Doctoral Thesis

Development of a temperature-vacuum swing process for CO2 capture from ambient air

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DEVELOPMENT OF A TEMPERATURE-VACUUM SWING PROCESS FOR CO₂ CAPTURE FROM AMBIENT AIR

A dissertation submitted to attain the degree of DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

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Abstract

Direct air capture (DAC) of CO₂ deals with the extraction of concentrated CO₂ from atmospheric air. Potential applications include future emission mitigation strategies, in particular storage and transportation of renewable energies in the form of synthetic hydrocarbon fuels. If these fuels are synthesized from CO₂ captured from the air, a closed carbon material cycle can be obtained.

Adsorption processes, in which species are chemically or physically bound at the surface of a solid sorbent material, are a common method for gas separation. Over the past years, several sorbents based on amine-functionalized porous materials have been developed for the purpose of CO₂ capture from concentrated or diluted sources. Many of these materials are in principle applicable for DAC; however, process concepts for the efficient extraction of CO₂ in a concentrated form are very rare.

In this thesis, a novel process referred to as temperature-vacuum swing (TVS) for CO₂ capture from ambient air using amine-functionalized, solid sorbent materials is developed as well as experimentally and numerically investigated. Starting with a general energy analysis of DAC processes, the combination of a temperature swing and the reduction of the absolute pressure around the sorbent is found to be an efficient way for the separation of concentrated CO₂ from air.

In a first experimental campaign the TVS process is demonstrated utilizing a packed bed of a sorbent material made of amine-functionalized commercial silica gel. Adsorption/desorption cycles are performed under equilibrium and non-equilibrium (short-cycle) conditions. Thereby, the CO₂ capture capacity of the material is determined over a wide range of operational parameters, namely 10-150 mbarₐₚs desorption pressure, 74-90 °C desorption temperature, and 0-80% relative humidity during adsorption. Up to 158 ml of CO₂ (6.8 ml per gram sorbent) with a purity of up to 97.6% are recovered per cycle. Adsorption isotherms of the sorbent material are experimentally determined by thermogravimetry and fitted to isotherm models, which are successfully applied to predict desorption capacities achieved in the TVS process. Under dry conditions, desorption pressures above 100 mbarₐₚs lead to strongly decreasing CO₂ capture capacities below 0.03 mmol/g. Under humid conditions with 40% relative humidity during adsorption, the desorption pressure can be raised to 150 mbarₐₚs with
Abstract

Capture capacities remaining above 0.2 mmol/g. Stable performance of the sorbent material in the TVS process is demonstrated over 40 consecutive adsorption/desorption cycles.

In a second experimental campaign the TVS process is applied to an amine-functionalized nanofibrilated cellulose material. This material has a higher CO\textsubscript{2} adsorption capacity than the silica-based material used for the first experiments and thus allows for more accurate measurements of the process performance, since parasitic effects such as air trapped in the dead volume have a smaller influence. The focus of the second campaign is the analysis of co-adsorption of CO\textsubscript{2} and H\textsubscript{2}O. For this purpose, a novel experimental setup is designed which allows for measuring the amount of water vapor released from the sorbent material during desorption under vacuum conditions. The promoting effect of the relative humidity on the CO\textsubscript{2} capture capacity and on the amount of co-adsorbed water is quantified. The measured specific CO\textsubscript{2} capacities range from 0.32 to 0.65 mmol/g and the corresponding specific H\textsubscript{2}O capacities range from 0.87 to 4.76 mmol/g for adsorption temperatures varying between 10 and 30 °C and relative humidities varying between 20 and 80%. Desorption of CO\textsubscript{2} is achieved at 95 °C and 50 mbar\text{abs}, yielding a purity exceeding 94%. Sorbent stability and a closed mass balance for both H\textsubscript{2}O and CO\textsubscript{2} are demonstrated for ten consecutive adsorption/desorption cycles. The specific energy requirements of the TVS process based on the measured H\textsubscript{2}O and CO\textsubscript{2} capacities are estimated to be 12.5 kJ/mol\textsubscript{CO2} of mechanical (pumping) work and between 493 and 640 kJ/mol\textsubscript{CO2} of heat at below 100 °C, depending on the air relative humidity. For a targeted CO\textsubscript{2} capacity of 2 mmol/g, the heat requirement would be reduced to between 272 and 530 kJ/mol\textsubscript{CO2}, depending strongly on the amount of co-adsorbed water.

Further, a transient heat and mass transfer model is developed to simulate the desorption step of the TVS process under dry and moist conditions. The model incorporates binary CO\textsubscript{2} and H\textsubscript{2}O adsorption equilibrium data, heat of adsorption, heat conduction and gas phase diffusion. A set of desorption experimental runs is carried out using a packed bed of amine-functionalized nanofibrillated cellulose sorbent material in the temperature range 20 – 95 °C and at 62 mbar\text{abs} desorption pressure. Numerically calculated temperature profiles are compared to those obtained experimentally. The simulation results indicate fast gas diffusion and local re-adsorption of CO\textsubscript{2} and H\textsubscript{2}O in colder zones of the reactor. The risk of O\textsubscript{2}-induced sorbent degradation is substantially reduced under humid air conditions as opposed to dry conditions, since air is purged out of the reactor by co-desorbed
H₂O before reaching a critical temperature. Further, the purity of the desorbed CO₂ stream is analyzed.

The proposed TVS process is found to be generally feasible for the extraction of concentrated CO₂ from air. The observed process performance indicates that the energy requirements of the process can in principle be in the range of 1’750 – 2’700 kWh/t CO₂ (280 – 430 kJ/mol CO₂) of heat at around 95 °C, which is the approximate amount of energy available as waste heat from a downstream fuel synthesis process. Aspects that should be investigated in more detail in the future include detailed adsorption equilibrium and kinetic models for the co-adsorption of CO₂ and H₂O for DAC conditions, especially for the temperatures prevailing during TVS desorption, mass transfer modelling of the adsorption process, and an analysis of the TVS process at adsorption temperatures below 0 °C.
Zusammenfassung


Adsorptionsprozesse, bei denen ein Stoff chemisch oder physikalisch an der Oberfläche eines festen Adsorptionsmaterials gebunden wird, sind eine übliche Methode zur Trennung von Gasgemischen. In den letzten Jahren wurden zahlreiche solcher Adsorptionsmaterialien basierend auf amin-funktionalisierten Trägerstoffen zur Abtrennung von CO₂ aus konzentrierten oder verdünnten Quellen entwickelt. Viele dieser Materialien sind prinzipiell zur CO₂ Abscheidung aus der Luft geeignet, jedoch fehlt es an Konzepten für dazugehörige Prozesse, welche eine effiziente Extraktion des CO₂ in konzentrierter Form ermöglichen.


In einer ersten Versuchsreihe wird die Funktionsfähigkeit des TVS Prozesses mittels eines Schüttgutbettes aus amin-funktionalisiertem Silikagel aufgezeigt. Es werden Adsorptions- und Desorptionszyklen unter transienten und Gleichgewichtsbedingungen durchgeführt. Dabei wird die CO₂-Abscheidungskapazität des Materials über einen grossen Parameterbereich bestimmt und zwar für Desorptionsdrücke zwischen 10 und 150 mbarₐₛ, Desorptionstemperaturen zwischen 74 und 90 °C und relative Luftfeuchten während der Adsorption zwischen 0% und 80%. Pro Zyklus werden bis zu 158 ml CO₂ (6.8 ml pro Gramm Sorptionsmaterial) mit einer Reinheit von bis zu 97.6%
aus der Luft abgetrennt. Mittels Thermogravimetrie werden Adsorptionsisothermen des Materials experimentell bestimmt und zur Parameteridentifizierung von zugehörigen Isothermen-Modellen herangezogen. Mittels der Isothermen können die im TVS Prozess erreichten Desorptionskapazitäten gut vorhergesagt werden. Unter trockenen Bedingungen führen Desorptionsdrücke über 100 mbar abs zu einer starken Abnahme der CO₂-Kapazitäten unter 0.03 mmol/g. Unter feuchten Bedingungen mit einer relativen Luftfeuchte von 40% während der Adsorption kann der Desorptionsdruck auf 150 mbar abs angehoben werden, wobei die CO₂-Kapazitäten oberhalb von 0.2 mmol/g bleiben. Der TVS Prozess erweist sich als stabil über 40 aufeinanderfolgende Adsorptions-/Desorptionszyklen.

In einer zweiten Versuchsreihe wird der TVS Prozess unter Verwendung von amin-funktionalisierter nanofibrillierter Zellulose als Adsorptionsmaterial untersucht. Dieses Material hat eine höhere CO₂-Adsorptionskapazität als das zuvor verwendete Silikagel-basierte Material und ermöglicht deshalb Messungen der Prozesseigenschaften mit höherer Genauigkeit, da Seiteneffekte wie z.B. Lufteinschlüsse im Totvolumen weniger ins Gewicht fallen. Der Schwerpunkt der zweiten Versuchsreihe liegt auf der Analyse der Co-Adsorption von CO₂ und H₂O. Hierzu wurde ein neuartiger Experimentaufbau entwickelt, welcher eine quantitative Bestimmung der während der Desorption abgegebenen Wasserdampfmenge unter Vakuumbedingungen ermöglicht. Somit werden der unterstützende Effekt der Luftfeuchte auf die CO₂-Adsorption sowie die Menge an co-adsorbiertem Wasser quantifiziert. Für Adsorptionstemperaturen zwischen 10 und 30 °C und relative Luftfeuchten zwischen 20% und 80% bewegen sich die gemessenen spezifischen CO₂-Kapazitäten im Bereich von 0.32 bis 0.65 mmol/g und die entsprechenden spezifischen H₂O-Kapazitäten im Bereich von 0.87 bis 4.76 mmol/g. Die Desorption wird bei 95 °C und 50 mbar abs durchgeführt und resultiert in einer CO₂-Reinheit von über 94%. Über zehn aufeinanderfolgende Zyklen wird ein stabiles Verhalten des Adsorptionsmaterials und eine geschlossene Massenbilanz demonstriert. Der spezifische Energiebedarf wird – basierend auf den gemessenen CO₂ und H₂O Kapazitäten – auf 12.5 kJ/mol CO₂ mechanische (Pump-)Arbeit und zwischen 493 und 640 kJ/mol CO₂ Wärme unter 100 °C geschätzt, wobei der Wärmebedarf von der relativen Luftfeuchte während der Adsorption abhängt. Für eine angestrebte CO₂ Kapazität von 2 mmol/g würde sich der Wärmebedarf auf 272 bis 530 kJ/mol CO₂ reduzieren, wiederum abhängig von der Menge des adsorbierten Wassers.

Im Ergebnis erweist sich der TVS Prozess als prinziell geeignet für die Abtrennung von konzentriertem CO₂ aus der Luft. Die gemessene Leistungsfähigkeit des Prozesses lässt darauf schliessen, dass sich dessen Energiebedarf prinziell im Bereich von 1'750 – 2'700 kWh/t CO₂ (280 – 430 kJ/mol CO₂) bewegen kann, was in etwa der aus einem nachgeschalteten Treibstoffsyntheseprozess zur Verfügung stehenden Abwärme entspricht. Aspekte, die in der Zukunft noch genauer untersucht werden sollten, sind detaillierte Gleichgewichts- und kinetische Modelle der Co-Adsorption von CO₂ und H₂O für DAC Bedingungen, insbesondere für die während der Desorption vorherrschenden Temperaturbereiche, eine Modellierung der Stofftransportvorgänge während der Adsorption und eine Analyse des TVS Prozesses für Adsorptionstemperaturen unter 0 °C.
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Declaration of financial interests

The author Jan Andre Wurzbacher declares to have financial interest in Climeworks Ltd. Climeworks Ltd. is a Zurich-based spin-off company of ETH Zurich aiming at the commercialization of a technology for CO₂ capture from ambient air.
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Nomenclature

Symbols

$b$ width of the sorbent bed

$b, b_0$ parameters of the Toth model

$c_{0, CO_2/H_2O}$ CO$_2$/H$_2$O concentration upstream of the adsorption reactor

$c_{1, CO_2/H_2O}$ CO$_2$/H$_2$O concentration downstream of the adsorption reactor

$c_{d, H_2O}$ H$_2$O concentration in the drying gas at the exit of the gas dryer

$c_{p/v}$ specific heat capacity at constant pressure/volume

$C_{G/G,0/m/m,0}$ parameters of the GAB model

$D$ averaged diffusion coefficient

$D_0$ averaged diffusion coefficient at ambient pressure and 310 K

$Err$ fitting error

$f_{RH}$ conversion factor between humid and dry CO$_2$ adsorption capacity

$h$ height of the sorbent bed

$h$ specific enthalpy

$\Delta h_{ads}$ mole-specific enthalpy of adsorption/desorption

$\Delta H_C, \Delta H_K$ parameters of the GAB model

$ar{j}$ diffusion flux

$k_{eff}$ effective thermal conductivity

$k_F$ parameter of the Freundlich model
$k_L$ parameter of the Langmuir model

$K_{ads}, K_0$ parameters of the GAB model

$l$ length of the sorbent bed

$m$ mass

$M$ molar mass

$\dot{n}_{air/CO_2/Ar/d}$ molar flow rate of air/CO$_2$/Argon/drying gas (dried air)

$n$ parameter of the Freundlich model

$n_s, n_{s,0}$ parameters of the Toth model

$n_x, n_y$ number of grid points in x/y direction

$N$ number of measured isotherm data points

$p$ absolute/partial pressure

$p_{ads,CO_2}$ CO$_2$ partial pressure during adsorption

$p_{tot}$ total gas phase pressure in the reactor

$p_{vap}$ vapor pressure of water

$q$ loading of adsorbed species on the sorbent material

$q_e$ equilibrium CO$_2$ loading on the sorbent material

$q_e(T(p))$ equilibrium CO$_2$ loading at temperature $T$ and pressure $p$

$q_\infty$ saturation CO$_2$ loading for Langmuir model

$\Delta q_{CO_2/H_2O}^{(ads)/(des)}$ cyclic CO$_2$/H$_2$O adsorption/desorption capacity

$\Delta q_e$ equilibrium adsorption/desorption CO$_2$ capacity in TVS process

$q$ conduction heat flux

$Q$ heat (required for desorption)
\( R \)  
ideal gas constant

\( t \)
time

\( \Delta t \)  
time step of the discretization

\( t, t_0 \)  
parameters of the Toth model

\( T \)
temperature

\( T_0 \)  
reference temperature for the Toth model

\( T_2 \)  
intermediate temperature in TVS process

\( T_{pump} \)
operating temperature of the vacuum pump

\( u \)  
specific internal energy

\( U \)  
internal energy

\( v \)  
specific volume

\( v_{i,g} \)  
specific volume of species \( i \) at its partial pressure in the gas phase

\( v_{i,p} \)  
specific volume of species \( i \) at pressure \( p_{tot} \)

\( V \)  
volume

\( V_{CV} \)  
volume of the control volume

\( W_{comp} \)  
mechanical compression work

\( \Delta x, \Delta y \)  
edge length of finite volumes in x/y direction

\( \delta x, \delta y \)  
distance between centers of neighboring finite volumes in x/y direction

\( \bar{x} \)  
control volume-specific property: \( \bar{x} = x/V_{CV} \)

\( \alpha, \chi \)  
parameters of the Toth model

\( \beta \)  
parameter of the GAB model

\( \eta \)  
efficiency
Nomenclature

**Relative humidity (RH)**

\[ \phi \]

**Density**

\[ \rho \]

**Nabla operator**

\[ \nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right) \]

**Sub-/superscripts**

- **0**: initial condition / value at previous time step
- **abs**: absolute (pressure)
- **ads**: adsorbed / adsorption
- **amb**: ambient
- **des**: desorption
- **el**: electricity
- **exp**: experimental/measured
- **g**: gas phase
- **i, j, r**: counters
- **mod**: modeled
- **N**: normal volume (at 1.01325 bar and 0 °C)
- **net**: net flow, leaving a control volume (outflow - inflow)
- **s**: sorbent/solid phase
- **sens**: sensible (heat)
- **p**: center point (discretization grid)
- **e / n / s / w**: “east”/“north”/“south”/“west” point (discretization grid)
## Acronyms

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<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>APDES</td>
<td>3-aminopropylmethyldiethoxysilane</td>
</tr>
<tr>
<td>APDES-NFC-FD</td>
<td>aminosilane-functionalized NFC sorbent material</td>
</tr>
<tr>
<td>APDES-NFC-FD-S</td>
<td>aminosilane-functionalized NFC sorbent material (scaled-up synthesis batch)</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller method</td>
</tr>
<tr>
<td>CV</td>
<td>control volume</td>
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<tr>
<td>DAC</td>
<td>direct air capture of CO₂</td>
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<tr>
<td>DAQ</td>
<td>data acquisition</td>
</tr>
<tr>
<td>GAB</td>
<td>Guggenheim-Anderson-de Boer model</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower heating value</td>
</tr>
<tr>
<td>NFC</td>
<td>nanofibrillated cellulose</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>SI-AEATPMS</td>
<td>aminosilane-functionalized silica gel sorbent material</td>
</tr>
<tr>
<td>TCS</td>
<td>temperature-concentration swing</td>
</tr>
<tr>
<td>TVS</td>
<td>temperature-vacuum swing</td>
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</table>
1 Introduction

1.1 CO₂ capture from air

Among several strategies to mitigate anthropogenic CO₂ emissions, capturing CO₂ directly from ambient air – usually referred to as direct air capture (DAC) – has recently attracted increasing interest.¹⁻¹⁴ DAC is not a mutually exclusive or competing alternative to other mainstream efforts to capture CO₂ from concentrated point sources (e.g. flue gases),¹⁵ but rather an additional tool within a set of various emission mitigation instruments with its own advantages, disadvantages, applications, and timelines.

Because of the low CO₂ concentration in the air, direct air capture is evidently a thermodynamically less favorable option. Nevertheless, there are a number of intriguing advantages that can compensate or overcompensate this drawback in certain applications.¹ DAC enables addressing present and past CO₂ emissions released by the transportation sector and other distributed sources. DAC systems can be decoupled in space and time from the existing power plant infrastructure and be strategically located next to a source of renewable energy and/or to a final storage site, such as uninhabited deserts with high solar irradiation and vast geological storage reservoirs. Thereby, long-distance transportation of CO₂ is eliminated. In particular, air capture systems can also be deployed next to a CO₂ processing/recycling plant. Ultimately, combining air capture with the solar-driven or electrochemical splitting of CO₂ enables a closed carbon material cycle for the production of synthetic hydrocarbon fuels.¹⁶⁻²¹ Thereby, DAC offers the possibility of a truly sustainable hydrocarbon fuel-based energy future. In the long term, air capture may become indispensable for stabilizing the global CO₂ concentration in the atmosphere in view of continuously increasing emissions above threshold limits.

CO₂ concentration in air, presently at around 400 ppm, is about 100 to 400 times lower than that in flue gases, typically 5-15%.²², ²³ The minimum required free energy to capture 90% of the CO₂ in a flue gas stream containing 10% CO₂ at 300 K, given by the thermodynamic free energy of mixing,²⁴ is around 7.5 kJ/mol CO₂ (47.5 kWh/t CO₂). On the other hand, the corresponding minimum free energy
required to completely extract the CO$_2$ out of an air stream at 300 K is around 22 kJ/mol CO$_2$. If the CO$_2$ content of the air is only reduced to 200 ppm, the required free energy reduces to around 20 kJ/mol CO$_2$ (128 kWh/t CO$_2$), i.e., only a factor of about 3 larger than that required for the flue gas separation case. If the comparison is done based on the free energy demand of a single-sorbent system with constant activity, the difference between both cases is even smaller.\textsuperscript{24} These numbers reveal that the difference in terms of energy requirement between DAC and CO$_2$ capture from concentrated sources is relatively small from a thermodynamic perspective and that there are no stringent, fundamental limitations on DAC from thermodynamics. In particular, the absolute values of the minimum required energy for DAC are relatively small. The most crucial aspect of air capture is the large mass flow rate of air per mass of CO$_2$ captured, which imposes corresponding constraints on the design of DAC systems and impacts their energy consumption and capital costs. The actual energy consumption of an industrial CO$_2$ capture plant will therefore rather be determined by the process design, plant engineering, and choice of the sorbent system than by the thermodynamic limit.

Supplying the energy required to drive a DAC process and any downstream processes creates again CO$_2$ emissions. For a DAC process to be overall carbon negative, it is therefore important that these emissions are small compared to the amount of CO$_2$ captured. Thereby, it is advantageous, if low-value energy, such as low-temperature heat, which is often available as waste heat from other processes, can be used to power the DAC process as opposed to high-value energy such as electricity. In this respect, coupling DAC with the production of synthetic fuels from renewable energy has another important advantage since the DAC process can be driven by the waste heat of the fuel synthesis process. If for an order-of-magnitude estimation it is assumed that the efficiency of a fuel synthesis process (high-temperature electrolysis followed by Fischer-Tropsch synthesis of -CH$_2$\textsuperscript{19}) is between 60\% and 70\% and that all energy losses can be recovered as heat, 1’750 – 2’700 kWh of waste heat would be available for the DAC process per ton of CO$_2$. While a detailed process engineering design will be required for an accurate analysis of the amount of recoverable heat, this value provides an upper limit on the heat consumption of a DAC process that is to be driven by the waste heat of a coupled fuel synthesis process.
Several different concepts of DAC technologies have been developed over the last years by a couple of research groups and start-up companies. A comprehensive overview can be found in the corresponding reviews.1, 13

A group around David Keith, the University of Calgary, and the Calgary-based start-up company Carbon Engineering has developed a wet scrubbing system in which CO₂ is absorbed from an air stream by an alkaline solution such as NaOH or KOH. Initial designs involved a spray tower design with a vertical flow pattern for adsorption,25 where the solution was regenerated through a caustic recovery process known from the pulp and paper industry.26 An alternative regeneration process based on a titanate cycle was also investigated.3, 27 Later designs were based on intermittently-wetted cross-flow packed tower geometries28, 29 A potential advantage of this approach is the fact that several standard processes known from the industry can be utilized where potential disadvantages are associated with the high-temperature heat required for solvent regeneration.

At the Professorship of Renewable Energy Carriers of Aldo Steinfeld, ETH Zurich, a thermochemical carbonation-calcination cycle for DAC was developed that is driven by concentrated solar irradiation.4, 30, 31 During the carbonation step, air and steam is passed through a fluidized bed reactor and CaO is converted to CaCO₃. During the subsequent calcination step, CaCO₃ is transformed back to CaO and pure CO₂ is recovered. The cycle was demonstrated on a solar simulator. While this process is entirely driven by solar energy, potential drawbacks are related to the adsorption step which needs to operate under elevated temperatures due to kinetic reasons and therefore requires heating of the air stream.

A group around Klaus Lackner, Columbia University, and the start-up company Kilimanjaro Energy has developed a humidity swing cycle to capture CO₂ out of relatively dry air streams.5 The process is based on CO₂ adsorption from an air stream on an anionic ion exchange resin. If the resin is subsequently wetted or exposed to moisture, the equilibrium partial pressure of CO₂ over the resin can be increased by 2 orders of magnitude32 and CO₂ desorption can be achieved, for example under vacuum conditions. Thermodynamic analyses have shown that the free energy required for the CO₂ concentration process is supplied through the evaporation of water during drying of the sorbent.24, 33 This process can be very favorable from an energy consumption perspective, since it is mainly driven by water evaporation into dry air. On the other hand, the requirements on the relative
humidity (RH) of the air during adsorption and the still relatively low partial pressure of the CO₂ recovered during desorption might limit its application range.

A DAC process based on solid amine-modified sorbents was investigated by the group of Christopher W. Jones, Georgia Institute of Technology, in collaboration with the start-up company Global Thermostat. Several different materials, ranging from PEI-impregnated silica, over hyperbranched aminosilicas to mesoporous alumina-supported amines were synthesized and analyzed for their CO₂ capture properties.\textsuperscript{7-9, 34-37} In order to achieve separation of pure CO₂ from an air stream a steam purge process was suggested,\textsuperscript{38} were steam at around 100 °C was introduced into a sorbent material bed for regeneration to achieve both, heating of the material and reduction of the CO₂ partial pressure around the material. Stability of different sorbent materials under steam exposure was also analyzed.\textsuperscript{34, 39} While the steam purge process allows for fast heating of the sorbent bed, it poses other practical challenges such as potential occurrence of condensate in the material.

Several of the different DAC concepts were analyzed on a bench scale; however, their large-scale industrial feasibility remains to be proven. While some studies claim that DAC will become cost competitive\textsuperscript{5, 40} and others question its near-term economic feasibility,\textsuperscript{41-46} it is evident that additional R&D on the fundamentals of DAC is required to reliably assess its ultimate industrial-scale applicability. Further, it is being discussed whether the development of DAC technology could potentially create a moral hazard in the sense that other mitigation technologies are neglected and climate policies rely on the future capture of today’s emissions from the air, which would clearly be a very risky strategy.\textsuperscript{47} On the other hand it can be argued that the deployment of DAC technology on a global scale, for example in the framework of renewable fuel production within a closed carbon cycle, will require very long lead times of 30 years or more, which in turn implies that substantial development efforts must start today, even if potential application scenarios will become globally relevant only in several decades.

For processes based on adsorption on solid sorbent materials, several amine-functionalized porous sorbent materials were developed over the recent years for both, DAC and CO₂ capture from concentrated sources such as flue gases.\textsuperscript{23, 48-55} Solid amine-functionalized materials have been identified as promising sorbents for DAC, as they offer relatively high specific CO₂ capacities and uptake rates under extremely low CO₂ partial pressures, such as in the case of ambient air.\textsuperscript{6-9, 11,}
In contrast to liquid scrubbing systems, solid sorbent materials for CO₂ adsorption offer reduced thermal mass, resistance to corrosion, and potentially smaller losses of volatile compounds to the air stream. Another intriguing advantage is their tolerance to air moisture. In contrast to physical sorbents such as zeolites, an increase of the CO₂ adsorption capacity was observed under humid conditions compared to dry conditions. However, substantial amounts of water are co-adsorbed from moist gases. Formation of carbamates and carbamic acid was postulated as the main underlying CO₂ adsorption mechanism on amine-modified silica under dry and humid conditions. Additional adsorption of H₂O presumably occurs through physical adsorption.

Within the doctoral thesis of Christoph Gebald that was conducted at the Professorship of Renewable Energy Carriers at ETH Zurich in parallel to this thesis, a novel class of amine-functionalized sorbent materials based on nanofibrillated cellulose was developed for the purpose of CO₂ capture from the air. While for initial studies a different, amine-modified silica gel sorbent material was used, for the main part of the experimental work in the present thesis these cellulose-based materials were employed.

The vast majority of previous studies on amine-functionalized sorbent materials focused on maximizing their CO₂ uptake capacities and rates, while sorbent regeneration was usually achieved by purging with an inert gas, yielding – again – highly diluted CO₂. Desorption of concentrated, high-purity CO₂ is evidently crucial for downstream applications, yet this issue remained mostly disregarded. A few studies, including some of those introduced above, applied steam stripping, moisture swing, or temperature-vacuum swing (TVS) processes to obtain concentrated CO₂, but most of the latter ones not for CO₂ capture from the air. The development of feasible processes for the extraction of concentrated CO₂ out of gas streams by using amine-functionalized sorbent materials is therefore crucial.

1.3 Thesis outline

The overall goal of this thesis is the development, demonstration, and characterization of a novel process for the extraction of concentrated CO₂ from atmospheric air using amine-functionalized solid sorbent materials. The process thereby needs to cope with the special conditions prevailing for the separation of CO₂ from air, most importantly the extremely low concentration of CO₂ and...
presence of humidity. It further needs to fulfill the energy requirements for a feasible DAC process.

Starting with an energy analysis of DAC processes in general, in Chapter 2, the temperature-vacuum swing (TVS) process is derived and explained in detail. It is found to meet the above described criteria. One major step towards the successful experimental demonstration of the TVS process for the extraction of concentrated CO₂ from the air was the development of a solid experimental setup for conducting automated and repeatable adsorption/desorption cycles. Both the setup and the first experimental demonstration of DAC with a TVS cycle on an amine-functionalized sorbent material are described in Chapter 3, including several process parameter studies. In Chapter 4, co-adsorption of CO₂ and H₂O is analyzed. In a second experimental campaign, both, CO₂ and H₂O adsorption and desorption is quantified over multiple, consecutive cycles using an extension of the experimental setup allowing for measuring the amount of desorbed H₂O under vacuum conditions. Finally, heat and mass transfer during TVS desorption is analyzed by employing a rigorous numerical model, which is validated through comparison with measurements on a scaled-up TVS reactor as described in Chapter 5. In Chapter 6, the obtained results are briefly summarized and potential future, follow-up work is indicated.
2 The temperature-vacuum swing process\textsuperscript{a,b}

Motivated by the lack of process concepts for the extraction of concentrated CO\(_2\) from the air by utilizing amine-functionalized solid sorbent materials, the first part of this thesis comprises the development of such a concept. Thereby, the energy requirements of a concept were chosen as main criteria for the evaluation of its feasibility. The temperature-vacuum swing process (TVS) was thereby found to be a promising approach for keeping the energy consumption within tolerable limits.

2.1 Energy analysis of direct air capture

To assess and compare different concepts, the energy consumption of various process steps were put into a perspective with general energy figures related to DAC. The focus was thereby set on adsorption-based processes. Typical adsorption-based processes for gas separation include temperature swing, concentration swing, pressure swing, vacuum swing, and combinations thereof. Table 2-1 shows approximate energy figures of selected processes and process steps which were standardized to the units kWh per ton CO\(_2\). The heating energy and ventilation work of the air stream were thereby calculated according to Equations (1.1) and (1.2).

Heating of air stream:

\[
Q_{\text{air-stream}} = \frac{c_{p,\text{air}} \cdot \Delta T \cdot \rho_{\text{air}}}{(\Delta c \cdot p_{\text{amb}})/(R \cdot T)} \tag{1.1}
\]

where \(\Delta c\) is the amount of CO\(_2\) extracted from the air stream, expressed as concentration difference, e.g., 200 ppm.

\textsuperscript{a} Material from this chapter has been published in: Wurzbacher J. A., Gebald C., Steinfeld A. Separation of CO\(_2\) from Air by Temperature-Vacuum Swing Adsorption Using Diamine-Functionalized Silica Gel. Energy & Environmental Science, Vol. 4, pp. 3584-3592, 2011

\textsuperscript{b} Material from this chapter has been filed as a patent: Gebald C., Steinfeld A., Wurzbacher J.A. Amine Containing Fibrous Structure for CO\(_2\) Capture from Atmospheric Air; WO 2010/091831
Ventilation work on air stream:

\[
W_{\text{vent}} = \frac{1}{\eta_{\text{fan}}} \frac{\Delta p}{(\Delta c \cdot P_{\text{amb}}) / (R \cdot T)}
\]

(1.2)

where \( \Delta p \) is the pressure drop on the air stream and \( \eta_{\text{fan}} \) the efficiency of the fan.

**Table 2-1. DAC related energy figures (per ton CO\textsubscript{2} captured) of different process steps.**

<table>
<thead>
<tr>
<th>Process</th>
<th>Required energy ( \text{(kWh/t CO}_2\text{)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat generation (LHV) with natural gas; as reference\textsuperscript{75}</td>
<td>5'060</td>
</tr>
<tr>
<td>Electricity generation (combined cycle plant, ( \eta_{\text{LHV}} =60% ) in rel. to LHV) with natural gas; as reference</td>
<td>3'040</td>
</tr>
<tr>
<td>Wind power (life cycle analysis-based equivalent CO\textsubscript{2} emissions for &gt; 100 kW nameplate turbine capacity);\textsuperscript{76,77} as reference</td>
<td>&gt;&gt; 30’000</td>
</tr>
<tr>
<td>Thermodynamic limit of work required for DAC (at 300 K, complete removal of CO\textsubscript{2} from the air stream)\textsuperscript{24}</td>
<td>140</td>
</tr>
<tr>
<td>Upper limit for heat consumption of a DAC process to be covered by waste heat of fuel production (see Introduction)</td>
<td>1’750 – 2’700</td>
</tr>
<tr>
<td>Enthalpy of CO\textsubscript{2} adsorption on amine groups (average of 60 kJ/mol CO\textsubscript{2})\textsuperscript{78}</td>
<td>380</td>
</tr>
<tr>
<td>Heat of water desorption (adsorption of 3 mmol H\textsubscript{2}O per mmol CO\textsubscript{2}, enthalpy of H\textsubscript{2}O adsorption of 49 kJ/mol\textsuperscript{78} assumed)</td>
<td>930</td>
</tr>
<tr>
<td>Heating of the adsorption air stream by 10 K\textsuperscript{#} (at 300 K)</td>
<td>9’300</td>
</tr>
<tr>
<td>Ventilation of the adsorption air stream with a pressure drop of 100 Pa\textsuperscript{#} (fan efficiency = 50%)</td>
<td>157</td>
</tr>
<tr>
<td>Ventilation of the adsorption air stream with a pressure drop of 0.1 bar\textsuperscript{#} (fan efficiency = 50%)</td>
<td>15’700</td>
</tr>
</tbody>
</table>

\textsuperscript{\#} 400 ppm CO\textsubscript{2} content assumed, of which 50\% are captured.

As described in the Introduction, the energy consumption of a DAC process should be below 1’750 – 2’700 kWh of low-temperature heat per ton CO\textsubscript{2} captured in order to be supplied by the waste heat of a corresponding fuel synthesis process. Table 2-1 additionally puts this figure into perspective with the CO\textsubscript{2} emissions associated with the energy generation from burning of natural gas as an exemplary fossil fuel and from wind power as exemplary renewable electricity. Natural gas or other fossil fuels are not the targeted power source for DAC. However, for the sake
of comparing orders of magnitude, it can be concluded that a DAC process that consumes, for example, 2'000 kWh of heat could theoretically be overall carbon negative if powered by natural gas. Utilizing large amounts of renewable electricity to power a DAC process is also not desirable, since costs will typically prohibit this option. Further, in many cases renewable electricity might alternatively – potentially more efficiently – be used to replace other fossil fuel-based power generation. However, the figures of Table 2-1 show that supplying electricity to a DAC process that requires a limited amount of power, e.g., less than 300 kWh per ton of CO\textsubscript{2} captured, does not create significant side emissions, especially if renewable electricity can be employed as power source.

Most importantly, it follows from Table 2-1 that for any DAC process to be feasible on a large scale, the adsorption step needs to be passive in the sense that no treatment of the air stream in the form of substantial heating, cooling, pumping or compression can be afforded from an energy point of view. This is due to the low concentration of CO\textsubscript{2} in the air. For example, heating or cooling of the air stream by as little as 10 K would require around 9'300 kWh/t CO\textsubscript{2} heating or cooling power, respectively. This shows that even concepts with heat recovery will not allow for a thermal treatment of the air stream since the remaining temperature differences over heat exchangers will typically be in the order of at least 5-10 K. Also any pumping or ventilation requirements on the air stream must be very small. A pressure drop over the adsorber of 100 Pa with an associated energy penalty of around 150 kWh\textsubscript{e}/t CO\textsubscript{2} illustrates the order of magnitude of the limits with respect to air ventilation. Already a pressure drop of 0.1 bar, which is not extremely high for industrial gas processing, exceeds the feasible limit by two orders of magnitude. This practically excludes any pressure swing processes in which adsorption occurs under other than ambient conditions for DAC applications.\textsuperscript{79}

On the other hand, the enthalpy of adsorption of CO\textsubscript{2} on amine-based sorbent materials is around 400 kWh/t CO\textsubscript{2}. While this energy needs to be provided as heat during desorption and cannot be recovered since the corresponding heat of adsorption is lost to the air stream during adsorption, it is relatively small compared to the target maximum energy consumption of the DAC process. Also, for moderate co-adsorption of water the associated energy penalty remains within feasible limits. For example, if 3 mmol H\textsubscript{2}O are co-adsorbed for each adsorbed mmol of CO\textsubscript{2}, the overall heat of desorption for both, CO\textsubscript{2} and H\textsubscript{2}O, is approximately 1'300 kWh/t CO\textsubscript{2}. Therefore, CO\textsubscript{2} adsorption on amine-modified
sorbent materials that are regenerated by heating during desorption can generally be feasible for DAC from an energy consumption point of view.

However, if the amount of co-adsorbed water substantially exceeds the amount of adsorbed CO$_2$, e.g., by one order of magnitude or more, the energy penalty becomes critical. Such large ratios of H$_2$O co-adsorption can potentially occur, since the water content of air is typically at least one order of magnitude higher than its CO$_2$ content. Thus, adsorption on physisorbents such as zeolites, on which CO$_2$ and H$_2$O adsorption are competitive and adsorbed CO$_2$ can even be displaced by additional adsorbed H$_2$O,$^{71}$ is typically not suitable for DAC.

### 2.2 TVS process description

The simplest approach of regenerating an amine-functionalized sorbent material after CO$_2$ adsorption would be sole heating of the material at ambient pressure until desorption of pure CO$_2$ starts. However, if previous adsorption was carried out under DAC conditions, i.e., at a CO$_2$ partial pressure of 0.4 mbar, pure CO$_2$ cannot be obtained. This is due to the typical shape of the adsorption isotherms of amine-based sorbents which do not allow for a substantial reduction in sorbent loading at 1 atmosphere and temperatures around 100 °C, as it will be quantitatively assessed in Chapter 3 below.

On the other hand, if a temperature swing is combined with a pressure reduction around the sorbent material, desorption of concentrated CO$_2$ is possible. This process is referred to as temperature-vacuum swing (TVS). As opposed to sole pressure swing or sole vacuum swing processes,$^{79}$ the proposed combined process eliminates compression of the gas stream during adsorption while enabling operation at moderate vacuum during desorption. Typical vacuum pressures range between 25 and 250 mbar$_{\text{abs}}$, which are achievable with standard industrial liquid ring vacuum pumps. Furthermore, it allows desorption at relatively low temperatures ($<100$ °C), thereby preventing degradation of the sorbent material and increasing the energy efficiency of the process.

An alternative approach would be a combination of a temperature swing and a concentration swing, which can be achieved by a purge gas flow around the sorbent material during desorption. Such a process is referred to as temperature-concentration swing (TCS) and was applied to measure the adsorption capacity of sorbent materials in this work. However, for applications aiming at the extraction
of concentrated CO₂ from the air, the purge gas must be easily separable from the CO₂, which excludes inert gases such as N₂ or Ar for this purpose. As described in the Introduction, purging with steam is an option where the purge gas can be separated from the desorbed CO₂ through condensation. Since the cyclic generation of condensate water in the sorbent material poses stringent technical challenges in this case, this approach was not further followed in the framework of this thesis.

Figure 2-1 depicts qualitatively an idealized TVS process for CO₂ adsorption from a dry gas stream under equilibrium conditions in an adsorption isotherm diagram. Uniform temperature within the sorbent material is assumed. In the process shown here, the desorption pressure \( p_{\text{des}} \) (e.g. 100 mbar\(_{\text{abs}}\)) is significantly larger than the CO₂ partial pressure during adsorption \( p_{\text{ads}, \text{CO₂}} \) (e.g. 0.4 mbar\(_{\text{abs}}\) corresponding to 400 ppm CO₂ concentration), as it will be the case for a typical TVS process for air capture. Point 1 represents the equilibrium state after the sorbent material has been saturated in an atmosphere with CO₂ partial pressure \( p_{\text{ads}, \text{CO₂}} \). The corresponding equilibrium CO₂ loading of the sorbent at this point is \( q_{e, \text{ads}} \). The desorption process starts with an evacuation of the system to the desired desorption pressure \( p_{\text{des}} \), which is typically completed within a few minutes or less. During the subsequent first phase of the heating process from \( T_{\text{ads}} \) to \( T_2 \) (point 1 \( \rightarrow \) 2), a typically small amount of CO₂ is desorbed into the volume around the sorbent material until the partial pressure of CO₂ equals the desorption pressure, indicated by point 2. At this point, the sorbent is contained in a pure CO₂ atmosphere at \( p_{\text{des}} \) and Equation (1.3) is fulfilled:

\[
q_{e,T_2}(p_{\text{des}}) = q_{e,T_{\text{ads}}}(p_{\text{ads}, \text{CO₂}}) =: q_{e, \text{ads}}
\]

(1.3)

where \( q_{e,T}(p) \) represents the equilibrium CO₂ uptake of the sorbent at CO₂ partial pressure \( p \) and temperature \( T \). It is thereby neglected that the sorbent loading at point 2 is slightly smaller than that at point 1 due to the typically small amount of CO₂ that is desorbed between points 1 and 2.
During the second phase of the heating process (point 2 → 3), CO₂ is constantly desorbed and removed by the vacuum pump until the sorbent temperature equals \( T_{des} \). After cooling (point 3 → 4) and exposing the sorbent again to a gas stream with CO₂ partial pressure \( p_{ads,CO₂} \), the next adsorption process is started until point 1 is reached, closing the cycle. Since the adsorption is a non-equilibrium process, line 4-1 does not represent intermediate states in the adsorption isotherm diagram. The idealized equilibrium capacity for CO₂ adsorption from a dry gas stream in a TVS process \( \Delta q_e \) can thus be calculated by:

\[
\Delta q_e = q_{e,T_{ads}}(p_{ads,CO₂}) - q_{e,T_{des}}(p_{des})
\]  

(1.4)

Note that Equation (1.4) represents an idealized approximation which is valid only under the following assumptions:

i) At the end of the desorption process the gas atmosphere around the sorbent material consists of CO₂ only, i.e., the partial pressure of the CO₂ equals the desorption pressure: \( p_{CO₂} = p_{des} \)

ii) The amount of CO₂ that remains in the reactor after desorption is small compared to the total amount of CO₂ extracted by the vacuum pump and can therefore be neglected.

iii) The amount of CO₂ that is diluted by air remainders in the system at the beginning of the desorption process is small compared to the total amount

**Figure 2-1.** Qualitative representation of TVS process in adsorption isotherm diagram.
of CO₂ extracted by the vacuum pump and dilution can therefore be neglected.

For very large desorption pressures the idealized process description according to Figure 2-1 and in particular Equation (1.4) may not be valid, since for this case the air remainders in the reactor after initial evacuation of the system and CO₂ remainders in the system after the end of desorption can be large compared to the amount of CO₂ desorbed during the process. In turn, assumptions i) – iii) might not be fulfilled. An accurate calculation of the cyclic CO₂ capacity of the TVS process requires a simulation of the complete desorption process, taking the purity of the CO₂ outlet stream into account. Such a simulation is provided in Chapter 5 below.

While the TVS process is a promising approach for the desorption of concentrated CO₂, its practical implementation implies a number of challenges. Firstly, the heat for the desorption process needs to be transferred to a solid material under vacuum conditions. To enable fast heat transfer, efficient heat exchange structures need to be employed. Secondly, co-adsorption of H₂O can be an issue, especially for high relative humidity in the air. Only very limited data about co-adsorption under DAC conditions is available in the literature. Thirdly, desorption under vacuum requires structures or containers enclosing the sorbent material that withstand the forces implied by the pressure difference.

Besides the fundamental demonstration of the TVS process for DAC conditions, this thesis deals with the detailed investigation of the first two challenges. The latter one needs to be addressed within an industrial, engineering design process which is outside the scope of this work.
3 Separation of concentrated CO₂ from air with the TVS process\textsuperscript{c,d}

This chapter describes the experimental demonstration of the separation of concentrated CO₂ from air using the temperature-vacuum swing process introduced above. To achieve this, an experimental setup for conducting multiple, computer-controlled column breakthrough adsorption/desorption experiments was designed and fabricated as described in Section 3.1. The setup allowed for performing consecutive cyclic experiments under repetitive conditions as well as controlled variation of process parameters such as adsorption and desorption temperatures, desorption pressure, gas flows, and cycle timing. It was used for most of the experimental investigations of this thesis.

Besides the demonstration of the TVS cycle, the influence of the desorption pressure, desorption temperature, and relative humidity during adsorption on the CO₂ extraction performance was investigated. Further, the difference of adsorption/desorption cycles conducted under equilibrium and non-equilibrium (short-cycle) conditions was analyzed and a stability study over 40 consecutive cycles was carried out.

A diaminosilane-grafted silica gel sorbent material, consisting of 2-5 mm diameter beads, was used in this study. No attempt was undertaken at optimizing the sorbent material for maximum CO₂ capture capacity and uptake rates, since the focus was investigating the process in detail rather than the material. While faster adsorption kinetics may be obtained with smaller particles,\textsuperscript{80} larger particles cause a lower pressure drop across the sorbent bed, which keeps the air pumping energy requirements during adsorption within tolerable limits for scaled-up systems.

\textsuperscript{c} Material from this chapter has been published in: Wurzbacher J. A., Gebald C., Steinfeld A. Separation of CO₂ from Air by Temperature-Vacuum Swing Adsorption Using Diamine-Functionalized Silica Gel. \textit{Energy & Environmental Science}, Vol. 4, pp. 3584-3592, 2011.

\textsuperscript{d} The sorbent material used in this chapter was prepared by X. Cai under the supervision of C. Gebald and J.A. Wurzbacher. The measurement and modelling of the adsorption isotherms was conducted in the framework of a Bachelor thesis by S. Deml under the supervision of J.A. Wurzbacher.
To the best of our knowledge, no cyclic TVS process extracting a stream of pure CO₂ from a low-concentration gas stream (≤ 5000 ppm CO₂ content) has been demonstrated yet. Previous studies analyzed vacuum swing and TVS processes based on physisorption on zeolite materials for gas streams with high CO₂ concentration (≥10%). In space applications, a TVS process based on an amine-impregnated material was applied to a stream containing CO₂ at a concentration of 0.8% and higher, but the purity of the desorbed CO₂ was not an issue. TVS cycles based on amine-grafted mesoporous silica were investigated by micro-scale thermogravimetric analysis. Yet, these studies do not reflect the conditions of a large-scale TVS process in which the atmosphere around the sorbent material is saturated with desorbed CO₂.

3.1 Experimental setup for cyclic TVS measurements

3.1.1 Description of the setup

The experimental setup that was developed for this study is schematically shown in Figure 3-1. CO₂ adsorption and desorption on the sorbent material took place in a 40 mm inner diameter 40 mm-height stainless steel cylinder. For conventional adsorption-based gas separation processes, the height of the column is usually chosen much larger than its diameter to achieve sharp breakthrough curves and thus nearly complete removal of the adsorbate from the gas stream. In contrast, when capturing CO₂ from the air, this requirement is not necessary and even undesired because of the pressure drop. Thus, the height of the column was chosen relatively short as it would be the case for a large-scale system with small pressure drops.

The steel cylinder could be filled with up to 50 cm³ of sorbent material and a K-type thermocouple was placed at the center of the sorbent bed. The cylinder was contained in a water bath to rapidly heat and cool for desorption and adsorption, respectively. The bath was connected to temperature controlled hot (70-95 °C) and cold (20 °C) water reservoirs through a system of valves and a pump.

The mass flow rates of the air during adsorption were controlled by two electronic mass flow controllers (Bronkhorst EL-FLOW®). One of the air streams was bubbled through a water bath at 25 °C (humidifier) and mixed with the dry air stream. Before each experiment, the water bath was saturated with CO₂ by bubbling air through it until the CO₂ concentration in the air leaving the water bath
was equal to the CO$_2$ concentration in the inlet air. The relative humidity was controlled by adjusting the ratio of the mass flow rates of both air streams and monitored by an electronic humidity sensor (Vaisala HMP110). The CO$_2$ content of the air leaving the cylinder was monitored by an IR gas analyzer (Siemens ULTRAMAT, equipped with two detectors for the ranges of 0-1000 ppm and 0-5%, at 1 Hz sampling rate and 0.2% range detection limit). Before and after each adsorption, the air stream bypassed the reactor for several minutes so that the inlet CO$_2$ concentration could be measured by the IR gas analyzer.

Figure 3-1. Schematic of the experimental setup for TVS cyclic runs.

For subsequent desorption, the cylinder was connected to a vacuum system using an arrangement of solenoid valves. The vacuum system comprised a vacuum pump (KNF Neuberger, N84.3 ANDC) providing vacuum down to 5 mbar$_{\text{abs}}$, a pressure controller (Bronkhorst EL-PRESS$^\text{®}$), and a flow meter (Bronkhorst EL-FLOW$^\text{®}$) measuring the flow rate of concentrated CO$_2$ leaving the vacuum pump at ambient pressure up to 25 ml$_N$/min. The cylinder was evacuated to the desired desorption pressure and the desorption process was initiated by heating the
cylinder to the desired desorption temperature. The purity of the desorbed CO₂ was determined by gas chromatography (Agilent Micro GC M200, equipped with a Molsieve 5A and a PPQ 6M column, 90 s sampling period). After desorption, the cylinder was cooled to below 25 °C and the cycle was restarted.

As an alternative to desorption under vacuum and for the sake of comparison, desorption could also be performed by streaming Ar as a purge gas through the cylinder while being heated to the desired desorption temperature. This process is referred to as temperature-concentration swing (TCS).

The complete setup, including all components shown in Figure 3-1, was computer controlled using an “NI CompactDAQ” (National Instruments, TM) data acquisition (DAQ) system with a total of 32 digital output channels, 16 analog voltage output channels, 32 analog voltage input channels, and 16 analog thermocouple input channels. The hardware was controlled by a software program that was designed in the LabVIEW (National Instruments, TM) programming environment and allowed for autonomous operation of the setup over several days. Control of consecutive adsorption/desorption cycles was achieved through a finite state machine-based programming scheme. In Table 3-1, a typical state sequence that was used to control consecutive TVS cycles is shown. Both, the software program and the electric control cabinet comprising all DAQ hardware were designed within the framework of this thesis. A photo of the setup is shown in Figure 3-2; a photo of the control cabinet is shown in Figure 3-3.

### Table 3-1.
Exemplary state sequence of the control software for consecutive TVS cycles.
The description of the states contains only the main actions during the states; “t” refers to the time of each state.

<table>
<thead>
<tr>
<th>No.</th>
<th>State</th>
<th>Description</th>
<th>Transition cond. to next state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INIT</td>
<td>Initialization, prepare data filing, start cooling of condenser</td>
<td>t = 2 sec</td>
</tr>
<tr>
<td>2</td>
<td>CHECK AIR 1</td>
<td>Measure inlet CO₂ and H₂O concentration: start air flow, bypass column</td>
<td>t = 5 min</td>
</tr>
<tr>
<td>3</td>
<td>ADS</td>
<td>Adsorption: pass flow through column, measure outlet CO₂ and H₂O concentration and sorbent temp.</td>
<td>t = tₐₜₕ</td>
</tr>
</tbody>
</table>
### 3.1. Experimental setup for cyclic TVS measurements

<table>
<thead>
<tr>
<th>No.</th>
<th>State</th>
<th>Description</th>
<th>Transition cond. to next state</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>CHECK AIR 2</td>
<td>Measure inlet CO₂ and H₂O concentration: bypass column</td>
<td>( t = 5 \text{ min} )</td>
</tr>
<tr>
<td>5</td>
<td>WAIT DES READY</td>
<td>Stop air flow; heat water bath to desorption temperature ( T_{heater} = T_{des} )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>PUMP WARM-UP</td>
<td>Start vacuum pump</td>
<td>( t = 10 \text{ sec} )</td>
</tr>
<tr>
<td>7</td>
<td>EVAC 1</td>
<td>Switch valves and evacuate reactor to desired desorption pressure ( p \leq p_{des} )</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>EVAC 2</td>
<td>Evacuate piping after pressure controller to steady-state pump pressure ( t = 10 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>DES</td>
<td>Desorption: start hot water circulation to heat up column, measure CO₂ mass flow leaving the vacuum pump, record sorbent temperature and column pressure ( t = t_{des} )</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>AFTER DES 1</td>
<td>Stop heating, switch valves ( t = 2 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>AFTER DES 2</td>
<td>Switch valves, prepare venting ( t = 2 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>VENT REACTOR</td>
<td>Vent the reactor with atmospheric air to equilibrate pressure ( t = 5 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>PURGE REACTOR</td>
<td>Purge the reactor briefly with air to remove CO₂ (prevent re-adsorption) ( t = 45 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>PUMP OUTGAS</td>
<td>Purge the vacuum pump with air to remove condensate water, empty water bath around column ( t = 5 \text{ min} )</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>BEFORE COOLING</td>
<td>Shut down vacuum pump, switch valves ( t = 2 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>COOLING</td>
<td>Start cold water circulation, cool column to adsorption temperature ( T_{sorb} = T_{ads} )</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>AFTER COOLING</td>
<td>Stop water circulation, empty water bath around column ( t = 5 \text{ min} )</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>END CYCLE</td>
<td>End of cycle, start next cycle or shut down all devices ( t = 2 \text{ sec} )</td>
<td></td>
</tr>
</tbody>
</table>
3. Separation of concentrated CO2 from air with the TVS process

**Figure 3-2.** Photo of the experimental setup used for computer controlled adsorption/desorption cycles.

**Figure 3-3.** Photo of the electric control cabinet comprising the control and data acquisition hardware.
### 3.1.2 Data processing

The CO$_2$ adsorbed during one cycle $\Delta q^{(ads)}_\text{CO$_2$}$ (mmol CO$_2$/g sorbent material) was calculated by integrating the adsorption breakthrough profile:

$$\Delta q^{(ads)}_\text{CO$_2$} = \int_{t=0}^{t=t_{ads}} \frac{\dot{n}_{\text{air}} \cdot (c_0 - c_1)}{m_s} dt$$

(2.1)

where $t_{ads}$ is the adsorption time, $\dot{n}_{\text{air}}$ the molar flow rate of the air stream, $c_0$ and $c_1$ the CO$_2$ concentrations upstream and downstream of the cylinder, and $m_s$ the mass of the sorbent material contained in the cylinder.

The CO$_2$ desorbed during one TVS cycle $\Delta q^{(des)}_{\text{CO$_2$}, TVS}$ (mmol/g) was calculated by integrating over the desorption process:

$$\Delta q^{(des)}_{\text{CO$_2$}, TVS} = \int_{t=0}^{t=t_{des}} \frac{\dot{n}_{\text{CO$_2$}}}{m_s} dt$$

(2.2)

where $t_{des}$ is the desorption time and $\dot{n}_{\text{CO$_2$}}$ the measured molar flow rate of desorbed CO$_2$.

The CO$_2$ desorbed during one TCS cycle $\Delta q^{(des)}_{\text{CO$_2$}, TCS}$ (mmol/g) was calculated by integrating the CO$_2$ content of the argon stream leaving the cylinder, measured by the IR gas analyzer:

$$\Delta q^{(des)}_{\text{CO$_2$}, TCS} = \int_{t=0}^{t=t_{des}} \frac{\dot{n}_{\text{Ar}} \cdot c_1}{m_s} dt$$

(2.3)

where $\dot{n}_{\text{Ar}}$ is the measured molar flow rate of Ar.

### 3.2 Experimental work

#### 3.2.1 Synthesis of the sorbent material

Solvent-free surface grafting of aminosilanes was applied on the silica gel.$^{82, 83}$ 20 g silica gel beads of 2-5 mm diameter (ZEObeads™ B2, Zeochem AG, Switzerland) were dried for 3 hours at 110 °C in a natural convection oven. Afterwards, the beads were loaded into a two-neck flask equipped with a reflux condenser and 11.12 g of [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane
(AEATPMS, ABCR, Germany) were added. The mixture was heated to 150 °C in a silicone oil bath and gently stirred for 3 h under reflux. After cooling to room temperature, the solid product was washed twice in diethyl ether (J.T Baker, Netherlands), dried in ambient air for 24 h, and labeled SI-AEATPMS.

3.2.2 Material characterization

The structural properties of the sorbent material were determined by N₂ adsorption at 77 K (Micromeritics TriStar). Prior to the measurement, the samples were degassed for 2 h in dry helium at 150 °C (Micromeritics FlowPrep 060). The specific surface area was calculated by the BET method. Pore volume and average pore width were determined by the BJH method. The nitrogen and with it the amine content of the sorbent material was determined by elemental analysis (LECO CHN 900, calibration substance: acetanilide).

3.2.3 Adsorption isotherms

Adsorption of dry CO₂ at equilibrium was measured on a thermogravimetric apparatus (TG, Netzsch STA 409 CD). A sorbent sample of 50 mg (approximately 6 beads) was loaded in a ceramic crucible, which was supported on a scale for weight change monitoring. The sample temperature was measured by a thermocouple. The reactive gas entered the furnace at the bottom at atmospheric pressure, flowing upward past the sample. Mass flow rates were controlled using electronic flow controllers (Vögtlin Q-FLOW). Measurements were performed using certified gas mixtures of 200 ppm to 25% of CO₂ in Ar, pure Ar, and pure CO₂ (Messer Schweiz AG). The composition of the off-gas was analyzed by gas chromatography (2-channel Varian Micro GC, equipped with a Molsieve-5A and a Poraplot-U column, at 0.66 min⁻¹ sampling rate and 100 ppm detection limit). Before each adsorption measurement, the sample was activated under 170 mlN/min of Ar at 130 °C for 4 hours to ensure complete desorption of CO₂ and H₂O. Afterwards, the temperature was adjusted to the desired adsorption temperature of 25, 70, 90 or 110 °C and the gas flow was switched to the desired gas mixture at 170 mlN/min. Measurements were continued at isothermal conditions until the sample weight change was smaller than 0.02 mg/h to ensure that equilibrium was attained.
3.2. Experimental work

3.2.4 Packed-bed adsorption/desorption cycles

The cyclic adsorption/desorption experiments were carried out using the setup described in Section 3.1. For a typical experiment, a sample of 23.25 g of SI-AEATPMS sorbent material was used and placed in the steel cylinder. For adsorption, more than 100 m$^3$ of pressurized air with CO$_2$ content between 400 and 440 ppm were used.

Two types of measurements were carried out: (i) TVS and TCS runs under equilibrium conditions with 24 h adsorption time; and (ii) cyclic TVS and TCS runs at non-equilibrium with 3 h adsorption time. For all equilibrium runs, adsorption time was long enough to allow for complete breakthrough, i.e., the column outlet CO$_2$ concentration and relative humidity at the end of adsorption were equal to the inlet concentration and relative humidity, respectively. Hence, for fixed relative humidity during adsorption, the CO$_2$ and water uptake of the sorbent at the beginning of desorption was equal for each run. For the cyclic runs, equilibrium was not reached during adsorption, resulting in a cyclic process between non-equilibrium states. Table 3-2 lists the operational conditions and parameter ranges of the relative humidity, desorption temperature, and desorption pressure for experiments under equilibrium conditions and for cyclic runs at non-equilibrium.

### Table 3-2. Experimental parameters of TVS and TCS processes under equilibrium and cyclic operational conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equilibrium</th>
<th>Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption time</td>
<td>24 h</td>
<td>3 h</td>
</tr>
<tr>
<td>Desorption time</td>
<td>2 h</td>
<td>1.25 h</td>
</tr>
<tr>
<td>Adsorption flow rate</td>
<td>1 l$_N$/min</td>
<td>2.5 l$_N$/min</td>
</tr>
<tr>
<td>Adsorption temperature</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>Adsorption relative humidity (at 25 °C)</td>
<td>0 / 40%</td>
<td>0 / 20 / 40 / 60 / 80%</td>
</tr>
<tr>
<td>Adsorption CO$_2$ concentration</td>
<td>400 – 440 ppm</td>
<td></td>
</tr>
<tr>
<td>Desorption temperature</td>
<td>74 / 90 °C</td>
<td>74 / 82 / 90 °C</td>
</tr>
<tr>
<td>Desorption pressure</td>
<td>10 / 25 / 50 / 75 / 100 mbar$_{ab}$</td>
<td>50 / 75 / 100 / 100 / 125 / 150 mbar$_{ab}$</td>
</tr>
<tr>
<td>Desorption flow rate</td>
<td></td>
<td>0.8 l$_N$/min</td>
</tr>
<tr>
<td>(only for purge desorption)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3 Adsorption isotherm models

In order to corroborate relation (1.4) for the TVS process, the TVS equilibrium capacities measured in this chapter were compared to the corresponding adsorption isotherms, which in turn were fitted to isotherm models. For the narrow pressure range pertinent to this study (< 0.6 bar), the adsorption isotherms were found to be represented well by the Freundlich model\(^8^4\) for low temperatures (25 °C, TVS adsorption) and by the Langmuir model\(^8^4\) for high temperatures (70 – 110 °C, TVS desorption), given by the correlations:

**Freundlich model:**

\[
q_e(p) = k_F \cdot p^{1/n}
\]  

**Langmuir model:**

\[
q_e(p) = q_\infty \cdot \frac{k_L \cdot p}{1 + k_L \cdot p}
\]

3.4 Results and discussion

3.4.1 Material characterization

The BET surface area, pore volume and average pore size of the non-modified silica gel support were 422 m\(^2\)/g, 1.07 cm\(^3\)/g, and 9.4 nm, respectively. The corresponding values for the SI-AEATPMS sorbent material were 216 m\(^2\)/g, 0.65 cm\(^3\)/g, and 9.6 nm, indicating that the surface area and pore volume have been reduced through the amine-grafting process by 49% and 39%, respectively. The average pore size did not change significantly during the grafting process, presumably due to blockage of small pores by the introduced organic species. The amine content of the SI-AEATPMS material was 2.48 mmol\(_N\)/g sorbent.

3.4.2 CO\(_2\) adsorption isotherms

The adsorption isotherms of dry CO\(_2\) on SI-AEATPMS sorbent material, measured by thermogravimetry, are shown in Figure 3-4, the corresponding numerical values are shown in Table 3-3. For the measured data points, the estimated uncertainty (caused by inaccuracies in the mass and temperature
measurements) is ±2% ±0.02 mmol/g for the sorbent loading, and ±3 K for the temperature. The 25 °C isotherm is fitted well by the Freundlich model while the high-temperature isotherms are fitted by the Langmuir model with reasonable accuracy. The model parameters are displayed in Table 3-4, together with their validity range and the fitting error within the validity range based on the normalized standard deviation according to Equation (2.5)

\[
Err = \sqrt{\frac{\sum((q_{e,exp} - q_{e,mod})/q_{e,exp})^2}{N-1}}
\]  

(2.5)

where \( q_{e,exp} \) are the measured values, \( q_{e,mod} \) are the modeled values obtained from the isotherm model fits, and \( N \) is the total number of measured data points in the validity range.

Figure 3-4. Adsorption isotherms of dry CO\(_2\) on SI-AEATPMS at 25 °C (circles), 70 °C (squares), 90 °C (diamonds) and 110 °C (triangles). Solid lines correspond to fitted Freundlich (at 25 °C) and Langmuir (at 70, 90, and 110 °C) models. Measurement uncertainty is indicated by error bars.
Table 3-3. Numerical values of the adsorption isotherms of dry CO$_2$ on SI-AEATPMS. $P_{CO2}$ in (mbar), $q_e$ in (mmol/g).

<table>
<thead>
<tr>
<th>$T = 25 , ^\circ$C</th>
<th>$T = 70 , ^\circ$C</th>
<th>$T = 90 , ^\circ$C</th>
<th>$T = 110 , ^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{CO2}$ (mbar)</td>
<td>$q_e$ (mmol/g)</td>
<td>$P_{CO2}$ (mbar)</td>
<td>$q_e$ (mmol/g)</td>
</tr>
<tr>
<td>0.33</td>
<td>0.40</td>
<td>3.6</td>
<td>0.19</td>
</tr>
<tr>
<td>0.89</td>
<td>0.44</td>
<td>8.8</td>
<td>0.25</td>
</tr>
<tr>
<td>4.1</td>
<td>0.52</td>
<td>35</td>
<td>0.49</td>
</tr>
<tr>
<td>9.2</td>
<td>0.59</td>
<td>88</td>
<td>0.50</td>
</tr>
<tr>
<td>35</td>
<td>0.70</td>
<td>440</td>
<td>0.57</td>
</tr>
<tr>
<td>87</td>
<td>0.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>520</td>
<td>0.92</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3-4. Adsorption isotherm model parameters, validity range, and fitting error within the validity range. For both models, the unit for the pressure $p$ to be used in the model equation is (bar).

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Freundlich</th>
<th>Langmuir</th>
<th>Validity range</th>
<th>Fitting error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_F$ (mmol/g)</td>
<td>$n$</td>
<td>$k_L$ (1/bar)</td>
<td>$q_\infty$ (mmol/g)</td>
</tr>
<tr>
<td>25 °C</td>
<td>1.001</td>
<td>8.758</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70 °C</td>
<td>-</td>
<td>-</td>
<td>108.4</td>
<td>0.578</td>
</tr>
<tr>
<td>90 °C</td>
<td>-</td>
<td>-</td>
<td>45.1</td>
<td>0.446</td>
</tr>
<tr>
<td>110 °C</td>
<td>-</td>
<td>-</td>
<td>16.1</td>
<td>0.295</td>
</tr>
</tbody>
</table>

The shape of the 25 °C adsorption isotherm curve is in agreement with previously reported data for amine-functionalized mesoporous materials at ambient temperature.\textsuperscript{64, 85-87} The Freundlich model gives a reasonably good fit. This can be explained by the fact that the regime where physisorption overlaps chemisorption, which would require a more complex isotherm model, is presumably not reached in the pressure range considered. In particular, the linear relation of $\log(p_{CO2})$ and $\log(q_e)$ in the considered pressure and temperature range implied by the Freundlich model has been previously observed.\textsuperscript{87} Transition to Langmuir model fitting occurs in the temperature range 70 – 110 °C. One possible reason can be the fact that adsorbate-adsorbate interactions become insignificant in this temperature range.
This transition for higher temperatures is consistent with previous measurement of the 55 °C isotherm of a similar material.\textsuperscript{87} Note that the modeled adsorption isotherms are based on a relatively small number of measured data points. This is because the measurements were carried out on a thermogravimetric apparatus in which adsorption takes place at ambient pressure and the CO\textsubscript{2} partial pressure is adjusted by feeding different gas mixtures to the apparatus. This is in contrast to other devices in which the CO\textsubscript{2} partial pressure can be automatically adjusted over a large range by varying the absolute pressure in the measurement chamber. The number of data points is therefore a trade-off between accuracy and measurement effort. While the observed shapes of the isotherms, including the transition from the Freundlich model to the Langmuir model, are consistent with previous observations from the literature, an accurate analysis of the underlying mechanisms would require additional measurements providing a larger set of data points and allowing for a statistical evaluation of the measurement uncertainty. In particular the observed Langmuir shape of the isotherm at 25 °C is substantially based on a single data point at 520 mbar. On the other hand, the shape of the 25 °C isotherm at partial pressures above 0.4 mbar (corresponding to the CO\textsubscript{2} concentration in the air) is not relevant for the analysis that follows which is why no additional measurements were carried out.

### 3.4.3 TVS at equilibrium conditions with dry air

The results of the equilibrium runs for the TVS and TCS processes with adsorption in dry air on SI-AEATPMS at 25 °C are shown in Figure 3-5. The desorption capacity is plotted as a function of desorption pressure and temperature. The estimated uncertainty due to mass, flow, and concentration measurements, as well as air remainders and leaks in the system is ±6% for the TCS desorption measurements and ±4% ±0.02 mmol/g for the TVS desorption measurements. The uncertainty is indicated by error bars in Figure 3-5. Thereby, the desorption capacities are calculated from the measured gas flow at the exit of the vacuum pump according to Equation (2.2), independent of its composition. I.e., $\hat{n}_{\text{CO}_2}$ is set to the measured gas flow, assuming that it consists of pure CO\textsubscript{2} at all times. While this is not true at the beginning of the desorption due to air remainders in the system, the air volume initially exiting the vacuum pump corresponds to an equivalent volume of CO\textsubscript{2} that is being desorbed in the reactor and pushes the air out of the system. Therefore, the CO\textsubscript{2} desorption capacities provided in Figure 3-5 correspond in good approximation to the amounts of CO\textsubscript{2} being actually desorbed.
from the sorbent material during TVS desorption. These capacities differ to a certain extent, depending on the process conditions, from the amounts of CO₂ being recovered in concentrated form, which are smaller due to dilution by initial air remainders and CO₂ remainders at the end of desorption. However, providing instead the amounts of CO₂ that can be recovered in a concentrated form in this experimental setup would not be representative, since due to the small scale of the setup the effects of dilution and air/CO₂ remainders are disproportionately high compared to a scaled-up system. Providing the amounts of CO₂ that are being actually desorbed from the sorbent material is therefore more meaningful since they are much less dependent on the scale of the experiments. The effects of initial CO₂ dilution and air/CO₂ remainders for a scaled-up system are addressed separately in the modelling section of Chapter 5.

The measurement inaccuracies associated with the varying gas composition at the outlet of the vacuum pump during TVS desorption are accounted for in the error estimation. To quantify the effects of dilution on the amount of CO₂ that can be recovered in a concentrated form for this small-scale setup, an analysis of the desorption gas flow and composition is provided below for selected measurements.

As expected, the largest desorption capacities are observed for the TCS process due to the purge gas. Desorption capacities of 0.40 mmol CO₂/g sorbent (mmol/g) and 0.32 mmol/g, were measured at 90 °C and 74 °C, respectively. The corresponding amine efficiencies (moles CO₂ adsorbed per moles of amine groups) were 0.16 and 0.13, respectively. They allow assessing the ratio of the amine groups incorporated in the sorbent material that actually adsorb CO₂ and are provided here for comparison with the literature. For the TVS process, a strong dependence on both desorption temperature and pressure is evident. At 10 mbar_{abs} desorption pressure, the capacity was 0.30 mmol/g and 0.16 mmol/g for 90 °C and 74 °C desorption temperature, respectively. The former value corresponds to a total volume of 158.4 mlN of CO₂ that was desorbed from 23.25 g of the sorbent material sample during one cycle. With increasing desorption pressure, the capacity dropped dramatically until no significant CO₂ desorption was observed for desorption pressures above 50 mbar_{abs} at 74 °C and above 100 mbar_{abs} at 90 °C.
3.4. Results and discussion

Figure 3-5. TVS equilibrium desorption capacity of SI-AEATPMS as a function of the desorption pressure and TCS equilibrium desorption capacity for dry adsorption at 25 °C and desorption temperatures of 74 °C (triangles) and 90 °C (squares). Closed symbols, with error bars: values measured with packed bed; open symbols: values predicted from adsorption isotherms.

The measured peak CO₂ purity during the peak of the desorption step for the measurements at 90 °C and 10, 25, 50 mbarₐₐₜ desorption pressure was 95.8%, 93.7%, and 89.4%. Due to the above described disproportionally high dilution effects for this small-scale setup, for desorption pressures above 50 mbarₐₐₜ, where the amounts of desorbed CO₂ were very small, no meaningful purity measurements could be taken.

Figure 3-6 exemplary shows the measured desorption flow, the integrated desorbed volume, and the measured CO₂ purity for the experiment at 25 mbarₐₐₜ desorption pressure. After the initial heating phase the desorption flow rises steeply to approximately 4.5 mlN/min after around 10 minutes and decays to less than 0.5 mlN/min after one hour, marking the end of the desorption step with an accumulated desorbed volume of around 100 mlN. The CO₂ purity reaches its peak of 93.7% after 20 min desorption time, remains at that level for around 25 min followed by a relatively steep decay. The deviation of the purity level at the “peak plateau” from 100% can be accounted to leaks in the system and measurement accuracy. One reason for the decrease of the measured purity after around 45 min is the fact that approximately from this point the sample volume flow of the gas chromatograph is larger than the desorption flow and therefore air is partly drawn.
into the sample flow. From the data of Figure 3-6 it follows that around 60% of the desorbed CO$_2$ can be recovered in a concentrated form with this small-scale setup. The remaining CO$_2$ is diluted by air in the beginning of the desorption or remains in the reactor, piping, armatures, and the vacuum pump at the end of desorption.

Figure 3-7 further shows the corresponding desorption curves for the measurement at 50 mbar$_{\text{abs}}$ desorption pressure. With around 2.5 ml$_N$/min, the peak of the desorption flow attained after around 20 min desorption time is significantly smaller compared to the experiment at 25 mbar$_{\text{abs}}$ desorption pressure. The total desorbed volume is around 60 ml$_N$. Also, the purity peak is reached only after around 30 min desorption time and no purity plateau is attained. Again, the purity drop after around 30 min is attributed to air mixing with the sample volume stream, since the desorption flow is not sufficient to supply the sample flow. It can be concluded that for this experimental setup and for the analyzed experimental conditions, in particular for dry adsorption, the bulk of the desorbed CO$_2$ cannot be recovered in a concentrated form for desorption pressures above around 50 mbar$_{\text{abs}}$. However, this observation is not representative for an industrial DAC system, which will operate at a much larger scale and typically under humid conditions, which strongly influence the obtained CO$_2$ purity as shown below.

Therefore, even though from the presented measurement data it can be concluded that lower desorption pressures lead to substantially higher CO$_2$ purities, tuning of process conditions for maximum CO$_2$ purity would require measurement data of a scaled-up experimental setup. On the other hand, the fact that even for a small-scale experimental setup, CO$_2$ purities on the order of 95% can be measured confirms that

i) the thermodynamic conditions of the proposed TVS process in principle allow for desorption of essentially pure CO$_2$; and

ii) the purity for scaled-up systems will most likely at least reach these levels but can presumably be further tuned just due to the fact that air remainders and leaks in the piping have a much smaller influence for scaled-up systems.
3.4. Results and discussion

Figure 3-6. Measured desorption flow (a), integrated desorbed volume (b), and measured CO₂ purity (c) during TVS desorption at 90 °C and 25 mbar_{abs} desorption pressure after equilibrium (24 h) adsorption under dry conditions.
Figure 3-7. Measured desorption flow (a), integrated desorbed volume (b), and measured CO$_2$ purity (c) during TVS desorption at 90 °C and 50 mbar$_{abs}$ desorption pressure after equilibrium (24 h) adsorption under dry conditions.

Figure 3-8 shows the adsorption isotherms of dry CO$_2$ on SI-AEATPMS at 25 °C, corresponding to the measured TVS and TCS adsorption temperature, and at 74 and 90 °C, corresponding to the respective desorption temperatures. The isotherm at 74 °C was obtained by linear interpolation of the modeled curves according to Figure 3-4, which were derived from thermogravimetric
measurements at 70 and 90 °C. The equilibrium uptake capacities at the analyzed adsorption and desorption conditions, \( q_{e,T_{\text{ads}}} (p_{\text{ads, CO\textsubscript{2}}}) \) and \( q_{e,T_{\text{des}}} (p_{\text{des}}) \), are shown as data points on the isotherms. These points are used to predict the TVS and TCS equilibrium desorption capacities \( \Delta q_{e} \) according to Equation (1.4). Thereby, for the case of the TCS process it is assumed that the purge gas reduces the partial pressure of CO\textsubscript{2} – and therefore the equilibrium CO\textsubscript{2} uptake – to zero. While interpolating between adsorption isotherms provides only approximate values, this approach is considered appropriate here since the “distance” of the interpolation is relatively small (4 K), the two isotherms between which it is interpolated have a very similar shape, and Equation (1.4), which uses the interpolated values, is an approximation itself.

The predicted desorption capacities are plotted in Figure 3-5 and reveal good agreement with the measured values. A plausible explanation for the fact that most of the measured values are slightly above the predicted values is given by the results of Chapter 5 below, which indicate that for dry conditions air remainders are likely present in the reactor until the end of desorption. This air reduces the partial pressure of the CO\textsubscript{2} during desorption and can therefore lead to slightly higher desorption capacities than those predicted from the total desorption pressure (see also assumptions along with Equation (1.4) in Section 2.2).

For the TCS process at 74 °C, the fixed desorption time of 2 h was too short to attain equilibrium, which explains the deviation at this point. The results are consistent with previous findings where no desorption was achieved at ambient pressure without a purge gas flow,\textsuperscript{73} while a decrease of pressure and an increase of temperature had a positive effect on the desorption capacity.\textsuperscript{56}

The results of this work provide a means of rationalizing the effects of different desorption pressures and temperatures for both TVS and TCS processes using adsorption isotherms. For dry conditions, the desorption capacity for the TVS process at desorption pressures of 10 mbar\textsubscript{abs} and 25 mbar\textsubscript{abs} is approximately 75% and 50% of that for the TCS process, respectively.
3. Separation of concentrated CO\textsubscript{2} from air with the TVS process

Figure 3-8. Equilibrium dry CO\textsubscript{2} uptake at analyzed adsorption and desorption conditions plotted as data points in the adsorption isotherm diagram. Adsorption: 25 °C, 430 ppm CO\textsubscript{2} (circle); desorption: 74 °C (squares) and 90 °C (diamonds) at various desorption pressures.

Notably, it can be concluded from Figure 3-8 that – as opposed to the TVS cycle – an isothermal vacuum swing cycle\textsuperscript{70-72, 74} on SI-AEAPTMS or similar materials is unfavorable for air capture. An isothermal process can only cycle between points on the isotherm corresponding to the adsorption temperature (e.g. 25 °C). This implies that the desorption pressure needs to be considerably lower than the CO\textsubscript{2} partial pressure in the air, e.g., 20 Pa, to achieve a practical cyclic capacity, which in turn requires expensive vacuum equipment and sealings. Furthermore, a decrease of the desorption pressure from 100 mbar\textsubscript{abs} to 20 Pa\textsubscript{abs} will substantially increase the required compression work for the desorbed CO\textsubscript{2} from approximately 9.6 kJ per mol CO\textsubscript{2} captured (kJ/mol\textsubscript{CO2}) to 35 kJ/mol\textsubscript{CO2} (isothermal compression at 350 K with 70% isothermal vacuum pump efficiency, see Equation (2.6) below). Along a similar line it can be argued that any isothermal pressure swing process in which pure CO\textsubscript{2} is desorbed at ambient pressure is inapplicable for air capture. To achieve a non-zero cyclic CO\textsubscript{2} capture capacity, the air stream would need to be compressed up to a level where the partial CO\textsubscript{2} pressure raises above ambient pressure, implying an unrealistic compression to above 2000 bar. Further, the associated energy penalty would be several orders of magnitude above tolerable limits as discussed in Chapter 2.
3.4.4 TVS at equilibrium conditions with humid air

Figure 3-9 shows the results of the equilibrium runs for the TVS and TCS processes with adsorption in moist air with relative humidity $\phi_{ads, 25^\circ C} = 40\%$ at 25 °C. The measured desorption capacity is plotted as a function of desorption pressure and temperature. The estimated uncertainty is the same as that for the experiments in dry air (Section 3.4.3) and is indicated by error bars in Figure 3-9. As described above, the desorption capacities are calculated from the measured gas flow at the exit of the vacuum pump, assuming that it consists of pure CO$_2$. Thus, they correspond approximately to the amounts of CO$_2$ being actually desorbed from the sorbent material during TVS desorption. Due to technical limitations of the vacuum pump under operation with moist gases, measurements could only be taken for desorption pressures of 50 mbar$_{abs}$ and higher.

Higher adsorption capacities are observed with humid air, presumably due to the partial formation of bicarbonates instead of carbamates.$^{64, 69}$ As for the case of dry air, the TCS process yields the highest desorption capacities of 0.44 and 0.38 mmol/g at 90 and 74 °C, respectively. The corresponding amine efficiencies were 0.18 and 0.15, respectively. Interestingly for the humid TVS process, the effect of increasing the desorption pressure is much smaller compared to the dry case. For example, the desorption capacity at 90 °C only drops from 0.27 mmol/g at 50 mbar$_{abs}$ to 0.21 mmol/g at 150 mbar$_{abs}$. As for dry air, the capacity drops as the desorption temperature decreases, but even at 74 °C and 150 mbar$_{abs}$ 0.07 mmol/g are desorbed. This finding has an impact on large-scale applications of a TVS process, since increased desorption pressure leads to considerable reduction of electrical energy requirements.

The peak CO$_2$ purity at 90 °C desorption temperature and 50, 75, 100, 125, 150 mbar$_{abs}$ desorption pressure was between 96.2 and 97.6% for all measurements. This indicates that under humid conditions for desorption pressures of up to 150 mbar$_{abs}$ desorption of concentrated CO$_2$ can be achieved and even for the small-scale setup under consideration, the desorption pressure in the considered range has little influence on the observed peak purities during desorption. As for the dry case the purity can presumably be further tuned for scaled-up systems where air remainders in the piping have a smaller influence.
Figure 3-9. TVS equilibrium desorption capacities of SI-AEATPMS for different desorption pressures and TCS equilibrium capacities for moist adsorption conditions (40% RH at 25 °C) and desorption temperatures of 74 °C (triangles) and 90 °C (squares). Error bars indicate measurement uncertainty.

Figure 3-10 exemplary shows the desorption curves for the measurement at 50 mbar\textsubscript{abs} desorption pressure. The desorption flow peaks at around 5 ml\textsubscript{N}/min after around 8 min and desorption is nearly completed after one hour with a total desorbed volume of around 135 ml\textsubscript{N}. The purity curve exhibits a long plateau of maximum purity around 97% between 10 and 50 min desorption time. From the data of Figure 3-10 it follows that 73% of the desorbed CO\textsubscript{2} is recovered at a purity of >95%. It is concluded that the recovery of concentrated CO\textsubscript{2} is increased under humid conditions compared to dry conditions. This will be confirmed and quantified by the modeling results of Chapter 5.
3.4. Results and discussion

Figure 3-10. Measured desorption flow (a), integrated desorbed volume (b), and measured CO\textsubscript{2} purity (c) during TVS desorption at 90 °C and 50 mbar\textsubscript{abs} desorption pressure after equilibrium (24 h) adsorption at 40% RH.

To quantify the reproducibility of the TVS desorption measurements for the data at 50 mbar\textsubscript{abs} desorption pressure, 90 °C desorption temperature, and 40% RH during adsorption, three independent adsorption-desorption measurements were carried out. The measured adsorption capacities were 0.265, 0.266, and 0.270 mmol/g, the corresponding desorption capacities were 0.256, 0.266, and 0.269
mmol/g, indicating a closed mass balance. All values lie within a range of ±3.5% of their overall average.

The temperatures in the sorbent bed center during desorption, which are plotted as a function of desorption time in Figure 3-11, provide further insight to the effects of humidity. The curves shown in Figure 3-11 correspond to the desorption measurements at 90 °C desorption temperature after 24 h adsorption in dry (compare Figure 3-5) and humid (compare Figure 3-9) air. Initially, the slope of the temperature profiles after dry adsorption is slightly smaller than that after humid adsorption. However, at a temperature between 40 and 60 °C, depending on desorption pressure, the profiles in the humid case flatten dramatically until the temperature reaches approximately 75 °C. This is presumably caused by desorption of a considerable amount of co-adsorbed water, consuming a large portion of the heat input and consequently strongly influencing the radial temperature front propagating through the reactor during desorption. The resulting water vapor surrounding the sorbent material reduces the CO₂ partial pressure and facilitates desorption at higher overall desorption pressures. These effects are investigated in more detail in Chapter 5 by employing a detailed heat and mass transfer model of the TVS desorption process. The observed reduction of the influence of desorption pressure on desorption capacity after humid adsorption can further be promoted by a different shape of the adsorption isotherms under humid conditions associated with a change in the CO₂ adsorption mechanism.
3.4. Results and discussion

Figure 3-11. Temperature evolution in sorbent bed center during TVS desorption at 90 °C after 24 h adsorption in dry air (dashed lines) and moist air (40% RH at 25 °C, solid lines) at different desorption pressures.

3.4.5 Non-equilibrium TVS cycles

For technical applications it is not economical to cycle the sorbent material between equilibrium states. Therefore, the influence of relative humidity, desorption pressure, and temperature on the cyclic non-equilibrium CO₂ capture capacity was analyzed. The “baseline” case is φ_{ads,25 °C} = 40%, p_{des} = 50 mbar, T_{des} = 95 °C. The resulting cyclic adsorption and desorption capacities are shown in Figure 3-12 as a function of relative humidity, desorption pressure, and desorption temperature, respectively. The plotted results represent the average of the last 3 cycles of 5 cyclic runs performed for each parameter combination. The estimated measurement uncertainty is the same as for the equilibrium measurements above. Deviations between adsorption and desorption capacity are caused by inaccuracies due to small CO₂ mass flow rates and remaining air in the system during desorption.
While, as expected, the cyclic adsorption and desorption capacities were smaller compared to those obtained during equilibrium measurements, the cycle time was reduced by a factor of approximately 5. For the baseline case, the adsorption and desorption capacities were 0.16 and 0.17 mmol/g, respectively. In complete absence of moisture, the cyclic capacity was reduced by about half, whereas the differences in cyclic capacity were small among the different moisture levels. The highest cyclic capacities of 0.22/0.20 mmol/g for adsorption/desorption were observed for the TCS mode. TVS capacity decreased slightly from 0.17 to 0.13 mmol/g desorption capacity by increasing the desorption pressure from 50 to 150 mbar abs. The influence of the desorption temperature in the considered range is stronger, causing a decrease from 0.17 to 0.11 mmol/g desorption capacity by decreasing the desorption temperature from 90 to 74 °C. Generally, the effect of variation of cycle parameters is smaller for cyclic, non-equilibrium runs, since the cyclic capacity is primarily limited by the adsorption time.
3.4.6 Stability

An experimental run with 40 consecutive TVS cycles desorbing concentrated CO$_2$ was performed to verify cyclability of SI-AEATPMS sorbent material in a TVS process for air capture. The adsorption and desorption capacities for each of the 40 cycles are shown in Figure 3-13. The capacities remain satisfyingly constant within the range 0.17 – 0.19 mmol/g, indicating stability of the system for short-term operation. The adsorption breakthrough, desorption, and temperature profiles in the center of the sorbent bed during desorption are shown in Figure 3-14 for the 40 consecutive cycles. Good repeatability is observed. In particular, no fast degradation due to the formation of urea groups occurs, as previously observed for TCS cycles under dry conditions. During desorption under vacuum, sufficient humidity in the atmosphere around the sorbent material is presumably maintained, preventing urea formation.

![Figure 3-13](image_url)  
**Figure 3-13.** Adsorption/desorption capacities for 40 consecutive TVS cycles.
3. Separation of concentrated CO₂ from air with the TVS process

Figure 3-14. Adsorption breakthrough (a), desorption (b), and sorbent temperature profiles during desorption (c) for 40 consecutive TVS cycles.

3.4.7 Energy requirements

The energy required for sorbent regeneration of the TVS process includes mechanical work for CO₂ compression from desorption to ambient pressure and heat for desorption of CO₂ and co-adsorbed water as well as for the thermal swing of the sorbent material. It was estimated here using the assumptions summarized in Table 3-5. Parasitic energy requirements for initial evacuation of the system prior to desorption and for compression of desorbed water vapor that is not condensed before the vacuum pump are estimated to less than 10% of the overall energy consumption and were not considered. Further, the specific energy requirements estimated here refer to the total amount of desorbed CO₂, neglecting the fact that some of the CO₂ cannot be recovered in a concentrated form due to dilution with air at the beginning of the desorption step. As shown by the modeling results of Chapter 5 below the fraction of CO₂ that can be recovered in a concentrated form (>99%) can be assumed to be in the range of 90% to 99% of the total desorbed CO₂ for typical operating conditions of a large-scale system. The energy requirements presented here are thus underestimated by around 1% to 10% due to
this effect. An energy analysis which takes the purity of the recovered CO₂ into account is provided in Chapter 4 below. The work $W_{\text{comp}}$ required for CO₂ compression was calculated according to Equation (2.6). The heat (low-temperature heat at below 95 °C) required for heating up the sorbent material to the desorption temperature $Q_{\text{sens}}$ and for desorption of CO₂ and co-adsorbed H₂O $Q_{\text{des}}$ was calculated according to Equations (2.7) and (2.8), respectively. The total required heat $Q$ is the sum of $Q_{\text{sens}}$ and $Q_{\text{des}}$ (2.9). As a preliminary estimation, a ratio of co-adsorbed H₂O and adsorbed CO₂ of approximately 1 was assumed.⁶⁴ A more detailed quantification of H₂O co-adsorption is carried out in Chapter 4.

$$W_{\text{comp}} = \frac{1}{\eta_{\text{pump}}} \cdot R \cdot T_{\text{pump}} \cdot \ln \left( \frac{P_{\text{amb}}}{P_{\text{des}}} \right)$$

$$Q_{\text{sens}} = \frac{1}{\Delta q_{\text{CO₂,TVS}}} \cdot c_{p,s} \cdot \Delta T_{\text{TYS}}$$

$$Q_{\text{des}} = h_{\text{ads,CO₂}} + h_{\text{ads,H₂O}}$$

$$Q = Q_{\text{sens}} + Q_{\text{des}}$$

### Table 3-5. Assumptions for energy requirement estimation.

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Symbol</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclic CO₂ capacity of sorbent (SI-AEAPTMS material used in this work)</td>
<td>$\Delta q_{\text{CO₂,TYS}}$</td>
<td>0.2 mmol/g</td>
<td>this work</td>
</tr>
<tr>
<td>Cyclic CO₂ capacity of sorbent (advanced sorbent material with higher cyclic capacity)</td>
<td>$\Delta q_{\text{CO₂,TYS}}$</td>
<td>2 mmol/g</td>
<td>⁷</td>
</tr>
<tr>
<td>Amount of co-adsorbed H₂O</td>
<td>$n_{H₂O}/n_{CO₂}$</td>
<td>1</td>
<td>⁶⁴</td>
</tr>
<tr>
<td>Heat capacity of the sorbent material (silica)</td>
<td>$c_{p,s}$</td>
<td>0.9 kJ/kg/K</td>
<td>⁹⁰</td>
</tr>
<tr>
<td>Temperature difference between adsorption and desorption</td>
<td>$\Delta T_{\text{TYS}}$</td>
<td>65 K</td>
<td>this work</td>
</tr>
<tr>
<td>Vacuum pump temperature</td>
<td>$T_{\text{pump}}$</td>
<td>350 K</td>
<td>estimation</td>
</tr>
</tbody>
</table>
3. Separation of concentrated CO\textsubscript{2} from air with the TVS process

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Symbol</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of adsorption of CO\textsubscript{2}</td>
<td>$\Delta h_{ads,CO_2}$</td>
<td>$\approx 90$ kJ/mol</td>
<td>69, 87</td>
</tr>
<tr>
<td>Heat of adsorption of H\textsubscript{2}O</td>
<td>$\Delta h_{ads,H_2O}$</td>
<td>$\approx 47$ kJ/mol</td>
<td>69</td>
</tr>
<tr>
<td>Desorption pressure</td>
<td>$p_{des}$</td>
<td>100 mbar\textsubscript{abs}</td>
<td>this work</td>
</tr>
<tr>
<td>Vacuum pump efficiency (with respect to isothermal compression at T = 350 K)</td>
<td>$\eta_{pump}$</td>
<td>0.7</td>
<td>estimation</td>
</tr>
</tbody>
</table>

For the SI-AEATPMS material with an approximate cyclic CO\textsubscript{2} capture capacity of 0.2 mmol/g, the required regeneration energies are 9.6 kJ/mol\textsubscript{CO2} (61 kWh/t CO\textsubscript{2}) mechanical work and 430 kJ/mol\textsubscript{CO2} (2’710 kWh/t CO\textsubscript{2}) heat at 95 °C. Recent developments\textsuperscript{6-8} indicate that amine-based sorbent materials with much higher cyclic capacity can be developed. For example, a sorbent material with 0.9 mmol/g cyclic TVS capacity was recently presented.\textsuperscript{91} Exemplary, the thermal energy required for regenerating a sorbent with 2 mmol/g cyclic capacity is 166 kJ/mol\textsubscript{CO2} (1’050 kWh/t CO\textsubscript{2}) heat at 95 °C, while the required mechanical work remains the same as for the case of SI-AEATPMS.

For comparison, a moisture-temperature swing process for air capture\textsuperscript{5} was estimated to require 50 kJ/mol\textsubscript{CO2} mechanical work and an unspecified amount of low-temperature heat, which can potentially be supplied by internal heat recovery. The 50 kJ/mol\textsubscript{CO2} include, however, compression of the CO\textsubscript{2} to the liquid state, initial evacuation of a vacuum system, and compression of water vapor. This process consumes a substantial amount of water, which is lost by evaporation to the environment. The energy requirement for the regeneration cycle of another air capture process based on liquid CO\textsubscript{2} absorption in a sodium hydroxide solution\textsuperscript{3} was estimated to be 150 kJ/mol\textsubscript{CO2} heat at 860 °C. To the best of our knowledge, desorption of pure CO\textsubscript{2} has not been yet demonstrated with either of the two aforementioned processes.

3.5 Conclusions

A TVS process using SI-AEATPMS sorbent material was analyzed over a wide range of parameters under equilibrium and non-equilibrium (short-cycle)
3.5. Conclusions

Extraction of CO\(_2\) from air with more than 97% purity was demonstrated using mainly heat at below 95 °C as the energy input. Adsorption isotherms of dry CO\(_2\) on SI-AEATPMS were described using the Freundlich and Langmuir isotherm models. It was found that the equilibrium desorption capacities of the TVS process can be predicted from the isotherms. The influence of desorption pressure on the TVS desorption capacity under humid conditions was significantly diminished as compared to dry conditions, reducing the energy requirements of the vacuum pump. Stability was demonstrated with 40 consecutive adsorption/desorption cycles. The mechanical work requirement for sorbent regeneration is approximately 9.6 kJ/mol\(_{\text{CO}_2}\). The thermal energy requirement can be reduced from 430 kJ/mol\(_{\text{CO}_2}\) to 166 kJ/mol\(_{\text{CO}_2}\) heat at below 95 °C provided the sorbent’s cyclic CO\(_2\) capture capacity can be increased from 0.2 mmol/g to 2 mmol/g, given the recent advances in materials research described above.
4  Co-extraction of CO2 and H2O from the air\textsuperscript{e,f}

In this chapter, co-adsorption and -desorption of CO\textsubscript{2} and H\textsubscript{2}O during the TVS process is experimentally quantified. For the experiments, an amine-functionalized nanofibrillated cellulose sorbent material\textsuperscript{58} was used. This material had significantly higher CO\textsubscript{2} adsorption capacities than the one used in the previous chapter, which allowed for more accurate measurements.

As opposed to flue gases, the molar water content of air is typically one to two orders of magnitude higher than its CO\textsubscript{2} content. Thus, water adsorption per gram of sorbent material can substantially exceed CO\textsubscript{2} adsorption\textsuperscript{57, 64}. This in turn implies significant heat requirements for water desorption during sorbent regeneration. The required heat of water desorption will typically be of the same order of magnitude as the heat of evaporation of the co-adsorbed water\textsuperscript{69}. Corrosion and fouling due to condensed water vapor might also be of concern in an industrial large-scale implementation. Therefore, quantitative data on co-adsorption of H\textsubscript{2}O is important for the design of a DAC process based on a solid sorbent material.

On the other hand, if H\textsubscript{2}O is co-extracted from ambient air, major logistical benefits can be achieved in the production of synthetic liquid hydrocarbon fuels using concentrated solar energy\textsuperscript{16, 17, 19, 21}. Solar fuel production plants will be located in deserted regions of the earth’s sunbelt with vast direct solar irradiation but limited or no fresh water resources. Water co-extracted in a DAC process can thus become a valuable by-product. Note that, if seawater is accessible, fresh water extraction via reverse osmosis desalination\textsuperscript{92} is about two orders of magnitude more energy efficient than water extraction from air via adsorption.

\textsuperscript{e} Material from this chapter has been published in: Wurzbacher J. A., Gebald C., Piatkowski N., Steinfeld A. Concurrent Separation of CO\textsubscript{2} and H\textsubscript{2}O from Air by a Temperature-Vacuum Swing Adsorption/Desorption Cycle. Environmental Science & Technology, Vol. 46, pp. 9191-9198, 2012.

\textsuperscript{f} The experimental setup used for the measurements in this chapter was designed and built in collaboration with Dr. N. Piatkowski (Professorship of Renewable Energy Carriers, ETH Zurich). The sorbent material used in this chapter was synthesized in the framework of the PhD thesis of C. Gebald.
Although several proposed DAC concepts are based on amine-functionalized materials, their co-adsorption of water during CO₂ capture has hardly been quantified. Data on H₂O adsorption on an amine-based sorbent was shown for spacecraft air regeneration without CO₂ concentration. Water adsorption isotherms on amine-grafted pore expanded mesoporous silica gel were measured but only for single component adsorption. Co-adsorption of CO₂ and H₂O on amine-functionalized silica was analyzed in column-breakthrough experiments but no concentrated CO₂ was extracted.

The objective of this chapter is the detailed measurement of co-adsorption of CO₂ and H₂O during the TVS process and the analysis of the effects of varying adsorption temperature, relative humidity of the air, and desorption pressure. For this purpose we have designed an experimental setup that uses a membrane-based gas dryer to selectively extract the water vapor from the desorbed stream under vacuum conditions prior to its condensation, enabling an accurate mass balance. These measurements further enable a more reliable estimate of the energy requirements of the TVS process.

4.1 Experimental work

4.1.1 Material synthesis and characterization

The sorbent material (acronym: APDES-NFC-FD) was obtained through a one-pot reaction of an aqueous suspension of nanofibrillated cellulose (NFC) and 3-aminopropylmethyldiethoxysilane (APDES) similar to a procedure described elsewhere. A 0.5% w/w NFC hydrogel was produced by a two-step mechanical isolation process of a refined fibrous beech wood pulp suspension (Arbocel P 10111, 13.5% w/w aqueous suspension, Rettenmeier & Söhne GmbH & Co. KG, Germany). The hydrogel was further concentrated to 8.46% w/w suspension by centrifugation. 3-aminopropylmethyldiethoxysilane (APDES, 97%, ABCR, Germany, used as received) was then added to the suspension to yield a 10% w/w concentration of APDES and the suspension was incubated for 2 h. Subsequently, it was dropped into liquid N₂ to yield a frozen granulate which was freeze dried for 48 h (Leybold Lyovac GT2). The dried material was then subjected to thermal treatment at 120 °C under N₂ flow in a natural convection oven for 2 h. The final material consisted of elongated grains with an average diameter of 5 mm and an average length of 10 mm.
The BET specific surface area of the APDES-NFC-FD sorbent material was determined by N\textsubscript{2} adsorption on a Micromeritics TriStar device at -196 °C. The samples were degassed for 2 h in dry N\textsubscript{2} at 105 °C (Micromeritics FlowPrep 060) prior to the measurement. The BET surface area was 12.2 \text{m}^{2}/g.

The nitrogen content of the sorbent material was determined by elemental analysis (LECO CHN 900). The amine content, corresponding to the nitrogen content, was 3.86 mmol\textsubscript{N}/g sorbent.

4.1.2 Co-adsorption/desorption measurements

The TVS adsorption/desorption cycles were performed on a modified version of the experimental setup described in Section 3.1. Instead of the previously used 40 mm-inner diameter cylinder, a 45 mm x 45 mm rectangular reactor with an oil-filled jacket for cooling and heating was used for cyclic adsorption and desorption. It was filled with a packed bed of 10 g of sorbent material for the measurements. This larger reactor was required due to the smaller density of the sorbent material used in this study. The bed length of 80 mm was chosen to obtain a low pressure drop because a sharp breakthrough, which would require a larger bed length, was not relevant. The reactor temperature was controlled by a heating and a cooling thermostat circulating oil through the jacket. The temperature inside the sorbent bed was measured with a type-K thermocouple.

As a further modification to the setup described in Section 3.1, CO\textsubscript{2} content and RH were measured before and after the reactor with electronic sensors (Vaisala GMP343 and Vaisala HMP110, respectively, 1 Hz sampling rate), accounting for temperature and pressure compensation. Prior to each adsorption, the sensors before and after the reactor were calibrated against each other by bypassing the reactor. A schematic of the modified setup is shown in Figure 4-1, a photo is shown in Figure 4-2.

All experiments used dried, technical-grade pressurized air for adsorption obtained by compressing ambient air with a CO\textsubscript{2} content varying between 400 – 510 ppm. By comparing several otherwise equal adsorption/desorption runs with different inlet CO\textsubscript{2} concentration, it was verified that this variation has negligible effect on the results: The specific CO\textsubscript{2} adsorption/desorption capacities of APDES-NFC-FD for several otherwise equal cycles as a function of the inlet CO\textsubscript{2} concentration varying between 408 and 500 ppm are shown in Figure 4-3. The deviation is below +/- 0.025 mmol/g and thus not relevant for this study. This can
be explained with the relatively flat shape – far beyond the Henry’s law regime – of the CO₂ adsorption isotherms of amine-modified porous adsorbents even at CO₂ concentrations of as low as 400 ppm.⁶

**Figure 4-1.** Schematic of the modified experimental setup.

**Figure 4-2.** Photo of the modified experimental setup.
To quantify the amount of H$_2$O desorbed under vacuum conditions, the gas flow exiting the reactor was passed through one channel of a Nafion® membrane gas dryer (Perma Pure MD-070-72S) before entering the vacuum pump. Dried pressurized air, controlled by an electronic mass flow controller (Bronkhorst ELFLOW®), was passed through the other channel as a “drying gas” in counter-current flow configuration. The piping between the reactor and the gas dryer was heated to avoid condensation. Nearly all water vapor contained in the desorption gas diffused through the Nafion® membrane into the drying gas, as corroborated by blank experiments. This amount of H$_2$O was quantified by measuring the RH of the drying gas at the exit of the channel with an electronic sensor (Vaisala HMP110).

For comparison, the CO$_2$ adsorption capacity for 10 h adsorption at 20 °C and 0/40% RH after N$_2$ purge desorption (TCS) was measured on the experimental setup described in Section 3.1.

The CO$_2$ and H$_2$O adsorbed during a single TVS cycle $\Delta q^{(ads)}_{CO_2}$ (mmol CO$_2$/g sorbent material) and $\Delta q^{(ads)}_{H_2O}$ (mmol H$_2$O/g sorbent material) are determined by integrating the breakthrough profiles according to Equation (2.1), where for the case of CO$_2$ the inlet and outlet concentrations of CO$_2$, $c_{0,CO_2}$ and $c_{1,CO_2}$, and for the case of H$_2$O the inlet and outlet concentrations of H$_2$O, $c_{0,H_2O}$ and $c_{1,H_2O}$, are used.
The CO₂ desorbed during a single TVS cycle \( \Delta q^{(\text{des})}_{\text{CO}_2} \) (mmol CO₂/g) is determined by integrating over the desorption process according to Equation (2.2).

The H₂O desorbed during a single TVS cycle \( \Delta q^{(\text{des})}_{\text{H}_2\text{O}} \) (mmol H₂O/g) is determined by integrating over the H₂O concentration profile in the drying gas stream at the exit of the membrane gas dryer

\[
\Delta q^{(\text{des})}_{\text{H}_2\text{O}} = \int_{t=0}^{t=\text{des}} \frac{n_d \cdot c_{d,H_2O}}{m_s} \, dt \tag{3.1}
\]

where \( n_d \) is the molar flow rate of the drying gas stream and \( c_{d,H_2O} \) the H₂O concentration in the drying gas leaving the gas dryer calculated from its RH, temperature, and pressure.

The baseline operational parameters of the adsorption/desorption experiments are listed in Table 4-1. In a first measurement series (see Section 4.2.1), the adsorption parameters were varied for the purpose of evaluating the effects of adsorption temperature and RH. All other operational conditions, in particular those during desorption, were fixed. Each adsorption cycle started therefore from the same equilibrium baseline state of the sorbent material to facilitate comparison of the individual cycles with varying adsorption conditions. The adsorption time of 5 h was required to attain sufficient loading of the sorbent material, but did not lead to full adsorption equilibrium. In a second measurement series (see Section 4.2.2), the desorption pressure was varied, while the adsorption parameters were fixed. For each parameter combination, two adsorption/desorption cycles were performed to ensure reproducibility; the reported results represent the average of both cycles. All experiments use the same sorbent sample. Periodic repetitions of a standard cycle during the parametric study verified that no measurable degradation of the sample occurred.
4.2 Results and discussion

4.2.1 CO₂ and H₂O capacities for varying adsorption conditions

The results of the TVS adsorption/desorption measurements for varying adsorption temperature and RH and fixed desorption conditions (95 °C, 50 mbar\textsubscript{abs}) are shown in Figure 4-4. The specific CO₂ and H₂O adsorption/desorption capacities are plotted as function of the air RH for adsorption temperatures of 10, 20, and 30 °C. The RH was varied between 20 and 80% at 10 and 20 °C, and between 20 and 60% at 30 °C, to prevent condensation in the piping in the latter case. The CO₂ adsorption/desorption mass balance is well closed for all parameter combinations, with average deviation < 2.5%. The corresponding H₂O mass balance exhibits discrepancy for some data points, caused by inaccuracies in the RH measurement during adsorption as laid out below.

The estimated uncertainty due to mass, flow, and concentration measurements, as well as air remainders and leaks in the system is ±3.5% ± 0.025 mmol/g for CO₂ adsorption, ±4% ± 0.035 mmol/g for TVS CO₂ desorption, ±3.5% ± 1.2 mmol/g for H₂O adsorption, and ±3% ± 0.3 mmol/g for TVS H₂O desorption. The relatively large uncertainty of the H₂O adsorption data is explained as follows: Compared to its CO₂ content, the water content of the air is up to two orders of magnitude higher. Most of the water passes therefore through the reactor without being adsorbed. Hence, an offset of up to 1% RH at 20 °C between the two RH sensors

### Table 4-1. Operational parameters of the CO₂ and H₂O adsorption/desorption experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption time</td>
<td>5 h</td>
</tr>
<tr>
<td>Desorption time</td>
<td>1 h</td>
</tr>
<tr>
<td>Adsorption flow rate</td>
<td>4 l\textsubscript{N}/min</td>
</tr>
<tr>
<td>Adsorption temperature</td>
<td>10/20/30 °C</td>
</tr>
<tr>
<td>Adsorption relative humidity (at adsorption temperature)</td>
<td>20/40/60/80%</td>
</tr>
<tr>
<td>Adsorption CO₂ concentration</td>
<td>400-510 ppm</td>
</tr>
<tr>
<td>Desorption temperature</td>
<td>95 °C</td>
</tr>
<tr>
<td>Desorption pressure</td>
<td>10/50/150 mbar</td>
</tr>
</tbody>
</table>
4. Co-extraction of CO2 and H2O from the air

before and after the reactor, which was observed during sensor equilibration, leads
to an inaccuracy of 1.2 mmol/g in the calculated amount of adsorbed water as
shown by Equation (3.2). Thus, the more accurate desorption values are used in the
analysis that follows.

\[
\left( \Delta q_{H_2O}^{(ads)} \right)_{\text{actual}} - \left( \Delta q_{H_2O}^{(ads)} \right)_{\text{observed}} =
\int_{t=0}^{t=\text{4 min}} \frac{n_{\text{air}} \cdot (c_{0,H_2O} - c_{1,H_2O})}{m_s} dt - \int_{t=0}^{t=\text{4 min}} \frac{n_{\text{air}} \cdot \left( c_{0,H_2O} - c_{1,H_2O} + \frac{1\% \cdot p_{\text{vap}}}{p_{\text{tot}}} \right)}{m_s} dt =
\int_{t=0}^{t=\text{4 min}} \frac{n_{\text{air}} \cdot \left( 1\% \cdot p_{\text{vap}} \right)}{m_s} dt
\]

(3.2)

Further, the experimental reproducibility can be quantified from the observed
deviation between the two measurements that were taken for each data point: The
maximum deviations during all of the measurements in this chapter for CO2
adsorption, desorption, as well as H2O adsorption, and desorption were 0.023,
0.032, 1.0, and 0.15 mmol/g.
Figure 4-4. Specific CO₂ and H₂O adsorption/desorption capacities of APDES-NFC-FD in the TVS cyclic process as a function of the air relative humidity for adsorption temperatures of 10 °C (a), 20 °C (b), and 30 °C (c) and 50 mbar desorption pressure. Error bars describing the measurement uncertainty of the desorption data points are shown at the right-hand side of each data point.
At 10 °C adsorption temperature, the CO₂ capacity increases from 0.36 mmol/g at 20% RH to 0.63 mmol/g at 80% RH, corresponding to amine efficiencies (moles CO₂ adsorbed per moles of amine groups) of 0.09 and 0.16, respectively. At 20 °C adsorption temperature, the CO₂ capacity varies from 0.39 mmol/g at 20% RH to 0.65 mmol/g at 80% RH. At 30 °C, it varies from 0.32 mmol/g at 20% RH to 0.50 mmol/g at 60% RH. The amine efficiencies are lower than reported elsewhere, because (i) the adsorption process was stopped after 5 hours before attainment of the complete full capacity, and (ii) desorption under TVS conditions, while resulting in a stream of concentrated CO₂, is known to yield lower capacities than desorption under inert purge gas, which results in a stream of diluted CO₂. The purity of the desorbed CO₂ for all data points was between 94.4% and 96.7%. The corresponding H₂O capacity at 10 °C adsorption temperature increases from 0.87 mmol/g at 20% RH to 4.20 mmol/g at 80% RH. At 20 °C adsorption temperature, the H₂O capacity increases from 0.94 at 20% RH to 4.76 mmol/g at 80% RH. At 30 °C, it increases from 0.96 at 20% RH to 3.02 mmol/g at 60% RH.

For the purpose of comparison with published data, Figure 4-4b contains in addition the values of the adsorption capacities of 0.82 and 0.94 mmol/g measured for 10 h adsorption at 0 and 40% RH, respectively after N₂ purge desorption.

Evidently, the measurements reveal a strong promoting effect of the RH during adsorption on both CO₂ and H₂O capacities for all investigated adsorption temperatures. The influence is larger on H₂O adsorption than on CO₂ adsorption. For example, the H₂O capacity increases by a factor of 5 while the CO₂ capacity increases by a factor of 1.7 when the RH varies from 20% to 80% at 20 °C adsorption temperature. These results are in agreement with the generally known promoting effect of humidity on CO₂ adsorption on amine-functionalized solid sorbent materials. The fact that a higher level of RH leads to a stronger increase of the CO₂ capacity has been previously observed. H₂O co-adsorption of 4.7 and 7.29 mmol/g was observed for 27% and 64% RH, respectively, on amine functionalized mesoporous silica that was regenerated by purging inert gas. Our results quantify for the first time the promoting effect of the RH of air on the co-adsorption/desorption capacities of CO₂ and H₂O for the TVS process extracting concentrated CO₂ from air.

While the detailed mechanisms of binary adsorption of CO₂ and H₂O are not yet fully understood, hydrogen bonding with the surface functional groups and multilayer adsorption have been proposed as general mechanisms for the co-adsorption of H₂O and CO₂ on porous sorbent materials. On cellulose fibrils, H₂O...
molecules are assumed to mainly adsorb in multilayers on the cellulose hydroxyl surface groups.\textsuperscript{97} Besides the chemical interaction of H\textsubscript{2}O and CO\textsubscript{2} with the surface functionalities, the smaller van der Waals diameter of H\textsubscript{2}O molecules compared to that of CO\textsubscript{2} molecules\textsuperscript{96} can be one reason for the observed H\textsubscript{2}O capacities largely exceeding the corresponding CO\textsubscript{2} capacities. Moreover, multilayer adsorption of H\textsubscript{2}O is presumably responsible for the stronger increase of the H\textsubscript{2}O capacity with RH \textit{vis-à-vis} that of the CO\textsubscript{2} capacity.

The TVS adsorption/desorption CO\textsubscript{2} capacities achieved in this study for an amine-functionalized nanofibrilated cellulose sorbent are about twice higher than those obtained previously for an amine-functionalized silica gel sorbent (see Chapter 3), while adsorption time was only 5 h instead of 24 h. This is associated with the higher amine content of the APDES-NFC-FD sorbent used in this study and its more favorable adsorption kinetics.\textsuperscript{58} In another TVS study, a CO\textsubscript{2} capacity of 0.13 mmol/g under moist conditions was reported for an amine-grafted silica sorbent.\textsuperscript{10}

From Figure 4-4 and Figure 4-5, which shows the desorption capacities as a function of the adsorption temperature, it can be seen that the influence of the adsorption temperature on the CO\textsubscript{2}/H\textsubscript{2}O capacities at fixed RH is minor. For example, the CO\textsubscript{2} capacities for adsorption temperatures of 10, 20, and 30 °C at a fixed 40% RH are 0.42, 0.44, and 0.38 mmol/g, respectively. The corresponding H\textsubscript{2}O capacities are 1.67, 1.69, and 1.74 mmol/g, respectively. Since the RH at different adsorption temperatures does not reflect the absolute water content of the air, the measured capacities are also plotted as a function of the partial pressure of H\textsubscript{2}O in Figure 4-6. For clarity, only the desorption values are shown. It becomes evident that, at constant H\textsubscript{2}O partial pressure, both CO\textsubscript{2} and H\textsubscript{2}O capacities strongly decrease with increasing adsorption temperature. For example, at a partial H\textsubscript{2}O pressure of about 9 mbar, the H\textsubscript{2}O capacities at 10, 20, and 30 °C are 4.20, 1.69, and 0.96 mmol/g, respectively. The corresponding CO\textsubscript{2} capacities are 0.63, 0.44, and 0.32 mmol/g, respectively. This coherence is a direct consequence of the relation between the three variables H\textsubscript{2}O partial pressure, temperature, and RH, of which only two are independent and the respective third one can be calculated from the corresponding vapor pressure of H\textsubscript{2}O.
4. Co-extraction of CO₂ and H₂O from the air

Figure 4-5. Specific CO₂ (a) and H₂O (b) desorption capacities in a TVS cyclic process as a function of the adsorption temperature at different relative humidity levels and 50 mbar abs desorption pressure. Error bars describe the measurement uncertainty.
Therefore, describing the H₂O/CO₂ capacities as a function of the relative humidity turns out to be most convenient, since this representation is nearly independent of the adsorption temperature in the temperature range considered in this study. This is in agreement with other studies in which water adsorption was observed to be only marginally influenced by temperature at constant RH.⁹⁸, ⁹⁹ In fact, both the strong temperature dependence of the adsorption capacities at constant H₂O partial pressure (Figure 4-6) and the negligible dependence at constant RH are predicted from thermodynamic principles. According to the Clausius-Clapeyron equation, the temperature dependence of the adsorption capacity scales with the isosteric heat of adsorption. As shown elsewhere,¹⁰⁰ when the H₂O capacity is expressed as a function of H₂O partial pressure, the

Figure 4-6. Specific CO₂ (a) and H₂O (b) desorption capacities in a TVS cyclic process as a function of the H₂O partial pressure for adsorption temperatures of 10, 20, and 30 °C and 50 mbar_{abs} desorption pressure. Error bars describe the measurement uncertainty.
corresponding isosteric heat of adsorption to be used for the evaluation of the Clausius-Clapeyron equation is the total heat of adsorption, \textit{i.e.}, the sum of the “net” heat of adsorption and the latent heat of evaporation. On the other hand, when the H$_2$O capacity is expressed as a function of RH, the Clausius-Clapeyron equation needs to be evaluated by using the “net” heat of adsorption only. The latter is relatively small, since the heat of adsorption for amine modified sorbent materials is known to approach the value of the heat of H$_2$O evaporation.$^{69}$

While thermodynamics predict a marginal decrease of the CO$_2$/H$_2$O capacities with increasing temperature, the observed minimal increase for several data points (Figure 4-5) is attributed to – besides measurement uncertainty – the non-ideal behavior of the binary CO$_2$/H$_2$O system.$^{96}$ For the CO$_2$ capacities further overlapping of equilibrium and kinetic effects is likely.

While a detailed analysis of mass transfer during adsorption is not targeted here, in order to compare the rates of CO$_2$ and H$_2$O adsorption, the breakthrough curves at 20 °C adsorption temperature and 40% RH are shown in Figure 4-7. Breakthrough of water occurs much faster than that of CO$_2$, which is consistent with previous results obtained with diluted CO$_2$ streams.$^{57}$ After approximately 1 h, H$_2$O adsorption reaches completion while CO$_2$ adsorption does not reach equilibrium within 5 h adsorption time. Thus, longer adsorption times yield higher CO$_2$ to H$_2$O adsorption ratios for a DAC process. This is confirmed by Figure 4-8, which shows the cumulative CO$_2$ and H$_2$O uptakes over the adsorption process for 20 °C adsorption temperature and various RH. After 5 h adsorption time, the CO$_2$ uptake curves are still considerably increasing while the corresponding H$_2$O curves have reached a constant plateau for all RH values. Slight variations are due to sensor deviations. Further, the CO$_2$ uptake curves exhibit the same profile for all RH levels, indicating the same underlying rate controlling mechanism determined presumably by diffusion and surface reaction with the amine groups.
4.2. Results and discussion

Figure 4-7. CO$_2$ and H$_2$O adsorption breakthrough curves at 20 °C adsorption temperature and 40% RH.

Figure 4-8. CO$_2$ (a) and H$_2$O (b) uptake during adsorption at an adsorption temperature of 20 °C and an air relative humidity of 20, 40, 60, and 80%.
4.2.2 CO₂ and H₂O capacities for varying desorption pressure

The results of the TVS adsorption/desorption measurements for varying desorption pressure are shown in Figure 4-9 and Figure 4-10 (zoom of Figure 4-9). The specific CO₂ and H₂O adsorption/desorption capacities are plotted as function of the desorption pressure, which was varied between 10 and 150 mbar\(_{abs}\), for relative humidity levels during adsorption of 40% and 80%, respectively. The adsorption temperature was kept constant at 20 °C for all experiments.

The CO₂ adsorption/desorption mass balance is well closed for 10 and 50 mbar\(_{abs}\) desorption pressure (average deviation < 2.5%) while for 150 mbar\(_{abs}\) desorption pressure the deviation between adsorption and desorption values is up to 0.1 mmol/g, presumably due to air/CO₂ remainders in the dead volume of the system, which are more significant for higher desorption pressures. The H₂O mass balance exhibits discrepancy for some data points, caused by the above described inaccuracies in the RH measurement during adsorption. Therefore, the more accurate H₂O desorption values are used in the following.

At 40% RH during adsorption, the CO₂ desorption capacity drops from 0.48 to 0.37 mmol/g as the desorption pressure is increased from 10 mbar\(_{abs}\) to 150 mbar\(_{abs}\). At the same time, the H₂O desorption capacity changes slightly from 1.5 to 1.3 mmol/g. At 80% RH, the corresponding CO₂ capacity drops from 0.66 to 0.58 mmol/g, while the H₂O capacity remains constant at 4.3 mmol/g. The observed, slight dependence of the CO₂ adsorption capacity on the desorption pressure for the humid case is in agreement with the findings of Chapter 3 (see Figure 3-9). On the other hand, considering the measurement uncertainty, it can be concluded that the H₂O adsorption/desorption capacity remains essentially constant in the analyzed desorption pressure range. E.g., for 80% RH, the H₂O desorption capacities remain within ±3%, while the desorption pressure is reduced 15-fold. This is in agreement with expectations since, as described in Section 4.2.1, the heat of adsorption of the water is very small compared to its heat of evaporation and water desorption is therefore approximatively determined by the vapor pressure of the water. Since in the complete parameter range considered the desorption pressure is substantially lower than the vapor pressure of water at 95 °C (desorption temperature), it can be assumed that substantially all of the adsorbed water is desorbed during each desorption cycle.
Therefore, the optimization of the desorption pressure for a scaled-up system should primarily be carried out with respect to the CO$_2$ desorption capacity and its influence on the H$_2$O desorption capacity can be neglected in a first step.

![Graph](image-url)

**Figure 4-9.** Specific CO$_2$ and H$_2$O adsorption/desorption capacities of APDES-NFC-FD in the TVS cyclic process as a function of the desorption pressure for 20°C adsorption temperature and air relative humidity during adsorption of 40% (a) and 80% (b). Error bars describing the measurement uncertainty of the desorption data points are shown at the right-hand side of each data point.
4. Co-extraction of CO₂ and H₂O from the air

4.2.3 Multicycle experiment

The stability of the material and repeatability of the measurements are examined by performing 10 equal, consecutive adsorption/desorption cycles. The adsorption temperature and RH were fixed at 20 °C and 40%, respectively and the desorption pressure was fixed at 50 mbar\textsubscript{abs}. The measured CO₂ and H₂O adsorption/desorption capacities for each cycle are shown in Figure 4-11. The CO₂ adsorption/desorption values remain stable over all cycles and the corresponding mass balance is accurately closed. The average adsorbed and desorbed amounts of CO₂ are 0.415 mmol/g and 0.421 mmol/g, respectively. The amount of desorbed
H$_2$O also remains stable with an average of 1.73 mmol/g. The water adsorption/desorption mass balance is well closed for cycles 3, 4, 5, 8, and 9. For the other cycles, discrepancy is associated with the sensitivity of the H$_2$O adsorption measurement to small drifts in the RH measurements.

![Figure 4-11. Specific adsorbed/desorbed amounts of CO$_2$ and H$_2$O in multi-cycle experiment at an adsorption temperature of 20 °C and an air relative humidity of 40%.

4.2.4 Energy requirements

Based on the CO$_2$ and H$_2$O capacities measured in this chapter for the cellulose-based sorbent material, the energy consumption of a TVS process can be estimated in more detail and the influence of the adsorption conditions can be quantified. Therefore, the mechanical compression work of desorbed CO$_2$, heat of desorption of CO$_2$ and H$_2$O, and heat for the thermal swing of the sorbent material are considered. As an extension to the energy calculations in Chapter 3, the thermal mass of the adsorbed species is also considered. Their heat capacities were approximated by the pure component heat capacities of gaseous CO$_2$ and liquid H$_2$O, respectively. Parasitic losses such as pressure drops across pipes, heat losses, and heat transfer irreversibilities are omitted from consideration. For the molar amount of desorbed water per mole of desorbed CO$_2$ the ratios of the measured values in this work are used. The assumptions are summarized in Table 4-2.
The energy requirement for sorbent regeneration in the TVS process is given by the electrical input $W_{comp}$ for operating the vacuum pump (3.3), the heat input $Q_{sens}$ for bringing the sorbent material to the desorption temperature (3.4), and the heat input $Q_{des}$ for the desorption enthalpies of CO$_2$ and H$_2$O (3.5). Equation (3.3) is identical to Equation (2.6) and is repeated here for convenience. The specific sensible heat, heat of desorption, and total required heat in kJ per mole of CO$_2$ separated are shown in Table 4-3 for 10, 20 and 30 °C adsorption temperatures and 20, 40, 60, and 80% RH. These values refer to the total amount of desorbed CO$_2$ independent of its purity.

\[ W_{comp} = \frac{1}{\eta_{pump}} \cdot R \cdot T_{pump} \cdot \ln \left( \frac{P_{amb}}{P_{des}} \right) \quad (3.3) \]

\[ Q_{sens} = \left( \frac{1}{\Delta q_{CO_2}^{(des)}} \cdot c_{p,s} + c_{p,CO_2} + \frac{\Delta q_{H_2O}^{(des)}}{\Delta q_{CO_2}^{(des)}} \cdot c_{p,H_2O} \right) \cdot (T_{des} - T_{ads}) \quad (3.4) \]
For example, at 20 °C adsorption temperature and 20% RH, the measured amounts of desorbed CO\textsubscript{2} and H\textsubscript{2}O are 0.39 mmol/g and 0.94 mmol/g, respectively, and the corresponding required total heat is 493 kJ/mol\textsubscript{CO2} (3’110 kWh/t CO\textsubscript{2}). On the other hand, increasing the RH to 80% while keeping all other parameters results in an increase in the amount of desorbed CO\textsubscript{2} and H\textsubscript{2}O to 0.65 mmol/g and 4.76 mmol/g, respectively, while the corresponding required heat is increased to 639 kJ/mol\textsubscript{CO2} (4’030 kWh/t CO\textsubscript{2}). The required mechanical work for the vacuum pump is 12.5 kJ/mol\textsubscript{CO2} (79 kWh/t CO\textsubscript{2}) for all cases. Thus, although a higher RH significantly promotes CO\textsubscript{2} adsorption and, consequently, reduces the mass of the sorbent material per mole of adsorbed CO\textsubscript{2} and the corresponding sensible heat input, the overall heat consumption may still increase with RH due to disproportionately higher co-adsorption of H\textsubscript{2}O and the corresponding heat of desorption. Therefore, unless increased water adsorption is

\[ Q_{\text{des}} = \Delta h_{\text{ads,CO}_2} + \frac{\Delta q_{\text{H}_2\text{O}}^{(\text{des})}}{\Delta q_{\text{CO}_2}^{(\text{des})}} \cdot \Delta h_{\text{ads,H}_2\text{O}} \]  

\[ (3.5) \]
explicitly desired despite the associated energy penalty – e.g., when a source of fresh water such as that obtained via reverse osmosis desalination of seawater is unavailable – it will be more favorable to operate the DAC system in air with low RH. In contrast, the effect of the adsorption temperature on the energy consumption is less pronounced. For example, the total required heats for a TVS at 10 and 30 °C adsorption temperatures and 40% RH are 588 kJ/mol\textsubscript{CO2} and 575 kJ/mol\textsubscript{CO2}, respectively. These effects have evidently an impact on the economic viability of the DAC process, especially when evaluating the costs of the sorbent material and the energy requirements.

For practical applications, the specific energy requirements of the process are more meaningful if they are provided in energy per amount of CO\textsubscript{2} that can be extracted at a given purity level. Therefore, the results regarding the purity of the desorbed CO\textsubscript{2} that are obtained with the heat and mass transfer model of Chapter 5 below are used to correspondingly convert the specific energy requirements given in Table 4-3 for 20 °C adsorption temperature. In Table 4-4 the fraction of the desorbed CO\textsubscript{2} that can be recovered at >99% purity (“recovery fraction”) as calculated with the model for a desorption pressure of 50 mbar\textsubscript{abs} and RH during adsorption between 20% and 80% is shown. The details of the modelling are described in Chapter 5. Based on these values, the converted specific heat requirements per mol CO\textsubscript{2} extracted at >99% purity are listed.

Naturally, the converted specific energy requirements are slightly higher than the ones presented in Table 4-3; however, due to the relatively large recovery fractions of concentrated CO\textsubscript{2} the values are similar. The converted values still indicate that it is advantageous from an energy consumption point of view to operate the system at lower RH. Yet, the differences are smaller, since the recovery fractions are smaller for lower RH. For example, the specific heat requirement only increases from 541 kJ/mol CO\textsubscript{2} extracted at >99% purity at 20% RH to 646 kJ/mol at 80% RH. This shows that at least in the analyzed parameter range the influence of the RH on the specific energy consumption is smaller, if it is considered per ton of CO\textsubscript{2} extracted at a given purity level.
Table 4-4. Heat requirements for sorbent regeneration per mol CO₂ extracted at >99% purity at 20 °C adsorption temperature and various relative humidities.

<table>
<thead>
<tr>
<th>% RH</th>
<th>%</th>
<th>kJ/molCO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>91</td>
<td>541</td>
</tr>
<tr>
<td>40</td>
<td>96</td>
<td>558</td>
</tr>
<tr>
<td>60</td>
<td>98</td>
<td>586</td>
</tr>
<tr>
<td>80</td>
<td>99</td>
<td>646</td>
</tr>
</tbody>
</table>

Figure 4-12 shows the requirements of heat at below 100 °C of the TVS process as a function of the specific CO₂ adsorption/desorption capacity varying between 0.5 mmol/g (experimentally verified in this study) to 2 mmol/g (targeted for an optimized sorbent), independent of the purity of the recovered CO₂. The adsorption temperature is 20 °C. The specific H₂O capacity is assumed to be 2.4, 3.9, 5.4, and 7.3 times that of CO₂ as measured in this work for 20, 40, 60, and 80% RH, respectively. At a H₂O:CO₂ capacity ratio of 2.4, the heat requirement decreases from 429 to 272 kJ/molCO₂ (1’720 kWh/t CO₂) when the specific CO₂ capacity increases by a factor of 4 from 0.5 to 2 mmol/g. At a H₂O:CO₂ capacity ratio of 7.3, it decreases from 687 to 530 kJ/molCO₂ (3’350 kWh/t CO₂). The required mechanical work remains constant at 12.5 kJ/molCO₂ for all cases. A higher CO₂ capacity beyond 2 mmol/g results in an ever decreasing heat requirement because the contribution of the sensible heat term becomes less significant. On the other hand, the influence of the specific H₂O capacity on the heat requirement is much larger, which again justifies its accurate quantification as accomplished in this study.
Figure 4-12. Requirement of heat at below 100 °C of the TVS process as a function of the specific CO₂ adsorption/desorption capacity, for the measured H₂O:CO₂ capacity ratios at 20 °C adsorption temperature.

4.3 Conclusions

CO₂ extraction from ambient air using the TVS cycle was demonstrated using a novel, amine-functionalized nanofibrillated cellulose sorbent material. The material had a higher CO₂ adsorption capacity than the silica-based sorbent material used for the analysis in Chapter 3 and thus allowed for more differentiated measurements. Up to 0.65 mmol/g cyclic TVS CO₂ capacity were observed. A novel experimental setup was successfully applied to measure the amount of co-adsorbed H₂O for both, TVS adsorption and desorption. A closed mass balance for CO₂ and H₂O was achieved and a detailed set of CO₂ and H₂O adsorption/desorption capacity data for adsorption conditions between 10 and 30 °C and 20 and 80% RH was generated. Both, CO₂ and H₂O adsorption were strongly promoted by increasing relative humidity. Further, it was found that a reduction of the desorption pressure had a slightly promoting effect on the cyclic CO₂ capacity but a negligible effect on the cyclic H₂O capacity.

Following up on the energy considerations of Chapter 3, a more detailed energy analysis was carried out taking into account the influence of different adsorption conditions, in particular the relative humidity. It was found that despite the promoting effect of the RH on CO₂ adsorption, the energy consumption for desorption slightly increases with raising RH during adsorption due to increased
co-adsorption of H\textsubscript{2}O. Given the above described, recent advances in material research that have revealed materials with, \textit{e.g.}, 0.9 mmol/g cyclic TVS capacity, the energy analysis was carried out for materials with up to 2 mmol/g cyclic TVS capacity. For such an optimized targeted sorbent material, the total heat requirement for desorption is estimated between 1’720 and 3’350 kWh/t CO\textsubscript{2} for relative humidities varying between 20 and 80\%, respectively. This shows that the target heat consumption of a DAC system to be powered by the waste heat of a fuel synthesis process of 1’750 – 2’700 kWh/t CO\textsubscript{2} can in principle be met by the TVS process investigated here, at least for moderate to medium RH levels during adsorption.
5 Heat and mass transfer of TVS desorption

This chapter describes the detailed investigation of heat and mass transfer during the TVS desorption process. The general reactor design guideline for the TVS process strives to an efficient mass transfer during the adsorption step and an efficient heat transfer during the desorption step. This is because both, high adsorption rates of CO₂ from the air flow and fast and uniform heating and corresponding high desorption rates imply shorter cycle durations and can in turn substantially reduce the capital costs of a DAC system. However, heating a highly porous bed of solid sorbent material under vacuum conditions with an external heat source is challenging because of the inherent poor thermal conductivity and negligible convective heat transfer.

Several modeling efforts were undertaken for CO₂ capture systems, but focused exclusively on the adsorption step for predicting column breakthrough curves. Previous studies from other fields have analyzed the heat transfer during regeneration of H₂O-loaded zeolite beds; however, their results are not directly applicable here because the TVS process for DAC is mainly driven by the interaction of adsorption, desorption, and mass transfer of both CO₂ and H₂O.

Here, a rigorous heat and mass transfer model of the TVS desorption step for DAC was developed and applied to a packed bed of amine-functionalized sorbent material to enable a better understanding of the TVS process. The main target was to analyze the radial heat transfer into the sorbent bed and the composition of the gas atmosphere in the reactor and that of the recovered gas stream during desorption, since these factors are crucial for the performance and the lifetime of a scaled-up design. The model was developed with focus on these aspects. The model accounts for heat conduction, heat capacities of the sorbent material and of the adsorbed and gas phase species, desorption and re-adsorption of CO₂ and H₂O, as well as diffusion and convection of the gas phase species CO₂, H₂O, and air. For the purpose of model validation, a set of experiments on a laboratory-scale TVS packed-bed reactor was performed and the measured and simulated temperature distributions were compared. As it will be shown in the analysis that follows, the

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Material from this chapter has been submitted for publication: Wurzbacher J. A., Gebald C., Brunner S., Steinfeld A. Heat and Mass Transfer of Temperature-Vacuum Swing Desorption for CO₂ Capture from Air. 2015.
model enables insight into the gas phase composition and the sorbent loading in the reactor cross section during the desorption process as well as the achievable CO₂ desorption capacities at a certain purity level for a broad range of operating conditions.

5.1 Experimental work

5.1.1 Material synthesis and characterization

The sorbent material (acronym: APDES-NFC-FD-S) was synthesized through a scaled-up one-pot reaction of an aqueous suspension of nanofibrillated cellulose (NFC) and 3-aminopropylmethyldiethoxysilane (APDES) similar to the procedure described in Section 4.1.1.58, 78 150 g of 3-aminopropylmethyldiethoxysilane (APDES, 97%, ABCR, Germany, used as received) was mixed with 1183.4 g of deionized water at room temperature for 15 h. The solution was thereupon mixed with 1666.6 g of fibrillated cellulose suspension (Borregaard SA, 9% w/w in deionized water) and further stirred at room temperature for 3 h. The suspension was frozen by pressing it through a perforated metal plate into a box containing liquid N₂. The obtained frozen granulate was freeze dried for 48 h (Telstar, Lyoquest -85) and subsequently further air dried at 50 °C in an oven for 1 h. The nitrogen content of the APDES-NFC-FD-S sorbent material was determined by elemental analysis (LECO CHN 900) and was 3.40 mmol N/g sorbent.

5.1.2 Thermal conductivity measurement

The effective thermal conductivity $k_{\text{eff}}$ of APDES-NFC-FD-S was measured with a laboratory hot plate device that was specially designed for small samples with low thermal conductivities.108 The cold and hot plate temperatures were set at 12 °C and 31 °C, respectively. A cubic 50 x 50 x 12 mm³ sample of packed sorbent material, initially dried for 60 min in N₂ at 90 °C, was contained in a sealed plastic foil for measurements at $p = 18$ mbar, $100$ mbar, and ambient pressure. The corresponding $k_{\text{eff}}$ were 45, 45, and 44 mW/m/K with an estimated uncertainty of ±2 mW/m/K. Thus, the influence of $p$ on $k_{\text{eff}}$ can be neglected for the ranges relevant in this study. Pictures of the sorbent sample and the setup are shown in Figure 5-1.

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h The thermal conductivity measurements were carried out in collaboration with Dr. S. Brunner (Laboratory of Building Science and Technology, Empa Dübendorf)
5.1. Experimental work

Figure 5-1. Picture of the sorbent sample in a sealed plastic foil (left-hand side) and the setup for measuring thermal conductivity (right-hand side).

5.1.3 CO₂ and H₂O adsorption capacity measurements

The total CO₂ and H₂O loadings of the APDES-NFC-FD-S sorbent material for different adsorption temperatures, relative humidities, and CO₂ concentrations after regeneration in dry N₂ were determined with a simplified version of the setup described in Section 3.1. A schematic is shown in Figure 5-2.

A sample of 1 g of APDES-NFC-FD-S sorbent material was loaded into a cylindrical, 40 mm-inner diameter, 30 mm-height packed bed reactor equipped with an electrical heating foil and a fan for temperature control. During adsorption, either dried, technical-grade pressurized air with a CO₂ content of 450 ppm, pure CO₂, or a mixture of both was used. The flow rate was controlled between 0.1 l_N/min (for pure CO₂ adsorption) and 1 l_N/min (for air adsorption) using two electronic mass flow controllers (Buerkert).

For measuring H₂O/CO₂ adsorption under humid conditions, the desired RH was adjusted by passing the gas flow through a bubbler-type humidifier placed inside a temperature-controlled water bath. The experimental duration of the adsorption phase was 1 h for H₂O adsorption and 10 h for dry and humid CO₂ adsorption. Subsequently, desorption was performed by heating the reactor for 60 min to 90 °C under 1 l_N/min dry N₂ flow. The H₂O loadings were determined during adsorption through integration of the H₂O breakthrough curve recorded with an electronic RH sensor (Vaisala HMP110). The CO₂ loadings were determined during desorption through integration of the CO₂ content in the desorption gas stream recorded by an electronic CO₂ sensor (Vaisala GMP343).
5. Heat and mass transfer of TVS desorption

5.1.4 Packed bed TVS desorption measurements

To verify the results predicted by the heat and mass transfer model, the temperature profiles within a packed bed of sorbent material during TVS desorption were determined using a scaled-up, rectangular reactor with 72 mm x 72 mm cross section and 500 mm length. It was equipped with an oil-filled jacked for heating and cooling and was made of aluminum to ensure a uniform temperature distribution at its walls. 85.9 g of APDES-NFC-FD-S sorbent material were filled into the entire cross-section of the reactor over a length of 299 mm. The density of the material in the packed bed was therefore 55.4 kg/m³. The resulting rectangular block of sorbent material was fixed between two perforated aluminum plates which were arranged the way that at the entrance and the exit of the reactor a space of approx. 100 mm length was left free of sorbent material in order to minimize boundary effects. A K-type thermocouple attached to the inner reactor wall was used to monitor the wall temperature and another K-type thermocouple was placed in the center of the sorbent material block by using a ceramic guiding tube. A cross section of the reactor geometry is shown in Figure 5-3; pictures are
shown in Figure 5-4. The reactor was operated within a simplified version of the setup described in Section 4.1.2. A schematic is shown in Figure 5-5.

![Figure 5-3. Cross section of the TVS reactor.](image)

![Figure 5-4. Picture of the scaled-up aluminum reactor within the experimental setup (left-hand side); internal view of the reactor (right-hand side).](image)
Before M1, the sorbent material was heated to 90 °C for 2 h and then cooled to 20 °C under a flow of 2 l/min of dry N₂. For M2, adsorption was carried out by passing 14 l/min of dry air through the sorbent material. For M3, a stream of 7 l/min of dry air and a stream of 7 l/min air that had passed through a bubbler-type humidifier were mixed before the reactor to set the RH to 58.3%. Dried, technical-grade pressurized air with a CO₂ content of 400 to 490 ppm was used, controlled by two electronic mass flow controllers (Bronkhorst EL-FLOW®). The adsorption was stopped after the outlet CO₂ concentration had reached the inlet CO₂ concentration within a tolerance of +/- 15 ppm (18 h for M2 and 12 h for M3). Since H₂O breakthrough occurs significantly faster than CO₂ breakthrough, it
was sufficient to use the CO$_2$ outlet concentration as stopping criterion for the adsorption process. The adsorption temperature was 20 °C.

For all measurements, TVS desorption was initiated by evacuating the reactor to 62 mbar$_{abs}$ with a vacuum pump (KNF Neuberger, N84.3 ANDC) using a pressure controller (Bronkhorst EL-PRESS®). The reactor was then heated by circulating hot oil at 95 °C inlet temperature through the jacket. The desorbed gases were constantly removed from the reactor through the vacuum pump while the pressure was kept at 62 mbar$_{abs}$. The temperatures of the reactor wall and in the center of the packed bed were recorded with a sampling rate of 1 s. The measurements were stopped after thermal equilibrium was attained for each measurement.

5.2 Modelling

5.2.1 Single-component adsorption isotherms

The single component adsorption isotherms of the sorbent material have been previously measured$^{78}$ and were used as a basis for this study. The H$_2$O adsorption isotherms were described by the temperature-dependent form of the Guggenheim-Anderson-de Boer (GAB) model,$^{78}$ which is represented by Equations (4.1) to (4.4). Therein, (4.4) represents an empirical fit for the parameter $C_m$. $p_{vap}(T)$ denotes the vapor pressure of water at the temperature $T$. The model parameters were fitted to the GAB isotherms determined previously at five different temperatures$^{78}$ using a non-linear least squares algorithm and are summarized in Table 5-1. To achieve the fit, the three parameter pairs $C_{G,0}$ and $\Delta H_C$, $K_0$ and $\Delta H_K$, as well as $C_{m,0}$ and $\beta$ were individually fit to the values of $C_G$, $K_{ads}$, and $C_m$, respectively, which had been previously fit to the measured data points for each of the five isotherms at 283, 296, 303, 343, and 353 K and are presented elsewhere.$^{78}$ For each of the three fits, the Matlab® routine “lsqcurvefit” was employed.

$$q_{H_2O}(T, p_{H_2O,g}) =$$

$$C_m(T) \cdot \frac{C_G(T) \cdot K_{ads}(T) \cdot \frac{p_{H_2O,g}}{p_{vap}(T)}}{\left(1 - \frac{K_{ads}(T) \cdot \frac{p_{H_2O,g}}{p_{vap}(T)}}{1 + \left(C_G(T) - 1\right) \cdot K_{ads}(T) \cdot \frac{p_{H_2O,g}}{p_{vap}(T)}}\right)}$$

(4.1)
\[ C_G(T) = C_{G,0} \cdot e^{\frac{\Delta H}{RT}} \]  
(4.2)

\[ K_{\text{ads}}(T) = K_0 \cdot e^{\frac{\Delta H}{RT}} \]  
(4.3)

\[ C_m(T) = C_{m,0} \cdot e^{\beta} \]  
(4.4)

**Table 5-1. Parameters of the GAB model.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{G,0} )</td>
<td>(-)</td>
<td>6.86</td>
</tr>
<tr>
<td>( \Delta H_C )</td>
<td>(J/mol)</td>
<td>-4120</td>
</tr>
<tr>
<td>( K_0 )</td>
<td>(-)</td>
<td>2.27</td>
</tr>
<tr>
<td>( \Delta H_K )</td>
<td>(J/mol)</td>
<td>-2530</td>
</tr>
<tr>
<td>( C_{m,0} )</td>
<td>(mmol/g)</td>
<td>0.0208</td>
</tr>
<tr>
<td>( \beta )</td>
<td>(K)</td>
<td>1540</td>
</tr>
</tbody>
</table>

The dry CO\(_2\) adsorption isotherms were described by the temperature-dependent form of the Toth model,\(^{78,93}\) which is represented by Equations (4.5) to (4.8). Its parameters were fitted to the previously measured adsorption isotherms\(^{78}\) with a non-linear least squares algorithm and are shown in Table 5-2. The parameter fit was achieved as follows: The parameter \( T_0 \) was defined to 296 K. The parameter \( \Delta h_{\text{ads},CO_2} \) was set to 60 kJ/mol in alignment with the value used in the model (see Table 5-3 below). The remaining five parameters were fitted using the routine “lsqcurvefit” in Matlab\(^\text{®}\). Thereby all data points of the three previously measured adsorption isotherms at 296 K, 323 K, and 343 K\(^{78}\) were fed to the “lsqcurvefit” routine in a single step to calculate all five parameters.

Note that the APDES-NFC-FD-S material used here was obtained from a scaled-up synthesis batch and had about 19\% lower amine content and corresponding lower dry CO\(_2\) adsorption capacity than the previously measured one.\(^{78}\) Thus, the model parameter \( n_s \) was linearly scaled by a coefficient of 1/1.18.
5.2. Modelling

\[ q_{CO2}^{dry}(T, p_{CO2,g}) = n_s(T) \cdot \frac{b(T) \cdot p_{CO2,g}}{\left(1 + \frac{b \cdot p_{CO2,g}}{T_0 \cdot T_k}\right)^\gamma} \]  

(4.5)

\[ b(T) = b_0 \cdot e^{\frac{\Delta h_{ads,CO2,0}}{R \cdot T_0 \cdot (T - T_0)}} \]  

(4.6)

\[ t(T) = t_0 + \alpha \cdot \left(1 - \frac{T_0}{T}\right) \]  

(4.7)

\[ n_s(T) = n_{s,0} \cdot e^{\frac{T}{T_0}} \]  

(4.8)

Table 5-2. Parameters of the Toth model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>( T_0 )</td>
<td>(K)</td>
<td>296</td>
</tr>
<tr>
<td>( b_0 )</td>
<td>(1/mbar)</td>
<td>22.5</td>
</tr>
<tr>
<td>( \Delta h_{ads,CO2,0} )</td>
<td>(kJ/mol)</td>
<td>60</td>
</tr>
<tr>
<td>( t_0 )</td>
<td>(-)</td>
<td>0.422</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>(-)</td>
<td>0.949</td>
</tr>
<tr>
<td>( n_{s,0} )</td>
<td>(mmol/g)</td>
<td>1.97</td>
</tr>
<tr>
<td>( \chi )</td>
<td>(-)</td>
<td>2.37</td>
</tr>
</tbody>
</table>

5.2.2 Binary CO₂ and H₂O adsorption

In a previous study\textsuperscript{78} it was shown that the H₂O adsorption capacity of amine-functionalized NFC material remains largely unaffected by the presence of ultra-diluted CO₂. Another study showed that also in the presence of higher CO₂ concentrations the H₂O adsorption capacity of amine-functionalized sorbent materials was not affected.\textsuperscript{93} For this study, the single-component GAB isotherms were therefore used to model the equilibrium H₂O loading of the sorbent material during TVS desorption.
While it is generally known that CO$_2$ adsorption is enhanced by the presence of moisture,\textsuperscript{11, 50, 51, 64, 109} quantitative data on the influence of RH on the equilibrium CO$_2$ adsorption capacity is rare, as described in Chapter 4. This is partly because co-adsorption measurements are complex as opposed to single-component gravimetric measurements.\textsuperscript{64} In a previous study\textsuperscript{78} it was found that the enhancing effect of the RH on CO$_2$ adsorption diminished with increasing CO$_2$ partial pressure, and that at 23 °C, CO$_2$ adsorption capacity increased with RH in accordance with literature.\textsuperscript{57, 64} Thus, an empirical bilinear interpolation of an enhancing factor $f_{RH}$, which is a function of the CO$_2$ partial pressure and the relative humidity $\phi$, was used in this study to describe the humid CO$_2$ adsorption capacity of the sorbent. Therein, $f_{RH}$ represents the ratio of the CO$_2$ adsorption capacity at a certain RH and the corresponding CO$_2$ adsorption capacity at dry conditions:

$$q^{\text{humid}}_{CO_2}(T, p_{CO_2,g}, \phi) = f_{RH}(p_{CO_2,g}, \phi) \cdot q^{\text{dry}}_{CO_2}(T, p_{CO_2,g})$$ (4.9)

$$f_{RH}(p_{CO_2,g}, \phi) = 1 + \phi \cdot \left(0.6 - \frac{p_{CO_2,g}}{59 \text{ mbar}} \cdot 0.47\right)$$ (4.10)

The empirical bilinear fit for $f_{RH}$ (4.10) was derived from four measurements representing the extreme cases of partial CO$_2$ pressure $p_{CO_2}$ and RH prevailing during the TVS desorption process modeled in this paper (Table 5-4).

It has to be noted that this approach for describing the CO$_2$ adsorption capacities under humid conditions provides only a very rough approximation, is purely empirical, and does not provide any insight into the underlying mechanistic phenomena. It was chosen due to the lack of suitable co-adsorption models in the literature, the development of which was beyond the scope of this work. However, it can be assumed that the inaccuracy in the calculated CO$_2$ equilibrium capacities is not detrimental to the general results of the subsequent model and the conclusions drawn from the analysis that follows. This was confirmed by a corresponding sensitivity analysis that showed that a variation of the CO$_2$ adsorption capacity of ±20% has practically no influence on the modeled temperature evolution in the reactor and only a small influence on the modeled gas phase composition in the reactor, which did not change the characteristic shape of the partial pressure profiles.
5.2.3 Diffusivity

The diffusion coefficients of the gas pairs CO$_2$-H$_2$O(g), CO$_2$-air, and H$_2$O(g)-air at 1 atm are 0.202 cm$^2$/s (at 307 K), 0.177 cm$^2$/s (at 317 K), and 0.277 cm$^2$/s (at 313 K), respectively.\textsuperscript{110} For simplification, the diffusion coefficient of the 3-component mixture of CO$_2$, H$_2$O, and air was assumed to be the average value $D_0 = 0.22$ cm$^2$/s at 310 K and 1 bar. A sensitivity analysis indicated that this assumption does not affect the accuracy of the simulation results. The diffusion coefficient $D$ at a given temperature and pressure is calculated by\textsuperscript{110}

$$D = D_0 \cdot \frac{1.013 \text{ bar}}{P} \left( \frac{T}{310 \text{ K}} \right)^{1.5}$$

(4.11)

5.2.4 Heat and mass transfer model

A transient, 2D heat and mass transfer model is developed for the TVS desorption process in the packed bed of sorbent material. The following assumptions are taken:

1) advection is considered only in the $z$-direction along the gas flow direction;
2) the total pressure $P_{\text{tot}}$ in the bed is uniform and constant during the entire desorption process as ensured by the pressure controller; this was corroborated by measurements showing that the pressure drop over the reactor during desorption is $< 2$ mbar and therefore negligible;
3) viscous forces and dissipative terms are neglected, since the flow velocities in the reactor are very small (in the order of several mm/s);
4) the reactor is heated uniformly from the walls, \textit{i.e.}, there are no gradients of the temperature boundary condition in the $x$-, $y$-, and $z$-direction;
5) gas and solid phase are at local thermal equilibrium ($T_s = T_g =: T$), as justified by the high surface area of the porous sorbent material;
6) the material properties, except for the diffusion coefficients, are in good approximation independent of the temperature; and
7) the thermal conductivity is constant over the entire adsorbent bed.

Thermal conduction in a packed bed is generally a complex phenomenon. Since the porosity of a packed bed near the column wall is typically different from that in the bulk of the packed bed, many models account for a radial variation of the thermal conductivity. Two models that are often used are the “$\alpha_w$ model”
utilizing a wall heat transfer coefficient in the form of a temperature jump boundary condition and the “$\Lambda_r(r)$ model” accounting for the thermal conductivity as a function of the distance from the wall. Those models are described in detail in the literature.\textsuperscript{90} Assumption 7) therefore implies a certain simplification. However, since the goals of the model were not the determination of very accurate temperature profiles over the bed cross section but rather the investigation of bulk figures for the required desorption times as well as an analysis of the gas phase composition in the reactor during desorption, spatial variation of the thermal conductivity was neglected and the resulting inaccuracy is accepted.

From assumptions 2), 3), and 4) the following further assumption is derived. Because the boundary conditions and the pressure are in good approximation constant in z-direction and the velocity that increases in z-direction is very small so that viscose forces and dissipative terms can be neglected, the model is lumped in the z-direction. This is further illustrated as follows: If the sorbent bed is segmented into several axial slices as illustrated in Figure 5-6, all slices have identical boundary conditions except for an accumulating mass flow and velocity in axial direction through each control volume in the x-y plane of the slices towards the reactor outlet. Starting from the first slice, the net mass flow $\bar{m}_{net,i}$ (as defined in Figure 5-6) leaving a control volume has the same temperature and composition as the following ones due to the lack of gradients in the boundary conditions in z-direction and therefore does not significantly affect energy and mass balance of the following slices. This is further justified by the following consideration: The influence of an axial flow on the mass balance can be neglected, since due to diffusion the gas atmosphere in the reactor is in good approximation uniform as shown below. Its influence on the energy balance would be due to transport of sensible heat in z-direction. However, the heat capacity of the overall amount of desorbed gas during the desorption step is very small compared to the heat capacity of the sorbent in the reactor (0.16 J/K vs. 2.1 J/K per gram of sorbent material for typical desorption capacities of 0.5 mmol/g CO$_2$ and 4 mmol/g H$_2$O). Therefore, the influence on the energy balance would be small. This is clearly another simplification however introducing a third dimension to the model equations would substantially increase their complexity, which would not justify a minor gain in accuracy.
Figure 5-7 shows schematically a finite volume of the (x,y) modeling domain, indicating the solid and gas phase species and the energy and mass flows. In the solid phase, the species are the sorbent material, adsorbed CO$_2$, and adsorbed H$_2$O, whereas in the gas phase the species are CO$_2$, H$_2$O, and air (remainder after initial evacuation of the system). In the x-y plane, heat transfer by conduction and mass transport by diffusion are accounted for.

\[ \dot{m}_{\text{tot},i} = \dot{m}_{\text{in},i} + \dot{m}_{\text{net},i} \]

**Figure 5-6.** Definition of the advection mass flows in z-direction.

\[ \begin{align*}
q_y(x) & \quad j_{x,CO_2}(x) \\
q_y(y+dy) & \quad j_{y,CO_2}(y+dy) \\
q_x(x) & \quad j_{x,H_2O}(x) \\
j_y(x+dx) & \quad j_{y,H_2O}(x+dx) \\
\end{align*} \]

**Figure 5-7.** Schematic of a finite volume in the (x,y) domain of the heat and mass transfer model.
5.2.5 Governing equations

The mass and energy conservation equations are

Volume balance:

\[
\frac{dV_{CV}}{dt} = \frac{d}{dt}(V_s + V_g) = 0 \quad (4.12)
\]

Solid phase mass balances:

\[
\frac{d\bar{m}_i}{dt} = 0 \quad (4.13)
\]

\[
\bar{m}_{i,ads} = M_i \cdot \bar{m}_s \cdot q_i(T, \ p_{CO2,g}, \ p_{H2O,g}) ; \quad i = CO_2, \ H_2O \quad (4.14)
\]

\[
\bar{m}_{air,ads} = 0 \quad (4.15)
\]

Gas phase mass balances:

\[
\frac{\partial \bar{m}_{i,g}}{\partial t} + \frac{\partial \bar{m}_{i,ads}}{\partial t} + \nabla \cdot \bar{j}_i + \dot{\bar{m}}_{net,i} = 0 ; \quad i = CO_2, \ H_2O, \ air \quad (4.16)
\]

\[
\nabla \cdot \bar{j}_i = \nabla \cdot (-D \cdot \nabla \bar{m}_{i,g}) \quad (4.17)
\]

\[
\dot{\bar{m}}_{net,i} = \frac{1}{\bar{V}_{i,g}} \cdot \dot{\bar{V}}_{net} \quad (4.18)
\]

Energy balance:

\[
\frac{\partial \bar{U}}{\partial t} = \frac{\partial}{\partial t} \sum_r \bar{m}_r \cdot u_r = -\nabla \cdot \bar{q} - \sum_i \dot{\bar{m}}_{net,i} \cdot h_i - \sum_i \nabla \cdot (\bar{j}_i \cdot h_i) \quad (4.19)
\]

\[
\bar{j}_i = -D \cdot \nabla \bar{m}_{i,g} \quad (4.20)
\]

\[
\nabla \cdot \bar{q} = -k_{eff} \cdot \nabla^2 T \quad (4.21)
\]

\[r = s, \ CO_{2,ads}, \ H_2O_{ads}, \ CO_{2,g}, \ H_2O_g, \ air_g ; \quad i = CO_{2,g}, \ H_2O_g, \ air_g\]
5.2. Modelling

Initial conditions:

\[
\text{at } t = 0 : \quad T = T_0 ; \quad p_{\text{CO}_2, g} = p_{\text{CO}_2, g, 0} ; \quad p_{\text{H}_2\text{O}, g} = p_{\text{H}_2\text{O}, g, 0} ; \\
p_{\text{air}, g} = p_{\text{tot}} - p_{\text{CO}_2, g, 0} - p_{\text{H}_2\text{O}, g, 0} \tag{4.22}
\]

Boundary conditions:

\[
T \left( x = 0, \ y = 0, \ t \right) = T_{\text{wall, experiment}} \left( t \right) \tag{4.23}
\]

\[
\frac{\partial \bar{m}_{i, g}}{\partial x} \bigg|_{x=0} = 0, \quad \frac{\partial \bar{m}_{i, g}}{\partial y} \bigg|_{y=0} = 0 ; \quad i = \text{CO}_2, \ \text{H}_2\text{O}, \ \text{air} \tag{4.24}
\]

Therein, the “hut” notation \( \bar{x} \) denotes a quantity \( x \) per volume of one control volume \( V_{CV} \), i.e., \( \bar{x} = x / V_{CV} \). In particular, the control volume-specific masses of the gas phase components \( \bar{m}_i \) are slightly different from their density \( \rho_{i, g} = 1 / V_{i, g} \) \( (i = \text{CO}_2, \ \text{H}_2\text{O}, \ \text{air}) \) in the gas phase, since the density refers to the mass per volume of the gas phase \( V_g \), differing from the volume of the control volume, which is occupied by both, the solid and the gas phase.

Note that, as implied by Equation (4.14) that algebraically links the masses of adsorbed \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) \( \bar{m}_{i, \text{ads}} \) to the corresponding equilibrium capacities \( q_i \) given by the adsorption isotherms, the intrinsic kinetics of the desorption process are assumed to proceed fast enough so that chemical equilibrium is attained at all times. This is the main underlying assumption of this model, justified by the fact that the required heating times are in the order of hours, whereas the \( \text{CO}_2 \) desorption kinetics at elevated temperatures have time constants of at least an order of magnitude smaller.\(^{106}\) The rate of \( \text{H}_2\text{O} \) desorption can be assumed to proceed even faster than that of \( \text{CO}_2 \).\(^{109}\)

The governing equations (4.12) to (4.24) were rearranged to yield the final equations (4.34) and (4.46) as shown in the following.

Taking the sum over the ideal gas equations of the individual gas phase species

\[
p_i \cdot \bar{V}_g = \bar{m}_i \cdot R_i \cdot T ; \quad i = \text{CO}_2, \ \text{H}_2\text{O}, \ \text{air} \tag{4.25}
\]

yields

\[
\bar{V}_g = \frac{T}{p_{\text{tot}}} \cdot \sum_i \bar{m}_i \cdot R_i ; \quad i = \text{CO}_2, \ \text{H}_2\text{O}, \ \text{air} \tag{4.26}
\]
with

\[ P_{\text{tot}} = P_{CO_2,g} + P_{H_2O,g} + P_{\text{air},g}. \]  

(4.27)

Evaluating the differentials of the volume balance (4.12) yields

\[ \frac{\partial \bar{V}_g}{\partial t} = -\frac{\partial \bar{V}_s}{\partial t} = -\frac{\partial \bar{m}_{CO_2,ads}}{\partial t} \cdot v_{CO_2,ads} - \frac{\partial \bar{m}_{H_2O,ads}}{\partial t} \cdot v_{H_2O,ads} \]  

(4.28)

and, inserting (4.26),

\[ \frac{\partial \bar{V}_g}{\partial t} = \frac{\partial T}{\partial t} \cdot \bar{V}_g \cdot \frac{T}{p_{\text{tot}}} \cdot \frac{\partial}{\partial t} \sum_i m_{i,g} \cdot R_i = \frac{\partial T}{\partial t} \cdot \bar{V}_g \cdot \frac{T}{p_{\text{tot}}} + \sum_i v_i^p \cdot \frac{\partial m_{i,g}}{\partial t} \]

(4.29)

\[ i = \text{CO}_2, \ H_2\text{O}, \ \text{air}. \]

From the ideal gas law, the following relation between the specific volume \( v_{i,g} \) of a gas phase species at its partial pressure \( p_{i,g} \) and its corresponding specific volume \( v_i^p \) at the total gas phase pressure at the same temperature follows.

\[ \frac{v_{i,g}}{v_i^p} = \frac{p_{\text{tot}}}{p_{i,g}} \]  

(4.30)

Inserting (4.18) and (4.30) into the mass balances of the gas phase species (4.16) and multiplying the resulting equation by \( v_i^p \) yields

\[ v_i^p \cdot \frac{\partial m_{i,g}}{\partial t} + v_i^p \cdot \frac{\partial m_{i,ads}}{\partial t} + v_i^p \cdot \nabla \cdot \vec{j}_i + \frac{p_{i,g}}{p_{\text{tot}}} \cdot \dot{V}_{\text{net}} = 0 \]  

(4.31)

\[ i = \text{CO}_2, \ H_2\text{O}, \ \text{air} \]

Summing up equation (4.31) for all gas phase species and using (4.27) yields

\[ \dot{V}_{\text{net}} = -\sum_i v_i^p \cdot \frac{\partial m_{i,g}}{\partial t} - \left( v_{CO_2}^p \cdot \frac{\partial m_{CO_2,ads}}{\partial t} + v_{H_2O}^p \cdot \frac{\partial m_{H_2O,ads}}{\partial t} \right) \]

(4.32)

\[ i = \text{CO}_2, \ H_2\text{O}, \ \text{air} \]

which, by inserting (4.28) and (4.29), is rearranged to
\[
\dot{\nu} = -\frac{\partial \hat{m}_{CO_2,ads}}{\partial t}(v^p_{CO_2} - v^f_{CO_2}) - \frac{\partial \hat{m}_{H_2O,ads}}{\partial t}(v^p_{H_2O} - v^f_{H_2O}) \\
+ \frac{\partial T}{\partial t} \cdot \frac{\bar{V}_g}{T} \cdot \sum_i v^p_i \cdot \nabla \cdot \vec{j}_i \\
i = \text{CO}_2, \text{H}_2\text{O}, \text{air}.
\]

By inserting (4.33) into equations (4.16) and (4.18), equation (4.34) is obtained.

\[
\frac{\partial \hat{m}_{i,g}}{\partial t} + \frac{\partial \hat{m}_{i,ads}}{\partial t} + \nabla \cdot \vec{j}_i + \frac{1}{v_{i,g}} \left[ -\frac{\partial \hat{m}_{CO_2,ads}}{\partial t} \cdot (v^p_{CO_2} - v^f_{CO_2}) \right] \\
- \frac{\partial \hat{m}_{H_2O,ads}}{\partial t} \cdot (v^p_{H_2O} - v^f_{H_2O}) + \frac{\partial T}{\partial t} \cdot \frac{\bar{V}_g}{T} \cdot \sum_r v^p_{r,g} \cdot \nabla \cdot \vec{j}_{r,g} = 0
\]

\(i = \text{CO}_2, \text{H}_2\text{O}, \text{air}; \quad \forall i: \quad r = \text{CO}_2, \text{H}_2\text{O}, \text{air}\)

Taking the differential of the left-hand side of the energy balance (4.19) yields

\[
\frac{\partial U}{\partial t} = \frac{\partial T}{\partial t} \cdot \sum_r \bar{m}_r \cdot c_{v,r} + \sum_r \frac{\partial \bar{m}_r}{\partial t} \cdot u_r
\]

\(r = s, \text{CO}_2\text{ads}, \text{H}_2\text{O}_\text{ads}, \text{CO}_2\text{g}, \text{H}_2\text{O}_\text{g}, \text{air}_\text{g}\)

Inserting (4.35), the gas phase mass balances (4.16), and (4.13) into the energy balance (4.19) yields

\[
\nabla \cdot \bar{q} = -\frac{\partial T}{\partial t} \cdot \sum_r \bar{m}_r \cdot c_{v,r} \\
+ \frac{\partial \hat{m}_{CO_2,ads}}{\partial t} \cdot (u^f_{CO_2} - u^f_{CO_2}) + \frac{\partial \hat{m}_{H_2O,ads}}{\partial t} \cdot (u^f_{H_2O,g} - u^f_{H_2O,ads}) \\
- \sum_l \hat{m}_{net,l} \cdot (h_l - u_l) \\
- \sum_l \nabla \cdot (\vec{j}_l \cdot h_l) + \sum_i u_i \cdot \nabla \cdot \vec{j}_i
\]

\(r = s, \text{CO}_2\text{ads}, \text{H}_2\text{O}_\text{ads}, \text{CO}_2\text{g}, \text{H}_2\text{O}_\text{g}, \text{air}_\text{g}; \quad i = \text{CO}_2\text{g}, \text{H}_2\text{O}_\text{g}, \text{air}_\text{g}\)

By using (4.27) and the relations

\[
\dot{m}_{net,l} \cdot (h_l - u_l) = \dot{m}_{net,l} \cdot p_l \cdot v_l = p_l \cdot \dot{\nu}_{net} \quad i = \text{CO}_2\text{g}, \text{H}_2\text{O}_\text{g}, \text{air}_\text{g}
\]
and
\[ \nabla \cdot \left( \vec{j}_i \cdot h_i \right) = h_i \cdot \nabla \cdot \vec{j}_i + \vec{j}_i \cdot c_{p,i} \cdot \nabla T ; \quad i = \text{CO}_2, \; \text{H}_2\text{O}, \; \text{air} \quad (4.38) \]

(4.36) is rearranged to
\[ \nabla \cdot \vec{q} = -\frac{\partial T}{\partial t} \cdot \sum_r \vec{m}_r \cdot c_{v,r} \]
\[ + \frac{\partial \vec{m}_{\text{CO}_2,\text{ads}}}{\partial t} \cdot \left( u_{\text{CO}_2} - u_{\text{CO}_2,\text{ads}} \right) + \frac{\partial \vec{m}_{\text{H}_2\text{O},\text{ads}}}{\partial t} \cdot \left( u_{\text{H}_2\text{O},\text{g}} - u_{\text{H}_2\text{O},\text{ads}} \right) \quad (4.39) \]
\[ -p_{\text{tot}} \cdot \vec{V}_{\text{net}} \]
\[ -\sum_i \left( \nabla \cdot \vec{j}_i \right) \cdot \left( h_i - u_i \right) - \sum_i \vec{j}_i \cdot c_{p,i} \cdot \nabla T \]

\[ r = s, \; \text{CO}_2,\text{ads}, \; \text{H}_2\text{O},\text{ads}, \; \text{CO}_2,\text{g}, \; \text{H}_2\text{O},\text{g}, \; \text{air} \; ; \quad i = \text{CO}_2,\text{g}, \; \text{H}_2\text{O},\text{g}, \; \text{air} \]

which, by inserting the net volume flow (4.33),
\[ u_r + p_{\text{tot}} \cdot v^p = h_r ; \quad r = \text{CO}_2,\text{ads}, \; \text{H}_2\text{O},\text{ads}, \; \text{CO}_2,\text{g}, \; \text{H}_2\text{O},\text{g}, \; \text{air} \, , \quad (4.40) \]

\[ p_{\text{tot}} \cdot \frac{\vec{V}_r}{T} = \sum_i p_i \cdot \frac{\vec{V}_i}{T} = \sum_i \vec{m}_i \cdot R_i ; \quad i = \text{CO}_2,\text{g}, \; \text{H}_2\text{O},\text{g}, \; \text{air} \, , \quad (4.41) \]

\[ c_{p,r} = c_{v,r} ; \quad r = s, \; \text{CO}_2,\text{ads}, \; \text{H}_2\text{O},\text{ads} \, , \quad (4.42) \]

and
\[ c_{p,i} = c_{v,i} + R_i ; \quad i = \text{CO}_2,\text{g}, \; \text{H}_2\text{O},\text{g}, \; \text{air} \, , \quad (4.43) \]

yields
\[ \frac{\partial T}{\partial t} \cdot \sum_r \vec{m}_r \cdot c_{p,r} = -\nabla \cdot \vec{q} \]
\[ + \frac{\partial \vec{m}_{\text{CO}_2,\text{ads}}}{\partial t} \cdot \left( h_{\text{CO}_2} - h_{\text{CO}_2,\text{ads}} \right) \]
\[ + \frac{\partial \vec{m}_{\text{H}_2\text{O},\text{ads}}}{\partial t} \cdot \left( h_{\text{H}_2\text{O},\text{g}} - h_{\text{H}_2\text{O},\text{ads}} \right) \quad (4.44) \]
\[ -\sum_i \vec{j}_i \cdot c_{p,i} \cdot \nabla T \]

\[ r = s, \; \text{CO}_2,\text{ads}, \; \text{H}_2\text{O},\text{ads}, \; \text{CO}_2,\text{g}, \; \text{H}_2\text{O},\text{g}, \; \text{air} \; ; \quad i = \text{CO}_2,\text{g}, \; \text{H}_2\text{O},\text{g}, \; \text{air} \, . \]
By inserting (4.20), (4.21), and

\[
\Delta h_{r,ads} = h_{r,g} - h_{r,ads} \quad ; \quad r = \text{CO}_2, \text{H}_2\text{O}, \text{ads}
\]

(4.45)

into (4.44), Equation (4.46) is obtained.

\[
\frac{\partial T}{\partial t} \sum_r \bar{m}_r \cdot c_{p,r} = k_{\text{eff}} \cdot \nabla^2 T
\]

\[
+ \frac{\partial \bar{m}_{\text{CO}_2,ads}}{\partial t} \cdot \Delta h_{\text{ads,CO}_2} + \frac{\partial \bar{m}_{\text{H}_2\text{O},ads}}{\partial t} \cdot \Delta h_{\text{ads,H}_2\text{O}}
\]

\[
+ \sum_i c_{p,i} \cdot D \cdot (\nabla \bar{m}_i \cdot \nabla T)
\]

\[
r = s, \ \text{CO}_2, \text{ads}, \text{H}_2\text{O}, \text{ads}, \text{CO}_2, \text{g}, \text{H}_2\text{O}, \text{g}, \text{air}; \quad i = \text{CO}_2, \text{g}, \text{H}_2\text{O}, \text{g}, \text{air}_g
\]

The numerical values of the material properties and parameters are summarized in Table 5-3. The specific particle volume of the sorbent material is defined as inverse of the particle density, not including any pore or void volume. Since the specific particle volume of the sorbent and the specific volumes of the adsorbed species are about two orders of magnitude smaller than their respective bulk volumes, estimations of these values are sufficient, which was confirmed by a corresponding sensitivity analysis.

Table 5-3. Material properties and model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total desorption pressure</td>
<td>(P_{tot})</td>
<td>62 mbar</td>
<td>experiment design</td>
</tr>
<tr>
<td>Width of reactor cross section</td>
<td>(b)</td>
<td>72 mm</td>
<td>experiment design</td>
</tr>
<tr>
<td>Height of reactor cross section</td>
<td>(h)</td>
<td>72 mm</td>
<td>experiment design</td>
</tr>
<tr>
<td>Length of the sorbent bed</td>
<td>(l)</td>
<td>299 mm</td>
<td>experiment design</td>
</tr>
<tr>
<td>Specific particle volume of sorbent</td>
<td>(v_s)</td>
<td>629 cm³/kg</td>
<td>^111, ^112</td>
</tr>
<tr>
<td>Specific volume of adsorbed CO(_2)</td>
<td>(v_{\text{CO}_2,ads})</td>
<td>1’000 cm³/kg</td>
<td>Estimated from liquid CO(_2)^90</td>
</tr>
<tr>
<td>Specific volume of adsorbed H(_2)O</td>
<td>(v_{\text{H}_2\text{O},ads})</td>
<td>1’000 cm³/kg</td>
<td>Estimated from liquid water</td>
</tr>
</tbody>
</table>
5. Heat and mass transfer of TVS desorption

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control volume-specific mass of sorbent (bulk density)</td>
<td>$\bar{m}_s$</td>
<td>55.4 kg/m³</td>
<td>Experiment</td>
</tr>
<tr>
<td>Specific heat capacity of sorbent</td>
<td>$c_{p,s}$</td>
<td>2.07 kJ/kg/K</td>
<td>fit, measurement</td>
</tr>
<tr>
<td>Specific heat capacity of adsorbed CO₂</td>
<td>$c_{CO_2,ads}$</td>
<td>2.0 kJ/kg/K</td>
<td>Estimated from</td>
</tr>
<tr>
<td>Specific heat capacity of adsorbed H₂O</td>
<td>$c_{H_2O,ads}$</td>
<td>4.19 kJ/kg/K</td>
<td>Estimated from</td>
</tr>
<tr>
<td>Specific heat capacity of CO₂(g)</td>
<td>$c_{CO_2,g}$</td>
<td>0.860 kJ/kg/K</td>
<td>102</td>
</tr>
<tr>
<td>Specific heat capacity of H₂O(g)</td>
<td>$c_{H_2O,g}$</td>
<td>1.90 kJ/kg/K</td>
<td>102</td>
</tr>
<tr>
<td>Specific heat capacity of air</td>
<td>$c_{air,g}$</td>
<td>1.006 kJ/kg/K</td>
<td>102</td>
</tr>
<tr>
<td>Effective thermal conductivity of sorbent material</td>
<td>$k_{eff}$</td>
<td>44.5 mW/m/K</td>
<td>Measurement</td>
</tr>
<tr>
<td>Heat of CO₂ adsorption</td>
<td>$\Delta h_{ads, CO_2}$</td>
<td>60 kJ/mol</td>
<td>78 (average)</td>
</tr>
<tr>
<td>Heat of H₂O adsorption</td>
<td>$\Delta h_{ads, CO_2}$</td>
<td>49 kJ/mol</td>
<td>78</td>
</tr>
<tr>
<td>Average diffusion coefficient (at 310 K and ambient pressure)</td>
<td>$D_0$</td>
<td>0.22 cm²/s</td>
<td>110 (average)</td>
</tr>
<tr>
<td>Initial condition (IC): temperature</td>
<td>$T_0$</td>
<td>20 °C</td>
<td>experiment design</td>
</tr>
<tr>
<td>IC: CO₂ partial pressure M1</td>
<td>$P_{CO_2,g,0}$</td>
<td>0 mbar</td>
<td>experiment design</td>
</tr>
<tr>
<td>IC: CO₂ partial pressure M2 &amp; M3</td>
<td>$P_{CO_2,g,0}$</td>
<td>0.4 mbar</td>
<td>experiment design</td>
</tr>
<tr>
<td>IC: H₂O partial pressure M1 &amp; M3</td>
<td>$P_{H_2O,g,0}$</td>
<td>0 mbar</td>
<td>experiment design</td>
</tr>
<tr>
<td>IC: H₂O partial pressure M3</td>
<td>$P_{H_2O,g,0}$</td>
<td>13.5 mbar</td>
<td>experiment design</td>
</tr>
</tbody>
</table>

### 5.2.6 Discretization

The mass and energy balances were discretized using a finite volume method. An equally spaced rectangular grid was defined over one quadrant of the x-y plane. The solution over the complete x-y plane was obtained from the solution over the quadrant by using symmetry conditions. Since computation time was not an issue,
the additional symmetry condition along the diagonal of the quadrant was not exploited for the simulations. Figure 5-8 shows the definition of the discretization grid. Therein, $\Delta x$ and $\Delta y$ denote the (constant) edge length of the finite volumes and $\delta x$ and $\delta y$ denote the distances between the center points of two neighboring finite volumes. The latter are also constant except for boundary points at the reactor walls, where the distance between the center points and the boundary, which is required to calculate the heat flux at the boundary, is only $\delta x/2$ and $\delta y/2$.

**Figure 5-8.** Definition of the discretization grid over one quadrant of the x-y plane.

Equations (4.47) and (4.48) represent the discretized energy balance for a non-boundary point “$p$”; Equations (4.49), (4.50), and (4.51) represent the discretized mass balances for CO$_2$, H$_2$O, and air in the gas phase for a non-boundary point “$p$”.
Therein, \( n \), \( e \), \( s \), and \( w \) denote the four neighboring points in the north, east, south, and west of point \( p \). \( x\big|_p \) denotes the value of \( x \) at point \( p \) and \( x^0 \) denotes the value of \( x \) at the previous time step. For the discretization of the source term \( c_{p,i} \cdot D \cdot (\nabla \bar{m}_i \cdot \nabla T) \) in the energy balance, the arithmetic mean of the spatial derivatives of \( \bar{m}_i \) and \( T \) towards the two neighboring points in each coordinate direction is employed. The notation \( x\big|_{p,e} \) denotes the arithmetic mean of the quantity \( x \) at point \( p \) and point \( e \).

\[
\sum_r \left( \bar{m}_r \cdot c_{p,r} \right) \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \left( T_p - T_p^0 \right)
- \frac{k_{\text{eff}}}{\Delta x} \left[ \left( T_e - T_p \right) - \left( T_p - T_w \right) \right] \cdot \Delta y
- \frac{k_{\text{eff}}}{\Delta y} \left[ \left( T_n - T_p \right) - \left( T_p - T_s \right) \right] \cdot \Delta x
- b_{\text{CO}_2} \left[ q_{\text{CO}_2} (T_p) - q_{\text{CO}_2} (T_p^0) \right] - b_{\text{H}_2\text{O}} \left[ q_{\text{H}_2\text{O}} (T_p) - q_{\text{H}_2\text{O}} (T_p^0) \right]
\]

\[
- \sum_i \left[ \left( \bar{m}_i \big|_{e} - \bar{m}_i \big|_p \right) \cdot \frac{D_i}{\Delta x} \left( \bar{m}_i \big|_p - \bar{m}_i \big|_w \right) \right]
\]

\[
= 0
\]

\[ r = s, \ \text{CO}_{2,\text{ads}}, \ \text{H}_2\text{O}_{\text{ads}}, \ \text{CO}_{2,\text{g}}, \ \text{H}_2\text{O}_{\text{g}}, \ \text{air}_g; \ \ i = \text{CO}_{2,\text{g}}, \ \text{H}_2\text{O}_{\text{g}}, \ \text{air}_g \]

\[
b_{\text{CO}_2} = m_s \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \cdot \Delta h_{\text{ads,CO}_2} ; \ b_{\text{H}_2\text{O}} = m_s \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \cdot \Delta h_{\text{ads,H}_2\text{O}} \]
\[
\left( \bar{m}_{\text{CO}_2,g}^p - \bar{m}_{\text{CO}_2,g}^0 \right) \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \\
- \left[ \bar{m}_{\text{CO}_2,\text{ads}}^p - \bar{m}_{\text{CO}_2,\text{ads}}^0 \right] \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \cdot \left( \frac{v_{\text{CO}_2}^p - v_{\text{CO}_2,\text{ads}}}{v_{\text{CO}_2}} - 1 \right)_{p} \\
- \left[ \bar{m}_{\text{H}_2\text{O},\text{ads}}^p - \bar{m}_{\text{H}_2\text{O},\text{ads}}^0 \right] \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \cdot \left( \frac{v_{\text{H}_2\text{O}}^p - v_{\text{H}_2\text{O},\text{ads}}}{v_{\text{CO}_2}} \right)_{p} \\
+ \frac{1}{v_{\text{CO}_2}} \cdot \frac{\bar{V}_g}{T} \cdot (T_p - T_0) \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \\
- \left[ \frac{D_{\text{CO}_2}^{w,w}}{\delta x} \cdot (\bar{m}_{\text{CO}_2,g}^p - \bar{m}_{\text{CO}_2,g}^0) - \frac{D_{\text{CO}_2}^{w,v}}{\delta x} \cdot (\bar{m}_{\text{CO}_2,g}^p - \bar{m}_{\text{CO}_2,g}^0) \right] \cdot \Delta y \cdot \left( 1 - \frac{v_{\text{CO}_2}}{v_{\text{CO}_2}} \right)^0_{p} \\
- \left[ \frac{D_{\text{CO}_2}^{n,n}}{\delta x} \cdot (\bar{m}_{\text{CO}_2,g}^p - \bar{m}_{\text{CO}_2,g}^0) - \frac{D_{\text{CO}_2}^{n,v}}{\delta x} \cdot (\bar{m}_{\text{CO}_2,g}^p - \bar{m}_{\text{CO}_2,g}^0) \right] \cdot \Delta y \cdot \left( 1 - \frac{v_{\text{CO}_2}}{v_{\text{CO}_2}} \right)^0_{p} \\
+ \left[ \frac{D_{\text{H}_2\text{O}}^{w,w}}{\delta x} \cdot (\bar{m}_{\text{H}_2\text{O},g}^p - \bar{m}_{\text{H}_2\text{O},g}^0) - \frac{D_{\text{H}_2\text{O}}^{w,v}}{\delta x} \cdot (\bar{m}_{\text{H}_2\text{O},g}^p - \bar{m}_{\text{H}_2\text{O},g}^0) \right] \cdot \Delta y \cdot \left( \frac{v_{\text{H}_2\text{O}}}{v_{\text{CO}_2}} \right)^0_{p} \\
+ \left[ \frac{D_{\text{H}_2\text{O}}^{n,n}}{\delta x} \cdot (\bar{m}_{\text{H}_2\text{O},g}^p - \bar{m}_{\text{H}_2\text{O},g}^0) - \frac{D_{\text{H}_2\text{O}}^{n,v}}{\delta x} \cdot (\bar{m}_{\text{H}_2\text{O},g}^p - \bar{m}_{\text{H}_2\text{O},g}^0) \right] \cdot \Delta y \cdot \left( \frac{v_{\text{H}_2\text{O}}}{v_{\text{CO}_2}} \right)^0_{p} \\
+ \left[ \frac{D_{\text{air}}^{w,w}}{\delta x} \cdot (\bar{m}_{\text{air},g}^p - \bar{m}_{\text{air},g}^0) - \frac{D_{\text{air}}^{w,v}}{\delta x} \cdot (\bar{m}_{\text{air},g}^p - \bar{m}_{\text{air},g}^0) \right] \cdot \Delta y \cdot \left( \frac{v_{\text{air}}}{v_{\text{CO}_2}} \right)^0_{p} \\
+ \left[ \frac{D_{\text{air}}^{n,n}}{\delta x} \cdot (\bar{m}_{\text{air},g}^p - \bar{m}_{\text{air},g}^0) - \frac{D_{\text{air}}^{n,v}}{\delta x} \cdot (\bar{m}_{\text{air},g}^p - \bar{m}_{\text{air},g}^0) \right] \cdot \Delta y \cdot \left( \frac{v_{\text{air}}}{v_{\text{CO}_2}} \right)^0_{p} \\
= 0
\]
\[
\left( \bar{m}_{H2O,g} \bigg|_p - \bar{m}_{H2O,g} \bigg|_p^0 \right) \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \\
- \left[ \bar{m}_{CO2,ads} \bigg|_p - \bar{m}_{CO2,ads} \bigg|_p^0 \right] \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \cdot \left( \frac{v_{CO2}^p - v_{CO2,ads}}{v_{H2O,g}} \right) \bigg|_p^0 \\
- \left[ \bar{m}_{H2O,ads} \bigg|_p - \bar{m}_{H2O,ads} \bigg|_p^0 \right] \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \cdot \left( \frac{v_{H2O}^p - v_{H2O,ads}}{v_{H2O,g}} - 1 \right) \bigg|_p^0 \\
+ \frac{1}{v_{H2O,g}} \cdot \frac{\bar{V}_g}{T} \bigg|_p^0 \cdot (T_p - T_p^0) \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \\
+ \left[ \frac{D_{CO2}^{ep}}{\delta x} \cdot \left( \bar{m}_{CO2,g} \big|_p - \bar{m}_{CO2,g} \big|_p^0 \right) - \frac{D_{CO2}^{zn}}{\delta x} \cdot \left( \bar{m}_{CO2,g} \big|_p - \bar{m}_{CO2,g} \big|_w \right) \right] \cdot \Delta y \cdot \left( \frac{v_{CO2}^p}{v_{H2O,g}} \right) \bigg|_p^0 \\
+ \left[ \frac{D_{CO2}^{zp}}{\delta y} \cdot \left( \bar{m}_{CO2,g} \big|_p - \bar{m}_{CO2,g} \big|_w \right) - \frac{D_{CO2}^{zss}}{\delta y} \cdot \left( \bar{m}_{CO2,g} \big|_p - \bar{m}_{CO2,g} \big|_s \right) \right] \cdot \Delta x \cdot \left( \frac{v_{CO2}^p}{v_{H2O,g}} \right) \bigg|_p^0 \\
- \left[ \frac{D_{H2O}^{ep}}{\delta x} \cdot \left( \bar{m}_{H2O,g} \big|_e - \bar{m}_{H2O,g} \big|_p \right) - \frac{D_{H2O}^{zn}}{\delta x} \cdot \left( \bar{m}_{H2O,g} \big|_p - \bar{m}_{H2O,g} \big|_w \right) \right] \cdot \Delta y \cdot \left( 1 - \frac{v_{H2O}^p}{v_{H2O,g}} \right) \bigg|_p^0 \\
- \left[ \frac{D_{H2O}^{zp}}{\delta y} \cdot \left( \bar{m}_{H2O,g} \big|_p - \bar{m}_{H2O,g} \big|_w \right) - \frac{D_{H2O}^{zss}}{\delta y} \cdot \left( \bar{m}_{H2O,g} \big|_p - \bar{m}_{H2O,g} \big|_s \right) \right] \cdot \Delta x \cdot \left( 1 - \frac{v_{H2O}^p}{v_{H2O,g}} \right) \bigg|_p^0 \\
+ \left[ \frac{D_{air}^{ep}}{\delta x} \cdot \left( \bar{m}_{air,g} \big|_e - \bar{m}_{air,g} \big|_p \right) - \frac{D_{air}^{zn}}{\delta x} \cdot \left( \bar{m}_{air,g} \big|_p - \bar{m}_{air,g} \big|_w \right) \right] \cdot \Delta y \cdot \left( \frac{v_{air}^p}{v_{H2O,g}} \right) \bigg|_p^0 \\
+ \left[ \frac{D_{air}^{zp}}{\delta y} \cdot \left( \bar{m}_{air,g} \big|_p - \bar{m}_{air,g} \big|_w \right) - \frac{D_{air}^{zss}}{\delta y} \cdot \left( \bar{m}_{air,g} \big|_p - \bar{m}_{air,g} \big|_s \right) \right] \cdot \Delta x \cdot \left( \frac{v_{air}^p}{v_{H2O,g}} \right) \bigg|_p^0 \\
= 0 \quad (4.50)
\]
\[
\left( \bar{m}_{\text{air},g} \big|_p - \bar{m}_{\text{air},g} \big|_p \right) \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \\
- \left[ \bar{m}_{\text{CO}_2,ads} \big|_p - \bar{m}_{\text{CO}_2,ads} \big|_p \right] \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \cdot \left( \frac{v_{\text{CO}_2}^p - v_{\text{CO}_2,ads}}{v_{\text{air},g}} \right)_p^{0} \\
- \left[ \bar{m}_{\text{H}_2\text{O},ads} \big|_p - \bar{m}_{\text{H}_2\text{O},ads} \big|_p \right] \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \cdot \left( \frac{v_{\text{H}_2\text{O}}^p - v_{\text{H}_2\text{O},ads}}{v_{\text{air},g}} \right)_p^{0} \\
+ \frac{1}{v_{\text{air},g}} \cdot \frac{\bar{T}_g}{T} \cdot \left( T_p - T_p^0 \right) \cdot \frac{\Delta x \cdot \Delta y}{\Delta t} \\
+ \left[ \frac{D_{\text{CO}_2}^{\text{ep}}}{\delta x} \cdot \left( \bar{m}_{\text{CO}_2,g} \big|_e - \bar{m}_{\text{CO}_2,g} \big|_p \right) - \frac{D_{\text{CO}_2}^{\text{ps}}}{\delta x} \cdot \left( \bar{m}_{\text{CO}_2,g} \big|_p - \bar{m}_{\text{CO}_2,g} \big|_w \right) \right] \cdot \Delta y \cdot \left( \frac{v_{\text{CO}_2}^p}{v_{\text{air},g}} \right)_p^{0} \\
+ \left[ \frac{D_{\text{H}_2\text{O}}^{\text{ep}}}{\delta x} \cdot \left( \bar{m}_{\text{H}_2\text{O},g} \big|_e - \bar{m}_{\text{H}_2\text{O},g} \big|_p \right) - \frac{D_{\text{H}_2\text{O}}^{\text{ps}}}{\delta x} \cdot \left( \bar{m}_{\text{H}_2\text{O},g} \big|_p - \bar{m}_{\text{H}_2\text{O},g} \big|_w \right) \right] \cdot \Delta y \cdot \left( \frac{v_{\text{H}_2\text{O}}^p}{v_{\text{air},g}} \right)_p^{0} \\
+ \left[ \frac{D_{\text{H}_2\text{O}}^{\text{ep}}}{\delta y} \cdot \left( \bar{m}_{\text{H}_2\text{O},g} \big|_e - \bar{m}_{\text{H}_2\text{O},g} \big|_p \right) - \frac{D_{\text{H}_2\text{O}}^{\text{ps}}}{\delta y} \cdot \left( \bar{m}_{\text{H}_2\text{O},g} \big|_p - \bar{m}_{\text{H}_2\text{O},g} \big|_s \right) \right] \cdot \Delta x \cdot \left( \frac{v_{\text{H}_2\text{O}}^p}{v_{\text{air},g}} \right)_p^{0} \\
- \left[ \frac{D_{\text{air}}^{\text{ep}}}{\delta x} \cdot \left( \bar{m}_{\text{air},g} \big|_e - \bar{m}_{\text{air},g} \big|_p \right) - \frac{D_{\text{air}}^{\text{ps}}}{\delta x} \cdot \left( \bar{m}_{\text{air},g} \big|_p - \bar{m}_{\text{air},g} \big|_w \right) \right] \cdot \Delta y \cdot \left( 1 - \frac{v_{\text{air}}^p}{v_{\text{air},g}} \right)_p^{0} \\
- \left[ \frac{D_{\text{air}}^{\text{ep}}}{\delta y} \cdot \left( \bar{m}_{\text{air},g} \big|_e - \bar{m}_{\text{air},g} \big|_p \right) - \frac{D_{\text{air}}^{\text{ps}}}{\delta y} \cdot \left( \bar{m}_{\text{air},g} \big|_p - \bar{m}_{\text{air},g} \big|_s \right) \right] \cdot \Delta x \cdot \left( 1 - \frac{v_{\text{air}}^p}{v_{\text{air},g}} \right)_p^{0} \\
= 0 \quad (4.51)
\]
The discretized equations were solved in Matlab® using a fully implicit scheme, where in each time step the nonlinear system of the grid equations was numerically solved. A spatial grid of 100 finite volumes per quadrant and a time step of 5 s were found to be sufficient for the simulations as confirmed by a grid conversion study.

5.2.7 Reactor outlet flows

The mass and volume flows at the outlet of the reactor were calculated by summing up the mass balances over the grid plane according to Equations (4.52) and (4.53), accounting for the fact that all diffusion mass flows over the grid plane add up to zero. The factor of 4 accounts for the four quadrants of the modelling plane.

\[
\dot{m}_{out,r} = \left( \sum_{i=1}^{n_i} \sum_{j=1}^{n_j} - \frac{\partial \dot{m}_{r,g}}{\partial t} - \frac{\partial \dot{m}_{r,ads}}{\partial t} \right) \cdot \Delta x \cdot \Delta y \cdot 4 \tag{4.52}
\]

\[
\dot{V}_{out,r} = \frac{\dot{m}_{out,r} \cdot 22.414 \ l_N}{M_r} \tag{4.53}
\]

\[
r = \text{CO}_2, \text{H}_2\text{O}, \text{air} \tag{4.54}
\]

The CO\(_2\) purity was calculated according to Equation (4.54). It is thereby assumed that the CO\(_2\) is only diluted by the non-condensable air and that the water vapor contained in the desorption flow is completely condensed out after the reactor outlet, as it will be the case in good approximation for an industrial vacuum pump system, for example a liquid ring pump.

\[
c_{CO2} = \frac{\dot{V}_{out,CO2}}{\dot{V}_{out,CO2} + \dot{V}_{out,air}} \tag{4.54}
\]

Note that by applying Equation (4.54) for the purity calculation parasitic effects such as air remainders in the piping and vacuum pump after the reactor outlet as well as leaks, which strongly depend on the engineering design of the DAC plant, are neglected.
5.3 Results and discussion

5.3.1 CO$_2$ and H$_2$O adsorption capacity measurements

The results of the single-component and binary CO$_2$ and H$_2$O adsorption capacity measurements are summarized in Table 5-4. The CO$_2$ adsorption capacities of the APDES-NFC-FD-S material at dry and moist (≥ 95% RH) conditions at 0.4 and 59 mbar CO$_2$ partial pressure and 23 °C were used to derive the bilinear interpolation of the enhancing factor $f_{RH}$. The other values were used for comparison with the previously measured material.\textsuperscript{78}

Table 5-4. Results of CO$_2$ and H$_2$O adsorption capacity measurements of APDES-NFC-FD-S.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$p_{CO2}$ (mbar)</th>
<th>RH</th>
<th>$q_{CO2}$ (mmol CO$_2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>0.4</td>
<td>dry</td>
<td>0.94</td>
</tr>
<tr>
<td>23</td>
<td>0.4</td>
<td>≥ 95%</td>
<td>1.50</td>
</tr>
<tr>
<td>23</td>
<td>59</td>
<td>dry</td>
<td>1.58</td>
</tr>
<tr>
<td>23</td>
<td>59</td>
<td>≥ 95%</td>
<td>1.79</td>
</tr>
<tr>
<td>23</td>
<td>1’000</td>
<td>dry</td>
<td>1.93</td>
</tr>
<tr>
<td>50</td>
<td>1’000</td>
<td>dry</td>
<td>1.72</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>RH</th>
<th>$q_{H2O}$ (mmol H$_2$O/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>48%</td>
<td>3.0</td>
</tr>
<tr>
<td>30</td>
<td>73%</td>
<td>5.4</td>
</tr>
</tbody>
</table>

5.3.2 Sorbent temperature and gas phase composition

Figure 5-9 shows the experimentally measured (solid) and numerically simulated (dashed) temperature in the reactor center as a function of time during TVS desorption for the three measurements: M1) heating in inert atmosphere; M2) desorption after saturation with dry CO$_2$; and M3) desorption after saturation with CO$_2$ and H$_2$O. The wall temperature for all three experiments is also indicated.
Experimentally measured (solid) and numerically simulated (dashed) temperature in the reactor center as a function of time during TVS desorption for M1 (“inert”), M2 (“dry”), and M3 (“humid”). Also shown is the wall temperature boundary condition (“wall”). For M1, the dashed line is almost covered by the solid line.

The heating temperature profile for M1 is characteristic of heat transfer by conduction with an initial steep slope followed by an asymptotic towards thermal equilibrium. That for M2 is of similar shape but with a flatter asymptotic above approx. 70 °C due to the heat sink caused by the enthalpy of CO₂ desorption. That for M3 exhibits a pronounced 25 min plateau around 42 °C due to the heat sink caused by the enthalpy of H₂O desorption and evaporation, followed by an asymptotic towards final thermal equilibrium after 180 min, as opposed to approx. 60 and 90 min for the other two measurements.

Interestingly, the initial temperature rise for M2 and M3 is faster than that of M1. This is particularly pronounced for the curve of the humid desorption measurement (M3), which reaches a temperature of 40 °C after 7 min as opposed to 13 min for the inert heating curve, i.e., almost twice as fast. This observation is counter-intuitive since a slower temperature rise would be expected for the desorption experiments than for the pure heating experiment due to the heat sinks caused by the desorption enthalpies. This effect is explained by the strong influence of diffusion in the gas phase as confirmed by the modeling.

Measurement M1 was used to determine the specific heat capacity $c_{p,s}$ of the sorbent material as heat conduction is the only mode of heat transfer. A least
squares fit yielded $c_{p,s} = 2'070 \text{ J/kg/K}$ and this value was used exclusively for all numeric calculations. The agreement between measured and simulated temperature profiles is very good for M1 and M2. For M3, the temperature level of the plateau is precisely predicted, but towards the end of the process, the modelled temperature is overestimated presumably due to the inaccuracy of the binary adsorption capacities and neglected kinetics. Figure 5-10 to Figure 5-12 show the temperature distributions over the first quadrant of the reactor cross-section at different points in time during desorption for measurement M1, M2, and M3, respectively and illustrate the progress of the heating process in the reactor cross section for all three cases.

**Figure 5-10.** Simulated temperature distribution over the first quadrant of the reactor cross-section at 1, 5, 15, and 30 min after start of heating for measurement M1 (inert heating).
Figure 5-11. Simulated temperature distribution over the first quadrant of the reactor cross-section at 1, 5, 15, and 30 min after start of heating for measurement M2 (dry TVS desorption).
5.3. Results and discussion

Figure 5-12. Simulated temperature distribution over the first quadrant of the reactor cross-section at 5, 15, 30, and 60 min after start of heating for measurement M3 (humid TVS desorption).

A sensitivity analysis was carried out to examine the relevance of diffusion in the transfer of heat for humid TVS desorption (M3). The modeled temperature in the center of the sorbent bed was computed as a function of time and for various values of the diffusion coefficient. Therein, all parameters were kept identical except for the diffusion constant $D$, which was calculated by Equation (4.11) with $D_0$ ($D_0 = 0.22 \text{ cm}^2/\text{s}$ at 310 K and 1 bar, as for all other simulations), $2 \cdot D_0$, $\frac{1}{2} \cdot D_0$, and zero. The results are shown in Figure 5-13. It turns out that the temperature profile for the case of zero diffusion differs significantly, which indicates that heat transfer is strongly controlled by diffusion and underlines its importance for process design. Part of the reason is that $D$ is inversely proportional to the absolute pressure (Equation (4.11)), i.e., it strongly increases in vacuum. On the other hand, the three other temperature profiles for the non-zero values of $D_0$ do not differ significantly from each other, justifying the simplifications aforementioned.
Besides predicting the temperature profiles, the simulation results can be used to gain insight into further process data, which are not easily accessible by measurements: Figure 5-14 and Figure 5-15 show the modeled gas phase composition, i.e., the partial pressure profiles of CO₂, H₂O, and air in the center of the sorbent bed and next to the reactor wall, as a function of desorption time for M2 and M3, respectively. Figure 5-16 and Figure 5-17 show the CO₂ and H₂O loading of the sorbent material in the bed center and next to the reactor wall as a function of desorption time for M2 and M3, respectively.
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Figure 5-14. Modeled partial pressure of CO$_2$, H$_2$O, and air in the center of the sorbent bed (solid) and next to the reactor wall (dashed, mostly hidden under the solid lines) for M2.

Figure 5-15. Modeled partial pressure of CO$_2$, H$_2$O, and air in the center of the sorbent bed (solid) and next to the reactor wall (dashed, mostly hidden under the solid lines) for M3.
As evident from Figure 5-14 and Figure 5-15, the partial pressure of all gas phase species is practically identical at the reactor wall and its center at all times during TVS desorption. This implies that the partial pressure of the gas phase species is in good approximation uniform over the entire sorbent bed cross section during the complete desorption step and essentially no composition fronts are
5.3. Results and discussion

Present in the reactor cross-section. This in turn shows that mass transfer by diffusion is fast in relation to the overall heating and desorption process so that disturbances, for instance induced by initial desorption of species near the reactor wall, are immediately balanced. Interestingly, the H₂O and CO₂ loading profiles in the center of the sorbent bed of Figure 5-17 (solid lines) exhibit an increase during the initial phase of humid TVS desorption for about 6 and 35 min, respectively, and only thereafter decline towards their final equilibrium values. This is because during the initial heating phase, substantial desorption takes place in the outer layers of the sorbent bed close to the reactor wall, as evidenced by the dashed curves of Figure 5-17. This, in turn, leads to an abrupt rise of the H₂O partial pressure in the entire bed’s cross section and, after about 6 min, the gas phase is almost entirely occupied by water vapor ($p_{H₂O,g} \approx 60$ mbar, see Figure 5-15).

During this phase, re-adsorption of H₂O occurs in the center region of the sorbent bed, which is still relatively cold compared to the wall. Analogously, the partial pressure of CO₂ increases during further heating, and CO₂ is re-adsorbed in the center region. The re-adsorption, mainly of H₂O, releases heat and causes the initial, counterintuitive, steep temperature increase in the sorbent bed center, as seen in Figure 5-9 for M3. It can be interpreted as heat transport by desorbed and re-adsorbed species from the reactor walls to its center. Similar re-adsorption effects have been observed during the regeneration of H₂O-loaded zeolite beds.\(^98\)

In particular, the peak in H₂O loading in the center of the bed (Figure 5-17) is first followed by a slight decrease during the temperature plateau (Figure 5-9) until about 40 min, and then succeeded by a steep drop to final equilibrium. The first slight decrease is caused by a drop in $p_{H₂O}$ due to partial displacement by constantly desorbing CO₂, as seen in Figure 5-15. The temperature stagnation and even marginal, temporary decrease in the center of the bed during this phase is thereby explained by the heat of H₂O desorption that is withdrawn from the sorbent material, since desorption during this phase is not induced by heating but rather by the partial pressure decrease. The subsequent steep drop is caused by the temperature increase after the plateau, as heat reaches the center of the bed. As the temperature increases, CO₂ is desorbed in the center region, which leads to a continuous increase of $p_{CO₂}$ and a corresponding decrease of $p_{H₂O}$, resulting in the final equilibrium values of $p_{CO₂} = 26$ mbar and $p_{H₂O} = 36$ mbar for M3. The increase of the CO₂ partial pressure eventually even causes re-adsorption of CO₂ in the sorbent close to the reactor wall, as indicated by the dashed CO₂-loading line in Figure 5-17. This is because the sorbent close to the wall had initially been
desorbed below the equilibrium loading that corresponds to the final temperature and CO₂ partial pressure in the gas phase.

The higher cyclic CO₂ adsorption capacities under humid air conditions\(^{109}\) can now be explained not only by the higher equilibrium CO₂ loading of the sorbent material but also by the prevailing partial pressures in the gas phase as the desorbed CO₂ is diluted by desorbed water vapor, resulting in a lower \(p_{CO₂}\) that shifts the equilibrium to the left-hand side of the adsorption isotherms. This effect was already indicated by the results of Chapter 3 and is now quantified by the modelling results.

Another important aspect that can be analyzed using the modelling results is the oxygen-induced degradation of the sorbent material under different process conditions. It is known that amine-based sorbent materials, are prone to degradation when exposed to O₂ at higher temperatures. Thereby, the stability depends on the amine type and proximity.\(^{113-116}\) For example, it was found that the adsorption capacity of amine-functionalized NFC is reduced by 30% after exposure to moist air at 90 °C for 15 h.\(^{91}\) Over longer time periods, even smaller O₂ concentrations induce degradation of amine-based sorbent materials at above 70 °C.\(^{117}\) Figure 5-15 shows that, for the case of humid TVS desorption (M3), the initial air content is immediately replaced by desorbed H₂O and CO₂ and \(p_{air}\) drops to below 0.001 mbar after 7 min. This explains the small degradation of amine-functionalized NFC sorbent observed after 100 humid TVS cycles, while at the same time large degradation rates were observed in an air atmosphere at the same temperatures for that material.\(^{91}\) On the other hand, for the case of dry TVS desorption (M2), Figure 5-14 shows that the air is not completely purged out during the entire desorption process because of the smaller amount of desorbed CO₂ and the absence of desorbed H₂O. The partial pressure of air remains at 2.4 mbar at thermal equilibrium, corresponding to an O₂ partial pressure of approx. 0.5 mbar. Oxygen-induced degradation is therefore expected to proceed much faster for dry TVS than for humid TVS.

It is therefore important to estimate the highest temperature reached by the sorbent before the air is purged out of the system. A cross-plot of Figure 5-9 and Figure 5-17 \((p_{air}\) vs. \(T\) during humid TVS desorption, Figure 5-18) indicates that, when the gas phase becomes substantially O₂-free, the bed center temperature is still below 45 °C and uncritical, while the reactor wall temperature reaches 65 °C and is already critical to oxidative degradation.\(^{115}\) Nevertheless, the exposure time is very short (see Figure 5-15). Although these results are obviously dependent on
the particular reactor and process conditions, it can be generally concluded that the risk of oxygen-induced degradation is substantially reduced for humid TVS desorption processes because of the purging effect of the desorbed H$_2$O.

Moreover, dry TVS promotes urea formation, which also leads to degradation of the sorbent material.\textsuperscript{89, 118, 119} From Figure 5-15 it follows that for moist TVS desorption the corresponding risk of urea formation can be considered small since the partial pressure of H$_2$O in the reactor atmosphere remains above 35 mbar until thermal equilibrium, even though the H$_2$O desorption peak occurs before the bulk of CO$_2$ desorption.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure5-18.png}
\caption{Simulated partial pressure of air as a function of the sorbent temperature at the center of the sorbent bed (solid) and next to the reactor wall (dashed) for humid TVS desorption (M3).}
\end{figure}

5.3.3 CO$_2$ purity and recovery

The model was further employed to analyze the stream of the recovered gas during TVS desorption and to describe the recovery of desorbed CO$_2$ at a given purity level, which is one key performance indicator for an industrial DAC system. This is to quantify the tradeoff between purity and recovery that was briefly discussed in Chapter 3 but could not be experimentally analyzed on the small-scale setup employed there.

Figure 5-19 shows the modeled desorption flows and integrated desorbed volumes of the non-condensable gases CO$_2$ and air in the desorption stream as well
as the modeled CO₂ purity for M3. From the desorption flows it can be seen that during the first few minutes of desorption the non-condensable part of the stream mainly consists of air and after 8 minutes the air flow sharply drops to zero. Between 5 and 8 minutes of desorption, the CO₂ flow increases steeply from around 5 to more than 20 mlN/min. Correspondingly, the CO₂ purity rises to above 99% after around 7 minutes. For the calculation of the purity it is thereby assumed that the water vapor is completely condensed out of the gas stream after the reactor outlet. As a result, 97.4% of the total of 1’100 mlN (0.57 mmol/g) desorbed CO₂ are recovered at >99% purity. This shows that, for the process conditions of M3 and under the assumptions made for the purity calculation, the CO₂ losses due to dilution with air are relatively small.

Figure 5-20, which shows the modeled desorption flow and integrated desorbed volume of H₂O during M3, elucidates the main reason for the quick, initial purge of the reactor avoiding dilution of a larger share of the CO₂ by air. The flow of desorbed water vapor rises by at least an order of magnitude faster than that of CO₂ and air and reaches its peak of around 380 mlN/min after 7 minutes (note the different scale of Figure 5-20). This provides a sufficiently large purge volume flow to completely remove the air from the reactor during the first 8 minutes of desorption as evident from Figure 5-19. This observation highlights another positive effect of humidity in the air and corresponding co-adsorption of CO₂ and H₂O, which is the purge of the reactor by water vapor. The vapor is desorbed relatively early during the desorption step and typically makes up a relatively large volume flow compared to the CO₂ and air flows leaving the reactor. (E.g., 7’400 mlN total desorbed water vapor compared to 1’200 mlN non-condensable gases for M3) The findings are in agreement with the above described modeled composition of the gas phase in the reactor (see Figure 5-15). The extent and the rate of the initial purge obviously depend on the amount of co-adsorbed water and therefore on the RH during adsorption as further analyzed below.
Figure 5-19. Modeled desorption flows (a) and integrated desorbed volumes (b) of the non-condensable gases CO$_2$ and air, as well as modeled CO$_2$ purity in the non-condensable desorption stream (c) during TVS desorption of M3 ($p_{des} = 62$ mbar$_{abs}$, RH during adsorption = 58%); “total” is the sum of the non-condensable gases CO$_2$ and air.
Figure 5-20. Modeled desorption flow (a) and integrated desorbed volume (b) of water vapor during TVS desorption of M3 ($p_{\text{des}} = 62$ mbar$_{\text{abs}}$, RH during adsorption = 58%); note different y-axis scales compared to Figure 5-19.

Figure 5-21 to Figure 5-24 show the corresponding modeled desorption flows, integrated desorbed volumes, and CO$_2$ purities for a desorption pressure of 200 mbar$_{\text{abs}}$ after adsorption at 58% RH and for a desorption pressure of 62 mbar$_{\text{abs}}$ after adsorption at 20% RH, respectively. The remaining process conditions and simulation parameters were identical to M3.

For the case of increased desorption pressure (Figure 5-21 and Figure 5-22) the total mass of air remaining in the reactor after evacuation to 200 mbar$_{\text{abs}}$ is obviously around 3 times larger compared to M3. Accordingly, the air flow peaks after 8 minutes with around 24 mlN/min decaying to nearly zero only after around 20 minutes, which is where the CO$_2$ purity reaches the 99% level. Therefore, in this case only 82% of the the total of 890 mlN (0.46 mmol/g) desorbed CO$_2$ are recovered at >99% purity. While the total amount of water vapor extracted from the column is similar to the case of M3 (6’400 vs. 7’400 mlN), the water desorption flow curve has a broader shape with a much lower peak (150 vs. 380 mlN/min).
This can be partly attributed to the fact that for higher desorption pressures water desorbs at higher temperatures, which in turn implies a slower desorption process due to smaller temperature gradients driving the heat transfer. Consequently, the slower initial purge through water vapor combined with the larger air mass remaining in the system leads to an increased initial dilution of the desorbed CO₂. Thus, increasing the desorption pressure from 62 to 200 mbar\textsubscript{abs} not only reduces the CO₂ desorption capacity from 0.57 to 0.46 mmol/g but also reduces the fraction of the CO₂ that can be recovered at >99% purity from 97% to 82%.

For the case of a RH of only 20% during adsorption at 62 mbar\textsubscript{abs} desorption pressure (Figure 5-23 and Figure 5-24) on the one hand, as expected, the achieved total CO₂ desorption capacity is smaller compared to M3 due to the corresponding CO₂ and H₂O co-adsorption equilibrium. On the other hand, as evident from Figure 5-24, also substantially less desorbed water vapor is available for the initial reactor purge (1’600 vs. 7’400 ml\textsubscript{N} for M3). This leads to a broader, lower peak of the air flow leaving the reactor and the 99% level of the CO₂ concentration is only reached after 15 minutes. Consequently, 88% of the total of 620 ml\textsubscript{N} (0.32 mmol/g) desorbed CO₂ are recovered at >99% purity. This shows again that less co-adsorption of H₂O also leads to a smaller recovery rate of concentrated CO₂. Interestingly, the CO₂ desorption peak is steeper than that of M3 even though overall less CO₂ desorbed, since the sorbent material is heated faster to the temperature range of CO₂ desorption due to the reduced thermal load through H₂O desorption.
Figure 5-21. Modeled desorption flows (a) and integrated desorbed volumes (b) of the non-condensable gases CO₂ and air, as well as modeled CO₂ purity in the non-condensable desorption stream (c) during TVS desorption at $p_{des} = 200$ mbar$_{abs}$ after adsorption at RH = 58%; “total” is the sum of the non-condensable gases CO₂ and air.
Figure 5-22. Modeled desorption flow (a) and integrated desorbed volume (b) of water vapor during TVS desorption at $p_{des} = 200$ mbar$_{abs}$ after adsorption at RH = 58%; note different y-axis scales compared to Figure 5-21.
Figure 5-23. Modeled desorption flows (a) and integrated desorbed volumes (b) of the non-condensable gases CO$_2$ and air, as well as modeled CO$_2$ purity in the non-condensable desorption stream (c) during TVS desorption at $p_{des} = 62$ mbar$_{abs}$ after adsorption at RH = 20%; “total” is the sum of the non-condensable gases CO$_2$ and air.
5.3. Results and discussion

Figure 5-24. Modeled desorption flow (a) and integrated desorbed volume (b) of water vapor during TVS desorption at $p_{des} = 62$ mbar$_{abs}$ after adsorption at RH = 20%; note different y-axis scales compared to Figure 5-23.

Since both desorption pressure and RH during adsorption strongly influence the CO$_2$ recovery at a given purity level, a corresponding parameter study was carried out, where both parameters were varied over the ranges that are considered interesting for practical application. Note that the desorption pressure is a parameter that can be chosen according to the process design, while the RH during adsorption is given by the environmental conditions at the plant site and is subject to daily and seasonal fluctuations which can hardly be influenced. Figure 5-25 shows the modeled CO$_2$ desorption capacities and CO$_2$ recovery fractions for desorption pressures varying between 25 and 200 mbar$_{abs}$ and RH during adsorption varying between 20 and 80%. The CO$_2$ recovery fraction is thereby defined as the fraction of desorbed CO$_2$ that is recovered at a purity >99%. The remaining process conditions and simulation parameters were identical to M3.
The modeled total CO₂ desorption capacities increase with increasing RH during adsorption and decrease with increasing desorption pressure, as expected from the results presented in Chapter 4. For low RH during adsorption the modeled recovery fractions are smaller, become a strong function of the desorption pressure, and strongly decrease with increasing pressure. In the extreme case, at 20% RH, the recovery fraction drops from 96.6% at 25 mbarₐₐₛ to almost zero at 200 mbarₐₐₛ desorption pressure. For higher RH the recovery fractions are larger and the influence of the desorption pressure becomes less pronounced until at 80% RH the recovery fraction only changes from 99.1% to 90.5% when the desorption pressure is increased from 25 to 200 mbarₐₐₛ. This shows that for low desorption pressures the CO₂ recovery rate remains relatively high, independent of the RH during adsorption. For example, at 62 mbarₐₐₛ desorption pressure the recovery rate remains between 87.7% and 98.5% in the analyzed RH range. Overall, for typical process conditions of desorption pressures ≤ 100 mbarₐₐₛ and RH during adsorption ≥ 40% (which can be assumed for most of the time during the day and year for many locations), more than 90% of the totally desorbed CO₂ can be recovered at >99% purity.

These values need to be taken into consideration when evaluating the performance of an industrial TVS system, including its energy consumption, which should be expressed in kWh per ton CO₂ extracted at a certain purity level in order to account for the initial dilution effects. Note that the above definition of the recovery fraction by using the 99% purity level was chosen based on a CO₂ utilization for a subsequent fuel synthesis process for which 99% purity (remainders being air) is considered appropriate. While for other applications other purity levels might be required, the above results would not change significantly if the purity threshold was for example increased to 99.9%, since the modeled purity profiles have a very “sharp” shape and thus reach the 99.9% level shortly after reaching the 99% level.
Figure 5-25. Modeled CO₂ desorption capacities and CO₂ recovery rates at a purity >99% for desorption pressures varying between 25 and 200 mbar/abs and RH during adsorption of 20% (a), 40% (b), 58% (c, as for M3), and 80% (d).
5.3.4 Scale-up

One purpose of the model is serving as a design tool for a scale-up of the TVS process. While the geometry of the sorbent bed of a scaled-up DAC system might be more complex than that of the modeled reactor and will typically depend on the fluid mechanic design of an adsorber structure, the model presented here can provide a guideline for the required bulk distances between heat exchanger elements in the bed.

For example, if the bed was heated by a plate-type heat exchanger, the behavior of such a scaled-up bed during the heating process would be similar to that of the modeled reactor, if the plate distances equal the side length of the reactor. I.e., the required plate distance to achieve a desired performance can be roughly determined by simulating a reactor with varying side length. As an example, a parameter study was therefore carried out in which the side length of the quadratic reactor cross section was varied between 18 and 72 mm. The remaining process conditions and simulation parameters were identical to M3. For each case, the time \( t_{95}^{(des)} \) after which 95% of the total CO\(_2\) desorption capacity was reached was determined. Figure 5-26 shows \( t_{95}^{(des)} \) as a function of the side length, which increases from 16 minutes for a side length of 18 mm to 81 minutes for a side length of 72 mm (see M3). Thus, if the desired desorption time of a process design is for example 30 minutes, Figure 5-26 shows that the required distance between heat exchanger elements in the sorbent material has to be on the order of 40 mm in order to achieve desorption of 95% of the full desorption capacity during this time. For a more detailed analysis the model could be further extended based on the geometry of a scaled-up design. This includes adjusting the temperature boundary conditions of the model to the characteristics of a specific heat exchanger in the sorbent material.

Another possible utilization of the model for the process scale-up can be the simulation of CO\(_2\) recovery fractions at a given purity level and given process conditions for a scaled-up bed geometry. For this purpose, complex geometries could be approximated by adjusting the density of the sorbent material in the model presented here to the overall (“bulk”) density of the sorbent material in the scaled-up bed.
5.4 Conclusions

The model developed in this study elucidates several key aspects of the TVS desorption process:

i) The heating process is controlled by conductive heat transfer, desorption, diffusive mass transport, and subsequent re-adsorption of CO$_2$ and H$_2$O.

ii) Due to fast diffusion under vacuum conditions, the gas phase composition during desorption is nearly uniform over the entire sorbent bed.

iii) The larger CO$_2$ adsorption capacity for humid air than that for dry air is due to the larger CO$_2$ uptake of the sorbent material in the presence of H$_2$O, and to the dilution of CO$_2$ and the corresponding decrease of its partial pressure by desorbed H$_2$O.

iv) The process parameters for humid TVS desorption can be chosen to minimize the risk of O$_2$-induced degradation of the sorbent material as air is purged out by co-desorbed H$_2$O before reaching critical temperatures. On the other hand, during dry TVS desorption, O$_2$-induced degradation is likely as air remains in the reactor until the end of the desorption process at temperatures approaching 90 °C.

v) The purge effect of the stream of desorbed water vapor also minimizes the amount of CO$_2$ that is diluted by air in the beginning of the desorption process. For typical conditions (>40% RH and < 100 mbar$_{abs}$ desorption pressure) more than 90% of the CO$_2$ can be recovered at >99% purity.

Figure 5-26. Required time to reach 95% of CO$_2$ desorption as a function of the reactor side length. (Process conditions and model parameters analogous to M3)
vi) If the side length of a quadratic sorbent bed that is heated from its walls at 95 °C after previous adsorption in 60% RH air is varied between 18 and 72 mm, the desorption time required to achieve 95% of the total desorption capacity varies between 16 and 81 minutes, which provides a reference point for the required geometric dimensions of a heat exchanger.
6 Conclusions and outlook

In this work, a temperature-vacuum swing process for extracting CO₂ from atmospheric air using amine-functionalized solid sorbent materials was developed and characterized in detail. While in most publications dealing with amine-modified solid sorbents for CO₂ capture the sorbent was regenerated with an inert purge gas, the process developed here is one of the few ones that achieve separation of the CO₂ in concentrated form. The process development was carried out in a systematic way starting with an energy analysis and targeting at a process that can be technically feasible at a large scale from an energy consumption point of view. Processes which require treatment of the air stream during adsorption, such as heating, cooling, or compression, were thus excluded from consideration, since they are too energy intensive. It was further shown that, partly due to the typical shape of the CO₂ adsorption isotherms of amine-modified sorbent materials, sole temperature swing or sole pressure swing processes are unfavorable for DAC. On the other hand, the combination of a moderate temperature increase to around 70 – 95 °C and application of moderate vacuum pressures in the range of 50 – 150 mbarₐₛₚ for sorbent regeneration turned out to be compatible with the challenging requirements on a DAC process.

One of the main achievements of this work was the establishment of a robust experimental setup to carry out automated, repeatable, cyclic TVS adsorption/desorption measurements under a wide range of DAC operating conditions. In particular the amount of co-adsorbed H₂O was experimentally quantified for the first time for both, TVS adsorption and desorption. In contrast to the majority of the studies published in the literature, the setup allowed for measurements using relatively large sorbent samples of up to several ten grams. This in turn allowed for creating a CO₂-enriched atmosphere around the sorbent during desorption, as it would be the case for a scaled-up system, and for measuring actual mass flows of desorbed CO₂ which were large compared to the air inclusions in the dead volume of the adsorption column and piping. The demonstration of closed adsorption/desorption mass balances for both, CO₂ and H₂O and two multi-cycle runs with repeatable measured capacities indicate reliability and accuracy of the measurements and a stable performance of the TVS cycle.
The experimental characterization of the TVS process provides a detailed performance map of the process under adsorption and desorption conditions relevant to the industrial implementation of a DAC system for separating a concentrated stream of CO₂ from ambient humid air considering a single adsorption column system. It is a valuable data set to be used as a starting point for the design of a scaled-up CO₂ capture system. Most importantly, the quantification of co-adsorption of H₂O allows for quantifying potential associated energy penalties and reveals the importance of the influence of the relative humidity during adsorption. Since the ambient air conditions can hardly be influenced or controlled, for a scaled-up DAC system designed to operate during daytime and nighttime and during summer and winter the corresponding performance fluctuations must be considered. The development of corresponding control strategies can be a challenging task and will require data such as that measured in this work. Further, it was found that the cyclic CO₂ capture capacity increases slightly with decreasing desorption pressure and strongly with increasing desorption temperature. These findings lead to an optimal system design point depending on the availability of electricity (required for the vacuum pump) and heat.

Moreover, a rigorous numerical model that was validated with measurements for a specific set of operational conditions provided insight to the heat and mass transfer within the sorbent material bed during TVS desorption. This model can serve as a tool for the design of a scaled-up DAC system. Further expansion of the model to incorporate kinetic rates, along with additional experimental validation to better tune the model parameters, will further elucidate the coupled transport and desorption phenomena. While heating of the solid sorbent bed under vacuum through an external heat source is generally challenging, it was shown that the order of magnitude of the required dimensions of heat exchangers to heat the sorbent material to desorption temperature, such as plate distances, is in principle feasible from a technical point of view. In addition, it was shown that due to rapid diffusion in the gas phase the risk of O₂-induced degradation of the sorbent material is very small under humid conditions. The reason for this is that the oxygen is purged out of the system by desorbed water vapor in the beginning of the desorption process. This is a very important finding, since the life time of the sorbent material can have a major influence on the capital cost of a DAC system. It can be an important advantage of the TVS process over other processes which are more likely to expose the sorbent material to oxidizing conditions. It was further found that due to the purging effect of the water vapor losses due to CO₂ dilution
by air remainders in the system are minimized and that for typical process conditions more than 90% of the desorbed CO\textsubscript{2} can be recovered at >99% purity.

Finally, based on the measured and modeled performance of the TVS process under DAC conditions, the energy consumption of the process was estimated, including the energy penalty caused by the desorption of co-adsorbed H\textsubscript{2}O. The energy calculations do not have the accuracy level of detailed process engineering design calculations, but provide an order-of-magnitude information about the feasibility of the process. The electricity requirement for vacuum generation of 60 – 80 kWh/t CO\textsubscript{2} is relatively small compared to the emissions associated with the generation of electricity. The heat requirement for desorption strongly depends on the cyclic CO\textsubscript{2} capture capacity of the sorbent and on the relative humidity during adsorption. While the heat requirement for the best material analyzed in this work is still relatively high (3’110 to 4’030 kWh/t CO\textsubscript{2}), it can be substantially reduced if optimized materials with higher CO\textsubscript{2} capture capacity are developed. Recent developments in material research indicate that such materials are likely to be developed in the mid-term. For example, a material with a cyclic TVS capacity of 0.9 mmol/g, \textit{i.e.}, almost twice the capacity of the best material used in this work, was recently presented.\textsuperscript{91} For a cyclic CO\textsubscript{2} capacity of 2 mmol/g and moderate to medium RH levels, the heat required is in the same range as the heat available as waste heat from a fuel synthesis process. In such a configuration, the DAC process can thus be operated without substantial external heat input except for the heat obtained from the fuel synthesis.

Several future research projects are motivated by the results of this work. These include, amongst others, the detailed measurement and modelling of co-adsorption equilibria and kinetics, the design of and optimization of the sorbent bed geometry and validation measurements with scaled-up systems.

The development of a novel, thorough model for CO\textsubscript{2} and H\textsubscript{2}O co-adsorption on amine-functionalized porous sorbent materials will be one major milestone towards a better understanding of the co-adsorption equilibria under DAC conditions. Such a model should be able to describe adsorption isotherms under various conditions, including those prevailing during TVS adsorption and desorption. In particular, this includes high temperatures up to 100 °C and CO\textsubscript{2} and H\textsubscript{2}O partial pressures up to several 100 mbar\textsubscript{abs}. The precise measurement of these data requires the development of a specific experimental setup such as a differential reactor enabling accurate control and/or measurement of the humidity and CO\textsubscript{2} levels over a sorbent sample that can be kept at a defined temperature.
Experimentally validated kinetic models of the adsorption and desorption of CO\textsubscript{2} and H\textsubscript{2}O on amine-functionalized materials can further extend the detailed understanding of the TVS process. Both, the co-adsorption equilibrium models and kinetic data can be employed to extend the TVS desorption process model. While the results obtained in this work indicate that neglecting kinetics during desorption is a reasonable assumption, their detailed knowledge will significantly enhance the understanding of the adsorption process.

Further possible extensions of the model of the TVS desorption process include validation experiments using extended experimental setups. Measurements of the CO\textsubscript{2}, H\textsubscript{2}O, and oxygen content directly within the bed of a scaled-up reactor could be used to validate the predicted gas phase species concentrations throughout the process. Multiple temperature measurements in a scaled-up reactor could be used to validate 3D temperature distributions.

A detailed modelling of the adsorption process, which was not within the scope of this work, will not only include adsorption equilibria and kinetics, but also the mass transfer in the porous sorbent bed. The latter will be strongly related to the development of sorbent bed geometries that are capable of achieving high mass transfer rates of the CO\textsubscript{2} contained in the gas phase to the sorbent material surface while at the same time the pressure drop is kept at a tolerable level with a maximum of several 100 Pa. A suitable model of the adsorption process shall therefore account for 3D advection and diffusion in the gas phase, kinetics and equilibria of CO\textsubscript{2} and H\textsubscript{2}O adsorption at the sorbent material surface and pressure drop in the air flow. The latter will most likely require CFD simulations which in turn require validation measurements for the pressure drop using different sorbent bed geometries.

Moreover, for the practical application of a DAC process which will operate throughout the year under outdoor conditions, it is necessary to extend the parameter range of analyzed adsorption conditions. This includes in particular measurements at temperatures at below 0 °C. At these conditions, complications due to freezing of water can occur which need to be understood in detail. Thereby, condensed water from previous cycles might be an issue. Also, co-adsorption data for very low temperatures is not available at present and it is not clear whether the adsorption process might behave fundamentally different under these conditions. For these measurements, the existing experimental setup using a thermal oil for heating and cooling the reactor can be utilized. Preferably, such experiments should be carried out using a larger sorbent bed of at least several 10 grams of
sorbent material to account for effects that only occur at larger scales, such as the formation of condensate streams.

Another important aspect is the optimization of transfer of heat during the desorption process. While novel heat exchanger concepts could optimize the heat transfer from an external heating/cooling fluid, fundamentally different concepts such as directly solar irradiated sorbent bed structures offer potentially faster heat transfer rates. The development of such concepts include the optimization of the optical properties of the sorbent material and the bed structure as well as the development of technically feasible structures that can withstand vacuum pressures at large geometrical dimensions and are at the same time transparent to solar irradiation.

Besides the more detailed analysis of the TVS process, the investigation of alternative processes for DAC is of interest and their potential performance should be compared to that of the TVS process. Such processes include desorption in steam or humidity swings as described above. For the comparison of different processes, the definition of appropriate metrics regarding their energy consumption and other properties is crucial.

Finally, in this work no economic considerations regarding the TVS process for capturing CO₂ from the air were performed. To carry out an economic analysis of the process, a large-scale process engineering design of a CO₂ capture plant will be required as a starting point. Based on such a design, the capital, operating, and maintenance costs as well as the actual energy consumption including the consumption of plant auxiliaries can be estimated. These values will finally decide about the economic feasibility of any DAC process. If a scaled-up DAC system is fabricated, validation experiments should be carried out to investigate any scale-up effects that could potentially limit the applicability of the measured data obtained in the laboratory to a large-scale plant.
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