Steam adsorption equilibrium data at 110°C on an activated carbon, Lewatit VP OC 1065, and CALF-20 using a microscale dynamic column breakthrough apparatus

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Abstract

Steam adsorption equilibrium data is important for many carbon capture applications, including direct-air capture, point-source, and pre-combustion carbon capture. However, there is a dearth of concentrated unary equilibrium data for H₂O at temperatures greater than 100°C. In this study, unary steam adsorption equilibrium data was measured at 110°C and up to approximately 1.0 bar partial pressure with a steam microscale dynamic column breakthrough (µDCB) apparatus using a milligram quantities of adsorbent. These partial pressures are equivalent to those used in industrial carbon capture processes. The construction of the apparatus is detailed, along with the necessary calibrations and validations to ensure accurate equilibrium measurement. Three adsorbents were considered in this study: an activated carbon (Calgon BPL), an amine-functionalized polymer (Lewatit VP OC 1065), and a metal-organic framework (Calf-20). It was observed that steam adsorbs strongly on all three materials at 110°C. Activated carbon and Lewatit displayed type-3 isotherm shapes, and Calf-20 displayed a type-5 isotherm shape. Activated carbon and Lewatit were modeled with the GAB isotherm, and Calf-20 was modeled with the cubic-Langmuir isotherm. The 110°C data was compared against H₂O equilibrium data collected at 25°C as a function of relative pressure. An in-house dynamic column breakthrough simulator coded in MATLAB was able to predict the µDCB composition breakthrough curves well for all three materials. The data obtained from the steam breakthrough experiments has important process implications and highlights the need to measure steam adsorption data for any proposed carbon capture material.

Keywords: dynamic column breakthrough, adsorption, equilibrium, water, steam, H₂O, experimental protocol

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1 Introduction

Steam is an important component of many adsorptive processes, including as a reactant in sorption-enhanced water-gas shift reactors [1], and as a purging gas [2, 3] in many industrial separations, such as post-combustion [4, 5], pre-combustion [6] and direct-air carbon capture [7]. The design and optimization of adsorption processes involving steam requires reliable steam adsorption equilibrium data to accurately predict process performance [8]. However, very little steam adsorption equilibrium data exists in the literature. In the NIST/ARPA-E database of novel and emerging adsorbent materials there are 13 publications that contain equilibrium data for water vapor at temperatures greater than 101°C; of these 13 papers, only 8 contain experimentally measured data [9–16]. Most of these steam measurements were made at dilute H₂O concentrations, at partial pressures less than 0.05 bar. The remaining 3 papers contained H₂O data at partial pressures greater than 1.0 bar [9,12,16].

A study by Gruszkiewicz et al. in 2005 was the earliest manuscript found that studied steam adsorption equilibrium above 0.05 bar [9]. Their aim was to determine the temperature dependence of water vapor hysteresis for various adsorbent materials. Gruszkiewicz et al. measured steam adsorption equilibrium on controlled pore glasses, activated carbon monoliths, natural zeolites, and geothermal reservoir rocks at temperatures between 105 and 250°C. Isotherms for different activated carbon samples were made at 105 and 150°C at pressures up to each temperature’s saturation pressure. Steam equilibrium data was measured with an isopiestic instrument with 3–15 grams of adsorbent per measurement. These activated carbon isotherms displayed a type-5 trend [17]. Boon et al. studied steam and CO₂ adsorption at 400°C on potassium-promoted hydrotalcite for a sorption-enhanced water-gas shift process [12]. Steam adsorption equilibrium data was measured using dynamic column breakthrough measurements at partial pressures up to \( \approx 21 \) bar. These experiments utilized a large column set-up that contained \( \approx 2.2–6.8 \) L of adsorbent (\( \approx 1.46–4.38 \) kg of adsorbent) [12]. Mixture CO₂/H₂O experiments were also performed by fixing the partial
pressure of one fluid, and allowing the other to vary. H$_2$O displays a type-2 isotherm trend on hydrotalcite [17]. Kampen et al. studied steam adsorption equilibrium on zeolite 3A at temperatures between 200 and 350°C for a sorption-enhanced reaction process [16]. Kampen et al. also utilized dynamic column breakthrough to measure steam adsorption, utilizing sample sizes of approximately 2–5 grams of adsorbent at 200 and 250°C. Steam adsorption equilibrium measurements were also performed on a thermogravimetric analyzer containing $\approx$ 200 mg of adsorbent between 200–350°C. Steam measurements using both apparatuses were made up to $\approx$ 4.5 bar partial pressure. H$_2$O displayed a type-1 isotherm trend on zeolite 3A [17]. It’s important to note that there is no published steam adsorption data on any metal-organic frameworks or amine-functionalized polymers. These materials are being heavily researched for their potential in pre-combustion, post-combustion, and direct air carbon capture processes [18].

The lack of steam adsorption equilibrium data in the region of interest (0–1 bar partial pressure steam) for carbon capture applications is likely due to the difficulty of the measurement. There are several challenges associated with measuring steam adsorption quantitatively. The steam generator should prevent two-phase flow and provide a stable and consistent flow of steam [19]. This requirement is essential if fixed compositions of dilute steam are required. For dilute or blended steam, a detector that is selective to steam needs to be mounted inside the apparatus at the test temperature ($>\ 100^\circ$C). For open systems such as dynamic column breakthrough, a flow sensor needs to be positioned at the outlet of the bed to monitor the effluent flow rate. This sensor must also be maintained at the test temperature to avoid complications from condensation. Commercial instruments meeting the requirements for quantitative steam adsorption, particularly at the microscale, are scarce and is likely the reason why every published article containing concentrated steam adsorption equilibrium data used either a custom-built apparatus or user-modified commercial equipment; this is another a possible barrier.

In T/PSA process simulations, steam is often assumed to be a non-adsorbing gas
when it is used to purge a heavy component from the adsorbent column [3, 6]. This assumption influences how long it takes the steam to saturate the bed and how much conditioning gas is required to prepare the bed for the next adsorption cycle. This assumption might be valid for hydrophobic materials like activated carbons, but are unlikely to be valid for hydrophilic materials, such as MOFs and amine-functionalized polymers. For these materials steam may adsorb strongly, even at temperatures greater than 100°C. As the search for suitable carbon capture materials continues, adsorption and desorption characteristics must be measured so that the process performance of an adsorbent can be predicted accurately.

Dynamic column breakthrough (DCB), sometimes referred to as “open volumetry”, is one of many experimental techniques that is able to measure single and multicomponent equilibrium [20, 21]. A breakthrough experiment measures the effluent response of a packed bed filled with an adsorbent of interest, to a known step-change introduced at the inlet of the packed bed. The transient response (in gas composition and volumetric flow) can be used to solve a mass balance for the adsorbate equilibrium loading. Dynamic column breakthrough has been classically employed to quantitatively measure equilibrium loadings using larger adsorbent sample sizes, often greater than 10 grams [22]. Quantitative measurements on milligram-scale samples still present many challenges [21–23], especially with condensible adsorbates.

The aim of this study is to build a micro-scale dynamic column breakthrough apparatus (µDCB) that can quantify unary steam adsorption equilibrium and column dynamics on milligram-scale sized adsorbent samples. The milligram sample size facilitates early stage screening of novel adsorbent candidates for carbon capture applications [24]. The details of the steam µDCB system and its operation are described, and the importance of steam adsorption on pressure and temperature swing adsorption process are demonstrated. The system was tested with a series of unary H₂O adsorption and desorption experiments using N₂ as an inert diluent on a metal-organic framework (CALF-20 [4]), an activated carbon (Calgon BPL 4 x 10 CAS #7440-44-00), and an anime-functionalized polymer (Lewatit VP OC 1065). All of these adsorbents have all
been considered in steam-based regeneration cycles for carbon capture. In particular, CALF-20 is used in the rapid-cycle TSA process by Svante Technologies Inc. [4, 5], Lewatit VP OC 1065 is a candidate material for direct-air capture applications [25], and activated carbon has been considered for precombustion carbon capture [6].

2 Materials and Methods

The CALF-20 sample used in this study is the same as the one reported in our previous studies [4, 26–28]. This was deliberately chosen in order to obtain consistent sets of equilibrium data. A more detailed description of the CALF-20 sample can be found in a previous publication [4]. The as-synthesized CALF-20 sample was originally a crystalline powder that formed first into a binderless puck using a hydraulic press, and then broken into 20 – 50 mesh pellets for this study. CALF-20 was activated at 150°C. The activated carbon used in this study (Calgon BPL 4x10 CAS#7440-44-00) is a widely studied commercial adsorbent [22,29–34]. The activated carbon sample was originally pelletized. For this study, it was crushed and sieved to 20 – 50 mesh to pack into the 1/4” Swagelok VCR fittings (used as a adsorbent column). The factory BPL pellets were too large to fit into the column mouth. The activated carbon sample was activated at 200°C. The amine-functionalized polyer, Lewatit VP OC 1065, is a material often considered in direct-air carbon capture (DAC) studies [7, 35]. For brevity, this study will refer to Lewatit VP OC 1065 as ‘Lewatit’. The Lewatit sample was obtained from Millipore-Sigma Canada and has a particle size of 0.5 mm. The Lewatit sample was activated at 110°C. All adsorbent materials in this study were considered to have an approximate skeletal density of 2.0 g/mL. The N₂ in this study (99.995% N₂) was obtained from Linde Canada. Reagent grade deionized water (ASTM 1) was obtained from Millipore-Sigma Canada; it contains less than 60 ppb dissolved solids. Before the deionized water was utilized, it was degassed with a vacuum pump for 2 hours.
2.1 Microscale Steam Dynamic Column Breakthrough Apparatus

The microscale steam dynamic column breakthrough apparatus (steam $\mu$DCB) system was built into a Shimadzu GC14 B gas chromatograph (GC). The internal plumbing and instrumentation in the GC was not used in the construction of the DCB instrument as it functioned simply as very stable convective air thermostatic bath. A manual chromatographic switching valve was installed via a factory made side-port in the oven enclosure so that the entire valve body was housed within the oven. The 6-port Vici valve (with 0.125” connectors) was plumbed as previously reported for an earlier microscale DCB system [22] to function as a 4-port switching valve. The operator could manually select between the two streams connected to a manual valve, which was placed on the outside of the GC oven enclosure. A schematic of the system is shown in Fig. 1 with photos of the apparatus in the Supporting Information.

A bank of flow controllers was mounted to the top of the GC and the associated process lines were fed through factory made access ports in the roof of the oven enclosure. MFC-1 and MFC-2 were Alicat Scientific mass flow controllers ranged to 0–200 Nccm. Nitrogen gas was fed to both mass flow controllers. The outlet from MFC-2 was connected to a T-fitting between the body of the switching valve and the outlet of the steam generator. A check valve was not installed as it was assumed that the backflow of steam up the diluent line would not be an issue when MFC-2 was set to zero. MFC-1 acts as the reference mass flow controller and the face value reported is taken to be the true flow into the system.

A syringe pump (Syringepump.com model NE-300) was equipped with a 2 mL ground glass syringe from Cadence Science (VWR Scientific). A ground glass syringe was selected as the effectively frictionless interference between the barrel and the piston provided the most pulseless flow. A 2 mL syringe volume was selected as it allowed for the most stable flow in the range of 0.01 mL/min because, it is assumed, the smaller diameter of the barrel allowed the stepper motor for the syringe pump to operate at

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more a consistent speed. The barrel of the syringe was fixed with adhesive to the cradle of the syringe pump and the syringe piston was fixed with adhesive to the pusher block. These modifications were necessary to ensure the piston only advanced due to the action of the pusher block and not from pressure changes downstream of the pump. The outlet of the syringe was adapted to connect to a 30 cm length of 0.0625” fluoropolymer (FEP) tubing which then connected to a 0.125” Swagelok union (via a rubber reducing ferrule) that led to the steam generator. Refilling the syringe was accomplished by placing the end of the 0.0625” tubing in a container of degassed, deionized water and slowly drawing the pusher block while holding in the drive nut button.

The steam generator was fabricated from a round, 400 mm long, 6 mm diameter Wakefield-Vette sintered heat pipe (Digikey). The internal sintered copper surface of the heat pipe is intended to increase water vapor adsorption and prevent 2-phase flow. These characteristics seemed ideal for a microscale steam generator and so the selection to use a heat pipe was made. It is important to note that an oven temperature of 105°C was required to have stable steam generation. The ends of the heat pipe were trimmed off to create an open length of tubing. The exhaust end of the heat pipe was adapted to a 1/4” Swagelok compression fitting using a stack of #10 (0.25” ID) silicone o-rings in place of the standard ferrule set. A 20 cm length of 20 gauge needle terminating with a Luer Lock connector was epoxied to the inlet end of the heat pipe such that the end of the needle was positioned ≈ 18 cm from the top of the heat pipe. This positioned the water outlet at roughly the vertical mid point of the oven. The Luer Lock connector was adapted to a 0.125” compression fitting so it could be joined to the delivery line from the syringe pump. An extensive survey of heat pipe length and diameter was not carried out nor was a study carried out to understand whether it would be equally possible to use standard copper or steel tubing in lieu of the length of copper heat pipe. The selection and construction of the steam generator worked to the requirements of the study (temperature of 110 ± 5°C) and the reader should not accept this selection as the only solution for the fabrication of an effective microscale
steam generator.

The configuration of the steam generator in the DCB apparatus introduces an experimental uncertainty that needs to be considered. The evaporator accumulates water vapor until the system reaches equilibrium. At equilibrium the volumetric steam flow from the evaporator is a function of the water flow rate into the heat pipe, the temperature of the evaporator, and the pressure downstream of the evaporator. Should any of these parameters be disturbed, the evaporator will reestablish equilibrium under the new conditions. It is possible that during an adsorption experiment the reduced downstream pressure (due to steam adsorption) could result in an increased steam flow rate. This could impact equilibrium loading measurement for adsorption experiments. While this pressure drop does exist for desorption, the evaporator would not be used during the experiment, and therefore no additional uncertainty would be introduced.

The DCB bed housing was assembled from Swagelok VCR fittings. The bed consisted of four elements. Two SS-4-VCR-6-200 bodies were connected using a SS-4-VCR-CG coupler with a 20 µm snubber frit installed between the glands of the mating parts. One of the bodies was drilled through to 0.1719”. Once all four parts were assembled, a quantity of granulated adsorbent (≈200 mg of 20–50 mesh granules) was poured into the drilled-out fitting and lighted tapped to densify the bed. The physical configuration of the instrument has the bed oriented vertically with the adsorbent resting on the 20 µm frit. The inlet flow is thus in the direction of gravity which mitigates the risk of fluidization at higher flow rates.

Steam was detected using the Sensirion SHT85 combined RH and temperature sensors. One sensor was located at the exit of the bed and the other was positioned at the bypass to monitor the stability of the steam flow before it was directed to adsorbent bed. The sensors were potted into 0.125” Swagelok unions by drilling one of the wrench flats out with a 0.1406” orifice to accept the head of the sensor. High-Heat epoxy putty (J-B Weld) was used to seal the sensor into the fitting. The sensors were oriented so that the edge of the sensor was coaxial with the flow direction. This orientation limited the pressure drop across the sensor housing. The signals from the
sensors were collected with Sensirion’s SEK Sensorbridge hardware and ControlCenter software. The SEK SensorBridge was located outside of the oven enclosure and connected to the sensor using one of Sensirion’s evaluation kit cables. A sampling rate of 10 Hz was used for all experiments.

The outlet flow from the bed was monitored using a microform thermal mass flow sensor supplied as an evaluation kit from Innovative Sensor Technology (IST-A05-Flowmodul mit MFS02, Mouser Electronics). The flow meter employs a microscale hot-wire anemometer and is thus referred to as the Anemometer Flow Meter (AFM). The entire flow channel component was reinforced with the original formulation JB Weld 2-part epoxy. When cured, the epoxy created a clamping force between the printed circuit board and the polycarbonate flow channel and prevented them from warping away from each other when exposed to high temperatures. The small sensor window in the flow channel was protected from epoxy ingress by blinding it with a small piece of high temperature putty. The same epoxy was similarly used to reinforce the hose barb connectors that threaded into the polycarbonate flow channel. The heater voltage on the board was set to 5.0 V. The gain for the board was set so that 50 ccm of N\textsubscript{2} provided a value of roughly 5 V (at ambient temperature). The zero signal for the board was tuned so that the signal at ambient temperature was zero under a condition of zero flow. The voltage output signal from the AFM was logged using a USB-6000 data acquisition system from National Instruments along with the associated DAQExpress software package from National Instruments. Data was collected at a rate of 10 Hz for all experiments. The use of two, independent logging programs necessitated the use of a master clock which could be used to synchronize the independent data streams.

A flow-matching sequence was used to verify the steam flow rates. This consisted of a series of syringe-pump set points, which were calibrated against a primary standard (in this case an Alicat flow controller). The flow-matching sequence was carried out at the experimental temperature which necessitated the use of metal, rather than plastic, tubing for the flow matching sequence. A 500 cm section of 0.25” OD, 0.028” wall
copper tube was bent into a coil with loops ≈ 21 cm diameter. This flow-matching reservoir was connected to the valve at one end and to the RH-AFM sensor cluster at the other. This length of metal tubing increased the fluid residence time so that a single-fluid signal would be measured for a length of time, even after the upstream valve was switched the other gas flow. This is the same means as described previously [22]: the steam flow rate at a selected syringe pump speed could be determined by tuning the N\textsubscript{2} flow from MFC-1 so that the signal at the AFM was constant when the valve was switched between the blended steam and purge N\textsubscript{2} lines.

The use of the AFM for in-situ flow measurement at temperatures above 100°C is highly advantageous but the instrument did require some accommodations. The AFM is situated as close to the outlet of the bed as possible so that the concentration profile measured by the RH sensor and the flow signal are effectively coincident in time. The reproducibility of the AFM instrument is high but its sensitivity is lower than traditional MFMs using thermal or pressure measurement, which somewhat increases the uncertainty of the measurement. Most importantly, however, the flow signal from the instrument is not linearized. The flow signal from the AFM is quasi-exponential with respect to flow and so a calibration was carried out to calibrate the voltage output from the instrument as a function of both N\textsubscript{2} and steam flow rates. The details of the calibration are provided in a later section, and the associated calibration plots are provided in Fig. 2. It should be noted that these calibration plots are valid only for an instrument with identical printed circuit board settings. Should the gain setting or heater voltage be different, the reported calibration values will not be valid. The quasi-exponential nature of the instrument output as a function of flow is consistent across a range of heater voltages and gain settings, so the calibration technique and the form of equation used to fit the profiles will be suitable for any settings used for one of the AFM instruments.

It should be mentioned that the application of both the RH and AFM sensors under the test conditions selected here is well outside of the specification sheets provided by the manufacturers. The authors, however, have not experienced failure or drift in either
of the devices despite repeated thermal cycling to temperatures as high as 120°C and weeks of isothermal experimentation spent at 110°C.

### 2.1.1 Anemometer Calibrations

The AFM voltage signal was found to be nonlinear with respect to fluid normal flowrate (flow at 25°C and 1.00 bar). The measured voltage was also dependent on the composition of the fluid mixture. Pure steam would register a higher voltage than dry N₂ for the same normal flowrate. Normal conditions are: 25°C and 1.00 bar absolute pressure. The AFM first required calibrations to estimate the unary normal flowrates of N₂ and H₂O vapor as a function of the measured AFM voltage. These calibrations were performed at 110°C. A series of measurements were first made by varying MFC-1 and MFC-2 (for N₂ purge, and N₂ diluent, respectively) from a set point of 0 to 200 Nccm, in increments of 5 Nccm until a set point of 30 Nccm, then 10 Nccm increments until at a set point of 100 Nccm, and finally 25 Nccm increments until a set point of 200 Nccm. The AFM signal voltage was measured after a steady voltage had been reached. The calibration points for N₂ are shown in Fig. 2(a) as black markers. As seen in Fig. 2(a), the measured AFM signal (in voltage) for both MFC-1 and MFC-2 is almost identical, with a small disagreement at set points of 15 and 20 Nccm. The calibration data displays an exponentially increasing curve with a vertical asymptote at 5.0 V, where the AFM signal becomes saturated. A similar set of calibration experiments was performed for H₂O by varying the syringe pump speed from 0.01 mL/min to 0.028 mL/min in 0.002 mL/min increments. Again, the AFM voltage signal was measured downstream after the flow came to steady-state. This calibration curve (in Nccm) is shown as blue markers in Fig. 2(a). From the measured data, it is clear that the H₂O AFM signal is also nonlinear. The syringe pump was not able to scan as wide of a flow region as the Alicat MFCs.

The two unary fluid calibration curves display similar nonlinear trends with respect to voltage. Eqn. 1 was used for each fluid to estimate the unary normal flowrate from
the measured voltage signal in the AFM:

\[
Q_i(I_{AFM}) = \frac{I_{AFM} - a_3}{a_1a_2 - a_2(I_{AFM} - a_3)}
\]  

(1)

where \(Q_i\) is the normal flowrate of fluid \(i\), \(I_{AFM}\) is the AFM voltage signal, and \(a_1\), \(a_2\) and \(a_3\) are fitting constants. The constants \(a_1\) (units of V), \(a_2\) (units of Nccm\(^{-1}\)), and \(a_3\) (units of V) are unique for each fluid, and were fitted to the experimentally collected data with an objective function to minimize the sum of squared errors. For N\(_2\) these parameters are: \(a_1 = 4.6510\) V, \(a_2 = 0.034170\) Nccm\(^{-1}\), and \(a_3 = 0.29994\) V. For H\(_2\)O these parameters are: \(a_1 = 4.5792\) V, \(a_2 = 0.054923\) Nccm\(^{-1}\), and \(a_3 = 0.25038\) V.

A series of binary H\(_2\)O/N\(_2\) flow calibrations were also performed. The aim of these calibrations was to determine the normal flow from the AFM voltage signal if the composition was known. The N\(_2\) flowrate was set in MFC-2 at either 10, 20, 30, 40, 50, or 60 Nccm, while the H\(_2\)O flowrate was set in the syringe pump at either 0.01, 0.015, or 0.02 mL/min. The AFM signal was measured downstream of MFM-2 and the syringe pump, once it reached a steady-state. The 18 N\(_2\) and H\(_2\)O set point combinations were measured to correlate measured voltage (\(I_{AFM}\)) with a mixed fluid flow (\(Q(t)\)). A few functions were tested to correlate the AFM voltage to the binary normal flowrate. The function that provided the best fit is given in Eqn. 2, with a parity plot shown in Fig. 2(b).

\[
Q(t) = Q_{H_2O}(I_{AFM}) \cdot y_{H_2O}^{0.460} + Q_{N_2}(I_{AFM}) \cdot y_{N_2}^{0.968}
\]  

(2)

In Eqn. 2, the measured AFM voltage signal, \(I_{AFM}\), is used to estimate the unary N\(_2\), \(Q_{N_2}\), and H\(_2\)O, \(Q_{H_2O}\), normal flowrates. These estimated normal flow values are multiplied with their respective molar fractions, \(y_{N_2}\) and \(y_{H_2O}\). The mole fraction terms needed to be exponential to account for the nonlinearity of the mixed-fluid flow. If the exponents were not used, the predicted normal flow would deviate up to 19% at a mixed H\(_2\)O/N\(_2\) flowrate of 87.5 Nccm. Equation 2 also returns correct flowrates when the fluid is 100 mol% H\(_2\)O or 100 mol% N\(_2\). The parity plot in Fig. 2(b) demonstrates
that the correlation is able to predict the binary normal flowrate within 5% of parity for all measured values. Eqn. 2 was used in all mass balance calculations.

Due to the nonlinearity of the calibration data and resulting equations, it was difficult to estimate the fluid normal flowrate at anemometer signals above 4 V. The noise associated with the AFM signal could cause the calibration to predict unreasonably high flowrates in this range. Due to this, mass balance calculations were only performed if the AFM remained below 4 V (≈ 110 Nccm for N₂) throughout the experiment. This meant that some dilute H₂O adsorption experiments (Qᵢn > 110 Nccm), and concentrated H₂O desorption experiments (Q(t) > 110 Nccm) were unable to provide reliable H₂O equilibrium loadings.

As previously mentioned, the calibration plots in Fig. 2 and fitted constants in Eqns. 1 and 2 are only valid for an instrument with identical tuning settings. The calibration procedure is left in the paper since we believe the procedure is applicable to these AFM devices regardless of their tuning, and is necessary to obtain accurate equilibrium loadings.

2.1.2 Blank Experiment

Blank measurements were performed in the same manner as our previous publication [22]. To measure the blank response, an equivalent empty Swagelok VCR fitting was installed in place of the adsorbent bed. An adsorption blank experiment is run by first initializing the column with a known fluid composition (the 100 mol% N₂ purging gas) and then, at a given time the upstream valve is flipped to the test gas (mixtures of H₂O and N₂). Sufficient time is given for the outlet test gas composition and effluent flow signals to reach a steady-state. Afterwards, the desorption blank response can be measured by flipping the upstream valve back to the purge gas (100 mol% N₂) and waiting for a new equilibrium to be established. This elution profile yields the blank response, which measures all extra-column, intra-column volume, and any time constants associated with instrumentation. The blank response is a slight overprediction
of the fluid volume in the packed VCR fitting, since the measured blank measurement includes volume that would be occupied with adsorbent in the composite response (blank plus adsorbent response). The blank response can be corrected by subtracting the adsorbent volume with the adsorbent’s pycnometric density [22].

A blank response for 100 mol% H$_2$O at 110°C and 0.94 bar pressure is shown in Fig. 3. The blank responses are shown as a function of flow-time, $Q_t$, which is the multiplication of the inlet flowrate (or initial flowrate for a desorption experiment) and the time to yield the number of bed volumes in mL. This transformation was made to directly compare the adsorption and desorption experiments, since most were not performed at the same flowrate. The raw RH meter signal is shown in Fig. 3(a). As previously mentioned, the Sensirion SHT85 measures a relative humidity, $P_{H_2O}/P_{sat}(T) \times 100\%$, where $P_{sat}(T)$ is the vapor pressure at temperature $T$. At 110°C, $P_{sat} = 1.4434$ bar for H$_2$O, so at an outlet pressure of 0.95 bar, an RH reading of around 65% would be expected from the device under a flow of pure steam. The instrument displays an RH value close to this value under pure steam and, critically, displays a linear dependence on the steam mole fraction across all compositions studied. The Sensirion RH meter signal was linear over the composition range of interest. This allowed a simple normalization of the measured signal to determine the mole fraction blank response in Fig. 3(b). This is confirmed by both signals in Figs. 3(a) and (b) crossing at approximately 50% of the full signal. This is more apparent in Fig. 3(b), where they cross at 46 mol%. In Fig. 3(c), the desorption curve is transformed by $1 - y_{H_2O}$, and is plotted with the adsorption blank curve. As seen in Fig. 3(c), both curves are coincident, breaking through at $\approx 1.30 \pm 0.05$ mL. The adsorption/desorption blank response coincidence is not as good as our previous apparatus, which utilized a thermal conductivity detector and programmable pneumatic switching valve [22]. This small discrepancy is mostly due to the manual value switch (repeatable within 300 ms), and partially due to the signal dynamics of the Sensirion RH meter.
2.1.3 Typical Experiment

The system temperature was monitored using the RH/T sensor at the outlet of the bed and once this temperature was stable for at least 10 minutes it was assumed that all of the metal components in the system were isothermal. Adsorbents were dried under purge flow at the test temperature. Each of the adsorbents studied were capable of being purged dry at 110°C under dry N₂. Complete activation was characterized by a stable zero signal for the RH sensor at the outlet of the bed.

Once the oven was at a stable temperature a water flow rate was selected and the syringe pump was started. The steam generator has a significant capacity for water vapor and establishing a stable steam flow could take up to an hour. Because there is no AFM at the outlet of the bypass, the stability of the steam flow rate is best monitored by introducing some diluent N₂ into the system. The presence of the diluent N₂ allows both positive and negative fluctuations in steam flow to be monitored using the RH sensor. Once the RH is constant for at least 10 minutes the system was considered stable. If pure steam is desired all that remains is to turn the diluent flow to zero.

All experiments start with the switching valve positioned to deliver dry purge gas to the bed. To collect the adsorption and desorption breakthroughs the logging softwares have to be synchronized. The master clock (chronometer) is started which establishes experimental zero time. After a desired period of time the Sensirion logging software is started and after another desired period of time the National Instruments logging software is started. Baseline signals under dry N₂ are then collected for a period of time (typically 2 to 5 minutes) after which the valve is switched to deliver steam or diluted steam to the bed. After a period of time long enough to achieve equilibrium (typically 15 minutes) the valve is returned to provide dry purge flow to the bed. All of these events are recorded relative to their time on the master clock and, in this way, the different data streams can be synchronized during signal processing. Synchronizing the streams is a necessity if to solve the mass balance. Having the composition and flow data offset by even a few seconds will corrupt the calculation of molar flow and
render the AFM calibration curves less accurate. Data was sampled at a frequency of 10 Hz.

A typical steam μDCB experiment for 82.1 mol% H₂O (balance N₂) on CALF-20 is shown in Fig. 4 at 0.94 bar and 110°C. The composite adsorption breakthrough curve is shown in Fig. 4(a) (in red). The composite response breaks through after the blank (in black) and pycnometrically corrected blank (in blue). The same is true for the composite desorption curve in Fig. 4(b). As seen in Figs. 4(a) and (b), there is very little noise associated with the RH meter. The associated flow events are given for adsorption in Fig 4(c) and desorption in Fig 4(d). The DCB breakthrough curves display behavior characteristic of a strongly adsorbing gas. For adsorption, there is a decrease in effluent flow (by ≈ 20 ccm) as steam adsorbs into CALF-20. The opposite is observed during desorption, where the effluent flow increases (by ≈ 28 ccm) compared to the initial flow due to the desorption of steam from CALF-20. It is worth noting that the effluent flow event due to adsorption or desorption is much larger than our previous H₂O vapor studies for zeolite 13X [36] or CALF-20 [4]. In these previous studies, the H₂O mole fraction was no greater than ≈ 2 mol%, and therefore its flow event did not contribute significantly to the equilibrium loading calculations, or spread of the breakthrough curves. As seen in Figs. 4(c) and (d), the AFM signal is noisy, and contributes the most uncertainty to the equilibrium measurement. The signal is noisiest during adsorption experiments when steam fills the instrument. This noise may signify an instability in the evaporator, or it could be the result of small temperature variations in the oven which could change the steam volume in the AFM and its measured signal. The latter cause is expected to contribute as the AFM was operated uninsulated in the oven, and was subject to the full force of the convention currents in the enclosure.
3 Mass Balances and Error Analysis

3.1 Experimental Mass Balances

Two separate experiments must be performed to obtain equilibrium data from the steam μDCB apparatus. The first is a “blank experiment”, which is performed through an empty bed, and the second is a “composite response”, which is the column/adsorbent response plus the blank response through an equivalent bed. The blank experiment is performed at a uniform temperature, pressure, inlet flow and composition without any adsorbent in the VCR fitting. It is not essential to run the blank experiment at the same experimental conditions as the composite experiment. However, it is convenient that the conditions for the blank and composite experiments are the same for data visualization purposes. The approach of running a blank for every unique H₂O/N₂ mixture was taken throughout this study.

The mass balance for a blank or an adsorption experiment can be written as:

\[
\text{Input} - \text{Output} = \text{Accumulation} \tag{3}
\]

For an adsorption experiment, the mass balance can be solved for the equilibrium loading of component \( i \) (\( q_{i,\text{ads}}^* \)) as:

\[
q_{i,\text{ads}}^* = \frac{P y_{i,\text{in}}}{RT} \frac{Q_{\text{in}}}{m_{\text{ads}}} \left[ \bar{t}_{\text{comp,ads}} - \bar{t}_{\text{blank,ads}} + \bar{t}_{\text{sync}} \right] \tag{4}
\]

where \( y_{i,\text{in}} \) is the inlet mole fraction of \( i \), \( Q_{\text{in}} \) is the inlet volumetric flow, \( T \) is the oven temperature, \( P \) is the total pressure, \( R \) is the universal gas constant, and \( m_{\text{ads}} \) is the mass of the adsorbent. \( \bar{t}_{\text{comp,ads}} \) is the mean retention time of the composite adsorption experiment and is measured experimentally as:

\[
\bar{t}_{\text{comp,ads}} = \int_0^{t_{\infty}} \left( 1 - \frac{Q(t)y_i(t)}{Q_{\text{in}}y_{i,\text{in}}} \right) dt \tag{5}
\]

where \( y_i(t) \) is the effluent mole fraction of component \( i \), and \( Q(t) \) is the effluent volumetric flow. \( \bar{t}_{\text{blank,ads}} \) is the mean retention time of the blank experiment. An equivalent
expression as Eqn. 5 can be made for $\bar{t}_{\text{blank,ads}}$. $\bar{t}_{\text{pync}}$ is the pycnometric correction, which is defined below:

$$\bar{t}_{\text{pync}} = \frac{m_{\text{ads}}}{\rho_{sk}Q_{\text{in}}}$$

where $\rho_{sk}$ is the skeletal (helium free-space) density of the adsorbent.

For a desorption experiment, the adsorbate is initially in equilibrium at $C_{i,\text{init}} = y_{i,\text{init}}P/(RT)$. The mass balance can be solved again to yield the desorption equilibrium loading ($q_{i,\text{des}}^*$):

$$q_{i,\text{des}}^* = \frac{P y_{i,\text{init}} Q_{\text{init}}}{RT} m_{\text{ads}} \left[ \bar{t}_{\text{comp,des}} - \bar{t}_{\text{blank,des}} + \bar{t}_{\text{pync}} \right]$$

In the case of desorption, there is no input term in the mass balance. Therefore, all subscripts are now denoted as “init” to signify the measured equilibrium is for the the initial conditions of the bed. $\bar{t}_{\text{comp,des}}$ is the mean retention time of the composite desorption experiment, and again is measured experimentally as:

$$\bar{t}_{\text{comp,des}} = \int_0^{t_{\infty}} \left( \frac{Q(t)y(t)}{Q_{\text{init}}y_{\text{init}}} \right) dt$$

The mean retention time of the blank, $\bar{t}_{\text{blank,des}}$, can again be calculated with an equation equivalent to Eqn. 8. The pycnometric correction is the same as for an adsorption experiment, except that $Q_{\text{in}}$ is replaced by $Q_{\text{init}}$.

Note that Eqns. 4 and 7 can be used for either a single-component or multicomponent experiment. When multicomponent experiments are involved, the measured loading corresponds to the competitive or cooperative loading for a given component. The loadings measured in the adsorption and desorption experiments should yield identical values and can be used as a experimental consistency check. Full derivations of the mass balances can be found in the Supporting Information.

### 3.2 Error Analysis

An error analysis was performed to determine the significance of the calculated data. The uncertainty associated with a variable $\gamma$ in a function $f$, $\delta f$, is given by:
\[ \delta f = \left| \left( \frac{\partial f}{\partial \gamma} \right) \delta \gamma \right| \] (9)

where \( \delta \gamma \) is the uncertainty of \( \gamma \).

There are eight measured quantities in the \( \mu \)DCB mass balances that contribute to the uncertainty in the equilibrium loading (\( q^* \)) calculation: \( m_{ads}, T, P, \rho_s, y_{in/init}, Q_{in/init}, y(t) \) and \( Q(t) \). The measurement of both \( y \) and \( Q \) at the inlet and outlet are split into two separate sets of variables since they are measured with different instruments. The sum of all of these errors yields the total system (plus/minus) error for the equilibrium loading:

\[ \delta q^* = \sum_i \left| \left( \frac{\partial q^*}{\partial \gamma_i} \right) \delta \gamma_i \right| \] (10)

The uncertainties associated with these measurements are shown in Table 1. The error propagation equations and derivations are shown in the Supporting Information. The error bars shown in all figures with \( \mu \)DCB equilibrium loading calculations are from these error propagation calculations.

4 Results and Discussion

4.1 Steam Measurements using Known Blank Volumes

The aim of this study is to quantify the adsorption of steam on various adsorbents. To achieve this goal, it is necessary that the steam \( \mu \)DCB can accurately and precisely measure relatively small volumes of gas; volumes commensurate with the quantities of steam adsorbed on small quantities of adsorbents. Validation experiments were performed on three lengths of 1/8” stainless steel tubing, cut at exact lengths of 5’, 10’ and 20’. The internal diameter of the tubing was taken from the Swagelok catalogue as 0.1753 cm and confirmed with a caliper. It was assumed that this diameter was constant throughout the length of the tubing. This resulted in internal geometric volumes of: 3.68 mL, 7.35 mL, and 14.70 mL, for the 5’, 10’, and 20’ lengths of tubing. For a 200 mg adsorbent sample, these volumes (at 110°C and 1.00 bar) would correspond to a
measured equilibrium loading of 0.5771 mol/kg, 1.1541 mol/kg, and 2.3083 mol/kg, respectively. These loadings are representative of the ones measured in this study. The experiments were performed by replacing the adsorbent bed with the 5’, 10’ and 20’ lengths of tubing and running adsorption and desorption experiments using 82.1 mol% H$_2$O (balance N$_2$) blank experiments at 110°C. 82.1 mol% H$_2$O was chosen (instead of 100 mol%) to include the signal and uncertainty from the diluent N$_2$ flow controller (MFC-2). This had the added benefit of monitoring the stability of the steam flow as explained earlier. The measured response can be used to estimate the tubing volume, $V_{\text{tube}}$ using an appropriate mass balance, either Eqn. 11 for adsorption or Eqn. 12 for desorption.

\[
V_{\text{tube}} = Q_{\text{in}} \int_0^{t_{\infty}} \left(1 - \frac{Q(t)y(t)}{Q_{\text{in}}y_{\text{in}}}ight) dt - V_{\text{extra}} \tag{11}
\]

\[
V_{\text{tube}} = Q_{\text{init}} \int_0^{t_{\infty}} \left(\frac{Q(t)y(t)}{Q_{\text{init}}y_{\text{init}}}ight) dt - V_{\text{extra}} \tag{12}
\]

The integrand is measured as a composite response of the intra-tubing and extra-tubing volumes. The extra-tubing volume must also be measured with a separate experiment where the length of tubing is removed. This measurement is different than the previously described blank measurement, since no VCR column is added to the system. Instead, the inlet pipe fitting, that would be attached to the beginning of the length of tubing, is attached to the outlet pipe fitting, which would be at attached to the ending of the length of tubing. This experiment measures the extra-tubing volume, $V_{\text{extra}}$. The extra-tubing volume can be measured from an adsorption experiment with Eqn. 13 or a desorption experiment with Eqn. 14.

\[
V_{\text{extra}} = Q_{\text{in}} \int_0^{t_{\infty}} \left(1 - \frac{Q(t)y(t)}{Q_{\text{in}}y_{\text{in}}}ight) dt \tag{13}
\]

\[
V_{\text{extra}} = Q_{\text{init}} \int_0^{t_{\infty}} \left(\frac{Q(t)y(t)}{Q_{\text{init}}y_{\text{init}}}ight) dt \tag{14}
\]
Three repetitions were made for each length of tubing to yield 6 volume estimations: three from adsorption and three from desorption. The calculated \( \mu \)DCB volume considered both the RH meter and AFM signals to include all noise and sources of uncertainty that would be present if an adsorbent bed was considered. A parity plot of the calculated \( \mu \)DCB volume against the geometric volume is shown in Fig. 5. The parity line is shown in black, with the gray shaded region representing a 5% error bound. The average measured volume was found to be: 3.88 ± 0.24 mL for the 5’ length, 7.17 ± 0.31 mL for the 10’ length, and 14.04 ± 0.39 mL for the 20’ length. The plus/minus error was estimated as a standard error from the repeated measurements. These values are all within 6% of the geometric tubing volume. Specifically, the steam \( \mu \)DCB is able to predict the geometric volume within 5.72% for the 5’ length of tubing, 2.54% for the 10’ length of tubing, and 4.50% for the 20’ length of tubing.

These results demonstrate that the steam \( \mu \)DCB is able to accurately measure small, known volumes to within 6% of their true values. It is also precise, with a standard error no larger than 0.39 mL. The apparatus can comfortably measure an accumulated volume of at least 3.68 mL, which would correspond to an approximate equilibrium loading of 0.5771 mol/kg for a 200 mg quantity of adsorbent at 1.00 bar and 110°C. These results give us confidence that the constructed steam \( \mu \)DCB can accurately and precisely quantify steam adsorption equilibrium.

4.2 Unary Steam Equilibrium on Activated Carbon

Steam and dilute steam breakthrough experiments were performed on activated carbon for \( \text{H}_2\text{O} \) (balance \( \text{N}_2 \)) at 110°C and \( \approx 0.95 \) bar total pressure. Activated carbon was chosen since it has been previously studied [9], and due to its relevance in precombustion carbon capture [6]. For these experiments, 139.7 mg of activated carbon was packed into the \( \mu \)DCB column. A summary of the breakthrough experiments is given in Table 2. Experiments were performed for \( \text{H}_2\text{O} \) compositions between \( y_{\text{H}_2\text{O}} = 0.186 – 1.00 \). The saturation vapor pressure of \( \text{H}_2\text{O} \) at 110°C is 1.4434 bar; this corresponds to equilibrium...
measurements made at relative pressures ($P_{H_2O}/P_{sat}$) between 0.131 – 0.598.

A sample set of breakthrough curves is shown in Fig. 6. The curves in Fig. 6 are plotted in normalized molar flow, either $y(t)Q(t)/(y_{in}Q_{in})$ for an adsorption experiment, or $y(t)Q(t)/(y_{init}Q_{init})$ for a desorption experiment [37]. The accumulation of adsorbate is less ambiguous using these non-dimensional terms than with the mole fraction breakthrough curve alone [37]. The $x$-axis is plotted in flow-time (in mL), either $Q_{in}t$ or $Q_{init}t$. This scaling was utilized since the experimental flowrates were not fixed at a single value. The conversion to flow-time allows for the direct comparison of breakthrough experiments with different inlet flowrates. Three breakthrough curves are shown in each subfigure in Fig. 6. The composite breakthrough curve is shown in red, with the experimentally measured blank response in black, and pycnometrically corrected blank in blue. As described in our previous work, the pycnometric correction becomes more significant at low adsorbate loadings [22]. The area between the (blue) pycnometrically corrected blank and the (red) composite breakthrough curves is proportional to the adsorbate equilibrium loading for a particular adsorption or desorption breakthrough experiment.

Two experimental elution curves are shown in Fig. 6. The first experiment was performed for 49.5 mol% H$_2$O/N$_2$ at 110°C and 0.97 bar total pressure. Panel (a) shows the adsorption experiment, where the pycnometric response breaks through at $\approx$ 1.6 mL, and the composite curve begins to break through at $\approx$ 4.9 mL as a shock. At $\approx$ 6.0 mL, the composite curve shock-propagation ends, and the curve begins to round. The composite breakthrough curve reaches an equilibrium at $\approx$ 40 – 50 mL. The corresponding desorption experiment for 49.5 mol% H$_2$O/N$_2$ is shown in panel (b). The composite desorption initially increases above $y(t)Q(t)/(y_{init}Q_{init}) = 1$ as the effluent flow, $Q(t)$, increases above the the initial flow $Q_{in}$. The effluent flow peak is reached between 0.45 – 1.20 mL, and then the composite curve drops to a value of zero at 15 mL. While the H$_2$O loading at 49.5 mol% steam is significant, it is not larger than the loadings measured for activated carbon at ambient temperature [29]. However, the concentration of steam is an order of magnitude more concentrated than at a similar
relative pressure at 25°C. It is this greater concentration of H\textsubscript{2}O which gives rise to the flow surge observed in the steam desorption experiments, and which is absent at low temperature H\textsubscript{2}O vapor measurements [4,36].

The second row of Fig. 6 shows the results for (c) adsorption and (d) desorption breakthrough curves for 82.1 mol\% H\textsubscript{2}O in N\textsubscript{2} on activated carbon. The adsorption breakthrough curve takes longer to reach an equilibrium than was observed for 49.5 mol\% H\textsubscript{2}O/N\textsubscript{2}, reaching an equilibrium around 100−120 mL. Other than the increased breakthrough time, the 82.1 mol\% H\textsubscript{2}O/N\textsubscript{2} experiment resembles the shape of the 49.5 mol\% H\textsubscript{2}O/N\textsubscript{2} experiment. The associated desorption breakthrough curve in Fig. 6(d) displays a distinct trend. There is a flow-spike associated with the desorption of H\textsubscript{2}O found at \approx 0.46 mL. After the flow-spike, the flow decreases with an apparent inflection between 5 and 6 mL. It reaches a new equilibrium at approximately 15 mL.

Using an appropriate mass balance for adsorption (Eqn. 4) or desorption (Eqn. 7) the equilibrium loading can be calculated from both the adsorption and desorption curves. These values are shown in Fig. 7(a), and are tabulated in Table 2. The adsorption equilibrium loading at \( y_{H\textsubscript{2}O} = 0.186 \) and desorption equilibrium loading \( y_{H\textsubscript{2}O} = 1.00 \) are not reported, since the recorded AFM signals were greater than 4.0 V and provided unreliable normal flow estimations. The calculated H\textsubscript{2}O equilibrium loadings are initially lower at lower steam mole fractions. The H\textsubscript{2}O loading slope increases around a steam pressure of about 0.6 bar after which the H\textsubscript{2}O loading increases rapidly to 5.8900 mol/kg at 0.93 bar. As seen in Fig. 7(a), the equilibrium loading displays a type-3 (anti-Langmuir) isotherm [17] for the range of pressures measured. This suggests that adsorbate-adsorbent interactions are weak [17]. This observation is reasonable since activated carbons tend to display hydrophobic characteristics [9]. Figure 7(d) shows the same adsorption equilibrium data as a function of relative pressure \( (P_{H\textsubscript{2}O}/P_{\text{sat}}) \) and includes a comparison with data from the literature at 25°C (blue circles) [29]. The low temperature H\textsubscript{2}O data from Qi and LeVan is on the same Calgon BPL activated carbon. Only the adsorption-branch of the data by Qi and LeVan is plotted in Fig. 7(d). As seen in Fig. 7(d), low temperature data has a greater loading...
than the data at 110°C at a fixed relative pressure. This observation is interesting, as it suggests that low temperature H\textsubscript{2}O equilibrium data cannot be assumed to be equal to the steam adsorption equilibrium data. The data from both temperatures appears to share the same isotherm shape, but it is not coincident. This suggests that high temperature H\textsubscript{2}O must be measured to accurately estimate unary H\textsubscript{2}O at high temperatures. It cannot be extrapolated from a dilute, low temperature measurement. This is not the case for a material like zeolite 13X [19,36].

Gruszkiewicz et al. found type-5 behavior for H\textsubscript{2}O on their activated carbons at 105 and 150°C [9]. For Gruszkiewicz et al., the inflection point was observed in the range of \( \approx 0.546 - 0.693 \) relative pressure at 105°C. The saturation vapor pressure at 105°C is 1.209 bar. The full isotherm by Qi and Levan also displayed a type-5 shape, with an inflection at \( \approx 0.536 \) relative pressure (off-scale in Fig. 7(d)) [29]. In this study, steam was measured up to a relative pressure of 0.598 at 110°C. The data reported in Gruszkiewicz et al. would appear type-3 if plotted up to 0.598 relative pressure. The same trend is observed with the data by Qi and LeVan at 25°C in Fig. 7(d) [29]. The H\textsubscript{2}O isotherm shape observed by both Gruszkiewicz et al., Qi and LeVan, and this study are the same for the range of H\textsubscript{2}O equilibrium data measured.

4.3 Unary Steam Equilibrium on CALF-20

Single-component H\textsubscript{2}O (balance N\textsubscript{2}) breakthrough experiments were also performed on CALF-20 at 110°C and \( \approx 0.97 \) bar total pressure. CALF-20 is a water-stable metal-organic framework that was recently described by Lin et al. [4], and has been deployed in industrial carbon capture processes [26–28,38]. Most importantly, CALF-20 is stable in steam [4,38]. The study by Lin et al. reported low concentration H\textsubscript{2}O equilibrium data at 100°C, demonstrated that CALF-20 remained stable after exposure to 450000 steam cycles at 150°C, and showed minor changes in N\textsubscript{2} isotherms at 77 K before and after steam-cycling [4]. This behavior should allow the use of steam-purging in carbon capture adsorptive separations process to yield a high-purity CO\textsubscript{2} extract product.
For this set of experiments, 209.8 mg of CALF-20 was packed into the μDCB column. A summary of the breakthrough experiments is given in Table 3. Experiments were performed for H_2O compositions between $y_{\text{H}_2\text{O}} = 0.147−1.00$. This corresponds to equilibrium measurements made at relative pressures ($P_{\text{H}_2\text{O}}/P_{\text{sat}}$) between 0.106−0.654 at 110°C.

A representative set of CALF-20 breakthrough curves is shown in Fig. 8. The first row corresponds the (a) adsorption and (b) desorption of 49.5 mol% H_2O/N_2 at 110°C and 0.98 bar. For the adsorption experiment, the pycnometrically corrected blank experiment again breaks through quickly at $\approx 1.6$ mL. The composite experiment begins to breakthrough at $\approx 34$ mL, and slowly increases to the inlet molar flow at $\approx 300$ mL. The adsorption breakthrough curve resembles the 49.5 mol% H_2O/N_2 breakthrough on activated carbon in Fig 6(a). The corresponding desorption experiment is shown in Fig. 8(b). After the desorption flow-spike between 0.4 and 2.1 mL, the molar flow decreases until $\approx 80$ to 100 mL where another transition is observed. After this transition, the molar flow decreases rapidly, where another equilibrium is established at $\approx 140$ mL. The 49.5 mol% H_2O/N_2 CALF-20 desorption experiment qualitatively resembles the 82.1 mol% H_2O/N_2 activated carbon desorption in Fig 6(d). The main difference is that there appears to be much more capacity for H_2O on CALF-20 than activated carbon.

The second row of Fig. 8 is for a mixture of 82.1 mol% H_2O/N_2 at 110°C. The adsorption breakthrough curve is shown in panel (c). There is also a significant drop in effluent flow in these concentrated steam experiments. The composite curve begins to breakthrough at $\approx 40 - 50$ mL. After $\approx 66$ mL, the breakthrough curve begins to round until and equilibrium is reached around $\approx 200$ mL. The adsorption breakthrough curve shape at 82.1 mol% similar to the previous adsorption curve at 49.5 mol%. An interesting trend is observed for the desorption breakthrough curve, shown in Fig. 8(d). A large amount of effluent flow is observed upon the initial desorption of H_2O. This causes the flow-spike to momentarily increase to a value almost 4.8 times greater than the inlet flow at a flow-time of 0.34 mL. The molar flow then decreases...
until approximately 140 mL where a new equilibrium is established. On first glance, it appears that there is no inflection in the 82.1 mol% H₂O/N₂ desorption curve. Upon closer examination, a similar transition to the 49.5 mol% H₂O desorption experiment is observed for 82.1 mol%, again between 80 – 100 mL. This transition is much less pronounced, and is likely due to the large initial effluent flow change. The change in effluent flow was not observed by Lin et al., since they preformed their experiments under dilute conditions [4].

Again, using an appropriate mass balance for adsorption (Eqn. 4) or desorption (Eqn. 7), the equilibrium loading could be calculated. These values are shown in Fig. 7(b), and are tabulated in Table 3. Some equilibrium points were measured, but had too much uncertainty associated with them for publication. They are shown in Table 3 with a dash and are specifically: adsorption loadings at $y_{H_2O} = 0.147$ and $0.186$, and a one desorption experiment at $y_{H_2O} = 1.0$. As shown in Fig. 7(b), the calculated equilibrium data displays a type-5 isotherm. The initial part of the isotherm, up to $\approx 0.30$ bar H₂O, the isotherm appears anti-Langmuirian. Between $\approx 0.30$ and $\approx 0.48$ bar there is an inflection point, which changes the isotherm shape to Langmuirian. The observation of a type-5 isotherm shape is consistent with previous H₂O equilibrium data on CALF-20 at 22°C [4].

Figure 7(e) shows the same isotherm data plotted in relative pressure, with a comparison with low temperature data (22°C) by Lin et al. (blue circles) [4]. Note that the sample in Lin et al. included about 25 wt% binder, while the sample used in this study was binderless. To compare the data directly, the data by Lin et al. was multiplied by 1.25 to account for the decrease in gravimetric loading of the binded sample. It should be noted that only the adsorption-branch of the data by Lin et al. was plotted in Fig. 7(e). As was observed for activated carbon, the low temperature equilibrium loading data from Lin et al. was consistently greater than our data collected at 110°C at equivalent relative pressure. It is interesting that the isotherm inflection point at 110°C does not appear to be at the same relative pressure as at 22°C. The inflection appears to move to a higher relative pressure at 110°C. Other mesoporous metal-organic
frameworks, such as MIL-101(Cr), have shown this trend [39]. Fei et al. found that as the isotherm temperature increased from $-6^\circ\text{C}$ to $70^\circ\text{C}$, the H$_2$O hysteresis loop shifted to higher relative pressures, and the saturation loading decreased [39]. This shift appears to be consistent with our observations. A recent paper by Chen et al. demonstrated that CALF-20 forms a distinct polymorph ($\beta$-CALF-20) between 11 & 23% relative humidity at room temperature, and that this coincides with the step in the type-5 isotherm [40]. It is possible that the $\beta$-CALF-20 polymorph forms at greater relative pressures as the temperature increases. The observation that the adsorption temperature can change the characteristics of the H$_2$O isotherm demonstrate the necessity of concentrated steam adsorption equilibrium data on CALF-20.

4.4 Unary Steam Equilibrium on Lewatit

Single-component H$_2$O (balance N$_2$) breakthrough experiments were also performed on Lewatit VP OC 1065 at $110^\circ\text{C}$ and $\approx 0.98$ bar total pressure. Lewatit is an amine-functionalized polymeric material that has been studied for direct-air carbon capture applications [7, 25, 35]. For this set of experiments, 156.4 mg of Lewatit was packed into the $\mu$DCB column. A summary of the breakthrough experiments is given in Table 4. Experiments were performed for H$_2$O compositions between $y_{\text{H}_2\text{O}} = 0.147 − 1.00$. This corresponds to equilibrium measurements made at relative pressures ($P_{\text{H}_2\text{O}}/P_{\text{sat}}$) between 0.109 − 0.647 at $110^\circ\text{C}$.

A representative set of breakthrough curves is shown in Fig. 9. The first row corresponds the (a) adsorption and (b) desorption of 49.5 mol% H$_2$O/N$_2$ at $110^\circ\text{C}$ and 0.96 bar. For the adsorption experiment (Fig. 9(a)), the pycnometric response breaks through at $\approx 1.6$ mL, and the composite curve begins to breakthrough as a shock at 4.3 mL. The adsorption breakthrough curve rapidly increases until $\approx 10.4$ mL, where the curve begins to round. An equilibrium is established around 90 − 100 mL. This breakthrough curve resembles the activated carbon and CALF-20 adsorption breakthrough curves (Figs. 6 & 8). For the desorption experiment (Fig. 9(b)), the
composite experiment (in red) initially increases to a factor of 2.00 above the normalized molar flowrate \((y(t)Q(t)/(y_{\text{init}}Q_{\text{init}}))\) at \(\approx 0.4\) mL flow-time. The normalized molar flow then decreases as a smooth curve until \(35 - 40\) mL flow-time, where a new equilibrium is established.

The second row corresponds the (a) adsorption and (b) desorption of 82.1 mol\% \(\text{H}_2\text{O}/\text{N}_2\) at 110°C and 0.94 bar. The adsorption experiment (Fig. 9(c)) appears to take a similar amount of time (80 – 100 mL) to reach equilibrium as the \(y_{\text{H}_2\text{O}} = 0.495\) experiment, and it has a similar breakthrough curve shape. It initially breaks through at \(\approx 7.0\) mL, and increases quickly to around \(\approx 13.1\) mL where the curve begins to round and slowly approach an equilibrium. It is important to note that the \(y_{\text{H}_2\text{O}} = 0.821\) experiment does initially breakthrough slightly later (\(\approx 3\) mL) than the \(y_{\text{H}_2\text{O}} = 0.495\) experiment. It is also possible that the \(y_{\text{H}_2\text{O}} = 0.821\) experiment required more time to establish an equilibrium, but it cannot be distinguished from the the effluent flowmeter noise. The desorption experiment (Fig. 9(d)) appears similar to the experiment at \(y_{\text{H}_2\text{O}} = 0.495\), but the normalized molar flow now approaches a value of 4.03 in the initial flow spike (at 0.3 mL) and then decreases until \(35 - 40\) mL flow-time.

Again, using an appropriate mass balance for adsorption (Eqn. 4) or desorption (Eqn. 7), the \(\text{H}_2\text{O}\) equilibrium loading can be calculated. These values are shown in Fig. 7(c), and are tabulated in Table 4. Some equilibrium points were measured, but had too much error associated with them to include in this manuscript, or had an anemometer reading above 4 V. They are shown in Table 4 with a dash and are specifically: adsorption loadings at \(y_{\text{H}_2\text{O}} = 0.147, 0.186, \text{ and } 0.314\). The calculated data displays a type-3 isotherm shape and is consistent with data previously measured on the material [25,35]. The \(\text{H}_2\text{O}\) loadings initially appear linear (type-1) to \(y_{\text{H}_2\text{O}} = 0.661\). At this point the isotherm slope begins to increase as a type-3 isotherm. The initial \(\text{H}_2\text{O}\) loading is quite high when compared to activated carbon, reaching a \(\text{H}_2\text{O}\) loading of 1.0 mol/kg at 0.385 bar steam pressure. This may be due to the uptake mechanism of \(\text{H}_2\text{O}\) on Lewatit, which is not microporous in nature and may instead adsorb \(\text{H}_2\text{O}\) into its polymer matrix.
Young et al. have published H$_2$O equilibrium data at 100°C on Lewatit to 0.40 bar [25]. This data is shown as the gray ‘x’ markers in Fig. 7(c). While it does not cover the entire range studied here, it remains an important point of comparison. Data by Young et al. at 100°C displays a fairly linear isotherm with equilibrium loadings that are greater than our calculated loadings at 110°C, but appear to follow the same isotherm profile as described by the data collected in this study. Young et al. published H$_2$O equilibrium data at lower temperatures and observed a consistent type-3 trend out to higher relative pressures [25]. Figure 7(f) shows the same isotherm data plotted in relative pressure, with a comparison with low temperature data (25°C) by Low et al. (blue circles) [35]. Only the adsorption-branch of the data by Low et al. is shown in Fig. 7(f). The same type-3 isotherm shape is seen in all three datasets [25,35]. As was observed for both activated carbon and CALF-20, the low temperature data at 25°C is consistently greater than our data at 110°C. The topography of the steam isotherms for all three materials bear a strong resemblance to their low temperature H$_2$O isotherm counterparts. These observations suggest that the steam isotherm classification is predicted by the low temperature H$_2$O isotherm. In all three cases, however, the equilibrium loadings for the steam isotherm lie below those calculated for the same materials at ambient temperature. In the case of CALF-20, not only is the H$_2$O loading lower, but the position of the inflection of its type-5 isotherm shifts in comparison to its low temperature counterpart; an observation which highlights the risk associated with adopting the low temperature H$_2$O isotherm as a proxy for the high temperature steam isotherm.

4.5 Modeling Steam Equilibrium Data

Among the three materials studied, two isotherm types were evident. Both activated carbon and Lewatit displayed a type-3 (anti-Langmuirian) isotherm, and CALF-20 displayed a type-5 isotherm. The measured isotherms need to be fit with appropriate models in order to accurately simulate the H$_2$O breakthrough curves for the three
The Guggenheim-Anderson-De Boer (GAB) isotherm [41] was chosen to model the type-3 isotherms. This isotherm model is widely used for H$_2$O on amine-functionalized materials with particular applications in direct-air capture [7,35,42]. This is partially due to its ability to model type 1, 2, and 3 isotherm shapes depending on the value of its parameters [41]. The formula describing the GAB isotherm is shown in Eqn. 15.

$$q_{\text{H}_2\text{O}}^* = \frac{q_{\text{H}_2\text{O}}^\text{sat} c_{\text{H}_2\text{O}} b_{\text{H}_2\text{O}} x_{\text{H}_2\text{O}}}{(1 - b_{\text{H}_2\text{O}} x_{\text{H}_2\text{O}})(1 + (c_{\text{H}_2\text{O}} - 1)b_{\text{H}_2\text{O}} x_{\text{H}_2\text{O}})}$$ (15)

where, $q_{\text{H}_2\text{O}}^\text{sat}$ is the monolayer saturation capacity of the adsorbent, $b_{\text{H}_2\text{O}}$ is one nonlinearity constant, $c_{\text{H}_2\text{O}}$ is a second nonlinearity constant and a parameter that determines the isotherm shape (either type-2 and type-3), and $x_{\text{H}_2\text{O}}$ is the relative pressure of H$_2$O. The relative pressure of H$_2$O ($x_{\text{H}_2\text{O}}$) is defined as: $x_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}/P_{\text{sat}}$, where $P_{\text{sat}}$ is the saturation (vapor) pressure of water. The $b_{\text{H}_2\text{O}}$ and $c_{\text{H}_2\text{O}}$ parameters can be made functions of temperature [25], but will only be considered at 110°C for this study.

The steam saturation pressure ($P_{\text{sat}}$) was determined with the International Association for the Properties of Water and Steam (IAPWS) 1995 equation of state (EOS) [43]. This will be referred to the IAPWS 1995 EOS. Its correlation for steam saturation pressure is given in Eqn. 16.

$$\ln\left(\frac{P_{\text{sat}}}{P_c}\right) = \frac{T_c}{T}(\beta_1 \nu + \beta_2 \nu^{1.5} + \beta_3 \nu^3 + \beta_4 \nu^{3.5} + \beta_5 \nu^4 + \beta_6 \nu^{7.5})$$ (16)

where $\nu = (1 - T/T_c)$, $T_c$ is the critical temperature of H$_2$O ($T_c = 647.096$ K), $P_c$ is the critical pressure of H$_2$O ($P_c = 220.64$ bar), and $\beta_1 - \beta_6$ are constants with the values: $\beta_1 = -7.85951783$, $\beta_2 = 1.84408259$, $\beta_3 = -11.7866497$, $\beta_4 = 22.6807411$, $\beta_5 = -15.9618719$, and $\beta_6 = 1.80122502$ [43]. The IAPWS 1995 EOS was chosen due to its high saturation pressure accuracy (within ±0.04% of the true value) and its recommendation by the National Institute of Standards and Technology (NIST) [43].

The GAB isotherm fits for activated carbon and Lewatit are shown in Figs. 7(a) and (c) respectively, as the black lines, with their parameters found in Table 6. As seen in Fig. 7, both datasets are fitted well. For activated carbon, there are a few
discrepancies with the measured equilibrium data and the GAB isotherm model once multilayer formation begins at $\approx 0.632$ bar. The low pressure range of the isotherm is fitted very well for activated carbon. The estimated error for each measured point below 0.632 bar bisects the GAB model prediction. The Lewatit GAB isotherm fit is very good, with the error of each point bisecting the GAB isotherm fit.

The cubic-Langmuir isotherm was chosen to model the (type-5) H$_2$O isotherm on CALF-20 [44]. This isotherm has been previously used to successfully model dilute H$_2$O equilibrium on CALF-20 between 22 and 100°C [28]. The cubic-Langmuir isotherm is shown in Eqn. 17.

$$q_{\text{H}_2\text{O}}^* = \frac{q_{\text{H}_2\text{O}}^{\text{sat}}(b_{1,\text{H}_2\text{O}}C_{\text{H}_2\text{O}} + 2b_{2,\text{H}_2\text{O}}(C_{\text{H}_2\text{O}})^2 + 3b_{3,\text{H}_2\text{O}}(C_{\text{H}_2\text{O}})^3)}{1 + b_{1,\text{H}_2\text{O}}C_{\text{H}_2\text{O}} + b_{2,\text{H}_2\text{O}}(C_{\text{H}_2\text{O}})^2 + b_{3,\text{H}_2\text{O}}(C_{\text{H}_2\text{O}})^3} + \frac{q_{\text{d}}^{\text{sat}}d_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}}{1 + d_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}}$$ (17)

where $C_{\text{H}_2\text{O}}$ is the concentration of H$_2$O ($C_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}}P/(RT)$ assuming an ideal gas) $b_{1,\text{H}_2\text{O}}$, $b_{2,\text{H}_2\text{O}}$, and $b_{3,\text{H}_2\text{O}}$ are nonlinearity parameters for the $b$-site, $d_{\text{H}_2\text{O}}$ is the nonlinearity parameter for the $d$-site, and $q_{\text{b}}^{\text{sat}}$ and $q_{\text{d}}^{\text{sat}}$ are the saturation capacities for the $b$ and $d$-sites, respectively. For this isotherm fit, the concentration (instead of relative pressure) was taken as the dependent variable [28].

The cubic-Langmuir isotherm fit for H$_2$O on CALF-20 is shown in Fig. 7(b) as the black line, with the fitted parameters found in Table 7. As seen in Fig. 7(b), the overall fit is quite good with more deviations from the model as the pressure approaches 1.0 bar, which is acceptable given the uncertainty in the calculated data. The isotherm model finds an inflection from a type-3 (anti-Langmuirian) isotherm shape to type-1 (Langmuirian) isotherm shape at approximately 0.30 bar ($P_{\text{H}_2\text{O}}/P_{\text{sat}} = 0.209$), which is consistent with the previous study by Lin. et al [4].

4.6 Dynamic Column Breakthrough Simulations

The dynamic column breakthrough simulator was previously developed in MATLAB using finite-volume techniques [45]. The column was assumed to be one-dimensional with 30 finite volume nodes and a van Leer flux limiter. The breakthrough simulator assumes the following:
1. The gas phase is ideal. While the fluid is a mixture of N\textsubscript{2} and concentrated H\textsubscript{2}O, the associated gas compressibility factors, Z, are within 1.3% of ideality (Z = 1 ± 0.013) [46].

2. The column is one-dimensional in the axial-direction, with no radial gradients in concentration or temperature.

3. An axially-dispersed plug-flow model adequately describes flow through the column.

4. The pressure-drop can be modelled adequately with Darcy’s Law. This assumption is justified since all experiments were carried out in the laminar flow regime (Re < 11).

5. The adsorbent column is isothermal. This assumption is justified due to the relatively small quantity of heat released for the large flowrate traveling through the column. Nonisothermal simulations were also performed, but yielded similar results.

6. Adsorbent and column properties are uniform throughout the column.

7. The linear driving force model adequately describes the solid phase mass transfer rate.

This simulator has been described in detail in the original paper by Haghpanah et al. [45] and one of our previous publications [8]. The equations incorporated into the model are shown in Table 5.

### 4.6.1 Blank Correction Procedures

An important point to stress is that the dynamic column breakthrough simulator will produce a result characteristic of a “true” column response, with no extra-column volume considered. Essentially, the simulation will only simulate the intra-column
volume. There are multiple strategies to compare simulation and experimental results, most of which aim to remove the extra-column response from the composite (measured) breakthrough response to yield a ‘true’ or intra-column experimental response [37, 47–49]. The μDCB contains a large extra-column volume compared to the column volume. This usually makes it difficult to correct the composite experimental response to an intra-column experimental response. The previously cited procedures can add a significant amount oscillations around sharp transitions (such as a shock propagation) [48]. However, these techniques can also be used in the opposite direction. The extra-column response can be modelled and then added to the intra-column (“true”) simulation result to provide a composite (intra- plus extra-column) simulation response. This strategy was used to compare simulations with the experimentally measured breakthrough curves.

The blank correction technique utilized in this study is the tanks-in-series (TIS) method [48]. The correction procedure assumes that the downstream extra-column volume can be modeled as the composition response through a defined number of well-mixed tanks with a fixed volume. The authors described both the inversion process, which corrects a composite experimental response to an intra-column response, and the correction without inversion, which adds an extra-column experimental response to the intra-column simulation results for a composite simulation. For this study, the latter approach was taken to compare simulation and experimental composite responses (including extra-column volume). In other words, the measured (composite) experimental breakthrough curve was compared with a simulated composite breakthrough curve. The tanks-in-series model requires two parameters, the volume of each tank and the number of tanks in series. These were fitted to values of 0.14447 mL (in $Qt$, flow-time) and 8 tanks, respectively. The TIS model predictions are shown for many different blank experiments in the Supporting Information.

The effect of the blank response on the composite simulation results depended on the steam-adsorbent system considered. For CALF-20, the effect was negligible. The shortest CALF-20 steam desorption considered ($y_{H_2O} = 0.147$) reached an equilibrium
at $\approx 100$ mL. This results in approximately a 1% change in simulated flow-time estimation. However, the simulated composite response for both activated carbon and Lewatit was noticeably changed due to the TIS blank response addition. This change is proportional to the duration of the desorption experiment. This change could be up to 10% of the flow-time for the lowest activated carbon experiment considered at $y_{H_2O} = 0.186$. The equivalent value for Lewatit ($y_{H_2O} = 0.147$) would result in a maximum 5% change in flow-time.

4.6.2 Composite Desorption Simulation Results

Desorption breakthrough simulations were generated for activated carbon, Lewatit, and CALF-20 using the previously described simulator and assumptions. Only desorption experiments were considered since the desorption flowrate (using an Alicat flow controller) was significantly more consistent than the blended steam adsorption flow rate. Also, for a desorption experiment it does not matter how its initial conditions came to an equilibrium, just that one had been reached during the previous adsorption experiment, regardless of any flow instabilities or pressure imbalances that may have occurred before equilibrium. Since the inlet desorption flowrates were lower than those in adsorption, this data was also of higher resolution. Finally, the desorption of steam using $N_2$ (or air) is an important process step. This step would be necessary to remove the loaded $H_2O$, and prepare the adsorbent bed for the feed gas in the next TSA cycle. For example, the Svante VeloxoTherm process consists of an adsorption step to adsorb $CO_2$ from a flue gas, followed by a steam regeneration step to capture the trapped $CO_2$, and finally a hot air conditioning step to cool the process and remove trapped $H_2O$ [5]. The conditioning step is equivalent to the desorption experiments presented in this study. The simulation parameters are given in Table 8. In this section, the $H_2O$ mole fraction breakthrough curves will be used to compare experiment and simulations. This is a departure from the normalized molar flowrates shown earlier, but was necessary due to the blank correction technique utilized [48].
Three activated carbon desorption experiments (at $y_{H_2O} = 0.186, 0.394,$ and 0.821) were chosen to validate the numerical simulations. $y_{H_2O} = 0.186$ and $y_{H_2O} = 0.821$ were chosen to study the extremes in the mole fraction desorption curves, while $y_{H_2O} = 0.394$ was chosen to study the transition between the two desorption profiles. All three experimental and simulated desorption breakthrough curves are shown in Fig. 10(a). Starting with $y_{H_2O} = 0.821$ (a partial pressure of 0.780 bar), the experimental curve (as red circles) appears to have two transitions, one at approximately 1–2 mL (in $Q_{init}t$) and another at approximately 6 mL. The simulation was only able to predict one of these transitions. It is able to approximate the experimental desorption curve, but does not capture all experimentally observed features. The desorption curve at $y_{H_2O} = 0.186$ (a partial pressure of 0.188 bar, shown as green triangles) only has a single transition that begins at approximately 1–2 mL and decreases gradually to its new equilibrium. The simulation captures this curve very well. However, the desorption curve at $y_{H_2O} = 0.394$ (a partial pressure of 0.388 bar) could not be estimated as well with the simulations. Experimentally, the desorption curve (as blue squares) first remains at $y_{H_2O} = 0.394$ until $\approx 3$ mL. At this point, $y_{H_2O}$ decreases rapidly to zero at $\approx 9 - 10$ mL. This contrasts with the $y_{H_2O} = 0.394$ simulation that predicts a response that more gradually returns to $y_{H_2O} = 0$ at $\approx 15$ mL. This difference in the curve is likely due to the choice of isotherm model and goodness of the fit to the equation. For these simulations, the mass transfer coefficient, $k_i$, was kept as a fitting parameter. This was done to estimate the mass transfer resistance in the $\mu$DCB column. For steam on activated carbon, $k_i = 0.2 \text{ s}^{-1}$. This suggests that there is not a large mass transfer resistance for steam adsorption on activated carbon.

Simulations were also performed for three Lewatit desorption experiments in Fig. 10(b). Desorption experiments at $y_{H_2O} = 0.147, 0.394,$ and 0.821 were chosen, again to study the effect of isotherm shape and the ability for the simulator to capture the experimentally observed trends. Overall, GAB isotherm model is fitted very well to the measured $\mu$DCB equilibrium data. The Lewatit H$_2$O desorption experiment at $y_{H_2O} = 0.821$ (partial pressure of 0.775 bar) displays a gradual descent from the initial composi-
tion to zero. The simulation does a good job describing the desorption experiment. The initial and final portions of the desorption experiment (red circles) are captured very well by the simulator (red line). The experimental desorption experiment at $y_{\text{H}_2\text{O}} = 0.394$ (partial pressure of 0.386 bar) decreases gradually to zero at $\approx 40$ mL (shown as blue squares). This curve is predicted by the simulation very well (blue line). The same is true for the experimental desorption experiment at $y_{\text{H}_2\text{O}} = 0.147$ (partial pressure of 0.157 bar), which is shown as the green triangles in Fig. 10(b). Overall, the GAB isotherm does an excellent job at predicting the observed experimental desorption curves, as well as the transition around the point where H$_2$O multilayer adsorption begins. Again, the mass transfer coefficient was kept as a fitting parameter. For steam on Lewatit, $k_i = 0.06$ s$^{-1}$. This again suggests that there is not a large mass transfer resistance for steam adsorption on Lewatit.

Simulations were also performed for the CALF-20 desorption experiments. The same range of steam compositions ($y_{\text{H}_2\text{O}} = 0.147, 0.394,$ and 0.821) were chosen to highlight different features of the CALF-20 isotherm observed in the experiments. All three experimental curves, plus their simulations, are shown in Fig. 10(c). The first CALF-20 experiment is at a composition of $y_{\text{H}_2\text{O}} = 0.821$ (partial pressure of 0.774 bar) shown as red circles. This partial pressure lies after the inflection point on the CALF-20 H$_2$O isotherm (Fig. 7(c)). The experimental breakthrough curve initially decreases gradually. At approximately 75 mL the experimental breakthrough curve transitions and rapidly approaches zero. The isotherm model and simulation are able to predict this transition very well. Importantly, this includes the change in effluent flow that happens during desorption, as this event will change the experimental mole fraction breakthrough curves. The second CALF-20 desorption experiment is at a composition of $y_{\text{H}_2\text{O}} = 0.394$ (partial pressure of 0.381 bar) and is shown as blue squares. This partial pressure also lies after the inflection point on the CALF-20 H$_2$O isotherm. A similar trend is observed experimentally as was observed for $y_{\text{H}_2\text{O}} = 0.821$, which is also captured well by the simulation. It is worth noting the the same transition is predicted at $\approx 75$ mL for $y_{\text{H}_2\text{O}} = 0.394$ as was predicted for $y_{\text{H}_2\text{O}} = 0.821$. The final
experiment (green triangles) was at a composition of \( y_{H_2O} = 0.147 \). This experiment has a low partial pressure 0.153 bar. This pressure is in a portion of the CALF-20 \( H_2O \) isotherm (Fig. 7(c)) that is slightly anti-Langmuirian (type-3). The resulting experimental breakthrough curve appears to have a transition at this point. This behavior is captured well by the simulator shown as the green line. These experiments show that the sharp transitions observed by Lin et al. [4] will be more dispersed when the effluent flow changes significantly. Like the previous two sets of simulations, the mass transfer coefficient was kept as a fitting parameter. For steam on CALF-20, \( k_i = 0.04 \text{ s}^{-1} \). This suggests that there is slightly more resistance to steam adsorption on CALF-20 than activated carbon, but approximately the same as was experienced for Lewatit. A recent study found that there are slight variations in the \( H_2O \) diffusion coefficients as a function of relative pressure [50]. In this analysis, a single, fixed value for the mass transfer coefficient was sufficient to model the range of CALF-20 desorption curves presented in Fig. 10(c).

5 Importance of Steam Equilibrium Data and Breakthrough Experiments for Process Design

The steam desorption experiments, and their simulations, highlight the necessity of high temperature, high concentration, \( H_2O \) breakthrough experiments for these processes. Bed conditioning, with either air or \( N_2 \), is an important process step to remove the loaded \( H_2O \) during the steam purge [5]. This prepares the adsorbent for the next adsorption step in order to maximize the amount of \( CO_2 \) captured. The \( H_2O \) desorption curves in Fig. 10 show the maximum time a conditioning step could last in a TSA process for the three presented materials. This will effect the TSA cycle duration, as well as related process performance metrics such as productivity (often expressed as tonnes \( CO_2 \) captured per adsorbent volume per cycle time).

The adsorption and desorption breakthrough data presented in study also highlights
the differences between dilute, low temperature, H$_2$O breakthrough experiments [51], like the ones for CALF-20 presented in Lin et al. at 22°C [4], and breakthrough experiments at steam partial pressures found in industrial processes [5]. The most significant difference seen with steam adsorption experiments is the change in effluent flow that accompanies the adsorption and desorption of steam. For comparison, the presented steam data in this study is $\approx$ 5 to 30× more concentrated than a saturated feed at 25°C. This result is highlighted in Fig. 4(c) and (d) for CALF-20.

Importantly, none of the studied systems can be assumed as nonadsorbing for steam. Steam adsorbed strongly in all three studied materials. Even a hydrophobic material like activated carbon loads a significant amount of steam at 110°C. Figure 6 shows that the desorption of H$_2$O on activated carbon produces a composite desorption curve (in red) different than an equivalent pycnometrically corrected blank experiment (blue). This alone is evidence that H$_2$O cannot be treated as a nonadsorbing gas in this system. In other words, two experiments could be preformed on a novel material to determine whether or not steam adsorbs at a given temperature. The first is a blank desorption experiment (with the pycnometric correction) for a desired partial pressure of steam at the desired purging temperature. The second is an equivalent desorption experiment with the novel material. If the two curves do not coincide, steam is cannot be considered nonadsorbing on the novel adsorbent. This further stresses the need to accurately simulate steam adsorption dynamics.

It is also interesting that our high temperature steam equilibrium data at 110°C seems to be consistently lower in value than data at lower temperatures (at the same relative pressure). This conclusion is the same for all three materials studied. This is especially interesting because the three chosen materials are all different adsorbent material types; one is an activated carbon, another is a metal-organic framework, and the final material was an amine-functionalized polymer. This result suggests that low temperature, dilute H$_2$O vapor measurements cannot be assumed to be equal to the concentrated steam data (at the same relative pressure). If this assumption was made, the simulations in Fig. 10 would overpredict the H$_2$O loading in the column. In other
words, the simulations would predict a later desorption (in time) than the experimental measurements. This result also suggests that a strictly relative pressure (or relative humidity) isotherm model (with no additional temperature dependencies) may produce incorrect predictions at high temperature and high partial pressures.

While these steam experiments, their associated unary equilibrium loadings, and simulations are an important first step, it is only a part of the required analysis. The adsorptive competition \[4\], or cooperation \[25\], between CO\(_2\) and H\(_2\)O must also be considered at high temperature. This is required to understand how dry the adsorbent bed must at the end of the conditioning step. More unary equilibrium data for H\(_2\)O at temperatures greater than 100\(^\circ\)C, and their associated binary CO\(_2\)/H\(_2\)O equilibrium data is required. Once these adsorbate-adsorbent systems are better understood, simulations and optimizations can be utilized to further understand and improve carbon capture processes involving steam.

6 Conclusions

A microscale dynamic column breakthrough (\(\mu\)DCB) apparatus was constructed to measure adsorption and desorption equilibrium loadings of steam using milligram quantities of adsorbent. The construction of the apparatus was detailed including discussions on necessary validations and calibrations. A steam adsorption and desorption breakthrough experiment took approximately 35 – 90 minutes using the \(\mu\)DCB apparatus (depending on the desired flowrate). Appropriate mass balances were derived and detailed for apparatus including both the blank and composite measurements. Empty volume experiments were performed to determine the accuracy of the instrument. These known volumes were measured using the \(\mu\)DCB within \(\pm6\%\) the true geometric value. Steam adsorption and desorption equilibrium data was measured with the \(\mu\)DCB apparatus at 110\(^\circ\)C for an activated carbon (Calgon BPL), Lewatit VP OC 1065, and CALF-20. Data was measured at various partial pressures up to approximately 1.0 bar. This is a relative pressure of approximately 0.65 at 110\(^\circ\)C.
data points were reported with linear error propagation, using uncertainties from the utilized instruments. Both activated carbon and Lewatit displayed a type-3 isotherm shape, while CALF-20 displayed a type-5 isotherm, for the measured data range (up to a relative pressure of 0.65). This qualitatively agrees with the available literature data. Since these experiments were performed using a high concentration of H₂O, the effluent flow changed significantly. This caused the transitions between isotherm inflection points to become more dispersed, and sometimes even blended into each other. These observations were validated using simulations.

This instrument demonstrates the ability to measure steam adsorption equilibrium data quickly and reliably using milligram quantities of adsorbent. This is representative of a first-batch synthesis sample size of a novel adsorbent material. Extensive calibrations are required to accurately measure the effluent flow. Once these calibrations were performed, they held true for all experiments in this study (a time period of a four months). The relative humidity sensors were linear and did not require extensive calibrations. Further developments to this apparatus are currently being performed to extend its applicability to multicomponent equilibrium measurements at multiple temperatures (> 100°C).

The analysis of the steam breakthrough experiments highlighted the importance of this data and their implications in carbon capture processes involving a steam purge. The measured steam desorption experiments can be used as an upper bound of the TSA conditioning step duration, which is a rough indication of process productivity. The dynamics of steam adsorption and desorption do not resemble the observed trends at low partial pressures and this impacts the dynamics of steam adsorption and their simulation. It was shown that steam adsorption at 110°C is significant, even for hydrophobic materials like activated carbon. The calculated H₂O equilibrium data and associated breakthrough curves demonstrate that steam adsorption cannot be considered nonadsorbing for activated carbon, Lewatit, or CALF-20. The high temperature steam equilibrium data also produced an unexpected result. Specifically, that when the data is plotted as a function of relative pressure it does not coincide with data col-
lected at a low temperature. This is contrary to what has been reported for a material like zeolite 13X. This has been observed in the literature for Lewatit and at least one metal-organic framework, MIL-101(Cr). However, this suggests that low temperature measurements on CALF-20 and activated carbon cannot be used to estimate a concentrated steam equilibrium at high temperature. Concentrated steam equilibrium data must be measured at high temperature to accurately model their equilibrium.

More work is required to understand the equilibrium and dynamics of steam on adsorbents considered for carbon capture; even for commonly considered adsorbents like activated carbon, Lewatit and CALF-20. This includes unary H$_2$O equilibrium measurements at multiple temperatures (greater than 100°C), binary CO$_2$/H$_2$O equilibrium measurements, as well as multicomponent adsorption and desorption breakthrough experiments to build accurate simulation models. This data will allow the rigorous simulation and optimization of adsorption processes to determine the best materials for carbon capture.

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8 Declaration of Interests

NSW is currently employed by Svante Technologies Inc. which has commercialized CALF-20 for industrial CO$_2$ capture. JAS and AR confirm that there is no conflict of interest to declare.
9 Supporting Information

A derivation of the mass balance equations, details of error analysis, all breakthrough curves measured in this study, tanks-in-series blank simulations, and pictures of the \( \mu \text{DCB} \) system are provided in the Supporting Information.
Nomenclature

Roman symbols

\(a\)  \(\) anemometer calibration constants \([\text{Ncm}^{-1}]\) or \([\text{V}]\)  
\(b\)  \(\) adsorption equilibrium constant \([\text{m}^3 \text{mol}^{-1}]\) or \([-\])  
\(c\)  \(\) adsorption equilibrium constant \([-\])  
\(C\)  \(\) concentration \([\text{mol m}^{-3}]\)  
\(d\)  \(\) adsorption equilibrium constant \([\text{m}^3 \text{mol}^{-1}]\)  
\(D_L\)  \(\) axial dispersion \([\text{m}^2 \text{s}^{-1}]\)  
\(f\)  \(\) function  
\(I\)  \(\) anemometer signal \([\text{V}]\)  
\(k\)  \(\) lumped mass transfer coefficient \([\text{s}^{-1}]\)  
\(L\)  \(\) length \([\text{m}]\)  
\(m_{\text{ads}}\)  \(\) adsorbent mass \([\text{kg}]\)  
\(n\)  \(\) index \([-\])  
\(P\)  \(\) pressure \([\text{bar}]\)  
\(q^*\)  \(\) equilibrium solid phase loading \([\text{mol kg}^{-1}]\)  
\(q\)  \(\) local solid phase loading \([\text{mol kg}^{-1}]\)  
\(Q\)  \(\) volumetric flow \([\text{m}^3 \text{s}^{-1}]\)  
\(Q(t)\)  \(\) effluent volumetric flow \([\text{m}^3 \text{s}^{-1}]\)  
\(Q_t\)  \(\) flow-time \([\text{mL}]\)  
\(r\)  \(\) radius \([\text{m}]\)  
\(R\)  \(\) universal gas constant \([\text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1}]\)  
\(Re\)  \(\) Reynolds number \([-\])  
\(t\)  \(\) time \([\text{s}]\)  
\(\bar{t}\)  \(\) mean retention time \([\text{s}]\)  
\(T\)  \(\) temperature \([\text{K}]\)  
\(v\)  \(\) interstitial velocity \([\text{m s}^{-1}]\)
$V$ volume $[m^3]$  
$x$ relative pressure $[-]$  
$y$ mole fraction $[-]$  
$y(t)$ effluent mole fraction $[-]$  
$z$ axial direction $[m]$  
$Z$ compressibility factor $[-]$  

**Greek symbols**

$\beta$ IAPWS 1995 EOS constant  
$\delta$ uncertainty  
$\epsilon$ void fraction $[-]$  
$\gamma$ uncertain variable  
$\mu$ viscosity $[kg \ m^{-1} \ s^{-1}]$  
$\nu$ $1 - T/T_c$, IAPWS 1995 EOS parameter  
$\rho$ density $[kg \ m^{-3}]$  
$\tau$ tortuosity $[-]$  

**Abbreviations, subscripts and superscripts**

$a$ adsorbed phase  
$ads$ adsorption or adsorbent  
$amb$ ambient  
$b$ adsorption site  
$blank$ blank response  
$c$ critical  
$col$ column  
$comp$ composite response or component  
$d$ adsorption site
des desorption
deca extra-column, extra-tubing
i index of species or inner
in inlet or internal
\infty equilibrium
init initial
j index
m molar
n index
o outer
out external
p particle
pync pycnometric
\ast equilibrium
sat saturation
sk skelletal
t time
tube tubing
z axial
0 Van’t Hoff prefactor

Acronyms

ADS adsorption
AFM anemometer flow meter
DAC direct air capture
DCB dynamic column breakthrough
DES desorption
EOS equation of state
FEP fluoropolymer
GAB Guggenheim-Anderson-De Boer isotherm
GC gas chromatograph
IAPWS International Association for the Properties of Water and Steam
µDCB microscale dynamic column breakthrough
MFC mass flow controller
MFM mass flow meter
MOF metal-organic framework
PSA pressure swing adsorption
RH relative humidity
RH/T combined relative humidity & temperature sensor
TIS tanks-in-series
TSA temperature swing adsorption
VCR vacuum coupling radiation
References


Figure 1: General arrangement of components and instrumentation for the steam μDCB apparatus.
Figure 2: Hot-wire anemometer calibrations for unary (a) N\(_2\) and H\(_2\)O, and binary (b) H\(_2\)O/N\(_2\) mixtures. The markers denote experimentally collected data and the lines are empirical fits. The gray shading in panel (b) denotes a ±5% error for the proposed empirical model. Normal conditions are: 25°C and 1.00 bar absolute pressure.
Figure 3: 100 mol% H\textsubscript{2}O adsorption and desorption blank responses at 0.94 bar and 110\degree C. 100 mol% N\textsubscript{2} was used as the purging gas in desorption. For these experiments, $Q_{in} = 29.2$ ccm and $Q_{init} = 31.1$ ccm. Panel (a) shows the unprocessed signal from the relative humidity meter in relative pressure, $P/P^\text{sat}(110\degree C) \times 100\%$. Panel (b) shows the calibrated adsorption and desorption curves, and panel (c) transforms the desorption curve by $1 - y_{\text{H}_2\text{O}}$ to be directly comparable to the adsorption blank. The adsorption curves are shown with hollow symbols, and the desorption curves are shown with solid symbols.
Figure 4: Single-component H$_2$O/N$_2$ adsorption and desorption µDCB experiments for 82.1 mol% H$_2$O in N$_2$ on CALF-20 at 0.94 bar and 110°C. The top row shows the (a) adsorption and (b) desorption mole fraction breakthrough curves. The corresponding effluent flow curves for (c) adsorption and (d) desorption are shown in the second row, below the mole fraction responses.
Figure 5: Mass balance calculations of a 5’, 10’ and 20’ length of 1/8” stainless steel tubing in the steam μDCB apparatus. The markers denote experimentally measured data and the line denotes parity. The gray shading denotes a ±5% deviation from parity. Error bars in this figure are a standard error of 3 repeated elution profiles (6 volume estimations, 3 from adsorption and 3 from desorption).
Figure 6: Single-component H$_2$O/N$_2$ adsorption (left) and desorption (right) breakthrough curves at 110°C on activated carbon. Panels (a) and (b) are for 49.5 mol% H$_2$O/N$_2$, and panels (c) and (d) are for 82.1 mol% H$_2$O/N$_2$. 
Figure 7: Unary H$_2$O adsorption equilibrium data at 110°C for (a) activated carbon, (b) CALF-20, and (c) Lewatit, with N$_2$ as a diluent. The circle and square markers denote measured data from adsorption and desorption experiments, respectively. Error bars are estimated from error propagation. Appropriate isotherm models are shown as black lines for each adsorbent. The same H$_2$O adsorption equilibrium data as a function of relative pressure for (d) activated carbon, (e) CALF-20, and (f) Lewatit, with low temperature data from the literature as blue circles. Note that the data from Lin et al. [4] was binder-corrected to be comparable with the powder CALF-20 sample used in this study.
Figure 8: Single-component H$_2$O/N$_2$ adsorption (left) and desorption (right) breakthrough curves at 110°C on CALF-20. Panels (a) and (b) are for 49.5 mol% H$_2$O/N$_2$, and panels (c) and (d) are for 82.1 mol% H$_2$O/N$_2$. 

https://doi.org/10.26434/chemrxiv-2023-dgf39 ORCID: https://orcid.org/0000-0001-6891-2434 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0
Figure 9: Single-component H$_2$O/N$_2$ adsorption (left) and desorption (right) breakthrough curves at 110°C on Lewatit. Panels (a) and (b) are for 49.5 mol% H$_2$O/N$_2$, and panels (c) and (d) are for 82.1 mol% H$_2$O/N$_2$. 
Figure 10: Single-component H$_2$O/N$_2$ experimental and simulated desorption breakthrough curves at 110°C on activated carbon (a), Lewatit (b), and CALF-20 (c). Markers denote the composition breakthrough experiments, while lines denote the simulations.
Table 1: Measured quantities and their associated uncertainties for the calculation of equilibrium loading with the microscale steam dynamic column breakthrough mass balances.

<table>
<thead>
<tr>
<th>Measured Variable</th>
<th>Uncertainty</th>
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<tr>
<td>$m_{ads}$</td>
<td>0.0005 g</td>
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<tr>
<td>$P$</td>
<td>$3.45 \times 10^{-4}$ bar</td>
</tr>
<tr>
<td>$T$</td>
<td>1 K</td>
</tr>
<tr>
<td>$\rho_{sk}$</td>
<td>0.2 g/mL</td>
</tr>
<tr>
<td>$y_{in/init}$</td>
<td>standard deviation of steady signal ($\approx 0.01$ to $0.1%$ of signal)</td>
</tr>
<tr>
<td>$y(t)$</td>
<td>standard deviation of steady signal ($\approx 0.01$ to $0.1%$ of signal)</td>
</tr>
<tr>
<td>$Q_{in/init}$</td>
<td>$(0.004)Q_{(set\ point)}$ Nccm</td>
</tr>
<tr>
<td>$Q(t)$</td>
<td>$(0.004)Q_{in/init}$ Nccm</td>
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Table 2: Experimental μDCB conditions for the unary H₂O (balance N₂) adsorption and desorption experiments performed on activated carbon (Calgon BPL 4x10 CAS#7440-44-00). All experiments were performed at 110°C. The subscript “in” refers to the inlet adsorption flow, while the subscript “init” refers to the inlet desorption flow. A “-” entry signifies that the AFM voltage signal was too large to accurately estimate the equilibrium loading or that the predicted error bisected zero.

<table>
<thead>
<tr>
<th>$y_{in/init}$</th>
<th>$P$</th>
<th>$Q_{in}$</th>
<th>$Q_{init}$</th>
<th>$q^*_{ads}$</th>
<th>$q^*_{des}$</th>
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<tr>
<td>[-]</td>
<td>[bar]</td>
<td>[ccm]</td>
<td>[ccm]</td>
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<td>30.187</td>
<td>29.720</td>
<td>5.8876</td>
<td>-</td>
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</table>
Table 3: Experimental µDCB conditions for the unary \( \text{H}_2\text{O} \) (balance \( \text{N}_2 \)) adsorption and desorption experiments performed on CALF-20. All experiments were performed at 110°C. The subscript “in” refers to the inlet adsorption flow, while the subscript “init” refers to the inlet desorption flow. A “-” entry signifies that the AFM voltage signal was too large to accurately estimate the equilibrium loading or that the predicted error bisected zero.

<table>
<thead>
<tr>
<th>( y_{\text{in/init}} )</th>
<th>( P )</th>
<th>( Q_{\text{in}} )</th>
<th>( Q_{\text{init}} )</th>
<th>( q_{\text{ads}}^{*} )</th>
<th>( q_{\text{des}}^{*} )</th>
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<tr>
<td>([\text{-}])</td>
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<td>[ccm]</td>
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<td>[mol kg(^{-1})]</td>
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Table 4: Experimental µDCB conditions for the unary H$_2$O (balance N$_2$) adsorption and desorption experiments performed on Lewatit (Lewatit VP OC 1065). All experiments were performed at 110°C. The subscript “in” refers to the inlet adsorption flow, while the subscript “init” refers to the inlet desorption flow. A “-” entry signifies that the AFM voltage signal was too large to accurately estimate or that the predicted error bisected zero.

<table>
<thead>
<tr>
<th>$y_{in/init}$</th>
<th>$P$ [bar]</th>
<th>$Q_{in}$ [ccm]</th>
<th>$Q_{init}$ [ccm]</th>
<th>$q_{ads}^*$ [mol kg$^{-1}$]</th>
<th>$q_{des}^*$ [mol kg$^{-1}$]</th>
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Table 5: Equations for modeling isothermal adsorption dynamics.

<table>
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<th>Mass Balance Type</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Mass Balance</td>
<td>$\frac{1}{P} \frac{\partial P}{\partial t} = -\frac{1}{P} \frac{\partial}{\partial z} (P v) - \frac{RT}{P} \frac{1 - \epsilon}{\epsilon} \sum_{i=1}^{n_{\text{comp}}} \frac{\partial q_i}{\partial t}$</td>
</tr>
<tr>
<td>Component Mass Balance</td>
<td>$\frac{\partial y_i}{\partial t} + \frac{y_i}{P} \frac{\partial P}{\partial t} = D_L \frac{\partial}{\partial z} \left( P \frac{\partial y_i}{\partial z} \right) - \frac{1}{P} \frac{\partial}{\partial z} (y_i P v) - \frac{RT}{P} \frac{1 - \epsilon}{\epsilon} \frac{\partial q_i}{\partial t}$</td>
</tr>
<tr>
<td>Solid Phase Mass Balance</td>
<td>$\frac{\partial q_i}{\partial t} = k_i (q_i^* - q_i)$</td>
</tr>
<tr>
<td>Pressure Drop</td>
<td>$-\frac{\partial P}{\partial z} = \frac{150 \mu v}{4} r_p^2 \left( \frac{1 - \epsilon}{\epsilon} \right)^2$</td>
</tr>
</tbody>
</table>
Table 6: GAB isotherm parameters for unary steam equilibrium on Lewatit (Lewatit VP OC 1065) and activated carbon (Calgon BPL) at 110°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>$q_{b}^{sat}$</th>
<th>$b$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[mol kg$^{-1}$]</td>
<td>[-]</td>
<td>[-]</td>
</tr>
<tr>
<td>Lewatit</td>
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</tr>
<tr>
<td>Activated Carbon</td>
<td>0.9086</td>
<td>1.3505</td>
<td>0.8328</td>
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</table>

Table 7: Cubic-Langmuir isotherm parameters for unary steam equilibrium on CALF-20 at 110°C

<table>
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<tr>
<th>$q_{b}^{sat}$</th>
<th>$q_{d}^{sat}$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_3$</th>
<th>$d$</th>
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<tbody>
<tr>
<td>[mol kg$^{-1}$]</td>
<td>[mol kg$^{-1}$]</td>
<td>[m$^3$ mol$^{-1}$]</td>
<td>[m$^3$ mol$^{-1}$]</td>
<td>[m$^3$ mol$^{-1}$]</td>
<td>[m$^3$ mol$^{-1}$]</td>
</tr>
<tr>
<td>1.6966</td>
<td>9.9969</td>
<td>7.0405$x$10$^{-5}$</td>
<td>5.8298$x$10$^{-4}$</td>
<td>5.0827$x$10$^{-4}$</td>
<td>2.5194$x$10$^{-2}$</td>
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</table>
Table 8: Detailed breakthrough simulation parameters for activated carbon (Calgon BPL), Lewatit (Lewatit VP OC 1065), and CALF-20.

<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
<th>Source</th>
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<td></td>
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<td>outer column radius, $r_o$ [m]</td>
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<td>assumed</td>
</tr>
<tr>
<td>tortuosity, $\tau$</td>
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<td>assumed</td>
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<td><strong>Properties and Constants</strong></td>
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<td></td>
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<td>standard value</td>
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<tr>
<td></td>
<td>880 (Lewatit)          [7]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1190 (CALF-20)         [38]</td>
<td></td>
</tr>
<tr>
<td>fluid viscosity, $\mu$ [kg m$^{-1}$ s$^{-1}$]</td>
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<td>standard value</td>
</tr>
<tr>
<td>mass transfer coefficient, $k_i$ [s$^{-1}$]</td>
<td>$2.0 \times 10^{-1}$ (Activated Carbon)</td>
<td>fitted</td>
</tr>
<tr>
<td></td>
<td>6.0 $\times 10^{-2}$ (Lewatit)</td>
<td>fitted</td>
</tr>
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<td></td>
<td>4.0 $\times 10^{-2}$ (CALF-20)</td>
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</tr>
<tr>
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<td>Chapman-Enskog</td>
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</table>