Characterization of Solid Sorbent for Direct Air Capture of CO_2 Using a CFD-Based Methodology

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2024 NETL Workshop on Multiphase Flow Science

Aug. 14, 2024

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Project Overview

- Started with an aminated PIM sorbent PF-15-TAEA developed by the NETL Integrated Project team
- PIM sorbent available in various form factors (particle and/or fiber)
- Intrinsic kinetics identified from mg-scale samples are not applicable at reactor scale
- Develop a laboratory-scale experiment in MFAL to investigate sorbent performance in a fixed bed configuration with active flow
- Calibrate sorbent kinetics using a CFD model of a small fixed bed reactor

Laboratory-scale experiments and CFD models NETL sorbents

Validate CFD modeling approach and model parameters

→

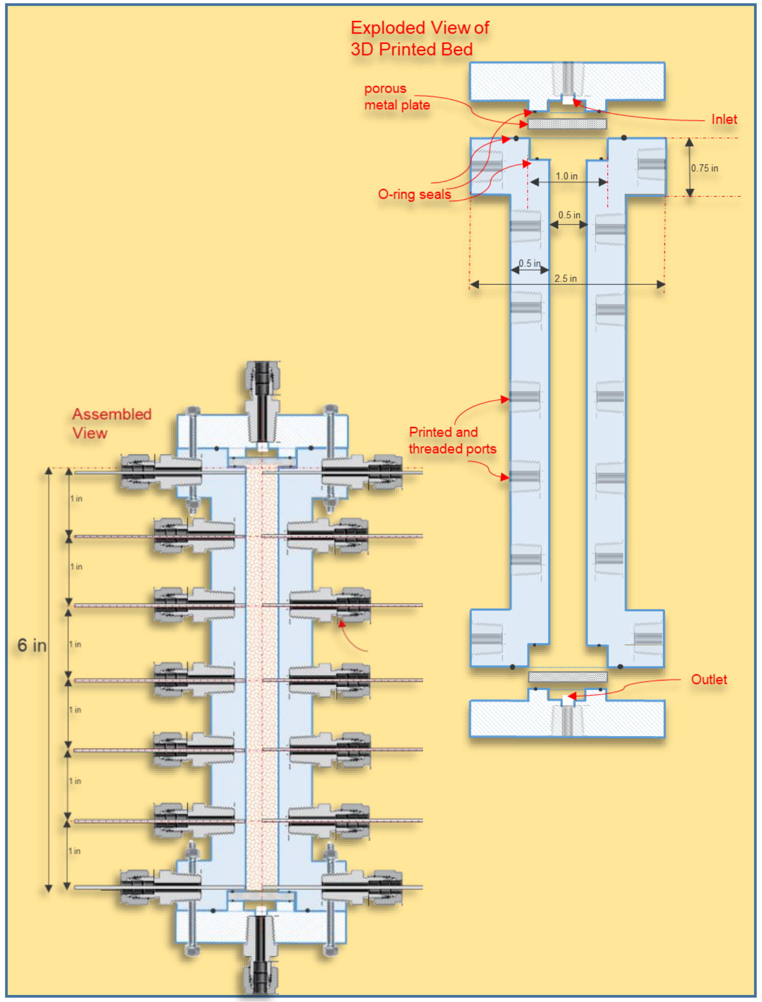
Use CFD models to scale up DAC based on NETL sorbents

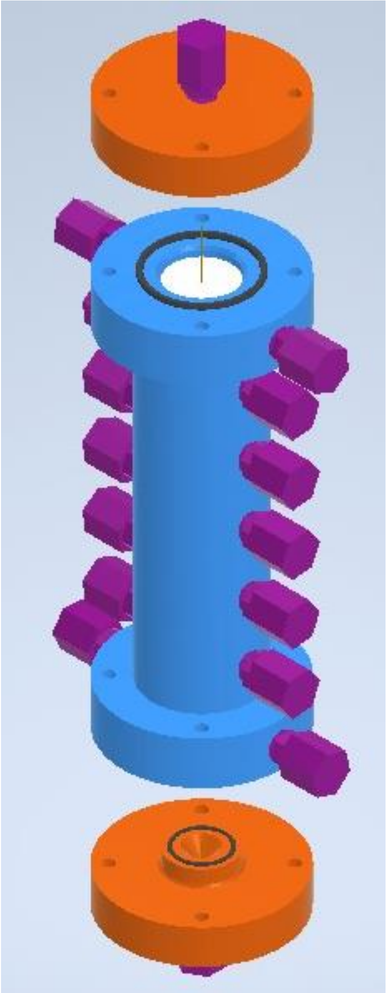
Small pilot scale: include ducting, fan, regeneration

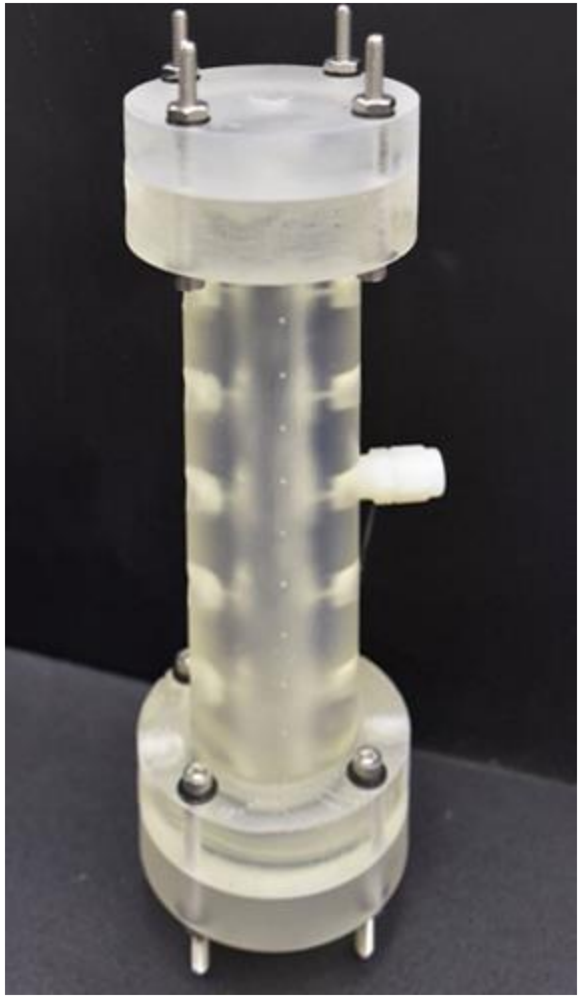
Optimize performance

Small-Scale Fixed Bed Testing

Concept → Design → 3D Printed







Porous Media Model Solution Approach

- A CFD model is developed for the small-scale fixed bed using the porous media model approach in Ansys Fluent
- A porosity of 0.56 (ε_s = 0.44) is specified for the fixed bed
- Both the equilibrium adsorption $n^* = f(P, T)$ and the dynamic/instantaneous adsorption n are stored in user-defined memory and explicitly updated every time step
- Mass source term accounts for depletion rate of gas-phase CO_2 due to adsorption

$$S_m = -(\varepsilon_s \rho_s)(MW_{\mathrm{CO2}})(dn/dt)$$

- Energy source term depends on the mass source and accounts for heat of adsorption

$$S_h = -\frac{[\Delta H][S_m]}{[MW_{CO2}]}; \quad \Delta H \equiv \text{Heat of adsorption}$$

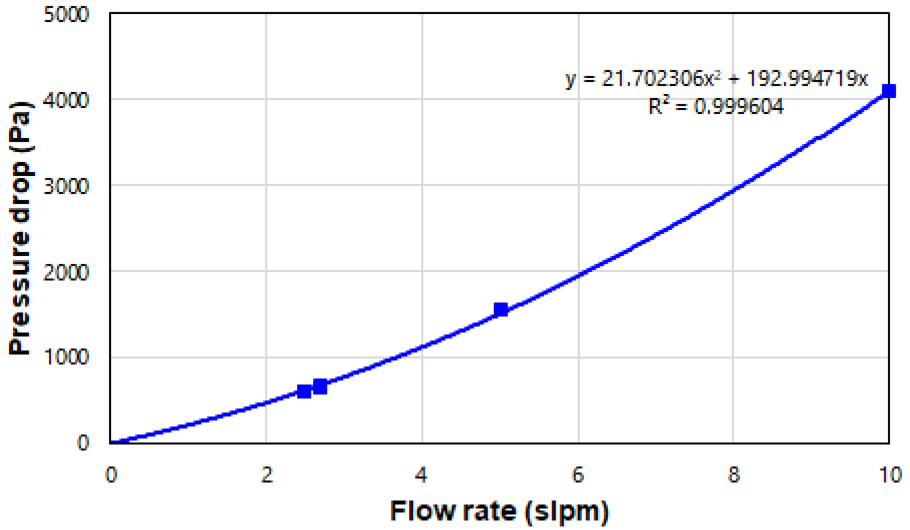
Porous Media Method Pressure Drop Calibration

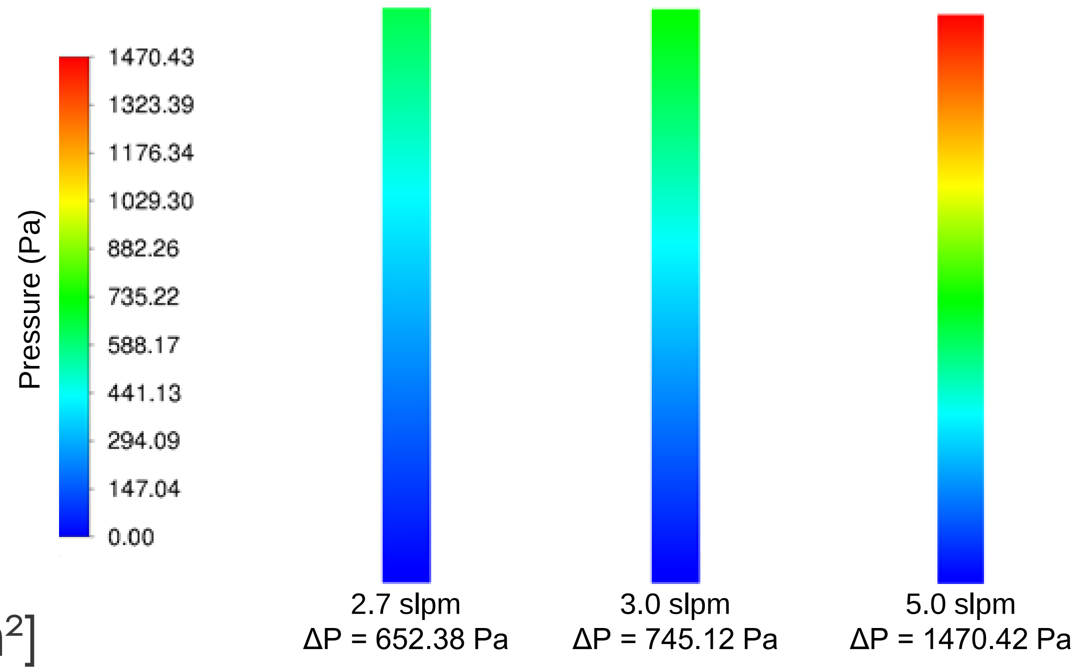
- For homogeneous/isotropic porous media, $S_i = -\left(\frac{\mu}{\alpha} v_i + \frac{1}{2} C_2 \rho |v| v_i\right)$

Viscous term

Inertial term

Flow rate (slpm)	Experimental ΔP (Pa)
2.5	602.35
2.7	661.85
5	1558.69
10	4091.90



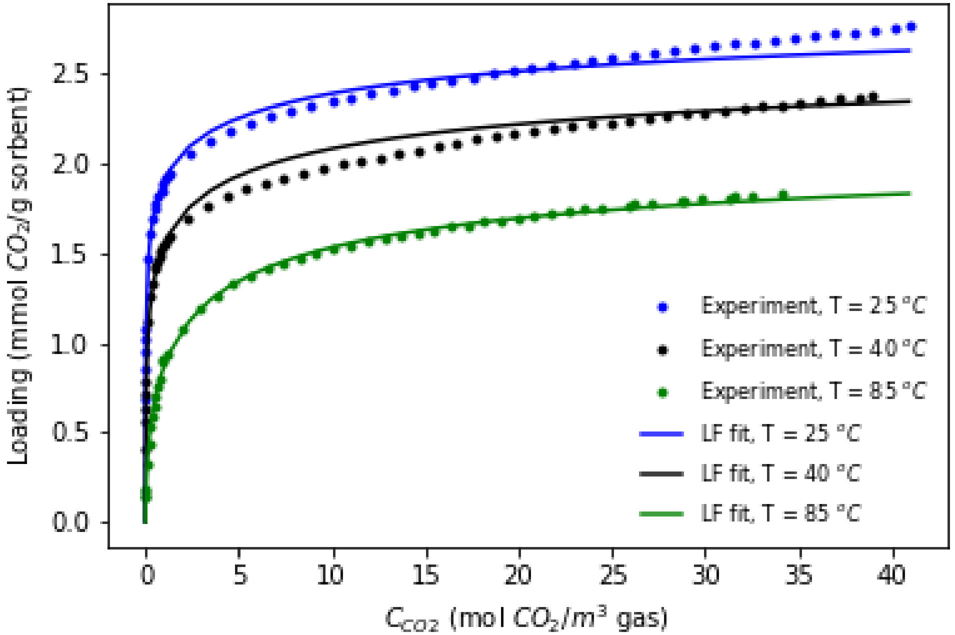


- Coeff. of viscous resistance = $5.11 \cdot 10^8$ [1/m²]
- Coeff. of inertial resistance = $1.25 \cdot 10^4$ [1/m]

Isotherm Fit for Adsorption of CO_2 from Dry Air

$$q_e = \frac{q_{max} K_{eq} C_{CO_2}^n}{1 + K_{eq} C_{CO_2}^n}$$

- Langmuir-Freundlich isotherm parameters q_{max}, K_{eq}, and n can be determined from isotherm data at different temperatures
- By considering these as exponential functions of temperature, a single-equation fit is generated that can be implemented into the CFD code



$q_{max} = k_1 \exp(k_2/T)$

$K_{eq} = k_5 \exp(k_6/T)$

$n = k_3 \exp(k_4/T)$

$k_1 = 3.053 \cdot 10^{-4}$ mol-CO2/g-sorbent

$k_2 = 708.7$ K

$k_3 = 1.570 \cdot 10^{-2}$ (mol-CO2/m³-gas)^n

$k_4 = 1332.1$ K

$k_5 = 13.02$

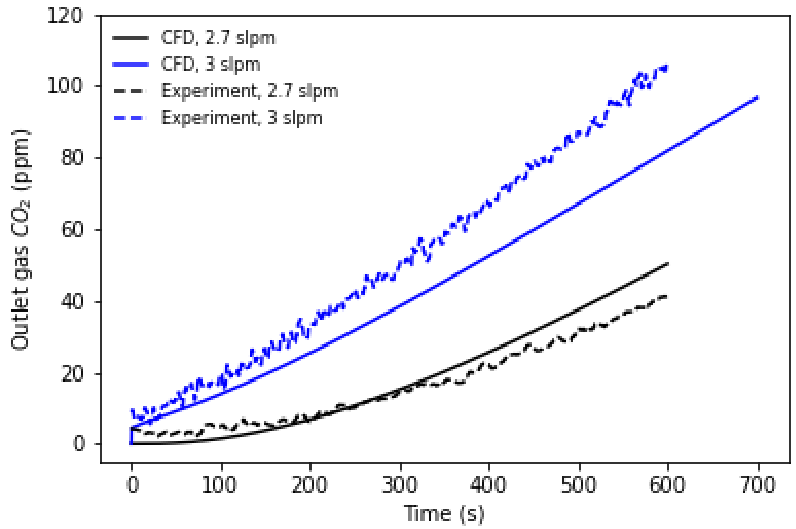
$k_6 = -1137.8$ K

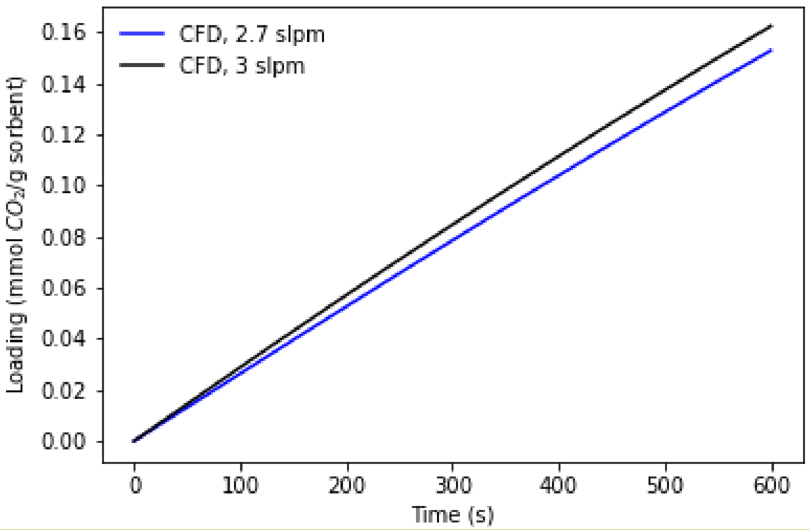
Dry Adsorption Rate Calibration

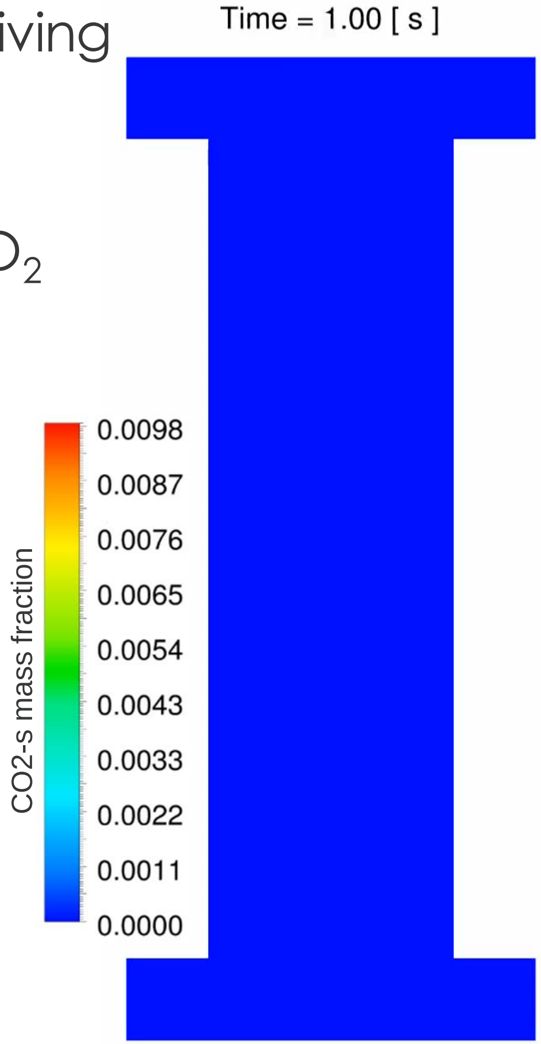
- Adsorption of CO_2 from dry air is modeled using the second-order linear driving force model with q_e implemented based on the isotherm

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$

- CFD simulations were performed with different values of k at 500 ppm CO_2 and T = 22℃ to match the experimental condition
- The effect of k on the breakthrough time underlines the methodology for calibrating k against the experimental data; $k = 0.00861$ (g-sorbent/g-CO_2)/s produces the best match for the range of flow rates studied







2.7 slpm @ 500 ppm CO_2
$k = 0.00861$ (g−sorbent/g−CO_2)/s

Effect of Humidity on CO_2 Adsorption

- Equilibrium CO_2 capacity increases as a result of humidity in air but H_2O adsorption is generally unaffected by the presence of CO_2
- Stampi-Bombibelli et al.[1] used the first-order linear driving force model to investigate co-adsorption of CO_2/ H_2O

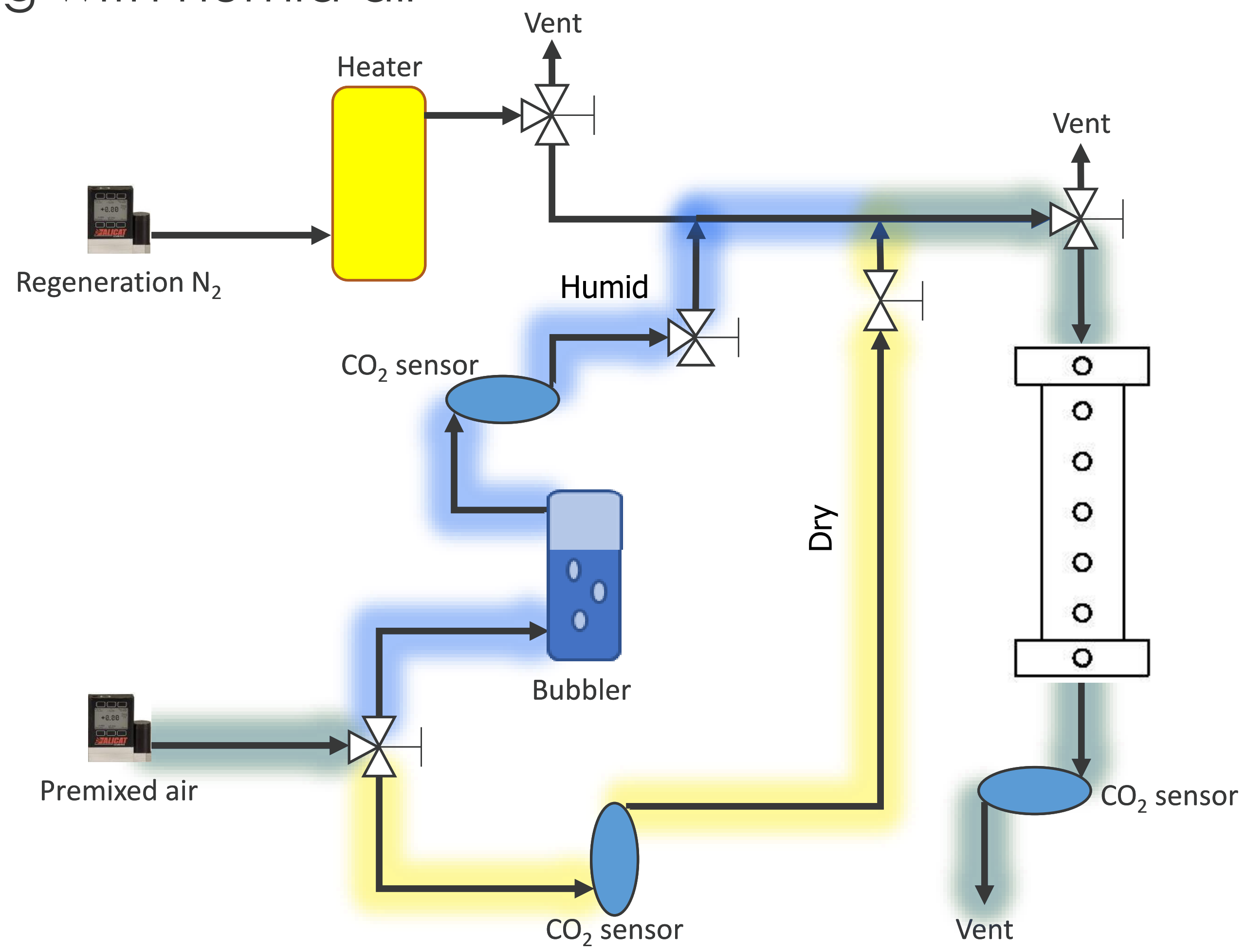
$$\frac{dq_{t,\mathrm{CO_2}}}{dt} = k_{\mathrm{CO_2}}\left(q_{e,\mathrm{CO_2}} - q_{t,\mathrm{CO_2}}\right);\quad \frac{dq_{t,\mathrm{H_2O}}}{dt} = k_{\mathrm{H_2O}}\left(q_{e,\mathrm{H_2O}} - q_{t,\mathrm{H_2O}}\right)$$

- Appropriate isotherm models must be used for $q_{e,\mathrm{CO_2}}$ and $q_{e,\mathrm{H_2O}}$ in co-adsorption conditions
- Most of the heat released during co-adsorption of CO_2/H_2O is due to H_2O adsorption; since H_2O is present in higher concentrations compared to the ppm levels of CO_2, accurate representation of the isosteric heat of adsorption becomes important

[1] V. Stampi-Bombibelli, M. vab der Spek, M. Mazotti, Analysis of direct capture of CO2 from ambient air via steam-assisted temperature vacuum swing adsorption, Adsorption, 2020, 26, 1183–1197.

Modified Setup for Humid Adsorption

- The small-scale fixed bed setup was modified to incorporate a bubbler for experimental breakthrough testing with humid air



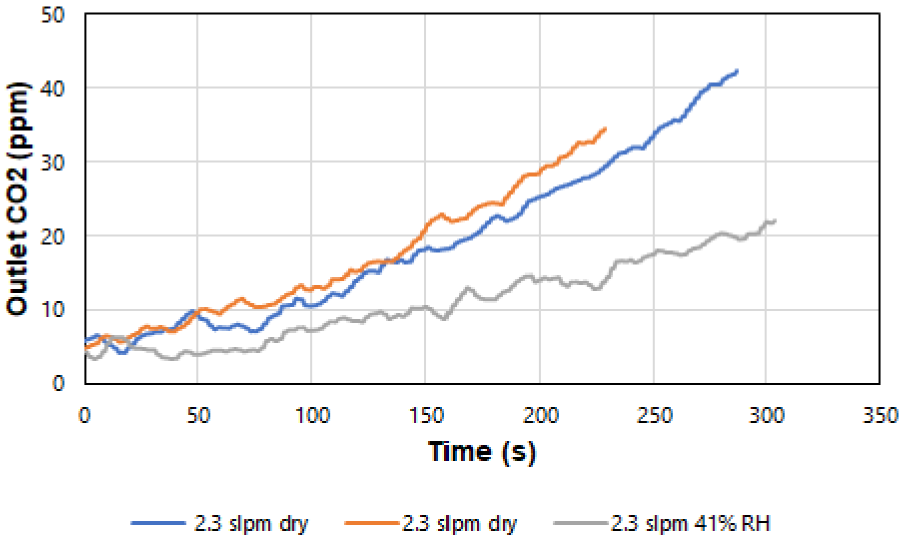
CO_2 uptake dry
- Air@500 ppm CO_2
- 22°C
- 0% RH

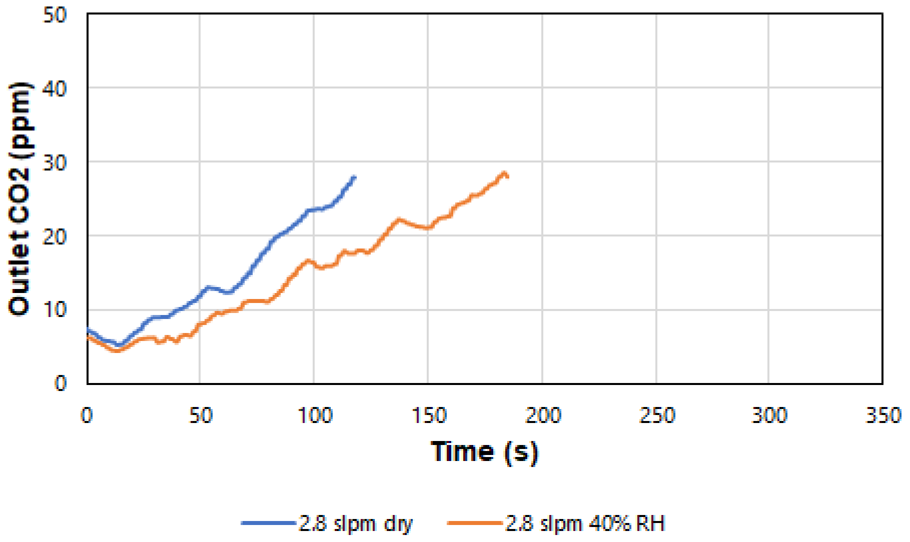
CO_2 uptake humid
- Air@500 ppm CO_2
- 22°C
- 40–45% RH

Regeneration
- N_2, dry, 70°C

Humid Adsorption Breakthrough Results

- Breakthrough testing is conducted with dry and humid air at different flow rates

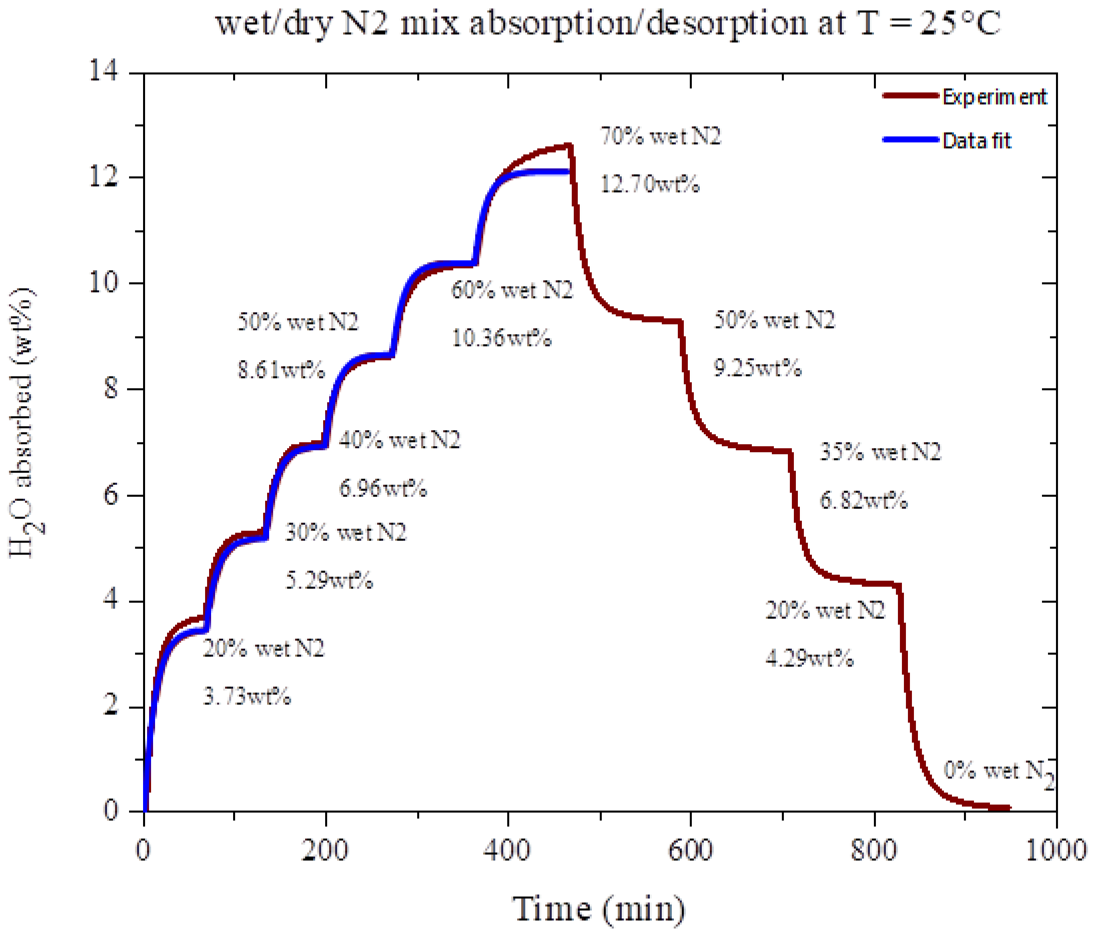




  - Repeats runs at the same flow rate show comparable breakthrough profiles
  - The breakthrough curve rises faster with increased flow rate since more CO_2 is available relative to the capacity
  - The breakthrough curve rises slower with humid air indicating larger capacity
- MFAL breakthrough profiles are used to calibrate k_{CO_2} in the fixed bed configuration only, not to measure uptake capacity; q_{e,CO_2} in co-adsorption CFD model is affixed based on data from NETL Integrated Project colleagues

Effect of Humidity on H_2O Uptake Capacity

- Experimental data provided by Integrated Project colleagues is used to fit a Henry's Law relationship between $q_{e,\mathrm{H_2O}}$ and relative humidity (RH)
- Rate constant $k_{\mathrm{H_2O}}$ is assumed constant since RH is being varied at constant temperature
- The data fit corresponds to a Henry's Law constant of 0.1736 wt.%/RH
- This allows H_2O uptake capacity to be incorporated into the CFD model as a continuous function of humidity



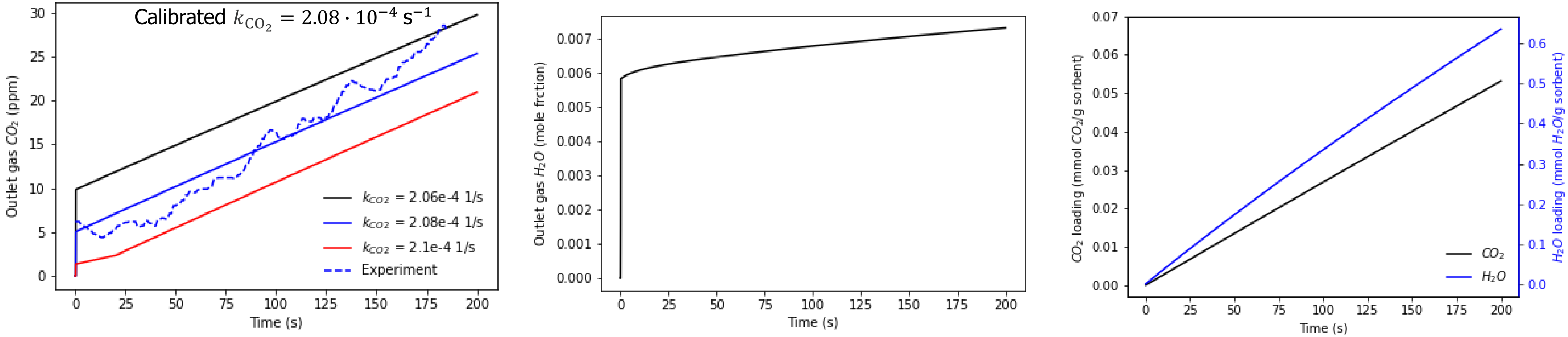
Modeling CO_2 Adsorption from Humid Air

- CFD model for dry adsorption was extended to model the co-adsorption of CO_2/H_2O
- CFD simulations were performed at different values of k at inlet flow rate of 2.8 slpm with 500 ppm CO_2 and 40% RH at T=25℃

$$\frac{dq_{t,CO_2}}{dt} = k_{CO_2}(q_{e,CO_2} - q_{t,CO_2})\,; \quad \frac{dq_{t,H_2O}}{dt} = k_{H_2O}(q_{e,H_2O} - q_{t,H_2O})$$

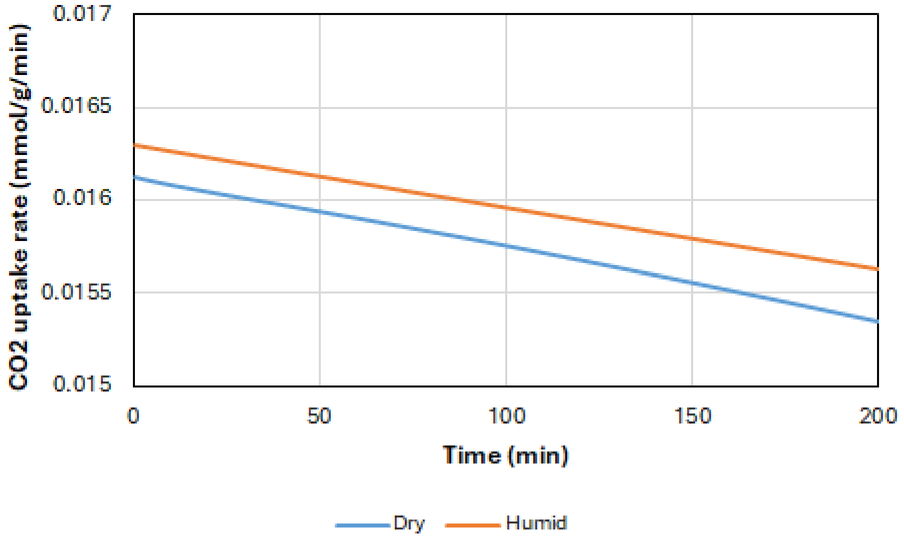
$q_{e,CO_2} = 1.31$ mmol−CO_2/g−sorbent at 25℃ from Micromeritics BTA

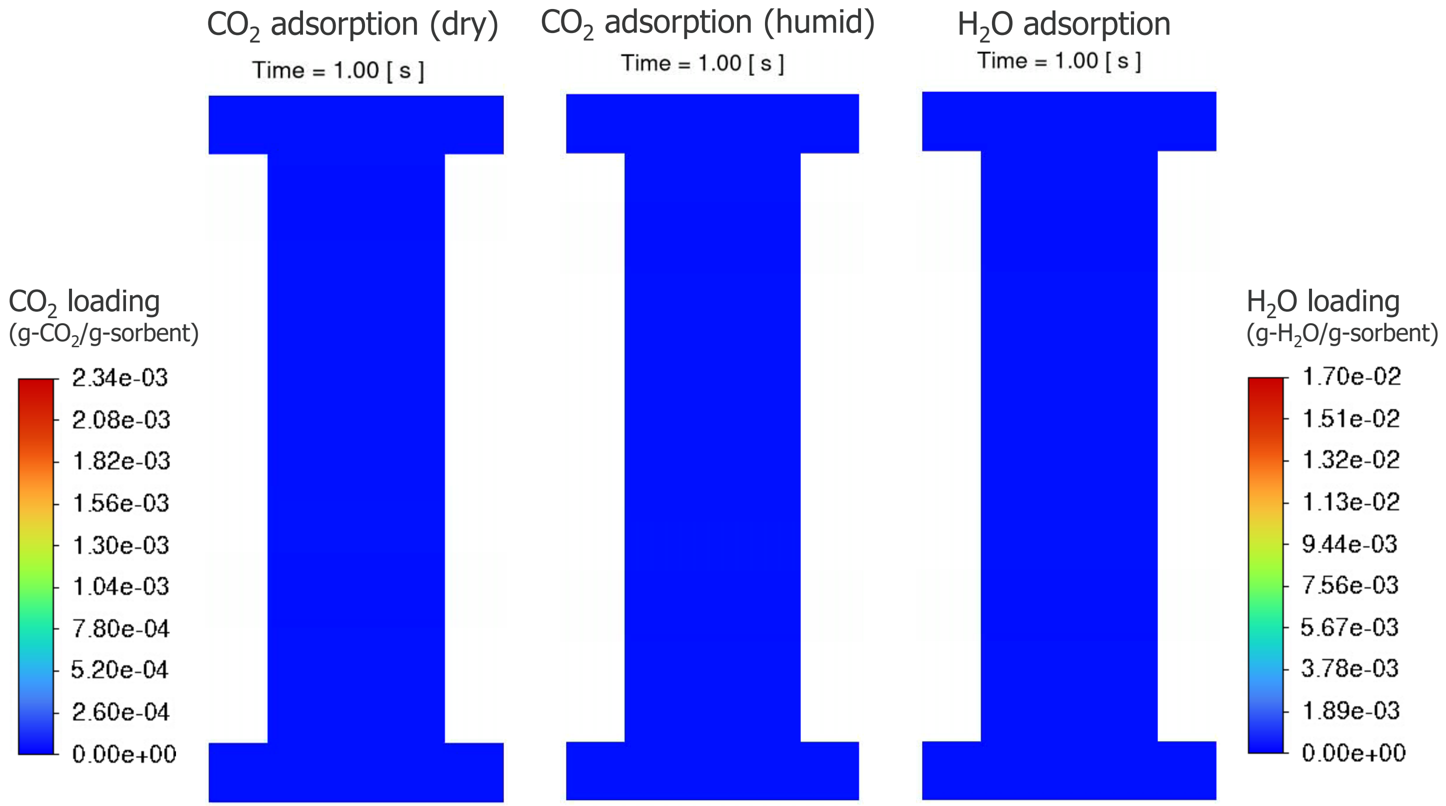
$q_{e,H_2O} = 0.1736 \cdot \mathrm{RH}(\%)$, $k_{H_2O} = 0.001366\ \mathrm{s}^{-1}$



Modeling CO_2 Adsorption from Humid Air

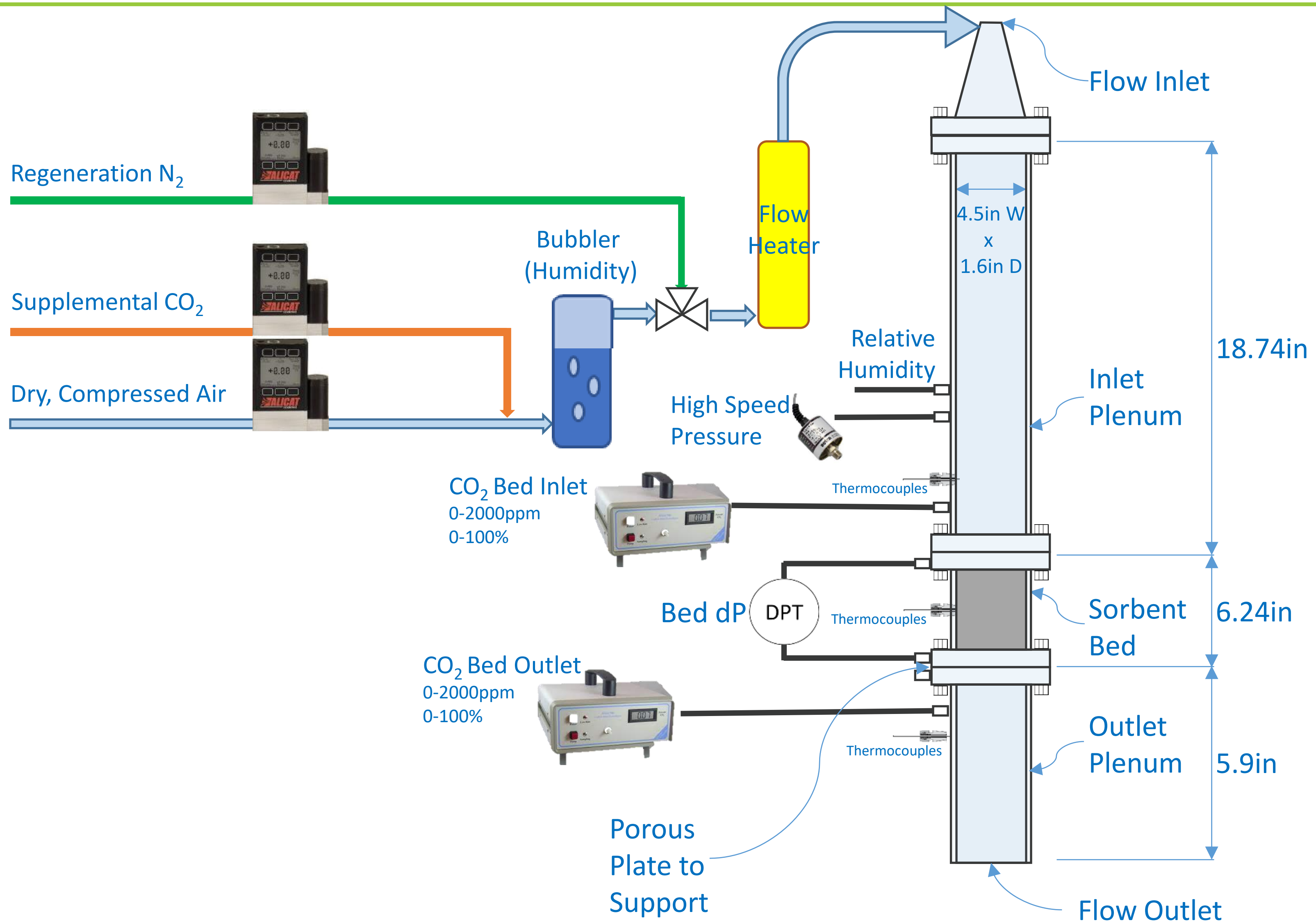
- Rate constant values cannot be compared directly for sorbents with different uptake capacities; for side-by-side comparison of the kinetics for CO_2 adsorption from dry and humid air, the net uptake rate of CO_2 is considered

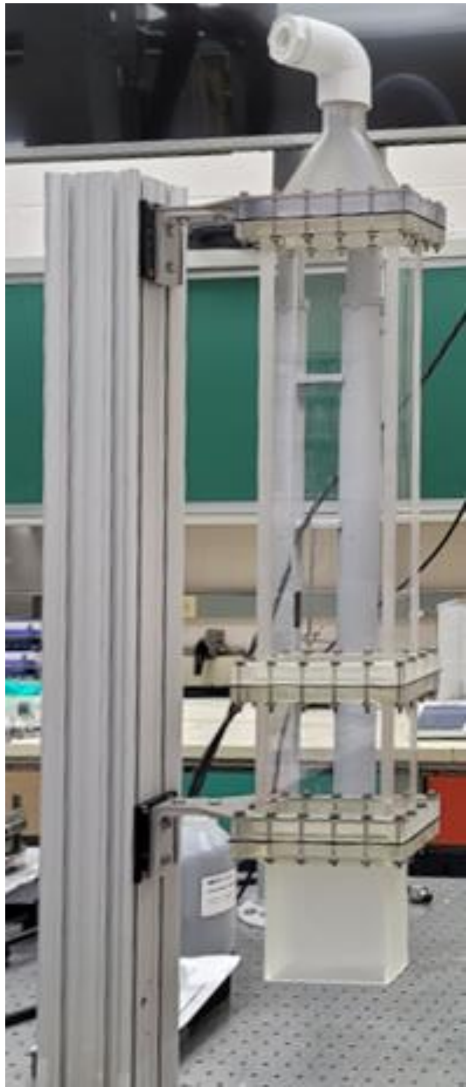




- CO_2 adsorption from humid air starts out 1% faster and the difference grows over time (+1% after 200 s)
- Current iteration of PF-15-TAEA has up to 25% increased capacity and will require a repeat of the sorbent characterization methodology

Ongoing/Future Work: Scale-up to Bench Scale



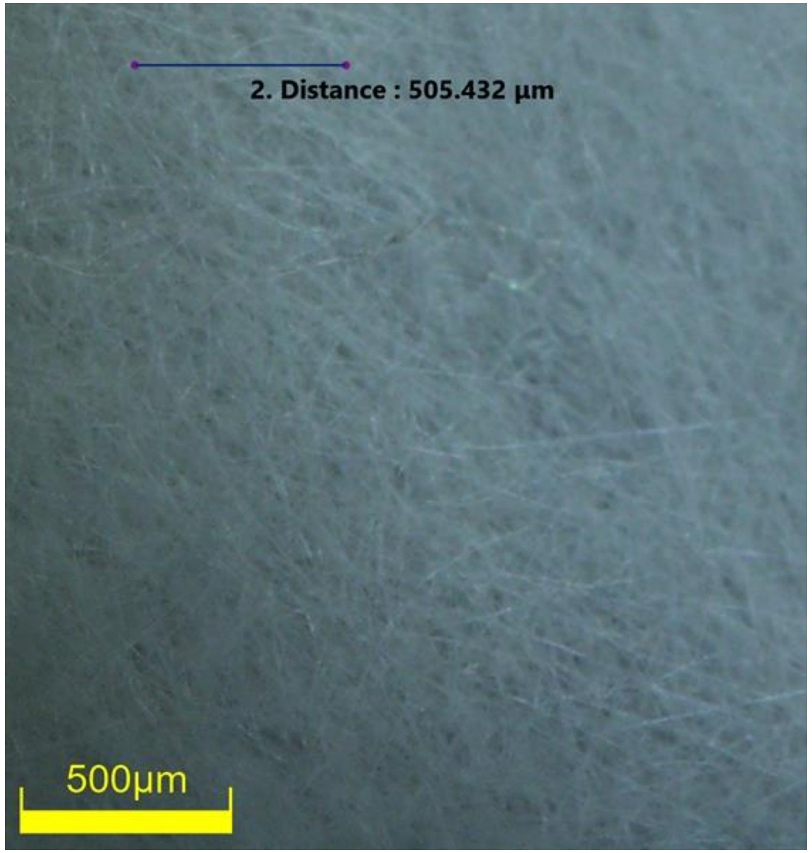


Ongoing/Future Work: Scale-up to Bench Scale

- Adsorption experiments in the bench-scale setup was conducted at MFAL by Integrated Project colleagues
- The CFD model of the small-scale fixed bed will be scaled up and validated against experimental bench-scale data
- In turn, the validated CFD model will be used to optimize bed design and operating conditions for best capture/pressure drop performance
- The rate calibration regimen may need to be repeated if significant changes to sorbent form factor or operating conditions occur

Ongoing/Future Work: Modeling of Fiber Shaped Sorbents

- PF-15-TAEA is currently available in different form factors, solid fibers, hollow fibers, and flat sheet with different uptake and kinetics properties
- Porous media model approach may not be appropriate to model the flow through the flat sheet arrangement because of non-uniform distribution of porosity
- To accurately predict pressure drop across the flat sheet, a CFD–DEM coupled simulation is developed in Ansys Rocky coupled with Ansys Fluent
- The flexible fibers are modeled by connecting multiple sphero-cylinders serially through virtual bonds[1]

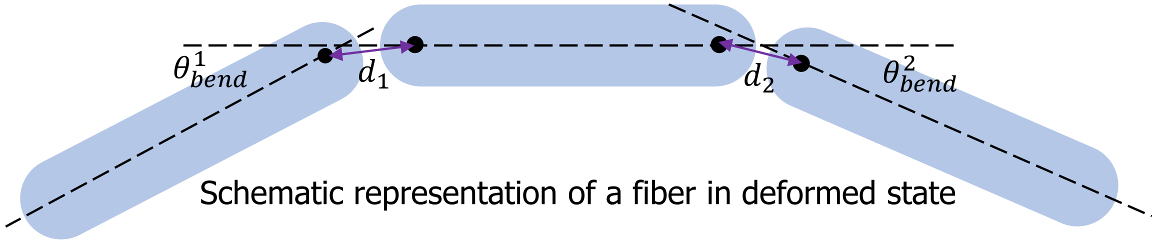


[1] Y. Guo, C. Wassgren, J. S. Curtis, D. Xu, A bonded sphero-cylinder model for the discrete element simulation of elasto-plastic fibers, Chemical Engineering Science, 2018, 175, 118–129.

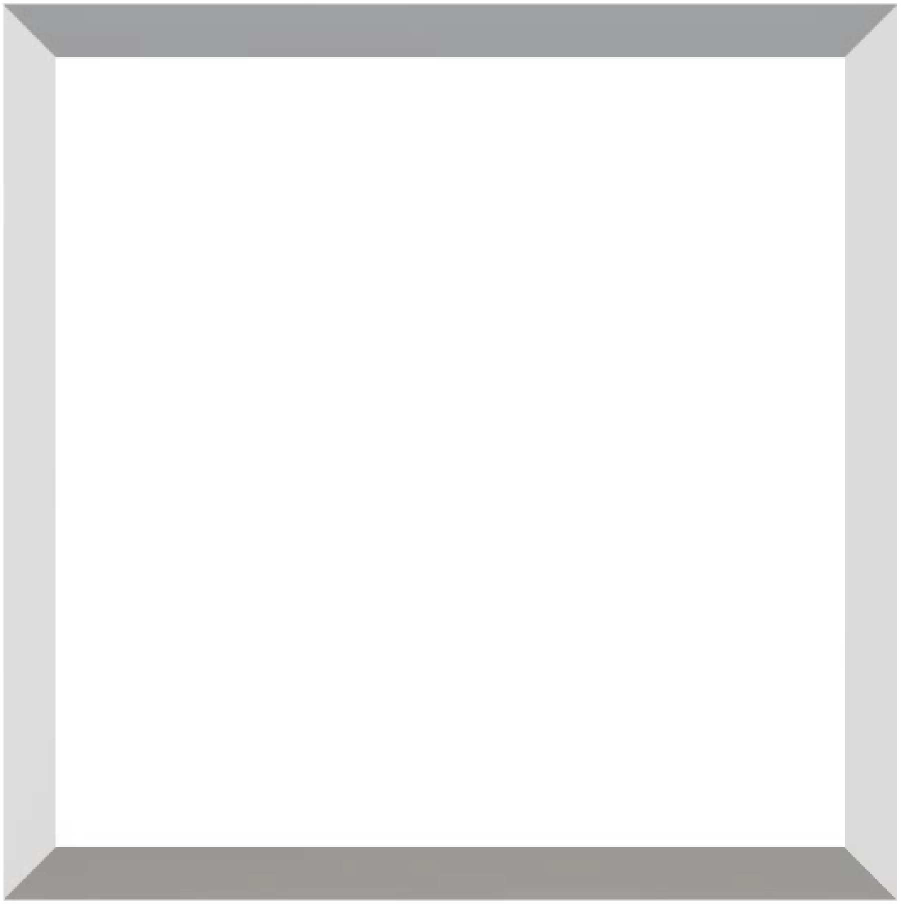
Ongoing/Future Work: Modeling of Fiber Shaped Sorbents

- The curved/deformed shape is generated because of the relative movement between sphero-cylinder elements
- The bond forces can be calculated using different models, e.g. linear elastic, bilinear elastoplastic, model, linear elastic & viscous damping, etc.
- Further sensitivity studies are necessary to develop an accurate representation of the flat sheet form factor in the coupled CFD-DEM model

Schematic representation of a fiber composed multiple elements



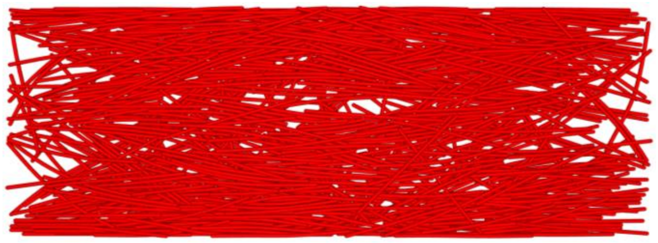
Schematic representation of a fiber in deformed state



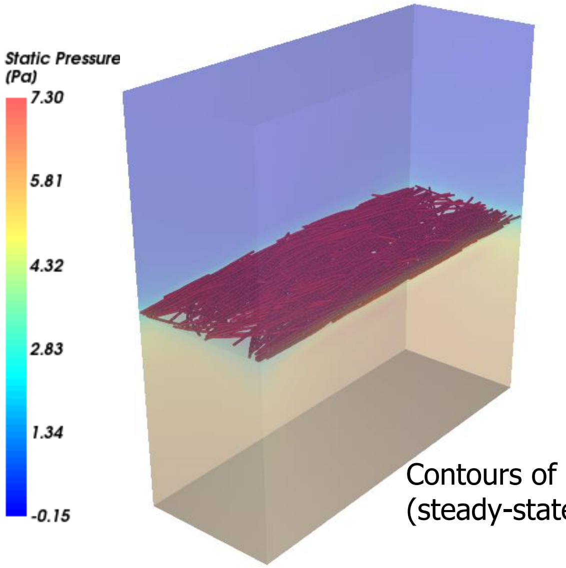
Deposition of multi-element flexible fibers on obtained from simulation

Ongoing/Future Work: Modeling of Fiber Shaped Sorbents

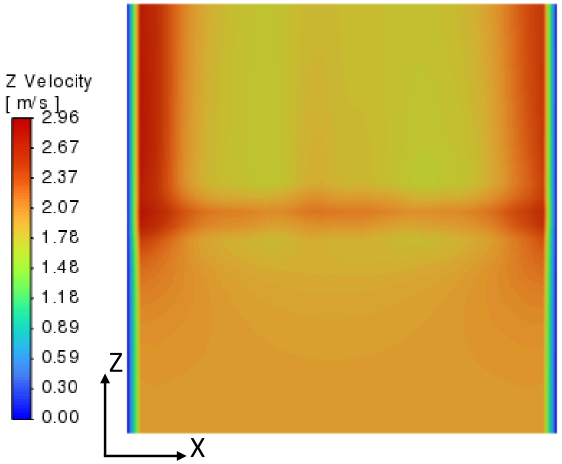
- The CFD-DEM model is used to analyze pressure drop across a representative fiber mat
- Fibers are deposited on a horizontal plane halfway up the 11.4 x 11.4 x 4.06 cm domain
  - Inlet air velocity = 2 m/s
  - Fiber diameter = 0.7 mm
  - Fiber length = 24.05 mm
  - Fiber element length = 1.85 mm (13 elements/fiber)
  - Drag law proposed by Marheineke & Wegener[1] was used to model the drag force



Fiber mat after 551 fibers deposited



Contours of pressure (steady-state)



Contours of centerline z-velocity (steady-state)

[1] N. Marheineke, R. Wegener, Modeling and application of a stochastic drag for fibers in turbulent flows, International Journal of Multiphase Flow, 2011, 37, 136-148.

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