

Enabling 10 mol/kg swing capacity via heat integrated sub-ambient pressure swing adsorption

Ryan P. Lively

Principal Investigator

Yoshiaki Kawajiri, Matthew J. Realff, David S. Sholl, Krista S. Walton

Co-Principal Investigators

Georgia Institute of Technology

School of Chemical & Biomolecular Engineering

Atlanta, GA 30332

DOE-NETL CO₂ Capture Technology Project review Meeting

Thursday, August 24th , 2017

Key Idea:

Combine:

- (i) Sub-ambient gas processing and energy recovery with**
 - (ii) ultra-porous metal-organic frameworks and**
 - (iii) space- and energy-efficient fiber sorbent contactors**
- to yield a game-changing process strategy**

Project scope—Re-thinking general assumptions about post-combustion CO₂ capture

ExxonMobil
Research and Engineering

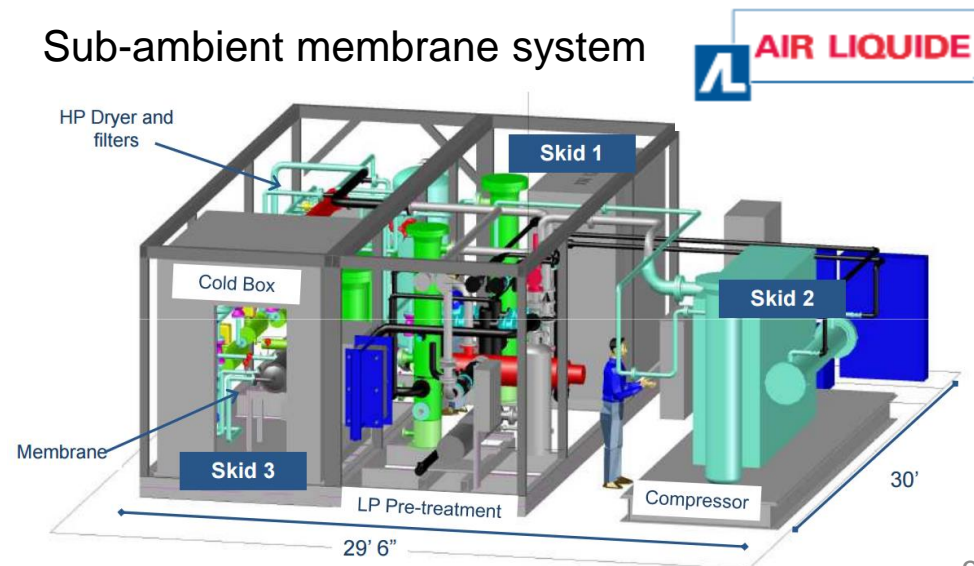
QuestAir
Pure Innovations®

- Rapid pressure swing adsorption is more straightforward than rapid temperature swing adsorption (the former has been commercialized)
- Immense pore volume and surface area of MOFs are advantageous at sub-ambient conditions and moderate CO₂ partial pressures (~1-2 bar)
- Sub-ambient conditions increase adsorption selectivity and working capacity—even without adsorbent structural changes
- Weaknesses of MOFs addressed through contactor (hollow fiber sorbents) and through process strategy

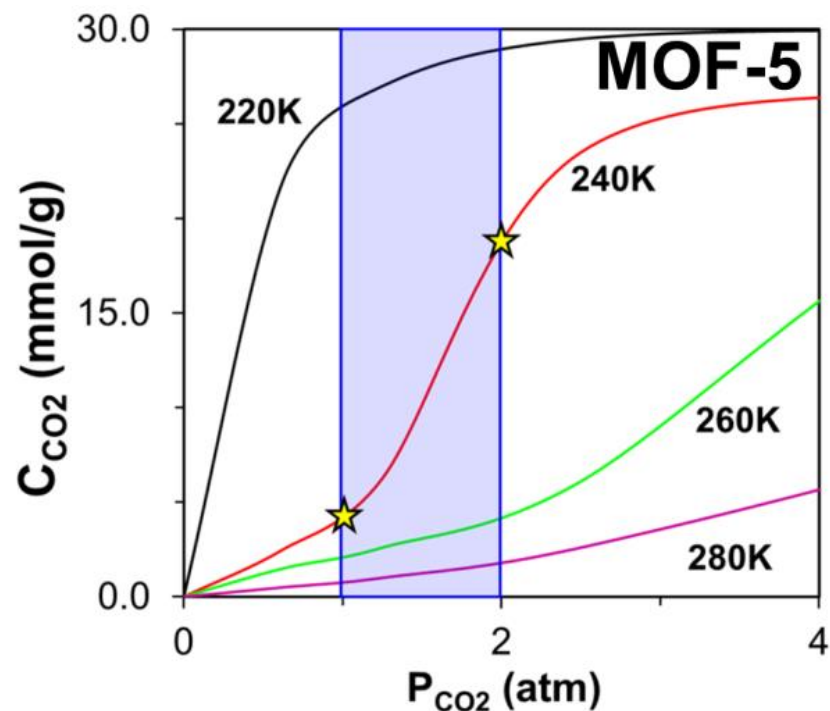
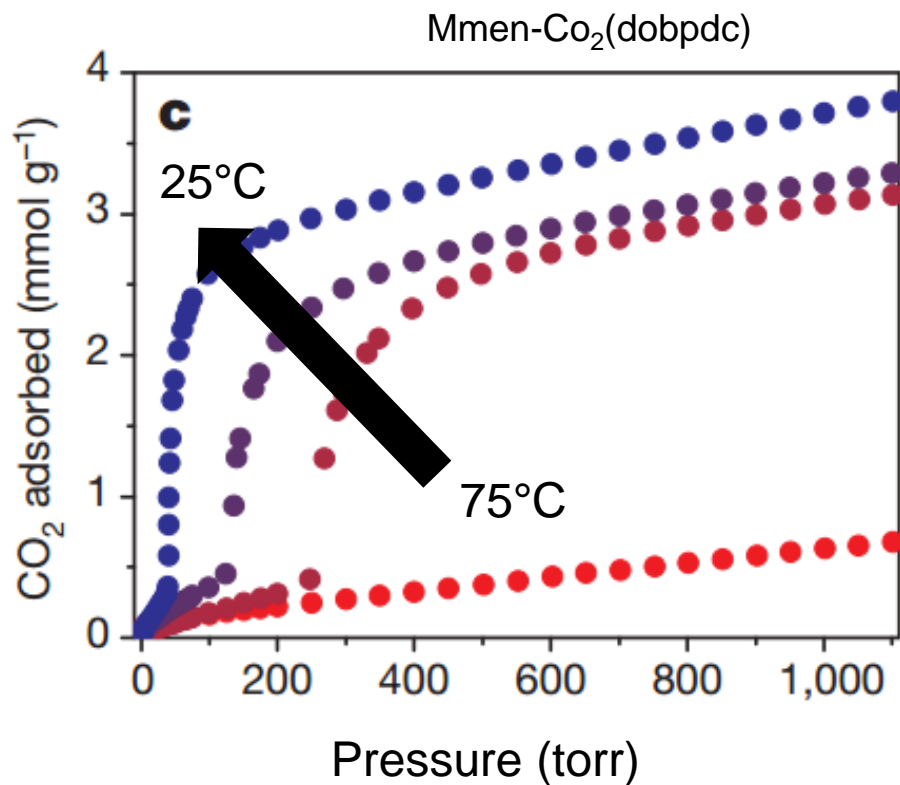
RCPSA



Sub-ambient membrane system



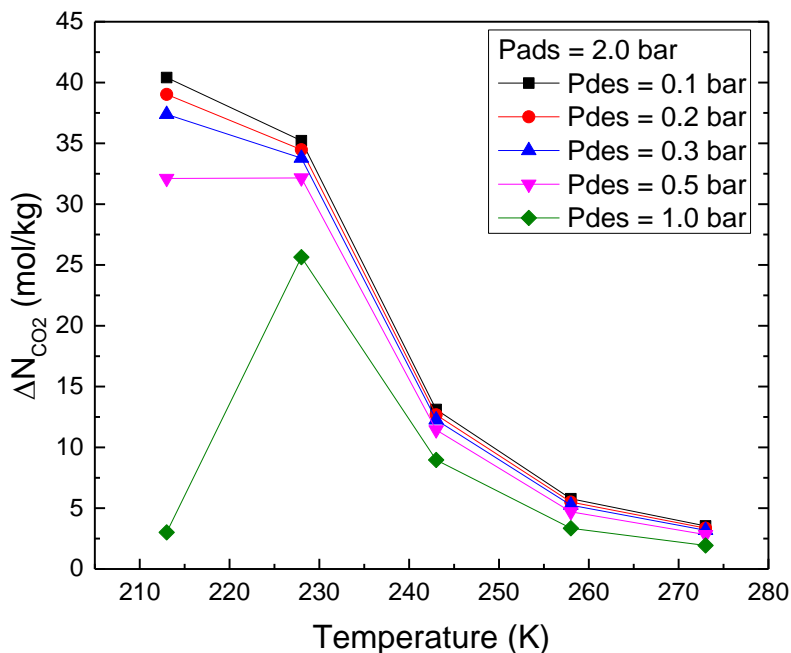
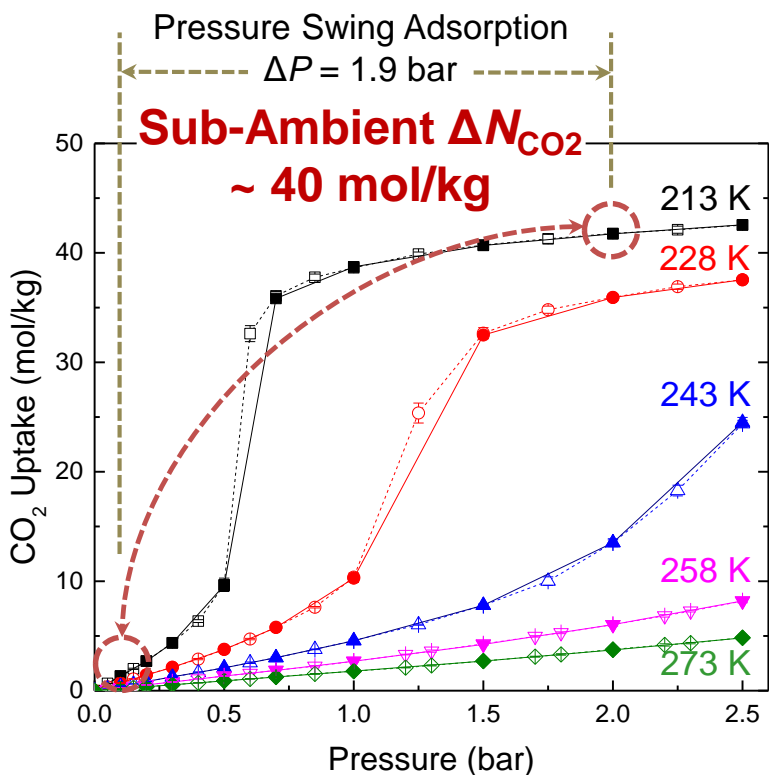
Background: Metal-organic frameworks—State-of-the-art



[1] TM McDonald, JR Long et al., *Nature*, 2015, 519, 303-308

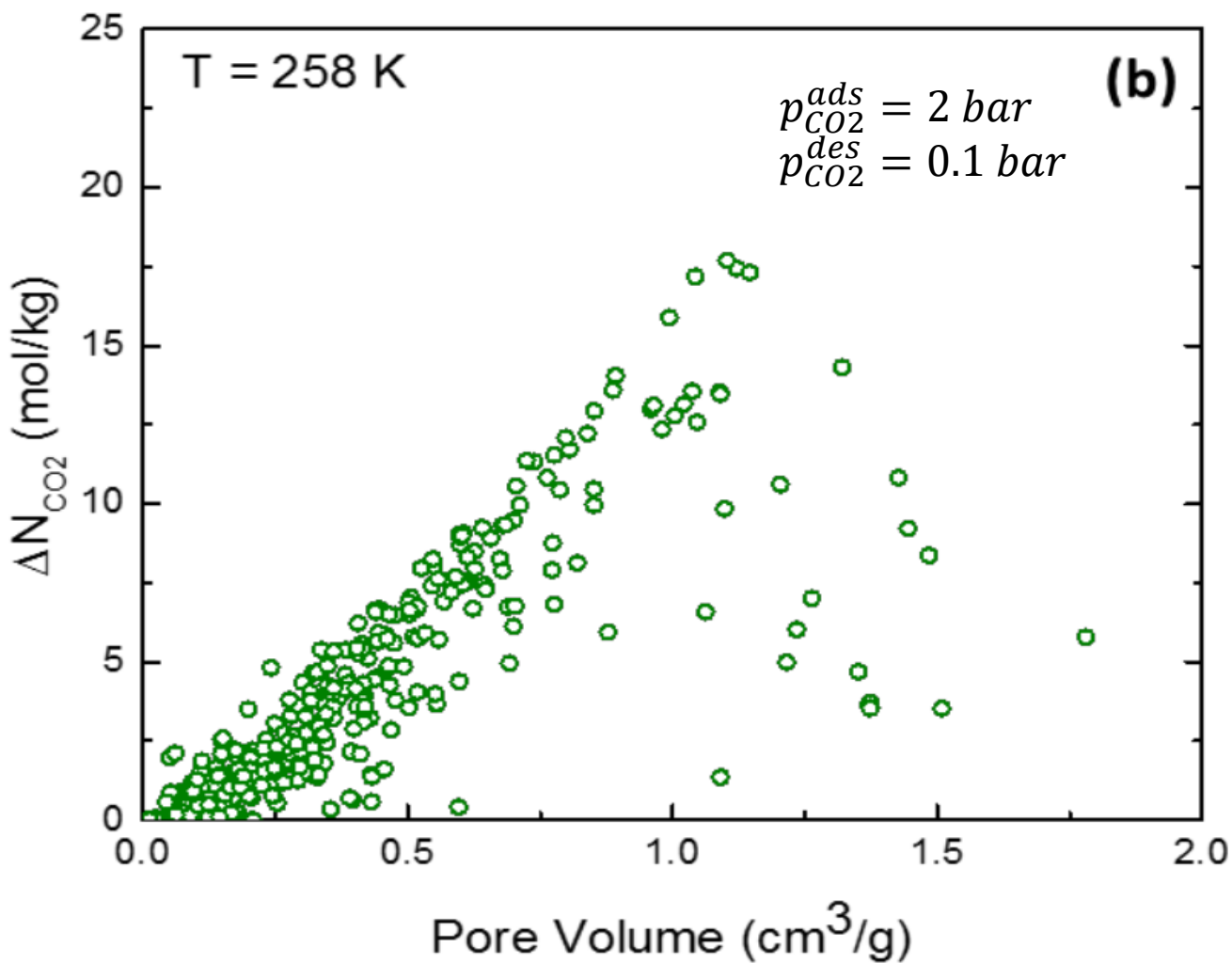
[2] JM Simmons, T Yildirim et al., *Energ. Env. Sci.*, 2011, 4(6), 2177-2185

A wide variety of MOFs can hit >10 mol/kg swing capacities at sub-ambient conditions

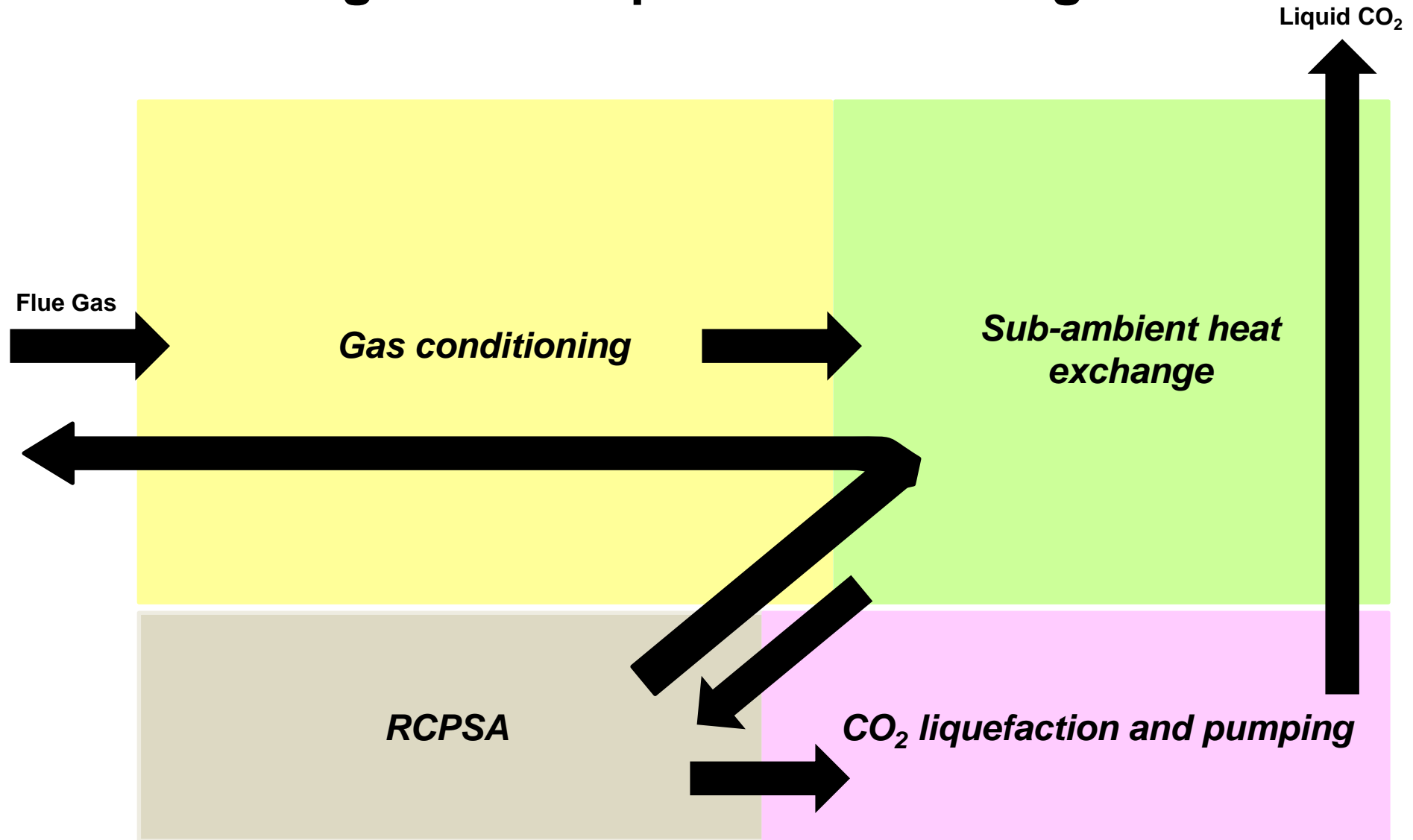


[1] J Park, RP Lively, DS Sholl, *J. Mater. Chem. A*. 2017, 5, 12258-12265

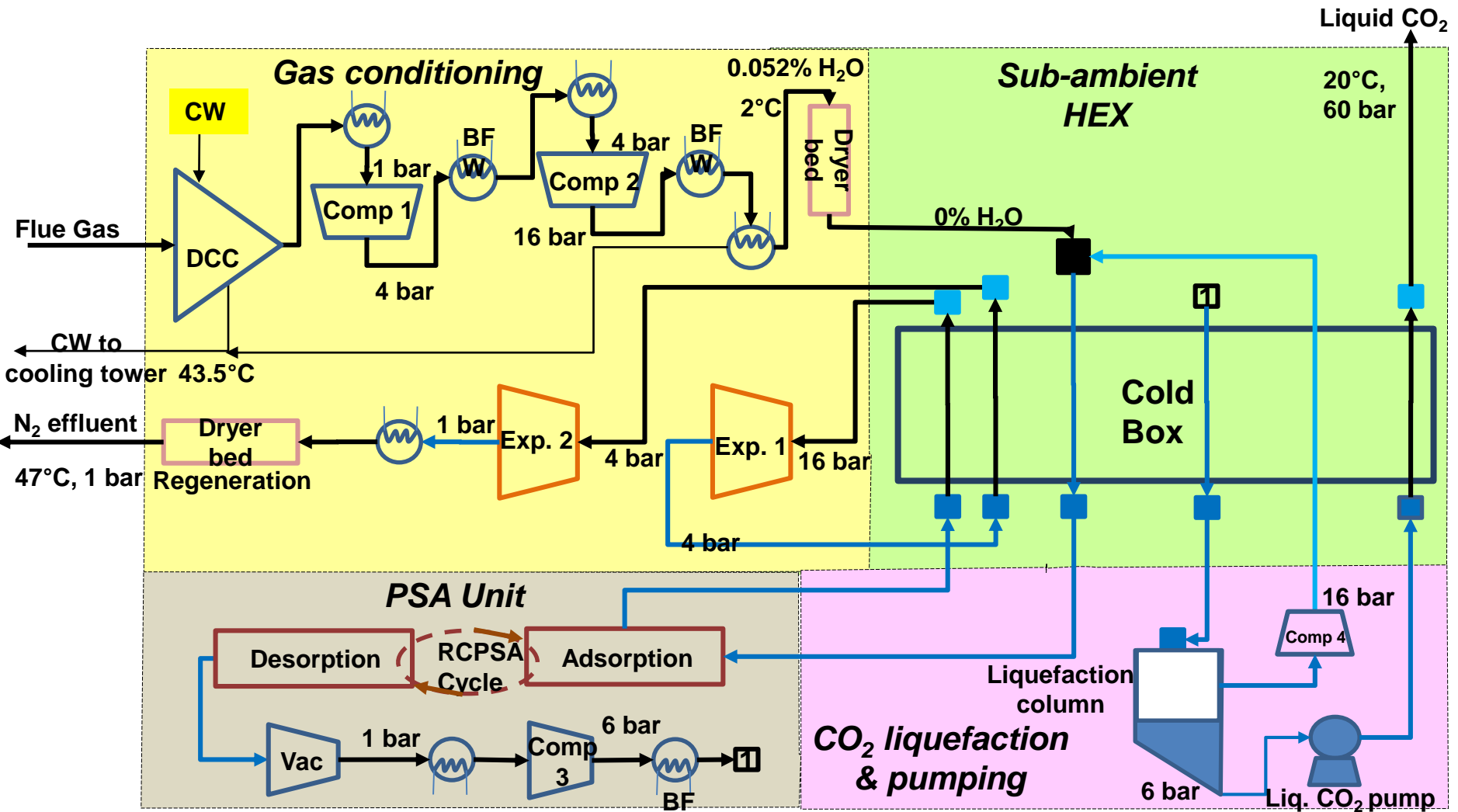
A wide variety of MOFs can hit >10 mol/kg swing capacities at sub-ambient conditions



2nd generation process flow diagram

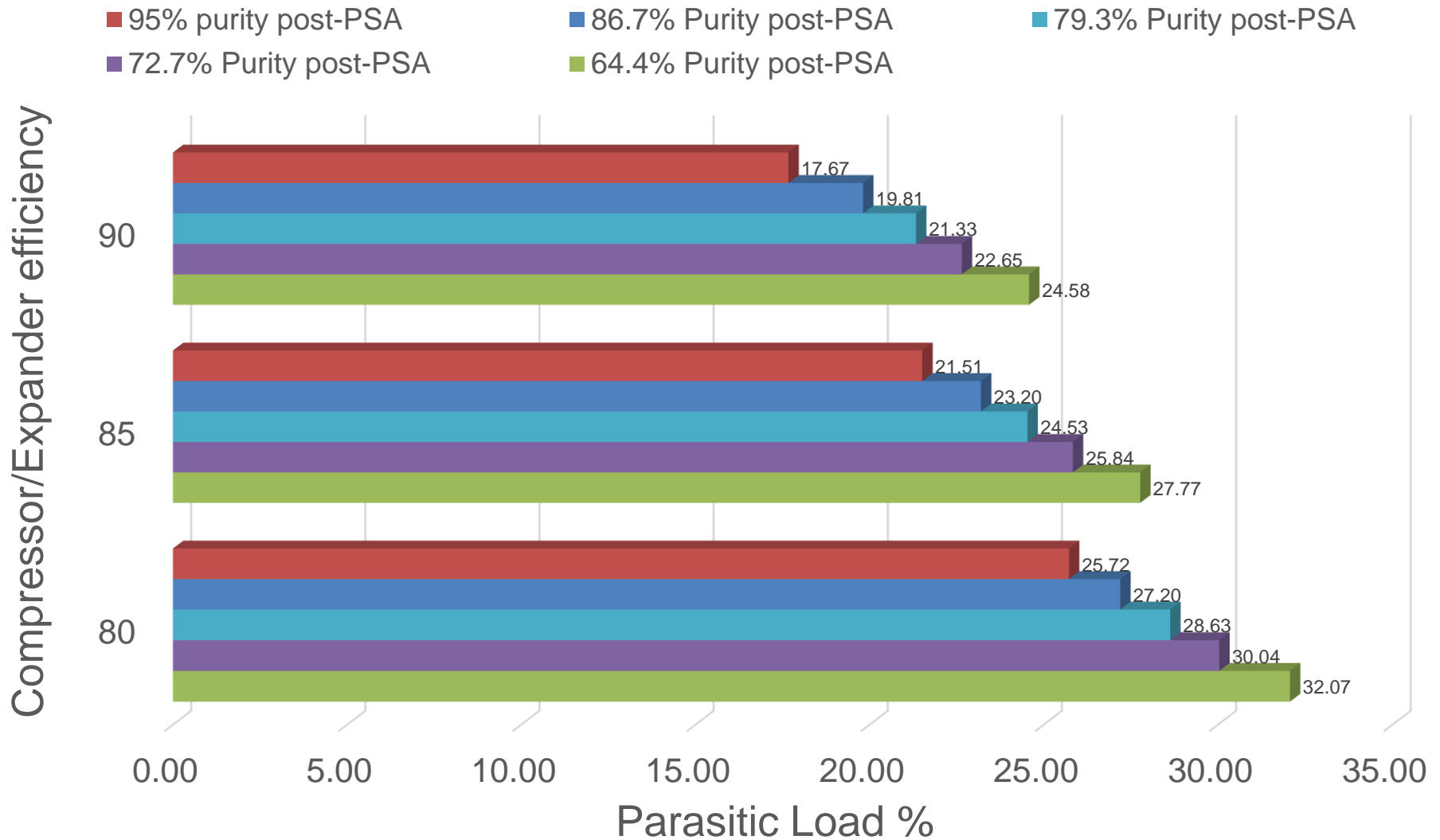


2nd generation process flow diagram



Preliminary techno-economic analysis

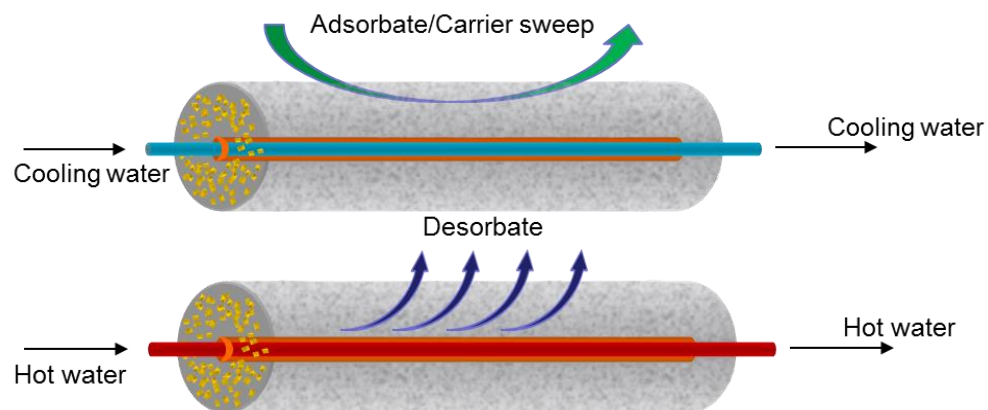
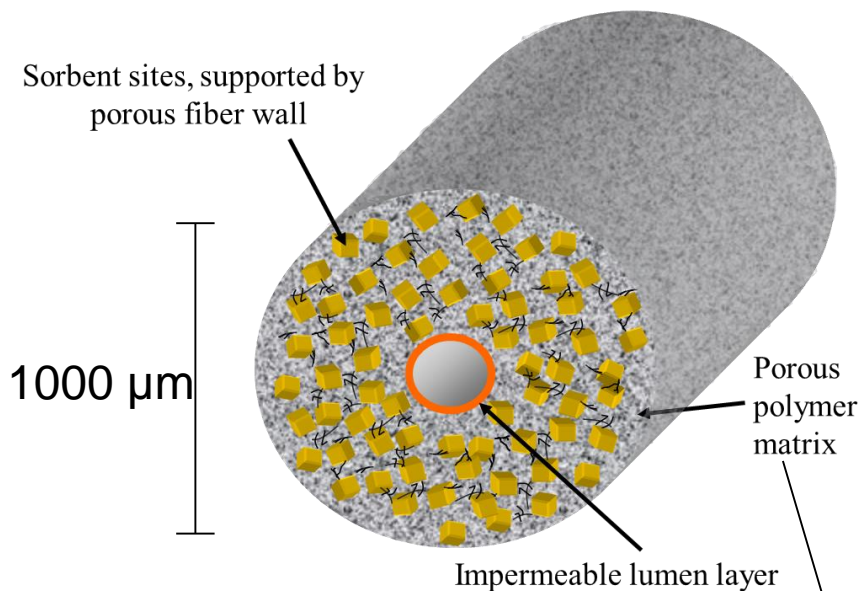
Parasitic load (NETL Base Case 550 MW power plant)



Preliminary techno-economic analysis

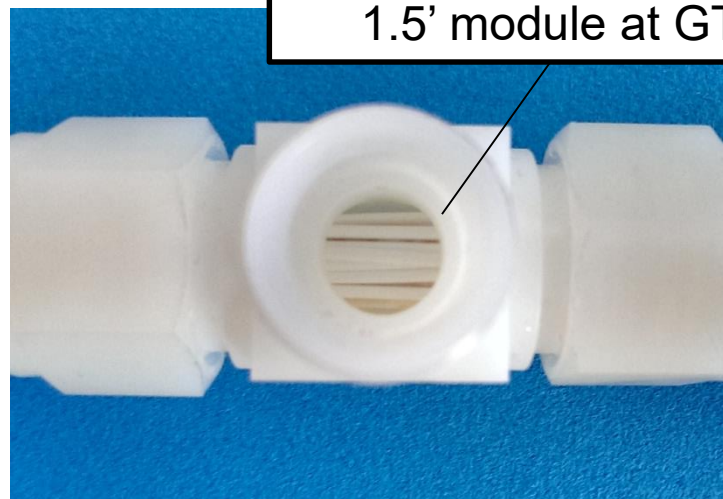
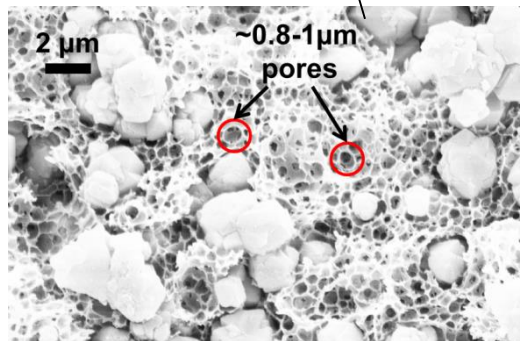
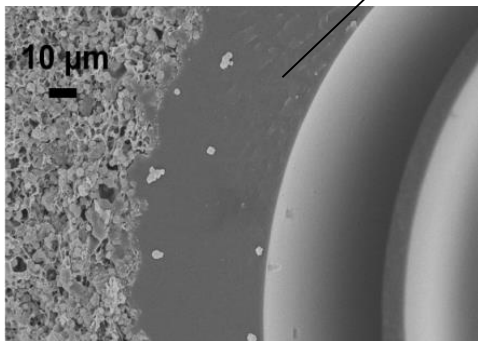
| Equipment | Cost (MM\$) |
|-----------------------------|-------------|
| compressors & expanders | 74 |
| HX | 38 |
| PSA | 38 |
| DCC & cooling tower | 2 |
| Liquid CO ₂ pump | < 0.1 |
| silica bed | < 0.1 |
| Total | ~155 |

Background: Hollow fiber sorbents, a mass producible structured sorbent inspired by hollow fiber membrane spinning

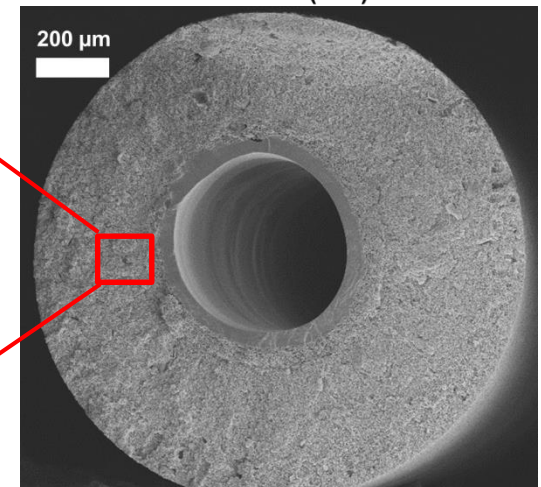
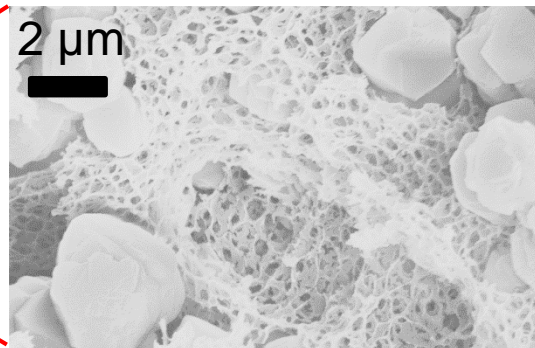
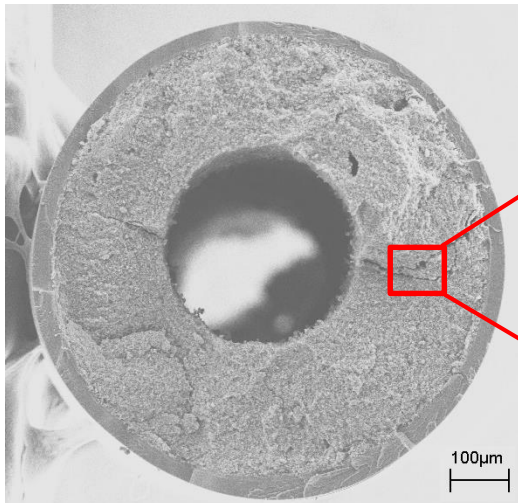
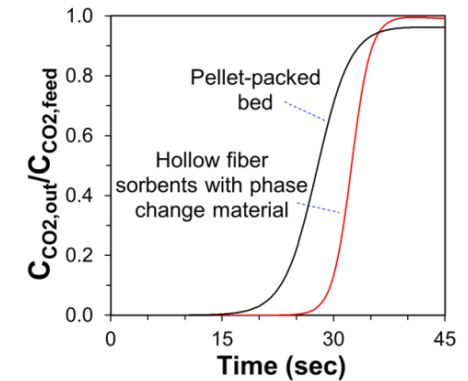
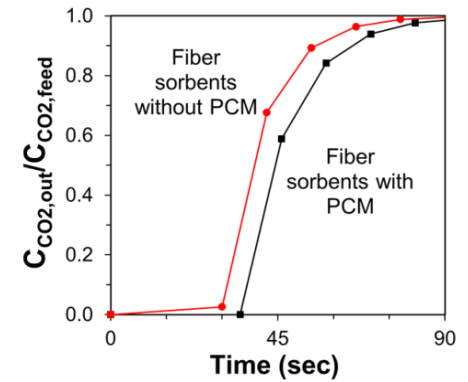
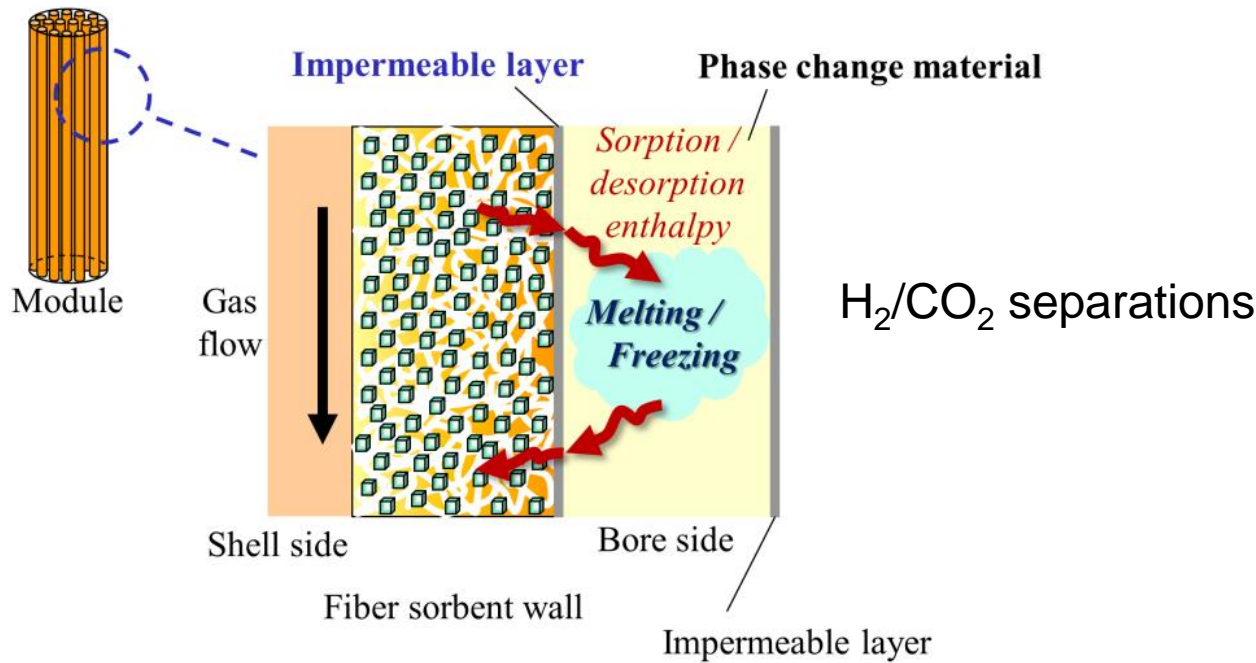


Ideal temperature swing adsorption

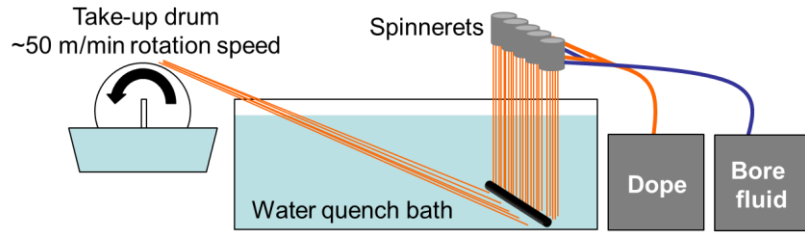
Bundle of 40 fibers in a 1.5' module at GT



Background: Fiber sorbents for PSA applications

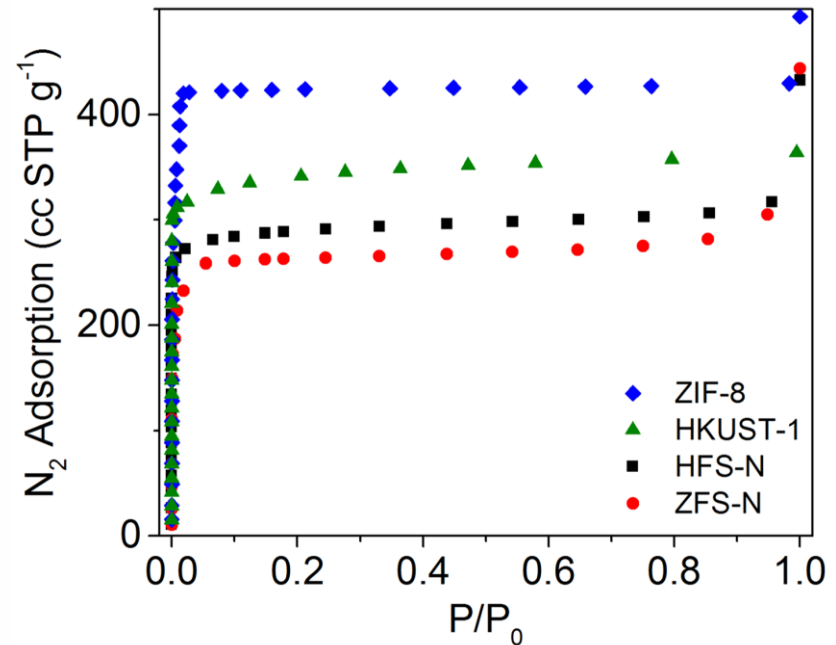
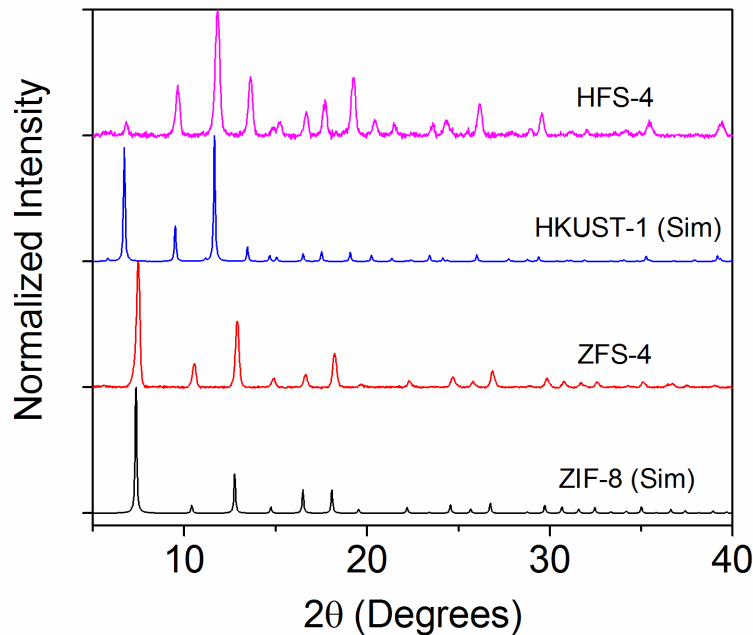
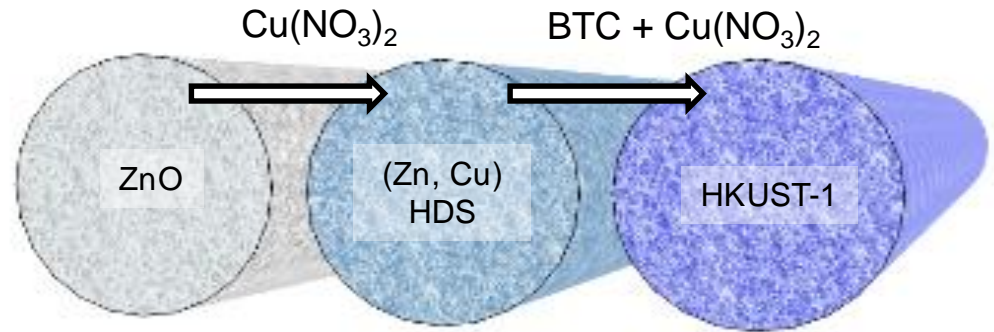
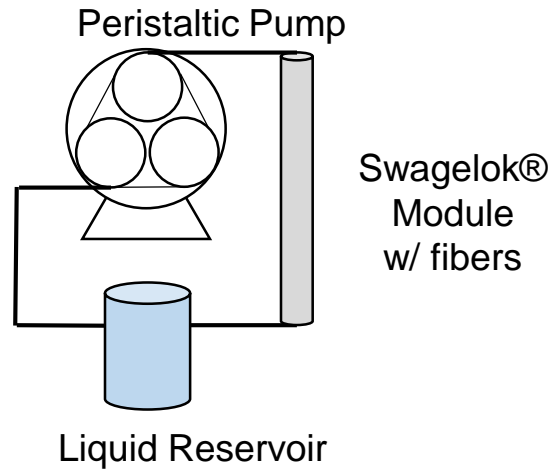


Post-synthesis formation of MOFs in fiber sorbents



Load metal oxide fibers into adsorption module

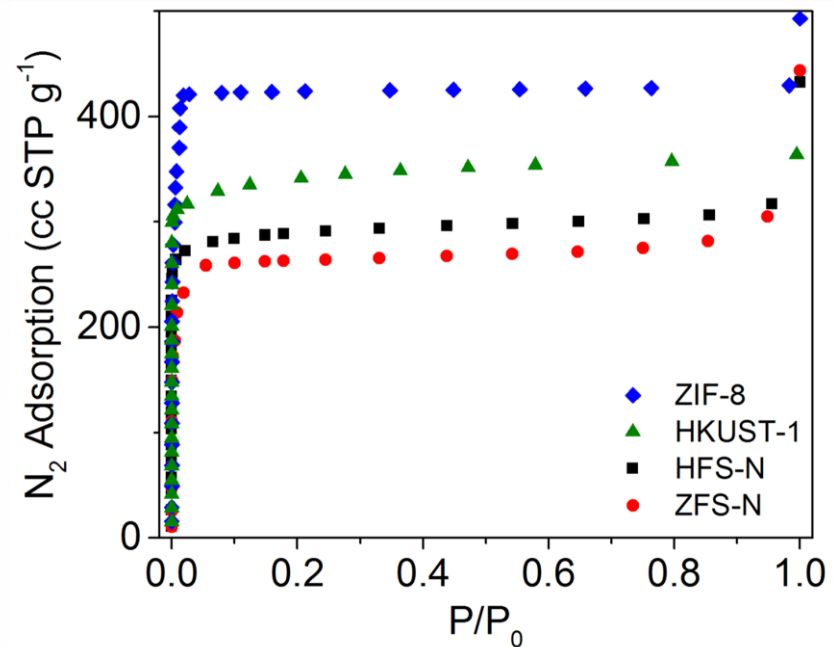
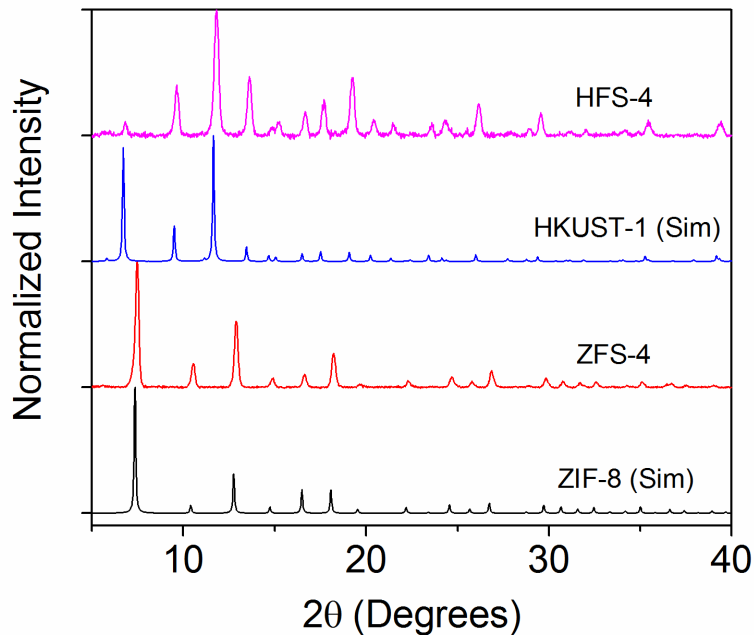
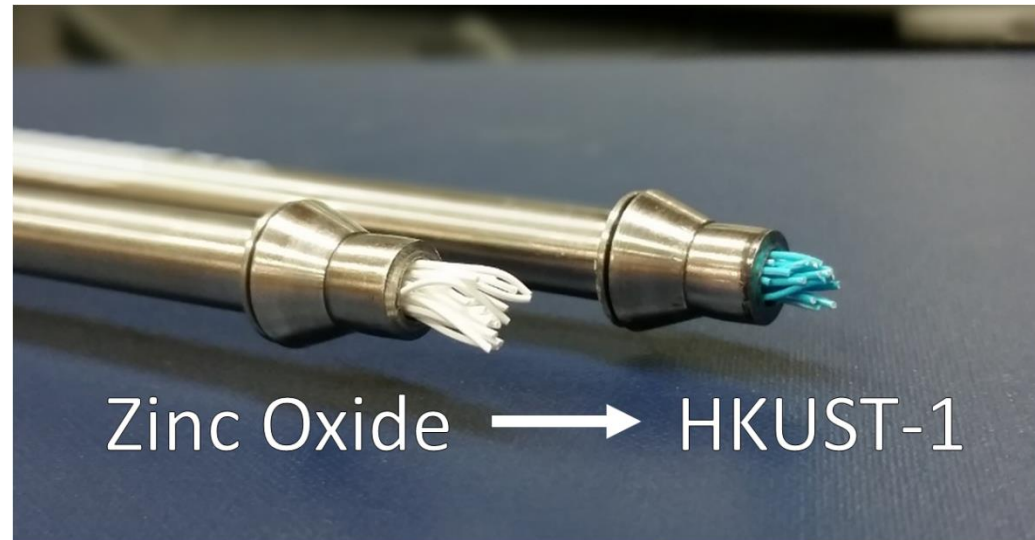
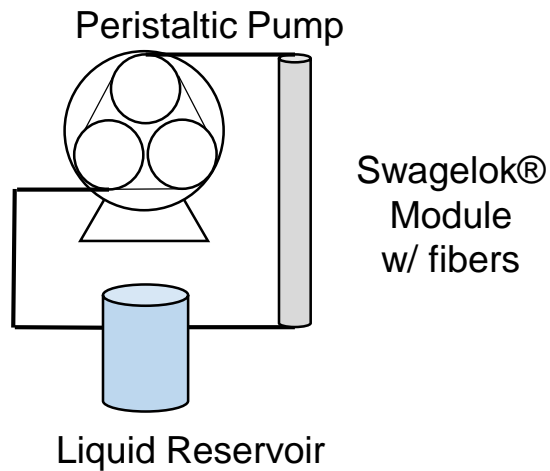
Post-synthesis formation of MOFs in fiber sorbents



✓ Task 7 (synthesize MOFs and spin fibers)

[1] BR Pimentel, RP Lively et al., *Ind. Eng. Chem. Res.* **2017**, 56(17), 5070-5077

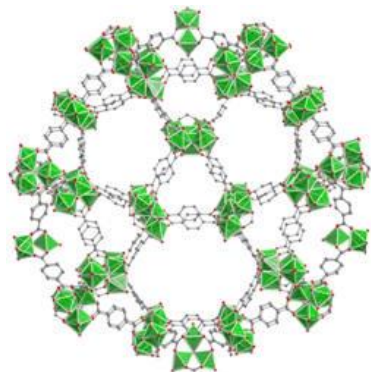
Post-synthesis formation of MOFs in fiber sorbents



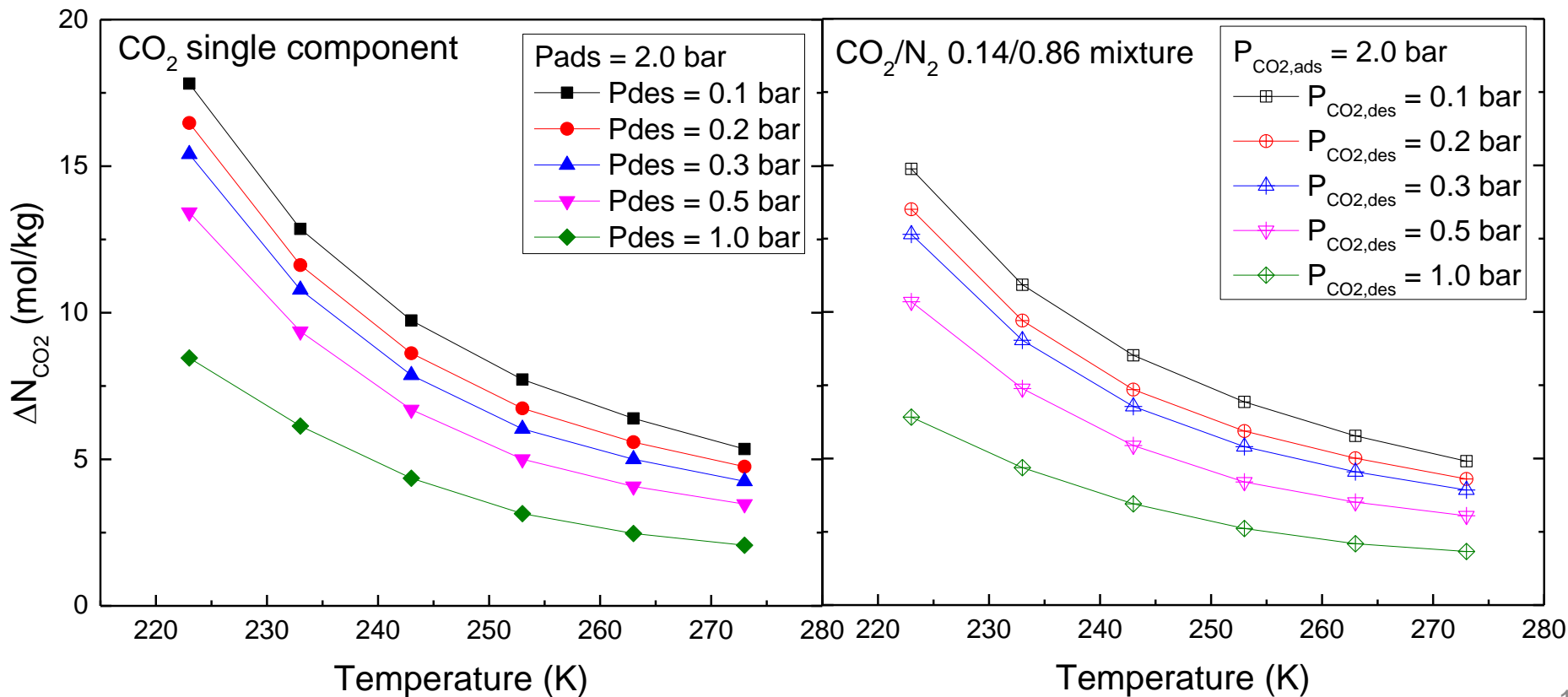
✓ Task 7 (synthesize MOFs and spin fibers)

[1] BR Pimentel, RP Lively et al., *Ind. Eng. Chem. Res.* **2017**, 56(17), 5070-5077

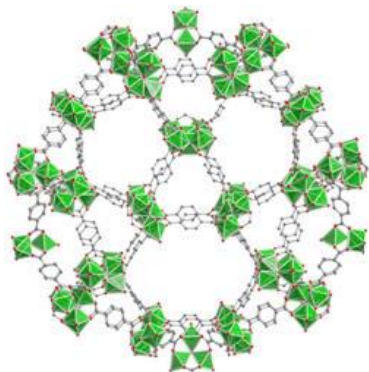
MIL-101(Cr) emerged as a promising candidate



Low cost ligands (benzene dicarboxylate)
Relatively low cost metal centers (chromium nitrate)
Scale-up is straight forward (70% yield on large batches)
Water stable

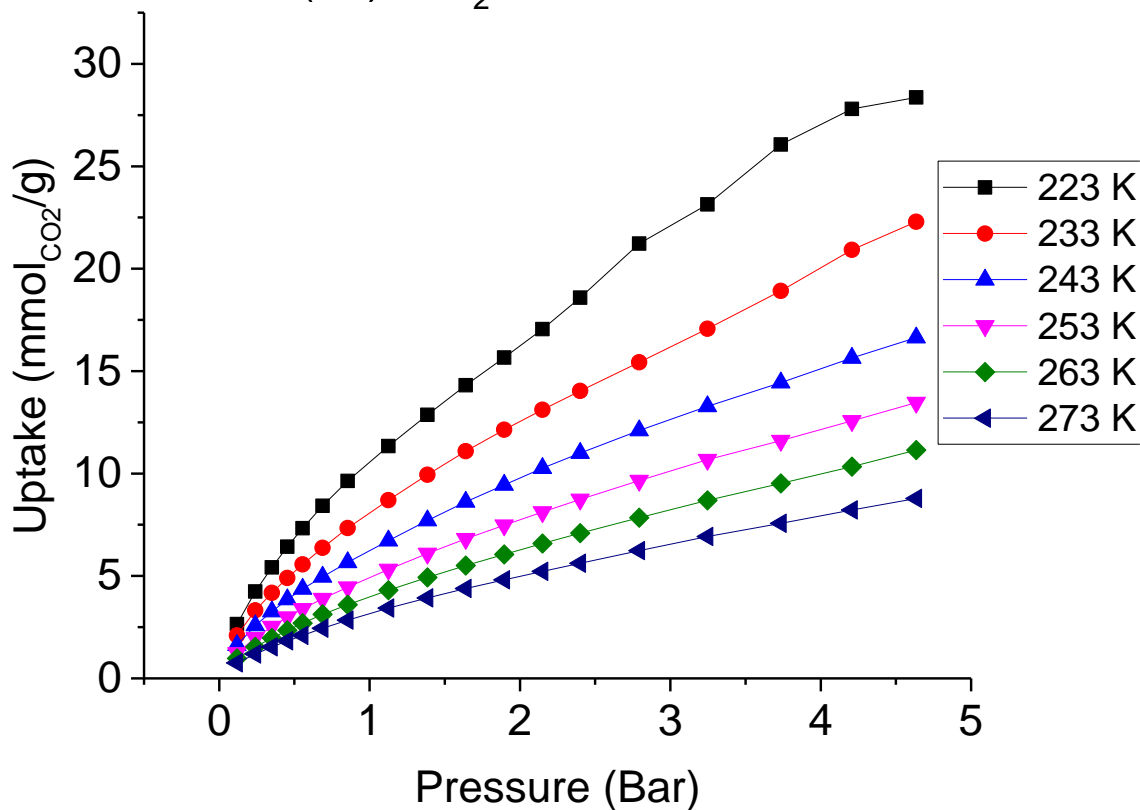


MIL-101(Cr) emerged as a promising candidate



Low cost ligands (benzene dicarboxylate)
Relatively low cost metal centers (chromium nitrate)
Scale-up is straight forward (70% yield on large batches)
Water stable

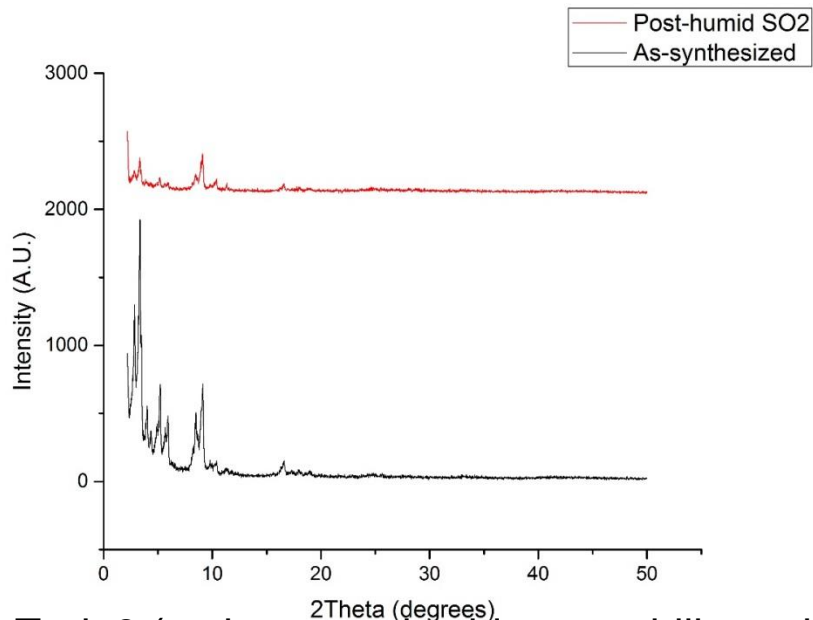
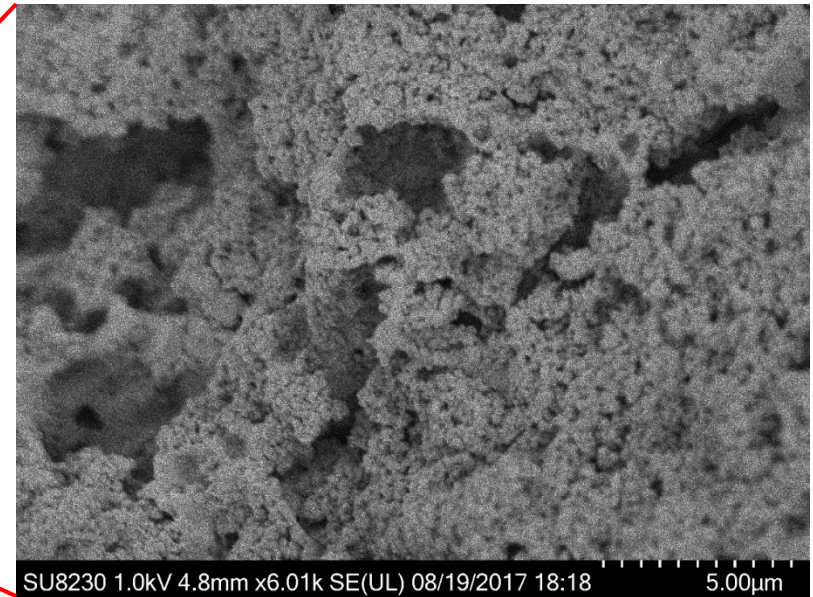
MIL-101(Cr) CO₂ Subambient Isotherm



[1] J Park, RP Lively, DS Sholl, *J. Mater. Chem. A*. 2017, 5, 12258-12265

[2] L Hamon, GD Weireld et al., *J. Am. Chem. Soc.* 2009, 131, 8775-8777

MIL-101(Cr) fiber sorbents



Solvent stability ✓

Water stability ✓

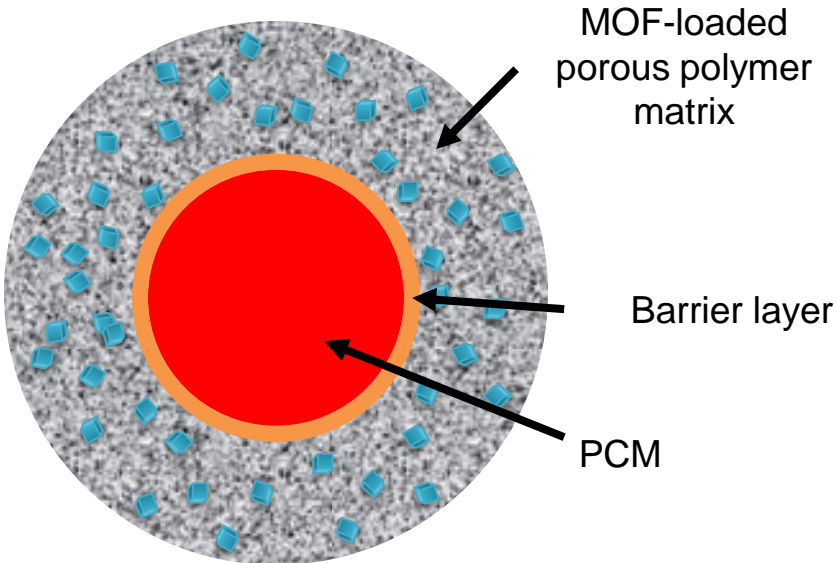
BET Specific Surface Area (m²/g)

| | |
|----------------------------|------|
| As-synthesized | 2740 |
| Post-humid SO ₂ | 2790 |

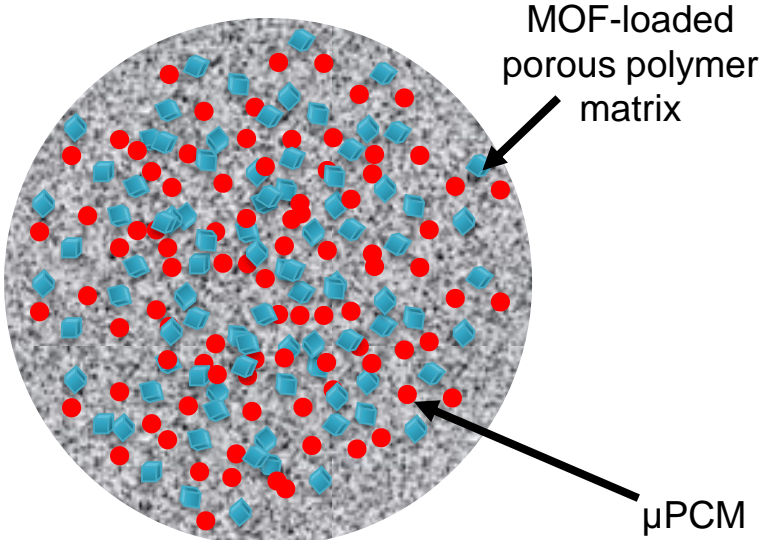


Task 8 (moisture and acid gas stability—also completed for UiO-66)

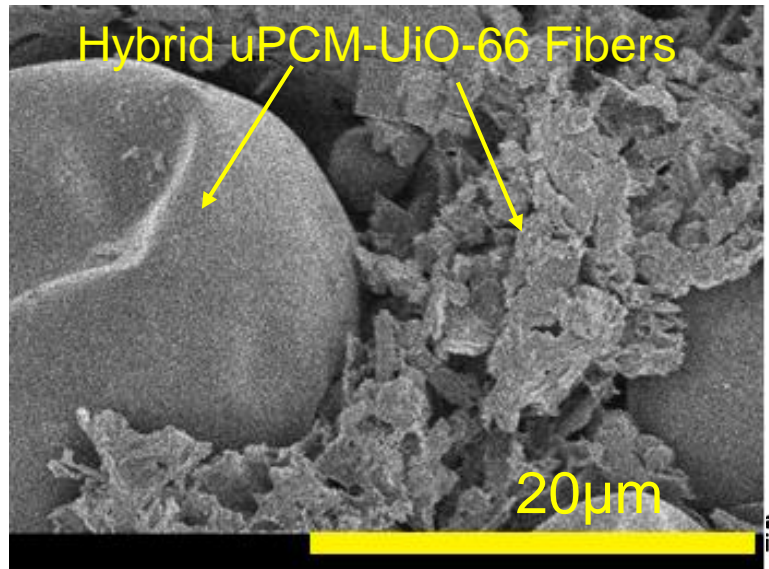
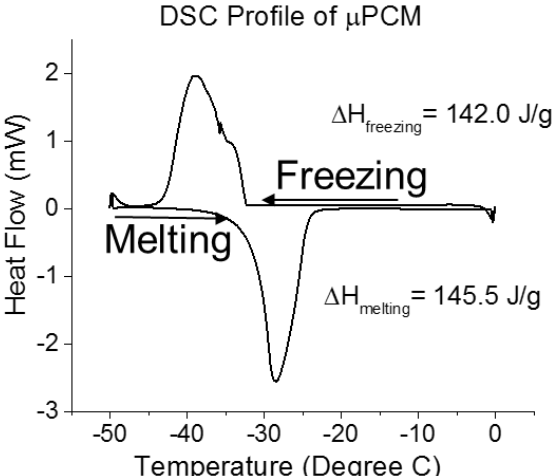
Installing thermal modulation into fiber sorbent contactors



3 steps: spinning, barrier layer installation, PCM installation



1 step: spinning

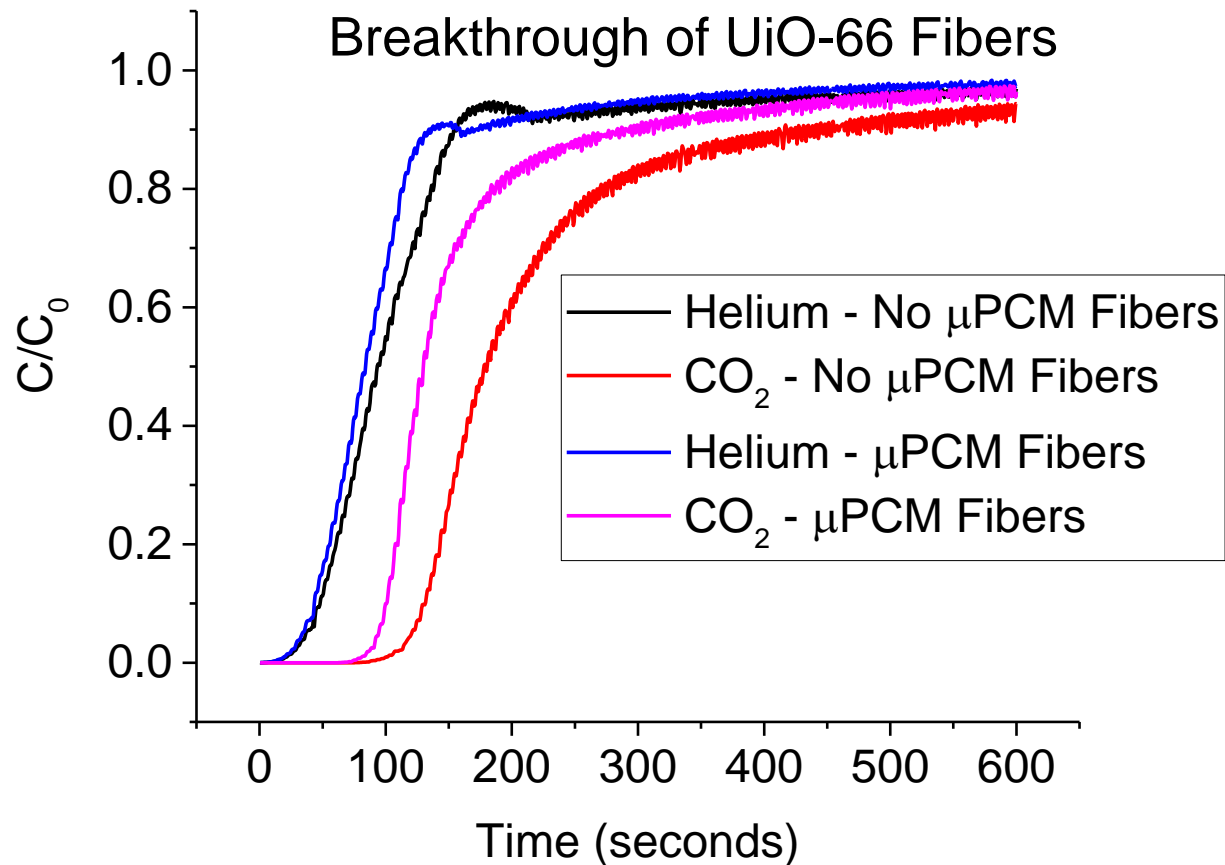


✓ Task 11 (integrate PCM into modules)

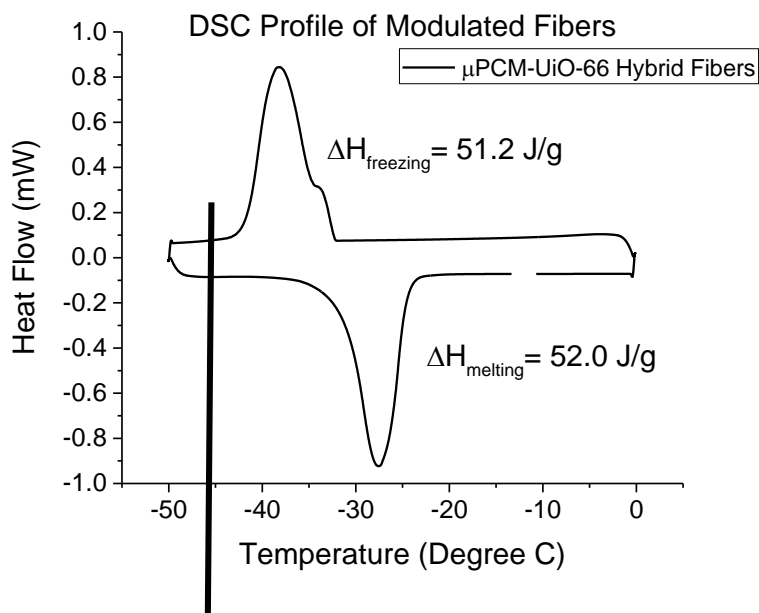
Performance of thermally modulated MOF fiber sorbents



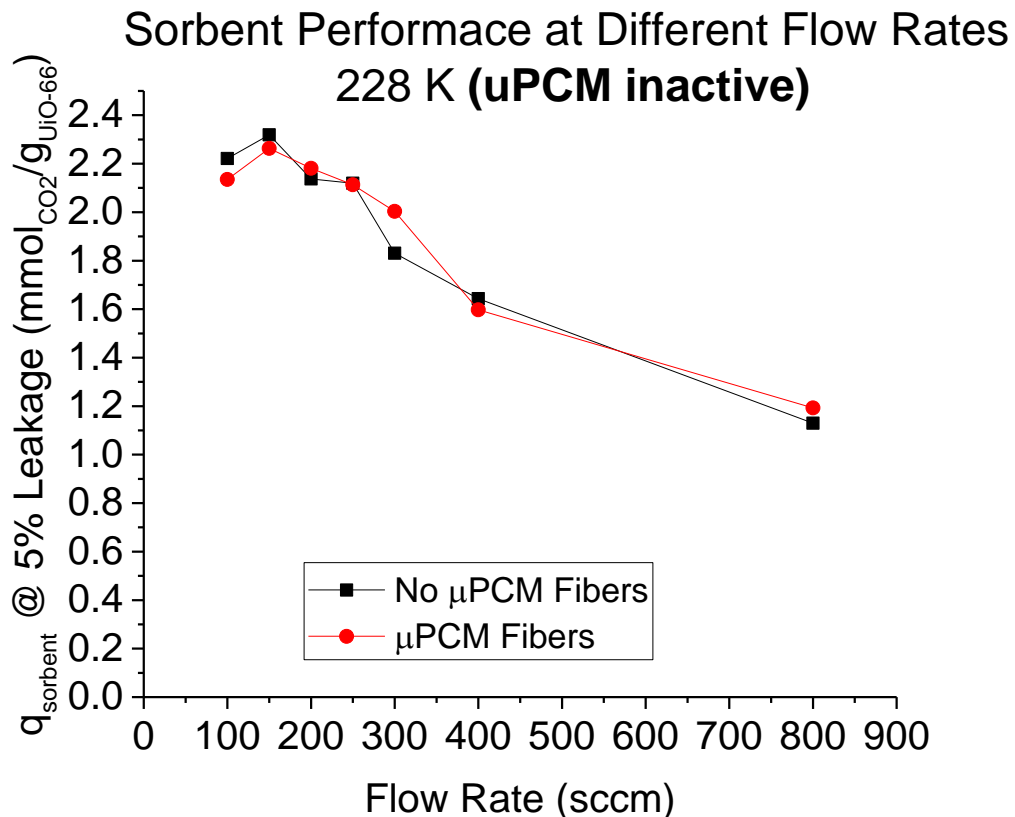
Effect of μ PCM incorporation on CO_2
Breakthrough of UiO-66 Fibers



Performance of thermally modulated MOF fiber sorbents

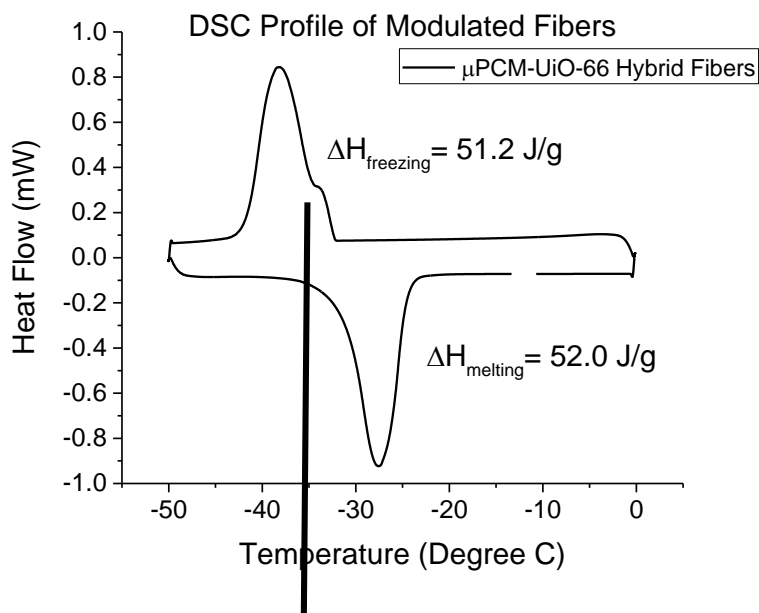


Operating
Temperature

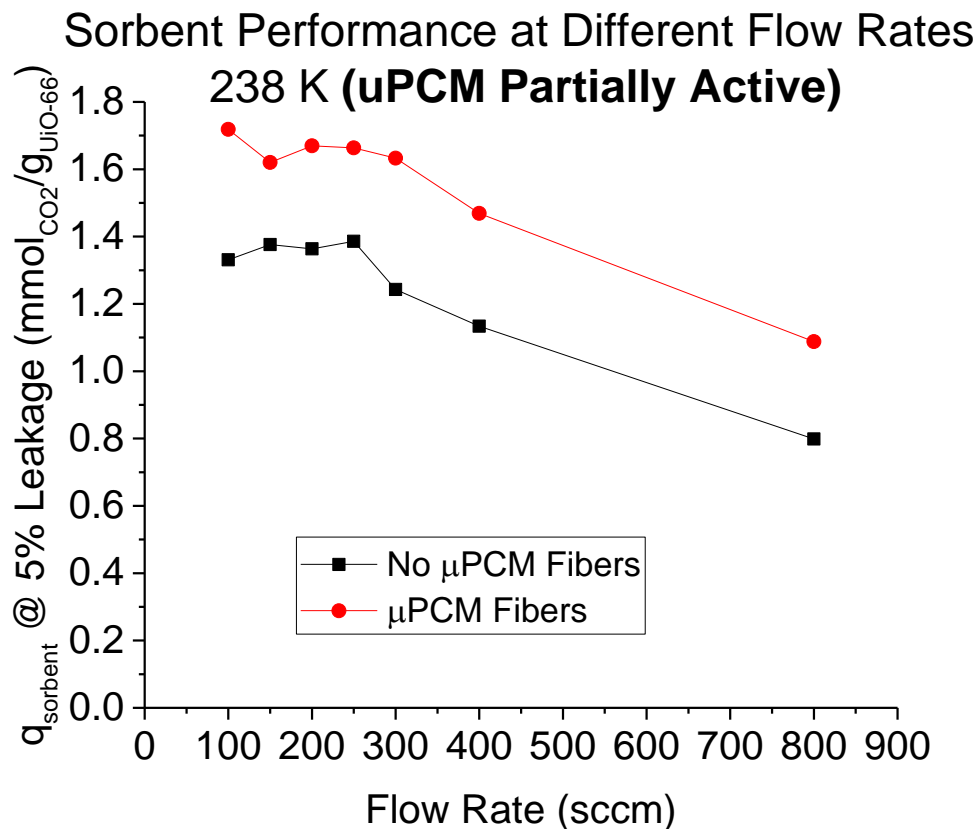


Task 10 (experimental PSA cycles)

Performance of thermally modulated MOF fiber sorbents



Operating
Temperature

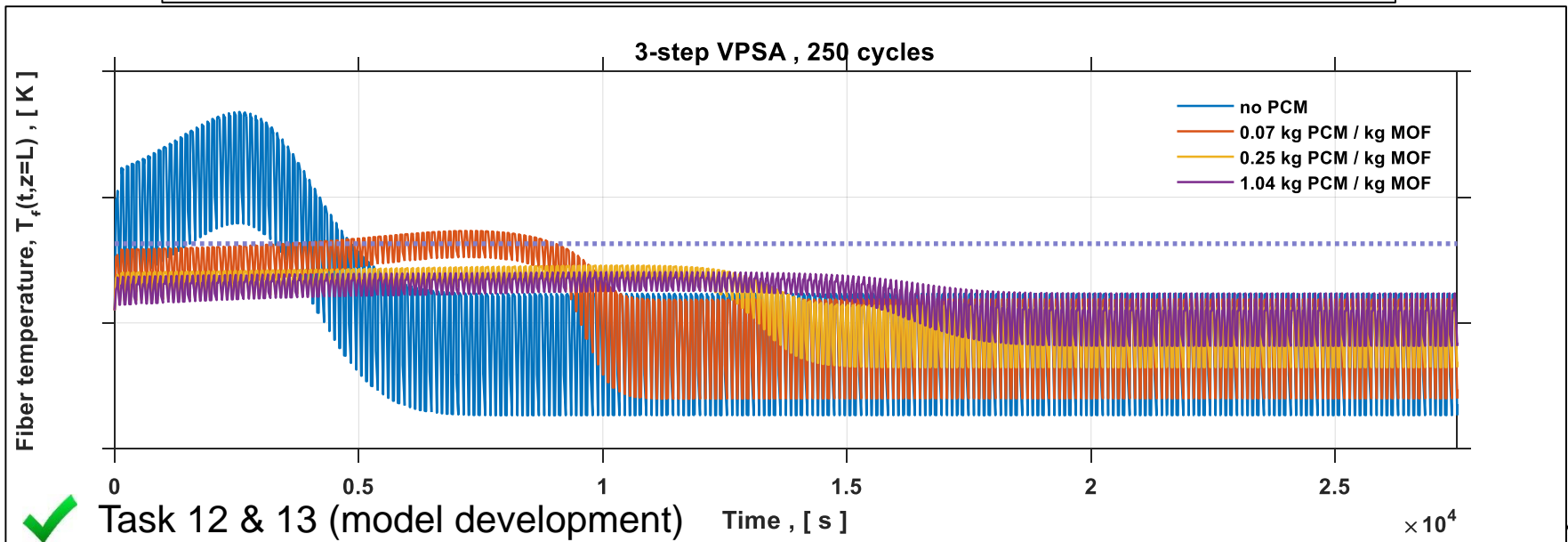
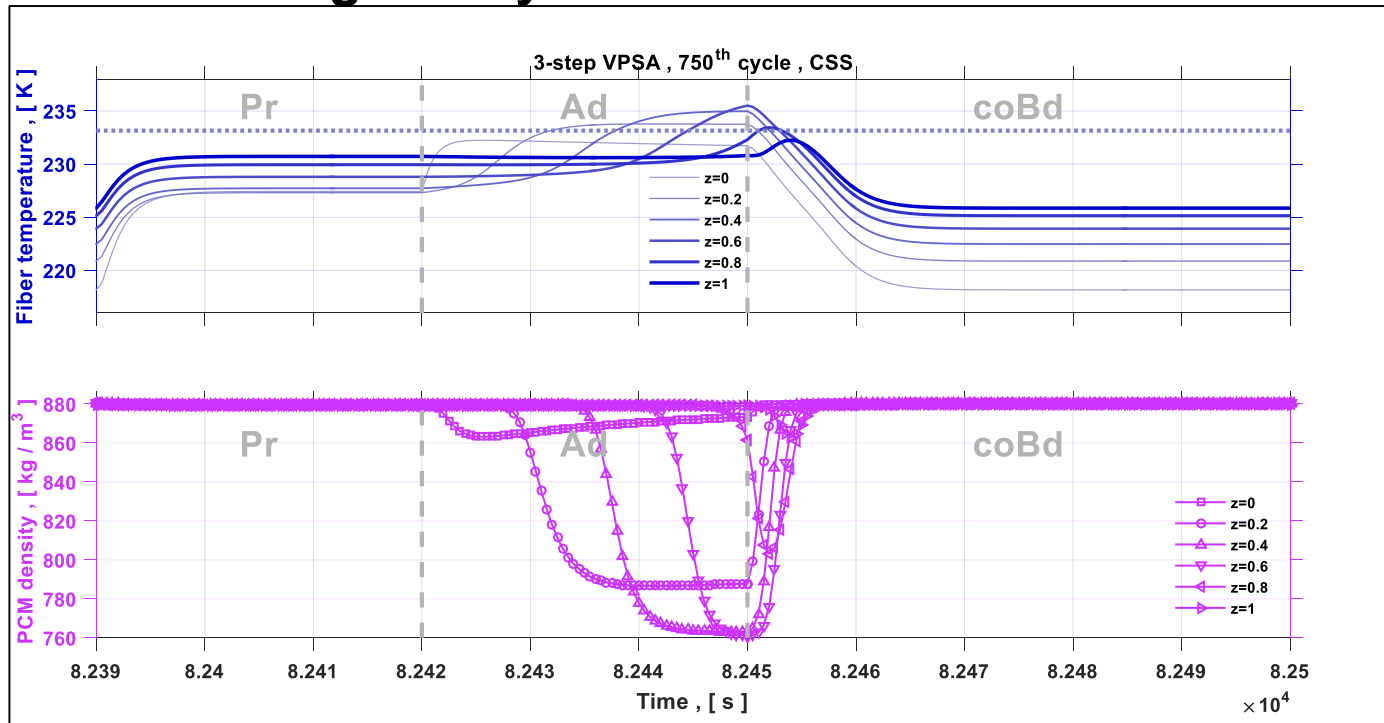


\$ (μPCM) \ll \$ (MOF)



Task 10 (experimental PSA cycles)

Cyclic PSA modeling clearly shows the benefit of thermal modulation



Process Scope—Key Topics, BP2

Seven major activity areas for BP2:

Task 7.0: Generate >250 g/quarter of UiO-66, sub-ambient sorption isotherms, and simple fiber sorbents—**Complete**

Task 8.0: Moisture and acid gas stability—**Complete**

Task 9.0: Lumen layer synthesis—**Obsolete via micro PCM**

Task 10.0: Cyclic RCPSA using clean gas—**Ongoing, 80% complete**

Task 11.0: PCM integration into modules—**Complete**

Task 12.0 & 13.0: Model development—**Complete**

Task 14.0: Flowsheet optimization—**Complete**

Summary

- Novel polymer/MOF sorbent composite hollow fibers will be used in new sub-ambient RPSA process for post-combustion CO₂ capture
 - 50% experimental demonstration
 - 50% prediction, modeling, optimization, and economic feasibility analysis
- Viability of concept is being demonstrated
 - Potential for game-changing swing capacities by utilizing MOFs in sub-ambient conditions
- Georgia Tech and Inmondo Tech are partners on this project
- Annual reports, annual review meetings and conferences presentations and quarterly reports have been used to update DOE on team activities
- DOE contribution: ~\$2.0M
Georgia Tech contribution: ~\$0.5M

