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

Eli Carter, Stephen DeWitt, Jongwoo Park, Hector Rubiera
Researchers

<u>Ryan P. Lively</u>
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

Bruce Lani
Program Manager, DOE-NETL

DOE-NETL CO_2 Capture Technology Project review Meeting
Thursday, August 11th , 2016

inmondo tech

Georgia Tech School of Chemical & Biomolecular Engineering

Key Idea:

***Combine*:**

(i) Sub-ambient gas processing and energy recovery with

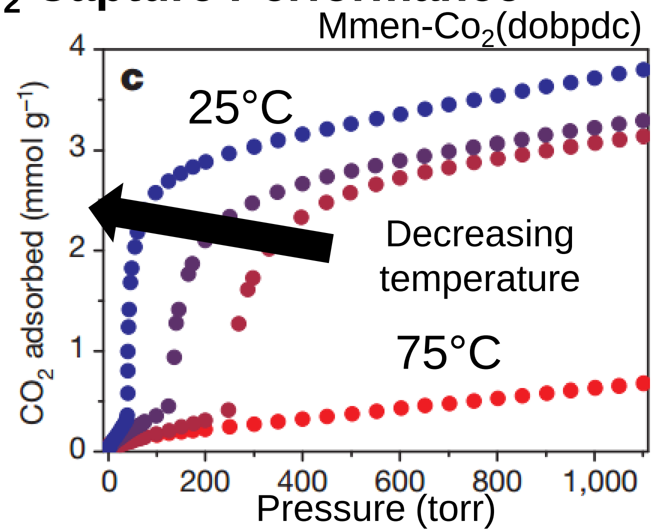
(ii) ultra-porous metal-organic frameworks and

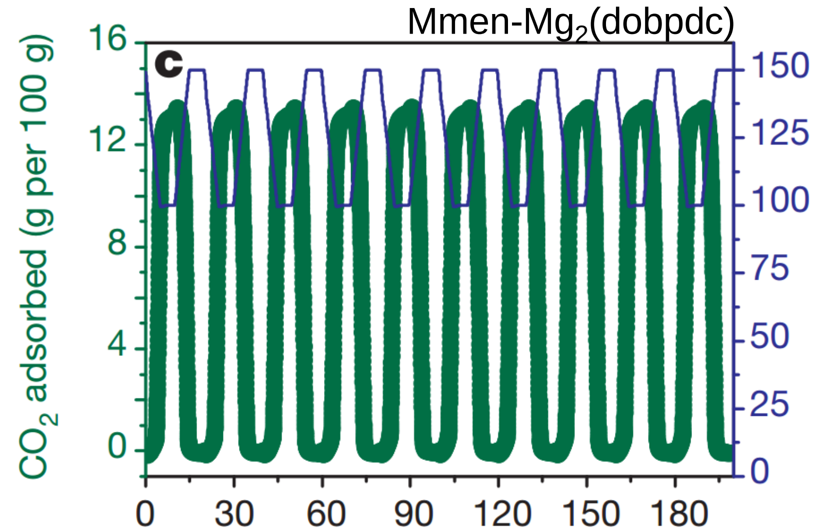
(iii) space- and energy-efficient fiber sorbent contactors

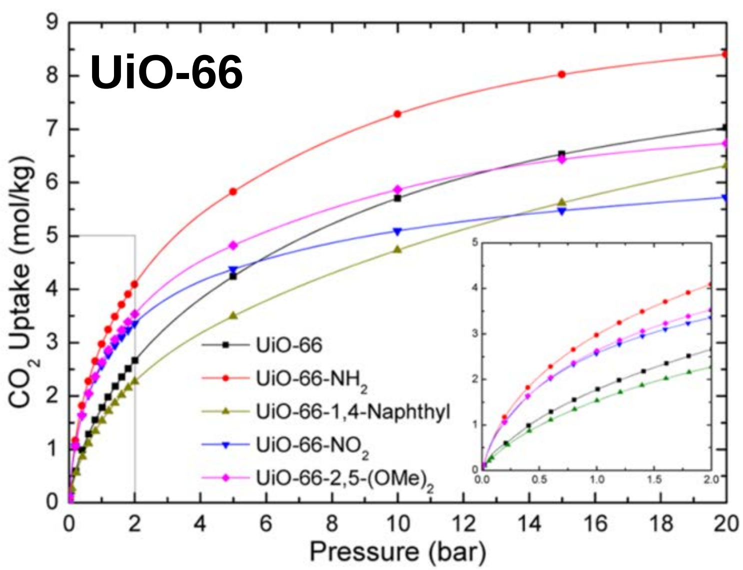
to yield a game-changing process strategy

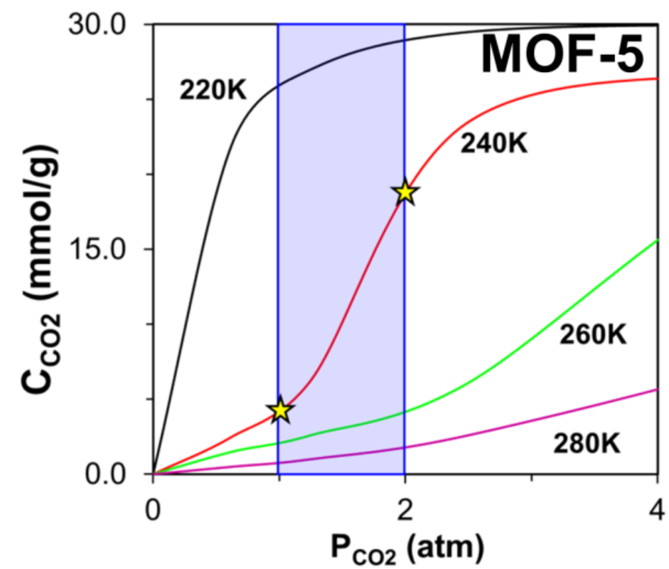
Background: Metal-organic frameworks—State-of-the-art

CO_2 Capture Performance







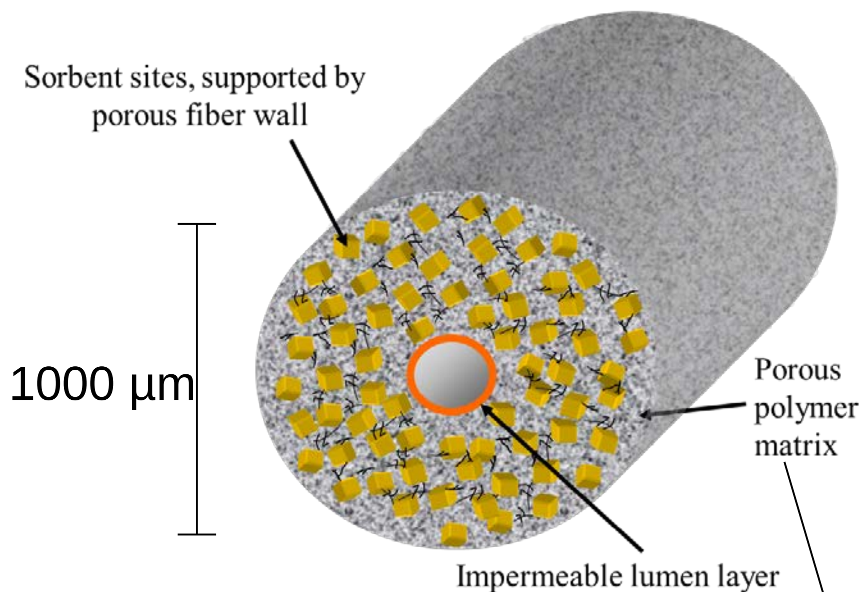


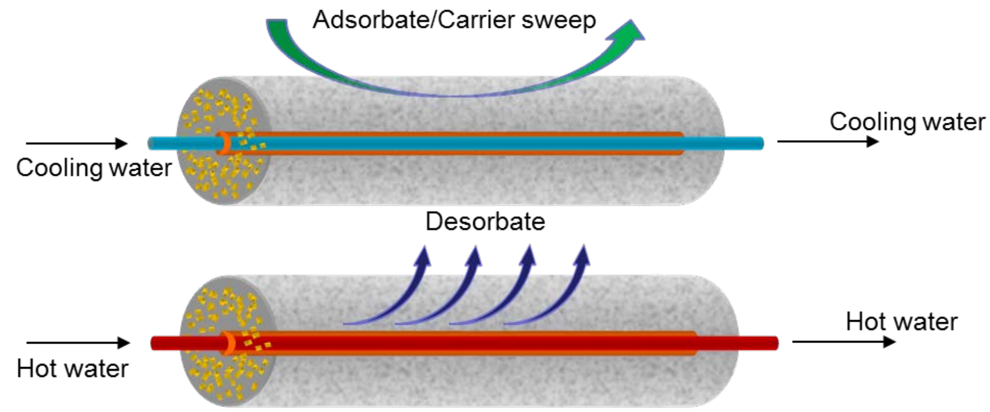
[1] TM McDonald, JR Long et al., *Nature*, 2015, 519, 303-308

[2] GE Cmarik, KS Walton et al., *Langmuir*, 2012, 28(44), 15606-15613

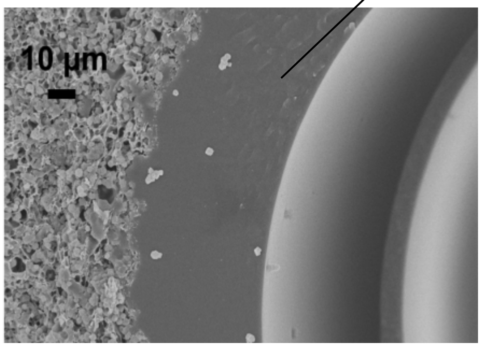
[3] JM Simmons, T Yildirim et al., *Energ. Env. Sci.*, 2011, 4(6), 2177-2185

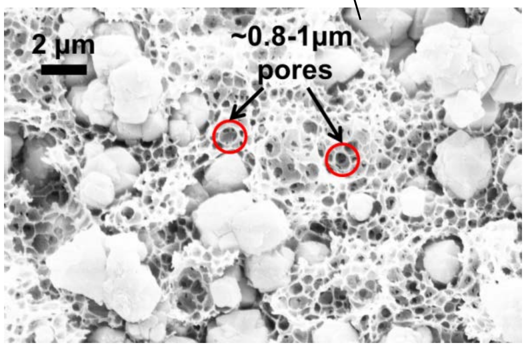
Background: Hollow fiber sorbents, a mass producible structured sorbent inspired by hollow fiber membrane spinning



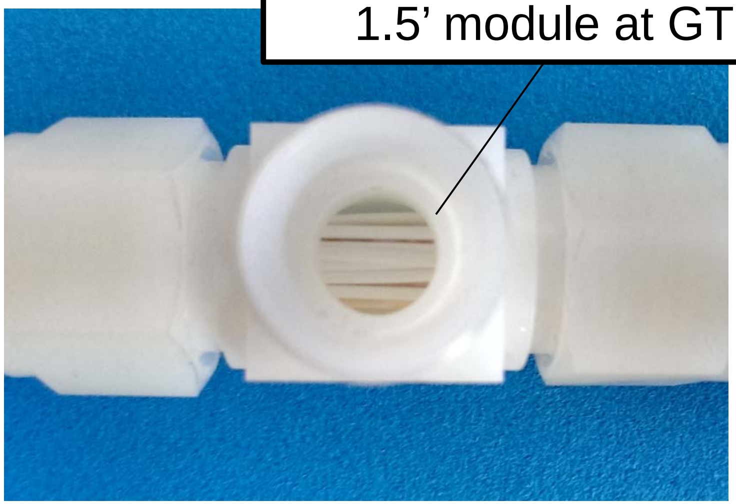


Ideal temperature swing adsorption



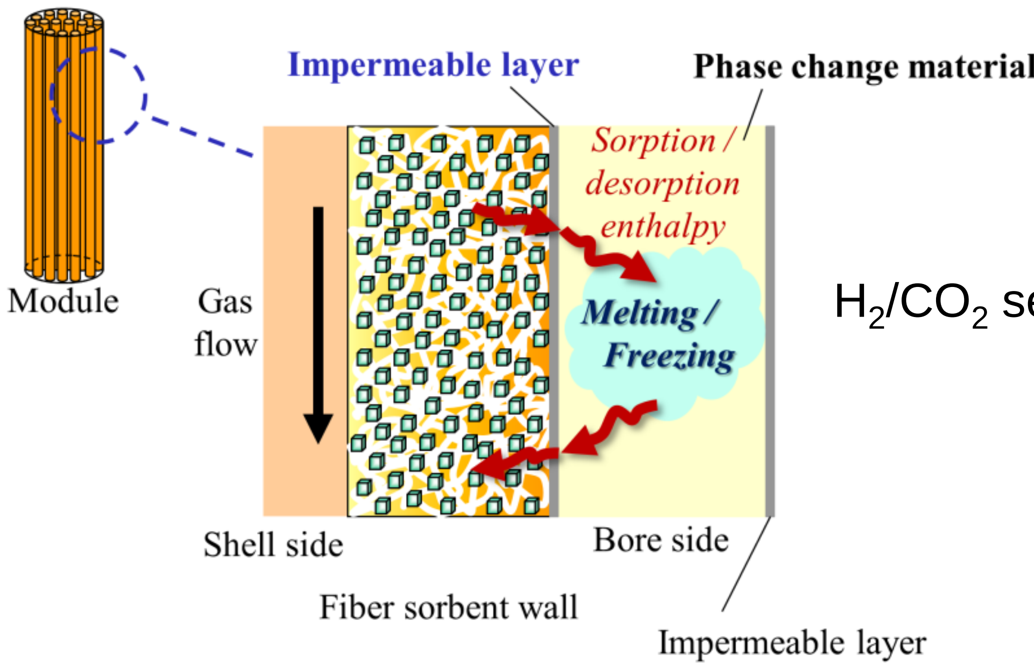


Bundle of 40 fibers in a 1.5’ module at GT

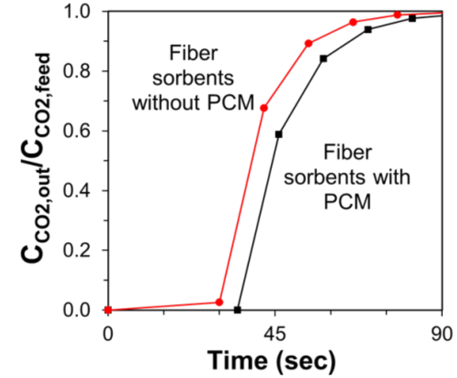


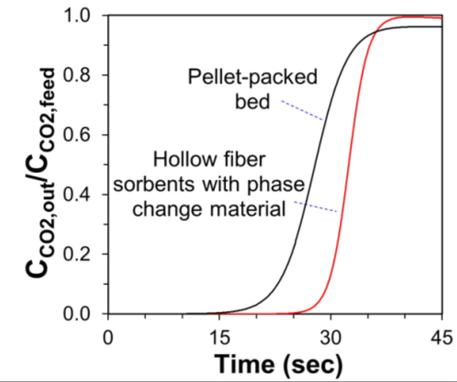
[1] RP Lively, WJ Koros et al., *Ind. Eng. Chem. Res.*, 2009, 48(15), 7314-7324

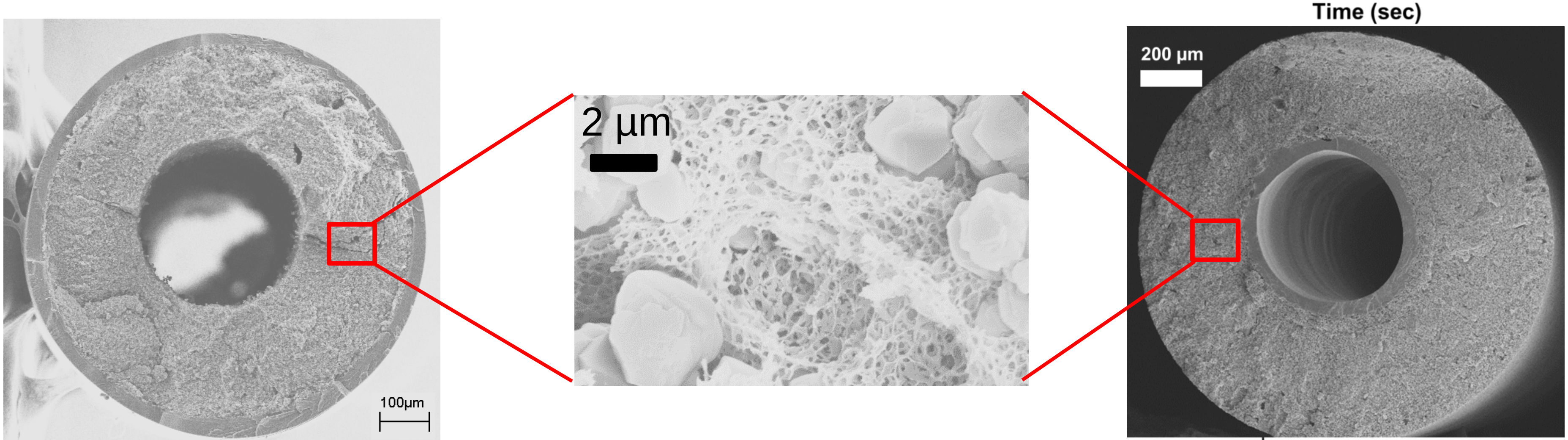
Background: Fiber sorbents for PSA applications



H_2/CO_2 separations







Georgia Tech School of Chemical & Biomolecular Engineering

[1] RP Lively, WJ Koros et al., *Int. J. Hydrogen Energ.*, 2012, 37(20), 15227-15240

Project scope—details on key ideas

ExxonMobil Research and Engineering

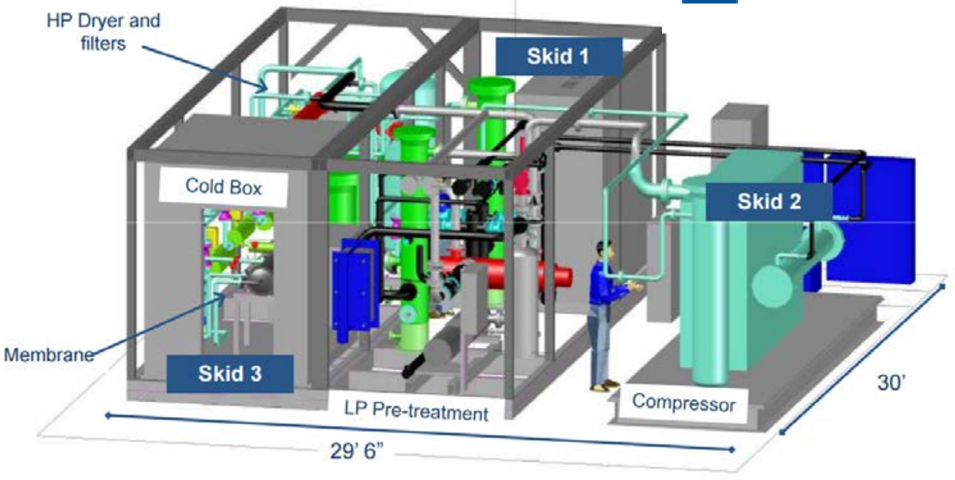
QuestAir Pure Innovations

- Rapid pressure swing adsorption is more straightforward than rapid temperature swing adsorption (has been commercialized)
- Sub-ambient conditions increase adsorption selectivity and working capacity
- Immense pore volume and surface area of MOFs are advantageous at sub-ambient conditions and moderate CO_2 partial pressures (~1-2 bar)
- Weaknesses of MOFs addressed through contactor (hollow fiber sorbents) and through process strategy

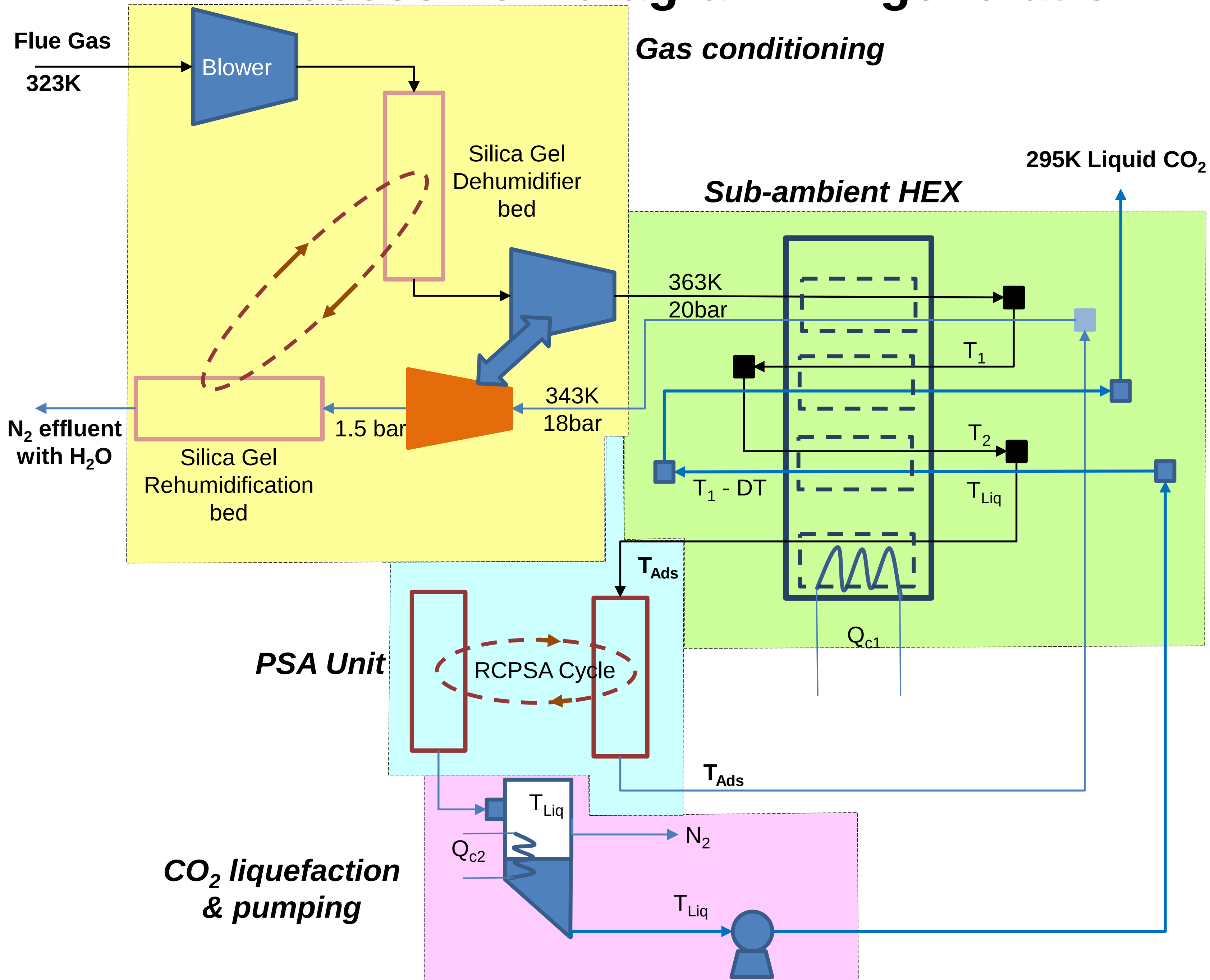
RCPSA

Sub-ambient membrane system

AIR LIQUIDE



Process flow diagram: 1st generation



Process Scope—Key Research Topics

Five major activity areas are proposed in this work:

(1) UiO-66 / MOF synthesis, sub-ambient adsorption characterization, and stability,

(2) Composite hollow fiber spinning (cellulose acetate/polysulfone fibers containing UiO-66 / MOF sorbents),

(3) RCPSA system construction and testing of fiber sorbent modules and hollow fiber sorbent modules with bore-side phase change material,

(4) Modeling and optimization of fiber and hollow fiber module operation as well as flue gas conditioning optimization, and

(5) Overall system techno-economic analysis.

Process Scope—Key Topics, BP1

Five major activity areas are proposed in this work for BP1:

Task 2.0: Generate >250 g/quarter of UiO-66, sub-ambient sorption isotherms, and simple fiber sorbents

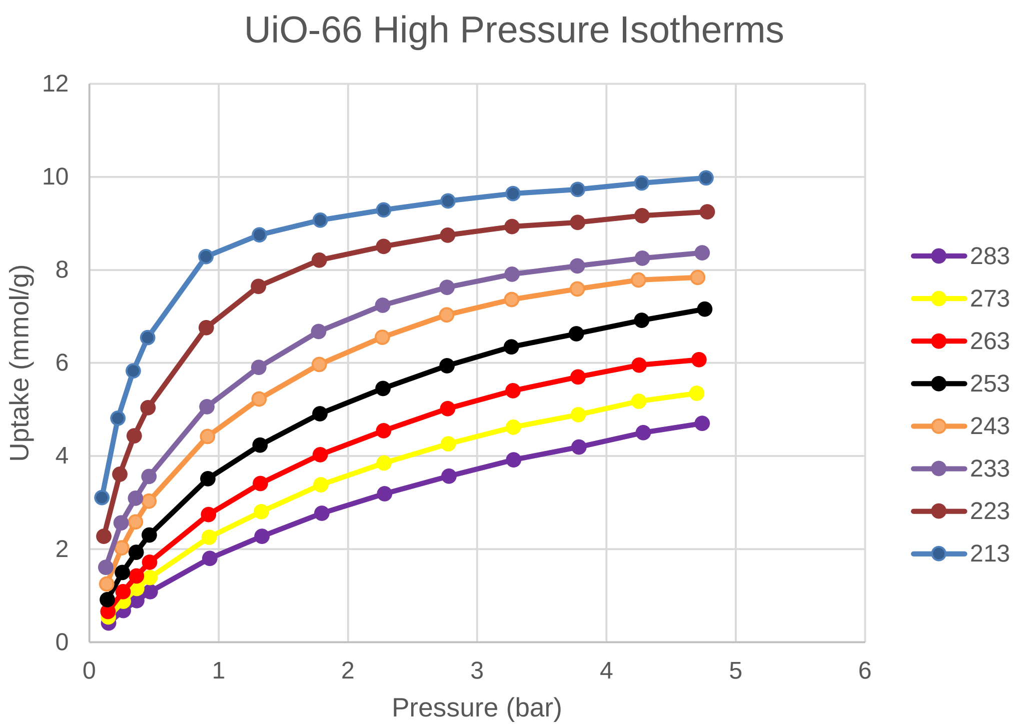
Task 3.0: Spin fiber sorbents

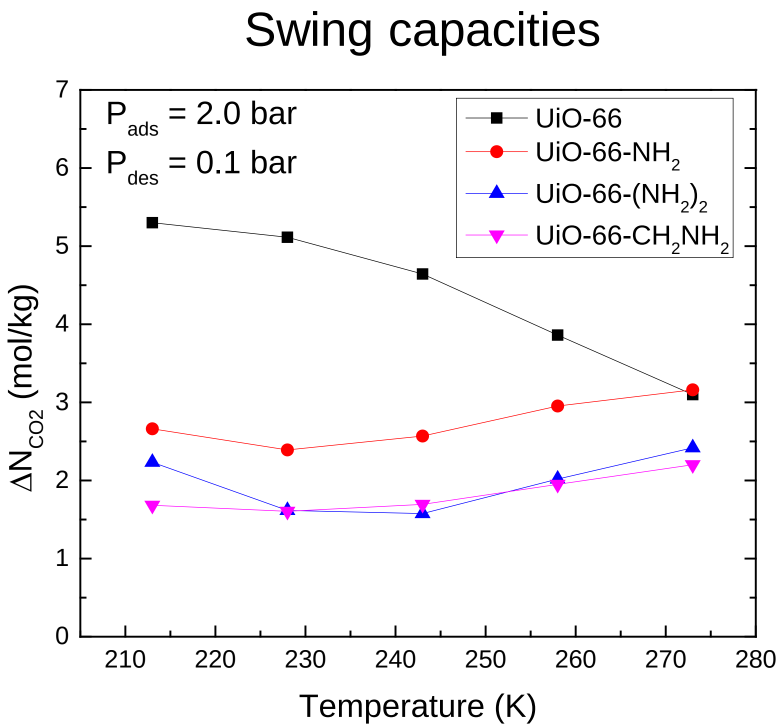
Task 4.0: Stability of module seals at sub-ambient conditions

Task 5.0: Develop model for hollow fiber sorbent module

Task 6.0: RCPSA Testing and construction

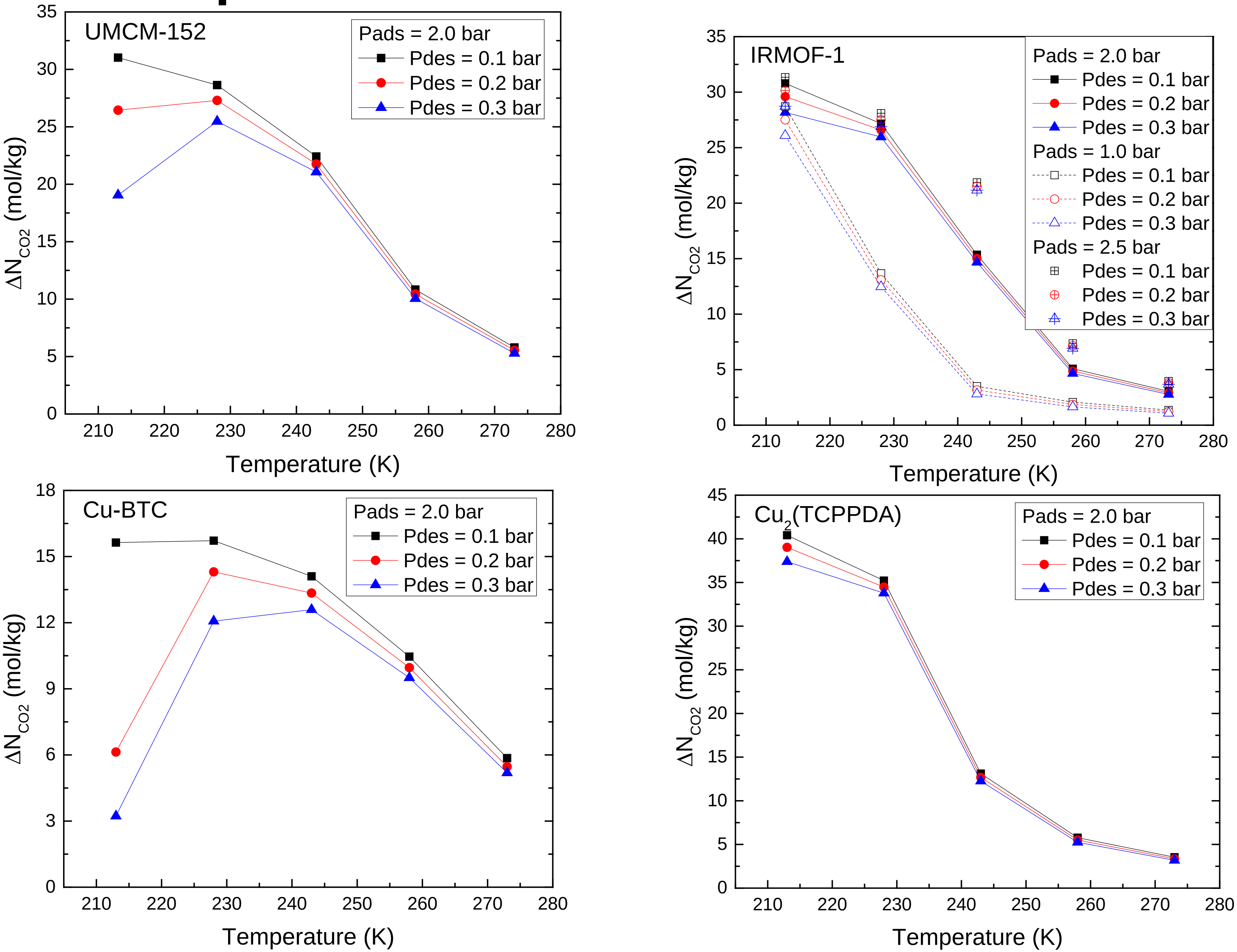
Task 2—sorption isotherms, experimental



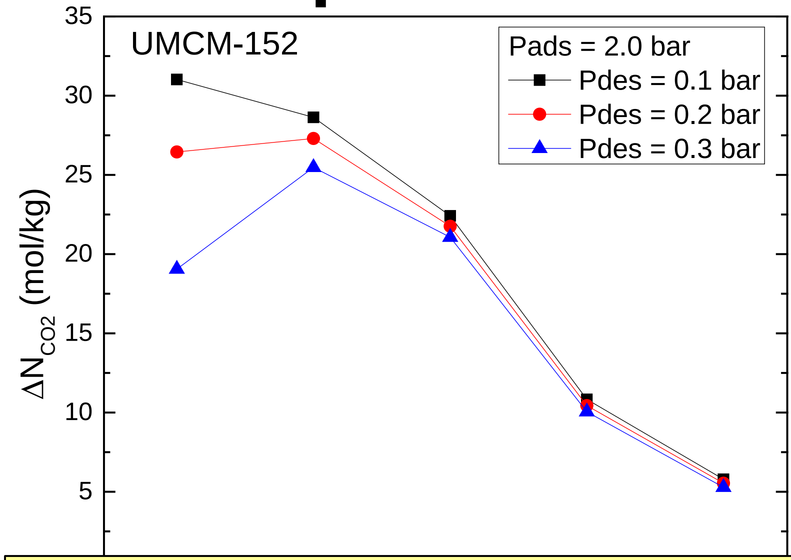


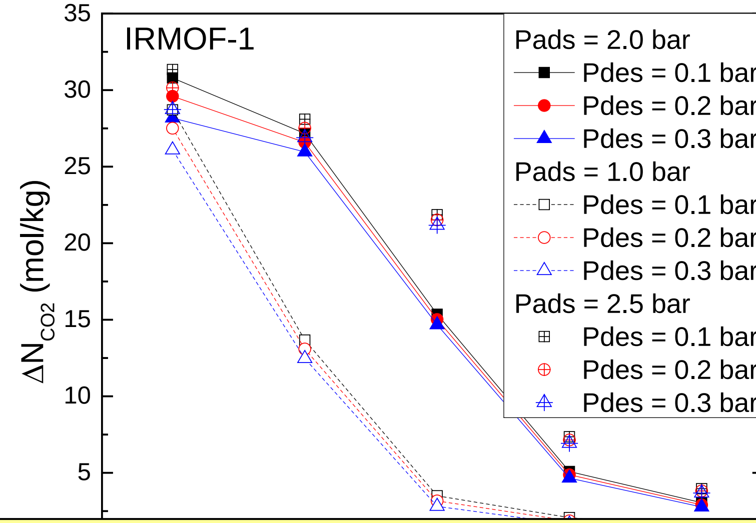
UiO-66 can achieve impressive swing capacities at sub-ambient conditions—but higher pore volumes needed for 10+ mol/kg

Task 2—sorption isotherms from GCMC

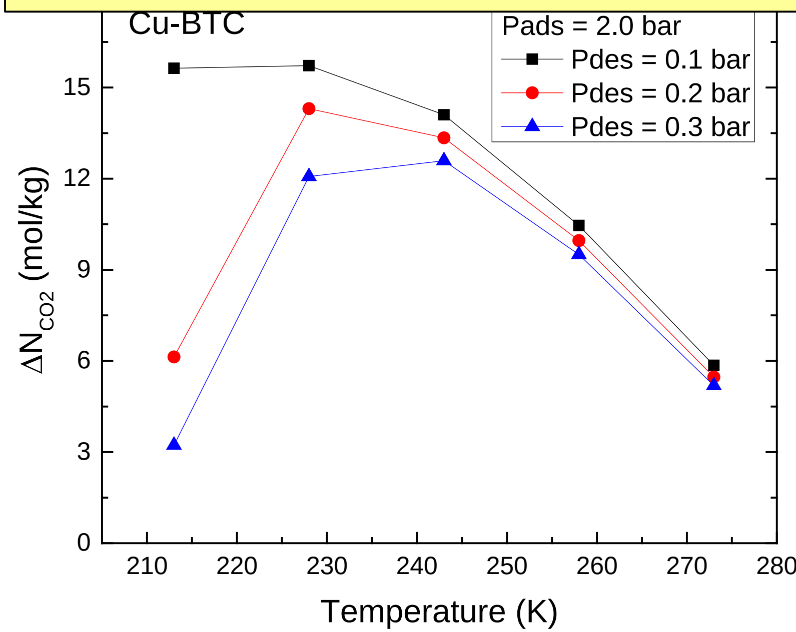


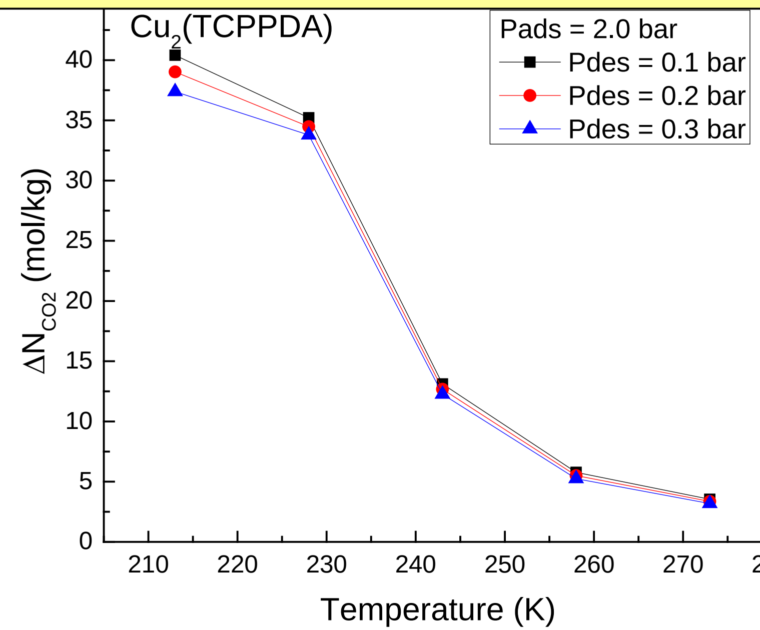
Task 2—sorption isotherms from GCMC



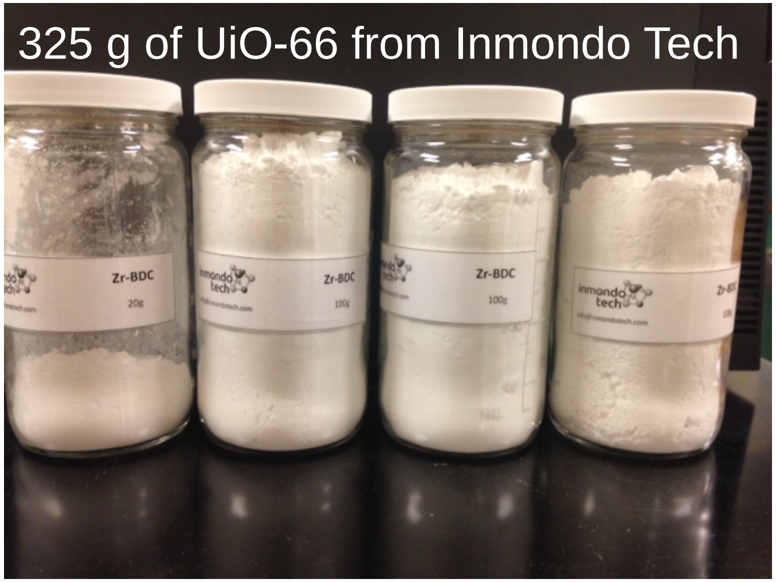


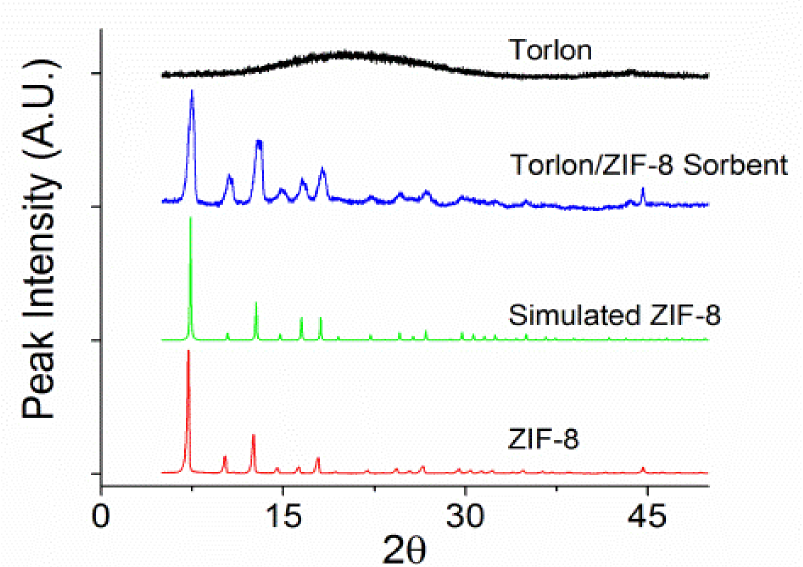
Many MOFs can achieve the 10+ mol/kg target! Integrating into fiber sorbents is a challenge

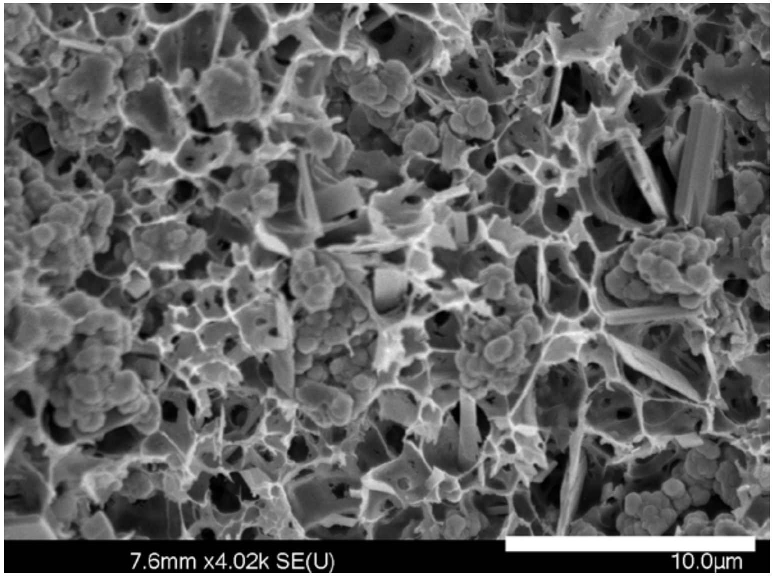




Task 2, 3: UiO-66 scale-up and hollow fiber sorbents

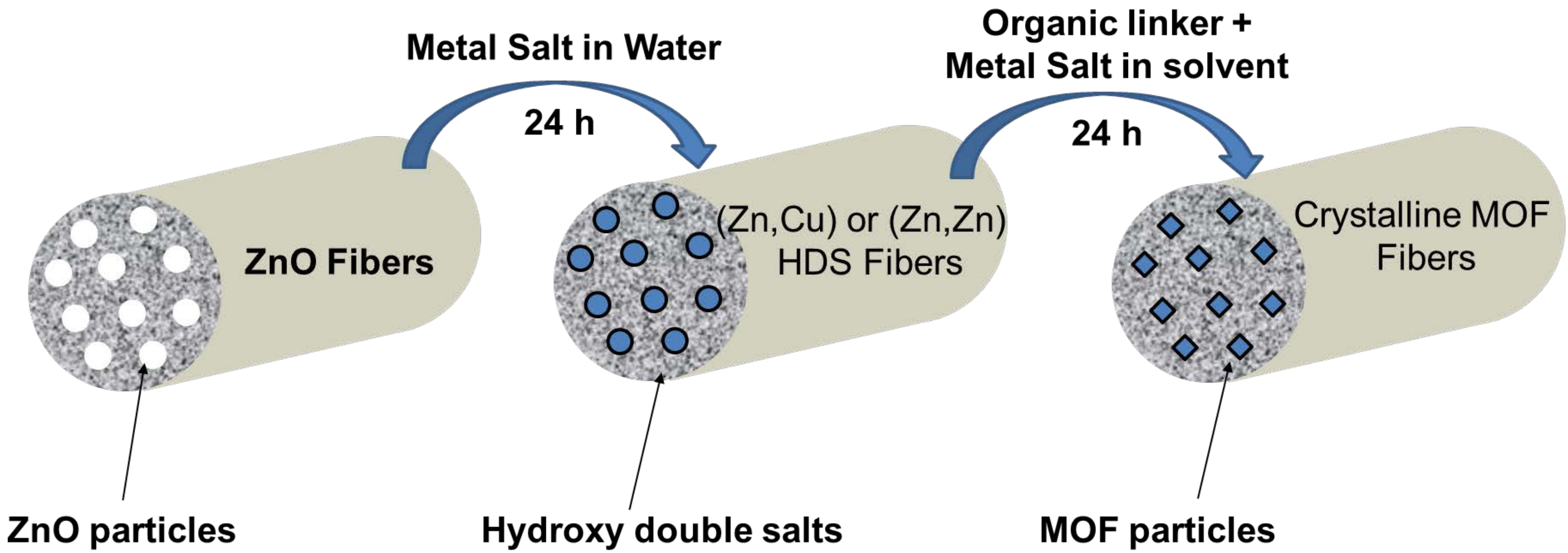


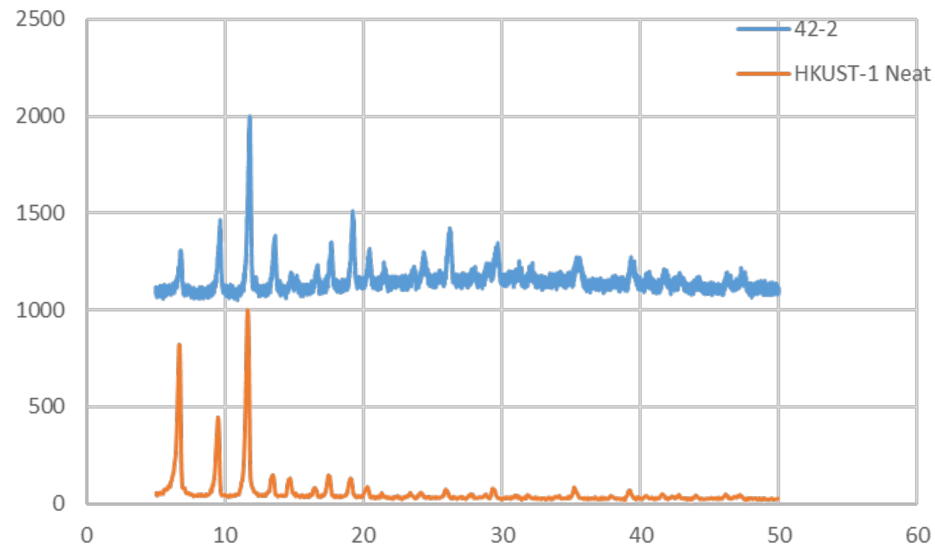




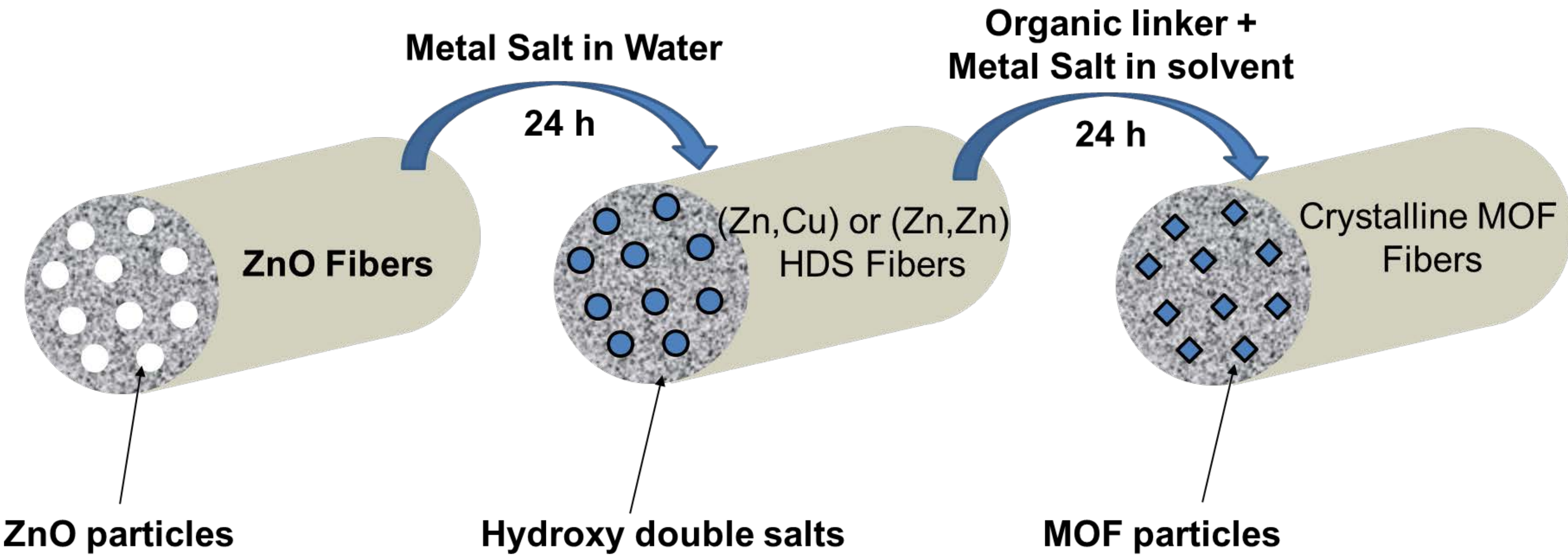
Water stable MOFs retain crystallinity and porosity after fiber sorbent spinning

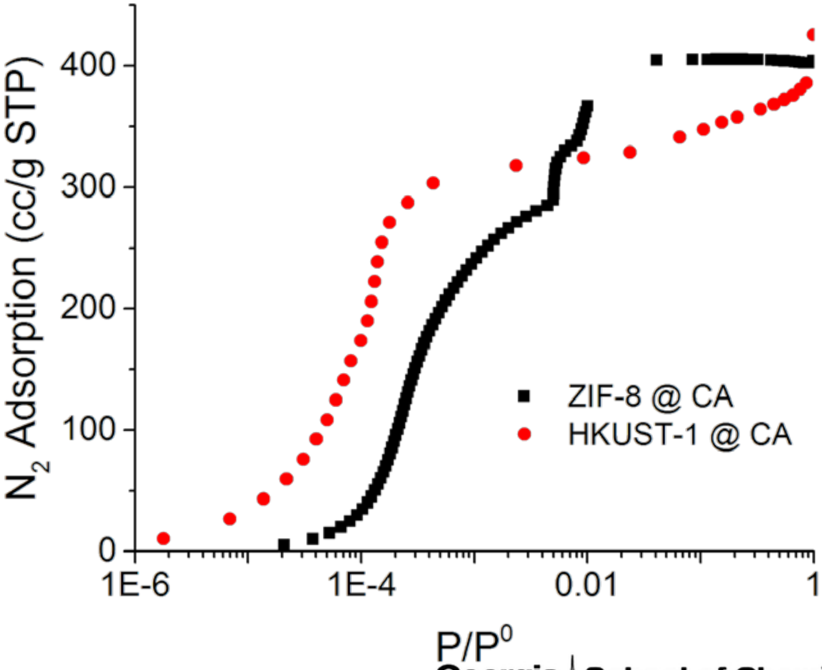
Task 2,3: What about water-sensitive MOFs?



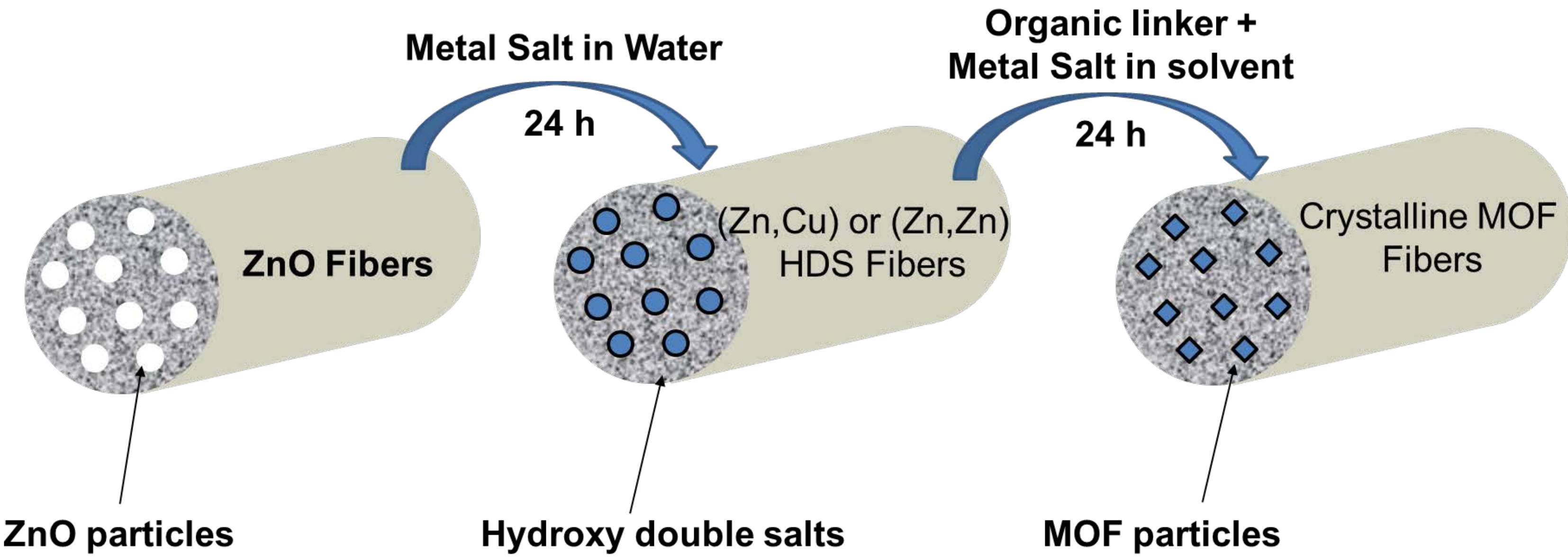


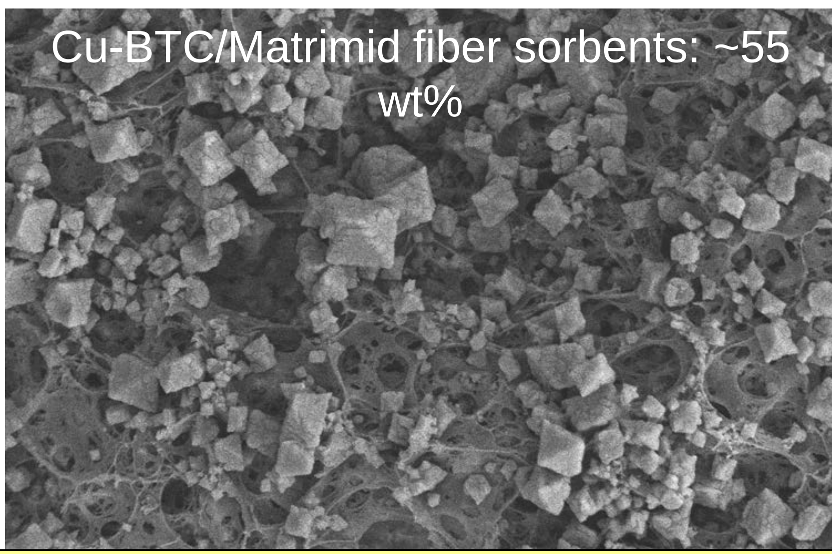
Task 2,3: What about water-sensitive MOFs?

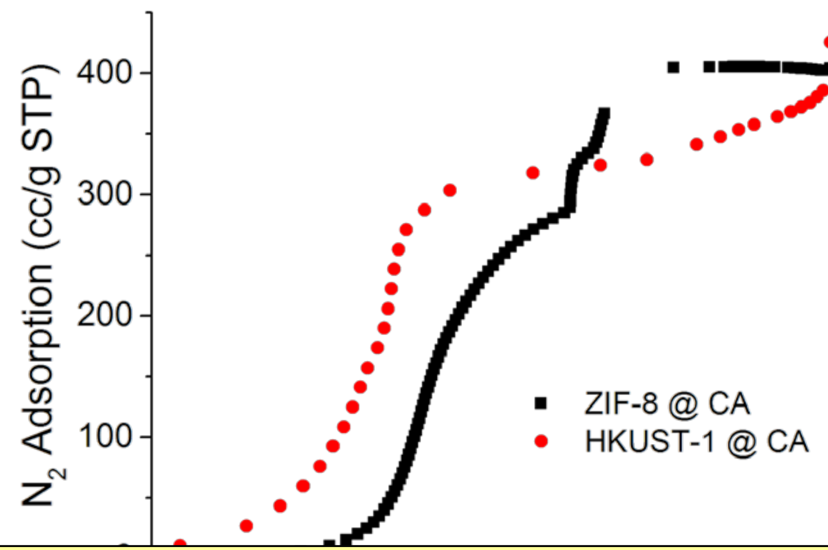




Task 2,3: What about water-sensitive MOFs?

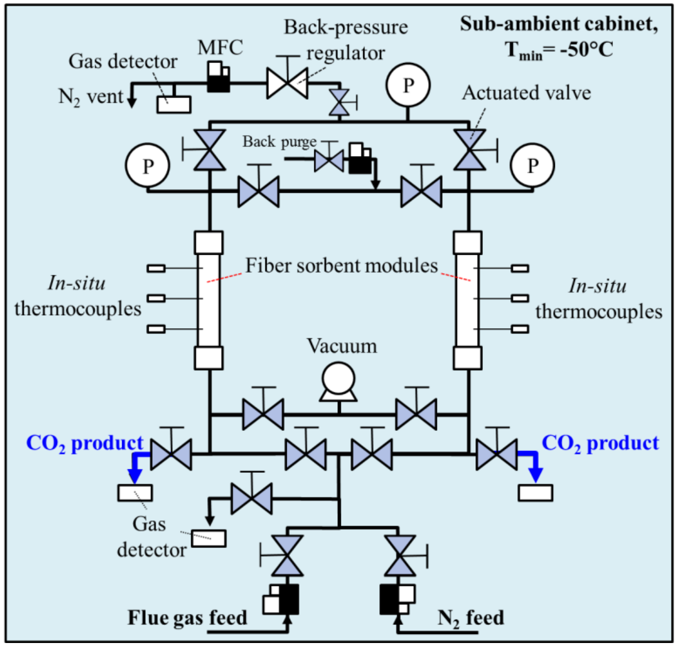




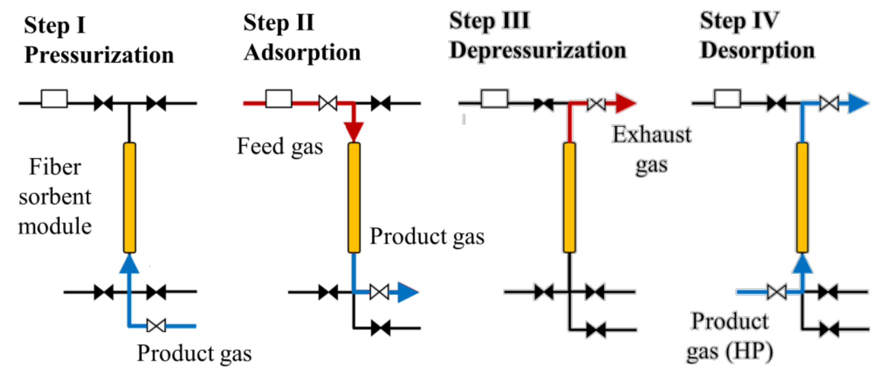


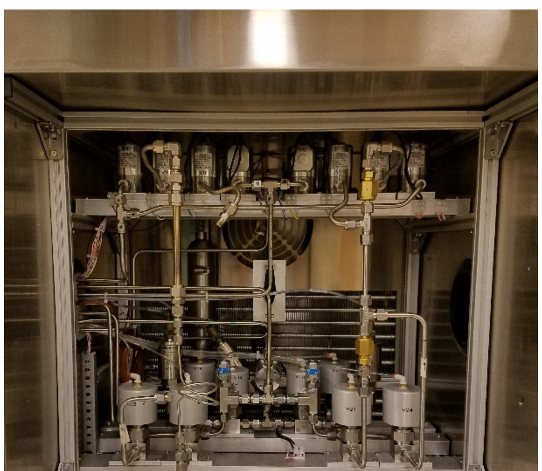
MOFs with water stability issues can now be integrated into fiber sorbents!
Operational stability is less of an issue as flue gas is dehydrated + substantial industry experience with water sensitive sorbents (e.g., LiX)

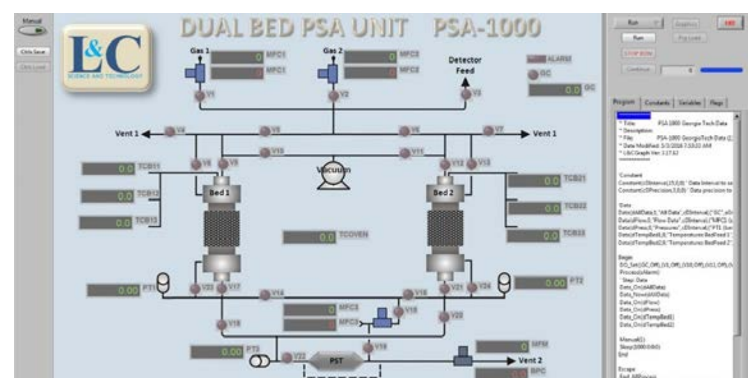
Task 4, 6—Rapid pressure swing adsorption



Shell side feed (low ΔP feed)



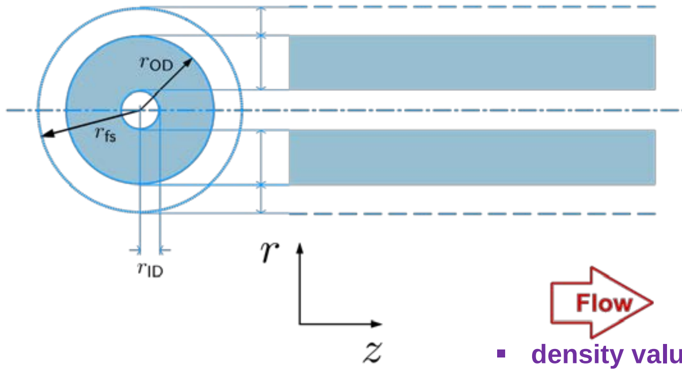


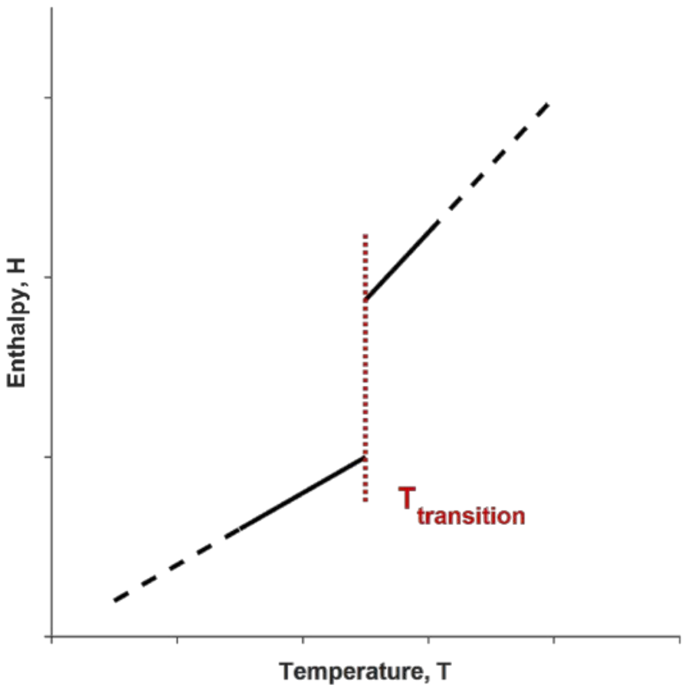


Sub-ambient breakthrough experiments on UiO-66 and UiO-66 fiber sorbents currently underway

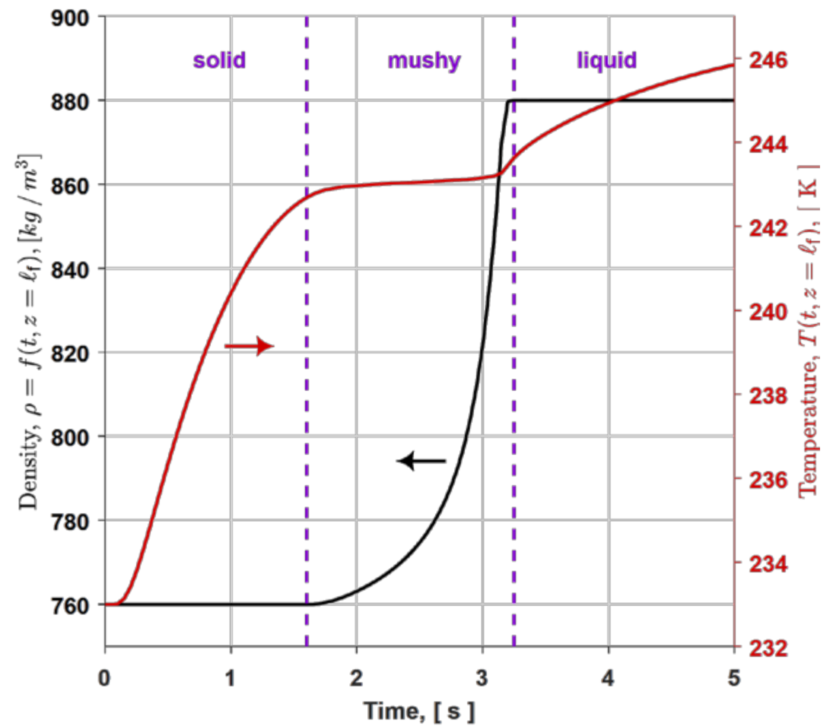
Task 4: Dynamic model development

- Combined heat, mass, and momentum balance on the fiber, including transient heat conduction w/ heat source





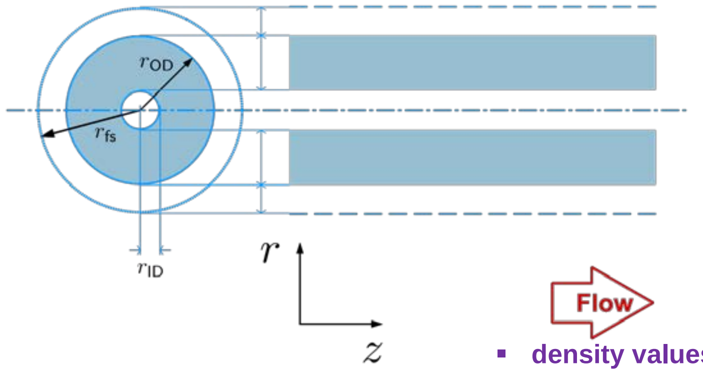
- density values help to track the melting front



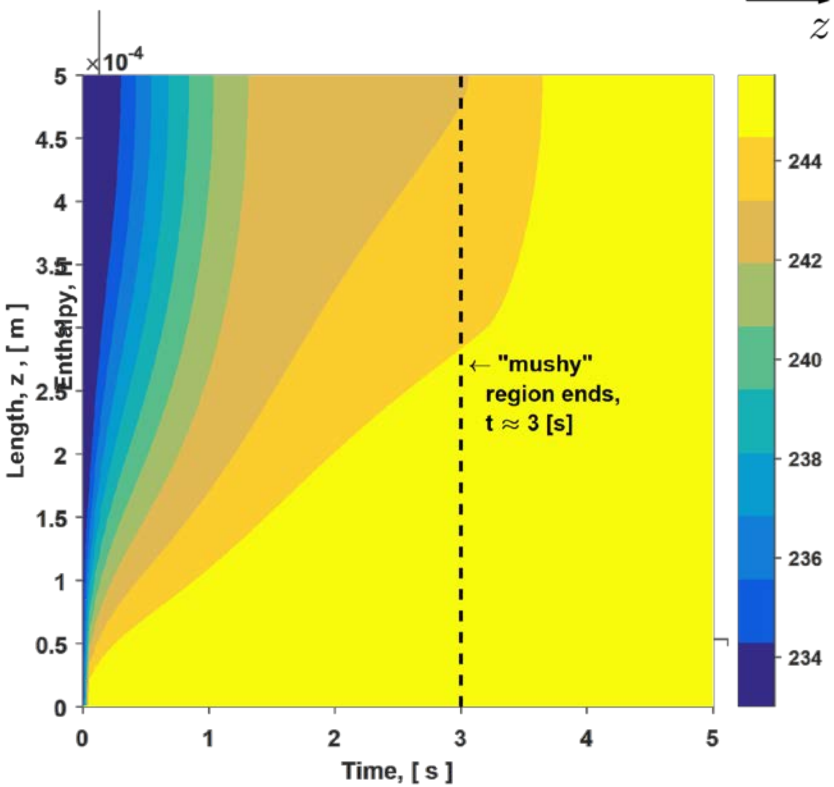
Dynamic model guides experiments and RCPSA cycle development

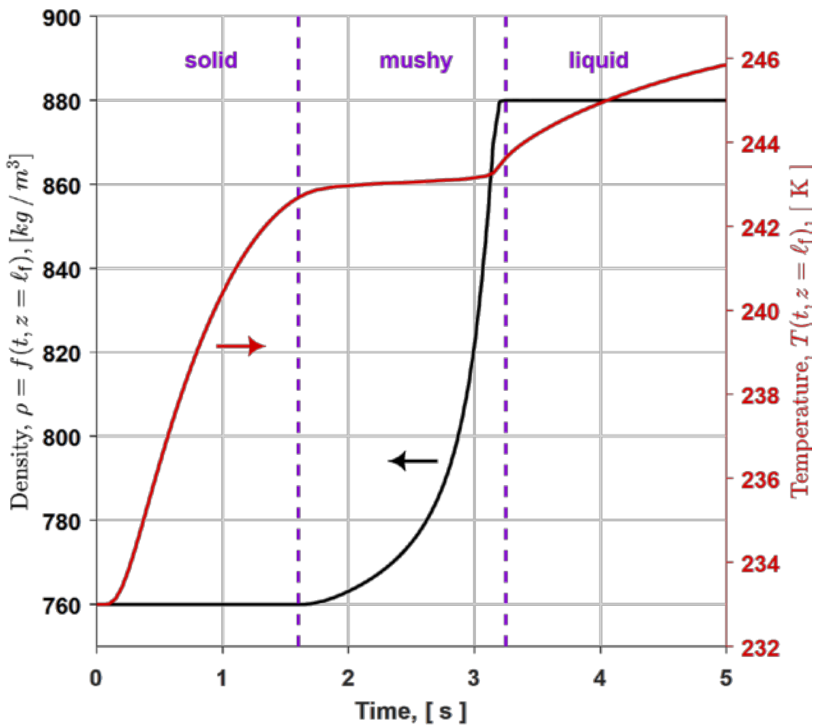
Task 4: Dynamic model development

- Combined heat, mass, and momentum balance on the fiber, including transient heat conduction w/ heat source



- density values help to track the melting front





Dynamic model guides experiments and RCPSA cycle development

Process Scope—Key Topics, BP1

Five major activity areas are proposed in this work for BP1:

Task 2.0: Generate >250 g/quarter of UiO-66, sub-ambient sorption isotherms, and simple fiber sorbents**—Complete**

Task 3.0: Spin fiber sorbents**—Complete**

Task 4.0: Stability of module seals at sub-ambient conditions**—Ongoing, 60% (sub-ambient exposure completed, leak rate of module seals ongoing)**

Task 5.0: Develop model for hollow fiber sorbent module**—Complete**

Task 6.0: RCPSA Testing and construction**—Ongoing, 80% complete (remaining items: breakthrough curves for UiO-66 powders and fibers).**

Summary

- Novel polymer/MOF sorbent composite hollow fibers will be used in new sub-ambient RPSA process for post-combustion CO_2 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 will be used to update DOE on team activities

- DOE contribution: ~$2.0M Georgia Tech contribution: ~$0.5M

Budget

DOE Contribution
1st year: $705,441
2nd year: $681,845
3rd year: $599,698
Total: $1,986,984 (79%)

Cost Share Provided by Georgia Tech: $513,792 (21%)

Total Budget: $2,500,776

5 primary researchers supported (2 post-doctoral researchers, 3 graduate student researchers)

5 PIs supported (Lively, Kawajiri, Realff, Sholl, Walton)

Major equipment purchases/construction: Sub-ambient rapid pressure swing adsorption units

Personnel

Principal Investigators:

Georgia Tech
Ryan Lively, *Project Director*, Inmondo liaison, hollow fibers and RCPSA system

Yoshiaki Kawajiri, Process optimization, cyclic adsorption processes

Matthew Realff, Process systems engineering, technoeconomic analysis

David Sholl, Adsorption and diffusion in nanoporous materials

Krista Walton, Adsorption in MOFs and MOF synthesis

Inmondo Tech
Dr. Karen Tuleg, Inmondo PI, Sorption and gas storage

Risks

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management Mitigation and Response Strategies
Technical Risks:			
MOFs do not exhibit ~10 mol/kg swing capacity between 1 and 2 bar CO_2 partial pressure	Moderate	Moderate	(a) Technoeconomic analysis and modeling effort will determine impact of > 10 mol/kg swing vs. 5-10 mol/kg swing. (b) Other scalable MOFs can be considered if >10 mol/kg is critical
MOF particles do not survive spinning process	Low	High	If required, MOFs can be grown within porous polymer supports post-spinning. Preliminary data from Lively indicates that MOFs retain their porosity and crystallinity post-spinning.
Failure of sealing for fiber modules	Low	Moderate	If required, specialty epoxies resistant to temperature changes will be used to seal modules.
Instability of MOF to flue gas contaminants	Low	High	Functionalized MOFs will be tested, providing various materials for use. Additional flue gas processing can be used if necessary.
Resource Risks:			
Delays in production of MOFs by Inmondo Tech	Low	High	MOFs will be produce in excess of minimum requirement in year 1 to ensure availability. Capability to deliver materials in this manner has already been demonstrated.
Management Risks:			
Difficulty in recruiting postdocs/grad students at GT	Low	Moderate	Shift personnel between tasks to manage temporary vacancies
Lack of coordination among project partners	Low	Moderate	Project partners already have a proven record of collaboration; regular project meetings are scheduled with all partners

BP 1 Task List & Milestones

Budget Period	Task/Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
1	1	Updated Project Management Plan	08/31/2015		Project Management Plan file
1	1	Kickoff Meeting	10/01/2015		Presentation file
1	2.1	Produce 250+ g of UiO-66 @ >900 m^2/g surface area and >2.5 mol CO_2/kg @ 273K & 1 bar	01/31/16		Report to DOE
1	2.2	Generate sub-ambient isotherms	04/30/16		Report to DOE
1	2.3	Syringe fibers using UiO-66	04/30/16		Report to DOE
1	3	Spin monolithic fibers	09/30/16		Report to DOE
1	4	RCPSA module construction & seal testing	09/30/16		Report to DOE
1	5	Bare fiber module model development	04/30/16		Report to DOE

BP2 Task List & Milestones

2	**6**	**Test PSA using syringe fiber samples**	**04/31/17**	**Report to DOE**
2	7	Produce 250+ g of UiO-66 @ >900 m^2/g surface area and >2.5 mol CO_2/kg @ 273K & 1 bar	01/31/17	Report to DOE
2	8	MOF moisture and acid gas test (SO2 and steam exposure)	09/30/17	Report to DOE
2	9	Lumen layer synthesis and barrier properties	04/31/17	Report to DOE
2	10	Demonstrate hollow fiber lumen layer synthesis	09/30/17	Report to DOE
2	11	PCM integration into modules	09/30/17	Report to DOE
2	12	Model development of fibers with PCM	09/30/17	Report to DOE
2	13	Modeling phase change and adsorption using experimental data	09/30/17	Report to DOE
2	14	Process flowsheet optimization	09/30/17	Report to DOE

BP3 Task List & Milestones

3	**15**	**Process flowsheet refinement**	**06/30/18**	**Report to DOE**
3	16	Produce 250+ g of UiO-66 @ >900 m^2/g surface area and >2.5 mol CO_2/kg @ 273K & 1 bar	01/31/18	Report to DOE
3	17	Construct/test RCPSA for dirty gas testing	04/30/18	Report to DOE
3	18	Model validation for hollow fiber module—model validation for composite fibers	04/30/18	Report to DOE
3	19	Monolithic fiber sorbent stability in dirty gas RCPSA	06/30/18	Report to DOE
3	20	Test hollow fibers containing phase change material in PSA	09/30/2018	Report to DOE
3	21	Complete Technoeconomic assessment	09/30/2018	Report to DOE
3	22	Test a demonstration module	09/30/2018	Report to DOE

Initial high level process analysis using 10 mol/kg swing

- Plant parasitic load: 16.7%
- Installed capital costs: \$188.2 x 10^6
- Total annual cost (operating expenses + amortized capital): \$72.8 x 10^6/yr
- CO_2 captured per year: 4.50 x 10^6 tons CO_2/yr
- CO_2 capture cost: \$19.0/ton, \$21/tonne
- Number of 8” module elements needed: 36,000
- Estimated footprint (assuming modules stacked 10 high): ~200 m^2 for a 500 MW_e coal-fired power plant