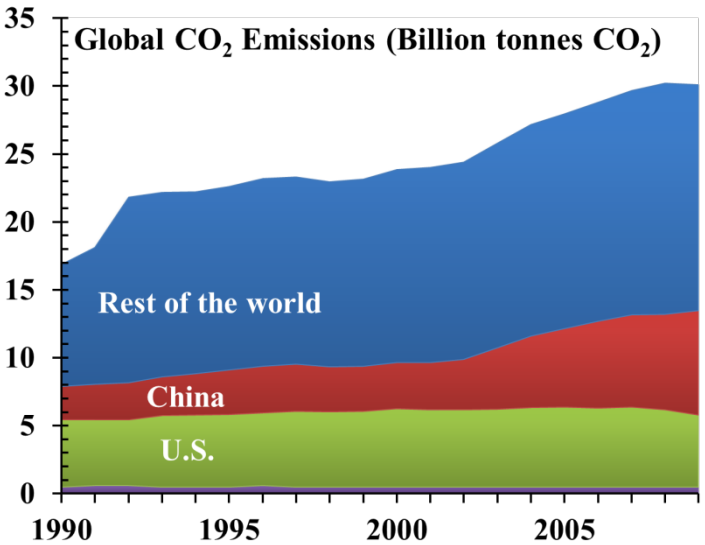
Rapid-Temperature Swing Adsorption Using Polymeric/Supported Amine Hollow Fiber Materials

Georgia Institute of Technology

DOE Award #: DE-FE0007804



International Energy Outlook 2013, US Energy Information Administration 2013, DOE/EIA-0484

Acknowledgements and Funding

Ms. Grace Chen
Dr. Yanfang Fan
Prof. Christopher W. Jones
Ms. Jayashree Kalyanaraman
Prof. Yoshiaki Kawajiri
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Dr. Ying Labreche
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Prof. Matthew Realff
Dr. Fateme Rezaei
Ms. Katherine Searcy
Prof. David S. Sholl
Dr. Subramanian Swernath
Dr. Simon Pang

Key Idea:

***Combine*:**

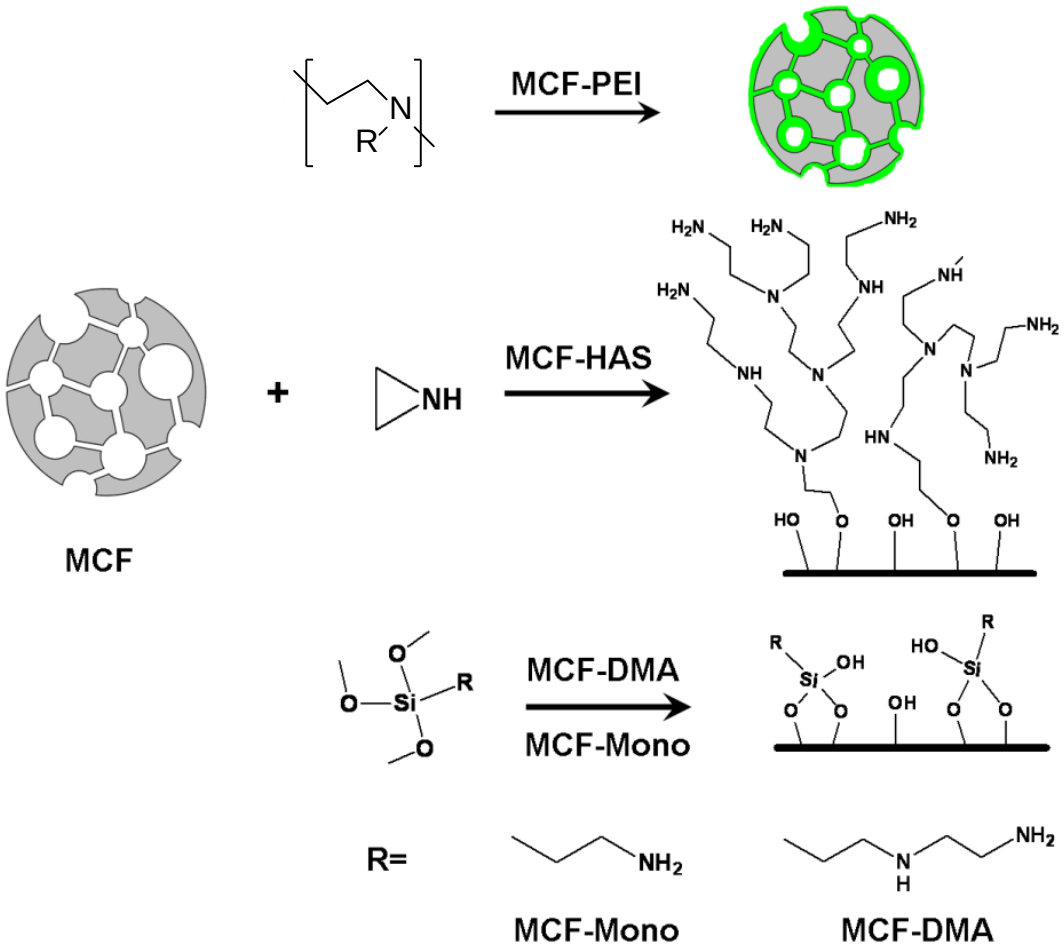
(i) state-of-the-art supported amine adsorbents, with

(ii) a new contactor tuned to address specific weaknesses of amine materials,

to yield a novel process strategy

Silica-Supported Amine Sorbents

Amine sorbents widely studied in academia – but little work on scalable contactors



Class 1
Impregnated polymer

Class 3
In-situ Polymerized

Class 2
Grafted silanes

- As chemisorbents, supported amine sorbents require efficient heat management, ΔH = 65-85 kJ/mol.

Amine-based approaches to CO_2 capture

Absorption (amine scrubbing)

- ✓ High recovery and purity easily attainable
- ✓ Mature
- x Evaporative water ballast

Fixed bed adsorption

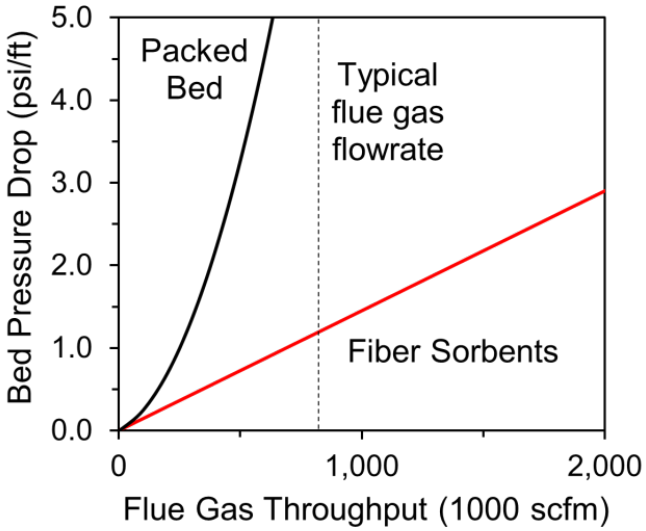
- ✓ No evaporative ballast
- ✓ Lower heat of reaction/sorption
- x Massive sensible heat loads (TSA) / massive compression (PSA)
- x Pressure drop
- x Cycle times (4h)

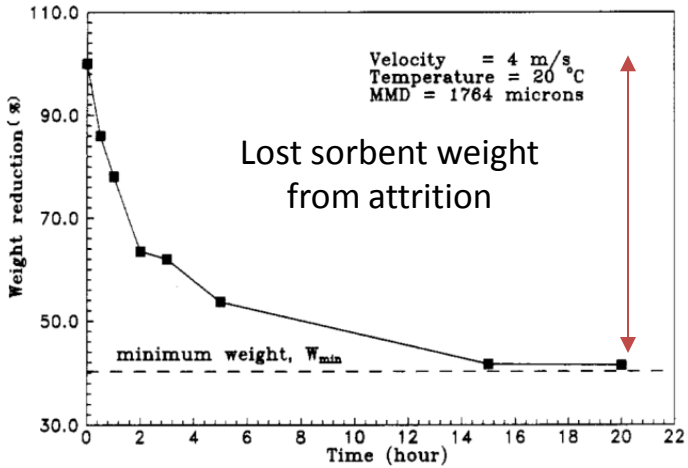
Looping beds

- ✓ No evaporative ballast
- ✓ Lower heat of reaction/sorption
- ✓ Rapid cycling
- x Irrecoverable sensible heat loads
- x Pressure drop
- x Sorbent attrition

Heat integrated fiber contactors

- ✓ **Directly integrate heat and mass transfer**
- ✓ No evaporative ballast
- ✓ Lower heat of reaction/sorption
- ✓ Rapid cycling
- ✓ Recoverable sensible heat
- ✓ Recoverable sorption enthalpy
- ✓ Low pressure drop
- ? Still in early stages of development
- ? Purity and recovery

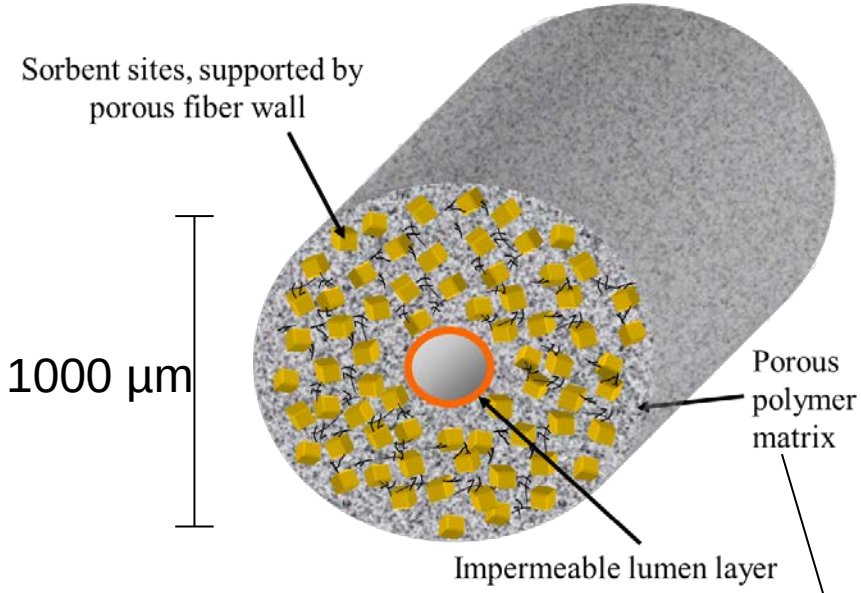


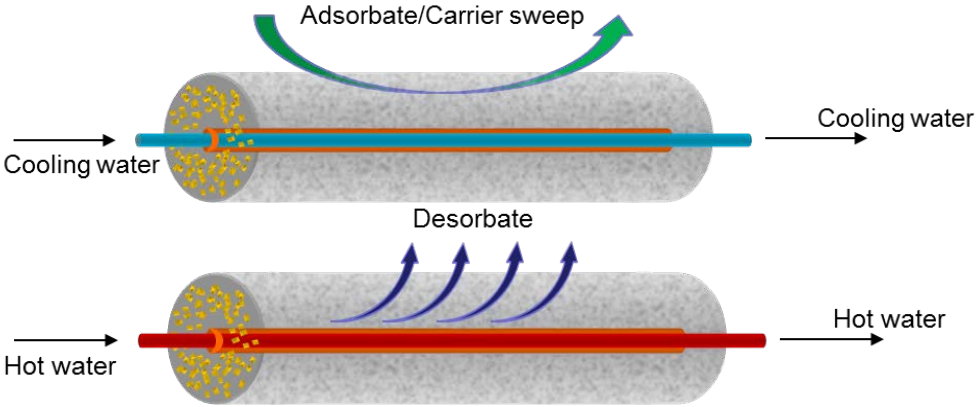


Lee, S-K ; Jiang, X ; Keener, TC ; Khang, SJ. *Ind. Eng. Chem. Res.* **1993**, 32, 2758

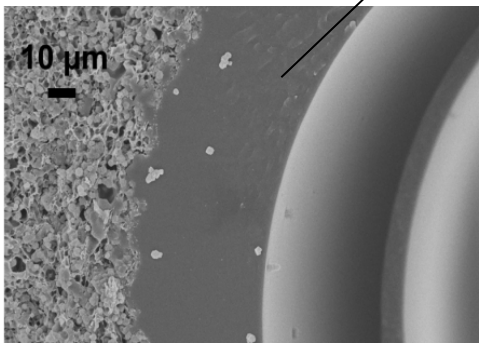
Hollow Fiber Sorbents
in
Rapid Temperature Swing Adsorption

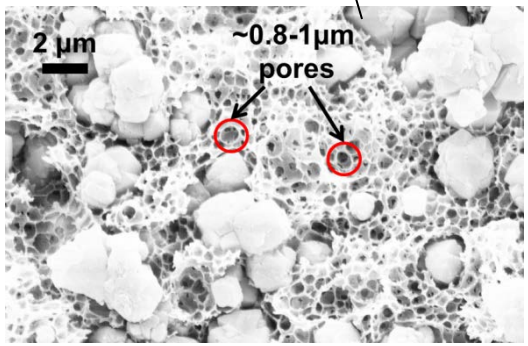
Hollow fiber sorbents: a mass producible structured sorbent inspired by hollow fiber membrane spinning



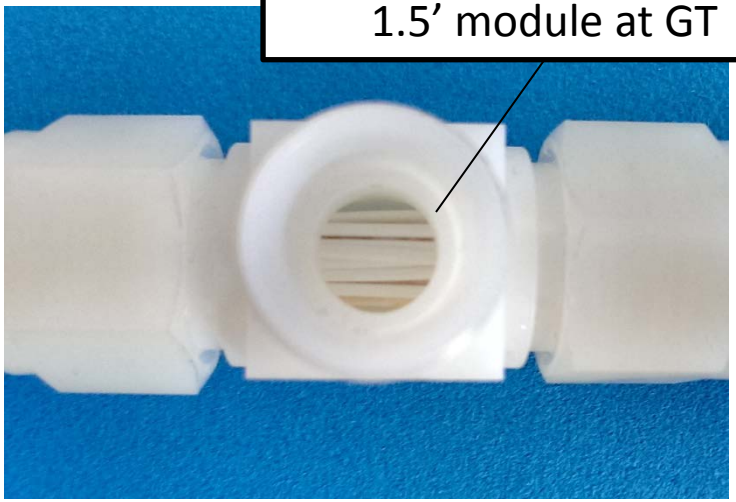


Ideal temperature swing adsorption





Bundle of 40 fibers in a 1.5’ module at GT



RP Lively et al., *Ind. Eng. Chem. Res.*, **2009**, 48, 7314-7324

Module evolution moved membranes from lab to large scale–and fiber sorbent modules are now on a similar path

Area packing density

10^2 m^2/m^3

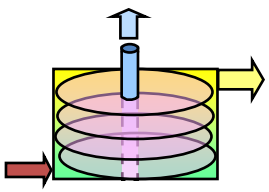
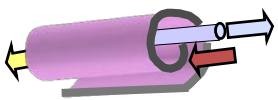


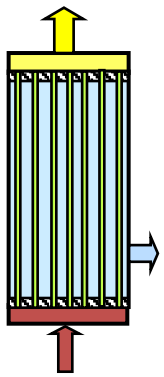
Plate & Frame

10^3 m^2/m^3



Spiral Wound

10^4 m^2/m^3

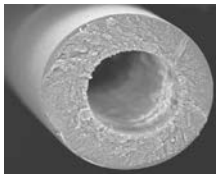


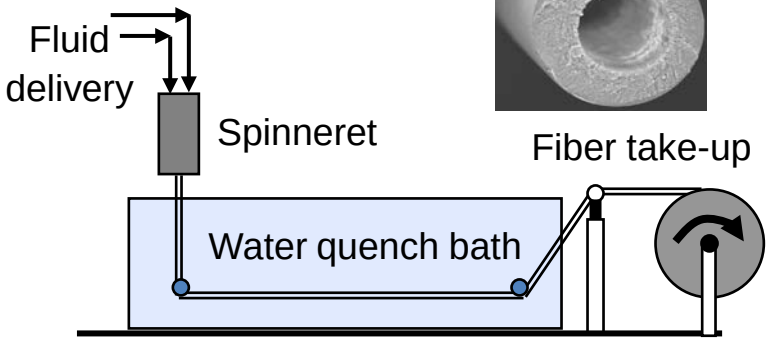
Hollow Fiber

Parallel connection of 20 cm OD modules (Desalination plant)
N. Alon: Demotix , Israel

High contact area, low pressure drop and mass transfer resistance make fibers the most evolved module form

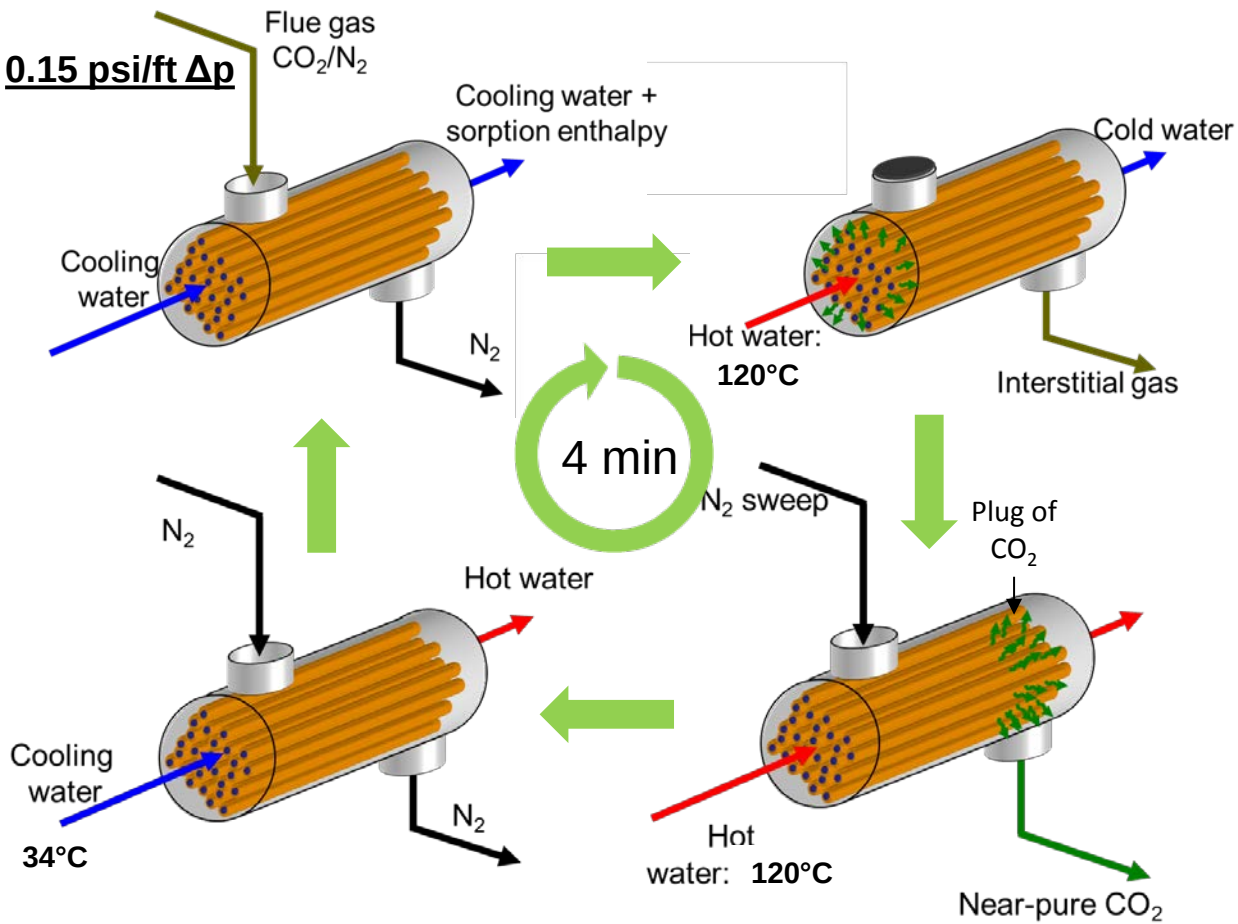
800-1200 µm OD





Large CO_2/CH_4 module
76 cm OD x 1.8 m
Used on 700 MMSCFD offshore platform
Courtesy, E. S. Sanders NAMS 2003 plenary

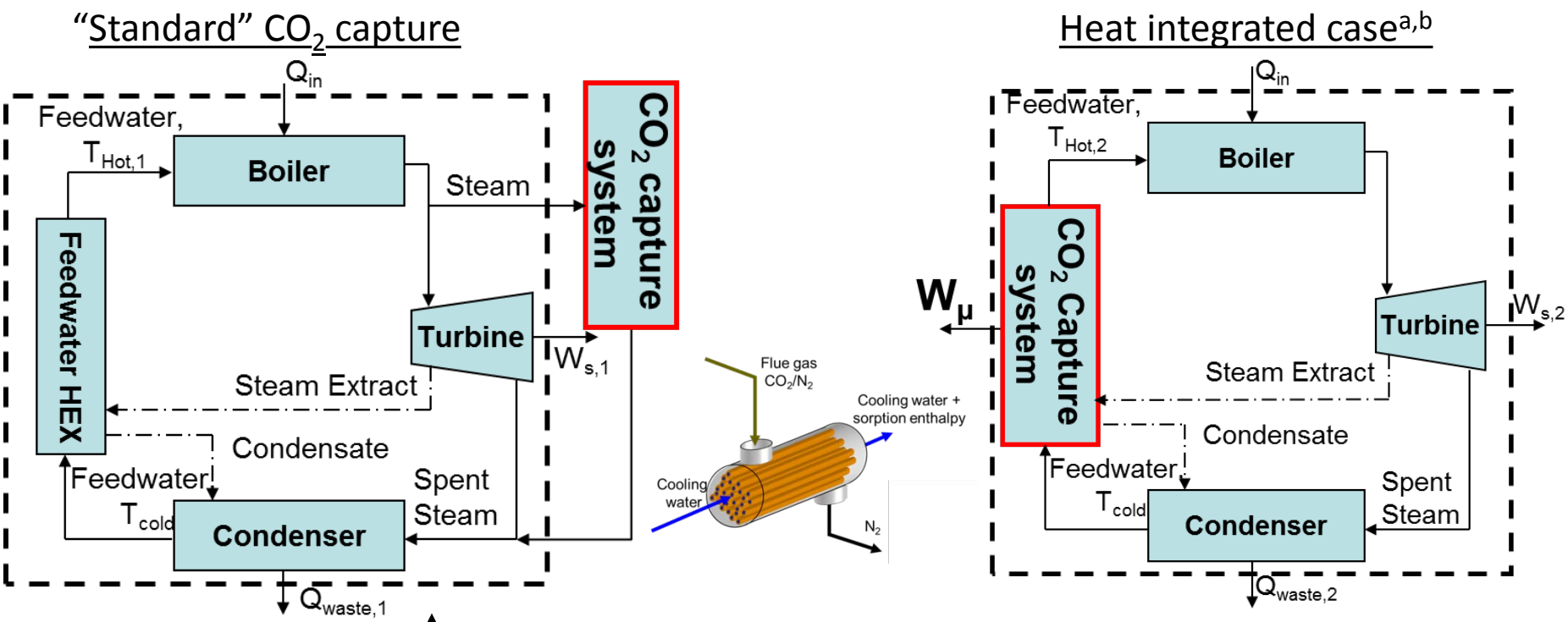
Rapid temperature swing adsorption (RTSA)



- 4 min cycle using zeolites (physisorbents), with amines, we can drop the cycle to 2 min.

Lively RP, et al., *Int. J. Greenhouse Gas Control* **2012**, 10, 285

Heat integration concepts—unique advantages of fiber sorbents



$Q_{waste,2} < Q_{waste,1}$

GT-Trimeric techno-economic analysis uses this approach

[a]Lively RP, Chance RR, Koros WJ, *Ind. Eng. Chem. Res.* **2010**, 49, 7550

[b]Lively RP, Chance RR, Koros WJ, US Patent Application, No. 20120324890

Project Components

- Task Area 1 – Sorbent Synthesis: Dr. Fateme Rezaei
- Task Area 2 – Hollow Fiber Spinning: Dr. Ying Labreche
- Task Area 3 – RTSA Experimental Testing: Dr. Yanfang Fan
- Task Area 4 – Single Fiber Model: Ms. Jayashree Kalyanaraman
- Task Area 5 – Optimization Model and Technoeconomic Analysis: Dr. Subramanian Swernath

Project Tasks

Year 1

Task 1: Reporting to DOE

Task 2: Preliminary Technology Feasibility Study
Subtask 2.1- Base Case Design Adaptation from Zeolite 13X data
Subtask 2.2 - Base Case Process Cost Estimation
Subtask 2.3 - Sensitivity Analysis

Task 3.0 – Amine Sorbent Formulation and Oxidation
Subtask 3.1 – Prepare Amine Sorbents for Fiber Spinning
Subtask 3.2 – Stability of Sorbents to O2

Task 4.0 – Preliminary Hollow Fiber Spinning

Task 5.0 – RTSA Module Construction

Task 6.0 – Initial Model Development
Subtask 6.1 - Subtask 6.1 Heat transfer model development.
Subtask 6.2 Heat transfer model implementation.
Subtask 6.3 Optimization model formulation

Project Tasks

Year 2

Task 7 – Update Technology Feasibility Study
Subtask 7.1 – Impact of Module Configuration on Operability and Cost
Subtask 7.2 - Cost Estimation Refinement

Task 8.0 – Amine Sorbent Stability and Performance
Subtask 8.1 – Sorbent CO_2 Adsorption Isotherms and Kinetics
Subtask 8.2 – Stability of Sorbents to SO_2 and NO_x

Task 9.0 – Hollow Fiber & Lumen Layer Synthesis
Subtask 9.1 – Spin Cellulose Acetate – Amine Sorbent Hollow Fibers
Subtask 9.2 – Lumen Layer Formation
Subtask 9.3 – Prepare Hollow Fibers for RTSA System Testing

Task 10.0 – RTSA Module Construction and Operation
Subtask 10.1 – Construction of RTSA Bench Scale Testing Stations
Subtask 10.2 – Single Fiber Operation – Temperature Profile Measurement
Subtask 10.3 – RTSA Operation – No Bore Heat/Cool – Clean Gas
Subtask 10.4 – RTSA Operation – Active Bore Heat/Cool – Clean Gas

Project Tasks

Year 2 (continued)

Task 11 – RTSA Model and Optimization Development
Subtask 11.1. Validation of heat transfer model
Subtask 11.2. Development of single-fiber adsorption/desorption model
Subtask 11.3 Implementation of single-fiber adsorption/desorption model
Subtask 11.4 Development of module model with adsorption and desorption
Subtask 11.5. Implementation of module model with adsorption and desorption
Subtask 11.6 Implementation of optimization model

Year 3

Task 12 – Composite Hollow Fiber Sorbent Stability

Task 13 – RTSA Testing and Operation
Subtask 13.1 – RTSA Operation - Clean Gas – Heat Management
Subtask 13.2 – RTSA Operation – Dirty Gas – Effect of Contaminants
Subtask 13.3 – RTSA Operation – Clean Gas – Front Matching

Project Tasks

Year 3 (continued)

Task 14.0 – Model Testing, Refinement and Validation, Optimization Studies
Subtask 14.1 Validation of single-fiber adsorption model
Subtask 14.2 Validation of single-fiber desorption model
Subtask 14.3 Validation of module model with adsorption
Subtask 14.4 Validation of module model with desorption
Subtask 14.5 Trade-off analysis by multi-objective optimization

Year 4

Task 15.0 – Final RTSA Technical Feasibility Study

Task 16.0 – Environmental Health & Safety Assessment

Project Milestones – All Milestones to Date Met on Time

Task/ Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
1	Reporting to DOE	12/31/2011	12/31/11 04/30/12 07/30/12	Year 1, Q1, Q2, Q3 reports
2	Preliminary Technology Feasibility Assessment	03/31/2012	03/31/2012	Year 1, Q2 report
3.1	Amine Sorbent Available for fiber spinning	9/30/2012	9/30/2012	Year 1, Q4 report
3.2	Stability of Sorbents to O_2	9/30/2012	9/30/2012	Year 1, Q4 report
4	Preliminary Hollow Fiber Spinning	9/30/2012	9/30/2012	Year 1, Q4 report
5	RTSA module construction	9/30/2012	9/30/2012	Year 1, Q4 report
6.1	Heat Transfer Model Development	9/30/2012	9/30/2012	Year 1, Q4 report
6.2	Heat transfer model implementation	9/30/2012	9/30/2012	Year 1, Q4 report
6.3	Optimization model formulation	9/30/2012	9/30/2012	Year 1, Q4 report

Project Milestones – All Milestones to Date Met on Time

Task/ Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
7	Update Technology Feasibility Study	9/30/2013	9/30/2013	Year 2, Q4 report
8.1	Sorbent CO_2 adsorption isotherms and kinetics	6/30/2013	6/30/2013	Year 2, Q3 report
8.2	Stability of sorbents to SO_2 and NOx	9/30/2013	9/30/2013	Year 2, Q4 report
9.1	Spin CA-Amine Sorbent Hollow Fibers	Year1 through Year 3	Year1 through Year 3	Year 1, 2, Q1,2,3,4 reports
9.2	Lumen Layer Construction	9/30/2013	9/30/2013	Year 2, Q4 report
9.3	Prepare Hollow Fibers for RTSA System Testing	Year1 through Year 3	Year1 through Year 3	Year 1, 2, Q1,2,3,4 reports
10.1.1	Assemble RTSA Testing Station 1	3/31/2012	3/31/2012	Year 2, Q2 report
10.1.2	Assemble RTSA Testing Station 2	6/30/2013	6/31/2013	Year 2, Q3 report
10.1.3	Assemble RTSA Testing Station 3	6/30/2013	6/30/2013	Year 2, Q3 report
10.2	Single Fiber Operation – Temperature Profile Measurement	12/31/2012	12/31/2012	Year 2, Q1 report

Project Milestones – All Milestones to Date Met on Time

Task/ Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
10.3	RTSA Operation – No Bore Heat/Cool – Clean Gas	12/31/2012	12/31/2012	Year 2, Q1 report
10.4	RTSA Operation – Active Bore Heat/Cool – Clean Gas	9/30/2013	9/30/2013	Year 2, Q4 report
11.1	Validation of Heat Transfer Model	3/31/2013	3/31/2013	Year 2, Q2 report
11.2	Development of single-fiber adsorption/ desorption model	3/31/2013	3/31/2013	Year 2, Q2 report
11.3	Implementation of single-fiber adsorption/ desorption model	6/30/2013	6/30/2013	Year 2, Q3 report
11.4	Development of module model with adsorption and desorption	3/31/2013	3/31/2013	Year 2, Q2 report

Project Milestones – All Milestones to Date Met on Time

Task/ Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
11.5	Implementation of single-fiber adsorption/ desorption model	6/30/2013	6/30/2013	Year 2, Q3 report
11.6	Implementation of optimization model	9/30/2013	9/30/2013	Year 2, Q4 report Year 3, Q1 report
12	Composite Hollow Fiber Sorbent Stability	3/31/2014	3/31/2014	Year 3, Q2 report
13.1	RTSA Operation - Clean Gas – Heat Management	3/31/2014	3/31/2014	Year 3, Q2 report
13.2	RTSA Operation – Dirty Gas – Effect of Contaminants	6/30/2014	6/30/2014	Year 3, Q3 report
13.3	RTSA Operation – Clean Gas – Front Matching	9/30/2014	9/30/2014	Year 3, Q4 report
14.1	Validation of single-fiber adsorption model	12/31/2013	12/31/2013	Year 3, Q1 report
14.2	Validation of single-fiber desorption model	6/30/2014	6/30/2014	Year 3, Q3 report

Project Milestones – All Milestones to Date Met on Time

Task/ Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
14.3	Validation of module model with adsorption	6/30/2014	6/30/2014	Year 3, Q3 report
14.4	Validation of module model with desorption	6/30/2014	6/30/2014	Year 3, Q3 report
14.5	Trade-off analysis by multi-objective optimization	9/30/2014	9/30/2014	Year 3, Q4 report
15	Final RTSA Technology Feasibility Study	3/31/2015	12/31/2014	Year 4, Q1 report
16	Environmental Health & Safety Risk Assessment	3/31/2015	12/31/2014	Year 4, Q1 report

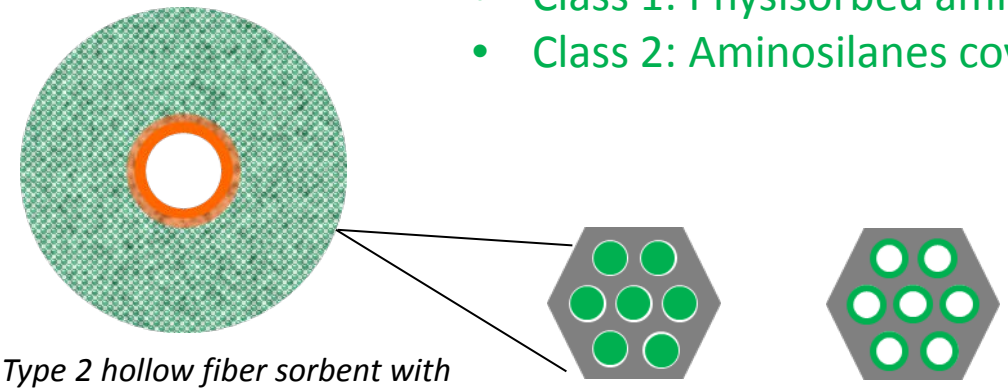
- Highlights from our work will be presented next in five sections:
  - Task Area 1 – Sorbent Synthesis
  - Task Area 2 – Hollow Fiber Spinning
  - Task Area 3 – RTSA Experimental Testing
  - Task Area 4 – Single Fiber Model
  - Task Area 5 – Optimization Model and Technoeconomic Analysis

Task Area 1 – Sorbent Synthesis

Original sorbent synthesis approach

Alkyl amines physisorbed or covalently bonded to mesoporous supports.

- Class 1: Physisorbed amines
- Class 2: Aminosilanes covalently tethered to support



Type 2 hollow fiber sorbent with lumen-side barrier layer

Silica	C803
Bulk density, g/cm^3	0.07-0.60
Particle size, µm	3.8
Pore diameter, nm	18.5-20
Pore volume cm^3/g	0.85
BET surface area m^2/g	209
Supplier	W.R. Grace

- Synthesize amine/silica sorbents, incorporate into polymer spinning dopes (polymer, water, THF, sorbent, etc.), spin fibers

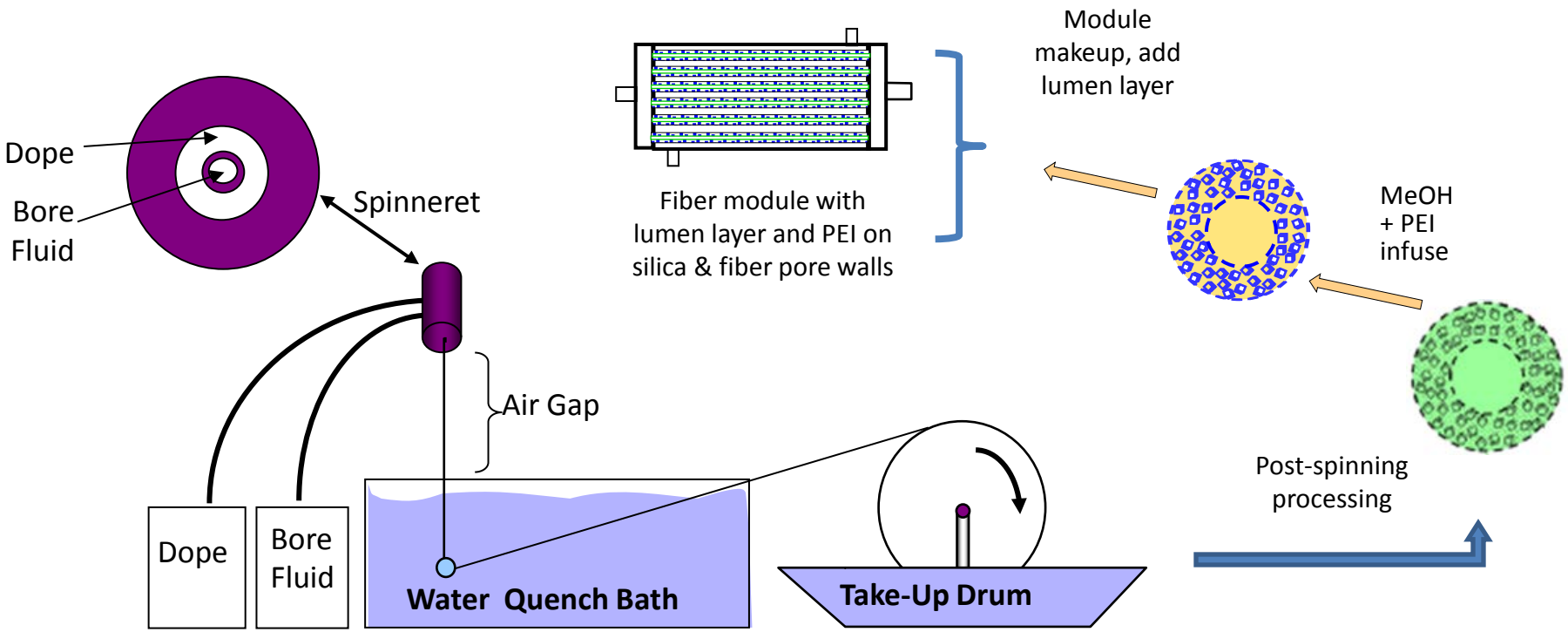
- Resulting fibers contain silica particles, but virtually no amine!
  - -- washes out of class 1 materials during dope preparation or fiber quenching
  - -- hydrolyzes amine-silica linkages in class 2 materials, with nearly complete amine loss in resulting fibers

Task Area 1 & 2 – Fiber & Sorbent Synthesis

Labreche et al., *Chem. Eng. J.*, **2013**, 221, 166-175.
Rezaei et al., *ACS Appl. Mater. Interf.*, **2013**, 5, 3921-3931.
Labreche et al., *ACS Appl. Mater. Interf.,* **2014**, 6, 19336-19346.
Labreche et al., *J. Appl. Polym. Sci.,* **2015**, 132, DOI: 10.1002/APP.41845.

Post-spinning amine infusion

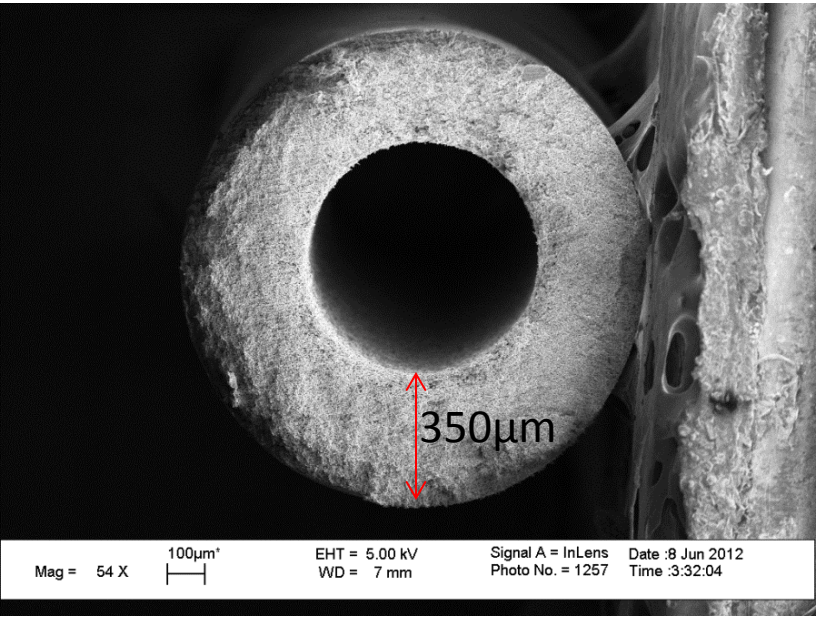
- **New method for amine-containing fiber sorbent synthesis**

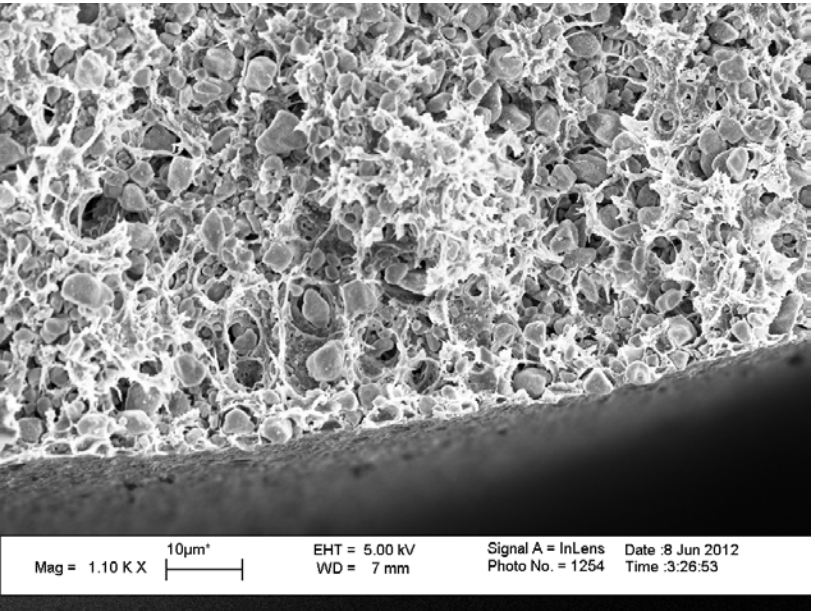


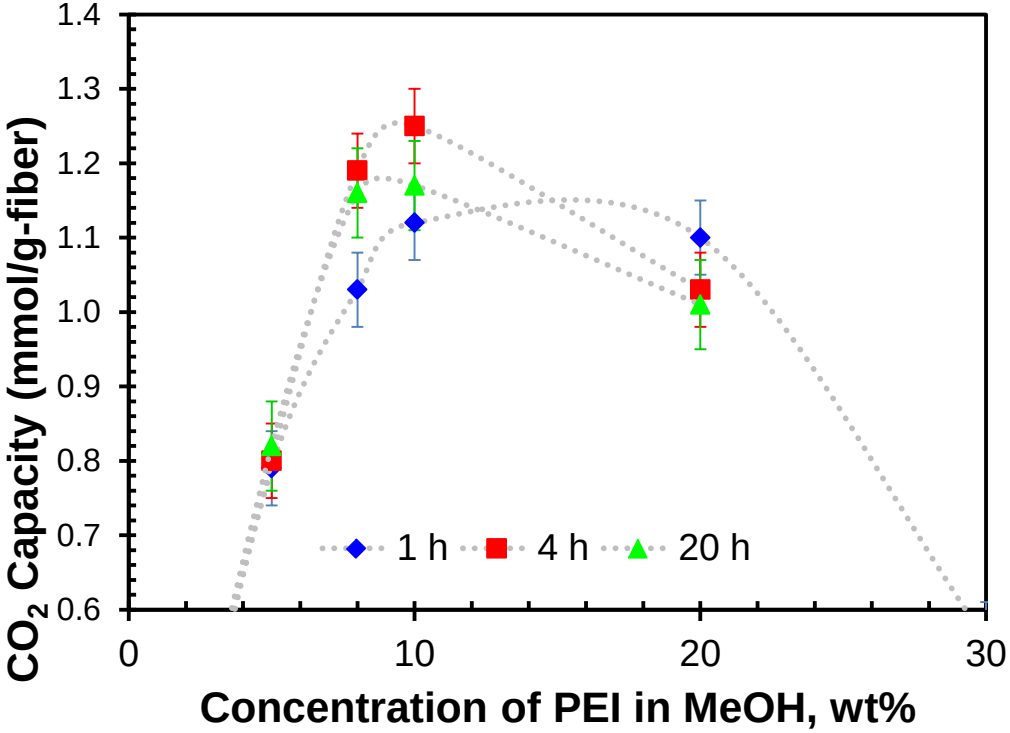
- **First successful spinning of polymer/silica/PEI hollow fiber sorbent**
- **Simple, scalable procedure**
- **Proved the concept with cellulose acetate (CA) - CA/silica/PEI**

Labreche et al., *Chem. Eng. J.*, **2013**, 221, 166-175.

CA-Silica fiber post-spinning infusion



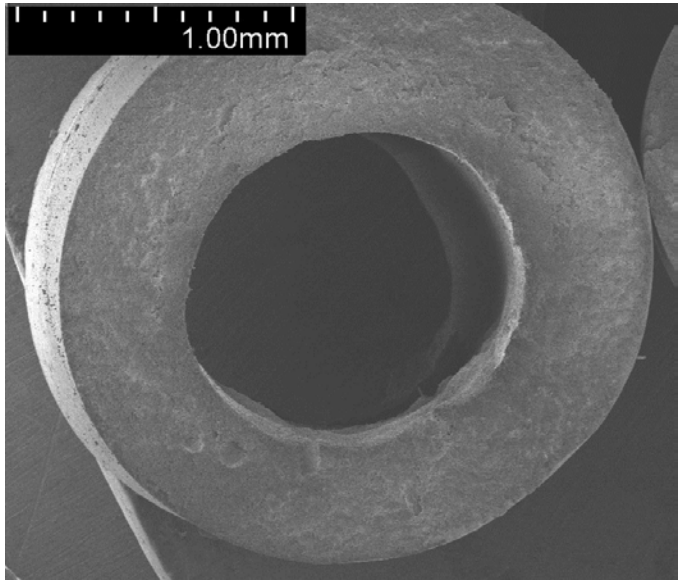


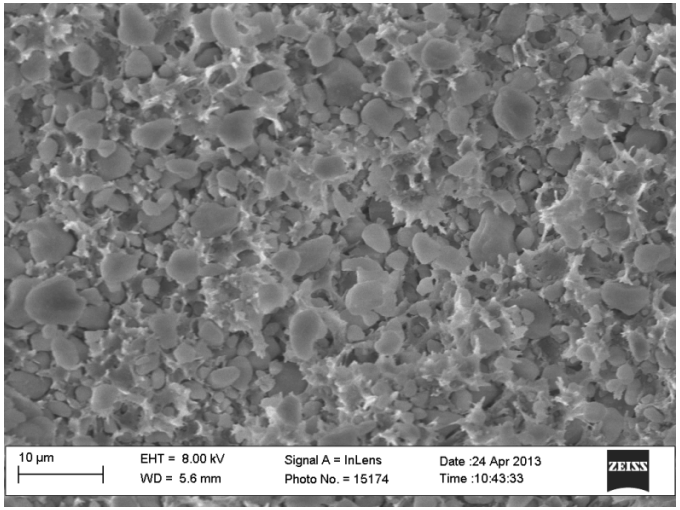


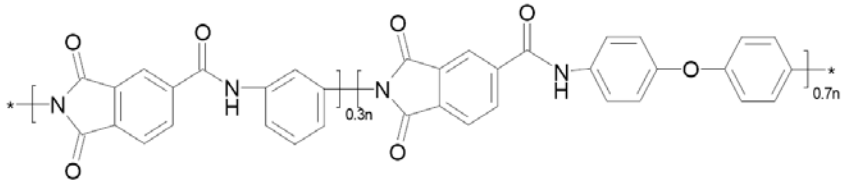
"Rechargeable" Hollow Fiber Sorbent

Fiber samples	CO_2 capacity, mmol/g-fiber
PSI, 10% PEI	1.25±0.08
RPSI, 10% PEI	1.07±0.03

Torlon®-Silica fiber synthesis







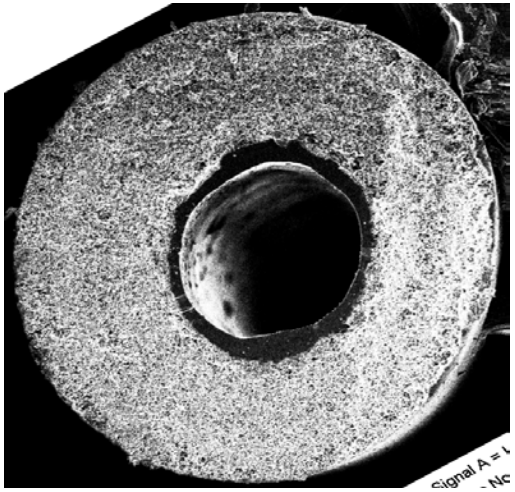
- Torlon®, like CA, is commercially available
- Improved thermal stability
- Chemically resistant
- Good mechanical strength
- Fiber sorbent rechargeable, as in the CA case

Hollow Fiber Contactor as Heat Exchanger

Constructing a barrier lumen layer in the fiber bore, allowing the fibers to act as a shell-in-tube heat exchanger.

Two approaches:

(i) **Post-treatment**: Flow of a polymeric, Neoprene® latex and cross-linker through fibers

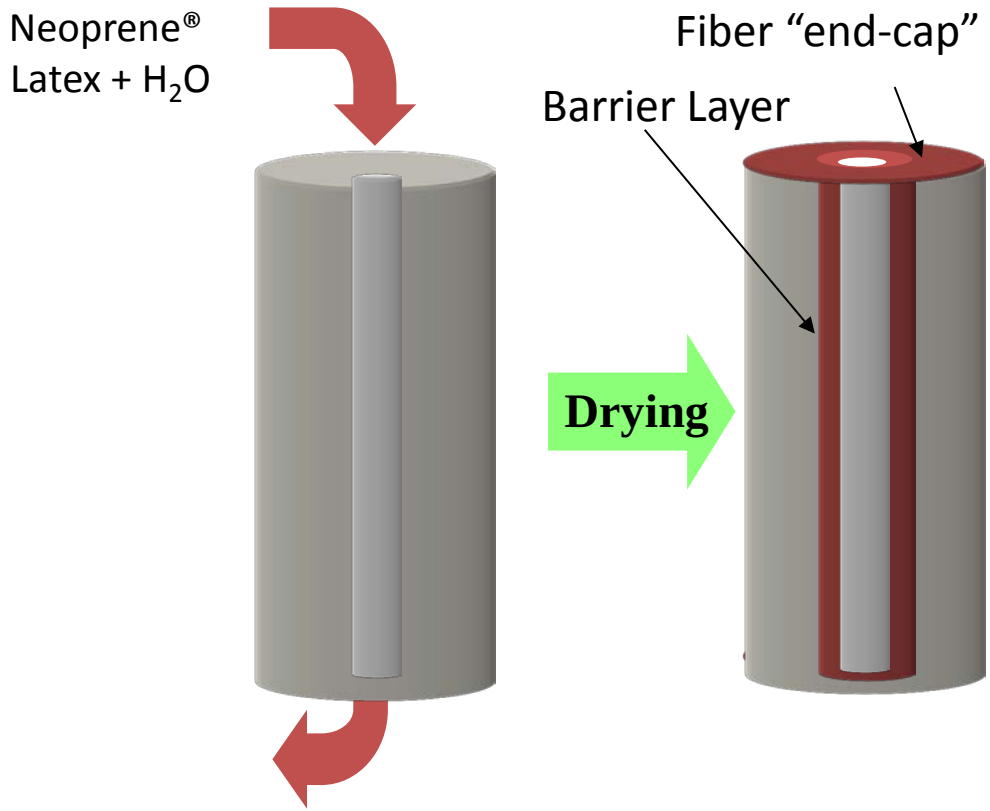


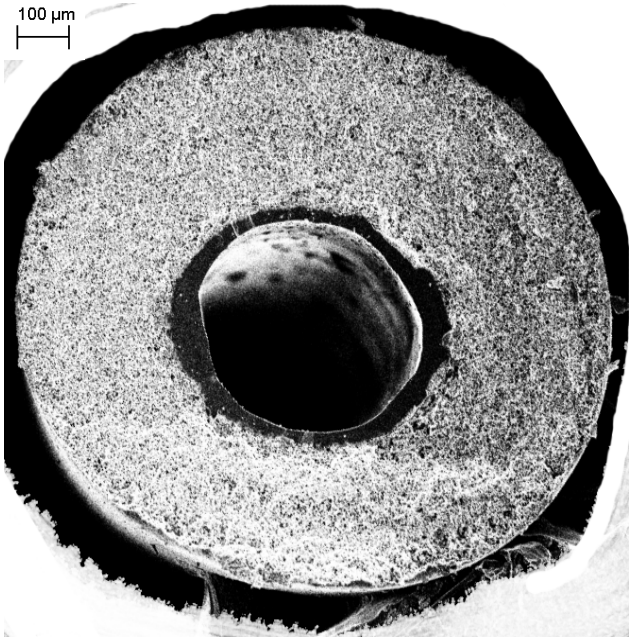
Sample	He permeance (GPU)
CA/Silica	72,200 (25 psi)
CA/Silica/Neoprene®/TSR-633	3.4

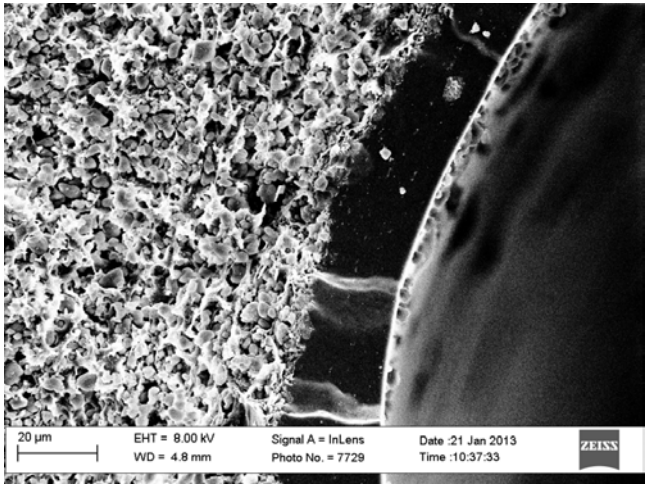
-- Large decrease in mass flux from bore to shell with lumen layer = good barrier layer

Labreche et al., *ACS Appl. Mater. Interf.*, **2014**, 6, 19336-19346.

Defect-Free, Lumen Layer Synthesis







- **Successful gas impermeable lumen layer prepared.**
- **Enables operation as nanoscopic heat exchanger.**
- **Some plugging of fibers occurs – challenge to scalability**

Hollow Fiber Contactor as Heat Exchanger

Constructing a barrier lumen layer in the fiber bore, allowing the fibers to act as a shell-in-tube heat exchanger.

Two approaches:

(i) **Post-treatment**: Flow of a polymeric, Neoprene® latex and cross-linker through fibers

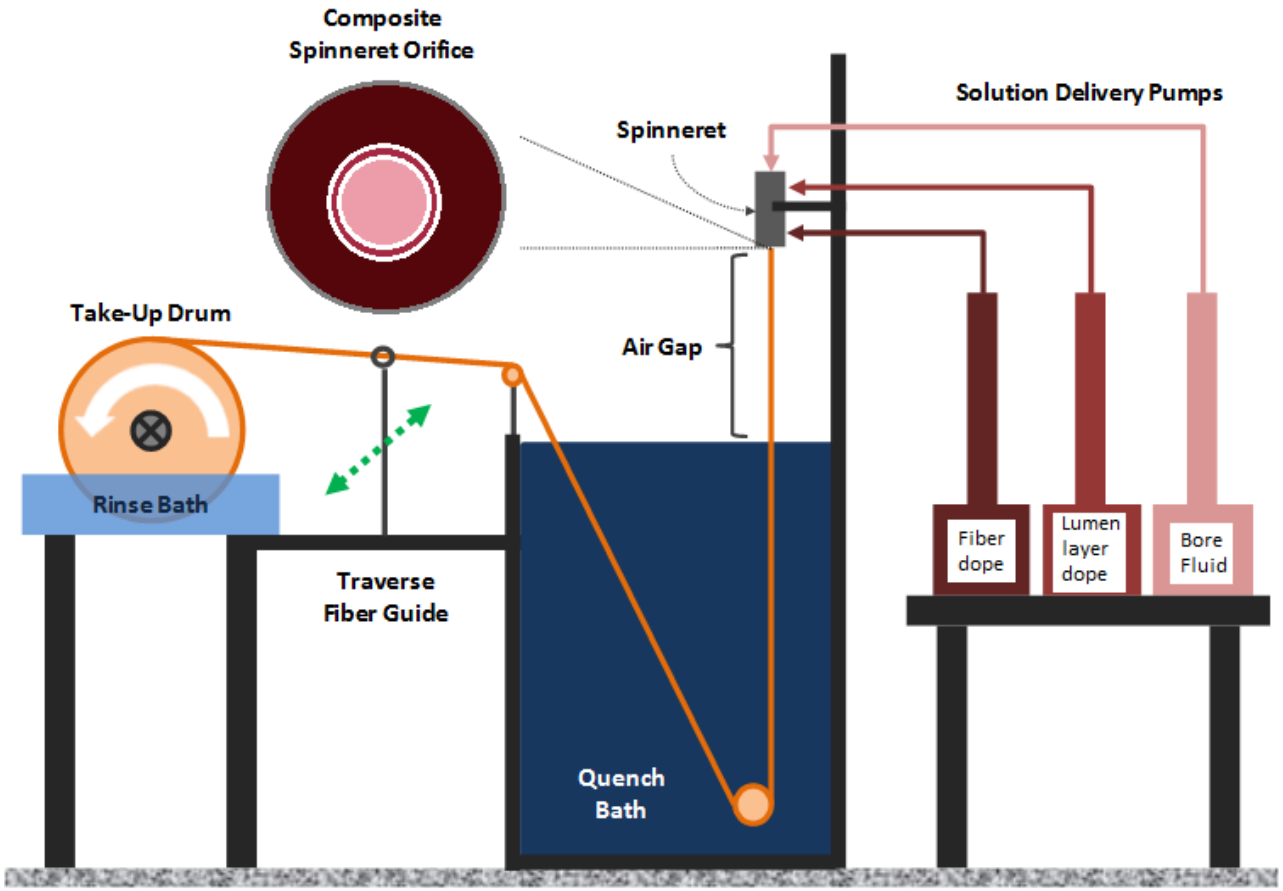
- Disadvantage – fibers can become clogged by latex, requires careful handling of latex

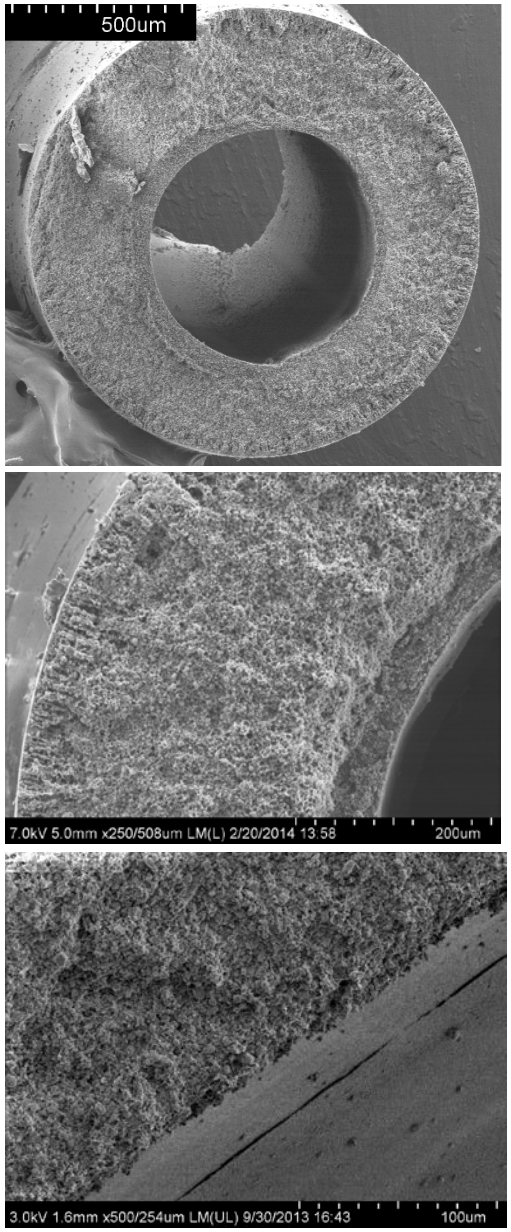
(ii) Dual layer fiber spinning – spin the lumen layer when initial fiber formed

- Advantage – highly scalable synthesis when poly(amide-imide) like Torlon® employed

- Main fiber: porous Torlon® containing 50-60 wt% silica;
  Lumen layer: dense Torlon®; post-treatment with PDMS gives excellent barrier properties

Lumen Layer Creation by Direct, Dual Layer Spinning





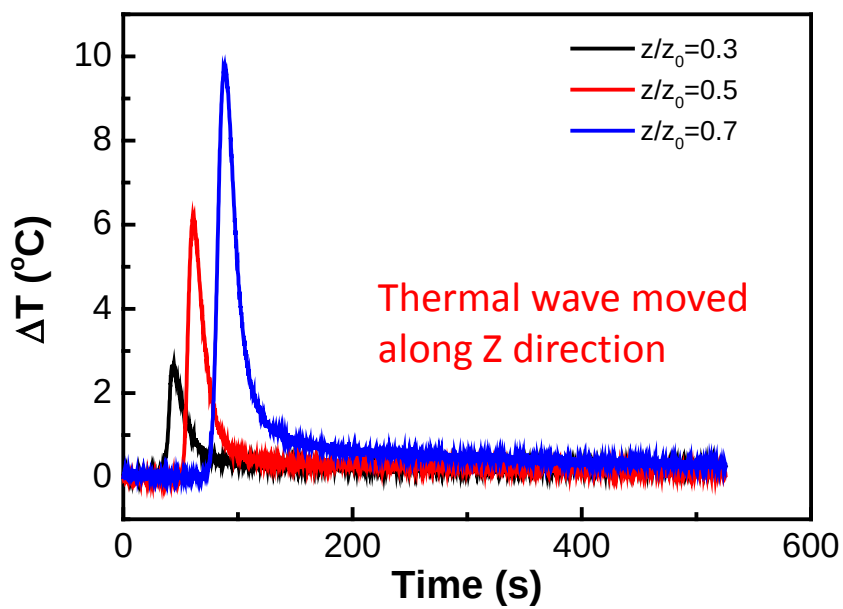
- Simplified spinning and lumen layer coating to one step
- Excellent barrier layer for both water and gases
- Outstanding scalability

Labreche et al., *J. Appl. Polym. Sci.*, **2015**, 132, 4185.

Hollow Fiber Contactor as Heat Exchanger

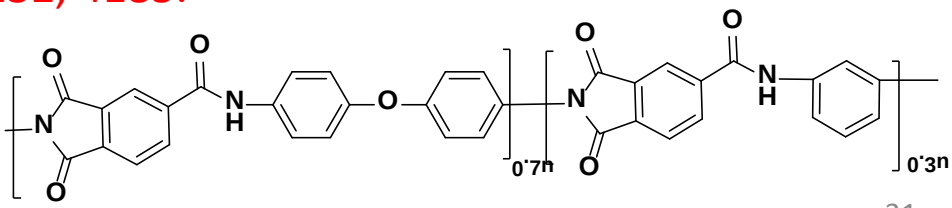
- Torlon®, commercially available
- Improved thermal & chemical stability
- Excellent barrier properties for both water and gases
- No need for problematic latex post-treatment

Lab scale heat capture efficiency during adsorption: ~72%



Fan et al., *AIChE J.*, **2014**, 60, 3878-3887.

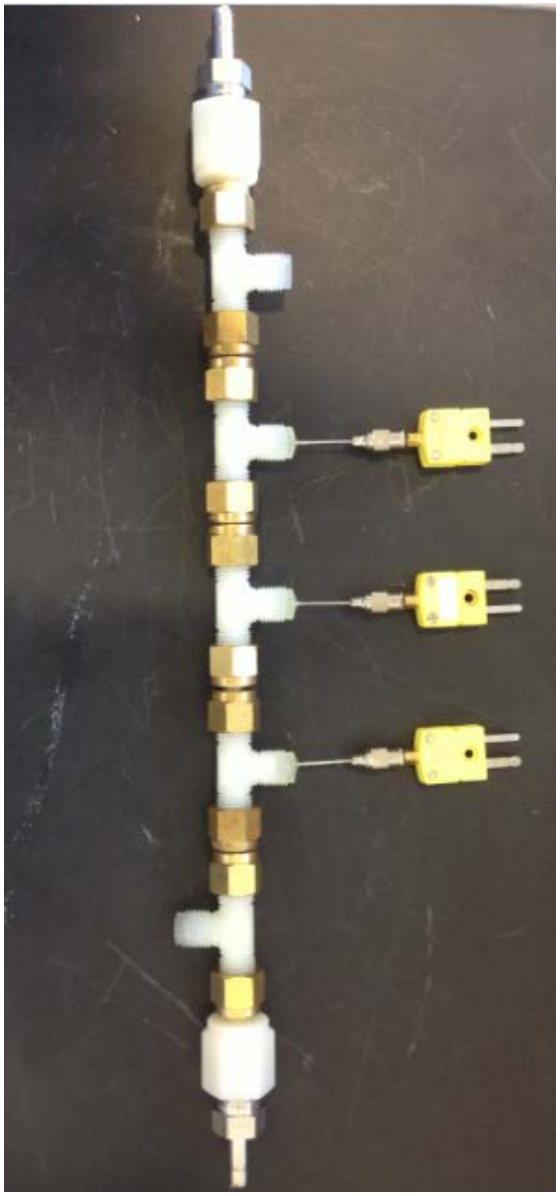
Labreche et al., *J. Appl. Polym. Sci.*, **2015**, 132, 4185.

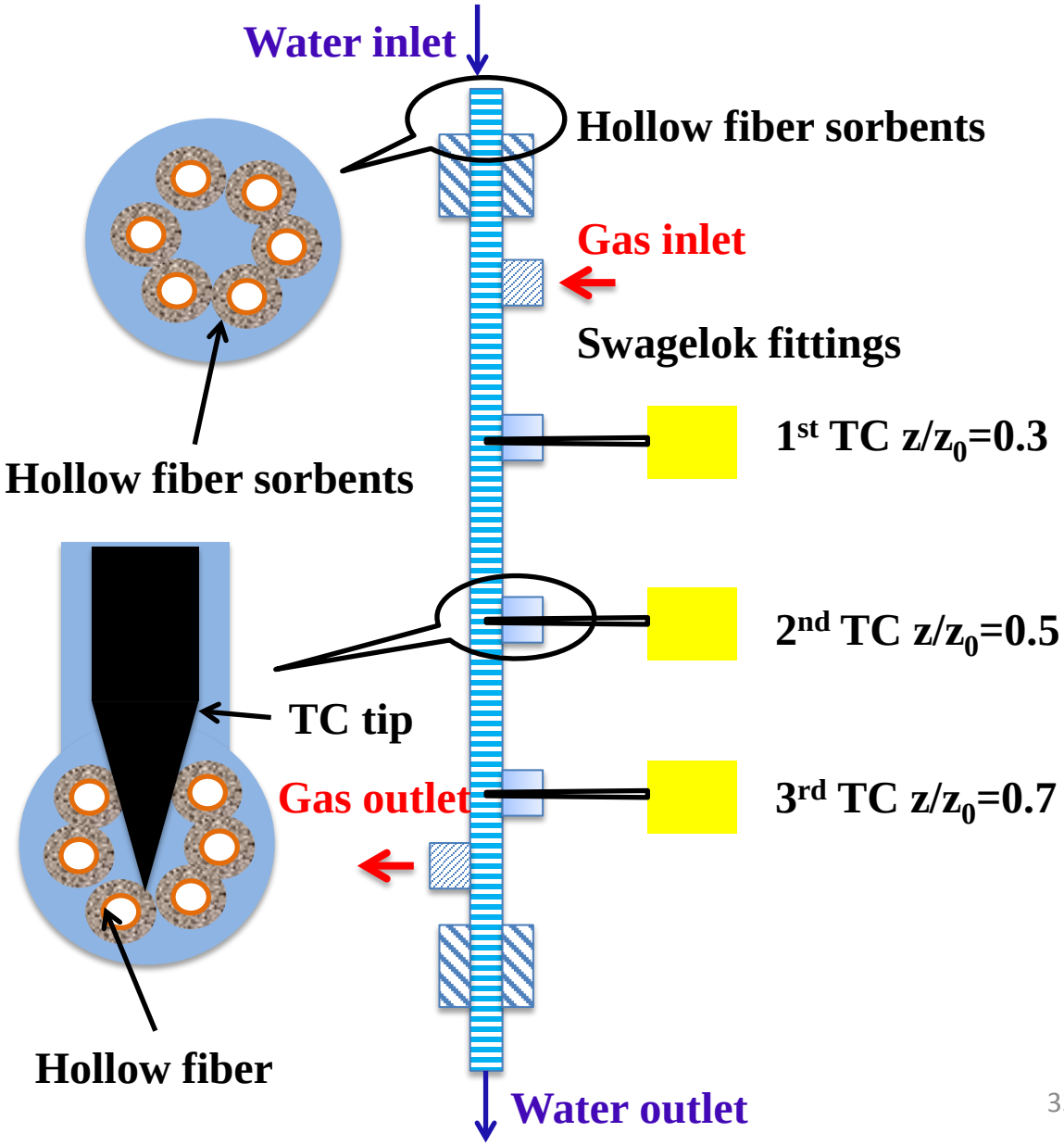


Task Area 3 – RTSA Experimental Testing

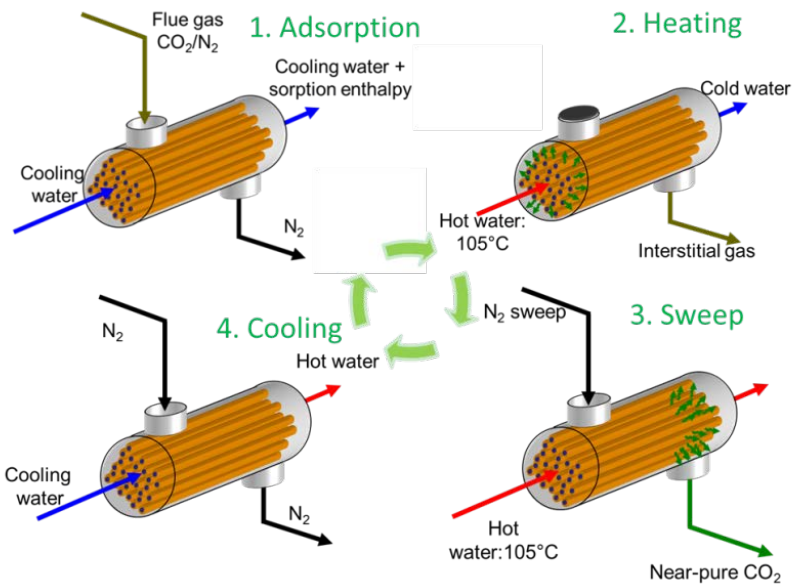
Fan et al., *Int. J. Greenhouse Gas Control*, **2014**, 21, 61-71.
Fan et al., *AIChE J.*, **2014**, 60, 3878-3887.
Fan et al., *Ind. Eng. Chem. Res.*, **2015**, 54, 1783-1795.
Fan et al., *Fuel*, to be submitted 04/2015

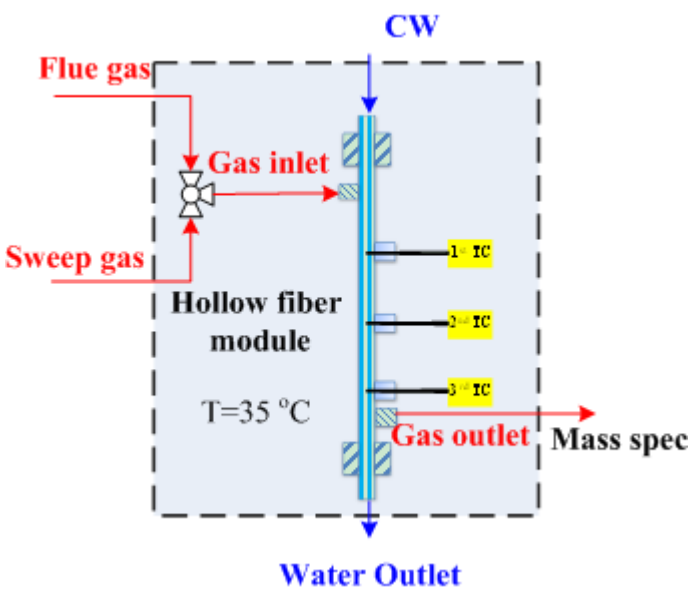
Lab Scale Hollow Fiber Module

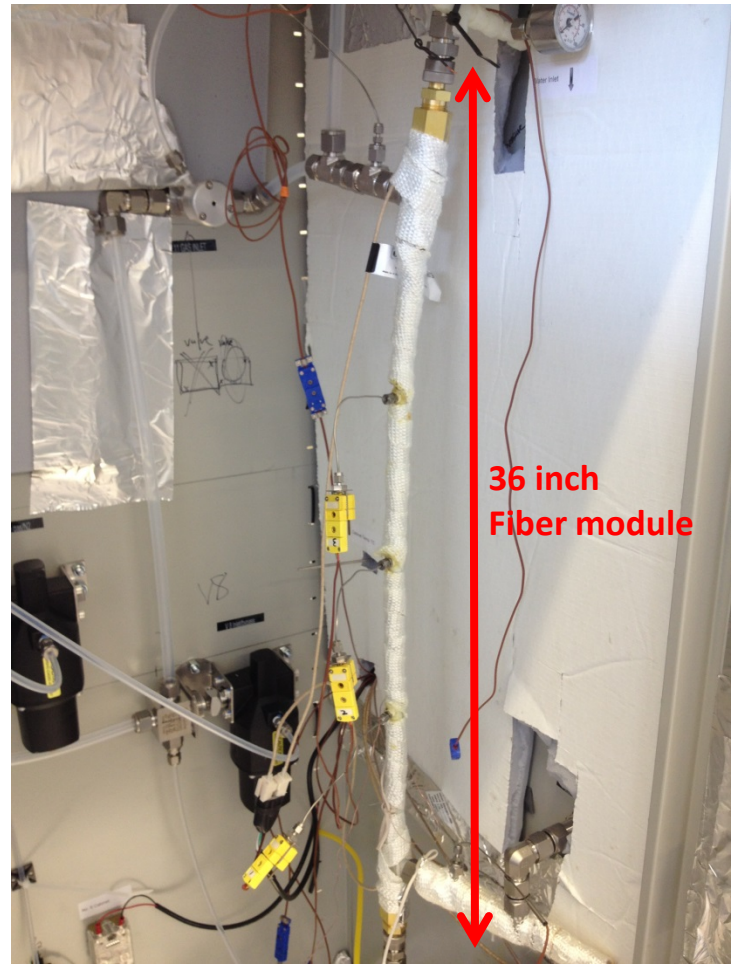




RTSA Design and Operation







Flue gas composition: 35 °C, 1 atm

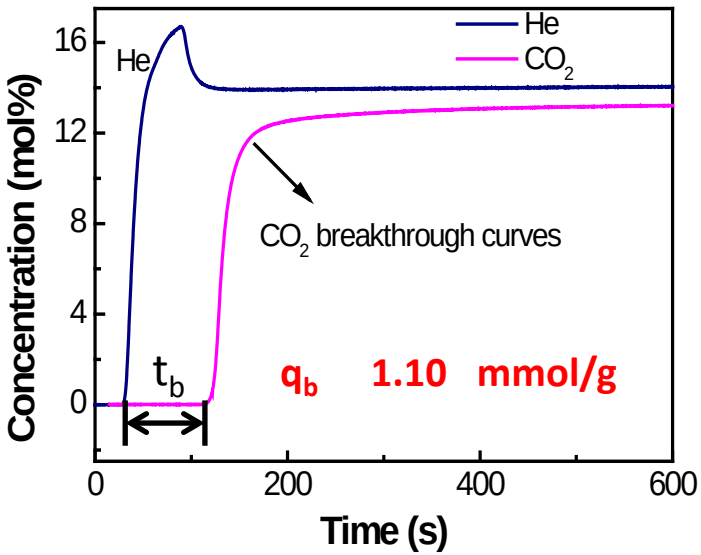
~ 13% CO_2, ~13% He (Inert tracer),

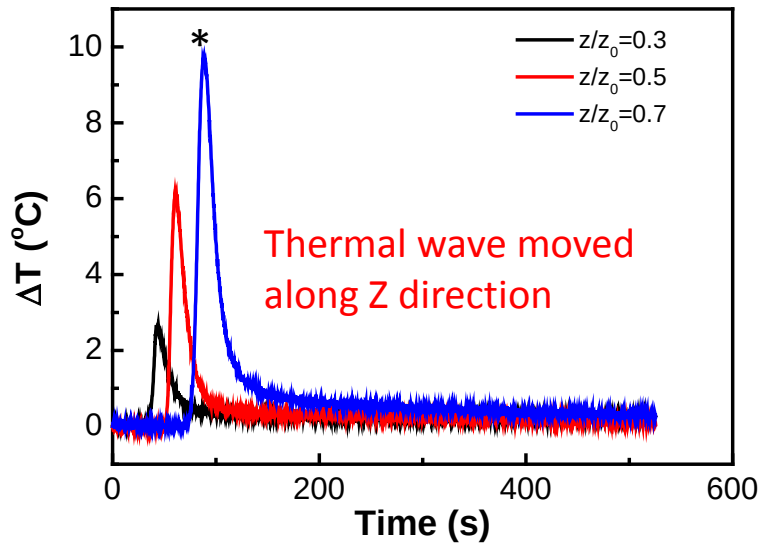
6% H_2O, balance gas N_2

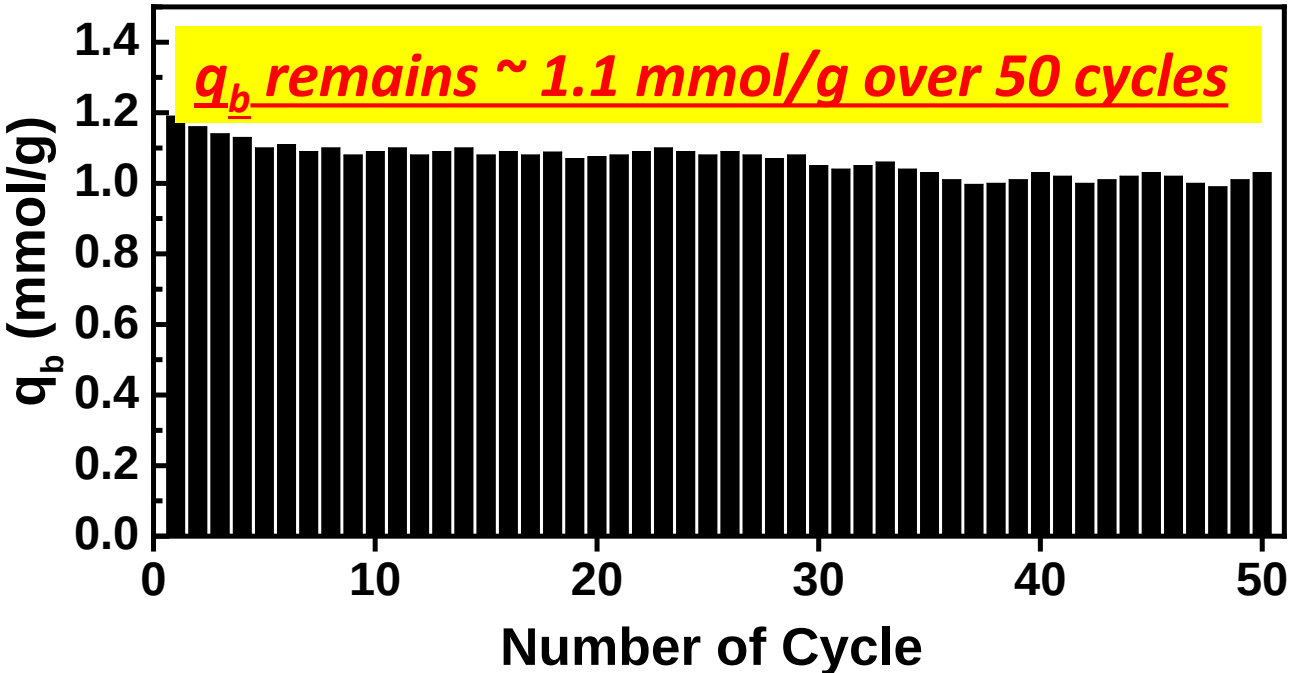
q_b: breakthrough capacity

CO_2 Sorption in Uncooled CA-C803-PEI Generation 2 Fibers

* Estimated thermal excursion is ~ 63 °C in full size module







Generation 3 Fibers

Dynamic process modeling and system technoeconomic analysis suggest there are several factors to lowering costs:

(i) **Improved sorption capacities** [pseudo-equilibrium (q_{pe}), breakthrough (q_b), swing capacities (q_s)]

(ii) **Improved process configuration** allowing for enhanced heat management without integrating with power plant

Generation 3 Fibers

Dynamic process modeling and system technoeconomic analysis suggest there are several factors to lowering costs:

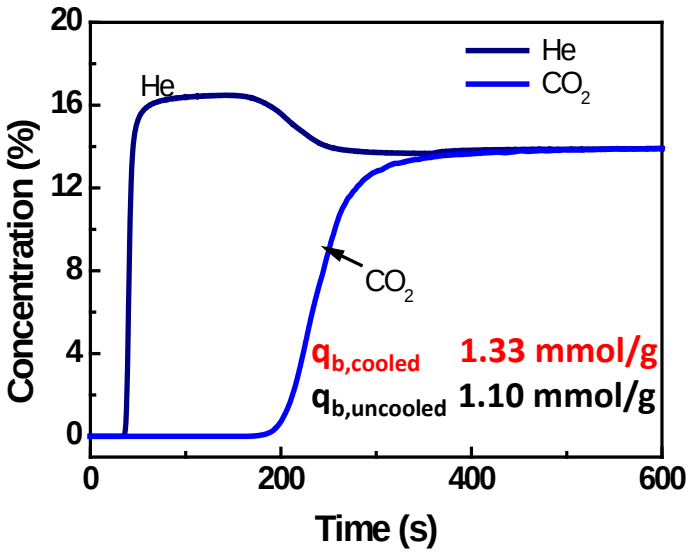
(i) **Improved sorption capacities** [pseudo-equilibrium (q_{pe}), breakthrough (q_b), swing capacities (q_s)]

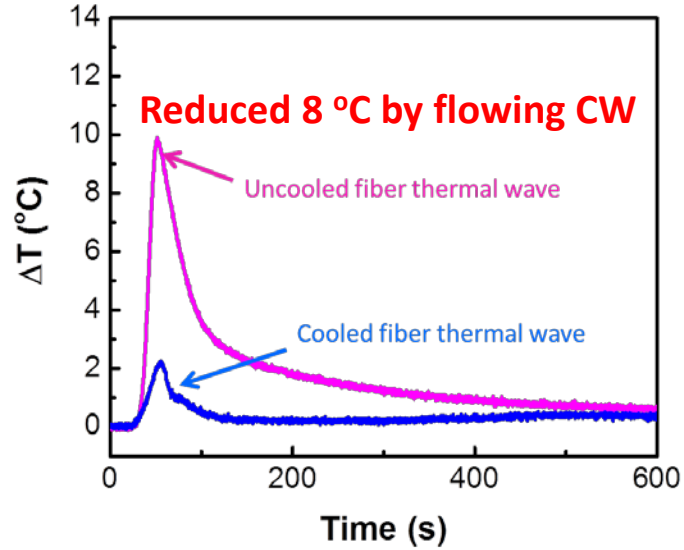
(ii) **Improved process configuration** allowing for enhanced heat management without integrating with power plant

(mol/kg fiber)	q_{pe}	q_b	q_s
Generation 1 fibers:	1.1	0.5	0.30
Generation 2 fibers:	1.5	1.1	0.65
Generation 3 fibers:	2.0	1.3	0.75 (0.83)

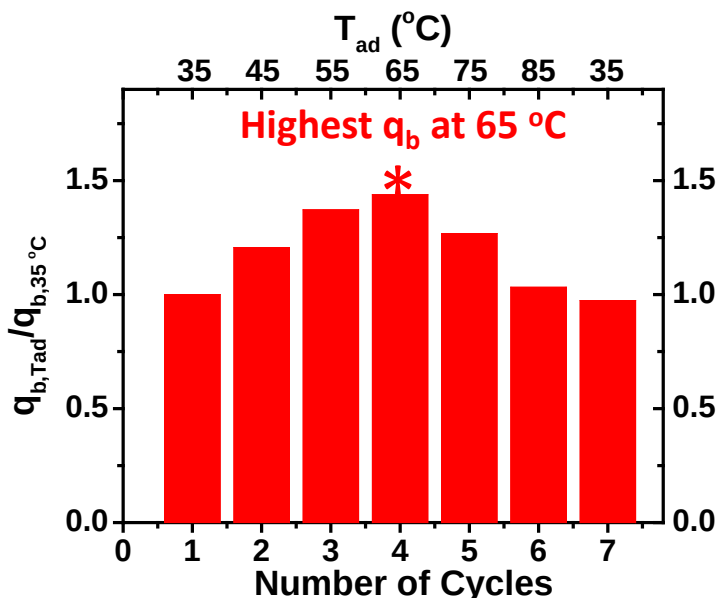
(260% increase in q_b in 2.5 years)

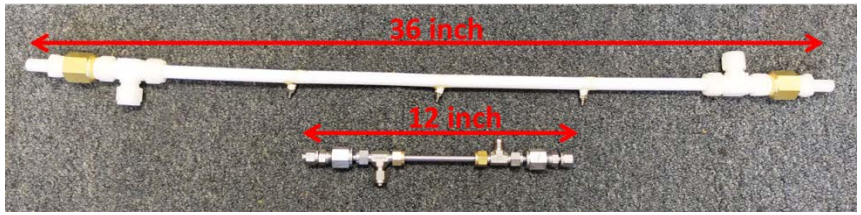
Cooled Torlon-C803-PEI Fiber Sorbent
Generation 3 Fibers





CW boosted CO_2 sorption capacity by removing heat





Torlon-C803-PEI properties improve at elevated temperature

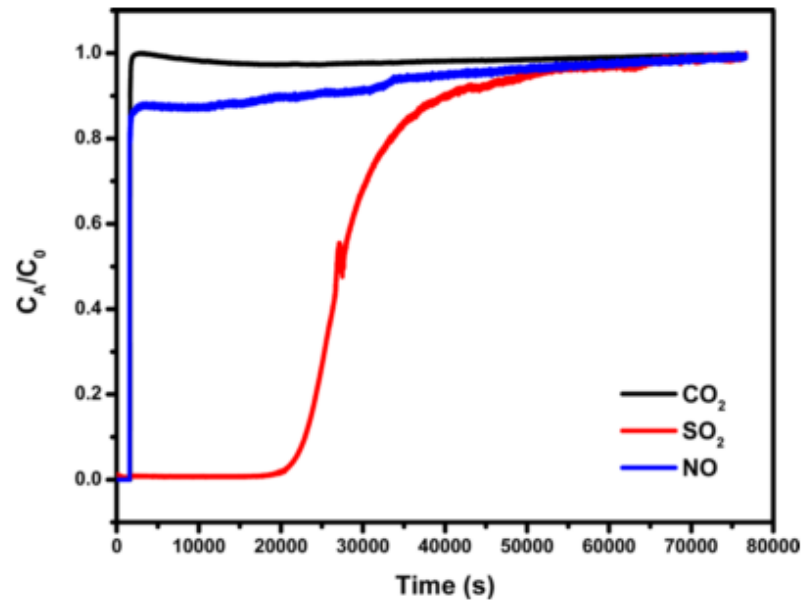
- Avoid process pre-cooling and pre-drying steps
- Reduce energy consumption and operational cost

Impact of SO_x/NO_x on Adsorbent Materials

Assessing the impact of operating conditions on deactivation via (i) oxidation, (ii) SO_x exposure, (iii) NO_x exposure is critical.

- Conditions whereby oxidation via residual oxygen in flue gas can be avoided identified
- Equilibrium and dynamic sorption measurements of NO, NO_2, SO_2 completed
- Pure component SO_2, NO_2 and NO adsorption studies on class 1 and class 2 aminosilicas show that only SO_2 and NO_2 adsorb appreciably.
- Multicomponent sorption studies showed no synergistic pathways to degradation for $CO_2/NO/SO_2$ adsorption.

10% CO_2/200 ppm SO_2/200 ppm NO, 35 °C co-adsorption with PD-MAPS_2

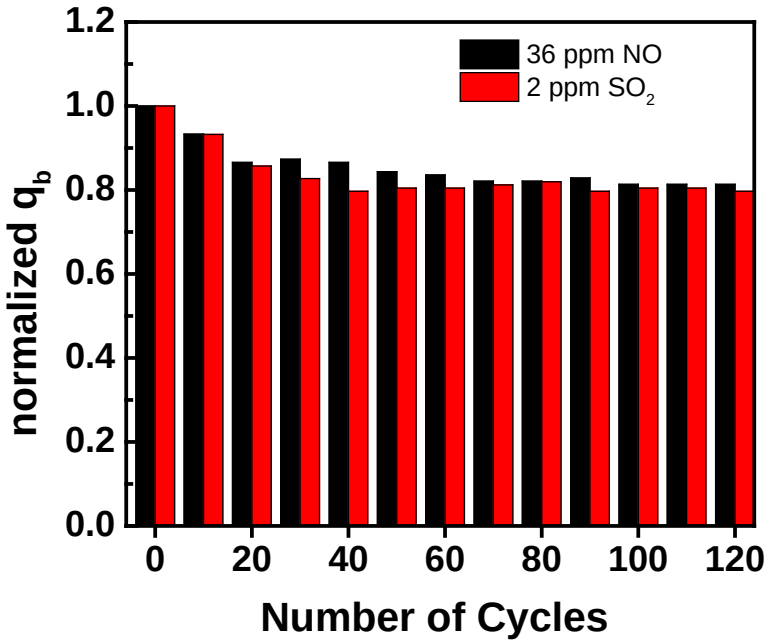


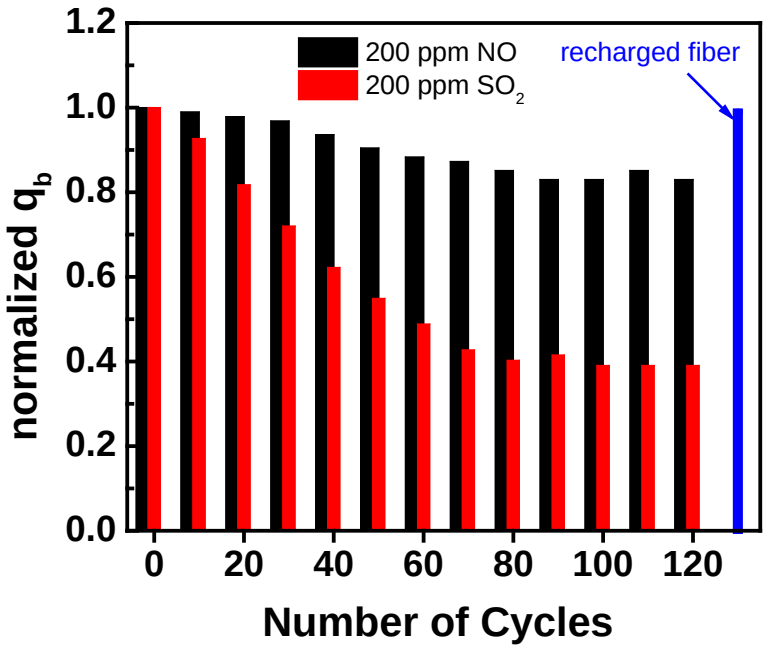
Rezaei et al., *Ind. Eng. Chem. Res.*, **2013**, 52, 12192-12201.

Rezaei et al., *Ind. Eng. Chem. Res.*, **2014**, 53, 12103-12110.

SO_x/NO_x studies facilitated by support of *Southern Company*.

Impact of SO_x/NO_x on Fiber Module Operation





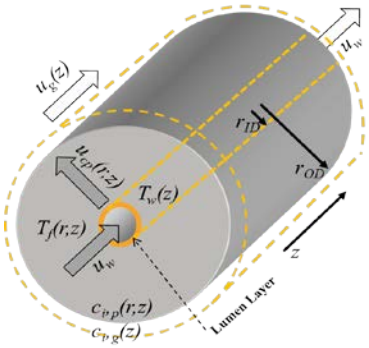
- **NO_2, SO_2** adsorb strongly, but have modest impact at low concentration
- Saturation capacity loss observed
- High concentration of gases (200 ppm) cause significant capacity loss, but a plateau was observed. Low concentration NO_2 had no measurable impact on capacity for class 1 fibers.
- Deactivated fibers can be stripped of amine and recharged in the field for **full capacity regeneration.**

Fan et al., *AIChE J.*, **2014**, 60, 3878-3887.

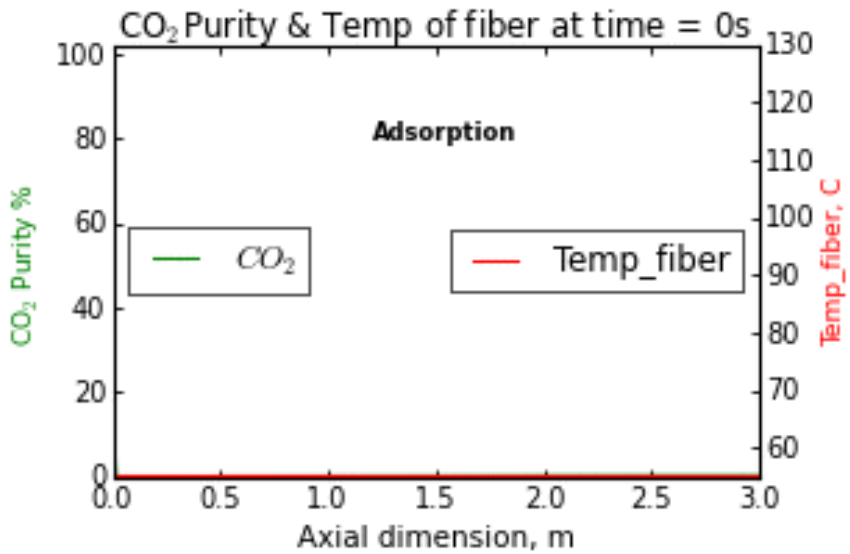
Task Area 4 – Single Fiber Modeling

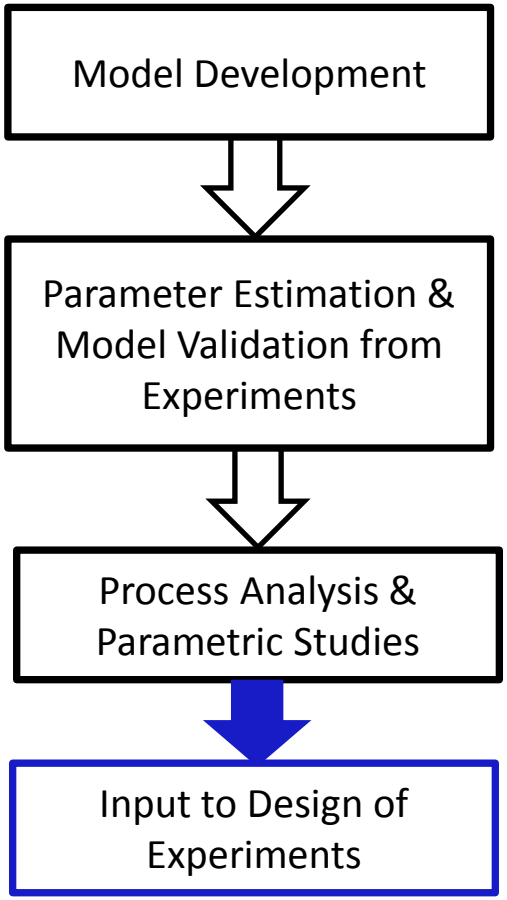
Rezaei et al., *Chem. Eng. Sci.*, **2014**, 113, 62-76.
Kalyanaraman et al., *Chem. Eng. J.*, **2015**, 259, 737-751.
Fan et al., *Ind. Eng. Chem. Res.*, **2015**, 54, 1783-1795.
Kalyanaraman et al, *Comp. Chem.Eng,* **2015**, *submitted.*

Model Development (Single Gen 2 Fiber Modeling)



Cyclic steady state simulation





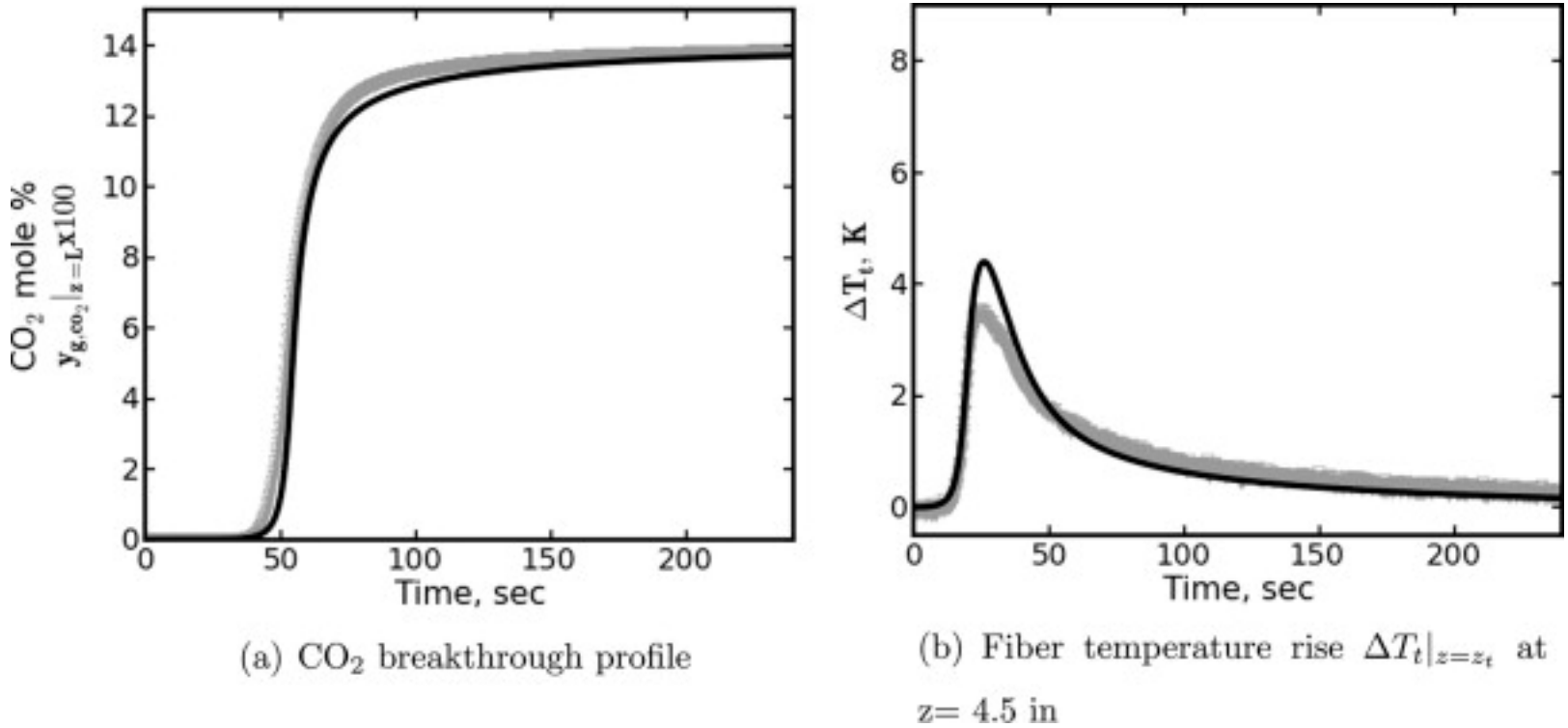
- Adsorption = 44 s
- Self Sweeping/Heating = 78 s
- N_2 sweeping = 23 s
- Cooling = 50 s

Cycle Time = 195 s

Rezaei et al., *Chem. Eng. Sci.*, **2014**, 113, 62-76.
Kalyanaraman et al., *Chem. Eng. J.*, **2015**, 259, 737-751

Mass and Heat Transfer Parameter Estimation

- **Breakthrough data from experiments used to estimate resistance parameters**



(a) CO_2 breakthrough profile

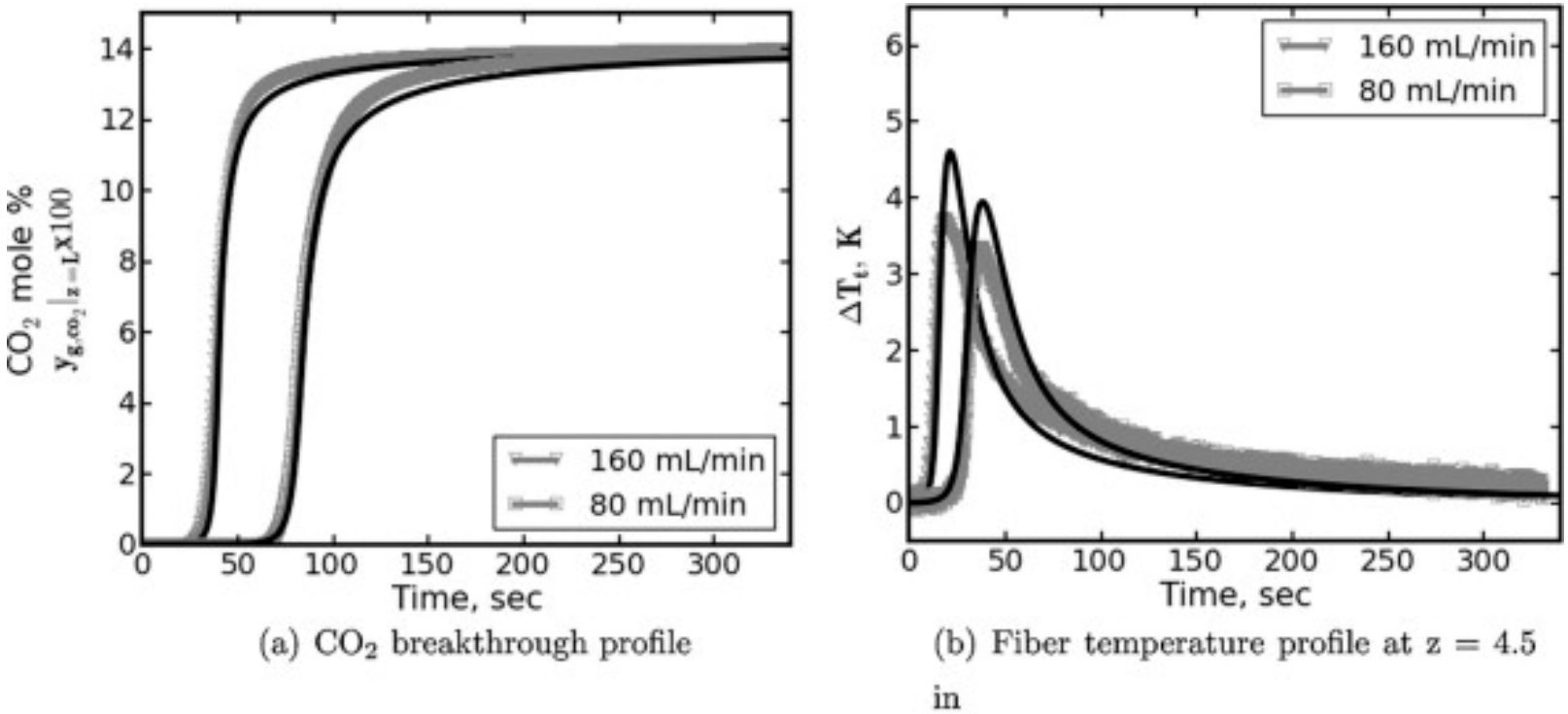
(b) Fiber temperature rise $\Delta T_t|_{z=z_t}$ at

Figure: Validation against different flue gas flow rates: solid line without marker is the model prediction

- **Model parameters tuned to match experimental temperature and concentration**

Kalyanaraman et al., *Chem. Eng. J.*, **2015**, 259, 737-751

Model Prediction Validation



(a) CO_2 breakthrough profile (b) Fiber temperature profile at z = 4.5 in

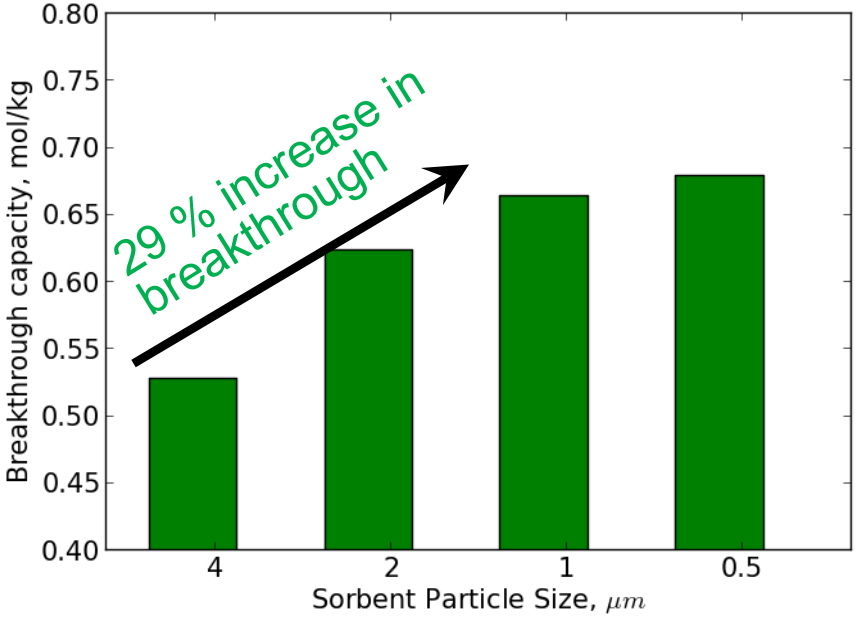
Figure: Validation against different flue gas flow rates: solid line without marker is the model prediction

- **Model prediction matches very well with Gen 2 fiber experiment data**

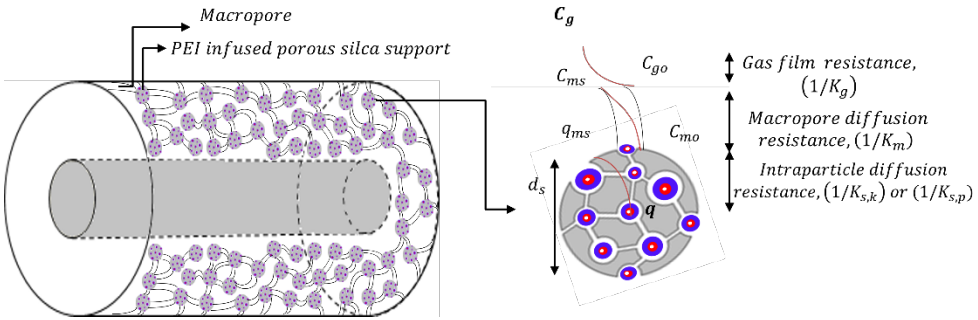
Kalyanaraman et al., *Chem. Eng. J.*, **2015**, 259, 737-751

Process Improvement from Modeling : Effect of Sorbent Size

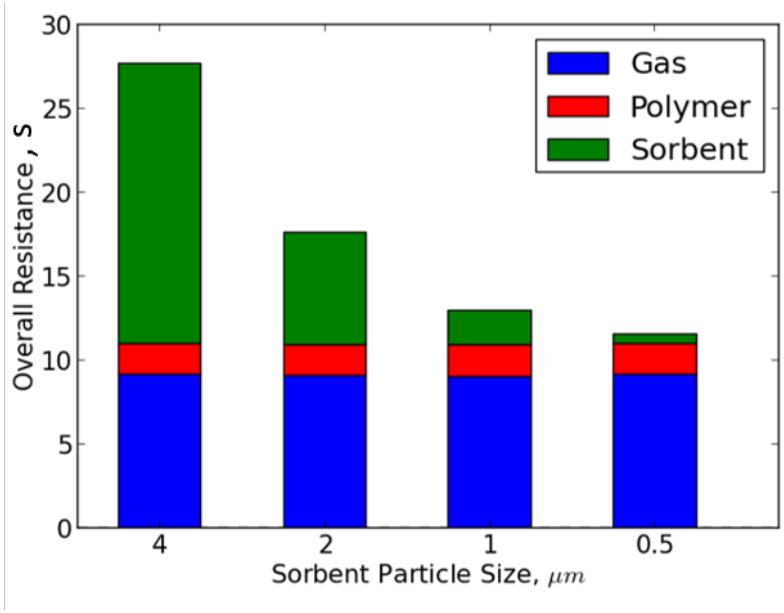
Model prediction of effect of sorbent size on breakthrough capacity



Hollow fiber schematic with different mass transfer resistance components



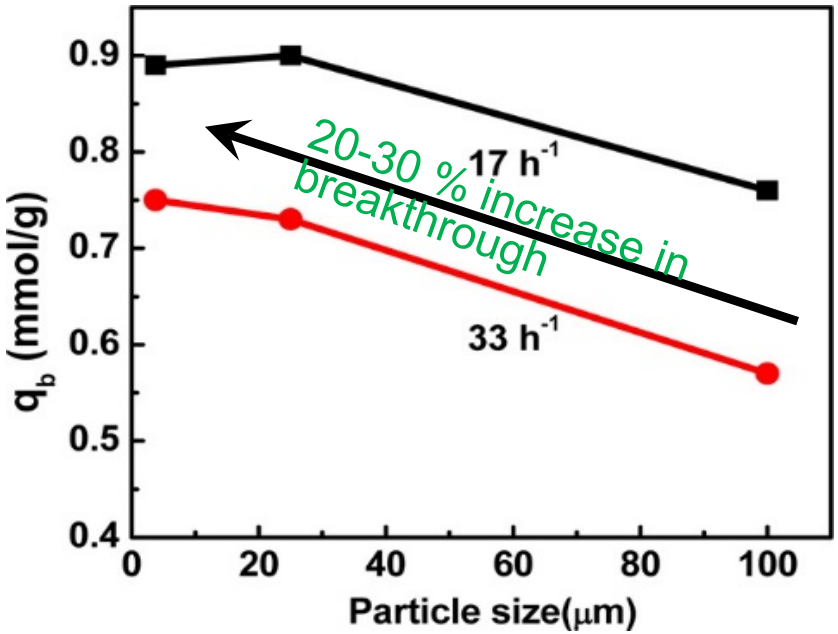
Overall mass transfer resistance vs. sorbent size



- Sorbent/ intra-particle diffusion is the limiting diffusion resistance
- Smaller silica particles can increase breakthrough capacity

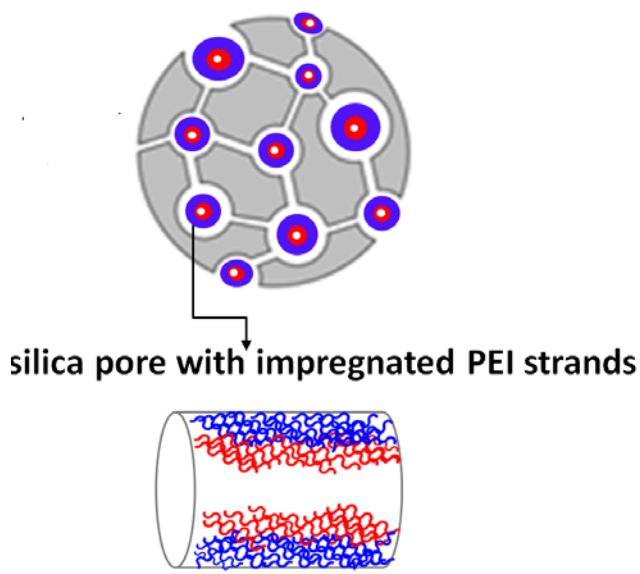
Experimental verification of sorbent particle size effect

[2] Experimental data of breakthrough capacity with different sorbent size at different flow rates



- ❑ Within intra-particle resistance, bulk PEI diffusion is limiting
- ❑ At very small particle sizes, pore volume reduced and there is less total PEI loaded

Blue: PEI in amino-polymer phase (bulk PEI)
Red: PEI silica pore surface (surface PEI)

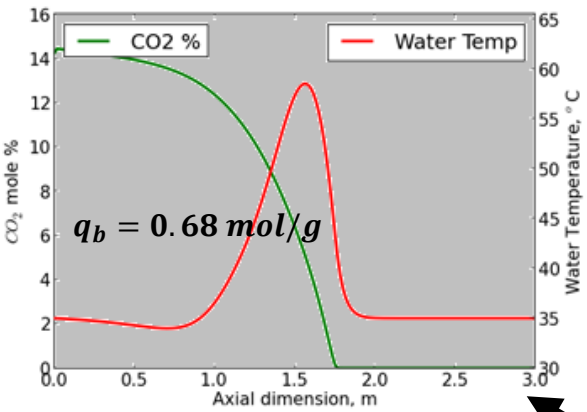


[1]Kalyanaraman et al., *Chem. Eng. J.*, **2015**, 259, 737-751
[2]Fan et al., *Ind. Eng. Chem. Res.*, **2015**, 54, 1783-1795.

Heat Recovery : Optimizing water velocity

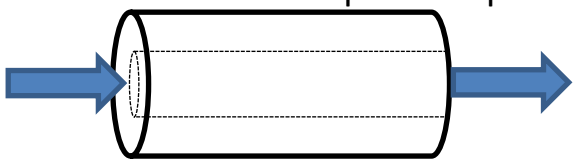
- **Adsorption heat recovery by controlling relative concentration and thermal front velocity**

Thermal front <= Conc front

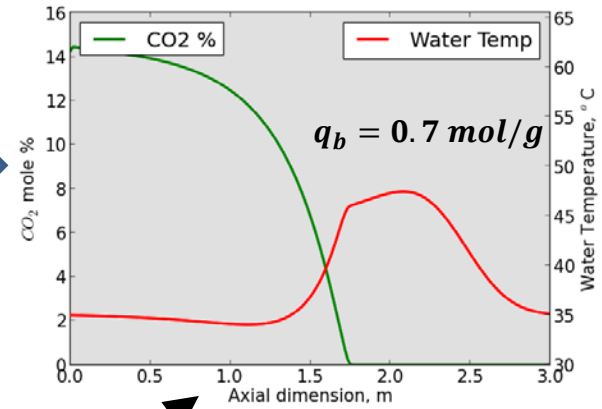


Cooling water

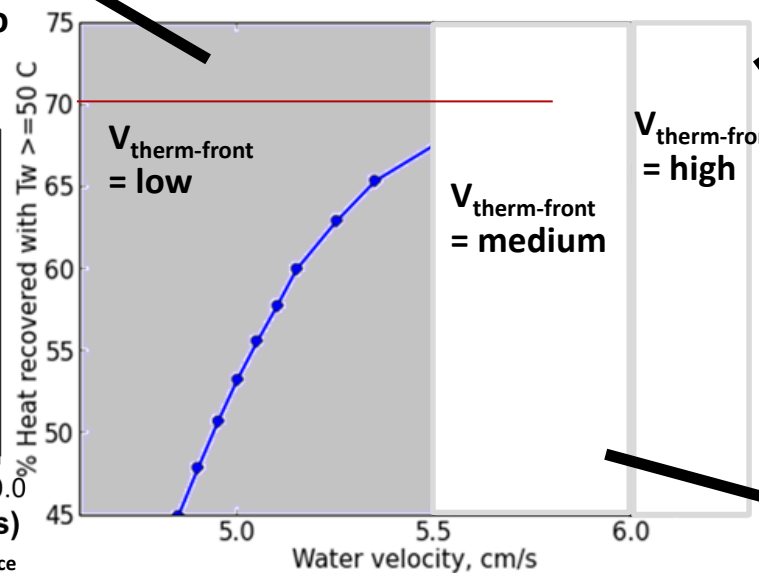
Fiber in adsorption step



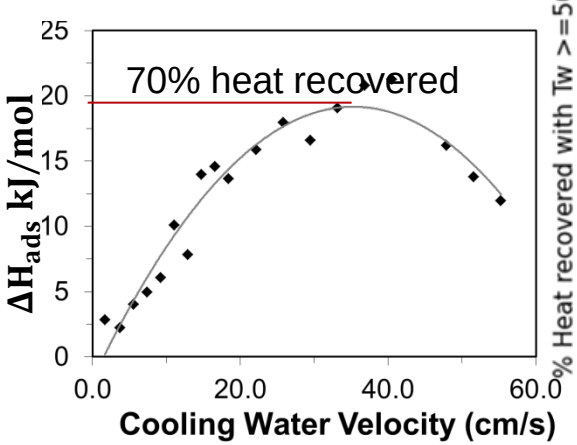
Thermal front >> Conc front



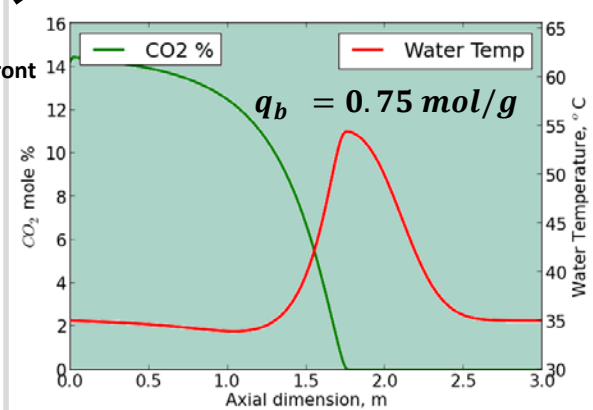
Recovered heat vs. Cooling water velocity



Heat recovery trend similar to experimentally observed[1]



Thermal front > Conc front

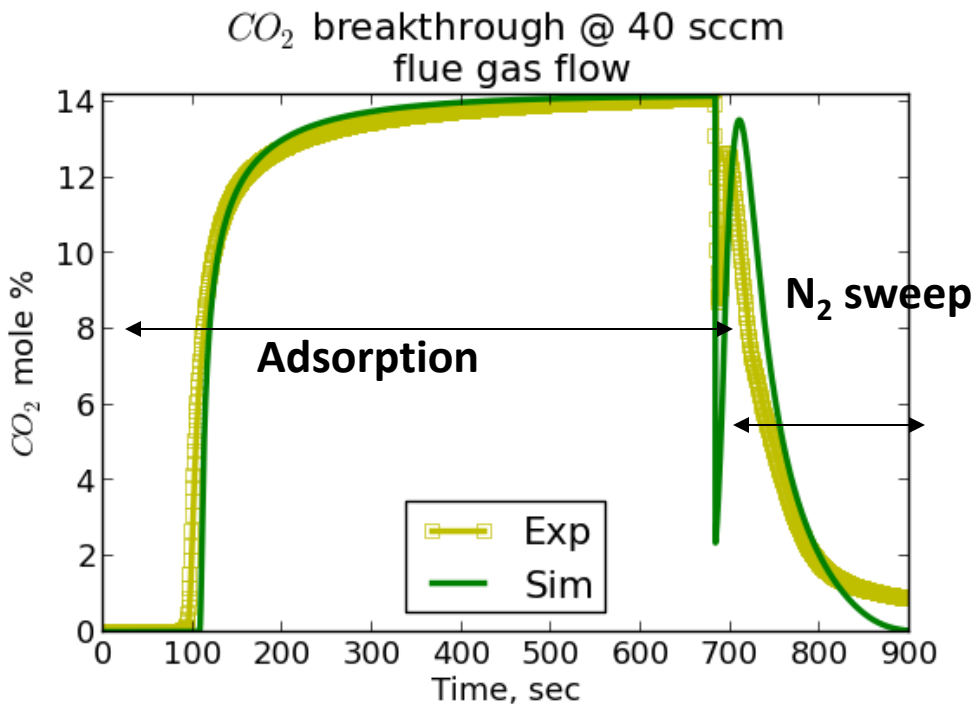


[1] Lively et al, CO_2 sorption and desorption performance of thermally cycled hollow fiber sorbents, 2012, Int. Greenhouse Gas control

Other Modeling efforts: Desorption Model Prediction Validation

- Desorption also experimentally validated with the model

Gen 1 fibers Adsorption/Desorption validation

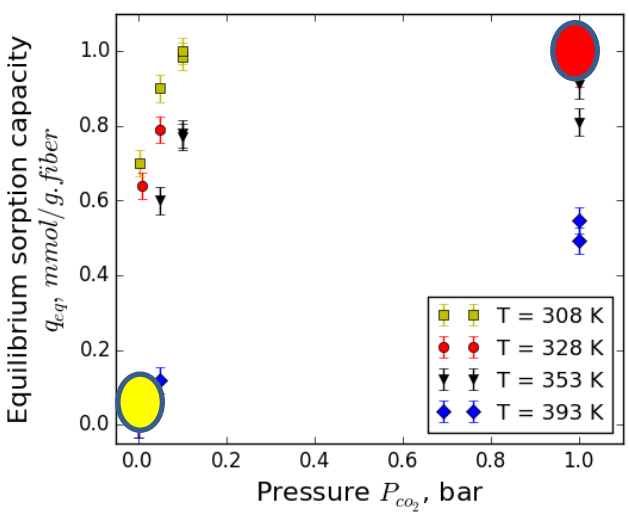


- Qualitatively and quantitatively good agreement with model prediction
- Low desorbed CO_2 concentration due to high flow rate of N_2 purge gas

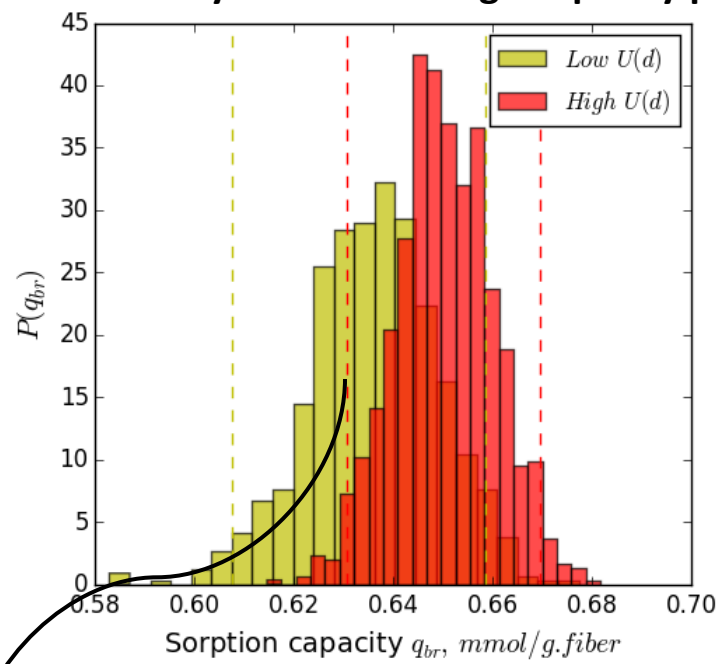
Other Modeling efforts: Optimal design of experiments under uncertainties

- **Optimal design of TGA experiment to reduce q_b prediction uncertainties due to measurement errors**
- **$U(d)$ - information gain from an experimental data**

TGA experiment of Class 2 fibers[1]



Uncertainty in breakthrough capacity prediction



- Breakthrough capacity considering uncertainty increased from 0.605 to 0.63 mmol/g fiber(5% increase) with one added data

[1] Kalyanaraman et al, Comput. Chem.Eng. Submitted

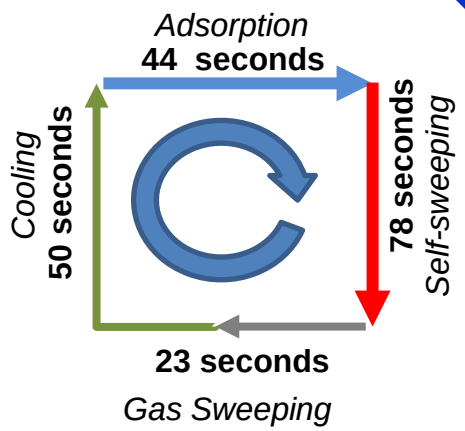
Task Area 5 – Optimization Model & Technoeconomic Analysis

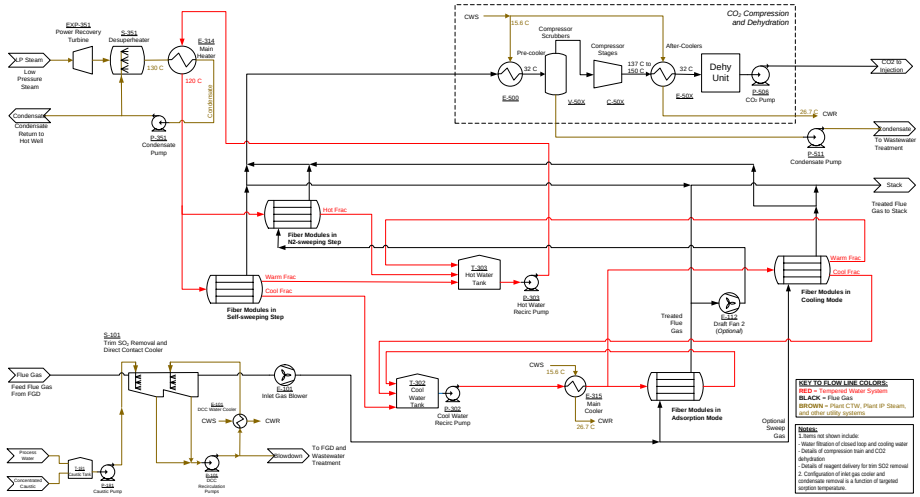
Swernath et al, *Comput. Aided Chem. Eng.*, **2015**, in press.

Overall approach

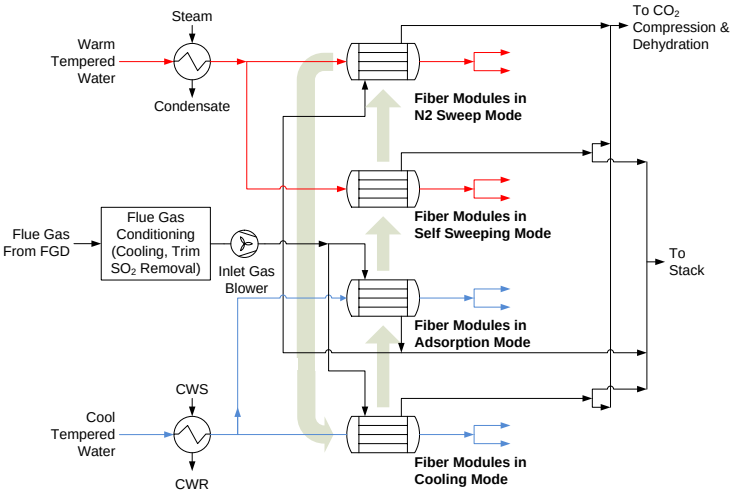
DOE Metric Calculation. Feedback to single fiber design and optimization

Cycle Design on Single Fiber (GT)





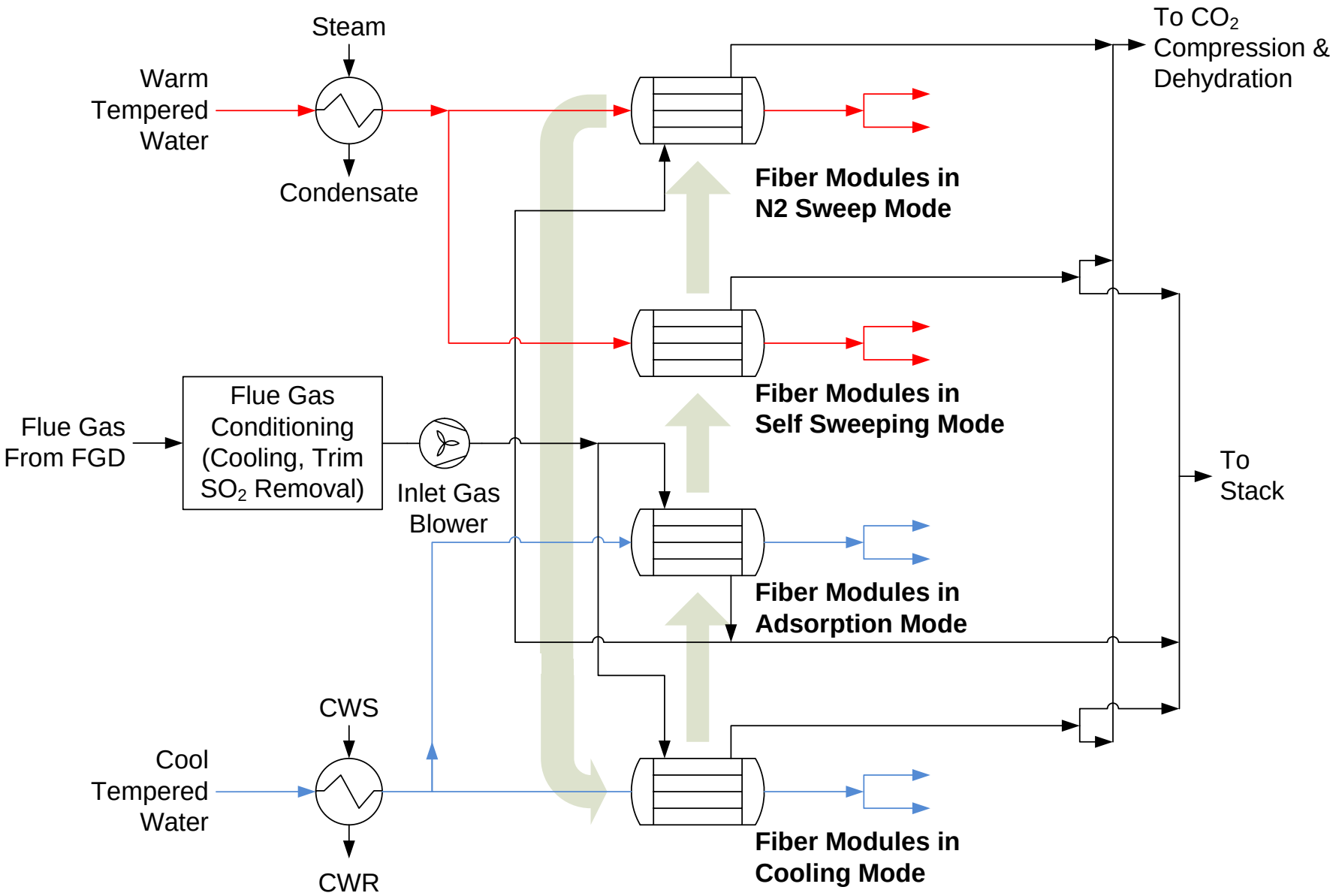
Cycle Model Validation and Scale Up to Module Level (GT and Trimeric)



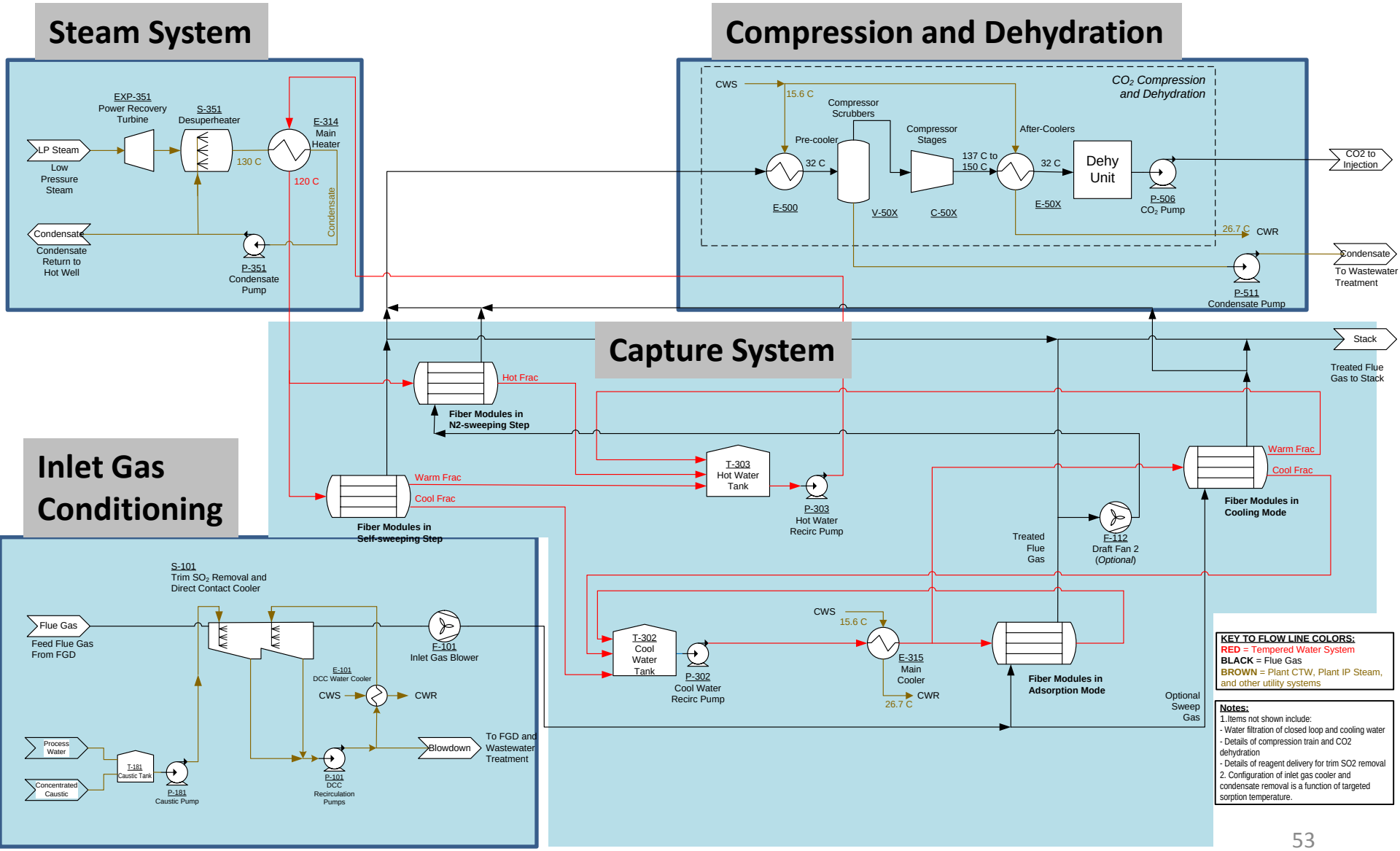
Water Looping for Heat Integration

Integration with Plant Design and Escalation for TEA (Trimeric)

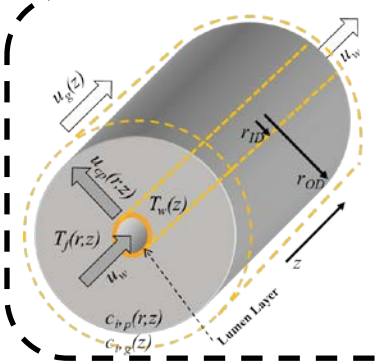
Process Flow Diagram - Cycle Steps



Process Flow Diagram



TEA Methodology: From Single Fiber to Utility Scale (Slide 1 of 3)

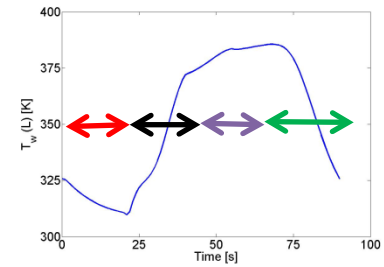


1. Detailed dynamic cyclic simulation of single fiber

Solving model

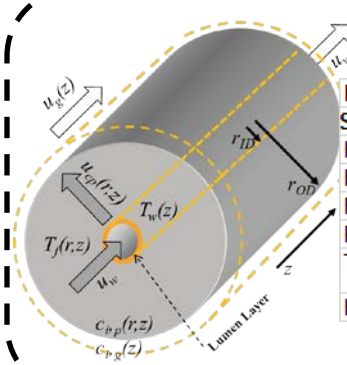
in gPROMS

Ensure purity & recovery constraints met!



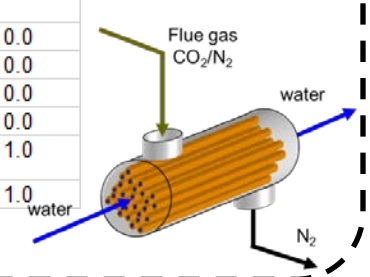
2. Input to TEA

	Sorption	Self Sweeping	N2 Sweep	Cooling
Cycle Time	44	78	23	50
Estimated number of modules	378	670	197	429
Initial bed temperature, C	54.9	60.9	119.9	118.9
Final bed temperature, C	60.9	119.9	118.9	54.9
Inlet gas temperature, C	55	55	55	55
Outlet gas temperature, C	62.8	139.9	137	54.9
Gas velocity, m/s	4.01	-	0.045	0.07
Avg retained water temperature at start of step, C	54.9	59.9	119.9	118.9
Water velocity, m/s	0.290	0.500	0.240	0.500
Inlet water temperature,C	55	120	120	55
"Cool" outlet water temperature, C	60.85	72.65	*138.85*	59.88
Percent of cycle time at "cool" outlet water temp, %	100.0	23.1	0.0	68.0
"Warm" outlet water temperature, C	*62.85*	113.97	118.85	111.22



3. Heat & material balance validation

Description	Units	Sorbing	Self-sweep	N2 Sweeping	Cooling	Error (abs)
Single Fiber Estimates						
Heat of sorption / desorption	J/fiber	45.5	-40.1	-5.3	-0.1	0.0
Fiber sensible heat	J/fiber	-11.3	-111.3	1.9	120.8	0.0
Flue gas sensible heat	J/fiber	0.0	-0.2	0.0	0.2	0.0
Retained water sensible heat	J/fiber	-5.0	-60.5	1.0	64.5	0.0
Tempered water I/O sensible heat	J/fiber	-25.7	209.6	1.9	-184.7	1.0
Heat Balance	J/fiber	3.4	-2.3	-0.5	0.4	1.0



TEA Methodology: From Single Fiber to Utility Scale (Slide 2 of 3)

4. Parasitic Energy and Escalation

		No Capture	Unescalated	Escalated
Equivalent Electrical Capacity	MWe	580.4	580.4	792.8
Steam derate for carbon capture	MWe	0.0	113.8	155.4
Steam turbine power	MWe	580.4	466.6	637.3
Steam power recovery	MWe	0.0	-49.2	-67.3
Base plant auxiliary load	MWe	30.4	30.4	41.5
CO2 Capture Direct Electrical Derate	MWe	0.0	82.8	113.0
Net Power	MWe	550	402.7	550

5. Equipment Selection and Pricing with Cost Curves

Equipment Name	Equipment type	Base cost	Base size	Base units	Base year	Base CPI	Min Size	Max Size	# Units	Size each	$/each	$ total
Trim SO2 Water Cooler	shell and tube	28,102	1,000	ft2	Q1 2011	564.8	1000	18000	1	10,886	151,000	151,000
Main Heater	Shell and tube, TEMA BEM	28,102	1,000	ft2	Q1 2011	564.8	1000	18000	16	17,038	210,000	3,360,000

6. Factored Capital Cost Estimate and Operating Cost Estimate

DOE Methodology (SAG) →

Total purchased equipment costs (PEC)
Fibers
CO2 capture
CO2 compression
Process Plant Cost (PPC)
Total Plant Cost (TPC)
Total Plant Investment (TPI)
Total Capital Requirement (TCR)
Annual Capital Charge

DOE O&M Inputs (Solicitation) →

Maintenance and materials
Labor
Fiber replacement
Cooling water
Makeup water
Wastewater treatment
Solid waste disposal
TS&M

TEA Methodology: From Single Fiber to Utility Scale (Slide 3 of 3)

7. Cost metrics

Escalation factor	
Levelized cost of electricity	mills/kWh
Increase in cost of electricity	%
Levelized cost of steam	$/1,000 lb
Cost of CO_2 Capture	$/ton
Change in Net Plant Efficiency	%
Net Plant Efficiency	%

8. Assess sensitivity to cycle parameters

- ❑ Cycle time
- ❑ Water temperature & velocities etc

9. Repeat step 1-8 for new operating conditions identified in 8

DOE Design Basis

- Specified in solicitation, similar but not identical to DOE baseline reports
- 550 MWe net, 90% CO_2 capture
- Supercritical steam cycle
- Inlet flue gas conditions and composition
- Outlet CO_2 at 95% purity and 15272 kPa (2215 psia)
- Cooling water supply, return, and approach temperatures
- Steam delivery conditions:
  - IP/LP crossover
  - 395 °C (743 °F) and 1156 kPa (168 psia)
  - Thermal energy penalty of 0.0911 kWe/(lb/h steam)
- Detailed inputs provided in final TEA report

Fiber and Cycle Parameters for RVTSA Case

RTSA Conditions and Cycle Inputs

Sorption temperature	55	C
Desorption temperature	120	C
Desorption pressure	0.2	bar
Adsorption swing capacity	0.854	mmol CO2 / g sorbent

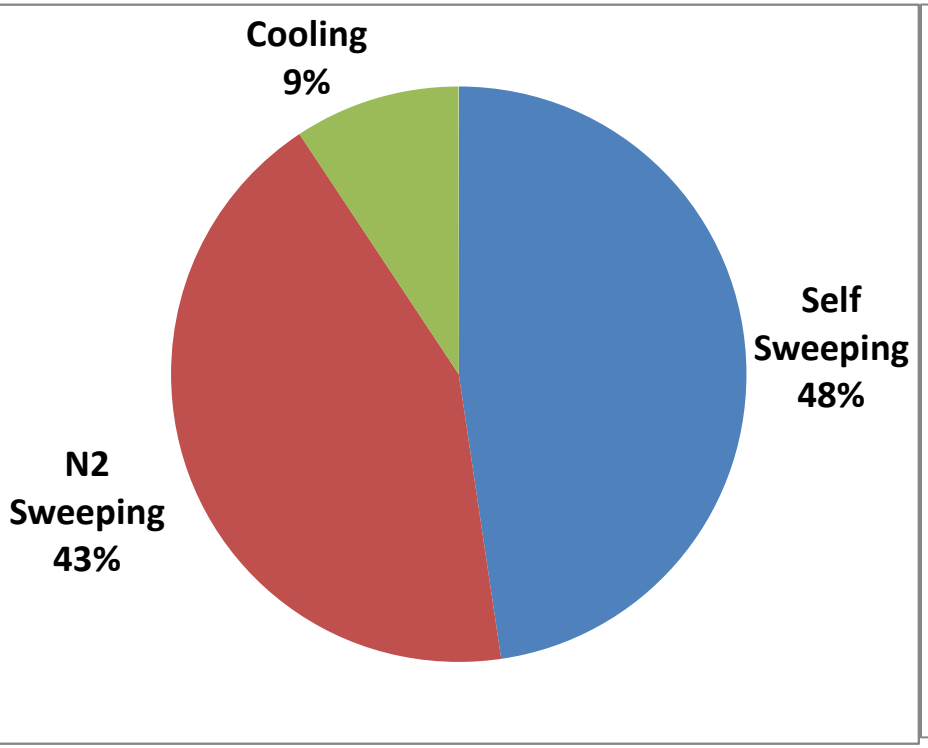
Fiber Characteristics

Heat of Sorption	59	kJ/gmol
Sorbent loading	57	wt%
Fiber module diameter	1	m
Fiber module length	3	m
Module packing fraction	60	vol %
Fiber OD	1200	µm
Fiber ID	320	µm
Fibers per module	420,000	fibers/module

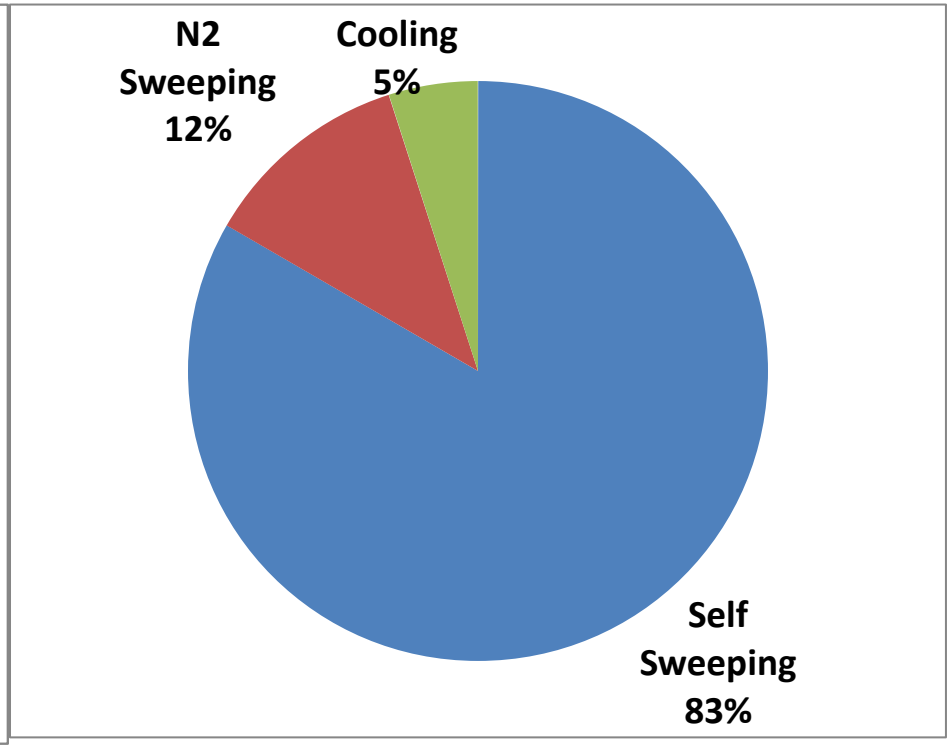
	Sorption	Self Sweep	N2 Sweep	Cooling	Cycle Total
Cycle time, seconds	44	78	23	50	**195 sec (3 minutes)**
Number of modules	380	670	200	430	1700 (Unescalated)
	520	920	270	590	**2300 (Escalated)**
					1350 tonne fiber (Esc)

CO_2 Balance in RTSA and RVTSA

RTSA



RVTSA



95% CO_2 purity
91% Recovery
Targets Met

Energy and Escalation Results – RVTSA

Description		Units	Value
Escalation Factor		-	1.37
Energy			
	Sorption enthalpy	MWth	162
	Sensible heat	MWth	315
	Total enthalpy per sorption or desorption step	MWth	477
	Main heater duty	MWth	375
	Main cooler duty	MWth	-367
	Intraprocess heat recovery	%	21
Steam usage		kg/h	771,000
Derate			
	Direct Electrical Derate	MWe	113.0
	Steam Derate	MWe	155.4
	Steam Turbine Energy Recovery	MWe	-67.3
	Total Derate for CO_2 Capture	MWe	201.2

Escalated Capital Costs

Description	Units	Year 3 (Jan 2015)	Comments
Total purchased equipment costs (PEC)	MM$	178	
Fibers	MM$	102	
CO_2 capture	MM$	43.6	
CO_2 compression	MM$	33.1	
Process Plant Cost (PPC)	MM$	507	PPC = PEC + Direct Costs
Total Plant Cost (TPC)	MM$	847	TPC = PPC + Engineering + Process Contingency + Project Contingency (30%)
Total Plant Investment (TPI)	MM$	898	TPI = TPC + Interest and Inflation
Total Capital Requirement (TCR)	MM$	923	TCR = TPI + Startup + Initial Fill + Working Capital + Land + Others
Annual Capital Charge	MM$/year	162	

Technoeconomic Metrics – RVTSA

Description	Units	Year 3 (Jan 2015)
Levelized Costs of Electricity and Steam		
Levelized cost of electricity	mills/kWh	126
Levelized cost of steam	$/1,000 lb	11.5
Cost of CO_2 Capture		
Total Annual Cost of CO_2 Capture	MM$/year	237
Impact of CO_2 Capture on Plant Efficiency		
Net Plant Efficiency without CO_2 Capture (HHV)	%	39.3
Net Plant Efficiency with CO_2 Capture (HHV)	%	28.8
Change in Net Plant Efficiency	%	-10.5

Metrics were calculated using simplified equations specified in the solicitation.
Net plant efficiency is based on supercritical steam cycle.

Performance Evolution during Project

Description	Units	Year 2 Q4 (Sept 2013)	Year 3 (July 2014)	Year 3 (Jan 2015)
		RTSA	RTSA	RVTSA – 0.2 bar
Escalation Factor		1.67	1.53	1.37
Levelized Costs of Electricity and Steam				
Levelized cost of electricity	mills/kWh	178	154	126
Levelized cost of steam	$/1,000 lb	16.2	14.0	11.5
Cost of CO_2 Capture				
Total Annual Cost of CO_2 Capture	MM$/year	277	302	237
Impact of CO_2 Capture on Plant Efficiency				
Net Plant Efficiency without CO_2 Capture (HHV)	%	39.3	39.3	39.3
Net Plant Efficiency with CO_2 Capture (HHV)	%	22.0	25.6	28.8
Change in Net Plant Efficiency	%	-17.3	-13.7	-10.5

Major Advances

Major Advances

- First chemisorbent-fiber composite contactors for RTSA
- Invention of post-spinning amine infusion method of creating and recharging sorbents
- Development of dual layer spinning method for scalable lumen layer formation
- Up to 70% recovery of the heat of adsorption via heat integration
- Detailed single fiber model validated with experiments
- Reduction of RTSA cycle times to 3 minutes
- Development of multi-scale model spanning the nanoscale to the plant scale, with rapid data transfer across scales

Remaining Challenges

Remaining Key Challenges

- Large scale, low cost process control – gas switching (for practical operation, not for lab scale)

- Understanding dynamics by long term operation of complete cycles with bore-side heating/cooling
  -- conducted >100 consecutive cycles with external heating/cooling
  -- conducted <10 consecutive cycles with bore-side heating/cooling

- Complexities associated with water (humidity)
  -- model results based on dry feeds
  -- experimental tests with humidity conducted, humidity helps capacity and kinetics
  -- approach to pseudo-steady-state humidity levels in fibers not yet modeled

- Incremental increases in breakthrough capacity

- Manufacturing cost estimates of fibers have significant uncertainty

Summary

- **Rapid Temperature Swing Adsorption (RTSA) enabled by a new contactor** combined with solid amine sorbents.

- Cycle allows **quasi-isothermal adsorption with significant sensible heat recovery** due to nanoscopic shell-tube heat exchanger design.

- Not refining a decades old process with decades old sorbents – rather, developing a fundamentally new contactor with modern sorbents – significant advances in first three years.

- Technoeconomic analysis suggests targets for improvement.
  -- Current parasitic load, Gen 3 fibers, RVTSA (1.37 escalation factor)
  -- Initial parasitic load, Gen 1 fibers, RTSA (1.67 escalation factor)

Publication and Inventions

Publications

1. Labreche, Ying., Lively, Ryan ; Rezaei, Fateme; Chen, Grace; Jones, Christopher W; Koros, William J., *Post-spinning infusion of poly(ethyleneimine) into polymer/silica hollow fiber sorbents for carbon dioxide capture.* Chemical Engineering Journal, 2013, 221, 166-175.
2. Rezaei, Fateme; Lively, Ryan; Labreche, Ying; Chen, Grace; Fan,Yanfang; Koros, William; Jones, Christopher, *Aminosilane-grafted polymer/silica hollow fiber adsorbents for CO_2 capture from flue gas.* ACS Applied Materials & Interfaces, 2013, 5, 3921-3931.
3. Rezaei, Fateme; Jones, Christopher, *Stability of Supported Amine Adsorbents to SO_2 and NO_x in Post-Combustion CO_2 Capture Process-1. Single Component Adsorption*.. Industrial & Engineering Chemistry Research, 2013, 52, 12192-12201.
4. Fan,Yanfang; Lively, Ryan; Labreche, Ying; Rezaei, Fateme; Koros, William; Jones, Christopher, *Evaluating CO_2 dynamic adsorption performance of polymer/silica supported poly(ethylenimine) hollow fiber sorbents in rapid temperature swing adsorption.* International Journal of Greenhouse Gas Control, 2014, 21, 61-71**.**
5. Labreche, , Ying; Fan, Yanfang; Rezaei, Fateme; Lively, Ryan; Jones, Christopher; Koros, William, *Poly (amide-imide)/Silica Supported PEI Hollow Fiber Sorbents for Postcombustion CO_2 Capture by RTSA.* ACS. Appl. Mater. Interfaces, 2014, 6, 19336-19346.
6. Rezaei, Fateme; Jones, Christopher, *Stability of Supported Amine Adsorbents to SO_2 and NO_x in Post-Combustion CO_2 Capture Process-2. Multicomponent Adsorption*.. Industrial & Engineering Chemistry Research, 2014, 53, 12103-12110.
7. Fan,Yanfang; Labreche, Ying; Lively, Ryan; Koros, William; Jones, Christopher, *Dynamic CO_2 Adsorption Performance of Internally Cooled Silica Supported Poly(ethylenimine) Hollow Fiber Sorbents.* AIChE J., 2014, 60, 3878-3887**.**
8. Rezaei, Fateme; Swernath, Subramanian; Kalyanaraman, Jayashree; Lively, Ryan; Kawajiri, Yoshiaki; Realff, Matthew, *Modelling of Rapid Temperature Swing Adsorption Using Hollow Fiber Sorbents.* Chem. Eng. Sci., 2014, 113, 62-67.
9. Kalyanaraman, Jayashree; Fan, Yanfang; Lively, Ryan; Koros, William; Jones, Christopher; Realff, Matthew; Kawajiri, Yoshiaki, *Modelling and Experimental Validation of Carbon Dioxide Sorption on Hollow Fibers Loaded with Silica-Supported Poly(ethylenimine).* Chem. Eng. J., 2015, 259, 737-751.
10. Labreche, Ying; Fan, Yanfang; Lively, Ryan; Jones, Christopher; Koros, William, *Direct Dual Layer Spinning of Aminosilica/Torlon® Hollow Fiber Sorbents with a Lumen Layer for CO_2 Separation by Rapid Temperature Swing Adsorption.* J. Appl. Polym. Sci., 2015, 132, 4185.
11. Fan,Yanfang; Kalyanaraman, Jayashree; Labreche, Ying; Rezaei, Fateme; Lively, Ryan; Realff, Matthew; Koros, William; Jones, Christopher; Kawajiri, Yoshiaki, *CO_2 Sorption Performance of Composite Polymer/Aminosilica Hollow Fiber Sorbents.* Ind. Eng. Chem. Res., 2015, 54, 1783-1795**.**
12. Swernath, Subramanian; Searcy, Kathine; Rezaei, Fateme; Labreche, Ying; Lively, Ryan; Realff, Matthew; Kawajiri, Yoshiaki, *Optimization and Techno-Economic Analaysis of Rapid Temperature Swing Adsorption (RTSA) Process for Carbon Capture from Coal-Fired Power Plant.* Comput. Aided Chem. Eng., 2015, in press.
13. Add Jayashree's paper that is submitted.
14. Fan, Yanfang; Rezaei, Fateme; Labreche, Ying; Lively, Ryan P.; Koros, William J.; Jones, Christopher W. *Stability of Amine-based Hollow Fiber CO2 Adsorbents to NO and SO_2*. Fuel, to be submitted 04/15.

Inventions

1. " Dual Layer Spinning with Lumen Layer PAI Polymer/Silica/PEI Hollow Fiber Sorbent for RTSA" submitted on 11/25/ 2013, The internal reference number is GTRC ID 6560. The invention is sponsored by GE and US DOE. Y. Labreche, W.J. Koros, R. P. Lively
2. "Novel Amine Post-Spinning Infused Polymer/Silica Composite Hollow Fiber Sorbents" submitted on 07/18/2012. The internal reference number is GTRC ID 6142. The invention is supported by GE and US DOE. Y. Labreche, W.J. Koros, R. P. Lively, F. Rezaei, G. Chen, C. W. Jones, D. S. Sholl