DOE Award #: DE-FE0007804

Rapid Temperature Swing Adsorption using Polymer/Supported Amine Composite Hollow Fibers

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Post-Combustion Sorbent-Based Capture
2014 NETL CO_2 Capture Technology Meeting
Sheraton Station Square, Pittsburgh, PA
Tuesday, July 29, 2014

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School of Chemical & Biomolecular Engineering

Budget:

DOE contribution:

Year 1:	$ 691,955
Year 2:	$ 847,672
Year 3:	$ 847,006
Total:	$2,386,633 (79%)

Cost Share Partners:

GE Energy:	$ 420,000
Algenol Biofuels:	$ 183,900
Southern Company:	$ 33,147
Total:	$ 637,047 (21%)

Total Budget: $3,023,680

Project Performance Dates – October 2011 to September 2014

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

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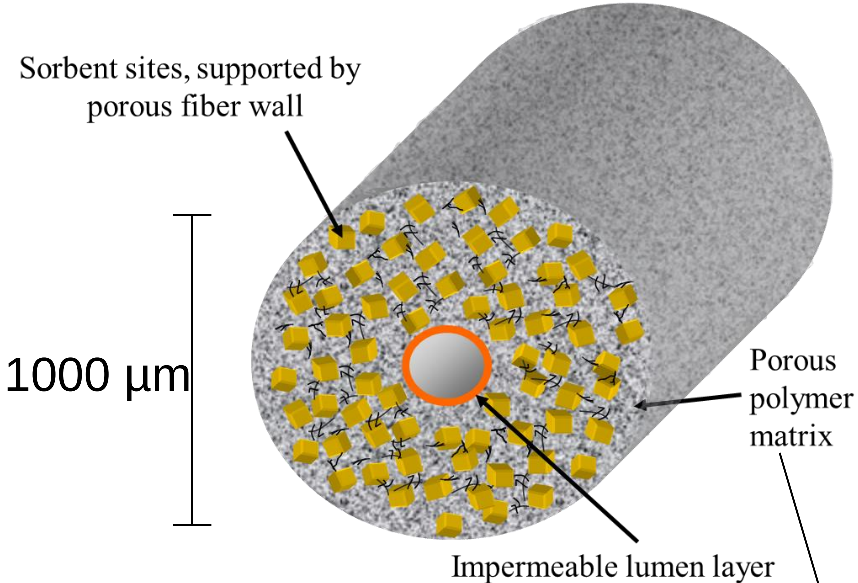
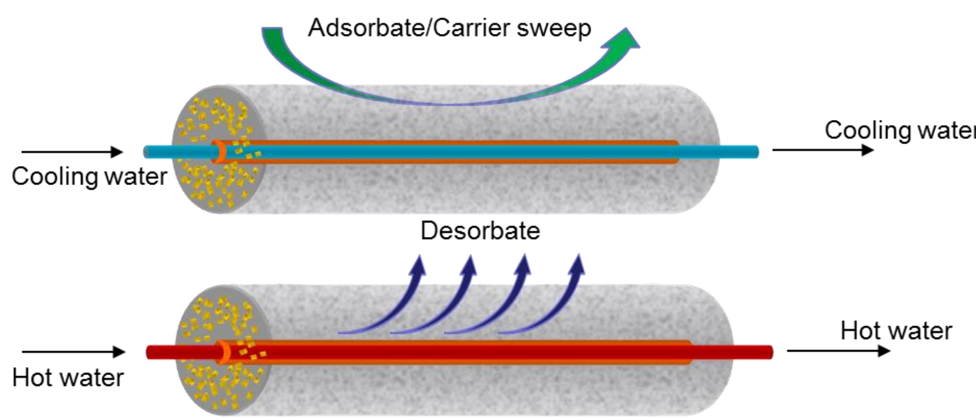
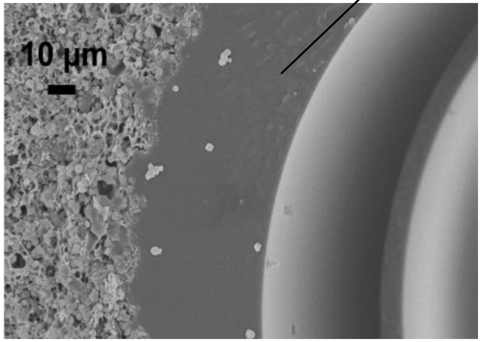
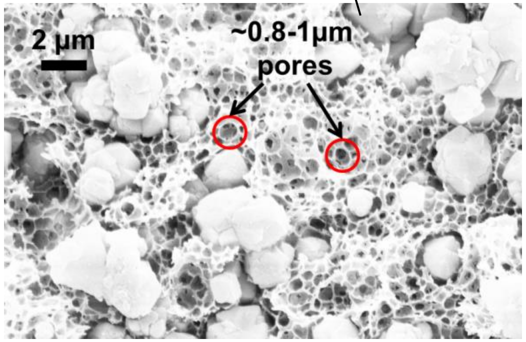
Hollow Fiber Contactor:



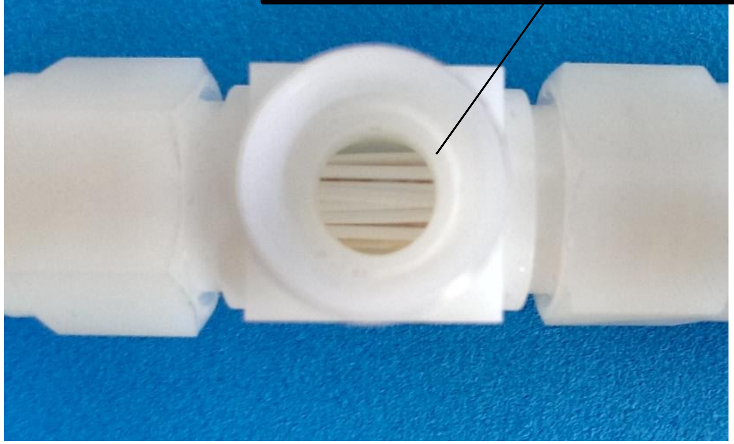


Ideal temperature swing adsorption





Bundle of 40 fibers in a 1.5' module at GT



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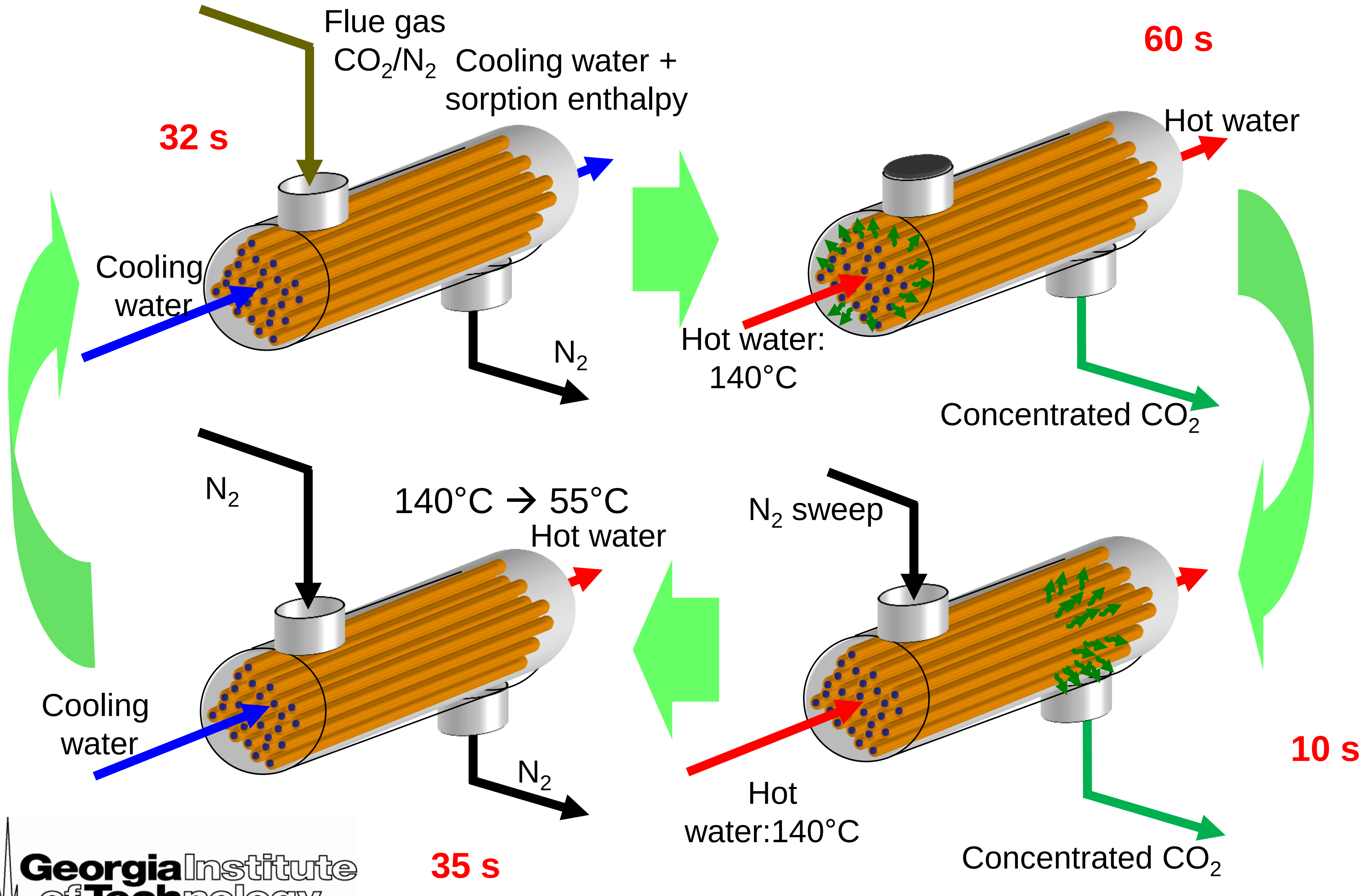
RP Lively et al., *Ind. Eng. Chem. Res.*, **2009**, 48, 7314-7324

RTSA Qualitative Cycle:



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Hollow Fiber Contactor:

Key Experimental Tasks:

1) **Spinning** of high solid content (50-66 volume%), flexible hollow fibers, using low cost commercial polymers (e.g. cellulose acetate, Torlon®).

2) **Incorporating amines** into composite polymer/silica hollow fibers.

3) Building and demonstrating **RTSA systems** for CO_2 capture from simulated flue gas.

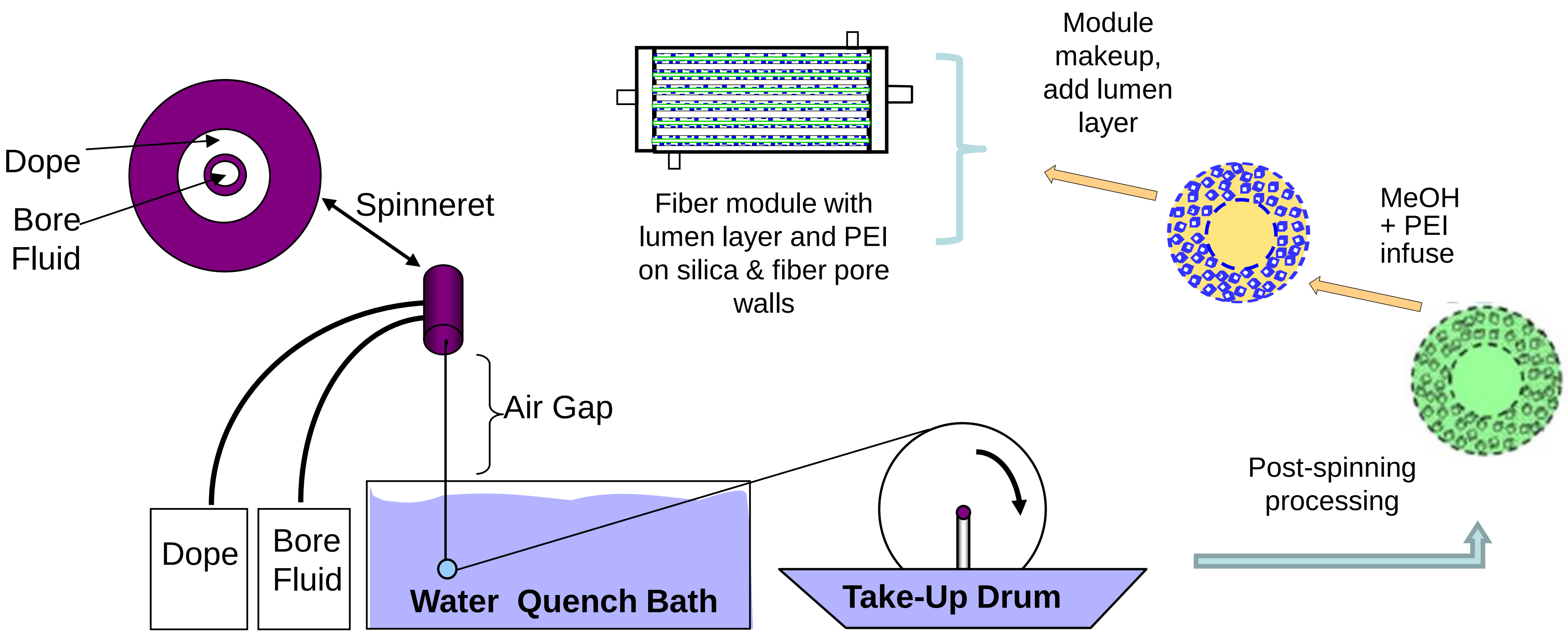
4) Assessing the impact of operating conditions on deactivation via (i) oxidation, (ii) **SOx** exposure, (iii) **NOx** exposure.

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

6) Demonstrating **steady-state cycling** of multi-fiber module with heating/cooling.

Post-Spinning Infusion:

1) Spinning of high solid content (50-66 volume%), flexible hollow fibers
2) Incorporating amines into composite polymer/silica hollow fibers.



Y. Labreche et al., *Chemical Engineering Journal*, **2013**, 221, 166-175.
F. Rezaei et al., *ACS Applied Materials & Interfaces*, **2013**, 5, 3921-3931.
Y. Fan et al., *International Journal of Greenhouse Gas Control*, **2014**, 21, 61-72.

SOx/NOx Experiments:

4) Assessing the impact of operating conditions on deactivation via (i) oxidation, (ii) SOx exposure, (iii) NOx exposure.

-- 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

-- single component and multicomponent sorption studies

F. Rezaei et al., *Industrial & Engineering Chemistry Research,* **2013**, 52, 12192-12201.

F. Rezaei et al., *Industrial & Engineering Chemistry Research,* **2014**, in press.

SOx/NOx studies facilitated by support of *Southern Company*.

SOx/NOx Experiments:

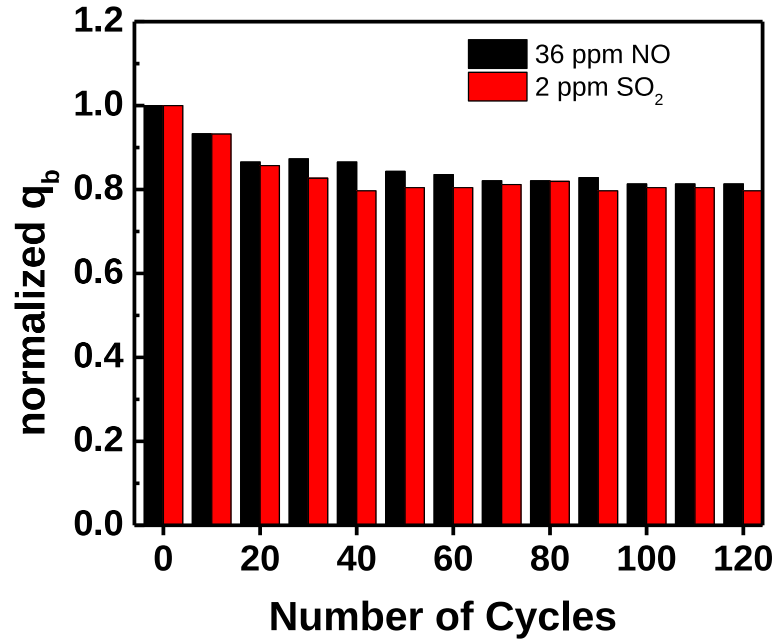
4) Assessing the impact of operating conditions on deactivation via (i) oxidation, (ii) SOx exposure, (iii) NOx exposure.

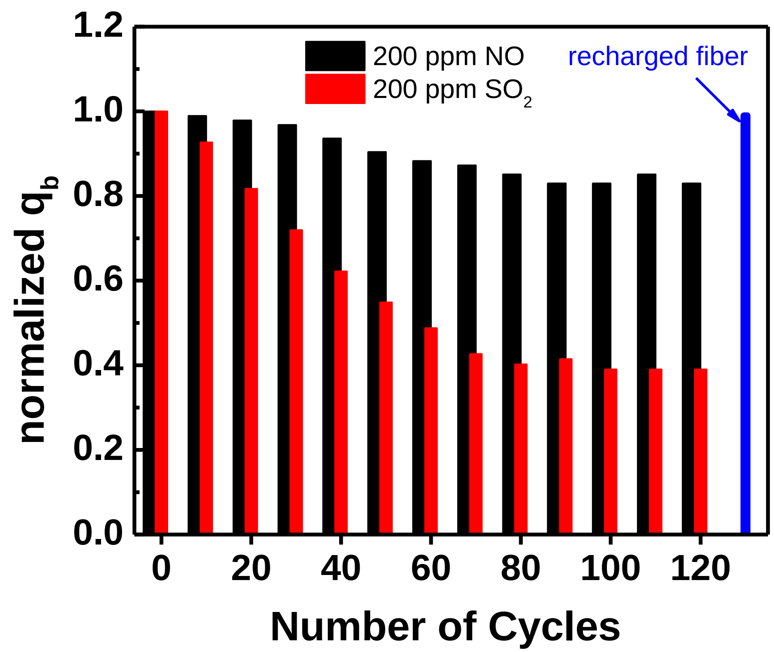
-- **NO_2, SO_2** adsorb strongly, but have modest impact at low concentration

-- saturation capacity loss observed

-- high concentration of gases (200 ppm) cause significant capacity loss

-- deactivated fibers can be stripped of amine and recharged in the field for **full capacity regeneration**



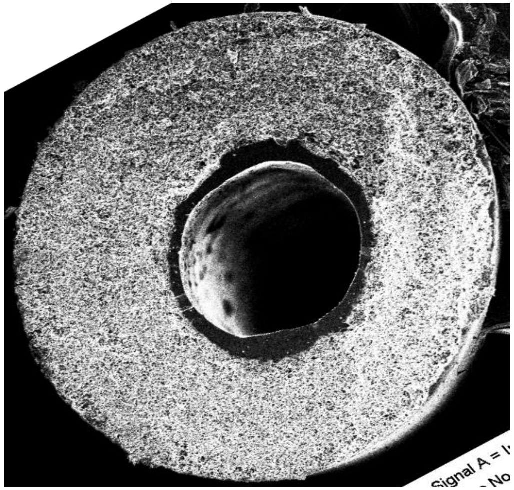


Hollow Fiber Contactor as Heat Exchanger:

5) **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

Y. Labreche et al., *ACS Applied Materials & Interfaces*, **2014**, submitted.

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- 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

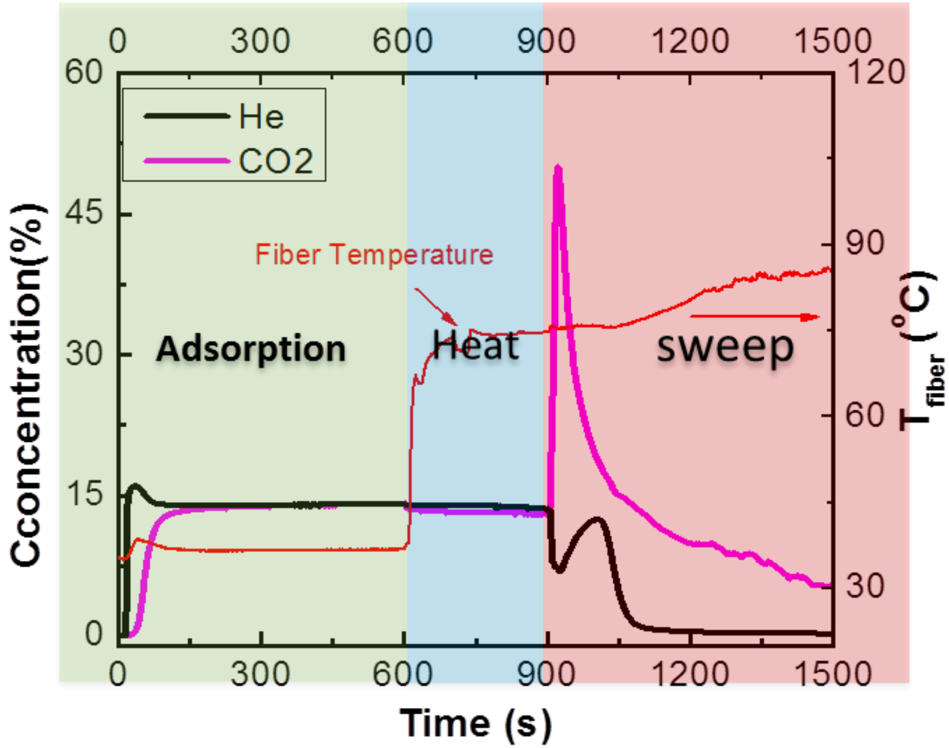
Hollow Fiber Contactor as Heat Exchanger:

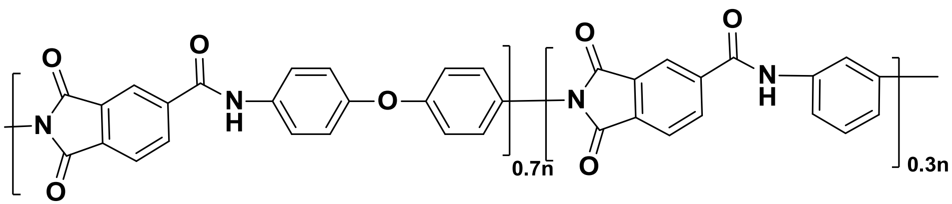
- Torlon®, commercially available
- Improved thermal & chemical stability
- Excellent barrier properties for both water and gases
- No need for problematic latex post-treatment

Y. Fan et al.,
AIChE Journal, **2014**, submitted.

Y. Labreche et al.,
Polymer, **2014**, in preparation.

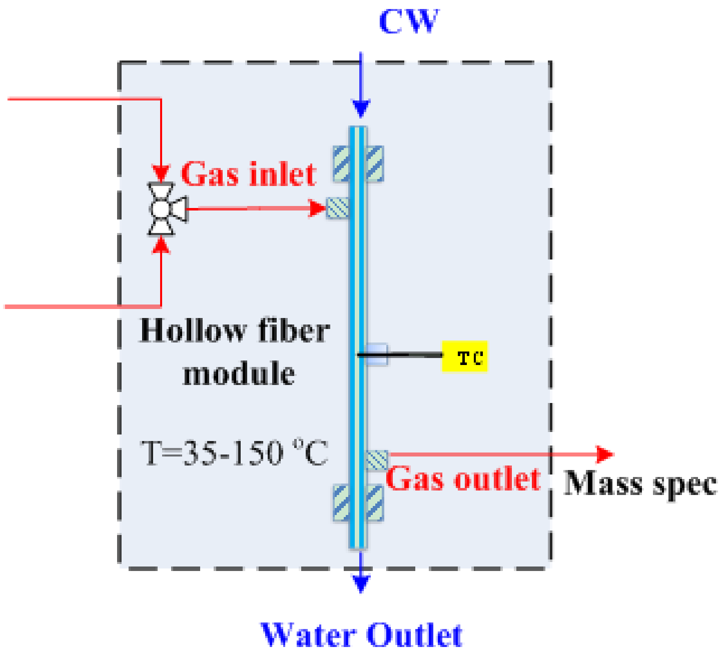
Lab scale heat capture efficiency during adsorption: ~72%

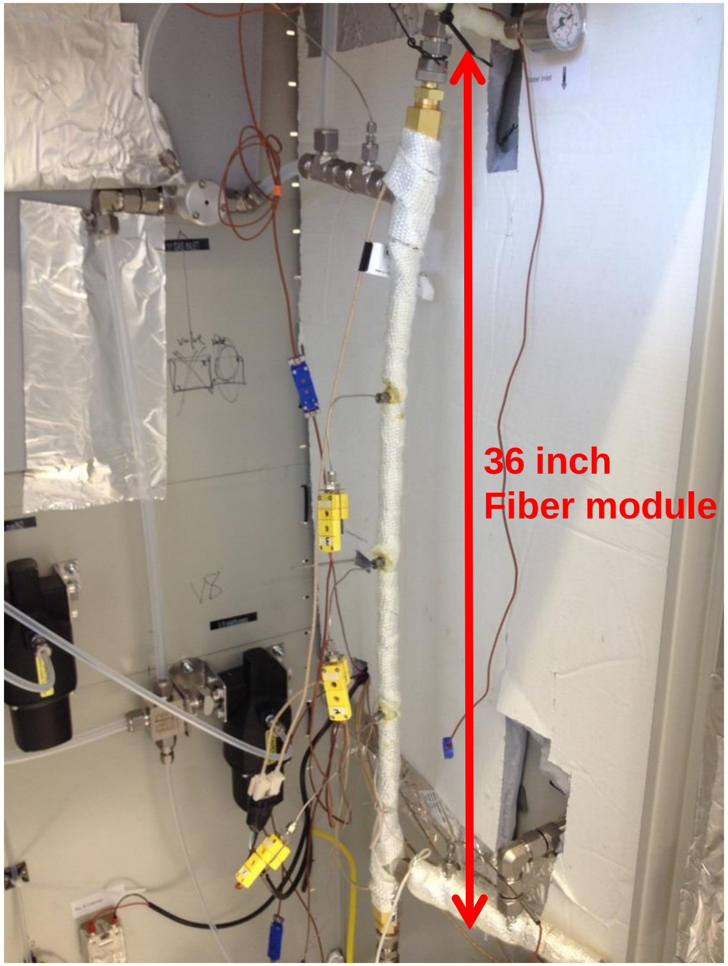




Fiber Cycling – Model and Realistic Conditions:

6) Demonstrating steady-state cycling of multi-fiber module with heating/cooling.



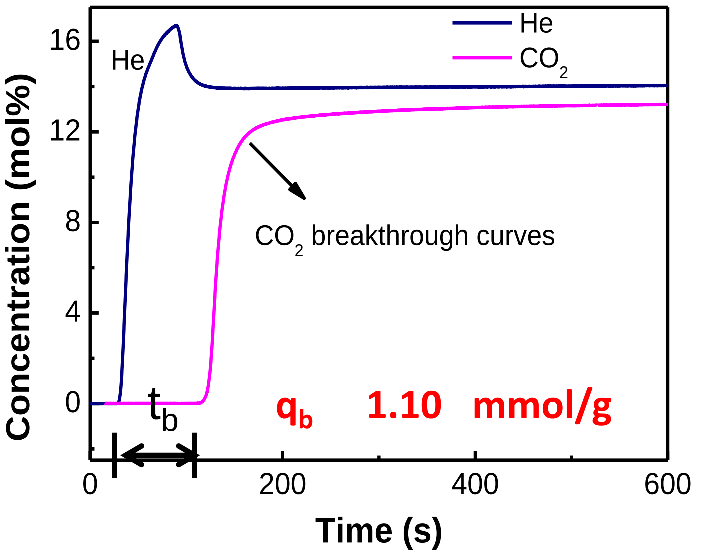


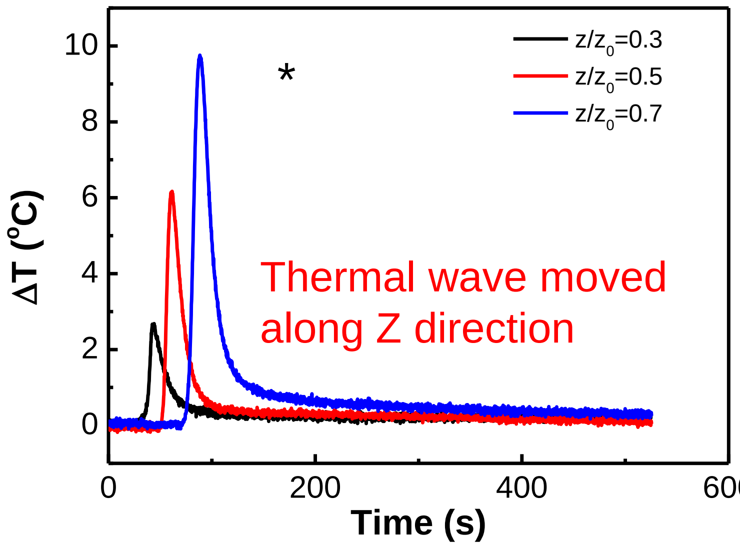
Flue gas composition: 35 ^{o}C, 1 atm

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

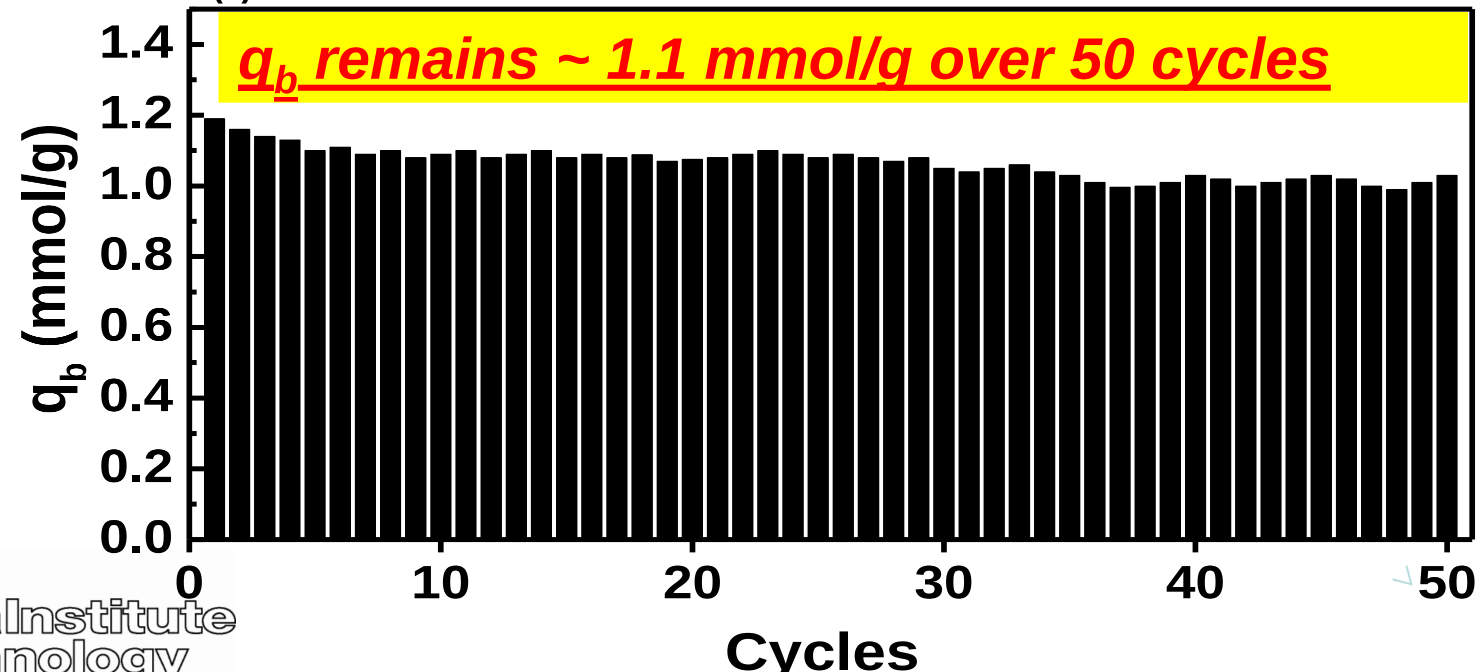
6% H_2O, balance gas N_2

CO_2 Sorption in Uncooled Generation 2 Fibers:





*** Estimated thermal excursion is ~ 63 ºC 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

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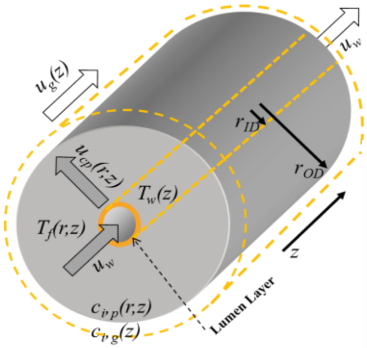
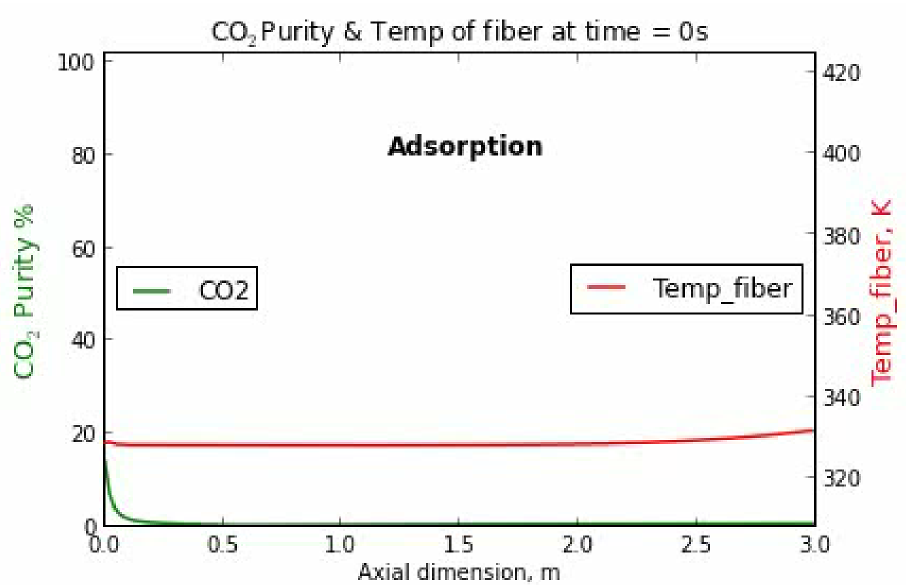
(mol/kg fiber)	q_{pe}	q_b	q_s
Generation 1 fibers:	1.1	0.5	0.30
Generation 2 fibers:	1.5	1.1	0.65
Generation 3 fibers:	2.0	1.3	0.75

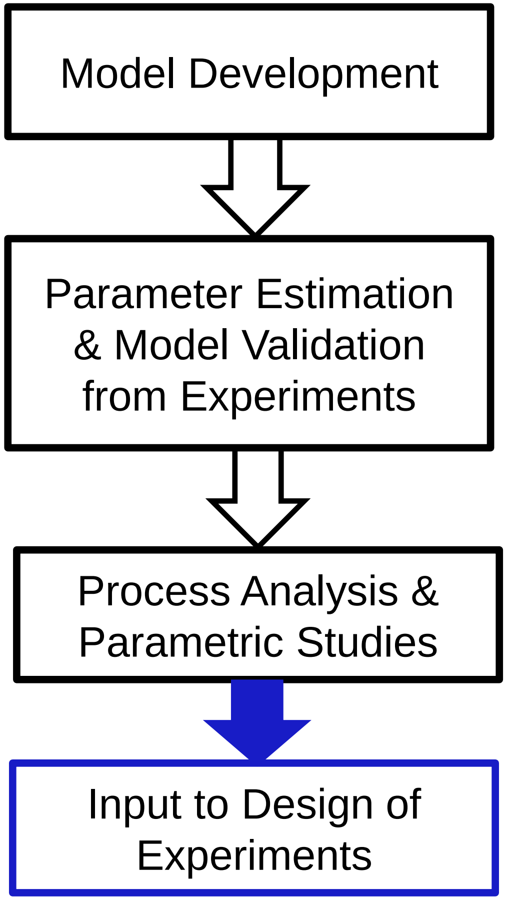
(260% increase in q_b in 2 years)

Model Development (Single Gen 2 Fiber Modeling):



Cyclic steady state simulation





- Adsorption = 32 s
- Self Sweeping/Heating = 60 s
- N_2 sweeping = 10 s
- Cooling = 35 s

Cycle Time = 137 s

F. Rezaei et al., *Chemical Engineering Science*, **2014**, 113, 62-76.

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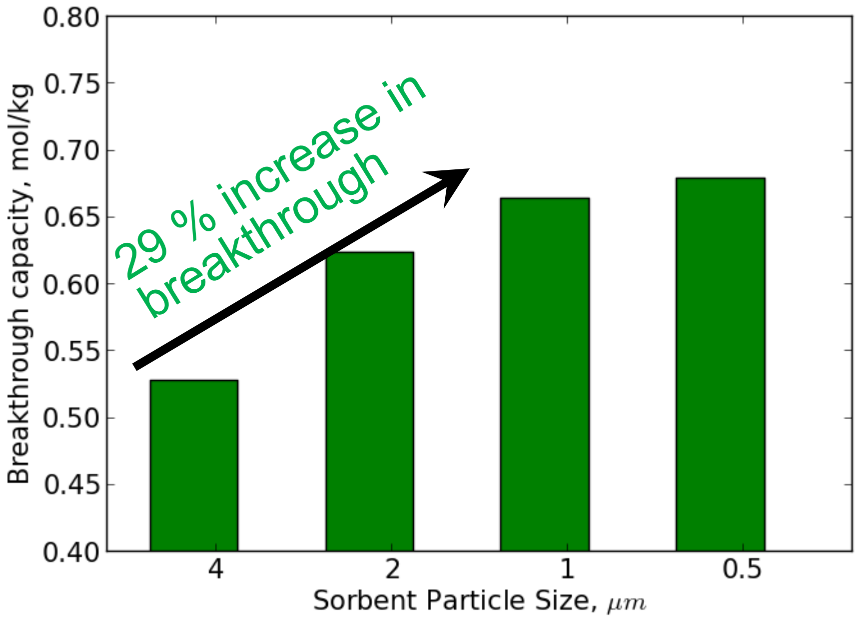
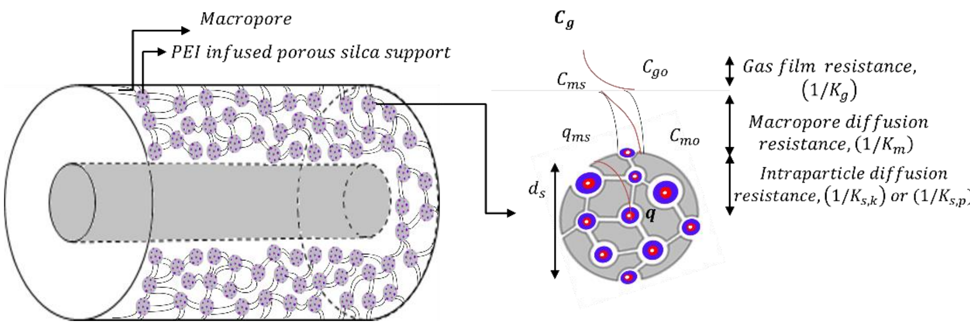
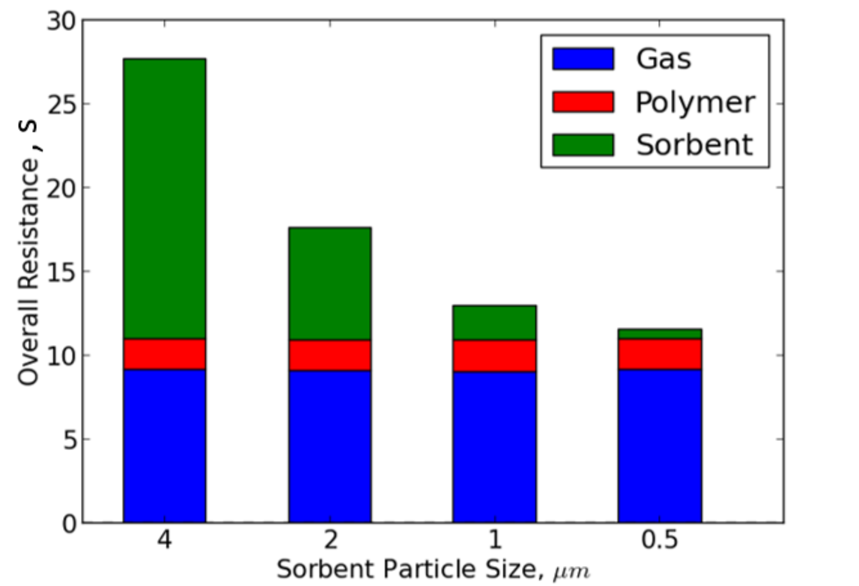
Process Improvement from Modeling : Effect of Sorbent Size:



Hollow fiber schematic with different mass transfer resistance components



Overall mass transfer resistance vs. sorbent size



- Model predicts increase in breakthrough capacity due to decrease of mass transfer resistance
- Smaller silica particles to be employed experimentally.

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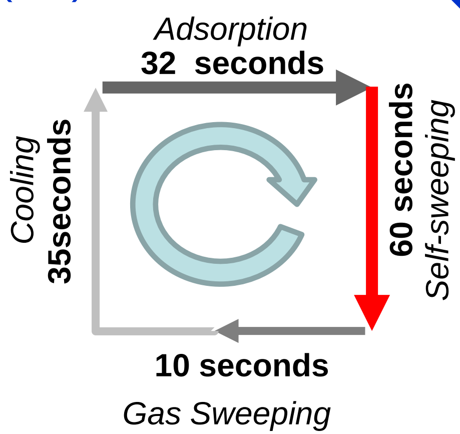
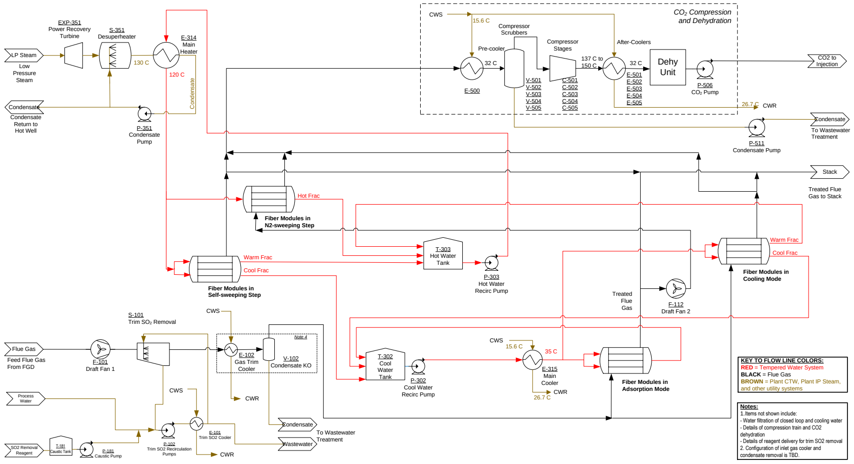
Overall approach:

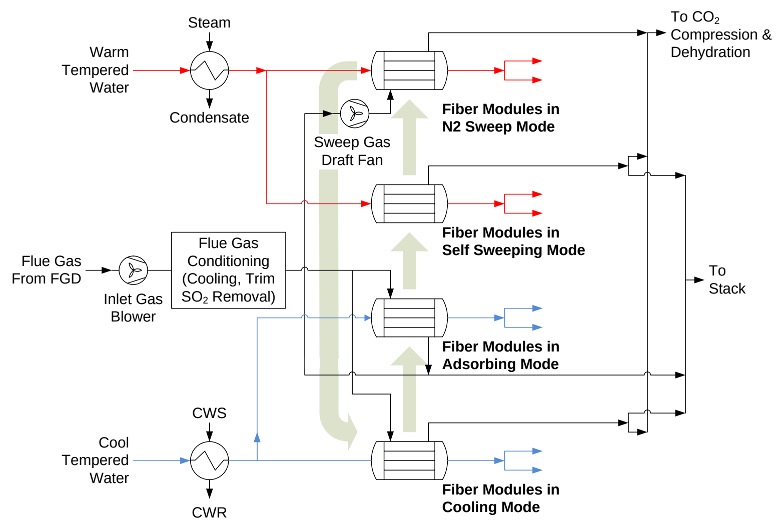
Cycle Design on Single Fiber (GT)



DOE Metric Calculation. Feedback to single fiber design and optimization



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)

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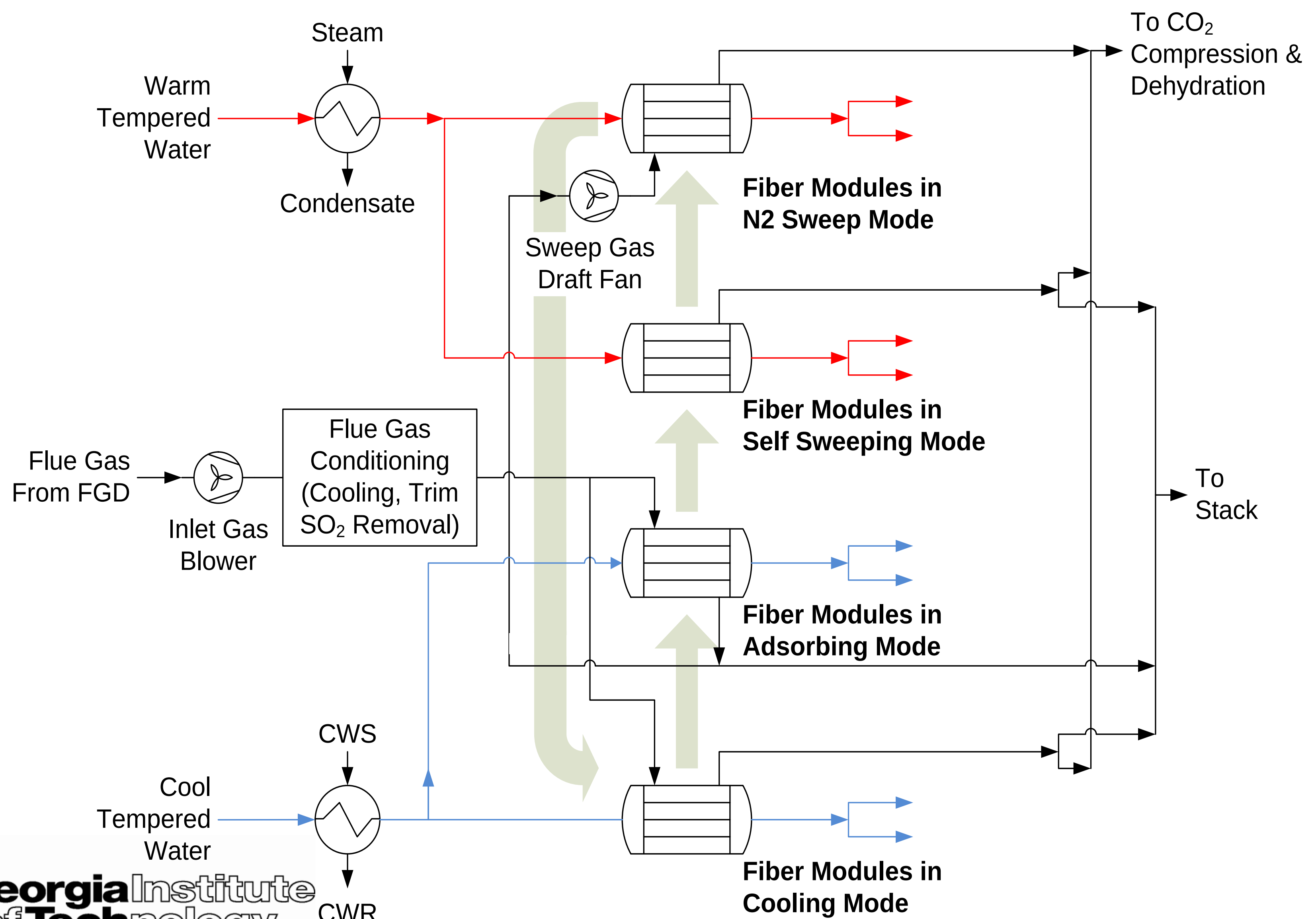
Process Flow Diagram - Cycle Steps:



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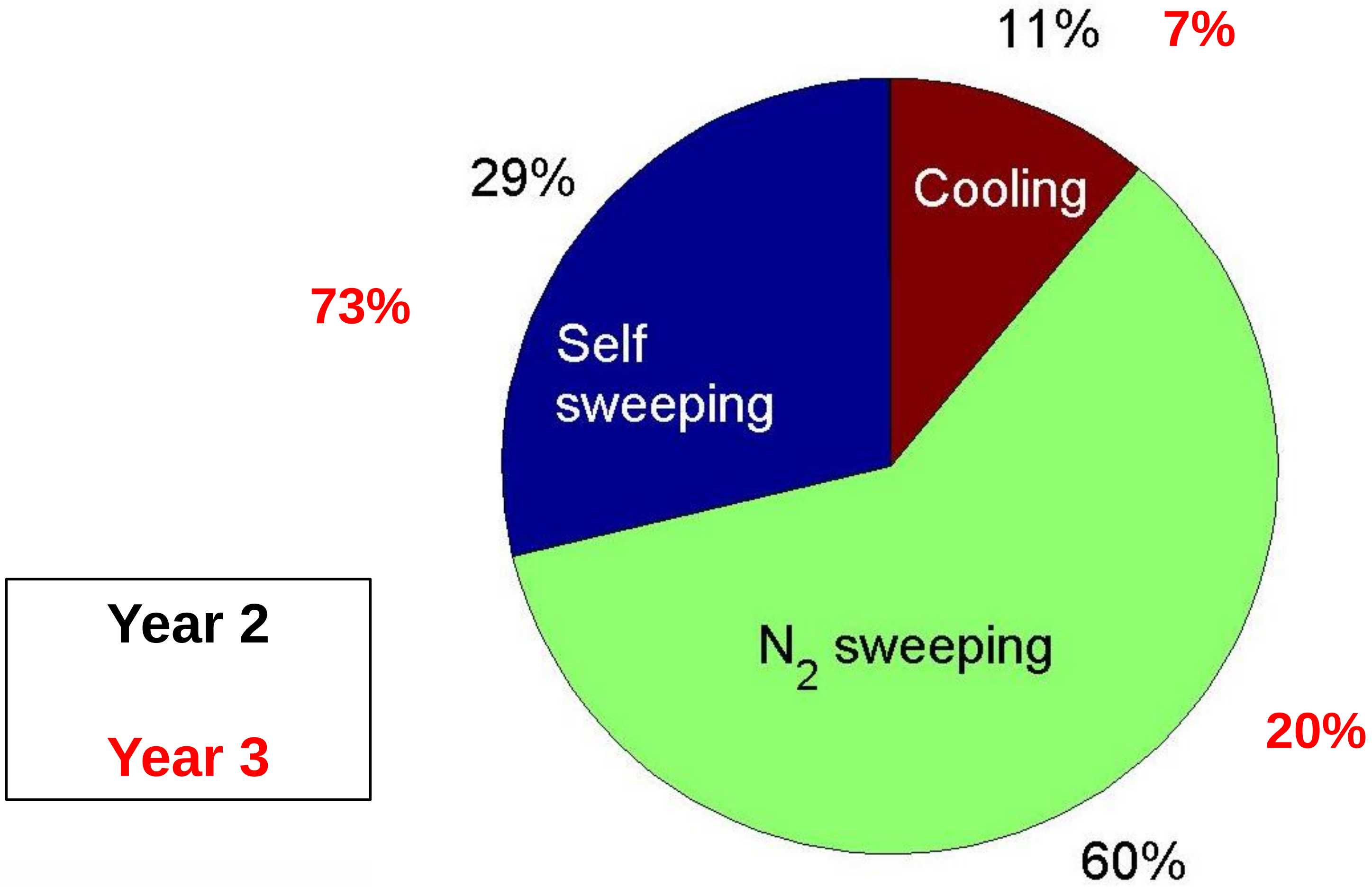
CO_2 Balance:

CO_2 purity of 95% and recovery of 90% per pass



Technoeconomic Evaluation Methodology:

The current technoeconomic evaluation employs a similar methodology to the first and second year:

- Outputs from cyclic steady state fiber model (e.g., tempered water flow rates and temperatures) were abstracted and used as inputs to steady-state process model
- Heat and material balances were used to size and select equipment
- Capital costs, operating costs, and technoeconomic metrics were calculated according to DOE methodology

Equipment pricing was improved over year 1:

- Equipment cost curves were developed to accommodate more rapid evaluation of process options by overall modeling team.
- Aspen In-plant Cost Estimator replaced PDQ$ as the equipment cost estimating software.

Year 2, CO_2 recovery target (93%) was met, but CO_2 purity was not (82%).

Year 3, CO_2 recovery (90%) and purity targets met, (95%).

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 kWh/lb

Energy and Escalation Results Year 3:

Description		Units	Value
Escalation Factor		-	1.532
Energy			
	Sorption enthalpy	MWth	183.2
	Sensible heat	MWth	1006
	Total enthalpy per sorption or desorption step	MWth	1190
	Main heater duty	MWth	550
	Main cooler duty	MWth	-563
	Intraprocess heat recovery	%	
Steam usage		kg/h	819000
Derate			
	Direct Electrical Derate	MWe	110.8
	Steam Derate	MWe	252.6
	Steam Turbine Energy Recovery	MWe	-71.0
	Total Derate for CO_2 Capture	MWe	292

Escalated Capital Costs:

Description	Units	Year 3	Comments
Total purchased equipment costs (PEC)	MM$	221.6	1850 modules
Fibers	MM$	135.9	450,000 fibers/module
CO_2 capture	MM$	57.6	
CO_2 compression	MM$	28.1	
Process Plant Cost (PPC)	MM$	641.5	PPC = PEC + Direct Costs
Total Plant Cost (TPC)	MM$	1078.5	TPC = PPC + Engineering + Process Contingency + Project Contingency (30%)
Total Plant Investment (TPI)	MM$	1142.6	TPI = TPC + Interest and Inflation
Total Capital Requirement (TCR)	MM$	1175.3	TCR = TPI + Startup + Initial Fill + Working Capital + Land + Others
Annual Capital Charge	MM$/year	205.7	

Technoeconomic Metrics Escalated Case:

Description	Units	Year 3 Q3
Levelized Costs of Electricity and Steam		
Levelized cost of electricity	mills/kWh	154
Levelized cost of steam	$/1,000 lb	14.0
Cost of CO_2 Capture		
Total Annual Cost of CO_2 Capture	MM$/year	303
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)	%	25.6
Change in Net Plant Efficiency	%	-11.2

Metrics were calculated using simplified equations specified in the solicitation.

Summary & Future Work:

- **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.

- Refined Technoeconomic analysis suggests targets for improvement.
  -- Current parasitic load, Gen 2 fibers (1.53 escalation factor)

- Refinement Approaches:

  -- Gen 3 fibers = 1.43 escalation factor

  -- Gen 3 fibers (**VTSA**, 0.33 bar desorption pressure)
  Lower bound steam savings = 30% less heat used

  -- Gen 3 fibers (**VTSA**, 0.33 bar desorption pressure)
  Upper bound steam savings = 50% less heat used

  -- Multi-bed adsorption

Acknowledgements:

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Algenol Biofuels
GE
Southern Company

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People

Dr. Ron Chance – Algenol Biofuels
Dr. Ying Labreche – hollow fiber spinning
Dr. Yanfang Fan – experimental system design and testing
Dr. Fateme Rezaei – sorbent synthesis and fiber modeling
Dr. Swernath Subramanian – fiber modeling
Ms. Jayashree Kalyanaraman – fiber modeling
Ms. Grace Chen – sorbent synthesis & characterization / fuel gas upgrading
Mr. Morgan French – Southern Company
Mr. Jerrad Thomas - Southern Company

Program officer Bruce Lani – NETL, DOE