DOE Award #: DE-FE0007804

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

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Post-Combustion Sorbent-Based Capture
2013 NETL CO_2 Capture Technology Meeting
Sheraton Station Square, Pittsburgh, PA
Monday, July 8, 2013

Georgia Institute of Technology
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

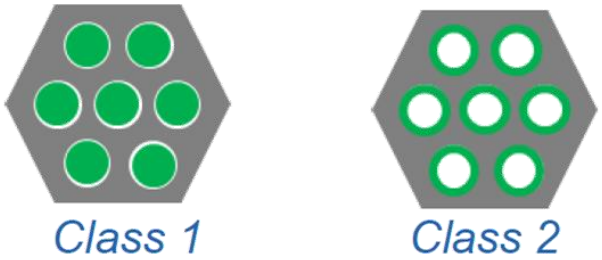
Supported Amine Adsorbent:

Pros:

1) Can achieve high capacity in lab studies
2) Appear to achieve acceptable kinetics
3) Simple, scalable synthesis
4) High heat of adsorption (heat integration!)

Cons:

1) High heat of adsorption
2) Deactivation with O_2, steam, NOx, SOx
3) Low working capacity or degradation in practical contactors (fluidized bed)
    - (i) can deactivate with direct steam contact
    - (ii) can deactivate at high T in concentrated CO_2



Porous silica (gray)

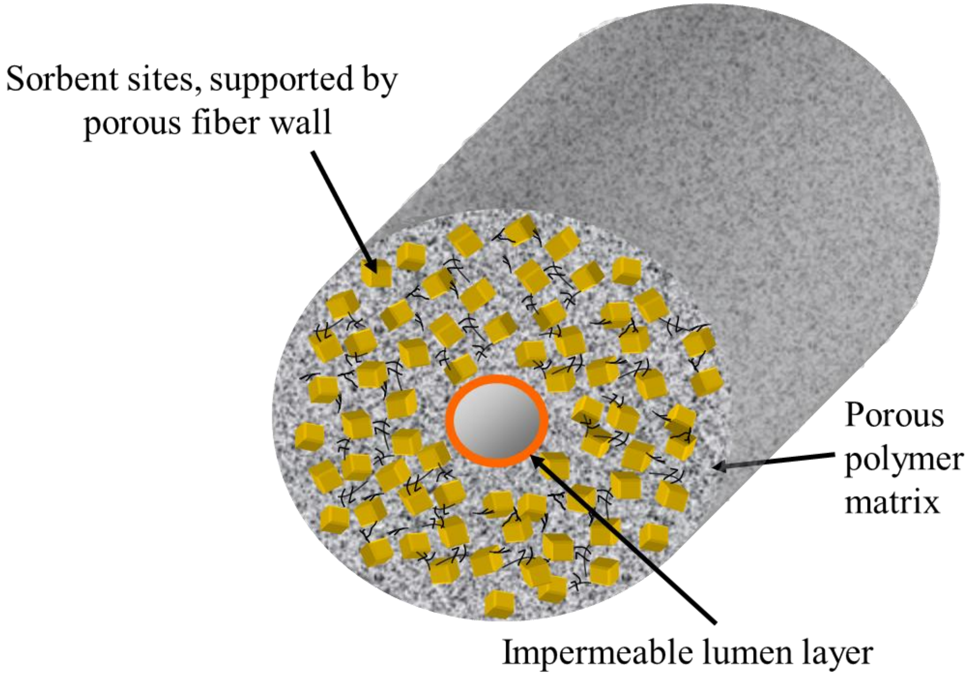
Amines (green)

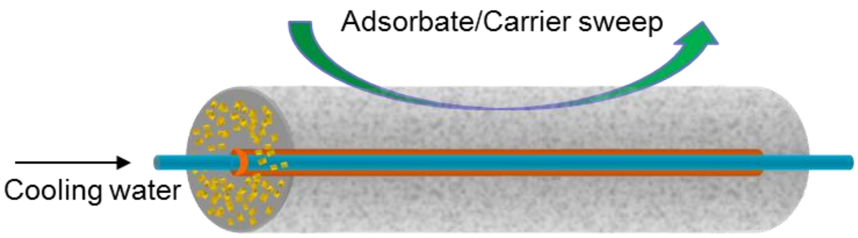
No effective contactor demonstrated that addresses multiple "cons."

Hollow Fiber Contactor:

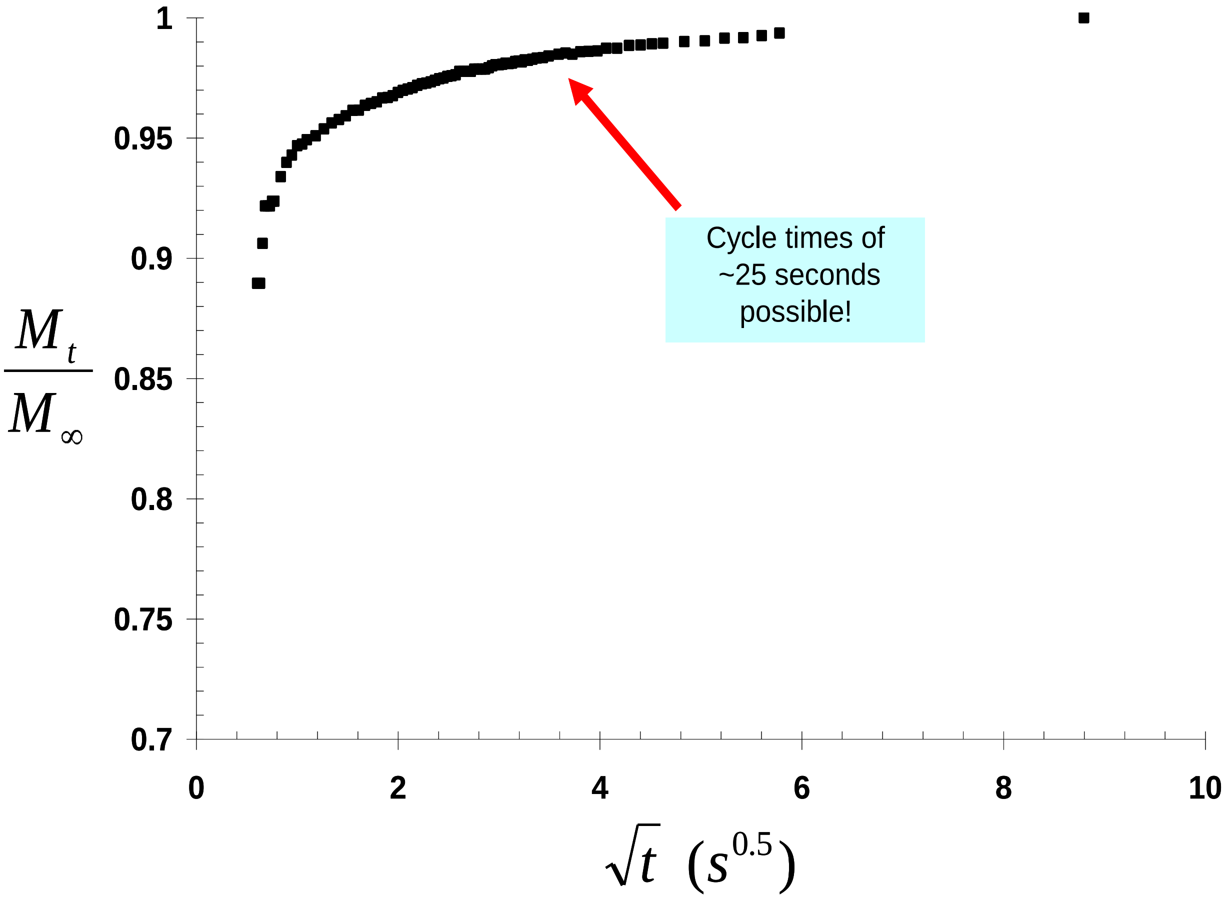
Fiber Bed: Achieves high surface area without excessive pressure drop

Hollow Fiber: Allows rapid heat transfer without contact of steam with amine





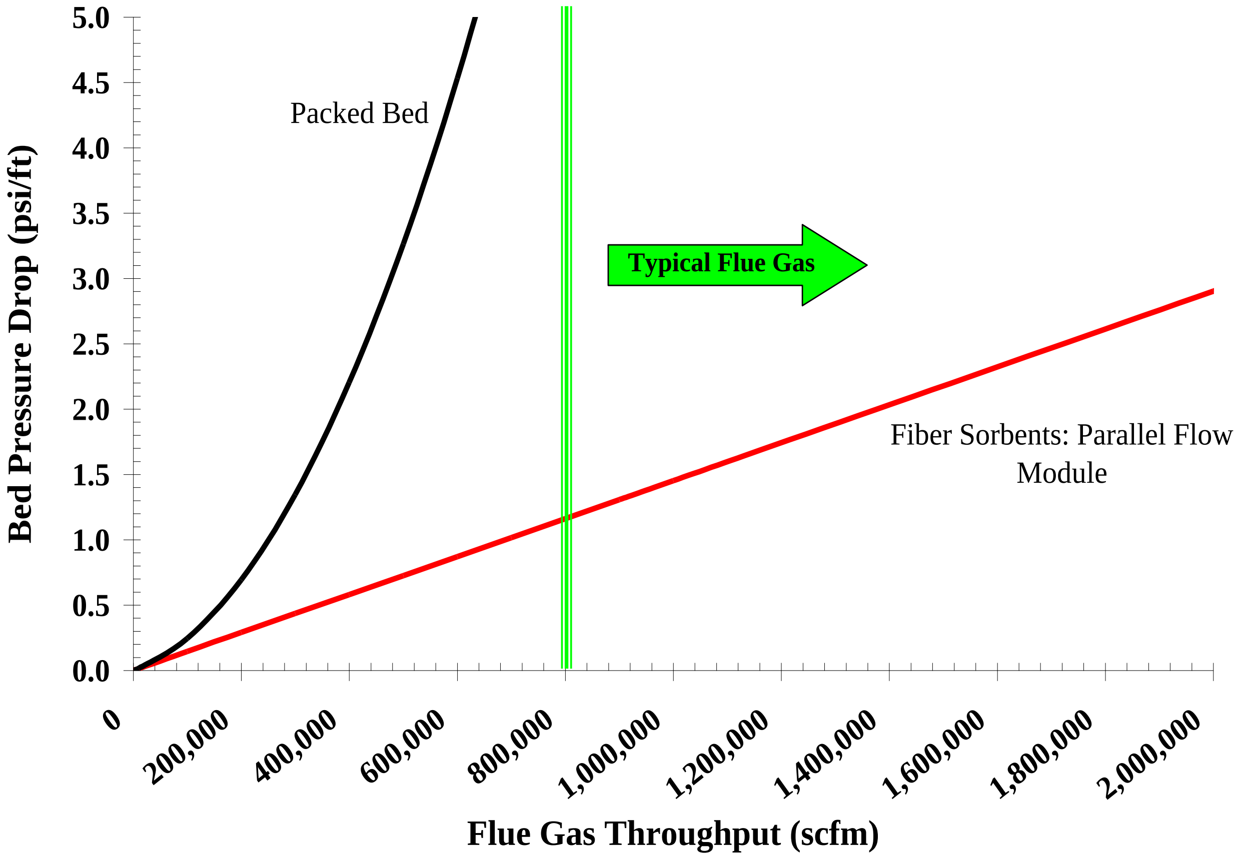
Parallel Flow Hollow Fiber Contactors:



Cycle times of ~25 seconds possible!

- Rapid adsorption cycles possible with zeolite 13X.
- First experimentally demonstrated here with amine sorbents

Parallel Flow Hollow Fiber Contactors:



- Pressure drop through fiber modules is very low compared to fixed beds

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).

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.

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).

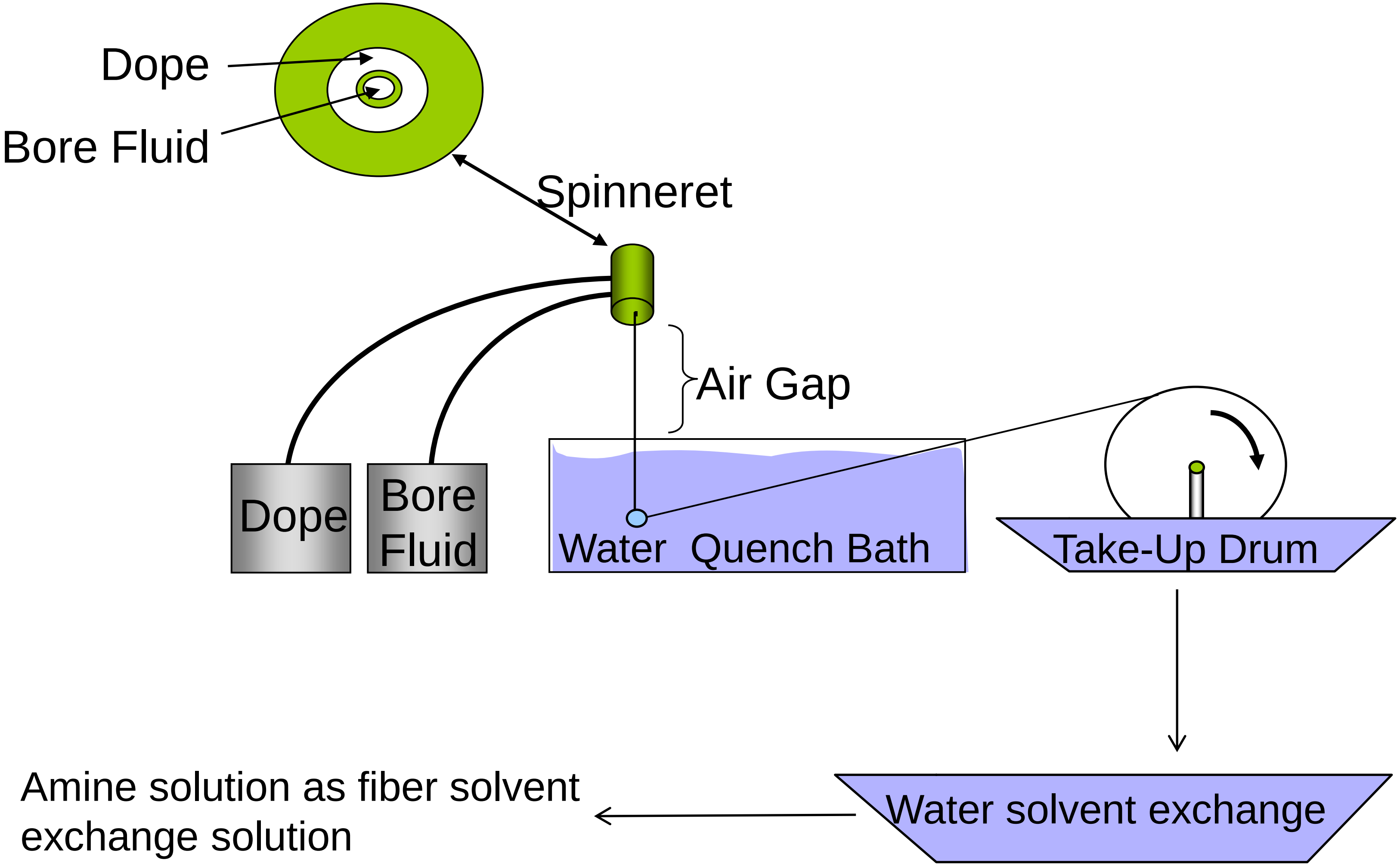
-- achieved using two commercial mesoporous silica materials

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

-- invented post-spinning amine infusion technique, creating class 1 (impregnated PEI) and class 2 (grafted 3-aminopropylsilane) fiber sorbents.

Y. Labreche et al., *Chemical Engineering Journal*, **2013**, 221, 166-175.
F. Rezaei et al., *ACS Applied Materials & Interfaces*, **2013**, 5, 3921-3931.

Post-Spinning Infusion:



Dope

Bore Fluid

Spinneret

Air Gap

Dope

Bore Fluid

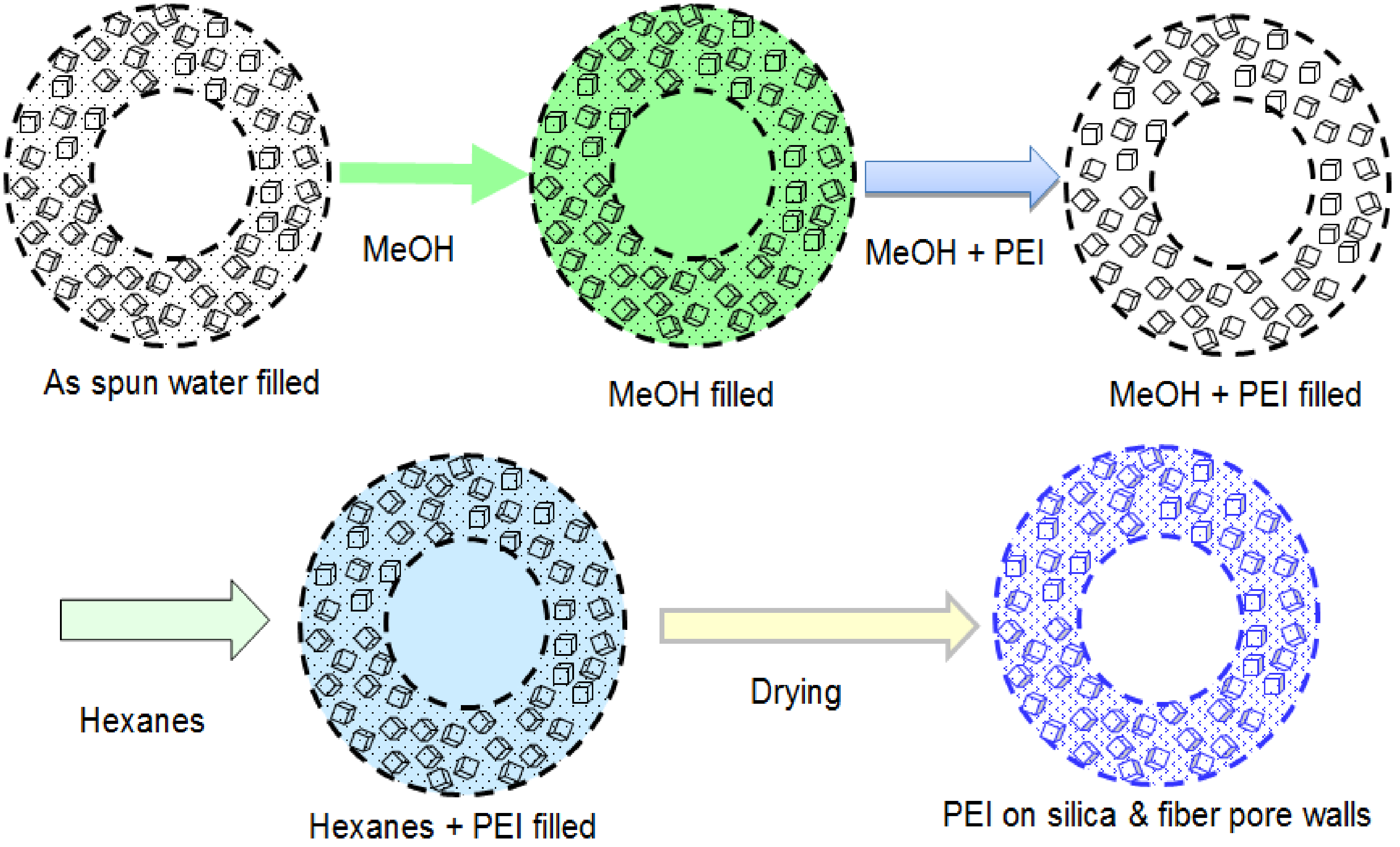
Water Quench Bath

Take-Up Drum

Water solvent exchange

Amine solution as fiber solvent exchange solution

Post-Spinning Infusion:



As spun water filled

MeOH

MeOH filled

MeOH + PEI

MeOH + PEI filled

Hexanes

Hexanes + PEI filled

Drying

PEI on silica & fiber pore walls

Hollow Fiber Contactor:

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

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

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

-- small scale station for breakthrough testing built and employed

-- medium scale station for thermal management tests built and commissioning

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

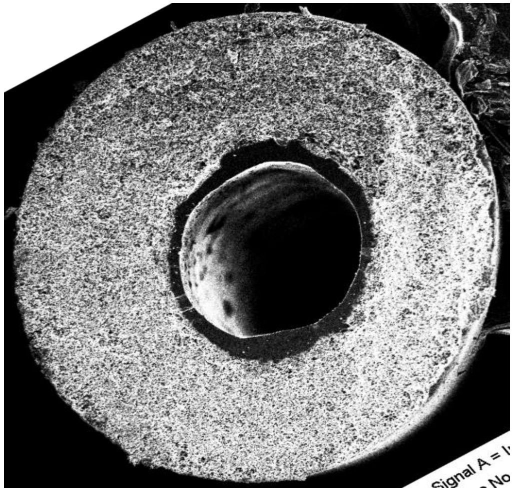
-- materials & operating conditions for minimal oxidative degradation identified

-- SOx/NOx experiments ongoing

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

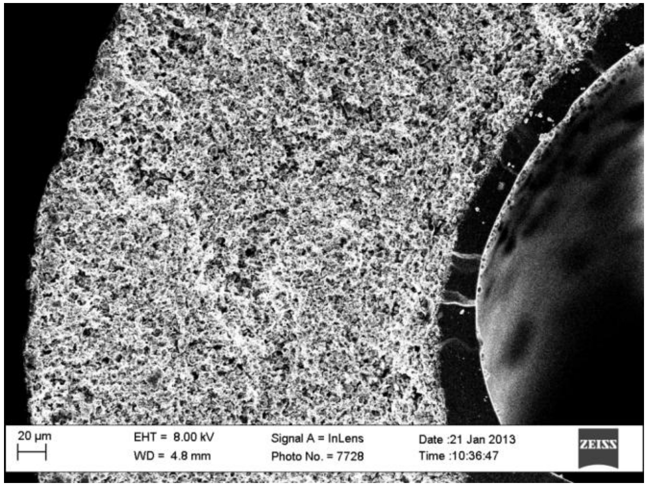
-- preliminary results promising

Lumen Layer Allows Cooling with Adsorption:



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

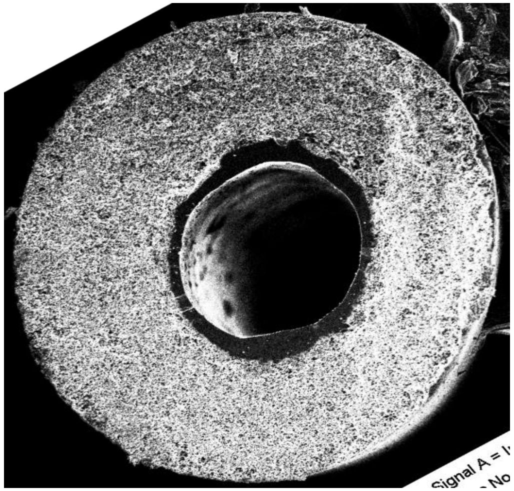
-- Large decrease in mass flux from bore to shell with lumen layer



Module (class 1)	CO_2 q_b mmol/g-fiber	CO_2 q_e mmol/g-fiber
W/O cooling	0.51	1.14
With cooling	1.16	2.32

-- Significant increase in breakthrough and equilibrium fiber capacity with cooling during adsorption

Lumen Layer Allows Cooling with Adsorption:



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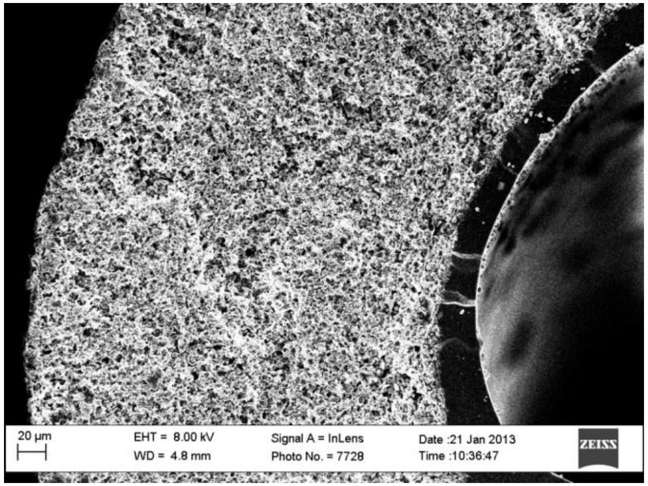
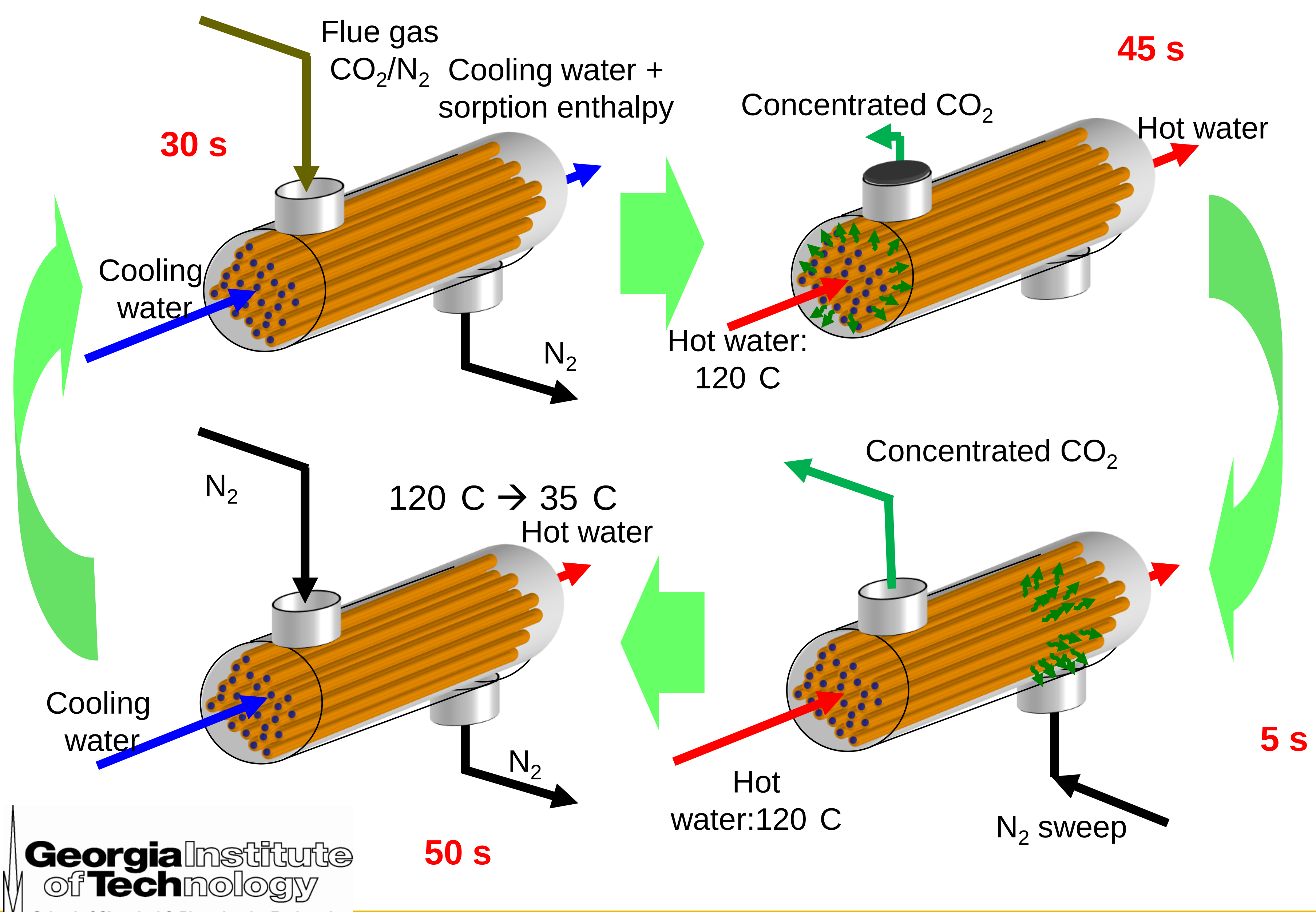


Module (class 1)	**CO_2 q_b mmol/g-fiber**	**CO_2 q_e mmol/g-fiber**
W/O cooling	0.51	1.14
Modeling Value	0.69	Swing capacity
With cooling	1.16	2.32

-- **Significant increase in breakthrough and equilibrium fiber capacity with cooling during adsorption**

RTSA Qualitative Cycle:



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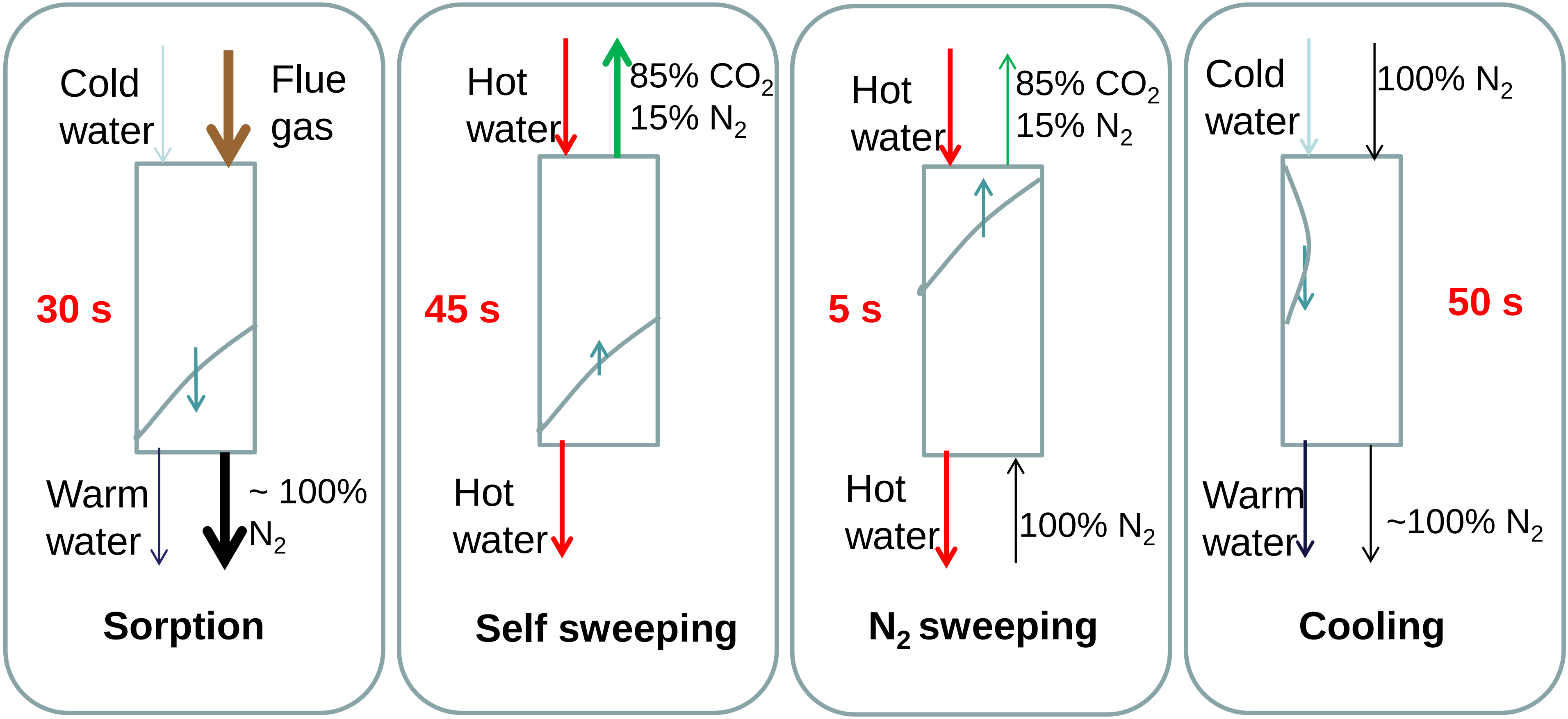
Bed Profiles in Individual Steps:



Cold water

Flue gas

30 s

Warm water

~ 100% N_2

Sorption

Hot water

85% CO_2
15% N_2

45 s

Hot water

Self sweeping

Hot water

85% CO_2
15% N_2

5 s

Hot water

100% N_2

N_2 sweeping

Cold water

100% N_2

50 s

Warm water

~100% N_2

Cooling

-- Thickness of arrows signify the magnitude of velocities

-- Internal profiles and arrows depict the movement of concentration fronts during the four steps (Mass transfer zone)

Technoeconomic Evaluation Methodology:

The current technoeconomic evaluation employs a similar methodology to the first 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
- Equipment costs were developed from quotes, literature, and cost estimating software
- Capital costs, operating costs, and technoeconomic metrics were calculated according to DOE methodology

Equipment pricing was improved:

- Equipment pricing sources and methods were updated and refined for numerous unit operations
- Aspen In-plant Cost Estimator replaced PDQ$ as the equipment cost estimating software
- Equipment cost curves were developed to accommodate more rapid evaluation of process options by overall modeling team.

Technoeconomic Evaluation, Changes from Year 1:

- Year 1 costs based on estimated parameters from literature (powder sorbents) and preliminary mass and heat flows. **Aggressive estimate.**
- Year 2 costs reflect new (dry gas) experimental data on aminosilica fibers and changes in heat integration. **Conservative estimate.**
- **Effective sorbent swing capacity decreased 31%** (from 1 to 0.69 mmol CO_2/g sorbent)
- **Recovery of sorption heat decreased by ~26%** (have no use for 50-60 ˚C water from capture of sorption enthalpy – DOE rules do not allow heat integration into plant)
- Results using preliminary inputs do not achieve purity specification but exceeded recovery targets [82% purity at 93% recovery]

- Reconciling and integrating the cyclic steady-state fiber simulation with the steady-state process simulation is ongoing
- Many options exist to improve the process with respect to purity and heat recovery beyond the results achieved with the initial inputs

Process Simulation - Results

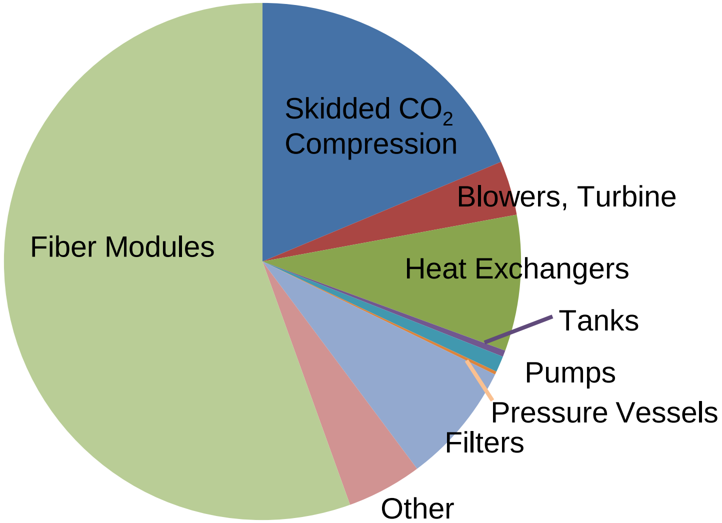
Escalation and Power / Steam Requirements		**Year 1 Aggressive Estimate**	**Year 2 Conservative Estimate**	**DOE Case 12 (Supercritical, Econamine)**
Escalation factor		1.248	1.471	1.382
Equivalent electrical capacity (with no steam or electrical draws)	MWe	727.4	857.0	782.9
Electrical capacity after steam draws	MWe	646.2	627.5	662.8
Net electrical power produced	MWe	550.0	550.0	550.0
Net parasitic power requirements for CO_2 capture	MWe	136.7	259.1	191.3
CO_2 capture auxiliary power requirements	MWe	21.8	32.3	26.3
Compression power requirements	MWe	58.6	82.8	44.9
Steam derate	MWe	81.2	229.5	120.1
Steam power recovery	MWe	-24.9	-85.5	0.0
Base plant auxiliary load	MWe	40.7	47.9	41.6

Purchased Equipment Costs:

		Year 1		**Year 2**	
		550 MWe net		**550 MWe net**	
		1.248		1.471	
Purchased equipment costs					
			%		%
Skidded CO_2 compression		23,226,000	17.6	34,392,000	18.7
Blowers, turbine		8,265,000	6.3	6,196,000	3.4
Heat Exchangers		7,856,000	6.0	15,655,000	8.5
Tanks		655,000	0.5	739,000	0.4
Pumps		2,713,000	2.1	1,915,000	1.0
Pressure Vessels		206,000	0.2	458,000	0.2
Filters		8,967,000	6.8	13,965,000	7.6
Others (except fiber mods)		6,757,000	5.2	8,657,000	4.7
Fiber modules		72,208,000	55.2	102,403,000	55.5
Purchased Equipment Costs by Class					
Fibers	MM$	72.2		102.4	
Other CO2 capture equipment	MM$	35.4		47.6	
Skidded CO2 compression	MM$	23.2		34.4	
Total purchased equipment costs	MM$	130.9		184.4	

Purchased Equipment Costs:

Purchased equipment costs	**Year 2** **550 MWe net** 1.471	%
Skidded CO_2 compression	34,392,000	18.7
Blowers, turbine	6,196,000	3.4
Heat Exchangers	15,655,000	8.5
Tanks	739,000	0.4
Pumps	1,915,000	1.0
Pressure Vessels	458,000	0.2
Filters	13,965,000	7.6
Others (except fiber mods)	8,657,000	4.7
Fiber modules	102,403,000	55.5



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Summary & Future Work:

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

- Cycle allows effective recovery of heat of sorption (not possible under DOE program guidelines) and sensible heat of module through integration of modules in different phases of operation.

- Preliminary Technoeconomic analysis indicates promise.
  -- Relatively low parasitic load (1.25 escalation factor – aggressive estimate)

- Refined Technoeconomic analysis suggests targets for improvement.
  -- Higher parasitic load (1.47 escalation factor – conservative estimate)

- Refinement Approaches:
  -- Improved sorbent capacity
    - evolution of post-spinning infusion (better methods)
    - experimental operation in humid conditions (model/expts dry; expts w/o cooling)
  -- Implement a CO_2 recycle loop to improve purity

Future Work:

- Refinement Approaches:
    - -- Improved sorbent capacity
        - - evolution of post-spinning infusion (better methods)
        - - experimental operation in humid conditions (model/expts dry; expts w/o cooling)
    - -- Implement a CO_2 recycle loop to improve purity
- Make multi-fiber modules with lumen layers for CO_2 capture testing with heat exchange
- Carry out dynamic experimental trials, measuring CO_2 capture and heat effects simultaneously – will improve dynamic process model
- Complete and refine dynamic process model – will improve technoeconomic analysis

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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

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