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of Technology

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

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Atlanta, GA 30332

DOE-NETL Kick-off Meeting
Monday, November 7, 2011

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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

Parties Involved:

Principal Investigators:

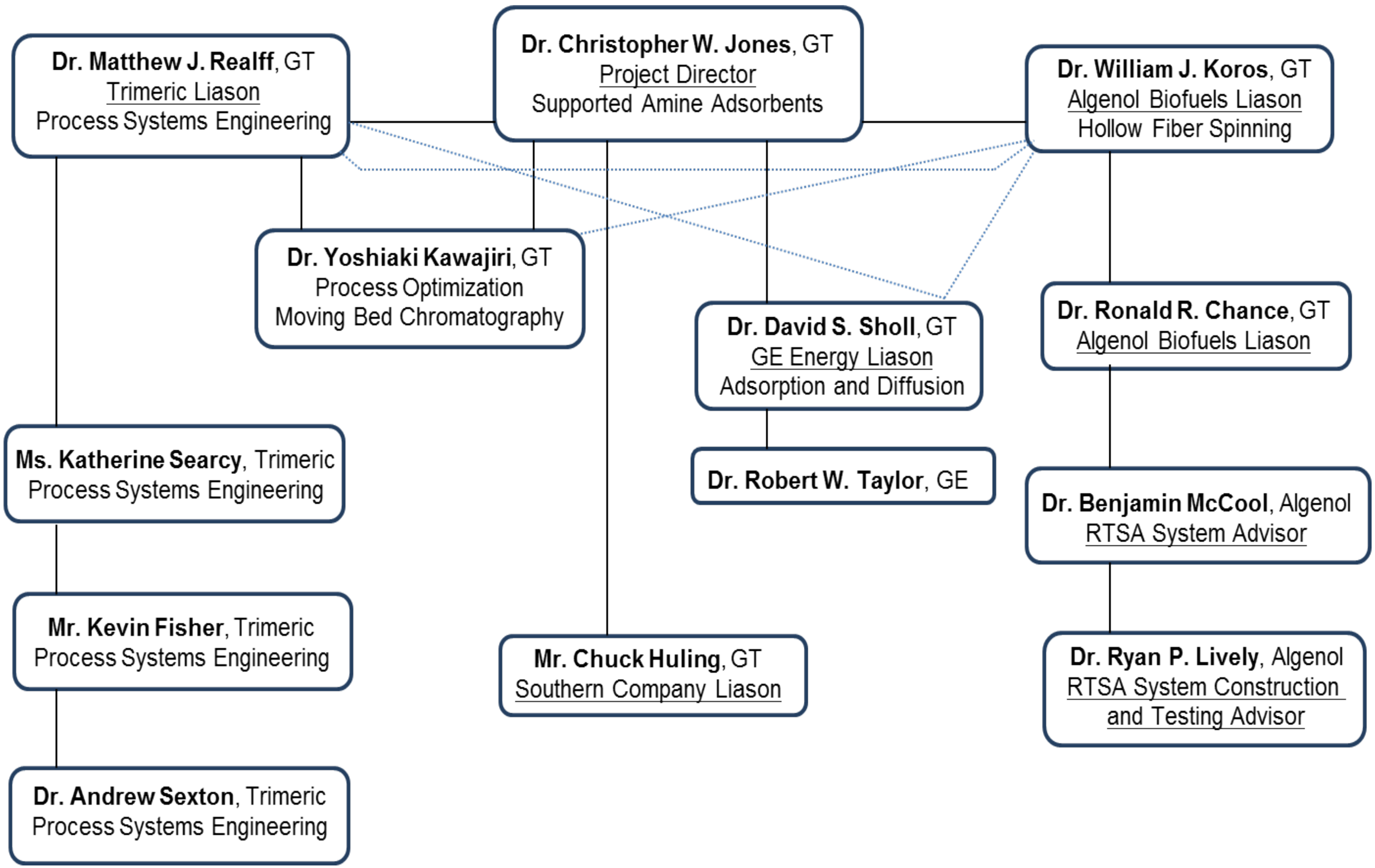
Georgia Tech
Chris Jones, *Project Director*, Amine Adsorbents and RTSA System
Bill Koros, *Algenol Biofuels Liason*, Hollow Fibers and RTSA System
Matthew Realff, *Trimeric Liason*, Process Systems Engineering
David Sholl, *GE Energy Liason*, Adsorption and Mass Diffusion
Yoshiaki Kawajiri, Process Optimization, Moving Bed Chromotography

Trimeric Corporation
Katherine Searcy, Kevin Fisher, Andrew Sexton

Cost Share Partners:

GE Energy: funding a parallel PhD student to use system for fuel gas cleanup
Algenol Biofuels: engineering and technical support on fiber systems
Southern Company: engineering and technical consulting

Organizational Chart:



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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Literature Review:

Chemisorbants

-High ΔH_{ads}

-Steep isotherm

-Strong binding

-- *amines*

-- *CaO*

--*hydrotalcites*

Physisorbants

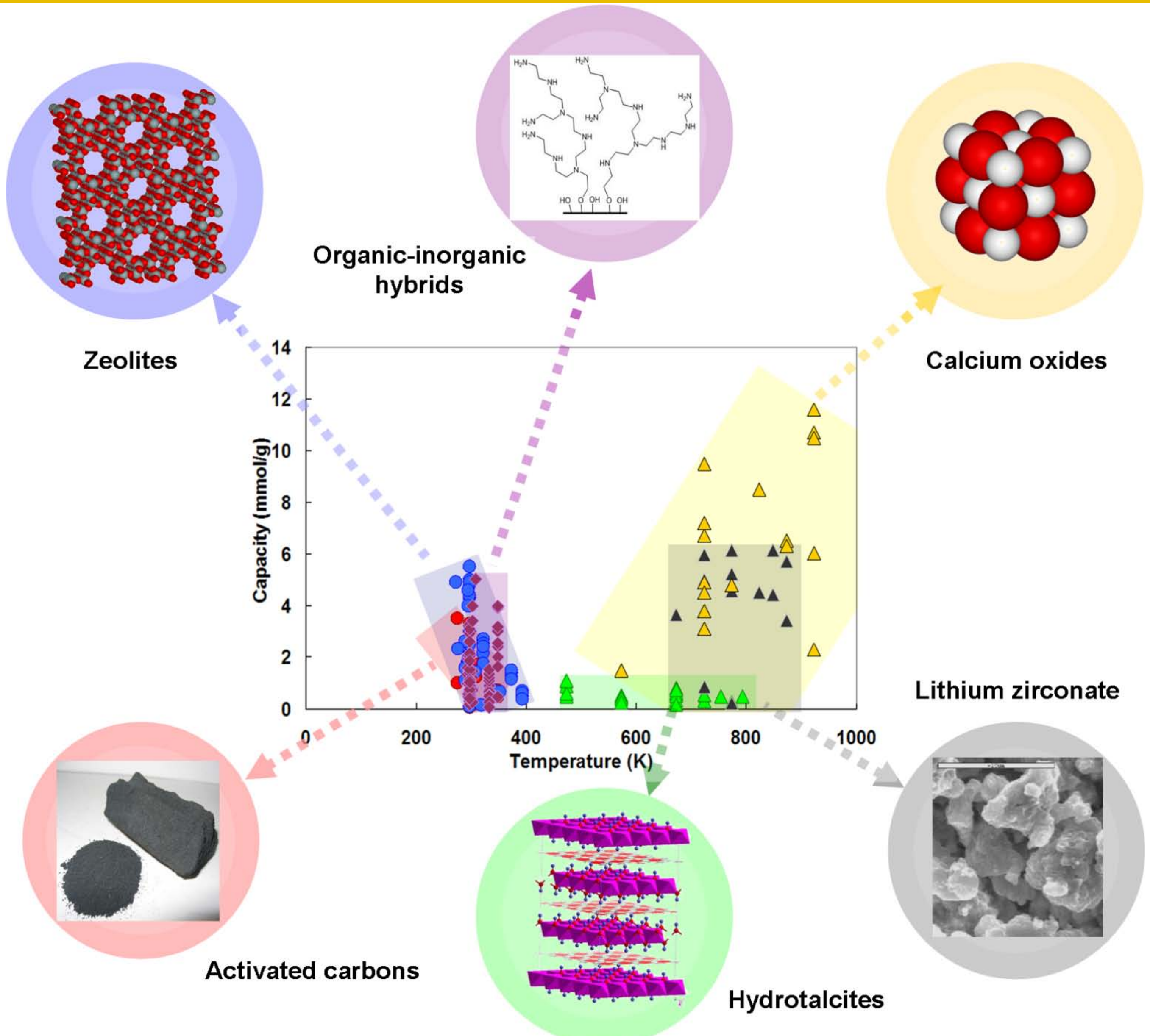
-Low ΔH_{ads}

-Shallow isotherm

-Weak binding

--*zeolites*

--*carbons*



Supported Amine CO_2 Adsorbents – State of the Art:

- Today, 100+ papers on different supported amine materials for CO_2 capture.

- Nearly singular focus on developing sorbents with high capacity with “make and test” strategy. Adsorption kinetics are increasingly reported.

- Despite all this work, few (maybe no) published studies actually concentrate the CO_2.

- Almost all authors regenerate sorbents by heating in flowing inert, thereby producing a dilute CO_2 stream unsuitable for sequestration.

- How might practical desorption be accomplished?

  -- heating in flowing concentrated CO_2 – low working capacity; urea
  -- heating at reduced pressure – massive vacuum pumps
  -- heating with flowing steam – sorbent degradation; water condensation

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Jones et al. *ChemSusChem* **2010**, 3, 899.
Jones et al. *J. Mater. Chem*. **2011**, 21, 15100.

Supported Amine CO_2 Adsorbents – State of the Art:

- **Limitations of state-of-the-art:**

-- lack of studies on practical sorbent regeneration; real contactors.
-- sorbent stability
-- practical working capacity
-- purity of CO_2 product

-- focus on studies using CO_2 + inert (N_2, Ar, He)
-- real flue gas has O_2, NO_x, SO_x, Hg, particulates
-- NO_x, SO_x will irreversibly adsorb

Khatri et al. *Energy Fuels* **2006**, 20, 1514
Beckman et al., *J. Appl. Polym. Sci*. **1994**, 53, 857.

-- Sayari shows O_2 does not adsorb, but will it react?

Sayari et al. *Ind. Eng. Chem. Res.* **2010**, 49, 359.

-- Jones has shown direct contact with steam can degrade aminosilica materials.

Jones et al. *ACS Appl. Mater. Interface* **2010**, 2, 3363.

Supported Amine CO_2 Adsorbents – Oxidative Stability:

- Amine solutions degrade via oxidative pathways.
  - -- catalyzed by metal ions in solution.
  - -- primarily in high temperature steam-stripping step.
  - -- for example with monoethanolamine:

Fe^{3+} H^+

MEA H^+ Fe^{3+}

\+ H_2O H_2O

\+ +

Rochelle et al. *Ind. Eng. Chem. Res.* **2002**, 42, 4178.
Rochelle et al. *Ind. Eng. Chem. Res.* **2004**, 43, 6400.

Supported Amine CO_2 Adsorbents – Oxidative Stability:

- Supported amine adsorbents and long term stability.

Advantages: -- no metal catalyst; no solution phase.

Disadvantages: -- sorbent loss by attrition
-- unknown oxidative, SO_x, NO_x stability

- Exposure to O_2 during processing:

Flue gas: 10-15% CO_2, 5-10% O_2, 4-5% water vapor, balance N_2
~2000 ppm SO_2 (before flue gas desulfurization)
~1500 ppm NO (before selective catalytic reduction)
T = 40-70 °C; P ~ 1atm

Desorption: Steaming at 90-120 °C; co-presence of O_2 and elevated T at outset of desorption cycle.

Supported Amine Adsorbents:

Class 1 Supported-Amine Adsorbents: Song et al., *Energy Fuels* **2002**, 16, 1463.

-- Oxides or polymer supports with alkyl amine groups **impregnated or physisorbed** in the support porosity.

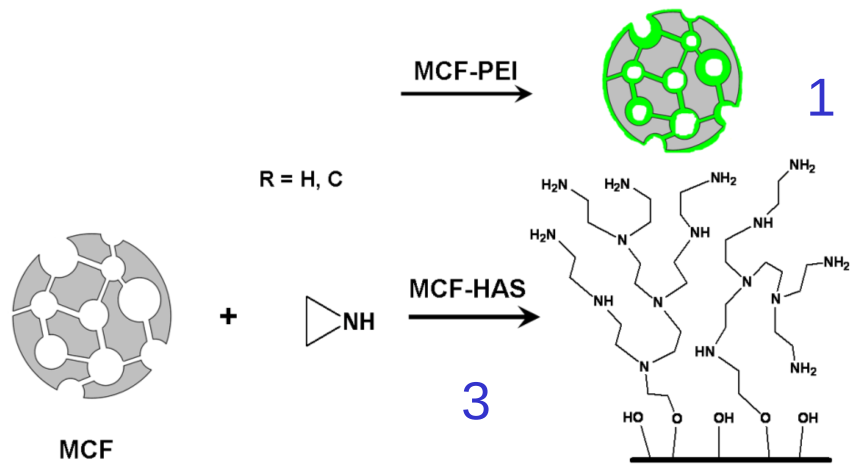
Tsuda et al, *Chem. Lett.* **1992**, 2161.

Class 2 Supported-Amine Adsorbents:

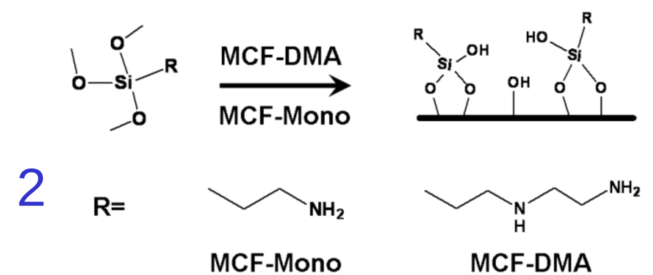
-- Oxides or polymer supports with alkyl amine groups **covalently bound** to the support (via Si-C or C-C) bonds.

Class 3 Supported-Amine Adsorbents:

-- Oxides or polymer supports with alkyl amine groups **covalently bound** to the support prepared via reactive, *in-situ* polymerization.



Jones et al., *J. Am. Chem. Soc.* **2008**, 130, 2902.



Supported Amine Adsorbents:

Class 1 Supported-Amine Adsorbents:

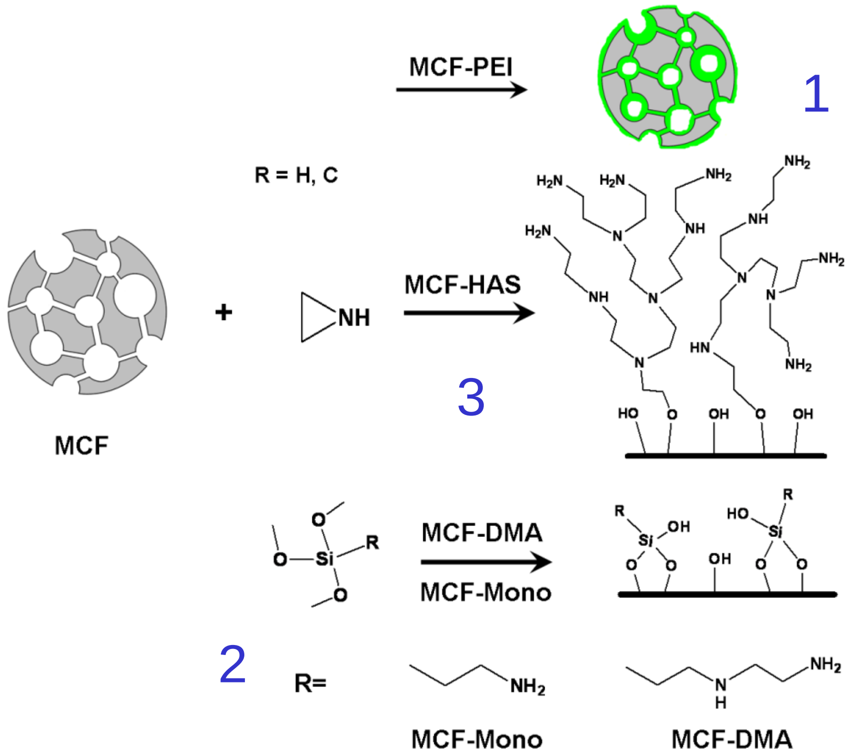
-- Easiest to scale-up. To be made at GT, with possible tests of proprietary NETL sorbents (Mac Gray)

Class 2 Supported-Amine Adsorbents:

-- Can be made on scale needed for bench studies.

Class 3 Supported-Amine Adsorbents:

-- New, presently more difficult to make on large scale.



Supported Amine Adsorbent Summary:

Pros:

1) Can achieve high capacity in lab studies
2) Appear to achieve acceptable kinetics
3) Simple, scalable synthesis

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1) High heat of adsorption (heat integration!)
2) Deactivation with O2, steam, NOx, SOx
3) Low working capacity in more practical contactors
    - (i) can deactivate with direct steam contact
    - (ii) can deactivate at high T in concentrated CO2

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No effective contactor demonstrated that addresses multiple "cons."

Improved Contactor for Supported Amines:

- Amine adsorbents provide good CO_2 capacity and acceptable adsorption desorption kinetics if they can be kept isothermal.

- Heat of adsorption for amine adsorbents is high compared to conventional adsorbents such as zeolites or carbons.

- An effective, scalable contactor for amine adsorbents that allows for acceptable adsorption/desorption properties, cost, and ability to yield high purity CO_2 has not yet been demonstrated.

    -- fluidized bed, looping processes give significant sorbent attrition and typically yield depressed working capacities.

    -- fixed bed processes make heat management highly problematic

- An ideal contactor would offer high surface areas at low cost, allow for isothermal adsorption, and would yield a concentrated CO_2 product.

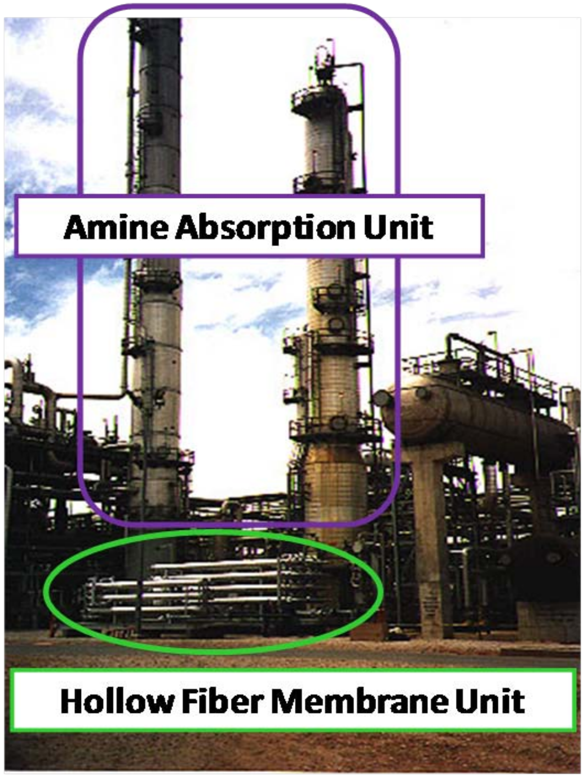
Background:

- In 2009, Koros and Lively introduced the concept of rapid-temperature swing adsorption (RTSA) using polymeric hollow fiber sorbents:

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

- Polymeric hollow fibers have been demonstrated on a commercial scale for gas separations. Polymeric hollow fiber spinning is a high-throughput, highly scalable process that could produce sorbents on the scale required for post-combustion CO2 capture applications.

- Hollow fiber gas separation installations have a small footprint.



Background:

- Koros and Lively made several important advances:

1) Spinning of high solid content (60-75 volume%), flexible hollow fibers, using low cost commercial polymers (e.g. cellulose acetate)

2) Building and demonstrating an RTSA system for CO_2 capture from simulated flue gas

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

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

- For their initial demonstration of the RTSA hollow fiber concept, they used zeolite 13X as the adsorbent particles that were embedded in the fibers.

- These would require dewatering of the flue gas, a very expensive option.

Process Scope

Project Scope – Marrying Amine Adsorbents and Hollow Fibers:

- Amine adsorbents have many promising properties, but their use requires a process design that enables rapid heat transfer.

- Hollow fiber RTSA process offers a scalable technology, with excellent heat and mass transfer characteristics.

The current project aims to produce polymeric hollow fiber contactors loaded with amine adsorbent particles for post-combustion CO2 capture.

-- use known supported amine adsorbents

-- use known polymers for fiber spinning

-- adapt lessons learned during 13X case to supported amine case.

-- evaluate base process economics and optimize to minimize costs.

Project Scope – Key Topics:

Five major activity areas are proposed in this work:

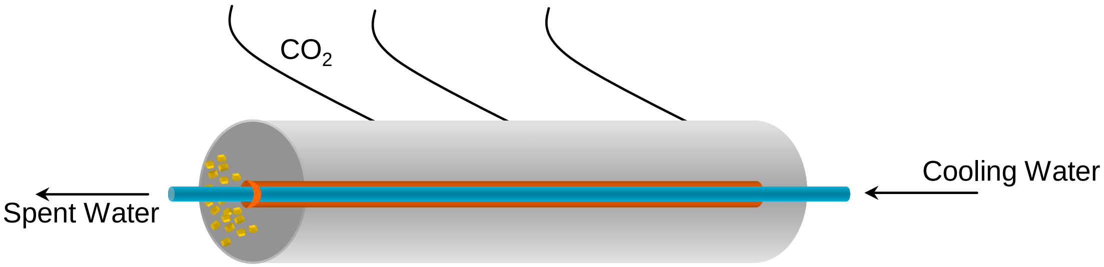
(1) Supported amine powder sorbent synthesis and stability testing,

(2) Composite hollow fiber spinning (cellulose acetate fibers containing silica-supported amine sorbents),

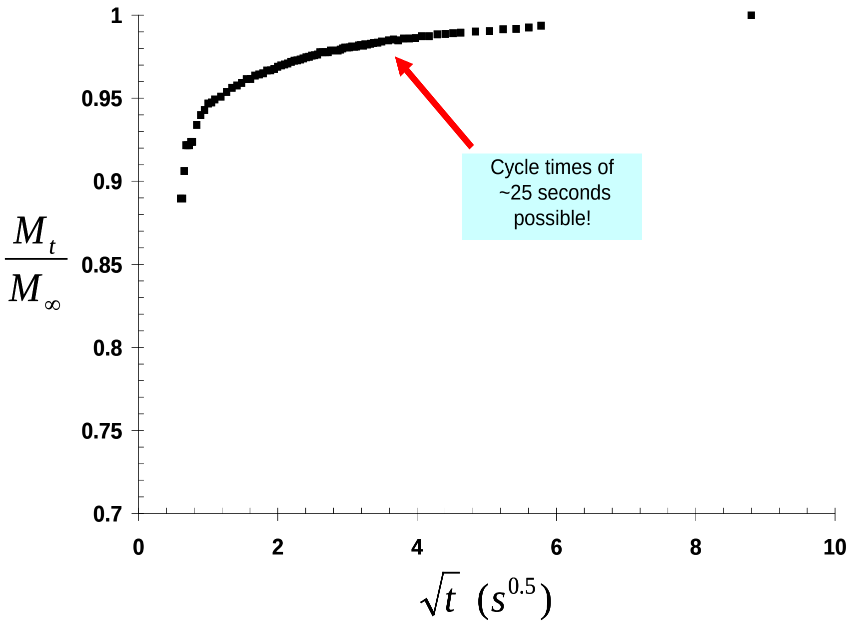
(3) RTSA system design, assembly and testing of hollow fiber modules,

(4) Modeling and optimization of hollow fiber module operation, and

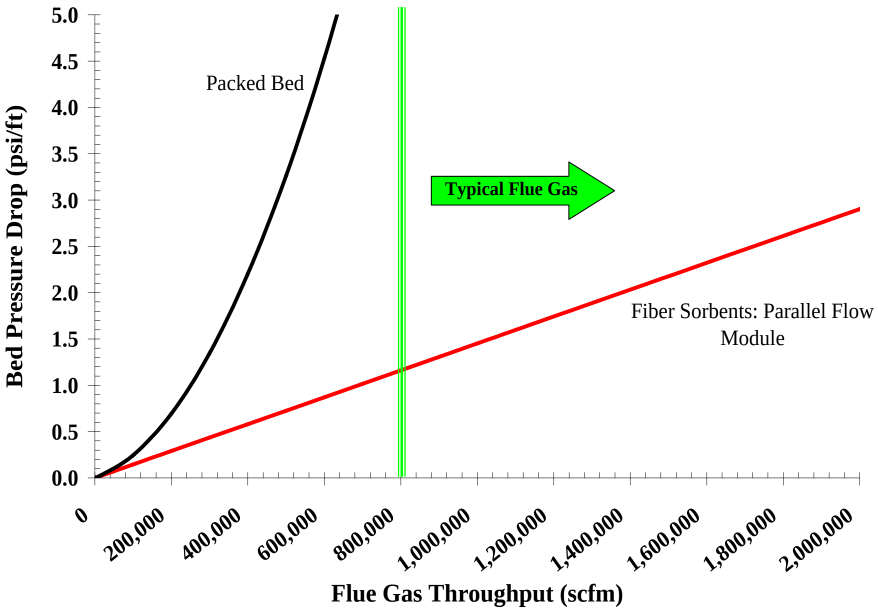
(5) Overall system techno-economic analysis and environmental health and safety analysis.


CO2
Cooling Water
Spent Water

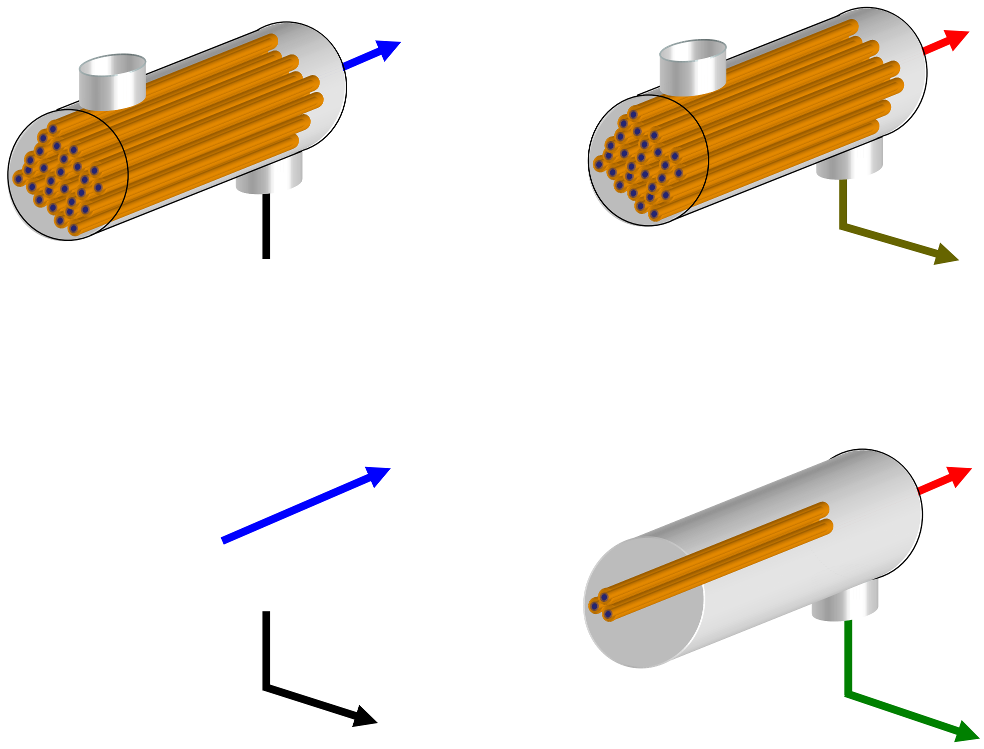
Parallel Flow Hollow Fiber Contactors:



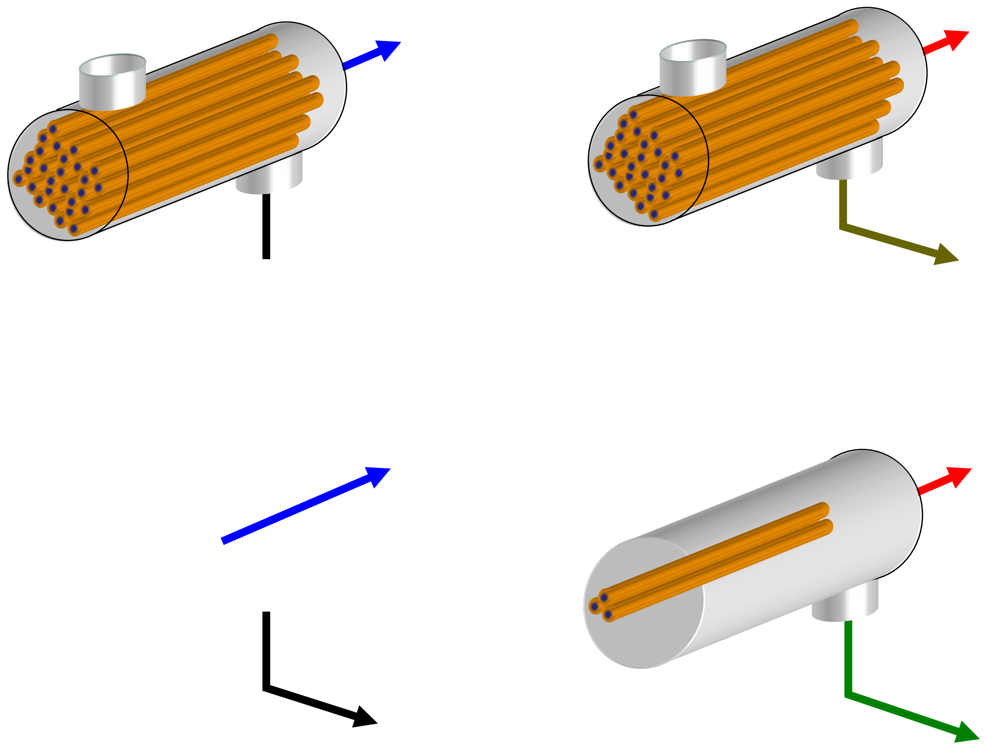
- Rapid adsorption cycles possible with zeolite 13X
- We will establish if/how this changes for supported amines
- Pressure drop through fiber modules is very low compared to fixed beds



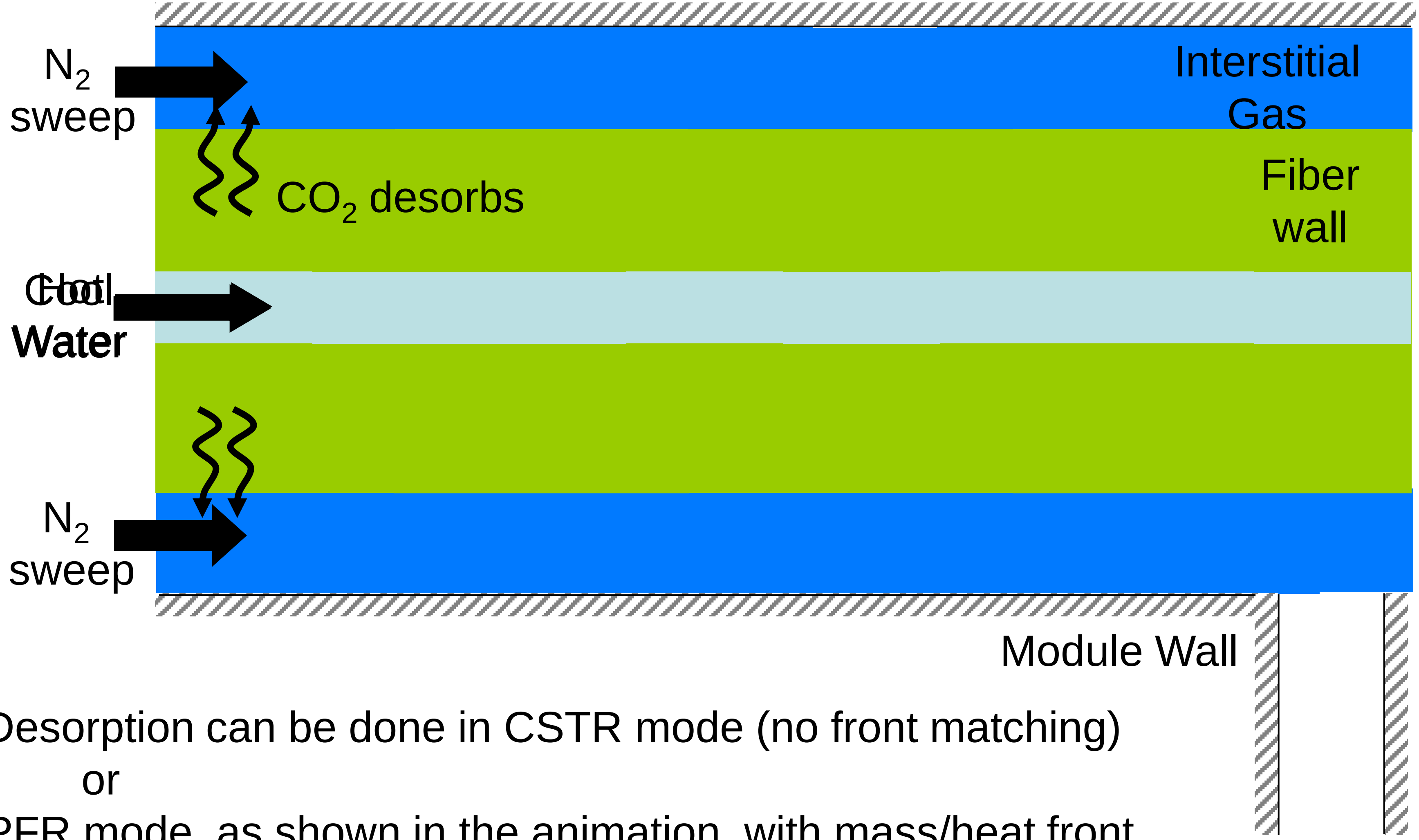
RTSA Operation with Parallel Flow Hollow Fiber Contactors:



RTSA Operation with Parallel Flow Hollow Fiber Contactors:



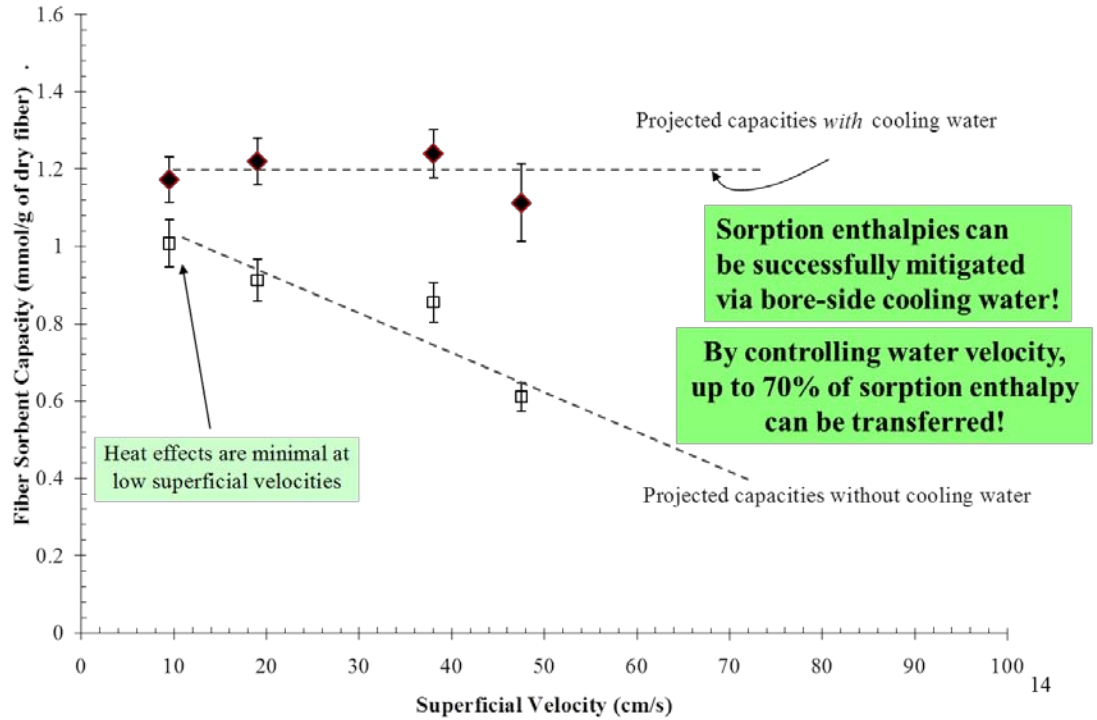
Route to a Concentrated CO_2 Product:

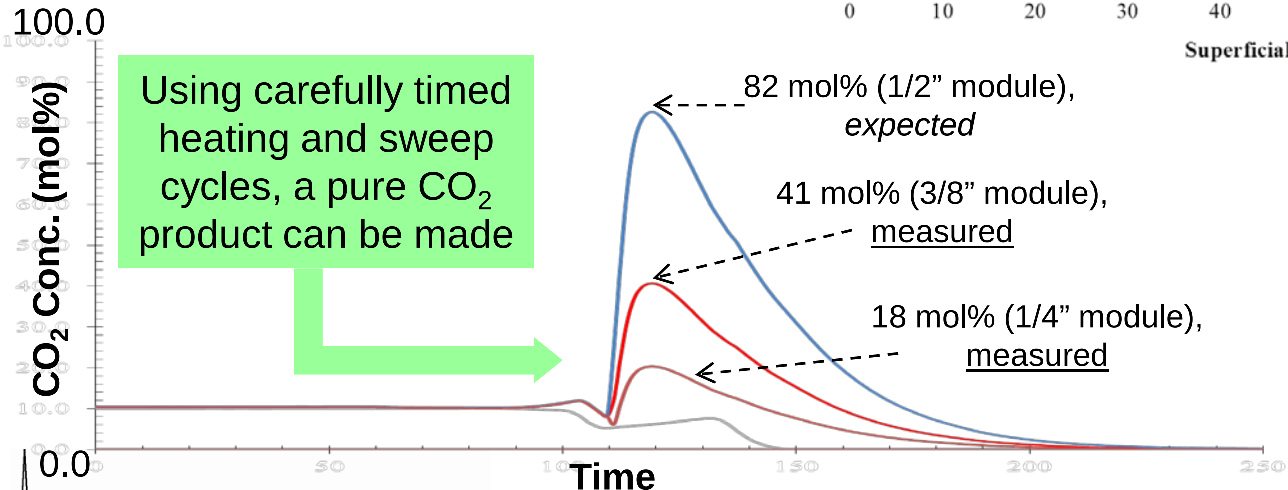


- Desorption can be done in CSTR mode (no front matching)
  or
  PFR mode, as shown in the animation, with mass/heat front matching.

Key Points from Zeolite 13X Studies:

- Fiber sorbents show rapid (<10 second) CO_2 uptakes
- Fibers can be repeatedly thermally cycled with no loss in capacity or physical damage
- External boundary layers can be removed via close fiber packing (ε~0.3)
- Low pressure drops (< 1.5 psig) at high superficial velocities (~ 1 m/s)



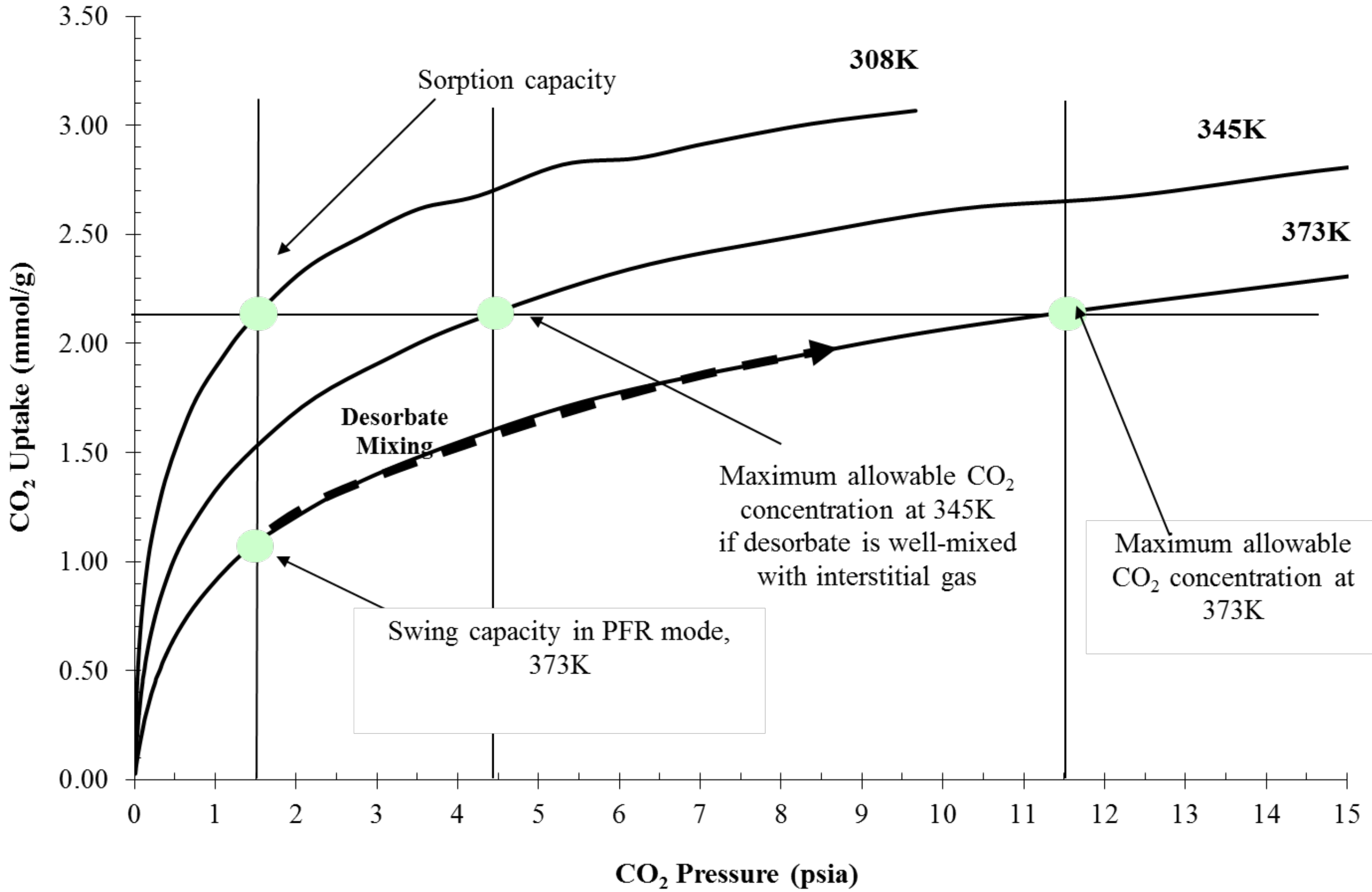


Larger modules should result in near-pure CO_2 product streams

PFR mode lab demonstration

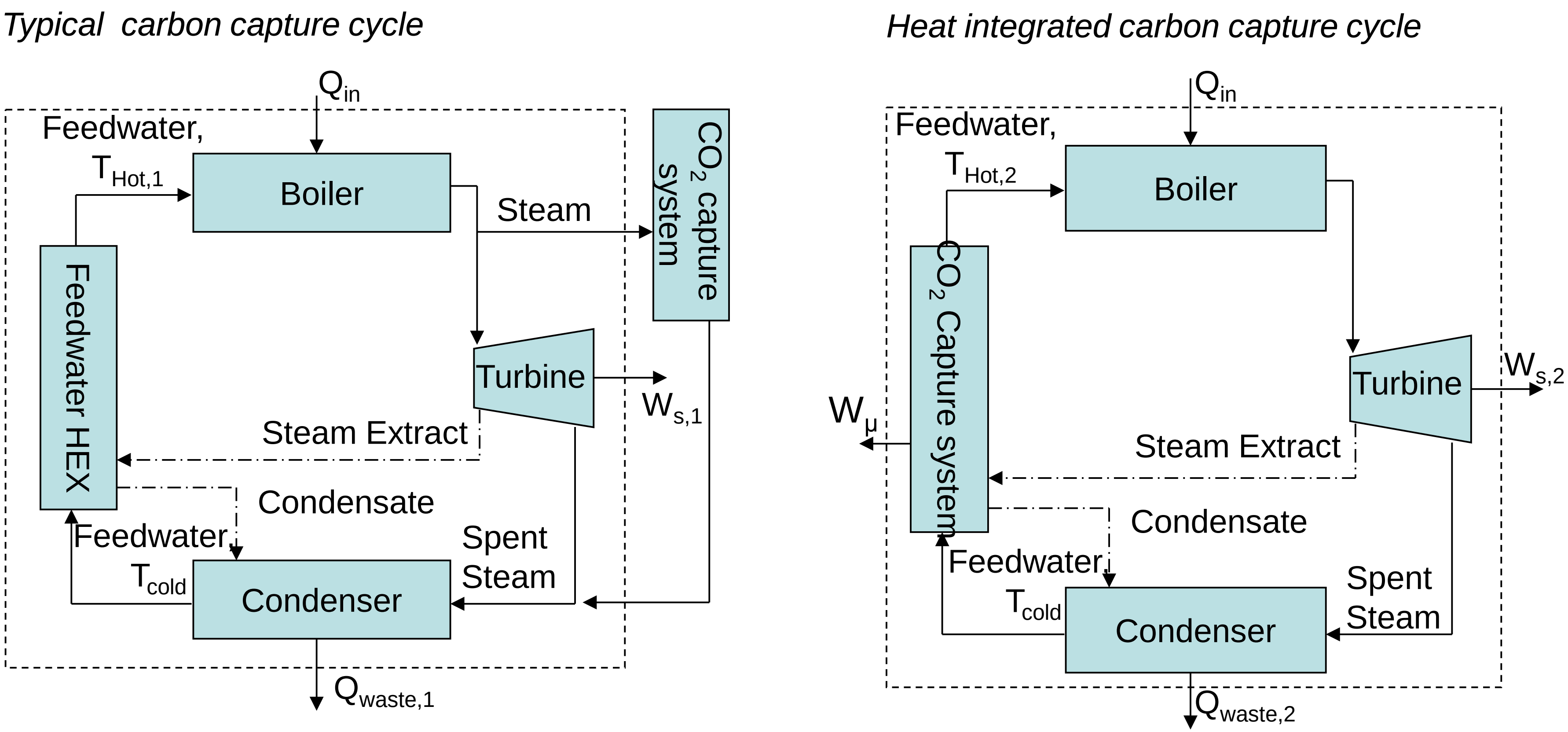
Desorption Modes:

Overview of “PFR” mode and “CSTR” mode desorption



CSTR mode offers simplicity at the cost of lower purities

Heat-Integration with Host Facility - Overview:

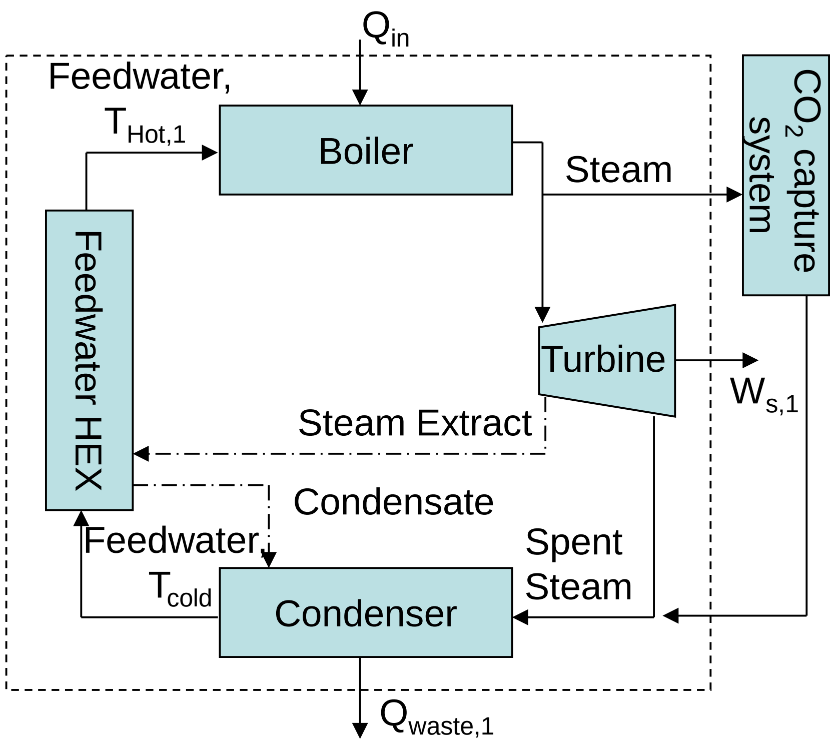


-- energetic comparison of RTSA with hollow fiber contactors with conventional post-combustion capture processes

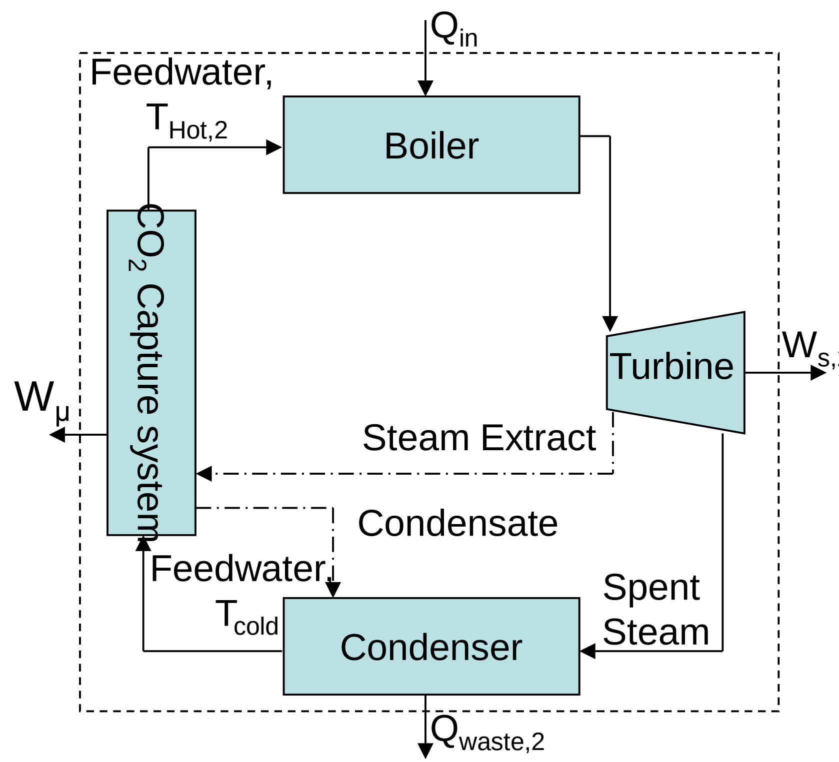
Lively et. al, *Ind. Eng. Chem. Res.*, **2009**, 49, 7550

Heat-Integration with Host Facility - Overview:

Typical carbon capture cycle

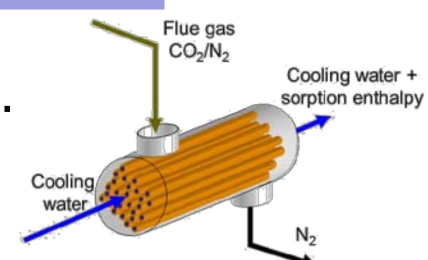


Heat integrated carbon capture cycle



Intrinsic energy penalty for CO_2 capture via adsorption = ΔH_{ads}
Typically 30-60 kJ/mol, or **18-36% parasitic load** for 90% capture

-- not including compression, pumps, fans compressors etc.



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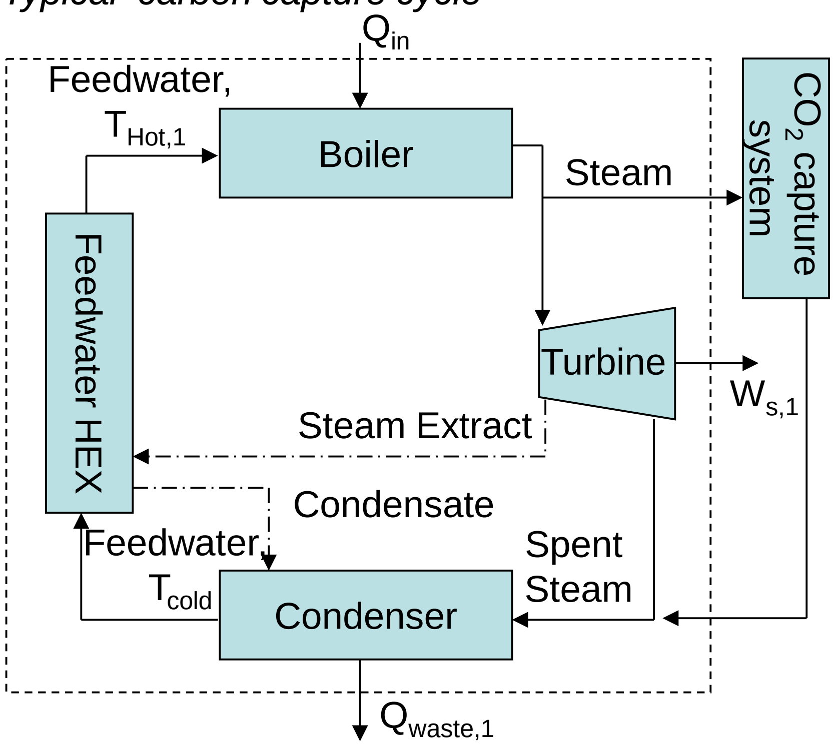

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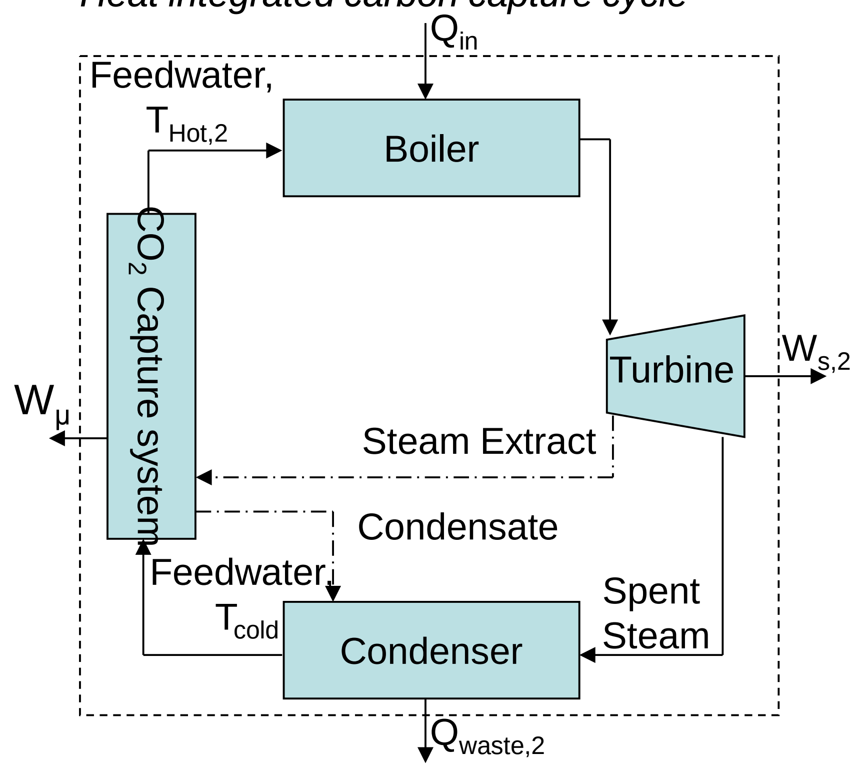

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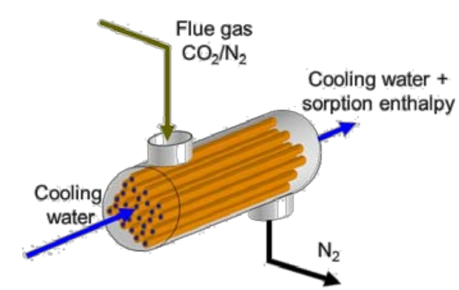
Typically 30-60 kJ/mol, or **18-36% parasitic load** for 90% capture

Experiments using 13X-based fiber sorbents have demonstrated **70% sorption enthalpy transfer** to cooling water; Intrinsic parasitic load can be reduced **to 5.4%-10.8%**



Advantages of RTSA/Amine System:

- Amines have high ΔH_{ads}; excellent heat integration required for an economic process; Hollow fiber system provides this.

- Hollow fibers already commercialized for membrane gas separations with multi-million fiber installations.

- Desorption mode for amine adsorbents critical:
  -- high T steam with direct contact of steam to adsorbent can degrade adsorbent.
  -- high T treatment with concentrated CO2 can degrade adsorbent, forming ureas.
  -- RTSA fiber process in PFR mode prevents contact with high gaseous CO2 concentrations and direct steam (lumen layer).

- Hollow-fibers are well-suited to give highly efficient heat transfer compared to a fixed or fluidized bed.

Risks:

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management (Mitigation and Response Strategies)
Technical Risks:			
Ability to switch and move large gas flow rates between modules on a commercial scale.	Low	Moderate	The ability to move large volumes of flue gas between several RTSA modules presents a technical challenge on the scale of a pulverized coal power plant. This risk does not impede the proposed work on the bench scale or even pilot scale studies, but the team must work to identify scalable engineering solutions to this potential problem.

Risks:

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Technical Risks:			
Impacts of SO_2, NO_x, Hg and particulates on composite fibers.	High	Low	For all amine-based capture processes, irreversible poisoning with NO_x and SO_2 will be an issue, necessitating effective gas clean-up prior to carbon capture. The extent to which these species will define the overall lifetime of a fiber module is critical information that is targeted as part of the proposed work.

Risks:

Description of Risk	**Probability (Low, Moderate, High)**	**Impact (Low, Moderate, High)**	**Risk Management (Mitigation and Response Strategies)**
Technical Risks:			
Fiber mechanical properties associated with gas flow pulsation.	Low	Moderate	If the gas pulsation associated with switching between adsorption and desorption modes leads to premature mechanical failure of the fibers, this could adversely shorten the lifetime of a module. Preliminary data suggests the fibers are robust to mechanical stresses.

Risks:

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management (Mitigation and Response Strategies)
Technical Risks:			
Stability of amines, lumen layer and fibers to oxidation.	Low	Moderate	At the low oxygen partial pressures in flue gas, the lumen layer, amines and fibers are expected to be quite stable to operating conditions. However, premature oxidative degradation could shorten the lifetime of fiber modules.
Commercial scale synthesis of the lumen layer.	Low	Low	it is expected that commercial scale application of a lumen layer to the composite hollow fibers is technically achievable, although the cost associated with doing this on a commercial scale is difficult to define.

Risks:

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Technical Risks:			
Process control allowing for high purity CO_2 product.	Moderate	Moderate	Two experimental desorption modes will be applied, CSTR mode and PFR mode. PFR mode requires the thermal (bore heating) and mass fronts (shell CO_2 desorption) be matched while purging the shell of the module with a nitrogen stream. This mode requires careful process control and optimization but should produce a high purity CO_2 stream.

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Technical Risks:			
Pressure drop of process	Low	Moderate	Pressure drop through the fiber modules depends on the packing density, module size, flow orientation and other factors. If the pressure drop required for flow is too high, compressors would be required rather than draft fans. Assessing accurately the pressure drop through the modules is an important component of the proposed work.

Risks:

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management (Mitigation and Response Strategies)
Technical Risks:			
Ease of spinning hollow fibers containing amines adsorbents	Moderate	Moderate	Spinning hollow fibers with different solid fibers initially requires a trial and error search for appropriate conditions. The ability to spin amine-hollow fibers composites might take weeks or months of optimization of conditions. It is critical to start as soon as possible.

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Tasks 1-6

Budget Period 1

October 2011 – September 2012

Tasks 1-2:

Task 1.0 – Project Management and Planning

The PI, Prof. Christopher Jones, will be responsible for all aspects of project management, including coordinating financial reporting information with business personnel at Georgia Tech (GT), providing reports as defined in the Deliverables section below to program officers at NETL, submission of required NEPA documentation, and maintaining and revising the Project Management Plan in conjunction with program officers at NETL.

Task 2.0 – **Preliminary Technology Feasibility Study**

During the first quarter of Budget Period 1, Georgia Tech and subcontractor Trimeric will complete the Preliminary Technology Feasibility Study prior to commencement of bench-scale testing.

Tasks 1-2:

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Subtask 2.1- Base Case Design Adaptation from Zeolite 13X data.
Based on laboratory research conducted prior to commencement of the proposed projects, Georgia Tech will develop a preliminary block flow diagram, material and energy balances, and stream tables for a full-scale facility as specified in the solicitation. This will be based on the preliminary calculations presented in Dr. Ryan Lively's thesis for zeolite 13X with operational modification of the cooling and heating to account for the higher heat of adsorption. The fiber number and amount of adsorbent will also be modified to account for the higher capacity of the amine adsorbent. The initial design will be for a parallel flow module in both adsorption and desorption. **This is already underway.**

Tasks 1-2:

Subtask 2.2 - Base Case Process Cost Estimation

Trimeric will adapt the block flow diagram into a process flow diagram (PFD). Then, Trimeric will develop capital and operating cost estimates for the full-scale process. First, Trimeric will size major process equipment based on the process data supplied by Georgia Tech. Trimeric will estimate the costs for major process equipment using commercially-available cost estimating software, published cost data and correlations available in the literature, and, as appropriate, by scaling equipment costs developed for similar equipment in recent projects., Trimeric will use the cost of hollow fiber membranes as a first approximation for the best-case sorbent fiber cost. A preliminary estimate for utility requirements (e.g., cooling water, steam) will be included with the feasibility study.

Tasks 1-2:

Subtask 2.3 - Sensitivity Analysis

Key issues impacting overall CO_2 capture cost will be identified for more detailed evaluation. Cost estimates will be developed in accordance with the DOE Quality Guidelines for Energy Systems Studies. Trimeric will apply a range of cost multipliers to the membrane cost to evaluate the sensitivity of total capital expenditures and cost of CO_2 capture to the cost of the sorbent fibers. Later revisions of the technology feasibility study will refine the cost of the sorbent fibers and will evaluate various adsorber designs and configurations. Two specific amine choices will be evaluated to understand the relative importance of different sorbent parameters, maximum capacity, sensitivity to oxygen, heat of adsorption, and shape of adsorption isotherm. Two amine loadings will be evaluated to probe whether optimization of the loading is significant for the bench scale module. This will lead to four specific cases that will serve as the starting point for further studies in subsequent budget periods.

Task 3:

Task 3.0 – Amine Sorbent Formulation and Oxidation

Two amine sorbents, one based on 3-aminopropyltrimethoxysilane-functionalized silica and one based on poly(ethyleneimine)-impregnated silica will be used in the RTSA systems. In this Task, the formulation and oxidative stability of the two amine sorbents will be evaluated.

Subtask 3.1 – Prepare Amine Sorbents for Fiber Spinning

The two sorbents will be prepared in quantities needed for hollow fiber spinning. Sorbents will be synthesized in-house from commercial precursors.

Subtask 3.2 – Stability of Sorbents to O_2

The two sorbents, in powder form, will be exposed to oxygen at partial pressures (0.1, 0.05, and 0.01 bar O_2) and temperatures relevant to post-combustion capture (55, 75, 95 and 115 °C) at various humidity levels (0%, 50% and 100% R_h). This will allow quantification of the lifetime of the sorbents with regard to oxidative degradation.

Tasks 4-5:

Task 4.0 – Preliminary Hollow Fiber Spinning
The experimental conditions required to spin hollow fibers of cellulose acetate containing the amine sorbent particles will be determined. The behavior of the supported amine adsorbents in the presence of cellulose acetate in various spinning solvents will be assessed. The fundamental phase behavior of polymer dopes (solutions of polymer and sorbent) needed to allow for spinning of cellulose acetate hollow fibers with high sorbent loadings will be determined.

Task 5.0 – RTSA Module Construction
Hollow fiber modules will be constructed from Swagelok® nylon fittings in the sizes needed for RTSA system testing. Integrity of potting and sealing techniques will be tested with existing hollow fibers.

Task 6:

Task 6.0 – Initial Model Development

In this task, a mathematical model for a single fiber will be developed that describes the heat transfer between the gas and fiber. An initial optimization model will be formulated utilizing the preliminary feasibility study in Task 2.

Subtask 6.1 - Subtask 6.1 Heat transfer model development.

A single, sorbent free, fiber model with no bore flow and only external gas flow will be developed. In this model, the focus will be on the heat transfer between the gas and the fiber, ignoring adsorption or desorption. Heat transfer parameters will be predicted by empirical correlations in literature (which will be corrected in later tasks).

Task 6:

Subtask 6.2 Heat transfer model implementation.

The above model will be implemented in a computational modeling environment (e.g. Matlab, gPROMS). Numerical approaches for the partial differential equation model will be tuned for this application.

Subtask 6.3 Optimization model formulation

A base-case optimization problem formulation will be developed. The result from Task 2 will be utilized to formulate reasonable design and operational constraints, operating parameter bounds, and objective functions.

Budget Period 1 Deliverables:

Task 2.0 – Preliminary Technology Feasibility Study at end of **Year 1, Q2**.

Task 3.0 –
Subtask 3.1 –Two supported amine sorbents will be prepared in quantities for fiber spinning, described in the **Year 1, Q4 report**.
Subtask 3.2 – Oxidative stability of two sorbents at various temperatures, oxygen partial pressures and humidities reported in the **Year 1, Q4 report**.

Task 4.0 - Conditions required to spin cellulose acetate fibers containing amine adsorbents communicated in the **Year 1, Q4 report**.

Task 5.0 - Construction of RTSA modules containing hollow fibers needed for RTSA module system testing reported in **Year 1, Q4 report**.

Task 6.0 – Written description of single fiber heat transfer model in **Year 1, Q4 report**.

Tasks 1, 7-11

Budget Period 2

October 2012 – September 2013

Task 7:

Task 7.0 – Update Technology Feasibility Study

Trimeric will refine equipment design and selection and will employ more detailed cost estimation approaches than the shortcut methods applied in the preliminary feasibility study. The update will evaluate equipment and methods to effectively integrate the cyclic adsorption and desorption processes with the continuous upstream and downstream processes.

Subtask 7.1 – Impact of Module Configuration on Operability and Cost

Various configurations of the sorbent module architecture will be evaluated, and options to control CO2 flow to the compressors during desorption will be evaluated. Crossflow versus parallel flow during the adsorption phase will be considered. Input from evaluation of initial heat and mass transfer resistance studies is anticipated. Equipment design decisions will consider not only process requirements but also plant operability and tradeoffs between capital and operating costs. Process flow diagrams will be updated accordingly.

Task 7:

Subtask 7.2 - Cost Estimation Refinement

Trimeric will update estimated purchased equipment costs using commercial cost estimating software (e.g., PDQ$ or similar), published cost data and correlations. For equipment having the greatest impact on capture cost, Trimeric will obtain vendor quotes. CO_2 capture costs will be factored cost estimates based on purchased equipment costs and will be developed in accordance with DOE Quality Guidelines for Energy Systems Studies. Trimeric will update the sensitivity calculations developed in Task 2 to reflect bench-scale and modeling results obtained via other tasks; the sensitivity study will reflect updated process configurations suggested by the evaluation of adsorber architecture options from Task 7.1. The study will address the sensitivity of CO_2 capture costs to sorbent properties and loading, cycle times, and adsorber design parameters.

Task 8:

Task 8.0 – Amine Sorbent Stability and Performance

Subtask 8.1 – Sorbent CO_2 Adsorption Isotherms and Kinetics

The two sorbent's CO_2 adsorption behavior is known from the literature in powder form. However, the sorbents have not been studied in polymeric hollow fibers. The composite hollow fiber sorbent's CO_2 adsorption properties will be evaluated and compared to the performance of the aminosilica sorbent in powder form. Heats of adsorption/desorption will also be measured.

Subtask 8.2 – Stability of Sorbents to SO_2 and NO_x

The two sorbents will irreversibly bind SO_2 and NO. The degree of irreversible binding will be assessed at three different concentrations relevant to post-combustion capture (low: 10 ppm SO_2, 25 ppm NO_x; medium: 42 ppm SO_2, 74 ppm NO_x; high 120 ppm SO_2, 150 ppm NO_x) at two temperatures (55 and 75 °C) using powdered sorbents. One NO_x/SO_2 mixture will also be used to assess any synergies in co-adsorption of these gases.

Task 9:

Task 9.0 – Hollow Fiber & Lumen Layer Synthesis

Subtask 9.1 – Spin Cellulose Acetate – Amine Sorbent Hollow Fibers

Cellulose acetate hollow fibers will be prepared containing the supported amine adsorbents at sorbent loadings of 50-75% by volume. The fibers will be used in CO_2 adsorption testing ex-situ, in a TGA or fixed bed for initial investigations (Task 8), followed by evaluation in single fiber and multi-fiber RTSA modules (Tasks 10 & 12-13).

Subtask 9.2 – Lumen Layer Formation

Building off subtask 9.1, the composite hollow fibers will be modified with a polymer latex to coat the fiber bore with a polymer film that will be largely impenetrable to gases (flue gases, steam) and liquids (heating or cooling water).

Subtask 9.3 – Prepare Hollow Fibers for RTSA System Testing

Hollow fibers will be prepared as needed for evaluation in Tasks 10 and 12-13

Task 10:

Task 10.0 – RTSA Module Construction and Operation

Subtask 10.1 – Construction of RTSA Bench Scale Testing Stations

Three RTSA testing stations will be built. Two will share a single mass spectrometer and will be used only for testing clean, simulated flue gas (N_2, CO_2, O_2, H_2O as only components). The third testing station will be designed to test gas adsorption cycles in the presence of dirty simulated flue gas containing the above components plus sulfur and nitrogen oxides.

Subtask 10.1.1 – Assemble RTSA Testing Station 1

RTSA station will be designed to test ¼" diameter and 8" length fiber modules for CO_2 uptake experiments, pressure drop measurements, and sorption enthalpy capture experiments.

Subtask 10.1.2 – Assemble RTSA Testing Station 2

RTSA station will be designed to accommodate ½" diameter and 3' length fiber modules for CO_2 desorption and heat management experiments.

Subtask 10.1.3 – Assemble RTSA Testing Station 3

The third RTSA station will be similar to station 1 but will be dedicated for CO_2 measurements using dirty feeds.

Task 10:

Task 10.0 – RTSA Module Construction and Operation

Subtask 10.2 – Single Fiber Operation – Temperature Profile Measurement

A single hollow fiber will be potted in a module with thermocouples wrapped around the inlet section, middle and exit section, to measure the temperature profile during adsorption, which is needed for validating modeling studies in subtask 11.1.

Subtask 10.3 – RTSA Operation – No Bore Heat/Cool – Clean Gas

Hollow fibers without lumen layers will be potted and tested in ¼" modules (6 fibers at maximum filling fraction) in cyclic CO_2 capture operation. Adsorption/desorption cycling will be facilitated with external heating and desorption with an inert gas purge.

Subtask 10.4 – RTSA Operation – Active Bore Heat/Cool – Clean Gas

Complete, composite hollow fibers with lumen layers will be assembled in ¼" modules and evaluated in cyclic CO_2 capture operation. Desorption will be achieved with hot water feed through the bore in CSTR mode.

Task 11:

Task 11 – RTSA Model and Optimization Development

The single fiber model developed in Task 6 will be further extended to consider the adsorption equilibrium. Partial validation with experimental data will be performed.

Subtask 11.1. Validation of heat transfer model

The model developed in subtask 6.1 will be validated against an experiment that measures the temporal and spatial profiles of the temperature on the surface of the fiber. A model parameter update will be performed which will correct the predicted parameters from Task 6.1.

Subtask 11.2. Development of single-fiber adsorption/desorption model

The model developed in 11.1 will be further extended to consider adsorption and desorption, utilizing the equilibrium data obtained in Task 8. Mass and heat transfer parameters will be predicted by empirical correlations in literature (which will be corrected in later tasks).

Subtask 11.3 Implementation of single-fiber adsorption/desorption model

The model developed in 11.2 will be implemented on a computational modeling environment (e.g. gPROMS).

Task 11:

Task 11 – RTSA Model and Optimization Development

Subtask 11.4 Development of module model with adsorption and desorption

The fiber sorbent module that handles adsorption and desorption will be modeled. This model includes the description of hot and cold water flows in desorption and adsorption steps, respectively. Mass and heat transfer parameters will be predicted by empirical correlations in literature (which will be corrected in later tasks).

Subtask 11.5. Implementation of module model with adsorption and desorption

The model developed in 11.4 will be implemented in a computational modeling environment (e.g. gPROMS).

Subtask 11.6 Implementation of optimization model

The optimization model developed in 6.3 will be implemented in a computational environment (e.g. gPROMS). Numerical approaches for the partial differential equation model and algorithms that solve the optimization problem efficiently and robustly will be investigated.

Budget Period 2 Deliverables:

Task 7.0 –
Subtask 7.1 - Impact of module configuration on operability and cost - describe the adsorber configurations considered, the advantages and disadvantages of the configurations, and a recommended configuration for inclusion in subsequent systems analyses, in **Year 2, Q4 report**.
Subtask 7.2 - Cost estimation refinement - summarize revisions to process economics and design recommendations based on the sensitivity study conducted under Task 7.2 in **Year 2 Q4** progress report.

Task 8.0 –
Subtask 8.1 - Sorbent CO_2 adsorption isotherms and kinetics reported in the **Year 2, Q3 report**.
Subtask 8.2 - The degree of irreversible binding of SO_2 and NOx to the supported amine sorbents after exposure at concentrations relevant to CO_2 capture communicated in the **Year 2, Q4 report**.

Budget Period 2 Deliverables:

Task 9.0 –
Subtask 9.1 - Spin cellulose acetate - amine sorbent hollow fibers demonstrated and described in the **Year 2, Q3 report**.
Subtask 9.2 - Lumen layer construction - construction of a lumen layer in the hollow fibers demonstrated and described in the **Year 2, Q4 report**.
Subtask 9.3 - Prepare hollow fibers for RTSA system testing - In each quarter of year 2, the continued ability to prepare sufficient volumes of fibers for Task 10 will be verified and reported.

Task 10.0 –
Subtask 10.1 - Construction of RTSA bench scale testing stations
Assemble RTSA testing station 1 - reported in the **Year 2, Q2 report**.
Assemble RTSA testing station 2 - reported in the **Year 2, Q3 report**.
Assemble RTSA testing station 3 - reported in the **Year 2, Q4 report**.

Budget Period 2 Deliverables:

Subtask 10.3 – operation of RTSA testing station 1 in CO_2 capture experiments without active heating and cooling in the bore demonstrated and communicated in the **Year 2, Q3 report**.

Subtask 10.4 - operation of RTSA testing station 1 in CO_2 capture experiments with active heating and cooling in the bore demonstrated and communicated in the **Year 2, Q4 report**.

Task 11.0 – Single Fiber Model Development

Subtask 11.6 – Implementation of optimization model - a description of the optimization model communicated in the **Year 2, Q4 report**.

Tasks 1, 12-16

Budget Period 3

October 2013 – September 2014

Tasks 12-13:

Task 12 – Composite Hollow Fiber Sorbent Stability

Hollow fibers containing amine sorbents will be evaluated for stability to O_2, SO_2 and NOx separately at the conditions deemed most important in subtask 8.2, to assess any changes in stability in composite form vs. the powder form.

Task 13 – RTSA Testing and Operation

Subtask 13.1 – RTSA Operation - Clean Gas – Heat Management

Complete, composite hollow fibers with lumen layers will be assembled in ½" modules and evaluated in cyclic CO_2 capture operation. Desorption will be achieved with hot water feed through the bore in CSTR mode.

Subtask 13.2 – RTSA Operation – Dirty Gas – Effect of Contaminants

Complete, composite hollow fibers with lumen layers assembled in ½" modules will be evaluated in cyclic CO_2 capture operation with gases containing sulfur and nitrogen oxides. Desorption will be achieved with hot water feed through the bore in CSTR mode.

Tasks 12-13:

Task 13 – RTSA Testing and Operation

Subtask 13.3 – RTSA Operation – Clean Gas – Front Matching

Complete, composite hollow fibers with lumen layers assembled in ½” modules will be evaluated in cyclic CO_2 capture operation. Desorption will be achieved with hot water feed through the bore in PFR mode to experimentally evaluate the ability to match propagating thermal and mass fronts, for improvement of CO_2 purity.

Task 14:

Task 14.0 – Model Testing, Refinement and Validation, Optimization Studies

In this final modeling task, the full mathematical description of the fiber module developed considering adsorption and desorption in Task 11, will be validated against experimental data. The mathematical model obtained will be used in a systematic trade-off study by numerical (computational) optimization.

Subtask 14.1 Validation of single-fiber adsorption model

The single fiber model implemented in Task 11.3 will be validated against adsorption breakthrough experiments. Model parameter update will be performed which will correct the predicted parameters.

Subtask 14.2 Validation of single-fiber desorption model

The single fiber model implemented in Task 11.5 will be validated against desorption experiments. Model parameter update will be performed which will correct the predicted parameters.

Task 14:

Task 14.0 – Model Testing, Refinement and Validation, Optimization Studies

Subtask 14.3 Validation of module model with adsorption

The full module model implemented in Task 11.6 will be validated against adsorption breakthrough experiments. Model parameter update will be performed which will correct the predicted parameters.

Subtask 14.4 Validation of module model with desorption

The validated model in Task 14.4 will be further compared against experimental data for desorption. The prediction of CO_2 concentration profile will be examined.

Subtask 14.5 Trade-off analysis by multi-objective optimization

An optimization study for design and operation will be performed using the mathematical model. Trade-offs of CO_2 purity, recovery, and pressure drop will be quantified systematically by multi-objective optimization.

Task 15:

Task 15.0 – Final RTSA Technical Feasibility Study

Georgia Tech and Trimeric will complete the Final Technology Feasibility Study. Georgia Tech will supply updated heat and material balances and stream tables using results from Tasks 10 and 13. Trimeric will revise process flow diagrams, equipment sizing and selection as appropriate, utility requirements (e.g., cooling water, steam) and cost estimates for CO_2 capture. Updated vendor quotes will be obtained for major pieces of equipment having the largest impact on capture costs. Trimeric will consult utility partner, Southern Company, to develop construction and installation costs that are consistent with costs encountered in the utility industry. A process description will discuss the final recommended process configuration, methods of heat removal and addition, and heat integration with the main power facility. Equipment lists will document key equipment design parameters (e.g., materials of construction, adsorber pressure drop). The study will also address operability-maintenance concerns such as removal of sorbent agglomerates and fines.

Task 16:

Task 16.0 – Environmental Health & Safety Assessment

The EH&S Risk Assessment will evaluate process emissions and wastes, process toxicological impacts, material properties, compliance and regulatory issues, opportunities for risk reduction, and considerations for handling, storage, disposal and releases. Trimeric will estimate the air and water emissions as well as solid waste generated by the process using the material balances developed in Task 15. Trimeric will collate relevant material properties to support the toxicological evaluation. The EH&S consultant will evaluate and document the compliance and regulatory issues for the process. As appropriate, Trimeric will investigate and document options for risk reduction. Trimeric will work with the EH&S consultant to develop precautions and recommendations for materials handling, storage, disposal, and accidental release measures.

Budget Period 3 Deliverables:

Task 12 - Composite fiber sorbents evaluated for stability to O_2, SO_2 and NO_x separately at one set of conditions from subtasks 3.2 and 8.2 and the results reported in the **Year 3, Q2 report**.

Task 13 –
Subtask 13.1 - RTSA Operation - successful operation of RTSA testing station 2 in CO_2 capture experiments with active heating and cooling in the bore demonstrated. Temperature profiles in the module reported in the **Year 3, Q2 report**.
Subtask 13.2 - RTSA Operation - successful operation of RTSA testing station 3 in CO_2 capture experiments using simulated flue gas containing SO_2, NO_x and O_2 contaminants with active heating and cooling in the bore demonstrated and reported in the **Year 3, Q3 report**.
Subtask 13.3 - RTSA Operation - successful operation of RTSA testing station 1 in CO_2 capture experiments using simulated flue gas with active heating and cooling in the bore demonstrated using PFR desorption and reported in the **Year 3, Q4 report**.

Budget Period 3 Deliverables:

Task 14.0 – Module Model development & Optimization - validation of single fiber desorption model described in the **Year 3, Q3 report**.

Task 15.0 - Final RTSA Technology Feasibility Study – final technology feasibility study will comprise updated PFDs, heat and material balances, equipment selection and costs, cost of CO_2 capture and impacts on plant efficiency, summary of design rationale and improvements developed during the project, and identification of key factors that impact costs for the proposed RTSA approach; end of the project, in **Year 3, Q4**.

Task 16.0 - Environmental Health & Safety Risk Assessment – document process emissions and wastes, process toxicological impacts, material properties, compliance and regulatory issues, opportunities for risk reduction, and considerations for handling, storage, disposal and releases; end of the project, in **Year 3, Q4**.

Milestones & Decision Points

Milestone Log:

Budget Period	Task/Subtask No.	Milestone Description	Planned Completion	Actual Completion	Verification Method
1	1a	Updated Project Management Plan	11/30/2011		Project Management Plan file
1	1b	Kickoff Meeting	12/31/2011		Presentation file
1	2	Preliminary Technology Feasibility Assessment	03/31/2012		Year 1, Q2 report
1	3	Amine Sorbents Available for Fiber Spinning	9/30/2012		Year 1, Q4 report
2	7	Updated Technology Feasibility Assessment	9/30/2013		Year 2, Q4 report
2	10	Demonstrated RTSA Operation using Hollow Fiber Module	9/30/2013		Year 2, Q4 report

Milestone Log:

Budget Period	**Task/Subtask No.**	**Milestone Description**	**Planned Completion**	**Actual Completion**	**Verification Method**
2	11	Transient Adsorption-Desorption Model for a Single Composite Hollow Fiber	9/30/2013		Year 2, Q4 report
3	13	RTSA Experimental Data for Verification of RTSA Model	03/31/2014		Year 3, Q2 report.
3	14	RTSA Model Validation with Experimental Data	06/30/2014		Year 3, Q3 report.
3	15	Final Technology Feasibility Study	09/30/2014		Year 3, Q4 report.
3	16	Environmental Health & Safety Assessment	09/30/2014		Year 3, Q4 report.

Decision Points:

Decision Point	Date	Success Criteria
Preliminary Technology Feasibility Study shows RTSA technology may offer a competitive approach for post-combustion CO_2 capture. (Milestone 2)	03/31/2012	No major technology flaws identified.
Supported amine sorbents can be prepared on the scale needed to synthesize hollow fibers. (Milestone 3)	9/30/2012	Demonstrated ability to prepare at least 250 g of supported amine adsorbent by this date.
Amine sorbent is sufficiently stable to oxidation (Milestone 3)	9/30/2012	Amine sorbent maintains >80% of its initial capacity after exposure to oxygen at flue gas concentrations and temperatures for 24 hours.
RTSA modules successfully constructed and operated in CO_2 capture experiments (Milestone 10)	9/30/2013	RTSA testing station operated using a multi-fiber module demonstrating ability to cycle through at least 3 adsorption and 3 desorption steps using clean feed, capturing >70% of CO_2.

Decision Points:

Decision Point	Date	Success Criteria
Transient Adsorption/Desorption Model for a Single Composite Hollow Fiber (Milestone 11)	9/30/2013	Model demonstrates that it can produce temperature and adsorption profiles that match within +/- 30% fiber behavior from previous experimental studies on Zeolite 13X .

Summary:

- Novel polymer/amine sorbent composite hollow fiber based RTSA process for post-combustion CO_2 capture.
  - -- 60% experimental demonstration
  - -- 40% modeling, optimization, and economic feasibility analysis

- Georgia Tech, Trimeric, GE Energy, Algenol Biofuels are major partners

- Annual reports, annual review meetings and conference presentations, and in some cases, quarterly reports.

- DOE budget ~$2.4M; Partner budget ~$0.6M;