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

primary project goals

Georgia Tech Research Corporation developed a rapid temperature swing adsorption (RTSA) carbon dioxide (CO_2) process and evaluated the cost and performance benefits of this novel hybrid capture approach via bench-scale testing of a module containing polymeric/supported amine hollow fibers, which are loaded with supported adsorbents and surround an impermeable lumen layer that allows for cooling and heating.

technical goals

- Produce polymeric hollow fiber contactors loaded with amine adsorbent particles for post-combustion (CO_2 capture.
- Develop a computational model of the fiber module and validate it in parallel with the experimental program.
- Assess adsorption/desorption and heat-exchange performance of hollow fiber modules using simulated clean and simulated dirty flue gas.

technical content

Supported amine adsorbents have many promising properties with regard to CO_2 capture from post-combustion flue gas. However, most previous studies of supported amine materials focus only on CO_2 adsorption, ignoring desorption. In addition, essentially all published studies describe the use of supported amine materials in fixed beds. This process configuration is difficult to use at practical scales due to heat integration challenges. This is especially important for supported amines; whose heats of adsorption are among the highest of known CO_2 adsorbents (50–80 kJ/mol), but which enables large swings in capacity with temperature. Thus, practical process designs for amine sorbents must include effective heat transfer.

Recently, the use of novel polymeric hollow fiber contactors loaded with CO_2 adsorbents has been introduced as a scalable process configuration for CO_2 capture. In this approach, polymeric hollow fibers, similar to those used for commercial-scale membrane gas separation, are prepared and loaded with large volumes of solid CO_2 adsorbing materials. However, unlike those used for membrane applications, these hollow fibers have several unique aspects. First, high volumes of adsorbent materials are included, typically 60–75 percent by volume. Second, the polymeric phase is designed to have many large voids, allowing rapid mass transfer to the sorbent particles. Third, a dense lumen layer is installed in the fiber bore to largely shutdown transport from the shell side of the fibers to the bore. This design yields fibrous structures that are ideally suited for application as combined sorption and heat transfer modules in an RTSA process. Total cycle times are in the order of 3 minutes.

In the amine-hollow-fiber RTSA process, flue gases flow over the shell of the fibers while cooling water flows through the bore. Given the small diameter of the fibers, the fibers

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Bench-Scale, Simulated Flue Gas

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Rapid Temperature Swing Adsorption

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percent complete:
100%

and adsorbents can be maintained in nearly isothermal conditions, with the cooling fluid providing an effective reservoir for heat of adsorption (Figure 1). At the appropriate time, the flue gas can be rerouted to another bed and the fibers can be switched to desorption mode by passing hot water through the fiber bore, driving off the CO_2.

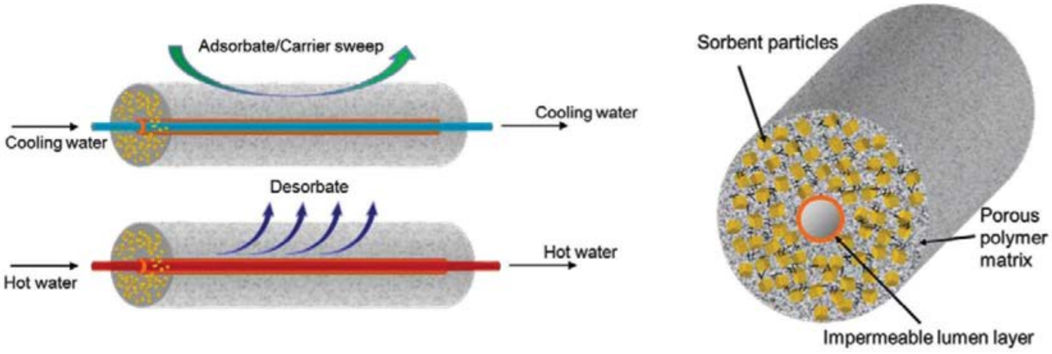

Figure 1: Sorption (top) and desorption (bottom) modes in hollow fiber sorbents

This RTSA approach was previously demonstrated using cellulose acetate fibers and zeolite 13X as the adsorbent in the fibers. Zeolite 13X is not an ideal sorbent for wet post-combustion CO_2 capture streams, but supported amines may be well suited for the task.

The hollow fiber architecture has three key attributes: (1) it provides the adsorption surface area needed to handle large volumes of flue gas, (2) it enables efficient heat transfer needed to handle the high heat of adsorption of supported amines, and (3) it is readily scalable given the current commercial capability to produce large surface area hollow fibers on an industrial scale.

The RTSA process based on hollow fibers containing supported amine adsorbents represents a novel new process configuration for post-combustion CO_2 capture. In a commercial process, multiple hollow fiber modules would be used, and modules would cycle synergistically between adsorption and desorption modes in a continuous process, as shown in Figure 2.

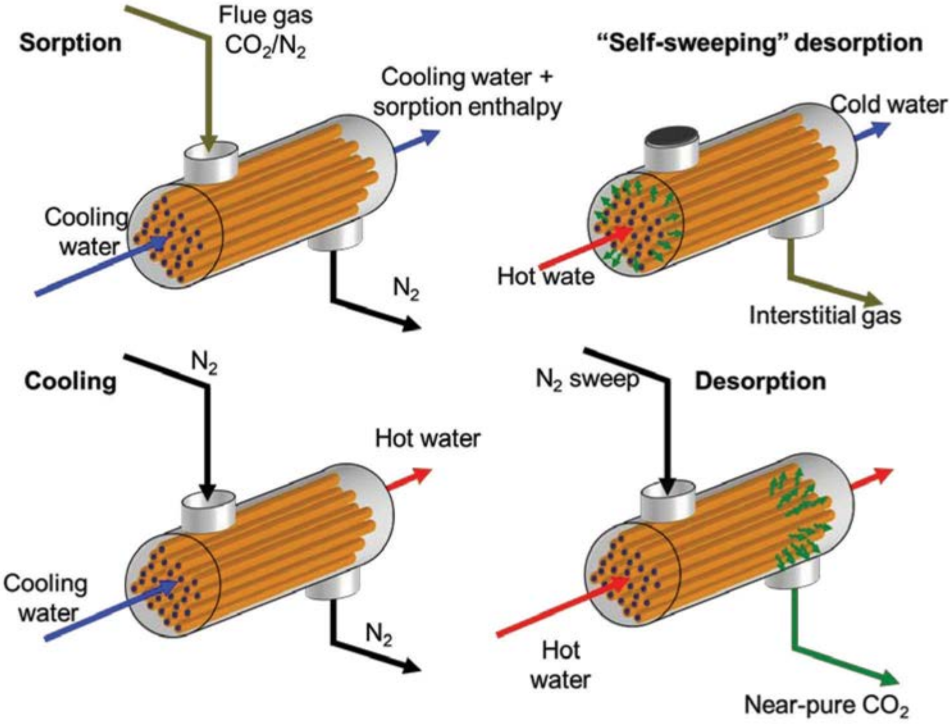

Figure 2: Potential RTSA process configuration

The sorbent and process parameters are shown in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,100	1,100
Bulk Density	kg/m^3	1,100	1,100
Average Particle Diameter	mm	1.2	1.0
Particle Void Fraction (void fraction of fiber bed)	m^3/m^3	0.4–0.5	0.28–0.3
Packing Density (packing density of fiber bed)	m^2/m^3	1,000	1,600
Solid Heat Capacity @ STP	kJ/kg-K	1,800	3,000
Crush Strength	kg_f	1.140	1.140
Manufacturing Cost for Sorbent	\$/kg	unknown	unknown
Manufacturing Cost for Fiber Module (includes hardware, fibers, sorbent)	\$/kg	unknown	\$10/m^2 or \$25–\$35/kg
Adsorption			
Pressure (partial pressure of CO_2)	bar	0.159	0.13
Temperature	°C	55	35
Equilibrium Loading	g mol CO_2/kg fiber	0.84	1.0–1.5
Heat of Adsorption	kJ/mol CO_2	59	55–65
Desorption			
Pressure	bar	0.2	1.0
Temperature	°C	120	90
Equilibrium CO_2 Loading	g mol CO_2/kg fiber	0.34	0.1
Heat of Desorption	kJ/mol CO_2	59	55–65
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	shell and tube	
Flue Gas Flowrate	kg/hr	200 sccm (lab), ≈2,900 (full scale, per module)	0.5 (lab), ≈2,900 (full scale, per module)
CO_2 Recovery, Purity, and Pressure	% / % / bar	91%/96 mol%/0.2 bar (0.19 bar partial pressure)	90%/95 mol%/1 bar or 80 mol% at 5.5 bar
Adsorber Pressure Drop	bar	<0.1	<0.15
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The underlying mechanism is primary and secondary amines reacting with CO_2 to produce carbamates or (bi)carbonates, depending on the nature of the amines, amine loading, and humidity level. Under most conditions, a mixture of species is formed on the adsorbent surface.

Sorbent Contaminant Resistance – Thus far, the solid supported amines developed for this project have displayed excellent oxidative stability, stability in humid conditions (5–90 percent relative humidity [RH]), and resistance to nitric oxide. The active amine fillers are poisoned by high concentrations of sulfur oxide (SO_x, 200 parts per million [ppm]), and extensive sulfur removal is needed.

Sorbent Attrition and Thermal/Hydrothermal Stability – Due to the sorbents being “protected” within the walls of the hollow fiber sorbents, the Georgia Institute of Technology has yet to experience any mechanical issues (such as attrition) in their studies. The fibers themselves are quite temperature-resistant, but the amines have a realistic upper temperature limit of ≈130 °C. The amines contained within the fiber walls exhibit higher CO_2 uptake capacities in the presence of water; moreover, the fibers themselves have been continuously cycled between 35°C and 120°C without damage to the fiber structure. These suggest that the materials are hydrothermally stable within the operating ranges of the RTSA process.

Flue Gas Pretreatment Requirements – Current analysis indicates that flue gas cooling to approximately 35 °C is required for low-cost CO_2 capture. Experimental work suggests that partial dehydration of the flue gas may prolong fiber lifetimes (i.e., 90 percent RH vs. 100 percent RH). Finally, further wet FGD may be required for additional SO_x removal for optimum long-term performance of the amines.

Sorbent Makeup Requirements – Analyses investigating the amine loss rates are needed. It has been demonstrated that deactivated amines can be removed when required, and fresh amines redeposited in the fibers, allowing fiber recycling and reuse.

Waste Streams Generated – Spent fiber sorbents represent the only process waste stream. Currently, the fibers are assumed to last 3 years before replacement is required. With appropriate flue gas scrubbing, such lifetime may be achievable.

Process Design Concept – See Figure 2.

technology advantages

- Deleterious thermal effects typically associated with packed-bed sorption can be mitigated and higher sorption efficiencies can be achieved by utilizing the hollow fiber morphology to supply cooling agents in the bore of the fiber during adsorption.
- The thin porous walls of the fiber sorbent allow for rapid heat and mass transfer equilibration, thereby allowing for more rapid thermal cycles and thus reducing device volume.
- Pressure drops through these beds will be correspondingly lower than those of packed or fluidized solid sorbent beds, which will reduce draft fan costs.
- Heat transfer fluids in the bore of the fibers can be as simple as hot water and cold water, providing an environmentally friendly overall process.
- Rapid heat transfer enables potential recovery of heat of adsorption and reuse of sensible heat of the bed. This affords heat integration both within the capture process and may facilitate heat integration with the boiler feed water preheat. This can dramatically reduce the overall parasitic thermal load of the RTSA process.

R&D challenges

- High heat of adsorption, with heat management improved by contactor design.
- Deactivation of sorbents upon exposure to SO_x and exposure to saturated humidity and temperature.
- Low-working capacity in more conventional contactors.
- Efficient heat integration with power plant.
- Long-term operation of complete cycles with bore-side heating and cooling.
- Manufacturing cost estimates of fibers have significant uncertainty.
- Design of efficient multibed cycles to improve recovery and purity.
- Adaptive scheduling and control to manage slow degradation over many cycles and variability between modules.

status

The project was completed on March 31, 2015. Georgia Tech has developed a post-spinning amine infusion method to create and recharge sorbents. A dual layer spinning method was developed for constructing a barrier lumen layer in the fiber bore, which allows the fiber to be used as an adsorbing shell-in-tube heat exchanger. Testing has been completed on hollow fiber RTSA modules. Heat integration in the RTSA process has allowed for up to 70 percent recovery of the heat of adsorption and the RTSA cycle time has been reduced to 3 minutes. A detailed process model of the cyclic pressure temperature swing adsorption module was developed and validated against experimental data. The process model was integrated with costing models for the overall process that included compression and flue gas conditioning. The CO_2 capture cost was estimated to be \$44.8/tonne CO_2.

available reports/technical papers/presentations

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