Project Title:

Metal Monolithic Amine-Grafted Silica for CO_2 Capture

Technology Area:	**Technology Maturity:**
Post-Combustion Sorbents	Bench-Scale, Simulated Flue Gas

Primary Project Goal:

To develop a low-cost carbon dioxide (CO_2) capture technology by integrating metal monoliths with a grafted amine sorbent.

Technical Goals:

- 1.5 mmol-CO_2/g-sorbent
- 1.0 mmol-sulfur dioxide (SO_2)/g-sorbent
- 500 repeated thermal cycles of sorbent between CO_2 adsorption at 25°C and desorption at 110°C with less than 10% degradation in original CO_2 capture capacity.

Technical Content:

The key innovation of this project is the utilization of metal foils with amine-grafted porous silica to fabricate a highly efficient and low-cost CO_2 adsorption system. Porous silica, alumina, zeolite, and carbon, which are used as commercial adsorbents for a wide range of applications, are impregnated with alkyl amine molecules such as monoethanolamine/tetraethylenepentamine. The adsorption capacity of this novel amine-grated silica was found to be greater than 1.5 mmol-CO_2/g-sorbent because of the abundance of available amine functional groups on the amine-grafted silica. The adsorption and desorption (i.e., CO_2 capture capacity) can be further fine-tuned and optimized by the sorbent preparation procedures.

The purpose of the metal foil is to fabricate the metal monolithic structure. The surface of the metal monolith is coated with a layer of silica, carbon fibers, and a binder. Calcination of the metal monolith with this coating produces the silica or zeolite layers structure with 10 µm diameter channels. The binder and carbon fiber concentration is fine-tuned to optimize the number of the micro channel pathways for CO_2 diffusion into the amine-grafted silica and zeolite.

The University of Akron, as part of this project, has also investigated using coal fly ash treated first with sodium hydroxide (NaOH) and/or hydrochloric acid (HCl) and then impregnated with the amine tetraethylene-pentamine. Coal fly ash is being investigated as a support for amine due to its ready availability and low cost.

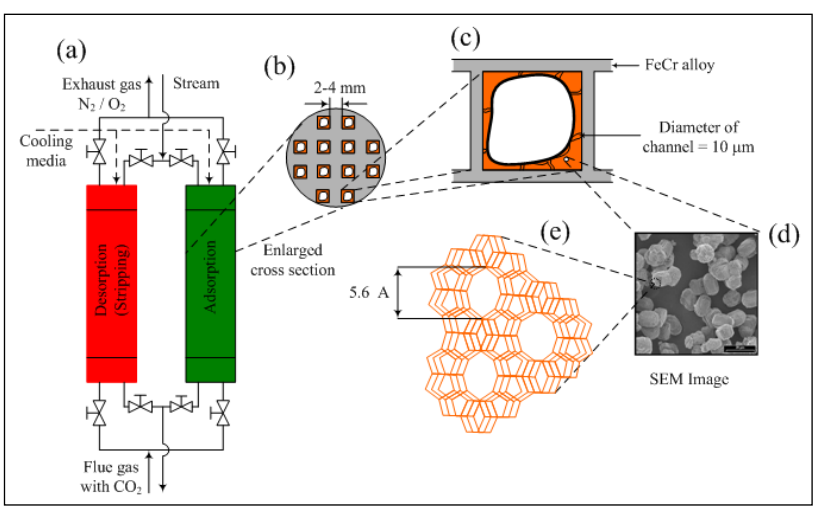

Figure 1: Metal Monolithic Amine-Grafted Silica Sorbents

Figure 1 displays the amine-grafted zeolite structure (5.6 Angstroms in length) inside an adsorption unit. The amine is located in the adsorption (a) chamber within holding tubes. The tubes housed in the adsorption unit that holds the individual metal (b) tubes with the amine about 2-4 mm apart. The silica or zeolite is coated inside the square metal tube. Gas enters the tube and flows through the channels (d) of the amine grafted silica, which are 10 µm

in diameter. The goal is that the CO_2 and SO_2 adsorption capacity of the amine will be greater than 1.5 mmol-CO_2/g-sorbent for CO_2 and 1.0 mmol-CO_2/g-sorbent for SO_2. The regeneration ability of the amine is >500 times, while having <10% degradation of the CO_2 capture capacity. The amine grafted silica sorbent is expected to exhibit a heat capacity of 1.5 kJ/kg K. The CO_2 will be captured at an approximate temperature of 50°C (140°F) and then released at approximately 110°C (230°F).

Table 1: Process Parameters for Metal Monolithic Amine-Grafted Silica Sorbents

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	PEG/TEPA/SiO_2	N/A
	Heat of adsorption (kJ/mole CO_2)	52	50-55
	CO_2 loading/working capacity, wt.%	6.4	6.0
	Surface area, m^2/g		
	Particle density, cm^3/g		
	Packing density, cm^3/g		
	Particle size (mm)	0.05-.3	0.25
	Heat capacity (kJ/K/kg)	1.49	1.3-1.5
	Thermal stability, °C	130°C	130°C
	Hydrothermal stability, °C	Not tested	
Process Configuration	Attrition rate (fluidized bed), %/year		
	Cycle time (fixed bed), minutes	30	
	Pressure drop (fixed bed), psia		
Operating Conditions	Adsorption temperature, °C	50	50
	Adsorption pressure, atm.	1	1
	CO_2 capture efficiency, %		
	Regeneration method	Thermal swing	Thermal swing
	Regeneration temperature, °C	100 - 110	100 - 110
	Regeneration pressure, atm.	1 - 1.05	1 – 1.05
Heat Integration	Required regeneration steam temperature, °C	100-110	100-110
Miscellaneous	Sorbent make-up rate, kg/kgCO_2	Not tested	
Product Quality	CO_2 purity, %	15%	
	N_2 concentration, %	balance	
	Other contaminants, %	N/A	
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	
	Heat requirement, kJ/kgCO_2	N/A	
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	

Technology Advantages:

- High stability for CO_2 adsorption and desorption.
- Accelerated removal of the heat of adsorption.
- Low regeneration heat duty due to the low heat capacity of the sorbent.
- Low-cost immobilized amine sorbent.

R&D Challenges:

- The scaleup transition from lab- to bench-scale tests.
- Temperature swing adsorption requires a long cycle time due to the heating and cooling of the sorbent.
- Contaminants, such as sulfur oxides (SO_X), will react with amine functional groups similar to the monoethanolamine process.
- Currently, the CO_2 capture capacity of the sorbent is too low.

Results To Date/Accomplishments:

Recent results show that the silica-supported amine sorbent with additives is able to capture more than 1.6 mmol CO_2/g-sorbent at 40°C and desorb at 100°C for more than 500 cycles with less 13% degradation. Degradation was found to be due to the overheating of those sorbents which were in contact the tube wall. During heating for CO_2 desorption, the wall temperature is 5°C to 15°C higher than that of the center of packed bed.

Tested three types of sorbent supports for the amines.

- Prepared and determined more than 15 samples of alkyl, amine-grafted zeolite/oxide for CO_2 capture and 10 samples of aryl, amine-grafted oxides for SO_2 capture.
- Conducted DRIFT adsorber studies for CO_2 capture and characterization studies of TEPA/Silica 68.
- Conducted tubular adsorber studies for silicon dioxide (SiO_2) amines in quartz and copper tubes.
- Observed that treating coal fly ash with hydrogen chloride (HCl) followed by sodium hydroxide (NaOH) increased its surface area by an approximate factor of 14.

Next Steps:

- Continue to improve CO_2 and SO_2 capture capacity and stability.
- Determine long-term stability of the sorbents.
- Fine-tune sorbent composition.
- Fabricate CO_2 absorber.
- Test performance of the absorber.
- Conduct economic analysis.

Available Reports/Technical Papers/Presentations:

"Metal Monolithic Immobilized Amine Absorber for Carbon Dioxide Capture," U.S. Patent Applications, Nov. 7, 2008, UA 685.

"Oxide-supported Tetraethylenepentamine for Carbon Dioxide Capture," J. C. Fisher II, J. Tanthana, and S. S. C. Chuang, Environmental Progress & Sust Energy, 28 (4), 589-598, 2009.

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