APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION SORBENTS

BENCH-SCALE DEVELOPMENT AND TESTING OF RAPID PRESSURE SWING ABSORPTION FOR CARBON DIOXIDE CAPTURE

primary project goals

WR Grace and the University of South Carolina are developing a rapid pressure swing adsorption (PSA) process to evaluate concept cost and performance benefits by testing a bench-scale system using a low-cost, structured adsorbent with low-pressure drop, high mass-transfer rates, high capacity, and high availability that will enable large feed throughputs.

technical goals

- Develop an attrition-resistant and low-pressure drop structured adsorbent based on a commercial zeolite that is compatible with the high velocities associated with rapid PSA operation.
- Develop a rapid PSA cycle configuration in concert with the structured adsorbent so that the resulting rapid PSA process delivers an exceptional performance at reduced capital and operating costs.

technical content

PSA is attractive because it only requires electricity and not any of the power plant's steam. A PSA cycle has recently been developed for carbon dioxide (CO_2) capture that has a total separation energy of 25 kJ/mol compared to 39.0 kJ/mol for a monoethanolamine (MEA) system. This new PSA cycle achieves more than 90 percent CO_2 recovery and more than 95 vol percent CO_2 purity using commercial zeolite pellets. Although it could be retrofitted to a coal-fired power plant today, the columns would be exceedingly large and thus capital-intensive. A rapid PSA process, taking advantage of a much shorter cycle time, could potentially solve this problem by reducing the cycle time from 300 seconds (conventional PSA cycle) to 30 seconds or less. This would increase the feed throughput, and thus decrease the size of the columns by a factor of 10 or more, significantly reducing both the capital and operating costs, as well as the plant footprint.

The key challenge to the success of this concept is two-fold: (1) an attrition-resistant and low-pressure drop structured adsorbent must be developed based on commercial zeolite that is compatible with the high velocities associated with rapid PSA operation; and (2) a rapid PSA cycle configuration must be developed in concert with the structured adsorbent so that the resulting rapid PSA process achieves necessary cost and performance metrics.

One advantage of a rapid PSA process over other CO_2 adsorption processes is simplified heat management. The rapid cycle times minimize temperature swings. Thus, the columns will heat up only slightly during adsorption and cool down only slightly during desorption, approaching nearly isothermal operation, which is optimal.

technology maturity:

Bench-Scale,
Simulated Flue Gas

project focus:

Rapid Pressure Swing
Adsorption

participant:

WR Grace

project number:

FE0007639

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partners:

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Battelle Memorial Institute

performance period:

5/1/12 – 4/30/15

Management of water will provide some operational challenges. Degradation of the PSA process performance in the presence of water is well documented. It is anticipated that for a rapid PSA CO_2 removal process, up to 95 percent of the water in the flue gas will need to be removed using commercial desiccant technology. This will increase capital and operating costs; however, any increases are more than offset by cost savings in other parts of the process.

The structured adsorbent to be developed will consist of zeolite crystals coated on a metal support. This process has been successfully demonstrated using metal foil, as shown in Figure 1.

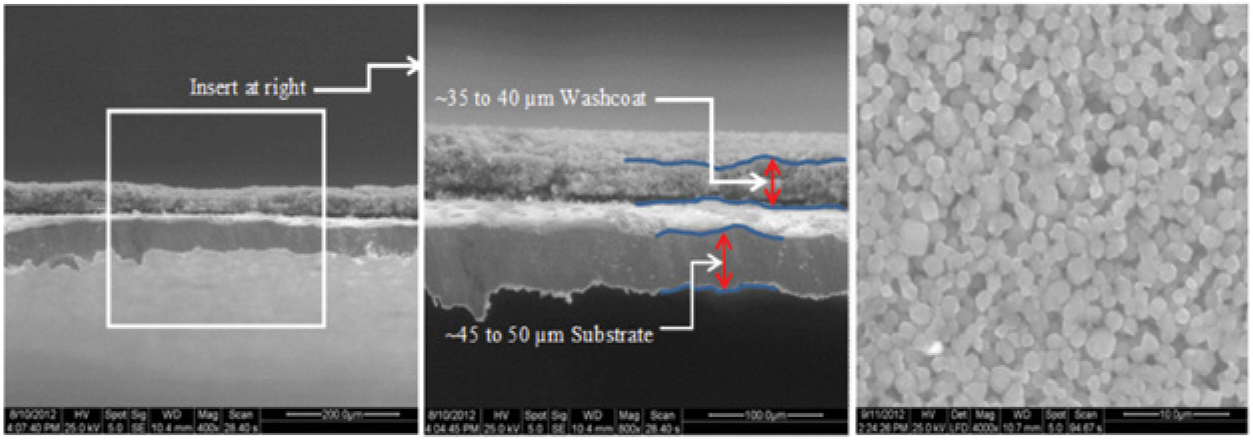

Figure 1: Edge View of Zeolite-Coated Metal Substrate at 400X Magnification (left); Edge View of Zeolite-Coated Metal Substrate at 800X Magnification Indicating Washcoat is 35-40 µm Thick (center); Top View of Zeolite-Coated Metal Foil Substrate at 4,000X Magnification (right)

Corrugated cores have been fabricated (Figure 2) to serve as the metal substrate for testing the rapid PSA process. These cores are currently being tested to evaluate pressure drop, and they will eventually be coated with zeolite crystals for process testing.

Figure 2: Side View of 1.5″ x 6″ x 289 cpsi Corrugated Cores

In addition, a dynamic volumetric frequency response (DVFR) apparatus (Figure 3) that is being used to characterize adsorbate mass-transfer rates in various adsorbents at cycle times up to 10 Hz, as well as a single-column rapid pressure swing adsorption (S-C rPSA) system (Figure 4), is being used to study the effect of cycle time on the mass-transfer rates at step times as short as 0.25 seconds.

Figure 3: Photograph of Dynamic Volumetric Frequency Response (DVFR) Apparatus

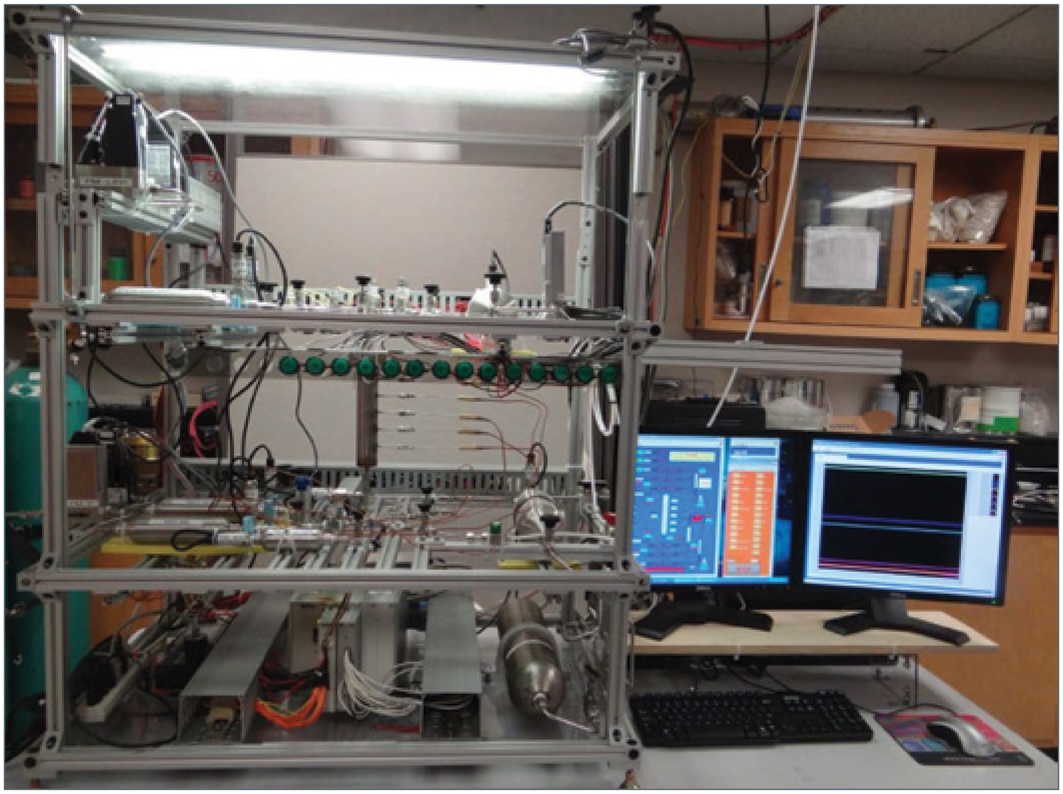

Figure 4: Photograph of Single-Column Rapid Pressure Swing Adsorption (S-C rPSA) System

TABLE 1: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP[2]	kg/m^3	1,090	2,518
Bulk Density[3]	kg/m^3	688	400
Average Particle Diameter[4]	mm	5.0	0.100
Particle Void Fraction	m^3/m^3	0.47	0.47
Packing Density	m^2/m^3	750	6,070
Solid Heat Capacity @ STP[2]	kJ/kg-K	0.92	0.82
Crush Strength[5]	kg_f	3.6	N/A
Manufacturing Cost for Sorbent	$/kg	20	37.4
Adsorption[6]			
Pressure[7]	bar	1.2/1.14	1.2/1.14
Temperature	°C	50	50
Equilibrium Loading[8]	g mol CO_2/kg	4.18	4.18
Average Bed Loading @ End of HR step	g mol CO_2/kg	2.46*	2.50
Heat of Adsorption	kJ/mol CO_2	37.5-46.0	37.5-46.0
Desorption			
Pressure[7]	bar	0.05/0.00085	0.05/0.00085
Temperature	°C	50	50
Equilibrium Loading[9]	g mol CO_2/kg	0.14	0.14
Average Bed Loading @ End of LR step	g mol CO_2/kg	1.20*	1.20
Heat of Desorption	kJ/mol CO_2	37.5-46.0	37.5-46.0
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	Fixed bed/cyclic	Fixed bed/cyclic
Flue Gas Flowrate	kg/hr	2.32×10^6	2.32×10^6
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 95%, 1.38 bar	
Adsorber Pressure Drop	bar	0.15	0.15
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	45.4	49.2

1. For the Current R&D Value, the calculation is based on 5-mm 13X beads. For the Target R&D Value, the calculation is based on a 52-micron thick stainless steel support containing a 100-micron thick zeolite crystal coating at each side.
2. The Target R&D Value includes the stainless steel support.
3. The Target R&D Value corresponds to mass of adsorbent (zeolite) per volume of bed.
4. The Target R&D Value corresponds to coating thickness.
5. The structured support for the target will be unaffected by PSA dynamic stresses.
6. The adsorption step is considered as the Heavy Reflux step, which follows the feed step in the PSA cycle and is highly enriched in CO_2 and obtained from another desorption step in the PSA cycle.
7. First value is total pressure; second value is partial pressure of CO_2.
8. The value corresponds to conditions of the heavy product gas.
9. The value corresponds to conditions of the light product gas.

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 coal (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.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The relative thermodynamic adsorption selectivity towards CO_2 over other gases such nitrogen (N_2), oxygen (O_2), and argon (Ar) on a commercial zeolite at partial pressures of CO_2 at around or below 1.0 bar.

Sorbent Contaminant Resistance – The effect of the contaminant sulfur dioxide (SO_2) is not clear yet; tests are planned. It is expected, however, that the 42 parts per million (ppm) in the fresh flue gas will be significantly reduced at the condensing heat exchanger that will be located upstream of the PSA unit. It is not expected that the zeolite will be irreversibly affected by nitrogen oxides (NO_x).

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent will be deposited on the surface of a metal structured support; thus, thermal or mechanical stresses present in pelletized/beaded systems will not be observed.

Flue Gas Pretreatment Requirements – The flue gas requires a blower to bring the pressure up to 120 kPa and then a condensing heat exchanger followed by a dryer to bring the content of water to less than 0.1 vol percent prior to entering the PSA unit.

Sorbent Make-Up Requirements – There are no sorbent make-up requirements in PSA units. The structured adsorbent is expected to last at least 5 years and possibly 10 years before it needs to be replaced. This is common in commercial PSA systems.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere. For example, the condensing heat exchanger will produce about 460,000 lb/h of condensed water that is recycled back as makeup water for the flue gas desulfurization (FGD) unit. It may contain up to 1125 mg/L of dissolved SO_2 and no other contaminants. In addition, about 3.69 x 106 lb/h of N_2-rich product at about 80°C is vented into the air. This stream will contain, by volume, about 1.8% CO_2, 4.0% H_2O, 3.3% O_2, 1.09% Ar, and balance N_2.

Proposed Module Design – Note the module location, as well as the pressure, temperature, and composition of the gas entering the module. The table below shows all the stream compositions and conditions throughout the proprietary process flowsheet. Column 7 (i.e., stream 7) is the feed to the PSA unit, which comes after the FGD unit and the water removal units described above. In addition, it is expected that stream 7 will have less than 2 parts per million by volume (ppmv) of sulfur oxides (SO_x) and about 92 ppmv of NO_x.

TABLE 2: STREAM COMPOSITIONS AND CONDITIONS IN EACH OF THE STREAMS (# COLUMNS) IN THE PROPRIETARY PROCESS FLOWSHEET

	1	2	3	4	5	6	7	8	9	10
V-L Mass Fraction										
CO_2	20.28%	20.28%	0.00%	22.28%			22.56%	2.60%	2.60%	2.81%
H_2O	10.87%	10.87%	100.00%	2.09%	100.00%	100.00%	0.06%	0.00%	0.00%	2.57%
N_2	65.11%	65.11%	0.00%	71.52%			73.17%	92.06%	92.06%	89.44%
O_2	2.62%	2.62%	0.00%	2.88%			2.95%	3.74%	3.74%	3.63%
Ar	1.12%	1.12%	0.00%	1.23%			1.26%	1.60%	1.60%	1.55%
V-L Mole Fraction										
CO_2	13.17%	13.17%	0.00%	15.36%			15.77%	1.69%	1.69%	1.80%
H_2O	17.25%	17.25%	100.00%	3.52%	100.00%	100.00%	0.10%	0.00%	0.00%	4.01%
N_2	66.44%	66.44%	0.00%	77.46%			80.34%	93.83%	93.83%	89.90%
O_2	2.34%	2.34%	0.00%	2.73%			2.83%	3.34%	3.34%	3.20%
Ar	80.00%	80.00%	0.00%	93.00%			0.97%	1.14%	1.14%	1.09%
V-L Mole Fraction (Dry Basis)										
CO_2	15.92%	15.92%	0.00%	15.92%			15.78%	1.69%	1.69%	1.87%
N_2	80.29%	80.29%	0.00%	80.29%			80.42%	93.83%	93.83%	93.66%
O_2	2.83%	2.83%	0.00%	2.83%			2.83%	3.34%	3.34%	3.33%
Ar	97.00%	97.00%	0.00%	97.00%			0.97%	1.14%	1.14%	1.14%
V-L Flowrate (10^6 lb/hr)	5.12	5.12	0.46	4.66	29.38	29.38	4.55	3.59	3.59	3.69
V-L Flowrate (10^4 lb mol/hr)	17.91	17.91	2.55	15.36	163.22	163.22	14.82	12.57	12.57	13.11
V-L Flowrate (10^4 SLPM)	3,039.38	3,039.38	432.62	2,607.36	27,698.57	27,698.57	2,514.09	2,132.28	2,132.28	2,225.55
Temperature (°F)	135.00	135.00	86.00	86.00	60.00	80.00	122.00	122.00	219.36	175.60
Pressure (psia)	14.70	14.70	14.70	17.38	20.00	19.00	17.24	15.06	14.86	14.72

	11	12	13	14	15	16	17	18	19	
V-L Mass Fraction										
CO_2	96.49%	96.49%	96.49%	96.49%					96.74%	
H_2O	0.28%	0.28%	0.28%	0.28%	100.00%	100.00%	100.00%	100.00%	2.00%	
N_2	3.23%	3.23%	3.23%	3.23%					3.24%	
O_2	0.00%	0.00%	0.00%	0.00%					0.00%	
Ar	0.00%	0.00%	0.00%	0.00%					0.00%	
V-L Mole Fraction										
CO_2	94.37%	94.37%	94.37%	94.37%					94.95%	
H_2O	66.00%	66.00%	66.00%	66.00%	100.00%	100.00%	100.00%	100.00%	5.00%	
N_2	4.97%	4.97%	4.97%	4.97%					5.00%	
O_2	0.00%	0.00%	0.00%	0.00%					0.00%	
Ar	0.00%	0.00%	0.00%	0.00%					0.00%	
V-L Mole Fraction (Dry Basis)										
CO_2	95.00%	95.00%	95.00%	95.00%					95.00%	
N_2	5.00%	5.00%	5.00%	5.00%					5.00%	
O_2	0.00%	0.00%	0.00%	0.00%					0.00%	
Ar	0.00%	0.00%	0.00%	0.00%					0.00%	
V-L Flowrate (10^6 lb/hr)	1.28	1.28	0.97	0.31	7.18	7.18	0.87	0.87	0.97	
V-L Flowrate (10^4 lb mol/hr)	2.97	2.97	2.25	0.72	55.66	39.91	4.85	4.85	2.24	
V-L Flowrate (10^4 SLPM)	504.34	504.34	381.81	122.53	9,445.33	6,772.09	823.84	823.84	379.48	
Temperature (°F)	122.00	122.00	122.00	122.00	60.00	80.00	60.00	80.00	104.00	
Pressure (psia)	1.20	20.00	20.00	20.00	20.00	19.00	20.00	19.00	2,215.00	

technology advantages

- Established large-scale technology for other applications.
- Needs no steam or water, only electricity.
- Tolerant to trace contaminants; possibly with use of guard or layered beds.
- Zeolite adsorbent commercial and widely available.
- Increase in cost of electricity (COE) lower than other capture technologies.
- If research and development (R&D) is successful, beds can be installed under a parking lot.

R&D challenges

- Energy-intensive, but better than current amines.
- Large beds required; implies large pressure drop, using more power.
- Large footprint.
- High capital cost.

results to date/accomplishments

- The PSA cycle was developed via process simulation that indicates a total separation energy of 24.6 kJ/mol (18.5 kJ/mol CO_2 removed for the PSA unit) and requires a small footprint (approximately 15 percent of a football field).
- A metal foil was successfully coated with commercial zeolite crystals, with the coating comprising approximately 85 percent zeolite and 15 percent inorganic binder, and having a nominal loading of 141 mg/in2.
- Several commercial zeolite crystals have been screened for CO_2 working capacity (using thermo gravimetric analysis [TGA]), and some candidate materials have been identified.
- Construction of an S-C rPSA system has been completed, and initial testing is underway. Construction of additional multi-bed, bench-scale demonstration systems is ongoing and about 50 percent complete.
- An in-house constructed volumetric frequency response system is being used to measure mass-transfer rates in various commercial adsorbents up to 10 Hz.
- Construction of the pressure drop system for measuring pressure drop through fixed and structured beds of adsorbents has been completed and testing with candidate beds is underway.
- A computational fluid dynamics (CFD) model for a geometry characteristic of a typical structured sorbent material has been developed and is currently under refinement.

next steps

- Continue to refine the PSA cycle using process simulation and continuously measured thermodynamic and mass-transfer data to reduce energy consumption.
- Continue to characterize structured adsorbent materials to find optimum CO_2 loading and mass-transfer characteristics.
- Continue to operate the S-C rPSA system to study the role of cycle time on the mass-transfer rates.
- Finish construction of the multi-bed experimental apparatus that will be used to demonstrate the rapid PSA technology at the bench scale.
- Continue to modify the coating process to optimize the zeolite loading on the metal foil.
- Continue to develop and refine the CFD model to optimize the geometry and minimize pressure drop through the structured adsorbent material.
- Based on CFD results, continue to manufacture new structured sorbent configurations to minimize pressure drop.

available reports/technical papers/presentations

Ritter, James A., " Bench-scale Development and Testing of Rapid PSA for CO2 Capture," presented at the 2012 NETL CO2 Capture Technology Meeting, Pittsburgh, PA, July 2012 *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/1-Monday/J%20Ritter-USC-RPSA.pdf*.

BENCH-SCALE DEVELOPMENT OF AN ADVANCED SOLID SORBENT-BASED CO_2 CAPTURE PROCESS FOR COAL-FIRED POWER PLANTS

primary project goals

The goal of this project is to address the technical and economic hurdles to developing a sorbent-based carbon dioxide (CO_2) capture process by transitioning a promising sorbent chemistry, based on molecular basket sorbent (MBS) materials, to a low-cost sorbent suitable for use in a fluidized-bed process and developing a scalable circulating fluidized, moving-bed reactor (FMBR) process arrangement.

technical goals

- Improve the thermal and chemical stability of the base polyethyleneimine (PEI) reactant while transitioning the current fixed-bed form MBS material into a fluidizable form.
- Collect critical process engineering data using bench-scale testing equipment to allow for a detailed design of a CO_2 capture prototype system based on improved MBS materials.
- Improve reactor design, optimize operability, and optimize heat integration strategies for the FMBR system.
- Scale-up advanced MBS materials to roughly 1,000 lbs production for use in the CO_2 capture prototype system.
- Demonstrate the technical and economic feasibility of a commercial embodiment of the MBS-based CO_2 capture process through a detailed technology feasibility study.

technical content

The project team is developing an advanced sorbent process that utilizes a polymeric amine-based CO_2 sorbent developed by Pennsylvania State University (PSU) under a previous project (DE-FE-0000458) to capture CO_2 from coal-fired power plant flue gas. The solid sorbent consists of a high-surface area support, such as silica, impregnated with branched PEI polymer, as exhibited in Figure 1.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Advanced Solid Sorbents and Processes for CO_2 Capture

participant:

RTI International

project number:

FE0007707

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performance period:

10/1/11 – 3/31/15

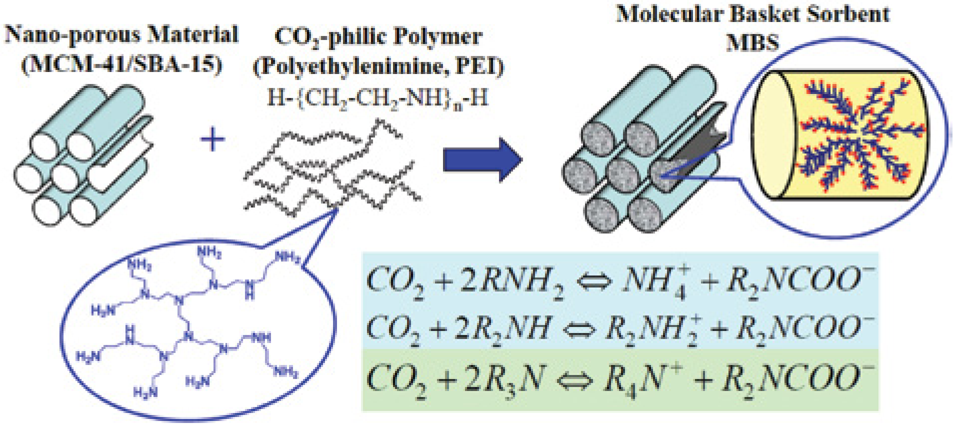

Figure 1: Molecular Basket Sorbent Concept

The branched polymer contains primary, secondary, and tertiary amine sites that absorb CO_2. Carbon dioxide adsorption is favored between 50 to 90°C (122 to 194°F), with a heat of reaction of ΔHAbs = 66 kJ/mol- CO_2 (645 Btu/lb- CO_2). At temperatures greater than 110°C (230°F), the reverse reactions predominate and the sorbent releases CO_2.

This advanced sorbent CO_2 capture process operates as a cyclic absorption-regeneration thermal swing process where the solid sorbent is continuously circulated between two FMBRs – a CO_2 absorber and a sorbent regenerator. A basic block flow diagram of this process, installed within a pulverized coal (PC)-fired power plant, is provided in Figure 2.

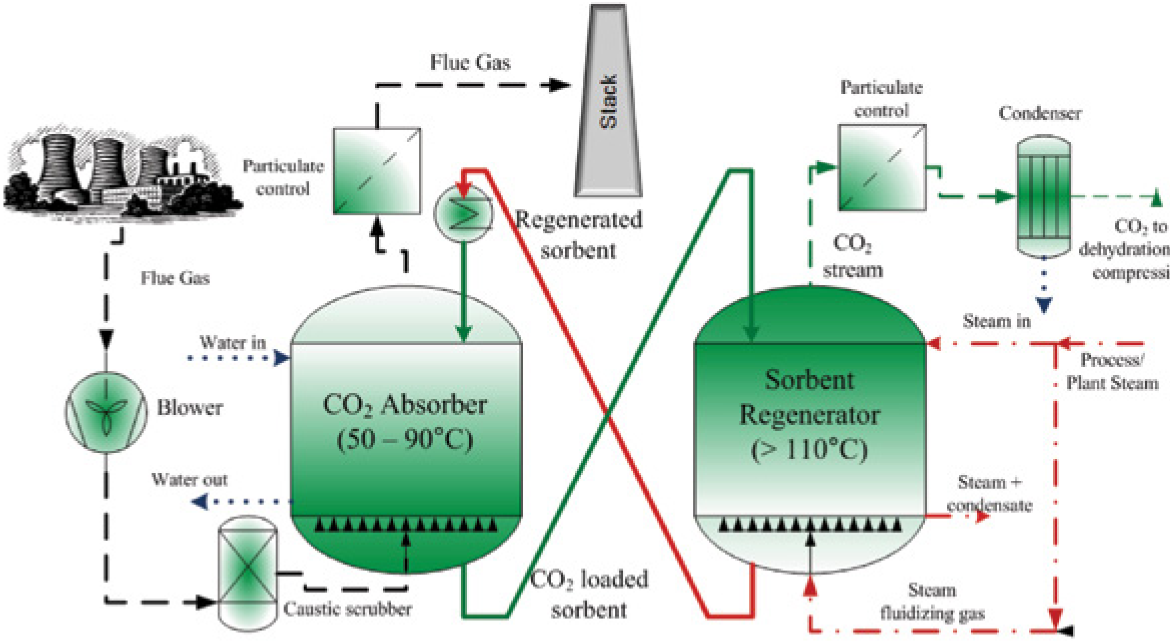

Figure 2: Block Flow Diagram of Advanced Solid Sorbent CO_2 Capture Process

Carbon dioxide-rich flue gas from the PC power plant goes through a caustic scrubbing system to remove strong acid gases prior to entering the CO_2 absorber. The CO_2 absorber is designed as an FMBR. Within the absorber, flue gas comes in contact with lean sorbent that is fed to the absorber from the sorbent regenerator. The sorbent selectively removes CO_2 and generates heat due to the heat of reaction for CO_2 removal. In order to control the sorbent bed temperature, cooling water is used to cool the sorbent through indirect contact. Treated flue gas exits the CO_2 absorber and enters a baghouse filter for removal of particulates, primarily attrited sorbent particles. Following particulate removal, the flue gas is then directed to the stack and vented.

The CO_2-rich sorbent exits the absorber and is transported to the sorbent regenerator. The sorbent regenerator design and operation is similar to the CO_2 absorber, except that the sorbent bed is indirectly heated with condensing steam in order to strip the sorbent of the absorbed CO_2. The regenerated sorbent produces a concentrated CO_2 gas stream that is swept out of the sorbent regenerator with a CO_2 sweep gas. The concentrated CO_2 gas stream is then sent to a dehydration and compression unit, and the sorbent is transferred through a sorbent cooling unit and on to the CO_2 absorber for continued CO_2 removal. Fresh sorbent is added to this stream to make up for attrited sorbent and diminished sorbent performance.

Project Scope: A preliminary technology feasibility study of the MBS-based process to provide baseline projections for energy penalty, capital, operating, and overall CO_2 capture costs has been conducted. RTI, PSU, and Clariant will transition PSU's current MBS-powdered material to a fluidizable sorbent that can be readily scaled-up. The team will use new preparation procedures, transition sorbent formulations to commercial precursor materials, and adapt acceptable manufacturing procedures to this new type of sorbent. RTI will lead an effort to conduct process evaluations in a bench-scale, single-stage, fluidized-bed unit capable of sustained CO_2 capture and sorbent regeneration. RTI, assisted by an engineering fabrication company, will then lead the design and fabrication of a bench-scale, continuous-flow CO_2 capture prototype system. This system will be integrated and commissioned at the University of North Carolina at Chapel Hill's (UNCH-CH) coal-fired power plant, where extensive parametric and long-term flue gas testing will be performed. Masdar New Ventures will co-fund the project.

TABLE 1: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	N/A	N/A
Bulk Density	kg/m^3	≈ 500	≈ 1,000
Average Particle Diameter	mm	≈ 0.1	0.05 to 0.2
Particle Void Fraction	m^3/m^3	not measured	TBD
Packing Density	m^2/m^3	not measured	TBD
Solid Heat Capacity @ STP	kJ/kg-K	1.53	1.1 to 1.5 (1.2)
Crush Strength	kg_f	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	N/A	< $10/kg
Adsorption			
Pressure	bar	1.01	1.01
Temperature	°C	75	60 to 90
Equilibrium Loading	g mol CO_2/kg-sorbent	2.27	3.18
Heat of Adsorption	kJ/mol CO_2	66	60 to 70
Desorption			
Pressure	bar	1.01	1.01
Temperature	°C	100	>110
Equilibrium Loading	g mol CO_2/kg-sorbent	0.68	0.45
Heat of Desorption	kJ/mol CO_2	78	70 to 80
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	—-	—-
Flue Gas Flowrate	kg/hr	—-	—-
CO_2 Recovery, Purity, and Pressure	% / % / bar	—-	
Adsorber Pressure Drop	bar	—-	—-
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—-	—-

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 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.

Other Parameter Descriptions:

Sorbent Contaminant Resistance – Most, if not all materials used for CO_2 capture, including aqueous amine solvents, alkaline and alkali-based solvents and sorbents, and the amine-based sorbents being developed in this project, have a high affinity for strong acid gases, including sulfur oxide (SO_x), nitrogen oxide (NO_x), and hydrogen chloride (HCl). Considerations have been made regarding how to implement contaminant control within the overall CO_2 capture system. Resistance to trace metal contaminants is unknown at this point.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent attrition will be a function of the process operating environment and physical strength of the sorbent. These will be measured and observed during larger-scale testing campaigns. The base PEI reagent suffers from performance instability at temperatures greater than 110°C. One of the focuses of this project is to improve the sorbent performance stability.

Flue Gas Pretreatment Requirements – Most likely, the flue gas will require a scrubbing of acid gases prior to entering the CO_2 absorber containing the sorbent being developed in this project.

Sorbent Make-Up Requirements – Continuous sorbent make-up will be required during operation of a commercial system in order to replenish sorbent lost to attrition, entrainment, and deactivation by reaction with contaminants.

Waste Streams Generated – As a whole, the process generates few waste streams. It is expected that a continuous purge of sorbent will be required to maintain a desired level of CO_2 removal within the sorbent bed. In addition, sorbent will be lost from the process through attrition and entrainment. The sorbent can either be treated and reused, or disposed of following minimal treatment.

technology advantages

- Potential for reduced parasitic loads and lower capital and operating costs than conventional technology.
- High CO_2 loading capacity.
- Relatively low heat of absorption.
- Reactor design offers superior gas-solid heat and mass transfer characteristics.
- Counter current gas-solids flow maximizes CO_2 driving force.
- Needed process equipment exists and is used industrially.

R&D challenges

- Performance stability above 100°C is not ideal.
- Further sorbent cost reduction is needed.
- Heat management and novel heat integration strategies are critical to reduce parasitic power losses.
- Water management is critical to avoid condensation.
- Novel process design has not been tested/evaluated at commercial-scale for CO_2 capture.

results to date/accomplishments

- Screened and tested more than 20 commercially available, low-cost support materials using an automated, packed-bed absorption system.
- Identified a low-cost support material yielding a sorbent with comparable performance to expensive, mesoporous silica.
- Demonstrated that adding a small amount of moisture to the regeneration gas dramatically improves the multi-cycle performance stability of the MBS material.
- Significant sorbent stability improvement demonstrated at 120°C through process condition selection, sorbent complexation, and cross-linking pathways.
- Sorbent has been prepared through spray drying to make fluidizable particles.
- Demonstrated that water can replace methanol (or any alcohol) as the amine impregnation solvent.
- Developed a fluidized-bed reactor model.
- Developed a preliminary bench-scale system design package.
- Completed a preliminary technology feasibility study projecting capture costs of \$36 to \$42/tonne CO_2 captured.

next steps

- Continue improvement of MBS stability by increasing amine-support interaction and novel cross-linking activities.
- Design a bench-scale FMBR system and internal heat-management system.
- Conduct parametric studies of economic/process variables for the bench-scale FMBR system.
- Develop a detailed design and engineering package for a high-fidelity, bench-scale prototype.
- Scale-up novel MBS materials to 1,000 lbs.
- Conduct long-term testing of the prototype system flue gas from a fossil fuel-fired facility.
- Conduct a detailed techno-economic study that results in a high confidence level that the technology can meet U.S. Department of Energy goals.

available reports/technical papers/presentations

Nelson, T, et al., “Advanced Solida Sorbents and Process Designs for Post-Combustion CO2 Capture,” presented at the 2012 NETL CO2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/1-Monday/T%20Nelson-RTI-Adv%20Solid%20Sorbents.pdf*.

EVALUATION OF SOLID SORBENTS AS A RETROFIT TECHNOLOGY FOR CO_2 CAPTURE FROM COAL-FIRED POWER PLANTS

primary project goals

ADA Environmental Solutions (ADA-ES) is designing and constructing a 1-megawatt (MW) pilot plant to demonstrate solid sorbent-based post-combustion carbon dioxide (CO_2) capture technology to reduce uncertainty of scale-up and accelerate the path to commercialization.

technical goals

Validate and optimize a solid sorbent-based post-combustion CO_2 capture technology through 1-MW slipstream pilot testing and process modeling to enable the conceptual development and techno-economic analysis of a 550-megawatt electric (MWe) facility.

technical content

ADA-ES is developing a post-combustion CO_2 capture process using solid sorbents. The viability assessment included laboratory-scale and 1-kilowatt (kW) pilot-scale sorbent screening and a commercial-scale equipment study in a separate U.S. Department of Energy (DOE) project (DE-NT0005649). The specific work completed under the viability assessment included:

- Evaluated more than 100 potential CO_2 sorbents, which were procured from various CO_2 solid sorbent developers worldwide. Sorbents were evaluated on the basis of cyclic stability, CO_2 capacity, working CO_2 capacity, availability, cost of raw materials, production process, manageable disposal costs (low toxicity), interaction with flue gas constituents, adequate physical strength, and theoretical regeneration energy. The CO_2 sorbents were investigated in such a way to assess their respective performances in a temperature swing adsorption (TSA) process. Table 1 displays the key properties used to evaluate CO_2 sorbents.

technology maturity:

Pilot-Scale, 1-MW Slipstream of Actual Flue Gas

project focus:

Solid Sorbents as Retrofit Technology

participant:

ADA-ES

project number:

NT0004343
NT0005649

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partners:

EPRI
Southern Company
Stantec Consulting, Ltd.

performance period:

9/30/08 – 12/31/14

TABLE 1: KEY PROPERTIES USED TO EVALUATE CO_2 SORBENTS

Physical Property	Current Range	Goal
True Density @ Sorbent Particle Size (mm)	Highly varied and controllable	≈0.1-5
Sorbent Surface Area (m^2/g)	0.5 – 3,000	0.5 – 1,500
Sorbent Active Component Concentration (wt%)	5 – 60	10 – 100
Shape of Sorbent	Varied	Spherical
Density of Sorbent (g/cm^3 [lb/ft^3])	0.2 – 0.6 [15 – 40]	Dependent on process design
Mechanical Strength	Not reported	Dependent on process design
Attrition Fines: Form, Processing, and Fate	Not reported	Low attrition, potential for re-use desired, non-volatile, non-hazardous disposal

The lab-scale tests typically consisted of <3 grams of the adsorbents exposed to simulated flue gas and then regenerated by a temperature swing with a humid nitrogen sweep gas. For the adsorption step, the simulated flue gas was 55°C (130°F) with oxygen and CO_2 concentrations of 4 percent and 12 percent, respectively. The moisture level was varied (0%, 50%, or 90% relative humidity). The regeneration temperature was varied between 65 to 250°C (150 to 480°F).

- A 1-kW transport-reactor pilot was constructed to more thoroughly investigate the most positively rated adsorbents tested at the laboratory scale. More than 90 percent CO_2 removal was achieved repeatedly in batch mode with one supported amine sorbent at two field sites.
- In a concurrent effort to the sorbent evaluation, a technology survey was completed to identify potential commercial and conceptual processes and equipment options for use in retrofitting the existing fleet of coal-fired power plants for post-combustion CO_2 capture. Different equipment options were selected for the adsorption, regeneration, and cooling sections and pieced together to form the conceptual design of the commercial-scale process. The technologies selected were proven the most reliable, cost-effective, and versatile options available.

The current project (DE-FE0004343) includes development of a commercial-scale (550 MWe) conceptual process and validation using a 1 MWe-scale pilot. The information gained from the 1-MW pilot operation will be used to complete a technical and economic analysis of the commercial-scale process. Three project phases are planned:

- In Phase 1, a 550-MW conceptual design was developed and a 1-MW pilot plant was designed. A simplified sketch of the commercial concept integrated into an existing coal-fired power plant is presented in Figure 1. The sorbent-based CO_2 capture process is implemented immediately upstream of the stack. Based on the properties of one promising sorbent, four adsorption/regeneration trains are required to remove 90 percent of the CO_2 being exhausted from a 550-MWe subcritical coal-fired power plant.

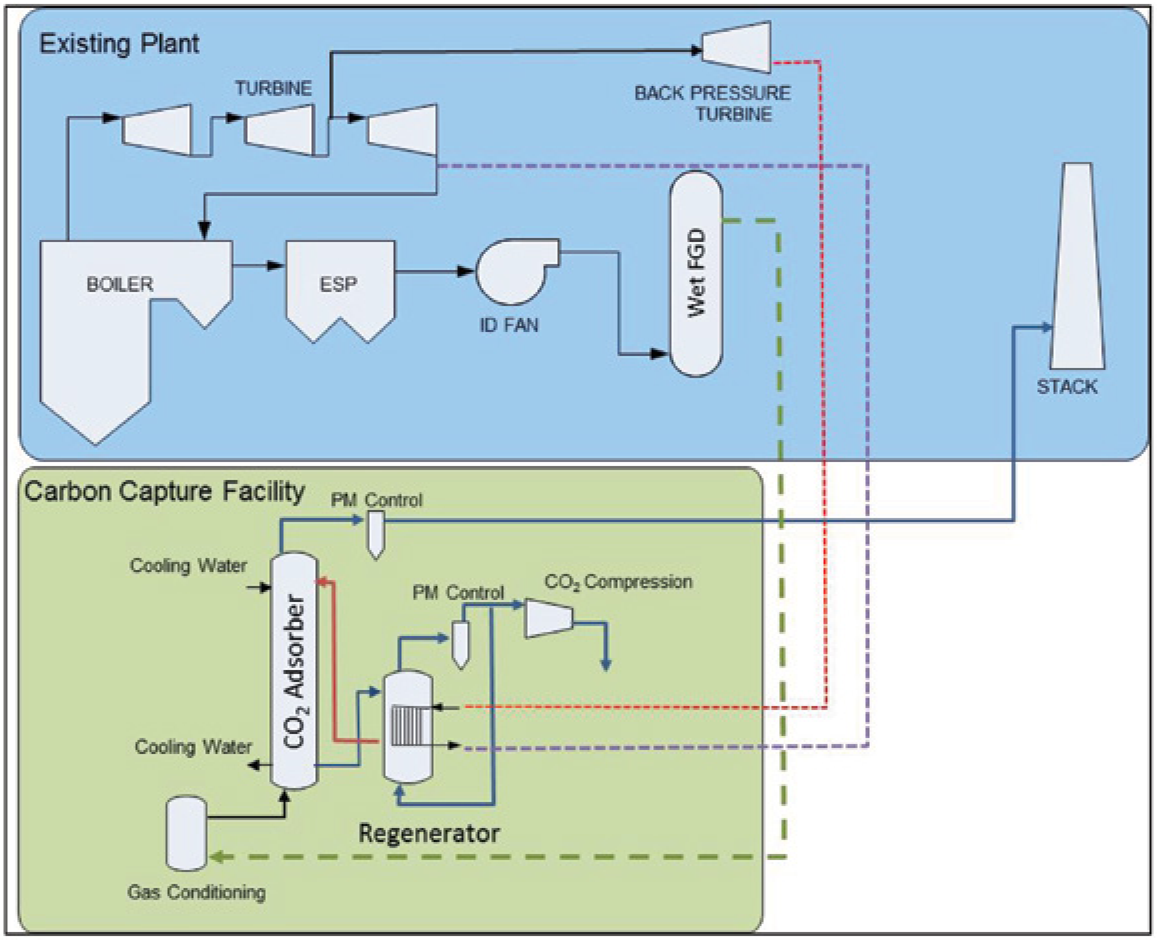

Figure 1: Process Flow Diagram of a Subcritical PC Power Plant Retrofitted with a Solid–Based CO_2 Capture Process

The process was designed to minimize CO_2 capture costs, primarily by providing the sorbent with the conditions necessary to achieve the highest possible CO_2 working capacity. This is accomplished through two important process characteristics: (1) isothermal operation and (2) approaching counter-current gas/solids contacting in the adsorber. Note that in Figure 1, the regenerator is shown as a single stage, but multiple stages could also be used if it was economically advantageous to use steam to drive off more CO_2 during regeneration. Improvements in sorbent CO_2 capture performance or altered operating conditions could decrease the overall process costs, but for all sorbents it is important to evaluate whether the process can be improved further by incorporating heat integration.

- Phase II is currently underway and includes 1-MWe detailed engineering, construction, installation, and tie-in of the pilot plant at a coal-fired power plant site. This phase is scheduled to be completed by the end of 2013. A 3D model of the pilot is shown in Figure 2.

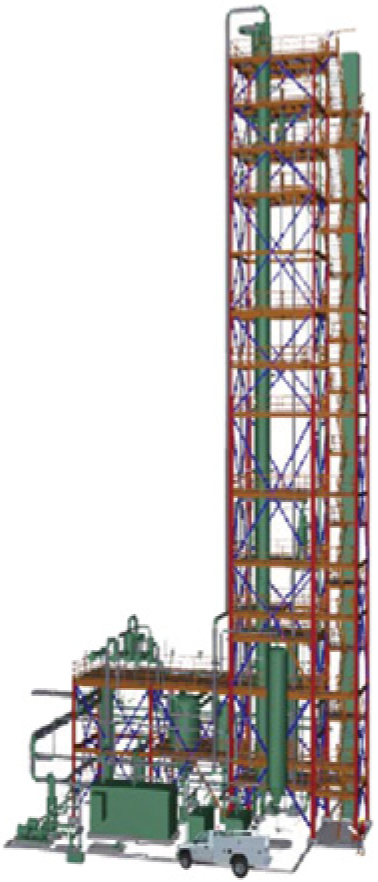

Figure 2: 3D Model of 1-MWe Pilot of CO_2 Capture Process

- Phase III will include field-testing with the 1-MWe pilot, system analysis, and a techno-economic assessment of the full-scale process. Planned field-testing includes parametric studies and up to two months of continuous pilot operation to validate pilot plant performance.

Specific objectives for the current project include:

- Demonstrate the technical, economic, and energy benefits of a promising CO_2 capture technology.
- Develop performance data through the operation of the system on flue gas, including temperature control and optimized system heat recovery.
- Measure process conditions, including sorbent heat of reaction, sorbent working capacity, sorbent attrition, system pressure drop, and CO_2 capture.
- Assess sorbent performance sensitivity to flue gas constituents.
- Operate continuously for at least two months to identify operating and maintenance issues and system reliability.
- Remove at least 90 percent of the incoming CO_2 from the flue gas.
- Produce high-purity CO_2 that will be capable of meeting pipeline standards.
- Conduct a techno-economic analysis of the commercial design.

The sorbent and process properties identified to date are provided in Table 2.

TABLE 2: PROCESS PARAMETERS FOR SOLID SORBENT

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	646	646
Bulk Density	kg/m^3	453	453
Average Particle Diameter	mm	0.1	0.1
Particle Void Fraction	m^3/m^3	0.418	0.418
Packing Density	m^3/m^3	N/A	N/A
Solid Heat Capacity @ STP	m^2/m^3	1.05	1.05
Crush Strength	kJ/kg-K	2.2	2.2
Manufacturing Cost for Sorbent	kg_f	≈$150	$20-$40
Adsorption			
Pressure	bar	1	1
Temperature	°C	40	40
Equilibrium Loading	g mol CO_2/kg-sorbent	2.4	2.4
Heat of Adsorption	kJ/mol CO_2	-60	-60
Desorption			
Pressure	bar	1	1
Temperature	°C	120	120
Equilibrium Loading	g mol CO_2/kg-sorbent	0.8	0.8
Heat of Desorption	kJ/mol CO_2	60	60
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	Fluidized bed, temperature swing adsorption	
Flue Gas Flowrate	kg/hr	3500	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 85% CO_2, 15% H_2O), Ambient	
Adsorber Pressure Drop	bar	0.55	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	TBD	

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 coal (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.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The sorbent selected for this project is an ion exchange resin with a primary benzyl amine that removes CO_2 in a TSA process. It is important to note that other supported amine sorbents with similar enthalpy of adsorption and physical properties could also be used in the same process without major equipment changes.

One of the most important sorbent properties for post-combustion CO_2 capture is the CO_2 working capacity. Isotherms were generated using experimental data and the Langmuir isotherm model, which are provided in Figure 3. To calculate the CO_2 working capacity of this sorbent, the adsorption conditions are assumed to be 40°C and $P_{CO2} = 0.15$ bar, while the regeneration conditions are assumed to be 120°C and 0.81 bar (note that the CO_2 in the regenerator exhaust will be slightly diluted with desorbing moisture). Using the isotherms provided in Figure 3, the CO_2 loading under adsorption conditions is approximately 10.5 g CO_2/100 g fresh sorbent, while the CO_2 loading under the regeneration conditions is approximately 3.5 g CO_2/100 g fresh sorbent; the CO_2 working capacity is approximately 7 g CO_2/100 g fresh sorbent, which is nearly an 80 percent improvement versus the working capacity of aqueous monoethanolamine provided in the 2010 version DOE Baseline Report.

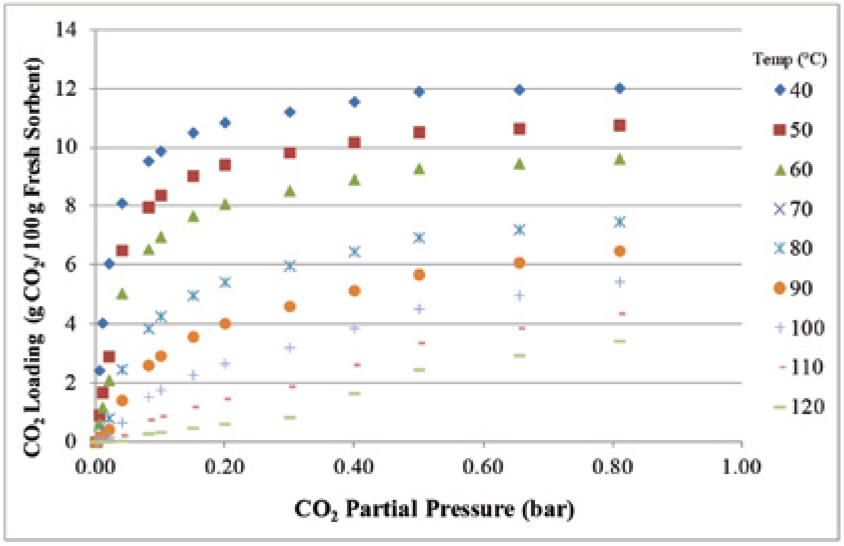

Figure 3: Sorbent Isotherms

Sorbent Contaminant Resistance – Amines will react with sulfur dioxide (SO_2) in the flue gas. The selected sorbent will react with SO_2 and, as a result, the overall working capacity for CO_2 will decrease. However, this is a reversible reaction and the sorbent can be regenerated to recover CO_2 capture effectiveness.

Sorbent Attrition and Thermal/Hydrothermal Stability – Based on laboratory testing, the selected sorbent is expected to have low mechanical attrition. Comparisons to fluid catalytic cracking (FCC) catalyst attrition are favorable. The moisture uptake on the sorbent is important because it results in an increase in the regenerator heat duty due to the enthalpy of vaporization/condensation (assuming that the H_2O is physically adsorbed). In addition, in the regenerator, the released H_2O will necessitate the addition of condensers to separate the H_2O from the CO_2 exhaust. This sorbent demonstrates a small (≈0.9 g H_2O/100 g fresh sorbent under expected 1-MWe pilot operating conditions) H_2O working capacity.

Flue Gas Pretreatment Requirements – A secondary scrubber has been incorporated into the pilot design to reduce the flue gas SO_2. An assessment of the cost-benefit of scrubbing SO_2 versus regenerating the sorbent that has reacted with SO_2 to recover CO_2 capture effectiveness must be conducted to determine the commercial process design and operating details.

Sorbent Make-Up Requirements – Current estimates used in cost projections are to replace the sorbent nominally once per year. Further testing is required, including pilot testing to refine the make-up requirements.

Waste Streams Generated – Waste streams will include spent sorbent, flue gas scrubber blow-down, and flue gas cooler condensate.

Process Design Concept – A simple schematic of the design of the 1-MWe pilot being designed and constructed is provided in Figure 4. In the schematic, three fluidized beds are shown for adsorption, but the actual number of fluidized beds must be selected based on the sorbent. However, while the number of beds may change, it is important to remember that the heat transfer surface area is based on the sensible heat that must be removed, the enthalpy of adsorption, and the amount of CO_2 being adsorbed. The regenerator is a single fluidized bed. Only one stage is necessary because the goal of the regenerator is to generate high partial pressure CO_2 and no stripping steam is used.

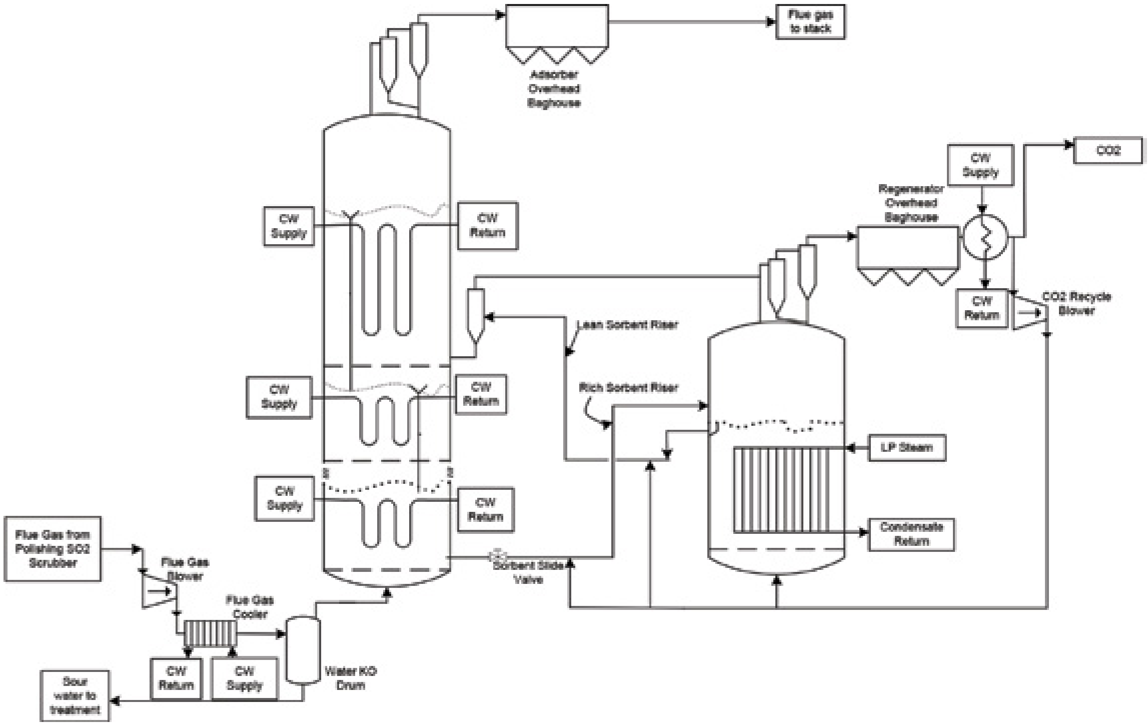

Figure 4: Schematic of ADA's CO_2 Capture Temperature Swing Adsorption System

Proposed Module Design – The CO_2 capture module will be located downstream of the plant's existing SO_2 scrubber. The gas stream from which CO_2 will be removed is representative of that from a coal-fired power plant with nominal conditions of P_{CO2} = 0.13 bar and T = 55°C. The adsorber is designed to operate isothermally at 40°C. The exhaust pressure for regeneration is approximately ambient pressure. The minimum superficial velocity of the flue gas will be limited to 1.2 m/s (4.0 ft/s) to minimize the number and footprint of reactors, and thus capital costs. Pneumatic conveying will be utilized for all required material conveying to increase reliability, decrease O&M costs, and increase technology acceptance. Because the sorbent and flue gas are contacted in a system that approaches counter-current flow, CO_2 working capacity can be maximized. In addition, the heat transfer has been optimized through the use of bubbling fluidized beds. The optimal mixing that is characteristic of bubbling fluidized beds also translates into effective gas/solids contacting. The design of the system employed established methods and principles used for gas-solid systems, including gas distribution, in-bed heat transfer, risers, standpipes, cyclones, and diplegs. Large-scale, two-stage fluidized beds have been used commercially for FCC processes. However, not all aspects of the design are commercially available. Wherever necessary, novel and innovative components, such as the trays used to support the fluidized beds, have been developed.

technology advantages

- Compared to an aqueous amine system:
    - No corrosion inhibitors are required.
    - Less water waste will be generated.
    - No process make-up water will be required.
    - Amine volatilization will be reduced or eliminated (indicated during laboratory testing and will be evaluated during 1-MWe pilot testing).
- Reduction in the regeneration energy requirements by minimizing heat input:
    - The heat capacity of solids is nominally 25 percent of liquids (heat recovery for solids has not been developed for this application).
    - The latent heat of vaporization is minimized (no liquid solvent is involved).
- High sorbent CO_2 capacities have been demonstrated (lab-scale).
- Fundamental sorbent chemistry is well-know (e.g., amine).
- Components of process equipment are mature (e.g., circulating fluidized bed).

R&D challenges

- Similar to aqueous amines, long-term stability of sorbents when exposed to flue gas is of concern. Laboratory tests indicate sorbent performance can be recovered using a secondary system.
- Availability of sorbents including the number of suppliers. Many developers are currently materials and several show promise in laboratory testing. Multiple suppliers are expected to emerge with a commercial market.
- Ability to scale-up sorbent manufacturing without impacting performance. Although the specific recipe is unique, the current sorbent is produced using a commercial-scale ion exchange resin manufacturing process. Larger-scale production lines should not be an issue for this material. Cost controls will be realized by developing a manufacturing process specific to this recipe.
- Ability to design a process that can control sorbent temperatures and counteract changes resulting from the heat of reaction, potential erosion, and/or corrosion of process equipment.

results to date/accomplishments

- Selected supported amines as the sorbent family for the 1-MW pilot. Selected an ion exchange resin with optimal physical and chemical characteristics for this application.
- Selected a staged fluidized bed for the adsorber design and a single fluidized bed for the regenerator design.
- Completed a 550-MWe conceptual design.
- 1-MWe pilot plant detailed engineering design complete.
- Onsite construction activities, including installation of the steam line for regeneration heat, have begun.
- Construction activities for the pilot have begun. The pilot will be built as several modules and moved to the host site. Fabrication of major vessels is complete and erection of the structural steel modules is underway.
- All major equipment and instrumentation is procured, sorbent has been manufactured, and quality testing of the major vessels is underway.

next steps

- Complete pilot module construction and ship to host site.
- Complete pilot foundations and all other required host site preparations.
- Complete field installation of modules and interconnects.
- Process sorbent to conform to specifications of process design.
- Complete operating, commissioning/start-up, and testing procedures.
- Demonstrate pilot plant operation.
- Complete techno-economic assessment of technology.

available reports/technical papers/presentations

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RAPID TEMPERATURE SWING ADSORPTION USING POLYMERIC/SUPPORTED AMINE HOLLOW FIBER MATERIALS

primary project goals

The Georgia Institute of Technology is developing a rapid temperature swing adsorption (RTSA) process and will evaluate the cost and performance benefits of this novel hybrid capture approach via bench-scale testing of a module containing 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 carbon dioxide (CO_2) capture.
- Develop a computational model of the fiber module and validate it in parallel with the experimental program.

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 to 80 kJ/mol). 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 to 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 expected to be on the order of two to three minutes.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Rapid-Temperature Swing Adsorption

participant:

The Georgia Institute of Technology

project number:

FE0007804

NETL project manager:

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partners:

Trimeric Corporation
Algenol Biofuels
Southern Company Services
GE Energy

performance period:

10/1/11 – 9/30/14

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 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 re-routed 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.

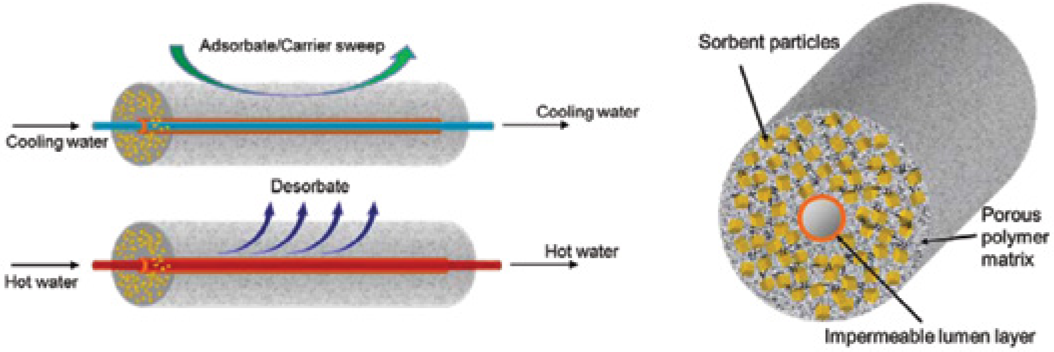

Figure 1: Sorption (top) and Desorption (bottom) Modes in Hollow Fiber Sorbents

This RTSA approach was recently 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.

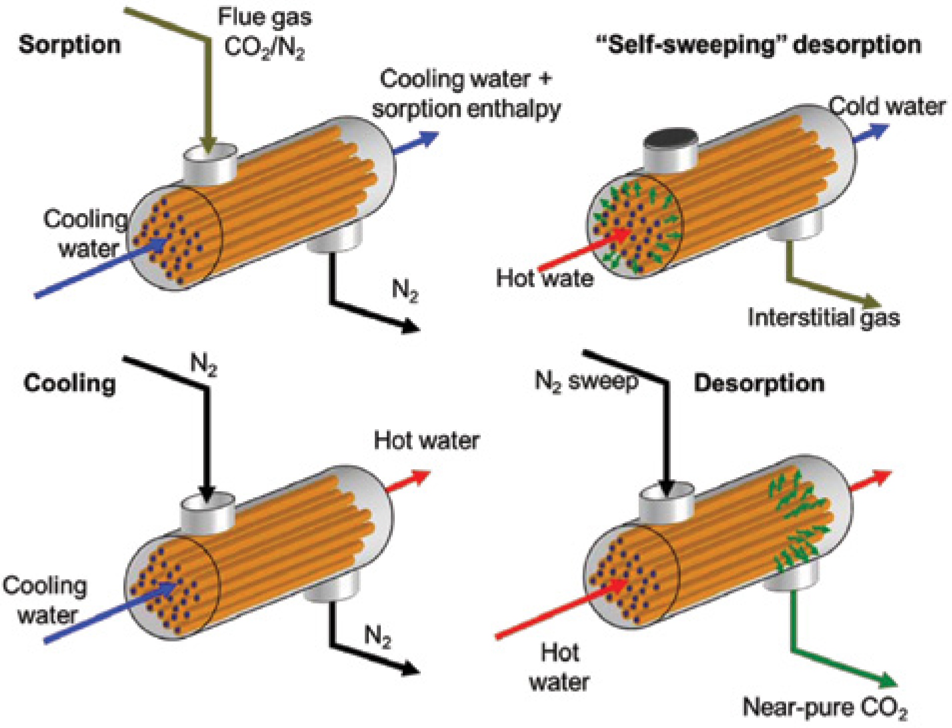

Figure 2: Potential RTSA Process Configuration

TABLE 1: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	1100	1100
Bulk Density	kg/m^3	1100	1100
Average Particle Diameter	mm	1.0	1.0
Particle Void Fraction	m^3/m^3	0.4-0.5	0.28-0.3
Packing Density	m^3/m^3	0.44	0.4-0.5
Solid Heat Capacity @ STP	m^2/m^3	1800	3000
Crush Strength	kJ/kg-K	1.140	1.140
Manufacturing Cost for Sorbent	kg_f	Unknown	Unknown
Manufacturing Cost for Fiber Module (includes hardware, fibers, sorbent)	$/kg	Unknown	$10/$m^2$, or $25-$35/kg
Adsorption			
Pressure	bar	0.13	0.13
Temperature	°C	35	35
Equilibrium Loading	g mol CO_2/kg-sorbent	0.9-1.1	1.0-1.5
Heat of Adsorption	kJ/mol CO_2	55-65	55-65
Desorption			
Pressure	bar	1.0	5.5
Temperature	°C	120	90
Equilibrium Loading	g mol CO_2/kg-sorbent	0.1	0.1
Heat of Desorption	kJ/mol CO_2	55	55-65
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	Co-current shell and tube	Co-current shell and tube
Flue Gas Flowrate	kg/hr	0.005 (lab), ≈2,900 (full scale, per module)	0.5 (lab), ≈2,900 full scale, per module)
CO_2 Recovery, Purity, and Pressure	% / % / bar	100%R, 42 mol%, 1 bar (0.42 bar partial pressure)	90%R, 95 mol%, at 1 bar or 80 mol% at 5.5 bar
Adsorber Pressure Drop	bar	< 0.1	< 0.15
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	N/A

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.

Fiber Bundle – collection of fibers to be used in a single module. Each fiber contains 50-55 percent wt. solid sorbent, and 30 to 50 percent of the solid sorbent is amine.

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 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.

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% RH – 90% RH), and resistance to nitric oxide (NO). 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 fibers can restructure upon extended exposure to high humidity at high temperature. However, the water sorption capacity of the fibers is much higher than the CO_2 capacity, so CO_2 breakthrough occurs while the majority of the fiber is still dry. Therefore, degradation due to humidity can be controlled.

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% RH vs. 100% RH). Finally, further wet flue gas desulfurization (FGD) may be required for additional SO_x removal for optimum long-term performance of the amines.

Sorbent Make-Up Requirements – Analyses investigating the amine loss mechanism and rate are ongoing.

Waste Streams Generated – Spent fiber sorbents represent the only process waste stream. Currently, the fibers are assumed to last three years before replacement is required.

Process Design Concept – Flowsheet/block flow diagram:

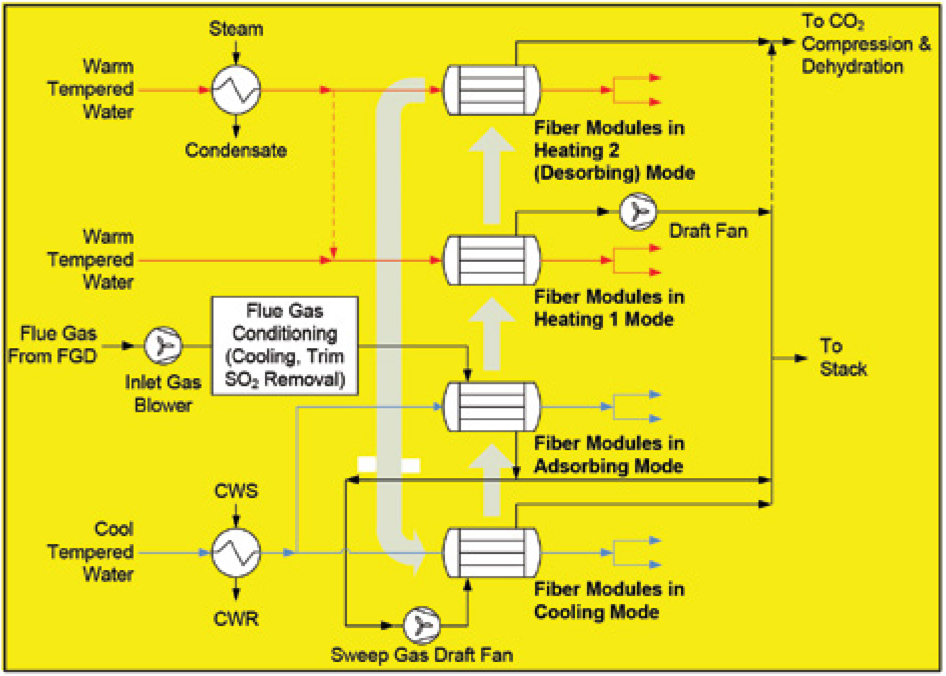

Figure 3: Flowsheet/block flow diagram

Proposed Module Design – Note the module location, as well as the pressure, temperature, and composition of the gas entering the module. Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

Several shell-and-tube hollow fiber sorbent modules are being considered. In this arrangement, the flue gas is sent through a valve manifold "cascade" that introduces the flue gas sequentially into the "rack" of modules. A similar approach is envisioned for water that will be valved and pumped through the bore side of the hollow fiber sorbents to enable rapid heating and cooling, thus driving down system footprint and increasing the overall sorbent productivity. The flue gas will enter through a gas diffuser ring at the "top" of the shell side of the module. The gas will proceed through the shell side until CO_2 breaks through the "bottom" of the module; the tightly packed hollow fibers prevent gas bypass. Water will enter the bore side of the fibers through a header system and will flow in the same directions as the flue gas (co-current design). The water eluent is segregated based on temperature and is recycled throughout the process in a tempered water system, which facilitates intra-process heat recovery.

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 oxygen, SO_x, and exposure to saturated humidity and temperature.
- Low-working capacity in more conventional contactors.

results to date/accomplishments

- Fibers and amine/silica sorbents synthesized.
- New, scalable amine/sorbent/fiber synthesis protocol developed.
- Construction and operation of RTSA Testing Station 1 for CO_2 uptake experiments and pressure-drop measurements.
- First demonstration of CO_2 capture from amine containing hollow fibers in small modules.
- Demonstration of resistance to O_2 and NO under conditions typical of flue gas.
- Models of adsorption-heating-desorption-cooling cycle developed.
- Preliminary techno-economic analysis conducted.

next steps

- Construct bench-scale modules (0.5” x 3’ 150 fibers) for RTSA Testing Station 2 for heat transfer measurements.
- Model validation against bench-scale experiments.
- Optimize cycle parameters to minimize cost per ton of CO_2 captured.
- Optimize sorbent, fiber, and module parameters to maximize heat recovery.
- Refine techno-economic model with experimental parameters.

available reports/technical papers/presentations

Realff, M, et al., “Rapid Temperature Swing Adsorption Using Polymer/Supported Amine Compostie Hollow Fibers,” presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/M%20Realff-GIT-RTSA.pdf*.

Lively, Ryan, “Hollow fiber sorbents for post-combustion CO_2 capture,” dissertation, Georgia Institute of Technology, January 2011. *http://smartech.gatech.edu/handle/1853/43758*.

Labreche, Y, et al., “Post-spinning infusion of poly(ethyleneimine) into polymer/silica hollow fiber sorbents for carbon dioxide capture,” Chemical Engineering Journal, Volume 221, 1 April 2013, Pages 166–175 . *http://www.sciencedirect.com/science/article/pii/S1385894713001320*.

LOW-COST HIGH-CAPACITY REGENERABLE SORBENT FOR CARBON DIOXIDE CAPTURE FROM EXISTING COAL-FIRED POWER PLANTS

primary project goals

TDA Research, Inc. (TDA) is developing a low-cost, high-capacity carbon dioxide (CO_2) adsorbent to demonstrate its technical and economic viability through sorbent evaluation and optimization, development of sorbent production techniques, and bench-scale testing of the process using actual flue gas.

technical goals

- Optimize chemical composition.
- Optimize physical properties and mechanical integrity of the sorbent to meet the specific requirements of the process.
- Identify optimum operating conditions and process parameters for design calculations.
- Assess the economic viability of the new carbon capture process.

technical content

TDA is developing a low-cost, high-capacity CO_2 adsorbent and demonstrating its technical and economic viability for post-combustion CO_2 capture for existing pulverized coal (PC)-fired power plants. The sorbent consists of a carbon material modified with surface functional groups that remove CO_2 via physical adsorption. It exhibits a much higher affinity to adsorb CO_2 than nitrogen, water, or oxygen, enabling effective CO_2 separation from the flue gas. The sorbent binds CO_2 more strongly than common adsorbents, providing the chemical potential needed to remove the CO_2. However, because CO_2 does not form a true covalent bond with the surface sites, regeneration can be carried out with only a small energy input. The heat input to regenerate the sorbent is only 4.9 kcal/mol of CO_2 (Figure 1), which is much lower than that for chemical absorbents (e.g., 29.9 kcal/mol CO_2 for sodium carbonate) or amine-based solvents (e.g., 14.2 kcal/mol CO_2 for monoethanolamine [MEA]).

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Low-Cost, High-Capacity Regenerable Sorbent

participant:

TDA Research, Inc.

project number:

FE0007580

NETL project manager:

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partners:

Babcock & Wilcox
Gas Technology Institute
University of California – Irvine

performance period:

10/1/11 – 9/30/14

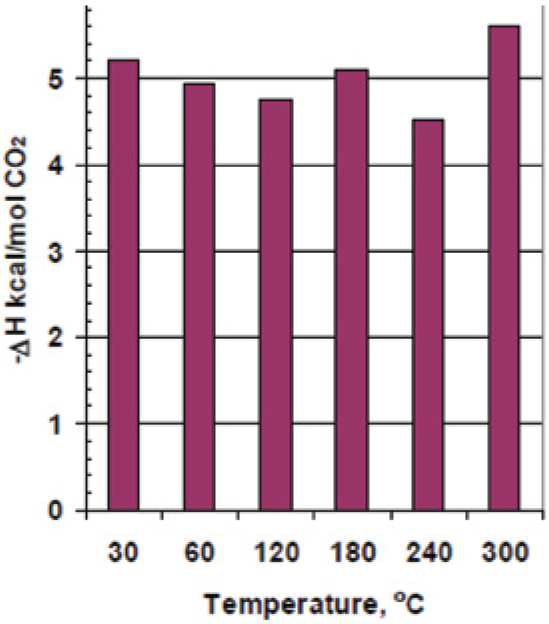

Figure 1: Heat of Adsorption Measurements (ΔH_{ads} = 4.9 ± 0.4 kcal/mol)

Initial sorbent testing under conditions simulating the environment downstream of a wet flue gas desulfurization unit showed stable CO_2 capacity for more than 220 cycles with no sign of degradation (Figure 2).

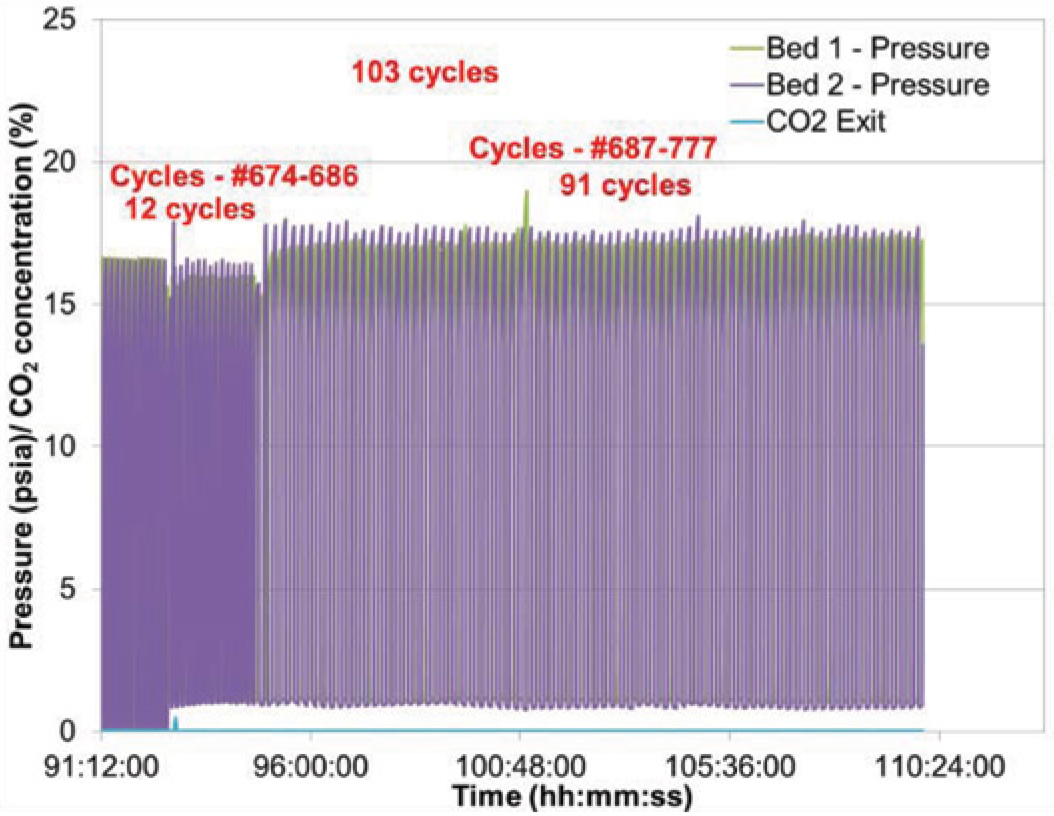

Figure 2: Capacity Testing Under Multiple VSA Cycles – Capacity Maintained Over 770 Cycles (T = 22°C; half-cycle time = 4-8 min; Pads= 16 psia; Pdes= 1 psia; simulated flue gas, 17 percent vol. CO_2, H_2O = 1.2 percent vol)

The presence of acid gases, such as sulfur dioxide (SO_2) and nitrogen oxide (NO_x), and water vapor up to 15 percent vol. caused no adverse effect on the CO_2 capacity (Figure 3)

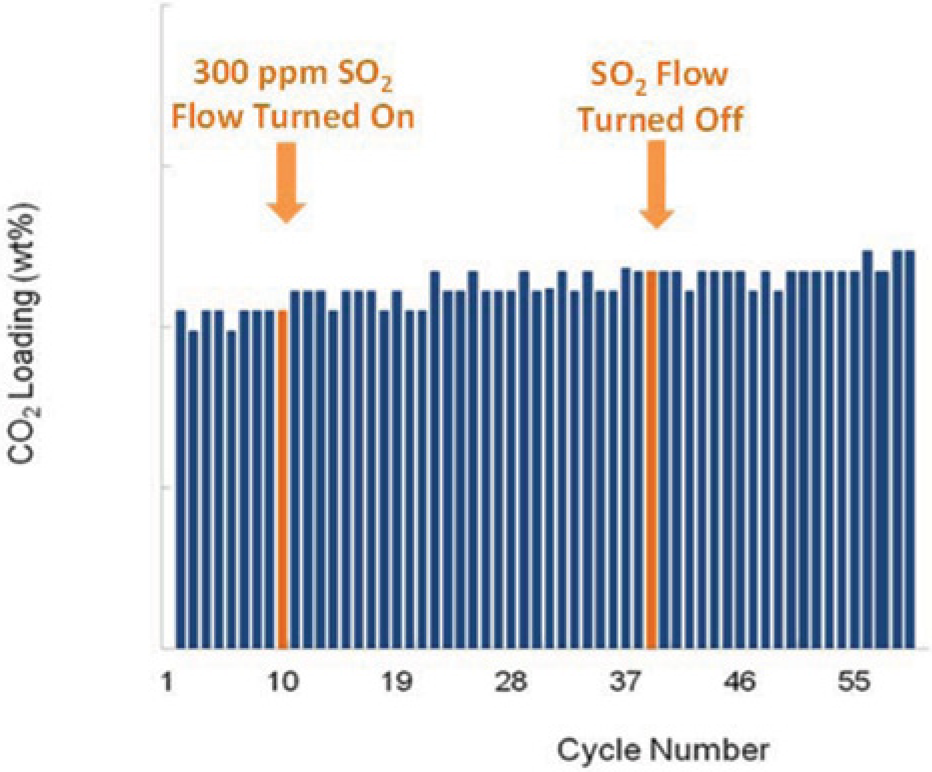

Figure 3: Capacity Analysis in Presence of SO_2 and Water (adsorption T = 62°C, 15.2 percent CO_2, 2.8 percentO_2, bal N_2, sat. with H_2O, 300 ppmv SO_2)

The regeneration of the sorbent and the recovery of CO_2 and its pressurization can then be achieved by several approaches, including temperature swing and vacuum swing. Figure 4 shows a schematic diagram of the process under temperature-swing operation.

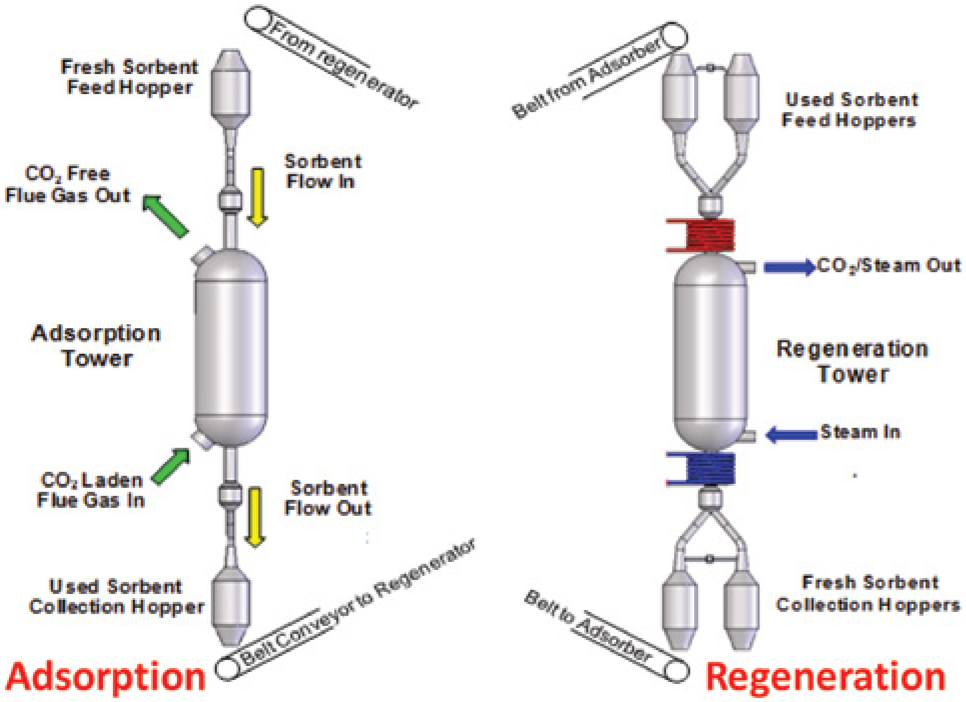

Figure 4: TSA Process Schematic

TABLE 1: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3		
Bulk Density	kg/m^3		
Average Particle Diameter	mm		
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3		
Solid Heat Capacity @ STP	kJ/kg-K	0.93	0.93
Crush Strength	kg_f		
Manufacturing Cost for Sorbent	$/kg		
Adsorption			
Pressure	bar	1.02	1.02
Temperature	°C	70	58
Equilibrium Loading	g mol CO_2/kg	0.3	0.4
Heat of Adsorption	kJ/mol CO_2	-20.5	-20.5
Desorption			
Pressure	bar	0.204	0.15 – 0.2
Temperature	°C	70	58
Equilibrium Loading	g mol CO_2/kg-sorbent		
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-		
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar	96–97%	
Adsorber Pressure Drop	bar		
Estimated Absorber/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 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.

technology advantages

- The sorbent does competitively adsorb CO_2 over water.
- The heat of adsorption of CO_2 is low (much lower than amine-based solvents; comparable to that of Selexol).
- The net energy loss in sorbent regeneration is expected to be lower than amine scrubbers.

R&D challenges

- Mechanical integrity of the sorbent material at the conditions of use must be demonstrated.
- The gas-solid contactor design must be proven with full capabilities to be demonstrated.

results to date/accomplishments

- The evaluation and optimization of sorbent chemical composition has been completed.
- A low-fidelity process design and system optimization to provide a basis for future experimental and system design work has been developed.

next steps

- Process design and system analysis.
- Long-term sorbent cycling.
- Design of a breadboard prototype test unit.
- High-fidelity process optimization and design.
- Fabrication of the prototype test unit.
- Concept demonstration.
- System analysis, economic evaluation, and environmental health and safety assessment.

available reports/technical papers/presentations

Alptekin, G., Jayaraman, A., Copeland, R., "Post-Combustion CO2 Capture System for Existing Coal-fired Power Plant," presented at the 2012 NETL CO2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/G%20Alptekin-TDA%20Research-Sorbent.pdf*.

Power Plant Air Pollutant Control "MEGA" Symposium, August 20-23, 2012, Baltimore, Maryland.

EVALUATION OF CARBON DIOXIDE CAPTURE FROM EXISTING COAL-FIRED PLANTS BY HYBRID SORPTION USING SOLID SORBENTS

primary project goals

The University of North Dakota (UND) is developing solid sorbent technology to decrease capture costs and energy use via bench-scale testing of a system that utilizes novel process chemistry, a low-cost method of heat management, and contactor conditions that minimize sorbent-carbon dioxide (CO_2) heat of reaction and promote fast CO_2 capture.

technical goals

- Combine existing technologies to create a new sorbent that will have a high CO_2 loading capacity and a process with a low regeneration energy penalty.
- Develop a process that will efficiently capture CO_2 from flue gas streams and regenerate it into a pure CO_2 stream with a lower operating cost than current methods.

technical content

UND is scaling-up and demonstrating a solid sorbent technology for CO_2 capture and separation from coal combustion-derived flue gas. The technology – Capture from Existing Coal-Fired Plants by Hybrid Sorption Using Solid Sorbents Capture (CACHYS™) – is a novel solid sorbent process based on the following principles:

- Reduction of energy for sorbent regeneration.
- Utilization of novel process chemistry.
- Contactor conditions that minimize sorbent-CO_2 heat of reaction and promote fast CO_2 capture.
- Low-cost method of heat management.

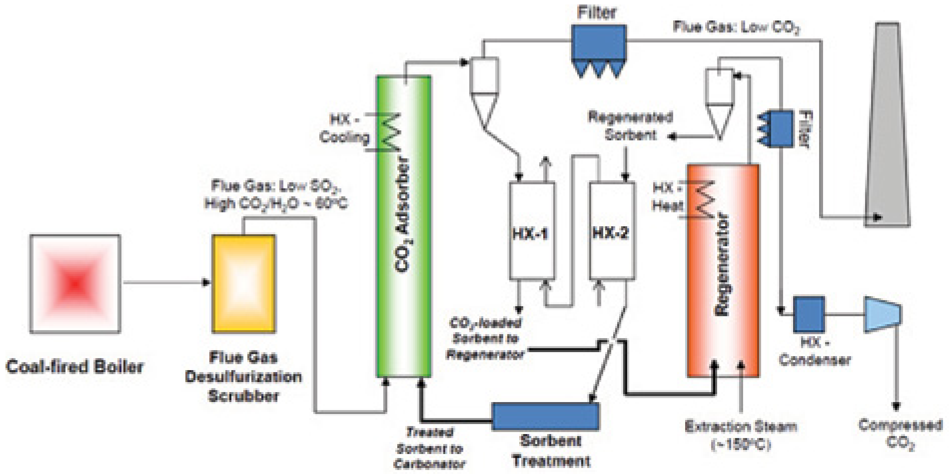

Figure 1: CACHYS™ Sorption Process

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Solid Sorbent-Based CO_2 Capture

participant:

University of North Dakota

project number:

FE0007603

NETL project manager:

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partners:

Industrial Commission of North Dakota
Envergex LLC
Barr Engineering
Solex Thermal Science Incorporated
ALLETE Incorporated
SaskPower

performance period:

10/1/11 – 9/30/14

Another key component of the technology is the use of a low-cost sorbent (consisting of active component, promoter, and support). UND is evaluating effective and cost-competitive sorbent formulations for CO_2 capture that have been identified in previous studies.

TABLE 1: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	1,800 – 2,200	1,800 – 2,200
Bulk Density	kg/m^3		
Average Particle Diameter	mm	0.1 – 1	0.1 – 1
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3		
Solid Heat Capacity @ STP	kJ/kg-K	0.8 – 1.4	0.8 – 1.4
Crush Strength	kg_f		
Manufacturing Cost for Sorbent	$/kg		
Adsorption			
Pressure	bar	1 – 1.5	1 – 1.5
Temperature	°C	50 – 90	50 – 90
Equilibrium Loading	g mol CO_2/kg-sorbent	1.5	2
Heat of Adsorption	kJ/mol CO_2	125	80
Desorption			
Pressure	bar	1 – 7	1 – 7
Temperature	°C	120 – 170	120 – 170
Equilibrium Loading	g mol CO_2/kg	0.4	0.4
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	Fluidized Bed	Fluidized Bed
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 95–99%,	
Adsorber Pressure Drop	bar		
Estimated Absorber/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 coal (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.

technology advantages

- Low heat of reaction observed.
- High sorbent capacity.
- Increased sorption kinetics.

R&D challenges

- Confirmation of energetic.
- Confirmation of sorbent capacity.
- Sorbent integrity.
- Sorbent handling.

results to date/accomplishments

- Performed initial heat and material balance calculations.
- Completed detailed initial process design.
- Conducted laboratory-scale sorbent performance tests; sorbent capacities ranged from 70 to 100 gm CO_2/kg sorbent, desorption energy values ranged from 30-80 kJ/mol CO_2.
- An initial technical and economic feasibility analysis of the process was conducted; calculated CO_2 capture costs were just above $36/ton.
- A detailed design of the bench-scale CACHYS™ adsorption and desorption system was developed.

next steps

- Bench-scale unit procurement and construction.
- Initial operation of the bench-scale unit.
- Bench-scale process testing.
- Final process assessment.

available reports/technical papers/presentations

Benson, S., et al., "Evaluation of CO_2 Capture from Existing Coal-fired Plants by Hybrid Sorption Using Solid Sorbents," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/evaluation-of-co2-capture-kickoff-nov2011.pdf*.

Preliminary Carbon Dioxide Capture Technical and Economic Feasibility Study - Topical Report [PDF-1MB] (Nov 2012).

Project Review Meeting Presentation [PDF-1.4MB] (Sep 2012). *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/und-co2-capture-budget-period1.pdf*.

Evaluation of CO_2 Capture from Existing Coal-Fired Power Plants by Hybrid Sorption Using Solid Sorbents (CACHYS™) [PDF-459KB] Project kick off meeting presentation, November 21, 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/und-co2-capture-budget-period1.pdf*.

BENCH-SCALE DEVELOPMENT AND TESTING OF A NOVEL ADSORPTION PROCESS FOR POST-COMBUSTION CO_2 CAPTURE

primary project goals

InnoSepra, LLC is developing a sorption-based technology using a combination of novel microporous materials and process cycles to determine the impacts of this unique combination on capture costs and performance via bench-scale testing of system components using actual coal-based flue gas.

technical goals

- Confirm the design basis for bench-scale testing based on lab-scale results and process modeling.
- Build and mechanically test the bench-scale unit in the lab.
- Test the bench-scale unit on an actual coal-based flue gas stream for a period of six to eight weeks.
- Develop capital cost, operating cost, and levelized cost of electricity (LCOE) for a commercial, 550-MW power plant.

technical content

InnoSepra is demonstrating the effectiveness of an innovative, adsorption-based carbon dioxide (CO_2) capture technology utilizing a combination of novel microporous materials and process cycles. The process utilizes physical sorbents with much lower heats of adsorption (around 200 kcal/kg, less than 25 percent of the total energy needed for amine-based systems) compared to competing processes. Lab-scale testing has produced greater than 99 percent CO_2 purity and greater than 90 percent CO_2 recovery from synthetic flue gas. Projections based on detailed engineering evaluations show that at commercial scale, the technology can reduce the power consumption for CO_2 capture by more than 40 percent, and reduce the capital cost for the CO_2 capture equipment by more than 60 percent; this results in a more than 40 percent reduction in the CO_2 capture cost compared to alternate technologies such as amines and chilled ammonia. The overall process schematic is shown in Figure 1.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Novel Adsorption Process

participant:

InnoSepra, LLC

project number:

FE0007948

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partners:

Adsorptech
New Mexico State University
Electric Power Research Institute (EPRI)
NRG Energy Inc
PNNL

performance period:

10/1/11 – 3/31/14

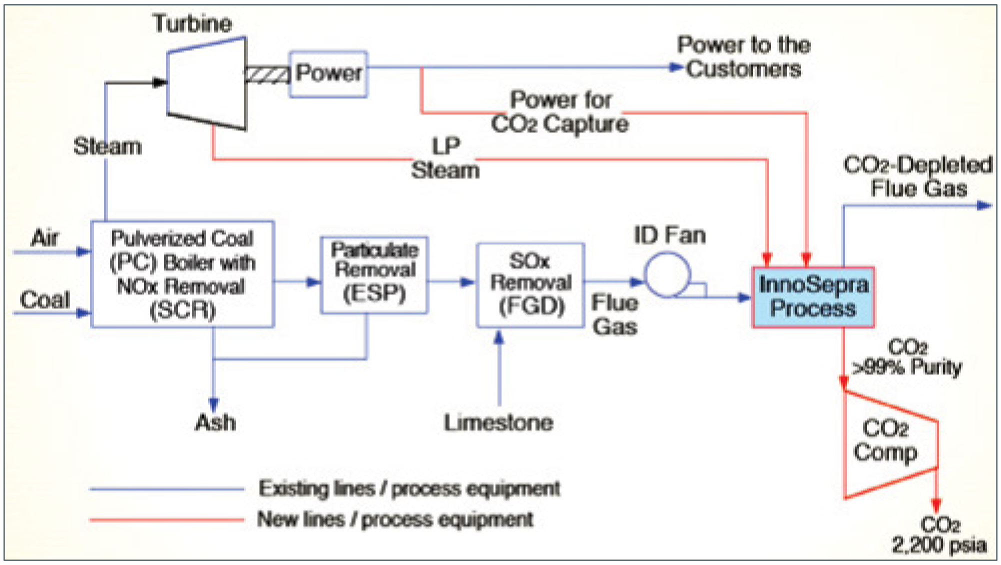

Figure 1: InnoSepra Capture Process Schematic

Figure 2 provides a schematic representation focusing on the CO_2 removal process. After the removal of moisture and sulfur oxides (SO_x) in a pretreatment system, the CO_2 is adsorbed, and high-purity CO_2 is produced during regeneration. The sorbents are heated and cooled using both direct and indirect cooling. Some of the heat of adsorption is removed during the adsorption process; the remaining heat is removed during the cooling steps. Regeneration heat is supplied via low-pressure steam, as well as by utilizing other process waste heat in the system.

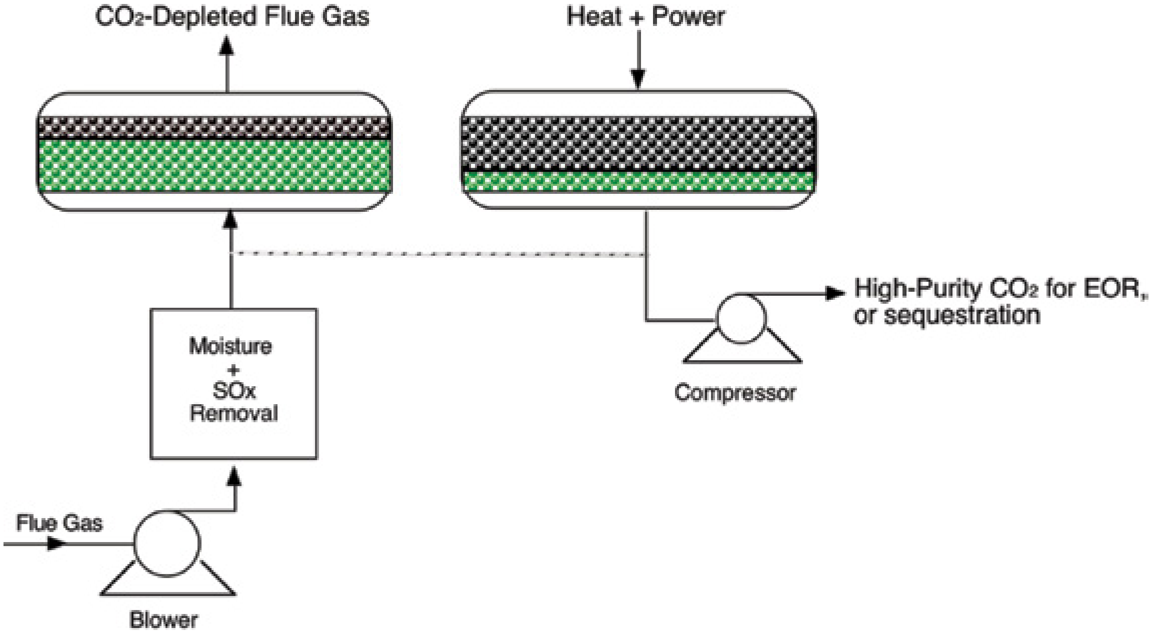

Figure 2: CO_2 Capture Process Schematic

Field-testing of the process at a one-ton-per-day scale in an actual power plant, as well as independent verification of process economics, will provide a firmer basis for techno-economic evaluation. This technology has the potential for earlier commercialization compared to some other technologies because most of the materials and unit operations used are commercial or near-commercial.

TABLE 1: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	1,990	1,990
Bulk Density	kg/m^3	690	690
Average Particle Diameter	mm	1.5-3.0	0.5-1.5
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1.79e8	1.79e8
Solid Heat Capacity @ STP	kJ/kg-K	0.96	0.96
Crush Strength	kg_f	2.9	2.9
Manufacturing Cost for Sorbent	$/kg	4.0	3.0-4.0
Adsorption			
Pressure	bar	1.15	1.1
Temperature	°C	25-32	25-32
Equilibrium Loading	g mol CO_2/kg	3.25	3.5-4.0
Heat of Adsorption	kJ/mol CO_2	38	38
Desorption			
Pressure	bar	0.3-1.0	0.3-1.0
Temperature	°C	100	90-110
Equilibrium Loading	g mol CO_2/kg	1.5	0.5-1.5
Heat of Desorption	kJ/mol CO_2	38	38
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	Fixed/cyclic	Fixed/cyclic
Flue Gas Flowrate	kg/hr	2,320,000	2,320,000
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 99%, 1.0 bar	
Adsorber Pressure Drop	bar	0.14	0.10
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	0.003	0.0025

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 coal (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.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The adsorption is physical sorption based on weak van der Waals forces. This leads to low heats of adsorption.

Sorbent Attrition and Thermal/Hydrothermal Stability – The process design protects the adsorbent from moisture and potential hydrothermal degradation. If moisture should break through onto the adsorbent, the adsorbent can be regenerated completely. The adsorbent is thermally stable at temperatures of more than 300°C.

Sorbent Make-Up Requirements – Based on prior experience with similar sorbents in similar operating environments, the adsorbent life would be between five and 10 years. An adsorbent life of five years has been assumed to estimate the make-up requirements.

Waste Streams Generated – Except for the sorbents loaded with flue gas components, SO_x and mercury, no other waste streams are generated in the process. These can be disposed off as per current power plant practices for materials loaded with SO_x and Hg.

Proposed Module Design – The CO_2 capture modules will be designed to capture CO_2 from a 550-MW PC power plant. Multiple modules will be used to minimize field fabrication and maximize off-site fabrication. The separation skid will consist of a feed preparation section (flue gas compression and cooling), the CO_2 adsorption section (removal of impurities, CO_2 adsorption, and desorption), and the CO_2 compression section. Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- The technology is able to utilize physical sorbents to obtain the same purity and recovery as chemical sorbents and amine-based absorption.
- The sorbents have lower heats of adsorption compared to reaction-based systems.
- The technology is able to produce >95 percent CO_2 at >90 percent recovery with an energy penalty of less than 60 percent of the energy penalty for the monoethanolamine (MEA) systems.
- The process is non-corrosive and can utilize carbon steel construction for the most part.

R&D challenges

- Heat management during both adsorption and regeneration.
- Water management.

results to date/accomplishments

- Two adsorbents with a CO_2 capacity greater than 5 wt% in cyclic steady state experiments have been identified.
- Adsorption and desorption isotherms, as well as the kinetic data for these adsorbents, have been measured.
- The heat and mass transfer data have been measured with different diameter beds (0.75 to 1.5 inch), and a preliminary design of the bench-scale unit for field-testing has been completed.
- Methods to remove contaminants such as nitrogen oxide (NO_x) and SO_x have been tested.
- A rigorous process model of the adsorption process has been developed, tested, and is undergoing modification.
- A preliminary technical and economic feasibility study of the process has been completed. The projected increase in LCOE is less than 45 percent, and the projected CO_2 capture cost is about $40/ton.
- A preliminary design and costing of a process unit capable of producing about one ton per day of CO_2 from flue gas was completed.
- Detailed mechanical design of the bench-scale test unit was completed and the components are being procured.

next steps

- Install tie-ins for the bench-scale unit in the field.
- Perform field-testing at NRG's Indian River power plant.
- Simulate the cyclic adsorption process using the modified adsorption process simulator.
- Update the techno-economic analysis based on field-test results and modeling results.
- Perform an environmental health and safety analysis.

available reports/technical papers/presentations

Jain, R., "Bench-scale Development and Testing of a Novel Adsorption Process for Post-Combustion CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/R%20Jain-InnoSepra-Adsorption%20Process.pdf*.

DEVELOPMENT OF NOVEL CARBON SORBENTS FOR CO_2 CAPTURE

primary project goals

SRI International (SRI) is developing an innovative, low-cost, low-energy, carbon dioxide (CO_2)-consuming capture technology based on adsorption with a high-capacity and low-cost carbon sorbent. The project is validating sorbent performance in a bench-scale system for post-combustion applications and performing parametric testing to determine optimum operating conditions.

technical goals

- Determine properties of the sorbent, such as surface area, heat of absorption and desorption, compressive strength and attrition resistance, and size and shape of sorbent particles.
- Validate the performance of the sorbent in a bench-scale, falling-bed reactor.
- Perform parametric experiments to determine the optimum operating conditions for the system.
- Validate the performance of the sorbent using an actual flue gas from a coal-fired boiler.
- Evaluate the technical and economic viability of the technology.

technical content

The novel sorbent developed for the project is composed of carbon microbeads, as shown in Figure 1. The sorbent was manufactured by ATMI, Inc. Initially, the characteristics of the sorbent were determined using the BET adsorption technique and thermogravimetric analysis (TGA) under various temperatures, pressures, and gas exposures. Bench-scale tests were performed in three stages: absorber parametric testing, regenerator parametric testing, and cyclic testing. An integrated absorber-regenerator system was designed and operated for determining long-term durability of the sorbents. Based on the favorable results from the bench-scale tests at SRI with a simulated gas, the bench-scale system was tested at the University of Toledo (Toledo, Ohio) using a flue gas from a coal-fired steam boiler.

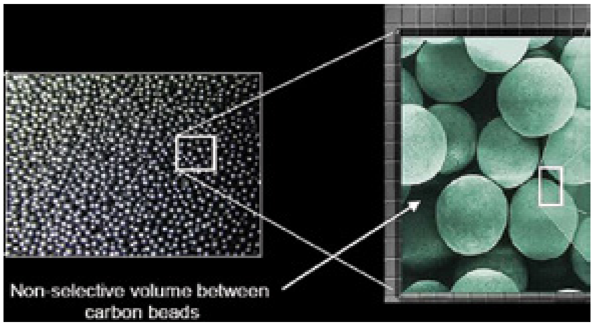

Figure 1: Graphic Displays of Novel Carbon Pellets Sorbent

technology maturity:
Bench-Scale Using Actual Flue Gas

project focus:
Novel Solid Sorbents

participant:
SRI International

project number:
NT0005578

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partners:
ATMI, Inc.

performance period:
10/1/08 – 11/30/13

Figure 2 depicts the proposed sorbent system for an existing coal-fired power plant. Flue gas first enters an existing flue gas desulfurization (FGD) system where most of the sulfur content is removed. The gas is then cooled before entering the cascading-bed adsorption reactor, which utilizes a high-capacity carbon sorbent (0.05 to 0.08 kg of CO_2 per kg of sorbent). As the gas stream passes over the lean sorbent, CO_2 is removed from the gas and adsorbed by the sorbent. The loaded sorbent cascades down the separation column and is heated by low-pressure steam, causing the sorbent to release the adsorbed CO_2. The CO_2 is siphoned off to a compressor where it can be prepared for sequestration. The sorbent is then dried, cooled, and sent back into the separation column for re-use and the cycle begins again.

Figure 3 represents the performance of the system after approximately 100 hours of operation. An 85 to 95 percent CO_2 capture and a CO_2 product gas purity of ≈100 percent was achieved. Note that a decrease in the CO_2 purity was observed due to an interruption of the steam feed. When the operation was resumed, the CO_2 purity value resumed to the original value, indicating the robust nature of the system.

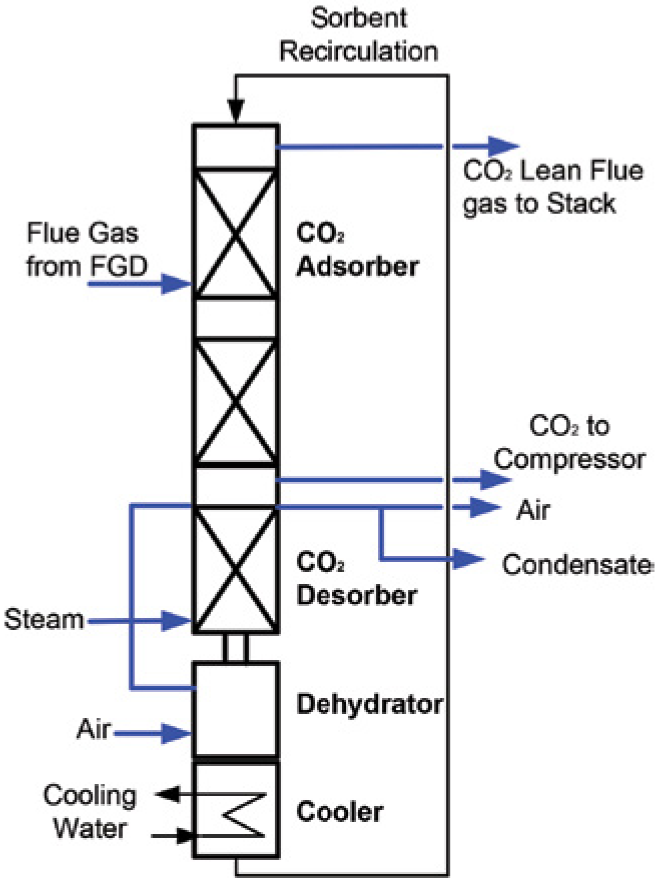

Figure 2: The Proposed Sorbent System

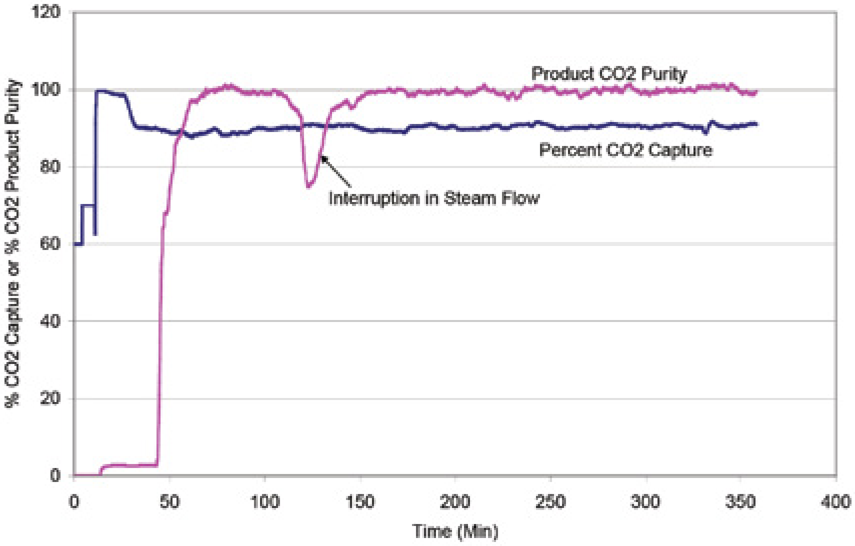

Figure 3: Typical Plot of CO_2 Capture Efficiency and Product Gas Purity in Field Test

TABLE 1: PROCESS PARAMETERS FOR SOLID CARBON SORBENT

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	2200	2200
Bulk Density	kg/m^3	700	700
Average Particle Diameter	mm	0.3	0.5
Particle Void Fraction	m^3/m^3	0.36	0.3
Packing Density	m^2/m^3	9 x108	1.1x109
Solid Heat Capacity @ STP	kJ/kg-K	1.0	1.0
Crush Strength	kg_f	3.3	3.3
Manufacturing Cost for Sorbent	$/kg	50	30
Adsorption			
Pressure	bar	1	1
Temperature	°C	15 – 25	25
Equilibrium Loading	g mol CO_2/kg-sorbent	1.1	1.3
Heat of Adsorption	kJ/mol CO_2	28	28
Desorption			
Pressure	bar	1	1
Temperature	°C	80 – 100	100
Equilibrium Loading	g mol CO_2/kg	0.01	0.01
Heat of Desorption	kJ/mol CO_2	25 to 28	25 to 28
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	Falling bead	Falling bead
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar	99%, 90%, 1 bar	
Adsorber Pressure Drop	bar	1 x 10-3	4 x10-3
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	200	200

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 coal (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.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Rapid physical adsorption and desorption rates: The adsorption of CO_2 occurs on the micropores of the sorbent with low activation energy (< 5 kJ/mole), allowing rapid equilibrium. Similarly, the adsorbed CO_2 is desorbed rapidly at the regeneration temperature (≈100°C), and the sorbent performance can be predicted by equilibrium models.

Sorbent Contaminant Resistance – The sorbent is pure carbon and generally resistant to many contaminants. The sulfur dioxide (SO_2) needs to be reduced to <10 parts per million (ppm) levels, preferably to 1 ppm level. Nitrogen oxides (NO_x) can be present at ≈50 ppm levels. Fly-ash particles in flue gas downstream of an electrostatic precipitator do not appear to interfere with CO_2 adsorption.

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent granules are hard and attrition-resistant. No observable attrition was noticed in a recent field test conducted over 7,000 cycles of adsorption and regeneration. The sorbent has a high hydrothermal stability and direct heating with steam can be used for CO_2 desorption. The sorbent regenerated at the elevated temperature can be cooled by evaporative cooling of moisture adsorbed on the sorbent.

Flue Gas Pretreatment Requirements – Reduce SO_2 levels to < 5 ppm. The flue gas needs to be cooled to ≈25°C.

Sorbent Make-Up Requirements – Preliminary data suggest multi-year lifetime for sorbent make-up.

Waste Streams Generated – The sorbent particles are hard and attrition-resistant, and no fine sorbent particles are generated during operation. Steam condensate from the dehydrator may need to be treated before cycling back to the steam boiler.

Proposed Module Design – The module will be located between FGD and flue gas chimney

technology advantages

- High CO_2 Capacity: The sorbent has a high capacity for CO_2 adsorption (20 wt% at 1 atm CO_2) and good selectivity for CO_2 over other flue gas components (CO_2-N_2 separation factor > 20).
- Rapid Adsorption and Desorption Rates: The adsorption of CO_2 occurs on the micropores of the sorbent with low activation energy (< 5 kJ/mole), allowing rapid equilibrium. Similarly, the adsorbed CO_2 is desorbed rapidly at the regeneration temperature (≈100°C), and the sorbent performance can be predicted by equilibrium models.
- Low Heat of Adsorption and Desorption: The relatively low heats (25 to 28 kJ/mole) indicate that this process has a low-heat demand for regeneration.
- High Hydrothermal Stability: Direct heating with steam can be used for CO_2 desorption. The sorbent regenerated at the elevated temperature can be cooled by evaporative cooling of moisture adsorbed on the sorbent.
- Mechanical Robustness for Long Lifetime: The sorbent granules are hard and attrition-resistant. No observable attrition was noticed in a recent field test conducted over 7,000 cycles of adsorption and regeneration.
- Spherical Morphology of the Sorbent Granules: The spherical nature of the sorbent granules (200 to 400 µm in diameter) eliminates sorbent dust generation during use by the breakage of sharp points on the outer edge of granules.
- Resistance to Agglomeration at the Operating Temperature: Carbon particles do not sinter at 100°C. Agglomeration of the sorbent microbeads is unlikely.
- Low-Heat Capacity: The low-heat capacity of the sorbent (1 J/g/K), as compared to that of water, minimizes the thermal energy needed to heat the sorbent to the regeneration temperature.

- High-Thermal Conductivity: The thermal conductivity of 0.8 w/m-K enables rapid thermal equilibrium between the surface and interior of the microbeads.
- Hydrophobicity: The sorbent is essentially hydrophobic, indicating little interaction between the condensed water and the sorbent. The thermal energy required to desorb the condensed water is significantly less than that required to evaporate water from oxide surfaces such as those found in molecular sieves (zeolites), alumina, and silica.

R&D challenges

- Other elements of the flue gas, such as sulfur oxides (SO_x), may compete with CO_2 in being adsorbed by the sorbent, reducing the amount of CO_2 that is adsorbed as the gas passes through the reactor.
- A low temperature needs to be maintained for optimal adsorption conditions. The flue gas needs to be cooled to approximately 25°C.
- Thermal management to recover part of the sensible heat present in the hot sorbent to preheat the sorbent entering the stripper. Proprietary heat exchangers have been designed to recover heat from the sorbent (thereby cooling the sorbent) and to use the heat to preheat the sorbent.

results to date/accomplishments

- Completed 135 hours of testing using the flue gas from a coal-fired steam boiler facility at the University of Toledo.
- Completed the long-term, 1,000-cycle test to determine the durability of the sorbent.
- Completed bench-scale parametric tests and evaluation of optimum process conditions.
- Completed field testing with their bench-scale unit using flue gas from a coal-fired boiler at the University of Toledo. Testing ended after 135 hours (approximately 7,000 cycles of adsorption and desorption).
- Evaluated several physical, chemical, and mechanical properties of the sorbent in the context of the CO_2 capture system using a bench-scale, fixed-bed reactor.
- Demonstrated regeneration using direct contact steam producing relatively pure CO_2.
- Simulated CO_2 capture using novel carbon sorbent in a pulverized coal (PC)-fired boiler from coal to electricity and compressed CO_2.
- Determined several physical and chemical properties of the advanced carbon sorbent in the context of flue gas CO_2 capture.

next steps

- Complete CO_2 capture tests with flue gas from a PC boiler.
- Install bench-scale reactor at the National Carbon Capture Center (NCCC).

available reports/technical papers/presentations

Krishnan, G., "Development of Novel Carbon Sorbents for CO_2 Capture," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Gopala%20Krishnan-NT0005578.pdf*.

Krishnan, G., "Development of Novel Carbon Sorbents for CO_2 Capture," presented at the 9th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2010.

Krishnan, G., "Development of Novel Carbon Sorbents for CO_2 Capture – Project Overview," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5578%20SRI%20carbon%20sorbent%20%28Hornbostel%29%20mar09.pdf*.

LOW-COST SORBENT FOR CAPTURING CO_2 EMISSIONS GENERATED BY EXISTING COAL-FIRED POWER PLANTS

primary project goals

TDA Research is designing and developing a low-cost solid sorbent that is capable of cost-effectively and efficiently capturing carbon dioxide (CO_2) from existing coal-fired power plants, as well as an adsorption/regeneration process designed around that material.

technical goals

- Use existing information to select candidates for a low-cost, highly efficient CO_2 sorbent.
- Perform thermogravimetric analysis (TGA), surface area (BET), and crush strength analyses to characterize the sorbent.
- To determine the effects of sulfur oxides (SO_x), nitrogen oxides (NO_x), and water (H_2O) on the working capacity of the optimum sorbent.
- Construct and demonstrate a novel CO_2 removal system for real flue gas stream.

technical content

TDA's CO_2 capture system uses a dry alkalized alumina sorbent. The regenerable sorbent acts as a physical adsorbent for CO_2. The CO_2 capture process runs near isothermally at around 150°C in both adsorption and regeneration. No heating or cooling of the sorbent between absorption and regeneration steps is required. The sorbent is regenerated with low-pressure (15.5 pounds per square inch absolute [psia]) steam. This regeneration is done at near the same temperature as adsorption.

The sorbent has shown excellent tolerance to contaminants. Laboratory tests using simulated flue gas with sulfur dioxide (SO_2) were performed for more than 2,000 cycles. Testing with NO_x has been conducted for more than 180 cycles. No loss of CO_2 loading capacity was observed during these tests. For this process, additional flue gas pretreatment upstream of the CO_2 capture unit may not be required beyond what is already in place with existing flue gas desulfurization (FGD) units.

Figure 1 shows an overall schematic of TDA's system, which consists of three primary components: (1) the absorber/regenerator unit; (2) the low-pressure steam generator; and (3) the CO_2 compression and purification unit. The process is designed for the sorbent to pull the dilute CO_2 out of the flue gas at intermediate temperature and near ambient pressure, and then be regenerated with low-pressure superheated steam. TDA is developing both the sorbent and the process designed around that material.

technology maturity:

Bench-Scale Using Simulated Flue Gas

project focus:

Low-Cost Solid Sorbent

participant:

TDA Research

project number:

NT0005497

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partners:

Babcock & Wilcox (B&W)
Louisiana State University (LSU)
Western Research Institute (WRI)

performance period:

11/1/08 – 8/31/13

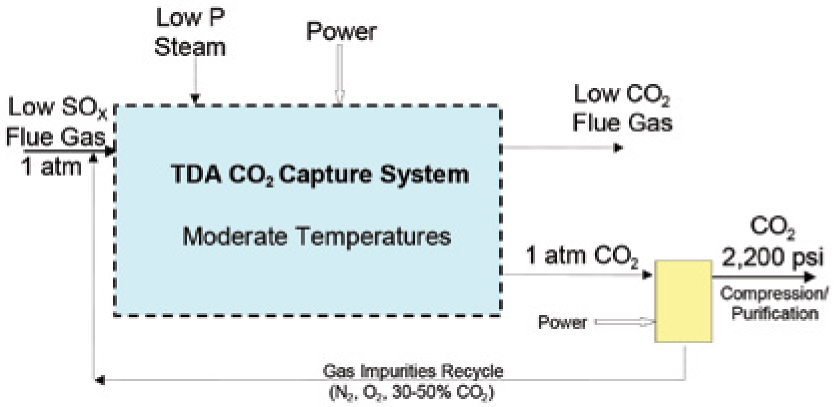

Figure 1: Schematic of TDA's CO$_2$ Emission Control System

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	750	750
Bulk Density	kg/m^3	520	520
Average Particle Diameter	mm	1.3	3.175
Particle Void Fraction	m^3/m^3	0.55	0.55
Packing Density	m^2/m^3		
Solid Heat Capacity @ STP	kJ/kg-K	0.72	0.72
Crush Strength	kg$_f$	8	8
Manufacturing Cost for Sorbent	$/kg		
Adsorption			
Pressure	bar	0.13	0.13
Temperature	°C	160	150
Equilibrium Loading	g mol CO$_2$/kg	1.5	1.5
Heat of Adsorption	kJ/mol CO$_2$	-12.5 to -41.9	-12.5 to -41.9
Desorption			
Pressure	bar	0.4	0.5
Temperature	°C	160	150
Equilibrium Loading	g mol CO$_2$/kg	1.5	1.5
Heat of Desorption	kJ/mol CO$_2$	12.5 to 41.9	12.5 to 41.9
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-		
Flue Gas Flowrate	kg/hr		
CO$_2$ Recovery, Purity, and Pressure	% / % / bar		
Adsorber Pressure Drop	bar		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

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 coal (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.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The sorbent is an adsorbent and is regeneration with steam.

Sorbent Contaminant Resistance – Based on extended cycling 1,500 hours with simulated flue gas with 13.8% CO_2, 104 parts per million (ppm) SO_2, 3% oxygen (O_2), and 9% H_2O, sorbent life was calculated to be one year with 5 ppm of SO_2. No effect of NO_x on capacity was seen after 200 cycles with 739 ppm nitric oxide (NO) and 84 ppm nitrogen dioxide (NO_2).

Flue Gas Pretreatment Requirements – Flue gas should have <5 ppm SO_X.

Proposed Module Design – TDA's CO_2 capture system is located downstream of the FGD unit. The adsorbent removes dilute CO_2 from the flue gas (10 to 14% CO_2, 8 to 10% H_2O, <5 ppm SO_2) at intermediate temperature (160°C) and near ambient pressure.

technology advantages

- Low regeneration energy.
- Rapid adsorption/regeneration kinetics due to surface-only adsorption.
- Isothermal operation.

R&D challenges

- Effectively produce a sorbent from low-cost raw materials with extensive regenerative life of the sorbent.
- Minimizing the parasitic demands from the sorbent system.

results to date/accomplishments

- Demonstrated bench-scale unit at Western Research Institute on coal-derived flue gas.
- Completed lab-scale reactor testing.
- Completed design of the bench-scale unit.
- Performed TGA, BET, and crush strength analyses on a variety of sorbent materials.
- Determined alkalized alumina to be the optimum sorbent with a loading capacity of 0.7 wt%.
- Performed extended period testing up to 1,800 cycles and found the sorbent maintained its loading capacity at near-constant levels throughout.
- Optimized the sorbent composition and production process.
- Performed sorbent testing and characterization.
- Initiated 1,500-hour sorbent cycling test to evaluate the SO_x contamination of the sorbent and to complete wear and service assessments of the sorbent.
- Evaluated the affect of NO_x in simulated flue gas. No loss of CO_2 loading capacity observed after 180 cycles with 820 ppm of NO_x.
- Created a CO_2 capture process design and ASPEN model that includes steam source, CO_2 compression, and heat sources, and calculates efficiency.
- Evaluated improved sorbent material with 40 percent higher loading capacity.

next steps

Evaluate new process designs.

available reports/technical papers/presentations

Elliot, J., and Srinivas, G., “Low Cost Sorbent for CO_2 Capture on Existing Plants,” presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/1-Monday/J%20Elliott-TDA-Low%20Cost%20Sorbent.pdf*.

Elliot, J., and Srinivas, G., “Post-Combustion CO_2 Capture with Alkalized Alumina,” presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/publications/proceedings/09/CO_2/pdfs/5497%20TDA%20sorbent%20%28Elliott%29%20mar09.pdf*.

Elliot, J.; Srinivas, G.; and Copeland, R., “Low-Cost Sorbent for Capturing CO_2 Emissions Generated by Existing Coal-Fired Power Plants,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Jeannine%20Elliott-NT0005497.pdf*.

Elliot, J.; Srinivas, G.; and Copeland, R., “Low Cost Solid Sorbent for CO_2 Capture on Existing Coal-Fired Power Plants,” presented at the 26th Annual International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September 2009. *http://www.tda.com/Library/docs/PCC%20Sept%202009%20v3.pdf*.

Elliot, J., and Srinivas, G., “Low-Cost Sorbent for Capturing CO_2 Emissions Generated by Existing Coal-Fired Power Plants – Project Overview,” presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO_2/pdfs/5497%20TDA%20sorbent%20%28Elliott%29%20mar09.pdf*.

METAL MONOLITHIC AMINE-GRAFTED SILICA FOR CO_2 CAPTURE

primary project goals

The University of Akron set out 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 a 10 percent 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 (MEA)/tetraethylenepentamine. The adsorption capacity of this novel amine-grated silica was determined 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 can be further optimized by the sorbent preparation procedures with additives.

The metal monolithic structure allows the rapid removal of heat of CO_2 adsorption. 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 tetraethylenepentamine. Coal fly ash was investigated as a support for amine due to its ready availability and low cost.

technology maturity:

Pilot-Scale Using Simulated Flue Gas, 15 kW

project focus:

Metal Monolithic Amine-Grafted Zeolites

participant:

University of Akron

project number:

FC26-07NT43086

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partners:

FirstEnergy

performance period:

2/21/2007 – 3/31/11

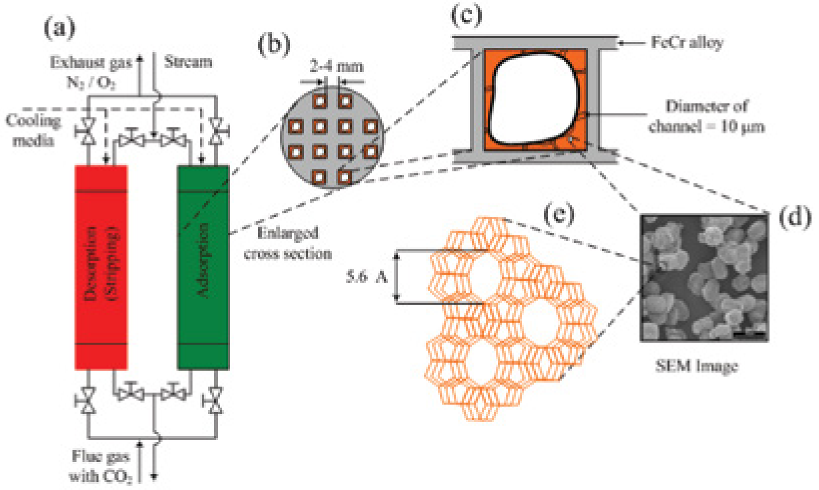

Figure 1: Metal Monolithic Amine-Grafted Silica Sorbents

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 holds the individual metal (b) tubes with the amine approximately 2 to 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. Heating for CO_2 desorption (i.e., regeneration) and cooling for adsorption are achieved by 40 pounds per square inch gauge (psig) steam and cooling water flowing through the jacket side of the adsorber. Desorbed CO_2 is purged from the channels of metal monoliths by pulses of steam and hot air. The goal is that CO_2 and SO_2 adsorption capacity of the amine will be greater than 1.5 mmol-CO_2/g-sorbent and 1.0 mmol-CO_2/g-sorbent, respectively. The amine is capable of greater than 500 times regeneration with less than 10 percent degradation in CO_2 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

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3		
Bulk Density	kg/m^3	0.5	0.5
Average Particle Diameter	mm	0.05-1	<1
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3	.43	<0.5
Solid Heat Capacity @ STP	kJ/kg-K		
Crush Strength	kg$_f$		
Manufacturing Cost for Sorbent	$/kg	14	12
Adsorption			
Pressure	bar	1	1
Temperature	°C	50	<55
Equilibrium Loading	g mol CO_2/kg	2.4	3.1
Heat of Adsorption	kJ/mol CO_2	60	55
Desorption			
Pressure	bar	1-1.05	1-1.05
Temperature	°C	100-110	100-110
Equilibrium Loading	g mol CO_2/kg	2.4	3.1
Heat of Desorption	kJ/mol CO_2		

TABLE 1: PROCESS PARAMETERS FOR METAL MONOLITHIC AMINE-GRAFTED SILICA SORBENTS

	Units	Current R&D Value	Target R&D Value
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-		
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar		
Adsorber Pressure Drop	bar		
Estimated Absorber/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 coal (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.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – $CO_2 + R\text{-}NH_2 \rightarrow$ Carbamate/ammonium ions and Carbamic acid

Sorbent Contaminant Resistance – Sorbent capacity decreased by more than 50 percent after 30 cycles in 15 percent CO_2 and 250 parts per million (ppm) SO_2.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent capacity decreased by less than 10 percent after more than 500 cycles under thermal/hydrothermal conditions.

Flue Gas Pretreatment Requirements – Less than 20 ppm SO_2.

Sorbent Makeup Requirements – Less than 10 percent after 500 cycles.

Waste Streams Generated – Degraded sorbents will be re-activated.

Proposed Module Design –

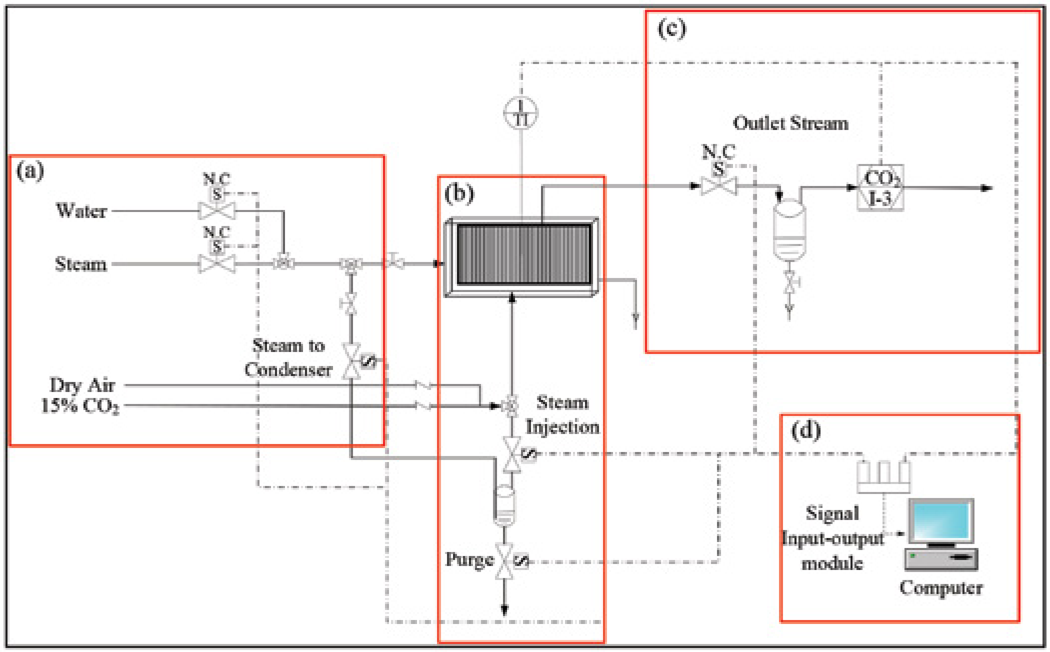

Figure 2: Process Schematic of the Monolith Adsorber

Adsorption temperature: < 40°C; desorption temperature: 105 to 115°C; pressure: 1 to 1.3 atm.

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 scale-up 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 MEA process.
- Currently, the CO_2 capture capacity of the sorbent is too low.

results to date/accomplishments

- The first generation of immobilized amine sorbents underwent 500 CO_2 capture cycles with less than 15 percent degradation. Refining in composition and preparation method resulted in sorbents with high stability for more than 1,100 CO_2 capture cycles, but lower capture capacity.
- Zeolite was shown to not be an effective support because of its hydrophilicity and small pore sizes.
- Developed a pilot-scale sorbent manufacturing process at a rate of 1 kg/hr.
- Enhanced the sorbent resistance to SO_2 poisoning by adding a proprietary additive to the CO_2 sorbent.

- A binder agent allows to agglomerate powder sorbents into rod or spherical pellets while maintaining the CO_2 capture capacity of the sorbent and yielding to low attrition rates.
- The operation under fixed-bed conditions present limitations in heat transfer: (1) slowing down the CO_2 capture process and (2) causing the sorbent to degrade.
- The CO_2 capture capacity could be increased 1.6 to 1.9 times when H_2O is present in the flue gas as compared to capture in dry conditions.
- Demonstrated the sorbent at pilot-scale, a 5-kg fixed bed. Adsorption was carried out at 55°C and desorption was with steam at 110°C.

next steps

This project ended on March 31, 2011.

available reports/technical papers/presentations

Chuang, S.S.C., “Amine absorber for carbon dioxide capture and processes for making and using the same,”

US 8377173 B_2, US Patent, Publication date: Feb. 19, 2013.

Chuang, S.S.C., “Metal Monolithic Amine-Grafted Zeolites for CO_2 Capture Power Plants,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Steven%20Chuang-NT43086.pdf*.

Chuang, S.S.C.; Fisher, J.; and Tanthana, J., “Metal Monolithic Amine-grafted Zeolites for CO_2 Capture,” presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO$_2$/pdfs/43086%20Akron%20amine-zeolite%20sorbent%20%28Chuang%29%20mar09.pdf*.

Tanthana, J., and Chuang, S.S. C., “In Situ Infrared Study of the Role of PEG in Stabilizing Silica-Supported Amines for CO_2 Capture,” Chemical & Sustainability Energy & Materials, 3, 957-964, 2010. *http://onlinelibrary.wiley.com/doi/10.1002/cssc.201000090/abstract*.

Fisher II, J.C.; Tanthana, J.; and Chuang, S.S.C., “Oxide-supported Tetraethylenepentamine for Carbon Dioxide Capture,” Environmental Progress & Sust Energy, 28 (4), 589-598, 2009. *http://onlinelibrary.wiley.com/doi/10.1002/ep.10363/abstract*.

CO_2 REMOVAL FROM FLUE GAS USING MICROPOROUS METAL ORGANIC FRAMEWORKS

primary project goals

UOP set out to design and develop a carbon dioxide (CO_2) removal system that employs metal organic framework (MOF) sorbents.

technical goals

- Use combinatorial chemistry to systematically synthesize and characterize a wide range of MOF and related materials.
- Screen materials for hydrothermal stability.
- Collect isotherm data for subsequent development and optimization.
- Determine the effects of water on CO_2 adsorption.
- Develop and validate material scale-up and forming procedures.
- Select the best one or two materials for final optimization and scale-up.
- Determine the effects of contaminants on the performance of scaled-up materials.
- Understand detailed kinetic and equilibrium data for incorporation in a process design and an economic analysis.

technical content

MOFs are extremely high surface area, crystalline, microporous, and thermally stable materials that have shown exceptional storage capacity for CO_2, methane, hydrogen, and other gases. MOFs typically consist of transition metal vertices, or hubs, attached three-dimensionally to other metal vertices by organic "linker" molecules. After removal of reaction solvent, the resulting porosity can be adjusted by simply changing the length or composition of the molecules used to link the metal vertices. Well-ordered openings, channels, and pockets in the structures are from a few angstroms to tens of angstroms. Figure 1 represents the building blocks used to create prototypical MOF-5, in which the green ball represents the metal-containing hub, and the yellow cylinder represents the organic linker.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

CO_2 Removal from Flue Gas Using Microporous MOFs

participant:

RTI International

project number:

FC26-07NT43092

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Vanderbilt University
Northwestern University

performance period:

3/12/07 – 6/30/10

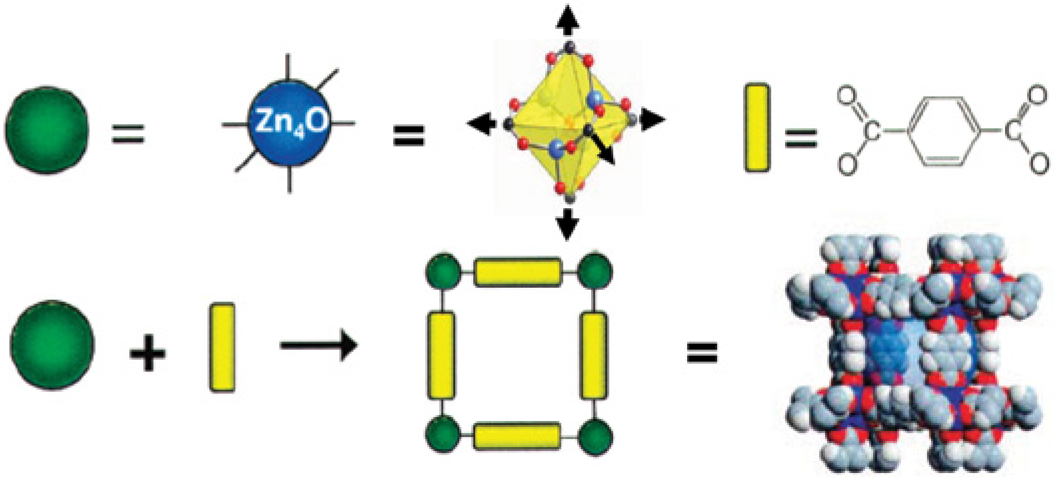

Figure 1: Building Blocks Used to Create Prototypical MOF-5

More than 50 MOFs for CO_2 adsorption were prepared from literature reports or designed by the experimenters. Table 1 displays the top MOFs for CO_2 capture.

TABLE 1: TOP 10 MOFS FOR CO_2 CAPTURE

Sample	Loading (mol/kg)	Loading (wt%)	Heat of Absorption (kJ/mol)
Mg\DOBDC (2)	4.73	20.9	60.1
Ni\DOBDC	3.40	15.0	27.2
Co\DOBDC	1.84	8.1	19.9
Mg\DOBDC (1)	1.28	5.6	21.3
HKUST-1 (CuBTC)	0.42	1.8	23.3
Zn\DOBDC	0.41	1.8	22.9
A1-MIL-110	0.24	1.1	21.7
Cr-MIL-101	0.18	0.8	13.3
Tb-MOF-76	0.18	0.8	21.7
A1-MIL-53	0.17	0.7	26
Zn-IRMOF-1	0.13	0.6	13.5

MOF-based adsorbents will be utilized in a vacuum pressure swing adsorption (VPSA) process for removal of CO_2 from flue gas. Figure 2 represents an example of MOF CO_2 adsorption capabilities as a function of pressure (for M/DOBDC, M represents the metal).

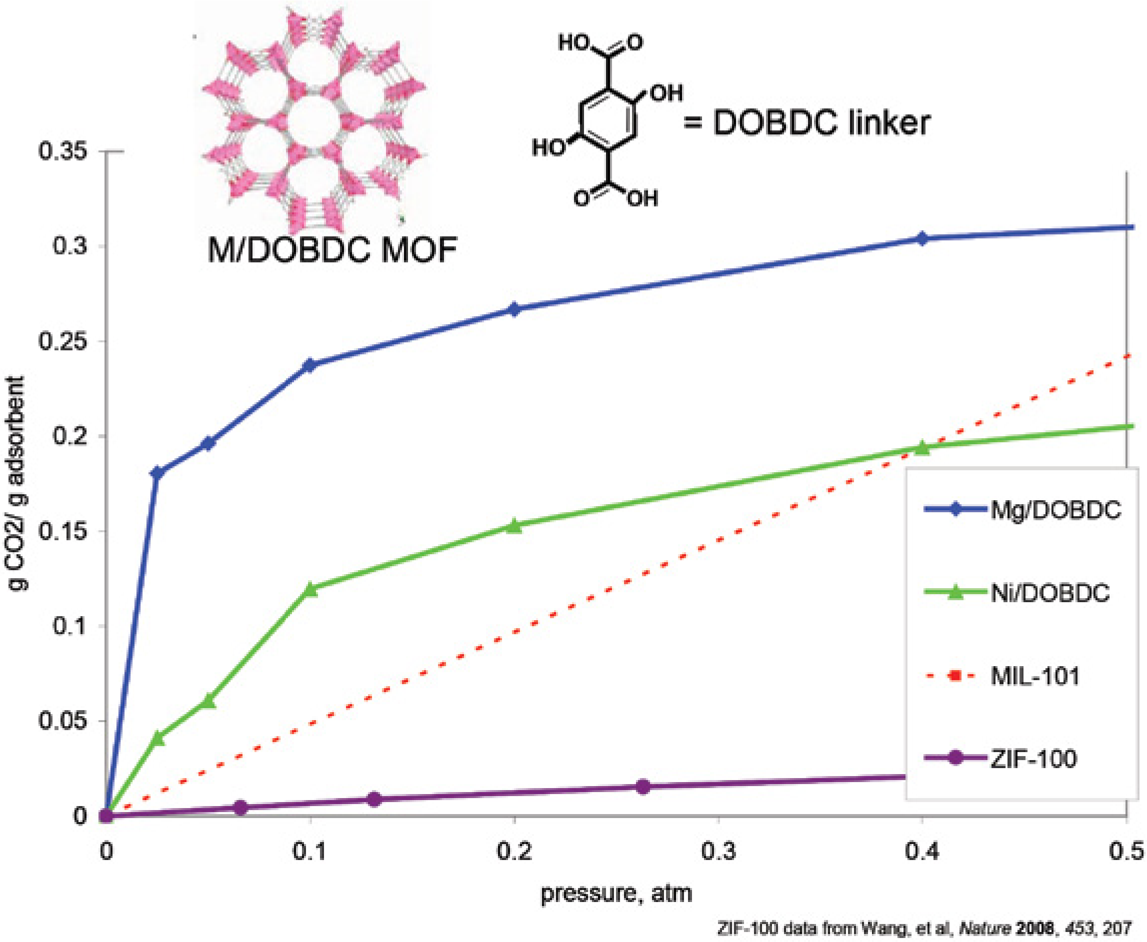

Figure 2: Example of MOF CO_2 Adsorption Capabilities as a Function of Pressure

The MOF-based VPSA CO_2 recovery system will be located after a contaminant-removal section and before the final CO_2 compression and drying section. The nitrogen (N_2)-rich waste stream (raffinate) will be sent to the stack. A process schematic is provided in Figure 3.

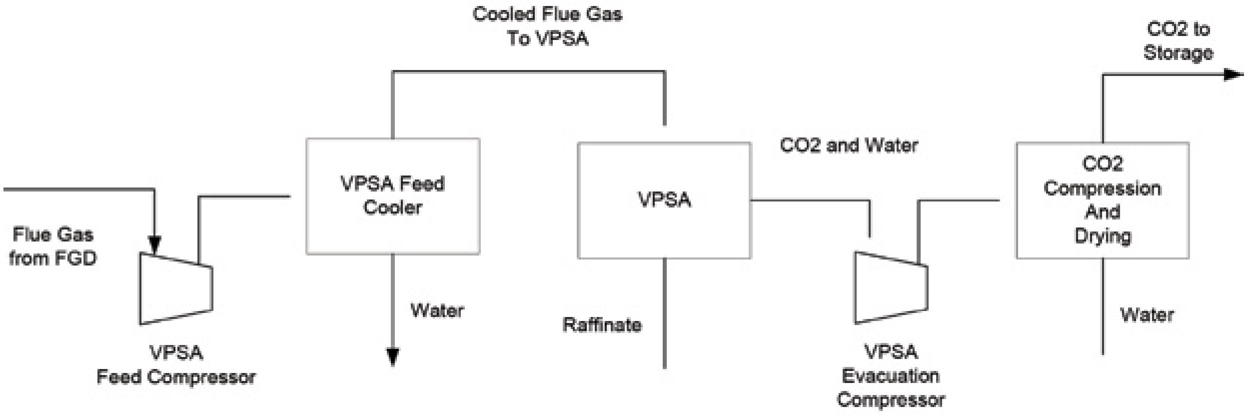

Figure 3: The MOF-Based CO_2 Capture System Process Schematic

Downstream from the flue gas desulfurization (FGD) and polishing scrubber, flue gas pressure is boosted in the VPSA feed compressor by approximately 4.8 pounds per square inch (psi) to make up for pressure drop in the contaminant-removal section and to maximize the adsorption of CO_2 in the VPSA unit. The VPSA feed compressor will be followed by a VPSA feed cooler to lower the temperature of the flue gas to approximately 100°F. It is likely that two parallel operating VPSA feed compressor and VPSA feed cooler trains will be required. Compressing and cooling the flue gas to 100°F will reduce the flue gas volume flow rate (actual cubic feet per minute [ACFM]) by up to 35 percent, and concurrently knock out at least 75 percent of the water vapor originally present in the flue gas. The combined lower-volume, lower-temperature, and lower-water content will allow the VPSA unit to operate more efficiently and effectively on the resultant flue gas stream.

The cooled flue gas enters the VPSA unit and will flow in a radial fashion through a short bed of adsorbent in either a vertical or horizontal configuration, depending upon the particular power plant's requirements. The adsorbent beds will consist of alumina for moisture polishing, and MOF for CO_2 removal. In the VPSA conceptual design at the end of the adsorption step, the vessel first vents N_2 raffinate to the stack to reduce the bed pressure to atmospheric pressure; pressure then equalizes with another vessel that had just completed the vacuum regeneration step. This would reduce the bed pressure to 7 to 8 pounds per square inch absolute (psia). These steps also reduce the N_2 stored in the vessel voids and minimize the amount that would be co-produced with the CO_2. The adsorbent bed would then be evacuated to 0.5 psia to produce the CO_2. For the purposes of the calculations, it was assumed that there was negligible co-adsorption of N_2 on the CO_2-loaded adsorbent and that the N_2 was primarily stored in the voids of the adsorbent vessel. The target CO_2 delta loadings were based on producing a >90 percent CO_2 purity stream during the regeneration step. The parasitic load for regeneration of the adsorbent is the compression energy associated with evacuating the vessel to 0.5 psia and compressing the contents to at least 8.8 pounds per square inch gauge (psig). The contribution of the N_2 stored in the voids is quite small compared to the compression energy associated with desorbing the CO_2. A purge step was not used in this process since the primary concern is producing a high-purity CO_2 stream.

The VPSA evacuation compressor will be used to remove CO_2 streams at 95 to 97 percent purity from the adsorbent beds. The water that comes along with the CO_2 will be removed during the CO_2 compression and drying stage of the process. In order to facilitate the gas compression and drying section CAPEX estimate, the VPSA evacuation compressor discharge pressure is 8.8 psig. This is the same pressure that the Econamine process delivers captured CO_2 to the gas compression and drying section. In the compression section, the CO_2 is compressed to 2,215 psia by a six-stage centrifugal compressor with inter-stage cooling to 100°F. The discharge pressures of the stages were balanced to give reasonable power distribution and discharge temperatures across the various stages. During compression in the multiple-stage, intercooled compressor, the CO_2 stream is dehydrated to a dew point of -40°F with triethylene glycol. The virtually moisture-free supercritical CO_2 stream is delivered to the plant battery limit as sequestration-ready.

There are no heating or cooling steps within the VPSA unit operation, which is typical of VPSA processes. Since this is still a conceptual design, however, there remain other types of processes to consider depending upon future pilot study and other experimental results. In a VPSA process, the heat of adsorption is released and is stored in the bed by a sensible temperature rise. The heat is removed during the desorption step as the adsorbent bed cools. Approximately 90 percent of the CO_2 in the feed gas is adsorbed onto the MOF adsorbent, and the rest leaves the VPSA section to the stack. Further, other than spent adsorbent, there is no waste generated in this process. The MOF-based VPSA process should generate little waste because the adsorbent itself is not hazardous waste, nor is it expected that the MOF will generate any hazardous waste products via degradation.

TABLE 2: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	0.8	1.0
Bulk Density	kg/m^3		
Average Particle Diameter	mm	0.5 – 2.0	1.0
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3	0.5	0.7
Solid Heat Capacity @ STP	kJ/kg-K	≈ 1	< 1
Crush Strength	kg_f		
Manufacturing Cost for Sorbent	$/kg		

TABLE 2: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Adsorption			
Pressure	bar	0.1	0.1 – 0.15
Temperature	°C	25 – 45	25 – 45
Equilibrium Loading	g mol CO_2/kg-sorbent		
Heat of Adsorption	kJ/mol CO_2	45	45 – 55
Desorption			
Pressure	bar	0.01 – 0.05	0.05
Temperature	°C	Ambient	Ambient
Equilibrium Loading	g mol CO_2/kg-sorbent		
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	—-	—-
Flue Gas Flowrate	kg/hr	—-	—-
CO_2 Recovery, Purity, and Pressure	% / % / bar	90–98	
Adsorber Pressure Drop	bar	—-	—-
Estimated Absorber/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 coal (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.

technology advantages

- High CO_2 adsorption capacity.
- Good adsorption/desorption rates.
- Good hydrothermal stability.
- Environmentally friendly.

R&D challenges

- Effects of water, sulfur oxides (SO_x), and nitrogen oxides (NO_x) on the MOF material.
- Need for large vacuum pumps to compress the CO_2 from the outlet of the VPSA.

results to date/accomplishments

- More than 50 MOF materials were evaluated; two were selected for further development and testing. The CO_2 capacity for these MOFs was determined in the presence of water and other contaminants and measured at several temperatures. Hydrothermal stability testing at accelerated conditions was also carried out for these MOFs.
- Mg/DOBDC outperformed all MOF and zeolite materials evaluated, with about 25 wt% CO_2 captured by this MOF at flue gas conditions (≈0.13 atm CO_2 pressure, 311°K).
- UOP's techno-economic analysis indicated that an MOF-based VPSA process has potential to be a less-expensive option than using amines to capture CO_2. Their analysis indicated a 65 percent increase in cost of electricity (COE) compared to a reference power plant without CO_2 capture.

next steps

This project ended on June 30, 2010. The final report was issued in October 2010.

available reports/technical papers/presentations

Carbon Dioxide Removal from Flue Gas Using Microporous Metal Organic Frameworks [PDF-2.7MB] (Oct 2010) Final Technical Report.

Benin, A., et al., "CO_2 Removal from Flue Gas Using Microporous Metal Organic Frameworks," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/43092%20UOP%20MOF%20sorbent%20%28Benin%29%20public%20version%20mar09.pdf*

DEVELOPMENT OF A DRY SORBENT-BASED POST-COMBUSTION CO_2 CAPTURE TECHNOLOGY FOR RETROFIT IN EXISTING POWER PLANTS

primary project goals

Research Triangle Institute (RTI) developed and tested a carbon dioxide (CO_2) capture process that utilizes a dry sodium carbonate (Na_2CO_3) sorbent that is based on the reaction of Na_2CO_3 with CO_2 and water vapor present in the flue gas from a coal-fired power plant.

technical goals

- Determine the optimal process configuration for the dry carbonate process.
- Construct and demonstrate a bench-scale CO_2 capture process using Na_2CO_3.
- Construct and demonstrate a pilot-scale, dry carbonate process that captures 0.9 tonnes of CO_2/day (1 ton of CO_2/day).
- Demonstrate the long-term chemical and mechanical stability of the sorbent.
- Update the economic analyses of the CO_2 sorbent capture process.
- Develop a commercialization plan for instituting the CO_2 capture process.

technical content

In an effort to develop a pre-pilot scale facility, RTI has been collecting data needed for designing, constructing, and operating the dry sorbent-based capture unit. RTI has designed and constructed a bench-scale heat transfer evaluation unit, shown in Figure 1, which is used to experimentally determine realistic gas and solid circulation rates and overall heat transfer coefficients for new reactor designs. A schematic diagram of the process is shown in Figure 1.

technology maturity:

Bench-Scale/Small Pilot-Scale

project focus:

A Dry Sorbent-Based Post Combustion CO_2 Capture

participant:

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project number:

FC26-07NT43089

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performance period:

3/7/07 – 12/31/09

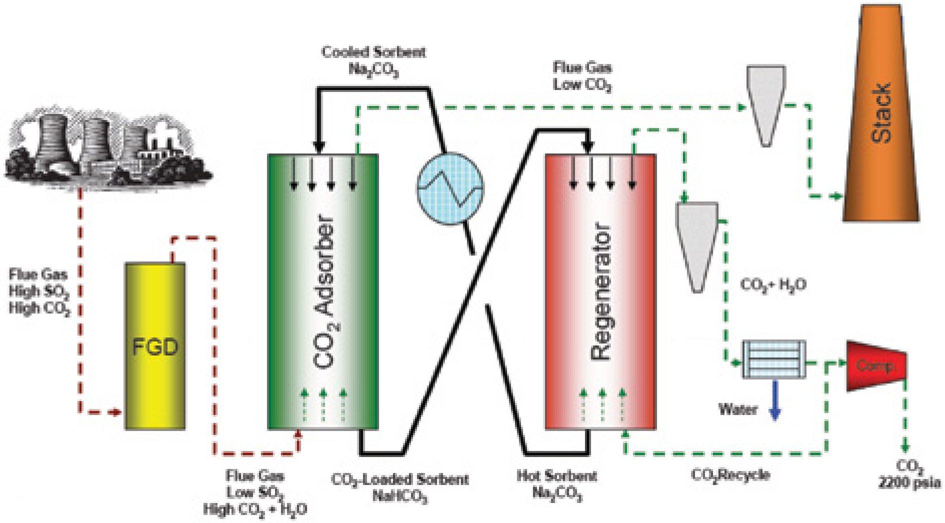

Figure 1: Schematic Diagram of CO_2 Capture Process

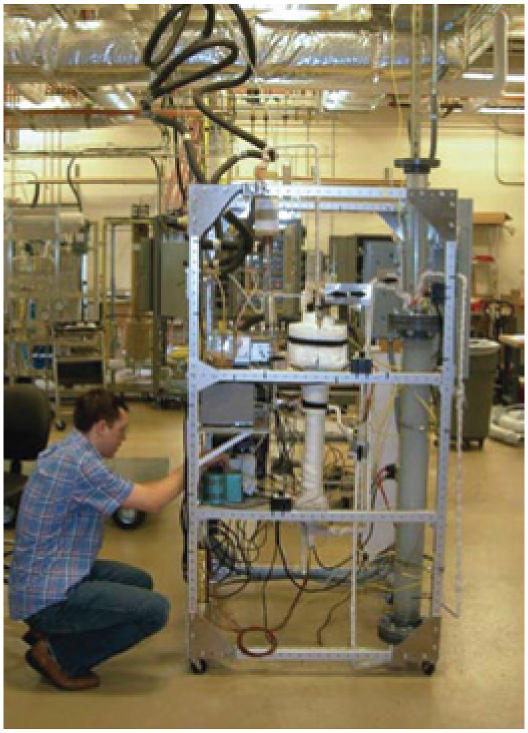

Figure 2: Lab-Scale CO_2 Absorption Reactor Skid

Pilot-scale testing will be performed on a slipstream from the air-blown gasifier at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama. SRI has designed a pilot-scale, continuous, integrated test system. The equipment is being procured and will be assembled. The pilot-scale test will emphasize stability of integrated operation. The effects of trace contaminants will be observed, as the pilot tests will use a gas stream from an operating gasifier that has undergone minimum cleanup and will contain trace contaminants.

The CO_2 capture unit is located after the wet flue gas desulfurization (FGD) unit. The Na_2CO_3 sorbent reacts with the CO_2 and water (H_2O) located in the gas stream through a cyclic temperature swing cycle by adsorbing the CO_2 and H_2O at 60°C and releasing the constituents at 120°C during the sorbent regenerating stage. Considering the high exothermic heat of absorption (3.08 MJ/kg), significant cooling fluid is required to maintain the adsorption temperature at the desired value.

Utilizing the information gathered from the bench-scale unit, as well as the lab-scale unit shown in Figure 2, RTI has developed engineered sorbents that exhibit improved CO_2 capture rate and physical characteristics (e.g., attrition resistance, fluidizibility, and density) over the supported (multi-layer) sorbents. These improvements will have a significant impact on a commercial, dry carbonate system by lowering the solids handling requirements and minimizing the heating and cooling duties in a commercial process. A long-term, multi-cycle testing of these sorbents to demonstrate chemical stability has been undertaken. Initial results indicate that the engineered sorbents are highly stable in the presence of contaminates such as hydrochloric acid (HCl), nitrous oxides (NO_x), H_2O, and oxygen (O_2). While sulfur dioxide (SO_2) forms irreversible chemical bonds to the sorbent, it is considered a minor issue, considering the rate of attrition is generally greater than the rate of deactivation due to SO_2.

TABLE 1: PHYSICAL PROPERTIES OF SODIUM CARBONATE SORBENTS

Property	Value
Bulk Density	1.0 – 1.1 g/mL
Average Particulate Size	65 – 75 µm
Surface Area	100 – 120 m^2/g
Physical Strength (A)	0.77
Na_2CO_3 Strength	10 – 40 wt%
Heat of Absorption	3.08 MJ/kg
Regeneration Energy	3.08 MJ/kg

The heat transfer experiments will be conducted in a fluidized bed contactor, as shown in Figure 2. The conveyors (one heated, the other cooled) will be used to move the Na_2CO_3 through the fluidized bed to introduce a simulated flue gas (from coal or natural gas) to the sorbent. The instrument is used to analyze the adsorption effectiveness and the attrition rate of the Na_2CO_3 sorbent. Data from the fluidized bed will be used to validate and develop the computational fluid dynamic (CFD) model called MFIX.

Some physical properties of the sorbent are provided in Table 1.

As seen in the aforementioned table, the theoretical maximum CO_2 loading for the sorbent is ≈40 wt%. While RTI has achieved loading as high as 30 wt%, it requires a cycle time much greater than would be practical. Allowing only 30 minutes per cycle phase results in loading capacities of ≈20 to 25 percent.

technology advantages

- Lower capital and operating costs for CO_2 removal.
- Sorbent is inexpensive and easy to acquire (≈$200/ton).
- Sorbent is non-hazardous, non-toxic, and does not produce hazardous waste.

R&D challenges

- Circulation of solids may be problematic.
- The reaction of Na_2CO_3 with H_2O is highly exothermic and requires effective heat transfer.
- Removal of CO_2 requires equimolar amounts of H_2O.
- Irreversible reactions of Na_2CO_3 with SO_2 and HCl during process conditions.
- Raw Na_2CO_3 is not a physically strong material, leading to high attrition rates.
- Raw Na_2CO_3 agglomerates upon contact with condensed H_2O.

results to date/accomplishments

- Constructed a heat transfer evaluation system used to evaluate the hydrodynamics and heat transfer characteristics of the reactor designs.
- Constructed a packed-bed reactor system to demonstrate sorbent stability over many adsorption and regeneration cycles and provide insight into reaction kinetics.
- Validated the operation of a bench-scale, coupled cold-flow system and collected data on gas-solid contactor bed height control, range of operability, sorbent bed densities, bed void volumes, and fluidization characteristics.
- Measured the heat transfer limitations of the existing screw conveyor system and determined that the screw conveyors cannot be used for sorbent regeneration in a 1-ton/day CO_2 capture pre-pilot system.
- Developed updated process simulations for the new dry carbonate process design using ASPEN Plus.

next steps

This project ended on December 31, 2009. The final report was completed in April 2010.

available reports/technical papers/presentations

Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology for Retrofit in Existing Power Plants – Final Report – April 2010.

Nelson, T., et al., "Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology Retrofit in Existing Power Plants," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO$_2$/pdfs/43089%20RTI%20sorbent%20%28Nelson%29%20mar09.pdf*.

The Dry Carbonate Process: Carbon Dioxide Recovery from Power Plant Flue Gas, 7th Annual Conference on Carbon Capture and Sequestration in Pittsburgh, Pennsylvania, May 2008.

The Dry Carbonate Sorbent Technology for CO_2 Removal from Flue Gas of Existing Coal-Fired Power Plants – Power Plant Air Pollutant Control "Mega" Symposium in Baltimore, Maryland, August 2008.

Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology for Retrofit in Existing Power Plants Fact Sheet, April 2008.

Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents, Topical Report, November 2004.