

APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS
POST-COMBUSTION SORBENTS

CO₂ CAPTURE FROM FLUE GAS USING SOLID MOLECULAR BASKET SORBENTS

Primary Project Goals

Pennsylvania State University (PSU) is developing a new generation of solid and regenerable polymeric molecular basket sorbent (MBS) for more cost-efficient capture and separation of carbon dioxide (CO₂) from flue gas of coal-fired power plants.

Technical Goals

- A regenerable working sorption capacity higher than 70 mg-CO₂/g-S.
- A significantly lower cost for the sorbent preparation compared to the early generations of MBS.

Technical Content

The current state-of-the-art post-combustion capture technology—aqueous amine scrubbing—is a highly energy-intensive process estimated to increase the cost of electricity (COE) by about 75–85%, according to U.S. Department of Energy (DOE) reports. The goal of DOE's Existing Plants, Emissions, and Capture (EPEC) Research and Development (R&D) Program is to achieve 90% CO₂ capture with an increase in COE less than 35%. Therefore, it is important to develop inexpensive, effective, and robust materials and technologies that can reduce CO₂ emission and are suitable for installation in power plants to maintain the cost-effectiveness of U.S. coal-fired power plants. Recently, a new sorbent concept called MBS has been developed for CO₂ capture from flue gas. The idea of MBS development, as shown in Figure 1, is to load CO₂-philic polymers on to high surface area mesoporous materials. This process increases the number of approachable sites on/in the sorbent and enhances the sorption/desorption rate by increasing the gas-sorbent contacting interface and by improving the mass transfer in the sorption/desorption process. The expected result of this project will be a concentrated CO₂ stream that can be directed to CO₂ sequestration or CO₂ utilization.

The researchers are using the following approaches to accomplish the technical project goals:

- Using cheaper nanoporous materials to replace SBA-15 and MCM-41 to reduce the cost for the sorbent.
 - Silica-gel, fumed silica, carbon.
- Using cross-linkers to improve the thermal stability and regenerability of MBS via chemical bonding.

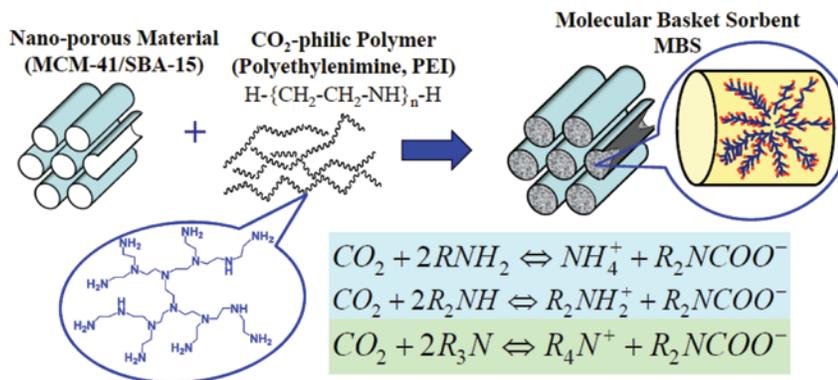


Figure 1: Molecular Basket Sorbent (MBS) Concept

Technology Maturity:
Bench-scale

Project Focus:
Solid Molecular Baskets

Participant:
Penn State University

Project Number:
FE0000458

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Partners:
None

Performance Period:
9/1/09 – 8/31/11

Table 1: Process Parameters for Sorbents

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Solid amine	Solid amine
	Heat of adsorption (kJ/mole CO ₂)	~69	—
	CO ₂ loading/working capacity, wt%	140/80	120/70
	Surface area, m ² /g	20–80	~60
	Particle density, g/cm ³	N/A	—
	Packing density, g/cm ³	0.4–0.8	~0.8
	Particle size (mm)	~0.05	~0.05
	Heat capacity (kJ/K/kg)	~1.6	—
	Thermal stability, °C	~100	120
	Hydrothermal stability, °C	<90	120
Process Configuration	Attrition rate (fluidized bed), %/year	N/A	N/A
	Cycle time (fixed bed), minutes	60	40
	Pressure drop (fixed bed), psia	<10	<5
Operating conditions	Adsorption temperature, °C	75	75
	Adsorption pressure, atm	1 (CO ₂ , 0.15%)	1
	CO ₂ capture efficiency, %	>90	>95
	Regeneration method	PSA+TSA	PSA/TSA
	Regeneration temperature, °C	100	100
	Regeneration pressure, atm	0.01	—
Heat Integration	Required regeneration steam temperature, °C	N/A	—
Miscellaneous	Sorbent make-up rate, kg/kg CO ₂	N/A	—
Product Quality	CO ₂ purity, %	~90%	>95%
	N ₂ concentration, %	N/A	—
	Other contaminants, %	N/A	—
Process Performance	Electricity requirement, kJ/kg CO ₂	N/A	—
	Heat requirement, kJ/kg CO ₂	N/A	—
	Total energy (electricity equivalent), kJ/kg CO ₂	N/A	—

Technology Advantages

- High capacity: 3.2 mol-CO₂/kg (or 14%) at CO₂ conc. of 15%.
- High selectivity: CO₂/N₂>1,000.
- No (or less of a) corrosion problem.
- Suitable operation conditions.
- High sorption/desorption rate.
- Positive effect of moisture.
- Regenerable at mild conditions.

R&D Challenges

- High cost of nanoporous materials (SBA-15 and MCM-41).
- Low packing density.
- Thermal and regenerable stability needs to be improved.

Results To Date/Accomplishments

- Four types of nanoporous supports, including silica-gel, Cab-O-Sil, carbon black, and mesoporous foam silica either purchased or synthesized in the lab, have been tested for polyethylenimine loading.
- More than 50 sorbent samples have been prepared and examined for CO₂ capture using thermogravimetric analysis, fixed-bed flow system, and temperature-programmed desorption methods.
- Several sorbents have showed comparable sorption capacity to SBA-15-based molecular basket sorbent, reaching about 140 mg-CO₂/g-sorbent, while the cost for the sorbent is much lower, being ~\$40/kg. It exceeds the project goals of higher than 70 mg-CO₂/g-sorbent with less than \$240/kg cost.
- A new approach, polymer cross-linking, has been proposed and tested to further improve the thermal and regenerable stability of molecular basket sorbents. More than 15 samples have been tested with thermal degradation at heating over 100 °C, CO₂ sorption at 75 °C, and desorption at 100 °C cycling.
- Primary computational calculations show that the addition of cross-linker can promote the stability of the cross-linked polymer and improve the sorption strength between CO₂ and amine sites; thus, both the thermal stability and regenerability may be enhanced.

Next Steps

- More experimental and computational work will be conducted to identify a proper way to prepare and obtain a highly thermal stable molecular basket sorbent, and it will be applied to the low-cost sorbents developed in this project.
- The best regeneration conditions and method (TAS and/or PSA) will be determined.
- Based on the developed MBS, scale-up of CO₂ sorption process using MBS will be carried out (about 200 ml sorber in the lab).
- Based on the selected materials and sorption performance, a primary analysis on the techno-economy of MBS technology will be conducted.

Available Reports/Technical Papers/Presentations

Peer-Reviewed Journal Papers:

DX Wang, C Sentorun-Shalaby, XL Ma, CS Song, High-capacity and low-cost carbon-based molecular basket sorbent for CO₂ capture from flue gas. *Energy Fuels* **2011**, 25, 456–458.

Presentations:

XX Wang, SQ Zhao, XL Ma, CS Song, CO₂ capture from gas streams with low CO₂ concentrations using solid molecular basket sorbent. 241st ACS National Meeting, Anaheim, CA, USA, March 27–31, **2011**.

XX Wang, SQ Zhao, XL Ma, CS Song, Carbon dioxide sorption over molecular basket sorbents: a detailed TPD study. 22th North American Catalysis Society meeting, Detroit, MI, June 2–10, **2011**.

XL Ma, ZH Zhang, J Zhu, XX Wang, CS Song, CO₂ capture from the atmosphere using nano-porous-material-supported polyethylenimine sorbents. 241st ACS National Meeting, Anaheim, CA, USA, March 27–31, **2011**.

XL Ma, XX Wang, CS Song, Advances and challenges in development of amine-functionalized and amine-immobilized solid sorbents for CO₂ capture. The International Chemical Congress of Pacific Basin Societies, Honolulu, HI, USA, December 15–20, **2010**.

XX Wang, DX Wang, EP Fillerup, E Peduzzi, ZH Zhang, XL Ma and Chunshan Song. CO₂ Capture from Flue Gas Using Solid Molecular Basket Sorbents. Oral Presentation. 2010 NETL CO₂ Capture Technology Meeting. Pittsburgh, September 13–17, **2010**. http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Xiaoxing_Wang-FE0000458.pdf

EP Fillerup, XX Wang, XL Ma, and CS Song. Utilization of Polymer Cross-linkers to Improve the Thermal Stability of Molecular-Basket Sorbents. Oral Presentation. American Chemistry Society 240th National Meeting, Boston, MA, August 22–26, **2010**.

XL Ma, XX Wang, CS Song, “Molecular Basket” Sorbents for CO₂ Capture from Flue Gas. 26th International Pittsburgh Coal Conference, Pittsburgh, PA, September 21–24, **2009**.

Manuscript in Preparation:

XX Wang, SQ Zhao, XL Ma, ZH Zhang, DX Wang, CS Song, SBA-15-supported polyethylenimine sorbents for CO₂ capture from flue gas. **2011**, in preparation.

XX Wang, SQ Zhao, XL Ma, CS Song, CO₂ sorption over polyethylenimine loaded SBA-15 sorbents: a TPD study. **2011**, in preparation.

XX Wang, XL Ma, V Schwartz, JC Clark, SH Overbury, SQ Zhao, XC Xu, CS Song, Superior solid sorbent for CO₂ capture and separation from gas streams with low CO₂ concentration at ambient conditions. **2011**, in preparation.

LOW-COST SORBENT FOR CAPTURING CO₂ 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 (CO₂) 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 CO₂ 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 (H₂O) on the working capacity of the optimum sorbent.
- Construct and demonstrate a novel CO₂ removal system for real flue gas stream.

Technical Content

TDA's CO₂ capture system uses a dry alkalized alumina sorbent. This regenerable sorbent acts as a physical adsorbent for CO₂. The CO₂ 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 (SO₂) were performed for more than 2,000 cycles. Testing with NO_x has been conducted for more than 180 cycles. No loss of CO₂ loading capacity was observed during these tests. For this process, additional flue gas pretreatment upstream of the CO₂ 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 CO₂ compression and purification unit. The process is designed for the sorbent to pull the dilute CO₂ 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.

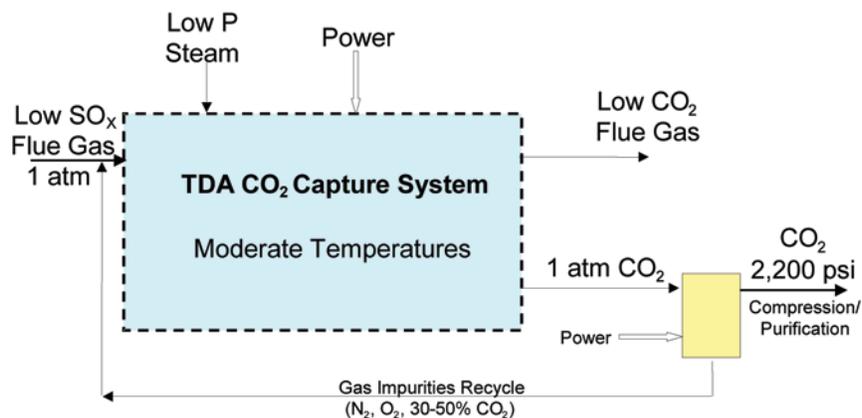


Figure 1: Schematic of TDA's CO₂ Emission Control System

Technology Maturity:

Bench-scale using simulated flue gas

Project Focus:

Alkalized Alumina

Participant:

TDA Research, Inc.

Project Number:

NT0005497

NETL Project Manager:

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Principal Investigator:

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Partners:

Babcock & Wilcox

Louisiana State University

Western Research Institute

Performance Period:

11/1/08 – 10/31/11

Table 1: Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Adsorbent	Adsorbent
	Heat of adsorption (kJ/mole CO ₂)	12–25	10–20
	CO ₂ loading/working capacity, wt%	0.7	1–3
	Surface area, m ² /g	100	100–150
	Particle density, cm ³ /g	0.63	0.6
	Packing density, cm ³ /g	1.05	1
	Particle size (mm)	1.6	9.5
	Heat capacity (kJ/K/kg)	0.8	0.8
	Thermal stability, °C	650	>250
	Hydrothermal stability, °C	110 < T < 650	110 < T < 650
Process Configuration	Attrition rate (fluidized bed), %/year	TBD	TBD
	Cycle time (fixed bed), minutes	5–15	5–15
	Pressure drop (fixed bed), psia	2–5	0.5
Operating Conditions	Adsorption temperature, °C	110 < T < 200	110 < T < 250
	Adsorption pressure, atm	1	1.05
	CO ₂ capture efficiency, %	90	90
	Regeneration method	Steam	Steam
	Regeneration temperature, °C	110 < T < 200	110 < T < 200
	Regeneration pressure, atm	1	1.05
Heat Integration	Required regeneration steam temperature, °C	TBD	TBD
Miscellaneous	Sorbent make-up rate, kg/kg CO ₂	TBD	Annual
Product Quality	CO ₂ purity, %	TBD	99.99998
	N ₂ concentration, %	TBD	1.8e–8
	Other contaminants, %	TBD	1.98e–5
Process Performances	Electricity requirement, kJ/kg CO ₂	N/A	—
	Heat requirement, kJ/kg CO ₂	N/A	—
	Total energy (electricity equivalent), kJ/kg CO ₂	N/A	—

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

- 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 CO₂ loading capacity observed after 180 cycles with 820 parts per million (ppm) of NO_x.
- Created a CO₂ capture process design and ASPEN model that includes steam source, CO₂ compression, and heat sources, and calculates efficiency.
- Designed bench-scale testing apparatus to show continuous absorption of CO₂ in simulated flue gas feed.
- Construction of CO₂ capture bench-scale unit is nearly complete.

Next Steps

- Demonstrate sorbent in new apparatus with continuous absorption and regeneration functions.
- Update system analysis with experimental data and determine process economics.
- Demonstrate system on coal-derived flue gas at Western Research Institute.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/lowcostsorbent.html>

Low-Cost Sorbent for Capturing CO₂ Emissions Generated by Existing Coal-Fired Power Plants; Presentation at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, September 13–17, 2010. http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Jeannine_Elliott-NT0005497.pdf

Low-cost Sorbent for Capturing CO₂ Emissions Generated by Existing Coal-fired Power Plants; Project Fact Sheet, January 2011. <http://www.netl.doe.gov/publications/factsheets/project/NT0005497.pdf>

Low Cost Solid Sorbent for CO₂ Capture on Existing Coal-Fired Power Plants; Presentation at the 26th Annual International Pittsburgh Coal Conference, September 20–23, 2009. http://www.tda.com/Library/docs/PCC_Sept_2009_v3.pdf

Low-Cost Sorbent for Capturing CO₂ Emissions Generated by Existing Coal-Fired Power Plants – Project Overview; Presentation at the Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 24–26, 2009. http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5497_TDA_sorbent_%28Elliott%29_mar09.pdf

DEVELOPMENT OF NOVEL CARBON SORBENTS FOR CO₂ CAPTURE

Primary Project Goals

SRI is developing an innovative, low-cost, low-energy, carbon dioxide (CO₂)-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, fixed-bed reactor.
- Perform parametric experiments to determine the optimum operating conditions for the system.
- Evaluate the technical and economic viability of the technology.

Technical Content

The novel sorbent developed for the project is composed of carbon pellets, as shown in Figure 1. The sorbent was manufactured by ATMI, Inc., and is designated as ACS-1. 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 being operated for determining long-term durability of the sorbents.

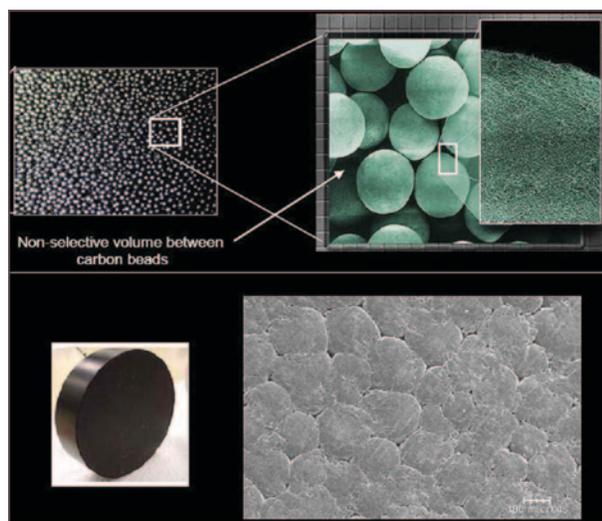


Figure 1: Graphic Displays of the Novel Carbon Pellets Sorbent

Technology Maturity:

Bench-scale using simulated flue gas

Project Focus:

Carbon-Based Sorbents

Participant:

SRI International

Project Number:

NT0005578
FE0000896

NETL Project Manager:

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Partners:

ATMI, Inc.

Performance Period:

10/1/08 – 9/30/11

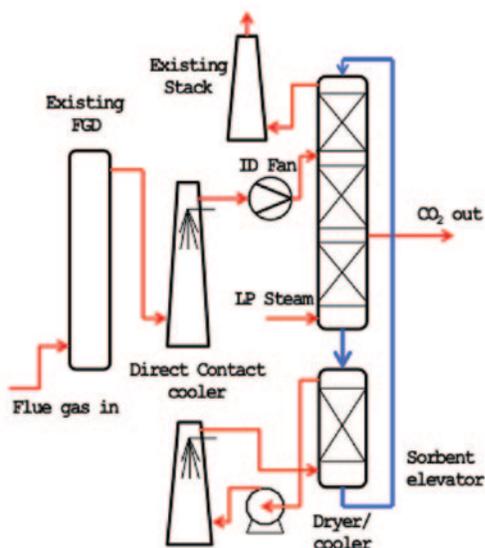


Figure 2: The Proposed Sorbent System

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 (0.1–0.2 kg of CO₂ per kg of sorbent). As the gas stream passes over the lean sorbent, CO₂ 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 CO₂. The CO₂ is siphoned off to a compressor where it can be prepared for sequestration. The sorbent is then dried and cooled and sent back into the separation column for re-use and the cycle begins again.

The primary waste stream will be carbon fines generated by attrition of the carbon sorbent granules.

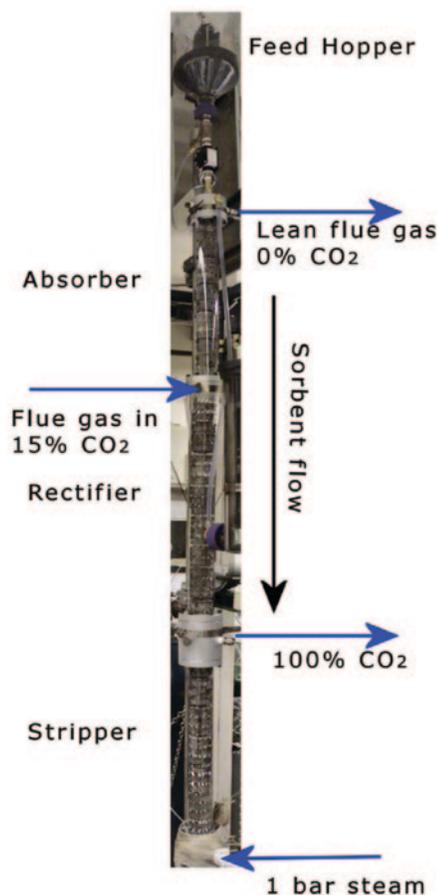


Figure 3: Photograph of 6-Inch ID x 24-Foot Tall Integrated System Column

Based on the results of parametric experiments using a two-inch bench-scale absorber and desorber, SRI designed and assembled the larger bench-scale, six-inch diameter integrated absorber-desorber system, shown in Figure 3. The system is being used to perform tests with varying gas and solid flow rates to determine the interaction between these variables. The amount of steam needed to strip the CO₂ and the water balance in the system will be determined. Later, the system will be setup for long-term tests.

Table 1: Process Parameters for Solid Carbon Sorbent

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Carbon	Carbon
	Heat of adsorption (kJ/mole CO ₂)	28	28
	CO ₂ loading/working capacity, wt%	5	8
	Surface area, m ² /g	1,600	1,600
	Particle density, cm ³ /g	1.1	1.1
	Packing density, cm ³ /g	0.7	0.7
	Particle size (mm)	0.2	0.2
	Heat capacity (kJ/K/kg)	1.0	1.0
	Thermal stability, °C	>400	>100
	Hydrothermal stability, °C	>100	>100
Process Configuration	Attrition rate (fluidized bed), %/year	<0.01 ¹	<0.05 ¹
	Cycle time (fixed bed), minutes	0.25 ²	N/A
	Pressure drop (fixed bed), psia	0.04 ³	N/A
Operating Conditions	Adsorption temperature, °C	15–25	25
	Adsorption pressure, atm	1	1
	CO ₂ capture efficiency, %	>95	>90
	Regeneration method	Direct steam	Indirect or direct
	Regeneration temperature, °C	80–100	100
	Regeneration pressure, atm	1	1
Heat Integration	Required regeneration steam temperature, °C	100	100
Miscellaneous	Sorbent make-up rate, kg/kg CO ₂	Not known	N/A
Product Quality	CO ₂ purity, %	>95	>95
	N ₂ concentration, %	<2	<10
	Other contaminants, %	N/A	SO ₂ , NO _x
Process Performance	Electricity requirement, kJ/kg CO ₂	N/A	450 ⁴
	Heat requirement, kJ/kg CO ₂	2,000	1,200 ⁵
	Total energy (electricity equivalent), kJ/kg CO ₂	N/A	720 ⁶

Notes:

1. Measured by ASTM D5757 accelerated attrition testing; long-term attrition rate has not been established.
2. 0.25 minutes estimated in a moving bed.
3. At a space velocity corresponding to 95% capture of air-15% CO₂ mixture.
4. Includes electricity for compression of released CO₂ to 150 atm.
5. No heat recovery savings is accounted.
6. Based on simulation of pulverized coal (PC)-fired boiler from coal to electricity enabling CO₂ capture and compression.

Technology Advantages

- The sorbent has a low cost and a stable operating range of 20–100 °C.
- The sorbent has a high capacity of CO₂ loading with 0.1–0.2 kg of CO₂ per kg of sorbent.
- The sorbent features a low heat of adsorption reaction of 25–28 kJ/mole of CO₂ and releases CO₂ at atmospheric pressure at a low temperature of 80–100 °C.

R&D Challenges

- Other elements of the flue gas, such as moisture, sulfur oxides (SO_x), and nitrogen oxides (NO_x) may compete with CO₂ in being adsorbed by the sorbent, reducing the amount of CO₂ that gets adsorbed as the gas passes through the reactor.
- A low temperature needs to be maintained for optimal adsorption conditions. Excess heat may have to be removed from the adsorption reactor in addition to the flue gas being cooled prior to treatment by the sorbent.
- The heat exchange between the cold, loaded sorbent and regenerated, hot sorbent will have to be kept to a minimum to maintain optimal temperatures for the adsorption process.

Results To Date/Accomplishments

- Determined the CO₂ adsorption and desorption characteristics and the heat of adsorption for the carbon sorbent.
- Determined the CO₂ loading on the sorbent as a function of CO₂ partial pressure and temperature.
- The desorption characteristics were tested in a temperature range of 40–100 °C using a TGA.
- Evaluated several physical, chemical, and mechanical properties of the sorbent in the context of the CO₂ capture system using a bench-scale, fixed-bed reactor.
- Demonstrated >95% CO₂ capture in a moving bed from air containing 15% CO₂ at ambient temperature.
- Demonstrated regeneration using direct contact steam producing relatively pure CO₂.
- Simulated CO₂ capture using novel carbon sorbent in a PC-fired boiler from coal to electricity and compressed CO₂.
- Determined several physical and chemical properties of the advanced carbon sorbent in the context of flue gas CO₂ capture.
- Demonstrated a unique sorbent for CO₂ capture.
 - Achieved ~98% CO₂ capture from air-CO₂ gas mixture.
 - Achieved >97% pure CO₂ during regeneration.
 - Capable of rapid adsorption and regeneration.
 - Low heat requirements for regeneration.
 - Fluid-like flow properties.
 - High attrition resistance.
- Developed an unique reactor system.
 - Integrated absorber-desorber geometry.
 - Minimize solids handling.
 - Minimize heat exchanger requirements.

Next Steps

- Conduct parametric testing on the absorber and regenerator, including gas velocity, temperature, CO₂ inlet level, sorbent pellet size and geometry, heating method, and the presence of SO_x or NO_x.
- Design and construct a bench-scale system for testing.
- Conduct 100 cycle tests on select sorbents.
- Conduct a long-term (1,000 cycle) test on the superior sorbent to determine durability.
- 1,000-cycle test under integrated adsorption-desorption conditions.
- Evaluation of the technical merits and increase in cost of electricity for CO₂ capture using the novel carbon sorbents.
- Field testing of the process using a flue gas from an operating PC-fired boiler.

Available Reports/Technical Papers/Presentations

Development of Novel Carbon Sorbents for CO₂ Capture; presented at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, September 13–17, 2010. [http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Gopala Krishnan-NT0005578.pdf](http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Gopala%20Krishnan-NT0005578.pdf)

Development of Novel Carbon Sorbents for CO₂ Capture; presented at the 9th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 10–13, 2010. [http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Gopala Krishnan-NT0005578.pdf](http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Gopala%20Krishnan-NT0005578.pdf)

Development of Novel Carbon Sorbents for Carbon Dioxide Capture – Continuation application report submitted to U.S. Department of Energy, August 2009.

Development of Novel Carbon Sorbents for CO₂ Capture – Project Overview; presented at the Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 24–26, 2009. [http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5578 SRI carbon sorbent %28Hornbostel%29 mar09.pdf](http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5578%20SRI%20carbon%20sorbent%20Hornbostel%29%20mar09.pdf)

EVALUATION OF SOLID SORBENTS AS A RETROFIT TECHNOLOGY FOR CO₂ 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 (CO₂) 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 CO₂ capture technology through 1-MW slipstream pilot testing and process modeling.

Technical Content

ADA-ES is utilizing progress it made on sorbent-based CO₂ capture as demonstrated in a viability assessment project. The viability assessment included laboratory-scale and 1-kW pilot-scale sorbent screening and a commercial-scale equipment study in a separate Department of Energy (DOE) project DE-NT0005649. The specific work completed under the viability assessment included:

Evaluated more than 100 potential CO₂ sorbents, which were procured from various CO₂ solid sorbent developers worldwide. Sorbents were evaluated on the basis of cyclic stability, CO₂ capacity, working CO₂ 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 CO₂ 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 CO₂ sorbents.

Table 1: Key Properties Used to Evaluate CO₂ Sorbents

Physical Property	Current Range	Goal
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)	Dependant on contractor design
Mechanical strength	Not reported	Dependant on contractor design
Attrition fines: form, processing, and fate	Not reported	To be determined

The lab-scale tests consisted of <3 grams of the adsorbents exposed to simulated flue gas and then regenerated by a temperature swing with a humid nitrogen (N₂) sweep gas. For the adsorption step, the simulated flue gas was 55 °C (130 °F) with oxygen (O₂) and CO₂ concentrations of 4% and 12%, respectively. The moisture level was varied (0%, 50%, or 90% relative humidity). The regeneration temperature was varied between 65 and 250 °C (150 and 480 °F).

Technology Maturity:

Pilot-scale using a 1-MW slip stream of actual flue gas

Project Focus:

Evaluation of Solid Sorbents

Participant:

ADA-ES, Inc.

Project Number:

FE0004343
NT0005649

NETL Project Manager:

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Principal Investigator:

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Partners:

EPRI
Southern Company
Stantec Consulting, Ltd.

Performance Period:

9/30/08 – 12/31/14

A 1-kW pilot was constructed to more thoroughly investigate the most positively rated adsorbents tested at the laboratory scale. At the first field test site, more than 90% CO₂ removal was achieved repeatedly in batch mode with one supported amine sorbent. Testing is underway at the second field site. The 1-kW pilot tests are parametric in nature to characterize sorbent performance under a range of realistic conditions. Figure 1 is a schematic of the 1-kW pilot, which consists of a transport reactor for adsorption and a fluidized bed for regeneration. A photo of the 1-kW pilot test equipment is shown in Figure 2.

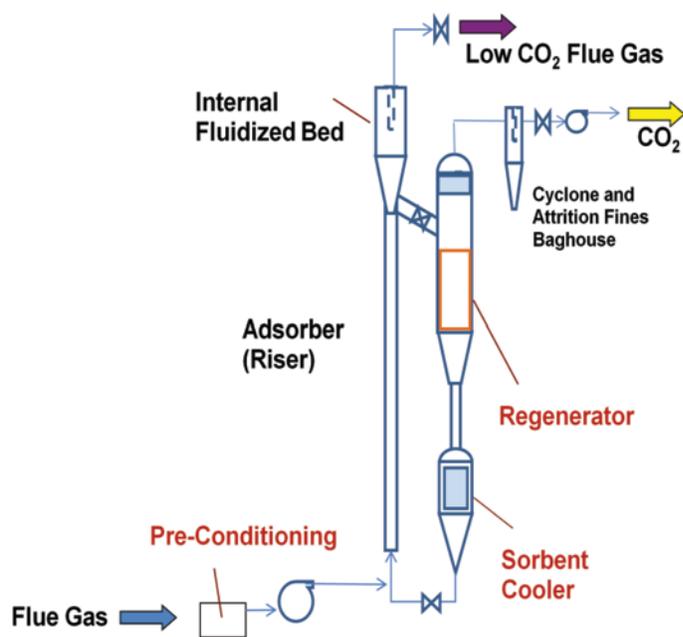


Figure 1: Diagram of Circulating Transport Reactor



Figure 2: 1-kW Pilot

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 CO₂ 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 to be the most reliable, cost-effective, and versatile options available. This conceptual design was not intended to be a final commercial-scale design, but rather serve as an example of one option that could be used to calculate high level cost estimates and identify the technology cost drivers. A schematic of the final technology selection integrated into a power plant is shown in Figure 3.

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

Table 2: Process Parameters for Solid Sorbent

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Supported amine, activated carbon	N/A
	Heat of reaction (kJ/mole CO ₂)	~ -60	-60
	CO ₂ loading (55°C, 12% CO ₂) wt%	14	≥15 (stable)
	Working capacity (regenerating in pure CO ₂), wt%	<6	10
	Surface area, m ² /g	20–1,500	TBD
	Particle density, g/cm ³	Pending	TB
	Bulk density, g/cm ³	0.2–0.6	0.3–1.0
	Particle size (mm)	10–1000	Depends on contactor design
	Heat capacity (kJ/kg•K)	1.4	0.8–1.3
	Thermal stability, °C	100	150
	Hydrothermal stability, °C, relative humidity in %	120, 5	150, 50
Process Configuration	Attrition rate (fluidized bed), %/year	Not measured	≤50
	Cycle time, minutes	Depends on contactor	≤30
	Pressure drop, psia	0.1	0.5 (depends on contactor)
Operating Conditions	Adsorption temperature, °C	55	55
	Adsorption pressure, atm	1	1
	CO ₂ capture efficiency, %	100 (lab-scale)	90
	Regeneration method	Temperature swing with sweep gas	Temperature swing with >95% CO ₂ in regen. gas
	Regeneration temperature, °C	100–120	100–120
Heat Integration	Regeneration pressure, atm	1 (lab-scale total pressure)	1 (>95% CO ₂)
	Required regeneration steam temperature, °C	Not measured	120–150
Miscellaneous	Sorbent make-up rate, kg/kg CO ₂	Will be measured for 1 kW pilot	≤0.0005
Product Quality	CO ₂ purity, %	20% (lab-scale with N ₂ purge)	≥95
	N ₂ concentration, %	Not measured	≤5
	Other contaminants, %	Not measured	≤1
Process Performance	Parasitic Electricity requirement ¹ , kJ/kg CO ₂	Not measured	≤20
	Heat requirement, kJ/kg CO ₂	Not measured	≤1,500
	Total energy (electricity equivalent) ² , kJ/kg CO ₂	Not measured	≤1,800

Notes:

1. Does not include makeup power or CO₂ compression.
2. Includes compression (estimated at 0.1 MW/ton CO₂).

Technology Advantages

- Reduction in the regeneration energy requirements by minimizing heat input (no liquid solvent is involved).
- High sorbent CO₂ capacities have been demonstrated (lab-scale).
- Fundamental sorbent chemistry is well-known (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. Can sorbents be reclaimed?
- Availability of sorbents including the number of suppliers.
- Ability to scale-up sorbent manufacturing without impacting performance.
- 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

- Detailed assessment of the current state of development of solid sorbents.
- Identified technology cost drivers in order to direct future technology development efforts.
- Selected supported amines as the sorbent family for the 1-MW pilot.

Next Steps

- Refine 500-MW concept with modeling and bench-testing.
- Design 1-MW pilot.
- Manufacture sorbents.
- Construct and install 1-MW pilot to validate 500-MW concept.
- Perform 1-MW testing.
- Develop 500-MW preliminary design.
- Conduct techno-economic analysis.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/eval-solid-sorbent.html>

Evaluation of Solid Sorbents as a Retrofit Technology for CO₂ Capture from Coal-Fired Power Plants; Presentation at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, September 13–17, 2010. [http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/thursday/Sharon Sjoström - ADA Environmental Solutions.pdf](http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/thursday/Sharon%20Sjostrom%20-%20ADA%20Environmental%20Solutions.pdf)

Solid Sorbents as a Retrofit CO₂ Capture Technology: Results from Field Testing; Presentation at the Power Plant Air Pollutant Control “MEGA” Symposium, Baltimore, MD, August 30–September 2, 2010. [http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/Sjostrom -ADA CO₂ Solid Sorbents - MEGA 2010.pdf](http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/Sjostrom%20-%20ADA%20CO2%20Solid%20Sorbents%20-%20MEGA%202010.pdf)

Solid Sorbents as a Retrofit CO₂ Capture Technology: Results from Field Testing; Paper #2010-A-131 submitted for presentation at the Power Plant Air Pollutant Control “MEGA” Symposium, Baltimore, MD, August 30–September 2, 2010. [http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/Sjostrom -ADA CO₂ Solid Sorbents - MEGA 2010 Paper.pdf](http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/Sjostrom%20-%20ADA%20CO2%20Solid%20Sorbents%20-%20MEGA%202010%20Paper.pdf)

Cameron Martin, Sjoström, S., Krutka, H., Richard, M., Cameron, D., *Topical Report 1, 2 and 3: Technology Survey, Screening, and Final Selection*, Reporting Period: October 1, 2008–January 31, 2010 for U.S. Department of Energy Contract No. DE-NT0005649, July 2010.

B-222 Sharon Sjostrom, Holly Krutka, Evaluation of solid sorbents as a retrofit technology for CO₂ capture, *Fuel*, Volume 89, Issue 6, Advanced Fossil Energy Utilization, June 2010, Pages 1298–1306. <http://www.sciencedirect.com/science/article/B6V3B-4XVH-HK9-1/2/71d79dcdd8ea282606d7e9c5c8f862cb>

Post-Combustion CO₂ Control Using Solid Sorbents: Results from 1 kW Pilot Tests, Presented at the Ninth Annual Conference on Carbon Capture and Sequestration, May 2010. <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/5649 CCS Conference May 2010.pdf>

Sjostrom, S.; Campbell, T.; Krutka, H.; O’Palko, A. *Solid Sorbents as a Retrofit CO₂ Capture Technology: Results from Pre-Pilot Field Testing*, Air Quality VII Conference, Arlington, VA, October 27, 2009. (Presentation and paper).

Evaluation of Solid Sorbents as a Retrofit Technology for CO₂ Capture from Coal-Fired Power Plants – Project Overview; Presentation at the Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting , Pittsburgh, PA, March 24–26, 2009. <http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5649 ADA-ES sorbents %28Sjostrom%29 mar09.pdf>

Results from Lab and Field Testing of Novel CO₂ Sorbents for Existing Coal-Fired Power Plants - Power Plant Air Pollutant Control “Mega” Symposium in Baltimore, MD - August 2008. <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/5649 ADA-ES sorbent evaluation 2008 MEGA paper.pdf>

Summary of Post-Combustion CO₂ Capture Technologies for Existing Coal-Fired Power Plants, Air and Waste Management Association Annual Conference, paper #808, Portland, OR, June 24–26, 2008.

CO₂ REMOVAL FROM FLUE GAS USING MICROPOROUS METAL ORGANIC FRAMEWORKS

B-223

POST-COMBUSTION SORBENTS

Primary Project Goals

UOP is designing and developing a carbon dioxide (CO₂) 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 CO₂ 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 CO₂, 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.

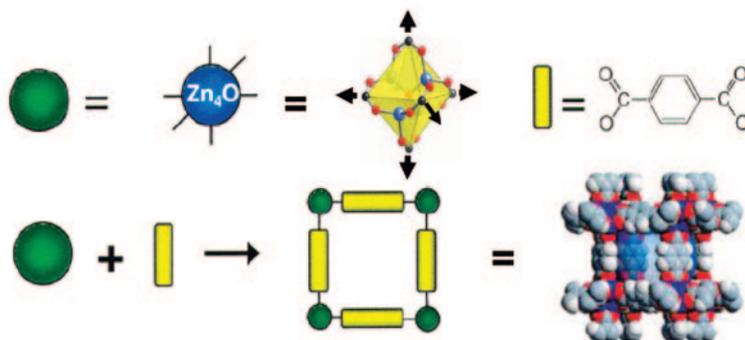


Figure 1: Building Blocks Used to Create Prototypical MOF-5

Technology Maturity:

Laboratory-scale using simulated flue gas

Project Focus:

Metal Organic Frameworks

Participant:

UOP, LLC

Project Number:

NT43092

NETL Project Manager:

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Principal Investigator:

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Partners:

University of Edinburgh
 University of Michigan
 Vanderbilt University
 Northwestern University

Performance Period:

3/12/07 – 6/30/10

More than 50 MOFs for CO₂ adsorption were prepared from literature reports or designed by the experimenters. Table 1 displays the top MOFs for CO₂ capture.

Table 1: Top 10 MOFs for CO₂ Capture

Sample	Loading (mol/kg)	Loading (wt%)	Heat of Adsorption (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	.041	1.8	22.9
Al-MIL-110	0.24	1.1	21.7
Cr-MIL-101	0.18	.08	13.3
Tb-MOF-76	0.18	.08	21.7
Al-MIL-53	0.17	.07	26.0
Zn-IRMOF-1	0.13	.06	13.5

MOF-based adsorbents will be utilized in a vacuum pressure swing adsorption (VPSA) process for removal of CO₂ from flue gas. Figure 2 represents an example of MOF CO₂ adsorption capabilities as a function of pressure (for M/DOBDC, M represents the metal).

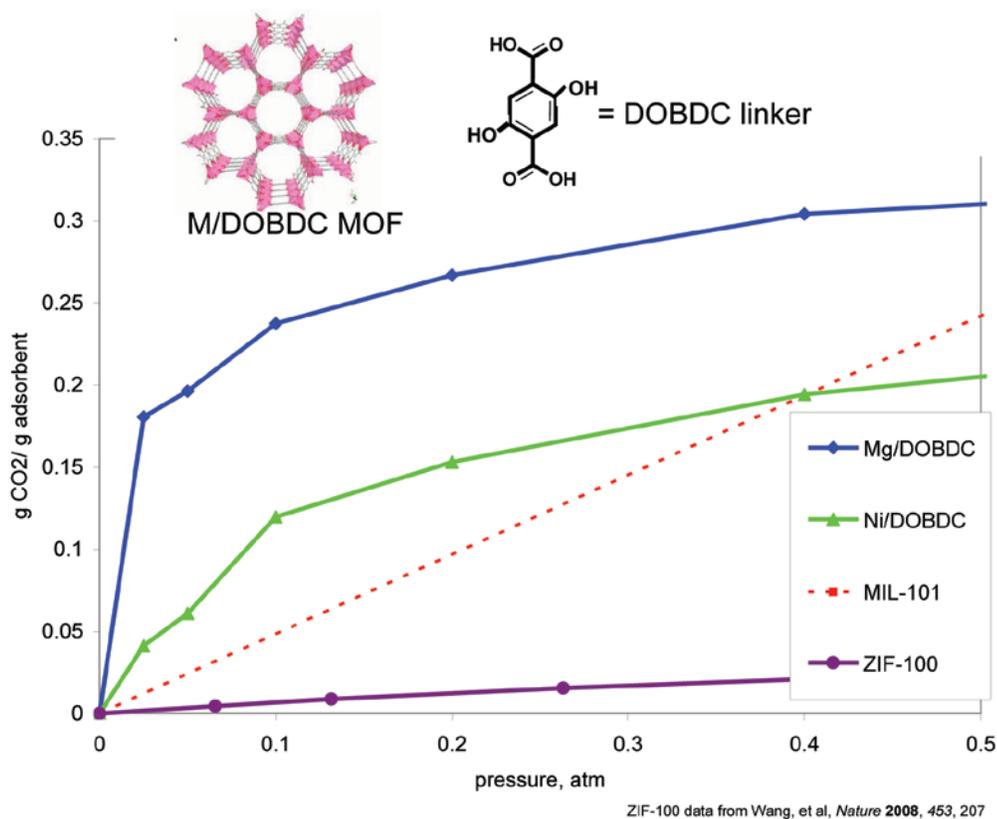


Figure 2: Example of MOF CO₂ Adsorption Capabilities as a Function of Pressure

The MOF-based VPSA CO₂ recovery system will be located after a contaminant removal section and before the final CO₂ compression and drying section. The nitrogen-rich waste stream (raffinate) will be sent to the stack. A process schematic is provided in Figure 3.

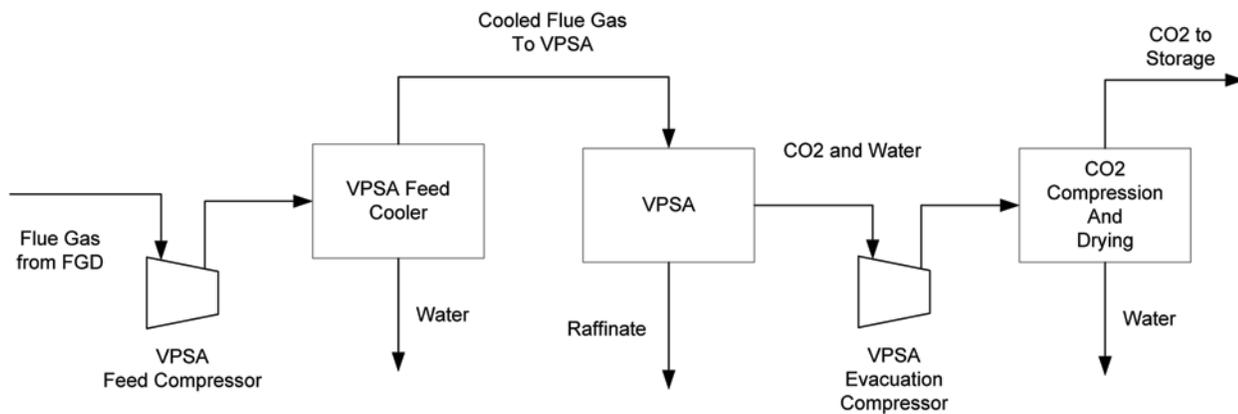


Figure 3: The MOF-Based CO₂ Capture System Process Schematic

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 CO₂ 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% and concurrently knock out at least 75% 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 CO₂ removal. In the VPSA conceptual design at the end of the adsorption step, the vessel first vents nitrogen (N₂) 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 7–8 pounds per square inch absolute (psia). These steps also reduce the N₂ stored in the vessel voids and minimize the amount that would be co-produced with the CO₂. The adsorbent bed would then be evacuated to 0.5 psia to produce the CO₂. For the purposes of the calculations, it was assumed that there was negligible co-adsorption of N₂ on the CO₂ loaded adsorbent and that the N₂ was primarily stored in the voids of the adsorbent vessel. The target CO₂ delta loadings were based on producing a >90% CO₂ 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 N₂ stored in the voids is quite small compared to the compression energy associated with desorbing the CO₂. A purge step was not used in this process since the primary concern is producing a high purity CO₂ stream.

The VPSA Evacuation Compressor will be used to remove CO₂ streams at 95–97% purity from the adsorbent beds. The water that comes along with the CO₂ will be removed during the CO₂ 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 CO₂ to the Gas Compression and Drying section. In the compression section, the CO₂ 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 CO₂ stream is dehydrated to a dew point of -40 °F with triethylene glycol. The virtually moisture-free supercritical CO₂ 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% of the CO₂ 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 very 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: Process Parameters for MOF Sorbents

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	MOF	MOF
	Heat of adsorption (kJ/mole CO ₂)	45	45–55
	CO ₂ loading/working capacity, wt%	15	>20
	Surface area, m ² /g	1,400	2,000
	Particle density, g/cm ³	0.8	1.0
	Packing density, g/cm ³	0.5	0.7
	Particle size (mm)	0.5–2.0	1.0
	Heat capacity (kJ/K/kg)	~1	<1
	Thermal stability, °C	250	400
	Hydrothermal stability, °C	200	200
Process Configuration	Attrition rate (fluidized bed), %/year	N/A	<5
	Cycle time (fixed bed), minutes	4–16	4
	Pressure drop (fixed bed), psia	1–2	<1
Operating Conditions	Adsorption temperature, °C	25–45	25–45
	Adsorption pressure, atm	0.1	0.1–0.15
	CO ₂ capture efficiency, %	95	95
	Regeneration method	VPSA	VPSA
	Regeneration temperature, °C	Ambient	Ambient
	Regeneration pressure, atm	0.01–0.05	0.05
Heat Integration	Required regeneration steam temperature, °C	N/A	N/A
Miscellaneous	Sorbent make-up rate, kg/kg CO ₂	N/A	< 0.1
Product Quality	CO ₂ purity, %	90–98	97–99
	N ₂ concentration, %	Balance	Balance
	Other contaminants, %	<1	<1
Process Performance	Electricity requirement, kJ/kg CO ₂	~1,000	800
	Heat requirement, kJ/kg CO ₂	N/A	N/A
	Total energy (electricity equivalent), kJ/kg CO ₂	~1,000	800

In commercial operation, the MOF-based PSA system will have a lower regeneration duty than the monoethanolamine (MEA) process because of higher relative CO₂ loading on a mass basis and because VPSA is a physical rather than chemical process. As such, no high quality steam from the coal-fired boilers will be required to regenerate the MOF adsorbent. By contrast, the MEA process will require high quality steam in order to get the amine to an elevated temperature to release the CO₂.

Technology Advantages

- High CO₂ adsorption capacity.
- Good adsorption/desorption rates.
- Good hydrothermal stability.
- Environmentally friendly.

R&D Challenges

- Effects of sulfur oxides (SO_x), and nitrogen oxides (NO_x) on the MOF material.
- Need for large vacuum pumps to compress the CO₂ 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 CO₂ 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% CO₂ captured by this MOF at flue gas conditions (~0.13 atm CO₂ 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 CO₂. Their analysis indicated a 65% increase in cost of electricity compared to a reference power plant without CO₂ capture.

Next Steps

Project completed June 2010. Final report issued October 2010.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/mofs.html>

Carbon Dioxide Removal from Flue Gas Using Microporous Metal Organic Frameworks (Oct 2010) Final Technical Report. <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/43092F1.pdf>

CO₂ Removal from Flue Gas Using Microporous Metal Organic Frameworks – Progress Update; presented at the Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting Pittsburgh, PA, March 24–26, 2009. <http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/43092 UOP MOF sorbent %28Benin%29 public version mar09.pdf>

DEVELOPMENT OF A DRY SORBENT-BASED POST-COMBUSTION CO₂ CAPTURE TECHNOLOGY FOR RETROFIT IN EXISTING POWER PLANTS

Technology Maturity:
Bench-scale/small pilot-scale

Project Focus:
Dry Sodium Carbonate

Participant:
Research Triangle Institute

Project Number:
NT43089

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Partners:
Arcadis
ADA-ES, Inc.
BOC
EPA
EPRI
Nexant
Süd-Chemie, Inc.

Performance Period:
3/7/07 – 12/31/09

Primary Project Goals

Research Triangle Institute (RTI) is developing and testing a carbon dioxide (CO₂) capture process that utilizes a dry sodium carbonate (Na₂CO₃) sorbent and is based on the reaction of Na₂CO₃ with CO₂ 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 CO₂ capture process using Na₂CO₃.
- Construct and demonstrate a pilot-scale, dry carbonate process that captures 0.9 tonnes of CO₂/day (1 ton of CO₂/day).
- Demonstrate the long-term chemical and mechanical stability of the sorbent.
- Update the economic analyses of the CO₂ sorbent capture process.
- Develop a commercialization plan for instituting the CO₂ 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.

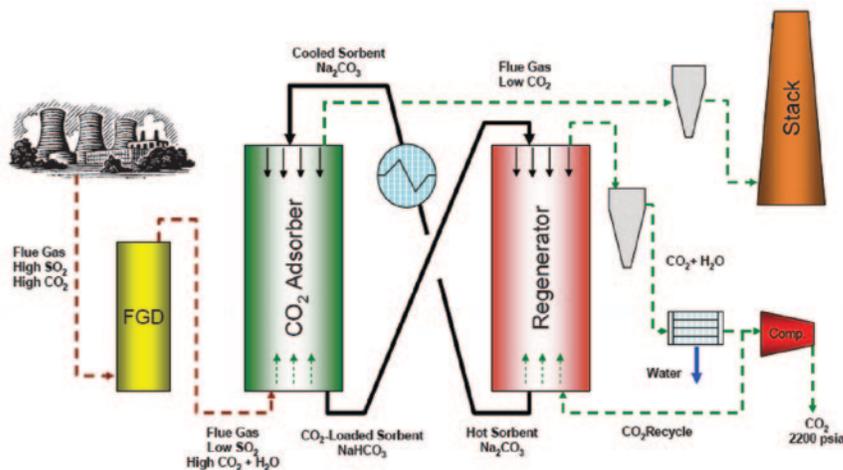


Figure 1: Schematic Diagram of CO₂ Capture Process

The CO₂ capture unit is located after the wet flue gas desulfurization (FGD) unit. The Na₂CO₃ sorbent reacts with the CO₂ and water (H₂O) located in the gas stream through a cyclic temperature swing cycle by adsorbing the CO₂ and H₂O 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 CO₂ capture rate and physical characteristics (e.g., attrition resistance, fluidizability, 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 contaminants such as hydrochloric acid (HCL), nitrous oxides (NO_x), H₂O, and oxygen (O₂). While sulfur dioxide (SO₂) forms irreversible chemical bonds to the sorbent, it is considered to be a minor issue, considering the rate of attrition is generally greater than the rate of deactivation due to SO₂.

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 Na₂CO₃ 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 Na₂CO₃ sorbent. Data from the fluidized bed will be used to validate and develop the computational fluid dynamic (CFD) model called MFIIX.

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

As seen in the aforementioned table, the theoretical maximum CO₂ 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 ~20–25%.



Figure 2: Lab-Scale CO₂ Absorption Reactor Skid

Table 1: Physical Properties of Sodium Carbonate Sorbents

Property	Value
Bulk density	1.0–1.1 g/mL
Average particle size	65–75 μm
Surface area	100–120 m ² /g
Physical strength (AR)	0.77
Na ₂ CO ₃ content	10–40 wt%
Heat of absorption	3.08 MJ/kg
Regeneration energy	3.08 MJ/kg

Technology Advantages

- Lower capital and operating costs for CO₂ 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 Na₂CO₃ with H₂O is highly exothermic and requires effective heat transfer.
- Removal of CO₂ requires equimolar amounts of H₂O.

- 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

Development activities for this technology are no longer part of the DOE/NETL portfolio.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/dry-regen.html>

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

Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology for Retrofit in Existing Power Plants – Progress Update, presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 24-26, 2009. <http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/43089 RTI sorbent %28Nelson%29 mar09.pdf>

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

Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents Fact Sheet – April 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.

METAL MONOLITHIC AMINE-GRAFTED SILICA FOR CO₂ CAPTURE

Primary Project Goals

The University of Akron is developing a low-cost carbon dioxide (CO₂) capture technology by integrating metal monoliths with a grafted amine sorbent.

Technical Goals

- 1.5 mmol-CO₂/g-sorbent.
- 1.0 mmol-sulfur dioxide (SO₂)/g-sorbent.
- 500 repeated thermal cycles of sorbent between CO₂ adsorption at 25 °C and desorption at 110 °C with less than 10% degradation in original CO₂ 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 CO₂ adsorption system. Porous silica, alumina, zeolite, and carbon, which are used as commercial adsorbents for a wide range of applications, are impregnated with alkyl amine molecules such as monoethanolamine/tetraethylenepentamine. The adsorption capacity of this novel amine-grated silica was determined to be greater than 1.5 mmol-CO₂/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 CO₂ 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 CO₂ 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 is being 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:

NT43086

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Performance Period:

2/21/07 – 3/31/11

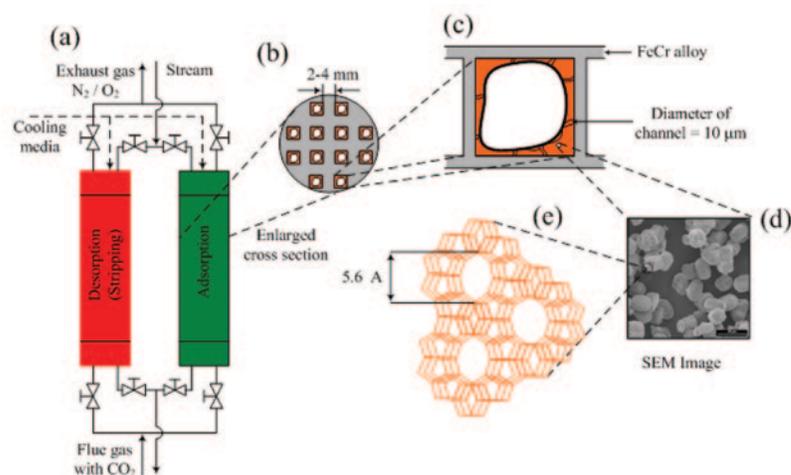


Figure 1: Metal Monolithic Amine-Grafted Silica Sorbents

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 about 2–4 mm apart. The silica or zeolite is coated inside the square metal tube. Gas enters the tube and flows through the channels (d) of the amine grafted silica, which are 10 µm in diameter. Heating for CO₂ 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 CO₂ is purged from the channels of metal monoliths by pulses of steam and hot air. The goal is that CO₂ and SO₂ adsorption capacity of the amine will be greater than 1.5 mmol-CO₂/g-sorbent and 1.0 mmol-CO₂/g-sorbent, respectively. The amine is capable of greater than 500 times regeneration with less than 10% degradation in CO₂ capacity. The amine grafted silica sorbent is expected to exhibit a heat capacity of 1.5 kJ/kg K. The CO₂ will be captured at an approximate temperature of 50 °C (140 °F) and then released at approximately 110 °C (230 °F).

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

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	PEG/TEPA/SiO ₂	N/A
	Heat of adsorption (kJ/mole CO ₂)	52	50–55
	CO ₂ loading/working capacity, wt%	8 (dry); >11 (wet)	10
	Surface area, m ² /g	30	40
	Particle density, cm ³ /g	0.5	<0.5
	Packing density, cm ³ /g	0.43	<0.5
	Particle size (mm)	0.05–1	<1
	Heat capacity (kJ/K/kg)	1.49	1.3–1.5
	Thermal stability, °C	130 °C	130 °C
	Hydrothermal stability, °C	110 °C	110 °C
Process Configuration	Attrition rate (fluidized bed), %/year	TBD	20
	Cycle time (fixed bed), minutes	12	10
	Pressure drop (fixed bed), psia	2	—
Operating Conditions	Adsorption temperature, °C	50	<55
	Adsorption pressure, atm	1	1
	CO ₂ capture efficiency, %	98	90
	Regeneration method	Thermal swing	Thermal swing
	Regeneration temperature, °C	100–110	100–110
	Regeneration pressure, atm	1–1.05	1–1.05

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

	Parameter	Current R&D Value	Target R&D Value
Heat Integration	Required regeneration steam temperature, °C	100–110	100–110
Miscellaneous	Sorbent make-up rate, kg/kg CO ₂	0 not tested	TBD
Product Quality	CO ₂ purity, %	95%	99.9%
	N ₂ concentration, %	Balance	—
	Other contaminants, %	250 ppm SO ₂	<40 ppm SO ₂
Process Performance	Electricity requirement, kJ/kg CO ₂	N/A	—
	Heat requirement, kJ/kg CO ₂	TBD	1,500
	Total energy (electricity equivalent), kJ/kg CO ₂	N/A	—

Technology Advantages

- High stability for CO₂ 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 monoethanolamine process.
- Currently, the CO₂ capture capacity of the sorbent is too low.

Results To Date/Accomplishments

- Silica-supported amine sorbent with additives is able to capture more than 1.5 mmol CO₂/g-sorbent at 40 °C and desorb at 100 °C for more than 500 cycles with less 10% degradation. Degradation was due to overheating of those sorbents which were in contact with the tube wall. During heating for CO₂ desorption, the wall temperature is 5–15 °C higher than that of the center of packed bed. The presence of 4% water (H₂O) in the CO₂/air stream increases the CO₂ capture capacity by more than 1.6 times and decreases the rate of degradation.
- 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 SO₂ poisoning by adding a proprietary additive to the CO₂ sorbent.
- Identified the structure of adsorbed CO₂ and SO₂ on the amine sorbents.
- More than 500 of sorbents have been prepared and tested for CO₂ capture.
- Fabricated a metal monolith CO₂ absorber.
- 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

- Continue to improve CO₂ and SO₂ capture capacity and stability by fine-tuning sorbent compositions.
- Improve the heat transfer rate of the absorber.
- Conduct economic analysis.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/zeolite.html>

Metal Monolithic Amine-Grafted Zeolites for CO₂ Capture Power Plants, presented at the 2010 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, September 13–17, 2010. [http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Steven Chuang-NT43086.pdf](http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Steven%20Chuang-NT43086.pdf)

Metal Monolithic Amine-Grafted Zeolites for CO₂ Capture Factsheet, U.S. DOE National Energy Technology Laboratory, May 2010. <http://www.netl.doe.gov/publications/factsheets/project/NT43086.pdf>

Metal Monolithic Amine-grafted Zeolites for CO₂ Capture, presented at the Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 24–26, 2009. [http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/43086 Akron amine-zeolite sorbent %28Chuang%29 mar09.pdf](http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/43086%20Akron%20amine-zeolite%20sorbent%20Chuang%20mar09.pdf)

“In Situ Infrared Study of the Role of PEG in Stabilizing Silica-Supported Amines for CO₂ Capture” J. Tanthana and S.S. C. Chuang, *Chemical and Sustainability Energy and Materials*, 3, 957–964, 2010. <http://onlinelibrary.wiley.com/doi/10.1002/cssc.201000090/abstract>

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

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

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