

Bench-Scale Development and Testing of Rapid Pressure Swing Adsorption for Carbon Dioxide Capture

primary project goals

W.R. Grace developed a rapid pressure swing adsorption (rPSA) 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.
- Design, develop, and test a bench-scale rapid PSA process using the structured adsorbent to deliver efficient and cost-effective separation of carbon dioxide (CO₂) from flue gas.

technical content

W.R. Grace worked to develop a rapid PSA process with a much shorter cycle time compared to conventional PSA, which could potentially reduce 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. Pressure swing adsorption is attractive because it requires only electricity and not any of the power plant's steam.

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 CO₂ 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.

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 CO₂ 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

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Rapid Pressure Swing Adsorption

participant:

W.R. Grace and Co.

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predecessor projects:

N/A

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percent complete:

100%

metal support. This process has been successfully demonstrated using metal foil, as shown in Figure 1.

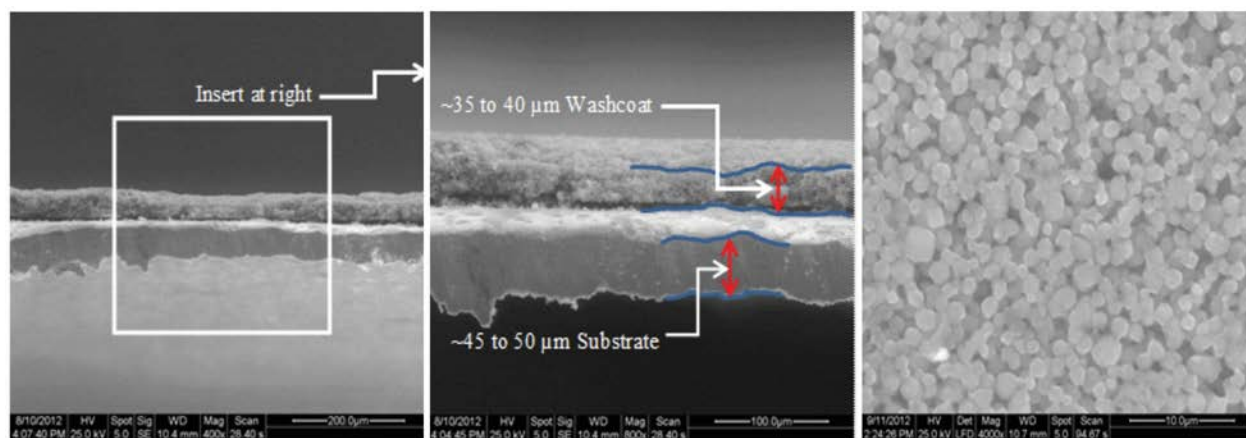


Figure 1: Edge view of zeolite-coated metal substrate at 400x magnification (left); edge view of zeolite-coated metal substrate at 800x magnification indicating washcoat is 35–40 μm thick (center); top view of zeolite-coated metal foil substrate at 4,000x magnification (right)

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



Figure 2: Side view of 1.5" x 6" x 289 psi 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 DVFR apparatus

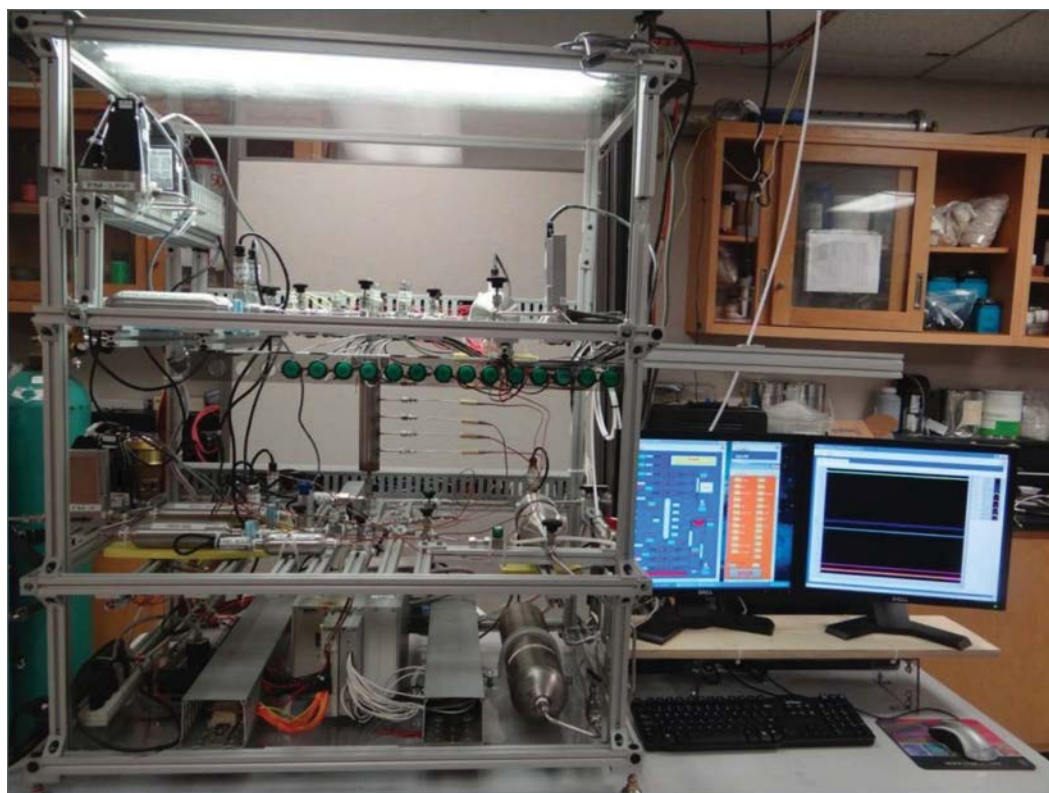


Figure 4: Photograph of S-C rPSA system

TABLE 1: SORBENT PROCESS PARAMETERS¹

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Sorbent	Units	Current R&D Value	Target R&D Value
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
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 CO ₂ Loading ⁹	g mol CO ₂ /kg	0.14	0.14
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	
Flue Gas Flowrate	kg/hr	2.32 × 10 ⁶	
CO2 Recovery, Purity, and Pressure	% / % / bar	90	95 1.38
Adsorber Pressure Drop	bar	0.15	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

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 CO₂ and obtained from another desorption step in the PSA cycle.

7. First value is total pressure; second value is partial pressure of CO₂.

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., CO₂-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 CO₂ 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 CO₂ in equilibrium with the sorbent. If the vapor phase is pure CO₂, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO₂. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO₂ is about 13.2 percent. Therefore, the partial pressure of CO₂ 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 CO₂ 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 CO₂ in CO₂-rich product gas; assuming targets are met.

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

Pressure	Temperature	Composition						SO _x	NO _x
		CO ₂	H ₂ O	vol% N ₂	O ₂	Ar			
psia	°F							ppmv	
14.7	135	13.17	17.25	66.44	2.34	0.80		42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The relative thermodynamic adsorption selectivity toward CO₂ over other gases such as nitrogen (N₂), oxygen (O₂), and argon (Ar) on a commercial zeolite at partial pressures of CO₂ at around or below 1.0 bar.

Sorbent Contaminant Resistance – The effect of the contaminant sulfur dioxide (SO₂) 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% prior to entering the PSA unit.

Sorbent Makeup Requirements – There are no sorbent makeup 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 1,125 mg/L of dissolved SO₂ and no other contaminants. In addition, about 3.69 x 10⁶ lb/h of N₂-rich product at about 80 °C is vented into the air. This stream will contain, by volume, about 1.8 percent CO₂, 4.0 percent H₂O, 3.3 percent O₂, 1.09 percent Ar, and balance N₂.

technology advantages

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

R&D challenges

- Energy-intensive (but better than current amines).
- Reducing bed size; larger bed implies large pressure drop, requiring more power.
- Minimizing pressure drop, mass transfer issues, and adsorbent attrition.

status

The project has ended. Three 6-inch Catacel core structures were successfully coated with a 50 μm thick layer of Zeolite crystals, with a density of 240 kg/m^3 . One-bed and three-bed bench-scale PSA apparatuses were constructed. Testing of the structured adsorbent began using these units. The dynamic adsorption process simulator was validated with experimental data from the testing.

available reports/technical papers/presentations

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO₂ Capture," presented at the 2015 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, June 2015. <https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/J-Ritter-USCarolina-Rapid-PSA.pdf>

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO₂ Capture," presented at the 2014 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, July 2014. [http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO₂%20Capture/J-Ritter-USCarolina-Rapid-Pressure-Swing-Adsorption.pdf](http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/J-Ritter-USCarolina-Rapid-Pressure-Swing-Adsorption.pdf)

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO₂ Capture," presented at the 2013 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, July 2013. [http://www.netl.doe.gov/File%20Library/Events/2013/CO₂%20Capture/J-Ritter-USC-Rapid-Pressure-Swing-Adsorption.pdf](http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/J-Ritter-USC-Rapid-Pressure-Swing-Adsorption.pdf)

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO₂ Capture," presented at the 2012 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, July 2012. <https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/rapid-pressure-swing-adsorption-july2012.pdf>

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO₂ Capture," presented at the Project Kickoff Meeting, Pittsburgh, PA, May 2012. <https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/rapid-pressure-swing-adsorption-kickoff-july2012.pdf>