

Lab- and Bench-Scale Applications for Research and Development of Transformational Carbon Dioxide Capture

primary project goals

Research Triangle Institute (RTI) is developing novel third-generation fluidizable solid sorbents for their sorbent-based carbon dioxide (CO₂) capture process. Two different types of sorbents are being developed, based on hybrid metal organic frameworks (MOFs) and hybrid phosphorus dendrimers (*P*-dendrimers), with long-term performance testing of the most promising sorbents in a fluidized-bed reactor.

technical goals

- Design, synthesize, and optimize two novel fluidizable CO₂ adsorbents based on hybrid MOFs and hybrid *P*-dendrimers.
- Demonstrate superior performance of these solid sorbents at lab-scale in a packed-bed reactor (PBR).
- Evaluate impact of flue gas contaminants such as sulfur oxides (SO_x), nitrogen oxides (NO_x), oxygen (O₂), and water (H₂O).
- Scale-up production of selected sorbents in fluidizable form.
- Complete performance testing in lab-scale fluidized-bed reactor.
- Conduct a high-level techno-economic analysis (TEA).

technical content

RTI is developing novel hybrid fluidizable sorbents for CO₂ capture based on hybrid MOFs and hybrid *P*-dendrimers. The hybrid MOF-based sorbents are based on impregnating polyethylenimine (PEI) on an MOF-silica support. For this sorbent, the silica provides attrition resistance, fluidizability, low cost, and acceptable density. The MOF has very high surface area and tunable pore sizes. The PEI is a polymer with a repeating amine unit, providing high amine content, high CO₂ affinity, and a relatively low cost. RTI has developed a new general approach to selectively grow well-dispersed MOF nanocrystals within mesoporous silica via novel “solid-state” synthesis, which will be used for preparing the novel MOF hybrid CO₂ sorbents. The ability to control and direct the growth of MOFs on confined surfaces (pores) paves the way for new prospective applications of such hybrid systems (i.e., CO₂ adsorption). As confirmed by a combination of different characterization techniques, an outstanding high loading of mesoporous cavities (up to 50 wt%) by the smallest MOF crystals yet reported (4.5±1 nm) leads to several improved properties, including diffusion, attrition resistance, handling, and, particularly for this project, fluidizability, which can approach, for the first time, MOFs to applications in a fluidized-bed reactor, in which MOFs have never been proposed.

Figure 1 shows the high MOF loading in the silica using a confocal microscope. Figure 2 shows the full characterization of the resulting hybrid material. Figure 2(a) shows the N₂ sorption isotherms at 77K (closed symbols correspond to adsorption branches while open symbols correspond to desorption branches, 20%MOF: green line, 40%MOF: blue line).

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Fluidizable Solid Sorbents

participant:

Research Triangle Institute

project number:

FE0026432

predecessor projects:

N/A

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N/A

start date:

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percent complete:

100%

X-ray diffractograms (Cu $K\alpha$ radiation) are shown in Figure 2(b). Figure 2(c) shows the pore-size distribution calculated from Barrett-Joyner-Halenda (BJH) adsorption pore volume versus pore diameter (dV/dD) plot (inset figure: pore diameter [nm] at X-axis and pore volume [cm³ g⁻¹ nm⁻¹] at Y-axis). Figure 2(d) shows the Fourier transform infrared spectroscopy (FTIR) spectra measured in attenuated total reflectance (ATR) mode [Reference lines: Pure MOF (black line, the FTIR intensity was divided by 3 for better comparison), Silica(A) (grey line) and MOF precursors loaded on Silica(A) (dark yellow line)].

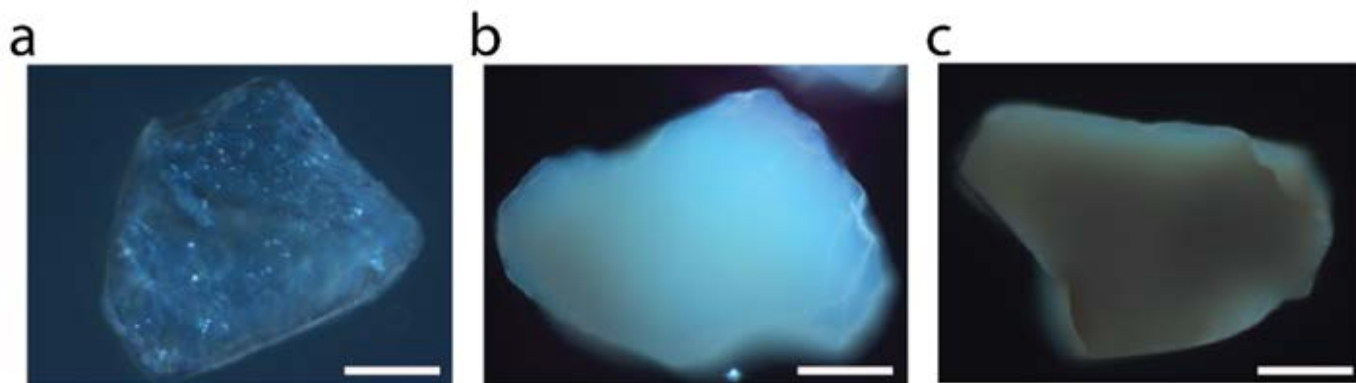


Figure 1: MOF loading in silica: (a) transparent amorphous silica; (b) 20% MOF; (c) 40% MOF.

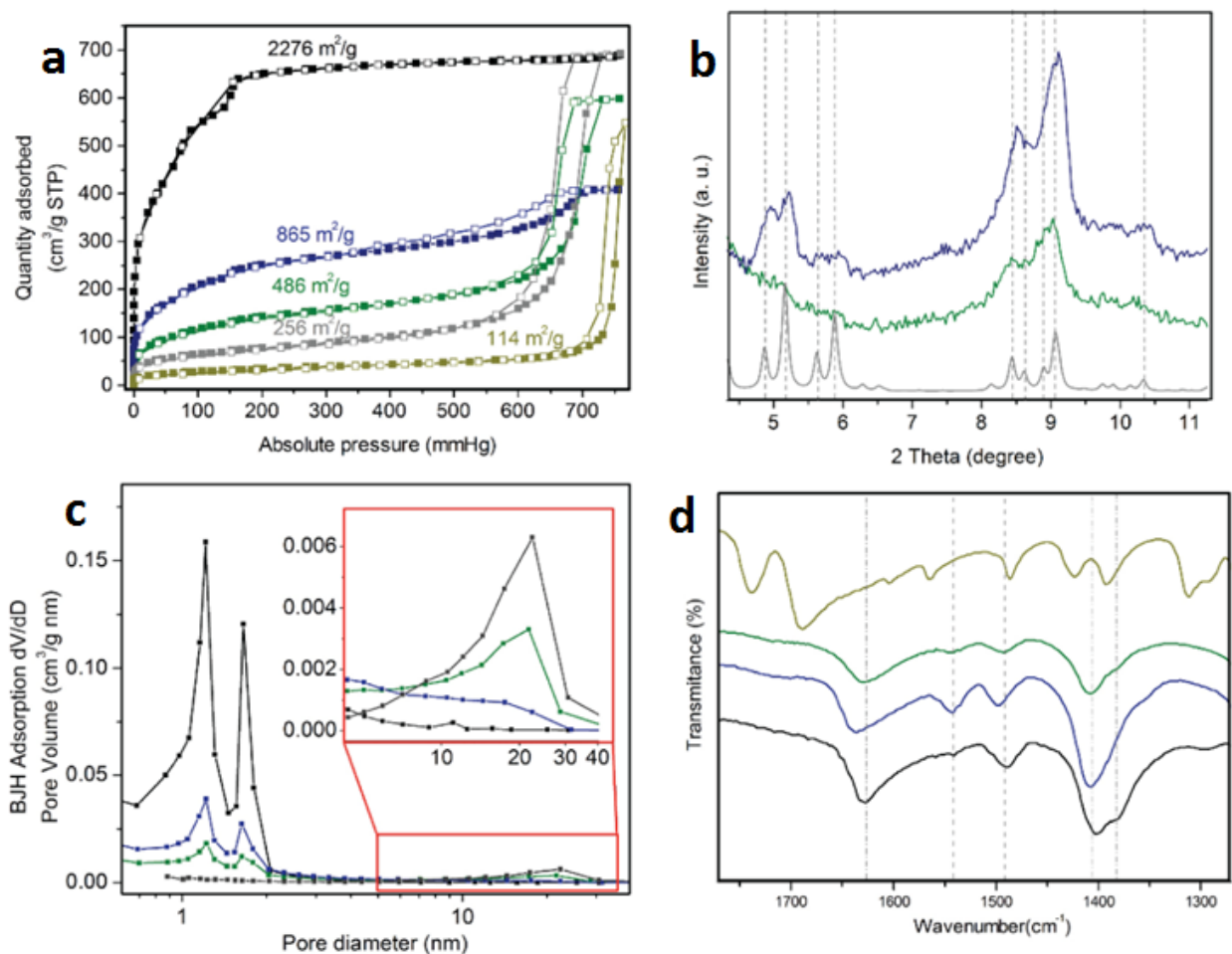


Figure 2: Characterization of the hybrid material: (a) N₂ sorption isotherms at 77K; (b) X-ray diffractograms; (c) pore-size distribution; (d) FTIR spectra measured in ATR mode.

In order to evaluate the utilization of these novel MOF hybrid materials prepared via solid-state synthesis for CO₂ capture from post-combustion flue gas, fluidized MOF/silicon dioxide (SiO₂) hybrid sorbents containing different polyamines and selected MOF

nanocrystals have been systematically studied. Hybrid sorbents containing a moderate loading of (Zn)ZIF-8 are the most promising sorbents in terms of CO₂ capacity and long-term stability (250 cycles) and were successfully prepared at the kilogram scale. Two sorbents exhibited excellent stability for 250 cycles under simulated flue gas conditions, as shown in Figure 3.

These hybrid sorbents demonstrated excellent fluidizability and performance under the relevant process conditions in a visible fluidized-bed reactor.

Dendrimers are repeatedly branched, large spherical molecules. *P*-dendrimers provide a rigid scaffold, hydrophobic interior, and well-defined spatial location of the functional groups, along with high thermal stability. An example of a dendrimer structure is shown in Figure 4. RTI is developing an approach to produce sorbents by covalently grafting amine-functionalized *P*-dendrimers on solid supports, such as silica, to improve stability and fluidizability.

Extensive cyclic adsorption/desorption testing was conducted with the best performing *P*-dendrimer sorbent (1-G0/600PEI) produced in this study, revealing an average CO₂ capacity of 13.1 wt% from simulated flue gas over 350 cycles running for 700 contiguous hours. A heat of adsorption value of 103 kJ mol⁻¹ was determined from CO₂ isotherms, providing evidence for chemisorption binding. The effect of common contaminants of flue gas (sulfur dioxide [SO₂], nitric oxide [NO], and nitrogen dioxide [NO₂]) were investigated with 1-G0/600PEI. The sorbent was significantly impacted by SO₂ exposure at low concentrations (50 parts per million [ppm]), binding the SO₂ irreversibly and blocking active amine sites. Like many solid amine sorbents, for 1-G0/600PEI to be utilized on a practical scale for post-combustion CO₂ capture, a desulfurization step would be required. The impact of NO_x contaminants, NO and NO₂, was less influential – with only a small decrease over 100 cycles presumably from the binding of NO₂ as a nitrite species. Extensive efforts were made to fluidize the 1-G0/600PEI sorbent so that it could be utilized in a fluidized-bed reactor. Unfortunately, this material was unable to reach high capacities and attain packed-densities greater than 0.6 g/mL required for fluidization. Alongside the poor physical properties for fluidization, the material also had much higher costs when projected for commercial-scale production in comparison to the MOF-based hybrid sorbents.

A PBR is used to screen the novel hybrid sorbents with multi-cycle adsorption-regeneration, measuring CO₂ loading and rate along with contaminant effects. A visual fluidized-bed reactor, shown in Figure 5, is utilized to verify the fluidizability of the sorbents under realistic process conditions and to test optimal fluidization conditions.

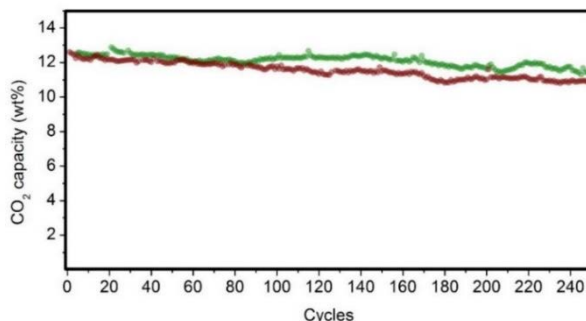


Figure 3: Long-term CO₂ adsorption performance stability for PEI/(Zn)ZIF-8/SiO₂ (green) and PEI/(Zn)ZIF-7/SiO₂ (dark red) under simulated flue gas conditions.

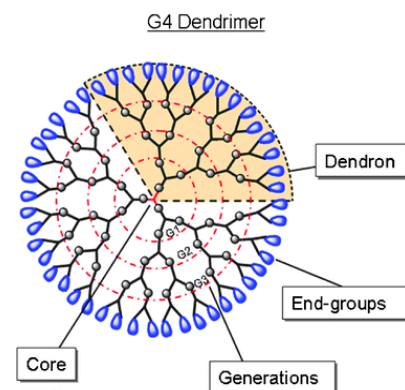


Figure 4: Dendrimer structure.

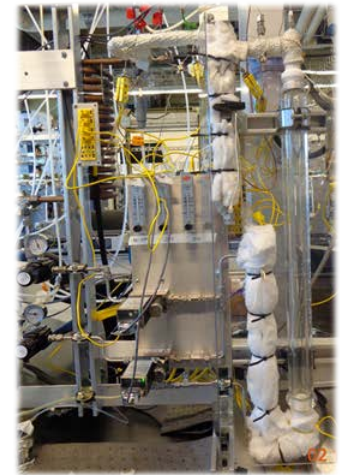
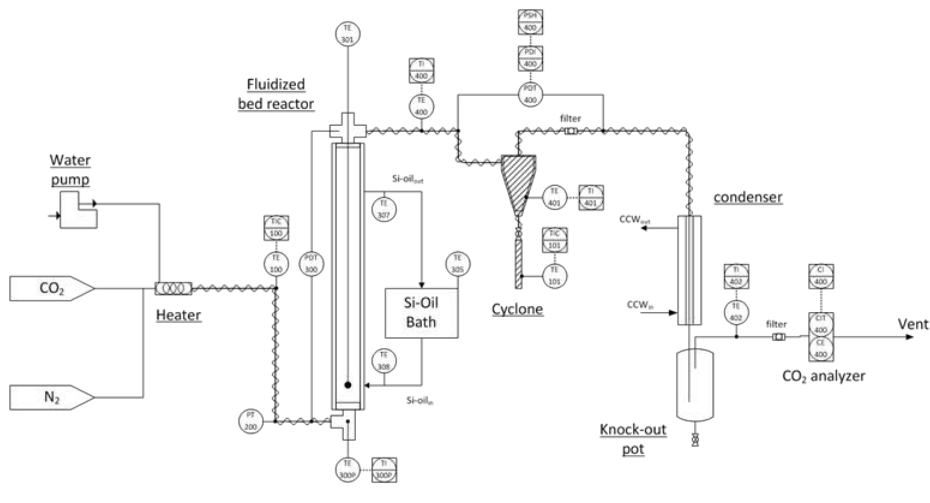


Figure 5: RTI visual fluidized-bed reactor.

TABLE 1: SORBENT PROCESS PARAMETERS

| Sorbent | Units | Current R&D Value | Target R&D Value |
|-------------------------------------|--------------------------------|-------------------|------------------|
| True Density @ STP | kg/m ³ | — | — |
| Bulk Density | kg/m ³ | 650-750 | — |
| Average Particle Diameter | mm | 165 | — |
| Particle Void Fraction | m ³ /m ³ | — | — |
| Packing Density | m ² /m ³ | — | — |
| Solid Heat Capacity @ STP | kJ/kg-K | 1.5 | — |
| Crush Strength | kg _f | 10% | — |
| Manufacturing Cost for Sorbent | \$/kg | 15 | — |
| Adsorption | | | |
| Pressure | bar | 1-1.2 | — |
| Temperature | °C | 60-70 | — |
| Equilibrium Loading | g mol CO ₂ /kg | 12.5 | — |
| Heat of Adsorption | kJ/mol CO ₂ | 85-90 | — |
| Desorption | | | |
| Pressure | bar | 1.3-1.4 | — |
| Temperature | °C | 110-120 | — |
| Equilibrium CO ₂ Loading | g mol CO ₂ /kg | 0.5-1 | — |
| Heat of Desorption | kJ/mol CO ₂ | 75-90 | — |

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [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 pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO₂ is about 13.2%. 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.

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – To provide insight regarding the influence that the presence of MOF nanocrystals causes on the CO₂ dynamics of impregnated PEI, the adsorption-desorption profiles for 35 wt% of PEI confined on 4.6 wt% of (Zn)ZIF-8/SiO₂ and bare SiO₂ at the tenth cycle are compared in Figure 6. The adsorption breakthrough profile for the MOF-containing solid sorbent shows a superior CO₂ adsorption compared with PEI/SiO₂. The characteristic adsorption-regeneration profiles for the PBR filled with inert silicon carbide SiC₄ are represented by the red line, which determines the dead volume of the PBR. However, the regeneration profile shows an interesting difference in terms of CO₂ desorption for the composite incorporating MOF nanocrystals. Larger concentrations of early release adsorbate are measured for the MOF/SiO₂ hybrid sorbent, which is attributed to weakly adsorbed CO₂ via physisorption because the temperature required to release them is lower than 80°C.

PEI/SiO₂ also exhibited an early release, but it is mainly attributed to CO₂ trapped in the dead volume of the PBR, as suggested by comparison with the profile for the inert SiC₄. In addition, PEI/MOF/SiO₂ exhibited higher CO₂ desorption between 80 and 100°C, which suggests slightly better use of the PEI amines for CO₂ chemisorption as well. This result highlights the unusual dual adsorption performance of our hybrid sorbents containing MOF nanocrystals compared with the pure silica counterpart.

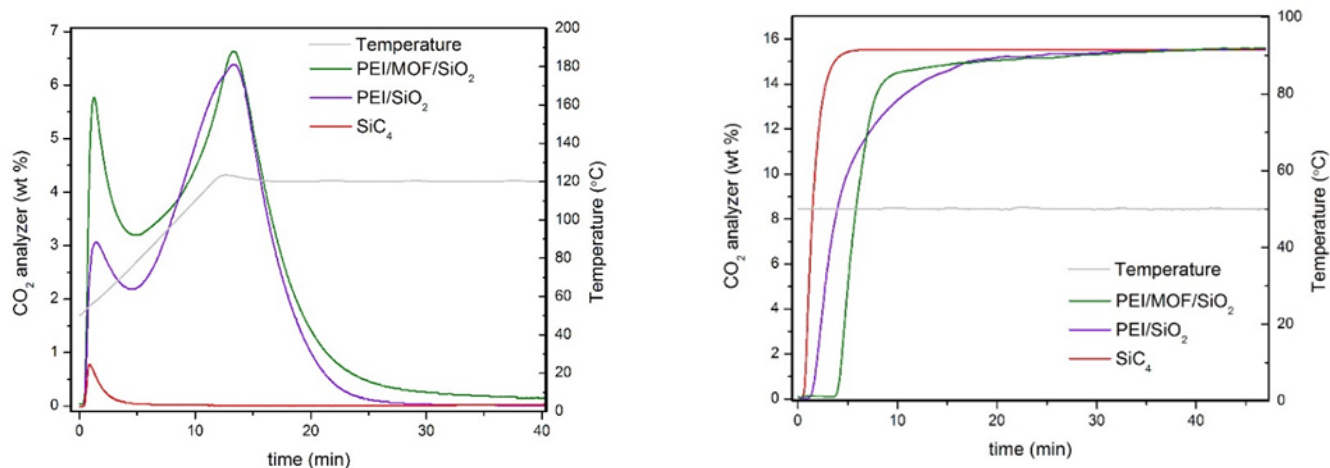


Figure 6: Adsorption (left) and regeneration (right) profiles for 35 wt% of PEI/4.6 wt% of (Zn)ZIF-8/SiO₂ and 35 wt% of PEI/SiO₂.

Sorbent Contaminant Resistance – Fluidized MOF/SiO₂ hybrid sorbents have demonstrated good CO₂ adsorption capacity under simulated flue gas conditions, since they exhibit 140% higher CO₂ capacity and similar deactivation (*ca* 10% after 250 cycles) than

the reference PEI impregnated on bare mesoporous silica. As flue gas from coal-fired power plants typically contains other acid gas impurities, such as SO₂ and NO_x, that can dramatically influence the CO₂ capture efficiency. The results show a clear deactivation of the CO₂ adsorption capacity of the sorbents under the presence of SO₂. This deactivation is due to the irreversible reaction occurring during the adsorption step between SO₂ and PEI amines, which are not further active for the CO₂ capture. On the other hand, excellent stability has been observed under elevated concentration of NO_x. Therefore, the presence of MOF nanocrystals within the hybrid solid sorbent does not reduce the tendency of PEI amines to be deactivated by irreversible binding with SO₂, as similar deactivation has been measured for PEI/SiO₂.

Sorbent Attrition and Thermal/Hydrothermal Stability – This work is the first example of CO₂ capture from simulated flue gas in a fluidized-bed configuration using an MOF-based CO₂ solid sorbent. The application of MOFs on this configuration have never been proposed due to the poor attrition, handling, and lack of fluidizability of bulk MOFs. By engineering MOFs within mesoporous silica, the final sorbent is demonstrating excellent fluidizability, handling, and improved attrition resistance (up to two to three times compared to SiO₂, and six to seven times compared to MOF). Very aggressive regeneration conditions (stream containing 80 volume/volume % H₂O balanced with nitrogen [N₂] at 100°C for one hour) were used to check the stability of this sorbent; the CO₂ adsorption capacity was practically maintained for PEI/MOF/SiO₂, whereas a significant drop was observed for the MOF-free sorbent.

Flue Gas Pretreatment Requirements – An additional unit should be included up-stream for scrubbing the SO₂ levels in the flue gas down to a single-digit ppm level prior to reaching the fluidized-bed reactor to elongate the life of the hybrid solid sorbents and reduce the makeup rate.

Sorbent Makeup Requirements – Fluidized MOF/SiO₂ hybrid sorbents demonstrate an excellent attrition resistance and therefore significantly reduced the makeup rate.

Waste Streams Generated – Two waste streams could be generated:

- Sorbent attrition fines could be reprocessed and used as sulfur guard-bed.
- Steam condensate from regenerator CO₂ capture steam usually has leached PEI. However, water-wash experiments of the sorbent showed no PEI leaching. This suggests that the condensed water will be easily processed and reused.

Process Design Concept – RTI proposes the use of a multi-stage, fluidized-bed, absorber-regenerator process for the capture and recovery of CO₂. By employing fluidized-bed reactors with heat transfer internals, the process temperature in each stage will be controlled precisely by removing heat during adsorption and adding heat in the regenerator. Multi-stage reactors are essential in maximizing sorbent-rich loading in the absorber and lean-loading in the regenerator, thereby maximizing working capacity.

technology advantages

- High theoretical CO₂ loading for *P*-dendrimers.
- MOF/silica fluidized hybrid materials offer several advantages:
 - High MOF loading (up to 50%).
 - Excellent MOF dispersion and homogeneity.
 - Good water and air stability.
 - Good chemical and thermal stability.
 - Tunable pore size distribution.
 - Elevated surface area (up to 900 m²/g) and density (0.65 g/cm³).
 - Enhanced attrition resistance.
 - Good fluidizability.
- High CO₂ capacity (≥12 wt%) and good stability of hybrid MOF-based adsorbents.

R&D challenges

- Reducing sorbent production costs, particularly for the *P*-dendrimer-based adsorbents.
- Transforming the *P*-dendrimer-based adsorbents to fluidizable form.

status

The project was completed on June 30, 2018. RTI has developed a novel technique to grow MOF inside the pores of silica supports. Testing of the three most promising PEI-impregnated silica-MOF sorbents has shown high (greater than 12%) CO₂ capacity with good MOF dispersion and homogeneity, good water and air stability, good chemical and thermal stability, enhanced attrition resistance, and excellent fluidizability. The sorbents exhibit better performance and long-term stability in a fluidized configuration. Production of the hybrid MOF-based sorbent has been scaled from 20-mg to 5-kg scale. Three *P*-dendrimer sorbents were evaluated and showed high (greater than 12.0 wt%) CO₂ capacities over at least 250 cycles. The project team has down-selected a PEI-impregnated silica-MOF sorbent, based on performance characteristics and the successful scale-up in a fluidized form to kilogram quantities, which was then tested in RTI's lab-scale fluidized moving-bed reactor prototype. This hybrid MOF sorbent was capable of achieving 90% CO₂ capture.

available reports/technical papers/presentations

Soukri, M., et al. "Lab-Scale Development of a Solid Sorbent for CO₂ Capture Process for Coal-Fired Power Plants," presented at the 2017 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, August 2017.

<https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/M-Soukri-RTI-Solid-Sorbent.pdf>.

Soukri, M., et al. "Lab-Scale Development of a Solid Sorbent for CO₂ Capture Process for Coal-Fired Power Plants," presented at the 2016 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, August 2016. <https://netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/M-Soukri-RTI-Lab-scale-Sorbent.pdf>.