Transformational Molecular Layer Deposition, Tailor-Made, Size-Sieving Sorbents for Post-Combustion CO_2 Capture

primary project goal

Rensselaer Polytechnic Institute (RPI) is developing a transformational molecular layer deposition (MLD), tailor-made, size-sieving sorbent/pressure swing adsorption (PSA) process (MLD-T-S/PSA) that can be installed in new (or retrofitted into existing) pulverized coal (PC) power plants for carbon dioxide (CO_2) capture. The project's technical activities include mathematical modeling, development of MLD tailor-made sorbents, MLD sorbent design, construction of an MLD-T-S/PSA system, and techno-economic analysis (TEA). The project team includes the University of South Carolina (USC), Gas Technology Institute (GTI), Trimeric Corporation, and the National Carbon Capture Center (NCCC). USC will conduct sorbent performance testing, PSA process optimization, and system design and construction. GTI will evaluate the influence of impurities on sorbent performance, construct a testing skid at USC, and transport the testing skid to the National NCCC in Wilsonville, Alabama, for field testing. Trimeric will perform the TEA based on the NCCC test results.

technical goals

- Generate tailor-made, size-sieving sorbents by using MLD to coat sorbents.
- Identify promising sorbent materials through computational screening.
- Optimize MLD process to develop sorbents with high CO_2 adsorption capacity and stability in the presence of water vapor.
- Perform single-bed testing and simulation with the developed sorbents.
- Identify allowable contaminant levels for sorbents by further single-bed testing and simulation.
- Design PSA cycle schedule tailored to best MLD-modified sorbent.
- Design and construct MLD-modified sorbent/PSA skid system.
- Test skid system under simulated flue gas and actual flue gas conditions.
- Perform a TEA of the process integrated with a 550-megawatt-electric (MWe) power plant.

technical content

RPI, in collaboration with USC and GTI, is developing a process that integrates transformational, tailor-made, MLD-modified sorbents with a novel PSA process concept to achieve U.S. Department of Energy (DOE) CO_2 capture performance and cost goals. RPI has developed sorbents with CO_2/nitrogen (N_2) selectivity as high as 130—much higher than state-of-the-art commercial sorbents, such as 13X zeolite, with similar CO_2 capacity under similar adsorption conditions—enabling achievement of 95% CO_2 purity in a single stage PSA for CO_2 capture from flue gas. The sorbents are coated with an inorganic material to achieve pore misalignment, which allows for fine-tuning the pore mouth size on the surface of sorbents (Figure 1). Using MLD, a vapor phase deposition technique utilizing self-

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Size-Sieving Sorbent Integrated with Pressure Swing Adsorption

participant:
Rensselaer Polytechnic Institute

project number:
FE0031730

predecessor projects:
N/A

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University of South Carolina; Gas Technology Institute; Trimeric Corporation

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percent complete:
82%

limiting surface reactions, the external surface of the base sorbent is uniformly coated by ultrathin (less than 20 nanometers [nm]) microporous coatings. A wide range of porous materials (zeolites, activated carbon, and metal-organic frameworks [MOFs]) in different forms (powder or pellets) can be used directly as the base material for MLD coating, and the pore mouth size can be precisely designed by controlling the coating layer composition and thickness, as well as the thermal treatment conditions. The MLD-modified sorbents provide precise pore mouth size control in the range of 0.01 nm, which is crucial for achieving highly selective separation of CO_2 from N_2, as illustrated in Figure 2. MLD treatment results in minimal loss to the CO_2 adsorption capacity of the base sorbent.

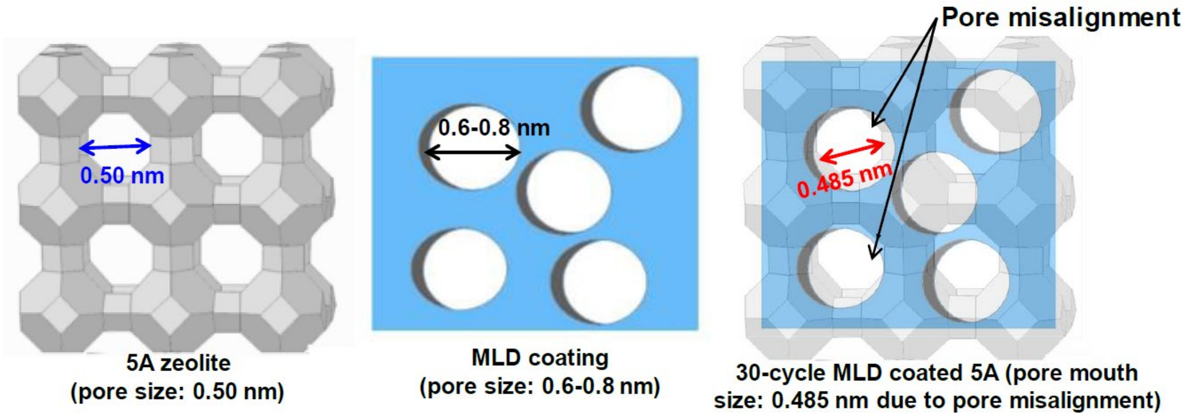

Figure 1: Schematic of pore misalignment for fine-tuning pore mouth size of sorbents.

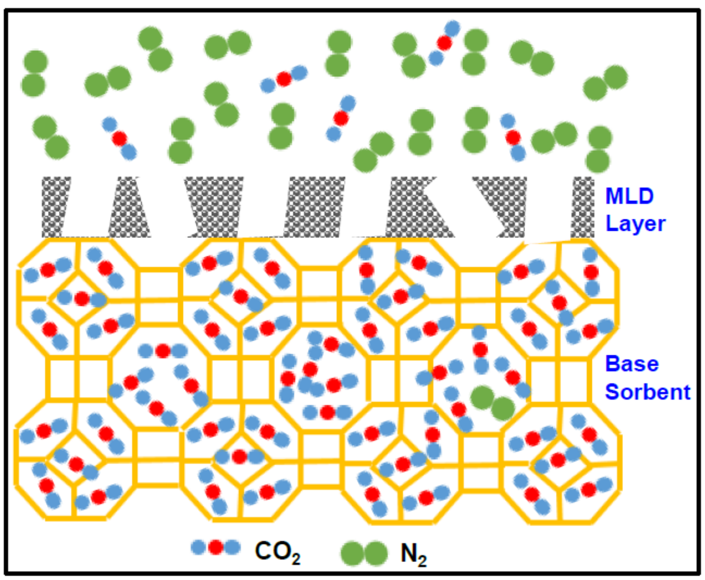

Figure 2: High CO_2/N_2 selectivity achieved by size-sieving for the MLD tailor-made sorbent.

Early studies on the pore misalignment concept show that 5A zeolite with and without MLD coatings have almost identical surface areas (343.5 ± 8.3 m^2/g) and micropore volume, suggesting that the coatings are only on the external surface and the internal cavity of the zeolite is maintained (Figure 3). Furthermore, the effective pore size of the treated 5A zeolite can be precisely controlled by the number of MLD cycles. Preliminary experiments on MLD-coated 13X zeolite show that almost no N_2 is adsorbed, suggesting a molecular sieving mechanism, and indicate a reduction in the heat of adsorption of CO_2. The sorbent and process parameters are provided in Table 1. In addition to 5A and 13X zeolites, other microporous sorbents have the potential to achieve high CO_2 adsorption capacity and CO_2/N_2 selectivity with MLD modification.

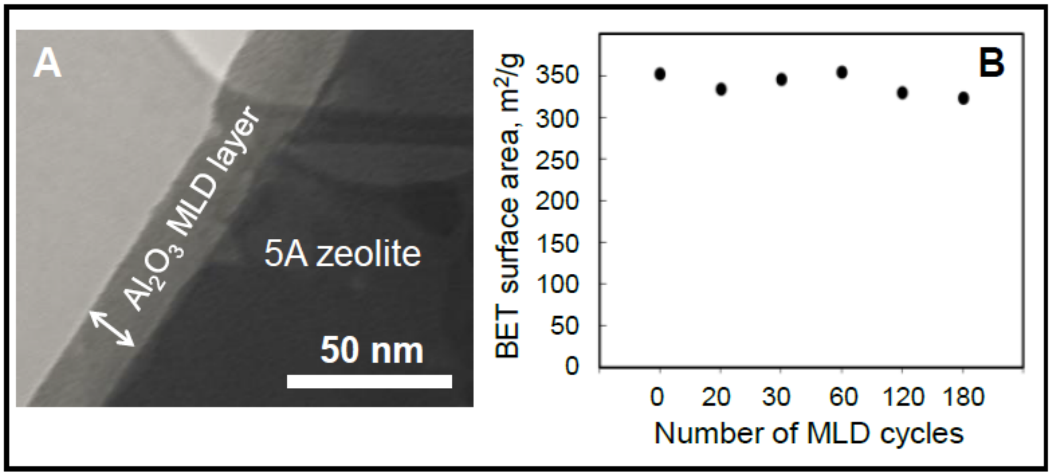

Figure 3: Characterization of MLD-modified 5A zeolite: (A) transmission electron microscopy (TEM) image of 5A zeolite with 60 cycles of aluminum oxide coating; (B) BET surface area of 5A zeolite with different cycles of MLD.

USC has recently developed a proprietary PSA cycle schedule concept for CO_2 capture from flue gas that involves the use of fewer number of beds than employed in their previously DOE-supported project DE-FE0007639, thereby reducing the CO_2 capture cost significantly. The number of required beds is reduced from 240 to 48 (i.e., six, eight-bed PSA systems operating in parallel) for the MLD-coated sorbent/PSA process integrated into a 550-MWe power plant. Figure 4 shows a diagram of the process, including identification of the numbered streams. The flow sheet incorporates desiccant wheels for water vapor removal upstream of the PSA process that are regenerated by a simple concentration swing with the light product from the PSA system and ambient air without the use of any heating. The dry light product (~2.4 mol% CO_2) produced by the PSA system is used to regenerate Dryer 2, and slightly compressed ambient air is used to regenerated Dryer 1. A reflux compressor produces a concentrated recycle stream containing approximately 83 mol% CO_2, facilitating the production of greater than 95 mol% CO_2 in the final CO_2 product. The system is uniquely designed with six adsorption beds being fed simultaneously, while two beds are being regenerated. This ensures low pressure drop during the feed step with a beaded adsorbent for large flow rate feed streams, allowing for the use of fewer number of adsorption beds in the PSA system since the adsorption bed height can be increased without a pressure drop penalty.

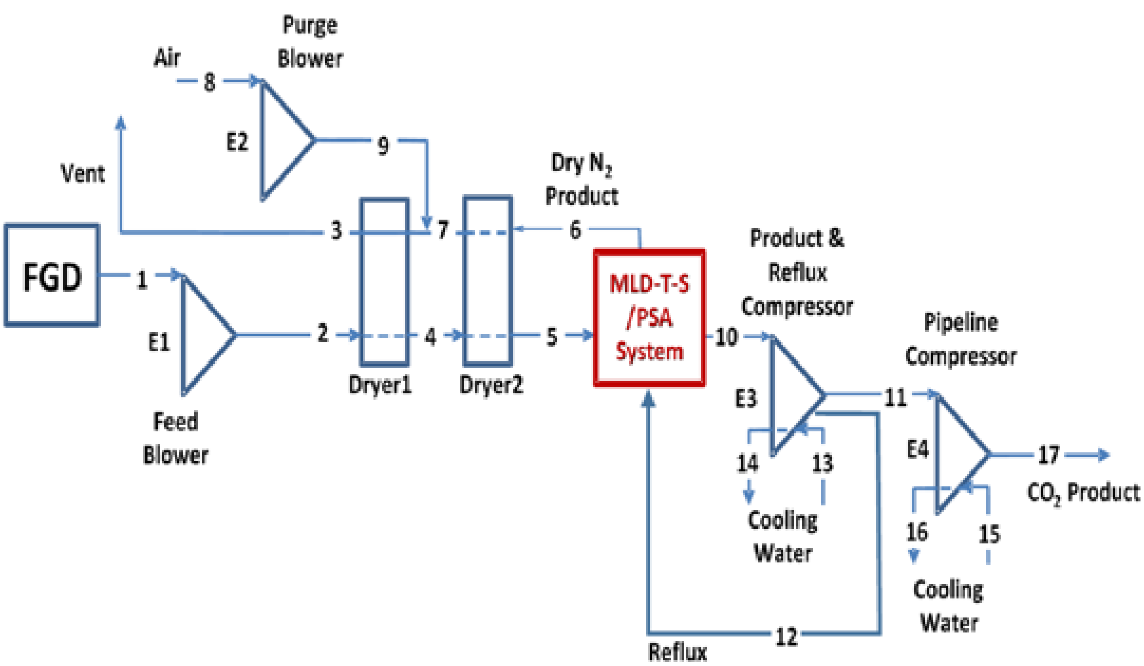

Figure 4: USC's PSA process flow diagram integrated with the MLD sorbent/PSA system.

USC's dynamic adsorption process simulator (DAPS) has been used to design a hypothetical MLD-treated sorbent/PSA system, showing a 6% reduction in separation energy when using MLD-coated 13X zeolite compared to commercial 13X. Preliminary TEA results compared to the DOE/National Energy Technology Laboratory (NETL) Base Case 9 (subcritical PC plant without CO_2 capture) and Base Case 10 (subcritical PC plant with amine scrubbing) are shown in Figure 5, indicating that the MLD-treated sorbent/PSA system can achieve 90% CO_2 capture rate with 95% CO_2 purity with a cost of $28/tonne CO_2.

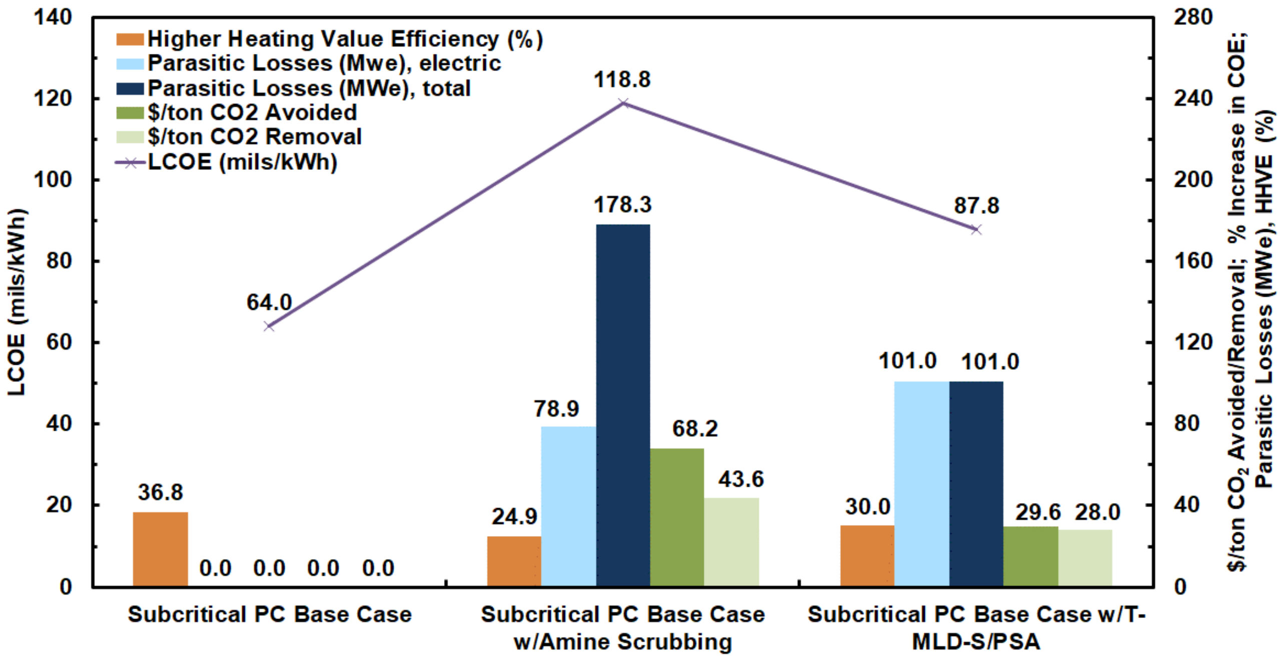

Figure 5: Comparison of the cost of CO_2 capture between DOE/NETL Base Case 9 (subcritical PC plant without CO_2 capture), Base Case 10 (subcritical PC plant with amine scrubbing), and the MLD-coated sorbent/PSA process.

technology advantages

- High CO_2/N_2 selectivity (greater than 130), enabling a 95 vol% CO_2 purity to be achieved in a single stage for a typical coal flue gas containing 12–15 vol% CO_2.
- Uses low-cost commercial sorbents as base material.
- Metal and organic precursors required to form the coating materials are low cost.
- MLD is comparable to commercially available atomic layer deposition technology and suitable for roll-to-roll manufacturing.
- MLD tailor-made sorbent technology allows for reduced vacuum level and reduced light reflux flow during regeneration, thereby reducing the size and energy required by the product and reflux vacuum pump.
- Advanced sorbent fabrication procedure reduces manufacturing cost.
- Low pressure drop during feed step leads to use of fewer adsorption beds in PSA cycle, reducing capital costs.
- Compact, stand-alone, and modularized system design, reducing upfront installation costs and footprint.
- Serves as a platform for CO_2 capture from both coal-fired and natural gas-fired power plants.

R&D challenges

- Precise control of the MLD coating properties to form appropriate pore misalignment for molecular sieving.
- Degradation of MLD sorbent performance in the presence of flue gas contaminants.
- Lower CO_2 purity when integrating MLD sorbent with the new PSA cycle.

status

The project team is using MLD to apply microporous coatings of less than 30 nm thickness on base sorbent material. Computational screening of various sorbent materials is being used to identify the sorbents for this technology. DAPS is being used to design the PSA system based on commercial 13X zeolite to establish baseline performance. A unique 100 Hz volumetric frequency response (VFR) was designed, constructed, and became operational at USC. This system will be used to measure mass transfer rates and mechanisms in virgin and MLD-modified zeolite beads. In addition, a unique six-bed PSA system was designed, constructed, and became operational at USC. It was modified and upgraded to operate with two feed or two light reflux beds. Start-up and troubleshooting have commenced, with preliminary results currently being evaluated. Molecular Dynamics (MD) simulations were used to identify how the transport at the MLD/base sorbent interface can enhance the overall selectivity. Future simulations that include modifications within the base sorbent will expand the design space of modified materials. MLD was shown as an effective technology to modify 13X zeolite and optimized its properties relevant to PSA. The optimized sorbent showed almost no loss in CO_2 working capacity and approximately a doubling of CO_2/N_2 selectivity under relevant PSA conditions. Simulations with DAPS have shown that it may be possible to have a two-unit, 10-bed, 13-step Vacuum Swing Absorption (VSA) cycle (i.e., a 20-bed VSA system when using a 9-mm-diameter 13X zeolite bead); a unique scaling procedure was developed to meet pressure drop requirements and bed design constraints while minimizing the total surface area of the beds required in the VSA system.

available reports/technical papers/presentations

Underhill, P., Ritter, J., Miao, Y. "Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture," presented at the 2021 NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Underhill.pdf*.

Yu, M., et al. "Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture," Kickoff Meeting Presentation, Pittsburgh, PA, November 2019. *http://netl.doe.gov/projects/plp-download.aspx?id=10733&filename=Transformational+Molecular+Layer+Deposition+Tailor-Made+Size-Sieving+Sorbents+for+Post-Combustion+CO2+Capture.pdf*.

Yu, M., et al. "Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture," presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/M-Yu-RPI-Tailor-Made-Sorbents.pdf*.