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

DE-FE0031730

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U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management and Natural Gas & Oil Research Project Review Meeting

Virtual Meetings August 2 through August 31, 2021

Project Overview

Funding: \$3,000,000 from DOE; \$759,206 Cost Share

Overall Project Performance Dates: 10/1/2019-9/30/2023

Project Participants:

Rensselaer

University at Buffalo
The State University of New York

University of South Carolina

gti

Trimeric Corporation

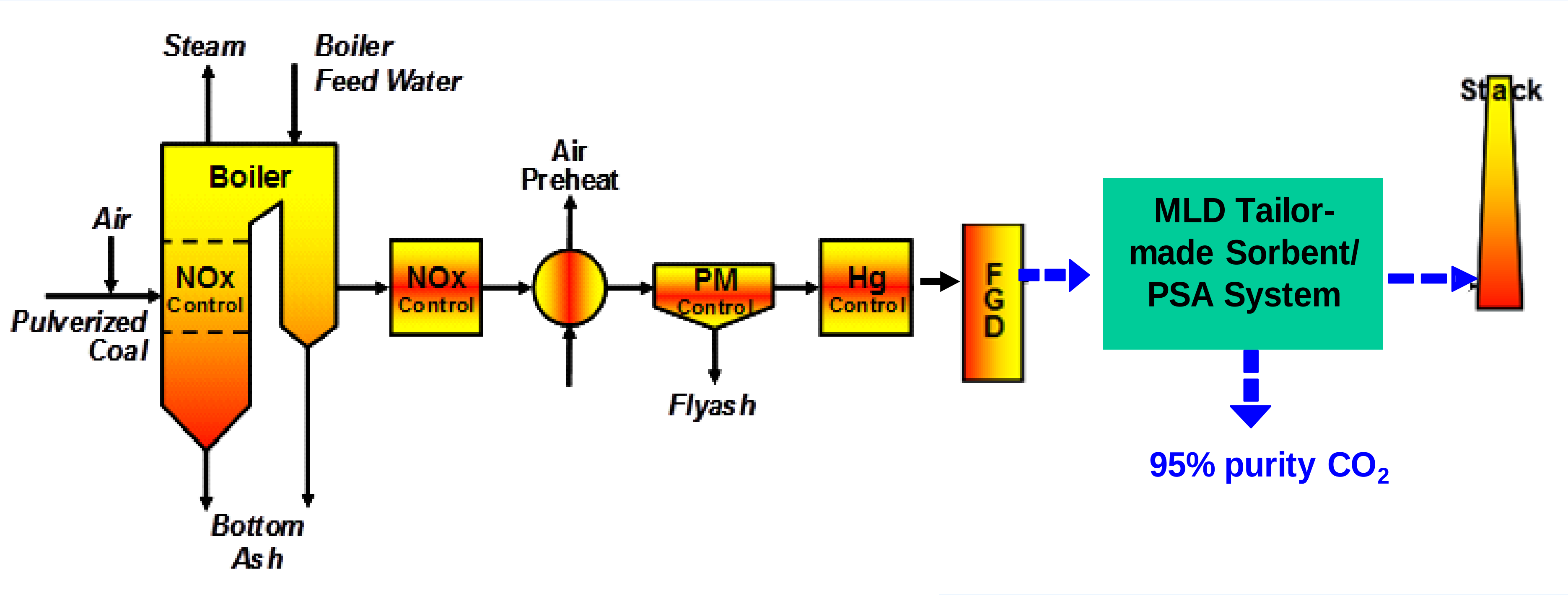
National Carbon Capture Center

Overall Project Objectives:

Develop a transformational molecular layer deposition tailor-made size-sieving sorbent/PSA process (MLD-T-S/PSA) that can be installed in new or retrofitted into existing pulverized coal (PC) power plants for CO_2 capture with 95% CO_2 purity and a cost of approximately \$30 per tonne of CO_2 captured; it will be ready for demonstration by 2030.

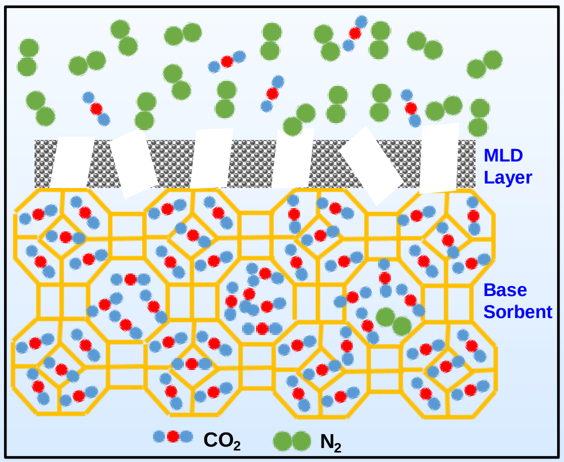
Technology Background

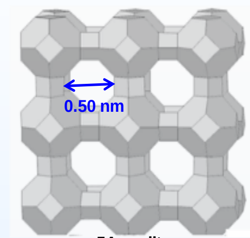
Integration with coal-fired power plants: installed downstream of FGD



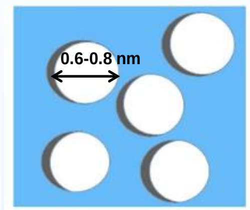
Technology Background

MLD-T-S for molecular sieving

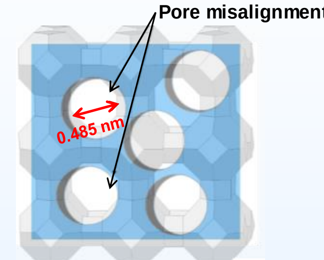




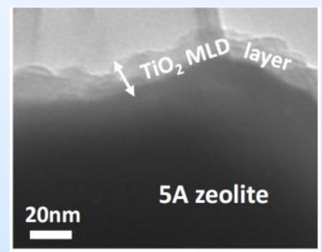
5A zeolite (pore size: 0.50 nm)



MLD coating (pore size: 0.6-0.8 nm)

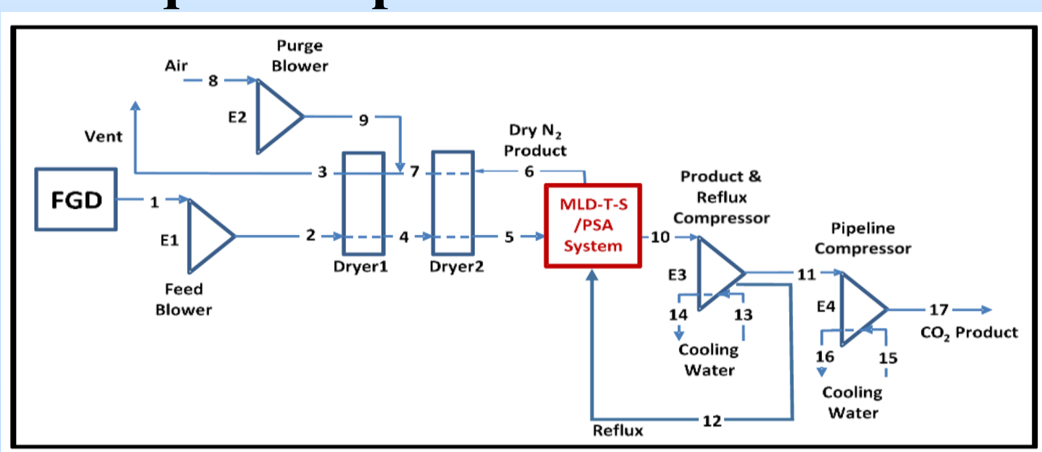


30-cycle MLD coated 5A (pore mouth size: 0.485 nm due to pore misalignment)



Adsorbents	Adsorption capacity (mmol/g)		CO_2/N_2 ideal selectivity
	CO_2	N_2	
5A zeolite	1.0	0.15	35
5A-MLD-250-2h	0.97	0.036	130
5A-MLD-250-4h	0.55	0.028	98
5A-MLD-250-8h	1.0	0.11	46

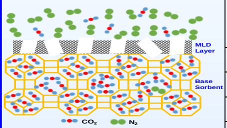
USC's unique PSA process flow sheet from FGD through CO_2 compression



Technology Background

Technical and economic advantages

Transformational Sorbents: ultrathin coating on low-cost commercial sorbents



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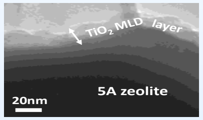
Advanced Sorbent Fabrication Procedure to Reduce Manufacturing Cost



- MLD for uniform external coating from vapor phase
- Low cost MLD precursors
- Successful commercial roll-to-roll production

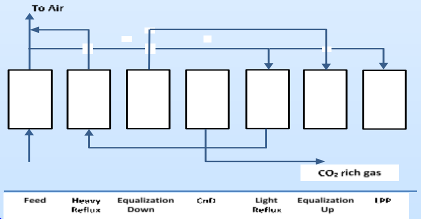
Ease of Scale-Up

- Pellets/beads of commercial sorbents can be directly used

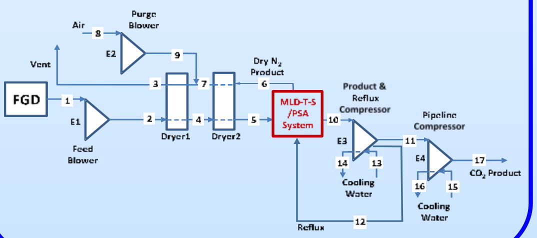
Anticipated Good Long-Term Stability and Recyclability

- MLD coatings are composed of inorganic materials (e.g., TiO_2)
- Stable base sorbent materials, such as zeolites, activated carbon

USC proprietary PSA Cycle Schedule Concept



Ease of Integration into Power Plants

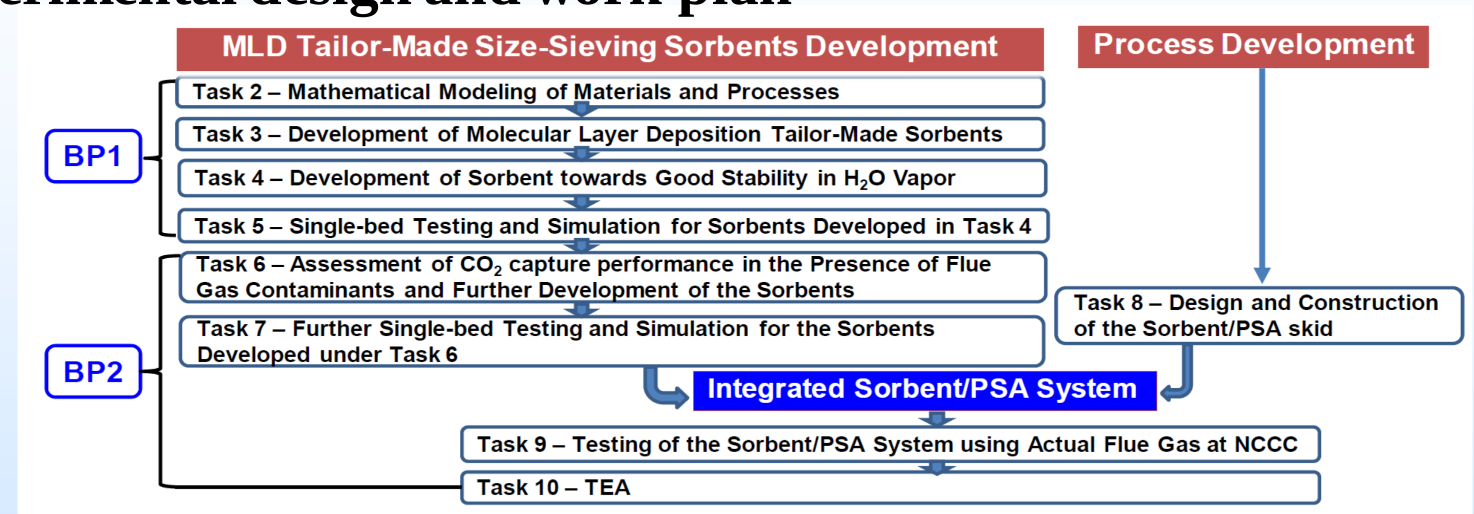


Challenges of our technology

- 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
- schedule concept

Technical Approach/Project Scope

Experimental design and work plan



Key milestones and success criteria

BP1: Achieve performance targets for the MLD tailed-made sorbents and achieve baseline PSA

Success criteria: i) MLD tailor-made sorbent showed CO_2/N_2 selectivity ≥130 with simulated flue gas containing water; the measured heat of adsorption for CO_2 is < 35 kJ/mol;
ii) 1-Bed PSA testing with MLD T-S and follow-on DAPS simulation validated that the required beds can be reduced to ≤ 48 for a 550 MWe (net) power plant.

BP2: Achieve 95% CO_2 purity and 90% CO_2 recovery with the MLD-T-S/PSAskid for actual flue gases at National Carbon Capture Center (NCCC) and validate DOE cost goal.

Success criteria: i) Sorbent/PSA skid testing at NCCC using flue gas complete, 70-90% CO_2 removal rate achieved, 95% CO_2 purity validated, and sorbent shows good stability during a 200-h continuous testing;
ii) Final TEA report issued. DOE cost goal (cost of electricity 30% less than baseline CO_2 capture approach Case B12B, or approximately \$30 per tonne of CO_2 captured) validated.

Technical Approach/Project Scope

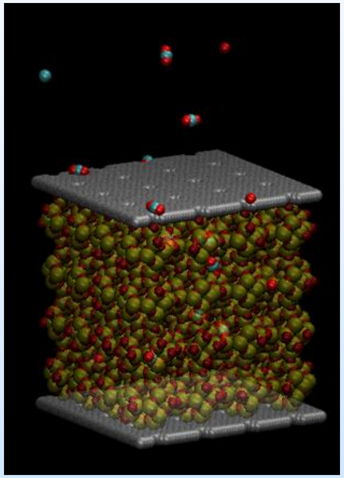
Risks and mitigation strategies

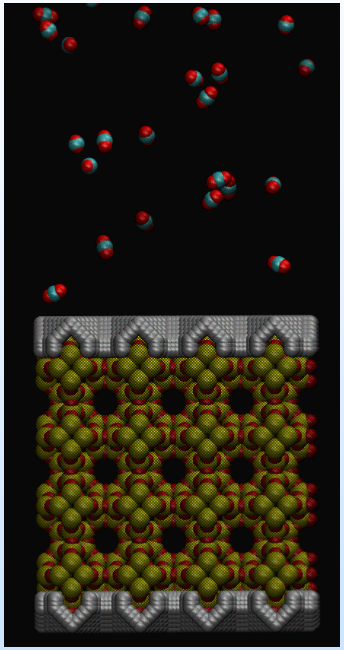
Description of Risk	Probability*	Impact*	Risk Management Mitigation and Response Strategies
Technical Risks:			
Separation selectivity of the MLD tailor-made sorbents not as high as ideal selectivity (>130)	Moderate	Moderate	• Identify new approaches to improve CO_2/N_2 separation selectivity besides the proposed approaches
Decrease in separation performance of the tailor-made sorbents in the presence of flue gas contaminants	Low	Moderate	• Identify approaches to improve stability of the sorbent in the presence of flue gas contaminants; • Measure allowable contaminant levels of the sorbent and identify flue gas clean-up requirements upstream of the CO_2 capture process; and • Design the PSA system based on the steady state performance of the sorbent in the presence of flue gas contaminants
Column pressure drop not sufficiently low when using the new PSA cycle schedule concept	Moderate	Moderate	• Improve PSA process design; and • Add more adsorption beds
95% CO_2 purity not achieved when integrating the size-sieving sorbents with the new PSA cycle schedule concept	Low	High	• Further improve performance of the MLD tailor-made sorbents; and • Based on the CO_2 purity obtained, Prof. Ritter's Research Group at USC will use their expertise to re-design the PSA process to achieve 95% CO_2 purity.
Cost of the process not in line with expected outcome	Moderate	High	• Improve manufacturing process to lower MLD sorbent costs; and • Further optimize process design of the PSA system integrated with the MLD sorbent
Resource Risks: Minimal – RPI, USC, GTI, Trimeric, and NCCC have qualified personnel and equipment in place.			
Management Risks: Minimal – RPI, USC, GTI, Trimeric, and NCCC are implementing project management systems to minimize management risks.			

Progress and Current Status of Project

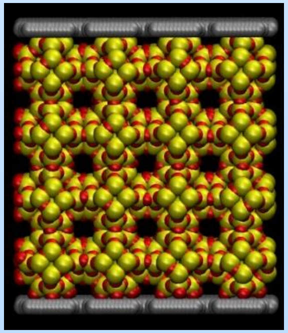
Atomistic simulations

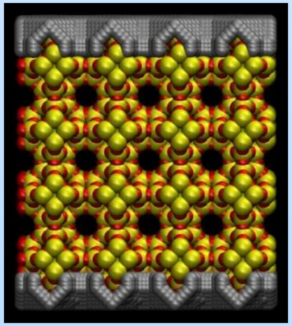
- Designed geometry to use molecular dynamic (MD) simulations to quantify preferential interfacial transport
  - Slab of base sorbent
  - MLD coating on top and bottom
  - Exposed to gas phase on top and bottom
  - Kinetics of transport of gas into middle of sorbent calculated over time





- Screened candidates for different
  - Pore size, mismatch, and shape
  - Base sorbent and exposed crystal plane





Atomistic simulations-cont'

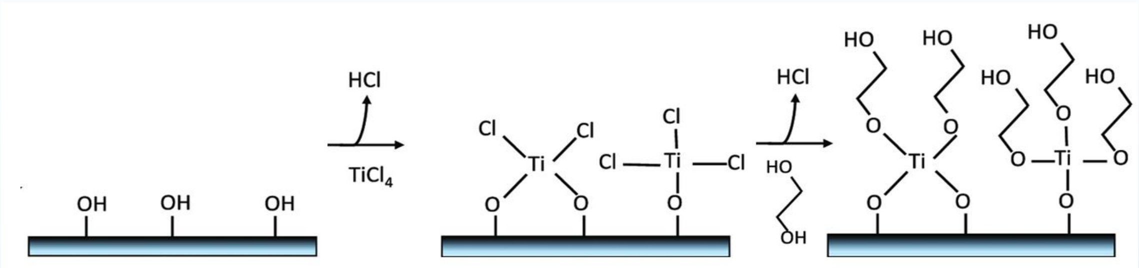
- Best candidates can help direct strategies to design better modified sorbents

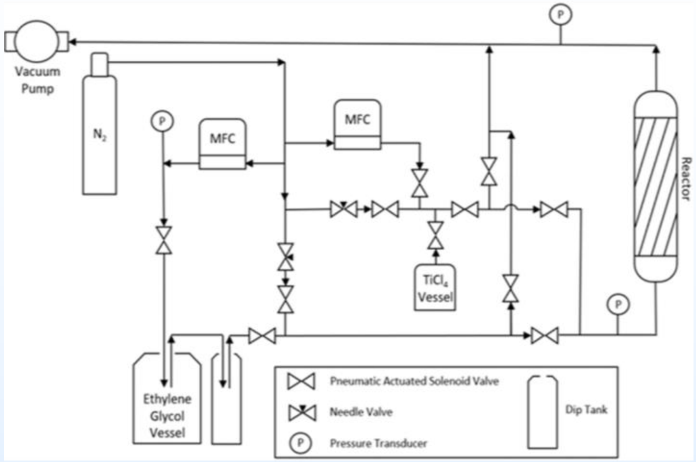
	Original 5A				Cut 5A		13X	
	Flat 0.4nm		Taper 0.6nm		Flat 0.4nm		Flat 0.4nm	
	Aligned	Misalign by 0.6nm	Aligned	Misalign by 0.3nm	Aligned	Misalign by 0.3nm	Aligned	Misalign by 1.2nm
Selectivity divided by case with no MLD	1.4	**4.3**	3.1	**5.1**	0.5	**1.2**	0.3	**2.9**

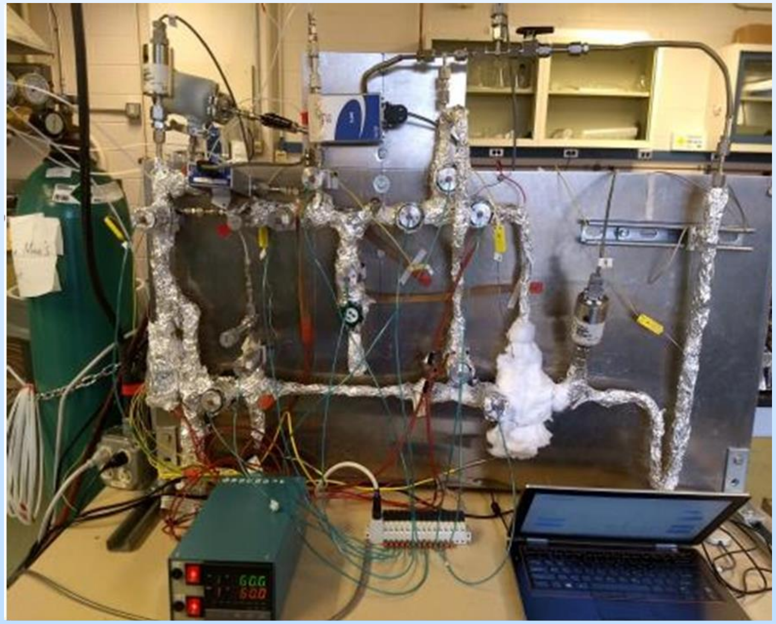
- Synergistic opportunities and future testing
  - Use simulations to understand modifications within interior of base sorbents

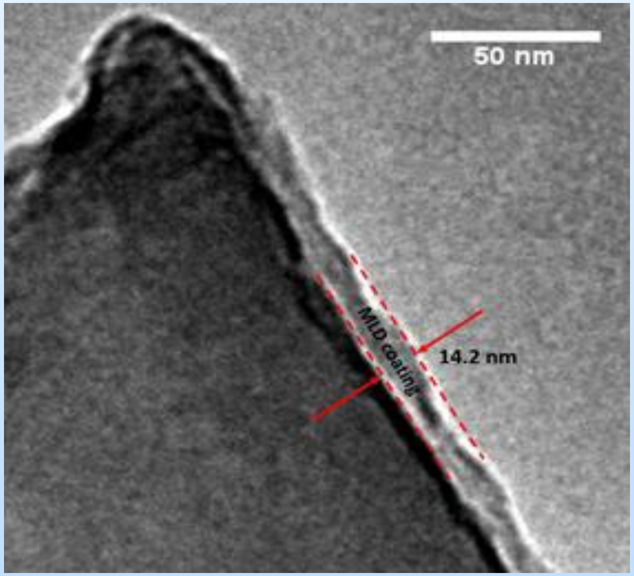
UB equipment description

1. Flow MLD system



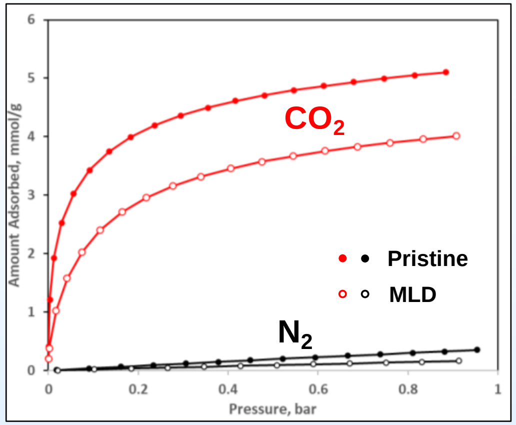




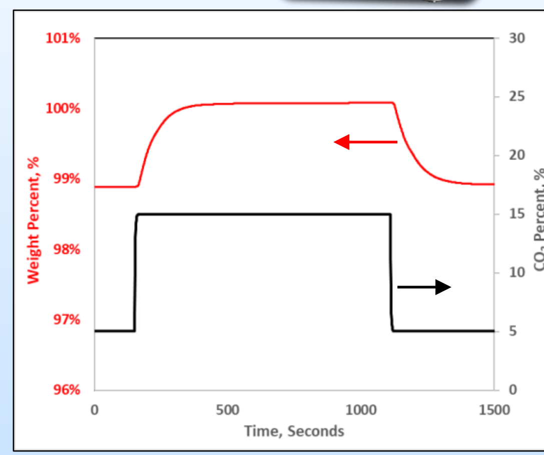


2. Single-component adsorption capacity, mixture capacity, and working capacity measurement systems

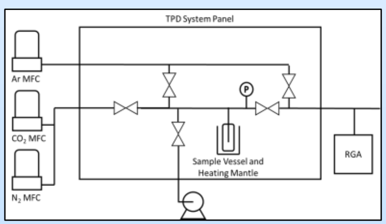
Single-component isotherm measurement system

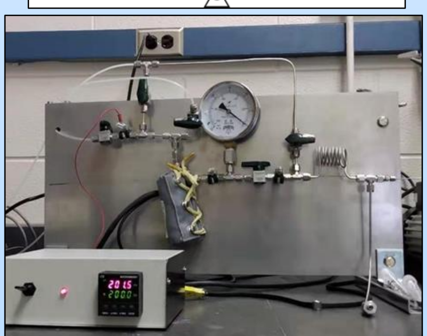


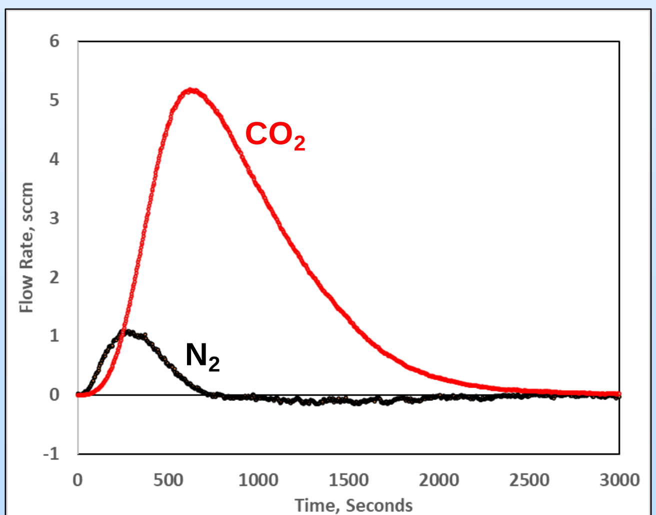
TGA: Cyclic CO_2/N_2 working capacity



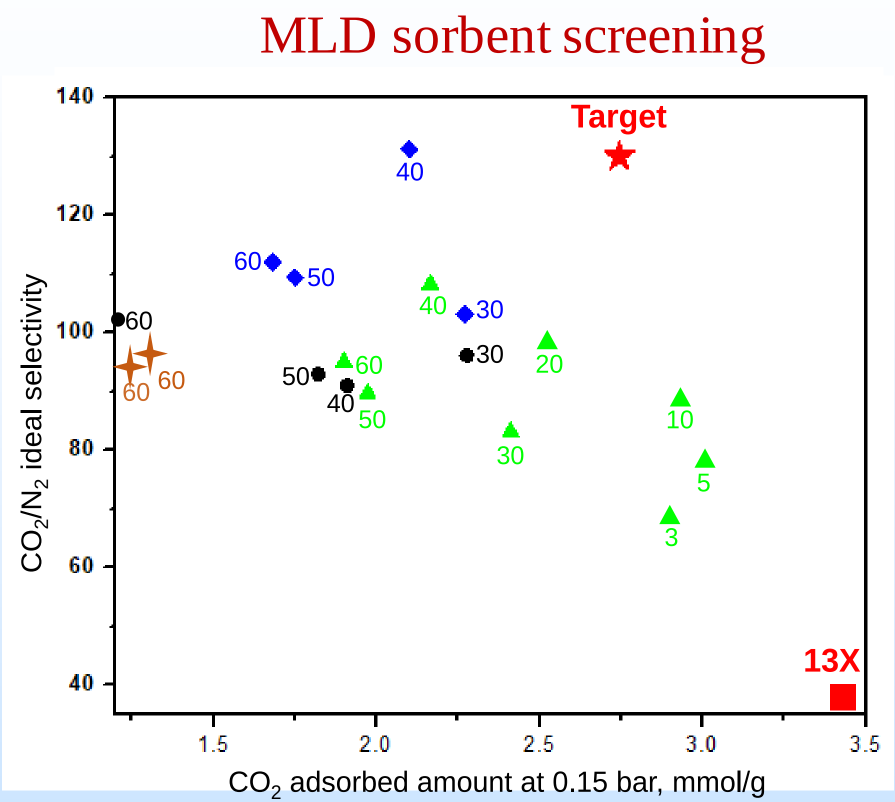
TPD-MS system: Mixture capacity

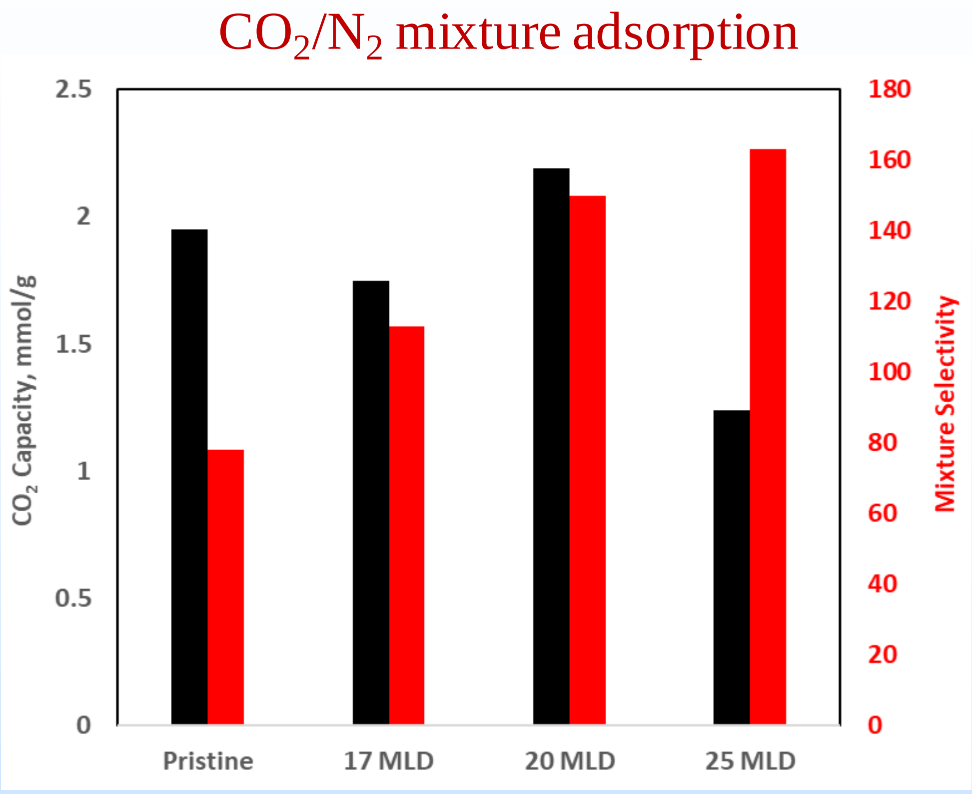






Sorbent optimization





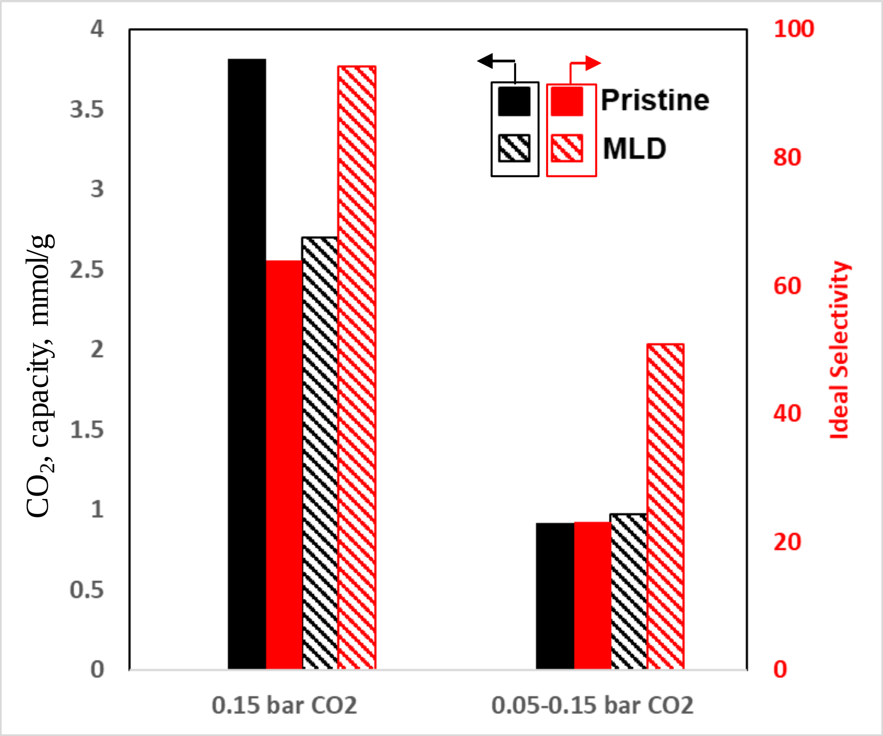
Note: numbers are MLD cycles

<u>Sorbent optimization:</u>

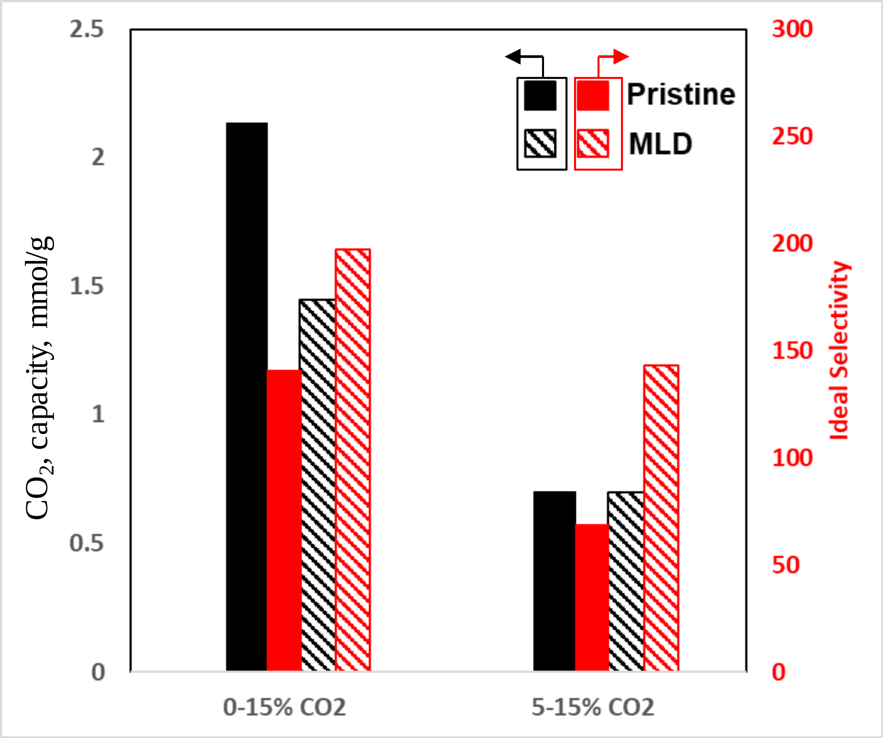
- Screened MLD modified samples with CO_2 and N_2 single-component isotherms
- Established relationship between MLD and CO_2 capacity and selectivity

Key findings of optimized sorbent

Single-component isotherm data



TGA cyclic data



<u>Optimized sorbent properties:</u>

- Maintain high CO_2 capacity under relevant PSA conditions (0.05 to 0.15 bar)
- Dramatically improved CO_2/N_2 selectivity
  - Reduced operating costs due to reduced PSA purification steps

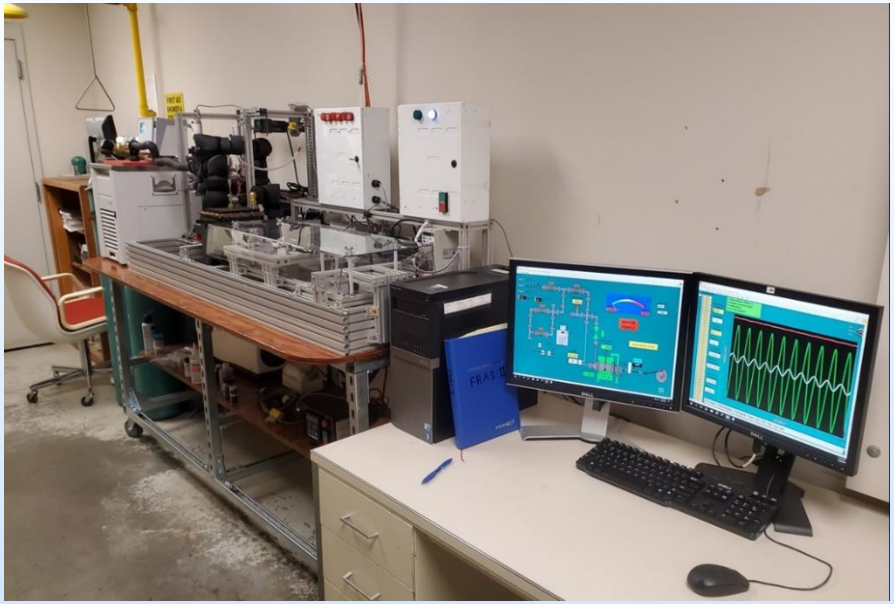
Three best large scale VSA systems simulated to date via DAPS

Achievement: The three-best simulated VSA systems that require the least number of beds are an 8-unit 10-bed 13-step VSA cycle (i.e., an 80 bed VSA system), a 2-unit 10-bed 13-step VSA cycle (i.e., a 20 bed VSA system) and an 8-unit 13-bed 20-step VSA cycle (i.e., a 104 bed VSA system).

- 80 bed VSA System Process Performance: 95.9 vol% CO_2 purity, 91.8% CO_2 recovery and 448 ppm O_2 concentration in the heavy product, with 23.2 kJ/mol of energy consumed and 127 L(STP)/h/kg throughput.
- 20 bed VSA System Process Performance: 99.0 vol% CO_2 purity, 90.0% CO_2 recovery and 59 ppm O_2 concentration in the heavy product, with 25.3 kJ/mol of energy consumed and 127 L(STP)/h/kg throughput. To reduce the number of beds from 80 to 20, the particle diameter of the adsorbent was increased from 3 mm (commercial) to 9 mm (potentially commercial), with only a 9% increase in the energy penalty.
- 104 bed VSA System Process Performance: 99.4 vol% CO_2 purity, 90.1% CO_2 recovery and 6.5 ppm O_2 concentration in the heavy product, with 31.8 kJ/mol of energy consumed and 102 L(STP)/h/kg throughput. To reach the 10 ppm limit on the O_2 content, the number of beds increased from 80 to 104, with a 37% increase in the energy penalty.

USC Experimental systems designed and constructed at USC

100 Hz Volumetric Frequency Response (VFR) System



Achievement: A unique100 Hz volumetric 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.

6-Bed PSA System: Modified and Upgraded for This Project

Achievement: A unique 6-bed PSA system was designed, constructed and became operational at USC. It was modified and upgraded operate with 2 feed or 2 light reflux beds. Start-up and troubleshooting have commenced, with preliminary results obtained soon.

Plans for future testing/development/ commercialization

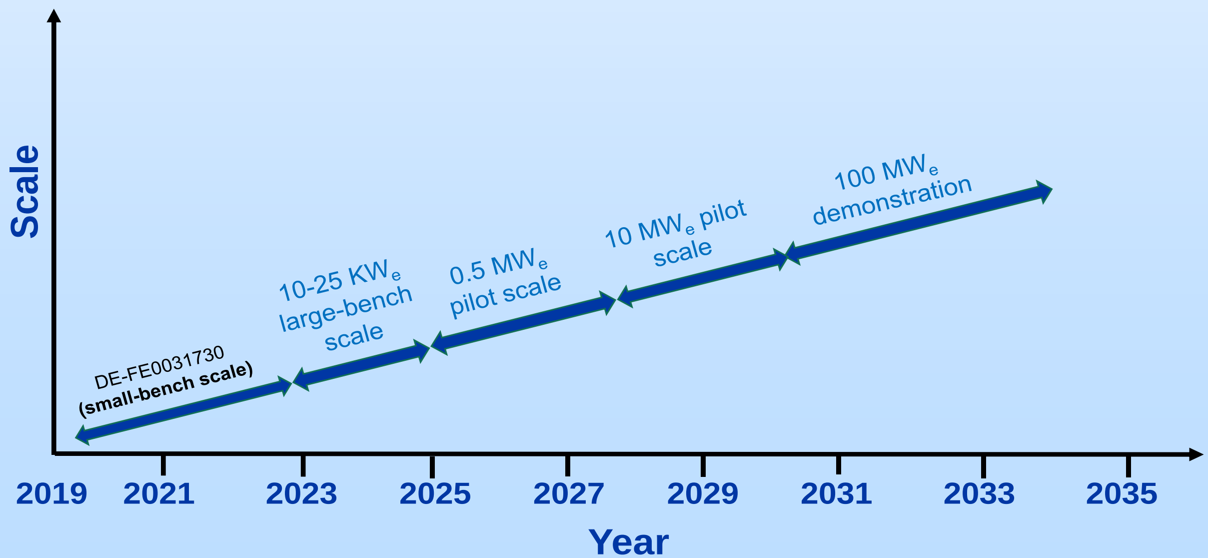
In this project

<u>MLD modified sorbents</u>: Further optimize MLD and calcination conditions to improve sorbent properties and conduct systematic evaluation of sorbent performance with the presence of water and contaminants.

<u>PSA</u>: Further DAPS simulation and 4-bed PSA testing; design and construction of a MLD-T-S/PSA system.

<u>TEA</u>: Conduct detailed techno-economic analysis based on experimental results.

After this project and scale-up potential

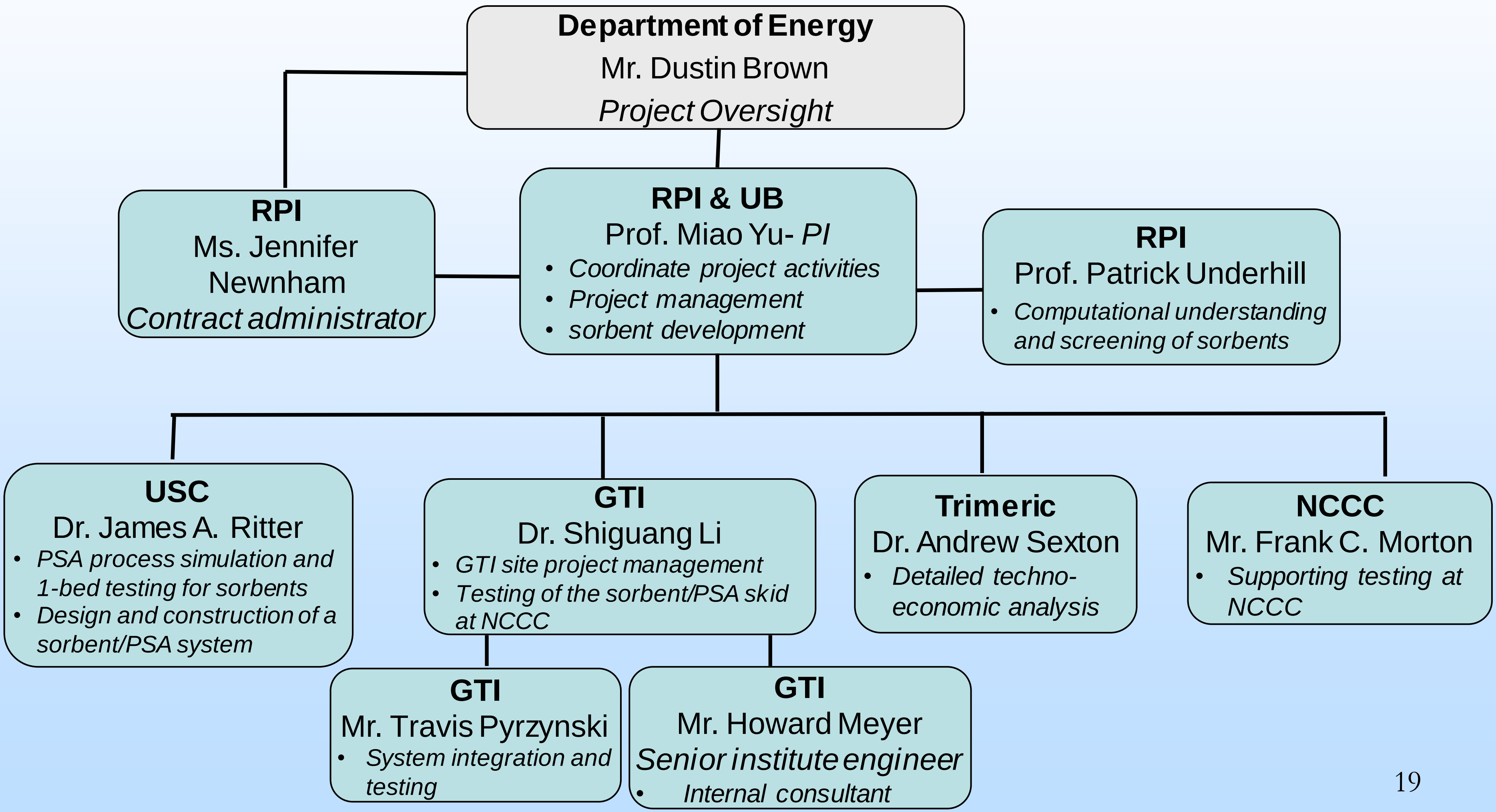


Summary

- 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 might be possible to have a 2-unit 10-bed 13-step 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.

Appendix

Organization Chart



Gantt Chart

ID	Task	Subtask	Milestone	Task Name	Start	Finish	Group
1				Budget Period 1	Tue 10/1/19	Wed 3/31/21	
2	1.0			Project Management and Planning	Tue 10/1/19	Fri 9/30/22	RPI, GTI, USC
3			1.1	Updated Project Management Plan	Wed 10/30/19	Wed 10/30/19	RPI, GTI, USC
4			1.2	Kickoff Meeting	Wed 12/30/20	Wed 12/30/20	RPI, GTI, USC
5			1.3	Technology maturation plan submitted	Wed 12/30/20	Wed 12/30/20	RPI, GTI, USC
6			1.4	Continuation application for BP2 submitted	Thu 12/31/20	Thu 12/31/20	RPI, GTI, USC
7			1.5	Submit BP1 Report	Fri 4/30/21	Fri 4/30/21	RPI, GTI, USC
8			1.6	Submit Final Technical Report	Fri 12/30/22	Fri 12/30/22	RPI, GTI, USC
9	2.0			Mathematical Modeling	Tue 10/1/19	Tue 6/30/20	RPI, USC
10		2.1		Computational Screening of MLD Tailor-made Size-sieving Sorbents	Tue 10/1/19	Tue 6/30/20	RPI
11			2.1	> three (3) promising sorbent materials screened by computational simulation	Tue 6/30/20	Tue 6/30/20	RPI
12		2.2		PSA Process Modeling with the New PSA Cycle Schedule Concept and Zeolite 13X	Tue 10/1/19	Tue 6/30/20	USC
13			2.2	Promising modeling with the new PSA cycle concept showed the number of beds required for a 550 MWe (new) power plant can be reduced from 240 to 48	Tue 6/30/20	Tue 6/30/20	USC
14	3.0			Development of Molecular Layer Deposition Tailor-made Sorbents	Tue 10/1/19	Tue 6/30/20	RPI
15			3.1	<30 nm thick MLD coatings deposited on screened base sorbents	Tue 3/31/20	Tue 3/31/20	RPI
16			3.2	MLD sorbent showed CO_2/N_2 selectivity>130 at 20 oC, CO_2 partial pressure of 0.15 bar, and N_2 partial pressure of 0.85 bar. The measured heat of adsorption for CO_2 is <35 kJ/mol	Tue 6/30/20	Tue 6/30/20	RPI
17	4.0			Development of Sorbent towards Good Stability in the Presence of Water Vapor	Wed 7/1/20	Wed 3/31/21	RPI
18			4.1	MLD sorbent showed CO_2/N_2 selectivity >130 with simulated flue gas containing water; effective desorption method to recover >80% of the CO_2 capacity	Wed 3/31/21	Wed 3/31/21	RPI
19	5.0			Single-bed Testing and Simulation for the Sorbents Development under Task 4	Wed 7/1/20	Wed 3/31/21	USC
20			5.1	1-Bed PSA testing with MLD sorbent and follow-on DAPS simulation validated that the required beds can be reduced to ≤ 48 for a 550 MWe (net) power plant.	Wed 3/31/21	Wed 3/31/21	USC
21				Budget Period 2	Thu 4/1/21	Fri 12/31/21	
22	6.0			Assessment of CO_2 capture performance in the Presence of Flue Gas Contaminants and Further	Thu 4/1/21	Fri 12/31/21	RPI
23			6.1	Allowable contaminant (including O_2, Ar, SO_2 and NO_2) levels identified	Fri 12/31/21	Fri 12/31/21	RPI
24	7.0			Further Single-bed Testing and Simulation for the Sorbents Development under Task 6	Thu 4/1/21	Fri 12/31/21	USC
25			7.1	Further simulation and 1-bed PSA testing with improved sorbents validated that CO_2 capture with 95% CO_2 purity and a cost of ~$30 per tonne of CO_2 captured can be achieved	Fri 12/31/21	Fri 12/31/21	USC
26	8.0			Design and Construction of a Sorbent System	Tue 6/1/21	Fri 12/31/21	GTI, USC
27		8.1		Determination of Required Pretreatment	Tue 6/1/21	Thu 9/30/21	GTI
28		8.2		Process Simulation and Design	Tue 6/1/21	Thu 9/30/21	USC
29		8.3		Construction of the S3 Skid	Fri 10/1/21	Fri 12/31/21	USC
30			8.1	Construction of sorbent/PSA skid complete; 95% CO_2 purity achieved when testing the constructed skid using simulated flue gas	Fri 12/31/21	Fri 12/31/21	USC
31	9.0			Testing of skid at NCCC using Actual Flue Gas	Sat 1/1/22	Fri 9/30/22	RPI, GTI, USC
32		9.1		Installation on On-site Shakedown	Sat 1/1/22	Mon 2/28/22	GTI
33			9.1	Commissioning complete and sorbent/PSA skid system ready for testing at NCCC	Mon 2/28/22	Mon 2/28/22	GTI
34		9.2		Field testing Sorbent Material Support	Sat 1/1/22	Fri 9/30/22	RPI
35			9.2	500 to 1000 grams of MLD tailor made sorbent shipped to NCCC	Mon 2/28/22	Mon 2/28/22	RPI
36		9.3		Field testing Process Support	Sat 1/1/22	Fri 9/30/22	USC
37			9.3	Skid testing at NCCC complete, 70-90% CO_2 removal rate achieved, 95% CO_2 purity validated, and system shows good stability during a 200-h continuous testing	Fri 9/30/22	Fri 9/30/22	RPI, GTI, USC
38		9.4		CO_2 Capture Testing of the System at NCCC using Actual Flue Gas	Tue 3/1/22	Fri 9/30/22	GTI
39	10.0			Detailed Techno-Economic Analysis	Wed 6/1/22	Fri 9/30/22	Trimeric
40			10.1	Issue techno-economic analysis report	Fri 9/30/22	Fri 9/30/22	Trimeric