Overall Project Objectives

- design, develop and demonstrate a bench-scale process for the efficient and cost effective separation of CO$_2$ from flue gas using Pressure Swing Adsorption (PSA)
- goal to reduce energy consumption, capital costs, and environmental burdens with novel PSA cycle/flow sheet designs
- applicable to both large (500-1000 MW) and small (5-50 MW) capacity power plants, and industries with 10 to 100 times less CO$_2$ production

Process simulations and experiments; structured adsorbent material development, CFDs and experiments; and complete flow sheet analyses being used for demonstrating and validating the concepts.
The Team

- Grace (Hoefer)
- Catacel (Cirjak)
- USC (Ritter & Ebner)
- Battelle (Saunders & Swickrath)

- Thin film materials development and characterization
- Specification
- Technology development and process integration
- Investigation
- Materials characterization, and process modeling and experimentation
- Validation
PSA Technology Advantages

- established, very large scale technology for other applications
- needs no steam or water; only electricity
- tolerant to trace contaminants; possibly with use of guard or layered beds
- zeolite adsorbent commercial and widely available
- increase in COE lower than other capture technologies
- beds can be installed under a parking lot
PSA Technology Challenges

- energy intensive, but better than today’s amines; possibly overcome by novel designs
- today, very large beds required → implies large pressure drop → more power; possibly overcome by structured adsorbents and faster cycling
- large footprint; possibly overcome by underground installation and faster cycling → smaller beds
- high capital cost; possibly overcome by faster cycling → smaller beds
Key PSA Technology Project Challenge

- although a commercial tri-sieve zeolite could be used today in an efficient PSA cycle, it would only minimize to some extent the pressure drop issues, but not the adsorbent attrition and mass transfer issues

- key challenge is to develop a structured adsorbent around an efficient PSA cycle that exhibits a high enough packing density to allow the fastest possible cycling rate (\(\rightarrow\) smallest possible beds), while improving pressure drop and mass transfer issues and eliminating attrition issues
Where are we going?
Scale of PSA System for CO$_2$ Capture from 500 MW Power Plant

Is it possible to achieve a 1/10th volume reduction?

- increase working capacity 10 fold (herculean)
- operate at 1/10$^{th}$ cycle time (achievable)
- known as rapid PSA

although rapid PSA offers potential for a low-cost solution for CO$_2$ capture, the extent of size reduction achievable is, at the moment, unknown
QuestAir H-6200 Rapid PSA-Installed at ExxonMobil Facility

H₂ Production Rapid PSA
~ 12,000 Nm³/h/module

H₂ Production
Conventional PSA
~ 20,000 Nm³/h

A 500 MW plant produces ~ 33,000 Nm³/h at > 30 times lower pressure!

Two of Questair’s modules do 20% better than this 6-bed PSA system and are much smaller.
Where are we now after completing first year?
Preliminary Technical and Economic Feasibility Study

Overall Outcome
Significant Outcomes from Year 1

- developed PSA cycle and process flow sheet with less than 35% LCOE increase; based on completed *preliminary technical and economic feasibility study*

- demonstrated zeolite crystals can be coated onto basic metal structure with at least 50 mm thick coating; *suggests it may be possible to achieve even 100 to 150 mm coatings, if needed*

- demonstrated Catacel core structures can be made with up to 400 cells per square inch (cpsi); *makes goal of achieving 600 cpsi, possibly even 800 cpsi, within reach*

- demonstrated needed limit of < 20 kPa/m pressure drop through 400 cpsi core at very high velocities up to 25 m/s; *pressure drop limit utilized in preliminary technical and economic feasibility study*
Significant Outcomes from Year 1

- Predicted pressure drop through Catacel core nearly quantitatively using CFD model with no adjustable parameters; paves way to fabricate even more optimum core structures using computational tools.

- Demonstrated, via PSA process simulation, possibly lowest energy, highest feed throughput PSA cycle for CO₂ capture; amazing when considering bulk density reduced from 710 kg/m³ (typical for packed bed of zeolite beads) to 400 kg/m³ (entirely feasible with Catacel core).

- PSA cycle boasts feed throughput of around 3,000 L(STP)/hr/kg and separations energy < 18 kJ/mol CO₂ captured.
How did we get to this point?
**CO₂ Isotherm on Adsorbent and Dual Process Langmuir Fit**

Dual Process Langmuir (DPL) Isotherm

\[
\begin{align*}
    n_i &= \left( \frac{n_{1,i}^s P_Y b_{1,i}}{1 + P_Y b_{1,i}} \right)_{site-1} + \left( \frac{n_{2,i}^s P_Y b_{2,i}}{1 + P_Y b_{2,i}} \right)_{site-2} \\
    n_{j,i}^s &= n_{j,i}^{s0} + n_{j,i}^{st} T \\
    b_{j,i} &= b_{j,i}^0 \exp \left( \frac{B_{j,i}}{T} \right)
\end{align*}
\]
N\textsubscript{2} Isotherm on Adsorbent and Dual Process Langmuir Fit

Dual Process Langmuir (DPL) Isotherm

\[ n_i = \left( \frac{n_{1,i}^s P y_i b_{1,i}}{1 + P y_i b_{1,i}} \right)_{\text{site-1}} + \left( \frac{n_{2,i}^s P y_i b_{2,i}}{1 + P y_i b_{2,i}} \right)_{\text{site-2}} \]

\[ n_{j,i}^s = n_{j,i}^{s0} + n_{j,i}^{st} T \]

\[ b_{j,i} = b_{j,i}^0 \exp \left( \frac{B_{j,i}}{T} \right) \]
O₂ Isotherm on Adsorbent and Dual Process Langmuir Fit

Dual Process Langmuir (DPL) Isotherm

\[ n_i = \left( \frac{n_{i,1}^s P_i b_{i,1}}{1 + P_i b_{i,1}} \right)_{site-1} + \left( \frac{n_{i,2}^s P_i b_{i,2}}{1 + P_i b_{i,2}} \right)_{site-2} \]

\[ n_{j,i}^s = n_{j,i}^{s0} + n_{j,i}^{st} T \]

\[ b_{j,i} = b_{j,i}^0 \exp \left( \frac{B_{j,i}}{T} \right) \]
Zeolite Coated Metal Foil

- preliminary fabrication
- coated on flat foil coupon at 30 mg/in²
- coating passed Catacel adhesion test
- goal: to make coating 100 – 150 µm thick
Rapid Adsorbent Characterization

- commercial zeolites
  - activation at 350 °C overnight in N₂
  - cycling at 90 °C
    - 2 min adsorption in 15% CO₂-N₂
    - 2 min desorption in 100% N₂
  - P_T = 1 atm
TGA Runs at 70 °C
Cycle: 100 s Stream with CO$_2$/100 s Pure N$_2$

15% CO$_2$ in N$_2$/100% N$_2$
100% CO$_2$/100% N$_2$

Working Capacities of washcoat between 50 and 100% higher than commercial beads!
Corrugated Catacel Cores

1” x 6” x 400 cells/in²

goal: to increase corrugation to 800 cpsi
Structured and Beaded Media Pressure Drop

Pressure Drop Apparatus

\[ Q_{\text{max}} = 1000 \text{ SLPM} \]

\[ \Delta P_{\text{max}} = 30, 70 \text{ or } 140 \text{ in H}_2\text{O} \]

goal: \( \Delta P_{\text{max}} < 20 \text{ kPa/m} \) at design velocity of 20 m/s
Volumetric Frequency Response Apparatus

- Frequency range: $5 \times 10^{-5}$ to 10 Hz
- 100 g adsorbent
- 80 °C and 0.2 atm
Volumetric Frequency Response Results

Correlation of Mass Transfer Models with Experimental Data

System and Conditions
CO\textsubscript{2}-commercial zeolite beads
T = 25 °C
P = 102, 185, or 744 torr
f = 5\times10^{-5} to 10 Hz

Mass Transfer Models
- Macropore Diffusion
- Micropore Diffusion
- Macropore Convection

only macropore diffusion model unequivocally fits the data over the pressure range investigated
1-Bed Rapid PSA Apparatus

- 0.1 to 2 Hz
- 100 g adsorbent
- 80 °C and 0.1 atm
1-Bed Rapid PSA Schematic
Two-Step CO$_2$ and N$_2$ Cycling Experiments

Information Obtained

a) Determination of Valve C$_v$

b) Determination of excluded volume

c) Validation of Single Component Isotherms

d) Validation Adsorption/Desorption Mass Transfer Coefficients
Pure Gas Cycling in 1-Bed Rapid PSA System

CO$_2$ on Beaded Zeolite at 22 °C

Pressure [kPa]

Time [sec]

Feed Tank

Bed

Model

Vacuum Tank

t$_s$ = 3 s
Pure Gas Cycling in 1-Bed Rapid PSA System

\( \text{CO}_2 \) on Beaded Zeolite at 22 °C

- \( t_s = 3 \text{ s} \)
- \( t_s = 2 \text{ s} \)
- \( t_s = 1 \text{ s} \)
- \( t_s = 0.5 \text{ s} \)
Comparison of Mass Transfer Coefficients

CO₂ on Beaded Zeolite

Volumetric Frequency Response Apparatus (25 °C)

<table>
<thead>
<tr>
<th>$P$ (Torr)</th>
<th>$hA$ (kJ/K/s)</th>
<th>$D_p/R_p^2$ (s⁻¹)</th>
<th>$k_{LDF}$ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>744</td>
<td>$1.7 \times 10^{-4}$</td>
<td>3.32</td>
<td>1.94</td>
</tr>
<tr>
<td>185</td>
<td>$1.7 \times 10^{-4}$</td>
<td>3.32</td>
<td>0.38</td>
</tr>
<tr>
<td>102</td>
<td>$1.7 \times 10^{-4}$</td>
<td>3.32</td>
<td>0.18</td>
</tr>
</tbody>
</table>

1-Bed Rapid PSA System (22 °C)

$k_{LDF} = 1.87$ s⁻¹
Typical Cycle Steps for PSA Operation

Snapshot of Multi-Bed PSA System

- **PH**
- **T**
- **PI1**
- **PI2**
- **PL**
- **PI1**
- **PH**
- **CO₂ Depleted Product**
- **CO₂ Rich Product**

- **Feed Gas**
- **Pressurization**
- **Heavy Reflux**
- **Equalization**
- **Co-Current**
- **Current Depressurization**
- **Light Reflux**
- **Equalization**
- **Light Product Pressurization**

\[ 0 \geq a, b, c, d, e \geq 1 \]

\[ 0 \geq \alpha, \beta, \gamma \geq 1 \]
PSA Process Conditions for DAPS*

**Feed Composition (Dry)**

\[ y_{CO2} = 0.1592 \]
\[ y_{N2} = 0.8029 \]
\[ y_{O2} = 0.0379 \]

**Mass Transfer Coefficients**

\[ k_{CO2} = 10.0 \text{ s}^{-1} \]
\[ k_{N2} = 1.0 \text{ s}^{-1} \]
\[ k_{O2} = 1.0 \text{ s}^{-1} \]

**Process Conditions**

\[ P_H = 120 \text{ kPa} \]
\[ P_L = 5 \text{ kPa} \]
\[ T_F = 75 \text{ °C} \]
\[ h = 0.0 \text{ W/m}^2 \text{ K (adiabatic)} \]
\[ t_c = 120 \text{ s} \]
\[ \theta = 2,600 - 3,100 \text{ L(STP)/kg/hr} \]

**Structured Bed Properties**

\[ L_b = 0.125 \text{ m} \]
\[ d_b = 0.09848 \text{ m} \]
\[ \rho_b = 400 \text{ kg/m}^3 \]
\[ \varepsilon_b = 0.64 \]

* DAPS: dynamic adsorption process simulator
DAPS Results of Bench Scale PSA Process

this is a low energy, high feed throughput PSA cycle for CO₂ capture that meets the DOE criteria, especially when considering the bed density is only 400 kg/m³
Motivation to Compare Solid Amine to Zeolite

- sorbents for post-combustion CO\textsubscript{2} capture
  - zeolites
    - have sufficient working capacity for CO\textsubscript{2}
    - not H\textsubscript{2}O tolerant: \textit{must be removed prior to PSA unit!}
  - solid amine sorbents
    - commercial amines grafted or immobilized within large pores of a high surface area support like silica gel
    - have sufficient working capacity for CO\textsubscript{2}
    - H\textsubscript{2}O tolerant: \textit{will it pass through the PSA unit with N\textsubscript{2}?}

solid amine sorbents have \textbf{NOT} been studied extensively for CO\textsubscript{2} capture from flue gas by PSA
CARiACT G10 Solid Amine Sorbent*  
- **substrate:** CARiACT G10 silicon dioxide (Fuji Silysia)  
  - surface area: 300 m²/g  
  - pore volume: 1.3 ml/g  
  - particle size: 75-150 µm  
- **polyethylenimine (PEI) (MN 423 Aldrich)**  
- 40 wt% PEI physically adsorbed (immobilized) onto G10

*Gray et al., Energy Fuels, 23 (2009) 4840.
Typical Cycle Steps for PSA Operation

Snapshot of Multi-Bed PSA System

0 \geq a, b, c, d, e \geq 1

0 \geq \alpha, \beta, \gamma \geq 1
### Comparison of PSA Process Performance

#### PEI vs Zeolite

<table>
<thead>
<tr>
<th></th>
<th>PEI</th>
<th>Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{cyc}$ (s)</td>
<td>300</td>
<td>120</td>
</tr>
<tr>
<td>Feed Throughput (L(STP)/kg/hr)</td>
<td>224</td>
<td>2870</td>
</tr>
<tr>
<td>CO$_2$ Recovery (%)</td>
<td>91.0</td>
<td>91.8</td>
</tr>
<tr>
<td>CO$_2$ Purity (%)</td>
<td>95.2</td>
<td>95.8</td>
</tr>
<tr>
<td>Energy (kJ/mol CO$_2$ Recovered)</td>
<td>34.2</td>
<td>17.6</td>
</tr>
</tbody>
</table>

For the same process performance and conditions (much different PSA cycle), zeolite beds are 10X smaller than PEI beds with PEI consuming 2X the energy => need amine with faster desorption kinetics.
Conclusions

- Metal foil coated with commercial zeolite and corresponding low pressure drop corrugated structure showing much promise for CO₂ capture from flue gas.
- Frequency response and 1-bed rapid cycling experiments both show very fast mass transfer rates of CO₂ in beaded zeolite.
- Very low energy, very high feed throughput PSA cycle configuration developed using validated DAPS.
- Novel hybrid adsorption process flow sheet resulted in < 35% COE increase.
- Shorter PSA cycle times showing potential to significantly reduce column size and thus plant footprint.
- PEI solid amine sorbent showing potential in PSA process; it may allow H₂O to pass through bed with N₂; need better kinetics to make PSA process performance more like zeolites.
Acknowledgements

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Thank You!