Combined Pressure and Temperature Contrast and Surface-enhanced Separation of Carbon-dioxide for Post-combustion Carbon Capture

DOE Project # DE0007531
Project Manager: Ms. Elaine Everitt

Dr. Michael S. Wong
Professor in Chemical and Biomolecular Engineering, Chemistry and Environmental Engineering

Rice University
NETL CO₂ Capture Technology Meeting
July 10th, 2013
• About Rice University
• Project Overview
• Project Team
• Combined Pressure and Temperature Contrast and Surface-enhanced Separation of Carbon-dioxide
• Selection of materials
• Integrated absorber and stripper – A proof-of-concept demonstration
• Substrate functionalization
• Project Budget
Rice University

- Located in Houston, TX
- 295-acre, heavily wooded campus
- Ranked 17th in the US and in the top 100 in the world
- 650 full-time faculty, 3500 undergraduates and 2300 graduate students
- Chemical and Biomolecular Engineering program, 13 faculty members, 70 graduate students
- Chemistry program, 38 faculty members, 130 graduate students
Project Team

**Project Director**

George Hirasaki  
A J. Hartsook Professor in Chemical & Biomolecular Engineering

**Co-Project Investigator**

Michael Wong  
Professor in Chemical & Biomolecular Engineering & Chemistry

**Co-Project Investigator**

Kenneth Cox  
Professor-in-practice in Chemical and Biomolecular Engineering

**Co-Project Investigator**

Edward Billups  
Professor in Chemistry

**Postdoctoral Associate**

Jerimiah Forsythe  
PhD, Chemistry (LSU, 2011)

**Undergrad Researcher**

Colin Shaw  
Chemical & Biomolecular Engineering

**Past member**

Sumedh Warudkar  
PhD (April 2013)
• Project funding under DOE agreement – DE-FE0007531
• Total project cost - $960,811 over three years. Federal share: $768,647 | Non-federal share: $192,164
• Contract awarded executed October 2011
• Project duration: 10/2011 – 9/2014
• Project objective - Performance of bench-scale R&D to demonstrate and develop Rice University’s “combined pressure and temperature contrast and surface-enhanced separation of CO₂ for post-combustion carbon capture to meet DOE’s goal of at least 90% CO₂ removal at no more than 35% increase in the cost of electricity”
Reference Carbon Capture Scenario

- Goals set by the DOE:
- Using 2\textsuperscript{nd} generation technologies in post-combustion capture:
  - Demonstrate 90% CO\textsubscript{2} capture
  - Less than 35% increase in COE
  - Less than $40/tonne with carbon capture utilization and storage
- Estimates based off of Case 10: post-capture subcritical unit
  - 550 MW coal-fired power plant with a net plant efficiency of 26.2%
Our Approach

**COMBINED PRESSURE, TEMPERATURE CONTRAST, AND SURFACE-ENHANCED SEPARATION OF CO₂**

- Functionalized substrates
- Amine Absorption for Carbon Capture
- Vacuum Stripping
- Integrated Absorber-Stripper

Waste Heat
Combining the Absorber and Desorber Units

A comparison of the conventional amine system with the proposed ‘combined’ process

Process Schematic
Integrated Absorber-Stripper

Lean Absorbent (in) → Low CO₂ gas (out) → Moist CO₂

Absorption Side
Desorption Side
Heat Exchanger

Cooled Flue gas → Lean Absorbent (out) → Reboiler

Steam
Selection of Foam Material

Ceramic Foam
- Low bulk density
- Very high macro-porosity (80%-90%)
- Very high geometric surface area
- Regulated pore-size
- Low pressure drop
- High structural uniformity
- Ease of reproducibility of structure

<table>
<thead>
<tr>
<th>Structure</th>
<th>S (m²/m³)</th>
<th>Porosity (ε)</th>
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</thead>
<tbody>
<tr>
<td>5 mm packing spheres</td>
<td>600</td>
<td>0.392</td>
</tr>
<tr>
<td>Raschig ceramic rings, 25 mm</td>
<td>200¹</td>
<td>0.646</td>
</tr>
<tr>
<td>Corrugated metal structured packing (AceChemPack) – 500 x/y</td>
<td>500³</td>
<td>0.93</td>
</tr>
<tr>
<td>30-PPI -Al₂O₃ foam, no washcoat</td>
<td>3360²</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Figure: Commercial Sample of Ceramic foam

SEM Micrographs of a Commercial Ceramic Foam Sample

**Figure:** Scanning Electron Micrographs of 40-ppi Ceramic Foam (a) 50x (b) 280x (c) 290x (d) 11,000x
## Material Properties

### Ceramic Foam

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Material</td>
<td>99.5 % (α-Al₂O₃)</td>
</tr>
<tr>
<td>Supplier</td>
<td>ASK-Chemicals, USA</td>
</tr>
<tr>
<td>Dimensions</td>
<td>For absorption studies: L = 2”, φ = 1”</td>
</tr>
<tr>
<td></td>
<td>For stainless steel prototype: 8” x 4” x 1”</td>
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</table>

### Porous Ceramic Membrane

<table>
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<th>Property</th>
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<tr>
<td>Material</td>
<td>99.5 % (α-Al₂O₃)</td>
</tr>
<tr>
<td>Supplier</td>
<td>Refractron Inc., USA</td>
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<tr>
<td>Dimensions</td>
<td>12” x 6” x 1”</td>
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<tr>
<td>Permeability &amp; Gas Entry Pressure</td>
<td>5.37 Darcy</td>
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</table>

### Gas-Liquid Separator Polymer Membrane

<table>
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<th>Value</th>
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<tbody>
<tr>
<td>Material</td>
<td>Polyethersulfone (Hydrophilic)</td>
</tr>
<tr>
<td>Supplier</td>
<td>Pall LifeSciences Corporation, USA</td>
</tr>
<tr>
<td>Dimensions</td>
<td>8” x 8”</td>
</tr>
<tr>
<td>Permeability &amp; Gas Entry Pressure</td>
<td>0.32–1.52 Darcy</td>
</tr>
</tbody>
</table>
Experimental Setup

CO₂ Absorption Experiments
Degree of CO$_2$ Removal
Dependence on the Height of Ceramic Foam Packing

Height of ceramic foam packing: 10.1 cm

Height of ceramic foam packing: 15.2 cm

Height of ceramic foam packing: 20.3 cm

Height of ceramic foam packing: 25.4 cm

Liquid Flow:
- 10 (cc/min)
- 20 (cc/min)
- 30 (cc/min)

Gas flow-rate (cc min$^{-1}$)
Combined Absorber and Stripper System
Experimental Setup for Proof-of-Concept Demonstration

Diglycolamine (DGA) (30 wt%)
0.01 LPM

Steam: 102°C, 109 kPa
0.01 kg min⁻¹

Effluent CO₂ loading
(not detectable)

Excess Amine Absorbent
Collected

Simulated flue gas
0.25, 0.5 and 1.0 SLPM

Stainless steel
Prototype

PR: Pressure Regulator
PG: Pressure Gauge
3-W-V: 3-way valve
TC: Thermocouple
DT-1: CO₂ Detector
HW: Hot water supply
MFC: Mass flow controller
PP: Peristaltic pump
BPR: Back Pressure Regulator
FAR: Fresh Absorbent Reservoir
SAR: Spent Absorbent Reservoir
RB: Reboiler
SSP: Stainless steel prototype
HWR: Hot Water Reservoir

Steam: 102°C, 109 kPa
0.01 kg min⁻¹
Combined Absorber and Stripper System
Experimental Setup
Combined Absorber and Stripper System

Degree of CO₂ Removal

Degree of CO₂ Removal (%)

Gas Flow-rate (SLPM)

Without Steam

With Steam

0.25

0.5

1

17
Combined Absorber and Stripper System
Lateral Flow of Absorbent

Pressure Differential (kPa)

Lateral Flow of Absorbent (Measured)
(Liters/minute)

Lateral Flow of Absorbent (Estimated)
(Liters/minute)

Experimental measurements
Darcy's Law Estimate
Our Approach: Substrate functionalization

Combined Pressure, Temperature Contrast, and Surface-enhanced Separation of CO₂
Ceramic Foam Surface Functionalization

**Absorber side**
- Liquid Film
- Gas Phase
- Metal oxide contactor surface (unfunctionalized)

**Desorber side**
- Liquid Film
- Gas Phase
- Metal oxide contactor surface (functionalized)

- Immobilized surface groups
- Surface liberated CO₂

- CO₂
- Carrier gas (N₂)
- CO₂ + amine (reacted, intermediate)

Surface modifications may be tailored to influence CO₂ release from carbamate intermediates.

→ Potential for faster breakdown kinetics with lower stripping temperatures, smaller unit, and less amine.
Silane Modification of $\text{Al}_2\text{O}_3$

Using established silane-based modifications of metal oxide ($\text{MO}_x$) surfaces

Calcinated $\alpha$-alumina powder ($74 - 44 \, \mu\text{m}$, with surface area = 360 m$^2$ g$^{-1}$)

Stability studies: exposure to 3 M MEA with 0.3 mol CO$_2$, pH 10.30

TGA: weight loss from 200 to 600 °C under air at 10 °C min$^{-1}$

<table>
<thead>
<tr>
<th>APTMS $\text{Al}_2\text{O}_3$</th>
<th>Weight Loss (%)</th>
<th>Grafting Density (molecules nm$^{-2}$)</th>
<th>Loss from exposure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>0.08</td>
<td>$7.4 \times 10^{-4}$</td>
<td>N/A</td>
</tr>
<tr>
<td>1 hr exposure</td>
<td>0.05</td>
<td>$6.6 \times 10^{-4}$</td>
<td>0.03</td>
</tr>
<tr>
<td>24 hr exposure</td>
<td>0.03</td>
<td>$6.2 \times 10^{-4}$</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Phosphonate Modification of Al₂O₃

Alternative to silanes, used for corrosion inhibition on steel and anti-biofilm on TiO₂

Phenylphosphonic acid (PPA) (10 vol%)

MeOH: water (80:20), 25 °C, 24 hrs

PPA1 = single PPA deposition, PPA2 = double PPA deposition

Stability studies: exposure to 3 M MEA with 0.3 mol CO₂, pH 10.30

TGA: weight loss from 200 to 600 °C under air at 10 °C min⁻¹

<table>
<thead>
<tr>
<th>PPA Al₂O₃</th>
<th>Weight Loss (%)</th>
<th>Grafting Density (molecules nm⁻²)</th>
<th>Loss from exposure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPA1</td>
<td>3.64</td>
<td>0.04</td>
<td>N/A</td>
</tr>
<tr>
<td>PPA1 + 1 hr</td>
<td>0.00</td>
<td>0.00</td>
<td>3.64</td>
</tr>
<tr>
<td>PPA2</td>
<td>5.72</td>
<td>0.1</td>
<td>N/A</td>
</tr>
<tr>
<td>PPA2 + 1 hr</td>
<td>0.01</td>
<td>0.00</td>
<td>5.72</td>
</tr>
</tbody>
</table>
APTMS Modification of SiO$_2$

Due to the instability of silane and phosphonate bonds on Al$_2$O$_3$, other substrates explored:

SiO$_2$: Evonik Areoperl colloidal silica 30 $\mu$m particles, 300 m$^2$ g$^{-1}$

APTMS (10 vol%) deposition in toluene at 90 $^o$C, 24 hours on SiO$_2$

Stability studies: exposure to 3 M MEA with 0.3 mol CO$_2$, pH 10.30
2 x wash with water, 2 x wash with EtOH, dry at 100 $^o$C for 24 hours

<table>
<thead>
<tr>
<th>APTMS SiO$_2$</th>
<th>Weight Loss (%)</th>
<th>Grafting Density (molecules nm$^{-2}$)</th>
<th>Loss from exposure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>6.64</td>
<td>5.0 X 10$^{-2}$</td>
<td>N/A</td>
</tr>
<tr>
<td>1 hr exposure</td>
<td>5.86</td>
<td>2.9 X 10$^{-2}$</td>
<td>0.8</td>
</tr>
<tr>
<td>24 hr exposure</td>
<td>5.30</td>
<td>2.0 X 10$^{-2}$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Typical Coverages: 2-4 molecules nm$^{-2}$

SiO$_2$ demonstrates a higher grafting density and slower loss of APTMS

Optimization should yield a stable functionalized surface under desorber conditions
Reactions between amine, CO$_2$, and bicarbonate

For MEA:

\[
\text{HOCH}_2\text{CH}_2\text{NH}_2 + \text{CO}_2 \rightleftharpoons \text{HOCH}_2\text{CH}_2\text{NHCO}_2\text{H}
\]

\[
\begin{align*}
 k_\text{7} & = 5.8 \times 10^{10} \ e^{(-4872/\text{T})} \ (\text{M}^{-1} \ \text{s}^{-1}) \\
 k_\text{7} & = 1.0 \times 10^{13} \ e^{(-7583/\text{T})} \ (\text{s}^{-1}) \\
 \text{Calculated Equilibrium} \ K_\text{7} & \\
 \text{Absorber} & \\
 30 \ ^\circ\text{C} & : \ 6.0 \times 10^3 \\
 70 \ ^\circ\text{C} & : \sim 3.9 \times 10^4 \\
 100 \ ^\circ\text{C} & : \sim 1.2 \times 10^5 \\
 150 \ ^\circ\text{C} & : \sim 5.8 \times 10^5 \\
 \text{Desorber} & \\
 & \\
 & \\
 Convery, W. et al. \ J. \ Phys. \ Chem. \ A \ 2011, 115, 14340.
pH Effects on CO₂ Desorption with Temperature

15 mL of 3 M MEA (~ 30 wt%) loaded with 0.3 mol CO₂
N₂ bubbling through solution at 800 mL min⁻¹, temperature from 25 °C to 86 °C at 12 °C min⁻¹

Initial pH values:
3 M MEA (no CO₂): 12.30
+ 0.3 mol CO₂: 10.26

pH of solution reduced with 12 M HCl
(no CO₂ release observed until heat applied)

Others have demonstrated aqueous acid release of CO₂ from carbamates before.
Do solid acids have a similar effect on CO₂ release?
Consider Acidity of Substrate Surface on CO₂ Desorption

Others have demonstrated ability of acids to liberate CO₂ from carbamates.

It is not very practical to add aqueous acid to the desorber (separation issues).

However, metal oxide surfaces can function as an acid/base from the view of isoelectric points (IEP) (aka Brønsted acids/bases):

\[
\begin{align*}
\text{pH < IEP} & : \ OH_2^+ & \text{Absorption of anions} \\
K_1 & \\
\text{pH = IEP} & : \ OH & \leftrightarrow [H^+] \ (\text{pH change}) \\
K_2 & \\
\text{pH > IEP} & : \ O^- & \text{Absorption of cations}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>pH&lt;sup&gt;25&lt;/sup&gt; of IEP at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.2 – 0.5</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.7 – 3.5</td>
</tr>
<tr>
<td>γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>7 - 8</td>
</tr>
<tr>
<td>α-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>8 - 9</td>
</tr>
<tr>
<td>ZnO</td>
<td>9.5</td>
</tr>
<tr>
<td>NiO</td>
<td>10 – 11</td>
</tr>
</tbody>
</table>

Preliminary Results: CO$_2$ Desorption in Presence of Metal Oxide

15 mL of 3 M MEA (~30 wt%) pre-loaded with 0.3 mol CO$_2$

To each solution, 1.5 g of MO$_x$ powder added, 15 min equilibration

N$_2$ bubbling through solution at 800 mL min$^{-1}$, temperature from 25 °C to 86 °C at 12 °C min$^{-1}$

Initial pH values:
- 3 M MEA: 10.26
- $\alpha$-Al$_2$O$_3$: 10.32
- SiO$_2$: 10.22

<table>
<thead>
<tr>
<th></th>
<th>Time (min)</th>
<th>Temp (°C)</th>
<th>Mol CO$_2$ Released</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>9.8</td>
<td>84</td>
<td>0.09</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.8</td>
<td>83</td>
<td>0.13 (+44%)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>8.6</td>
<td>82</td>
<td>0.14 (+56%)</td>
</tr>
</tbody>
</table>

→ The presence of metal oxide substrates has an effect on the extent of CO$_2$ desorption
Summary and Conclusions

• **Combined absorber/desorber for CO₂ removal**
  – We have identified commercially available materials – ceramic foams that can be used to combine the absorber and desorber
  – 1-D CO₂ absorption studies were conducted to select conditions suitable for achieving 90% CO₂ removal in a bench-scale system
  – Feasibility of the combined absorber/desorber system was demonstrated in a bench-scale, stainless steel prototype (90% CO₂ removal could be achieved for simulated flue gas containing 13% CO₂ with 30 wt% diglycolamine (DGA) as the absorbent)

• **Substrate functionalization and metal oxide effects**
  – α-Al₂O₃ is a poor substrate for silane and phosphonate functionalization due to low surface coverage and instability at high pH
  – Surface functionalization chemistry can be optimized to improve grafting density and stability at high pH
  – Presence of metal oxides increases CO₂ desorption amount, suggesting a simple approach to improve stripper performance
Research Tasks for 2013-14

• **Modeling combined absorber/desorber CO₂ separation process**
  – A commercial fluid flow simulation software such as COMSOL Multiphysics will be used to develop a flow model
  – A simpler, 1-D model is the first step, followed by models with greater complexity

• **Completion of surface functionalization**
  – Increase coverage and stability of APTMS on SiO₂ substrates
  – Test the hypothesis that metal oxides 'catalyze' carbamate decomposition
  – Demonstrate functionalized vs. non-functionalized substrates in absorption/desorption process
## Project Budget

<table>
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<tr>
<th>Budget Period</th>
<th>Budget Period 1 (10.01.11 – 09.30.12)</th>
<th>Budget Period 2 (10.01.12 – 09.30.13)</th>
<th>Budget Period 3 (10.01.13 – 09.30.14)</th>
<th>Total</th>
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<tbody>
<tr>
<td><strong>Object Class</strong></td>
<td><strong>Category</strong></td>
<td><strong>Personnel</strong></td>
<td><strong>Fringe Benefits</strong></td>
<td><strong>Travel</strong></td>
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<td>$180,738</td>
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<td>$10,480</td>
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<td>$22,680</td>
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<td><strong>Total Direct Charges</strong></td>
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<td><strong>Total</strong></td>
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<td>$378,916</td>
<td>$248,801</td>
<td>$960,811</td>
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Acknowledgements

Personnel
- Dr. Joe Powell, Chief Scientist at Shell Oil Company
- Dr. TS Ramakrishnan, Scientific Advisor at Schlumberger-Doll Research Center
- Hirasaki Group & Wong Group members at Rice University

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- Energy and Environmental Systems Institute (EESI) at Rice University
- Rice Consortium on Processes in Porous Media
- Schlumberger