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 of Chemical and Biomolecular Engineering
Rice University
NETL CO₂ Capture Technology Meeting
July 31, 2014
Outline

- Project Overview
- Project Budget
- Project objectives and technical approach
- Progress on process model to simulate gas/liquid flow and reaction in integrated CO₂ absorber/desorber
- Screening of metal oxide for CO₂ desorption/amine regeneration
- Summary and Conclusions
Project Overview

- Project funding under DOE agreement – DE-FE0007531
- Total project cost - $960,811 over three years. Federal share: $768,647 | Non-federal share: $192,164
- Contract awarded executed October 2011
- **Project duration**: 10/2011 – 3/2015
- **Primary project goal**: Performance of bench-scale R&D to demonstrate and develop Rice University’s “combined pressure and temperature contrast and surface-enhanced separation of CO$_2$ for post-combustion carbon capture to meet DOE’s goal of at least 90% CO$_2$ removal at no more than 35% increase in the cost of electricity”
Project Team

Project Director

Michael Wong
Professor in Chemical & Biomolecular Engineering & Chemistry

Co-Project Investigator

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

Co-Project Investigator

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

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Edward Billups
Professor in Chemistry

Postdoctoral Associate

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Postdoctoral Associate

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Undergrad Researcher

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Past Members

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PhD (April 2013)

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PhD, Chemistry (LSU, 2011)
## Project Budget

<table>
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<th>Budget Period Object Class Category</th>
<th>Budget Period 1 (10.01.11 – 09.30.12)</th>
<th>Budget Period 2 (10.01.12 – 12.31.13)</th>
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<td><strong>$248,801</strong></td>
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Objectives

- Develop a CO₂ capture process that uses a single integrated unit that combines both the absorber and desorber columns.
- Use waste heat for absorbent regeneration instead of low-pressure steam by operating the desorber section of the integrated unit under vacuum.
- Develop a 2-D model to simulate the CO₂ absorption process, to test different configurations, and to optimize the material properties (i.e., pore-size distribution, aspect ratio, etc.).
- Reduce energy requirement by lowering the desorption temperature with the addition of a metal oxide.
Technical Approach

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

- Waste Heat
- Amine Absorption for Carbon Capture
- Vacuum Stripping
- Metal Oxides
- Integrated Absorber-Stripper

Diagram:
- Lean Absorbent (in)
- Low CO₂ gas (out)
- Moist CO₂
- Absorption Side
- Desorption Side
- Heat Exchanger
- Reboiler
- Cooled Flue gas
- Lean Absorbent (out)
- Steam
Advantages

- Reduction of space requirement and capital cost due to integration of absorber and desorber sections into a single unit.

- Favorable characteristics for mass transfer because ceramic gas-liquid contactors have large geometric surface areas.

- Cost saving and less energy requirement due to low desorption temperature:
  - Metal oxide catalyzes the desorption of CO₂
  - Moderate vacuum helps desorption to be carried out at reduced temperatures.
Key milestones

- Preliminary Technical and Economic Feasibility Study
- Bench-scale Prototype Design and Test
- Process modeling and simulation (1D and 2D model)
- Addition of metal oxide in desorption zone
- Technical and Economic Feasibility Study; Technology EH&S Risk Assessment

Timeline:
- 10/2011-6/2012
- 6/2012-4/2013
- 9/2012-12/2014
- 4/2014-10/2014
- 10/2014-3/2015
Content of Today’s Talk

- Progress on process model to simulate gas/liquid flow and reaction in integrated CO\textsubscript{2} absorber/desorber unit (COMSOL)
  - Pressure drop, flooding prediction in 1D model
  - CO\textsubscript{2} absorption performance prediction in 1D model
  - Gas/liquid flow simulation in 2D model

- Screening of metal oxides that can enhance CO\textsubscript{2} desorption from amine solution at lower stripping temperature
Experimental Setup for Pressure Drop in 1D Column

α-Al₂O₃ ceramic foam

P<sub>top</sub>

P<sub>bottom</sub>

Gas

Liquid

20 PPI

30 PPI

45 PPI

Scanning Electron Micrographs of Ceramic Foam: (a) 50x (b) 280x
## Material Properties

### Advantages of ceramic foam:
1. Low bulk density and pressure drop
2. Very high geometric surface area and macro-porosity (80%-90%)
3. Regulated pore-size and ease of reproducibility of structure
4. Low pressure drop
5. High structural uniformity

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<th>Packing Type</th>
<th>Structure</th>
<th>Porosity (%)</th>
<th>S (m²/m³)</th>
<th>Bulk density (g/cm³)</th>
<th>Equivalent Pore diameter (mm)</th>
<th>Permeability (m²)</th>
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<td>85</td>
<td>700&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.60&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.28</td>
<td>8.0x10⁻⁹</td>
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<td>30-PPI</td>
<td>85</td>
<td>900&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>1.00</td>
<td>7.3x10⁻⁹</td>
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<td>45-PPI</td>
<td>84</td>
<td>1400&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.71&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.60</td>
<td>6.2x10⁻⁹</td>
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<td><strong>Random Packing&lt;sup&gt;c&lt;/sup&gt;</strong></td>
<td>Raschig Ring</td>
<td>62.6</td>
<td>239</td>
<td>0.58&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.50</td>
<td>3.87x10⁻⁸</td>
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<tr>
<td></td>
<td>Pall Ring</td>
<td>94.2</td>
<td>232</td>
<td>0.48&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.50</td>
<td>3.53x10⁻⁷</td>
</tr>
</tbody>
</table>

(a) PPI: Number of pores per linear inch length; (b) C.P.Stemmet, IChemE, 2006 (c) Jerzy Maćkowiak, IChemE, 2011 (d) www.ask-chemicals.com
(e) http://www.tower-packing.com (f) permeability of packing was calculated by \[ k = \frac{3\phi d^2}{50} \]
Predicted Pressure drops under Different Gas Velocities

- **Continuity equation (Steady-state)**

\[ \rho_i \nabla \cdot U_i = 0 \]

- **Momentum Balance Equation (Steady-state)**

\[ -\nabla \cdot p_L - \frac{\mu_L}{f_L K} U_L + \rho_L g \nabla D = 0 \quad \text{Darcy's Law} \]

\[ -\nabla \cdot p_G - \frac{\mu_G}{f_G K} U_G + \rho_G g \nabla D = 0 \quad \nabla \cdot p_G = \nabla \cdot p_L \]
Predicted and Experimental Pressure Drops in 20ppi Ceramic Foam

(a) Liquid flow rate 10 mL/min
(b) Liquid flow rate 30 mL/min
(c) Liquid flow rate 50 mL/min

Packing Height: 30.5 cm
Liquid phase: water @25 °C
Gas Phase: air

(a) Liquid flow rate 10 mL/min
(b) Liquid flow rate 30 mL/min
(c) Liquid flow rate 50 mL/min
Predicted and Experimental Drops in Ceramic foams

Packing Height: 30.5 cm
Liquid phase: water @25 °C
Gas Phase: air
Liquid flow rate 50 mL/min
Flooding Point Prediction

Liquid holdup = \(\frac{\text{Volume of liquid in porous media}}{\text{void volume}}\)

Typical liquid holdup for different gas and liquid Reynolds numbers. (Stemmet et al. 2005)
Operating Zone in 20-PPI Ceramic Foam

Figures: Modelling results of the liquid holdup versus gas flow rate:

- 20-PPI ceramic foam; Packing Height: 30.5 cm; Liquid phase: water @25°C; Gas Phase: air
**Absorbent:**
Aqueous Diglycolamine (DGA) 30 wt%

**Structure:**
\[
\text{HO} - \text{O} - \text{NH}_2
\]

**Operating conditions:**
- Inlet CO\(_2\) concentration: 13 v/v%
- Absorption temperature: 25 °C
- Ceramic foam: 20-PPI
Model Equations and Major Reactions

- **Mass Balance of Species i**
  \[ \nabla \cdot ( - D_i \nabla c_i + c_i U ) = S_i \n\]

- **Source Terms for Gas Phase**
  \[ S_i = - K_{ov} a_{eff} \left[ \frac{C_{Gi}}{H_i} - C_{Li} \right] \]

- **Source Terms for Liquid Phase**
  \[ S_i = K_{ov} a_{eff} \left[ \frac{C_{Gi}}{H_i} - C_{Li} \right] - R_{ij} \]
  \[ S_j = - 2 R_{ij} \]

**Main Kinetic Reactions**
- \( \text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- \)
- \( \text{HCO}_3^- \rightarrow \text{CO}_2 + \text{OH}^- \)
- \( \text{DGA}^- + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{DGACOO}^- + \text{H}_3\text{O}^+ \)
- \( \text{DGACOO}^- + \text{H}_3\text{O}^+ \rightarrow \text{DGA}^- + \text{H}_2\text{O} + \text{CO}_2 \)

**Main Equilibrium Reactions**
- \( \text{DGAH}^- + \text{H}_2\text{O} \leftrightarrow \text{DGA}^- + \text{H}_3\text{O}^+ \)
- \( \text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^- + \text{CO}_3^{2-} \)
CO$_2$ Concentration Profile along Column under Different Liquid Velocities

Liquid flow rate: 30 mL/min
Gas flow rate: 0.15 SLPM

Liquid flow rate: 3 mL/min
Gas flow rate: 0.15 SLPM

Liquid flow rate: 0.3 mL/min
Gas flow rate: 0.15 SLPM

Packing length: 20.4 cm
Diameter: 2.54 cm
Liquid: 30 wt% DGA, 25C
Gas: 13% CO$_2$/87% N$_2$

Unit: %
Temperature Profiles with Changing Liquid Velocities

Liquid flow rate: 0.076 mL/min  Liquid flow rate : 0.76 mL/min  Liquid flow rate : 7.6 mL/min

(constant gas flow rate 0.6 SLPM )
Experimental and Simulated CO$_2$ Removal Ratio
(ceramic foam column= 20.4 cm)

Liquid phase: 30% DGA, Gas phase: 13% CO$_2$/87% N$_2$; Temperature: 25 °C
Experimental and Simulated CO₂ Removal Ratio
(ceramic foam column= 10.2 cm)

Liquid phase: 30% DGA, Gas phase: 13% CO₂/87% N₂; Temperature: 25 °C
Prototype of Integrated CO₂ Absorber and Desorber Unit

- Fiber Glass Wool Blanket: 19cmx0.5cmx10cm
- Alumina Foam: 20cmx2.35cmx10cm
- Porous Alumina Membrane: 19cmx2.5cmx10cm
- PES Membrane: 19cmx0.14umx10cm

Photograph of the experimental setup developed for the proof-of-concept demonstration.
Representative of Liquid Phase Velocity and Temperature Profiles

- Liquid: 30 wt% DGA
- Gas: 13% CO₂/87% N₂
- Liquid flow rate: 50 mL/min
- Gas flow rate: 4 SLPM

Liquid phase velocity field

Temperature ranges:
- Steam outlet: 120°C
- Gas outlet: 25°C
Our Approach:
Using Metal Oxides during Desorption

COMBINED PRESSURE, TEMPERATURE CONTRAST, AND SURFACE-Enhanced Separation of CO₂

- Metal Oxides
- Waste Heat
- Amine Absorption for Carbon Capture
- Integrated Absorber-Stripper
- Vacuum Stripping
**Experimental Setup**

- 15 mL of an amine solution pre-loaded with 0.3 mol CO₂
- To each solution, 1.5 g of MOₓ powder added, 15 min equilibration
- N₂ bubbling through solution at 800 mL min⁻¹, temperature from 25 °C to 86 °C at 10 °C min⁻¹
• WO$_3$, V$_2$O$_5$, and MoO$_2$ increased the release of CO$_2$ from MEA
• V$_2$O$_5$ and MoO$_2$ started desorbing CO$_2$ at 40 °C during the initial 15-minute equilibrium step
• WO$_3$ caused more CO$_2$ release than MEA only after 76 °C
### Screening of Metal Oxides for CO₂ Desorption

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<th>MOₓ (1.5 g)</th>
<th>Cumulative %CO₂ released by 30 min at 86 °C</th>
<th>Cumulative %CO₂ released by 60 min at 86 °C</th>
<th>Time (min), temperature °C of max CO₂ release peak</th>
<th>IEP</th>
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<td>MEA only</td>
<td>31.6</td>
<td>49.2</td>
<td>14, 84</td>
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<td>WO₃</td>
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<td>V₂O₅</td>
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<td>MgO</td>
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<td>22.3</td>
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- No correlation between IEP and CO₂ desorption
- WO₃, V₂O₅, and MoO₂ caused CO₂ to desorb at lower temperatures than CO₂-loaded MEA solution
- WO₃ did not dissolve, which implies that ceramic foams made using WO₃ may be suitable in a stripper unit
Screening of Metal Oxides for CO$_2$ Desorption (Piperazine)

No correlation between IEP and CO$_2$ desorption
- WO$_3$, V$_2$O$_5$, and MoO$_2$ caused more CO$_2$ release than piperazine (PZ) only solution
- Similar to MEA, WO$_3$ did not dissolve in PZ.
Developed a process model to simulate gas/liquid flow and reaction in integrated CO₂ absorber/desorber unit

- Complete development of a 1D process model.
- Successful to predict pressure drop, flooding and CO₂ absorption in 1D ceramic foam column.
- Predicted fluid flow and temperature profiles of integrated absorber/desorber unit in 2D model

Screened various metal oxides for CO₂ desorption

- Metal oxides represent a new approach to reduce the desorption temperature
- Our process can potentially reduce the cost of existing amine-based CO₂ capture technology by addressing the major challenges due to high desorption temperatures. These challenges are- high energy requirement, degradation and evaporation of amine solutions
Research Tasks for 2014-15

- Model combined absorber/desorber CO₂ separation process
  - Continue the development of a 2-D model to simulate gas and liquid flow in the capture process and compare simulation results with experimental measurements
  - Perform a sensitivity analysis and process optimization

- Develop low temperature desorption zone
  - Develop highly active and stable catalysts that can further lower the desorption temperature.
  - Perform appropriate tests to examine the amine solutions after experiments to check for any degradation products.
  - Design foams containing metal oxides
  - Reduce the cost of existing amine-based CO₂ capture technology by addressing major challenges due to high desorption temperatures.

- Complete an exergy (available energy) and techno-economic analysis and perform an EH&S assessment of the process
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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• Rice Consortium on Processes in Porous Media
• Schlumberger
Material Properties of alumina membrane and polymer (PES) membrane

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