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. George Hirasaki
A J. Hartsook Chair Professor in Chemical Engineering, Rice University
NETL CO$_2$ Capture Technology Meeting
July 9$^{th}$, 2012
• About Rice University
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• Combined Pressure and Temperature Contrast and Surface-enhanced Separation of Carbon-dioxide
• Supporting experimental and simulation results
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• Project Objectives
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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**

Edward Billups  
Professor in Chemistry

Michael Wong  
Professor in Chemical & Biomolecular Engineering & Chemistry

**Co-Project Investigator**

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

**Graduate Student**

Sumedh Warudkar  
PhD Candidate

**Postdoctoral Associate**

Jerimiah Forsythe  
PhD, Chemistry (LSU, 2011)
Project Overview

- Project funding under DOE agreement – DE-FE0007531
- Total project cost - $960,811 over three years with 20% cost-share agreement
- Contract awarded executed October 2011
- Project objective - Performance of bench-scale R&D to demonstrate and develop Rice University’s “combined pressure and temperature contrast and surface-enhanced separation of CO$_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”
Conventional Amine Absorption Adapted for Carbon Capture

Flue gas in

Absorber:
40 - 70 °C
1 atm

Lean amine in
45 °C

Desorber:
100 - 150 °C
1 - 5 atm

CO₂ rich solvent

Captured CO₂ out

Reboiler/Reclaimer

Regenerated lean amine out

CO₂ rich solvent

Heat Exchanger

Flue Gas:
40 °C
12% CO₂
7% H₂O
3-6% O₂

Low CO₂ gas (out)
Drawbacks of Conventional Amine Absorption

- Amine absorption was developed and optimized for Natural gas sweetening not Carbon Capture
- Absorbent regeneration is very energy intensive and requires diverting low pressure steam from the LP steam turbine at coal-fired utilities
- Parasitic load due to Carbon capture can be in excess of 50% of rated capacity of power plant
- Commonly used amines like MEA and DEA are very corrosive at high CO₂ loadings
- Corrosion problems are worse at higher operating temperatures which correspond to higher stripper pressure
- Requires space for a separate absorber and desorber column which can be a problem while retrofitting existing coal-fired utilities
Our Approach

**Combined Pressure and Temperature Contrast and Surface-enhanced Separation of CO₂**

**Amine Absorption for Carbon Capture**

- Waste Heat
- Functionalized substrates
- Vacuum Stripping
- Integrated Absorber-Stripper
Process Schematic
Integrated Absorber-Stripper

Cool Lean Absorbent (in)
Low CO$_2$ gas (out)
Humid CO$_2$

Absorption Side

Desorption Side

Heat Exchanger

Cooled Flue Gas
Hot Lean Absorbent (out)
Waste Heat
Reboiler
Flue gas (in)

Absorbent (in)

Ceramic foam

Cleaned flue gas (out)

Liquid permeable membrane

Moist CO₂ (out)

Waste Heat (in)

Ceramic foam

Regenerated Absorbent (out)
# Gas-liquid contactor – Ceramic Foam

## Ceramic Foam
- Low bulk density
- Very high macro-porosity (80%-90%)
- Very high geometric surface area (upto 4756 m²/m³ (solid))
- Regulated pore-size
- Low pressure drop
- High structural uniformity
- Ease of reproducibility of structure

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

(a) 70x

(b) 300x

(c) 2900x

(d) 12400x
Schematic of Plexiglas Setup

Water (in) to Peristaltic Pump, then to Combined Pressure and Temperature Swing Process prototype. Water flows from the absorption side to the desorption side through a Needle Valve. Air (in) to Needle Valve. Desorption side water (out).
Result of Flow Experiments
A Proof-of-concept

Flow Rate of Water from Absorption to Stripping side (cc/min) vs Pressure Drop Across Ceramic Membrane (psi)

- Inflow Rate = 27.5 cc/min
- Inflow rate = 32 cc/min
- Inflow rate = 41 cc/min

Absorption chamber floods at:
- 41 cc/min
- 32 cc/min

No flooding at:
- 27.5 cc/min

Inflow rates and pressure drop are shown graphically. The graph indicates the flow rates and pressure drops across the ceramic membrane under different inflow rates, demonstrating the flooding points and the range of no flooding.
1-D Column for Mass Transfer Evaluation
Pressure drop in 30-ppi ceramic foam at varying gas and liquid flow-rates
Mass transfer characteristics of various tower packing materials

![Bar chart showing % CO₂ pick-up for different packing materials]
**Substrate Functionalization**

**Silanization Chemistry Approach**

Silane functionalization not stable in amine solutions

Other directions:
- Phosphonates
- Other organic linkages (e.g. carboxyl)
- Protecting polymer layer
- Other surface coating to increase bond strength

### Table

<table>
<thead>
<tr>
<th>Surface Modifier</th>
<th>Grafting Density ((\rho), molecules nm(^{-2})) (S(BET) = 250 \text{ m}^2 \text{ g}^{-1})</th>
<th>Grafting Density ((\rho), molecules nm(^{-2})) (S(BET) = 155 \text{ m}^2 \text{ g}^{-1})</th>
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<td>APTMS</td>
<td>1.00</td>
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<tr>
<td>APTMS (Post-Bubbler #1)</td>
<td>0.90</td>
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<td>APTMS (Post-Bubbler #2)</td>
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100 to 325 mesh \(\alpha\)-alumina substrate

Grafting density determined by thermogravimetric analysis (TGA)

10 wt% diglycolamine (DGA)/water with 1 hour contact time

**Figure**

- (3-aminopropyl)trimethoxysilane (APTMS)
- Toluene, 100 °C
Parasitic Power Losses
Vacuum vs. Conventional stripping

Reboiler steam requirement for MEA>
Steam Flow-rate to LP Turbine. Same case for 60 wt% DGA at 30 kPa

Vacuum Stripping
Steam: 60 psia, 160°C

Parasitic Duty (% of Rated Plant Output)

Stripper Pressure (kPa)

CO2 Capture with DEA 40%  CO2 Capture with DGA 60%
Technical & Economic Feasibility

Comparison of cost of electricity for various processes

- No Carbon Capture: 64.0
- Fluor: 131.6
- Rice-Process (Worst Case): 134.3
- Rice-Process (Best Case): 100.3
Merits of Proposed Technology

- Ceramic foam has a geometric surface area up to 10x that of conventional packing (e.g. Raschig rings).
- Functionalized packing can increase the rate of CO$_2$ absorption into absorbent solution thus making it attractive to use slow reacting amines which also have low heat of regeneration.
- High geometric surface area packing, along with surface enhancement by functionalization can reduce the height of tower packing.
- Integrated absorber – desorber arrangement reduces space requirements. This will be an important factor when retrofitting existing coal-fired power plant with CO$_2$ capture technology.
- Waste heat usage for absorbent regeneration significantly reduces parasitic duty for power plant and thus, limit the increase in cost of electricity.
- Operating the desorber at lower temperatures decreases amine losses and equipment corrosion problems.
Project Objectives

1. Project Initiation – Technical and Economic Feasibility Study
   - At project initiation, a technical and economic feasibility study will be performed on this project to determine the possibilities of scaling up this process to pilot scale and beyond.
   - As a part of the feasibility study, an environmental risk assessment will also be performed to evaluate the potential environmental impacts of the proposed technology.

2. Hydrodynamics and Mass Transfer Studies
   - We will conduct studies to measure the hydrodynamic properties of the ceramic foam.
   - We will conduct studies to measure the mass transfer properties for ceramic foam as compared to a standard tower packing material like ceramic Raschig rings.

3. Design of stainless steel prototype
   - A stainless steel prototype will be designed and fabricated for demonstrating absorption and stripping of CO\(_2\) in the combined absorber/desorber arrangement. In addition, absorbent regeneration will be carried out under vacuum.

4. Demonstrate absorption and stripping using stainless steel prototype
   - Once the stainless steel prototype is designed and fabricated, the complete CO\(_2\) capture process will be implemented and demonstrated
   - Various factors affect CO2 absorption and desorption. Some of these are (i) Absorbent and gas flow-rate (ii) Macro-pore sizing in ceramic foam (iii) Vacuum on stripping side
5. Substrate functionalization
   - Amine and polycarboxylate functionalization on absorption and desorption side substrate
   - Basic and acidic functionalities influence local pH conditions and increase forward and reverse reactions between amine and CO₂ respectively
   - Effectiveness of substrate functionalization will be evaluated by measuring changes in the heat and mass transfer coefficients.

6. Process modeling
   - Both horizontal and vertical mass and heat transport are significant.
   - Develop a 2-D model to capture the influence of reaction kinetics, gas-liquid mass and heat transfer properties, operating pressure and temperature.

7. Sensitivity analysis and process optimization
   - Large number of degrees of freedom like properties of ceramic foam and porous slab, operating pressure and temperature, gas and liquid flow rate, choice of absorbent
   - Overall process optimization to reduce the energy requirement and costs

8. Project Completion – Feasibility and Economics Analysis
   - The Feasibility and Economics analysis performed at project initiation will be updated based on information generated as a part of this project.
   - This feasibility and economic analysis will indicate the possibility of scaling up the project to a pilot demonstration.
<table>
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<th>Personnel</th>
<th>Role</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 (10.01.12 – 09.30.13)</th>
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<td>Prof. George Hirasaki</td>
<td>Project Director, Lead Investigator</td>
<td>✓</td>
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<td>Prof. Michael Wong</td>
<td>Co-Project Investigator</td>
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<td>Prof. Kenneth Cox</td>
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<td>Prof. Ed Billups</td>
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<tr>
<td>Mr. Sumedh Warudkar</td>
<td>Graduate Student</td>
<td>✓</td>
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<td>Dr. Jerimiah Forsythe</td>
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**TBD**
## Project Budget

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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

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• Rice Consortium on Processes in Porous Media
• Schlumberger
• US DOE DE0007531
Questions