Advancing Post-Combustion CO$_2$ Capture through Increased Mass Transfer and Lower Degradation

FE-00031661

Jesse Thompson and Kunlei Liu

University of Kentucky - Center for Applied Energy Research
caer.uky.edu/power-generation/
Project Overview

• Funded as part of the Novel and Enabling CO₂ Capture Technologies

• Project consists of three primary area: (1) using novel 3-D printed polymeric absorber packing; (2) modifying solvent physical properties to increase solvent wetting on absorber packing; (3) developing an effective process to decompose nitrosamines from waterwash systems

• **Project Period:** 10/1/2018 - 9/30/2021 (3 years)

• **Funding:** Federal - $2.9M; CS - $725K; Total - $3.6M
Project Objectives

Developing process enhancements/technologies that can be broadly applied to amine-based post-combustion CO₂ capture systems:

1. 3-D printed hydrophobic/hydrophilic packing material to increase solvent turbulence and CO₂ mass transfer

2. A better understanding of solvent physical properties, specifically those related to increasing CO₂ mass transfer

3. Nitrosamine decomposition using electrochemical decomposition within the waterwash
How does packing wettability translate to CO₂ Flux?

- \[ \text{flux} = A \cdot k_G \cdot (P_{CO_2}^g - P_{CO_2}^*) \]

Where \( k_G \propto \frac{\sqrt{D_{CO_2} \cdot k_2 \cdot [amine]}}{H_{CO_2}} \)

<table>
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<tr>
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<th>MEA</th>
<th>PZ</th>
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<tbody>
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<td>Rate Constant</td>
<td>5.94</td>
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- Most solvents do not take full advantage of packing
- Improved mixing can help to overcome this issue
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Technology Background – Dynamic Packing

Dynamic Packing + 3D Printing

- Hydrophilic-hydrophilic interaction
- Larger contact angle
- Greater surface contact

- Hydrophilic-hydrophobic interaction
- Smaller contact angle
- Internal turbulence from solvent drawing up

- Hydrophilic-hydrophilic
- Packing re-wetting
- More internal turbulence and mixing

Surface wetting and contact angle

Flue Gas Flow
Technology Background – Dynamic Packing

Target: Polymers that are stable to amine solvents and typical absorber temperatures

Contact angle differences between the two polymeric materials of >15° up to 30°

Stolaroff, 2017 NETL CO₂ Capture Technology Meeting
Polymer stability when exposed to amine solvents

- High Density Polystryene (HDPS)
- Acrylonitrile butadiene styrene (ABS)
- Nylon
- Polylactic Acid (PLA)

Measure contact angle of water (reference) and CO₂-rich solvent

Measure mass, thickness and tensile strength of each coupon

Place coupons into CO₂-rich solvent for 1000 hrs

Re-measure and calculated changes to mass, thickness and tensile strength

Re-measure contact angle of water (reference) and CO₂-rich solvent

Repeat measurements after exposure at 60 °C for 1000 hours
## Polymer stability when exposed to amine solvents

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Treatment (1000 hrs)</th>
<th>Contact Angle w/ water</th>
<th>Contact angle w/ amine</th>
</tr>
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<tbody>
<tr>
<td><strong>High density polystyrene (HDPS)</strong></td>
<td>Before</td>
<td>82.57</td>
<td>62.19</td>
</tr>
<tr>
<td></td>
<td>After amine exposure at 60 °C</td>
<td>82.87</td>
<td>70.51</td>
</tr>
<tr>
<td><strong>ABS</strong></td>
<td>Before</td>
<td>84.51</td>
<td>69.03</td>
</tr>
<tr>
<td></td>
<td>After amine exposure at 60 °C</td>
<td>84.06</td>
<td>69.04</td>
</tr>
<tr>
<td><strong>Nylon</strong></td>
<td>Before</td>
<td>63.72</td>
<td>56.87</td>
</tr>
<tr>
<td></td>
<td>After amine exposure at 60 °C</td>
<td>63.35</td>
<td>57.65</td>
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<tr>
<td><strong>PLA</strong></td>
<td>Coupon unstable after 60 °C amine exposure</td>
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Polymer stability when exposed to amine solvents
Dynamic Packing Patterns

- LLNL has an initial finite element model to help tune the pattern of the hydrophilic/hydrophobic areas. The model uses a Multiphysics approach combining level set and laminar flow equations (turbulent conditions can also be applied)

- Post treatments can also be used to modify the hydrophobicity and hydrophilicity of the base polymers

- Currently performing FDM test printing of ABS/Nylon and evaluating solvent wettability and CO₂ capture enhancement at the lab-scale
Physical Properties of Amine Solvents

- Focus on ways to modify physical properties of solvents to increase CO₂ mass transfer (decrease diffusion resistance)
- Additives can be used to modify physical properties, including surface tension and contact angle (wettability)
Mass Transfer Enhancement with Additives

Increased CO₂ mass transfer was observed as the result of micro-bubble/froth formation in solutions containing a small amount of surfactant-type additive.
Modify Physical Properties of Amine Solvents

![Graph showing the relationship between contact angle (°) vs ABS and surface tension (mN/m) for Amine Solvents.](image_url)
A very small amount of surfactant-type additive (< 0.1%) can be used to reduce the surface tension (ave. ↓30%) and contact angle (ave. ↓23%) of common amine solvents, helping to increase the wettability of these solvents on the hydrophobic polymer packing.
Small-Bench Testing

Next steps: Fabrication of 3” diameter Dynamic Packing sections and installation into our small-bench CCS, followed by integrated solvent/packing testing in Phase II
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Nitrosamine Mitigation

Photochemical Reduction (UV) w/ Ozone treatment

Zeolite Membrane

Catalytic Hydrogenation

Activated Carbon Adsorption

Nitrosamine Mitigation

**Challenge:**
Removing nitrosamines at very low concentrations from the circulating waterwash solution

Part of DE-FE-0007395
Nitrosamine Mitigation

Two-step process:
1) Adsorption of the nitrosamines onto the carbon CX electrodes
2) Electrochemical decomposition of the nitrosamines

Challenge:
Removing nitrosamines at very low concentrations from the circulating waterwash solution
Current Progress– Nitrosamine Mitigation

Nitrosamine adsorption onto high surface area, high porosity, highly conductive Carbon Xerogel (CX) electrodes

NPY; polar nitrosamine

NDEA; non-polar nitrosamine
Current Progress—Nitrosamine Mitigation

Target: >60% nitrosamine removal with a Faradic (charge) efficiency of >10% from a waterwash solution

Surface modifications of the CX can be used to increase adsorption and/or electrochemical reaction rates
Current Progress– Nitrosamine Mitigation

Primary byproduct is regeneration of the parent amine through a reduction reaction

\[
\text{NO} \quad \xrightarrow{\text{H}} \quad \text{N}
\]

with minimal additional amine decomposition
Current Progress—Nitrosamine Mitigation

Next steps: Fabrication of flow-through cell and test using authentic waterwash collected at our 0.7 MWe Small Pilot CCS
Key Knowledge Gained

• 3D printed dynamic packing is a promising and potentially lower-cost alternative for amine CO$_2$ capture absorbers

• Amine solvent physical properties can be modified through the addition of additives to decrease surface tension and increase wettability on hydrophobic packing surfaces

• Nitrosamine decomposition can be achieved using an electrochemical treatment process.
Acknowledgements

• DOE-NETL: Andy Aurelio, José Figueroa, Lynn Brickett

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• UKy-CAER: Moushumi Sarma, Saloni Bhatnagar, Keemia Abad, Shino Toma, Ayo Omosebi, James Landon, Lisa Richburg