Transformational Technologies: Approach and Successes

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Integrated Technology Development

**Material Synthesis & Fabrication**

**Molecular Design & Optimization**

**Characterization**

**Process Synthesis & Techno-economic assessment**

**Performance Assessment In Real Environments**

**Material Processing & Device Development**

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**COE Sensitivity to Module Separation Efficiency**

Case 6 1% Efficiency:

- COE = $291/MWh
- Membrane ~77% of TPC

Case 6 100% Efficiency:

- COE = $88.3/MWh
- Membrane ~3% of TPC

3.5% COE increase (Case 6)

7% COE increase (Case 6)
Integrated Technology Development

Technology Pathway

- **Stage 0**: Materials Design: Modeling, Synthesis, and Characterization
- **Stage 1**: Performance Testing (Ideal)
  - Generation 1 Advanced Materials
  - Generation 2 Advanced Materials
  - Generation 3 Advanced Materials
  - Generation 4 Advanced Materials
  - Generation 5 Advanced Materials
- **Stage 2**: Performance Testing (Realistic)
- **Stage 3**: Bench Scale Slipstream
- **Stage 4**: Scale-up & Module Development
  - Technology Transfer
  - Industry
- **Stage 5**: Pilot Scale Slipstream

FY 12 | FY 13 | FY 14 | FY 15 | FY 16 | FY 17
What Is the NETL-ORD Role in Transformation Technology Development?

And what is it not?

• It’s not:
  – Basic science
  – Creation/discovery of new classes of materials
  – Pilot-scale testing
  – Commercialization

• It is:
  – Examination of novel classes of materials for capture
  – Exploration of innovative process configurations
  – Development of advanced screening approaches
Three Types of Projects

• Material type with unique properties:

• Novel process configuration:

• Testing method or device allowing accelerated R&D:
Eutectic Solvents

- ILs forming crystalline solids tend to have a sharp melting point and low viscosity in the liquid phase.
- These materials also tend to melt well above room temperature.
- Forming eutectic mixtures could lead to low viscosity liquids.
- It proved challenging to locate mixtures showing both reduced viscosity and a depressed melting point.

Identify Simpler compounds (Minimize interactions)

Eutectic

Suppression of $T_m$

Low viscosity
1. Weakened ionic interaction
2. Packing/Defect

$y = -0.056.74x^2 + 303.24x$
$R^2 = 0.9999$

106°C

46.5°C

Viscosity is 22 Cp
Structured Liquids

**IL Confinement**
- ILs for semi-ordered structures when confined in pores under 50 nm.
- Structures show unique properties not attainable in bulk ILs.
- Formation of IL micelles results in similar property changes.
- Computational results appeared promising, but fabrication of the materials proved challenging.

**Unconfined Structured ILs**

Hydrophilic Head Groups

Hydrophobic Tails

\[ \text{CO}_2 \]
Hybrid Organic-Inorganic Hydroxide Solvents

- Phosphorous-Nitrogen core lends excellent stability and good interaction with CO$_2$.
- Molecular foliage used to control molar volume and add additional CO$_2$ affinity.
- Initial results do not appear favorable.
Core-shell MOFs

- Many MOFs with desirable properties for CO$_2$ capture are water sensitive.
- It is possible to grow MOFs with similar crystal lattices in intimate contact with one another.
- MOF particles may be created with a core of CO$_2$-philic, water sensitive MOF and a hydrophobic protective shell.
- Producing a practical capture material from the MOFs was not possible.
Hybrid Nanoparticle Solvents

- Nanoparticles with appropriate ligands attached may behave as liquids.
- Depending upon the ligand and core, CO\textsubscript{2} capacity could be considerable.
- Cu-based nanoparticles of 10 nm size with targeted ligands were developed.
- Viscosity of the resulting liquids was too great, and they proved impractical.

Poster
Porous Borazine-coated Silica

- Boron containing materials have high CO₂ uptake and good stability.
- Capture materials may be made by supporting them on high surface area materials.
- Material fabrication underway.

Can we improve CO₂ interaction by developing a Bidentate type interaction?
Flexible Inorganic Polymer Membranes

Polyphosphazenes:

- High performance elastomers (aerospace)
- Phosphorous-nitrogen backbone shows good CO$_2$ affinity.
- Several new polymers synthesized with properties targeted for CO$_2$ separations.
- Film formation in progress.

\[
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\left[ \begin{array}{c}
R \\
\vdots \\
R
\end{array} \right] \\
\vdots \\
\left[ \begin{array}{c}
P \\
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N
\end{array} \right]
\end{array}
\]

Hydrophobic fibers

Surface modification by plasma or chemical etching

Contact angle of water droplets, over 100°
Structured Polymers (PILs)

- Plasticization is a problem in CO$_2$-selective membranes.
- Block copolymers can phase segregate at the nanoscale to produce separate domains.
- The property can be used in a membrane with separate transport and structural phases.
- Membrane films have been created using poly(IL)s as the transport phase.

Poster
Processes
Solvent-Membrane Hybrid System

- An amine solvent cycle may be used with a sweep gas to compress the CO₂ in the flue gas to higher pressure and concentration.
- A membrane can then be used to produce pure CO₂ ready for sequestration.
- Systems analyses were performed examining the economics of the process and it was found to be competitive with existing processes without materials development.
- Membrane development was undertaken to improve the process.
Integrated Water Removal

• Many potentially useful CO₂ capture techniques are infeasible because to the presence of water in flue gas.

• Using a low energy physical adsorption and making use of residual heat, the water may be removed concurrent to capture.

• Systems analyses were performed examining the economics of the process and it was found to be potentially competitive based on the capture technology used.
Methods
Microfluidic Apparatus for Solvent Characterization

- Screening of solvents can require large volumes of material and substantial time commitment.
- A microfluidic device was developed which examines bubble shrinkage over time in contact with a liquid solvent to determine gas solubility and mass transfer rate.
Conclusions

- NETL-ORD uses an integrated technology development approach which examines a large number of technologies to determine their promise for CO$_2$ capture.
- A variety of materials, processes, and testing methods have been evaluated for their ability to achieve long term CO$_2$ capture targets.
- Some of the technologies show promise and further evaluation will be conducted.
Choline-based ILs

- Strong interactions with CO$_2$ are desirable for ILs as solvents and membranes.
- Inter-molecular hydrogen bonding leads to increased viscosity and reduced mass transport.
- Intra-molecular hydrogen bonding, which may be encouraged with spacer groups allows for reduced viscosity.

<table>
<thead>
<tr>
<th>RFIL</th>
<th>viscosity (cP)</th>
<th>$T_g$ (°C)</th>
<th>Setaram CO$_2$ uptake, mol CO$_2$/mol IL</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NH$_2$(CH$_2$)$_2$NMe$_2$(CH$_2$)$_2$OH]Tf$_2$N(N2, O2)</td>
<td>4530</td>
<td>-39.4</td>
<td>0.017</td>
</tr>
<tr>
<td>[NH$_2$(CH$_2$)$_2$NMe$_2$(CH$_2$)$_2$OH]Tf$_2$N(N2, O3)</td>
<td>1146</td>
<td>-44.6</td>
<td>not determined</td>
</tr>
<tr>
<td>[NH$_2$(CH$_2$)$_3$NMe$_2$(CH$_2$)$_2$OH]Tf$_2$N(N3, O2)</td>
<td>1303</td>
<td>-49.6</td>
<td>not determined</td>
</tr>
<tr>
<td>[NH$_2$(CH$_2$)$_3$NMe$_2$(CH$_2$)$_2$OH]Tf$_2$N(N3, O3)</td>
<td>1424</td>
<td>-39.2</td>
<td>0.018</td>
</tr>
<tr>
<td>[NH$_2$(CH$_2$)$_3$NMe$_2$(CH$_2$)$_2$OH]Tf$_2$N(N3, hex)</td>
<td>1084</td>
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<td>0.018</td>
</tr>
<tr>
<td>[NH$_2$(CH$_2$)$_4$NMe$_2$(CH$_2$)$_2$OH]Tf$_2$N(N4, O2)</td>
<td><strong>280</strong></td>
<td><strong>-66.6</strong></td>
<td><strong>0.028</strong></td>
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</table>
Cyclic ether-based polymers have tailorable free volume and molecular affinity for CO₂.

- Methodologies invented to synthesize monomers with desirable groups and polymerized these monomers.
- Film fabrication techniques developed for new materials.
Coal Gasification with In-Situ CO$_2$ Capture

- The process uses alkali hydroxides and alkali earth metal oxides inside the gasifier as combined gasification catalysts and capture agents.
- The exothermic heat of reaction of the CO$_2$ capture reaction is utilized to offset the endothermic steam-coal gasification reactions.
- Lab scale coal gasification experiments and systems analyses are underway to examine the feasibility of the process.
Redox-driven Regeneration of Amines

- Electrically driven pH swing may be used to drive CO₂ capture and solvent regeneration in a cycle based on quinone.

- A capture device has been constructed and results show CO₂ concentration swing.
- Device may be employed in a membrane configuration.
Neural Network Modeling

- NN is a processing system composed of a large number of highly interconnected processing elements.
- They work in unison to transform input data into output.
- Each neuron is defined by an activation function, which takes a weighted output of multiple input neurons as an argument.
- This input is used to train the force fields.
- An ab initio database for the specific case of CO$_2$-[CH$_3$COO]$^-$ anions is being generated.