Development and Testing of Aerogel Sorbents for CO₂ Capture

2015 CO₂ Capture Technology Meeting
Pittsburgh, Pennsylvania
June 23 – 26, 2015

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Aspen Aerogels, Inc.
**Project Overview**

*Develop and bench-scale test an advanced aerogel sorbent for post-combustion CO₂ capture from coal-fired power plants*

"AFA"

Amine Functionalized Aerogel Sorbent

Form Pellets with Binder

**Develop Aerogel Sorbent at Bench Scale for CO₂ Capture**
- Improve Amine Functionalized Aerogels (AFA)
- Convert optimized sorbent into bead form
- Develop pellet binder formulations, and forming process
- Develop SOₓ diffusion barrier for AFA sorbents
- Test & evaluate sorbent technology at bench scale

Develop Compatible SOₓ Resistant Binder

Bench Scale Evaluation
Project Objectives

1. Optimize sorbents for improved CO₂ capacity and SOₓ poisoning resistance.
2. Convert optimized sorbent into durable pellet and bead form for analysis.
3. Produce the best candidate sorbent form (bead or pellet) in larger quantities for fluidized bed testing.
4. Assess the sorbent in fluidized bed bench-scale testing.
5. Conduct a technical and economic assessment of the sorbent technology and process.
Project Team

- Period of Performance:
  - 10-1-2013 through 09-30-2016
- Funding:
  - U.S.: Department of Energy: $2.99M
  - Cost share: $0.77 million
  - Total: $3.76 million
<table>
<thead>
<tr>
<th>BP#</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP1 (2013 – 2014)</td>
<td>AFA Sorbent Development</td>
</tr>
<tr>
<td></td>
<td>Pellet Development and Optimization</td>
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<tr>
<td></td>
<td>Sorbent Evaluation</td>
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<td></td>
<td>Coating Development</td>
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<td></td>
<td>Coated Pellet and Bead Evaluation</td>
</tr>
<tr>
<td>BP3 (2015 – 2016)</td>
<td>Pellet (or Bead) Production</td>
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<tr>
<td></td>
<td>Fluidized Bed Evaluation</td>
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<tr>
<td></td>
<td>Techno-Economic Evaluation</td>
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<td>Environmental Health and Safety Evaluation</td>
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</tbody>
</table>
Amine Functionalized Aerogel (AFA) Development

AFA benefits

- High surface/high porosity material
- Hydrophobic to enhance CO$_2$ adsorption selectivity and stability
- Low specific heat, thus low energy regeneration
- High temperature stability
- Good routes for manufacture at reasonable cost and at high volume
Accomplishments to Date

Sorbent CO₂ Capture Performance
- High total and working CO₂ adsorption capacities ( ~ 20 wt.%, ~ 8 wt.%)*
- Fast CO₂ adsorption kinetics (<15 min. to reach 80% of total CO₂ capacity)**
- Stable for at least 250 adsorption/desorption cycles

Regeneration Temperature and Delta Temperature (ΔT)
- Reduced the required regeneration temperature below 130 °C and kept the CO₂ working capacity above 6 wt.% target.

Moisture Uptake
- AFA moisture uptake > 1 wt.%
- However, AFA has high preferential adsorption of CO₂ vs. H₂O
- Maintaining acceptable CO₂ loading performance by reducing cycling time.

* BP1 targets: > 12 wt.%, and > 6 wt.% (@ 40 – 100 °C, adsorption/desorption cycle)
** 40 °C and 0.15 CO₂ bar
Accomplishments to Date

**Pellet Sorbent Development**
- 300 – 350 micron size pellets prepared.
- 85% capacity retention of the corresponding powder.

**SO₂ Resistant Coating Development (on-going)**
- Different coatings have been tested on sorbents in the presence of SO₂.
- Continuing SO₂ resistant coating optimization with goal of minimizing degradation of CO₂ capture performance.

**Sorbent Bead Development (on-going)**
- Optimum sorbent formulation used to produce aerogel beads.
- Bead sizes 0.3 – 1.5 mm have been fabricated.
Technical Progress
AFA Formulation Optimization

Top two AFA formulations from BP1

- **AFA Sorbent Type #1**
  - Direct amine grafting process, using amino-silane precursors/sol-gel process.
  - High thermal stability (~ 190 °C), CO$_2$ capacity (~ 14.3 wt. %).

- **AFA Sorbent Type # 2**
  - “Double functionalization” process by amine-grafting and impregnation methods.
  - Thermally stable up to 100 – 110 °C, high CO$_2$ capacity (> 15.4 – 20 wt.%).

Performance Trade?
Enhanced Capacity vs. Thermal Stability
AFA CO₂ Capture Performance

Top AFA sorbent performance under 100% CO₂ (TGA):

Sorbent Type #1

<table>
<thead>
<tr>
<th></th>
<th>Temp. swing adsorption/desorption cycle</th>
<th>Total CO₂ capacity (wt.%)</th>
<th>Working CO₂ capacity (wt.%)</th>
<th>Heat of reaction (kJ/mole CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>@ 40°C - 100°C</td>
<td>@ 40°C - 120°C</td>
<td>@ 70°C - 120°C</td>
<td></td>
</tr>
<tr>
<td>Sorbent Type #1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.8</td>
<td>6.2</td>
<td>50 – 60 (MEA ~ 84 kJ/mole CO₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.3</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.9</td>
<td>6.4</td>
<td></td>
</tr>
</tbody>
</table>

Sorbent Type #2

<table>
<thead>
<tr>
<th></th>
<th>Temp. swing adsorption/desorption cycle</th>
<th>Total CO₂ capacity (wt.%)</th>
<th>Working CO₂ capacity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>@ 40°C - 100°C</td>
<td>@ 40°C - 120°C</td>
<td></td>
</tr>
<tr>
<td>Sorbent Type #2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.3</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.2</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.8</td>
<td>6.5</td>
</tr>
</tbody>
</table>

- High working capacity
- Low ΔT (thus low energy regeneration)
- Sorbent is thermally stable
### Pelletization of Powder Aerogel (AFA) Sorbent

#### Issues
- Degradation of CO₂ performance by 50% when AFA pelletized with Standard Binder Solution (StdBS).
- Sorbent Type #1 (1N) not compatible (dissolved) with StdBS.

#### Progress
- Applied SRE* coating.
- Sorbent Type #1 pellets (with SRE): 12.5 wt.% (~ 13.7% loss)
- Attrition test using ASTM D5757. **Attrited weight < 0.1%**

#### Plan of Action
- Optimize pelletization process (mixing, extrusion and drying) to reduce performance degradation

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*SRE is a coating designed by UA for SO₂ poisoning resistance. Also used for pelletization.
SO₂ Removal Strategy and Process

- Amine-based sorbents suffer from SO₂ poisoning.
- There is currently not a sorbent which only adsorbs CO₂ without adsorbing SO₂.
- SO₂ not only poisons the sorbents but also decreases the purity of desorbed CO₂.
- The degree of SO₂ removal depends on important factors such as the sorbent tolerance to SO₂ and cost of the sorbent replacement and/or regeneration.
- Current design of flue gas desulphurization (FGD) units can achieve more than 95% removal of SO₂.
- Effectiveness of the SO₂-resistant coating (develop by UA) is verified to reduce the SO₂ poisoning on the aerogel sorbents.
- Recent results exhibited only 4% degradation in the CO₂ capture capacity after a 20-cycle exposure to 40 ppm SO₂ in the simulated flue gas.
- UA has also proposed a desorption process to achieve both high-purity CO₂ with an insignificant energy penalty.
SO₂ Resistant Coating Development for AFA Pellets

**Issues**
- SO₂ poisons Sorbent Type #2
- ~ 13% degradation in CO₂ capture capacity after 20 cycles in presence of 40 ppm SO₂

**Progress**
- Developed SRE series SO₂ resistant coating
- SRE-10 & SRE-15: < 4% degradation with cycling
- < 25% capture capacity loss on cycle 1 due to coating

**Plan of Action**
- Reduce 1ˢᵗ-cycle capture capacity drop (compensate amines)
- Study effect of moisture on the SRE coating
- Higher SO₂ conc. testing

### Table: CO₂ Capacity Degradation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer</th>
<th>Linker</th>
<th>Cycle 1 CO₂ Capacity (Wt. %)</th>
<th>Cycle 20 CO₂ Capacity (Wt. %)</th>
<th>Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRE-5</td>
<td>5% sln.</td>
<td>/</td>
<td>12.80</td>
<td>10.50</td>
<td>18.48%</td>
</tr>
<tr>
<td>SRE-7</td>
<td>7% sln.</td>
<td>/</td>
<td>11.88</td>
<td>10.52</td>
<td>11.48%</td>
</tr>
<tr>
<td>SRE-10</td>
<td>10% sln.</td>
<td>/</td>
<td>11.09</td>
<td>10.65</td>
<td>3.97%</td>
</tr>
<tr>
<td>SRE-15</td>
<td>15% sln.</td>
<td>/</td>
<td>10.82</td>
<td>10.47</td>
<td>3.18%</td>
</tr>
<tr>
<td>CQA 12</td>
<td>/</td>
<td>/</td>
<td>14.83</td>
<td>12.89</td>
<td>13.00%</td>
</tr>
</tbody>
</table>
The objective of making sorbent beads is to skip the pelletization process; thus reducing the cost of production if the AFA sorbent beads perform better (or “as good as”) the pellets.
Bead AFA Sorbent CO$_2$ Capture Performance

- Optimum AFA formulations used in bead process optimization
- Bead size and quality depends on:
  - Mixing speed of the “inert medium”
  - Gel time of the AFA sol
  - Temperature of the “inert medium”

* Desorption @ 1 atm CO$_2$

Type #2 sorbent beads

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Total CO$_2$ capacity</th>
<th>CO$_2$ capacity @ desorption*</th>
<th>Working CO$_2$ capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>@ 40°C - 100°C</td>
<td>14.1</td>
<td>10.0</td>
<td>4.1</td>
</tr>
<tr>
<td>@ 40°C - 120°C</td>
<td>14.2</td>
<td>5.1</td>
<td>2.6</td>
</tr>
<tr>
<td>@ 70°C - 120°C</td>
<td>9.1</td>
<td>4.7</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Type #1 sorbent beads

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Total CO$_2$ capacity</th>
<th>Total CO$_2$ @ desorption*</th>
<th>Working CO$_2$ capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>@ 40°C - 100°C</td>
<td>8.26</td>
<td>1.63</td>
<td>0.87</td>
</tr>
<tr>
<td>@ 40°C - 110°C</td>
<td>7.58</td>
<td>6.13</td>
<td>6.71</td>
</tr>
<tr>
<td>@ 40°C - 120°C</td>
<td>7.23</td>
<td>7.17</td>
<td>7.17</td>
</tr>
</tbody>
</table>

Working CO$_2$ capacity ~ 80-99% of Total CO$_2$ capacity for Type #1
AFA Sorbent Fabrication in Bead Form

Different size beads (density ~0.25 g/cc) have been prepared and are being tested at ADA:

- 0.60 – 1.00 mm
- 0.35 – 0.60 mm
- < 0.35 mm

**Issues**

- Amine leaching out during bead process fabrication.
- Long gel time of AFA sol formulations.
- “medium inert” might affect bead sorbent CO₂ capture performance.

**Plan of Action**

- Improve the conditions of bead prep.
- Increase working CO₂ capacity of the beads above 6 wt.% at reduced ΔT.
- Apply SO₂ resistant coating on beads and assess performance.
- CQA-12 sorbent powder exhibits definitively the optimum performance.
- CQA-12 beads have slightly better capacity than pellets.
- Binder/coating decreases CQA-12 pellet performance.
- Total and working CO₂ capacities are maximized when temperature of adsorption is 40 °C and temperature of desorption is 120 °C.
Performance Comparison for Water Uptake

Water uptake @ 40 °C and 60% RH

< 1 wt.% water adsorption @ < 6 minutes

The sorbent cycling time may be reduced to control moisture loading and still maintain acceptable CO₂ loading performance.
SO₂ Resistant Coating Development on AFA Beads

<table>
<thead>
<tr>
<th>Sample</th>
<th>Process</th>
<th>CO₂ Capture Capacity (wt. %)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFA Bead*, uncoated</td>
<td>/</td>
<td>11.18</td>
<td>/</td>
</tr>
<tr>
<td>AFA Bead, coated, SRE-10</td>
<td>1</td>
<td>6.38</td>
<td>- 42.9%</td>
</tr>
<tr>
<td>AFA Bead, coated, 1% XL</td>
<td>2</td>
<td>13.11</td>
<td>+ 17.3%</td>
</tr>
<tr>
<td>AFA Bead, coated, 3% XL</td>
<td>2</td>
<td>14.12</td>
<td>+ 26.4%</td>
</tr>
<tr>
<td>AFA Bead, coated, 5% XL</td>
<td>2</td>
<td>14.52</td>
<td>+ 29.9%</td>
</tr>
</tbody>
</table>

*Bead form is well retained

➢ The total CO₂ capture capacity increased using Process #2
Future Plans

• Finalize bead fabrication process (Aspen).
• Finalize the optimization of SRE coating composition and process application (Akron).
• Crush strength (ADA).
• Perform the attrition tests according to the standard protocol based on the Jet Cup Attrition Standard Procedure (representative of the process to be used) (ADA).
• Test cyclic stability of the most promising sorbent over 1000 cycles (ADA).
• Investigate alternative regeneration process (low CO$_2$ partial pressure with steam as sweep gas) to increase CO$_2$ desorption of sorbent and improve working capacity (ADA).
Future Plans

- Determine the CO₂ vs. H₂O uptake in MSFB (mass spec fixed bed) for promising sorbents (ADA).
- Bench-Scale CO₂ Capture Unit (Akron):
  - Build and optimize 1-kW bench-scale fluidized bed CO₂ capture unit.
## Performance vs. Goals

<table>
<thead>
<tr>
<th>Verification Method</th>
<th>BP2 Performance Target</th>
<th>Planned completion date</th>
<th>Actual completion date</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total CO₂ adsorption capacity&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>&gt; 17 wt.%</td>
<td>06/30/2015</td>
<td>09/15/2015</td>
<td>Close to target (14 wt.%)</td>
</tr>
<tr>
<td>Working CO₂ capacity&lt;sup&gt;(2)&lt;/sup&gt;</td>
<td>&gt; 6 wt.%</td>
<td>06/30/2015</td>
<td>04/01/2015</td>
<td>Exceeded target (9.1 wt.%)&lt;sup&gt;(3)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Adsorption/desorption kinetics&lt;sup&gt;(4)&lt;/sup&gt;</td>
<td>Fast</td>
<td>03/31/2015</td>
<td>03/31/2015</td>
<td>Met target</td>
</tr>
<tr>
<td>Water adsorption&lt;sup&gt;(5)&lt;/sup&gt;</td>
<td>&lt; 1 % @ 40 °C</td>
<td>06/30/2015</td>
<td>06/01/2015</td>
<td>Met target</td>
</tr>
<tr>
<td>Cycling stability (CO₂ adsorption/desorption)</td>
<td>Stable over 500 cycles.</td>
<td>06/30/2015</td>
<td>09/15/2015</td>
<td>Testing scheduled</td>
</tr>
<tr>
<td>Size (micron)</td>
<td>300 - 350</td>
<td>04/30/2015</td>
<td>03/31/2015</td>
<td>Met target</td>
</tr>
<tr>
<td>Attrition Index</td>
<td>&lt;3%(&lt;sup&gt;(6)&lt;/sup&gt;)</td>
<td>06/30/2015</td>
<td>03/31/2015</td>
<td>Met target</td>
</tr>
<tr>
<td>Total CO₂ capacity in the presence of 40 – 60 ppm SO₂ and 80 ppm NO in flue gas.</td>
<td>&lt; 10%</td>
<td>09/30/2015</td>
<td>04/30/2015</td>
<td>Met target&lt;sup&gt;(7)&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>(1)</sup> Adsorption @ 40 °C, Desorption @ 100 - 120°C and 0.15 CO₂ bar.
<sup>(2)</sup> Adsorption @ 40 °C, Desorption @ 100 - 120°C and 1.0 CO₂ bar
<sup>(3)</sup> Desorption @ 120 °C and 1.0 CO₂ bar
<sup>(4)</sup> < 15 min. to reach 80% of total CO₂ capacity at 40 °C and 0.15 CO₂ bar
<sup>(5)</sup> During adsorption/desorption cycle (i.e. water adsorption should be < 1% wt. during the first 6 min of adsorption)
<sup>(6)</sup> loss under fluidizing condition for 3 hours.
<sup>(7)</sup> Testing in presence of NO and SO2 in flue gas is scheduled during the remaining of BP2.
Summary

- All BP2 milestones met and completed on schedule.
- Optimized process of AFA bead and pellet fabrication.
- High CO₂ capture performance of top AFA (beads) sorbent:
  - Total CO₂ capacity ~14 wt.%
  - Working CO₂ capacity ~ 6 - 9.1 wt.%
- Fast adsorption kinetics
  - The rate of moisture uptake is < 1 wt.%
- SRE coating proven as efficient SO₂ resistant coating.
  - Uncoated AFA: ~ 13% CO₂ capacity degradation
  - AFA pellets: < 4 % CO₂ capacity degradation
  - AFA beads: Increased CO₂ capacity by 30%
- The degree of SO₂ removal depends on:
  - Sorbent tolerance to SO₂ /cost of the sorbent /replacement and/or regeneration
Acknowledgements

Project Funding (DE-FE0013127):

U.S. Department of Energy (DOE-NETL)

DOE-NETL Project Manager - I. Andrew Aurelio

Team Acknowledgements:

- Aspen Aerogels Inc. (R&D group)
- ADA-ES (M. Sayyah, M. Lindsay, W.J. Morris)
- University of Akron (L. Zhang, J. Yu, Y. Zhai, and S. Chuang)
Thank You