National Carbon Capture Center: Post-Combustion

2012 NETL CO₂ Capture Technology Meeting

July 10, 2012
Project Funding
DOE-Funded CO₂ Capture Test Facilities in Wilsonville, Alabama


In May 2009 PSDF transitioned to the National Carbon Capture Center (NCCC).

Existing facilities used to support development of pre-combustion CO₂ capture.

Additional facility, the Post-Combustion CO₂ Capture Center (PC4) built and started testing March 2011.

Located at adjacent power plant, Alabama Power’s Plant Gaston.
Flue gas drawn from downstream of FGD and returned upstream so any contaminants introduced are removed by FGD before passing to stack.
Recap of MEA Baseline Run

• The 1140-hour MEA baseline test was completed May 2011
  – Achieved steady operation under controlled conditions
  – Competed 23 balance periods with good mass balance closures
  – Concluded that PSTU is ready to test developer’s solvents and collect reliable data in support of commercialization
• Some issues identified that required further investigation
  – MEA carryover greater than vapor equilibrium value
    • Exceeds VOC limits: excessive solvent make up rates
  – Labs used declined to measure degradation products in solvent
  – Degradation products in regenerated CO₂ stream not sampled
  – End-of-run analysis of solvent revealed selenium and chromium contents, each in excess of 1 ppm
Second MEA Test Campaign

- Follow-up program required to investigate issues raised in first MEA Test Campaign
  - Around 55% of solvent used was from previous run
- 400 hours of operation, March 6-23, 2012.
- 9 test periods with 30% MEA supported with mass and heat balances.
- Held at one set of flow rates but varied beds and intercoolers in service
  - 5000 lb/hr flue gas with 20,000 lb/hr solvent: L/G = 4.0
  - Steam 1400 lb/hr: S/L = 0.07
  - 3 beds, 0 and 2 intercoolers
  - 2 beds, 0 and 1 intercooler
  - CO$_2$ capture efficiency in line with previous results
Other Testing at PC4

- B&W OptiCap™ solvent tested for ~2000 hours
- Currently testing Hitachi’s H3-1 solvent
- Preparing to test Cansolv and Chiyoda solvents
- Aker’s Mobile test Unit collected data for over 2,000 hours in latter half of 2011
  - Amine solvent tested developed as part of SOLVit Program in Norway
- MTR’s 0.05-MW CO$_2$ separation membrane approaching 500 hours of testing
  - Modified version of unit tested at Arizona Public Service Cholla plant
- Tested Codexis enzyme in MDEA using their pilot module

MTU being installed next to PSTU
### Post-Combustion Test Plan for 2012

<table>
<thead>
<tr>
<th>Quarter</th>
<th>PSTU</th>
<th>2nd Pilot Bay</th>
<th>Bench Scale #1</th>
<th>Bench Scale #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st qtr</td>
<td>2nd MEA Solvent Test</td>
<td>Aker CleanCarbon</td>
<td>CODEXIS</td>
<td>MTR Membrane Technology &amp; Research</td>
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<tr>
<td>2nd qtr</td>
<td>HITACHI Inspire the Next</td>
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<td>4th qtr</td>
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- Preparing to test MTR’s 1-MW CO₂ separation membrane in 2013.
- Recently announced Linde had received $15M award from DOE to build 1-MW integrated pilot plant to test CO₂ solvent (supplied by BASF) at NCCC. To be operational in 2014.
PC4 Test Locations

- Pilot Bay 2: BASF/Linde
- Pilot Bay 3: MTR 1-MW

Bench-Scale Area

A. Codexis then Akermin
B. MTR 0.05-MW
C. SSTU
PC4 Pilot Bay Units

- NCCC provides industrial experience to support developers on site integration, construction, and safety/environmental compliance.
PC4 Bench-Scale Units

・NCCC provides similar support to that for pilot-bay units and makes modifications to allow testing to proceed.

MTR 0.05-MW Membrane Module
M = Metals Measurement
D = Degradation Products
NCCC Sampling System for Amine and Degradation Products

Front End Adapted from EPA MM5

Flue Gas Sample From Probe

Condenser Coil

Knock-Out Trap

Empty Impingers

Ice Bath

Submersible Pump

Temperature (~40°F)

Back End Custom Designed Using Industrial Hygiene Sampling Techniques

Sorbent Tube Sampling Section for Nitrosamines, Aldehydes, Ketones, Amines, and Solvent Vapors

Flow Metering and Control

Silica Gel

Two additional impingers can be added for testing chemical scrubbing of vapors.
Solvent Carryover

• During the baseline test, the MEA emissions from the PSTU were in excess of 100 ppmv
• Vapor emissions level was predicted to be less than 3 ppmv
• SO$_3$ aerosol (~0.1 micron) present in flue gas leaving Gaston scrubber
  – Too small to scatter much light so flue gas appears clear
• In warm absorber aerosol grows to sizes that scatter light efficiently (>1 micron) and a fog appears
  – These small droplets are not collected efficiently in wash tower and many escape with CO$_2$-depleted flue gas
  – Theorized controlling absorber temperature (higher or lower) may increase droplet size, making them more easily removed, and lower MEA carryover
# Results of MEA Carryover Tests

<table>
<thead>
<tr>
<th>Test</th>
<th>Beds</th>
<th>Inter-Coolers</th>
<th>Max Temp °F</th>
<th>MEA in Wash Water, %</th>
<th>MEA Emission Rate Total, lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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**Alabama Bituminous Coal (flue gas SO$_3$ 1.8 ppmv)**

<table>
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<tr>
<th>Test</th>
<th>Beds</th>
<th>Inter-Coolers</th>
<th>Max Temp °F</th>
<th>MEA in Wash Water, %</th>
<th>MEA Emission Rate Total, lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>0</td>
<td>174</td>
<td>1.05 (1)</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>2</td>
<td>160</td>
<td>0.98 (2)</td>
<td>7.3</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1</td>
<td>162</td>
<td>1.06 (2)</td>
<td>4.9</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1</td>
<td>163</td>
<td>0.22 (3)</td>
<td>3.8</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>0</td>
<td>174</td>
<td>0.92 (1)</td>
<td>1.1</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>1</td>
<td>164</td>
<td>5.58 (1)</td>
<td>5.9</td>
</tr>
</tbody>
</table>

**Higher Sulfur Illinois Coal (flue gas SO$_3$ 3.2 ppmv)**

<table>
<thead>
<tr>
<th>Test</th>
<th>Beds</th>
<th>Inter-Coolers</th>
<th>Max Temp °F</th>
<th>MEA in Wash Water, %</th>
<th>MEA Emission Rate Total, lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>2</td>
<td>0</td>
<td>176</td>
<td>1.16 (1)</td>
<td>1.8</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>0</td>
<td>175</td>
<td>1.02 (1)</td>
<td>2.1</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>0</td>
<td>175</td>
<td>1.08 (1)</td>
<td>1.7</td>
</tr>
</tbody>
</table>

(1) Intrinsic values  (2) Adjusted to ~ 1%  (3) Reduced using fresh water

**MEA carryover:**

- Increased with and SO$_3$ level and upper absorber bed inactive
- Decreased with wash water MEA content and solvent temperature
SO$_3$ and MEA Carryover

- Single-stage wash tower designed from data collected with bottled gases.
  - Shows value of using coal-derived flue gas.
- Investigating adding wash stages incorporating condensate from regenerator that has low MEA concentration.
- Contacting suppliers to identify more efficient demisters.
- Acid wash column or wet ESP after wash tower may help.
  - Ideas such as these could be investigated on slipstream solvent test unit (SSTU).
- Hitachi and MHI have processes that cool flue gas to between acid and water dew points so SO$_3$ condenses on fly ash to be neutralized by alkali present.
- Alstom has Integrated Emissions Control System combining SDA with FGD, SDA removing chlorine and SO$_3$. 
## Amine and Degradation Product Carryover

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Wash Tower Outlet, ppm</th>
<th>Regenerator Outlet, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vapor (1)</td>
<td>Liquid (2)</td>
</tr>
<tr>
<td>MEA</td>
<td>4.40</td>
<td>131</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.035</td>
<td>0.28</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.63</td>
<td>0.063</td>
</tr>
<tr>
<td>Ammonia</td>
<td>53.7</td>
<td>86.4</td>
</tr>
<tr>
<td>Ethyl amine</td>
<td>0.036</td>
<td>ND</td>
</tr>
<tr>
<td>Acetone</td>
<td>NM</td>
<td>0.18</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>NM</td>
<td>0.039</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>NM</td>
<td>0.021</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>NM</td>
<td>0.23</td>
</tr>
<tr>
<td>N-Nitrosodimethylamine</td>
<td>0.000225</td>
<td>ND</td>
</tr>
<tr>
<td>N-Nitrosodiethanolamine (NDELA)</td>
<td>0.00106</td>
<td>ND</td>
</tr>
</tbody>
</table>

(1) As vapor sample by sample tubes  
(2) Removed in sample train condensed liquid but expressed as ppmv in vapor stream  

ND - not detected  
NM - not measured
<table>
<thead>
<tr>
<th>Metals</th>
<th>Inlet Gas, ppb</th>
<th>Liquid Concentrations, ppb</th>
<th>Suspected Source of Metal Buildup</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fresh MEA</td>
<td>Makeup Water</td>
</tr>
<tr>
<td>Arsenic</td>
<td>3.62</td>
<td>&lt;12</td>
<td>0.46</td>
</tr>
<tr>
<td>Barium</td>
<td>10.90</td>
<td>&lt;12</td>
<td>54.3</td>
</tr>
<tr>
<td>Cobalt</td>
<td>&lt;0.23</td>
<td>&lt;12</td>
<td>0.43</td>
</tr>
<tr>
<td>Chromium</td>
<td>1.01</td>
<td>&lt;12</td>
<td>0.93</td>
</tr>
<tr>
<td>Manganese</td>
<td>239</td>
<td>&lt;60</td>
<td>83.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.66</td>
<td>24.8</td>
<td>2.42</td>
</tr>
<tr>
<td>Selenium</td>
<td>31.3</td>
<td>44.1</td>
<td>&lt;0.23</td>
</tr>
<tr>
<td>Zinc</td>
<td>9.5</td>
<td>&lt;120</td>
<td>27.4</td>
</tr>
<tr>
<td>Iron</td>
<td>56.6</td>
<td>191</td>
<td>18,410</td>
</tr>
</tbody>
</table>

Elements below detection limits: Silver, Beryllium, Cadmium, Copper, Lead, Antimony, Thallium

(*) 50:50 fresh MEA and MEA from 2011 tests
Major Constituents of 316L

- Proportions of Fe:Cr:Ni:Mn in solvent are close to those in 316L
- Stainless selected to resist corrosion but inhibitor appears still to be required
Selenium Chemistry

- At end of run 50% selenide, 25% selenite, 25% elemental, selenate below LDL.
- pH of solvent in range 9 to 10.
- Adding hydrogen peroxide (for example) changes valence state from selenide (-2) to selenate (+6).
- At VS 4 the non-toxic selenite can precipitate out using iron or polymers.
- Speciating other metals to identify how they also might be removed.

Selenium Findings

• Levels of total selenium in the MEA exceed allowable RCRA limits of 1 ppm for hazardous waste classification.
• Established water treatment processes but may need to be adapted to this new requirement.
• Contacting water treatment experts to identify removal approaches.
• Laboratory program to evaluate approaches with potential for commercial application.
• Test selected approaches on SSTU.
• Working closely with other carbon capture research projects to find a path forward.
• Gaston has an ESP for particulate clean up. Selenium transmissions may be lower with a baghouse.

Results are preliminary. Work is being done with partners and technology developers to confirm and determine the details of the issue.
Summary

- PC4 is a flexible facility that allows multiple technologies to be tested simultaneously at different scales.
  - Almost 6,500 data collecting hours since March 2011 supporting five developers plus MEA baseline testing on PSTU.
- Provide real industrial expertise to support developers looking to test their technology on real coal derived flue gas.
  - Engineering support to facilitate site integration as well as compliance with safety and environmental regulations.
  - On site E&I, I&C, and mechanical maintenance support for on-the-go upkeep on equipment for continuous operation.
- Continuously upgrading infrastructure to support other developers.
- Contract negotiations in progress to bring future developers to site.
- MEA results from PSTU show significant value to be gained from testing with coal-derived flue gas.
  - Some unexpected results were found but research infrastructure is well established to resolve issues as they arise.