Pilot Plant Testing of Piperazine (PZ) with High T Regeneration

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Objective is to demonstrate PZ with advanced regeneration at 150°C in coal-fired flue gas

| PZ                | • Optimize process  
<table>
<thead>
<tr>
<th></th>
<th>• Demonstrate solvent robustness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regeneration</td>
<td>• Advanced flash stripper (AFS)</td>
</tr>
</tbody>
</table>
| Aerosols          | • Formation and characterization  
|                   | • Control                     |
Phased testing at UT SRP and NCCC to optimize PZ absorption/regeneration

- **SRP 2011**: 2SF, 8m PZ (Completed)
- **SRP 2013**: 1SF, 5m PZ, Aerosol (Completed)
- **SRP 2014**: AFS, 5 vs 8m, Aerosol (In Progress)
- **NCCC 2016**: AFS, Aerosol (Pending SRP 2014 Results)

CO₂ in air: 0.1 MW, 0.5 MW Flue gas
Budget Period 1

$1.65 M  Federal Share
$0.92 M  Cost Share
$ 2.57 M  Total BP1

Cost share by CO$_2$ Capture Pilot Plant Project (C2P3)
5m Piperazine is a Superior Solvent
Solubility Window for 5 m & 8 m PZ

CO₂ loading (mol/mol alkalinity)

Transition T (°C)

5 m PZ
8 m PZ

Solution

Overstrip
Saturation

Operating Range

PZ·6H₂O (s)

0.22
0.26
### Piperazine: Superior Energy Performance

<table>
<thead>
<tr>
<th>Amine</th>
<th>m</th>
<th>$k_{g,avg}' \times 10^7$</th>
<th>μ</th>
<th>$\Delta C_\mu$</th>
<th>$T_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZ</td>
<td>8</td>
<td>8.5</td>
<td>11</td>
<td>0.84</td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11.3</td>
<td>4</td>
<td>0.81</td>
<td>163</td>
</tr>
<tr>
<td>AMP/PZ</td>
<td>4_2</td>
<td>8.6</td>
<td>5</td>
<td>0.90</td>
<td>128</td>
</tr>
<tr>
<td>MEA</td>
<td>7</td>
<td>4.3</td>
<td>3</td>
<td>0.67</td>
<td>121</td>
</tr>
<tr>
<td>MDEA/PZ</td>
<td>5_5</td>
<td>8.5</td>
<td>13</td>
<td>0.91</td>
<td>117</td>
</tr>
</tbody>
</table>
# Absorber Performance

## 40°C Intercooling

<table>
<thead>
<tr>
<th></th>
<th>5 m PZ</th>
<th>8 m PZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean Ldg at solid limit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mol CO₂/mol alk)</td>
<td>0.22</td>
<td>0.26</td>
</tr>
<tr>
<td>Rich Loading</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>(mol CO₂/mol alk.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L/G (mol/mol)</td>
<td>3.03</td>
<td>2.55</td>
</tr>
<tr>
<td>Equivalent Work</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(kJ/mol CO₂)</td>
<td>36.0</td>
<td>36.3</td>
</tr>
<tr>
<td>Packing Required</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(m²/mol CO₂)</td>
<td>126</td>
<td>298</td>
</tr>
</tbody>
</table>
PZ: superior solvent management

Resistant to oxidation

• Cyclic : PZ (160°C) = 1.3  MEA (120°C) = 4.7  mM/hr

Volatility just right

• At lean absorber: PZ = 8   MEA=30   ppm
• Thermal reclaiming removes nonvolatile impurities
• PZ & MEA may condense out as aerosols in absorber

Nitrosamine manageable

• PZ + NO₂/NO₂⁻ → mononitrosopiperazine (MNPZ)
• Decomposes at 150°C giving 1 mM MNPZ at SS
The Advanced Flash Stripper (AFS) minimizes Energy Use and Capital Cost.
Irreversibility of simple stripper using 5 m PZ

![Graph showing irreversibility of various processes with lean loading on the x-axis and irreversibility (kWh/tonne CO₂) on the y-axis. The processes include Cross exchanger, Condenser, Reboiler, Compression+Pump, and Trim cooler.]
Advanced flash stripper using 5 m PZ

Cold Rich BPS
8%

Warm Rich BPS
34% 113 °C

Rich Solvent
0.40 Ldg

Lean Solvent
0.22 Ldg

20K LMTD

∆P=2.5 bar

∆P=2.1 bar

∆P=2.6 bar

∆P=0.6 bar

150 °C

5.9 bar

∆T=7.5 K
Irreversibility of AFS using 5 m PZ

Irreversibility (kWh/tonne CO₂)

Lean loading (mol CO₂/mol alkalinity)

Simple stripper

Trim cooler

Stripper

Compression+Pump

Steam heater

Condenser

Cross exchanger
Total Annualized Cost of Regeneration
(Does not include absorber)

Annualized cost includes:
- **CAPEX**: steam heater, cross exchanger
- **OPEX**: steam cost, pumping cost

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**Annualized cost ($/tonne CO2)**

- **8 m PZ Ldg=0.30**
- **5 m PZ Ldg=0.26**
- **8 m PZ Ldg=0.26**
- **5 m PZ Ldg=0.22**

**Cross exchanger LMTD (K)**

- $23$
- $25$
- $27$
- $29$
- $31$
Total Energy

- Simple stripper (5m PZ, 7.5 K LMTD)
- AFS (5m PZ, 7.5K LMTD)
- AFS (8m PZ, 10K LMTD)
- AFS (5m PZ, 5K LMTD)

Lean loading (mol CO₂ / mol alkalinity)

Energy (W_EQ (kWh / tonne CO₂))

- 190
- 200
- 210
- 220
- 230
- 240
- 250
- 260

- 0.20
- 0.22
- 0.24
- 0.26
- 0.28
- 0.30
- 0.32
- 0.34
AFS saves 10% over SS
($/metric ton CO_2 Captured, not rigorous DOE method)
(593 MWe Gross)

<table>
<thead>
<tr>
<th></th>
<th>MEA-SS</th>
<th>PZ-SS</th>
<th>PZ-AFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Derating (MW_e)</td>
<td>145</td>
<td>97.5</td>
<td>90.1</td>
</tr>
<tr>
<td>CAPEX</td>
<td>22</td>
<td>22.1</td>
<td>19.4</td>
</tr>
<tr>
<td>OPEX</td>
<td>37</td>
<td>25.1</td>
<td>23.2</td>
</tr>
<tr>
<td>Cost of CO_2 Capture</td>
<td>59.5</td>
<td>47.2</td>
<td>42.6</td>
</tr>
<tr>
<td>(excluding TS&amp;M)</td>
<td>(1.00)</td>
<td>(0.79)</td>
<td>(0.72)</td>
</tr>
</tbody>
</table>
Amine Aerosols can be measured by FTIR and Phase Doppler Interferometer (PDI).
Amine aerosols cause high amine emissions

Nucleation sites in flue gas
- $\text{SO}_3/\text{H}_2\text{SO}_4$
- Submicron fly ash
- $\text{SO}_2$/amine

+ Amine condensation
  - Amine/$\text{CO}_2/\text{H}_2\text{O}$ from solvent to aerosol

+ Poor collection of small drops in water wash

= Unacceptable amine emissions
Effect of H2SO4 Injection
FTIR Absorber out

H2SO4 Generator Turned on
Effect of 25 ppm SO$_2$ on PZ Aerosol

- SO$_2$ ON
- Intercooling

Graph showing the effects of 25 ppm SO$_2$ on PZ Aerosol with CO$_2$ levels and manual control points.
Phase-Doppler Interferometer (PDI)
Size & concentration: 0.5 – 10 µm up to 10⁶ particle/cm³
2G Bypass Extractive Sampler (tested 11/13)

Diagram:
- 1-½” Ball Valve
- PDI Analysis Cell
- Regenerative Blower
- 8” Sch. 10 Duct Absorber Outlet
PDI at Absorber Outlet – Startup

(11/22/2013)

Counts vs. Diameter (μm)

- 1.41x10^2 part./cm^3
- 1.02x10^2
- 5.02x10^1
Absorber Outlet – Steady-State
(LVI H$_2$SO$_4$: 11/22/2013)
Modifications for 3G PDI

• Use custom transmitter/receiver
  • to see down to 0.1 µm
• Use sapphire heated windows
  • to prevent liquid sheeting
• Set windows in flow body
  • To minimize wall geometry effects
Aerosol and AFS Test Plans for SRP 2014

• Energy performance of AFS
• Energy performance of 5 m PZ vs. 8 m PZ
• Aerosol formation
  – Add SO$_2$ and H$_2$SO$_4$ to the inlet gas
  – Use 3G PDI purchased by NCCC
  – Manual and FTIR measurements of amines
  – Impingement tray at top of the absorber
Conclusions

• 5 m PZ is a superior, demonstrated solvent.
• The advanced flash stripper provides 10% better energy performance for PZ and other solvents.
• Aerosol measurements by FTIR and PDI will quantify aerosol emissions for further control.
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