Pilot Plant Testing of Piperazine (PZ) with Advanced Flash Regeneration

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Andrew Sexton (PjM), Trimeric

Bruce Lani, DOE PM
Advanced Flash Stripper (AFS)

CO₂ (90% removal)

Heat recovery exchanger

Cold Rich BPS
7.5%
47°C
Rich solvent
0.39 mol CO₂/mol alk

Lean solvent
L/G=3.9 kg/kg
0.24 mol CO₂/mol alk

Cross exchanger

Warm Rich BPS
29.6%
116°C

Stripper
(2 m RSR #0.5
2 m RSR #0.7)

Steam heater

Vented gas

H₂O

0.5 MW

Absorber

Flue gas

ΔT=10.0°C

ΔT=10.0°C

ΔT=8.7°C

ΔT=8.7°C

ΔT min =3.3°C

6.3 bar
32.3% H₂O

150°C

D T=7.4°C

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New Equipment on Skid

CO₂ (90% removal)

Vented gas

Absorber

Flue gas 0.5 MW

Lean solvent
L/G=3.9 kg/kg
0.24 mol CO₂/mol alk

Cross exchanger

Heat recovery exchanger

Cold Rich BPS
7.5%
47°C
Rich solvent
0.39 mol CO₂/mol alk

Warm Rich BPS
29.6%
116°C

Stripper (2 m RSR #0.5
2 m RSR #0.7)

Steam heater

6.3 bar
32.3% H₂O

71°C

ΔT=10.0°C

ΔT=8.7°C

ΔT=7.4°C

ΔTₘᵢₙ=3.3°C

150°C

D T=7.4°C

D Tₘᵢₙ=3.3°C

150°C
Outline

• Funding and objectives : NCCC fall 2017
• Capital and Energy << MEA
• Solvent Management of PZ - Prepared
## Project Budget ($million)

<table>
<thead>
<tr>
<th></th>
<th>BP1</th>
<th>BP2</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Federal</td>
<td>1.6</td>
<td>3.3</td>
<td>5.2</td>
</tr>
<tr>
<td>Cost Share</td>
<td>1.1</td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>2.7</td>
<td>3.6</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Cost share by CO₂ Capture Pilot Plant Project (C2P3)
Objective is to develop PZ with advanced regeneration at 150°C

PZ
- Optimize solvent (8m vs 5m)
- Demonstrate resistance to oxidation, nitrosation, & corrosion

Regeneration
- Two stage flash (2SF)
- Advanced flash stripper (AFS)

Aerosols
- Formation and control
- Characterization
Phased testing at UT SRP and NCCC to optimize PZ absorption/regeneration
Phased testing at UT SRP and NCCC to optimize PZ absorption/regeneration

**SRP 2017**
- AFS
- 5m PZ
- 4-20% CO$_2$
- Aerosol
- Corrosion

Completed MTR/DOE

**NCCC 2017**
- AFS
- 5m PZ
- Aerosol
- Corrosion
- Oxidation

Ready to operate

**MTR/DOE BP2**
- 0.1 MW
- CO$_2$ in air

**AECOM/DOE BP2**
- 0.5 MW
- Flue gas
Our test window:
Fall 2017 parametric
Spring 2018 long-term

<table>
<thead>
<tr>
<th>Activity</th>
<th>2017</th>
<th>2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skid Installed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Test</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commissioning</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start-Up</td>
<td></td>
<td></td>
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<tr>
<td>Parametric Field Campaign</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Long-term Field Campaign</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site Restoration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis/Reporting</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note: The table includes a legend for colors and symbols used to indicate different statuses.*
Advanced amine scrubbing gives 50% efficiency
Limited by capital-energy tradeoff

$W_{eq} \text{ (kJ/mol CO}_2\text{)}$

- **DOE Case 10**
  MEA/SS
  (120°C, $P_{\text{strp}}=1.6$ bar)

- **SRP 2015**
  PZ/AFS
  (150°C, $P_{\text{strp}}=6$ bar)

**Power Balance Components:**
- $W_{\text{min,comp}}$
- $W_{\text{lost,absorber}}$
- $W_{\text{lost,cross X}}$
- $W_{\text{lost,reboiler}}$
- $W_{\text{lost,comp}}$
- $W_{\text{lost,others}}$
AFS also works with other solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>kg’ (10^{-7} mol/Pa-s-m^2)</th>
<th>W_{eq} (kJ/mol CO_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Simple stripper</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7m MEA</td>
<td>4.3</td>
<td>36.3</td>
</tr>
<tr>
<td>10m DGA</td>
<td>3.6</td>
<td>37.0</td>
</tr>
<tr>
<td>8m PZ</td>
<td>8.5</td>
<td>34.9</td>
</tr>
<tr>
<td>5m PZ</td>
<td>11.3</td>
<td>36.5</td>
</tr>
<tr>
<td>2m PZ /3m HMPD</td>
<td>10.1</td>
<td>34.9</td>
</tr>
</tbody>
</table>

- Rich \(P_{CO_2}^* = 5 \text{ kPa}, \) Lean \(P_{CO_2}^* = 0.2 \text{ kPa}\)
- Optimum cross exchanger \(\Delta T_{LM} = 5K \left(\frac{\mu}{\mu_{MEA}}\right)^{0.175}\)
AFS provides reversible stripper performance
90% removal, 0.24 lean ldg
Possible long term conditions at NCCC
0.24 lean ldg, 150ºC/82 psia stripper, 2x20 ft absorber packing

<table>
<thead>
<tr>
<th>CO₂ removal (%)</th>
<th>Gas Rate (MW)</th>
<th>Rich Ldg (mol CO₂/eq PZ)</th>
<th>L/L_{min}</th>
<th>W_{eq} (kwh/tonne)</th>
<th>Q (GJ/tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.5</td>
<td>0.387</td>
<td>1.006</td>
<td>256</td>
<td>2.56</td>
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<tr>
<td>98.5</td>
<td>0.5</td>
<td>0.366</td>
<td>1.16</td>
<td>260</td>
<td>2.61</td>
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<tr>
<td>95.4</td>
<td>0.8</td>
<td>0.380</td>
<td>1.10</td>
<td>274</td>
<td>2.77</td>
</tr>
</tbody>
</table>
PZ losses and environmental impact

• Resistant to corrosion, use more carbon steel
• Moderate volatility
  – Manage losses with water wash
  – Manage impurities with thermal reclaiming
• Manage aerosol with grow and capture
• Resistant to Degradation
  – Thermally stable to 150°C
  – Oxidation, 4x less than MEA
  – Nitrosation, decompose at 150°C
• Manage solid precipitation with rich storage
• Two ER corrosion probes in stripper
  – 316L SS
  – 1010 CS
• One ORP Probe
• In addition, one ER probe in absorber sump
## SRP Pilot Plant Corrosion 2017

<table>
<thead>
<tr>
<th>Location</th>
<th>Alloy</th>
<th>T (°C)</th>
<th>Avg. Loading (mol CO₂/mol N)</th>
<th>Corrosion (μm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorber</td>
<td>C1010</td>
<td>30</td>
<td>0.33</td>
<td>331</td>
</tr>
<tr>
<td>Stripper</td>
<td>C1010</td>
<td>150</td>
<td>0.21</td>
<td>325</td>
</tr>
<tr>
<td>Stripper</td>
<td>316L</td>
<td>150</td>
<td>0.21</td>
<td>174</td>
</tr>
</tbody>
</table>

- Absorber corrosion greater than expected

### Corrosion (μm/yr)

<p>| | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td><strong>Good</strong></td>
<td>100 - 500</td>
</tr>
<tr>
<td><strong>Poor</strong></td>
<td>1000 - 500</td>
</tr>
<tr>
<td><strong>Unacceptable</strong></td>
<td>5000+</td>
</tr>
</tbody>
</table>
• Low $\text{Fe}^{2+}$ solubility in PZ may result in $\text{FeCO}_3$ protective layer.
Dissolved oxygen and metals increase oxidation when cycling from 55 to 150°C

- 5-8 m PZ
- Cycled to 150 °C
- ○ D.O. Stripping
- ● No D.O. Stripping
- ▲ >1 wt. % Inh A

1.9 mol NH₃/(kg-hr-mol Fe²⁺)

<0.03 mmol/kg Fe²⁺ required to catalyze oxidation

0.4 mmol NH₃/(kg-hr) due to D.O.
Oxidation Mitigation

• Reaction w D.O.: 0.05 mmol/kg/cycle in HTOR
  • Minimize holdup at high temperature before stripper
  • Strip O₂ with N₂ mmol/(kg-cycle-mmol/kg Fe²⁺)
• Fe²⁺ solubilized by degradation products
  • Oxidation → Fe²⁺ accumulation → more oxidation
  • NO₂ → MNPZ → Oxidation in pilots w/ coal flue gas
    • Prescrub NO₂ and reclaim solvent to minimize Fe²⁺
Growth slows down at high part. number conc
5 m PZ, NCCC conditions

Diameter (µm)

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

ABS BOT  Z/Z_{tot}  Dry Bed  WW  ABS TOP

1 part./cm$^3$

$10^7$

$5 \times 10^7$

$10^8$

Growth slows down at high part. number conc
Baghouse at NCCC

Coal Combustion

- Selective Catalytic Reduction
- Electro-Static Precipitator
- Bag House (2016)
- Flue Gas Desulfurization
- Pre-Scrubber
- CO₂ Capture

Hg
Fly Ash
SO₃
SO₂
SO₂
CO₂

NOₓ
Fly Ash
SO₃

Activated Carbon
Baghouse at NCCC significantly reduced MEA emissions.
Produced 1.7 grams/minute SO$_3$ during UT-SRP tests
10 to 30 ppm SO$_3$ usually not always produce aerosol
Conclusions

• The Advanced Flash stripper will reduce $W_{eq}$ by 10-20% for PZ and other solvents

• 5 m PZ is a superior solvent
  • Fast absorption, thermally stable, high P stripper
  • Good resistance to corrosion, oxidation
  • Managed aerosol
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