Piperazine (PZ) with Advanced Flash Stripper (AFS)
NCCC pilot Plant Results
Gary T. Rochelle (PI), Eric Chen, Korede Akinpelumi, Joe Selinger, Tianyu Gao, Ching-Ting Liu, Yuying Wu, Kent Fischer
The University of Texas at Austin
Karen Farmer (PM), AECOM
Andrew Sexton (PjM), Katherine Dombrowski, Trimeric
Bruce Lani, DOE PM
A baseline process for 2G amine scrubbing

- Reliable Design and Operation
- 2.1 GJ/t CO$_2$ producing CO$_2$ at 6 bar
- 90-98% removal with 40 ft packing
- Degradation < 0.2 lbs PZ/t CO$_2$
- 0.5 – 5 ppm PZ emissions at 0 – 4 ppm SO$_3$
- Carbon steel frequently protected by FeCO$_3$
Demonstrate robustness of PZ & advanced regeneration processes at 0.5 MW

• Team
  • AECOM (Prime Contractor)
  • UT Austin (Technology Provider)
  • Trimeric Corporation (TEA, Process Design)

• Initiation
  • October 1, 2010

• Total Funding Agreement
  • DOE-NETL: $5.1M
  • Cost Share (C2P3): $1.4M

• Target:
  • 90% capture with significant progress to less than 35% increase in COE
Advanced Flash Stripper: New Equipment on Skid

- CO₂ (90% removal)
- Lean solvent: L/G = 3.9 kg/kg, 0.24 mol CO₂/mol alk
- Cold Bypass exchanger: Cold Rich BPS (7.5%, 47°C)
- Cross exchanger
- Warm Rich BPS (30%, 116°C)
- Rich solvent: 0.39 mol CO₂/mol alk
- Flue gas: 0.5 MW
- Vented gas
- H₂O: 6.3 bar, 32% H₂O
- Absorber
- Stripper (2 m RSR #0.5, 2 m RSR #0.7)
- Steam heater
- CW
- ∆T = 7.4°C
- ∆T = 10°C
- ∆T = 9°C
- ∆T = 150°C
- ∆T = 3.3°C

Note: The diagram shows the flow of gases and solvents through the equipment, with temperature and pressure changes indicated.
Objectives for 2000 hrs in the PSTU at NCCC

Start-up
- Water test
- Solvent loading
- Operational development

Parametric
- AFS Factorial
  - Absorber Factorial

Simple Stripper
- Match best AFS
- Compare

Long-term
- Reliability
- Performance
- Degradation
- Aerosol

12/12/17
2/22/18
600 hrs
2/23
4/12
250 hrs
4/18
6/4
1100 hrs
6/5
8/15

6+ host plant outages of days to weeks
NCCC Operations

PZ Solids Successfully managed
Reliable operation
Seasonal T managed
PZ solids successfully managed

• PZ delivered as 68% solid in mini-ISO container
  – Melted and loaded with CO$_2$ in circulating hot water
• Numerous boiler shutdowns without PZ precipitation
  – Solvent gravity drained to rich storage
• Plugged CO$_2$ product flow meter
  – Once during AFS stripper flooding
    • cleaned manually offline
  – Similar plugging with simple stripper (no reflux)
Controlling T across the absorber

- Lean Solvent: 104 F - 110-130 F
- Trim Cooler: 86 F
- Gas Outlet: 104 F, 115 F
- Gas Inlet: 104 F, 115 F
- In-Out IC: 104 F, 110-130 F
- Wash Tower: Gas Outlet 106 F, 117 F
- DCC: 86 F
2.1 GJ/t CO$_2$
150$^\circ$C Stripper producing CO$_2$ at 6 bar

90-98% removal
40 ft packing, 0.5 – 0.62 MW gas

More in the next presentation
Energy Use of 5 m PZ with Advanced Flash Stripper
No correction for heat loss
Simple Stripper requires 50% more heat.
Heat Duty (GJ/tonne) at NCCC
Not corrected for heat loss, Mostly Simple Stripper

- B&W RSAT 2011: 2.5
- Hitachi H3-1 2012: 2
- Chiyoda T-3 2014: 2.5
- CCS APBS 2015: 2.5
- Cansolv DC103 2017: 2.5
- Linde AOSIbl 2017: 2.5
- Ion 2017: 2.1
- AECOM PZ-AFS 2018: 3
- AECOM PZ-SS 2018: 3
Oxidation by NH$_3$< 0.17 lb PZ/t CO$_2$
Total Formate: SRP < NCCC 2018 << Tarong, PP2
Oxidation Management

• Stripper sump residence time - Fe$^{+3}$ mechanism
  • 80% level – first 6 weeks
  • 15% level – second 6 wks
  • 7% level – impacts energy performance

• Dissolved Oxygen
  • Warm rich bypass residence time at 250°F
  • Flashing in hot exchanger to remove O$_2$
  • Nitrogen sparging in absorber sump - second 6 wks

• NO$_2$
  • SCR and Bag filter eliminate NO$_2$
  • Uncertain residual, SCR reliability
  • Thiosulfate added to prescrubber - second 6 wks
PZ Oxidation estimated from \( \text{NH}_3 = 0.17 \text{ lb PZ/t CO}_2 \)
Assume 1 mol \( \text{NH}_3/\text{mol PZ Oxidized} \)

Simple Stripper

AFS Low Ox
(15% Stripper Level, \( \text{N}_2 \) Sparging, \( \text{NO}_2 \) Removal)

AFS High Ox
(80% Stripper Level)
PZ oxidation as suggested by dissolved Fe

Operating Hours (hr)

Dissolved Fe (mmol/kg)

AFS High OX

Simple Stripper

AFS High OX

NCCC 2018

AFS Low OX
Comparison of Dissolved Fe to other PZ pilot data

- AFS Low OX
- AFS High OX
- Simple Stripper
- AFS
- PP2
- CSIRO Tarong
- NCCC 2018
- SRP

Operating Hours (hr)

Fe$^{2+}$ (mmol/kg)
Normalized Degradation Products (Total Formate and EDA)

- AFS High OX (80% Stripper Level)
- Simple Stripper
- AFS Low OX (15% Stripper Level, N₂ Sparging, NO₂ Removal)

- Total Formate
- EDA
0.5 – 5 ppm PZ emissions at 0 – 4 ppm SO$_3$  
Aerosol managed by high Lean T  
and additional pump-around water wash
Managing PZ emissions

Water Wash
Bag Filter
Greater Lean T
Pump-around

Hydrated Lime addition

Bag Filter

2 – 8 ppm SO₃ Injection

DCC

3rd Bed Pump-around ON

Gas Outlet

Max Cooling

<1 – 60 ppm PZ

Lean Solvent
110 F
120 F
130 F

DCC

Max cooling

In-Out IC

Gas Inlet
110 F – 115 F

Rich Solvent
Low Ca(OH)$_2$ correlates with high PZ

Low lime injection in spring
Mostly > 600 in summer

Avg. PZ (ppm)
Avg. Hydrated Lime addition (lbs/hr)
Higher lean T & 3rd Bed Pump-around suppress PZ

Wash Tower Outlet

\[ \text{SO}_3 \text{ Injected (ppm)} \]

\[ \text{PZ (ppm)} \]

- Lean 110 F
- Lean 120 F
- Lean 130 F
- Lean 130 F Pump-around
Carbon Steel frequently protected by FeCO$_3$
Stainless mostly untouched
Degradation products increase corrosion
Corrosion occurs at a critical concentration of degradation products. 
Bench-scale measurement by ER probe at reducing conditions, 120°C.
Not all FeCO₃ films are protective.

Not corroded
36 wt% Tarong PZ

Corroded
60 wt% Tarong PZ
Protective $\text{FeCO}_3/\text{Fe}_3\text{O}_4$ forms on C1010 at high T

118 µm/yr
50 °C
(incomplete layer)
cold rich bypass, 115 hr.

94 µm/yr
150 °C
(protective layer)
AFS sump, 115 hr
### NCCC C1010 Coupon Corrosion, 114 hrs of contact

<table>
<thead>
<tr>
<th>Location</th>
<th>Corrosion (μm/yr)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorber sump</td>
<td>79</td>
<td>Slow oxidation</td>
</tr>
<tr>
<td>Absorber middle</td>
<td>105</td>
<td>Slow oxidation</td>
</tr>
<tr>
<td>Cold, lean</td>
<td>350</td>
<td>High velocity?</td>
</tr>
<tr>
<td>Cold rich bypass</td>
<td>118</td>
<td>Slow oxidation</td>
</tr>
<tr>
<td>Warm rich bypass</td>
<td>92</td>
<td>protected</td>
</tr>
<tr>
<td>Hot rich</td>
<td>173</td>
<td>Flashing</td>
</tr>
<tr>
<td>AFS sump</td>
<td>94</td>
<td>Protected</td>
</tr>
</tbody>
</table>

- Stainless analysis in progress, but no signs of high corrosion
A baseline process for 2G amine scrubbing

• Reliable Design and Operation

• 2.1 GJ/t CO$_2$ producing CO$_2$ at 6 bar

• 90-98% removal with 40 ft packing

• Degradation < 0.2 lbs PZ/t CO$_2$

• 0.5 – 5 ppm PZ emissions at 0 – 4 ppm SO$_3$

• Carbon steel frequently protected by FeCO$_3$
Acknowledgements

• Cost Sharing: Luminant, Southern Co, EPRI, LG&E, Chevron,
• Operations by Southern Co.: Tony Wu, Laura Uhrig, Graham Bingham

• Acknowledgement: “This material is based on work supported in part by the Department of Energy under Award Number DE-FE0005654.”

• Disclaimer: “This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.”