Safeguarding Amines from Oxidation by Enabling Technologies

DOE Contractors Meeting

DE-FE0031861

Fred Closmann, Ph.D., The University of Texas at Austin

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management Project Review Meeting
August 15 - 19, 2022
Outline

• Project objectives and structure
• Background on solvent oxidation and losses
• SRP pilot modifications
• SRP pilot data
• Dissolved oxygen stripping
• Plans for NCCC campaign (Q4 2022 – Q1 2023)
Develop technologies to safeguard scrubbing from solvent loss by oxidation. Project directly addresses safeguarding amine solvents against $O_2$ and $NO_2$. 
<table>
<thead>
<tr>
<th>Budget Period</th>
<th>Start Date</th>
<th>End Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>March 1, 2020</td>
<td>May 31, 2021</td>
</tr>
<tr>
<td>2</td>
<td>June 1, 2021</td>
<td>April 30, 2022</td>
</tr>
<tr>
<td>3</td>
<td>May 1, 2022</td>
<td>June 30, 2023</td>
</tr>
</tbody>
</table>
## Project budget

<table>
<thead>
<tr>
<th>Description</th>
<th>BP1 ($)</th>
<th>BP2 ($)</th>
<th>BP3 ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salaries (PI/staff/grad students/SRP)</td>
<td>342,316</td>
<td>416,116</td>
<td>278,123</td>
</tr>
<tr>
<td>Fringe</td>
<td>95,361</td>
<td>118,687</td>
<td>91,036</td>
</tr>
<tr>
<td>Travel</td>
<td>7,016</td>
<td>9,601</td>
<td>23,498</td>
</tr>
<tr>
<td>Equipment*</td>
<td>230,100</td>
<td>5,000</td>
<td>102,657*</td>
</tr>
<tr>
<td>Supplies</td>
<td>54,450</td>
<td>74,153</td>
<td>73,801</td>
</tr>
<tr>
<td>Tuition</td>
<td>38,658</td>
<td>39,435</td>
<td>40,260</td>
</tr>
<tr>
<td>Indirect/Overhead (56.5%)</td>
<td>282,015</td>
<td>349,766</td>
<td>263,549</td>
</tr>
<tr>
<td>Total by BP</td>
<td>1,049,915</td>
<td>1,012,759</td>
<td>872,924</td>
</tr>
<tr>
<td>Total cumulative</td>
<td>1,049,915</td>
<td>2,062,674</td>
<td>2,935,598</td>
</tr>
<tr>
<td>Total cost share</td>
<td>209,983</td>
<td>202,552</td>
<td>174,585</td>
</tr>
</tbody>
</table>

*Reflects redirection of Equipment budget for purchase of amino acid identification/quantification system.
Why is this project important?
## Why this project is important

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Rate (kg/t CO₂)</th>
<th>Flue gas</th>
<th>CO₂ (%)</th>
<th>O₂ (%)</th>
<th>NOₓ/NO₂</th>
<th>Facility</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASTOR1, CASTOR 2</td>
<td>1.4</td>
<td>coal</td>
<td>12</td>
<td>NA</td>
<td>&lt;65 ppm NOₓ</td>
<td>Esbjergvaerket, Denmark</td>
<td>Knudsen, 2009</td>
</tr>
<tr>
<td>CESAR1</td>
<td>0.45</td>
<td>coal (lignite)</td>
<td>15.2</td>
<td>5</td>
<td>6-8 ppm NO₂, 100-160 ppm NOₓ</td>
<td>Niederaussem</td>
<td>Moser, 2022</td>
</tr>
<tr>
<td>CDRMax</td>
<td>2</td>
<td>coal</td>
<td>14-16</td>
<td>NA</td>
<td>NA</td>
<td>CAER, UK</td>
<td>Frimpong, 2021</td>
</tr>
<tr>
<td>MEA</td>
<td>0.8-1.6</td>
<td>CHP (NGCC)</td>
<td>3.6-4</td>
<td>13-14</td>
<td>&lt;5 ppmv NOₓ</td>
<td>TCM</td>
<td>Morken, 2019</td>
</tr>
<tr>
<td>PZAS™</td>
<td>0.3/0.75</td>
<td>NGCC</td>
<td>4</td>
<td>12-14</td>
<td>&lt;1 ppm</td>
<td>NCCC, Wilsonville, AL</td>
<td>Wu, 2021</td>
</tr>
<tr>
<td>PZAS™</td>
<td>0.6</td>
<td>synth NGCC</td>
<td>4</td>
<td>20</td>
<td>1 ppm</td>
<td>SRP, UT</td>
<td>Closmann, 2022</td>
</tr>
<tr>
<td>Aker ACC S26</td>
<td>0.15-0.2</td>
<td>cement kiln</td>
<td>17.8</td>
<td>7.5</td>
<td>180-250 mg/Nm³ NOₓ</td>
<td>Norcem; Brevik, Norway</td>
<td>Knudsen, 2014</td>
</tr>
<tr>
<td>Solvent</td>
<td>Rate (kg/t CO₂)</td>
<td>Flue gas</td>
<td>CO₂ (%)</td>
<td>O₂ (%)</td>
<td>NOₓ/NO₂</td>
<td>Facility</td>
<td>Author</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>----------</td>
<td>---------</td>
<td>--------</td>
<td>-------------------</td>
<td>-----------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>CASTOR1, CASTOR 2</td>
<td>1.4</td>
<td>coal</td>
<td>12</td>
<td>NA</td>
<td>&lt;65 ppm NOₓ</td>
<td>Esbjergvaerket, Denmark</td>
<td>Knudsen, 2009</td>
</tr>
<tr>
<td>CESAR1</td>
<td>0.45</td>
<td>coal (lignite)</td>
<td>15.2</td>
<td>5</td>
<td>6-8 ppm NO₂, 100-160 ppm NOₓ</td>
<td>Niederaussem</td>
<td>Moser, 2022</td>
</tr>
<tr>
<td>CDRMax</td>
<td>2</td>
<td>coal</td>
<td>14-16</td>
<td>NA</td>
<td>NA</td>
<td>CAER, UK</td>
<td>Frimpong, 2021</td>
</tr>
<tr>
<td>MEA</td>
<td>0.8-1.6</td>
<td>CHP (NGCC)</td>
<td>3.6-4</td>
<td>13-14</td>
<td>&lt;5 ppmv NOₓ</td>
<td>TCM</td>
<td>Morken, 2019</td>
</tr>
<tr>
<td>PZASTM</td>
<td>0.3/0.75</td>
<td>NGCC</td>
<td>4</td>
<td>12-14</td>
<td>&lt;1 ppm</td>
<td>NCCC, Wilsonville, AL</td>
<td>Wu, 2021</td>
</tr>
<tr>
<td>PZASTM</td>
<td>0.6</td>
<td>synth NGCC</td>
<td>4</td>
<td>20</td>
<td>1 ppm</td>
<td>SRP, UT</td>
<td>Closmann, 2022</td>
</tr>
<tr>
<td>Aker ACC S26</td>
<td>0.15-0.2</td>
<td>cement kiln</td>
<td>17.8</td>
<td>7.5</td>
<td>180-250 mg/Nm³ NOₓ</td>
<td>Norcem; Brevik, Norway</td>
<td>Knudsen, 2014</td>
</tr>
</tbody>
</table>

**Why this project is important**
• Absence of NO$_2$ at SRP and NCCC – investigate role of NO$_2$ in oxidation
• PZAS$^\text{TM}$ flashes dissolved/entrained O$_2$ before stripper sump
• Stripper sump $\tau_{\text{avg}}$ at UT-SRP and NCCC <2 minutes, which may minimize oxidation of amine by Fe$^{+3}$
Three oxidation mechanisms of interest
Amine oxidation mechanisms

- **Vented gas**
- **Absorber**
- **Water Wash**
- **Intercooler**
- **Trim cooler**
- **Rich pump**
- **Cold cross exchanger**
- **Hot cross exchanger**
- **Condenser**
- **Cold rich exchanger**
- **Cold rich bypass**
- **Warm rich bypass**
- **Stripper**
- **Steam heater**
- **Flash**

No. 1: NO$_2$ in flue gas
Amine oxidation mechanisms

1: NO$_2$ in flue gas
2: DO/entrained O$_2$ in rich amine
Amine oxidation mechanisms

1. NO₂ in flue gas
2. DO/entrained O₂ in rich amine
3. Fe²⁺ → Fe³⁺ in rich amine
4. Fe³⁺ → Fe²⁺
SRP pilot campaign modifications
<table>
<thead>
<tr>
<th>Modification</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inject and measure NO$_2$ at 1 ppm</td>
<td>Create baseline oxidation similar to commercial flue gas</td>
</tr>
<tr>
<td>N$_2$ sparging and entrained bubble coalescence in the absorber sump</td>
<td>Test efficacy of DO stripping and entrained bubble/oxygen removal</td>
</tr>
<tr>
<td>Increase $\tau$ on warm rich bypass (WRB) from &lt;0.5 to &gt;1 min</td>
<td>Confirm high-T degradation in rich amine</td>
</tr>
<tr>
<td>Add carbon bed in rich amine line to remove iron</td>
<td>Test impact of removing oxidation catalysts</td>
</tr>
</tbody>
</table>
Pilot campaign results
NO$_2$ measurement in flue gas – initial test

- Vented gas
- Absorber
- Condenser
- Cold rich bypass
- Cold rich
- Warm rich bypass
- Stripper
- Steam heater
- Flash
- Intercooler
- Water Wash
- Injection point
- Air
- Rich pump
- Cold cross exchanger
- Cold exchanger
- Hot cross exchanger

American Ecotech S60 analyzer:
- Direct NO$_2$ analysis
- Cavity Attenuated Phase Shift
- Accurate over 0 - 2 ppm range

Observed ~42% NO$_2$ absorption into solvent

~0.6 ppm

~1 ppm

Injection point

NO$_2$ measurement in flue gas – initial test

American Ecotech S60 analyzer:
- Direct NO$_2$ analysis
- Cavity Attenuated Phase Shift
- Accurate over 0 - 2 ppm range

Observed ~42% NO$_2$ absorption into solvent

~0.6 ppm

~1 ppm

Injection point
Mononitrosopiperazine (MNPZ) and NO$_2$ absorption at SRP

**Baseline**

NO$_2$ absorbed/MNPZ formed ~ 1/1

WRB $\tau$ increase

NO$_2$ absorbed/MNPZ formed ~ 1/1
Piperazinone (PZone) & MNPZ at SRP

\[ \Delta \text{PZone}/\Delta \text{MNPZ} > 25 \text{ mol/mol} \]

Baseline  \(\text{1 ppm NO}_2\)  \(\text{N}_2\)  \(\text{No N}_2\)  Carbon

PZ-one-lean  MNPZ-lean
Piperazinol (PZOH) and total aldehydes at SRP
Amine oxidation in PZ – NO$_2$ pathway

**Absorber**

\[
\text{NO}_2^- + \text{PZ} \rightarrow (\text{PZ} \cdot \cdot) + \text{NO}_2^- + \text{H}^+
\]

*Free radical propagation:*

\[
\text{PZ} \cdot + \text{O}_2 \rightarrow \text{PZO} \cdot \cdot
\]

\[
\text{PZO} \cdot + \text{PZ} \rightarrow \text{PZ} \cdot + \text{PZO} \cdot \cdot
\]

*Termination:*

\[
2\text{PZ} \cdot + \text{H}_2\text{O} \rightarrow (\text{PZO} \cdot \cdot \cdot) + \text{PZ}
\]

\[
\text{PZO} \cdot \cdot \cdot \cdot \rightarrow 2\text{PZO} \cdot \cdot
\]

\[
\text{PZO} \cdot \cdot \cdot \cdot \rightarrow \text{PZO} \cdot + \cdot \text{OH}
\]
Dissolved oxygen stripping through N$_2$ sparging
Wire mesh mist eliminator

Mist eliminator and sparge pipe installed in absorber

DO and entrained oxygen removal
Three tests conducted in absorber sump at N₂ sparging rates of 6, 10, and 20 SCFM

Test at 6 SCFM N₂
- Flue gas rate of 600 SCFM; N₂ ~1% of total gas traffic in abs column
- Solvent rate of 4 gpm → $\tau_{abs} \sim 15$ minutes
- Rich amine DO decreased from 7.4 ppm to 1.0 ppm
- ~2.3 NTUs; abs sump level ~29 inches, so HTU ~ 12 inches
- Sump level then increased from 29 to 35 inches -&gt; increased NTU & lowered DO

Foaming in absorber sump
- As foam developed mass transfer improved & DO decreased
- Operational issues managing abs sump liquid level - added anti-foam
- Foam disappeared → DO increased, but N₂ sparging still effective
Did N₂ sparging reduce solvent oxidation?

- Best evidence in NH₃ data
- NH₃ experienced a drop during the 6 SCFM N₂ sparging test, followed by increase
- 6 SCFM N₂ sparge test coincided with WRB res time increase being brought online
- Possible test outcome: N₂ stripped NH₃ from solvent (apparent at abs knock-out)
SRP campaign conclusions

- PZone detected at greatest conc. (~85 mmol/kg) among products and likely evidence of catalytic reactions
- Observed 42% NO$_2$ absorption rate with each pass of flue gas through absorber
- MNPZ formed at 1:1 ratio w/ NO$_2$ absorbed (not catalytic)
- $\Delta$PZone/$\Delta$MNPZ $\sim$40
- N$_2$ sparging in abs sump at 1% of column gas traffic reduced DO by >85%; unclear how much oxidation reduction occurred
NCCC campaign overview
• Currently scheduled for Q4 2022 -> Q1 2023
• NGCC flue gas (4% CO₂, 8% H₂O) at ~110 °C from gas boiler
• Reduce NO₂ concentration to ≤1 ppm with thiosulfate/sulfite
• Test N₂ sparging in absorber sump for DO removal
• Test carbon bed at slipstream rates of 1 – 5 gpm
• Use acid wash loop for NH₃ control
• Bottom packed section pump-around intercooling
• Multiple corrosion coupon locations
<table>
<thead>
<tr>
<th>Parameter</th>
<th>SRP (UT Austin)</th>
<th>NCCC (Southern Co.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size equivalent (MW_{eq})</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Solvent inventory (gal)</td>
<td>~350(a)</td>
<td>1300(b)</td>
</tr>
<tr>
<td>Abs diameter (inches)</td>
<td>16.8</td>
<td>25.3</td>
</tr>
<tr>
<td>Abs packing height (feet)</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Abs sump residence time (min)</td>
<td>15(c)</td>
<td>8(d)</td>
</tr>
<tr>
<td>Flue gas source</td>
<td>Synthetic</td>
<td>Commercial - natural gas boiler or coal</td>
</tr>
<tr>
<td>Flue gas rate (lb/hr)</td>
<td>3,000</td>
<td>8,000</td>
</tr>
<tr>
<td>Flue gas (NO_{2}) ppm</td>
<td>0 (blended to 1 ppm)</td>
<td>1 – 2</td>
</tr>
</tbody>
</table>

(a) Lean amine tank bypassed; (b) includes carbon bed loop; (c) at L = 4 gpm; (d) calc at L ~ 12 gpm (~3.5 gpm/ft²) & 3.5 ft liquid height.
## Project participants

<table>
<thead>
<tr>
<th>Party</th>
<th>Person</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>NETL</td>
<td>Krista Hill</td>
<td>Project Manager</td>
</tr>
<tr>
<td>UT-Austin</td>
<td>Dr. Gary Rochelle</td>
<td>Principal Investigator</td>
</tr>
<tr>
<td></td>
<td>Dr. Fred Closmann</td>
<td>Deputy PM</td>
</tr>
<tr>
<td>GRAs</td>
<td>Yuying Wu</td>
<td>HTOR, FTIR - pilot support</td>
</tr>
<tr>
<td></td>
<td>Ching-Ting Liu</td>
<td>Corrosion, Titrations – pilot support</td>
</tr>
<tr>
<td></td>
<td>Chih-I Chen</td>
<td>HGF - NO₂ studies</td>
</tr>
<tr>
<td></td>
<td>Ariel Plantz</td>
<td>Iron studies</td>
</tr>
<tr>
<td></td>
<td>Miguel Abreu</td>
<td>Pilot support</td>
</tr>
<tr>
<td></td>
<td>Athreya Suresh</td>
<td>Pilot support</td>
</tr>
<tr>
<td>SRP Staff</td>
<td>Dr. Frank Seibert</td>
<td>Director SRP</td>
</tr>
<tr>
<td></td>
<td>JR Campos</td>
<td>Operations technician</td>
</tr>
<tr>
<td></td>
<td>Yee Lee Chen</td>
<td>Night shift operator, pilot data analysis</td>
</tr>
</tbody>
</table>
Questions?
Piperazinone (PZone) and other degradation products at SRP

Baseline

NO₂

N₂

No N₂

Carbon

WRB τ increase

Time (hrs)

HEP, MPZ (mmol/kg)
PZone, EDA, AEP (mmol/kg)
Did carbon bed reduce solvent oxidation?

- Best evidence in UV-Vis absorbance data
- Absorbance (A) dropped when carbon bed brought online
- Iron continued a decreasing trend; chelated metal ion species were being removed
- Possible test outcome: Iron solubility limit was changing with step changes
Amine (PZ) oxidation – role of NO₂

Total N in Products (EDA, PZ-ol, PZ-one, FPZ, MNPZ, NH₃, AEP)

- **CSIRO Tarong 125 ºC**
  - 0.43 mmol/kg/hr
  - NO₂ Abs. Rate: 0.07 mmol/kg/hr (1.3 ppmv)
- **CSIRO Tarong 155 ºC**
  - 1.11 mmol/kg/hr
  - $E_a = 44$ kJ/mol
- **PP2**
  - 0.38 mmol/kg/hr
- **NCCC Coal**
  - 0.12 mmol/kg/hr
- **SRP**
  - 0.11 mmol/kg/hr
- **NCCC NGCC w/ Carbon**
  - 0.11 mmol/kg/hr

Estimated Total N in Deg. Products and C. NH₃ (mmol/kg)

Time (hrs)
Where do we expect oxidation to occur?

\[ \tau < 30 \text{ seconds} \]
\[ \text{DO} < 1 \text{ ppm (flashing)} \]
\[ T \sim 150 \degree C \]

\[ \tau \sim 15 \text{ min} \]
\[ \text{DO} \sim 5 \text{ ppm} \]
\[ T \sim 55 \degree C \]
Amino acids in degraded amine solutions

- Why investigate amino acids?
  - Ability of bicine to chelate metal ions (Lawson, 2003)
  - 2% mole N as amino acids in MDEA/PZ blends in gas conditioning plants (Thompsen, 2013)
  - Correlation to corrosion
- Ternary ligand complex formation stable at pH>7 (Mohamed, 2005)
- Amino acid analytical method history at UT (Closmann, 2011)
  - Dionex ICS-3000 with AminoPac PA10 column (Dionex AAA™-Direct)
  - Gold-oxide catalyzed oxidation of amino acids
  - Pulsed electrochemical detector
  - Bicine, glycine, HEG and HES all identified in degraded MDEA/PZ
  - Glycine detected at 5 mmol/L in temperature cycled (125 °C) 8 m PZ
Modifications at NCCC
## Modification

<table>
<thead>
<tr>
<th>Modification</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce NO$_2$ to $&lt; 1$ ppm and measure</td>
<td>Use sulfite/thiosulfate in pre-scrubber to remove NO$_2$</td>
</tr>
<tr>
<td>N$_2$ sparging in the absorber sump</td>
<td>Test efficacy of DO stripping in the absorber sump</td>
</tr>
<tr>
<td>Remove iron (as chelates) with carbon bed</td>
<td>Test impact of removing oxidation catalysts over slipstream range 1–5 gpm</td>
</tr>
<tr>
<td>Test water wash configured as acid wash loop</td>
<td>Ammonia control</td>
</tr>
<tr>
<td>Perform pump-around intercooling of bottom packed section</td>
<td>Remove heat for process performance and lower emissions in stack</td>
</tr>
<tr>
<td>Adding corrosion coupons</td>
<td>Monitor corrosion simultaneous with oxidation</td>
</tr>
</tbody>
</table>
NO₂ reduction in flue gas prescrubber

- Chemistry in prescrubber (Selinger, 2018)
  - Sulfite (SO₃²⁻) added as Na₂SO₃ to achieve 400 ppm to react with NO₂
  - Thiosulfate added as Na₂S₂O₃ to achieve (180 mM) and inhibit sulfite oxidation
  - NaOH added to maintain pH > 8
  - Reactions occur in liquid boundary layer
## NCCC pilot campaign – planned strategies

<table>
<thead>
<tr>
<th>Modification</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce NO₂ to &lt; 1 ppm and measure</td>
<td>Use sulfite/thiosulfate in pre-scrubber to remove NO₂</td>
</tr>
<tr>
<td>N₂ sparging in the absorber sump</td>
<td>Test efficacy of DO stripping in the absorber sump</td>
</tr>
<tr>
<td>Remove iron (as chelates) with carbon bed</td>
<td>Test impact of removing oxidation catalysts over slipstream range 1 – 5 gpm</td>
</tr>
<tr>
<td>Test water wash configured as acid wash loop</td>
<td>Ammonia control</td>
</tr>
<tr>
<td>Perform pump-around intercooling of bottom packed section</td>
<td>Remove heat for process performance and lower emissions in stack</td>
</tr>
<tr>
<td>Adding corrosion coupons</td>
<td>Monitor corrosion simultaneous with oxidation</td>
</tr>
</tbody>
</table>
Dissolved oxygen stripping with N₂

- Will use new Mott sparge pipe with more $A_{XS}$ than used in past to lower $D_{bub}$
- Abs pump-around intercooling will increase $L$ by 4X in abs sump; will this affect sparge effectiveness?
- At ~2,400 SCFM, N₂ rates of 24 and 50 SCFM will be tested (start at 1% of abs gas traffic)
- N₂ sparge rate will be adjusted to maintain 5 - 25 fpm at nozzle/sparge pipe and $*D_{bub} < 1$ mm
- Will measure DO downstream and estimate NTU and HTU; expect ~2.5 NTU from SRP results

*Design Guide & Part Selection, Mott Corporation (www.mottcorp.com); recommendations for water service.
## NCCC pilot campaign – planned strategies

<table>
<thead>
<tr>
<th>Modification</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce NO₂ to &lt; 1 ppm and measure</td>
<td>Use sulfite/thiosulfate in pre-scrubber to remove NO₂</td>
</tr>
<tr>
<td>N₂ sparging in the absorber sump</td>
<td>Test efficacy of DO stripping in the absorber sump</td>
</tr>
<tr>
<td>Remove iron (as chelates) with carbon bed</td>
<td>Test impact of removing oxidation catalysts over slipstream range 1 – 5 gpm</td>
</tr>
<tr>
<td>Test water wash configured as acid wash loop</td>
<td>Ammonia control</td>
</tr>
<tr>
<td>Perform pump-around intercooling of bottom packed section</td>
<td>Remove heat for process performance and lower emissions in stack</td>
</tr>
<tr>
<td>Adding corrosion coupons</td>
<td>Monitor corrosion simultaneous with oxidation</td>
</tr>
</tbody>
</table>
Remove degradation products & iron with carbon bed

- Will use existing equipment that has been used in past campaign(s)
- Fourteen sets of two cannisters (28 total); offers flexibility - will run 6 cannisters
- Desired flow range (1 – 5 gpm) at nominal L of 12 gpm (8 to 40%)
- Adds ~300 gallons of solvent inventory
- Will run minimum four weeks; capture breakthrough as color change (UV-Vis)
## NCCC pilot campaign – planned strategies

<table>
<thead>
<tr>
<th>Modification</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce NO$_2$ to &lt; 1 ppm and measure</td>
<td>Use sulfite/thiosulfate in pre-scrubber to remove NO$_2$</td>
</tr>
<tr>
<td>N$_2$ sparging in the absorber sump</td>
<td>Test efficacy of DO stripping in the absorber sump</td>
</tr>
<tr>
<td>Remove iron (as chelates) with carbon bed</td>
<td>Test impact of removing oxidation catalysts over slipstream range 1 – 5 gpm</td>
</tr>
<tr>
<td>Test water wash configured as acid wash loop</td>
<td>Ammonia control</td>
</tr>
<tr>
<td>Perform pump-around intercooling of bottom packed section</td>
<td>Remove heat for process performance and lower emissions in stack</td>
</tr>
<tr>
<td>Adding corrosion coupons</td>
<td>Monitor corrosion simultaneous with oxidation</td>
</tr>
</tbody>
</table>
Test acid wash loop for ammonia control

- Water wash loop required for water balance
- Water wash does not remove ammonia if wash water is returned to the process; accumulates until emissions equal to rate of production
- Bleed of wash water or stripper condensate with high NH$_3$ can reduce emissions
- Acid wash (H$_2$SO$_4$) with bleed will be tested to remove NH$_3$
- Challenge will be to operate long enough to obtain steady state ammonia concentrations with and without acid wash
NCCC pilot campaign – planned strategies

<table>
<thead>
<tr>
<th>Modification</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce NO$_2$ to &lt; 1 ppm and measure</td>
<td>Use sulfite/thiosulfate in pre-scrubber to remove NO$_2$</td>
</tr>
<tr>
<td>N$_2$ sparging in the absorber sump</td>
<td>Test efficacy of DO stripping in the absorber sump</td>
</tr>
<tr>
<td>Remove iron (as chelates) with carbon bed</td>
<td>Test impact of removing oxidation catalysts over slipstream range 1 – 5 gpm</td>
</tr>
<tr>
<td>Test water wash configured as acid wash loop</td>
<td>Ammonia control</td>
</tr>
<tr>
<td>Perform pump-around intercooling of bottom packed section</td>
<td>Remove heat for process performance and lower emissions in stack</td>
</tr>
<tr>
<td>Adding corrosion coupons</td>
<td>Monitor corrosion simultaneous with oxidation</td>
</tr>
<tr>
<td>Modification</td>
<td>Purpose</td>
</tr>
<tr>
<td>-------------------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Reduce NO₂ to &lt; 1 ppm and measure</td>
<td>Use sulfite/thiosulfate in pre-scrubber to remove NO₂</td>
</tr>
<tr>
<td>N₂ sparging in the absorber sump</td>
<td>Test efficacy of DO stripping in the absorber sump</td>
</tr>
<tr>
<td>Remove iron (as chelates) with carbon bed</td>
<td>Test impact of removing oxidation catalysts over slipstream range 1 – 5 gpm</td>
</tr>
<tr>
<td>Test water wash configured as acid wash loop</td>
<td>Ammonia control</td>
</tr>
<tr>
<td>Perform pump-around intercooling of bottom packed section</td>
<td>Remove heat for process performance and lower emissions in stack</td>
</tr>
<tr>
<td>Adding corrosion coupons</td>
<td>Monitor corrosion simultaneous with oxidation</td>
</tr>
</tbody>
</table>
Proposed corrosion coupon locations

Circles – disc coupons; squares – strip coupons (see photos)
Red – old locations; blue – new locations
SRP corrosion coupon locations

- Existing
- Added 2021

Diagram showing the corrosion coupon locations in a chemical process. Icons and labels include WW, Water, CO₂, Trim Cooler, Lean solvent, Intercooler, Rich solvent, Cold rich bypass, Warm rich bypass, Cross exchanger, Striper, and Residence T mod.
SRP pilot campaign – add carbon bed in rich amine line

- Pass 5-10% liquid rate slip-stream through carbon bed
- Single-pass removal sock design
- Size will limit time on stream due to break-through
- Using pressure of rich amine line downstream of pump to push liquid through carbon bed; return to absorber
- Same fresh carbon used at NCCC
SRP pilot campaign – formate and N-formyl amides

![Graph showing formate, total formate, NFPZ, and WRB increase over time](image)

- Baseline
- NO$_2$
- N$_2$
- No N$_2$
- Carbon

WRB $\tau$ increase

Formate, Total Formate, NFPZ, (mmol/kg)

Time (hrs)
SRP pilot campaign – NH₃ in absorber knock-out drum (FTIR)

- Baseline
- NO₂
- N₂
- No N₂
- Carbon

WRB τ increase

Avg NH₃ (ppm) vs. Time (hrs)
Oxygen measurement in CO$_2$ gas

Sample pulled from horizontal CO$_2$ accumulator (>15 psi)

- Vented gas
- Absorber
- Condenser
- Cold rich exchanger
- Cold rich bypass
- Cold cross exchanger
- Hot cross exchanger
- Stripper
- Steam heater
- Flash

Air

- Rich pump
- DO probe
- Water Wash
- Intercooler

- DO probe
- Air