Piperazine and nitrosamine degradation in pilot plants

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Commonwealth Scientific and Industrial Research Organisation (CSIRO)
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Outline

- Introduction
  - Description of pilot plants and cycling apparatus
  - Safe shipping of Tarong samples

- Results
  - Nitrosamine accumulation
  - Solvent oxidation
  - Corrosion
  - Flue gas contaminant accumulation

- Conclusions
1.2 kPa CO$_2$
Volatile amines

\( \text{NH}_3 \)
Increased emissions

150 bar CO$_2$

12 kPa CO$_2$

5 kPa O$_2$

1 – 5 ppm NO$_2$

SO$_2$, NO$_x$, HCl, Fly ash

Aerosols

D.O., peroxides

Nitrite

Sulfate, nitrate, Cl, Hg, Se, As, Cr, etc.

Absorber

Rich

Nitrosamine formation & decomposition

Stainless steel metal ions: Fe$^{2+}$, Mn$^{2+}$

Corrosion

Thermal degradation: Carbamate polymers, S$_{N2}$

High temp oxidation: \( \text{NH}_3 \), formate, heat stable salts,
Benefits:
- Faster absorption rate, 2x capacity of MEA
- Thermally stable beyond 150 °C: far greater energy performance
- More resistant to oxidation than MEA

Drawbacks:
- More viscous than MEA
- Limited solubility window
- >2x price of MEA per tonne
# PZ Pilot plants/cycled degradation apparatus

<table>
<thead>
<tr>
<th></th>
<th>Tarong</th>
<th>PP2</th>
<th>SRP</th>
<th>HTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas</td>
<td>Coal</td>
<td>Coal</td>
<td>Air + CO₂</td>
<td>Air + CO₂</td>
</tr>
<tr>
<td>$M_W$&lt;sub&gt;e&lt;/sub&gt;</td>
<td>0.1</td>
<td>N/A</td>
<td>0.1</td>
<td>Bench scale</td>
</tr>
<tr>
<td>$O_2$ (kPa)</td>
<td>5</td>
<td>5</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>$SO_2$ (ppm&lt;sub&gt;v&lt;/sub&gt;) (avg)</td>
<td>0.6</td>
<td>&lt;0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$NO_2$ (ppm&lt;sub&gt;v&lt;/sub&gt;) (avg)</td>
<td>1.3</td>
<td>1 – 5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$NO_x$ (ppm&lt;sub&gt;v&lt;/sub&gt;) (avg)</td>
<td>~200</td>
<td>Controlled</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Materials of construction</td>
<td>SS304</td>
<td>SS</td>
<td>SS304, some CS</td>
<td>SS316, plastic, glass</td>
</tr>
<tr>
<td>Stripper $T_{op}$</td>
<td>120 / 155 C</td>
<td>150 C</td>
<td>135 / 150 C</td>
<td>120 – 160 C</td>
</tr>
<tr>
<td>Notes</td>
<td></td>
<td></td>
<td>1 wt% Inh A</td>
<td>Run w/ fresh 8 m PZ and degraded SRP solvent</td>
</tr>
</tbody>
</table>

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**Notes**

- Run w/ fresh 8 m PZ and degraded SRP solvent
Safe shipping of Tarong samples

- Sealed in 30 mL vials with tape, then placed in Ziploc bags and surrounded by packing material
- Opened and stored in fume hood at room temperature
- No samples leaked in transit
Results
1-Nitroso-PZ (MNPZ)

Tarong 1.3 ppm NO₂

120 °C 155 °C

PP2 150 °C, 1 – 5 ppm NO₂
Oxidation at Tarong

No significant accumulation of thermal degradation products (< 10 mmol/kg)

PZ + O₂ → 2-PZOH → EDA → Formate
Catalyzed by metal ions (corrosion)

Stainless steel metal ions (SSM) (mmol/kg)

Oxidation products (mmol/kg)

Cycles

120 °C, 155 °C
Iron accumulation

Fresh 8 m PZ in HTOR 40 – 150 °C

PP2

155 °C

0.3 mM Fe$^{2+}$ added

SRP

SRP in HTOR 40 – 150 °C 60% Inhibited

“Corrosion event”
Formate accumulation

Fresh 8 m PZ in HTOR 40 – 150 °C

“Corrosion event”

SRP in HTOR 40 – 150 °C 40 – 70% Inhibited

0.3 mM Fe²⁺ added

Tarong

PP2

155 C
Contaminant (mmol/kg)

Flue gas contaminants

Cycles

Sulfate

Nitrate

Tarong

155 °C

PP2

Sulfate

Nitrate
Conclusions

- MNPZ accumulation in PZ pilot plants controlled by thermal degradation to less than 3 mmol/kg at 150 °C
- Oxidation dominates over thermal degradation as cause of amine loss
  - Ammonia and formate final products
  - Ethylenediamine and 2-PZOH major intermediates
- Rate of formate accumulation linked to accumulation of stainless steel metal ions
- Corrosion and oxidation at SRP inhibited by Inh A
Questions?

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