Amine Scrubbing for CO2 Capture

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Technology Strategy and Planning
June 21, 2021
• Amine scrubbing overview
• Advanced absorption
• Advanced regeneration systems
• Advanced solvent systems
Leading CO₂-capture technology is amine absorbent based.

Amine Scrubbing (Bottoms, 1930)

- 30 wt% PZ
- CO₂
- ΔT=5°C
- Stripper
  - 6 bar
  - Packing or Trays
- 12% CO₂
- 5% O₂
- 1 ppm SO₂
- 40°C
- Reboiler
  - 6 bar
  - 150°C
- Packed Absorber
  - 1 bar
- Dec. 2, 1930.
- R.R. Bottoms
- Process for Separating Acidic Gases
- Filed Oct. 7, 1930
Amine scrubbing overview

Commercial plants of amines for flue gas carbon capture

- More than 30 commercial plants have been constructed to capture CO2 from gas-fired flue gas
  - > 20 employing Fluor technology using 30% MEA
  - > 10 plants employing MHI technology using KS-1

- Only a few plants have been constructed to capture CO2 from coal-fired flue gas.
  - Four operating units employing Lummus technology using 20% MEA
  - Boundary Dam capture project employing Shell Cansolv technology
  - Petra Nova capture project employing MHI technology
# Basic chemistry & rates

<table>
<thead>
<tr>
<th>Class</th>
<th>Typical reaction</th>
<th>$-H_{\text{abs}}$ (kJ/mol)</th>
<th>Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate</td>
<td>$\text{CO}_3^- + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons 2 \text{HCO}_3^- $</td>
<td>40</td>
<td>Very slow</td>
</tr>
<tr>
<td>Tertiary Amine</td>
<td>$\text{R}_3\text{N} + \text{CO}_2 \rightleftharpoons \text{R}_3\text{NH}^+ + \text{HCO}_3^-$</td>
<td>60</td>
<td>Slow</td>
</tr>
<tr>
<td>Hindered Amine</td>
<td>$\text{AMP} + \text{CO}_2 \rightleftharpoons \text{AMPH}^+ + \text{HCO}_3^- $</td>
<td>60-70</td>
<td>Moderate</td>
</tr>
<tr>
<td>Secondary or Primary Amines</td>
<td>$2\text{R}_2\text{NH} + \text{CO}_2 \rightleftharpoons \text{R}_2\text{NHCOO}^- + \text{R}_2\text{NH}_2^+$</td>
<td>70-80</td>
<td>Fast</td>
</tr>
</tbody>
</table>

These four classes of aqueous solvents differ in heat of CO$_2$ absorption, kinetics of CO$_2$ absorption, and intrinsic CO$_2$ stoichiometry.
# Applications for amine scrubbing

<table>
<thead>
<tr>
<th>Application</th>
<th>Total P (bar)</th>
<th>$P_{CO2 \text{ in}}$ (bar)</th>
<th>$P_{CO2 \text{ out}}$ (bar)</th>
<th>Gas Volume (m$^3$/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas</td>
<td>20-100</td>
<td>1-20</td>
<td>0.001 - 0.005</td>
<td>$2 \times 10^4 - 5 \times 10^5$</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>20-100</td>
<td>4-20</td>
<td>0.002 - 0.01</td>
<td>$1.5 \times 10^5$</td>
</tr>
<tr>
<td>LNG</td>
<td>30-100</td>
<td>0.5-4</td>
<td>0.002</td>
<td>$5.0 \times 10^6$</td>
</tr>
<tr>
<td>Coal flue gas</td>
<td>1</td>
<td>0.12</td>
<td>0.01</td>
<td>$5.0 \times 10^6$</td>
</tr>
<tr>
<td>Simple cycle gas turbine</td>
<td>1</td>
<td>0.035</td>
<td>0.0035</td>
<td>$5.0 \times 10^6$</td>
</tr>
</tbody>
</table>
Amine system energy performance continues to improve with time

- At Lubbock in 1983 the reboiler duty decreased with the substitution of 30% MEA for 20% MEA.
- At the MHI plant in 1999, 30% MEA was replaced with KS-1.
- At a newer MHI plant in 2009, additional energy savings from stripper process modifications.
- Cansolv plant at Boundary Dam achieved energy savings with a new aqueous amine and the use of lean vapor compression at the stripper.

Source: G.T. Rochelle, 2016
**Analogy to limestone slurry scrubbing**

<table>
<thead>
<tr>
<th>CaCO₃</th>
<th>Event</th>
<th>Amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1936</td>
<td>1st commercial plant</td>
<td>1980</td>
</tr>
<tr>
<td>1958</td>
<td>“Almost Insurmountable difficulties” (Bienstock et al. 1958)</td>
<td>1991</td>
</tr>
<tr>
<td></td>
<td>”Although ... technically feasible, it is an expensive method”</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Booras and Smelzer, 1991)</td>
<td></td>
</tr>
<tr>
<td>1960-75</td>
<td>Government funds research on advanced alternatives</td>
<td>1995-</td>
</tr>
<tr>
<td>1970-85</td>
<td>Government &amp; EPRI fund test facilities</td>
<td>2010-</td>
</tr>
<tr>
<td>1968</td>
<td>60-250 MW prototypes</td>
<td>2014-</td>
</tr>
<tr>
<td>1977</td>
<td>500+ MW deployed per regulations</td>
<td>2025</td>
</tr>
<tr>
<td>2015</td>
<td>First choice dominates</td>
<td>???</td>
</tr>
</tbody>
</table>
Absorber intercooling in CO2 absorption
**Effect of intercooling on packing area, 8 m PZ**

- An isothermal absorber would require less packing and a lower liquid rate to achieve the same performance.

- In many cases intercooling may be used to reduce the absorber packing cost and increase the rich loading.

Source: Sachde and Rochelle, 2014
Effect of intercooling on liquid rate

- At a lean loading of 0.21 the minimum flow is more than 3.5 times that of an isothermal absorber.

- A single stage of in-and-out intercooling reduces this effect to a factor of two at a greater lean loading of 0.26.
Absorber design

• The larger demonstrations use modern structured packing with larger corrugation angle
• The earliest absorbers in capture systems were round vessels
• Boundary Dam uses a rectangular absorber
• The MHI design at Thompsons uses a rectangular absorber
• Full-scale commercial designs will probably use a single rectangular absorber

Source: G.T. Rochelle, 2016
Three stripper enhancements to that of simple stripping

- Simple stripper loses efficiency because of water vapor that passes overhead and is condensed without heat recovery.
- Large scale commercial applications will probably utilize these or similar configurations to enhance energy performance.

Source: G.T. Rochelle, 2016
Advanced flash stripper (UT Austin)

This configuration has been successfully tested in the pilot plant at the University of Texas.

Source: Rochelle, 2014
Inter-heated stripper (MHI)

- An important part of the Energy Saving Process used by MHI in several commercial units
- The design has no optimization variables, so it is usually less efficient than the advanced flash stripper

Source: Rochelle, 2014
Lean vapor compression (Cansolv)

- This configuration is included with the Saskpower Boundary Dam project.
- It is not as flexible as the advanced flash stripper since the compressor needs to run at a maximum single-stage compression ratio (1.8 to 2.2).

Source: Rochelle, 2015
Electricity burden of commercial units

- The electricity burden with advanced amine scrubbing is approaching the minimum work (113 kWh/tonne CO₂ removed).

- It is possible to expect ultimate requirement of 200 kWh/tonne CO₂, with a thermodynamic efficiency of 56%.

Source: Rochelle, 2014
Energy criteria for amine selection

The primary basis for amine selection is built on four energy properties:

1. Capacity
2. CO2 absorption rate
3. Heat of CO2 Absorption
4. $T_{\text{max}}$ from thermal degradation
Absorbent management criteria

Other important amine properties include:

- Oxidative degradation
- Nitrosamine
- Amine volatility
- Amine aerosol emissions
- Molecular weight
- Amine cost and availability
- Amine corrosion
# PZ is an excellent alternative to MEA

<table>
<thead>
<tr>
<th>Property</th>
<th>7 m MEA</th>
<th>5 m PZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption rate(^{a}) ((10^{-7} \text{mol/s-Pa-m}^2))</td>
<td>4.3</td>
<td>11.3</td>
</tr>
<tr>
<td>Capacity(^{b}) ((\text{mol CO}_2/\text{mol alkalinity}))</td>
<td>0.62</td>
<td>0.76</td>
</tr>
<tr>
<td>(T_{\text{max}}) (^{c}) ((^\circ \text{C}))</td>
<td>120</td>
<td>160</td>
</tr>
<tr>
<td>(P_{\text{max}}) ((\text{bar}))</td>
<td>2.2</td>
<td>14</td>
</tr>
<tr>
<td>Heat of absorption(^{d}) ((\text{kJ/mol}))</td>
<td>71</td>
<td>64</td>
</tr>
<tr>
<td>Viscosity(^{e}) ((\text{cP}))</td>
<td>2.5</td>
<td>3</td>
</tr>
<tr>
<td>Solid precipitation(^{f})</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

\(^{a}\) Average liquid side mass transfer rate between 0.5 and 5 kPa of P*CO2 at 40 °C (Dugas, 2009)

\(^{b}\) Difference of lean and rich loading between 0.5 and 5 kPa of P*CO2 at 40 °C (Dugas, 2009)

\(^{c}\) Corresponds to 2% amine loss per week (Davis, 2009; Freeman, 2011)

\(^{d}\) Differential heat of absorption at 1.5 kPa of P*CO2 (Li, Voice, et al., 2013)

\(^{e}\) Average between 0.5 and 5 kPa of P*CO2 at 40 °C (Amundsen et al., 2009; Freeman et al., 2011)

\(^{f}\) No

Source: G.T. Rochelle, 2016
## PZ blends are comparable but with no issues of solid solubility

<table>
<thead>
<tr>
<th>Property</th>
<th>5 m PZ</th>
<th>2 m PZ/7 m MDEA</th>
<th>2 m PZ/4 m AMP</th>
<th>2 m PZ/3 m HMPD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption rate</strong> &lt;sup&gt;a&lt;/sup&gt; (10^{-7} mol/s-Pa-m²)</td>
<td>11.3</td>
<td>6.9</td>
<td>8.3</td>
<td>10.1</td>
</tr>
<tr>
<td><strong>Capacity</strong> &lt;sup&gt;b&lt;/sup&gt; (mol CO₂/mol alkalinity)</td>
<td>0.76</td>
<td>0.82</td>
<td>0.86</td>
<td>0.92</td>
</tr>
<tr>
<td><strong>T&lt;sub&gt;max&lt;/sub&gt;</strong> &lt;sup&gt;c&lt;/sup&gt; (°C)</td>
<td>160</td>
<td>120</td>
<td>128</td>
<td>149</td>
</tr>
<tr>
<td><strong>P&lt;sub&gt;max&lt;/sub&gt;</strong> (bar)</td>
<td>14</td>
<td>1.4</td>
<td>3.4</td>
<td>8.8</td>
</tr>
<tr>
<td><strong>Heat of absorption</strong> &lt;sup&gt;d&lt;/sup&gt; (kJ/mol)</td>
<td>64</td>
<td>68</td>
<td>73</td>
<td>-</td>
</tr>
<tr>
<td><strong>Viscosity</strong> &lt;sup&gt;e&lt;/sup&gt; (cP)</td>
<td>3</td>
<td>9</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td><strong>Solid precipitation</strong>&lt;sup&gt;f&lt;/sup&gt;</td>
<td>Yes</td>
<td>No</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
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Source: G.T. Rochelle, 2016

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<sup>a</sup> Average liquid side mass transfer rate between 0.5 and 5 kPa of P*CO₂ at 40 °C (Dugas, 2009)

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<sup>e</sup> Average between 0.5 and 5 kPa of P*CO₂ at 40 °C (Amundsen et al., 2009; Freeman et al., 2011)
Conclusions

• Conventional amine scrubbing will be a dominant technology for post-combustion capture

• 2nd generation amine scrubbing provides improved energy performance, with electricity burden approaching 200 kWh/ton CO2 in coal-fired application

• 5 m PZ with absorber intercooling and the advanced flash stripper should serve as the baseline for future improvements in post-combustion capture

• Amine aerosol emissions and amine oxidation are not yet completely understood and managed