Emissions from a post-combustion CO$_2$ capture plant running on MEA

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SINTEF Materials and Chemistry

19 May 2011, Abu Dhabi

PCCC1
Outline

- Background
- General thoughts on emissions
- A simple model for predicting relative emissions
- Conclusions
Background

- There is at present a significant focus on the emissions from post-combustion CO$_2$ capture plants
- Extremely limited literature data on emissions from such plants
  - Partly because a lot of work has been done in industry
  - Post-combustion CO$_2$ capture is only now being implemented in full-scale
- Emission data, even when available, can be hard to interpret
Contributions to emissions

- Gas-phase emissions

- Aerosol formation

- Liquid entrainment
  - The only form of emission that can result in emissions of non-volatile degradation products

Aerosols with diameter around 0.2-0.5 µm are difficult to capture in demisters
Factors affecting emission levels of specific components

- Volatility/solvation energy/vapour pressure
- Molecular weight

- Concentration in the liquid phase/formation rate
- Reactions in liquid phase (liquid speciation)
  - amines protonate and bind to $\text{CO}_2$
  - acids deprotonate
The free energy of solvation

- Is a direct expression of the gas-liquid equilibrium
- Models are often parameterized for infinite dilution in water
- Relates to the Henry’s law constant:
  \[ \Delta G_s = RT \ln K_H \]
- Examples of values:
  - water: -6.3 kcal/mol  ammonia: -4.3 kcal/mol
- In present work the SM5.4A model is utilized (Hawkins, Cramer and Truhlar 1998)
Factors affecting emission levels

- Water-wash operation and design
- Demisters
- Gas and liquid velocities
- Temperature profile in the absorber and water wash section
- Exhaust gas impurities (potential condensation nuclei)
- Solvent degradation
  - Temperatures
  - Exhaust gas composition (O$_2$, NO$_x$, SO$_x$...)
  - Reclaimer operation
What are solvent emission levels?

For MEA we regard 0.5 ppm (volume basis) as readily achievable.

**Qualifying comments:**
Further reduction of emissions is certainly possible, but this may come at a price

A number of technology providers are working on emission control (but limited data has been published)

Most pilot plants have not been designed for optimal emission control. Data from a pilot-plant should therefore not be equated with what is achievable
A simple model for relative emissions

Emissions assumed proportional to concentration and volatility

\[ E_i = E_{\text{solvent}} \frac{X_i}{X_{\text{solvent}}} e^{\frac{\Delta G_{s,i} - \Delta G_{s,\text{solvent}}}{RT}} \]
Application to MEA pilot-plant data

Estimated emissions based on liquid phase concentrations

Pilot plant data from Esbjerg: Lepaumier, da Silva et al GHGT10, 2010
Application to MEA pilot-plant data

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Potential refinements in model

\[ E_i = E_{\text{solvent}} \frac{\chi_i}{\chi_{\text{solvent}}} e^{\frac{\Delta G_{s,i} - \Delta G_{s,\text{solvent}}}{RT}} \]

- Add term for entrainment/mist formation
- Couple to models of solvent degradation
- Couple to model of water-wash system
What degradation products to worry about?

- Potential health and environmental impact
- Concentration in process
- Volatility
## Calculated free energy of solvation for some relevant compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$dG_{solv}$ [kcal/mol]</th>
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</thead>
<tbody>
<tr>
<td>Ethanolamine</td>
<td>-9.0</td>
</tr>
<tr>
<td>N-nitroso ditethanolamine</td>
<td>-9.8</td>
</tr>
<tr>
<td>N-nitrosodimethylamine</td>
<td>-2.6</td>
</tr>
<tr>
<td>Methylamine</td>
<td>-4.6</td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>-4.3</td>
</tr>
<tr>
<td>Oxazolidinone</td>
<td>-10.1</td>
</tr>
<tr>
<td>4-(2-hydroxyethyl)piperazin-2-one (HEPO)</td>
<td>-12.7</td>
</tr>
<tr>
<td>N-(2-hydroxyethyl)formamide (HEF)</td>
<td>-11.6</td>
</tr>
<tr>
<td>N-(2-hydroxyethyl)-glycine (HeGly)</td>
<td>-66.2</td>
</tr>
</tbody>
</table>
## Classification by volatility

<table>
<thead>
<tr>
<th>Classification</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile degradation products</td>
<td>Ammonia, aldehydes and alkylamines</td>
</tr>
<tr>
<td>Volatility comparable to ammonia</td>
<td></td>
</tr>
<tr>
<td>Low volatility degradation products</td>
<td>Most amine and alcohol compounds</td>
</tr>
<tr>
<td>Volatility comparable to MEA</td>
<td></td>
</tr>
<tr>
<td>Non-volatile degradation products</td>
<td>Acids and amino-acids</td>
</tr>
<tr>
<td>Ionic species</td>
<td></td>
</tr>
</tbody>
</table>
What degradation products to worry about?

- Aldehydes / Ketones
- Carboxylic Acids
- Amides
- Cyclic Compounds
  - Aliphatic
  - Aromatic
- Volatile amines
- Nitrites / Nitrates
- Ureas
- Amino-acids
- + Nitrosamines
  - + Nitramines?

* Deg. Products more uncertain
Conclusions

- We regard emissions of 0.5 ppm MEA as readily achievable.

- Many degradation products are less volatile than MEA and present in much smaller quantities. Emissions for such compounds would be expected to be very low.

- A solvation model can give valuable input on which compounds to track in emissions and be used to interpret emission data.
Thank you for your attention!

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