Assessment of Solvent Degradation within a Global Process Model of Post-Combustion CO$_2$ Capture

Grégoire Léonard, Dominique Toye, Georges Heyen

Budapest, Escape 24, June 2014
Global context

**CO₂ capture and storage as a possible answer to**

- Environmental issues
- Growing energy demand and large contribution of fossil fuels

![Diagram showing World net electricity generation by fuel, 2008-2035](image)
1. Introduction: CO$_2$ capture and solvent degradation

2. Experimental study of solvent degradation

3. Simulation of the CO$_2$ capture process with assessment of solvent degradation

4. Conclusion and perspectives
1. Introduction
1. Introduction

Post-combustion CO$_2$ capture

www.bellona.org
1. Introduction

Most studies on CO$_2$ capture with amines: energy penalty
⇒ New solvents, Process intensification…

However, simulation does not consider all important parameters!

1. Introduction

Focus set on solvent degradation

• Process operating costs:
  - Solvent replacement: up to 22% of the CO$_2$ capture OPEX$^{[1]}$!
  - Removal and disposal of toxic degradation products

• Process performance:
  - Decrease of the solvent loading capacity
  - Increase of viscosity, foaming, fouling…

• Capital costs
  - Corrosion

• Environmental balance
  - Emission of volatile degradation products!

1. Introduction

The goal of this work is to develop a model assessing both energy consumption and solvent degradation.

Two steps:

- **Experimental study** of solvent degradation
- **Process modeling** with assessment of solvent degradation

Methodology based on 30 wt% MEA (Monoethanolamine)
2. Experimental study of solvent degradation
Degradation is a slow phenomenon (4% in 45 days\textsuperscript{[1]}).

\Rightarrow Accelerated conditions (base case):

- 300 g of 30 wt% MEA
- Loaded with CO\textsubscript{2} (~0.40 mol CO\textsubscript{2}/mol MEA)
- 120°C, 4 barg, 600 rpm
- 7 days
- Continuous gas flow: 160 Nml/min,
  5% O\textsubscript{2} / 15% CO\textsubscript{2} / 80% N\textsubscript{2}

2. Experimental study

Identification of degradation products:

- HPLC-RID
  => MEA
- GC-FID
  => degradation products
- FTIR
  => Volatile products ($NH_3$)
2. Experimental study

Comparison of the base case with degraded samples from industrial pilot plants:
2. Experimental study

Similar degradation products (GC spectra)!

=> 20% degradation after 7 days!

=> Nitrogen mass balance can be closed within 10%

=> Repetition experiments lead to similar results (<5% deviation)
2. Experimental study

Study of the influence of operating variables:

=> Gas feed flow rate and composition (O₂, CO₂)
=> Temperature
=> Agitation rate
=> Presence of dissolved metals and degradation inhibitors
2. Experimental study

Leads to a kinetic model of solvent degradation:

=> 2 main degradation mechanisms

=> Equations balanced based on the observed proportion of degradation products

**Oxidative degradation**

\[ \text{MEA} + 1,3 \ O_2 \]
\[ \downarrow \]
\[ 0,6 \ NH_3 + 0,1 \ HEI + 0,1 \ HEPO + 0,1 \ HCOOH + 0,8 \ CO_2 + 1,5 \ H_2O \]

**Thermal degradation with CO_2**

\[ \text{MEA} + 0,5 \ CO_2 \rightarrow 0,5 \ HEIA + H_2O \]
2. Experimental study

Arrhenius kinetics (kmol/m³.s):
Parameters are identified by minimizing the difference between calculated and observed degradation rates.

- Oxidative degradation: \[ r = 535 \, 209 \cdot e^{-\frac{41730}{8314 \cdot T}} \cdot [O_2]^{1.46} \]
- Thermal degradation with CO₂: \[ r = 627.1011 \cdot e^{-\frac{143106}{8314 \cdot T}} \cdot [CO_2]^{0.9} \]
3. Simulation of the CO$_2$ capture process with assessment of solvent degradation
Degradation model has been included into a global process model built in Aspen Plus
⇒ Steady-state simulation, closed solvent loop
⇒ Additional equations in the column rate-based models

3. Process simulation

Base case degradation:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Absorber</th>
<th>Stripper</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA degradation</td>
<td>kg/ton CO₂</td>
<td>8.1e-2</td>
<td>1.4e-5</td>
<td>8.1e-2</td>
</tr>
<tr>
<td>NH₃ formation</td>
<td>kg/ton CO₂</td>
<td>1.4e-2</td>
<td>8.4e-7</td>
<td>1.4e-2</td>
</tr>
<tr>
<td>HEIA formation</td>
<td>kg/ton CO₂</td>
<td>1.1e-5</td>
<td>1.1e-5</td>
<td>2.2e-5</td>
</tr>
<tr>
<td>MEA emission</td>
<td>kg/ton CO₂</td>
<td>8.7e-4</td>
<td>9.4e-9</td>
<td>8.7e-4</td>
</tr>
<tr>
<td>NH₃ emission</td>
<td>kg/ton CO₂</td>
<td>9.5e-3</td>
<td>3.0e-3</td>
<td>1.3e-2</td>
</tr>
<tr>
<td>HCOOH emission</td>
<td>kg/ton CO₂</td>
<td>1.1e-4</td>
<td>1.4e-5</td>
<td>1.2e-4</td>
</tr>
</tbody>
</table>

=> Degradation mainly takes place in the absorber:

=> 81 g MEA/ton CO₂
3. Process simulation

Base case degradation:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Absorber</th>
<th>Stripper</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA degradation</td>
<td>kg/ton CO₂</td>
<td>8.1e-2</td>
<td>1.4e-5</td>
<td>8.1e-2</td>
</tr>
<tr>
<td>NH₃ formation</td>
<td>kg/ton CO₂</td>
<td>1.4e-2</td>
<td>8.4e-7</td>
<td>1.4e-2</td>
</tr>
<tr>
<td>HEIA formation</td>
<td>kg/ton CO₂</td>
<td>1.1e-5</td>
<td>1.1e-5</td>
<td>2.2e-5</td>
</tr>
<tr>
<td>MEA emission</td>
<td>kg/ton CO₂</td>
<td>8.7e-4</td>
<td>9.4e-9</td>
<td>8.7e-4</td>
</tr>
<tr>
<td>NH₃ emission</td>
<td>kg/ton CO₂</td>
<td>9.5e-3</td>
<td>3.0e-3</td>
<td>1.3e-2</td>
</tr>
<tr>
<td>HCOOH emission</td>
<td>kg/ton CO₂</td>
<td>1.1e-4</td>
<td>1.4e-5</td>
<td>1.2e-4</td>
</tr>
</tbody>
</table>

=> Oxidative degradation is more important than thermal degradation with CO₂
3. Process simulation

Base case degradation:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Absorber</th>
<th>Stripper</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA degradation</td>
<td>kg/ton CO₂</td>
<td>8.1e-2</td>
<td>1.4e-5</td>
<td>8.1e-2</td>
</tr>
<tr>
<td>NH₃ formation</td>
<td>kg/ton CO₂</td>
<td>1.4e-2</td>
<td>8.4e-7</td>
<td>1.4e-2</td>
</tr>
<tr>
<td>HEIA formation</td>
<td>kg/ton CO₂</td>
<td>1.1e-5</td>
<td>1.1e-5</td>
<td>2.2e-5</td>
</tr>
<tr>
<td>MEA emission</td>
<td>kg/ton CO₂</td>
<td>8.7e-4</td>
<td>9.4e-9</td>
<td>8.7e-4</td>
</tr>
<tr>
<td>NH₃ emission</td>
<td>kg/ton CO₂</td>
<td>9.5e-3</td>
<td>3.0e-3</td>
<td>1.3e-2</td>
</tr>
<tr>
<td>HCOOH emission</td>
<td>kg/ton CO₂</td>
<td>1.1e-4</td>
<td>1.4e-5</td>
<td>1.2e-4</td>
</tr>
</tbody>
</table>

=> Ammonia is the main emitted degradation product after washing, coming from both absorber and stripper
3. Process simulation

Comparison with industrial CO$_2$ capture plants:

81 g MEA/ton CO$_2$ < 284 g MEA/ton CO$_2$\textsuperscript{[1]}

=> Degradation under-estimated (although 324kg MEA/day at large-scale ~ 4000 tCO$_2$/day)!

=> Maybe due to simplifying assumptions:

- Modeling assumptions for the degradation kinetics
- Presence of SO$_x$ et NO$_x$ neglected
- Influence of metal ions neglected

3. Process simulation

Influence of process variables on solvent degradation:

=> Regeneration pressure

Exponential increase of the thermal degradation, but still much lower than oxidative degradation
3. Process simulation

Influence of process variables on solvent degradation:

⇒ MEA concentration

*Influence of MEA concentration on the $O_2$ mass transfer!*
3. Process simulation

⇒ Identification of optimal process operating conditions for the CO$_2$ capture process:

- **Concentrated MEA solvent:** 40 wt% MEA (if degradation inhibitors are available).

- **Optimized solvent flow rate:** 24 m$^3$/h in the simulated configuration.

- **Low oxygen concentration in the flue gas:** 0% O$_2$ (or minimum)

- **High stripper pressure:** 4 bar.

- **Equipment for absorber intercooling and lean vapor compression.**
4. Conclusion and perspectives
4. Conclusion

Two of the main CO$_2$ capture drawbacks are considered:

• Solvent degradation is experimentally studied and a kinetic model is proposed

• This model is included into a global process model to study the influence of process variables

$\Rightarrow$ Both energy and environmental impacts of the CO$_2$ capture are considered!

$\Rightarrow$ This kind of model could and should be used for the design of large-scale CO$_2$ capture plants.
4. Conclusion

• Many challenges are still up to come for the CO$_2$ capture process!

=> ~ 1 Mton CO$_2$ has been emitted during this presentation

• Demonstration plants are the next step to evidence large-scale feasibility!

• Further works: CO$_2$ re-use for methanol synthesis
Thank you for your attention!
• Mass transfer enhancement due to the chemical reaction in the liquid film

\[ \mathcal{N}_\text{O}_2 = k_L \cdot a \left( C_{\text{O}_2}^{\text{interface}} - C_{\text{O}_2}^{\text{bulk}} \right) \cdot E \]

\[ E = Ha = \frac{\sqrt{D_{A,L} \cdot k \cdot C_{B,L}}}{K_L^0} \]
Table 1. Main peaks identified in GC spectra of degraded MEA samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Retention time (min)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MEA</td>
<td>monoethanolamine</td>
<td>7.6</td>
<td>Start amine</td>
</tr>
<tr>
<td>2 DEG</td>
<td>diethylene glycol</td>
<td>15.0</td>
<td>Internal standard</td>
</tr>
<tr>
<td>3 HEEDA</td>
<td>$N$-(2-hydroxyethyl)ethylenediamine</td>
<td>17.0</td>
<td>Quantified</td>
</tr>
<tr>
<td>4 HEF</td>
<td>$N$-(2-hydroxyethyl)formamide</td>
<td>21.1</td>
<td>Identified</td>
</tr>
<tr>
<td>5 OZD</td>
<td>2-oxazolidinone</td>
<td>22.5</td>
<td>Quantified</td>
</tr>
<tr>
<td>6 HEI</td>
<td>$N$-(2-hydroxyethyl)imidazole</td>
<td>24.9</td>
<td>Quantified</td>
</tr>
<tr>
<td>7 HEIA</td>
<td>$N$-(2-hydroxyethyl)imidazolidinone</td>
<td>31.5</td>
<td>Quantified</td>
</tr>
<tr>
<td>8 HEPO</td>
<td>4-(2-hydroxyethyl)piperazine-2-one</td>
<td>34.3</td>
<td>Quantified</td>
</tr>
<tr>
<td>9 HEHEAA</td>
<td>$N$-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide</td>
<td>36.8</td>
<td>Identified</td>
</tr>
<tr>
<td>10 BHEOX</td>
<td>$N,N'$-bis(2-hydroxyethyl)oxamide</td>
<td>38.7</td>
<td>Quantified</td>
</tr>
</tbody>
</table>
3. Process simulation

Influence of process variables on solvent degradation:

=> Solvent flow rate

=> Oxygen concentration in the gas feed

Minimum in the solvent flow rate has been experimentally evidenced.