Optimal design of a CO$_2$ absorption unit and assessment of solvent degradation

Mid-term Presentation

Grégoire Léonard

14th December 2011
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1. Introduction
1. Introduction

CO$_2$ capture in coal power plants
Chemical reactions taking place during the CO\textsubscript{2} capture in Monoethanolamine (MEA):

\[
\begin{align*}
\text{2 H}_2\text{O} & \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \\
\text{C}_2\text{H}_7\text{NO} + \text{H}_3\text{O}^+ & \leftrightarrow \text{C}_2\text{H}_8\text{NO}^+ + \text{H}_2\text{O} \\
\text{CO}_2 + 2 \text{H}_2\text{O} & \leftrightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- + \text{H}_2\text{O} & \leftrightarrow \text{H}_3\text{O}^+ + \text{CO}_3^{2-} \\
\text{C}_2\text{H}_7\text{NO} + \text{HCO}_3^- & \leftrightarrow \text{C}_3\text{H}_6\text{NO}_3^- + \text{H}_2\text{O}
\end{align*}
\]
2. Objectives
2. Objectives

Context: reduction of the CO₂ capture cost for large scale power plants

=> Energy requirement and degradation induced costs are among the largest operative costs!
2. Objectives

- To establish a link between **modeling** and **degradation**
2. Objectives

• To establish a link between modeling and degradation

• The result will be

  a proposal
  … for optimal operating conditions in the CO$_2$ capture process
  … taking into account process efficiency and solvent degradation
  … i.e. cost and environmental impacts of PCC
3. Modeling and optimal design
3.1 Objectives

• Model building

• Sensitivity study of key parameters

• Simulation of process improvements

• Validation based on experimental results

• Implementation of degradation results

• Multi-objective optimization
3.1 Objectives

- Model building
- Sensitivity study of key parameters
- Simulation of process improvements
- Validation based on experimental results
- Implementation of degradation results
- Multi-objective optimization
3.2 Model Building

Two different modeling approaches

Model parameters: 2500 NM³ flue gaz, 14vol-% CO₂, 90% Capture rate, MEA 30wt-%
3.2 Model Building

Simulation tool: Aspen Plus V7.2

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3.3 Sensitivity study

**Sensitivity study of process key variables**

- **Stripper Pressure (bar)**
  - Equilibrium
  - Ratesep

- **Solvent flow rate (m³/h)**
  - Equilibrium
  - Ratesep

<table>
<thead>
<tr>
<th>Results</th>
<th>Stripper Pressure</th>
<th>Solvent concentration</th>
<th>Solvent flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case Value</td>
<td>1.2 bar</td>
<td>30 wt-%</td>
<td>15 m³/h</td>
</tr>
<tr>
<td>Optimized Value</td>
<td>2.2 bar</td>
<td>37 wt-%</td>
<td>12.4 m³/h</td>
</tr>
<tr>
<td>Gain in regeneration energy</td>
<td>-16.9%</td>
<td>-5.4%</td>
<td>-2.8%</td>
</tr>
</tbody>
</table>
3.4 Model improvements

Impact study of process improvements
3.4 Results summary

**Impact study of process improvements**

<table>
<thead>
<tr>
<th>Process modifications</th>
<th>Lean vapor compression</th>
<th>Absorber intercooling</th>
<th>Split-flow configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gain in regeneration energy</td>
<td>-14% (exergy)</td>
<td>-4%</td>
<td>-4%</td>
</tr>
</tbody>
</table>

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3.5 Conclusion

- It is possible to identify optimal operating conditions using modeling.

- Simulation results are less costly than lab experiments and can help to the decision for process improvements.

- Good model knowledge has been gained and can be useful for further simulation.

- However, simulation results still don’t take secondary effects into account (degradation, corrosion, …)
3.6 Perspectives

- Writing of an article and submission for publication to a journal in the field *Energetics and Engineering* => planned at the beginning of 2012.

- Validation of the model may occur soon, depending on pilot experimental results => validation based on:
  - Regeneration energy = \( f(\text{solvent flow rate}) \)
  - Absorber and stripper temperature profiles
  - Solvent lean and rich loading
3.6 Perspectives

• Follow-up of a master thesis with subject « Simulation of the dynamic behavior of a pilot plant for CO$_2$ capture »
  => First semester 2012
  => Objective is to develop a dynamic model using Aspen Dynamics
  => Eventually modeling of process improvements

• First tests for the implementation of degradation parameters in Aspen Plus
4. Solvent degradation
4.1 Objectives

- Design and construction of a degradation test rig
- Detailed screening of MEA degradation
- Study of the impact of operating conditions (temperature, gas composition, flow, …)
- Study of the effect of additives (degradation inhibitors, metal)
- Test of 1 or 2 other solvents
- Results implementation in the process model
4.1 Objectives

- Design and construction of a degradation test rig
- Detailed screening of MEA degradation
- Study of the impact of operating conditions (temperature, gas composition, flow, …)
- Study of the effect of additives (degradation inhibitors, metal)
- Test of 1 or 2 other solvents
- Results implementation in the process model
4.2 Literature review

3 types of degradation mechanisms: Temperature, O$_2$, CO$_2$

- **Aldehydes / Ketones**
  - Formaldehyde
  - Acetone
  - Acetaldehyde

- **Carboxylic Acids**
  - Formic acid
  - Acetic acid
  - Glycolic acid

- **Amides**
  - Formamide
  - Acetamide

- **Volatile amines**
  - Ammonia
  - Methylamine

- **Nitrites / Nitrates**
  - Nitrite

- **Amino-acids**
  - HEGly

- **Amines derivatives**
  - HEEAD
  - HEHEAA
  - HHEA
  - BHEOX
  - MMEA

- **Cyclic Compounds**
  - **Aliphatic**
    - OZD
    - HEIA
    - HEF
    - HEA
    - 4-HEPO
  - **Aromatic**
    - *Deg. Products more uncertain
    - NDELA

- **Nitrosamines**
  - *
### 4.2 Literature review

<table>
<thead>
<tr>
<th>Reference</th>
<th>Description</th>
<th>Volume (ml)</th>
<th>Gas feed mode</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>Solvent</th>
<th>Analysis</th>
<th>Run time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supap et al, 2001</td>
<td>Kinetic law for MEA-degradation in function of solvent concentration, O2, Temperature and stirring</td>
<td>230</td>
<td>Discontinuous with gas feed to compensate for pressure losses</td>
<td>120-150</td>
<td>2,41-3,45 bar O2</td>
<td>MEA (2-11 mol/L)</td>
<td>GCMS</td>
<td>2 - 12 days</td>
</tr>
<tr>
<td>Lawal and Idem, 2005; Lawal et al, 2005 &amp; 2006</td>
<td>Influence of O2, CO2, MDEA-MEA-ratio, Temperature, amine concentration + Product formation mechanisms, Ecotoxicty</td>
<td>230</td>
<td></td>
<td>55-120</td>
<td>2.5 bar O2/CO2</td>
<td>MEA-MDEA blends (7-8mol/L)</td>
<td>GCMS (HPLC from 2006)</td>
<td>6 - 22 days</td>
</tr>
<tr>
<td>Bello and Idem, 2006</td>
<td>Pathways of degradation reaction, influence of O2, CO2, Temperature, MEA concentration, ... Analysis techniques: comparison and methods</td>
<td>230</td>
<td></td>
<td>55-120</td>
<td>2,5-3,5 bar O2/CO2</td>
<td>MEA (5-7 mol/L)</td>
<td>GCMS</td>
<td>6 - 30 days</td>
</tr>
<tr>
<td>Supap et al, 2006</td>
<td>Influence of the corrosion inhibitor NaVc3 on Degradation kinetics</td>
<td>450</td>
<td></td>
<td>55-120</td>
<td>2,5-4,5 bar O2/CO2</td>
<td>MEA (5 mol/L)</td>
<td>GCMS, HPLC, CE</td>
<td>18-24 days</td>
</tr>
<tr>
<td>Bello and Idem, 2006</td>
<td>Influence of the corrosion inhibitor NaVc3 and of SO2 on kinetics, Kinetics model</td>
<td>450</td>
<td></td>
<td>55-120</td>
<td>3,5-4,5 bar O2/CO2</td>
<td>MEA (5-7 mol/L)</td>
<td>HPLC</td>
<td>6-30 days</td>
</tr>
<tr>
<td>Uyang and Idem, 2007</td>
<td>Kinetics data for O2 and SO2-induced Degradation</td>
<td>450</td>
<td></td>
<td>55-140</td>
<td>2,5 bar O2/N2/CO2/SO2, 2,5 bar O2/N2/O2/SO2</td>
<td>MEA (3-7 mol/L)</td>
<td>HPLC</td>
<td>5-10 days</td>
</tr>
<tr>
<td>Supap et al, 2009</td>
<td>Influence of CO2-loading and inhibit (Fe, Bicine, EDTA) on NH3 production rate</td>
<td>500</td>
<td>Up to 8 l/min Air/Air + CO2</td>
<td>55</td>
<td>1</td>
<td>MEA (13-42 wt-%)</td>
<td>FTIR</td>
<td>up to 8 hours</td>
</tr>
<tr>
<td>Chi and Rochelle, 2000</td>
<td>Importance of O2-mass transfer and agitation rate, influence of Fe-Cu and of the presence of degradation products on degradation rate, Test of several oxidative degradation inhibitors for Fe-Cu catalysed degradation</td>
<td>550 g</td>
<td>Low flow (100ml/min 2%CO2/98%CO2) and high flow (7,5 L/min Air/N2/2%CO2)</td>
<td>55</td>
<td>1</td>
<td>MEA (42 wt-%)</td>
<td>FTIR, IC (AC&amp;CC), HPLC</td>
<td>12-15 days</td>
</tr>
<tr>
<td>Goff and Rochelle, 2004; Goff, 2005; Goff and Rochelle, 2006</td>
<td>Test of different gas flow rate, influence of degradation catalysts (Fe, Cr-Ni, Cu, V) and inhibitors, test of MEA-P2 blends, amine screening</td>
<td>350-400</td>
<td></td>
<td>55</td>
<td>1</td>
<td>MEA (15-40 wt-%)</td>
<td>IC (cationic), HPLC, MS</td>
<td>Few days to several months</td>
</tr>
<tr>
<td>Sexton, 2008; Sexton and Rochelle, 2009</td>
<td>Dependance of Degradation rate on Temperature, Pressure and amine concentration, Thermal degradation of different amines, Kinetics model</td>
<td>10</td>
<td>Batch +CO2</td>
<td>100-150</td>
<td>1-8</td>
<td>MEA (15-40 wt-%)</td>
<td>IC (cationic), HPLC, MS</td>
<td>Few days to several months</td>
</tr>
<tr>
<td>Davis and Rochelle, 2009; Davis 2009</td>
<td>Degradation and corrosion screening for 20 amines</td>
<td>Not reported</td>
<td>Batch</td>
<td>140</td>
<td>5 bar O2/CO2/N2</td>
<td>Different amines</td>
<td>GC, GCMS, HPLC, IC</td>
<td>14 days</td>
</tr>
<tr>
<td>Bacot et al, 2007</td>
<td>Degradation rate of primary, secondary amines, and activator (83%)</td>
<td>350g</td>
<td>10 nml/min 40%N2, 30%CO2, 30%CO2</td>
<td>90</td>
<td>1</td>
<td>Different amines</td>
<td>GC, RMN</td>
<td>14 days</td>
</tr>
<tr>
<td>Notz et al, 2007</td>
<td>Solvent degradation induced by contact with gas, Castor 1&amp;2, MEA</td>
<td>350g</td>
<td>10 - 20nl/min N2/O2/CO2</td>
<td>40-120</td>
<td>1-4</td>
<td>MEA</td>
<td>GC-RID</td>
<td>14 days</td>
</tr>
<tr>
<td>Notz 2009</td>
<td>Thermal degradation</td>
<td>7 ml</td>
<td>Batch</td>
<td>140-180</td>
<td>N2 atmosphere max 2 bar</td>
<td>MEA (30wt-%) +Castor1&amp;2</td>
<td>GC-RID</td>
<td>7 days</td>
</tr>
<tr>
<td>Notz 2009</td>
<td>Results from test campaigns on Esbjerg pilot</td>
<td>~20m³/h</td>
<td>Plant conditions</td>
<td>up to 125°c</td>
<td></td>
<td>MEA (30wt-%)</td>
<td>Not reported</td>
<td>Several months</td>
</tr>
<tr>
<td>Knudsen et al, 2007</td>
<td>Degradation studies for the Capttech program. Few details available.</td>
<td>100ml</td>
<td>Batch O2/CO2/N2/Air</td>
<td>150</td>
<td>1.2</td>
<td>Different amines</td>
<td>GC, GCMS, RMN</td>
<td>2 weeks</td>
</tr>
<tr>
<td>Capttech, 2007</td>
<td>Degradation Mechanisms and products for different amines</td>
<td>100ml</td>
<td>Batch O2/CO2/N2/Air</td>
<td>140</td>
<td>20</td>
<td>Different amines</td>
<td>GC, GCMS, RMN</td>
<td>2 weeks</td>
</tr>
</tbody>
</table>
4.3 Degradation Test Rig

1. Reactor
2. Gas supply
3. Water balance
4. Gas flow
5. Control panel
4.3 Degradation Test Rig

Test rig continuously improved to face experimental problems
4.4 Analytical Methods

**Liquid phase:**
- **HPLC** (High Pressure Liquid Chromatography): MEA quantification
- **GC-FID** (Gas Chromatography): identification & quantification of the degradation products
- **IC** (Ionic Chromatography): quantification of organic anions
- **Karl-Fischer** Titration: water quantification
- **AAS** (Atomic Absorption Spectroscopy) and **CE** (Capillary Electrophoresis): quantification of inorganic ions

**Gas phase:**
- **FTIR** (Fourier Transform Infrared Spectroscopy): \( \text{NH}_3 \) and MEA quantification
4.4.1 HPLC

Quantification of MEA: 3 different columns have been tested

- C18 Pyramid

- Nucleosil 100-5 SA

- HILIC
4.4.1 HPLC

With different results…

• C18: no retention
4.4.1 HPLC

- Nucleosil 100-5 SA: Better separation but bad peak shape
4.4.1 HPLC

- Nucleosil 100-5 SA: quantification of MEA possible: => calibration curve

![Graph showing linear relationship between MEA concentration and peak area]

\[ y = 0.0239x + 0.0259 \]

\[ R^2 = 0.9989 \]
4.4.1 HPLC

- HILIC: Better peak shape but separation still to be improved...

Degraded MEA
4.4.2 GC-FID

GC-FID:
- Analytical method has been developed
- Identification of degradation products possible
- Quantification using an internal standard (1% of 2-Methoxyethanol)
4.4.3 Organic Ions Analysis

- Organic ions may lead to heat stable salts (HSS)
- HSS can not be regenerated and lead to a loss of efficiency
- Analysis of Formate, Acetate, Glycolate, Oxalate
4.4.4 Karl Fischer Titration

Potentiometric titration of water based on the equation:

$$2 \text{H}_2\text{O} + \text{SO}_2 + \text{I}_2 \rightarrow \text{SO}_4^{2-} + 2 \text{I}^- + 4 \text{H}^+$$

$=>$ Water quantification in degraded amine samples

$=>$ In relation with the mass balance
4.4.5 Inorganic Ion Analysis

Quantification of elementar ions because their presence can be directly related to corrosion

<table>
<thead>
<tr>
<th>Ion</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Atomic absorption</td>
</tr>
<tr>
<td>Cr</td>
<td>Atomic absorption</td>
</tr>
<tr>
<td>Ni</td>
<td>Atomic absorption</td>
</tr>
<tr>
<td>Si</td>
<td>Atomic absorption</td>
</tr>
<tr>
<td>F</td>
<td>Capillary electrophoresis</td>
</tr>
<tr>
<td>Cl</td>
<td>Capillary electrophoresis</td>
</tr>
</tbody>
</table>

Fe, Cr, Ni: components of SS 316
Si: found in many analyses
F, Cl: corrosion accelerator
4.4.6 FTIR

- Quantification of NH$_3$ and MEA in the gas phase at the reactor exhaust
- Quantification of H$_2$O, CO$_2$, MEA and NH$_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength interval (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>926 – 1150</td>
</tr>
<tr>
<td>MEA</td>
<td>2700 – 3200</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3200 – 3401</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>910 – 1150</td>
</tr>
</tbody>
</table>
4.4.6 FTIR

- Heating rope from reactor to FTIR

=> Combined with a pre-heating of the dilution gas
=> Prevents condensation of the gas sample in the line
4.4.6 FTIR

- Calibration of liquid samples

Air outlet to FTIR

Air supply

Syringe pump

Heated plate

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4.4.6 FTIR

- Calibration of NH$_3$ and MEA

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## 4.5 Results Summary

### Operating conditions

<table>
<thead>
<tr>
<th>Name</th>
<th>Experiment Start</th>
<th>Experiment End</th>
<th>Length [Days]</th>
<th>Parameter tested</th>
<th>T [°C]</th>
<th>$P_{\text{tot}}$ [bar]</th>
<th>$P_{\text{O}_2}$ [bar]</th>
<th>$P_{\text{CO}_2}$ [bar]</th>
<th>$P_{\text{N}_2}$ [bar]</th>
<th>Gas flow [min/min]</th>
<th>Solvent [wt% MEA]</th>
<th>Mass balance [%]</th>
<th>Problems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td>19/02/2011</td>
<td>05/03/2011</td>
<td>14</td>
<td>Base case</td>
<td>120</td>
<td>4</td>
<td>0.2</td>
<td>3</td>
<td>0.8</td>
<td>80</td>
<td>30.00</td>
<td>not recorded</td>
<td>-</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>24/03/2011</td>
<td>05/04/2011</td>
<td>12</td>
<td>Exp. Length/strong cond.</td>
<td>140</td>
<td>20</td>
<td>1</td>
<td>15</td>
<td>4</td>
<td>200</td>
<td>30.00</td>
<td>-3.33</td>
<td>Gas exhaust stopped due to crystal formation in the condenser, pressure up to 25 bar</td>
</tr>
<tr>
<td>Experiment 3</td>
<td>11/04/2011</td>
<td>25/04/2011</td>
<td>14</td>
<td>Temperature</td>
<td>120</td>
<td>20</td>
<td>1</td>
<td>15</td>
<td>4</td>
<td>200</td>
<td>30.01</td>
<td>10.07</td>
<td>-</td>
</tr>
<tr>
<td>Experiment 4</td>
<td>10/05/2011</td>
<td>19/05/2011</td>
<td>9</td>
<td>Pressure (N$_2$)</td>
<td>140</td>
<td>20</td>
<td>0.2</td>
<td>3</td>
<td>16.8</td>
<td>500</td>
<td>30.05</td>
<td>-1.43</td>
<td>Foaming, temperature sensor defective =&gt; heating stopped automatically</td>
</tr>
<tr>
<td>Experiment 5</td>
<td>27/05/2011</td>
<td>10/06/2011</td>
<td>14</td>
<td>Repetability</td>
<td>120</td>
<td>4</td>
<td>0.2</td>
<td>3</td>
<td>0.8</td>
<td>80</td>
<td>30.01</td>
<td>-62.33</td>
<td>Crystal formation in the condenser, pressure up to 20 bar for a few hours, mass losses</td>
</tr>
<tr>
<td>Experiment 6</td>
<td>1/07/2011</td>
<td>15/07/2011</td>
<td>14</td>
<td>Repetability</td>
<td>120</td>
<td>4</td>
<td>0.2</td>
<td>3</td>
<td>0.8</td>
<td>80</td>
<td>30.02</td>
<td>-47.60</td>
<td>-</td>
</tr>
<tr>
<td>Experiment 7</td>
<td>20/07/2011</td>
<td>3/08/2011</td>
<td>14</td>
<td>Batch</td>
<td>120</td>
<td>20</td>
<td>0.2</td>
<td>3</td>
<td>0.8</td>
<td>0</td>
<td>29.99</td>
<td>-0.33</td>
<td>Corrosion of the temperature sensor</td>
</tr>
<tr>
<td>Experiment 8</td>
<td>24/08/2011</td>
<td>31/08/2011</td>
<td>7</td>
<td>Temperature and gas flow</td>
<td>120</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>20</td>
<td>30.00</td>
<td>-2.33</td>
<td>-</td>
</tr>
<tr>
<td>Experiment 9</td>
<td>31/08/2011</td>
<td>09/09/2011</td>
<td>9</td>
<td>Temperature and gas flow</td>
<td>120</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>200</td>
<td>30.00</td>
<td>-3.70</td>
<td>Gas bottle empty (2 days), current shortage</td>
</tr>
<tr>
<td>Experiment 10</td>
<td>13/09/2011</td>
<td>27/09/2011</td>
<td>14</td>
<td>New base case</td>
<td>120</td>
<td>4</td>
<td>0.2</td>
<td>0.6</td>
<td>3.2</td>
<td>160</td>
<td>29.99</td>
<td>-11.30</td>
<td>Mass losses</td>
</tr>
</tbody>
</table>

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4.5 Results Summary

Experimental feed-back of the 1st test campaign

- Corrosion
- Crystal formation
- Mass balance regulation
- Temperature regulation
- Agitation
HPLC quantification of MEA in degraded samples

Experiment number

MEA concentration (wt-%)

Base case
New base case

Temperature
Pressure
Batch
BC Strong
Repetability
T° and gas flow

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# GC Identification of degradation products

<table>
<thead>
<tr>
<th>Std</th>
<th>Exp</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEEDA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HEA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>OZD</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
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</tbody>
</table>

14th December 2011
GC Identification of degradation products: Experiment 10

14th December 2011
GC Identification of degradation products: Experiment 10
4.5.2 GC-FID

GC Comparison with pilot plant results

Experiment 7

Long Term testing at Esbjerg
GC Comparison with pilot plant results

=> Experiment 10 has been chosen as the new base case for next test campaign:
- 120°C
- 4 bar
- 5%O₂, 15%CO₂, 80%N₂
- 160 mln/min gas flow
- 2 weeks
### 4.5.3 Inorganic Ions

**Quantification of inorganic ions**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Cl</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA 30%</td>
<td>0.44</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
<td>-</td>
<td>&lt; 2.00</td>
<td>38.944</td>
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<tr>
<td>Experiment 1</td>
<td>7.57</td>
<td>1.55</td>
<td>4.24</td>
<td>-</td>
<td>&lt; 2.00</td>
<td>416.08</td>
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<tr>
<td>Experiment 2</td>
<td><strong>22.40</strong></td>
<td><strong>8.60</strong></td>
<td><strong>9.75</strong></td>
<td>13.01</td>
<td>513.16</td>
<td>1826.18</td>
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<tr>
<td>Experiment 3</td>
<td>6.80</td>
<td>3.10</td>
<td>2.66</td>
<td>10.66</td>
<td>522.32</td>
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<tr>
<td>Experiment 4</td>
<td>1.90</td>
<td>1.30</td>
<td>1.01</td>
<td>15.57</td>
<td>291.36</td>
<td>307.13</td>
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<td>Experiment 6</td>
<td><strong>14.70</strong></td>
<td><strong>2.75</strong></td>
<td><strong>159</strong></td>
<td><strong>2754.21</strong></td>
<td>&lt; 5.00</td>
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<tr>
<td>Experiment 7</td>
<td><strong>66.10</strong></td>
<td><strong>7.50</strong></td>
<td><strong>571</strong></td>
<td>147.78</td>
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<td>321.14</td>
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<td>Experiment 8</td>
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<td>&lt; 5.00</td>
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<td>Experiment 9</td>
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<td>&lt; 5.00</td>
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<tr>
<td>Experiment 10</td>
<td>3.46</td>
<td>6.41</td>
<td>0.87</td>
<td><strong>557.55</strong></td>
<td>29.34</td>
<td>532.38</td>
</tr>
</tbody>
</table>

=> More ions during Experiments 2, 6 and 7

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4.5.4 Organic Ions

Identification of organic ions performed at Laborelec

Experiment 5

Experiment 10

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4.5.5 Karl Fischer Titration

- Quantification of water in degraded amine sample
- Good correspondance with mass balance results!

![Graph showing mass and water balances](image)
4.6 Conclusion

• First test campaign has brought practical experience using the degradation test rig that may be very useful for future experiments

• Analysis methods are numerous and allow for a complete screening of MEA degradation

• Observed degradation products were expected and may be explained in relation with previous studies

• Unexpected degradation products are also obtained, but similar to pilot plant results
4.6 Conclusion

• First tests have permitted the definition of a new base case, with results similar to pilot plant’s

• Influence of temperature, gas flow rate, gas composition and pressure may already be observed. Results are in accordance with previous litterature

• Corrosion follow-up is pursued
4.7 Perspectives

- Development of analytical methods, especially FTIR and GC-FID for quantification of degraded products

- Next degradation tests must ensure repetability
  => the new base case experiment will be repeated

- Second test campaign with MEA to determine more precisely the influence of gas composition and temperature
  => first experiments will study the influence of O$_2$ and CO$_2$ separately
4.7 Perspectives

• Bibliography studies about degradation inhibitors and additives that may be tested with MEA

• Test of alternative solvents furnished by Laborelec

• Collaboration with the University of Mons in order to determine the influence of degradation on the $\text{CO}_2$ capture process

• Participation to a conference at the University of Texas in Austin
5. Conclusion and perspectives
5 Conclusions

• Good knowledge about the CO₂ capture process considers the **energetical efficiency** but also takes **solvent degradation** into account!

• Results prove that the study of MEA degradation under accelerated conditions can be related to pilot scale results.

• In the coming year, the construction of a **model including solvent degradation** parameters will begin. This model will have to be **validated** with experimental data in order to perform a **multi-objective optimisation** of the CO₂ capture process.
Thanks for your attention!

14th December 2011