ENVIRONMENTAL IMPACTS OF CAPTURE

9TH IEAGHG INTERNATIONAL CCS SUMMER SCHOOL - 6TH-12TH DECEMBER 2015
UNIVERSITY OF WESTERN AUSTRALIA, PERTH, AUSTRALIA

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CONTENT

• Background
• Nitrosamine and nitramine
• Atmospheric degradation
• Capture plant
• Limits for nitrosamines and nitramines in air and drinking water
• Atmospheric formation, destruction and dispersion
• Nitrosamines and nitramines in the media (Norway)
• Concluding remarks
• Further reading
NORWAY: GOVERNMENT: CONTINUED COMMITMENT TO CCS ACTIVITIES ALONG THE WHOLE VALUE CHAIN

DEMO by 2020

R&D
PILOT TESTING
DEMO: CAPTURE
DEMO: STORAGE
COMMERCIALISATION

CLIMIT-PROGRAMME
TECHNOLOGY CENTRE (TCM)

COST-EFFECTIVE CCS
TCM NEWS:

- CCSL test amine technology from Nov. 2015

US Funding for TCM Testing:

- NETL has awarded GE, Alstom and University of Kentucky phase 1 funding to advance planning of their CO$_2$ capture technologies towards large scale pilot testing.
- Phase 2 award for construction and execution of the tests is anticipated mid. 2016
FULL SCALE NORWAY:

• Pre-feasibility study 2015 - results:
  - Identified emission sources and storage sites which may be technically suitable for a full-scale CCS project
  - More studies needed to identify the most suitable of the storage options
  - On stream 2020/2021, at earliest.

Norcem, Brevik
Yara, Porsgrunn
Klemetsrud, Oslo
BACKGROUND: AMINE EMISSION

2006: Kårstø - plan for capture from CCGT, 1 million ton CO$_2$ per year:
   – Emission of 1 – 4 ppm amines => 40 – 160 ton per year

2008: First literature and worst case assessment:
   – Release of maximum 24 tonne amine per year (1 mill ton CO$_2$ per year)
   – Assumptions:
     • Literature data: 2% of amines convert to nitrosamines
     • Instantaneous conversion at stack exit and no further degradation

2009: First time in the national Norwegian news:
Flue gas → \( \text{Absorber} \) → \( \text{Desorber} \) → To stack ppm, ppb → To CO\(_2\) storage

- Amine waste
- Heat
Cleaned flue gas + amine...

Degradation

Dispersion

Flue-gas

CO₂ Capture

CO₂

Amine waste

Environment
WHAT ARE WE LOOKING FOR?

- Degradation components of special interest:
  - nitrosamines and nitramines

- \(N\)-nitrosamines, \(R_1 R_2 N-N=O\), synthetic and naturally occurring compounds. Approximately 90% of the 300 nitrosamines tested have shown carcinogenic effects in bioassays and laboratory animals.

- \(N\)-nitramines, \(R_1 R_2 N-NO_2\), are structurally related to \(N\)-nitrosamines. The nitramines seem to be less potent than the corresponding nitrosamines.

- Låg et al., Health effects of possible degradation products of different amines relevant for the CO2 capture. NILU: OR 7/2009.
- www.wikipedia.org
ATMOSPHERIC DEGRADATION

Degradation during daytime: OH oxidation chemistry
• This may end in nitrosamines and nitrarnines

Example MEA - hydrogen abstraction from the amino group:

Nitramine: 0,3 to 1,5% (dependent of NOx level)  Nitrosamine: 0%

Source: Nielsen et.al. , Atmospheric chemistry of 2-aminoethanol (MEA), GHGT 10
ATMOSPHERIC FORMATION, DESTRUCTION AND DISPERSION

• The ADA programme provided relevant experimental data:
  – Photo-oxydating experiments in Valencia (Euphore)
  – MEA, methyl-, dimethyl-, trimethyl-, ethyl-, diethyl, triethyl-amine and piperazine
  – Basis for modelling other amines

• Vendor amines have also been tested in Valencia
Capture Plant (1)

- Amine chemistry in capture plant (experimentally):
  - MEA degradation dependent of oxygen, temperature and NO\textsubscript{X}
  - Found: DEA, NDELA, NDMA, NMOR, MMA

- Methodology used in the technology qualification amine program for Full Scale Capture at Mongstad – CCM (Norway)
  - Vendors did own tests in small solvent degradation rigs

Source: Fostås et.al, Effects of NOx in the Flue Gas Degradation of MEA, GHGT 10
Se also: Einbu et.al, A new test rig for studies of degradation of CO\textsubscript{2} absorption solvents..., GHGT 11
Capture Plant (2)

- **Initiatives for emission reduction:**
  - An extra water wash section on top of the absorber
  - High efficiency demisters and filters
  - Acid wash in the final washing section on the absorber top
  - UV treatment of lean amine, wash water or gaseous outlet
  - Amine mist control

- **Sampling and analytical techniques:**
  - Sample, identify and quantify nitrosamines and nitramines
  - Total nitrosamine analysis

- **Results:**
  - Sub ppm in emission
  - Level of detection of 0.1 ppb for amines, nitrosamines and nitramines.
  - Total nitrosamine mass balance
Capturing Plant (3)

- Current focus: Amine mist – aerosol based amine emission
- Health and environment & cost of amine loss

Absorber:

See also:
Bade et al., Controlling Amine Mist Formation in CO2 Capture from Residual Catalytic Cracker., GHGT 12
Moser et al., Demonstrating Emission Reduction – Results from the Post-combustion Capture., GHGT 12
Khakharia et al., Predicting Aerosol Based Emissions in a Post Combustion CO2 Capture Process., GHGT 12
LIMITS FOR NITROSAMINES AND NITRAMINES IN AIR AND DRINKING WATER

• International values for NDMA:

<table>
<thead>
<tr>
<th></th>
<th>WHO</th>
<th>Health Canada</th>
<th>US EPA</th>
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<tbody>
<tr>
<td>Drinking water</td>
<td>ng/l (10^{-5})</td>
<td>100</td>
<td>40</td>
</tr>
<tr>
<td>Drinking water</td>
<td>ng/l (10^{-6})</td>
<td>4</td>
<td>0,7</td>
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• Norwegian values
  – Recommendation from Norwegian Institute of Public Health (NIPH 2011)
  – Based on nitrosodimethylamine (NDMA)
  – Annual average

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<thead>
<tr>
<th></th>
<th>nitrosamine + nitramines</th>
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<tbody>
<tr>
<td>Drinking water</td>
<td>ng/l</td>
</tr>
<tr>
<td>Air</td>
<td>ng/m^3</td>
</tr>
</tbody>
</table>

ATMOSPHERIC FORMATION, DESTRUCTION AND DISPERSION

Modelling approach:

• Instantaneous conversion at absorber exit (first assessment 2008)
• Post-processing amine chemistry (discharge permit 2011)
• Integrated amine chemistry (current development)

TCM discharge (2011): Annual average sum of nitrosamines and nitramines.

<table>
<thead>
<tr>
<th></th>
<th>NIPH guideline values</th>
<th>MEA Worst case</th>
<th>MEA Likely case</th>
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<tbody>
<tr>
<td>Drinking water</td>
<td>ng/l</td>
<td>4</td>
<td>0,009</td>
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<tr>
<td>Air</td>
<td>ng/m³</td>
<td>0,3</td>
<td>0,52</td>
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</table>
ATMOSPHERIC FORMATION, DESTRUCTION AND DISPERSION

Modelling approach:

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- Post-processing amine chemistry (discharge permit 2011)
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TCM discharge (2011): Annual average sum of nitrosamines and nitramines.

ppm/ppb

ng/m$^3$

ng/liter
Nitrosamines and Nitramines in the Media (Norway)

- Debated in public since 2009
- Published reports on web and conferences
- National and local media discuss:
  - Nitrosamines, nitramines and atmospheric degradation

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CONCLUDING REMARKS

• Carcinogenicity – Some nitrosamines are classified as probably carcinogenic to humans
• Nitrosamines and nitramines are taken into account when assessing capture process and emissions
• Risk reduction through closing knowledge gaps
• Generated new know-how of high scientific and technical quality
• Results from Mongstad not directly transferable to other locations
  – However, methodology and approach applicable elsewhere
• Sharing knowledge:
  – Close to 100 reports and publications prepared and made available
• Current focus on amine mist
**Further reading**

Overview article presented at GHGT-11 in Kyoto (2012):

- Health and environmental impact of amine based post combustion CO$_2$ capture (Gjernes, Helgesen, Maree)
  

TCM studies and research projects:


Full scale CO$_2$ Capture Mongstad (CCM):