A new test rig for studies of degradation of CO₂ absorption solvents at process conditions; comparison of test rig results and pilot plant data for degradation of MEA

Aslak Einbu*, Eirik DaSilva, Geir Haugen, Andreas Grimstvedt, Kristin Giske Lauritsen, Kolbjørn Zahlsen and Terje Vassbotn

SINTEF Materials and Chemistry, 7465 Trondheim, Norway

Abstract

SINTEF Materials and Chemistry has recently designed an advanced laboratory test rig for studies of solvent degradation. This solvent degradation test rig (SDR) emulates the process conditions observed in an absorber/stripper configuration designed for CO₂ capture. Aqueous solvent is degraded by cycling in a combined absorber and stripper setup with realistic temperatures and CO₂ loadings of the solvent in addition to a defined synthetic flue gas mixture. A 14 week test campaign with degradation of 30 wt.% 2-ethanolamine (MEA) was performed in the rig. Comparison between group methodology and specific nitrosamine analysis of the solvent showed that 42 % of the nitrosamines were unidentified species. This indicates that many of the MEA degradation products are likely precursors for nitrosamine formation. Two nitrosamines were identified in the solvent; nitrosodietanolamine (NDELA) and the nitrosamine of the degradation product N-(2-hydroxyethyl)-glycine (HEGly); nitroso-(2-hydroxyethyl)-glycine (NHEGly). 56% of the total nitrosamine was identified as NHEGly, while 2% was NDELA. Nitrosodimethylamine (NDMA) was detected in the absorber gas emission, but was below the quantification limit in the solvent. Results indicate that the degradation of nitrosamines and nitramine in the solvent is highly temperature dependent, and that the levels of total nitrosamines and MEA-nitramine are significantly reduced by elevated stripper temperature. The results show that the SDR results give a realistic picture on the solvent degradation to be expected in a real CO₂ capture plant; degradation products formed in the SDR MEA solvent reflects those previously found in pilot plant studies. This demonstrates how the SDR enables bench-scale studies of solvent process degradation previously only available from pilot plant studies. SDR results should provide valuable input to health and environmental risk evaluations for different solvent systems for CO₂ capture.

© 2013 The Authors. Published by Elsevier Ltd.
Selection and/or peer-review under responsibility of GHGT

Keywords: CO₂ Capture, solvent degradation, MEA, nitrosamines, absorber emissions, environmental impact

* Corresponding author. Tel.: +47 982 83 933
E-mail address: aslak.einbu@sintef.no
1 Introduction

Previous works on solvent degradation have applied batch reactors for studies of oxidative degradation [1], stainless steel cylinders [2] and micro-calorimeters [3] for screening of solvents for thermal degradation. In these experimental setups, the mechanisms for oxidative and thermal degradation are studied separately and the combined effects occurring in a real capture plant are not considered. Process degradation of amine solvents is a complex mixture of reactions, in which reactants, intermediates and end degradation products in the solvent are circulated in the plant and exposed to changing conditions throughout the process cycle. Different degradation and formation mechanisms compete in different parts of the plant and the chemical composition of the degradation-product mixture depend on the combined effects of formation and degradation of compounds in the process.

Knowledge of the total process degradation of solvents has traditionally been obtained from pilot plant studies. Closmann and Rochelle (2010) reported studies of solvent degradation in an ”Integrated Solvent Degradation Apparatus” (ISDA), which alternately exposed the solvents to oxidative and thermal degradation conditions in a single system [4]. However, the ISDA experiments also deviate from realistic process conditions in that the CO\textsubscript{2} loading is constant during the cycling, and that it lacks the presence of NO\textsubscript{X} in the flue gas.

SINTEF Materials and Chemistry has recently designed an advanced laboratory test rig for studies of solvent degradation. The test rig simulates the process conditions observed in an absorber/stripper configuration designed for CO\textsubscript{2} capture; aqueous solvent is degraded by cycling in a combined absorber and stripper setup with realistic temperatures and CO\textsubscript{2} loadings of the solvent in addition to a defined synthetic flue gas mixture. The developed solvent degradation test rig (SDR) can be applied for studies on process-related degradation or nitrosation and provides qualitative data on compounds potentially present in the absorber emissions for different solvent systems.

2 Experimental

2.1 Test rig design

The SDR is built to fit into a standard laboratory fume hood cabinet; it has a relatively compact rig setup with a footprint of 120x60 cm and a height of less than 2 meters. Total solvent inventory is about 5 litres. Figure 1 shows a simplified process flow diagram (PFD) of the rig.

The SDR allows operation with desorber temperatures from 110-150°C and absorber temperatures between 25-80°C. Buffer tanks enable adjustable solvent residence time in the absorber/desorber. Typical rich and lean CO\textsubscript{2} loading of the solvent is aimed at 0.5 and 0.2, (mol CO\textsubscript{2}/mol solvent) respectively. An electric heater in the desorber sump enables stripping in order to obtain a realistic lean loading. A synthetic flue gas is produced by mixing of pure N\textsubscript{2}, O\textsubscript{2}, CO\textsubscript{2} and defined NO\textsubscript{X}-mixture and/or other flue gas components of interest. In order to limiting the consumption of synthetic gas and to obtain realistic gas/liquid loads in the column packing, the rich solvent and flue gas is recycled over the absorber. The rig has several sampling points for solvent, gas and condensate in order to obtain information on both the gas and liquid compositions during experiments. The rig is designed for unmanned operation, but relies on regular manual inspection and adjustments. A piping and instrumentation diagram (P&ID) is shown in Figure 2.
2.2 Test protocol experimental design

The SDR rig was operated for 14 weeks with 30 wt.% MEA (CAS 141-43-5) in water. Regular sampling and analysis was performed of gas and liquids. The results presented in this paper focuses on the solvent analyses, and less on the absorber gas emission measurements. In the experiments, typical process conditions found in a real capture plant were simulated. The absorber liquid temperature was 40°C and lean and rich loading around 0.20 and 0.45 mol CO₂/mol amine respectively over the entire test period. The campaign was divided into four consecutive protocols with different process conditions with duration of 5 weeks and then 3x3 weeks duration. Parameters to be changed in the test protocols were stripper temperature, flue gas oxygen and NOₓ content. The test rig process conditions and operation times are summarised in Table 1 for all test protocols. Overall, the rig was operated for 83 days during the 14 weeks campaign period which correspond to a total operational time of 87%.

Table 1. Summary of variations in test rig process conditions during the 14 week test campaign with 30 wt% MEA.

<table>
<thead>
<tr>
<th>Test protocol</th>
<th>Stripper temperature [°C]</th>
<th>Flue gas oxygen content [mol %]</th>
<th>Flue gas NOx content [ppmv]</th>
<th>Operation [days (total days)]</th>
<th>Operation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Standard&quot;</td>
<td>120</td>
<td>12</td>
<td>5</td>
<td>26 (35)</td>
<td>74%</td>
</tr>
<tr>
<td>&quot;High oxygen&quot;</td>
<td>120</td>
<td>18</td>
<td>5</td>
<td>16 (17)</td>
<td>93%</td>
</tr>
<tr>
<td>&quot;High temperature&quot;</td>
<td>140</td>
<td>12</td>
<td>5</td>
<td>21 (21)</td>
<td>100%</td>
</tr>
<tr>
<td>&quot;High NOₓ&quot;</td>
<td>120</td>
<td>12</td>
<td>50</td>
<td>20 (22)</td>
<td>89%</td>
</tr>
</tbody>
</table>
The second and fourth protocols ("High NO\textsubscript{X}", "High oxygen") involved change in the synthetic exhaust gas composition, and all other operation parameters for the SDR were fixed. The third protocol "High Temperature" was the only protocol with any "major" operational change in the SDR rig where desorber pressure was increased to 3.65 bar and the reboiler duty was increased to compensate for higher heat loss and to meet the target of 140 °C in the reboiler. No amine makeup was performed during the test campaign. Demineralized water was added daily in order to compensate for sample withdrawal and vapour loss with the exiting absorber gas. On average, 23 grams was added per day in order to keep a stable solvent inventory.

During the experiment rich and lean solvent samples were sampled at regular intervals. Condensates and gas emission samples were sampled at the end of each protocol. Components analysed for included amines, ammonia, alkylamines a range of nitrosamines and nitramines in addition to a list of selected MEA degradation products. Concentrations of different metal ions were also monitored in order to study corrosive effects. MEA and all degradation products were analysed by LC-MS-QQQ except total nitrosamine which were analysed by GC-NCD. In addition MEA was also determined by titration method (titration with $H_2SO_4$) for some of the solvent samples, $CO_2$ loading (moles $CO_2$/moles amine) (were determined by a TOC analyser operated in inorganic modus and the metals were analysed by HR-ICP-MS.

![P&ID of the bench scale test rig (SDR) designed by SINTEF](image)

Fig. 2. P&ID of the bench scale test rig (SDR) designed by SINTEF. The rig enables solvent degradation studies at simulated process conditions observed in an absorber/stripper configuration designed for $CO_2$ capture.
3 Results

3.1 Solvent amine analysis

During the execution of the test protocols lean solvent were sampled and analysed at regular intervals. The determined MEA concentration in the samples as a function of time is given in Figure 3. The results show a relatively linear decrease in MEA concentrations as a function of time with a total 32 % loss of MEA over the 14 week test campaign.

![Figure 3. MEA concentration in test rig lean solvent as a function of running time (weeks). The test campaign consisted of four subsequent test protocols; 1) Standard conditions, 2) High flue gas O₂ level, 3) High stripper temperature and 4) High flue gas NOₓ level.](image)

The overall degradation rate of MEA did not appear to change significantly throughout the campaign, despite the changes applied in process conditions of the different test protocols.

3.2 Solvent degradation products

Lean solvent samples were analysed for a range of known degradation product in MEA including: methylamine, ethylamine, diethyamine, dimethyamine, diethanolamine (DEA), 4-(2-hydroxyethyl)piperazin-2-one (HEPO), N-(2-hydroxyethyl)imidazole (HEI), N-(2-hydroxyethyl) glycine (HEGly), N-(2-hydroxyethyl)formamide (HEF), N,N’-bis(2 hydroxyethyl)oxamide (BHEOX), N-(2-hydroxyethyl)acetamide (HEA) and 2-oxazolidinone (OZD). The concentrations of these products were plotted as a function of time during the test campaign. Results for DEA are plotted in Figure 5. Alkylamines are shown in Figure 6, while the rest of the listed compounds are shown in Figure 4.
The test campaign consisted of four subsequent test protocols; 1) Standard conditions, 2) High flue gas O$_2$ level, 3) High stripper temperature and 4) High flue gas NO$_x$ level.

The results show that all the listed degradation products appear in the solvent upon time and increase in concentration during the SDR test campaign. The concentration of HEPO has a significant increase in rate of formation during the test protocol with elevated stripper temperature. Also for HEF there is a significant increase when the temperature of the stripper is increased. This indicates that the reaction for formation of these compounds is temperature dependent. HEPO concentration in the solvent is reduced during the test protocol with elevated NO$_x$ level in the flue gas. HEGly is the secondary amine that is present in highest concentration among the analysed degradation products. This suggests that the nitrosamine formed from HEGly may be a significant contributor to the total nitrosamine levels.
Results show that DEA is present in the unused MEA solvent in a concentration of approximately 250 μmol/liter. During the test campaign, there is a steady increase in DEA-concentration during the first three test protocols followed by a significant reduction during the last protocol involving increased NOx-level in the flue gas.

Fig. 6. Alkylamine concentration in lean solvent as a function of running time (weeks). The test campaign consisted of four subsequent test protocols; 1) Standard conditions, 2) High flue gas O2-level, 3) High stripper temperature and 4) High flue gas NOx-level.

Methylamine is the most dominant species among the alkylamines analysed for in the solvent; it also shows the highest increase in formation during the high stripper temperature case. Diethylamine was not found above the quantification limits in any of the solvent samples, it is however present in the gas emission. Ethylamine shows a relative large increase in concentration for the high stripper temperature case. Solvent concentration of dimethylamine increases for the high stripper temperature followed by a decrease for the high NOx case.

3.3 Nitrosamine and nitramine analysis

Nitrosamines were analysed for by two different approaches; by group methodology giving the total nitrosamine concentration and by a set of specific nitrosamines analysed for. The following specific nitrosamines were analysed for: nitrosodiethanolamine (NDELA), nitrosopiperidine (NPIP), nitrosodiethylamine (NDEA), nitrosodimethylamine (NDMA), nitrosomethylethylamine (NMEA), nitrosomorpholine (NMOR), nitrosodibutylamine (NDBA), nitrosodipropylamine (NDPA), nitrosopyrrolidine (NYPR) and nitroso-(2-hydroxyethyl)-glycine (NHEGly).

Two specific nitramines were analysed for i.e. MEA-nitramine and AMP-nitramine. Only MEA-nitramine was detected. Table 2 shows results from solvent analysis of total nitrosamine and MEA-nitramine during different SDR test protocols. Total nitrosamine is given as μg/ml NDMA equivalents.
Table 2. Solvent analysis of total nitrosamine and MEA nitramine during the different SDR test protocols.

<table>
<thead>
<tr>
<th>Solvent sample</th>
<th>Test protocol</th>
<th>Total nitrosamine [µg NDMA/ml]</th>
<th>MEA-NO₂ [ng/ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unused</td>
<td></td>
<td>16.6</td>
<td>16.6</td>
</tr>
<tr>
<td>Week 3</td>
<td>Standard</td>
<td>12.3</td>
<td>49.7</td>
</tr>
<tr>
<td>Week 5</td>
<td>Standard</td>
<td>9.2</td>
<td>44.6</td>
</tr>
<tr>
<td>Week 7</td>
<td>High Oxygen</td>
<td></td>
<td>140.0</td>
</tr>
<tr>
<td>Week 8</td>
<td>High Oxygen</td>
<td>11.6</td>
<td>98.5</td>
</tr>
<tr>
<td>Week 11</td>
<td>High Temperature</td>
<td>4.8</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Week 14</td>
<td>High NOₓ</td>
<td>11.1</td>
<td>72.8</td>
</tr>
</tbody>
</table>

Analytical results show that the MEA nitramine is present in the unused solvent. Nitramine is present in much lower concentrations than nitrosamine. Nitramine formation seemed to increase with higher flue gas oxygen level and decreased below the quantification limit upon elevated stripper temperature. The total nitrosamine level was reduced by more than 50% during the high stripper temperature test protocol. This indicates that the process of degradation of nitrosamines and nitramine in the solvent is highly temperature dependent. During the elevated NOₓ case, the total nitrosamine concentration returned to the same level as during the standard and high oxygen cases. This could indicate that the total nitrosamine has reached a steady-state level in these cases with a common stripper temperature, which is not affected by the change in NOₓ-level or elevated oxygen concentration in the flue gas.

For the specific nitrosamines in the solvent, only NHEGly and NDELA were found to be above the quantification limit (10 ng/ml). The total nitrosamine levels determined by group methodology were significant higher than the sum of the identified nitrosamines; NHEGly accounted for 56% of the total nitrosamine concentration and NDELA 2%, the remaining 42% were not identified in this work.

NDMA concentrations were below quantification limits for all solvent samples. However, NDMA was detected in the emissions: the level was elevated during the high NOₓ test protocol. The observation of NDMA in the emission only, can be explained by its volatility and the fact that gas measurements were performed by accumulative methods.

3.4 Comparison with pilot plant data

Table 3 shows the ratio of the concentrations found in the SDR rig relative to solvent concentrations found during an MEA pilot plant campaign at Esbjerg, Denmark. The solvent analysis from Esbjerg was performed 20 weeks into the campaign and is from the lean solvent [5]. Comparison of the degradation products identified in the SDR experiment with the pilot plant shows that the SDR experiment gives a representative picture of MEA degradation occurring in a real life capture plant. The levels of degradation products in the SDR rig and the pilot-plant are quantitatively relatively similar. At week 8 the level of all major degradation products is within 70% of the value at the Esbjerg pilot plant.
Table 3. Results of selected degradation products in the SDR solvent relative to concentrations found in the Esbjerg pilot plant.

<table>
<thead>
<tr>
<th>Solvent sample</th>
<th>Test protocol</th>
<th>OZD</th>
<th>BHEOX</th>
<th>HEA</th>
<th>HEGly</th>
<th>HEPO</th>
<th>HEF</th>
<th>HEI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Week 0</td>
<td>Standard</td>
<td>0.03</td>
<td>0.06</td>
<td>0.04</td>
<td>0.2</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Week 3</td>
<td>Standard</td>
<td>14.1</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>1.0</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Week 5</td>
<td>Standard</td>
<td>12.9</td>
<td>0.4</td>
<td>0.5</td>
<td>0.8</td>
<td>1.2</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Week 8</td>
<td>High Oxygen</td>
<td>13.6</td>
<td>1.2</td>
<td>0.7</td>
<td>0.8</td>
<td>1.1</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Week 10</td>
<td>High Temperature</td>
<td>1.5</td>
<td>0.9</td>
<td>4.1</td>
<td>3.7</td>
<td>2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Week 11</td>
<td>High Temperature</td>
<td>1.9</td>
<td>1.0</td>
<td>5.2</td>
<td>4.4</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Week 13</td>
<td>High NOx</td>
<td>2.0</td>
<td>1.1</td>
<td>4.7</td>
<td>3.8</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Week 14</td>
<td>High NOx</td>
<td>2.3</td>
<td>1.2</td>
<td>4.6</td>
<td>4.5</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results suggest that the SDR rig does capture the degradation chemistry taking place in CO₂ capture plants. Both the relative concentration between degradation products and overall levels are in good agreement between the SDR and the Esbjerg pilot campaign. The SDR results show significantly higher levels of 2-oxazolidinone (OZD) than at Esbjerg. OZD is however a minor degradation product. OZD is known to be a transient degradation product and it may be that the steady state concentration is higher in the SDR due to different residence times in the absorber and stripper.

It can also be seen that at high stripper temperature conditions the ratio of some degradation products starts to differ in the SDR and the pilot plant. This is as expected, since the solvent in this case is exposed to more severe conditions than in the pilot plant. For volatile degradation products a direct quantitative comparison is more difficult to make, since the SDR rig has recirculation of absorber gas and a different emission control system than a pilot-plant. It does however seem that all degradation products found in pilot plants can be found and quantified in the SDR rig. For the nitrosamines we have less available data to carry out quantitative comparisons. Our overall impression is however that the nitrosation chemistry in the SDR rig is comparable to that we see in pilot plants.

Overall the results suggest that the SDR not only qualitatively captures the relevant degradation chemistry taking place in CO₂ capture plants, it also gives a reasonable quantitative picture of the level of build-up of degradation products.

4 Conclusions

Our results show that results from experiments with MEA in the new solvent degradation rig (SDR) give a realistic picture on the solvent degradation to be expected in a real CO₂ capture plant. The results provide a qualitative picture of the degradation products to be formed and list potential components present in the gas exiting the absorber column.

Solvent analysis shows that the total nitrosamine levels in the used solvent were significantly higher than the sum of identified nitrosamines. This means that there are significant amounts of unidentified nitrosamines in used MEA solvent. Many of the degradation products which have secondary amine groups are likely precursors for nitrosamine formation. The nitrosamine of HEGly contributed to 56% of the total nitrosamine and NDELA 2%. 42% of the total nitrosamine content in the solvent was not identified in this study.
Results indicate that the degradation of nitrosamines and MEA-nitramine is highly temperature dependent, and that the levels in the solvent are significantly reduced by elevated stripper temperature.

Our results demonstrate that the solvent degradation rig can provides valuable input to health and environmental risk evaluations for different solvent systems for CO₂ capture. The new SDR designed by SINTEF enables bench-scale studies of solvent process degradation previously only available from pilot plant studies.

Acknowledgements

This work has been part of the Amine Technology Qualification Program (TQP Amine), an extensive investigation program with the object of developing a set of methods and procedures for evaluating health and environmental impact of amine based solvents, under the CO₂ Capture Mongstad project (CCM), funded by the Norwegian State and organized as a joint effort by Gassnova SF and Statoil ASA.

References