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Degradation and Emission Results of Amine Plant Operations from MEA Testing at the CO₂ Technology Centre Mongstad

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Abstract

In 2015, the CO₂ Technology Centre Mongstad (TCM DA), operated a test campaign using aqueous monoethanolamine (MEA) solvent at 30 wt%. The main objective was to demonstrate and document the performance of the TCM DA Amine Plant located in Mongstad, Norway. This paper will present several aspects concerning degradation of the solvent and atmospheric emissions from amine based CO₂ removal processes. The work aims to; (1) quantify the amounts and compositions of the degraded solvent (2) report results from atmospheric emissions measurements of amines and amine based degradation products; and (3) present Ambient Air measurement done during a 2 month campaign.

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1. Introduction

The CO₂ Technology Centre Mongstad (TCM DA) is located next to the Statoil refinery in Mongstad, Norway. TCM DA is a joint venture set up by Gassnova representing the Norwegian state, Statoil, Shell, and Sasol. The facility run by TCM DA entered the operational phase in August 2012 and it is one of the largest post-combustion CO₂ capture test centres in the world. A unique aspect of the facility is that either a flue gas slipstream from a natural gas turbine based combined heat and power (CHP) plant or an equivalent volumetric flow from a residual fluidized catalytic cracker (RFCC) unit can be used for CO₂ capture. The CHP flue gas contains about 3.5% CO₂ and the RFCC flue gas contains about 13-14% CO₂. One of the main test plants at TCM DA is a highly flexible and well-instrumented amine plant. The amine plant was designed and constructed by Aker Solutions and Kværner to accommodate a variety of technologies, with capabilities of treating flue gas streams of up to 60,000 standard cubic meters per hour. The plant is being offered to vendors of solvent based CO₂ capture technologies to, among others, test; (1) the performance of their solvent technology, and (2) technologies aimed to reduce the atmospheric emissions and environmental impact of amines and amine based degradation products from such solvent based CO₂ capture processes. The objective of TCM DA is to test, verify, and demonstrate CO₂ capture technologies suitable for deployment at full-scale. Up to now the vendors Aker Solutions, Alstom, Cansolv Technologies Inc. and Carbon Clean Solutions Ltd. have successfully used the TCM DA facilities to verify their CO₂ capture technologies. From July to October 2015 TCM DA, in collaboration with partners, operated a test campaign using the non-proprietary aqueous monoethanolamine (MEA) solvent at 30 wt%.

2. The amine plant and operating conditions

The MEA campaign was started 6th of July 2015 with flue gas introduction to the amine plant. The campaign lasted to 17th of October 2015. Operational hours are counted as hours with both flue gas and solvent circulation. The entire campaign gave a total of 1960 hours of operation (figure 1).

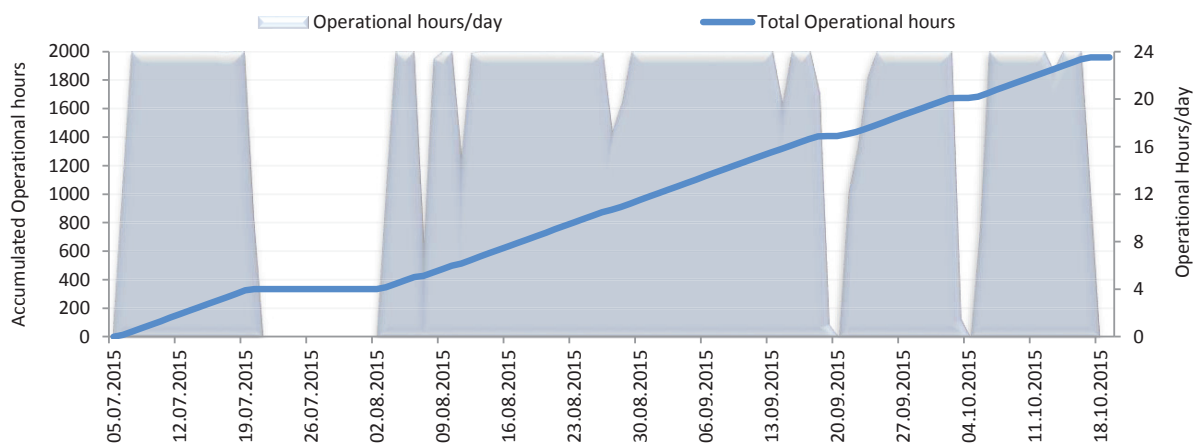


Figure 1. Overall MEA campaign operational hours, from 6th of July to 18th of October 2016.

A process flow diagram including sample points for the amine plant is given in figure 2. A more detailed description of the TCM DA amine plant and the TCM sample handling system can be found elsewhere [1,2,3]. Liquid and gas sampling, target component groups and analytical measurement techniques are described in sections 2.3 to 2.5 below.

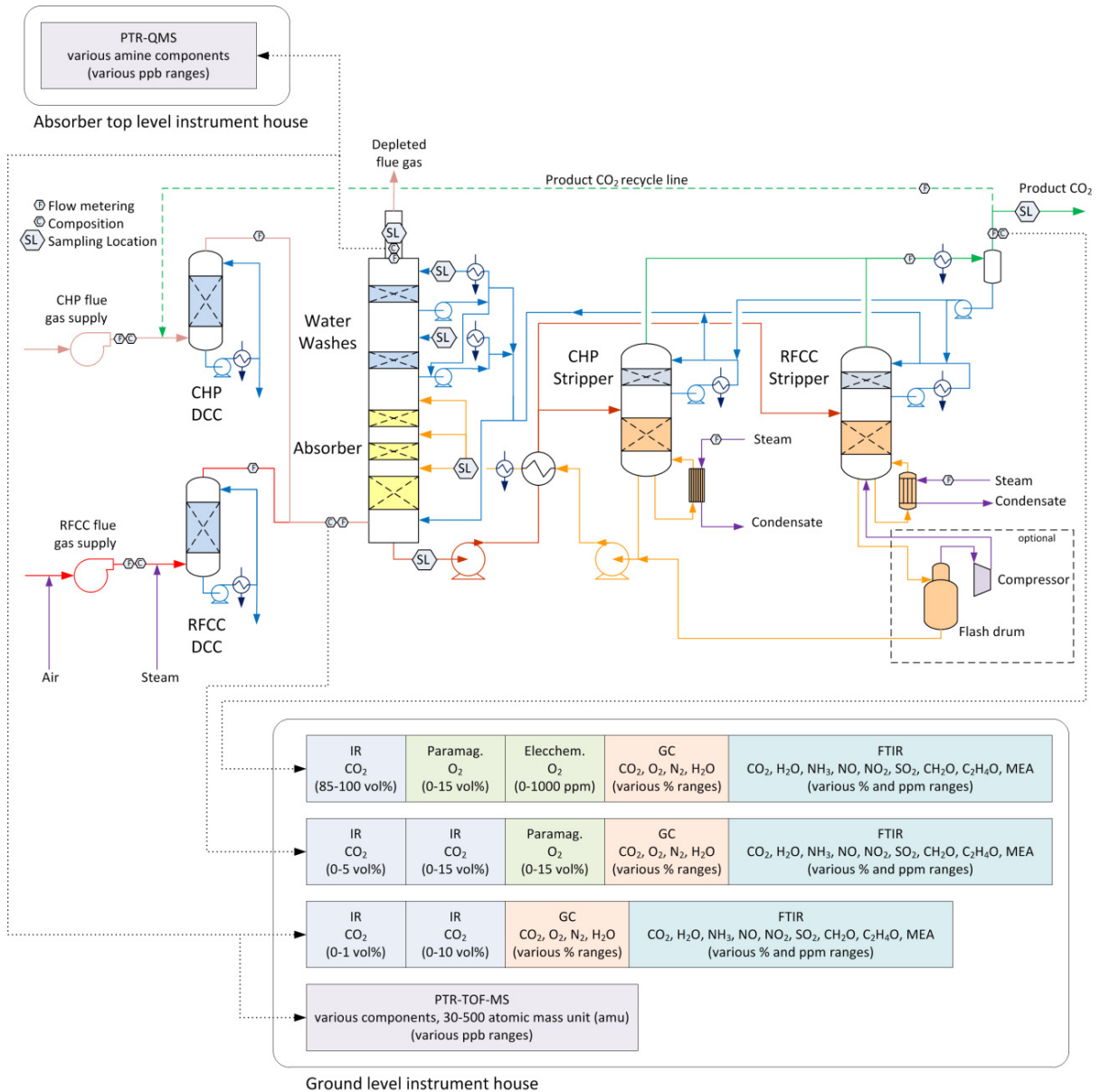


Figure 2. Process flow diagram for TCM, including online equipment's and manual sampling locations

Several operating conditions are important with respect to the solvent degradation and emission rates of amines and degradation products. Detailed information about the operating conditions and all the test activities and performance results from the MEA campaign, can be found in Gjernes et al [12].

The flue gas composition downstream the Direct Contact Cooler (DCC) from the CHP and the RFCC are providing a range of test conditions and the solvent will be exposed to a corresponding range in CO₂ and O₂ concentrations, as well as NO_x, SO_x and particles. Solvent amines react with the flue gas components and give rise

to the degradation products as illustrated in figure 3. Degradation reactions of MEA and specific degradation products that were monitored during this campaign is given in section 3 below.

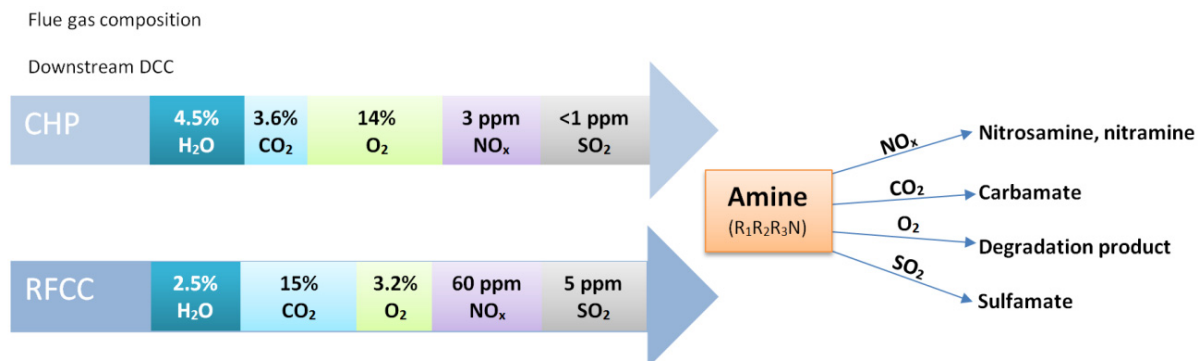


Figure 3. Typical flue gas composition influence of reaction with amines

When the solvent is exposed to higher temperatures in combination with the flue gas components, the degradation reactions are accelerated. Also the accumulation in the solvent of transition metal elements due to corrosion may contribute to degradation [11]. Process units with high temperature exposure are the stripper and reboiler system and the hot part of the solvent circulation loop. For more process details see Table 1. The inventory and the residence time of solvent in the hot areas are decisive for degradation, for more details regarding the inventory see Flø et al [13].

Table 1. Process parameters in the solvent circulation loop

| Process parameters | Unit | Hot Lean Solvent | Hot Rich Solvent | Cold Lean Solvent | Cold Rich Solvent |
|--------------------|-----------|------------------|------------------|-------------------|-------------------|
| Temperature | °C | 120 | 110 | 35 - 37 | 30 - 40 |
| Flow rate | Tons/hour | 55 - 120 | 55 - 120 | 55 - 120 | 55 - 120 |
| pH | - | 10.4 | 9 | 10.4 | 9 |
| Pipe size | Inches | 8 | 6 | 8 | 6 |
| Velocity | m/s | 0.45-0.97 | 0.74-1.62 | 0.45-0.97 | 0.74-1.62 |

2.1. Liquid samples

The solvent amine, ammonia, and some degradation products were analyzed by TCM DA and Statoil Crude Oil and Products laboratories (CP Lab). Alkyl amines, aldehydes, ketone, generic nitrosamines, solvent specific nitrosamines and nitramines were analyzed by SINTEF laboratories. Total Nitrogen (Kjeldahl) was analyzed by LabNett Stjørdal, table 2 gives an overview of the different techniques used.

Organic acids and anions were measured by Ion Chromatograph (IC) and Total Heat Stable Salts (HSS) by ion exchange and following titration.

Table 2. Analytical measurements techniques

| Component groups | Analysis methods | Supplier | Analysed by |
|-------------------------------------|-------------------------------|----------|------------------|
| Amines (solvent) | LC MS QQQ | Agilent | Statoil CP lab |
| Amines (alkyl) | LC MS QQQ | Agilent | Sintef |
| Ammonia | Cation chromatography, IC-ECD | Dionex | TCM Lab |
| Aldehydes | LS MS QQQ | Agilent | Sintef |
| Nitrosamines (TONO) | See * | - | Sintef |
| Nitrosamines (specific and generic) | LC MS QQQ | Agilent | Sintef |
| Nitramines | LC MS QQQ | Agilent | Sintef |
| Organic acids, anion | Anion chromatography, IC-ECD | Dionex | TCM Lab |
| Total Heat Stable Salts | Ion exchange and titration | Metrohm | TCM Lab |
| Total Nitrogen | - | - | LabNett Stjørdal |

*TONO; Quench of solved nitrite followed by break of N-NO bond in a reaction chamber. Total NO released from the N-nitroso groups detected by chemiluminescence analyser.

2.2. Emission samples

TCM DA applies different measurement techniques to monitor and quantify the amounts and concentrations of emitted compounds. There are three different flue gas streams, flue gas inlet to the absorber (downstream DCC), absorber outlet and CO₂-stripper outlet. Online instruments are connected via heated sampling lines to sampling probes. The amine and other emissions were monitored and confirmed by isokinetic sampling and the following online analyzers in Table 3. A full description of emission monitoring at TCM is given in Morken et al [1]. For a more detailed description of the general online equipment see Lombardo and Gjernes [6,12].

Table 3. Online instrumentation for emission monitoring at TCM

| Instrument | Gasmet FTIR FCX | FTIR Anafin2000 | PTR-TOF-MS | PTR-QMS |
|------------------------|-----------------------------|-----------------------------|----------------------------------|-------------------|
| Supplier | Gasmet Technologies Oy | Analect | Ionicon | Ionicon |
| Temp | Cell 180°C | Cell 85°C | Drift tube 100°C | Drift tube 100°C |
| Cell path length | 5 m | 7 m | - | - |
| Resolution | 8 cm ⁻¹ | 2 cm ⁻¹ | ($\Delta(m/z)/((m/z)) > 3000$) | $\Delta(m/z) = 1$ |
| Flow rate | 120 – 600 L/h | 100 L/h | 30 L/h | 30 L/h |
| Range | 900 – 4200 cm ⁻¹ | 500 – 7000 cm ⁻¹ | 10-200 | 20-200 |
| LOD | 0.5 - 1 ppmv * | 0.5 -1 ppmv * | 0.0001 ppmv | 0.001 ppmv |
| SD | * | * | ± 20 % | ± 20 % |
| Inlet Flue Gas | | x | | |
| CO ₂ -stack | x | | x** | |
| Absorber | x | x** | x | x |

*Limit of detection (LOD) value depends on compound, level of compound, the way of calculation and measurement time.

**Occasionally measurements on these streams for QA/QC and comparing different instruments.

2.3. Ambient Air measurements, instrumentation and locations

The ultra-sensitive proton-transfer-reaction quadrupole ion guide time-of-flight mass spectrometer (PTR-QiToF-MS) from IONICON was used for detecting trace gases at low pptv levels in ambient air in the vicinity of Technology Centre Mongstad. These novel ambient air measurements were performed in August and September 2015 by University of Oslo. Measurements were carried out in three different geographic locations, Sundsbø (60°46'10.1''N, 5°09'08.6''E), Sande (60°50'56.6''N, 5°00'21.0''E) and Mongstad West (60°48'45.7''N, 5°00'43.4''E). These sites were chosen from earlier measurement done by Norwegian Institute for Air Research (NILU) and dispersion models done by NILU [5]. For more technical details and results regarding this surveillance see Mikoviny et al [10].

3. MEA solvent and degradation theory

3.1. Oxidative and Thermal degradation

The degradation mechanisms for MEA have been extensively studied in the literature [4,5,8,11,14]. The main degradation reaction pathways with most important degradation products are indicated and proposed in figure 7 below. Oxidative degradation is induced by O₂ and produces oxidized fragments of the solvent. Organic acids, ammonia and aldehydes are the main products from this degradation route. Ammonia and aldehydes are observed in the emission samples. The organic acids react with MEA and various degradation products are formed in subsequent reactions. These products are identified in the solvent samples.

The carbamate degradation route requires CO₂ and fairly high temperatures. The thermal degradation of MEA occurs predominantly in the reboiler and stripper packing due to exposure to high temperature. While the initial products of thermal degradation have been identified, the kinetics of the thermal degradation pathways has not been clearly defined. Davis and Rochelle [14] indicate that thermal degradation is minor when reboiler temperature is held below 110°C but it accelerates above 130 °C. Carbamate polymerization due to high temperature is the main cause of thermal degradation of MEA. This degradation is also compounded when the CO₂ loading of the solution is increased. MEA concentrations can be kept at 30 wt % to minimize thermal degradation and prevent corrosion in industrial applications.

3.2. HSS components

Heat Stable Salts (HSS) are salts in the amine solution that is not affected by heat. The heat stable salt does not regenerate in the regenerator and remains in the circulating amine system. Total HSS are measured by a titration procedure which prepares the sample with a strong cation exchange resin. Individual HSS anions are measured by Ion Chromatography (IC). The different anions measured by IC are summarized in table 4.

Table 4. Heat stable salts anions analyzed by TCM laboratory using Ion Chromatography

| Component | Abb | CAS No | Mw |
|------------|---|------------|-----|
| Acetate | (AA ⁻) | 71-50-1 | 59 |
| Glycolate | (GA ⁻) | 79-14-1 | 75 |
| Formate | (FA ⁻) | 71-47-6 | 45 |
| Oxalate | (OA ⁻) | 144-62-7 | 125 |
| Nitrate | (NO ₃ ⁻) | 14797-55-8 | 62 |
| Nitrite | (NO ₂ ⁻) | 14797-65-0 | 46 |
| Sulphate | SO ₄ ²⁻ | 14808-79-8 | 96 |
| Propionate | (C ₂ H ₅ COO ⁻) | 72-03-7 | 73 |

The identified anions are summed to provide a total HSS. In general, Total HSS by titration should be the same or larger than the sum of anions by IC, figure 6 (h). Total HSS are reported as the wt% of the equivalent amount of amine. This means if HSS concentration were 1 mole/kg (eq/kg) of solution, it will be 6.1 wt% as MEA (1).



3.3. Degradation components in solvent, from emission and in Ambient Air

The degradation components measured during the MEA campaign were based on information found from literature [4]. All components from solvent and emission samples in Table 5 were analyzed by Sintef. The analyzing measuring technique was primarily LC-MS-QQQ. The mixture of the different degradation components are hereafter called D-mix. Analysis of Ambient Air components were done by University of Oslo [10].

Table 5. Degradation products and measurements in solvent, emission from amine plant absorber stack and in Ambient Air.

| Component | Abb | CAS No | Mw | Solvent | Emission to Air | Ambient Air |
|---|-----------------|-------------|-----|---------|-----------------|-------------|
| Monoethanolamine | MEA | 141-43-5 | 61 | x | x | x |
| Ammonia | NH ₃ | 7664-41-7 | 17 | x | x | |
| Formaldehyde | FA | 50-00-0 | 30 | x | x | |
| Acetaldehyde | AA | 75-07-0 | 44 | x | x | x |
| N-Nitroso-diethanol-amine | NDELA | 1116-54-7 | 134 | x | x | |
| N-(2-hydroxyethyl) acetamide | HEA | 142-26-7 | 103 | x | | |
| 1-hydroxyethane 1,1-diphosphonic acid | HEDP | 2809-21-4 | 206 | x | | |
| N-(2-hydroxyethyl)ethylenediamine | HEEDA | 111-41-1 | 104 | x | | |
| N-(2-hydroxyethyl)formamide | HEF | 693-06-1 | 89 | x | | |
| N-(2-hydroxyethyl)glycine | HeGly | 5835-28-9 | 119 | x | | |
| N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide | HEHEAA | 144236-39-5 | 162 | x | | |
| Pyrazine | - | 290-37-9 | 80 | x | x | |
| N-(2-hydroxyethyl)imidazole | HEI | 1615-14-1 | 112 | x | | |
| N-(2-hydroxyethyl)imidazolidinone | HEIA | 3699-54-5 | 130 | x | | |
| 4-(2-hydroxyethyl)piperazin-2-one | HEPO | 23936-04-1 | 144 | x | | |
| Dimethylamine | DMA | 124-40-3 | 45 | x | x | x |
| Methylamine (Monomethylamine) | MA (MMA) | 74-89-5 | 31 | x | x | x |
| Ethylamine | EA | 75-04-7 | 45 | x | x | x |
| Diethylamine | DiEA | 109-89-7 | 73 | x | x | x |
| Morpholine | Mor | 110-91-8 | 87 | x | x | |
| Trimethylamine | TMA | 75-50-3 | 59 | x | x | x |
| 4,4-dimethyl-2-oxazolidinone | 4,4-DMO | 26654-39-7 | 115 | x | x | |
| N-Nitroso(2-hydroxyethyl)glycine | NO-HeGly | 80556-89-4 | 148 | x | x | |
| 2-(Nitroamino)ethanol | NO2-MEA | 74386-82-6 | 106 | x | x | |
| N-methyl,N-nitroso-methanamine | NDMA | 62-75-9 | 74 | x | x | |
| N-nitro-N-methyl-methanamine | DMNA | 4164-28-7 | 90 | x | x | |
| N-Nitrosomethylethylamine | NMEA | 10595-95-6 | 88 | x | x | |
| N-Nitrosodiethylamine | NDEA | 55-18-5 | 102 | x | x | |
| N-Nitrosodi-n-propylamine | NDPA | 621-64-7 | 130 | x | x | |
| N-Nitrosodi-n-butylamine | NDBA | 924-16-3 | 158 | x | x | |
| N-Nitrosopyrrolidine | NPYR | 930-55-2 | 100 | x | x | |
| N-Nitrosopiperidine | NPIP | 100-75-4 | 114 | x | x | |
| N-nitrosodiethanolamine | NDELA | 1116-54-7 | 134 | x | x | |
| 2-Oxazolidone | OZD | 497-25-6 | 87 | x | x | |
| Alkylpyrazine | - | | | | x | |
| NN'-Bis(2-hydroxyethyl)oxamide | BHEOX | 1871-89-2 | 176 | x | x | |
| Diethanolamine | DEA | 111-42-2 | 105 | x | x | |

4. Results and discussions

The first observable sign of degradation was color change of the solvent. The color of the solvent changed rapidly after the first contact with the flue gas. Samples taken before introduction of flue gas show a colorless solvent. Only hours after start up, the color started to change from colorless to yellow, and more and more orange and dark brown as seen in figure 4. After reclaiming 12th of October, the color is more like the color that appeared in the start of the campaign when the solvent was fresh.



Figure 4. Pictures of samples taken during the campaign. The color change gives an indication on how degraded the solvent is. The samples are from left to right after: 0, 1300, 1830, 1870 and 1920 hours of operation.

4.1. Heat stable salts in the solvent

Figure 5 and 6 shows how the levels of organic acids and anions developed during the entire campaign. Figure 5 shows overall heat stable salts development where 5a) are Total Heat Stable salts reported as wt% MEA, and 5b) results from individually IC results from each component. Figure 6 (a-g) shows more detailed development of all the individual components. The main anion formed is formate and the level of this component reach 3000 mg/L before reclaiming. Glyoxylic acid is assumed to be one of the formed organic acids during the degradation process [7]. It was not possible to analyze for this component as there were no available method at the time. An unknown component of significant response on the IC chromatogram was found. The area of the unknown component in the chromatogram was significant, and the component was calibrated with a mix of the other components. The result from this unknown component is rather uncertain, see figure 6 g). All other IC results have a repeatability uncertainty of $\pm 20\%$.

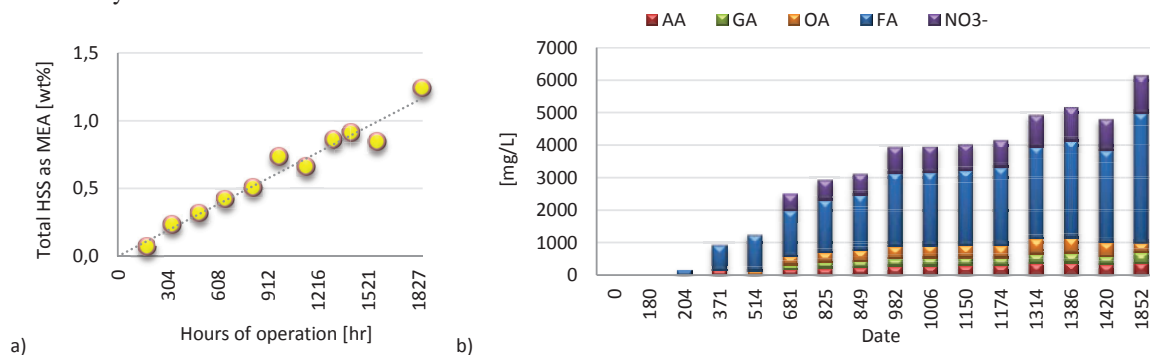


Figure 5. (a) Total Heat stable salt concentration; (b) Results from Anion IC analysis

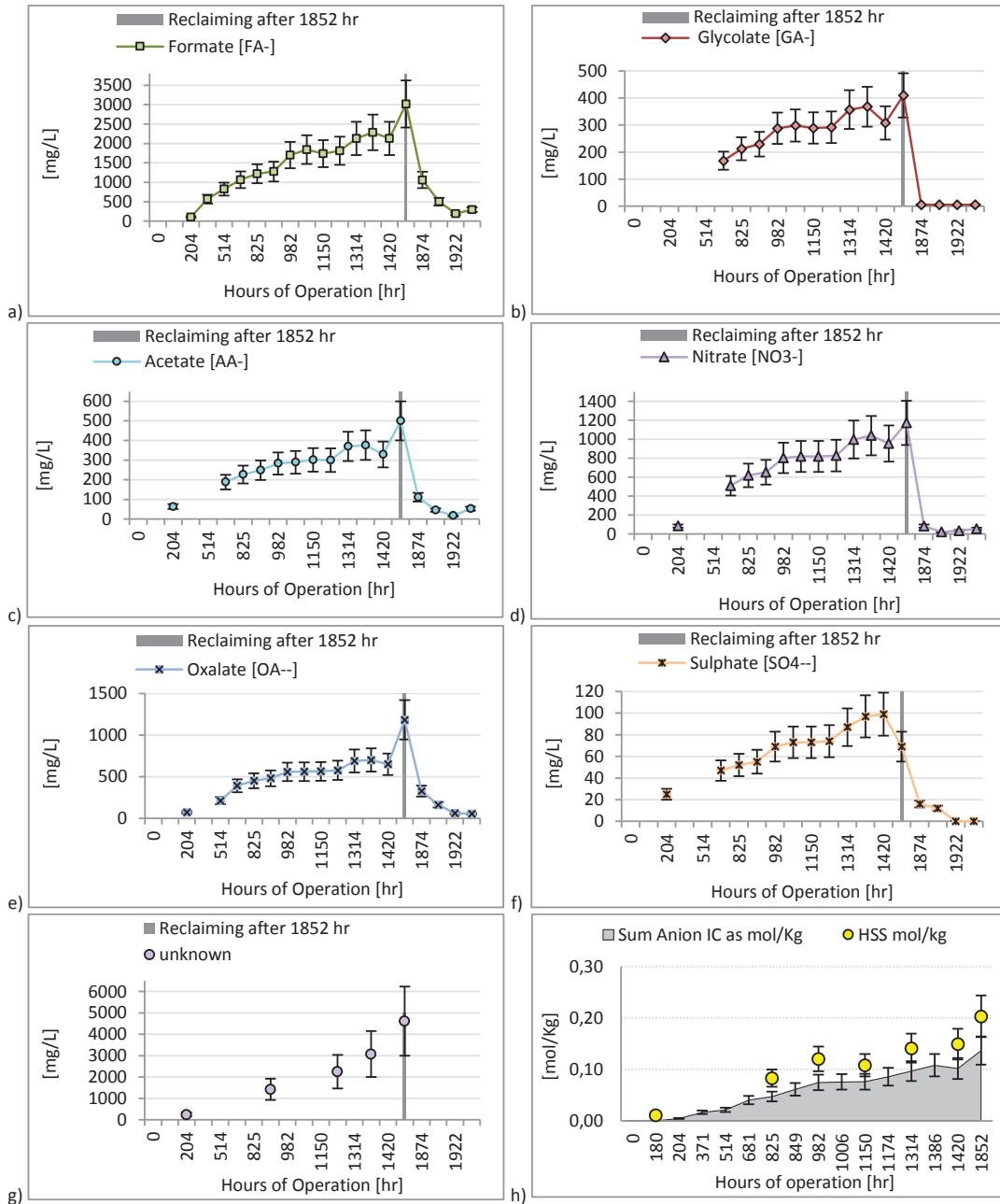


Figure 6. (a) Formate concentration, mg/L; (b) Glycolate concentration, mg/L; (c) Acetate concentration, mg/L; (d) Nitrate concentration, mg/L; (e) Oxalate concentration, mg/L; (f) Sulphate concentration, mg/L (g) unknown component, mg/L; (h) Total HSS and sum anions presented as mole/kg

Propionate ($C_2H_5COO^-$) and nitrite (NO_2^-) were not detected above 10 mg/L which is the limit of detection on the Ion Chromatograph.

4.2. Degradation products in the solvent

A simplified scheme for MEA degradation is proposed in figure 7. Oxidation reactions lead to formation of the organic acids and the emission products ammonia and aldehydes. This is indicated in the left blue square of the figure. Reactions between MEA and the organic acids, CO₂ and additional free MEA lead to formation of the degradation products identified in the lean solvent samples. This is indicated in the large red square of the figure. A nitrogen mass balance based on solvent analysis are presented and compared to literature data in section 4.5 below.

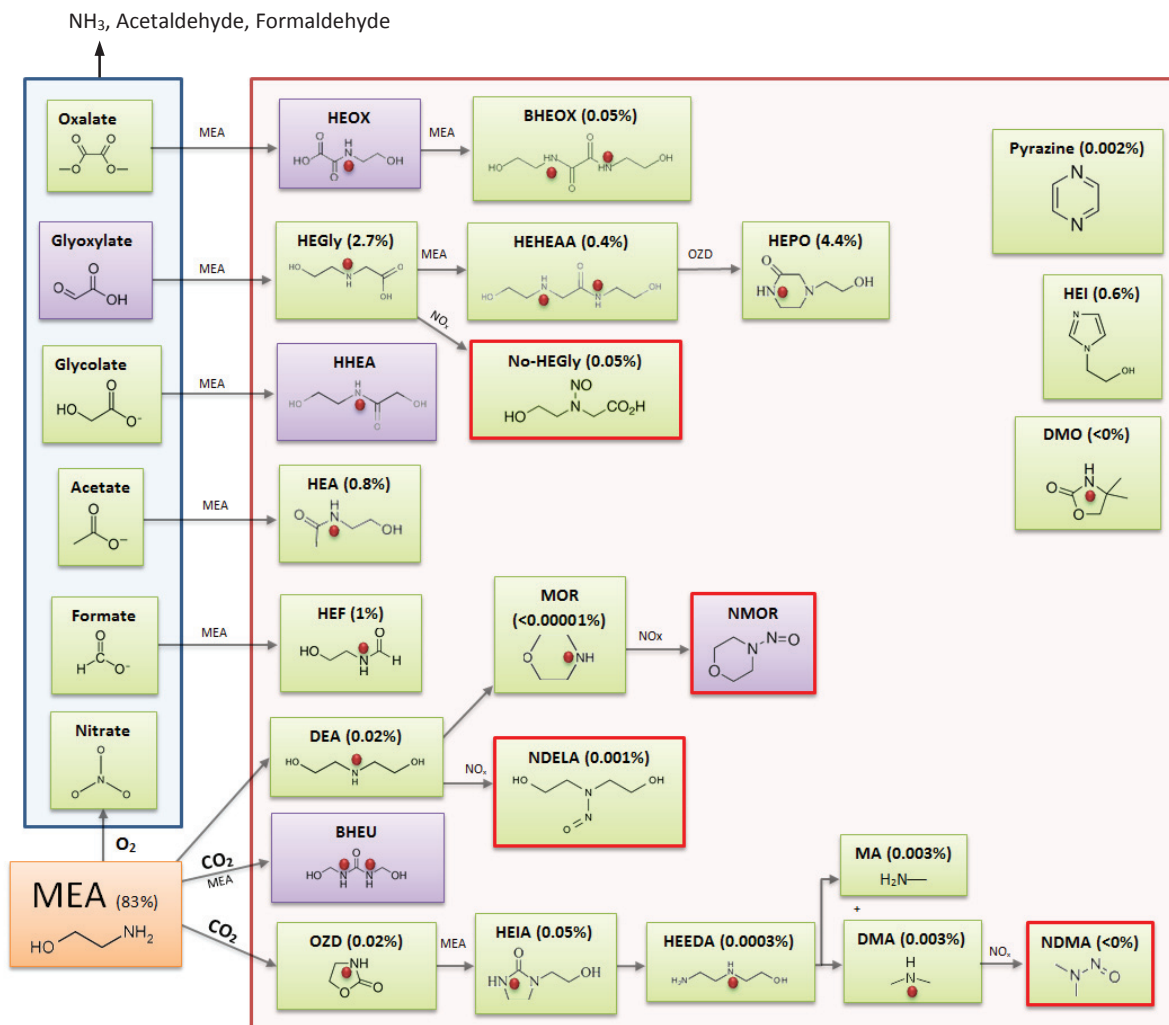
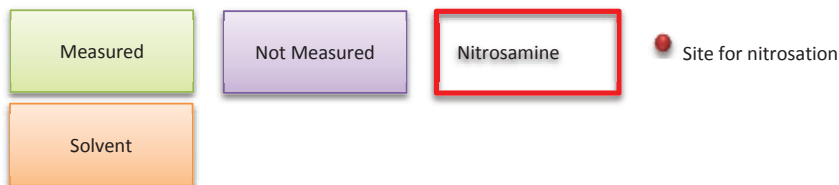


Figure 7. Proposed overall degradation scheme for monoethanolamine. Scheme is simplified and intermediate amine compounds may form.



The rate of formation of the degradation products is a function of temperature (faster kinetics), CO₂ loading (more carbamate present), and MEA concentration. The identified degradation products in the solvent samples and the accumulation of these as function of operational hours are shown in figure 8. TCM performed a MIST test after 1314 hours of operation and also did a CO₂ recycling test with higher CO₂ content in the CHP flue gas [12]. The results shown after 1314 hours are not consistent with the other samples and cannot be explained. Results from the reclaiming part of the 2015 MEA campaign is given in [13].

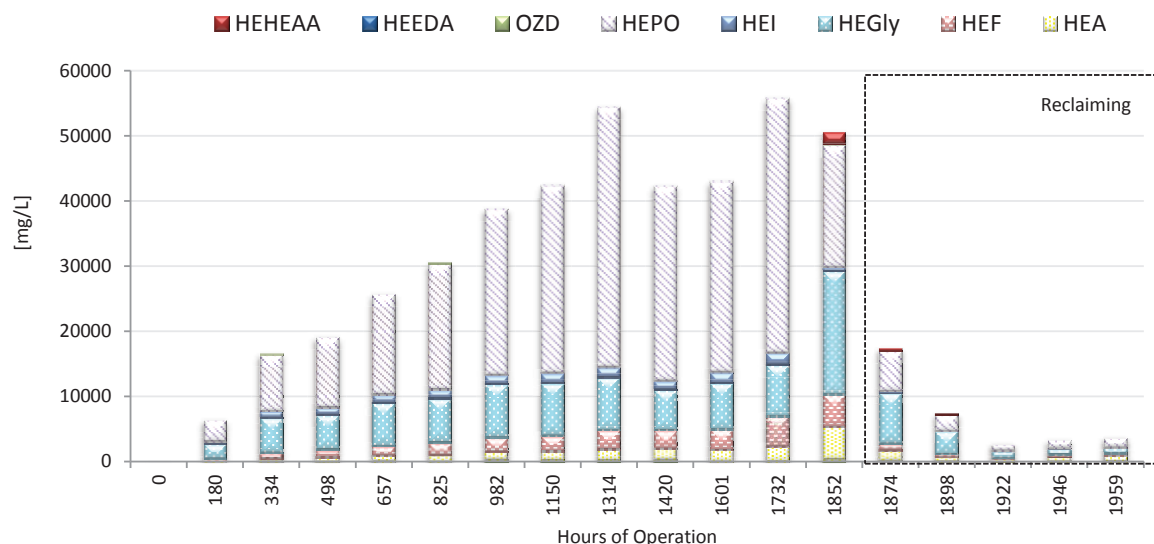


Figure 8. Main degradation products during the entire campaign. The component names and abbreviation is given in table 5 above.

It is seen that the dominant degradation products in the solvent are N-(2-hydroxyethyl)glycine (HeGly) and 4-(2-hydroxyethyl)piperazine-2-one (HEPO). This corresponds to the oxidation pathway via glyoxylate and subsequent reaction with MEA given in figure 7. The identification of the nitroso-compound nitroso-HeGly (No-HeGly) in the solvent further confirms this degradation route.

4.3. Nitroso- and Nitramines in solvent

Two solvent specific nitrosamines, N-nitrosodiethanolamine (NDELA) and N-nitroso-2-hydroxyethyl-glycine (Nitroso-HeGly), were detected in the solvent as the degradation process progressed. The total concentrations of nitrosamines (TONO) were measured to be 2351 $\mu\text{mol/L}$ after 1850 hours of operation, see figure 9. Since MEA is a primary amine it is not expected to form a stable nitrosamine. The identified compounds are thus formed from secondary amines occurring as impurities in the solvent or being formed during the degradation reactions. As is shown in Figure 9 a), there are still some unidentified nitrosamines in the degraded solvent sample. These nitrosamines are formed from high molecular weight amines and have low volatility. Figure 9 b) shows a decrease in the level of total nitrosamines after reclaiming of the solvent.

Nitrosamines are formed after reaction with NO_x in the flue gas [8]. During the MIST test, RFCC flue gas was used, and as this flue gas contains more NO_x than flue gas from the Combined Heat and Power Plant, this could explain the higher amount of nitrosamines in this MEA2 campaign compared with the first MEA1 campaign from TCM [1].

The solvent specific nitramine (MEA-NO₂) was detected at a concentration of approximately 4 mg/L after 1850 hours of operation. Methyl nitramine (MA-NO₂) and Dimethyl nitramine (DMA-NO₂) were also analyzed, but the responses on the LC MS QQQ were below the limit of detection (< 0.1 mg/L).

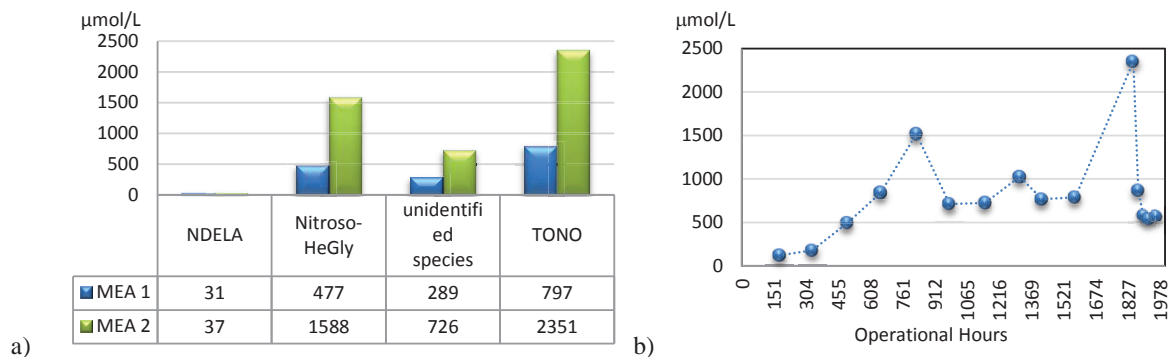


Figure 9. a) Nitrosamines in Lean MEA after 1850 operational hours. Results from the first MEA campaign (MEA 1) and this campaign (MEA 2) b) TONO measurements through the entire campaign

4.4. Nitrogen mass balance of the solvent

A nitrogen balance of the solvent was done after 1850 hours of operation, just before reclaiming, see table 6.

Table 6. A nitrogen mass balance of the solvent was done after 1850 operational hours

| Component | mg/L | mg/Kg | tot Kg | mole N | $\mu\text{mole/L}$ | % |
|------------------------------|--------|--------------|--------|---------------|--------------------|------------|
| MEA | 326473 | | 11263 | 184403 | | 82.7 |
| BHEOX | 274 | | 9.4 | 107 | | 0.048 |
| HEA | 4963 | | 171 | 1660 | | 0.74 |
| HEF | 5062 | | 175 | 1960 | | 0.88 |
| HEGly | 18922 | | 653 | 5480 | | 2.46 |
| HEI | 1826 | | 63 | 1124 | | 0.50 |
| HEPO | 18788 | | 648 | 8997 | | 4.04 |
| OZD | 82 | | 2.8 | 32 | | 0.015 |
| HEIA | 181 | | 6.3 | 96 | | 0.043 |
| HEEDA | 1.0 | | 0.03 | 0.7 | | 0.00031 |
| HEHEAA | 1870 | | 65 | 795 | | 0.36 |
| 4.4-DMO | <1 | | <0.1 | <1 | | <0.0004 |
| Morpholine | <1 | | <0.1 | <1 | | <0.0004 |
| Bicine | 62 | | 2.1 | 13 | | 0.0059 |
| Pyrazine | 8.0 | | 0.3 | 3.4 | | 0.0015 |
| DEA | 152 | | 5.3 | 50 | | 0.022 |
| DMA | 7.1 | | 0.2 | 5.5 | | 0.0024 |
| DiEA | 0.3 | | 0.01 | 0.14 | | 0.00006 |
| MA | 5.7 | | 0.2 | 6.3 | | 0.0028 |
| EA | 0.2 | | 0.005 | 0.12 | | 0.00005 |
| Formamid | 11 | | 0.4 | 8.2 | | 0.0037 |
| Acetamid | 12 | | 0.4 | 7.0 | | 0.0031 |
| NDELA* | 4.9 | | 0.2 | 2.5 | | 0.0011 |
| No-HEGly* | 235 | | 8.1 | 110 | | 0.049 |
| TONO | 306 | | 11 | 162 | 2351 | 0.073 |
| MEA-NO ₂ | 4.0 | | 0.1 | 2.6 | | 0.0012 |
| NO ₃ ⁻ | 1173 | | 40 | 653 | | 0.29 |
| Sum Identified components | | | 13116 | 205567 | | 92.2 |
| Unidentified | | | | 17397 | | 7.80 |
| Tot N | | 83000 | | 222964 | | 100 |

*NDELA and No-HeGly are included in the TONO results, and hence not summarized

Total Nitrogen in lean amine was measured to be 8.3 wt%, which give a total of 222964 mole N. The sum of the different degradation products found gives a total of 205567 moles. This gives 7.8 mole% of nitrogen that is not found by analysis, these components are hereafter called unidentified components. Some of the unidentified components are assumed to be long chain molecules. Dissolved ammonium and ammonia in the solvent were not measured; this means that they will presumably have some contribution to the amount of the unidentified components. Table 6 shows an overview of all the components that were analyzed, and the contributions of each component to the total amount of nitrogen.

4.5. Solvent loss

Excluding plant leakage, MEA loss can occur in the following ways:

- MEA emitted via Absorber (after water wash section)
- MEA emitted via stripper upper product after the condenser
- MEA degraded product via NH_3 formation, which is detected after the wash section and from the CO_2 -product stream
- Liquid sampling, which was taken for analysis
- Unexpected loss due to leakage through joints and pumps
- Wash water (absorber, stripper)
- Reclaimer waste

Lab samples and reclaimer waste are a part of the total inventory calculation. MEA was charged into the amine makeup tank from trucks. From the amine make up tank, MEA can either be charged into the storage tank or directly to the process loop. A total of 30088 Kg of pure MEA was filled into the makeup tank, while a total of 23208 Kg of MEA was discharged from the plant after the end of campaign. This gave a total loss of 7622 Kg pure MEA. Total CO_2 capture in the campaign was 4941 ton, and this give a loss of 1.5 kg MEA/ton CO_2 captured.

A nitrogen mass balance of the total solvent system was also done. The accumulated NH_3 emission from the absorber and stripper corresponds to approximately 67% of the total MEA loss, while the nitrogen detected identified degradation compounds (D-mix) constitutes approximately 16% of the MEA loss. Table 7 gives a short summary of the degraded product produced per mole amine lost. These results are similar to the results reported by IEAGHG [11]. Total Nitrogen analysis was performed, and it is reasonable to assume that long-chain degradation compounds constitute some amount of the unidentified loss.

The nitrogen mass balance for the entire campaign gives a loss of MEA that corresponds to 1.6 kg MEA/ton CO_2 captured. There is a small gap between the two different methods of calculation, and average value is used. From this MEA 2 campaign it is concluded that the loss of solvent was 1.6 ± 0.1 kg/ton CO_2 captured.

Table 7. Stoichiometry of Products Produced per Mole of Degraded Amine

| Product | Mole produced/mole amine lost | Mole produced/mole amine lost ^{a)} |
|-----------------------|-------------------------------|---|
| Ammonia | 0.67 | 0.67 |
| Total formate + HEF | 0.03 | 0.12 |
| Oxalate + oxylamide | 0.003 ^{b)} | 0.01 |
| Nitrate | 0.005 | 0.01 |
| HEI | 0.01 | 0.06 |
| HeGly | 0.04 | 0.05 |
| HEHEAA + HeGly + HEPO | 0.12 | - |

^{a)} Reported values from IEAGHG "Evaluation of reclaimer sludge disposal from post-combustion CO_2 capture", 2015/02, March 2014 [11]

^{b)} Oxylamide was not analyzed

5. Emissions of amines and amine based degradation products

5.1. Analysis of emission from depleted flue gas

Emission to Air from TCM DA amine plant has two sources, the amine absorber and the CO₂-stack. At TCM the CO₂ product stream is sent into the atmosphere, which will not be the case for a full-scale CO₂ capture plant. As the contribution from this stream is small considered to the absorber (1-3%), data from this stream is not given in this paper.

TCM DA applies different measurement techniques to monitor and quantify the amounts and concentrations of emitted compounds. A description of the TCM DA overall system for emission control and monitoring is given elsewhere [1]. The emission was followed up by FTIR, PTR-TOF-MS, PTR-QMS, isokinetic sampling and by 3rd party (FORCE Technology) [9].

MEA emissions are highly related to aerosols in the flue gas [6]. Even at low mass concentrations of aerosols, increased MEA emissions have been measured and reported. In September 2015 TCM investigated the relation between flue gas particle content, mainly related to sulphuric acid mist particles and dust, and corresponding MEA amine emissions. This “MIST test” was based on aerosol number concentration and size distribution, to evaluate the maximum aerosol number concentration acceptable for operation with a solvent based on MEA [6]. TCM received a temporary emission permit given for this campaign from the Norwegian environmental agency (NEA). The temporary permit gave allowance to increase MEA emission from 6 ppmV to 500 ppmV for maximum 4 days of testing.

The Mist test was a planned temporary campaign lasting for only two weeks. The rest of the MEA campaign were performed without issues regarding mist, impurities and aerosols, as flue gas from the combined heat and power plant does not contain particles and impurities. Detailed information about all the test activities and performance from the MEA campaign can be found in Gjernes et al [12].

Figures 10 - 13 provide the daily average ammonia, MEA, acetaldehyde and formaldehyde emissions and operational hours throughout the campaign. Some daily averages of ammonia emissions indicate higher emissions than allowed in the TCM DA emission permit. Any such emission peaks were communicated to the NEA. These incidents were administratively handled by NEA, and the campaign continued as planned. These higher levels were due to amine plant start-up activities, where molecular ammonia (or other amine compounds), i.e. ammonia (or other amine compounds) are unreacted with CO₂, are by convection transferred by the flue gas through the absorber and eventually emitted to atmosphere. The emissions follow a Gaussian like trend, i.e. an emission peak is observed until the emission levels settles at a lower steady state level. Test activities with increased CO₂-content in the flue gas combined with high temperatures in the solvent, water washes and flue gas, gave high ammonia emissions.

A start-up procedure conducted in the following order will reduce such start-up emission peaks;

- MEA solvent circulation starts at ambient temperatures
- Flue gas is introduced and the CO₂ loading process of the entire MEA solvent inventory occurs at ambient temperatures, until CO₂ in the MEA solvent are in equilibrium with CO₂ in the incoming flue gas ($\alpha =$ close to 0.5 mole CO₂ / mole MEA in the case of the CHP flue gas)
- Heat is applied to the stripper section in order start the continuous CO₂ removal process

By following the aforementioned start-up order, the amount of emitted molecular ammonia and amine compounds are decreased as the presence of these compounds in the gas phase inside the absorber is reduced, and hence less gaseous ammonia and amine compounds are transferred through the absorber by convection. 19th of May 2016, TCM received a new permanent emission permit from NEA allowing 100 ppmV ammonia emissions as a daily average.

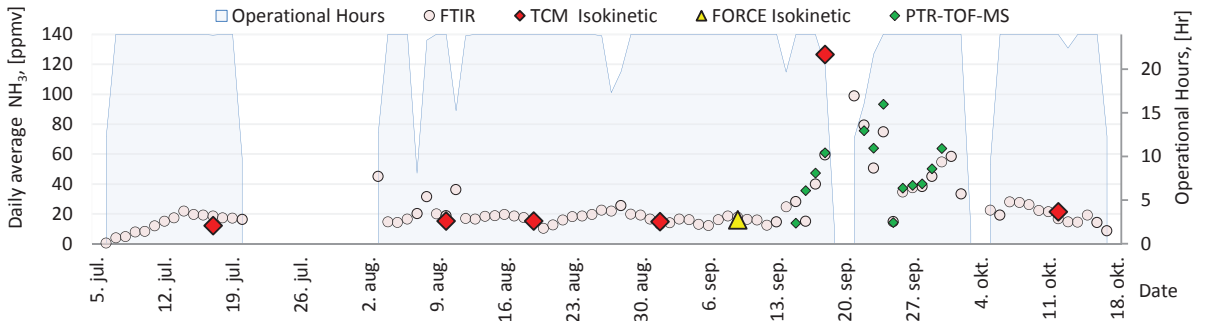


Figure 10. Daily average Ammonia (NH₃) ppmV emission from absorber measured by online FTIR, PTR-TOF-MS and isokinetic sampling, (isokinetic sampling is for a 2 hour period)

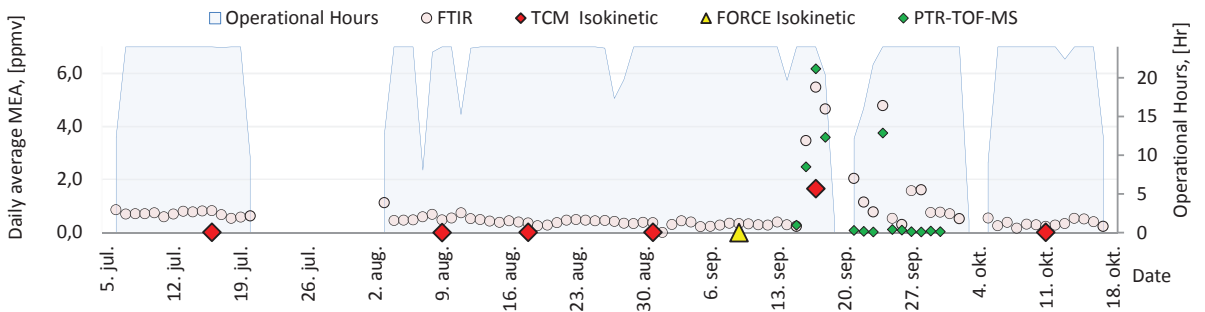


Figure 11. Daily average Monoethanolamine (MEA) ppmV emission from absorber measured by online FTIR, PTR-TOF-MS and isokinetic sampling, (isokinetic sampling is for a 2 hour period)

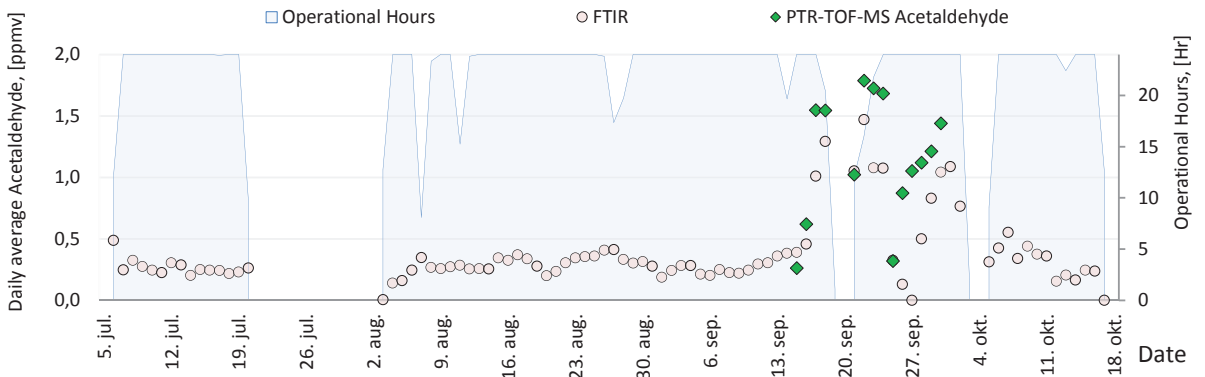


Figure 12. Daily average Acetaldehyde ppmV emission from absorber measured by online FTIR and PTR-TOF-MS

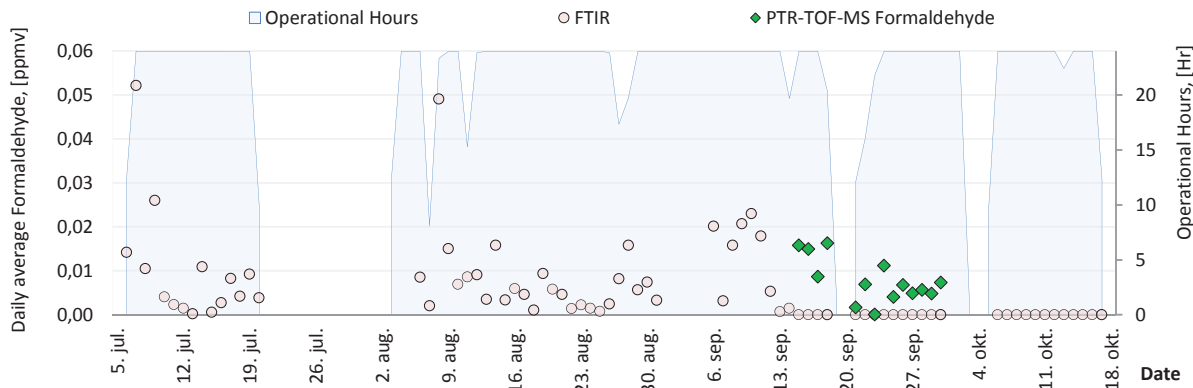


Figure 13. Daily average Formaldehyde ppmV emission from absorber measured by online FTIR and PTR-TOF-MS

For achieving the TCM objectives, it is important that variables are measured with high degree of accuracy. This will ensure that high quality data are obtained and thus a high quality of test results can be provided. This is significant not only for technology test reports but also for emissions reporting to the Norwegian Environmental Agency (NEA). A failure to estimate the inaccuracies of measurements will complicate the test planning, reporting to NEA and operation and maintenance of the test facility. Apart from accuracies of different variables, repeatability or precision of measurements for each of the variables on different streams also needs to be estimated. One quality assurance (QA) test is to compare different monitoring techniques. This was done during the MIST test, and depleted flue gas out of the absorber was measured by four different independent measurements; two FTIR's, PTR-TOF-MS and PTR-QMS. All the different measurement techniques showed very similar results. The result of this QA is shown in figure 14 and 15. TCM is a demo-plant where many types of online emission measurement equipment are tested, providing useful information for commercial projects.

Seven emission isokinetic sampling campaigns have been carried out in order to follow up on emissions form the absorber. Results from these measurements can be found in table 8. Overall the results are similar to the results reported by Morken et al [1].

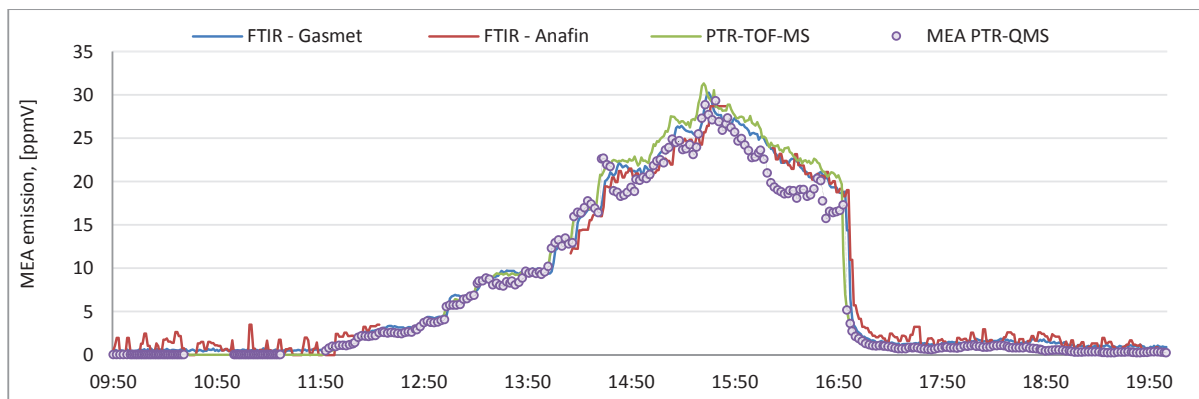


Figure 14. Simultaneously online measurement of MEA emission from amine absorber 16th of September 2015. The online equipment's are two independent FTIR's, PTR-TOF-MS and PTR-QMS.

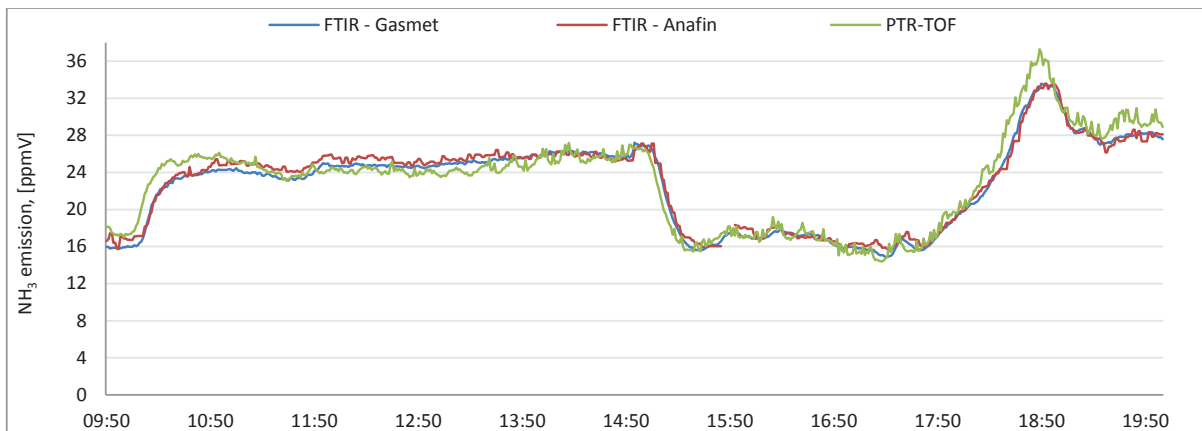


Figure 15. Simultaneously online measurement of ammonia (NH₃) emission from amine absorber 16th of September 2015. The online equipment's are two independent FTIR's and PTR-TOF-MS.

TCM has shown earlier that the absorber wash water sections are found to effectively reduce possible atmospheric emissions from amine based solvent system [1]. Atmospheric emissions of monoethanolamine (MEA) were very low throughout the entire campaign, and determined to be in the parts per billion (ppb) ranges.

Atmospheric emissions of MEA amine based degradation products such as nitrosamines and nitramines were below detectable levels. Atmospheric emissions of alkyl amines in the low ppb range. Results from isokinetic measurements can be seen in table 8. These results confirm the emission results from earlier MEA campaign at TCM [1].

Table 8. Result from isokinetic gas emission measurements from the entire MEA campaign

| Date | 17.07.2015 | 10.08.2015 | 19.08.2015 | 01.09.2015 | 09.09.2015* | 18.09.2015 | 12.10.2015 |
|-------------------------------------|------------|------------|------------|------------|-------------|------------|------------|
| MEA, µg/m ³ | 19.0 | 11.1 | 24.9 | 18.6 | 5.9 | 4281 | 18.5 |
| MEA, ppmv | 0.007 | 0.004 | 0.010 | 0.007 | - | 1.66 | 0.007 |
| DMA, µg/m ³ | 56.4 | 35.4 | 42.2 | 35.4 | 37 | 228 | 494 |
| DMA, ppmv | 0.030 | 0.019 | 0.023 | 0.019 | - | 0.120 | 0.255 |
| EA, µg/m ³ | 0.42 | 0.76 | 1.1 | 1.4 | 1.2 | 19.1 | 4.6 |
| EA, ppmv | 0.0002 | 0.0004 | 0.0006 | 0.0007 | - | 0.010 | 0.0024 |
| MA, µg/m ³ | 29 | 11.2 | 17.8 | 33 | 30 | 238 | 166 |
| MA, ppmv | 0.022 | 0.008 | 0.014 | 0.025 | - | 0.181 | 0.124 |
| DiEA, µg/m ³ | 0.025 | 0.065 | 0.062 | 0.032 | 9.7 | 0.428 | <0.007 |
| DiEA, ppmv | 0.00001 | 0.00002 | 0.00002 | 0.00001 | - | 0.00014 | <0.000002 |
| EMA, µg/m ³ | 0.39 | 0.37 | 0.34 | 0.24 | <0.8 | 2.2 | 3.0 |
| EMA, ppmv | 0.0002 | 0.0001 | 0.0001 | 0.0001 | - | 0.0009 | 0.0012 |
| PA, µg/m ³ | 0.34 | 0.22 | 0.17 | 0.11 | <0.8 | 1.3 | 1.1 |
| PA, ppmv | 0.00013 | 0.00009 | 0.00007 | 0.00004 | - | 0.00053 | 0.00041 |
| NH ₃ , µg/m ³ | 9335 | 11667 | 11467 | 11370 | 13000 | 96329 | 16571 |
| NH ₃ , ppmv | 12.3 | 15.3 | 15.4 | 14.9 | 16 | 126.5 | 21.4 |

*Third party measurements done by FORCE Technology [9]. All other sampling and measurements are done by TCM.

Conclusions

During the MEA 2015 campaign at TCM the degradation products being formed in the solvent and released to the atmosphere were closely monitored. Based on an overall nitrogen mass balance it was concluded that less than 8% of total nitrogen introduced into the plant was not identified. The solvent loss calculated as pure MEA was 1.6 ± 0.1 kg/ton CO₂ captured. The major contributors to the loss were ammonia emission (67% of loss) and identified degradation products in the solvent (16% of loss). Emissions to air from the absorber stack were monitored by five different independent on-line measurement instruments and by regular manual sampling. The four on-line methods provided very similar results. The manual sampling results confirmed results from earlier MEA campaign at TCM. The MEA and alkyl amines emissions are in the parts per billion ranges and nitrosamines and nitramines were below detectable levels.

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