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06

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CO₂ capture with monoethanolamine: Solvent management and environmental impacts during long term operation at the Technology Centre Mongstad (TCM)



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ABSTRACT

The owners of the Technology Centre Mongstad (TCM DA) started a monoethanolamine (MEA) test campaign in June 2017. The main objective was to produce knowledge and information that can be used to reduce the cost as well as technical, environmental and financial risks of commercial scale deployment of post-combustion capture (PCC). The campaign covered experimental activities in the amine plant from the 12th of June 2017 until the 30th of July 2018. A wide range of operating conditions were applied, thus giving a unique opportunity to study the impacts on the solvent quality, degradation behavior, corrosion tendency and emissions to the atmosphere. The current work describes how solvent quality and low emissions to atmosphere can be maintained during long-term operation by appropriate solvent management.

For futher information: https://www.sciencedirect.com/science/article/abs/pii/S1750583618307576?via%3Dihub

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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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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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Keywords: Monoethanolamine, MEA, Amine, Emission, Degradation, CO2-capture

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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 CO_2 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 CO_2 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 nonproprietary 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.



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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 CO_2 and O_2 concentrations, as well as NOx, SOx and particles. Solvent amines react with the flue gas components and give rise

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to the degradation products as illustrated in figure 3. Degradation reactions of MEA and specific degradation products that where 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 chemiluminscence 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 path length Resolution Flow rate Range LOD SD	Cell 180°C 5 m 8 cm ⁻¹ 120 – 600 L/h 900 – 4200 cm ⁻¹ 0.5 - 1 ppmv * *	Cell 85°C 7 m 2 cm ⁻¹ 100 L/h 500 – 7000 cm ⁻¹ 0.5 -1 ppmv * *	Drift tube 100°C - (Δ (m/z))/((m/z)) > 3000 30 L/h 10-200 0.0001 ppmv ± 20 %	Drift tube 100°C - Δ (m/z) = 1 30 L/h 20-200 0.001 ppmv \pm 20 %
Inlet Flue Gas		х		
CO ₂ -stack	Х		x**	
Absorber	х	x**	Х	х

*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

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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 O_2 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 CO_2 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 CO_2 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.

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	$(C_2H_5COO^{-})$	72-03-7	73

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

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).

$$MEA + RCOOH \rightarrow MEAH^{+} + RCOO^{-}$$

(1)

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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	х	х	х
Ammonia	NH ₃	7664-41-7	17	х	х	
Formaldehyde	FA	50-00-0	30	х	х	
Acetaldehyde	AA	75-07-0	44	х	х	х
N-Nitroso-diethanol-amine	NDELA	1116-54-7	134	х	х	
N-(2-hydroxyethyl) acetamide	HEA	142-26-7	103	х		
1-hydroxyethane 1,1-diphosphonic acid	HEDP	2809-21-4	206	х		
N-(2-hydroxyethyl)ethylenediamine	HEEDA	111-41-1	104	х		
N-(2-hydroxyethyl)formamide	HEF	693-06-1	89	х		
N-(2-hydroxyethyl)glycine	HeGly	5835-28-9	119	х		
N-(2-hydroxyethyl)-2-(2- hydroxyethylamino)acetamide	HEHEAA	144236-39-5	162	х		
Pyrazine	-	290-37-9	80	х	х	
N-(2-hydroxyethyl)imidazole	HEI	1615-14-1	112	х		
N-(2-hydroxyethyl)imidazolidinone	HEIA	3699-54-5	130	х		
4-(2-hydroxyethyl)piperazin-2-one	HEPO	23936-04-1	144	х		
Dimetylamine	DMA	124-40-3	45	х	х	х
Methylamine (Monometylamine)	MA (MMA)	74-89-5	31	х	х	х
Ethylamine	EA	75-04-7	45	х	х	х
Diethylamine	DiEA	109-89-7	73	х	х	х
Morpholine	Mor	110-91-8	87	х	х	
Trimethylamine	TMA	75-50-3	59	х	х	х
4,4-dimethyl-2-oxazolidinone	4.4-DMO	26654-39-7	115	х	х	
N-Nitroso(2-hydroxyethyl)glycine	NO-HeGly	80556-89-4	148	х	х	
2-(Nitroamino)ethanol	NO2-MEA	74386-82-6	106	х	х	
N-methyl,N-nitroso-methanamine	NDMA	62-75-9	74	х	х	
N-nitro-N-methyl-methanamine	DMNA	4164-28-7	90	х	х	
N-Nitrosomethylethylamine	NMEA	10595-95-6	88	х	х	
N-Nitrosodiethylamine	NDEA	55-18-5	102	х	х	
N-Nitrosodi-n-propylamine	NDPA	621-64-7	130	х	х	
N-Nitrosodi-n-butylamine	NDBA	924-16-3	158	х	х	
N-Nitrosopyrrolidine	NPYR	930-55-2	100	х	х	
N-Nitrosopiperidine	NPIP	100-75-4	114	х	х	
N-nitrosodiethanolamine	NDELA	1116-54-7	134	х	х	
2-Oxazolidone	OZD	497-25-6	87	х	х	
Alkylpyrazine	-				х	
NN'-Bis(2-hydroxyethyl)oxamide	BHEOX	1871-89-2	176	х	х	
Diethanolamine	DEA	111-42-2	105	х	Х	

4. Results and discussions

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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



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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

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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 µmol/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 NOx in the flue gas [8]. During the MIST test, RFCC flue gas was used, and as this flue gas contains more NOx 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. Methylnitramine (MA-NO₂) and Dimethylnitramine (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.

Component	mg/L	mg/Kg	tot Kg	mole N	µmole/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

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

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

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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 NH₃ formation, which is detected after the wash section and from the CO₂product 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.

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 CO₂ capture", 2015/02, March 2014 [11]

^{b)} Oxylamide was not analyzed

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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 CO_2 -stack. At TCM the CO_2 product stream is sent into the atmosphere, which will not be the case for a full-scale CO_2 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 (α = 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.



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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



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].

Date	17.07.2015	10.08.2015	19.08.2015	01.09.2015	09.09.2015*	18.09.2015	12.10.2015
MEA, $\mu g/m^3$	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, $\mu g/m^3$	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, $\mu g/m^3$	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, $\mu g/m^3$	29	11.2	17.8	33	30	238	166
MA, ppmv	0.022	0.008	0.014	0.025	-	0.181	0.124
DiEA, $\mu g/m^3$	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, $\mu g/m^3$	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, $\mu g/m^3$	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
$NH_3, \mu g/m^3$	9335	11667	11467	11370	13000	96329	16571
NH ₃ , ppmv	12.3	15.3	15.4	14.9	16	126.5	21.4

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

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

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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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References

- [1] Morken AK, Nenseter B, Pedersen S, Chhaganlal M, Feste J, Tyborgnes RB, Ullestad Ø, Ulvatn H, Zhu L, Mikoviny T, Wisthaler A, Cents T, Bade OM, Knudsen J, De Koeijer G, Falk-Pedersen O, Hamborg ES. Emission results of amine plant operations from MEA testing at the CO₂ Technology Centre Mongstad, Energy Procedia 63, 6023-6038.
- [2] Thimsen D, Maxson A, Smith V, Cents T, Falk-Pedersen O, Gorset O, Hamborg E S. Results from MEA testing at the CO₂ Technology Centre Mongstad. Part I: Post-Combustion CO₂ Capture Testing Methodology. Energy Procedia 2014.
- [3] Hamborg ES, Smith V, Cents T, Brigman N, Falk-Pedersen O, Chhaganlal M, Feste J K, Ullestad Ø, Ulvatn H, Gorset O, Askestad I, Gram L K, Fostås B F, Shah M I, Maxson A, Thimsen D. Results from MEA testing at the CO₂ Technology Centre Mongstad. Part II: Verification of baseline results. Energy Procedia 2014
- [4] Da Silva EF, Hoff KA, Booth A; Emissions from CO2 capture plants; an overview, Energy Procedia 37 (2013) 784-790
- [5] Lepaumier H, Picq D, Carrette P-L, New Amines for CO2 Capture. I. Mechanisms of Amine Degradation in the Presence of CO2, Ind. Eng. Chem. Res., 2009, 48 (20), pp 9061–9067
- [6] Lombardo G, Fostås BF, Shah MI, Morken AK, Hvidsten OA, Mertens J, Hamborg ES. Results from aerosol measurement in amine plant treating gas turbine and residue catalytic cracker flue gases at the CO₂ Technology Centre Mongstad. Energy Procedia (GHGT-13), Forthcoming 2017.
- [7] Vevelstad SJ, Eide-Haugmo I, Da Silva EF, Svendsen HF, Degradation of MEA; a theoretical study, Energy Procedia 4 (2011) 1608–1615
- [8] Fostås B, Gangstad A, Nenseter B, Pedersen S, Sjøvoll M, Sørensen AL, Effects of NOx in the flue gas degradation of MEA, Energy Procedia 4 (2011) 1566–1573
- [9] Faramarzi L, Thimsen D, Hume S, Maxson A, Watson G, Pedersen S, Gjernes E, Fostås BF, Lombardo G, Cents T, Morken AK, Shah MI, de Cazenove T, Hamborg ES. Results from MEA testing at the CO2 Technology Centre Mongstad: Verification of baseline results in 2015. Energy Procedia (GHGT-13), Forthcoming 2017.
- [10] Mikoviny T, Nielsen C.J, Tana W, Wisthaler A, Zhu L, Morken A.K, Nilsen T.N, Ambient Measurements of Amines by PTR-QiTOF: Instrument Performance Assessment and Results from Field Measurements in the Vicinity of TCM, Mongstad, Forthcoming 2017.
- [11] IEAGHG "Evaluation of reclaimer sludge disposal from post-combustion CO₂ capture", 2015/02, March 2014
- [12] Gjernes E, Pedersen S, Cents T, Watson G, Fostås BF, Shah MI, Lombardo G, Desvignes C, Flø NE, Morken AK, de Cazenove T, Faramarzi L, Hamborg ES. Results from 30 wt% MEA performance testing at the CO2 Technology Centre Mongstad. Energy Procedia (GHGT-13), Forthcoming 2017.
- [13] Flø NE, Faramarzi L, de Cazenove T, Hvidtsten OA, Morken AK, Hamborg ES, Vernstad K, Watson G, Pedersen S, Cents T, Fostås BF, Shah MI, Lombardo G, Gjernes E. Results from MEA degradation and reclaiming processes at the CO₂ Technology Centre Mongstad. Energy Procedia (GHGT-13), Forthcoming 2017.
- [14] Davis J, Rochelle G, Thermal degradation of monoethanolamine at stripper conditions, Energy Procedia 1 (2009) 327-333.

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Results from MEA Degradation and Reclaiming Processes at the CO₂ Technology Centre Mongstad

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Abstract

In 2015, the CO_2 Technology Center 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. As part of the test campaign, thermal reclaiming was performed in order to eliminate accumulated degradation products and improve the solvent performance. This paper presents results and discussions concerning formation and monitoring of amine degradation products along with experiences related to the thermal reclaiming process and its operational procedure. Evaluations of the efficiency of thermal reclaiming and the solvent improvement after reclaiming are also presented.

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Keywords: Thermal reclaiming; degradation monitoring; MEA reclamation; MEA degradation

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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, Shell 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 nonproprietary aqueous monoethanolamine (MEA) solvent at 30 wt%. After testing a variety of process conditions for a total of 1843 hours, clear evidence of solvent degradation was observed. The test campaign proceeded with thermal reclaiming of the solvent in order to eliminate accumulated degradation products and demonstrate improvement of solvent performance. This work presents results concerning MEA degradation monitoring and reclaiming operation at TCM DA. Various design and operational factors that affect degradation rates are discussed, the efficiency of thermal reclaiming is estimated and experiences related to the reclaiming process and its operational procedure is shared.

1.1. Solvent degradation mechanisms

Amine solvents degrade due to exposure to heat (thermal degradation), presence of oxygen (oxidative degradation) and reactions of the amine with flue gas contaminants such as SO_x , NO_x , halogenated compounds, hydrocarbons and other impurities. Thermal degradation occurs mainly in the stripper section and is strongly dependent on the stripper operating temperature. The main thermal degradation products in MEA are Oxazolidin-2-one (OZD), MEA urea, HEIA, HEEDA [1]. The rate of formation of these products depend on the operating temperature (faster kinetics), CO_2 loading (more carbamate present) and MEA concentration. Oxidative degradation is mainly an issue for post-combustion CO_2 capture where the solvent is exposed to oxygen present in the flue gas. This occurs mainly in the absorber, where the level of oxygen is significant. Amine oxidation is also shown to be catalyzed by transition metal ions and will typically results in formation of ammonia and different organic acids [2]. In a second step, the organic acids will form heat stable salts (HSS) which are difficult to regenerate under normal regeneration conditions (atmospheric pressure and temperature around 120°C) [1]. These salts will therefore remain and accumulate in the circulated solvent. Amine degradation may also be induced by flue gase contaminants such as sulfur, polysulfide and CO. This issue has become especially evident for oil refinery flue gases such as gas originating from RFCC units [2]. Nonvolatile contaminants causing amine degradation can also arise from other sources such as make-up water, anti-foam agents, lubricants and corrosion inhibitors [2].

Several degradation processes often occur simultaneously to produce a wide range of degradation products. Accumulation of amine degradation products affects the solvent properties. They are known to increase the solvent viscosity and surface tension which again affects heat transfer coefficients, diffusion coefficients, and mass transfer rates [3]. This will again lead to loss of solvent capacity and increased energy numbers. Further, degradation products might lead to corrosion, fouling and foaming [2], which again increases operational and maintenance costs and might cause long-term technical integrity issues. Dissolved metal elements originating from corrosion are also as mentioned above expected to contribute as catalysts for oxidative degradation [1].

1.2. Solvent refreshing options

In order to reduce the impact of unwanted impurities and minimize the operational and maintenance issues listed above, a number of techniques have been suggested. Wang et al. (2015) have published an extensive review of amine reclaiming technologies and other techniques to handle this issue, including purging (bleed and feed), neutralization, ion exchange, adsorption, electrodialysis, and different thermal reclamation techniques [4]. Dumée et al. (2012) also presents a thorough comparison of the most promising techniques [1]. A summary is provided below.

• Bleed and feed

Bleed and feed is a simple operational procedure where a portion of the degraded solvent is continuously or periodically purged and replaced with fresh solvent. However, amine replacement and disposal might make this technique rather costly, particularly for specialized and expensive solvents. Further, a certain level of degradation products needs to build up before effecting bleed and feed in order to minimize replacement and disposal costs.

Neutralization

Neutralization converts amine HSS to sodium or potassium HSS by addition of NaOH or KOH, according to the following reaction using NaOH as an example:

NaOH + [AmineH⁺ RCOO⁻] \rightarrow Amine + H₂O + [Na⁺ RCOO⁻] (1) Neutralization maintains the amine capacity; however, there is no reduction in salt content of the solvent. The amine becomes more and more contaminated by salts that contribute to higher solvent density and viscosity, reduced surface tension, and possibly foaming and fouling. Eventually, the solvent needs to be discarded.

• Ion exchange

Ion exchange is a technology where the amine HSS ion is replaced with a friendlier ion. For example, an anion exchange removes HSS anions, replacing them with hydroxide ions, which frees the amine and let it return together with water to the process. The HSS anions are later removed from the resin by regeneration with NaOH. The practice of removing HSS from amine systems by ion exchange has presented many technical and operational challenges, and several researchers report doubt in the practical efficiency for amine applications. High consumption of chemical and water for resin regeneration together with generation of large amounts of waste are mentioned as other disadvantages. Further, ion exchangers are not capable of removing uncharged contaminants, i.e. degradation products originating from thermal degradation. It is still regarded a relatively economical method, especially for low levels of contaminants. However, if poorly designed and/or operated it can cause significant solvent losses and sodium slippage into the main amine process.

Adsorption

Adsorption on activated carbon is a widely used method to remove high-boiling or surface active organic compounds [5]. However, activated carbon it is not able to remove significant amount of degradation products [2].

• Electrodialysis

Electrodialysis has also been suggested as a method to purify amine solutions. It uses a stack of alternating anionic and cationic ion-exchange membranes to selectively remove charged contaminants from the solvent [1]. The main disadvantage also for this method is inability to remove uncharged amine degradation products originating from thermal degradation and hydrocarbons [2].

• Thermal reclaiming

Thermal reclaiming is usually conducted on a small slipstream extracted from the stripper reboiler on a semicontinuous basis [2, 5]. The amine solution is vaporized in the reclaimer vessel and returned as vapour to the main process, while the less volatile degradation products and other contaminants accumulate in the reclaimer vessel bottoms. Stoichiometric addition of NaOH during thermal reclaiming allows recovery of the amine from the amine heat stable salts by conversion to sodium salts, according to Reaction (1). Thermal reclaiming has long been a recognized reclamation method for MEA. Compared with secondary and tertiary amines, MEA has a low normal boiling point allowing it to vaporize without degrading significantly. For other amines with higher boiling points vacuum might be required in order to prevent thermal degradation during reclaiming. The fact that MEA reclaiming units can be operated at the stripper pressure eliminates the need for a separate condenser for the reclaiming system and reduces the overall energy demand. In this approach the reclaimer product vapour which contains MEA is directly sent to the stripper [1, 5]. A major disadvantage of thermal reclaiming is the formation of an aqueous slurry waste whose disposal poses a challenge for the CO₂ capture process. The amount of waste depends on various parameters such as the flow rate of the slip stream fed to the reclaimer, the amount of basic solution used to liberate

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MEA from heat stable salts, solvent conditions and overall operating conditions of the plant. According to the International Energy Agency (IEA) about 3.2 kg of amine reclaimer waste is generated per ton of CO_2 captured from coal fired flue gases using MEA [3]. However, depending on gas pre-treatment, combustion fuel, the type of amine used and the capture process itself, the reclaimer waste generation can vary in the range of 0.1-14.9 kg waste/ ton CO_2 [3]. Collecting representative samples of reclaimer waste is complicated and so far there is limited information in the public domain that fully represents amine reclaiming waste for CO_2 capture processes. Using the Flour Econamine FGSM system as a reference, Nurrokhmah et al. (2013) have investigated methods to characterize MEA reclaiming waste along with possible waste treatment and reuse options. Thermal reclaiming is also mentioned to be energy extensive. However, alternative reclaiming technologies such as ion exchange and electrodialysis are not able to remove metals and non-ionic products and the potential efficiency of HSS removal is not as high as for thermal reclaiming [1].

Nomenclature	
СНР	Combined Heat and Power
DCC	Direct Contact Cooler
HSS	Heat Stable Salts
IBC	Intermediate Bulk Container
IEA	International Energy Agency
MEA	Monoethanolamine
MP	Medium Pressure
RFCC	Residue Fluidized Catalytic Cracker
SRD	Specific Reboiler Duty
TCM	CO ₂ Technology Centre Mongstad

2. The TCM DA amine plant

An illustration of the TCM DA amine test unit is presented in Figure 1, and a short description is given in the following. Flue gas is cooled down and saturated with water in a direct contact cooler (DCC) before it enters the absorber. At TCM DA there are two possible sources of flue gas, i.e. exhaust gas originating from the natural gas fired combined heat and power plant and industry gas originating from the residue fluidized catalytic cracker. Both flue gas sources have their individual flue gas fans and DCCs as illustrated in Figure 1. Product CO₂ can also be recirculated back to the CHP gas absorber inlet to adjust the CO₂ content. For RFCC gas there is an option of mixing in air to adjust the CO₂ content. The conditioned flue gas is contacted counter-currently with the amine solvent in the absorber tower. CO₂ from the flue gas is released to the atmosphere after passing two sections of water wash. Typical absorber conditions are close to ambient pressure and temperatures of 40 - 80 °C, depending on the CO₂ content in the incoming flue gas. The CO₂ rich solvent is pre-heated in the lean/rich cross heat exchanger before it enters the stripper column where the chemical reactions are reversed to desorb CO₂ and regenerate the solvent. Heat is provided through steam in a thermosiphon reboiler to maintain regeneration conditions, i.e. 100 - 120 °C and pressure around 1 barg. The product CO₂ is released to the atmosphere, while the regenerated lean solvent is pumped back to the absorber via the lean/rich cross heat exchanger and the lean cooler.

The TCM DA amine test unit is also equipped with a thermal reclaimer which treats a slip stream of the lean solvent coming from the stripper. The thermal reclaimer uses additional heat provided by steam to separate the useful solvent from the degradation products which are accumulated in the solvent over time. The reclaimer vapour contains useful solvent which is recycled back to the main process, while the waste remains in the reclaimer and is periodically discharged. Water and NaOH can be added to the reclaimer unit on demand. The operating pressure corresponds to the stripper pressure.

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The reclaiming system consists of a flash vessel and a steam heater, as illustrated in Figure 1. The dimensions of the reclaimer vessel is 2.3m x 3.0 m (IDxTT) and it is designed for an operating volume of 1 - 7 m³, which corresponds to approximately 2 - 14 % of the total solvent inventory of the plant.



Figure 1: Schematic illustration of the TCM DA amine plant

2.1. MEA campaign overview

The MEA test campaign was conducted from 06/07/2015 to 17/10/2015. During the total 1960 hours of operation a wide range of operational process conditions were executed and a total of 4941 tons of CO₂ was captured. The variation of gas and solvent flow rates and stripper bottom temperatures are presented in Figure 2, while further details on typical operating process conditions are presented in Table 1 of Gjernes et al. (2017) [7]. The test campaign was operating on 30 ± 2 wt% MEA and the ranges of the lean and rich CO₂ loadings during the campaign was 0.19 - 0.29 and 0.46 - 0.53 mol CO₂/mol MEA, respectively. The majority of the campaign was operated with CHP flue gas; however, for a shorter period of 9 days from 16/09/2015 to 24/09/2015 it was operated on a mixture of CHP and RFCC gas, as indicated in Figure 2. Thermal reclaiming was performed towards the end of the campaign, after 1838 hours of operation. Reclaiming was performed for 92 hours, and the plant was run for an additional 28 hours after the reclaiming period before the campaign was concluded 17/10/2015.



Figure 2: Overview of the daily gas and solvent flow rates and stripper temperatures during the MEA test campaign

3. Solvent degradation during the test campaign

3.1. Process conditions that influenced solvent degradation

The MEA test campaign was conducted by executing a wide range of process conditions with frequent operational set-point changes. Such a shifting operating environment might accelerate solvent degradation. The average stripper bottom temperature was 120 °C, with a maximum of 122.5 °C. Superheated MP steam in the temperature range of 130 - 150 °C was used as heat source in the stripper reboiler. The reboiler skin temperature for which the solvent is exposed to, can therefore be assumed to be around 130°C. The solvent will undergo thermal degradation when exposed to temperatures at this level.

The majority of the campaign was operated with CHP flue gas. However, as part of specific mist testing where the aim was to induce formation of aerosols and study its effect on emissions, the plant was operated on a mixture of CHP and RFCC gas [8]. The mist testing where more specifically conducted by;

- 1. Increasing the concentration of CO_2 in the feed flue gas up to 12 vol% by recycling parts of the captured CO_2 to the absorber flue gas inlet.
- 2. Mixing portions of the RFCC flue gas with the CHP flue gas.

Up to 10 % mixing of RFCC gas in CHP gas was tested. Typical CHP and RFCC gas concentrations downstream the DCCs are presented in Table 1. As seen in the table, the CHP flue gas contains significant amounts of oxygen which causes oxidative degradation. Exposure to higher concentrations of CO_2 and RFCC gas impurities during the mist testing accelerated the rate of solvent degradation. Further, metal particulate material present in the RFCC gas might have contributed as catalysts for oxidative degradation.

Description	Unit	Conditioned CHP gas	Conditioned RFCC gas
Temperature	°C	25 - 50	15 - 50 ⁽¹⁾
Pressure	mbar g	Up to 250	Up to 250
Nitrogen	mol %	73 - 79	73 - 79
Oxygen	mol %	13 - 14	3 - 8
CO ₂	mol %	3.5 - 4.0 (2)	13.0 - 14.5 ⁽³⁾
H_2O	mol %	Saturated	Saturated
SO_2	ppmv	< 0.3	<5
NO _x	ppmv	<5	60
NH ₃	ppmv	<5	<1
СО	ppmv		<3
Particulates	mg/Nm ³		(4)

Table 1: Typical CHP and RFCC flue gas conditions downstream DCC conditioning at TCM DA.

Note:

1. With steam injection.

2. Facility is provided to enable CO_2 recycling, thereby allowing tests with CO_2 concentrations up to about 15 vol%.

 Facility is provided to enable air dilution, thereby allowing tests with CO₂ concentrations down to about 2.5 vol %.

3.2. The impact of process design on solvent degradation

As mentioned above, the main factors causing solvent degradation was elevated operating temperature in the stripper section and exposure to oxygen and contaminants in the flue gas. The effect of thermal and oxidative degradation will not only depend on these factors themselves, but also on the solvent residence times in the sections of the plant where these factors are significant, i.e. the part of the plant where the solvent is exposed to higher temperatures and oxygen and gas contaminants.

The hot solvent inventory (desorber packing, desorber sump, reboiler, hot part of the lean/rich cross heat exchanger and the hot lean and rich solvent piping) calculated for CHP baseline operating conditions are presented in Table 2. For details about the CHP baseline operating conditions it is referred to Faramarzi et al. (2017) [9]. The total of 13.4 m³ hot solvent inventory is quite significant and corresponds to about 35% of the total solvent inventory. The corresponding solvent residence time is about 20 minutes for CHP baseline operating conditions. The main contributor to the hot solvent inventory is clearly the rather long hot lean solvent pipe, which contributes to 60% of the total hot solvent inventory. The reboiler itself has a rather low solvent residence time; however, the beforementioned reboiler skin temperature of about 130 °C might also contribute to significant thermal degradation as degradation increases exponentially with the temperature.

The solvent inventory exposed to oxygen and the corresponding oxygen exposure time is also presented in Table 2. It is expected that the largest effect of oxygen exposure is seen in the absorber packing, where the actual inventory and exposure time is estimated to about 8 m^3 and 12 minutes, respectively, considering CHP baseline operating conditions. This abovementioned exposure time is also relevant for flue gas contaminants when operating on CHP/RFCC gas mixture.

In order to minimize solvent degradation it is clearly of interest to perform plant design such that the exposure times to oxygen and elevated temperatures are limited. For scale-up purposes it is therefore of specific importance to minimize solvent hold-up in hot parts of the plant.

Continu of the ulant	Solv	ent inventory [m ³]	Exposure/residence time [min]	
Section of the plant	Exposed to oxygen	Exposed to temperature > 100°C	Oxygen	Temperature > 100°C
Absorber packing	7.8		11.5	
Absorber sump	9.0		13.3	
Desorber packing		0.9		1.3
Desorber sump		2.3		3.4
Reboiler		0.4		0.6
Lean/rich cross heat exchanger		0.5		0.7
Hot rich solvent piping		1.1		1.6
Hot lean solvent piping		8.2		12.1
Total	16.8	13.4	24.8	19.8

Table 2: Estimated solvent inventory and residence times for solvent exposed to oxygen and elevated temperatures based on CHP baseline
operating conditions (for details about the CHP baseline conditions it is referred to Faramarzi et al (2017) [9].

3.3. Monitoring of solvent degradation

Solvent degradation was observed and monitored by a number of parameters during the test campaign. Lean and rich solvent samples were frequently withdrawn for solvent analysis. The analytical methods are described by Morken et al (2017) [10]. Firstly the physical properties of the solvent changed during the campaign as shown by the increase of solvent viscosity in Figure 3. The viscosity was measured in TCM DA lab and reported at two different temperatures (30°C and 60°C) and a clear increase of about 50% is observed from the test campaign start until reclaiming started on 12/10/2015.



Figure 3: Change in solvent viscosity during the MEA test campaign

A clear observation of solvent degradation was also the change of solvent color during the test campaign. The fresh 30 wt% MEA solvent started out as a clear liquid, which changed color quite fast after contact with flue gas. The solvent became gradually darker during the campaign, until it reached the dark brown color illustrated by the third sample glass from 11/10/2015 in Figure 4.



Figure 4: Picture of solvent samples taken during the campaign. The color change indicates solvent degradation.

Further, the level of volatile degradation products in the gas phase increased significantly during the period of Mist testing. Morken et al (2017) presents detailed results regarding ammonia emissions, which is associated with presence of ammonia in the solvent originating from solvent degradation [10]. Emission of ammonia is also highly dependent on operating conditions; however the observed build-up of ammonia in the solvent is regarded as a clear sign of solvent degradation.

Heat stable salts started building up in the solvent as shown in Table 3 before it reached a maximum of 0.203 mol/kg just before reclaiming started on 12/10/15. More detailed results concerning HSS analysis are presented by Morken et al (2017) [10]. The concentration of main degradation products was also monitored continuously and shows a significant increase as the test campaign progressed. It is referred to Morken et al (2017) for details [10].

Concentration of heat stable salts (HSS) [mol/kg]
0.011
0.038
0.052
0.069
0.083
0.120
0.108
0.141
0.149
0.138
0.203

Table 3: Total concentration of heat stable salts (HSS) during the campaign.

Additional parameters which are important to monitor during operation of the amine plant are solvent foaming tendency and metal ion concentration. The latter gives indications of plant corrosion and was also monitored during the test campaign. The results are presented by Hjelmaas et al. (2017) [11].

4. Reclaiming procedure and operational experience.

The reclaimer was operated in a semi-continuous operation mode, meaning that solvent was continuously fed to the reclaimer vessel, while the reclaimer waste was allowed to accumulate and was only disposed at the end of the test campaign. The process was operated continuously for 3 days with exception of one unexpected plant stoppage for about 3 hours on the 13/10/2015.

The reclaimer vessel was initially filled with water. Water circulation and steam heating was started before the solvent feed to the reclaimer vessel. The rather large volume of initial water evaporated during the reclaiming operation and resulted in dilution of the solvent as shown in Figure 5.

The reclaimer liquid was circulated in the reclaiming system loop through the steam heat exchanger at a circulation rate of approximately 165 m³/h. No boiling occurs in the steam heater, but the liquid flashes when it enters the evaporator vessel. The evaporating level was controlled by adjusting the steam rate supply. As the liquid became more concentrated, its boiling temperature increased and the rate of evaporation was reduced. The percentage of degradation products in the reclaimer, and the resulting temperature were slowly increasing. Upon reaching high temperature, high viscosities and high amounts of precipitates, the reclaimer feed was stopped.





Figure 5: MEA concentration in the lean solvent during reclaiming

4.1. Solvent and water feed rate.

The reclamation unit was fed with a continuous slip stream of the lean amine solvent from downstream the stripper. The reclaimer was also fed simultaneously with water in order to control the boiling temperature of the reclaimer fluid below 160 °C. Figure 6 presents the solvent and water flow rates along with the reclaimer liquid temperature.

The solvent slip stream corresponded to 4 - 5 % of the lean solvent circulation and was up to a maximum of about 3 000 kg/h as illustrated in Figure 6. A total accumulated amount of 46 000 kg solvent was fed to the reclaimer during the whole period of 3 days. This corresponds to about 110 % of the total solvent inventory.

4.2. Steam consumption

The reclaimer heat duty variations were according to the changing amount of the lean solvent slip stream directed to the reclaimer vessel. As shown in Figure 7, in order to vaporize MEA in the reclaimer a significant amount of heat was required. At times, the amount of heat used for reclaiming was almost equal to the heat used to regenerate the solvent in the stripper. As reclamation of MEA is energy intensive, it is important to optimize the amount of lean amine slip stream sent to the reclamation unit. However, as shown in Figure 6 the flow of slip stream varied due to the fluctuations in the process conditions and it was not possible to achieve a constant flow during the reclaiming procedure.

The reboiler heat duty increased significantly when the reclaimer was brought on stream and then plateaued at about 2 500 kW. This was due to the large amount of water that was initially added to reclaimer unit, which evaporated from the reclaiming vessel and caused dilution of the solvent. The concentration of MEA was consequently reduced to about 21 wt% as shown in Figure 5. Thus the amount of water to be boiled off in the stripper was much larger, causing higher energy numbers.

The reclaimer liquid circulation and steam heating continued for 2 days after the solvent feed was stopped in order to evaporate as much as possible of the useful MEA solvent and concentrate the waste.







Figure 7: Steam consumption during reclaiming.

4.3. Dosage of NaOH

Aqueous solution of 50 wt% NaOH was added to the reclaimer vessel via the reclaimer liquid circulation loop in order to stabilize anions of amine heat stable salts by converting them to sodium salts and liberating the amine according to Reaction (1). The recovered amine and water vapor was returned to the stripper sump.

A dosage rate of 3 L NaOH/m³ solvent was applied during reclaiming based on previous experience at TCM DA. In total 227 liters 50% NaOH was added, which corresponds to 4299 mol Na⁺.

According to Reaction (1), the stoichiometric ratio of NaOH to HSS should ideally be 1:1. This is a very rough estimate since the actual ratio depends on the electrical charge of the anions. The concentration of HSS components was 0.203 mol MEA-eq/kg solvent at the point of reclaiming start 12.10.15 (see Table 3). With a total solvent inventory of 40 800 kg in the plant at the time, this corresponds to 8282 mol HSS. A stoichiometric check shows excess HSS compared to NaOH, which might cause additional MEA loss in the reclaimer waste.

4.4. Reclaimer waste

After the reclaiming operation was concluded the majority of the concentrated waste was drawn off to the flushing line and passed through the sea water cooler to the IBC (Intermediate Bulk Container) drainage system. The reclaimer fluid was quite concentrated and viscous at the time, thus some water was added in order to dilute the waste and enable unloading of the vessel. The total concentrated waste was collected in IBCs and added up to a total of about 6 m³. This corresponds to about 1.3 kg reclaimer waste/ton CO₂ captured during the overall campaign, which is well below reported numbers in the literature. Further, the reclaiming process was initiated when HSS concentration reached 0.203 mol/kg, as beforementioned. The actual necessity of reclaiming at this level of HSS must be considered based on the actual solvent condition and potential plant corrosion issues, i.e. at this moment the reclaiming campaign was not necessary but rather conducted for demonstration purposes in the test campaign. The waste/ton CO_2 capture would thus be even lower in an actual necessary reclaimer case. The reclaimer vessel and piping was afterwards flushed with water.

5. Efficiency of thermal reclaiming

In order to investigate the reclaiming efficiency and demonstrate how the solvent quality is recovered and maintained by the reclaiming process, samples were frequently taken from the lean amine solvent, the reclaimer liquid and reclaimer vapor. The samples were analyzed for MEA, degradation products, HSS and metals, and the results are summarized in Table 4.

The concentration of degradation products in lean amine was analyzed throughout the test campaign and the results are presented by Morken et al (2017) [10]. Figure 8 below shows the concentration of degradation products in the lean amine solvent during the reclaiming operation. It is seen that the degradation products is efficiently cleaned from the lean amine and about 95% percent of the degradation products was removed. A small increase in concentration from day three indicates that degradation is significant during reclaiming, likely due to thermal degradation due to operation at elevated temperatures inside the reclaimer vessel.



Figure 8: Concentration of degradation products (D-mix) in lean amine during reclaiming

A very similar trend is seen for the concentration of metal elements iron (Fe), Nickel (Ni) and Chromium (Cr) in Figure 9 below. The concentration is reduced by more than 95% after reclaiming.



Figure 9: Concentration of metal elements in lean amine during reclaiming

The trends for heat stable salts in the lean solvent, reclaimer liquid and the reclaimer vapor are shown in Figure 10. Again, the concentration of HSS in lean amine is rapidly reduced to less than 5% of the start concentration, as shown by the blue columns in the graph. The accumulation of HSS in the reclaimer liquid is also clearly seen by the

red columns. HSS could not be detected in the reclaimer vapor return to stripper, as expected. Figure 11 presents the concentration of MEA, NaOH and HSS in the reclaimer liquid during the reclaiming process. Most of the MEA is evaporated during the period as seen in the figure. HSS and Na^+ is accumulated, however MEA seems to be in excess, also at the end of the reclaiming.



Figure 10: Concentration of HSS in lean amine and the reclaimer liquid



Figure 11: Concentration of MEA, NaOH and HSS in the reclaimer liquid

The color of the solvent changed back to a lighter color after reclaiming as illustrated by the fifth sample glass from 15/10/2015 in Figure 4. Based on analysis of the reclaimer waste and assessment of the total MEA inventory in the plant before and after reclaiming, it is estimated that about 500-550 kg MEA was lost to waste during

reclaiming. This corresponds to 4% of the total inventory (according to Table 4) and 0.11 kg MEA/ton CO_2 captured.

		12.10.2015	17.10.2015	Removal
		Before reclaiming	After reclaiming	
Total solvent inventory	[kg]	40800	37600	
MEA	[kmol]	199	191	4 %
HSS	[mol]	8280	413	95 %
Degradation products	[kg]	1837	129	93 %
Metals	[g]	1133	56	95 %

Table 4: Amount of HSS, degradation products and metals removed from the solvent and MEA lost in reclaimer waste

6. Solvent performance after reclaiming

After the reclaiming operation had been concluded the plant was operated for another 28 hours at a flue gas flow rate of 47,000 Sm³/h. Two test cases were conducted during this period, and these are used for comparison to other similar tests conducted previously in the campaign with a fresh solvent. The two test cases after reclaiming is designated "T4" and "T5", while the optimum energy case with the use of anti-foam (case 2B6) from previously in the campaign is used for comparison. The total operating hours at the point in time when case 2B6 was conducted was approximately 950 hours. The overall 2015 MEA campaign and the entire specific test series carried out to investigate the capture plant performance is described by Gjernes et al. (2017) [7].

Figure 12 summarizes the operation before and after reclaiming. T4 and T5 were operated with 24 and 18 m absorber packing height, respectively. During T4 the amine plant was a bit unstable while there were stable conditions during T5. Case 2B6 was operated with 24 meters of packing height. The plant performance after reclaiming was comparable to the optimum performance achieved earlier in the campaign and there were no significant indications of reduced solvent quality.



Figure 12: Results for test cases 2B6, T4 and T5: To the left rich- (squares) and lean-loading (diamonds) and stripper bottom temperature (triangles) and to the right SRD (diamonds) and lean amine flow (squares).

7. Discussion and future work

Monitoring the amine concentration and CO_2 loading is very important for optimal operation. At TCM DA the solvent concentrations are mainly followed on a daily basis with manual samples and analysis. Further, a number of analyzers are available for real-time online monitoring, i.e. conductivity, density and pH analyzers. These online results can be correlated to enable a closer follow-up of the solvent condition.

As an effect of reclaiming start-up, the solvent in the main process was diluted by water evaporating from the reclaimer vessel. In future campaigns, extra care will be taken not to disrupt the main process during reclaiming. The deviation in solvent concentration could have been corrected at an earlier stage with an online estimate of solvent concentration.

The reclaiming environment is very harsh to the solvent due to high temperatures (up to 160 °C). The elevated temperatures represent a risk of additional thermal degradation. Care must therefore be taken in order to limit the residence time of the reclaimer solvent and thereby unnecessary degradation. Thus frequent manual solvent sampling or online analyses are required in order to monitor the progress of reclaiming and terminate the reclaiming process when the target is reached. In this test campaign it was very successfully demonstrated a 95 % cleaning efficiency when circulation a 4-5 % slip stream through the reclaimer for three days, which added up to an accumulated reclaimed volume of about 110% of the total solvent inventory.

The total HSS analysis indicates that the amount of NaOH added during reclaiming was on the stoichiometric low side to limit the MEA loss in the reclaimer waste. It is therefore reason to believe that additional MEA was lost in HSS to the waste. Thus, the total MEA loss of 4% could be reduced even further by optimizing the NaOH dosage. However, the actual effect of NaOH addition on MEA release from HSS should be investigated more in detail.

There is little information available in the literature that addresses how the build-up of impurities impacts the energy demand for regenerating MEA in the stripper i.e. reboiler heat duty. However, the density and viscosity of the solvent increased with the increasing level of contaminants as discussed in Section 3. This will cause reduction of the solvent heat transfer coefficient and consequently the heat transfer efficiency in the reboiler. The impact of accumulation of the contaminants on the specific heat capacity of amines is also very little addressed in the literature. However, it is expected that degraded MEA has higher specific heat capacity than MEA which in turn could increase the sensible heat needed to regenerate the solvent in the stripper. It is recommended to investigate these effects in the future.

As the amine plant was only operated for 28 hours after solvent reclaiming, a very limited investigation of the effect of removing the aqueous phase contaminants on the energy requirement of the stripper reboiler was performed. In future tests, sufficient time should be allowed to investigate in detail and compare the solvent performance at the beginning of the test campaign to the performance just before reclaiming and just after reclaiming.

In order to further optimize the process and reduce disposal problems both the reclaiming procedure itself and the collection and drainage of the reclaimer waste can be improved. The rapid cleaning of the lean solvent suggests running the reclaimer more frequently for shorter time periods (for example 12 hours a week) as one option to avoid degraded solvent to accumulate in lean amine. In this way the acceleration of degradation reactions could also be minimized. The draining and flushing operation can be improved by using less water or even small amounts of steam for keeping the reclaimer vessel fit for purpose. This will reduce the amounts of waste.

8. Conclusions

A test campaign with 30 wt% MEA has been conducted for a total of 1960 hours at the CO_2 Technology Centre Mongstad. The present paper discusses main causes of solvent degradation and various parameters for monitoring degradation products. Further, the effect of process design and operating conditions on solvent degradation is discussed, and thermal reclaiming is evaluated as a technique for removal of degradation products and other contaminants in the MEA solution.

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The solvent condition was closely monitored during the test campaign and several observations such as increasing solvent viscosity and darker solvent color indicated solvent degradation. Solvent exposure to oxygen and flue gas contaminants in the absorber and operation at elevated temperatures (above 100 °C) in the stripper section are highlighted as main causes for degradation. When performing scale-up to commercial CO₂ capture units it is recommended to minimize the hot solvent residence time in the plant, in order to minimize solvent degradation.

Thermal reclaiming has demonstrated an efficient clean-up of the MEA solvent. The cleaning efficiency was about 95% with respect to degradation products, HSS and metal elements. The solvent viscosity returned to normal values and the solvent color was normalized to a clearer and more yellow appearance. The quality recovery of the solvent was further assessed by an evaluation of the capture process after the reclaiming was concluded by comparing the solvent performance to results obtained at earlier stages of the test campaign and there were no significant indications of reduced solvent quality.

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References

- [1] Dumée L, Scholes C, Stevens G, Kentish S. *Purification of aqueous amine solvents used in post combustion CO*₂ *capture: A review.* International journal of Greenhouse Gas Control 10 (2012): 443-455.
- [2] Abdi MA, Golkar MM. Improve contaminant control in amine systems. Hydrocarbon Processing 63 (2011): 102C 102-I.
- [3] IEAGHG, "Evaluation of Reclaimer Sludge Disposal from Post-Combustion CO₂ Capture", 2014/02 (March 2014).
- Wang T, Hovland J, Jens, KJ. Amine reclaiming technologies in post-combustion carbon dioxide capture. Journal of Environmental Science 27 (2015): 276 – 289.
- [5] Kohl AL, Nielsen RB. Gas purification. Gulf publishing Company, Houston, Texas, USA, 5th edition (1997).
- [6] Nurrokhmah L, Mezher T, Abu-Zahra MRM. The evaluation of monoethanolamine-based CO₂ post-combustion capture process waste handling approaches considering the regulations in UAE. Energy Procedia 37 (2013): 751 – 758.
- [7] Gjernes E, Pedersen S, Cents T, Watson G, Fostås BF, Shah MI, Lombardo G, Desvignes C, Flø NE, Morken AK, de Cazenove T, Faramarzi L, Hamborg ES. *Results from 30 wt% MEA performance testing at the CO₂ Technology Centre Mongstad*. Energy Procedia (GHGT-13), Forthcoming 2017.
- [8] Lombardo G, Fostås BF, Shah MI, Morken AK, Hvidsten OA, Mertens J, Hamborg ES. Results from aerosol measurement in amine plant treating gas turbine and residue fluidized catalytic cracker flue gases at the CO2 Technology Centre Mongstad. Energy Procedia (GHGT-13), Forthcoming 2017.
- [9] Faramarzi L, Thimsen D, Hume S, Maxson A, Watson G, Pedersen S, Gjernes E, Fostås BF, Lombardo G, Cents T, Morken AK, Shah MI, de Cazenove T, Hamborg ES. *Results from MEA testing at the CO₂ Technology Centre Mongstad: Verification of baseline results in 2015*. Energy Procedia (GHGT-13), Forthcoming 2017.
- [10] Morken AK, Pedersen S, Kleppe ER, Wisthaler A, Vernstad K, Ullestad Ø, Flø NE, Faramarzi L, Hamborg ES. Degradation and Emission Results of Amine Plant Operations from MEA Testing at the CO₂ Technology Centre Mongstad. Energy Procedia (GHGT-13), Forthcoming 2017.
- [11] Hjelmaas S, Storheim E, Flø NE, Thorjussen ES, Morken AK, Faramarzi L, de Cazenove T, Hamborg ES. Results from MEA amine plant corrosion processes at the CO₂ Technology Centre Mongstad. Energy Procedia (GHGT-13), Forthcoming 2017.

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