

SINTEF F22608- Restricted

# Process Protocol

## Final Report

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## Report

## **Final Report**

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#### ABSTRACT

#### Process protocol

The present report describes the execution of a solvent degradation protocol in the SDR rig. The SDR rig has been designed to simulate the degradation of solvents utilized in post-combustion  $CO_2$  capture plants. The purpose is to be able to predict solvent degradation and gain knowledge on what components may be emitted from a plant running on a given solvent. The building and documentation of the SDR rig have been a part of the present project. The rig is described in a separate "Design package" deliverable.

The solvent degradation protocol was carried out for 30 wt% 2-ethanolamine (MEA). The results show that the rig operates as intended. The rig appears to give a realistic picture of the solvent degradation. Degradation products that SINTEF has previously identified in pilot-plants were also found in the SDR rig. There was also reasonably good quantitative agreement between levels of degradation products in the rig and a pilot plant campaign at Esbjerg.

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#### 1 Introduction

The Solvent Degradation Rig (SDR) was designed by SINTEF as part of the Amine Technology Qualification Program (TQP Amine) under the  $CO_2$  Capture Mongstad Project (CCM).

The objective has been to establish a laboratory scale protocol for examination of process degradation and emission properties of solvents for post combustion  $CO_2$  capture, i.e. primarily aqueous solution of amines and amino acids.

The 14 week long SDR test campaign with degradation of 30 wt.% MEA demonstrates that the rig operates as intended. The results show that the SDR results give a realistic picture on the solvent degradation to be expected in a real  $CO_2$  capture plant; degradation products formed in the SDR MEA solvent reflects those previously found in pilot plant studies.

SDR results should provide valuable input to health and environmental risk evaluations for different solvent systems for  $CO_2$  capture. Execution of the test protocol demonstrates how the SDR enables bench-scale studies of solvent process degradation previously only available from pilot plant studies.



#### 2 Rig design

#### 2.1 General

The SDR is an advanced laboratory test rig for studies of solvent degradation at process conditions. The test rig simulates typical process conditions found in absorption based  $CO_2$  capture. Solvent is degraded by long term cycling in a combined absorber and stripper setup with a defined synthetic absorber flue gas mixture. Compared with purely oxidative or thermal experimental setups for solvent degradation, the SDR enables studies of the combined effects of different degradation mechanisms occurring in a real-life process. The test rig simulates realistic temperatures and solvent  $CO_2$  loadings found in absorber/stripper configurations for  $CO_2$  capture. The SDR can be applied for studies on process-related degradation or nitrosation and provides qualitative estimates of compounds potentially present in absorber emissions for different solvent systems. We refer to the previous "Design package" deliverable for details regarding the SDR design.

Based on the experience obtained from the SDR test campaign, SINTEF considers the rig design to be successful. Long term stable operation was achieved despite significant degradation of the MEA solvent. The re-absorber unit proved to function as intended resulting in controllable and realistic solvent  $CO_2$  loading in the absorber and desorber sections. The relatively simple regulation principle of the rig also functioned as intended with automatic regulation of desorber pressure and solvent cycle flow. Severe foam formation in the two columns did not hinder operation of the SDR.

#### 2.2 Potential operational issues - precipitation

Precipitation of solvent or degradation products is seen as a potential problem for future test campaigns with other solvent systems; the fine metal sinter in the re-absorber unit was clogged by solid precipitates well into the test campaign (week 10). This specific problem could be solved by using a sinter with bigger pore size or by having new sinters available for quick exchange upon clogging. Precipitate is also a potential challenge for the pressure regulation valve of the desorber (PC01), which is a fine-tuned instrument. Possible future pressure regulation problems due to precipitation in PC01, could be prevented by heating of  $CO_2$  gas line N & O out of the desorber in order to avoid condensation and subsequent precipitation of solids in the valve.

#### 2.3 Deviation from intended design – absorber gas cooler

Operation of the cooling section of the absorber column was found to hinder proper temperature control of the absorber solvent temperature; the line A solvent coil placed in the thermostatic bath (HX01) had insufficient heating effect in order to counter the cooling effect on the solvent from recirculated gas. Because of this, the cooling water flow was set to zero in the absorber cooler (AC-G cool1) during the test campaign. If regarded as necessary, a future modification could solve the issue by applying a longer solvent heating coil in line A (HX01). Less cooling of the gas exiting the absorber could lead to reduction in life-time of the gas pump (KE01) due to increased exposure to moisture. No problems with the gas pump were observed during the 14 week test campaign.



#### 3 Operation of the rig, experiences

The SDR rig was operated for 14 weeks with 30 wt. % MEA (CAS 141-43-5) solvent during 31.10.2011 to 15.02.2012. The campaign was divided into four "Test Protocols" (see chapter 4) with duration of 5 and 3x3 weeks duration. The Table 3-1 give a short operation summary with time, numbers of days in operation and percentage operational time for each test protocol. Overall, the SDR was operated for 83 days during the 14 weeks campaign period which correspond to a total operational time of 87% for the SDR.

Three of the protocols (*Standard, High NO<sub>x</sub>, High O<sub>2</sub>*) were only minor change in the synthetic exhaust gas composition, and all the operation parameters for the SDR were basically fixed for these protocols, except the exhaust gas composition of course. The forth protocol (*High Temp.*) was the only protocol with any "major" operational change in the SDR rig where desorber pressure was increased to 3.65 bar and the reboiler duty was increased to compensate for higher heat loss and to meet the target of 140 °C in the reboiler. A summary of all the controls variables for each protocol and P&ID are given in the appendix.

Test protocol Start/end		Operation days (Total days)	Operation time	
Standard	31.10-05.12	26 (35)	74%	
High O2	05.12-22.12	16 (17)	93%	
High Temp.	02.01-23.01	21 (21)	100%	
High NOx	23.01-15.02	20 (22)	89%	
Total		83 (95)	87%	

#### Table 3-1: Operation of the SDR rig

A picture of the prototype SDR installed in a fume cupboard during operation is given in Figure 3-1, while Figure 3-2 shows some pictures of the solvent and the inspection glasses after 13 weeks of operation. As seen, the solvent was red-brownish indicating degradation while it was initial completely transparent. Also, a lot of foam can be seen in the absorber sump, but this was only seen at the end of the14 week's campaign. In the desorber, foam could often be observed however it's expected to see some foam/boiling since the inspections glass is located right above the reboiler heating element. Tiny gas bubbles could also be observed after the Re-Absorber, indicating a well-functioning gas sparger (sinter) inside the Re-Absorber (Re-ABS). Most of the CO2 is reabsorbed, but small amounts probably escape and are captured in the absorption column.





Figure 3-1: Picture of solvent degradation rig prototype installed in fume cupboard





Figure 3-2: Pictures from the SDR prototype rig at the 13<sup>th</sup> week. A: Absorber inspections glass; B: Desorber inspections glass; C: Re-Absorber inspection glass; D: Solvent after 13 weeks

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#### 3.1 Problems experienced during 14 weeks of operation

The SDR rig is designed for unmanned operation and continuous operation, but several operational issues during the 14 weeks led to down-time as seen in Table 3-1. First problem experienced was software related where the control system (LABVIEW 2011) "froze" randomly, often during night, which caused in total several days of down time in the first campaign. This software issue was especial hard to identified due it was a software "bug" in Labview, and the only fix was to turn of the multicore CPU support to the PC . Several mitigation actions were tested before identifying the correct cause. It's estimated that approximately 8 of the 9 days of downtime in the standard protocol was related to this software issues. However, no problem has been experienced with the software after the fix.

The rest of the problems experienced were purely operational issues. The first problem was solvent in the pressure controller (PC01) after a shutdown trigger by an alarm. The solvent was found downstream of PC01 and the fluid resulted in clogging of the valve, which further led to flow restrictions and improper venting of the desorber overhead gas. Hence, several hours of purging with instrument air was needed to remove the solvent from the relative small valve in the PC01 (actually a mass flow controller). A check valve is installed to prevent back flow of solvent to the pressure controller. Furthermore, a check valve is installed in the desorber column to prevent vacuum build-up during shut-down. Anyway, solvent was found downstream the pressure controller probably due the gases CO2 and H2O condense slowly or reversible in the gas line downstream. Hence, the pressure difference over the check valve is probably too small to engage the back flow restrictions, and solvent creeps slowly up to the pressure controller from the re- absorber. Purging the gas line before cooling with nitrogen will remove this problem which explains why this is a problem only for a shutdown triggered by an alarm.

Another problem with the pressure controller was precipitations upstream which clogged the inlet to the pressure controller (PC01) and also inlet to the pressure transmitter (PT01). A picture of the white precipitate is in the desorber overhead gas line is shown in Figure 3-3 which is taken after a shutdown trigger by a pressure alarm in the absorber due to improper (or missing) venting of the desorber overhead gas. Two incidents were registered during the 14 weeks of operation, and the precipitate is probably building up over a long time period before the precipitate in the gas line reach a critical level where the flow restriction are too high to proper vent the desorber overhead gas, resulting in a pressure build up in the desorber and a shutdown triggered by the pressostat. It's estimated that the precipitate mechanically with a pipe cleaner and by flushing with water. A strong ammonia smell was noticed from the precipitate. Later, a liquid analysis with LC-MS-QQQ identified 23% ammonia in the precipitate. For instance ammonia carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>) and ammonia bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) contains respectively around 17% and 22% NH<sub>3</sub>. It is expected that the precipitation of these carbonates.



Figure 3-3: Precipitations in desorber overhead gas line

As seen in the emission measurement in chapter 4, ammonia emissions and ammonia levels in lean sample were high. Ammonia is a more volatile than water, hence the desorber overhead gas is relative rich in ammonia and also

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highly rich in CO2. Cooling by natural heat loss can favour condensation and precipitation of ammonia carbonate compounds. Better insulation or heat tracing could reduce the water condensation and risk for precipitation in the gas line to the pressure controller. Also, a thorough inspection after each test protocol is recommended to reduce the risk of precipitation build up over time.

At the end of the 14 weeks campaign, it was experienced several shut down due pressure build up in the desorber. First suspect was precipitations in the desorber overhead gas line, but physical inspections revealed no precipitations. After some work, the cause was found to be the gas sinter located downstream the pressure regulator (PC01). Scaling or dirt inside the gas sinter reduced the gas flow to a critical level where CO2 vented trough the pressure controller was less than produced, resulting in pressure build up and shutdown triggered by alarm. The original gas sinter at 15 um was replaced with a 2 um (only available at present time) which restored the venting capacity and fixed the problem. Two days were lost due to the clogging of the gas sinter.

Another smaller problem experienced once or twice was friction build up in the lean return line. At some time the friction became so large that the return flow were smaller than the rich feed, even with the return valve fully open (LCO1), resulting in a shutdown trigged by level alarm in the desorber. Less than a day of operation time was lost due to this particular problem.

Last, a small leakage was detected in the pipe connections to the rich/lean heat exchanger at the cold side. The leakage was measured to approximately 2-3 g pr day for the first protocol while tightening the connections during the second campaign reduced the leakage to 0.2 to 0.3 g/day. At the high temperature protocol, the leakage increased to 2 g/day due the increased pressure. A similar leakage was experienced at the hot side during commissioning and was fixed. Hence, the pipe connections to HPO1 were a weak point for the SDR.

#### 3.2 Solvent inventory

Initial fill was 4.4 kg of preloaded 30 wt.% MEA to the SDR prototype rig as first batch. Initial liquid analysis showed a drop in MEA concentration to 27 wt. % due residue water from the washing of the SDR. Additional 1.1 kg of 30 wt. % solvent was added during the first week to compensate for the dilution and for compensation of filling of the several voids in the plant. After the first week no more solvent was added to the plant. Liquid sampling, purge gas and leakage will reduce the solvent inventory to the SDR and makeup must be added over time to compensate. De-mineralized water was the only makeup after the first week, and all makeup were weighed and logged. It's estimated that 27g of water is lost every operation day if dry purge gas leaves the SDR saturated at 20°C, which in total sum up to almost 600 gram for a three week test protocol. Furthermore, liquid sampling of solvent and condensate removes approximately 80 gram for the same protocol. Also, a leakage of solvent was experienced near the heat exchanger with a max rate of 40 to 60 grams per protocol. Hence, its estimated to approximately 700 g of solvent inventory must be replaced for a 3 week test protocol. Accumulated water makeup to the SDR over 14 weeks is plotted in Figure 3-4, and linear regression gave an average of 23 grams or almost 500 g pr protocol.





Figure 3-4: Accumulated water makeup for the SDR

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#### 4 Results, Execution of test protocol

The experiment with 30% MEA was run according to the test protocol (D1- Planned Test Protocol: CCM TQP amine 4 - Process Protocol). The experiment involved 4 cases with changes in some of the process parameters which are summarized in Table 4-1. In all cases the absorber liquid temperature was 40°C and with a lean and rich loading around 0.20 and 0.45 respectively (see also Table 4-4).

#### Table 4-1 Summary of different cases in test protocol

Condition	T <sub>Stripper</sub>	0 <sub>2</sub>	NO <sub>x</sub>	Duration
	[°C]	[mol%]	[ppmv]	
Standard	120	12	5	5 weeks
High Ox	120	18	5	3 weeks
High Stripper	140	12	5	3 weeks
High NOx	120	12	50	3 weeks

During the experiment solvent samples were sampled at regular intervals, in addition also condensate and emission samples were sampled at the end of each sub campaigns (condition). This is further described in the test protocol (D1- Planned Test Protocol: CCM TQP amine 4 - Process Protocol) and is also summarized in Table 4-2.

 Table 4-2 Proposed sample matrix for chemical analysis

Condition	Week	Lean Solvent	Rich Solvent	Condensate	Emission
		(V29)	V30)	(V01)	(Entrapped Gas)
Unused solvent	0	Х			
	0	х			
Standard	1	х	х		
5010010	3	х		х	
	5	Х	Х	Х	Х
High Ox	7	х			
	8	Х	Х	Х	Х
High Strigger	10	Х			
	11	х	х	х	Х
	13	Х			
	14	х	х	х	Х

The collected samples were analysed according to the test protocol (D1- Planned Test Protocol: CCM TQP amine 4 - Process Protocol). All MEA and all degradation products were analysed by LC-MS-QQQ except total nitrosamine which were analysed by GC-NCD. In addition MEA was also determined by titration method (titration with  $H_2SO_4$ ) for some of the solvent samples,  $CO_2$  were determined by a TOC analyser operated in inorganic modus and the metals were analysed by HR-ICP-MS. The obtained results are given in the following sections.

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#### 4.1 Analysis MEA solvent

During the execution of the test protocol lean solvent were sampled at regular intervals the determined MEA concentration in these samples are given in Table 4-3 and the results are also plotted versus time in Figure 4-1. In Table 4-3 the absolute decrease ( $\Delta$ MEA) in MEA concentration with respect to the unused solution is given as well as the relative decrease.

# Table 4-3 Results MEA (LC-MS) of Lean Solvent at different times. $\Delta$ MEA is the absolute difference in MEA concentration with respect to the unused solution (MEA<sub>0</sub>)

Jornal no	Sample id	Condtions	Date	Time	MEA [mol/L]	<b>∆MEA</b> [mol/L]	<b>∆MEA/MEA</b> ₀ [%]
P112631	Unused				4.93	0.00	
P112632	LEAN Week O	Standard	31.10.11	19:50	4.60	0.32	
P112633	LEAN Week 1	Standard	10.11.11	10:40	4.75	0.18	
P112635	LEAN Week 3	Standard	28.11.11	14:10	4.45	0.48	
P112637	LEAN Week 5	Standard	04.12.11	18:20	4.35	0.58	11.8 %
P113055	LEAN Week 7	High Ox	19.12.2011	11:05	4.09	0.84	
P113056	LEAN Week 8	High Ox	22.12.2011	12:40	3.94	0.99	20.0 %
P12119	LEAN Week 10	High Stripp temp.	16.01.2012	12:25	3.68	1.25	
P12120	LEAN Week 11	High Stripp temp.	23.01.2012	12:36	3.70	1.23	24.9 %
P12400	LEAN Week 13	High NOx	06.02.2012		3.38	1.54	
P12401	LEAN Week 14	High NOx	14.02.2012		3.35	1.57	31.9 %





For selected rich and lean samples the amine concentration was determined by wet chemistry (amine titration),

 $CO_2$  were determined on a TOC analyzator run in inorganic mode and density on a density meter (Mettler Toledo). The results are given in Table 4-4 where also the loading is calculated.

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Jornal nr	Sample id	Date	Time	Amine titration [mol amine/kg]	Density [g/ml]	CO2 [mol CO2/kg]	Loading [mol CO <sub>2</sub> /mol amine]
P112631	Unused			4.513		1.778	0.39
P112632	LEAN Week O	31.10.11	19:50	4.410			
P112633	LEAN Week 1	10.11.11	10:40	4.581	1.0599	1.088	0.24
P112634	Rich Week 1	10.11.11	10:40		1.1052	2.106	
P112635	LEAN Week 3	28.11.11	14:10	4.267	1.0553	0.984	0.23
P113053	Rich Week 5	4.12.11	10:44	4.078		1.957	0.48
P113054	Rich Week 5	4.12.11	19:35			1.953	
P113056	LEAN Week 8	22.12.11	12:40	3.855		0.784	0.20
P113374	Rich Week 8	22.12.11	07:15	3.662		1.732	0.47
P113375	Rich Week 8	22.12.11	14:28	3.640		1.719	0.47
P12120	LEAN Week 11	23.01.12	12:36	3.540		0.572	0.16
P12127	Rich Week 11	23.01.12	07:20	3.781		1.682	0.45
P12400	LEAN Week 13	06.02.12		3.225	1.0488		
P12401	LEAN Week 14	14.02.12		3.226		0.567	0.18
P12408	Rich Week 14	14.02.12		3.102		1.396	0.45

#### Table 4-4 Results of density, CO<sub>2</sub> and amine (amine titration) of lean and rich samples

Lean solvent samples were also analysed for a range of known degradation product in MEA including: Diethanolamine (DEA), 4-(2-hydroxyethyl)piperazin-2-one (HEPO), N-(2-hydroxyethyl)imidazole (HEI), N-(2hydroxyethyl)-glycine (HEGly), N-(2-hydroxyethyl)formamide (HEF),N,N'-bis(2-hydroxyethyl)oxamide (BHEOX), N-(2-hydroxyethyl)acetamide (HEA) and 2-oxazolidinone (OZD) and the results for these products are shown in Table 4-5. All of these results except DEA are also plotted against time in Figure 4-2. DEA is plotted separately in Figure 4-3.

Table 4-	5 Results of	selected	degradation	products	determined t	y LC-MS-QQ	IQ in Lean	Solvent at	different
times									

Jornal no	Sample id	Condtions	DEA	OZD	BHEOX	HEA	HeGly	HEPO	HEF	HEI
			[µmol/l]	[µg/ml]						
P112631	Unused		260	< 10	< 100	< 10	< 10	< 10	75	2
P112632	LEAN Week O	Standard		< 10	< 100	20.4	459.6	87.91	95.2	31.4
P112633	LEAN Week 1	Standard	318							
P112635	LEAN Week 3	Standard	282	35	< 100	180	3211	1390	427	341
P112637	LEAN Week 5	Standard	400	32	< 100	237	4098	1834	507	393
P113055	LEAN Week 7	High Ox								
P113056	LEAN Week 8	High Ox	531	33.8	28.5	443	6152	2635	787	728
P12119	LEAN Week 10	High Stripp temp.	574	< 100	< 100	898	7117	9730	1568	1102
P12120	LEAN Week 11	High Stripp temp.	719	< 100	< 100	1146	7494	12542	1846	1066
P12400	LEAN Week 13	High NOx		< 100	< 100	1166	8475	11310	1623	1198
P12401	LEAN Week 14	High NOx	310	< 100	< 100	1386	9288	11001	1901	1315





Figure 4-2 Selected degradation product in Lean solvent as a function of running time (weeks)





Figure 4-3 DEA concentration in Lean solvent as a function of running time (weeks)

Furthermore results for nitroseamines and  $\cdot$ 2-nitroamino ethanol (MEA-NO<sub>2</sub>) in lean solvent is given in Table 4-6 and Table 4-7

Table 4-6 Results of nitrosamines in Lean Solvent at different times. All specific nitroseamines were analysed by LC-MS-QQQ. Total nitroseamine (Total NA, group detection) was analysed by GC.

Jornal no	Sample id	Condtions	Total NA	NDELA	NDMA	NMOR	NPYR	NMEA	NDEA	NPIP	NDPA	NDBA
			[µg NDMA/ml]	[ng/ml]								
P112631	Unused			< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
P112635	LEAN Week 3	Standard	12.3	174	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
P112637	LEAN Week 5	Standard	9.2	134	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
P113056	LEAN Week 8	High Ox	11.6	< 10	< 10	< 10	< 10	< 10	< 100	< 100	< 100	< 100
P12120	LEAN Week 11	High Stripp temp.	4.8	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100
P12401	LEAN Week 14	High NOx	11.,1	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100

The used abbreviations for these compounds are :

NDELA	Nitrosodiethanolamine
NPIP	Nitrosopiperidine
NDEA	Nitrosodiethylamine
NDMA	Nitrosodimethylamine
NMEA	Nitrosomethylethylamine
NMOR	Nitrosomorpholine
NDBA	Nitrosodibutylamine
NDPA	Nitrosodipropylamine
NYPR	Nitrosopyrrolidine
	DEBODT NO



Jornal no	Sample id	Condtions	MEA-NO2 [ng/ml]
P112631	Unused		16.6
P112635	LEAN Week 3	Standard	49.7
P112637	LEAN Week 5	Standard	44.6
P113055	LEAN Week 7	High Ox	140
P113056	LEAN Week 8	High Ox	98.5
P12120	LEAN Week 11	High Stripp temp.	< 10
P12401	LEAN Week 14	High NOx	72.8

#### Table 4-7 Results MEA nitramine (MEA-NO<sub>2</sub>) by LC-MS in Lean Solvent at different times

Also alkylamines and  $NH_3$  was analysed in lean solvent and the results are given in Table 4-8 and the alkylamines are also plotted in Figure 4-4.

#### Table 4-8 Results of alkylamines and $NH_3$ in Lean Solvent at different times

Jornal no	Sample id	Condtions	NH₃	Dimethylamine	Methylamine	Ethylamine	Diethylamine
			[µg/ml]	[ng/ml]	[ng/ml]	[ng/ml]	[ng/ml]
P112631	Unused		95.7	< 100	< 100	<100	< 100
P112635	LEAN Week 3	Standard	787	277	2047	196	< 100
P112637	LEAN Week 5	Standard	706	439	2861	257	< 100
P113056	LEAN Week 8	High Ox	1097	491	5742	46.0	< 100
P12120	LEAN Week 11	High Stripp temp.	1274	2657	13780	1411	< 100
P12401	LEAN Week 14	High NOx	1001	1912	16360	1819	< 100





Figure 4-4 Concentration of alkylamines in lean solvent

To monitor possible corrosion during the campaign lean samples were regularly analysed for metals (V, Cr, Fe, Ni and Mo) by HR-ICP-MS. The results are given in Table 4-9 and are also shown graphically versus operational time in Figure 4-5.

Jornal	Sample id	Condtions	V	Cr	Fe	Ni	Mo
no			[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]
P112631	Unused		<0.001	<0.003	0.063	<0.007	<0.01
P112632	LEAN Week O	Standard	<0.1	0.828	3.56	2.41	0.196
P112635	LEAN Week 3	Standard	<0.1	1.96	10.1	4.27	0.43
P112637	LEAN Week 5	Standard	<0.1	2.14	10.9	4.48	0.492
P113056	LEAN Week 8	High Ox	0.023	2.00	10.8	3.99	0.479
P12120	LEAN Week 11	High Stripp temp.	0.034	3.23	11.5	5.44	0.654
P12401	LEAN Week 14	High NOx	0.034	3.30	9.9	5.56	0.678

#### Table 4-9 Results of metal analysis (HR-ICP-MS) of Lean Solvent at different times

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Figure 4-5 Plot of metal concentration s versus time for lean solvent.

#### 4.2 Analysis condensate

In connection with the weekly sampling condensate was also collected from sampling point V01. Additionally also condensate from sampling point V28 were collected. The MEA concentration determined by LC-MS-QQQ for these condensates is given in Table 4-10.



Jornal no	Sample id	Sampling	Condtions	Date	Time	MEA
		Point				[mmol/l]
P112636	Condensate Week 3 VO1	v01	Standard	28.11.11	14:10	0.16
P112639	Condensate Week 5 VO1	v01	Standard	04.12.11	19:45	0.11
P113061	Condensate Week 8 VO1	v01	High Ox	22.12.11	07:15-14:30	0.13
P12121	Condensate Week 11 VO1	v01	High Stripp temp.	23.01.12	08:19-14:47	0.11
P12402	Condensate Week 14, VO1	v01	High NOx	14.02.12		0.14
P112638	Condensate Week 5 V28	v28	Standard	4.12.11	18:23	4.56
P113057	Condensate Week 8 V28	v28	High Ox	22.12.2011	12:36-13:06	4.13
P12126	Condens Week 11 V28	v28	High Stripp temp.	23.01.2012	12:24-12:57	2.89
P12407	Condens Week 14 V28	v28	High NOx	14.02.12	14:10	4.19

#### Table 4-10 Results MEA (LC-MS) in condensate at different times.

Results for nitrosamines in the condensate samples are shown in Table 4-11. The results for NDMA are also shown graphically in Figure 4-6 (the other analysed nitrosamines is below or close to the respective LOQ).

Table 4-11 Results nitrosamine	s (LC-MS-QQQ) in condensate at different times.
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Jornal	Sample id	Sample	Condtions	NDELA	NDMA	NMOR	NPYR	NMEA	NDEA	NPIP	NDPA	NDBA
no		Point		[ng/ml]								
P112636	Condensate Week 3 VO1	v01	Standard	< 0.1	2.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
P112639	Condensate Week 5 VO1	v01	Standard	< 0.1	1.81	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
P113061	Condensate Week 8 VO1	v01	High Ox	< 1	4.88	< 1	< 1	< 1	< 1	< 1	< 1	< 1
P12121	Condensate Week 11 VO1	v01	High Stripp temp.	< 1	3.92	< 1	< 1	< 1	< 1	< 1	< 1	< 1
P12402	Condensate Week 14, VO1	v01	High NOx	< 1	26.4	< 1	< 1	< 1	< 1	< 1	< 1	< 1
P112638	Condensate Week 5 V28	v28	Standard	< 0.1	1.23	0.0977	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
P113057	Condensate Week 8 V28	v28	High Ox	< 0.1	2.80	< 0.1	< 0.1	< 0.1	< 1	< 1	< 1	< 1
P12126	Condens Week 11 V28	v28	High Stripp temp.	< 1	2.02	< 1	< 1	< 1	< 1	< 1	< 1	< 1
P12407	Condens Week 14 V28	v28	High NOx	< 1	16.8	1.42	< 1	< 1	< 1	< 1	< 1	< 1





Figure 4-6 Plot of NDMA in condensate for the different conditions. (sample point V01)

In Table 4-12 the results for MEA nitramine determined by LC-MS-QQQ in the condensate samples are given.

Jornal	Sample id	Sample	Condtions	MEA-NO <sub>2</sub>
no		Point		[ng/ml]
P112639	Condensate Week 5 VO1	v01	Standard	< 0.1
P113061	Condensate Week 8 VO1	v01	High Ox	< 0.1
P12121	Condensate Week 11 VO1	v01	High Stripp temp.	< 0.1
P12402	Condensate Week 14, VO1	v01	High NOx	< 0.5
P112638	Condensate Week 5 V28	v28	Standard	< 0.1
P113057	Condensate Week 8 V28	v28	High Ox	< 0.1
P12126	Condens Week 11 V28	v28	High Stripp temp.	< 0.1
P12407	Condens Week 14 V28	v28	High NOx	< 0.5

Table 4-12 Results MEA nitramine  $(MEA-NO_2)$  in condensate at different times.

Finally the determined alkylamines and  $NH_3$  in the condensate is shown in Table 4-13. The determined concentrations are also plotted versus time in Figure 4-7 and Figure 4-8.



Jornal	Sample id	Sample	Condtions	NH3	Dimethylamine	Methylamine	Ethylamine	Diethylamine
no		Point		[µg/ml]	[ng/ml]	[ng/ml]	[ng/ml]	[ng/ml]
P112636	Condensate Week 3 VO1	v01	Standard	2401	1037	340	93.3	< 10
P112639	Condensate Week 5 VO1	v01	Standard	1807	935	474	104	< 10
P113061	Condensate Week 8 VO1	v01	High Ox	2549	787	618	123	6.35
P12121	Condensate Week 11 V01	v01	High Stripp temp.	3416	1136	2273	531	6
P12402	Condensate Week 14, VO1	v01	High NOx	2700	817	2621	541	10.5
P112638	Condensate Week 5 V28	v28	Standard	1105	3252	1956	325	18.3
P113057	Condensate Week 8 V28	v28	High Ox	1224	2788	3894	511	12.8
P12126	Condens Week 11 V28	v28	High Stripp temp.	1452	2654	9224	1263	12
P12407	Condens Week 14 V28	v28	High NOx	1128	2477	11645	1632	13.6

#### Table 4-13 Results alkylamines and $NH_3$ (LC-MS-QQQ) in condensate at different times.



Figure 4-7 Plot of alkylamines in condensate for the different conditions. Dotted lines are from sample point V28, solid lines from sample point V01





Figure 4-8 Plot of  $NH_3$  in condensate for the different conditions. Dotted lines are from sample point V28, solid lines from sample point V01



#### 4.3 Emission measurements

Gas sampling of the dry emitted gas was performed by the use of a gas washing bottle sampling train. The gas was sucked from valve V33 (VSG3) through a series of gas washing bottles before drying and volume measurement prior to final venting of the gas flow. A detailed description of the gas sampling procedure is referred to D1- Planned Test Protocol: CCM TQP amine 4 - Process Protocol.

The flow measurement of FG-03 was used to ensure that a small surplus of gas goes through the rotameter in order to avoid sampling of air from the vent by reversed flow through FG-03. In addition to gas sampling from V23, condensate from AC-Gcool2 was collected at the same time. Based on these two "measurements" one may calculate:

- 1. Emission measurements in the "purge" gas leaving the SDR (Line R in P&ID)
- 2. Gas measurements of the recycled gas exiting the absorber top (Line K in P&ID)

The SDR was operated in semi-closed manner where only a small purge-gas exit the SDR, and also cooling (20 C) was applied on the purge gas to reduce water loss. Hence, the emissions measurements of the purge gas will differ from an equivalent pilot plant due to:

- 1. More cooling (20 C) will reduce emissions of water soluble compounds (MEA, NH3 etc)
- 2. Less purge-gas gives more accumulation of the volatile degradation products.

Anyway, the SDR was not meant to give quantitative numbers of the emissions in carbon capture. A simple mass balance in the SDR give that the degradation products created must be equal the venting rate if we assume no accumulation (steady state). Hence, it could be possible to back-calculate the emissions in a fully open system with the assumption of an equal degradation rate, but the assumptions of zero accumulation is probably questionable, at least for the most water soluble degradation products.

The emission measurement results are shown in Table 4-14, while NDMA and NH<sub>3</sub> are also shown graphically in Figure 4-9 and Figure 4-10. The gas measurement of the recycled gas is given in Table 4-15.



Week	5		8		11		14		
	Standa	rð	High Ox		High Stripp temp.		High NOx		
	µg/Nm³ <sub>a</sub>	ppmv <sub>b</sub>	µg/Nm³ <sub>a</sub>	ppmv <sub>b</sub>	µg/Nm³ª	ppmvb	µg/Nm³ª	ppmv <sub>b</sub>	
MEA	9	3.2E-03			10	3.8E-03			
MEA-NO2									
NDELA							0.04	7.4E-06	
NDMA	0.04	1.4E-05	0.22	6.8E-05	0.09	2.8E-05	0.72	2.2E-04	
NMOR									
NPYR									
NMEA									
NDEA									
NPIP									
NDPA									
NDBA									
NH3	164 000	216	175 000	231	267 000	352	207 000	272	
Dimethylamine	1	4.1E-04	0	1.4E-04	0	1.5E-04	1	3.2E-04	
Methylamine	0	5.5E-05			0	4.6E-05			
Ethylamine							0	5.8E-06	
Diethylamine	0.08	2.6E-05	0.04	1.2E-05	0.04	1.3E-05	0.07	2.1E-05	
a: mass pr dry Normal cubic meter. b: Parts per million (dry vol gas)									

#### Table 4-14 Emission measurement results: blank indicates concentrations below limit of quantification.

From Table 4-14 it can be seen that the levels of emission (for the defined conditions) were below the detectable limits for the majority of Nitrosamines except NDMA and to a lower extent NDELA. However, even for those other components that could be detected and quantified, the emission levels are far less than 1 ppm. The levels of  $NH_3$  seem to be consistent under all conditions, but slightly higher (in comparative terms) for week 11.

The recycled gas measurement (Table 4-15) has general higher levels of all the compounds found in the emissions measurements. The level of MEA has gone up to 0.1 ppm which is similar to a real pilot plant. MEA is presumably not produced in the SDR hence the MEA level will not be influenced by the low purge gas rate in same extent as the degradation products. Ammonia is an example of a degradation product where the low purge gas rate in the SDR give elevated levels in the gas due venting rate must be equal production rate. The alkyl amines levels were higher relative to the emissions and also all alkyl amines were detected in the recycled gas in all protocols. No additional Nitrosamines were found in the recycled gas, but the levels were approximately 2-3 times higher for the detected nitrosamines.



Week	5		8		11		14		
	Standa	ord	High Ox		High Stripp temp.		High NOx		
	µg/Nm³ <sub>a</sub>	ppmvb	µg/Nm³ <sub>a</sub>	ppmvb	µg/Nm³ <sub>a</sub>	ppmvb	µg/Nm³ª	$ppmv_b$	
MEA	335	0.12	343	0.13	343	0.13	461	0.17	
MEA-NO2									
NDELA							0.04	7.4E-06	
NDMA	0.13	4.0E-05	0.44	1.3E-04	0.28	8.4E-05	2.16	6.5E-04	
NMOR									
NPYR									
NMEA									
NDEA									
NPIP									
NDPA									
NDBA									
NH3	252 000	332	288 000	379	431 000	567	354 000	466	
Dimethylamine	46	0.02	35	0.02	55	0.03	45	0.02	
Methylamine	23	0.02	27	0.02	109	0.08	142	0.10	
Ethylamine	5.0	2.5E-03	5	2.7E-03	25	1.3E-02	29	1.5E-02	
Diethylamine	0.08	2.6E-05	0.32	9.8E-05	0.33	1.0E-04	0.64	2.0E-04	
a: mass pr dry Normal cubic meter. b: Parts per million (dry vol gas)									

#### Table 4-15 Recycled gas measurement results: blank indicates concentrations below limit of quantification.









#### 5 Discussion

#### 5.1 Comparison of the different cases

In Figure 5-1 the estimated degradation rate for MEA in the solvent is shown for each case. The degradation rate is calculated from the difference in MEA divided by the running time within each case. When also the uncertainties in these degradation rates are considered it is difficult to see any significant effect of the different conditions on the rate. The uncertainty in the rate is based on 1% relative uncertainty in the MEA concentrations.



Figure 5-1 Estimated degradation rate for each condition the experiment were run. The error bars is based on a combined uncertainty of the MEA concentrations determined by LC-MS.

Also for the MEA in the condensate and the emission measurement there is difficult to see any clear effect of the different cases, only indication of somewhat lower levels for the high stripper temperature case.

Even if there is no or small effect on the MEA degradation rate there are large effect for some of the degradation products. For instance there is a large increase of HEPO (see Figure 4-2) when the stripper temperature is increased, also for HEF there is a significant increase when the temperature of the stripper is increased. This indicates that the reaction for formation of these compounds is temperature dependent.

For DEA the largest effect seems to be when the NOx is increased, see Figure 4-3, where a decrease in DEA is observed. A reason for this may be a consumption of DEA in the formation of nitrosamines. As can be seen from Table 4-6 there is an increase in total nitrosamines for the High NOx case, however there is no detectable increase in NDELA.

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For the nitrosamines in the solvent only NDELA is above the quantification limit in the standard case all other specific nitrosamines is below their respective quantification limits. However the determined total nitrosamine is significant higher than the NDELA amount which indicate that significant amount of unidentified nitrosamines is be present in the solvent. For the total nitrosamines the results indicate a decrease in the high stripper case followed by an increase for the high NOx case. In the condensate and emission measurements mainly NDMA showed values above the quantification limits, see Table 4-11 and Table 4-14. In the condensate there can be observed a large increase in the case with high NOx, also for the high oxygen case there is observed some increase while a small decrease in the high stripper temperature case, see Figure 4-6. For the emission samples, see Figure 4-9, there appear to be an increase of NDMA for the high oxygen case followed be a decrease in the high stripper temperature case. As the condensate is sample before the emission measurement these results should be considered together.

For the MEA nitramine in the solvent seems to increase with higher oxygen but decreases significantly when the oxygen is decreased (back to the standard case) and stripper temperature is increased. The concentration is then increasing again when the stripper temperature is decreased and the NOx level is increased (the high NOx case).





For the ammonia level there seems to be a good correlation of the trends between the condensate, emission measurements and in the solvent as shown in Figure 5-2. The ammonia level increases when the oxygen level is increased (high Ox case) and it further increases when going to the high stripper temperature case, while a decrease is observed for the last case with higher NOx. One may expected that the MEA degradation rate were highly correlated to the ammonia levels, from these data however it is difficult to see such correlation.

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Figure 5-3 Alkylamines in Lean Solvent, condensate and emission for the different cases.

Also for the alkylamines the time trends is much similar for the solvent, condensate and emission samples, see Figure 5-3. For DMA the trend for the solvent and condensate is similar an increase for the high stripper temperature followed by a decrease for the high NOx case. DMA in the emission samples do not follow that trend, here a large increase is observed for the high oxygen case. For MA the trend in the solvent and condensate are similar with a large increase for the high temperature case (for the emission measurements only the last case yielded values above quantification limit). For DiEA no values were above the quantification limit for solvent samples, while the emission and condensate to a certain degree seems to be correlated, both with an increase for the high oxygen case and a small decrease for the high stripper temperature case. EA also shows a fairly good correlation between the solvent and condensate samples with a relative large increase for the high stripper temperature case.

During the experiments the lean samples were also analyzed for metals. The results showed an increase in the start of the experiment (week 3) followed by a mainly stable level during the rest of the experiment (possible a small increase during the high stripper temperature case), see Figure 4-5. These results do not indicate any severe corrosion problems during the experiment.

#### 5.2 Comparison with Pilot data

In Table 5-1 we show the ratio of the concentrations found in the SDR rig relative to concentrations found during a pilot plant campaign at Esbjerg. The MEA campaign at Esbjerg is from the EU-project Cesar, the analysis was 20 weeks into the campaign and is from the lean solvent (Lepaumier, H. da Silva, E. F., et al. Comparison of MEA

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degradation in pilot-scale with lab-scale experiments, GHGT10, Amsterdam). It can be seen that the level of degradation products in the SDR rig and the pilot-plant is quantitatively similar. At week 8 the level of all major degradation products is within 70% of the value at the Esbjerg pilot plant.

Jornal no	Sample id	Conditions	OZD	BHEOX	HEA	HeGly	HEPO	HEF	HEI
P112631	Unused								
P112632	LEAN Week 0	Standard			0.034	0.060	0.037	0.225	0.073
P112633	LEAN Week 1	Standard							
P112635	LEAN Week 3	Standard	14.1		0.303	0.421	0.580	1.01	0.792
P112637	LEAN Week 5	Standard	12.9		0.398	0.537	0.765	1.20	0.913
P113055	LEAN Week 7	High Ox							
P113056	LEAN Week 8	High Ox	13.6	1.11	0.745	0.806	1.10	1.86	1.69
P12119	LEAN Week 10	High Stripp temp.			1.51	0.933	4.06	3.70	2.56
P12120	LEAN Week 11	High Stripp temp.			1.93	0.982	5.23	4.36	2.48
P12400	LEAN Week 13	High NOx			1.96	1.11	4.72	3.83	2.78
P12401	LEAN Week 14	High NOx			2.33	1.22	4.59	4.49	3.05

Table 5-1 Results of selected degradation products determined by LC-MS-QQQ in Lean Solvent at different times relative to concentrations found in the Esbjerg pilot plant

The results suggest that the SDR rig does capture the degradation chemistry taking place in  $CO_2$  capture plants. Both the relative concentration between degradation products and overall levels are in good agreement between the SDR and the Esbjerg pilot campaign.

For the SDR we do have higher levels of 2-oxazolidinone OZD than we see in Esbjerg. OZD is however a minor degradation product. OZD is known to be a transient degradation product and it may be that the steady state concentration is higher in the SDR due to different residence times in the absorber and stripper.

It can also be seen that at high stripper temperature conditions the ratio of some degradation products starts to differ in the SDR and the pilot plant. This is entirely as expected since the solvent in this case is exposed to more severe conditions than in the pilot plant.

For volatile degradation products a direct quantitative comparison is more difficult to make. This since SDR rig has recirculation and a different emission control system than a pilot-plant. It does however seem that all degradation products found in pilot plants can be found and quantified in the SDR rig.

For the nitrosamines we have less available data to carry out quantitative comparisons. Our overall impression is however that the nitrosation chemistry in the SDR rig is comparable to that we see in pilot plants. NDELA is found in significant concentrations, while some other nitrosamines are found in lower concentrations.

Overall the results suggest that the SDR not only qualitatively captures the relevant degradation chemistry taking place in  $CO_2$  capture plants, it also gives a reasonable quantitative picture of the level of build-up of degradation products.



#### 5.3 Suggestion for improvements

One of the issues that have been discussed is to what extent one should refill solvent during the campaign. It is desirable to keep the solvent as close as possible to concentrations actually utilized by a given technology vendor, on the other hand it is desirable to keep the protocol as simple as possible. We might suggest adding solvent once during the campaign (after high Ox test) to keep concentrations reasonably close to specifications.

For the volatile degradation products, the SDR rig has a higher build-up then would be expected in a real capture plant. Ideally one would like to have a set up where the emission levels could be directly compared.

On the operation side it has been observed that precipitation can be an issue in the rig. MEA is not a solvent where precipitation is a major issue, for other solvents this could therefore be a greater issue than it is for MEA.

There are a number of steps that can be taken in order to minimize difficulties with precipitation. Some lines in the rig can be heated. Other components can be inspected and cleaned regularly.



#### 6 Conclusion

The present report describes the execution of a solvent degradation protocol in the SDR rig.

The solvent degradation protocol was carried out for 30 wt% MEA. The results show that the rig operates as intended. The rig appears to give a realistic picture of the solvent degradation. Degradation products that SINTEF has previously identified in pilot-plants were also found in the SDR rig. There was also reasonably good quantitative agreement between levels of degradation products in the rig and a pilot plant campaign at Esbjerg.

It is clear from the campaign that the build-up of different degradation products depends on conditions such as oxygen levels and temperature. The overall degradation rate did however not appear to change significantly throughout the campaign.

Total nitrosamine levels were found to be significantly higher than the sum of identified nitrosamines. This means that there most likely are significant amounts of unidentified nitrosamines in the system. Among the identified degradation product HeGly is the secondary amine that is present in highest concentration. This suggests that the nitrosamine formed from HeGly may be a significant contributor to the total nitrosamine levels.

Overall the results show that the rig works as intended and we expect that most degradation products that can form to significant degree in a  $CO_2$  capture plant will also be found in the SDR rig.



# A Appendix: Piping and instrumentation diagram

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### P&ID legend





**B** Appendix: Operation Data



Unit	Туре	Units	Standard	High O2	High Temp	High NOX
FG01	Rotameter	[%]	0	0	0	0
FG02	Rotameter	[%]	100	100	100	100
FG03	Rotameter	[%]	100	100	100	100
FG04	Rotameter	[%]	10	10	10	10
HX01	Heat-bath	[C]	50C	50C	50C	50C
FX01	Heat-tracing	[C]	50C	50C	50C	50C
FE01	Boiler	[%]	40%	40%	44%	40%
FC01	Flow controller	[NL/min]	0.85	0.79	0.85	0.825
FC02	Flow controller	[mNL/min]	30	30	30	30
FC03	Flow controller	[mNL/min]	120	180	120	120
FC04	Flow controller	[mNL/min]	2.5	2.5	2.5	25
FC05	Flow controller	[NL/min]	0.0	0.0	0.0	0.0
LC01	Level controller	[mbar]	20	20	20	20
PC01	Pressure controller	[bar]	1.82	1.82	3.65	1.82
PG01	Pump recycle	[L/hr]	10	10	10	10
PG02	Pump rich	[L/hr]	5	5	5	5
KE01	Fan recycle	$[m^3/hr]$	3	3	3	3

#### Table 6-1: Operational control variable for the four test protocols



# C Appendix: Detection of N-nitroso HeGly in SDR rig



#### Detection of N-nitroso HeGly in SDR rig

Based on study of known degradation products in MEA and pathways for nitrosamine formation we have in SINTEF concluded that it was very likely that the nitrosamine N-nitroso HeGly (N-(2-hydroxyethyl)-N-nitroso-Glycine) was being formed in degraded MEA.

As a result of this SINTEF recently develop an analysis method for this compound.

We analysed 1 sample from the SDR rig for this nitrosamine. The sample chosen was lean amine from week 14 (SINTEF journal id P12401).

The detected level was 11.9  $\mu$ g/mL. This would correspond to 56% of the nitrosamine level found with total nitrosamine analysis. This nitrosamine may be the dominant nitrosamine in MEA utilized in CO<sub>2</sub> capture plants. Further studies are required to determine how large a fraction of nitrosamines it will represent in pilot-plants and full scale CO<sub>2</sub> capture plants.

0 ×<sub>N</sub>  $\cap$ HO OH

Figure 4 Molecular structure of N-nitroso HeGly



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