



Formation and Destruction of NDELA in 30 wt% MEA (Monoethanolamine) and 50 wt% DEA (Diethanolamine) Solutions

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Hanna Knuutila, Naveed Asif, Solrun Johanne Vevelstad, Hallvard F. Svendsen. Formation and Destruction of NDELA in 30 wt% MEA (Monoethanolamine) and 50 wt% DEA (Diethanolamine) Solutions. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, 2014, 69 (5), pp.805-820. <10.2516/ogst/2013168>. <hal-01933406>

HAL Id: hal-01933406

<https://hal.science/hal-01933406v1>

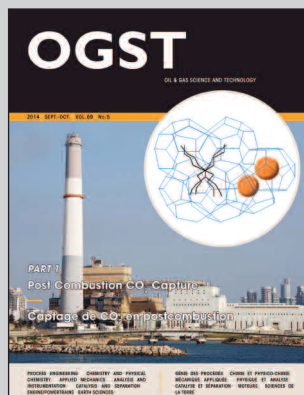
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This paper is a part of the hereunder thematic dossier published in OGST Journal, Vol. 69, No. 5, pp. 773-969 and available online [here](#)

Cet article fait partie du dossier thématique ci-dessous publié dans la revue OGST, Vol. 69, n°5, pp. 773-969 et téléchargeable [ici](#)

DOSSIER Edited by/Sous la direction de : **P.-L. Carrette**

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Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 69 (2014), No. 5, pp. 773-969

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Formation and Destruction of NDELA in 30 wt% MEA (Monoethanolamine) and 50 wt% DEA (Diethanolamine) Solutions

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Résumé — Formation et destruction de NDELA dans des solutions de 30 %m de MEA (monoéthanolamine) et de 50 %m de DEA (diéthanolamine) — La formation de nitrosodiéthanolamine (NDELA) dans une installation pilote de laboratoire a été étudiée en injectant des quantités contrôlées d'oxyde d'azote et de dioxyde d'azote dans le flux de gaz entrant dans l'absorbeur. La destruction par irradiation UV de la NDELA présente dans le solvant a aussi été étudiée sur la même installation pilote. Deux campagnes de mesure ont été menées, la première utilisant une solution de 30 %m de monoéthanolamine (MEA) et la seconde utilisant une solution de 50 %m de diéthanolamine (DEA). Durant la campagne de mesure sur la DEA, la destruction de la NDELA dans les eaux de nettoyage a aussi été testée. De plus, la dégradation thermique d'échantillons de solution dégradée prélevés dans l'installation pilote a été testée. Les résultats indiquent que de la NDELA se forme en présence d'oxyde d'azote et de dioxyde d'azote. Il a été constaté que la destruction de la NDELA par la lumière UV dans la boucle de solvant était lente. La destruction de la NDELA par la lumière UV dans le compartiment des eaux de nettoyage a été démontrée. La dégradation de la NDELA durant des études de dégradation thermique à 135 °C a été établie.

Abstract — Formation and Destruction of NDELA in 30 wt% MEA (Monoethanolamine) and 50 wt% DEA (Diethanolamine) Solutions — The formation of nitrosodiethanolamine (NDELA) in a lab scale pilot was studied by feeding known amounts of nitrogen oxide and nitrogen dioxide into the gas entering the absorber. In the same pilot, the destruction by UV-irradiation of NDELA present in the solvent was studied. Two campaigns were performed, one with 30 wt% monoethanolamine (MEA) and one with 50 wt% diethanolamine (DEA). During the DEA campaign the destruction of NDELA in the water wash section was also tested. Additionally, degraded solution samples withdrawn from the pilot were tested for thermal degradation. The results show that NDELA was formed when nitrogen oxide and nitrogen dioxide were present. Destruction of NDELA with UV-light in the solvent loop was found to be slow. In the water wash section, the UV-light destroyed the NDELA effectively. NDELA was found to degrade during the thermal degradation studies at 135°C.

INTRODUCTION

Global warming caused by anthropogenic CO₂ emissions is one of the most severe problems presently. Carbon capture and storage may offer a route to significantly reducing these emissions. Of the capture technologies, reactive absorption seems to be the most viable option. However, in order to operate absorption processes on a global scale, one has to make certain that the processes are benign and do not create additional environmental problems. One of the issues that could be detrimental to the application of this technology is the formation and potential emissions of nitrosamines when using amines or amino acids as absorption reagents.

Amine processes have been in use on modest scale for many years. One of the most used amines, MEA, has been a popular reagent for capture of CO₂ from power plant exhaust gases, *e.g.* the Warrior Run plant with ABB-Lummus technology (Kohl and Nielsen, 1997). Formation or emissions of nitrosamines from these plants have not been reported in the open literature.

The formation of nitrosamines from absorption plants can stem from two sources. One is atmospheric formation from emissions of solvent amines from the plant, as discussed by Bråten *et al.* (2008), Wisthaler (2010) and Nielsen *et al.* (2010). However, a proper wash process can limit the emitted exhaust gas amine content below 0.1 vppm (Graff *et al.*, 2013). Thus this problem seems to be under control, at least for MEA, and is not the focus of the present work.

However, nitrosamines may also be formed in the process itself. Fostås *et al.* (2010) found that gas containing NO_x and oxygen led to the formation of levels of 20–50 µg/g of DEA in their AMINOX plant after 25–75 hours. The formation of nitrosamines was also studied and NDELA (Nitrosodiethanolamine) was the main product, forming at a rate of 200–700 ng/g after 25–100 hours. The end concentration of NDELA was 0.5 µg/g in the solvent solution. Traces of two volatile nitrosamines, nitrosodimethylamine (NDMA) and nitrosomorpholine (NMOR) were also detected.

Most of the nitrosamines formed in the plant will most likely stay in the solvent loop, but nitrosamines have been detected in the gas leaving the water wash section located above the absorber (Kolderup *et al.*, 2012). Even though these measurements were performed in a research pilot that was not designed to minimize nitrosamine or amine slip, it is reasonable to consider that nitrosamines would be found in the water wash solutions also in other plants if they are formed in the solvent liquid. The volatile nitrosamines will penetrate to the water wash section in gaseous form, whereas droplets

and aerosols might transfer non-volatile nitrosamines from the absorber into the water wash.

The formation rate of nitrosamines under normal operation is not known, but will depend on temperature, liquid phase composition and the oxygen and NO_x content of the gas phase. NO₂ is believed to be the critical component in NO_x and will dissolve in the liquid phase and may disproportionate into nitrate and nitrite. The nitrite formed will be reactive toward secondary amine groups and can form nitrosamines, typically NDELA (Fostås *et al.*, 2011). This is one possible route to nitrosamine formation, but there may be others. Direct UV radiation could be an option to destroy the nitrosamines in both the solvent and water wash liquids.

Direct UV photolysis is currently used to remove NDMA from drinking water and treated wastewater and most of the literature available on destruction of nitrosamines with UV-light is related to water treatment applications (Sharma, 2012; Nawrocki and Andrzejewski, 2011). Some literature is available for amine applications. Jackson and Attala (2012) have a patent on treating an amine solvent with UV-radiation.

In this paper, the formation and destruction of NDELA in pilot conditions are studied. The formation of NDELA is studied by feeding known amounts of NO and NO₂ in the pilot, and the destruction of NDELA is studied by irradiating the solvent with UV-light. Two campaigns were made: one with 30 wt% MEA and another with 50 wt% DEA. During the DEA campaign the destruction of NDELA in the water wash section was also tested. Additionally degraded solution samples withdrawn from the pilot are tested for thermal degradation to determine if NDELA degrades at high temperatures.

1 EXPERIMENTAL APPARATUSES

1.1 UV-Light Reactor

The setup shown in Figure 1 was used to study the destruction of nitrosamines in the pilot plant. The reactor setup contained a centrifugal circulation pump, a valve to control the circulation rate, a commercial UV-light reactor (Sterilight silver S8Q-PA) and sampling points at the UV-reactor inlet and outlet. Main technical data of the commercial UV-light reactor with lamp effect of 37 W are presented in Table 1.

1.2 Lab Scale Pilot Plant

The lab scale pilot plant located at the Gløshaugen campus in Trondheim was used in the experiments and a

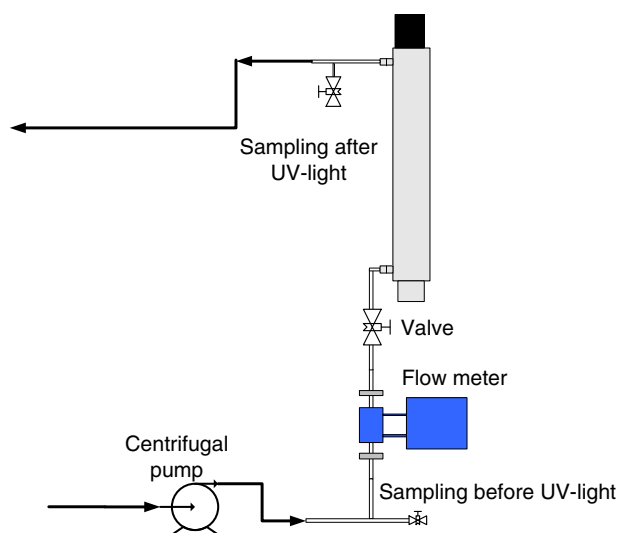


Figure 1

UV-reactor, connected to a centrifugal pump and flow meter.

TABLE 1

Technical information about Sterilight silver S8Q-PA UV-light reactor

	Value
Power consumption	46 W
Lamp power	37 W
Max. flow rate	37.9 L/min
Chamber material	304 stainless steel
Chamber length	90.0 cm
Chamber diameter	6.4 cm
Lamp	Sterilume-EX model S810RL
Sleeve	Quartz Model QS-810

simplified flow sheet of the fully automated pilot plant is given in Figure 2. In Table 2 some additional information about the pilot is given. Lean amine exits the reboiler, flows through the cross flow heat exchanger HEX1, into a mixing tank, and is pumped through the heat exchanger (cooler) HEX2 to cool the solvent if the temperature into the mixing tank is too high. After passing through the absorption column, the rich amine exits the absorber, and is pumped through the heat exchanger HEX1 entering the top of the stripper.

The vapor from the top of the stripper enters two water-cooled condensers in series (one condenser shown

in the figure). The condensate returns to the reboiler, and the CO₂ is mixed with the outlet gas from the water wash column and sent back as feed gas to the absorber. It should be noted that the complete plant is run as a closed system, thus all CO₂ that is stripped is transferred back to the absorber.

From the outlet of the absorber the gas enters either the water wash section, or in case this section is bypassed, goes directly to the fan and into the absorber. The fan is dimensioned to overcome the pressure drop in the absorber column and water wash sections. In the water wash section, wash water is circulated from the water tank to the top of the water wash column, and trickles counter currently to the gas downwards to the water tank.

Samples, for liquid analysis to obtain liquid species concentrations, were withdrawn at the inlets and outlets of the absorber and desorber and at the outlet of the reboiler as shown in Figure 2. The concentration of CO₂ was determined in the inlet and outlet gas of the absorber by 2-channel IR analyzers. The CO₂ analysers were calibrated with known mixtures of N₂ and CO₂ on regular basis. The oxygen level was measured at the absorber inlet with a Servoflex 5200 multipurpose oxygen analyser from Servomex (accuracy 0.2%). During this campaign, a factory calibrated portable DX4000 FTIR by Gasmeter was connected to the inlet of the absorber and was mainly used to measure the NO and NO₂ levels.

While running the pilot, the liquid and gas flows, the temperature profiles in the packed columns, the CO₂ concentrations in and out the absorber, the reboiler heat duty and temperatures and pressures in the pipes were all continuously logged. A more detailed description of the plant is found in Tobiesen et al. (2007).

During this campaign, the UV-reactor setup shown in Figure 1 was connected either to the lean solvent outlet from the mixing tank or to the outlet from the mixing tank in the water wash system towards the end of the campaigns. In both cases the liquid was returned to the mixing tank after exposure to UV-light. Since the same UV-reactor setup was used in both the solvent loop and the water wash loop, no experiments were made where UV-light was simultaneously applied to the solvent circulation and the water wash circulation loop. The flow rate through the UV-light reactor was 3 L/min in all the experiments.

Known amounts of NO, NO₂, air and CO₂ were added to the gas leaving the absorber before the fan/water wash column using Bronkhorst HI-TEC mass flow controllers. The mass flow controllers were calibrated before the campaign (estimated accuracy of calibration $\pm 2\%$). A total of 4 mass flow controllers were used,

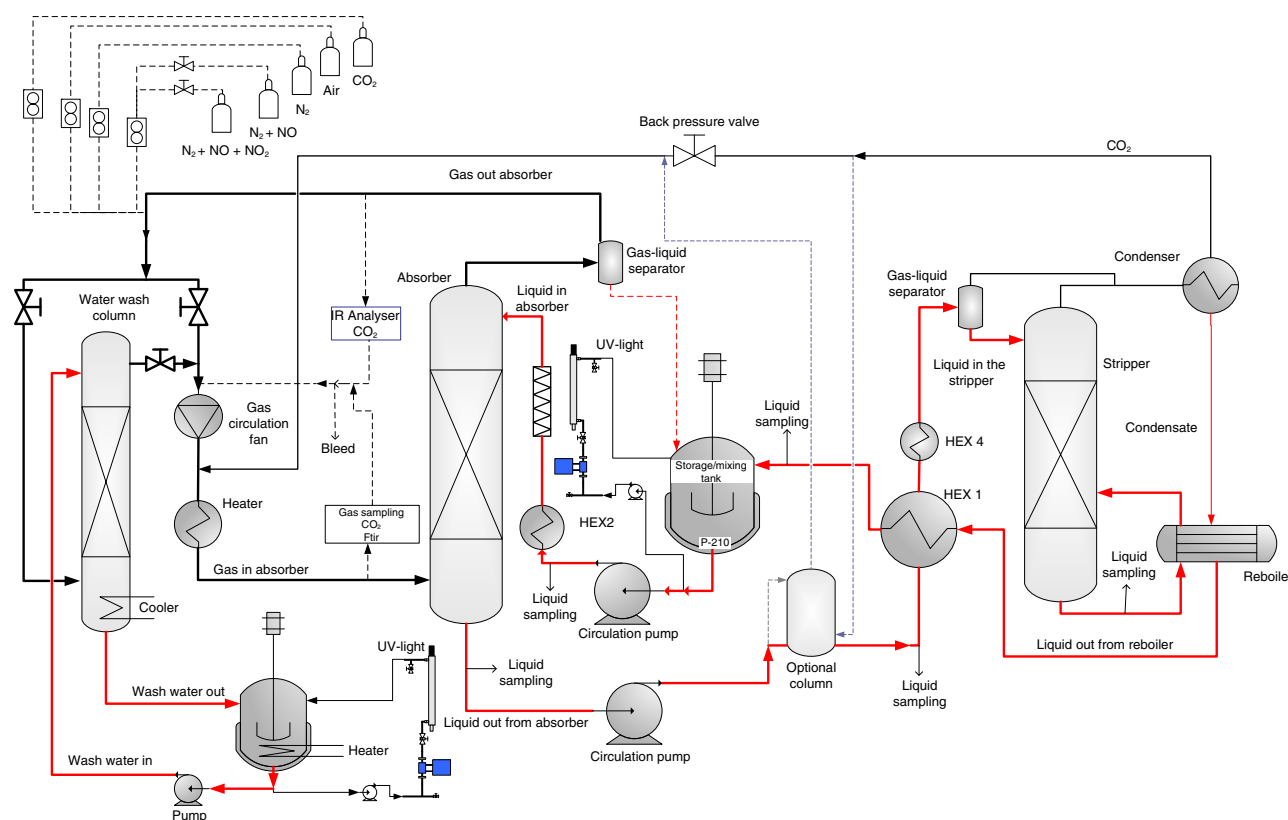


Figure 2

Flow diagram of the modified pilot plant. The UV-light reactor system with a pump, flow meter and UV-light reactor was used. The UV-light reactor system was connected either to the lean amine mixing tank or the water wash loop.

TABLE 2

Brief description of typical process parameters in the used pilot plant

Packing type	
Wash water section	Mellapak250Y
Absorber section	Mellapak250Y
Stripper section	Mellapak250Y
Wash water diameter/height (m)	0.15/2.10
Absorber diameter/height (m)	0.15/4.39
Stripper diameter/height (m)	0.1/3.89
Temperature difference between rich amine inlet and lean amine outlet in LRX	Typically (-6)-(-8)
Reboiler heat duty (kW)	Up to 18 kW
Solvent flow (L/min)	3-9
Gas flow (m ³ /h)	100-150

one for air, one for CO₂ (99.999% pure) and one for N₂ (99.999% pure). The fourth flow controller was used to control the flow of premixed N₂/NO or N₂/NO/NO₂ gas mixtures. The N₂/NO gas mixture contained 1 800 ppm NO (relative uncertainty 2%) mixed with N₂ and the N₂/NO/NO₂ mixture contained 1 800 ppm NO (relative uncertainty 2%) and 200 ppm NO₂ (relative uncertainty 5%). With these flow controllers it was possible to control the amounts of NO, O₂ and NO₂ fed to the system. Small amounts of CO₂ were added to the gas phase to compensate for the CO₂ leaving through the bleed. The amount of O₂ was manually recorded whereas NO and CO₂ levels in the gas phase at the absorber inlet were recorded electronically.

The FTIR was able to measure the amount of NO in the gas phase but did not detect NO₂ in the gas phase during the campaign. This was probably due to the water condensate in the absorber inlet pipe absorbing the NO₂ from the gas phase before the FTIR. When the premixed NO/NO₂/N₂ was feed to FTIR, the FTIR was able to detect the NO₂. However since a ready mixture of

N₂/NO/NO₂ was used together with calibrated flow controllers, it was possible to calculate the amount of NO and NO₂ feed to the system.

1.3 Analytical Methods

The total alkalinity of the solutions was determined by acid titration (0.1 M H₂SO₄) and CO₂ concentrations were measured using the BaCl₂ method (Ma'mun et al., 2007). IC was used to measure nitrite, nitrate and formate with method described in Vevelstad et al., (2013) and LC-MS was used to analyse for DEA, MEA, nitrosamines, HEI, HEF, OZD, HEA, HEPO, HeGly and BHEOX. Methylamine, dimethylamine, ethylamine, diethylamine and ammonia were analysed using GC-MS. More thorough descriptions of the analytical methods for LC-MS and GC-MS can be found in da Silva et al. (2012) and Lepaumier et al. (2011).

2 PILOT PLANT EXPERIMENTS

Two pilot campaigns were run, one with 30 wt% MEA and one with 50 wt% DEA. The main objective of the campaigns was to study the formation and destruction of NDELA with NO and NO₂ present in the gas phase. For that reason the goal was to operate the pilot under stable operating conditions. Both campaigns were divided into three phases:

- the campaigns started with feeding small amounts of NO/N₂ mixture and O₂ to have a NO concentration around 100 ppm and an O₂ level between 5-7 vol% in the gas entering the absorber;
- after some time, the NO/N₂ mixture was switched to a NO/NO₂/N₂ mixture. The goal was to keep the NO level around 100 ppm, which would give NO₂ level of about 11 ppm if the same amount of NO and NO₂ were absorbed. The O₂ feeding was continued;
- in the third phase, the feed of all gases was stopped and the effect of UV-irradiation was measured in the solvent loop during the campaigns. In the 50 wt% DEA campaign, UV-irradiation was also tested in the water wash loop.

During the campaigns the solvent degradation and formation of NDELA was monitored by regular liquid sampling.

2.1 Pilot Operation During 30 wt% MEA and 50 wt% DEA Campaigns

During both of the campaigns the lean solvent flow rate was 3 L/min and the gas flow rate was around 120 m³/h.

The pressure in the stripper and reboiler was held around 2 bara. Typical operating conditions during the MEA and DEA campaigns are presented in Table 3. As seen from the table for MEA, the rate of stripped and absorbed CO₂ was 5.0 kg/h giving a heat demand of 4.49 kJ/kg. This is in very good agreement with previous MEA campaigns performed in the same pilot (Tobiesen et al., 2008). In Figure 3, the temperature profiles in the stripper and absorber are presented for the conditions presented in Table 3. During the MEA campaign, some adjustments to both reboiler duty (varied from 3 kW to 7 kW) and lean loading were made due to operational problems. However the data presented in Table 3 gives a good picture of the operational conditions during the campaigns. During the DEA campaign, there were no operational problems.

The 30 wt% MEA solution used in this campaign was previously used for 700 hours in the same pilot. During those 700 hours no NO, NO₂ or O₂ was added to the system. In the present campaign, 30 wt% MEA was tested in the lab pilot for 990 hours as shown in Table 4. During the first 670 hours of the campaign, only NO and O₂ was added to the gas as shown in Figure 4. During this time, the NO feed was on for 528 hours. Starting from campaign hour 674, a pre-mixed gas containing both NO and NO₂ was fed into the gas phase until campaign hour 890 as can be seen in Figure 4. During this time, both NO and NO₂ were fed for 187 hours. The objective of the combined NO and NO₂ feeding was to monitor the formation of nitrosamines and degradation products. After 890 campaign hours, the NO, NO₂, O₂ feeds were stopped and the UV-light reactor was connected to the lean solvent mixing tank for UV-light tests.

The lab pilot campaign with 50 wt% DEA was similar to the MEA present campaign where lab pilot was operated for 990 hours. However, the DEA campaign lasted only 410 hours. As for the MEA campaign, the DEA campaign was started by feeding small amounts of the NO + N₂ mixture as well as O₂ and CO₂ to the gas phase. After 150 hours of NO + N₂ feed, the feed was switched to a mixture of NO + NO₂ + N₂ as shown in Table 4. The 50 wt% DEA solution was exposed to NO₂ for 100 hours. The NO and NO₂ feed as a function of campaign hours is shown in Figure 4b. After the NO and NO₂ feeds were stopped UV-radiation was tested for NDELA degradation.

The total amount of gas added to the system was between 1-1.5 L/min and assuming that the system was completely closed and stable, the added amount would only leave through the system bleed. Based on the mass flow controller and the composition of the added

TABLE 3
Typical operational parameters during MEA and DEA campaign

		30 wt% MEA (27.4.2011)	50 wt% DEA (24.5.2011)
Absorber			
<i>Flow conditioning column</i>			
Gas	(m ³ /h)	120	110
Liquid	(L/min)	3	3
Superf. velocity inlet ABS	(m/s)	1.9	1.8
Gas load	(m ³ /m ² , h)	6 800	6 230
Liquid load	(m ³ /m ² , h)	10	10
Gas/liquid ratio		666	610
Absorbed CO ₂	(kg/h)	5.0	4.2
<i>Pressure</i>			
P _{gas} upstream Fl.meter (a)	(kPa a)	107	103
<i>Concentration liquid</i>			
Amine group	(mole MEA/L)	5.6	5.0
Lean loading	(mole/mole)	0.35	0.17
Rich loading	(mole/mole)	0.45	0.26
<i>Concentration gas</i>			
CO ₂ inlet	(vol% dry)	8.2	8.4
CO ₂ outlet	(vol% dry)	5.4	6.0
CO ₂ inlet	(vol% wet)	6.9	7.7
CO ₂ outlet	(vol% wet)	4.6	5.5
<i>Temperature</i>			
Gas inlet	(°C)	55	49
Gas outlet	(°C)	57	45
Liquid inlet	(°C)	41	38
Liquid outlet	(°C)	54	48
Reboiler			
Reboiler duty	(kW)	6.8	5.6
<i>Temperature</i>			
T-06 (R-solvent downstream EX01)	(°C)	109	108
T-07 (R-solvent inlet DES)	(°C)	106	105
T-09 (DES, swamp, L-solvent outlet)	(°C)	110	106
T-11 (steam out DES)	(°C)	103	100

(continued)

TABLE 3 (continued)

		30 wt% MEA (27.4.2011)	50 wt% DEA (24.5.2011)
TK (overflow L-solvent reboiler)	(°C)	116	113
T-14 (steam reboiler)	(°C)	116	113
<i>Flow</i>			
Flowrate condensate (Coriolis)	(kg/h)	2.48	1.80
Reflux ratio	(kg H ₂ O/kg CO ₂)	0.45	0.48

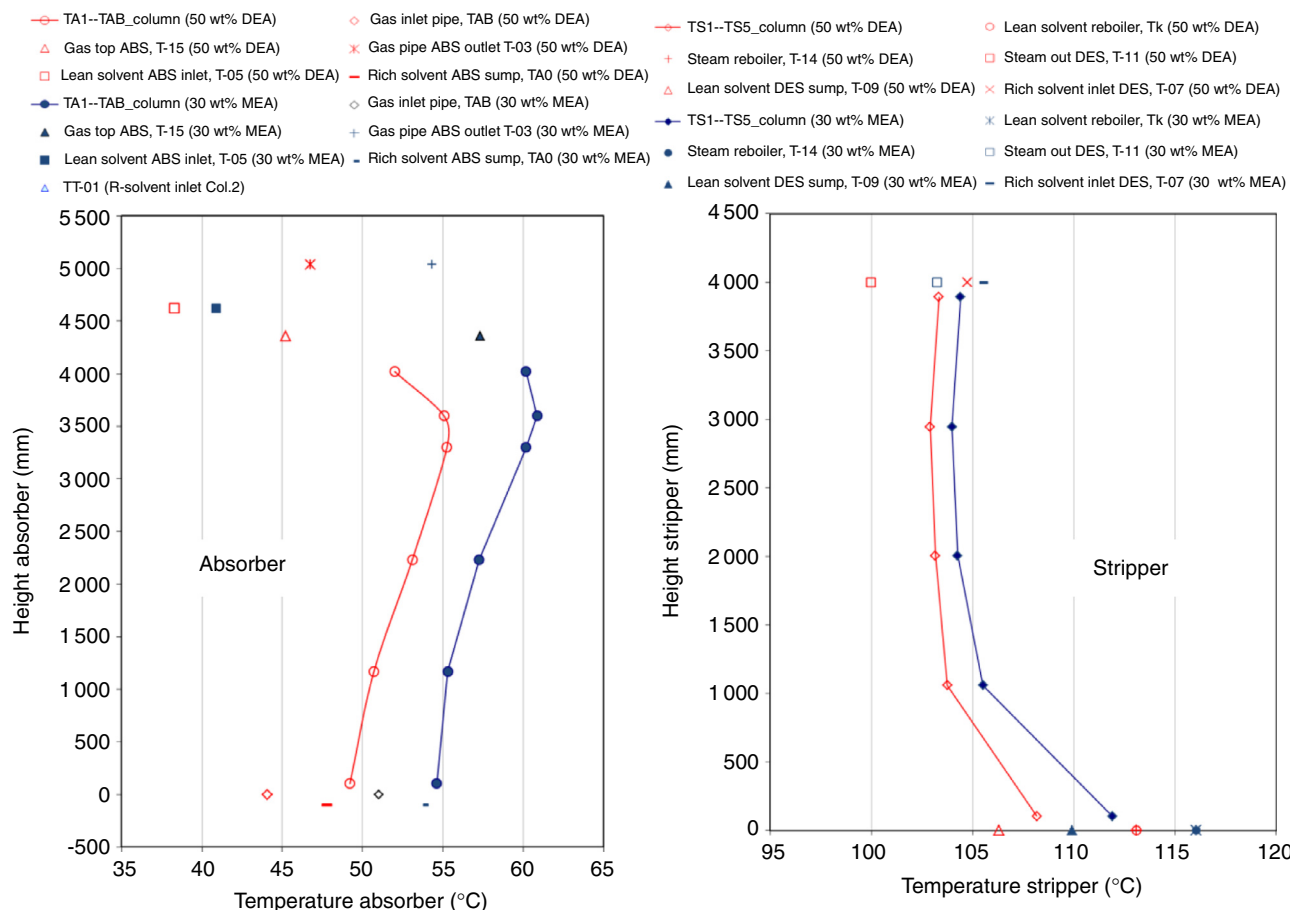


Figure 3

The temperature profiles in the absorber and stripper during 30 wt% MEA on (in blue) and 50 wt% DEA campaigns on (in red).

N₂ + NO and N₂ + NO + NO₂ gas mixtures provided by the supplier, the amount of added NO and NO₂ could be calculated.

During the 30 wt% MEA campaign, the NO concentrations measured were between ~70-110 ppm (dry) in the absorber inlet. The oxygen level at the absorber inlet

TABLE 4
Basic information about the 30 wt% MEA and 50 wt% DEA pilot campaigns

	30 wt% MEA	50 wt% DEA
Campaign duration (h)	990	410
NO feed (actual feeding hours) (h)	715	250
NO ₂ feed (actual feeding hours) (h)	187	100
UV-light radiation in the main solvent circulation (h)	37	48
UV-light radiation in water wash section (h)	-	5

varied from 5 to 10 vol% (dry). During DEA campaign the NO concentration at the absorber inlet was ~110 ppm (dry), whereas the oxygen level decreased during the first 70 campaign hours from above 10 to 6 vol% (dry). After that the oxygen level stayed at a very constant level around 5.5 vol% (dry).

3 RESULTS FOR THE 30 WT% MEA CAMPAIGN

3.1 Solvent Degradation During 30 wt% MEA Campaign

Degradation of the solution was monitored during the whole campaign by taken liquid samples regularly. The liquid samples were analysed with IC and LC-MS. The analysed concentrations of HEI, HEF, OZD, HEA, HEPO, HeGly and BHEOX during the campaign are shown in Figure 5. From the figure it can be seen that the solvent was partially degraded from the campaign start because of the earlier use for approximately 700 hours where no NO/NO₂ was added to the system. The results at 0 hours thus show the degradation products accumulated without NO/NO₂ in the gas phase after approximately 700 hours. It can be seen that the order of these degradation products with respect to relative amounts formed, does not seem to be affected by the NO and NO₂ addition. The DEA concentration was quite stable over the whole campaign as seen from Figure 6. Additionally, from Figure 6 it can be seen that the formate and nitrate concentrations increased throughout the campaign. Formate is a degradation product and also a reactant further to HEF. The formate concentration is clearly increasing during the UV-radiation of 34 hours (campaign hours from 958 to 992). The nitrate concentration seems to be slowly increasing. Nitrate concentration in lean amine sample withdrawn after the mixing tank and sample withdrawn at UV-reactor outlet seems to increase during the 34 hour UV-radiation (sample at 958 and 992 hours). Nitrite concentration was below detection limit throughout the campaign.

Selected samples were also analysed for methylamine, dimethylamine, ethylamine and diethylamine, from which only methylamine was detected in mg/L whereas ammonia, another volatile degradation compound, was detected at 200 times higher concentrations.

Based on analysis of LC-MS scan N-(2-hydroxyethyl)-ethylenediamine (HEEDA) and 1-(2-Hydroxyethyl)-2-imidazolidinone (HEIA) were identified based on mass and retention time. These compounds have been previously reported by da Silva *et al.* (2012) to be formed in thermal degradation experiments. Similarly, 2-(2-hydroxyethylamino)-2-oxoacetic acid (HEO) has been reported by da Silva *et al.* (2012) and a peak at the right mass was also seen in the scans.

The samples were also analysed for following nitrosamines: NDMA, NDEA, NPIP, NMEA, NPYR, NMOR, NDPA, NDPA and NDELA. During addition of NO gas, no formation of NDELA or any other nitrosamine was detected. After combined NO and NO₂ addition 230 ng/mL of NDELA was detected (*see Sect. "Formation of NDELA"*). The other nitrosamines (NDMA, NDEA, NPIP, NMEA, NPYR, NMOR, NDPA and NDPA) were not detected. However, total nitrosamine after 940 hours was analysed externally by Henkel AG & Co with a method described in Langenohl *et al.* (2011) and it showed much higher nitrosamine concentration than that of NDELA. This indicates that unknown nitrosamines were present. This agrees with Einbu *et al.* (2012) who reported that only few percent of nitrosamines present during their tests were found to be NDELA.

Formation of NDELA

The formation of NDELA during the campaign is presented in Figure 7. Additionally in the figure, the accumulative amounts of NO and NO₂ are presented. During NO feeding the NDELA concentration was below the Limit Of Quantification (LOQ).

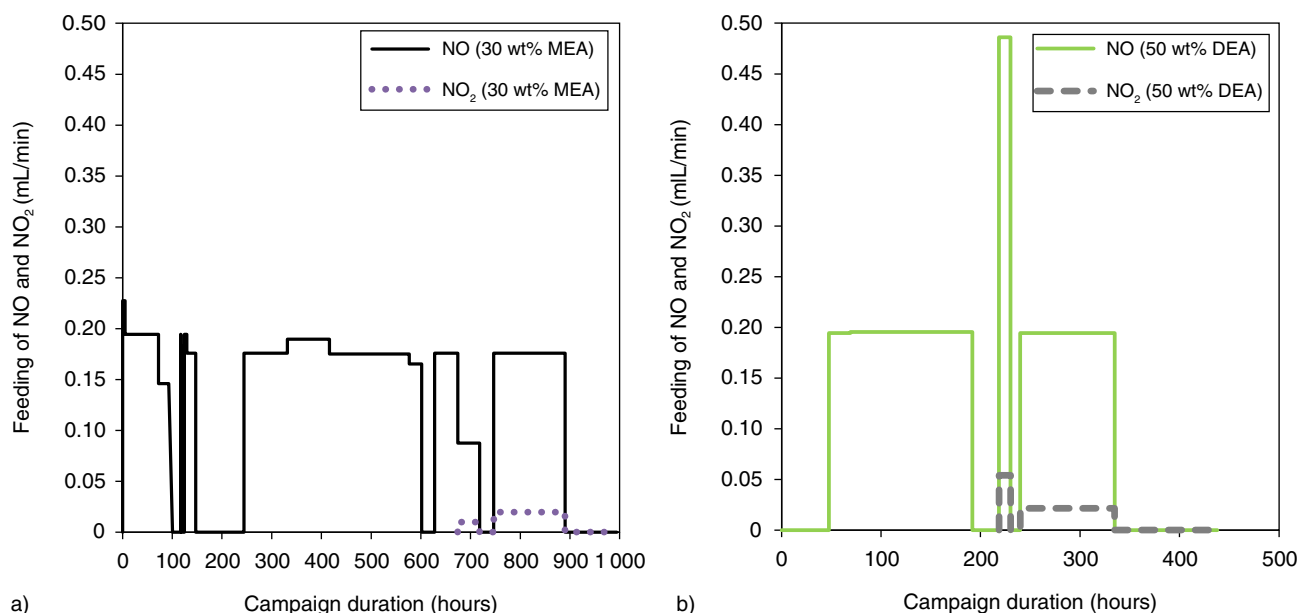


Figure 4

Added NO and NO₂ during a) 30 wt% MEA and b) 50 wt% DEA campaigns. Oxygen was added at the same times, when NO and/or NO₂ was added.

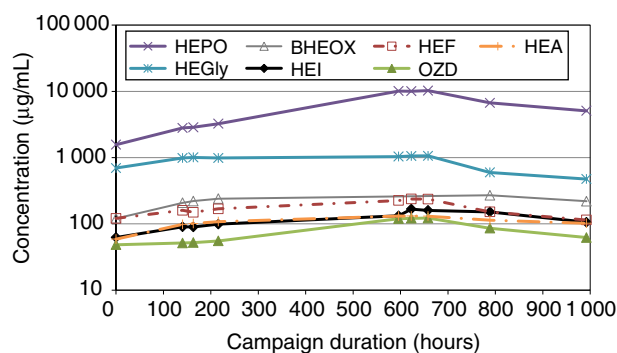


Figure 5

Concentration of degradation products during MEA campaign.

After 660 campaign hours the NO₂ feeding was started (NO and O₂ feed were continued) and after 740 campaign hours NDELA was detected at a concentration of 1.7 nmol/mL (230 ng/mL). Pedersen *et al.* (2010) reported a NDELA concentration of 500 ng/g solvent after 95 hours with NO_x levels of 25-50 ppmv. They did not report what was the NO/NO₂ ratio during the tests. Even though the results are not exactly the same,

they are of the same order of magnitude and considering that experimental conditions were different, the results agree reasonable well with each other. After 890 hours the solution was spiked with NDELA to ensure high enough NDELA concentrations during the UV-light tests (shown with a black line) and the feed of NO, NO₂, O₂ and CO₂ were stopped.

3.2 Destruction of NDELA with UV-Light

As mentioned above, after 890 hours the solvent was spiked with NDELA to increase the concentration with ~300 ng/mL_{solution} of NDELA (2.24 nmol/mL) to ensure high enough NDELA concentration for UV-light tests. At campaigning hours between 932 and 935, the circulating solution was exposed to UV-light for 3 hours. The start NDELA concentration was 550 ng/mL. Three sampling points were used: one at the UV-reactor inlet, one at the UV-reactor outlet and the third sampling was the return of lean solvent from the reboiler. The sampling points before and after the UV-light reactor tell about the effect of UV light whereas the out of reboiler sample tells more how the UV-light effects the NDELA concentration in the amine solution in the whole pilot. However 3 hours of UV-radiation had no significant effect on the NDELA concentration in the solution. Therefore a longer UV-light campaign was started two

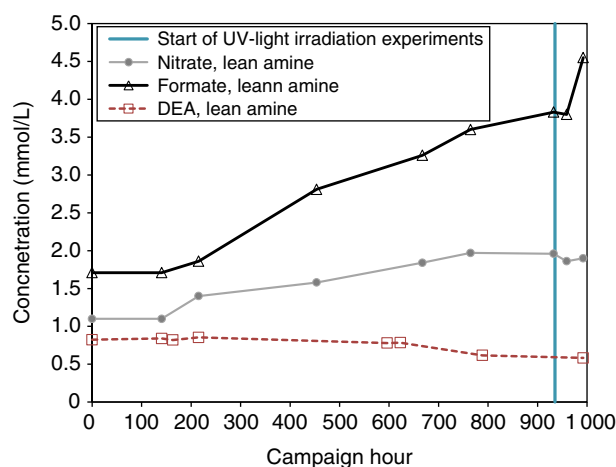


Figure 6

Concentration of DEA, formate and nitrate during 30 wt% MEA campaign. The measurement at campaign hour 932, is a lean solvent after first 3 hours of UV-irradiation; the sample at campaign hour 958 is taken just before starting the second UV-irradiation and the sample at campaign hour 992 is taken after 34 hours of UV-radiation.

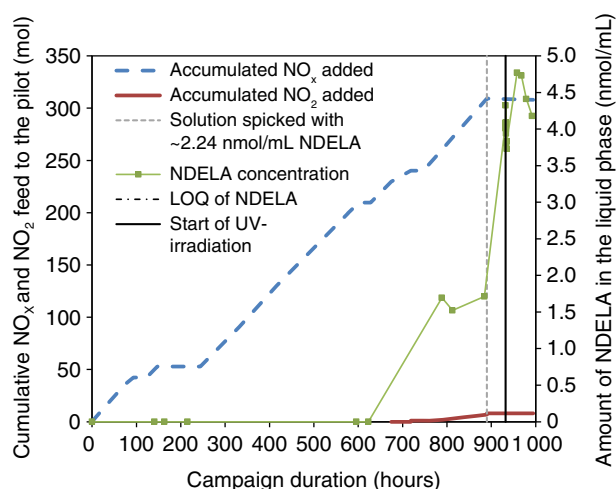


Figure 7

Cumulative NO and NO₂ feed together with NDELA concentration during the 30 wt% MEA campaign. For the first 660 hours, the concentration of NO_x is only NO since no NO₂ is added.

days later. This time the UV-light was on for 34 hours and from Figure 8, it can be seen that the concentration of NDELA decreased approximately 10%. Additionally it can be seen from the results that the NDELA concentration after the UV-light reactor is very close to the NDELA concentration entering the UV-light. This indicates that the UV radiation was not very effective. Interesting point here is also that at the start of the first UV

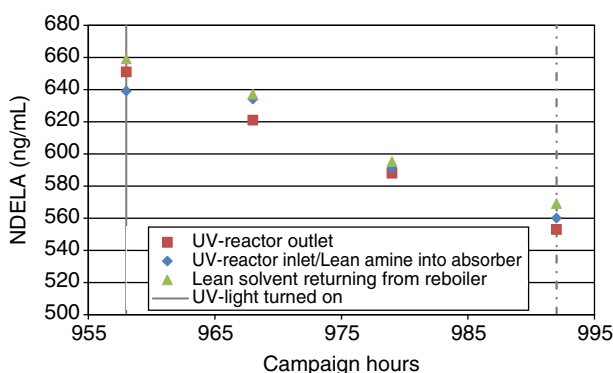


Figure 8

NDELA concentration during the 34 h UV-radiation.

campaign the NDELA concentration was 550 ng/mL where as two days later the concentration was 640–660 ng/mL. However NO and NO₂ feed to the system was turned off two day before both of these tests. This indicated that the reactions towards NDELA continued after feeding of NO and NO₂ is stopped. One final remark is that the first samples (956 hours) for the long term UV-radiation tests should be equal. The analytical results vary from 639 to 659 ng/mL which are within 3%. This value indicates a good analytical accuracy.

During the long term radiation the destruction of NDELA seems to be 0-order reaction. The solvent in the pilot campaign was coloured and had a low penetration depth throughout the campaign (below 0.5 cm). The low penetration depth can also explain why short time irradiation of UV-light did not degrade NDELA significantly. The short penetration depth can explain why we see 0-order reaction. NDELA had a limited access to UV-light and the light was absorbed by other components in the solution. This is in line with results from Knuutila *et al.* (2012) with fresh and used MEA solutions, where 1st order reaction behaviour was seen in fresh solutions but where coloured solutions would exhibit 0th-order behaviour. In Knuutila *et al.* (2012), the total liquid amount was ~30 L, where in the pilot plant there is around 180 L of solvent. In this paper and in Knuutila *et al.* (2012), the same UV-reactor and same liquid flow was used. So during the pilot campaign the solvent passed the UV-reactor once an hour (since also the solvent circulation rate was 3 L/min) whereas in the batch scale experiments presented in Knuutila *et al.* (2012) the 30 wt% MEA passed the UV-reactor every 10 minutes. This difference can also explain some of the difference in the degradation rates between Knuutila *et al.* (2012) and this work.

In the literature, nitrite and nitrate has been reported to be formed during decomposition of NDMA (Plumlee and Reinhard, 2007; Lee *et al.*, 2005). In this work, the amount of degraded NDELA during the 34 hour UV-light campaign was 0.59 nmol/mL (from 639 ng/mL to 560 ng/mL). Even if all this amount would give nitrate, the 0.59 nmol/mL is too small to be seen in the nitrate concentration shown in Figure 6, when comparing to the increase in nitrate seen throughout the campaign.

4 PILOT TESTS WITH 50 WT% DEA

4.1 Solvent Degradation During 50 wt% DEA Campaign

During the DEA campaign, some liquid samples were analysed for degradation products using LC-MS. The results are shown in Figure 9. The concentration of NDELA is also shown in Figure 9. The decrease in the NDELA concentration from 70 to 22 $\mu\text{g/mL}$ from 337 to 385 hours is due to the UV-radiation, which will be discussed more detailed in the next chapter. From the figure, it can be seen that NDELA is the most common degradation compound from those that were analysed followed by HEPO, HEGly and BHEOX. NDELA was below LOQ (50 ng/mL) before the campaign, but already after 150 hours, the concentration was 24 $\mu\text{g/mL}$. The samples were also analyzed for other nitrosamines (NDMA, NDEA, NPIP, NMEA, NYPR, NMOR, NDPA and NDBA) but all concentrations were below the detection limit. Formate was below LOQ in all samples analysed. Nitrate was detected only in the sample taken after UV-light campaign (after 385 campaign

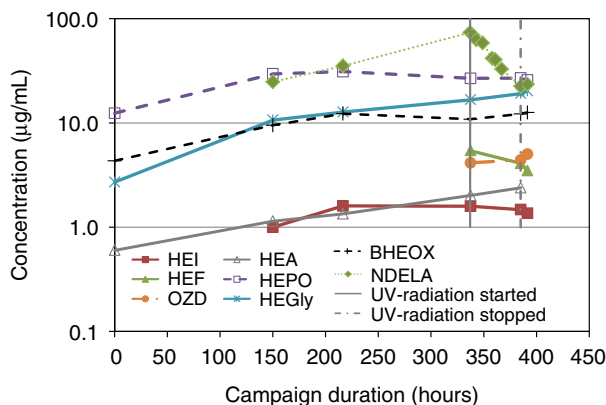


Figure 9

Formation of degradation products as a function of campaign hours. After campaign hour 385 the UV-irradiation was connected to the water wash system and no samples from the main loop were analysed for degradation after that.

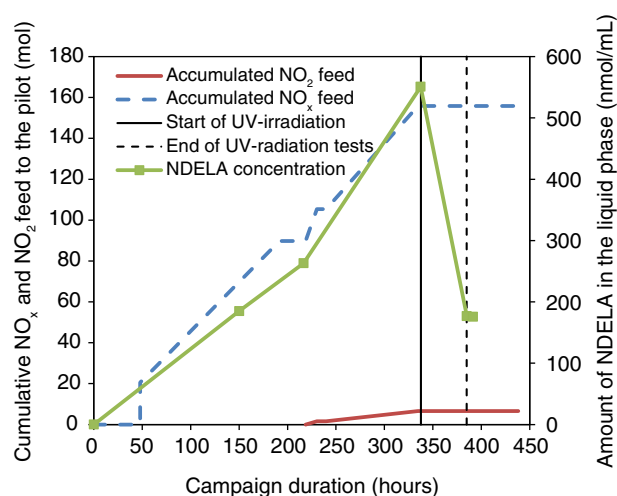


Figure 10

Cumulative NO_x and NO_2 feed (on the left hand axis) together with NDELA concentration (on the right hand axis) during 50 wt% DEA campaign. For the first 220 hours the concentration of NO_x is only NO since no NO_2 is added.

hours). HEI was below limit of quantification (LOQ = 1 $\mu\text{g/mL}$) until 150 hours. OZD and HEF were below LOQ (LOQ = 1 $\mu\text{g/mL}$) until 337 hours.

Formation of NDELA

The accumulative amounts of NO and NO_2 feed into the system together with the formation of NDELA during the campaign are presented in Figure 10. The figure clearly shows that the NDELA started to form already during the NO feeding and after 220 hours the NDELA concentration was 260 nmol/mL. During the 30 wt% MEA campaign, no NDELA was detected during 660 hours of NO feeding. The reason is likely to be the very different DEA concentrations (5 000 mmol/L in DEA campaign, and 0.6 mmol/L in MEA campaign, since NDELA is formed from DEA. After 220 hours feeding of NO_2 and NO was started. The formation of NDELA continues to increase. It is however difficult to conclude based on the data, if the formation rate of NDELA increased during feeding of NO/ NO_2 mixture.

4.2 UV-Light Tests with 50 wt% DEA

The UV-light reactor was connected to the solvent mixing tank in the same manner as during the MEA campaign. The liquid flow rate through the UV-light reactor was 3 L/min and the total experimental time was 48 hours. Since the NDELA concentration was

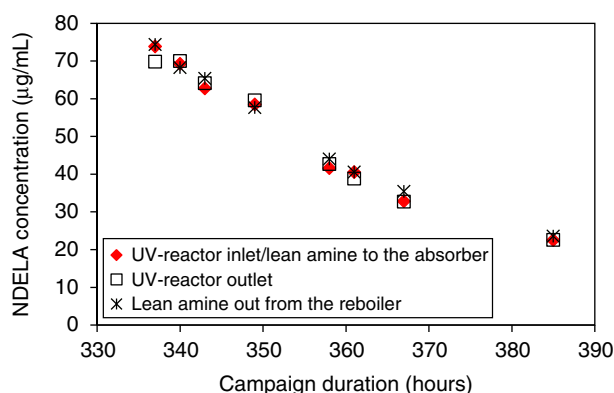


Figure 11

NDELA concentration during UV-radiation.

not known before starting the UV-light tests, the solution was spiked with NDELA. The concentration that would have been reached with the spiked NDELA was estimated to ~ 0.3 $\mu\text{g/mL}$. After the first UV-light campaign, the NDELA concentrations for the whole campaign were analysed and it was found that the starting concentration was 70 $\mu\text{g/mL}$ from which 0.3 $\mu\text{g/mL}$ was spiked NDELA. The decomposition of NDELA during the UV-radiation campaign is shown in Figure 11.

During 48 hours approximately 70% of the NDELA was decomposed. This is much faster than with MEA. The penetration depth of the 50 wt% DEA solution was below 0.5 cm and very close to that of 30 wt% MEA during the MEA campaign. However visual comparison of the MEA and DEA solution showed a colour difference, with 30 wt% MEA being much darker colour. Maybe, the fact that the NDELA concentration during the DEA campaign was more than 10 times higher, could be part of the explanation, why degradation of NDELA was faster in DEA solution.

Before UV-light was started no nitrite or nitrate were detected with IC analyses. After the UV-light campaign in the lean amine sample 0.43 mmol/L of nitrate was detected. This value is very close to the limit of quantification and samples taken from other parts of the pilot were below LOQ. During the UV-light campaign and concentration of NDELA decreased from 74 to 22.5 $\mu\text{g/mL}$ which corresponds to 0.4 mmol/L, which is close to the value of nitrate found in the solution. It could be speculated if this detected nitrate is due to the decomposition of NDELA into nitrate. Nitrate and nitrite have been reported in literature to be formed under NDMA photodegradation in weakly acidic water solution (Plumlee and Reinhard, 2007). However literature findings also suggest

that in alkaline solutions, other inorganic nitrogen products than nitrate and nitrite like N_2 and N_2O are formed (Xu *et al.*, 2009a; Stefan and Bolton, 2002).

During the pilot campaigns, the penetration depth for both of the amine solutions was low, and even during 50 wt% DEA campaign which was started with fresh 50 wt% DEA the penetration depth was around 0.5 cm after 180 hours of running. The low penetration depth can explain the slow degradation of NDELA in the DEA solution. The results are similar to those reported in Knuutila *et al.* (2012) where the 50 wt% DEA was tested in a batch reactor was tested and the decomposition of NDELA was found to be slow.

UV-Light in the Water Wash Circulation

The effect of UV-light in the water wash section was tested at the end of DEA campaign. One day before the experiment the water wash section was spiked with a small amount of DEA and NDELA solution to ensure an NDELA concentration that could be detected by LC-MS and also to have DEA concentration representative of what can be expected in a water wash, about 0.5 wt%. The UV-light was connected to a mixing tank as shown in Figure 2 and the liquid flow through the UV-light reactor was approximately 3 L/min. The total amount of liquid in the water wash section is approximately 35 L.

The decomposition of NDELA is shown in Figure 12. The destruction of NDELA in the water wash solution is much faster compared to destruction rates found in the solvent loops. Here, the NDELA concentration decreases from 360 ng/mL to 6 ng/mL in 90 minutes. This can be explained by the colourless solution and low amine concentration which both decreases the

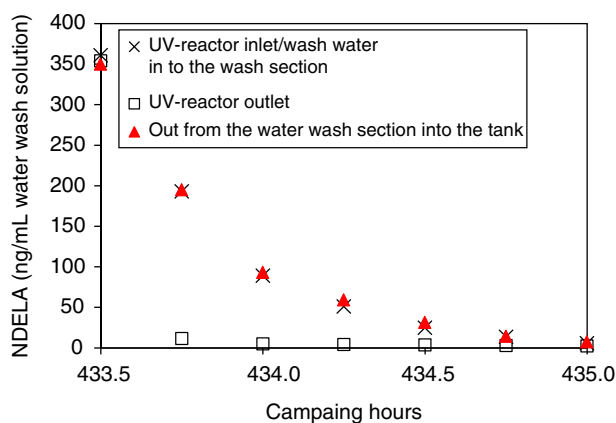


Figure 12

NDELA concentration in the water wash circulation loop during the UV-light reactor experiment.

penetration depth and thereby also the effect of the UV-light (Knuutila *et al.*, 2012). From the results with UV-irradiation, one can see that when the solution goes through the UV-light reactor, almost all the NDELA is decomposed during one pass through. Additionally the destruction seems to be 1st order in respect to NDELA. These results clearly indicate that the use of UV-light is much more efficient in the water wash section compared to the solvent loop.

5 THERMAL DEGRADATION OF NDELA

Pilot solutions after the 30 wt% MEA and 50% DEA campaigns were tested for thermal degradation. Thermal degradation metal cylinders (316 stainless steel tubes) were used. The cylinders were filled with the end solutions from 30 wt% MEA and 50 wt% DEA and closed in a glove box under a nitrogen atmosphere. For each experiment 10 cylinders were prepared. To check for leakages, the cylinders including solution were weighed before and after the experiment.

The cylinders were stored in a thermostatic chamber at an upright position at 135°C and were not moved or agitated until sampled. Every week, 2 cylinders with 30 wt% MEA and 50 wt% DEA were sampled. The solution was analysed to determine the degradation of NDELA, MEA and DEA and the concentration of nitrate, nitrite, formate, HEA, HEI, HEPO, OZD, HEF, BHEOX and HeGly. The total experimental time was 5 weeks. Cylinders opened for sampling were not returned to the chamber. Parallel cylinders removed from the thermostatic chamber day 21 and 35 were both analysed. From other samplings days only one cylinder was sent to analyses.

5.1 Experiment with MEA Taken from the Pilot

The MEA solution was analysed for amine and CO₂ before starting the experiments. The amine concentration was 28 wt% and loading was 0.35 mol_{CO₂}/mol_{amine}. The concentration of MEA during the thermal degradation tests are shown in Figure 13. It can be seen that the MEA concentrations decreases from 5 to 2.88 mol/L, which equals a 43% loss of MEA. This is quite similar to the results presented by da Silva *et al.* (2012). Additionally it can be seen that DEA concentration increases throughout the experiment, which was expected since DEA is a known product of MEA degradation (Fostås *et al.*, 2011). In Figure 14, the NDELA concentration is shown to decrease under quantification limit (100 ng/mL) during the first week and it stays under limit of quantification until the end of the experiment.

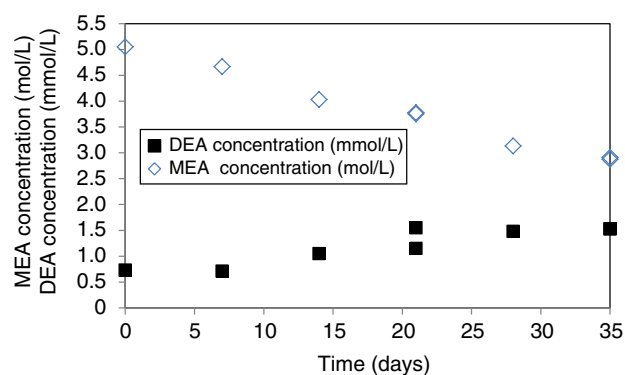


Figure 13

Concentration of MEA and DEA during thermal degradation test with 30 wt% MEA previously used in a pilot plant.

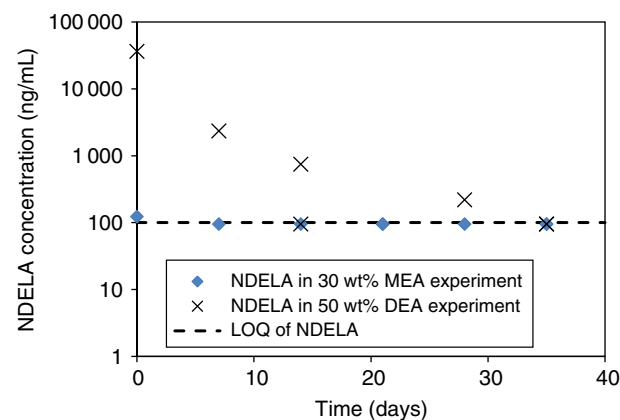


Figure 14

NDELA concentrations during MEA and DEA experiments. NDELA concentrations below 100 ng/mL are under quantification limit.

HEPO, HEA, HEF and HEI, concentrations stayed constant during the experiment whereas the HeGly decreased throughout the experiment. HEA, HEF, HEI and OZD were detected at levels of hundreds of µg/mL, while HEPO concentration was 10 times higher compared to HEA, HEF and HEI. The concentration of formate, doubled during the experiment ending up to 0.6 g/kg_{solution}. Nitrate, nitrite and oxalate were only detected in the original sample (day 0), but the concentrations were too low to be quantified.

Thermal degradation of DEAThermal degradation of DEA

The DEA previously used in the pilot was analysed for amine and CO₂ loading prior the experiment. The

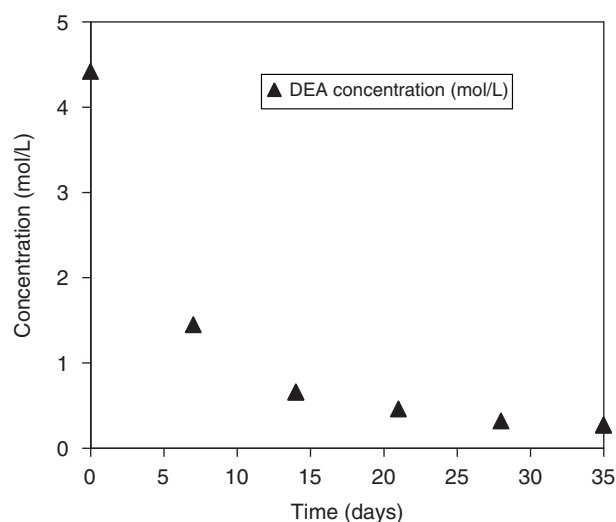


Figure 15

Concentration of DEA during thermal degradation test with 50 wt% DEA previously used in a pilot plant.

DEA concentration was 48.5 wt% and loading was $0.16 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{amine}}$. DEA degraded almost fully (93%) during the thermal degradation experiment as shown in Figure 15. This is in a good agreement with results from Eide-Haugmo (2011) who found that 96% of DEA degraded during thermal degradation tests with fresh DEA at a CO_2 loading of $0.5 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{amine}}$. The concentration of NDELA is shown in Figure 14. From the figure, it is clear, that NDELA decomposes at 135°C . After one week, the concentration of NDELA comes down from 36 000 ng/mL to 2 400 ng/mL and after 4 weeks, the concentration is down to 280 ng/mL and after 5 weeks, it is below the limit of quantification (100 ng/mL).

HEPO was detected at levels of few hundred micrograms/mL and HeGly concentration was around 4 times smaller compared to HEPO. The concentrations of HEA and HEF were below the limit of quantification (10 $\mu\text{g/mL}$), except for the first sample for HEA and last sample of HEF which were just above it. OZD, HEI and BHEOX (10, 10 and 100 $\mu\text{g/mL}$, respectively) were below the limit of quantification throughout the experiment. Similarly as with MEA, the analysed amount of formate increased throughout the experiment ending up to 500 $\mu\text{g/g}_{\text{solution}}$. Oxalate and nitrate were detected in the start sample, but the concentrations were below limit of quantification. Nitrite was not detected at all.

CONCLUSIONS

During the pilot campaigns UV-destruction was tested for both 30 wt% MEA solution and 50 wt% DEA

solution. In both cases, the UV-light was working, even though the rate of decay was low. For the DEA solution the decrease in NDELA concentration was higher compared to 30 wt% MEA campaign. This is believed to be related to the high NDELA concentration during the DEA campaign. The small scale experiments presented in Knuutila *et al.* (2012) support and agree well with the pilot results.

During 50 wt% DEA campaign destruction of NDELA in water wash loop was found to be fast. 98% of NDELA decomposed during 90 minutes of UV-irradiation. This is much faster compared to the UV-irradiation tests done in the solvent loop indicating the optimal location for UV-radiation would be in the water wash section. However, it should be remembered that the destruction rates are dependent on the nitrosoamine (Knuutila *et al.*, 2012; Plumlee and Reinhard, 2007; Xu *et al.*, 2009b) and in this work, only NDELA was tested.

During the pilot campaign, the formation of nitrosamines was also studied. From the nitrosamines analysed, only NDELA was detected. During the MEA campaign 660 hours of NO feeding did not give a detectable NDELA concentration. After, this NO and NO_2 were added for 100 hours, and the NDELA concentration rose to around 220 ng/mL. During the DEA campaign, the NDELA started to form already during NO feeding and no change in the formation rate was seen when the solvent was exposed to both NO and NO_2 . In total, after 250 hours of NO_x feed, the NDELA concentration was 70 $\mu\text{g/mL}$. Other degradation products were also monitored. The relative order of the analyzed degradation compounds analyzed during the 30 wt% MEA and 50 wt% DEA campaigns did not depend on the presence of NO and NO_2 in the gas phase.

The thermal degradation experiments done with degraded MEA and DEA solutions at 135°C , showed that NDELA degrades at high temperatures.

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Manuscript accepted in July 2013
Published online in October 2013

APPENDIX

ABBREVIATIONS AND CAS-NUMBERS

BHEOX	<i>N'</i> -bis(2-hydroxyethyl)oxalamide	1871-89-2
DEA	Diethanolamine	111-42-2
DMA	Dimethylamine	124-40-3
HEA	<i>N</i> -(2-hydroxyethyl)acetamide	142-26-7
HEEDA	<i>N</i> -(2-hydroxyethyl)ethylenediamine	111-41-1
HEF	<i>N</i> -(2-hydroxyethyl)formamide	693-06-1
HeGly	<i>N</i> -(2-hydroxyethyl) glycine	5835-28-9
HEI	<i>N</i> -(2-hydroxyethyl)imidazole	1615-14-1
HEIA	<i>N</i> -(2-hydroxyethyl)imidazolidinone	3699-54-5
HEO	2-(2-hydroxyethylamino)-2-oxoacetic acid	5270-73-5
HEPO	4-(2-hydroxyethyl)piperazin-2-one	23936-04-1
MEA	Monoethanolamine	141-43-5
MNPZ	<i>N</i> -Nitrosopiperazine	5632-47-3
NDBA	Nitrosodibutylamine	924-16-3
NDEA	<i>N</i> -Nitrosodiethylamine	55-18-5
NDELA	<i>N</i> -Nitrosodiethanolamine	1116-54-7
NDMA	<i>N</i> -nitrosodimethylamine	62-75-9
NMEA	Nitrosomethylethylamine	10595-95-6
NMOR	Nitrosomorpholine	59-89-2
NPIP	<i>N</i> -Nitrosopiperidine	100-75-4
NPYR	<i>N</i> -Nitrosopyrrolidine	930-55-2
OZD	2-oxazolidinone	497-25-6
PZ	Piperazine	110-85-0