Decomposition of nitrosamines in aqueous monoethanolamine (MEA) and diethanolamine (DEA) solutions with UV-radiation

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Abstract

CO_2 capture based on chemical absorption using amine solutions is considered to be the most feasible way to remove CO_2 from low pressure sources. However, amines, when exposed to nitrous oxides, may form nitrosamines which are known to be carcinogenic. In this work the destruction of two nitrosamines, NDELA (Nitrosodiethanolamine) and NDMA (Nitroso-dimethylamine), with UV-light is studied in a batch reactor at room temperature and at 45°C. Additionally, the effect of UV-light on the degradation of MEA is investigated.

The results from this project clearly show that the rate of UV-induced decay of NDMA and NDELA are different. Additionally the efficiency of UV-light for decomposition of NDMA and NDELA depends on the type of solution. In dilute amine solutions (water wash solutions), the decay is much faster compared to more concentrated solutions. Colouring of the solutions, caused by degradation products, was found to decrease the effect of UV-light dramatically. A dynamic model for the reactor setup used is developed and used for interpretation of the results. In all solutions the decay was found to be 1st order with respect to NDELA and NDMA concentrations.

INTRODUCTION

Global warming caused by anthropogenic CO_2 emissions is one of the most severe problems at present. Carbon Capture and Storage may offer a route to significantly reducing these emissions, and of the capture technologies, reactive absorption seems to be the most viable option. However, in order to put absorption processes in operation 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 decades. One of the most used amines, MEA, has been a popular reagent for capturing of CO_2 from slip streams from power plant exhaust gases, e.g. the Warrior Run plant with ABB-Lummus technology (Kohl and

Nielsen, 1997). Formation or emission data for nitrosamines from these plants have not been reported in the open literature.

Formation of nitrosamines in laboratory MEA based absorption processes has been reported by several authors like Pedersen et al. (2010), Einbu et al. (2013) and Knuutila et al. (2013a). All of the authors reported formation of NDELA (Nitrosodiethanolamine) in the process. Additionally NHEGly (nitroso-(2-hydroxyethyl)-glycine)(Einbu et al., 2013), NDMA (nitrosodimethylamine) (Pedersen et al. 2010, Einbu et al., 2013) and NMOR (nitrosomorpholine)(Pedersen et al., 2010) have been identified.

Since most nitrosamines have low volatility, when formed in the plant they will tend to stay mainly in the solvent loop. However, even non-volatile nitrosamines have been detected in the gas leaving the water wash section located above the absorber (Kolderup et al., 2012). These measurements were performed in a research pilot that was not designed to minimize nitrosamine or amine slip, but 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. Direct UV radiation could be an option to destroy nitrosamines in both the solvent and water wash liquids. Jackson and Attala (2012) have a patent on treating an amine solvent with UV-radiation.

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. The nitrosamine most frequently studied in water treatment is NDMA. Xu et al. (2009a) reported that the reaction rate constantly decreased with increasing initial concentration of NDMA and that the NDMA photo-degradation in acidic solution was faster than that in neutral and alkaline solutions. Similar results were reported by Lee et al. (2005) and Stefan and Bolton (2002). In amine absorbents the pH is high and not adjustable, but given by the amine used, its concentration and the CO_2 loading. However, in wash water solutions it may be imagined that acidic solutions may be used, in particular for the last wash section (acid wash).

Oxygen saturated waters have been reported to enhance the destruction of NDMA compared to N_2 saturated water (Xu et la., 2009a; Lee et al., 2005). Additionally Xu et al. (2009a) verified that singlet oxygen $^1O_2$ was the reactive oxygen species present in the process of NDMA degradation. Nitrite and nitrate have been reported to be produced during UV-photodegradation of NDMA (Plumlee and Reinhard, 2007; Lee et al., 2005). Other degradation products containing nitrogen were methylamine (MA) and dimethylamine (DMA).

The destruction kinetics are reported to be dependent on the nitrosamine (Plumlee and Reinhard, 2007; Xu et al. 2009b). NDMA, NPyr and NPIP are all reported to follow first-order kinetics (Xu et al.2009a and 2009b). Additionally, the effectiveness of treatment might be reduced if the water is turbid, coloured or contains chemicals that can interfere with the short wavelength UV light (Mezyk et al., 2004; Knuutila et al., 2013a; Knuutila et al., 2013b).

In this paper the destruction of NDELA and NDMA with UV-irradiation in a laboratory scale setup is reported. The effect of UV-light is measured in a fresh 30 wt% MEA solution, in an artificial water wash liquid and in 30wt% MEA and 50wt% DEA solutions previously used in a pilot plant. Additionally, degradation of 30wt% MEA solution under long term exposure to UV-radiation is studied. A dynamic model for the reactor setup used is developed and used for interpretation of the results.

EXPERIMENTAL METHODOLOGY

2 The batch reactor setup used in this study is shown in Figure 1. It contains a 45L mixing tank, a centrifugal circulation pump, a valve to control the circulation rate, a commercial UV-light reactor (Sterilight silver S8Q-PA), a heating element located in the mixing tank and sampling points before and after the UV-light reactor. Main technical data of the commercial UV-light reactor with lamp effect of 37W are presented in Table 1. The liquid volume inside the UV-light reactor was 2 litres.

The experiments were started by placing a known amount of solution into the mixing tank and starting the mixing of solution in the tank. After ensuring a homogeneous aqueous phase, the circulation of the solution through the UV-light was started by turning on the centrifugal pump. The flow rate through the UV-light was controlled with the valve located between the flow meter and UV-light reactor. The flow was measured with a calibrated flow meter and was set to 3 kg/min. After a steady liquid flow rate was achieved a liquid sample from the sampling point located after the UV-light was withdrawn. Then the UV-light was turned on and liquid sampling was started based on the sampling plan made before the experiments. The main sampling point was located at the outlet of the UV-light reactor, but samples from the mixing tank and at the inlet of the UV-light were also taken in some of the experiments. Most of the experiments were performed at room temperature, but a few experiments were done at 45^{o}C.

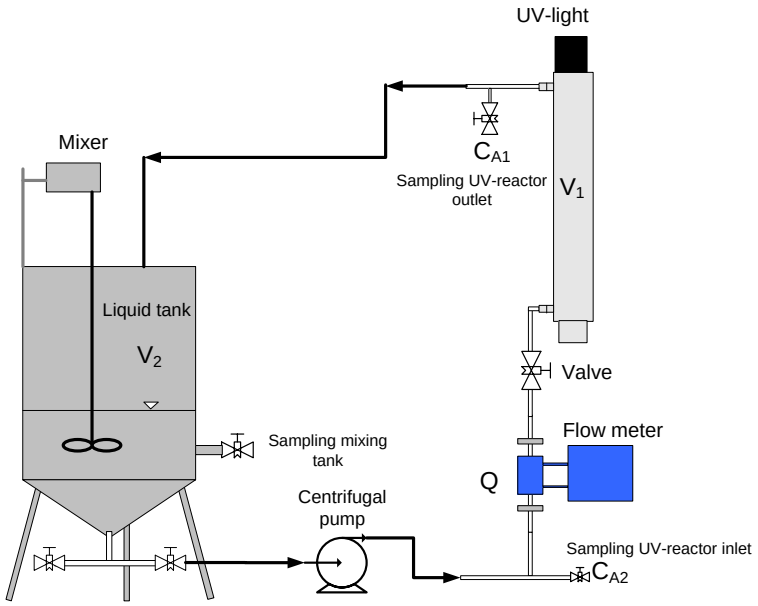

Figure 1: Experimental set-up used for laboratory experiments.

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
UV-reactor liquid volume	2 L

SOLUTIONS

Fresh MEA solutions were made by weighing commercially purchased MEA (>99% pure) and DI water. NDMA and NDELA were purchased from commercial companies and weighed into the 30wt% MEA solutions.

Artificial water wash solution was prepared by mixing several components into DI water. The solution did not imitate a specific solution present in a water wash section but instead it was a cocktail of potential chemicals present in a water wash systems of several amine solvents, and was made for laboratory experiments. The composition of the artificial wash water is presented in Table 2. Solvents present in the solution were 2-amino-2-methylpropanol (AMP),

monoethanolamine (MEA) and Piperazine (Pz). Additionally the solution contained several degradation products like ammonia (NH_3), alkylamines and nitrosamines. Alkyl amines, analysed with GC-MS, present in the solution were dimethylamine (DMA), diethylamine (DiEA), metylamine (MA) and ethylamine (EA). Additionally N-Nitrosodiethanolamine (NDELA) and Nitrosodimethylamine (NDMA) were added to the solution.

Table 2 Composition of the artificial water wash solution.

Component	Amount	Unit
NH3	15.2	ng/ml
Dimethylamine	695	ng/ml
Methylamine	415	ng/ml
Ethylamine	380	ng/ml
Diethylamine	569	ng/ml
AMP	1.1	mg/ml
PZ	1.1	mg/ml
MEA	17.6	mg/ml
NDELA	301	ng/ml
NDMA	293	ng/ml

Experiments with pilot plant solutions were made with 50wt% DEA and 30wt% MEA solutions. The solutions were extracted from two pilot plant campaigns and stored in 20 litre containers in a dark room at room temperature. A detailed presentation of the pilot plant campaigns can be found in Knuutila et al. (2013a). The MEA solution was run in the pilot for 1690 hours during which it was exposed to ~100 ppm of NO for 715 hours and to ~10 ppm of NO_2 for 187 hours. Additionally the solution was irradiated with UV-light for 37 hours. The DEA solution was tested in the pilot for 410 hours, during which it was exposed to ~100ppm NO for 250 hours and ~10ppm NO_2 for 100 hours as presented in Table 3. The NDELA detected in the 50wt% DEA was formed during the pilot campaign. The NDELA analysed in the MEA solutions was a combination of formed NDELA and added NDELA (for more info, see Knuutila et al. 2013a). Both solutions were analysed for NDMA, before addition of NDMA, but it was not detected.

Table 3 Basic data about the used 30 wt% MEA and 50wt% DEA solutions.

	30 wt% MEA	50 wt% DEA
Campaign duration	1690 hours	410 hours
NO feed (actual feeding hours)	715 hours	250 hours
NO_2 feed (actual feeding hours)	187 hours	100 hours
UV-light radiation in the main solvent circulation	37 hours	48 hours

ANALYTICAL METHODS

IC was used to measure nitrite, nitrate and formate with methods 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).

The water wash samples were analyzed without further dilution and the 30wt% MEA samples were diluted 1/100 in water before injection. The lower limit of quantification (LOQ) for NDMA in 30wt% MEA was 250 ng/ml and for the water wash samples 2.5ng/ml. For NDELA the limit was 50 ng/ml for both 30wt% MEA and 50wt% DEA. For water wash samples, the limit for NDELA was 0.5 ng/ml.

All concentrations of NDMA and NDELA presented in the paper are based on LC-MS analyses.

DYNAMIC MODEL OF SMALL SCALE UV APPARATUS

The basis for the reactor model is the experimental set-up shown in Figure 1. For the UV-reactor itself, plug flow is assumed and, since the volume of the UV-reactor is small compared to the total liquid volume, the transients in the UV-reactor inlet are governed by the slow changes in the whole liquid volume, mainly the mixing tank:

$$dC_{A1} = -\frac{r}{Q_1} dV_1 \qquad (1)$$

In Eq. (1), C_{A1} is the concentration in the UV-reactor in moles/m^3, Q_1 is volumetric flow rate (m^3/s), V1 is the liquid volume inside the UV-reactor(m^3) and r is the destruction rate of nitrosamine(mole/s m^3). When the volume in the connecting pipes is disregarded, an equation can be set up for the nitrosamine concentration in the liquid in the holding tank. This volume is assumed well mixed and no reaction takes place here.

$$V_2 \frac{dC_{A2}}{dt} = Q_1 \cdot (C_{A1} - C_{A2}) \qquad (2)$$

In Eq. (2), C_{A2} is the concentration in the mixing tank(moles/m^3), also equal to the concentration in the liquid phase entering the UV-reactor, V_2 is the volume of liquid in the mixing tank in m^3. Eqs. (1) and (2) are coupled by C_{A1} being the concentration leaving the UV-reactor and entering the holding tank, and reversely, C_{A2} leaving the holding tank and being the inlet to the UV reactor.

Various reaction orders for the destruction of NDELA or NDMA with respect to their concentrations can be assumed. The literature suggests both 1st order and 0th order. If we assume

1st order with respect to the NDELA and NDMA concentrations the reaction can be described by $r=k\,C_{A1}$ and integrating Eq.(1) gives:

$$C_{A1} = C_{A2}\exp(-\frac{k \cdot V_1}{Q_1}) \quad (3)$$

This can be inserted into Eq.(2) and integrated:

$$C_{A2} = C_{A20}\exp(-\frac{Q_1}{V_2}(1-\exp(-\frac{k \cdot V_1}{Q_1}))\cdot t) \quad (4)$$

In Eq. (4) C_{A20} is the starting concentration. Using eq.(3) we get:

$$C_{A1} = C_{A20}\cdot\exp(-\frac{k \cdot V_1}{Q_1})\cdot\exp(-\frac{Q_1}{V_2}(1-\exp(-\frac{k \cdot V_1}{Q_1}))\cdot t) \quad (5)$$

At time t = 0 Eq. (5) is seen to reduce to Eq. (3) as it should.

In the case of 0th order kinetics, Eqs. (4) and (5) become respectively:

$$C_{A2} = C_{A20} - \frac{r \cdot V_1}{V_2}\cdot t \quad (6)$$

$$C_{A1} = C_{A20} - \frac{r \cdot V_1}{Q_1} - \frac{r \cdot V_1}{V_2}\cdot t \quad (7)$$

6 RESULTS

Results from 12 experiments are presented here. The results are presented in figures, but the numerical values are available in Appendix 1. An overview of the experiments is shown in Table 4 and in Table 5 the total time of UV-radiation, limits of quantification (LOQ) for NDMA and NDELA as well as the start concentrations are given.

222 **Table 4 Overview of the batch reaction experiments.**

ID	Solution	Total amount of solution (kg)	Amine $mol/kg_{solution}$	Loading mol/mol	Temp. °C	Source
EX1	Water wash solution	22.3	*	0	22	This work
EX2	Water wash solution	29.4	*	0	22	Knuutila et al. (2013)
EX3	Fresh 30 wt% MEA	29.9	4.9	0	22	Knuutila et al. (2013)
EX4	Fresh 30 wt% MEA	32.4	4.9	0	22	Knuutila et al. (2013)
EX5	30 wt% MEA taken from the pilot	31.5	4.7	0.35	22	Knuutila et al. (2013)
EX6	30 wt% MEA taken from the pilot	31.5	4.7	0.35	45	This work
EX7	30 wt% MEA taken from the pilot	32	4.7	0.35	45	This work
EX8	50 wt% DEA taken from the pilot	32	4.7	0.22	45	This work
EX9	50 wt% DEA taken from the pilot	33	4.6	0.22	22	Knuutila et al. (2013)
EX10	50 wt% DEA taken from the pilot	31	4.6	0.22	22	Knuutila et al. (2013)
EX11	50 wt% DEA taken from the pilot	30.5	4.6	0.22	22	This work
EX 12	Fresh 30wt% MEA	32.4	4.9	0	22	This work

223 *See Table 2

224

225 **Table 5 Start concentrations of NDELA and NDMA as well as LOQs in different experiments**

ID	Solution	NDELA (ng/ml)	NDMA (ng/ml)	LOQ NDELA (ng/ml)	LOQ NDMA (ng/ml)	Time of UV-radiation
EX1	Water wash solution	304	294	2.5	25	75min
EX2	Water wash solution	290	307	5	25	75min
EX3	Fresh 30 wt% MEA	236	7620	50	250	180min
EX4	Fresh 30 wt% MEA	624	-	50		180min
EX5	30 mass% MEA taken from the pilot	248	-	50		72h
EX6	30 mass% MEA taken from the pilot	<50*	-	50		72h
EX7	30 mass% MEA taken from the pilot	570	-			72h
EX8	50 mass% DEA taken from the pilot	27 620	-	50		72h
EX9	50 mass% DEA taken from the pilot	5500	-	50		72h
EX10	50 mass% DEA () taken from the pilot	20 070	-	50		24 h
EX11	50 mass% DEA taken from the pilot	28700	-	50		72 h
EX 12	30 mass% MEA	<50*	-			482h

226 *Used in degradation studies

EXPERIMENTS WITH ARTIFICIAL WATER WASH SOLUTION

Two experiments (EX1 and EX2) were performed with the artificial water wash solution (pH= 10.3). EX1 was performed with a total liquid volume of 22 kg as shown in Table 4 and EX2 was performed with 30 kg of solution. Other than that the experiments were similar. In these tests the UV-reactor outlet concentration, C_{A1}, was sampled and analysed as function of time. In Figure 2, as depicted by Eq. (5), the normalized outlet UV-reactor nitrosamine concentrations (C_{A1}/C_{A20}) are shown on a logarithmic scale as a function of dimensionless time($t \cdot Q_1/V_2$) normalized against total solution volume for EX 1 and 2. It can be seen from Figure 2 that there is a good agreement between the two tests, but EX1 has somewhat more scatter in the results than EX2. The results fit well with a linear relationship between logarithmic normalized concentration and dimensionless time as predicted by Eq. (5). This implies that the reduction of nitrosamine by UV-light in the wash water solution follows first order kinetics in nitrosamine concentration. This finding is in a good agreement with the literature where several authors have reported that destruction of nitrosamine follows first order kinetics with respect to nitrosamine (Xu et al.2009a and 2009b). The results also clearly show that the rate of decay for NDMA is approximately half of that of NDELA. This finding is supported by literature related to water treatment where the destruction kinetics are reported to be dependent on the type of nitrosamine (Plumlee and Reinhard, 2007; Xu et al. 2009b). The penetration depth for the used UV-radiation into the artificial water wash solutions was shown to be about 28 cm, see Knuutila et al.(2013b). The thickness of the solution irradiated in the UV reactor was 2.5 cm so absorption of UV-radiation by the solution itself would not play a significant role. The rate constants in Eq. (5) used for the lines in Figure 2 were 2.6 and 1.6 min^{-1} for NDELA and NDMA respectively.

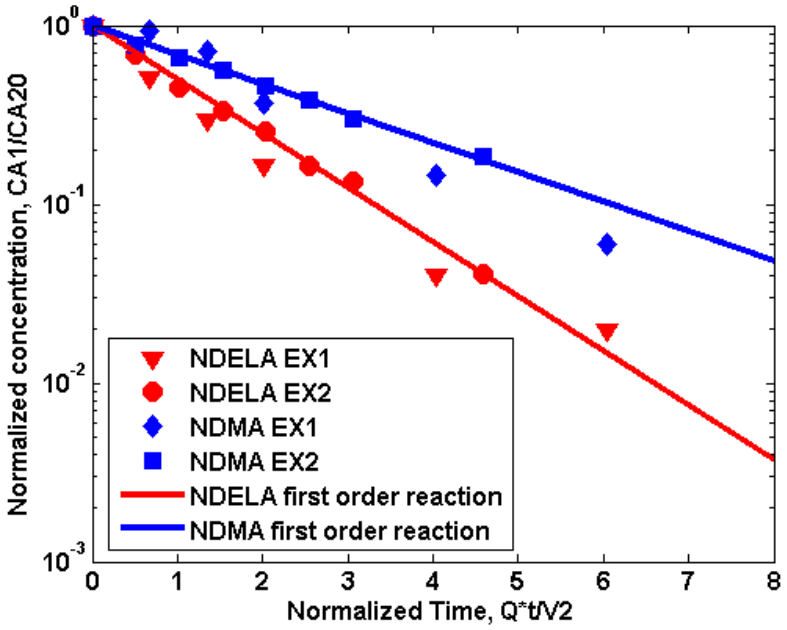

Figure 2 Experimental results from EX1 and EX2.

6.2 EXPERIMENTS WITH FRESH AMINE SOLUTION

Experiments EX3 and EX4 were done with 30 mass% MEA in water. Both of the solutions were prepared by weighing known amounts of fresh MEA into the water wash liquid presented in Table 2. The solution used in EX3 was spiked with NDMA to increase the NDMA concentration above the detection limit of the LC-MS analyses. The solution used in EX4 was spiked with NDELA. In both experiments the solutions were unloaded, i.e. no CO_2 present.

The decomposition results are presented in Figure 3 and data given in Table A2. Comparing Figures 2 and 3 shows clearly that the decay of both nitrosamines is significantly slower in 30mass% MEA than in artificial water wash solutions. A comparison with first order reaction kinetics is also shown in Figure 3. Although there is significant scatter in the data for NDELA in EX3, caused by the concentration level being close to the detection limit, it is reasonably clear that also in 30 mass% MEA the reactions are of first order with respect to the nitrosamine concentration. The lines inserted in Figure 3 have the same slope ratio as in Figure 3 indicating that the relative destruction rates of NDELA and NDMA are approximately the same in both wash water and 30 mass% MEA solutions. The first order kinetic constants, k in Eq. (5) for 30 mass% MEA, were found to be 1.12 and 0.6 min^{-1} for NDELA and NDMA, respectively. The main reason for the reduction in destruction rate is believed to be the difference in penetration depth as discussed in Knuutila et al. (2013b). The penetration depth, measured with a UV-spectrophotometer, decreases with increasing MEA concentration. In wash water it is estimated to be 28 cm whereas for 30 mass% MEA solutions, it is about 10 cm. Even though the penetration depth measurements seem to explain the decrease in reaction kinetics, the results with degraded solutions presented later, show that penetration depth alone cannot explain all the differences seen in destruction kinetics.

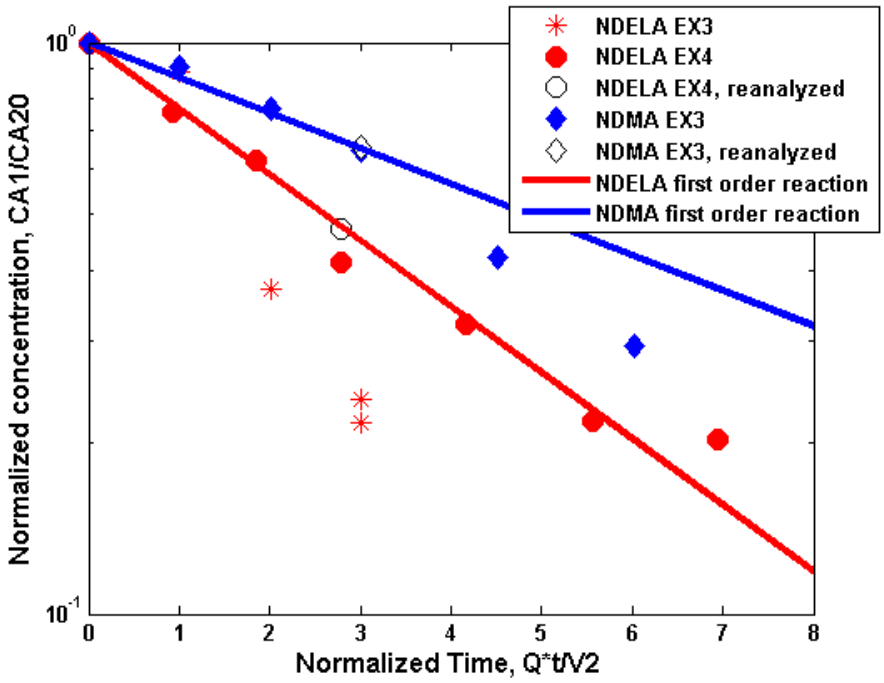

Figure 3: Normalised concentration of NDELA and NDMA during EX3 and EX4 together with fit to first order kinetics.

Two samples from EX3 and EX4 were analysed twice to check whether the nitrosamine concentrations in stored samples would be stable over time. Samples withdrawn after 30 min (normalized time ~ 3 in Figure 3) in EX3 were analysed once right after the experiment and a second time 1 month later. As can be seen the agreement is good. In EX3 the analysed NDMA concentrations were 4935 and 5000 ng/ml and in EX4 NDLEA showed respectively 294 and 258 ng/ml. The changes seen are considered to be within the analytical uncertainty although the difference in EX4 is somewhat high. This indicates that the nitrosamines studied are stable in samples stored properly at about 5°C and in darkness at least for non-degraded solutions.

Plumlee and Reinhard (2007) as well as Lee et al. (2005) reported that nitrate and nitrite were formed during NDMA photo-degradation in weakly acidic water solutions. For this reason the start and end samples from EX3 were analysed using ion chromatography (IC). In EX3 with 30mass% MEA (pH= ~11.8), nitrite was detected both in the start and end samples, whereas nitrate was above LOQ only in end sample as shown in Table 6. Based on the results presented in Table 6, the sum of nitrite and nitrate formed during the experiment was 0.0002 mmol/ml (assuming that no nitrate was present at the start of the experiment). The start sample contained 236 ng/ml NDELA and 7697 ng/ml NDMA and if we assume that all NDELA and NDMA were decomposed during UV-radiation (which is an assumption since the last samples were below LOQ), the sum of N from decomposed NDELA and NDMA would be 0.0001 mmol/ml. These results could thus be seen as support of the findings of Plumlee and Reinhard (2007) and Lee et

al. (2005) mentioned above. Yet two things should be noted. First the mass balance is uncertain due to the fact that the nitrate concentration is very close to the LOQ. Secondly; based on the literature, in alkaline solutions formed nitrate and nitrite only explains part of the degradation products and possibly other compounds like DMA and MA are formed (Xu et al., 2009a; Stefan and Bolton, 2002). The samples withdrawn during EX3 were not analysed for DMA or MA.

Table 6 Samples from EX3 analyzed with IC.

Time	Nitrite (mg/mL)	Nitrate (mg/mL)
0 min	0.000294	-
180 min	0.00747	0.002896

6.3 EXPERIMENTS WITH DEGRADED 30MASS% MEA SOLUTION

Two experiments were performed with 30 mass % MEA that had earlier been used in pilot plant operation (Knuutila et al.,2013a); EX5 and EX7. EX5 and EX7 were nitrosamine destruction tests performed at 22ºC and 45ºC respectively, whereas in EX6 the NDELA concentration was below detection limit and for that reason, EX6 is only discussed in Chapter 6.5.1 where degradation during UV-radiation is discussed. The decrease in NDELA concentrations with time in EX5 and EX7, are presented in Figure 4 and data given in Table A3 and A4. EX7 was a long experiment where the solution was first irradiated for 72 hours after which the UV-light was turned off and the circulation of the solution in the setup was continued another 72 hours to see if NDELA would be reformed. As seen from Figure 4 no sign of reforming of NDELA could be detected. In EX5 and EX7 samples were withdrawn from both the inlet and outlet of the UV-reactor. Additionally the mixing tank was sampled three times during EX5. The samples withdrawn at normalized time 0 were taken before the UV-light was turned on. For EX7, the samples at the UV-reactor outlet and inlet agree very well at 0 min/kg, as would be expected since the solution has not been in contact with UV-light. In EX5 a bit more scatter is seen, but the agreement can still be considered to be good. It can be seen that the differences between the UV-light inlet and outlet samples are very small in both experiments, though in most of the samples the inlets have a little higher nitrosamine concentration compared to the outlet samples. This is not surprising as the decomposition of NDELA is slow in the used 30 mass% MEA solution, taking place over 72 hours, whereas the liquid retention time in the UV lamp was about 40 sec. A comparison between Figure 3 and Figure 4 shows the effect of having a used degraded MEA solution compared to a fresh one. In EX3, Figure 3, 50 minutes was needed to decrease the concentration of NDELA to below LOQ, in EX5, Figure 4, more than 50 hours were needed.

Interpreted with first order reaction rate kinetics, the rate constant in the used MEA solution was about 140 times smaller than in the artificial water wash solution, presented in Figure 2, and 60 times smaller than for unused MEA solution of the same strength. The dark color and

degradation product content of the used MEA solution are believed to be the main reasons for the seen decrease in rate as both color and MEA concentration affect the penetration depth. The effect of color/degradation is much stronger than that of amine concentration. The penetration depth in the MEA taken from the pilot was about 0.08 cm, while for the artificial water wash liquid it was found to be around 28 cm (Knuutila, et al., 2013b). This means that only a very small part of the UV-reactor would be effective in the used 30 wt% MEA case and that this is the reason for the low "apparent" kinetic constant values found. Interestingly, the temperature does not seem have a strong influence on the rate of decay as can be observed when comparing results from EX5 and EX7. The effect of temperature is further discussed in the next sections.

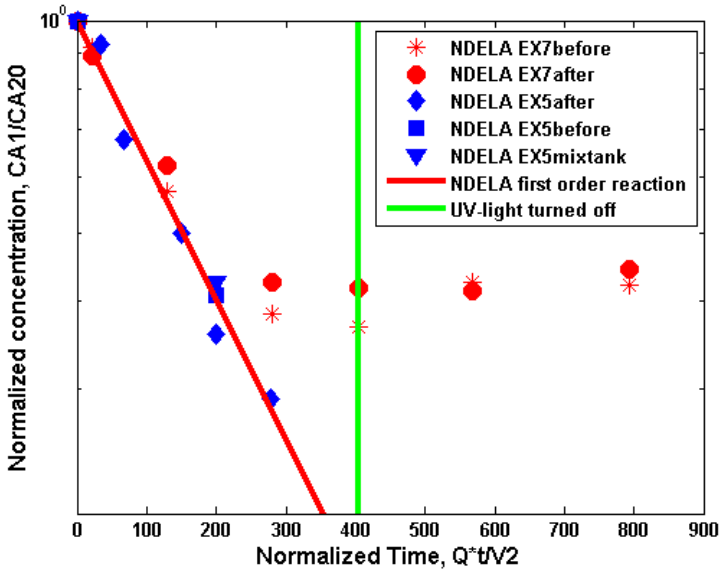

Figure 4. Results from EX5 (22ºC) and EX7 (45ºC).

6.4 EXPERIMENTS WITH USED 50MASS% DEA SOLUTION

A shown in Table 4, four experiments were performed with degraded 50mass% DEA solution taken from the pilot plant after the DEA campaign, see Knuutila et al.(2013a). In EX8 the destruction of NDELA during UV-radiation at 45 ºC was studied. After this the solution was cooled down to 22ºC and the UV-radiation was continued for another 72 hours (EX9) with the same solution. In Figure 5 are shown the normalized C_{A1} values, Eq. (5), as function of dimensionless time and the actual values are given in Table A5. It can be seen that the NDELA concentration decreases with time and after about 50 hours the further reduction in NDELA content becomes slower. At 72 hours the concentration at the inlet and outlet of the UV-reactor are almost the same indicating low destruction rate.

As mentioned above, after irradiating for 72 hours, the UV-light was turned off and the solution was cooled down to 22 ºC over 2 hours, after which a new start sample was withdrawn and the UV-light turned on, formally starting EX9. It was expected that the NDELA concentration at the

start of EX9 at 22°C would be the same as the last sample in EX8 at 45°C. However, as seen from Table A5, the concentration of NDELA increased from 400 ng/ml to 5500 ng/ml during the cooling period (the sample at 74 hours is taken just before turning the UV-light on again). This could be a sign that the decomposition products, like nitrite, nitrate etc. have reacted back to NDELA after the UV-light was turned off and the solvent cooled down, possibly through a reversion or change of equilibrium.

Also in the case of used 50 mass % DEA solution it seems that a 1st order rate dependency holds. However, in EX8 and EX9, at respectively 45 and 22 °C it seems that the temperature does have an influence on the rate. The "apparent" 1st order rate constants found for the DEA solutions were 0.076 and 0.035 min^{-1} at 45 and 22 °C respectively, meaning that the nitrosamine destruction is significantly faster in the used 50 mass% DEA solution than in the used 30 mass% MEA solution. This is reasonable as the penetration depth in the two solutions were 0.2 and 0.08 cm respectively. The effect of temperature found for this case will be discussed a bit more later.

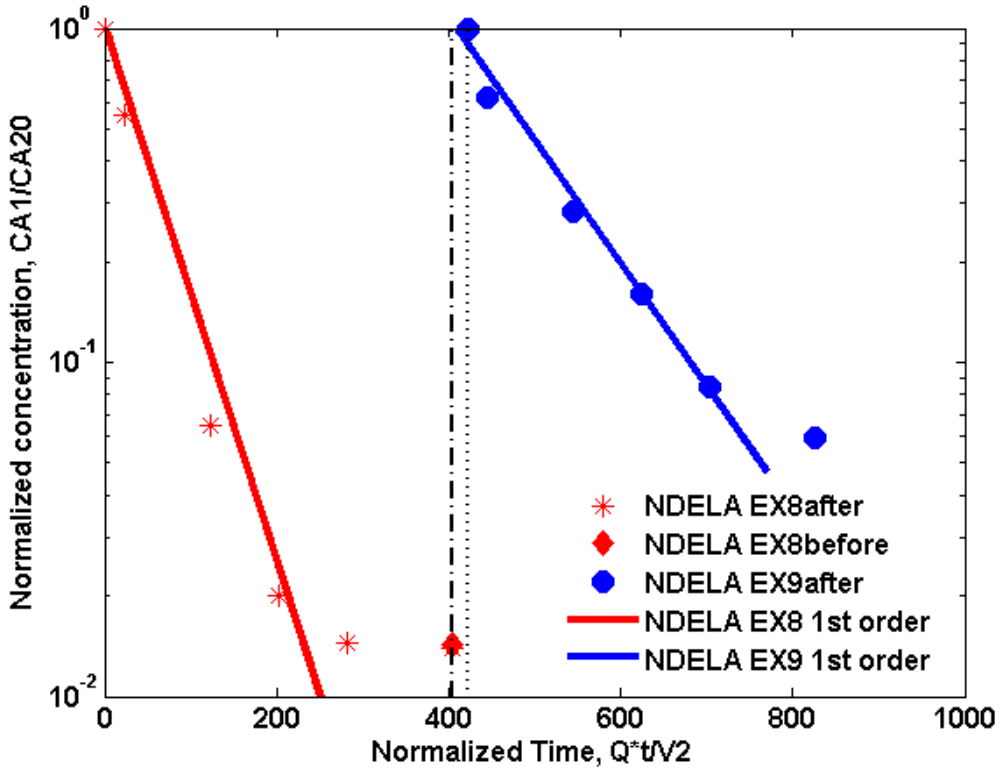

Figure 5. NDELA concentration during experiments EX8 (45°C) and EX 9 (22°C). Liquid samples withdrawn after the UV-light reactor. One sample withdrawn also at the inlet of UV-light reactor. Y-axis is in logaritmic scale.

In order to check the suggested possibility of an equilibrium reversion, two additional experiments (EX10 and EX11) were performed, where the possibility of a back-reaction was

monitored. In EX10 the used 50mass% DEA solution was irradiated with UV-light for 24 hours at room temperature. After this the circulation of solvent was continued for another 24 hours at the same temperature to see if NDELA was formed from the degradation products. To minimize the possibility for NDELA to either form or decompose between sampling and analysis, the samples were analysed as soon as possible. Most of the samples were analysed within 1 hour of sampling and the maximum was a few hours after sampling. The results for EX10 are given in Figure 6
and Table A6 both for C_{A1} and C_{A2} in Eqs. (5) and (4) respectively. The results show that no NDELA was formed during the 24 hours when the UV-light was turned off. The samples withdrawn at time 5 hours (Table A6) were analysed twice, due to increased NDELA concentration seen for later samples. These parallel analyses gave the same values as the first ones.

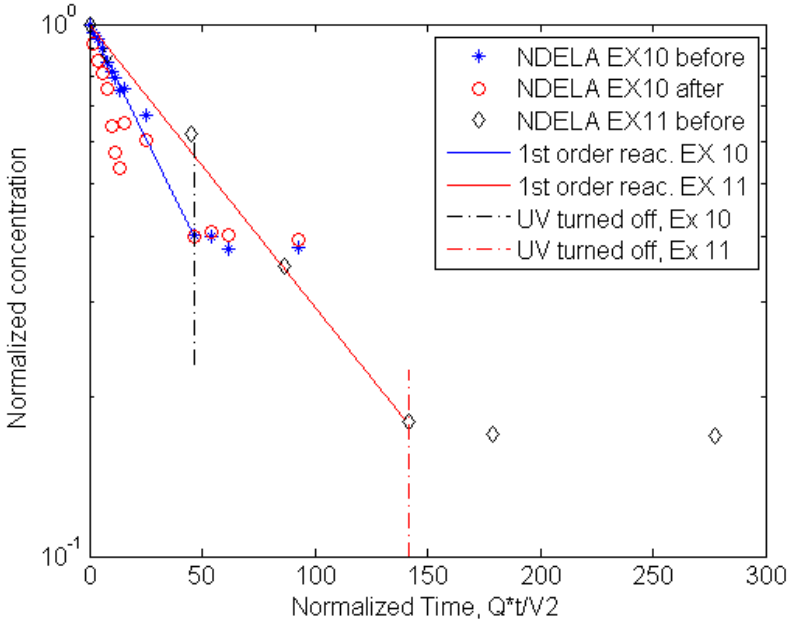

Figure 6 Results for the EX10 and 11 at 22ºC.

In EX11 the UV-light was first on for 72 hours at 22ºC, after which it was turned off and the solution circulated for another 72 hours in the setup. The results for the reactor inlet, C_{A2}, are presented in Figure 7 and Table A7. Again, no formation of NDELA after the UV-light was turned off was seen. This agrees well with what was seen with 30mass% MEA in EX7 and with 50mass% DEA in EX10 and indicates that the increase of NDELA concentration during cooling down between EX 8 and EX9, probably has to do with the decrease in temperature. This phenomenon should be further studied. In Figure 6 it is also seen that the NDELA decay is slower for EX11 than for EX10. No good explanation for this is found at present.

In Figure 7, EX8 at 45 °C is compared to EX10 at 22 °C. The "apparent" rate constant used for the line drawn is the one found from EX8, k = 0.076 min^{-1}. The two experiments agree well with each other, now indicating that temperature does not have an effect on nitrosamine decay. Results in this work are thus inconclusive with regard to the effect of temperature, but the tendency is toward no effect of temperature.

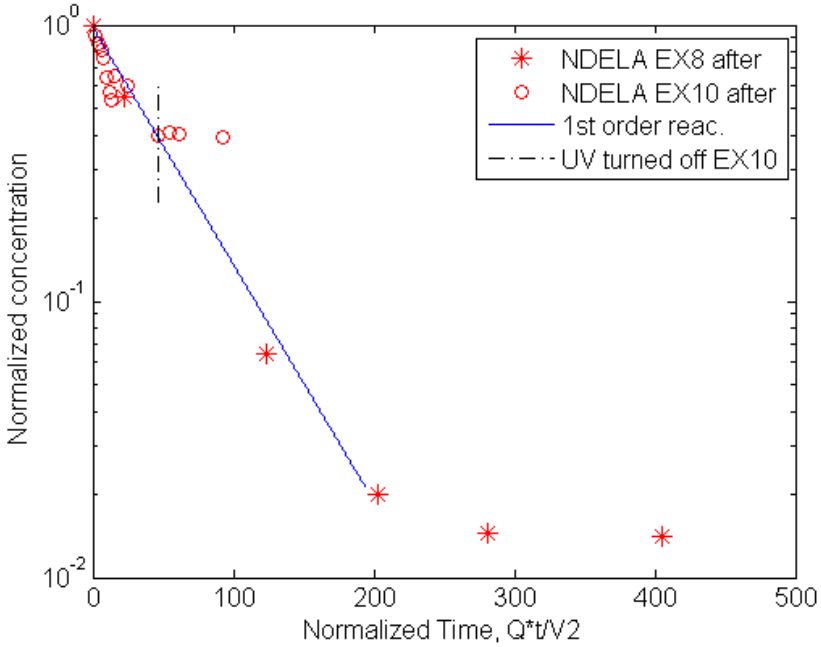

Figure 7. NDELA concentration during experiment 8 and 10 with 50mass% DEA at respectively 45 and 22°C.

In Figure 8 results from EX10 are used to test hypothesies of either a 0th or 1st order reaction mechanism. In this experiment we have a set of values for both UV-reactor inlet and outlet concentrations. For a 0th order reaction Eq. (7) can be subtracted from Eq. (6) giving:

$$C_{A2} - C_{A1} = \frac{r \cdot V_1}{Q_1} \qquad (8)$$

An for a 1st order reaction Eq (4) divided by Eq. (5) gives:

$$C_{A2} / C_{A1} = 1 / \exp(-\frac{k \cdot V_1}{Q_1}) \qquad (9)$$

Both of these are time invariant. In Figure 8, normalized forms of Eqs. (8) and (9) are plotted as function of time. The normalization is against initial values. Indication of either a 0th or 1st order rection mechanism would be a constant value equal to 1. From Figure 8 it can be seen that the data set does not fulfil this criterion for any of the mechanism, giving an indication of the experimental uncertainty in the data. However, it is quite clear that the 1st order provides a far better fit that the 0th order mechanism.

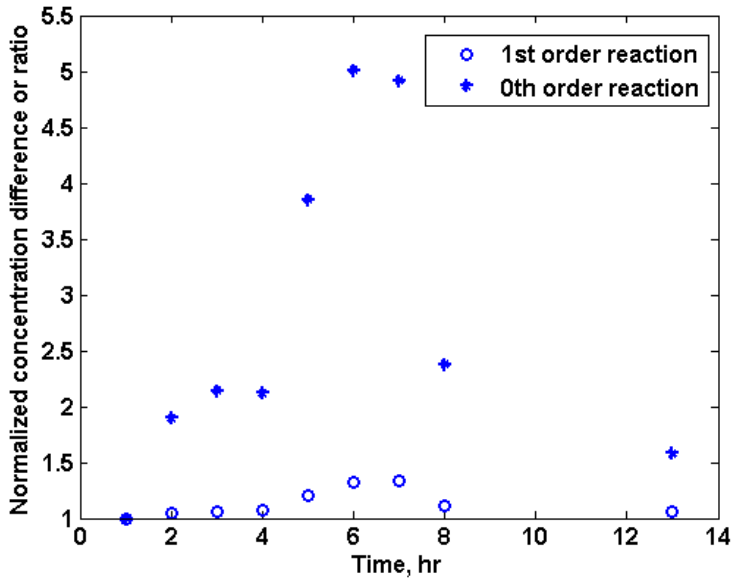

Figure 8 Comparison between 0th and 1st order reaction mechanism for Ex10.

6.5 AMINE DEGRADATION DURING UV RADIATION

6.5.1 Degraded MEA solution

The MEA degradation compounds analysed were: HeGly, BHEOx, HEI, HEA, HEPO, HEF and OZD. In EX5 the degradation was monitored at 22°C and in EX6 and EX7 at 45 °C. During all the experiments, the solutions were UV-irradiated for 72 hours. After this, monitoring was continued for 72 hours in EX7 and for 216 hours in EX5. As seen from Figure 9 the concentrations of HEPO, HeGly, HEA and OZD were not significantly affected by the UV-light, and the concentrations were very stable for all experiments. HEI and HEF, shown in Figure 10, were detected at the same levels as HEA. The concentrations of HEI and HEF were quite stable in the experiments done at room temperature, but it seems that both of them are formed more rapidly at 45°C. This could be due to increased radical activity at higher temperature or due to a change in chemical equilibrium towards HEI and HEF at higher temperatures. As also seen from Figure 10, the rate of formation of HEI and HEF seem to be more affected by temperature than by the presence of UV-light. BHEOX was below detection limit during all these tests. These results all indicate that UV-light does not lead to more rapid degradation of the amine itself. However the exposure to UV-light was short and results from a longer exposure experiment are discussed later.

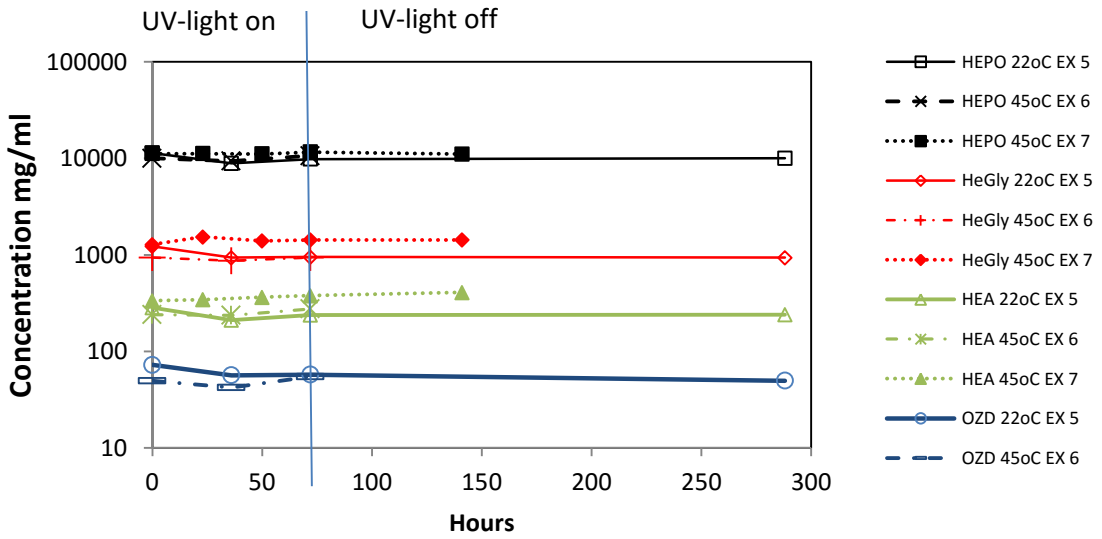

Figure 9 Concentration of HeGly, HEPO, HEA and OZD during lab scale experiments with the 30wt% MEA previously used in a pilot campaign.

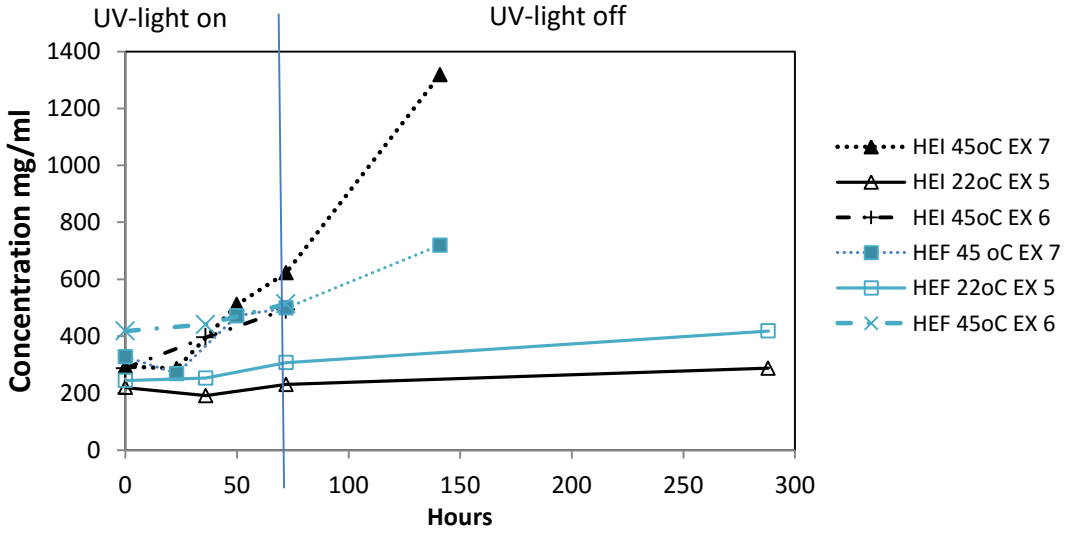

Figure 10 Concentration of HEI and HEF during lab scale experiments with the 30wt% MEA previously used in a pilot campaign.

6.5.2 Degraded DEA solution

As for the MEA experiments, the 50wt% DEA solution used in EX8, EX9 and EX10, were analysed for the following degradation compounds: HeGly, BHEOx, HEI, HEA, HEPO, HEF and OZD. HeGly, BHEOX and HEPO were detected in concentrations around 50 µg/mL whereas HEI and HEA were quantified close to the detection limit of 1 µg/mL as seen from Figure 12. The concentrations of HEF and OZD were too low to be quantified. The low concentrations of degradation compounds found was related to the short time of operation of the

pilot plant in the DEA campaign; only 410 hours wheras the MEA solution was run first for 700 hours in one campaign and then reused for another 990 hours in a new campaign, see Knuutila et al. (2013b). It should also be noted that the HeGly, BHEOX, HEI, HEA, HEPO, HEF are common degradation compounds for MEA, but DEA might also form other degradaion compounds not analysed for in this study (da Silva et al. 2012).

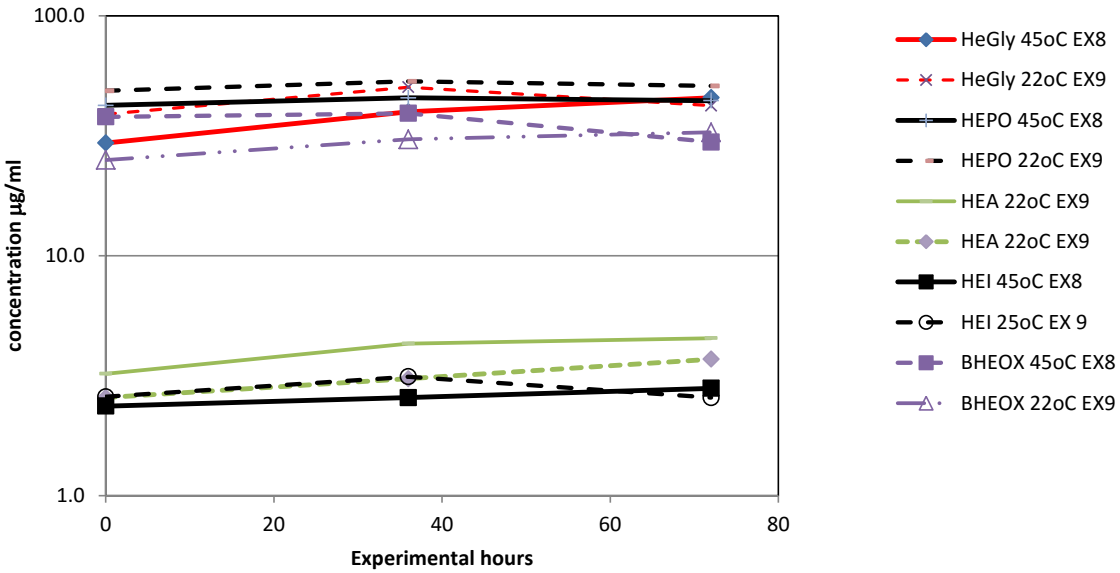

Figure 11 Concentration of HeGly, HEPO, HEA, HEI and BHEOX during lab scale experiments with the 50wt% DEA with the solution previously used in the pilot campaign.

6.5.3 Fresh 30wt% unloaded MEA

As a follow up of the relatively short exposure time in the earlier tests shown in Figures 9 and 10, specific tests were designed to investigate whether the degradation of MEA changed when exposed to UV-light over longer periods of time. In EX 12 the unloaded MEA solution used in experiment 4 was exposed to UV-light for 20 days using the setup in Figure 1 at 22^{o}C and with a liquid flow rate of 3 kg/min. During the experiment liquid samples were withdrawn almost daily and a selection of them were analysed for degradation products. In a similar setup without UV-radiation one would not expect any degradation at 22^{o}C.

From Figure 12 it can be seen that the main degradation products found are formate, HEF and HEI, followed by HEGly. UV-radiation produces radicals and the results indicate that the formation of HEI, HEF and HeGly are dependent on the radicals which either contribute by direct reaction or by forming intermediate products. During the UV-radiation the concentration of formic acid and HEF increases throughout the experiment. This is reasonable taking into account that Lepaumier et al. (2011) suggested that HEF is formed in a reaction between MEA

and formic acid. The formation of HEI was previously detected in oxidative degradation experiments and in pilot plants (da Silva et al. 2012; Lepaumier et al. 2011; Vevelstad et al. 2013) the formation from glyoxal, formaldehyde, MEA and ammonia was verified by Vevelstad et al. (2013).

Other degradation products quantified were HEA, BHEOX, OZD and HEPO. The concentrations of BHEOX, OZD and HEPO were close to the LOQ and did not show any significant increase during the experiment. OZD on the other hand, even though present at low concentration, shows a constant increase during the experiment. HEPO is a one of the two dominant degradation products typically found in pilot plants, however in oxidative degradation experiments, performed typically at 55°C it is only seen in small quantities indicating that high temperatures are needed for its formation (da Silva et al. 2012).

Methylamine (MA) was found in levels of few µg/ml and in some samples also dimethylamine (DMA) was detected at the same levels. However, it should be noted that the DMA results were close to the LOQ. Both EA and DiEA were below LOQ during this test. Based on LC-MS scan N-(2-hydroxyethyl)-ethylenediamine (HEED), N-(2-Hydroxyethyl)lacetamide, 2,3-Morpholinedione (NO3C4H5) and N,N-di(2-hydroxyethyl)urea/MEA-urea were identified as likely degradation compounds present during and at the end of the 20 days UV-radiation period. From the samples analysed with IC it was possible to quantify only formate. Nitrate and nitrite were not detected. This is however not very surprising since the solution had not had contact with NO/NO_2 and the NDELA and NDMA concentrations were below the deteaction limit throughout the experiment. pH did not change during the 20 days of UV-radiation.

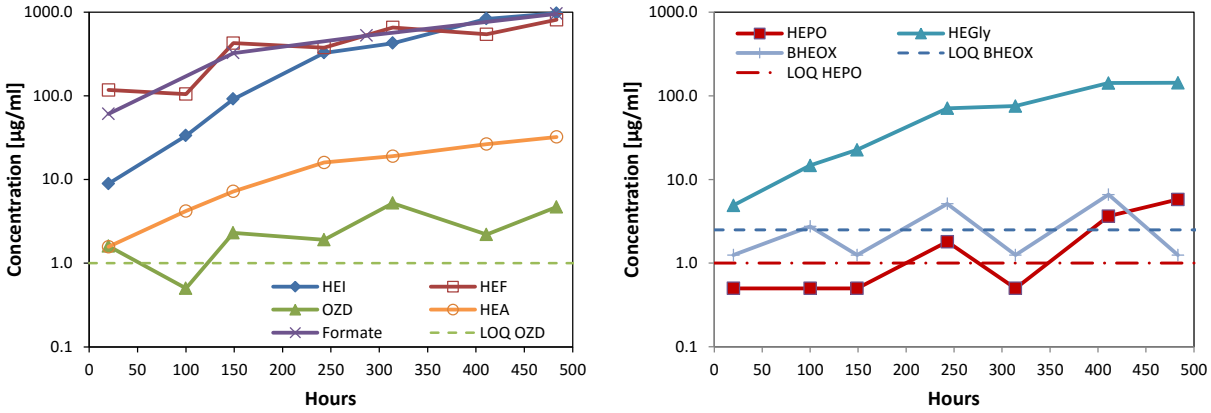

Figure 12: Amount of degradation products as a function of UV-radiation time at 22 °C.

CONCLUSIONS

CO_2 capture based on chemical absorption using amine solutions is considered to be a feasible way to capture CO_2 from power plants. However, amines, while degrading, may form nitrosamines which are known to be carcinogenic. In this work the destruction of two nitrosamines, NDELA and NDMA, with UV-light was studied in a batch reactor.

The results from this project clearly show that the rate of decay for NDMA is about half of that of NDELA in artificial water wash solutions. In fresh 30 wt% MEA solution the destruction of NDMA and NDELA was found to be 1/3 of that in the artificial water wash liquid. This can be explained by the changes in penetration of UV light into the solution: UV light has higher penetration depth into the artificial water wash solution compared to 30 wt% MEA.

In coloured solutions containing degradation compounds, the destruction rate in degraded 30wt% MEA solution was 33 times slower compared to the colourless, dilute artificial water wash solution. The decay in degraded 50wt% DEA was faster compared to the degraded MEA solution. This difference could be due to the darker colour and shorter penetration depth found in the MEA solution compared to DEA. The decomposition was not dependent on temperature.

Nitrite and nitrate were found in the fresh 30wt% MEA solutions in higher concentrations after the UV-initiated decomposition of NDELA. This indicates that these compounds are formed during decomposition of NDELA with UV-light.

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List of Abbreviations and CAS-numbers

Abb.	Name	CAS-number
BHEOX	*N'*-bis(2-hydroxyethyl)oxalamide	1871-89-2
HEA	*N*-(2-hydroxyethyl)acetamide	142-26-7
HEEDA	*N*-(2-hydroxyethyl)ethylenediamine	111-41-1
HEF	*N*-(2-hydroxyethyl)formamide	693-06-1
HEI	*N*-(2-hydroxyethyl)imidazole	1615-14-1
HEIA	*N*-(2-hydroxyethyl)imidazolidinone	3699-54-5
HEPO	4-(2-hydroxyethyl)piperazin-2-one	23936-04-1
NDELA	N-Nitrosodiethanolamine	1116-54-7
NDMA	N-nitrosodimethylamine	62-75-9
OZD	2-oxazolidinone	497-25-6
AMP	2-amino-2-methylpropanol	124-68-5
DiEA	Diethylamine	109-89-7
DMA	dimethylamine	124-40-3
EA	Ethylamine	75-04-7
MA	Methylamine	74-89-5
MEA	Monoethanolamine	141-43-5
NH3	Ammonia	7664-41-7
PZ	Piperazine	110-85-0
	N-(2-Hydroxyethyl)lacetamide	5422-34-4
	2,3-Morpholinedione, NO3C4H5	86310-85-2
	N,N-di(2-hydroxyethyl)urea/MEA-urea	15438-70-7

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APPENDIX 1

Table A1 Analyzed NDELA and NDMA concentrations in EX1 and EX2. Sampling point: UV-reactor outlet, i.e. concentration C_{A1}.

	EX1			EX2	
Time min	**NDELA [ng/ml]**	**NDMA [ng/ml]**		**NDELA [ng/ml]**	**NDMA [ng/ml]**
0	304	294		289	307
5	102	274		145	237
10	59	212		95	203
15	33	108		69	171
20				54	141
25				34	118
30	8	43		28	92
45	4	18		9	57
60	<2.5	< 25		< 5	< 25
75	<2.5	< 10		< 5	< 25

Table A2 Analyzed NDELA and NDMA concentrations in EX3 and EX4. Sampling point: UV-reactor outlet, i.e. concentration C_{A1}.

	EX3			EX4	
Time min	**NDELA ng/mml**	**NDMA ng/ml**		**NDELA ng/mml**	**NDMA ng/ml**
0	236	7617		624	< 250
10	209	6886		473	< 250
20	88	5828		388	< 250
30	51	4935		258	< 250
30	56	5000		294	< 250
45	< 50	3211		201	< 250
60	< 50	2250		136	< 250
75				126	< 250
90	< 50	993		66	< 250
105				60	< 250
120	< 50	319		54	< 250
150	< 50	< 250		< 50	< 250
180	< 50	< 250		< 50	< 250

Table A3: Analysed NDELA concentration during EX5 with 30wt% MEA.

Time (hr)	NDELA (ng/ml)		
	UV reactor outlet	UV-reactor inlet	Mixing tank
0	248	277	228
2	263		
6	229		
12	168		
27	124		
36	89	113	97
50	72		
72	<50	<50	<50

Table A4. Experimental results from EX7 with 30wt% MEA. UV-light was turned off after 72 hours.

Time (hr)	UV-light outlet NDELA (ng/ml)	UV-reactor inlet NDELA (ng/ml)
0	568	
4	520	505
23	325	354
50	218	242
72	209	237
101	242	235
141	240	252

Table A5. NDELA concentrations during EX 8 and EX9 with 50wt% DEA.

After UV	EX8		EX9
Time (hr)	UV-reactor outlet NDELA (ng/ml)	UV-reactor inlet NDELA (ng/ml)	UV-reactor outlet NDELA (ng/ml)
0	27616		5498
4	15251		
6			3426
22	1777		1560
36	554		884
50	398		463
72	387	393	327

Table A6. NDELA concentration during EX10 with 50wt% DEA. UV-light was turned off after 24 hours.

Time (hr)	UV-reactor inlet NDELA (ng/ml)	UV-reactor outlet NDELA (ng/ml)
0	20 065	
1	19 357	18 476
2	18 834	17 162
3	18 097	16 208
4	17 048	15 179
5	16 291	12 895
6	15 922	11 511
7	15 068	10 737
8	15 164	13 071
13	13 535	12 143
24	8 079	8 004
28	8 010	8 150
32	7 577	8 071
48	7 631	7 899

Table A7. NDELA concentration during EX11 with 50wt% DEA. UV-light was turned off after 72hours.

Time (hr)	UV-reactor inlet NDELA (ng/ml)	UV-reactor outlet NDELA (ng/ml)
0	28728	
4	25189	8840
23	17921	6024
44	10075	973
72	5149	2246
91	4873	4879
141	4839	4891