Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 37 (2013) 701 – 716

Energy Procedia

GHGT-11

Nitrosamine degradation by UV light in post-combustion CO_2 capture: Effect of solvent matrix

Ferran de Miguel Mercader[a]*, Alexander K. Voice[b], Henk Trap[a], Earl L.V. Goetheer[a]

[a] *TNO, Gas Treatment, Leeghwaterstraat 46, 2628CA Delft, The Neterlands*
[b] *University of Texas at Austin, 1 University Station C0400, Austin, Texas 78712, USA*

Abstract

Potential production and emission of nitrosamines during post-combustion CO_2 capture has drawn some attention due to their toxicity and potential carcinogenicity. One of the possible ways to reduce the concentration of nitrosamines is irradiation of the liquid streams of the capture plant with UV light. This paper shows experimental results of the degradation of nitrosamines such as N-nitroso-diethanolamine (NDELA) and N-mononitroso-piperazine (MNPZ) in different solvent matrices. These solvent matrices include water and laboratory grade monoethanolamine (MEA) aqueous solutions, as well as aqueous MEA solution and wash water that had been used in a CO_2 capture pilot plant connected to a coal-fired power plant. Experiments were conducted in dedicated batch set-ups and in a continuous mini CO_2 capture plant. Results show that the UV absorbance of impurities (degradation products and/or dissolved metals) present in MEA solvent that had been used in a pilot plant significantly reduces the UV degradation rate of nitrosamines. Furthermore, UV light seems to accelerate the degradation of the capture solvent itself. For these reasons, if UV light treatment is to be used in full-scale post-combustion CO_2 capture plants, suitable locations would be the absorber's washing section or the stripper's condensate. At these locations, less interference of degradation products can occur and there is less solvent to be degraded.

Selection and/or peer-review under responsibility of GHGT

*Keywords:*Nitrosamine degradation; Post-combustion; CO_2 capture; piperazine; MEA; NDELA; MNPZ

* Corresponding author. Tel.: +31 88 86 62 868.
E-mail address: ferran.demiguelmercader@tno.nl.

1876-6102
Selection and/or peer-review under responsibility of GHGT
doi:10.1016/j.egypro.2013.05.159

1. Introduction

One of the challenges in post-combustion CO_2 capture using an amine scrubbing system is the formation of nitrosamines. These compounds are formed by the reaction of NO_2 present in the flue gas with the solvent amine [1,2,3]. Nitrosamines are a non-desired product due to their toxicity and potential carcinogenicity (the toxicity depends on the type of nitrosamine) [4,5]. Because of this, measures to prevent their formation or to enhance their degradation are of high interest. One of the proposed measures for the degradation of nitrosamines is the use of UV light [6,7].

Degradation of nitrosamines using UV light has been studied in drinking water purification [8]. Due to the photosensitivity of nitrosamines, their degradation under UV light is possible [9]. Plumlee and Reinhard [9] analysed the UV spectra of several nitrosamines (NDMA, NMEA, NDEA, NDPA, NDBA, NPyr and MNPZ) and it was observed that they all had similar UV absorption in two main bands; one with a maximum around 230 nm and a second one with a maximum around 330 nm. This second band overlaps with solar radiation, explaining why nitrosamines can degrade in the atmosphere under sun light [10]. Because of the first absorption band (with a maximum at 230 nm), UV-C light (100-280 nm) can also be used to degrade nitrosamines.

The present study shows results of the degradation of nitrosamines using UV-C light in two different set-ups. The first one is a batch set-up in which degradation of a known initial concentration of nitrosamine can be carried out in a more controlled way. The second set-up is a continuous mini CO_2 capture unit (500 L/h synthetic flue gas) in which gaseous NO_2 is introduced to create nitrosamines, followed by irradiation of the solvent by UV light to attempt to degrade them. This paper focuses on the effect of different solvent matrices on the degradation of nitrosamines.

Nomenclature

NDBA	N-nitrosodi-n-butylamine
NDEA	N-nitrosodiethylamine
NDMA	N-nitrosodimethylamine
NDPA	N-nitrosodi-n-propylamine
NDELA	N-nitrosodiethanolamine
NMEA	N-nitrosomethylethylamine
MNPZ	N-mononitrosopiperazine
NPyr	N-nitrosopyrrolidine
UV	Ultraviolet

2. Experimental section

In this section, the experimental set-ups, solvents and model nitrosamines used in this study are presented. Subsequently, the analytical equipment used is also described.

2.1. Batch set-up

Figure 1 shows the flow diagram of the batch set-up for controlled UV degradation of nitrosamines. This set-up consisted of a 2 L glass bottle, a heater/magnetic stirrer, a peristaltic pump and a UV light flow through cell. The glass bottle was completely covered with aluminium foil to avoid exposure of the liquid to ambient light.

In a typical experiment, 2 L of solvent with a known amount of nitrosamine (typically 1 g/L) was used. The liquid stirring rate was kept constant at 900 RPM and, if heating was desired, a hot plate with a temperature indicator submerged in the liquid, controlled the temperature. The system was deemed stable after 60 min (with the UV light off), after which the light was turned on (considered experimental time 0 min). The UV light chamber had an internal volume of approximately 300 mL (~15% of the total hold-up) and used an 11 W UV-C lamp (Philips TUV PL-S). As mentioned earlier, this specific UV band was chosen because nitrosamines degrade when they are exposed to it. A sample point was placed after the UV light chamber (typically 1 mL of sample was taken).

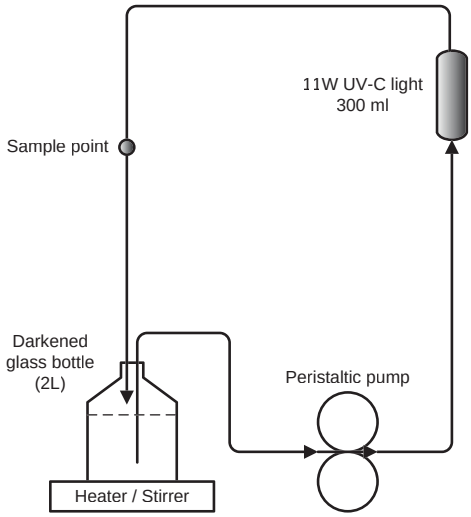

Fig. 1. Schematic representation of the batch set-up for UV degradation of nitrosamines

2.2. Continuous set-up

Nitrosamine formation and degradation experiments were also conducted in a mini CO_2 capture unit (see Figure 2 for flow diagram). In a typical experiment, 500 L/h of synthetic flue gas (with a tuneable composition including air, CO_2, NO_2 and/or N_2) was fed to the absorber. For this study, a membrane contactor (SuperPhobic, MEMBRANA) was used as absorber. In this step, the “lean solvent” entered the membrane module with a flow of approximately 12 kg/h and absorbed CO_2 and NO_2, becoming “rich solvent” (the total solvent inventory in the entire capture unit was approximately 7 L). The spent flue gas was analysed for CO_2 and NO_2. The rich solvent was then passed through the UV light chamber (for these experiments, the same UV light chamber as for the batch experiments was used). The solvent was sent to the stripper via a heat exchanger. The hot rich solvent was introduced into the stripper (packed column) in which CO_2 was desorbed. The gas stream exiting the stripper was cooled (condensing some water) and

vented. Some of the condensate was automatically fed to the stripper when the level in it was lower than a fixed value. The lean solvent was sent back to the absorber, via the heat exchanger, closing the cycle.

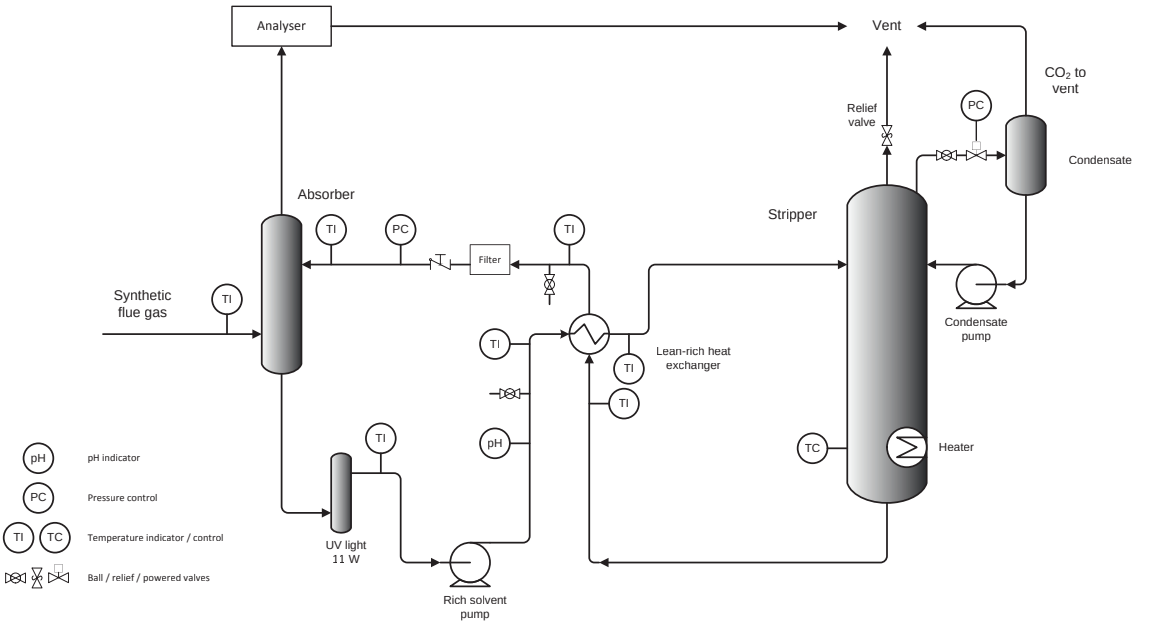

Fig. 2. Flow diagram for the mini CO_2 capture unit including UV lamp

2.3. Solvents and model compounds

In the batch set-up, four different solvent matrices were evaluated:

- Water: deionised water
- Clean MEA: aqueous 30 wt.% MEA solution (laboratory grade)
- Pilot MEA: aqueous MEA solution that was used at TNO's pilot plant for CO_2 capture. This pilot plant is connected to E.ON's power plant at the Maasvlakte (The Netherlands) [11]. This solvent had been used for few weeks at the pilot plant, had an MEA content of approximately 20 wt.% and was amber coloured. Although this specific sample was not analysed, it included degradation products and dissolved metals
- Wash water: Water taken from absorber's washing section at TNO's pilot plant

For the experiments in the continuous set-up, the clean and pilot MEA were used.

For the batch experiments, NDELA was chosen as model compound to represent those nitrosamines that are found when MEA is used as solvent. NDELA (the product of the reaction of DEA with absorbed NO_2) was chosen because nitrosamines from secondary amines (such as DEA) are more stable than those formed from primary amines (such as MEA) [1, 12, 13]. Moreover, NDELA has been reported to be found when MEA is exposed to NO_x [1].

Additionally, UV degradation of MNPZ in an aqueous solution of 40 wt.% piperazine was also evaluated in the batch set-up.

For the continuous experiments, NO_2 gas was added to the flue gas, leading to different types of nitrosamines. In this case too, the concentration of nitrosamines in the liquid was monitored by analysing NDELA as the model compound.

2.4. Analyses

For the batch and continuous experiments, nitrosamines (i.e. NDELA and MNPZ) in the liquid were analysed using an HPLC with UV detection at 245 nm (UV max for MNPZ) or 234 nm (UV max for NDELA).

NO_3^- in the liquid was analysed using a spectrophotometer and commercial kits (Hach-Lange).

The amine concentration in the solvent was determined by titration with 0.1M HCl. The inflection point was considered as the end point in which all the moles of amine were neutralised. The term alkalinity is used to define the amine concentration in the solvent.

For the gas analysis in the continuous set-up (feed and absorber exit gas), a Horiba PG-250 multi gas analyser was used to analyse the following gases: O_2, CO_2 and NO_x. It uses non-dispersive IR detection for CO_2; chemiluminescence (cross-flow modulation) for NO_x; and a galvanic cell for O_2.

3. Results

3.1. Batch set-up

3.1.1. UV light degradation of NDELA in different solvent matrices

The first experiment conducted was the UV degradation of NDELA in water. This experiment lasted for 3 weeks, in which samples were taken at regular intervals. Figure 3 shows the evolution of the concentration of NDELA in the solvent. It shows that after 1.2 days, all the NDELA was degraded (at least, its concentration was under the detection limit of the HPLC used for analysis of approximately 0.1 mg/L). The constant zero-order reaction visible during the 1.2 days, made shorter experiments possible (the standard time used for the rest of the experiments was 5 h). It should be noted that for all the experiments performed, no NDELA degradation was observed during the system stabilisation time (first hour of experiment) in absence of UV light (three samples were always taken during this period), indicating no interference from ambient light in the experiments.

Figure 4 shows the reduction of concentration of NDELA in four different solvent matrices: Water, clean MEA, pilot MEA and wash water (see Section 2.3 for details on these solvents). For all the cases, UV light degradation of NDELA was possible but at different rates. The figure also shows the degradation rate obtained by linear fitting, giving a clear idea on the differences in NDELA degradation using difference solvent matrices. The degradation rate of NDELA in deionised water, clean MEA or water wash was very similar. However, the figure clearly shows that the degradation rate of NDELA when pilot MEA was used as solvent was much lower than when the other solvents were used (approximately 3.5 times lower).

As already mentioned, the pilot MEA had an amber colour indicating the presence of other compounds in it. To elucidate the influence of this colour in the UV degradation, UV spectra of clean MEA and pilot MEA were measured (see Figure 5). These measurements show that the pilot MEA absorbed more UV light in the region between 200 and 280 nm (within UV-C band) than clean MEA. As an indication, the area under the pilot MEA curve is roughly double than that of the clean MEA. This indicates that some components present in the pilot MEA absorb UV light, decreasing its availability to degrade NDELA.

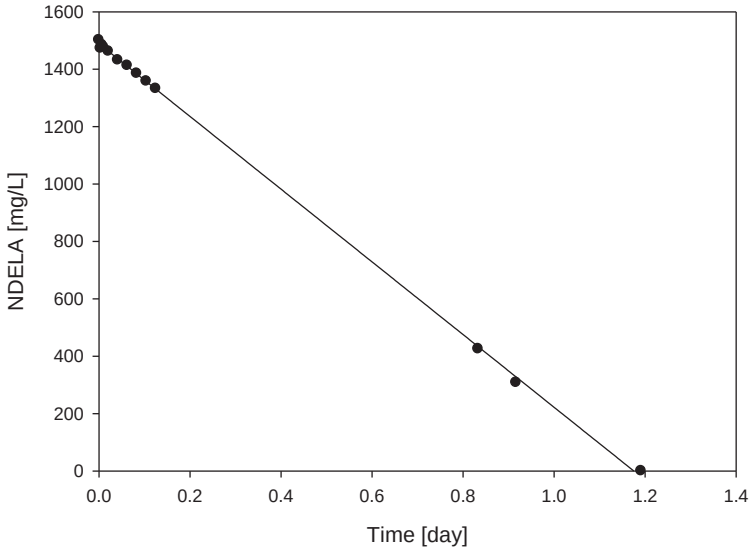

Fig. 3. UV light degradation of NDELA in water. Conditions: room temperature, 15% holdup in 11W UV-C lamp, 240 mL/min flow rate, 2 L inventory, 900 RPM agitation in the glass bottle

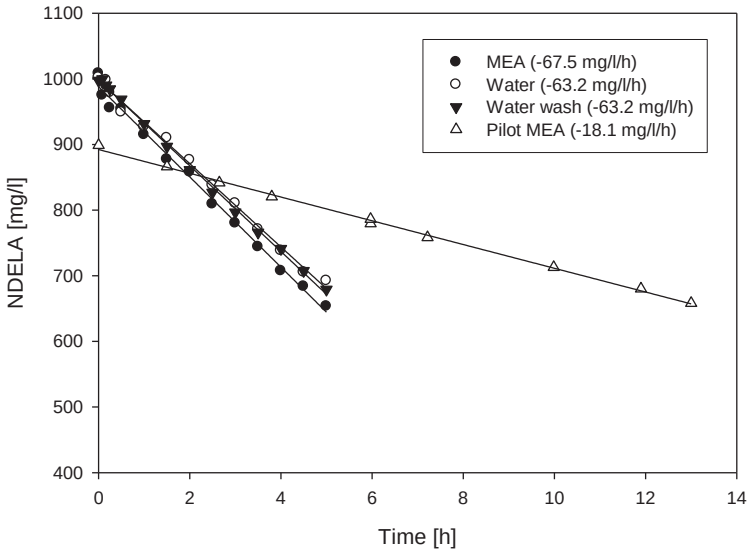

Fig. 4. UV light degradation of NDELA dissolved in different solvents matrices. The legend gives the degradation rate for each of the experiments. Conditions: room temperature, 15% holdup in 11W UV-C lamp, 130 mL/min flow rate, 2 L inventory, 900 RPM agitation in the glass bottle

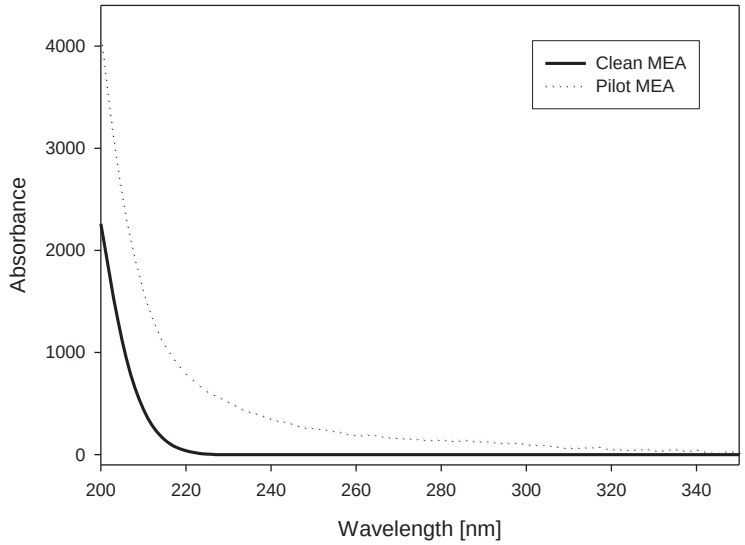

Fig. 5. UV spectra of aqueous 30 wt.% MEA solution (clean MEA) and the aqueous MEA solution that had been used in the Maasvlakte pilot plant (pilot MEA)

3.1.2. UV light degradation of MNPZ in aqueous 40 wt.% piperazine

As an additional experiment, the degradation of MNPZ present in 40 wt.% piperazine (advanced capture solvent [14]) was evaluated. Two experiments using different CO_2 loading (i.e. 0.27 and 0.36 mol CO_2/mol alkalinity) were performed. The rest of experimental conditions were kept the same as for the NDELA experiments (room temperature, 15% hold-up in 11W UV-C lamp, 2 L inventory, 900 RPM stirring in the glass bottle).

Figure 6 shows the decrease of concentration of MNPZ during UV light exposure. For the first 1.5 h, the UV light was off and no MNPZ degradation was observed. This indicated that interferences from ambient light were avoided. The figure shows that MNPZ degraded in UV light following (initially) zero order reaction. After 24 hours of experiment, a change in the colour of the solution was observed (into a light orange colour) and the degradation rate of MNPZ appeared to decrease. This can be attributed to the formation of piperazine degradation products that also absorbed UV light, decreasing the degradation rate of MNPZ.

To evaluate the influence of oxygen during the UV degradation of MNPZ, nitrogen was sparged into the glass bottle for the first 6 hours of the experiment. At this point, in inlet gas was switched from nitrogen to air introducing oxygen into the solution. Figure 6 shows no change in degradation rate when changing sparging gas, indicating that the degradation rate was not affected by the presence of dissolved oxygen.

Figure 7 shows the results of the degradation of MNPZ in aqueous 40 wt.% piperazine with a loading of 0.36 mol CO_2/mol alkalinity. The degradation rate of MNPZ at higher loading appears to be slightly higher than at lower loading. Similar to the lower loading and to the NDELA experiments, the initial degradation rate appears to follow zero order reaction, but it deviates at the end of the experiment. In this

case, the solvent also changed colour indicating the formation of degradation products that could absorb some UV light and interfere with the degradation of MNPZ.

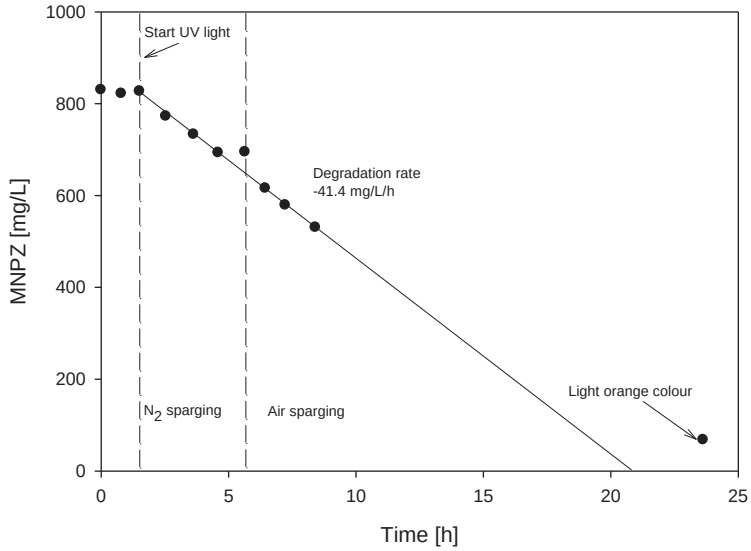

Fig. 6. UV degradation of MNPZ in 40 wt. % piperazine at 0.27 mol CO_2/mol alkalinity. Conditions: room temperature, 130 mL/min flow rate, 15% holdup in 11W UV-C lamp, pH=10.10, 2 L inventory, 900 RPM agitation in the glass bottle

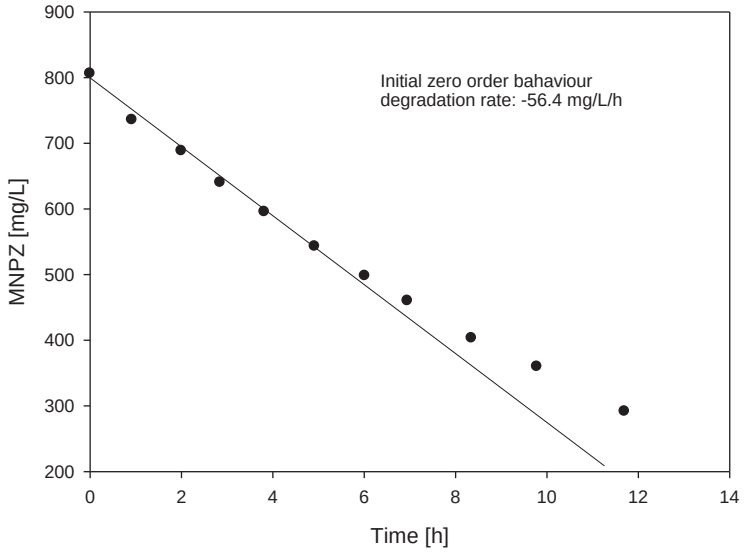

Fig. 7. UV degradation of MNPZ in 40 wt. % piperazine at 0.36 mol CO_2/mol alkalinity. Conditions: room temperature, 130 mL/min flow rate, 15% holdup in 11W UV-C lamp, pH=8.95, 2 L inventory, 900 RPM agitation in the glass

3.1.3. UV light solvent degradation

After observing the change in colour of the piperazine solution after UV light exposure for 24 h, dedicated experiments were conducted to evaluate the degradation of the solvent itself.

An experiment was carried out, exposing the piperazine solution to UV light for more than 2 days. In this case, air was sparged in the solution. As Figure 8 shows, the solution lost alkalinity indicating the degradation of the piperazine. When evaluating the rate of degradation of piperazine (-307 mg/L/h), it appears to be considerably higher than the rate of degradation in the presence of oxygen at 55 °C with no UV light (<50 mg/L/h) [15]. This indicates that UV can contribute to the oxidative degradation of the amine solvent itself. This comparison should be assessed with caution because very different conditions and experimental set-ups were used for these cases.

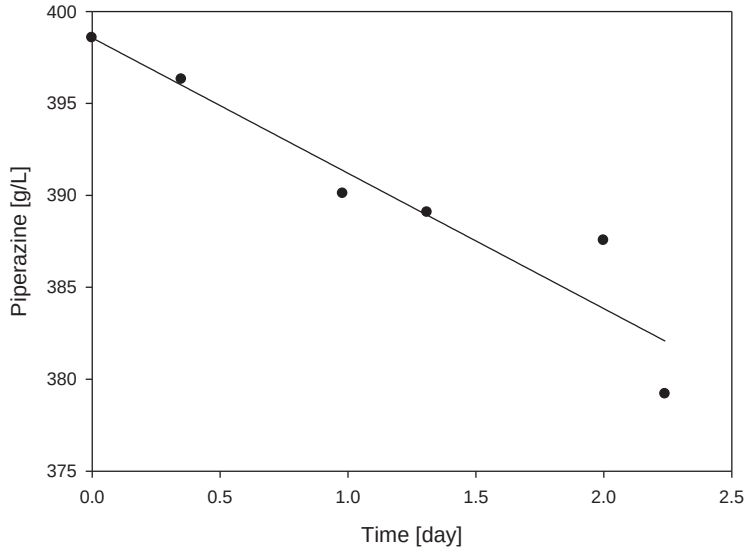

Fig. 8. Degradation of piperazine by UV light in the presence of air. Conditions: 40 wt. % piperazine, at 0.36 mol CO_2/mol alkalinity, room temperature, 130 mL/min flow, 15% holdup in 11 W UV-C lamp, 2 L inventory, 900 RPM agitation in the glass bottle

The same type of experiments were carried out using 30 wt.% MEA as solvent. A two day experiment did not accomplish any reduction of alkalinity in the solution (results not shown). Therefore, a three weeks experiment was carried out. Two equal batch set-ups were used in which the same aqueous 30 wt.% MEA solution was added. During the three weeks, CO_2 and air were sparged in both liquids kept at 40 °C. In one of the set-ups, the UV light was turned on and in the other one, the UV light was left off. A substantial decrease of alkalinity was not measured in any of the end products. However, the visual appearance of the solvent was completely different. While the solvent that was not exposed to UV had a pale yellow colour, the solvent that had been exposed to UV light, had a dark red colour (see Figure 9). To obtain more information on the amount of degradation products in both solutions, qualitative HPLC analysis was performed. Figure 10 shows the chromatograms resulting from the analysis. It can be seen that the MEA that was irradiated with UV light has more peaks and some of those with more area under them. This qualitatively indicates that more degradation occurred when the MEA solution was irradiated

with UV light. Quantitative analyses are needed to evaluate these results completely. This work is currently in progress.

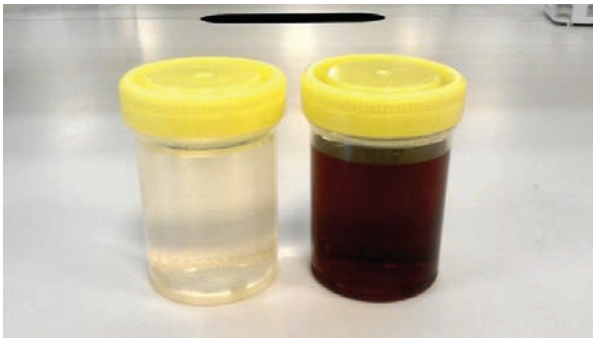

Fig. 9. Picture of the aqueous 30 wt.% MEA after 3 weeks at 40 °C and sparged with CO_2 and air. The sample in the left container was not exposed to UV light. The sample in the right container was exposed to UV light

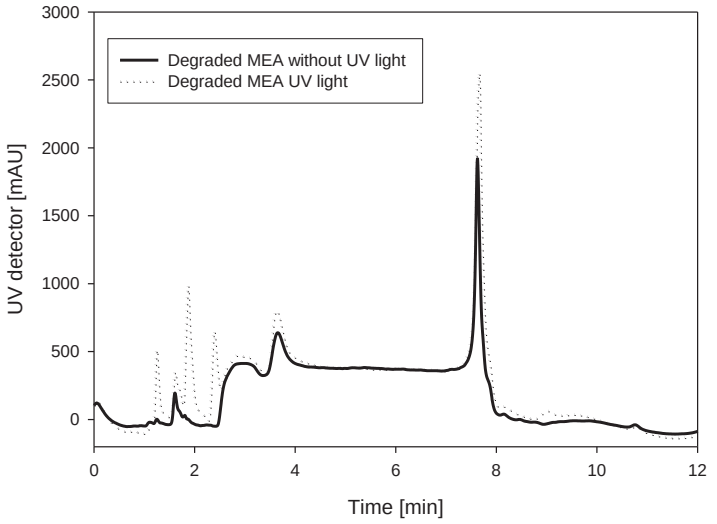

Fig. 10. HPLC chromatogram of degraded MEA for 3 weeks with and without UV exposure

3.2. Continuous set-up

In this section, experimental results on formation and degradation of nitrosamines during CO_2 capture process are given. Two experiments were conducted using a mini CO_2 capture unit, simulating CO_2 capture operation using aqueous MEA as solvent. Similar to the batch experiments, the main difference between the two continuous experiments was the use of clean or pilot MEA.

In both experiments, NO_2 gas was added to flue gas mixture (together with CO_2, air and/or N_2) to generate nitrosamines. Also in both experiments, the same UV set-up used in the batch experiments was used to degrade nitrosamines. Further experimental details can be found hereunder.

The first experiment (Experiment A) was conducted using laboratory grade aqueous 30 wt.% MEA together with 5 wt.% DEA. Although such a concentration of DEA will never occur in a MEA-based post-combustion system, DEA was added because, as previously stated, secondary amines are more prone to nitrosamine formation [1,13]. In this way, accelerated nitrosamine (NDELA) formation would be possible and results could be obtained faster. For this same reason, 100 ppmv NO_2 was added with the synthetic flue gas. This concentration is much higher than what it is typically found in a coal fired power plant. The NO_2 and secondary amine concentrations should be investigated further to see their dependence on nitrosamine formation (outside the scope of this paper).

Table 1 shows the experimental program of Experiment A. During the first 16 h only CO_2 and air were added to stabilise the system. Then 100 ppmv of NO_2 was added for 24 h to create NDELA. After this time, the UV light was turned on, while keeping the NO_2 gas concentration at 100 ppmv (an equilibrium between formation and degradation was expected). After 48 h, NO_2 flow was stopped and the capture plant was allowed to run for 72 h using 12 vol.% CO_2 with air.

Table 1. Experimental program for formation and degradation on NDELA during CO_2 capture (Experiment A)

Time used [h]	Accumulated Time [h]	Flue gas	UV-light setting
16	0-16	12% CO_2 (rest air)	Off
24	16-40	12% CO_2 + 100ppmv NO_2 (rest air)	Off
48	40-88	12% CO_2 + 100ppmv NO_2 (rest air)	On
72	88-160	12% CO_2 (rest air)	On

Figure 11 shows the concentration of NO_3^- in the rich and the lean solvent. It can be seen, that when the flue gas contained NO_2, NO_3^- was accumulating in the solvent.

Figure 12 shows the concentration of NDELA during Experiment A. The figure clearly shows that when NO_2 was added, NDELA was formed. After 40 h of experiment, the UV light was turned on. Because the flue gas still contained 100 ppmv of NO_2, an equilibrium concentration of NDELA that balanced formation and degradation was expected. However, NDELA degradation by UV light was much faster than formation, achieving an NDELA concentration under the detection limit of the analyser.

For the second experiment (Experiment B), a similar procedure as for Experiment A was followed, but in this case, pilot MEA was used. Table 2 shows the experimental program of Experiment B. For the first 17.5 h, only CO_2 and air were used as flue gas to stabilise the system. After this time, 100 ppmv of NO_2 was added during 23.5 h to form NDELA. Then, the supply of NO_2 was stopped and the system was left to stabilise during 24.5 h using only CO_2 and air as flue gas. Then, the UV light was turned on to evaluate its effect on nitrosamine degradation.

Table 2. Experimental program for formation and degradation on NDELA during CO_2 capture (Experiment B)

Time used [h]	Accumulated Time [h]	Flue gas	UV-light setting
17.5	0-17.5	12% CO_2 (rest air)	Off
23.5	17.5-41	12% CO_2 + 100ppmv NO_2 (rest air)	Off
24.5	41-65.5	12% CO_2 (rest air)	Off
32	65.5-97.5	12% CO_2 (rest air)	On

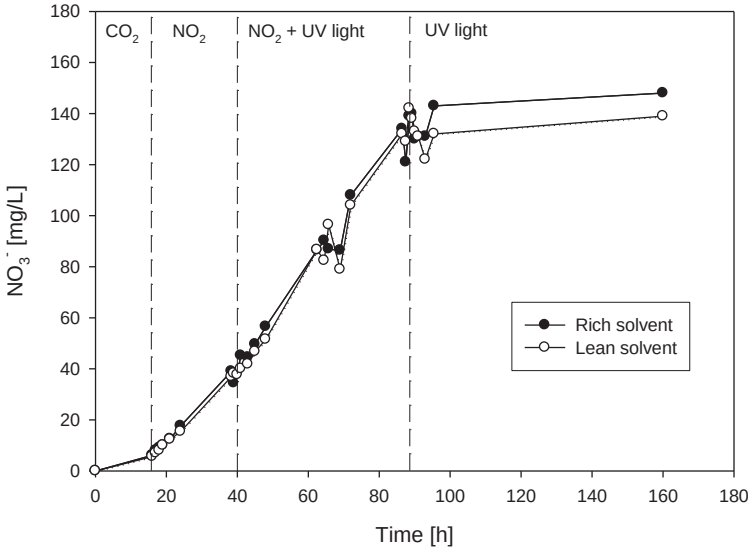

Fig. 11. NO_3^- concentration in lean and rich solvent. Vertical lines indicate event changes (gas composition or UV light setting)

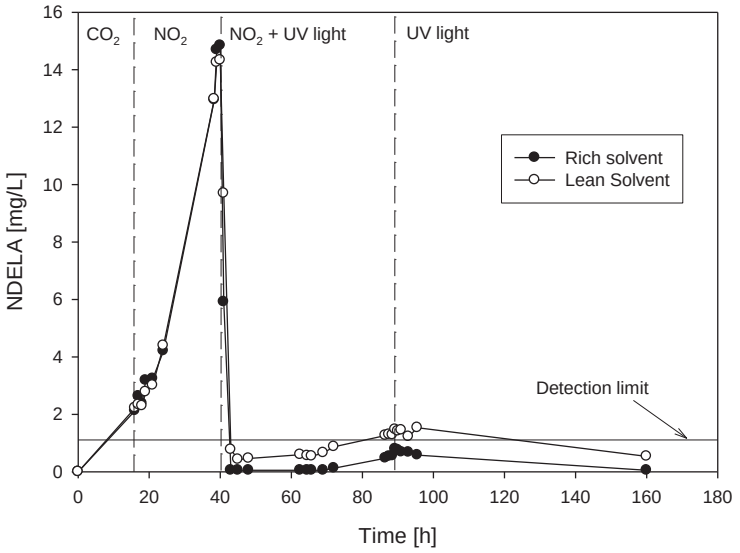

Fig. 12. Experiment A. NDELA concentration in rich and lean solvent (clean MEA). Vertical lines indicate event changes (gas composition or UV light setting)

Figure 13 shows the concentration of NDELA in the rich and lean solvents for Experiment B. It can be observed that during the first 17.5 h when only CO_2 and air were added, the concentration of NDELA already increased even without the addition of NO_2. This can be attributed to residual NDELA and/or NO_2 that was in the set-up from previous runs. Although the set-up was thoroughly rinsed with water (3 times), it is possible that some residue from previous experiments might have stayed inside.

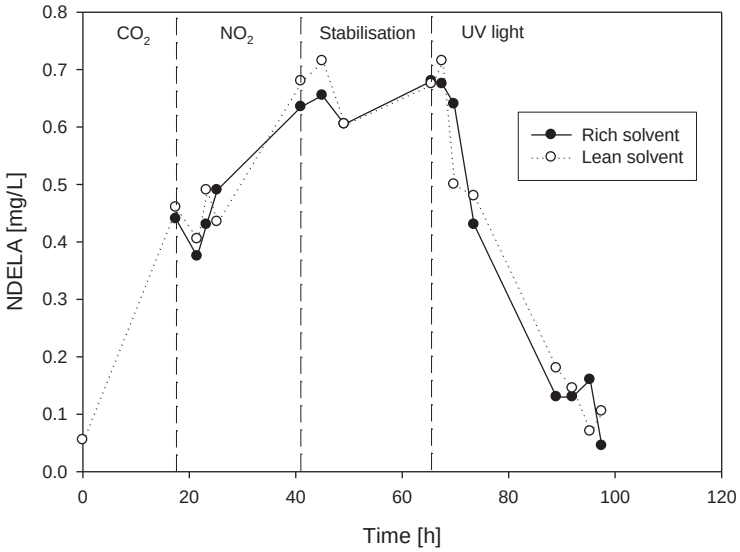

Fig. 13. Experiment B. NDELA concentration in rich and lean solvent (pilot MEA). Vertical lines indicate event changes (gas composition or UV light setting)

After 17.5 h running the experiment with only CO_2 and air, 100 ppmv of NO_2 was added to the flue gas, causing an increase in NDELA concentration. Overall, a much lower concentration of NDELA was detected in this experiment compared to Experiment A (the maximum concentration of NDELA is approximately 20 times lower). This is because in Experiment B, no extra DEA was added to the solvent. Therefore, the availability of one of the reactants to produce NDELA was limited.

When the supply of NO_2 was stopped (23.5 h after it was started), the concentration of NDELA also stabilised. Then, the UV light was turned on and NDELA degradation was again observed. However, the degradation rate observed during Experiment B (approximately -0.02 mg NDELA/l/h) appeared to be lower compared to Experiment A (approximately -4.5 mg NDELA/l/h). Similar to the batch experiments, this reduction of degradation rate can be attributed to the higher UV absorbance of the components that are present in the pilot MEA (e.g. solvent degradation products, dissolved metals, etc.).

It should be noted that the NDELA degradation rates observed in these experiments were much lower than those of the batch experiments. However, the relative residence time of the solvent in the UV light chamber compared to the total solvent inventory were completely different.

The indications of solvent degradation due to UV light exposure during the batch experiments, together with the results (of both batch and continuous experiments) showing the interferences created by

the solvent impurities, suggest that UV light treatment should be applied where amine solvent is not present. Therefore, if UV treatment is implemented in a full-scale post-combustion CO_2 capture plant, recommended locations would be the washing section water loop of the absorber and/or the stripper's condensate.

3.3. Degradation rate: batch vs. continuous

Experiments using laboratory grade MEA solution (clean MEA) and MEA that had been used at the pilot plant (pilot MEA) were performed in both batch and continuous systems. In this section, a comparison between the NDELA degradation rates observed in both systems is given. Table 3 shows the degradation rates of NDELA for the four cases. It also provides a corrected rate taking into account the different relative residence time of the liquid in the UV light compared to the total liquid inventory. These corrected values will be used for the comparison.

The results show much higher degradation rate for the batch experiments compared to the continuous. For the clean MEA, although the degradation rates are in the same order of magnitude, the continuous experiment show a degradation rate approximately four times lower than the batch. It should be noted that during the continuous experiment using MEA as solvent, the solutions also contained 5 wt.% DEA and that during UV degradation period, NO_2 was also present in the flue gas. This means, that during UV degradation, NDELA was probably also being formed, resulting in a net lower degradation rate. It is also possible that, due to the longer experimental run time of the continuous experiments (30 times longer), solvent degradation products and dissolved metals interfered with the UV degradation.

The results for the experiments using pilot MEA, showed that the degradation rate for the continuous system was more than two orders of magnitude lower than the batch system. A possible explanation of this large difference is the much higher total concentration of NDELA in the batch system (1000 times higher at the maximum concentration level) compared to the continuous system. This could make the interference of the impurities more significant during the continuous experiment. It is also possible that, although NO_2 was not added during the UV degradation, NDELA was being formed due to NO_2^- present in the solvent, for example, from oxidation of MEA (to NH_3 and finally to NO_2^-) or from NDELA degradation. The formation of NDELA would be enhanced in the continuous experiments due to the higher temperatures of the heat exchanger and the stripper (which are not present in the batch experiments).

Table 3. . NDELA degradation rates using clean MEA and pilot MEA as solvent for the continuous and batch systems. The correction is based on the relative residence time of the solvent in the UV light chamber

	NDELA UV degradation rate [mg/L/h]			
	Batch	Batch corrected [a]	Continuous	Continuous corrected [b]
Clean MEA	- 67.5	- 450	- 4.5	- 105
Pilot MEA	- 18.1	- 121	- 0.02	- 0.47

[a] Correction considering that the residence time of the liquid in the UV light is 15% of the total residence time (UV light volume is 300 ml, total liquid volume is 2 L)

[b] Correction considering that the residence time of the liquid in the UV light is 4.3% of the total residence time (UV light volume is 300 ml, total liquid volume is ~7 L)

4. Conclusions

Experimental work was carried out on the degradation of nitrosamines using UV light. Experiments were conducted in both a batch and a continuous system.

Using UV light in batch experiments, it was possible to degrade N-nitroso-diethanolamine (NDELA) dissolved in water and monoethanolamine (MEA) based matrices. NDELA was used as model nitrosamine present during post-combustion CO_2 capture using aqueous MEA as solvent. Although in all cases the UV light degradation of NDELA was possible, the degradation rate was highly influenced by the solvent matrix. When either water, wash water obtained from pilot plant absorber's washing section or laboratory grade MEA aqueous solution were used as matrix, the UV light NDELA degradation rate was significantly faster than when aqueous MEA that had been used in a pilot plant was used as solvent matrix. This reduction of degradation efficiency was attributed to the UV absorbance of impurities that were present in the pilot MEA such as degradation products and/or dissolved metals.

Similar interference from the solvent matrix was also observed during the UV light degradation of N-mononitroso-piperazine dissolved in 40 wt.% aqueous piperazine.

Dedicated extended experiments were carried out to measure the stability of the solvent (MEA and piperazine) under UV light exposure. Although no conclusive results were obtained, reduction in alkalinity (measured by titration) was observed in a 40 wt.% aqueous piperazine solution after 2 days exposure to UV light, indicating reduction of piperazine concentration. When the experiment was conducted using 30 wt.% aqueous MEA, no significant reduction of MEA concentration was measured by titration. However, strong change in colour of the solution when UV light was used compared to the reference experiment without UV light was observed, possibly indicating solvent degradation. The detailed analysis of these samples for degradation products is currently on-going.

Experiments conducted in a continuous mini CO_2 capture unit using both clean and pilot MEA, also showed interference of impurities in the solvent on the UV light degradation efficiency. When clean MEA was used as solvent, the UV light degradation of NDELA was faster than its formation even when the flue gas contained 100 ppmv of NO_2. However, when pilot MEA was used, the degradation rate of NDELA decreased significantly.

With these results, it appears that if UV light treatment for degradation of nitrosamines is to be implemented in full-scale post-combustion CO_2 capture plants, it should be located in a stream in which the UV light can not degrade the solvent or impurities from the solvent can not reduce the nitrosamine degradation efficiency. Two recommended locations for UV light treatment are the washing section loop of the absorber or the stripper condensate stream.

Acknowledgements

This work has been sponsored by the CATO2 program (http://www.co2-cato.org).

References

[1] Fostås B, Gangstad A, Nenseter B, Pedersen S, Sjøvoll M, Sørensen AL. Effects of NOx in the flue gas degradation of MEA. *Energy Procedia* 2011;**4**:1566–1573.

[2] Strazisar BR, Anderson RR, White CM. Degradation Pathways for Monoethanolamine in a CO_2 Capture Facility. *Energy Fuels* 2003;**17**:1034–1039.

[3] Challis BC, Shuker DEG. Chemistry of nitroso-compounds. Part 16. Formation of N-nitrosamines from dissolved NOCl in the presence of alkanolamines and related compounds. *Food Cosmet. Toxicol.*1980;**18**:283–288.

[4] Lin JK. Nitrosamines as potential environmental carcinogens in man. *Clin. Biochem.*1990;**23**:67–71.

[5] Magee PN. Toxicity of nitrosamines: Their possible human health hazards. *Food Cosmet. Toxicol.*1971;**9**:207–218.

[6] Swaim P, Royce A, Smith T, Maloney T, Ehlen D, Carter B, Effectiveness of UV Advanced Oxidation for Destruction of Micro-Pollutants. *Ozone Sci. Eng.* 2008;**30**:34–42.

[7] Xu B, Chen Z, Qi F, Ma J, Wu F, Comparison of N-nitrosodiethylamine degradation in water by UV irradiation and UV/O3: Efficiency, product and mechanism. *J. Hazard. Mater.*2010;**179**:, 976–982.

[8] Nawrocki J, Andrzejewski P. Nitrosamines and water. *J. Hazard. Mater.* 2011;**189**:1–18.

[9] Plumlee MH, Reinhard M.Photochemical Attenuation of N-Nitrosodimethylamine (NDMA) and other Nitrosamines in Surface Water. *Environ. Sci. Technol.*2007;**41**:6170–6176).

[10] Nielsen CJ, D'Anna B, Karl M, Aursnes M, Boreave A, Bossi R, et. al. Atmospheric Degradation of Amines (ADA). Summary report: Photo-oxidation of methylamine, dimethylamine and trimethylamine. CLIMIT project no. 201604. Kjeller, NILU (NILU OR, 02/2011).

Available at: http://www.nilu.no/DesktopModules/NiluWeb.UserControls/Resources/File.ashx?filename=02-2011-mka-ADA-final%20report.pdf&filetype=file

[11] Goetheer ELV, Nell L. First pilot results from TNO's solvent development workflow. *Carbon Capture Journal*. 2009;2–3.

[12] Jackson P, Attalla M. Environmental impacts of post-combustion capture-New insights. *Energy Procedia* 2011;**4**:2277–2284.

[13] Rochelle GT, Bishnoi S, Chi S, Dang H, Santos J. Research Needs for CO_2 Capture from Flue Gas by Absorption/Stripping DOE Report DE-AF26-99FT01029 2001.

[14] Freeman SA, Dugas R, Van Wagener DA, Nguyen T, Rochelle GT. Carbon dioxide capture with concentrated, aqueous piperazine. Int. J. Greenhouse Gas Control 2010;**4**:119–124.

[15] Freeman SA. Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture. *PhD Thesis, University of Texas* 2011.