# Oxidative degradation of amines using a closed batch system

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Abstract
Oxidative degradation experiments on five amines and two amino acids were performed in a new closed setup at atmospheric pressure. For most of the amines/amino acids significant degradation was not present under these conditions, except for MEA and MMEA. The degradation compounds found seem to follow the same patterns as described in literature. Volatile compounds as ammonia and alkylamine play an important role in understanding the initial degradation mechanisms. For MMEA, methylamine and ammonia were found in the same order of magnitude. Oxygen stochiometry of the degradation compounds could not be explained by initial air in the system. Oxygen in some of the degradation compounds could come from oxygen diffusing into the system as seen from proposed model and/or water reacting with iminium giving aldehyde and amine/ammonia. Temperature and dissolved metal seemed to influence oxygen and degradation rate for the MEA experiments.

Keywords: amine degradation; closed setup; oxygen; gas and liquid phase

## 1. Introduction

As a reasonably mature technology for CCS, post-combustion $CO_2$ capture by absorption can be applied both for retrofit and Greenfield plants. The best absorbents combine high net cyclic capacity, equilibrium temperature sensitivity and reaction/absorption rates for $CO_2$, good chemical stability, low vapour pressure and low corrosiveness. Unfortunately, all organic solvents, amines and amino acids, suffer from problems related to absorbent degradation.

Several types of degradation occur in post-combustion plants for $CO_2$ capture. Autoxidation takes place in the absorber, resulting in both primary and secondary degradation compounds as explained in a previous publication (Vevelstad et al., 2013). Degradation due to temperature alone is likely to happen in the reboiler, while a combination of temperature and $CO_2$ might give degradation in the stripper. Laboratory experiments were conducted to clarify factors influencing degradation, formation of degradation compounds and in general to study stability of amines under different conditions. The last decade several systematic degradation studies have been performed. Thermal degradation with $CO_2$ was studied by Davies, Lepaumier and Eide-Haugmo (Davis, 2009; Eide-Haugmo, 2011; Lepaumier et al., 2009a) and oxidative degradation by Lepaumier (Lepaumier et al., 2009b). Increased attention on oxidative degradation was seen after pilot plant samples showed high degree of similarity to degradation compounds found in oxidative degradation experiments (da Silva et al., 2012; Lepaumier et al., 2011a; Strazisar et al., 2003). The oxidative degradation experiments reported have been performed in variations of two setups, either in a closed-batch reactor at elevated temperature and oxygen pressure (Lepaumier et al., 2009b; Supap et al., 2001; Wang and Jens, 2011) or in an open-batch reactor at 55 °C, where the solution would be sparged with a wet gas blend of $CO_2$ and $O_2$/air (da Silva et al., 2012; Goff and Rochelle, 2004; Lepaumier et al., 2011b; Sexton and Rochelle, 2011). Lately, also the temperature swing

influence of degradation in a pilot plant was taken into consideration prompting building new laboratory apparatuses where the solvent would be exposed successively to both absorber and stripper conditions (Closmann and Rochelle, 2011; Einbu et al., 2013). Results from the latter solvent degradation rig seem to reflect the degradation compounds found in pilot plant samples.

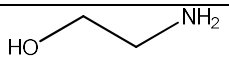
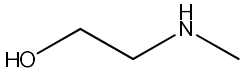
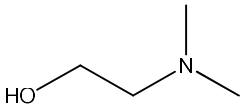
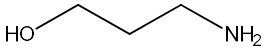
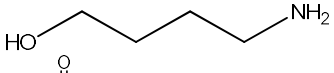
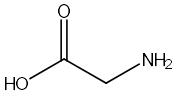
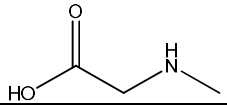
The initial steps of oxidative degradation of amines, both alkanolamines and other amines, are believed to take place through a radical mechanism. Amines have been shown to oxidize in air (Beckwith et al., 1983; Boukouvalas and Haynes, 2001; Chen et al., 1990; Correa et al., 1988; Kovtun and Aleksandrov, 1973). In addition oxidation can be induced using chemical methods (initiators) (Audeh and Smith, 1970; Dennis et al., 1967; Hull et al., 1969b; Leonard and Rebenstorf, 1945; Lindsay Smith and Mead, 1976; Rosenblatt et al., 1968; Rosenblatt et al., 1963), electrochemical methods (Portis et al., 1970; Smith and Mann, 1969), photosensitizers (Schaefer and Zimmermann, 1970) and other methods (Chow et al., 1978). The mechanisms postulated by the different research groups show some variation depending on the intermediates suggested. However, most studies suggest an aminium radical ion as an important intermediate and that the end products are aldehyde(s) and amine. The explicit details around the mechanism of oxidation of amines are still unclear, but the general impression is that the initial step either involves abstraction of an electron from the lone pair of nitrogen, abstraction of hydrogen from the nitrogen, α-carbon, or β-carbon or a combination of these depending on the amine structure, nature of oxidants, pH, solvent effects and whether oxygen is an active participant or not (Beckwith et al., 1983; Bedell, 2009; Chi and Rochelle, 2002; Davis et al., 1972; Goff, 2005; Goff and Rochelle, 2004; Hull et al., 1967; Hull et al., 1969c; Rosenblatt et al., 1967). The last step of both the electron and hydrogen abstraction mechanisms for monoamines is a nitrogen-carbon scission step. However, introducing a heteroatom β to the amine function for primary and secondary amines seems rather to give products formed from carbon-carbon scission as indicated by Dennis et al. and Nicolet et al. for MEA and DEA, both giving formaldehyde and ammonia as end products (Dennis et al., 1967; Nicolet and Shinn, 1939). Tertiary β-hydroxy amines gave products indicating C-N fragmentation using lead tetra-acetate as oxidant (Leonard and Rebenstorf, 1945). Lindsay Smith showed that monoamines had higher reactivity towards formation of aminium radicals than corresponding diamines. This effect was less pronounced when the separation of the nitrogen atoms increased (Lindsay Smith and Mead, 1976).

The present paper describes results from oxidative degradation experiments on five amines and two amino acids in a laboratory scale closed setup at atmospheric pressure. The amines were chosen based on structure. The setup was constructed to introduce new aspects to the previous open batch system described in earlier publications (da Silva et al., 2012; Vevelstad et al., 2013). Both gas and liquid phase analyses were performed. The advantage using a closed system is that volatile degradation compounds are contained to a larger extent, shedding light on the formation mechanisms and which role reversibility and intermediates play. The amines and amino acids were chosen to obtain information on how the structure influences the formation of degradation products. In this work potassium hydroxide was used to neutralize the amino acids.

## 2. Experimental section

The amines used are given in Table 1. AB was purchased from Syntastic, purity 98%. The rest of the amines were purchased from Sigma-Aldrich with purity higher than 98%. Potassium hydroxide pellets were obtained from Merck and ammonia (25wt% in water) from VWR.

**Table 1: Short, full name, structure and cas for amines used.**

| Amine | Abbr. | Structure | Cas |
|---|---|---|---|
| 2-ethanolamine | MEA |  | 141-43-5 |
| 2-(methylamino)-ethanol | MMEA |  | 109-83-1 |
| 2-(dimethylamino)-ethanol | DMMEA |  | 108-01-0 |
| 3-Amino-1-propanol | AP |  | 156-87-6 |
| 4-amino-1-butanol | AB |  | 13325-10-5 |
| Glycine | Gly |  | 56-40-6 |
| Sarcosine | SAR |  | 107-97-1 |

Amine or amino acid solutions (30 wt%) were prepared gravimetrically using distilled water. Potassium hydroxide was added to the amino acids (glycine and sarcosine) in 1:1 relation. A loading of 0.4 mole $CO_2$ per mole amine group was obtained by bubbling $CO_2$ gas through the solution until the desired weight was obtained.

In order to investigate the effect of ammonia on the degradation rate, one experiment was run with an MMEA-$NH_3$ mixture. An MMEA/water solution was prepared and loaded with $CO_2$ ($\alpha$=0.4 mole $CO_2$/mole MMEA). Ammonia in water (25 wt%) was added to give a final solution of 30 wt% MMEA and 7 wt% ammonia, loaded with $CO_2$.

Actual amine/amino acid concentrations were measured using LC-MS and alkalinity titration. $CO_2$ concentrations were measured for the start and end samples using the $BaCl_2$ method (Ma'mun et al., 2007). In addition, selected samples were analysed for "heat stable salts" ("HSS"), nickel, chromium and iron (Inductively Coupled Plasma Mass Spectroscopy, ICP-MS), nitrogen (Kjeldahl), density, anions (Ion Chromatography, IC), alkylamines and ammonia (Gas chromatography-Mass Spectrometry, GC-MS/ Liquid Chromatography–Mass Spectrometry, LC-MS), nitrosamine (LC-MS-MS-QQQ), degradation compounds in the "LC-MS mix" (LC-MS) shown in Table 2 and LC-MS analysis in full scan mode.

**Table 2: Short and full name of the degradation compounds in "LC-MS mix".**

| | | |
|---|---|---|
| BHEOX | *N,N'*-Bis(2-hydroxyethyl)-oxamide | 1871-89-2 |
| HEA | *N*-(2-hydroxyethyl)-acetamide | 142-26-7 |
| HEF | *N*-(2-hydroxyethyl)-formamide | 693-06-1 |
| HEGly | *N*-(2-hydroxyethyl)-glycine | 5835-28-9 |
| HEI | *N*-(2-hydroxyethyl)-imidazole | 1615-14-1 |
| HEPO | 4-(2-hydroxyethyl)-2-piperazinone | 23936-04-1 |
| OZD | 2-Oxazolidinone | 497-25-6 |

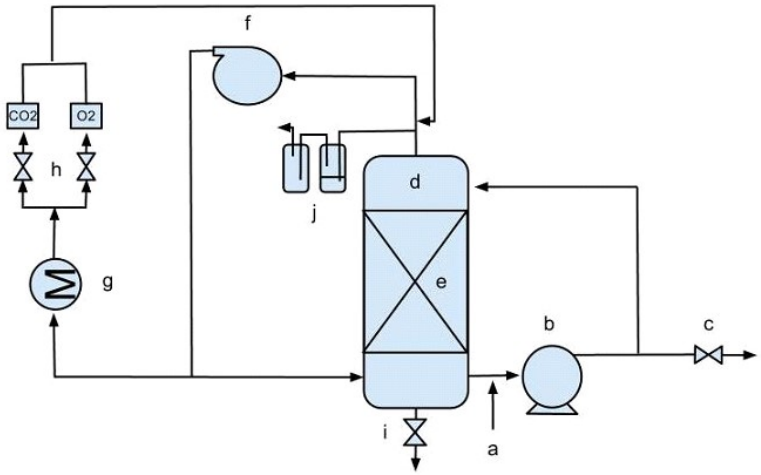
Almost all of the analytical techniques used are previously described by Vevelstad (Vevelstad et al., 2013). Nitrosamines were analysed on a LC–MS/MS 6460 Triple Quadrupole Mass Spectrometer coupled with a 1290 Infinity LC Chromatograph and Infinity Autosampler 1200

Series G4226A from the supplier Agilent Technologies. The quantification was performed diluting the samples 1/1000 in water and adding deuterated internal standards. Column, ion source and mobile phase were the same as described for amine and full scan analysis by Vevelstad (Vevelstad et al., 2013). The amine quantification for all amines, except MEA, was performed without internal standard. System and methods used for LC-MS analysis (alkylamine, ammonia, degradation compounds, amine, full scan) are described in more details by da Silva and Vevelstad (da Silva et al., 2012; Vevelstad et al., 2013). Details for the alkylamine and ammonia analysis for MEA experiment 1, KSAR and KGly on GC-MS are described by Vevelstad (Vevelstad et al., 2013), while more thorough details on method and system used for the GC-MS analysis (MEA, MMEA, DMMEA, KSAR) of degradation compounds are given by Lepaumier (Lepaumier et al., 2011b).
All systems and methods used for the rest of analyses, except "HSS", were described in detail in previous publications (Vevelstad et al., 2013). "Heat stable salts" were measured for the end sample by a wet chemistry method based on ion exchange followed by titration with NaOH. Additionally a test was conducted to verify what information this method gives. Two samples were prepared. The first sample consisted of 30 wt% MEA solution (5.07 g) and HEF (0.080 g, 0.90 mmol) and the second sample of water (5.00 g) and HEF (0.074 g, 0.83 mmol). Both of these samples were then analysed using the "HSS" method.

**Oxidative degradation setup**

Closed batch setup

The amine/amino acid solutions, loaded with $CO_2$ ($\alpha$= 0.4 mole $CO_2$ per mole amine group), were introduced into a closed batch reactor (a mini-absorber with an inner diameter of 80mm) according to the flow diagram shown in Figure 1.




a Valve for loading solution into the system
b Liquid pump
c Valve for taking sample
d Reactor
e Packing area
f Gas pump
g Cooler before gas analysers
h Flow meters for the $CO_2$ and $O_2$ analysers
i Valve used to empty the reactor
j Water lock to avoid pressure build up

**Figure 1: Simplified flow diagram for closed batch setup.**

Air was circulated in closed loop, counter-currently to the liquid flow, from the absorber sump to the top and liquid was distributed across the top of the packing. Gas/liquid mass transfer was enhanced by using a structured packing (Sulzer DX, SS316) with a diameter of 80mm and a total height of 275 mm (Figure 2).

**Figure 2: The closed batch system.**

The absorber was heated to 50-55 °C with the help of an ISOHEAT temperature sensor/system. Temperature sensors were placed in the absorber sump and in the packing. The gas was analysed for $CO_2$ and $O_2$. Temperature and gas composition ($O_2$ and $CO_2$) were continuously logged using Labview software (National Instruments). Samples were taken

regularly from the liquid phase (c) and analysed by the analytical techniques mentioned above. A water lock open to the surroundings was used to assure that deviations from atmospheric pressure were kept below a few mbar.

## 3 Results and discussion

### Gas phase analyses

Gas phase oxygen and $CO_2$ composition were continuously logged in Labview together with temperature measurements. Initial gas and liquid volumes varied a few percent because loading of liquid into the reactor was based on visual evaluation, and the amount of liquid extracted when sampling varied with time and between experiments. In addition there might have been small variations in the residual amount of nitrogen in the gas volume prior to start-up of the experiments although the apparatus was purged with air before every test.

The development in oxygen and carbon dioxide concentrations in the gas phase for the three amines MEA, MMEA and DMMEA are given in Figure 3 and 4. It has to be pointed out that the peak around 200 hours for the MEA experiment is related to a stop in the experimental run. The setup was not opened to air during this period, however circulation of gas and liquid was stopped for a period and the temperature decreased to around 25-30 °C before the problem was solved.

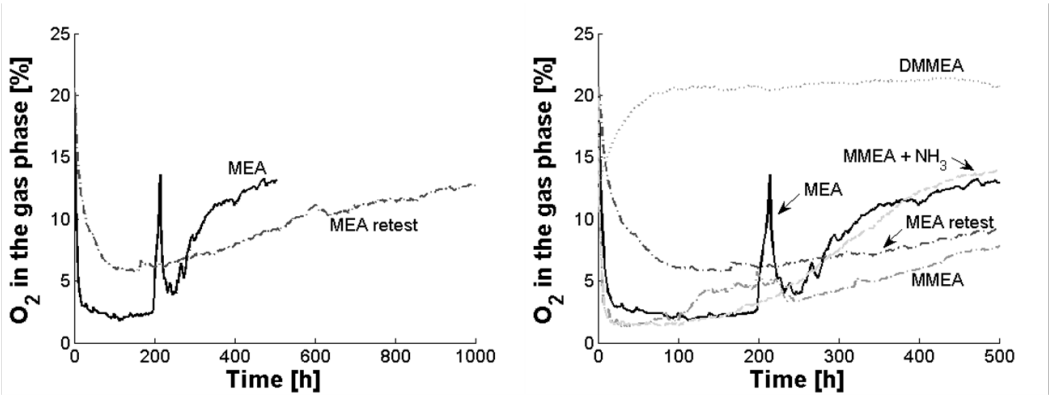



**Figure 3: Oxygen (%) in gas phase over time (h) for MEA (summer 2011), MEA retest (summer 2012), MMEA, MMEA-$NH_3$ and DMMEA.**

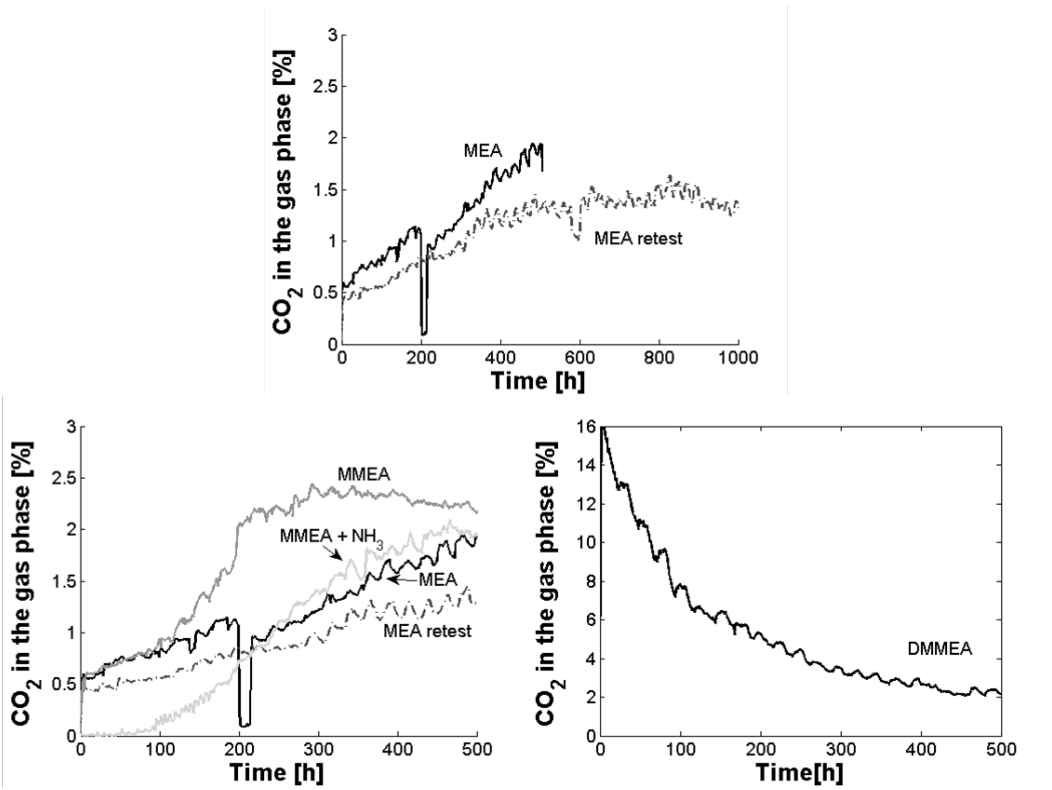



**Figure 4: $CO_2$ (%) in the gas phase over time (h) for MEA (summer 2011), MEA retest (summer 2012), MMEA, MMEA-$NH_3$ and DMMEA.**

DMMEA shows different profiles than the other two amines for $CO_2$ and $O_2$. It seems like oxygen stays in the gas phase, while $CO_2$ increases fast to 16 % and then decline toward 2%. The analysis of the initial sample shows that the DMMEA solution was loaded to 0.6 mole $CO_2$ /mole amine. This might explain the fast increase in the gas phase. Analyses also show that DMMEA is the only amine where the loading decreases to a significant extent during the experimental run, ending up at 0.2 for the end sample.

Gas phase oxygen and $CO_2$ profiles for the alkanolamines with increasing carbon chain-length are given in Figure 5.

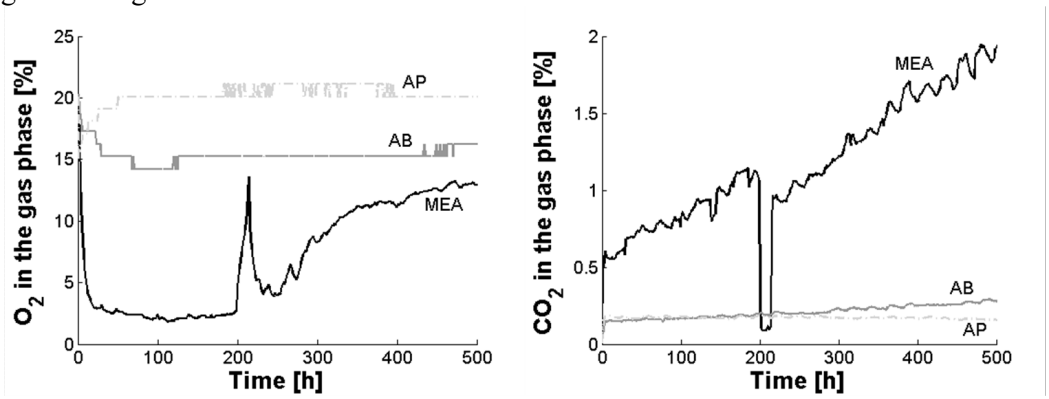



**Figure 5: Oxygen (left, %) and $CO_2$ (right, %) in gas phase over time (h) for MEA (summer 2011), AP and AB.**

AP shows a similar behaviour to DMMEA. The oxygen level decreases fast in the beginning and then increases back to the initial concentration. AB seems to gradually reach a level of 15% oxygen. The gas phase $CO_2$ concentrations for AP and AB increase slightly with time, but much less than for MEA and MMEA. Because of low degradation the $CO_2$ loading is almost constant.

The oxygen and $CO_2$ profiles for amino acid analogues to MEA and MMEA are given in Figure 6.

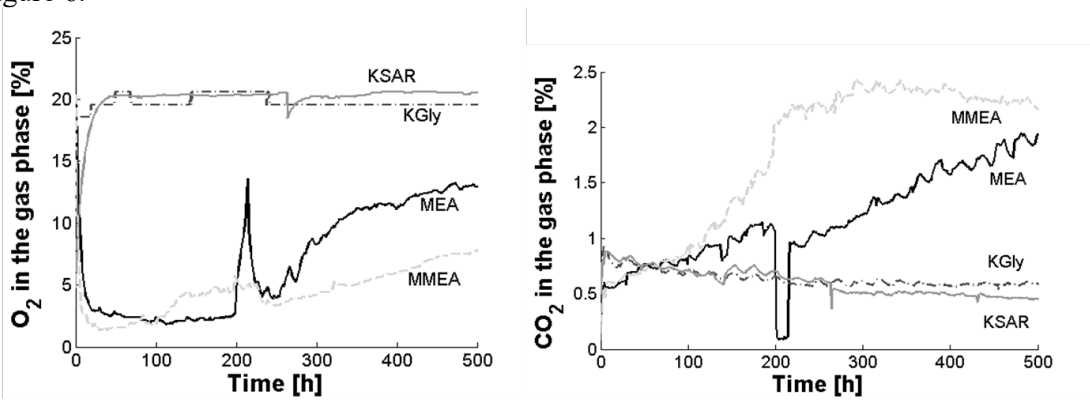



**Figure 6: Oxygen (left, %) and $CO_2$ (right, %) in gas phase over time (h) for MEA (summer 2011), MMEA, KGly and KSAR.**

KSAR and KGly show a similar behaviour to the amines with low/no degradation regarding gas phase oxygen content, and the $CO_2$ level decreases gradually.

The gas phase oxygen profiles for DMMEA, AP, KGly and KSAR show similar trends. The same can be said about AB, MEA, MEA retest, MMEA and MMEA-$NH_3$, even if the $O_2$ levels are not the same. The first set of amines show low or no degradation, and the shape of the oxygen curve suggests a sudden drop caused by for instance nitrogen pockets in the apparatus, and then a diffusion based re-entry of oxygen into the system. A mass transfer based model was postulated and could explain the shape of the curve for DMMEA by fitting a mass transfer coefficient, $k_g$. The same model could also predict the concentration of oxygen for the AP and KGly tests. In the cases where there is oxygen consumption by degradation, the partial pressures of oxygen can be explained by the combination of re-entry of oxygen due to diffusion and consumption through the degradation reactions. This latter contribution can be calculated according to Sexton (Sexton and Rochelle, 2011) where oxygen consumption was estimated from the reaction between MEA and oxygen resulting in ammonia and the chosen degradation compounds. When both mechanisms are taken into consideration, it is possible to show that the oxygen consumption prediction is in reasonable agreement with the observed profiles.

**Amine loss**

In Table 3 the amine losses (%) calculated from both LC-MS and titration results after 3 weeks for the different experiments are given. Amine loss is calculated by

$$a = \left( \frac{C_0^m - C_i^m}{C_0^m} \right) * 100$$

where $C_0^m$ is initial amine concentration and $C_i^m$ is the molar concentration at a specific time i.

**Table 3: Amine loss after 3 weeks determined by titration and LC-MS.**

| Experiment | LC-MS | Titration |
|---|---|---|
| MEA | 26 | 23 |
| MEA retest | 19 | 15 |
| MMEA | 32 | 26 |
| DMMEA | <5 (1.5[a]) | <5 |
| AP | <5 | <5 |
| AB | <5 (4.6[a]) | < 5 (0.8[a]) |
| KGly | <5 | <5 |
| KSAR | <5 | <5 |

[a]Measured amine loss.

It is in general seen that titration predicts lower losses than analyses based on LC-MS, this might be due to uncertainty of the analytical method and formation of small amount of other amines contributing to a lower alkalinity loss. However, the agreement is deemed satisfactory for MEA and MMEA where the losses are significant, but for the other components the losses are too small. The amine losses for the individual amines (LC-MS) over time are given in Table S5 in the supporting information.

In Figure 7 the normalised amine concentrations over time are given. Normalised concentrations are found by $b = \frac{C_i^m}{C_0^m}$ using results from LC-MS (mol/L).

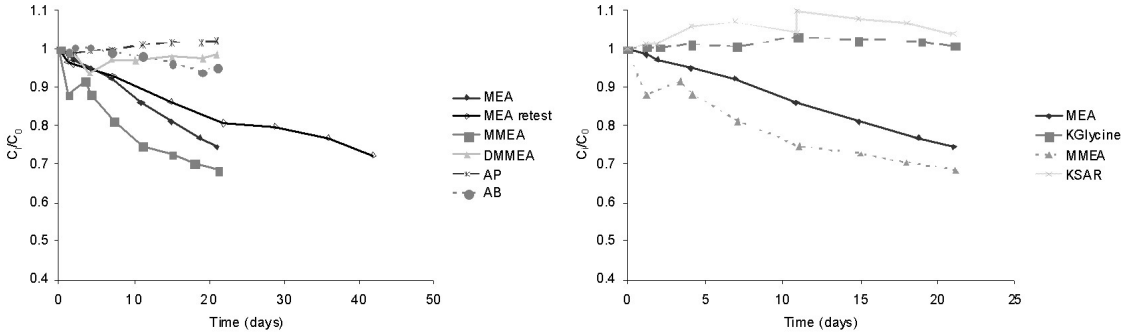



**Figure 7: Normalised amine concentration over time (days).**

Amine loss was found to be significant for MEA and MMEA. For AB and DMMEA there is indication that degradation took place, however the loss was within the level of uncertainty. The order of increasing degradation rate was found to be DMMEA < MEA < MMEA for amines with increasing steric hindrance on the amine functionality. In contrast Lepaumier found that MEA degraded slightly faster than MMEA while another secondary amine, DEA, degraded faster than MEA (Lepaumier et al., 2009b). DMMEA showed lowest degradation of these three. Rooney found that DEA was more stable than MEA and MDEA (Rooney et al., 1998) which is contrary to Lepaumier's results. However, degradation rate in the present and Lepaumier's work are based on amine loss, while Rooney based his conclusions on the formation of anions. Looking at formation of anions, MMEA in the present work was found to be more stable than MEA.

Both the MEA experiments performed in this work showed the same oxygen consumption, nitrogen recovery and amine losses. However, the last experiment lasted for 6 weeks compared to 3 weeks for the first one. The first experiment was run at a mean temperature about 4-5°C higher than the last experiment, 55°C compared to close to 50°C for the second experiment. In Figure 14 is seen that the iron concentration increases more rapidly in the first

MEA test compared to the re-test. Also the day one concentration in the first test is higher. Why the first experiment shows a higher concentration on the first day is not known, but this higher starting point could be a contributor to the more rapid degradation. Temperature has also a very strong effect on degradation rate and the combination of lower initial iron concentration and temperature could be an explanation for the lower degradation rates seen in the MEA re-test.

Oxidation degradation of MMEA has also been conducted in an open batch setup (Lepaumier et al., 2011b) and in this case only 19 % of the MMEA was recovered after 311 hours. As comparison, more than 68 % of MMEA was recovered in the closed setup after 500 hours. It was postulated that loss off volatile degradation compounds, notably $NH_3$, could accelerate degradation in open setup. To test this hypothesis, another experiment was performed in the closed setup with MMEA, ammonia and $CO_2$ (30wt% MMEA, 6wt% $NH_3$, $\alpha$=0.2 mole $CO_2$/mole amine). In this experiment the degradation was reduced to half the amount of the previous experiment. This strongly suggests that reversible reactions play an important role in degradation, and that retaining volatile degradation products in the gas phase, as $NH_3$, may actually be one method to slow down degradation. Rooney suggested that increased $CO_2$ concentration, and thereby ionic strength, may lower the $O_2$ solubility (Rooney et al., 1998). Supap showed that the MEA degradation rate decreased with increasing $CO_2$ loading (Supap et al., 2009). If this holds also for MMEA, the effect of gas phase $NH_3$ could be even stronger that found in the above experiments as the $CO_2$ loadings in the two experiments were respectively $\alpha$=0.4 and $\alpha$=0.2 without and with added ammonia. More tests should be conducted to verify these preliminary results for ammonia as “inhibitor” of degradation.

Increase in carbon chain length between alcohol and amine function did not increase the degradation compared to MEA. On the contrary, low and no degradation were found for AB and AP respectively. AB with a carbon chain of four makes formation of an energetically favourable five-membered ring possible. Lepaumier reported formation of 1-methylpyrrolidine in their oxidative degradation experiments of *N,N,N',N'*-tetramethylbutylenediamine (TMBDA) (Lepaumier et al., 2010). The formation of 5-membered ring from cyclisation of AB, pyrrolidone, has been identified in thermal degradation experiments with $CO_2$ (Davis, 2009; Eide-Haugmo, 2011). This compound was not analysed in the present work, but it is very likely that it was formed under our conditions. Lepaumier showed that polyamines with a 4 carbon chain between tertiary amine functions degraded more than both MEA and polyamines with two or three carbons between the tertiary amine functions (Lepaumier et al., 2010).

Amino acids salts have received increased attention as alternatives to amine solvent used for $CO_2$ capture (Aronu et al., 2010a; Hook, 1997). However, degradation data are limited. Amino acids are zwitterions which have to be neutralized to activate the amino group for $CO_2$ absorption. In this work potassium hydroxide was used to neutralize the amino acids, however other bases could also be used and both potassium sarcosinate (KSAR) and amine-aminoacids, as for example 3-(methylamino)propylamine/sarcosine (SARMAPA), have been tested for $CO_2$ absorption in a laboratory pilot plant (Aronu et al., 2010b; Knuutila et al., 2011). KSAR and KGly showed low or no oxidative degradation. Loaded KSAR did give around 50% degradation under thermal degradation conditions with $CO_2$ as shown by Eide-Haugmo (Eide-Haugmo, 2011). The low degradation found under the conditions used in this study might be explained by low temperature and low oxygen solubility in the strongly ionic solution. KSAR did show GC-MS peaks suggesting formation of several anhydrides and

intermediates for these anhydrides. However, some of these compounds might be impurities in sarcosine solutions.

## Degradation compounds

### MEA

Since MEA was the only compound where the degradation products could be quantified properly, these were followed as function of time. Percentage formation of the degradation products ( $\tau_{f,i}$ ) was calculated by the method described by Lepaumier (Lepaumier et al., 2011b) and shown as $\tau_{f,i} = \nu_i * \frac{C_i^m}{C_0^m} * 100$

Here $\nu_i$ is the number of nitrogen in the degradation product, $C_i^m$ is the molar concentration of the degradation product and $C_0^m$ is the initial concentration of MEA. % formation of degradation compounds as function of time (days) for the LC-MS mix, ammonia, nitrite and nitrate for the two MEA experiments are given in Figure 8 and the concentration (mmol/L) as function of time (days) of formate and oxalate are given in Figure 9.

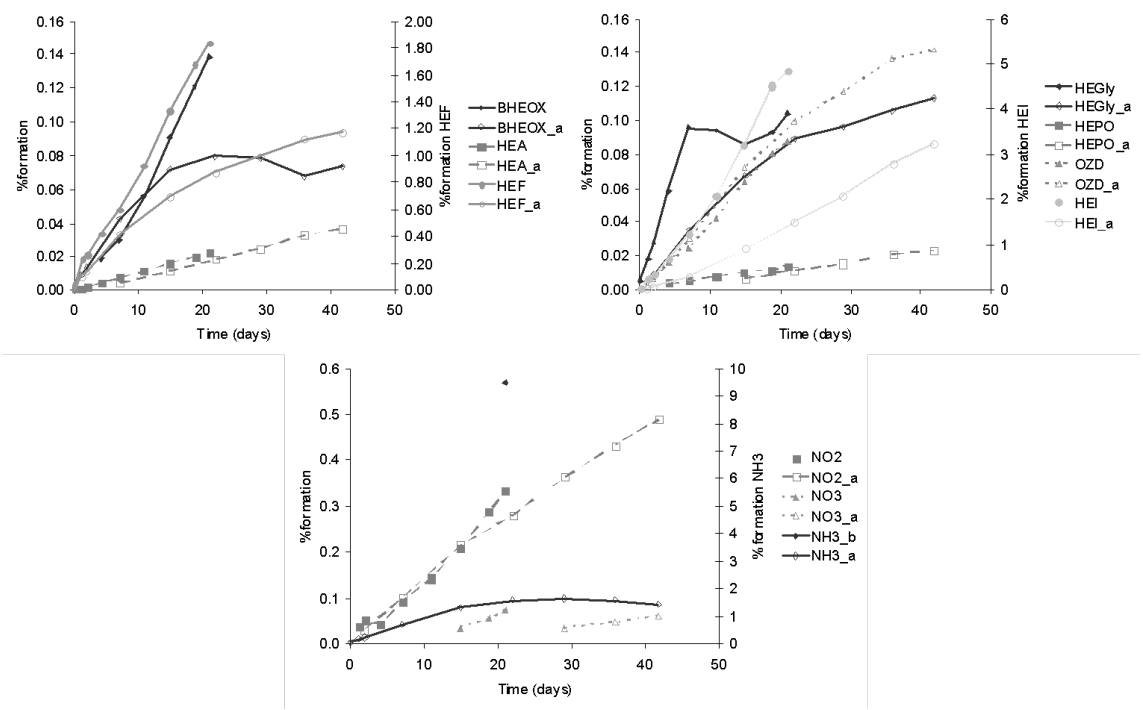



**Figure 8: % formation of degradation compounds as function of time (days) found in the two different MEA experiments, [a]MEA retest (6 weeks), [b]ammonia results from GC-MS for the first MEA experiment.**

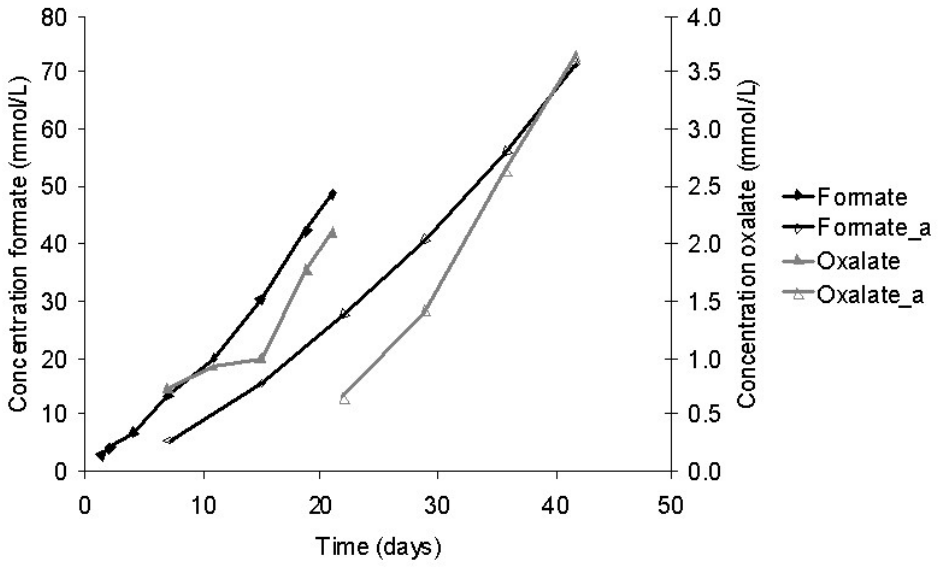



**Figure 9: Concentration (mmol/L) as function of time (days) of formate and oxalate for the two different MEA experiments, [a]MEA retest, (6 weeks).**

The time period between conducting the two MEA experiments was about 1 year. Small concentration changes for the degradation compounds in these experiments could therefore be explained by analytical procedures being under continuous development. In some cases new methods have been developed as for ammonia and alkylamines. Results for most of the degradation compounds (LC-MS mix and IC mix) show that the first MEA experiment (summer 2011) gave higher formation rates than the MEA retest. As seen from Figure 14 the metal concentrations rise more rapidly in the first MEA test compared to the re-test. All this is consistent with the more rapid degradation of MEA in the first test as discussed earlier and the slower absorption of oxygen as shown in Figure 3.

Exceptions are the formation rates for OZD, HEPO, HEA and nitrite which seem to be comparable for the two experiments. HEPO and HEGly were earlier indicated to be independent of oxygen concentration (Vevelstad et al., 2013). Measured gas phase oxygen concentration for the two experiments shows higher oxygen levels for the re-test, Figure 3, and that it takes longer for the oxygen level to reach its minimum. In addition the nitrogen recovery was found to be the same for both of the MEA experiments, see Table 10. Another interesting observation is that the MEA re-test shows the same degradation rate as for the MEA experiments at 21 % $O_2$ in an open setup (Vevelstad et al., 2013).

## Other amines

Degradation compounds for all amine tested were analyzed using techniques described earlier. The LC-MS results for the samples after 3 weeks for all experiments are given in Table 4.

**Table 4: Concentration (µg/mL) of degradation compounds after 3 weeks (LC-MS analysis).**

| Experiment | OZD | BHEOX | HEA | HeGly | HEPO | HEF | HEI | NDELA |
|---|---|---|---|---|---|---|---|---|
| MEA | 306 | 491 | 94 | 498 | 41 | 6560 | 10923 | 0.092 |
| MEA retest | 402 | 328 | 87 | 495 | 38 | 3630 | 3939 | no analysis |
| MMEA | 17 | < 10 | < 10 | 361 | 66 | 94 | 263 | <0.001 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| DMMEA | < 10 | < 100 | < 10 | < 10 | < 10 | 13 | 2.9 | <0.1 |
| AP | < 1 | < 10 | < 1 | < 1 | < 1 | < 1 | 0.8 | <0.05 |
| AB | < 10 | < 10 | < 10 | < 10 | < 10 | < 10 | < 10 | <0.01 |
| KGly | < 1 | < 10 | < 1 | 4.7 | < 1 | < 1 | 0.60 | <0.05 |
| KSAR | < 10 | < 10 | < 10 | < 10 | < 10 | < 10 | < 10 | <0.01 |

The typical MEA degradation compounds as for example OZD, BHEOX, HEA and HEI are generally formed in smaller amounts from the other amines. Most of the amines tested showed very little oxidative degradation and this makes it difficult to propose degradation mechanisms for the formation of new degradation compounds. In general it seems like the formation of degradation compounds follows the same patterns as earlier described for the formation of de-methylated amines (secondary and tertiary amines) or secondary products as HEF analogues, HEI, OZD analogues, alkylamines and ammonia (da Silva et al., 2012; Lepaumier et al., 2011b; Lepaumier et al., 2009b; Strazisar et al., 2003; Vevelstad et al., 2013).

Volatile compounds as ammonia, methylamine, dimethylamine, diethylamine and ethylamine were only analysed for the amines which did not influence the analytical method. A GC-MS method using derivatisation was used to analyse for ammonia and alkylamine, the results (after 3 weeks) are shown in Table 5.

**Table 5: Concentration (µg/mL) of volatile degradation compounds after 3 weeks in liquid samples (GC-MS).**

| Experiment | $NH_3$ (µg/mL) | Methylamine (ng/mL) | Dimethylamine (ng/mL) | Ethylamine (ng/mL) | Diethylamine (ng/mL) |
|---|---|---|---|---|---|
| MEA | 6495 | 4700 | <500 | <500 | <500 |
| KGly | 712 | 4500 | 3000 | <100 | <100 |
| KSAR | <1000 | <10000 | 1600 | <100 | <100 |

This GC-MS method was not suitable for analysis of DMMEA and MMEA as the amines themselves were found to introduce noise into the chromatogram. Later on an LC-MS method for ammonia and alkylamine was developed and used to analyse the MEA retest and MMEA+$NH_3$ experiment. Additionally MEA and MMEA samples were re-analysed using the new LC-MS method as shown in Table 6 (concentration in the sample after 3 weeks is given).

**Table 6: Concentration (µg/mL) of volatile degradation compounds in liquid samples after 3 weeks using LC-MS.**

| Experiment | $NH_3$ (µg/mL) | Methylamine (ng/mL) | Dimethylamine (ng/mL) | Ethylamine (ng/mL) | Diethylamine (ng/mL) |
|---|---|---|---|---|---|
| MEA retest | 1275 | 9679 | 79 | 120 | < 50 |
| MMEA[a] | 1743 | 2300000 | 2895 | 223 | < 50 |
| MMEA+$NH_3$ | 7020 | no analysis | no analysis | no analysis | no analysis |

[a]Analyses performed on old samples (1 year old samples).

The analyses on the original MEA samples on GC-MS, Table 5, showed that ammonia was formed in much higher amounts than methylamine. In the LC-MS analysis performed on the same MEA samples 1 year later neither ammonia nor methylamine was above quantification limit. This might be explained by these compounds being volatile and thus disappear over time. For MMEA, GC-MS analysis was not possible, but the re-analysis on LC-MS showed methylamine and ammonia in the same order of magnitude. It is general consensus that ammonia, volatile alkylamine and aldehydes are formed by radical mechanisms. Both electron

and hydrogen abstraction mechanisms have been suggested in studies on monoamine without oxygen present (Audeh and Smith, 1970; Hull et al., 1969a; Hull et al., 1967) resulting in aldehyde and ammonia or alkylamine through carbon-nitrogen scission. Dennis suggested that β-amino and β-hydroxyamines instead started with a carbon-carbon cleavage, in the end giving formaldehyde and ammonia for MEA (Dennis et al., 1967). In addition Nicolet showed that DEA was split to 4 moles of formic acid and 1 mole of ammonia using periodic acid (Nicolet and Shinn, 1939).

Oxygen was only added as air in the start-up of the present experiments, the gas volume is between 3 - 4L in the reactor. Using Sexton's (Sexton and Rochelle, 2011) suggested oxygen stoichiometry, as explained earlier, for formic acid, HEI, HEF $HNO_2$, oxalic acid and $HNO_3$ would consume about 97 mmoles of $O_2$ for the first MEA experiment in the closed setup. Calculating $O_2$ present for the system resulted in 30 mmoles $O_2$ available at start-up (gas volume 4L). As suggested earlier oxygen can come from mass transfer into the apparatus in addition to oxygen present in the initial organic compounds and possibly also water (hydrogen or electron abstraction). From the present results it is not possible to prove whether oxygen in degradation products is taken from water or not.

The samples were in addition analysed for anionic compounds using IC, concentrations (µg/g) for the end samples are given in Table 7.

**Table 7: Concentration (µg/g) of anionic degradation compounds in the end samples (IC).**

| Experiment | Nitrite | Nitrate | Formate | Oxalate | Acetate |
|---|---|---|---|---|---|
| MEA[a] | 570 | 171 | 2020 | 171 | <50 |
| MEA retest[b,d] | 969 | 165 | 2970 | 296 | <50 |
| MMEA | <30 | <30 | 1270 | 175 | <110 |
| DMMEA | - | - | <30 | <11 | - |
| AP | <50 | <50 | <60 | <50 | - |
| AB | 397 | 196 | 459 | <48 | <50 |
| KGly | < 50 | < 135 | 464[c] | 199 | 2130[c] |
| KSAR | - | - | <30 | - | - |

[a]Analysed on both AS15 and AS11HC. Mean values are calculated for analyses of samples with different dilutions and for both of the columns.
[b]Analysed on AS11HC. Mean values are calculated for analyses of samples with different dilutions.
[c]These values are highly uncertain since analysing glycolate, acetate and formate spiked with KGly only gave two peaks which were far from baseline separated, additionally it was seen that KGly in itself gave peaks in this area, see Vevelstad (Vevelstad and Svendsen, 2013).
[d]End sample (42 days).

Acetate and glycolate were in general below or close to the quantification limit. The exception is acetate in KGly, where acetate could be a result of the solution matrix as shown by Vevelstad (Vevelstad and Svendsen, 2013). However, the uncertainty around the early peaks (glycolate, acetate, formate, 2-[(2-hydroxyethyl)amino]-2-oxo-acetic acid (HEOX)) is in general higher than for nitrite, nitrate and oxalate because of insufficient base line separation, wider peaks because of lower KOH concentration in the eluent and to a higher impact of the solution matrix (Vevelstad and Svendsen, 2013). It has also to be pointed out that identification is based on commercially available standards, and that it is possible that two anions have similar retention time and therefore could be misinterpreted even if the standard is added to the unknown sample.

Samples were analysed for "heat stable salts". However it was unclear what this test actually showed. A test was therefore conducted to investigate if amide would contribute to the HSS. Two samples, one with known amount of HEF in water and the other sample with HEF in

30 wt% MEA were analysed using the method for heat stable salt, the results are shown in table 8, where % HEF = $C_{HSS}/C_{HEF,0}$.

**Table 8: HSS for HEF in 30 wt% MEA and water.**

| | HEF (mol/kg) | HSS (eq/kg) | % HEF |
|---|---|---|---|
| Water | 0.16 | 0.07 | 43 |
| 30wt % MEA | 0.17 | 0.07 | 39 |

As seen from table 8, the heat stable salt method seems to some extent to give amide hydrolysis. This shows that it is necessary to conduct more tests to verify what the method is giving and to clarify the expression "heat stable salt".

The end samples from all degradation experiments were analysed using the "heat stable salts" method. The results are given in Table 9.

**Table 9: HSS for end samples (3 or 6 weeks).**

| | Formate [mol/kg] | Total anion[a] [mol/kg] | HSS [eq/kg] | Identified (%) | Formate (%) |
|---|---|---|---|---|---|
| MEA | 0.045 | 0.068 | 0.090 | 75 | 50 |
| MEA retest[b] | 0.066 | 0.101 | 0.190 | 53 | 35 |
| MMEA | 0.028 | 0.035 | 0.140 | 25 | 20 |
| DMMEA | | | <0.01 | | |
| AP | | | <0.01 | | |
| AB | 0.010 | 0.022 | 0.030 | 73 | 34 |

[a]Sum quantified anions from IC and HEGly from LC-MS.
[b]After 6 weeks.

The trend is that less "heat stable salts" were formed for low degradation levels. This is reasonable. Formate was found to be the largest contributor to HSS. The order of contribution to HSS for the MEA experiments was found to increase in the following order Nitrate < HEGly/Oxalate < Nitrite < Formate. However from the test, in table 8, it was also clear that amide could contribute to some extent to "HSS". Calculation showed that 40% of HEF in MEA and MEA retest gives respectively 30 and 10 % of "HSS".

**GC-MS/LC-MS analysis**

Some of the samples were analysed on GC-MS in chemical ionisation (CI) mode giving the molecular mass of the compounds. In addition LC-MS positive ($M+H^+$) and negative ($M-H^+$) scans enabled us to suggest degradation compounds by checking the masses in the full scan spectrum. Both techniques give only indications regarding qualitative results. LC-MS full scan usually gives a large number of masses, in some cases the masses in the positive scan are $M-Na^+$ or an MS fragment of the compound making it complicated to interpret. Mass to charge ratios (m/z) which could be related to known degradation patterns is of special interest and will be discussed in the following. Figure 10 gives a general mechanism for formation of secondary degradation products from different amines and acids. In Table 10 is given which amines showed m/z in the positive LC-MS scan. This could indicate formation of the products given in Figure 10.

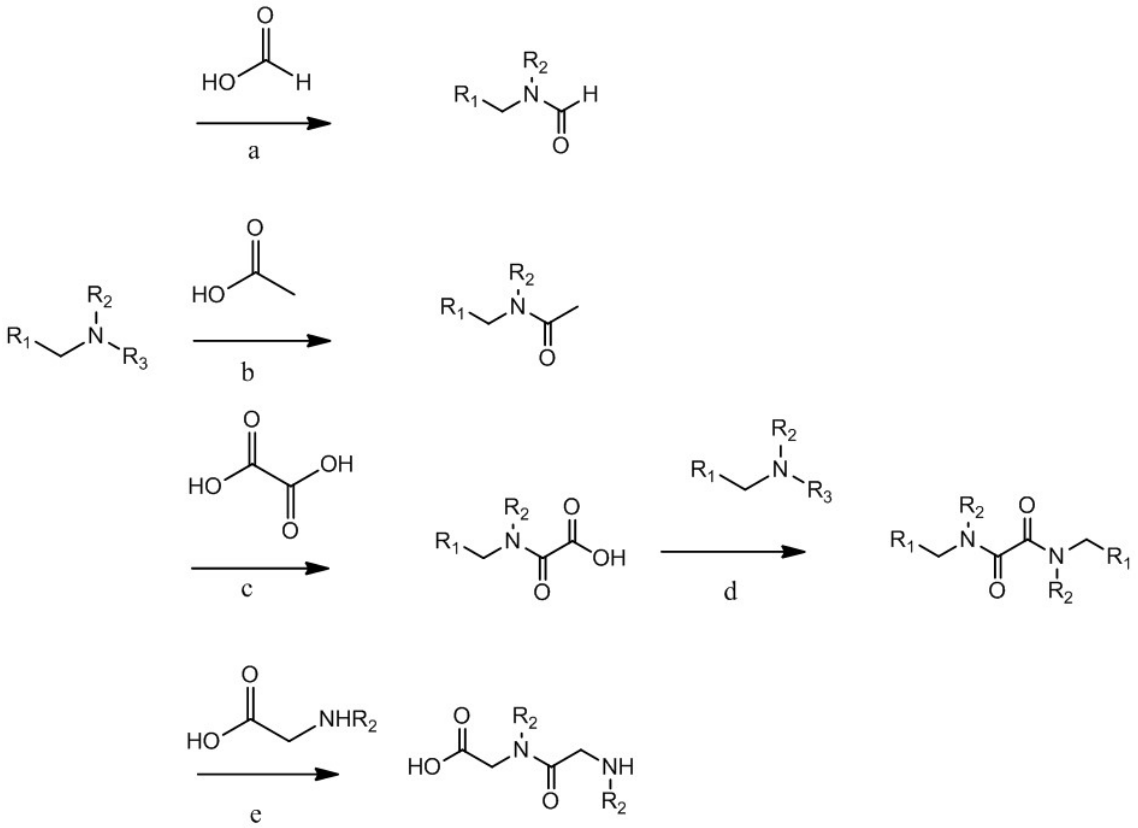



**Figure 10: General mechanism for formation of secondary degradation products between acids and amines.**

**Table 10: m/z found from LC-MS positive scan indicating products formed by the general mechanism shown in figure 10.**

| Amine | $R_1$ | $R_2$ | $R_3$ | a | b | c | d | e |
|---|---|---|---|---|---|---|---|---|
| MEA | $CH_2OH$ | H | H | x | | x | x | |
| MMEA | $CH_2OH$ | $CH_3$ | H | x | | | x | x[b] |
| DMMEA | $CH_2OH$ | $CH_3$ | $CH_3$ | | x[a] | | | |
| AP | $(CH_2)_2OH$ | H | H | x | x | | | |
| AB | $(CH_2)_3OH$ | H | H | x | | x | | |
| Glycine | COOH | H | H | x | | | | x |
| Sarcosine | COOH | $CH_3$ | H | x | | | | x |

[a]de-methylated DMMEA formed this product
[b]$R_2$ in the acid is hydrogen (glycine) (MMEA+glycine)

All studied compounds except DMMEA (de-methylated DMMEA) seem to form their HEF analogue. The MMEA experiment also showed an OZD analogue, MOZD, where MOZD has earlier been reported by Lepaumier (Lepaumier et al., 2011b). In addition the LC-MS positive scan gave an m/z =204 which might be a BHEOX analogue. The GC-MS (CI mode) results for MMEA showed a molecular peak at an m/z=172 which is still unknown but verified with LC-MS positive scan (m/z=173).

DMMEA showed m/z for MMEA in the LC-MS positive scan supporting the existence of de-methylation reactions earlier suggested by Lepaumier (Lepaumier et al., 2009b), and which makes it possible to form secondary degradation products from acids and amine (de-methylated DMMEA). However, it is slightly surprising that both AP and DMMEA show m/z suggesting formation of amides from acetate since acetate in general seems not to be formed, and if at all, only in small amounts. GC-MS (CI mode) gave no peaks for DMMEA.

GC-MS (CI mode) for KSAR showed molecular peaks at m/z=128 and 142 which are respectively the sarcosine anhydride (**3**: cas 5076-82-4) and the glycine sarcosine anhydride (**4**: cas 5625-52-5), where the last one is formed after de-methylation of sarcosine to glycine. The LC-MS positive scan for sarcosine shows in addition m/z=161 which might be the intermediate between sarcosine and sarcosine anhydride as shown in figure 11.

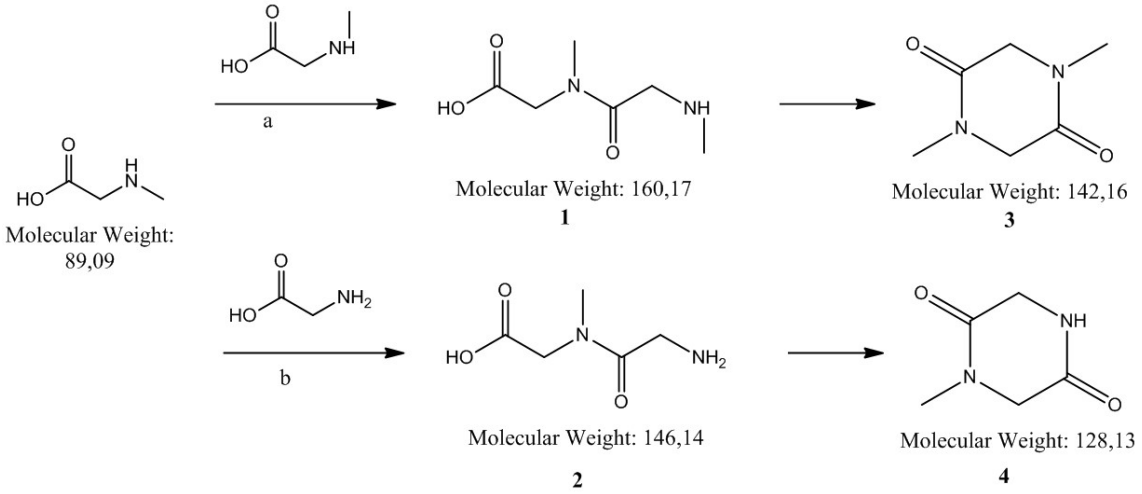



**Figure 11: Possible formation of different types of sarcosine anhydrides through route a and b.**

Neither sarcosine anhydride nor glycine sarcosine anhydride were visible with the available analytical methods and cyclodiglycine (106-57-0) could therefore not be verified in the glycine experiment since degradation data from GC-MS (CI mode) were not available. However, the formation of this compound is highly likely since both glycine sarcosine anhydride and sarcosine anhydride were found in the sarcosine experiment. In addition, LC-MS positive scan showed m/z=132 which is the glycine analogue to compound **1** shown in Figure 11 using glycine instead of sarcosine. Both of the glycine and sarcosine experiments showed a peak (only in positive scan for glycine, but both in negative and positive scan for sarcosine) which might suggest a reaction between the amino acid and 2-oxiranone (42879-41-4) giving *N*-carboxymethyl)glycine (142-73-4) or *N*-(carboxymethyl)-*N*-methylglycine (4408-64-4). However, 2-oxiranone has never been isolated in bulk and has up to this point only been identified using MS.

## Nitrogen balance

The end samples from each experiment were analysed for nitrogen according to the Kjeldahl method (Kjeldahl, 1883). Table 11 shows how MEA and the sum of known degradation compounds (LC-MS mix and $NH_3$) contribute to the organic nitrogen recovery ($R_N$) for the liquid phase end sample. The N unaccounted column is the balance up to 100%. Assumptions, together with the calculations for the uncertainty are given in the supporting information.

**Table 11: Nitrogen balance for end sample (3 or 6 weeks) liquid phase.**

| | Amine | Amine % | N known degr. cpd (%) | $R_N$ (%) | N unaccounted (%) |
|---|---|---|---|---|---|
| MEA | MEA | 70 | 15 | 85+/-5 | 15 |
| MEA retest[a] | MEA | 79 | 7 | 86+/-5 | 14 |
| MMEA | MMEA | 75 | 5 | 80+/-5 | 20 |
| DMMEA | DMMEA | 111 | 0 | 111+/-7 | -11 |
| AP | AP | 100 | 0 | 100+/-6 | 0 |
| AB | AB | 97 | 0 | 97+/-6 | 3 |
| KGly | Glycine | 92 | 1 | 93+/-6 | 7 |
| KSAR | Sarcosine | 99 | 0 | 99+/-6 | 1 |

[a]After 6 weeks

As expected, the amine with low degradation showed the highest nitrogen recovery.
The distribution of main nitrogen-containing degradation compounds together with total unaccounted nitrogen for MEA and MEA retest is given in Figure 12

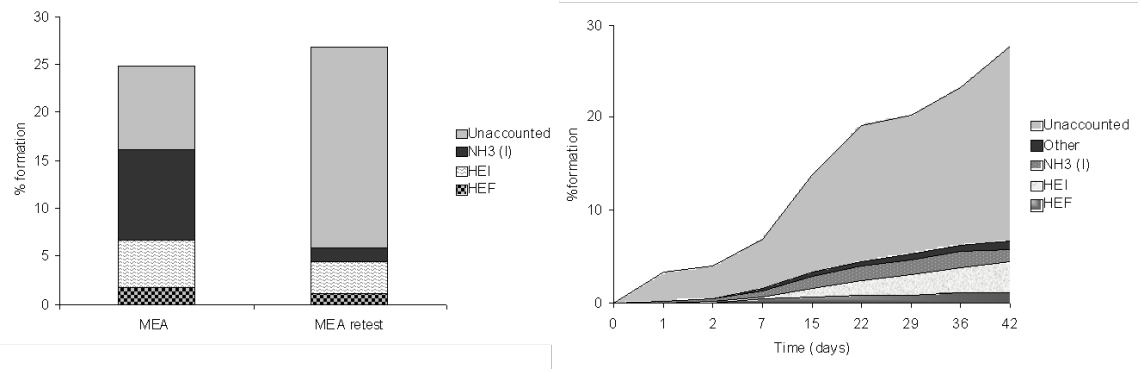



**Figure 12: % formation and unaccounted Nitrogen for end sample for MEA (21 days) and MEA retest (42 days) (left) and % formation over time (days) for MEA retest (right).**

Ammonia was quantified by GC-MS for the first MEA experiment and it is believed that this method over-predicts the liquid phase ammonia concentration which probably explains the lower ammonia concentration seen for the MEA retest which was analysed by LC-MS. Assuming the missing nitrogen is gas phase ammonia gives a higher partial pressure of ammonia than the total pressure in the system. This is no surprise, since there are still several nitrogen-containing degradation compounds in liquid phase without quantitative analysis. One of these compounds is HEOX, which was identified by a combination of lab experiment and IC as shown in previous publication (Vevelstad et al., 2013). Comparing the area in the IC-chromatogram make this the second largest peak after formate, which means that HEOX might have higher significance than some of the other degradation compounds for the nitrogen balance. A commercial standard was not available for HEOX, and this compound was therefore not quantified.

The % formation of degradation compounds for the MMEA experiment over time (days) is given in Figure 13.

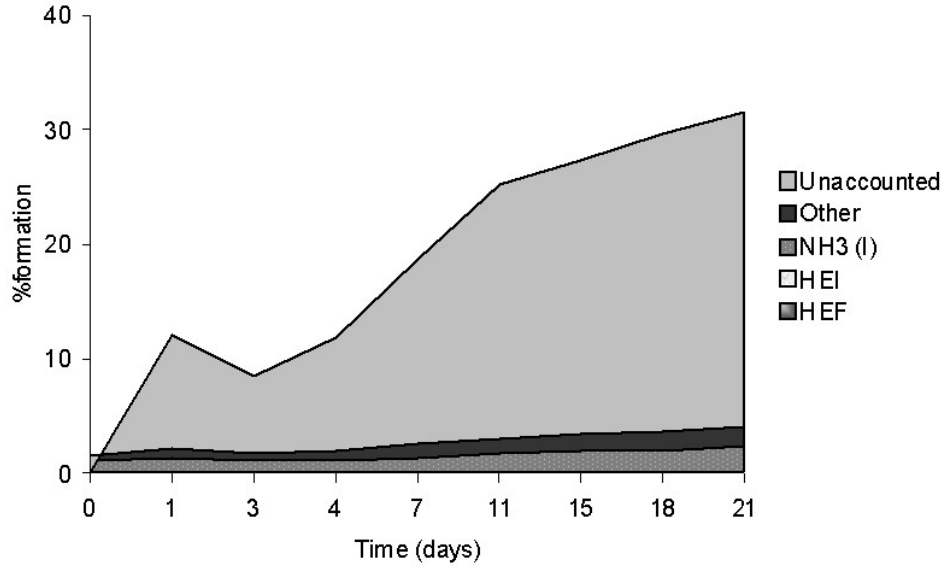



**Figure 13: % formation and unaccounted Nitrogen over time (days) for MMEA experiment.**

HEI and HEF are formed in small amounts. The main contributor to "Other" in the MMEA case in Figure 13 is methylamine which was found in comparable amounts to ammonia.

## Metals

Most of the experimental setup is built from glass. However, the packing and the gas lines are of stainless steel material (SS316). Iron, chromium and nickel concentrations were therefore measured for all the experiments. The results for the MEA, MMEA and DMMEA experiments are given in Figure 14.

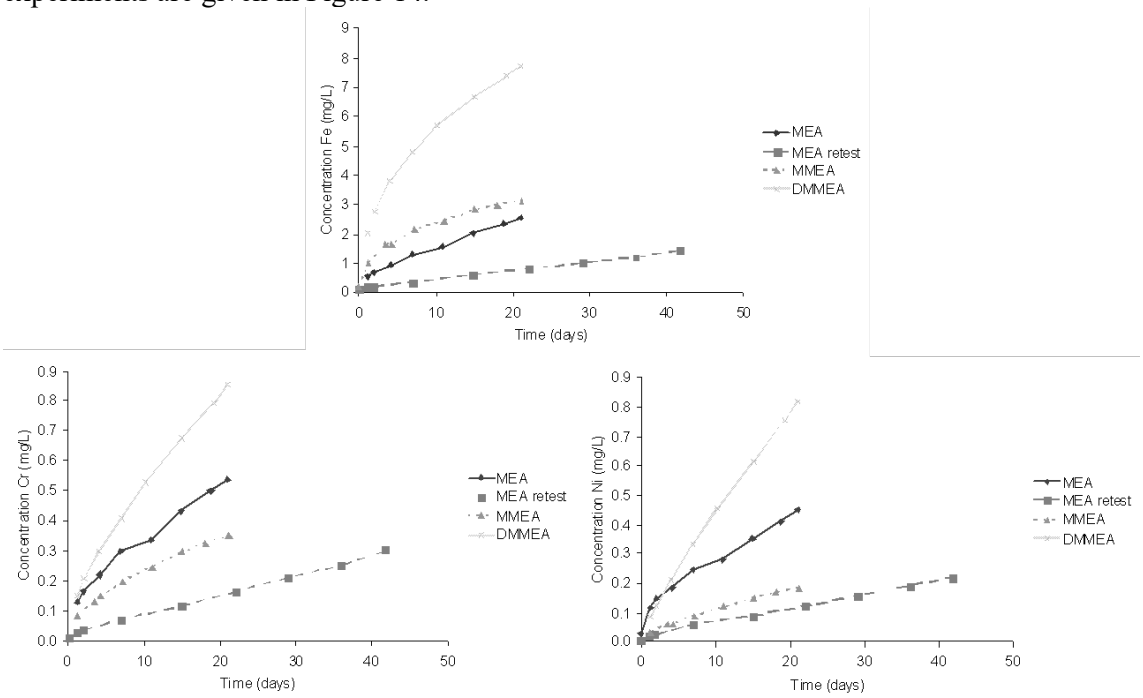



**Figure 14: Metal concentration (mg/L) as function of time (days) for MEA, MMEA and DMMEA.**

As expected the iron concentration increases with time in all systems. There is a large difference between the early MEA experiment and the MEA retest. This is in line with the degradation development seen for some of the products. Also higher iron concentrations are found in the MMEA system than for MEA. This was not unexpected as MMEA degrades faster. On the other hand, DMMEA gives very rapid dissolution of iron in spite of being very stable. It is expected DMMEA is corrosive in itself, but degradation is not triggered by iron. Chromium is found in slightly higher amounts than nickel and both of them increase in the same way.

The metal concentration build-ups in the MMEA and MMEA-$NH_3$ experiments are given in Figure 15.

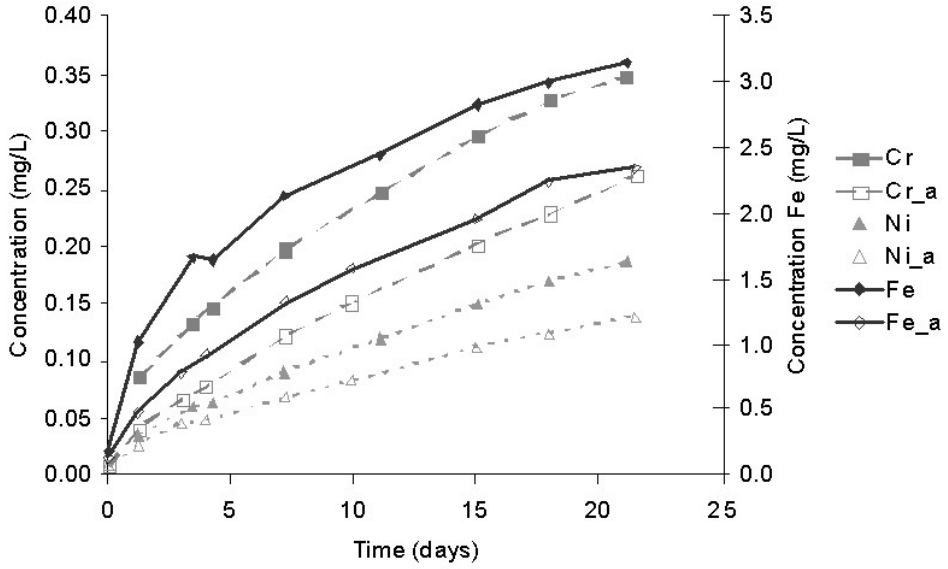



**Figure 15: Metal concentration (mg/L) as function of time (days) for MMEA and MMEA-$NH_3$ experiment. [a]MMEA-$NH_3$ experiment.**

The MMEA experiment with added ammonia shows lower degradation rate and has lower concentrations of all the metals. The concentration order is the same as without ammonia: iron > chromium > nickel.

The development in metal concentrations for the amines when increasing the carbon chain is given in Figure 16

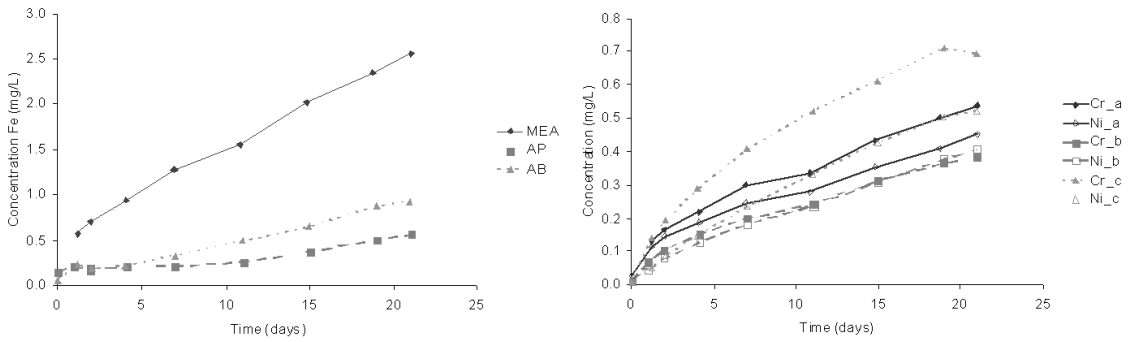



**Figure 16: Metal concentration (mg/L) as function of time (days) for MEA (a), AP (b) and AB (c).**

Iron follows the same trend as amine loss with MEA giving the highest rate of dissolution and AP the lowest. For nickel and chromium the picture is more complex and the spread in dissolution rates is relatively small.

The amino acid analogues to MEA and MMEA were also tested and the dissolution rates are given in Figure 17.

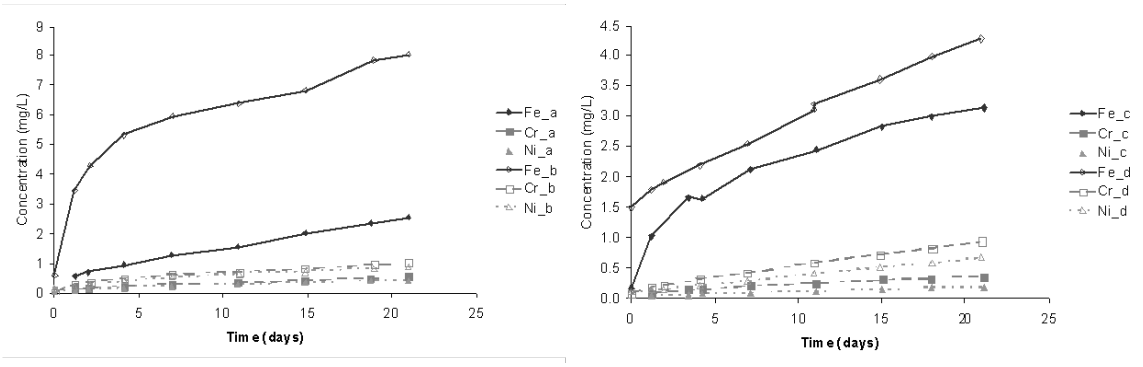



**Figure 17: Metal concentration (mg/L) as function of time (days) for MEA (a) and KGly (b) (left) and MMEA (c) and KSAR (d) (right).**

High metal concentrations were found for the amino acids and KGly was the worst. Both the amino acids show higher dissolution rates than their alkanolamine analogue. This is likely due to the ionic nature of the amino acids.

The iron concentrations seem to decrease in the following order KGly > DMMEA > KSAR > MMEA > MEA > MMEA-$NH_3$ > AB > MEA retest > AP. The order is slightly different looking at nickel and chromium, the most significant change is that AB, MEA and AP show higher or similar concentrations than for MMEA.

## 4. Conclusions

For most of the amines/amino acids significant degradation was not present under these conditions, except for MEA and MMEA. Absence of significant degradation for most of the amines made it difficult to propose mechanism based on the structural changes to the amine used. However the degradation compounds found seem to follow the same patterns as described in literature, demethylation reaction of secondary and tertiary amines, ring formation if 5- or 6-membered could be formed and formation of secondary products as HEF analogues, HEI, OZD analogues. It was also shown that oxygen stoichiometry for degradation products are not explained by initial air in the system. Oxygen in some of the degradation products could come from water reacting with iminium giving aldehyde and amine or/and from oxygen diffusing into the system as seen from the proposed model. Additionally it seems like there is no mass transfer limitation for oxygen in the liquid phase. Temperature and dissolved metal seemed to influence oxygen and degradation rate for the MEA experiments giving the same nitrogen recovery and amine loss for both of the experiment, even when duration of the last experiment was twice as long. Volatile compounds are difficult to analyse in liquid phase, both taking into account the volatility, but also the analytical technique used. However, the formation and behaviour of volatile compounds are important to understand the primary mechanisms taking place. For MMEA, methylamine and ammonia were found in the same order of magnitude.

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