Influence of experimental setup on amine degradation

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Abstract

Chemical stability of amines under CO_2 capture conditions is a well known problem both for process operability and related to economy and environmental issues. Many degradation studies have been conducted under different conditions and in different apparatuses. In this work the chemical stability of a set of amines and their degradation products using 3 different setups have been studied. A new degradation compound for 2-ethanolamine (MEA), *N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide (HEHEAA) was quantified resulting in a total of 21 degradation compounds for MEA. Liquid phase metal and gas phase oxygen concentrations, temperature and volatility of degradation products (intermediates) all influence degradation and differences in results from the various apparatuses are observed. Conditions favoring formation of primary degradation compounds are difficult to identify and explain, but generally low metal and oxygen concentrations and temperature reduce their formation. For some of the secondary degradation compounds volatility of intermediates was an issue and higher formation rates were seen in the closed setup which preserved more of these products in the solvent compared to the open setup with gas throughput. Amines believed to form volatile degradation compounds showed lower chemical stability in the open setup compared to the closed setup. A new mechanism for the important degradation product *N*-(2-hydroxyethyl)-glycine (HEGly) is suggested.

Keywords: Oxidative degradation, oxygen, metal, setups, temperature, volatility

1. Introduction

Fossil fuel based power plants are one of the main sources to human carbon dioxide emissions and contribute to an increase in the greenhouse effect. Post combustion CO_2 capture using absorption processes is currently the most mature technology for CCS and over the last years several pilot plants and test centres have been or are being built to test a variety of absorbents, e.g. Technology Centre Mongstad (TCM) in Norway (Andersson et al., 2013; Jönsson and Telikapalli, 2013), International test Centre (ITC) in Canada (Skoropad et al., 2003; Wilson et al., 2003), several pilots in Australia (CSIRO) (Cousins et al., 2012). Additionally a full scale plant has been built at Boundary Dam Canada. Ideal absorbents should have high net cyclic capacity, good chemical stability, high equilibrium temperature sensitivity and reaction/absorption rates for CO_2, low vapour pressure and low corrosiveness. It has been difficult to find an absorbent combining all of these properties, and 2-ethanolamine (MEA) is still a reference case for amine systems.

One major problem with organic absorbents is their stability in the process where degradation will cause additional operating costs related to solvent losses, corrosion, fouling, foaming and the potential risk of degradation products entering the environment (Chakma and Meisen, 1986; Kohl and Nielsen, 1997; Strazisar et al., 2003). Degradation in pilot plants is often divided into thermal degradation, with or without CO_2, and oxidative degradation. Thermal degradation with CO_2 is likely to occur in the stripper, while thermal degradation without CO_2 is of less importance, but might take place in the reboiler. Oxidative degradation is normally

associated with the absorber but oxygen will dissolve in the solvent and also be present to some extent, until depleted, in other parts of the plant. For thermal degradation studies with CO_2, a general procedure has been accepted and used for the experiments (Davis, 2009; Eide-Haugmo, 2011; Lepaumier et al., 2009a). However, oxidative degradation experiments are conducted in various setups at different conditions making them more complicated to compare. For example, experiments were conducted in open apparatuses (da Silva et al., 2012; Goff and Rochelle, 2004; Sexton and Rochelle, 2011; Vevelstad et al., 2013b) and in closed setups (Lepaumier et al., 2009b; Supap et al., 2011b; Wang and Jens, 2011). Especially the conditions in the open setups varied among the research groups with variation in gas composition (in particular oxygen concentration), gas flow, with or without gas throughput, variation in temperature, using glass or metal setups, gas introduced in headspace or bubbled through solution and with or without additives as metals or inhibitors. Degradation compounds from oxidative degradation experiments are among the degradation compounds most frequently found in continuous operation (da Silva et al., 2012; Lepaumier et al., 2011a; Strazisar et al., 2003). However, the relative rates of formation of these compounds vary between pilot plant and oxidative lab degradation experiments. This observation has resulted in developing a new lab system, comprising a full absorption-stripping cycle, that also could give representative rates of formation of the degradation compounds which were observed in pilots.

Through the last decade, the degradation compounds themselves have received increased attention with more focus on their formation mechanisms and the similarities between compounds resulting from degradation of different amines (da Silva et al., 2012; Gouedard et al., 2012; Lepaumier et al., 2010; Lepaumier et al., 2009b; Vevelstad et al., 2013b). This has resulted in a relative comprehensive mapping of certain amines as MEA (da Silva et al., 2012; Lepaumier et al., 2011a) or systematic studies on the effects of structural variations on degradation products formed (both for alkanolamines and polyamines) (Lepaumier et al., 2010; Lepaumier et al., 2009a, b). However, no study, to our knowledge, has earlier compared the effect of variation in experimental setup on degradation and evaluation of mechanisms. In this work a total of 5 amines were compared in two different setups. MEA, 2-(methylamino)-ethanol (MMEA), 3-amino-1-propanol (AP) and 4-amino-1-butanol (AB) were tested in both a closed batch (CB) setup and an open batch (OB) setup whereas 3-amino-1-(methylamino)-propane (MAPA) was tested in OB and in a low gas flow (LGF) setup. More details on amines tested in CB are given by Vevelstad *et al.* (Vevelstad et al., 2013a), for MEA in OB see (Vevelstad et al., 2013b), for MMEA in OB see (Lepaumier et al., 2011b) and for MAPA in LGF see (Voice et al., 2013). The data for MAPA, AP and AB in OB are new in this work. This work also includes updates in MEA degradation by giving quantitative and qualitative data for earlier suggested degradation compounds and suggesting mechanisms for compounds which are seen in high amount in pilot plant samples.
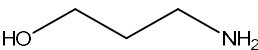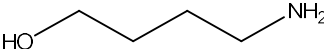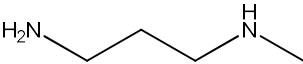
Analytical results from degradation studies will vary depending on which analytical methods were available at the time of analysis. This may influence the absolute values reported and therefore in this work normalised concentrations are used for comparison.

2. Experimental section

The amines experimentally studied in this work are presented in Table 1. AB was purchased from Syntastic, purity 98%. MAPA was purchased from Alfa Aesar (93 %) or Sigma-Aldrich (98%). AP was purchased from Sigma-Aldrich with purity higher than 98%. The experiments were performed using open batch setup (OB) previously presented in Vevelstad (Vevelstad et al., 2013b). A typical experiment last for 3 weeks at 55 ℃. The amine solution, loaded with

CO_2 (α= 0.4 mol CO_2 per mol of amine), was introduced into the open batch reactor (1L). A recycle loop maintained a circulation rate of about 50 L/h of a gas blend of air with 2% CO_2. The gas was humidified by passing through a contactor and sparged into the solution in the reactor. A net throughput of gas was obtained by adding (0.35 L/min air or + 7.5 mL/min CO_2) to the recycle loop. The reactor temperature was maintained at 55 ˚C. The exhaust gas was bubbled through gas bubble flasks containing water or 0.05 M H_2SO_4 as shown in the flow sheet by Vevelstad et al. (Vevelstad et al., 2013b). Samples were taken regularly from the liquid phase and analysed by the analytical techniques mentioned below.

Table 1: Short, full name, structur and CAS for amines used.

Amine	Abbreviation	Structure	CAS
3-amino-1-propanol	AP		156-87-6
4-amino-1-butanol	AB		13325-10-5
3-amino-1-(methylamino)-propane	MAPA		6291-84-5

Aqueous amine solutions (30 wt% for AP and AB and 43-45wt% (9m) MAPA) were prepared with a loading of 0.4 mole CO_2 per mole amine obtained by bubbling CO_2 gas through the solution until the desired weight was achieved. The total alkalinity of the solution was determined by acid titration (0.1 M H_2SO_4) using a standard procedure, and 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 nitrogen using the Kjeldahl method (Kjeldahl, 1883). Quantitative data was obtained for degradation compounds described in Table 2. Initial and end samples were in addition analysed in full scan mode (Liquid Chromatography – Mass Spectrometry (LC-MS)) (Vevelstad et al., 2013b) for investigation of degradation compounds which were not a part of Table 2. The concentrations of amine and degradation compounds were corrected based on the change in the amount of water before and after the experiment as described by Vevelstad (Vevelstad et al., 2013b).

Table 2: Abbreviation and full name of quantified degradation compounds, including HEHEAA, aldehydes and acetone.

Abbreviation	Compound	CAS	Structure	Analytical method
BHEOX	*N,N'*-Bis(2-hydroxyethyl)-oxamide	1871-89-2		LC-MS ("LC-MS mix")
HEA	*N*-(2-hydroxyethyl)-acetamide	142-26-7		LC-MS ("LC-MS mix")
HEF	*N*-(2-hydroxyethyl)-formamide	693-06-1		LC-MS ("LC-MS mix")
HEGly	*N*-(2-hydroxyethyl)-glycine	5835-28-9		LC-MS ("LC-MS mix")
HEHEAA	*N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide	144236-39-5		LC-MS ("LC-MS mix")
HEI	*N*-(2-hydroxyethyl)-imidazole	1615-14-1		LC-MS ("LC-MS mix")
HEPO	4-(2-hydroxyethyl)-2-piperazinone	23936-04-1		LC-MS ("LC-MS mix")
OZD	2-Oxazolidinone	497-25-6		LC-MS ("LC-MS mix")
DEA	Diethanolamine			LC-MS
	Formate			IC-anion
	Nitrite		NO_2	IC-anion
	Nitrate		NO_3	IC-anion
	Oxalate			IC-anion
	Ammonia	7664-41-7	NH_3	GC-MS or LC-MS
MA	Methylamine	74-89-5		GC-MS or LC-MS
DMA	Dimethylamine	124-40-3		GC-MS or LC-MS
EA	Ethylamine	75-04-7		GC-MS or LC-MS
DiEA	Diethylamine	109-89-7		GC-MS or LC-MS
	Formaldehyde	50-00-0		LC-MS
	Acetaldehyde	75-07-0		LC-MS
	Acetone	67-64-1		LC-MS

More thorough descriptions of the analytical methods for Kjeldahl, density and Ion Chromatography (IC) are given in Vevelstad (Vevelstad et al., 2013b). For LC-MS and Gas Chromatography – Mass Spectrometry (GC-MS) see (da Silva et al., 2012; Lepaumier et al., 2011b; Vevelstad et al., 2013b). Formaldehyde, acetaldehyde and acetone were analysed on the same LC-MS system as described by Vevelstad (Vevelstad et al., 2013b) using derivatisation of the samples. The analytical column Ascentis Express C8 (7.5cm x 2.1 mm, 2.7 μm, Cat#:53843-U,) Supelco Analytical, Bellefonte, USA) was used for aldehyde and acetone analysis. The mobile phase was 0.1 % ammonium acetate in acetonitrile and the molecules were converted to ions using electrospray ionization (ESI).

2.2 Mixing experiments

Mixing experiments were performed to investigate formation of specific degradation compounds in MEA, such as HEHEAA and HEGly, or for investigation of factors influencing formation of *N*-(2-hydroxyethyl)-formamide (HEF) and *N*-(2-hydroxyethyl)-acetamide (HEA). The results were used as basis for discussing, and as support for, results obtained in the degradation experiments. The results and experimental procedures from the mixing experiments are given in detail in supporting information.

3. Comparison of the setups and overview of experiments discussed

The experiments compared in this work are listed in Table 3. All experiments except experiments with MAPA were performed with 30 wt% solutions. As listed, all solutions were loaded with CO_2 up to loading of 0.4 mole CO_2 per mole of amine. A metal mixture of $FeSO_4*7H_2O$ (Fe: 0.4 mM), $Cr_2(SO_4)_3*xH_2O$ (Cr: 0.1 mM), and $NiSO_4*6H_2O$ (Ni:0.05mM)) was added to the MAPA (9m) solution for both the OB and LGF experiments. The flow sheet for the LGF is given by Sexton (Sexton and Rochelle, 2011). As seen from the Table 3, in the CB experiments the initial amine concentrations were typically 1-2% lower compared to in the OB experiments. This was due to small amounts of water already present in the CB setup when the solution to be tested was added. The flow sheet for the CB setup is given by Vevelstad (Vevelstad et al., 2013a). Table 4 gives an overview of the analyses performed in each experiment.

Table 3: Overview of experiment and setups compared.

Amine	Setup	Experiment	Initial concentration and loading	Reference
MEA	CB	MEA_CB_1	25 / 0.4	(Vevelstad et al., 2013a)
	CB	MEA_CB_2	30	(Vevelstad et al., 2013a)
	OB	MEA_OB_1	30	(Vevelstad et al., 2013b)
	OB	MEA_OB_2	30	(Vevelstad et al., 2013b)
MMEA	CB	MMEA_CB	30	(Vevelstad et al., 2013b)
	OB	MMEA_OB	30	(Lepaumier et al., 2011b)
AP	CB	AP_CB	30	(Vevelstad et al., 2013b)
	OB	AP_OB	30	This work
AB	CB	AB_CB	30	(Vevelstad et al., 2013b)
	OB	AB_OB_1	30	This work
	OB	AB_OB_2	30	This work
	OB	AB_OB_3	30	This work
MAPA	OB	MAPA_OB	43	This work
	LGF	MAPA_LGF	45	(Voice et al., 2013)

Table 4: Overview of degradation compounds analysed for in each experiment.

Experiment	Anion IC	LC-MS mix	HEHEAA[b]	Alkyl-amine	NH$_3$	Aldehyde /Acetone[b]	LC-MS Scan	Kjeldahl (N)	Other
MEA_CB_1	x	x	x	x[a]	x[a]		x	x	
MEA_CB_2	x	x	x	x	x	x		x	
MEA_OB_1	x	x		x[a]	x[a]		x	x	
MEA_OB_2	x	x	x	x	x	x		x	
MMEA_CB	x	x		x	x		x	x	
MMEA_OB								x	
AP_CB	x	x					x	x	
AP_OB	x			x	x		x	x	
AB_CB	x	x					x	x	
AB_OB_1	x			x	x			x	
AB_OB_2	x			x	x		x	x	
AB_OB_3	x			x	x		x	x	
MAPA_OB	x						x	x	
MAPA_LGF	x								Scan GC-MS and LC-MS

[a]Analysed on GC-MS.
[b]Analysed in this work.

In Table 5 the experimental conditions used in the different setups are compared. The composition of the gas phase in OB and LGF was more constant compared to in the closed batch (CB) because of the small amount of gas constantly added during the OB and LGF experiments. The initial gas composition corresponded to air in all the setups except for LGF where only oxygen and CO$_2$ were used(98%O$_2$/2%CO$_2$). The gas in the OB setup was bubbled through the solution while in the CB setup the gas/liquid contact was enhanced by counter-current flow over a SULZER DX packing. In the LGF contactor the gas entered the headspace of the reactor. All the experiments were performed at 50-55 ^{o}C. The OB and CB setups were previously described by Vevelstad (Vevelstad et al., 2013a; Vevelstad et al., 2013b) and the LGF reactor by Sexton and Voice (Sexton and Rochelle, 2011; Voice and Rochelle, 2011).

Table 5: Conditions for the OB, CB and LGF setup.

Condition	OB	CB	LGF
Added dry gas rate (NL/min)	0.35 (air)	0 (air)	0.10 (98% O$_2$/2%CO$_2$)
Added dry gas rate (CO$_2$) (NL/min)	0.0075	0	
Recirculation gas rate (L/min)	50	24.6	0
Liquid agitation/flow	Agitation	0.9 L/min	1400 RPM
Temperature (°C)	55	50-55	55
Total amount of liquid (L)	~1	~0.7	~0.35

3 Results and discussion

In this section results from the OB and CB setups are compared. Both new and literature results are discussed together. First the amine loss is discussed, then the various degradation products that are formed from MEA and how their formation varies in the two setups. After this, the other primary and secondary amines are discussed, and finally a section on the nitrogen balance is included.

3.1 Amine loss

Amine loss gives a measure for the amount of degradation in the system. In Table 6 the amine losses (%) calculated from both LC-MS and titration results for the different experiments are given. Amine loss is calculated by $a = \left(\dfrac{C_0^m - C_i^m}{C_0^m} \right) * 100$

where C_0^m is the initial amine concentration and C_i^m is the molar concentration at a specific time i. In general it is seen that amine loss using titration for alkalinity and amine specific analyses by LC-MS give comparable results for both setups. This indicates that only small amounts of other amines are formed. MMEA and MAPA show the highest differences. Both of them are suspected of going through de-methylation reactions giving new amines. For all the amines, except MEA, a higher degree of degradation was found for the OB setup compared to CB which later will be discussed based on differences in degradation compounds formed in the two setups. The order of degradation was found to be MAPA_LGF > MMEA_OB > MAPA_OB > MMEA_CB > MEA_CB_1 > MEA_CB_2 > MEA_OB_1&2 > AB_OB_1 > AP_OB > AB_OB_2&3 > AB_CB & AP_CB. As seen from Table 6 the AB_OB_1 experiment showed a higher deviation (12 %) in the water balance than normally accepted (5-6 %) and these results are therefore somewhat more uncertain. In experiment AB_OB_3 the solution from experiment AB_OB_2 was used, but fresh AB and CO_2 were added to obtain an initial concentration of 30 wt% and a loading of 0.4 mole CO_2/mole amine. AB_OB_2 was performed with gas flows of CO_2 and air which were respectively twice and half of the amounts used for the rest of the OB experiments. However, the amine losses for AB_OB_2 and 3 are comparable in spite of lower oxygen concentration and higher CO_2 concentration. The higher concentration of CO_2 did not seem to increase the formation of oxazolidinone. Oxazolidinone formation for MEA is low at 55 °C (Vevelstad et al., 2013b).

Table 6: Comparison of amine loss for the end sample between two analytical methods, titration and LC-MS (this work, Vevelstad 2013a and Vevelstad 2013b).

	LC-MS	Titration	Remarks	Reference
MEA_CB_1	26	23	Initial MEA concentration 25wt%	(Vevelstad et al., 2013a)
MEA_CB_2	19[a]/28	15[a]/27		(Vevelstad et al., 2013a)
MEA_OB_1	13	14		(Vevelstad et al., 2013b)
MEA_OB_2	11	13		(Vevelstad et al., 2013b)
MMEA_CB	32	26		(Vevelstad et al., 2013a)
MMEA_OB	82			(Lepaumier et al., 2011b)
AP_CB	<5	<5		(Vevelstad et al., 2013a)
AP_OB	10	7		
AB_CB	<5 (4.6[b])	<5 (0.8[b])		(Vevelstad et al., 2013a)
AB_OB_1	12	12	12% difference in water balance	This work
AB_OB_2	7	6	CO_2 feed = 0.0035NL/min and air feed =0.175 NL/min	This work
AB_OB_3	8	9	Part of the solution from AB_OB_2 was used.	This work
MAPA_OB	33	27		This work
MAPA_LGF	100	100		(Voice et al., 2013)

[a]After 22 days
[b]Measured amine loss

3.2 MEA degradation

In Figure 1 the normalised MEA concentrations as function of time are given for the MEA experiments performed using the OB and CB setups. Normalised concentrations are defined by

$$b = \frac{C_i^m}{C_0^m} \qquad (1)$$

using the concentrations from LC-MS. C_i^m is the molar concentration as function of time and C_0^m is the initial molar concentration of MEA.
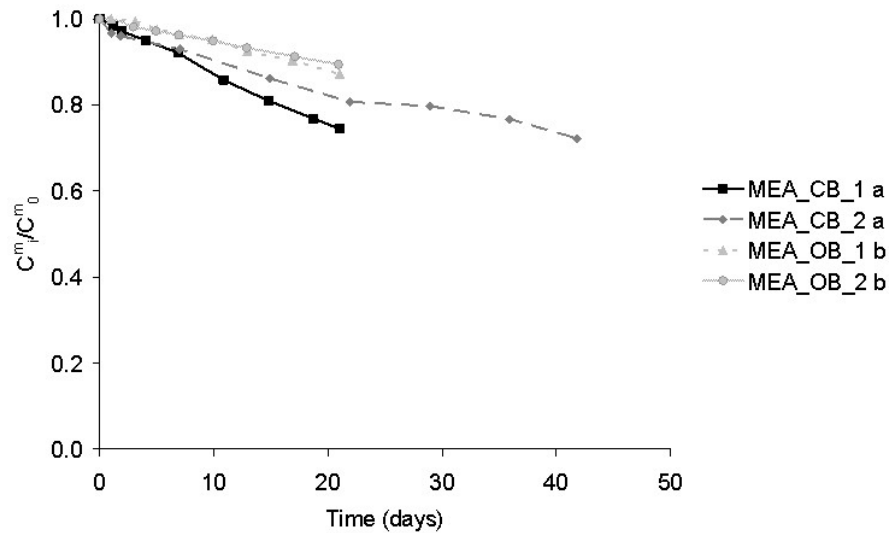

Figure 1: Normalised amine concentration over time for MEA. Data from [a](Vevelstad et al., 2013a), [b](Vevelstad et al., 2013b).

The results show a higher amine loss for MEA in the CB setup compared to the OB setup. The difference in amine loss comparing MEA_CB_2 and MEA_OB_1&2 was smaller than for MEA_CB_1. The closed setup is more similar to absorber conditions when it comes to contact between liquid and gas as a packing is used, but the degradation might be limited due to the limited amount of CO_2 and O_2 present. In the OB setup oxygen and CO_2 were added during the experiment. The variations between the setups regarding gas availability and contact between liquid and gas might influence degradation differently and could also possibly cancel each other out.

In the CB setup, oxygen concentrations should decrease according to the oxygen consumption caused by the degradation reactions. However, based on the oxygen profile in the gas phase for the CB setup it was proposed that oxygen diffused into the system (Vevelstad et al., 2013a). Even though oxygen concentration influences degradation (Vevelstad et al., 2013b), in the CB setup the oxygen concentration should never exceed the concentration in the open batch (run with air) since in the worst case, with a leakage of air into the CB setups, the setups would have similar O_2 concentrations. So the diffusion/leakage should not give higher amine degradation in the closed setup for MEA. The faster amine degradation and higher concentrations of degradation compounds in the closed setup experiments with MEA could be due to metals present in the CB. From Figure 1 it can be seen that MEA_CB_1 had faster amine degradation compared to MEA_CB_2. This was explained by the higher concentration of metals in MEA_CB_1 and difference in oxygen profile between the two experiments (Vevelstad et al., 2013a).

3.2.1 Primary degradation compounds
There are several factors to consider when studying formation of primary degradation compounds such as aldehydes, acids, nitrite, nitrate, ammonia and alkylamine. Oxygen availability, degradation product volatility, the mechanisms of formation of the studied degradation compound and their intermediates and volatility of intermediates play important roles. The formate and nitrite concentrations in the CB experiments (MEA_CB_1 and MEA_CB_2) were higher compared to experiments in OB (MEA_OB1&2). These differences could be due to the catalytic effect of metals, oxygen limitations in the closed setup favouring formation of nitrite compared to nitrate, and higher concentrations of intermediates (e.g. ammonia for nitrite).

The liquid phase was also analysed for formaldehyde, acetaldehyde, acetone, ammonia, methylamine (MA), dimethylamine (DMA), ethylamine (EA) and diethylamine (DiEA) for MEA_CB_2 and MEA_OB_2. The normalised concentrations of degradation compounds were based on equation 1 and all of them, except for DiEA, were higher in the CB setup than in the OB setup for the experiments with comparable amine loss, as seen for DMA, EA and MA in Figure 2 and for ammonia and formaldehyde in Figure 3. Acetaldehyde was only seen in the CB setup. DiEA and acetone were not seen above the quantification limit in any of the setups. Higher concentrations of volatile compounds in CB would be expected to be related to the setup itself loosing less volatile compounds together with the presence of metals catalysing the formation of primary degradation compounds.
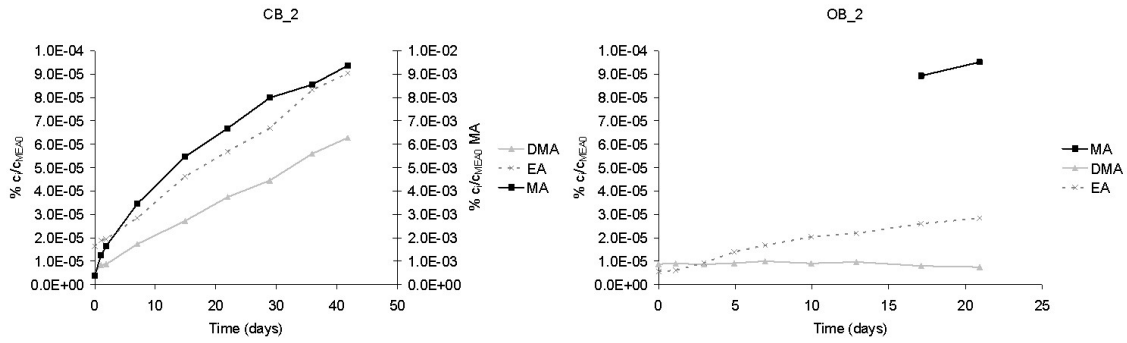
Figure 2: Normalised concentration of DMA, EA and MA in MEA_CB_2 and MEA_OB_2.
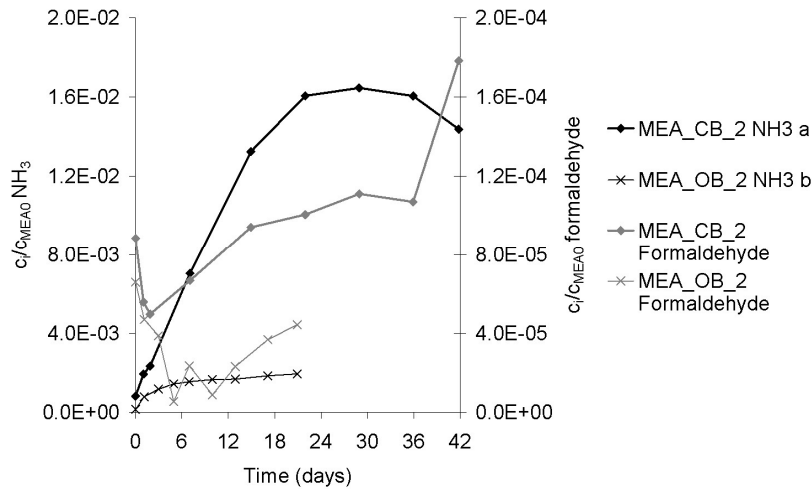

Figure 3: Normalised concentration of ammonia (black curve) and formaldehyde (grey curve) in MEA_CB_2 and MEA_OB_2 (right). Data from [a](Vevelstad et al., 2013a) and [b](Vevelstad et al., 2013b).

3.2.2 Secondary degradation compounds

Secondary degradation compounds are formed from the primary degradation compounds (ammonia, acids, aldehydes) and amine (Vevelstad et al., 2013b). Therefore the formation of secondary degradation compounds is dependent on both the reaction chemistry of the secondary reactions and the formation of intermediates (for example ammonia, aldehydes or acids).

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The levels of HEA and HEF both in the OB and CB experiments, as seen in Figure 4 at 55°C, increased steadily and did not reach a maximum. This is in contrast to Supap's observations (Supap et al., 2011a). However, for the MEA_CB_2 it can be seen that *N,N'*-Bis(2-hydroxyethyl)-oxamide (BHEOX) went through a maximum before it stabilised.
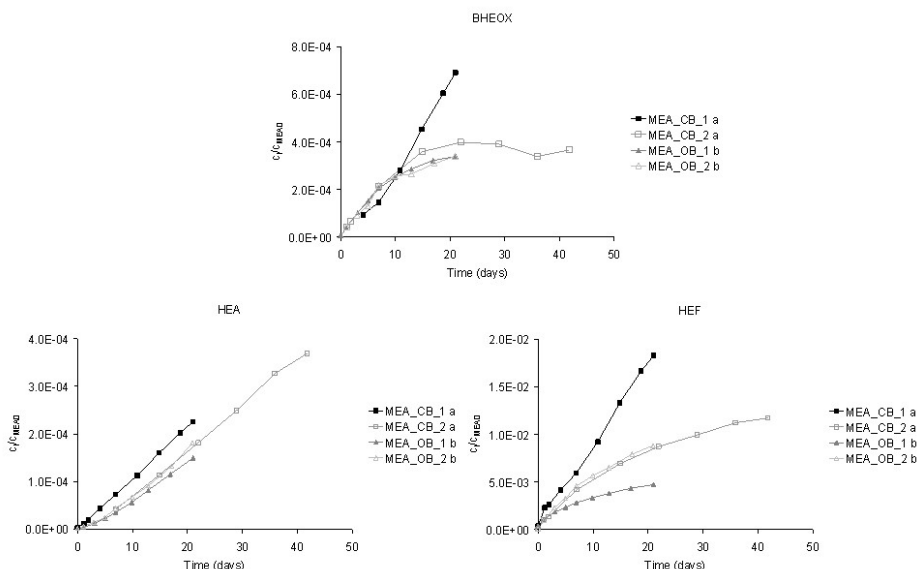

Figure 4: Normalised concentration of BHEOX, HEA and HEF, 55°C. Data from [a](Vevelstad et al., 2013a) and [b](Vevelstad et al., 2013b).

The formation of HEA was for all practical purposes seen to be the same in the OB and CB experiments. For HEF the CB and OB experiments differ more than for HEA, but comparable amounts were seen for OB_2 and CB_2 which also showed comparable amounts of formate. HEA was also seen to be only a few percent of the formed HEF. Acetate was never seen above trace amounts in any of the experiments and the formate concentration was high compared to the rest of the anions. Thus it is reasonable that more HEF than HEA is formed in both setups. HEA and HEF were found in higher concentrations in the MEA_CB_1 compared to MEA_CB_2, which might indicate an indirect influence of metal through increased formation of intermediates such as formate and acetate or their aldehyde analogues. In order to investigate possible reasons for this, laboratory mixing experiments were conducted to study the formation of HEF and HEA with and without metals as described in supporting information. HEA was formed in low amounts compared to HEF (as also seen in Figure 4) and both of them were formed in comparable amounts with and without metal ions. This indicates that metal influence on these compounds is related to formation of intermediates (aldehydes and acids) and not as a direct influence on the reaction itself. A more sterically hindered acid as intermediate for HEA might explain the higher formation of HEF compared to HEA. Additionally both HEF and HEA were formed in low amounts compared to available acid (see supporting information for details). This is supported by results from Supap (Supap et al., 2011a). An increase of HEF and HEA formation with temperature was also seen in lab mixing experiment (supporting information).

The formation of 4-(2-hydroxyethyl)-2-piperazinone (HEPO) and HEGly has been difficult to explain so far since no mechanism has been suggested for HEGly and since the intermediate, HEHEAA, between HEGly and HEPO, first had to be synthesised (by a chemical supplier) before qualitative and quantitative analyses could be conducted (see Figure 5).
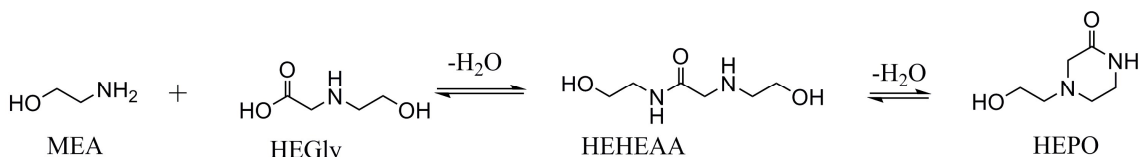
Figure 5: HEPO formation from HEGly and HEHEAA.

Lab mixing experiments verified that HEHEAA could form from MEA and HEGly (details described in supporting information).

HEGly and HEPO were formed in higher amounts in MEA_OB_2 compared to MEA_CB_1&2 (Vevelstad et al., 2013a; Vevelstad et al., 2013b). The difference seen for these compounds between the OB and CB setup cannot be explained by differences in oxygen concentration in the two setups since HEGly and HEPO formation seems to be independent of oxygen concentration (Vevelstad et al., 2013b). The formation of HEHEAA in MEA_CB_2 and MEA_OB_2 was very similar (see Figure 6). In contrast to HEPO and HEGly, HEHEAA showed a faster formation rate and reached higher concentrations in the MEA_CB_1 experiment compared to MEA_CB_2 and MEA_OB_2.
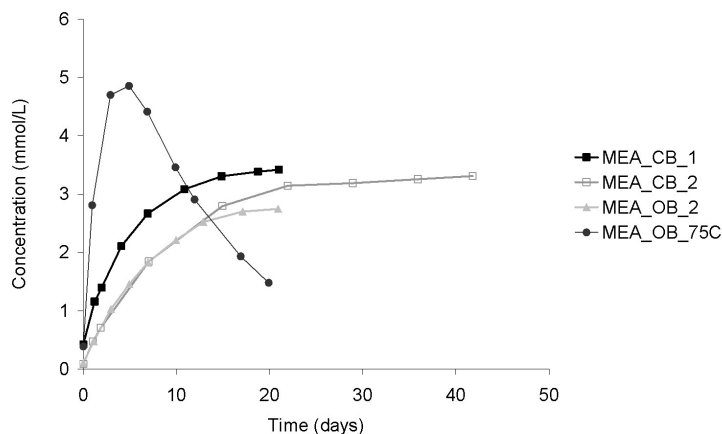

Figure 6: HEHEAA concentration (mmol/L) as a function of time (days) for MEA_CB_1&2, MEA_OB_2 and MEA_OB_75C.

At lower temperature the HEHEAA concentration seemed to stabilise after some time. The same was seen for HEPO at higher temperature (Vevelstad et al., 2013b), for BHEOX in MEA_CB_2 at ~50 °C and for HEF in MEA_OB_75C (Vevelstad et al., 2013b). HEPO, BHEOX and HEF are believed to be end products in reversible reactions and a shift in equilibrium with temperature would be expected. HEHEAA in the experiment at 55 °C might be considered as end product due to the very low formation rate of HEPO or any other secondary degradation compound formed from HEHEAA at this temperature. This can explain why the HEHEAA concentration levels out at a stable value.

HEPO was found in low concentrations in the lab experiments at 50-55 °C (both OB and CB) compared to other degradation compounds including HEGly (Vevelstad et al., 2013a; Vevelstad et al., 2013b) and HEHEAA (see Figure 6 for HEHEAA in CB and OB at 55 and 75 °C). Pilot samples have shown that both HEPO and HEGly are important secondary degradation compounds (da Silva et al., 2012). This may indicate that we have a reaction sequence, at least partly controlled by equilibrium, and that at low temperature the equilibria are shifted toward HEGly and HEHEAA, whereas at higher temperatures the formation of HEPO is favoured. A temperature effect for the formation of HEPO and HEGly has also been

reported in literature (Vevelstad et al., 2013b) and a temperature effect was also seen for HEHEAA (Figure 6). The higher concentrations of HEGly and HEHEAA compared to HEPO at lower temperatures might also suggest that there are more factors than temperature influencing the HEGly and HEHEAA formation as e.g. fewer reaction steps to HEGly and HEHEAA and higher concentration of intermediates. The HEHEAA/HEGly ratio as a function of time (days) is given in Figure 7.
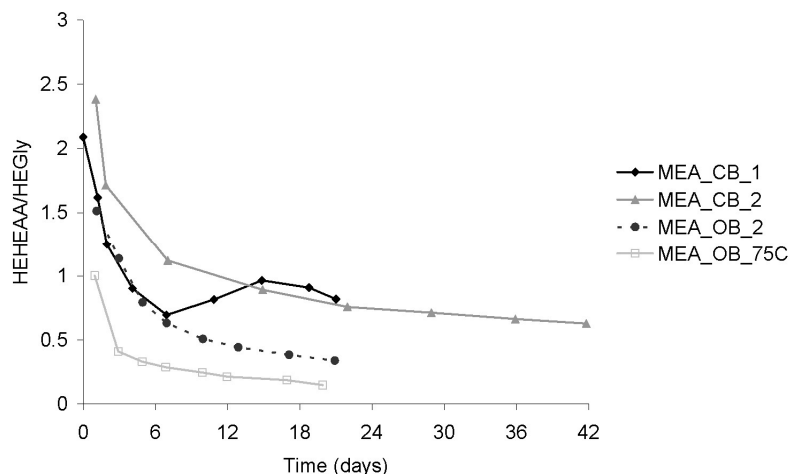

Figure 7: Ratio HEHEAA/HEGly as a function of time (days).

Figure 7 indicates that the reaction between HEGly and HEHEAA reaches equilibrium around the same time for both setups, but earlier at higher temperature. This indicates that factors as metal and oxygen concentration, varying between the setups, have less influence on the equilibrium reaction between HEGly and HEHEAA. This was also seen for HEA and HEF with regard to metal. However, a higher concentration of HEGly was seen in OB than in CB indicating that the setup has a direct or indirect effect on HEGly's behaviour. Basically several explanations can be given. Possibly the intermediate for the formation of HEGly may be favoured in the OB setup. There could be competitive reactions consuming HEGly's intermediate, favoured in the CB, or HEGly could be an intermediate in other secondary reactions favoured in the CB setup. Investigating important intermediates for HEGly led to the suggestion of glyoxylic acid. Glyoxylic acid has been suggested as a degradation compound in several mechanisms (Gouedard et al., 2012). However, no qualitative or quantitative data are given for this compound. A new mechanism for formation of HEGly from this compound is suggested in this paper based on a Clarke-Eschweiler methylation reaction (Clarke et al., 1933) where formaldehyde is substituted with glyoxylic acid, as shown in Figure 8. HEGly was positively quantified in a lab mixing experiment where MEA, glyoxylic acid and formic acid (in excess) were mixed and stirred at 40-55 °C for 3 days (details given in supporting information). More thorough experiments have to be conducted to verify the formation of HEGly from glyoxylic acid since this reaction is likely to be less favoured under basic conditions.
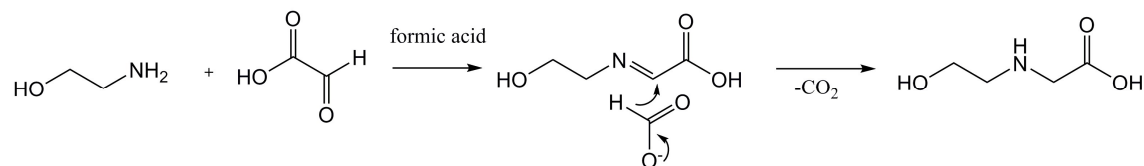

Figure 8: Suggestion of formation mechanism for HEGly from MEA and glyoxylic acid in presence of formic acid.

Similarly, glyoxylic acid has been suggested as one of the intermediates in the formation of imidazoles (compounds similar to *N*-(2-hydroxyethyl)-imidazole (HEI)), see Vevelstad (Vevelstad et al., 2013b). Imidazole formation was favoured in CB compared to OB and could therefore partly explain higher concentrations of HEGly in OB compared to CB if glyoxylic acid is a common intermediate. The differences could also be explained by HEGly being an intermediate in more than only the HEHEAA formation reaction. This is supported by the OB experiment conducted at 75 °C which showed that the concentration of HEHEAA and HEPO could not explain the decrease in HEGly (Vevelstad et al., 2013b). It was also observed that HEPO formation could not explain the decline in HEHEAA concentration. HEHEAA continued to decline even after the HEPO concentration stabilised which explains the increase in ratio between HEPO/HEHEAA as shown in Figure 9 for MEA_OB_75C. HEGly and HEHEAA for example have amine groups which could result in new degradation compounds (e.g. amides) following the degradation mechanisms reported for MEA.
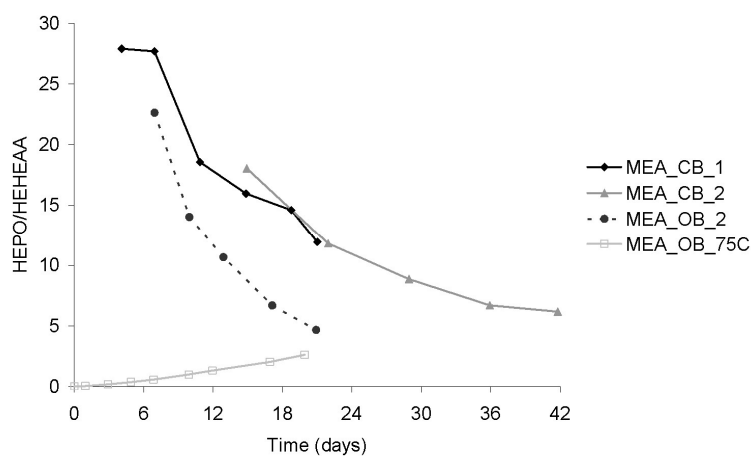

Figure 9: Ratio HEPO/HEHEAA as a function of time (days)

The chemistry in oxidative degradation experiments is complex. Several of the degradation compounds are intermediates in one or more reactions and several of the reactions are possible equilibrium reactions and unknown degradation compounds can still be present. Isolating the behaviour of a degradation compound is difficult and it is therefore difficult to explain the behaviour of degradation compounds such as HEGly and HEHEAA which seem to have more than one role in the system.

The highest formation of HEI in the CB setup was seen for experiment MEA_CB_1, being about 3 times as high as for MEA_CB_2 which showed the highest MEA degradation rate and the highest concentration of metals. The experiments in the CB setup also showed 15 to 45 times higher concentrations of HEI than for the MEA experiments in the OB setup. Formation of HEI depends on several intermediates where some of them are volatile and most of them are intermediates for more than one reaction. Formation of HEI must therefore be linked to the formation and consumption of glyoxal, ammonia and formaldehyde. An analytical method for quantification of glyoxal was not available. Ammonia and formaldehyde are both volatile and the CB will contain more of these products than the OB.

Comparing the results for MEA from the OB and CB setups, we can see that 2-Oxazolidinone (OZD) was found at similar concentrations. This is reasonable assuming OZD is formed from CO_2 and MEA.

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3.3. Degradation products from other primary amines: AB and AP

Increasing the carbon chain in MEA between the alcohol and amine functions gives AP and AB. Both of these amines showed low or no degradation in the CB setup. However, in the OB setup amine loss was found to be around 10% after 21 days which is similar to MEA_OB_1&2. Normalised amine concentrations over time are given in Figure 10.
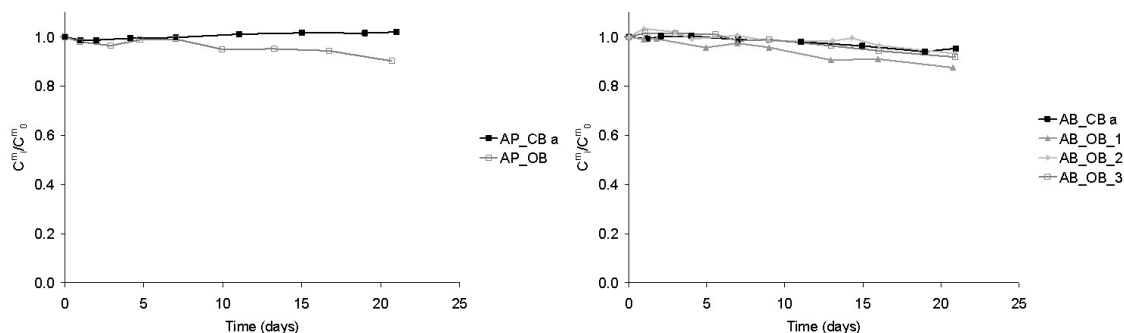

Figure 10: Normalised amine concentration over time for AP (left) and AB (right). Data from [a](Vevelstad et al., 2013a).

The CB experiments were analysed for the "LC-MS mix" (see Table 2 for compounds in the "LC-MS mix") while the OB setup was in addition analysed for ammonia and alkylamines. Normalised concentrations after 21 days for the experiments with different amines in the OB setup and for MEA_CB_2, are given in Table 7.

The "LC-MS mix" is basically a set of degradation compounds identified from MEA degradation experiments. Some of these degradation compounds are still of interest for other amines because of demethylation reactions which have been shown to happen (Lepaumier et al., 2009b).

Table 7: Normalised concentrations of ammonia and alkylamine for MEA_OB_2, AP_OB and AB_OB_1-3 and after 22 days for MEA_CB_2 (a).

	Ammonia	Methylamine	Dimethylamine	Ethylamine	Diethylamine	Reference
MEA_CB_2[a]	1.6E-02	6.7E-05	3.7E-07	5.7E-07	b	(Vevelstad et al., 2013a)
MEA_OB_2	1.9E-03	9.5E-07	7.5E-08	2.8E-07	b	
AP_OB	1.0E-03	9.6E-07	b	2.4E-06	b	This work
AB_OB_1	1.8E-03	5.5E-05	b	4.1E-06	b	This work
AB_OB_2	3.1E-03	4.8E-05	2.0E-07	5.4E-06	4.7E-06	This work
AB_OB_3	1.7E-03	7.7E-05	1.3E-07	8.4E-06	4.7E-06	This work

[a]MEA_CB_2, after 22 days.
[b]Lower than quantification limit.

For MEA the CB setup showed higher amounts of ammonia and all alkylamines compared with the OB setup. Ammonia is, as expected, the degradation product found in highest amounts. Result for AB_OB_1&3 were comparable to MEA_OB_2. There are small variations for the alkylamines and most of them were found in small amounts in the liquid phase. Normalised concentrations of nitrite, nitrate, formate and oxalate for the OB experiments for all the amines, are given in Table 8.

Table 8: Normalised concentrations of nitrite, nitrate, formate and oxalate in the end sample.

	Nitrite	Nitrate	Formate	Oxalate
MEA_OB_2	1.2E-03	3.5E-04	6.4E-03	3.0E-04
AP_OB	1.7E-03	1.4E-03	3.8E-03	4.1E-04
AB_OB_1	2.8E-03	2.1E-03	3.9E-03	a
AB_OB_2	1.6E-03	1.0E-03	a	a
AB_OB_3	4.0E-03	3.0E-03	6.6E-03	6.2E-04

[a]Lower than the detection limit

As seen in Table 8, concentrations of nitrite and nitrate are generally of the same order of magnitude for all the amines. The concentration differences for the AB_OB_1-3 experiments are most likely connected to differences in gas composition, water balance and solvent composition for these experiments. For example AB_OB_3 was an experiment where the solution used in AB_OB_2 was reused and the concentration of the start solution was adjusted with fresh AB and CO_2 to reach 30 wt% solution and loading 0.4. This means that the start solution for AB_OB_3 contained small amounts of degradation compounds.

According to the study by Lepaumier on the effect of alkyl length between amine functions in diamines (Lepaumier et al., 2010), the length of the carbon chain could induce degradation in cases where ring formation would be favourable and where Hofmann or Cope elimination to some extent could take place for propylene di- and triamine. AP and *N,N,N',N'*-tetramethylpropylenediamine (TMPDA) (Lepaumier et. al., 2010) both have a three carbon chain between the functional groups. They might therefore give similar degradation compounds. AP showed $M+H^+$ (LC-MS positive scan results in the molecular mass plus a proton) of 58 as degradation product, suggesting 3-amino-1-propene (allylamine) which is an analogue to *N,N*-dimethyl-1-amino-2-propene formed from TMPDA as reported by Lepaumier. Her study suggested a Cope elimination mechanism giving allylamine. Cope elimination does not necessary explain the formation of allylamine from AP. However, Zhang showed that etheneamine could be formed from ethanolamine through ester formation (Zhang and Hao, 2012). 3-amino-1-propene has in this study not been quantified and was identified based on similarity to Lepaumier's work and the mass of the compound. However in the study by Lepaumier, *N,N*-dimethyl-1-amino-2-propene was found to be the second main degradation compound only surpassed by a compound formed in a de-methylation reaction (Lepaumier et al., 2010). AB has a favourable structure for ring formation giving a five membered ring. However, the five membered ring was not verified in the present work. In Lepaumier's study a polyamine with 4 carbons between the tertiary amine functions, *N,N,N',N'*-tetramethylbutylenediamine (TMBDA) gave 1-methylpyrrolidine as degradation product (Lepaumier et al., 2010).

3.4 Degradation products from secondary amines: MAPA and MMEA

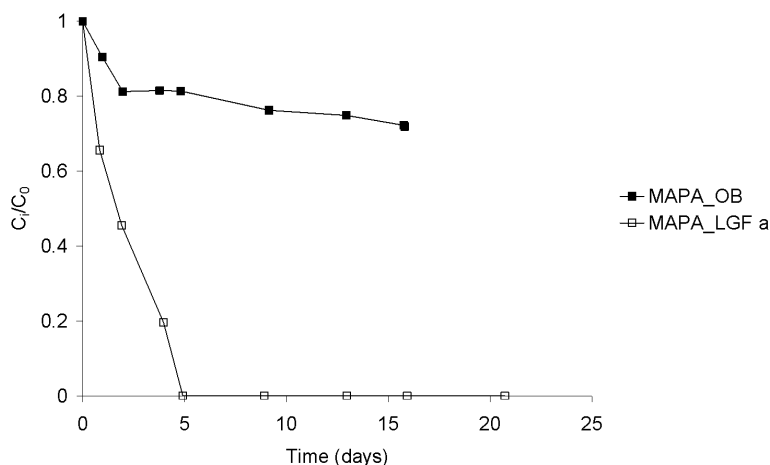Normalised amine concentrations for the MAPA_LGF and MAPA_OB are given in Figure 11.

Figure 11: Normalised amine concentration over time for MAPA. [a]Data from Voice (Voice et al., 2013).

As seen in Figure 11, MAPA_LGF showed a much higher degradation rate ending up with zero MAPA left after 5 days. MAPA_OB showed a high degradation rate the first 2 days and then it started to decline. The combination of higher oxygen concentration (98%) and a more open setup for LGF might explain the difference in amine loss of MAPA since a similar behaviour was seen when comparing the MMEA experiments performed in the OB (Lepaumier et al., 2011b) and CB setup (Vevelstad et al., 2013a), see Figure 12.
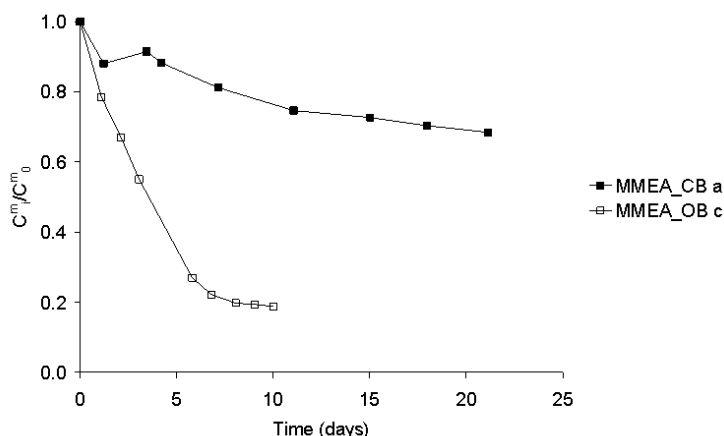

Figure 12: Normalised amine concentration over time for MMEA. Data from Vevelstad [a](Vevelstad et al., 2013a), [b](Lepaumier et al., 2011b).

The MMEA loss in the OB setup was 4 times higher than in the CB setup. The LGF and OB setups are similar in the way that both are open. A continuous gas flow enters the LGF setup and there is stirring of the solution. The main differences and factors possibly influencing degradation are that volatile compounds can escape the LGF setup more easily than in the OB setup. The behaviour of the normalised concentrations over time for MMEA and MAPA in the OB, see Figure 11 and 12, is similar in the way that both of them show fast degradation initially and later a much lower rate. None of the other amines shows this behaviour and it is not seen in the closed setup. The difference in oxygen concentration and a more open system might explain the faster degradation rate of MAPA in the LGF setup compared to OB, see Figure 11. In the OB experiments, MAPA showed 3 times and MMEA 8 times higher degradation rates than MEA_OB, and both of them have structures which could give formation of volatile compounds under degradation conditions. These could be allylamine (3-

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amino-1-propene) by Cope elimination for MAPA and methylamine for MMEA through a mechanism suggested by Lepaumier and coworkers (Lepaumier et al., 2011b). The mass of allylamine was found in the MAPA experiment (MAPA_OB) and methylamine was found in comparable amounts to ammonia in the liquid phase in the closed MMEA experiment (MMEA_CB) (Vevelstad et al., 2013a). The OB setup might therefore increase degradation of amines which form volatile compounds as they may escape from the setup and therefore influence any equilibrium involving these compounds in the liquid phase.

As shown by Vevelstad (Vevelstad et al., 2013a) for the MMEA_CB test OZD, HEGly, HEPO, HEF and HEI were formed. However the formation of HEF, HEI and OZD in MMEA_CB was low compared to what was found in the MEA_CB_1 and MEA_CB_2 experiments. Also, their occurrences were shifted to later on in the experiment. However, formation of HEGly and HEPO in the MMEA_CB experiment was comparable to that found for MEA_CB_1 and MEA_CB_2. For MMEA, the HEGly formation started later than in MEA_CB_2, but then the formation rates were similar. This might be explained by demethylation of MMEA to MEA before a HEGly intermediate is formed. However, it does not explain why smaller amounts of e.g. HEF is formed from MMEA compared to from MEA. Lepaumier (Lepaumier et al., 2011b) identified and described several degradation products formed by MMEA. Some of the molecular masses from the positive LC-MS scan observed in this work have the same molecular masses as the degradation compounds for MMEA suggested by Lepaumier and may thus indicate that they are the same degradation compounds as found for MMEA.

In Figure 13 the normalised anion concentrations over time are given for the degradation experiments on MAPA performed in the LGF reactor (MAPA_LGF) (Voice et al., 2013) and from the OB setup (MAPA_OB). Normalised anion concentrations were defined as

$$c = \frac{C_i}{C_{alkalinity_0}}$$ where C_i is the concentration of the anion in mmol/kg and $C_{alkalinity_0}$ is the initial alkalinity concentration in mmol/kg.
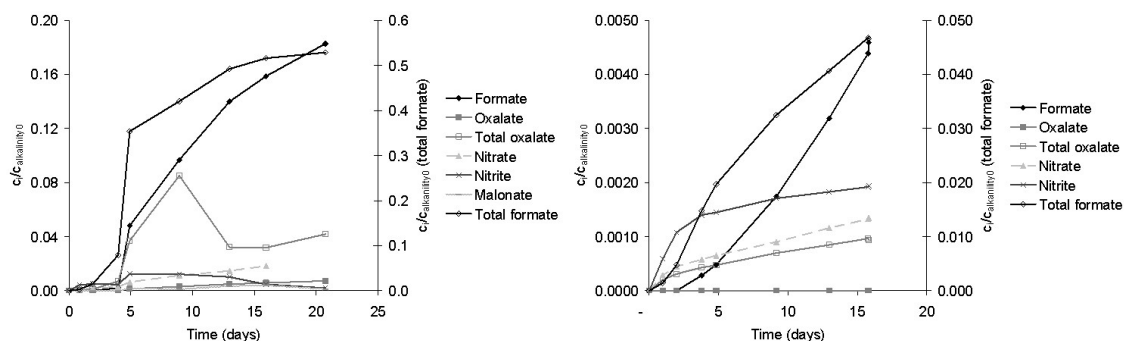

Figure 13: Normalised anion concentration for MAPA_LGF (Voice 2013) (left) and MAPA_OB (right).

The anion concentrations, especially formate and total formate, where total formate is formate after reaction with NaOH (total amide), for the LGF setup mimics the amine loss behaviour seen in Figure 11. Formate and total formate are found to be the biggest contributors to the quantified degradation compounds for both MAPA_LGF and MAPA_OB. The combination of higher oxygen concentration and a more open setup might explain the faster degradation rate seen for MAPA_LGF compared to MAPA_OB. Volatile compounds like 3-amino-1-propene are likely to be formed, and these will more easily escape from the LGF reactor. Formation of these degradation compounds is supported by LC-MS positive scan for

the MAPA_OB experiment and by MS-MS for the MAPA_LGF setup. The escape of volatile compounds will affect the equilibrium in the reactor giving higher formation of products that otherwise would be limited by the volatile degradation compound, e.g. ammonia. The observations are similar to those discussed above for MMEA in the CB and OB.

3.5 Nitrogen balance

The percentage formation of the degradation products ($\tau_{f,i}$) is calculated by the method described by Lepaumier (Lepaumier et al., 2011b) and given by $\tau_{f,i} = \nu_i * \dfrac{C_i^m}{C_0^m} * 100$.

Here ν_i is the number of nitrogen molecules in the degradation product, C_i^m is the molar concentration of the degradation products and C_0^m is the initial concentration of the amine.

The end samples from each experiment were analysed for nitrogen according to the Kjeldahl method (Kjeldahl, 1883). In Table 9 is shown how amine and the sum of known degradation compounds ("LC-MS mix" and NH_3) contribute to the liquid phase organic nitrogen balance for the end sample. The N unaccounted column is the balance up to 100%.

Table 9: Nitrogen balance for end sample liquid phase.

	Amine %	N known degr cpd %	R_N %	N unaccounted (l) %	Ref.
MEA_CB_1	70	16	86	14	(Vevelstad et al., 2013a)
MEA_CB_2	89	7	86	14	(Vevelstad et al., 2013a)
MEA_OB_1	89	4	93	7	(Vevelstad et al., 2013b)
MEA_OB_2	94	2	96	4	(Vevelstad et al., 2013b)
MMEA_CB	75	5	80	20	(Vevelstad et al., 2013a)
AP_CB	100	0.0004	100	0	(Vevelstad et al., 2013a)
AP_OB	94	0.1	94	6	This work
AB_CB	97	-	97	3	(Vevelstad et al., 2013a)
AB_OB_1	96	0.2	96	4	This work
AB_OB_2	96	0.3	97	3	This work
AB_OB_3	92	0.2	92	8	This work
MAPA_OB	88	-	88	12	This work

A better nitrogen recovery was seen for the OB setup compared to the CB setup for MEA. This might support the suggested new degradation compounds analogue to HEI, and as shown earlier, HEI formation was favoured in the CB setup. In contrast to MEA, where in depth studies have given a a relative comprehensive set of compounds to analyse for, other amines are still at an early stage with regard to identification of all degradation compounds. The nitrogen recovery balance for other amines is therefore dominated by recovered amine. For MMEA, several imidazoles are likely to be formed and these contribute to the nitrogen balance. Lepaumier reported 3 different imidazoles for MMEA_OB (Lepaumier et al., 2011b). For MAPA, *N*-methyl-*N,N'*-trimethyleneurea (Eide-Haugmo, 2011; Voice et al., 2013), is likely to be formed together with amide formed the same way as for example HEF for MEA. *N*-methyl-*N,N'*-trimethyleneurea and amide (MAPA + acid) are not volatile and would therefore contribute to the liquid phase nitrogen balance.

4. Conclusions

Chemical stability of amines under CO_2 capture conditions is a well-known problem both for process operability and related to economy and environmental issues. Many degradation studies have been conducted to simulate conditions in a capture plant. For oxidative degradation studies, conditions and setups have varied. In this work the chemical stability of a set of amines and their degradation products using 3 different degradation apparatuses has been studied.

The apparatuses studied were a closed batch (CB), an open batch (OB) and an open low gas flow (LGF) apparatus. For MEA, higher or comparable amine losses were seen for the CB compared to the OB apparatus. The other amines studied showed higher degradation in the OB setup. Amine losses for AP, AB and MEA in the OB setup were about the same. Metal concentrations in the liquid phase, oxygen gas concentration and temperature all influence degradation. In particular the two first directly impact the primary degradation mechanisms. Amine with a structure favouring formation of volatile intermediates or end degradation products, as for example MAPA, MMEA and possibly AP, showed typically less stability in the OB setup compared to the CB setup.

For MEA, a new compound (HEHEAA) was quantified for the first time in this work resulting in a total of 21 degradation compounds analysed for in the degradation solutions. Temperature was found to be the most important parameter in the formation of both primary and secondary degradation compounds, both through influencing the formation of intermediates for the secondary degradation compounds and by changing the equilibria. Metal content and oxygen level are more likely to have indirect impact by increasing the formation of intermediates required for the formation of secondary products. For example for HEI, which is formed from several volatile compounds, the difference between OB and CB was large mainly because the CB setup maintained a higher concentration of volatile compounds in the liquid phase.

A new mechanism for the important degradation product HEGly is suggested based on Clarke-Eschweiler methylation reaction where formaldehyde is replaced with glyoxylic acid.

Degradation compounds found for the other amines tested were a mix of degradation compounds also seen for MEA, degradation compounds formed by the same type of mechanisms as for MEA or formed by mechanisms suggested in the literature for other amines with similar structure as the compounds studied. In principle the same types of mechanisms seem to occur in degradation reactions: demethylation reactions of secondary and tertiary amines, ring formation if 5- or 6-membered rings can be formed and the formation of aldehydes, acids, ammonia and alkylamines, amides, imidazoles and oxazolidinones.

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