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Thermal degradation on already oxidatively degraded solutions

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Abstract

CO_2 capture with alkanolamines has been in use since 1930, where 2-ethanolamine (MEA) is the most studied absorbent for post-combustion. In order to prevent degradation, it is important to understand the degradation mechanisms, which in turn requires knowledge of both stoichiometry and kinetics of the reactions and chemical pathways associated with degradation. In the present work thermal degradation with CO_2 in closed cylinders at 135 °C is performed on already oxidatively degraded solutions from both an open batch and a closed batch setup. Thermal degradation with CO_2 on oxidatively degraded solutions seems to give typical thermal degradation compounds.

1. Introduction

Degradation in reactive absorption systems may occur thermally with CO_2 present, or through oxidative degradation, depending on the conditions. Thermal degradation has been studied by several research groups over a long period of time [1-4] while oxidative degradation has received increased attention the last decade [5-7]. Increased insight into the mechanisms, through knowledge of both stoichiometry, kinetics, and chemical pathways associated with degradation, may result in methods for

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strongly reduced degradation [8]. The oxidative degradation experiments described in the literature are mainly performed in variations of two setups. Either the amine loss was studied working in a closed-batch reactor at elevated temperatures and oxygen pressures [9, 10], or in an open-batch reactor at 55 °C where the CO_2-loaded amine solution would be sparged with a wet gas blend of CO_2 and air [5, 11]. Thermal degradation experiments are normally done in stainless steel cylinders [1, 2] or in a reactor as described by Lepaumier [3].

The different conditions in the various parts of a capture plant create challenges related to understanding the degradation mechanism. It has been shown that separate laboratory experiments for thermal or oxidative degradation alone do not explain all the compounds found from pilot plant samples [11]. Lately a degradation setup taking both degradation types into account was introduced, an integrated solvent degradation apparatus (ISDA), where the solvent is exposed to both oxidative and thermal degradation conditions in a single system [12]. This setup may produce more of the degradation products found in pilots, but does not necessarily give the information needed to understand the mechanisms behind the different degradation pathways because of the complexity of the system.

Short name for amine and degradation products	
AB	4-amino-1-butanol (13325-10-5)
AEEA/HEEDA	*N*-(2-hydroxyethyl)ethylenediamine (111-41-1)
AEHEIA	*N*-(2-aminoethyl)-*N'*-(2-hydroxyethyl)imidazolidinone (-)
BHEOX	*N,N'*-bis(2-hydroxyethyl)oxamide (1871-89-2)
BHMEDA	*N,N'*-bis(2-hydroxyethyl)-*N,N'*-dimethylenediamine (14037-83-3)
DMHEED	*N,N'*-dimethyl-*N'*-(2-hydroxyethyl)ethylenediamine (17225-70-6)
DMIDZ	*N,N'*-dimethylimidazolidinone (80-73-9)
DMMEA	*N,N*-dimethyletahnolamine (108-01-0)
DMP	*N,N'*-dimethylpiperazine (106-58-1)
HEA	*N*-(2-hydroxyethyl)acetamide (142-26-7)
HEF	*N*-(2-hydroxyethyl)formamide (693-06-1)
HEGly	*N*-(2-hydroxyethyl)-glycine (5835-28-9)
HEHEAA	*N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide (144236-39-5)
HEI	*N*-(2-hydroxyethyl)imidazole (1615-14-1)
HEIA	*N*-(2-hydroxyethyl)imidazolidone (3699-54-5)
HEPO	4-(2-hydroxyethyl)-2-piperazinone (23936-04-1)
KGlycine	Potassium Glycine (Glycine (56-40-6)
KSAR	Potassium Sarcosine (Sarcosine (107-97-1))
MEA	2-ethanolamine (141-43-5)
MMEA	*N*-methylethanolamine (109-83-1)
MOZD	*N*-methyl-2-oxazolidinone (19836-78-3)
OZD	2-Oxazolidinone (497-25-6)

2. Experimental

The test solutions were oxidatively degraded using an open or closed batch setup for three weeks. The conditions for the oxidation degradation experiments (open and closed experiment 3) are given in table 1. Closed experiments 1 and 2 were test experiments, so adjustments were done during the experimentation period.

Table 1: Conditions for the open and closed experiment 3.

Condition	Open batch	Closed batch
Gas feed	Air + CO_2	No
Dry gas rate (L/min)	0.35 (air), 0.0075 (CO_2)	24.6
Oxygen (%)	21	21
Carbon dioxide (%)	2	0
Nitrogen (%)	77	79
Liquid agitation/flow	agitation/no flow	0.9 L/min
Temperature (°C)	55	50-55
Volume (L)	1	0.7-0.8
Duration (weeks)	3	3
Introduction of gas	Bubbled through the solution	Over liquid sump
Mass transfer	Stirrer + bubbled through	SS316 packing
Metals	No	From packing

In the thermal degradation tests the solutions were placed in 316 stainless steel cylinders (7 ml in each) and heated for 5 weeks at 135 °C. One cylinder was taken out every week and analysed by the following analytical procedures; Liquid Chromatography – Mass Spectrometry (LC-MS), inductively coupled plasma mass spectroscopy (ICP-MS), Ion Chromatography (IC) and titration for CO_2 and amine content. Initial and end samples for some of the experiments were analysed by Gas Chromatography – Mass Spectrometry (GC-MS) according to the method described by da Silva.[13] Potential leakages were also checked by a weight comparison of each cylinder before and after experiment. More details about the open oxidative degradation setup and the thermal degradation setup is given by da Silva [13] and Lepaumier [14]. All the samples are analysed and quantified for HEI, HEF, HEA, BHEOX, OZD, HEGly and HEPO (LC-MS mix) on LC-MS using the method described by da Silva [13] and for formate, oxalate, nitrite and nitrate on an ICS-5000 Dual RFIC Ion Chromatography Dionex System using a gradient method. This system was equipped with IonPac AG15 guard column (2*50mm)/AS15 analytical column (2*250mm), ASRS300 suppressor (2mm), a carbonate removal device (CRD-200, 2mm), a CD conductivity detector and EG eluent Generator Module (KOH cartridge) connected to an ICW-3000 water purification system (Millipore system).

3. Results

The amine losses for the different oxidative degradation open and closed experiments for MEA varied between 13 – 26 % after three weeks. Amine losses resulting from thermal degradation of the MEA solutions from these 4 different oxidative degradation experiments are given in Figure 1 and the initial MEA concentrations and loadings (mol CO_2/mol amine) are given in table 1.
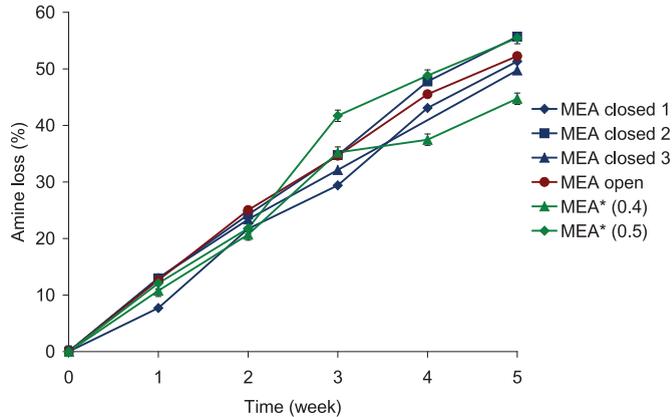

Figure 1: Amine loss. *Data from Ingvild Eide-Haugmo [2]

Table 2: Initial MEA concentration and loading for the different thermal with CO_2 MEA experiments.

Initial sample	MEA (mol/L)	Loading (mol CO_2/mol amine)	Amine loss after 5 weeks (%)
MEA Closed Ex1	3.70	0.42	51
MEA Closed Ex2	4.00	0.42	56
MEA Closed Ex3	3.36	0.44	50
MEA Open	4.20	0.45	52
MEA (=0.4)*	4.83	0.4	45
MEA (=0.5)*	4.22	0.5	56

*Data from Ingvild Eide-Haugmo [2]

Amine losses after 5 weeks in the thermal cylinders were from 50 – 56 % for all the MEA experiments even when the initial concentration and loading were slightly different. These amine losses are comparable to amine losses after 5 weeks for thermal degradation of fresh 30 wt% MEA (= 0.4 – 0.5) which were around 45 - 56% [2]. It has earlier been shown that the CO_2 loading influences the thermal degradation [13], and this is also seen for experiments done the different oxidatively degraded MEA solutions. It is interesting to notice that the previous oxidative degradation does not seem to have any effect on the MEA loss in the thermal cylinders.

Several tests with different amines were also performed. Comparisons for initial amine concentration and loading together with the amine loss after 5 weeks between this work and work of Eide-Haugmo [2] on fresh 30 wt% amine solutions are given in table 3.

All of the solutions in table 2, except MMEA, were only slightly degraded oxidatively before the present experiments. Comparing the amine loss after 5 weeks for these amines shows that MMEA, DMMEA and AB has similar thermal degradation with CO_2 even after they have been a priori oxidatively degraded. For all of these experiments, except for DMMEA, the loadings were around 0.4-0.5. According to Eide-Haugmo [2] DMMEA probably demethylates to MMEA, giving the MMEA oxazolidinone. Support for this is found when comparing the degradation compounds found for DMMEA against the compounds found for MMEA in Lepaumier *et al.* [3]. The LC-MS scan for MMEA in the present experiment shows some of the same masses as for DMMEA. Earlier findings by Eide-Haugmo and Lepaumier [2, 14] indicate that the masses found in DMMEA and MMEA samples are MOZD, DMP or DMIDZ (these have the same mass and cannot be distinguished by LC-MS scan), DMHEED, *N,N',N''*-trimethyl-*N''*-(2-hydroxyethyl)diethylene triamine and *N,N',N'',N'''*-tetramethyl-*N'''*-(2-hydroxyethyl)triethylenetetramine. In addition DMMEA also showed formation of BHMEDA.

Table 3: Initial amine and loading conditions together with amine loss after 5 weeks for different thermal degradation experiments with CO_2.

Amine	Amine (mol/L)		Amine loss (% -5 weeks)	Amine (mol/L)*	*	Amine loss (%-5 weeks)*
MMEA	2.6	0.4	89	4.6	0.5	96
DMMEA	3.2	0.2	23	3.3	0.5	29
AB	3.1	0.4	16	3.3	0.5	19
KSAR	3.7	0.4	33	4.1	0.5	46
Kglycine	4.7	0.5	49	-	-	

*Data from Ingvild Eide-Haugmo [2]

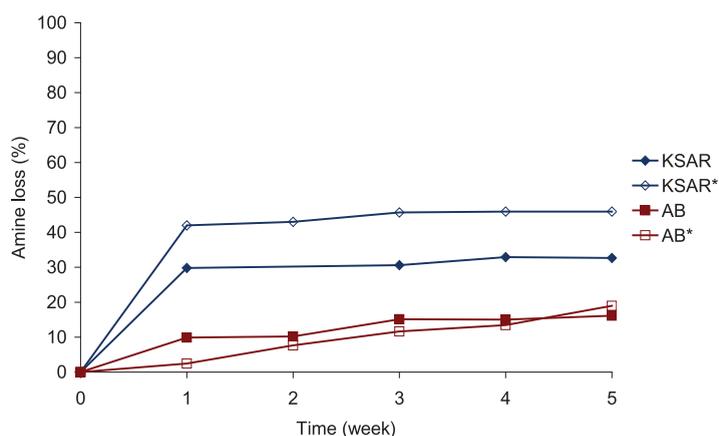The amine loss over time for AB and KSAR compared to results from Eide-Haugmo [2] are given in figure 2.

Figure 2: Amine loss over time for KSAR and AB (*Data from Ingvild Eide-Haugmo [2]).

The curves for the rest of the amines showed slightly less degradation over time than for thermal degradation with CO_2 on fresh samples. Previously degraded AB seemed however to have a faster degradation rate the first week and then slowing down ending up barely below the amine loss for fresh 30 wt% AB (=0.5) after 5 weeks. The behavior for KSAR for both fresh and pre-degraded samples is similar. However, previously degraded KSAR has a lower degradation rate the first week, before it stabilizes. Eide-Haugmo [2] also showed that KSAR with CO_2 (=0.5) had higher degradation than without CO_2. The two curves show similar behavior. However, the slightly lower curve found in the present work can be explained by the lower loading used.

All the samples were analysed for typical MEA degradation compounds (LC-MS-mix) as listed in the experimental section. LC-MS scan has been used to verify degradation compounds outside this mix. For the MEA open and closed experiment 3 the LC-MS scans are in addition supported by GC-MS results. As earlier mentioned, the amine loss results for the present experiments show the same behavior as described by Eide-Haugmo [2] for pure thermal degradation. It is therefore likely that the degradation compounds formed, outside the LC-MS-mix, are more or less the same as the ones reported by Eide-Haugmo [2]. This is supported comparing the LC-MS scans for the pure thermal degradation experiments with CO_2 with the present experiments. GC-MS results for MEA open and MEA closed experiment 3 also verify that HEF, OZD, HEI, HEIA, AEHEIA, BHEIA and a variant of HEI are present. However, quantification was not performed on compounds outside the LC-MS mix.

HEPO is normally classified as an oxidative degradation compounds. However, lab scale experiments often show small amounts of this compound, while several pilots studies report much higher amounts [13]. The samples subjected to thermal degradation with CO_2 in this study contained oxidative degradation compounds. Analysis of these degradation compounds after thermal degradation can give valuable information about what can happen to these degradation compounds when they are introduced to the desorber. Several of the degradation compounds decompose or react further during the first week, for example BHEOX, nitrite, nitrate, HEOX and to some extent oxalate. The behavior for the rest of the degradation mix found in the oxidatively pre-degraded solutions is shown in figure 3 for the solutions from the closed setup and in figure 4 for solutions from the open setup. HEI is shown on the right-hand y-axes for both figures.
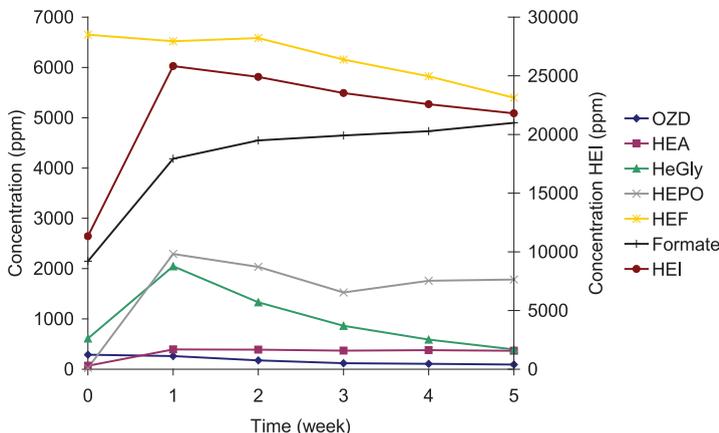

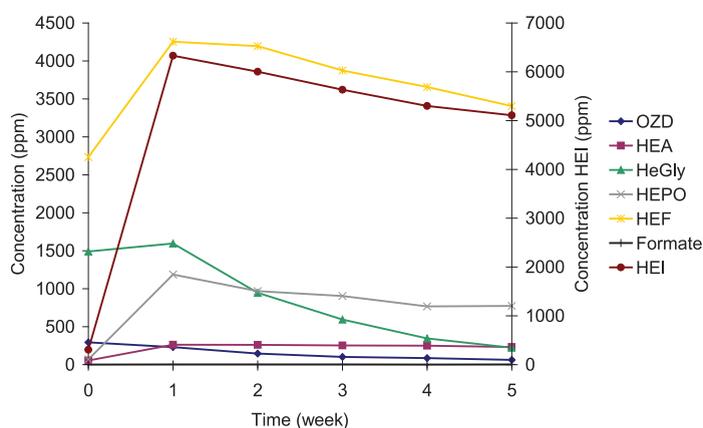Figure 3: Degradation compounds closed experiment 3

Figure 4: Degradation compounds open MEA.

Several of the degradation compounds seem to be affected by temperature to some degree; formation is rapid in the beginning, but then leveling off. The leveling off, or decrease, could be a combination of less intermediates available to form these particular degradation compounds or that these compounds are intermediates in further degradation reactions. The total moles of quantified degradation compounds (LC-MS-mix) in the initial and end samples only varies by 0.13 moles/L or less indicating that these degradation compounds only have a small influence on the amine loss for these experiments.

HEF is believed to be formed from formic acid/formaldehyde and MEA [11, 13]. After one week the rate of formate formation decreases both in the open and closed apparatus. Comparing the decrease of HEF towards the increase of formate from week 1-4, the formation of formate may be explained by a reversion of the HEF to formic acid reaction.

The first week the solution from the open MEA experiment, figure 4, shows a higher rate of formation of some degradation compound compared to the closed experiment, figure 3. This could partly be explained by comparing the different experiments for oxidative degradation and the setups showing that the metal and, to a smaller extent, temperature catalyse the HEF reaction. The open batch oxidative degradation setup did not contain metals, however, the closed batch system contained a SS316 packing. The lower slope of formate and increased rate of HEF in the first week for the experiment with pre-degraded solution from open batch could thus be explained by dissolved metal from the cylinders catalysing the HEF reaction. The metal concentration for the open batch system follows the same trend as in the closed setup experiment 3, only slightly higher concentrations are seen (see Figure 5).
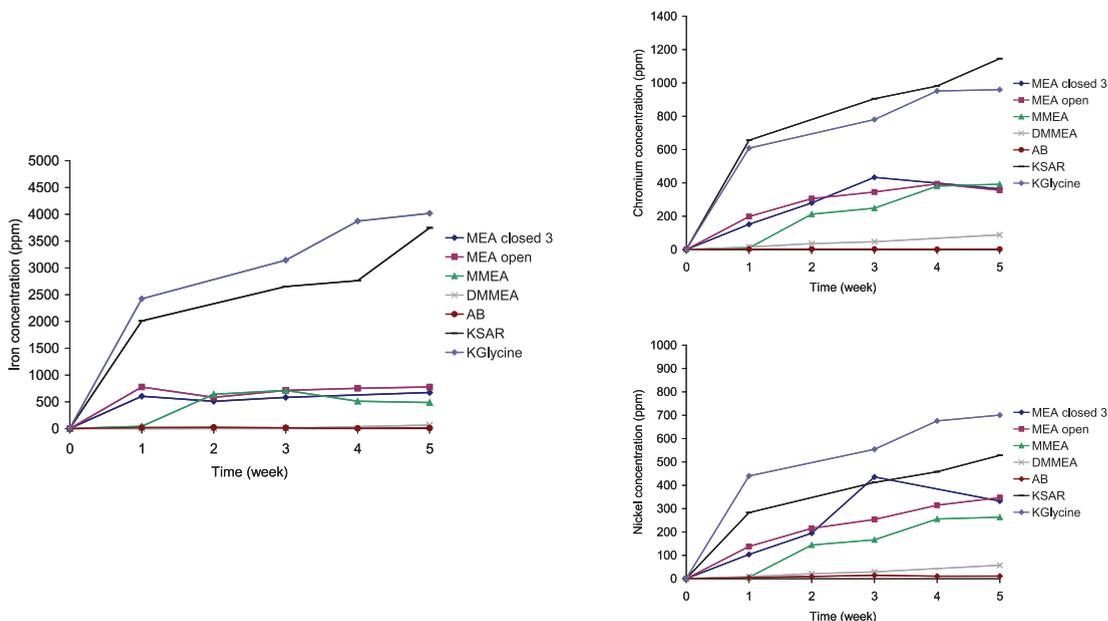
Figure 5: Iron, chromium and nickel concentration (ppm) for different amine solutions

The chromium and nickel concentrations show the same trends as those of iron, however their concentrations are lower. In general the metal concentrations seem to be similar for amines with same amine loss. The exceptions are MMEA and the potassium salt of amino acids. MMEA shows slightly lower metal concentration than MEA even if the amine loss was almost twice that of MEA. The high conductivity and ionic nature of the potassium salt of amino acids could explain the high metal concentrations found in these samples. The metal concentrations for DMMEA are around 10 times higher than for AB, however the concentrations are low and the uncertainty around the numbers is significant.

According to da Silva and Lepaumier [11, 13], HEPO is formed by a cyclisation reaction of HEHEEA, where HEHEEA is formed of MEA and HEGly. Figures 3 and 5 do not show a clear correlation between the amounts of HEGly and HEPO. The slopes for the formation of HEGly and HEPO the first week are respectively 13 and 2 for the solution from the open setup. This may indicate that HEGly in itself is not the limiting factor for the formation of HEPO. However, more information around the behavior of HEHEAA is needed for verification of limiting reactions. HEGly is, together with OZD, the only degradation product with an end concentration lower than initial one. This either means that HEHEAA formation is favored under these conditions or that HEGly is an intermediate for other degradation compounds.

4. Conclusion

The complex and variable operating conditions in a CO_2 capture plant makes it difficult to understand the mechanisms behind the formation of various degradation products. There are several factors contributing differently in different parts of the plant. In thermal degradation the amine losses for

previously degraded solutions were found comparable to amine losses for fresh 30 wt% amine solution (
= 0.4 – 0.5). Analyses indicate that most of the thermal degradation compounds formed are the same as
the compounds earlier described for fresh solutions by Eide-Haugmo and Lepaumier [2, 14]. The thermal
degradation behaviour of several of the oxidative degradation compounds corresponds well with earlier
results from pilot samples.

Acknowledgements

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