

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

Influence of dissolved metals and oxidative degradation inhibitors on the oxidative and thermal degradation of monoethanolamine in post-combustion CO₂ capture.

Journal:	<i>Industrial & Engineering Chemistry Research</i>
Manuscript ID:	ie-2014-036572.R1
Manuscript Type:	Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Léonard, Grégoire; University of Liège, Applied Chemistry Voice, Alexander; The University of Texas , Chemical Engineering Toye, Dominique; University of Liège, Applied Chemistry Heyen, Georges; University of Liège, Applied Chemistry

SCHOLARONE™
Manuscripts

1
2
3
4
5
6
7 Influence of dissolved metals and oxidative
8
9
10
11 degradation inhibitors on the oxidative and thermal
12
13
14
15 degradation of monoethanolamine in post-
16
17
18
19
20 combustion CO₂ capture
21
22
23
24

25 *Grégoire Léonard^{d,*}, Alexander Voice^b, Dominique Toye^a, Georges Heyen^a*
26
27

28 ^aDepartment of Applied Chemistry, University of Liège, Allée de la chimie B6a, Liège Sart
29
30
31 Tilman, 4000, Belgium.
32

33 ^bDepartment of Chemical Engineering, University of Texas, E Dean Keeton St. 200 C0400,
34
35
36 Austin, Texas 78712-1589, USA.
37
38
39

40
41 KEYWORDS: Post-combustion CO₂ capture, monoethanolamine degradation, dissolved metals,
42
43 oxidative degradation inhibitors.
44
45
46
47
48

49
50 ABSTRACT: In the present work, the influence of metal ions and oxidative degradation
51
52 inhibitors on the stability of monoethanolamine solvents (MEA) is studied. Solvent degradation
53
54

55
56 * Corresponding Author: Grégoire Léonard, g.leonard@ulg.ac.be
57
58
59
60

1
2
3 induces additional costs and impacts the environmental balance of the CO₂ capture process as
4 well as its efficiency. The two main degradation pathways of MEA are studied under accelerated
5 conditions: oxidative degradation with continuous gas feed and thermal degradation in batch
6 reactors. It is confirmed that metal ions (resulting from solvent impurities and wall leaching)
7 enhance the oxidative degradation of MEA, while they do not impact its thermal degradation.
8 Moreover, different oxidative degradation inhibitors are tested with varying results according to
9 the inhibitor. It appears that at the selected concentration, radical scavengers like Inhibitor A and
10 DMTD (2,5-dimercapto-1,3,4-thiadiazole) are more efficient than chelating agents like HEDP
11 (1-hydroxyethylidene diphosphonic acid) at inhibiting oxidative degradation. Furthermore,
12 attention must be paid to the influence of oxidative degradation inhibitors on the thermal
13 degradation of MEA. Indeed, some inhibitors like DMTD, DTPA (diethylenetriaminepentaacetic
14 acid) and DTDP (3,3'-Dithiodipropionic acid) appeared to decrease the MEA thermal stability,
15 which cannot be accepted in industrial applications. Finally, a further drawback of DTPA is its
16 high affinity for metal ions leading to a more corrosive solution, so that its use is not
17 recommended for CO₂ capture applications.
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39

40 **1. Introduction**

41 **1.1 General Context**

42
43 CO₂ capture and storage technologies represent one of the main technologies to rapidly reduce
44 the anthropogenic emissions of carbon dioxide in response to the increasing environmental
45 concerns and to the growing world energy demand. According to the International Energy
46 Agency¹, CCS may represent up to 17% of the CO₂ emission reduction in 2050. Among other
47 capture methods, the CO₂ post-combustion capture with amine solvent treats the flue gas after
48 the combustion so that already operating power plants can be retrofitted to rapidly reduce their
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 CO₂ emissions. The CO₂ is captured by absorption into an amine solvent and the current
4
5 benchmark solvent is an aqueous solution of 30 wt% monoethanolamine (MEA). After the
6
7 absorption, the CO₂-loaded solvent is regenerated at a higher temperature to release the captured
8
9 CO₂ that can be re-used or stored underground.
10
11

12
13
14
15 Besides the high energy requirement of the process, the degradation of the amine solvent and
16
17 its consequences represent the second main operational drawback of post-combustion CO₂
18
19 capture. First, the cost of the solvent make-up which is necessary to compensate for solvent
20
21 losses may represent up to 22% of the process operational expenses². Then, the degradation of
22
23 amine solvents leads to the formation of a large range of products that may modify the solvent
24
25 properties and decrease the process efficiency, implying additional costs. Finally, the emission of
26
27 amine solvents and volatile degradation products like ammonia is a critical issue in CO₂ capture
28
29 plants. Although emission reduction technologies exist (among others the (acid) water washing
30
31 of the flue gas at the column outlet), the problem of volatile products emissions is still significant
32
33 in large-scale operating plants³. As underlined by Svendsen et al.⁴, there is no advantage at
34
35 capturing CO₂ if this implies the emission of other products like ammonia.
36
37
38
39
40
41
42

43
44 In the last decade, some attention has been paid to the understanding of solvent degradation
45
46 mechanisms. In the case of aqueous MEA, three main degradation mechanisms have been
47
48 listed⁵: oxidative degradation, thermal decomposition (i.e. the cleavage of the MEA molecule at
49
50 temperatures higher than 200°C) and thermal degradation with CO₂ (corresponding to
51
52 irreversible reactions between CO₂ and the amine solvent). Epp et al.⁶ also reported about a
53
54 fourth mechanism, i.e. solvent degradation with flue gas contaminants like SO_x or NO_x. Previous
55
56
57
58
59
60

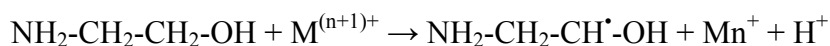
1
2
3 studies performed at the University of Liège have demonstrated that accelerated degradation
4 conditions may reproduce similar degradation pathways in comparison to the degradation
5 observed in samples coming from different industrial pilot plants⁷, especially when lab
6 experiments are performed under oxidative degradation conditions. At the same time, the
7 degradation rate was strongly accelerated (20% degradation over 7 days in oxidative conditions
8 and 37% degradation over 3 weeks in thermal conditions) compared to the degradation rate
9 reported in pilot plants (4% degradation over 45 days⁸). As a consequence, the experimental
10 equipment allowed for a detailed study of MEA thermal and oxidative degradation within
11 reasonable time ranges⁹. In these studies, only pure MEA solutions were tested, and the presence
12 of dissolved metals or additives in the solution has been neglected in first approach. However, in
13 industrial conditions, MEA solutions are never absolutely pure, due to the presence of unwanted
14 dissolved metals and to the addition of degradation inhibitors to improve the solution stability.
15 Thus, the objective of the present study is to gain a better understanding about the influence of
16 metal ions and degradation inhibitors on the stability of MEA solvents. First, a brief review of
17 the literature regarding dissolved metals and degradation inhibitors in MEA solutions is
18 performed. Then, after the materials and methods section, the experimental results of MEA
19 oxidative and thermal degradation are presented and discussed.

20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 **1.2 Influence of dissolved metals on solvent degradation**

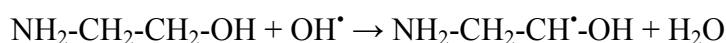
47
48 Dissolved metals like iron (Fe), chromium (Cr), nickel (Ni) and manganese (Mn) may leach
49 from stainless steel columns and pipes walls into the solution, while copper (Cu) and vanadium
50 (V) are sometimes deliberately added to amine solvents as corrosion inhibitors. Several works
51 reported that the presence of these metal ions may catalyze the oxidative degradation of amine
52
53
54
55
56
57
58
59
60

1
2
3 solvents. This effect was first observed by Blachly and Ravner¹⁰ that studied the stability of
4 MEA solutions for CO₂ capture in sub-marine applications. Then, Chi and Rochelle¹¹ confirmed
5 a catalytic effect on MEA oxidative degradation when Fe, Cu or Mn was present in the amine
6 solution. Uyanga and Idem¹² evidenced that the corrosion inhibitor NaVO₃ also catalyzes the
7 degradation of MEA due to the presence of Vanadium (V).
8
9
10
11
12
13
14
15
16
17

18 From these studies, it appears that the presence of metal ions catalyzes the formation of free
19 radicals, and thus the initiation of chain reactions that are responsible of MEA oxidative
20 degradation. Bedell^{5, 13} proposes three main reaction mechanisms. First, the direct one-electron
21 oxidation by a metal ion proceeds via the formation of a complex between MEA and the metal or
22 between MEA, oxygen and the metal. The metal ion is reduced while a MEA radical is generated
23 as represented in the equation below. This MEA radical may then initiate a chain reaction,
24 leading to solvent degradation. Formation of metals complexes was observed¹⁴ in the case of
25 Ag²⁺ with MEA. Bedell⁵ also reported complexes of Fe²⁺ and Cu⁺ with various amines.
26
27
28
29
30
31
32
33
34
35



41 The second mechanism is the hydrogen abstraction by a hydroxyl radical as represented in the
42 equation hereunder. In this case, metals facilitate the propagation steps by catalyzing the
43 generation of radicals from hydroperoxides as presented in Figure 1^{15, 16}. Hydroperoxides are
44 generated by the presence of O₂ in water and their presence in oxidized MEA solutions has been
45 evidenced previously¹⁰, which further supports this reaction pathway.
46
47
48
49
50
51
52



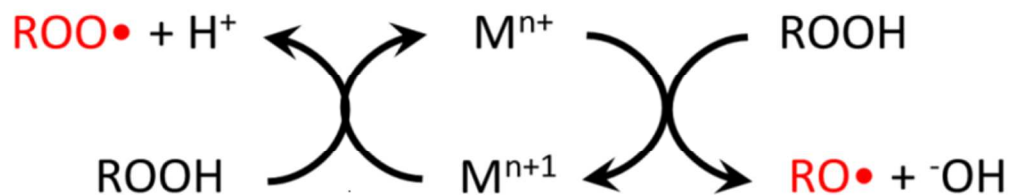
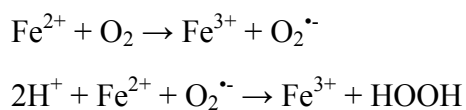
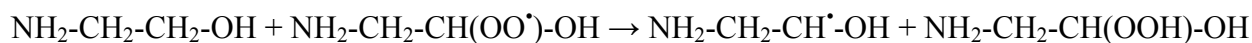


Figure 1. Decomposition of hydroperoxides by the catalytic action of metals.

Moreover, the presence of hydroperoxides is also due to the catalytic action of metals. For instance, Bedell⁵ proposes the following reaction pathways with iron:



The third mechanism of MEA degradation resulting from the action of dissolved metals may be the hydrogen abstraction by an organoperoxy radical following the equation hereunder. The organoperoxy radical $\text{NH}_2\text{-CH}_2\text{-CH}(\text{OO}\cdot)\text{-OH}$ is the reaction product of O_2 and $\text{NH}_2\text{-CH}_2\text{-CH}\cdot\text{-OH}$ resulting from direct one-electron oxidation by a metal ion or hydrogen abstraction by a hydroxyl radical. The MEA peroxide $\text{NH}_2\text{-CH}_2\text{-CH}(\text{OOH})\text{-OH}$ as well as the generated radicals further reacts to form the stable degradation products that may be observed in degraded MEA solutions.



Finally, Davis¹⁷ showed that dissolved metals have no influence on MEA thermal degradation, so that the catalytic effect of dissolved metals seems to be limited to oxidative degradation. No study could be found on the influence of dissolved metals on thermal decomposition or on MEA degradation with SO_x or NO_x .

1.3 Degradation inhibitors

In response to these degradation mechanisms taking place in the presence of both oxygen and dissolved metals, many inhibitors for MEA oxidative degradation have been proposed. These inhibitors may be separated into three main categories which are related to the oxidative degradation mechanisms described in the previous section. First, chelating agents form a complex with dissolved metals, inhibiting their catalytic activity and limiting the initiation/propagation steps of the chain reaction. Then, radical and O₂ scavengers react with peroxides to form stable products and stop the chain reaction. They are called O₂ scavengers since they stoichiometrically react with dissolved O₂. Disadvantage of many radical scavengers is that they are consumed during the reaction and must be renewed. Finally, stable salts like KCl, KBr or KCOOH increase the ionic strength of water, so that the solubility of gases (especially O₂) in the solvent decreases¹⁸ and the degradation rate is reduced.

A detailed bibliographic study has been performed to identify the most efficient inhibitors for MEA degradation¹⁹. Most studies have been conducted at the University of Texas at Austin, the University of Regina, and at the Institut Français du Pétrole-Energies Nouvelles. Their main conclusions can be summarized as following. First, depending on the operating conditions, both chelating agents and radical/O₂ scavengers seem to be very promising inhibitors. On the contrary, stable salts appear to be poor inhibitors, decreasing the degradation rate by only 15% in the best case. Then, a combination of different inhibitors may also lead to an excellent inhibition effect. Chelating agent HEDP may advantageously be combined with radical scavengers Inhibitor A or DTPA to decrease the MEA oxidative degradation¹⁶. Finally, good results were

1
2
3 also reported for TDE, DTDP and DMTD, and TDE^{20, 21, 22} as radical/O₂ scavengers. The exact
4
5 formulation of these inhibitors is given in the next section.
6
7
8
9

10 In conclusion, although previous studies have led to a better understanding of the solvent
11 degradation mechanisms in the presence of metals and degradation inhibitors, research is still on-
12 going to identify efficient and stable inhibitors for MEA oxidative degradation. So far, most
13 inhibitors were only tested in oxidative degradation conditions, i.e. at moderate temperature
14 (~ 55°C-80°C) in the presence of oxygen. However, oxidative degradation inhibitors may be
15 unstable at stripping temperatures or even worse, have a negative influence on the thermal
16 stability of CO₂-loaded MEA solutions. The objective of the present study is thus to evaluate the
17 influence of promising inhibitors on MEA stability. This influence will be studied under both
18 oxidative and thermal degradation conditions.
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33

34 **2. Materials and methods**

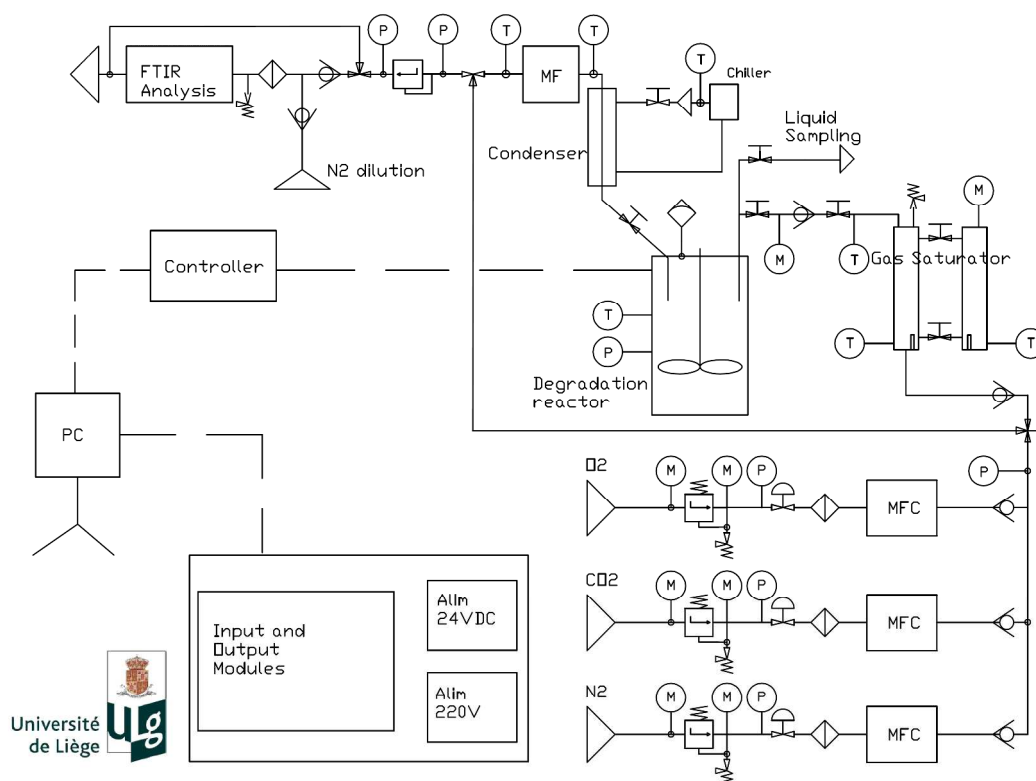
35
36 As already mentioned, solvent degradation is a slow phenomenon taking place over months in
37 industrial capture plants. Thus, it was necessary to develop appropriate experimental equipment
38 and procedures to accelerate solvent degradation within a reasonable timeframe at the lab scale.
39 In the present work, the two main degradation pathways of MEA (oxidative degradation and
40 thermal degradation of MEA with CO₂) have been considered, while the MEA thermal
41 decomposition and the reactions with flue gas contaminants like SO_x or NO_x have been neglected
42 in a first approach. Indeed, thermal decomposition does not take place at the temperatures
43 observed in CO₂ capture conditions and the presence of SO_x and NO_x may be considerably
44 reduced, assuming a high efficiency of the flue gas cleaning steps occurring before the CO₂
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 capture. However, one must keep in mind that even low concentrations of SO_x and NO_x will
4
5 accumulate in real CO₂ capture operations, so these flue gas contaminants will have an effect on
6
7 long-term solvent degradation. Thus, SO_x and NO_x degradation may be included in further works
8
9 to refine the present approach.
10
11

12
13
14
15 The degradation study is performed using specially developed equipment depending on the
16
17 degradation pathway. Because it does not require the presence of a gas phase, thermal
18
19 degradation with CO₂ may be studied under batch conditions. On the contrary, oxidative
20
21 degradation requires a continuous gas feed since it is limited by the rate of gas-liquid transfer²³.
22
23 Thus, oxidative degradation experiments were conducted in an experimental Degradation Test
24
25 Rig with continuous gas flow (see Figure 2) while the thermal degradation experiments with CO₂
26
27 were performed in batch cylinders⁷. On the first side, the Degradation Test Rig for MEA
28
29 oxidative degradation allows temperatures up to 140 °C and pressures up to 2 MPa, with flexible
30
31 gas composition and variable agitation rate. Typically, 300 g of 30 wt% MEA (1.47 mol MEA
32
33 and 11.67 mol H₂O) are weighted into the reaction vessel and loaded with CO₂ to reach a loading
34
35 of about 0.40 mol CO₂/mol MEA. The degradation experiment runs for one week at 120°C,
36
37 0.4 MPa (gauge) and 600 rpm with a continuous gas flow rate (160 NmL/min) composed of 5%
38
39 O₂, 15% CO₂ and 80% N₂. After one week, the experiment is completed and a sample is taken
40
41 for liquid analysis. On the other side, MEA thermal degradation was studied in batch reactors
42
43 consisting in 150 ml-cylinders made of stainless steel 316L that were set into a laboratory oven.
44
45 In a typical experimental run, the cylinders are filled with 100 g of the solvent to be tested,
46
47 usually MEA 30 wt% that has been loaded with CO₂ to reach a loading of about 0.40 mol
48
49
50
51
52
53
54
55
56
57
58
59
60

CO₂/mol MEA. Typical experiments run for 3 weeks at 140°C and a sample is taken every week for analysis.

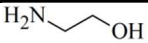


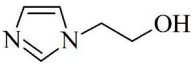
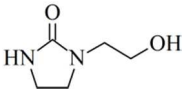
Figure 2. Degradation Test Rig used for the oxidative degradation experiments.

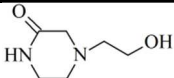
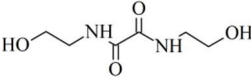


In order to characterize the degraded solvent samples, different analytical methods have been developed. The MEA content is determined by high performance liquid chromatography (HPLC) while the liquid degradation products are quantified using gas chromatography (GC). The relative error of the HPLC method was calculated to 0.76% by multiple measurements of a known sample, while the relative error of the GC method varies from 2.5% to 12% in the case of low concentrated products. Gaseous degradation products in the gas exhaust of the Degradation Test Rig are quantified on-line by Fourier transformed infra-red spectroscopy (FTIR) with a

relative error of 0.2%. The main compounds quantified in oxidative and thermal degradation experiments and the corresponding analytical techniques are reported in Table 1. HEEDA and HEIA are typical thermal degradation products while HEI, HEPO, BHEOX and NH₃ were only observed in oxidative degradation experiments. OZD was reported for both degradation pathways. Besides these components, the concentration of dissolved metal ions (Fe, Cr, Ni and Mn) is measured in liquid solvent samples by Atomic Absorption Spectrometry (AAS). The relative standard deviations of AAS measurements are usually below 10% for each metal but they may reach up to 45% in case of low metal concentrations. A detailed description of the equipment and procedures has been published in a previous work⁷. Based on such equipment, degradation rates of 24% over 1 week and 37% over 3 weeks could be achieved in oxidative and thermal degradation conditions respectively. Moreover, a nitrogen balance check was performed for oxidative degradation experiments. It evidenced that the experimental error could be kept within 10% and that the repeatability of the results could be demonstrated with a relative difference on the total nitrogen content lower than 4%.

Table 1. Main organic compounds identified in degraded MEA samples.

Abb.	Compound	Structure	Analytical method
MEA	Monoethanolamine		HPLC
HEEDA	<i>N</i> -(2-hydroxyethyl)ethylenediamine		GC
OZD	2-oxazolidinone		GC
HEI	<i>N</i> -(2-hydroxyethyl)imidazole		GC
HEIA	<i>N</i> -(2-hydroxyethyl)imidazolidinone		GC

HEPO	4-(2-hydroxyethyl)piperazine-2-one		GC
BHEOX	<i>N,N'</i> -bis(2-hydroxyethyl)oxamide		GC
NH ₃	Ammonia	NH ₃	FTIR

Under base case conditions with no addition of dissolved metals, no metal leaching from the reactor vessel to the solution was observed. Indeed, the dissolved metal concentrations at the end of the experiments have been measured to be lower than 3 ppm for iron and lower or equal to 1 ppm for chromium, nickel and manganese. Thus, in order to get closer to real CO₂ capture operations for oxidative degradation experiments while still working under accelerated degradation conditions, a mix of stainless steel metal ions (Fe²⁺, Cr³⁺, Ni²⁺, Mn²⁺) was added to the solvent solution before the experiment start. Based on the concentrations of Fe, Cr, Ni and Mn ions measured during a MEA test campaign in a European CO₂ capture pilot plant (samples provided by our industrial partner), corresponding amounts of metal salts were added to the experiment solutions. As an example, Table 2 compares the initial concentrations of dissolved metals in the base case oxidative degradation experiment with the concentrations measured in the pilot plant.

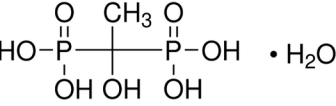
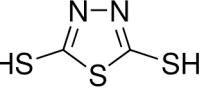
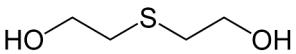
Table 2. Metal concentrations observed in MEA solvents.

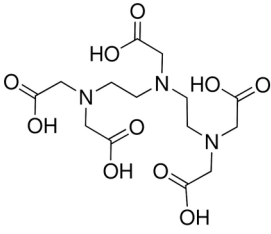
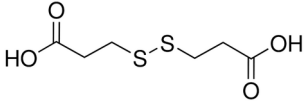
Metal	Metal concentrations measured in pilot plant (ppm)	Initial concentrations in the oxidative base case (ppm)	Corresponding metal salt
Fe ²⁺	52	52.8	FeSO ₄ · 7H ₂ O
Cr ³⁺	5	1.4	CrKO ₈ S ₂ · 12H ₂ O
Ni ²⁺	6	5.3	NiSO ₄ · 6H ₂ O

Mn ²⁺	2	1.4	MnSO ₄ · H ₂ O
------------------	---	-----	--------------------------------------

In addition to this metal mix, an inhibitor may be added to the solvent solution. Table 3 lists the six inhibitors tested in the present study, all of them at an inhibitor concentration of 1 wt% except for Inhibitor A whose concentration was 100 mMol/kg. The concentration of 1 wt% was selected for TDE, DTDP and DMTD since it corresponds to the best results obtained in previous experiments for these inhibitors^{20, 21, 22}. The same concentration was selected for HEDP and DTPA, for which no optimal concentration has been reported. Inhibitor A is a radical scavenger that has already been studied previously¹⁸ but whose composition has not been divulged. All other inhibitors are also radical scavengers, apart from of HEDP which is a chelating agent. Moreover, a combination of 100 mMol/kg Inhibitor A and 1 wt% HEDP was also tested. In this case, the total inhibitor concentration was then higher than 1 wt%.

Table 3. Oxidative degradation inhibitors tested in the present study.

Compound	Structure	CAS number
Inh. A Inhibitor A	Not divulged	n.a.
HEDP 1-hydroxyethylidene diphosphonic acid		25211-86-3
DMTD 2,5-dimercapto-1,3,4-thiadiazole		1072-71-5
TDE 2,2'-thiodiethanol		111-48-8

1			
2			
3			
4			
5			
6	DTPA	diethylenetriaminepentaacetic acid	67-43-6
7			
8			
9			
10			
11			
12			
13	DTDP	3,3'-Dithiodipropionic acid	1119-62-6
14			
15			
16			

3. Experimental results

The first objective of the experimental study is to define a base case experiment for each degradation pathway of MEA. Based on this base case experiment, the influence of metal ions and degradation inhibitors is studied for both oxidative and thermal degradation of MEA.

3.1 Oxidative degradation

In this section, the influence of dissolved metals and degradation inhibitors on MEA oxidative degradation is studied in the Degradation Test Rig. Two experiments are conducted in the absence of inhibitors, respectively with and without the metal mix described in the previous section. Then, experiments with varying degradation inhibitors in the MEA solution are compared to the base case experiment with metal mix. Four inhibitor compositions are tested in the Degradation Test Rig to evaluate the potential of inhibitors at reducing the degradation extent: Inhibitor A, HEDP, DMTD and a combination of Inhibitor A and HEDP. This last composition was selected to quantify the improvement that can be achieved by combining a radical scavenger (Inhibitor A) with a chelating agent (HEDP).

3.1.1 Influence of metal ions

1
2
3 The conditions and the relevance of the base case experiment for the accelerated study of MEA
4 oxidative degradation have been discussed in previous works^{7, 9}. However, the identified base
5 case did not consider the presence of metal ions in the solvent solution although they are present
6 in industrial CO₂ capture plants. Thus, the first experiment performed in the present study
7 evaluates the impact of metal ions on solvent oxidative degradation in order to decide whether
8 metal ions should be included to the base case experiment or not. The metal mix added to the
9 MEA solution has been described in the previous section. From Figure 3a, it appears that the
10 presence of dissolved metals enhances MEA oxidative degradation. The MEA loss rises by 58%
11 from 0.31 mol up to 0.49 mol with dissolved metals in the solution (initial MEA content equals
12 1.47 mol). Similarly, the total emission of ammonia increases from 0.14 mol up to 0.20 mol in
13 the presence of metal ions, confirming their influence on MEA oxidative degradation. This
14 influence can also be observed in Figure 3b which represents the distribution of liquid
15 degradation products. The formation of HEI is significantly increased by the addition of metal
16 ions, as well as the formation of BHEOX. Since HEI has been identified as a typical product of
17 MEA oxidative degradation²⁴, this increase further evidences the catalytic effect of dissolved
18 metals on this degradation pathway. As a consequence, the presence of metal ions needs to be
19 considered when comparing the effect of different degradation inhibitors on MEA oxidative
20 degradation.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

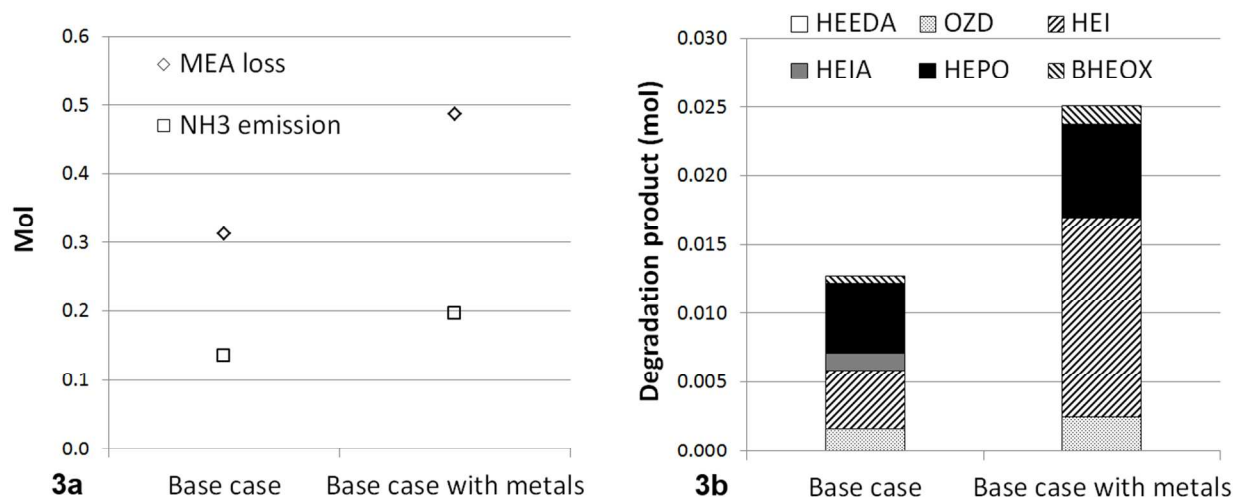
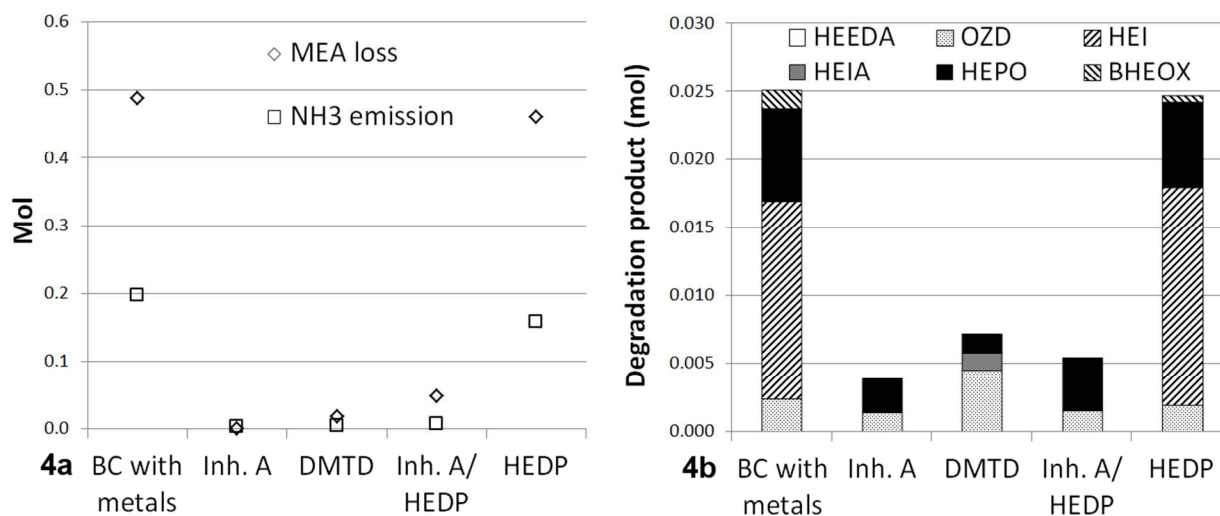


Figure 3. Influence of dissolved metals on MEA degradation and NH₃ emission (3a) and on liquid degradation products (3b) (300 g, 30 wt% CO₂ loaded MEA, 600 rpm, 120°C, 4 barg, 160 NmL/min gas feed, 5% O₂/15% CO₂/80% N₂, 1 week).

3.1.2 Influence of degradation inhibitors

In the literature, degradation inhibitors have usually been tested in oxidative degradation conditions, i.e. at moderate temperature (~ 55°C-80°C) in the presence of oxygen¹⁸. The objective of the present study is to evaluate their influence on MEA degradation in accelerated degradation conditions. In order to get as close as possible to real CO₂ capture operations, the same metal mix as previously described (Fe²⁺, Cr³⁺, Ni²⁺ and Mn²⁺) is added to the amine solution with the inhibitor to be tested. As a consequence, experiments with degradation inhibitors are compared to the base case with metals described in the previous section. Four compositions of degradation inhibitors are tested in the Degradation Test Rig: Inhibitor A, HEDP (1-hydroxyethylidene diphosphonic acid), DMTD (2,5-dimercapto-1,3,4-thiadiazole) and a combination of Inhibitor A and HEDP.

1
2
3
4
5
6 Figure 4a presents the MEA loss and the total ammonia emission for each experiment. It
7
8 appears that Inhibitor A and DMTD are very efficient at reducing the emission of ammonia and
9
10 thus the oxidative degradation rate. On the contrary, HEDP is not successful at limiting MEA
11
12 degradation or NH_3 emission in the test conditions. Moreover, the combination of radical
13
14 scavenger Inhibitor A with chelating agent HEDP seems to be less efficient than Inhibitor A
15
16 only. The inefficiency of HEDP may be due to its low thermal stability²⁵. The inhibitive effect of
17
18 Inhibitor A and DMTD is confirmed by the absence of HEI in these experiments as evidenced in
19
20 Figure 4b. However, more OZD is produced in the DMTD experiment, which could not be
21
22 explained. Finally, similar amounts and types of degradation products are formed with HEDP
23
24 compared to the base case with metals, confirming the inefficiency of HEDP at inhibiting MEA
25
26 degradation.
27
28
29
30
31
32
33



1
2
3 Figure 4. Influence of oxidative degradation inhibitors on MEA degradation and NH₃ emission
4
5 (4a) and on liquid degradation products (4b) (300 g, 30 wt% CO₂ loaded MEA, 600 rpm, 120°C,
6
7 4 barg, 160 NmL/min gas feed, 5% O₂/ 15% CO₂/80% N₂, 1 week).
8
9
10

11 12 13 14 **3.2 Thermal degradation**

15
16 The thermal degradation of MEA has been studied in batch reactors since there is no need for
17
18 continuous gas supply for this degradation pathway if the solution is initially loaded with CO₂.
19
20 First, the influence of dissolved metals on MEA thermal degradation is evaluated. Then,
21
22 degradation inhibitors that have been proposed to reduce MEA oxidative degradation are tested
23
24 under thermal degradation conditions. Indeed, oxidative degradation inhibitors do not remain in
25
26 the absorber during the CO₂ capture process but are also sent to the stripper where they face
27
28 higher temperatures. As a consequence, attention has to be paid to their influence on the thermal
29
30 stability of MEA.
31
32
33
34
35
36

37 38 **3.2.1 Influence of metal ions**

39
40 The same metal mix as described in section 2 is used to study the influence of dissolved
41
42 metals. Figure 5a confirms that the degradation pathway that is studied in batch reactors is
43
44 indeed the thermal degradation of MEA with CO₂: when the solution is not loaded with CO₂,
45
46 there is almost no MEA loss over 3 weeks, while the MEA loss reaches 37.4% in the presence of
47
48 CO₂. However, no influence of the metal ions may be observed independently of the presence of
49
50 CO₂ in the solvent. Figure 5b clearly evidences that the main identified products of MEA thermal
51
52 degradation are the same whether metal ions are present in the solution or not. These products
53
54 are HEEDA and HEIA, and in a less extent OZD as reported by Davis¹⁷. The small amounts of
55
56
57
58
59
60

degradation products formed in non-loaded solutions may be due to CO₂ contamination as the solutions were not degassed before testing. As a conclusion, metal ions have no effect on MEA thermal degradation.

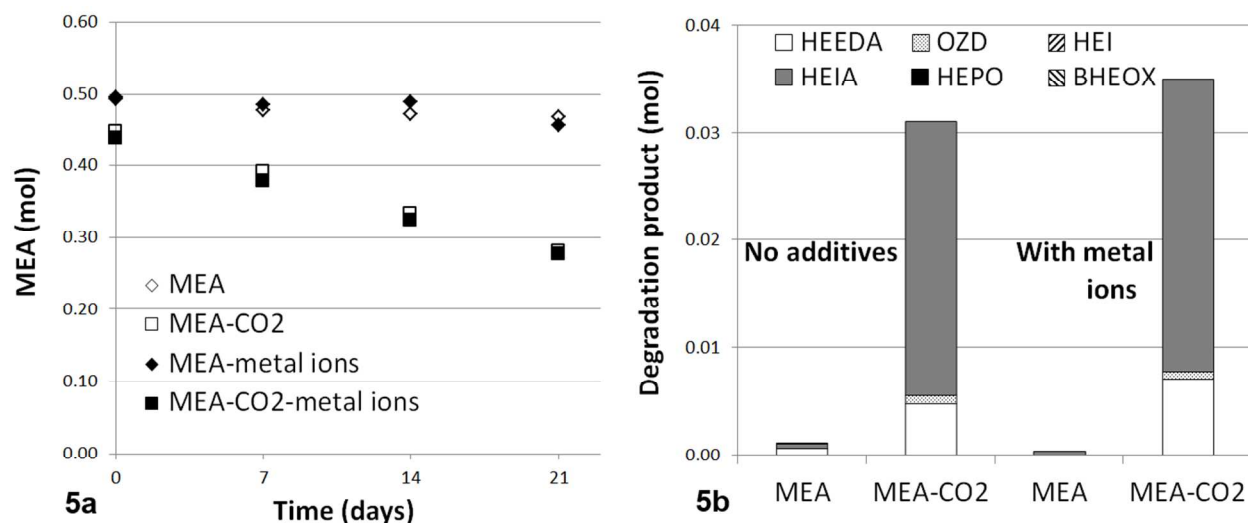


Figure 5. Influence of CO₂ and dissolved metals on MEA thermal degradation (5a) and on liquid degradation products (5b) (100 g, 30 wt% MEA, no gas feed, 140°C, 3 weeks). The initial mole number of MEA is lower in the case of loaded solutions due to the dilution effect of the CO₂ loading.

3.2.2 Influence of degradation inhibitors

Most proposed degradation inhibitor aim at preventing MEA oxidative degradation because it is the dominant degradation pathway under industrial conditions²⁶. However, no study has been reported so far to observe if existing inhibitors may be degraded at stripping temperatures or even worse, have a negative influence on the thermal stability of CO₂ loaded MEA solutions. Thus, some promising oxidative degradation inhibitors were tested in the present work under thermal degradation conditions. In comparison to the oxidative degradation experiments, three

1
2
3 further degradation inhibitors were tested at a concentration of 1 wt%: TDE (2,2'-thiodiethanol),
4
5 DTPA (diethylenetriamine-pentaacetic acid) and DTDP (3,3'-dithiodipropionic acid). The
6
7 experiments were performed without any addition of metal ions into the solution since the
8
9 presence of metal ions does not influences MEA thermal degradation as evidenced in the
10
11 previous section.
12
13
14
15
16
17

18 Figure 6 shows the distribution of degradation products for each solvent solution after 3 weeks
19
20 (bars, left vertical axis) as well as the MEA loss (line, right vertical axis). It appears that three
21
22 oxidative degradation inhibitors clearly enhance MEA thermal degradation with CO₂, leading to
23
24 a MEA loss higher than 0.20 mol: DMTD, DTPA and DTDP (compared to a value of 0.17 mol
25
26 for MEA with no inhibitors). TDE also seems to slightly increase the MEA loss. Inhibitor A and
27
28 HEDP have no significant effect on the thermal stability of the solution. From Figure 6, it also
29
30 appears that HEEDA and HEIA are the major degradation products. A further product was
31
32 reported in all GC spectra but was not identified. This product may correspond to MEA urea
33
34 (N-N'-di(2-hydroxyethyl)urea) as reported by Davis¹⁷.
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

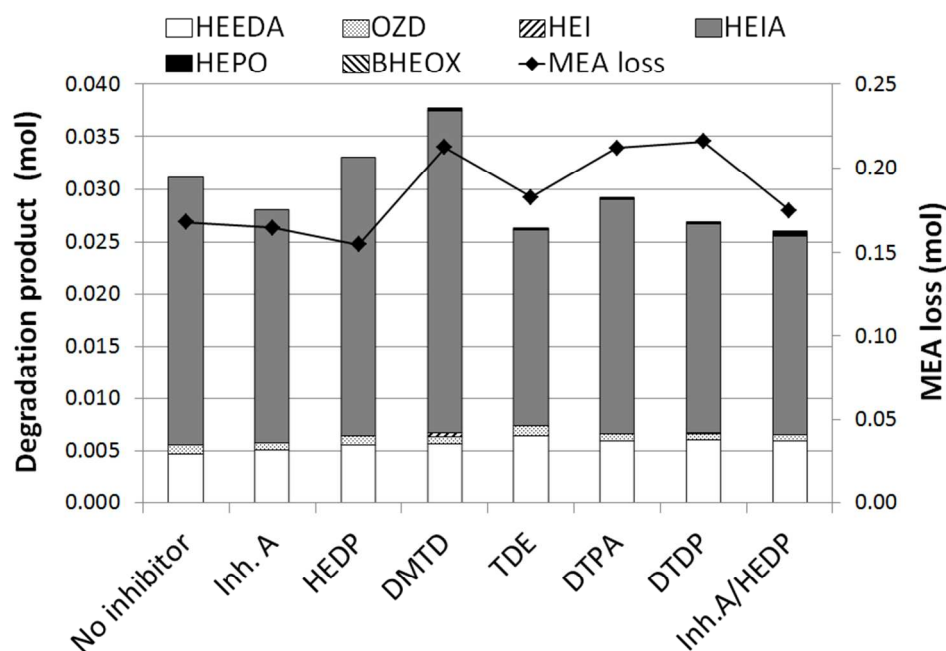


Figure 6. Influence of oxidative degradation inhibitors on MEA thermal degradation with CO₂ (line) and on the repartition of degradation products (bars) (100 g, 30 wt% CO₂ loaded MEA, no gas feed, 140°C, 3 weeks).

No other major product was observed in GC apart from a large unidentified peak recorded in the experiment with TDE. This peak could not be observed in any other sample, meaning that an additional degradation product was formed due to the presence of TDE. Further degradation products may be present in the solutions but were not detected in GC. Their presence may be confirmed by the color of the degraded solutions. Indeed, the degraded solutions containing DMTD, TDE, DTPA and DTDP did not remain transparent contrarily to the other solutions. Figure 7 evidences the different sample colors after 3 weeks of thermal degradation at 140°C. A liquid-liquid phase separation was also observed in the degraded solvent samples containing DMTD and DTDP. Moreover, a strong smell of rotten eggs (characteristic of H₂S), was detected

1
2
3 in degraded samples containing DMTD and DTDP, further indicating the degradation of the
4
5 sulfur-containing inhibitors. This smell was also present for TDE, although to a lower extent.
6
7
8
9



10
11
12
13
14
15
16
17
18
19
20
21
22 Figure 7. Influence of oxidative degradation inhibitors on the color of the degraded solution (100
23
24 g, 30 wt% CO₂ loaded MEA, no gas feed, 140°C, 3 weeks).
25
26
27
28
29

30
31 Finally, Figure 8 shows that the concentrations of metal ions measured in the solution inhibited
32
33 with DTPA are much larger than in the other samples. This may be due to the high affinity of
34
35 DTPA for metal ions since it is a well-known chelating agent similar to EDTA
36
37 (Ethylenediaminetetraacetic acid). Indeed, the equilibrium constant for the formation of metal
38
39 chelates with DTPA is about 100 times higher than with EDTA²⁷. This is among others the case
40
41 for chelates formed with iron, nickel and manganese which are all components of stainless steel
42
43 316L. As a conclusion, DTPA, DMTD, DTDP and TDE lead to undesired reactions under
44
45 thermal degradation conditions, so they may not be suitable for real CO₂ capture systems. In
46
47 particular, DTPA must be imperatively avoided in CO₂ capture applications to prevent the high
48
49 corrosivity that it would induce towards carbon and stainless steels.
50
51
52
53
54
55
56
57
58
59
60

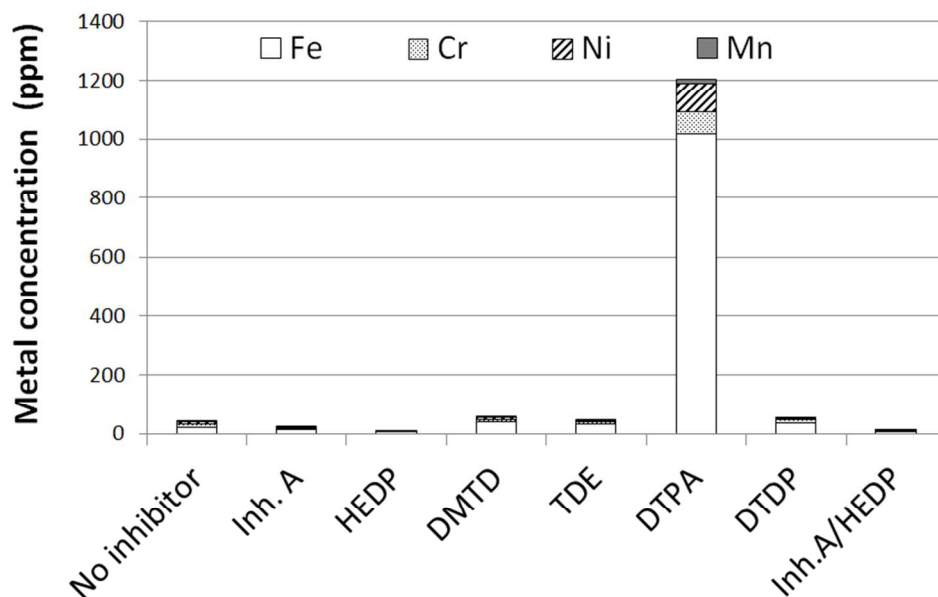


Figure 8. Influence of oxidative degradation inhibitors on metal ions concentrations in degraded solutions (100 g, 30 wt% CO₂ loaded MEA, no gas feed, 140°C, 3 weeks).

4. Conclusion

The environmental impact related to solvent degradation and to the emission of degradation products is one of the most important operational drawbacks of the CO₂ post-combustion capture with amine solvents. In the present work, the degradation of the benchmark solvent (30 wt% MEA) is studied and the influences of metal additives and degradation inhibitors are quantified. The two main degradation pathways of MEA are considered using specially developed equipment for accelerating MEA degradation: the oxidative degradation is evaluated in an experimental Degradation Test Rig with continuous gas feed and the thermal degradation with CO₂ is performed in batch cylinders.

As expected from the literature, the presence of metal ions in the solvent catalyzes the oxidative degradation, leading to a significant increase (58 %) of the degradation extent. It also

1
2
3 appears that the addition of degradation inhibitors may reduce the oxidative degradation more or
4 less successfully depending on the tested inhibitor. However, one should keep in mind that the
5 efficiency of these inhibitors has been tested at one inhibitor concentration only, which may
6 differ from the optimal concentration so further tests would be necessary to identify optimal
7 inhibitor concentrations. Experimental results show that radical scavengers like Inhibitor A and
8 DMTD seem to be more efficient at inhibiting MEA oxidative degradation than the only
9 chelating agent tested in oxidative degradation conditions (HEDP). The combination of HEDP
10 with Inhibitor A does not bring any improvement compared to Inhibitor A alone.
11
12
13
14
15
16
17
18
19
20
21
22
23

24
25 Regarding thermal degradation, the present study confirms that metal ions in the solvent have
26 no influence on thermal degradation as suggested by Davis¹⁷. However, the experimental results
27 evidence that some oxidative degradation inhibitors like DMTD, DTPA, and DTDP clearly
28 enhance the solvent thermal degradation. TDE inhibitor also leads to increased thermal
29 degradation, although to a lower extent. Further degradation products than those reported for the
30 thermal degradation of MEA are also observed, but they have not been identified. Moreover, it is
31 reported that the presence of degradation inhibitor DTPA dramatically increases the solution
32 corrosivity during thermal degradation experiments. This may be due to the high affinity of
33 DTPA for metal ions as a chelating agent. On the contrary, it seems that Inhibitor A and HEDP
34 do not influence the thermal degradation of MEA.
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49

50
51 Finally, the present study underlines the influence of oxidative degradation inhibitors on the
52 thermal stability of MEA solvents. This point must imperatively be considered in the design of
53 solvent solutions containing additives for applications in CO₂ capture. Furthermore, radical
54
55
56
57
58
59
60

1
2
3 scavengers appear to be more efficient at inhibiting MEA oxidative degradation. This is
4
5 reinforced by the observation that efficient chelating agents like DTPA may also induce a higher
6
7 solution corrosivity, which has not been reported for radical scavengers. Based on both oxidative
8
9 and thermal degradation results, Inhibitor A seems to be the most promising inhibitor for
10
11 reducing the oxidative degradation of MEA without enhancing its thermal degradation.
12
13
14

15 16 **Acknowledgements**

17
18
19 The Belgian Fund for Scientific Research (F.N.R.S., bourse FRIA) and the company
20
21 Laborelec, member of the GDF SUEZ group are gratefully acknowledged for their financial and
22
23 technical support.
24
25
26
27
28
29
30

31 **References**

- 32
33
34 (1) IEA. *Technology Roadmap, Carbon Capture and Storage*. International Energy Agency,
35
36 OECD/IEA: Paris, 2013.
37
38
39
40 (2) Abu Zahra, M.; Schneiders, L.; Niederer, J.; Feron, P.; Versteeg, G. CO₂ capture from
41
42 power plants. Part II. A parametric study of the economical performance based on mono-
43
44 ethanolamine. *Int. J. Greenhouse Gas Control* **2007**, *1*, 135.
45
46
47
48 (3) Mertens, J.; Lepaumier, H.; Desagher, D.; Thielens, M.-L. Understanding ethanolamine
49
50 (MEA) and ammonia emissions from amine based post combustion carbon capture: Lessons
51
52 learned from field tests. *Int. J. Greenhouse Gas Control* **2013**, *13*, 72.
53
54
55
56
57
58
59
60

1
2
3 (4) Svendsen, H.; Essen, E.; Mejdell, T. Carbon dioxide capture by absorption, challenges and
4 possibilities. *Chem. Eng. J.* **2011**, *171*, 718.
5
6

7
8
9 (5) Bedell, S. Amine autoxidation in flue gas CO₂ capture – Mechanistic lessons learned from
10 other gas treating processes. *Int. J. Greenhouse Gas Control* **2011**, *5*, 1.
11
12

13
14 (6) Epp, B.; Fahlenkamp, H.; Vogt, M. Degradation of solutions of monoethanolamine,
15 diglycolamine and potassium glycinate in view of tail-end CO₂ absorption. *Energy Procedia*
16 **2011**, *4*, 75.
17
18

19
20 (7) Léonard, G.; Toye, D.; Heyen, G. Relevance of accelerated conditions for the study of
21 monoethanolamine degradation in post-combustion CO₂ capture. *Can. J. Chem. Eng.* **2014**,
22 <http://dx.oj.org/10.1002/cjce.22094>.
23
24
25
26

27
28 (8) Lepaumier, H. *Etude des mécanismes de dégradation des amines utilisées pour le captage*
29 *du CO₂ dans les fumées*. PhD thesis at the University of Savoie, 2008.
30
31
32

33
34 (9) Léonard, G.; Toye, D.; Heyen, G. Experimental study and kinetic model of
35 monoethanolamine oxidative and thermal degradation for post-combustion CO₂ capture. *Int. J.*
36 *Greenhouse Gas Control* **2014**, *30*, 171.
37
38
39
40

41
42 (10) Blachly, C.; Ravner, H. *The stabilization of monoethanolamine solutions for submarine*
43 *carbon dioxide scrubbers*; Report 6189, U.S. Naval Research Laboratory, 1965.
44
45
46
47

48
49 (11) Chi, S.; Rochelle, G. Oxidative degradation of monoethanolamine. *Ind. Eng. Chem. Res.*
50 **2002**, *41*, 4178.
51
52

53
54 (12) Uyanga, I.; Idem, R. Studies of SO₂- and O₂-induced degradation of aqueous MEA during
55 CO₂ capture from power plant flue gas streams. *Ind. Eng. Chem. Res.* **2007**, *46*, 2558.
56
57
58
59
60

1
2
3 (13) Bedell, S. Oxidative degradation mechanisms for amine in flue gas capture. *Energy*
4
5 *Procedia* **2009**, *1*, 771.

6
7
8
9 (14) Kumar, A. Kinetics of complexation and oxidation of ethanolamine and diols by silver
10
11 (II). *J. Phys. Chem.* **1982**, *86*, 1674.

12
13
14 (15) Walling, C. *Free Radicals in Solution*; John Wiley & Sons Inc.: New York, 1957.

15
16
17 (16) Voice, A.; Rochelle, G. MEA oxidation in CO₂ capture, inhibitor screening with hot gas
18
19 FTIR. *Presentation at Luminant Carbon Management Program's Research Review Meeting*:
20
21 Trondheim, 2011.

22
23
24 (17) Davis, J. *Thermal degradation of aqueous amines used for carbon dioxide capture*. PhD
25
26 Thesis at the University of Texas at Austin, 2009.

27
28
29 (18) Goff, G.; Rochelle, G. Oxidation inhibitors for copper and iron catalyzed degradation of
30
31 monoethanolamine in CO₂ capture processes. *Ind. Eng. Chem. Res.* **2006**, *45*, 2513.

32
33
34 (19) Léonard, G. *Optimal conception of a post-combustion CO₂ capture unit with assessment*
35
36 *of solvent degradation*. PhD Thesis at the University of Liege, 2013.
37
38 <http://orbi.ulg.ac.be/handle/2268/158739>

39
40
41 (20) Carrette, P.-L. ; Delfort, B. *Absorbing solution containing a sulphurated organic*
42
43 *degradation inhibitor and method for limiting the degradation of an absorbent solution*;
44
45 International Patent WO2009/156622 A1, 2009.

46
47
48 (21) Carrette, P.-L. ; Delfort, B. *Absorbing solution containing a degradation sulphur-*
49
50 *containing inhibitor having a carboxyl group and method for limiting the degradation of an*
51
52 *absorbent solution*; International Patent WO2009/156621 A1, 2009.

1
2
3 (22) Carrette, P.-L.; Delfort, B. *Absorbing solution containing a thiadiazole-derived*
4 *degradation inhibitor and method for limiting the degradation of an absorbing solution*;
5
6 International Patent WO2009/156619 A2, 2009.
7
8

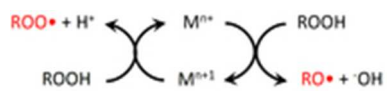
9
10
11 (23) Goff, G. *Oxidative degradation of aqueous monoethanolamine in CO₂ capture processes:*
12 *iron and copper catalysis, inhibition, and O₂ mass transfer*. PhD Thesis at the University of
13
14 Texas at Austin, 2005.
15
16

17
18
19 (24) Voice, A.; Wei, D.; Rochelle, G. Sequential degradation of aqueous monoethanolamine
20
21 for CO₂ capture. *Recent advances in post-combustion CO₂ capture chemistry* Chapter 13, *ACS*
22 *Symposium Series* **2012**, 1097, 249.
23
24

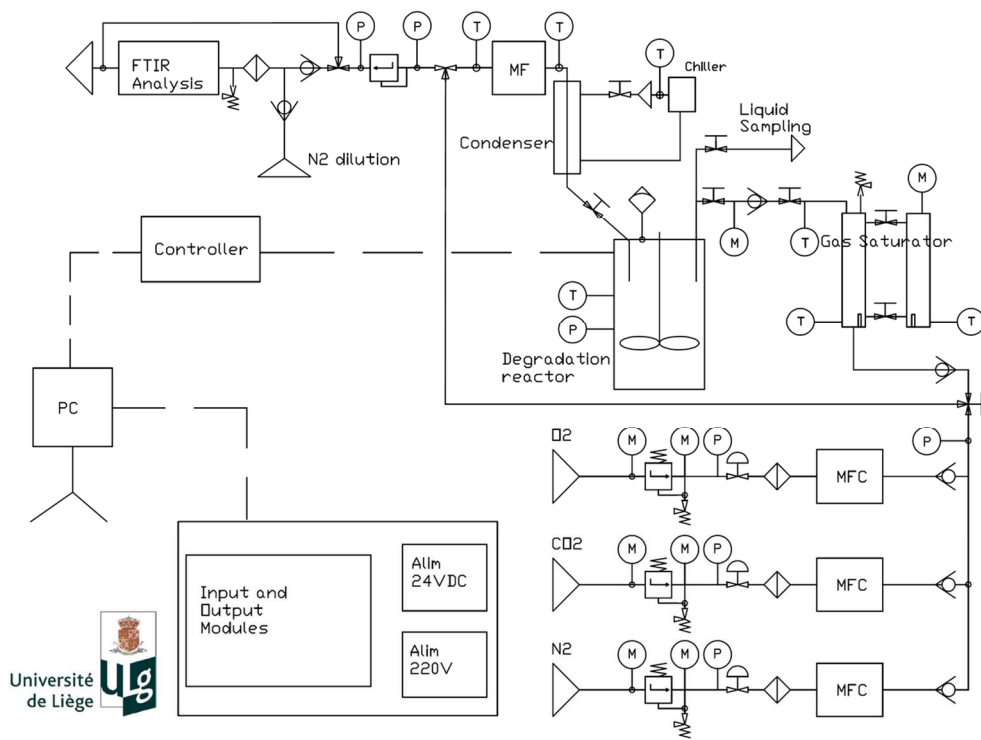
25
26
27 (25) Voice, A.; Rochelle, G. Inhibitors of monoethanolamine oxidation in CO₂ capture
28
29 processes. *Ind. Eng. Chem. Res.* **2014**, 53 (42), 16222.
30
31

32
33 (26) Lepaumier, H.; da Silva, E.; Einbu, A.; Grimstvedt, A.; Knudsen, J.; Zahlsen, K.;
34
35 Svendsen, H. Comparison of MEA degradation in pilot-scale with lab-scale experiments. *Energy*
36
37 *Procedia* **2011**, 4, 1652.
38
39

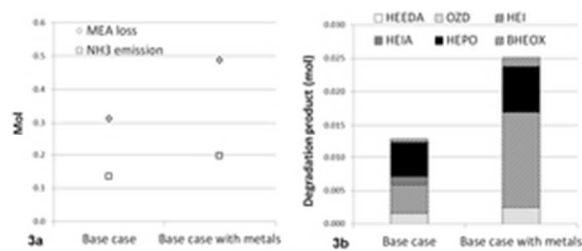
40
41 (27) Hart, R. Ethylenediaminetetraacetic Acid and Related Chelating Agents. *Ullmann's*
42 *Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim,
43
44 2005.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



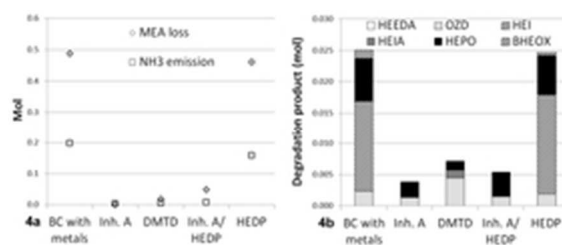
Decomposition of hydroperoxides by the catalytic action of metals.
16x3mm (300 x 300 DPI)



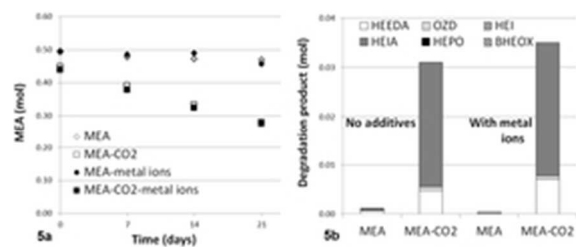
Degradation Test Rig used for the oxidative degradation experiments.
116x85mm (300 x 300 DPI)



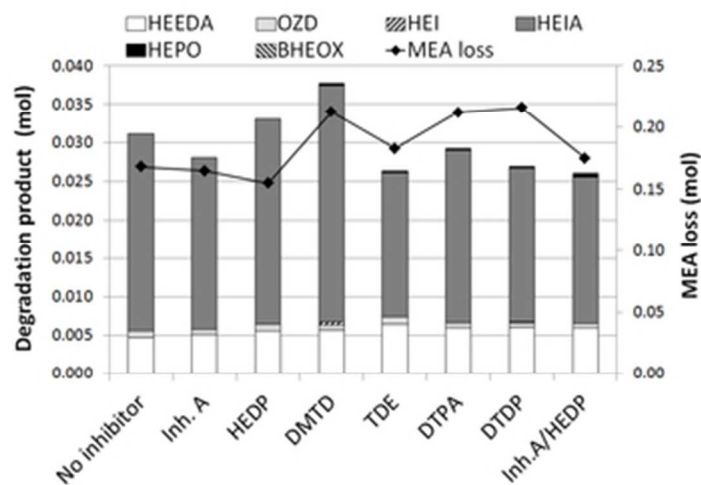
Influence of dissolved metals on MEA degradation and NH₃ emission (3a) and on liquid degradation products (3b) (300 g, 30 wt% CO₂ loaded MEA, 600 rpm, 120°C, 4 barg, 160 NmL/min gas feed, 5% O₂/15% CO₂/80% N₂, 1 week).
24x10mm (300 x 300 DPI)



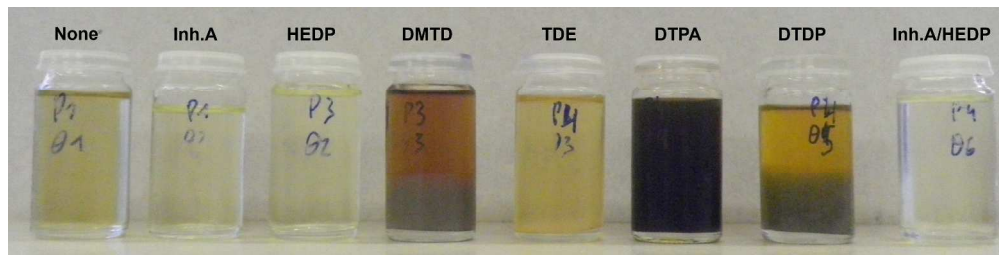
Influence of oxidative degradation inhibitors on MEA degradation and NH₃ emission (4a) and on liquid degradation products (4b) (300 g, 30 wt% CO₂ loaded MEA, 600 rpm, 120°C, 4 barg, 160 NmL/min gas feed, 5% O₂/ 15% CO₂/80% N₂, 1 week).
24x10mm (300 x 300 DPI)



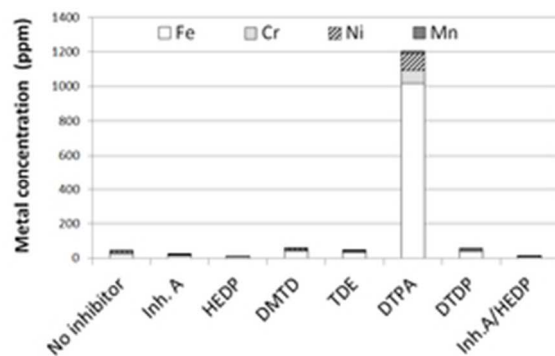
Influence of CO₂ and dissolved metals on MEA thermal degradation (5a) and on liquid degradation products (5b) (100 g, 30 wt% MEA, no gas feed, 140°C, 3 weeks). The initial mole number of MEA is lower in the case of loaded solutions due to the dilution effect of the CO₂ loading.
23x10mm (300 x 300 DPI)



Influence of oxidative degradation inhibitors on MEA thermal degradation with CO₂ (line) and on the repartition of degradation products (bars) (100 g, 30 wt% CO₂ loaded MEA, no gas feed, 140°C, 3 weeks). 29x22mm (300 x 300 DPI)



Influence of oxidative degradation inhibitors on the color of the degraded solution (100 g, 30 wt% CO₂ loaded MEA, no gas feed, 140°C, 3 weeks).
305x76mm (300 x 300 DPI)



Influence of oxidative degradation inhibitors on metal ions concentrations in degraded solutions (100 g, 30 wt% CO₂ loaded MEA, no gas feed, 140°C, 3 weeks).
23x15mm (300 x 300 DPI)