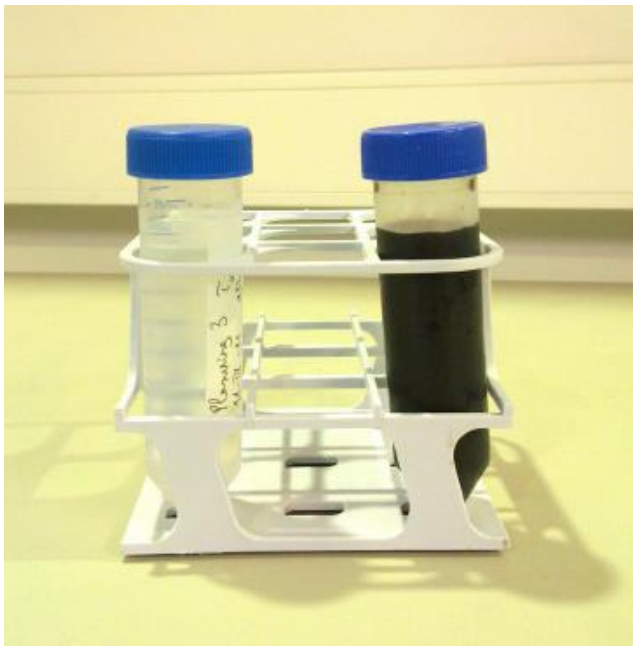
LABORELEC
GDF SUEZ

Université de Liège

Degradation inhibitors and metal additives: impact on solvent degradation



April 2012

Grégoire Léonard

Index

1. Introduction 4
2. Degradation types 5
3. Metal effect on MEA degradation 6
   3.1 Effect of metals on oxidative degradation 7
      3.1.1 Oxidative degradation mechanism 7
      3.1.2 Effect of iron 8
      3.1.3 Effect of copper 11
      3.1.4 Effect of nickel 12
      3.1.5 Effect of chromium 12
      3.1.6 Effect of vanadium 12
      3.1.7 Effect of manganese 13
      3.1.8 Effect of silver 14
      3.1.9 Effect of other metals 14
      3.1.10 Effect of combined metals 14
      3.1.11 Comparison of the different metals 15
   3.2 Effect of metals on CO_2 degradation 17
   3.3 Effect of metals on MEA thermal degradation 18
   3.4 Effect of metals on SO_x and NO_x degradation 18
   3.5 Conclusion on metal effect 19
4. Degradation inhibitors 20
   4.1 Chelating agents 22
      4.1.1 Bicine 22
      4.1.2 EDTA 23
      4.1.3 HEDTA 25
      4.1.4 TEA 25
      4.1.5 Gluconate 25
      4.1.6 Potassium-sodium tartarate 25
      4.1.7 HEDP, DTPA, DTPMP, citric acid, NTA 26
      4.1.8 Conclusion about chelating agents 26
   4.2 Radical and O_2 scavengers 27
      4.2.1 MDEA 27
      4.2.2 Formate and formaldehyde 27
      4.2.3 Na_2SO_3 28
      4.2.4 NH_2OH 29

4.2.5 Inhibitor A 29
4.2.6 Inhibitor B 31
4.2.7 Various sulfur continuing products 31
4.2.8 Conclusion about radical and O_2 scavenger 32
4.3 Conclusion about degradation inhibitors 32
5. Conclusion 33
6. List of abbreviations 35
7. Table of Figures 36
8. Bibliography 37

1. Introduction

This report is part of a PhD thesis currently taking place at the University of Liège in collaboration with the company Laborelec. A Degradation Test Rig (DTR) has been built in order to evaluate solvent degradation in CO_2 capture conditions. Details about degradation effects and about the DTR may be found in a previous report (PhD mid-term report, G. Léonard, 2011). Experiments to study the effect of process conditions on degradation are in progress with 2-ethanolamine (MEA) as benchmark solvent.

This report presents first a brief overview of the different degradation mechanisms and associated products, followed by a literature review about metal influence on MEA degradation and a state of the art review about degradation inhibitors.

2. Degradation types

In order to understand the effect of metals and inhibitors on solvent degradation, it is necessary to distinguish the different degradation mechanisms.

Four main degradation types have been identified. It is important to note that the boundaries between the different types are not always clear, so that different classifications of degradation reactions may coexist. Here are the main ones, based on the work of Epp et al (2011):

- **Thermal degradation.** With the only effect of temperature, MEA degrades and decomposes above 200°C (Epp et al., 2011). However, Lepaumier has shown that MEA (4M in water) can also degrade at 140°C but in a much lower extent than in presence of CO_2 and/or O_2 (Lepaumier, 2008). The degradation products proposed were NH_3 and HEEDA (N-(2-Hydroxyethyl)ethylenediamine).

- **Degradation with CO_2,** sometimes referred to as thermal degradation in presence of CO_2. This type of degradation occur by irreversible reactions between MEA and CO_2. In presence of CO_2, the main degradation products of MEA are HEIA (N-(2-hydroxyethyl)imidazolidone), HEEDA and OZD (2-Oxazolidinone) (Lepaumier, 2008).

- **Oxidative degradation**. Many authors agree on the fact that oxidative degradation is a free radical chain reaction (Lepaumier, 2008; Bedell et al., 2011; Voice, 2011). The main degradation products are ammonia and organic acids (formic, acetic, glycoli and oxalic acids). Moreover, ions resulting from organic acids may further react with MEA to form Heat Stable Salts (HSS).

- **Reaction of MEA with flue gas contaminants such as SOx and NOx.** SOx and NOx are hydrolyzed into inorganic acids when in solution. Those acids react with the amine via a reversible acid-base reaction to form salts. These salts can be recovered by thermal reclaiming (Epp et al., 2011).

3. Metal effect on MEA degradation

The presence of dissolved metals in the solution may promote solvent degradation. Several works have reported that the presence in the solvent of dissolved metals like iron (Fe), copper (Cu), chromium (Cr), nickel (Ni) and vanadium (V) may catalyze oxidative degradation reactions. Fe, Cr and Ni may leach from columns and pipes walls, and Cu and V are sometimes used as corrosion inhibitors. It is then important to consider dissolved metals for representative results. The different studies published on this subject are listed in Table 1.

Table 1: Studies about metal effects on MEA degradation

Reference	Objectives of the study	Metal	Degradation tracer
Blachly and Ravner, 1965a	Stability of a MEA solution containing degradation inhibitors	Fe^0, Fe^{2+}, Fe^{3+}, Cr^0, Cr^{6+}, Ni^0, Ni^{2+}, Cu^{2+}	NH_3, total N, peroxides
Blachly and Ravner, 1965b	Case study of a CO_2 capture process in submarines	Undesired presence of Fe and Cu[1]	Total N, MEA
Blachly and Ravner, 1966	Published results from Blachly and Ravner, 1965a	-	-
Ravner and Blachly, 1968	Patent on results from Blachly and Ravner, 1965a	-	-
Kumar, 1982	Effect of silver on complexation and oxidation of ethanolamines and diols	Ag^{2+}	Not reported
Chi and Rochelle, 2002	Effect of iron and of several degradation inhibitors on MEA oxidation	Fe^{2+}, Fe^{3+}, Mn^{7+}	NH_3
Goff and Rochelle, 2003	Oxidative degradation of MEA at absorber conditions	Fe^{2+}, Cu^{2+}	NH_3
Goff and Rochelle, 2004	O_2 mass transfer effects	Fe^{2+}, Cu^{2+}	NH_3
Goff and Rochelle, 2006	Oxidation Inhibitors for copper and iron catalyzed degradation	Fe^{2+}, Cu^{2+}, Mn^{2+}, Mn^{7+}	NH_3
Bello and Idem, 2006	Effect of corrosion inhibitor $NaVO_3$ on MEA oxidative degradation	V^{5+}	MEA
Sexton and Rochelle, 2006	Oxidation products of amines in CO_2 capture	Cu^{2+}, Fe^{3+}, V^{5+}	Carboxylic acids, EDA, Nitrite, Nitrate
Uyanga and Idem, 2007	Effect of corrosion inhibitor $NaVO_3$ on MEA O_2 and SO_2 degradation	V^{5+}	MEA
Sexton and Rochelle, 2009	Catalysts and inhibitors for MEA oxidation	Cu^{2+}, Cr^{3+}, Ni^{2+}, Fe^{2+}, V^{5+}	NH_3, carboxylic acids, …

Davis, PhD, 2009	Effect of metal on MEA thermal degradation	Cu, Cr, Ni, Fe, V[1]	MEA, HEEDA
Captech 2007	Effect of iron	Fe[1]	Not reported
Voice and Rochelle, 2011a	Oxidation of different amines at absorber conditions	Fe^{2+}, Cr^{3+}, Ni^{2+},	NH_3, MEA
Voice and Rochelle 2011b	Inhibitor screening with hot gas FTIR	Fe^{2+}, Cu^{2+}, Mn^{2+}, V, Cr, Ni, Ti, Mo, Co, Sn, Se, Ce, Zn[1]	NH_3
Voice and Rochelle 2011c	Catalysts and inhibitors screening for MEA oxidation	Mn^{2+}, Mn^{x+}, Fe^{2+}, Cr^{3+}, Cu^{2+}, V^{7+}	NH_3

In this section, we will mainly address oxidative degradation. The effect of each metal will be described separately, as well as the effect of the metal concentration for iron and copper, the effect of combined metals and the metal influence on the observed degradation products. Finally, the effect of metals on other types of degradation will briefly be evocated.

3.1 Effect of metals on oxidative degradation

3.1.1 Oxidative degradation mechanism

Many authors agree on the fact that oxidative degradation proceeds according to a chain reaction (Lepaumier, 2008; Bedell et al., 2011; Voice and Rochelle, 2011a). Free-radical chain reactions can be described by initiation, propagation and termination steps. During the initiation step, a free radical is formed by the cleavage of a homolytic covalent bond. This initiation may be due to temperature, light, or metal catalyst (Belfort et al., 2011).

$RH \rightarrow R^{\bullet} + H^{\bullet}$ Initiation
$R\text{-}R \rightarrow 2\ R^{\bullet}$

The generated radicals may then react with Oxygen to form peroxy radicals, which further react with a C-H bond via a hydrogen abstraction reaction, generating hydroperoxides. The chain reaction can progress further via the cleavage of hydroperoxide into two radicals (Belfort et al., 2011).

$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ Propagation
$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$

$ROOH \rightarrow RO^{\bullet} + HO^{\bullet}$
$2\ ROOH \rightarrow ROO^{\bullet} + RO^{\bullet} + H_2O$

The termination step is the recombination of two radicals to form a stable molecule, the degradation product. In the case of MEA, NH_3 and formic acid are among the main final degradation products (Voice and Rochelle, 2011a).

Studying this chain reaction in details, Bedell (2009, 2011) proposes three main degradation pathways for MEA where metals play different roles:

[1] Oxidation state not reported

- **Direct one-electron oxidation by a metal ion:**

$$NH_2\text{-}CH_2\text{-}CH_2\text{-}OH + M^{(n+1)+} \rightarrow NH_2\text{-}CH_2\text{-}CH_2\text{-}OH^{\bullet} + M^{n+}$$

This reaction may occur via the formation of a complex between MEA and the metal or between MEA, O_2 and the metal. The generation of MEA radicals initiates the chain reaction. Complexation of metals by MEA has been observed by Kumar (1982) in the case of Ag^{2+}. Bedell has also reported complexes of Fe^{2+} and Cu^{+} with various amines (Bedell, 2011).

- **Hydrogen abstraction by a hydroxyl radical:**

$$NH_2\text{-}CH_2\text{-}CH_2\text{-}OH + OH^{\bullet} \rightarrow NH_2\text{-}CH_2\text{-}CH^{\bullet}\text{-}OH + H_2O$$

In this case, metals facilitate the propagation steps by catalyzing the generation of radicals from hydroperoxide as presented on Figure 1 (Voice and Rochelle, 2011b).

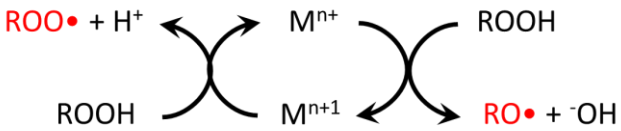


Figure 1: Decomposition of hydroperoxides by catalytic action of metals

Moreover, the presence of hydroperoxides is also due to the action of the metal catalyst. For instance, with iron, Bedell (2011) proposes the following reactions:

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O^{\bullet}_2{}^{-}$$
$$2H^{+} + Fe^{2+} + O^{\bullet}_2{}^{-} \rightarrow Fe^{3+} + HOOH$$

- **Hydrogen abstraction by an organoperoxy radical:**

$$NH_2\text{-}CH_2\text{-}CH_2\text{-}OH + NH_2\text{-}CH(OO^{\bullet})\text{-}CH_2\text{-}OH \rightarrow NH_2\text{-}CH^{\bullet}\text{-}CH_2\text{-}OH + NH_2\text{-}CH(OOH)\text{-}CH_2\text{-}OH$$

where $NH_2\text{-}CH(OO^{\bullet})\text{-}CH_2\text{-}OH$ is the reaction product of $NH_2\text{-}CH^{\bullet}\text{-}CH_2\text{-}OH$ and O_2. The MEA peroxide $NH_2\text{-}CH(OOH)\text{-}CH_2\text{-}OH$ may further react to form stable degradation products.

To summarize, metals have an essential catalytic effect by generating free radicals that will initiate and propagate chain reactions, leading to formation of degradation products and MEA degradation.

3.1.2 Effect of iron

Iron is the main component of stainless steel, so that its presence cannot be prevented during CO_2 capture. In solution, iron can be present under the form of Fe^{2+} or Fe^{3+} (it can respectively be added as $FeSO_4$ or $FeCl_3$). It seems from Chi and Rochelle (2002) that Fe^{2+} has a larger catalytic effect on MEA degradation than Fe^{3+}. The higher catalytic effect of Fe^{2+} compared to Fe^{3+} is represented on Figure 2 at both CO_2 lean and rich loading. The production of NH_3 is used as tracer for the oxidative degradation of MEA.

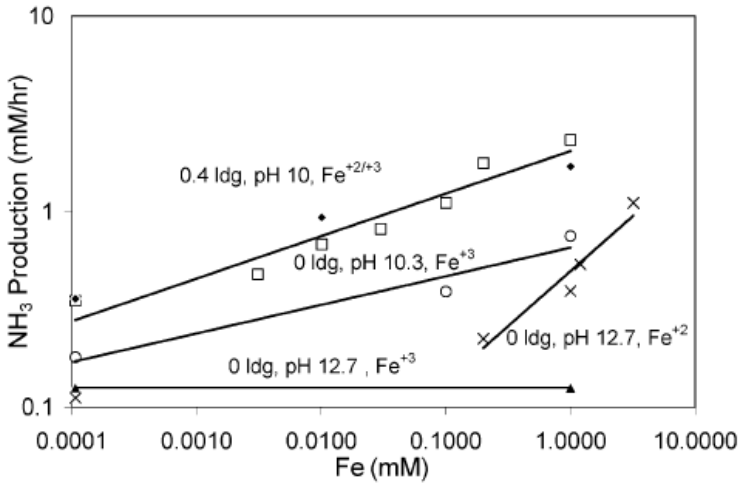


Figure 2: Effect of Fe^{2+} and Fe^{3+} on NH_3 evolution (Chi and Rochelle, 2002)

Explanation for the higher influence of Fe^{2+} compared to Fe^{3+} may come from the Fe^{2+}-catalyzed pathway for hydroperoxide formation proposed by Bedell (2009) and presented in section 3.1.1.

Although Blachly and Ravner (1965a) have performed all their experiments with degradation inhibitors (see chapter 4 about degradation inhibitors), they have also stated that Fe^{2+} has a larger catalytic effect on NH_3 production than Fe^{3+} (Figure 3). Moreover, in the presence of degradation inhibitor, bulk iron has no impact on NH_3 production.

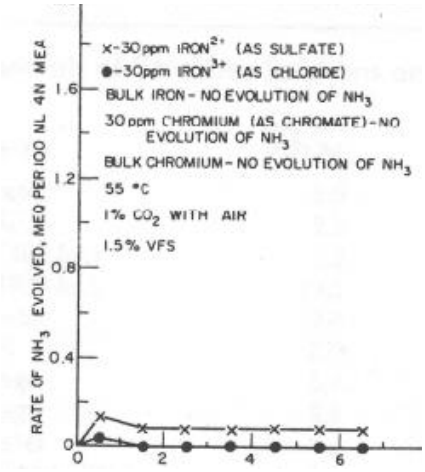


Figure 3: Effect of Iron on NH_3 evolution (Blachly and Ravner, 1966)

All the authors from Table 1 that have studied the influence of Fe^{2+} have confirmed its catalytic effect on the oxidative degradation of MEA. Chi and Rochelle (2002) have also evidenced (Figure 4) that a higher metal concentration induces a higher oxidative degradation, both with Fe^{2+} (dissolved $FeSO_4$, left chart) and Fe^{3+} (dissolved $FeCl_3$, right chart).

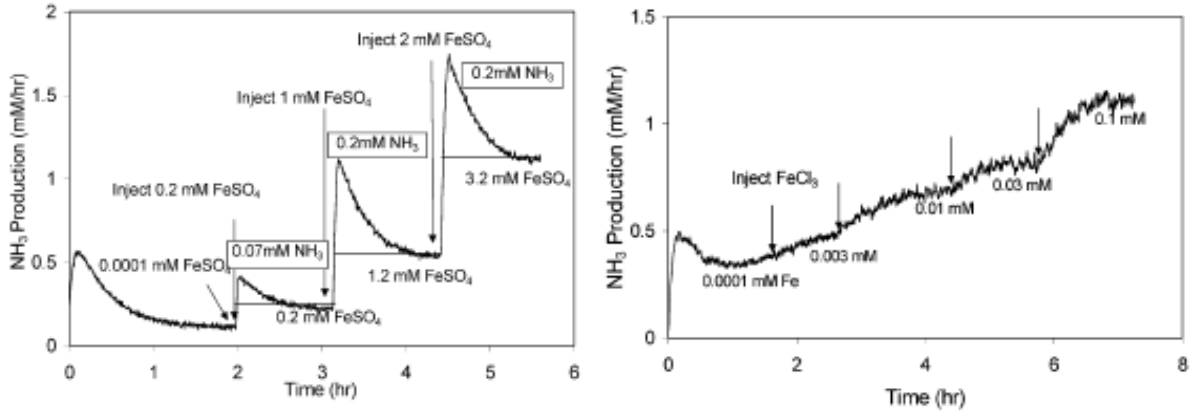


Figure 4: Influence of the iron concentration (Chi and Rochelle, 2002)

Only one other work (Goff and Rochelle, 2004) has studied the impact of varying Fe^{2+} concentration, with similar evidence of a NH_3 production increasing when the metal concentration is increased (Figure 5). However, the authors have stated that the degradation rate dependence on iron concentration was much lower than first order. They attribute this to the limiting O_2 mass transfer due to insufficient agitation rate during their experiment.

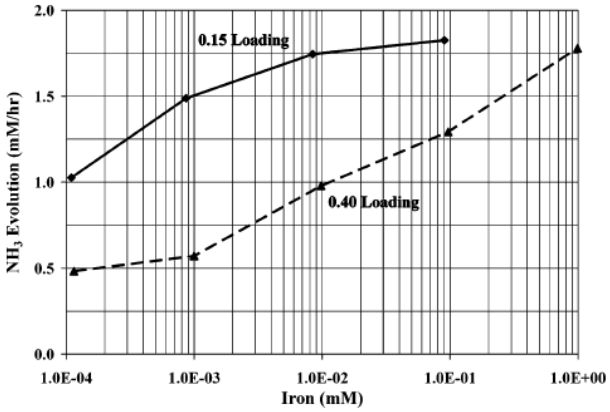


Figure 5: Influence of the Fe^{2+} concentration (Goff and Rochelle, 2004)

Furthermore, Figure 5 shows that CO_2 loading has an impact on the MEA degradation rate. Diverging from previous results of Chi and Rochelle (2002, see also Figure 2) and from the results they first obtained (Goff and Rochelle, 2003, see Figure 6), they have shown that the degradation rate was higher in case of unloaded solutions (Goff and Rochelle, 2004). This latest result has been confirmed in the case of metal-free solutions as well as in presence of vanadium catalyst (Bello and Idem, 2006). The reason for this lower degradation rate would be a decrease of O_2 solubility in loaded MEA solutions.

Finally, according to Chi and Rochelle (2002), the CO_2-loading has a further effect on MEA oxidation since only Fe^{2+} presents a catalytic effect in unloaded solutions. This may be due to an influence of the solution pH. Unloaded solutions are more basic, so that Fe^{3+} may precipitate under the form of $Fe(OH)_3$, which could however not be confirmed visually.

3.1.3 Effect of copper

Since 1966, the large catalytic effect of Cu^{2+} on the oxidative degradation of MEA has been evidenced (Blachly and Ravner, 1966). This has been later confirmed by several studies (Goff and Rochelle, 2003, 2004; Voice and Rochelle, 2011c).

Goff and Rochelle (2003, see Figure 6) have evidenced the influence of Cu^{2+} on NH_3 production rate at both rich (left chart) and lean CO_2 loading (right chart). They have found that the NH_3 production rate first increases with the Cu^{2+} concentration, and then decreases, so that a maximal NH_3 production rate is achieved. However, like for Iron, the rate dependency on Cu^{2+}concentration was lower than first order, also due to O_2 mass transfer limitations in the bulk liquid.

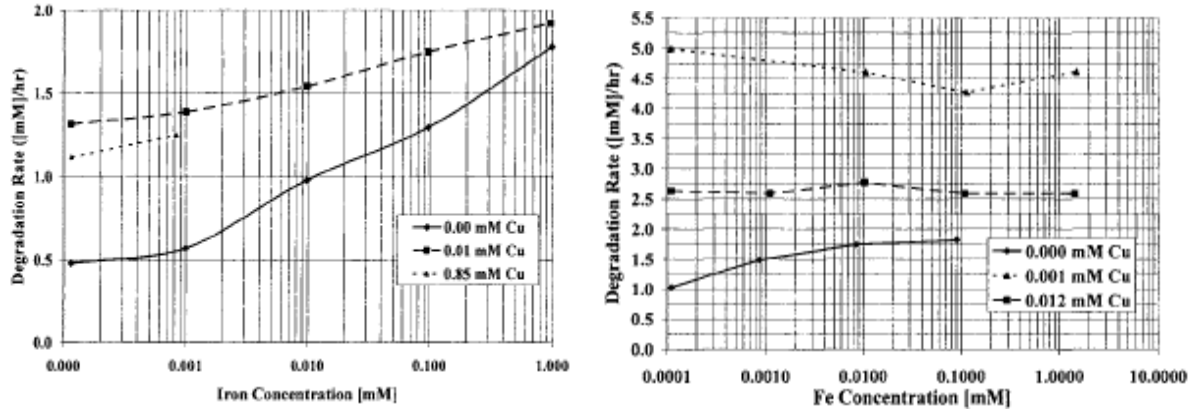


Figure 6: Influence of Cu^{2+} concentration at rich (left) and lean CO_2 loading (right)

In the presence of bicine (tradename VFS), a degradation inhibitor (see chapter 4), Blachly and Ravner (1966) have shown that the Cu^{2+} concentration has a large influence on the oxidative degradation. Even at 1ppm Cu, Figure 7 shows an effect on MEA degradation in presence of bicine. However, they did not report about a maximal NH_3 production rate.

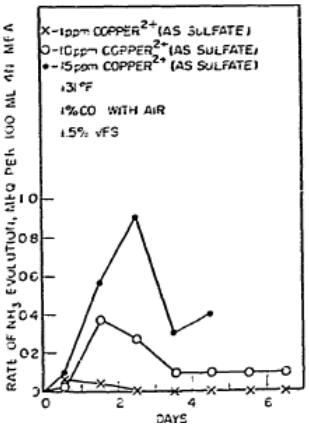


Figure 7: Effect of Cu^{2+} concentration on NH_3 evolution (Blachly and Ravner, 1966)

3.1.4 Effect of nickel

Blachly and Ravner (1966) have studied the effect of nickel in presence of degradation inhibitor bicine (VFS). Their study has been performed at 55°C. Bulk nickel rapidly corroded, inducing severe amine degradation. Dissolved nickel (Ni^{2+} dissolved from $NiCl_2$) at low concentration (3.7ppm) had no effect but larger amount (37ppm) induced perceptible degradation as observed on figure 8.

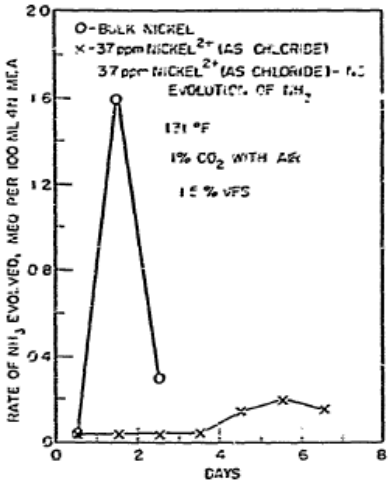


Figure 8: Effect of Ni^{2+} on NH_3 evolution

However, in a more recent study, Voice and Rochelle (2011b) indicate that Ni^{2} has no significant effect on MEA oxidative degradation at 70°C.

3.1.5 Effect of chromium

Voice and Rochelle (2011b and c) have evidenced a mild catalytic effect of chromium[2]. According to Blachly and Ravner (1966), chromium has no effect on MEA oxidative degradation when bicine is present, neither under the form of bulk chromium nor under the form of chromate. However, a mild effect has been observed when the inhibitor is EDTA.

3.1.6 Effect of vanadium

Vanadium may be present in MEA solutions under the form of $NaVO_3$, a corrosion inhibitor. Bello and Idem (2006) have tested the effect of V^{5+} (from dissolved $NaVO_3$) at 55 and 120°C as represented on Figure 9. In both cases, the addition of V^{5+} induced higher oxidative degradation rates.

[2] Oxidation state not reported

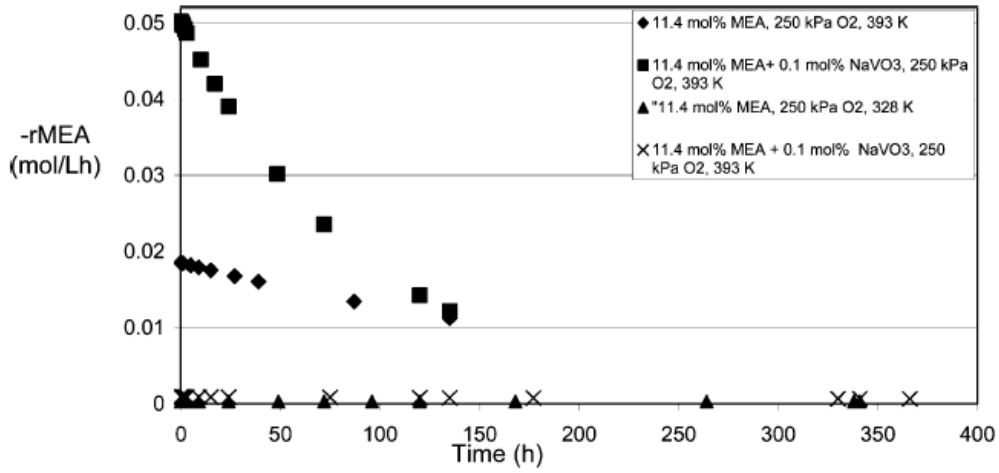


Figure 9: Effect of V^{5+} on MEA oxidative degradation rate (Bello and Idem, 2006)

The catalytic effect of V^{5+} ($NaVO_3$) has been confirmed by Sexton and Rochelle (2006). Uyanga and Idem (2007) have also confirmed an effect on MEA degradation in presence of both O_2 and SO_2. Voice and Rochelle (2011b) have reported a mild catalyst effect of vanadium[3], but in a second publication (2011c), they have presented vanadium (VO_4^-) as an inhibitor. This point must be considered with care since vanadium does not exist at the oxidation state 7+.

3.1.7 Effect of manganese

Chi and Rochelle (2002) have tested the influence of Mn^{7+} ($KMnO_4$) as a potential oxidant of MEA. The presence of this metal induced a rapid MEA degradation. They have also stated that the production rate of NH_3 was 1mol NH_3/mol $KMnO_4$, which would mean a linear variation of MEA degradation with the Mn^{7+} concentration. Goff and Rochelle (2004) confirmed the catalytic effect of manganese. They have studied the impact of Mn^{2+} ($MnSO_4$) and Mn^{7+} ($KMnO_4$) and observed that both oxidation states seriously increased the MEA oxidative degradation. However, they have supposed that Mn was reacting in a different way than Fe or Cu since the NH_3 evolution rate was varying with time differently than other metals as shown in Figure 10 (to compare with Figure 4, left chart).

This profile has been confirmed by Voice and Rochelle (2011b) (see also Figure 12). In a second paper, Voice and Rochelle (2011c) have confirmed the catalytic effect of Mn, making though a distinction between Mn^{2+}, rather a degradation inhibitor and Mn^{7+}, a serious oxidant. They have supposed that Mn^{2+} changes its oxidation state at stripper temperatures, without giving any further details.

[3]Oxidation state not reported

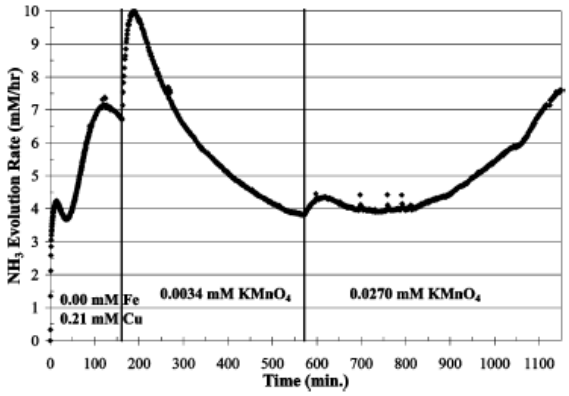


Figure 10: Profile of NH_3 production after $KMnO_4$ addition in MEA (Goff and Rochelle, 2004)

3.1.8 Effect of silver

Kumar (1982) has studied the effect of silver on the oxidation of low amounts of MEA. He has reported that Ag^{2+} oxidizes MEA. MEA first forms a complex with the metal ions. The MEA oxidation proceeds by an intramolecular electron transfer within the complex.

3.1.9 Effect of other metals

Voice and Rochelle (2011b) have performed a large screening of metal effects on MEA oxidative degradation. Besides the results already described, they have also tested Ti, Mo, Co, Se, Ce, Sn and Zn[4]. None of these metals showed significant catalytic effect on MEA degradation.

3.1.10 Effect of combined metals

- *Fe^{2+} and Cu^{2+}:*

Goff and Rochelle (2003, 2004) have tested the effect of both Fe^{2+} and Cu^{2+} on MEA oxidation (see Figure 6). It seems that the concentration of Cu^{2+} has a larger influence than the Fe^{2+} concentration on the NH_3 evolution, especially at lean CO_2 loading.

While testing the effect of Inhibitor A, Goff and Rochelle (2006) observed that it was more difficult to inhibit the degradation when both Fe and Cu were in solution in comparison with only one metal in solution. This can be observed in figure 11. Sexton and Rochelle (2009) have confirmed the combined effect of Cu^{2+} and Fe^{2+}. They described the influence of the metal combination on the observed degradation products (see next section).

[4] Oxidation state not reported

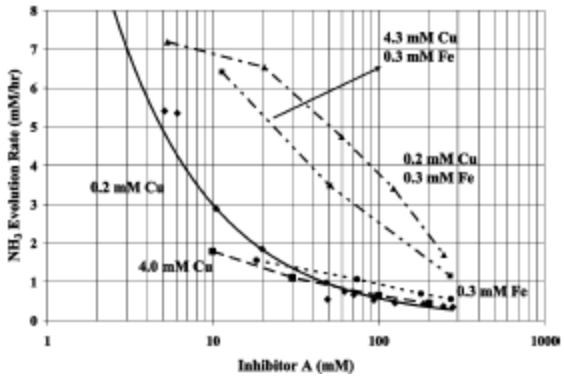


Figure 11: combined effect of Fe^{2+} and Cu^{2+} in presence of inh. A

- *Cr^{3+} and Ni^{2+}*

Sexton and Rochelle (2009) have tested the combination of Cr^{3+} and Ni^{2+}. They observed a higher catalytic effect on MEA degradation rate than with Fe^{2+} alone. This was not expected from discussions in Sections 3.1.4 and 3.1.5 describing the rather low activity of separate metals.

3.1.11 Comparison of the different metals: Degradation rate

In the absence of degradation inhibitor, Goff and Rochelle (2004) have shown that Cu presents a higher catalytic effect than Fe. This has been evidenced by Voice and Rochelle (2011b) in Figure 11 when comparing Fe^{2+}, Cu^{2+}, as well as Mn^{2+} at equal molar concentrations (1mM, respectively 56, 63.5 and 55ppm). According to the authors, Cr and V only show a mild effect, while the other metals tested (Ti, Co, Mo, Ni, Sn, Se, Ce, Zn) don't show any significant effect.

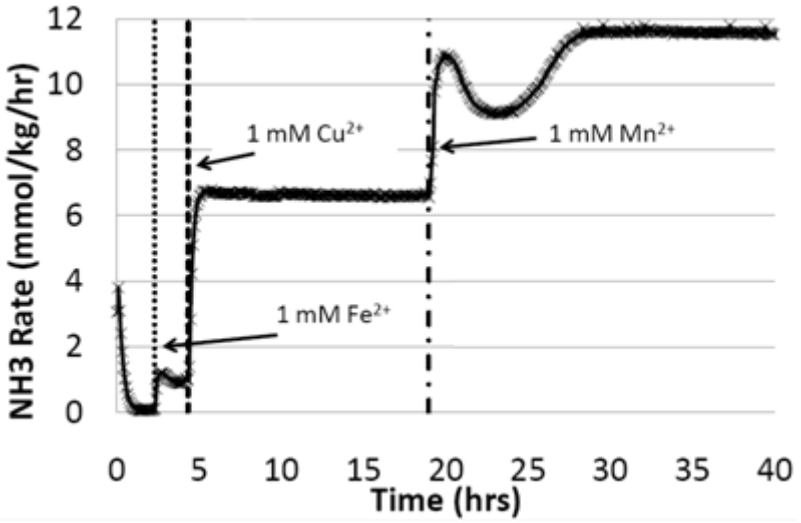


Figure 12: Comparison of the effects of Fe^{2+}, Cu^{2+} and Mn^{2+} (Voice, 2011b)

In a second study (Voice and Rochelle, 2011c), the catalytic effect decreases as following: Mn^{x+} > Cu^{2+} > Fe^{2+} > Cr^{3+}. The exact oxidation state of Mn^{x+} has not been defined. The oxidation state has an effect but this effect for Mn is still unclear in the literature. In this study, Mn^{2+} and VO^{4-} are presented as having rather a strong respectively mild inhibiting effect on MEA oxidation. In the case of Mn^{2+}, this is in direct contradiction with the results presented on Figure 12, where there may be confusion between Mn^{2+} and Mn^{x+}.

Sexton and Rochelle (2009) list the metal with decreasing oxidative degradation potential as following: Cu^{2+} (or Fe^{2+}/Cu^{2+}) > Cr^{3+}/Ni^{2+} > Fe^{2+} > V^{5+}.

According to Blachly and Ravner (1966), the most serious oxidative degradation of MEA in presence of the inhibitor EDTA is observed with Fe^{2+} (30ppm) (Figure 13). The catalytic activity of Cu^{2+} is neutralized by EDTA. Cr^{3+} (10ppm) and Ni^{2+} (30ppm) also influence the degradation but in a much lower extent than Fe^{2+}. This evidence the fact that the classification of the respective catalytic effect of metals depends on the degradation conditions.

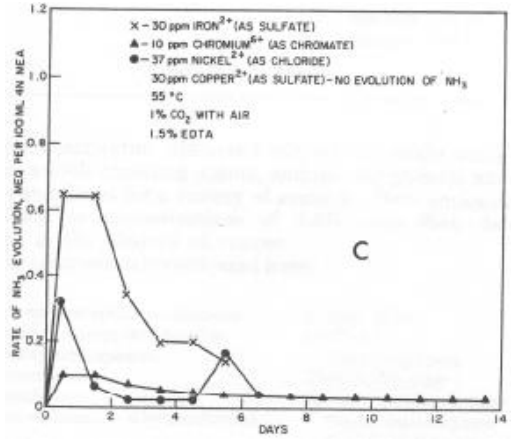


Figure 13: Comparison of metal effect in presence of EDTA

So it is possible to summarize these studies with the following decreasing order of oxidation potential:

Mn^{7+} > Fe^{2+}/Cu^{2+} ≥ Cu^{2+} > Cr^{3+}/Ni^{2+} > Fe^{2+} > Fe^{3+} > Cr^{3+} > V^{5+} >> Ti, Co, Mo, Ni, Sn, Se, Ce, Zn

Moreover, the combination of different metals may increase their respective effect. Mn^{2+} is not listed since it is considered as a degradation inhibitor. The effect of Ag^{2+} has not been compared to other metals.

3.1.12 Comparison of the different metals: Products observed

Most studies relate the evolution of NH_3 in the experiment flue gas to the degradation rate of MEA. However, some studies also performed liquid phase analysis and related the results to the metal added to the solution. This was the case for Sexton and Rochelle (2006 and 2009). In their first paper, they observed that more formate and glycolate were formed when both Fe and Cu were in solution compared to only Cu (oxidation states not specified). In the same way, more NO_2 and NO_3 were produced, as represented in Table 2.

Table 2: Influence of Fe and Fe/Cu on degradation products (Sexton and Rochelle, 2006)

Experiment	12/2004	09/2005
Distinguishing Conditions	0.2 mM Cu	0.2 mM Cu and Fe
Acetate/Glycolate (mM/hr)	0.26	0.34
Formate (mM/hr)	0.33	0.64
Oxalate (mM/hr)	0.03	0.03
Nitrate (mM/hr)	0.07	0.20
Nitrite (mM/hr)	0.18	0.26
EDA (mM/hr)	N/A	N/A

Those assumptions seem to confirm the larger oxidation potential of Cu/Fe compared to Cu only. Indeed, the ratio Formate over Acetate/Glycolate (their respective peaks could not be separated) increases when Fe is present, and formate is a more oxidized degradation product. The same argument can be applied to the ratio NO_3/NO_2.

This behavior is confirmed in Sexton and Rochelle (2009). The presence of Fe^{2+} multiplies by 3 the amount of formate, HEI (1-(2-HydroxyEthyl)Imidazole) and HEF (N-(2-HydroxyEthyl) Formamide) produced compared to Cu^{2+} only. However, when the metal catalyst is V^{5+} instead of Fe^{2+}, less formate and HEI is produced, but more oxamide.

To summarize, degradation products may be observed in different proportions according to the metal catalyst. Degradation pathways must be further studied.

3.2 Effect of metals on CO_2 degradation

Only little research has been performed to study the effect of metals on the MEA degradation when the solution is only loaded with CO_2 (no O_2). Chi and Rochelle (2002) have observed

no NH_3 production at 55°C when the feed gas only contains N_2 and CO_2, whether Fe had been added to the solution or not. The only exception was the production of NH_3 when Mn^{7+} ($KMnO_4$) was added. The stoichiometry between NH_3 production and $KMnO_4$ addition was 0.97.

The second study performed on this subject showed no influence of V^{5+} ($NaVO_3$) on MEA degradation when only CO_2 was present in the reactor feed gas (Figure 14). This study was performed at 120°C by Bello and Idem (2006).

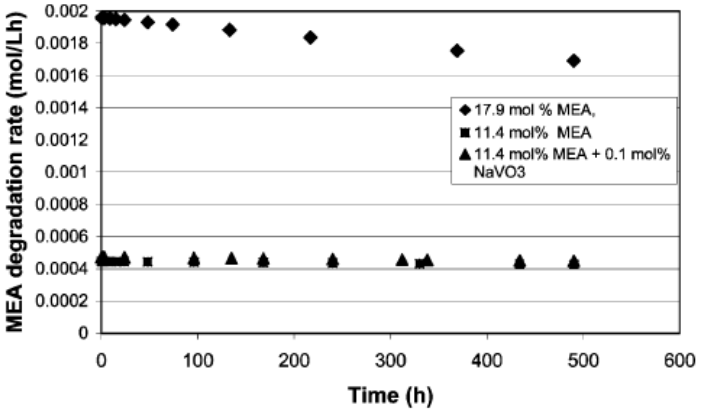


Figure 14: Effect of V^{5+} on MEA degradation with CO_2 (Bello and Idem, 2006)

Davis (2009) has spiked CO_2 loaded MEA at 150°C with 100mM of Fe, Cr, Ni, Cu, V^5 (respectively 5600, 5200, 5900, 6350 and 5100ppm). No degradation could be observed.

3.3 Effect of metals on MEA thermal degradation

No research could be retrieved on the effect of metals on MEA thermal degradation in the absence of CO_2 and O_2.

3.4 Effect of metals on SO_x and NO_x degradation

Pure SO_2 degradation has not been studied in presence of metals. However, Uyanga et Idem (2007) have studied the influence of V^{5+} ($NaVO_3$) on the MEA-H_2O-O_2-SO_2 system. They observed an increase of the degradation due to $NaVO_3$ as presented in Figure 15. However, they did not distinguish between SO_2 and O_2 degradation, so that no conclusion can be made.

[5] Oxidation state not reported

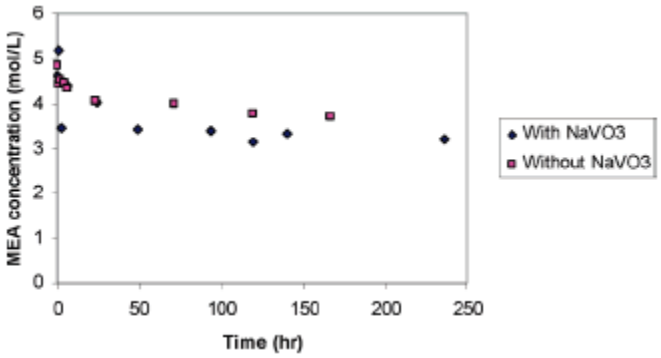


Figure 15: Influence of $NaVO_3$ on the MEA-H_2O-O_2-SO_2 system (Uyanda et Idem, 2007)

No research has been made on the influence of metals on NO_x degradation.

3.5 Conclusion on metal effect

The influence of metals on MEA degradation has only been studied for the case of oxidative degradation and degradation with CO_2. The influence of metal catalysts on oxidative degradation has clearly been established. The oxidation potential of metals can be listed as following:

$Mn^{7+} > Fe^{2+}/Cu^{2+} \geq Cu^{2+} > Cr^{3+}/Ni^{2+} > Fe^{2+} > Cr^{3+} > V^{5+} >$ Ti, Co, Mo, Ni, Sn, Se, Ce, Zn

Mn^{2+} is not listed since it is considered as a degradation inhibitor. It has also been evidenced that the combination of different metals may increase their respective effect.
Moreover, degradation products may be observed in different proportions according to the metal catalyst. This highlights the fact that degradation pathways still have to be studied.

Finally, different studies have evidenced that the presence of metal has no influence on degradation with CO_2. The influence of metals on MEA degradation with temperature only, SO_x and NO_x has not been studied so far.

4. Degradation inhibitors

The role of a degradation inhibitor is to prevent or minimize the MEA degradation during the CO_2 capture process. However, no degradation inhibitor has been proposed so far to prevent thermal degradation, CO_2 degradation, or NOx degradation, and only few studies about degradation inhibitors consider MEA degradation due to SO_2. The reasons are the following:

- Thermal degradation occur at temperatures higher than 200°C (Epp et al., 2011), so that it is not necessary to consider it in classical CO_2 capture processes.
- Degradation due to CO_2 results from the CO_2 absorption in MEA, a mechanism that is desired, so that inhibiting this mechanism does not make much sense.
- Degradation with NO_x and SO_x has rarely been studied because of the low SO_2 and NO_x content achievable in power plant flue gas.

As a consequence, the large majority of studies about degradation inhibitors concern oxidative degradation. Oxidative degradation inhibitors may be separated into two main categories based on the oxidative degradation mechanisms described in section 3.1.1 (Bedell, 2009):

- Chelating agents. They form a complex with dissolved metals, inhibiting their catalytic activity and stopping the initiation/propagation steps of the chain reaction.
- Radical and O_2 scavengers. As presented in section 3.1.1, dissolved O_2 forms peroxides in water. Radical scavengers react with the peroxides to form stable products and stop the chain reaction. They are also called O_2 scavengers since they stoichiometrically react with the dissolved O_2. Disadvantage of many radical scavengers is that they are consumed during the reaction and must be renewed.

A third category has been tested by Goff and Rochelle (2006). Stable salts like KCl, KBr or KCOOH increase the ionic strength of water, so that the solubility of gases in the solvent decreases. However, these salts appeared to be poor inhibitors, decreasing the NH_3 production by only 15% in the best case. They will not be further considered.

Finally, attention must be paid for distinguishing degradation inhibitors from corrosion inhibitors. Some corrosion inhibitors have already been evocated in the chapter on metals (Cu and $NaVO_3$). Their role is to reduce the corrosive character of the MEA solution. As presented in previous chapter, they usually catalyze the oxidative degradation of MEA.

Table 3 lists the main studies. The inhibitors in bold characters have been presented by the study's authors as effective. Some inhibitors may then be presented as effective or ineffective according to the author. The other inhibitors won't be discussed further.

Table 3: Studies about degradation inhibitors

Reference	Objectives of the study	Degradation inhibitor	Degradation tracer
Johnson and McElwain, 1964	Stability of a MEA solution	**Bicine**, **HEDTA**, **EDTA**, NH_4VO_3	NH_3, Solution alcalinity
Blachly and Ravner, 1965a	Stability of a MEA solution	**Bicine**, **EDTA**, Sodium mercaptobenzo thiazole, Disalycylal propylenediamine, p-acetylaminophenol, o-aminophenol, Quinalizarin, bis-acetylacetene ethylenediimine, Propyl gallate, Sorbitol, n-dimethylglycine, Phthaloylglycine, Diethylcyclohexylamine	NH_3, total N, peroxides
Blachly and Ravner, 1965b	Case study of CO_2 capture process in submarines	**Bicine**, **EDTA**	Total N, MEA normality
Singh, 1970a	Patent on deg. inhibitor	**Triethanolamine**	MEA
Singh, 1970b	Patent on deg. inhibitor	**Gluconate**	MEA
Faucher, 1989	Patent on deg. inhibitor	**MDEA**	HSS, solution alcalinity
McCullough et al., 1990	Patent on deg. inhibitor	**MDEA-Sb**	HSS, solution alcalinity
Chi and Rochelle, 2002	Effect of iron and deg. inhibitors	**Bicine**, **EDTA**, glycine, formaldehyde, DMMEA	NH_3
Goff and Rochelle, 2003	Oxidative degradation of MEA at absorber conditions	**EDTA**, bicine, MDEA, phosphate	NH_3
Goff and Rochelle, 2004	O_2 mass transfer effects	Formaldehyde	NH_3
Lawal and Idem, 2005	Oxidative degradation of MEA-MDEA blends	**MDEA**	MEA, MDEA
Lawal et al., 2005	Inhibitor effect of MDEA	**MDEA**	MEA, MDEA
Lawal and Idem, 2006	Oxidative degradation kinetics of MEA-MDEA	**MDEA**	MEA, MDEA
Goff and Rochelle, 2006	Oxidation Inhibitors for Copper and iron catalyzed degradation	Hydroquinone, ascorbic acid, Mn salts, **inh. A**, **Na_2SO_3**, **formaldehyde**, **EDTA**, Na_3PO_4, Na_2S_4, potassium salts	NH_3
Sexton and Rochelle, 2006	Oxidation products of amines in CO_2 capture	**Inh. A**	Carboxylic acids, EDA, nitrite, nitrate
Sexton and Rochelle, 2009	Catalysts and inhibitors for MEA oxidation	**Inh. A, inh. B, EDTA**, formaldehyde, Na_2SO_3, formate	NH_3, carboxylic acids, …
Carrette and Delfort, 2009a	Patent on degradation inhibitor	Hydroquinone, **Cystamine, 2-mercaptoethylether, 1-thioglycerol, 2-2'-thiodiethanol, 2-2'-dithiodiethanol**	HSS
Carrette and Delfort, 2009b	Patent on degradation inhibitor	Hydroquinone, **2-2' thiodiacetic acid, 2-2' dithiodiacetic acid, 3-3'-thiodipropionic acid, 3-3-dithiodipropionic acid, thioglycolic acid**	HSS

Carrette and Delfort, 2009c	Patent on degradation inhibitor	Hydroquinone, **5-5'-dithiobis(1,3,4-thiadiazole-2(3H)-thione), DMTD**	HSS
Delfort and Carrette, 2009a	Patent on degradation inhibitor	Hydroquinone, **Zn-diethyldithiocarbamate, Na-diethyldithiocarbamate, Bis(dimethylthiocarbamyl)disulfide, O-O'-Diisopropyldithiobis(thioformate)**	HSS
Delfort and Carrette, 2009b	Patent on degradation inhibitor	Hydroquinone, **potassium-O,O'-diethyldithiophosphate, ammonium-O,O'-diethyldithiophosphate**	HSS
Carrette and Delfort, 2010	Patent on degradation inhibitor	Hydroquinone, **Na-L-cystine, Na-L-cystéine**	
Carrette and Delfort, 2011	Patent on degradation inhibitor	Na_2SO_3, **Na-1H-1,2,4-triazole-3-triol, Na-4-methyl-4H-1,2,4-triazole-3-thiol, 5-methyl-4H-1,2,4-triazole-3-thiol, 4-isopropyl-4H-1,2,4-triazole-3-thiol, 4-phenyl-4H-1,2,4-triazole-3-triol, 1-methyl-1H-tetrazole-5-thiol, 1-[2-(dimethyl amino)ethyl]-1H-tetrazole-5-thiol**	MEA, NH_3
Supap et al., 2011	Inhibitors for oxidative and SO_2 degradation	**Na_2SO_3, K-Na-tartarate, EDTA, NH_2OH**	MEA
Lemaire et al., 2011	Optimized CO_2 capture Process HiCapt+	**U2, V1, V2, Y1**	MEA, NH_3, HSS
Delfort et al., 2011	Inhibitors for MEA oxidation	Hydroquinone, ascorbic acid, hindered phenols, p-benzoquinone, hindered amines, **V1->V8**	MEA, NH_3, HSS
Voice and Rochelle, 2011a	Oxidation of different amines at absorber conditions	**Inh. A**	NH_3, MEA
Voice and Rochelle 2011b	Inhibitor screening with hot gas FTIR	**MDEA**, **HEDP**, Na_2SO_3, **DTPA, DMTD, DTPMP**, **inh. A**, **citric acid**, nitrilotriacetic acid, …	NH_3
Voice and Rochelle 2011c	Catalysts and inhibitors screening for MEA oxidation	Inh. O, **V**, X, Y, **Z**	NH_3

However, many of the inhibitors presented in Table 3 appeared to be ineffective, or even to increase the MEA degradation rate.

4.1 Chelating agents

4.1.1 Bicine

N,N-diethanolglycine, also called bicine or VFS (Dow Chemical trade name, Versene Fe-3 Specific), is a metal complexant. Johnson and McElwain (1964) reported in a patent that the

addition of bicine reduced the emitted amount of air contaminant (supposed to be NH_3) by 95% over 48hours at 55°C. No metal had been added to the solution. Blachly and Ravner (1966) tested bicine in metal-free solutions for 6 weeks at 55°C without observing any degradation.

In the presence of metals, Chi and Rochelle (2002) showed that bicine reduces the NH_3 production rate by 50% in the presence of 56ppm Fe^{2+} at both lean and rich loading (Figure 16).

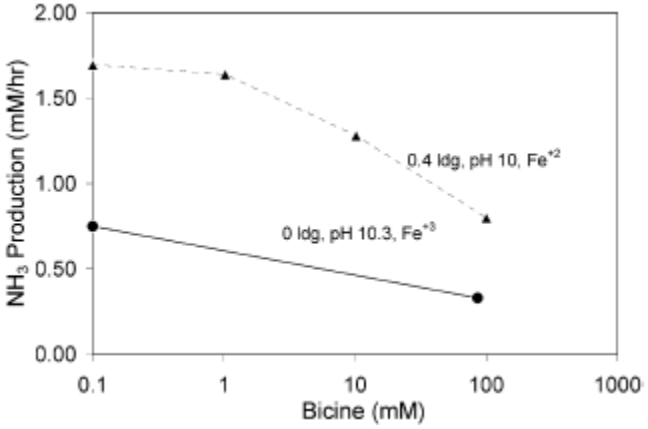


Figure 16: Effect of bicine in presence of 56ppm Fe^{2+} (Chi and Rochelle, 2002)

However, Blachly and Ravner (1966) noted that 100 mM bicine (1,5wt-%) was not effective in presence of Cu^{2+} at concentrations varying from 1 to 15ppm. Finally, Goff and Rochelle (2003) tested bicine but listed it as an ineffective degradation inhibitor when Fe^{2+} and Cu^{2+} were both present in solution.

4.1.2 EDTA

EDTA (EthylenDiamine TetraAcetic Acid) is a well-known chelating agent for metals. Johnson and McElwain (1964) reported that the addition of EDTA reduced the emitted amount of air contaminant (supposed to be NH_3) by 75% over 48hours at 55°C.

Chi and Rochelle (2002) have confirmed a mild inhibition effect of EDTA in loaded MEA (20-40% reduction of the NH_3 formation) at 55°C. Goff and Rochelle (2003) also observed a reduction by approximately 50% of the NH_3 production rate at 55°C.

Blachly and Ravner (1966) reported that EDTA was only mildly effective (less effective than bicine) into inhibiting MEA oxidation at 98°C in metal-free solution (Figure 17, left), as well as in Fe^{2+}-spiked solutions. Sexton and Rochelle (2009) showed however that at higher EDTA concentrations (3wt-% instead of 1.5 wt-%), MEA oxidative degradation due to Fe^{2+} could be completely inhibited.

In the presence of several metals including both Fe^{2+} and Cu^{2+}, EDTA induced a reduction of the NH_3 production rate that could not be achieved with bicine alone (Figure 17, right). The efficient inhibition of Cu^{2+}-catalyzed (in comparison with Fe^{2+}-catalyzed) degradation has also been observed by Goff and Rochelle (2003, 2004).

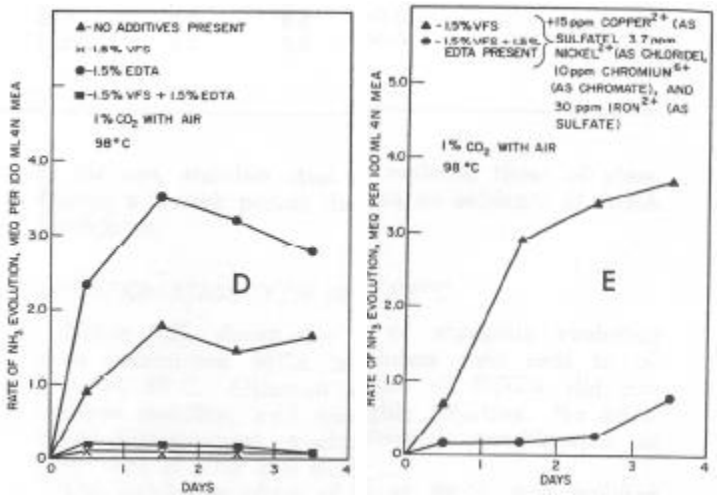


Figure 17: Effect of EDTA and Bicine on MEA oxidative degradation without (left) and with metals (right)

According to Chi and Rochelle (2002), EDTA did not show any inhibiting effect in unloaded MEA. Furthermore, Goff and Rochelle (2004) reported that the effect of EDTA decreased with time probably due to EDTA oxidation. According to Sexton and Rochelle (2009), due to continuous corrosion, the endless supply of Fe^{2+} may saturate all the EDTA active sites, so that the Fe-EDTA complexes will have to be regularly reclaimed or fresh EDTA will have to be regularly fed to the amine solution.

According to Supap et al. (2011), the optimal EDTA concentration for inhibiting O_2 and SO_2-induced degradation was 0,07wt-% in metal-free solutions, reducing the MEA degradation rate by 68% in presence of 6ppm SO_2. Higher EDTA concentrations induced more degradation with O_2 and SO_2 as represented on Figure 18. Both CO_2 loaded and unloaded solutions degraded slower under SO_2 and O_2 with EDTA.

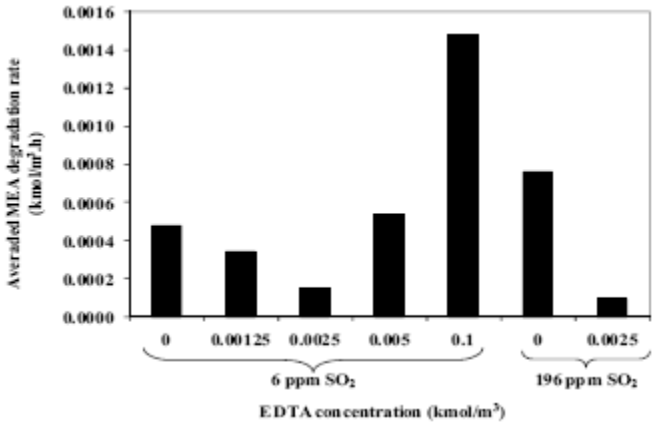


Figure 18: Effect of EDTA concentration on O_2-SO_2 induced degradation

4.1.3 HEDTA

HEDTA (*N*-HydroxyEthylDiamine TriAcetic acid, trade name Versenol 120) has only been tested by Johnson and McElwain (1964). They reported that HEDTA reduced the emitted amount of air contaminant (supposed to be NH_3) by 90% over 48hours at 55°C.

4.1.4 TEA

TriEthanolAmine (TEA) has been patented as a degradation inhibitor for H_2S and CO_2 degradation by Singh (1970a). The authors observed that at 150°C, the MEA degradation rate over 4 hours was reduced by 85% in presence of TEA. However, no test was performed in the presence of O_2. An advantage of TEA is that this tertiary amine can absorb CO_2.

4.1.5 Gluconate

Singh (1970b) has patented gluconate as degradation inhibitor for H_2S and CO_2 degradation. He observed that at 150°C, the MEA degradation rate over 4 hours was reduced by 85% in presence of sodium gluconate. However, no test was performed in the presence of O_2.

4.1.6 Potassium-sodium tartarate

Supap et al. (2011) have tested potassium-sodium tartarate ($KNaC_4H_4O_6.4H_2O$) in presence of O_2 and SO_2. In CO_2-loaded (respectively unloaded) solutions, the MEA degradation rate decreases by 83% (resp. 91%). They also reported that the blending of potassium-sodium tartarate with Na_2SO_3 produced the best inhibiting results compared to other inhibitors (see Figure 19).

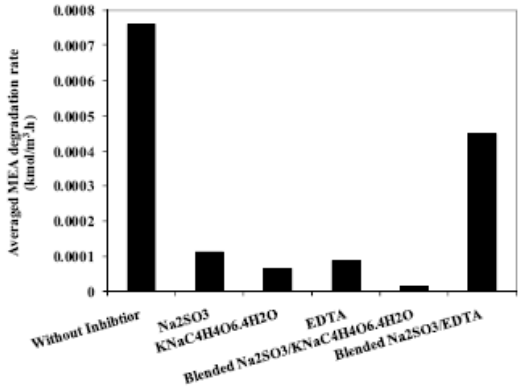


Figure 19: Comparison of blended potassium-sodium tartarate/Na_2SO_3 with other inhibitors

4.1.7 HEDP, DTPA, DTPMP, citric acid, NTA

Voice and Rochelle (2011b) screened various inhibitors but they have not published the detailed results of their studies yet (Figure 20). They have classified the inhibiting potential of chelating agents as following:

DTPA (DiethyleneTriaminePentaAcetic acid) >> EDTA >> NTA (NitriloTriAcetic acid)

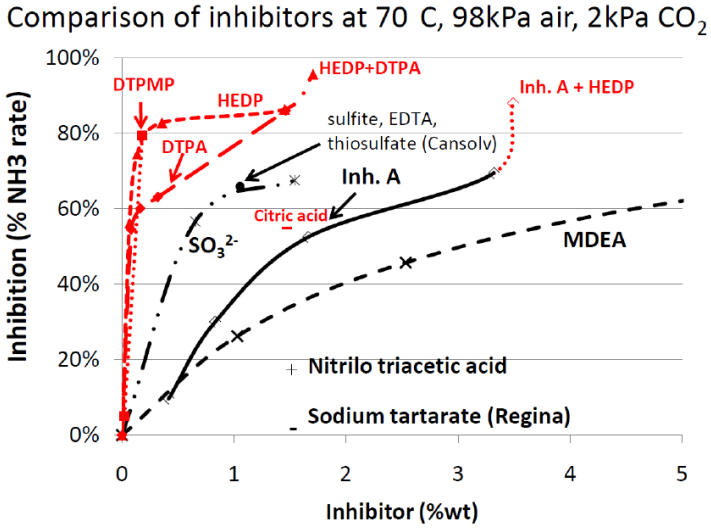


Figure 20: Screening of new inhibitors (Voice and Rochelle, 2011b)

On the other side, they also reported HEDP (Etidronic acid, 1-hydroxyethane 1,1-diphosphonic acid), DTPMP (diethylenetriamine penta(methylene phosphonic acid)) and citric acid as promising chelating agents for inhibiting MEA oxidative degradation.

4.1.8 Conclusion about chelating agents

Many chelating agents have been studied. First generation ligands have shown their limits:

- Bicine is not stable with Cu^{2+}
- EDTA is slowly oxidized with Fe^{2+}

- HEDTA, TEA, gluconate still require more studies

Second generation ligands may prove interesting inhibiting effects (Figure 20):

- Potassium-sodium tartarate presents very interesting properties, especially in combination with Na_2SO_3. This has to be confirmed by further studies.
- HEDP also seems very promising, especially in combination with DTPA.
- Citric acid and NTA seem less interesting

4.2 Radical and O_2 scavengers

4.2.1 MDEA

Faucher (1989) first patented the use of MDEA (methylDiEthanolAmine) blended with MEA for inhibiting MEA degradation. Under oxidative conditions, MDEA preferentially reacts with O_2 to protect MEA, so that the MEA degradation rate is reduced by about 80% (Lawal et al., 2005). To achieve a 90% reduction of the NH_3 production rate, Voice and Rochelle (2011b) have shown that the MDEA concentration must be equal or higher than 20wt-%. This is much more than conventional inhibitors evocated so far, but it shall be noted that MDEA has the capacity of absorbing CO_2. According to McCullough et al. (1990), the combined use of MDEA with Antimony is used to inhibit both corrosion and degradation. Antimony is a rather toxic element that is used in this context as corrosion inhibitor.

MDEA has many disadvantages:

- The amount of degradation products remains high, these products resulting from MDEA degradation (Lawal et al., 2005).
- MEA degradation is slowed down but not stopped (Voice et Rochelle, 2011b).
- The protective effect of MDEA is only active at temperature >100°C. At absorber temperatures, MEA degrades more than MDEA (Lawal et al., 2005).

4.2.2 Formate and formaldehyde

Formate and formaldehyde are degradation products of MEA oxidative degradation. According to Goff and Rochelle (2006), degradation products may compete with MEA for available oxygen to further react. Chi and Rochelle (2002) and Goff and Rochelle (2004) have not observed a large inhibition effect due to formaldehyde. However, Goff and Rochelle (2006) have observed the inhibition effect of formaldehyde, this effect being larger in presence of Cu^{2+} than Fe^{2+} (Figure 21).

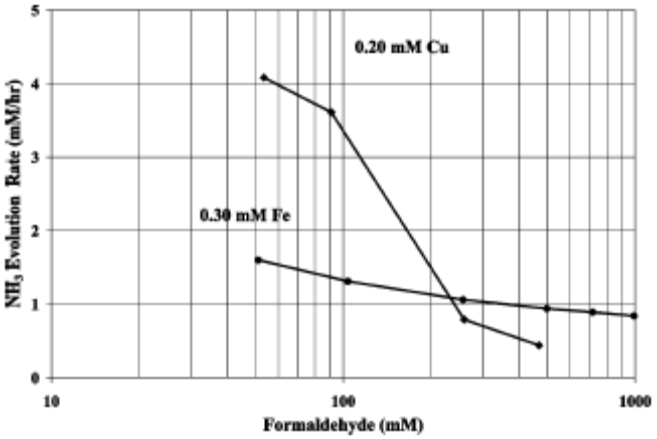


Figure 21: Effect of formaldehyde on NH_3 evolution rate (Goff and Rochelle, 2006)

However, Sexton and Rochelle (2009) could not confirm those results. They stated that the addition of formaldehyde increased the MEA loss rate by 30%. Similarly, the presence of formate increased the MEA loss rate by 20%.

4.2.3 Na_2SO_3

According to Goff and Rochelle (2006), sulfite (obtained by adding Na_2SO_3) is rapidly oxidized into sulfate, competing with MEA for the available O_2. Goff and Rochelle (2006) have shown in Figure 22 that sulfite can reduce the NH_3 production rate in systems catalyzed by Cu^{2+} and Fe^{2+}, achieving a better reduction with Cu^{2+} systems. However, above a limit concentration (~1000mM), Na_2SO_3 is not soluble anymore and precipitates.

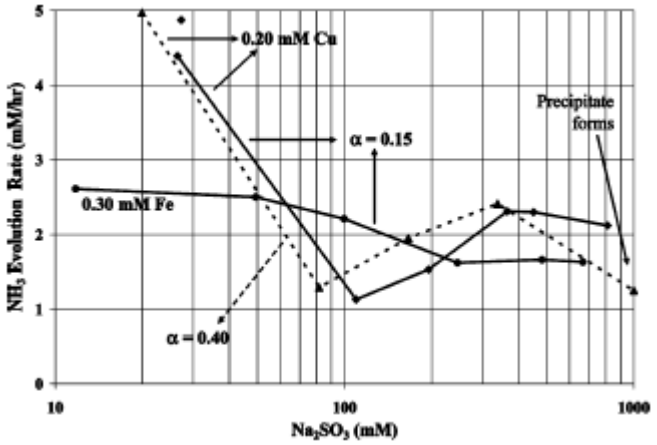


Figure 22: Effect of Na_2SO_3 on NH_3 evolution rate (Goff and Rochelle, 2006)

Even if sulfite is not very efficient as a degradation inhibitor in comparison to inhibitor A for instance, it would be a cheap degradation inhibitor since it can be derived from SO_2 contained in power plant flue gas (Goff and Rochelle, 2006).

Supap et al. (2011) confirm the benefic effect observed with sulfite on O_2 and SO_2-induced degradation. They determine the optimal sulfite concentration at 0.05kmol/m³, i.e. 50mM (Figure 23).

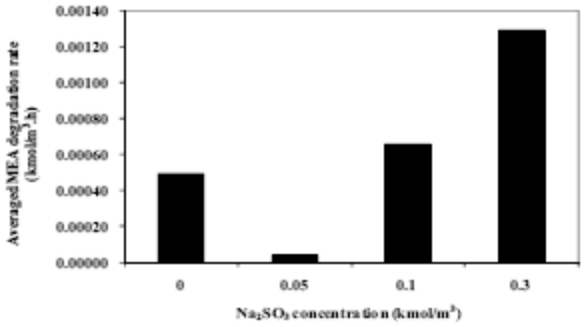


Figure 23: Effect of Na_2SO_3 concentration on NH_3 evolution rate (Supap et al., 2011)

However, Sexton and Rochelle (2009) did not observe any inhibition effect for Na_2SO_3. They showed that the addition of 100mM sulfite increased the MEA loss rate by 30% in comparison to Fe^{2+}-catalyzed system.

4.2.4 NH_2OH

NH_2OH (hydroxylamine) has been tested by Supap et al. (2011) which propose 25mM as an optimal inhibitor concentration for inhibiting O_2 and SO_2 degradation. No other study has been performed using this interesting inhibitor.

4.2.5 Inhibitor A

Inhibitor A is an inorganic additive developed at the University of Texas (Goff and Rochelle, 2006). Inhibitor A possesses at least three different oxidation states, but the reduced oxidation states clearly appear to be more effective (Figure 24).

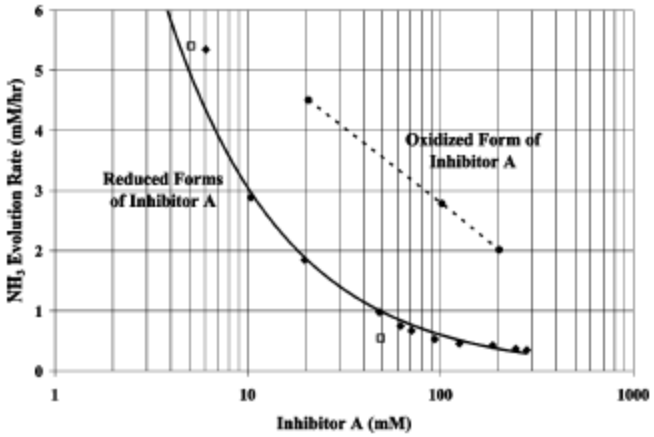


Figure 24: Effect of oxidation state for inhibitor A (Goff and Rochelle, 2006)

According to Goff and Rochelle (2006), inhibitor A is very stable at absorber conditions, so that it is not consumed with time. This has been confirmed by Voice and Rochelle (2011b). Goff and Rochelle (2006) described it as a radical scavenger effectively inhibiting MEA oxidative degradation caused by both Fe^{2+} and Cu^{2+} (Figure 25). A higher concentration of inhibitor A induces a lower NH_3 evolution rate in all systems.

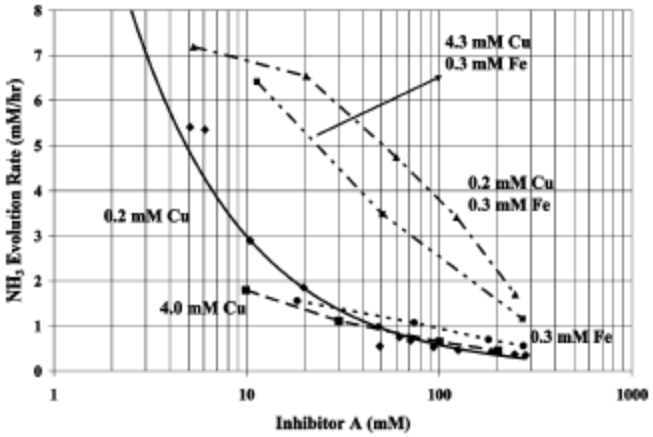


Figure 25: Effect of inhibitor A on Fe^{2+} and Cu^{2+} catalyzed degradation

According to Sexton and Rochelle (2009), the presence of inhibitor A in a Cr^{3+}/Ni^{2+}-catalyzed system decreased the formation of degradation products by 99%. The MEA losses decreased by 87,5%, approaching the detection limits of the MEA quantification analysis.

In the presence of Fe and Cu, Sexton and Rochelle (2006) observed that proportionally more glycolate was formed in MEA solutions inhibited with inhibitor A, but the amount of carboxylic acid formed is much lower than in inhibitor-free systems.

However, according to Voice and Rochelle (2011a) the inhibiting effect of inhibitor A decreases at higher temperatures in the presence of Fe^{2+}, Cr^{3+} and Ni^{2+} (Figure 26), whatever the inhibitor concentration. At 70°C, steady state in the production rate of NH_3 was not often observed, even after several days.

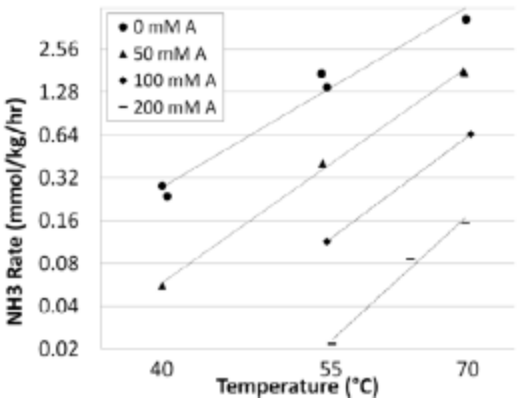


Figure 26: Effect of temperature and Inhibitor A concentration on NH_3 evolution

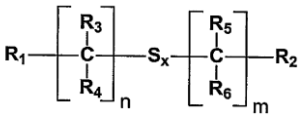
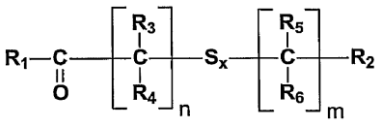
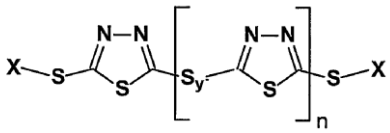
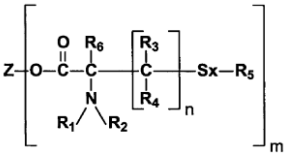
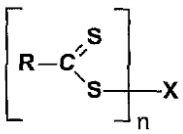
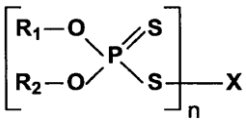
4.2.6 Inhibitor B

Sexton and Rochelle (2009) have presented inhibitor B as an effective inhibitor for preventing MEA oxidative degradation since it decreased the MEA losses by 75% at 55°C in Fe^{2+}-catalyzed systems. However, it could not reach the efficiency of inhibitor A.

4.2.7 Various sulfur continuing products

IFPEN has patented various sulfur containing inhibitors at 80°C (Carrette and Delfort, 2009a-b-c; Carrette and Delfort, 2010; Carrette and Delfort, 2011; Delfort and Carrette, 2009a-b). Those inhibitors are listed in Table 4, as well as their general formula. Based on the formate production rate compared to the uninhibited system, the best inhibitor of each family is presented.

Table 4: sulfur-containing inhibitors patented by IFP

Reference	Formula	Best inhibitor	Formate reduction
Carrette and Delfort, 2009a		2-2'-thiodiethanol	99,7%
Carrette and Delfort, 2009b		3-3-dithiopropionic acid	99,8%
Carrette and Delfort, 2009c		DMTD (Dimercaptothiadiazole)	99,1%
Carrette and Delfort and Carrette, 2010		Sodium L-Cysteine	82,8%
Carrette and Delfort, 2011	Triazole and tetrazole	All tested inhibitors produced equal results	No MEA losses observed
Delfort and Carrette, 2009a		O-O'-Diisopropyl dithiobis(thioformate)	98,1%
Delfort and Carrette, 2009b		ammonium-O,O'-diethyldithiophosphate	98,4%

Among the inhibitors presented in Table 4, only DMTD (Dimercaptothiadiazole) has been tested in another study. Voice and Rochelle (2011b) identified DMTD as one of the best inhibitors tested, but they note that it requires additional testing.

4.2.8 Conclusion about radical and O_2 scavenger

First generation radical scavengers have shown their limits:

- MDEA does not completely prevent MEA degradation
- Formaldehyde, formate and sulfite increased the MEA losses
- Inhibitor A seems to become less effective at higher temperatures (70°C)

Second generation scavengers, especially sulfur containing inhibitors patented by IFP seem however very promising, reducing the amount of degradation products by more than 99%.

4.3 Conclusion about degradation inhibitors

Chelating agents and radical/O_2 scavengers are the two main types of degradation inhibitors. Depending on the operating conditions, both seem to be very promising inhibitors. Combinations of different inhibitors may also lead to excellent inhibition effect.

Chelating agent HEDP (Hydroxyethylidene diphosphonic acid) may advantageously be combined with radical scavengers Inhibitor A or DTPA (diethylenetriamine pentaacetic acid) to decrease the emission of NH_3 at 70°C. Good results were also achieved for DTPMP (diethylenetriamine pentamethylene phosphoric acid), less stable but which can also be used as a corrosion inhibitor and DMTD (dimercaptothiadiazole) even if this latest requires more tests.

5. Conclusion

Many inhibitors have been tested for limiting MEA oxidative degradation. Some of those inhibitors also show good results into inhibiting SO_2-O_2 systems. Tests of new inhibitors are still in progress.

Most recent MEA degradation inhibitors were developed and tested at absorber temperatures (equal or lower than 80°C) to study their influence on oxidative degradation. However, inhibitor stability at stripper temperatures seems to be one of the biggest upcoming challenges, since the solvent system will be heated up to 120°C during the CO_2 capture process.

Contrary to many test benches, the Degradation Test Rig (DTR) at the University of Liège allows the testing of degradation inhibitors at that temperature range, which is a good opportunity to contribute to research on efficient and stable degradation inhibitors for MEA.

Table 5 represents the planning of coming tests on the DTR. Experiments 11 to 15 will not include any additives. Experiments 16 to 20 will include a mix of stainless steel metals (Fe^{2+}, Cr^{3+}, Ni^{2+} and potentially Mn^{2+}). Moreover, degradation inhibitors will be included to experiments 17 to 20:

- Inhibitor A has been furnished by the University of Texas at a concentration of 100mM. Inhibitor A is a benchmark radical scavenger at absorber temperature. The effect of temperature on the inhibition efficiency will be studied. Temperature tests will be performed at 55°C and 120°C.

- The combination of inhibitor A with a chelating agent like HEDP seems promising. Voice and Rochelle (2011b) reported an inhibition rate of 90% at 70°C. The stability of this additive package at higher temperature (120°C) will be studied.

- DMTD has been patented by IFPEN, and promising results has been reported by Voice and Rochelle (2011b). An experiment to study its stability at 120°C in combination with HEDP, would be very interesting.

Table 5: Planning of upcoming experiments on the DTR

Experiment	Start	End	Days	Test	T° (°C)	P_{tot} (bar)	P_{O2} (bar)	P_{CO2} (bar)	P_{N2} (bar)	Gas flow (mln/min)	Additives
11	11/04/12	25/04/12	14	Base case repetability	120	4	0.2	0.6	3.2	160	-
12	31/04/12	14/05/12	14	Influence of CO2	120	4	0	0.6	3.4	160	-
13	21/04/12	4/06/12	14	Influence of O2	120	4	0.2	0	3.8	160	-
14	6/06/12	20/06/12	14	Influence of Temperature	55	4	0.2	0.6	3.2	160	-
15	25/06/12	9/07/12	14	Influence of Temperature	140	4	0.2	0.6	3.2	160	-
16	11/07/12	25/07/12	14	Influence of SS metals	120	4	0.2	0.6	3.2	160	Addition of stainless steel metals (0.4 mM Fe2+, 0.1 mM Cr3+, and 0.05 mM Ni2+, evtl. 0.1mM Mn2+)
17	30/07/12	6/08/12	14	Influence of inh. A	55	4	0.2	0.6	3.2	160	SS metals + 100 mM Inh. A
18	8/08/12	22/08/12	14	Influence of inh. A	120	4	0.2	0.6	3.2	160	SS metals + 100mM Inh. A
19	27/08/12	10/09/12	14	Influence of inh. A + HDPE	120	4	0.2	0.6	3.2	160	SS metals + 100 mM Inh A + HEDP 1wt-%
20	12/09/12	26/09/12	14	Test of metal additives/2	120	4	0.2	0.6	3.2	160	SS metals + HEDP 1wt-% + DMTD 0.4 wt-%

6. List of abbreviations

DMMEA	DiMethylMonoEthanolAmine
DMTD	DiMercaptoThiaDiazole
DTPA	Diethylenetriaminepentaacetic acid
DTPMP	DiethyleneTriamine Penta(Methylene Phosphonic acid)
EDTA	EthylenDiamine TetraAcetic Acid
HEDP	1-HydroxyEthane 1,1-DiPhosphonic acid
HEDTA	*N*-HydroxyEthylDiamine TriAcetic acid
HEEDA	HydroxyEthylEthyleneDiAmine (2-(2-Aminoethylamino)ethanol)
HEF	N-(2-HydroxyEthyl)Formamide
HEI	1-(2-HydroxyEthyl)Imidazole
HSS	Heat Stable Salts
MDEA	MethylDiEthanolAmine
MEA	MonoEthanolAmine
NTA	NitriloTriAcetic acid
TEA	TriEthanolAmine
VFS	Versene Fe-3 Specific (bicine)

7. Table of Figures

Figure 1: Decomposition of hydroperoxides by catalytic action of metals 8
Figure 2: Effect of Fe^{2+} and Fe^{3+} on NH_3 evolution (Chi and Rochelle, 2002) 9
Figure 3: Effect of Iron on NH_3 evolution (Blachly and Ravner, 1966) 9
Figure 4: Influence of the iron concentration (Chi and Rochelle, 2002) 10
Figure 5: Influence of the Fe^{2+} concentration (Goff and Rochelle, 2004) 10
Figure 6: Influence of Cu^{2+} concentration at rich (left chart) and lean loading (right chart) ... 11
Figure 7: Effect of Cu^{2+} concentration on NH_3 evolution (Blachly and Ravner, 1966) 11
Figure 8: Effect of Ni^{2+} on NH_3 evolution 12
Figure 9: Effect of V^{5+} on MEA oxidative degradation rate (Bello and Idem, 2006)..... 13
Figure 10: NH_3 evolution profile after $KMnO_4$ addition in MEA (Goff and Rochelle, 2004) 14
Figure 11: combined effect of Fe^{2+} and Cu^{2+} in presence of inh. A..... 15
Figure 12: Comparison of the effects of Fe^{2+}, Cu^{2+} and Mn^{2+} (Voice, 2011b)..... 15
Figure 13: Comparison of metal effect in presence of EDTA 16
Figure 14: Effect of V^{5+} on MEA degradation with CO_2 (Bello and Idem, 2006) 18
Figure 15: Influence of $NaVO_3$ on the MEA-H_2O-O_2-SO_2 system (Uyanda et Idem, 2007) .. 19
Figure 16: Effect of bicine in presence of 56ppm Fe^{2+} (Chi and Rochelle, 2002)..... 23
Figure 17: Effect of EDTA and Bicine on MEA oxidative degradation without (left) and with metals (right) 24
Figure 18: Effect of EDTA concentration on O_2-SO_2 induced degradation 25
Figure 19: Comparison of blended potassium-sodium tartarate/Na_2SO_3 with other inhibitors 26
Figure 20: Screening of new inhibitors (Voice and Rochelle, 2011b)..... 26
Figure 21: Effect of formaldehyde on NH_3 evolution rate (Goff and Rochelle, 2006)..... 28
Figure 22: Effect of Na_2SO_3 on NH_3 evolution rate (Goff and Rochelle, 2006) 28
Figure 23: Effect of Na_2SO_3 concentration on NH_3 evolution rate (Supap et al., 2011) 29
Figure 24: Effect of oxidation state for inhibitor A (Goff and Rochelle, 2006) 29
Figure 25: Effect of inhibitor A on Fe^{2+} and Cu^{2+} catalyzed degradation..... 30
Figure 26: Effect of temperature and Inhibitor A concentration on NH_3 evolution..... 30
Figure 20: Screening of new inhibitors (Voice and Rochelle, 2011b).....**Erreur ! Signet non défini.**

8. Bibliography

Bedell S., 2009. Oxidative degradation mechanisms for amine in flue gas capture. *Energy Procedia, 1: 771–778.*

Bedell S., Worley C., Darst K., Simmons K., 2011. Thermal and oxidative disproportionation in amine degradation—O_2 stoichiometry and mechanistic implications. *International Journal of Greenhouse Gas Control, 5(3): 401-404.*

Bello A. and Idem R., 2006. Comprehensive Study of the Kinetics of the Oxidative Degradation of CO2 Loaded and Concentrated Aqueous Monoethanolamine (MEA) with and without Sodium Metavanadate during CO2 Absorption from Flue Gases. *Ind. Eng. Chem. Res., 45: 2569-2579.*

Blachly C. and Ravner H., 1965a. The Stabilization of Monoethanolamine Solutions for Submarine Carbon Dioxide Scrubbers. Report 6189, U.S. Naval Research Laboratory.

Blachly C. and Ravner H., 1965b. Studies of Submarine Carbon Dioxide Scrubber Operation: Effect of an Additive Package for the Stabilization of Monoethanolamine Solutions. Report 1598, U.S. Naval Research Laboratory.

Blachly C. and Ravner H., 1966. Stabilization of Monoethanolamine Solutions in Carbon Dioxide Scrubbers. *J. Chem. Eng. Data*, *11*: *401-403.*

Captech, 2007. Openbaareindrapport Captech jaar 1 (2006-2007), Advanced Solvents. *www.co2-captech.nl*.

Carrette P.-L. and Delfort B., 2009a. Absorbing solution containing a sulphurated organic degradation inhibitor and method for limiting the degradation of an absorbent solution. International Patent WO2009/156622 A1.

Carrette P.-L. and Delfort B., 2009b. Absorbing solution containing a degradation sulphur-containing inhibitor having a carboxyl group and method for limiting the degradation of an absorbent solution. International Patent WO2009/156621 A1.

Carrette P.-L. and Delfort B., 2009c. Absorbing solution containing a thiadiazole-derived degradation inhibitor and method for limiting the degradation of an absorbing solution. International Patent WO2009/156619 A2.

Carrette P.-L. and Delfort B., 2010. Absorbing solution containing a sulphur-containing degradation inhibitor derived from an amino-acid and method for limiting the degradation of an absorbent solution. International Patent WO2010/004119 A1.

Carrette P.-L. and Delfort B., 2011. Absorbing solution containing a degradation inhibitor derived from a triazole or from a tetrazole and process for the absorption of acid compounds contained in a gaseous effluent. International Patent WO2011/012777 A1.

Chi S. and Rochelle G., 2002. Oxidative Degradation of Monoethanolamine. *Ind. Eng. Chem. Res.*, *41: 4178-4186.*

Davis J., 2009. Thermal Degradation of Aqueous Amines Used for Carbon Dioxide Capture. PhD Thesis, University of Texas at Austin, USA.

Delfort B. and Carrette P.-L., 2009a. Absorbent solution containing a degradation inhibitor having a thiacarbonyl functional group and method for limiting the degradation of an absorbent solution. International Patent WO2009/156618 A1.

Delfort B. and Carrette P.-L., 2009b. Absorbent solution containing a degradation inhibitor of the family of dithiophosphates and method for limiting the degradation of an absorbent solution. International Patent WO2010/004118 A1.

Delfort B., Carrette P.-L., Bonnard L., 2011. MEA 40% with Improved Oxidative Stability for CO_2 Capture in Post-Combustion. *Energy Procedia, 4: 9-14.*

Epp B., Fahlenkamp H., Vogt M., 2011. Degradation of solutions of monoethanolamine, diglycolamine and potassium glycinate in view of tail-end CO_2 absorption. *Energy Procedia, 4: 75-80.*

Faucher, 1989. Process for inhibiting mono and diethanolamine degradation. US Patent 4,840,777.

Goff G. and Rochelle G., 2003. Oxidative degradation of aqueous monoethanolamine in CO_2 capture systems under absorber conditions. *Greenhouse Gas Control Technologies, 1: 115-120.*

Goff G. and Rochelle G., 2004. Monoethanolamine Degradation: O_2 Mass Transfer Effects under CO_2 Capture Conditions. *Ind. Eng. Chem. Res., 43: 6400-6408.*

Goff G. and Rochelle G., 2006. Oxidation Inhibitors for Copper and Iron Catalyzed Degradation of Monoethanolamine in CO_2 Capture Processes. *Ind. Eng. Chem. Res.*, *45: 2513-2521.*

Johnson W. and McElwain R., 1964. Stabilization of aqueous alkanolamine solutions in gas treating processes. US Patent 3,137,654.

Kumar A., 1982. Kinetics of complexation and oxidation of ethanolamine and diols by silver(II). *J. Phys. Chem., 86: 1674-1678*.

Lawal A. and Idem R., 2005. Effects of Operating Variables on the Product Distribution and Reaction Pathways in the Oxidative Degradation of CO_2- Loaded Aqueous MEA-MDEA Blends during CO2 Absorption from Flue Gas Streams. *Ind. Eng. Chem. Res.*, *44*: *986-1003.*

Lawal A., Bello A. and Idem R., 2005. The Role of Methyl Diethanolamine (MDEA) in Preventing the Oxidative Degradation of CO_2 Loaded and Concentrated Aqueous Monoethanolamine (MEA)-MDEA Blends during CO_2 Absorption from Flue Gases. *Ind. Eng. Chem. Res.*, *44: 1874-1896.*

Lawal A. and Idem R., 2006. Kinetics of the Oxidative Degradation of CO_2 Loaded and Concentrated Aqueous MEA-MDEA Blends during CO_2 Absorption from Flue Gas Streams. *Ind. Eng. Chem. Res.*, *45: 2601-2607.*

Lepaumier H., 2008. Etude des mécanismes de dégradation des amines utilisées pour le captage du CO_2 dans les fumées. PhD thesis at the University of Savoie, France.

Lemaire E., Bouillon P.A., Gomez A., Kittel J., Gonzalez S., Carrette P. L., Delfort B., Mougin P, Alix P., Normand L., 2011. New IFP optimized first generation process for post-combustion carbon capture: HiCapt+™. *Energy Procedia, 4: 1361-1368.*

McCullough J., Faucher J., Kubek D., Barr K., 1990. Alkanolamine gas treating composition and process. US Patent 4,971,718.

Ravner H. and Blachly C., 1968. Stabilization of Monoethanolamine Solutions in Carbon Dioxide Scrubbers. US Patent 3,372,981.

Sexton A. and Rochelle G., 2006. Oxidation products of amines in CO_2 capture. *www.che.utexas.edu/rochelle_group/Pubs/Pubs/SextonGHGT8.pdf*

Sexton A. and Rochelle G., 2009. Catalysts and Inhibitors for MEA Oxidation. *Energy Procedia, 1: 1179–1185.*

Singh K., 1970a. Method of stabilizing a monoethanolamine solution by adding a trialkanolamine. US Patent 3,535,260.

Singh K., 1970b. Ethanolamine solutions stabilized with an aldonic acid or an aldonate. US Patent 3,535,263.

Supap T., Idem R., Veawab A., Aroonwilas A., Tontiwachwuthikul P., Chakma A., Kybett B., 2001. Kinetics of the Oxidative Degradation of Aqueous Monoethanolamine in a Flue Gas Treating Unit. *Ind. Eng. Chem. Res.*, *40: 3445-3450.*

Uyanga I. and Idem R., 2007. Studies of SO_2- and O_2-Induced Degradation of Aqueous MEA during CO2 Capture from Power Plant Flue Gas Streams, *Ind. Eng. Chem. Res.*, *46,* 2558-2566

Voice A. and Rochelle G., 2011a. Oxidation of amines at absorber conditions for CO_2 capture from flue gas. *Energy Procedia 4 : 171-178.*

Voice A. and Rochelle G., 2011b. MEA Oxidation in CO_2 capture, Inhibitor screening with hot gas FTIR. Presentation at Luminant Carbon Managment Program.

Voice A. and Rochelle G., 2011c. Catalysts and Inhibitors of Monoethanolamine Oxidation. Presentation at 1st Post Combustion Capture Conference.