

# Degradation and corrosion inhibitors for MEA-based CO<sub>2</sub> capture plants

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## Abstract

In amine based post-combustion CO<sub>2</sub> capture and storage, solvent degradation and corrosion of steel materials are the main operational challenges. In this paper the focus was on minimizing degradation and corrosion by addition of inhibitors. The tested amine solution was 30wt% of the benchmark solvent ethanolamine (MEA). The tested inhibitors were pyrogallol, alpha,alpha'-(1-Methylethylenediimino)di-ortho-cresol, carbonylhydrazide, 2-butanone oxime (MEKO), tricine and 1,3-Diaminopropane-*N,N,N',N'*-tetraacetic acid (PDTA). The tests were performed under oxidative degradation conditions. After two weeks, PDTA showed the best inhibition performance. In addition to the oxidative degradation experiments, the thermal stability of carbonylhydrazide and PDTA were tested at 120 °C. After 2 weeks at stripper conditions, the PDTA loss was less than 50%. However, PDTA showed high metal concentration, indicating possible corrosion problems on the steel surface. Carbonylhydrazide, on the other hand, showed excellent corrosion protection properties, but it is not stable at 120 °C.

*Keywords: Corrosion; MEA; CO<sub>2</sub> capture; degradation; corrosion inhibition;*

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<b>Nomenclature</b>	
AADP-cresol	alpha,alpha'-(1-Methylethylenediimino)di-ortho-cresol
Bicine	<i>N,N</i> -Bis(2-hydroxyethyl) glycine
DEA	Diethanolamine
HEA	<i>N</i> -(2-hydroxyethyl) acetamide
HEEDA	<i>N</i> -(2-hydroxyethyl) ethylenediamine
HEF	<i>N</i> -(2-hydroxyethyl) formamide
HeGly	<i>N</i> -(2-hydroxyethyl) glycine
HEI	<i>N</i> -(2-hydroxyethyl) imidazole
HEIA	<i>N</i> -(2-hydroxyethyl) imidazolidone
HEPO	4-(2-hydroxyethyl)-2-piperazinone
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LC-MS	Liquid Chromatography Mass Spectrometry
MEA	Ethanolamine
MEKO	2-Butanone oxime
MDEA	Methyldiethanolamine
NaVO <sub>3</sub>	Sodium metavanadate
OZD	2-oxazolidinone
PDTA	1,3-Diaminopropane- <i>N,N,N',N'</i> -tetraacetic acid

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## 55           1. Introduction

56 CO<sub>2</sub> capture and storage (CCS) applications have the potential to reduce greenhouse gas  
57 emissions, while allowing the continued use of fossil fuels[1]. Of the various processes, post-  
58 combustion CCS with amines is one of the most mature, and has already reached commercial  
59 stage[2]. The benchmark solvent, ethanolamine (MEA) has been studied extensively and has  
60 been used in pilot plants[3-6].

61 However, two of the main challenges of MEA-based CCS are solvent degradation and  
62 equipment corrosion. MEA degradation can be oxidative or thermal. Oxidative degradation is  
63 expected to occur in the absorber in the presence of dissolved oxygen [7]. Thermal  
64 degradation takes place in the stripper as a result of CO<sub>2</sub> presence and heat. Furthermore,  
65 amine degradation affects system performance by decreasing the efficiency of CO<sub>2</sub> capture.  
66 MEA itself is not corrosive, but some degradation products can enhance equipment corrosion  
67 [8].

68 Additives can be used to inhibit degradation and corrosion in MEA based post-combustion  
69 CCS plants. Degradation and corrosion are closely tied, and therefore, additives should  
70 inhibit both degradation and corrosion. So far, the majority of studies have focused either on  
71 degradation or corrosion inhibitors but not on the combined inhibition.

72 Degradation inhibitors can be either chelating agents, which form a complex with dissolved  
73 metals, or scavengers (e.g. radical, oxygen scavenger)[9]. Corrosion inhibitors can either be  
74 oxidizing passivators (e.g. NaVO<sub>3</sub>), which promote the formation of a protective layer onto  
75 steel surface, or film forming inhibitors[10] (e.g. the carboxylic acid presented in [11] ).

76 Some important considerations in selection of corrosion inhibitors are the type of corrosion  
77 (uniform or localized), effect of temperature, and the effect of inhibitors on degradation. The  
78 corrosion inhibitors are usually heavy metal salts of vanadium or copper[12]. One of the main  
79 problems of inhibitors is that many of them are highly toxic in even small concentrations  
80 (very low LD<sub>50</sub> values)[13]. Vanadium compounds, particularly sodium metavanadate  
81 (NaVO<sub>3</sub>), are the most extensively and successfully used in amine treating plants, but these  
82 inorganic inhibitors are toxic to humans and to the environment[11]. In laboratory  
83 experiments, for MEA solutions containing CO<sub>2</sub> and heat-stable salts, NaVO<sub>3</sub> showed  
84 excellent inhibition efficiency and the best inhibition performance. [14]. Veawab et al.[11]  
85 reported that organic compounds, i.e. a specific carboxylic acid and a specific sulfoxide,  
86 showed promising corrosion reduction results (75-92%) and the best performance was given  
87 by carboxylic acid[11]. The tested temperatures were 40 °C and 80 °C. Sodium thiosulfate  
88 (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), in a short term exposure, is a very effective corrosion inhibitor, and the presence  
89 of chloride or formate does not affect its performance[15].

90 Voice and Rochelle [16] have tested various degradation inhibitors for MEA oxidation in  
91 CO<sub>2</sub> capture process. Of the various inhibitors, the patented inhibitor A, which is a free-  
92 radical scavenger, and 2,5-dimercapto-1,3,4-thiadiazole, which is a sulfur containing  
93 antioxidant, showed promising results. However, none of the tested inhibitors were effective  
94 in stripper conditions. Léonard et al. [9] proposed that radical scavengers can be more  
95 efficient in degradation inhibition compared to chelating agents. Moreover, extra attention  
96 should be paid, because some inhibitors can decrease the thermal stability of MEA[9]. As  
97 discussed above, many of the suggested degradation inhibitors are either thermally stable  
98 under stripper conditions or the stability has not been tested. Thus, it's important to include  
99 thermal stability tests when testing and developing degradation and corrosion inhibitors.  
100

101 In general, inhibitors' efficiency depends on molecular structure, concentration of the  
102 inhibitor, temperature, type of solution and on the metal surface nature and charge[17]. The  
103 kinetics of the inhibition processes should be studied under various parameters every time a  
104 new inhibitor is being tested. It is of great importance that the chosen inhibitor does not cause  
105 additional problems to the CO<sub>2</sub> capture process.

106 Based on the above literature review and on internal data [18], this paper focused on  
107 investigating non-toxic to humans additives for their performance in degradation and  
108 corrosion inhibition. Carbohydrazide, 2-Butanone oxime (MEKO) and alpha,alpha'-(1-  
109 Methylethylenediimino)di-ortho-cresol (AADP-cresol) are oxygen scavengers while 1,3-  
110 Diaminopropane-*N,N,N',N'*-tetraacetic acid (PDTA), pyrogallol and tricine are chelating  
111 agents. For carbohydrazide and MEKO there is data indicating that they can be degradation  
112 inhibitors [18]. AADP-cresol and pyrogallol have shown effective oxidation stability for  
113 biodiesels[19]. A compound with similar structure with PDTA have been tested by Voice et  
114 al.[16] and showed promising degradation inhibition results.

115 Six non-toxic to humans degradation inhibitors were tested under oxidative degradation  
116 conditions, with a custom made apparatus. The amine loss and the formate formation are  
117 reported. In addition, the stability and corrosivity of two promising inhibitors was tested  
118 under thermal degradation conditions.

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## 120 **2. Materials and Methods**

### 121 **2.1 Experimental setup**

122 An existing apparatus[7] was modified and used to investigate the effect of various  
123 degradation inhibitors in 30wt% loaded MEA solutions (0.4 mol CO<sub>2</sub>/ mol MEA). The basis  
124 for the construction of the apparatus was a Heidolph star-fish multi-experiment setup with 5  
125 reactors. The setup included a MR Hei-End stirrer, a temperature sensor and gas coolers.  
126 200 g of 30wt% MEA solution was put into each of the three-necked 250 mL flasks. For the  
127 initial oxidative degradation experiment, 0.05 M of inhibitor was added. Each reactor is  
128 connected to a gas cooler, gas sparger and a top septum cover. At all connections, grease was

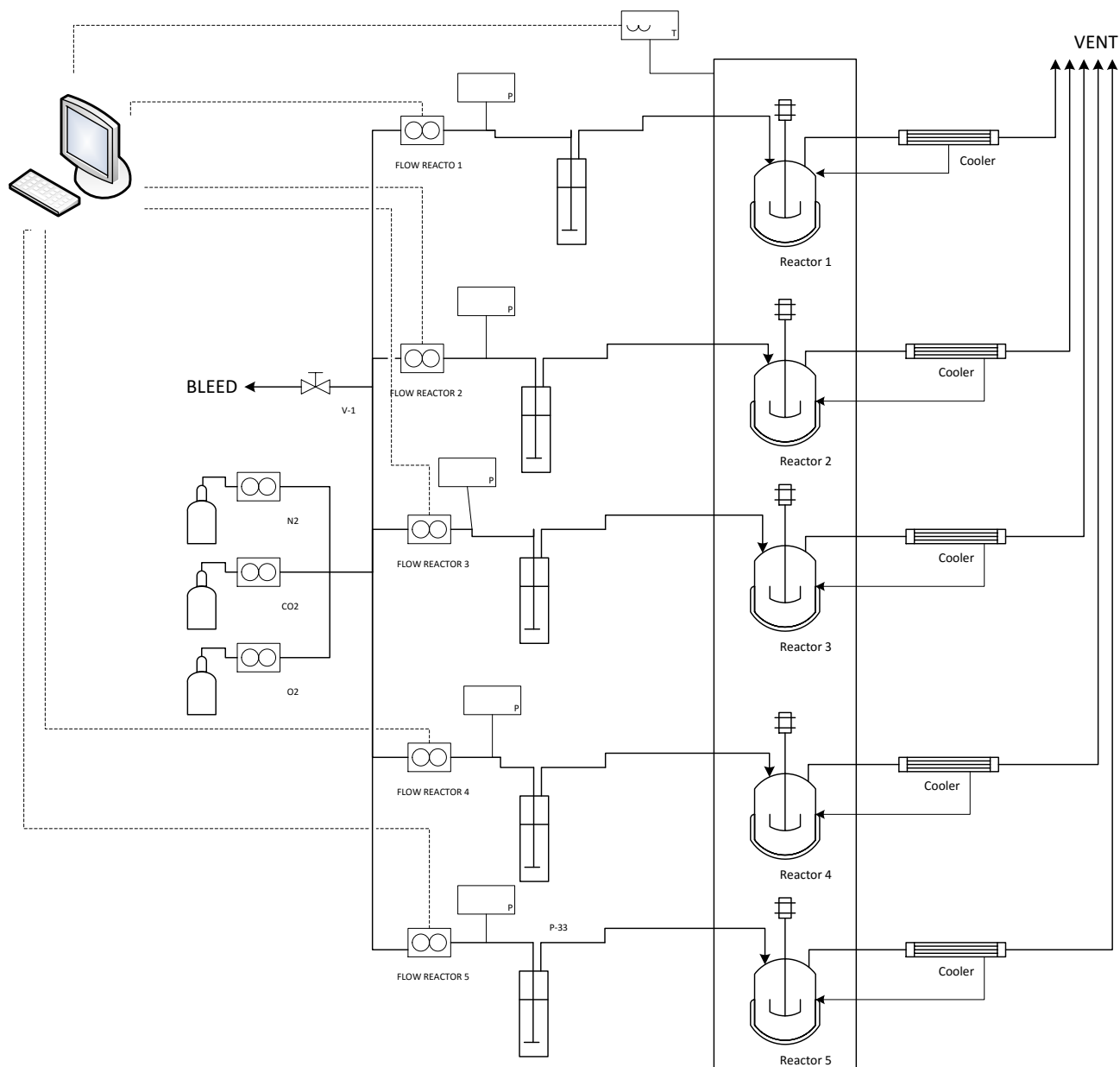
129 used to minimize vapor losses. Samples were taken with a HAMILTON 1005 TLL syringe  
130 equipped with a 150 mm stainless steel needle.

131 Three Alicat mass flow controllers were used in order to achieve the desired gas composition.  
132 In the experiments that were conducted, the gas composition was 98% O<sub>2</sub>, 2% CO<sub>2</sub> and 0%  
133 N<sub>2</sub>. After the gas mixing, five more mass flow controllers were used to distribute the same  
134 gas flow (20 cm<sup>3</sup>/min) to each reactor. These mass flow controllers were calibrated before the  
135 experiments. The gas mix is pre-saturated with water before it enters each reactor with the  
136 use of gas water washing flasks.

137 To speed up MEA degradation, 0.5 mM of FeSO<sub>4</sub> was added to all the reactors for all the  
138 experiments. The total experimental time was 2 weeks for each experiment. Samples were  
139 taken out at the beginning of the experiment, after 2 days, 7 days, 10 days and 14 days.

140 A detailed schematic diagram of the apparatus is presented in Fig. 2.2.

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Figure 2.2: Schematic diagram of the inhibitors screening setup.

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## 2.2 Experimental conditions

147 As a starting experiment, only 30wt% loaded MEA was used. Although there are 5 parallel  
 148 reactors, small variations in MEA loss were observed (MEA loss range 9.8-11.4%).  
 149 Moreover, in the reactor with lower MEA loss, the CO<sub>2</sub> loading after the experiment was  
 150 lower compared to the other (0.03 mol CO<sub>2</sub>/mol MEA lower). That is why the results from  
 151 this reactor were not used in this paper. The remaining 4 reactors showed similar CO<sub>2</sub>  
 152 loadings after the experiments (0.32 mol CO<sub>2</sub>/mol amine). Water loss was kept low thanks to  
 153 the water washing flasks and the grease that was used in all connections. The temperature  
 154 was set to 60 °C, and magnetic stirring was performed at 400 rpm.

155 As presented earlier, the following MEA degradation inhibitors were tested: pyrogallol,  
156 alpha,alpha'-(1-Methylethylenediimino)di-ortho-cresol, carbonylhydrazide, 2-Butanone oxime,  
157 tricine and 1,3-Diaminopropane-*N,N,N',N'*-tetraacetic acid. All the inhibitors were purchased  
158 from Sigma-Aldrich, with a purity of >98%. The inhibitors that were used are listed in Table  
159 2.1. None of the tested inhibitors was toxic to humans. Carbonylhydrazide is toxic to aquatic  
160 organisms but not to humans. The LD<sub>50</sub> values of the tested inhibitors are given in Table 2.2.  
161 The LD<sub>50</sub> value (rat, oral) for MEA is 1089 mg/kg. The LD<sub>50</sub> values of PDTA and AAPD-  
162 cresol are higher than MEA's while carbonylhydrazide is more toxic compared to MEA. MEKO  
163 has very similar toxicity to MEA.

### 164 **2.3 Amine, CO<sub>2</sub> and formate analysis**

165 Amine loss (i.e. the % of amine that is lost from the original 30wt% MEA solution due to  
166 degradation) was determined by titration with sulfuric acid, using a method described in [20].  
167 Anion IC was used for formate quantification at the end of experiments by an ICS-5000  
168 ThermoScientific Dionex IC system equipped with AS15 as column. The system had an  
169 ASRS300 suppressor (2 mm), a carbonate removal device and a CD conductivity detector. A  
170 gradient method with KOH as eluent was used. Finally, the precipitation-titration method of  
171 Ma'mun et al. [21] was used for determining CO<sub>2</sub> concentrations for the start and end  
172 samples.

### 173 **2.4 Thermal degradation experiment**

#### 174 **2.4.1 ICP-MS for corrosion evaluation**

175 In addition to the oxidative degradation experiments, solutions of 30wt% MEA containing  
176 1wt% of carbonylhydrazide and of 30wt% MEA containing 1wt% PDTA were tested under  
177 thermal degradation conditions and compared with 30wt% MEA. All the solutions were  
178 loaded (0.4 mol CO<sub>2</sub>/ mol MEA) and were placed into stainless steel cylinders as described in  
179 more detail by Lepaumier[22]. They were heated in a thermostat chamber at 120 °C for 2  
180 weeks.

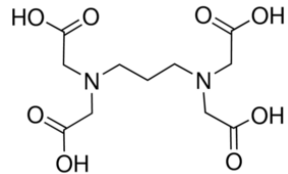
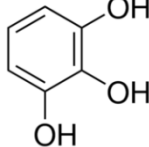
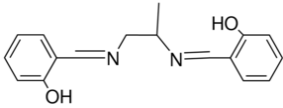
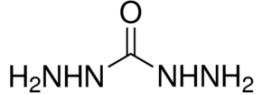
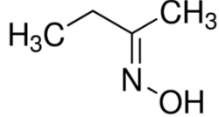
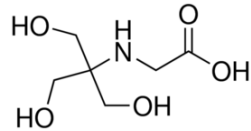
181 Parallels have been used for all the sampling that was taken after 2, 7, 10 and 14 days. In the  
182 end liquid samples, total Fe, Cr, Ni and Mo were analyzed by a high resolution Thermo  
183 Fischer Element 2 ICP-MS, as an indication of corrosivity.

#### 184 **2.4.2 LC-MS for inhibitors' thermal stability**

185 Furthermore, after sampling, an Agilent 1290 Infinity liquid chromatography system coupled  
186 to an Agilent 6490 Triple Quadrupole Mass Spectrometer equipped with an Agilent Jet  
187 Stream ion source (Agilent Technologies, Santa Clara, CA, USA) was used to investigate the  
188 inhibitors' stability. The inhibitor PDTA was determined by using the Ascentis express RP-  
189 amide column (4,6mmx150mm) with 25 mM formic acid as mobile phase. For the  
190 quantification of carbonylhydrazide, the Supelco Discovery HS F5 column (4,6x150 mm) with  
191 25 mM formic acid as mobile phase was utilized.

192 In addition to carbonylhydrazide and PDTA concentration, the end samples were analyzed by  
 193 LC-MS for MEA loss and for the oxidative degradation products HEI, HEF, HEPO, HeGly,  
 194 and HEA, and also for the thermal degradation products HEEDA and HEIA and OZD. More  
 195 information in regard to the LC-MS method is given by Vevelstad et al. [23].

196 **Table 2.1: Short, full name, CAS and molecular structure for inhibitors used.**

Abbreviation	Compound	CAS	Structure
PDTA	1,3-Diaminopropane- <i>N,N,N',N'</i> -tetraacetic acid	1939-36-2	
Pyrogallol	1,2,3-Trihydroxybenzene	87-66-1	
AAPD-cresol	alpha,alpha'-(1-Methylethylenediimino)di-ortho-cresol	94-91-7	
Carbohydrazide		497-18-7	
MEKO	2-Butanone oxime	96-29-7	
Tricine	N-[Tris(hydroxymethyl)methyl]glycine	5704-04-1	

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199 **Table 2.2: LD<sub>50</sub> values of the tested inhibitors obtained from Sigma-Aldrich MSDS.**

Inhibitors	Animal, Route	LD <sub>50</sub>
Tricine	No data available	No data available
AAPD-cresol	Rat, Oral	4560 mg/kg
PDTA	Rat, Oral	1600 mg/kg
MEKO	Rat, Oral	930 mg/kg
Carbohydrazide	Rat, Oral	311 mg/kg
Pyrogallol	Mouse, Oral	300 mg/kg

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201 **3. Results and Discussion**

202 **3.1 Oxidative degradation inhibition**

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 204 During the oxidative degradation experiment, the total alkalinity from the titration method  
 205 gives an approximation of the MEA concentration. In Table 3.1 and in Fig 3.1. the % MEA  
 206 loss for the various solutions with the addition of 0.05 M of inhibitor is presented. 30wt%  
 207 MEA and 30wt% MEA+PDTA plots are the averages of two experiments. The 30wt%  
 208 MEA+PDTA values are very close for the 2 experiments (max. 0.5 % differences for all  
 209 samples) and for 30wt% MEA the differences are between 1-2%. It can be seen that after 14  
 210 days, all inhibitors except Pyrogallol and Pyrogallol+AAPD-cresol, which showed 15.83 and  
 211 16.67% MEA loss respectively, showed less degradation compared to 30wt% MEA solutions  
 212 without additives. The MEA loss vs time graph (Fig. 3.1) is plotted for the tested inhibitors  
 213 except for Pyrogallol and Pyrogallol+AADP-cresol which clearly increased degradation.

214 **Table 3.1: MEA loss % vs time for the various solutions**

Days	MEA loss%						
	30wt% MEA*	30wt% MEA + 0.05 M MEKO	30wt% MEA + 0.05 M PDTA*	30wt% MEA + 0.05 M Tricine	30wt% MEA + 0.05 M Carbohydrazide	30wt% MEA + 0.05 M Pyrogallol	30wt% MEA + 0.05 M Pyrogallol+ AAPD-cresol
2	3.0	1.1	0.1	0.4	1.3	5.7	6.5
7	5.3	4.4	0.9	4.4	5.2	12.2	11.2
10	7.2	6.8	1.8	5.5	8.2	13.7	14.5
14	10.2	9.4	2.7	8.0	10.4	15.8	16.7

215 **\*Average of two experiments.**

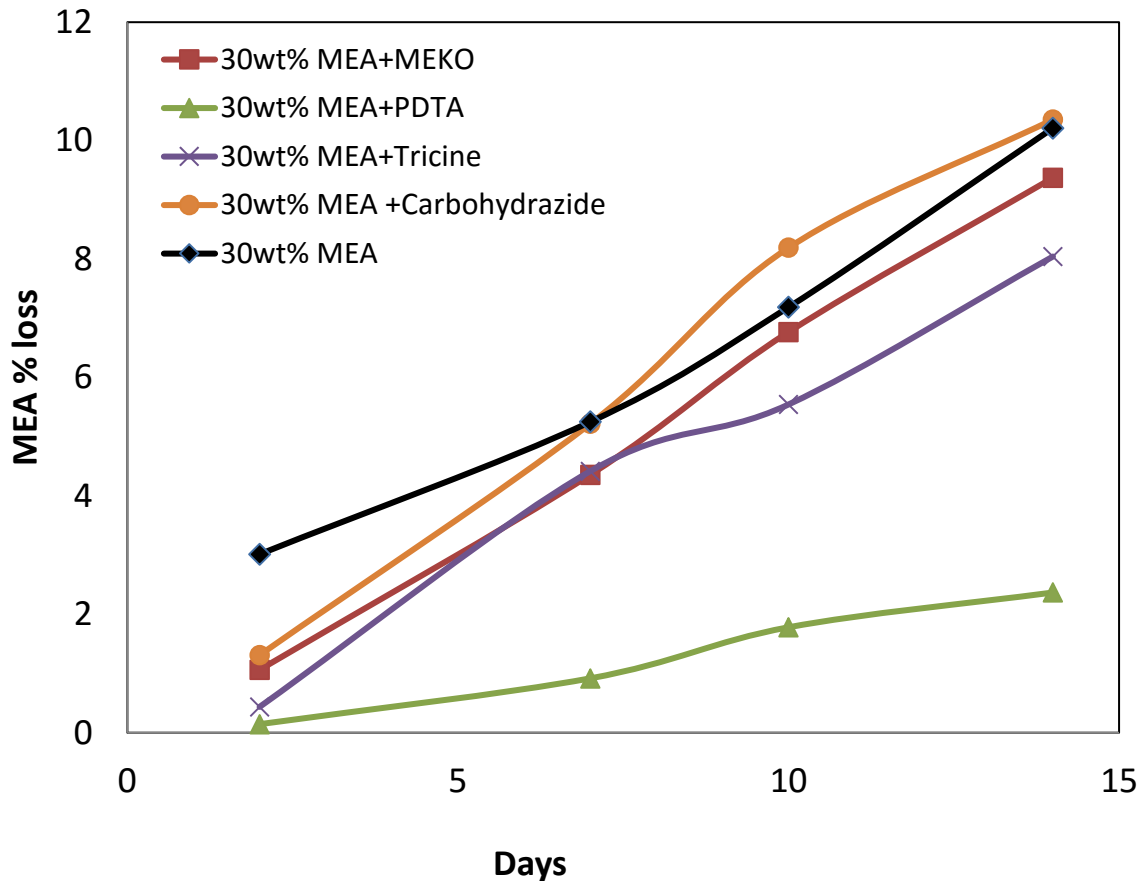


Figure 3.1: MEA % loss with the addition of inhibitors

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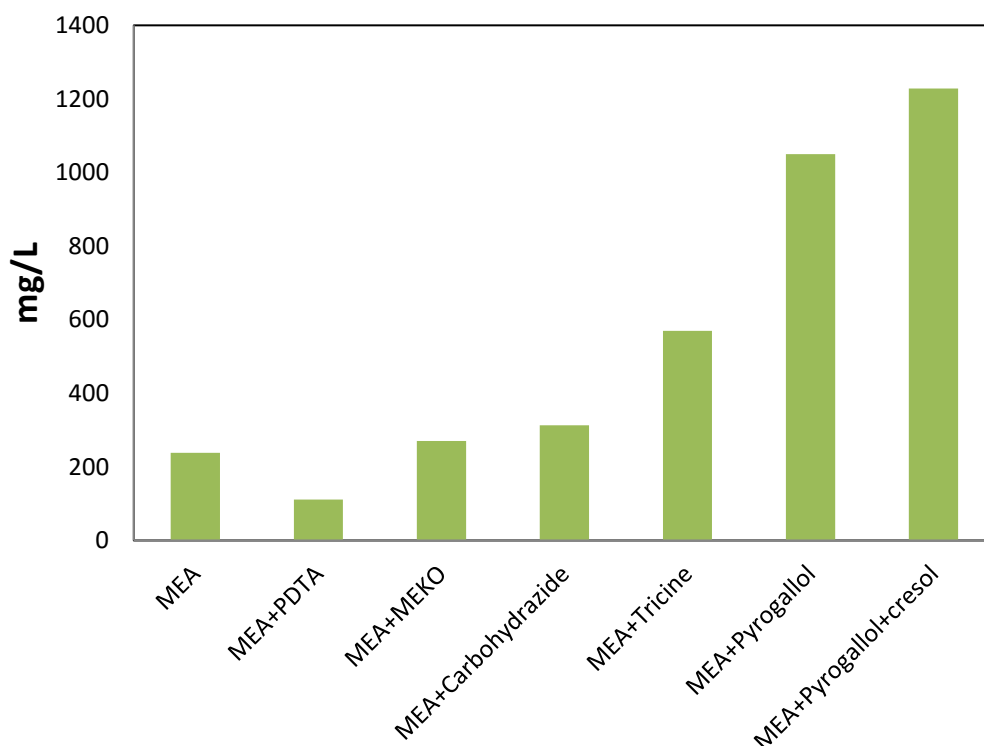
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219 It can be observed from Fig 3.1 that with the addition of PDTA, the MEA loss was the lowest.  
 220 The good degradation inhibition performance of PDTA is due to its chelating agent behavior  
 221 and the formation of complexes with dissolved iron. After 2 days, all additives presented in  
 222 Figure 3.1 seem to inhibit degradation. However, after 7, 10 and 15 days only PDTA, Tricine  
 223 and MEKO have lower MEA loss than uninhibited MEA, whereas the addition of  
 224 carbohydrazide doesn't seem to have a positive effect on the degradation inhibition. The  
 225 results with carbohydrazide were not as expected since it has shown promising degradation  
 226 inhibition performance in the past [18]. It is possible that by the end of the first week of  
 227 experiments, the additives are consumed or degraded, and that they cannot inhibit further the  
 228 degradation.

229 The end samples were analyzed with anion chromatography for formate, and the results are  
 230 presented in Fig. 3.2. Formate is linked with oxidative degradation, and has in several cases  
 231 been used to evaluate degradation [24]. Inhibitors are expected to inhibit formate formation  
 232 as well. In addition, formate can cause severe corrosion problems[25, 26] and is an unwanted  
 233 byproduct in amine-based post-combustion CO<sub>2</sub> capture[27].

234 Comparing Table 3.1 and Figure 3.2, the association between formate concentration and  
 235 degradation can be examined. MEA+Pyrogallol and MEA+Pyrogallol+AAPD-cresol had 5

236 and 6 times higher formate concentration than MEA respectively. This is as expected, since  
 237 they didn't inhibit the degradation, and higher amine degradation was observed compared to  
 238 30wt% MEA without inhibitor, see Table 3.1. On the other hand, the only inhibitor that  
 239 clearly gave lower amine degradation was PDTA and, as expected, lower amounts of formate  
 240 (111 mg/L) compared to 30wt% MEA without inhibitors (240 mg/L). When it comes to both  
 241 the amine loss and formate concentration in MEA+MEKO and MEA+carbohydrazide  
 242 solutions are, as expected, close to each other. However, MEA+Tricine, which had lower  
 243 amine loss compared to uninhibited MEA, showed twice as high formate concentration. The  
 244 high formate concentration observed from MEA+Tricine is unexpected and no data could be  
 245 found from literature that support decomposition of tricine to formate. Tricine was not  
 246 investigated further because of the high formate concentration since formate forms heat stable  
 247 salt with MEA which increases corrosion [25].



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 249 Figure 3.2: Formate concentration (mg/L) at the end of experiments  
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251 Based on the results it was decided that PDTA, with its superior performance compared to the  
 252 others, would be taken for further testing. Even though carbohydrazide did not give any  
 253 degradation inhibition, promising degradation inhibition performance in the past [18] and its  
 254 role as corrosion inhibitor (i.e. oxygen scavenger) [28], make it worthwhile to investigate the  
 255 observed results. These further studies are presented in chapter 3.2.

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### 3.2 Inhibitor efficiency vs Concentration

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An additive can inhibit degradation in one specific concentration while, in another concentration, can intensify degradation. Finding the optimal concentration for a specific inhibitor is of great importance for the process. In this chapter, three concentrations were checked for carbohydrazide and PDTA and the results are presented in Fig. 3.3. In the case of 0.05 M of PDTA and 0.05 M carbohydrazide, the results on this graph are the same as in Figure 3.1.

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From the results, the excellent inhibition performance of PDTA can be observed, and the degradation decreased with increasing PDTA concentration after 14 days. Also, for carbohydrazide, the increase of concentration from 0.05 M to 0.1 M improved the degradation inhibition effect. The data for 0.2M, for reasons unclear, show high degradation after 2 days, but after that the performance improved. However, the performance of the 0.2 M carbohydrazide got much better after 2 days, and between 2 to 10 days the amine degradation was lower in 0.2 M carbohydrazide solution, as compared to 0.1 M carbohydrazide solution as seen from the lower slope in Figure 3.3. Still, after 10 days, the performance was once again close to that of 0.1 M carbohydrazide. These results are somewhat inconclusive when it comes to the optimal concentration. Overall, however, it can be concluded that both carbohydrazide and PDTA seem to inhibit MEA degradation in presence of oxygen at 60 °C. Additionally, it seems that the performance is somewhat dependent on the concentration after 2 days. This is a possible indication that the additive was consumed before the seventh day. The optimal PDTA concentration found in this study is 0.2 M.

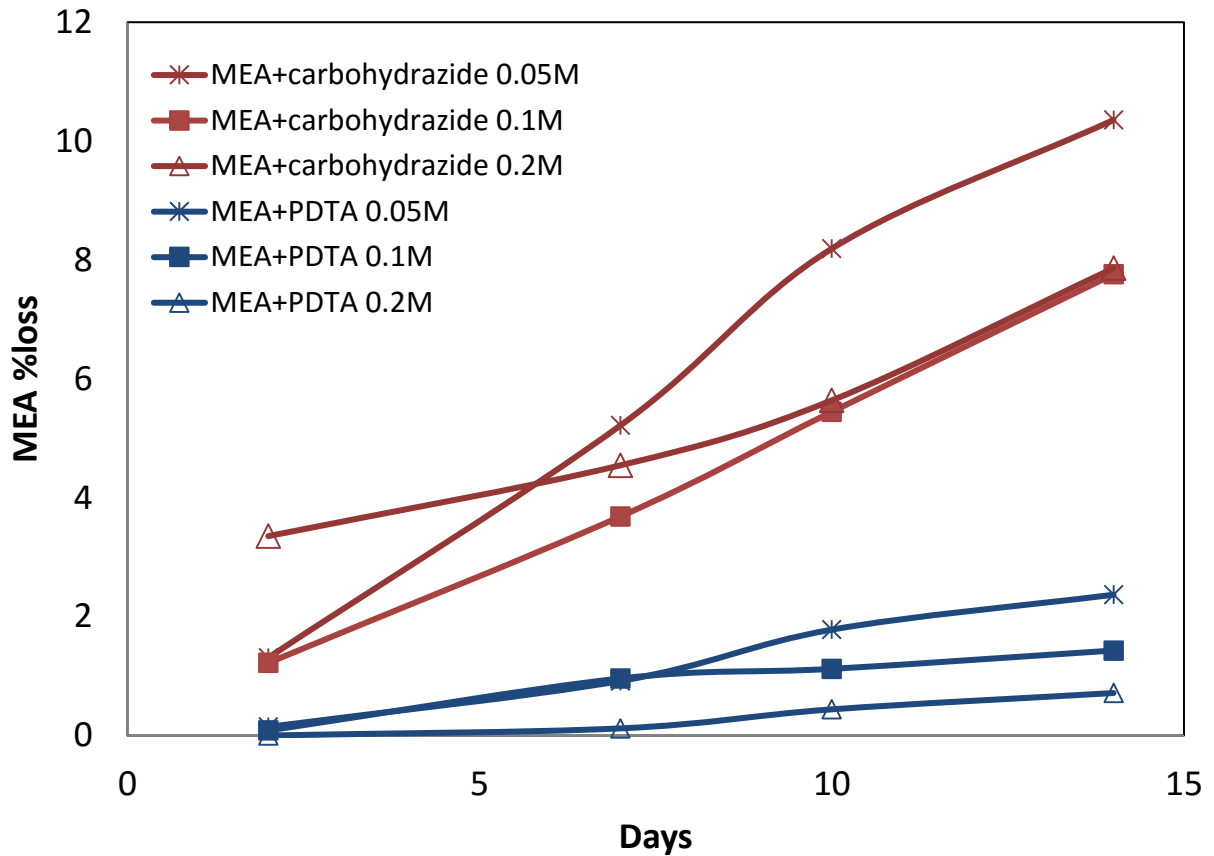


Figure 3.3: MEA % loss with the addition of inhibitors at different concentrations

### 3.3 Thermal stability and degradation of inhibitors

#### 3.3.1 Stability test at stripper conditions

As discussed earlier, carbohydrazide and PDTA were the chosen candidates for thermal stability test. Carbohydrazide was chosen because it is a known corrosion inhibitor, and PDTA was chosen because it showed the best degradation inhibition. During the thermal degradation experiment as described in chapter 2.4, two samples of each solution were analyzed for carbohydrazide and PDTA by LC-MS in order to check the stability of the inhibitor. In Fig. 3.4, the average of the two parallels is presented for the MEA+carbohydrazide and MEA+PDTA solutions. Around 50% of PDTA is lost after 2 days. However, after that, concentration decreases only slowly, indicating that PDTA is partly thermal stable under these conditions. The LC-MS analysis for PDTA was repeated, but the results were the same. The reason for this high loss during the first 2 days is unknown, but it could indicate that some equilibrium reactions between PDTA and the solutions take place. At 120 °C, carbohydrazide was not stable, and after 2 days, 90% of it was lost. After 7 days, carbohydrazide had decomposed completely. This was not unexpected since it is known that carbohydrazide is stable below 100 °C and decomposes between 100 and 155 °C [28]. Carbohydrazide decomposes to hydrazine. Although hydrazine is a known oxygen scavenger at fossil fuel plants, there are health, safety and environmental concerns about it[28].

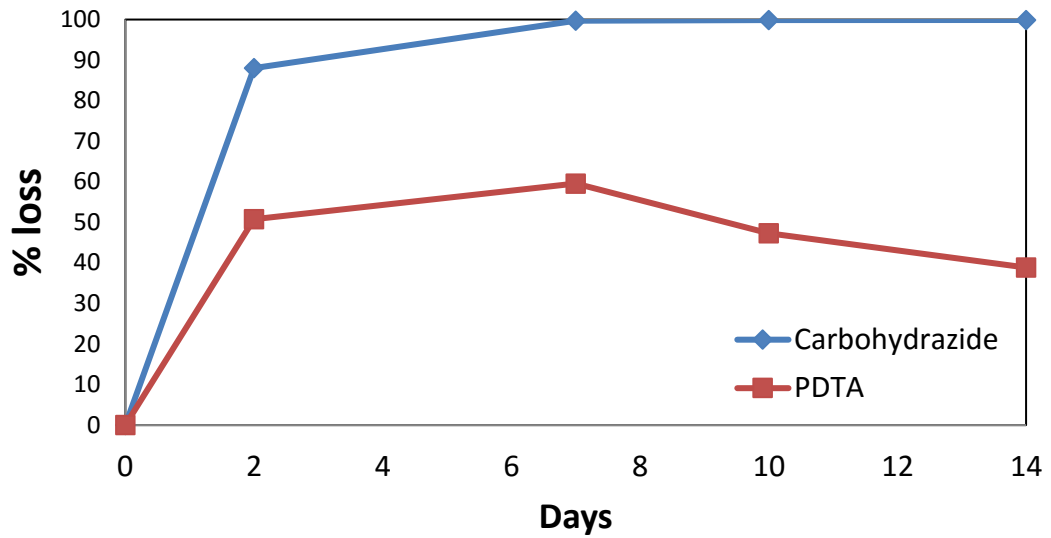
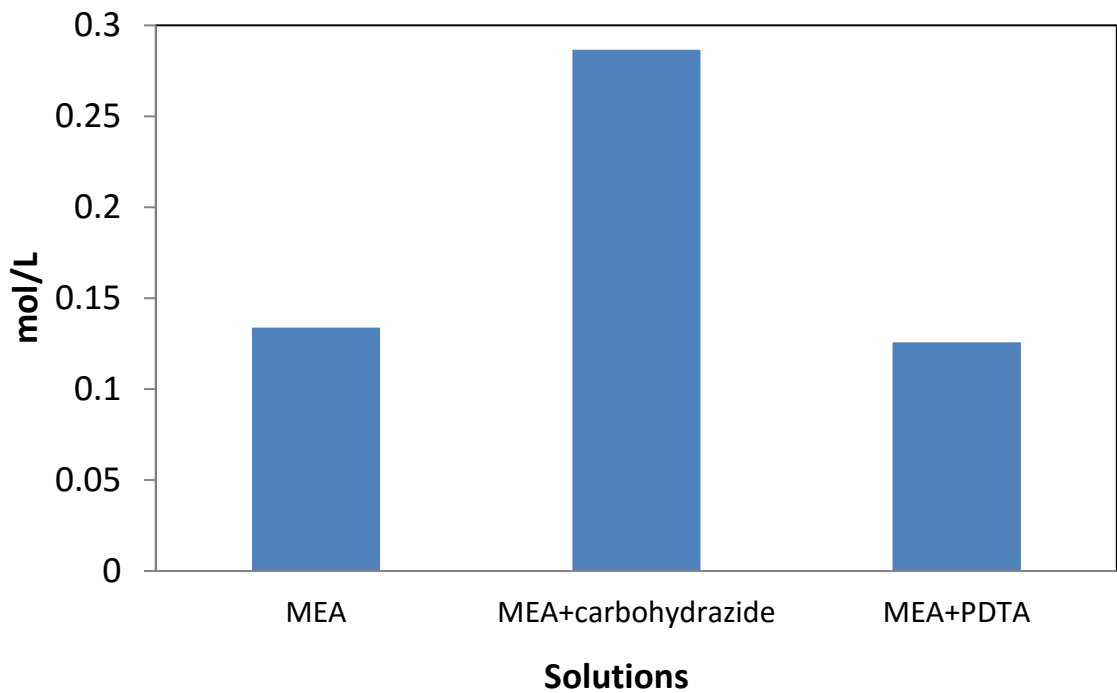


Figure 3.4: Carbohydrazide and PDTA loss% vs time at stripper conditions

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### 3.3.2 Degradation products formation at stripper conditions

308 In addition to the thermal stability, the same samples were analyzed for MEA loss (Fig. 3.5)  
309 and for the quantification of the thermal degradation products, i.e. HEEDA, HEIA and OZD  
310 (Fig 3.6). The results were compared with the average of two 30wt% MEA samples that were  
311 used as reference.



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Figure 3.5: MEA loss (mol/L) after 14 days at stripper conditions

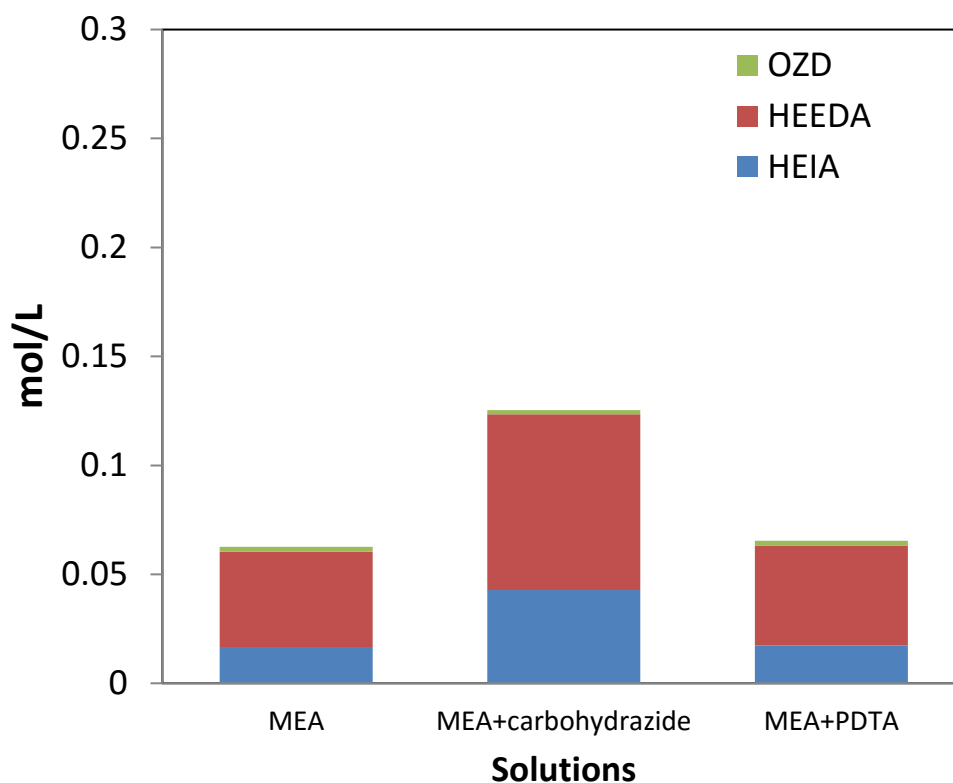


Figure 3.6: HEEDA, HEIA and OZD concentrations (mol/L) after thermal degradation experiment

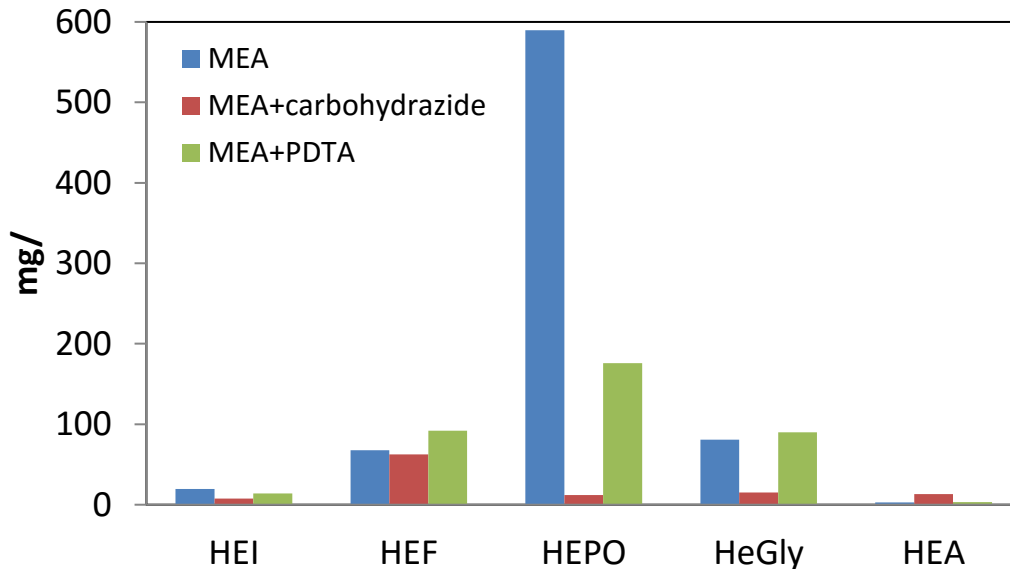
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319 Under stripper conditions, the addition of PDTA doesn't change anything when it comes to  
320 MEA loss and to thermal degradation products formation, as it can be seen from Fig. 3.5-6.  
321 On the other hand, the addition of carbohydrazide enhanced thermal degradation, and the  
322 concentration of the degradation products HEEDA and HEIA is two times higher compared  
323 to MEA and to MEA+PDTA. The concentration of MEA that was lost, and the  
324 concentrations of HEEDA and HEIA that were formed, are in good agreement with the  
325 carbamate polymerization mechanism for MEA that was suggested by Polderman et al.[29].

326 In addition to thermal degradation products' quantification, the end samples of the thermal  
327 degradation experiment were analyzed for the oxidative degradation products HEI, HEF,  
328 HEPO, HeGly, and HEA (Fig. 3.7).

329 HEPO and HEI concentrations are low for MEA+carbohydrazide solutions. HeGly and HEI  
330 are directly formed from primary degradation compounds, like aldehydes, carboxylic acids  
331 and ammonia. Primary degradation products are formed by radical reactions, which are  
332 catalyzed by iron[30]. Since iron concentration was very low in MEA+carbohydrazide  
333 solutions, as presented later in Chapter 3.3, the formation of HEGly and HEI is expected to  
334 be less than in MEA.

335 Under thermal degradation conditions, the formation of the formamide HEF, which is related  
336 to formate, does not seem to be influenced by the addition of inhibitors even if formate is a  
337 primary degradation compound. However, as Fig. 3.2 shows, formate formation is low in the  
338 case of MEA+PDTA under oxidative degradation conditions.



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341 Figure 3.7: Oxidative degradation products concentrations (mg/L) after thermal  
342 degradation experiment

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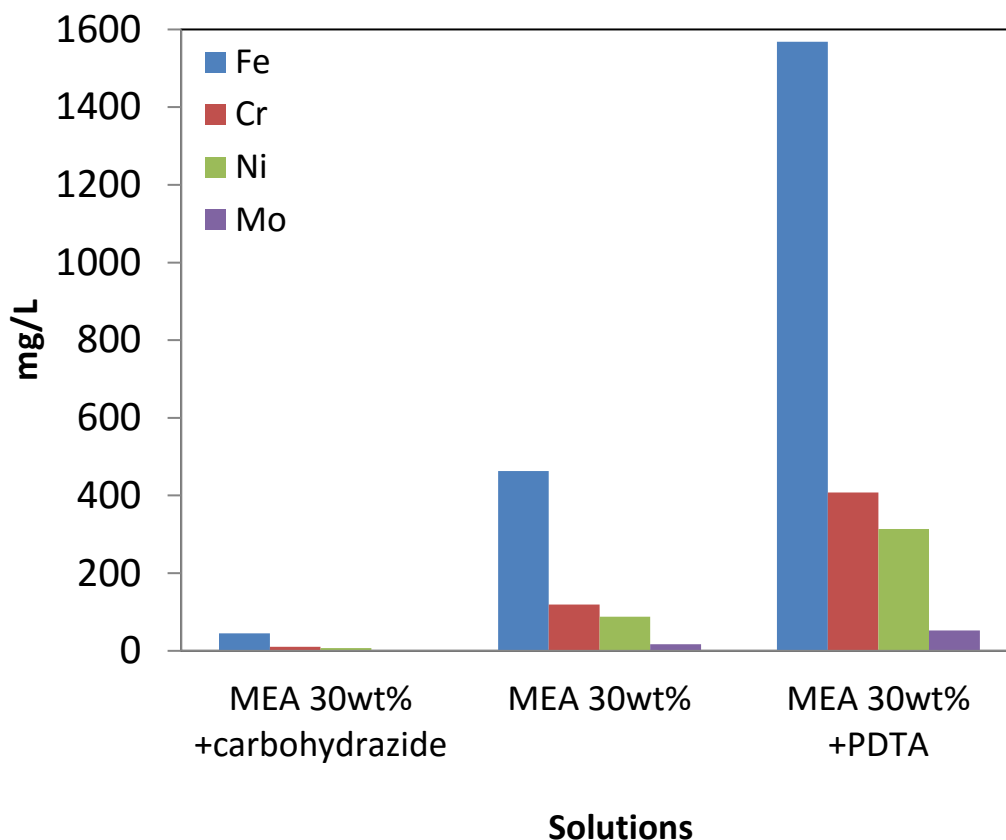
### 344 3.4 Corrosivity of inhibitors

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346 At the end of thermal degradation experiment, samples were analyzed for metal concentration  
347 as indication of corrosion by ICP-MS. ICP-MS gives essential information on the solvent  
348 corrosivity during thermal degradation experiments [31]. The results are presented in Fig 3.8.  
349 It can be seen that the addition of carbohydrazide inhibited corrosion. Even though  
350 carbohydrazide decomposed, the decomposition product of carbohydrazide, i.e. hydrazine, is  
351 known to inhibit corrosion as well. However, it has been classified by EPA as a probable  
352 human carcinogen[32].

353 In the case of PDTA, although a very promising degradation inhibitor, the high metal  
354 concentrations indicate a negative effect on steel surface. It would be interesting to  
355 investigate the combination effect of carbohydrazide and PDTA on degradation and corrosion,  
356 since carbohydrazide showed excellent corrosion protection properties, and PDTA  
357 remarkable degradation inhibition. However, one should keep in mind that carbohydrazide is  
358 not thermally stable above 100 °C, and this can hinder its use in chemical absorption-based  
359 CO<sub>2</sub> capture plants with thermal regeneration of solvent.





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Figure 3.8: Metal concentrations (g/L) after thermal degradation experiment

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#### 4. Conclusions

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In this paper, the degradation and corrosion inhibition performance of the additives pyrogallol, AAPD-cresol, pyrogallol+AAPD-cresol, carbohydrazide, MEKO, tricine and PDTA was tested. From the various additives that were examined under oxidative degradation conditions, carbohydrazide has the potential to be a corrosion inhibitor in MEA-based post-combustion CO<sub>2</sub> capture. Moreover, the addition of 0.1 M of carbohydrazide could have a positive effect on MEA degradation. Furthermore, PDTA showed excellent degradation inhibition properties, but there is a concern about its effect on corrosion. Even though, no perfect inhibitor suitable for both corrosion and degradation inhibition was identified, an interesting approach could be to combine a promising corrosion inhibitor with a degradation inhibitor and investigate the possibilities to optimize the blends for degradation and corrosion inhibition.

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389 **References**

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