Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 63 (2014) 1869 – 1875

Energy Procedia

GHGT-12

# Effect of MEA's degradation products on corrosion at $CO_2$ capture plants

Georgios Fytianos[a], Andreas Grimstvedt[b], Hanna Knuutila[a]* and Hallvard F. Svendsen[a]

[a]Institutt for kjemisk prosessteknologi, NTNU, 7491 Trondheim, Norway
[b]SINTEF Materials and Chemistry, 7465 Trondheim, Norway

---

**Abstract**

Amine degradation and corrosion can be a severe operational problem in the $CO_2$ absorption process. In this paper the effect of MEA's degradation products on corrosion is studied. Different solutions of MEA 30wt% containing also 1wt% of a specific degradation product were placed in 316 stainless steel cylinders and stored in a thermostat chamber at 135°C. Samples are analysed for Fe, Cr, Ni and Mo by ICP-MS as an indication of corrosivity. The results showed that after 5 weeks loaded MEA 30wt% with 1wt% oxalic acid was the most corrosive solution.

Peer-review under responsibility of the Organizing Committee of GHGT-12

*Keywords:* $CO_2$ capture; thermal degradation; corrosion; degradation products; ICP-MS

---

## 1. Introduction

Carbon dioxide ($CO_2$) is the primary greenhouse gas emitted through human activities mainly from the combustion of fossil fuels (coal, natural gas, and oil). The development of innovative technologies for $CO_2$ emission reduction is of great importance. In this direction, post combustion $CO_2$ capture processes can be used to minimize the emissions of carbon dioxide in fossil fuel power plants.

---

* Corresponding author. Tel.: +47 73594119; fax: +47 735 94080.
*E-mail address:* hanna.knuutila@ntnu.no

Peer-review under responsibility of the Organizing Committee of GHGT-12
doi:10.1016/j.egypro.2014.11.195

Regarding $CO_2$ post-combustion, chemical absorption with aqueous alkanolamines solutions is the most commonly used method and has already reached commercial stage. However, corrosion can potentially be a severe operational problem in the $CO_2$ absorption process.

Although progress has been made in understanding of degradation and corrosion in $CO_2$ capture plants, further research, both theoretical and experimental, has to be done. This work investigates which degradation products found in 30wt% MEA lead to corrosion and specifically to what extend each of them aggravate corrosion. Moreover, the role of formation of heat stable salts (HSS) on corrosion and the role of $CO_2$ loading are studied. Tanthapanichakoon et al. [1] studied the effect on corrosion of HSS at 80 $^oC$ with an electrochemical approach. In this paper, results from a different experimental method at 135 $^oC$ are presented and compared to the already published ones.

**Nomenclature**

| | |
|---|---|
| HEA | *N*-(2-hydroxyethyl) acetamide |
| HEEDA | *N*-(2-hydroxyethyl) ethylenediamine |
| HEF | *N*-(2-hydroxyethyl) formamide |
| HeGly | *N*-(2-hydroxyethyl) glycine |
| HEI | *N*-(2-hydroxyethyl) imidazole |
| HEIA | *N*-(2-hydroxyethyl) imidazolidone |
| HEPO | 4-(2-hydroxyethyl)-2-piperazinone |
| MEA | Monoethanolamine |
| OZD | 2-oxazolidinone |

## 2. Experimental

This work investigates the effect of MEA's degradation products on corrosion. Therefore, five of the identified degradation products of MEA are tested for their corrosivity using metal cylinders constructed from 316 stainless steel tubes with an outer diameter of ½ inch and equipped with Swagelok® end caps. 9g of $CO_2$-loaded solution of 30wt% MEA containing 1wt% of degradation product was injected into each cylinder. For every solution in order to check for possible leakages, the cylinder was weighed before and after incubation. The cylinders were held in an upright position and stored in a thermostat chamber at 135$^oC$ [2]. Two replicates were used for each solution and every week two cylinders of each solution were taken out for analysis. The total experimental time was 5 weeks. Solutions are analysed for Fe, Cr, Ni and Mo by inductively coupled plasma mass spectroscopy (ICP-MS) as an indication of corrosivity. Similar methodology has previously been used by Grimstvedt et al. [3]. MEA and the following degradation products are analysed using Liquid Chromatography – Mass Spectometry (LC-MS): HEIA, HEEDA, OZD, Hegly, HEF, BHEOX, HEA, HEPO and HEI. Ion Chromatography (IC) is used for identification and quantification of glycolate, propionate, formate, oxalate and acetate. The anions are analysed on an ICS-5000 RFIC ThermoScientific System equipped with AS15 analytical column, an ASRS300 suppressor and a conductivity detector.

In this paper the degradation products listed in Table 1 are tested for their corrosivity. Most of the experiments are performed using loading 0.4 $molCO_2/molMEA$, but the influence of loading into corrosivity is also tested by performing some experiments with loading 0.2 $molCO_2/molMEA$. The acids of Table1 dissolute in MEA aqueous solutions and give their anion form which is also called heat-stable salt anion.

Scanning electron microscope (SEM) was used to examine the stainless steel surface before and after the experiments in order to determine the type of corrosion.

Table 1. MEA's Degradation Products.

| | 0.2 loading | 0.4 loading |
|---|---|---|
| Glycolic acid | Not Tested | Tested |
| Propionic acid | Not Tested | Tested |
| Formic acid | Not Tested | Tested |
| Oxalic acid | Tested | Tested |
| Acetic acid | Tested | Tested |

## 3. Results

### 3.1. Degradation of MEA

In Fig. 1 the MEA concentration in presence of different acids (30wt% MEA + 1wt% acid) is shown at week 5. 30wt% MEA corresponds to 4.9mol/l. It can be seen that after 5 weeks, the loss of MEA was the highest in presence of acetic acid 1wt%, followed by glycolic and oxalic acid solutions. Generally, the presence of the acids increased the MEA loss as discussed later. The degradation for the two solutions with the 0.2 loading is less than the 0.4 loading solutions. Both the MEA+oxalic acid solution and MEA+acetic acid solution had 30% more MEA loss for 0.4 $CO_2$ molar loading compared to the 0.2 loading. Same influence of loading has been reported by Davis [4] who presented that doubling the molar loading from 0.2 to 0.4 almost doubles the MEA degradation rate during a thermal degradation study at 135 °C.

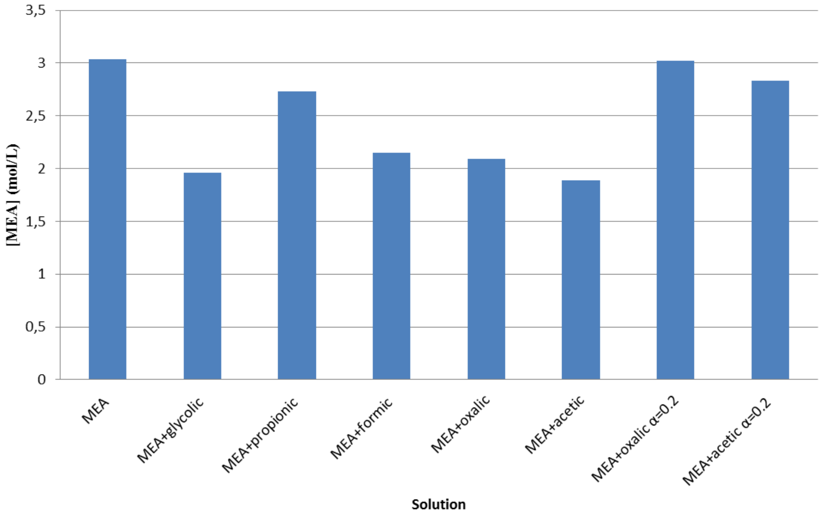


Fig. 1. MEA concentration after 5 weeks for different solutions containing 30wt% MEA + 1wt% different acids. The solutions are loaded to 0.4 mol/mol except the two on the right hand side which have loadings 0.2mol/mol.

Quantitative results for HEI, OZD, HEPO, HEA, HEF and HeGly by LC-MS are presented in Fig. 2. Typical oxidative degradation compounds e.g. HEPO and HeGly were quantified in very small concentrations. LC-MS results showed high concentrations of HEF for the MEA 30wt% + formic acid solution followed by the MEA 30wt% + oxalic acid solutions. Moreover, HEA concentration was high for the MEA 30wt% + acetic acid solutions. After 5 weeks, there is still some acetate left in the MEA+acetic acid solution. It has been reported in the literature and in this study that MEA reacts with formic acid to give HEF [5, 6], but the interesting part in this work is that HEF was produced also in the MEA+oxalic acid solution. Further study with IC indicated that part of the oxalic acid via thermal decomposition became formic acid after 1 week at 135 $^{o}$C, and all of the oxalic decomposed after 2 weeks. Voice et al. [7], while studying sequential degradation of aqueous MEA, stated that oxalate species converted one-to-one to formate at 135 $^{o}$C. Quantitative results for two of the main thermal degradation compounds, HEEDA and HEIA, are presented in Fig. 3. HEIA is the main thermal degradation compound found in this study. HEIA concentration varied a lot in the presence of different acids. However, HEEDA concentration is not influenced as much as HEIA's in the different solutions. Ammonia and N,N'-bis(2-hydroxyethyl) urea and ammonia were not analysed in this study. As shown in Fig. 1 and 3, the most degraded solutions had higher concentrations of HEEDA and HEIA i.e. MEA+glycolic acid solution and MEA+acetic acid solution.

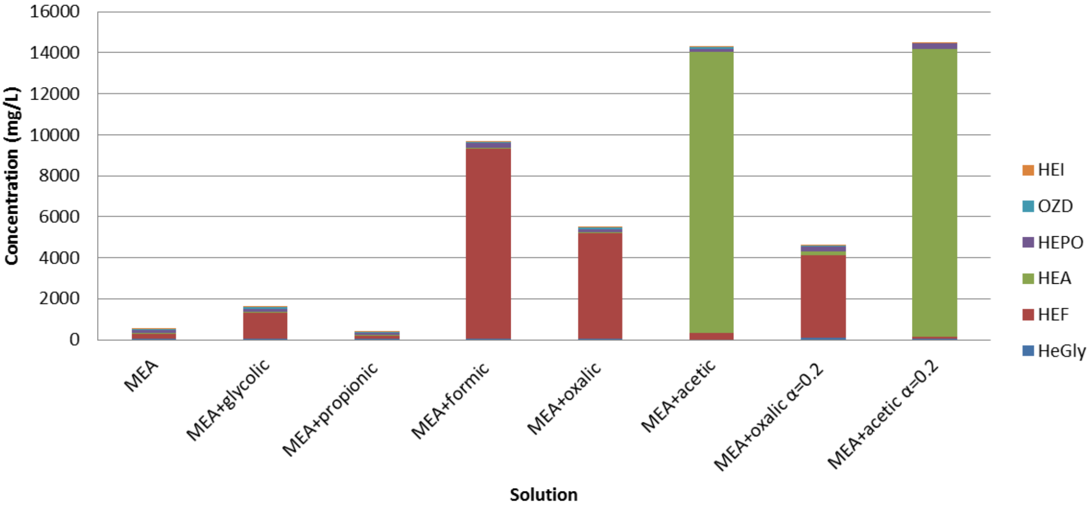


Fig. 2. Concentration of degradation products after 5 weeks determined by LC-MS.

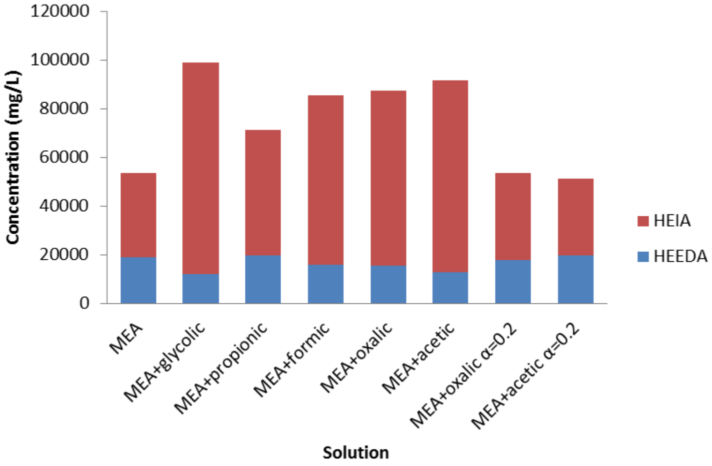
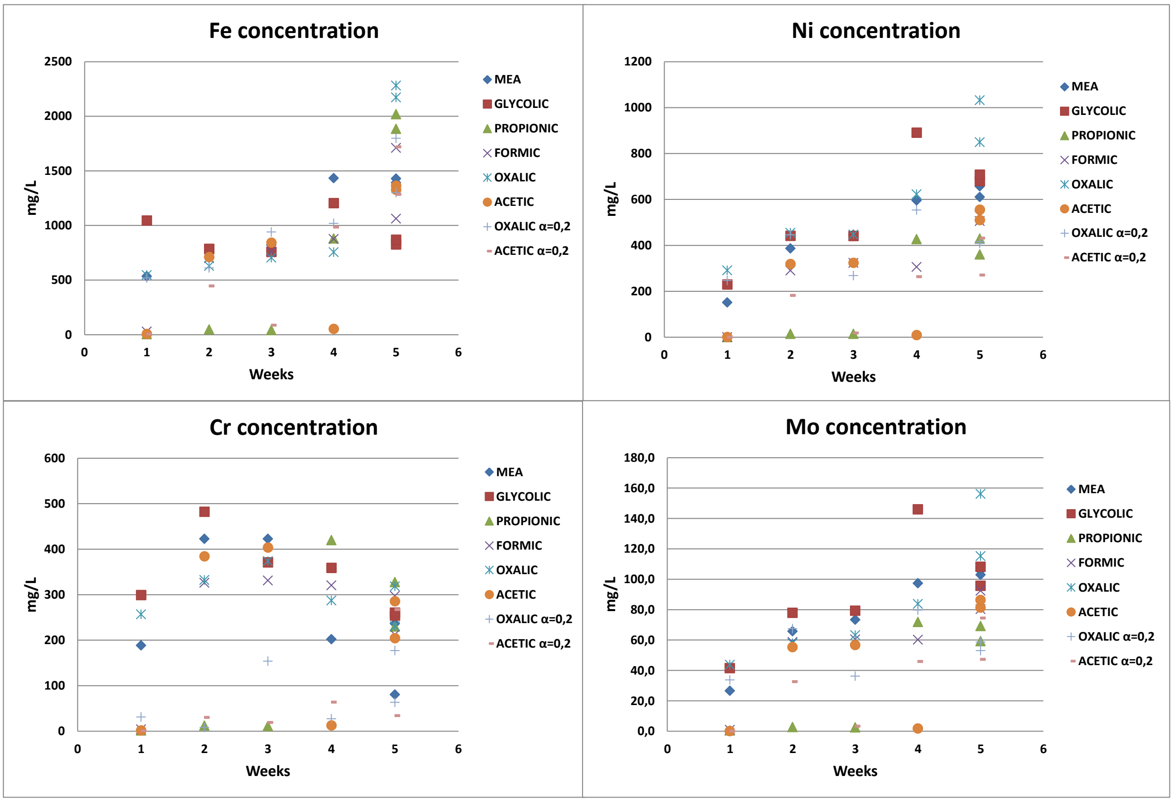


Fig. 3. Concentration of HEIA and HEEDA determined by LC-MS after 5 weeks for the different solutions.

### 3.2. Corrosion

The ICP-MS results for the metals Fe,Ni,Mo and Cr for every week are presented in Fig. 4. The methodology that is used is based on the simple approach that higher metal concentration in the solutions means more corrosion. The parallel samples from the first until fourth week are not listed because there is no discernible difference between any of the metal concentrations. However, for the last week of the experiment, the results from the two parallels are shown. For the 0.2 loading solutions and for the MEA+formic acid with 0.4 loading there is a noticeable difference for the iron concentration.


Fe concentration

Ni concentration

Cr concentration

Mo concentration

Fig. 4. Fe, Mo, Ni and Cr concentration over time during the experiment.

From the results, it can be seen that the iron concentration is the highest for all the solutions. Mo concentration in the various solutions do not exceed 100mg/L. Furthermore, Cr and Ni follow the increasing trend of Fe concentration but still, Fe profile gives a better picture of the corrosion. Therefore, in addition to Fig. 4, the iron concentrations of the solutions after 5 weeks are summarized in Fig. 5. After 5 weeks loaded MEA 30wt% with 1wt% oxalic acid was the most corrosive solution and MEA 30wt% with glycolic acid was the least corrosive one. Tanthapanichakoon et al. [1], during an electrochemical investigation on the effect of HSS on corrosion at aqueous solution of loaded MEA, stated that oxalate induced the highest corrosion, followed by formate. For acetate and glycolate they noticed that glycolate and acetate have not an important effect on corrosion of Stainless Steel 304. When comparing these results to Fig. 5 we can see that the results are in agreement. After 5 weeks, the 30wt% MEA aqueous solution caused cracks and some pitting corrosion on the surface as can been seen in Fig. 6 where SEM images show the inner part of the cylinder before and after the experiment.

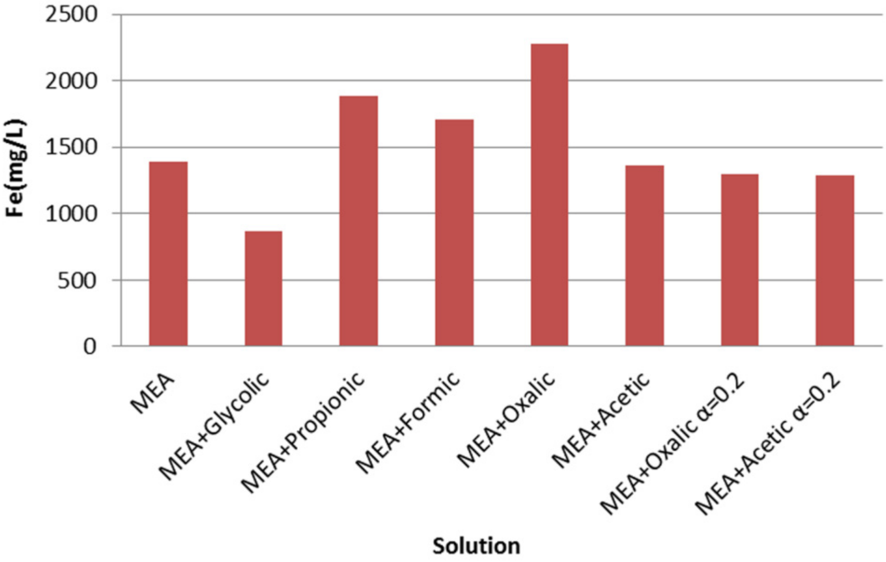


Fig. 5. Fe concentration (indication for corrosion) for different solutions containing 30wt% MEA + 1wt% acid. The solutions are loaded to 0.4 mol/mol except the two on the right hand side which have loadings 0.2mol/mol.

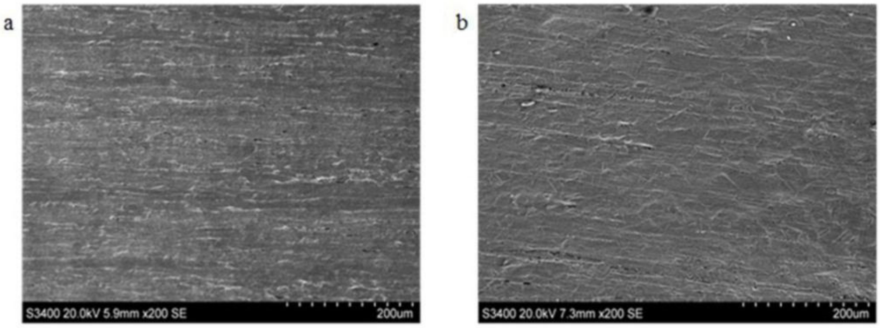


Fig. 6. SEM images for MEA 30wt% solution with 0.4 loading (200X Magnification) (a) Before the Experiment; (b) after 5 weeks.

## 4. Conclusions

In this paper degradation and corrosion of MEA with different degradation products solutions was studied. Of the various solutions, MEA 30wt% with acetic acid 1wt% caused the highest degradation of MEA. When the $CO_2$ loading was doubled from 0.2 to 0.4 the MEA loss increased by 30%. The methodology that was used for estimation of corrosivity gave a satisfactory idea of the relative corrosivity for the different solutions. At 135 $^{o}$C, MEA 30wt% with oxalic acid 1wt% with 0.4 $CO_2$ molar loading had the highest effect on corrosion, followed by MEA with propionic acid and MEA with formic acid solutions. Furthermore, glycolic acid and acetic acid didn't seem to increase the corrosion. The metal concentration profiles for the two most corrosive solutions (MEA+oxalic and MEA+acetic) are close due to the fact that oxalic decomposed to formic after 2 weeks at 135 $^{o}$C.

## Acknowledgements

The work is done under the SOLVit SP4 project, performed under the strategic Norwegian research program CLIMIT. The authors acknowledge the partners in SOLVit, Aker Solutions, Gassnova, EnBW and the Research Council of Norway for their support.

## References

[1] Winyu Tanthapanichakoon, Amornvadee Veawab and Bryce McGarvey. Electrochemical Investigation on the Effect of Heat-stable Salts on Corrosion in $CO_2$ Capture Plants Using Aqueous Solution of MEA. Ind. Eng. Chem. Res. 2006, 45, 2586-2593

[2] Eide-Haugmo, Ingvild. Environmental impacts and aspects of absorbents used for $CO_2$ capture. Doctoral theses, NTNU, ISSN 1503-8181; 2011:242

[3] Andreas Grimstvedt, Eirik Falck da Silva and Karl Anders Hoff. Thermal degradation of MEA, effect of temperature and $CO_2$ loading. TCCS7, SINTEF Materials and Chemistry, 7465 Trondheim, Norway

[4] Davis, J.D. "Thermal Degradation of Aqueous Amines used for Carbon Dioxide Capture." Ph.D. Dissertation (2009). The University of Texas at Austin.

[5] Helene Lepaumier, Eirik F. da Silva, Aslak Einbu, Andreas Grimsvedt, Jacob N. Knudsen, Kolbjørn Zahlsen, Hallvard F. Svendsen. Comparison of MEA degradation in pilot-scale with lab-scale experiments. GHGT-10. Energy Procedia Volume 4, 2011, Pages 1652–1659

[6] Eirik F. da Silva, Hélène Lepaumier, Aslak Einbu, Andreas Grimstvedt, Kai Vernstad, Solrun Johanne Vevelstad, Hallvard F. Svendsen and Kolbjørn Zahlsena. 'Understanding MEA degradation in post-combustion $CO_2$ capture' SINTEF and NTNU. Ind. Eng. Chem. Res., 2012, 51 (41), pp 13329–13338

[7] Alexander K. Voice, Daniel Wei, and Gary T.Rochelle. Sequential Degradation of Aqueous monoethanolamine for $CO_2$ Catpure. Recent Advances in Post-Combustion $CO_2$ Capture Chemistry. Chapter 13, pp 249–263. University of Texas at Austin, Dept. of Chemical Engineering, Publication Date (Web): May 3, 2012