

Corrosion in CCS

Alongside degradation, corrosion can be a severe problem when operating a CO_2 absorption process ¹. Although a lot of research has been done in the field and valuable insights have been gained, the corrosion process that takes place in the post combustion capture plants is not well understood.

Overall, corrosion is a complex problem, and it has been found that multiple factors contribute, including composition of the amine solution, temperature, acid gases, and flue gas impurities. Carbon steel corrodes by a charge transfer reaction between the metal surface and the surroundings, accompanied by a reduction. Stainless steel have the important ability to form $Ni(OH)_2$ and Cr_2O_3 on the surface. At high pH levels, these will work as a protective layer for the metal underneath. However, if the system experience sufficiently oxidizing conditions, the protective layer will become unactive and corrosion will occur similarly to carbon steel corrosion². Most of the electrochemical reactions involved in corrosion are thermally activated ^{3,4}. This is in line with what has been observed and reported in the literature, where increased temperature has been reported to result in increased corrosion rates ^{1,5,6}.

The composition of the amine solution also influences the corrosion rates. Generally, amines by themselves are not corrosive ⁷. Increased loading of the amine, however, result in increased corrosivity ^{1,5}. At areas with the combination of high loading and high temperature, the likelihood of excessive corrosion is, therefore, high. Such a point can be found in the rich amine line between the heat exchanger and the stripper ³.

The choice of amine does not affect corrosion rates if the amine is not loaded. When the amine is loaded, however, the choice of amine becomes highly influential ³. The corrosion potential of the amine classes is proposed to go from most to least corrosive in the order primary > secondary > tertiary ⁸. Studies have suggested that corrosivity of the amine solution is linked to the rate of carbamate formation ⁶. Also, sterically hindered amines are not very corrosive, as they for a protective layer of iron carbonate (FeCO₃) on the metal surface. Both Stericallyhindered amines and tertiary amines are capable of this, as they are both a source of the carbonate species needed for this formation ⁸. A consensus of the effect of the amine concentration has not been reached ³.

As the amine degrades during operating hours, the formation of degradation products will also contribute to the corrosion problem. Some basic degradation products have been found to increase corrosion rates, but heat-stable salts (HSS) are generally considered the main contributors ^{1,9–12}. The higher the concentration of these components, the higher the corrosion rates. The reason why, and by which mechanisms this happens, is not understood.

Studying corrosion is usually done using coupons. Here, the weight loss is measured ^{1,13}, and in some cases visual inspection of the surface of the coupons is also conducted ¹⁴. Metal concentration in the solvent can also give insight into of the state of the solvent with regards to corrosion. These are measured using by ICP-MS/-OES ¹⁵.

Experiments

A thermal degradation study of amines in water-lean solvents was conducted over 5 weeks (12 weeks for the tertiary amines) to study the thermal stability of water-lean solvents. The presence of metals is not expected to affect the thermal degradation mechanism of amines ¹⁶, and so, corrosion measurements of the degraded solvents were performed as a side study to gain insights into the corrosivity of the solvents. An overview of the series of solvent systems studied, where metals were measured, are listed below. Comprehensive experimental details are presented in deliverable D.3.2.2. under the LAUNCH Project.

- a. Increasing concentrations of loaded MEA (CAS: 141-43-5) in water with a constant absolute concentration of CO_2 (0.19 mol $CO_2/100$ g unloaded solution).
- b. Loaded MEA (5 Molal, α =0.5) in changing ratios of triethylene glycol (TEG, CAS: 112-27-6) and water.
- c. Loaded primary (5 Molal, α=0.5), secondary (5 Molal, α=0.5), and tertiary (5 Molal, α=0.3) amines in solutions of TEG and water. Amines included were AP (1°, CAS: 156-87-6), MMEA (2°, CAS: 109-83-1), EAE (2°, CAS: 110-73-6), DMMEA (3°, CAS: 108-01-0), and DEEA (3°, CAS: 100-37-8).
- d. Loaded MEA (5 Molal, α=0.5) in organic solvents TEG, diethylene glycol (DEG, CAS: 111-46-6), monoethylene glycol (MEG, CAS: 107-21-1) and a 20mol% *N*-Formyl morpholine/water solution (NFM, CAS: 4394-85-8).

Measurement of metals in solutions by ICP-MS was done externally. The main metal components from stainless steel, i.e. Mo, Cr, Ni, Fe, were measured. It should be noted that this is not a proper corrosion test for the solvents, but it gives an indication of the corrosivity of the actual systems.

a. The results for the solutions with increasing concentrations of loaded aqueous MEA is shown in Figure 1. In these experiments, the MEA concentration was varied, while the absolute concentration of CO_2 was kept constant. Some unexpected results were observed. At low concentrations of MEA, the metal concentration increased with the increase in MEA. At

the midrange concentrations, the concentration of metals stabilized, before decreasing as the concentration increased further. Though the concentrations of the separate metals were not the same, the total amount of metals were found to be the same for the solutions with 8mol% and 100mol% MEA. In the literature, no consensus has been reached with regards to the effect of amine concentration on corrosion. Form these results, it seems to have an effect, though it is not a clear trend.

b. The metal concentration in the solutions with loaded MEA in various ratios of TEG and water is shown in Figure 2. It is worth noticing that the 0mol% TEG in Figure 2 corresponds to the 8mol% MEA in Figure 1. Figure 2 shows that, at lower concentrations of TEG, the metal concentration increases with an increasing ratio of TEG. Between 20mol% and 50mol%, however, there is a sharp change and all the solutions with high TEG content have very low metal concentrations. Higher TEG concentrations, therefore, might have an inhibitory effect on corrosion. The change in metal content might also be due to insufficient solubility of the metal ions in TEG. We have unfortunately not found any published data on the solubility of any of the metals in TEG.

c. A comparison of solutions with various loaded amines in water and solutions of the same loaded amines in 50mol% TEG in water is shown in Figure 3. From the results of the different amines, it is clear that the choice of amine strongly influences the corrosion. The results for the amines in water compared with their corresponding solution with TEG and water shows that the presence of TEG has a strong effect on the corrosivity of the amine solutions. Similar to the trend seen for loaded MEA, the various loaded amines show significantly lowered metal content with TEG present. As an exception, the solutions with DMMEA are less affected by TEG, though why this is is not clear. It is feasible that the concentration at which TEG results in the protective property that is seen for the other amines, is higher for DMMEA.



Figure 1: Metal concentrations in thermally degraded solutions (5 weeks, 135 °C) of loaded aqueous MEA (0.19 mol CO₂/100 g unloaded solution) with increasing MEA concentrations.



Figure 2: Metal concentrations in thermally degraded solutions (5 weeks, 135 °C) of loaded MEA (5 Molal, α =0.5) in changing TEG/water ratios.



Figure 3: Comparison of metal concentrations in thermally degraded solutions (5-12 weeks, 135 °C) of loaded primary (5 Molal, α =0.5), secondary (5 Molal, α =0.5) and tertiary amines (5 Molal, α =0.3) in water and TEG/water mixtures thermally degraded for 5 weeks.



Figure 4: Metal concentrations in thermally degraded solutions (5 weeks, 135 °C) of loaded MEA (5 Molal, α =0.5) in a selection of organic solvents.

d. The metal concentration in solutions of loaded MEA in some organic solvents are presented in Figure 4. In this experiment, thermal degradation experiments were conducted with MEA in a selection of organic solvents. The three glycols, MEG, DEG and TEG, were tested with loaded MEA without any water present. Loading MEA in pure NFM, however, resulted in phase separation. To avoid this, solutions of loaded MEA in mixtures of NFM and water (20:80 mol ratio) was studied. The three glycols all had a low metal content, while the NFM water mixture had a noticeably higher concentration of metals. This is probably due to the high water content of this solution.

Conclusion

In this study, corrosion tendencies of amines in water-lean solvents have been studied. This was done through measurements of the metal content in the solvents after a finished thermal degradation experiment. In these experiments, the water content was reduced both by increasing the amine concentration, and by introducing organic solvents as replacements for the water as diluents.

Experiments with increasing MEA concentrations showed that the amine concentration has an effect on the corrosion, though there is no clear correlation. At low MEA concentrations the metal content increased with increasing amine concentration. In the midrange, though, the trend reversed. After this, the metal content decreased as the MEA concentration increased. The solution of 8mol% MEA in water and pure MEA had the same total metal concentration.

The effect of introducing the organic solvent TEG was studied. At low concentrations of TEG, the metal concentration of the solutions with MEA increased with the increasing TEG content. Between 20mol% and 50mol% TEG, there was a sharp change, and for all solutions with higher TEG concentration the metal content was low. TEG also showed this effect for all other amines tested.

Loaded MEA was also tested with other organic solvents. For the solvents tested with no water present, MEG, DEG, and TEG, the same effect on the corrosion was observed. For the organic solvent, NFM, tested in a blend with water, the metal content was considerably higher. The results from these tests indicate that a low water content results in lower or similar corrosion tendencies compared to loaded aqueous 5M MEA solutions.

References

- Kittel, J.; Idem, R.; Gelowitz, D.; Tontiwachwuthikul, P.; Parrain, G.; Bonneau, A. Corrosion in MEA Units for CO2 Capture: Pilot Plant Studies. *Energy Procedia* 2009, *1* (1), 791–797. https://doi.org/10.1016/J.EGYPRO.2009.01.105.
- (2) Fischer, K. B. Corrosion of Stainless and Carbon Steel in Aqueous Amine for CO2 Capture, University of Texas at Austin, 2019.
- (3) Kittel, J.; Gonzalez, S. Corrosion in CO2 Post-Combustion Capture with Alkanolamines a Review. *Oil Gas Sci. Technol.* **2014**, *69* (5), 915–929. https://doi.org/10.2516/OGST/2013161.
- (4) Nielsen, R. B.; Lewis, K. R.; McCullough, J. G.; Hansen, D. a. Controlling Corrosion in Amine Treating Plants. *Proc. Laurence Reid Gas Cond. Conf.* **1995**.
- (5) Cousins, A.; Ilyushechkin, A.; Pearson, P.; Cottrell, A.; Huang, S.; Feron, P. H. M. Corrosion Coupon Evaluation under Pilot-Scale CO2 Capture Conditions at an Australian Coal-Fi Red Power Station. *Greenh. Gases Sci. Technol.* 2013, *3* (3), 169– 184. https://doi.org/10.1002/GHG.1341.
- (6) DuPart, M. S.; Bacon, T. R.; Edwards, D. J. Understanding Corrosion in Alkanolamine Gas Treating Plants. *Hydrocarb. Process.* **1993**, *72* (5), 89–94.
- (7) Campbell, K. L. S.; Zhao, Y.; Hall, J. J.; Williams, D. R. The Effect of CO2-Loaded Amine Solvents on the Corrosion of a Carbon Steel Stripper. *Int. J. Greenh. Gas Control* 2016, 47, 376–385. https://doi.org/10.1016/J.IJGGC.2016.02.011.
- (8) Sadeek, S. A.; Williams, D. R.; Sedransk Campbell, K. L. Using Sodium Thiosulphate for Carbon Steel Corrosion Protection against Monoethanolamine and 2-Amino-2-Methyl-1-Propanol. *Int. J. Greenh. Gas Control* 2018, 78, 125–134. https://doi.org/10.1016/J.IJGGC.2018.08.004.
- (9) Fytianos, G.; Ucar, S.; Grimstvedt, A.; Hyldbakk, A.; Svendsen, H. F.; Knuutila, H. K. Corrosion and Degradation in MEA Based Post-Combustion CO2 Capture. *Int. J. Greenh. Gas Control* 2016, 46, 48–56. https://doi.org/10.1016/J.IJGGC.2015.12.028.
- (10) Kohl, A. L.; Nielsen, R. B. Alkanolamines for Hydrogen Sulfide and Carbon Dioxide Removal. In *Gas Purification*; 1997; pp 40–186. https://doi.org/10.1016/b978-088415220-0/50002-1.
- (11) Davoudi, M.; Safadoust, A. R.; Akbar Mansoori, S. A.; Mottaghi, H. R. The Impurities Effect on Thermal Degradation and Corrosivity of Amine Solution in South Pars Gas Sweetening Plants. *J. Nat. Gas Sci. Eng.* **2014**, *19*, 116–124. https://doi.org/10.1016/J.JNGSE.2014.05.001.
- (12) Fytianos, G.; Grimstvedt, A.; Knuutila, H.; Svendsen, H. F. Effect of MEA's Degradation Products on Corrosion at CO2 Capture Plants. In *Energy Procedia*; Elsevier Ltd, 2014; Vol. 63, pp 1869–1875. https://doi.org/10.1016/j.egypro.2014.11.195.

- (13) Davoudi, M.; Heidari, Y.; Safadoost, A.; Samieirad, S. Chemical Injection Policy for Internal Corrosion Prevention of South Pars Sea-Pipeline: A Case Study. J. Nat. Gas Sci. Eng. 2014, 21, 592–599. https://doi.org/10.1016/J.JNGSE.2014.09.017.
- (14) Moser, P.; Schmidt, S.; Uerlings, R.; Sieder, G.; Titz, J. T.; Hahn, A.; Stoffregen, T. Material Testing for Future Commercial Post-Combustion Capture Plants Results of the Testing Programme Conducted at the Niederaussem Pilot Plant. *Energy Procedia* 2011, *4*, 1317–1322. https://doi.org/10.1016/J.EGYPRO.2011.01.189.
- (15) Fytianos, G.; Ucar, S.; Grimstvedt, A.; Svendsen, H. F.; Knuutila, H. Corrosion Evaluation of MEA Solutions by SEM-EDS, ICP-MS and XRD. In *Energy Procedia*; 2016; Vol. 86, pp 197–204. https://doi.org/10.1016/j.egypro.2016.01.020.
- (16) Eide-Haugmo, I. Environmental Impacts and Aspects of Absorbents Used for CO2 Capture, 2011.