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Study of degradation products at different MEA based capture pilot plants

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Abstract

In the past, several research programs were undertaken at European Carbon Capture (CC) pilot plants. The results of these individual MEA based campaigns are brought together in order to better understand the solvent degradation at CC pilot plants. The data correlation analysis shows that nickel catalyzes significantly the formation of some degradation products (e.g. HEPO) at low concentrations of 2 mg/l. The iron impact was less clear than determined for nickel. All pilot plants show HEGly and HEPO as the main degradation products, followed by HEF. Within the group of carboxylic acids, formate is the major degradation product.

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Keywords: CO_2 capture; CC pilot plants; MEA; degradation products; HEGly-HEHEAA-HEPO system; metal catalysis

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1. Introduction

For post-combustion carbon capture, flue gas scrubbing with amine solvents is the most common option. 2-ethanolamine (MEA) has been widely used for long time for gas sweetening in refineries, and also for post-combustion capture from gas-fired plants. Due to the different composition of the flue gas from coal fired plants compared to e.g. gas turbines, the degradation occurring in the amine solvents has been found to be more complex. Much research has been undertaken on different amine solvents to find an efficient, degradation-resistant solvent with a low energy penalty. Despite all the different amines analysed, MEA remains the benchmark solvent for

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carbon capture plants since it has been widely researched (Da Silva et al [1]).

The EU funded many research projects in the past and also currently, to investigate the behaviour of MEA solvents under simulated (lab) conditions and in pilot plants. E.ON actively supported and co-funded these research projects. Additionally, EON has been involved in other industry funded carbon capture projects where MEA has been the benchmark solvent. During these projects, the degradation of the MEA solvent has been analysed at different intensities. Besides the degradation itself, corrosion was another aspect of interest in many campaigns as elevated Fe, Ni and Cr levels were observed in the amine solvent.

The aim of this study is to compare the different pilot plant campaigns in order to identify any correlations within the solvent chemistry. This comparison is done anonymously as it is not our intention to make a comparison in respect to material selection or process technology of any individual plant. The focus lies rather on understanding, how the degradation compounds interact and how the degradation process could be interfered. Therefore, references [2] to [6] give an overview of the different research programs, from which data was taken for this study. Solvent reclaiming was done during some of these pilot plant campaigns, but usually towards the end of a campaign. Such data was not considered for evaluation, despite availability, as the solvent composition is changed by reclaiming.

2. Methods

The chemical analyses of the different solvent samples were done within the individual CC pilot plant campaigns. The determination of the primary degradation products (mainly carboxylic acids) is typically done by Ion Chromatography (IC); laboratories proficient in this kind of technique and matrix were used throughout the different programs. All secondary degradation products (e.g. degradation products formed from other MEA-based degradation products) were determined by SINTEF, also within the individual research programs. SINTEF uses a combination of different analytical techniques, including GC-MS (Gas Chromatography – Mass Spectrometry), LC-MS (Liquid Chromatography – Mass Spectrometry) and IC-EX (Ion Chromatography with electrochemical detection) as described by Da Silva et al [1].

3. Results

3.1. Solvent degradation

Having a closer look to the degradation products of MEA, they can be divided into two groups: primary and secondary degradation products (Vevelstad et al. 2013 [7]). Goff [8] described the initial oxidation of MEA to be a radical reaction, allowing for the development of different radical species, which further reacts with MEA or other degradation products. Figure 1 shows the typical primary degradation products observed in degraded MEA solvents.

Comparing several pilot plant campaigns undertaken in the past years to optimize carbon capture at coal fired power plants it can be seen that formate is the dominant, primary oxidation product as shown in Figure 2.

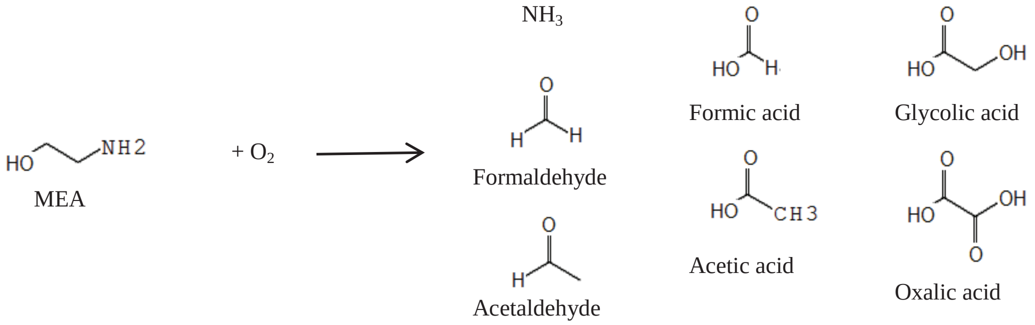


Figure 1: Oxidative degradation products as described by da Silva et al [1]

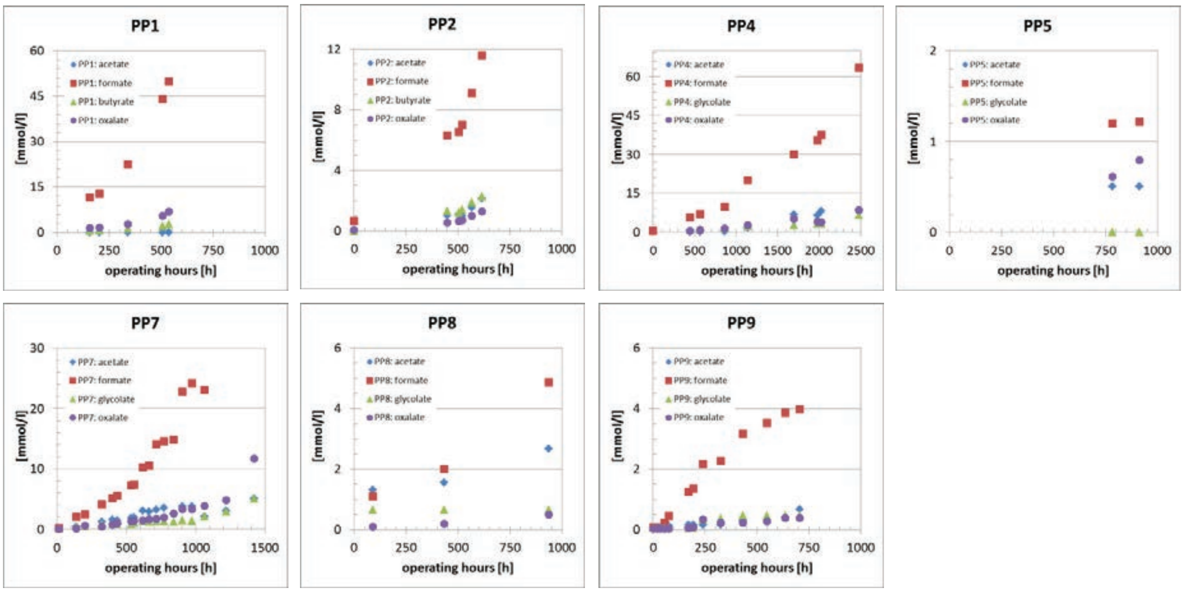
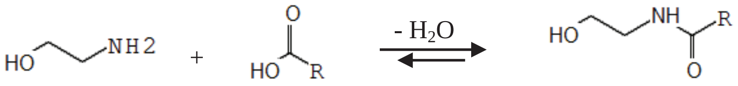


Figure 2: Primary degradation products (1^{st} DPs) for the different pilot plants compared in this study

These carbonic acids are involved in further reactions with MEA forming the corresponding amide compound by dehydration (Figure 3). Other degradation products most likely will occur by further reactions between the different molecules present in solution. The formation of (2-Hydroxyethyl)-glycine (HEGly), for example, was described by Vevelstad [9] to be a two-step reaction between MEA, glyoxylic acid and formic acid (Figure 4).



R = H → HEF
R = CH_3 → HEA
R = CH_2OH → HHEA

Figure 3: Reaction scheme between MEA and organic acids as described amongst others by da Silva et al [1]

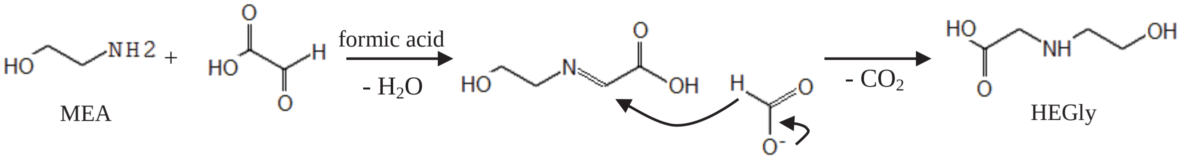


Figure 4: Formation mechanism of HEGly as suggested by Vevelstad [9]

3.2. HEF and formate

The simplest reaction product is (2-Hydroxyethyl)formamide (HEF); formed by the reaction of formic acid with MEA. Lab studies found HEF to be one of the major degradation products formed during MEA degradation [1;7]. Even though it was already determined to be not the major degradation product at pilot plants (da Silva et al [1]), it was found in significant concentrations across all pilot plants compared in this study as shown in Figure 5.

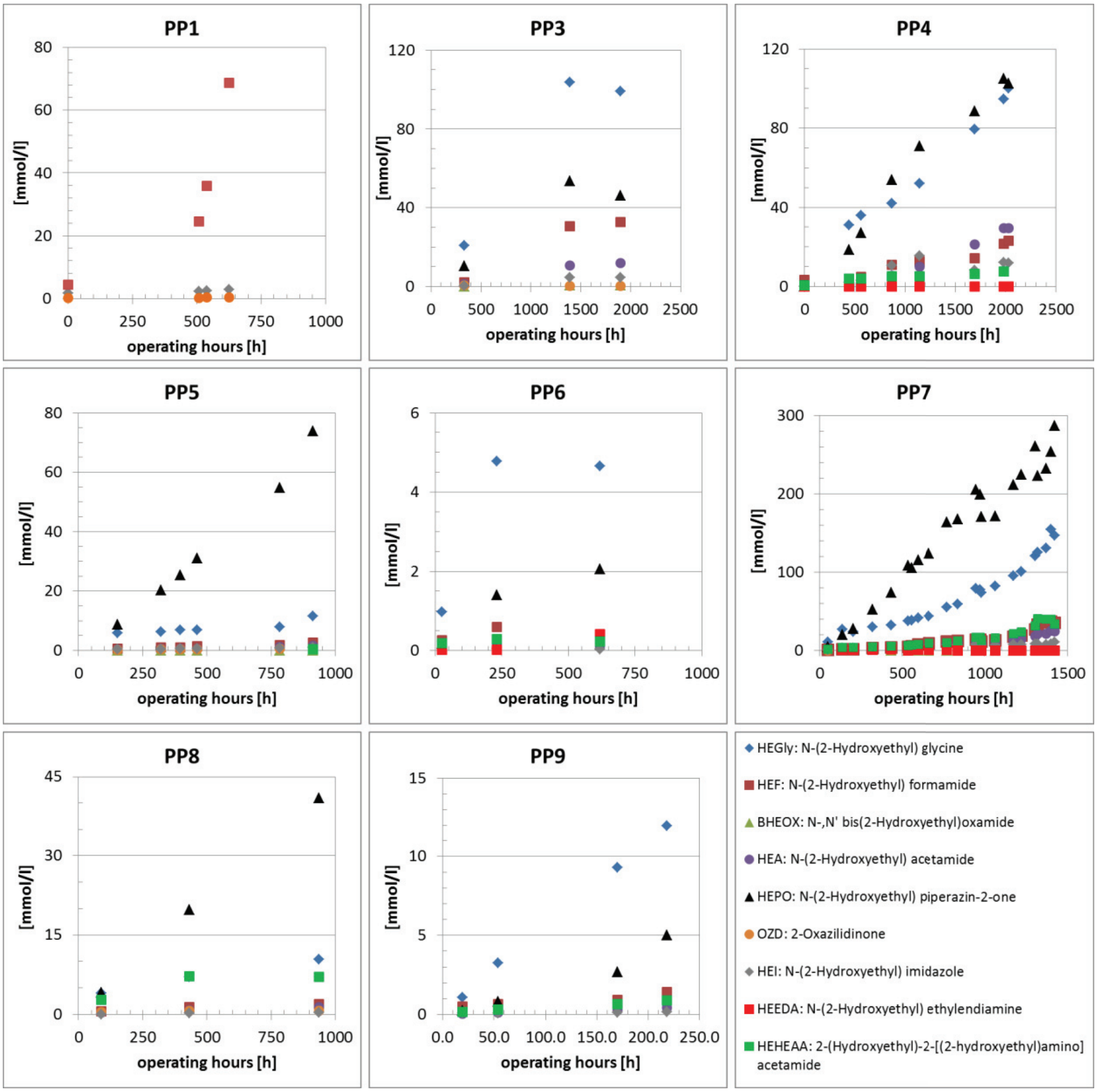


Figure 5: Secondary degradation products (2nd DPs) as determined for the different pilot plant campaigns compared in this study

While Vevelstad et al [10] reported that the formation of HEF is probably metal catalyzed; the pilot plant data did show varying dependencies on the typical dissolved heavy metals ions found in the solvent, e.g. iron, chromium and nickel. However, the reaction between MEA and formate to HEF is a simple condensation reaction. Figure 6 shows the correlation between HEF and formate concentration. All plants show a very similar correlation, accordingly, the amount of HEF present in the pilot plant campaigns depends mainly on the concentration of formate in the solvent, which varies for the different campaigns (Figure 7). The initial MEA oxidation rate of each plant is influenced by factors like oxygen availability in the solvent and radical formation; the latter one of course can be influenced by dissolved metals. Figure 8 shows the correlation of formate concentration with iron, chromium and nickel, respectively; of course, all three metals were present in the solvent at the same time. Some linear correlation with iron at low concentrations up to 1 mmol/l can be seen, but the magnitude of correlation differs between the plants. Chromium and nickel show only a strong correlation for one campaign at levels below 0.2 mmol/l; the effect in the other campaigns appears to be lower. The available data did not allow for quantitative evaluation of plant parameters like oxygen saturation, but a tendency towards higher formate formation in plants with higher oxygen concentrations in the flue gas, lower flue gas temperature and additional higher metal concentration in the solvent could be seen.

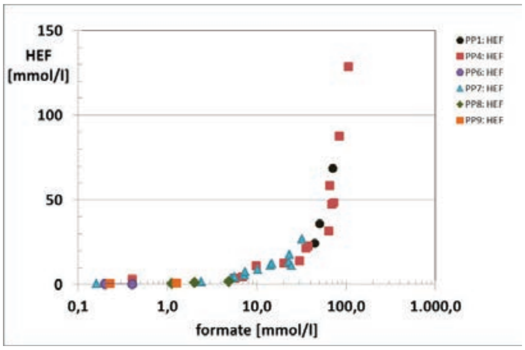


Figure 6: Correlation of HEF with formate for the studied campaigns

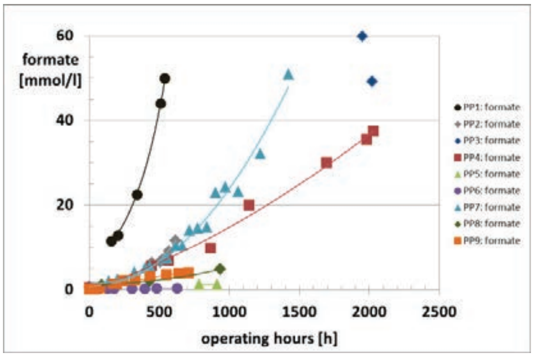


Figure 7: Formate formation for the studied CC pilot campaigns

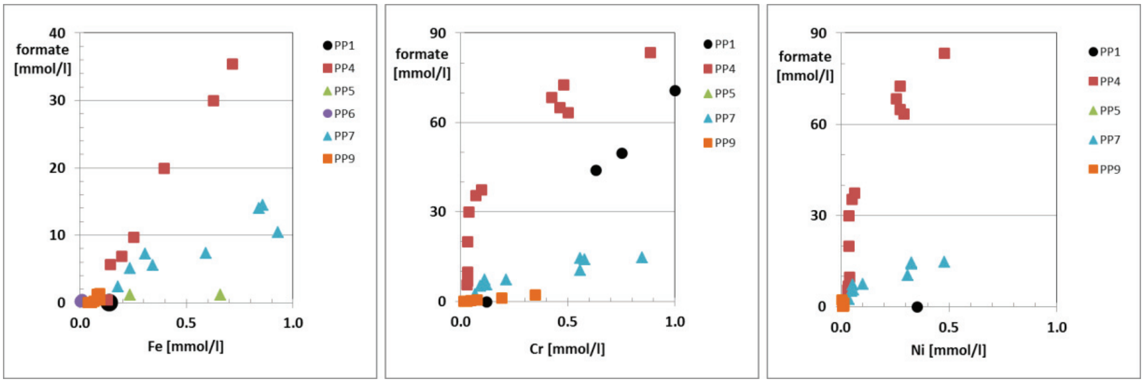


Figure 8: Formation of formate in correlation to iron, chromium and nickel in solution for the studied CC pilot plant campaigns

The absolute equivalents of HEF and formate determined in the solvents were in a similar magnitude of about 0.8-0.9 (HEF) to 1.0 (formate). Acetate is another simple carbonic acid, which follows a similar reaction scheme like formate by forming (2-Hydroxyethyl)acetamide (HEA). But in contrast to the HEF-formate system, the ratio between HEA to acetate is often stronger on the HEA side. In general, the analytical determination of acetate is more challenging compared to the other carbonic acids as the acetate signal is difficult to separate from glycolate within the commonly used ion chromatographic columns. Hence, the pilot plant data should be evaluated carefully. The correlation between HEA and acetate was as clear as found for the HEF-formate correlation for the studied pilot plants. Besides analytical uncertainty, this could also be due to competing reaction paths.

3.3. HEGly, HEHEAA and HEPO

As widely known in the CCS community, N-(2-Hydroxyethlyl)glycine (HEGly) and N-(2-hydroxyethyl)piperazin-2-one (HEPO) are the major degradation products in MEA based CC pilot campaigns [1;7]. Da Silva et al suspected that the difference in HEGly to HEPO ratios of the different pilot plants is caused by differences in stripper operation [1]. In the following, the data of up to seven different pilot campaigns will be assessed to better understand the dependencies. The reaction from HEGly to HEPO was suggested by da Silva et al [1] and Strazisar [11] to be a two-step reaction, involving N-(2-Hydroxyethyl)-2-[(2-hydroxyethyl)amino]acetamide (HEHEAA) as interim product (Figure 9).

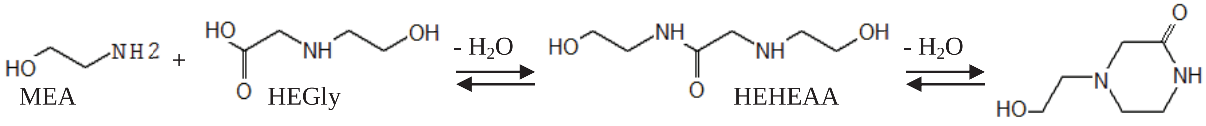


Figure 9: Mechanism of HEPO formation [1;11]

The first lab studies did not show HEGly and HEPO as important degradation products, only after adding metals and / or fly ash to the reaction vessels, formation of these compounds was observed [1;9]. Accordingly, the impact of typical metals present in pilot plant solvent was analyzed during the present study. Iron values were available for six cases, while chromium and nickel were only above detection limit for five of these six cases. Plotting HEGly, HEHEAA and HEPO against these metals was done for the available data in order to identify any correlations. However, one has to keep in mind that all metals are present within the solvents and that overlapping effects might occur.

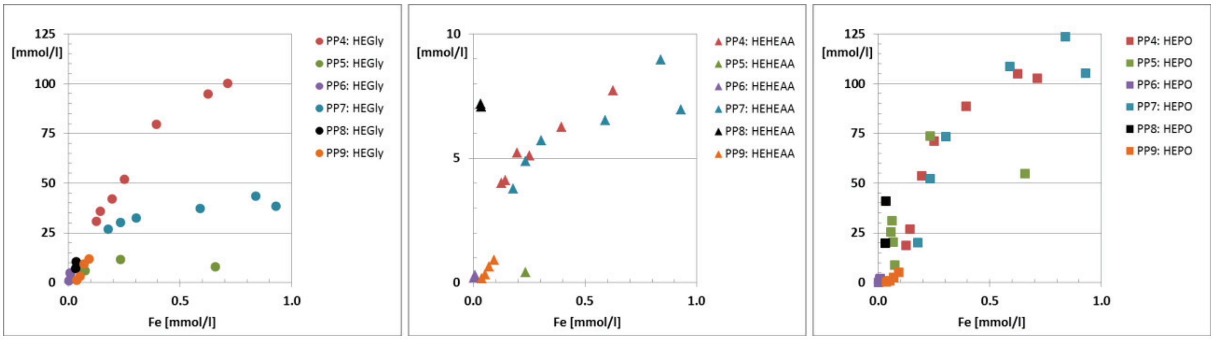


Figure 10: Correlation of HEGly, HEHEAA and HEPO with iron for the different pilot plants in this study

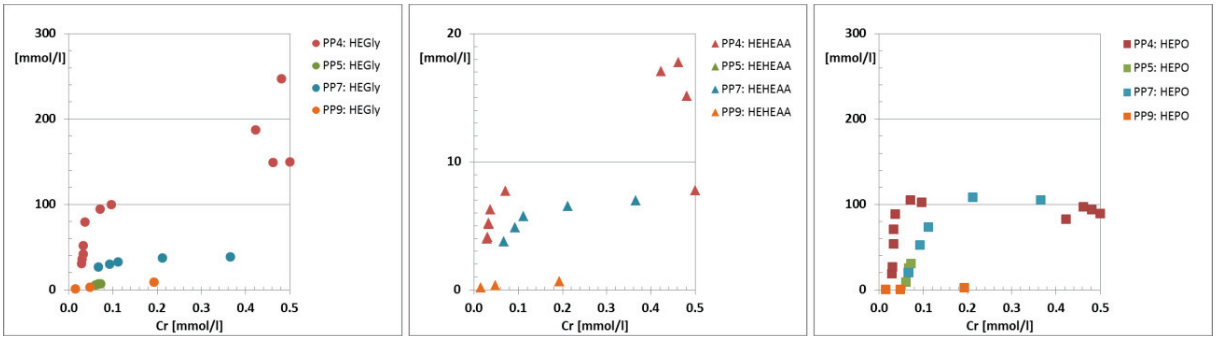


Figure 11: Correlation of HEGly, HEHEAA and HEPO with chromium for the different pilot plants in this study

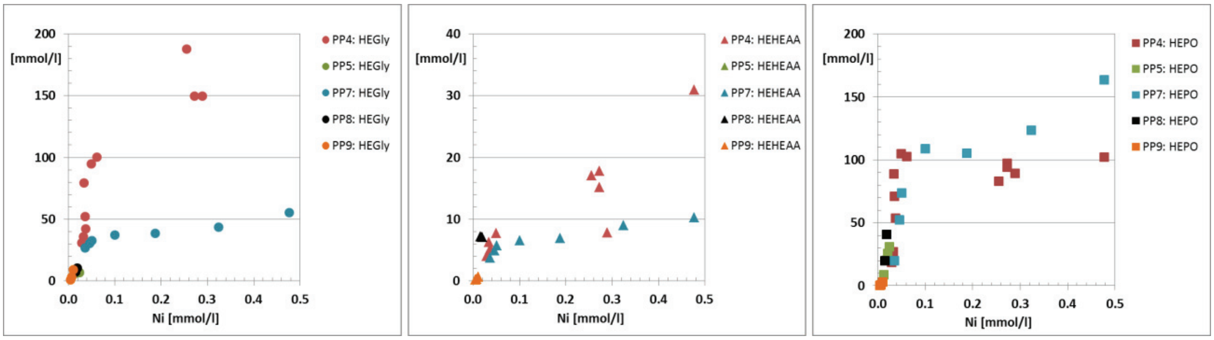


Figure 12: Correlation of HEGly, HEHEAA and HEPO with nickel for the different pilot plants in this study

A clear correlation between HEGly and any of the three metals could not be identified as the different trends drift apart quickly and other factors might be more important. HEHEAA shows some correlation with iron and nickel at very low concentrations. In case of iron, the campaigns show a correlation over a wider concentration range (up to 1 mmol/l) compared to nickel (up to 0.05 mmol/l), but the differences between the campaigns are stronger for iron than for nickel. However, less nickel data was available. The correlation with chromium suggests a stronger impact by other factors. A strong correlation was identified for HEPO formation. A strong linear increase in HEPO concentration was identified for a nickel concentration of up to 0.06 mmol/l. The data of five different pilot test campaigns align very well in this concentration range, indicating a dominant role of nickel in the formation of HEPO. The correlation to iron or chromium was less clear. Since the three metals appear in certain ratios, interferences between the individual correlations are possible, e.g. a slight positive correlation with the iron data can be caused by the good correlation with nickel, as nickel was present in the solvent as well. Sexton [12] used a mixture of chromium and nickel in his oxidative degradation experiments on MEA and found that the Cr/Ni mixture catalyzes the MEA oxidation to a greater extent than iron. However, at that time, degraded solvent samples were not analyzed for HEGly or HEPO, and about 90% of the raw peak area remained unidentified. It is clearly recommended to investigate further, if nickel solely or in combination with other metals catalyzes the degradation reaction. After a positive influence of nickel on the HEPO formation was identified, the correlation between HEGly, HEHEAA and HEPO was studied to better understand their dependencies within the reaction equilibrium; formation of HEPO in dependence on HEGly and HEHEAA, respectively is shown in Figure 13.

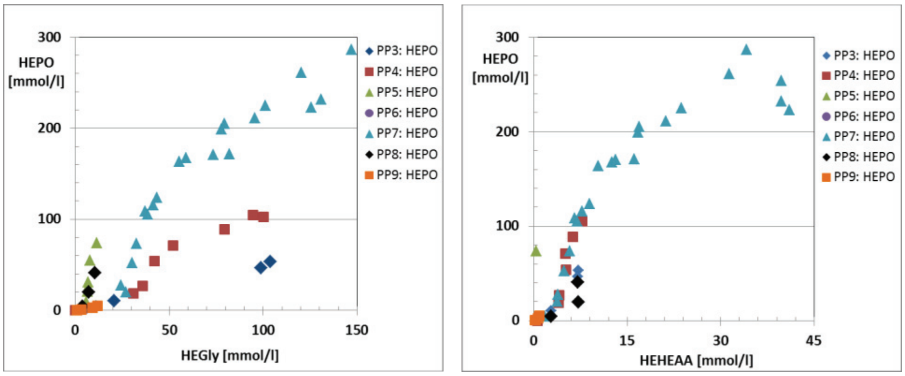


Figure 13: HEPO concentration against HEGly and HEHEAA concentration for the different pilot plant campaigns in this study

The correlation of HEPO against HEGly shows significant differences between the pilot plant campaigns. For one, the amount of HEPO formed per HEGly is not the same for the different campaigns. Additionally, it appears that there is a campaign specific limit on how much HEPO will be formed. The second step of the reaction appears to be a quick reaction as the HEPO values correlate well with the HEHEAA values of seven pilot plant campaigns. The concentration of HEPO is 7-10 times higher than the HEHEAA concentration, pointing to a strong equilibrium shift towards HEPO. Having this in mind, the first reaction step (HEGly to HEHEAA, Figure 9) is probably better characterized by plotting the sum of HEPO and HEHEAA against the HEGly concentration (Figure 14).

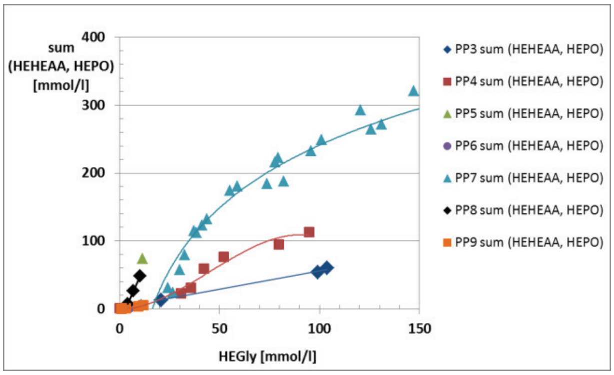


Figure 14: Sum (HEPO and HEHEAA) concentration against HEGly concentration for the different pilot plant campaigns in this study

Very different correlations were found for the seven different pilot campaigns. Some data show linear trends while others appear to follow a logarithmic function. But this could also be due to lower concentration ranges of the linear trending plants; with longer operation time a change might have been occurred. Additionally, the reaction from HEGly to HEHEAA is most likely impacted by plant specific factors like operation regime, plant design, solvent cycle time and alternate reactions. Based on this the formation of HEHEAA is the limiting step in HEPO formation. The amount of HEHEAA formed should possibly be manipulated by adjusting plant operation regime or plant design.

3.4. Magnitude of solvent degradation

Figure 15 depicts the total accumulation of HEGly, HEHEAA and HEPO over time by plotting the sum of these compounds against operating hours. A linear trend was found for each pilot campaign. The typical mid-range formation rate of the system HEGly-HEHEAA-HEPO is between 0.06 mmol/(l*h) and 0.12 mmol/(l*h). The two pilot plant campaigns which are not falling into this range have a formation rate of 0.31 mmol/(l*h) and < 0.01 mmol/(l*h), respectively. The other secondary degradation products were found in significantly lower concentrations; HEF, for example, was determined in the range of 3 % to 20 % from the sum (HEGly, HEHEAA, HEPO) depending on the operating hours and pilot campaign.

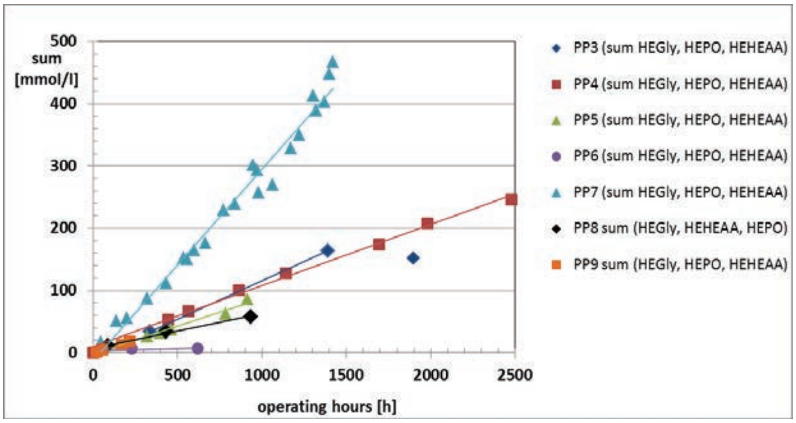


Figure 15: Sum (HEGly, HEHEAA, HEPO) concentration over time for the different pilot plant campaigns in this study

Since the development over time is not linear for all compounds, Figure 16 shows the amount of secondary degradation products (2^{nd} DP) determined at around 600 operating hours at each CC pilot plant campaign. Of course, only compounds analyzed are shown, the absence of a compound does not necessarily mean that it was not present in the corresponding solvent of a campaign. The system HEGly-HEHEAA-HEPO dominated with mid-range concentrations between 45 mmol/l and 70 mmol/l. The HEF concentration ranges from 0.3 mmol/l to 8.9 mmol/, with the majority falling into the range from 1.6 mmol/l to 4.8 mmol/l. the HEA concentration is mainly in the range from 0.1 mmol/l to 1.6 mmol/l, HEI concentrations are between 0.3 mmol/l to 2.9 mmol/l and OZD and HEEDA levels range from 0.1 mmol/l to 0.9 mmol/l. Figure 17 also shows the most typical primary degradation products (1^{st} DP) for the individual campaigns at around 600 operating hours. The formate concentration ranges from 3.4 mmol/l to 11.6 mmol/l, acetate concentration is between 0.1 mmol/l and 2.9 mmol/l, oxalate between 0.6 mmol/l and 1.6 mmol/l and glycolate between 0.5 mmol/l and 1.2 mmol/l. Strong variation is found across all campaigns and no mid-range section can be defined.

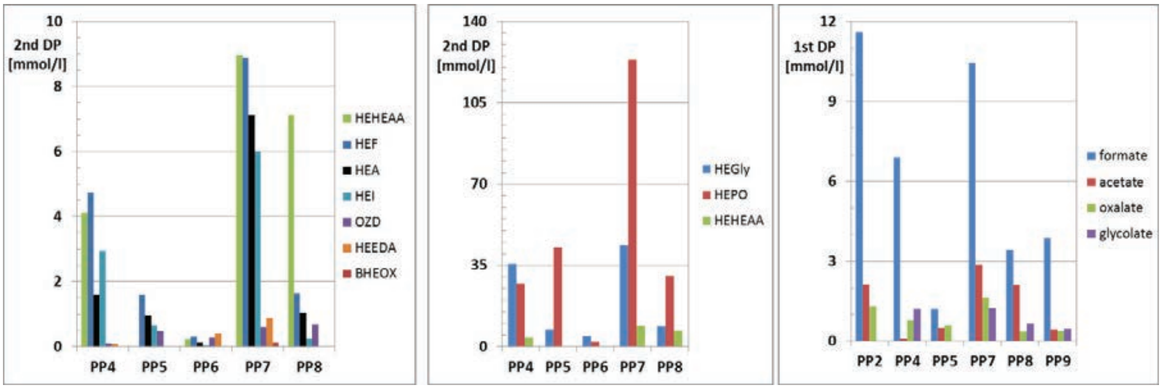


Figure 16: Amount of secondary and primary degradation products at around 600 operating hours for the different pilot campaigns in this study

The different behavior over time, meaning linear, exponential or other, causes a shift in concentration ratios with operation time. For a simplified comparison, the accumulated amount of degradation products was assumed to behave almost linearly due to the domination of the HEGly-HEHEAA-HEPO system. The accumulated amount of primary degradation products on the other hand shows a more exponential development. Hence, the ratio between secondary to primary degradation products will change with operating time. Accordingly, the solvent chemistry will change and alternate reactions might take place. TOC analysis of one plant indicated, that at the end of the campaign, a significant amount of unknown, organic degradation products was present in the solvent. Hence, the current, typical analytical scope does not cover the whole reaction chemistry.

4. Summary

The correlation of the available, MEA based CC pilot plant campaign data as discussed above can be summarized as follows:

- The HEPO concentration shows a strong correlation with the nickel concentration in the solvent at low concentrations (< 0.04 mmol/l).
- The corresponding correlation between HEPO and iron was less significant, but some correlation at low concentrations might be given (< 1 mmol/l).
- HEHEAA formation is the limiting step in the equilibrium reaction of HEPO formation from HEGly.
- The HEF concentration correlates well with the formate concentration for all plants across all concentration ranges.
- The formate concentration shows some linear correlation with iron at iron levels below 1 mmol/l, which occurs to different extents for the different campaigns.
- A correlation between HEA and acetate could be seen, but showed more variation compared to HEF, which might be due to analytical issues.
- HEGly and HEPO are the most dominant degradation products and their sum together with HEHEAA shows a linear increase over time.

5. Conclusions

The comparison of the different CC pilot campaigns leads to following conclusions:

- Longer operation time for pilot campaigns is required as degradation product distribution will change with time. The impact on solvent behavior needs to be determined.
- Reliable, analytical data is required to investigate and understand dependencies. Hence the analytical scope of pilot campaigns should not neglect periodic sampling of the solvent.
- At this point, it is not clear, if the HEGly formation is catalyzed in any form or if the reaction depends on other factors. However, since HEGly consumes MEA by further reactions, it needs to be limited within the solvent to reduce the overall MEA loss.
- The initial oxidation to carbonic acids should be minimized in order to reduce amide formation, since this is another pathway of MEA consumption.
- Nickel and potentially iron play an important role in some of the degradation reactions. The correlations have shown that a limitation to 0.02 - 0.04 mmol/l (1.2 – 2.4 mg/l) nickel and 0.1 mmol/l (~ 6 mg/l) iron within the solvent is preferable.
- Further recommended studies:
  - Impact of other metals on solvent degradation. Potential candidates could be molybdenum (as it occurs as part of stainless steel corrosion) and metals commonly found in fly ash (e.g. vanadium and manganese).
  - More research into the initial MEA oxidation mechanism is required. And more importantly, how to control this initial degradation in a pilot plant (on site variation of oxygen saturation and / or cycle time, if possible).
  - Comparison of the campaigns from different CC pilot plants provided a valuable insight into the chemistry, but plant design and operational conditions need to be considered to complete the data assessment.

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