EVALUATION OF RESULTS FROM SDR CAMPAIGNS AND PILOT DATA

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Abstract

For ethanolamine (MEA) many degradation products have been identified and quantified, and the formation of these compounds at different process conditions should be verified. This short paper shows that lab scale experiments, especially cycled degradation rigs, are capable of mimicking formation of the major degradation compounds found in larger pilot campaigns. A larger build-up of HEEDA in the cycled degradation experiment, compared to pilot samples, was observed. Observations like this could play a role to understand why deviations between lab scale and pilot plant or pilot plants occurs.

Keywords: CO₂ capture, amine solvents, degradation products, comparison lab and pilot data

1. Introduction

In post-combustion CO_2 capture with chemical absorbents, the absorbent chemically binds to the CO_2 and then it is cycled to the desorber where the reaction is reversed. In addition to the main reaction, other unwanted reactions also take place leading to products that often are called degradation compounds. Formation of these compounds are not necessarily reversible, and their formation could lead to operational problems as foaming, fouling and corrosion. Furthermore, the formation of these compounds reduces the CO_2 capacity of the solvent and may also produce compounds that are of environmental or health concern. Studying the chemical stability of the solvent at various process conditions is therefore a necessity in screening programs for new solvents [1]. Low chemical stability, formation of volatile compounds that could have an HSE impact are risks that need to be evaluated for different solvent systems. Further, chemical stability also includes evaluation of a solvent corrosivity since they are closely related, and these properties are potential showstoppers for a given solvent technology. However, there are several existing and future mitigation technologies to for example reduce emission levels and improve chemical stability.

Ethanolamine (MEA) is the most studied amine when it comes to identification and quantification of degradation compounds. This involve advanced analytical techniques which are not available on site [2]. Mechanisms of several of the major degradation compounds for MEA have been suggested and a summary of this could be found by Gouedard [3]. For some of the degradation compounds several pathways have been suggested and it is likely that more than one reaction can take place in the capture plant. Due to variation in operational conditions in a plant, as well as differences related to flue gas impurities and other additives or mitigation technologies introduced, comparison is never easy.

Amines in the CO_2 capture process reacts to other amines (non-volatile or volatile, polyamine, alkylamine), ammonia, aldehydes, acids (organic and inorganic, as well as amino acids), ring structures (oxazolidinone, oxazoline, piperazinone, imidazole, pyrazine, pyridine), nitramines, nitrosamine (formed from secondary amine), amide. Even if many degradation compounds are formed, several of them are only present in amounts lower than 100 mg/kg. The parent amine molecular structure is a requirement to predict which compounds are formed and to evaluate if actions must be taken for mitigation regarding safe working conditions and emissions. Various analytical instruments are required to fully map the degradation products, since no single instrument can detect all the compounds. An overview of different analytical techniques used for different compounds could be found in Cuccia et al. [4] while exploration of degradation chemistry using advanced chemical analysis is described by Grimstvedt et al. [2].

The aim of this work is to share light on several of the major and important degradation compounds formed in MEA solvent and how different process conditions influence them. Here this is based on observations from bench scale experiments mimicking the capture process (solvent degradation rig - SDR) and available pilot data e.g., from Technology Centre Mongstad (TCM).

2. Experimental set-up

SINTEF's solvent degradation rig (SDR) is an advanced laboratory test rig for studies of solvent degradation at process conditions. The total solvent inventory is about 5 liters. The solvent is cycling in a combined absorber and desorber setup where the temperature of the absorber and desorber is set at different levels (absorber: 25 - 80°C, desorber: 110-150 °C). The flue gas is a synthetic mixture of different gases (e.g., N_2, CO_2, O_2, NOx, SOx) where the composition could be varied. Compared with separate setups for oxidative or thermal degradation, the SDR enables studies of the combined effect of different

degradation mechanisms occurring in a real-life process. More details around the rig are given by Einbu et. al 2012 [5]. Three different MEA campaigns have been conducted, and the duration and conditions have varied for all of them as shown in Figure 1. The factors that have been varied are the oxygen concentration (12 or 18 vol%), reboiler temperature (120 or 140 °C) and NOx concentration (5 or 50 ppmv for campaign in 2012 and 2016 and 10 or 100 ppmv in 2020) [5, 6]. For the last campaign (2020) the MEA concentration was increased to 40wt% (30wt% used in the earlier campaigns) and absorber sump stripping using N_2 was also tried for two periods (week 5 and week 8). The impact of NOx is mostly related to possible nitrosamine formation.
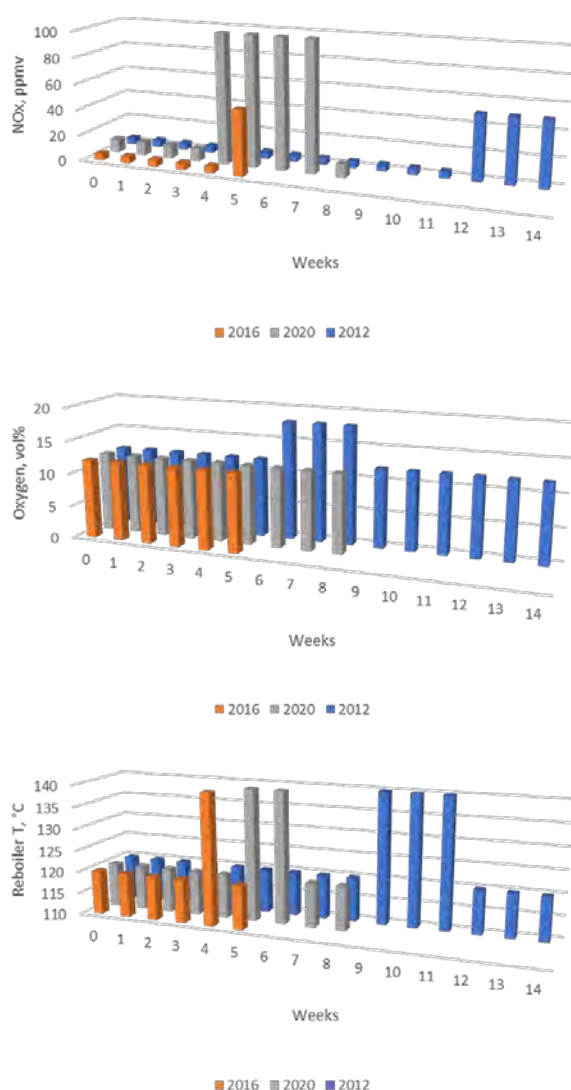

Figure 1: NOx (ppmv), reboiler temperature (°C) and oxygen (vol%) variations for the different campaigns.

LC-MS (Liquid Chromatography – Mass Spectrometry) is our preferred method for analyses of degradation compounds. Analysis of the degraded samples were carried out on a LC-MS/MS system, a 6490 triple quadrupole mass spectrometer that is coupled with a

1290 Infinity LC chromatograph and an Infinity autosampler 1290 Series G4226A from the supplier Agilent Technologies. The analytical column for degradation compounds described in Figure 3 was Discovery® HS F5 HPLC Column from Sigma-Aldrich.

General abbreviations and short name for chemical compounds used are given in Table 1.

Table 1: Abbreviations and short name for chemical compounds.

Abb		CAS
CO₂	Carbon dioxide	124-38-9
O₂	Oxygen	7782-44-7
N₂	Nitrogen	7727-37-9
NOx	Nitrogen oxide	
SOx	Sulfur oxide	
MEA	Ethanolamine	141-43-5
FeSO₄*7H₂O	Ferrous sulfate heptahydrate	7782-63-0
HEA	N-(2-hydroxyethyl)-acetamide	142-26-7
HEF	N-(2-hydroxyethyl)-formamide	693-06-1
HEGly	N-(2-hydroxyethyl)-glycine	5835-28-9
HEI	1H-imidazole-1-ethanol	1615-14-1
HEPO	4-(2-hydroxyethyl)-2-piperazinone	23936-04-1
OZD	2-oxazolidinone	497-25-6
HEEDA	2-[(2-aminoethyl)amino]-ethanol	111-41-1
HEHEAA	N-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide	144236-39-5
MEA-urea	N,N'-bis(2-hydroxyethyl)-urea	15438-70-7

3. Results

3.1 Principal component analysis for bench scale degradation experiments and pilot data

Chemical stability of the different solvents has been studied under various process conditions mimicking different parts of the capture process [7-14]. The different studies also have variations in laboratory set-ups, process conditions as well as chemical components. A principal component analysis (PCA) was conducted to investigate how these bench scale degradation experiments, either separate oxidative degradation studies or cycled studies, compares with respect to the degradation profile (concentrations of several degradation compounds) against pilot scale. In PCA the original variables are reduced to a few new variables (principal components) in directions that explain the main variation in the data set. Mathematically this is done by determine the eigenvalues and eigenvectors of the covariance matrix where the vectors with highest eigenvalues are chosen. The value for each sample in this new coordinate system is called the score, which describe the data structure in terms of sample patterns, and more generally show sample differences or similarities. In this case a range normalization of the data prior to the PCA was done.

The obtained score plot for principal component 1 versus principal component 2 is shown in Figure 2 and shows that the SDR campaigns have similar trends as the Pilot campaigns. For the oxidative experiments, the experiments with low oxygen (6%O_2) and high temperature (75°C) show a trend that is close to the SDR and Pilot campaigns.
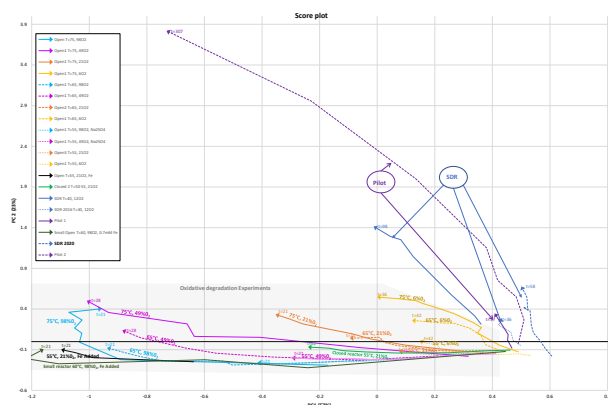

Figure 2: PCA score plot comparing lab-scale experiment with SDR and pilot data for following degradation compounds: HEGly, HEF, BHEOX, HEA, HEPO, OZD and HEI. Duration of experiments (t) is in the unit of days.

3.2 SDR comparison

As mentioned earlier, three MEA campaigns have been conducted since 2011 with the solvent degradation rig. Different process conditions have been varied in the campaigns to study the different conditions influence on the formation and destruction (decomposition or as middle product) of degradation compounds. The operational hours of the campaigns have varied from 860 to 2352 hours. Since the first campaign, more degradation compounds have been identified and quantified for MEA. A thorough mapping of degradation compounds from different amine structures requires a combination of advanced analytical instrumentation as well as understanding related to amine structure and their destruction mechanisms.

For MEA, mechanisms have been suggested for several of the degradation compounds, and some of these are transferable to other amines if one consider the structure of the parent amine. Lepaumier et al. have suggested more generalized mechanisms for both alkanolamines and polyamines [11, 12, 15] while Gouedard has summarized mechanisms related to MEA degradation compounds in her thesis [3].

Figure 3 shows the development of eight degradation compounds (2 of them were not available in 2012) for the three campaigns. These compounds are also quantified in the MEA campaign at Mongstad described by Morken et al. 2017 [16]. However, the SDR campaigns in 2016 and 2020 also quantified additional compounds. More details regarding these degradation compounds for the 2016 campaign are available in Vevelstad et al. [6]. Since there are no pilot data to compare with, these compounds will not be discussed in this short paper. However, it is worth noticing that one of these compounds, MEA-urea, was a

major contributor to the degradation in the SDR rig. It is likely that MEA-urea also is present in MEA pilot samples, but this must be verified by chemical analysis. There is currently no standard analytical method for analysis of degradation compounds in MEA, thus there exists a large variation in degradation compounds reported from the different pilot campaigns [17].
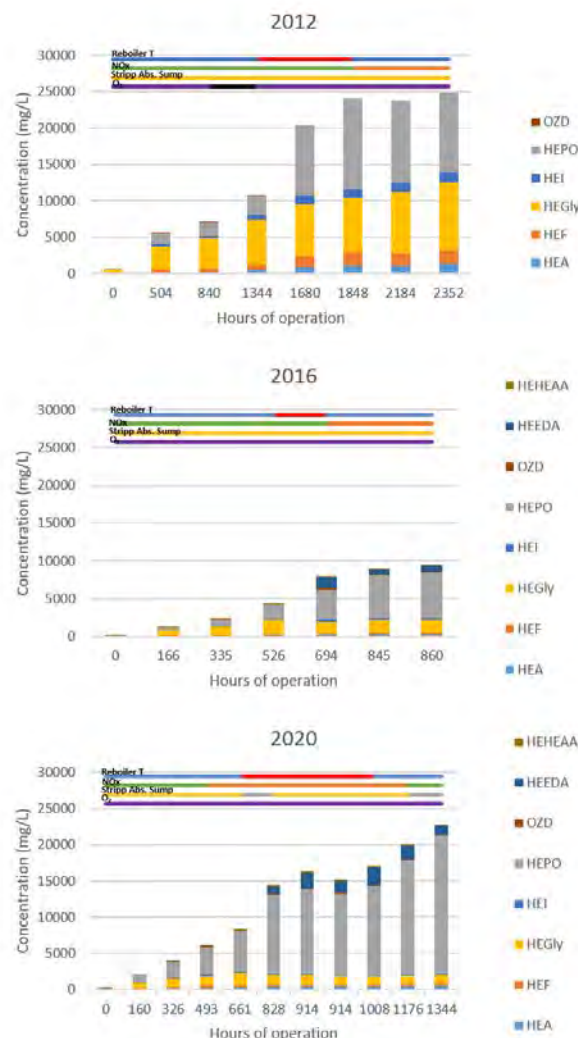

Figure 3: Development of eight degradation compounds (concentration mg/L) as a function of time (hours of operation) in the different SDR campaigns (standard conditions; reboiler temperature 120 °C (blue), NOx 5 or 10 ppm (green), no stripping absorber sump (yellow) & oxygen concentration 12% (purple)).

As shown in Figure 3, the major degradation compounds amongst these eight compounds are HEPO and HEGly. Similar observations were also found in pilot samples from MEA campaigns at Tiller [8], Esbjerg [8] and Technology Centre Mongstad (TCM) [16, 18]. HEA, HEI and HEF are also important degradation compounds in pilot samples. In general, the same major degradation compounds are identified both in the MEA campaigns in the SDR and in TCM (comparing the degradation components compared at both places). Although, some deviations can be observed for compounds at trace levels

(concentrations close to lower limit of quantification - LOQ).

An interesting observation is the process conditions in the SDR rig seem to favor more build-up of HEEDA compared to the campaign at TCM. HEEDA is a diamine, which has been suggested to be an intermediate in the reaction toward several imidazolidinone and piperazinone [3], where the imidazolidinone pathway is more familiar. HEEDA's role as known intermediate has often been used to explain the low concentration observed in pilot samples and in thermal degradation experiments. Recently several formation reactions of HEEDA have been suggested [3, 19], and reactions with nitrite has an important role for one of these. In the TCM campaign, nitrite was not observed above the LOQ (10 mg/L) [16]. Unfortunately, data for nitrite were not available for the different SDR campaigns and a hypothesis regarding nitrite and HEEDA could therefore not be verified. It has also been postulated that fly ash could inhibit nitrite-induced MEA degradation [19]. Further investigation should include analysis of other degradation compounds that are expected to be formed in higher amounts in the presence of nitrite, such as MEA-urea.

It is difficult to support degradation mechanism pathways suggested for different compounds due to variation in which components that are quantified in different pilot samples. Therefore, lab experiments combined with pilot data with focus on mapping and quantification of large set of degradation compounds, even for MEA as a solvent, are still important to explain the degradation loss of MEA, and to give input to solvent management strategies to maintain a fresh and healthy solvent.

4. Summary

Lab scale experiments, especially cycled degradation rigs, are capable of mimicking formation of the major degradation compounds in pilot campaigns. For some smaller compounds, some deviations between cycled degradation experiment and pilot data, e.g., HEEDA, could be observed, however more information is required to fully understand these observations. Such observations could however play a role to understand why deviations between lab scale and pilot plant or between pilot plants occurs.

Acknowledgements

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