17th International Conference on Greenhouse Gas Control Technologies **GHGT-17**

20th -24th October 2024, Calgary Canada

CESAR1 solvent degradation in pilot and laboratory scale

Vanja Buvik[a]* Andreas Grimstvedt[a], Kai Vernstad[a], Hanna K. Knuutila[b], Muhammad Zeeshan[c], Sundus Akhter[c], Matthew Campbell[c]

[a] *SINTEF Industry, NO-7465 Trondheim, Norway*
[b] *Department of Chemical Engineering, University of Science and Technology (NTNU), N-7491 Trondheim, Norway*
[c] *Technology Centre Mongstad, 5954 Mongstad, Norway*

Abstract

The non-proprietary CESAR1 amine blend has been widely studied for use as a solvent for post-combustion CO_2 capture.[1–5] Despite of its relative popularity in the solvent market, there are still many knowledge gaps connected to the stability of CESAR1. The mixture of 2-amino-2-methyl propanol (AMP, CAS 124-68-5) and piperazine (PZ, CAS 110-85-0) is known to be much more stable than ethanolamine (MEA, CAS 141-43-5), both under oxidising conditions, thermal stress, and at the cyclic conditions in the CO_2 capture plant. Despite of solvent degradation being low compared to other solvents, degradation phenomena need to be fully understood before a solvent can be safely implemented for large or full-scale CO_2 capture from industrial sources, to fully comprehend potential environmental and operational impacts, and ensure safety for operators and neighbours.

In this work, we aim to fully elucidate the degradation patterns of CESAR1 at industry relevant conditions. Oxidative and thermal degradation experiments with AMP, PZ, and CESAR1 will be performed, and their degradation patterns and chemistry will be compared to solvent samples from industrial operations. In the Norwegian CCS research centre (NCCS) and the HEU project AURORA, new CESAR1 degradation compounds have been identified and quantified. Currently, LC-MSMS methods for the quantification of more than 30 CESAR1 specific degradation compounds are available at SINTEF, in addition to generic amine degradation compounds such as carboxylates, aldehydes, and alkylamines. A total nitrogen (TN) analysis was also performed to assess whether all nitrogen containing degradation compounds have been identified in the used solvent.

A CESAR1 solvent sample from a pilot scale operation at the Technology Centre Mongstad (TCM) is currently partly characterised. Figure 1 shows the concentrations of 29 of the components present in the used solvent. In addition to these, acetone (148 mg/L), formaldehyde (89 mg/L), and acetaldehyde (4 mg/L), as well as the solvent amines AMP (264 g/kg) and PZ (94 g/kg) were also quantified. Furthermore, 20 other compounds were also included in the analysis of the sample, but none of them were found above their respective limits of quantification (0.1-1 mg/kg, depending on compound).

* Corresponding author. Tel.: +47 73 78 03 60, *E-mail address:* vanja.buvik@sintef.no

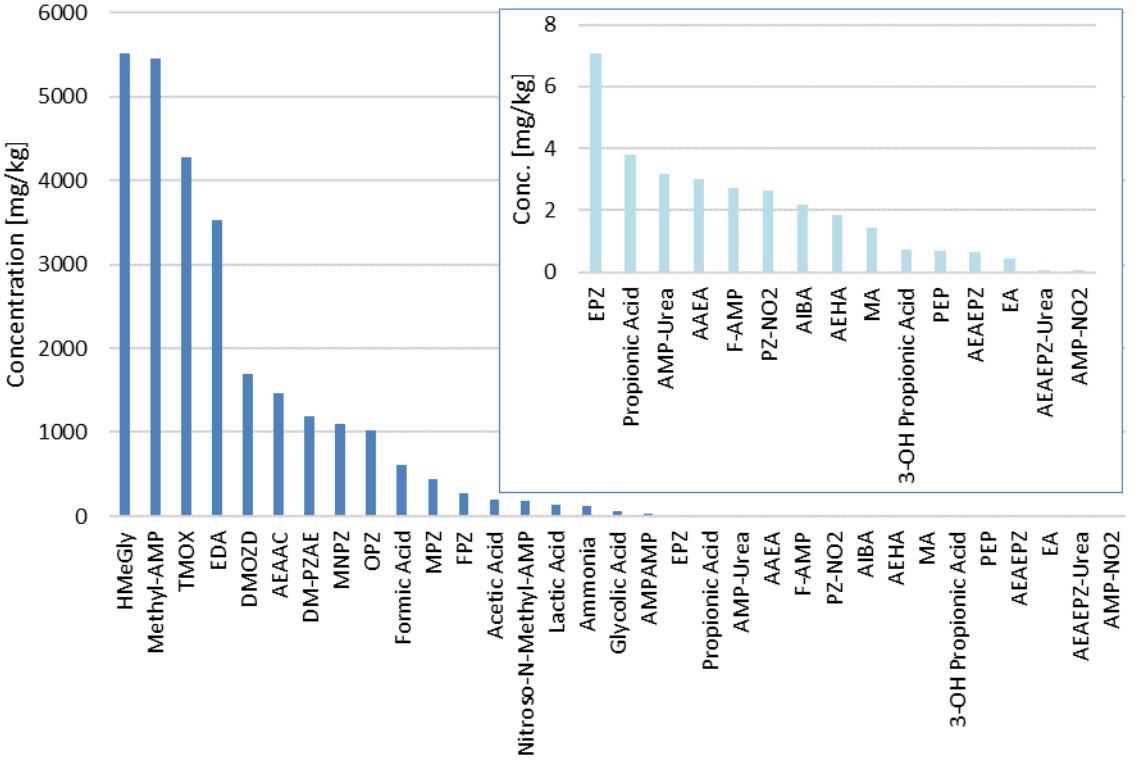
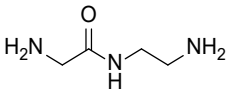
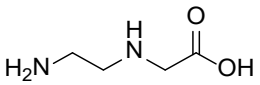
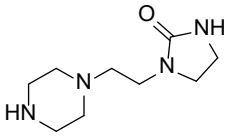
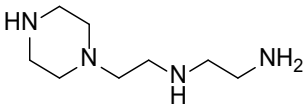
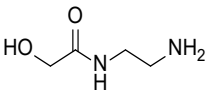
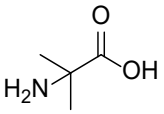
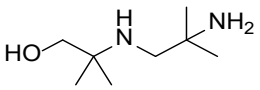
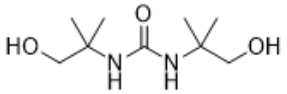
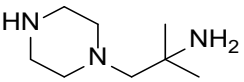
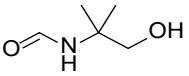
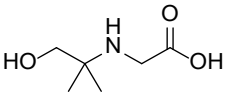
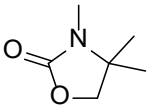


Figure 1: Concentrations of degradation compounds in CESAR1 solvent after ended operation at TCM.

The majority of the quantified compounds, like HMeGly (CAS 1154902-47-2), TMOX (CAS 15833-17-7), DMOZD (CAS 26654-39-7), EDA (CAS 107-15-3), and AEAAC (CAS 24123-14-6) seem to originate from oxidative degradation reactions. Oxidative degradation experiments with the single amines, as well as the mixture, it will be possible to establish which mechanistic routes are more likely to take place. The high concentration of methyl-AMP (CAS 27646-80-6) is likely due to its presence as a contaminant in fresh AMP, as a side product of AMP synthesis. As expected, there is also a significant presence of nitrosamines in the used CESAR1 solvent, mainly that originating from PZ nitrosation, MNPZ (CAS 5632-47-3), but also nitroso-*N*-methyl-AMP (CAS 27646-81-7). Smaller amounts of the corresponding nitramines, PZ-NO_2 (CAS 42499-41-2), and AMP-NO_2 (CAS 1239666-60-4) are also present in the solvent. TN analysis of the same solvent sample as was characterised with LC-MSMS, indicates that all, or nearly all nitrogen containing degradation compounds have been identified in the used CESAR1 sample from TCM.

At the GHGT-17 conference we will present some degradation compounds that have not been quantified in CESAR1 previously (or other amine solvents), including the ones depicted in Table 1. In addition, results from purely oxidative and thermal degradation experiments are compared with the TCM operational sample to identify the conditions at which each compound is formed. The findings will aid in the understanding, controlling, and mitigation of degradation during large-scale CO_2 capture operations with the CESAR1 solvent.

Table 1: Identified degradation compounds that have previously not been quantified in CESAR1, PZ, or AMP.

Abbrev.	Name	Structure	CAS-number
AAEA	2-amino-*N*-(2-aminoethyl)-acetamide		84354-31-4
AEAAC	*N*-(2-aminoethyl)-glycine		24123-14-6
AEAEPZ urea	1-[2-(1-Piperazinyl) ethyl]-2-imidazolidinone		104087-61-8
AEAPZ	N_1-[2-(1-Piperazinyl) ethyl]-1,2-ethanediamine		24028-46-4
AEHA	*N*-(2-aminoethyl)-2-hydroxy-acetamide		83019-76-5
AIBA	2-Aminoisobutyric acid		62-57-7
AMPAMP	2-[(2-amino-2-methylpropyl)amino]-2-methyl-1-propanol		72622-74-3
AMP urea	*N*,*N*'-bis(2-hydroxy-1,1-dimethylethyl)-urea		162748-76-7
DMPZEA	α,α-Dimethyl-1-piperazineethanamine		1259927-55-3
F-AMP	*N*-(2-Hydroxy-1,1-dimethylethyl)formamide		682-85-9
HMeGly	*N*-(2-hydroxy-1,1-dimethylethyl)-Glycine		1154902-47-2
TMOX	3,4,4-trimethyl-2-oxazolidinone		15833-17-7

Keywords: AMP; PZ; stability; oxidative degradation; thermal degradation

Acknowledgements

1) The AURORA project, which has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No. 101096521. https://aurora-heu.eu/
2) This publication has been produced with support from the NCCS Research Centre, performed under the Norwegian research programme Centre for Environment-friendly Energy Research (FME). The authors acknowledge the following partners for their contributions: Aker BP, Aker Carbon Capture, Allton, Ansaldo Energia, Baker Hughes, CoorsTek Membrane Sciences, Elkem, Eramet, Equinor, Gassco, Hafslund Oslo Celsio, KROHNE, Larvik Shipping, Norcem Heidelberg Cement, Offshore Norge, Quad Geometrics, Stratum Reservoir, TotalEnergies, Vår Energi, Wintershall DEA and the Research Council of Norway (257579/E20). https://nccs.no/

References

(1) Knudsen, J. N.; Andersen, J.; Jensen, J. N.; Biede, O. Results from Test Campaigns at the 1 t/h CO2 Post-Combustion Capture Pilot-Plant in Esbjerg under the EU FP7 CESAR Project; Abu Dhabi, 2011.
(2) Campbell, M.; Akhter, S.; Knarvik, A.; Muhammad, Z.; Wakaa, A. CESAR1 Solvent Degradation and Thermal Reclaiming Results from TCM Testing. **2022**.
(3) Moser, P.; Wiechers, G.; Schmidt, S.; Veronezi Figueiredo, R.; Skylogianni, E.; Garcia Moretz-Sohn Monteiro, J. Conclusions from 3 Years of Continuous Capture Plant Operation without Exchange of the AMP/PZ-Based Solvent at Niederaussem – Insights into Solvent Degradation Management. *International Journal of Greenhouse Gas Control* **2023**, *126*, 103894. https://doi.org/10.1016/j.ijggc.2023.103894.
(4) Mangalapally, H. P.; Hasse, H. Pilot Plant Study of Two New Solvents for Post Combustion Carbon Dioxide Capture by Reactive Absorption and Comparison to Monoethanolamine. *Chemical Engineering Science* **2011**, *66* (22), 5512–5522. https://doi.org/10.1016/j.ces.2011.06.054.
(5) Rabensteiner, M.; Kinger, G.; Koller, M.; Hochenauer, C. Pilot Plant Study of Aqueous Solution of Piperazine Activated 2-Amino-2-Methyl-1-Propanol for Post Combustion Carbon Dioxide Capture. *International Journal of Greenhouse Gas Control* **2016**, *51*, 106–117. https://doi.org/10.1016/j.ijggc.2016.04.035.