Towards understanding CESAR1 degradation

Vanja Buvik, Kai Vernstad, Andreas Grimstvedt, and Eirik Falck da Silva

SINTEF Industry, NO-7465 Trondheim, Norway

Corresponding author's e-mail address: vanja.buvik@sintef.no

Keywords: post-combustion capture, absorption, solvent stability, amine, AMP, PZ

ABSTRACT

A reason why aqueous ethanolamine (MEA) is still considered a benchmark solvent for CO_2 capture by some, despite of its relatively high energy consumption and relative instability compared to other solvents, is the abundance of knowledge and public data on MEA performance and chemistry. With more than 50 identified degradation compounds and successful attempts to find all nitrogen "lost" through MEA degradation in these degradation compounds, one can say that the mass and nitrogen balance of MEA during degradation, is closed. MEA is, however, no longer the solvent of choice for post-combustion CO_2 capture, but rather replaced with more stable and more energy efficient solvents and solvent blends. One of the most frequently used solvents that is non-proprietary, is an aqueous mixture of piperazine (PZ) and 2-amino-2-methylpropan-1-ol (AMP), mostly known by the name CESAR1, as it was developed during the EU project CESAR (**C**O_2 **E**nhanced **S**eparation **a**nd **R**ecovery) from 2008 to 2011. Despite many contributions from several research environments in the past decade on identification of degradation products and mechanisms of their formation, there still seems to be many compounds that need to be identified. CESAR1 is very stable during long-term operation and does not degrade much, especially compared to MEA (1). Still, it is important to elucidate the degradation paths that this solvent takes when it first decomposes, to find out if the degradation compounds it may form are of any concern to the environment or smooth operation of the plant. Acquiring the missing knowledge about CESAR1 degradation will facilitate safe and predictable operation of the CO_2 capture process. It might not be necessary to always keep track of all components in the solvent, but we must identify all its constituents once and for all, to find out which ones of them require close monitoring. Some of these may pose a threat to the environment, such as certain carcinogenic nitrosamine compounds, others can be problematic for the operation i.e., being corrosive or acting as degradation catalysts or foaming agents.

Continuing the work of (2–8) we are aiming to complete the whole CESAR1 degradation picture through efforts in the Norwegian CCS Research Centre (NCCS) and the newly started Horizon EU project AURORA. To do this, a substantial effort is in process to develop analytical methods for identification and quantification of more compounds, mechanisms must be elucidated and samples from laboratory and pilot scale will be studied.

T. Wang (7) managed to identify 47% of the nitrogen containing compounds after oxidative PZ degradation and 57% of them for AMP, meaning that there were still significant amounts of oxidative degradation products from laboratory scale experiments missing to identify and quantify. Many of these were suggested in the thesis, but their presence in the degraded amines has yet to be confirmed or disproved. CESAR1 forms the degradation component that each amine forms separately (8), but also new products are expected in the blend of the two.

We are developing methods for the identification and quantification of 41 suspected degradation compounds, in addition to already having in-house methods for quantifying some degradation compounds found in either AMP, or PZ, whereof at least 20 have never been identified or quantified in these mixtures, and many of MEA's degradation products. Looking for these new compounds in used CESAR1 from laboratory-scale degradation experiments, as well as CESAR1 used for pilot-scale testing with real flue gas, will bring us closer to closing the knowledge gaps on CESAR1 degradation.

At the Trondheim CCS conference, we want to present the status of this work at this point, where we expect to have analysed some samples from laboratory-scale oxidative degradation experiments. We will discuss the compounds found with suggested formation routes and say something about their potential consequences for the operation and safety of the CO_2 capture process.

Acknowledgements
This publication has been produced with support from two projects:
1) 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).
2) The AURORA project, which has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No. 101096521.

References
1. 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. Pz-Based Solvent Niederaussem–Insights Solvent Degrad Manag Oct 27 2022. 2022;
2. Davis JD. Thermal degradation of aqueous amines used for carbon dioxide capture. The University of Texas at Austin; 2009.
3. Freeman SA, Rochelle GT. Thermal degradation of aqueous piperazine for CO2 capture: 2. Product types and generation rates. Ind Eng Chem Res. 2012;51(22):7726–35.
4. Lepaumier H, Picq D, Carrette PL. New amines for CO2 capture. I. Mechanisms of amine degradation in the presence of CO2. Ind Eng Chem Res. 2009;48(20):9061–7.

5. Lepaumier H, Picq D, Carrette PL. New amines for CO2 capture. II. Oxidative degradation mechanisms. Ind Eng Chem Res. 2009;48(20):9068–75.
6. Nielsen PT, Li L, Rochelle GT. Piperazine degradation in pilot plants. Energy Procedia. 2013;37:1912–23.
7. Wang T. Degradation of aqueous 2-Amino-2-methyl-1-propanol for carbon dioxide capture. 2013;
8. Campbell M, Akhter S, Knarvik A, Muhammad Z, Wakaa A. CESAR1 Solvent Degradation and Thermal Reclaiming Results from TCM Testing. 2022;