



De-oxygenation as countermeasure for the reduction of oxidative degradation of CO₂ capture solvents

Juliana Monteiro, Isabella Stellwag, Martin Mohana, Arjen Huizinga, Purvil Khakharia, Peter van Os, Earl Goetheer¹

¹TNO, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

Keywords: CO₂ capture, MEA, solvent management, oxidative degradation, removal of dissolved oxygen.

Abstract

Solvent degradation is one of the major challenges in the operation of post-combustion CO₂ capture plants. Oxidative degradation of amines is a complex catalytic mechanism. Primary oxidative degradation products include volatile products (such as ammonia) and heat stable salts (such as acetate, formate, glycolate and oxalate) [1].

Based on results from several pilot plant runs, mostly using monoethanolamine (MEA), an out-of-control solvent chemistry is observed. This has been attributed to oxidative degradation. The main factors controlling the rate of oxidative degradation are the dissolved oxygen content, temperature and residence time. In a model formulated by TNO [2], these factors are explicitly considered in a framework consisting of the main unit operations of a CO₂ capture plant. The model was validated based on TNO's own pilot plant campaign. The validated model was then used predict the results from other pilot plants. All the results pointed towards the dissolved oxygen (DO) content being the most important factor leading to oxidative degradation. Therefore, solutions aiming towards reducing the DO content would result in decreased oxidative degradation.

Furthermore, the solvent is exposed to oxygen in the absorber packing and in the absorber sump. While the solvent exposure time of the solvent to oxygen may be comparable in the absorption sump to that in the packing [3] (depending on the plant's operational conditions and design), the quantity of dissolved oxygen is higher in the absorber sump. Therefore, a solution for reducing the oxidative degradation should target the oxygen removal in/before the absorber sump.

Given these aspects, TNO aims to develop and demonstrate a countermeasure for oxidative degradation. For this purpose, TNO has developed the Dissolved Oxygen Removal Apparatus (DORA). A gas-liquid (or liquid-liquid) contactor is used, and different strategies to remove the dissolved oxygen from 30wt% MEA rich solution (0,5 molCO₂/mol MEA, saturated with oxygen) are experimentally tested. The first strategy is the use of sweep gases, including N₂, CO₂ and air/N₂ mixtures (see initial results in Figure 1, left). The second strategy is to apply vacuum to desorb oxygen. The third strategy is to use an oxygen scavenger, and in this case a liquid-liquid contactor is used (see initial results in Figure 1, right).

The experimental parameters investigated include the contact temperature (20 to 60°C) and pressure, the ratio between the liquid and gas flowrates (L/G) and the chemical used as oxygen scavenger. After the various proposed solutions are screened, the best performing solution is further tested by connecting DORA to an in-house CO₂ absorption/desorption microplant (see Figure 2) also running

with 30wt% MEA. The performance of the technology is verified by monitoring quantity of removed oxygen, as well as the emissions of ammonia. The system design is such that DORA can be by-passed at any time, while keeping the cyclic operation of the microplant,. This allows for establishing baselines of the operation without DORA in order to properly demonstrate the technology impact. The demonstration tests will be performed using freshly prepared MEA solution, as well with MEA solution used in a pilot campaign (RWE's Coal Innovation Centre at Niederaussem, Germany).

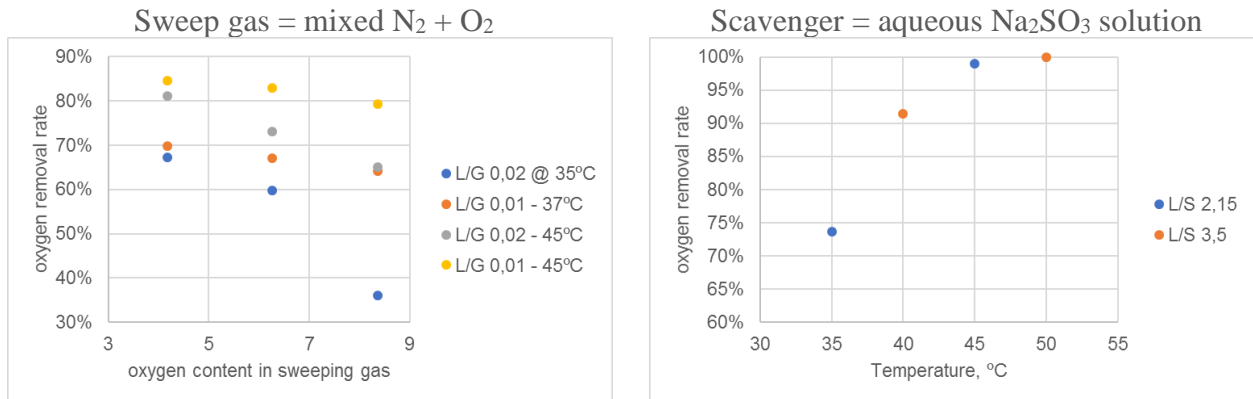


Figure 1: Initial results using the DORA set-up. L = amine solution flowrate, m³/h; G = artificial flue gas flowrate, Nm³/h; S = scavenger solution flowrate, m³/h.

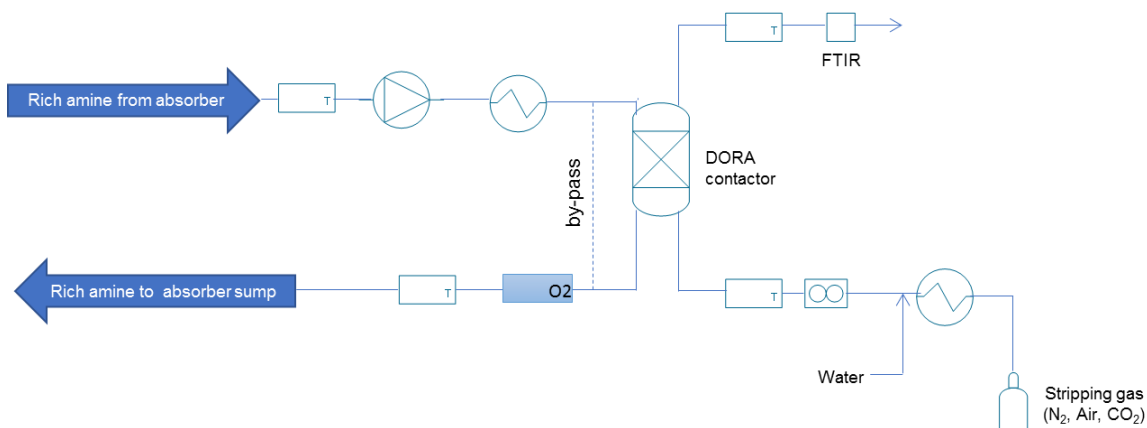


Figure 2: Schematic representation of the dissolved oxygen removal apparatus (DORA) using a sweeping gas

The oxygen removal process is simulated in ASPEN Plus, and the experimental data is used to validate the simulations results. The validated model is used to optimize the design of the contactor, as well as determine the optimum operational parameters, taking into consideration the technical and economic impact of each proposed solution. The TNO degradation model is used to predict the avoided amine loss.

In future studies, the optimal countermeasure will also be tested for other CO₂ capture solvents.

Acknowledgements

ACT ALIGN CCUS Project No 271501

This project has received funding from RVO (NL), FZJ/PtJ(DE), Gassnova(NO), UEFISCDI (RO), BEIS (UK) and is cofunded by the European Commission under the Horizon 2020 programme ACT, Grant Agreement No 691712

www.alignccus.eu

This publication has been produced with support from the NCCS Centre, performed under the Norwegian research program Centres for Environment-friendly Energy Research (FME). The authors acknowledge the following partners for their contributions: Aker Solutions, ANSALDO Energia, CoorsTek Membrane Sciences, Gassco, KROHNE, Larvik Shipping, Norcem, Norwegian Oil and Gas, Quad Geometrics, Shell, Statoil, TOTAL, and the Research Council of Norway (257579/E20).

References

- [1] G. Fytianos, S. J. Vevelstad, and H. K. Knuutila, “Degradation and corrosion inhibitors for MEA-based CO₂ capture plants,” *Int. J. Greenh. Gas Control*, vol. 50, no. Supplement C, pp. 240–247, 2016.
- [2] S. Dhingra *et al.*, “Understanding and Modelling the Effect of Dissolved Metals on Solvent Degradation in Post Combustion CO₂ Capture Based on Pilot Plant Experience,” *Energies*, vol. 10, no. 5, p. 629, May 2017.
- [3] N. E. Flø *et al.*, “Results from MEA Degradation and Reclaiming Processes at the CO₂ Technology Centre Mongstad,” *Energy Procedia*, vol. 114, no. Supplement C, pp. 1307–1324, 2017.