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The Effect of Solvent Aging on the Performance of CESAR1 at Highest CO_2 Capture Rates from 98.0% to >99.9%

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Abstract

Application of high CO_2 capture rates at amine-based capture plants has a huge potential to minimise the need for the offset of residual emissions by carbon dioxide removal (CDR) technologies, such as direct air capture, which has high costs and a high specific energy consumption due to the low CO_2 partial pressure in air. As part of the Clean Energy Transition Partnership project DRIVE (Deep Removal of CO_2 and InnoVative Electrification concepts) key performance data of amine-based CO_2 capture from flue gas with highest capture rates are assessed in extended testing campaigns (24/7) at the capture pilot plant at Niederaussem with the CESAR1 solvent, an aqueous solution of 3.0 M 2-amino-2-methylpropan-1-ol (AMP) and 1.5 M piperazine (PZ) [1]. Flue gas source is a lignite-fired power plant (CO_2 content of the flue gas around 15vol.%) and the capture plant capacity is 317 kg CO_2/h at 95% capture rate. To investigate the process and operational performance at CO_2 concentrations in the treated flue gas <400 ppm an IR CO_2 analyser with the necessary accuracy is used (0-3000 ppm; detection limit 1%, linearity deviation +/-15 ppm; calibration gas: mixture of 99.98 vol.% N_2 and 200 ppm CO_2). The holistic evaluation of deep removal, corresponding to CO_2 capture rates of 98.0% to >99.9%, is based on a wide range of systematic parameter studies and tests of different process configurations at the CO_2 capture pilot plant and validated process models for highest capture rates using the mass-transfer rate-based simulator ProTreat®. No additional components were installed in the capture pilot plant to realise deep removal. In addition to the effect of solvent flow, desorption temperature, intercooler positioning, and the level of the solvent feed-in into the absorber column (3 or 4 active beds of structured packing) on the process performance, the impact of the aging of the CESAR1 solvent is analysed. Due to an exchange of the solvent inventory after more than 15,000 hours capture plant operation without application of any reclaiming system, in which degradation products and trace compounds from the flue gas accumulated to 9wt.%, it was possible to compare directly the energetic performance of the very aged and fresh CESAR1 solvent. Additionally, organic degradation products, metals and accumulated inorganic trace compounds in the solvent are analyzed.

Oxidative degradation occurs when dissolved oxygen reacts with the amines. To predict oxidative degradation of solvents, the degradation network model (DNM) was developed. Unlike fundamental degradation models, the DNM does not require knowledge of specific degradation mechanisms. Within the DRIVE project, the DNM has been updated and expanded. It now predicts

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degradation more accurately for (fresh) CESAR1 in a broader range of temperatures and loadings. Additionally, it has been cross-compared with laboratory experiments on degraded CESAR1 to ensure the model remains accurate for degraded solvent systems. The stoichiometric factor *a*, which represents oxygen consumption relative to solvent consumption, was treated as a fitting parameter to achieve modeled degradation rates in line with degradation rates obtained at the capture pilot plant at Niederaussem. The degradation rates of aged CESAR1 will be obtained during a 6-month campaign which will focus on investigating solvent losses due to degradation under optimal conditions for deep removal.

The pilot plant tests at Niederaussem demonstrated that with fresh CESAR1 solvent residual CO_2 concentrations in the depleted flue gas down to 90 ppm are achievable using the complete absorber length (4 beds) at a solvent regeneration temperature of 120°C, which corresponds to just 20% of the current CO_2 concentration in ambient air. For the aged solvent just 885 ppm could be achieved due to a lower amine concentration in the solvent. Instead of the amine concentration, the water content of the solvent was kept constant during the test campaign to avoid any issues with precipitation which might occur by exceeding any solubility limits in the solvent. For the aged solvent it is necessary to increase the temperature in the desorber to 130°C in order to reach a CO_2 content below 400 ppm in the depleted flue gas.
For the fresh solvent the specific energy demand for the solvent regeneration at 120°C using four active beds in the absorber increases by ca. 40% for raising the capture rate from 95.0% (2,951 MJ/kg CO_2, 8210 ppm CO_2 concentration in the depleted flue gas) to 99.8% (4,228 MJ/kg CO_2, 328 ppm) and by 50% to reach 99.95% (4,440 MJ/kg CO_2, 90 ppm), see Figure 1. Between capture rates of 95.0% and 99.9% the specific energy demand for the regeneration of the aged solvent is 300 to 500 MJ/kg CO_2 higher compared with the fresh CESAR1.

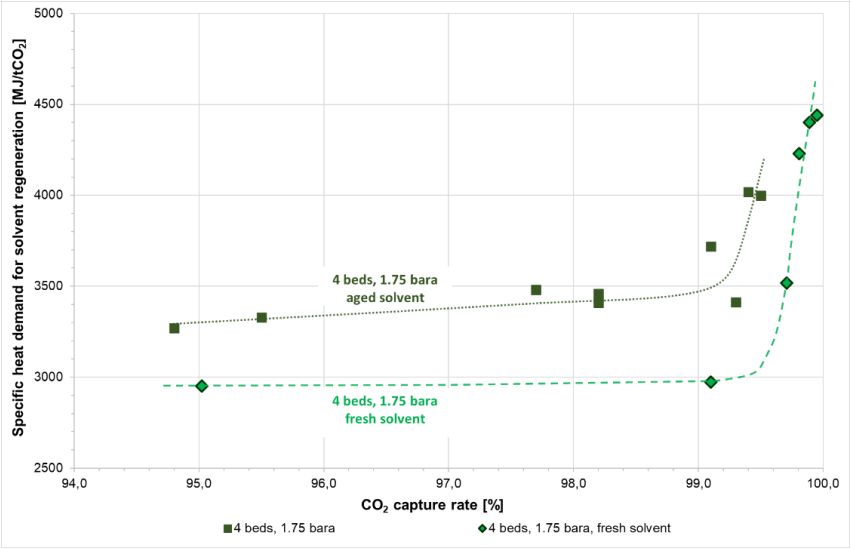

Fig. 1. Specific heat demand for the regeneration of the CESAR1 solvent depending on the CO_2 capture rate and solvent aging for capture plant operation with full absorber height (four active beds with structured packings) and a solvent regeneration temperature of 120°C.

It was shown that no self-accelerating degradation processes are initiated for the CESAR1 solvent despite extreme operating conditions regarding the CO_2 capture rate and the desorber temperature, and only moderate increases of solvent degradation occurred [3,4]. While an elevated desorber temperature seems to be an effective measure to increase the capture rate at moderate increase of the specific energy demand of the solvent regeneration and to control the nitrosamine concentration in CESAR1, there is always a trade-off between the positive aspects of an increased desorber temperature (higher CO_2 capture rates, higher CO_2 pressure, control of nitrosamine concentration in the solvent) and negative effects (higher pressure and value of the steam needed for the solvent regeneration, increased formation of volatile and non-volatile degradation products, which must be handled or might form hazardous components in consecutive reactions).

Results of the systematic operational parameter tests carried out in 8 months testing time are presented and are compared with the results from the optimised simulation models for aged and fresh CESAR1 solvent.

Keywords: AMP, PZ, solvent degradation, capture rate, longtime testing, CESAR1, highest capture rates, deep removal, solvent aging

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