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Solvent aging-effect on emissions of CESAR1 and performance of emission mitigation technologies after 500 h and 32,000 h operation

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Abstract

The effect of solvent aging on the emissions of an amine-based CO_2 capture plant is complex. On one hand the emissions of volatile degradation products should increase with an increasing degradation rate of the solvent which is observed for monoethanolamine (MEA) over the course of time. On the other hand and referring to Raoult's law (for ideal solutions and at infinite dilution, respectively) the vapor pressure of the volatile solvent components, like the amines, should decrease with increasing concentration of non-volatile contaminants in the solvent. However, as a unique testing campaign with a duration of 34,000 hours at the capture pilot plant at Niederaussem has shown, the degradation behavior of the CESAR1 solvent, an aqueous solution of 3.0 molar 2-amino-2-methylpropan-1-ol (AMP) and 1.5 molar piperazine (PZ), is generally linear over time. The lowest degradation rate was not found for the very fresh solvent, but for an aged one until 15,000 hours of operation without solvent inventory exchange. Removal of anions, which can act as ligands in metal cation complexation and thus influencing their catalytic redox capability in degradation reactions and their accessibility for rection partners, doubled the degradation rate. This degradation rate of CESAR1 was almost exactly reproduced 7,000 operating hours later when anions and cations have been removed by >80% simultaneously. De facto an increase of the ammonia emissions was detected as consequence of "making the solvent cleaner" (increase of the NH_3 emissions from 4 to 8 mg/m³, dry).

The contaminants which are accumulating over time and can decrease the vapor pressure of the solvent comprise degradation products (e.g. residues of the organic acids), corrosion products (e.g. iron, nickel cations) and species that are captured from the flue gas (chloride, sulfate anions). As a colligative property of the solution the vapor pressure depression depends on the number of ions formed in the solvent and the degree of dissociation and association of the contaminants. The effect of the solutes can be expressed by the van 't Hoff factor, which is the ratio between the actual concentration of particles produced when the substances are dissolved and the concentrations of substances as calculated from their mass. However, two aspects must be regarded in this context: the solvent is not representing an infinite diluted ideal solution and the relative contribution of the contaminants to the sum of dissolved ions is limited. Raoult's law may be adapted to a non-ideal system by incorporating fugacity coefficients which account for the interactions between molecules in the gas phase and deviations from the ideal-gas law and activity coefficients as a

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correction for interactions in the liquid phase. Regarding the sum of dissolved ions in the solvent it must be considered that even after a long time of operation without their removal their molar concentrations are considerably lower than the number of ions which are formed in connection with the carbamate formation. Another indirect operational effect of increasing concentrations of contaminants on the emissions which depends on the applied solvent management strategy might be important. When the concentration of inactive contaminants is increasing and the share of amines and alkaline compounds in the solvent is decreasing the solvent flow must be increased to remain a constant CO_2 capture rate. Therefore, the effect of an increasing L/G ratio on the level of emissions should be considered.

To analyze the effect of solvent aging on volatile and aerosol-based emissions of the CESAR1 solvent two testing campaigns are executed at the capture pilot plant at Niederaussem, Germany. The performance of emission mitigation technologies is tested after 32,000 operating hours without exchange of the solvent inventory and for a relatively fresh solvent inventory after 500 operating hours. Flue gas source is a lignite-fired power plant and the capture plant capacity is 300 kg CO_2/h @90% capture rate. The capture plant is operated 24/7. In each of the campaigns 20 emission mitigation configurations, comprising water wash as a benchmark, dry bed, double water wash, acid wash, two flue gas pretreatment technologies, and combined configurations of these technologies are applied. The measuring methodology comprises long measuring times between 1-5 days per configuration and repeat measurements to achieve reliable performance data at steady-state. The particle number concentration and size distribution in the flue gas at the inlet of the CO_2 absorber are determined using an ELPI+ system (14 size classes, size 6-5,400 nm) in longtime measurements, and the concentrations of AMP, PZ, and NH_3 in the flue gas downstream the last emission mitigation process step by FTIR. Additionally, for selected tests the amine concentrations in the water wash inventory is analyzed. To better understand the aerosol formation mechanism also solid aerosol particles have been collected and analyzed by SEM/EDX. For the test regarding the mitigation of aerosol-based emissions the aerosols are generated upstream the capture plant using a wet electric precipitator (WESP). The aerosol nuclei entering the CO_2 absorber consist for the largest part of $Na_xS_yO_z$. Only small particle concentrations occur of ca. 28,500 particles/cm³ (maximum 79,000 particles/cm³). By activating the WESP the particle number is increased by a factor of ca. 65 to ca. $1.9x10^6$ particles/cm³ which cause step-like increases of the amine emissions when no appropriate emission mitigation measures are taken. Through this the loss of piperazine increases with aerosol formation compared with AMP.

To explain the level of emissions depending on solvent aging, to understand the impact of the particle number concentration and size distribution in the feed gas, and to predict the individual and combined effects of the emissions reduction technologies, optimized models for volatile and aerosol-based emissions are set up. The optimization starts with ascertaining accurate input data for the modeling. Even for the basic benchmark technology water wash, most models use vapor-liquid equilibrium data that are fitted for concentration ranges pertinent for the absorber operation, which means for concentrations one order of magnitude higher than can be expected for the water wash inventory. Here, improving the model regarding the CO_2 loadings at the lower amine concentration in the water wash section is also important. Therefore, vapor-liquid equilibrium experiments of unloaded and loaded CESAR1 at compositions relevant to water wash systems have been carried out. The data are used to improve thermodynamic models used in process models. Additionally, the growth of aerosols for selected configurations of the capture plant and the emission mitigation systems are investigated based on an existing aerosol droplet growth model, which is further developed and validated with the results of the testing campaigns at Niederaussem. This strengthens the mechanistic understanding of the effect of emission mitigation technologies, the formation of volatile versus aerosol-based emissions and possible effects of solvent aging.

The testing campaigns are carried out as part of the three-year project SCOPE (Sustainable OPEration of post-combustion Capture plants) from the third ERA-NET Co-fund ACT program, project no 327341, with 24 partners from industry, authorities, research, and academia and six ACT countries, Germany, India, The Netherlands, Norway, United Kingdom, and the USA. The overarching goal is to close existing knowledge gaps and ensure that emission reduction for amine-based, commercial and large-scale CCUS is technically feasible, cost-efficient, and robust enough to mitigate environmental risks and to gain more public awareness and acceptance for this indispensable climate protection path. A prerequisite for establishing reasonable guidelines for controlling emissions and validating and optimizing emission models is the test of individual mitigation technologies in an industrial environment for an appropriate range of industrial use cases and amine-based solvents. SCOPE comprises pilot plant testing and investigations at six sites which go hand-in-hand with experimental solvent characterization to provide the required reliable process modeling data, real operational data, samples, and costs for the assessment of the individual emission mitigation technologies.

It is demonstrated that very effective emission reduction configurations are available to reduce the emissions below the detection limit of the FTIR for AMP and <2 mg/m³ for PZ (estimated measurement uncertainty 1 mg/m³), regardless of the particle number concentration in the flue gas and the aging state of the solvent. Selected results regarding the performance of the tested emission mitigation technologies and the first findings from the comparison of measured data with simulated volatile and aerosol-based emissions will be presented.

Keywords: post-combustion capture; amine; CESAR1; AMP; piperazine; emission mitigation; longtime testing; pilot plant; volatile emissions; aerosol; particles; simulation; vapour-liquid equilibrium; solvent aging, solvent degradation