



16th International Conference on Greenhouse Gas Control Technologies **GHGT-16**

23-27th October 2022, Lyon, France

Conclusions from 3 years of continuous capture plant operation without exchange of the AMP/PZ-based solvent at Niederaussem – Insights into solvent degradation management

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Abstract

Recently, it has been suggested that amine-based solvents should generally be clear and transparent, that “significant” changes of the solvent colour should automatically require the application of reclaiming, and that all non-solvent constituents should be removed from the solvent inventory as fast as they are added during operation, to avoid their accumulation [1,2]. However, the experimental basis for these recommendations is usually limited to simplified laboratory experiments or testing campaigns at pilot plants which are short compared to the time-scale of solvent degradation processes, and are related to the solvent 30 wt% aqueous monoethanolamine (MEA). It is important to scrutinize the effect of this solvent management approaches and the underlying assumptions about solvent degradation based on results from real long-time pilot plant or full-scale tests using fully representative, industrial flue gases to avoid waste streams and efficiency losses that may result from contra-productive overshooting efforts for solvent management.

As part of the transatlantic project LAUNCH (Project No. 299662; co-funded by the ERA-NET Accelerating CCS Technologies initiative), three solvent management strategies with different effect mechanisms are investigated and evaluated in a long-time test campaign (testing time >36 months; 24/7 operation) with the CESAR1 solvent (aqueous solution of 3.0 molar (26.7 wt%) 2-amino-2-methylpropan-1-ol (AMP) and 1.5 molar (12.9 wt%) piperazine (PZ)) at the capture pilot plant at the lignite-fired power plant in Niederaussem: removal of ionic compounds and elements from the solvent by ion exchange, adsorptive removal of trace elements from the solvent by active carbon and removal of NO₂ from the flue gas by thiosulfate/sulfite dosing. Also the effect of solvent refills and plant downtime on the degradation rate is evaluated.

The results of this unique test campaign of solvent management technologies with CESAR1 are contrary to the above mentioned general recommendations. It is shown that solvent treatment by active carbon reduced the visible absorbance of the solvent and the iron and nickel concentration, but this has no clear effect on the solvent degradation rate [3].

Anionic compounds, trace components and complexes can be removed from the solvent by ion exchange with an anionic resin, but after the application of anion exchange, the degradation rate increased rapidly (approx. 4% of the solvent inventory were treated per cycle; typically five cycles per week; in total: 48 cycles and treatment of approx. 2 times of the solvent inventory). A significant result of tests with aged solvent (after 645 days of operation before the

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start of the solvent treatment by ion exchange in the capture plant) is that the anionic ion exchange resin can remove a significant portion of the iron content from the solvent, but no nickel. Also the concentration of zinc and chromium can be significantly reduced. This result implies that metal cations which are dissolved in the solvent partially exist as anionic complexes and underpins also the importance of the solvent matrix for the properties and the catalytic effects of metal ions on amine degradation, as the properties of the ligands can control the redox behaviour and the catalytic activity of a metal ion. We will present the results of a 2-months campaign on solvent treatment by ion exchange using a serial set up of an anionic and a cationic exchange resin and the long-time effect on the degradation rate of the solvent.

The reduction of amine degradation by removal of the aggressive component NO₂ from the feed gas should reduce the amine degradation rate. At Niederaussem the NO₂ concentration in the flue gas is in the range between 1-4 mg/m³, dry (STP). The long-time test (approx. 2,000 h) of the NO₂ removal by dosing of thiosulfate into a pre-treatment column with structured packing material (specific surface 600 m²/m³) started at day 854 of the testing campaign and ended at day 937. The analysis of the scrubbing solution resulted in concentrations of thiosulfate up to 15,000 mg/l (134 mmol/l) and sulfite up to 16,500 mg/l (21 mmol/l). The reduction of the NO₂ concentration which enters the CO₂ absorber by around 80% had no measurable effect on the formation rate of oxidative amine degradation products. The NO₂ removal has no effect on the level of ammonia emissions in the CO₂-lean flue gas downstream the water wash of the CO₂ absorber. Explanations might be the negligible role of NO₂ as oxidant compared to oxygen or alternatively a too fast backformation of NO₂ from NO in the CO₂ absorber. It was shown by measurements at different locations along the flue gas path downstream the NO₂ removal that some “fresh” NO₂ is formed from NO - which is available in excess (concentration between 100 and 140 mg/m³, dry) in the flue gas. The residence time of the treated flue gas between both measurement positions was estimated to approx. 20 seconds and the increase in the NO₂ concentration to approx. 0.3 mg/m³, dry. New results from laboratory tests on the equilibrium reaction of NO and NO₂ will be presented to explain the investigated solvent degradation behaviour.

The presented results are supposed to avoid the waste of solvent and resources and to optimise the environmental benefit from amine-based carbon capture. Commercial capture plants should carefully analyse their individual operating and plant conditions depending on the solvent and the feed gas composition before they start to treat the solvent with the intention to reduce the formation rate of degradation products. Excessive reclaiming might have the opposite effect as intended.

Keywords: AMP, piperazine, CESAR1, solvent management, solvent degradation, ion exchange, NO₂ removal, pilot plant, demonstration

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Acknowledgements

The LAUNCH project is funded through the ACT programme (Accelerating CCS Technologies, Horizon2020 Project No 294766). Financial contributions have been made by Ministry of Economic Affairs and Climate Policy, the Netherlands; The Federal Ministry for Economic Affairs and Energy, Germany; Gassnova of Norway through the CLIMIT program; and the Department for Business, Energy & Industrial Strategy, UK, with extra funding from the US Department of Energy. All funders are gratefully acknowledged