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Predicting Oxidative Degradation for CESAR1 using a Degradation Network Model

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Abstract

Amine based post combustion CO_2 capture (PCCC) is a mature technology aimed at combatting effects of climate change through reduction of CO_2 emissions from various industries. PCCC plants can capture CO_2 from point sources such as power plants, waste-to-energy facilities, chemical industries and ships. The large scale implementation of PCCC is, however, hindered by a variety of issues that are adverse for the environment and the process economics. Key among these issues is the degradation of the capture solvents. Aqueous amines suffer from degradation – oxidative and thermal – under different operating conditions in the capture plant [1].

Oxidative degradation of amines occurs due to the reaction of dissolved oxygen with the amines and degradation products found in the solvent. This degradation is normally observed at temperatures below 100°C with loaded solvents. The oxidative degradation of amines leads to formation of several undesirable products like ammonia, carboxylic acids and aldehydes. These acidic products can further react with the amines forming Heat Stable Salts (HSS) [2], [3]. The accumulation of these products in the solvent leads to reduction of cyclic capacity, and can cause increased fouling, corrosion and foaming. Additionally, generation of volatile by-products like ammonia also leads to increased emissions from the capture plant. These issues make plant operation more difficult and expensive, in addition to having adverse environmental impacts.

Various techniques for mitigating oxidative degradation have been studied. Examples include removing dissolved oxygen by the use of oxygen scavengers, nitrogen sparging or membranes [4]. Proper and effective application of these mitigation techniques requires an understanding of the extent and rate of oxidative degradation in various parts of the capture plant. This can be predicted using degradation models that usually follow a fundamental approach in which knowledge of degradation reactions and mechanisms is required [5].Normally these models do not account for plant specific factors like residence times in various parts of the plant, quality of flue gas and plant operation that leads to an inability to reasonably predict degradation in real plants.

Within the ALIGN-CCUS project, TNO started the development of a practical degradation network model aimed at prediction of the oxidative degradation of monoethanolamine (MEA) in various operating units within a PCCC plant – absorber, absorber sump, piping between the absorber column and cross heat exchanger and the solvent cross heat exchanger. This model takes into account the plant specific factors mentioned above. The degradation network model

has been further expanded and adapted to also predict degradation for CESAR1 (aqueous solution of 3 molar AMP and 1,5 molar piperazine) within the LAUNCH project.

Model inputs include rate constants for oxygen depletion in CESAR1, residence times and operating conditions in different parts of the plant. The rate constants for oxygen depletion are obtained through degradation experiments performed in TNO's Oxygen Depletion Installation (ODIN) setup [4]. Oxygen decay is measured over time in CESAR1 under various temperatures and CO_2 loadings. The rate constants obtained from degradation experiments are used to predict the formation of primary degradation products such as formate, acetate, oxalate, and ammonia. The extent of formation of these products provides an insight into the amount of amines lost due to oxidative degradation.

The degradation network model will be validated with data from the CO_2 pilot capture plant associated with RWE's lignite fired power plant at Niederaussem. Long term testing of CESAR1 (more than 23,000 hours continuous 24/7 operation) has been carried out at this pilot facility resulting in new insights into degradation behaviour and the rate of formation of degradation products. Using pilot plant specific data on column sizes, operating temperatures and residence times, formation and amounts of the aforementioned primary degradation products will be calculated for this plant using the model. The results will be compared with data available from the pilot plant operation on amounts of degradation products for validation of the model.

The degradation network model will be a practical tool for understanding and prediction of solvent quality. This will allow for better selection and application of countermeasures to successfully long term operation of amine based CO_2 capture plants.

Keywords: Solvent degradation; CO_2 capture pilot; CESAR1, degradation network modelling

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