Influence of experimental setup on amine degradation

Solrun Johanne Vevelstad [a], Andreas Grimstvedt [b], Hanna Knuutila [a],
Eirik Falck da Silva [b], Hallvard F. Svendsen [a,*]

[a] *Norwegian University of Science and Technology, 7491 Trondheim, Norway*
[b] *SINTEF Materials and Chemistry, 7465 Trondheim, Norway*

ABSTRACT

Chemical stability of amines under CO_2 capture conditions is a well known problem both for process operability and related to economy and environmental issues. Many degradation studies have been conducted under different conditions and in different apparatuses. In this work the chemical stability of a set of amines and their degradation products using 3 different setups have been studied. A new degradation compound for 2-ethanolamine (MEA), *N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide (HEHEAA) was quantified resulting in a total of 21 degradation compounds for MEA. Liquid phase metal and gas phase oxygen concentrations, temperature and volatility of degradation products (intermediates) all influence degradation and differences in results from the various apparatuses are observed. Conditions favouring formation of primary degradation compounds are difficult to identify and explain, but generally low metal and oxygen concentrations and temperature reduce their formation. For some of the secondary degradation compounds volatility of intermediates was an issue and higher formation rates were seen in the closed setup which preserved more of these products in the solvent compared to the open setup with gas throughput. Amines believed to form volatile degradation compounds showed lower chemical stability in the open setup compared to the closed setup. A new mechanism for the important degradation product *N*-(2-hydroxyethyl)-glycine (HEGly) is suggested.

© 2014 Published by Elsevier Ltd.

1. Introduction

Fossil fuel based power plants are one of the main sources to human carbon dioxide emissions and contribute to an increase in the greenhouse effect. Post combustion CO_2 capture using absorption processes is currently the most mature technology for CCS and over the last years several pilot plants and test centres have been or are being built to test a variety of absorbents, e.g. Technology Centre Mongstad (TCM) in Norway (Andersson et al., 2013; Maree et al., 2013), International test Centre (ITC) in Canada (Skoropad et al., 2003; Wilson et al., 2003), several pilots in Australia (CSIRO) (Cousins et al., 2012). Additionally a full scale plant has been built at Boundary Dam Canada. Ideal absorbents should have high net cyclic capacity, good chemical stability, high equilibrium temperature sensitivity and reaction/absorption rates for CO_2, low vapour pressure and low corrosiveness. It has been difficult to find an absorbent combining all of these properties, and 2-ethanolamine (MEA) is still a reference case for amine systems.

One major problem with organic absorbents is their stability in the process where degradation will cause additional operating costs related to solvent losses, corrosion, fouling, foaming and the potential risk of degradation products entering the environment (Chakma and Meisen, 1986; Kohl and Nielsen, 1997; Strazisar et al., 2003). Degradation in pilot plants is often divided into thermal degradation, with or without CO_2, and oxidative degradation. Thermal degradation with CO_2 is likely to occur in the stripper, while thermal degradation without CO_2 is of less importance, but might take place in the reboiler. Oxidative degradation is normally associated with the absorber but oxygen will dissolve in the solvent and also be present to some extent, until depleted, in other parts of the plant. For thermal degradation studies with CO_2, a general procedure has been accepted and used for the experiments (Davis, 2009; Eide-Haugmo, 2011; Lepaumier et al., 2009a). However, oxidative degradation experiments are conducted in various setups at different conditions making them more complicated to compare. For example, experiments were conducted in open apparatuses (da Silva et al., 2012; Goff and Rochelle, 2004; Sexton and Rochelle, 2011; Vevelstad et al., 2013b) and in closed setups (Lepaumier et al., 2009b; Supap et al., 2011b; Wang and Jens, 2011). Especially the conditions in the open setups varied among the research groups with variation in gas composition (in particular

oxygen concentration), gas flow, with or without gas through-put, variation in temperature, using glass or metal setups, gas introduced in headspace or bubbled through solution and with or without additives as metals or inhibitors. Degradation compounds from oxidative degradation experiments are among the degradation compounds most frequently found in continuous operation (da Silva et al., 2012; Lepaumier et al., 2011a; Strazisar et al., 2003). However, the relative rates of formation of these compounds vary between pilot plant and oxidative lab degradation experiments. This observation has resulted in developing a new lab system, comprising a full absorption-stripping cycle, that also could give representative rates of formation of the degradation compounds which were observed in pilots.

Through the last decade, the degradation compounds themselves have received increased attention with more focus on their formation mechanisms and the similarities between compounds resulting from degradation of different amines (da Silva et al., 2012; Gouedard et al., 2012; Lepaumier et al., 2009b, 2010; Vevelstad et al., 2013b). This has resulted in a relative comprehensive mapping of certain amines as MEA (da Silva et al., 2012; Lepaumier et al., 2011a) or systematic studies on the effects of structural variations on degradation products formed (both for alkanolamines and polyamines) (Lepaumier et al., 2009a,b, 2010). However, no study, to our knowledge, has earlier compared the effect of variation in experimental setup on degradation and evaluation of mechanisms. In this work a total of 5 amines were compared in two different setups. MEA, 2-(methylamino)-ethanol (MMEA), 3-amino-1-propanol (AP) and 4-amino-1-butanol (AB) were tested in both a closed batch (CB) setup and an open batch (OB) setup whereas 3-amino-1-(methylamino)-propane (MAPA) was tested in OB and in a low gas flow (LGF) setup. More details on amines tested in CB are given by Vevelstad et al. (2013a), for MEA in OB see Vevelstad et al. (2013b), for MMEA in OB see Lepaumier et al. (2011b) and for MAPA in LGF see Voice et al. (2013). The data for MAPA, AP and AB in OB are new in this work. This work also includes updates in MEA degradation by giving quantitative and qualitative data for earlier suggested degradation compounds and suggesting mechanisms for compounds which are seen in high amount in pilot plant samples.

Analytical results from degradation studies will vary depending on which analytical methods were available at the time of analysis. This may influence the absolute values reported and therefore in this work normalised concentrations are used for comparison.

2. Experimental

The amines experimentally studied in this work are presented in Table 1. AB was purchased from Syntastic, purity 98%. MAPA was purchased from Alfa Aesar (93%) or Sigma–Aldrich (98%). AP was purchased from Sigma–Aldrich with purity higher than 98%. The experiments were performed using open batch setup (OB) previously presented in Vevelstad (Vevelstad et al., 2013b). A typical experiment last for 3 weeks at 55 °C. The amine solution, loaded with CO_2 (α = 0.4 mol CO_2 per mol of amine), was introduced into the open batch reactor (1 L). A recycle loop maintained a circulation rate of about 50 L/h of a gas blend of air with 2% CO_2. The gas was humidified by passing through a contactor and sparged into the solution in the reactor. A net throughput of gas was obtained by adding (0.35 L/min air +7.5 mL/min CO_2) to the recycle loop. The reactor temperature was maintained at 55 °C. The exhaust gas was bubbled through gas bubble flasks containing water or 0.05 M H_2SO_4 as shown in the flow sheet by Vevelstad et al. (2013b). Samples were taken regularly from the liquid phase and analysed by the analytical techniques mentioned below.

Aqueous amine solutions (30 wt% for AP and AB and 43–45 wt% (9 m) MAPA) were prepared with a loading of 0.4 mol CO_2 per mol amine obtained by bubbling CO_2 gas through the solution until the desired weight was achieved. The total alkalinity of the solution was determined by acid titration (0.1 M H_2SO_4) using a standard procedure, and CO_2 concentrations were measured for the start and end samples using the $BaCl_2$ method (Ma'mun et al., 2007). In addition, selected samples were analysed for nitrogen using the Kjeldahl method (Kjeldahl, 1883). Quantitative data was obtained for degradation compounds described in Table 2. Initial and end samples were in addition analysed in full scan mode (Liquid Chromatography–Mass Spectrometry (LC–MS)) (Vevelstad et al., 2013b) for investigation of degradation compounds which were not a part of Table 2. The concentrations of amine and degradation compounds were corrected based on the change in the amount of water before and after the experiment as described by Vevelstad (Vevelstad et al., 2013b).

More thorough descriptions of the analytical methods for Kjeldahl, density and Ion Chromatography (IC) are given in Vevelstad (Vevelstad et al., 2013b). For LC–MS and Gas Chromatography–Mass Spectrometry (GC–MS) see da Silva et al. (2012), Lepaumier et al. (2011b), and Vevelstad et al. (2013b). Formaldehyde, acetaldehyde and acetone were analysed on the same LC–MS system as described by Vevelstad (Vevelstad et al., 2013b) using derivatisation of the samples. The analytical column Ascentis Express C8 (7.5 cm × 2.1 mm, 2.7 μm, Cat#:53843-U, Supelco Analytical, Bellefonte, USA) was used for aldehyde and acetone analysis. The mobile phase was 0.1% ammonium acetate in acetonitrile and the molecules were converted to ions using electrospray ionisation (ESI).

2.1. Mixing experiments

Mixing experiments were performed to investigate formation of specific degradation compounds in MEA, such as HEHEAA and HEGly, or for investigation of factors influencing formation of *N*-(2-hydroxyethyl)-formamide (HEF) and *N*-(2-hydroxyethyl)-acetamide (HEA). The results were used as basis for discussing, and as support for, results obtained in the degradation experiments. The results and experimental procedures from the mixing experiments are given in detail in supporting information.

2.2. Comparison of the setups and overview of experiments discussed

The experiments compared in this work are listed in Table 3. All experiments except experiments with MAPA were performed with 30 wt% solutions. As listed, all solutions were loaded with CO_2 up to loading of 0.4 mol CO_2 per mol of amine. A metal mixture of $FeSO_4\cdot 7H_2O$ (Fe: 0.4 mM), $Cr_2(SO_4)_3\cdot xH_2O$ (Cr: 0.1 mM), and $NiSO_4\cdot 6H_2O$ (Ni:0.05 mM)) was added to the MAPA (9 m) solution for both the OB and LGF experiments. The flow sheet for the LGF is given by Sexton (Sexton and Rochelle, 2011). As seen from the Table 3, in the CB experiments the initial amine concentrations were typically 1–2% lower compared to in the OB experiments. This was due to small amounts of water already present in the CB setup when the solution to be tested was added. The flow sheet for the CB setup is given by Vevelstad (Vevelstad et al., 2013a). Table 4 gives an overview of the analyses performed in each experiment.

In Table 5 the experimental conditions used in the different setups are compared. The composition of the gas phase in OB and LGF was more constant compared to in the closed batch (CB) because of the small amount of gas constantly added during the OB and LGF experiments. The initial gas composition corresponded