Full Length Article

Degradation behaviour of fresh and pre-used ethanolamine

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ABSTRACT

The oxidative degradation of previously used ethanolamine from three different CO_2 capture pilot plants was studied in a laboratory-scale degradation setup. Different solvents behave differently under the same experimental conditions, indicating that different solvent contaminants, resulting from different operational conditions, can act either stabilising or destabilising under oxidising conditions. Some ionic compounds in the solvent seem beneficial to amine stability under oxidising conditions, while the presence of some inorganic compounds appears to have a negative effect on the stability of the solvent. The most stable pre-used ethanolamine solutions were those that contained the highest total concentrations of heat-stable salts, calcium, sodium, sulphur, potassium, and silicon. These solutions were previously used for CO_2 capture from a lignite-fired power plant and a waste-to-energy plant. The least stable amine solution had a higher concentration of metal ions like chromium, magnesium, and zinc, making these suspects of deteriorating solvent stability.

Abbreviations

EG	eluent generator
HPU	hydrogen production unit
HSS	heat stable salt
IC	ion chromatography
ICP	inductively coupled plasma
LC	liquid chromatography
LOD	limit of detection
M	mol kg^{-1}
MEA	ethanolamine
MS	mass spectrometry
N	mol$_{H+}$ L^{-1}
ppm	parts per million
TOC	total organic carbon
(U)HPLC	(ultra) high performance liquid chromatography

Introduction

Liquid amine scrubbing is one of the most mature technologies for capturing carbon dioxide (CO_2) from large industrial sources and will be an important part of the suit of technologies if we are to achieve our targets to significantly reduce our greenhouse gas emissions and mitigate human-induced climate change (Rogelj et al., 2018). One of the challenges the technology faces is solvent degradation, occurring during long-term operation. Degradation does not only lead to a loss in capture capacity but also associated problems like foaming, corrosion and fouling of equipment. We have come a long way in understanding solvent degradation and can now describe many aspects of the phenomenon, but despite several large research studies looking at amine degradation in the past decades, we cannot explain its whole extent. We are aware that degradation is temperature-controlled, that oxygen (O_2) (Vevelstad et al., 2013), nitrous oxides (NO_X) (Dai et al., 2012; Fostås et al., 2011), dissolved or suspended metals (Blachly and Ravner, 1963; Dhingra et al., 2017; Goff, 2005; Léonard et al., 2014; Nielsen and Rochelle, 2017), particulate matter (da Silva et al., 2012), as well as some products of solvent degradation (Fytianos et al., 2014) increase the rate of degradation, and that some degradation inhibitors are able to impede certain aspects of degradation (Buvik et al., 2021b; Fytianos et al., 2016; Goff and Rochelle, 2006; Léonard et al., 2014; Sexton and Rochelle, 2009; Supap et al., 2011; Voice and Rochelle, 2014). What is still missing is a holistic picture of degradation as a part of the whole capture process and specifically

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which compounds pose a particularly high threat to the stability of the solvent. In pilot-scale studies of CO_2 capture from industrial sources, we have seen in the past that some pilots are able to operate their capture plant without significant degradation or solvent loss over a very long period of time (Moser et al., 2020), whilst other experience a rapid loss in solvent stability, inevitably leading to interruption of the studies due to uncontrollable degradation (Dhingra et al., 2017). A typical observation is that degradation of monoethanolamine (MEA) suddenly goes from occurring at a more or less constant rate, to a sudden exponential growth of degradation product formation. This accelerated behaviour strongly indicates that there are conditions, for example, in the form of a particular solvent composition, that would strongly favour degradation to take place, and that can occur during operation with real flue gas.

MEA has been used for many years, including at pilot scale, and its degradation chemistry is the best understood of the amines used for CO_2 capture (Vevelstad et al., 2022). Of the degradation products that are found in high concentrations during pilot-scale CO_2 capture with MEA, those that require at least one oxidation step seem to dominate, such as small organic acids, 4-(2-hydroxyethyl)-2-piperazinone (HEPO), *N*-(2-hydroxyethyl)-glycine (HEGly) (da Silva et al., 2012; Morken et al., 2014, 2017), and 1H-imidazole-1-ethanol (HEI) (Reynolds et al., 2015b; Thompson et al., 2017), which is why there has been a large focus on understanding oxidative degradation of amines over the last decades. Laboratory-scale oxidative degradation tests can qualitatively reproduce the oxidation products found on pilot-scale (da Silva et al., 2012). In experiments performed in the type of setup used in this work, small organic acids and HEI are some of the main degradation compounds produced. They do, however also form higher relative amounts of *N*-(2-hydroxyethyl)-formamide (HEF) and lower concentrations of HEGly, and HEPO compared to pilot scale (Vevelstad et al., 2016).

In this study, we have mapped the content of degradation products and dissolved inorganic compounds in fresh and pre-used MEA from pilot-scale testing with industrial flue gases. The different MEA solutions were exposed to oxidising conditions over a three-week period, and their relative stabilities were assessed. Despite the extreme conditions experienced in lab-scale testing, where oxidative degradation occurs rapidly, the results will reflect the general stability of the solutions under real industrial oxidising conditions. The experimental setup is not meant to represent or reflect the exact reactions that take place within the CO_2 capture plant, but the degradation products found in pilot samples are also produced here, just more rapidly. We aim to identify some components in the solvents that seem to increase or decrease the solvent stability under oxidising conditions, not to represent a fully realistic degradation scenario in the CO_2 capture plant.

Materials and methods

Chemicals

Oxygen (O_2, N5.0) and carbon dioxide (CO_2, N5.0) were purchased from AGA. Deionised water was obtained from a local water purification system at NTNU. Ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$, CAS: 7782-63-0, purity $\geq$ 99.0%), Dowex 50W-X8 ion exchange resin (CAS: 69011-20-7), sodium hydroxide (NaOH, CAS: 1310–73–2), and monoethanolamine (CAS: 141–43–5, purity $\geq$99.0%) were purchased from Merck Life Science/Sigma Aldrich Norway. Potassium hydroxide (EGC III KOH, CAS: 1310–58–3) was purchased from Thermo Scientific in EG cartridges.

Oxidative degradation experiments

Accelerated amine degradation was performed at 60 °C, with magnetic stirring (ca. 200 rpm) and continuous sparging with a mixture of O_2 (98%) and CO_2 (2%) through a gas dispersion tube. Each experiment was performed in 275 mL reactors containing ca. 200 mL of solution, in three parallels. A more detailed description of the equipment

can be found in Buvik et al. (2021b). All solution preparation was performed gravimetrically, and MEA and CO_2 were added to all pre-used MEA solutions to achieve 30 wt% (*aq*.) MEA and 0.4 mol_{CO2} mol_{MEA}^{-1}. Additionally, 0.5 mM $FeSO_4$ was added to all solutions to increase their degradation rate. Pre-used MEA solutions were stored in the refrigerator prior to use in the accelerated degradation experiments. The solutions were used for 4–18 months after sampling from the pilot plants.

Two experiments were performed with MEA solutions from Pilot A and B, diluted/combined with fresh 30 wt% (*aq.*) MEA. These dilutions were made by taking 50 wt% pre-used solution and adding water and MEA to the desired MEA concentration (based on alkalinity titration). The experiment using pre-used MEA from Pilot A was performed using a mixture from two different operation times. Exact details on solution preparation are found in the supplementary information.

One experiment was performed using a fresh 30 wt% (*aq*.) MEA solution with an extract of the fly ash obtained from the electric precipitators of the power plant that supplies the flue gas for Pilot A. This solution was prepared by adding 30 g of fly ash to 750 g of 30 wt% (*aq*.) MEA and letting it stir at elevated temperature (ca. 50 °C) for three days and subsequently filtering the solution from all particulates prior to the degradation experiment. Another experiment was also run with fly ash particulates (Pilot A) added, in accordance with da Silva et al. (2012), with an addition of 0.4 wt% fly ash to fresh 30 wt% MEA. A much larger amount of fly ash was used to prepare the fly ash extract, to study the effect its ionic compounds have on stability. An experiment with the same amount of ash, not filtered, would yield a thick reaction mixture that is difficult to stir and monitor and was therefore not performed. With the amount of catalytic surface added by the fly ash itself, an inhibitory effect is not expected from such a mixture.

Pilots

The MEA solutions used in this work originated from three different pilot plants. Some key facts about the plants can be found in Table 1, including the initial concentration of heat-stable salts (HSSs) measured by titration in this work.

A previously used MEA solution obtained from the CO_2-capture pilot plant treating flue gas from a lignite-fired power plant in Niederaussem was provided by RWE and is denominated "Pilot A" in this study. More information about the long-term campaign, which lasted more than 12,000 h, can be found in Moser et al. (2020). During "Bleed and Feed" on day 328 after the start of the campaign, most of the MEA-solution in Pilot A got replaced with fresh 30 wt% (*aq*.) MEA, purposely leaving some used solvent in the plant to investigate whether a Bleed and Feed strategy could limit solvent degradation. As described by Moser et al. (2020) this was not the case, and a rapid increase in degradation product concentrations was observed immediately after the Bleed and Feed. The solvent samples used in this study were taken in the period after the Bleed and Feed on days 349 and 398, and a mixture of the two samples was used to perform the degradation experiments.

The solution denominated "Pilot B" in this study was provided by Preem and Aker Carbon Capture, who performed CO_2-capture from flue gas deriving from the hydrogen production unit (HPU) at the Preemraff Lysekil refinery. In this case, Aker Carbon Capture's Mobile Test Unit was employed for performing the CO_2 separation. Since this campaign was exploratory in nature, different process parameters were varied throughout the testing period. Nevertheless, flue gas conditions were kept more or less the same across the campaign. More details about this campaign can be found in Biermann et al. (2022).

The "Pilot C" MEA campaign was performed under proprietary conditions, and therefore operational conditions cannot be disclosed in this work. The flue gas source of "Pilot C" was a waste-to-energy plant.

Analytical methods

All amine concentrations given in the results section are corrected to CO_2-free concentration and for water loss throughout the experi-

Table 1

Key differences between pilot A and B studied in this work. Details about the campaign in Pilot C are proprietary.

	Pilot A	Pilot B	Pilot C
Flue gas source	Lignite-fired power plant	Refinery for H_2 production	Waste-to-energy
Time in operation when sample was taken	349 days (69 wt%) and 398 days (31 wt%)	510 h	
Flue gas flow	1150 m^3/h	340–360 m^3/h	
c_{CO2}	14.2 vol% (dry)	18–20 vol% (wet)	
CO_2 capture rate	90%	85–95%	
c_{O2}	5.0 vol% (dry)	Up to 20%	
$T_{absorber\ inlet}$	38–40 °C	30–32 °C	
$T_{desorption}$	120 °C	120 °C	
$p_{desorption}$	1.75 bar(a)	1.9	
c_{HSS} [mol kg^{-1}]	0.19	0.050	0.17
Storage time	18/15 months	3 months	4 months
Storage conditions	16/12 months at room temperature, 2 months in refrigerator	2 months at room temperature, 2–4 weeks in refrigerator	0.5 month at room temperature, 3.5 months in refrigerator

mental period. The concentration of alkalinity, corresponding to the total amine concentration, was determined by titration with sulphuric acid (H_2SO_4, 0.2 N) in accordance with the method described by Ma'mun et al. (2006). This method has an uncertainty of ± 2% compared to the analysis of known standards. To determine the concentration of CO_2, total inorganic carbon analysis was performed on a Shimadzu TOC-L_{CPH} analyser. The inorganic carbon concentrations were verified by regular analysis of $NaHCO_3$ standards of known concentrations. The analytical uncertainty of the TOC method is ± 3% when compared to the analysis of known standards.

The concentration of heat-stable salts (HSS) was determined by ion exchange in activated cation exchange resin according to the procedure described in Reynolds et al. (2015a). Approximately 2 g of accurately weighed sample was added to a mixture of ca. 40 mL resin and 40 mL of deionised water and stirred, partly covered, for one hour at 70 °C. The amount of acid released from the resin was then determined by titration of the liquid filtrate as well as the combined filtrates of repeated washing of the resin with sodium hydroxide (0.05 M). All HSS analyses were performed in duplicates, and the reproducibility of this method was ± 5%.
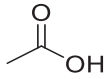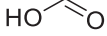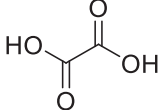
Viscosity was measured using a MCR 100 rheometer from Paar Physica. The measurements were performed at 25 °C and 1 atm. A torque calibration was performed prior to measurement, ensuring torque values within ± 0.05 μNm. Validation of the procedure was performed using a known reference standard (Viscosity & Density Reference standard, Paragon scientific Ltd, Blend of CAS 64742-47-8 and 8042-47-5), where a deviation between measured and known (by ISO 17025/ISO Guide 34) dynamic viscosity was < 2%. The method was deemed valid. A sample volume 3.8 mL was injected into a DG26.7 double-gap concentric cylinder, and the viscosity was determined between 10 and 1000 s^{-1} rotations by correlating shear rate and shear stress.

Quantification of dissolved metals and other elements in the amine solutions was performed by inductively coupled plasma mass spectrometry (ICP-MS) using Agilent 8800 Triple Quadrupole from Agilent Technologies, USA. All solutions and dilutions were prepared using ultra-purified water 18.2 MΩ from OmniaTap 10 UV system (Stakpure, Germany) and concentrated nitric acid (65% HNO_3) purified by a Savillex DST-1000 Acid Purification System (Savillex, USA). Standards for calibration curves were prepared from single element and mixed standard solutions from Inorganic Ventures, USA.

Anion chromatography was performed in the facilities of the University of South-Eastern Norway, on a Thermo Scientific™ Dionex™ ICS-5000 system, with a Dionex™ AG11-HC RFIC™ analytical and guard column (4 • 250 mm, and 2 • 50 mm) and a conductivity detector. A concentration gradient of KOH was used as eluent, in the range of 3–60 mM and generated by an EG system. The method is thoroughly described by Buvik et al. (2021a). Samples were diluted 1:100 or 1:350 in Millipore water, depending on the known amount of HSS observed by total HSS

Table 2

Names, chemical structures, and CAS numbers of the studied degradation products of MEA, quantified by anion IC analysis.

CAS	Name	Structure
64-19-7	Acetic acid	
64-18-6	Formic acid	
144-62-7	Oxalic acid	

analysis. Formate, acetate, and oxalate (Table 2) were quantified with this method, with an uncertainty of ± 3%, when analysing known standards. Calibration was performed in the range of 1 to 30 ppm.

Liquid chromatography coupled with mass spectrometry (LCMS) analyses were performed by SINTEF Industry with a UHPLC Agilent 1290 Infinity System with Agilent 6490 Triple Quadrupole detection. The separation of the degradation compounds given in Table 3, and MEA, was performed on Ascentis® Express Phenyl-Hexyl, 2.7 μm HPLC and Discovery® HS F5 HPLC columns.

As the largest source of uncertainty originates from the variability in the different parallel experiments with the same conditions and solutions and not the analytical methods, the uncertainties are plotted as the mean absolute or standard deviation for each sampling point.
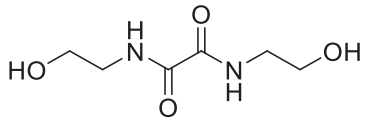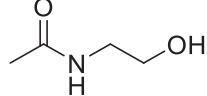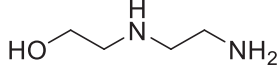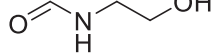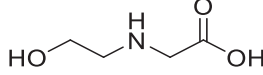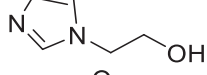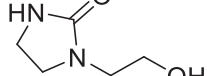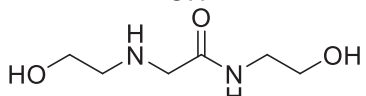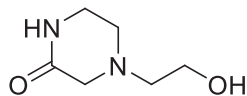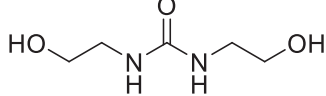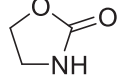
Results

When exposed to identical conditions, there is a difference in oxidative stability and degradability of MEA from different pilot plants and whether it contains fly ash or an extract of fly ash. All in all, it was seen that two of the MEA solutions, which came from pilot campaigns, showed higher stability under oxidising conditions than the third and that adding an extract of fly ash increased the solvent stability, while the addition of fly ash reduced the stability of MEA.

To begin with, we will compare the loss of alkalinity of the different MEA solutions for the duration of the oxidative degradation experiments, as this directly correlates with the solvent's ability to capture CO_2. The pre-used 30 wt% (*aq*.) MEA from Pilot A and C had higher stability under oxidising conditions than the pre-used solution from Pilot B, and fresh MEA, as can be seen in Fig. 1. This was despite the Pilot A solution having had to be diluted with fresh MEA to obtain a sufficient volume to perform three parallel experiments. The stability of the pre-used MEA from Pilot B is comparable to fresh MEA, but when it is combined with fresh 30 wt% (*aq*.) MEA, the stability decreases and is

Table 3

Names, chemical structures, and CAS numbers of the studied degradation products of MEA, quantified by LCMS analysis.

| CAS	Abbreviation	Name	Structure
1871-89-2	BHEOX	N, N'- bis(2- hydroxyethyl) -ethanediamide	
142-26-7	HEA	N- (2- hydroxyethyl) -acetamide	
111-41-1	HEEDA	2- [(2- aminoethyl) amino] -ethanol	
693-06-1	HEF	N- (2- hydroxyethyl) -formamide	
5835-28-9	HEGly	N- (2- hydroxyethyl) -glycine	
1615-14-1	HEI	1H- imidazole- 1- ethanol	
3699-54-5	HEIA	1- (2- hydroxyethyl) -2- imidazolidinone	
144236-39-5	HEHEAA	N- (2- hydroxyethyl) - 2- [(2- hydroxyethyl) amino] -acetamide	
23936-04-1	HEPO	4- (2- hydroxyethyl) -2- piperazinone	
15438-70-7	MEA-urea	N, N'- bis(2- hydroxyethyl) -urea	
497-25-6	OZD	2- oxazolidinone	
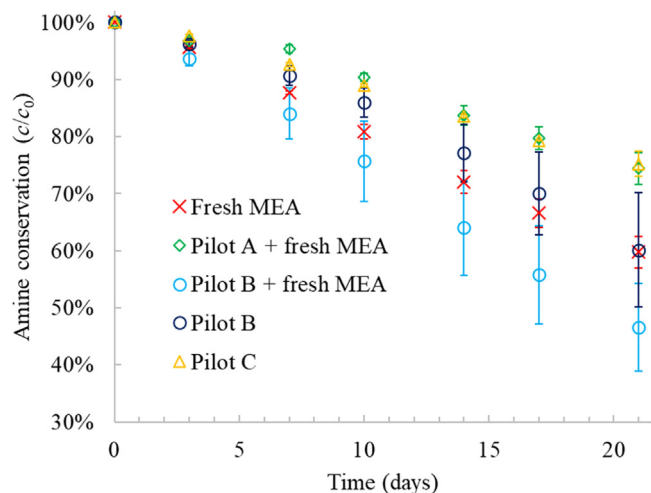
Fig. 1. Loss of alkalinity of fresh and pre-used 30 wt% MEA (*aq.*) from pilot scale, under oxidative conditions at 60 °C. Error bars represent the mean absolute deviation of the average concentrations of three parallel experiments. Degradability of fresh MEA was previously published in Buvik et al. (2021b).

even lower than in fresh MEA. Even with the low reproducibility of the experiments using MEA from Pilot B, reflected in the large error bars in Fig. 1, the stability of these solutions was significantly lower than that of the MEA from Pilots A and C.

Fig. 2 shows that using an extract of the fly ash obtained from Pilot A gives less amine loss than in fresh MEA, yet slightly more than the MEA from Pilot A. In Fig. 3, the total concentration of HSSs is compared before and after the oxidative degradation experiments, showing a large increase in HSS concentration in all experiments. It can also be seen in Fig. 2 that the addition of fly ash to the solvent, without filtering the solution, decreases its oxidative stability. This agrees with the observations of da Silva et al. (2012).

Since an increase in ionic strength also changes the physical properties of the solvent, we measured the viscosity of all the start solutions and compared this to the viscosity of fresh 30 wt% (*aq.*) MEA as shown in Fig. 4. Increasing the solvent viscosity can impact the mass transfer, possibly increasing the stability of the more viscous solution. In our oxidative degradation experiments, the solutions; *Pilot A + fresh MEA, Pilot C,* and *Fresh MEA + fly ash extract* have very similar stabilities under the experimental conditions, despite having varying viscosity at 25 °C. All experiments were performed at 60 °C, where the viscosity of the different solvents will vary even less. The viscosity of the CO_2-loaded fly ash extract is equal to that of fresh MEA, while the two pre-used so-
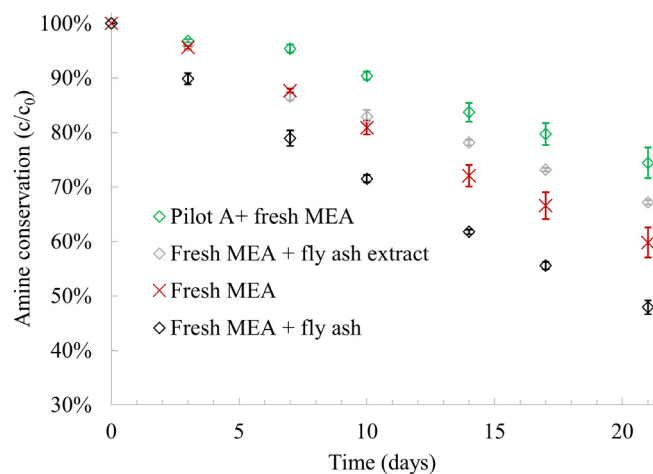
Fig. 2. Oxidative degradability of 30 wt% MEA (*aq.*) with and without the addition of fly ash, fly ash extract or pre-used MEA from Pilot A. Error bars represent mean absolute deviations of the average concentrations of three parallel experiments.
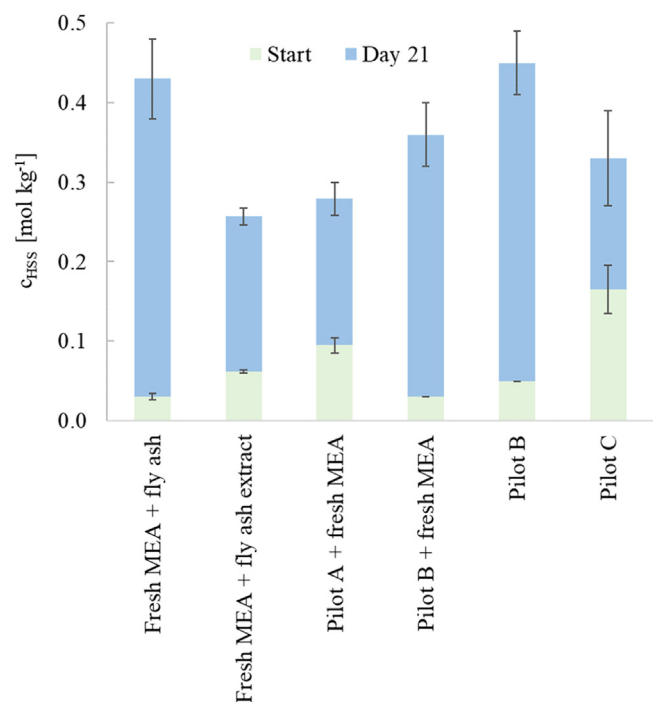

Fig. 3. Concentrations of total HSS before and after oxidative degradation of pre-degraded MEA 30 wt% (*aq.*)., and MEA 30 wt% (*aq.*) with fly ash and fly ash extracts. Error bars represent standard deviations of the average concentrations of three parallel experiments for the Day 21 solutions and the analytical uncertainty in the start solutions.

lutions have a slightly higher viscosity. Increasing the viscosity alone, does, therefore, not seem to be the cause of increased stability of these solutions.

The concentration of some acidic HSSs was measured by ion chromatography (IC) at the University of South-Eastern Norway (USN). None of the MEA solutions were exposed to alkaline hydrolysis prior to IC or HSS titration. As seen in Fig. 5, the pre-used MEA solutions already contained some HSSs, where formate, acetate and oxalate make up about half of their HSS content. Of the studied compounds, formate was the most dominant HSS. Formate continues to be the most dominant HSS of the ones studied, also after the experiment, and this observation
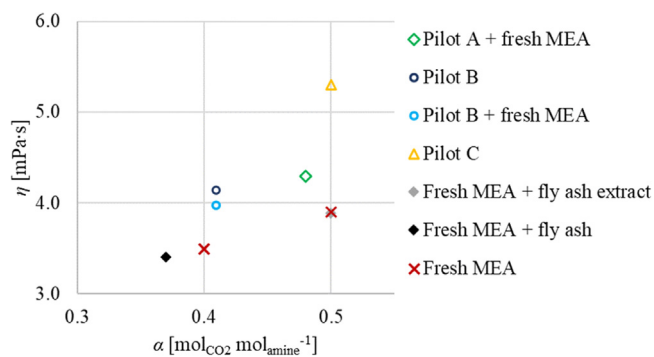
Fig. 4. Viscosity of the start solutions at 25 °C and atmospheric pressure, prior to oxidative degradation experiments, plotted against CO_2 loading. The viscosity of fresh 30 wt% (*aq.*) MEA is from Amundsen et al. (2009), and the viscosity of MEA is from Pilot C from Thorstad (2021).
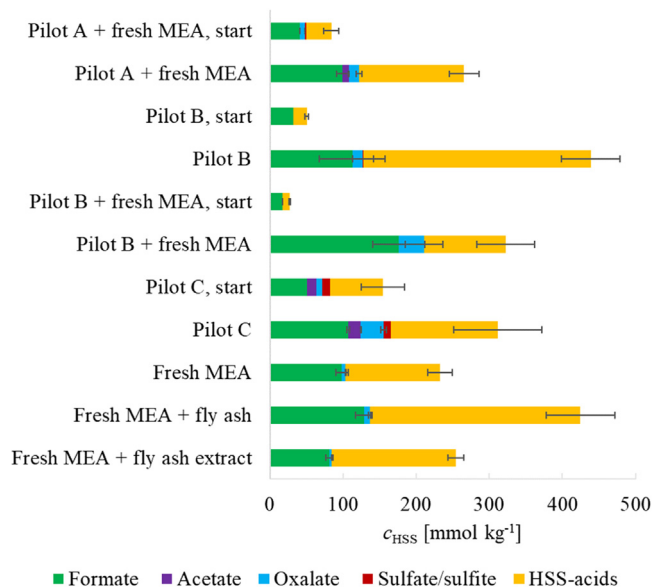
Fig. 5. Concentrations of the HSSs formate, acetate and oxalate measured by IC, as well as the remaining concentration of HSS, measured by titration, in the pre-used MEA solutions prior to the oxidative degradation experiments. Error bars represent the standard error of the means from three parallel oxidative degradation experiments.

agrees with previous experiments performed under the same conditions (Buvik et al., 2021a). As a matter of fact, acetic acid was below the limit of detection (LOD) of the IC method in all samples, except for the start solution obtained from Pilot A and C, as well as after 21 days in the solution from Pilot C.

In Fig. 6 it can be seen that all of the pre-degraded MEA solutions contained relatively high concentrations of the oxidative degradation products HEPO and HEGly, agreeing with previous observations from the pilot scale (da Silva et al., 2012; Morken et al., 2014, 2017). The MEA from Pilot A differs from the other two by also containing a quite high concentration of HEI. Of the studied degradation products, it can be seen in Fig. 7 that the thermal degradation product HEEDA is in the lowest concentration of the degradation products that were quantified in all the pre-used MEA solutions.

After oxidative degradation of the studied degradation compounds, HEI is dominant in all cases, followed by HEF, as can be seen in Fig. 8. In all the MEA solutions from the pilots, HEPO and HEGly seem to be consumed by the degradation reactions and are measured in lower concentrations than in the start solutions. In Fig. 9, it can be seen that the degradation experiments have caused an increase of BHEOX and OZD
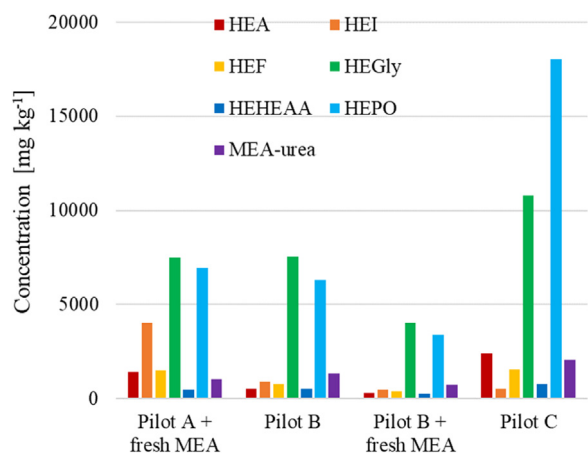
Fig. 6. Concentrations of a selection of known degradation products found in relatively high concentrations in the pure pilot-degraded MEA samples, measured by LCMS.
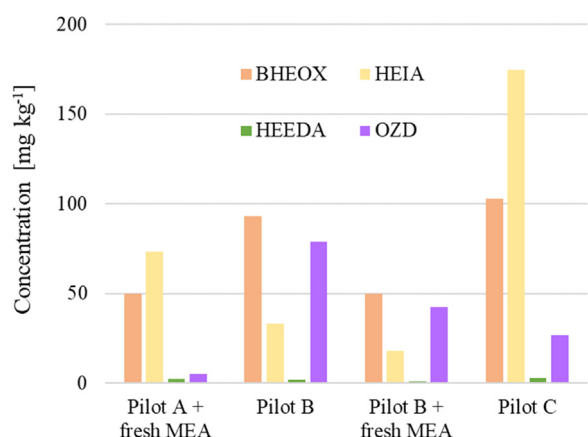

Fig. 7. Concentrations of a selection of known degradation products found relatively low concentrations in the initial pilot-degraded MEA samples, measured by LCMS.
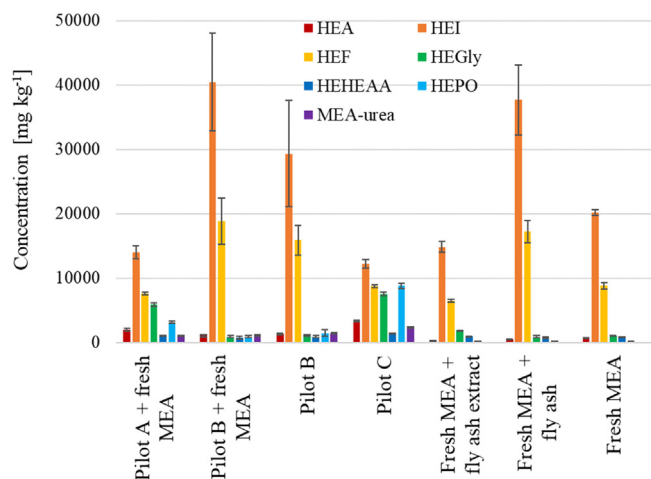

Fig. 8. Concentrations of a selection of known degradation products after oxidative degradation of the pilot-degraded MEA-solutions, or MEA with fly ash or fly ash extract added, measured by LCMS. Error bars represent the mean absolute deviation between the three parallel oxidative degradation experiments.
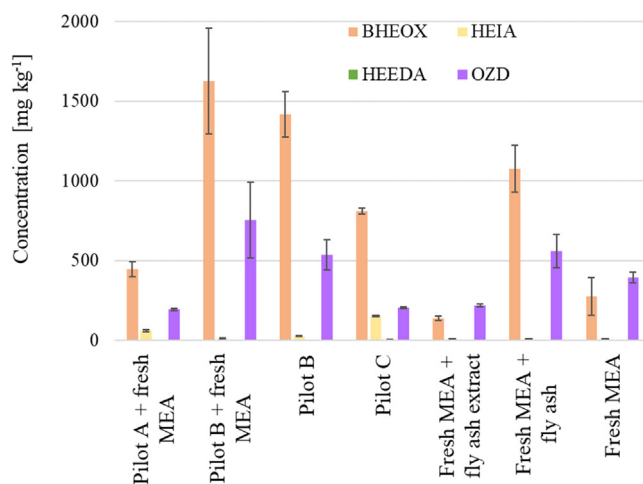

Fig. 9. Concentrations of a selection of known degradation products found relatively low concentrations after oxidative degradation of the pilot-degraded MEA-solution, or MEA with fly ash or fly ash extract added, measured by LCMS. Error bars represent the mean absolute deviation of the three parallel oxidative degradation experiments.
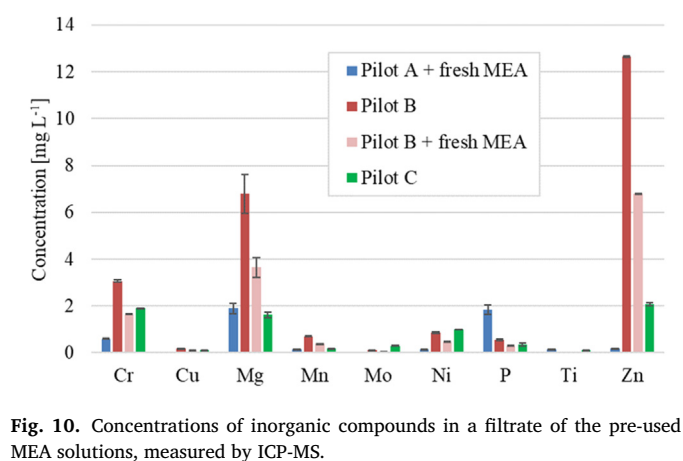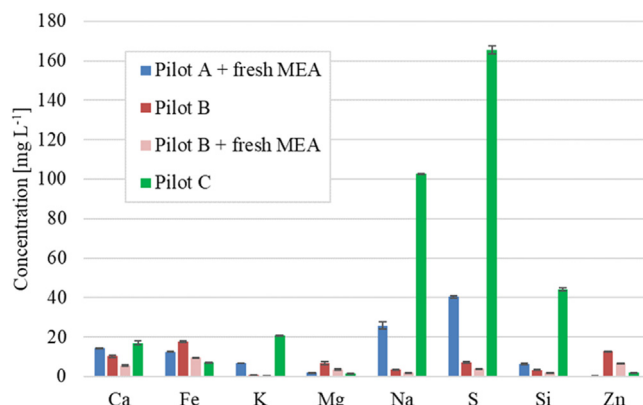

Fig. 10. Concentrations of inorganic compounds in a filtrate of the pre-used MEA solutions, measured by ICP-MS.

for all solutions but have not significantly changed the concentrations of HEEDA and HEIA. Neither fresh MEA nor MEA with added fly ash or extract of fly ash from Pilot A produced MEA-urea or HEEDA above the LOD, which is expected, as these products form at higher temperatures than 60 °C.

Since we know that trace components such as dissolved metals influence degradation, a component screening was performed using ICP-MS on filtrates of the pre-used MEA. Fig. 10 shows that the more
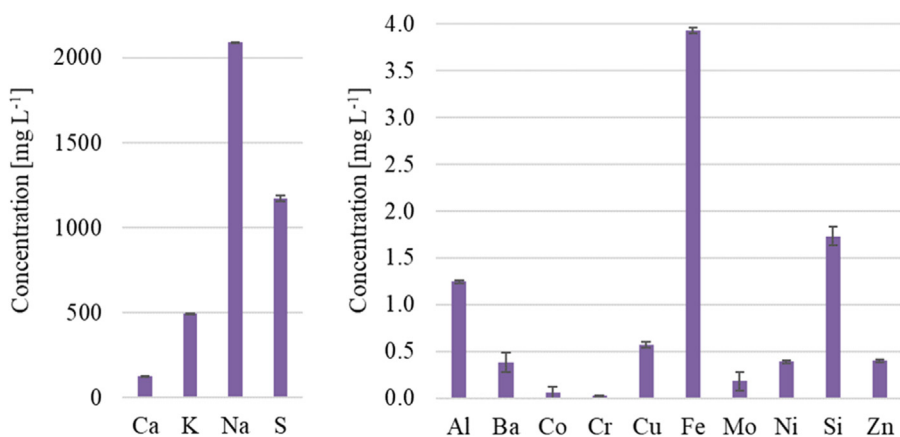
stable Pilot A and C solutions contain relatively high concentrations of calcium, potassium, sodium, and sulphur, which are likely to be present in the form of HSS (Ca^{2+}, K^+, Na^+, SO_4^{2-}, SO_3^{2-}). If sulphur is present in the form of SO_3^{2-}, it could act as a stoichiometric oxidation inhibitor. Silicon (Si) is also found in higher concentrations in Pilot A and C than in B. The less stable Pilot B solution contains more chromium, magnesium, and zinc (Cr, Mg, Zn) than the two others. The concentrations of trace metals were also determined by ICP-MS in the MEA with an extract of fly ash. As the concentrations of many elements were notably higher in this solution, the results from this analysis are given in Fig. 11.

Discussion

It is often assumed that a "clean" solvent is a good solvent for the CO_2 capture process, and that keeping your MEA or another amine solvent free from all contaminants will increase the solvent lifetime. This study indicates that we cannot generalise and deem all contaminants bad for solvent stability and that there may be more beneficial ways of looking at, i.e., solvent management strategies. The findings in this study give some insight into which compounds should be monitored more closely, and which should preferably be left in the solution, as long as the operability of the plant is not affected by their presence.

As can be seen in Table 1, the solvents originating from Pilot A and C contained higher concentrations of ionic compounds in the form of heat-stable salts (HSSs) than that from Pilot B. Since these two solutions were more stable than that from Pilot B, our first suspicion for the increased stability was that the ionic strength of the solvent could play a stabilising role. Upon dilution of the Pilot B solution, its ionic strength was further reduced, yet possible catalytic effects of the contained degradation compounds or contaminants were retained. This could explain the increased degradation observed when fresh and pre-degraded MEA solutions from Pilot B are combined. Whether a pure solution from Pilot A would be more or equally stable as in dilution is not known.

The higher concentration of ionic compounds could possibly reduce the concentration of dissolved oxygen in the amine solution, and thereby reduce the degradation rate of MEA. The presence of most electrolytes is known to decrease oxygen solubility in aqueous solutions (Schumpe et al., 1978). This is known as "salting out" of the gas from the liquid phase. Since the concentration of CO_2-products is 0.4 mol per mol MEA throughout each experiment, the ionic strength of the solution coming from (mainly) carbamate ($MEACOO^-$) and protonated MEA ($MEAH^+$) is already ca. 2 mol kg^{-1} solution. At such a high concentration of the CO_2-products, much higher than that HSS concentration of the solutions, the contribution of CO_2 products to salting out is expected to dominate. The total ionic strength of the starting solutions varies between 2.0 and 2.2 in all the used MEA solutions. This very small difference in general ionic strength is not sufficient to explain the large difference in oxidative stability observed in the different MEA solutions.

When looking at how the total HSS concentration increases throughout the experiments in Fig. 3, without seeing any decrease in degradation rates, as seen in Figs. 1 and 2, it seems even less likely that the increased stability can be explained by changes in concentration of salts in general.

It is also possible that the ionic species in the solution help stabilise $MEAH^+$ and $MEACOO^-$, or reaction intermediates, preventing these from taking part in radical reactions, which are the initial steps of oxidative degradation. The ionic compounds in the solution may also be forming complexes with the metals present, which are not as efficient catalysts for oxidative degradation as in i.e., the metals dissolved in the fresh MEA solution. This "shielding effect" of certain ligands has previously been suggested by Moser et al. (2022). Other elements may also contribute to shielding if they are dispersed as nanoparticles, such as silicon in the form of silica (SiO_2).

When looking at Fig. 5, it is evident that a portion of HSS is not identified in this study. It can be assumed, although not measured in this work, that a part of the unidentified HSS fraction consists of nitrate (NO_3^-), both originating from the flue gas and formed through degradation reactions. Additionally, other flue gas contaminants, such as SO_X and Cl^- can be present and shown in the total HSS analysis.

All MEA solutions seem to follow the same degradation patterns. Even though their degradation rates vary, the order of the formed degradation compounds is the same ($c_{HEI} > c_{HEF} > c_{HEGly} > c_{HEHEAA} > c_{HEA} > c_{OZD} > c_{BHEOX} > c_{HEPO} > c_{HEIA}$). This observation also highlights one of the shortcomings of these single-condition experiments. All the mechanisms that take place in the actual CO_2 capture plant, where temperature cycling, fluctuations in CO_2 concentrations, variation in redox conditions, or static storage periods, i.e., in the absorber sump or storage tanks all may play a role will not be seen with this experimental setup. Accelerating the degradation reactions, however, has the great advantage of allowing us to perform more tests in a less time-consuming and costly manner while obtaining important insights into some aspects of the total degradation chemistry.

An interesting observation in Fig. 8 is the fact that, after degradation, the content of degradation compounds in the fresh MEA, the "pure" and diluted MEA from Pilot B, and that which was added fly ash, are very similar. It can also be seen that the solutions from Pilot A and C contain much more HEGly than the other solutions, despite the Pilot A and B solutions containing comparable HEGly-concentrations at the start of the experiments (Fig. 6). This indicates that the mechanisms of degradation are different in the different MEA solutions. The breakdown of HEGly, as well as that of MEA, is inhibited in the solutions from Pilot A and C.

Chromium is a known catalyst for oxidative degradation (Blachly and Ravner, 1964; Voice, 2013), and like other transition metals, so is zinc expected to be, despite there being no targeted Zn-catalysis studies with ethanolamine or other alkanolamines. Voice (2013) did, however, study ZnO as a potential oxidation inhibitor

and concluded it had no inhibition effect on ammonia development from MEA under oxidising conditions. The concentrations of iron are similar in all three pilot solutions, but the accelerated conditions under which the experiments in this work were performed also provide an excess with the addition of 28 mg iron per kg solution, making it impossible to draw any conclusions on the role played by these initial iron concentrations. It does, however, look like other metal species are significant in catalysing the degradation reactions and that the removal of Cr, Mg and Zn could be beneficial for solvent stability. It should be noted that the fresh MEA solution is also highly degradable, despite only containing 28 mg/kg iron and none of the other metals, meaning that this alone also doesn't explain the low stability of the Pilot B MEA.

The elemental composition of the pre-used MEA can possibly explain the stabilising or destabilising effects under oxidative conditions. Metals are known to catalyse degradation; therefore, the content of chromium and zinc may be the reason why Pilot B's pre-used MEA is less stable. When diluted, the chromium content of the Pilot B solution is, however, comparable to that of Pilot C, so this cannot be the only explanation. A more probable reason for the variation in stability of the different solutions is a higher content of inert ions in the Pilot A and C solutions. A recent study showed that having a "clean", meaning contaminant-free solvent, does not necessarily mean having the most stable solvent (Moser et al., 2022). As a matter of fact, calcium, potassium, sodium, and sulphur are also found in relatively high abundance in the fly ash extract from Pilot A, seen in Fig. 11, further supporting the hypothesis of stabilising effects given by these ionic compounds. As the MEA solutions from Pilot A and C are more stable than the fresh MEA with fly ash extract, but all contain less Na, K and Ca, these three may not necessarily be the most beneficial components found in the solvent, although they can still have a positive impact on the stability. On the other hand, Sulphur is found in very high concentrations in the fly ash extract.

Looking at Fig. 1, the experimental repeatability where MEA from Pilot B was used is higher than for all other MEA solutions. There is no clear explanation for this effect, except for possible variation in bubble sizes from the gas dispersion tubes used in these experiments. Purchasing tubes with the same porosity does not necessarily mean that the spargers are always identical, and the bubble sizes may still vary. The effect of the large experimental variation between parallels is therefore also clearly visible in the other graphs presenting degradation product concentrations with error bars representing variation between the triplicates.

Conclusions

The composition of the 30wt% ethanolamine (MEA, *aq*.) solution affects its stability and degradability, and containing more contaminants does not necessarily mean that a solvent is less stable. Some previously used and partly degraded aqueous MEA solutions are more stable under oxidative conditions than others. A common denominator for the more stable solutions is a relatively high content of inert inorganic compounds, specifically calcium, sodium, potassium, silicon, and sulphur. Many of these were also present in high concentrations in the fly ash extract that was found to increase the stability of fresh MEA. Having these present does not seem to deteriorate the solvent stability. On the contrary, it could be beneficial to have them there, meaning that a "clean" solvent is not necessarily the most stable solvent under process conditions. The most stable of the previously used MEA solutions also had a relatively low content of some metal ions, especially chromium, magnesium, and zinc. The removal of one or several of these metal ions could potentially be positive for solvent stability. The more stable solutions also contained a higher concentration of heat-stable salts in general than the unstable solution. Two of the pre-used solutions were more stable than fresh ethanolamine, while the third was less. The solvent with the lowest content of degradation products and total heat-stable salts was the least stable under oxidising conditions.

Degradation mechanisms are complex and not yet fully understood. This work adds data to the current knowledge base and points in the direction of which compounds seem to have a significant impact on the oxidative degradation rate of MEA. The reactions also take place in a very complex matrix, making mechanistic studies harder than in simpler systems and making it harder to isolate one effect or the effect of one species from that of another. Without a way of simplifying the CO_2-capture process conditions, batch experiments with complex matrixes will to some degree, represent the conditions in the actual process. The insights found under accelerated degradation conditions like these are not reproducing the exact reactions as we find on a large scale but give information on overall stability under oxidising conditions. However, these conditions never present the exponential degradation regime seen in the pilot scale, which is why testing under cyclic conditions will always be important when assessing overall stability, not just stability under oxidising conditions. The same degradation compounds are formed during oxidative degradation of all the tested MEA solutions, independently of whether or not they were previously used in a pilot plant to capture CO_2 but differ significantly from the degradation compounds that dominantly build up in the capture plants.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccst.2023.100110.

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