Important Aspects Regarding the Chemical Stability of Aqueous Amine Solvents for CO$_2$ Capture

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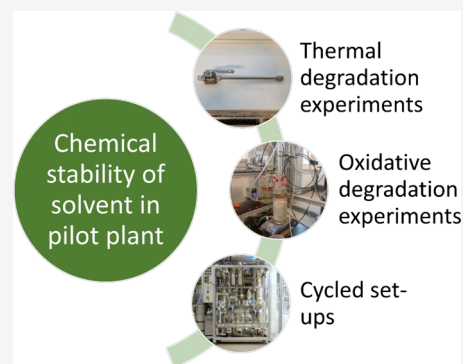
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ABSTRACT: The chemical stability of aqueous amines is an essential property to study before new amines are introduced in pilot plants, to reduce risks related to the operation, cost and environment. There are no standard methods for studying degradation and no standardized way of knowing which components to search for. This work will give an overview of the current status of amine degradation research with recommendations for further work within this field. Degradation of aqueous amines in the CO$_2$ absorption process will always occur, though some amines are more stable than others. Degradation leads to compounds with various functional groups, some of which require monitoring from an environmental or health perspective. Future experimental activity should focus on closing the knowledge gaps. Improved knowledge could help to better predict and monitor degradation, help design better mitigation technologies, and minimize solvent degradation by fine-tuning the plant operation.

Chemical stability of solvent in pilot plant

Thermal degradation experiments

Oxidative degradation experiments

Cycled set-ups

INTRODUCTION

One of the methods to mitigate global warming is by capturing CO$_2$ from industrial flue gas sources or power plants. Postcombustion CO$_2$ capture using amines is a mature process. The full-scale operation has been employed at Saskatchewan in Canada (Boundary Dam) since 2014 and Petra Nova in Austin/Texas for three years (2017−2020). The solvent technologies in these plants are based on proprietary solvents provided and developed by MHI and Shell Cansolv, while the first full-scale plant in Norway will operate with Aker Carbon Capture's proprietary solvent technology. The large capture projects mentioned above use proprietary solvent systems, but we expect to see plants using generic solvents and solvent blends with known compositions in the future. Generic solvent systems proposed include, among others, ethanolamine (MEA), piperazine (Pz), and Cesar 1 (a blend of 2-amino-2-methylpropanol/piperazine and AMP/Pz).

Different amines show varying stability in the CO$_2$ capture process, and every solvent to be used industrially must have high capture efficiency and acceptably high chemical stability under operating conditions. Some solvents are inherently unsuitable for CO$_2$ capture from flue gases because of their degradation and corrosion behavior, like diethylenetriamine (DETA) and ethylenediamine (EDA). There are no general guidelines for when a solvent should be rejected for its chemical stability or corrosive behavior, even though some have developed their own categorization based on testing many amines using the same setup and experimental conditions.[1] However, the limits found there are not necessarily directly transferable to other setups and experimental conditions, as small changes in operating conditions and the presence of different contaminants may significantly impact chemical stability.

The process conditions also impact the chemical stability of all amine-based solvents. For example, exposing the CO$_2$-loaded solvent to high temperatures (typically around 120 °C) during solvent regeneration and the presence of oxygen and nitrogen oxides (NOx) in the gas to be treated can negatively impact the solvent stability. Furthermore, the presence of sulfur oxides (SOx), metals, or other particulate matter and impurities can either react with the solvent, participate in the degradation reactions, or enhance degradation due to catalytic effects. Independently of the reasons, the result is the formation of unwanted degradation compounds in reactions occurring in parallel with the primary chemical reaction between the absorbent and CO$_2$. Mitigation technologies can reduce, or ideally eliminate, the formation of these unwanted compounds. Technologies proposed include, for example, using various inhibitors to remove oxygen, radicals, or metals, or remove oxygen from the absorber sump, either using a

dissolved oxygen removal apparatus (DORA)[2] or nitrogen stripping.

How much degradation can be tolerated depends on the solvent, process conditions, presence of impurities, and formed degradation compounds. However, some guidelines are available. Morken et al. presented threshold values for, among others, total heat stable salt (HSS) concentration, metals (Fe^{2+}/Fe^{3+}), ammonia emissions, and degradation compounds.[3] The paper discusses recommended actions when the threshold is reached.[3] Additionally, Freeman et al. developed a method to estimate the maximum desorber temperature for various amines, typically at rich loadings.[4] As the method is based on constant loadings and at a certain concentration, it is most suitable for relative comparison between the amines. For MEA, the maximum recommended temperature was around 115 °C, and for piperazine, around 160 °C.

Reducing the formation and presence of degradation compounds is vital. Degradation compounds can be removed, i.e., by replacing solvent inventory (bleed and feed), filtration of particulates (mechanical or active carbon), or using different reclaiming technologies such as thermal reclaiming, ion exchange, and electrodialysis. As given above, Morken et al.[3] describe actions to be taken when concentrations of degradation compounds and impurities become too high. Further, a recent publication by Moser et al.[5] describes solvent management strategies during the MEA campaign at the RWE pilot plant.

Degradation compounds influence the CO_2 absorption capacity of the solvent and increase corrosion, foaming, and fouling. For MEA, losses of 0.21−3.65 kg MEA per ton CO_2 captured have been observed for various MEA campaigns at different capture pilot plants.[5] Other solvents such as Pz and a blend of AMP and Pz have shown less solvent loss than MEA.[6] Replacing a part of the solvent by feed and bleed or reclaiming, using pretreatment technologies for the flue gas, and mitigation technologies for reducing emission or degradation all come at a cost, and influence which amines may be used on a commercial scale. Solvent degradation may also impact health, safety, and the environment by forming potentially harmful components, such as volatile components and nitrosamines. These will require monitoring to safeguard the health of people surrounding and operating the plant and the environment.

Understanding degradation mechanisms and performing lab-scale experiments are crucial for the use at the industrial scale. Knowledge about degradation mechanisms and how the process conditions impact them helps to develop and design mitigation technologies. Degradation experiments during solvent development help researchers to find optimal solvent composition and operating conditions, i.e., how high temperatures can be used during regeneration. Finally, laboratory data can be used to develop degradation models connected to process simulators allowing detailed studies on how process design impacts degradation. In the future, the models could also be used during industrial operations to predict the need for costly liquid analyses and the operation of mitigation technologies.

Studies that investigated the chemical stability of various solvents started in the 1930s when amines were used for gas treatment offshore and in submarines.[7−10] Until the end of the 20th century, the experimental focus was on high-temperature degradation in the presence of CO_2, carbamate polymerization reactions being the main degradation pathways. However, the

complexity increased when CO_2 removal from oxygen-containing flue gas from power plants was suggested, as oxygen radical reactions could occur. This work gives an overview of the current state of the work on degradation, including degradation mechanisms, known compounds, and experimental approaches for studying degradation. The advantages and disadvantages of different experimental approaches are addressed and discussed. Finally, we summarize some key learnings and recommendations for knowledge gaps to be filled next, helping the research community focus on the knowledge gaps.

2. DEGRADATION STUDIES

At first sight, the chemical stability of various solvents looks complicated since many variables influence the formation of unwanted degradation compounds. These include factors like temperature, flue gas composition (O_2, NOx, SOx, CO_2, particle impurities), plant construction material, hold-up time, and circulation rate. Over the years, simplified lab-scale experiments have focused on specific aspects or factors of degradation chemistry. Combining the understanding from these simplified experiments has resulted in the design of more complex setups that have been capable of capturing the behavior of degradation products in large pilot and demonstration plants such as the SINTEF Tiller CO_2 plant and the plant at Technology Centre Mongstad (TCM).[11]

Amine solvents without CO_2 are relatively stable even under accelerated conditions in lab-scale experiments.[12,13] But when CO_2 is present, the oxidative and thermal stability is reduced. So, ironically, the component we are removing reduces the solvent stability.

In terms of chemical stability, simplified lab-scale systems either focus on oxidative or thermal degradation. Although this division between thermal and oxidative degradation is commonly used, it is not precise as thermal degradation compounds are also formed during oxidative degradation studies. Further, some thermal degradation compounds influence oxidative degradation and vice versa. In reality, in the CO_2 capture plant, it is the combination of oxidative and thermal conditions that induce the degradation pathways that take place. Thus, separating oxidative and thermal degradation studies will not reproduce all the pathways taking place in a process.

In the laboratory, the degradation studies typically focus on either amine loss and the effect of structural changes in a molecule[12−18] or investigation of one single amine or amine blend to better understand the solvent degradation pathways.[19−29] Examples of solvent systems investigated in more detail are MEA, Pz, and AMP/Pz.

The motivation in the laboratory scale is, often, identifying stable amines and amine blends, identifying degradation compounds to be followed during piloting and demonstration, and understanding the degradation mechanisms helping to choose operation conditions during piloting and/or demonstration.

An overview of amines that have been part of degradation studies is given in Table S1 in the Supporting Information. The Supporting Information also includes an overview of abbreviations and CAS of other components (Table S2).

Oxidative Degradation Studies. For oxidative degradation, the amount of oxygen present always plays a role. Oxygen is needed to initiate the degradation[30] through the formation of radicals. Radicals have short lifetimes and high reactivity in

Table 1. Overview of Oxidative Degradation Studies, Including Which Amines Were Studied, Their Goals and Main Findings

Amines	Goals	Main findings
MEA[10,32]	Stabilizing the *aq.* amine solvents used for CO_2 capture in submarines using inhibitors.	Fe and Cu catalyze degradation, while EDTA and sodium salt of *N,N*-diethanolglycine inhibit oxidative degradation.
MEA[34,35]	Studying the formation oxidative degradation products in samples from a CO_2 capture plant.	Many degradation mechanisms were proposed.
MEA[46,55]	Comparing laboratory and pilot scale degradation.	Significant overlap was found between degradation products from pilot and laboratory scales. Oxidative degradation is the dominant pathway dominant in the pilot scale.
MEA[36,37,57,58]	Studying oxidative stability in varying amine concentrations, with and without CO_2 or $NaVO_3$ or SOx in pressurized reactors.	Conclusions about the influence of concentration of amine, O_2, CO_2, SOx, temperature, and corrosion inhibitor were made. Power-law rate model presented.
MEA[40]	Studying stability under typical absorber conditions, investigating the effect of iron and inhibitor concentrations on ammonia evolution.	The presence of CO_2 hugely increases the rate of degradation.
MEA[25,41,42]	Testing oxidative stability under various parameters: pH, CO_2 loading, O_2/Fe/Cu/MEA concentrations, and inhibitor presence.	Mass transfer of O_2 is the limiting factor for the degradation rate of MEA.
MEA[39,45]	Studying inhibitors for oxidative degradation of MEA (*aq.*), and the influence of degradation and corrosion inhibitors on MEA stability.	Inhibitors that successfully worked under simulated absorber conditions were unsuccessful at hindering degradation under cyclic conditions. No inhibitors suitable for both corrosion and degradation inhibition were found.
MEA[38]	Studying the effect of stable salts on CO_2 solubility, viscosity, thermal and oxidative degradation, and corrosion.	1−2 wt % KI gave an increase in oxidative stability, without influencing CO_2 solubility, viscosity, thermal degradation, and corrosion.
MEA[27,54,59]	Studying oxidative stability at different temperatures and pO_2 in an open-batch setup.	Monitored MEA loss and 17 different degradation compounds.
MEA, TEA, DIPA[7]	Testing resistance of the amine solvents at 85 °C with constant O_2 sparging.	MEA was the most resistant amine toward oxidation, followed by TEA and DIPA.
MEA, DEA, MDEA[33]	Studying a series of *aq.*, CO_2 free amines under oxidative conditions.	Mechanisms for the formation of the primary degradation compounds formic, acetic, oxalic, and glycolic acid were proposed.
16 amines[14,15]	Studying degradation of amine solutions in a pressurized vessel at high temperature (140 °C) in the absence of CO_2.	Many oxidative degradation mechanisms were postulated in this work based on results from GC, GC/MS, NMR, and IC.
25 amines[13,18]	Studying structural effects in amines on oxidative stability, and correlations between that and ecotoxicity, biodegradability and thermal stability.	For primary and tertiary alkanolamines, increasing the carbon chain increased oxidative stability. Size/length of alkyl substituents seemed to increase stability. Steric hindrance effect had more impact than electronic effects. A correlation between biodegradation and oxidative degradation was observed, but not between oxidative degradation, ecotoxicity, or thermal degradation.
8 amines[16,17]	Studying oxidative stability in an open and closed batch system. The closed system had gas phase recycling.	Temperature and dissolved metals influence degradation and degradation rate. The open setup generally gave higher amine losses than the closed, with some exceptions.
5 amines (imidazoles)[60]	Studying degradation and toxicity of alkylated imidazoles.	Polyalkylated imidazoles had low oxidative stability. Degradation pathways suggested.
Several amines and blends[43,44]	Studying oxidative amine stability and solutions to amine oxidation. Monitoring degradation product formation with and without presence of metals or inhibitors.	Identification of degradation products.
Pz[48]	Studying rate of oxidation in the presence of catalysts.	Fe^{2+}, Ni^{2+}, and Cr^{3+} are only weak oxidation catalysts compared to Cu^{2+}.
Pz[49]	Studying oxidation rates and products in a bench-scale cyclic degradation apparatus. Comparing with oxidation in pilot-scale campaigns.	Created a model for degradation and solvent management costs in full-scale.
Pz[50]	Studying amine stability under oxidative conditions in an advanced flash stripper.	The stripper configuration seemed to reduce Pz degradation.
AMP[51]	Studying oxidative degradation (*aq.*) in an autoclave type reactor at 100−140 °C.	Degradation rate was found to be mass transfer limited like in Goff and Rochelle.[42]
AMP/Pz blends[21]	Studying oxidative stability at temperatures between 80 and 140 °C	The degradation rate of Pz increased in blend with AMP, despite of the same compounds detected in the single amine solutions as in the blends.
AMP/KSAR, MMEA, 1-(2HE)PRLD, 2-PPE[29,52,56]	Studying degradation of various amines	1-(2HE)PRLD and AMP/KSAR more stable than MEA. Volatile compounds were formed during degradation of MMEA.
MAPA[24]	Studying MAPA as a solvent for CO_2 capture. Degradation properties are included in this evaluation.	MAPA had lower oxidative stability than MEA.
EDA[61]	Investigating EDA as a solvent for CO_2 capture	Oxidative degradation reduced using inhibitor.

solutions, and the chemistry around them is complicated to verify. What is known is that when a radical is formed, the proximity of other radicals plays a role in the termination of the reaction (forming a neutral molecule). The identity of the

formed radicals is unknown, and no studies exist that follow these radicals toward termination. This is understandable as this would require very complex and expensive experimental work without a guarantee that the efforts will be rewarded with

Table 2. Overview of Thermal Degradation Studies, Including Which Amines Were Studied, the Goals of the Studies and Their Main Findings

Amines	Goals	Main findings
MEA[8]	Understanding and explaining different compounds' contributions to the corrosion, and solution contamination observed in gas-treating plants	HEIA and AEEA/HEEDA were identified. First suggestion of carbamate polymerization mechanisms. AEEA/HEEDA was proven to be corrosive.
MEA[67,68]	Identifying the main impurities in *aq.* MEA solution used for gas treatment process	Main impurities identified using ^{1}H and ^{13}C NMR spectroscopy. Mechanisms for formation proposed.
MEA[69,70]	Investigation of reaction rates and studying side reactions in aqueous MEA in gas treatment.	Degradation pathway suggested.
MEA[66]	Studying the impact of flue gas contaminants on the thermal stability of MEA.	Fly ash, sodium sulfate, and sodium thiosulfate had no impact on degradation rate. Nitrite increased thermal degradation. Fly ash inhibited the nitrite induced thermal degradation. Degradation pathways were suggested.
MEA[77]	Data collection for developing a kinetic model for oxidative and thermal degradation.	A kinetic model for oxidative and thermal degradation was proposed based on experimental data.
DEA[63]	Understanding degradation of DEA and the compounds it forms in the gas treating process.	Identification of degradation compounds from DEA, and pathway suggestion for its formation.
DEA[78,79]	Studying degradation under various conditions and identifying degradation compounds.	No thermal degradation observed up to 205 °C when no CO_2 or other acids were present. Major degradation compounds identified, the reaction rates discussed, and degradation pathways suggested.
DEA[80,81]	Studying degradation, degradation kinetics, and identifying degradation compounds	Several degradation compounds were identified, and pathways were suggested.
MDEA and its blends[84,85]	Studying degradation rate and identification of degradation products.	Stable up to 240 °C without CO_2. Negligible degradation with CO_2 up to 120 °C. Many degradation compounds identified and pathways suggested.
DIPA[95]	Studying degradation and degradation kinetics as well as identifying degradation compounds.	Several degradation compounds were identified and pathways were suggested.
DGA[93]	Studying DGA degradation with CO_2, and comparing to MEA for gas sweetening.	Reaction pathway for the formation of certain degradation compounds suggested.
MAPA[24]	Studying degradation of MAPA.	MAPA had lower thermal stability than MEA.
EDA[61]	Investigating EDA as CO_2 capture solvent.	Low thermal degradation at 100−120 °C. At high temperatures, formation of cyclic urea and related compounds was observed.
AEEA/HEEDA[98]	Studying thermal degradation with and without CO_2. Identifying degradation compounds and suggesting pathways for their formation.	High loss was observed in the presence of CO_2, while little degradation without CO_2. Major degradation compound identified.
DEEA[96]	Studying thermal stability of DEEA. Looking into the influence of T, CO_2 loading, and initial concentration.	Higher thermal stability than MEA observed. Degradation increased with T, CO_2 loading, and DEEA concentration. Thermal degradation products identified, pathway suggested, and a model proposed.
AMP[92]	Developing a kinetic model for degradation of AMP and studying the degradation compound formation under thermal degradation conditions.	A power law rate equation for thermal degradation of AMP to a specific degradation compound as a function of amine and CO_2 concentration was given. The degradation compound formation was more dependent on AMP concentration than CO_2 concentration.
1-(2HE)PRLD, 2PPE[56]	Characterization of amines as strong bicarbonate forming solvents for CO_2 capture	Both were found to have higher thermal stability than MEA.
18 amines[28,64]	Evaluation of degradation of various amines, including MEA degradation rate. Degradation compounds identified and pathways for formation suggested.	Degradation kinetics of MEA given, main degradation compounds identified, and pathways suggested. The least stable amines were DETA and AEEA/HEEDA, while the long-chained alkanolamines, AB and 5-amino-1-pentanol, DGA, AMP, and MIPA were relatively stable.
16 amines[12,14]	Investigating structural influence on degradation.	Degradation products identified and general pathways suggested for ethanolamines and ethylenediamines. For the tertiary polyamines the compounds with 4 or 5 atoms separating the amino groups were unstable due to ring formation when degrading. The other polyamines tested were stable.
22 amines[72]	Evaluating degradation and corrosion properties at 140 °C in the presence of CO_2 and O_2.	A quantitative structure property relationship model (QSPR) was built to predict degradation. Seven compounds were less corrosive and more stable than MEA.
42 amines[29,55,62,73]	Investigating biodegradation, ecotoxicity and thermal degradation of 40 amines.	Identification of degradation compounds and pathways were commented on.
Pz and 7 structural analogues to Pz[4,22,48,53,89]	Studying oxidative and thermal degradation of Pz. The effect of changing heteroatoms, ring size in monoamines and diamines, and methyl substitution was investigated.	Main degradation compounds identified. Reaction order determined. The stability of Pz and its structural analogues were given.
8 amines[71]	Studying thermal degradation of linear amines.	Degradation rate decreased with chain length. Some amines reached a thermodynamic equilibrium with their degradation products. EDA was the most corrosive of the studied amines.
5 amines (imidazoles)[60]	Studying degradation and toxicity of alkylated imidazoles.	All imidazoles showed high thermal stability. Some of them were corrosive. Degradation pathways suggested.
6 amines and blends[75]	Studying thermal and oxidative stability in the absence and presence of CO_2.	O_2 and CO_2 influence the thermal stability. Sterically hindered amines have higher thermal stability. In the absence of CO_2, low oxidative stability for AMP and AHPD. AHPD higher oxidative stability in the presence of Pz.
Sodium salts of amino acids and 8 amines[76,97,99]	Studying of amino acid salts to investigate their potential for CO_2 capture. Investigating degradation from a structural standpoint.	Salts of amino acids have lower thermal stability than MEA. For amino acid salts, a secondary amine functionality increased the stability, for alkanolamine and diamine the opposite was shown. Steric hindrance around amine group in alkanolamine increased stability. Major degradation compounds identified and degradation pathways were suggested for some of the investigated solvents.

Table 2. continued

Amines	Goals	Main findings
Amine and amino acids[74]	Studying thermal degradation on already oxidatively degraded solutions.	Typical thermal degradation compounds observed. Comparable amine losses to fresh amine solutions.
13 amines, and some blends[88,100]	Investigating thermal stability and corrosion of various amines in aqueous amine and amine-organic diluent-water solutions.	Organic diluents influenced the amine stability. No single explanation was found to why the stability is reduced in the presence of organic diluent. For MEA, typical degradation compounds were also observed in the experiment with organic diluents.
MDEA-DEA-AMP blends[82]	Studying the degradation of eight aqueous solutions in the presence of CO_2 and H_2S.	MDEA degraded slower than DEA. MDEA and DEA degradation almost independent of AMP concentration. Minimal degradation of DEA and MDEA up to 200 °C.
Pz based amine blends[91,94,101]	Studying thermal stability of piperazine (Pz)-based amine blends to understand the relationship between structure and stability.	18 thermally stable Pz-based amine blends were identified based on degradation rate in CO_2 loaded solutions at 150 and 175 °C. Some degradation pathways were identified.
MDEA/Pz, MDEA, Pz[47,86,87]	Investigating MDEA/Pz as solvent for CO_2 capture, including thermal and oxidative stability.	MDEA/Pz more stable than MEA. Pz in MDEA/Pz seems to inhibit thermal degradation of MDEA. Less formate observed for the blend compared to MEA or MDEA alone.
AMP/KSAR[52]	Studying degradation and heat of dissolution of solids in an aqueous blend of AMP and KSAR with CO_2.	The blend was slightly more stable than MEA under both thermal and oxidative conditions. In the blend, AMP was more stable than SAR.
MDEA/Glycine[102]	Investigating thermal stability with and without CO_2.	Higher stability was observed for MDEA/glycine than MDEA alone.
Pz/DEA[83]	Investigating thermal stability at various CO_2 loadings.	Higher loss of PZ in this blend compared to other blends. Pathways proposed for major degradation compounds. Empirical rate law for loss of Pz given.

new insight and knowledge. Thus, the research has focused on the termination products like ammonia, alkylamines, aldehydes, and acids.

The general problem with oxidative degradation experiments is that setups and experimental conditions vary greatly, making it difficult to compare data from different research institutions/universities. In our experience, minor differences in the experimental conditions may play significant roles in the outcome of the experiments, as differences in the reactor temperature, gas flow, condenser temperature, and setup (open/closed) impact the amine loss. Typically, a glass or stainless-steel reactor is used for the experiments. The reactor can be pressurized with gas added to the headspace. However, in most cases, the experiments are formed under atmospheric pressures introducing gas continuously into the reactor. The gas introduced contains air or oxygen (6−98%) mixed with N_2 with/without CO_2 and sometimes other impurities like SOx. The reactor temperature varies between 55−140 °C, and the solution might be preloaded with CO_2. The experiments last from 15 days to a month. Additives such as Fe, particulate matter, or fly ash are sometimes present. Variations of the factors described above are ways of accelerating the degradation to reduce the duration of the degradation experiments from months or years to weeks or days. However, no study has investigated how these accelerated conditions influence the formation mechanisms of different degradation compounds or the relative order in which they are formed. Vevelstad et al. performed a principal component analysis (PCA) for MEA and its degradation compounds, comparing samples from two different open degradation setups with varying oxygen and iron concentrations, a cycled setup, and three different samples obtained from pilot campaigns, capturing CO_2 from industrial sources.[31] The results showed that the cycled experiment gave a degradation profile similar to pilot samples in terms of degradation compound distribution, and for the open setup, the experiments with oxygen concentration (6% O_2) and without the addition of iron were more similar than the experiments at higher oxygen concentration.[31]

Table 1 gives a full overview of the studies conducted with the main goals and findings. The most studied amines are MEA[7,10,13−18,25,27,32−46] and Pz,[21,43,47−50] while AMP,[13,15,18,21,51,52] and MDEA[13,15,18,33,47] are also extensively studied. Some early studies were related to gas conditioning applications and gas purification in submarines.[7,10,32,33] Several studies focus on changes in the molecular structure,[13−16,18,44] showing that some structural features seem to improve oxidative stability. Also, metals' impact on degradation[10,25,32,40−44,53] and degradation or corrosion inhibitors[10,25,32,36−44] have been investigated. Furthermore, numerous works have proposed pathways for degradation compounds,[14−17,20,21,27,29,33−35,40,43,44,54,55] and extensive work has been performed to identify degradation products of selected solvents.[14,15,19−21,26,27,29,44,48,55,56] Finally, there are studies focusing on the impact of amine concentration, CO_2, O_2, and temperature variations.[19,20,25,36,37,41,42]

Lepaumier et al.[14,15] conducted the most comprehensive mechanistic studies of both amine degradation and degradation pathways. The studies investigated six alkanolamines, one alkanolamine/diamine, five ethylenediamines (where a minimum of one nitrogen was a tertiary or a secondary amine), and four additional polyamines. Several of the main conclusions from these works are applicable to other amines, and they can be summarized as follows:

- Most amines participate in demethylation, methylation, dealkylation reactions, and, to some extent, carboxylic acid formation.
- Volatile compounds are always formed.
- Ethanolamines oxidize to amino acids (typically found in small amounts).
- Ethylenediamines degrade to piperazinone.
- Tertiary amines are slightly more stable than primary and secondary amines, but an exception is observed when the chain length between two amino groups makes it possible to form five- and six-membered rings.
- Steric hindrance (AMP) decreases degradation (only AMP investigated). Later, Buvik et al. and Muchan et al. showed that steric effects such as chain length, substituents location in relation to the nitrogen atom, and bond strain positively affect stability.[13,18]

Although the studies mentioned above only studied particular amines, we believe that sterically hindered amines will behave similarly to AMP. Decreasing bond flexibility seems to play a stabilizing role under oxidative conditions. For example, the ring structure of Pz makes the N−H bond more

rigid than the N−H bond in MEA, making the initial radical reaction less likely to occur and improving the stability of Pz compared to MEA.

Thermal Degradation Studies. Thermal degradation studies, like oxidative degradation studies, have focused on understanding degradation trends due to the molecular structure of the amines or understanding the thermal degradation and its pathways in specific solvent systems. Most of the published thermal degradation experiments are conducted in either stainless steel cylinders or stainless steel autoclaves. In the case of stainless-steel cylinders (the size varies from study to study), they are filled with absorption solutions that contain CO_2, which are placed in an oven at the desired temperature (often 110−150 °C). For every sampling, one or two cylinders are taken out of the oven, and the content is analyzed using available analytical schemes.[22,28,29,55,62] The other experiments use a jacketed autoclave in stainless steel, where gas is introduced in the headspace. These experiments are also conducted at a similar temperature as the closed cylinder experiments.[12] The degradation compounds formed in these experiments are mainly described as carbamate polymerization products, meaning that the presence of CO_2 is essential for the reaction to occur. Mechanisms and pathways suggested for the identified degradation compounds go back to the 1950s.[8,63] Davis and Eide-Haugmo[62,64] give good overviews of the thermal degradation of different amines, while a comprehensive overview of degradation compounds is given by Gouedard et al.[65] A study has also been conducted to investigate the impact of flue gas contaminants on the thermal degradation of MEA.[66]

The thermal degradation experiments are typically conducted in relatively simple laboratory set-ups, and a large number of studies have been conducted, as shown in Table 2. Thermal stability in the presence of CO_2 has been more thoroughly studied than stability in the presence of oxygen. This is because, historically, the focus has been on aqueous amine solutions used in natural gas treatment, not for CO_2 capture from oxygen-containing flue gases. Most studies focus on specific blends or single amines, and thoroughly studied amines are MEA,[8,12,28,62,64,66−77] diethanolamine (DEA),[12,62,63,73,78−83] N-methyldiethanolamine (MDEA),[12,47,62,64,73,82,84−88] Pz,[4,22,47,53,62,64,75,83,86,89−91] AMP,[12,52,62,64,72,73,75,82,92] and diglycolamine (DGA).[62,64,71,93,94] Studies on the following amines could also be found: diisopropanolamine (DIPA), 1-(2-hydroxyethyl)pyrrolidine (1-(2HE)PRLD), 2-piperidineethanol (2PPE), 3-amino-1-methylaminopropane (MAPA), various imidazoles, 2-(diethylamino)-ethanol (DEEA), sodium salts of various amino acids, N-(2-hydroxyethyl)ethylenediamine (AEEA/HEEDA), and ethylenediamine (EDA).[24,56,60,61,76,95−98] Davies (2009) and Eide-Haugmo (2011)[62,64] systematically investigated large sets of amines. Most of their work is described in their Ph.D. theses,[62,64] making the results less available. Thus, in recent years, we have seen publications[61,98] discussing the potential of amines, like EDA and AEEA/HEEDA, which Davies (2009) and Eide-Haugmo (2011) found to be corrosive and/or unstable. Davies and Eide-Haugmo also give good overviews of thermal degradation pathways suggested from the 1950s to 2009. Furthermore, Lepaumier et al. gave a general overview of degradation mechanisms for alkanolamines and polyamines.[12,14] In this case, structural variation significantly impacts the chemical stability, where tertiary amines and

amines with steric hindrance close to nitrogen often are more stable than others. It is also important to note that the chain length between functional groups in polyamines is essential since longer chains can form stable ring structures. This is often observed for tertiary polyamines such as N,N,N′,N′-tetramethylbutylenediamine (TMBDA) and N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA).[14]

Process Degradation. Lab-scale single-condition experiments (thermal and oxidative degradation experiments) are important for identifying new potential solvents for CO_2 capture and the identification of degradation compounds. Although both oxidative and thermal degradation conditions separately produce many of the compounds found in large-scale pilot plants, neither of them can produce the same degradation profile as observed in pilot samples. Some of the most prominent degradation products formed in pilot-scale CO_2 capture plants are not found to any considerable extent under any of the single condition experiments. Therefore, several lab-scale cyclic degradation setups have been built and are now available for solvent testing. Here, the solvent circulates between low and high temperatures. Oxygen is available in the low-temperature part of the cycle. A detailed description of two cyclic degradation rigs can be found elsewhere.[11,87] These setups mimic the CO_2 capture process and provide more realistic conditions. For example, the SINTEF solvent degradation rig[11] has been shown to give a more similar degradation profile as seen in pilot samples for MEA than in the single condition experiments. The cyclic experiments are needed in the scaling-up of solvent technologies, as it allows the identification of prominent degradation compounds before taking the solvent to the pilot scale. This will ensure that the most critical degradation compounds, either influencing the operation, emission, or operation of flue gas wash sections, can be monitored during piloting. Only a few studies and amines have been investigated in cycled laboratory setups. One reason for the low abundance of cyclic degradation studies is the complexity of these rigs, in effect increasing the experimental cost. The following amines have been studied in cycled systems: MDEA, MEA, AMP, Pz, 2-methylpiperazine (2-MPZ), and MDEA/Pz.[11,45,87,90,103,104] Mostly, the main focus of these studies has been assessing the solvents' chemical stability when repeatedly exposed to low and high temperatures. However, one study also investigated how different inhibitors behave under these conditions.[45]

Buvik et al. give an overview of degradation studies at the pilot scale.[105] The review points to the importance of flue gas pretreatment technologies, such as the removal of SO_X, NO_X, and particulates, to increase solvent lifetime and reduce amine degradation. Another main conclusion is the fact that no single degradation compound of the ones studied stands out as the only one to monitor and to assess solvent degradation.

Modeling Studies. Some kinetic thermal[64,77,79,81,85,106] or oxidative[37,40,42,58,107] degradation models have been developed based on experimental data. Most models consider amine loss and not the formation of degradation compounds, mainly due to the lack of knowledge of actual degradation pathways, kinetics, and often the concentration or even identity of degradation compounds themselves. Some simplified approaches have also been used to calculate the reaction rate for amine loss, assuming that the reactions for amine to various degradation compounds are first order with respect to the amine. These simplified models typically correlated factors such as oxygen, temperature, CO_2, or amine concentration to

amine loss.[4,59] However, experimental practices and uncertainties influence the possibility of using data on model development. For example, different studies analyze different degradation compounds. In open batch reactors, the amine and ammonia loss through evaporation is not quantified, and analytical uncertainties are not reported. Chakma and Meisen proposed a model for thermal degradation of MDEA, and Kennard and Meisen, and Kim and Sartori for DEA.[79,81,85] Davis, Léonard et al., and Braakhuis et al. proposed kinetic models to describe the thermal degradation of MEA.[64,77,106] The Léonard et al. model is based on the analyzed amount of MEA. The kinetic models by Davis and Braakhuis et al. are more detailed and include the formation of several degradation products.

For oxidative degradation, various works have been conducted for MEA or a blend of MEA-MDEA and are described by Goff and Rochelle, Chi and Rochelle, Supap et al., Pinto et al., and Lawal and Idem.[37,40,42,58,107] The degradation compounds taken into account in the models and the amount of data used to fit the model vary significantly.

3. CHARACTERIZATION OF SOLVENT (MAPPING OF DEGRADATION COMPOUNDS)

In postcombustion CO_2 capture using chemical absorbents, the principle is based on a reversible chemical reaction between the absorbent and CO_2. Therefore, the compounds that can partake in degradation reactions are both the free amines and the products formed in the reactions between amine and CO_2, e.g., carbamates. Environmental friendliness and safe work conditions can only be ensured by knowing the structure of the chemical compounds formed during amine degradation. Thus, studying degradation pathways and degradation component identification are crucial tasks during solvent development. Based on previous work, chemistry knowledge, and the structure of the solvent, some predictions can be made about the degradation mechanisms and compounds that can be formed for many amines. There is, however, no single analytical method that can be used to identify, let alone quantify, the degradation products formed in a new, previously unstudied amine. Studying the degradation of new solvents will always require the development of analytical methods and detective work to propose likely degradation compounds, then identify and finally quantify them. Even two amines, where the only difference is one more $-CH_2-$ in its alkyl chain, will go through different degradation pathways, and the degradation compounds and their mechanism of formation cannot be entirely predicted based on one of them. To illustrate, let us look at the carbamate polymerization mechanism occurring with amines in the presence of CO_2. In the case of MEA and 3-amino-1-propanol (AP), the mechanism leads to two different ring compounds, as illustrated in Scheme 1. The mechanism is the same, but the products are different, needing two different analytical methods for quantification.

Despite these challenges, alkanolamines and, to some extent, polyamine studies give an indication of the classes of compounds that can be expected. It is important to note that in these laboratory-scale studies, the solvents were degraded to a high degree, under partly unrealistic conditions, to produce sufficiently high concentrations of degradation products to surpass the detection limits of the analytical instruments. This means that the reaction schemes and

Scheme 1. : MEA and AP Reacting with CO_2 Forming, Respectively, 2-Oxazolidinone (OZD) and 1,3-Oxazinan-2-one (OZN)
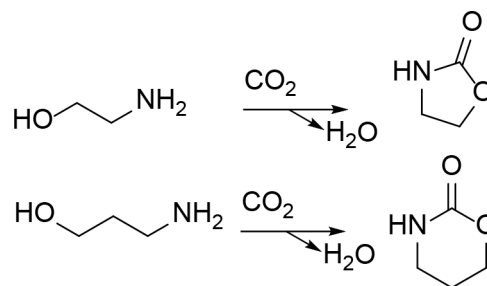
degradation compound concentrations are typically higher than what would be seen in a full-scale plant.

Generally, the compounds formed contain a combination of two or more of the following species: N, C, H, and O. The following functional groups and component types are generally observed in degradation studies: ammonia, aldehydes, alkylamines, carboxylic acids, amides, amino acids, ketones (in some cases), urea, cyclic structures such as piperazinone, imidazolidinone, oxazolidinone, and pyrazines. Most of these are not volatile components and will therefore accumulate in the solvent system, giving rise to more operational and cost issues than environmental or health concerns. One might say they could still be a health concern; however, these single components are not present in concentrations believed to cause any danger to operators, especially since personal protective equipment is already used when working with chemical compounds in the lab and industry. As long as the component is not volatile, it would, therefore, be hard to see that it can pose a larger risk than the risks we are surrounded by in our daily life (i.e., detergent, antifreeze, cosmetics).

There are numerous general analyses used for solvent monitoring, due to the variation of functional groups among the degradation compounds. This means that a combination of analytical instrumentation is required to detect them. Buvik et al.[105] give a thorough overview of analytical methods used in pilot campaigns, including both more general methods and degradation compound-specific methods. Numerous analytical equipment has been used in lab-scale experiments to identify and understand the formation of degradation compounds. This includes instrumentation for both gas and liquid chromatography (GC and LC, respectively), often coupled with mass spectrometry (MS) or other detectors. Common variations of GC and LC are GC–MS,[12,15,29,46,108−112] GC coupled with nitrogen chemoluminescence detection (GC-NCD)[56,104] or flame ionization detection (GC-FID),[113] LC with tandem mass spectrometry (LC−MS/MS),[27,29,46,54,56,109] high-performance LC (HPLC)[22,23,26,66,114,115] and HPLC coupled with time-of-flight MS detection (HPLC TOF-MS).[66,108,116] Other important analytical methods include ion chromatography (IC),[15,22,23,26,27,46,54,66,108,109,111,115,116] capillary electrophoresis (CE),[114,117] nuclear magnetic resonance (NMR),[15,22,109,110,118] and Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR−MS).[1,109] A combination of several of these is required for analyzing all degradation compounds; GC-NCD is often used specifically for the analyses of total nitrosamines, while IC is often used for carboxylic acids or other anionic compounds or the amine itself. GC−MS and LC−MS/MS, HPLC techniques are used for various degradation compounds. The choice is often related

to the availability of competence and instrumentation. Table S3 in the Supporting Information gives more details regarding analytical instrumentation and analytical methods for degradation components.

The amount of metals in the solvent is often monitored by inductively coupled plasma mass spectrometry (ICP-MS) and water content by Karl Fisher titration or by an internal standard added to the solution. Titration with a strong acid is used for determining the total amine concentration, and the amount of absorbed CO_2 is analyzed by total inorganic carbon (TIC)/total organic carbon (TOC) analyzer or by titration using e.g., $BaCl_2$.[119] Using a total nitrogen (TN) analyzer or total organic nitrogen using the Kjeldahl method[120] gives the amount of nitrogen in the solutions. Finally, a wet chemistry method based on ion exchange followed by titration[118] has been used to analyze for the heat-stable salts (HSS, total ionic content in the solution). Density can be used to monitor CO_2 loading of the solvent.

## 4. ENVIRONMENTAL AND HEALTH ASPECTS OF SOME DEGRADATION COMPOUNDS

Certain degradation compounds need to be monitored, either from an emission or a health perspective, or both, and many of these compounds are formed in tiny amounts. Until more research on the potential effects of specific components is done, their presence, even in very concentrations, requires monitoring. An example here is nitrosamines, a group of generally carcinogenic compounds.[121] However, few studies are available for the nitrosamines that are typically formed in the CO_2 capture process. For some, there are indications of them being less carcinogenic than, for example, N-methyl-N-nitroso-methanamine (NDMA); which is a nitrosamine that is found in some processed foods. If the specific toxicity or carcinogenicity of the identified nitrosamines is not tested, a generalization is made by putting them in the same class as nitrosamines that already have been tested, such as NDMA. The formation of nitrosamines depends on the molecular structure of the amine, and all aqueous amine solutions in a CO_2 capture process will result in some nitrosamine formation. Stable nitrosamines are formed from secondary amines. Nevertheless, to some extent, nitrosamines are formed from all aqueous amine solvent systems. This is because the primary or tertiary amines are observed to form secondary amines, and these degradation compounds can, in turn, form nitrosamines, meaning that the nitrosamine formation in primary and tertiary amines typically is much lower than in secondary amines. Many solvent-specific nitrosamines formed are nonvolatile compounds and will, therefore, primarily be contained in the solvent. For several of the smaller nitrosamines (often not solvent specific), which have been of interest to other applications than CO_2 capture, (standardized) analytical methods are available. These are often referred to as the EPA mix (water analysis EPA 521[122]), and include nitrosamines such as NDMA, N-nitrosomethylethylamine (NMEA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA), N-nitrosodi-n-butylamine (NDBA), N-nitrosopyrrolidine (NPYR), and N-nitrosopiperidine (NPIP). A group methodology for analyzing nitrosamines exists. However, in a round-robin test conducted in the OCTAVIUS project, this method did not give reliable quantification of the nitrosamine content in the range of 0.1−1.2 mg N-NO/kg sample.[123] The same work shows that the laboratories were able to give reliable results for nitrosamine in the sulfamic matrix. Further,

only a few laboratories could analyze low levels of nitrosamines in the solvent matrix and the whole specter of nitrosamines requested in that work. In carbon capture and storage (CCS) research, many studies related to nitrosamines have been conducted, and these studies give information about the formation and decomposition in the process. They have highlighted factors contributing to the formation and mapped nitrosamines in many open solvents.[124] Work has also been done looking into the mitigation technologies based on adjusting the process conditions (temperature in the desorber), inhibitor use, and nitrosamine destruction (e.g., catalytic hydrogenation or with ultraviolet (UV) light).[125] Many of the mitigation methods will be challenging to use in industrial scale. For example, the effect of UV-light is reduced significantly in solvent with discoloration. Formation of nitrosamines in nonaqueous or water-lean solvents that include an amine has not been adequately investigated.

All amines will form ammonia, alkylamines, and aldehydes when they degrade. Ammonia, smaller alkylamines, and aldehydes such as methylamine and formaldehyde are volatile and will be emitted with the purified gas from the absorber. Since these are well-known components, their behavior after being emitted is known, and emissions permits that take these into account can be provided.
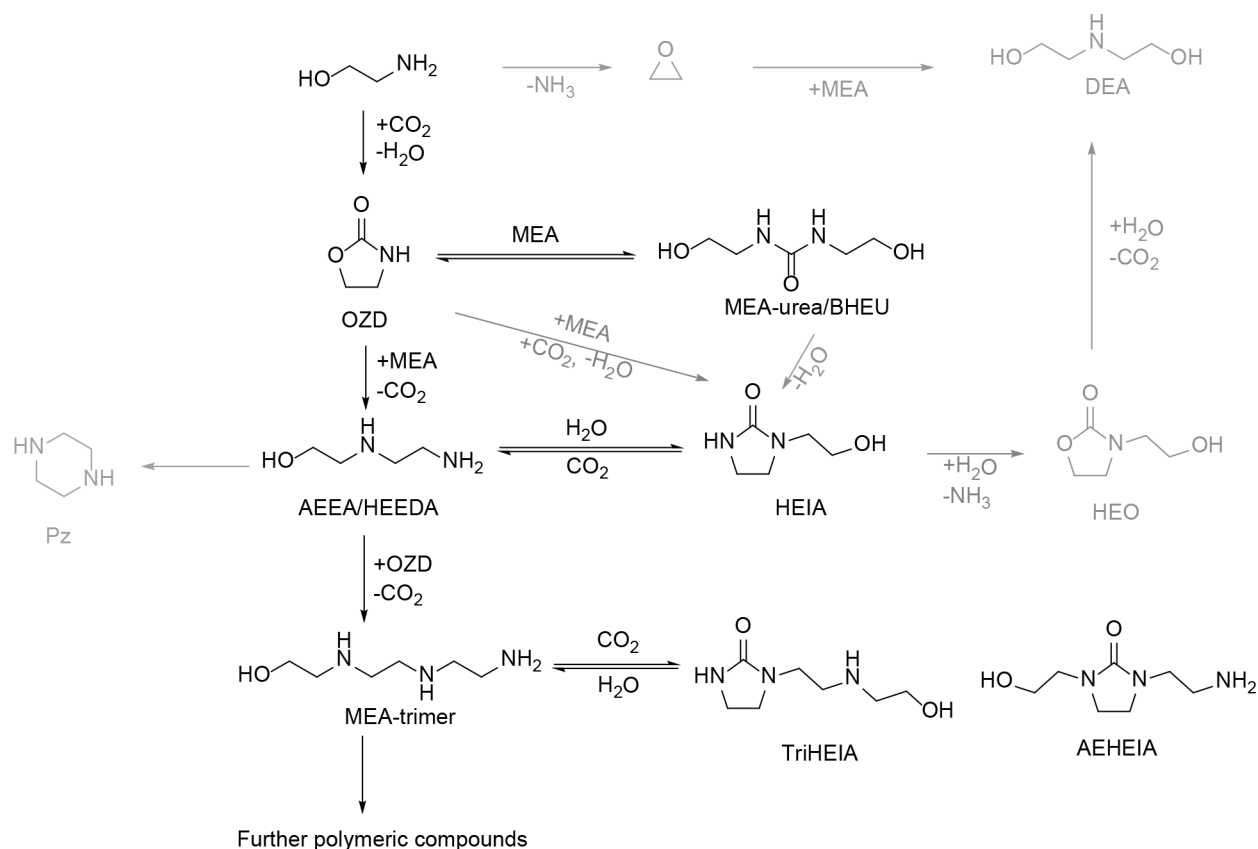
5. DEGRADATION PATHWAYS

MEA is the most studied amine in terms of degradation, where a large number of degradation compounds are identified, in some cases quantified, and pathways of formation have been suggested. A general overview of amines investigated combined with degradation compounds identified for different amines and formation pathways has been summarized by Gouedard et al.[126] Morken et al.[127] published a comprehensive data set related to MEA degradation on a pilot scale. Lepaumier et al.[12,14,15] suggested degradation compounds and pathways for a set of alkanolamines, ethylenediamine, and some other polyamines both thermal and oxidative degradation, as did Gouedard,[65,110] particularly for MEA. Vevelstad et al.[16,17,54] suggested pathways and degradation compounds for oxidative degradation of a set of alkanolamines, Eide-Haugmo[62] suggested schemes for the thermal degradation of over 40 amines. Davis and Rochelle,[28] Voice et al.,[24] Freeman et al.[22] (Pz), and Wang et al.[19−21] also add valuable contributions to amine degradation mechanisms. MEA is the most studied amine in terms of degradation, where a large number of degradation compounds are identified and, in some cases, quantified, and pathways of formation have been suggested. A general overview of amines investigated combined with degradation compounds identified for different amines and formation pathways has been summarized by Gouedard et al.[126] Morken et al.[127] published a comprehensive data set related to MEA degradation on a pilot scale. Lepaumier et al.[12,14,15] suggested degradation compounds and pathways for a set of alkanolamines, ethylenediamine, and some other polyamines, both thermal and oxidative degradation. Gouedard et al.[65,110] suggested pathways and degradation compounds, particularly for MEA. Vevelstad et al.[16,17] studied oxidative degradation of several alkanolamines, while Eide-Haugmo[62] focused on the thermal degradation of over 40 amines. Davis and Rochelle,[28] Voice et al.,[24] Freeman et al.,[22] and Wang et al.[19−21] also add valuable contributions to amine degradation mechanisms.

Scheme 2. Suggested Pathways for the Formation of HEGly, HEHEAA, 1HEPO, and 4HEPO[15,17,35,46,65]
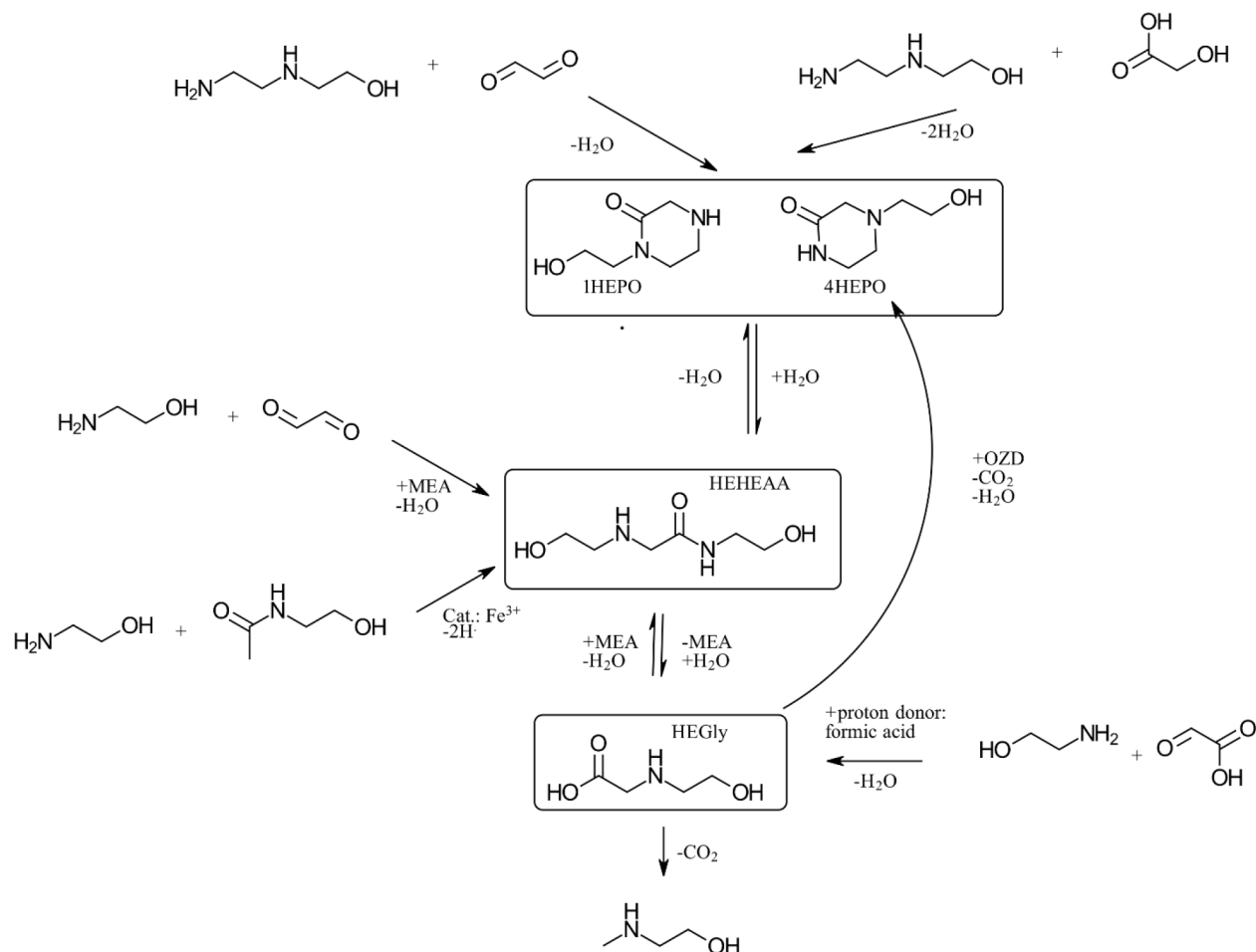
Scheme 3. Suggested Pathway of Formation for the Amides HEF, HEA, 2-Hydroxy-N-(2-hydroxyethyl)-acetamide (HHEA), HEO/HEOX, N1,N2-Bis(2-hydroxyethyl)-ethanediamide (BHEOX), and Oxazolines, 2-oxazoline and 2-methyloxazoline.[55,65,109,110] **The Amides Could Also Be in Their Salt Form, as Described by Ref 117.**
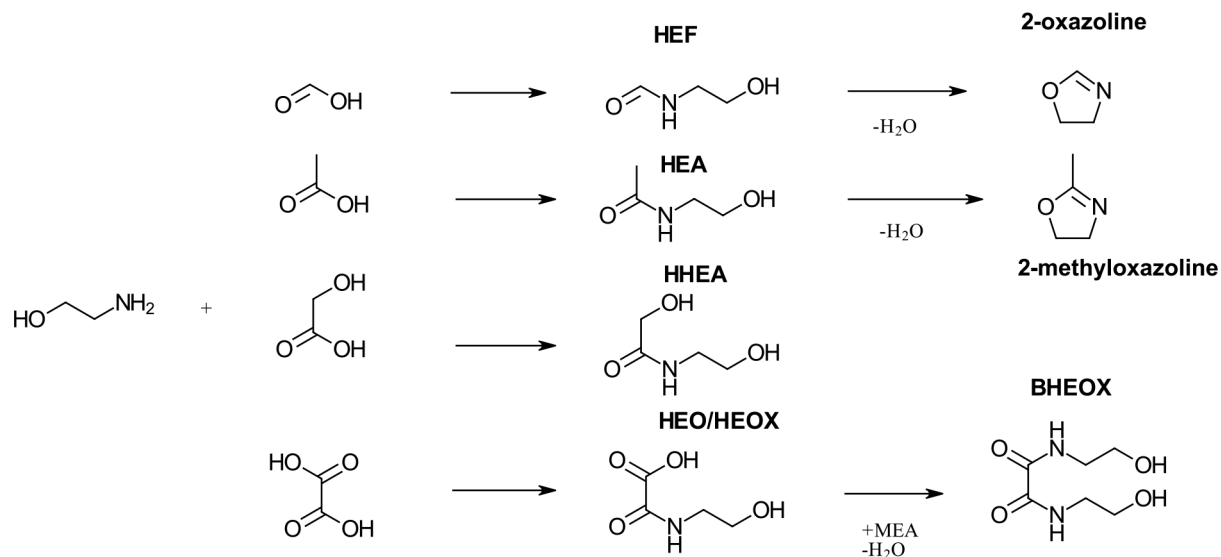
For oxidative degradation products, more than one pathway is needed to explain the identified compounds. Thus, MEA oxidative degradation is divided into different pathways for different degradation compounds. The compounds described here are also present in pilot samples. In most cases, several pathways have been suggested for the same compound, and several suggested degradation compounds are still not identified in pilot samples. It is not expected that any of

Scheme 4. : Carbamate Polymerization Pathways^a for MEA[8,12,62,64,68,70]

^{a}The black pathways are the most accepted mechanism the last ten years, while those shown in grey are less commonly accepted.

them are major degradation compounds since, in several cases, the nitrogen balance has been closed, meaning that nearly all the nitrogen contained in the initial MEA solution is recovered in MEA and its known degradation compounds after degradation. The initial reactions in the absorber are believed to be radical reactions which will give oxidative fragmentation of the amine either by electron or hydrogen abstraction. Both mechanisms occur for various amines depending on their molecular structure. It has been suggested that the electron abstraction mechanisms dominate for tertiary amines, while hydrogen abstraction mechanisms are more important going from secondary to primary amines.[128] Both mechanisms give similar degradation products, e.g., aldehydes (formaldehyde, acetaldehyde), carboxylic acids (formic, acetic, oxalic, glycolic, glyoxylic acid), ammonia, alkylamine (methylamine, dimethylamine etc.), and variations of the same intermediates, e.g., imine (either as iminium or as imine radical) either resulting in splitting between C−C or C−N. A thorough overview of several of these mechanisms/pathways is given in the review by Gouedard et al.[126] Typically, one sees a buildup of formic, oxalic, and, in some cases, acetic acid in addition to ammonia. In some cases, alkylamines, depending on the molecular structure of the solvent amine, are formed.

A summary of some of the suggested reaction schemes to form a range of the most significant degradation compounds of MEA is given in Scheme 2 and Scheme 3. For MEA, 4-(2-hydroxyethyl)-2-piperazinone (4HEPO/HEPO) and *N*-(2-hydroxyethyl)-glycine (HEGly) are major degradation compounds in pilots plants (SINTEF Tiller CO$_2$ plant, Esbjerg, TCM) as well in cyclic degradation equipment.[46,104,127] These

degradation compounds contribute heavily to the solvent sample nitrogen balance. There are no standard methods for analyzing solvent samples and no regulations regarding which components need to be quantified in the solvent samples from pilot plants. Different components are often reported from different campaigns due to availability and limited analytical capabilities, and different components being reported does not necessarily mean that these components are not formed. The result is large variations in degradation compounds reported in various experiments and pilots.

In Scheme 2, it is clear that some of the degradation components both are products and intermediates. This is the case for HEGly, *N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)-amino]-acetamide (HEHEAA), 1-(2-hydroxyethyl)-2-piperazinone (1HEPO), and 4HEPO/HEPO. Thus, isolating their behavior will be hard. HEEDA and OZD are suggested intermediates in the formation of respectively 4HEPO and 1HEPO or only 4HEPO. The formation of 1HEPO and 4HEPO also requires first-generation degradation products like aldehydes or their corresponding acids, e.g., glyoxal, glyoxylic acid, and glycolic acids. Currently, for the mentioned carboxylic acids, only quantitative data for glycolic acid has been reported from MEA samples.[15,26,127] Glyoxal forms oligomers in water and has only been indirectly identified as an expected intermediate product and as part of the oxidation pathway.[26,54,65] We have quantified small amounts of glyoxylic acid in pilot samples. However, formic, acetic, and glycolic acids are major acidic components in these samples (glyoxylic acid less than 1% of formic acid concentration). HEGly and 4HEPO are found in the largest amounts in SINTEF solvent

Scheme 5. Some of the Suggested Pathways for the Formation of OZD and OZD Reaction Pathways to Form Other Compounds[28,54,55,65a]
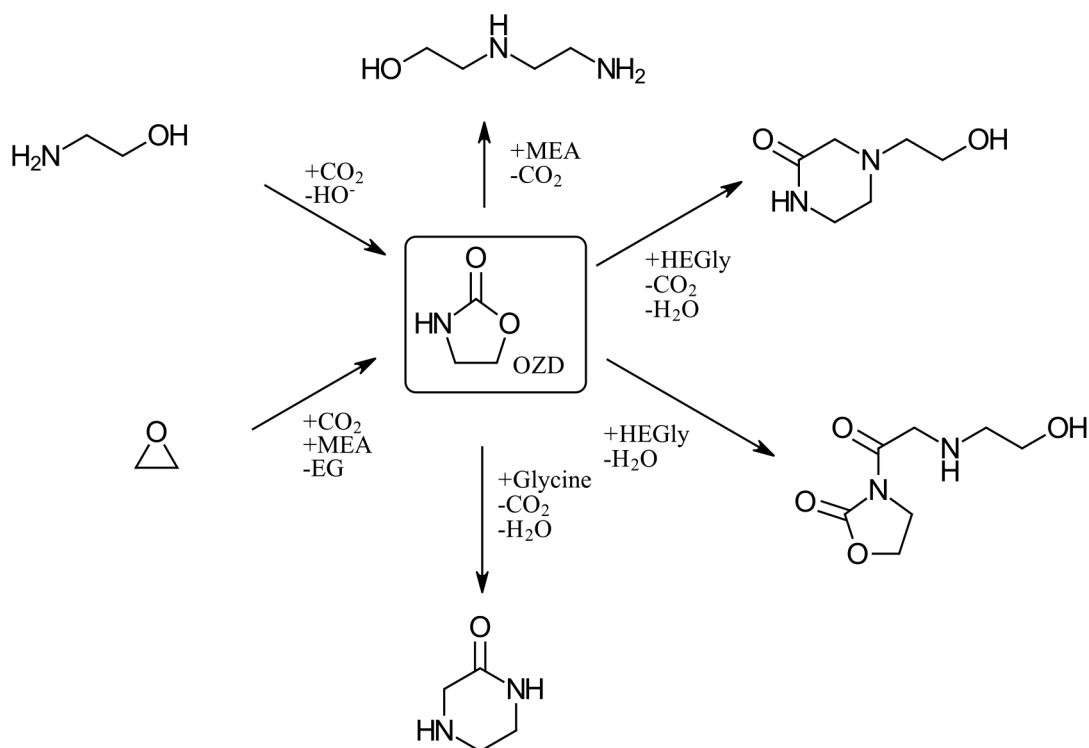
[a]Some of these compounds are not positively identified in pilot samples, such as piperazinone, epoxide, and substituted OZD component.

degradation rig as well as other pilot samples. In the few cases where 1HEPO has been quantified, it is found in small amounts.[31] The concentrations of 1HEPO, OZD, HEEDA, and HEHEAA are typically less than 1 mmol/L.

Degradation compounds in Scheme 3 have all been identified and, in most cases, quantified in MEA samples in samples from SINTEF solvent degradation rig and various pilots. 2-[(2-Hydroxyethyl)amino]-2-oxoacetic acid (HEO/HEOX) is only qualitatively identified.[54,109,129] Among the products in Scheme 3, N-(2-hydroxyethyl)-formamide (HEF), N-(2-hydroxyethyl)-acetamide (HEA), and 2-oxazoline are the most prominent components.

Carbamate polymerization reactions are described thoroughly in the dissertations of Davis and Eide-Haugmo,[62,64] and an overview is given in Scheme 4. The reaction scheme shows several suggested routes to the same products. The pathways in black have been more accepted in the past decade, while those in gray are less commonly accepted. For the carbamate polymerization reactions, the initial step is the formation of OZD from MEA and CO_2 (a cyclization reaction). Then a ring opening occurs, resulting in a diamine (AEEA/HEEDA) or a urea compound (N,N'-bis(2-hydroxyethyl)-urea(MEA-urea/BHEU)). The diamine can either react with OZD and form triamine or undergo another cyclization reaction to imidazolidinone (1-(2-hydroxyethyl)-2-imidazolidinone (HEIA)). Also, the triamine could form several imidazolidinones (1-[2-[(2-hydroxyethyl)amino]ethyl]- 2-imidazolidinone (TriHEIA) or 1-(2-aminoethyl)-3-(2-hydroxyethyl)-2-imidazolidinone (AEHEIA)). Quantitative data (based on commercial standards) for OZD, AEEA/HEEDA, and HEIA are available from thermal degradation experiments, e.g.,[28,46,55] SINTEF solvent degradation rig,[104] and from the MEA campaign at

Technology Centre Mongstad (TCM).[127] Additionally, MEA-urea data is available from thermal degradation experiments and from SINTEF's solvent degradation rig.[28,104] MEA-trimer and TriHEIA were identified by Davis,[64] and AEHEIA was quantified using a compound of similar structure da Lepaumier et al. and Silva et al.[46,55] In thermal degradation experiments, HEIA is often a significant component. It is a far less significant degradation component in cycled degradation setups and pilot plants. In the SINTEF solvent degradation rig, however, MEA-urea was one of the major degradation compounds. Additionally, HEEDA was present at a relatively high concentration in this setup compared to samples from TCM.

OZD is another important intermediate for both the carbamate polymerization route and the formation of 4HEPO, and an overview of the formation and consumption pathways for OZD is shown in Scheme 5. Currently, quantitative data for 4HEPO and HEEDA are available, while the rest are suggested components.

6. SUMMARY AND RECOMMENDATIONS

There are several lessons that we would like to summarize in the nine following points:

(1) Absorption of CO_2 using chemical solvents is a chemical process where unwanted side reactions forming degradation compounds will occur. A more stable chemical solvent is the goal. Alternatively, clever use of degradation mitigation technology is needed.

(2) For MEA, loss of 0.21−3.65 kg MEA per ton of CO_2 captured has been observed for various MEA campaigns at different capture pilot plants.[5] The proprietary solvents in the market typically show lower amine loss.

Anyhow, for the operation of the technology, information regarding which amines the solvent contains and which degradation compounds are present, and in which amount, should be made available for risk assessment. This will most likely be needed in many countries as input to emission permits.

(3) There are no shortcuts to be taken. The chemical stability of new solvents has to be tested on a lab scale, preferably in cycled systems, to identify major compounds as input to emissions permits and health and risk assessments before large-scale piloting. This requires lab facilities and analytical instruments for identifying degradation compounds such as a combination of IC, LC−MS, and/or GC−MS. Degradation and corrosion are show-stoppers if mitigation technologies cannot be used. Batch experiments are easier to perform and can give an initial starting point for identifying degradation products and potentially eliminate really unsuitable amines and solvent blends before costly cycled system testing is performed.

(4) Degradation compounds can be divided into different groups:

    a. more general components, like ammonia, smaller alkylamine, aldehydes, and smaller acids

    b. solvent-specific degradation compounds, including larger amines (e.g., diamine, methylated/alkylated amine, demethylated/alkylated amine etc.)

    c. cyclic structures (imidazole, piperazinone, oxazolidinone, imidazolidinone etc.)

    d. amino acids (some acids) and amide

    e. nitrosamines and nitramines

(5) Some degradation compounds require monitoring both in the solvent and gaseous phase. At least nitrosamine, nitramine, aldehyde, ammonia, alkylamine, and potentially other volatile compounds should be monitored. It is also wise to keep an eye on the health of the solvent as input to the operation of the plant. Some generalized methods can easily be conducted on-site. I.e., amine titration and analyzing for heat stable salts are simple methods which would give feedback daily or weekly. Monitoring specific degradation compounds often requires both offline and off-site methods. The optimal combination of on-site and off-site analysis depends on the solvent and the specific industrial site.

(6) Knowledge about the degradation and degradation mechanisms of MEA and other conventional amines and amine blends is essential for elucidating degradation compounds for new amines. However, it should be remembered that each solvent will have solvent-specific degradation compounds that should be known before large-scale piloting/demonstration. Thus, a good understanding of amine degradation and degradation mechanisms is needed to predict which compounds are formed.

(7) For full-scale implementation, analyzing all compounds is not necessary from an operational or environmental perspective, but the focus should be kept on the compounds that require monitoring from operational or environmental/health perspectives.

(8) Knowledge of degradation behavior will also help to operate the plant in a way that minimizes solvent degradation. This will also faciliate the selection of solvent specific management and degradation mitigation technologies.

(9) All aqueous amine solvents form nitrosamines. The concentration of nitrosamines will depend on the amine structure, where a secondary amine structure is particularly inclined to form a high concentration. Primary and tertiary amines may form secondary amine degradation products and are, therefore, also prone to nitrosamine formation. The hazard classification of nitrosamine is based on the group of compounds, and specific toxicity information for the solvent-specific nitrosamine observed in amine solvents does not exist. However, some initial results show that some solvent-specific nitrosamines are less carcinogenic than NDMA. Thus, analyzing for solvent-specific nitrosamines can reduce the overall risks compared to assuming that all nitrosamines are equally hazardous.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c02344.

    Overview of amines that have been part of degradation studies, abbreviations used for other components in this work, and analytical instrumentation used for identifying degradation compounds (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

1HEPO = 1-(2-hydroxyethyl)-2-piperazinone
4HEPO/HEPO = 4-(2-hydroxyethyl)-2-piperazinone
1-(2HE)PRLD = 1-(2-hydroxyethyl)pyrrolidine
2-PPE = 2-piperidineethanol
AEEA/HEEDA = N-(2-hydroxyethyl)ethylenediamine
AP = 3-amino-1-Propanol
AMP = 2-amino-2-methyl-1-propanol
DEA = diethanolamine
DEEA = 2-(diethylamino)-ethanol
DETA = diethylenetriamine
DGA = diglycolamine
DIPA = diisopropanolamine
EDA = ethylenediamine
EG = ethylene glycol
GC = Gas Chromatography
GC-FID = Gas Chromatography - Flame Ionization Detection
GC-MS = Gas Chromatography − Mass Spectrometry
GC-NCD = Gas Chromatography − Nitrogen Chemiluminescence Detection
HEEDA/AEEA = N-(2-hydroxyethyl)ethylenediamine
HEGly = N-(2-hydroxyethyl)-glycine
HEHEAA = N-(2-hydroxyethyl)-2-[(2-hydroxyethyl)-amino]-acetamide
HEIA = 1-(2-hydroxyethyl)-2-imidazolidinone
HPLC = High Performance Liquid Chromatography
IC = Ion Chromatography
LC = Liquid Chromatography
LC−MS = Liquid Chromatography−Mass Spectrometry
MEA = ethanolamine
MAPA = 3-amino-1-methylaminopropane
MEA-urea = N,N'-bis(2-hydroxyethyl)-urea
MDEA = N-Methyldiethanolamine
MS = Mass Spectrometry
NOx = Nitrogen oxides
NMR = Nuclear Magnetic Resonance
OZD = 2-oxazolidinone
p = pressure
SOx = Sulfur oxide
T = temperature
TCM = Technology Centre Mongstad
TOF = Time-Of-Flight

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