Deliverable Report: DT2_2017_1 Degradation and corrosion of amines (from a structural perspective)

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SUMMARY:

Degradation and corrosion of amine solutions in post combustion CO_2 capture plants increases the cost of the process due to operational problems, the need for high quality material in the plant and reduction of the solvent's CO_2 capacity. A literature review over degradation and corrosion in CO_2 capture processes have been performed with focus on mechanism for degradation and corrosion as well as experimental data from laboratory experiments and pilot data when available.

Degradation and corrosion are influenced by amine structure, CO_2 loading, temperature and impurities or other gas components present (O_2, SO_2, H_2S). Oxygen solubility in aqueous amine solutions and biodegradability of these amines could give valuable information in regard to chemical stability of amines in the presence of oxygen. Corrosion and degradation studies in long-term pilot plant campaigns have recently showed an accelerating degradation/corrosion which has not been observed in lab experiments.

KEYWORDS: Degradation, corrosion, post-combustion, pilot, amine structure, CO_2.

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1. Introduction

For post combustion CO_2 capture using absorption technology chemical stability of the solvent is vital to reduce/avoid corrosion, foaming, fouling, loss of CO_2 capacity, reducing the need for solvent make-up and limit the environmental impact caused by degradation compounds through emission or by spill to soil/water. The major challenge in studying degradation or corrosion is the complexity of the system, the variation of the conditions in different parts of the plant that influences both of them differently and the influence corrosion and degradation has on each other. The conditions and operation of the plant will influence degradation and corrosion mechanisms. A general introduction of degradation and corrosion is given in chapter 2 and 3 respectively.

2. Degradation

Generally, degradation in the plant is divided into oxidative and thermal degradation with or without CO_2. The vital part for oxidative degradation is oxygen and the main challenge here is formation of radicals, which can take place at high and low temperatures. Degradation reported in the literature as thermal degradation is a result of high temperature and high CO_2 concentration. Under the temperature conditions in CO_2 capture plant, little thermal degradation is observed (Lepaumier, Picq et al. 2009). Throughout the year's, oxidative and thermal degradation have been studied in batch set-ups separately. Recently, cycled systems were used to study degradation under more realistic process conditions (Closmann and Rochelle 2011, Einbu, da Silva et al. 2013, Voice, Closmann et al. 2013).

Oxidative degradation is conducted in stainless-steel or glass batch reactors (Lepaumier, Picq et al. 2009, Wang and Jens 2012, Vevelstad, Grimstvedt et al. 2013, Voice and Rochelle 2013). There are small differences in the experimental procedures conducted by different groups, like how the gas is introduced (in the headspace or bubbled through solution) and variation in gas flow. Usually the systems are slightly open, but closed reactors have also been used (Davis and Rochelle 2009, Lepaumier, Picq et al. 2009, Lepaumier, Grimstvedt et al. 2011, Freeman and Rochelle 2012, Freeman and Rochelle 2012). Degradation compounds identified in pilot samples had higher recemblance to products observed in the oxidative degradation experiments (Lepaumier, da Silva et al. 2011, da Silva, Lepaumier et al. 2012), however the oxidative experiment was not able to mimic the order of the compounds. It was clear that even if oxygen is an initiator for formation of these compounds, the conditions in the absorber could not explain the quantitative results.

For thermal degradation, the procedures and set-up are more similar; stainless steel cylinders of various sizes are used. These cylinders are placed in an oven at high temperature for several weeks and one cylinder is taken out at regular time interval. Several of the carbamate polymerization products were observed in pilots, but usually in small amounts, which contradicts the results from the cylinders. However, solvent residence time in the cylinders are weeks compared to minutes/hours in the plant.

Even though the separate experiments are not able to mimic the solvent behaviour in the plant, the experiments give vital information necessary to understand the degradation and to get a feeling of how the solvent will behave e.g. corrosion and foaming. However, before introducing a solvent to a full scale plant, degradation studies under more realistic conditions should be conducted. This is normally conducted in cycled set-ups, which are a mini-CO_2 capture plants. Most of the groups studying degradation have a set-up like this, and as a part of the planning for the full scale project Mongstad (CO_2 capture Mongstad, CCM), several solvent degradation rigs were designed and built for this purpose. The plan for these rigs was to allow vendors to test their solvent in accordance to a process protocol before qualifying to test at Mongstad (Haugen, Einbu et al. 2012).

Degradation of amines is influenced by both their structure and factors like O_2, CO_2 and initial amine concentration, temperature, flue gas composition and impurities. Some systematic degradation studies have been conducted to understand relationship between molecular structure and degradation. These studies are usually based on single experiments focusing either on oxidative or thermal degradation conditions which means that most of the factors e.g. gas composition and temperature are constant throughout the experiment and do not necesary reflect the solvent behavior in the pilot plant. The impact of oxygen concentration and temperature on ethanolamine (MEA) degradation were studied by (Supap, Idem et al. 2009, Vevelstad, Grimstvedt et al. 2013, Vevelstad, Johansen et al. 2014, Vevelstad, Johansen et al. 2016). Supap et al. also studied the impact of CO_2 concentration, initial amine concentration and and other gas components as SO_2, on MEA degradation (Supap, Idem et al. 2009). In the work by Lepaumier et al. 12 ethanolamines and ethyleneamines were investigated for oxidative and thermal degradation (Lepaumier, Picq et al. 2009, Lepaumier, Picq et al. 2009, Lepaumier, Martin et al. 2010). This work showed that secondary amines were less stable than primary and tertiary amines and some moleculare structures favored formation of different types of compounds as imidazoles, ogliomers or cyclic compounds. (Lepaumier, Picq et al. 2009). Eide-Haugmo studied a large set of amines (43) for thermal degradation and biodegradation in marine environment (Eide-Haugmo 2011). Both the work by Lepaumier (Lepaumier, Picq et al. 2009, Lepaumier, Picq et al. 2009, Lepaumier, Martin et al. 2010) and Eide-Haugmo (Eide-Haugmo 2011) shown that degradation compounds could be predicted based on structure, and that amines with similar structure follow the same degradation reaction pathways. The reaction mechanisms were supported based on advanced organic chemistry (Carey and Sundberg 2000, Carey and Sundberg 2001), specific name reactions (e.g. Eschweiler-Clarke) and qualitative or quantitative data for the degradation compound formed. Detailed mechanistic studies of the transition state or isotope exchange studies (Carey and Sundberg 2000) have not been conducted for CO_2 capture system. To describe a reaction mechanism, it is important to look at electronic, steric and solvent effects as well as thermodynamic and kinetic data for the reaction. To understand or evaluate charge stabilization, factors as charge density, electronegativity, polarizability, resonance, substitution (electron withdrawing or donating groups), orbitals, aromaticity and medium (solvent/gas) have to be investigated. Amines could react both as base and as nucleophile depending on conditions. The above factors necessary to study the degradation reaction mechanism are also used to evaluate new solvent candidates. However, an optimal solvent candidate is difficult to find, fast reaction kinetic often result in low chemical stability and lower cyclic capacity, while high cyclic capacity often give a slow reaction kinetic (tertiary amines). The solvent has to be optimized for the process and selected based on the overall picture.

Degradation compounds are often divided in two categories based on their formation mechanism; primary and secondary degradation compounds:

- In this case, primary degradation compounds are the initial degradation compound and compounds expected to be formed by radical reactions. These include compounds like ammonia, alkylamine, aldehydes and acids. The formation pathways are in this case more unclear, for the initial step both an electron and a hydrogen abstraction steps are suggested. A summary of this is given in paragraph 2.1.
- The secondary degradation compounds are the next stage compounds or compounds not expected to be formed by radical reactions. Examples of reaction/degradation mechanisms are ring closure, substitution reactions, carbamate polymerization reactions and these reactions often involve a reaction between amine and a primary degradation compound or amine and CO_2. These mechanisms are more straightforward and easier to follow.

The mechanism suggested for thermal degradation with CO_2 lead to secondary degradation compounds. Thermal degradation of amine without CO_2 would likely involve radical reactions and would therefore form primary degradation compounds, however this requires higher temperatures than in a post-combustion CO_2 capture plant. Today, there are several reaction pathways suggested for the same degradation compound, and it is likely that these occur to some extent. One of the major problems in studying chemical stability of solvents are that the purpose of the studies is different and it is therefore difficult to find the bigger picture in the studies. Most of the degradation compounds are present in ultra trace or traceamounts, their reaction pathway is not favourable and to synthesize these compounds more favourable reaction pathways are used. Explaining reaction mechanism for formation of small compounds that are not formed by a favourable reaction pathway is challenging. It is therefore important to realize that the pathway suggested could be one of several pathways and that normal textbook rules do not necessarily apply.

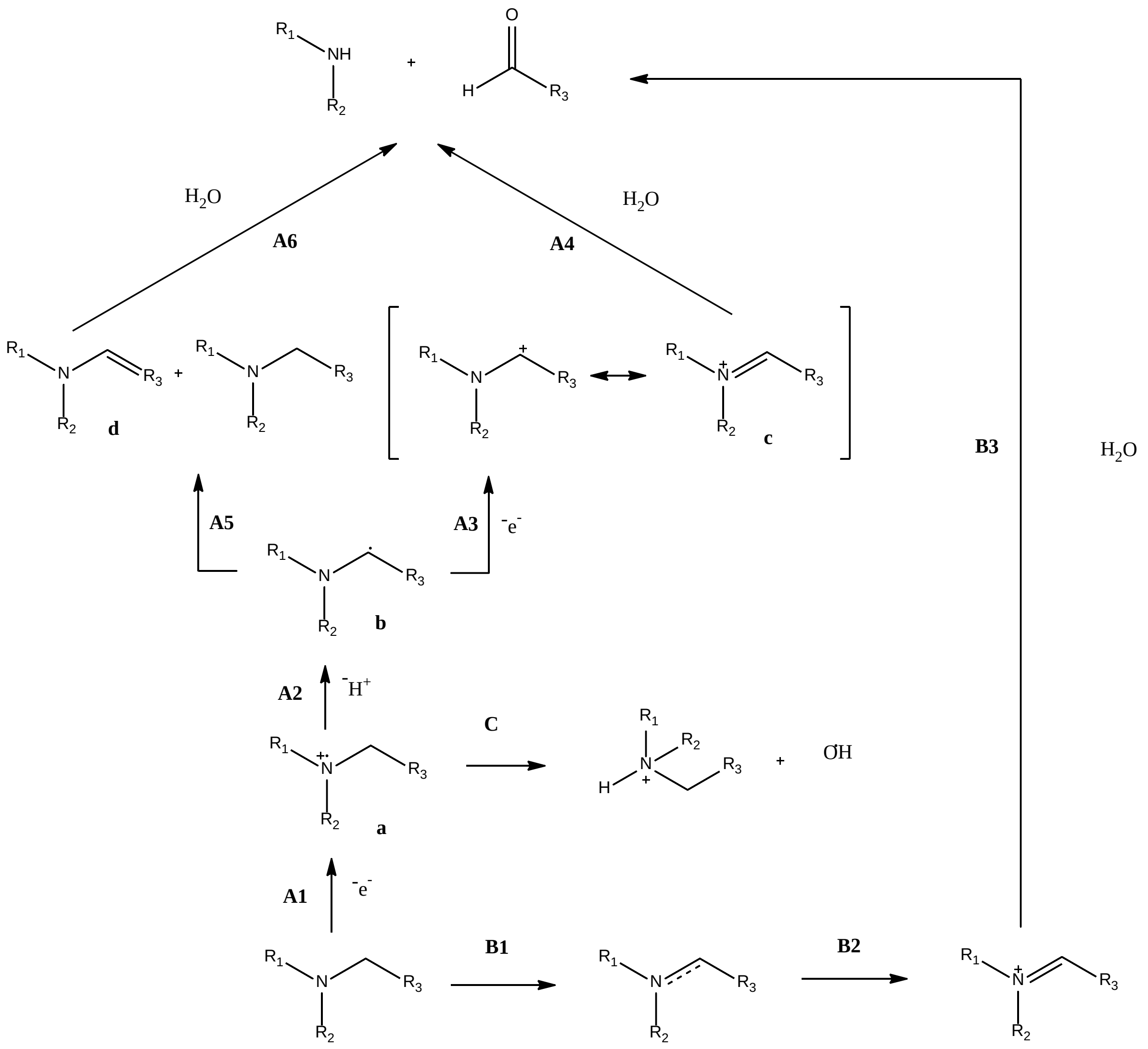
2.1 Radical/oxidation reactions – primary reactions

The radical reactions occuring in a post-combustion CO_2 capture plant are not well understood and the lifetime of intermediate radicals is normally short. As for all other reactions, there are general knowledge in regard to e.g generation of radicals, stability of radicals and structural and stereochemical properties of these intermediates (Carey and Sundberg 2000, Carey and Sundberg 2001). However, the degradation products observed in pilot plants and degradation experiments are the products from the termination step. The initiation step has not been verified experimentall, but reactions pathways have been suggested by several researchers (Nicolet and Shinn 1939, Hull, Davis et al. 1967, Smith and Mann 1969) and these end up with aldehyde(s) and amine/ammonia observed in the pilot campaigns or in laboratory experiments. The pathways suggested also share a common intermediate, aminium radical. These pathways either start with the abstraction of electron from the lone pair of nitrogen or with the abstraction of hydrogen. Which of the hydrogen atoms being abstracted, is dependent on the amine structure, nature of oxidants, pH, solvent effects and whether oxygen participates in the reaction (Hull, Davis et al. 1967, Rosenblatt, Hull et al. 1967, Hull, Giordano et al. 1969, Davis, Demek et al. 1972, Beckwith, Eichinger et al. 1983, Chi and Rochelle 2002, Goff and Rochelle 2004, Goff 2005, Bedell 2009). A summary of the different pathways for electron abstraction and hydrogen abstraction is given in Scheme 1 (Vevelstad 2013):

- Route A, electron abstraction using a one electron oxidant or electrochemical oxidation (Hull, Davis et al. 1967, Smith and Mann 1969).
- Route B, hydrogen abstraction (Hull, Davis et al. 1967).
- Route C, reaction between aminium radical reaction and water (alternative suggested by (Smith and Mann 1969)).

A review of non-aromatic aminium radicals, discussing generation, spectral properties, energetics and chemical reactions is given by Chow et al. (Chow, Danen et al. 1978).

Scheme 1: Electron abstraction using a one electron oxidant or electrochemical oxidation (route A, (Hull, Davis et al. 1967, Smith and Mann 1969)), hydrogen abstraction (route B, (Hull, Davis et al. 1967)) for mono-functional amines. (Vevelstad 2013)



R$_1$, R$_2$ and R$_3$ are hydrogen or alkyl groups with no heteroatoms in close vicinity. Route A5 requires that R$_3$ is an alkyl group. The intermediates; an aminium radical cation (a) (Walter 1955), an α-amino-radical (b), an iminium ion (c) and a carbinolamine (hemiaminal) have been supported either by product identification, kinetic studies, by use of linear free-energy correlations or a combination of these techniques. Lindsay Smith and coworkers managed to trap an iminium ion intra-molecularly (Lindsay Smith and Mead 1972). Kinetic studies using isotope (Rosenblatt, Davis et al. 1968) substitution showed that the rate determining step involved electron transfer for tertiary amines (Rosenblatt, Hayes et al. 1963, Hull, Davis et al. 1967, Rosenblatt, Hull et al. 1967, Ferris, Gerwe et al. 1968, Hull, Davis et al. 1969, Hull, Davis et al. 1969, Hull, Giordano et al. 1969, Smith and Mann 1969, Audeh and Smith 1970, Lindsay Smith and Mead 1972, Lindsay Smith and Mead 1976). Formation of the iminium ion from loss of α-proton was also suggested to be the product determining step (Ferris, Gerwe et al. 1968, Audeh and Smith 1970). Hydrogen abstraction depends on thermodynamic, polar, stereo-electronic and geometric effects (Feray, Kuznetsov et al. 2001). Geometric factors dominate for intra-molecular hydrogen abstraction.

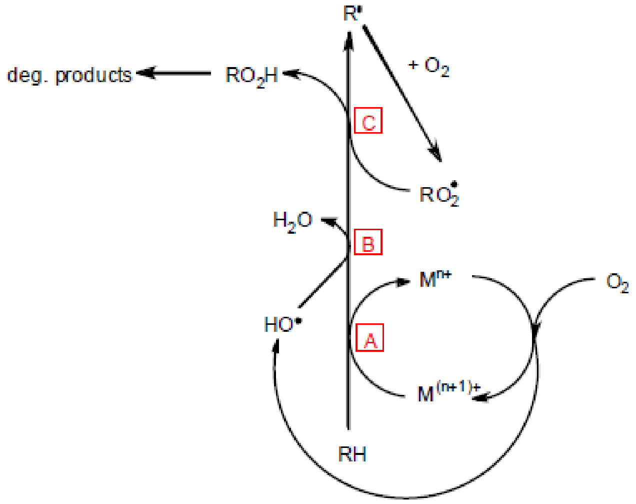
Kinetic experimental studies support both pathways in Scheme 1. The general opinion was that electron abstraction dominates for tertiary amines while hydrogen abstraction was more important for secondary and especially primary amines (Hull, Davis et al. 1967, Rosenblatt, Davis et al. 1968, Rosenblatt and Burrows 1982). More general factors like ionization potential and α-H dissociation energy of the amines could be used to explain the ratio between the pathways for different amines (Streitwieser 1960, Hull, Giordano et al. 1969).

Route C, a competitive reaction where aminium radical and water react producing protonated amine and hydroxyl radical was suggested by (Smith and Mann 1969). The hydroxyl radical can then form peroxide that belongs to the two-electron oxidants group together with peroxy acids, ozone and hypochlorous acid. These two-electron oxidations form amine oxide or hydroxylamine (Oswald and Guertin 1963, Hull, Giordano et al. 1969, Chow, Danen et al. 1978). Chen et al. and Correa et al. have reported formation of *N*-oxide from tertiary amines (Correa, Hardy et al. 1988, Chen, Linehan et al. 1990). Under low oxygen concentration *N*-oxides were only formed as minor by-products (Beckwith, Eichinger et al. 1983). According to Craig and Ferris and co-workers these tertiary *N*-oxides go through metal-complex catalysed rearrangements (Craig, Dwyer et al. 1961, Craig, Mary et al. 1964, Craig, Mary et al. 1964, Ferris and Gerwe 1964, Ferris, Gerwe et al. 1967, Ferris, Gerwe et al. 1968). Ferris et al. suggested a mechanism for this reaction where Fe(II) initiated formation of aminium radical and end products were secondary amine and aldehyde (Ferris, Gerwe et al. 1967, Ferris, Gerwe et al. 1968).

Scheme 1 describes the pathway for mono-functional amines or for amines with distance to heteroatoms. The last step for this type of amines is a nitrogen-carbon scission step. For carbon capture with amines, alkanolamines or polyamines are often used; these compounds have heteroatom (either oxygen or nitrogen) that is in close vicinity to the reacting nitrogen. Dennis et al. and Nicolet et al. showed that formaldehyde and ammonia were formed as end products from MEA (primary) and DEA (secondary) indicating carbon-carbon scission as the end step (Nicolet and Shinn 1939, Dennis, Hull et al. 1967). However tertiary β-hydroxy amines still seemed to give products indicating C-N fragmentation (Leonard and Rebenstorf 1945). According to Lindsay Smith et al., monoamines have higher reactivity toward aminium radical formation than corresponding diamines (Lindsay Smith and Mead 1976). The effect was shown to be less pronounced when distance between nitrogen atoms increased.

The amine autoxidation route (Scheme 2) given by Bedell shows how the electron or hydrogen abstraction could be initiated (Bedell 2011).

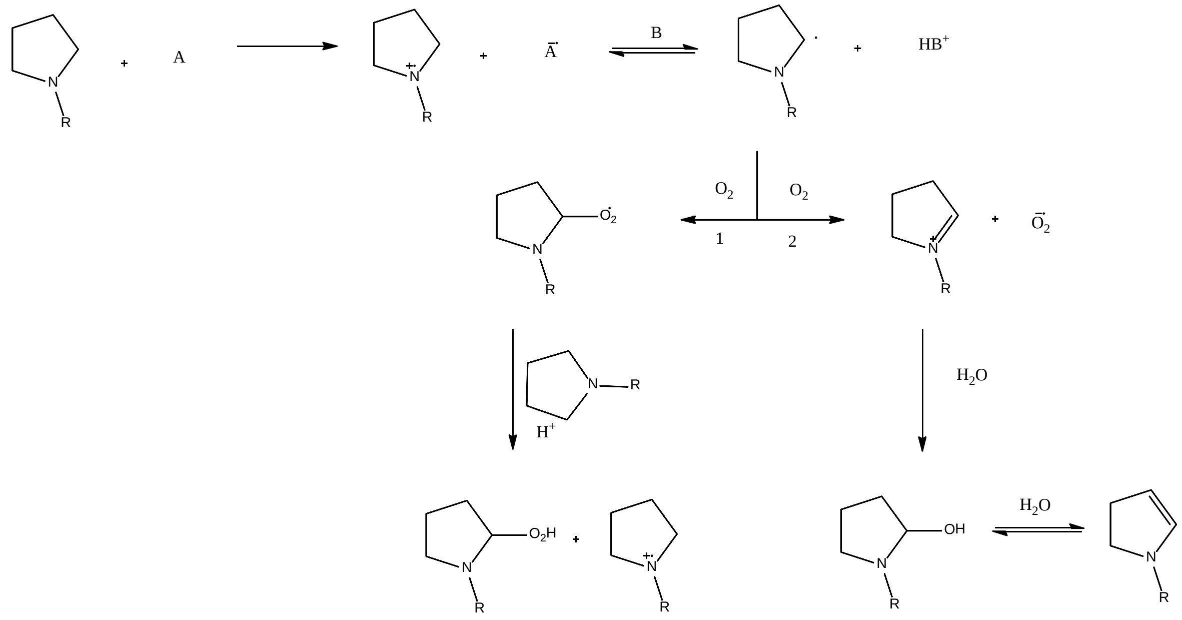
Scheme 2: Amine autoxidation routes (Bedell 2011).



Electron abstraction occurs when there is an appropriate metal ion in the solution, the metal ion could be a result of corrosion or come from impurities in flue gas e.g. fly ash (route A). Hydrogen abstraction could be initiated by hydroxyl radical (B) or an organoperoxy radical (C).

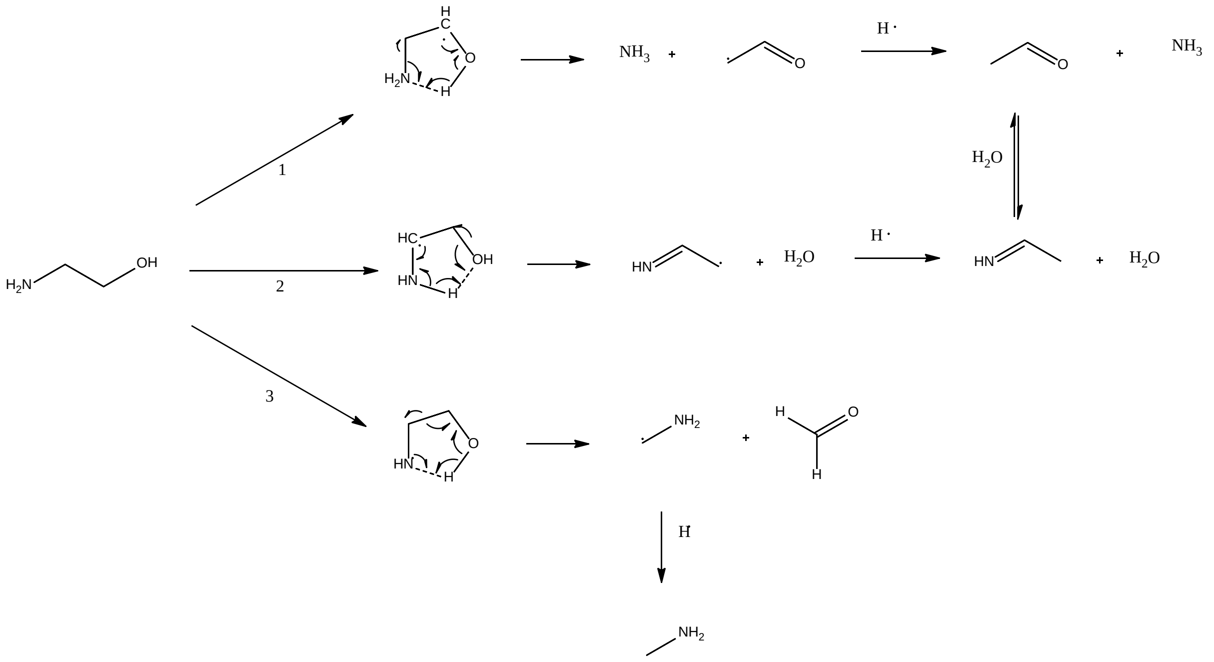
Oxidation of amines also occurs without added oxidants when air is present (autoxidation). The mechanism has been suggested to be similar to that of alkanes. An example of mechanism of autoxidation of *N*-alkylpyrrolidines (see Scheme 3) in non-polar and polar solvents is given by Beckwith et al (Beckwith, Eichinger et al. 1983). Reaction 1 and 2 are competing reactions in water, and reaction 2 will result in termination since superoxide is destroyed in protic solvents.

Scheme 3: Autoxidation of *N*-alkylpyrrolidine (Vevelstad 2013).



Mechanical pathways for amines used as absorbents for CO_2 capture has also been suggested. Petryaev (Petryaev, Pavlov et al. 1984) suggested that MEA degrades through hydrogen abstraction from N (3), α-carbon (2) or β-carbon (1) though a concerted mechanism as shown in Scheme 4.

Scheme 4: Hydrogen abstraction mechanism for degradation of MEA adapted from (Petryaev, Pavlov et al. 1984, Gouedard, Picq et al. 2012)



Molecular simulation studies support the suggested cyclic transition structure in Scheme 4 (Button, Gubbins et al. 1996, Alejandre, Rivera et al. 2000, Vorobyov, Yappert et al. 2002). A hydrogen abstraction mechanism has also been suggested for degradation compounds such as glycolic acid (Lepaumier, Picq et al. 2009, Gouedard, Picq et al. 2012) and glycine (Bedell 2009).

In addition to the described mechanisms, demethylation and methylation reactions and oxidation reactions could be mentioned. A mechanism for demethylation and methylation reactions is given by (Lepaumier, Picq et al. 2009).

2.2 All other degradation reactions in CO_2 capture - Secondary reactions

Amines are capable of sharing/donating electrons, as they are nucleophiles. In cases where these electrons are shared with a hydrogen, the process is called a Brönsted acid/base reaction, where the amine act as a Brönsted base. The Brönsted acid/base reaction is controlled by a (thermodynamic) equilibrium while amine reacting as a nucleophile is controlled by kinetics. A molecule's chemical properties depend on its structure. Important factors to consider when evaluating acidity or basicity of a chemical compound is charge distribution in the molecule and electronegativity and polarizability of the anion. A strong base is characterized by an anion with large electron charge on an atom of low electronegativity. Factors that stabilize negative charge are electronegativity, polarizability, resonance, electron withdrawing groups, orbitals (more s-character), aromaticity and smaller charge (Carey and Sundberg 2000, Carey and Sundberg 2001). These factors together with factors as steric hindrance are important for evaluation of nucleophilic properties. Solvation and the nature of the electrophile (e.g.

properties of leaving groups) are of importance for the reaction between nucleophile and electrophile.

Typical secondary degradation compounds are e.g. oxazolidinone, imidazoles, amides, piperazinone, amines and urea compounds. Studying reaction mechanisms is complex. Data from all aspects of the reaction is required, to study and describe the processes, , e.g. thermodynamic data is necessary to evaluate the feasibility of the reaction while kinetic data is necessary for insight into the reaction mechanism. To further study the reaction mechanism, additional aspects have to be evaluated:

- substituents effects (linear free-energy relationships),
- product composition controlled kinetically or thermodynamically
- isotope studies (isotope effects)
- characterization of intermediates
- role of catalyst (acid, base, Lewis acid)
- role of reaction medium (solvent, gas (substituents effect in gas phase)) and stereochemical course of the reaction.

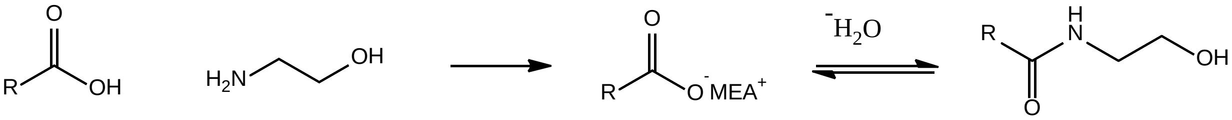
But: "In the end, a proposed mechanism can never be proven; rather, it is a case of alternative mechanisms being eliminated" (Carey and Sundberg 2000).

In the last decades, several pathways have been suggested for degradation compounds observed in degradation or pilot studies. More than one pathway can be suggested for the same compound, and in most cases, no studies have been conducted to get a deeper insight into the reaction mechanism. For post-combustion CO$_2$ capture, most of the research and development work is focused on the overall performance of the process rather than on the detailed reaction mechanism for degradation compounds present in insignificant amounts. However, some of the degradation compounds could cause problem in the process, e.g. fouling, foaming or corrosion, or they could cause enviornmental problems due to high volatility, toxicity, carcinogenity. A certain level of understanding of the reactions is therefore important.

Some of the suggested pathways for degradation compounds from MEA are given below. Compounds of similar structure have been shown to give degradation compounds by the same mechanism as for MEA, only accounting for the structural difference between MEA and the other amine. For blends, both degradation compounds belonging to each amine and combination products are observed.

Acids, e.g. formic acid, acetic acid, nitric acid, nitrous acid, glycolic acid and oxalic acid, have been quantified in MEA (and other amines) solutions from degradation experiments in the laboratory or in pilot samples. The acids could form salts with the amines producing so called heat stable salts, which reduces the amount of free amine available to capture CO$_2$. Another effect could also be that they reduce the solubility of gases as O$_2$ (and CO$_2$) in the amine solution. Amides have also been quantified in the same samples, and the acids are believed to have an important role in their formation. A general condensation reaction take place between acid and amine resulting in amide components. (*N*-(2-hydroxyethyl)formamide (HEF), *N*,*N'*-Bis(2-hydroxyethyl)oxamide (BHEOX), *N*-(2-hydroxyethyl)acetamide (HEA), 2-hydroxy-*N*-(2-hydroxyethyl)-acetamide (HHEA), and 2-[(2-hydroxyethyl)amino]-2-oxo-acetic acid (HEOX)) are quantified in pilot samples and lab experiments (Strazisar, Anderson et al. 2003, Lepaumier, Picq et al. 2009, Lepaumier, da Silva et al. 2011, Supap, Idem et al. 2011, da Silva, Lepaumier et al. 2012). Supap and coworkers (Supap, Idem et al. 2011) suggested that the amine salt of the acid is in equilibrium with the corresponding amide (Scheme 5), where R is either H, CH3, CH2OH or C(O)NHCH2CH2OH.

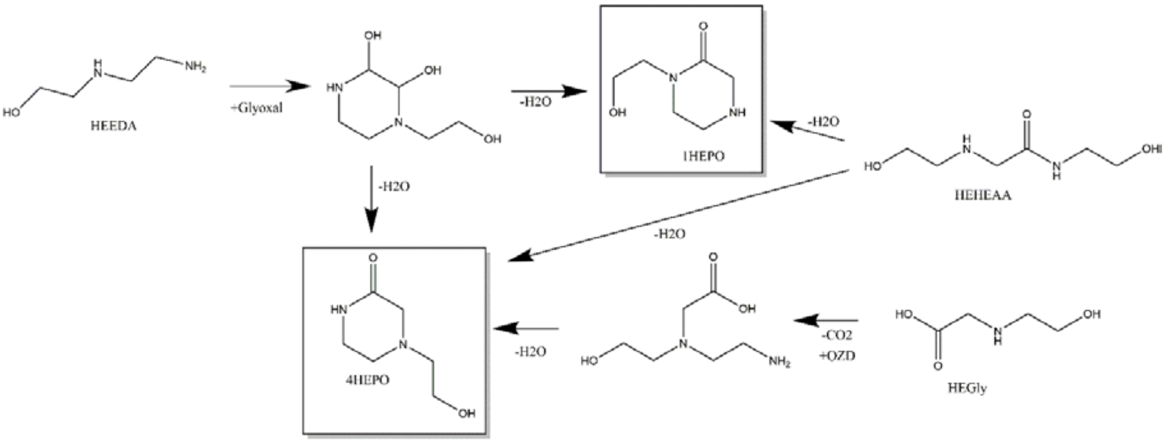
Scheme 5: Equilibrium reaction between amine salt and the corresponding amide, R e.g. H, CH3, CH2OH, C(O)NHCH2CH2OH.



Formation of these amides from MEA and corresponding acid have been verified with simplified lab experiment where the components have been mixed together and then the solution have been analyzed for the corresponding amide (Lepaumier, da Silva et al. 2011, Vevelstad, Grimstvedt et al. 2013, Vevelstad, Johansen et al. 2014).

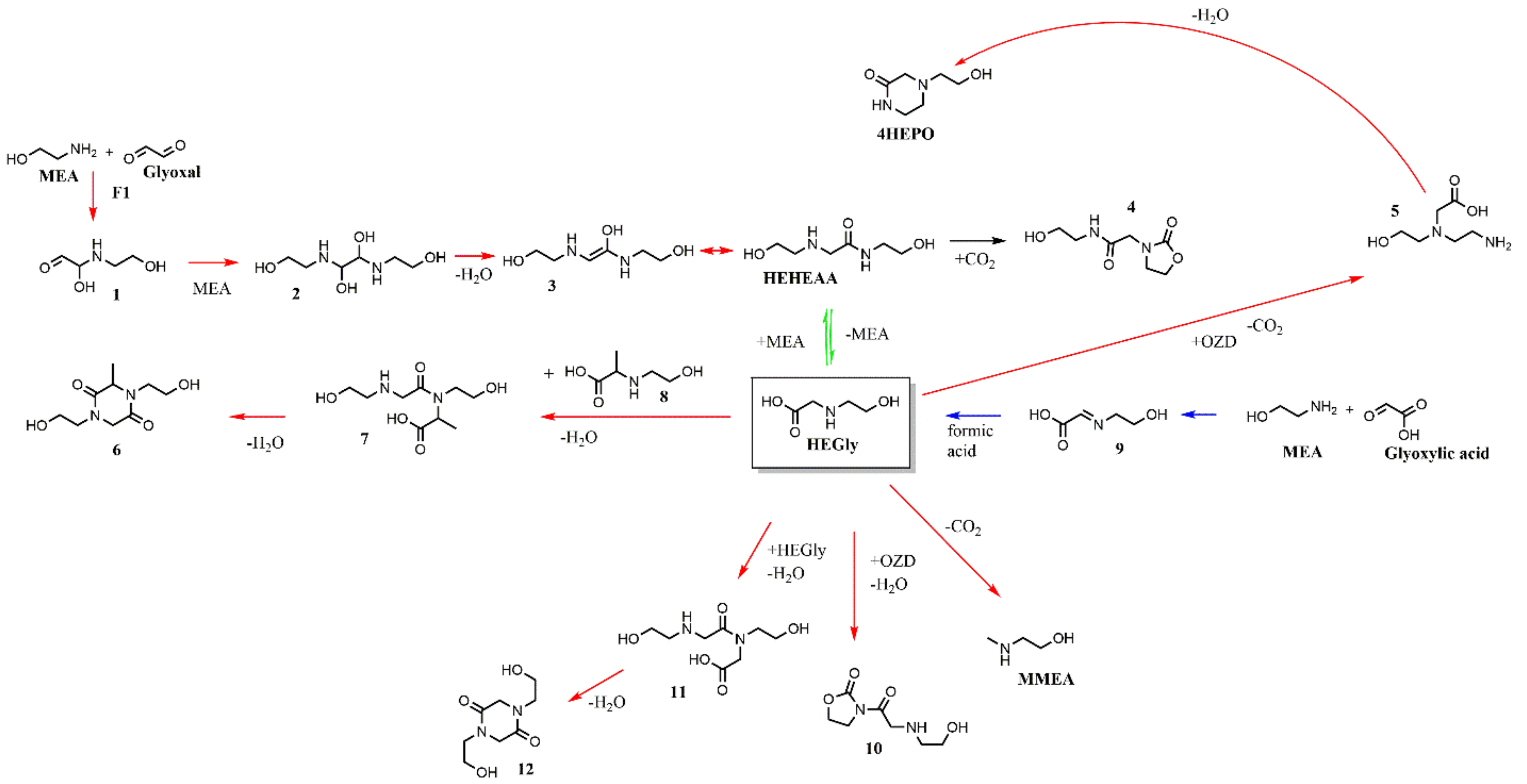
N-(2-hydroxyethyl)-glycine (HEGly) and 4-(2-hydroxyethyl)-2-piperazinone (4HEPO) are two of the largerst components quantified in pilot samples (da Silva, Lepaumier et al. 2012). A pathway was suggested by Strazisar that gives HEPO from *N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide (HEHEAA) (Strazisar, Anderson et al. 2003). Later, a pathway for 1-(2-hydroxyethyl)-2-piperazinone (1HEPO) and 4HEPO were suggested from HEGly, with HEHEAA as intermediate (da Silva, Lepaumier et al. 2012). In the work by Gouedard, critical questions were raised concerning the intramolecular pathway between HEHEAA and HEPO and this resulted in two new pathways for 4HEPO and one for 1HEPO, see Scheme 6.

Scheme 6: Suggested pathways for 1HEPO and 4HEPO formation adapted from Gouedard (Gouedard 2014) and da Silva (da Silva, Lepaumier et al. 2012).



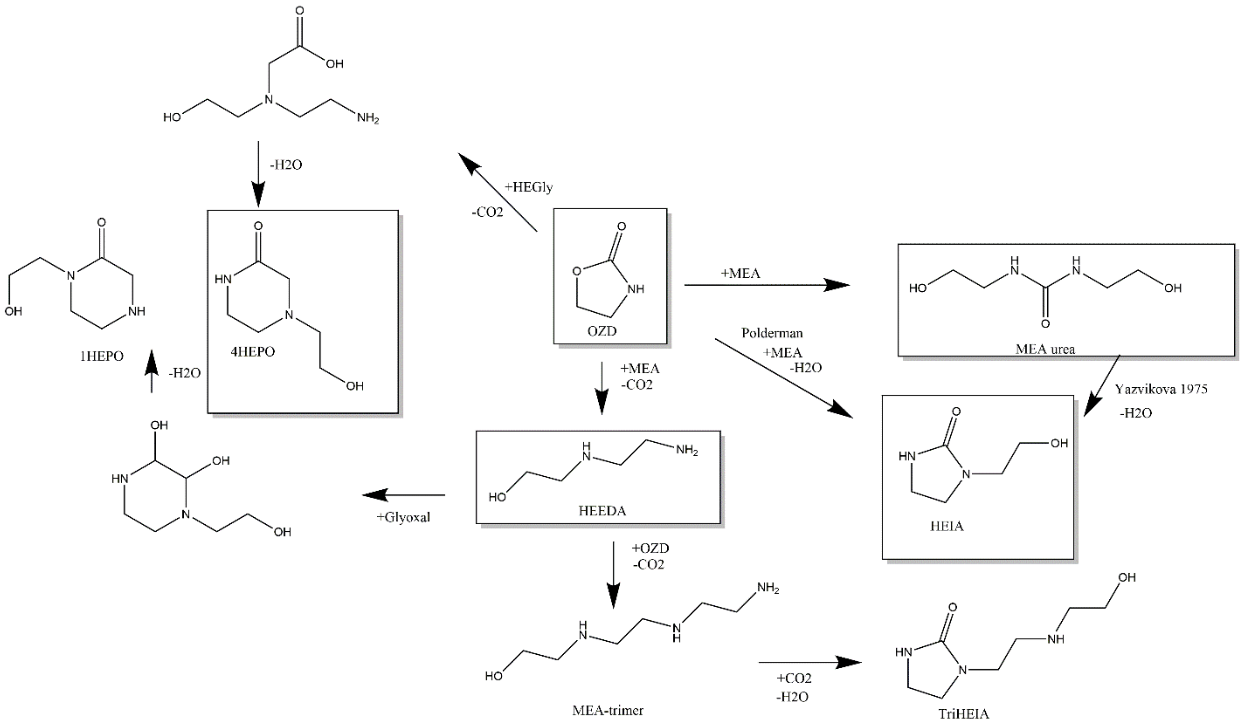
Pathways for HEGly formation were only suggested in 2014, one pathway starting from glyoxylic acid and MEA and involving a reductive amination step in the presence of formic acid (Vevelstad, Grimstvedt et al. 2014), while the other is a reaction between MEA and glyoxal, giving HEHEAA as an intermediate that is in equilibrium with HEGly (Gouedard 2014). Both pathways were tested in lab mixing experiments; however, in depth studies are lacking. A summary of suggested pathways of formation and consumption for HEGly was given by (Vevelstad, Grimstvedt et al. 2014), see Scheme 7 (pathways with red arrows was suggested by (Gouedard 2014), green arrows (da Silva, Lepaumier et al. 2012), blue arrows (Vevelstad, Johansen et al. 2016)).

Scheme 7: Formation and consumption reactions of HEGly; red arrows (Gouedard 2014), green arrows (da Silva, Lepaumier et al. 2012), blue arrows (Vevelstad, Johansen et al. 2016).



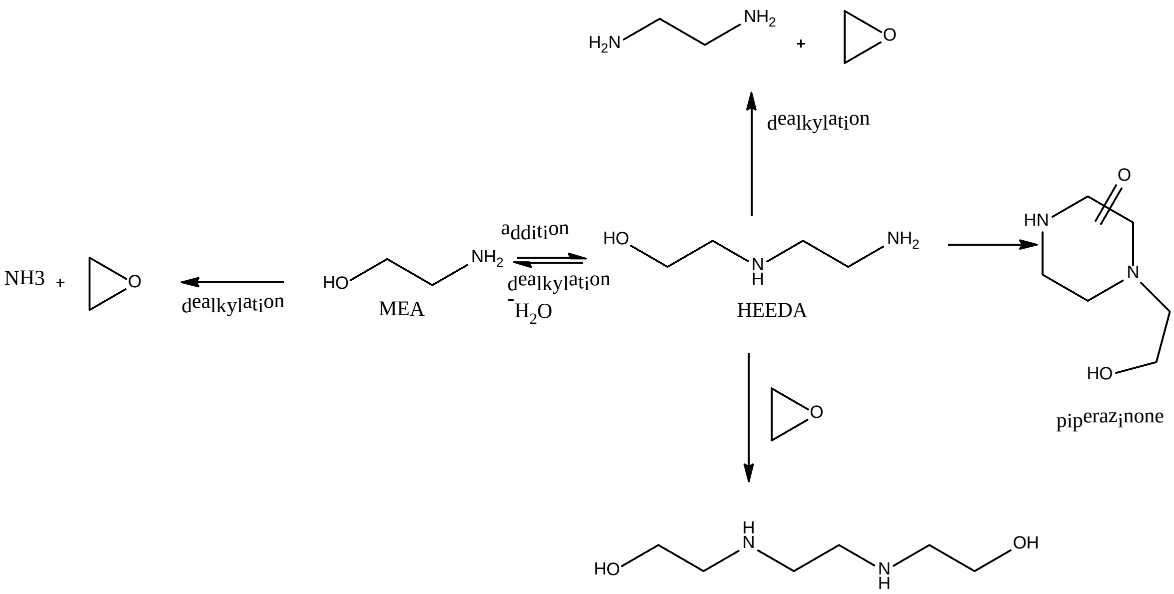
In the work by Vevelstad and co-workers, degradation of MEA was studied at different oxygen concentrations and temperatures and a set of degradation compounds was quantified (Vevelstad, Johansen et al. 2016). This work indicated the same conclusion as (Gouedard, Picq et al. 2012), formation of 1HEPO and 4HEPO from HEHEAA is not a the main formation reaction and that formation of 4HEPO from 2-oxazolidinone (OZD) is supported by their behavior at different oxygen concentrations. In the work by (Vevelstad, Johansen et al. 2016), *N*-(2-hydroxyethyl)ethylenediamine (HEEDA) was not quantified, and its importance as an intermediate for the formation of 1HEPO and 4HEPO could not be evaluated. In Scheme 8, suggested pathways for formation of four of the major degradation compounds, observed in the solvent degradation rig (Vevelstad, Grimstvedt et al. 2017), formed from OZD, is given.

Scheme 8: Suggested pathways of 4 of the major degradation compounds observed in solvent degradation rig (Vevelstad, Grimstvedt et al. 2017), explained from OZD as a start material.



In the work by Vevelstad and co-workers (Vevelstad, Grimstvedt et al. 2013) it was observed that OZD concentration increased with oxygen concentration. The existing pathway for OZD formation (from MEA and CO_2 through cyclization) is not sufficient to explain this behavior. OZD could be synthesized from CO_2 and epoxide (Patil, Tambade et al. 2008). Epoxide formation from dealkylation of MEA has been suggested by Lepaumier, see Scheme 9 for general pathway for ethanolamine degradation in the presence of air. Epoxide is a highly reactive compound.

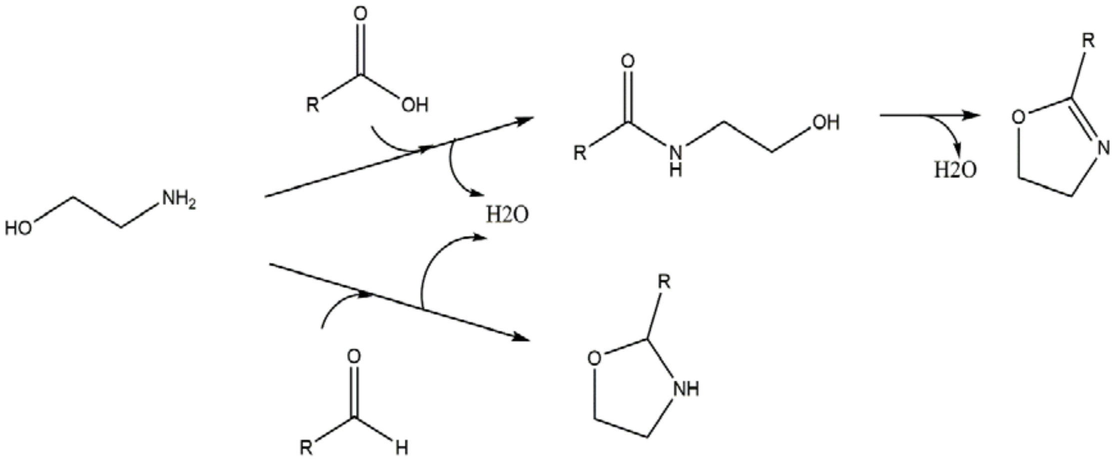
Scheme 9: General pathways for primary ethanolamine degradation with air (Lepaumier, Picq et al. 2009).



Systematic studies of several ethanolamines and ethyleneamines have been conducted under thermal degradation conditions (with or without CO_2) and oxidative degradation conditions (Lepaumier, Picq et al. 2009, Lepaumier, Picq et al. 2009, Lepaumier, Martin et al. 2010). This was the first study investigating structure-properties relationships in degradation of amines under CO_2 capture conditions. The work has been followed by other; Eide-Haugmo provided data on biodegradation, ecotoxicity and thermal degradation with CO_2 for various amines (30-40) (Eide-Haugmo, Brakstad et al. 2009, Eide-Haugmo 2011, Brakstad, Booth et al. 2012, Eide-Haugmo, Brakstad et al. 2012), oxidative degradation data for of a small set of alkanolamines and aminoacids were reported by (Vevelstad, Grimstvedt et al. 2013). In addition, several amines have been studied in detail; for piperazine (Freeman, Davis et al. 2010, Freeman 2011, Freeman and Rochelle 2011, Freeman and Rochelle 2012, Freeman and Rochelle 2012), 2-amino-2-methylpropanol (AMP) (Wang and Jens 2012, Wang 2013), *N*-methyldiethanolamine (MDEA) (Closmann, Nguyen et al. 2009, Closmann and Rochelle 2010), 2-(Methylamino)ethanol (MMEA) (Lepaumier, Grimstvedt et al. 2011) and MEA (Supap, Idem et al. 2001, Chi and Rochelle 2002, Strazisar, Anderson et al. 2003, Goff and Rochelle 2004, Goff 2005, Sexton and Rochelle 2009, Supap, Idem et al. 2009, Sexton and Rochelle 2011, Supap, Saiwan et al. 2011, da Silva, Lepaumier et al. 2012, Gouedard, Picq et al. 2012, Reynolds, Verheyen et al. 2013, Vevelstad, Grimstvedt et al. 2013, Voice and Rochelle 2013, Gouedard, Rey et al. 2014, Cuzuel, Gouedard et al. 2015, Reynolds, Verheyen et al. 2015, Vevelstad, Johansen et al. 2016) or blends of the amines given. A detailed overview of reported degradation compounds for MEA under thermal or oxidative conditions as well as an overview of compounds suggested without mechanism are given by Gouedard (Gouedard, Picq et al. 2012). In Gouedard's thesis, a mechanism has been suggested for some of these compounds (Gouedard 2014).

Quantitative data for the degradation compounds and understanding of their formation has got increased attention the last ten years. The structure of the amine is important in regard to its stability under different conditions. Amines of similar structures result in similar degradation compounds. Typical reactions are carbamate polymerization, dealkylation, deamination, oxidation and ring closure. The smaller carboxylic acids have been reported for several of the amines. Formation of degradation compounds from amines, acids and aldehydes are well known. Lately, two 5 rings, given in Scheme 10 (R=H or CH_3), have been suggested (Reynolds, Verheyen et al. 2013, Voice 2013); oxazoline and oxazolidine, and their formation pathway (Gouedard 2014).

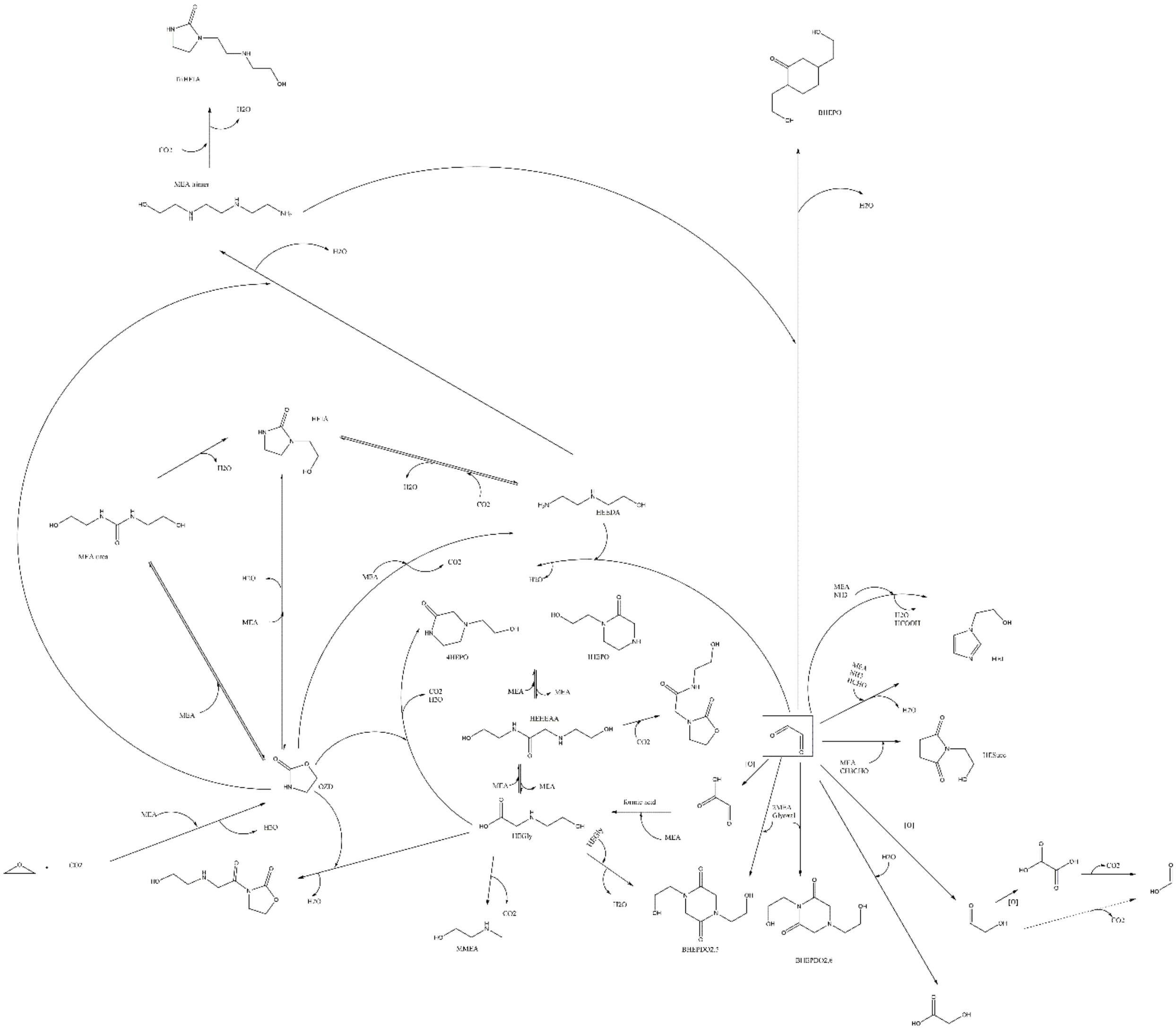
Scheme 10: Pathway for formation of amide, oxazoline and oxazolidine (R=H or CH_3).



Another compound and derivatives recently suggested and quantified, is pyrazine. A mechanism for the formation of pyrazine derivatives was suggested from 2-aminoacetaldehyde, formaldehyde and acetaldehyde (Rey, Gouedard et al. 2013).

Presence of glyoxal has also been suggested (Lepaumier 2008, Sexton and Rochelle 2011, Vevelstad, Grimstvedt et al. 2013, Vevelstad, Grimstvedt et al. 2014). This compound has not been verified; the compound is unstable and forms hydrates in water. Lately, glyoxal has been suggested as a starting material for several pathways. An overview of suggested degradation compounds with glyoxal as a starting material is given in Scheme 11. Please note, this is a suggestion from several authors, some degradation compounds have different pathways, and the degradation compounds are not necessarily observed in pilot samples (some are from lab mixing experiments). Authors suggesting these pathways are: (Polderman, Dillon et al. 1955, Yazvikova, Zelenskaya et al. 1975, Davis 2009, da Silva, Lepaumier et al. 2012, Vevelstad, Grimstvedt et al. 2013, Gouedard 2014, Vevelstad, Johansen et al. 2014).

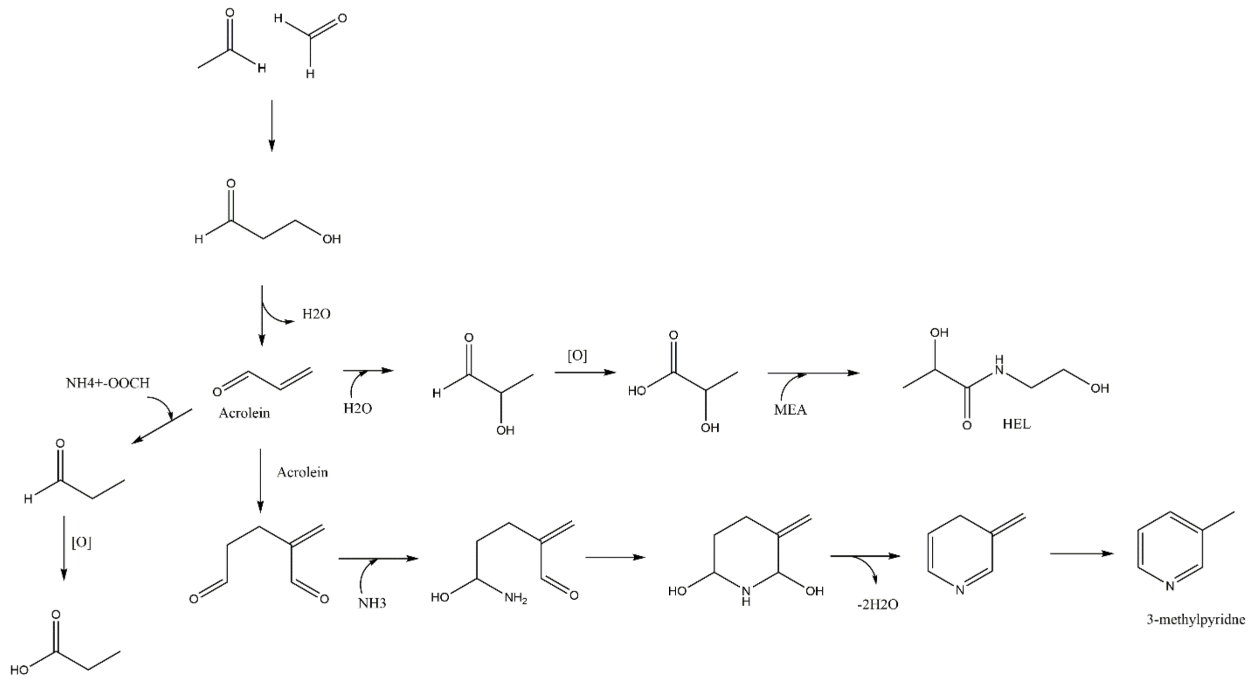
Scheme 11: Pathways suggested for various compounds (pilot samples, degradation studies or mixing experiments) – all starting from glyoxal.



The reactions with the acids toward amide, oxazoline and oxazolidine are not included in this scheme. However, MEA is participating in several of the reactions. Other amines could react in a similar way, increasing the amount of degradation compounds. MEA is the main amine present, and would contribute to larger amounts of degradation compounds than other amines. From a pilot perspective these additional degradation compounds should, if formed, be formed in small quantities compared to HEGly and HEPO.

Another degradation compound suggested, acrolein, has the potential to form a new set of compounds (Gouedard 2014). Acrolein is suggested to be formed from acetaldehyde and formaldehyde via an aldolization reaction. See Scheme 12 for formation and consumption reaction for acrolein.

Scheme 12: Formation and consumption of acrolein suggested by Gouedard (Gouedard 2014).



Nitrosamine and nitramine have got increased attention last 10-15 years. Nitrosamine is present in several daily use products, suchas processed meat, cigarette smoke, beer, as an additive in lubricants, food and dish soap. The nitrosamine group is believed to be carcinogenic or mutagenic due to formation of highly reactive diazonium ions which are capable of inducing alkylating DNA damage (Hebels, Briedé et al. 2010). Stable nitrosamines are formed from secondary amines. Nitrosamine formation is observed also for solvent system without secondary amines in the solvent blend due to formation of degradation compounds with a secondary amine function. Information is still lacking in regard to the carcinogenic potency of specific nitrosamines, there are indications that the carcinogenic potency of different nitrosamines are not the same (Douglass, Kabacoff et al. 1978). It is expected that the next decade will give more data for the specific nitrosamines observed in the solvent-based post-combustion CO_2 capture process. Monitoring of these compounds is necessary, and regulation in regard to nitrosamine concentration in air and drinking water are given for different countries (for Norway ((Klif) 2011, Morken, Nenseter et al. 2014). Emission permits also regulates emission of other compounds as e.g. ammonia and aldehydes. Destruction of nitrosamine also occur under the conditions in the plant, e.g. under high temperature in the desorber; the introduction to this topic could be found in the work by Fine et. al (Fine, Goldman et al. 2013, Fine and Rochelle 2013, Fine, Nielsen et al. 2014). Other nitrosamine mitigation techniques have been also investigated (Gui, Gillham et al. 2000, Frierdich, Shapley et al. 2007, Jackson and Attalla 2013, Knuutila, Asif et al. 2014, Knuutila, Svendsen et al. 2014).

For an overview of new degradation compounds suggested or found in MEA solutions, see (Gouedard, Picq et al. 2012, Gouedard 2014). For degradation work related to Pilot plant campaigns with MEA, see (da Silva, Lepaumier et al. 2012, Reynolds, Verheyen et al. 2015, Dux and Schallert 2016, Morken, Pedersen et al. 2017, Rieder, Dhingra et al. 2017).

2.3 Oxygen solubility

Degradation compounds identified and/or quantified in pilot samples show more recemblance to products observed in laboratory experiment simulating absorber conditions (oxidative degradation) (da Silva, Lepaumier et al. 2012). Oxidative degradation could occur in other locations in the plant due to transport of solvent with dissolved oxygen. Oxygen is vital factor for chemical stability of amine in the post combustion CO_2 capture processes. However, only one work has studied oxygen solubility in various alkanolamine/water mixtures (Rooney and Daniels 1998). In this study oxygen solubility in aqueous solutions of MDEA (30 and 50 wt%), Diglycolamine (DGA, 50 wt%), MEA (20 wt%), MDEA (50 wt%) and diethanolamine (DEA, 30 wt%) at temperatures from 15.5 – 82 °C was investigated. The oxygen in the solution in the experiments was measured with an oxygen probe. It was shown that the oxygen solubility in aqueous alkanolamine solutions, except for DEA, was comparable to water. For the temperature range tested in this work the oxygen solubility decreased with increasing temperature. Rooney et al. also report that oxygen solubility can increase at temperatures above 100 °C. It is also expected that CO_2 and heat stable salts (HSS) could reduce oxygen solubility (salting out effect) (Rooney and Daniels 1998). Data for oxygen solubility in dilute aqueous solution could be found in (Benson and Krause 1976, Wilhelm, Battino et al. 1977, Benson, Krause et al. 1979, IUPAC 1981).

2.4 Environmental studies: biodegradation and ecotoxicity

Over the years several biodegradation and ecotoxicity studies have been conducted for various alkanolamines. The experimental conditions have varied. Aerobic biodegradation of alkanolamines in soil have been studied by (Emtiazi and Knapp 1994, West and Gonsior 1996, Mrklas, Chu et al. 2004, Ndegwa, Wong et al. 2004, Hawthorne, Kubatova et al. 2005) in river or lake water (Emtiazi and Knapp 1994, West and Gonsior 1996), or using mixed microbial cultures (Rosenblatt, Hayes et al. 1963, Gieg, Coy et al. 1999, Rabenstein, Koch et al. 2009, Li, Landon et al. 2017). Anareobic biodegradation reported by (Knapp, Jenkey et al. 1996, Speranza, Morelli et al. 2006). Biodegradation and ecotoxicity of amines in marine environment has been studied by (Hansen, Altin et al. 2010, Libralato, Volpi Ghirardini et al. 2010, Brakstad, Booth et al. 2012, Eide-Haugmo, Brakstad et al. 2012). Biodegradation to handle waste or waste water from post-combustion pilot plants has been reported by (Li 2008, Campo, Platten et al. 2011, Henry, Kowarz et al. 2017). In the work by (Brakstad, Booth et al. 2012, Eide-Haugmo, Brakstad et al. 2012), a marine phytoplankton (ISO/DIS guideline 10253) and a marine biodegradation (OECD guideline 306) tests were conducted, both methods are standaradized methods. The results were summarized in two figures; ecotoxicity EC-50 (effective concentration of test substance inhibiting growth by 50%) and biodegradation BOD28 (biological oxygen demand after 28 days), see Figure 2-1 (adapted from (Eide-Haugmo, Brakstad et al. 2012)).

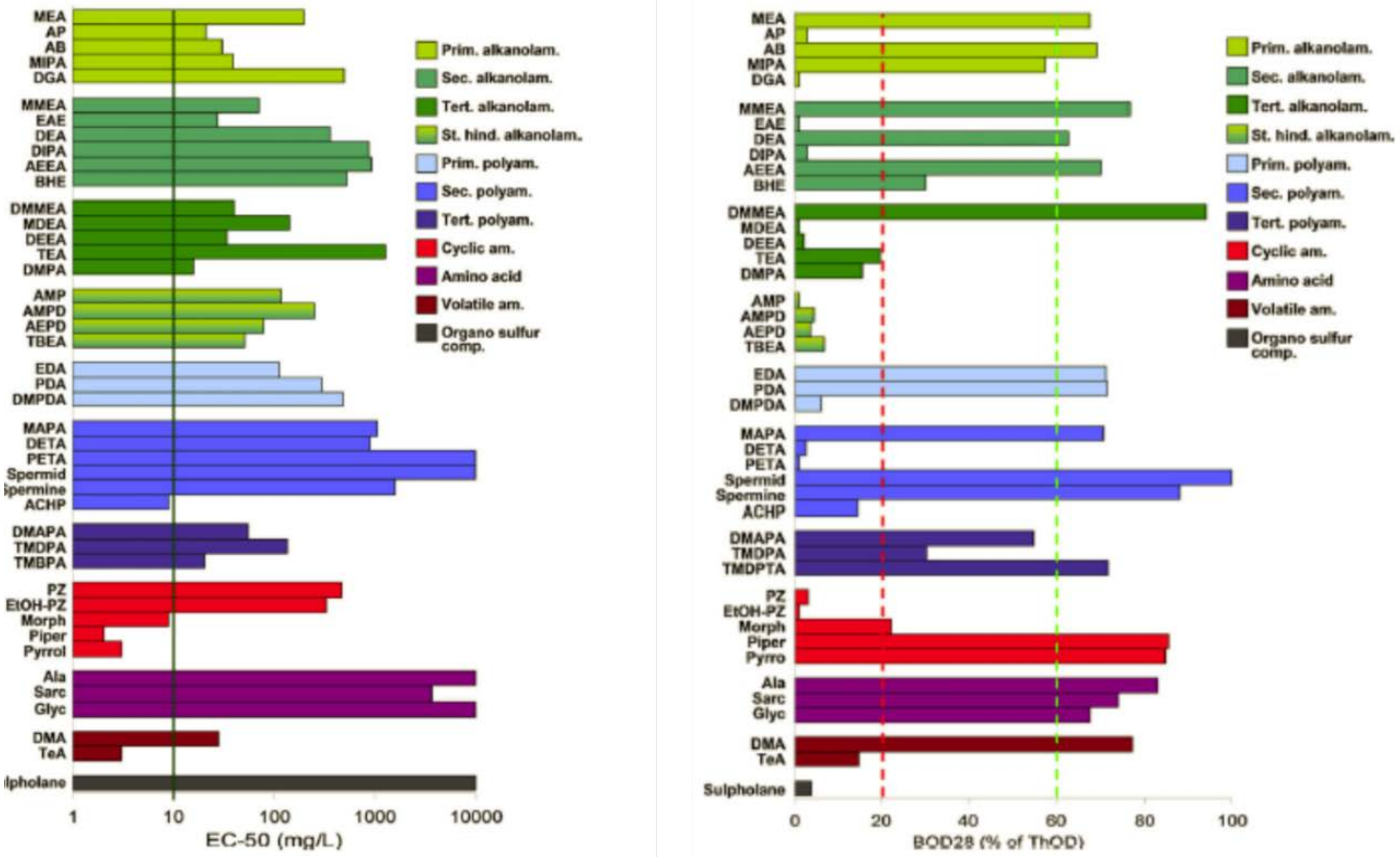


Figure 2-1: Ecotoxicity (EC-50) and biodegradation (BOD28) of 43 amines, adapted from (Eide-Haugmo, Brakstad et al. 2012).

Most of the amines have EC50 higher than 10 mg/L, which is acceptable. The amines of concern are 3-amino-1-cyclohexylaminopropane (ACHP), morpholine, piperidine, pyrroldine and triethylamine (TeA). For biodegradation, variation in the defined groups, given in Figure 2-1, are observed. Biodegradation higher than 20% is acceptable.23 of 43 compounds had biodegradability over this limit. Of the 43 compounds tested, 26 are classified as natural compounds. Six of these compounds had lower biodegradability than 20%; these are 2-ethylamineethanol (EAE), MDEA, diethylaminoethanol (DEEA), *N*-tertbutyletahnolamine (TBEA), ACHP and sulpholane. Low biodegradability has been observed for sterically hindered compounds, the cyclic compounds which were not natural, and most of the tertiary alkanolamines (Eide-Haugmo, Brakstad et al. 2012). Brakstad et al. reported that biodegradation rates followed the order primary/secondary > tertiary > sterically hindered alkanolamines (Brakstad, Booth et al. 2012). It was also reported that water temperature could influence the biodegradation rate for some of the alkanolamines, e.g. diethanolamine.

3-amino-1-(methylamino)propane (MAPA) and MMEA have shown low chemical stability in the presence of oxygen (Lepaumier, Grimstvedt et al. 2011, Voice, Vevelstad et al. 2013, Vevelstad, Grimstvedt et al. 2014). These compounds have biodegradability higher than 60% in seawater. There is likely a relation between biodegradability and oxidative stability, but the biodegradability alone can not explain why MEA and 4-amino-1-butanol (AB) have higher stability in the presence of oxygen than MAPA and MMEA.

3. Corrosion

Corrosion and degradation are related where each of them accelerate the other. Some degradation compounds are known to increase corrosion, and dissolved metals catalyse degradation. As for degradation, corrosion is also influenced by amine concentration, type of amine, temperature, CO_2 and O_2 concentration, other gas components (SO_2, H_2S, NH_3), impurities in solvent or gas, material in the plant and operation of the plant.

The main components and operating principles for natural gas processing, treatment of refinery gases and post-combustion CO_2 capture are the same (Kittel, Fleury et al. 2012). There are some differences in gas composition, preferred amine and the lean loading level (Kittel, Fleury et al. 2012). For post-combustion CO_2 capture, the presence of O_2 and amine type, has resulted in degradation problems together with corrosion problems which also has been associated with natural gas processing and treatment of refinery gases. Natural gas processing and treatment of refinery gases are industry processes and corrosion has therefore been studied for amine systems since the early 60s. A major part of maintenance budget is spend toward controlling corrosion or fixing problems caused by corrosion. The corrosion studies conducted have investigated the type of amine, amine concentration, acid gas concentration (CO_2, H_2S), process parameters (temperature, solvent flow rate, gas injection zones) and flue gas contaminants (O_2, SO_2,) (Saiwan, Supap et al. 2011). Severe corrosion is usually attributed to poor plant design and operation e.g. high flow velocity in pipelines, high operating temperature in reboiler, insufficient steam for solvent regeneration or the presence of process contaminants (Soosaiprakasam and Veawab 2008).

Corrosion is an electrochemical reaction which occurs at the surface of the metal. Corrosion could be uniform and localized and could further be divided into general, galvanic, crevice, pitting, intergranular, selective leaching, erosion, stress corrosion cracking and hydrogen damage (Dupart, Bacon et al. 1993, Soosaiprakasam and Veawab 2008). More details about the corrosion types is given by (Dupart, Bacon et al. 1993). Investigation of corrosion has been conducted both in lab scale using different set-ups, and in pilot plants with e.g. coupons. The evaluation methods in lab scale was often by potentiostat or/and studying coupons (weight). For experiments with coupons, longer experimental time is needed and the results sometimes deviate from shorter experiments with potentiostat. Application of mixed potential theory allows determination of the corrosion rate (Saiwan, Supap et al. 2011).

3.1 Corrosion mechanisms

Carbon steel is the common material for alkanolamine plants; some sections could be of stainless steel or other alloys to reduce corrosion. The mechanism for carbon steel corrosion in absent of inhibitor is an electrochemical reaction where iron is oxidized to ferrous ion (metal dissolution, anodic reaction) and hydrogen is reduced (oxidizer reduction, cathodic reaction (Kohl and Nielsen 1997, Veawab, Tontiwachwuthikul et al. 1999). The reaction occur at the surface of the metal.

$Fe = Fe^{2+} + 2e^-$ (3-1)
$H^+ + e^- = H°$ (3-2)
Net reaction: $Fe + 2H^+ = 2H° + Fe^{2+}$ (3-3)

The reaction is irreversible and the rate will increase with increasing hydrogen ion concentration, increasing temperature and increasing conductivity of the liquid medium (electrochemical reaction) (Kohl and Nielsen 1997).

The corrosion in the plant is usually divided into two groups (Kohl and Nielsen 1997, Kittel, Fleury et al. 2012):

- wet acid gas corrosion and
- amine solution corrosion

Wet acid gas corrosion occurs when high concentration of dissolved CO_2 and/or H_2S is present in an aqueous environment with little or no amine present e.g. top of desorber and below first tray in the absorber (Kittel, Fleury et al. 2012), while amine solution corrosion happens in the presence of aqueous amine, for rich amine solution e.g. rich amine line after heat exchanger to the desorber (Kittel, Fleury et al. 2012). The different type of corrosion occurs in different sections in the plant and are explained by the conditions at these sections. (Kohl and Nielsen 1997) has summarized this in a flow diagram, see Figure 3-1.

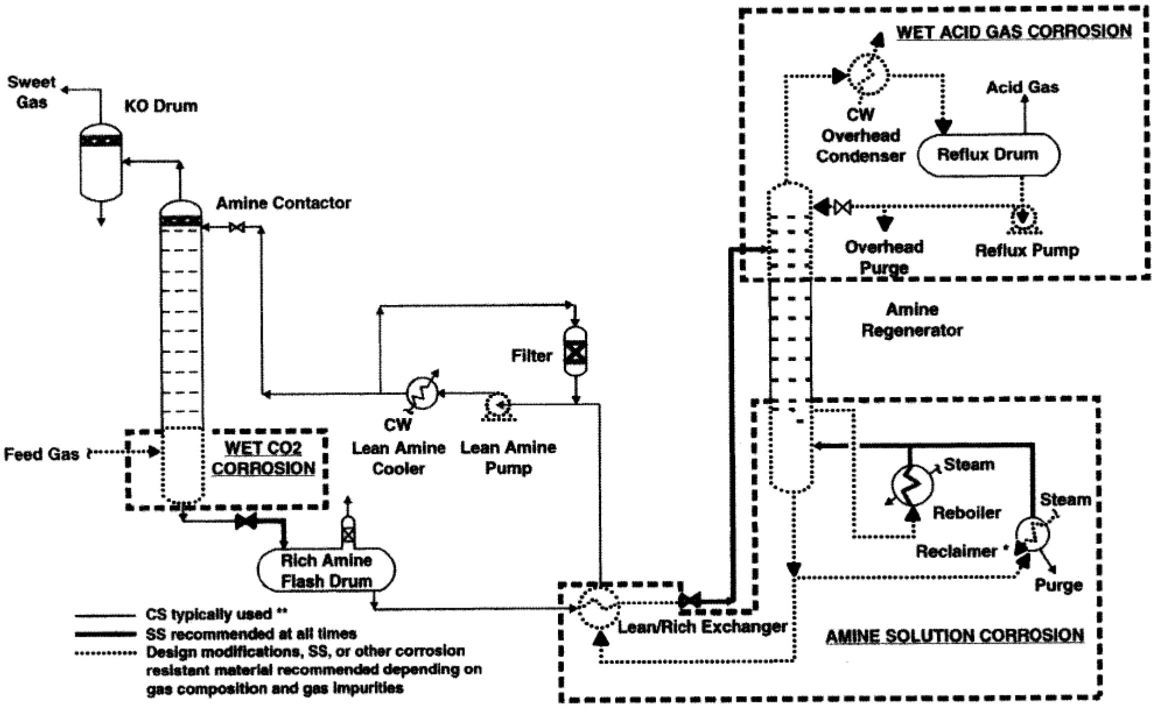


Figure 3-1: Flow diagram of amine plant with overview of construction material and where corrosion could occur adapted from (Kohl and Nielsen 1997).

3.1.1 Wet acid gas corrosion

There are two areas in the plant where wet acid gas corrosion could occur: in the top of the desorber or in the bottom of the absorber as long as the feed-gas is water saturated (see Figure 3-1). The mechanism varies depending on which gases are presents; CO_2, H_2S, NH_3 and HCN, where the two latter are present in refinery. The focus here will be mainly on CO_2, but the mechanism for H_2S is also given.

The overall reaction for CO_2 is:

$Fe + 2CO_2 + 2H_2O = Fe^{2+} + 2HCO_3^- + 2H°$ (3-4)

The overall reaction for H_2S is:

$Fe + H_2S = FeS + 2H°$ (3-5)

There are two mechanisms for CO_2, both resulting in the same overall reaction. The most general one is the reaction of CO_2 with water giving bicarbonate and hydrogen proton that will accept electron (reaction 2-2) from the iron (reaction 3-1).

$CO_2 + H_2O = 2HCO_3^- + H^+$ (3-6)

In the alternative mechanism suggested by Waard and Lotz (Kohl and Nielsen 1997), the carbonic acid accepts electron directly (from reaction 3-1) and gives elemental hydrogen and bicarbonate.

$H_2CO_3 + e^- = H^\circ + HCO_3^-$ (3-7)

For both pathways (3-6 and 3-7) the corrosion increases with increasing CO_2 concentration in water or CO_2 partial pressure in the gas phase.

In the corrosion process, ferrous ion could react with acid anions to either reduce or increase corrosion. For CO_2, ferrous carbonate is insoluble and gives scale deposition. However, ferrous carbonate is porous and corrosion protection is limited. For H_2S, a dense, non-porous scale is formed which reduces contineuous corrosion (ferrous sulphide). Oxalic acid forms insoluble iron chelates that seems to increase solution corrosivity (Rooney, Bacon et al. 1996). In the work by De Waard and Lotz is was observed that corrosion rate reaches a maximum as the temperature increases for water saturated with CO_2 (Kohl and Nielsen 1997). This was explained by formation of $FeCO_3$ or Fe_3O_4.

3.1.2 Amine solution corrosion

It is believed that acid gases are responsible for the corrosion of carbon steel by amine solutions (Kohl and Nielsen 1997), however several mechanisms have been suggested. The reaction is a redox reaction, where iron is oxidized and proton is reduced (equation 3-3), the proton could come from H_2CO_3 (equation 3-7) or alkanolammonium ion ((R_3NH^+ and $R_3NH_2^+$), resulting in elemental hydrogen and oxidized iron.

Riesenfeld and Blohm observed significant amine corrosion at the same time as evolution of acid gases from the rich amine solution occurred (Kohl and Nielsen 1997). This resulted in the following net reaction:

$Fe + CO_2 + H_2O = FeCO_3 + 2H^\circ$ (3-8)

The evolution of CO_2 from rich amine solution could occur through reaction 3-9 or 3-10 (Kohl and Nielsen 1997).

$R_3NH^+ + HCO_3^- = R_3N + H_2O + CO_2$ (3-9)

$R_2NH_2^+ + R_2NCO_2^- = 2R_2NH + CO_2$ (3-10)

Higher corrosion was observed for primary and secondary amines as MEA and DEA compared to tertiary amines as MDEA. This could be explained by higher temperature necessary to strip CO_2 from primary and secondary amines compared to tertiary amines, or by presence of some carbamate in primary amines after desorption acting as heat stable salt.

One source of proton is alkanolammonium ions, these could be formed through equation 3-11 – 3-13 depending on the acid gas present.

$CO_2 + R_3N + H_2O = R_3NH^+ + HCO_3^-$ (3-11)
$CO_2 + 2R_2NH = R_2NH_2^+ + R_2NCO_2^-$ (3-12)
$H_2S + R_3N = R_3NH^+ + HS^-$ (3-13)

The alkanolammonium ions are more abundant in aqueous amine solutions and are therefore a likely source of protons in corrosion reactions. This could then give the following net reaction:

The overall net reaction:

$Fe + 2R_3NH^+ = Fe^{2+} + 2H^\circ + 2R_3N$ (3-14)

Other reactions occurring in amine solution in the absorption process are:

$RNH_3^+ = RNH_2 + H^+$ (3-15)
$HCO_3^- = CO_3^{2-} + H^+$ (3-16)

Corrosion in amine solution is influenced by several factors e.g. process parameters (temperature, solvent flow rate, gas injection zones), acid gas loading, presence of other gas components (O_2, SO_2, H_2S, NH_3) and contaminants in the solvent or the gas (impurities, degradation compounds), amine solution concentration, amine type and construction material in the plant.

3.1.2.1 Process parameters

Corrosion increases with temperature. Both cathodic and anodic reactions show an increase in current densities at higher temperature for MEA and AMP (Veawab, Tontiwachwuthikul et al. 1999, Veawab, Tontiwachwuthikul et al. 1999, Soosaiprakasam and Veawab 2008, Kittel, Fleury et al. 2012). This is explained by increasing rate of iron dissolution and oxidizer reduction with increasing temperature (Soosaiprakasam and Veawab 2008). Lower passive current densities were observed at 40 °C than for 80 °C, but with higher fluctuations. This indicate that the passive film for MEA is more protected at 40 °C, but that the film is less stable than at 80 °C (Soosaiprakasam and Veawab 2008).

Increasing solution velocity increases corrosion rate (Soosaiprakasam and Veawab 2008) in both active and passive regions. This was explained by enhanced transport rates of corroding agents between metal surface and bulk solution.

Normally, corrosion tests in the laboratory are conducted using clean surfaces, while pilot plant campaigns are long-term processes, where surfaces are exposed to amine solution for longer periods. (Soosaiprakasam and Veawab 2008) studied corrosion for pre-corroded specimens for MEA solutions.

Faster corrosion rate was observed, which was a combination of faster rates of iron dissolution and oxidizer reductions reactions.

3.1.2.2 CO_2 loading

CO_2 loading has the highest impact on the cathodic current density (Veawab, Tontiwachwuthikul et al. 1999, Kittel, Fleury et al. 2012). By increasing the CO_2 loading, the concentrations of HCO_3^- and H^+ increases which causes rates of oxidizer reduction to increase (Veawab, Tontiwachwuthikul et al. 1999, Soosaiprakasam and Veawab 2008). Figure 3-2 shows corrosion rate in MEA at different temperature and CO_2 loading (Kittel, Fleury et al. 2012).

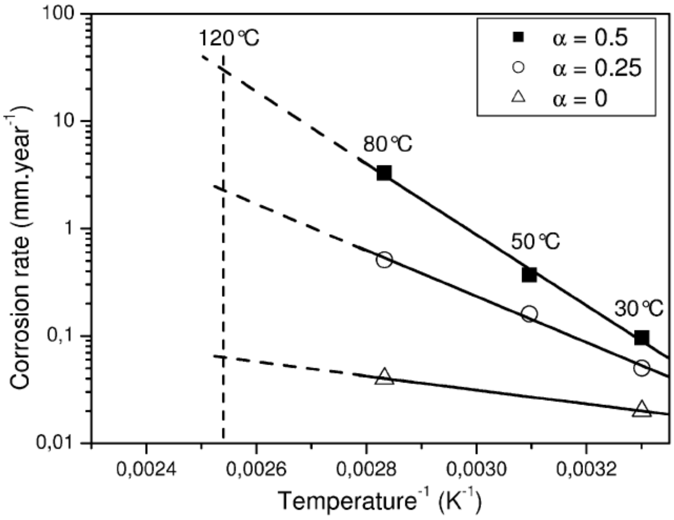


Figure 3-2: Corrosion rate (mmyear-1, from electrochemical measurements) as a function of temperature (K), material carbon steel, solution 30 wt% MEA. Extrapolation to reach 120 °C. (Kittel, Fleury et al. 2012).

3.1.2.3 Other gas components

Kittel et al. investigate oxygen's effect on corrosion in the laboratory (Kittel, Fleury et al. 2012). A solution of 30 wt% MEA saturated with CO_2 were used. The experiment was conducted at 80 °C with either flow of pure CO_2 or 75% CO_2 and 25% air. The loading for both systems were 0.5 molCO_2/mol MEA. Oxygen content in second experiment was 5%. The results showed that a solution of CO_2 saturated MEA at 80 °C results in corrosion rate of several mm/years, however the rate was not significantly changed in the presence of oxygen. It was also mentioned that corrosion rate measured using electrochemical evaluation, was higher than for coupons. The difference here is the time aspect: coupons normally exposed to the solutions over longer time, while electrochemical evaluation done short time after start-up of the experiment. Formation of iron carbonate, that forms a protective layer, is a slow process.

The early experiments with O_2 were investigated at constant O_2 concentration and no significant impact on corrosion were observed. At various partial pressures of O_2 the corrosion rate was shown to increase (Veawab, Tontiwachwuthikul et al. 1999, Soosaiprakasam and Veawab 2008). It was explained by higher oxidizer concentration in solution at higher partial pressure of O_2. However, the presence of O_2 in the region where hematite is formed, strengthen the passive film of hematite. Veawab et al. suggested that iron reacts with O_2 resulting in ferrous hydroxide and ferrix hydroxide (Veawab, Tontiwachwuthikul et al. 1999).

3.1.2.4 Contaminants in the solvent or the gas

In the post-combustion CO_2 capture process salts of carboxylic acids are formed as a result of solvent degradation. These products can increase corrosivity by two distinct ways: either by decreasing the pH and increasing the conductivity of the solvent, or by increasing the solubility of metals (formation of complexes), thus decreasing the precipitation tendency (Rooney, Bacon et al. 1996, Kittel, Fleury et al. 2012). In early work on degradation products from DEA and MDEA effect on corrosion, no effect on the corrosion rate of carbon steel was observed (Blanc, Grall et al. 1982). The observation was explained by the degradation compounds either being basic products and therefore not participating in acid corrosion process or that the concentration of acidic compounds in the amine were too low. Experiments with up to 5 wt% carboxylic acids were investigated. More recent studies have shown that especially some of the carboxylic acids influence the corrosion (Rooney, Bacon et al. 1996, Tanthapanichakoon, Veawab et al. 2006, Fytianos, Grimstvedt et al. 2014). Fytianos et al. also investigated influence on corrosion of some of MEA's secondary degradation compounds, e.g. amide, piperazinone, oxazolidinone (Fytianos, Ucar et al. 2016). In the work by (Rooney, Bacon et al. 1996), coupons of carbon steel were added to aqueous solution of *N*-methyldiethanolamine (MDEA) which contained various concentrations (500-10000 ppm) of acids as acetic, formic, oxalic and sulfuric acid or their salts. The experiments were conducted at 82 and 121 °C. The result for 82 °C is given in Figure 3-3 (Rooney, Bacon et al. 1996).

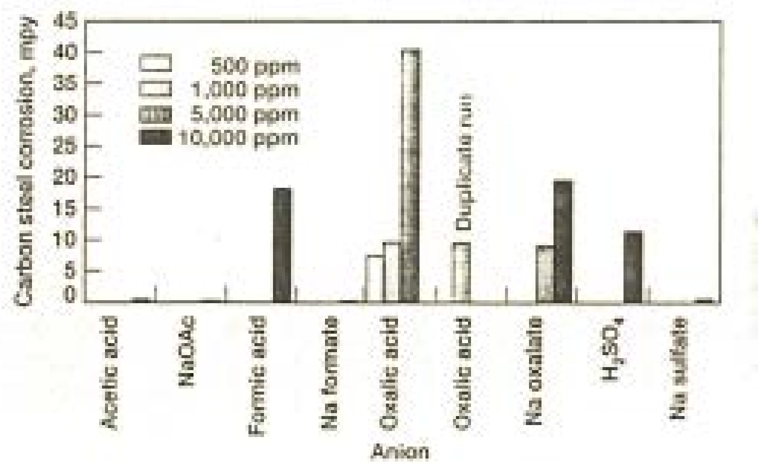


Figure 3-3: Corrosion of carbon steel in a aqueous MDEA solution with different concentration of anions (Rooney, Bacon et al. 1996).

Corrosion rate of carbon steel was highest for oxalic acid. The corrosion increased with acid concentration and with temperature. The corrosiveness of oxalic acid has later been verified by (Tanthapanichakoon, Veawab et al. 2006, Fytianos, Grimstvedt et al. 2014, Fytianos, Ucar et al. 2016). Little of no effect of heat stable salts on corrosion rate of stainless steel was observed (Rooney, Bacon et al. 1996, Tanthapanichakoon, Veawab et al. 2006). Recommended limits of individual acids were given by (Rooney, Bacon et al. 1996) and it was also shown that neutralization with caustic soda reduced the corrosion in two refinery plants. Oxalic acid has been shown to be more corrosive in MEA (Tanthapanichakoon, Veawab et al. 2006, Fytianos, Grimstvedt et al. 2014) and MDEA (Rooney, Bacon et al. 1996). For blend of MEA/piperazine (Pz) (Nainar and Veawab 2009), formic acid showed highest corrosivity in the absence of O_2. Some of the salts were shown to alter the mechanisms of iron dissolution and oxidizing reduction and in some cases the passive film formation was more difficult (Tanthapanichakoon, Veawab et al. 2006). Corrosion of the stainless steel in the presence of heat stable salts was also investigated, no significant change was observed (Tanthapanichakoon, Veawab et al. 2006). In the work by Fytinaos et al., corrosion of the stainless steel in the presence of degradation compounds was investigated using thermal degradation cylinders, where corrosion behavior was investigated combining analytical methods as ICP-MS (inductively coupled plasma mass spectroscopy), SEM-EDS (scanning electron microscopy-energy dispersive X-ray spectroscopy) and XRD (X-ray powder diffraction) (Fytianos, Grimstvedt et al. 2014, Fytianos, Ucar et al. 2016). The concentration of dissolved iron seems to give a good indication on the corrosivity of the solution when testing under similar conditions. Compounds as oxalic acid, fromic acid, HEGly, HEEDA, Bicine and BHEOX, increased the corrosivity of 30 wt% MEA solution (Fytianos, Grimstvedt et al. 2014, Fytianos, Ucar et al. 2016) while only a small effect was obeserved for HEA, HEF, OZD. No effect observed for HEPO, *N*-(2-hydroxyethyl)imidazole (HEI) and *N*-(2-hydroxyethyl)imidazolidone (HEIA).

3.1.2.5 Amine solution concentration

Amine concentration has shown to effect corrosion differently. Pure amine and mixtures of amine and water are not corrosive, they have low conductivity and high pH (Dupart, Bacon et al. 1993, Kohl and Nielsen 1997). In the presence of acid gas, several researchers have observed that corrosion rate increases with increasing amine concentration for the same amine (Dupart, Bacon et al. 1993, Veawab, Tontiwachwuthikul et al. 1999), but for AMP this changed at concentration above 3 kmol/m3 (Veawab, Tontiwachwuthikul et al. 1999), see Figure 3-4. This could be explained by less oxidizer (HCO_3^-) present at higher amine concentration because less water available for carbamate dissociation. The result is lower corrosion rate (Veawab, Tontiwachwuthikul et al. 1999). Other studies showed no effect of MEA concentration (Kittel, Fleury et al. 2012). The experiments have been conducted in different set-ups under different conditions e.g. CO_2 loading, temperature and amine concentration which could explain the deviating conclusions.

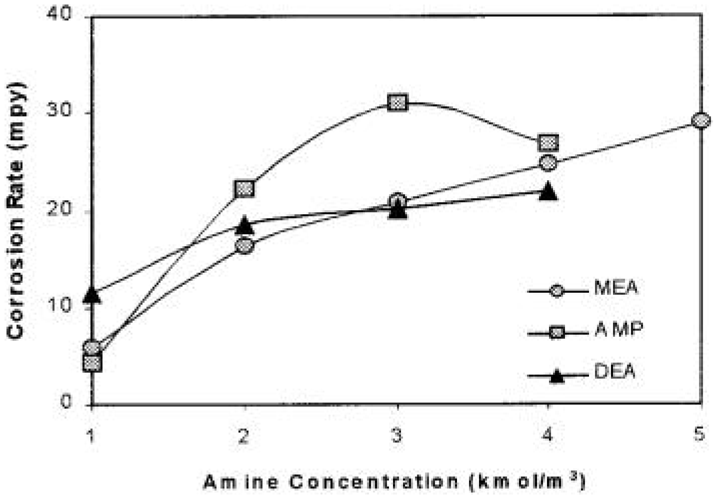


Figure 3-4: Corrosion rate as a function of amine concentration for MEA, AMP and DEA (T=80 °C and 0.2 mol CO_2/mol amine) (Veawab, Tontiwachwuthikul et al. 1999).

3.1.2.6 Amine type

According to (Dupart, Bacon et al. 1993), corrosion increases in the following order:

MDEA < DEA < MEA.

Veawab et al. also observed this order, however only for solutions of same amine concentration saturated with CO_2 (Veawab, Tontiwachwuthikul et al. 1999). In the work by (Veawab, Tontiwachwuthikul et al. 1999), AMP was less stable than DEA, but more stable than MEA. Experiment taking into account variation of CO_2 solubility in different amines, showed similar corrosion rate for MEA and DEA, while AMP had highest corrosion rate, which is connected to higher concentration of bicarbonate in AMP solutions. Corrosion rates for blends were also studied showing a mix of the behaviour for single amines (only one ratio for the mix was tested). AMP is a sterically hindered amine and do not form stable carbamate, formation of bicarbonate is therefore higher. The high concentration of bicarbonate (oxidizer) is believed to explain higher corrosion observed for AMP compared to MEA. The mechanisms for CO_2 absorption and solubility of CO_2 in different amines are essential to explain their corrosion behaviour.

3.1.2.7 Construction material in the plant

Carbon steel is often used in pilot plants. Most studied conducted looked at corrosion in regard to carbon steel. However, (Kohl and Nielsen 1997) compared corrosion rates of metals (monel, 302 and 304SS, 316 SS, 410 SS, aluminium 2S and 3S, mild steel and cast iron) in MEA or DEA solution in laboratory or in pilot plants (coupons) under different conditions, e.g. from no acid gas to acid gas present in the solution, amine concentration from 11 to 95 wt%, temperature from 107 to 190 °C, duration from 21 to 483 days (Kohl and Nielsen 1997). In general, less corrosion was observed for Monel and steel 300 series. Figure 3-1 gives an overview of material used in plants. Stainless steel or other corrosion resistant materials are suggested in the areas where wet acid gas or amine solution corrosion are expected to occur.

3.2 Previous studies (laboratory and pilot)

Several lab scale studies have recently been conducted for single amines or amine blends where conditions have been changed e.g. concentration of amine, amine composition (concentration of each component), temperature, CO_2 or O_2 concentration. Usually these experiments have been conducted by different groups and direct comparison are sometimes difficult since the tests are not standardized. An overview of some of these studies are given in Table 3-1. MDEA, DEA and MEA have been studied since 1930's in relation to acid gas removal from natural gas (Hofmeyer, Scholten et al. 1956, Chakma and Meisen 1986, Dupart, Bacon et al. 1993, DuPart, Bacon et al. 1993, Nielsen, Lewis et al. 1995, Rooney, Bacon et al. 1996, Kohl and Nielsen 1997).

Table 3-1: Recent corrosion studies conducted for various amines.

Amine	Studied	Method	Reference
Aminoacids	Concentration, amino acid type, temperature, CO_2 loading, adding piperazine, corrosion inhibitor	Coupons (weight), carbon steel 1018	(Ahn, Song et al. 2010)
MDEA/Pz	CO_2 loading, O_2, temperature, ratio blend	Coupons (weight), carbon steel and stainless steel	(Zhao, Sun et al. 2011)
MEA/Pz	Ratio blend, total amine concentration, CO_2 loading, temperature, O_2, HSS	Coupons, carbon steel (1018), stainless steel (430)	(Nainar and Veawab 2009)
AMP	Toal amine concentration, O_2, inhibitor	Coupons, carbon steel	(Veawab, Tontiwachwuthikul et al. 1997)
AMP		Electrochemical method, carbon steel	(Zheng, Matin et al. 2016)
MEA	Degradation compounds (HSS)	Electrochemical method, carbon and stainless steel	(Tanthapanichakoon, Veawab et al. 2006)
MEA	Degradation compounds	ICP-MS, SEM-EDS, stainless steel	(Fytianos, Grimstvedt et al. 2014)

(Martin, Lepaumier et al. 2012) studied degradation and corrosion of 22 different compounds, amines and aminoacids. The experiments were conducted in a batch reactor for 14 days at 140 °C. After stabilization of temperature the system was pressurized to 0.5 MPa with the gas mixture of (75% CO_2, 5% O_2 and 20% N_2). For most of the amines a concentration of 2.5 mol/l and 5 mol/L in water were used. A stainless steel and a carbon steel coupons were either immersed in the solution or held in the vapor phase. 7 amines were found to be less corrosive than MEA. These are AMP, 2-(2-

dimethylaminoethoxy)-ethanol, 3-dimethylamino-propan-1-ol, morpholine, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA), tris(hydroxymethyl)aminomethane and 4-methylmorpholine.

During the last 5 years, the studies focusing on corrosion in post-combustion CO_2 capture pilots have increased. Evaluation of corrosion in these studies have been conducted using online monitoring techniques (e.g. electrochemical measurements), coupons and pilot plant inspections. The solvent has been usually MEA. There are some publications for properitary solvents, however the information is usually scarce (Gao, Wang et al. 2011). In the last ten years, several corrosion studies from various pilot plants around the world have been published (Kittel, Idem et al. 2009, Moser, Schmidt et al. 2011, Cousins, Ilyushechkin et al. 2013, De Vroey, Huynh et al. 2013, Khakharia, Mertens et al. 2015, Hjelmaas, Storheim et al. 2017, Li, Landon et al. 2017), see Table 3-2. These pilot plants involve pilots in different scale with various flue gas source, from synthetic to slip stream from power generation from coal. In some cases the flue gas is pre-treated, in others - no pre-treatment was necessary. Most of the studies use coupons placed in various location in the plant, combined with monitoring of dissolved metals and HSS. The duration of the campaings varies, operation from 345 to 2200 hours has been reported. A short summary of the corrosion studies in these plants are given in Table 3-2.

Table 3-2: Overview of pilot studies also investigating corrosion. Good!

Pilot	**Pretreatment**	**Flue gas**					**Solvent**		**Plant material**	**Operating time (hrs)**	**Capacity**	**Corrosion monitoring**	**Reference**
		Source	**O_2 (vol%)**	**CO_2 (vol%)**	**Other components**	**Flue gas flow rate**	**Flow rate**	**Type**					
Esbjerg		DONG Energy (Coal fire power plant)	5.6-6					MEA		500 hrs	1 ton CO_2/hrs	Coupons: carbon steel (AISI1018), stainless steel (AISI 316 & 304)	(Kittel, Idem et al. 2009)
International Test Centre of CO2 capture, ITC		Natural gas burner		4 & 8				MEA				Corrosometer probes	(Kittel, Idem et al. 2009)
Tsinghua University		Synthetic	18	12	0-300 ppm SO2	86 m3/h	0.2-1.2 m3/h	Toshiba's solvent	Major equipment and pipelinge (316L)	345-500		Coupons: carbon, stainless (304 and 316)	(Gao, Wang et al. 2011)
Esbjerg		DONG Energy (Coal fire power plant)						MEA		500-3000		Coupons: carbon (AISI1018), austenitic stainless (304L, 316L), duplex (2101, 2205 and 2705)	(De Vroey, Huynh et al. 2013)
Maasvlakte	Scrubbing with aqueous sodium carbonate, cooled to 40 °C	E.ON's coal fire power plant	7-17	4-13		Max 1210 m3STP/h (STP; 0°C and 101.325 kPa)	2.5-6.5 ton/h	MEA	Austenistic steel (304L and 316L)	1700-2200	6 tons CO_2/day	Electrochemical measurements (online)	(Khakharia, Mertens et al. 2015)
Kentucky	Low NOx control,	Power generation	6-12	14-16	<5 ppm SO_2, <50 ppm		0.3-0.5 m/s	MEA		1000 hrs		Coupons: carbon steel	(Li, Landon et al. 2017)

Pilot	Pretreatment	Flue gas					Solvent		Plant material	Operating time (hrs)	Capacity	Corrosion monitoring	Reference
		Source	O_2 (vol%)	CO_2 (vol%)	Other components	Flue gas flow rate	Flow rate	Type					
	desulfurization unit, electrostatic precipitator	flue gas (0.7 MWe), E.W. Brown Generating station			NOx							(A106), Ni-coated A106, Ni2Al3/Al2O3 coated A106 and AISI 304 stainless steel	
Technology Center Mongstad (TCM DA)		Natural gas turbine based combined heat and power (CHP) or residual fluidized catalytic cracker (RFCC)	CHP 13-14 RFCC 3-8	CHP 3.5-4 RFCC 13-14.5	Defined in (Hjelmaas, Storheim et al. 2017)	CHP <60000 Sm3/h RFCC <45000 Sm3/h	55-120 tons/hrs	MEA	Main plant equipment and piping system in contact with amine: 22% Cr duplex	1960 hrs		Coupons: austenitic stainless steel with Stellite welding, ferric austenitic stainless steel with synthetic rubber	(Hjelmaas, Storheim et al. 2017)
Tarong Post-Combustion Capture Pilot	Pretreatment column	Coal combustion flue gas	1.9-20.9	0-12.3		600 kg/hrs	0-70 L/min	MEA	Piping, columns, heat exchangers, fitting: 316 stainless steel	593 or 745 hrs		Coupons: 316L, 316L welded, C1018, C1018 galvanized	(Cousins, Ilyushechkin et al. 2013)
Niederaussem	Prescrubber	Power station Niederaussem (1000MW$_{el}$, lignite fired)	5	14.2		1550 m_N^3/hrs		MEA		3875-4920 hrs	7.2 ton CO_2/day	Coupons: austenitic ss (1.4541 & 1.4571), austenitic-ferritic ss (1.4462), nickel base alloy material (2.4858). Flange-tube-flange components.	(Moser, Schmidt et al. 2011, Moser, Schmidt et al. 2011)

Corrosion in two pilots, Esbjerg pilot (coal) and International Test Centre of CO_2 capture, ITC's pilot (natural gas burner) was investigated placing out coupons or corrosometer probes in various locations in the plant with MEA as solvent (Kittel, Idem et al. 2009). Both pilots showed low corrosion in the colder parts of the plant, as absorber inlet and outlet. For Esbjerg, highest corrosion observed in the outlet from the stripper (4500-8500 µm/yr), while for ITC, highest corrosion observed for inlet of the stripper. The corrosion rate for carbon steel in the Esbjerg pilot was (535-538 µm/yr) in the stripper overhead and (533-1075 µm/yr) in the rich solvent going to the stripping column (Kittel, Idem et al. 2009).

Gao et al. presented corrosion and degradation studies on Toshiba's solvent in a pilot plant at Tsinghua University using synthetic flue gas (Gao, Wang et al. 2011). Coupons of different materials were placed in the pilot and evaluated. The lab pilot was operated in closed loop, gases out of absorber and desorber, and the condensate were returned to the pilot. Highest corrosion rate for carbon steel observed for the rich solvent out of heat exchanger, a lower rate observed at this point for the campaign with 200 ppm SO_2. But this was not the case for coupons located in different part of the plant. Lower corrosion rate observed for stainless steel (304 and 316), highest rate observed for lean liquid out of desorber. Same as for carbon steel, in some cases lower corrosion rate observed when SO_2 is present.

Moser et al. describes tests conducted for different materials and gaskets placed at different locations in a post-combustion capture plant in Germany at the lignite-fired 1000 MW_{el} power station Niederaussen (Moser, Schmidt et al. 2011). Coupons of different types of stainless steel (austenitic, austenitic-ferritic, nickel base alloy material) were placed in the pre-scrubber, the absorber and the desorber. Flanges, tubes and gaskets were placed at different locations in the solvent cycle and a concrete module was placed in the lean CO_2 solvent flow. Few details are described regarding the campaign itself in this publication (Moser, Schmidt et al. 2011), however more information could be obtained from (Moser, Schmidt et al. 2011, Moser, Schmidt et al. 2011, Moser, Schmidt et al. 2011). The tests were conducted with 30wt % MEA with an operating time around 6 months (3875 – 4920 hrs). The tested stainless-steel materials and the flange-tube-flange materials showed good corrosion resistance. For the gasket, the best results obtained for PTFE (Moser, Schmidt et al. 2011).

In the study by De Vroey et al. (De Vroey, Huynh et al. 2013) the focus was to identify critical zones, find appropriate material, understand corrosion mechanisms and relate it to the operation of the plant. Coupouns of different material were placed in different locations in the Esbjerg pilot plant (flue gas from coal fire plant), the different locations are given in Figure 3-5 (De Vroey, Huynh et al. 2013).

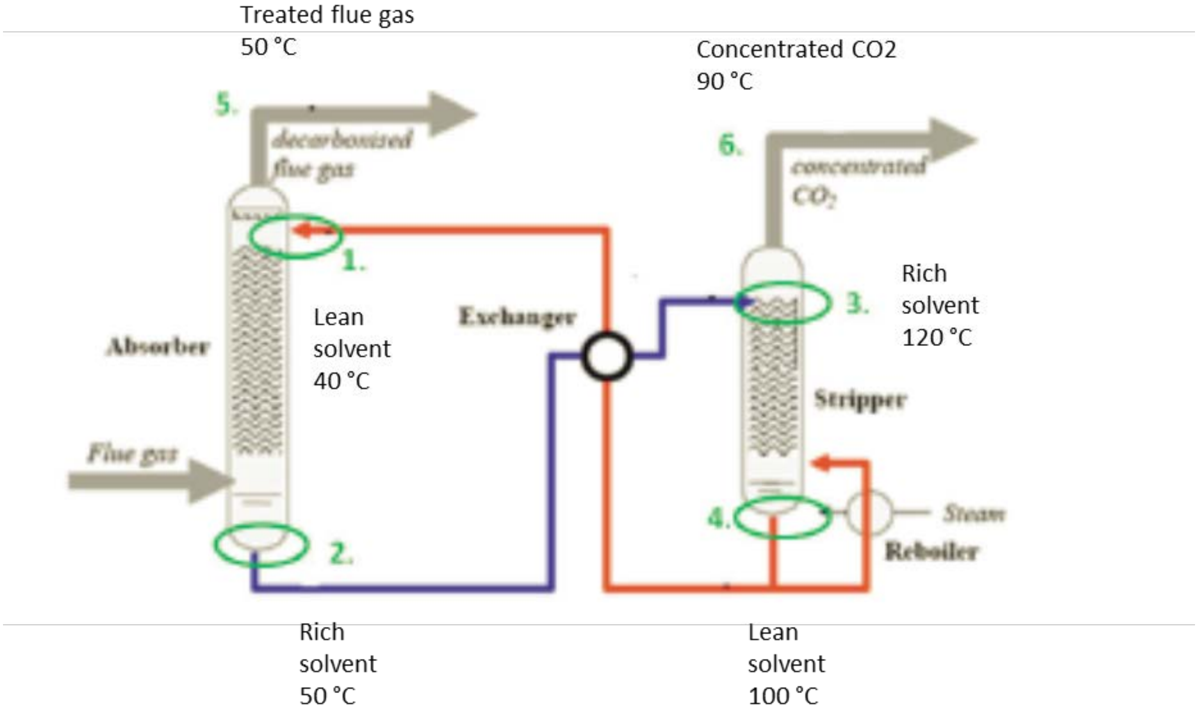


Figure 3-5: Locations where the coupouns are placed in the Esbjerg pilot plant, adapted from (De Vroey, Huynh et al. 2013).

Carbon steel and 304L performed well in most places in the pilot, the exception where for the lean solvent stripper outlet and for concentrated CO_2 out of the stripper (De Vroey, Huynh et al. 2013). The critical zones were identified; stripper sump, high temperature lean sovent lines exposed to flow turbulence, reboiler and reclaimer.

A pilot campaign with 30 wt% MEA were conducted at Tarong Post Combustion Capture pilot plant, the operating time was 593 or 745 hours (Cousins, Ilyushechkin et al. 2013). Coupons of carbon steel, galvanized carbon steel, stainless steel and welded stainless steel were placed at 8 different loactions in the plant (several coupons of same material placed at the same location). These locations were below packed sections or in the solvent storage tanks in absorber and stripper. The details in regard to plant operation conditions and temperature are given by (Cousins, Ilyushechkin et al. 2013). Some spread observed between coupons of same material at same locations, indicate that it is necessary to use multiple coupons when discussing trends (Cousins, Ilyushechkin et al. 2013). The general trend was that galvanized carbon and carbon steel were more corrosive than welded stainless and stainless steel. Except for wash water outlet, higher corrosion observed for galvanized carbon steel than carbon steel. In the absorber the corrosion rates for these two materials were from 200 to 800 µm/yr. Corrosion rate for stainless steel and welded stainless steel was less than 3 µm/yr at all locations. No clear trend observed for corrosion rates of different materials.

In the work by Khakharia et al., a method for online corrosion monitoring in TNO's post-combustion CO_2 capture pilot in Maasvlakte (receives part of the flue gas from E.ON's coal fire plant) was described and tested on two different MEA campaigns (Khakharia, Mertens et al. 2015). A SmartCET real-time measurements system from Honeywell was used, this is based on electrochemical measurements. Output variables from the method are general corrosion rate, B-value or Stern-Geary constant, pitting factor and corrosion mechanism indicator. The probe was placed at the outlet of the stripper. Corrosion coupons were also placed at the same location and evaluated visually and using weight loss. The test were conducted at the TNO's post-combustion CO_2 capture plant at Maasvlakte, the specification for the plant is given by (Khakharia, Mertens et al. 2015). Two campaigns at repspectively 2200 and 1700 operating hours were performed. For campaign 2, corrosion rates from both the coupon and the online system were lower than 25 µm/y. Both campaigns showed a rapid increase in metal concentration, corrosion rate and ammonia emission. This is not fully understood, but seems to happen when operation is continued after a no operation period. It was also observed that adding fresh MEA only gave temporarily reduction in solvent degradation and corrosion rate.

Corrosion resistance of carbon steel, coated carbon steel and stainless steel was tested in a pilot plant at Kentucky Utilities (KU) E.W. Brown Generating Station in Harrodsburg (Li, Landon et al. 2017). Coupons were placed at 4 locations in the plant; in the absorber and in the stripper, in the CO_2 lean amine line prior to the absorber inlet and in the CO_2 rich amine line prior to the stripper inlet. Significant corrosion was observed for carbon and coated carbon steel in the stripper columns and in the line prior to the stripper inlet. For carbon and coated carbon steel the corrosion rate at these locations was > 5mm/yr. Surface characterization using SEM was also conducted for the coupons.

Test Centre at Mongstad has been in operation since 2012. Several campaigns have been conducted at different conditions using different solvents. During this period, MEA campaigns have been conducted as baseline. In (Hjelmaas, Storheim et al. 2017), the corrosion results for the MEA campaign performed in 2015, is given. A thorough description is given of the operation conditions as well as the conditions for the test itself and the analysis of the results. In addition to the evaluation of the copouns by weight and by using microscopy at magnification of 25X, some were also examined using SEM (scanning electron microscopy) connected to EDS (Energy dispersive spectrometer) or microscopy combined by use of dye penetrant fluid (details given by (Hjelmaas, Storheim et al. 2017). Carbon steel coupons (alloy S235) showed a corrosion rate to be above 1.4 mm/yr. For the alloys 304L, 316L and 22 Cr duplex stainless steel the corrosion rate was less than 0.1 mm/yr. The Inconel 600 coupon had a corrosion rate of 0.84 mm/yr in the lean solvent and below in 0.1 mm/yr for the rich solvent. Alloy Stellite 6 and 12 showed no corrosion. Pitting was observed for 316L exposed to rich solvent (pitting depth 0.15 mm/yr). No pitting observed for 304L, Inconel 600 and 22 Cr Duplex at all locations and for 316L in the lean solvent. For more details see (Hjelmaas, Storheim et al. 2017). HSS and dissolved metal were also monitored.

4. Conclusion

Systematic studies investigating amine structure effect on degradation have been conducted. Few or no systematic studies have been conducted relating the corrosive behavior of amine toward its structure. Degradation and corrosion are influenced by amine structure, CO_2 loading, temperature and impurities or other gas components present (O_2, SO_2, H_2S). Oxygen solubility in aqueous amine solutions as well as the biodegradatability of these amines are also important when studying chemical stability of amines.

The last decade several studies have been conducted studying corrosion or degradation in pilot plants. Several of these studies have shown that long time campaigns are necessary to evaluate the chemical stability of the amine as well as the resistance of the material in the plant. The lab experiments do not mimick the accelerating degradation/corrosion that often is observed in the pilot plant after several thousand hours.

There is a relation between degradation and corrosion, and important factors to monitor in this aspect are metal concentration and concentration of heat stable salts (HSS) in solvent as well as ammonia emitted. These give important information in regard to corrosion in the plant and the chemical stability of the solvent. It is also clear that stainless steel are still important to use in areas more prone to corrosion.

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