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4  Experimental study of monoethanolamine oxidative and thermal degradation under
5  accelerated conditions.

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# Experimental study and kinetic model of monoethanolamine oxidative and thermal degradation for post-combustion CO₂ capture.

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## Abstract

In the present work, a kinetic model is proposed for the prediction of amine solvent degradation in the post-combustion $CO_2$ capture process. Solvent degradation combined to the emission of degradation products represents one of the main operational drawbacks of this process. It induces additional costs and it impacts the process efficiency and its environmental balance. In the present work, degradation is studied under accelerated conditions for the case of monoethanolamine solvent (MEA). The influence of the temperature and of the $O_2$ and $CO_2$ concentrations in the gas feed are studied, and their effect on the MEA loss and the emission of degradation products is quantified. Based on the experimental results, a kinetic model for both oxidative and thermal degradation of MEA is proposed and compared to previous attempts to model MEA degradation. The present kinetic model may be further used to develop a practical tool assessing solvent degradation in large-scale capture plants.

**Highlights:**
1. MEA degradation is studied in conditions representative of industrial $CO_2$ capture.
2. The influence of the temperature and the feed gas composition is studied.
3. Major products of MEA oxidative and thermal degradation are quantified.
4. A kinetic model is proposed to describe MEA oxidative and thermal degradation.
5. The MEA degradation under industrial conditions may be predicted.

Keywords: Post-combustion $CO_2$ capture, monoethanolamine degradation, degradation kinetics.

## 1. Introduction

$CO_2$ capture and storage (CCS) technologies represent one of the main technologies to rapidly reduce the anthropogenic emissions of carbon dioxide. It may be part of the response for facing the combination of increasing environmental concerns and growing world energy demand. According to the International Energy Agency (IEA, 2013), CCS may account for up to 17% of the $CO_2$ emission reduction in 2050. Among other capture methods, the $CO_2$ post-combustion capture with amine solvent treats the flue gas after the combustion so that already operating power plants can be rapidly retrofitted. The $CO_2$ is captured by absorption into an amine solvent, the benchmark solvent being an aqueous solution of 30 wt% monoethanolamine (MEA). After the absorption, the $CO_2$-loaded solvent is regenerated at a higher temperature to release the captured $CO_2$ that can be re-used or stored underground.

Besides the high energy requirement of the process, the degradation of the amine solvent (and its consequence, i.e. the emission of degradation products to the environment) represents the second main operational drawback of the post-combustion $CO_2$ capture. First, the cost of solvent make-up necessary to compensate for solvent losses may represent up to 22% of the process operative costs (Abu Zahra et al., 2007). Moreover, the degradation of amine solvents leads to the formation of a large range of products that may modify the solvent properties and decrease the process efficiency. Some volatile degradation products like ammonia may then be emitted, potentially resulting into a significant issue in $CO_2$ capture plants. Although emission reduction technologies exist (among others the (acid) water washing of the flue gas at the column outlet), the problem of volatile products emissions may still be significant in large-scale operating plants (Mertens et al., 2013). As summarized by Svendsen et al. (2011), there is no advantage at capturing $CO_2$ if it implies the emission of other products like ammonia.

In the last decade, some attention was paid to the understanding of solvent degradation mechanisms. In the case of aqueous MEA, Bedell (2011) listed three main degradation mechanisms: oxidative degradation, thermal decomposition and thermal degradation with $CO_2$. Thermal decomposition occurs in the absence of $O_2$ and $CO_2$ by the cleavage of the MEA molecule at temperatures higher than 200°C, while thermal degradation with $CO_2$ implies irreversible reactions between $CO_2$ and the amine solvent. Moreover, Epp et al. (2011) also reported about a fourth mechanism, i.e. solvent degradation with flue gas contaminants like $SO_x$ or $NO_x$. These four mechanisms have been diversely studied. The thermal degradation of MEA with $CO_2$ was studied by Davis (2009) and a kinetic model of this degradation pathway was proposed. Supap et al. (2009) and Sexton & Rochelle (2009) both studied the influence of operating parameters on MEA oxidative degradation. In addition, a kinetic model of MEA $O_2$- and $SO_2$- induced degradation was proposed by Supap et al. (2009). However, the degradation experiments underlying this model took place with discontinuous gas feed while industrial $CO_2$ capture plants operate with a gas feed continuously flowing through the liquid. This different operating mode leads to degradation pathways that are not representative of industrial degradation. Conditions closer to industrial plants were adopted by Lepaumier et al. (2011) and in a previous work (Léonard et al., 2014), but no kinetic model of solvent degradation was proposed. It appeared from both works that MEA oxidative degradation is the main degradation pathway in industrial conditions. Moreover, these studies have evidenced that accelerated lab-scale degradation could reproduce similar degradation rates and products to those observed in samples coming from industrial pilot plants.

In conclusion, although previous studies have led to a better understanding of the solvent degradation mechanisms, there is currently no validated kinetic model of MEA degradation that is able to predict industrial scale degradation. This is however essential for a proper process evaluation and design. Thus, the objective of the present work is to study solvent degradation in accelerated conditions that are representative of real $CO_2$ capture plants. Based on these experimental results, we propose a kinetic model for solvent degradation that is relevant for large-scale process simulation.

## 2.    Materials and methods

Solvent degradation is a slow phenomenon taking place over months in industrial capture plants. Thus, it was necessary to develop appropriate experimental equipment and procedures to accelerate solvent degradation within a reasonable timeframe at the lab scale. In the present

work, the two main degradation pathways of MEA (oxidative degradation and thermal degradation of MEA with $CO_2$) have been considered, while the MEA thermal decomposition and the reactions with flue gas contaminants like $SO_x$ or $NO_x$ have been neglected in a first approach. Indeed, thermal decomposition does not take place at the temperatures observed in $CO_2$ capture conditions and the presence of $SO_x$ and $NO_x$ may be considerably reduced, assuming a high efficiency of the flue gas cleaning steps occurring before the $CO_2$ capture.

The degradation is studied using specially developed equipment depending on the degradation pathway. Because it does not require the presence of a gas phase, thermal degradation with $CO_2$ may be studied under batch conditions. On the contrary, oxidative degradation requires a continuous gas feed since it is a gas-liquid transfer limited phenomena (Goff, 2005). Thus, oxidative degradation experiments were conducted in an experimental Degradation Test Rig with continuous gas flow while the thermal degradation experiments with $CO_2$ were performed in batch cylinders. On the first side, the Degradation Test Rig for MEA oxidative degradation allows temperatures up to 140 °C and pressures up to 2 MPa, with flexible gas composition and variable agitation rate. Typically, 300 g of 30 wt% MEA (1.47 mol) are weighted into the reaction vessel and loaded with $CO_2$ to reach a loading of about 0.40 mol $CO_2$/mol MEA. The degradation experiment runs for one week at 120°C, 0.4 MPa (gauge) and 600 rpm with a continuous gas flow rate (160 Nml/min) composed of 5% $O_2$, 15% $CO_2$ and 80% $N_2$. On the other side, MEA thermal degradation was studied in batch reactors consisting in 150 ml-cylinders made of stainless steel 316L that were set into a laboratory oven. In a typical experimental run, the cylinders are filled up with 100 g of the solvent to be tested, usually MEA 30 wt% that has been loaded with $CO_2$ to reach a loading of about 0.40 mol $CO_2$/mol MEA. Typical experiments usually run for 3 weeks at 140°C and a sample is taken every week. Finally, in order to characterize the degraded solvent samples, different analytical methods have been developed. The MEA content is determined by high performance liquid chromatography (HPLC) while the liquid degradation products are quantified using gas chromatography (GC). Gaseous degradation products are quantified by Fourier transformed infra-red spectroscopy (FTIR). A total nitrogen analysis is performed in the liquid phase using the Dumas method and the concentration of dissolved metal ions (Fe, Cr, Ni and Mn) is quantified in liquid solvent samples by Atomic Absorption Spectrometry. A detailed description of the equipment and procedures has been published in a previous work (Léonard et al., 2014).

## 3.    Experimental results

As already mentioned, it appears from previous works that oxidative degradation is the main degradation mechanisms in industrial pilot plants. As a consequence, the focus of the present experimental study is mainly set on MEA oxidative degradation. Besides these tests, some thermal degradation tests with $CO_2$ are also performed in order to get a comparison with the kinetic model proposed by Davis (2009) for MEA thermal degradation.

### 3.1 Oxidative degradation

In this section, the influence of different process operating parameters on MEA oxidative degradation is experimentally studied. These parameters are the gas feed composition and the temperature. The degradation tests occurred in the Degradation Test Rig with continuous gas flow. Most experiments were performed in the presence of both $O_2$ and $CO_2$ since $CO_2$ is always present in $CO_2$ capture applications, even in lean-loaded solvents.

### 3.1.1 Influence of the $CO_2$ and $O_2$ concentrations in the gas feed

The influences of the $CO_2$ and $O_2$ concentrations were successively studied by varying the corresponding component concentration in the gas feed. Since the gas feed consists in a mix of $O_2$, $CO_2$ and $N_2$, the variation of the $O_2$ or $CO_2$ concentration was compensated for with $N_2$ in order to keep a constant gas feed flow rate. Experiments varying the $CO_2$ concentration were conducted at a constant $O_2$ concentration of 5%. Similarly, the experiments varying the $O_2$ concentration were performed at a constant concentration of 15% $CO_2$ in the gas feed. Figure 1 (left) shows that the MEA loss equals about 0.35 mol whatever the $CO_2$ concentration as far as it is different from zero. In the absence of $CO_2$, the MEA loss reaches up to 0.55 mol (initial MEA content was 1.47 mol). The $NH_3$ emission follows the same trend when the $CO_2$ concentration is varied. It thus appears that the oxidative degradation of MEA does not depend on the $CO_2$ concentration as far as $CO_2$ is present in the gas feed, and that a higher degradation rate is observed at 0% $CO_2$. It must be noted that experiments with $CO_2$ in the gas feed underwent an initial $CO_2$ loading before the experiment start, which was not the case for experiments without $CO_2$ in the gas feed. As a conclusion, the $CO_2$ loading inhibits MEA oxidative degradation, but this inhibitive effect does not depend on the $CO_2$ concentration in the gas feed.

Regarding the influence of oxygen, it appears from Figure 1 (right) that the increase of the oxygen concentration in the gas feed leads to an increase of both the MEA degradation rate and the $NH_3$ emission. Doubling the oxygen concentration from 5% to 10% increases the MEA degradation rate by 160% to reach a MEA loss of 0.81 mol. These results also confirm that the main degradation pathway occurring in the Degradation Test Rig is the oxidative reaction since no MEA loss can be observed in the absence of oxygen. The increase of the $NH_3$ emission with the oxygen concentration also confirms the oxidative degradation mechanism since $NH_3$ was reported to be one of the main products of MEA oxidative degradation (Chi and Rochelle, 2002).
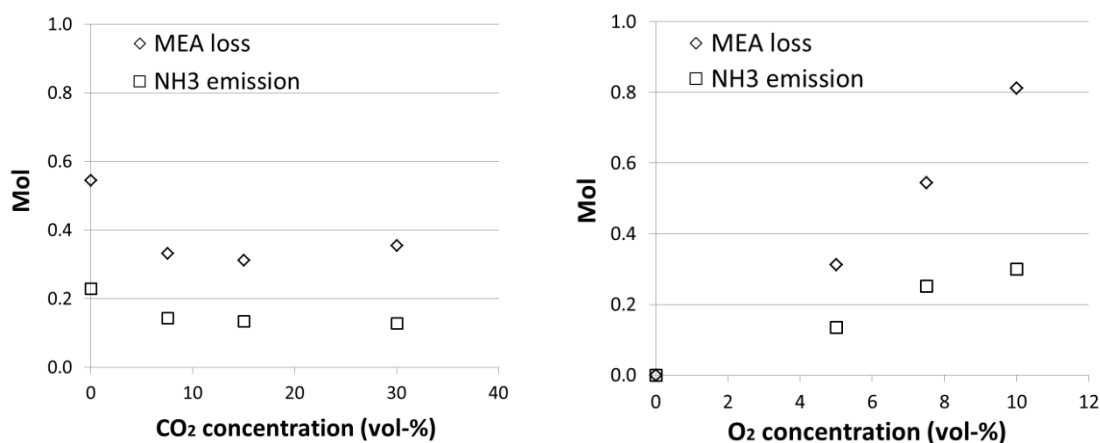


**Figure 1. Influence of the $CO_2$ concentration (left) and of the $O_2$ concentration (right) in the gas feed on MEA degradation and $NH_3$ emission (300 g, 30 wt% $CO_2$-loaded MEA, 120°C, 0.4 MPa (gauge), 600 rpm, 160 Nml/min gas feed, 1 week). There is no initial $CO_2$ loading in experiments with no $CO_2$ in the gas feed.**

When observing the resulting degradation products, Figure 2 (left) shows that the presence of $CO_2$ implies the apparition of products like HEIA and BEOX, while less HEI is produced. However, no clear influence of the $CO_2$ concentration could be observed on the distribution of degradation products, apart from the influence of the initial $CO_2$ loading. When varying the $O_2$ concentration in the gas feed, Figure 2 (right) evidences that more HEI is formed at higher

200  $O_2$ concentrations. This is coherent with HEI as a major oxidative degradation product as
201  proposed by Voice et al. (2012). On the contrary, the formation of HEPO and BHEOX does
202  not depend on the $O_2$ concentration although they are only formed when $O_2$ is present in the
203  system.



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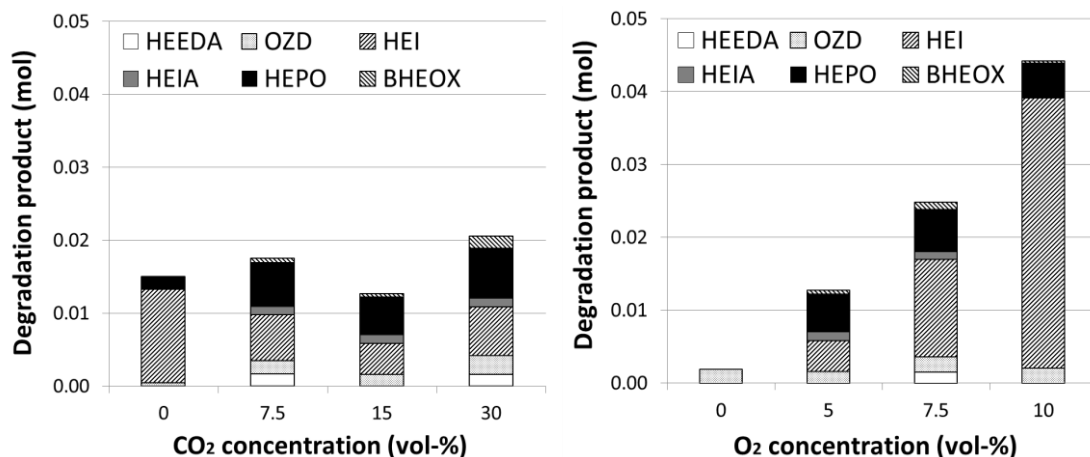
**Figure 2. Influence of the $CO_2$ concentration (left) and of the $O_2$ concentration (right) in**
**the gas feed on liquid degradation products (300 g, 30 wt% $CO_2$-loaded MEA, 120°C,**
**0.4 MPa (gauge), 600 rpm, 160 Nml/min gas feed, 1 week). There is no initial $CO_2$**
**loading in experiments with no $CO_2$ in the gas feed.**

### 3.1.2 Influence of the temperature

211  In the industrial $CO_2$ capture process with MEA, the solvent temperature may vary from 40°C
212  at the absorber entrance up to 120°C in the stripper reboiler, and even up to 150°C in case of
213  MEA thermal reclaiming (Cummings et al., 2007). Figure 3 (left) shows that both MEA
214  degradation and $NH_3$ emission increase more than proportionally with temperature. Almost no
215  degradation is observed at 55°C while the MEA loss reaches 0.5 mol at 140°C (initial MEA
216  content: 1.47 mol). At the same time, the $NH_3$ emission increases from 0 up to 0.17 mol. This
217  evidences that higher temperatures clearly enhance MEA oxidative degradation under usual
218  operating conditions.



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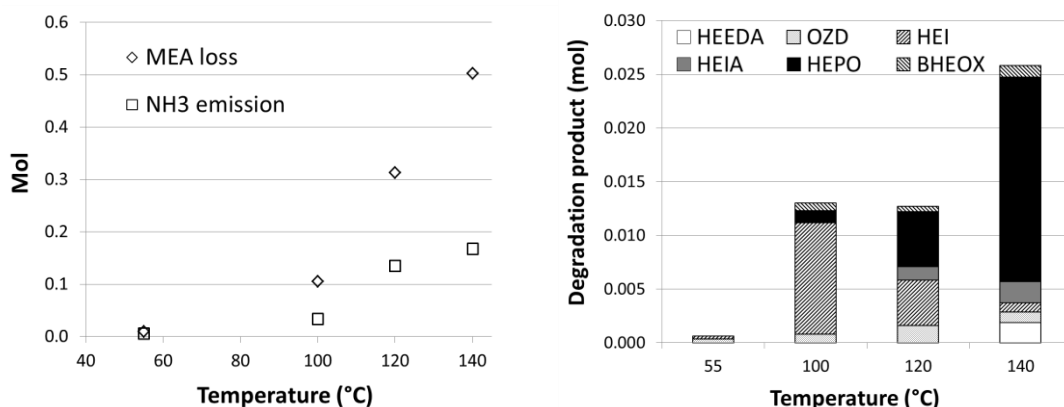
**Figure 3. Influence of the temperature on MEA degradation and $NH_3$ emission (left) and**
**on liquid degradation products (right) (300 g, 30 wt% $CO_2$-loaded MEA, 600 rpm,**
**0.4 MPa (gauge), 160 Nml/min gas feed, 5% $O_2$/ 15% $CO_2$/80% $N_2$, 1 week).**

223

224 It appears from Figure 3 (right) that the formation of HEI is maximal at 100°C and decreases
225 at higher temperatures. This maximum occurs although the oxidative degradation keeps
226 increasing as evidenced by the higher $NH_3$ emission. This may be related to the lower thermal
227 stability of HEI (Voice et al., 2012). On the contrary, the formation of HEPO (which is also
228 an oxidative degradation product like HEI) is dramatically increased at 140°C, confirming the
229 condensation mechanism proposed by Strazisar et al. (2003). Moreover, the formation of
230 HEIA and HEEDA also increases at higher temperature, although to a lower extent than
231 HEPO. Since HEIA and HEEDA were identified by Lepaumier (2008) as typical products of
232 MEA thermal degradation with $CO_2$, this suggests that thermal degradation with $CO_2$ also
233 takes place more significantly at 140°C. Finally, this evidences that the increasing MEA loss
234 between 120°C and 140°C is due to both thermal and oxidative degradation.

## 3.2 Thermal degradation with $CO_2$

236 The thermal degradation of MEA with $CO_2$ was studied in batch reactors because there is no
237 need for continuous gas supply for this degradation pathway if the solution is initially loaded
238 with $CO_2$. A detailed study of MEA thermal degradation with $CO_2$ was performed by Davis
239 (2009) who also proposed a kinetic model. In the present work, only a few experimental
240 points were performed for comparison purpose with the results of Davis (2009) and in order
241 to adjust the model parameters. The influence of the temperature and the $CO_2$ loading on the
242 MEA thermal degradation is described in the present section.

### 3.2.1 Influence of the $CO_2$ loading

244 The influence of an initial $CO_2$ loading on the thermal degradation of MEA over 3 weeks is
245 shown in Figure 4 (left). When the solution is not loaded with $CO_2$, the MEA loss is almost
246 negligible after 3 weeks (0.02 mol). The small degradation extent in non-loaded solutions may
247 be due to $CO_2$ and $O_2$ contamination since the solutions were not degassed before testing. On
248 the contrary, the MEA loss reaches 0.17 mol in the presence of $CO_2$, evidencing that MEA
249 thermal degradation effectively takes place in the test conditions in the presence of $CO_2$. It
250 appears from Figure 4 (right) that the main identified products of MEA thermal degradation
251 with $CO_2$ are HEEDA and HEIA, and in a less extent, OZD, which confirms the results of
252 Davis (2009). Moreover, Davis (2009) also reported about a fourth degradation product
253 (MEA urea, N,N'-di (2-hydroxyethyl) urea), which was not quantified in the present study.

254
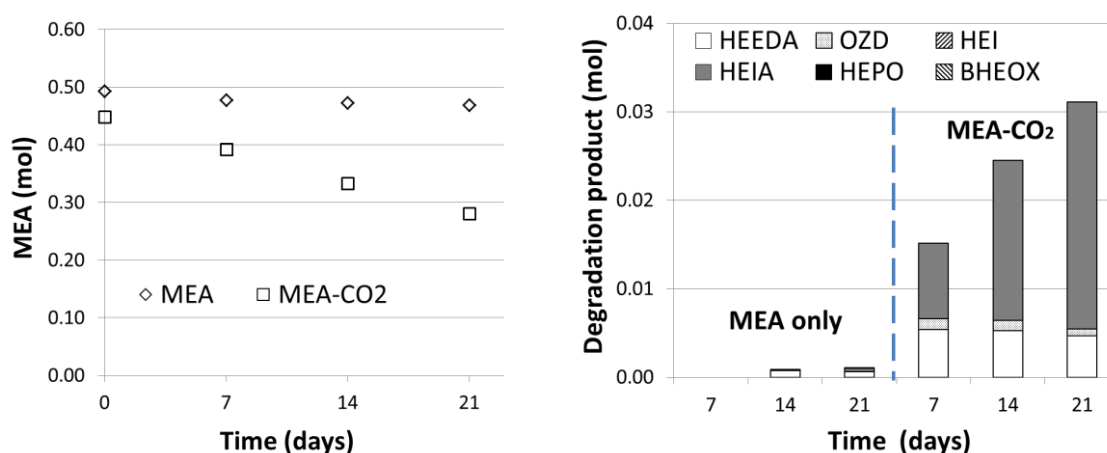


**Figure 4. Influence of $CO_2$ on MEA thermal degradation (left) and on liquid
degradation products (right) (100 g, 30 wt% MEA, no gas feed, 140°C, 3 weeks). The
initial mole number of MEA is lower in the case of loaded solutions due to the dilution
effect of the $CO_2$ loading.**

### 3.2.2 Influence of the temperature

From Figure 5 (left), it appears that the MEA loss due to thermal degradation with $CO_2$ was very low at 120°C, decreasing from 0.45 to 0.43 mol MEA after 3 weeks. On the contrary, the $CO_2$-loaded MEA clearly degraded at 140°C since the MEA content decreased from 0.45 mol to 0.28 mol. Figure 5 (right) indicates that the formation of HEEDA already took place at 120°C, although to a lower extent. Moreover, increasing the temperature up to 140°C especially increased the formation of HEIA, which was proposed by Lepaumier (2008) as a typical end-product of MEA thermal degradation with $CO_2$. On the contrary, the relative independency of HEEDA and OZD over time at 140°C confirms their role as intermediate thermal degradation products as suggested by Lepaumier (2008). As expected, oxidative degradation products like HEI, HEPO and BHEOX do not form in the test conditions so that the MEA loss can be attributed to thermal degradation only.
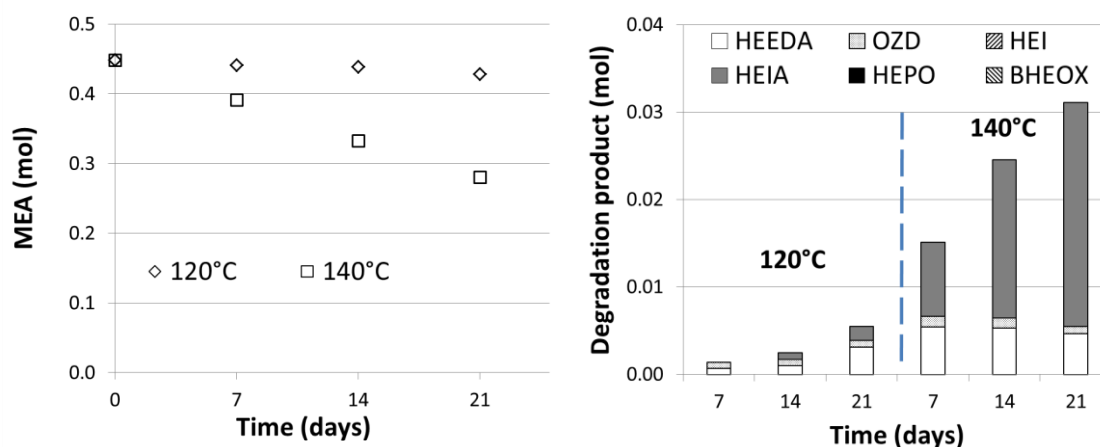


**Figure 5. Influence of the temperature on MEA thermal degradation (left) and on liquid degradation products (right) (100 g, 30 wt% $CO_2$-loaded MEA, no gas feed, 3 weeks).**

## 4.    Discussion

In this section, a kinetic model of MEA thermal and oxidative degradation is proposed. Based on the main results of the experimental study, some assumptions are made and discussed. First, the kinetics of oxidative degradation is derived from the results of the Degradation Test Rig with continuous gas supply. Then, the corresponding model for thermal degradation with $CO_2$ is based on the experiments in batch reactors. Finally, the relevance of the resulting model is evidenced by a comparison with existing kinetic models reported in the literature.
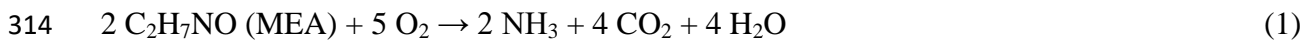
### 4.1 Kinetic model of MEA oxidative degradation

The oxidative degradation of MEA was the most studied degradation pathway in the present study and it occurred in the Degradation Test Rig. The relevance of this equipment and of selected experimental conditions for studying accelerated MEA degradation was established in a previous study by the comparison with degraded samples from two industrial pilot plants (Léonard et al., 2014). In the present experimental study, we first determined the influence of the oxygen and carbon dioxide concentrations in the gas feed. It appeared that the MEA loss and the emission of degradation products both increased with the oxygen concentration. An inhibiting effect of $CO_2$ could also be observed, although not depending on the $CO_2$ concentration as far as $CO_2$ was present. Moreover, these experiments with varying gas feed composition confirmed previous results (Léonard et al., 2014) reporting that $NH_3$ accounts for about half of the MEA loss and that HEI and HEPO are the main identified liquid products of MEA oxidative degradation. Finally, the influence of temperature on the MEA oxidative degradation was clearly evidenced.

Based on these experimental results, we propose to model the oxidative degradation of MEA by an apparent reaction mechanism that is based on several irreversible reactions implying the main identified degradation products. We consider ammonia, HEI, HEPO and formic acid ($CH_2O_2$) as the main degradation products resulting from MEA oxidative degradation. Formic acid is the acidic form of formate, and it is included in the model in order to consider the formation of heat stable salts. Indeed, although it was not identified in our test conditions, formate is the main carboxylic acid identified in degraded MEA samples from industrial pilot plants and its formation was reported in many experimental studies (among others by Sexton and Rochelle, 2009 and by Lepaumier, 2008). For each degradation product, a formation reaction is proposed and balanced with $CO_2$ and water, with ammonia appearing as a degradation product in all reactions. Since the exact reaction mechanisms are still unknown, the reactions (1) to (4) are thus apparent reactions that have been selected for their ability to represent the phenomenon called "oxidative degradation". These reactions are then weighted in accordance with the experimentally observed distribution of degradation products to lead to an overall reaction balance (5):
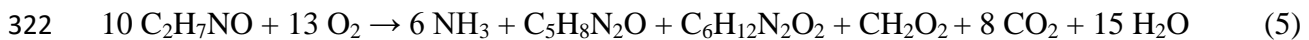
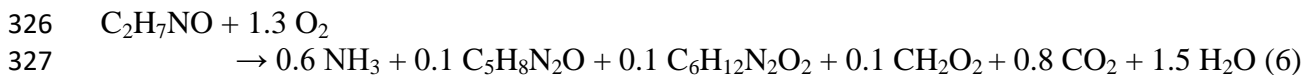$$2\ C_2H_7NO\ (MEA) + 5\ O_2 \rightarrow 2\ NH_3 + 4\ CO_2 + 4\ H_2O \tag{1}$$

$$4\ C_2H_7NO + 5\ O_2 \rightarrow 2\ NH_3 + C_5H_8N_2O\ (HEI) + 3\ CO_2 + 7\ H_2O \tag{2}$$

$$3\ C_2H_7NO + O_2 \rightarrow NH_3 + C_6H_{12}N_2O_2\ (HEPO) + 3\ H_2O \tag{3}$$

$$C_2H_7NO + 2\ O_2 \rightarrow NH_3 + CH_2O_2 + CO_2 + H_2O \tag{4}$$

$$10\ C_2H_7NO + 13\ O_2 \rightarrow 6\ NH_3 + C_5H_8N_2O + C_6H_{12}N_2O_2 + CH_2O_2 + 8\ CO_2 + 15\ H_2O \tag{5}$$

Weighting this equation to describe the degradation of one mol MEA leads to equation (6):

$$C_2H_7NO + 1.3\ O_2$$
$$\rightarrow 0.6\ NH_3 + 0.1\ C_5H_8N_2O + 0.1\ C_6H_{12}N_2O_2 + 0.1\ CH_2O_2 + 0.8\ CO_2 + 1.5\ H_2O \tag{6}$$

This latest reaction may be considered as the apparent reaction of MEA oxidative degradation. In order to determine its kinetics based on an Arrhenius' equation, three additional simplifying assumptions have been made. First, since MEA is not the limiting reactant and is present in large excess in the bulk, its influence on the degradation kinetics is neglected in a first approach. Then, in agreement with the experimental results observed in section 3.1, the influence of the $CO_2$ concentration on oxidative degradation is neglected as long as $CO_2$ is present in the system. Since $CO_2$ is always present in the capture process, even in lean solvents (typical lean loading values are 0.2 mol $CO_2$/mol MEA), the influence of $CO_2$ is neglected in the kinetics model of MEA oxidative degradation. Third, the concentration of dissolved $O_2$ in the solvent has been approximated by Henry's law for oxygen in water. Henry's law describes the dissolved concentration of a gas at saturation, which is not the case in the mass-transfer limited system of the Degradation Test Rig. Thus, the oxygen transfer may be overestimated and the kinetic constant of the reaction rate underestimated. It may be noted that the only other relation that has been retrieved for describing the oxygen solubility is a correlation proposed by Rooney and Daniels (1998) which describes the dissolved oxygen concentration in a solvent saturated with $O_2$. However, the use of this latest correlation leads to questionable results and physically inconsistent values for the kinetic parameters, like for instance a reaction order of 5 regarding oxygen.

347

348 Finally, based on these assumptions, the reaction rate of the MEA oxidative degradation (in
349 mol/L.s) can be expressed by equation (7):

350

351 $$-r_{\text{MEA, oxidative}} = 5.35 \; 10^5 \cdot e^{-41\,730/RT} \cdot [O_2]^{1.46} \tag{7}$$

352

353 R is the universal gas constant (8.314 J/mol.K), T the temperature (K), and $[O_2]$ the
354 concentration of dissolved oxygen (mol/L). The value for the activation energy is given in
355 J/mol and the pre-exponential unit is $(\text{mol/L.s})/(\text{mol/L})^{1.46}$.

356

357 The pre-exponential constant, the activation energy and the kinetic order of oxygen appearing
358 in equation (7) have been determined by minimizing the sum of squared differences between
359 the model-predicted degradation rates and the observed degradation rates based on a set of
360 eleven degradation experiments. The parameter regression has been performed with the solver
361 tool embedded in the Microsoft Excel 2010 software. The operating conditions of the eleven
362 degradation experiments used for the regression are reported in Table 1. Non-specified
363 conditions are similar to the base case experiment (1 week, 600 rpm, 0.4 MPa (gauge),
364 160 Nml/min gas feed). The observed degradation rate for each experiment (in mol/L.s) has
365 been calculated by dividing the mol number of degraded MEA by a run time of one week
366 (604 800 s) and a solvent volume of 0.3 L. Although the initial quantity of solvent equals
367 0.3 kg, the effect of density has been neglected since the density of fresh 30 wt% MEA has
368 been measured as 1.004 kg/L.

369

370 **Table 1. Experiments for determining the kinetics of MEA oxidative degradation**

| Temperature | $O_2$ concentration in gas feed | $CO_2$ concentration in gas feed | Observed degradation rate | Model-predicted degradation rate |
|---|---|---|---|---|
| °C | vol% | vol% | mol MEA/L.s | mol MEA/L.s |
| 55 | 5 | 15 | $1.00 \; 10^{-8}$ [a] | $1.30 \; 10^{-7}$ |
| 100 | 5 | 15 | $5.79 \; 10^{-7}$ | $8.25 \; 10^{-7}$ |
| 100 | 5 | 15 | $3.08 \; 10^{-7}$ | $8.25 \; 10^{-7}$ |
| 120 | 0 | 15 | 0 | 0 |
| 120 | 5 | 7.5 | $1.83 \; 10^{-6}$ | $1.64 \; 10^{-6}$ |
| 120 | 5 | 15 | $1.72 \; 10^{-6}$ | $1.64 \; 10^{-6}$ |
| 120 | 5 | 15 | $1.86 \; 10^{-6}$ | $1.64 \; 10^{-6}$ |
| 120 | 5 | 30 | $1.96 \; 10^{-6}$ | $1.64 \; 10^{-6}$ |
| 120 | 7.5 | 15 | $3.00 \; 10^{-6}$ | $2.95 \; 10^{-6}$ |
| 120 | 10 | 15 | $4.48 \; 10^{-6}$ | $4.50 \; 10^{-6}$ |
| 140 | 5 | 15 | $2.77 \; 10^{-6}$ | $3.03 \; 10^{-6}$ |

[a] In this case, no MEA degradation could be observed. However, in order to facilitate the parameter regression, the observed degradation rate has been arbitrarily set to $1.00 \; 10^{-8}$.

Finally, Figure 6 compares the observed degradation rates with the model-predicted degradation rates based on the results presented in Table 1. The model predicts most experimental degradation rates with less than 15% deviation (represented by the dashed lines). However, the uncertainty is higher in case of low degradation rates, for which the precise determination of the degradation rate is not easy due to experimental uncertainties.
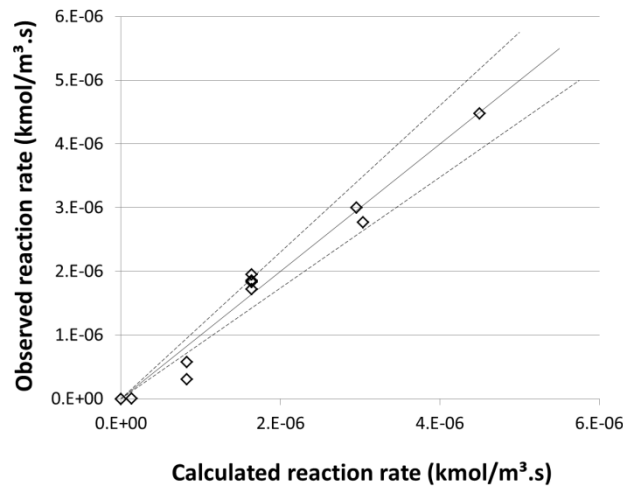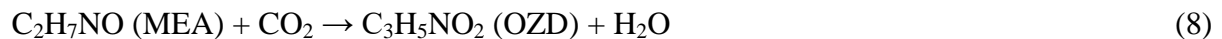


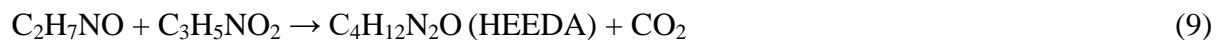**Figure 6. Model agreement with observed degradation rates for the oxidative degradation of MEA**

## 4.2 Kinetic model of MEA thermal degradation

Since thermal degradation with $CO_2$ is not the main degradation pathway in industrial pilot plants, it was less studied and only a few experimental points were collected. The experimental study confirmed the results reported by Davis (2009), i.e. the influence of the temperature and of the $CO_2$ concentration on MEA thermal degradation. Similarly to the kinetic model proposed for the oxidative degradation of MEA, we propose to describe MEA thermal degradation by an apparent reaction mechanism implying the main identified degradation products and to express the degradation rate using Arrhenius' equation. As for MEA oxidative degradation, we assume that thermal degradation reactions are also irreversible. Then, we consider HEIA as the main end-product of MEA thermal degradation while OZD and HEEDA are intermediate degradation products. Based on the degradation mechanisms proposed by Lepaumier (2008), the degradation pathway described by equations (8) to (10) has been assumed for MEA thermal degradation with $CO_2$.

$$C_2H_7NO \text{ (MEA)} + CO_2 \rightarrow C_3H_5NO_2 \text{ (OZD)} + H_2O \tag{8}$$

$$C_2H_7NO + C_3H_5NO_2 \rightarrow C_4H_{12}N_2O \text{ (HEEDA)} + CO_2 \tag{9}$$

$$C_4H_{12}N_2O + CO_2 \rightarrow C_5H_{10}N_2O_2 \text{ (HEIA)} + H_2O \tag{10}$$

$$2\ C_2H_7NO + CO_2 \rightarrow C_5H_{10}N_2O_2 + 2\ H_2O \tag{11}$$

Equation (11) may be weighted to describe the degradation of one mol MEA, leading to equation (12).

407  $C_2H_7NO + 0.5\ CO_2 \rightarrow 0.5\ C_5H_{10}N_2O_2 + H_2O$         (12)
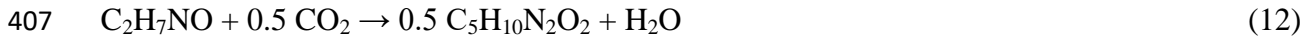
408

409  Equation (12) is considered as the apparent reaction of MEA thermal degradation. In order to
410  determine its kinetics, the influence of the MEA concentration on the degradation rate has
411  been neglected, assuming that MEA is not the limiting reactant. Moreover, in accordance with
412  the reaction mechanism and with the results reported by Davis (2009), the kinetic order of
413  carbon dioxide has been set to 1. Finally, the reaction kinetics can be described as following:

414

415  $-r_{MEA,\ Thermal} = 8.00\ 10^{11} . e^{-144\ 210/RT} . [CO_2]$         (13)

416

417  R is the universal gas constant (8.314 J/mol.K), T the temperature (K), and $[CO_2]$ the
418  concentration of $CO_2$ in the solvent solution (mol/L). The value for the activation energy is
419  given in J/mol and the pre-exponential unit is (mol/L.s)/(mol/L).

420

421  The values for the pre-exponential constant and the activation energy given in equation (13)
422  have been determined following the same method than described for the MEA oxidative
423  degradation. Since the MEA thermal degradation with $CO_2$ has already been studied in details
424  by Davis (2009), only three degradation experiments have been used for parameter regression.
425  The operating conditions of these experiments are reported in Table 2. They have been
426  performed in batch cylinders with no gas supply. The observed degradation rate for each
427  experiment (in mol MEA/L.s) has been calculated by dividing the mol number of degraded
428  MEA by a run time of three weeks (1 814 400 s) and a solvent volume of 0.0909 L. This
429  volume corresponds to a solution weight of 0.1 kg divided by a density of loaded solvent that
430  has been measured as 1.1 kg/L.

431

432  **Table 2. Experiments for determining the kinetics of MEA thermal degradation**

| Temperature | Initial $CO_2$ loading | Model-predicted degradation rate | Observed degradation rate |
|---|---|---|---|
| °C | mol $CO_2$/mol MEA | mol MEA/L.s | mol MEA/L.s |
| 120 | 0.44 | $1.19\ 10^{-7}$ | $1.19\ 10^{-7}$ |
| 140 | 0.44 | $1.02\ 10^{-6}$ | $1.02\ 10^{-6}$ |
| 140 | 0 | 0 | $1.44\ 10^{-7}$ |

433

## 4.3 Comparison with literature models

435  In this section, the MEA degradation model is compared to the models previously proposed
436  by Supap et al. (2009) and Davis (2009). First, the kinetic model developed by Supap et al.
437  (2009) does not distinguish the different types of degradation in the rate expression for the
438  MEA loss. Instead, it proposes an expression for the global degradation rate that considers the
439  $O_2$ and $CO_2$ concentrations, as well as the concentrations of MEA and $SO_2$. According to the
440  authors, $O_2$, $CO_2$ and $SO_2$ can be absent of the system without affecting the model usability.
441  The reaction rate is expressed by equation (14) and Table 3 compares the kinetic parameters
442  proposed by Supap et al. (2009) with those determined in the present work.

443

444  $$-r_{MEA} = \frac{k_0.e^{-\frac{E_a}{RT}}.[MEA]^a.([O_2]^b + [SO_2]^c)}{1 + k[CO_2]^d}$$         (14)

445

446 **Table 3. Comparison of kinetic parameters for oxidative degradation**

| Parameter | | Unit | Supap et al. (2009) | This work |
|---|---|---|---|---|
| Pre-exponential constant | $k_0$ | $(kmol/m^3)^{1-a}/[(kmol/m^3)^{\wedge b}+ (kmol/m^3)^{\wedge c}].s$ | $1.87\ 10^6$ | $5.35\ 10^5$ |
| $CO_2$ kinetic constant | $k$ | $(kmol/m^3)^{-d}$ | 1.18 | 0 |
| Activation energy | $E_a$ | J/mol | 29 403 | 41 729.8 |
| MEA order | $a$ | - | 0.015 | 0 |
| Oxygen order | $b$ | - | 2.91 | 1.46 |
| $SO_2$ order | $c$ | - | 3.52 | - |
| $CO_2$ order | $d$ | - | 0.18 | 0 |

447

448 Different observations can be made. First, based on experiments varying the MEA
449 concentration between 18 wt% and 43 wt%, Supap et al. (2009) reported an almost negligible
450 influence of the MEA concentration on the rate of degradation (MEA order = 0.015). This is
451 in agreement with our assumption to neglect the MEA concentration in a first approach for the
452 reaction rate expression. Then, $CO_2$ shows an inhibiting influence on MEA degradation
453 according to Supap et al. (2009), whatever the operating conditions. In the present work, we
454 confirm the inhibiting influence of $CO_2$, but only in the case of oxidative degradation. On the
455 contrary, we observe that thermal degradation with $CO_2$ is enhanced at higher $CO_2$
456 concentrations. Thus, thermal degradation with $CO_2$ is not properly considered by Supap et al.
457 (2009). In the present study, the influence of the $CO_2$ concentration is not considered for
458 MEA oxidative degradation as previously justified. Moreover, the reaction order proposed by
459 Supap et al. (2009) for oxygen is unexpectedly high and does not seem to reflect physical
460 reaction pathways. This is related to the use of the correlation proposed by Rooney and Daniel
461 (1998) for estimating the solubility of oxygen in the amine solvent. Similarly to Henry's law,
462 this correlation also estimates the concentration of dissolved oxygen in a solvent that is
463 saturated with oxygen. However, this correlation leads to inconsistent results as already
464 mentioned. Significant differences are also observed between the values proposed by Supap et
465 al. (2009) and this work for the pre-exponential constant and the activation energy. Besides
466 the determination of the oxygen concentration, this may also be related to the discontinuous
467 gas feed mode used by Supap et al. (2009) for the degradation experiments. Indeed, it was
468 evidenced that accelerated degradation with no continuous gas feed is not representative of
469 industrial plant degradation (Léonard et al., 2014). As a result, the present model brings a
470 significant improvement and describes more properly the MEA oxidative degradation because
471 its underlying assumptions are closer to the reality of industrial $CO_2$ capture plants.

472

473 Similarly, it is possible to compare the kinetic model proposed for the thermal degradation of
474 MEA with the model developed by Davis (2009). Davis (2009) proposes five thermal
475 degradation reactions with $CO_2$, leading to five different degradation products (HEEDA,
476 MEA Trimer, Polymeric products, HEIA, TriHEIA). In the present work, only the irreversible
477 formation of HEIA is considered. Indeed, HEIA has been found to be the main end-
478 degradation product, which is in agreement with the experimental results presented by Davis

479 (2009). Table 4 compares the values of the kinetic parameters proposed by Davis (2009)
480 based on his own results with the values proposed in this work.
481

482 **Table 4. Comparison of kinetic parameters for the formation of HEIA**

| Parameter | Unit | Davis (2009) | This work |
|---|---|---|---|
| Pre-exponential constant | Depending on the rate equation | $4.14 \ 10^{11}$ | $8.00 \ 10^{11}$ |
| Activation energy | J/mol | 138 072 | 144 210 |
| $CO_2$ order | - | 1 | 1 |

483

484 The reaction order of $CO_2$ has not been experimentally determined by Davis (2009) but it is
485 assumed based on degradation pathways and we decided to keep the same value. Finally,
486 although the rate equation proposed by Davis (2009) for the formation of HEIA considers
487 intermediate products, the kinetic parameters proposed in both models are in the same order
488 of magnitude which suggests that both models would lead to similar results.


489 ## 5.    Conclusion

490 Solvent degradation and its consequences on the process are one of the most important
491 operational drawbacks of the post-combustion $CO_2$ capture. In the present work, the
492 degradation of the benchmark solvent (30 wt% MEA) is studied and the influences of the
493 main process parameters are quantified. The two main degradation pathways of MEA are
494 considered: the oxidative degradation is evaluated in an experimental Degradation Test Rig
495 with continuous gas flow and the thermal degradation with $CO_2$ is performed in batch
496 cylinders. Appropriate analytical techniques are used to characterize solvent degradation by
497 quantifying the amine content (HPLC) and the formation of liquid (GC) and vapor (FTIR)
498 degradation products.
499

500 The influence of different process parameters like the temperature and the gas feed
501 composition was studied in the Degradation Test Rig for MEA oxidative degradation. The
502 experimental results show that the oxidative degradation is enhanced by the $O_2$ concentration
503 in the gas feed, while the $CO_2$ concentration of the gas feed has no influence as far as $CO_2$ is
504 present in the system, which is always the case in $CO_2$ capture applications. Moreover, it
505 appears that the oxygen-mass transfer limited oxidative degradation of MEA is also strongly
506 depending on the temperature. Regarding MEA thermal degradation, significant degradation
507 is only observed in the presence of $CO_2$ and at a high temperature (140°C). Based on these
508 results, a kinetic model of solvent degradation has been proposed for both oxidative and
509 thermal degradation of MEA. Its assumptions are discussed in details and justified. Each
510 degradation mechanism is described by an apparent reaction pathway and the parameters of
511 the Arrhenius' rate equation are determined in each case. This model is compared with
512 previously published attempts to describe the degradation kinetics of MEA and its
513 contribution is highlighted in regard to previous works. Particularly, the model developed for
514 the oxidative degradation of MEA is based on experiments with continuous gas feed which is
515 essential to properly reproduce the degradation pathways occurring in industrial conditions.
516 This is a major improvement in comparison to the model proposed by Supap et al. (2009).
517 The model developed for the thermal degradation of MEA is similar to the one proposed by
518 Davis (2009).

519

520 Finally, further developments plan to include the proposed kinetic model of MEA degradation
521 into a global model of the $CO_2$ capture process previously described (Leonard and Heyen,
522 2011; Leonard and Heyen, 2013). The results of the global model regarding degradation will
523 be validated against pilot plant data. The final objective is to develop a practical tool that is
524 able to predict solvent degradation in an industrial $CO_2$ capture process. This innovative
525 methodology may also be extended to other promising solvents like piperazine. Such a model
526 could and should be used for the design of industrial $CO_2$ capture plants to contribute to their
527 large-scale deployment.

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