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Evaluation of solvent degradation in amine-based post-combustion capture process simulations.

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Abstract

It is important to limit solvent degradation in amine-based post combustion capture systems, as it can lead to challenges, such as solvent losses, reductions in process performance, increased emissions, and corrosion of process equipment. In this work a degradation model is developed for oxidative and thermal degradation of monoethanolamine (MEA) based on experimental data and models from literature. The degradation model is then used to evaluate degradation in a typical coal fired post-combustion capture plant and investigate the effects of process design decisions on the degradation. The total degradation in the plant is predicted to be 0.064 kg MEA/ton CO₂, of which around 80% is caused by oxidative degradation. Degradation in the structured packing of the absorber accounts for 56% of the oxidative degradation as a result of increased temperatures due to CO₂ absorption. A single intercooler stage in the absorber can nearly halve oxidative degradation in the packing but has limited impact on degradation in the sump and heat exchanger, which is caused by dissolved O₂. The overall degradation is reduced 19% in comparison to the base case process. Additional intercooling has the potential to reduce the overall degradation by 33%. Higher O₂ concentrations in the flue gas are found to lead to more oxidative degradation in the absorber packing and sump as well as in the heat exchanger, where the effect is most significant.

Keywords: CO₂ capture; solvent degradation; monoethanolamine; process simulation

1. Introduction

Absorption-based post-combustion carbon capture is among the most promising technologies for the reduction of CO₂ emissions. The process revolves around an aqueous amine solvent, which is used to absorb CO₂ from a flue gas in an absorber. Subsequent heating in a desorber regenerates the solvent as the CO₂ is stripped and collected to be pressurized for transportation and further use or storage. Although the solvent is not consumed in the thermal-swing absorption process, solvent losses and a reduction in solvent activity have been observed as a result of emissions, degradation, and deactivation. [1], [2]

Degradation of the solvent does not only lead to loss in solvent activity, but also to inefficient operation, increased emissions, additional degradation, and damage to process equipment through corrosion. A good understanding of the degradation mechanisms is required to develop effective solvent management strategies that can reduce these negative effects. [3] Predictive solvent degradation models can give valuable insight in degradation in the process and can be used to evaluate the impact of operational strategies and design choices.

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Monoethanolamine (MEA) is one of the most studied and commonly used solvents and extensive work has been done on the acquisition of degradation data and the development of degradation models. [4]–[7] This work aims to combine these data and develop a degradation model that can evaluate thermal and oxidative degradation, which are the most significant mechanisms with respect to solvent consumption. [8] Thermal degradation occurs at relatively high temperatures in the presence of CO₂, while oxidative degradation is the result of dissolved O₂ from the flue gas reacting with MEA. [9]

The developed degradation model is connected to a process simulation of a typical coal-fired post-combustion carbon capture plant. Changes in solvent concentrations as a result of degradation are updated over time to reflect the impact of solvent degradation over time. Degradation is evaluated for each process unit and as a function of process conditions and unit sizes, to create an overview of where degradation is most significant. Furthermore, the model is used to run several case studies to investigate the effect of process parameters and modification on degradation, such as the impact of the O₂ content of the flue gas or intercooling in the absorber. Although the degradation model is developed for aqueous MEA solvents, the trends are expected to be similar for several other amine solvents because of similar degradation mechanisms.

2. Methodology

2.1. Degradation framework

The kinetic rates for absorption and desorption of CO₂ are several orders of magnitude higher than the kinetic rates of solvent degradation. It can thus be challenging to evaluate the degradation models dynamically for longer campaigns, which are typical for absorption-based capture processes. Therefore, in this work, a pseudo steady state approach is used.

First, a steady state process simulation is run, and the results are retrieved from the simulation and stored. These results contain information about the process, such as temperature profiles, concentrations, and liquid flow rates or holdups. The solubility and degradation models are then evaluated for each of the unit operations in the plant. The simulation is updated at regular intervals to take into account changes in solvent composition.

Consumption of CO₂ in the thermal degradation reactions has limited to no effect on the loading of the solvent and is thus neglected. The consumption of O₂, on the other hand, is taken into account, since the concentration of dissolved O₂ is low, and the majority of the O₂ is expected to be consumed on the way from the absorber to the stripper. Therefore, the degradation models are evaluated for the process units in a sequential order and the concentration of remaining O₂ is passed on.

2.2. Oxygen solubility

The solubility of O₂ in the loaded aqueous MEA solvent is predicted using the O₂ solubility model developed by Buvik et al. [10]. This model is based on the gas solubility model in electrolyte solutions by Schumpe et al. [11]. Buvik et al. [10] determined the ion-specific parameters for protonated MEA and the MEA carbamate using experimental data for the solubility of N₂O in a loaded aqueous MEA solvent.

The concentrations of the protonated MEA and the MEA carbamate are required to calculate the O₂ solubility and are assumed to be equal to the concentration of dissolved CO₂. In reality, at higher loadings, when the solvent is close to saturation, some bicarbonate will form instead of the MEA carbamate, which results in an overprediction of the concentration of the MEA carbamate. Since the molar fraction of bicarbonate is relatively small [12] and the model parameters for MEA carbamate and bicarbonate are similar, significant deviations in O₂ solubility are not expected.

The gas and liquid concentrations of O₂ are assumed to be in equilibrium. Liquid phase mass transfer resistances were estimated for a structured packing using the correlation by Billet et al. [13] and the reaction rate for oxidative degradation was found to be limiting for temperatures up to 75 °C. This should be verified experimentally, as the presence of mass transfer limitations can lower degradation rates significantly.

2.3. Thermal degradation

A thermal degradation model for MEA that was developed in previous work [5] is implemented and used in the degradation framework. The degradation reactions and reaction rate parameters for this model are given in Table 1. The reaction rate coefficient (k) is determined using the Arrhenius equation given in equation (1.1), where T_{ref} is the reference temperature at 400 K.

$$k = k_{\text{ref}} \cdot \exp\left(\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \quad (1.1)$$

The degradation model is valid for 30-wt% aqueous MEA solution with a loading of 0.1 – 0.5 mol CO₂/mol MEA, and temperatures in the range of 100 – 160 °C. At lower temperatures, thermal degradation in reality as well as predicted by the degradation model is negligible, so the model can be safely used with temperatures below 100 °C.

Data for BHEU was only available at 135 °C, so the activation energy could not be determined for this reaction. This will lead to an overprediction of BHEU production and MEA consumption at lower temperatures. To counter this behavior, the activation energy for the formation of BHEU is assumed to be the same as the activation energy for the formation of HEEDA. It is expected that both degradation mechanisms involve a common precursor whose formation is rate limiting. The precursor is either OZD as suggested by Davis [14] or isocyanate as suggested by Yoon et al. [15]. In both cases the activation energy is thus expected to be similar for the formation of HEEDA and BHEU. The reaction rate coefficient at reference temperature (400 K) has been recalculated using the assumed activation energy.

Table 1: Degradation reactions and reaction rate equations and parameters for the thermal degradation model. [5] *The activation energy for the formation of BHEU is estimated and the rate coefficient the reference temperature of 400 K is determined.

No.	Reaction	Reaction rate [mol/m ³ /s]	k_{ref} [m ³ /mol/s]	E_A [kJ/mol]
1	2 MEA → HEEDA + H ₂ O	$R_1 = k_1[\text{MEA}][\text{CO}_2]$	$1.599 \cdot 10^{-11}$	151.1
2	MEA + HEEDA → TRIMEA	$R_2 = k_2[\text{HEEDA}][\text{CO}_2]$	$3.054 \cdot 10^{-10}$	142.6
3	HEEDA + CO ₂ → HEIA	$R_3 = k_3[\text{HEEDA}][\text{CO}_2]$	$1.117 \cdot 10^{-10}$	121.5
4	TRIMEA + CO ₂ → AEHEIA	$R_4 = k_4[\text{TRIMEA}][\text{CO}_2]$	$2.839 \cdot 10^{-10}$	136.2
5	2 MEA → BHEU + H ₂ O	$R_5 = k_5[\text{MEA}][\text{CO}_2]$	$5.170 \cdot 10^{-13} *$	151.1 *

2.4. Oxidative degradation

A simple oxidative degradation model for MEA is proposed and fitted using experimental degradation data from Vevelstad et al. [16], for which oxidative degradation of 30 wt-% MEA was investigated in an open-batch stirred bubble reactor. The experiments were conducted with O₂ concentrations in the gas phase from 6% to 98% and temperatures from 55 °C to 75 °C.

The mass transfer resistance for O₂ in the gas phase is assumed to be negligible, and the liquid phase mass transfer coefficient (k_{L,O_2}) is estimated using the correlation for gas bubbles in a stirred tank from Cussler [17], see equation (1.2). This equation uses the bubble diameter (d_b), diffusivity of O₂ in the liquid (D_{O_2}), stirrer power per volume (P/V), and the liquid density (ρ) and kinematic viscosity (ν). The density and dynamic viscosity has been calculated using the correlation for aqueous MEA by Weiland et al. [18] and the diffusivity of O₂ has been estimated using the Wilke-Chang correlation [19]. The other experimental parameters, such as bubble diameter and stirring power, have been estimated in correspondence with the authors.

$$k_{L,O_2} = \frac{0.13D_{O_2}}{d_b} \left(\frac{(P/V)d_b^4}{\rho v^3} \right)^{\frac{1}{4}} \left(\frac{v}{D_{O_2}} \right)^{\frac{1}{3}} \quad (1.2)$$

Léonard et al. [4] proposed a weighted overall reaction balance for the oxidative degradation of MEA, in which 1.3 moles of O₂ are consumed per mole of MEA, and in this work the same assumption has been made. The type and quantity of degradation products (Prod.) is not considered in this simple model, and only consumption of MEA and O₂ is investigated.

Aside from the O₂ concentration in the flue gas and the temperature, the concentration of MEA was also found to be influencing the degradation rate. [20] The presence of CO₂ in the solvent appears to inhibit oxidative degradation to some extent, however, the concentration of CO₂ does not appear to have a significant impact on the degradation rate. [4] Supap et al. [21] observed a slight decrease in degradation rate at higher CO₂ loadings, but argued this was more likely a consequence of reduced solubility of O₂, due to the salting-out effect, than an decrease in the reaction rate. For this reason, the concentration of CO₂ is not included in the rate equation in this work.

The reaction rate equation and fitted parameters are given in Table 2. The same expression from the Arrhenius equation (see equation (1.1)) is used as for the thermal degradation model, however, a reference temperature of 338.15 K (65 °C) has been selected. The average absolute relative deviation (AARD) of the model considering the concentration of MEA is 8.0%, and no clear deviation trends were found with respect to temperature or O₂ concentration in the gas.

Table 2: Degradation reactions and reaction rate equations and parameters for the oxidative degradation model. The reference temperature for the oxidative rate coefficients is 338.15 K.

No.	Reaction	Reaction rate [mol/m ³ /s]	k_{ref} [(m ³ /mol) ^{0.58} /s]	E _A [kJ/mol]
1	MEA + 1.3O ₂ → Prod.	$R_1 = k_1[\text{MEA}][\text{O}_2]^{0.58}$	$6.35 \cdot 10^{-7}$	70.0

2.5. Simulated capture plant

A simulation in AspenPlus V10 of a coal-fired post-combustion carbon capture plant is used to evaluate the degradation and conduct the sensitivity studies. The ENRTL-RK property method is used, and other method parameters and equilibrium chemistry coefficients are selected after the ones used in the example file included in AspenPlus (ENRTL_Rate_Based_MEA_Model). An overview of the process is given in Figure 1 and the simulation parameters are given in Table 3.

The absorber (S101) and stripper (S102) are equipped with a structured Mellapak 250Y packing and are modelled with the rate based RadFrac model using Bravo et al. 1992 correlation for interfacial area and mass transfer coefficients. The column diameters are sized to operate at 75% flooding. The heat exchanger (HEX101) is modeled using the shortcut method with a temperature approach of 10 °C. The liquid holdup of the heat exchanger is estimated using the liquid flow rates and exchange area with a shortcut design methodology for a plate heat exchanger based on the approach by Sinnott et al [22].

A make-up is added for the water (SWMU) and MEA (SSMU) to account for losses in the gas streams exiting the absorber (SF2) and stripper (SC1). Note that solvent losses due to degradation are not considered for this balance.

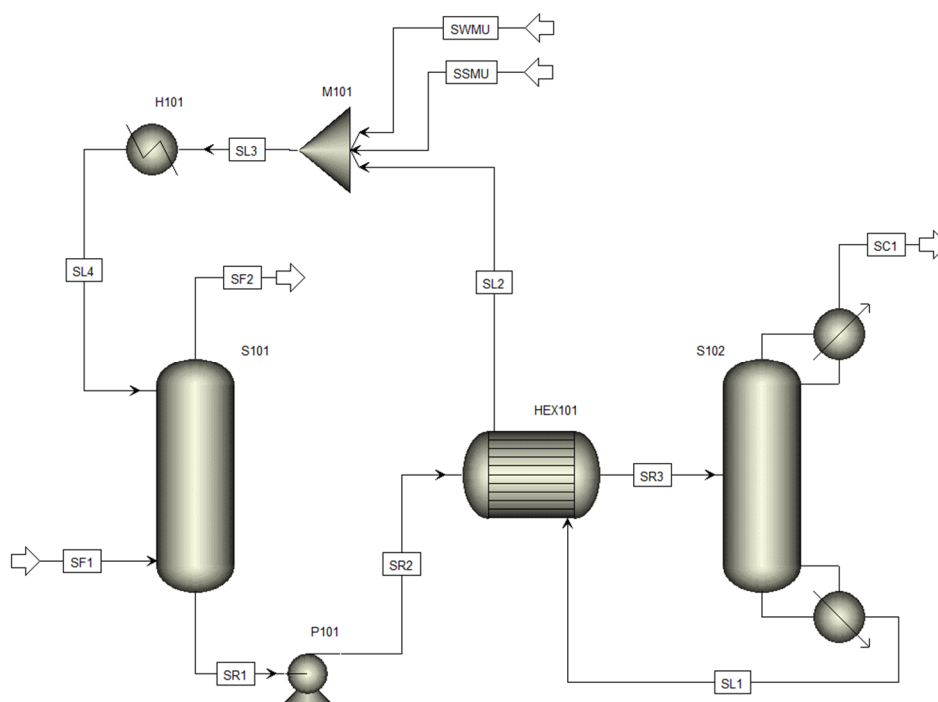


Figure 1: Process flow diagram of the post-combustion capture plant simulation in AspenPlus.

Table 3: Overview of the process parameters used in the simulation.

Absorber		Stripper	
Packing height	12.0 m	Packing height	10.0 m
Packing	Mellapak 250Y	Packing	Mellapak 250Y
Pressure top	1.1 bar	Pressure top	1.8 bar
Sump residence time	180 s	Reboiler residence time	240 s
Temperature liquid inlet	40 °C	Temperature liquid inlet	109 °C
Temperature gas inlet	40 °C	Temperature reboiler	119 °C
Gas velocity	1.7 – 2.1 m/s	Temperature condenser	20 °C
Liquid-to-gas ratio	2.6 [wt/wt]	Reboiler duty	3.5 MJ/kg CO ₂
Gas composition	5% O ₂ , 12% CO ₂ , 6.7% H ₂ O, 76.3% N ₂	<hr/>	
Lean loading	0.19	Heat exchanger	
Rich loading	0.54	Exchanger type	Plate
CO ₂ captured	90.0%	Approach	10 °C
		Duty	3.3 MJ/kg CO ₂

3. Results

3.1. Predicted degradation in base case

The degradation models are evaluated for a period of five weeks to analyze degradation at the start of a campaign.

Table 4 shows the predicted oxidative and thermal degradation in the different parts of the plant. The results show that the contribution of oxidative degradation to the overall degradation is most significant at around 80%. This is in line with other modelling works in literature [1], [23], [24]. Thermal reclaiming is predicted to be most significant in the stripper reboiler, due to the high liquid holdup volume and high temperatures. A reduction of temperature or residence time thus appears to be the most effective method of reducing thermal degradation.

The total estimated loss of solvent due to degradation is around 0.064 kg/ton CO₂. Moser et al. [25] reported a specific solvent consumption of 0.21 kg/ton CO₂ after 55 days in the pilot plant at the Niederaussem coal-fired powerplant. Note that this consumption also includes solvent losses as a result of entrainment, evaporation, and impurities, such as NO_x and SO_x, which are not considered in this work. The model thus appears to give a reasonable prediction of degradation in a plant. The loss of solvent only due to degradation results in a slight decrease in process efficiency, since at the end of the five-week period, 89.1% of the CO₂ is captured, instead of the initial 90.0%. In practice, solvent losses are usually addressed by addition of fresh amine or an adjustment of the water balance.

Table 4: Predicted initial oxidative and thermal degradation in the simulated plant.

Degradation [g/ton CO ₂]	Oxidative	Thermal	Total
Absorber	37.6	–	37.6
<i>packing</i>	28.7	–	28.7
<i>sump</i>	8.9	–	8.9
Stripper	–	13.1	13.1
<i>condenser</i>	–	–	–
<i>packing</i>	–	1.9	1.9
<i>reboiler</i>	–	11.2	11.2
Heat Exchanger	12.3	0.3	12.6
<i>rich side</i>	12.3	0.2	12.4
<i>lean side</i>	–	0.2	0.2
Other equipment	0.6	0.4	1.0
<i>pumps</i>	0.5	–	0.5
<i>pipng</i>	0.1	0.4	0.5
Total	50.6	13.7	64.3

Oxidative degradation occurs mostly in the absorber packing, absorber sump and on the rich side of the heat exchanger. Although the holdup volume in the absorber sump is larger than in the packing, higher temperatures in the packing, due to the exothermal nature of the chemical absorption, result in more degradation at this location. Oxidative degradation in the heat exchanger is a result dissolved O₂.

Figure 2 shows the temperature profile and predicted concentration of dissolved O₂ as the rich solvent is transported from the absorber sump to the heat exchanger. The sump is modelled as a CSTR and is accountable for around 20% of the consumption of dissolved O₂, given a residence time of 180 seconds. O₂ consumption in the pump and piping to the heat exchanger is limited. In the heat exchanger, the temperature increases up to 109 °C and most of the remaining O₂ is consumed. Note that the degradation rates above 75 °C are extrapolated, since they are outside of the range of the experimental dataset used for fitting the model.

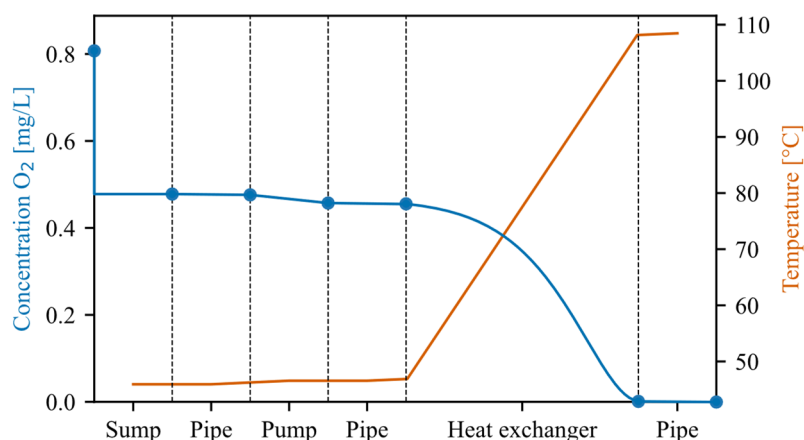


Figure 2: Temperature and predicted concentration of dissolved O₂ in the rich solvent.

3.2. Case study: Oxygen content of the flue gas

The effect of the O₂ content of the flue gas on degradation is investigated using a case study. The volume fractions of O₂ and nitrogen are adjusted, while the concentration of CO₂ is kept constant. The predicted total degradation, and the contribution of both oxidative and thermal degradation, are given in Figure 3. The oxidative degradation rate appears to be proportional to the concentration of O₂ in the flue gas and generally has the largest contribution towards the total degradation. Only at lower O₂ concentrations will thermal degradation become prominent, as it is not affected by the concentration of O₂ in the flue gas. However, post-combustion flue gasses with such low O₂ concentrations are uncommon.

The distribution of oxidative degradation in the different process units is given in Figure 4. The largest part of the oxidative degradation is predicted to occur in the packing of the absorber. The exothermic nature of the absorption reaction causes temperatures up to 73 °C and increased degradation rates, despite the lower solubility of O₂. At lower O₂ concentrations, most of the dissolved O₂ is consumed in the absorber sump and degradation in the heat exchanger is limited. Mitigation strategies that aim to remove dissolved O₂ after the absorber sump will thus be less effective in cases with low O₂ concentrations.

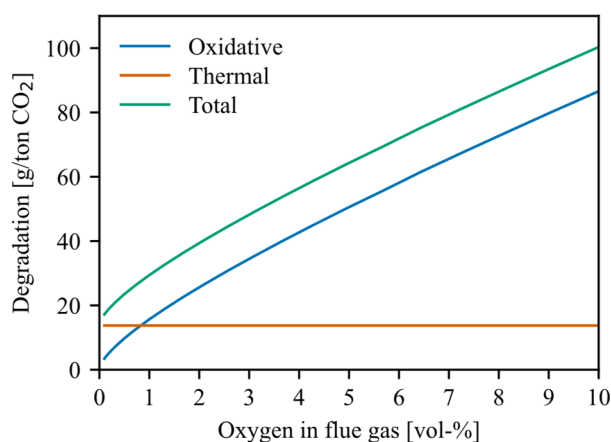


Figure 3: Predicted oxidative, thermal, and total degradation as a function of O₂ concentration in the flue gas.

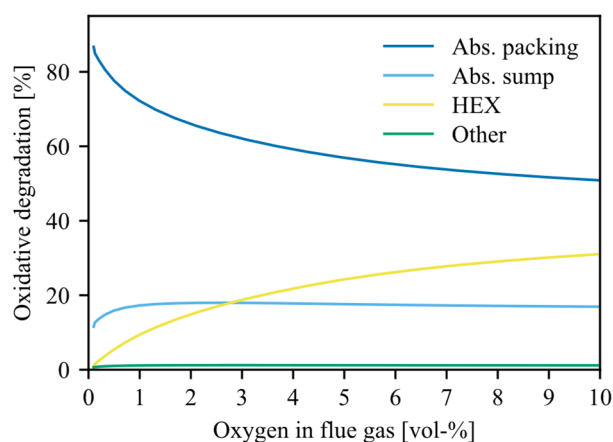


Figure 4: Distribution of oxidative degradation in the process units as a function of O₂ concentration in the flue gas.

3.3. Case study: Absorber intercooling

The effect of absorber intercooling on the degradation rate is also investigated. The base case simulation is modified, and the solvent is intercooled to 40 °C at a packing height of 2 m. Intercooling at this position was found to result in the lowest liquid peak temperature in the absorber. The liquid temperature profiles for the base case and intercooled case are given in Figure 5. The degradation rate profiles for both cases are given in Figure 6. Thermal degradation is negligible compared to oxidative degradation in the absorber. In addition to the intercooled case, degradation in an isothermal absorber at 40 °C is evaluated to investigate the potential of additional intercooling. An overview of the degradation rates for the three cases is given in Table 5.

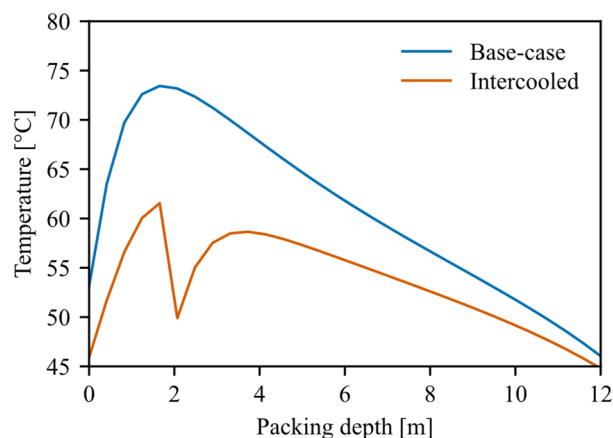


Figure 5: Liquid temperature profile in the absorber for the base case and intercooled case.

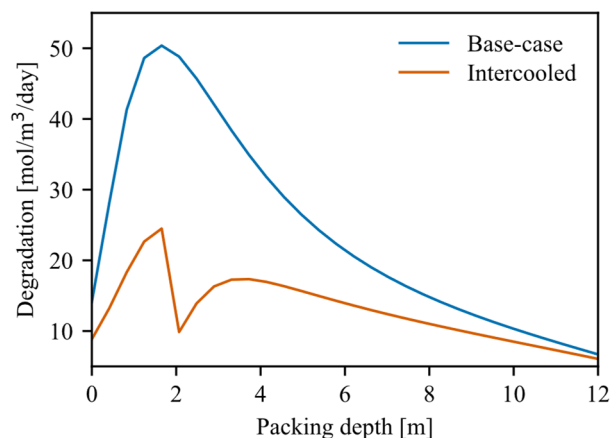


Figure 6: Degradation rate profile of MEA in the absorber for the base case and the intercooled case.

Intercooling reduces degradation in the absorber by 35%, where the degradation in the packing is reduced by 45%. Based on the degradation rate profiles in the absorber shown in Figure 6, however, a larger difference is expected. The results can be explained by the higher liquid viscosities, which are a consequence of the decreased temperatures, resulting in an increase the liquid holdup of the packing and consequently the reaction volume. An interesting side effect of intercooling is the slightly lower temperature in the sump, which favors O₂ solubility. However, the higher concentration of dissolved O₂ in the sump does not increase the degradation significantly in the sump, because the degradation rate is reduced due to the lower temperature in the sump. The additionally dissolved O₂ is consumed in the pump, heat exchanger, and piping as the solvent is transported to the stripper.

Table 5: Predicted degradation for the simulated base, intercooled, and isothermal case.

Degradation [g/ton CO ₂]	Base case	Intercooled	Isothermal (40 °C)
Absorber	37.6	24.3	12.1
Stripper	13.1	13.1	13.1
Heat Exchanger	12.6	13.5	16.3
Other equipment	1.0	0.9	1.3
Total	64.3	51.8 (-19%)	42.8 (-33%)

Overall, the intercooled case shows a reduction of 19% in total degradation. The isothermal case shows that there is a potential to reduce degradation by 68% in the absorber, and by 33% in the entire plant. However, the

implementation of an intercooling system may lead to increased residence times for the liquid, resulting in more degradation. It is thus important to keep this in mind when designing an intercooling system.

4. Conclusions

The current study shows that predicted solvent degradation rates are comparable to those measured at the start of pilot plant campaigns. Oxidative degradation is the predominant degradation mechanism for typical coal fired post-combustion flue gasses. Thermal degradation is dominant only in case of a flue gas with an O₂ content below 0.8 vol-%. Around half of the oxidative degradation takes place when the solvent is in direct contact with the flue gas in the absorber packing, whereas the other half is caused by degradation through dissolved O₂. In the simulated plant, 40% of the O₂ that is dissolved at the bottom of the absorber packing is already consumed in the sump.

Despite a low solvent holdup in the absorber packing, the elevated temperatures due to absorption of CO₂ cause oxidative degradation to be significant. It should be experimentally validated that mass transfer limitations are not significant for a structured packing at these conditions. Intercooling is found to reduce oxidative degradation in the absorber, but the effects of a longer residence time in the absorber due to implementation of intercooling should be investigated.

Future work should look into predicted degradation in capture plants which treat other flue gasses, such as those from a natural gas fired power plant or cement plant. The framework can be extended by including degradation models for other solvents and/or solvent blends. Furthermore, models can be developed and/or implemented to evaluate solvent and degradation product emissions as a result of evaporation and entrainment in aerosols. With respect to MEA, the degradation models can be extended by taking into account interactions between oxidative and thermal degradation mechanisms, the formation of degradation products, corrosion and concentration of dissolved iron and other metals and their catalytic effects on the degradation rates.

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