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Monoethanolamine Degradation Rates in Post-combustion CO_2 Capture Plants with the Capture of 100% of the Added CO_2

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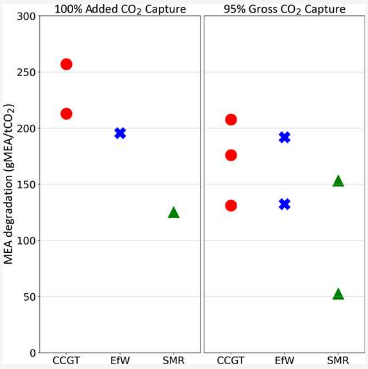

ABSTRACT: Residual emissions from post-combustion CO_2 capture plants must be reduced to zero or recaptured from the atmosphere to be compatible with long-term climate change goals. For amine-based CO_2 capture, increasing CO_2 capture fractions requires maintaining sufficient driving force of absorption at the top of the absorber column by reducing lean solvent loadings. To produce low lean loadings without excessively increasing the specific thermal energy input, increased operational pressures are required in the CO_2 stripper, inevitably leading to higher temperatures, which may increase the specific thermal degradation rate of the solvent. Concurrently, for solvents that react rapidly with dissolved O_2, increased residence time in the absorber due to the increased packing heights also associated with high capture fractions may increase the specific oxidative degradation rate as the direct contact with O_2 in the flue gas is extended. Through process modeling and the application of a newly developed monoethanolamine (MEA) degradation framework, we investigate the effect on solvent degradation rates of increasing CO_2 capture rates up to those that result in no net CO_2 addition to the atmosphere. We do this for three key energy-producing processes: a combined cycle gas turbine, an energy from waste facility, and a steam methane reformer. In a first-of-a-kind study, we demonstrate that for a 35 wt % MEA-based solvent under steady-state conditions, solvent degradation is predicted to increase by 24−138% as a result of decreasing lean loadings and increased absorber residence time (process modifications that are thought to be beneficial when increasing CO_2 capture fractions) from 53 to 208 gMEA/tCO_2 when a 95% CO_2 gross capture fraction is achieved to 125−257 gMEA/tCO_2 when 99.2−99.8% is achieved (i.e., when 100% of the added CO_2 is captured). Further analysis provides evidence that process modifications, such as intercooling of the absorber column and reduced stripper sump residence times, may be useful in reducing the rates of solvent degradation, providing critical insights to future test campaigns and project developments. However, limitations of this study remain; the degradation framework provides the instantaneous predicted MEA consumption rate of the system at a point in time and does not consider the catalytic effects that many impurities present in an operation plant will have on the reactions, potentially impacting degradation rates. Nonetheless, this serves as the first step toward understanding the effect of increasing CO_2 capture fractions in post-combustion CO_2 capture plants. Long-term tests with appropriate solvent management practices are required to fully quantify solvent degradation rates when operating at 100% added CO_2 capture fractions.

1. INTRODUCTION

Global anthropogenic CO_2 equivalent (CO_2e) emissions continue to rise year on year, resulting in a predicted global surface temperature rise of 3.2 °C (2.2−3.5 °C) by 2100 if all implemented climate policy targets are reached,[1] the Sixth Assessment Report by the International Panel on Climate Change (IPCC) states that "All global modeled pathways that limit warming to 1.5°C (>50%) with no or limited overshoot, and those that limit warming to 2°C (>67%), involve rapid and deep and, in most cases, immediate greenhouse gas emissions reductions in all sectors this decade". Within the global emissions scenarios considered within the sixth assessment report, those that have a greater than 67% chance of limiting global temperature rise to less than 2 °C include between 196−280 Gt of sequestered CO_2 from fossil CO_2 alone by 2100,[2] not including atmospheric CO_2 removal via bioenergy with CCS (BECCS) or direct air CO_2 capture and storage (DACCS). The International Energy Agency's (IEA) Sustainable Development Scenario, in which global emissions from the energy sector reach net zero by 2070, includes 240 Gt CO_2 sequestered by 2070, accounting for 15% of emission reductions.[3] As of 2023, around 40 carbon capture and storage (CCS) facilities are in operation globally, capturing approximately 0.045 GtCO_2/pa, with an additional 50 planned to come online by 2030, capturing an additional 0.125 GtCO_2/pa.[4] Although ambitious, this is an order of magnitude short of the approximate 1.2 GtCO_2/pa capacity needed in the Sustainable Development Scenario, highlighting the wide gap

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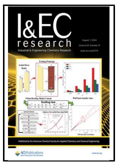

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between aspirations and actions. It is clear that if CCS is to contribute significantly to global climate change mitigation efforts, a rapid increase in the deployment of CCS facilities is required.

Post-combustion capture (PCC) encompasses any technology that separates CO_2 from a gas mixture downstream of an industrial process. Typically, this is a high-volume flow rate of combustion products and possibly additional CO_2 released from process materials, e.g. limestone, at atmospheric pressure, containing mainly nitrogen, water, and oxygen, with varying quantities of CO_2 (2−25 vol %). Depending on the process, the flue gas to be treated may contain trace impurities to varying degrees, including CO, NO_x, SO_x, volatile organic compounds (VOCs) and ammonia (NH_3), to name a few. Potential applications for PCC deployment cover all facets of the industrial decarbonization landscape, from the energy sector by decarbonizing critical dispatchable power infrastructure such as combined cycle gas turbines (CCGT) and coal-fired power plants and decarbonizing home heating and transport with blue hydrogen production to raw material production such as cement, glass and metal. Additional cross-industry applications lie in waste and biogenic fuel combustion, contributing to energy production, waste management, raw material recovery and negative emissions. Numerous technologies are under consideration for large-scale post-combustion capture, including solid adsorption, CO_2 selective membranes, and cryogenic separation; however, the most technologically and commercially mature and the focus of this article is amine-based CO_2 capture.

Amine-based post-combustion CO_2 capture functions on the principle that amine groups will bond with acid gases, such as CO_2, to form a carbamate or bicarbamate compound in a temperature-reversible reaction and, as such, can be used to separate acid gases from a dilute gas stream in a two-step absorption and desorption thermal swing process. Absorption typically occurs in a packed bed absorber column at close to atmospheric conditions. Within this column, the flue gas contacts in a counter-current fashion with descending CO_2 lean liquid solvent, transferring CO_2 in the gas phase to the amine solution as it travels up through the column. For a given liquid-to-gas ratio, the residence time of the liquid solvent in the packed bed absorber column, and so also the duration of exposure of the liquid solvent to the gases, in particular CO_2, O_2, NO_x and combustion impurities, contained in the flue gas, is proportional to the packing height.

CO_2 lean flue gas leaves the top of the absorber column after emission control techniques to minimize unwanted carryover of amine and amine-derived products, while CO_2-rich liquid solvent leaves the bottom of the column for regeneration. Regeneration occurs in a separate pressurized stripper packed bed column; CO_2-rich solvent descends through the stripper and condenses steam, which has been generated at the bottom of the column. As the steam condenses, it heats the rich solvent and reverses the carbamate/bicarbamate forming reaction, liberating CO_2. Mostly, CO_2 lean solvent exits the stripper packing and passes through a reboiler, where a thermal energy source heats the solvent, further liberating CO_2 and generating the stripping steam. The highest temperature in the post-combustion capture process occurs in the reboiler. CO_2/H_2O vapor leaves the top of the stripper column for drying, conditioning and compression for export while the now CO_2 lean solvent is returned to the absorber. At all stages the steam also provides a stripping function, by reducing the partial pressure of the CO_2; the ratio of CO_2 to H_2O vapor at equilibrium with the solvent depends on total pressure, solvent loading and temperature.

Amine CO_2 capture solvents are ammonia (NH_3) derivatives where a substituent, such as an alkyl or aryl group, has replaced one or more hydrogen atoms. They can be broadly characterized into primary (with monoethanolamine (MEA) being the most widely known example for CCS applications), secondary and tertiary amines, representing how many hydrogen atoms have been substituted for alkyl or aryl groups. Due to its reactivity, low cost and ease of reclamation, MEA continues to serve as a viable solution for CO_2 capture from low-concentration CO_2 flue gases. Stainless steel construction or corrosion inhibitors for carbon steel constructions can mitigate the corrosion concerns present for higher concentration solutions, while advanced configurations and control processes continually improve thermodynamic efficiency, particularly at high CO_2 capture fractions.

Historically, CO_2 capture fractions, defined as the mass of CO_2 exported divided by the mass of CO_2 entering the absorber, of 90% were targeted. However, in recent years, net-zero commitments have challenged this assumption's viability, as 10% residual emissions from PCC is clearly incompatible with these goals unless some form of permanent negative CO_2 emission technology is concurrently employed to recapture the residual emissions. The economically optimal CO_2 capture fraction will be the point at which the marginal cost of increasing the CO_2 capture fraction is more than the lowest cost permanent negative CO_2 emission technology that is available to recapture and permanently store the emitted CO_2 (a point that will change as both technologies are deployed at scale). In the absence of a definitive economic optimum, the CO_2 capture fraction that results in no net addition of CO_2 to the atmosphere is considered for this work. This CO_2 capture fraction is dependent on the ratio of atmospheric CO_2 entering the boundary of the facility with atmospheric air (typically used for combustion) and the added CO_2 generated by that combustion or other processes within the facility, and, as such, varies from application to application (see eq 1). However, it typically falls between 99.2% for a CCGT up to 99.8% for a steam methane reformer (SMR). Mullen et al.[5,6] term this CO_2 capture fraction as 100% fossil CO_2 capture; however, 100% added CO_2 will be used in this article to account for biogenic CO_2. This terminology will be adopted throughout this article, while capture fractions below this will be reported as gross CO_2 capture fractions, as is typical for the industry.

$$\text{Fossil CO}_2\text{ capture fraction} = \frac{m_{\mathrm{CO_2,T\&S}}}{m_{\mathrm{CO_2,produced}} - m_{\mathrm{CO_2,atmospheric}}}(\%) \tag{1}$$

where $m_{\mathrm{CO_2,T\&S}}$ is the mass of CO_2 exported to transport and storage, $m_{\mathrm{CO_2,produced}}$ is the mass of CO_2 produced during the process, and $m_{\mathrm{CO_2,atmospheric}}$ is the mass of atmospheric CO_2 entering the process.

Increasingly, CO_2 capture fractions above 95% up to, or slightly above, 100% added CO_2 capture is the focus of emerging research. Mullen and Lucquiaud[5] provide a detailed analysis of the currently available literature, critically assessing seven modeling studies[6−12] and six pilot plant facilities[13−18] where CO_2 capture fractions over 95% were achieved. The authors identify lean loading as the critical factor to ensure thermodynamically efficient operation at increased CO_2

capture fractions. Lean loading must be sufficiently low to provide a strong driving force of absorption at the top of the absorber despite decreased CO_2 concentrations, a consideration typically absent or insufficiently considered in the current literature. As well as increasing the absorption rate throughout the absorber, low lean loadings facilitate increased cyclic capacity of the solvent (CO_2 absorbed per unit of solvent), minimizing the quantity of water to be moved through the system and maximizing rich loading. These factors will contribute to a decreased energy requirement for solvent regeneration. Where the importance of low lean loadings was recognized, solvent regeneration to the loadings required is typically mismanaged. Michailos and Gibbins[12] describe what has been termed the stripper "inflection point". They present a modeling study using a 35 wt %. MEA solution on a flue gas representative of a commercial CCGT and study 95 and 99% gross CO_2 capture fractions over a range of lean loadings and absorber packing heights. They show that as lean loadings decrease under constant stripper pressure and incoming rich loading conditions, the energy requirement for regeneration per unit of CO_2 captured, known as the specific reboiler duty (SRD), increases exponentially below a low loading value that depend on the specific conditions. This phenomena has historically led to the conclusion reducing lean loadings and, by extension, increasing CO_2 capture fractions will result in exponential increases in SRDs.

However, Michailos and Gibbins showed that the inflection point can be shifted to lower lean loadings by increasing the stripper pressure, noting, though, that reboiler temperatures will increase proportionately as a result. This change in inflection point loading arises because the rapid increase in SRD corresponds to the point where the water vapor to CO_2 ratio in the reboiler rises to a level at which it cannot be condensed to near-equilibrium partial pressure and temperature with the incoming rich solvent at the top of the stripper column. This leads to increasing levels of water vapor in the CO_2 at the top of the column, representing a significant heat loss. An increase in stripper pressure shifts the vapor liquid equilibrium (VLE) in the reboiler toward lower water vapor/CO_2 ratios for a given lean loading, at the expense of higher reboiler temperatures.

Mullen et al.[5,6] build upon the work of Michailos and Gibbins by completing an in-depth techno-economic assessment on 100% added CO_2 capture for both an SMR and a CCGT using a 35 wt %. MEA solution. They find that, although the thermal efficiency of the process decreases and the cost of the product increases relative to achieving 95% CO_2 capture fractions, the effect is modest and is primarily due to the increase in the absolute quantity of CO_2 captured rather than any nonlinearity in the specific cost to capture CO_2 as the CO_2 capture fraction increases.

The authors further conclude that, for the assumed conditions of this study, unless the cost of negative emission technologies with permanent CO_2 storage falls below 184 £/tCO_2, increasing CO_2 capture fractions to 100% of the added CO_2 is the most economical method of fully decarbonizing a CCGT. Mullen et al. also show that the CO_2 intensity of the counterfactual to hydrogen combustion, i.e. natural gas combustion, means that the cost of CO_2 avoided falls as the CO_2 capture fraction increases for the SMR process considered, despite the increase in product cost. Mullen et al. suggest two design changes to achieve 100% added CO_2 capture: increased reboiler operating pressures and, by extension, temperatures, which facilitate efficient solvent regeneration for low lean loadings, and, in the CCGT case, a moderately increased absorber packing height, from 20 to 24 m, to increase the mass transfer area. Although moderate from a process and technological perspective, these two design changes will expose the solvent to previously largely unexplored process conditions, with higher regeneration temperatures, lower lean loadings and increased duration of exposure to the oxygen content of the flue gas. Each of these process modifications may lead to an increase in specific solvent degradation rates. Mullen et al. note that this is a knowledge gap and assumes an MEA replacement rate of 2 kg/tCO_2, quoting experience from MEA-based pilot plant studies, which report a range of 0.17−1.5 kg/tCO_2.[14,19−23] This article uses emerging models[24,25] developed by Braakhuis and Knuutila, two coauthors, to shed light on the effect on MEA degradation rates of the process conditions thought to be thermodynamically beneficial when operating at 100% added CO_2 capture.

MEA will degrade when exposed to oxygen-rich atmospheres (oxidative degradation)[26] or high temperatures (thermal degradation).[27] Unless effectively controlled, solvent degradation products in the circulating solvent can reduce CO_2 capture performance, increase atmospheric emissions and operational costs and accelerate equipment corrosion.[28] Degradation causes a loss of solvent directly while further solvent losses may occur as part of solvent reclaiming, which is required for sustained operation to remove all degradation products at the rate they are formed and maintain constant solvent health.

One of the main degradation mechanisms for MEA is carbamate polymerization, often referred to as thermal degradation. This mostly occurs at elevated temperatures within the CO_2 capture process, most notably within the stripper sump and reboiler, where temperatures often exceed 120 °C for extended periods. It also occurs when the solvent is descending through the stripper packing and during preheating of the solvent, albeit for relatively short periods and at lower temperatures than the reboiler. When the carbamate, formed when CO_2 reacts with MEA, is subjected to increased temperatures ring closure and dehydration occur to form 2-oxazolidinone (OZD). OZD is sensitive to nucleophilic attacks and reacts with MEA, forming dimers, oligomers, imidazolidinones, and other cyclic compounds. The cyclization of the carbamate leading to the formation of OZD is the rate-limiting reaction. This rate was found to be dependent on both temperature and CO_2 loading. Higher CO_2 loadings have been shown to increase degradation rates, possibly by forming more of the carbamate or increasing the availability of proton donors, which can catalyze dehydration. A detailed review of thermal degradation methods is available in Braakhuis et al.[24]

Oxidative degradation of an amine is a two-step process involving the dissolution of O_2 from the flue gas into the solvent, followed by a liquid phase reaction between the dissolved O_2 and the amine. The observed amine degradation rate is thus a function of O_2 solubility, mass transfer resistances, and kinetic reaction parameters. Process parameters, such as temperature, O_2 partial pressure, amine concentration, and CO_2 loading, influence each of these mechanisms. A detailed review of oxidative degradation methods is available in Braakhuis and Knuutila.[25] Braakhuis et al. define two categories of oxidative degradation: direct and indirect. Direct oxidative degradation occurs within the absorber where the solvent is in direct contact with the flue

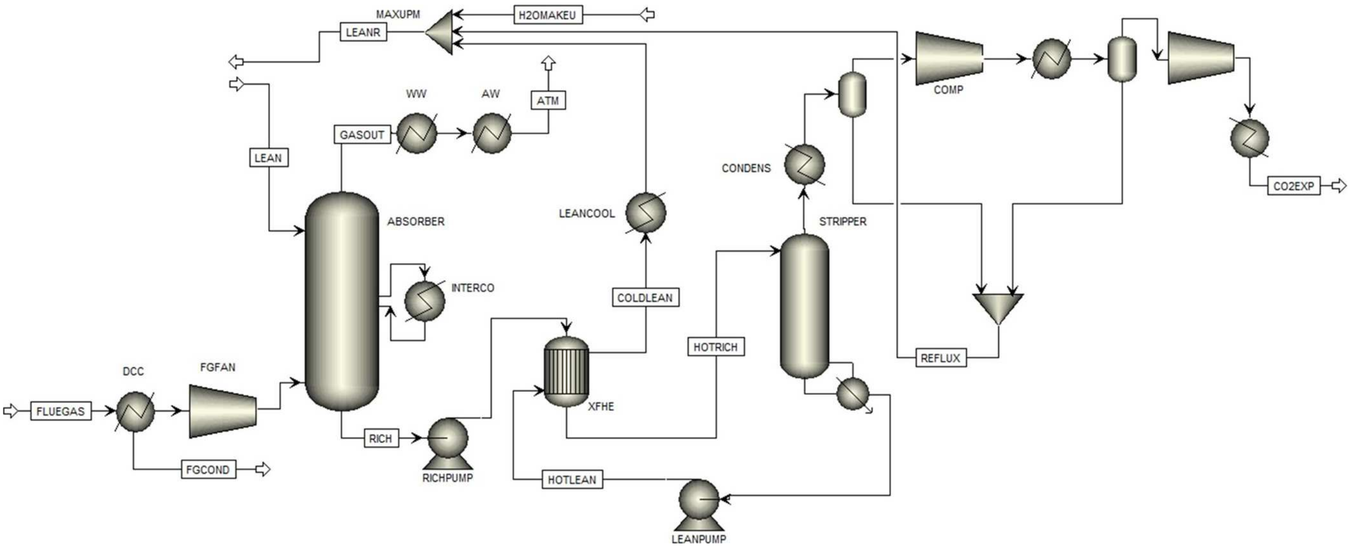

Figure 1. ASPEN PLUS process model.

gas, and the quantity of dissolved oxygen is replaced while consumed. The magnitude of this effect is a function of the rate of mass transfer of O_2 from the gas phase to the liquid phase and is expected to vary depending on the location within the absorber as the bulk temperature and the solvent loading change. Indirect degradation happens downstream of the absorber, where no further contact with an oxygen-rich flue gas occurs; in this case, the degree of oxidative degradation is limited to the quantity of dissolved oxygen in the solvent when no longer in contact with the flue gas. This can be mitigated with process modifications that reduce the quantity of dissolved O_2 that is carried over to the absorber sump, for example, flashing or N_2 sparging of rich solvent.

The process considerations proposed by Mullen et al. for 100% added CO_2 capture might be expected to adversely affect the degree of MEA degradation within post-combustion CO_2 capture plants. Higher reboiler temperatures will obviously increase the degree of thermal degradation, all other things being equal. However, the associated reduced loading (i.e., carbamate concentration) in the reboiler may somewhat mitigate this. Concurrently, a reduced average loading in the absorber may increase the solubility of O_2 overall and lead to increased oxidative degradation. Additional packing, the inclusion or absence of intercooling, and liquid-to-gas ratios will also all contribute to the uncertainty surrounding MEA degradation rates at 100% added CO_2 capture fractions.

This work applies the oxidative (Braakhuis and Knuutila[25]) and thermal degradation (Braakhuis et al.[24]) models for an MEA solvent with process modeling completed by Mullen et al.[5,6] to compare the specific quantity of MEA degradation for three industrial flue gas sources (CCGT, EfW and SMR processes) at two distinct CO_2 capture fractions (95% gross CO_2 capture and 100% added CO_2 capture), with the inclusion or not of intercooling serving as a third variable. For the first time, we quantify the expected additional solvent degradation rate when operating at a 100% added CO_2 capture fraction, facilitating an assessment of the resulting impact on process economics. It is important to note that the operational conditions proposed for 100% added CO_2 capture operation would also provide a reduced energy penalty for lower CO_2 capture fraction operation should the resulting solvent degradation rates be deemed economically acceptable. Likewise, if solvent degradation is more critical to a project than thermal efficiency, lean loadings sufficient to achieve high CO_2 capture fractions can be achieved at lower temperature regeneration conditions. Advance process configurations such as "pump-around" intercooling in the absorber, as opposed to the "in-and-out" scheme used in this study, may aid in increasing CO_2 capture rates while using higher lean loading than those considered in this study. This has been proposed in a modeling study by Gao,[29] where 99% CO_2 capture was achieved using a 30 wt % MEA solution at a lean loading of 0.2 mol/mol and two pump-around intercooling loops.

The goal of the inclusion of intercooling in this study was to investigate the effect of reduced absorber temperatures on oxidative degradation, which can be achieved with in-and-out intercooling. Therefore, this configuration has not been included in this work to limit the number of cases presented; however, it would be expected to result in a reduction in thermal degradation proportionate to the reduction in regeneration temperatures. This should be considered in conjunction with any change in CAPEX or SRD due to increased absorber heights, additional intercooling loops or changes in solvent properties.

This work aims to compare the solvent degradation rates at proposed design points for the considered CO_2 capture fractions that the authors consider to be valid and viable, acknowledging that such design points are project-specific and do not represent an absolute economic optimum, as no such point can exist except for specific project conditions.

1.1. Limitations of the Study.

This study serves as a first step toward quantifying the effect of achieving 100% added CO_2 capture in post-combustion CO_2 capture plants using an MEA solvent solution. However, limitations of this study remain; the degradation framework provides only the instantaneous predicted MEA consumption rate of the system at a point in time. As such, it does not consider the effect of cumulative production of degradation compounds within the solvent as the operation continues over an extended period and their concentrations balance with removals by reclaiming; degradation compounds within the solvent may catalyze MEA degradation and thus accelerate the reaction. Additionally, although thermal and oxidative degradation mechanisms are considered in the framework, they are considered independent,

Table 1. CO_2 Capture Case

process	CO_2[a] (vol %)	O_2[a] (vol %)	flow[a] rate (kg/s)	case	lean loading (mol/mol)	CO_2 capture (%[b])	intercooler (#)	absorber packing (m)	stripper packing (m)	stripper pressure (KPa)
CCGT	4.7	11.0	792	0.1 CCGT	0.1	99.2	0	24	20	275
				0.1 CCGT IC	0.1	99.2	1	24	20	275
				0.2 CCGT	0.2	95	0	20	20	149
				0.2 CCGT IC	0.2	95	1	20	20	149
				0.1 CCGT 95	0.1	95	0	24	20	275
EfW	11.1	6.7	31	0.1 EfW IC	0.1	99.7	1	20	20	275
				0.2 EfW	0.2	95	0	20	20	149
				0.2 EfW IC	0.2	95	1	20	20	149
SMR	19.5	1.2	275	0.1 SMR IC	0.1	99.8	2	20	20	275
				0.2 SMR	0.2	95	0	20	20	149
				0.2 SMR IC	0.2	95	2	20	20	149

[a]Saturated at 40 °C. [b]Gross CO_2 capture fraction.

and no interactions between the respective degradation compounds are accounted for. Finally, this study does not consider the catalytic effect of corrosion compounds on solvent degradation due to the complexity of the reaction mechanisms and the limited experimental data; these will also rise until balanced by removals in reclaiming. Considering the limitations highlighted above, the results presented in this article should be considered predictive only for a perfectly clean solvent. Over an extended period of operation, actual MEA degradation rates are expected to diverge from those predicted by the framework, likely trending toward increasing degradation, unless contaminants within the solvent are maintained at a very low level through a high rate of solvent reclaiming.

Additionally, the cases presented here are not intended to represent an optimum for CO_2 capture fraction, thermodynamic performance or solvent degradation but merely to demonstrate the effect process parameters can have on each of the above. Case-by-case optimization will be required on a project basis. However, the results presented in this work can serve to advise designers on methods of reducing or controlling solvent degradation rates.

2. METHODOLOGY

2.1. Process Modeling for CO_2 Capture. The process modeling of the CO_2 capture plant (Figure 1) is conducted using an open-source MEA model funded by the US Department of Energy and developed by the Carbon Capture Simulation for Industry Impact (CCSI) in ASPEN PLUS.[30] This model is validated against pilot-scale data from the US National Carbon Capture Centre (NCCC).[31] The reader is referred to Mullen et al.[5,6] for a detailed description of the process modeling. However, the process does not notably differ from that of a traditional amine CO_2 capture plant.

Three distinct CO_2 capture applications covering a range of CO_2 flue gas concentrations have been considered for this work. A GE H-Class 1 × 1 combined cycle gas turbine (GE 9HA.01) with a rated thermal efficiency of 63.5% (LHV) serving a CCGT application, A 500 t/day of municipal solid waste (MSW) moving grate plant serving as the energy from waste (EfW) application and a 1000 MWh_{th} (HHV) steam methane reformer (SMR) for hydrogen production as the final case. Two CO_2 capture fractions were considered for each case, 95% (gross) and 100% (added), and two lean loadings of 0.1 and 0.2 mol/mol, while the inclusion or not of intercooling served as an additional variable. An additional CCGT case was considered where 95% CO_2 capture was achieved at low lean loading and increased absorber packing to illustrate the energy-saving potential of these design modifications irrespective of CO_2 capture fractions. This leads to a total of 11 cases assessed in this work (see Table 1). A 35 wt %. MEA solution was used in all cases. Flue gas compositions and flow rates were extracted from previously completed works by Mullen et al.[5,6] and Su et al.[11]

For each of the cases described in Table 1, the stripper pressure is modified to ensure that the inflection point described in Michailos and Gibbins[12] is not passed. This leads to variable stripper operational pressures and, by extension, solvent regeneration temperature. Stripper packing was maintained at 20 m for all cases as per Eliot,[34] however reduced packing beds, if thermodynamically acceptable, would reduce residence times and therefore thermal degradation. This is a project by project consideration.

Plated heat exchangers were assumed for all heat exchangers within the system, with holdup volume and residence time calculated using eq 2.

$$\text{Residence Time} = \frac{\text{Holdup Volume}}{\dot{V}} = \frac{Q \times \text{Surface compactness} \times \dot{V}}{k \times \text{LMTD}} \tag{2}$$

where $\dot{V}$ is the lean solvent volumetric flow rate, LMTD is the log mean temperature difference, and k is the thermal conductivity. Surface compactness is assumed to be 150 m^2/m^3 as per Zohuri,[32] while thermal conductivity values of 3894 w/m^2 K for the reboiler and 1932 w/m^2 K for the cross heat exchanger were taken from Woods.[33] The LMTD was maintained at 6 °C for the reboiler and a minimum approach temperature of 5 °C was applied for the cross HX, leading to an LMTD of ca. 7−8.5 °C in all cases. Should high residence times in these pieces of equipment be found to increase

Table 2. Reactions and Kinetic Parameters for the Thermal Degradation Model as per Braakhuiset and Knuutila[25][a]

	reaction	reaction rate [$mol{\cdot}m^{-3}{\cdot}s^{-1}$]	k_{ref} [$m^3{\cdot}mol^{-1}{\cdot}s^{-1}$]	activation energy [J/mol]
1	$MEA \rightarrow HEEDA + H_2O$	$R_1 = k_{r,1}[MEA][CO_2]$	1.599×10^{-11}	1.511×10^5
2	$MEA + HEEDA \rightarrow TRIMEA$	$R_2 = k_{r,2}[HEEDA][CO_2]$	1.117×10^{-10}	1.215×10^5
3	$HEEDA + CO_2 \rightarrow HEIA$	$R_3 = k_{r,3}[HEEDA][CO_2]$	3.054×10^{-10}	1.426×10^5
4	$TRIMEA + CO_2 \rightarrow AEHEIA$	$R_4 = k_{r,4}[TRIMEA][CO_2]$	2.839×10^{-10}	1.362×10^5
5	$2\ MEA \rightarrow BHEU + H_2O$	$R_4 = k_{r,5}[MEA][CO_2]$	5.170×10^{-13}	1.511×10^5[b]

[a] Reference temperature ((T_{ref}) is 400 K). [b] Could not be determined in the original work and was assumed to be equivalent to reaction no. 1.

Table 3. Degradation Reactions, Reaction Rate Equations, and Parameters for the Oxidative Degradation Model[24][a]

	reaction	reaction rate [$mol{\cdot}m^{-3}{\cdot}s^{-1}$]	k_{ref} [$m^3{\cdot}mol^{-1}{\cdot}s^{-1}$]	activation energy [J/mol]
5	$MEA + 1.3O_2 \rightarrow 0.1\ HSS$	$R = k[MEA][O_2]^{0.469}$	6.790×10^{-7}	7.908×10^4

[a] Reference temperature for the oxidative rate coefficients is 338.15 K.

degradation excessively, this can be mitigated by increasing the LMTD at the cost of increased irreversibility in the system, however this may result in adverse effects due to higher metal skin temperatures as only bulk liquid temperatures were considered in this analysis.

Absorber and stripper sump levels were taken at 1.1 and 5 m, respectively, as per Elliot.[34] This maintains the hydraulic head to critical components similar to that of published FEED studies. This contributes to the varying residence times between cases. Should extended residence times in absorber and stripper sumps be required for operational reasons, an increase in sump level may be required. A flooding limit of 80% of the flooding value was imposed on all columns, leading to varying column diameters (see Mullen et al.[5,6] and Su et al.[11] for design parameters), and the total solvent inventory was assumed to be 150% of the summation of all equipment volumes and packing holdup. A complete list of model assumptions and equipment residence times is available in Table S1 of the Supporting Information.

2.2. Degradation Model. The kinetic degradation models for MEA used in this work have been adapted from previously developed oxidative and thermal degradation models described in Braakhuis and Knuutila[25] and Braakhuis et al.[24] The kinetic rate constants in both models are defined using the adjusted form of the Arrhenius equation shown in eq 3. The equations use a reference temperature and reaction rate coefficient at this temperature, simplifying the parameter fitting and optimization.

$$k = k_{ref} \cdot \exp\left[-\frac{E_A}{R_{id}}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{3}$$

2.2.1. Thermal Degradation. The thermal degradation model for MEA describes the consumption of the solvent and the formation of intermediates and degradation products. The model is developed for 30 wt % MEA and is valid at loadings between 0.1−0.5 mol CO_2/mol MEA and temperatures up to 160 °C. This model has been extrapolated to apply to a 35 wt % solution, as similar degradation rates are expected, as reported by Høisæter et al.[35] Although no experimental data was available below 100 °C, the predicted reaction rates are insignificant at these temperatures, and the model can be extrapolated.[24] The modeled degradation reactions, reaction rate equations, and fitted parameters are given in Table 2. Braakhuis et al. note that the direct measurement of intermediate reactant in the polymerization of carbamate, 2-oxazolidinone (OZD), is challenging, with limited reliable data available. However, at loadings below 0.5 mol/mol, as is the case for the processes considered in this study, Braakhuis et al. assumed that the vast majority of CO_2 in the solution is present in the form of carbamate, and as such, the free concentration of CO_2 in the solvent could then be used as a surrogate for the concentration of OZD.

There was insufficient experimental data to effectively assess the formation of 1,3-bis(2-hydroxyethyl)urea (BHEU) at various temperatures, and it was impossible to determine this reaction's activation energy accurately. The reaction mechanisms for forming BHEU are expected to resemble those of HEEDA (reaction no. 1) closely. Therefore, Braakhuis et al. consider it reasonable to assume that the activation energies for both reactions are similar. As such, the same activation energy is applied to model the formation of BHEU.

2.2.2. Oxidative Degradation. The kinetic model for oxidative degradation of MEA has been adapted from the work by Braakhuis and Knuutila.[25] The model is developed using experimental data produced by Vevelstad et al.,[36] who used an agitated bubble reactor at temperatures between 55 and 75 °C and gas phase oxygen concentrations between 6 and 98 vol %. Liquid phase mass transfer resistances for O_2 were expected to be present in the agitated bubble reactor, especially at higher temperatures. This would reduce the availability of dissolved O_2 and limit the overall degradation rate. Therefore, mass transfer resistances have been approximated and accounted for during the development of the degradation mode.[25]

The oxygen solubility model by Buvik et al.[37] is used in this work. This novel solubility model considers the effects of temperature and concentration of ionic species in the solvent and thus accounts for reduced solubilities in CO_2-loaded solvents. Dissolved metals, such as iron and copper, have been shown to catalyze the degradation reaction significantly.[38,39] However, dissolved metals were not present during the degradation experiments used in the model development.[35] Therefore, the degradation model does not consider the catalytic effect of dissolved metals. Additionally, the experimental data set[36] utilized by Braakhuis and Knuutila is limited to experiments completed at 55−75 °C with the model extrapolated to lower temperatures, therefore increased uncertainty at lower temperatures can be expected.

The reaction rate and rate coefficients for the oxidative degradation model for MEA are shown in Table 3. The oxygen stoichiometry in the overall oxidative degradation reaction is estimated to be around 1.30 to 1.44 mol O_2/mol MEA.[40] The degradation model assumes a stoichiometry of 1.30, which

Table 4. Process Modeling Results for the EfW and SMR Cases, 100% Added CO_2 Capture Is Unachievable without Intercooling

process	CO_2[a] (vol %)	O_2[a] (vol %)	case	lean loading (mol/mol)	CO_2 capture (%[b])	intercooler (#)	L/G (kg/kg)	SRD (GJ/tCO_2)	rich loading (mol/mol)	cycle (min)	reboiler temperature (°C)
CCGT	4.7	11.0	0.1 CCGT	0.1	99.2	0	0.89	3.67	0.441	36.7	135.6
			0.1 CCGT IC	0.1	99.2	1	0.90	3.74	0.436	36.4	135.2
			0.2 CCGT	0.2	95	0	1.24	4.04	0.440	31.1	114.9
			0.2 CCGT IC	0.2	95	1	1.25	4.09	0.438	31.0	114.7
			0.1 CCGT 95	0.1	95	0	0.78	3.42	0.473	40.0	135.7
EfW	11.1	6.7	0.1 EfW IC	0.1	99.7	1	1.72	3.63	0.451	30.8	135.5
			0.2 EfW	0.2	95	0	2.49	3.65	0.471	27.0	114.8
			0.2 EfW IC	0.2	95	1	2.49	3.67	0.471	26.1	114.6
SMR	19.5	1.2	0.1 SMR IC	0.1	99.8	2	3.31	3.64	0.454	27.6	135.2
			0.2 SMR	0.2	95	0	4.16	3.61	0.475	24.7	114.9
			0.2 SMR IC	0.2	95	2	4.44	3.85	0.457	25.6	114.7

[a] Saturated at 40 °C. [b] Gross CO_2 capture fraction.

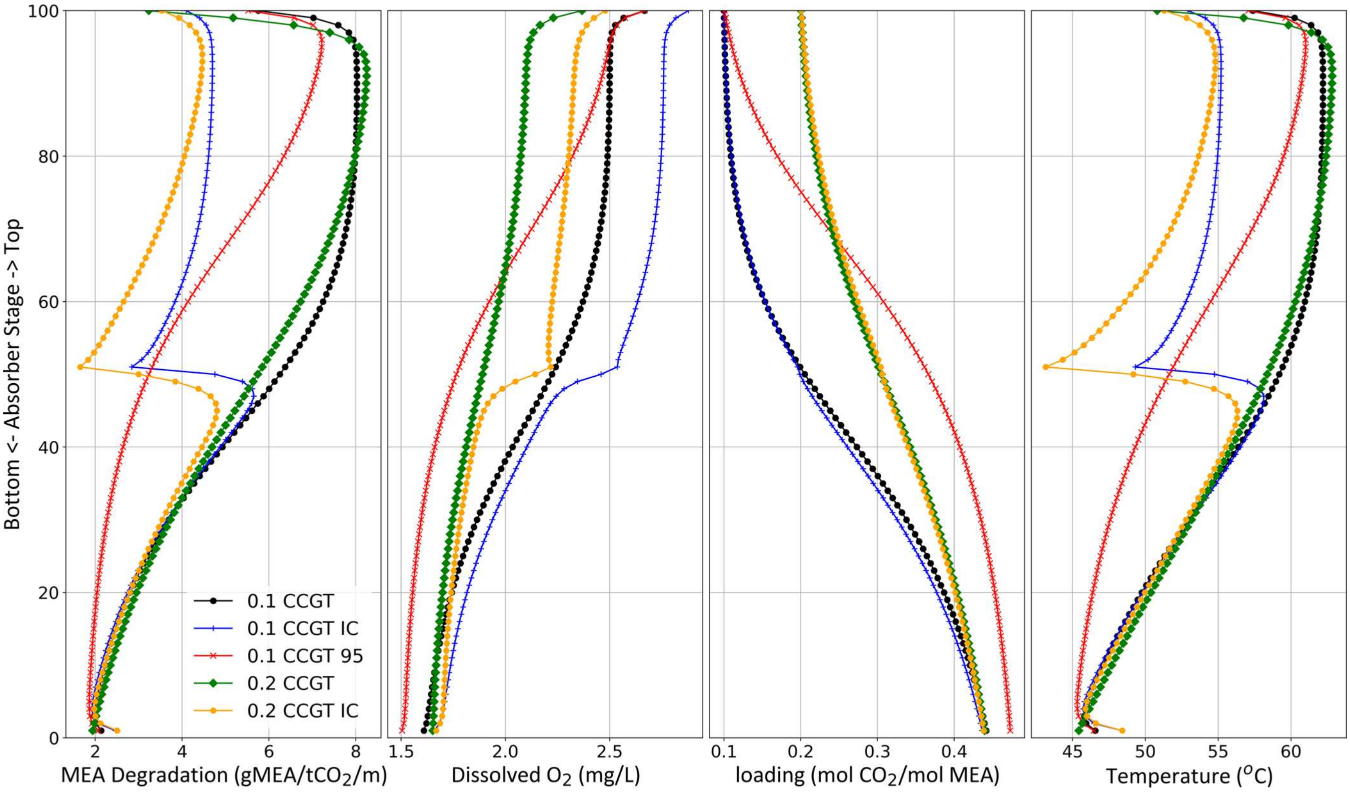

Figure 2. CCGT absorber profiles for MEA degradation rates, dissolved O_2 content in the liquid phase, and CO_2 loading of the solvent and bulk temperature.

serves as a worst-case assumption.[25] Braakhuis et al. account for the depletion of MEA and dissolved O_2 but do not predict the rates of degradation compound formation as the complex nature of oxidative degradation mechanisms makes such predictions challenging.

3. RESULTS AND DISCUSSION

3.1. Process Modeling. The outputs of the process modeling are described in Section 3.1 are detailed in Table 4. As previously described by Mullen et al.[5,6] and Su et al.,[11] when lean loading is reduced accordingly as CO_2 capture fraction increases and regeneration conditions are optimized, minimal differences in the specific energy requirements are observed, and in some cases, a reduction is seen. This is most pronounced in the CCGT case as the driving force of absorption at the top of the absorber is still moderately low, even for a 95% CO_2 capture rate at a lean loading of 0.2 mol/mol. A reduced SRD is predicted in all 95% CO_2 capture cases if lean loading is reduced below 0.2 mol/mol, as per Mullen et al. and Su et al. However, this research aims not to optimize thermal efficiency but to compare solvent degradation rates at typical operational conditions with those considered beneficial when achieving 100% added CO_2 capture. Nonetheless, an additional case was included where a 95% CO_2 capture rate was achieved for a CCGT flue gas at 0.1 mol/mol lean loading and 24 m of absorber packing. A 15.3% reduction in SRD was observed, representing a substantial energy saving at the expense of a 23.7% increase in solvent degradation rates, which

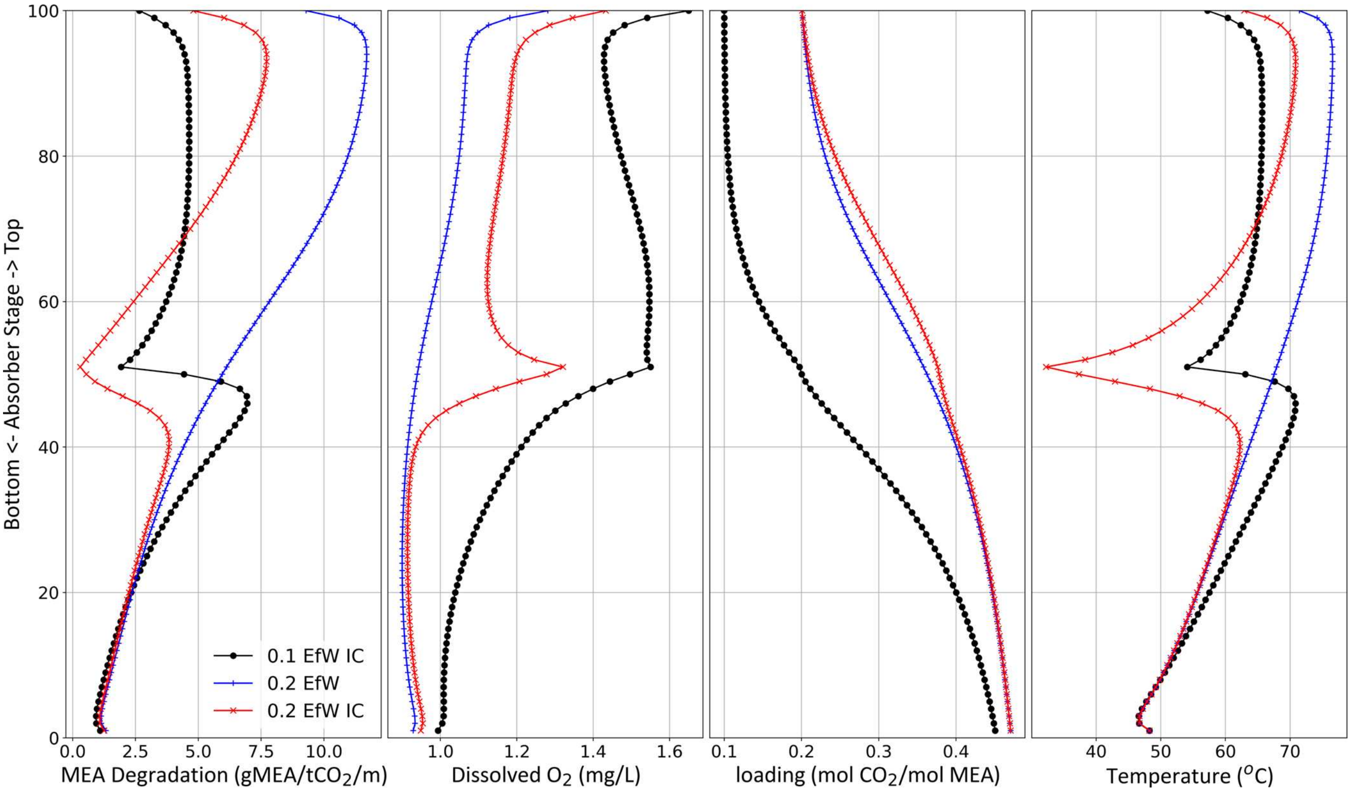

Figure 3. EfW absorber profiles for MEA degradation rates, dissolved O_2 content in the liquid phase, and CO_2 loading of the solvent and bulk temperature.

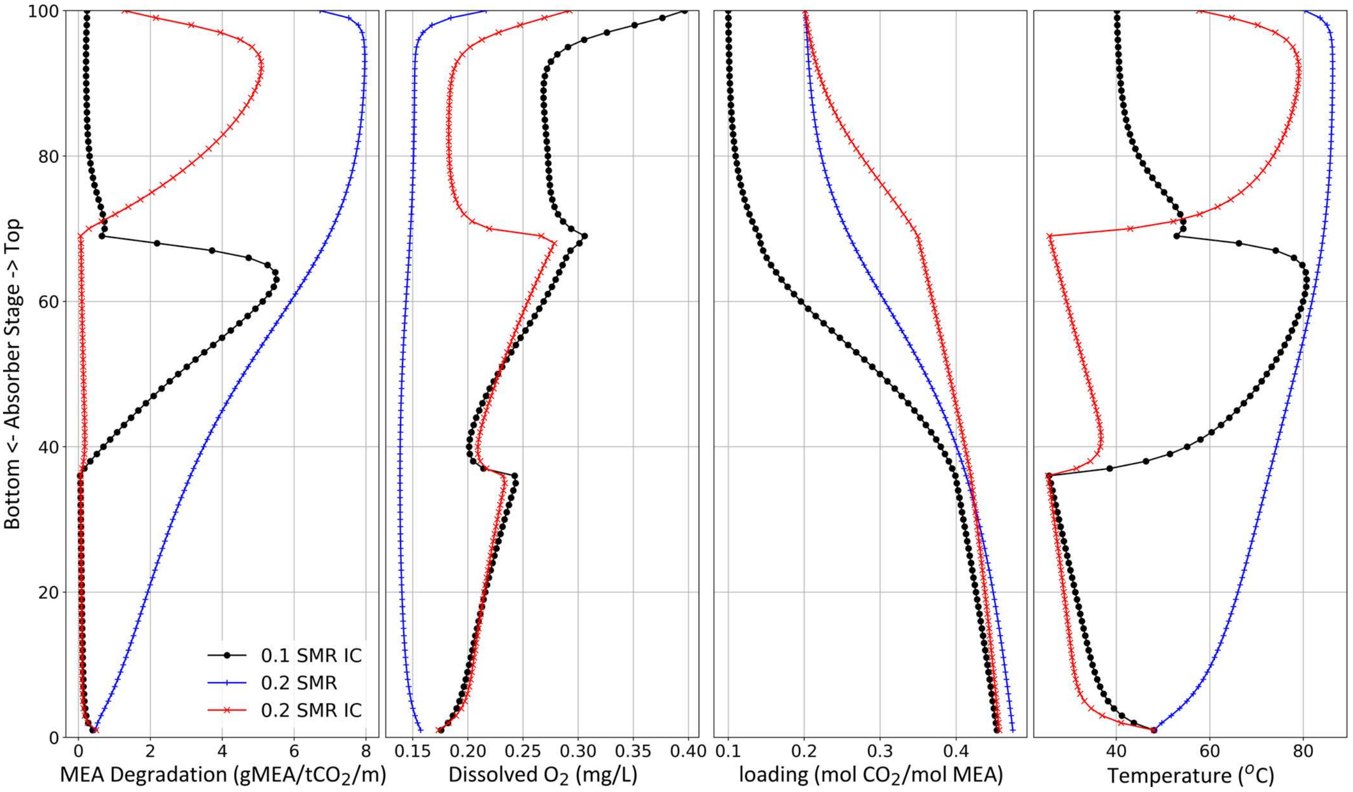

Figure 4. SMR absorber profiles for MEA degradation rates, dissolved O_2 content in the liquid phase, and CO_2 loading of the solvent and bulk temperature.

is discussed in Section 3.2, and an undetermined effect on plant CAPEX and CO_2 compressor power. This demonstrates that the energy benefits of low lean loading operation are not specific to high CO_2 capture fractions and must be a project by project cost optimization decision. Indeed, if solvent degradation is more critical to a project than thermal efficiency, lean loadings sufficient to achieve high CO_2 capture fractions can be achieved at lower pressure/temperature regeneration conditions.

The inclusion or otherwise of an intercooler had minimal effect on CO_2 capture in the CCGT cases. Due to the low concentration of CO_2 in the flue gas, the quantity of heat released in the exothermic reaction is not sufficient to increase the bulk gas temperature to the degree that the driving force of absorption is reduced sufficiently to necessitate intercooling. This is not the case for the EfW and SMR 100% added CO_2 capture cases. The reduced solvent flow rate (due to the reduced lean loading) coupled with the increase in CO_2 concentration in the flue gases leads to absorber pinching, where low/no mass transfer occurs. As a result, 100% added CO_2 capture is not achievable for these specific design cases without intercooling. Intercooling appears to have a minimal or negative effect on thermal efficiency for the 95% CO_2 capture cases as the driving force limiting higher temperatures is pushed to the top of the absorber; further optimization of return temperatures, intercooler location or additional packing beds may mitigate this. However, this is beyond the scope of this work. It should also be noted that, for simplicity, in the CCGT cases with 24 m meters of packing, the intercooler location was maintained at the center of the absorber. In reality, this is unlikely as it does not relate to an interbed location where the installation of intercooling would be most simple; as this case represents a 3 bed × 8 m packing absorber, an intercooler would be situated between one or both of the liquid collection/redistribution sections between each bed. Additionally, in situ absorber intercooling was assumed within the degradation framework with no residence time or hold-up volume ascribed to the intercoolers; this may result in an underestimation of the oxidative degradation rates in the intercooler cases. However, this effect is expected to be minor if residence times and intercooler return temperatures are low.

3.2. Solvent Degradation.

Figures 2, 3, and 4 show the profiles of O_2 concentration and CO_2 loading of the solvent along the absorber length for each case, along with bulk temperature and the predicted oxidative MEA degradation rate. The results presented are intersection averages of each modeled absorber section (1−100). The high O_2 concentration seen at the top of the absorber occurs due to the rapid dissolution of O_2 into the liquid phase over the final section of the absorber. A lower lean loading in itself does not appear to largely affect oxidative degradation rates. This is due to the order of the degradation reaction with respect to O_2 being low at 0.47, so an increase in the concentration of dissolved O_2 will have a progressively smaller impact on the degradation rate and the subtle effect of increased solubility and unloaded MEA concentration at lower lean loadings appears eclipsed by the much more dominant effect temperature has on the reaction rate.

More critically, and an entirely novel observation, is that, by the same virtue, total MEA degradation rates within the absorber are approximately comparable over the range of flue gas O_2 concentration studied. While increasing O_2 concentration will increase the concentration of O_2 in the solvent, the resulting increase in MEA degradation is muted by the low reaction order. However, O_2 leaner flue gases have increased concentrations of CO_2 in post-combustion applications; in the absence of intercooling, the high CO_2 concentration will tend to lead to higher temperatures in the absorber as more energy is released by the exothermic reaction between MEA and CO_2 per unit of flue gas processed. As the oxidative degradation reaction is strongly influenced by temperature, the increase in bulk temperature throughout the absorber present in low O_2/high CO_2 concentration flue gases appears to, at least partially, offset the effect of decreased dissolved O_2 concentrations; this is clearly illustrated in Figure 5.

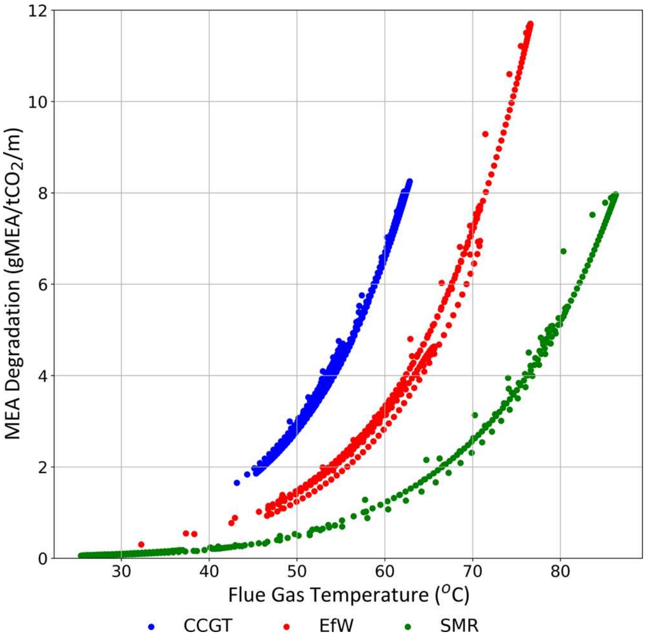

Figure 5. MEA degradation in the absorber packing vs flue gas temperature at different locations in the absorber.

This is most prominently observed in the cases with intercooling included, with a 30−80% decrease in oxidative degradation predicted. This indicates that regardless of the CO_2 capture rate or loading, intercooling can be an effective measure for reducing solvent degradation rates. This must, however, be considered in conjunction with the increased CAPEX and operational requirements that result from including intercooling. Notably, a 43% increase in oxidative degradation in the absorber packing is seen when comparing the 100% added capture and 95% gross capture CCGT cases at 0.1 mol/mol lean loading without intercooling in both cases. This is the result of increased temperatures in the absorber at the higher CO_2 capture fractions. Comparable degradation rates can be seen between the same 95% case and the 100% added capture case (with intercooling), a novel conclusion which indicates that intercooling may be a particularly potent mechanism for reducing solvent degradation in CCGTs at high CO_2 capture fractions despite giving a minor increase in SRD in the cases presented in Table 4 (likely due to decreased reaction rates at lower solvent temperatures). Likewise, the intercooler arrangement presented here does not represent an optimum; further benefits may be observed by revising return temperatures or the inclusion of an additional intercooler, which may have benefits outwit reducing oxidative degradation as this optimization may allow a marginally higher lean loading to be utilized while maintaining the same CO_2 capture performance, reducing thermal degradation.

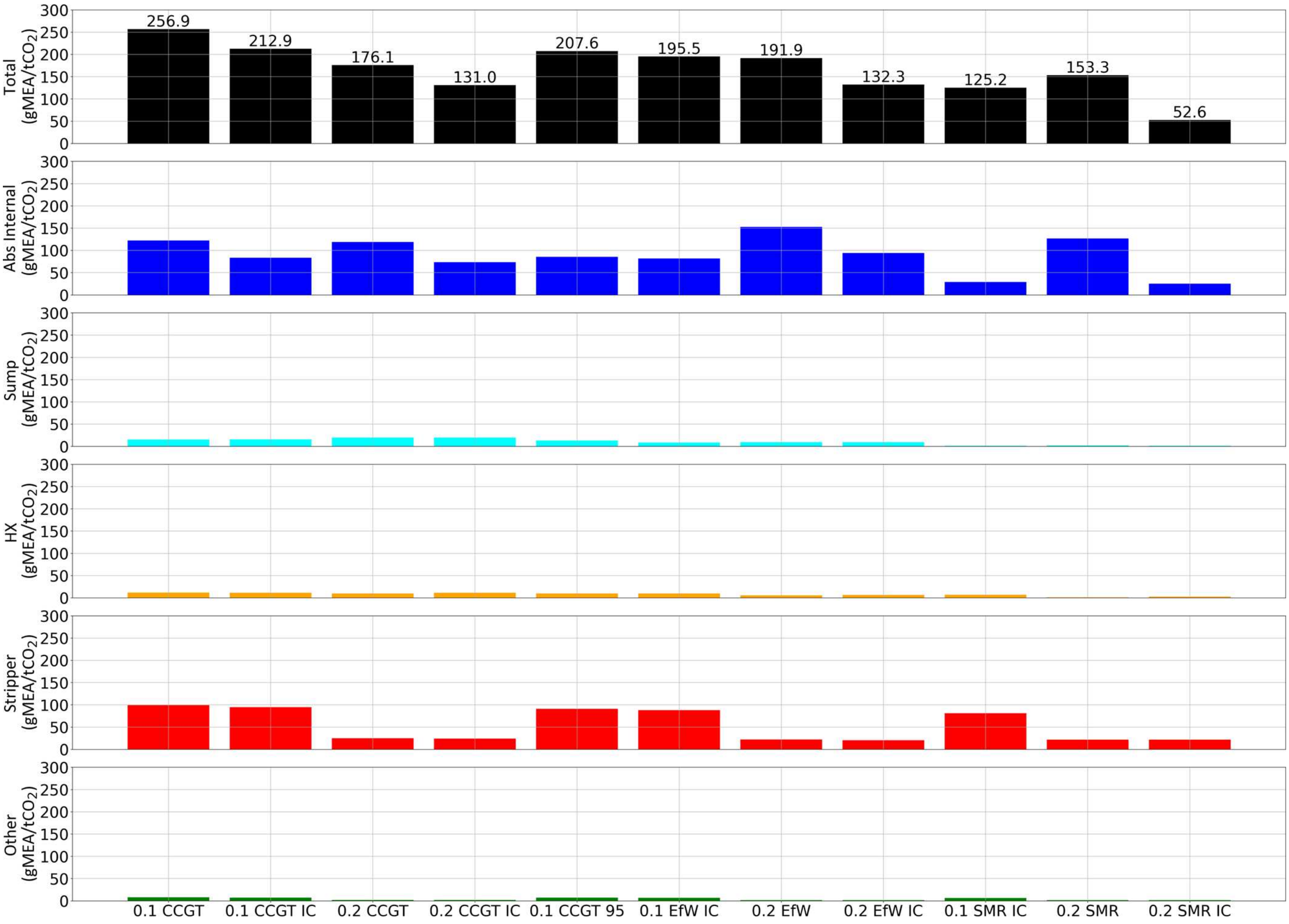

Figure 6. Total and location-specific MEA degradation rates.

Figure 6 and Table 5 detail the predicted total and location-specific MEA degradation rates in the CO_2 capture process. As MEA reacts rapidly with oxygen, the majority of the oxidative degradation occurs within the absorber internals, with the absorber sump and downstream equipment contributing minimally as the remaining dissolved O_2 in the solvent is consumed. The effect is more prominent in O_2-rich flue gases as a higher concentration of dissolved O_2 is carried over into the absorber sump.

Table 5. MEA Degradation Rates

case	total	Abs internal	Abs sump	cross HX	stripper (including reboiler)	other
0.1 CCGT	256.9	122.2	15.6	12.0	99.2	7.9
0.1 CCGT IC	212.9	83.4	15.7	11.8	94.8	7.3
0.2 CCGT	176.0	119.1	19.9	9.9	25.3	1.8
0.2 CCGT IC	131.0	73.7	19.9	11.5	24.2	1.8
0.1 CCGT (95)	207.6	85.7	13.5	9.8	91.2	7.4
0.1 EfW IC	195.6	81.8	8.7	10.0	88.2	6.9
0.2 EfW	191.9	152.9	9.7	5.7	22.0	1.5
0.2 EfW IC	132.3	94.2	9.5	6.7	20.4	1.6
0.1 SMR IC	125.2	29.0	1.5	6.9	81.3	6.4
0.2 SMR	153.3	126.9	2.2	1.2	21.6	1.4
0.2 SMR IC	52.6	25.4	1.5	2.7	21.6	1.3

For the 100% added CO_2 capture cases, i.e. lean loadings of 0.1 mol/mol, thermal degradation increases by a factor of 3−4 due to the increased temperatures experienced by the solvent in the regeneration system. The increase in reaction rate due to increased temperatures outstrips the decrease from the reduced carbamate concentration in leaner solutions, resulting in the net increase in degradation seen, albeit dampened to some degree. This indicates that a designer should utilize the lowest regeneration pressure that will achieve the required trade-offs between solvent degradation, energy efficiency and CAPEX. This is clearly shown in Figure 7, which details the distribution of MEA thermal degradation at key plant locations. A grouping of degradation profiles by lean loading is immediately apparent, with minimal difference seen between the three processes analyzed. The assumed residence times for each piece of equipment are available in Table S2 of the Supporting Information.

Figure 8 illustrates the consumption of O_2 dissolved within the solvent once direct contact with the flue gas ceases. The degradation framework assumes that once the solvent exits the absorber packing and enters the sump (modeled as a continuously stirred tank reactor), it is no longer in contact with O_2 from the flue gas. From this point onward, degradation occurs indirectly through previously dissolved O_2. For clarity, only the CCGT cases are shown; however, the EfW and SMR cases follow similar trends and can be seen in Figures S1 and S2 of the Supporting Information.

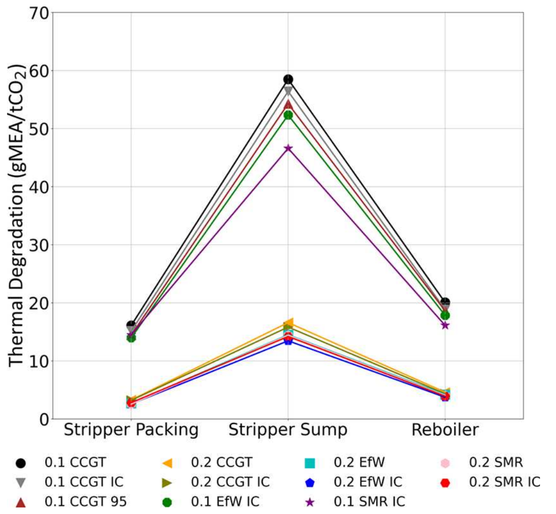

Figure 7. MEA degradation due to thermal degradation at key plant locations.

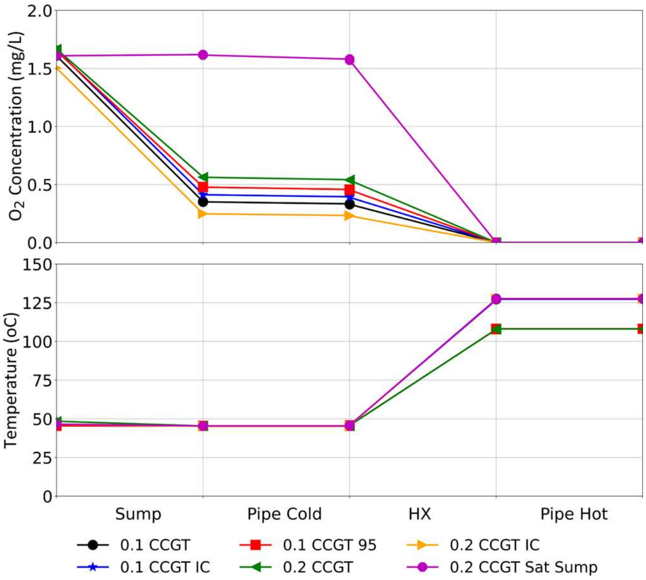

Figure 8. O_2 concentration within solvent at key plant locations (CCGT).

In reality, it is anticipated that the solvent in the absorber sump will still have some exposure to the flue gas, either through contact at the interface or due to the introduction of entrained bubbles resulting from the downcoming solvent. To assess the impact of this kind of exposure on the degradation rate, we predicted the degradation rates under a worst-case scenario by assuming that the solvent in the sump is fully saturated with O_2 throughout the residence time, see Figure 8. Therefore, the solvent leaving the sump is also fully saturated with O_2. In this case, the total MEA degradation rate is increased from the baseline 256.9 to 291.3 g/tCO_2, a 13.4% increase. However, it is unlikely that the solvent will be entirely saturated with O_2 in the absorber sump, as previous oxidative degradation experiments conducted in agitated bubble reactors found that mass transfer limitations for O_2 are present.[25] Nevertheless, it is essential to consider this effect, especially when operating with long sump residence times or flue gases rich in O_2, resulting in high dissolved O_2 concentrations. Process modifications that mitigate prolonged contact between the solvent and the flue gas may be beneficial, as also discussed in.[25] Likewise, process modifications that remove dissolved O_2 from the solvent solution, either prior to or post sump, i.e. flashing or sparging, should reduce indirect oxidative degradation proportional to its removal efficiency.

Minimal MEA consumption occurs in the cold-rich solvent pipeline to the heat exchanger (both pipework and heat exchangers are modeled as plug flow reactors) due to the low residence time and temperature. Within the heat exchanger, dissolved O_2 consumption increases rapidly due to the increased reaction rate stemming from the increased temperatures. By the time the solvent reaches the stripper column, O_2 is predicted to have been entirely consumed in all cases, as also seen in previous work.[25] Minimal O_2 in the export CO_2 stream is a crucial CO_2 pipeline specification due to downstream pipeline integrity concerns. As a result, deoxygenation systems are often included in the design downstream of the stripper at considerable capital expenditure. That being the case, confirmation of total O_2 consumption in the solvent prior to the stripper through pilot or operational studies may allow the omission or reduction in the capacity of the deoxygenation system, leading to a reduction in capital and operational expenditure for systems using aqueous MEA as solvent. This may not be the case for alternative solvents with greater resistance to oxidative degradation.

A design variable available to designers is the hold-up volume of solvent in column sumps. Having a high volume of hold-ups can buffer against operational upsets but comes with the cost of increased solvent exposure to degradation conditions as residence times increase. To investigate the magnitude of this effect, a sensitivity study was conducted wherein the residence time in both the absorber and stripper sumps was varied independently; the results are presented in Figure 9.

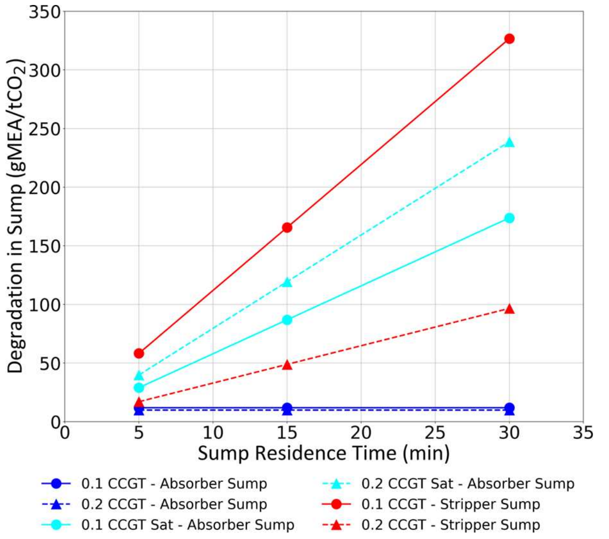

Figure 9. Sump residence time sensitivity study.

When considering the absorber sump, the sensitivity of the stored rich solvent is highly dependent on the assumptions made regarding the degree of O_2 mass transfer into the rich solvent. Where no mass transfer of O_2 occurs, analogous to an independent storage system with minimal contact with atmospheric air or gas capping, no increase in oxidative degradation occurs as the degradation reaction quickly reaches

Table 6. Predicted MEA Consumption Rates (gMEA/tCO_2)

95% gross CO_2 capture	MEA degradation (g/tCO_2)	100% added CO_2 capture	MEA degradation (g/tCO_2)	change in MEA consumption (g/tCO_2)	relative change in MEA consumption (%)
0.1 CCGT	207.6	0.1 CCGT	256.9	+49.3	+23.7
0.2 CCGT	176.0	0.1 CCGT	256.9	+80.8	+45.9
0.2 CCGT IC	131.0	0.1 CCGT IC	212.9	+81.9	+62.5
0.2 EfW IC	132.3	0.1 EfW IC	195.6	+63.2	+47.8
0.2 SMR IC	52.6	0.1 SMR IC	125.2	+72.6	+138.2

equilibrium as the dissolved O_2 in the solvent is consumed. However, if the stored solvent remains saturated with O_2, the increase in degradation is linear with residence time. As previously mentioned, the likely effect is somewhere between these two extremes as O_2 is carried into the solvent via mass transfer at the boundary or flue gas entrainment driven by the downcoming solvent. The risk of flue gas entrainment may be mitigated by the inclusion of a liquid collector at the bottom of the absorber packing; however, this should be considered in conjunction with the resultant increase in absorber height and pressure drop, which would result from its inclusion. The reduction of absorber sump residence times with independent rich solvent storage systems may provide a benefit if longer-term storage is required. As these results are presented on a specific basis, i.e. per tCO_2 captured, a divergence is observed in the reported MEA degradation occurring in the absorber sump between the 0.1 and 0.2 CCGT saturated sump cases, despite similar dissolved O_2 concentrations and temperatures, as the 0.2 CCGT case is exposed to more cycles of absorption/desorption per article of CO_2 captured than the 0.1 CCGT case.

For the stripper sump, the degree of expected thermal degradation experienced by the solvent per cycle increases linearly with residence time. This is particularly critical at higher temperatures as the slope of the additional degradation is increased due to the less favorable conditions. A buffer store of lean and rich solvent can aid in operational flexibility by enabling the rapid response to changing absorber conditions without the delay of producing additional lean solvent. However, the results presented here indicate that utilising the stripper sump to provide this storage capacity will lead to excessive thermal degradation. Storage of any lean solvent in excess of the minimum level required by the regeneration system in a separate storage tank after the cross-heat exchanger (i.e., ambient storage) could mitigate this by minimizing the holdup time in the stripper sump.

Table 6 details the absolute and relative change in MEA degradation rates predicted to occur when transitioning from 95% gross CO_2 capture to 100% added CO_2 capture for the design points presented in this work. The increase ranges between 21 and 112%, primarily due to the increased rate of thermal degradation in the regeneration section. Solvent replacement OPEX is a function of solvent consumption rate and solvent cost and, therefore, Table 6 can indicate OPEX incurred as a result of replacing this degraded solvent. To provide economic context, using a representative cost for an MEA solvent of 0.5−5£/kg MEA results in an increased OPEX of between 0.02−0.38 £/tCO_2. However, the cost indication provided here does not include any additional costs associated with the increased intensity of emission mitigation or solvent management (i.e., increased rates of thermal reclaiming) that are likely if solvent degradation increases, or any increase in volatile solvent losses due to the lower lean loading or higher absorber exit temperatures—these considerations are beyond the scope of this work.

Finally, it is worth noting that the MEA degradation rates presented here i.e. 53−257 g/tCO_2 is lower than the MEA make up rates reported as part of test campaigns i.e. 0.17−1.5 kg/tCO_2.[13−18] This is partially due to the limitations of this study (Section 1), but also that the values reported in these campaigns include additional losses in the system such as the loss of amines through atmospheric emission or emission control systems, process upsets and spills or any losses in the solvent reclamation system, to mention a few.

4. CONCLUSIONS

This article presents, for the first time, an assessment of monoethanolamine (MEA) degradation rates when capturing 100% of the added CO_2 produced as part of three distinct energy production processes fitted with a postcombustion CO_2 capture (PCC) process utilizing a 35 wt %. MEA solvent. The three processes considered, a combined cycle gas turbine (CCGT), energy from the waste facility (EfW) and a steam methane reformer (SMR), cover the expected range of O_2 (1.2−11.0 vol %) and CO_2 concentrations (4.7−19.5 vol %) within industrial flue gases likely to be relevant in PCC applications. Thus, the MEA degradation rates presented can form a likely range for PCC systems using an MEA solvent within the bounds of the study limitations highlighted throughout.

Flue gas conditions are extracted from the previously published works of Mullen et al.[5,6] and Su et al.[11] and form the input to the process model of the CO_2 capture plant, which uses an open-source model developed by the Carbon Capture Simulation for Industry Impact (CCSI) in ASPEN PLUS.[30] For each process, two distinct CO_2 capture fractions are considered: 95% gross CO_2 capture, which forms the basis for comparison and a CO_2 capture fraction resulting in the capture of 100% of the added CO_2 produced by the process (99.2, 99.6, and 99.7% for the CCGT, EfW and SMR respectively). The process modifications used to achieve 100% added CO_2 capture have previously been described by Mullen et al. and involve the reduction of the solvent lean loading from the typical value of ca. 0.2 mol/mol to ca. 0.1 mol/mol and, in the case of the CCGT, 4 m of additional packing within the absorber column. Mullen et al. have shown that the additional specific thermodynamic penalty of operating at 100% added CO_2 capture is minimal if these process modifications are implemented and conclude that to operate efficiently at the reduced lean solvent loading, an increase in stripper operational pressure is required to suppress the production of surplus steam within the regeneration system and minimize energy losses. This increase in operating pressure necessitates an increase in regeneration temperature within the reboiler, a process modification that the authors suggest may increase the thermal degradation of the solvent. Concurrently, a reduced average loading in the absorber may increase the solubility of O_2 overall and, coupled with increased residence time due to the increased packing height, may lead to increased oxidative degradation.

This study applies thermal and oxidative degradation models developed by Braakhuis et al.[24,25] to investigate how these process modifications affect the predicted MEA degradation rates compared to operational conditions, which achieve a gross 95% CO_2 capture fraction. Additionally, we investigate the effect absorber intercooling, sump O_2 dissolution and residence times rates have on total degradation.

Initially, we show that for an MEA solvent, oxidative degradation primarily occurs within the absorber packing and that, while the solubility of O_2 into the solvent and the partial pressure of O_2 in the flue gas will affect total oxidative degradation rates, the effect is dampened by the low order of reaction relative to O_2 concentration. In the absence of intercooling, higher CO_2 concentrations in the flue gas will tend to lead to higher temperatures in the absorber, as more energy is released by the exothermic reaction between MEA and CO_2 per unit of flue gas processed. As the oxidative degradation reaction is strongly influenced by temperature, the increase in flue gas temperature present in low O_2/high CO_2 concentration flue gases appears to, at least partially, offset the effect of decreased dissolved O_2 concentrations. We find that, for the conditions analyzed in this work and for equivalent intercooling regimes, oxidative degradation rates within the absorber packing are approximately equal over the three processes analyzed, as decreased dissolved O_2 concentrations are offset by increased temperatures.

The inclusion of intercooling consistently reduces total oxidative degradation rates as the bulk temperature within the absorber is reduced, and the reaction rate is proportionately reduced. This effect is predicted to result in a 30−70% reduction in oxidative degradation within the absorber packing. This indicates that, regardless of CO_2 capture fraction or loading, intercooling can be an effective measure for reducing solvent degradation rates. This must, however, be considered in conjunction with the increased CAPEX and operational complexity of including intercooling plus possibly a slight reduction in rich loading. Notably, a 43% increase in oxidative degradation in the absorber packing is seen when comparing the 100% added capture and 95% gross capture CCGT cases at 0.1 mol/mol lean loading (both without intercooling). This is the result of a compounded effect of increased temperatures in the absorber at the higher CO_2 capture fraction and the 20−24 m increase in absorber packing height, increasing residence times. But comparable degradation rates can be seen between the same 95% case and the 100% added capture case when intercooling is included. This novel conclusion indicates that intercooling may be a particularly potent mechanism for reducing solvent degradation in CCGTs at high CO_2 capture fractions.

The degradation framework assumes that once the solvent exits the absorber packing and enters the sump it is no longer in contact with O_2 from the flue gas. The authors consider this assumption optimistic as, in reality, the solvent in the absorber sump will still have some exposure to the flue gas or downcoming solvent, replacing the consumed O_2 to some degree. To investigate the magnitude of this effect, a sensitivity analysis shows that when a continually O_2-saturated sump is assumed, the magnitude of total MEA degradation within the system for the CCGT case with 100% added CO_2 capture increases by 13.4%, placing an upper bound on the magnitude of this effect as it expected that dissolved O_2 in the sump is unlikely to be entirely replaced by the stated mechanisms. Likewise, process modifications that remove dissolved O_2 from the solvent solution, either prior to or post sump, i.e. flashing or sparging, should reduce indirect oxidative degradation proportional to its removal efficiency. Due to the increased temperatures seen in the cross-heat exchanger, by the time the solvent reaches the stripper column, the dissolved O_2 is predicted to have been entirely consumed in all cases. Reduced O_2 concentration in the export CO_2 stream is a crucial CO_2 pipeline specification due to downstream pipeline integrity concerns. As a result, deoxygenation systems are often included in the design downstream of the stripper at considerable capital expenditure. That being the case, should this be confirmed through pilot or operational studies, it may allow the omission or reduction in the capacity of the deoxygenation system, leading to a reduction in capital and operational expenditure. This may not be the case for alternative, less reactive, solvents.

When considering thermal degradation, a pronounced effect is evident. Despite the decreased carbamate concentration in the leaner solvent reducing the rate of thermal degradation at a given temperature, the increased regeneration temperature required to achieve a lower lean loading outstrips this limiting effect, resulting in a 3−4-fold increase in thermal degradation when regeneration pressure (and temperature as a result) is increased to efficiently produce a solvent with a lean loading of 0.1 mol/mol vs 0.2 mol/mol. This appears to be an unavoidable consequence of operating at higher regeneration pressures and indicates that a designer should utilize the lowest regeneration pressure, and hence temperature, that will achieve the required trade-offs between solvent degradation, energy efficiency and CAPEX while being aware of the increased degradation rate and adjusting the solvent management regime accordingly. Additionally, advanced process configurations and/or optimized intercooling regimes may allow high CO_2 capture fractions to be achieved at a higher lean loading than those considered in this work; if so, an associated reduction in the expected degree of thermal degradation could be expected.

This work highlights stripper sump residence time as a key design variable for minimizing thermal degradation. A buffer store of lean solvent can aid in operational flexibility by enabling the rapid response to changing absorber conditions without the delay of producing additional lean solvent. However, utilizing the stripper sump to provide this storage capacity will lead to excessive thermal degradation. Storage of cold lean solvent after the cross-heat exchanger could mitigate this.

Some key limitations apply to this study. The degradation framework used in this work does not consider the effect of long-term degradation compound accumulation and removal within the circulating solvent, interactions between the thermal and oxidative degradation compounds or the catalytic effect of corrosion compounds on solvent degradation. As such, the results presented in this article should be considered predictive only for a perfectly clean solvent. Over an extended period of operation, actual MEA consumption rates are expected to diverge from those predicted by the framework, particularly as dissolved metals catalyze oxidative degradation, likely trending toward increasing consumption unless contaminants within the solvent are maintained at a low level via an effective solvent reclamation system. Also, we do not consider the effect any additional solvent degradation will have on atmospheric emissions or the associated control techniques, solvent management regimes or waste production. Additionally, the operational conditions proposed for 100% added CO_2 capture operation would also provide a reduced energy penalty for lower CO_2 capture fraction operation should the resulting solvent degradation rates be deemed economically acceptable. Likewise, if solvent degradation is more critical to a project than thermal efficiency, lean loadings sufficient to achieve high CO_2 capture fractions can be achieved at lower temperature regeneration conditions. Finally, the intercooler arrangements presented here are not considered optimum, and it is likely that further benefits, both thermodynamic and degradation-related, could be achieved with a dedicated optimization effort. This work aims to compare the solvent degradation rates at proposed design points for the considered CO_2 capture fractions that the authors consider to be valid and viable, acknowledging that such design points are project-specific and do not represent an absolute economic optimum, as no such point can exist.

Even so, this study serves as a first step toward quantifying the effect increasing CO_2 capture fractions in post-combustion CO_2 capture plants will have on solvent degradation. We identify key areas for further study and validation in test facilities as well as design considerations that may help mitigate solvent degradation. The learnings presented here can serve to advise project designs and researchers alike when considering operating at 100% added CO_2 capture, a development the authors believe to be critical if post-combustion CO_2 capture is to be compatible with a Net Zero world.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.4c01525.

Additional model parameters sufficient for reproduction and supporting graphics (PDF)

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Notes

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NOMENCLATURE

CCS	Carbon Capture and Storage
CCGT	Combined Cycle Gas Turbine
EfW	Energy from Waste
SMR	Steam Methane Reformer
MSW	Municipal Solid Waste
PCC	Post Combustion Capture
NCCC	National Carbon Capture Centre
MEA	Monoethanolamine
CAPEX	Capital Expenditure
OPEX	Operational Expenditure
T&S	Transport and Storage
CCSI	Carbon Capture Simulation Initiative
GE	General Electric
L/G	Liquid over Gas ratio (kg/kg)
VLE	Vapor Liquid Equilibrium
SRD	Specific Reboiler Duty (GJ/tCO_2)
DACCS	Direct Air CO_2 Capture and Storage
BECCS	Bioenergy with CCS
IEA	International Energy Agency
VOCs	Volatile Organic Compounds
HHV	Higher Heating Value (kJ/kg)
LHV	Lower Heating Value (kJ/kg)
LMTD	Log Mean Temperature Difference (°C)
HX	Heat Exchanger

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