

## ACT LAUNCH Project No 299662



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**Lowering Absorption process **UN**certainty, risks  
and **C**osts by predicting and controlling amine  
degradation**

**D1.3.2 Generalizing and Validating the DNM-LAUNCH rigs and  
pilot runs**

**D1.3.3 Optimised design and operation of capture units to  
reduce degradation**

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## Executive summary

The goal of work package 1.3 was to combine the data gathered in work package 1.1 with the models developed in work package 1.2 to inform CO<sub>2</sub> capture plant design with the aim of minimising and controlling solvent degradation to within manageable levels. This report pertains to two sub tasks taken over by the University of Sheffield on the request of Doosan.

- **Subtask 1.3.2 verifying the representativeness of accelerated degradation tests**
- **Subtask 1.3.3 Utilise the degradation network model to optimise design and operation of capture units to reduce degradation**

The oxidative degradation model developed by TNO as part of WP1 was used in conjunction with a thermal degradation model published by Braakhuis et al, 2022. A tool was developed that simulates the long-term operation of a CO<sub>2</sub> capture plant. Both oxidative and thermal degradation contributions are reported for each plant component as well as the total predicted solvent consumption rate resulting from degradation and the resulting variation in predicted impurity levels with time. The output from this tool was compared to results from the LAUNCH rigs to estimate a ratio of MEA molar consumption to non-volatile degradation compounds as 1:0.32. This ratio then forms an input in the continued use of the tool.

This tool is used to estimate the effect of plant parameters and solvent management techniques on solvent consumption rates. An Aspen Plus / CCSI model of the CO<sub>2</sub> capture plant proposed in the recent Sherman FEED study<sup>1</sup> was used with information publicly available in the study to estimate plant parameters such as absorber/stripper temperature and loading profiles and equipment residence time's, among others for three distinct lean loading/capture fraction cases; 0.12, 0.20, 0.24 mol CO<sub>2</sub>/mol MEA and for CO<sub>2</sub> capture fractions of 95%, 95% and 99.1% respectively. Oxidative degradation was predicted to contribute 1-2 kg/tCO<sub>2</sub> of MEA consumption over the base cases investigated while thermal degradation resulted in 0.05-0.1 kg/tCO<sub>2</sub>. This ratio of oxidative to thermal degradation is highly dependent on reboiler residence time and will shift accordingly. The estimated effects of O<sub>2</sub> removal techniques, residence time manipulation and thermal reclaiming rates are reported.

Continuous thermal reclaiming was predicted to be effective in maintaining a constant impurity level in the solvent over time, the steady state impurity level being dependant on the rate of reclaiming. An additional MEA consumption rate of 0.17-0.66 kg/tCO<sub>2</sub> was estimated to be associated with thermal reclamation, due to a combination of additional thermal degradation during the reclaiming process and MEA loss due to incomplete reclaiming. With effective thermal integration of the reclaiming process a minimal increase in specific reboiler duty of 0.2-1% was predicted.

Reducing residence times was found to be an effective method of reducing thermal degradation while the effect on oxidative degradation was limited. Reboiler and absorber sump residence time was decreased by 50%. The relatively fast kinetics of oxidative degradation and moderately low rich loading of 0.43-0.46 mol CO<sub>2</sub>/mol MEA ensured that the dissolved O<sub>2</sub> present in the absorber sump was consumed in the order of seconds rather than minutes and that a 50% reduction had no effect. Reduction in reboiler residence time had a more marked impact on MEA consumption with a 30-35% reduction in thermal degradation over the cases investigated.

Due to the consumption rate of O<sub>2</sub> observed in the sump only pre-sump O<sub>2</sub> removal was investigated. An oxygen removal fraction of 90% was assumed to occur directly after the last stage of the absorber column. Although effective at reducing sump and post-sump oxidative degradation, the majority of degradation was predicted to take place in the absorber, meaning that a minimal reduction was observed in total oxidative degradation with even pre-sump O<sub>2</sub> removal, a decrease of 2-4% over the

<sup>1</sup> <https://ukccsrc.ac.uk/open-access-sherman-feed/>



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cases investigated. A review of the dissolved oxygen model used in this work is advised as a disparity between the models proposed by TNO and Aspen with respect to predicted dissolved O<sub>2</sub> was observed.



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## 1 Introduction

Effective solvent management is one of the major obstacles facing long term operation of CO<sub>2</sub> capture plants as runaway solvent degradation can dramatically increase both the variable OPEX and maintenance costs of CO<sub>2</sub> capture plants, potentially leading to equipment failure or economic unviability. Solvent degradation can occur due to thermal degradation, oxidative degradation, and chemical reactions with impurities present in the flue gas. Thermal degradation is the breakdown of amine molecules caused by the high temperatures in the regeneration sections of CO<sub>2</sub> capture processes. Oxidative degradation is caused by the oxidation of amine solvents with oxygen present in the flue gas. Chemical reactions with impurities in the flue gas can also lead to amine degradation, as these impurities can react with the amine molecules to form new compounds.

One of the main consequences of amine solvent degradation is the loss of CO<sub>2</sub> capture efficiency. As the amine solvent degrades the formation of by-products and associated decrease in solvent availability negatively effects its ability to absorb CO<sub>2</sub>, which leads to an increase in the amount of solvent per unit of CO<sub>2</sub> that must be treated to achieve a given level of capture. This can result in increased energy consumption, as the regeneration section of the CO<sub>2</sub> capture process must work harder to release the same amount of CO<sub>2</sub> from the degraded amine solution.

Degraded solvent also contains non-volatile compounds that are not easily released during the regeneration process. These by-products can corrode the materials used in the CO<sub>2</sub> capture process, which can lead to increased maintenance costs and reduced system life as well as contribute to reduced efficiency of the process through fouling of equipment, increased sensible heat demands and foaming of the solvent.

Perhaps the most significant consequence of amine solvent degradation is the formation and emission of ammonia and nitrous amines during the degradation process. If unmitigated this can cause damage to the environment, plant and animal life as well as human health. Although emission control techniques such as water and acid washes have been shown to effectively control emission levels a reduction in the formation of these hazardous compounds can further reduce risks and costs.

To mitigate the impact of amine solvent degradation, various strategies have been developed. These include the use of more robust amine solvents, the addition of stabilizing agents to the amine solution, and the implementation of operational strategies to minimize exposure to high temperatures and oxidative conditions.

The LAUNCH (Lowering Absorption process **UN**certainty, risks and **C**osts by predicting and controlling amine degradation) project aims to systematically develop quantification and predictive tools for amine degradation to advise operational and design techniques for mitigation and control. This report presents the results from Work package (WP) 1.3 sub package 1.3.2 and sub package 1.3.3 as described below.

- **Subtask 1.3.2 verifying the representativeness of accelerated degradation tests**
- **Subtask 1.3.3 Utilise the degradation network model to optimise design and operation of capture units to reduce degradation**

## 2 Methodology

### 2.1 Thermal Degradation model

For this work a thermal degradation model published by Braakhuis et al [1] is used to predict the thermal degradation of MEA throughout a CO<sub>2</sub> capture plant. A relative deviation of 17.5% from experimental data is reported by the authors.

Braakhuis et al presents a kinetic model of thermal degradation of MEA fitted to 24 sets of experiments over a range of MEA loadings and temperatures. The degradation reactions proposed by Braakhuis et al are shown in Figure 1.

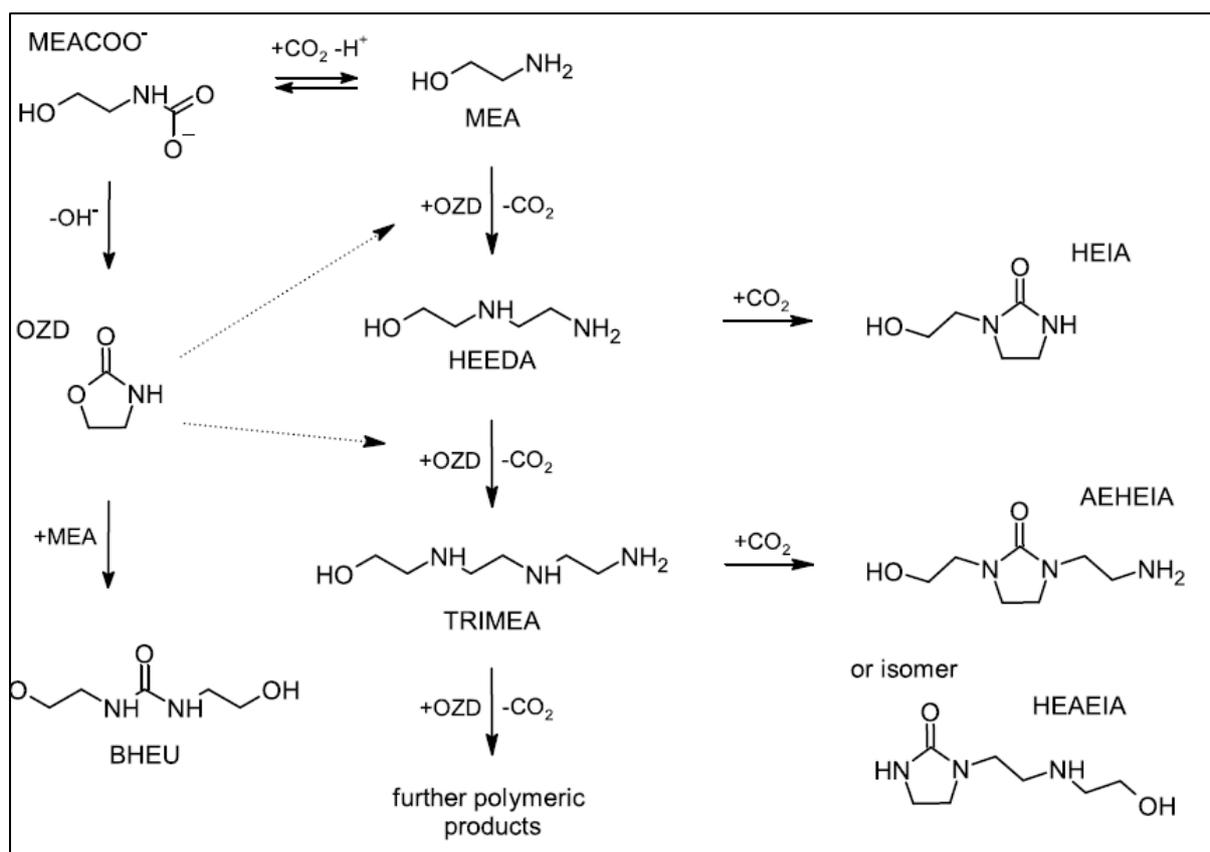


Figure 1 Overview of degradation reactions for carbamate polymerization of MEA[1]

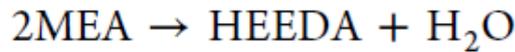
Optimized rate constants and activation energies are presented and described in Figure 2 while the equilibrium reactions are shown in Figure 3; all reactions are presented as first order reactions. Over the course of this work an error in the parameters presented in Figure 2 was observed. The rate constants and activation energy for equations 2 & 3 appear to be reversed. This has been rectified in order to successfully recreate the results presented in Braakhuis et al [1]. This has been confirmed with Braakhuis et al. who are in the process of updating the publication.

reaction	$k_{ref} [m^3 \cdot mol^{-1} \cdot s^{-1}]$	$E_A [kJ/mol]$
1 (MEA to HEEDA)	$1.599 \times 10^{-11}$	151.1
2 (HEEDA to TRIMEA)	$3.054 \times 10^{-10}$	142.6
3 (HEEDA to HEIA)	$1.117 \times 10^{-10}$	121.5
4 (TRIMEA to AEHEIA)	$2.839 \times 10^{-10}$	136.2
5 (MEA to BHEU)	$1.281 \times 10^{-12}$	

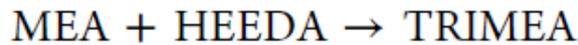
Figure 2 Optimized parameters for the Carbamate polymerization model [1]

Table 1: Updated reaction rates and activation energies used in this study

Reaction	$K_{ref} [m^3 \cdot mol^{-1} \cdot s^{-1}]$	$E_a [kJ/mol]$
1 (MEA to HEEDA)	$1.599 \times 10^{-11}$	151.1
2 (HEEDA to TRIMEA)	$1.117 \times 10^{-10}$	121.5
3 (HEEDA to HEIA)	$3.054 \times 10^{-10}$	142.6
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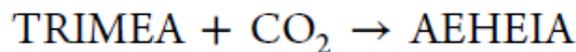
$$R_1 = k_1[\text{MEA}][\text{CO}_2] \quad (1)$$



$$R_2 = k_2[\text{HEEDA}][\text{CO}_2] \quad (2)$$



$$R_3 = k_3[\text{HEEDA}][\text{CO}_2] \quad (3)$$



$$R_4 = k_4[\text{TRIMEA}][\text{CO}_2] \quad (4)$$



$$R_5 = k_5[\text{MEA}][\text{CO}_2] \quad (5)$$

Figure 3 Equilibrium reactions for the Carbamate polymerization model [1]



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## 2.2 Oxidative Degradation model

An oxidative model developed by TNO as part of the Degradation Network Model (DNM) in WP1 was used to estimate the oxidative degradation of MEA solvent under process conditions.

Reference rate constants and activation energy for O<sub>2</sub> degradation within a loaded MEA solution at 3 distinct loading values are presented in the model and shown in Table 2

Table 2: Reference activation energy and rate constants for O<sub>2</sub> consumption in loaded MEA

Loading (mol/mol)	0.2	0.3	0.5
E <sub>a</sub> (KJ/mol)	8.12E+04	8.46E+04	6.19E+04
K <sub>o</sub> (mol/L.hr)	2.12E+12	7.21E+12	7.53E+08

Linear interpolation between data points was advised in the DNM to generate reference values over the range of loadings present in a CO<sub>2</sub> capture plant.

The Arrhenius equation is used to produce a rate constant for a given operational temperature as per Equation 1

$$K_t = K_o e^{\frac{-E_a}{RT}} \quad (1)$$

The rate of dissolved O<sub>2</sub> consumed is described by Equation 2 while Equation 3 describes the stoichiometry of the reaction.

$$O_2 \text{ Final} = \frac{[-K_t * \text{residance time} + 2\sqrt{O_2 \text{ Inital}}]^2}{4} \quad (2)$$



The stoichiometric factor of 1.3 was informed by experimental results.

The DNM also presents a model for estimating dissolved O<sub>2</sub> in a loaded MEA solution and is described by Equation 4

$$\begin{aligned} \text{dissolved } O_2 &= aT + b\alpha + C \\ a &= -8.54E - 06 \\ b &= -2.38E - 04 \\ c &= 1.08E - 03 \end{aligned} \quad (4)$$

Where T is the temperature of the liquid in °C, α is the loading in mol/mol and dissolved O<sub>2</sub> is reported in mol/L.

When comparing the estimated dissolved O<sub>2</sub> using Equation 4 to the estimations made by the modeling software Aspen Plus a large discrepancy was noted (see Figure 4) with Aspen Plus predicting dissolved O<sub>2</sub> concentrations approximately 20 times that of the TNO model. This disparity will have a large impact on the predictive capacity of the oxidative model if not resolved, particularly in the absorber sump, and further investigation is advised.

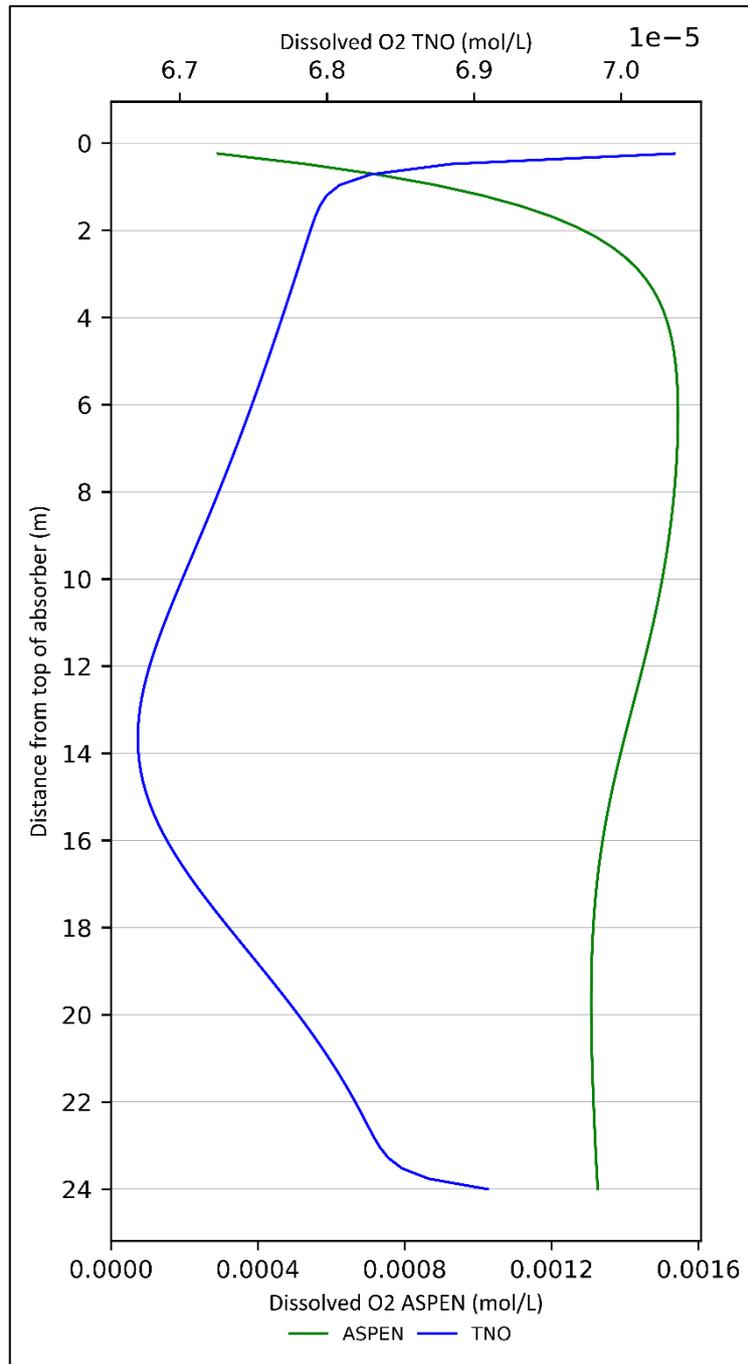


Figure 4 Comparison of dissolved O<sub>2</sub> concentrations in the 24m absorber modeled in Aspen Plus; lean loading is 0.12mol/mol and the CO<sub>2</sub> capture fraction is 99.1%

Preliminary testing of dissolved O<sub>2</sub> at the midpoint and bottom of the absorber was completed at the TERC facility on a synthetic flue gas containing 19% O<sub>2</sub> vol (wet) (see Figure 5). Dissolved O<sub>2</sub> measurements part way down the absorber roughly align with the TNO dissolved O<sub>2</sub> model but with somewhat lower absolute values, about a factor of 3 or half an order of magnitude lower. Rich solvent DO measurements also roughly align with the TNO model but are somewhat higher, a factor of 3 or half an order of magnitude higher. Whether the lower dissolved O<sub>2</sub> measurements in the semi lean solvent

is due to rapid O<sub>2</sub> consumption or slow dissolution of O<sub>2</sub> into the solvent is currently unclear and further investigation is advised.

The Aspen DO model appears to give higher predictions (order 10<sup>3</sup> mol/l) even than are measured at the rich solvent at the bottom and much higher than partway down.

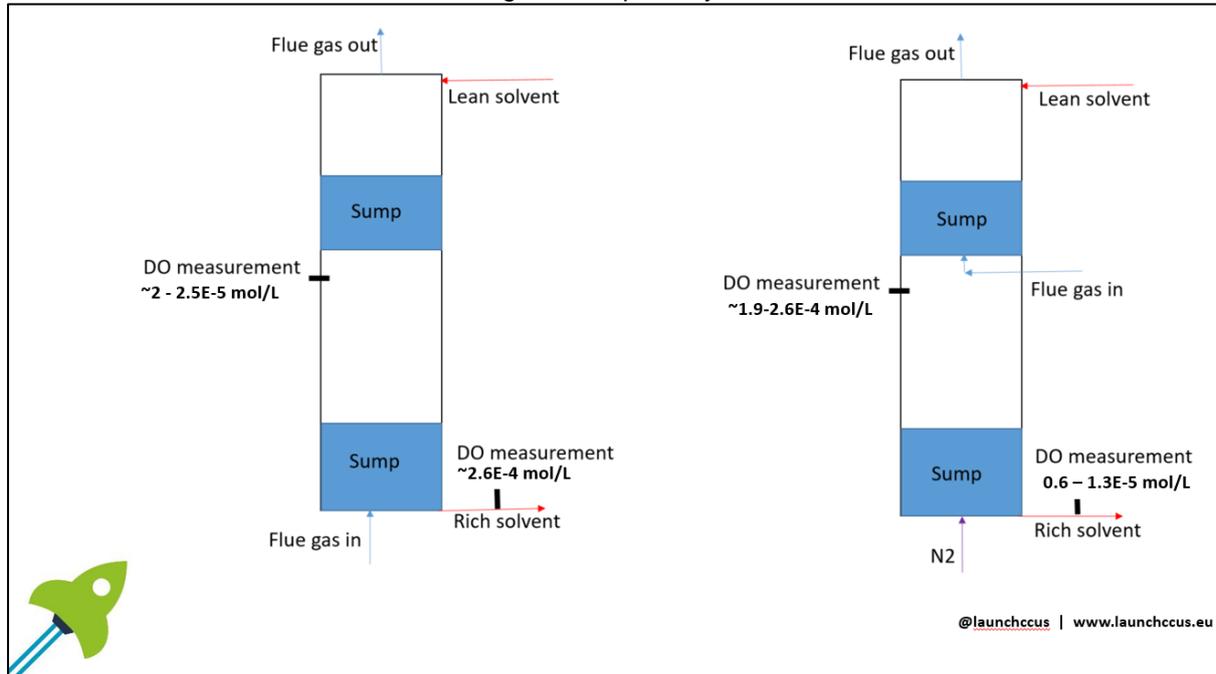


Figure 5 Preliminary Dissolved O<sub>2</sub> measurement at the TERC facility with a flue gas containing ~ 19% vol O<sub>2</sub>

## 2.3 Experimental Data

Experimental data in the form of time series concentrations of degradation products (Figure 5), and operational conditions (Figure 6) for test campaigns completed using the TERC pilot plant at the University of Sheffield and Launch Rig #2 at TNO was extracted from deliverable number D4.1.1 of the LAUNCH project. The SRD2020 campaign shown in Figure 6 is reproduced from academic literature [2] and is not included in the analyses as it is a non-LAUNCH campaign.

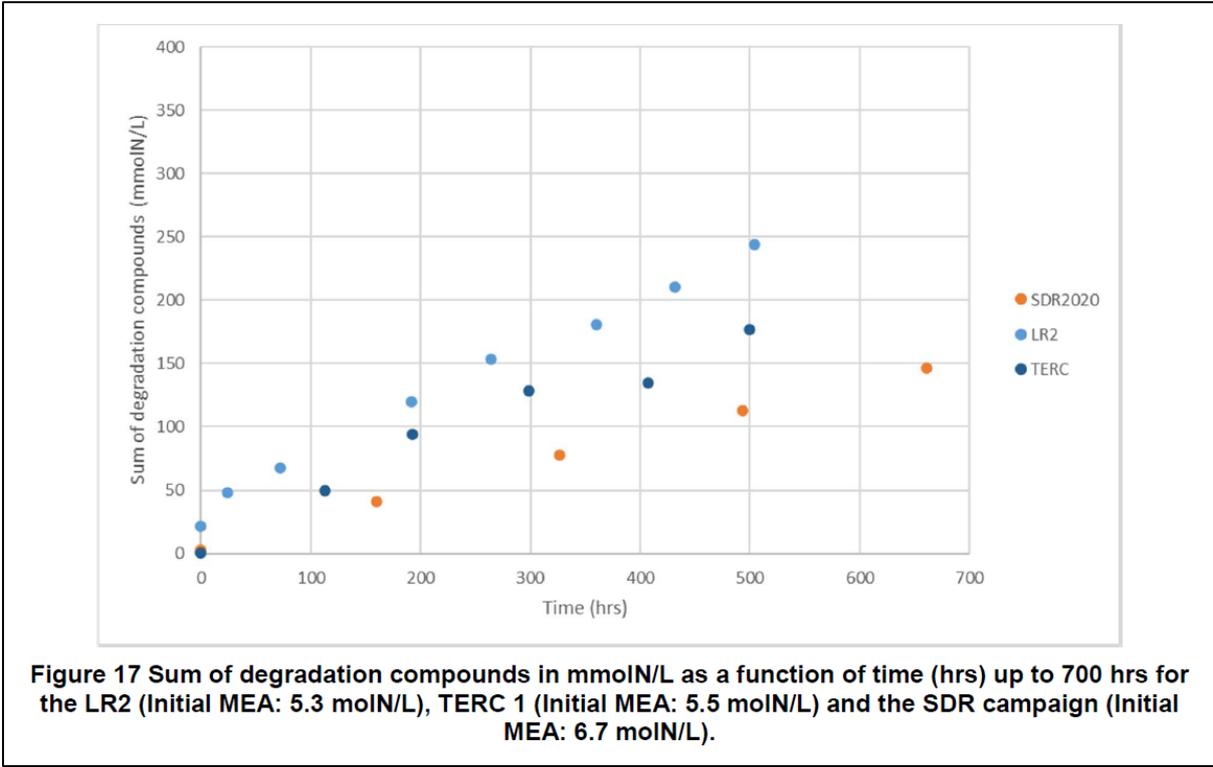


Figure 17 Sum of degradation compounds in mmolN/L as a function of time (hrs) up to 700 hrs for the LR2 (Initial MEA: 5.3 molN/L), TERC 1 (Initial MEA: 5.5 molN/L) and the SDR campaign (Initial MEA: 6.7 molN/L).

Figure 6 Time series concentration of degradation products from LAUNCH rigs

Parameter	Unit	LR2 Mean value	Parameter	Unit	TERC Mean value	Parameter	Unit	LR2 Mean value	Parameter	Unit	TERC Mean value	Parameter	Unit	LR2 Mean value	Parameter	Unit	TERC Mean value
<b>ABSORBER</b>																	
Temperature Gas inlet	°C	37.8	Temperature Gas inlet	°C	27.9	abs T profile	°C	59.80	Absorber 2	°C	37.6	stripper T profile (bottom)	°C	114.0	stripper T profile (bottom)	°C	112.9
Pressure Gas inlet	mbarg	54.20	Pressure Gas inlet	mbarg	30	abs T profile	°C	56.5	Absorber 2	°C	42.2	Reboiler duty	kW	0.88	Reboiler duty	kW	
Air inlet flowrate	nL/h	4224	Air inlet flowrate	nL/h	189000	abs T profile (bottom)	°C	50.5	Absorber 2	°C	35.2	Liquid level in the reboiler	%	44.83			
CO <sub>2</sub> inlet flowrate	nL/h	887							Absorber 2	°C	34.9	Liquid volume in reboiler	m <sup>3</sup>	0.005	Liquid volume in reboiler	litres	450
CO <sub>2</sub> inlet flowrate	nL/h	247							Absorber 2	°C	34.2	Temperature in reboiler liquid	°C	120.09	Temperature in reboiler liquid	°C	118
Inlet flowrate dry total	nL/h	4471							Absorber 2 (bottom)	°C	33	Residence time in reboiler	min	30.9	Residence time in reboiler	min	90
H <sub>2</sub> O inlet flowrate	gh	235							Absorber 1 (Top)	°C	30.7	Pressure in stripper	barg	0.75	Pressure in stripper	barg	0.5
H <sub>2</sub> O inlet flowrate	nL/h	293							Absorber 1	°C	44.8	Temp CO <sub>2</sub> product from condenser	°C	14.76	Temp CO <sub>2</sub> product from condenser	°C	15
Inlet flowrate wet total	nL/h	4765							Absorber 1	°C	59.6	Flow CO <sub>2</sub> product from condenser	L/h	227.93			
Gas inlet composition, CO <sub>2</sub>	vol(%) dry	5.53	Gas inlet composition, CO <sub>2</sub>	vol(%) dry	5.14				Absorber 1	°C	61.4						
Gas inlet composition, CO <sub>2</sub>	vol(%) wet	5.19	Gas inlet composition, CO <sub>2</sub>	vol(%) wet	5.1				Absorber 1	°C	60.4						
Gas inlet composition, O <sub>2</sub>	vol(%) dry	19.8	Gas inlet composition, O <sub>2</sub>	vol(%) dry					Absorber 1	°C	57.9						
Gas inlet composition, O <sub>2</sub>	vol(%) wet	18.6							Absorber 1	°C	53.35						
Gas inlet composition, H <sub>2</sub> O	vol(%)	6.2	Gas inlet composition, H <sub>2</sub> O	vol(%)	0.8				Absorber 1 (bottom)	°C							
Lean solvent inlet temperature	°C	39.7	Lean solvent inlet temperature	°C	40												
Lean solvent inlet pressure	mbarg	524.00															
Lean solvent inlet flowrate	kg/h	11.5	Lean solvent inlet flowrate	kg/h	300	Liquid level in the absorber sump	%	20.68	Liquid level in the absorber sump	m <sup>3</sup>	0.000	Liquid level in the absorber sump	m <sup>3</sup>	0.070			
Lean solvent density	kg/m <sup>3</sup>	1080	Lean solvent density	kg/m <sup>3</sup>	1029	Liquid volume in absorber sump	m <sup>3</sup>	0.006	Temperature in the absorber sump	°C	Not available						
Lean solvent outlet flowrate	m <sup>3</sup> /h	0.011	Lean solvent outlet flowrate	m <sup>3</sup> /h	300	Residence time in absorber sump	min	3.5	Residence time in absorber sump	min	14						
Gas outlet temperature	°C	43.4	Gas outlet temperature	°C	35.5	Pressure outlet to vent	mbarg	26.7	MEA outlet to vent	mg/nm <sup>3</sup>	105						
L/G (dry gas/lean solvent)	kg/kg	1.94	L/G (dry gas/lean solvent)	kg/kg	1.2	NH <sub>3</sub> outlet to vent	mg/nm <sup>3</sup>	5.31									
Pressure outlet	mbarg	26.7	Pressure outlet	mbarg	26	<b>STRIPPER</b>											
Rich solvent outlet temperature	°C	40.9	Rich solvent outlet temperature	°C	31	Rich solvent inlet temperature	°C	93.100	Rich solvent inlet temperature	°C	90						
Rich solvent outlet pressure	mbarg	1180				Rich solvent inlet pressure	mbarg	1060									
Rich solvent outlet flowrate	kg/h	12.1	Rich solvent outlet flowrate	kg/h	300	Rich loading range	mol/mol	0.45	Rich loading range	mol/mol	0.45 - 0.46						
Gas outlet composition, H <sub>2</sub> O	kg/m <sup>3</sup>	1110.0	Gas outlet composition, H <sub>2</sub> O	kg/m <sup>3</sup>	1045	Pressure outlet to condenser	barg	802.00	Pressure outlet to condenser	barg	0.5						
Rich solvent outlet flowrate	m <sup>3</sup> /h	0.011	Rich solvent outlet flowrate	m <sup>3</sup> /h	39.7	Lean solvent outlet temperature	°C	Not available	Lean solvent outlet temperature	°C	112						
abs T profile (top)	°C	57.20	Absorber 2	°C	39.4	Lean loading range	mol/mol	0.3	Lean loading range	mol/mol	0.24 - 0.26						
abs T profile	°C	61.50	Absorber 2	°C	38.6	Lean solvent outlet pressure	mbarg	666	stripper T profile (top)	°C	93.9	stripper T profile (top)	°C	107.4			
									stripper T profile	°C	95.2	stripper T profile	°C	104			
									stripper T profile	°C	96.2	stripper T profile	°C	111			
									stripper T profile	°C	101.0	stripper T profile	°C	112.2			

Figure 7 Operational parameters of LAUNCH rigs

## 2.4 Aspen Plus model

An Aspen Plus [3] model developed by Michailos and Gibbins [4] of a CCGT plant fitted with 35% wt MEA based post combustion CCS operating at ultra-high CO<sub>2</sub> capture rates of 95-99.1% and based on the open source Sherman FEED [5] study was used to generate absorber and stripper temperature, pressure, loading and O<sub>2</sub> profiles as well as solvent flow rates and temperatures throughout the PCCC plant. A two-stage reclaiming system (see Figure 8) was thermally integrated into the model to investigate the energy penalty associated with continuous reclaiming. 3 distinct cases were investigated, defined by varying lean loading values; these are 0.12, 0.20 and 0.24 molCO<sub>2</sub>/molMEA.

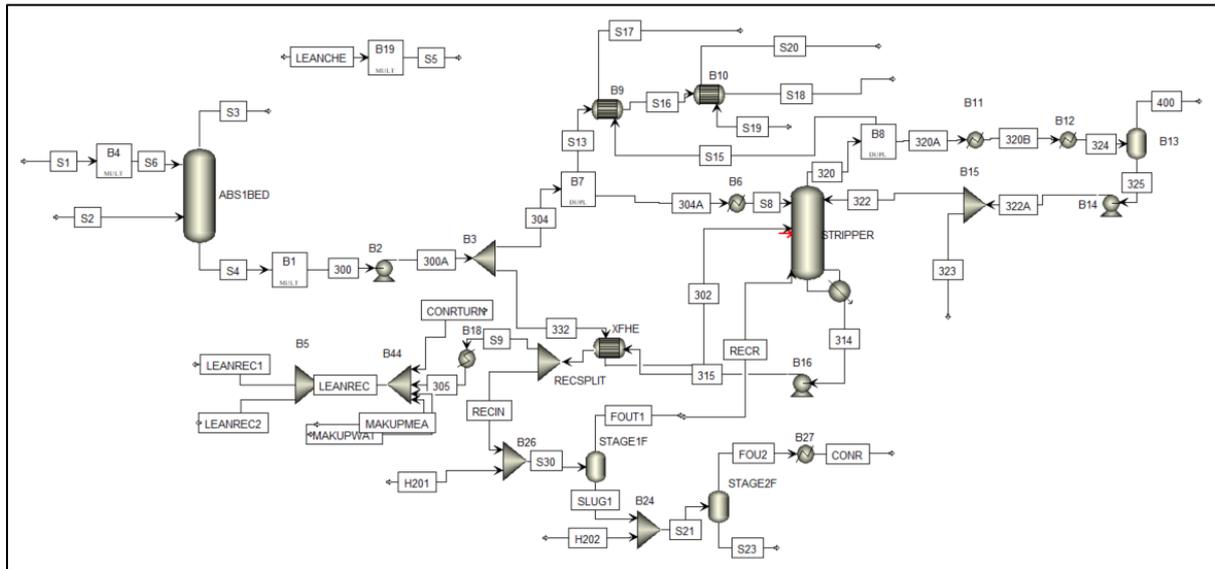
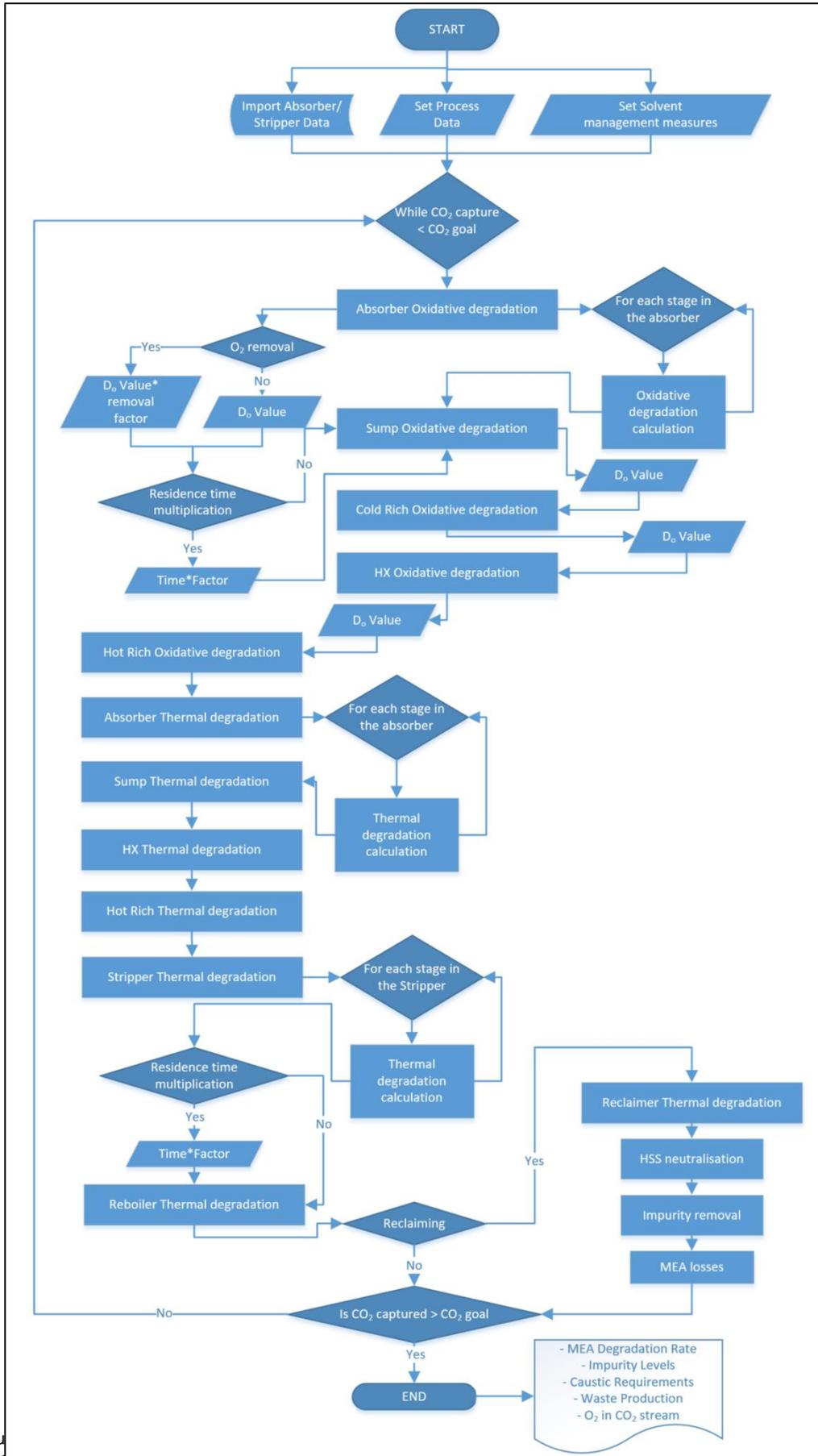


Figure 8 Aspen Plus PCCC model



## 2.5 Predictive Tool

A rigorous and interactive predictive tool combining both oxidative and thermal degradation models described above and informed by Aspen modelling and experimental data was produced in Python 3.9. Taking user inputs on process parameters, solvent control techniques and absorber/stripper profiles this tool models the long-term operation of a post combustion CO<sub>2</sub> capture plant by simulating the transit of 1 m<sup>3</sup> of MEA solvent through each piece of plant equipment i.e. absorber, sump cross heat exchanger, stripper, reboiler etc. over multiple cycles of CO<sub>2</sub> absorption and desorption. As the solvent is exposed to both oxidative and thermal degradation cycles MEA consumption occurs and impurity levels build up. Once a user-specified quantity of CO<sub>2</sub> has been captured by the plant, typically 500 tCO<sub>2</sub>/m<sup>3</sup> of solvent (corresponding to approximately 1 year of operation) the program ends and MEA consumption rate, impurity levels, caustic requirements and waste production rate from the reclaimer (if applicable) is reported. A flowchart describing the main operations of the tool is shown in Figure 9 while the full code is available in Appendix 1.





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*Figure 9 Flowchart describing solvent degradation predictive tool developed in Python 3.9*

## 3 Results

### 3.1 LAUNCH rig comparison

Simulations of degradation runs completed as part of the LAUNCH campaign (see Figure 6) were completed using the predictive tool described in section 2.5. These LAUNCH campaigns report an impurity value per unit of solvent. This is a measure of the total quantity of non-volatile degradation compounds arising from both oxidative and thermal degradation over the course of the campaign. While MEA consumption can be estimated using the predictive tool, the oxidative model developed by TNO and described in section 2.2 provides no stoichiometric factor for the production of non-volatile products, whereas the thermal degradation model described in section 2.1 does. A fitting exercise was completed to estimate the stoichiometric factor for oxidative degradation using the experimental data from the LAUNCH campaigns and the predictive tool.

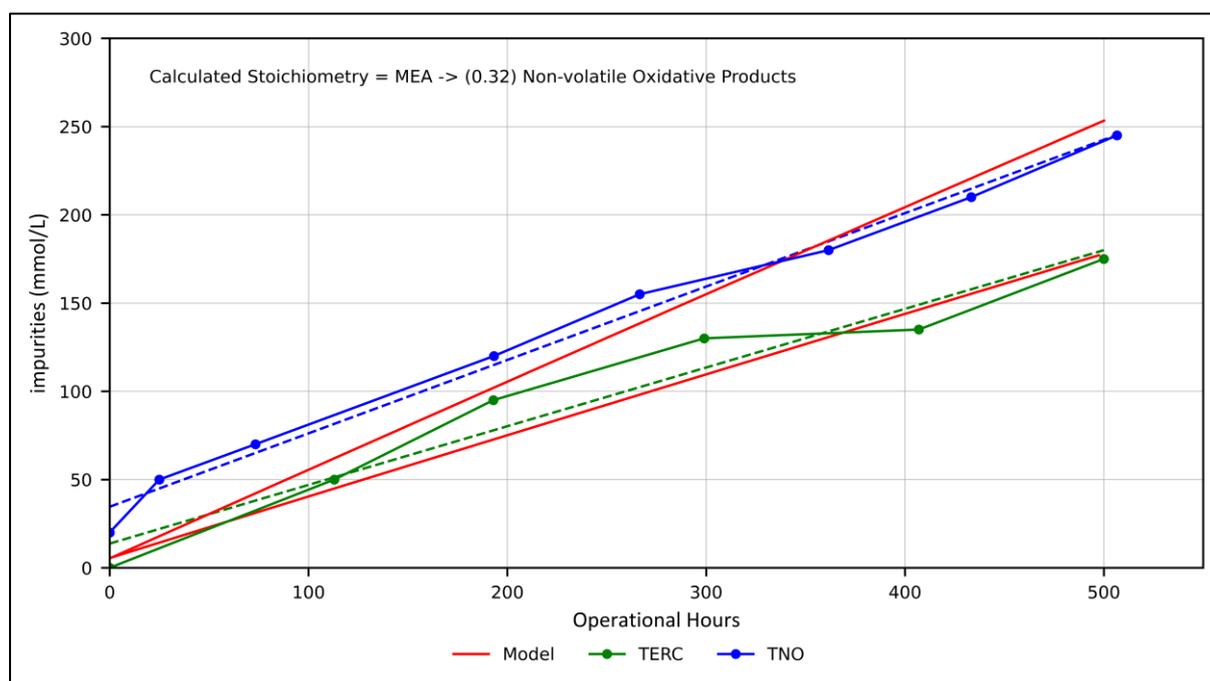


Figure 10 Comparison between experimental and simulation data from LAUNCH runs

As can be seen from Figure 10, a stoichiometric factor of 0.32 mol of non-volatile degradation compounds to 1 mol of oxidized MEA provides a good fit for campaigns at both the TERC and TNO rigs.

### 3.2 Thermal Degradation

Thermal degradation was explored in isolation to investigate the effect of lean loading on overall thermal degradation rates. As thermally efficient operation at low lean loading requires higher reboiler temperatures, due to the increased stripper pressure required to maintain stripper operation below the so called “inflection point” [4], the prevailing assumption is that operation at low lean loadings will increase MEA consumption rates dramatically, due to increased thermal degradation. However, as thermal degradation is thought to be rate limited by the quantity of absorbed CO<sub>2</sub> in the MEA solvent (i.e. loading), see Figure 1, a lower lean loading is thought to counteract the increase in solvent degradation due to increased temperatures. Figure 11 investigates this phenomenon; a constant rich loading of 0.47 mol/mol is assumed, no reclaiming is in operation and the reboiler only is modelled. Reboiler operational temperature is set for each lean loading values at the approximate minimum temperature to maintain energy consumption below the inflection point [4]. The simulation is run until

500 tCO<sub>2</sub>/m<sup>3</sup> of solvent is captured using various assumed reboiler residence times. An optimum loading of 0.2 mol/mol is observed across all residence times, however, for reboiler residence times below 45 minutes minimal differences are predicted between loadings of 0.25 down to approximately 0.10 molCO<sub>2</sub>/molMEA, indicating that low lean loading operation may not induce as much thermal degradation as previously thought. It is worth noting that as the work presented in Figure 11 models only the reboiler, it does not take an holistic view on the operation of the plant; equipment hold up rates and solvent circulation rates may change for different lean loadings and as such the residence time in the reboiler (and stripper) may vary with lean loading unless the plant is appropriately designed.

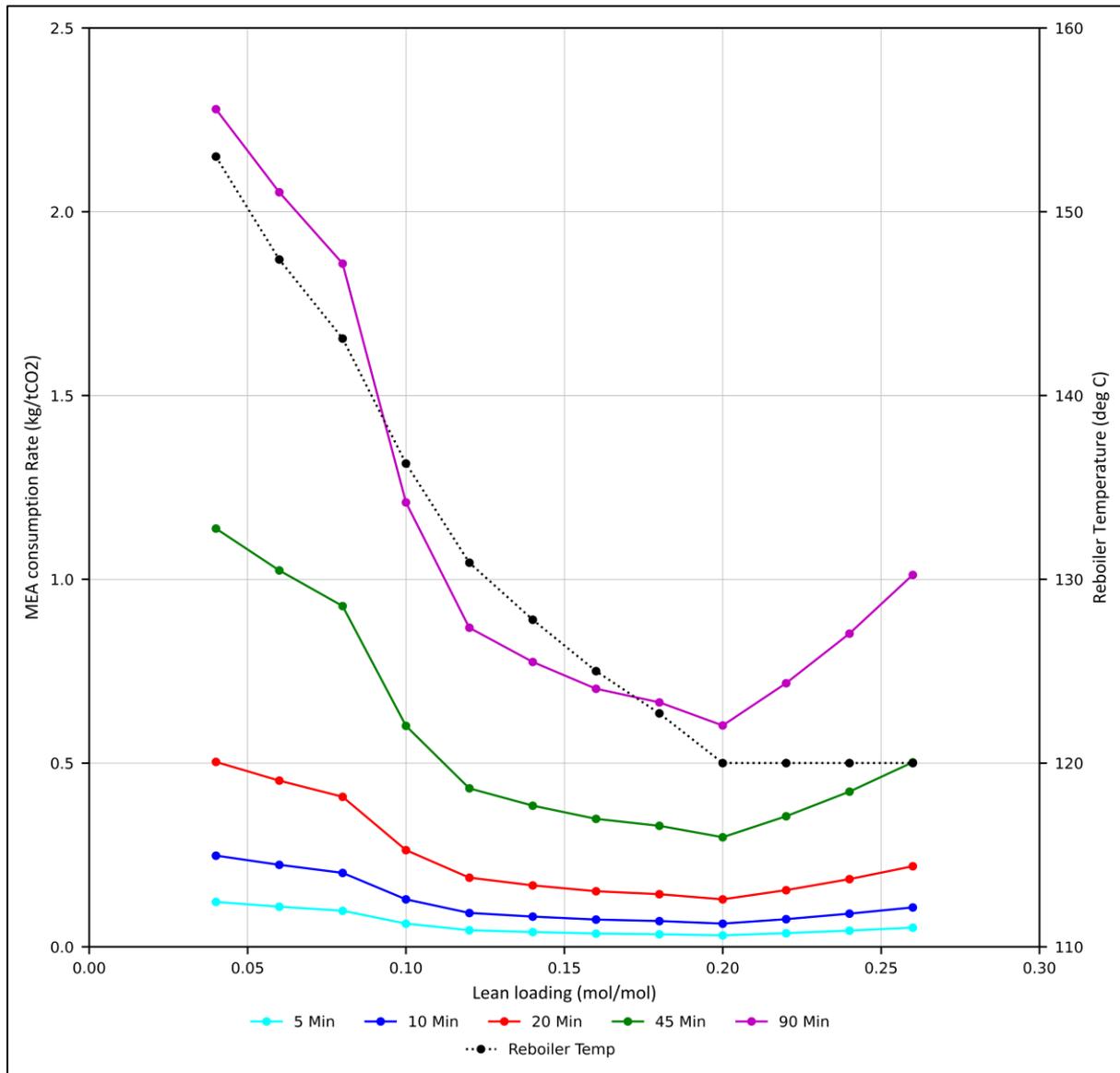


Figure 11 Lean loading vs MEA consumption rate

### 3.3 Oxidative Degradation

As described in section 2.3 a large disparity is noted between the estimated dissolved O<sub>2</sub> levels in the solvent when calculated using Aspen Plus vs the dissolved O<sub>2</sub> model provided in the DNM. This leads to vastly different predictions for the rate of MEA degradation in the system (see

Figure 12). Further experimental investigation is advised to attempt to explain and reconcile this disparity. For the purpose of this report the dissolved O<sub>2</sub> model provided in the DNM and described by equation 4 is used.

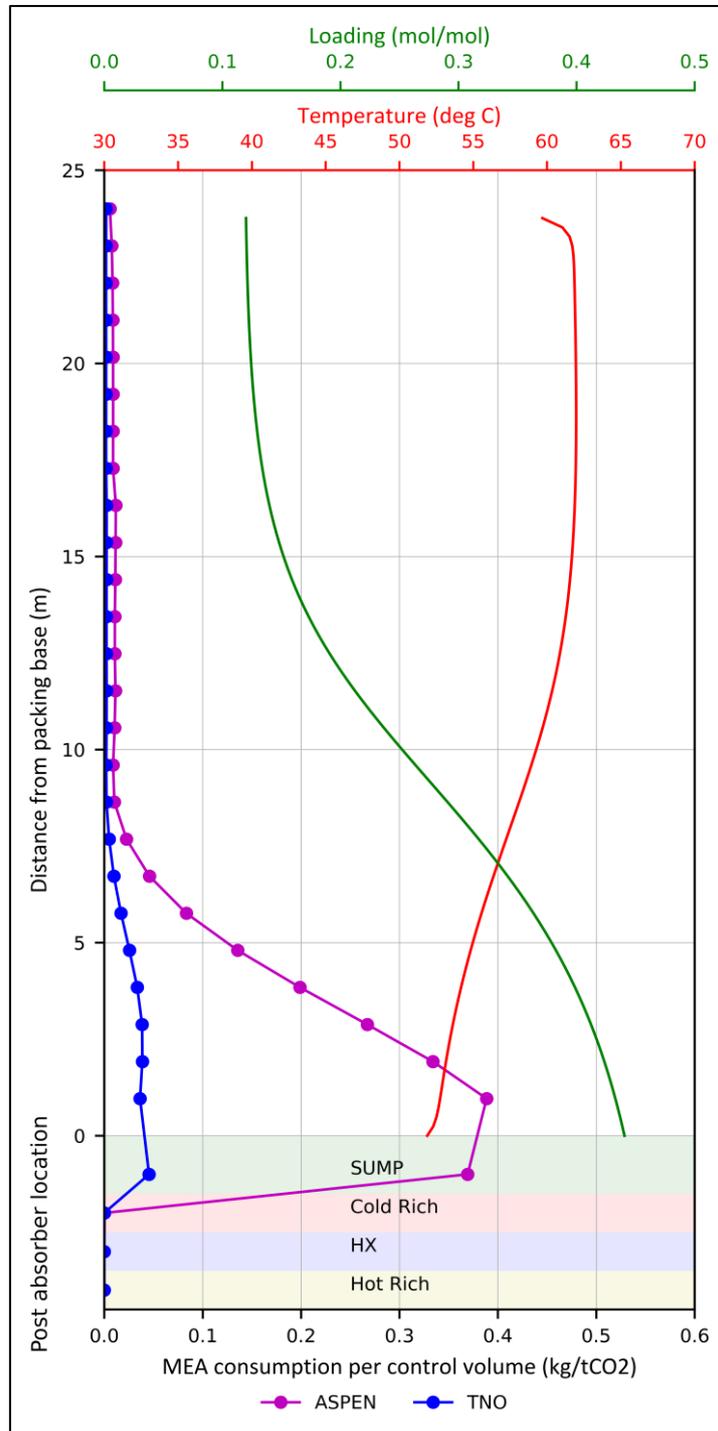


Figure 12 Comparison on MEA consumption between Aspen and TNO models for dissolved O<sub>2</sub> (Lean loading = 0.12)



Figure 13 illustrates the variation in oxidative degradation rates across the lean loading ranges investigated. A rapid increase in the amount of oxidative degradation is predicted in all cases at a loading above approximately  $0.35 \text{ molCO}_2/\text{molMEA}$ , this indicates a rate limitation on  $\text{O}_2$  consumption in the absorber below this loading value. This is further illustrated by Figure 14 which shows the reaction rate constant  $K$  for  $\text{O}_2$  consumption in a loaded 35%wt MEA solution for a range of solvent loadings and temperatures.

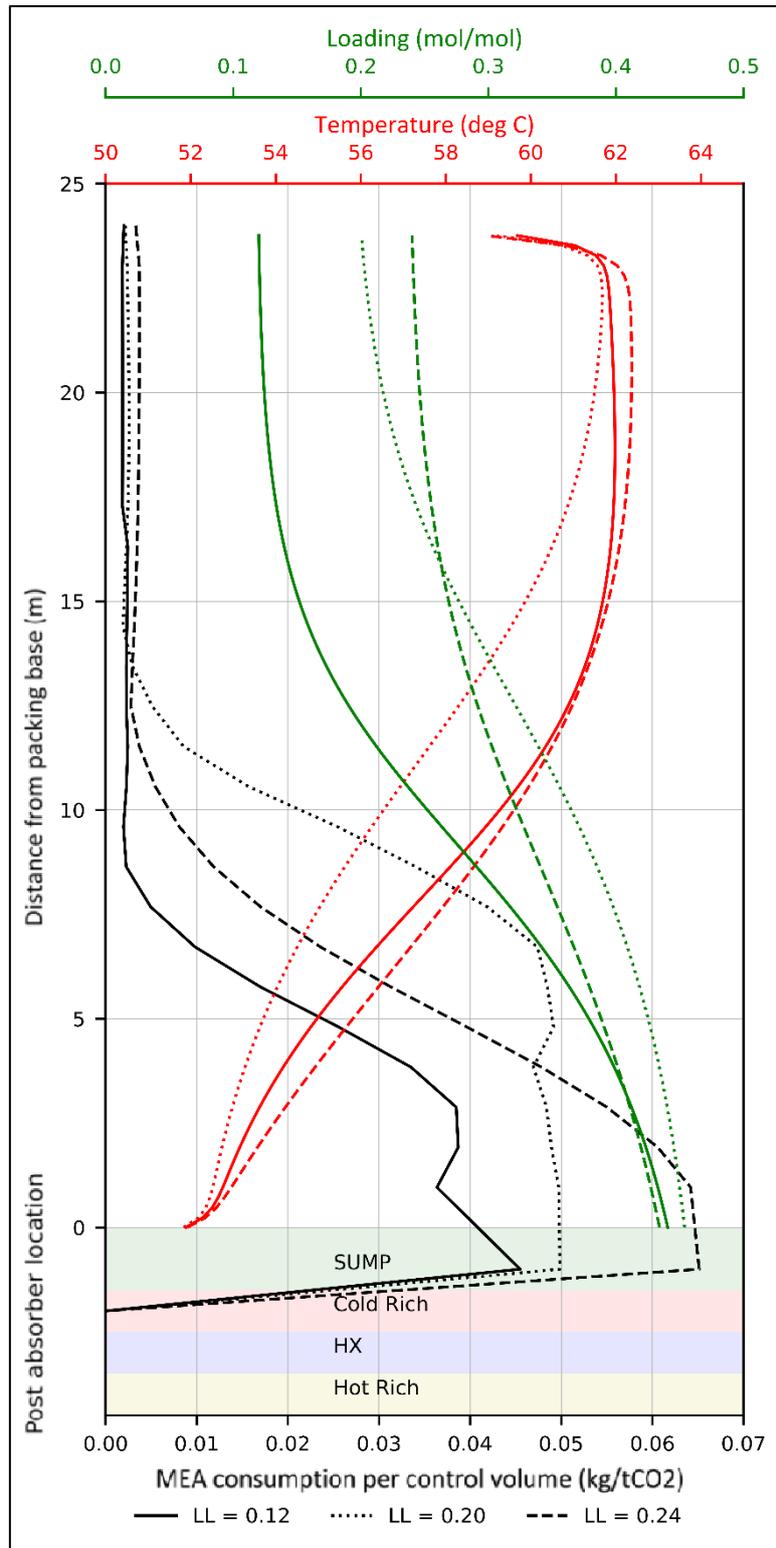


Figure 13 Comparison of Oxidative degradation across lean loading range

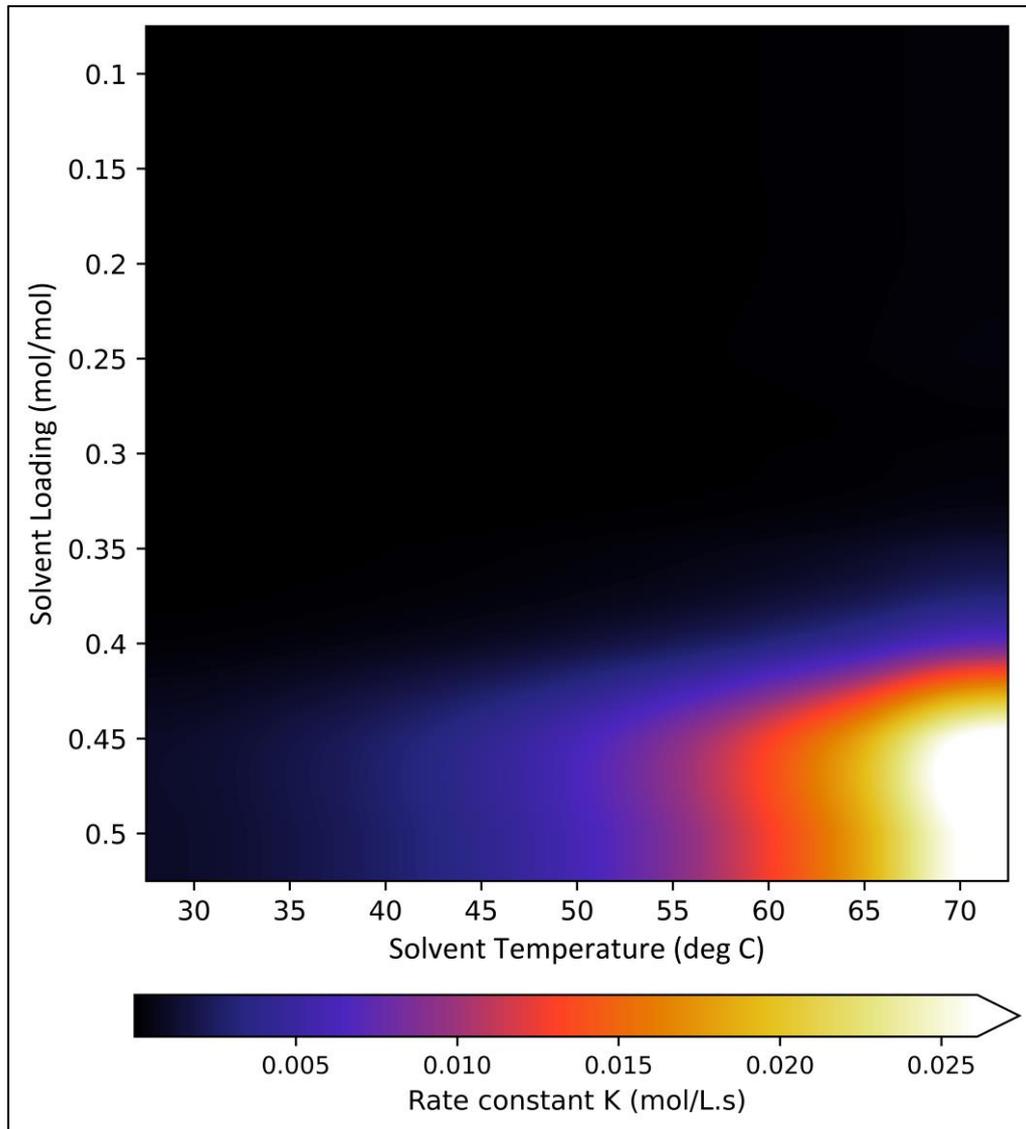


Figure 14 O<sub>2</sub> consumption reaction rate constant vs loading and temperature

### 3.4 Degradation management techniques

#### 3.4.1 Sherman FEED study

To form a basis for the investigation into the effective management of solvent degradation the PCCplant proposed in the recently published open source FEED study completed by Bechtel for the Sherman plant in the USA [5] is modelled under a variety of lean loading conditions and with the inclusion of three proposed solvent management techniques: thermal reclaiming, reboiler/absorber sump residence time manipulation and O<sub>2</sub> removal from the rich solvent. Process data from Aspen Plus [3] model developed by Michailos and Gibbins [4] was then used in the predictive tool described in section 2.5 while residence

Table 3) were based on inventory, levels in the reboiler and exchanger column hold up extracted from Solvent

<b>Residence Time</b>	<b>Unit</b>	<b>A</b>	<b>B</b>	<b>C</b>
Lean Loading	<i>mol/mol</i>	0.24	0.20	0.12
Absorber	<i>min</i>	5.4	6.5	7.1
Absorber Sump	<i>min</i>	8.0	10.6	13.0
Stripper	<i>min</i>	1.3	1.5	1.6
Reboiler/Sump	<i>min</i>	5.0	7.2	9.8
Cross HX (per side)	<i>min</i>	1.7	2.3	1.9
Pipework	<i>min</i>	2.4	4.8	6.2

times (see estimated solvent operational sump and heat surface areas, time were Aspen Plus. inventory and

operational levels in the sump and reboiler were assumed to be constant across all cases.

*Table 3 Sherman FEED study residence times*



Table 4 details the effect lean loading has on solvent degradation when no solvent management techniques are implemented. Although thermal degradation is predicted to increase in absolute terms as lean loading decrease (due to increasing reboiler operational temperatures) the increased CO<sub>2</sub> capture capacity per mol of solvent means that the specific degradation rate of MEA is seen to be lower at 0.12 mol/mol than 0.2 or 0.24; this is thought to be because the solvent is subject to less exposure to thermal and oxidative degradation conditions per unit of CO<sub>2</sub> captured (i.e. fewer circulations through the absorber and reboiler per unit time). Increased reboiler operational temperature is also explored in



Table 4 by means of increased stripper pressure. A consistent but minimal increase of ~1.5-2% in specific MEA degradation is observed across all cases. After the capture of 500 tCO<sub>2</sub>/m<sup>3</sup> solvent (corresponding with ~ 1 year of operation) impurity levels in the solvent were found to be very high, with levels between 1.0 - 0.51 mol/mol MEA, likely leading to drastic reductions in solvent performance.

Table 4 MEA Consumption with no solvent control techniques

Case	Unit	A.1	A.2	B.1	B.2	C.1	C.2
Capture Rate	%	95%	95%	95%	95%	99%	99%
Lean Loading	<i>mol/mol</i>	0.24	0.24	0.20	0.20	0.12	0.12
Rich Loading	<i>mol/mol</i>	0.434	0.434	0.454	0.454	0.441	0.441
Reboiler Temperature	<i>Deg C</i>	127.1	122.0	128.7	123.4	130.9	133.4
Stripper Pressure	<i>Bara</i>	2.4	2.0	2.4	2.0	2.4	2.6
SRD	<i>GJ/tCO<sub>2</sub></i>	3.81	3.84	3.54	3.63	3.73	3.65
Solvent Cycle Time	<i>min</i>	27.3	27.3	37.7	37.7	41.5	41.5
Residence Time Multiplayer	%	0	0	0	0	0	0
O <sub>2</sub> Removal	%	0%	0%	0%	0%	0%	0%
Reclaiming	<i>Week/inventory</i>	N/A	N/A	N/A	N/A	N/A	N/A
Oxidative MEA Consumption	<i>kg/tCO<sub>2</sub></i>	1.717	1.717	2.044	2.044	1.006	1.006
Thermal MEA Consumption	<i>kg/tCO<sub>2</sub></i>	0.085	0.053	0.096	0.059	0.074	0.104
Reclaiming MEA Consumption	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A	N/A	N/A	N/A
MEA recovery (HSS)	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A	N/A	N/A	N/A
Total MEA Consumption	<i>kg/tCO<sub>2</sub></i>	1.802	1.769	2.141	2.103	1.08	1.10
Waste Production Rate	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A	N/A	N/A	N/A
Caustic Requirement	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A	N/A	N/A	N/A
Impurities	<i>mol/mol MEA</i>	0.842	0.8208	0.9992	0.9747	0.5109	0.5261
Absorber % of Oxidative	%	96.2%	96.2%	97.6%	97.6%	95.5%	95.5%

### 3.4.2 Thermal Reclaiming

Thermal reclaiming takes advantage of the relative volatility of MEA when compared to its degradation compounds by boiling off the solvent inventory to be reclaimed. The vapour from the process, containing primarily clean MEA and water, is returned to the system, while the liquid waste, containing mostly degradation compounds and some remaining MEA and water, is collected and disposed of. Thermal reclaiming is typically completed in batch processes, where the entire solvent inventory is reclaimed in one process at set intervals, or on a semi continuous basis, where a slip stream of solvent is removed from the lean amine stream, reclaimed and the vaporised products, principally water vapour, MEA and CO<sub>2</sub>, are returned to the stripper. Semi-continuous reclaiming is investigated in this work due to the potential for thermal integration into the system, minimizing the energy penalty associated with it. A two-step thermal reclaiming system is modelled in Aspen Plus and integrated into a model of the Sherman FEED study PCC unit. Table 5 details the process parameters for the thermal reclaimer while a detailed process description can be found in [5].

Table 5 Thermal Reclaiming operational parameters

Parameter	Unit	Value
1 <sup>st</sup> stage flash Pressure	Bara	2.45
1 <sup>st</sup> stage flash Temperature	°C	155
1 <sup>st</sup> stage flash MEA recovery	%	72
2 <sup>nd</sup> stage flash Pressure	Bara	1.01
2 <sup>nd</sup> stage flash Temperature	°C	155

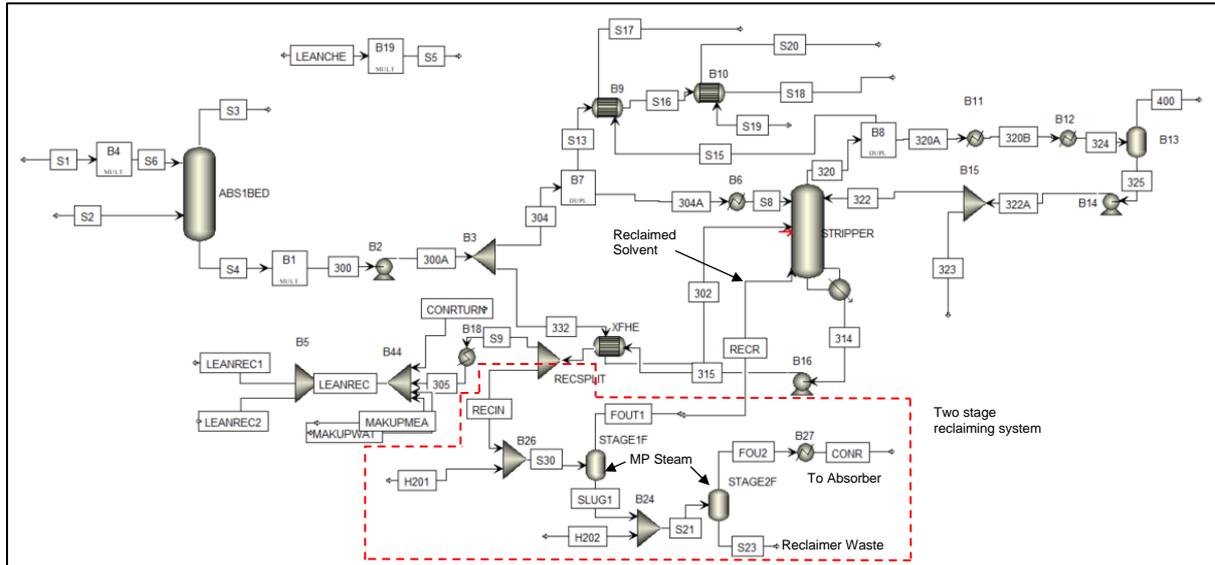


Figure 15 Two stage semi continuous thermal reclaiming system thermally integrated into PCC unit

Three different reclaiming rates, characterised by the time taken to pass the entire solvent inventory through the reclaiming process, are investigated for this work. The specific energy requirement, steady state impurity level and the additional MEA consumption (resulting from additional thermal degradation in the reclaimer and MEA losses with the waste product) is reported. The recovered amine from the first stage flash is returned to the bottom of the stripper column to improve thermal efficiency while the vapour from the second stage flash is returned to the absorber column. The impact on specific reboiler duty is reported in Table 6. A 1% increase was noted at the most aggressive reclaiming regime investigated with increases of 0.5% and 0.2% for 2 and 4 week reclaiming periods respectively.

Table 6 Specific energy impact of Thermal Reclaiming

Reclaiming Rate	SRD (GJ/tCO <sub>2</sub> )	Increase %
1 Week	3.766	1.0
2 Week	3.749	0.5
4 Week	3.739	0.2
None	3.730	N/A

Figure 16 illustrates how the reclaiming rate is predicted to influence the final steady state impurity levels in the solvent. All investigated regimes successfully maintained a constant impurity level after an initial period of increase but more aggressive reclaiming regimes achieved a lower steady state level. More work is, however, required to establish what level of impurities is acceptable, and more aggressive reclaiming rates will have CAPEX and OPEX implications with the level of MEA consumption in the reclaimer increasing at more intensive regimes (see Table 7). Importantly, though, the degradation models do not include any mechanisms by which maintaining a cleaner solvent inventory would contribute to reduced rates of degradation or reduced rates of emissions to atmosphere. Anecdotally it appears that this positive feedback on degradation may occur, but further long-term trials, with reclaiming, would be needed to investigate this.

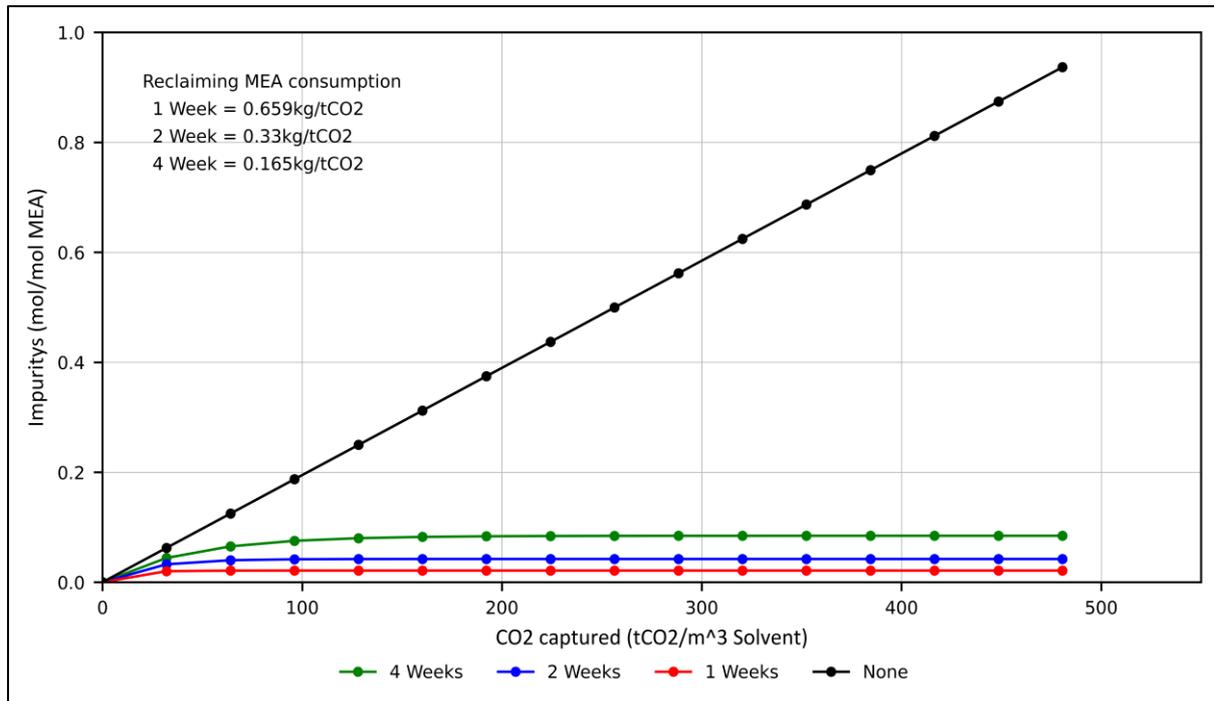


Figure 16 Build of up impurities in solvent for various reclaiming regimes (Lean loading = 0.20 mol/mol)

Table 7 Effect on thermal reclaiming on MEA consumption rates

Case	Unit	A.3	A.4	B.3	B.4	C.3	C.4
Capture Rate	%	95%	95%	95%	95%	99%	99%
Lean Loading	mol/mol	0.24	0.24	0.20	0.20	0.12	0.12
Rich Loading	mol/mol	0.434	0.434	0.454	0.454	0.441	0.441
Reboiler Temperature	deg C	122.0	122.0	123.4	123.4	130.9	130.9
Stripper Pressure	bara	2.0	2.0	2.0	2.0	2.4	2.4
SRD	GJ/tCO <sub>2</sub>	3.84	3.84	3.63	3.63	3.73	3.73
Solvent Cycle Time	min	27.3	27.3	37.7	37.7	41.5	41.5
Residence Time Multiplier	%	0	0	0	0	0	0
O <sub>2</sub> Removal	%	0%	0%	0%	0%	0%	0%
Reclaiming	Week/inventory	1	4	1	4	1	4
Oxidative MEA Consumption	kg/tCO <sub>2</sub>	1.717	1.717	2.044	2.044	1.006	1.006
Thermal MEA Consumption	kg/tCO <sub>2</sub>	0.051	0.051	0.057	0.057	0.072	0.072
Reclaiming MEA Consumption	kg/tCO <sub>2</sub>	0.864	0.216	0.659	0.165	0.521	0.13
MEA recovery (HSS)	kg/tCO <sub>2</sub>	-0.132	-0.126	-0.157	-0.147	-0.077	-0.07
Total MEA Consumption	kg/tCO <sub>2</sub>	2.5	1.858	2.604	2.12	1.522	1.138
Waste Production Rate	kg/tCO <sub>2</sub>	1.312	0.642	1.186	0.658	0.816	0.402
Caustic Requirement	kg/tCO <sub>2</sub>	0.088	0.084	0.105	0.098	0.051	0.047
Impurities	mol/mol MEA	0.0136	0.0544	0.0211	0.0845	0.014	0.056



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Absorber % of Oxidative	%	96.2%	96.2%	97.6%	97.6%	95.5%	95.5%
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### 3.4.3 Residence Time Manipulation

*To investigate the effect on of reboiler and absorber sump residence times on overall MEA consumption rates a 50% reduction in the residence time was applied and the results reported in*

Table 8. Due to the fast O<sub>2</sub> degradation kinetics reported in the DNM and the moderately low rich loadings seen, a 50% reduction in absorber residence time was found to have no effect on oxidative degradation. This is because dissolved O<sub>2</sub> in the absorber sump was found to have been fully consumed within the order of seconds not minutes; an expansion of the DNM to include more data points for O<sub>2</sub> degradation kinetics at higher loadings may serve to improve this assessment.

Reducing reboiler residence time was found to have a more promising effect with a 50% reduction in residence time corresponding to an approximate 30-35% reduction in thermal degradation.

*Table 8 Effect of residence time reduction on MEA consumption rates*

Case	Unit	A.5	B.5	C.5
Capture Rate	%	95%	95%	99%
Lean Loading	<i>mol/mol</i>	0.24	0.20	0.12
Rich Loading	<i>mol/mol</i>	0.434	0.454	0.441
Reboiler Temperature	<i>Deg C</i>	122.0	128.7	130.9
Stripper Pressure	<i>Bara</i>	2.0	2.4	2.4
SRD	<i>GJ/tCO<sub>2</sub></i>	3.84	3.54	3.73
Solvent Cycle Time	<i>min</i>	27.3	34.0	41.5
Residence Time Multiplier	%	-50%	-50%	-50%
O <sub>2</sub> Removal	%	0%	0%	0%
Reclaiming	<i>Week/inventory</i>	N/A	N/A	N/A
Oxidative MEA Consumption	<i>kg/tCO<sub>2</sub></i>	1.717	2.044	1.006
Thermal MEA Consumption	<i>kg/tCO<sub>2</sub></i>	0.035	0.042	0.05
Reclaiming MEA Consumption	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A
MEA recovery (HSS)	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A
Total MEA Consumption	<i>kg/tCO<sub>2</sub></i>	1.752	2.086	1.056
Waste Production Rate	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A
Caustic Requirement	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A
Impurities	<i>mol/mol</i>	0.809	0.963	0.4944
Absorber % of Oxidative	%	96.2%	97.6%	95.5%

### 3.4.4 Oxygen Removal

An O<sub>2</sub> removal devise was simulated by assuming that it would remove 90% of the O<sub>2</sub> dissolved in the solvent directly after the last stage of the absorber (prior to the sump). This was found to be effective at reducing post absorber oxidative degradation (see Table 9). However, as ~ 95% of the oxidative degradation is observed to occur in the absorber, the effect on the overall MEA consumption rate is modest, reducing oxidative degradation by 2-4%. The primary reason for this is that low rates of dissolved O<sub>2</sub> are predicted to be present in the sump by the current dissolved O<sub>2</sub> model, expansion on this model may lead to a review of this conclusion.

Table 9 Effect of O<sub>2</sub> removal on MEA consumption rates

Case	Unit	A.6	B.6	C.6
Capture Rate	%	95%	95%	99%
Lean Loading	<i>mol/mol</i>	0.24	0.20	0.12
Rich Loading	<i>mol/mol</i>	0.434	0.454	0.441
Reboiler Temperature	<i>Deg C</i>	122.0	128.7	130.9
Stripper Pressure	<i>Bara</i>	2.0	2.4	2.4
SRD	<i>GJ/tCO<sub>2</sub></i>	3.84	3.54	3.73
Solvent Cycle Time	<i>min</i>	27.3	28.6	41.5
Residence Time Multiplayer	%	0%	0%	0%
O <sub>2</sub> Removal	%	90%	90%	90%
Reclaiming	<i>Week/inventory</i>	N/A	N/A	N/A
Oxidative MEA Consumption	<i>kg/tCO<sub>2</sub></i>	1.658	1.998	0.965
Thermal MEA Consumption	<i>kg/tCO<sub>2</sub></i>	0.053	0.059	0.075
Reclaiming MEA Consumption	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A
MEA recovery (HSS)	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A
Total MEA Consumption	<i>kg/tCO<sub>2</sub></i>	1.711	2.057	1.04
Waste Production Rate	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A
Caustic Requirement	<i>kg/tCO<sub>2</sub></i>	N/A	N/A	N/A
Impurities	<i>mol/mol</i>	0.794	0.9536	0.4922
Absorber % of Oxidative	%	99.6%	99.8%	99.5%

### 3.4.5 Optimized Solvent Management

Table 10 reports the effect of MEA consumption rates and solvent impurities when all three solvent management techniques are applied. The modest reductions in overall MEA consumption rate observed by residence time reductions and O<sub>2</sub> removal is found to approximately offset the estimated MEA loss through thermal reclaiming. Using the assumptions in this study thermal reclaiming at a rate of 1 solvent inventory every 4 weeks was found to effectively maintain solvent impurities at a low level while having minimal impact on plant efficiency.

Table 10 MEA Consumption rates with solvent management techniques applied

Case	Unit	A.7	B.7	C.7
Capture Rate	%	95%	95%	99%
Lean Loading	<i>mol/mol</i>	0.24	0.20	0.12
Rich Loading	<i>mol/mol</i>	0.434	0.454	0.441
Reboiler Temperature	<i>Deg C</i>	122.0	128.7	130.9
Stripper Pressure	<i>Bara</i>	2.0	2.4	2.4
SRD	<i>GJ/tCO<sub>2</sub></i>	3.84	3.54	3.73
Solvent Cycle Time	<i>min</i>	27.3	37.7	41.5
Residence Time Multiplayer	%	-50%	-50%	-50%
O <sub>2</sub> Removal	%	90%	90%	90%
Reclaiming	<i>Week/inventory</i>	4	4	4
Oxidative MEA Consumption	<i>kg/tCO<sub>2</sub></i>	1.658	1.998	0.965
Thermal MEA Consumption	<i>kg/tCO<sub>2</sub></i>	0.035	0.041	0.049
Reclaiming MEA Consumption	<i>kg/tCO<sub>2</sub></i>	0.216	0.165	0.13
MEA recovery (HSS)	<i>kg/tCO<sub>2</sub></i>	-0.122	-0.143	-0.067
Total MEA Consumption	<i>kg/tCO<sub>2</sub></i>	1.787	2.061	1.077
Waste Production Rate	<i>kg/tCO<sub>2</sub></i>	0.615	0.634	0.374
Caustic Requirement	<i>kg/tCO<sub>2</sub></i>	0.081	0.096	0.045
Impurities	<i>mol/mol</i>	0.0518	0.0816	0.0521
Absorber % of Oxidative	%	99.6%	99.8%	99.5%

## 4 Conclusions

### 4.1 Model limitations

- No interactions between the oxidative and thermal degradation models is included in the predictive tool, positive or negative feedback loops between degradation products may be present in real operations.
- No benefits from reclaiming in terms of reduced degradation rates.
- No allowance for corrosion effects or flue gas impurities is included.
- MEA loss through the emission to air is not included.

### 4.2 Future Work

- Develop an integrated degradation model including any interactions between thermal and oxidative degradation compounds, corrosion effects and flue gas impurities.
- Expand the O<sub>2</sub> degradation kinetics data in the DNM model to include more loading points; current linear interpolation between distant loading points may induce large errors.
- Review dissolved O<sub>2</sub> model, with a particular view on the build-up of O<sub>2</sub> in the rich solvent entering the absorber sump.
- Investigate the effect of impurity level on degradation; establish a maximum steady state solvent impurity level to advise reclaiming regimes.
- Undertake appropriate long-term trials, including reclaiming and DO removal, to test modelling assumptions.

### 4.3 Main Takeaways

- Lower lean loadings (requiring higher reboiler temperatures) do not appear to necessarily increase plant MEA consumption rates, an holistic view of the entire plant operation is required. Increased solvent absorption capacity (i.e. lean to rich loading differential), leading to reduced solvent exposure to oxidative degradation conditions in the absorber per tonne of CO<sub>2</sub> captured, this may offset or reverse the effect of any additional thermal degradation.
- Thermal reclaiming can effectively maintain solvent impurities at low levels over extended periods with minimal effect on the specific reboiler duty when effectively thermally integrated. Unnecessarily aggressive reclaiming regimes can lead to substantial MEA losses in the reclaiming system and so rates must be optimized, although no way to do this exists in current modelling.
- Oxidative degradation was found to contribute to between 91-97% of all MEA degradation observed ~ 95% of which occurs in the absorber. This ratio of oxidative to thermal degradation is, however, highly dependent on reboiler residence time. The Sherman FEED study was calculated to have a low reboiler residence time of 5-10 minutes; this may not be representative for all cases.
- O<sub>2</sub> removal was found to be effective at reducing post-absorber MEA degradation. However, as the majority of degradation is seen to occur in the absorber, the overall benefit is minimal.
- Reducing reboiler residence time was found to be effective at reducing the rate of thermal degradation. No effect on overall oxidative degradation rates were seen when absorber sump residence time was reduced.



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## APPENDIX A – PREDITIVE MODEL

```
""
Created on Sun Feb 12 16:46:44 2023

@author: Daniel Mullen
""
import numpy as np
import math
import pandas as pd

Path = "X:/XXX/XXX/XXX/XXX/XXX/XXX.xlsx"

Cols_Abs = ["Stage", "Packing Height (m)", "Vapour T", "Liquid Flow Stage
(KG/s)", "Volume (m^3/s)", "Mole MEA", "Mole CO2", "Loading", "Liquid holdup
(m^3)", "Res Time", "O2 mole"]
Cols_Str = ["Stage", "Packing Height (m)", "Vapour T", "Liquid Flow Stage
(KG/s)", "Volume (m^3/s)", "Mole MEA", "Mole CO2", "Loading", "Liquid holdup
(m^3)", "Res Time"]

#Call file containing column data
Absorber = pd.read_excel(Path, sheet_name="X", usecols=Cols_Abs)
Stripper = pd.read_excel(Path, sheet_name="Y", usecols=Cols_Str)

#Create Arrays for columns
Absorber_T = np.array(Absorber["Vapour T"]); Absorber_Load =
np.array(Absorber["Loading"]); Absorber_Res = np.array(Absorber["Res
Time"]); Absorber_Vol = np.array(Absorber["Liquid holdup (m^3)"]);
Absorber_O2 = np.array(Absorber["O2 mole"])/1000;
Stripper_T = np.array(Stripper["Vapour T"]); Stripper_Load =
np.array(Stripper["Loading"]); Stripper_Res = np.array(Stripper["Res
Time"]); Stripper_Vol = np.array(Stripper["Liquid holdup (m^3)"]);

Oxidative_On = "Y"; Thermal_On = "Y"; #Choose what aspects to calculate

#Solvent managment
Reclaiming_On = "Y"; O2_Removal_On = "Y"; Reduce_Restime_On = "Y"
Reclaiming_Rate = 4; Reclaiming_Eff = 0.98; Reclaim_T = 155; # deg C

O2_Removal = 0.9
Res_Time_Mult = 0.5

#Plant Parameters
Lean_Loading = 0.12; Rich_Loading = 0.441; # mol/mol
MEA_wt = 0.35 # %wt CO2 free
Stripper_P = 2.4 # bara
```



```
O2_MF = 0.12; FG_Pressure = 1.08677 # bara
CO2_To_Capture = 500 # tCO2/m^3 solvent
T_Sump = 43.4; # deg C
Hot_Rich_T = 125.4; # deg C
Reboiler_Temp = 130.9; # deg C
T_Lean = T_Sump + 10 # deg C

# Assume linear temperature profile across HX
Temp_HX_Rich = [T_Sump, T_Sump + (Hot_Rich_T-T_Sump)/5, T_Sump +
2*(Hot_Rich_T-T_Sump)/5, T_Sump + 3*(Hot_Rich_T-T_Sump)/5, T_Sump +
4*(Hot_Rich_T-T_Sump)/5, Hot_Rich_T]
Temp_HX_Lean = [T_Lean, T_Lean + (Reboiler_Temp-T_Lean)/5, T_Lean +
2*(Reboiler_Temp-T_Lean)/5, T_Lean + 3*(Reboiler_Temp-T_Lean)/5, T_Lean +
4*(Reboiler_Temp-T_Lean)/5, Reboiler_Temp]

#Residence times (minutes)
Res_time_Absorber = np.sum(Absorber_Res)/60
Res_time_Absorber_Sump = 13;
Res_time_Pipes = 6.2;
Res_time_HX = 1.9;
Res_time_Stripper = np.sum(Stripper_Res)/60
Res_time_Reboiler = 9.8;
Res_time_Reclaim = 5;

# Sum of all residence times
Cycle_Time = 2*Res_time_HX + Res_time_Reboiler + Res_time_Pipes +
Res_time_Absorber_Sump + Res_time_Stripper + Res_time_Absorber

#Setting constants
R = 8.314; K = 273.15; MEA_moles_m3 = 16383; Rec_Rate =
0.006/Reclaiming_Rate; Ox_Stoich_Factor = 0.32
MEA_initial = MEA_wt*MEA_moles_m3; MEA_Con = MEA_initial
Rich_CO2_Con = MEA_initial*Rich>Loading; Lean_CO2_Con =
MEA_initial*Lean>Loading
Stoch_F = 1.3
MolWeight =
np.array([61.08, 44.01, 104.15, 130.15, 147.315, 173.31, 148.16, 31.998, 18.015])/1
000
Thermal_Deg_MW = 100/1000; Oxi_Deg_MW = 50/1000

if Reduce_Restime_On == "Y": # Apply residence time reduction factor if
applicable
    Res_time_Reboiler = Res_time_Reboiler*Res_Time_Mult
    Res_time_Absorber_Sump = Res_time_Absorber_Sump*Res_Time_Mult

if O2_Removal_On == "N": # Apply O2 removal if applicable
    O2_Removal = 1
else:
    O2_Removal = 1 - O2_Removal

def Interpol(Upper, Lower, Value):
    X = (Value-Lower)/(Upper-Lower); #Function for linear interpolation
    return X

def ThermalDeg(Res_time, Res_Temp, CO2_Con, Flow_Rate): # Function for
Thermal Degradation
```



```
global MEA_Con, HEEDA, TRIMEA, HEIA, AEHEIA, BHEU, CO2_Mol, H2O_Mol
# Rate constants and activation energys Braakhuis et al. 2022
Kthref = np.array([1.599e-11,1.117e-10,3.054e-10,2.839e-10,1.281e-12])
Eth = np.array([151100,121500,142600,136200,0])

Kth_array = np.array([])
# Temperature dependant rate constant for each reaction in the thermal
degradation model
for i in range(len(Kthref)):
    Kth = Kthref[i]*math.exp((-Eth[i]/R)*((1/(Res_Temp+K))-(1/400)))
    Kth_array = np.append(Kth_array,Kth)

for i in range(int(Res_time*60*Res_Time_Mult)): #Thermal degradation
per second
    HEEDA_S = Kth_array[0]*MEA_Con*CO2_Con # HEEDA production
    BHEU_S = Kth_array[4]*MEA_Con*CO2_Con # BHEU production

    MEA_Con -= 2*(HEEDA_S)*Flow_Rate # MEA consumption
    MEA_Con -= 2*(BHEU_S)*Flow_Rate # MEA consumption

    HEEDA += HEEDA_S*Flow_Rate # Increase HEEDA Concentration
    BHEU += BHEU_S*Flow_Rate # Increase BHEU Concentration
    CO2_Con -= BHEU_S*Flow_Rate # CO2 consumption

    TRIMEA_S = Kth_array[1]*CO2_Con*HEEDA # TRIMEA production
    HEIA_S = Kth_array[2]*CO2_Con*HEEDA # HEIA production

    HEEDA -= TRIMEA_S *Flow_Rate # HEEDA consumption
    HEEDA -= HEIA_S*Flow_Rate # HEEDA consumption

    MEA_Con -= TRIMEA_S*Flow_Rate # MEA consumption
    CO2_Con -= HEIA_S*Flow_Rate # CO2 consumption
    HEIA += HEIA_S*Flow_Rate # Increase HEIA Concentration
    TRIMEA += TRIMEA_S*Flow_Rate # Increase TRIMEA Concentration

    AEHEIA_S = Kth_array[3]*CO2_Con*TRIMEA # AEHEIA production
    TRIMEA -= AEHEIA_S*Flow_Rate # TRIMEA consumption
    AEHEIA += AEHEIA_S*Flow_Rate # Increase AEHEIA Concentration
    CO2_Con -= AEHEIA_S*Flow_Rate # CO2 consumption
    CO2_Mol += (AEHEIA_S + BHEU_S + HEIA_S)*Flow_Rate # Number of CO2
Mols consumed
    H2O_Mol += (HEEDA_S + BHEU_S + HEIA_S + TRIMEA_S +
AEHEIA_S)*Flow_Rate # Number of H2O Mols consumed

def Oxidative(R_Time,Temp>Loading,O2_initial): # Function for Oixdative
Degradation
    # Loading, Activation Energy, Rate constants ref DNM LAUNCH project
    O2_Kinetic_Array = np.array([[0.2,0.3,0.5],

[8.115603343E+04,8.455417390E+04,6.188256201E+04],

[2.117385069E+12/3600,7.212039151E+12/3600,7.525030566E+08/3600]])
    if O2_initial == 0:
        MEA_Consumed = 0; O2_Consumed = 0; O2_Final = 0 # If there is no
Dissolved O2
```



```
else:
    if Loading <= O2_Kinetic_Array[0][0]: # Loading Less than 0.2
        Ea = O2_Kinetic_Array[1][0]
        Ko = O2_Kinetic_Array[2][0]
    elif Loading > O2_Kinetic_Array[0][0] and Loading <=
O2_Kinetic_Array[0][1]: # Loading 0.2 - 0.3
        X = Interpol(0.3, 0.2, Loading)
        Ea = O2_Kinetic_Array[1][0] + X*(O2_Kinetic_Array[1][1]-
O2_Kinetic_Array[1][0]) # Linear interpolation
        Ko = O2_Kinetic_Array[2][0] + X*(O2_Kinetic_Array[2][1]-
O2_Kinetic_Array[2][0]) # Linear interpolation
    elif Loading > O2_Kinetic_Array[0][1] and Loading <
O2_Kinetic_Array[0][2]: # Loading 0.3 - 0.5
        X = Interpol(0.5, 0.3, Loading)
        Ea = O2_Kinetic_Array[1][1] + X*(O2_Kinetic_Array[1][2]-
O2_Kinetic_Array[1][1]) # Linear interpolation
        Ko = O2_Kinetic_Array[2][1] + X*(O2_Kinetic_Array[2][2]-
O2_Kinetic_Array[2][1]) # Linear interpolation
    else: # Greater than 0.5
        Ea = O2_Kinetic_Array[1][2]
        Ko = O2_Kinetic_Array[2][2]

    K1 = Ko*math.exp(-Ea/(R*(Temp+K))) # Temperature dependant Rate
constant

    O2_Consumed = 0; O2_1 = O2_initial
    for i in range(int(R_Time*60)): # Oxidative degradation per second
        O2_2 = ((-K1+(2*math.sqrt(O2_1)))**2)/4
        if (O2_1 - O2_2) < 0 or (O2_Consumed + (O2_1 - O2_2))/O2_initial
> 0.999: # Programing efficiency, exit at 99.9% O2 consumption if applicable
            break
        else:
            O2_Consumed += O2_1 - O2_2
            O2_1 = O2_2 # New O2

    O2_Final = O2_initial - O2_Consumed
    O2_Consumed = 1000*(O2_initial-O2_Final) # Mols O2 consumed per m^3
    MEA_Consumed = (O2_Consumed/Stoch_F) # MEA consumed based on DNM
factor
    return [O2_Consumed,MEA_Consumed,O2_Final]

# Set variables to zero
HEEDA = 0; TRIMEA = 0; HEIA = 0; AEHEIA = 0; BHEU = 0; Ox_Products = 0; HSS
= 0; O_Waste_Unrecover = 0; O_Waste_Thermal = 0;
CO2_Cap = 0; Total_Waste = 0; MEA_Make_up = 0; H2O_Mol = 0; CO2_Mol = 0;
Ox_MEA = 0; count = 0
Caustic_Weight = 0; O2_product = 0; Ox_Mol_Impur = 0; Reclam_MEA = 0;
MEA_Caustic = 0

while CO2_Cap < CO2_To_Capture: # While CO2 captured is less than the goal
CO2
    count += 1 # Number of capture and regeneration cycles

    if Oxidative_On == "Y": # If including Oxidative Degradation
        Absorber_Deg = 0; Ox_Sump = 0;
        for i in range(len(Absorber_T)):
```



```
Do = (-8.53673240468999E-06*Absorber_T[i] + -
0.0002381010855393191*Absorber_Load[i] +
0.00107762934963769)*FG_Pressure*O2_MF # Dissolved O2 as per TNO model
Array = Oxidative(Absorber_Res[i]/60, Absorber_T[i],
Absorber_Load[i], Do) # Oxidative degradation per absorber stage
Absorber_Deg += Array[1]; # MEA consumed

Sump_O2 = (-8.53673240468999E-06*T_Sump + -
0.0002381010855393191*Rich>Loading +
0.00107762934963769)*FG_Pressure*O2_MF*O2_Removal # Dissolved O2 as per TNO
model

Sump =
Oxidative(Res_time_Absorber_Sump,T_Sump,Rich>Loading,Sump_O2) # Oxidative
degradation Absorber Sump
Rich_Cold = Oxidative(Res_time_Pipes/4,T_Sump,Rich>Loading,Sump[2])
# Oxidative degradation Rich Pipe before HX

HX_Deg = 0
for i in range(len(Temp_HX_Rich)): # Oxidative degradation HX
if i == 0:
HX_Array = Oxidative(Res_time_HX/6, Temp_HX_Rich[i],
Rich>Loading, Rich_Cold[2])
else:
HX_Array = Oxidative(Res_time_HX/6, Temp_HX_Rich[i],
Rich>Loading, HX_Array[2])
HX_Deg += HX_Array[1]

Rich_Hot =
Oxidative(Res_time_Pipes/4,Hot_Rich_T,Rich>Loading,HX_Array[2]) # Oxidative
degradation Rich Pipe after HX
MEA_Con -= Sump[1] + Rich_Cold[1] + Rich_Hot[1] + Absorber_Deg +
HX_Deg # Total MEA consumption due to Oxidative degradation
Absorber_percentage = 100*Absorber_Deg/(Sump[1] + Rich_Cold[1] +
Rich_Hot[1] + Absorber_Deg + HX_Deg) # amount of Oxidative degradation in
absorber
Ox_Mol_Impur = (MEA_initial - MEA_Con)*Ox_Stoich_Factor # Impuritys
due to Oxidative degradation

O_Waste_Unrecover += Ox_Mol_Impur*0.6; HSS += Ox_Mol_Impur*0.25;
O_Waste_Thermal += Ox_Mol_Impur*0.15 # Breakdown in Impuritys due to
Oxidative degradation

O2_product += Rich_Hot[2]*1000*MolWeight[7] # O2 in CO2 stream
Ox_MEA += MEA_initial - MEA_Con

if Thermal_On == "Y": # If including Thermal Degradation
for i in range(len(Absorber_T)): # Thermal Degradation in Absorber
Absorber_Thermal = ThermalDeg(Absorber_Res[i]/60,
Absorber_T[i], Absorber_Load[i]*MEA_Con, 1)
Cold_Rich_Pipe = ThermalDeg(Res_time_Pipes/4, T_Sump, Rich_CO2_Con,
1) # Thermal Degradation in Cold Rich Pipe
for i in range(len(Temp_HX_Rich)):
HX_Rich = ThermalDeg(Res_time_HX/6, Temp_HX_Rich[i],
Rich_CO2_Con, 1) # Thermal Degradation in HX
```



```
Hot_Rich_Pipe = ThermalDeg(Res_time_Pipes/4, Hot_Rich_T,
Rich_CO2_Con, 1) # Thermal Degradation in Hot Rich Pipe
for i in range(len(Stripper_T)):
    Stripper = ThermalDeg(Stripper_Res[i]/60, Stripper_T[i],
Stripper_Load[i]*MEA_Con, 1) # Thermal Degradation in Stripper
    Reboiler = ThermalDeg(Res_time_Reboiler, Reboiler_Temp,
Lean_CO2_Con, 1) # Thermal Degradation in Reboiler
    for i in range(len(Temp_HX_Lean)):
        HX_Lean = ThermalDeg(Res_time_HX/6, Temp_HX_Lean[i],
Lean_CO2_Con, 1) # Thermal Degradation in Lean Pipe

CO2_Cap += (Rich_Loading - Lean_Loading)*MEA_Con*(MolWeight[1]/1000) #
CO2 captured

if Reclaiming_On == "Y": # If including Reclaiming
    MEA1 = MEA_Con
    Reclaiming = ThermalDeg(Res_time_Reclaim, Reclaim_T, Lean_CO2_Con,
Rec_Rate)
    Reclam_MEA += MEA1 - MEA_Con # MEA consumed due to thermal
degradation in the reclaimier
    Reclam_MEA += MEA_Con*Rec_Rate*(1-Reclaiming_Eff) # MEA recovered in
the reclaimier
    MEA_Con += HSS*Rec_Rate*Reclaiming_Eff # MEA recovered due to HSS
netrulisation
    MEA_Caustic += HSS*Rec_Rate*Reclaiming_Eff # Caustic required
    Total_Waste += Reclaiming_Eff*Rec_Rate*(HEEDA*(MolWeight[2]) +
HEIA*(MolWeight[3]) + TRIMEA*(MolWeight[4]) + AEHEIA*(MolWeight[5]) +
BHEU*(MolWeight[6]) + O_Waste_Unrecover*Oxi_Deg_MW +
O_Waste_Thermal*Thermal_Deg_MW) + Rec_Rate*HSS*(1-
Reclaiming_Eff)*(MolWeight[0]) + MEA_Con*Rec_Rate*(1-
Reclaiming_Eff)*MolWeight[0] # Waste produced in KG
    HEEDA -= HEEDA*Rec_Rate*Reclaiming_Eff # reduction in impurities due
to reclaiming
    TRIMEA -= TRIMEA*Rec_Rate*Reclaiming_Eff
    HEIA -= HEIA*Rec_Rate*Reclaiming_Eff
    AEHEIA -= AEHEIA*Rec_Rate*Reclaiming_Eff
    BHEU -= BHEU*Rec_Rate*Reclaiming_Eff
    Caustic_Weight += HSS*Rec_Rate*(39.9971/1000)
    HSS -= HSS*Rec_Rate
    MEA_Con -= MEA_Con*Rec_Rate*(1-Reclaiming_Eff)
    O_Waste_Unrecover -= O_Waste_Unrecover*Rec_Rate*Reclaiming_Eff
    O_Waste_Thermal -= O_Waste_Thermal*Rec_Rate*Reclaiming_Eff

Impurity_Mol = HEEDA + TRIMEA + HEIA + AEHEIA + BHEU +
O_Waste_Unrecover + HSS + O_Waste_Thermal
MEA_Make_up += (MEA_inital - MEA_Con)*MolWeight[0]; # MEA makeup per
cycle
MEA_Con = MEA_inital

Impuritys_Mass = HEEDA*(MolWeight[2]) + HEIA*(MolWeight[3]) +
TRIMEA*(MolWeight[4]) + AEHEIA*(MolWeight[5]) + BHEU*(MolWeight[6]) +
O_Waste_Unrecover*Oxi_Deg_MW + HSS*(MolWeight[0]) +
O_Waste_Thermal*Thermal_Deg_MW

#Printing results
```



```
print("Cycle Time: "+ str(round(Cycle_Time,1)) + " min")
print("Lean Loading: " + str(Lean>Loading) + " mol/mol, Pressure: " +
str(Stripper_P) + " bar, O2 Removal:" + O2_Removal_On + ", Restime
Multiple: " + Reduce_Restime_On + ", Reclaiming: " + Reclaiming_On )
print("MEA consumption: " + str(round(MEA_Make_up/CO2_Cap,3))+ " kg/tCO2")
print("MEA consumption Ox: " + str(round(Ox_MEA*MolWeight[0]/CO2_Cap,3))+ "
kg/tCO2")
print("MEA consumption Reclaiming: " +
str(round(Reclam_MEA*MolWeight[0]/CO2_Cap,3))+ " kg/tCO2")
print("MEA Recovery Caustic: -" +
str(round(MEA_Caustic*MolWeight[0]/CO2_Cap,3))+ " kg/tCO2")
print("Impuritys: " + str(round(Impurity_Mol/MEA_Con,4)) + "mol/mol MEA")
print("Waste Production: " + str(round>Total_Waste/CO2_Cap,3)) + "kg/tCO2")
print("Caustic: " + str(round(Caustic_Weight/CO2_Cap,3)) + "kg/tCO2")
print("O2 in product: " + str(round(O2_product/CO2_Cap,7)) + "mg/tCO2")
print("% of oxidative degradation occurring in absorber: " +
str(round(Absorber_precentage,1)) + "%")
```