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Understanding solvent degradation: A study from three different pilot plants within the OCTAVIUS project

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Abstract

Degradation of amines is one of the most important issues to be addressed for absorption-desorption based post-combustion CO_2 capture. Several laboratory studies have been performed to identify the degradation products and understand the mechanisms of degradation. However, there seems to be a gap in knowledge from translating the lab scale studies to observations from the pilot campaigns. Moreover, the observations from different pilot plant campaigns can be quite different. The objective of this study is to compare the solvent degradation behavior from different campaigns and highlight their causes in terms of solvent metal content and ammonia emissions. Results from the following different pilot plants are evaluated: (a) TNO's CO_2 capture plant at Maasvlakte, the Netherlands, (b) EnBW's CO_2 capture plant at Heilbronn, Germany and (c) ENEL's CO_2 capture plant at Brindisi, Italy. The different rate of oxidative degradation are correlated to the different operating conditions and layout of the pilot plants. Along with these results, kinetic models based on laboratory studies are used to compare the pilot plant observations, highlighting the differences between lab-scale studies and pilot plant studies.

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Keywords: 2-Ethanolamine; Oxidative degeneration; Operating Conditions; Metals; Prediction of Ammonia emissions

1. Introduction

Absorption on amine solvents to remove acid gases is a mature technology and has been widely used to remove SO_2 and H_2S in oil refineries[1]. However, extending this solution on removal of CO_2 from oxidizing environments such as flue gases can cause serious problems of solvent loss, decreased solvent capacity, formation of degradation

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products, ammonia emissions and aerosols emissions[2,3,4,5]. Thus, understanding of solvent degradation is necessary to have a deeper insight into these issues, which hinder the applicability of the process in power plants.

Solvent degradation in a post-combustion CO_2 capture (PCC) set-up is categorized mainly into oxidative degradation and thermal degradation. Thermal degradation occurs mainly at high temperatures of stripper (120^0C) in abundance of CO_2. Contrary to this, oxidative degradation is a complex catalytic mechanism occurring in the absorber at lower temperature conditions (55^0C) [1,6]. The solvent reacts with oxygen to form primary degradation products, such as organic acids (heat stable salts) and ammonia, which further react to form secondary degradation products. Heat stable salts (HSS) are non-regenerable and might accelerate corrosiveness of the system[7]. When metals leaches into the solvent system, it initiates an auto-oxidative degradation mechanism, making it difficult to understand and predict[8,9]. These degradation pathways reduce the solvent's CO_2 capturing capacity and account for 4% of the total cost of CO_2 sequestration[10].

A significant amount of laboratory scale experiments on accelerated degradation have been reported for better understanding of the system[3,11,12,13]. However, some of the degradation products like HEPO and HEGly are reported only in pilot plant operations. This is attributed to effect of cycling on solvent degradation[11]. The solvent has to undergo constantly varying operating conditions and dynamic cycles making it difficult to replicate the operating conditions at lab-scale.

The objective of this study is to compare the observations from three pilot plants (TNO's capture plant at Maasvlakte, The Netherlands, ENEL's capture plant at Brindsi, Italy and EnBW's capture plant at Heilbronn, Germany) in terms of ammonia emissions and metals present in the system. Subsequently, explaining them on the basis of differences in operating conditions and plant layout. As ammonia is the eventual product of any primary amine solvent, oxidative degradation of the solvent can be quantified through ammonia emissions[9]. Moreover, degradation models based on lab scale studies are used to compare the observations of the different pilot plant campaigns, exhibiting the gap between lab-scale and pilot scale operations.

Nomenclature

BHEOX	*N,N'*-bis(2-hydroxyethyl)oxamide
HEF	*N*-(2-hydroxyethyl)formamide
HEGly	*N*-(2-hydroxyethyl)-glycine
HEI	*N*-(2-hydroxyethyl)imidazole
HEPO	4-(2-hydroxyethyl)piperazin-2-one
HSS	Heat Stable Salts
MEA	2-ethanolamine
BDU	Brownian Demister Unit
FTIR	Fourier Transform Infrared Spectroscopy
FRP	Fiber – reinforced polymer

2. Pilot plant campaigns

2.1 Overview of pilot plants

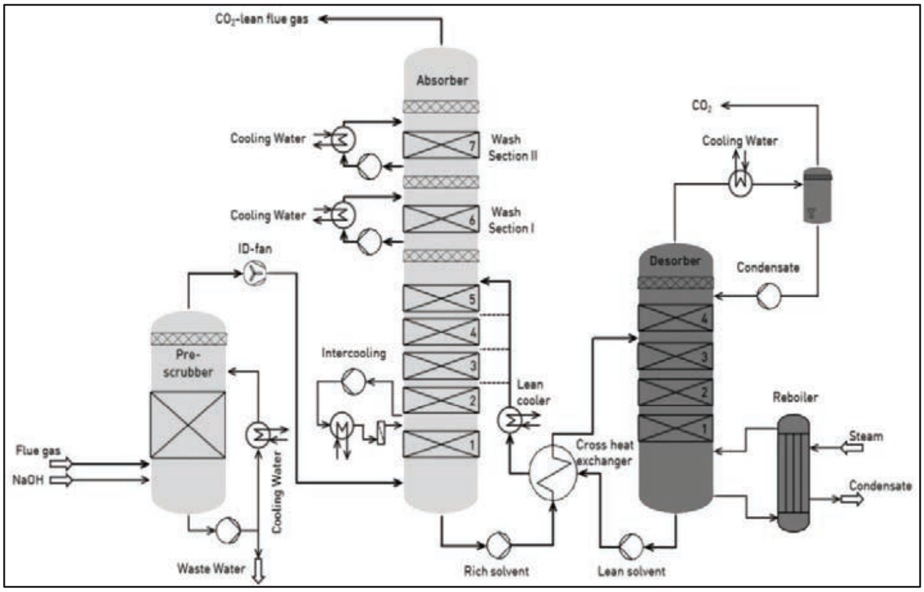
This study is based on three pilot plant campaigns namely at TNO's capture plant at Maasvlakte, The Netherlands (TNO), ENEL's capture plant at Brindsi, Italy (ENEL) and EnBW's capture plant at Heilbronn, Germany (EnBW). The details of the plant and techniques for analysis are already reported in [14,15,16]. Hence these pilot plants are discussed briefly in this study and description is focused on highlighting the differences in equipment in an otherwise typical absorber- desorber setup of the plant. The process flow schemes for the pilot plants are shown in Figure 1.

An inter-cooler section is available at EnBW's CO_2 capture pilot plant between the lowest two beds as shown in Figure 1(a). The absorber tower includes two packed beds at the top to act as water washing section and an acid wash section. Along with the absorber and stripper sumps, the solvent is stored in a tank in the inter-cooling line. It also has an option for different entry heights for the lean solvent, however only the top most inlet point was used. The absorber section is made up of FRP pipes with polypropylene in liner. The rest of the plant is made up of SS316L.

At TNO's CO_2 capture pilot plant, a BDU is installed downstream the SO_2 scrubber and prior the absorber in order to remove particles from the flue gas to avoid excessive amine aerosol based emissions, as in Figure 1(b). BDU units are made up of a polypropylene filter which removes particles larger than 1-2 µm[17]. The absorber tower has a section at the top which acts as a water wash. Another wash section, an acid wash is installed downstream the water wash. The principal material for equipment of pilot plant are SS 304L and SS 316L.

The pre-treatment section (Figure 1(c)) at ENEL's CO_2 capture pilot is constituted of flue gas desulphurization (DeSOx) unit based on limestone and two wet electrostatic precipitators in series to capture particulate matter but these were not operational for most part of the campaign. The absorber section in ENEL too has multiple inlet points for the lean solvent (Figure1(c)), however only the top most inlet line was used for this campaign. A conventional pump around type of water wash is located in the absorber tower. In addition to sump, storage tank of $36m^3$ capacity was also used to hold the solvent. The material of the columns and equipment is SS 316L.

a)



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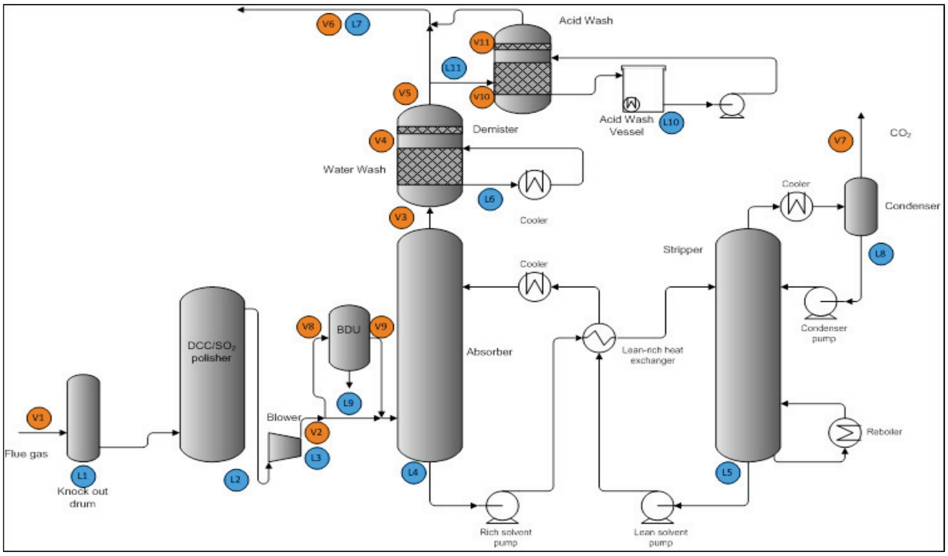

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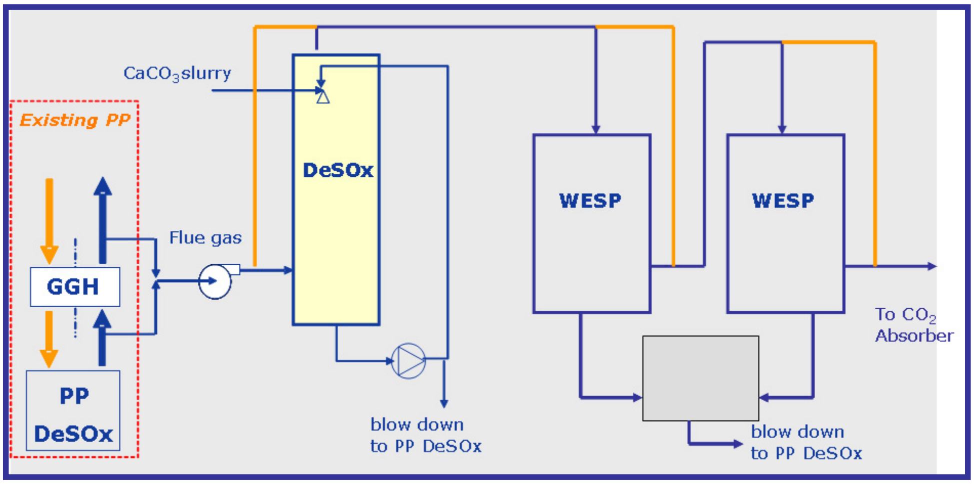

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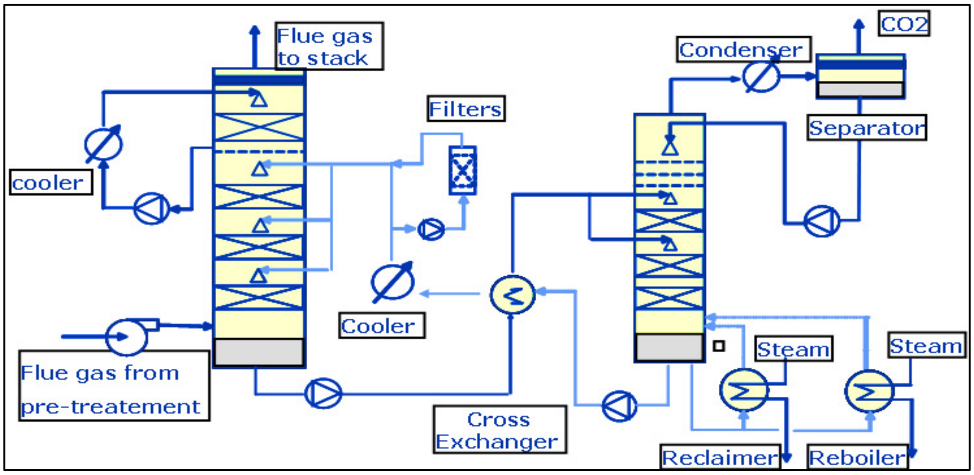

Fig. 1. Process flow diagram (a) EnBW[14] ; (b) TNO, V = Vapor, L = Liquid [15]; (c) Flue gas treatment section at ENEL (Orange lines represent bypass flow scheme); (d) ENEL[16]

2.2 Comparison of operating conditions

All the pilot plant campaigns were based on MEA (30 wt.%). One refilling of 760 kg of MEA was done at 952 hours of operation in EnBW’s campaign. At the end of EnBW campaign, water was added to the system resulting in a decrease of the concentration to around 25 % wt. In ENEL’s campaign, additionally 40 m^3 of 30 wt.% MEA was added midway in the campaign. This additional solvent was used till the end of the campaign. No fresh MEA or solvent was added in TNO’s MEA campaign.

All the three campaigns received their flue gas from coal based power plants. As flue gas quality plays an important role in carbon capturing process, Table 1 compares the typical values of flue gas quality observed at absorber inlet.

Table 1. Flue gas quality at the three CO_2 capture pilot plants

	TNO	EnBW	ENEL
Typical absorber inlet CO_2 concentration *(vol. % dry)*	11	12.3	11.5
Typical O_2 concentration *(vol.% dry)*	7.4	6.4	6.3 - 8.2
Typical SO_x concentration at flue gas withdrawal point *(mg/Nm^3)*	93	150-170	20-600
Typical absorber inlet SO_x concentration *(mg/Nm^3)*	Not measured	3	0-20
Typical NO_x concentration at flue gas withdrawal point *(mg/Nm^3)*	55-70	160 -180	40-120
Typical absorber inlet NO_x concentration *(mg/Nm^3)*	Not measured	Not measured	24-68
Particulate matter *(mg/Nm^3)*	Not measured	Not measured	1

The temperatures in different sections of the plant are important from the point of view of solvent degradation. Table 2 summarizes the process temperatures at the equipment which were prone to oxidative degradation in the solvent loop. The temperatures in TNO’s and ENEL’s plants were quite similar, while EnBW’s pilot plant was operated with a relatively lower absorber sump temperature. EnBW had an inter-cooling section operating at 32°C , which resulted in a lower rich solvent temperature.

Table 2. Operating temperatures at the three pilot plants

	TNO *(℃)*	EnBW *(℃)*	ENEL *(℃)*
Flue gas to absorber	40	35	47-50
Rich solvent temperature/ Rich Inlet cross HEX	51	37	51
Rich outlet cross HEX	110	100	109

Table 3 summarizes the holdup volumes and corresponding residence time in each process equipment based on a typical solvent flow rate. Depending on the design of the plant, the solvent inventory could vary even for plants of similar CO_2 capture capacity as seen between TNO’s and EnBW’s CO_2 capture plants. This impacts the residence time of the solvent in each process equipment. Since different operating conditions, i.e. temperature and CO_2 loading, exists at different sections of the plant, a different residence time in equipment can have a significant impact on the solvent degradation. The main hold up/residence time of the solvent at TNO and EnBW’s plant was in the sumps, while for ENEL the main hold up/residence time of the solvent was in the storage tanks.

Another important aspect for comparison is the ratio of solvent inventory to the flue gas flow rate inventory. Table 4 shows the solvent inventory at the three pilot plants with respect to the flue gas flow rate. The ratio at TNO’s pilot plant is much lower, however, EnBW’s and ENEL’s ratio are quite similar in standard operation.

Table 3 . Solvent inventory and typical residence times including the major equipment at the three pilot plants.

	TNO			EnBW			ENEL		
	Hold up volume *(L)*	Typical solvent flow rate *(L/h)*	Residence time *(min)*	Hold up volume *(L)*	Typical solvent flow rate *(L/h)*	Residence time *(min)*	Hold up volume *(L)*	Typical solvent flow rate *(L/h)*	Residence time *(min)*
Absorber sump	1438	3200	27	2500	5000	30	10000	28300	21.2
Rich side cross HEX	34.5		0.65	113		1.3	694		1.47
Inter-cooling tank	-		-	1500		18	-		-
Total plant inventory	2800		53	9000		108	60000		127

Table 4. Specific solvent inventory to gas flow rates at the three pilot plants.

	TNO	EnBW	ENEL
Flue gas flow rate *(Nm^3/h)*	800	1500	10000
Solvent inventory *(L)*	2800	9000	60000/100000
Specific Solvent inventory to gas flow *($L/Nm^3/h$)*	3.5	6	6/10

3. Results

3.1 Ammonia Emissions

Ammonia is an eventual oxidative degradation product of MEA[9]. Being highly volatile at the operating pH, it is stripped of the solvent and since a typical water wash uses the same water in a pump-around without a purge, ammonia is not captured in water washes.

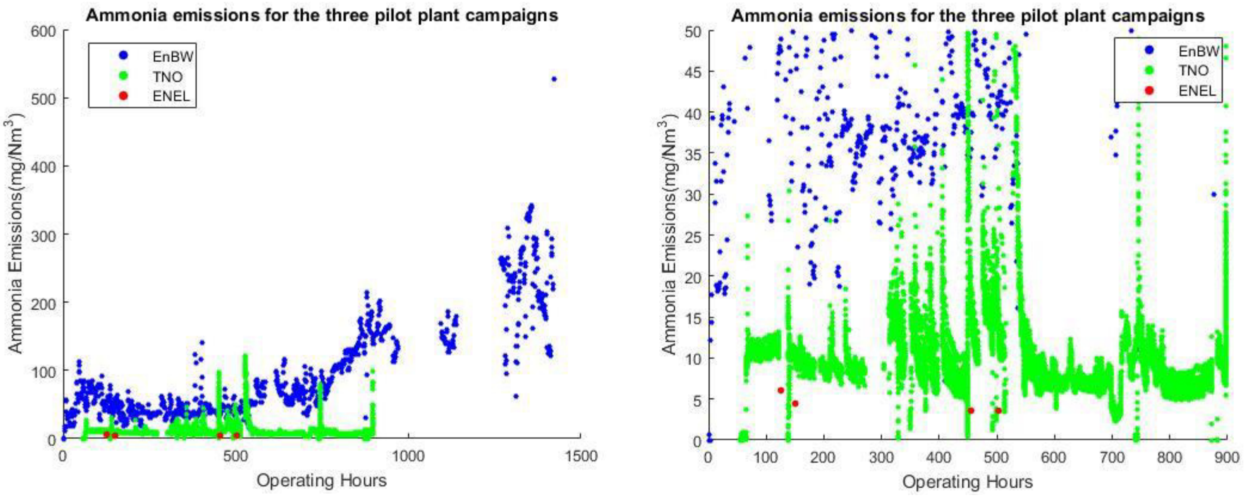
a) b)

Fig.2. (a) Ammonia emissions in treated flue gas stream for three campaigns; (b) Ammonia emissions zoomed up to 50 mg/Nm^3

It is clear from Figure 2, that the ammonia emissions at the three campaigns were quite different. At the EnBW campaign (hourly averages), it showed a rapid increase already in the first 50 operation hours. Further increases were seen at about 700 operation hours. Thereafter, it continued to rise and reached a maximum of 350 mg/Nm^3, at the end of the campaign.

The ammonia emissions at the ENEL campaign were below 5 mg/Nm^3(Fig. 2(b)). Similarly, at TNO's campaign (continuous data of every minute) emissions were mostly below 10 mg/Nm^3 as measured before the acid wash (V5 in Fig.1(b)). Few peaks in ammonia emissions were observed in TNO campaign and were due to the following reasons:

- a multiplexer system was used to sample the gas before and after the acid wash. While switching, some residual gas and condensation in the line leads to temporary artificial peaks
- Change in the flue gas flow rate or acid wash liquid flow rate.

3.2 Metals

The presence of metals is essential for oxidative degradation[3,18]. The Fe content in the solvent as a function of operating hours for the three campaigns was as shown in Figure 3. At TNO's and ENEL's campaign, the Fe content remained below 3 mg/L and 1 mg/L, respectively throughout the campaign (Fig.3(b)). The Fe content in the EnBW campaign showed a steady increase, initially, and after about 400 operating hours the Fe content started increasing rapidly, showing almost an exponential trend in the end (Fig.3(a)). Metal concentration for Ni and Cr also followed the same trend.

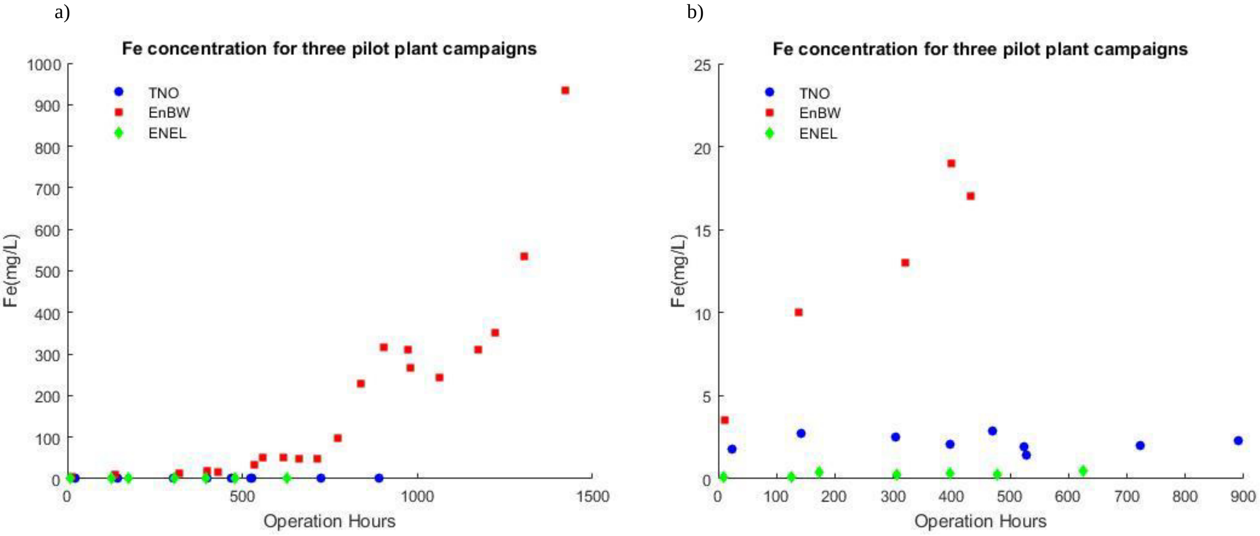

Fig.3. (a) Solvent Fe content for entire campaign; (b) Fe concentration zoomed up to 25 mg/L

4. Discussion

An interesting trend was observed for the metal concentration and ammonia emissions of EnBW campaign. In Figure 4(a), initially the metal concentration was a constant value, it then increased rapidly and a maximum was reached after which the concentration tended to remain constant for some time before repeating the trend again. The rapid increase in the metal concentration can be expected from auto-catalytic role of metals in MEA oxidative degradation[8,9]. However, the cause of change from one stable maximum to the other stable maximum couldnot be explained. A similar trend was observed in ammonia emissions for the EnBW campaign (Figure 4(b)).

Significantly higher metal content and ammonia emissions were observed at EnBW's campaign as compared to the campaigns at TNO and ENEL, all using MEA as the solvent. It is important to mention that duration of campaigns at TNO and ENEL were shorter than at EnBW (EnBW~ 1500 hours; TNO ~ 890 hours; ENEL ~ 550 hours). Although lower emissions were observed at TNO’s and ENEL’s campaign, significant degradation cannot be ruled out, if the campaign duration would have been longer. As ammonia emissions can be correlated to solvent degradation, therefore, it can be said that the rate of degradation observed at EnBW’s campaign was much higher than at TNO’s and ENEL’s campaign. The key elements for the rate of degradation are the amount of oxygen and temperature. Moreover, the presence of metals such as Fe, Cr and Ni significantly affect the degradation of MEA. Further in this section each of these factors are discussed in detail, however, these factors are closely inter-related.

4.1 Oxygen

As shown in Table 1, the oxygen content in flue gas to the three pilot plants was quite similar. However, the dissolved oxygen content, which is essential for degradation, can differ. This depends on the temperature and CO_2 loading. As expected, the oxygen solubility decreases with increase in temperature and CO_2 loading. The rich loading at the pilot plants is in the range of 0.4 to 0.5 mol CO_2/mol amine. The biggest difference in between the three pilot plants is the rich solvent temperature. The rich solvent temperature at EnBW was much lower, 37°C, as compared to 51°C at TNO and ENEL’s plant. The lower temperature is due to the use of inter-cooling, lower flue gas inlet temperature and lower lean solvent temperature. This lower temperature leads to much more dissolved oxygen in the EnBW campaign, thus higher degradation rate in the system.

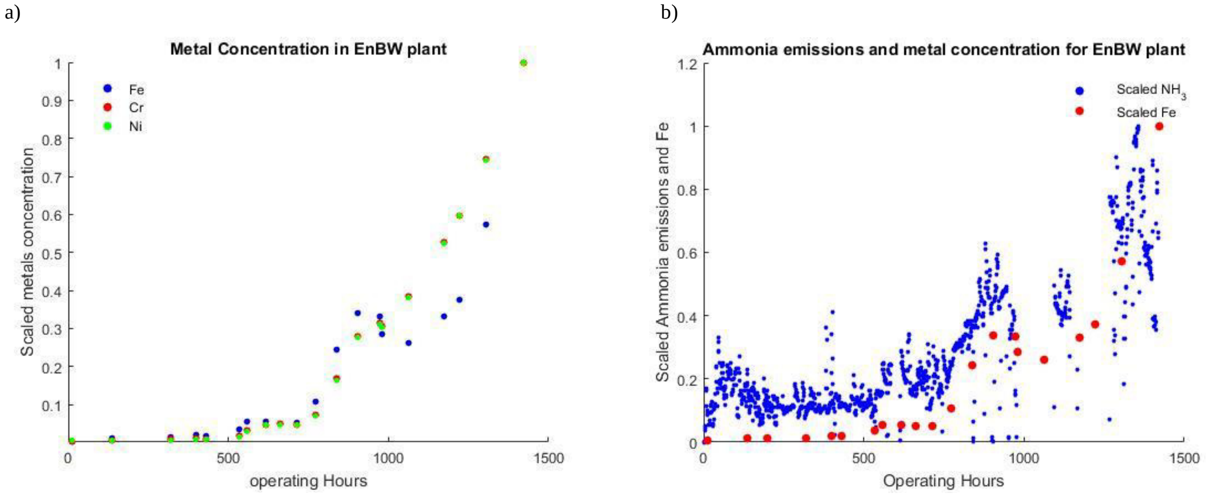

Fig. 4. EnBW plant concentration scaled to maximum (a) Metal; (b) Comparison of ammonia emission and Fe concentration

4.2 Temperature

As can be expected longer residence time in high temperature zones can significantly increase the rate of degradation, especially in the presence of oxygen. Typically, high temperature zone includes the rich line to cross heat exchanger, rich line from cross heat exchanger, stripper, reboiler and lean line to cross heat exchanger. The dissolved oxygen will be immediately released at the inlet of the stripper. However, some of the degradation products already formed can further react in the stripper at the high temperatures. Only the rich solvent temperature at EnBW campaign was low, the other temperatures in the above mentioned sections were quite similar at the three pilot plants as shown in Table 2.

4.3 Residence Time

The largest difference in the residence time is in the stripper sump/reboiler which is a high temperature zone. The residence time in EnBW’s plant was about 48 min while, at TNO’s and ENEL’s plant it was about 19 and

27 minutes, respectively. The residence times in the other sections of the plant were similar. Longer residence time in higher temperature zone can also contribute to increased thermal degradation. Table 4 shows the solvent inventory at the three pilot plants with respect to the flue gas flow rate. The ratio at TNO's pilot plant was much lower, however, EnBW's and ENEL's ratio were quite similar in standard operation. These factors can significantly affect the leaching process and relative ammonia emissions.

4.4 Metals as Catalyst

The source of metals can be either the stainless steel from the equipment or fly ash. On its own MEA is not known to be corrosive, therefore, metals from stainless steel at the start of the campaign are not to be expected[19]. Fly ash which can be present in the flue gas to the absorber contains heavy metals. This can leach in to the solvent and its concentration can increase over time, although to a limited extent[20,21,22]. However, this could be sufficient to trigger increased rate of oxidative degradation. An important difference is the presence of a BDU before the absorber at TNO's pilot plant campaign, which removes submicron particles. This could also lead to reduced fly ash or other particulates entering the pilot plant, thereby reducing the presence of heavy metals, and thus, oxidative solvent degradation. Similarly, at ENEL, a bag filter was used in the flue gas treatment train of the power plant which is also known to remove particulates from the flue gas. No special particulate removal system was used at EnBW's pilot plant, other than an electrostatic precipitator in the flue gas treatment train of the plant.

5. Comparison with literature models

Several models have been reported in literature to predict the degradation rate of PCC solvents[23,24,25,26,27]. These models are based on observations made in laboratory scale experiments. Models by Leonard et al. [23] and Pinto et al.[24] focus solely on the solvent losses due to MEA oxidative degradation. Hence, these models have been used to compare the ammonia emissions for the three pilot plant campaigns with the predicted ammonia emissions from the laboratory based models.

5.1 Comparison with the degradation model as proposed by Leonard et al.

Leonard et al. explains the degradation of MEA through a single equation, which is weighted in accordance to experimentally observed distribution of degradation products and is based on certain assumptions, as represented in Equation (1)[23].

$$\text{MEA} + 1.3\ O_2 \rightarrow 0.6\ NH_3 + 0.1\ \text{HEI} + 0.1\ \text{HEPO} + 0.1\ \text{HCOOH} + 0.8\ CO_2 + 1.5\ H_2O \qquad (1)$$

The reaction rate of MEA oxidative degradation (mol/L.s) is expressed by Equation (2). R is the universal gas constant (8.314 J/mol.K), T is the temperature (K) and $[O_2]$ is the concentration of dissolved oxygen (mol/L). The activation energy is of units J/mol and pre-exponential unit is defined in $(\text{mol/L.s})/(\text{mol/L})^{1.46}$.

$$-r_{MEA,Oxidative} = 5.35 \times 10^5 . e^{-41730/RT} . [O_2]^{1.46} \qquad (2)$$

Equation (2) was modelled in MATLAB R2015b using the ordinary differentiation solver ode15s to predict the ammonia emissions using the stoichiometry of Equation (1). Since most of the oxygen is stripped at the high temperatures of stripper, it is reasonable to assume that nearly all of the oxidative degradation takes place in the absorber sump and rich side cross heat exchanger (HEX) in presence of constant amount of oxygen. Thus, the comparison of model accounts for oxidative degradation taking place in absorber sump and HEX. Additionally, an intercooling tank is associated with EnBW campaign which is a large residence time zone with high O_2 content and hence, provides suitable conditions for oxidative degradation and is accounted for in the model.

The computation is initialized with temperatures and dissolved oxygen experienced in the absorber sump and HEX of the three pilot plant campaigns. Dissolved oxygen is estimated by fitting oxygen solubility measurements (Table 5) of Wang et al. for $MEA/CO_2/H_2O$ mixture using 0.5 mol of CO_2/mol of MEA loading as the three campaigns operate on the same loading[28]. The curve fitting (Figure 5) was executed using Equation (3) with a squared R of 0.99 and a 95% confidence interval for parameters.

$$(0.968/T^3) + (0.139/T^2) - (0.003/T) + (2.484 \text{ x } 10^5) = [O_2]\,, \tag{3}$$

Where T is temperature in ^{0}C and $[O_2]$ is dissolved oxygen concentration in mol/L. As explained in section 4.3, residence time of absorber sump and rich heat exchanger, number of dynamic cycles and flue gas flow rate to solvent ratio affect the ammonia emissions significantly. Hence they are accounted for in the model. The given inputs to the model are summarized in Table 6.

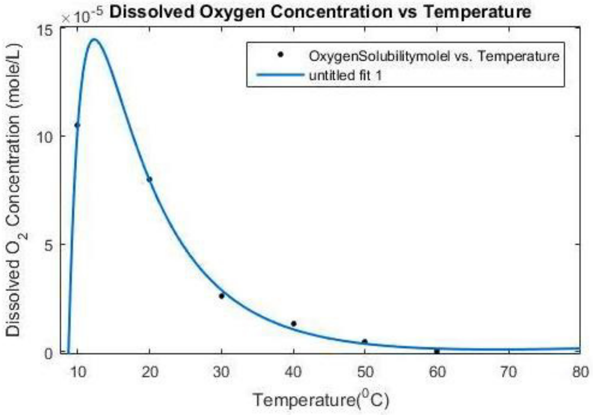

Fig. 5. Curve Fitting on Wang's Oxygen solubility measurements using Eq. 3

Table 5. Wang's oxygen solubility measurements at atmospheric pressure[28]

MEA Concentration (100 *w*)	CO_2 Loading *mol of CO_2/mol of MEA*	Temperature *(°C)*	Dissolved O_2 mass fraction ($x \cdot 10^6$)
30	0.5	10	3.35
		20	2.56
		30	0.83
		40	0.42
		50	0.14
		60	0.00

The model predicts higher emissions than that observed at TNO and ENEL pilot plant throughout the campaign(Figure 6 (a),(c)). On the other hand, for EnBW campaign, the model predicts the same order of magnitude of ammonia emissions up to 500 cycles. However, the high ammonia emissions without the role of catalyst suggest that the model over-estimates the ammonia emissions.

ENEL campaign operates on the highest sump temperature from the other campaigns and hence experiences the lowest dissolved oxygen concentration (Figure 5). This low dissolved oxygen concentration is responsible for prediction of low ammonia emissions for ENEL in Fig. 6(d). TNO and EnBW campaigns have comparable dissolved oxygen concentration and hence similar ammonia emissions (in Fig. 6(d)). It can be concluded that the model is significantly influenced by dissolved oxygen concentration.

Table 6. Summary of Input values for initialization of model

Given Input	Value			Comments
	TNO	EnBW	ENEL	
Temperature (*^0C*)				- Temperature for HEX is formulated as log mean temperature of inlet and outlet streams of exchanger
- Absorber Sump	40	35	48.5	
- HEX	76.7	76.3	63.3	
Dissolved O_2 Concentration (x 10^{-05}*mol/L)*				- Dissolved O_2 Concentration at inlet temperature of HEX.
- Absorber Sump	1.020	1.067	0.435	
- HEX	0.127	0.127	0.114	
Operating Hours	890	1500	550	- Duration of each campaign
Number of Cycles	1008	833	260	- Operating Hours/ Residence time

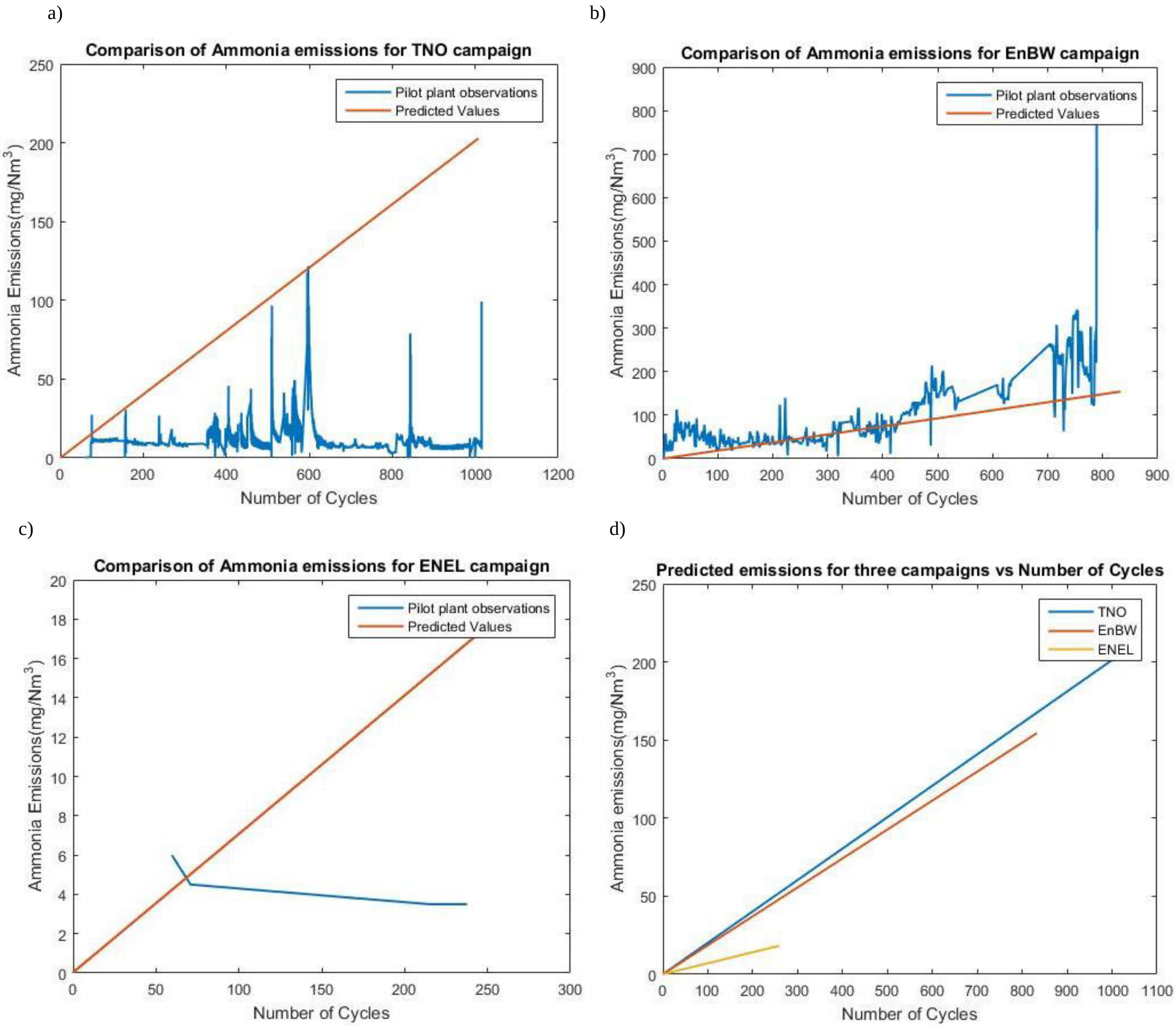

Fig. 6. Comparison of ammonia emissions from Leonard's model for (a) TNO; (b) EnBW; (c) ENEL; (d) three pilot plant campaigns with respect to number of cycles

5.2 *Comparison with the degradation model as proposed by Pinto et al.*

Pinto et al. explains the degradation of solvent with a set of equations based on suggested mechanisms of several degradation products[24]. The kinetic expressions and respective parameters for these set of equations are tabulated in appendix A. The kinetic expressions were modelled using ode15s in MATLAB R2015b by initializing the model with the conditions observed in pilot plants as mentioned in Table 6.

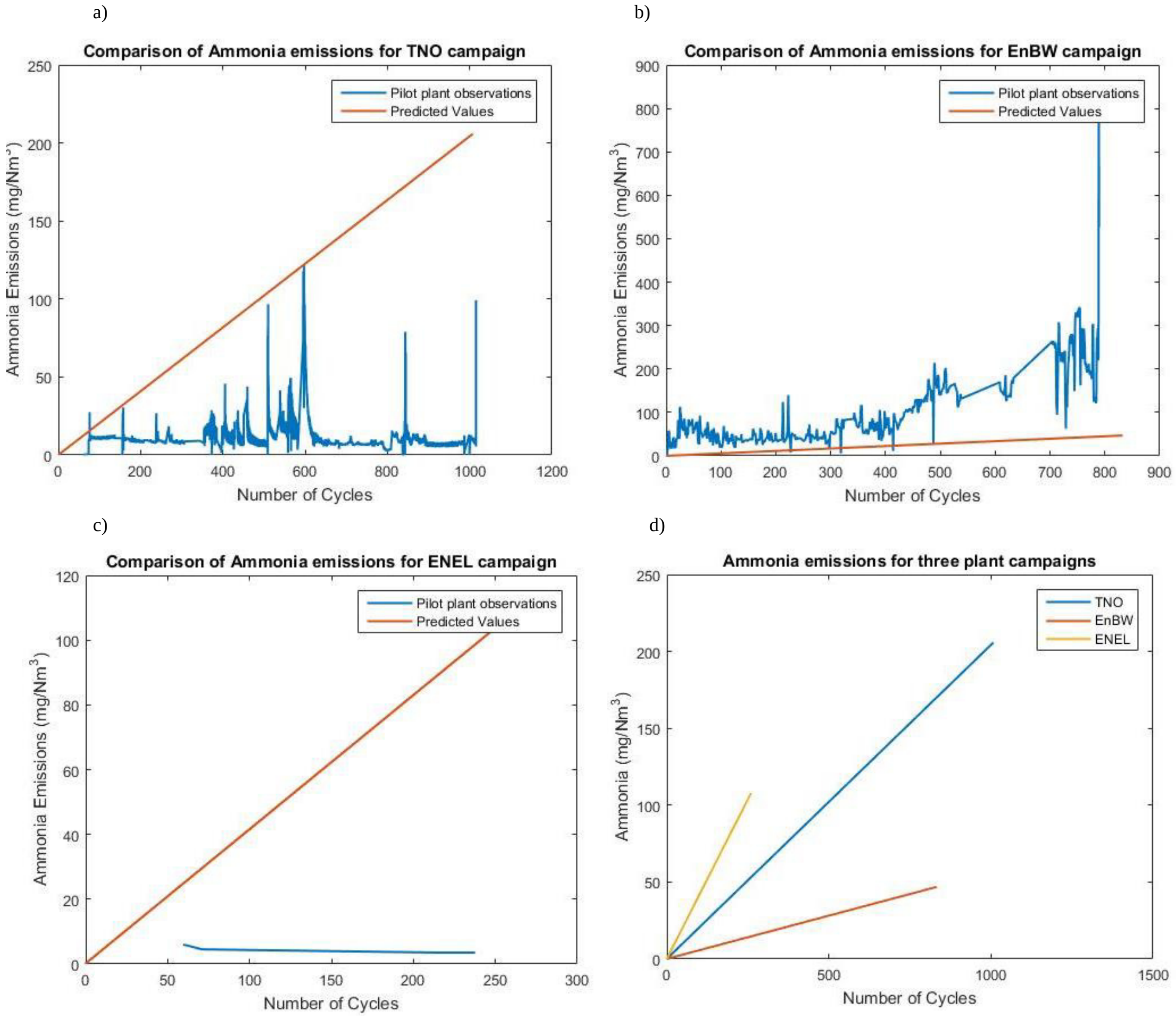

Fig.7. Comparison of ammonia emissions from Pinto's model for (a) TNO; (b) EnBW; (c) ENEL; (d) three pilot plant campaigns with respect to number of cycles

$$\text{MEA} + 3\ H_2O \rightarrow 2\ \text{Formaldehyde} + NH_3 + 2\ H_3O^+ \tag{4}$$

$$\text{Formaldehyde} + 0.5\ O_2 \rightarrow \text{Formic acid} \tag{5}$$

$$\text{MEA} + \text{Formic acid} \rightleftarrows \text{HEF} + H_2O \tag{6}$$

$$\text{MEA} + O_2 \rightarrow \text{Glyoxal} + H_2O + NH_3 \tag{7}$$

$$\text{MEA} + \text{Formaldehyde} + \text{Glyoxal} + NH_3 \rightleftarrows \text{HEI} + 3\ H_2O \tag{8}$$

$$\text{Glyoxal} + O_2 \rightleftarrows \text{Oxalic Acid} \tag{9}$$

$$2\ \text{MEA} + \text{Oxalic Acid} \rightleftarrows \text{BHEOX} + 2\ H_20 \tag{10}$$

$$2\ \text{MEA} + 0.5\ O_2 + 2\ H_20 \rightleftarrows \text{HEGly} + NH_3 + 2\ H_30^+ \tag{11}$$

The model fairly over-estimates the ammonia emissions for TNO and ENEL campaign contrarily under-estimating the emissions for EnBW campaign. From figure 7, rate of ammonia emissions is highest for ENEL and lowest for EnBW at a given number of cycles. This is indicative of the considerable influence temperature has on rate of reaction than dissolved oxygen concentration.

The results clearly stress upon the gap between lab scale experiments and pilot plant observations. In order to replicate pilot plant results, accelerated lab scale experiments were performed. The modelling of these accelerated studies tend to over-estimate the MEA degradation. Adding to this, very few studies highlight the role of metals in solvent degradation. Moreover, no study explicitly observes the auto-catalytic effect of metals. Understanding of this mechanism is important to have a representative model for the prediction of oxidative degradation at pilot plant scale and eventually, for full scale plants.

6. Conclusion

The pilot plant campaigns at TNO, EnBW and ENEL have provided significant amount of valuable information. Although it is based on, mainly MEA as the solvent, the learnings can be applied to other amines, too. The degradation rate observed in the three pilot plant campaigns were significantly different. The ammonia emissions and metal concentration were relatively stable during the TNO and ENEL campaign. However an overall combination of linear and exponential increase in the emission of ammonia and metal concentration was observed in the EnBW campaign. This exponential trend points towards the auto-catalytic role of metals in the oxidative degradation of amines.

The different observations could be mainly attributed to combination of multiple factors,

- Flue gas quality: The different flue gas quality could be due to the additional cleaning devices at these campaigns (BDU at TNO and WESP at ENEL) which possibly reduced the fly ash input to the solvent system.
- Dissolved oxygen concentration: EnBW campaign experienced the highest dissolved oxygen concentration leading to higher ammonia emissions. However, as dissolved concentration is further dependent on temperature, so the lower rich solvent temperature at EnBW could also be linked to higher ammonia emissions.

Lab-scale experiments certainly provide an insight into the degradation process but they fail to predict the pilot plant’s degradation rate to a satisfactory degree. Further focus should be given to understand and predict the auto-oxidative degradation mechanism observed in pilot plants for PCC.

Acknowledgements

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Appendix A.

The corresponding kinetic rate expressions and kinetic parameters for the equations 4-11 are tabulated as followed[24].

$$Rx_1 = A_1 exp\left(\frac{-E_1}{RT}\right)[MEA][O_2]$$

$$Rx_2 = A_2 exp\left(\frac{-E_2}{RT}\right)[CH_2O][O_2]$$

$$Rx_3 = A_3 \exp\left(\frac{-E_3}{RT}\right)[MEA][CH_2OH] - A_{-3}\exp\left(\frac{-E_{-3}}{RT}\right)[HEF]$$

$$Rx_4 = A_4 exp\left(\frac{-E_4}{RT}\right)[MEA][O_2]$$

$$Rx_5 = A_5 \exp\left(\frac{-E_5}{RT}\right)[MEA][CH_2O][NH_3][Glyoxal] - A_{-5}\exp\left(\frac{-E_{-5}}{RT}\right)[HEI]$$

$$Rx_6 = A_6 \exp\left(\frac{-E_6}{RT}\right)[Glyoxal]^{0.9}[O_2]^{0.5} - A_{-6}\exp\left(\frac{-E_{-6}}{RT}\right)[Oxalic]$$

$$Rx_7 = A_7 \exp\left(\frac{-E_7}{RT}\right)[MEA]^2[Oxalic] - A_{-7} \exp\left(\frac{-E_{-7}}{RT}\right)[BHEOX]$$

$$Rx_8 = A_8 \exp\left(\frac{-E_8}{RT}\right)[MEA]^2[O_2]^{0.5} - A_{-8}\exp\left(\frac{-E_{-8}}{RT}\right)[HEGly][NH_3][H_3O^+]^2$$

Pre-exponential factor	[-]	Activation energy	[J/mol]
A_1	5.898E+20	E_1	1.267E+05
A_2	4.004E+04	E_2	2.466E+04
A_3	1.3787E+05	E_3	1.981E+04
A_{-3}	3.5188E+20	E_{-3}	1.140E+05
A_4	2.0224E+22	E_4	1.332E+05
A_5	1.323E+29	E_5	1.703E+05
A_{-5}	7.808E+44	E_{-5}	2.728E+05
A_6	1.1589E+22	E_6	1.403E+05
A_{-6}	2.8483E+06	E_{-6}	3.848E+04
A_7	2.1854E+34	E_7	2.184E+05
A_{-7}	8.6309E+52	E_{-7}	3.286E+05
A_8	9.0063E+13	E_8	1.059E+05
A_{-8}	1.2517E+16	E_{-8}	1.047E+05

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