Australian National Low Emissions Coal Research and Development

Project:
Environmental Impacts of Amine-based CO$_2$ Post Combustion Capture (PCC) Process

Activity 3: Process Modelling for Amine-based Post-Combustion Capture Plant

Deliverable 3.2 Progress Report

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EXECUTIVE SUMMARY

The scientific literature concerning the formation of oxidative and thermal degradation products of MEA, MDEA, AMP, PZ and their select blends have been reviewed in this report. Despite high overall activity in this field, the amount of experimental work carried out for fully characterising and quantifying the degradation of amine solvents and the applicability of these findings to an industrial scale amine-based post combustion capture plant in terms of predicting the atmospheric emissions of solvent degradation products has been found to be far less than anticipated beforehand.

The wide spread of reported reaction conditions and applied analytical methods make direct comparison of both the laboratory and pilot plant based degradation studies rather difficult. Nevertheless the laboratory studies, pilot plant scale experiments and public domain technical information from various commercial technology vendors on degradation of amino solvents clearly indicates that in an industrial environment of post combustion CO_2 capture, these solvents will most certainly undergo both oxidative and thermal degradation. The extent of degradation and the type of degradation products formed are found to depend upon the structure of amine and the process operating conditions. Of these conditions we highlight the concentration of amine, its CO_2 loading, absorber reaction temperature, solvent regenerator temperature, content of oxygen, SO_X, NO_X and particulate matter in flue gas, composition of particulate matter (Fe, Ni, V, P, Cr, CO etc), catalytic effect of the material of construction of plant equipment towards degradation etc. The plant operating practices, such as the process control and how often a solvent is reclaimed, will also decide both the extent of solvent degradation and the type of degradation products formed.

In general, potential degradation products of amine solvents (combination of oxidative and thermal degradation) are likely to be one or more of the following:

Ammonia, primary amines / alkanolamines, secondary amines / alkanolamines, tertiary amines / alkanolamines, aldehydes (formaldehyde, acetaldehyde), carboxylates, amides, piperazines, piperazinones, oxazolidpnes, nitrosamines, imidazolidones, N,N-distributed ureas and nitramines. Other compounds may be added to the list if the ongoing research has identified any additional product.

The exact chemical structure of these degradation products depends upon the chemical structure of parent amine and the degradation reaction pathways it has followed.

Whilst there are a number of pilot plant scale CO_2 capture campaigns ongoing around the world, there has been so far not even a single study that has attempted to close the material balance around plant where formation of degradation products within the plant and the atmospheric emissions of these products are fully accounted. Nevertheless, these campaigns do confirm the following:

a) More degradation products are formed in an industrial plant environment than what various research groups have so far determined in their laboratory studies.

b) In an industrial environment, it is the oxidative degradation that is contributing more towards overall solvent degradation than the thermal degradation.

c) Vapour phase atmospheric emissions of heat stable salts and thermal degradation products of amines are likely to be minimal to the point of no concern.

d) Formation of nitroso compounds in the industrial plant environment is a reality since both Boundary Dam and ITC pilot plants in Canada confirm formation and detection of

1,2,3,6-tetrahydro-1-nitrosopyridine during their MEA and MEA/MDEA campaigns. It should be noted that the Boundary Dam pilot plant was originally built by Union Carbide and later refurbished by Fluor Ltd for SaskPower as per the Fluor Econamine technology and it used proprietary corrosion inhibitors for both amine campaigns. Thus, Strazisar et al., 2003, are correct in asserting that they detected nitrosamines in the lean amine solution at Kerr-MCGee/ABB Lumus technology based post combustion CO_2 capture plant at Trona, California, and these compounds may have been formed up to 2.91 µmol per mL of solution. It should be noted that the Trona plant also uses proprietary corrosion inhibitors despite the lean amine (MEA) concentration being less than 20% w/w.

e) Corrosion inhibitors currently being recommended and perhaps used by commercial technology vendors for post combustion CO_2 capture may be acting as catalyst towards the solvent degradation. Certainly, the corrosion inhibitors containing Copper, Vanadium, Cobalt and other metals used in the reducing environment of gas processing industry are catalyst for solvent degradation in the oxidative environment of post combustion capture. Laboratory studies of solvent degradation by Rochelle and other investigators confirm this.

f) The wash tower downstream of absorber plays critical role in controlling atmospheric emissions of various amine solvents and their volatile degradation products from a CO_2 capture plant. The AspenPlus process simulation results clearly indicate that the wash tower performance is affected by ambient conditions, particularly the cooling water temperature. Operating this tower at temperature as low as possible in practice can substantially reduce the emissions of volatile degradation products. No doubt other process or equipment performance improvement measures such as intercooling the absorber or separating the condensable species downstream of the absorber (using reflux condenser) prior to water washing the CO_2 lean flue gas will certainly help in reducing atmospheric emissions.

Published information on operating performance of the capture plant at Trona, California, and the technology related information from MHI Ltd clearly states that the flue gas impurities viz. the particulate matter, SO_X and NO_X contribute significantly towards solvent degradation and atmospheric emissions of amine solvents. In fact, the MHI data categorically shows that by reducing SO_X content at inlet to the absorber from 3 ppmv to 1 ppmv reduces atmospheric emissions of both KS-1 and MEA solvents by more than half. Recently published information from MHI further states that in order to eliminate formation of aerosols in the CO_2 lean exhaust stream, the SO_X content of flue gas at inlet to the absorber should be less than 0.1 ppmv. Similarly, to avoid the sludge build up in absorber and resulting foaming and flooding of the absorber as well as to reduce the metal catalysed degradation of solvent, the particulate level in the lean amine solvent should not be allowed to exceed 1 ppm by weight. All of this means that for stable performance of CO_2 absorption/desorption system with high efficiency, minimum solvent degradation and minimum atmospheric emissions, the direct contact cooler and the water wash tower in post combustion CO_2 capture plant must be performing efficiently. This is particularly important in Australian context since Australian power stations do not have de-SO_X and de-NO_X systems.

In terms of choosing an amine solvent for amine-based post combustion capture with minimal environmental adverse impact, one should note the guidelines below:

i. Secondary amines have highest risk of nitrosamine formation, followed by tertiary amines, while primary amines have the lowest risk of nitrosamine formation.

ii. All other things being equal, solvents with low vapour pressure are safer than solvents with high vapour pressure.

iii. All other things being equal, a more stable solvent that will resist degradation is safer than a less stable one since the more stable solvent will have lower emissions of degradation products.

Using the above guidelines, the amine solvents considered in this report can be ranked in order of their likely maximum adverse impact to minimal adverse impact as:

$$PZ > AMP > MEA > MDEA$$

The available publication from the ongoing pilot plant programs in different parts of the world shows that the characterisation and quantifications of gas and liquid streams at inlet and outlet to the absorber, stripper and water wash towers downstream of both absorber and stripper has not yet been fully understood. At this stage, there has been only one pilot plant based degradation study (RWE/LINDE/BASF Niderauβem Pilot Plant, Section 9.3) that has attempted to close material balance with respect to amine consumption and included formation of degradation products and their atmospheric emissions in the material balance. Unfortunately, the material balance does not close with acceptable accuracy and in addition, the liquid phase emissions have not been quantified.

It must be pointed out that the above study has been performed at a lignite-fired power plant in Europe where the coal based power plants are equipped with state of the art de-SO_X, de-NO_X and particulate filtration systems which is not the case with Australian coal-fired power plants. Thus, there is a strong parameter of flue gas quality that needs to be considered before using a European solvent degradation study for anticipating the solvent degradation and resulting atmospheric emissions from a post combustion CO_2 capture plant linked to an Australian coal-fired power plant. In addition, the ambient conditions for both summer and winter seasons in Europe are markedly different from Australian ambient conditions for both inland and coastal locations. Thus, impact of ambient conditions on performance of the water wash tower must also be accounted for when using a European study in Australian context.

Since, the Australian flue gas quality and ambient conditions are considerably different from equivalent European or US/Canadian situation, both direct contact cooler (DCC) and the water wash towers downstream of absorber and stripper will need to be designed accordingly. It will be preferable, if the flue gas desulphurisation as well as the removal of oxides of nitrogen can be carried out in the DCC tower itself for an Australian post combustion capture plant. This has potential to reduce the cost of CO_2 capture from an Australian coal-fired power plant and may even have a positive impact on the net power plant efficiency.

In light of the above findings, a future work program should include the following:

I. Full characterisation and quantification of degradation products of amine solvents both in the gas and liquid streams in an Australian pilot plant scale CO_2 capture plant accompanied by a closed material balance around the input and output streams of the plant. It is expected that this pilot plant will be operating at steady state in the gas-liquid flow regimes representative of currently operating industrial scale post combustion CO_2 capture plants.

II. Process improvements around the DCC tower and the water wash towers downstream of both absorber and stripper in an Australian pilot plant scale to minimise first the adverse impact of flue gas impurities on amine solvents and then atmospheric emissions of amine solvents and their degradation products.

III. Development of mathematical models from first principle (for example, using the molecular modelling principles) – bottom up approach – which account for the solvent degradation kinetics and yields of the degradation products observed through steps I and II above to improve predictive capability of anticipated atmospheric emissions from a full scale amine solvent based post combustion capture plant linked to an existing black coal-fired power plant in Australia.

1. PROJECT OBJECTIVES AND CURRENT MILESTONE

Aqueous amino solvent based acid gas removal processes for the natural and synthetic gas processing industry have been universally recognised to have potential for immediate reduction in the emissions of carbon dioxide (CO_2) from fossil fuel-fired power plant flue gas streams. As a result, commercially available technologies that use these solvents have recently acquired prominence as a short term technological solution to curb globally rising CO2 levels in the atmosphere. Recent laboratory and pilot plant data show that these solvents may undergo oxidative and thermal degradation during the post combustion capture application resulting into the formation of volatile and non-volatile organic compounds including nitrosamine and nitramine compounds. Some of these compounds can potentially be released to the atmosphere in both the vapour phase and the droplet phase along with the parent solvents that may cause adverse impacts on the environment. The objective of this project is therefore:

1. To identify the impact of process operating conditions on the degradation of amino solvents during the post combustion capture application,

2. To identify and summarise the major degradation products of amino solvents, and

3. To estimate the likely emissions of amino solvents and their degradation products into the atmosphere, if these solvents are utilised in a large scale post combustion plant connected to an black coal-fired power plant.

This report attends to the above objectives by undertaking a detailed literature survey on the oxidative and thermal degradation of aqueous amine solvents as observed during laboratory experiments and pilot plant trials. It also reports the likely emissions of these solvents and their degradation products to the atmosphere using available in the public domain or if it is possible to estimate them by process modelling using commercial tools such as the Aspen-Plus process simulation software. Since, the overall project objective is to understand the environmental impact of amino solvents when implemented for post combustion CO2 capture at large scale from a black coal-fired power plant flue gas stream, the emphasis in this report has been given to those amino solvents that are being used at present either commercially or at the technology demonstration scale for such an application. These solvents are monoethanolamine (MEA), methyl-diethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), piperazine (PZ) and their blends.

2. STATE OF KNOWLEDGE

Aqueous alkanolamines have been used for decades in the gas processing industry for acid gas removal such as carbon dioxide (CO_2), hydrogen sulphide (H_2S), carbonyl sulphide (COS), carbon disulfide (CS_2) and mercaptans. Monoethanolamine (MEA), Diethanolamine (DEA), methyl-diethanolamine (MDEA), di-isopropylamine (DIPA) and diglycolamine (DGA) have been the solvents of choice for this purpose[1]. For the last two decades, the sterically hindered amine such as 2-amino-2-methyl-1-propanol (AMP) has been suggested as an attractive solvent for acid gas removal due to its high equilibrium loading capacity and low energy requirement for regeneration[2]. Flexisorb, Kerr-McGee, Fluor Econamine, MHI, Ucarsol and BASF-activated-MDEA are some of the examples of commercial alkanolamine based acid gas removal process technologies[3]. In spite of resistance of these alkanolamines to chemical breakdown, the plant and laboratory reports indicate that, on prolonged use particularly in the oxidative environment, these solvents can transform into products from which they are not easily regenerated. This phenomenon, commonly referred to as 'amine degradation', not only reduces the acid gas removal capacity but also leads to operational problems such as foaming, corrosion, high solution viscosity, fouling and decreased plant

equipment life. Figure 1 below depicts the zones or equipment sections in a gas absorber and a solvent regenerator (stripper) system of an aqueous amine based gas treatment process where solvent degradation is observed to occur when processing post combustion flue gas[4].
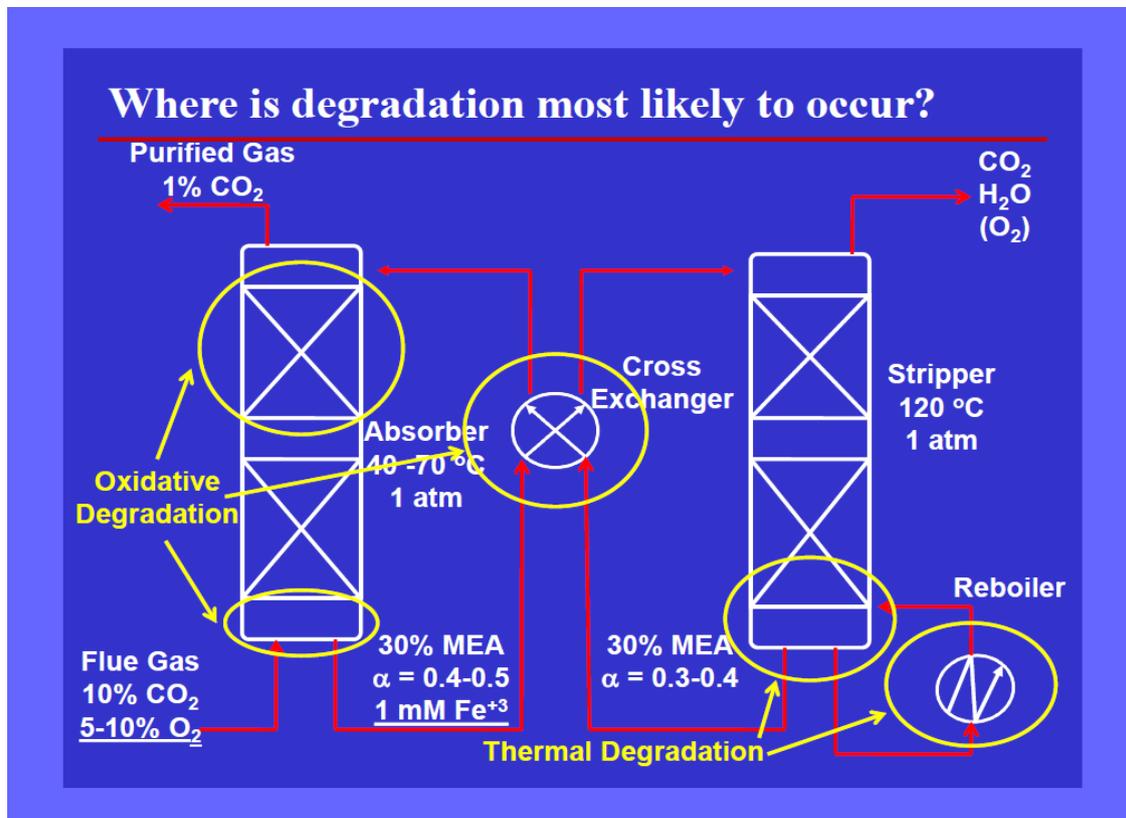
Figure 1 – Schematic of a typical amine based gas absorption-stripping system

The oxidative degradation is a chemical reaction of amine with oxygen dissolved in the amine solution that has entered the system either with the gas stream or due to the air-ingress. It occurs primarily in the absorber sump, absorber packing, piping leading to the cross exchanger (lean/rich solvent heat exchanger) and the cross exchanger. Any oxygen remaining after the cross exchanger will flash at the top of the stripper. In the case of post combustion capture of CO_2 from a coal-fired power plant flue gas, oxygen is present in the gas stream at around 4 to 8% by volume. The solvent hold up time in a commercial scale absorber sump is generally around 5 to 10 minutes allowing oxidation reactions sufficient time to degrade the solvent and cause the solvent loss[5]. In addition to oxygen, the impurities in flue gas, viz. particulate matter (metal oxides), HCL, HF, SO_X and NO_X present particularly in coal combustion off gas streams, also contribute towards the amine degradation. NO_X components of flue gas do react with amine species to form nitrosamines and nitramines that are known to be carcinogenic. Oxidation reactions, in general, involve fragmentation of N-C bond in amine and formation of O-C bond resulting into a number of degradation products that in turns can react with each other or with more oxygen or the amine itself to produce more degradation products[4]. These reactions are invariably catalysed by the metal ion impurities (Fe^{3+}, Fe^{2+} or Cu^+ etc) present in the flue gas as is usually the case with coal-fired power plant flue gas[6]. The laboratory data show that an amine solution loaded with dissolved CO_2 is much more prone to oxidative degradation than the unloaded one. In general, the rate of oxidative degradation of amines seems to depend upon the temperature, the concentrations of amine, metal ions, dissolved oxygen and CO_2 in the solution and the concentration of impurities such as SO_X in the flue gas[7]. Whilst oxidation of amines is not

well characterised for most amines since the primary degradation products are still being identified, the oxidative degradation of MEA is known to produce ammonia, aldehydes, ketones, amides and carboxylic acids[6-9]. Some of these degradation products have high volatility and can be emitted to the atmosphere both in the vapour and droplet phases during the post combustion CO_2 capture and thus could potentially affect the environment adversely. The laboratory and plant data also show that the oxidative degradation products of amine react with the materials of construction of the plant equipment and produce heat stable salts (HSS) which accumulate in the process system over time causing foaming, fouling and corrosion[10].

The thermal degradation of amine involves degradation of its carbamate form which occurs due to exposure to 100 $\overset{\circ}{C}$ or higher temperatures during CO_2 stripping. At these temperatures, the kinetic rates of degradation reactions that are suppressed in the absorber due to its lower temperature get elevated and cause enhanced solvent loss. Thermal degradation primarily occurs in the stripper packing, stripper sump, reboiler, solvent reclaimer (if present) and piping leading from the stripper to the cross exchanger. Novel stripper designs that do not include packing, such as flash-based designs, are still subject to thermal degradation. As with the absorber, the stripper sump hold-up is between 5 to 10 minutes, allowing adequate time for significant degradation. It is generally understood from the laboratory studies that temperature, CO_2 loading of the amine solution and concentration of amine strongly influence the rate of thermal degradation of amine. The CO_2 loading seems to have first order effect on the degradation rate whereas the amine concentration has more than first order effect[11]. Commonly known amines such as MEA, DEA and MDEA have been used for decades in the refinery off-gas and natural gas processing industries where thermal degradation is more predominant and hence, the thermal degradation products of these amines and their blends are generally well characterised. However, full characterisation of the thermal degradation products of amines in recent use, such as AMP and PZ, are yet to be determined. The laboratory investigations of thermal degradation of MEA show that oxazolidone, 1-(2-hydroxyethyl)-2-imidazolidone (HEIA), N-(2-hydroxyethyl)-ethylenediamine (HEEDA), MEA urea, N-(2-hydroxyethyl)-diethylenetriamine (trimer of MEA), 1-[2-[(2-hydroxyethyl)amino]ethyl]-2-imidazoline (cyclic urea of MEA trimer), N-(2-hydroxyethyl) triethylenetetramine (quatramer of MEA) and higher polymeric products are formed[11]. Since most of these products are high boiling and low volatility compounds, they are less likely to be emitted to the atmosphere in the vapour phase during the post combustion capture of CO_2.

In the cross exchanger, the amine solvent temperature could rise to as high as 100 ℃ or more, specially near its stripper ends, and cause the thermal degradation of amine. This is also the primary area where the oxidative degradation could be ongoing due to the presence of dissolved oxygen in the CO_2 rich amine. The study of combined oxidative and thermal degradation is an area of research that is decidedly lacking whereas all research to date has focussed on either oxidative or thermal degradation of amines separately. The combined effect of oxidative and thermal degradation needs to be fully understood to ascertain the degradation characteristics of an amino solvent.

Oxidative and thermal degradation of amines contributes towards the solvent loss, decrease in the solvent capacity to purify the gas stream, hydrodynamic instability of the operating systems (foaming, increased viscosity etc.), fouling of the heat transfer surfaces and corrosion of the plant equipment, thus contributing towards higher cost of gas purification. In addition to the cost, the environmental impact of atmospheric emissions of these degradation products should be addressed with the right scientific knowledge. Hence, identifying the process operating conditions that initiate the oxidative and thermal degradation of amines, identifying the exact nature of degradation products formed and their concentrations in the solvent circulating within the absorber/stripper system and determining

the likely emissions of these products into the atmosphere is extremely important, particularly when large scale post combustion carbon dioxide emission reduction is targeted for coal-fired power stations to achieve the greenhouse gas (GHG) mitigation globally.

To achieve the above objective, the oxidative and thermal degradation of select amines viz. MEA, MDEA, AMP and PZ is investigated and their anticipated atmospheric emissions estimated when aqueous solutions of these amines are used for recovering 90% CO_2 from a black coal-fired power plant flue gas. MEA is most commonly used amine for CO_2 removal commercially. The Kerr-McGee/ABB Lummus Crest process uses 10-20% w/w aqueous MEA[12]. The Fluor Daniel Econamine[TM] process uses 30% w/w aqueous MEA with an inhibitor to resist carbon steel corrosion and is especially tailored for treating flue gas with oxygen content as high as 15% v/v[13]. BASF and Ucarsol processes use aqueous MDEA solution with a rate promoter such as PZ[14]. Kansai Electric Power Co./Mitsubishi Heavy Industries Ltd KEPCO/MHI process uses sterically hindered amine, KS-1, which apparently does not require corrosion inhibitors and other additives[15]. Whilst the exact nature of KS-1 solvent is proprietary, AMP with a rate promoter, such as PZ, could be an analogous solvent[16].

Identification of the oxidative and thermal degradation products of the above selected amines in this report is based on the experimental data from the relevant literature studies. Likely emissions to atmosphere of these solvents and their degradation products is reported where available in the public domain or if it is possible to estimate by process modelling using the commercial tools such as the Aspen-Plus process simulation software. This review is necessary as a first step to enhance the accuracy of the process modelling results.

3. MONOETHANOLAMINE (MEA) DEGRADATION - REVIEW

Since early 1960s MEA has been in use for removal of CO_2 from gas streams due to its biodegradability, low cost and high reactivity towards CO_2. Its thermal degradation in the reducing environment of natural gas processing and oxidative degradation during CO_2 removal from air supply of nuclear submarines has been studied for long with a view to develop the corrosion inhibitors for protecting plant equipment and the anti-foaming agents for stabilising equipment performance. However, the proposed application of this solvent to globally remove 70 to 90% of CO_2 from commercial coal-fired power station flue gas streams has raised concerns about the environmental impact of its degradation products. As a result, several investigators have undertaken extensive characterisation and quantifications of the atmospheric emissions of MEA and its degradation products based on laboratory experiments and pilot plant operations. These studies conclude that both oxidative and thermal degradations of MEA occur during CO_2 removal from a coal-fired power plant flue gas stream and the degradation increases with temperature. The following sections describe the current status of knowledge on the oxidative and thermal degradation of MEA and the atmospheric emissions of its degradation products as observed at least during the pilot plant trials. It should also be noted that MEA has been treated in this report as a base line solvent for the post combustion CO_2 capture against which the degradation performance of other selected amines is compared.

3.1 Oxidative Degradation of MEA

Despite the latest progress achieved over the last five years in the understanding of the oxidative degradation mechanism for MEA where the electron and hydrogen abstractions were proposed as pathways towards the degradation[6] of MEA, there are still gaps in the knowledge that require to be elucidated. Fe, Cu, Cr, Ni and V ions were found to catalyse these paths. Figure 2 shows formation of the aminium and peroxide radicals via the electron abstraction mechanism which results into ammonia, formaldehyde and hydroxyacetaldehyde

formation as primary degradation products. Figure 3 shows the hydrogen abstraction mechanism towards formation of ammonia and formaldehyde as primary products. It is well known that aldehydes react with oxygen to form the carboxylic acids. Since MEA solutions have pH in the range 9 to 12, the carboxylic acids dissociate to form heat stable salts with MEA. The presence of aldehydes and organic acids in the degraded MEA solutions has been documented in a study by The Dow Chemical Co[17]. In addition, ammonia formed during the degradation process reacts with MEA in the presence of oxygen to form amides and alkylamines[6-11]. These reactions can be summarised as below:

$$C_2H_7NO + 0.5O_2 \Leftrightarrow HOCH_2CHO + NH_3 \text{------------------------- (1)}$$
$$C_2H_7NO + 0.5O_2 \Leftrightarrow 2HCHO + NH_3 \text{------------------------------- (2)}$$
$$HCHO + 0.5O_2 \Leftrightarrow HCOOH \text{--- (3)}$$
$$C_2H_7NO + 1.5O_2 \Leftrightarrow 2HCOOH + NH_3 \text{------------------------------ (4)}$$
$$C_2H_7NO \Leftrightarrow CH_3CHO + NH_3 \text{---------------------------------- (5)}$$
$$CH_3CHO + 0.5O_2 \Leftrightarrow CH_3COOH \text{-------------------------------------- (6)}$$
$$2C_2H_7NO + O_2 \Leftrightarrow 2CH_3COOH + 2NH_3 \text{------------------------- (7)}$$
$$C_2H_7NO + 0.5O_2 + NH_3 \Leftrightarrow HCONH_2 + CH_3NH_2 + H_2O \text{-------- (8)}$$
$$C_2H_7NO + 2O_2 \Leftrightarrow HOCOCOOH + NH_3 + H_2O \text{-------------------- (9)}$$
$$C_2H_7NO + 2O_2 + NH_3 \Leftrightarrow H_2NCOCONH_2 + 3H_2O \text{------------------ (10)}$$
$$C_2H_7NO + 0.5O_2 \Leftrightarrow H_2NCH_2COH + H_2O \text{------------------------- (11)}$$
$$2C_2H_7NO + 0.5O_2 \Leftrightarrow HOCH_2CH_2NHCHO + CH_3NH_2 + H_2O \text{--- (12)}$$
$$2C_2H_7NO + 0.5O_2 \Leftrightarrow HOCH_2CH_2NHCOCH_3 + NH_3 + H_2O \text{----- (13)}$$

In general, the stoichiometric equation given below represents the above reactions,

$$MEA + \Delta O_2 \Leftrightarrow NH_3 + Degradation\ Products$$

Figure 2 – Electron abstraction mechanism for the oxidative degradation of MEA
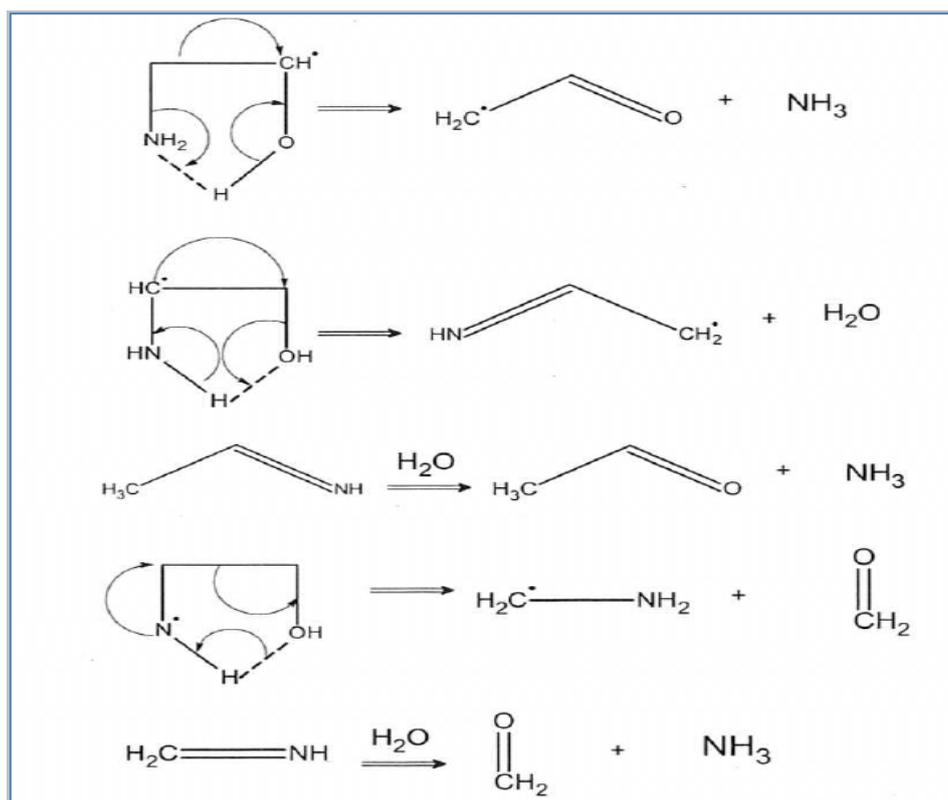
Figure 3 – Hydrogen abstraction mechanism for the oxidative degradation of MEA

Thus, the oxidative degradation of MEA involves a complex mixture of series and parallel reactions with ammonia as a primary product. Knowing the rate of ammonia evolution and the rate of dissolved oxygen consumption, the overall oxygen stoichometry (Δ) can be determined for the oxidative degradation of MEA as:

$$\text{Oxygen Stoichiometry } (\Delta) = (\text{Rate of O}_2 \text{ consumption} / \text{Rate of NH}_3 \text{ evolution})$$

Its value varies from 0.5 to 2.5 depending on what degradation product is being formed[6, 7]. It should be noted that the stoichiometry for acetaldehyde formation is 0.0, which means it can be formed by any free radical and does not require presence of oxygen. Vevelstad et al[18] have recently used continuum solvation models and performed quantum mechanical calculations to determine the heat of reaction (ΔH) and the Gibbs free energy change (ΔG) for the reactions 1 to 13 summarised above. These authors have not specified the temperature range at which these calculations were made. Consequently, these data have limited use towards building non-mechanistic kinetic rate models of the oxidative degradation of MEA and determining the degradation product distribution.

Laboratory studies of the oxidative degradation of MEA in sparged and agitated reactors by Goff[6] indicate that the degradation of MEA is a function of temperature and concentrations of metal ions (Fe, Cu, Cr, Ni, V etc), MEA and dissolved oxygen in the solution. The degradation can be O_2 mass transfer limited under laboratory conditions and the NH_3 evolution increases linearly with the oxygen concentration in gas stream up to 17 % by volume. Their results also indicate that the MEA solution with lower CO_2 loading has higher rate of oxidative degradation but lower oxygen stoichiometry in comparison with the MEA solution which has higher CO_2 loading. Under industrial conditions, the degradation of MEA can be both kinetics and O_2 mass transfer limited depending upon the liquid to gas ratio maintained in the gas/liquid system and the hydrodynamics of the system. NH_3 evolution

generally increases with higher MEA concentrations. At aqueous concentrations above 7 molar MEA (~ 42% w/w), the degradation rate appears to be O_2 mass transfer controlled and for solutions below 2 molar MEA (~ 12% w/w) appears to be kinetics controlled. Intermediate solution concentrations exhibit the effects of both kinetics and O_2 mass transfer control. Goff and Rochelle[19] reported that in industrial applications the oxidative degradation related MEA loss could be 0.29 to 0.73 kg of MEA per ton of CO_2 captured. Table 1 below summarises the results of various laboratory studies for the oxidative degradation of MEA reported in the literature.

Table 1 – Comparison of key studies for the oxidative degradation of MEA

Study	T (°C)	MEA (molar)	Gas	Liquid Volume (Litre)	Space Time (min)	Degradation Rate (milimoles/hr)	K_G (milmoles/ hr/bar)
Rooney et al[17]	82	5.4	Air	1.0	181.8	0.03 to 0.07	0.2 – 0.4
Blachly et al[20]	55	5.4	Air	0.3	1.0	0.02 to 0.14	0.1 – 0.8
Girdler[21]	80	3.1	50% O_2	0.1	1.0	0.36 to 1.32	0.7 – 2.6
Hofmeyer et al[22]	75	5.4	Pure O_2	0.2	0.35	5.0	5.0
Chi et al[23]	55	7.0	Air	0.4	0.05	0.1 to 2.32	0.6 – 12.9
Goff et al[24]	55	7.0	Air	0.3	0.04	0.48 to 5.0	2.7 – 27.8
Goff et al[19]	55	7.0	Air	0.5	0.06	0.25 to 8.25	1.4 – 45.8

Space Time = (Liquid Volume / Gas flow rate)
K_G = Apparent mass transfer co-efficient = (Degradation rate / Partial Pressure of O_2 in gas)

In the case of a coal-fired power plant, the impurities such as SO_X, NO_X and particulate matter (metal oxides) are invariably present in the flue gas stream in addition to un-reacted oxygen. SO_X are known to degrade MEA as per the reactions 14 to 16 below forming organo-sulphates and thiovanic acid[25]. The particulate matter has potential to not only act as a degradation catalyst but also form sludge within the gas/liquid contactor which causes corrosion and erosion of the plant equipment.

$$2(C_2H_5ONH_2) + SO_3 + H_2O \Leftrightarrow (C_2H_5ONH_3)_2SO_4 \text{----------------------- (14)}$$

$$2(C_2H_5ONH_2) + SO_2 + 0.5O_2 + H_2O \Leftrightarrow (C_2H_5ONH_3)_2SO_4 \text{------------- (15)}$$

$$C_2H_5ONH_2 + SO_2 \Leftrightarrow C_2H_4O_2S + NH_3 + 0.5O_2 \text{-------------------------- (16)}$$

There is limited information available in the public domain on the mechanism of degradation of MEA due to presence of NO_X in the flue gas. However, Pedersen et al[26-29] have recently shown that degradation of MEA in the presence of NO_X resulted into the formation of nitrosamines in their Aminox^{TM} rig and in a high-pressure autoclave. In these experiments, the authors exposed 30 to 40 wt% MEA solution at CO_2 absorber (44 °C) and stripper (120 °C) conditions to a flue gas containing 3.5 vol% CO_2, up to 14 vol% oxygen and as much as 100 ppmv NO_X. These investigators observed that NO is oxidised to NO_2 in the absorber inlet and roughly 20% of NO_2 is absorbed into the liquid phase due to the following reaction taking place in the presence of oxygen in flue gas:

$$NO + NO_2 + 0.5O_2 + H_2O \Leftrightarrow HNO_2 + HNO_3 \text{------------------ (17)}$$

The above reaction is known to occur even at room temperature[43]. Jackson et al[30] indicate that HNO_2 acts as a nitrosating agent in alkaline environment (pH >7) and the secondary amines such as Diethanolamine (DEA) are reactive towards the nitrosamines formation in the presence of NO_X. Results of Pedersen et al indicate that ammonia is the primary degradation product of MEA and its production is strongly correlated with the NO_X concentration in flue gas. Whilst these investigators expected MEA being a primary amine not to form stable nitrosamine, they however detected 0.5 ppm (by weight) nitrosodiethanolamine (NDELA) under the absorber environment after 100 hours of solution exposure to NO_X (25 to 50 ppmv). Pedersen et al believe that NDELA may have been formed from DEA, a secondary amine, that may have been either present in the MEA solution as an impurity or formed as a result of NO_X induced degradation of MEA which has undergone the nitrosation reactions with NO and HNO_2. Figures 4 to 6 show formation of NDELA and DEA in MEA solution as a function of its exposure time and the concentrations of O_2 and NO_X in flue gas. These results clearly show that even at NO_X concentration as low as 5 ppmv, NDELA is formed. Other investigators[31-33] do confirm the conclusion of Pedersen el al that for the formation of stable nitrosamines, the presence of a secondary amine in the reaction mixture is necessary.

Formation of nitrosamines at a concentration of 2.91 µmol/mL of lean MEA solution has also been confirmed by Strazisar[34] et al who analysed lean MEA, fresh MEA and reclaimer bottom streams at Kerr MCcGee technology based CO_2 capture plant of IMC Chemicals Inc, Trona, California. This plant has been in operation since 1978 and uses 15 to 18% w/w MEA solution to capture CO_2 from a coal-fired boiler flue gas slip stream. In addition to nitrosamines, organo-sulphates were also detected in the lean MEA solution. Unfortunately, Strazisar et al did not attempt to identify individual nitrosamine chemical in their study. Whilst this study has been first of its kind in the sense that actual power plant flue gas was used to understand oxidative degradation of MEA, because neither the spent MEA solution nor the reclaimer bottom stream or CO_2 lean flue gas was analysed, the quantification of volatile degradation product such as NH_3 was not available. While quantitative data on the rates of oxidative degradation of MEA can not be determined from this study, it does confirm the formation of carboxylic acids in the degraded solution as observed by other laboratory based studies.
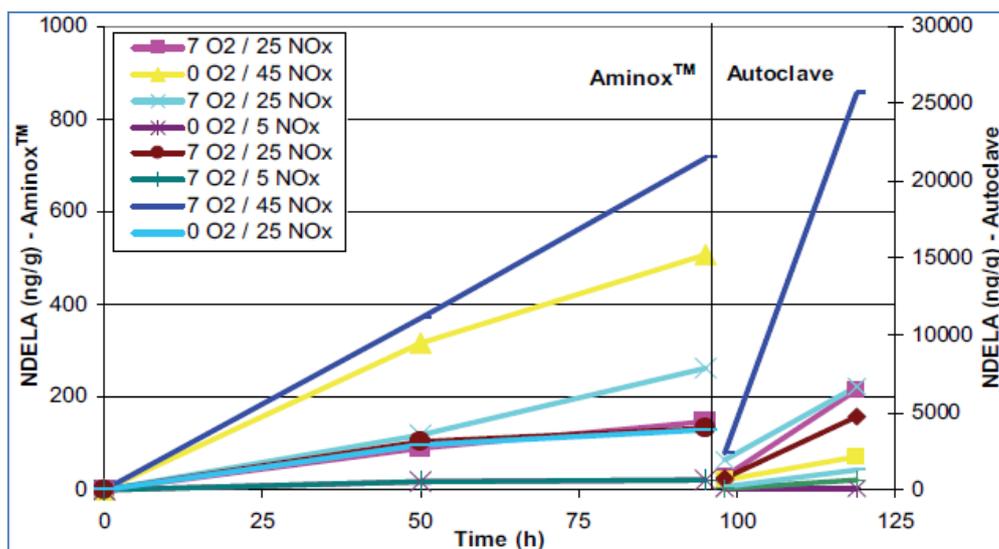

Figure 4 – Formation of NDELA in MEA solvent (Legend: $7O_2$ / $25NO_X$ denotes flue gas with 7 volume % Oxygen and 25 ppmv NO_X)
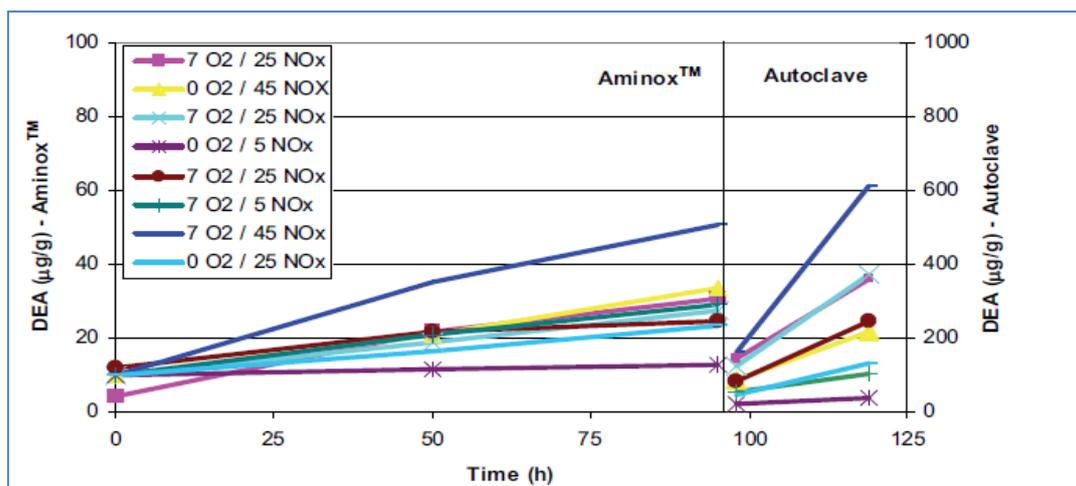
Figure 5 - Formation of DEA in MEA solvent (Legend: $7O_2$ / $25NO_X$ denotes flue gas with 7 volume % Oxygen and 25 ppmv NO_X)
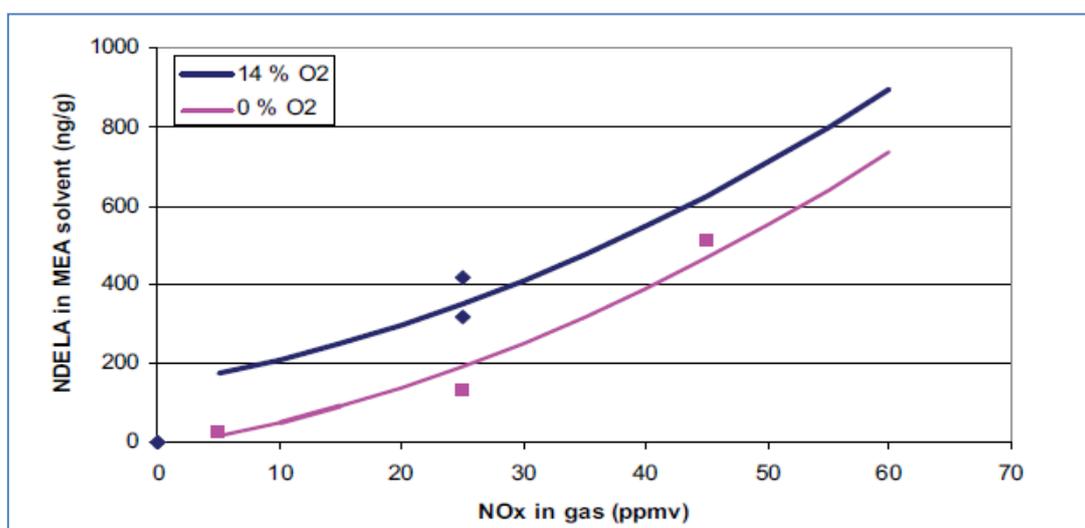

Figure 6 – Predicted (solid lines) and observed (dots) concentrations of NDELA in MEA solvent Aminox[TM] absorber condition.

Whilst previous laboratory studies on the oxidative degradation of MEA assessed the effect of oxygen mass transfer rate, CO_2 loading of MEA, MEA concentration and catalytic effect of the metal ions in solution and related these parameters to the evolution of NH_3 as a measure of MEA loss, the research group from University of Regina has focussed on measuring MEA degradation rate as a function of temperature, CO_2 loading of MEA and concentrations of oxygen and sulphur dioxide (SO_2) dissolved in solution to evaluate the contributions of SO_2 and O_2 to the degradation of MEA during CO_2 capture from power plant flue gas streams[35-38]. Uyanga and Idem[37] have developed a data regression based empirical rate expressions for oxidative degradation of MEA on the basis of such studies which are valid over the temperature range of 328 – 413 K, MEA concentrations in the range of 3 – 7 moles per litre of solution, SO_2 concentrations in flue gas ranging from 6 to 196 ppmv and oxygen concentrations in the range of 6 – 100 mole%. Both linear (Equation 18) and non-linear (Equation 19) power-law rate expressions have been provided as kinetic rate models assuming that all reactions occur in the liquid phase. These expressions are listed below. To eliminate any mass transfer resistance, the liquid phase (reaction mixture) was vigorously stirred at 505 rpm during the laboratory experiments.

$$-R_{MEA} = 0.7189 \exp[-(20752/8.314*T)] [MEA]^{1.359}[SO_2]^{2.0}[CO_2]^{-0.333}[O_2]^{0.03} \text{------- (18)}$$

$$-R_{MEA} = 0.00745 \exp[-(45258/8.314*T)] [MEA]^{1.9}[CO_2]^{-0.333}\{[SO_2]^{3.4} + [O_2]^{2.8}\} \text{------- (19)}$$

Where R_{MEA} is rate of degradation of MEA (moles/litre/hr), [MEA], $[CO_2]$, $[SO_2]$ and $[O_2]$ are molar concentrations (moles/litre) of MEA, CO_2, SO_2 and O_2 in solution and T is absorber temperature (K). The first expression accounts for the scenario in which the concentrations of all the species in the kinetic rate model are greater than zero. The second rate expression is a more-general model and allows the SO_2 and/or O_2 concentration to be zero or greater than zero.

Recently, Supap et al[38] have improved upon the above mentioned degradation rate models and suggested the following non-linear rate expression that is claimed to better represent the experimental results:

$$-R_{MEA} = \{6.74 \times 10^9 e^{-(29403/RT)}[MEA]^{0.02}([O_2]^{2.91}+[SO_2]^{3.52})\}/\{1+1.18x[CO_2]^{0.18}\} \text{------- (20)}$$

Where, R is universal gas constant (8.314 J/mole/K). Unlike previous models, this model shows an improvement in that any of the parameters, i.e. $[O_2]$, $[SO_2]$ and $[CO_2]$ terms can be removed without affecting the usability of the model.

From the process operations point of view, it is now accepted that minimising the absorber temperature rise, reducing the O_2, SO_2, NO_X and particulate content of flue gas, maintaining optimal CO_2 loading of MEA solution and MEA concentration, using appropriate materials of construction and the select use of corrosion inhibitors are all necessary to minimise oxidative degradation of MEA. Bicine, Ethylene diamine-tetra-acetic acid (EDTA), sodium sulphite (Na_2SO_3), potassium sodium tartarate tetrahydrate ($KNaC_4H_4O_6.4H_2O$), hydroxylamine (NH_2OH), diethylene triamine penta acetic acid (DTPA), dimercaptothiadiazole (DMTD) and a mixture of these compounds have been suggested in the literature[4,6,7,11,39,40] as the corrosion inhibiting compounds for the amine based post combustion CO_2 capture apparatus. However, not all of them are effective as observed by Rochelle and his researcher group[4,6,7,11].

Oxidative degradation related emissions of MEA and its degradation products observed in the pilot plant scale trials or noted in commercial scale (300 to 600 tonnes per day CO_2) operations and predictions of such emissions by means of process engineering simulation tools such as the Aspen-Plus have been discussed and summarised in the relevant sections of this report.

3.2   Thermal Degradation of MEA

The thermal degradation of MEA occurs predominantly in the stripper packing and reboiler due to exposure to high temperature. Davis and Rochelle[41] indicate that thermal degradation is minor when reboiler temperature is held below 110 °C but it accelerates above 130 °C. These authors indicate that carbamate polymerisation due to high temperature is the main cause of thermal degradation of MEA which is compounded when CO_2 loading of the solution is increased. Figure 7 shows the reaction pathway for thermal degradation of MEA as envisaged by Davis and Rochelle[11, 41].
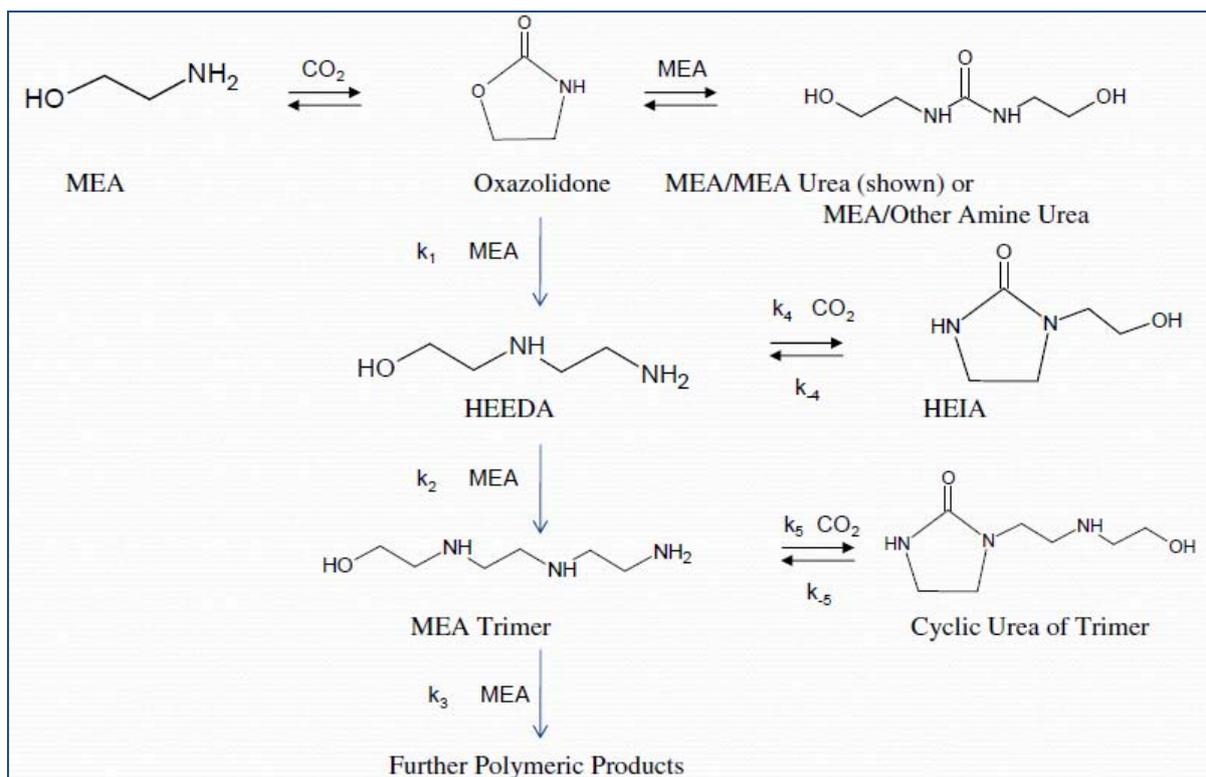
Figure 7 – Reaction mechanism for thermal degradation of MEA

According to this reaction mechanism, MEA carbamate cyclises internally through dehydrolysis step to form oxazolidone. Another molecule of MEA attacks oxazolidone at the ketone group to form MEA urea. MEA molecule can also attack oxazolidone to form N-(2-hydroxyethyl)-ethylenediamine (HEEDA). HEEDA then reacts with dissolved CO_2 in spent solution to form a HEEDA carbamate similar to MEA and ends up as 1-(2-hydroxyethyl)-2-imidazolidone (HEIA) or reacts with oxazolidine to form the trimer of MEA. The trimer of MEA in turn reacts with dissolved CO_2 in spent solution to form cyclic urea of MEA trimer. This polymerisation can continue indefinitely through the quatramer of MEA and its corresponding cyclic urea. Figure 8 shows the reaction sequence for MEA thermal degradation with Table 2 showing values for various rate constants.
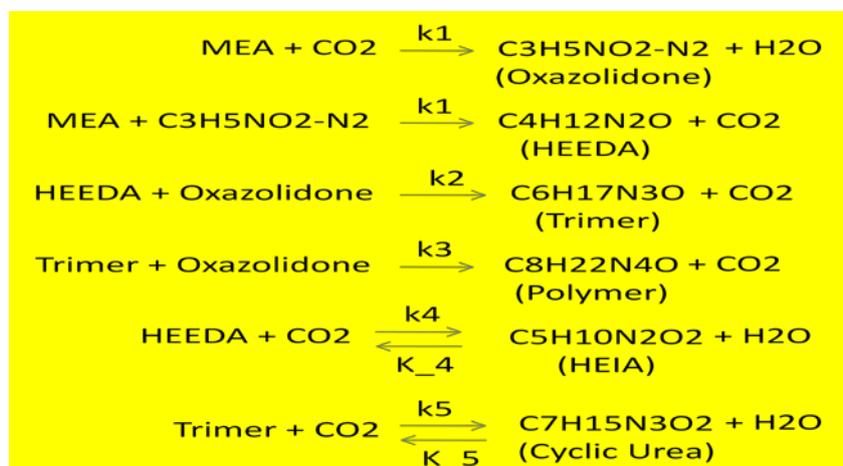
Figure 8 – Thermal degradation reaction sequence for MEA

Table 2 – Thermal degradation reaction rate constants and activation energies

Rate Constant	Pre-Exponential Constant (L/day/mole)	Activation Energy (Kcal/mole)
K1	1.05E16	34.4
K2	2.15E16	33.3
K3	3.28E15	31.5
K4	3.58E16	33.0
K-4	4.47E15	32.6
K5	3.65E15	31.3
K-5	4.56E14	31.3

Figure 9 shows thermal degradation product distribution for 7 molal MEA at 135 °C and CO_2 loading of 0.4 mole per mole of MEA as measured experimentally by Davis[11]. However, HEEDA/HEIA product distribution trend could change with temperature as observed by Davis[11] at 100 °C for the same solution concentration and CO_2 loading where more HEEDA formed than HEIA.
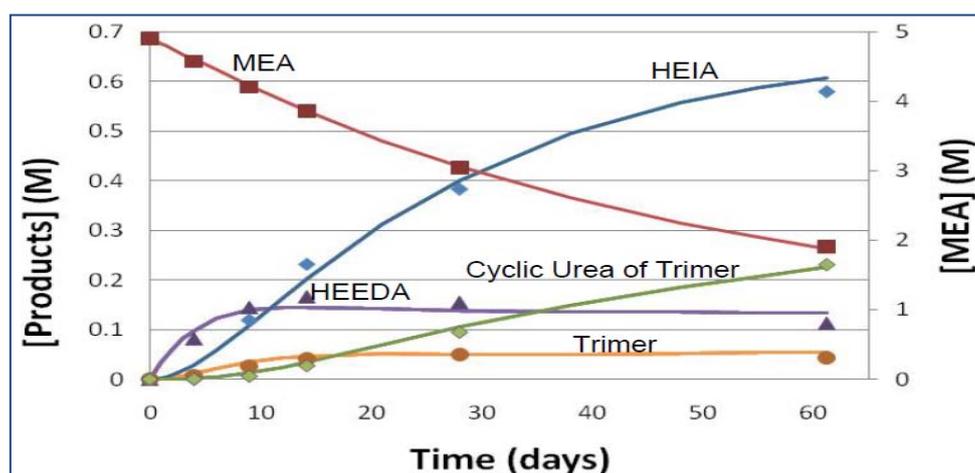

Figure 9 – Thermal degradation product distribution for 7 molal (30 % w/w) MEA at 135 °C and 0.4 mole/mole CO_2 loading

Figure 10 shows the effects of MEA concentration, CO_2 loading and stripper reboiler temperature on the amine loss due to thermal degradation as observed by Jason and Rochelle[41]. These results clearly indicate that the rate of degradation quadruples at every 17 °C rise in the stripper reboiler temperature or approximately every time the pressure of stripper is doubled. Decreasing the CO_2 loading is roughly a first order effect causing similar decrease in the degradation rate. Increasing MEA concentration from 30 to 40% w/w shows slightly more than first order effect. In practice, increasing MEA concentration will increase the reboiler temperature due to elevation in the boiling point of solution. Using this information and Aspen-Plus software, Jason and Rochelle[11, 41] have developed the stripper performance curve (Figure 11) that depicts optimum operating conditions for MEA stripper with respect to energy and MEA consumption costs ($ per metric ton of CO_2) when CO_2 capture is carried out using 30% w/w MEA solution and the product CO_2 pressure is 150 atm. The results show that for post combustion CO_2 capture with 30% w/w MEA, optimum stripper bottom pressure and temperature are 3.5 atm and 120 °C respectively when MEA

loss due to degradation is accounted. In this case, as per Closmann[125] the cost of MEA loss due to degradation is approximately US $1.5 per metric ton of CO_2.
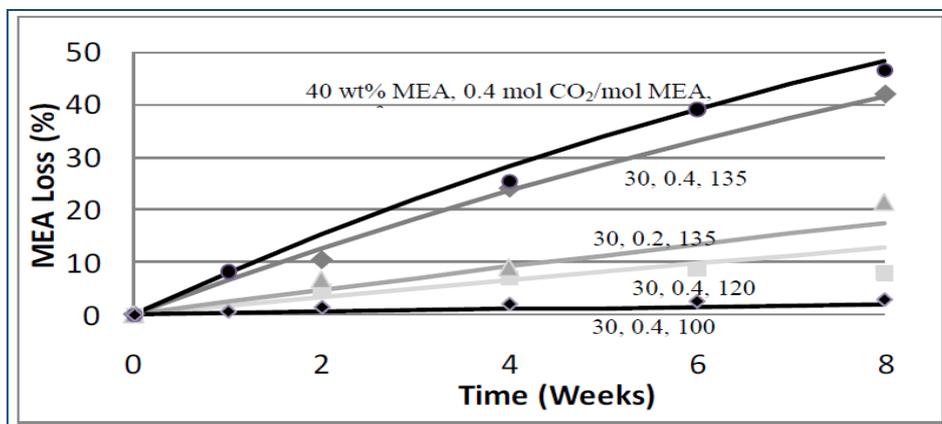
Figure 10 – MEA loss over time as a function of MEA concentration, CO_2 loading and stripper reboiler temperature
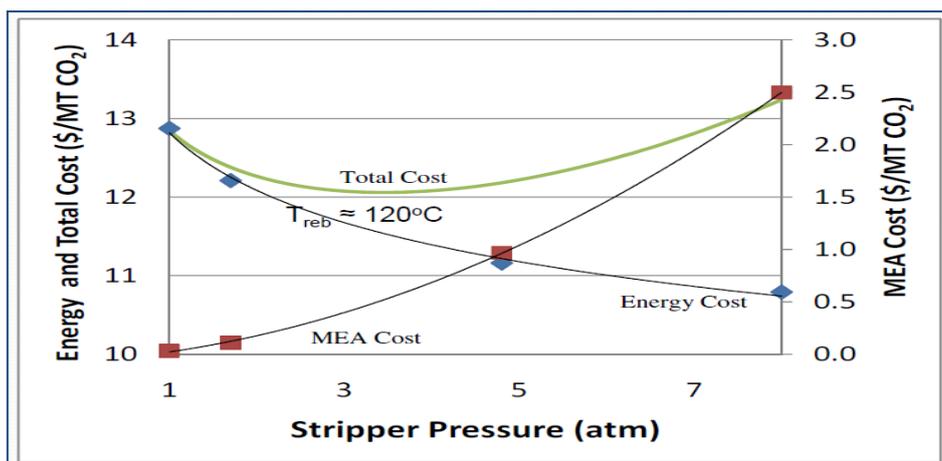
Figure 11 – Energy and MEA costs as a function of stripper pressure 30% w/w MEA with 0.2 CO_2 lean and 0.52 CO_2 rich loadings

Recently, Lepaumier et al[42] have compared oxidative and thermal degradation characteristics of MEA observed in the laboratory environment with those observed in the pilot plant at Esbjergvaerket in Denmark. This pilot plant captures 1 ton/hr of CO_2 from a slip stream (5000 Nm^3/h) of flue gas from a 400 MW coal-fired power station using 30% w/w MEA. Whilst these investigators concur with the observations of Davis and Rochelle[41], they identified several more degradation products in the MEA solution from pilot plant than in the laboratory solution though initial MEA concentration, CO_2 loading, reaction temperature and aging of both solutions were identical. This implies that MEA degradation pathways could be different in an actual plant environment from those of the laboratory environment where mostly sparged or continuously stirred batch reactors made of glass or steel are used with either air/CO_2 mixture or synthetic flue gas free of fly ash. Process factors such as the use of demineralised water in solution preparation and the lack of metal ions in solution due to fly ash free synthetic gas are most likely concealing the relative effect of catalysis on various

MEA degradation reactions in the laboratory environment. Accordingly, in addition to Oxazolidone, and N-(2-hydroxyethyl)ethylenediamine (HEEDA) and N-(2-hydroxyethyl)imidazolidinone, (HEIA), Lepaumier et al[42] detected N-(2-aminoethyl)-N'-(2-hydroxyethyl)imidazolidone (AEHEIA) in the laboratory solution which they could not detect in the pilot plant solution. Similarly, HEEDA was not detected at all in the pilot plant sample. The pilot plant sample however had a number of high molecular weight amide derivatives resulting from the reaction of MEA with carboxylic acids, viz. formic, acetic, glycolic and oxalic acid which were not at all present in the laboratory sample. This implies that the carboxylic acids, usually referred to as "Heat Stable Salts", are not stable and can react further in an industrial plant environment to give more complex compounds. Lepaumier et al[42] identified these additional degradation products as N-(2-hydroxyethyl)acetamide (HEA), 2-hydroxy-N-(2-hydroxyethyl)acet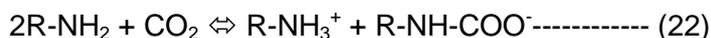amide (HHEA), N,N'-bis(2-hydroxyethyl)oxalamide (BHEOX), 4-(2-hydroxyethyl)piperazin-2-one (HEPO) and N-(2-hydroxyethyl)-2-(2-hydroxyethylamino) acetamide (HEHEAA) in the pilot plant solution sample.

It should be noted that in contrast to Strazisar et al[34], Lepaumier et al[42] analysed the lean MEA, the CO_2 rich MEA and the reclaimer bottom solutions to identify both oxidative and thermal degradation products of MEA in an actual operating process environment of Esbjergvaerket pilot plant. Lepaumier et al results for MEA degradation are essentially similar to those of Strazisar et al[34] where these investigators determined the degradation products by simply analysing the lean MEA solution circulating between the stripper and absorber of Trona, California, based Kerr McGee plant. This implies that the degradation products once formed may not get reversed to MEA either in the absorber or the stripper and continue to build with time.

In summary, the oxidative and thermal degradation of MEA is a complex phenomenon that leads to a number of different organo-chemicals that may not yet have been fully characterised and quantified. In an actual plant environment, the degradation products represent a combined effect of oxidative and thermal degradation which is perhaps different from the sum total of effects measured separately in the laboratory environment. For increasing the confidence in assessing and predicting the degradation products of a selected solvent, it is important to have knowledge about the laboratory studies as well as the correspondent results from pilot plant measurements

4. DEGRADATION OF 2-AMINO-2-METHYL-1-PROPANOL (AMP) - REVIEW

AMP (2-Amino-2-Methyl-1-Propanol) is a sterically hindered primary amine that forms bi-carbonate ions on reaction with the dissolved CO_2 in solution as against the carbamate ions produced by MEA in the same situation.

$$R\text{-}NH_2 + CO_2 + H_2O \Leftrightarrow R\text{-}NH_3^+ + HCO_3^- \text{ ----------- (21)}$$

$$2R\text{-}NH_2 + CO_2 \Leftrightarrow R\text{-}NH_3^+ + R\text{-}NH\text{-}COO^- \text{------------ (22)}$$

As a result, its CO_2 carrying capacity is twice that of MEA on mole per mole basis. However, AMP is a slow reacting amine and PZ (Piperazine) is normally added to the solution to accelerate CO_2 absorption reaction[44-48]. AMP is also less corrosive compared to MEA its corrosion potential can be controlled by adding simple inorganic salts such as Na_2SO_3 and $NaVO_3$ as shown experimentally by Veawab[49]. Aqueous solution of AMP (3 molar) and PZ (2 molar) mixture is supposedly CESAR1 solvent[50] that has been trialled at 1 ton/hr post combustion CO_2 capture pilot plant at Esbjergvaerket in Denmark. This solvent gives better performance in terms of reduced reboiler energy requirement in comparison with MEA. Mitsubishi Heavy Industries (MHI) technology solvent, KS-1, is also a mixture of primary

hindered amine and a rate promoter such as PZ, though the exact details of this solvent are proprietary knowledge.

4.1   Oxidative Degradation of AMP

The public domain literature information on the oxidative degradation of hindered amines, particularly AMP, is very limited. Only very recently, Wang and Jens[51] have made available experimental data on the oxidative degradation of AMP. They performed oxidative degradation experiments on 3 to 5 molar aqueous solution of AMP in a 200 mL glass autoclave under pure oxygen (250 to 350 kPa) at 100 to 140 ℃ and air/CO_2 mixture at 50 to 70 ℃ for 16 days. Amine concentration was determined periodically by the cation-exchange chromatography and the degradation products identified by the anion chromatography, gas chromatography-mass spectrometry and Fourier transform infra red spectroscopy. Figures 12 to 19 show their results. These results show that the oxidative degradation rate of AMP is close to that of Methyldiethanolamine (MDEA) but less than that of MEA under identical conditions. AMP is not a stable amine despite steric hinderance and the Oxazolidone formation can not be prevented. However, the steric hinderance of amine function stops ring opening of oxazolidone to further high molecular weight degradation products as seen with MEA. Degradation of AMP is oxygen mass transfer limited and strongly depends upon oxygen pressure. Transition metal ions (Fe^{2+}, Fe^{3+} and Cu^{2+}) have no obvious effect on oxidative degradation rates and that explains low corrosion potential of AMP observed by Veawab et al[49, 52]. However the oxidative degradation rates seem to increase with CO_2 loading as shown in Figure 18. Various carboxylates, ammonia, acetone, 2,4-Lutidine (Dimethyl pyridine) and 4,4-deimethyl-2-oxazolidone are the main oxidative degradation products of AMP[53].
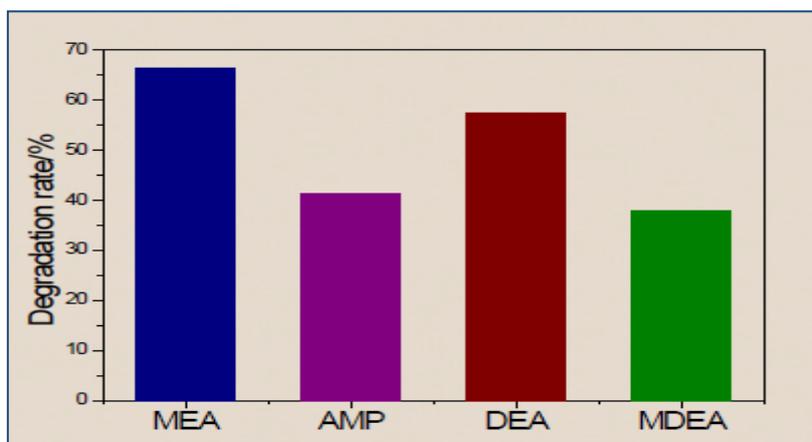
Figure 12 – Comparison of oxidative degradation of various amines at 120℃, 5 molar aqueous solutions, 350 kPa pure Oxygen and 16 days time
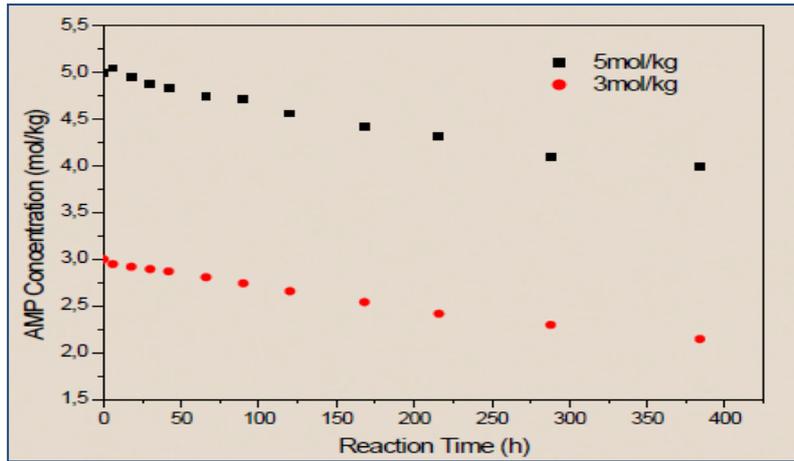
Figure 13 – Effect of AMP concentration on oxidative degradation, 250 kPa Oxygen and 120 ℃
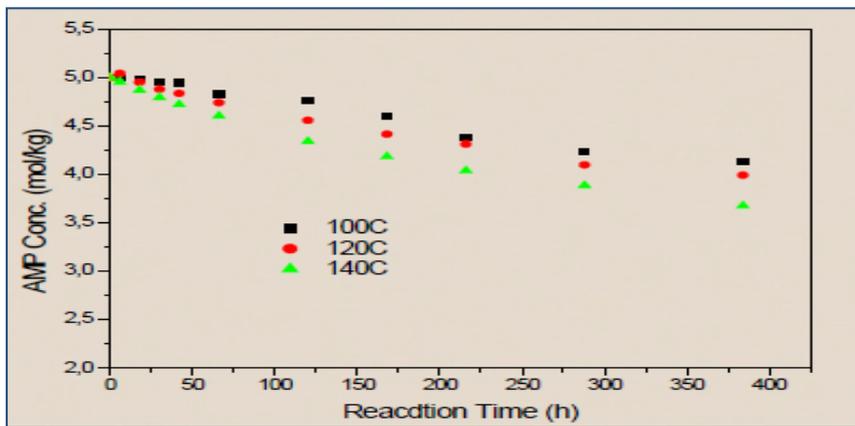
Figure 14 – Effect temperature on oxidative degradation of AMP, 250 kPa pure oxygen
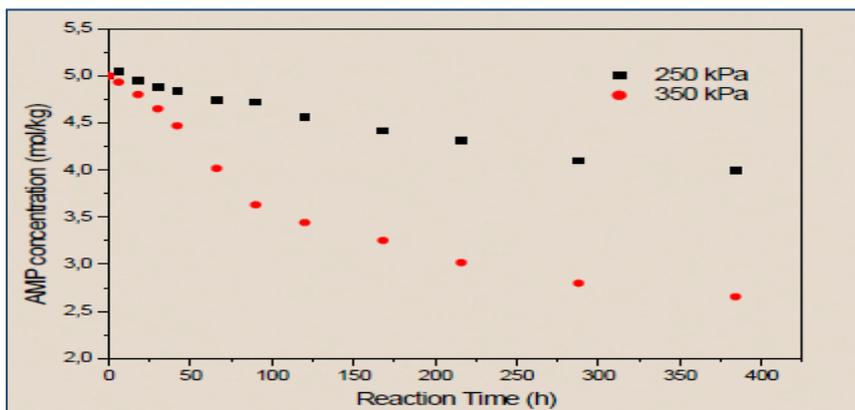
Figure 15 – Effect of Oxygen pressure at 120 ℃
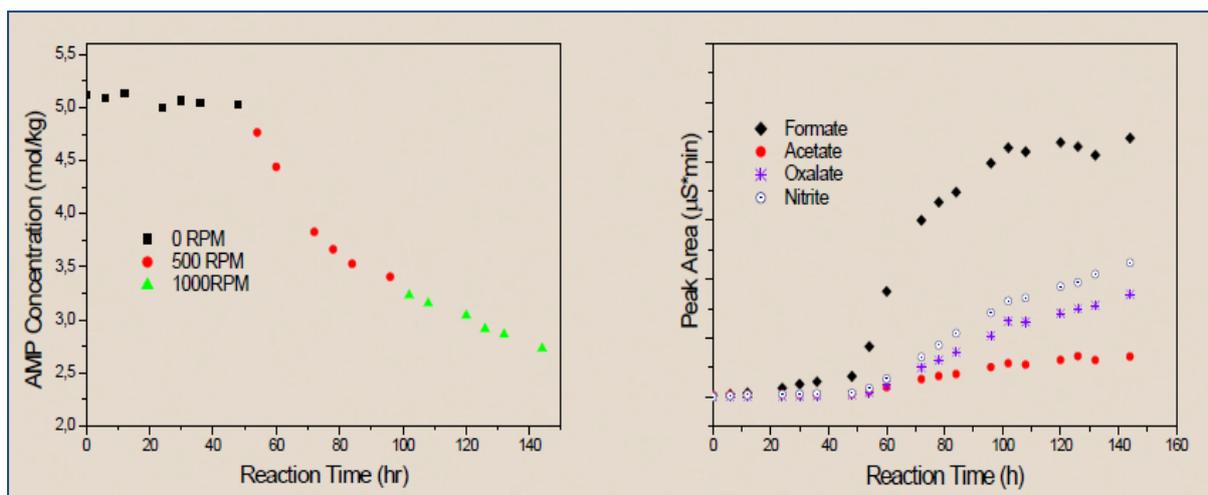
Figure 16 – Effect of solution agitation rate on oxidative degradation with corresponding anion determination, 120 ℃ and 250 kPa oxygen pressure
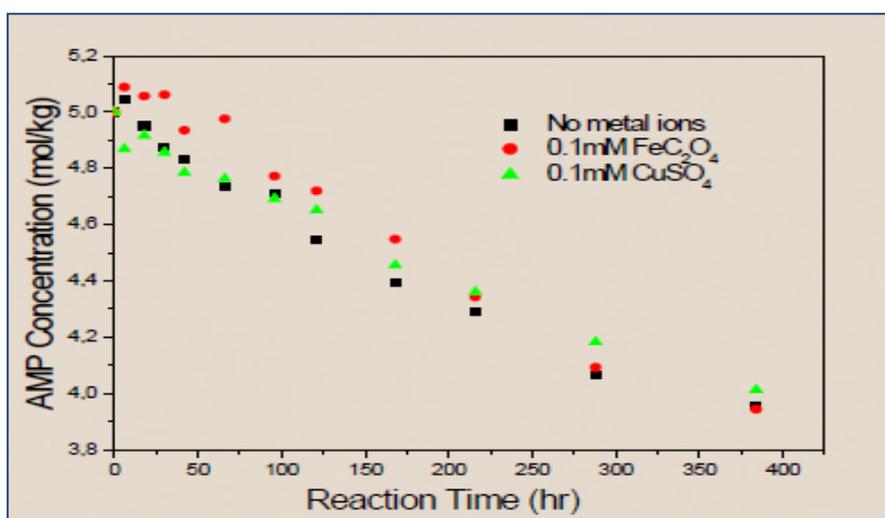
Figure 17 – Effect of metal ions on oxidative degradation of AMP, 120 ℃ and 250 kPa Oxygen pressure
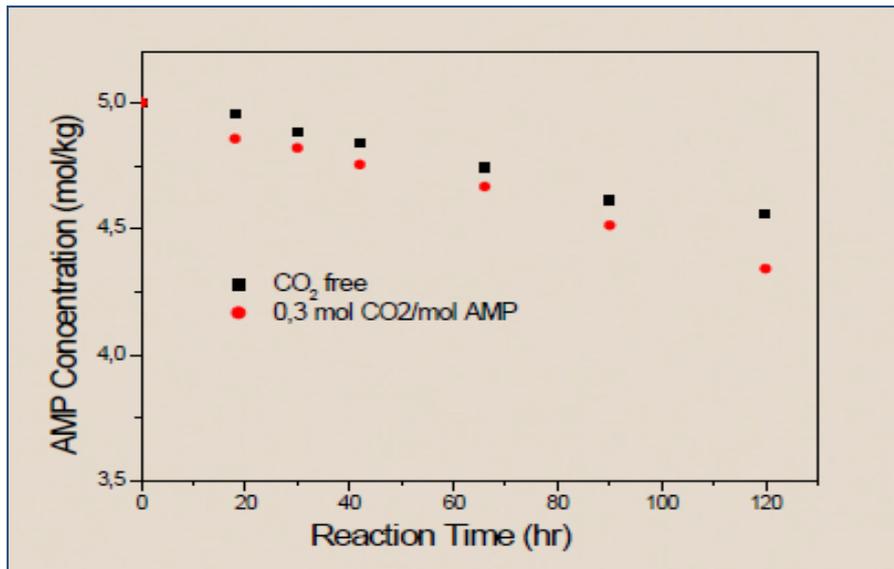
Figure 18 – Effect of CO₂ loading on oxidative degradation of AMP, 120℃ and 250 kPa Oxygen pressure
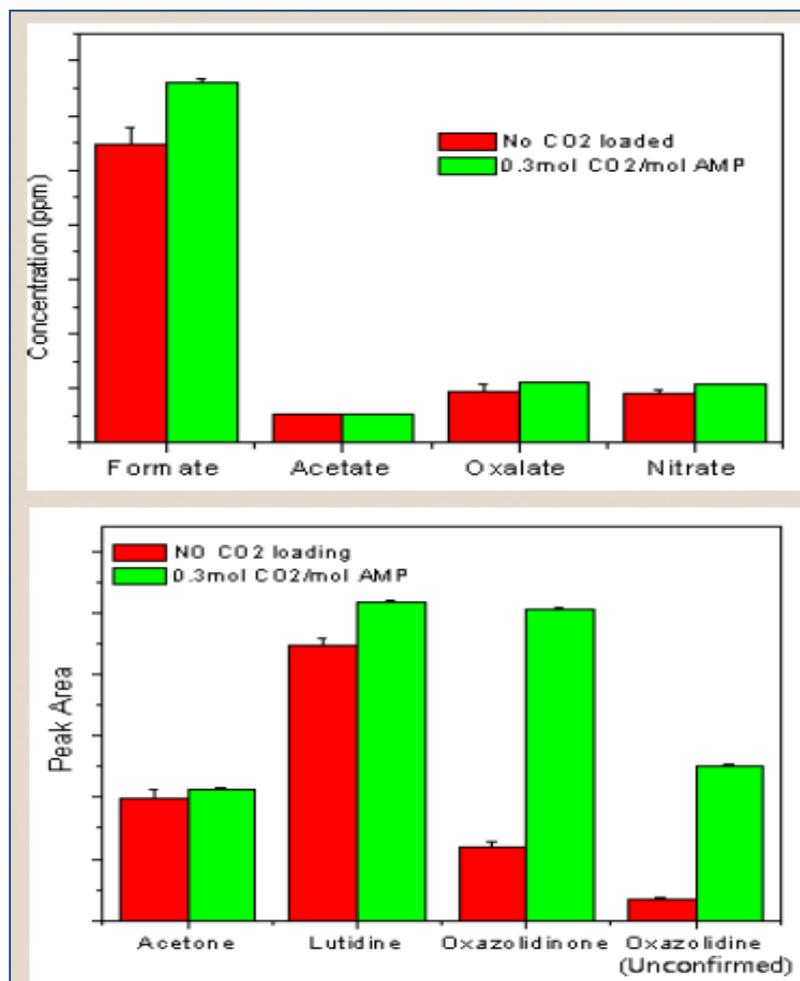
Figure 19 – Effect of CO₂ loading on oxidative degradation product distribution, 5 mole/kg of AMP degraded at 120℃ and 250 kPa Oxygen pressure

Voice and Rochelle[54] and Lepaumier et al[55, 56] have recently investigated the oxidative degradation of several new amines for their potential to form volatile products including ammonia. They confirm that the steric hindrance nature of amine function in AMP causes less formation of volatile products including ammonia at the CO_2 absorber temperature of most likely industrial practice (~ 55 to 80 $^{\circ}$C) when compared with the performance of MEA. This implies that in industrial practice, the atmospheric emissions of volatile degradation products due to use of AMP as a solvent will be less than that for MEA as a solvent.

At present, there is no laboratory or pilot plant experimental data available for either identifying or quantifying the oxidative degradation products of AMP due to SO_X and NO_X. However, the laboratory data from Oh et al[57], Choi et al[58] and Seo et al[59] for absorption of CO_2 from a gas mixture containing SO_2 indicate that the aqueous solution of 30% w/w AMP reacts with SO_2 as per the following reaction:

$$SO_2 + H_2O + 2AMP \Leftrightarrow 2AMPH^+ + SO_3^{2-} \text{------------ (23)}$$

This implies that AMP may be consumed by SO_X impurities in flue gas during absorption of CO_2. Mimura et al[60] have proposed the use of AMP at 40°C with and without rate promoter (Piperazine) to simultaneously absorb CO_2 and NO_2 from a gas stream. The published data shows that in the absence of oxygen in the gas phase, 30% w/w AMP solution without any CO_2 loading or a rate promoter has the liquid side mass transfer co-efficient value of 3.8 x 10^{-8} mol/s.Pa.m^2 for NO_2 absorption which increases to 6.5 x 10^{-8} mol/s.Pa.m^2 when Piperazine concentration in the solution is increased from zero to 3% w/w. This implies that addition of a rate promoter such as Piperazine accelerates AMP-NO_2 reaction. However, to accurately assess the rate of AMP-NO_2 reaction in a CO_2 absorber, data with CO_2 loaded amines are required.

In light of the above literature information, it should be noted that Mimura et al[60] are the originators of MHI process technology that uses KS-1 hindered amine solvent with a rate promoter and in this context, it is interesting to note that the published information[61-64] on MHI process technology states clearly that the KS-1 solvent loss due to the formation of heat stable salts is minimised, if SO_X concentration at inlet to the absorber is kept as low as 0.1 ppmv. These publications also point out the relationship of atmospheric emissions (both vapour and droplet phase) of KS-1 solvent to the SO_3 concentration of flue gas at inlet to the absorber as shown in Table 3. In addition, the relevant MHI publications clearly state that none of NO_X in flue gas gets absorbed in the direct contact cooler upstream of the absorber but 1 to 3% of the inlet NO_X is absorbed by KS-1 solvent producing however low levels of heat stable salts.

Table 3 – Atmospheric emissions of KS-1 solvent v/s SO₃ content of flue gas

SO₃ Concentration of flue gas @ absorber inlet	KS-1 Emissions
Zero	0.4 ppmv
1 ppmv	9.1 ppmv
3 ppmv	23.2 ppmv

4.2   Thermal Degradation of AMP

Similar to the oxidative degradation of AMP, data on the thermal degradation of AMP has become only recently available though it is very limited. Figure 20 below shows the thermal degradation behaviour observed by Wang and Jens[53] in the nitrogen environment. It shows that AMP does not degrade in a non-oxidative environment at least up to 140°C.
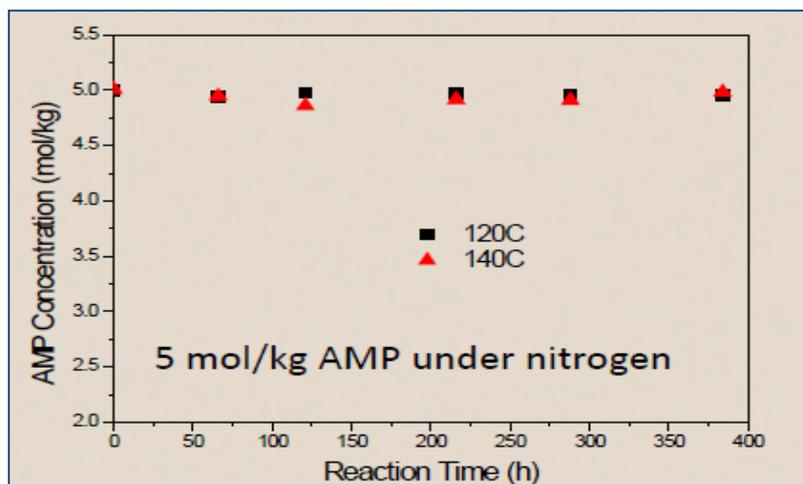
Figure 20 – Thermal degradation of AMP

However, comparing Figure 18 with Figure 20 shows that the presence of dissolved CO_2 does influence oxidative degradation of AMP. Therefore CO_2 loading should similarly influence thermal degradation of AMP somewhat. This type of degradation is most likely to be much less than that observed for MEA because AMP does not produce carbamate ions and hence, carbamate polymerisation related degradation products are unlikely to be formed. This is confirmed recently by Freeman et al[65] who have compared apparent first order degradation constant for thermal degradation of 7 molar AMP at CO_2 loading of 0.4 mole per mole of amine and 135°C with the MEA solution of identical concentration under identical degradation conditions of CO_2 loading and temperature. They found that this constant for AMP was 21×10^{-9} sec^{-1} whereas for MEA it was 134×10^{-9} sec^{-1}, thus confirming at least 6 times lower thermal degradation tendency for AMP in comparison with an equivalent MEA solution, when CO_2 is dissolved in the solution.

In summary, the oxidative and thermal degradation of AMP is less likely compared with MEA, when it is used for removing CO_2 from oxygen containing flue gas. Various carboxylates, ammonia, acetone, 2,4-Lutidine (Dimethyl pyridine) and 4,4-deimethyl-2-oxazolidone are the main oxidative degradation products of AMP. Increasing the CO_2 loading of AMP causes oxidative and thermal degradation of AMP to increase. Increase in the temperature increases its rate of oxidative degradation though the thermal degradation of AMP is less likely to be an issue until the solution temperature is more than 140°C and the solution is loaded with CO_2. Transition metal ions (Fe^{2+}, Fe^{3+} and Cu^{2+}) have no obvious effect on the oxidative degradation rates and that explains low corrosion potential of AMP. In addition, it should be noted that AMP has no α-hydrogen and hence it is unable to form an imine which is assumed to be a first step in the electron abstraction based oxidative degradation mechanism for the primary amines (AMP is a sterically hindered primary amine) as shown in Figure 2.

5. Degradation of Piperazine (PZ)

PZ is a cyclic diamine (molecular formula of $C_4H_{10}N_2$) that shows enhanced kinetic absorption rates for CO_2, almost 1.5 to 2 times that of MEA. Hence, it is being used for quiet sometime as a rate promoter for the slow reacting amine systems such as MDEA and AMP[4]. The concentration of PZ in blends, when used as a rate promoter, is usually low (between 0.5 - 2.5 molal) because it is not highly water soluble at room temperature. When exposed to water, either in aqueous solution or absorbed from air, PZ easily hydrates to hexahydrate ($PZ.6H_2O$). In aqueous solution with CO_2, the two amino functions on PZ can react and create numerous PZ-based species. The PZ species present in solution, as shown in Figure 21, include PZ carbamate ($PZCOO^-$), PZ dicarbamate [$PZ(COO^-)_2$], protonated PZ (H^+PZ), diprotonated PZ ($H_2^{+2}PZ$) and protonated PZ carbamate (H^+PZCOO^-)[4]. The speciation of PZ in solution is a function of its CO_2 loading as shown in Figure 22. Since PZ has two amine groups – in simple terms – double alkalinity compared to MEA, the CO_2 loading of its solution is usually described in terms of moles of CO_2 per mole of alkalinity which is one half of traditional loading, i.e. mole of CO_2 per mole of amine[4]. In the absence of CO_2 in solution, PZ exists primarily as free PZ with a small portion of H^+PZ. As the CO_2 concentration increases, carbamate of PZ, $PZCOO^-$, begins to form with the H^+PZ concentration increasing and the free PZ concentration decreasing. Once a CO_2 loading of about 0.28 mole CO_2 per mole alkalinity is reached, $PZCOO^-$ reaches its maximum concentration and H^+PZ begins to level out[4]. Leading up to this loading, the concentration of H^+PZCOO^- is steadily increasing, lagging the production of both H^+PZ and $PZCOO^-$. After a loading of 0.28 mole CO_2 per mole alkalinity, the concentrations of H^+PZ, $PZCOO^-$ and free PZ are decreasing while H^+PZCOO^- is increasing. A loading of 0.5 mole CO_2 per mole alkalinity represents the amount of CO_2 needed in order to have half of the PZ basic groups react with CO_2, while the other half are protonated. This is essentially the maximum realistic loading. At this point, the solution is primarily made of zwitterions H^+PZCOO^- with a small concentration of H^+PZ present. Through the entire range of loading, the concentration of $PZ(COO^-)_2$ is very small, demonstrating that this species is not a preferred form of PZ. The concentrations of H^+PZH^+ and $PZ(COO^-)_2$ are not represented in Figure 22 because their concentrations are nearly negligible. Whilst in the laboratory environment maximum CO_2 loading of 0.5 mole per mole of alkalinity is achievable with PZ, for industrial post combustion capture situation as applicable to a coal-fired power plant, the maximum loading is unlikely to be more than 0.41 CO_2 mole per mole alkalinity due to limitations of equipment size and maximum concentration of CO_2 possible in flue gas[4, 66].
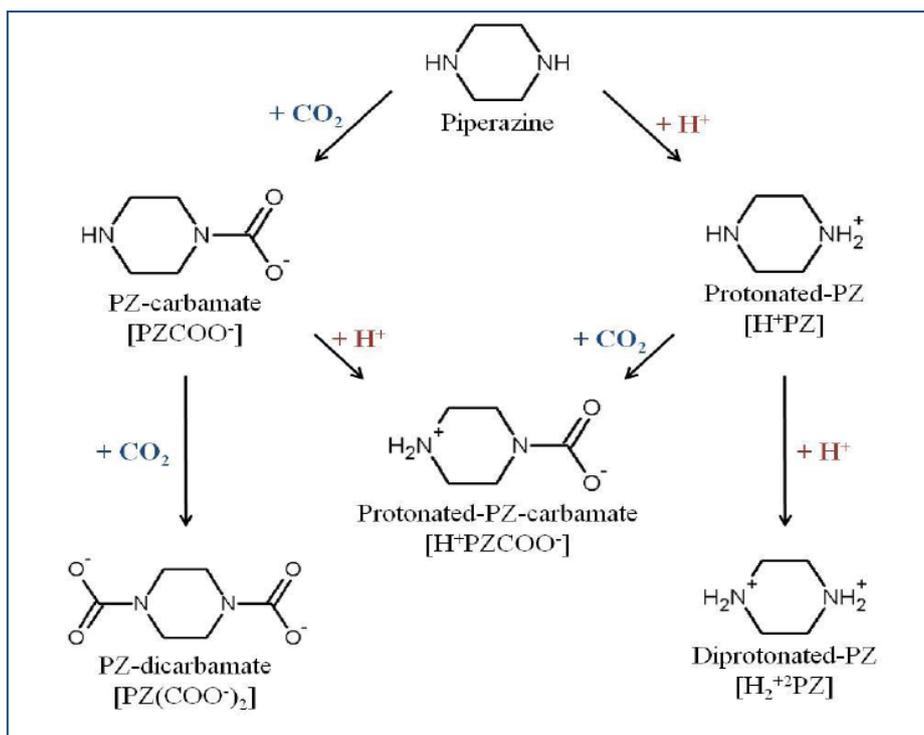
Figure 21 – Speciation of PZ in aqueous solutions
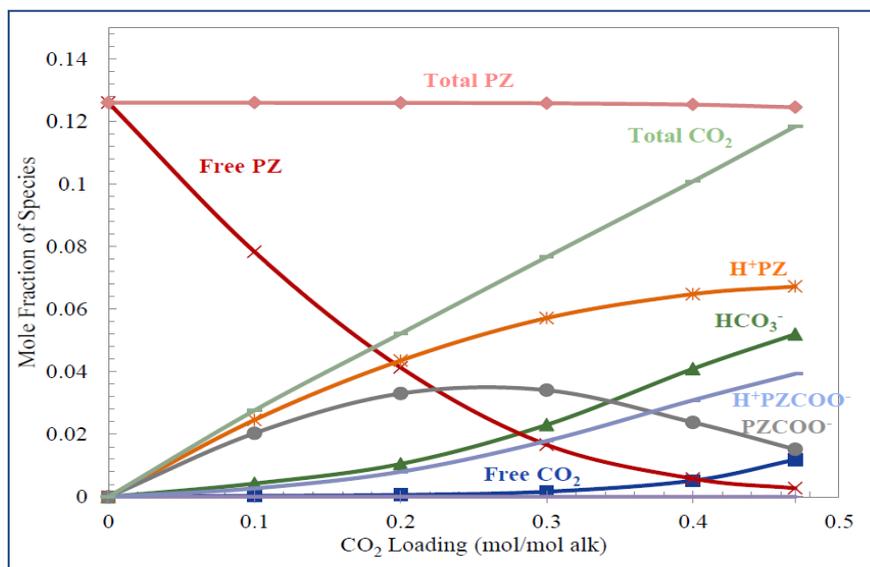
Figure 22 – Speciation of 8 m (molal) PZ at 40 ℃

Whilst the solid-liquid transition temperature – the temperature at which a liquid solution will first precipitate when cooled slowly - for plain aqueous solution of PZ increases with concentration of PZ (Figure 23), Figure 24 shows that increasing the CO_2 loading of solution reduces the solid-liquid transition temperature[4, 67-71]. Thus, aqueous solutions of PZ with concentrations as high as 8 to 10 molal (40 to 50% w/w) can be employed for CO_2 absorption, if the solution is correctly loaded initially. This has the potential to reduce the size of gas/liquid absorption system. Unfortunately, though PZ has boiling point lower than that for MEA (146.5 ℃ v/s 170 ℃), its volatility is similar to MEA due to non-ideal behaviour of

solution which has potential to result into the vapour phase losses of PZ comparable to MEA, when used for CO_2 emissions reduction[4].
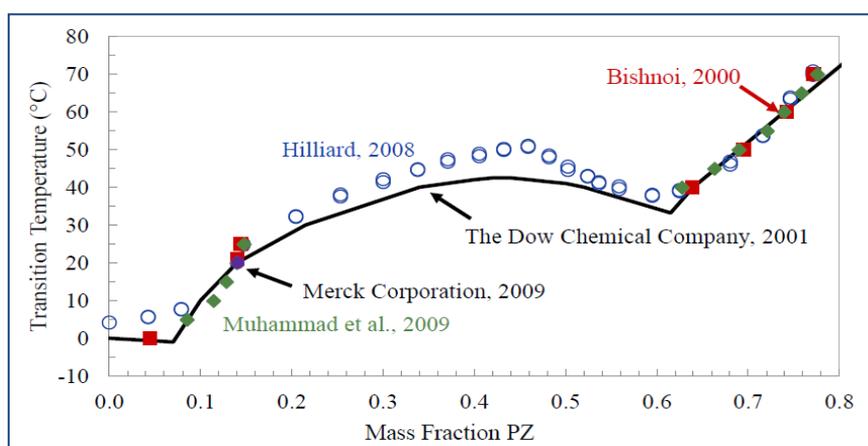
Figure 23 – Solid-liquid transition temperature for PZ with experimental data from various investigations
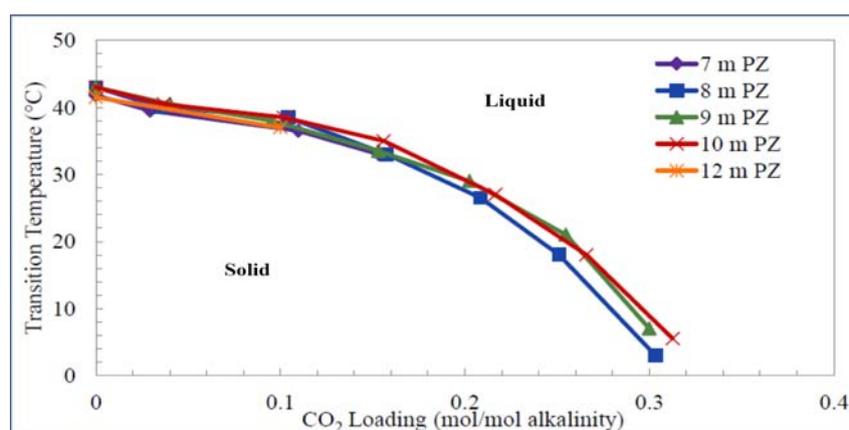
Figure 24 – Solid-liquid transition temperature for CO_2 loaded PZ solutions

5.1 Oxidative Degradation of PZ

Among various international research groups, the oxidative degradation of PZ has been investigated exhaustively by Professor Garry Rochelle and his research students due to their interest in investigating 8 molal (~40% w/w) PZ solution as one of the cost and energy efficient alternatives to 30% w/w MEA. Two bench scale reactors, the Teflon oxidation reactor (TOR) and the Integrated solvent degradation apparatus (ISDA), were used to study oxidative degradation[4]. The TOR is a batch reactor. It was used to investigate the oxidative degradation of PZ at low gas flow rate (100 mL/min) and rapidly oxidize PZ solutions with higher levels of oxygen than expected in an industrial CO_2 absorber. It was equipped with an agitator (1400 rpm) to increase the mass transfer of oxygen in the solution. The ISDA system cyclically created oxidizing and thermally degrading conditions in a single system. It circulated 200 mL/min of solvent and simulated degradation conditions observed in an absorber/stripper configuration designed for CO_2 capture. Figure 25 shows the schematics of the ISDA system. Technical description of both systems has been given elsewhere[4, 72].

The oxidative degradation characteristics of 8 molal PZ were studied in these bench scale reactors from 55 to 125 °C with inlet gas containing 40 to 98% oxygen and 2 to 6% CO_2. The CO_2 loading of 8 molal PZ was kept 0.6 mole per mole of amine (or 0.3 mole CO_2 per mole alkalinity). Metal salts as aqueous sulphates were added to the PZ solution to study the catalytic effect of iron (1 mM Fe^{2+}), stainless steel metals or SSM (0.4 mM Fe^{2+}, 0.1 mM Cr^{3+} and 0.05 mM Ni^{2+}) and copper (4 mM Cu^{2+}) on the rate of oxidative degradation[4]. Here as well as in the entire report, the units, mM, stand for milimoles of the particular species in the solution.
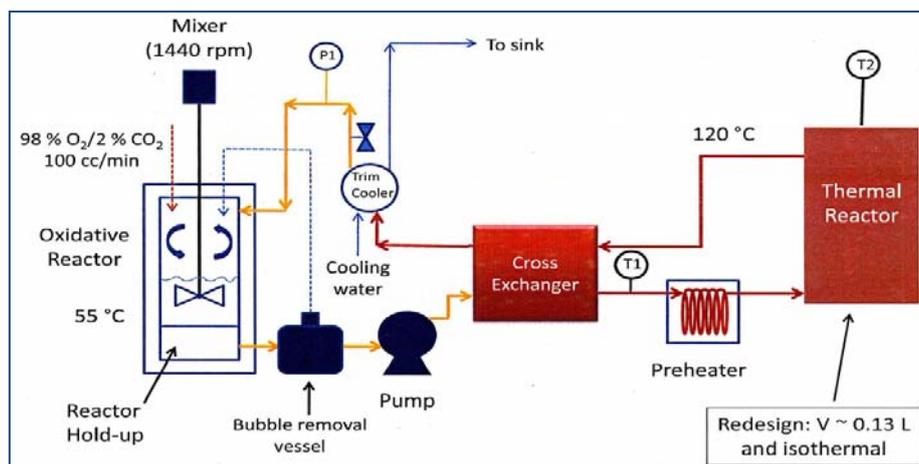
Figure 25 – Integrated solvent degradation apparatus for oxidative degradation study

The results of these investigations showed that the activation energy of PZ loss during oxidative degradation is 40 ± 4.5 kJ per mole of PZ. PZ loss has a first order relationship with partial pressure of oxygen in the inlet gas. The major identified oxidation products of PZ are Ethylenediamine (EDA), N-Formyl Piperazine (FPZ), formate, ammonia, oxalate and oxalyl amides[4]. Minor oxidative degradation products include acetate, acetyl amides, other formyl amides, nitrite and nitrate when PZ is heavily oxidised. The rate of generation of total formate (R_{TF}) i.e., the sum of formate and formyl amides, was seen as a good indicator of the overall level of PZ oxidation and this relationship was determined by data regression as:

$$R_{TF} = 0.1098 \times R_{PZ} \text{---------------- (24)}$$

Table 4 below shows the results of oxidative degradation of 8 molal PZ with 0.3 mole CO_2 loading per mole of PZ in the presence of iron, stainless steel metals and copper[4].

Table 4 – Effect of metals on oxidative degradation of PZ @ 55 °C

Metals	Average PZ Loss or Product formation Rate (mM/kg Solution/hr/kPa O_2)		
	R_{PZ} (measured)	R_{TF} (measured)	R_{PZ} (estimated)
None	6.2 ± 2.5	0.07 ± 0.04	0.6 ± 0.3
Iron	7.7 ± 7.0	0.08 ± 0.03	0.7 ± 0.3
Stainless steel	3.1 ± 4.3	0.09 ± 0.03	1.2 ± 0.9
Copper	84.4 ± 31	9.7 ± 4.0	107 ± 65

These results imply that iron and stainless steel metals (Fe^{2+}, Cr^{3+} and Ni^{2+} ions in solution) do not catalyse degradation of PZ, however, copper (Cu^{2+}) is a strong catalyst for PZ oxidation. Comparing the oxidative degradation behaviour of PZ in the presence of iron and stainless steel with that of 30% w/w MEA under similar conditions shows that PZ is 5.5 to 6 times more resistant to degradation than MEA. A similar comparison between PZ and MEA in the presence of copper shows that PZ is 2.6 times more resistant to copper catalysed oxidative degradation than MEA is. This implies that carbon steel and stainless steel as materials of construction for post combustion CO_2 absorber are suited for PZ application but copper based corrosion inhibitors such as copper borates or carbonates used for preventing corrosion in sour gas treatment industry cannot be used for PZ based post combustion capture plant.

The effect of temperature on the rate of PZ loss (R_{PZ}) due to oxidative degradation over the temperature range 55 to 125 °C in the presence of stainless steel material was determined as:

$$R_{PZ} = 9.29e^{-5389/T} \text{ ---------------------- (25)}$$

Where R_{PZ} has units of mili-mole PZ/kg of solution/hr/kPa O_2 and T has units of °K.

With the oxidative degradation characteristics of PZ established in the bench scale reactors, Freeman et al[4, 65, 66] have estimated that for a 500 MWe (installed) power plant, a post combustion CO_2 capture plant based on 8 molal PZ solvent and operating at 90% CO_2 capture with 120°C as the stripper operating temperature, will have the oxidative degradation loss of PZ as 2.1 moles (or 181 g) per metric ton of CO_2 captured.

Whilst the ISDA system allowed the designated research group to study the oxidative degradation of PZ at temperatures as high as 125 °C – bordering on to the region of thermal degradation – and thereby understand the extent of likely oxidative degradation of CO_2 loaded lean PZ solution in the stripper ends of cross exchanger (see Figure 1), The obtained results have the following limitations:

- The impact of CO_2 loading on the extent of oxidative degradation and the resulting product distribution were not studied over the CO_2 carrying capacity [0.79 mole CO_2 per kg (H_2O + PZ)] of 8 molal PZ solvent.

- The ISDA system is not a true absorber/stripper system in the sense that CO_2 was not cycled in and out of the solvent.

- Thermal reactor did not flash oxygen as is the case with industrial stripper and the laboratory investigations had the situation of pure thermal degradation products also undergoing high temperature oxidation.

- Accelerated degradation (98% O_2 / 2% CO_2) did not represent the industrial practice where oxygen concentration seldom increases beyond 15% by volume in flue gas and where CO_2 concentration could be as high as 14% by volume, hence the degradation product distribution could be skewed or extreme and unrepresentative of what could occur in an industrial post combustion capture plant. This has potentially a significant impact on the likely atmospheric emissions of PZ and its degradation products when either PZ is used as a singular solvent or blended with other amines.

In light of the above limitations, the oxidative degradation results for PZ reported here should be viewed with caution. In addition, there is currently no data available on the impact of SO_X on piperazine solvent, though NO_X impact towards formation of relevant nitrosamines has been investigated by Ashouripashaki and Rochelle[73] and Jackson and Attala[74].

Ashouripashaki and Rochelle[73] have studied the kinetics of nitrosamine formation over 21 to 75 °C range in 8 molal PZ that had CO_2 loading of 0.3 moles per mole of alkalinity. They used Teflon Oxidation Reactor (TOR) referred earlier both in the low gas flow (100 mL/min) and the high gas flow (8 Litre/min) modes. The gas stream contacting PZ solution contained 98% by volume O_2 and 2% by volume CO_2. It was further spiked with 55 ppmv NO_2. The PZ solution had metal ions representing the stainless steel as material of construction added in the form of water soluble sulphates. Mostly mono-nitrosopiperazine (MNPZ) formation was detected in the liquid phase though Di-nitrosopiperazine (DNPZ) could have also formed. The nitrosation reaction had activation energy of 47 kJ/mole of PZ and the order of reaction was one with respect to both PZ and NO_2 concentrations. Addition of formaldehyde in PZ solution as a `corrosion inhibitor catalysed the nitrosation reaction slightly. Figures 26 shows that the formation of nitrite in solution increases with time due to absorption of NO_2 and there is corresponding rise in the concentration of MNPZ due to reaction of PZ with nitrite at 55 °C in the low gas flow reactor. Figure 27 shows the similar result for the high gas flow reactor. These results clearly show that the yield of formation of nitrosation products is very low in the laboratory environment.
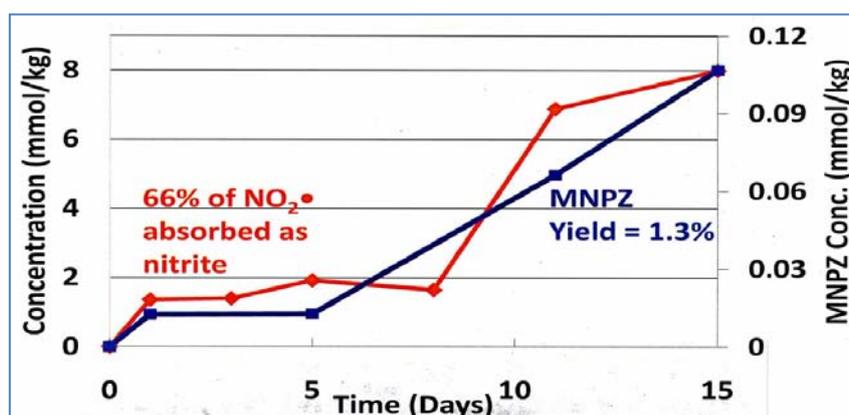
Figure 26 – Formation of Nitrite from NO_2 absorption and MNPZ production with time 100 mL/min, 55 °C, 50 ppmv NO_2, 0.4 mM Fe, 0.1 mM Cr & 0.05 mM Ni
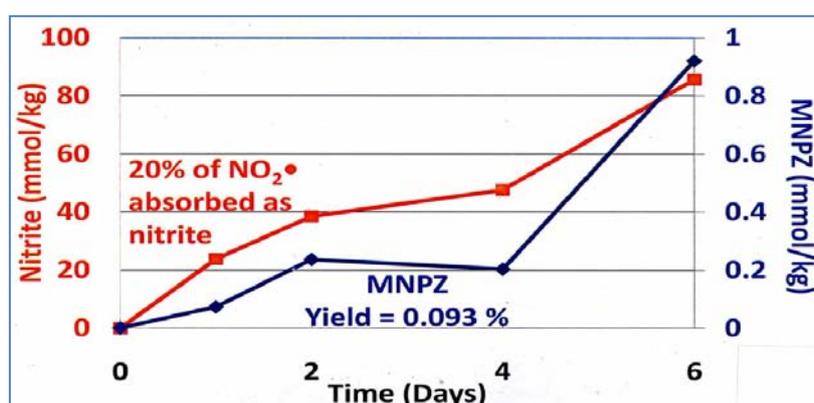
Figure 27 – Formation of Nitrite from NO_2 absorption and MNPZ production with time 7.65 L/min, 55 °C, 50 ppmv NO_2, 0.4 mM Fe, 0.1 mM Cr & 0.05 mM Ni

Low level of absorption of NO_2 and corresponding low yield of MNPZ in the high gas flow batch reactor of the identical reactor volume can be attributed to smaller residence time for gas in the reactor. This implies that for the industrial scale absorption operation, the packing

height, liquid hold up in the absorber, liquid to gas ratio in the absorber and the liquid residence time up to the stripper end of cross exchanger will decide the yield of MNPZ in addition to NO_2 concentration in the flue gas stream and the absorber temperature.

Jackson and Attala[74] used 15% w/w PZ solution at 60 ℃ and synthetic flue gas with 8000 ppmv NO_X to study the formation of nitroso products. The gas stream composition was 13% by volume CO_2, 5% by volume oxygen and the rest nitrogen. In addition to MNPZ and DNPZ, N-Oxopiperazine and Piperazine nitramine were detected by Attala in the degraded liquid sample. Figure 28 shows that Nitrosapiperazines are thermally stable at the operating temperature of stripper and therefore their formation is unlikely to be reversed in the reboiler. It should however be noted that 8000 ppmv NO_X concentration in the synthetic flue gas stream is way above what is usually noted with the industrial scale coal-fired power plant flue gas stream (roughly 200 to 300 ppmv in the absence of FGD). Allowing for complete conversion of NO_X (NO + NO_2) to Nitrosapiperazines, it is unlikely that CO_2 rich piperazine solution will carry nitroso compounds more than the stoichiometric equivalent weight of 300 ppmv NO_X.
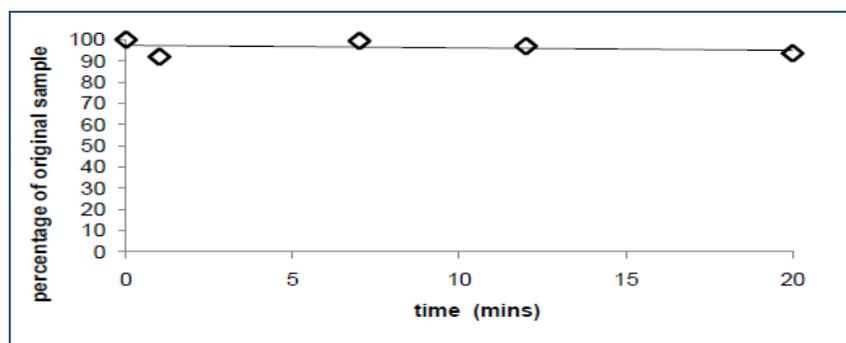
Figure 28 – Thermal resistance of MNPZ at 160 ℃

At present, the quantification of individual products of NO_X related degradation of PZ is not available in the public domain literature. Additionally, there is no information available in the public domain on the inhibitors for nitrosamines formation during post combustion capture of CO_2.

5.2 Thermal Degradation of PZ

Thermal degradation of PZ has been extensively studied by Professor Garry Rochelle and his research[4, 75, 76, 77] group at Texas University due to their interest in 8 molal PZ as a solvent to replace 30% w/w MEA. They studied the thermal degradation characteristics of PZ over the temperature range 135 to 175 ℃, PZ concentration range 4 to 20 molal and CO_2 loading from zero to 0.47 mole per mole alkalinity. They also studied the degradation effect of metal ions in solution at 175 ℃. Their results indicate that thermal degradation of PZ follows first order and therefore the concentration of PZ in solution, C_{PZ}, at any given time, t, can be expressed as:

$$C_{PZ} = C_{PZO} \times e^{-kt}$$

Where, C_{PZO} is the initial concentration of PZ. The reaction rate constant, k (sec^{-1}), could be defined as:

$$k = a \times e^{-E/RT}$$

Where, E is the activation energy for the thermal degradation step, R is the universal gas constant and T is °K. Table 5 below shows experimentally determined degradation rate constants for PZ solutions of different concentration with different CO_2 loadings at different temperatures. The activation energy E remains around 184 to 191 kJ per mole for PZ.

Table 5 – Measured k values for 4 to 20 molal PZ at different temperatures

PZ Concentration (molal)	CO$_2$ Loading (mole/mole alkalinity)	k x 10^{-9} (sec^{-1})			
		135 °C	150 °C	165 °C	175 °C
4	0.3			36	114
8	0	-	0.1	0.8	7.0
8	0.1	-	-	18	66
8	0.2	-	-	-	79
8	0.3	1.0	6.1	31	132
8	0.4	-	7.9	41	171
8	0.47	-	-	-	24
12	0.3	-	-	50	156
20	0.3	-	24	-	269

The above results indicate that unloaded PZ solution as well as those with low CO_2 loading (<0.2 mole per mole alkalinity) are fairly resistant to thermal degradation at normal stripper temperatures in the range 120 to 135 °C. There is a slight increase in the rate constant, k, for increased PZ concentration in the range 4 to 12 molal. In comparison with changes in CO_2 loading and temperature, which produce over two orders of magnitude change in, k, the effect of PZ concentration is definitely minor. The change in 'k' for 20 molal PZ is significant in comparison with 4 to 12 molal data, and probably reflects the drastic changes in solution composition and its degradation product distribution since the solution has high concentration (62% w/w PZ) and high viscosity (>300 cP). The effect of CO_2 loading is more complex as the rate constant, k, seems to rise with loading up to 0.4 mole per mole alkalinity but then drops at 0.47 value for 175 °C. Based on modelling work, Freeman and Rochelle[75] explain that the concentration of free PZ and PZ carbamate (PZCOO$^-$) are low above 0.4 mole CO_2 per mole alkalinity while concentration of bicarbonate (HCO$_3^-$) reaches a significant level (see also Figure 22). The presence of CO_2 in the form of HCO$_3^-$ appears to deactivate the catalytic effect of CO_2 when present in the form of other species, as seen at lower loadings.

Table 6 below compares the first order thermal degradation rate constants for PZ, AMP, MDEA and MEA at various concentrations and CO_2 loading to indicate their relative degradation tendencies[4, 65, 75, 76, 77]. This data shows that PZ is most thermal degradation resistant amine followed by AMP, a hindered amine, then MDEA, a tertiary amine and finally MEA, a primary amine. The thermal degradation activation energy for 7 molal AMP is 112 kJ per mole and for 7 molal MEA it is approximately 134 to 156 kJ per mole.

Table 6 – First order k values for thermal degradation of various amines

Amine	Concentration (molal)	CO₂ Loading (mole/mole alkalinity)	k x 10⁻⁹ (sec⁻¹) 120 °C	135 °C	150 °C
PZ	8 (40% w/w)	0.3	-	1.0	6.1
AMP	7 (38% w/w)	0.4	8	21	86
MDEA	7 (45% w/w)	0.1	-	-	283
MDEA	7	0.2		42	438
MEA	3.5 (18% w/w)	0.2	13	41	
MEA	3.5	0.4	22	109	
MEA	7 (40% w/w)	0.2	28	90	397
MEA	7	0.4	29	134	828

To study the effect of metal ions on thermal degradation of PZ, Freeman et al[65] subjected 8 molal PZ with 0.3 CO_2 loading to 5 mM Cu^{2+}/0.1 mM Fe^{2+} and 0.25 mM Fe^{2+}/0.6 mM Cr^{3+}/0.25 mM Ni^{2+} ions in solution at 175 °C and found no catalytic effect of metals on the thermal degradation rates. Thus, iron, stainless steel and copper materials of construction are suitable in the stripper for the post combustion capture application of PZ. However as mentioned in the previous section, the oxidative degradation of PZ is accelerated by presence of copper ions in the solution, therefore copper based construction materials and corrosion inhibitors must be avoided for CO_2 absorption using PZ.

Taking into account, little catalytic effect of iron and steel materials on both oxidative and thermal degradation of PZ, particularly in the concentration range of 4 to 8 molal with CO_2 loading up to 0.4 mole per mole alkalinity, a significant message from the data shown in Tables 5 and 6 is that PZ has potential for a least corrosive and stable reboiler operation at 150 °C. Assuming 10 minutes of liquid residence time in the stripping section and using the known CO_2 carrying capacity of 8 molal PZ as 0.79 mole CO_2 per kg of (H_2O + PZ), Chen and Rochelle[78] have estimated the thermal degradation loss of PZ at 150 °C as 0.043 mM PZ per mole of CO_2 captured, i.e. 84 gm per tonne of CO_2.

The characterisation and quantification of thermal degradation products at 135 to 175 °C carried out by Freeman[4] in the laboratory environment for concentrated aqueous PZ loaded with CO_2 shows that N-formylpiperazine (FPZ), N-(2-aminoethyl)piperazine (AEP) and NH_4^+ (ammonium) are major products. Other products include 2-imidazolidone (IMID), N-(2-hydroxyethyl) Piperazine (HEP), N-Ethyl Piperazine (EPZ), Ethylenediamine (EDA), N-Methyl Piperazine (MPZ), formate, acetate, and other heat stable salts such as oxalate and glycolate. In the absence of CO_2, PZ degradation does occur but half as fast as the loaded solution. Without CO_2 loading, IMID and formates including FPZ are not formed, instead ethylenediamine (EDA) is formed. Table 7 shows the thermal degradation products formed from 8 molal CO_2 loaded PZ after 20 weeks at 165 °C and their distribution. It shows that only 74% and 63% of N and C lost from initial PZ can be accounted from mass balance with known degradation products. In other words, the remaining lost N and lost C is present in the degradation product mixture as unidentified products. Of the total degradation products, FPZ, NH_4^+ (ammonium) and AEP account for 57% and 45% of N and C lost. The detailed results for other temperature, PZ concentration and CO_2 loading conditions are given in the tabulated form in the PhD dissertation by Freeman[4]. The significance of choosing only 165 °C thermal degradation condition for presenting Freeman's results in this report is explained further below.

Table 7 – Thermal degradation mass balance for PZ
(8 molal PZ, 0.3 mole CO$_2$ per mole alkalinity loading, 165 °C)

Compound	Concentration (mM/kg of solution)	Lost N (%)	Lost C (%)
PZ lost in 20 weeks	1729		
CO$_2$ lost in 20 weeks	888		
N-Formyl Piperazine (FPZ)	558	33	36
NH$_4^+$	496	14	-
N-(2-Aminoethyl) Piperazine (AEP)	118	10	9
Total		**57**	**45**
2-Imidazolidone (IMID)	109	6	4
N-(2-hydroxyethyl) Piperazine (HEP)	61	4	5
N-Ethyl Piperazine (EPZ)	54	3	4
Ethylenediamine (EDA)	53	3	1
N-Methyl Piperazine (MPZ)	21	1	1
Formate	108	-	1
Total Acetate	36	-	1
Total		**74**	**63**

Freeman[4] has postulated that the thermal degradation of PZ proceeds through a variety of S$_N$2 type substitution reactions that result in the ring opening and polymerisation products. In the first step of mechanism, 1-[2-[(2-aminoethyl) amino] ethyl] PZ (AEAEPZ) is believed to be formed from a ring opening S$_N$2 reaction of PZ with H$^+$PZ. The limiting rate was found to require protonated amine, but not CO$_2$. AEAPZ then reacts with dissolved CO$_2$ to form urea of AEAEPZ which is suspected to create other products. Protonated AEAEPZ in the solution produces N-(2-Aminoethyl) Piperazine (AEP) and ethylenediamine (EDA) as well as NH$_4^+$ ions. EDA reacts for creating 2-Imidazolidone (IMID) while Hoffman elimination and subsequent hydration of AEP produces N-(2-hydroxyethyl) Piperazine (HEP). More details of the thermal degradation reaction mechanisms are given in the PhD dissertation by Freeman[4].

Table 6 not only indicates relative thermal degradation tendencies of various amines in terms of their apparent first order degradation rate constants at a particular temperature of interest, this data can also be used to determine the maximum equivalent stripper temperature (MEST) for any amine for which the thermal degradation rate is required to remain the same as that of 30% w/w MEA, the base case amine solvent currently used commercially for post combustion capture. For 7 molal or 30% w/w MEA, the optimum stripper temperature with respect to minimum cost of energy for steam stripping and minimum cost of solvent replacement has been estimated by Davis[11] as approximately 120 °C (see Figure 11). This result is supported by the historical operation of MEA systems successfully at temperature between 115 and 120 °C. Assuming that the rich loading for MEA in the reboiler is 0.4 mole CO$_2$ per mole of MEA – same as mole CO$_2$ per mole alkalinity – in this case, its thermal degradation rate is expressed by its apparent first order rate constant, 2.91 x 10^{-8} sec^{-1}. Therefore, maximum thermal degradation temperature for an amine of interest that matches this apparent first order rate constant value is its maximum equivalent stripper temperature (MEST), if the degradation rate needs to not exceed that of MEA. Figure 29 below show`s this concept of MEST limit applied to 8 molal PZ and the stripper temperature determined for this solvent as approximately 163 °C[77].
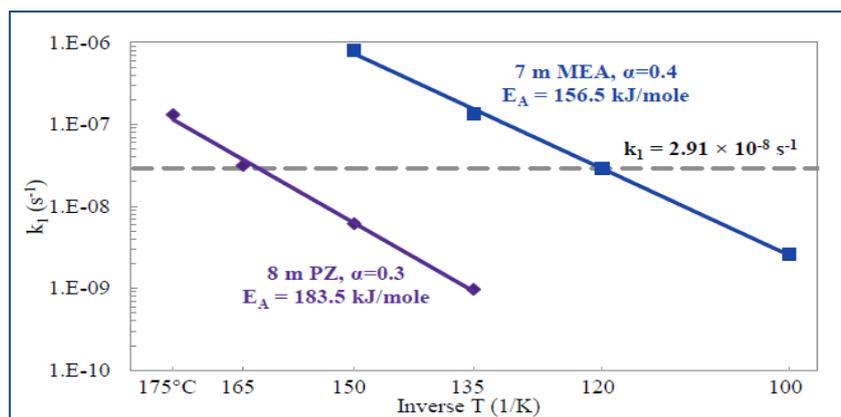
Figure 29 – Determination of MEST for 8 molal PZ with 0.3 mole CO_2/mole alkalinity

Figure 29 also demonstrates that the thermal stability of 8 molal PZ is two orders of magnitude more than 7 molal MEA. This methodology of determining MEST for any amine involves the assumption that all amines degrade thermally in a manner that follows first order rate or the degradation data can be approximated as first order. It does not take into account the cost of amine involved, for example in the case of an expensive amine such as PZ (cost per kg at least 2.5 times more than that of MEA) it may be prudent to operate at lower temperature than the MEST point in order to reduce the degradation rate even lower than that encountered with 7 molal MEA. However, this methodology of determining MEST provides a reasonable starting for the stripper design and suggests maximum propensity of an amine to thermally degrade. Table 8 presents the MEST values for a select number of amines and their blends[4].

Table 8 – Estimated MEST for select amines and their blends for CO_2 capture
(@ k =2.91x10^{-8} Sec^{-1}, Source: Freeman's PhD Dissertation[4])

Amine	Concentration (Molal)	CO_2 Loading (Mole/mole alkalinity)	Temperature Range (^{o}C)	Activation Energy (kJ/mole)	MEST (^{o}C)
PZ	8	0.3	135 -175	184	163
PZ	8	0.4	135-175	191	162
AMP	4.81	0.5	135		140
AMP	7	0.4	120-150	112	137
MDEA	3.6	0.5	135		120
MDEA	7	0.1	150		128
MDEA	7	0.2	100-135		128
MDEA	8.4	0.4	135		119
MEA	3.5	0.4	100-135	129	122
MEA	3.5	0.5	100-135	86	111
MEA	7	0.2	120-150	123	121
MEA	7	0.4	100-150	157	121
MEA	7	0.5	100-150	162	117
MEA	11	0.2	120-135		125
MEA	11	0.4	120-135		116
MEA	11	0.5	120-135		112
PZ/AMP	6/4	0.4	135-150		134
MDEA/PZ	7/2	0.11	135-150		138
MEA/PZ	7/2	0.4	100-150	84	104
MEA/AMP	7/2	0.4	100-150	146	123

The MEST results for the blended CO_2 capture results shed interesting light on the interaction of PZ and other amines in a blend at high temperature. Davis[11] as well as Closmann[72] report that PZ is preferentially degraded when blended with both MEA and MDEA. Their analysis of 'k' values indicates that PZ is degraded 12 to 15 times faster than MDEA and 4 to 8 times faster than the total amine concentration when in 7 molal MDEA/2 molal PZ blend. In 7 molal MEA/2 molal PZ blend, PZ degrades only 1.2 to 1.7 times faster than MEA and 1.1 to 1.9 times faster than total amine. Based on overall amine loss, the blend of MEA and PZ is seen as significantly less stable with MEST value 34 $^{\circ}$C lower than that for MDEA/PZ blend because MEA and PZ are both highly unstable in this blend. In the MDEA/PZ blend, however, MDEA degrades at similar rates as it does alone while PZ loss is accelerated.

In summary, PZ is a solvent with high resistance to both oxidative and thermal degradation and can be used at high concentration to compact the CO_2 absorption/desorption system and thereby reduce its cost, provided the process operating conditions are maintained within its solubility limits. Its degradation products such as ammonia and ethylenediamine can potentially emit to atmosphere. It does degrade in the presence of NO_X to produce mono-nitrosopiperazine. Currently, there is little information available on its degradation due to SO_X, particularly in the coal-fired power plant flue gas. Though, iron and steel do not seem to catalyse its degradation particularly below 150 $^{\circ}$C and these materials could be used in the construction of absorber and stripper, it is very susceptible to degradation by copper. Therefore, copper based materials of construction and corrosion inhibitors are detrimental to efficient performance of PZ as a solvent. Unfortunately, PZ gets preferentially degraded when mixed with other amines such as MDEA and MEA.

6.   DEGRADATION OF METHYL-DIETHANOLEAMINE (MDEA)

MDEA is a tertiary amine and unlike MEA, a primary amine, forms bicarbonate ions in solution as shown below instead of carbamate ions when CO_2 is absorbed in its aqueous solution. This gives MDEA the CO_2 carrying capacity per mole twice that of MEA.

$$\text{MDEA} + \text{CO}_2 + \text{H}_2\text{O} \Leftrightarrow \text{MDEAH}^+ + \text{HCO}_3^-$$

MDEA has been used for decades in the gas processing industry for acid gas removal (a mixture of CO_2, H_2S, COS, CS_2, mercaptans etc) where feed gas composition is typically 75% C1 to C5 alkanes and no oxygen, SO_X or NO_X. Under these conditions, solvent degradation is dominated by thermal and CO_2 catalysed processes. MDEA, being a tertiary amine, is slow reacting and needs a catalytic rate promoter such as piperazine, PZ, or a fast reacting amine such as, monoethanolamine, MEA, in solution to accelerate CO_2 absorption. A blend of 7 molal MDEA with 2 molal PZ is often commercially used in the gas processing industry[72]. Whilst thermal degradation of MDEA has been studied by Chakma and Meisen[79] under non-oxidative environment, the detailed information on its oxidative degradation has become available only recently due to interest of Garry Rochelle and his research group[72, 80, 81] at the University of Texas at Austin, USA, in assessing blends of MDEA and PZ as suitable alternative for MEA as a solvent for the post combustion capture of CO_2.

6.1 Oxidative Degradation of MDEA

Early work on the oxidative degradation of MDEA, though of a limited nature, has been by Rooney et al[17] who found that 30% w/w aqueous solution of MDEA, when exposed at 80 $^{\circ}$C to 100 mL/min of a gas stream containing 50% by volume CO_2 and 50% by volume O_2, had only 1.6% amine loss compared to 33% amine loss for 15% w/w MEA solution under identical conditions. The degraded MDEA solution contained heat stable salts, primarily the

acetate, formate and glycolate. They also found that 50% w/w MDEA solution had less heat stable salts in comparison with 30% w/w MDEA solution, when 5.5 mL/min of air was bubbled through solutions for 28 days. Tables 9 and 10 below present their results.

Table 9 – Results of oxidation studies of 30% w/w MDEA at 80 °C

Days	0	7	14	21	28
Acetate (ppm)	<10	82 to 120	202 to 205	332 to 353	437 to 449
Formate (ppm)	<10	80 to 107	121 to 126	167 to 187	220 to 249
Glycolate (ppm)	<10	278 to 186	411 to 430	561 to 593	667 to 704

Table 10 – Results of oxidation studies of 50% w/w MDEA at 80 °C

Days	0	7	14	21	28
Acetate (ppm)	<10	21	54	83	111
Formate (ppm)	<10	93	155	215	236
Glycolate (ppm)	<10	224	338	431	512

To study the effect of CO_2 loading on oxidative degradation of MDEA, both 30 and 50% w/w MDEA solutions were loaded with 0.25 mole CO_2 per mole amine and 5.5 mL/min of air was bubbled through the solution at 80 °C for 28 days. Tables 11 and 12 show the results of these investigations.

Table 11 – Results of oxidation studies of CO_2 loaded 30% w/w MDEA at 80 °C

Days	0	7	14	21	28
Acetate (ppm)	<10	24	81	158	265
Formate (ppm)	<10	60	101	152	209
Glycolate (ppm)	<10	156	261	379	504

Table 12 – Results of oxidation studies of CO_2 loaded 50% w/w MDEA at 80 °C

Days	0	7	14	21	28
Acetate (ppm)	<10	12	35	65	93
Formate (ppm)	<10	70	143	225	312
Glycolate (ppm)	<10	120	225	341	431

These results show that CO_2 loaded 50% MDEA has better resistance to degradation than CO_2 loaded 30% w/w MDEA. In addition to the heat stable salts, Rooney et al[17] detected approximately 1600 ppm DEA in the MDEA solution samples with or without CO_2 loading after 4 weeks. When the solutions were heated in nitrogen blanket to 80 °C, no DEA was detected which meant that oxygen was contributing towards DEA formation.

The research group at University of Regina, Canada, has studied the oxidative degradation of MDEA invariably as a blended amine with MEA. Several studies[82-86] on the kinetics and product distribution from the oxidative degradation of MDEA/MEA blends have been

reported. The temperature range for their investigations was typically 55-120 °C, the overall amine concentration was 5-9 moles/Litre, the oxygen pressure was 250 kPa and CO_2 loading was 0 to 0.4 mole per mole of total amine. Supap et al, Bello and Idem and Lawal and Idem reported vast amount (80 to 100) of degradation products. The results do not seem to reflect the systematic variations in reaction conditions, neither are they supported by plausible reaction schemes. The expected demethylation of MDEA to diethanolamine (DEA) and formation of methyl aminoethanol (MAE) are identified for some but not all experiments. Some general trends however do appear, for example MDEA is more prone to oxidative degradation than MEA and it is preferentially oxidised in the blend. The stability of MDEA/MEA blends to oxidative degradation decreases in the order MDEA/MEA/O_2 > MDEA/MEA/O_2/CO_2 > MDEA/MEA/CO_2.

Closmann[72] studied oxidative degradation of MDEA as a single amine and as a blend with 2 molal PZ. He used both the low gas flow and the integrated solvent degradation apparatus (ISDA) mentioned at Section 6.1. The temperature condition for the low gas flow reactor varied from 55 to 70 °C whereas for the ISDA system (Figure 25), the oxidative degradation temperature remained at 55 °C and the thermal degradation section temperature varied up to 130 °C. To study the oxidative degradation at accelerated rate a gas mixture of 98% by volume O_2 and 2% by volume CO_2 was used in the headspace above the solution. Metal ion catalysis effect towards the oxidative degradation was assessed using aqueous solutions of $FeSO_4.7H_2O$, $Cr(SO_4)_3.23H_2O$ and $NiSO_4.6H_2O$ at concentrations of 0.4 mM Fe^{2+}, 0.1 mM Cr^{3+} and 0.05 mM Ni^{2+} respectively. 7 molal MDEA at a nominal initial loading of 0.1 mole CO_2 per mole alkalinity (or 0.1 mole CO_2 per mole of MDEA) was the solvent utilised in all experiments. In the ISDA system, the solvent circulation rate was maintained at 200 mL/min.

Closmann[72] identified major oxidative degradation products of MDEA as primary amine monoethanol amine (MEA), secondary amines Methyl-aminoethanol (MAE) and Diethanolamine (DEA), the amino acids bicine, glycine, and hydroxyethyl sarcosine (HES), formyl amides of MAE and DEA, ammonia and heat stable salts formate, glycolate, acetate and oxalate. He used the production rate of total formate (formate plus formyl amides of MAE and DEA) as an indicator to differentiate the impact of various degradation parameters on the oxidative degradation. Closmann's results for the oxidative degradation in low gas flow reactor show that in the temperature range 55 to 70 °C, MDEA degradation rate was 0.4 mM/hr and alkalinity (nitrogen) loss rate was less than 0.1 mM/hr. The total formate production rate was also less than 0.03 mM/hr in this range despite the Fe^{2+} concentration in solution at 1 mM. This implies that in an industrial scale MDEA based CO_2 capture plant, oxidative degradation of MDEA is most likely to shift to the cross exchanger where temperatures in excess of 70°C are possible and carbon steel as a material of construction for the absorber has no significant adverse impact. When the ISDA system was used to study the effect of temperature cycling on the solvent degradation with the oxidative reactor temperature in the system at 55 °C but the thermal reactor temperature varying from 55 to 120 °C, the rates of MDEA and alkalinity loss and the rate of total formate production was as given in Table 13. In this case, 7 molal MDEA carried stainless steel metal salts at the concentration of 0.4 mM Fe^{2+}, 0.1 mM Cr^{3+} and 0.05 mM Ni^{2+}. These results help in understanding the effect of temperature on oxidation rates. The results clearly indicate that MDEA degradation increased as the solvent was cycled to a higher temperature. MDEA and alkalinity loss rates increased with thermal reactor temperature as did the rates of formate and total formate production. This trend supports the conclusion that degradation of MDEA is a high-temperature oxidative process. However, the data also demonstrate that the increase in formate production between 100 and 120 °C is lower than the increase observed between 90 and 100 °C, indicating that the oxidation processes become dissolved oxygen limited between 100 and 120 °C.

Table 13 – Oxidative degradation of 7 molal MDEA in ISDA system
0.1 mole CO_2/mole alkalinity loading, 98% O_2/2% CO_2 gas

Temperature (°C)	MDEA Loss (mM/hr)	Alkalinity Loss (mM/hr)	Formate Production (mM/hr)	Total Formate Production (mM/hr)
55	0.9	0.9	0.005	0.01
80	0.9	1.0	0.034	0.039
90	2.9	2.2	0.12	0.15
100	4.1	3.1	0.18	0.31
120	4.6	4.9	0.28	0.34

To study the effect of dissolved oxygen concentration, Closmann ran the ISDA system's oxidative section at 55 °C and the thermal section at 90 °C but with 98% air/2% CO_2 gas mixture in one case and 98% N_2/2% CO_2 in other case. The results are shown in Table 14. Both formate and total formate production rates relate to oxygen concentration.

Table 14 – Effect of dissolved O_2 on degradation of 7 molal MDEA in ISDA system
0.1 mole CO_2/mole alkalinity loading, 1mM Fe^{2+}

Gas Mixture	MDEA Loss (mM/hr)	Alkalinity Loss (mM/hr)	Formate Production (mM/hr)	Total Formate Production (mM/hr)
98% N_2/2% CO_2	1.9	1.6	0.013	0
98% Air/2% CO_2	0.2	0.2	0.044	0.058
98% O_2/2% CO_2	2.9	2.,2	0.12	0.15

Using experimental observations of the ISDA system and the assumptions given below, Closmann[72] has proposed the oxidative degradation model (Equation 26) for 7 molal MDEA over the temperature range 55 to 130 °C:

- Degradation of MDEA follows the first order reaction rate kinetics in terms of the dissolved oxygen concentration,
- The ISDA system behaves as an ideal plug flow reactor (PFR),
- The PFR operates almost isothermally,
- Very little degradation occurs at low temperature (< 70 °C) and hence, the oxidative reactor in the ISDA system merely saturates the MDEA solution with oxygen,
- Most of the oxidative degradation occurs in the thermal reactor of the ISDA system, and
- The PFR volume is that of the thermal reactor.

$$\Delta [Prod] = \{(P_{O2} * S * Q * t) / (K_H * V_{TOT})\} * \{1 - exp(-k_1 * V_{TR}/Q)\} \text{----------- (26)}$$

Where various terms in Equation 26 have the following meaning:

$\Delta [Prod] =$ The quantity of degradation product formed, mM

$P_{O2} =$ The partial pressure of Oxygen in the gas stream, kPa

S = Stoichiometric coefficient for Oxygen for a particular product formation

Q = Solvent flow rate, m^3/hr

t = Time for the oxidative degradation, hr

K_H = Henry's coefficient for oxygen solubility at the operating temperature of oxidative reactor in the ISDA system

V_{TOT} = Total volume of the ISDA system, m^3

K_1 = First order reaction rate constant for product formation at temperature T_1, hr^{-1}

V_{TR} = Volume of the thermal reactor in the ISDA system, m^3

The first order reaction rate constant K_1 for formation of a particular degradation product at temperature T (^{o}K) is related to the rate constant K_0 for the base case temperature T_0 by the Arrhenius Equation 27.

$$K_1 = K_0 * exp[-E_A/R\{1/T_1 – 1/T_0\}] ---------- (27)$$

Where, E_A is the activation energy for formation of a particular degradation product and R is the universal gas constant.

The above model has essentially three parameters viz., E_A, K_0 and S. Table 15 lists the values of these parameters for the formation of formate, total formate (includes amides) and Bicine as determined by Closmann[72] which gave him the best fit between the experimentally observed and predicted initial rates of formation of these degradation products from 7 molal MDEA over the temperature range 55 to 130 $^{\circ}$C.

Table 15 – 7 molal MDEA oxidative degradation model results

Parameter	K_0 (hr^{-1})	E_A (kJ/mole)	S (mole Product per mole O_2)
Formate	2.6	151	0.09
Total Formate	3.4	152	0.14
Bicine	0.32	244	0.35

Closmann utilised the above model to estimate the limit for MDEA solution exposure to high temperature in the cross heat-exchanger (Figure 1) and in piping to the steam stripper. An assumption was made that most of the dissolved oxygen will strip out of the solution at the top of the stripper and the residence time for solution in the cross exchanger plus piping is 30 seconds. Accordingly, for 10% oxygen consumption towards degradation in the cross exchanger/piping region of 7 molal MDEA based CO_2 capture plant, the average temperature tolerance was estimated to be 104 $^{\circ}$C. For 20% and 50% oxygen consumption, the temperature tolerance increases to 108 and 116 $^{\circ}$C. Finally using the oxidative degradation model results, Closmann estimated that for a 500 MW coal-fired power plant, 7 molal MDEA based post combustion CO_2 capture plant that has 90% CO_2 capture duty will have 0.29 moles of MDEA loss per ton of CO_2 captured, if the CO_2 carrying capacity of the solution is 0.5 mole CO_2 per kg of MDEA solvent.

The oxidative degradation model of Closmann described above has limitations as below:

- The ISDA system is not a true absorber/stripper system in the sense that CO_2 was not cycled in and out of the solvent.

- Thermal reactor did not flash un-reacted oxygen as is the case with industrial stripper and the laboratory investigations had the situation of pure thermal degradation products also undergoing high temperature oxidation.

- Accelerated degradation (98% O_2 / 2% CO_2) did not represent the industrial practice where oxygen concentration seldom increases beyond 15% by volume in flue gas and where CO_2 concentration could be as high as 14% by volume, hence the degradation product distribution seen by Closmann could be skewed or extreme and unrepresentative of what could occur in an industrial post combustion capture plant. This has potentially a significant impact on the likely atmospheric emissions of MDEA and its degradation products.

- The oxidative degradation model assumes isothermal plug flow reactor behaviour which is rarely the case for an industrial absorber/stripper system.

- The oxidative degradation model looks at the rate of degradation of MDEA in terms of only oxygen consumption and involves estimation of floating parameters E_A, K_0 and S. The initial values (guess) for these parameters were obtained by plotting the rate of degradation of MDEA or the rates of degradation products formation as a function of temperature and/or oxygen partial pressure. These values were improved upon in steps using the error minimisation mathematical techniques till the predicted rates of degradation product formation matched with the experimentally measured rates. In that sense, the parametric estimation is at best a curve fitting exercise and the parameter values derived from the laboratory investigations may not hold for the industrial situation.

- The oxidative degradation model is valid for estimating only the initial rate of degradation products formation and not the accumulation of degradation products over time. This model is also applicable over only a limited temperature range and assumes the maximum concentration of dissolved oxygen in the spent solvent as that decided by Henry's law at 55 $^{\circ}$C which assumes absorber operating isothermally at that temperature which is not usually the case with industrial absorbers.

In summary, the oxidative degradation of MDEA produces primary amine monoethanolamine (MEA), secondary amines Methyl-aminoethanol (MAE) and Diethanolamine (DEA), the amino acids bicine, glycine, and hydroxyethyl sarcosine (HES), formyl amides of MAE and DEA, ammonia and heat stable salts formate, glycolate, acetate and oxalate. At present, the study of oxidative degradation of MDEA is still progressing and there is no data available to explain the impact of SO_X and NO_X on the oxidative degradation, though Mimura et al[60] indicate that 30% w/w MDEA absorbs NO_2 and CO_2 simultaneously with the liquid side mass transfer co-efficient value of 1.5 x 10^{-7} mol/s/Pa/m^2. A patented CANSOLV process[87] uses an aqueous amine solution for high selective absorption of SO2 from large variety of gas streams. The experimental evidence by Closmann[72] of dealkylation of MDEA to form secondary amines, DEA and MAE, points towards the potential for the formation of nitroso-compounds (N-nitroso diethanolamine and 2-methylnitrosoamino-ethanol) in an industrial situation. Moreover, there is a possibility that MDEA could degrade to diethylamine which can form diethylnitrosamine and diethylnitramine.

6.2 Thermal Degradation of MDEA

Thermal degradation of MDEA was studied first by Chakma and Meisen[79] purely in terms of understanding the applicability of 20 to 50% w/w MDEA as a solvent for CO_2 capture from the commercial gas treatment operations where oxidative environment is non-existent. They used 600 mL stirred autoclave to expose 20 to 50% w/w aqueous MDEA solution to CO_2 (partial pressure 1.38 to 4.24 MPa) mixed with N_2 at 100 to 200 $^\circ$C. Thermal degradation products were identified by gas chromatography and mass spectrometry. These researchers found that MDEA did not degrade even after 240 hours at 200 $^\circ$C when it was exposed to only nitrogen gas but the presence of CO_2 immediately catalysed thermal degradation. Degradation however remained slow at temperatures below 120 ^{o}C even after 300 hours. The degradation products formed at temperatures well in excess of 120 ^{o}C were same as those at 120 $^\circ$C. Higher temperatures merely accelerated the rate of degradation. Overall MDEA degradation followed first order rate kinetics up to 170 $^\circ$C but beyond that the kinetics moved to higher order. The overall degradation rate constant increased with initial solution concentration up to about 3.5 moles MDEA per litre but then started to decrease with higher concentration because with increasing MDEA concentration, availability of water to form protonated MDEA started to decrease, thus slowing down the degradation reaction. Increasing CO_2 partial pressure increased its solubility and therefore accelerated degradation rate.

Overall, Chakma and Meisen[79] determined that CO_2 catalysed thermal degradation of MDEA produced 2-dimethylaminoethanol (DMAE) as a primary product which then further degraded into various other products as per the reaction equations given below. Table 16 lists the degradation products that were identified with GCMS techniques by these researchers.

$$MDEA + CO_2 + H_2O \overset{Keq}{\leftrightarrow} MDEAH^+ + HCO_3^- \text{ --------------- (28)}$$

$$MDEA + MDEAH^+ \overset{K2}{\rightarrow} DMAE + EO + DEA \text{ -------------- (29)}$$

$$2DMAE + CO_2 \overset{K3}{\rightarrow} TMA + EO + MAE \text{ ----------- (30)}$$

$$2MAE + CO_2 \overset{K4}{\rightarrow} DMP \text{ ------------------------ (31)}$$

$$EO + H_2O \overset{K5}{\rightarrow} EG \text{ -------------- (32)}$$

$$DEA + CO_2 + MAE \overset{K6}{\rightarrow} HMP \text{ ---------------------- (33)}$$

$$DEA + EO \overset{K7}{\rightarrow} TEA \text{ ------------- (34)}$$

$$HMP + EO \overset{K8}{\rightarrow} BHEP \text{ ------------ (35)}$$

$$TEA + DEA + CO_2 \overset{K9}{\rightarrow} TEHEED \text{ ------------------ (36)}$$

$$DMP + EO \overset{K10}{\rightarrow} HMP \text{ ------------- (37)}$$

$$DEA + CO_2 \overset{K11}{\rightarrow} HEOD \text{ ------------ (38)}$$

$$2DEA + CO_2 \overset{K12}{\rightarrow} THEED \text{ ----------- (39)}$$

$$THEED \overset{K13}{\rightarrow} BHEP \text{ ------ (40)}$$

Where K_{eq} is the equilibrium rate constant for reaction of MDEA with dissolved CO_2 and rest of the K are individual reaction rate constants. Table 17 lists the individual Arrhenius frequency factor and activation energy values for these rate constants.

Table 16 – CO₂ catalysed thermal degradation products of MDEA

Compound Name	Abbreviation
Methanol	Me-OH
Ethylene Oxide	EO
Trimethylamine	TMA
N,N-Dimethylethanamine	DMEA
Ethylene Glycol or 1,2 Ethanediol	EG
2 - Dimethylamino Ethanol	DMAE
4 - Methyl Morpholine	MM
1,4 Dimethyl Piperazine	DMP
Methyl Diethanolamine	MDEA
Diethanolamine	DEA
1 - (2 - hydroxyethyl) – 4 – Methyl Piperazine	HMP
Unidentified	
Triethanolamine	TEA
N,N-bis-(2 – hydroxyethyl) – Piperazine	BHEP
3 – (hydroxyethyl) – 2 – Oxazolidone	HEOD
N,N,N-tris-(hydroxyethyl) Ethylenediamine	THEED
Tetra – (hydroxyethyl) Ethylenediamine	TEHEED

Table 17 – The Arrhenius parameters for MDEA degradation rate constants

Rate Constant	Units	K_{Freq} (Sec^{-1})	Activation Energy (kJ/mole)
K2	Litre-ions/mole^2/hr	2.34×10^4	57.4
K3	Litre^2/ mole^2/hr	4.77×10^5	50.9
K4	Litre^2/ mole^2/hr	2.42×10^5	60.6
K5	Hr^{-1}	2.60×10^4	56.2
K6	Litre^2/ mole^2/hr	5.82×10^4	52.4
K7	Litre/ mole/hr	2.70×10^6	65.4
K8	Litre/ mole/hr	2.28×10^4	54.4
K9	Litre^2/ mole^2/hr	6.13×10^4	56.3
K10	Litre/ mole/hr	3.47×10^4	79.4
K11	Litre/ mole/hr	5.39×10^6	75.2
K12	Litre/ mole/hr	2.00×10^7	79.4
K13	Hr^{-1}	3.80×10^{11}	12.8

Using the above kinetic model, Chakma and Meisen[79] showed that the predicted values for the degradation product concentrations matched very closely with the experimentally observed values. However, it should be noted that these researchers used the degradation temperatures and the CO₂ partial pressures way above the values encountered with post combustion capture mainly to accelerate the degradation chemistry and obtain the results within hours. Since thermal degradation involves a number of competing reactions in series as well as in parallel, the acceleration of degradation by utilising very high temperatures and CO₂ partial pressures may have impacted on the product distribution, even if the chemical nature of the products remains same with what was observed by these researchers at 120 ᵒC. Interestingly, these researchers confirm that there was no appreciable thermal

degradation even in the presence of CO_2 at 120 °C and therefore, operating CO_2 stripper for MDEA based post-combustion capture process around 120 °C will leave no major cause for thermal degradation products formation and their likely atmospheric emissions. This is also being pointed out by Freeman[4] in her concept of MEST for stripper in Table 8 for 3.6 to 8.4 molal MDEA solutions loaded with CO_2.

In addition to Chakma and Meisen[79], Closmann[72] has also studied thermal degradation of MDEA in the temperature range 120 to 150 °C for 7 molal solution concentration and CO_2 loading up to 0.2 mole per mole alkalinity. Table 18 below shows MDEA loss rate. Based on the earlier work by Chakma and Meisen[79], Closmann estimated that the degradation kinetics followed first order rate and accordingly estimated the overall degradation rate constant for 7 molal MDEA as a function of temperature. For 150 °C, Closmann determined the first order rate constant as 8.06×10^{-7} sec^{-1} which closely matches the value of Chakma and Meisen. In addition to this, Closmann's estimate of 60 kJ per mole MDEA for the activation energy for thermal degradation is in line with Chakma and Meisen's estimate of 57.4 kJ per mole MDEA. However, there is some disagreement between these two bodies of work in relation to the products of thermal degradation. Table 19 lists the products observed by Closmann in his thermal degradation work where ethylene oxide, ethylene glycol and other compounds were not observed as products of degradation.

Table 18 – MDEA loss rate in thermally degraded 7 molal MDEA

Loading (Mole CO_2/ mole Alkalinity)	Temperature (°C)	MDEA Loss (Milimoles/hr)
0	150	0.0 ± 0.37
0.1	120	0.0 ± 0.5
0.1	135	0.5 ± 0.3
0.1	150	1.2 ± 1.5
0.2	120	1.6
0.2	135	2.2
0.2	150	3.0 ± 0.7

Table 19 – Thermal degradation products of 7 molal MDEA

Compound Name	Abbreviation
N,N-Dimethylethanamine	DMEA
2-Dimethylamino Ethanol	DMAE
N-(2-hydroxyethyl)-N-methyl Formamide	MAE-Amide
Diethanolamine	DEA
1,4 Dimethyl Piperazine	DMP
N,N-bis-(2-hydroxyethyl) Formamide	DEA-Amide or AEMP
1-(2-hydroxyethyl)–4–Methyl Piperazine	HMP
Triethanolamine	TEA
N,N-bis-(2–hydroxyethyl)-Glycine	Bicine
N,N-bis-(2-hydroxyethyl)-Piperazine	BHEP
N,N,N-tris-(hydroxyethyl) Ethylenediamine	THEED
Methyl-N,N,N-tris-(hydroxyethyl) Ethylenediamine	MTHEED

In summary, thermal degradation of MDEA follows first order rate kinetics at temperatures below 150 to 170 °C, with secondary amines such as DEA and MAE as the degradation

products. Above 170 °C, thermal degradation of MDEA follows higher order. MDEA is more resistant to thermal degradation in comparison with MEA.

7 AMINE BLENDS

The previous sections have summarised both thermal and oxidative degradation characteristics of common amine solvents that are commercially used for CO_2 capture. Table 20 lists their CO_2 carrying capacity, heat of reaction (absorption) with CO_2 and the reaction rate constant for CO_2 capture[88-92].

Table 20 – Comparison of CO_2 capture characteristics of common amines

Amine	Maximum Theoretical CO_2 Carrying Capacity (mole CO_2/mole amine)	Heat of Absorption (MJ/kg CO_2)	Reaction Rate Constant @ 25°C (m^3/mol/sec)
MEA	0.5	1.9	6.0
MDEA	1	1.1	5×10^{-3}
AMP	1	1.6	0.58
PZ	2	1.6	70.0

It can be seen from this data that while MEA is a fast reacting amine, its high heat of absorption for CO_2 and low CO_2 carrying capacity are distinct disadvantages. Similarly, whilst MDEA has lower heat of absorption in comparison with MEA and twice the CO_2 carrying capacity, it is handicapped by slow reaction kinetics as typified by 3 orders of magnitude lower reaction rate constant. Piperazine, on the other hand, has all favourable characteristics, provided it is within its solid/liquid transition temperature limit shown in Figure 24. AMP, a hindered amine has better characteristics for CO_2 capture compared to MDEA. Therefore, blending MDEA with MEA or Piperazine (PZ) or blending AMP with PZ can produce a solvent that has CO_2 absorption rate as well as CO_2 carrying capacity higher than either MEA or MDEA or AMP. Accordingly, Dubois and Thomas[89, 92] have experimentally measured improvements (Figure 30 and Figure 31) in the CO_2 absorption efficiency at 25 °C over that of 30% w/w MDEA solvent by using different single and blended amines for CO_2 removal in a given contactor where the inlet gas stream contained 10% v/v CO_2. Figure 32 shows the absorption enhancement factor or the "activation ratio" as a result of a particular level of blending in 30% w/w MDEA. Similarly, Choi et al[45, 93] have experimentally measured CO_2 absorption rates at different temperatures and the absorption activation ratio at these temperatures (Tables 21 and 22) for 30% w/w AMP and its blends with MDEA and PZ.
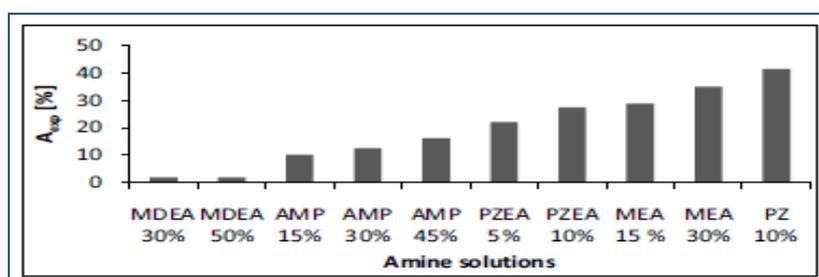
Figure 30 – CO_2 absorption efficiency (A_{exp}%) with single amine solutions in a fixed size contactor, [PZEA = (Piperazinyl -1)-2-ethylamine]
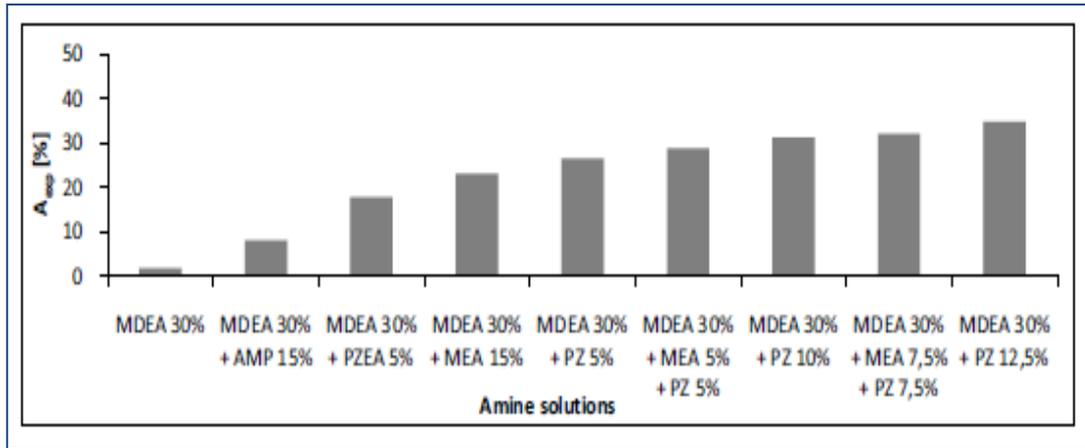
Figure 31 - CO_2 absorption efficiency (A_{exp}%) with mixed amine solutions for 30% w/w MDEA in a fixed size contactor, [PZEA = (Piperazinyl -1)-2-ethylamine]
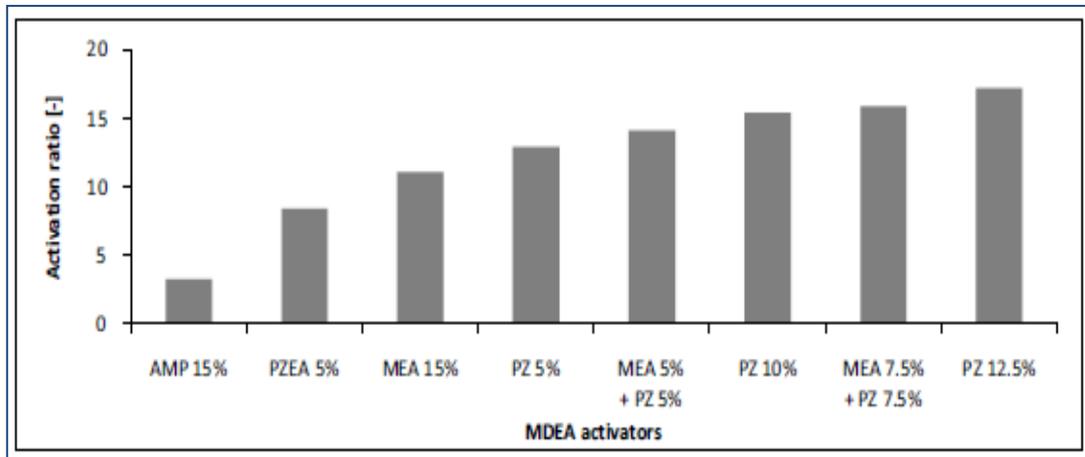
Figure 32 – CO_2 absorption enhancement or "Activation Ratio" for various additives in 30% w/w MDEA in a fixed size contactor, [PZEA = (Piperazinyl -1)-2-ethylamine]

Table 21 – Specific absorption rates of CO_2 in blends of AMP at various temperatures

CO_2 Absorption Rate	kmole of CO_2 per m^2 per sec			
Temperature (C)	30	40	50	70
Solvent (% w/w)				
AMP (30)	3.03	3.75	4.25	4.92
AMP (30) / MDEA (1)	3.08	3.86	4.45	5.13
AMP (30) / MDEA (3)	3.15	3.95	4.60	5.45
AMP (30) / MDEA (5)	3.27	4.07	4.68	5.74
AMP (30) / PZ (1)	3.09	3.90	4.44	5.17
AMP (30) / PZ (3)	3.21	4.03	4.63	5.57
AMP (30) / PZ (5)	3.34	4.18	4.89	6.02

Table 22 – Absorption "Activation Ratio" for AMP/MDEA & AMP/PZ blends

Temperature (°C)	30	40	50	70
Solvent (% w/w)				
AMP (30)	1.00	1.00	1.00	1.00
AMP (30) / MDEA (1)	1.02	1.03	1.05	1.04
AMP (30) / MDEA (3)	1.04	1.05	1.08	1.11
AMP (30) / MDEA (5)	1.08	1.09	1.10	1.17
AMP (30) / PZ (1)	1.02	1.04	1.05	1.06
AMP (30) / PZ (3)	1.06	1.08	1.09	1.14
AMP (30) / PZ (5)	1.10	1.12	1.15	1.23

These results clearly show that blending a primary amine or a fast reacting cyclic diamine with a tertiary or hindered amine has the potential to reduce the liquid circulation rate, the size of absorber and the associated equipment as well as the overall energy demand for CO_2 capture in an industrial situation. In essence, it can improve the techno-economic viability of an amine based post combustion capture plant for carbon capture and storage. This could be the reason why blended amine based CO_2 capture technologies for gas processing have been lately investigated for the post combustion capture application. The MHI Process[94] that uses a blend of AMP and PZ as a preferred solvent, the BASF process[95] that uses the PZ activated MDEA as a solvent and the PSR process[96-98] from University of Regina that uses a blend of MDEA and MEA are the examples of blended amine based capture processes. With these upcoming new post combustion capture processes in mind, the following sections delve into the oxidative and thermal degradation of three blended amine solvents; viz. a blend of MDEA and MEA, a blend of MDEA and PZ, and a blend of AMP and PZ.

7.1 Oxidative and Thermal Degradation of MDEA/MEA Blend

Combined oxidative/thermal degradation of MDEA/MEA blend has been studied by the research group[82, 83] from University of Regina, Canada. Table 23 below shows their laboratory based experiment conditions. The degradation product characterisation and identification was done using the gas chromatography and mass spectrometry techniques.

Table 23 – Oxidative and thermal degradation conditions for MDEA/MEA blends

Temperature (°C)	100	120	120
MEA Concentration (moles/Litre)	5	5	7
MDEA Concentration (moles/Litre)	2	2	2
CO_2 Loading (mole/mole total amine)	0.18	0.502	0.43
O_2 Pressure (kPa)	250	250	250

The degradation products seemed to vary with varying the ratio of MEA and MDEA concentration in the blends. More degradation products were formed with increasing the solution temperature and increasing the CO_2 loading. MDEA seemed to get preferentially degraded when blended with MEA, though as a standalone amine, it is more resistant to degradation in comparison with MEA. 2-(methylamino)ethanol, 1-amino-2-propanol, 1,3-propanediamine and 1,2-propanediamine were identified as major degradation products with a host of minor degradation products including 3-methylpyridine, N,N-dimethylurea, N-hydrohycarbaminic acid etc. No kinetics of combined degradation was determined and no

product distribution was quantified. One of the strongest limitations has been no degradation experiments in the joint presence of CO_2 and O_2 at conditions that typify a CO_2 absorber operation (typically 40 to 70 °C) and no identification of the expected formation of DEA and MAE. Similarly, N,N-dimethyl-2-ethanolamine (DMAE) and the carbamate polymerisation products were also not identified in the degradation product mixture.

Whilst, the University of Regina researchers[82, 83, 85] state to use MDEA/MEA blend in the ratio 1:4, there is no information provided by them on the impact of SO_X and NO_X on the degradation characteristics of the blend. Degradation of MEA by SO_X species has been narrated in the earlier sections and formation of NDELA in the presence of NO_X has been confirmed by Pedersen et al[26, 29] as described in the earlier sections. Given that MDEA is a tertiary weak amine and SO_X species are strongly acidic, degradation of MDEA by reaction with SO_2 and SO_3 is inevitable. There is indeed literature evidence for the flue gas desulphurisation using tertiary or hindered amines, for example the CANSOLV process[87]. Similarly, Mimura et al[60] indicate that 30% w/w MDEA absorbs NO_2 and CO_2 simultaneously with the liquid side mass transfer co-efficient value of 1.5×10^{-7} mol/s/Pa/m^2. However, the experimental evidence by Closmann[72] for the formation of secondary amines, DEA and MAE, points towards the potential for the formation of nitroso-compounds (N-nitroso diethanolamine and 2-methylnitrosoamino-ethanol) in an industrial situation that could have certainly adverse environmental impact. Moreover, there is a possibility that MDEA could degrade to diethylamine which can form diethylnitrosamine and diethylnitramine[14]. Thus, the blend of MEA and MDEA may have potentially adverse impact in terms of the atmospheric emissions perhaps to the extent same as the sum total of individual impact.

7.2 Oxidative and Thermal Degradation of AMP/PZ Blend

Currently, there is no data available on the oxidative and thermal degradation of AMP/PZ blend though the kinetics of CO_2 absorption in this blend has been investigated. Since both AMP and PZ have individually lower tendency towards degradation in comparison with MEA, it could be speculated that the combined oxidative and thermal degradation products of this blend could be a product mixture that represents the sum total of individual oxidative and thermal degradation products at least in terms of characterisation if not in quantification. It should be though noted that in an industrial post combustion capture situation, PZ in the presence of NO_X will produce MNPZ as indicated by Freeman[4] (Figures 26 and 27) and other additional nitroso compounds of PZ such as DNPZ, N-Oxopiperazine and Piperazine nitramine may also get formed as indicated by Jackson and Attala[30, 74] in their laboratory situation.

7.3 Oxidative and Thermal Degradation of MDEA/PZ Blend

The oxidative and thermal degradation of MDEA/PZ blend has been studied extensively by Closmann[72] using the low gas flow reactor (TOR) and the integrated solvent degradation assembly (ISDA) described in the previous sections. The TOR was used to study the oxidative degradation separately whereas the ISDA was used to study the combined effect of oxidative and thermal degradation. In addition, they used cylindrical batch reactors to exclusively study the effect of thermal degradation. For all of their experiments a blend of 7 molal MDEA and 2 molal PZ was used. Table 24 below shows their experimental conditions.

As shown in Table 24, both unloaded and loaded blends of MDEA and PZ were tested for assessing the degradation. Closmann argues that the low CO_2 loadings of 0.1 and 0.14 mole per mole alkalinity with 55 to 70 °C TOR temperature relate to the absorber condition in an industrial situation (a coal-fired power plant post combustion capture scenario with 90% CO2 recovery) whereas the thermal reactor temperature of 100 to 120 °C and the CO_2 loading

conditions of 0.3 and 0.43 mole per mole alkalinity relate to the rich amine stream undergoing regeneration in the stripper reboiler.

The oxidative degradation at 55 °C in the TOR produced mostly formates (0.013 mM/hr). The MDEA and PZ loss rate was not measured at this temperature. At 70 °C, both formyl amides and bicine were formed in addition to the formates. MDEA and PZ initial loss rates at this temperature were 0.17 ± 0.35 and 0.07 ± 0.05 mM/hr respectively. In terms of overall molar quantity, the secondary amines (DEA+ MAE) represented the largest degradation product, formed at a rate of 0.2 mM/hr. The total formate production rate (formates plus formyl amides) was 0.08 mM/hr whereas the formates only production rate and bicine formation rate were 0.031 and 0.024 mM/hr respectively. This signifies that ammonia produced during oxidative degradation does not react with the heat stable salts at lower temperature and the emissions of amides could be lowered in industrial practice by controlling the temperature bulge in the absorber.

Table 24 – 7 molal MDEA / 2 molal PZ blend degradation conditions

Reactor Type	Temperature (^{o}C)	Gas Composition (%O_2/%CO_2)	Initial CO_2 Loading (Mole CO_2/mole alkalinity)	Metal Ion Additives (mM)
TOR	55	92.5/7.5	0.3	1 Fe^{2+}
TOR	55	92.5/7.5	0.24	0.1 Fe^{2+}, 0.6 Cr^{3+}, 0.1 Ni^{2+}
TOR	55	92.5/7.5	0.23	0.1 Fe^{2+}, 5 Cu^{2+}
TOR	70	92.5/7.5	0.14	0.4 Fe^{2+}, 0.1 Cr^{3+}, 0.1 Ni^{2+}
Thermal Reactor	100, 120		0.25, 0.23, 0.43	
Thermal Reactor	100, 120		0.1, 0.2	
Thermal Reactor	100, 120		0.18	1 Fe^{2+}
Thermal Reactor	135		0.12, 0.23	
Thermal Reactor	135, 150		0.11, 0.26	
Thermal Reactor	135, 150		0.0, 0.02, 0.3	
Thermal Reactor	120, 135, 150		0.0, 0.1, 0.25	
ISDA	55/120	98.0/2.0	0.14	0.4 Fe^{2+}, 0.1 Cr^{3+}, 0.1 Ni^{2+}
ISDA	55/90	98.0/2.0	0.14	0.4 Fe^{2+}, 0.1 Cr^{3+}, 0.1 Ni^{2+}
ISDA	55/100	98.0/2.0	0.14	0.4 Fe^{2+}, 0.1 Cr^{3+}, 0.1 Ni^{2+}
ISDA	55/125	98.0/2.0	0.14	0.4 Fe^{2+}, 0.1 Cr^{3+}, 0.1 Ni^{2+}

Closmann[72] ranks amines in terms of their tendency towards high total formate production as 7 molal MEA > 7 molal MDEA/2 molal PZ > 7 molal MDEA. He also detected that the formyl amides specific to PZ degradation were formed at higher level suggesting PZ degrades faster when blended with MDEA though one would expect less PZ degradation due to its higher resistance to the oxidative degradation in comparison with MDEA. There is no proper explanation in the open literature why MDEA and PZ, though individually robust

solvents, get preferentially degraded when blended with MEA and MDEA respectively. This could be considered as an open subject for further investigations.

The thermal degradation experiments conducted separately in the thermal reactor showed the degradation products listed in Table 25.

Table 25 – Thermal degradation (only) products of 7 molal MDEA/2 molal PZ

Compound Name	Abbreviation
2 – Dimethylamino Ethanol	DMAE
Methyl Paperazine	1-MPZ
N-(2-hydroxyethyl)-N-methyl Formamide	MAE-Amide
Diethanolamine	DEA
1,4 Dimethyl Piperazine	DMP
3 – (hydroxyethyl) – 2 – Oxazolidone	HEOD
4 – Methyl – 1 – piperazine-ethanamine	MPZEA
N,N-bis-(2-hydroxyethyl) Formamide	DEA-Amide or AEMP
1 - (2 - hydroxyethyl) – 4 – Methyl Piperazine	HMP
N,N-bis-(2–hydroxyethyl)-Glycine	Bicine
2-[[2-(1-piperazinyl)ethyl]amino]ethanol	PEAE
N,N-bis-(2 – hydroxyethyl) – Piperazine	BHEP`
2-[[2-(4-methyl-1-piperazinyl)ethyl]amino]ethanol	MPZEA-OH
Methyl-N,N,N-tris-(hydroxyethyl) Ethylenediamine	MTHEED

These results showed that MDEA/PZ blend is thermally stable up to 150 $^{\circ}$C in the absence of CO_2 loading similar to MDEA is up to 120 $^{\circ}$C. The formation of amides of DMAE and DEA imply that ammonia is definitely a product of thermal degradation that reacts with carboxylic acids which may have been formed in the MDEA/PZ blend despite lack of oxygen due to the formation of oxygen in-situ as a result of CO_2 induced degradation of MDEA as observed by Lawal and Idem[82] in their studies. Closmann has used the thermal degradation results to develop a "Universal activation energy" based theoretical model that estimates the degradation product formation. It has an underlying assumption that the rate limiting step in the degradation of the MDEA/PZ blend is the first order protonation of MDEA, i.e. the formation of MDEAH$^+$ and that the overall degradation rate of the blend is independent of the concentration of PZ. With these assumptions, Closmann proposes the following equations to predict the rates of losses of MDEA and PZ:

$$\frac{d[MDEA]}{dt} = -K_T*[MDEA]_T*\alpha \text{ ---------- (41)}$$

$$K_T = K_{408}*\exp\left\{-\frac{104300}{8.314}*\left(\frac{1}{408} - \frac{1}{T}\right)\right\} \text{ --------- (42)}$$

Where, $\frac{d[MDEA]}{dt}$ is the MDEA loss rate in moles per hour, K_{408} is the first order degradation rate constant at 408 K in hr^{-1}, T is the reaction temperature in $^{\circ}$K, 104300 J/mole is the "universal activation energy" for the degradation of MDEA/PZ blend and 8.314 J per mole per $^{\circ}$K is the universal gas constant, $[MDEA]_T$ is molal concentration of MDEA in the solution at temperature T ($^{\circ}$K) and time t (hr), and α is initial moles of CO_2 loading per mole alkalinity of the blend solution.

The PZ loss rate, $\frac{d[PZ]}{dt}$, is calculated as:

$$\frac{d[PZ]}{dt} = 1.13 * \frac{d[MDEA]}{dt} \text{ ------------ (43)}$$

Closmann calculated the value for K_{408} as 0.001751 hr^{-1}.

The combined oxidative and thermal degradation experiments in the ISDA system conducted by Closmann showed that the degradation products of 7 molal MDEA/2 molal PZ blend over the temperature range 55 to 125 °C are formate, acetate, oxalate, DMAE, a mixture of MAE and DEA, 1-MPZ, DMP, AEP, N-formyl PZ, MAE-amide, DEA-amide, Bicine, HES and Glycine. In this case, the loss of MDEA, PZ and alkalinity as a function of time, t, were regressed as:

$$\text{MDEA loss (milimole)} = 3452.23*\exp{(-0.001*t)} \text{ ------- (44)}$$

$$\text{PZ loss (milimole)} = 969.68*\exp{(-0.002*t)} \text{ ---------- (45)}$$

$$\text{Alkalinity loss (milimole)} = 5050.13*\exp{(-0.00056*t)} \text{ ------- (47)}$$

Using equations 26 and 27, Closmann[72] calculated the first order rate constant and the activation energy for the total formates production during combined oxidative and thermal degradation as 10 hr^{-1} and 80 kJ per mole of total amine at 363 °K. Accordingly, the upper temperature limits for 10%, 20% and 50% oxygen consumption by the CO_2 rich MDEA/PZ blend in the cross exchanger and the piping leading to the stripper (Figure 1) was calculated by Closmann as 92 °C, 97 °C and 106 °C respectively, if the solution residence time in this section of the CO_2 absorber / regeneration system is approximately 30 sec. Closmann has further calculated that for a 500 MW coal-fired power plant using 7 molal MDEA/2 molal PZ blend with initial CO_2 loading of 0.14 mole per mole alkalinity, if the flue gas contains oxygen at 5 kPa and 90% CO_2 capture is required, then the overall amine loss due to the combined oxidative and thermal degradation will be 0.27 moles per ton of CO_2 captured.

In summary, the behaviour of 7 molal MDEA/2 molal PZ is in between the behaviour of 7 molal MDEA and 8 molal PZ solvents. Currently, there is no data available on the impact of SO_X/NO_X on the degradation characteristics of the MDEA/PZ blend but the comments made on MDEA and PZ as separate amines for the impact of SO_X/NO_X on their degradation and subsequent likely atmospheric emissions upon usage of these amines for the post combustion capture should be kept in mind.

8. EMISSIONS OF DEGRADATION PRODUCTS: ASPEN-PLUS SIMULATIONS

The preceding sections have reviewed the literature data on the oxidative and thermal degradation of MEA, MDEA, AMP, PZ and their blends. These amines are primary, tertiary, hindered, and secondary cyclical types and therefore, span most of the emission risk presented by amine solvents. The degradation data as presented by various investigators though not entirely obtained under the process conditions that are relevant to an industrial post combustion capture environment, however, do provide a list of likely degradation compounds. With identification of these compounds and their physical/chemical properties as well as their kinetics of formation known, it is possible to estimate their likely atmospheric emissions in an industrial scale post combustion capture environment using the process modelling tools such as CO2SIM, Aspen-Plus, PRO-II or ProTreat. The previous milestone report[99] for the Task 3 of the research project, "Environmental Impact of Amine based Post-combustion Processes" submitted to the ANLEC R&D has discussed a base case scenario

of capturing 90% CO_2 from a typical Australian black coal-fired power plant flue gas stream using the un-inhibited 30% w/w MEA solvent based post combustion CO_2 capture technology. This report estimates for this base case atmospheric emissions, both vapour and droplet phase, of MEA and its degradation products using the Aspen-Plus process simulation software. The underlying assumptions and methodology employed for the estimation of emissions have been discussed in detail in that report[99]. These assumptions and methodology could be used to estimate the atmospheric emissions of blended amine solvents such as a mixture of AMP and PZ or a mixture of MDEA and MEA.

8.1 Aspen-Plus Simulation Task

Using the methodology referred above and the Aspen-Plus process simulation software, the following tasks have been carried out for the current phase of the ANLEC R&D funded post combustion capture project:

a) Estimate the impact of wash water temperature on the atmospheric emissions of MEA and its degradation products for the base case scenario.
b) Estimate the vapour and the droplet phase atmospheric emissions of amine solvents when blended amine solvents B and C described below replace the un-inhibited 30% w/w MEA solvent in the base case scenario.
c) Estimate the impact of wash water temperature on the atmospheric emissions solvents B and C.

Solvent B Composition: 25% w/w AMP, 15% w/w PZ, 60% w/w Water
Solvent C Composition: 25% w/w MDEA, 5% w/w MEA, 70% w/w Water

For the tasks (b) and (c), the estimation of atmospheric emissions of the degradation products of AMP, PZ, MDEA and MEA has not been incorporated into the current process simulations since the characterisation and the quantification of the oxidative and thermal degradation products of the blends of AMP/PZ and MDEA/MEA is still uncertain particularly with respect to the impact of SO_X and NO_X on the degradation processes as described in the earlier sections. As these uncertainties diminish with more laboratory and pilot plant based solvent degradation data become available from various research organisations including CSIRO, these Aspen-Plus process models will be updated. It is envisaged that the next milestone report will have the results from the Aspen-Plus process models that have incorporated full degradation information on these blends.

8.2 Impact of Wash Tower Performance – MEA Base Case

The previous milestone report[99] had estimated the atmospheric emissions of MEA and its combined oxidative and thermal degradation products for one set of the Wash Tower operating condition. The report had also highlighted that in a conventional MEA based post combustion capture plant, the Wash Tower is the last line of defence against uncontrolled emissions of volatiles to the atmosphere from the CO_2 absorber.
Based on the pilot plant emissions data from Moser et al[119,120] and Aas[111], mentioned in the report[99] the estimated concentration of several degradation products on a dry gas basis in the CO_2 lean gas after absorber are estimated below:

DEA ~ 0.3 mg/Nm3, Formaldehyde ~ 0.35 mg/Nm3, Acetaldehyde ~ 0.35 mg/Nm3, Acetone ~ 0.5 mg/Nm3, NH3 ~ 27 mg/Nm3, Methylamine ~ 0.3 mg/Nm3, Acetamide ~ 0.5 mg/Nm3

The above chemicals could be present in vapour phase at the above stated concentration levels either in the process stream G1 or the process stream G3 of the flow sheet shown in Figure 33. Assuming the capture plant operating at steady state and solvent reclamation occurring at the end of 3rd week after start-up, likely atmospheric emissions of MEA and its oxidative as well as thermal degradation products were calculated in ASPEN simulation using the above data. The ASPEN calculations involved introducing the above chemicals at their above stated concentration levels in Stream G1 or Stream G3 as the case may be and normalising the stream flow rate. The atmospheric emissions of these chemicals in the droplet phase carryover of wash water from the Wash Tower was calculated using 0.13 m3 droplets carry-over per million m3 of CO2 Lean gas stream.

Since water balance has to be maintained around the capture plant during the steady state operation, only one degree of freedom is available for an existing capture plant where the Wash Tower has already been designed and installed with a set value for maximum liquid to gas flow ratio i.e., only the wash water temperature could be varied to control emissions. Figure 33 below shows the Aspen-Plus generated material and energy balance flow sheet for the base case of entire CO_2 capture plant where the Wash Tower is assumed to be operating at 45 °C. By activating the cooler HX7 on the wash water stream WW3, it is possible to operate the Wash Tower at lower temperature. In Australia, the inland summer temperature for cooling water could be as much as 30 to 35 °C whereas in winter, it could drop to as low as 5 °C. Thus, there is a possibility that the Wash Tower temperature could be lowered to 15 °C safely depending upon the cooling water temperature once the heat exchanger HX7 is activated. Such a process operating situation can potentially reduce the level of atmospheric emissions of MEA and its degradation products significantly.

Aspen simulation results for the base case considered reactivity of DEA (which could be present in the MEA as impurity or it is a by-product of oxidative degradation of MEA) with CO_2 in flue gas leaving the absorber as well as the possibility of maximum concentration of the volatiles either at the outlet of the absorber (Stream G1) or at the inlet to the Wash Tower (stream G3) depending upon how the basic design of the capture plant is carried out to effectively counter the temperature bulge occurring in the absorber due to the heat of absorption of CO_2 in aqueous amine. For the sake of completing the exercise, the impact of wash water temperature on the atmospheric emissions due to the volatiles being present at the maximum level either in the stream G1 or in the stream G3 was calculated. Tables 26 to 29 show the atmospheric emission results for both the cases (G1 and G3) where the reaction of DEA with CO2 is allowed in the Wash Tower. The Wash Tower temperature as a result of cooling water temperature change is allowed to vary as 45 °C, 35 °C, 25 °C and 15 °C. Figure 34 shows the impact of drop in the Wash Tower temperature on the emissions of MEA and its degradation products.

Figure 33 – Base case operation of the Wash Tower (Temperature 45 °C)

Table 26 – Atmospheric emissions (Stream G4) of MEA and its degradation products predicted at 45 °C

Chemical Emissions	For Maximum Volatiles input In Stream G3						For Maximum Volatiles input In Stream G1					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 CO_2 dry Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
MEA	2.45E-02	1.10E-01	1.35E-01	7.92E+01	3.57E+02	4.37E+02	2.63E-02	1.10E-01	1.37E-01	8.53E+01	3.58E+02	4.43E+02
NITROSOMORPHOLINE	2.36E-06	4.01E-07	2.76E-06	7.63E-03	1.30E-03	8.93E-03	2.36E-06	4.02E-07	2.76E-06	7.64E-03	1.30E-03	8.95E-03
NDELA	4.75E-15	8.62E-13	8.67E-13	1.54E-11	2.79E-09	2.81E-09	4.76E-15	8.63E-13	8.68E-13	1.54E-11	2.80E-09	2.81E-09
NH3	1.13E-01	2.32E-03	1.16E-01	3.67E+02	7.52E+00	3.74E+02	8.56E-04	1.89E-05	8.75E-04	2.77E+00	6.11E-02	2.83E+00
HEEDA	0	0	0	0	0	0	0	0	0	0	0	0
OXAZOLIDONE	3.88E-12	2.08E-12	5.96E-12	1.26E-08	6.75E-09	1.93E-08	3.88E-12	2.09E-12	5.97E-12	1.26E-08	6.76E-09	1.93E-08
HEIA	0	0	0	0	0	0	0	0	0	0	0	0
TRIMER	0	0	0	0	0	0	0	0	0	0	0	0
CYCLIC UREA	0	0	0	0	0	0	0	0	0	0	0	0
POLYMER	0	0	0	0	0	0	0	0	0	0	0	0
DEA	1.08E-07	2.59E-05	2.60E-05	3.49E-04	8.39E-02	8.43E-02	1.05E-12	2.37E-10	2.38E-10	3.39E-09	7.67E-07	7.71E-07
FORMALDEHYDE	2.73E-01	6.16E-06	2.73E-01	8.85E+02	2.00E-02	8.85E+02	2.62E-01	5.91E-06	2.62E-01	8.48E+02	1.91E-02	8.48E+02
ACETALDEHYDE	2.98E-01	3.97E-06	2.98E-01	9.66E+02	1.29E-02	9.66E+02	2.88E-01	3.84E-06	2.88E-01	9.34E+02	1.24E-02	9.34E+02
ACETONE	3.32E-01	1.39E-05	3.33E-01	1.08E+03	4.50E-02	1.08E+03	3.12E-01	1.31E-05	3.12E-01	1.01E+03	4.23E-02	1.01E+03
METHYLAMINE	2.17E-01	6.80E-06	2.17E-01	7.03E+02	2.20E-02	7.03E+02	2.06E-01	6.46E-06	2.06E-01	6.68E+02	2.09E-02	6.68E+02
ACETAMIDE	6.99E-05	4.32E-05	1.13E-04	2.26E-01	1.40E-01	3.66E-01	1.05E-07	6.46E-08	1.69E-07	3.39E-04	2.09E-04	5.48E-04

Table 27 – Atmospheric emissions (Stream G4) of MEA and its degradation products predicted at 35 °C

Chemical Emissions	For Maximum Volatiles input In Stream G3						For Maximum Volatiles input In Stream G1					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 CO_2 dry Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
MEA	1.26E-02	1.06E-01	1.19E-01	4.08E+01	3.44E+02	3.85E+02	1.36E-02	1.06E-01	1.20E-01	4.40E+01	3.44E+02	3.88E+02
NITROSOMORPHOLINE	1.81E-06	3.86E-07	2.20E-06	5.87E-03	1.25E-03	7.12E-03	1.82E-06	3.87E-07	2.20E-06	5.88E-03	1.25E-03	7.13E-03
NDELA	2.94E-15	8.30E-13	8.33E-13	9.52E-12	2.69E-09	2.70E-09	2.94E-15	8.31E-13	8.34E-13	9.54E-12	2.69E-09	2.70E-09
NH3	7.52E-02	2.24E-03	7.74E-02	2.43E+02	7.25E+00	2.51E+02	5.68E-04	1.82E-05	5.86E-04	1.84E+00	5.89E-02	1.90E+00
HEEDA	0	0	0	0	0	0	0	0	0	0	0	0
OXAZOLIDONE	3.02E-12	2.01E-12	5.03E-12	9.80E-09	6.50E-09	1.63E-08	3.03E-12	2.01E-12	5.04E-12	9.82E-09	6.51E-09	1.63E-08
HEIA	0	0	0	0	0	0	0	0	0	0	0	0
TRIMER	0	0	0	0	0	0	0	0	0	0	0	0
CYCLIC UREA	0	0	0	0	0	0	0	0	0	0	0	0
POLYMER	0	0	0	0	0	0	0	0	0	0	0	0
DEA	5.33E-08	2.49E-05	2.50E-05	1.73E-04	8.08E-02	8.09E-02	5.20E-13	2.28E-10	2.28E-10	1.68E-09	7.38E-07	7.40E-07
FORMALDEHYDE	2.66E-01	6.55E-06	2.66E-01	8.62E+02	2.12E-02	8.62E+02	2.55E-01	6.28E-06	2.55E-01	8.26E+02	2.03E-02	8.26E+02
ACETALDEHYDE	2.92E-01	4.38E-06	2.92E-01	9.45E+02	1.42E-02	9.45E+02	2.82E-01	4.23E-06	2.82E-01	9.14E+02	1.37E-02	9.14E+02
ACETONE	3.08E-01	1.55E-05	3.08E-01	9.96E+02	5.02E-02	9.96E+02	2.89E-01	1.45E-05	2.89E-01	9.35E+02	4.71E-02	9.35E+02
METHYLAMINE	2.09E-01	7.23E-06	2.09E-01	6.77E+02	2.34E-02	6.77E+02	1.98E-01	6.87E-06	1.98E-01	6.43E+02	2.22E-02	6.43E+02
ACETAMIDE	5.03E-05	4.16E-05	9.19E-05	1.63E-01	1.35E-01	2.98E-01	7.54E-08	6.22E-08	1.38E-07	2.44E-04	2.02E-04	4.46E-04

Table 28 – Atmospheric emissions (Stream G4) of MEA and its degradation products predicted at 25 ^{o}C

Chemical Emissions	For Maximum Volatiles input In Stream G3						For Maximum Volatiles input In Stream G1					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 CO_2 dry Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
MEA	5.81E-03	1.02E-01	1.08E-01	1.88E+01	3.31E+02	3.50E+02	6.28E-03	1.02E-01	1.09E-01	2.03E+01	3.31E+02	3.52E+02
NITROSOMORPHOLINE	1.34E-06	3.72E-07	1.71E-06	4.35E-03	1.21E-03	5.56E-03	1.35E-06	3.73E-07	1.72E-06	4.36E-03	1.21E-03	5.57E-03
NDELA	1.68E-15	7.99E-13	8.01E-13	5.45E-12	2.59E-09	2.60E-09	1.69E-15	8.00E-13	8.02E-13	5.47E-12	2.59E-09	2.60E-09
NH3	4.66E-02	2.16E-03	4.87E-02	1.51E+02	6.99E+00	1.58E+02	3.51E-04	1.75E-05	3.69E-04	1.14E+00	5.68E-02	1.20E+00
HEEDA	0	0	0	0	0	0	0	0	0	0	0	0
OXAZOLIDONE	2.30E-12	1.93E-12	4.23E-12	7.43E-09	6.26E-09	1.37E-08	2.30E-12	1.93E-12	4.23E-12	7.45E-09	6.27E-09	1.37E-08
HEIA	0	0	0	0	0	0	0	0	0	0	0	0
TRIMER	0	0	0	0	0	0	0	0	0	0	0	0
CYCLIC UREA	0	0	0	0	0	0	0	0	0	0	0	0
POLYMER	0	0	0	0	0	0	0	0	0	0	0	0
DEA	2.32E-08	2.40E-05	2.40E-05	7.51E-05	7.78E-02	7.79E-02	2.27E-13	2.20E-10	2.20E-10	7.36E-10	7.11E-07	7.12E-07
FORMALDEHYDE	2.57E-01	7.03E-06	2.57E-01	8.33E+02	2.28E-02	8.33E+02	2.46E-01	6.74E-06	2.46E-01	7.98E+02	2.18E-02	7.98E+02
ACETALDEHYDE	2.83E-01	4.93E-06	2.83E-01	9.17E+02	1.60E-02	9.17E+02	2.74E-01	4.76E-06	2.74E-01	8.87E+02	1.54E-02	8.87E+02
ACETONE	2.77E-01	1.74E-05	2.77E-01	8.98E+02	5.64E-02	8.98E+02	2.60E-01	1.63E-05	2.60E-01	8.43E+02	5.29E-02	8.43E+02
METHYLAMINE	1.99E-01	7.76E-06	1.99E-01	6.45E+02	2.51E-02	6.45E+02	1.89E-01	7.36E-06	1.89E-01	6.13E+02	2.39E-02	6.13E+02
ACETAMIDE	3.45E-05	4.00E-05	7.45E-05	1.12E-01	1.30E-01	2.41E-01	5.17E-08	5.99E-08	1.12E-07	1.68E-04	1.94E-04	3.62E-04

Table 29 – Atmospheric emissions (Stream G4) of MEA and its degradation products predicted at 15 $^{\circ}$C

| Chemical Emissions	For Maximum Volatiles input In Stream G3						For Maximum Volatiles input In Stream G1					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 CO_2 dry Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
MEA	2.40E-03	9.87E-02	1.01E-01	7.78E+00	3.20E+02	3.27E+02	2.60E-03	9.87E-02	1.01E-01	8.42E+00	3.20E+02	3.28E+02
NITROSOMORPHOLINE	9.58E-07	3.59E-07	1.32E-06	3.11E-03	1.16E-03	4.27E-03	9.60E-07	3.59E-07	1.32E-06	3.11E-03	1.16E-03	4.28E-03
NDELA	8.92E-16	7.71E-13	7.72E-13	2.89E-12	2.50E-09	2.50E-09	8.94E-16	7.72E-13	7.73E-13	2.90E-12	2.50E-09	2.50E-09
NH3	2.68E-02	2.08E-03	2.89E-02	8.68E+01	6.75E+00	9.36E+01	2.02E-04	1.69E-05	2.19E-04	6.55E-01	5.48E-02	7.10E-01
HEEDA	0	0	0	0	0	0	0	0	0	0	0	0
OXAZOLIDONE	1.70E-12	1.86E-12	3.56E-12	5.50E-09	6.03E-09	1.15E-08	1.70E-12	1.87E-12	3.57E-12	5.51E-09	6.04E-09	1.16E-08
HEIA	0	0	0	0	0	0	0	0	0	0	0	0
TRIMER	0	0	0	0	0	0	0	0	0	0	0	0
CYCLIC UREA	0	0	0	0	0	0	0	0	0	0	0	0
POLYMER	0	0	0	0	0	0	0	0	0	0	0	0
DEA	8.85E-09	2.32E-05	2.32E-05	2.87E-05	7.50E-02	7.51E-02	8.69E-14	2.12E-10	2.12E-10	2.82E-10	6.86E-07	6.86E-07
FORMALDEHYDE	2.47E-01	7.61E-06	2.47E-01	7.99E+02	2.46E-02	7.99E+02	2.36E-01	7.29E-06	2.36E-01	7.66E+02	2.36E-02	7.66E+02
ACETALDEHYDE	2.71E-01	5.68E-06	2.71E-01	8.78E+02	1.84E-02	8.78E+02	2.62E-01	5.49E-06	2.62E-01	8.50E+02	1.78E-02	8.50E+02
ACETONE	2.42E-01	1.96E-05	2.42E-01	7.83E+02	6.34E-02	7.83E+02	2.27E-01	1.84E-05	2.27E-01	7.35E+02	5.95E-02	7.35E+02
METHYLAMINE	1.88E-01	8.38E-06	1.88E-01	6.08E+02	2.72E-02	6.08E+02	1.78E-01	7.96E-06	1.78E-01	5.78E+02	2.58E-02	5.78E+02
ACETAMIDE	2.26E-05	3.86E-05	6.11E-05	7.31E-02	1.25E-01	1.98E-01	3.38E-08	5.78E-08	9.16E-08	1.09E-04	1.87E-04	2.97E-04
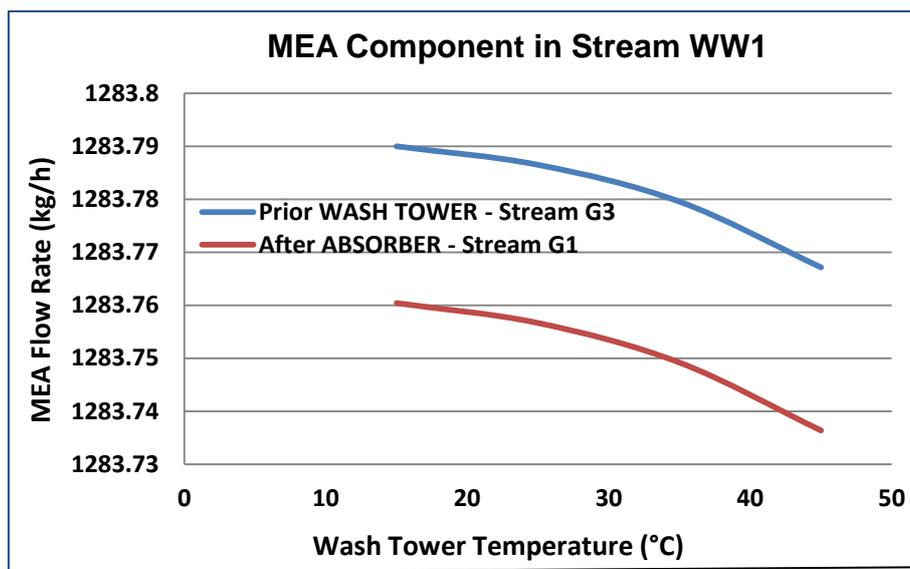
Figure 34 – Impact of decreasing Wash Tower temperature on MEA content

Figure 34 shows that as the Wash Tower temperature drops due to cooling the wash water stream WW3, the MEA content of stream WW1 leaving the wash tower increases. In other words, the atmospheric emissions of MEA decrease which is what Tables 26 to 29 shows. Similarly, these tables show that the atmospheric emissions of the degradation products of MEA including ammonia and NDELA decrease. For example, assuming maximum presence of volatiles at inlet to the Wash Tower, i.e. in Stream G3, total ammonia emissions (vapour plus droplet phase) decrease from 0.12 mg/Nm^3 of dry CO_2 lean gas or 374 mg/tonne of product CO_2 at 45 °C to 0.03 mg/Nm^3 of dry CO_2 lean gas or 93.6 mg/tonne of product CO_2 at 15 °C. Similarly, Nitrosomorpholine emissions decrease from 8.93 x 10^{-3} mg/tonne of product CO_2 at 45 °C to roughly half at 15 °C. Reduction in emissions of other compounds such as formaldehyde, acetaldehyde, acetone, methylamine and acetamide with reduction in the wash water temperature can be tracked through Tables 26 to 29. It should be noted that the droplet phase emissions are based on a general rule of thumb for the droplet entrainment from gas/liquid contactors as proposed by the Handbook of Gas Producers' Association and therefore, these values are purely indicative. In reality, the droplet phase emissions would depend upon the hydrodynamics within the CO_2 absorber and the design of its internals. Nevertheless, Tables 26 to 29 provide some sort of base line for the environmental regulatory bodies to set an emission standard for the amine based post combustion capture technologies.

8.3   Atmospheric Emissions of AMP/PZ Solvent

AMP/PZ blend is supposedly the preferred solvent of MHI technology[16, 94] and several investigators[57-60] have indicated that AMP could be used to co-absorb NO_2 and CO_2. Currently, there is not much information available on the oxidative and thermal degradation characteristics of the blend, though for the individual components of the blend some data is available. As a result for the present case, only the atmospheric emissions of AMP and PZ have been determined using the Aspen-Plus software. The AMP/PZ aqueous blend with 25% w/w AMP and 15% w/w PZ is almost same as 3 molar AMP and 1.5 molar PZ blend. Therefore, as a check for the validation of Aspen-Plus based process simulations, Aspen-Plus (Version 7.3 updated) generated vapour-liquid equilibrium (V-L-E) data for the AMP-PZ-H_2O system as a function of CO_2 loading was compared with the experimental data available from Bruder et al[100] and Yang et al[101]. Figures 35 to 39 compare predictions of Aspen-Plus

results with the experimental results over the operating temperature range (40 to 120 °C) of the AMP/PZ based post combustion capture plant.

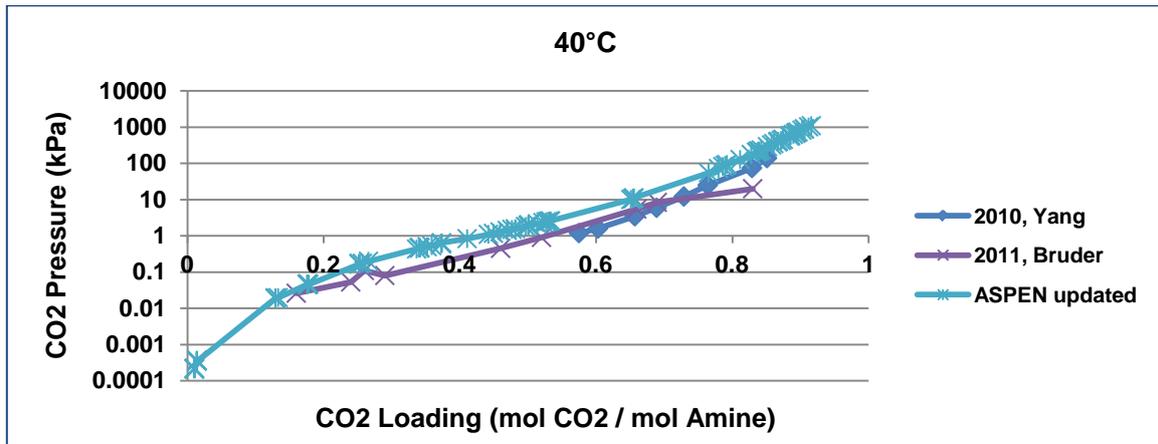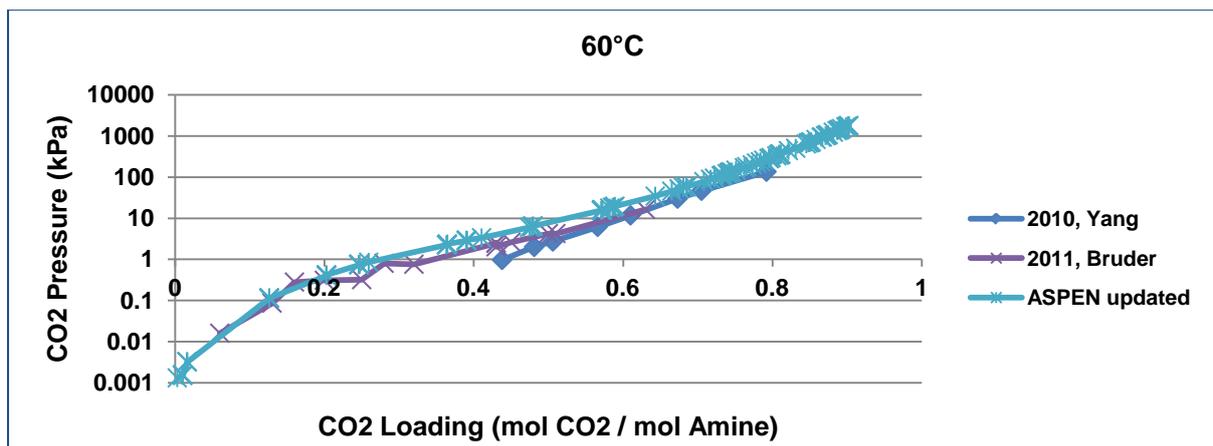**Figure 35 – V-L-E data for 3M AMP/2M PZ/H$_2$O system with CO$_2$ loading at 40 °C**

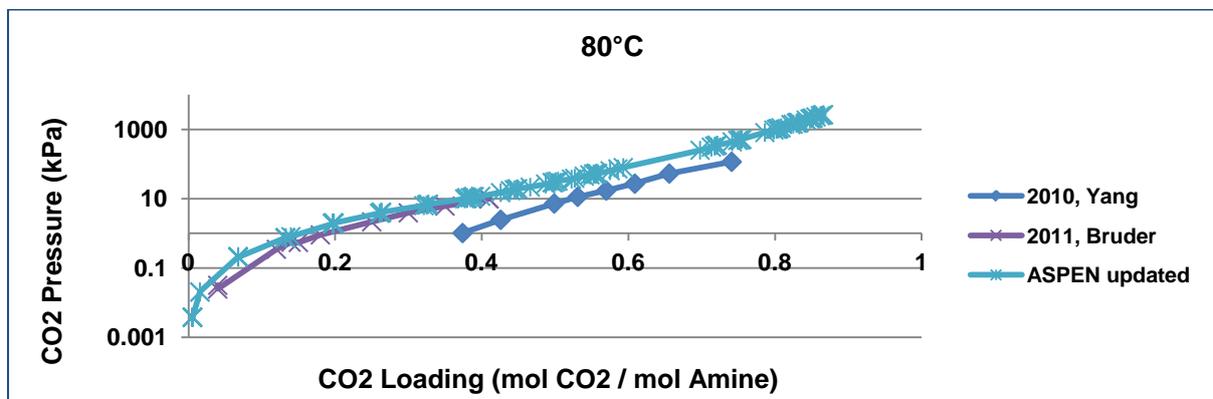**Figure 36 – V-L-E data for 3M AMP/2M PZ/H$_2$O system with CO$_2$ loading at 60 °C**

Figure 37 – V-L-E data for 3M AMP/2M PZ/H$_2$O system with CO$_2$ loading at 80 °C
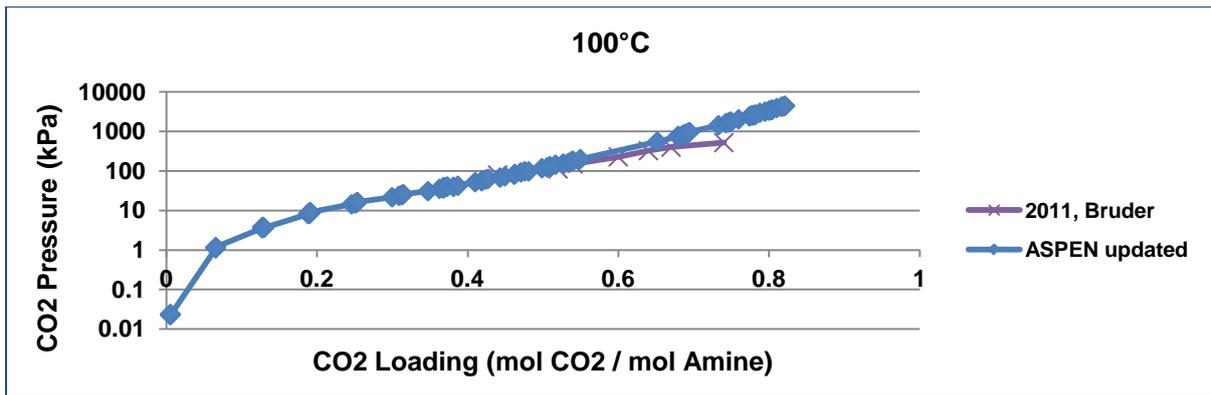
Figure 38 – V-L-E data for 3M AMP/2M PZ/H$_2$O system with CO$_2$ loading at 100 ^{o}C
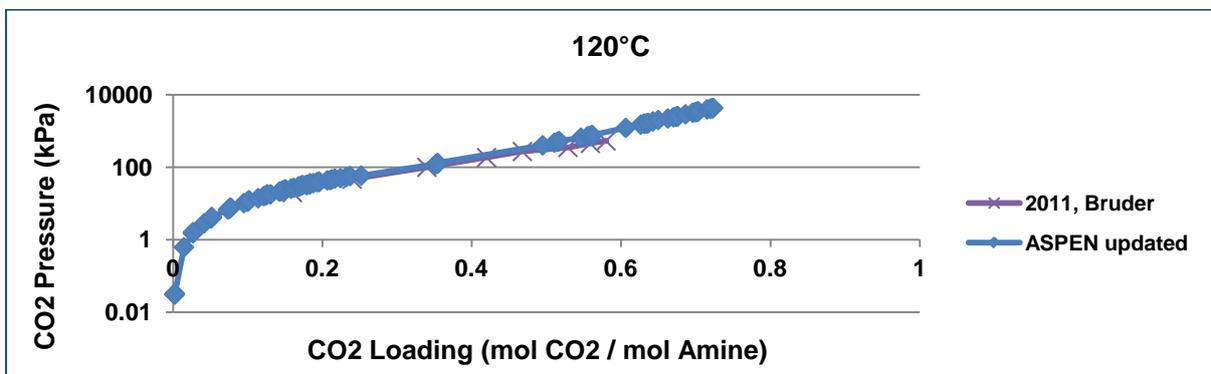

Figure 39 – V-L-E data for 3M AMP/2M PZ/H$_2$O system with CO$_2$ loading at 120 ^{o}C

These results show that the Aspen-Plus (Version 7.3 Updated) software is a reasonably reliable tool for predicting V-L-E data for AMP/PZ/H$_2$O/CO$_2$ system – a pre-requisite for accurate material and energy balance. Similar checks were also made for the other blends of AMP/PZ where AMP concentration varied from 1 molar to 3 molar and the PZ concentration varied from 0.5 molar to 2 molar. With this validation, Aspen-Plus software was used to develop the material and energy balance flow sheets using the same flue gas input data and other operating process information (for example, the Direct contact cooler) as for the base case which is described in detail in the previous milestone report. Figures 40 and 41 show material and energy flows for a capture plant with and without the condenser for recovering the volatiles from the CO$_2$ lean gas stream VENT1 leaving the absorber. These figures show that the reboiler pressure and temperature are 211 kPa and 125 $^{\circ}$C respectively. The reboiler energy demand for regenerating the spent amine blend is roughly 3.8 MJ/kg of CO$_2$ captured. It is roughly 11% less than the energy demand for the base case (4.23 MJ/kg of CO$_2$ – Please see Figure 33). The CO$_2$ lean and CO$_2$ rich amine loadings for this case are 0.075 moles CO$_2$ per mole of (AMP/PZ) and 0.312 moles CO$_2$ per mole of (AMP/PZ) respectively. Figures 42 and 43 show that content of AMP and PZ in the Wash Tower outlet stream W1 increases as temperature of the wash water at inlet to the Wash Tower drops. In other words, the atmospheric emissions of AMP and PZ decrease with lowering the temperature of wash water circulating in the Wash Tower. Tables 30 to 33 list the atmospheric emissions of various chemical species leaving the capture plant with the CO$_2$ lean gas stream VENT2, where there is a condenser for volatiles downstream of the absorber and the wash water temperature is changing over a range. Tables 34 to 37 list the atmospheric emission results when there is no condenser for the volatiles downstream of the absorber. These results clearly signify the role of Wash Tower temperature control in reducing the atmospheric emissions. Figures 44 and 45 also show that the vapour phase

emissions of AMP, PZ, and total amines measured as ppmv decrease as the wash water temperature at inlet to the Wash Tower decreases. These results clearly show that in an industrial situation either a condenser downstream of absorber or inter-cooling of the absorber for reducing the temperature rise due to heat of absorption reaction is necessary to reduce the atmospheric emissions, if a blend of AMP/PZ is preferred solvent for CO_2 capture.

The Aspen-Plus results show that when the lean solvent loading is 0.075 moles CO_2 per mole of AMP plus PZ, the lean solvent temperature is 40 °C and the flue gas temperature at inlet to the absorber is 45 °C, then temperature of the CO_2 lean gas at outlet of the absorber is 55.4 °C and at this temperature, the gas stream carries approximately 1220 ppmv of AMP plus PZ. Of course, the flue gas stream in this case is a typical Australian black coal-fired power plant off gas. Using the CO2SIM process simulation software, SINTEF[102] shows that under identical absorber operating conditions except for the flue gas representing a natural gas combined cycle power plant off gas stream and the lean solvent inlet loading being 0.1 mole CO_2 per mole of total amine, the vapour phase content of AMP plus PZ in the CO_2 lean gas stream at the outlet of the absorber will be roughly 555 ppmv. When comparing the Aspen-Plus and the CO2SIM simulation results, it should be noted that in addition to the difference in lean solvent loading and the flue gas composition, there has been a difference in the rich loading as well as the Liquid to Gas (L/G) ratio for the absorber. The Aspen-Plus simulations show 0.312 moles CO_2 per mole of total amine as the rich loading and 3.76 as the mass basis L/G ratio in the absorber, whereas the CO2SIM uses the rich loading as 0.64 moles CO_2 per mole of total amine and only 0.52 as the mass basis L/G ratio in the absorber.
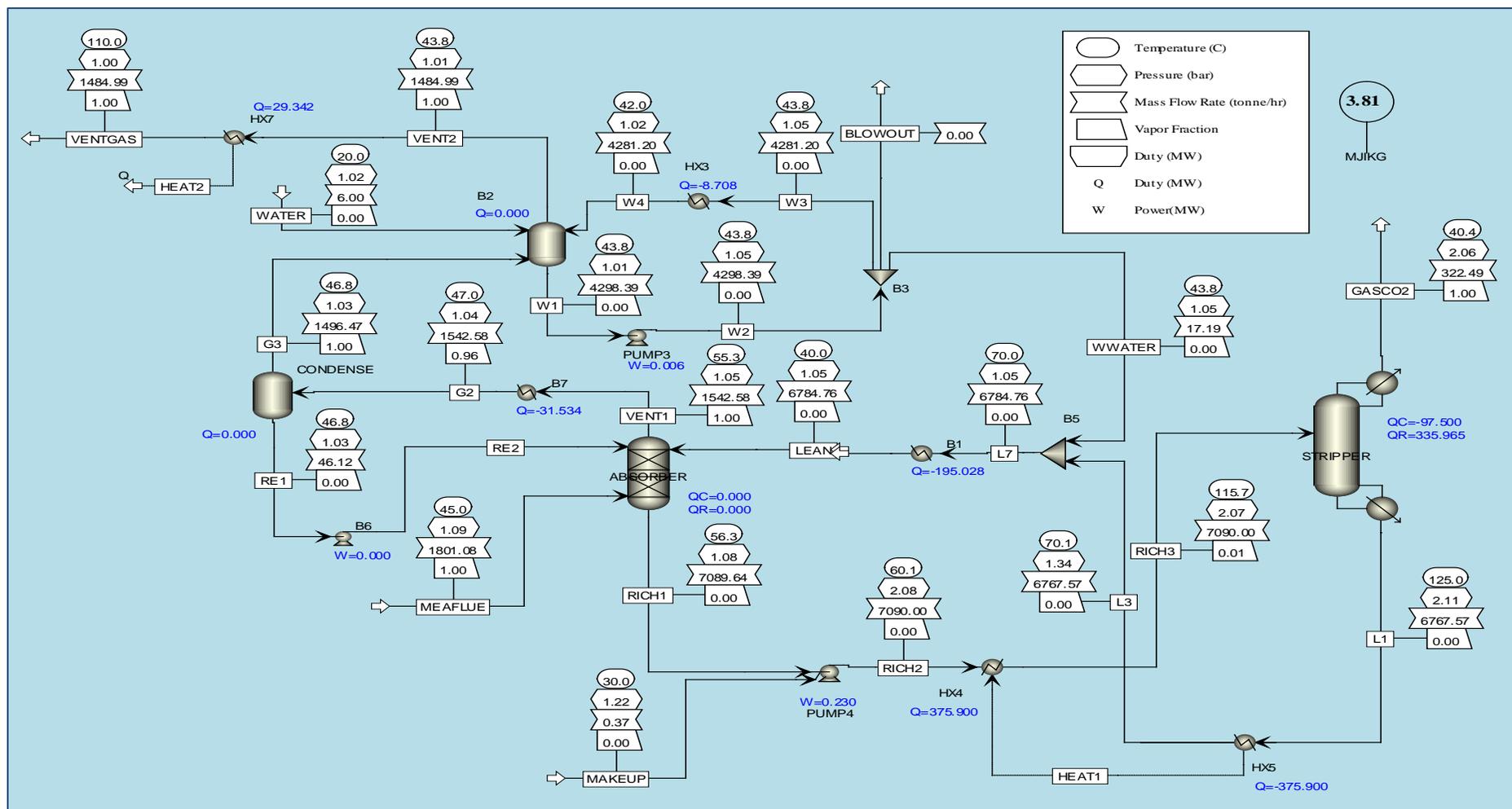
Figure 40 – AMP/PZ based CO₂ capture plant material and energy flow sheet with condenser at the absorber outlet
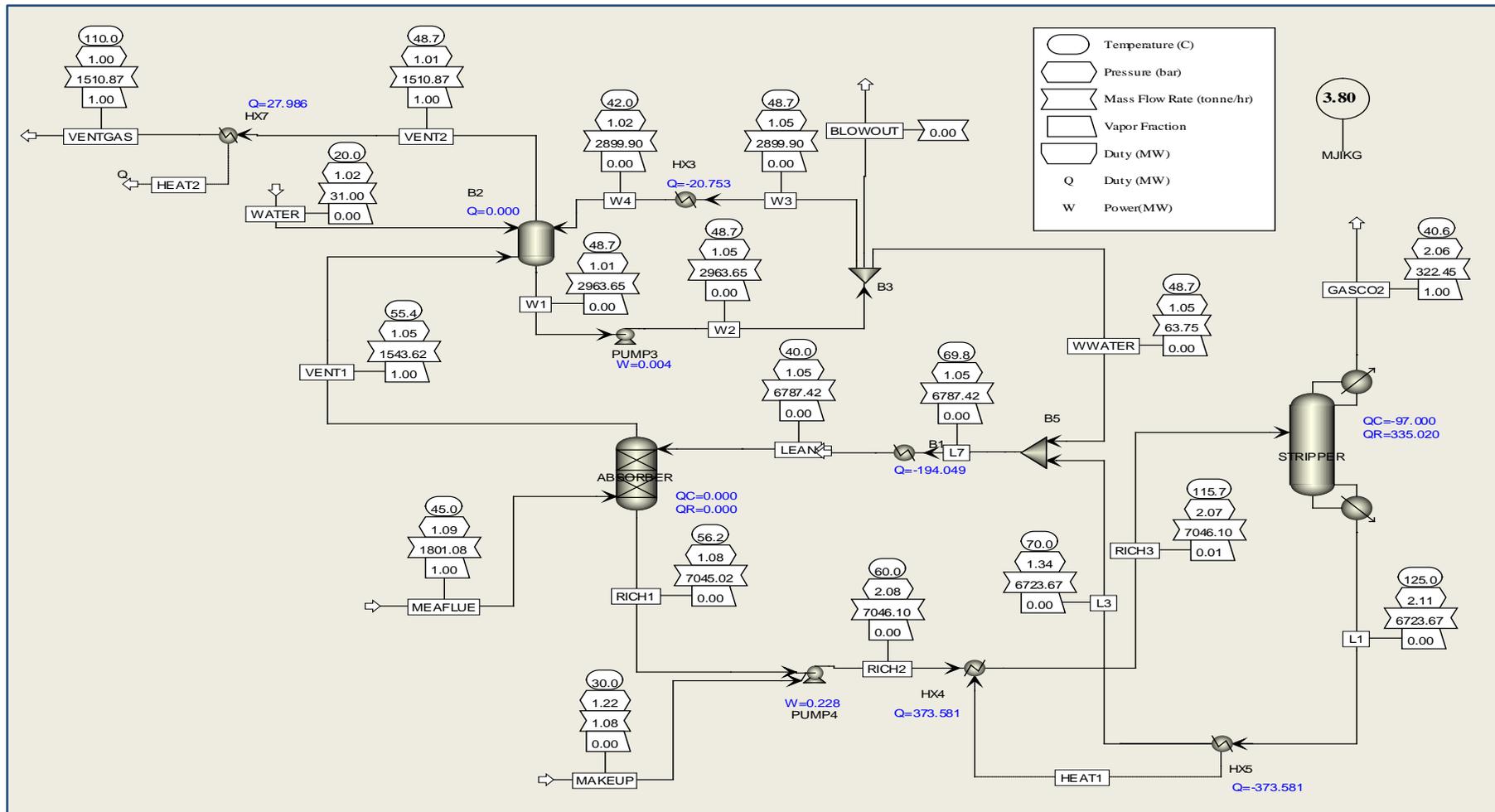
Figure 41 - AMP/PZ based CO₂ capture plant material and energy flow sheet without condenser at the absorber outlet
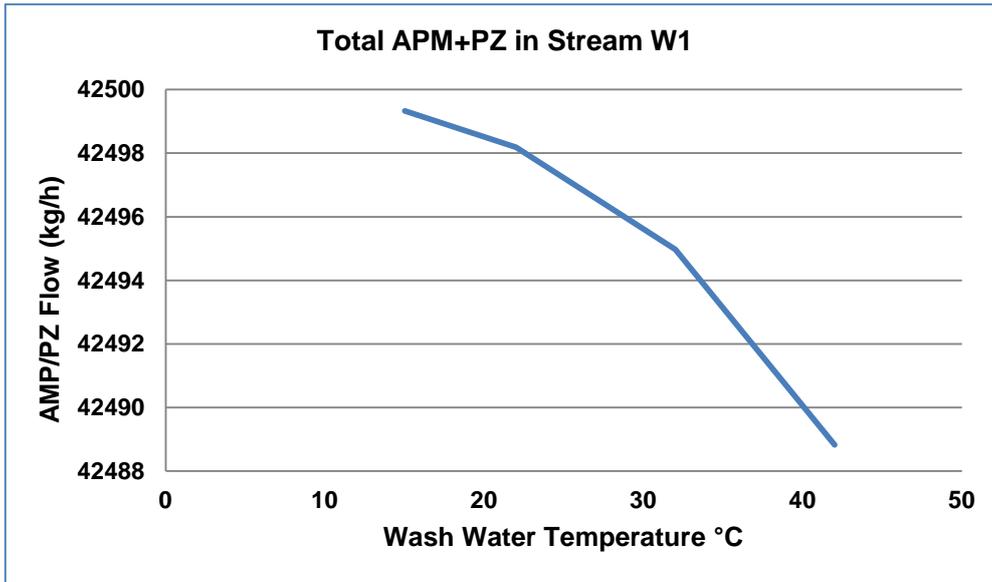
Figure 42 – Impact of the wash water temperature on AMP/PZ content of stream W1 (CO$_2$ Capture plant design with condenser for volatiles downstream of absorber)

Figure 43 – Impact of the wash water temperature on AMP/PZ content of stream W1 (CO$_2$ Capture plant design without condenser for volatiles downstream of absorber)

Table 30 - Atmospheric emissions of AMP, PZ and other compounds at 43.8 ^{o}C (Absorber with condenser, Wash water @ 42 ^{o}C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/tonne CO$_2$	mg/tonne CO$_2$	mg/tonne CO$_2$
AMP	8.99E+00	1.15E+00	1.01E+01	3.14E+04	4.02E+03	3.54E+04
PZ	1.52E+00	4.35E-01	1.96E+00	5.31E+03	1.52E+03	6.83E+03
SO2	2.90E+00	7.97E-05	2.90E+00	1.01E+04	2.78E-01	1.01E+04
NO2	1.13E-02	7.78E-07	1.13E-02	3.95E+01	2.72E-03	3.95E+01
NO	4.77E+02	6.67E-05	4.77E+02	1.67E+06	2.33E-01	1.67E+06

Table 31 - Atmospheric emissions of AMP, PZ and other compounds at 37.8 ^{o}C (Absorber with condenser, Wash water @ 32 ^{o}C)

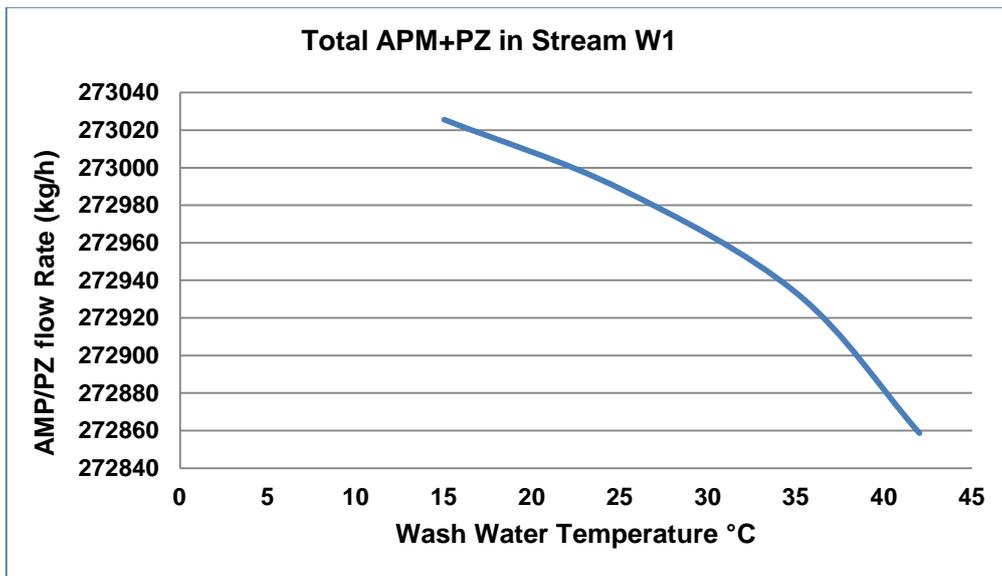| Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/tonne CO$_2$	mg/tonne CO$_2$	mg/tonne CO$_2$
AMP	4.27E+00	1.11E+00	5.39E+00	1.49E+04	3.88E+03	1.88E+04
PZ	7.10E-01	4.22E-01	1.13E+00	2.48E+03	1.47E+03	3.95E+03
SO2	2.67E+00	8.52E-05	2.67E+00	9.33E+03	2.98E-01	9.33E+03
NO2	9.47E-03	8.15E-07	9.47E-03	3.31E+01	2.84E-03	3.31E+01
NO	4.77E+02	8.54E-05	4.77E+02	1.66E+06	2.98E-01	1.66E+06

Table 32 - Atmospheric emissions of AMP, PZ and other compounds at 31.3 ^{o}C (Absorber with condenser, Wash water @ 22 ^{o}C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/tonne CO$_2$	mg/tonne CO$_2$	mg/tonne CO$_2$
AMP	1.79E+00	1.06E+00	2.85E+00	6.25E+03	3.71E+03	9.96E+03
PZ	2.91E-01	4.04E-01	6.94E-01	1.01E+03	1.41E+03	2.42E+03
SO2	2.41E+00	9.16E-05	2.41E+00	8.41E+03	3.19E-01	8.41E+03
NO2	7.63E-03	8.49E-07	7.63E-03	2.66E+01	2.96E-03	2.66E+01
NO	4.76E+02	1.12E-04	4.76E+02	1.66E+06	3.91E-01	1.66E+06

Table 33 - Atmospheric emissions of AMP, PZ and other compounds at 26.3 ^{o}C (Absorber with condenser, Wash water at 15 ^{o}C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
AMP	9.01E-01	1.03E+00	1.93E+00	3.14E+03	3.60E+03	6.74E+03
PZ	1.45E-01	3.92E-01	5.36E-01	5.04E+02	1.37E+03	1.87E+03
SO2	2.21E+00	9.64E-05	2.21E+00	7.70E+03	3.36E-01	7.70E+03
NO2	6.39E-03	8.71E-07	6.39E-03	2.23E+01	3.04E-03	2.23E+01
NO	4.76E+02	1.37E-04	4.76E+02	1.66E+06	4.79E-01	1.66E+06

Table 34 - Atmospheric emissions of AMP, PZ and other compounds at 48.7 ^{o}C (Absorber without condenser, Wash water @ 42 ^{o}C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
AMP	1.31E+02	7.84E+00	1.39E+02	4.59E+05	2.74E+04	4.86E+05
PZ	5.16E+01	7.97E+00	5.95E+01	1.80E+05	2.79E+04	2.08E+05
SO2	2.90E+00	6.02E-05	2.90E+00	1.01E+04	2.10E-01	1.01E+04
NO2	1.13E-02	5.52E-07	1.13E-02	3.95E+01	1.93E-03	3.95E+01
NO	4.77E+02	4.61E-05	4.77E+02	1.67E+06	1.61E-01	1.67E+06

Table 35 - Atmospheric emissions of AMP, PZ and other compounds at 45.5 ^{o}C (Absorber without condenser, Wash water @ 35 ^{o}C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
AMP	9.10E+01	7.58E+00	9.86E+01	3.18E+05	2.64E+04	3.44E+05
PZ	3.54E+01	7.71E+00	4.31E+01	1.24E+05	2.69E+04	1.51E+05
SO2	2.83E+00	6.32E-05	2.83E+00	9.87E+03	2.20E-01	9.87E+03
NO2	1.06E-02	5.79E-07	1.06E-02	3.70E+01	2.02E-03	3.70E+01
NO	4.78E+02	5.27E-05	4.78E+02	1.67E+06	1.84E-01	1.67E+06

Table 36 - Atmospheric emissions of AMP, PZ and other compounds at 41.2 °C (Absorber without condenser, Wash water @ 25 °C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm³ dry CO_2 Lean gas	mg/Nm³ dry CO_2 Lean gas	mg/Nm³ dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
AMP	5.51E+01	7.28E+00	6.24E+01	1.92E+05	2.54E+04	2.17E+05
PZ	2.14E+01	7.40E+00	2.88E+01	7.44E+04	2.58E+04	1.00E+05
SO2	2.72E+00	6.73E-05	2.72E+00	9.48E+03	2.35E-01	9.48E+03
NO2	9.61E-03	6.16E-07	9.61E-03	3.35E+01	2.14E-03	3.35E+01
NO	4.78E+02	6.30E-05	4.78E+02	1.67E+06	2.19E-01	1.67E+06

Table 37 - Atmospheric emissions of AMP, PZ and other compounds at 36.3 °C (Absorber without condenser, Wash water @ 15 °C)

| Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm³ dry CO_2 Lean gas	mg/Nm³ dry CO_2 Lean gas	mg/Nm³ dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
AMP	3.11E+01	7.01E+00	3.81E+01	1.08E+05	2.44E+04	1.33E+05
PZ	1.21E+01	7.12E+00	1.92E+01	4.21E+04	2.48E+04	6.69E+04
SO2	2.59E+00	7.23E-05	2.59E+00	9.02E+03	2.52E-01	9.02E+03
NO2	8.54E-03	6.55E-07	8.54E-03	2.97E+01	2.28E-03	2.97E+01
NO	4.79E+02	7.67E-05	4.79E+02	1.66E+06	2.67E-01	1.66E+06
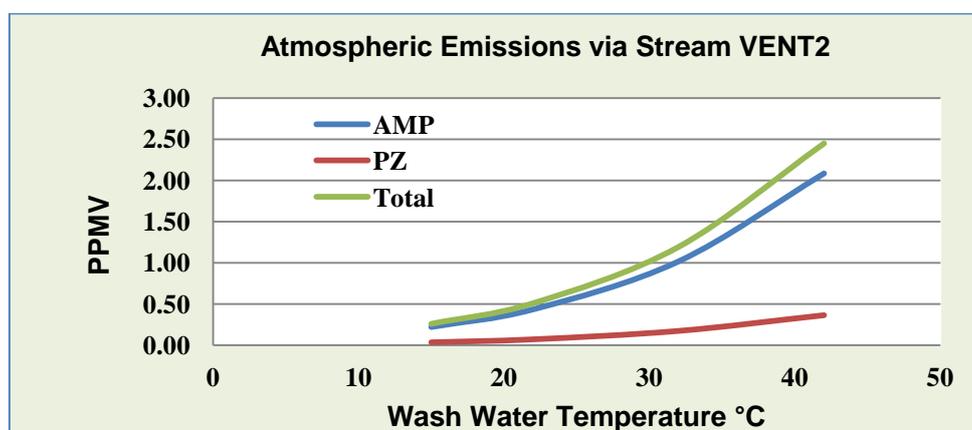
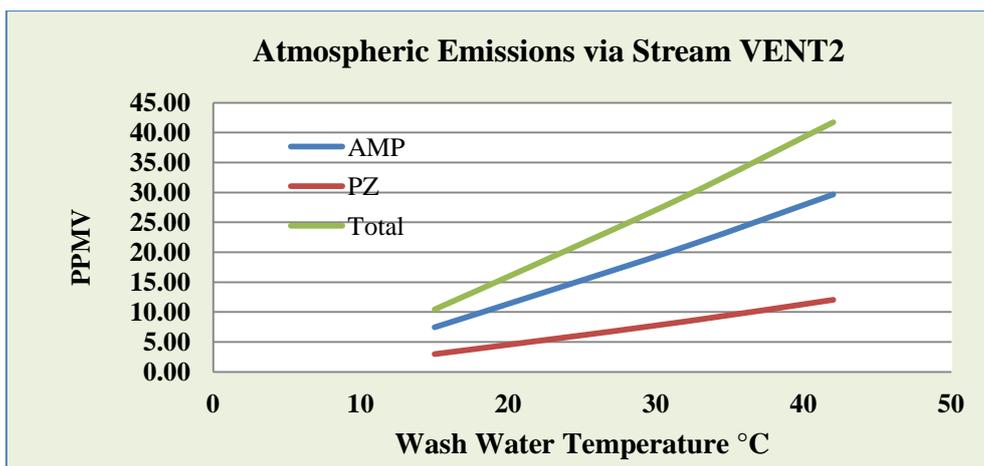Figure 44 – Vapour phase emissions of AMP and PZ (With condenser)

Figure 45 – Vapour phase emissions of AMP and PZ (Without condenser)

The Aspen-Plus results show that the use of a condenser in between the absorber and the Wash Tower reduces the Wash Tower load and the atmospheric emissions. Taking into account Australian inland summer and winter temperatures for the cooling water, Table 38 below shows the maximum and minimum levels of atmospheric emissions of AMP and PZ for both cases of capture plant designs i.e. with and without a condenser upstream of the Wash Tower.

Table 38 – Maximum and minimum atmospheric emissions of AMP/PZ
(mg per Nm³ of Dry CO₂ Lean Gas Basis)

Chemical	Capture Plant With Condenser				Capture Plant Without Condenser			
	Maximum Emissions @ 43.8 °C		Minimum Emissions @ 26.3 °C		Maximum Emissions @48.7 °C		Minimum Emissions @ 36.3 °C	
	Vapour	Liquid	Vapour	Liquid	Vapour	Liquid	Vapour	Liquid
AMP	8.99E+00	1.15E+00	9.01E-01	1.03E+00	1.31E+02	7.84E+00	3.11E+01	7.01E+00
PZ	1.52E+00	4.35E-01	1.45E-01	3.92E-01	5.16E+01	7.97E+00	1.21E+01	7.12E+00
Total	10.5E+00	1.58E+00	1.05E+00	1.42E+00	1.83E+02	15.8E+00	4.32E+01	14.1E+00

8.4 Atmospheric Emissions of MDEA/MEA Solvent

A blend of 4 molar MDEA and 1 molar MEA is supposedly the preferred solvent for PSR process for CO₂ capture that originated from the University of Regina, Canada. This process takes advantage of high absorption reaction rates with MEA and twice the CO₂ carrying capacity of MDEA without causing an excessive rise in the reboiler energy demand for the regeneration of blended solvent. Moreover, MDEA has better oxidative and thermal degradation resistance than un-inhibited aqueous MEA solution. Whilst the degradation characteristics of MDEA/MEA blend have been studied by the research group from the University of Regina, no degradation kinetics and no detailed degradation product distribution have been quantified as yet. Moreover, MDEA seems to degrade preferentially when blended with MEA as observed by Idem et al. Therefore in the present Aspen-Plus process analysis, the degradation kinetics of MDEA and MEA have not been included. However, as new information on degradation of MDEA and MEA blend in a post combustion environment becomes available in future, the Aspen-Plus process models will be upgraded and the atmospheric emissions of MDEA/MEA blend and its degradation products updated.

Figure 46 shows the Aspen-Plus simulation based material and energy flow for a capture plant that uses the aqueous solution of 25% w/w or 2.1 molar MDEA and 5% w/w or 0.82 molar MEA. In arriving at these results the same flue gas input data and other operating process information (for example, the Direct contact cooler) as for the base case which is described in detail in the previous milestone report were used. The CO_2 loadings of lean solvent at inlet to the absorber and of rich solvent at outlet of the absorber were set at 0.1 and 0.3 moles of CO_2 per mole of total amine respectively for this exercise. The Aspen-Plus simulation results show that the reboiler energy requirement in this case is 4.28 MJ per kg of CO_2, roughly same as in the case of 30% w/w un-inhibited aqueous MEA solvent and temperature of the CO_2 lean gas stream at outlet of the absorber is only 41.4 ̇C. This allows for not having a condenser for removing the volatiles prior to water washing since the total vapour phase concentration of MDEA and MEA in stream VENT1 is only 5.25 ppmv. Figure 47 shows the impact of varying temperature of wash water stream W4 and thereby the Wash Tower temperature as the summer and winter period cooling water temperature changes in inland Australia. As the wash water temperature decreases, the total amine content of Stream W1 at outlet of the Wash Tower increases i.e., in other words, the atmospheric emissions of the amines MDEA and MEA decrease. Figure 48 shows the vapour phase atmospheric emissions of MDEA, MEA and total amines expressed as ppmv decreasing with the dropping temperature of wash water stream W4. Tables 39 to 42 list the atmospheric emissions of various chemical species leaving the capture plant with the CO_2 lean gas stream VENT2. In arriving at these results, the chemical reactions of SO_2 and NO_2 with MDEA as well as MEA were not considered, though in the previous milestone report degradation products of MEA including nitrosamines were included. In addition, the degradation data available on individual amines can not be applied as sum total to predict the degradation product distribution for the blend since MDEA is known to degrade preferentially in the presence of MEA as observed by Idem et al. Nevertheless these results clearly signify the role of Wash Tower temperature control in reducing the atmospheric emissions. Taking into account Australian inland summer and winter temperatures for the cooling water, Table 43 below shows the maximum and minimum levels of atmospheric emissions of MDEA and MEA.
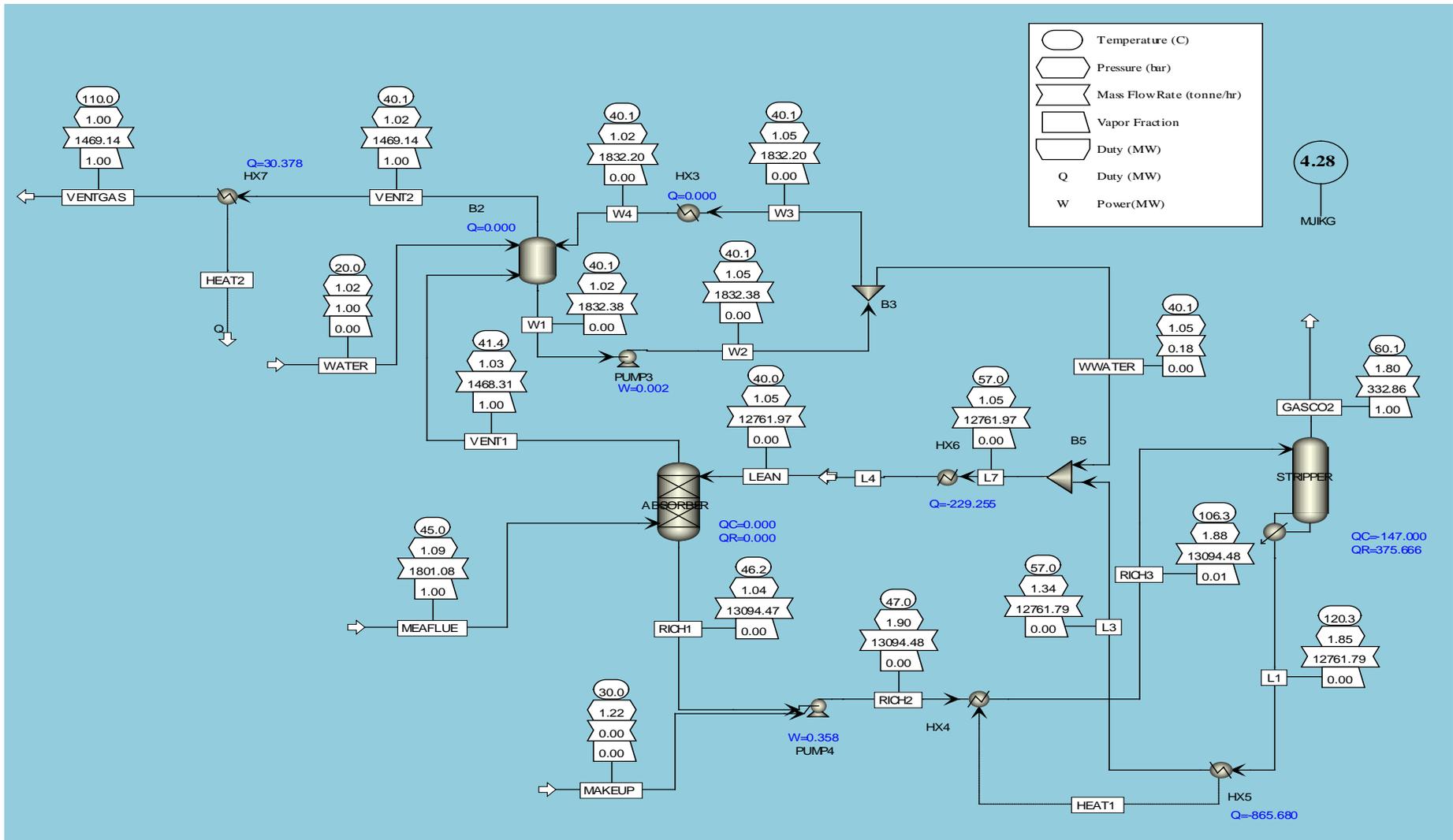
Figure 46 – MDEA/MEA blend based CO₂ capture plant material and energy balance flow sheet
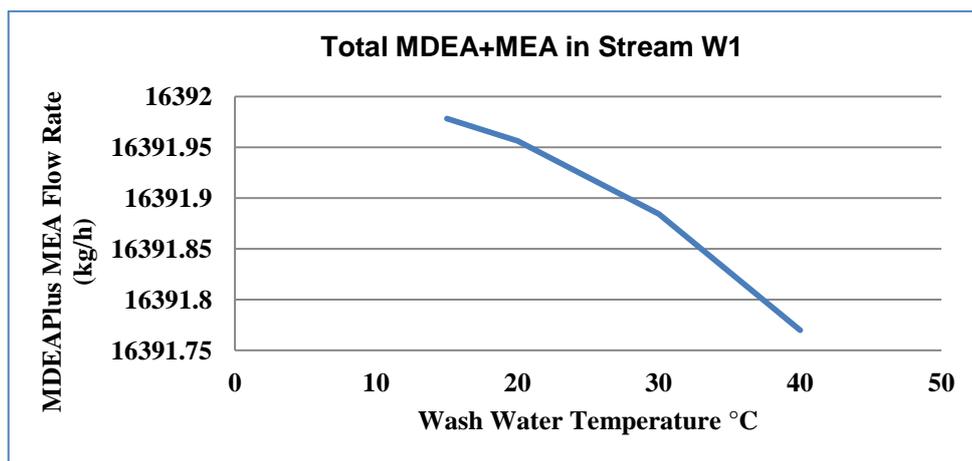
Figure 47 – Impact of wash water temperature on MDEA/MEA content of Stream
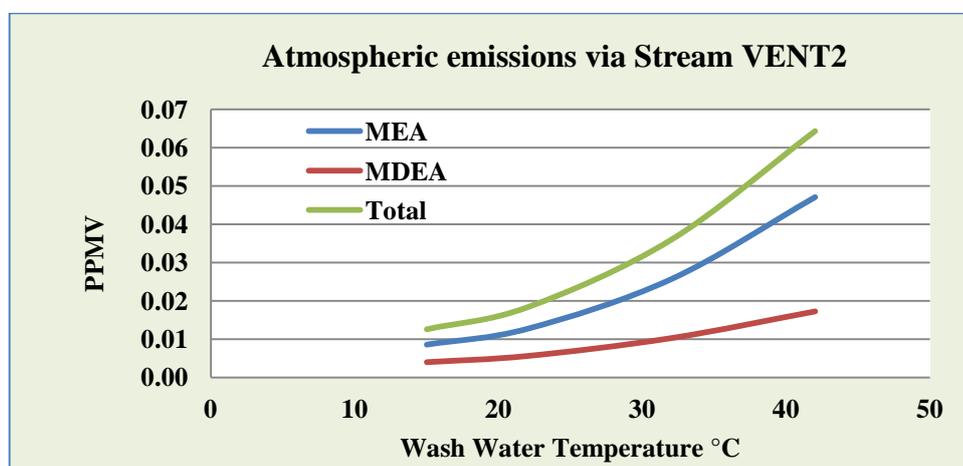
Figure 48 – Vapour phase emissions of MDEA and MEA

Table 39 - Atmospheric emissions of MDEA, MEA and other compounds at 40.1 $^{\circ}$C (Wash water @ 40 $^{\circ}$C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/Nm^3 dry CO_2 Lean gas	mg/tonne CO_2	mg/tonne CO_2	mg/tonne CO_2
MEA	1.37E-01	5.98E-01	7.35E-01	4.80E+02	2.10E+03	2.58E+03
MDEA	9.79E-02	8.09E-01	9.07E-01	3.44E+02	2.84E+03	3.18E+03
SO2	1.63E+00	4.93E-05	1.63E+00	5.73E+03	1.73E-01	5.73E+03
NO2	2.86E-03	2.27E-07	2.86E-03	1.00E+01	7.96E-04	1.00E+01
NO	4.75E+02	7.79E-05	4.75E+02	1.67E+06	2.73E-01	1.67E+06

Table 40 - Atmospheric emissions of MDEA, MEA and other compounds at 35.8 $^{\circ}$C (Wash water @ 30 $^{\circ}$C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/tonne CO$_2$	mg/tonne CO$_2$	mg/tonne CO$_2$
MEA	7.34E-02	5.77E-01	6.50E-01	2.58E+02	2.02E+03	2.28E+03
MDEA	5.73E-02	7.80E-01	8.38E-01	2.01E+02	2.74E+03	2.94E+03
SO2	1.57E+00	5.31E-05	1.57E+00	5.51E+03	1.86E-01	5.52E+03
NO2	2.60E-03	2.43E-07	2.60E-03	9.12E+00	8.52E-04	9.12E+00
NO	4.75E+02	9.30E-05	4.75E+02	1.67E+06	3.26E-01	1.67E+06

Table 41 - Atmospheric emissions of MDEA, MEA and other compounds at 31 $^{\circ}$C (Wash water @ 20 $^{\circ}$C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/tonne CO$_2$	mg/tonne CO$_2$	mg/tonne CO$_2$
MEA	3.59E-02	5.57E-01	5.93E-01	1.26E+02	1.95E+03	2.08E+03
MDEA	3.08E-02	7.53E-01	7.84E-01	1.08E+02	2.64E+03	2.75E+03
SO2	1.50E+00	5.76E-05	1.50E+00	5.26E+03	2.02E-01	5.26E+03
NO2	2.31E-03	2.60E-07	2.31E-03	8.09E+00	9.14E-04	8.09E+00
NO	4.75E+02	1.13E-04	4.75E+02	1.67E+06	3.98E-01	1.67E+06

Table 42 - Atmospheric emissions of MDEA, MEA and other compounds at 28.5 $^{\circ}$C (Wash water @ 15 $^{\circ}$C)

Chemical Emissions	Atmospheric Emissions (Stream VENT2)					
	Vapour Phase	Droplet Phase	Total	Vapour Phase	Droplet Phase	Total
	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/Nm^3 dry CO$_2$ Lean gas	mg/tonne CO$_2$	mg/tonne CO$_2$	mg/tonne CO$_2$
MEA	2.41E-02	5.47E-01	5.71E-01	8.46E+01	1.92E+03	2.01E+03
MDEA	2.17E-02	7.40E-01	7.62E-01	7.62E+01	2.60E+03	2.68E+03
SO2	1.46E+00	6.02E-05	1.46E+00	5.12E+03	2.11E-01	5.12E+03
NO2	2.15E-03	2.69E-07	2.15E-03	7.55E+00	9.46E-04	7.55E+00
NO	4.75E+02	1.26E-04	4.75E+02	1.67E+06	4.42E-01	1.67E+06

Table 43 – Maximum and minimum atmospheric emissions of MDEA/MEA
(mg per Nm³ of Dry CO₂ Lean Gas Basis)

Chemical	Capture Plant With Condenser			
	Maximum Emissions @ 40.1 ᵒC		Minimum Emissions @ 28.5 ᵒC	
	Vapour	Liquid	Vapour	Liquid
MEA	1.37E-01	5.98E-01	2.41E-02	5.47E-01
MDEA	9.79E-02	8.09E-01	2.17E-02	7.40E-01
Total	2.35E-01	1.41E+00	4.58E-02	1.29E+00

8.5 Comparison of MEA, AMP, PZ and MDEA Emissions

Comparing the Aspen-Plus process simulation results given in Tables 32 and 41 for the vapour phase atmospheric emissions of AMP/PZ and MDEA/MEA blends, it is clear that at identical temperature the vapour phase emissions of AMP are highest, followed by PZ, then MEA and finally MDEA. This is in accordance with the literature data for the volatility of various amines when in aqueous solution as a single amine solute except for MEA. The explanation for lower vapour phase emission of MEA than that of PZ is its low concentration in the MDEA/MEA blend (only 5% w/w). At this low concentration, most of MEA in solution could be already in the carbamate form due to its higher reactivity with CO_2 compared to MDEA and thereby suppressing its volatility. Nevertheless, Nguyen et al[103-105] explain that when experimentally generating the vapour-liquid-equilibrium data for aqueous solutions of different types of amines, they observed that the vapour phase mole fraction of an amine was influenced by the molecular groups in the amine structure and the shape of the structure. Amines having one or more polar groups such as hydroxyl and ether, tended to be less volatile when in solution due to favourable interactions with water. The presence of one or more methyl groups in a structure seemed to contribute to non-polarity or greater volatility as is observed in the present case for AMP. Nguyen et al concluded that as a second order effect, the presence of an $N-CH_3$ contribution in a straight chained amine, or a $C-CH_3$ contribution in a cyclic amine, correlates to lower volatility. Similarly, to a small extent, the cyclic amines appear to be less volatile than the straight chain amines. Thus, the amines with higher volatility invariably have high values for Henry's constant. Table 44 below shows the boiling points of a number of pure amines and their Henry's constant values when in aqueous solution at 40 ᵒC. Thus, it is obvious that one amine may be more volatile than another in its pure form but the opposite is true when each amine is in water. Equation 48 below shows the Henry's constant at 40 ᵒC as a function of various polar and non-polar group contributions according to Nguyen et al.

$$\ln (H_{amine,\ 40\ ^oC}) = [4.19 \pm 0.09] - [1.65 \pm 0.17](N) - [0.21 \pm 0.07](NH) - [1.55 \pm 0.17](R\text{-}O\text{-}R)$$
$$+ [0.7 \pm 0.08](\text{Non Cyclic } C\text{-}CH_3) + [2.63 \pm 0.21](\text{Cyclic } N\text{-}CH_3) \text{ ------ (48)}$$

The analysis of Nguyen et al[103-105] therefore shows what could be generally expected for vapour phase atmospheric emissions of amines and their degradation products in an industrial situation when aqueous solutions of individual amine or their blends are used for post combustion CO_2 capture, i.e. Irrespective of the normal boiling points, the amines with higher values for Henry's constant at a given stream temperature for the CO_2 lean gas leaving the wash tower will have greater vapour phase atmospheric

emissions or conversely these amines will require a larger wash water circulation in the wash tower in order to meet a given atmospheric emission limit than the amines with lower values, if these amines are either used as solvent for CO_2 capture or they are formed as degradation products of a different amine as solvent.

Table 44 – Comparison of boiling points and measured Henry's constant for amines

Amine	Boiling Point (°C)	Henry's Constant (Pa)
Methyl-diethanolamine (MDEA)	245	12.7
Diglycolamine (DGA)	223	13.9
Piperazine (PZ)	146	43.4
2-Methyl-piperazine (2-MPZ)	155	48.2
Ethylenediamine (EDA)	117	62.7
Monoethanolamine (MEA)	170	70.7
1-Methyl-piperazine (1-MPZ)	119	114
2 –Amino-2-methyl-1-propanol (AMP)	166	288

9. Pilot Plant Based Solvent Degradation Observations

As mentioned in the introduction section, post combustion capture of CO_2 from power plant flue gas streams using the amine based gas separation technologies that were originally developed for the gas processing and oil industries has been practised for the last several decades. These plants have been built predominantly to supply CO_2 for enhanced oil recovery (EOR) and meet the demand for CO_2 from food industry. Currently, there are 4 large scale plants (200 to 800 TPD CO_2) operating in the world that are exclusively recovering CO_2 from flue gas stream generated by the coal-fired power plants. Table 45[102] lists the post combustion capture plants currently operating in the world at capacity more than 100 TPD CO_2. These plants use inhibited 18 to 30% w/w aqueous MEA or an aqueous solution of hindered amine with a rate promoter for example KS-1. Lately, CANSOLV technology is being implemented at SaskPower's Boundry Dam based coal-fired power plant site to co-capture SO_2 and CO_2 from flue gas.

Whilst the plants listed in Table 45 have been operating for several years and the technology providers have concentrated over the years mainly on the corrosion, solvent loss due to degradation, cost of equipment and energy consumption issues, only lately environmental impact of the atmospheric emissions of solvent and its degradation products particularly nitrosamines and nitramines has become a serious issue. With regard to this latest issue, these process technologies are being re-examined at the process development and pilot plant scale. Table 46[102] lists the pilot plants currently operating in the world that are geared to investigate the solvent degradation, corrosion and environmental impact (atmospheric emission) issues in addition to assessing the performance of amine solutions in actual service.

Table 45 – Amine based CO_2 capture plants

Capture Technology	Location	Size (TPD)	Flue Gas	CO₂ Use
Kerr-MCGee/ABB Lumus	Trona, California	600	Coal-fired	Soda Ash
Kerr-MCGee/ABB Lumus	Shady Point, Oklahoma	200	Coal-fired	Food
Kerr-MCGee/ABB Lumus	Botswana, Africa	300	Coal-fired	Soda Ash
Kerr-MCGee/ABB Lumus	Warrior Run, Maryland	200	Coal-fired	Food
Fluor Econamine	Uttar Pradesh, India	150	Gas Furnace	Urea
Fluor Econamine	Sechuan Province, PRC	160	Gas Furnace	Urea
Fluor Econamine	Bellingham, Massachusetts	320	Gas-fired	Food
Fluor Econamine	Chiba, Japan	160	Gas-fired	Food
Mitsubishi Heavy Industries	Kedah Darul Aman, Malaysia	200	Gas Furnace	Urea
Mitsubishi Heavy Industries	Fukoka, Japan	330	Gas Furnace	General
Mitsubishi Heavy Industries	Aonla, India	450	Gas Furnace	Urea
Mitsubishi Heavy Industries	Phulpur, India	450	Gas Furnace	Urea
Mitsubishi Heavy Industries	Kakinada, India	450	Gas Furnace	Urea
Mitsubishi Heavy Industries	Abu Dhabi, UAE	400	Gas Furnace	Urea
Mitsubishi Heavy Industries	Bahrain	450	Gas Furnace	Urea
Mitsubishi Heavy Industries	Ghotoki, Pakistan	340	Gas Furnace	Urea
Mitsubishi Heavy Industries	Phu My, Vietnam	240	Gas Furnace	Urea
CERI	Shanghai, China	360	Coal-fired	General

To the credit of technology providers, it must be said that the issue of solvent loss due to degradation and the degradation of solvents causing corrosion particularly in the equipment parts made out of carbon steel, stainless steel and copper alloys is well understood by them from the point of keeping the fixed and operating costs of the capture plants low. This is the reason why the use of oxygen scavengers such as sodium sulphite (Na_2SO_3), hydrazine (N_2H_4), carbohydrazide (H_6N_4CO), erythorbate, methylethylketoxime (MEKO), hydroquinone, dietylhydroxylamine and their mixtures is listed in the public domain literature[106] for either passivating metal surfaces by creating an oxide layer or binding chemically the dissolved oxygen in amine solutions. Similarly, proprietary corrosion inhibitors, for example Max-amine GT-741C made by GE[107] are

used to prevent corrosion of process equipment caused by dissolved CO_2 and organic acids.

Table 46 – Pilot plant scale test facilities

Owner	Location	Size (kg/h)	Flue Gas
SINTEF/NTNU	Trondheim, Norway	10	Propane burner
Dong Energy/Vattenfall	Esbjerg, Denmark	1000	Coal-fired power plant
RWE/BASF/Linde	Niderauβem, Tsykland	300	Lignite-fired power plant
RWE Power	Didcot, UK	42	Coal-fired power plant
Aberthaw Power Station	UK	2083	Coal-fired power plant, CANSOLV technology
University of Texas	Texas, USA	200	Coal-fired boiler
DOE	Wilsonville, Alabama		Coal/Bio-fuel fired
ITC for CO_2 Capture	University of Regina	167	
SaskPower	Boundary Dam, Canada	4000	Lignite-fired power plant
Huaneng	Beijing, China	500	Coal-fired power plant
ENEL	Brindisi, Itali	2000	Coal-fired power plant
Loy-Yang Power/CSIRO	Loy-Yang, Australia	100	Lignite-fired power plant
Tarong Energy/CSIRO	Tarong, Australia	150	Coal-fired power plant
Hazelwood Power/CO2CRC	Hazelwood, Australia	25 to 50 TPD	Lignite-fired power plant

The following sections describe the solvent degradation studies conducted at some of the plants listed in Table 46. Any atmospheric emissions measurements of either solvents and/or their degradation products, where measured and put in public domain, are also included in the discussion.

9.1 Solvent Degradation Emissions – Dong Energy Plant

Dong Energy pilot plant study[108-112] is a joint venture under EU Project Castor where Dong Energy and Vattenfall Nordic built a 1 ton/hr CO_2 capture plant at Esbjergvaerket, 400 MW coal-fired power plant, site in Denmark. The plant uses bituminous coal and roughly 0.5% of flue gas is used as the feed gas stream for the capture plant. The power plant is equipped with state of the art de-NOX (high dust selective catalytic reactor), cold-sided electrostatic precipitator (ESP) and wet limestone based flue gas desulphurisation (FGD) plants.

A slip stream of flue gas is taken at a position immediately after the SO_2 scrubber. The flue gas does not undergo any pre-scrubbing or cooling before it enters the CO_2 absorber. The absorber consists of four consecutive packed-beds for CO_2 absorption and one water wash bed at the top. The absorber has an internal diameter of 1.1 metre. Each bed for CO2 absorption is 4.25 metres in height and filled with IMTP50 random packing. The water wash bed is 3 metres in height and filled with structured packing. The water wash section functions as a closed loop. The rich solvent from the absorber is pumped through two mechanical filters in series and a plate heat exchanger (Rich-Lean exchanger with 10 $^{\circ}$C ΔT) before it is fed to the stripper. The

stripper has an internal diameter of 1.1 metre and consists of two 5 metre high beds filled with IMTP50 random packing and a water wash bed at the top (3 metres of IMTP50 random packing). The stripper is driven by 350 kPa (absolute) saturated steam via a thermosiphon reboiler. The overhead vapours from the stripper are quenched in a condenser and the condensate returned to the stripper wash section. Essentially pure CO_2 product gas stream is returned to the main power plant flue gas duct. The regenerated solvent after Lean/Rich heat exchange is cooled to the absorber inlet temperature in a water-cooled trim cooler before returning to the absorber. A slipstream of approximately 10% of the solvent flow is passed through a carbon filter to remove organic products. Also part of the pilot plant is a reclaimer vessel where soda ash is used to remove impurities. Table 47 below gives the CO_2 capture plant specifications.

Table 47 – Dong Energy Pilot Plant Specifications

Parameter	Design Value
Flue gas capacity	5000 Nm^3/h
CO_2 removal (at 12% by volume CO_2)	1000 kg/h
CO_2 capture efficiency	90%
Maximum solvent flow	40 m^3/h
Maximum stripper pressure	300 kPa (absolute)
Flue gas condition	47 C @ inlet to absorber, <10 ppmv SO_2, <65 ppmv NO_X, <10 mg/Nm^3 (wet basis)

With the above plant uninhibited 30% w/w MEA, 3M (or 27% w/w) AMP blended with 1M (or 9% w/w) PZ and several other solvents were tested for determining the solvent effectiveness as well as solvent degradation. Sections 9.1.1 and 9.1.2 below present the results from the MEA and the AMP/PZ campaigns respectively.

9.1.1 Uninhibited MEA Solvent Campaign

Knudsen et al[109] found that under optimal operating conditions for MEA campaign, the liquid to gas ratio (L/G) in the absorber is between 2.5 and 3. At this ratio, the steam demand for 90% CO_2 recovery was 3.7 GJ/ton of CO_2 captured and MEA consumption was 1.4 kg/ton of CO_2 captured. For CO_2 recovery from gaseous fuels with no SO_2, MEA consumption of 1.6 kg/ton CO_2 has been reported by Chapel et al[113]. Knudsen et al[109] assert that the uninhibited MEA solvent campaign lasted for only 500 continuous hours and the solvent used during the campaign was fresh, therefore the overall MEA consumption was somewhat low despite the fact that flue gas (after FGD section) contained 6 ppmv SO_2. However, the authors detected 0.19 kg of heat stable salts per ton of CO_2 captured in the lean solvent (or 0.5% w/w) after 500 hours of operation. The uptake of sulphur by MEA solvent as a result of chemical reactions (see reaction equations 14 to 16) was 85%; i.e. 85% of sulphur coming into absorber as SO_2 reacted with amine. At the end of 500 hours, detailed emission measurements conducted on flue gas leaving the absorber (after the wash section) and the CO_2 gas from stripper condenser revealed the presence of volatile degradation products, e.g. ammonia, formaldehyde, acetaldehyde and acetone in both streams. In particular the emission of ammonia (25 mg/Nm^3) from absorber was significant, though no MEA (<0.01 mg/Nm^3) was detected. Since ammonia is formed mainly as a result of oxidative degradation of MEA, assuming 1:1 mole basis between ammonia and MEA, 0.4 kg MEA per ton of CO_2 or roughly 30% of the total MEA loss (consumption) could be due to oxidative

degradation. Assuming irreversible reactions between SO_2 and MEA, and 1:1 mole basis, Knudsen et al[109] calculated that 0.15 kg of MEA per ton of CO_2 (or 10% of the total MEA loss) occurs due to SO_2 induced degradation. The remaining MEA loss (≈ 60%) or 0.85 kg MEA per ton of CO_2 may be due to thermal degradation and reaction with NO_X. Aas and da Silva[111] state that the atmospheric emissions of formaldehyde with CO_2 lean gas (leaving the water wash tower) were 0.06 mg per Nm^3 of lean gas and oxygen concentration in the lean gas stream was 7.5% by volume on dry basis. Similarly, the NO_X content of CO_2 lean gas leaving the wash section was 73 mg/Nm^3.

In 2009, same pilot plant was operated for 3360 hours (20 weeks) under EU Project CESAR to closely monitor oxidative and thermal degradation of uninhibited 30% w/w MEA. After 11 weeks of operation, liquid samples were taken from different parts of the plant: the lean amine in the absorber, the rich amine in the stripper and the water washes (both for the absorber and stripper). In addition, final lean MEA solution corresponding to the end of the campaign was analysed. Lepaumier et al[42] state that more degradation products were observed in the final lean MEA solvent than what their own laboratory studies at equivalent conditions had determined. In the real plant environment, Lepaumier et al[42] found that the contribution of thermal degradation was quite limited. Accordingly, N-(2-hydroxyethyl)imidazolidone (HEIA) was identified but in a very small amount and N-(2-hydroxyethyl)ethylenediamine (HEEDA) was not detected at all. This point is in agreement with Strazisar[34] et al's observation when they analysed the degraded lean amine solution at Kerr-McGee/ABB Lumus technology based 800 tons/day CO_2 capture plant at Trona, California. Oxazolidone, N-(2-hydroxyethyl)imidazole (HEI) and N-(2-hydroxyethyl)formamide (HEF) – the products of oxidative degradation of MEA – were all detected with other amide derivatives N-(2-hydroxyethyl)acetamide (HEA), 2-hydroxy-N(2-hydroxyethyl)acetamide (HHEA) and N,N'-bis(2-hydroxyethyl)oxalamide (BHEOX). In addition, two major products 4-(2-hydroxyethyl)piperazin-2-one (HEPO) and N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide (HHEA) were identified as major oxidative degradation products. The last two products were also identified by Strazisar et al[34] at CO_2 capture plant based in Trona, California. Lepaumier et al[42] state that HEA, HHEA and BHEOX, which were detected in reasonable good amounts, are formed by reaction of MEA with respectively acetic, glycolic and oxalic acids. This observation confirms that in a real plant environment, the heat stable salts are not really stable but they form amide derivatives depending upon the plant operating conditions and how long the solvent has been circulating between the absorber and stripper without reclamation step. Aas and da Silva[111] present the results of gas sample analysis conducted during this long uninhibited MEA solvent campaign as given in Table 48. Figures 49 and 50 present the measurements of atmospheric emissions of acids, dust and constituents of dust taken during the 3360 hours of operation at absorber inlet and at outlet of the absorber wash section.

Table 48 – Atmospheric emission measurements (mg/Nm^3 of dry CO_2 lean gas)

Compound	Absorber Inlet	Absorber Outlet	Water Wash Outlet
MEA	<0.1	0.7	<0.3
DEA	<0.2	<0.3	<0.2
Formaldehyde	<0.1	0.7 to 1.1	<0.1
Methylamine	<0.2	<0.3	<0.2
Acetamide	<0.6	<1.0	<1.0
Ammonia	<0.1	23	20

It is interesting to note that neither Knudsen et al[109] nor Lepaumier[42] et al comment on the formation and detection of nitrosamines or nitramines as a result of NO_X induced degradation of MEA, though DEA formation has been detected during the CESAR campaign (Table 48). As observed in the lab-scale experiments by Pedersen et al[26], one would expect formation of nitrosamines during both CASTOR and CESAR campaigns.
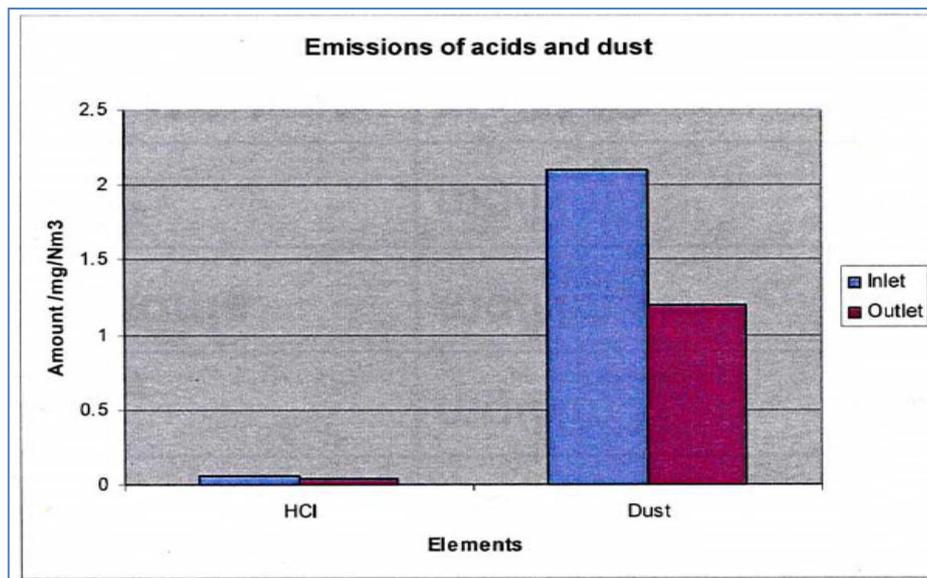

Figure 49 – Atmospheric of acids and dust at Dong Energy Pilot plant
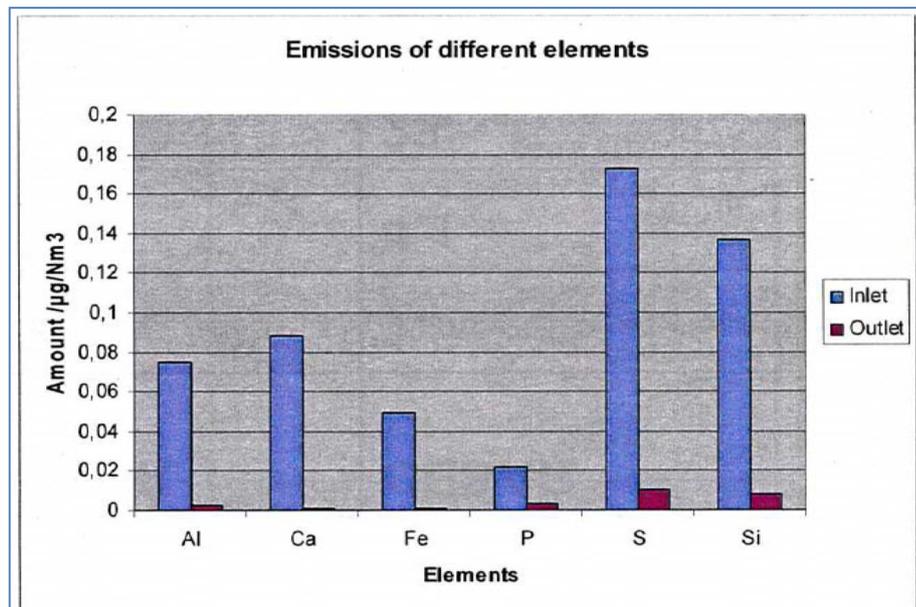

Figure 50 – Atmospheric emissions of dust constituents at Dong energy's pilot plant.

The results shown in Figures 49 and 50 clearly indicate the contribution of the water wash section of CO_2 capture plant in reducing the atmospheric emissions of volatile organics and the particulate matter. It is interesting to note from Figure 50 that as the dust particles get washed out in the absorber, the iron (Fe) present in the dust particles must end up in the CO_2 rich amine stream and catalyse both the oxidative and thermal degradation of uninhibited MEA solvent as observed by Goff[6] and Sexton[7].

It should be noted that the atmospheric emission results of Dong Energy's pilot plant have been used for the ANLEC R&D Project, "Process Modelling for Amine-based Post-Combustion Capture Plant" Milestone 3.1 Report[99] and that has further been a basis in this report for determining the atmospheric emissions as a function of the Wash Tower operating conditions in Australian context (See section 8). In reality, the ambient conditions at the capture plant site, the design of capture plant and the overall plant operating practice will greatly influence the actual extent of degradation product formation and its subsequent atmospheric emissions.

9.1.2 AMP/PZ Campaign

In a recent publication, Mertens et al[112] describe how Dong Energy's CO_2 capture plant at Esbjergvaerket has been utilised lately to understand the effectiveness of 3M AMP/1M PZ blend as an alternative of 30% w/w MEA solvent. For this campaign, the plant was equipped with on-line continuous measurement techniques to monitor the impact of various process parameters such as the wash tower operating conditions, lean amine solvent temperature at inlet to the absorber, CO_2 content of flue gas etc on the atmospheric emissions of AMP and PZ. These authors state that increasing CO_2 content of flue gas left less "free" amine in the solvent and therefore, emissions of AMP and PZ at outlet of the wash section decreased. Similarly, lowering the CO_2 loading of lean solvent increased the wash tower load for the same operating conditions and resulted into higher emissions. Lowering the wash water temperature or increasing the frequency of changing water (more makeup water) lowered emissions of both AMP and PZ. In the case of AMP, 70% of total AMP loss was determined as vapour phase emissions whereas for PZ, this figure was 3%. This is in accordance with the observations of Nguyen et al[103-105] (see Section 8.5), that AMP has a higher volatility than PZ. The remaining 30% for AMP and 97% for PZ was determined to be lost through several other mechanisms: formation of heat stable salts, gaseous emissions of degradation products, AMP and PZ losses with waste water from the plant etc. This suggests that volatility of amines rather than droplet entrainment is a dominant pathway for atmospheric amine emissions with AMP/PZ blend. Volatile organics such as formaldehyde, acetaldehyde and ammonia were not detected at the outlet of the wash section due to the functional limits of on-line measurement equipment. Surprisingly, Mertens et al[112] give no gas or liquid sample analysis results for the AMP/PZ blend campaign and do not present any evidence for detection or otherwise of either oxidative or thermal degradation products of AMP and PZ including Mono-nitrosopiperazine (MNPZ) and Di-nitrosopiperazine (DNPZ) which are expected to be formed due to nitrosation of PZ in the presence of NO_X in the flue gas (see Sections 4 to 5.2).

9.2 University of Regina (ITC) & SaskPower's Boundary Dam Plants

The International test Centre (ITC) for CO_2 capture technologies at the University of Regina, Canada, has been operating a CO_2 capture pilot plant from around 2001 to develop the formulated amine solvent (mostly a mixture of MEA and MDEA) as an

economically viable alternative of 30% w/w MEA[114]. It uses 4800 m^3/day of natural gas combustion flue gas (11.6% v/v CO_2, 1.1% v/v O_2 and 87.3% v/v N_2) to produce 1 tonne/day of CO_2. The absorber is composed of 0.3 m-diameter sections for a total height of 10 m and equipped with a series of temperature sensors and gas sampling points at a regular interval of 0.6 m to allow measurements of temperature and gas-phase CO_2 concentration during testing. The stripper is also of same dimensions as the absorber. A natural gas fired, 250 kW, steam boiler supplies saturated steam to the stripper for the solvent regeneration.

SaskPower, Canada, has research collaboration for carbon capture and sequestration with the ITC at University of Regina. Its Boundary Dam based CO_2 capture plant[115-117] uses a slip stream (14160 m^3/day) of flue gas from 150 MW lignite-fired power plant to produce 4 tons of CO_2 per day. The slip stream has composition of 15% v/v CO_2, 5% v/v O_2, 15% v/v H_2O, 380 ppmv SO_2 and 350 ppmv NO_X[116, 117]. It is first passed through a high efficiency bag-house followed by an Anderson 2000 SO_2 scrubbing unit[116] before entering the capture plant. The absorber has 0.45 m diameter and 19.5 m height whereas the stripper has 0.4 m diameter and 18 m height. The Anderson 2000 FGD unit improves the flue gas quality prior to entering the absorber to virtually free of fly ash and <10 ppmv SO_2 and NO_2.

At the above plants, 30% w/w MEA and a blend of MEA/MDEA have been tested as solvents. The MEA/MDEA blend had total concentration of MEA and MDEA as 30% w/w but MEA/MDEA ratio was 4:1. It should be noted that though MDEA is known to act as a corrosion inhibitor, a proprietary corrosion inhibitor was added to the solvents used in the Boundary Dam plant but no corrosion inhibitor was used at the ITC plant[117].

It should be noted that though the scope of work for this report restricts to dealing with the solvent degradation where flue gas is only from a black coal-fired power plant, the MEA and MEA/MDEA degradation data for treating the flue gas from a lignite-fired power plant is considered here because the flue gas composition for Boundary Dam plant is surprisingly looks similar to that of a black coal-fired plant in Australia, at least in terms of CO_2, O_2, SO_X and NO_X concentrations. Therefore, the section 9.2.1 below presents the solvent degradation results for MEA and MEA/MDEA solvents as observed at ITC and Boundary Dam plants.

9.2.1 MEA and MEA/MDEA Blend Degradation at Pilot Plants

Idem et al[117] describe that at both the ITC and Boundary Dam plants the amine emissions increased when the CO_2 loading of lean amine for both MEA and MEA/MDEA blend solvents was reduced. With the decreasing lean loading, a corresponding increase in the reboiler heat duty was observed at both plants for the same CO_2 capture capacity. Thus, in the industrial situation one will have to trade off the energy efficiency of process with the atmospheric emissions.

In the case of Boundary Dam plant straight chain amines such as 1-propanamine, cyclic compounds such as 1,2,3,6-tetrahydro-1-nitrosopyridine and 2-pyrrolidinone, dialcholos such as 1,2-ethanediol, as well as sulphur compounds such as isothiocynatoethane and 1,1-dioxid-tetrahydrothiophene were observed as major degradation products of MEA and MEA/MDEA mixed solvents. Idem et al[117] further state that the sulphur compounds may have resulted from contact of aqueous MEA and MDEA with trace amounts of SO_2 that survived the scrubbing process in the Anderson 2000 SO_2 unit. Since, the detection limit of the SO_2 analyser was about 5 ppmv, SO_2 in

the flue gas at absorber inlet must have been less than 5 ppmv. The wide variety of degradation products observed in the Boundary Dam demonstration plant samples, despite the use of proprietary corrosion inhibitors and oxygen scavenging additives, illustrates the effect of a harsher environment brought about by a coal-fired power plant flue gas. In the case of the ITC plant, lean amine sample analysis for both MEA and MEA/MDEA solvents indicated insignificant degradation and the presence of only trace amounts of degradation products, which included 1-propanamine and 2-pyrrolidinone, and just more than trace amounts of 1,2-ethanediol and 1,2,3,6-tetrahydro-1-nitrosopyridine. It should be noted that the ITC flue gas was natural gas combustion based and with lower oxygen level compared to flue gas for the Boundary Dam plant. Also, the lean amine solution for the ITC plant did not have either corrosion inhibitors or oxygen scavenging additives in it[117].

Idem et al[117] further state that the degradation rate for the aqueous MEA used in the Boundary Dam plant was 0.5 mole% per day. In the case of mixed MEA/MDEA solution for the same plant, the MEA degradation rate was 2.3 mole% per day while the rate of MDEA was 1.5 mole% per day. Thus, MEA degraded preferentially in the presence of MDEA contrary to what was observed by these authors in their laboratory scale degradation studies[82, 83]. Since, the reboiler temperatures (115 to 120 °C) and the lean amine concentrations were identical for both the Boundary Dam and ITC capture plants, the only reason for extensive solvent degradation in the case of Boundary Dam plant could be the quality of flue gas (coal-fired v/s gas fired) and catalytic effect of corrosion inhibitor for degradation). Unfortunately, Idem et al[117] neither clarify the exact nature of the corrosion inhibitor nor the quantification of degradation products for both the pilot scale capture plants.

It is unfortunate that Idem et al[117] neither state the characterisation and quantification of heat stable salts nor they mention presence of any thermal degradation products in the lean amine solvent samples for both the pilot scale capture plants. Comparison of the laboratory based degradation studies (see Table 49) by Lawal et al[82, 83] with the pilot plant solvent degradation study[117] implies that in an industrial situation, the solvent degradation products formed are quite different from those detected in the laboratory environment due to inability to replicate the exact flue gas quality, hydrodynamics and degradation process conditions.

Table 49 – Solvent degradation products in laboratory environment
(55 to 120 °C, 250 kPa O_2 Pressure)

MEA-H_2O-O_2-CO_2 System (7 molar MEA, 0.27 mol CO_2/mol MEA)		MEA-MDEA-H_2O-O_2-CO_2 System (7 molar MEA, 2 molar MDEA, 0.43 mol CO_2/mole total amine)	
Product	Formula	Product	Formula
Methyl-pyrazine	$C_5H_6N_2$	3-Methyl pyridine	C_6H_7N
7-Oxabicyclo-ketone	$C_6H_6O_2$	1,2-Propanediamine	$C_3H_{10}N_2$
Ethylamine	C_2H_7N	2-Butanamine	$C_4H_{11}N$
1-Propanamine	C_3H_9N	1-Amino-2-propanol	C_3H_9NO
1,3,5-Triazine	$C_3H_3N_3$	N-Hydrocarbaminic acid	$C_7H_{14}N_2O_5$
12-Crown-4	$C_8H_{16}O_4$	Dimethylamine	C_2H_7N
2-(2-ethoxy)ethanol	$C_6H_{14}O_3$	15-Crown-5	$C_{10}H_{20}O_5$
15-Crown-5	$C_{10}H_{20}O_5$	2-Ethenoxy-ethanol	$C_4H_8O_2$
Oxacyclo-octadecane	$C_{12}H_{24}O_6$	Ethyl-urea	$C_3H_8N_2O$
		Dimethyl-1,2-ethanediamine	$C_4H_{12}N_2$

9.3 RWE/LINDE/BASF Niderauβem Pilot Plant

In July 2009, RWE, Linde and BASF jointly commissioned 7.2 tons/day (300 kg/h) CO_2 capture plant at Niderauβem, Germany, based 1000 MW lignite-fired power plant[118-121]. This plant was operated for 5000 hours with 30% w/w uninhibited MEA solvent at 90% CO_2 capture efficiency. A slip stream of 1550 Nm^3/h flue gas containing 14.2% v/v CO_2 (dry basis) with 190 mg/Nm^3 NO_X (dry basis at 6% O_2), 93 mg/ Nm^3 SO_X (dry basis at 6% O_2) and 5% v/v O_2 (dry basis) was treated with roughly 4025 kg/h of aqueous MEA solvent. Upstream of the capture plant a wet FGD and electrostatic precipitators were used. The direct contact cooler of the capture plant reduced flue gas temperature from 65 ˚C to 40 ˚C at the absorber inlet and since it was operated with dilute caustic soda solution, the SO_X content of flue gas at inlet to the absorber was less than 5 ppmv. Similarly the NOx content of flue gas at inlet to the absorber fluctuated between 110 and 130 mg/Nm^3. The absorber was intercooled and equipped with water wash tower at the top to minimise the atmospheric emissions of MEA and its volatile degradation products. The temperature of CO_2 lean flue gas leaving the water wash tower was usually around 35 to 40 ˚C. The liquid to gas ratio (L/G) in the absorber was 3.1 on mass basis.

With the above background information, Moser et al[121] state that the overall MEA loss or specific MEA consumption during 5000 hours of plant operation was 290 g/ton of CO_2. The concentration of MEA in CO_2 lean gas leaving the plant was only 0.02 to 0.03 mg/Nm^3 (dry basis) but the product CO_2 stream leaving the stripper condenser carried between 8.1 and 11.8 mg of MEA per Nm^3 of product gas (dry basis). Thus, the vapour phase loss of MEA (combination of absorber and stripper) was roughly 6 g per ton of CO_2. The CO_2 lean gas leaving the capture plant contained ammonia (26.9 to 46.6 mg/Nm^3), acetaldehyde (0.5 to 1 mg/Nm^3) and acetone (0.2 mg/Nm^3). The product CO_2 gas contained 1.1 mg/Nm^3 ammonia, 11.6 to 12.9 mg/Nm^3 acetaldehyde and 0.3 to 1 mg/Nm^3 acetone. Thus, the total specific loss of MEA was determined as: 323 to 563 g/ton of CO_2 due to ammonia formation, 4 to 8 g/ton of CO_2 due to acetaldehyde formation and less than 1 g/ton of CO_2 due to acetone formation. Comparing with the data on specific consumption of MEA, the total specific loss of MEA does not match as far as the plant material balance is considered and this could be attributed to incorrect stoichiometry applied by Moser et al[121] for the formation of various volatile degradation products such as ammonia, acetaldehyde and acetone from MEA due to oxidative degradation.

Moser et al[121] further claim that the lean solvent analysis after 5000 hours of operation showed that the oxidative degradation of MEA contributed significantly towards the formation of heat stable salts (203 g/ton CO_2) which consisted of 1.8 % w/w acetate, 0.2% w/w formate and less than 0.1% w/w oxalates. In addition, traces of thermal degradation product 1-(2-hydroxyethyl)imidazolidone-2 (HEIA) were detected. However, other thermal degradation products that are related to the carbamate polymerisation such as Oxazolidine, HEEDA, trimer and polymer of MEA and cyclic urea were not detected in the circulating solvent even after 5000 hours of operation. Moser et al[121] are silent on the detection of any nitrosamines and nitramines either in the gas or liquid samples after 5000 hours. These investigators seem to have not found 1,2,3,6-tetrahydro-1-nitrosopyridine or 2-pyrrolidinone which Idem et al[117] found in the liquid sample at the Boundary Dam plant which is expected since these plants are lignite-fired and have roughly similar flue gas composition.

This shows that in an industrial situation, the extent of solvent degradation depends upon the plant operating practice and impact of process scale-up factors on degradation which are normally difficult to reproduce at the laboratory scale degradation studies.

9.4 University of Texas Pilot Plant Studies

The University of Texas has been operating 200 kg/h CO_2 capture plant for a number of years where the flue gas is derived from a coal combustion based steam generator. The pilot plant is based within the Pickle Research Centre of the university. Its absorber is made out of carbon steel and has internal diameter of 0.43 m. It is equipped with 6.1 m high packed bed made in two equal sections with a collector plate and redistributor for liquid between the two packed beds. The facility has been used for testing the novel solvents, corrosion, mass transfer, chemical kinetics, energy efficiency and cost issues associated with the chemical solvent based post combustion capture process. The solvent degradation aspects have been tested mostly in the laboratory scale experiments and the results of these investigations have been described in previous sections. The primary focus of these degradation studies has been to develop cost effective corrosion inhibitors and additives to suppress the oxidative degradation of amine solvents. Voice and Rochelle[40] claim Diethylene triamine Penta acetic acid (DTPA) as one of the best corrosion inhibitors for application with MEA solvent. Among the sulphur containing inhibitors, Dimercaptothiadiazole (DMTD) has also been considered to be a very effective corrosion inhibitor, though it is relatively costly. In addition to DTPA and DMTD, Voice and Rochelle recommend Diethylene triamine penta methylene phosphonic acid (DTPMP) and Hydroxy ethylidene diphosphonic acid (HEDP). These additives suppress ammonia and formic acid formation as a result of oxidative degradation by as much as 80% and only required to be added to lean MEA solution at less than 1% w/w. Some recent results from Prof. Rochelle's research group suggest that a mixture of HEDP and DTPA, when added to lean MEA solution at 1.5% w/w, suppresses ammonia formation as much as 97%.

9.5 CSIRO Pilot Plant Studies

CSIRO has been operating two CO_2 capture pilot plants that use 30% w/w uninhibited MEA as solvent to treat a slip stream of flue gas in one case, from a lignite coal fired power plant, and in another case, from a bituminous coal fired power plant. The first capture plant at Loy Yang in the La Trobe Valley of Victoria is based at Loy Yang Power's lignite coal-fired power plant whereas the second plant is based at Tarong, Queensland, at the black coal-fired power plant site of Stanwell. Both power plants have no de-NO_X and FGD facilities but only bag filters for particulate removal.

The Loy Yang based capture plant[123] has been designed to treat a maximum of 150 kg/h of flue gas at 90% CO_2 capture efficiency. The plant has two absorbers (211 mm internal diameter) made of stainless steel, each 9.4 m high with 2.7 m high packed bed of Pall rings. The two absorbers can be run in series or in parallel as required. The stripper is also made of stainless steel with 161 mm internal diameter and 6.9 m height which is packed with 3.9 m high Pall ring bed.

The Tarong based capture plant[122] is also all stainless steel construction but has 4 times bigger capacity for flue gas (600 kg/h). As a result, at 85% CO_2 capture

efficiency, it is designed to produce 100 kg/hr of pure CO_2. The absorber has internal diameter of 0.35 m and total of 4 packed sections of Sulzer Mellapack M250X, each 1.78 m high and thus rendering a total packed height of 7.14 m. The stripper has an internal diameter of 0.25 m. It contains two packed sections of Sulzer Mellapak 350X packing in the stripping section, with a further 1.12 m in the condensate return. Whilst the absorber is running close to atmospheric pressure, the stripper operates at around 1.8 atm pressure (absolute).

The uninhibited 30% w/w MEA campaign results[122, 123] for the solvent degradation and atmospheric emissions are as below:

a) It was observed that decreasing the CO_2 loading of lean amine at Loy Yang plant contributed towards higher emissions MEA to the atmosphere. Similarly, increasing the liquid flow rate in the absorber or operating the absorber at higher L/G ratio increased the atmospheric emissions of MEA. Thus, at L/G ratio of 2.2, MEA emissions were recorded as 20 g/h which nearly doubled when L/G ratio was increased to 4. Ammonia emissions from the absorber seemed to fluctuate between 1 and 4 g/h. These emissions also tended to increase with increasing L/G ratio and decreasing lean solvent loading. The high values for MEA and ammonia emissions could be attributed to the design of the capture plant in the sense that the Loy Yang pilot plant was not equipped with the water wash section downstream of the absorber. Recently, the water wash process step has been installed at the plant and a rigorous campaign with respect to detecting and quantifying the solvent degradation products is underway.

b) The Tarong pilot plant MEA campaign lasted for 500 hours. Table 50 shows the typical flue gas composition, flow rate and temperature recorded at various locations in the capture plant during the campaign.

Table 50 – Flue gas composition during MEA campaign at Tarong capture plant

Component	Unit	Plant Inlet	Absorber Inlet	Absorber Outlet	Wash Tower Outlet	Product CO_2
CO_2	Vol%	10.1	10.9	1	0.9	98.2
H_2O	Vol%	7.8	4.3	8.3	3.2	1.8
O_2	Vol%	6.3	7.1	6.6	6.8	0
N_2	Vol%	75.8	77.7	84	89.2	0
SO_2	ppmv	197	<5	5.3	<5	<5
SO_3	ppmv	<5	<5	<5	<5	<5
NO	ppmv	135	135	136	135	7.4
NO_2	ppmv	<5	<5	<5	<5	<5
N_2O	ppmv	<5	<5	<5	<5	<5
MEA	ppmv	<5	<5	<5	<5	<5
HCL	ppmv	7	<5	<5	<5	<5
HF	ppmv	11	<5	<5	<5	<5
Gas Flow Rate	Kg/h	500	496	428	410	71
Gas Temperature	^{o}C	104.5	28.1	41.4	27.6	23.2

The capture plant was operated at L/G ratio between 2.4 and 5.4. The CO_2 loadings of lean and rich amine solutions, in and out of the absorber, remained in the range 0.08 to 0.36 and 0.124 to 0.524 respectively. The minimum reboiler energy demand was measured as 3.8 MJ/kg CO_2 at the L/G ratio of 2.4. The lean MEA analysis showed that the heat stable salts seemed to increase linearly with time on-stream for the capture plant. At the end of 500 hrs, the lean MEA solvent carried 0.37% w/w heat stable salts.

This result is in line with the observation of Knudsen et al[109] for the formation of heat stable salts at Esbjergvaerket plant during uninhibited MEA campaign (see Section 9.1.1). The rich amine solution analysis also showed that over 500 hours, the iron content of solution varied with a maximum level of 1.5 mg per litre of the solution measured. This could be due to corrosion of the corrosion coupons installed at the pilot plant during the operation with MEA. 128 coupons in total were installed at the pilot plant and consisted of carbon and stainless steels.

The gas analysis involved measurements of 24 species including water vapours, carbon dioxide, carbon monoxide (CO), nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), sulphur trioxide (SO_3), ammonia (NH_3), hydrogen chloride (HCl), hydrogen fluoride (HF), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), n-propane (C_3H_8), n-hexane (C_6H_{14}), formaldehyde (CH_2O), acetaldehyde (C_2H_4O), ethanol (C_2H_6O), ethanolamine (MEA, C_2H_7NO), Piperazine ($C_4H_{10}N_2$), Ethylenediamine ($C_2H_8N_2$), N-Formylpiperazine ($C_5H_{10}N_2O$), NO_X (as sum of NO and NO_2), Total organic carbon (TOC) and Oxygen. The detection limit for the industrial Fourier Transform Infra Red spectroscopy (FTIR) based gas sample analyser was only 5 ppmv. Hence, the solvent degradation product components detected at the wash tower outlet at less than 5 ppmv have very limited accuracy. Table 51 shows the values for various chemicals detected in the gas samples at the beginning and at the end of the 500 hr campaign.

Table 51 – Gas sample analysis at the start and end of 500 hr campaign

Compound	Campaign Start (ppmv)			Campaign End (ppmv)		
	Absorber Outlet	Wash Tower Outlet	Stripper Outlet	Absorber Outlet	Wash Tower Outlet	Stripper Outlet
CO	1.2	6.5	<5	8.4	48.1	0
N2O	<5	<5	<5	<5	<5	<5
NO	135	229.6	6.07	0	204.7	7.4
NO2	<5	<5	<5	<5	<5	<5
SO2	<5	<5	6	<5	<5	5.1
SO3	<5	<5	<5	<5	<5	<5
NH3	8.4	19.5	<5	43.6	31.7	<5
HCl	<5	<5	<5	<5	<5	<5
HF	<5	<5	<5	<5	<5	<5
CH4	<5	<5	<5	<5	<5	<5
C2H6	<5	<5	<5	<5	<5	<5
C2H4	<5	<5	<5	<5	<5	<5
C3H8	<5	<5	<5	<5	<5	<5
C6H14	<5	<5	<5	<5	<5	<5
CH2O	<5	<5	<5	<5	<5	<5
C2H4O	<5	<5	<5	<5	<5	<5
C2H6O	<5	<5	<5	<5	<5	<5
MEA	<5	<5	<5	123.7	<5	<5
C4H10N2	<5	<5	<5	<5	<5	<5
C2H8N2	<5	<5	<5	<5	<5	<5
C5H10N2O	<5	<5	<5	<5	<5	<5
NO_X	135	230.3	6.07	0	205.7	7.6

Whilst the accuracy of detection below 5 ppmv is questionable, the results presented in Tables 51 are important for ammonia formation as a signpost for the extent of oxidative degradation of MEA. Ammonia emission at the outlet of the absorber on the start of campaign is seen as 8.4 ppmv which rises to roughly 44 ppmv by the end of 500 hr

campaign. This result points towards increasing degradation of MEA over time. At the wash tower outlet the atmospheric emissions of ammonia after 500 hrs is 32 ppmv. NO seems to simply pass through the absorber.

Currently, efforts are being made to improve the characterisation and quantification of gaseous emissions of the MEA degradation products.

10. Commercial CO_2 Capture Technologies – Solvent Degradation

As a result of the environmental regulatory bodies and other statutory authorities becoming increasingly aware of the potential risk of adverse environmental impact of amine based CO_2 capture technologies if used for global Greenhouse gas mitigation purposes, the commercial technology providers have started to open up recently and provide in a limited way information on the solvent degradation and resulting emissions from the capture plants based on their technology. This information has been given below.

Kerr-McGee/ABB-Lumus Technology

Arnold et al[12] and Strazisar et al[34] describe Trona, California based 600 tons/day CO_2 production plant and provide the atmospheric emissions data as well as the solvent degradation information. According to these authors, the plant uses 10 to 20% w/w MEA solution containing a proprietary corrosion inhibitor and other additives to treat the coal-fired boiler flue gas stream that carries 10 to 15% CO_2, 5 to 10% O_2, 5 to 15% H_2O, approximately 80% N_2, 10 to 100 ppmv SO_2 300 to 500 ppmv NO_X. In the plant, condensate from stripper condenser carries roughly 0.04% w/w MEA and it is used as wash water in the absorber wash tower. The wash water circulating in the wash tower carries 0.5% w/w MEA. The CO_2 lean gas leaving the wash tower carried aerosol of monoethanol sulphate and ammonium sulphate which are the products of reaction of MEA and ammonia with SO_X respectively. The wash water entrained in the CO_2 lean gas had the droplet size of less than 5 microns with majority less than 3 microns. A later date installation of a Brink mist eliminator downstream of the wire-mesh demister in the wash tower has mostly eliminated atmospheric emissions of the aerosols and fine droplets from the plant. Table 52 and 53 give the analysis of various liquid samples. Arnold et al further state that the solvent reclamation operation at the plant usually indicated insignificant solvent degradation. Un

Table 52 – Liquid sample analysis

Analysis	Absorber wash water	Stripper reflux water	MEA absorber exhaust line condensate
pH	8.7	6.4	9.0
Cl- (%)	<0.001	<0.001	<0.01
SO_4^{2-} (%)	0.06	0.008	<0.01
SO_3^{2-} (ppmw)	<10	<10	<10
CO_2 (%)	0.6	0.08	0.32
NH3, ppmw (%)	17	34	40
NO_3^- ppmw	38	<8	-
NO_2^-, ppmw	17	<1	-
MEA (%)	0.5	0.04%	0.5

Table 53 – Amine solution analysis

Analysis	Rich Amine	Lean Amine	Reclaimer Sample "A"	Reclaimer Sample "B"
pH	9.1	10.3	11.0	10.0
K^+ (%)	0.0002	0.002	0.001	0.009
Na^+ (%)	0.012	0.013	0.7	2.0
Cl^- (%)	0.006	0.005	0.04	0.2
SO_4^{2-} (%)	1.6	1.7	4.8	15.5
SO_3^{2-} (ppmw)	800	700	80	140
CO_2 (%)	3.2	0.5	1.7	1.0
NH3, ppmw (%)	180	160	1700	1100
NO_3^- ppmw	650	650	5300	7000
NO_2^-, ppmw	250	250	<1	<1
MEA (%)	10.7	11.2	46	33
Insoluble (%)	0.004	0.01	0.02	0.08

Whilst Arnold et al[12] describe the Trona plant operation and various liquid stream composition analysis under taken in 1982, Strazisar et al[34] have studied the solvent degradation issue in 2003 while analysing the plant performance separately. They analysed virgin concentrated MEA solution from storage tank for presence of impurities and lean MEA solution at inlet to the absorber and the reclaimer bottoms for solvent degradation impurities. Table 54 lists the solvent degradation products identified by these authors in the reclaimer bottoms sample.

Table 54 – Solvent degradation products identified at Trona plant

Compound	Chemical Formula
N-Formylethanolamine	$C_3H_7NO_2$
N-Acetylethanolamine	$C_4H_9NO_2$
2-Oxazolidone	$C_3H_5NO_2$
N-(hydroxyethyl)succinimide	$C_6H_9NO_3$
N-(2-hydroxyethyl)-lanthamide	$C_5H_{11}NO_3$
1-Hydroxyethyl-3-homopiperazine	$C_7H_{14}N_2O_2$
1-(2-hydroxyethyl)-2-imidazazolidnone	$C_5H_{10}N_2O_2$
1-Hydroxyethyl-2-piperazinone	$C_6H_{12}N_2O_2$
4-Hydroxyethyl-2-piperazinone	$C_6H_{12}N_2O_2$
3-Hydroxyethylamino-N-hydroxyethyl propanamide	$C_7H_{16}N_2O_3$
2-Hydroxyethylamino-N-hydroxyethyl acetamide	$C_6H_{14}N_2O_3$
Ammonia	NH_3
Acetic acid	$C_2H_4O_2$
Propionic acid	$C_3H_6O_2$
n-Butyric acid	$C_4H_8O_2$
MEA	C_2H_7NO
2,6-Dimethyl-4-pyridinamine	$C_7H_{10}N_2$
2-Imidazolecarboxaldehyde	$C_4H_4N_2O$
1-Methyl-2-imidazolecarboxaldehyde	C_5H_6N2O

Strazisar et al[34] further state that in the lean MEA sample nitrosamines were found to be present at a concentration of 2.91 µmol/mL. This is believed to be due to the reaction between MEA and nitrogen oxides, which are known constituents of flue gas. Assuming all of the nitrosamines present as nitrosodiethanolamine (NDELA as proposed by Schallert[31, 33]), the measured concentration of nitrosamines is equivalent to 390 mg of NDELA per litre of lean amine solvent which seems rather high. It should, however, be noted that Strazisar et al's quantification of nitrosamine concentration in lean amine was based on a generalised functional group test for NO and no **specific** nitrosamines were detected. These authors further state that nitrosamines were not detected in the reclaimer bottoms perhaps due to their low boiling point.

Fluor Econamine FG Plus[SM] Technology

This technology uses 30% w/w MEA solvent with a corrosion inhibitor that tolerates oxygen concentration in flue gas as much as 15% v/v. In fact, the corrosion inhibitor requires oxygen in flue gas and dissolved in lean amine solution to remain active as reported by Reddy et al[13]. This implies that the corrosion inhibitor works via passivating the carbon steel surface with a film of oxides of iron (mostly Fe_2O_3 and Fe_3O_4). The corrosion inhibition via surface passivation has design implications for the capture plant equipment in the sense that ultimate design should be conducive of minimising the sloshing and splashing of liquid within the absorber and flash vessels due to high gas velocity. Sloshing and splashing causes erosion of oxide based protective film. Once, a small portion of protective layer has eroded, it allows the corrosion reactions to propagate underneath the remaining protective film. Published information[12] on L/G ratio and absorber diameter indicates that the superficial gas and liquid velocities in the CO_2 absorber and flash vessels need to be no more than 1.5 m/s and 15 cm/s respectively to avoid surface erosion.

It should be noted that Fluor Econamine FG Plus[SM] technology incorporates recent process improvements such as inter-cooling of absorber, split flow feed, vapour compression and solvent flash prior to stripping in order to reduce the energy demand of the process to the lowest level. A publication by Reddy et al implies that it could be using either Piperazine type rate promoter to accelerate the reaction rate or MEA concentration in the solution could be as much as 40% w/w. Most of the information on this technology put in public domain by Fluor Ltd is sanitised and silent on the issue of solvent degradation and atmospheric emissions of the degradation products. However, Fluor Ltd admits that the capture plant does need a solvent reclaimer when treating a coal-fired power plant flue gas and the flue gas should not have SO_X/NO_X more than 10 ppmv. Also the particular matter content of flue gas should be less than 3 mg per Nm^3.

Mitsubishi Heavy Industries (MHI) Technology

This[61] technology uses an aqueous solution of hindered amine blended with an amine based rate promoter to enhance the kinetics of CO_2 absorption. The solvent known as KS-1 is claimed to have far better corrosion resistance characteristics and CO_2 carrying capacity than conventional MEA solvent. It is claimed to not require a corrosion inhibitor at all. Unfortunately, KS-1 is at least 5 times more expensive than MEA[12]. A recent publication by MHI[63] states that at least nine post combustion CO_2 capture plants around the world have been operating that are built with their technology and four more will be built by 2012 end. Most of the currently operating MHI plants have CO_2 capture capacity in the range 350 to 450 tonnes per day. Unfortunately none of these plants are based on coal-fired power plant flue gas. With this technology only

one pilot plant at 10 tons per day CO_2 capture capacity has been operating since 2006 at Matsushima power station in Southern Japan where over 6000 hours of cumulative on-stream time recorded[62].

Published information[64] from MHI states that in comparison with conventional MEA solvent, KS-1 requires 40% less solvent circulation rate for the same CO_2 capture duty and 20% less energy for solvent regeneration. In addition, the solvent loss due to degradation is only 10% of what is encountered with conventional MEA. However to achieve such superior performance when processing a coal-fired power plant flue gas, the build of particulate matter in the lean solvent will need to be less than 10 ppmw and the SO_X content of flue gas at inlet of the absorber must not be more than 0.1 ppmv[61]. Table 55 below compares the influence of SO_3 content of flue gas on the atmospheric emissions (total of vapour plus droplet phase) of KS-1 and conventional MEA solvents.

Table 55 – Influence of SO_X content on atmospheric emissions of KS-1 and MEA

SO3 Concentration @ Absorber Inlet (ppmv)	KS-1 Emissions (ppmv)	MEA Emissions (ppmv)
3	23.2	67.5
1	9.1	29.8
0	0.4	0.8

MHI further state that in their 10 tons per day pilot plant, they observed that 1 to 3% of flue gas NO_X was consumed by solvent KS-1 resulting into the formation of heat stable salts at low levels after 5000 hours of operation. The overall solvent loss (including loss due to degradation) is claimed to be less than 1 kg per ton of CO_2 by MHI[15]. No further information is available from MHI on either the characterisation and quantification of degradation products from KS-1 or their atmospheric emissions. However, a recent publication by Svendsen[94] implies that the MHI solvent KS-1 could be a blend of 3 molar AMP with 1 to 2 molar PZ. If that is true then the presence of PZ in solution is most likely to produce mono and di-nitrosopiperazines upon reaction with NO_X from flue gas as described in the earlier sections on solvent degradation for AMP and PZ. The formation of nitrosopiperazines and their potential for atmospheric emissions points to adverse environmental impact with the use of AMP/PZ blends for CO_2 capture.

11. ANTICIPATED VOLATILE DEGRADATION EMISSIONS

Both the laboratory and plant based solvent degradation information presented in the preceding sections points towards uncertainty of characterisation and questionable accuracy with quantification of various solvent degradation products due to mismatch of the operating process environment between the laboratory scale experiments and the actual plant operations. In addition, other issues such as the materials of construction of equipment for degradation studies acting as catalyst for solvent degradation, flashing or otherwise of dissolved oxygen prior to the solvent being regenerated and resubjected to the oxidative environment and the presence or absence of corrosion inhibitors in the amine solution have made prediction of atmospheric emissions of amines and their degradation products rather a very difficult task. In addition to the above difficulties, however, the process simulations point

towards significance of the efficiency of wash tower as key equipment for minimising the solvent loss via atmospheric emissions and thereby reduce the cost of makeup solvent. Thus, the extent of atmospheric emissions of an amine based solvent and its degradation products have not only a direct impact on environment but also on the cost of capital involved in building a most efficient water wash tower and the cost of consumables for operating a CO_2 capture plant around the clock. A simple way to screen any amine solvent for its propensity to be emitted from the process is to assess its volatility and the volatility of its all possible degradation products. Whilst, this may not take into account the effect of reaction kinetics, hydrodynamics, materials of construction etc, it will provide some glimpse into what lays ahead, should a particular amine or a blend of amines were to be chosen for the capture duty. In essence, it is a preliminary check of comparative advantages or disadvantages of using a group of amine solvents.

Nguyen et al[104] quantify volatility of an amine or its degradation product via an apparent activity coefficient, Y_i, defined by the modified Rault's law:

$$Y_{i} = P_i \div [X_i \times P^o_i] \text{ ------------ (48)}$$

Where,

P_i = Partial pressure of amine or its degradation product i in the gas phase,

X_i = Liquid phase mole fraction of the amine or its degradation product i, and

P^o_i = Vapour pressure of the amine or its degradation product i at a given temperature.

According to the above expression, higher the mole fraction of component i, higher its partial pressure for given activity co-efficient or volatility. All other things being equal, this would result in a higher emission level. It should be noted that vapour pressure of a chemical species i is a function of its free state in the liquid. Thus, the reactions that bind up an amine as a carbamate or protonated amine will result in its lower concentration as a free amine and lower vapour pressure.

According to equation 48, the volatility of the component i also depends on its vapour pressure which can be predicted by using an empirical equation as follows:

$$Ln [P^o_i] = b_1 + b_2/T + b_3 \ln(T) + b_4 T^{b}_5 \text{ ----------- (49)}$$

Where P^o_i is in Pascal and T is in ^oK.

For MEA, PZ, MDEA and AMP the values of co-efficient b_1 to b_5 are available in the literature and can be used to compare the volatility of these amines. Using this concept, da Silva et al[124] have recently estimated likely emissions of various amines and their likely degradation products. These anticipated emission levels are reproduced in Table 56 to 58 from the SINTEF report[102]. The underlying assumptions for arriving at these numbers are:

  i.   Degradation product emission rate is proportional to its rate of formation.
  ii. The rate of formation for a degradation product can be represented as a fraction of the ammonia emission rate.
  iii. Ammonia formation rate is an indicator of overall degradation rate of an amine.

iv. Ammonia emission for MEA is 1 ppmv, for MDEA 0.5 ppmv and 0.05 ppmv for AMP and Piperazine.

v. Any degradation product that has a free energy of solvation >-5kcal/mol is a volatile product. Volatile degradation products do not accumulate in the plant.

vi. For medium volatility degradation products (components with free energy of solvation <-5kcal/mol and that are non-ionic) vapour emissions are proportional to volatility and concentration in the liquid. Da Silva et al have used the numbers for concentrations in liquid as informed guesses.

vii. Ionic degradation products are non-volatile.

The assumption (iv) could be interpreted as whatever is the rate of ammonia formation during the degradation of MEA half of that is with MDEA and 1/20th is with either AMP or PZ or their blend as a solvent. Accordingly, emission rate of ammonia for MDEA degradation is half of what could be with MEA and 1/20th is for AMP and PZ. This same logic should be applied when reading the numerical values for the anticipated emission levels of other degradation products.

Table 56 – Emissions of non volatile degradation products

Degradation Product	CAS No.	Emissions (ppmv)	Solvent	Comment
Formic acid/formate	64-18-6	0.003	MEA	Oxidative degradation product
		0.002	PZ	
		0.003	MDEA	
		0.002	AMP	
Acetic acid/acetate	64-19-7	0.03	MEA	Oxidative degradation product
		0.002	PZ	
		0.003	MDEA	
		0.002	AMP	
Oxalic acid	144-62-7	0.003	MEA	Oxidative degradation product
		0.002	PZ	
		0.003	MDEA	
		0.002	AMP	
Propanoic acid	79-09-4	0.0003	MEA	
Glycolic acid/glocolate		0.0003	MEA	
Lactic acid/lactate	598-83-3	0.0003	MEA	
Glycine	56-40-6	0.0003	MEA	Possible oxidative degradation product
N-Glycylglycine	556-50-3	0.0002		Likely oxidative degradation product

Table 57 – Emissions of medium volatility degradation products

Degradation Product	CAS No.	Emission (ppmv)	Solvent	Comments
Formamide		0.007	MEA	
		0.003	PZ	
		0.006	MDEA	
		0.003	AMP	
Oxazolidin-2-one		0.004	MEA	
1-(2-hydroxyethyl)-2 imidazoliinone	3699-54-5	0.003	MEA	
N-(2-hydroxyethyl)-ethylenediamine	111-41-1	0.003	MEA	
N-(2-hydroxyethyl)-acetamide	142-26-7	0.003	MEA	
1-(2-hydroxyethyl)-2,5-Pyrrolidinone	18190-44-8	0.003	MEA	
N-(2-Hydroxyethyl)lactamide	5422-34-4	0.003	MEA	
N,N-di(2-hydroxyethyl)-Urea	15438-70-7	0.003	MEA	
N-(2-hydroxyethyl)-3-[(2-hydroxyethyl)amino]Propanamide	587876-41-3	0.003	MEA	
N-(2-hydroxyethyl)-3-[(2-hydroxyethyl)amino]acetamide	144236-39-5	0.003	MEA	
1-(2-hydroxyethyl)-2-piperazinone	59702-23-7	0.003	MEA	
4-(2-hydroxyethyl)-2-piperazinone	23936-04-1	0.003	MEA	
2-((2-[(hydroxyethyl)amino]ethyl)amino)ethanol	4439-20-7	0.003	MEA	
2-methylaminoethanol	109-83-1	0.01	MEA	
2,2'-[[2-[(2-hydroxyethyl)amino)ethyl]imino]bis-Ethanol	60487-26-5	0.003	MEA	
1,3-bis(2-hydroxyethyl)-2-Imidazolidinone)	71298-49-2	0.003	MEA	
Oxalamide	471-46-5	0.003	MEA	
1-(2-hydroxyethyl)imidazole	1615-14-1	0.03	MEA	
1H-imidazole-2-carboxaldehyde	10111-08-7	0.003	MEA	
1-methyl-1H-imidazole-2-carboxaldehyde	13750-81-7	0.003	MEA	
N,N-bis(hydroxyethyl)piperazine	122-96-3	0.003	MEA	
Glycine	56-40-6	0.003	MEA	
Hydroxy-acetaldehyde	141-46-8	0.003	MEA	

Table 57- Emissions of medium volatility degradation products (continued)

Degradation Product	CAS No.	Emission (ppmv)	Solvent	Comments
2-imidazolidinone	120-93-4	0.003	MEA	
Morpholine	119-91-8	0.02	MEA	
Diethanolamine	111-42-2	0.003	MEA	
Methylnitramine	598-57-2	0.02	MEA	
		0.002	PZ	
2-(Nitroamino)ethanol	74386-82-6	0.006	MEA	Extent of nitramines formation unknown in CO_2 capture plant
N-nitrosodiethanolamine	1116-54-7	0.0005	MEA	Detected in capture plants
		0.001	MDEA	
2-Oxopiperazine	5625-67-2	0.002	PZ	
2,5-Piperazinedione	106-57-0	0.002	PZ	
Ethylenediamine	107-15-3	0.002	PZ	
1-Piperazinecarboxaldehyde	7755-92-2	0.003	PZ	
1-Acetylpiperazine	13889-98-0	0.003	PZ	
1,1'-Carbonyl-bis-piperazine	17159-16-9	0.002	PZ	
1-Piperazine-ethanol	103-76-4	0.005	PZ	
N-(hydroxymethyl)piperazine	90324-69-9	0.002	PZ	
1-Nitrosopiperazine	5632-47-3	0.002	PZ	Possible nitrosamine degradation product
1,4-dinitrosopiperazine	140-79-4	0.2	PZ	Possible nitrosamine degradation product
1-Nitropiperazine	42499-41-2	0.003	PZ	Possible nitramine degradation product
4-methyl-1-Piperazine-ethanol	5464-12-0	0.2	MDEA	Observed experimentally
Triethanolamine	102-71-6	0.006	MDEA	
N-nitroso-diethanolamine	1116-54-7	0.0008	MDEA	
2-(Methylnitrosoamino)ethanol	26921-68-6	0.3	MDEA	
4,4-dimethyl-2-Oxazolidinone	26654-39-7	0.01	AMP	
Nitro-2-amino-2-methylpropanol		0.0003	AMP	

Table 58 – Emissions of volatile degradation products

Degradation Product	CAS No.	Emission (ppmv)	Solvent	Comments
Ammonia	7664-41-7	1	MEA	Oxidative degradation product for all solvents
		0.05	PZ	
		0.5	MDEA	
		0.05	AMP	
Methylamine	74-89-5	0.006	MEA	Possible oxidative degradation product
Formaldehyde	50-00-0	0.08	MEA	
		0.004	PZ	
		0.004	MDEA	
		0.004	AMP	
Acetaldehyde	75-07-0	0.02	MEA	
		0.001	PZ	
		0.009	MDEA	
		0.001	AMP	
Acetone	67-64-1	0.002	MEA	
Dimethylamine	124-40-3	0.01	MEA	
		0.00005	PZ	
		0.0005	MDEA	
		0.00005	AMP	
Ethylamine	75-04-7	0.01	MEA	
		0.000035	PZ	
		0.00035	MDEA	
		0.000035	AMP	
Diethylamine	109-89-7	0.01	MEA	
		0.00007	PZ	
		0.0007	MDEA	
		0.00007	AMP	
N-nitrosodimethylamine	62-75-9	0.02	MEA	
		0.001	PZ	
		0.01	MDEA	
		0.001	AMP	
4-nitroso-morpholine	59-89-2	0.01	MEA	
		0.0004	MDEA	
2-Methyl-3-nitroso-oxazolidone	39884-53-2	0.003	MEA	
1,4-dinitropiperazine	140-79-4	0.0001	PZ	

Table 58 – Emissions of volatile degradation products (continued)

Degradation Product	CAS No.	Emission (ppmv)	Solvent	Comments
Dimethylnitramine	4164-28-7	0.02	MEA	
		0.0001	PZ	
		0.001	MDEA	
		0.0001	AMP	
1,4 Dimethylpiperazine	106-58-1	0.004	MDEA	
2-methyl-2-(methylamino)-1-Propanol	27646-80-6	0.0003	AMP	Observed by H. Lepaumier
3,4,4-trimethyl-oxazolidin-2-one	15833-17-7	0.0005	AMP	Observed by H. Lepaumier
4,4 dimethyl-2-isopropyl-3-nitrosooxazolidine	39884-58-7	0.015	AMP	

da Silva et al[124] clarify in their report that the above values of emissions are rather conservative and on high side. They have tried to cover all possible degradation compounds including those likely to be formed only in a laboratory environment and those with some degree of uncertainty for their occurrence in an industrial environment. In addition, da Silva et al state that there is a great deal of uncertainty about formation of nitrosoamines and their emissions. Therefore, when using these tables caution should be exercised. For example, with N-nitrosodiethanolamine (NDELA) listed in Table 57, if ammonia emissions are 1 ppmv when using MEA solvent, then NDELA emissions will be 0.5 ppb. If the emission level of ammonia drops to 0.2 ppm (due to say process improvement) then NDELA emissions will reduce to 0.1 ppb. Similar understanding should be used with other degradation products and solvents.

12. RANKING OF SOLVENTS

The amine solvents considered in this report are representative of primary (MEA, AMP), secondary (PZ) and tertiary amines (MDEA). They exhibit a varied level of CO_2 carrying capacity and reactivity to CO_2. Whilst, it is easy to rank them in terms of their capacity to carry CO_2 or reactivity, in order to assess their environmental impact, they should be ideally ranked for their potential to form and emit harmful compounds to atmosphere, particularly when their usage for global mitigation of Greenhouse effect is desired. This ranking should also consider the toxicity of the solvent degradation products and their eventual fate in the environment. At present, there is no protocol or weighting template available to CSIRO to account for all the parameters (tendency to degrade, volatility of degradation products, toxicity of degradation products and fate of these products in atmosphere) on a single basis. In such a situation, we know that the compounds that have greatest health and environmental risk are the nitrosamines. The risk for their formation is highest with secondary amines, lower with tertiary amines and the lowest with primary amines. Based on this, one could rank the solvents from greatest to lowest risk as:

PZ > MDEA > AMP = MEA

Another way to look at the solvents for their ranking is to consider the extent of degradation to alkylamines, secondary amines (that may eventually form nitrosamines) and volatile products. Therefore, in terms of degradation rates, the following ranking is possible:

MEA > MDEA > PZ=AMP

Combining the above two rankings and giving more weight to the risk of nitrosamine formation, the following ranking is likely:

PZ > MDEA > MEA > AMP

If we now superimpose on the above ranking the volatility of amines and consider that most volatile amine will have maximum emissions in quantity for a worst case of industrial accident then the following nominal ranking is obtained:

PZ > AMP > MEA > MDEA

Thus, the following generalisation can be derived for the above solvents:

a) Secondary amines have highest risk of nitrosamine formation, followed by tertiary amines, while primary amines have the lowest risk of nitrosamine formation.

b) All other things being equal, solvents with low vapour pressure are safer than solvents with high vapour pressure.

c) All other things being equal, a more stable solvent that will resist degradation is safer than a less stable one since the more stable solvent will have lower emissions of degradation products.

13. CONCLUSIONS

Literature review of the laboratory studies, pilot plant scale experiments and public domain technical information from various technology vendors on degradation of amino solvents clearly indicates that in an industrial environment of post combustion CO_2 capture, these solvents will most certainly undergo both oxidative and thermal degradation. The extent of degradation and as a result, the type of degradation products formed will, however, depend upon not only the structure of amine but also the process operating conditions, such as the concentration of amine, its CO_2 loading, absorber reaction temperature, solvent regenerator temperature, content of oxygen, SO_X, NO_X and particulate matter in flue gas, composition of particulate matter (Fe, Ni, V, P, Cr, CO etc), catalytic effect of the material of construction of plant equipment towards degradation etc. The plant operating practices, such as the process control and how often a solvent is reclaimed, will also decide both the extent of solvent degradation and type of degradation products formed.

In an industrial operating environment, potential degradation products of amine solvents (combination of oxidative and thermal degradation) will be one or more of the following:

Ammonia, primary amines / alkanolamines, secondary amines / alkanolamines, tertiary amines / alkanolamines, aldehydes (formaldehyde, acetaldehyde), carboxylates, amides, piperazines, piperazinones, oxazolidpnes, nitrosamines, imidazolidones, N,N-distributed ureas and nitramines.

Exact chemical structure of these degradation products depends upon the chemical structure of parent amine and the degradation reaction pathways it has followed.

The above list is by no means complete or entirely accurate since characterisation of the degradation products is still ongoing internationally among various research groups both at the laboratory and pilot plant scales. There are also differences in identification of degradation products among various research groups due to either the differences in analytical techniques employed or the kinetic and mass transfer limitations during degradation have forced open different degradation pathways and formed different products. Unfortunately, both the characterisation and quantification of degradation products carried out in the laboratory environment are not entirely applicable to the operating plant situation because the process environment and scale factors of industrial plant are not duplicable or transferable at the laboratory scale. This is evident, for example, between the findings of laboratory studies by Rochelle group at University of Texas and the results of both ITC and Boundary Dam pilot plant results from University of Regina. A similar conclusion could be drawn by comparing results of pilot plant campaigns by various research groups.

Whilst there are a number of pilot plant scale CO_2 capture campaigns ongoing around the world, there has been so far not even a single study that has attempted to close the material balance around plant where formation of degradation products within the plant and the atmospheric emissions of these products are fully accounted. Nevertheless, these campaigns do confirm the following:

a) A large number of degradation products are formed in an industrial plant environment than what various research groups have so far determined in their laboratory studies.

b) It is the oxidative degradation that is contributing more towards degradation than thermal degradation in the industrial environment.

c) Vapour phase atmospheric emissions of heat stable salts and thermal degradation products of amines are likely to be minimal to the point of no concern.

d) Formation of nitroso compounds in the industrial plant environment is a reality since both Boundary Dam and ITC pilot plants in Canada confirm formation and detection of 1,2,3,6-tetrahydro-1-nitrosopyridine during their MEA and MEA/MDEA campaigns. It should be noted that the Boundary Dam pilot plant was originally built by Union Carbide and later refurbished by Fluor Ltd for SaskPower[116] as per the Fluor Econamine technology and it used proprietary corrosion inhibitors for both amine campaigns. Thus, Strazisar et al[34] are correct in asserting that they detected nitrosamines in the lean amine solution at Kerr-MCGee/ABB Lumus technology based capture plant at Trona, California, and these compounds may have been formed up to 2.91 μmol per mL of solution. It should be noted that Trona plant also uses proprietary corrosion inhibitors despite the lean amine (MEA) concentration being less than 20% w/w.

e) Corrosion inhibitors currently being recommended and perhaps used by commercial technology vendors for post combustion CO_2 capture may be acting as catalyst towards the solvent degradation. Certainly, the corrosion inhibitors containing Copper, Vanadium, Cobalt and other metals used in the reducing environment of gas processing industry are catalyst for solvent degradation in the oxidative environment of post combustion capture. Laboratory studies of solvent degradation by Rochelle and other investigators confirm this.

f) The wash tower downstream of absorber plays critical role in controlling atmospheric emissions of various amine solvents and their volatile degradation products from a CO_2 capture plant. The AspenPlus process simulation results clearly indicate that the wash tower performance is affected by ambient conditions, particularly the cooling water temperature. Operating this tower at temperature as low as possible in practice can substantially reduce the emissions of volatile degradation products. No doubt other process or equipment performance improvement measures such as inter-cooling the absorber or separating the condensable species downstream of the absorber (using reflux condenser) prior to water washing the CO_2 lean flue gas will certainly help in reducing atmospheric emissions.

Published information on operating performance of the capture plant at Trona, California, and the technology related information from MHI Ltd clearly states that the flue gas impurities viz. the particulate matter, SO_X and NO_X contribute significantly towards solvent degradation and atmospheric emissions of amine solvents. In fact, the MHI data categorically shows that by reducing SO_X content at inlet to the absorber from 3 ppmv to 1 ppmv reduces atmospheric emissions of both KS-1 and MEA solvents by more than half. Recently published information from MHI further states that in order to eliminate formation of aerosols in the CO_2 lean exhaust stream, the SO_X content of flue gas at inlet to the absorber should be less than 0.1 ppmv. Similarly, to avoid the sludge build up in absorber and resulting foaming and flooding of absorber as well as to reduce the metal catalysed degradation of solvent, the particulate level in lean amine solvent should not be allowed to exceed 1 ppm by weight. All of this means that for stable performance of CO_2 absorption/desorption system with high efficiency, minimum solvent degradation and minimum atmospheric emissions, the direct contact cooler and the water wash tower in post combustion CO_2 capture plant must be performing efficiently. This is particularly important in Australian context since Australian power stations do not have de-SO_X and de-NO_X systems.

In terms of choosing an amine solvent for post combustion capture with minimal environmental adverse impact, one should note the guidelines below:

i. Secondary amines have highest risk of nitrosamine formation, followed by tertiary amines, while primary amines have the lowest risk of nitrosamine formation.

ii. All other things being equal, solvents with low vapour pressure are safer than solvents with high vapour pressure.

iii. All other things being equal, a more stable solvent is safer than a less stable one since the more stable solvent will have lower emissions of degradation products.

Using the above guidelines, the amine solvents considered in this report can be ranked in order of their likely maximum adverse impact to minimal adverse impact as:

PZ > AMP > MEA > MDEA

14. RECOMMENDATIONS & FUTURE WORK

From the perspective of identifying accurately and anticipating amine solvent degradation and resulting atmospheric emissions of both solvent and its degradation products in an industrial scale post combustion CO_2 capture plant, this report clearly states that various laboratory based degradation studies have been less than helpful due to several reasons: forced or accelerated degradation by using either very high oxygen concentration in feed gas or high reactor temperatures, mismatch of operating flow regimes, i.e. mass transfer v/s chemical kinetics control, lack of representative feed gas including impurities in the feed gas (particulate matter, SO_X and NO_X), lack of actual corrosion inhibitors and oxygen scavengers that are used in the industrial environment and lack of hydrodynamics that are representative of the industrial practice. Nevertheless, these studies have provided some useful insights of what could be happening to an amine solvent circulating between the absorber operating at low temperature and the solvent regenerator operating at high temperature (at least twice of the absorber temperature). For example, ammonia formation rate is indicative of oxidation degradation rate and the rate of formation of formates is indicative of heat stable salts due to corrosion. These studies have also established clearly the possibility of nitrosoamines and nitramines formation in an actual plant environment which has been confirmed from the pilot plant results. In addition, the laboratory studies clearly imply that overdesigning an industrial absorber for the purpose of high CO_2 capture rate or using a packing that increases the dynamic liquid holdup within both absorber and stripper will contribute towards higher solvent degradation simply due to increased residence time for oxygen dissolution in absorber and CO_2 catalysis in stripper. These studies have, of course, provided some understanding of the degradation reaction pathways and the mathematical models of reaction kinetics which have been useful towards calculating the likely atmospheric emissions of both solvent and its degradation products using the process simulation tools such as AspenPlus. However, validation of these estimates requires the pilot plant scale studies to characterise and quantify the degradation products both in the gas phase and liquid phase accurately and close the material balance around all the input and output streams of the plant. Since degradation of amine solvent is an ongoing phenomenon within a capture plant that is operating at steady state, the characterisation and quantification of degradation products and the resulting reconciliation of plant material balance must be done continually as on-stream time of the plant builds.

The pilot plant programs ongoing so far in different parts of the world give impression from their publications that the characterisation and quantifications of gas and liquid streams at inlet and outlet to the absorber, stripper and water wash towers downstream of both absorber and stripper has not yet been complete. So far there has been only one pilot plant based degradation study (RWE/LINDE/BASF Niderauβem Pilot Plant, Section 9.3) that has attempted to close material balance with respect to amine consumption and included formation of degradation products and their atmospheric emissions in the material balance. Unfortunately, the material balance does not close with acceptable accuracy and in addition, the liquid phase emissions have not been quantified.

It must be pointed out that the above study has been performed at a lignite-fired power plant in Europe where the coal based power plants are equipped with state of the art de-SO_X, de-NO_X and particulate filtration systems which is not the case with Australian coal-fired power plants. Thus, there is a strong parameter of flue gas quality that needs to be considered before using a European solvent degradation study for anticipating the solvent degradation and resulting atmospheric emissions from a post combustion CO_2 capture plant linked to an Australian coal-fired power plant. In addition, the ambient conditions for both summer and winter seasons in Europe are markedly different from Australian ambient conditions for both inland and coastal locations. Thus, impact of ambient conditions on performance of the water wash tower must also be accounted for when using a European study in Australian context.

Since, the Australian flue gas quality and ambient conditions are considerably different from equivalent European or US/Canadian situation, both direct contact cooler (DCC) and the water wash towers downstream of absorber and stripper will need to be designed accordingly. It will be preferable, if the flue gas desulphurisation as well as the removal of oxides of nitrogen can be carried out in the DCC tower itself for an Australian post combustion capture plant. This has potential to reduce the cost of CO_2 capture from an Australian coal-fired power plant and may even have a positive impact on the net power plant efficiency.

Since post combustion capture of CO_2 needs to meet not only the criteria of minimal impact on the power plant efficiency and cost of electricity generation but also minimal adverse environmental impact, the solvent development program currently ongoing in Australia should follow the guidelines for solvent ranking given at Section 12.

In light of the above recommendations, the following work program is proposed:

I. Full characterisation and quantification of degradation products of amine solvents both in the gas and liquid streams in an Australian pilot plant scale CO_2 capture plant accompanied by a closed material balance around the input and output streams of the plant. It is expected that this pilot plant will be operating at steady state in the gas-liquid flow regimes representative of currently operating industrial scale post combustion CO_2 capture plants.

II. Process improvements around the DCC tower and the water wash towers downstream of both absorber and stripper in an Australian pilot plant scale to minimise first the adverse impact of flue gas impurities on amine solvents and then atmospheric emissions of amine solvents and their degradation products.

III. Development of mathematical models from first principle (for example, using the molecular modelling principles) – bottom up approach – which account for the solvent degradation kinetics and yields of the degradation products observed through steps I and II above to improve predictive capability of anticipated atmospheric emissions from a full scale amine solvent based post combustion capture plant linked to an existing black coal-fired power plant in Australia.

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