



Australian National Low Emissions Coal
Research and Development

Project:
**Environmental Impact of Amine-based CO₂ Post-
combustion Capture (PCC) Process**

**Activity 3: Estimated emissions to the
atmosphere from amine based PCC processes
for a black coal fired power station based on
literature and modelling.**

Deliverable 3.1 for ANLEC R&D

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Project Team

Do Thong
Narendra Dave
Paul Feron
Merched Azzi

Enquiries should be addressed to:

Merched Azzi
Phone: 61 2 9490 5307
Email: merched.azzi@csiro.au

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REVIEWER COMMENTS AND AUTHOR'S REPLIES

1. *Discussion of Results – The point is made that caustic soda could be used in Australian power stations for SO_x removal instead of FGD followed by a caustic wash. Please provide brief comment on the relative cost of chemicals for the two processes and also on the management/disposal options for each of the bi-products (Calcium sulphate or sodium sulphate).*

Response: Additional information is needed to address the cost/benefit analysis of caustic wash against conventional wet FGD. However, to help in clarifying this point we understand that 99% pure Caustic soda flakes cost \$350 to \$400 per tonne as bulk purchase market price, i.e. roughly 35 to 40 cents per kilo. At 2.5% aqueous concentration and 46.3 tonnes/hr of spent solution from the Caustic Wash tower, the hourly cost of chemical use is roughly \$460 /hr. The spent solution may need to pass through chemical treatment before disposal.

2. *Discussion of Results – The last point notes that the MEA emissions of 9ppbv can be achieved under certain wash water conditions. Can the process water balance also be maintained under these conditions (i.e. is sufficient water consumed in the process to allow the MEA concentration to be maintained at or below 643 ppm).*

Response: This level of emission reduction is possible with water balance maintained in the plant. But please note that these results are based on Aspen Plus simulations where the plant equipment is assumed to be constantly operating at its design conditions.

SUMMARY

The potential degradation products expected to be emitted to the atmosphere from MEA-based post combustion CO₂ capture plant (PCC) installed in an Australian black coal fired power plant, have been estimated using the Aspen-Plus process simulation package. This case study has been based on the latest information available in the public domain on the degradation products of MEA solvent used in the CO₂ capture system for black coal-fired power station flue gas. Different solvent degradation products formed at different stages within the process are mainly driven by thermal and oxidative degradation pathways. Whilst oxygen present in the flue gas is known to cause oxidative degradation of MEA, it is the carbamate polymerisation that initiates thermal degradation of MEA. The information related to the degradation products used in this study is mainly based on experimentally observed degradation of MEA in the laboratory and from selected pilot plant data. Available chemical reactions and their rate constants were embedded into Aspen-Plus to simulate the potential volatile products expected to be emitted from the plant.

Emissions to the atmosphere can be directly related to the amount of volatile compounds formed in the process and to the amount of compounds emitted in the form of droplets that are entrained with the flue gas. Knowledge about the likely entrainment rate from the plant and the volatility of the degradation products that are of major concerns is used as input for the Aspen Plus simulations.

It is important to highlight that there are still different challenges related to the analytical methods that are or to be used to determine the types and the quantities of selected degradation products.

The process design adopted is based on standard chemical engineering principles that are used for absorption and desorption of CO₂ using amine based solvent. In the absence of real data from an industrially operating CO₂ capture plant, the data from laboratory research and a few available pilot plants is used to estimate the process efficiency and performance. The concept of integrating the amine-based CO₂ post combustion capture (PCC) process into a coal fired power plant has been discussed in this report. In addition, the fundamental concepts, and process validation were discussed in light of the obtained results. Process simulations provide the appropriate information about the design, the heat and mass flows, and the type and amount of waste material expected from the process. The anticipated waste material from the plant would assist in determining if the plant would be licensed to operate under environmentally safe conditions for a given plant design.

The process simulations cover an existing Australian black coal (Tarong coal) fired power plant retrofitted with conventional 30% w/w MEA based CO₂ capture plant. At the present stage of the project, available information in the open literature related to the MEA-CO₂ chemistry and the thermodynamics of oxidative as well as thermal degradation of MEA to some known components is used. As the MEA degradation chemistry gets better defined and new scientific information related to the degradation products becomes available, the Aspen Plus process models will be improved over the life of the project.

The current process simulation results clearly show that there is a need to wash the flue gas of Australian black coal-fired power plants with 2.5% w/w caustic soda solution in the Direct Contact Cooling (DCC) tower of the capture plant. This procedure has potential to reduce the amount of SO_x entering the absorber to levels below 10 ppmv and meet the stipulated requirement for minimising MEA degradation.

Whilst the vapour phase emission estimates of MEA and its degradation products can be determined using the Aspen-Plus process simulator, the droplet phase emission estimates

require either a pilot plant or industrially operating plant data, particularly the water wash tower performance and the entrained liquid droplet size distribution, flux and its composition. For the purpose of this study, the droplet phase emissions have been estimated by assuming that the composition of entrained liquid leaving the water wash tower is the same as the composition of circulating wash water in the wash tower. The droplet flux is estimated using an empirical rule proposed by Gas Suppliers' Handbook (2004) for liquid entrainment from counter-currently operating packed towers, i.e. the liquid carryover from various types of mist extraction devices as 0.01 to 0.13 m³ per million m³ of gas stream.

At the current stage of the study, the process simulation results show that the range of atmospheric emissions (vapour and droplet phase combined) of MEA and its degradation products from Tarong coal-fired power plant would be as given below:

Chemical Emissions	Minimum Per Nm3 (dry) CO₂ Lean Gas	Maximum Per Nm3 (dry) CO₂ Lean Gas	Minimum Per tonne of CO₂	Maximum Per tonne of CO₂
MEA	0.14 mg	0.14 mg	436 mg	443 mg
NH ₃	1 µg	0.12 mg	2.8 mg	374 mg
DEA	-	0.03 µg	-	84 µg
FORMALDEHYDE	0.26 mg	0.27 mg	848 mg	885 mg
ACETALDEHYDE	0.3 mg	0.3 mg	934 mg	966 mg
ACETONE	0.31 mg	0.33 mg	1.01 g	1.08 g
ACETAMIDE	-	1.1 µg	-	0.4 mg
METHYLAMINE	0.21 mg	0.22 mg	668 mg	703 mg
NITROSOMORPHOLINE	-	0.003 µg	8.9 µg	8.9 µg

The above results have been obtained after augmenting the Aspen-Plus process simulated estimations with Moser et al (2010) and Aas (2009) pilot plant emission data.

The Aspen-Plus process simulation results further show that during the capture process the degradation products of MEA, i.e. heat stable salts, Oxazolidone-2, 1-(2 Hydroxyethyl) imidazolidone-2 (HEIA), N-(2-Hydroxyethyl)-ethylenediamine (HEEDA), N-(2-hydroxyethyl)-diethylenetriamine (Trimer), N-(2-hydroxyethyl)-triethylenetetramine (Polymer), and Cyclic Urea of Trimer are unlikely to be materially emitted to atmosphere though their concentrations may increase with time in the lean MEA solution. Whilst the concentration of degradation products in MEA circulating between the absorber and the stripper rise with time their volatility determines how much of these products and which one will be emitted to the atmosphere. Therefore, high boiling compounds with poor volatility such as HEEDA, HEIA and Oxazolidone will be less likely to be emitted noticeably

When compared with CSIRO's own pilot plant measurements of ammonia emissions, the Aspen-Plus generated ammonia emission estimates are rather low since the absorption process models used in this study are currently devoid of the data on kinetics of decomposition of MEA. However, when the pilot plant observations of Moser et al (2010) and Aas (2009) are taken as the basis then total ammonia emissions to atmosphere will be in the range 2.8 to 374 mg per tonne of CO₂ captured.

Aspen-Plus process models need appropriate kinetic rate data for reliable emission estimates of other degradation products of MEA such as DEA, formaldehyde, acetaldehyde, acetone, methylamine, acetamide, nitrosamines etc. This data is currently lacking or unreliable in the open literature. The estimate of emissions of such compounds in the present study has been restricted to relying on pilot plant measurements carried out and

reported by one or two public domain studies. Hence such estimates are to be treated as mere qualitative observations particularly when considering nitrosamine emissions to atmosphere.

The formation of nitrosamines from MEA degradation is still a controversial topic. However, based on very few publications reported on the subject with no description of the operational conditions, we have attempted to use a very conservative approach using the reported numbers to estimate the emissions of nitrosamines to the atmosphere. Despite the above stated inherent limitations of the current stage of the study, it conclusively proves that the absorber operating temperature and the wash tower operating parameters (wash water circulation rate, its temperature and the effectiveness of the demister) will decide the level of atmospheric emissions of MEA and its degradation products.

In conclusion, this study shows that there is a strong need for an experimental research program at a scale of pilot plant operations that tracks the formation of solvent degradation products and their vapour phase as well as droplet phase atmospheric emissions with the design of capture plant internals, such as the type of packing, liquid distributors, demisters and wash tower, and the capture process operating conditions. There is indeed a critical shortage of pilot plant scale observations of the droplet size distribution and the droplet mass flux as a function of hydrodynamic conditions within the absorber/wash tower and accumulation of degradation products over time. Reliable gas and liquid sampling and analytical methods to identify and quantify various degradation products in the vapour and liquid phases need to be determined. This data when gathered and analysed will provide a basis for fine-tuning the process simulation models and improve their accuracy for predicting atmospheric emissions from the amino solvent based post combustion capture technologies, should they be implemented at the technology demonstration/commercial scales for CO₂ emission reduction. Such an outcome will enable the regulatory bodies to determine emission guidelines or protocols for vendors looking to provide the PCC-solutions.

1. INTRODUCTION

Chemical solvents using amines are the most likely technologies to be deployed in the near future to capture CO₂ from industrial flue gases. The advantage of these solvents is related to the fact that they have excellent effectiveness and efficiency to absorb CO₂ in the flue gas from fossil fuel power plants operating with low partial pressures. In addition, these solvents can be regenerated and injected back into the process to capture more CO₂. For the acceptance and deployment of this process, the technology should be optimised for efficiency, cost and environmental consequences.

Operating the power plants with this technology can certainly reduce the atmospheric emissions of CO₂. However, different degradation products will be produced as results of the following three degradation pathways of the MEA solvent:

- Thermal degradation that mainly occurs in the stripper due to carbamate polymerization at temperatures higher than 100 °C ;
- Oxidative degradation initiated by the presence of O₂, SO₂, NO₂ and other impurities present in the flue gas

The degradation products produced during the solvent degradation may produce new pollutants which could be emitted to the atmosphere when the CO₂ lean flue gas is released. Some of these new pollutants may have different effects on human health and the environment when compared with those emitted from operating traditional power generation facilities.

The proponents of PCC demonstration projects in Europe note that there are knowledge gaps in the information needed to carry out proper environmental impact assessments for future commercial deployment of PCC processes (Shao and Stangeland, 2009). The report here, assesses the gaps in the knowledge using the ASPEN Plus process simulation approach and available public domain information in order to inform a robust environmental impact assessment process.

Nitrosamines and nitramines are two species of special concern due to their potential health risks. These species are formed under selected conditions where NO_x and amines can undergo some complex chemical reactions. Clearly, this issue must be addressed with some urgency in the context of the Australian PCC demonstration projects since the Australian coal-fired power plants are not equipped with the de-SO_x and de-NO_x equipments as required statutorily in Europe and USA. These and other degradation products may escape the PCC plants both in the gaseous state due to their vapour pressures and as droplets due to physical entrainment in the CO₂ lean flue gas. It is therefore crucial that the formation of degradation products of amine solvents and their likely atmospheric emission be determined in a pro-active manner for development of emission guidelines or protocols for vendors looking to provide PCC-solutions.

This study employs Aspen-Plus process simulator to estimate the atmospheric emissions of a base case 30 % w/w aqueous MEA solvent and its degradation products.

2. PROCESS DESCRIPTION

2.1 ASPEN Process Simulations

ASPEN Plus, <http://www.aspentech.com/products/aspen-plus.aspx> is being widely used to simulate the amine-based PCC processes. However, it is also recognised that because the

capture process is operating at steady state conditions and the solvent degradation is non-reversible process during solvent circulation but eventually cleared by the solvent reclamation step, one can treat the capture plant as a large continuous stirred tank reactor with variable residence times for the spent amine and lean amine solvent feed streams. This variable residence time could be taken as an equivalent time for various degradation reactions occurring. Knowing the kinetics of degradation reactions, one can come to an estimate of formation of degradation products and eventually their likely atmospheric emissions. In the following application, the nature of the capture process and degradation kinetics has merely allowed the researchers in this instance to expand the use of ASPEN and get the required information.

A generic CO₂ capture plant flow sheet developed by Fluor Daniel Ltd and given in the IEA GHG PH4/33 report typically represents the industrial process concept for the post combustion capture of CO₂ where an aqueous solution of amine is used as solvent. Figure 1 below shows this generic process flow sheet. It formed the basis for the Aspen-Plus process simulation of the aqueous MEA based post combustion CO₂ capture process undertaken in this study. A detailed description of the capture process is, however, given elsewhere (IEA GHG PH4/33 report).

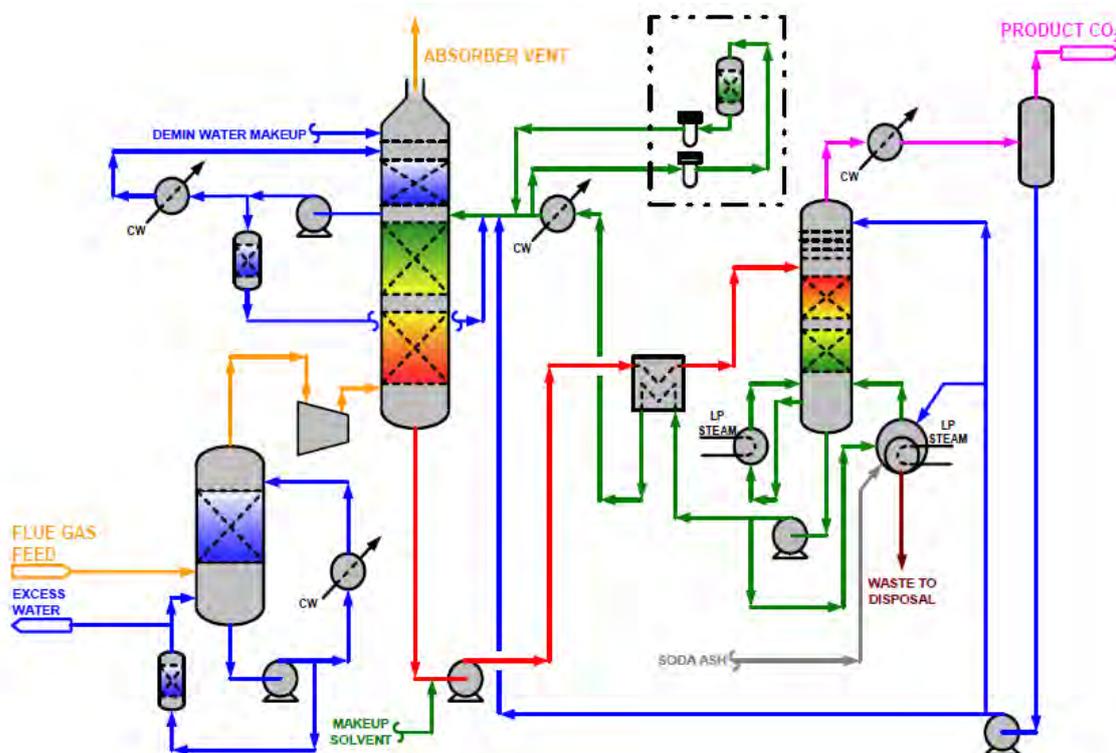


Figure 1– Standard amine based PCC process flow sheet

The CO₂ capture process releases CO₂ lean flue gas to atmosphere from the top of the absorber. During the process, chemical compounds are produced as a result of complex chemical reactions occurring in the absorber. Some of these products continue to recycle in the plant while others such as amines, ammonia, aldehydes, carboxylic acid etc are released to the atmosphere. Generally, the operating conditions of the absorber top control the amount of concentrated vapour that is expected to be emitted to the atmosphere. According to the vapour pressures of gas constituents that are dependent on the absorber temperature and chemical concentrations, MEA and its degradations products may be entrained to the atmosphere.

For the capture process simulation, the flue gas temperature at inlet to the absorber was kept at 45°C and the stripper bottom temperature at 120°C. The lean MEA solvent temperature at inlet to the absorber was kept at 40°C and its CO₂ loading was set at 0.2 mole per mole of MEA. The capture plant efficiency for CO₂ removal and recovery was kept at 90%.

Tarong coal with composition shown in Table 1 was chosen as fuel for the base case scenario.

Table 1– Tarong coal composition

Ultimate Analysis	Weight (%)
Moisture	14.0
Ash	28.0
Carbon	46.75
Hydrogen	3.07
Nitrogen	0.87
Chlorine	0.0
Sulfur	0.23
Oxygen	7.08
Total	100
Coal HHV (MJ/kg)	19.38

In the present study, for the process analysis the ambient conditions for the capture plant were set as per the “Technical Guidelines - Generator Efficiency Standards” (GES) released in December 2006 by the Australian Government through the Australian Greenhouse Office, i.e. 25°C ambient temperature with 60% relative humidity, the demineralised process water and cooling water inlet temperatures as 20°C and the maximum rise in cooling water temperature restricted to 7°C.

The SO₂ and SO₃ concentrations in the flue gas leaving the power plant were determined to be 200 ppmv and 1.9 ppmv respectively using the Steam-Pro software to simulate the base load (600 MW) performance of power plant at steady state. The Steam-Pro simulations of the power plant show that despite having a fabric filter with dust collection efficiency of 99.9% roughly 30 mg of particulate matter is present in flue gas per Nm³ of the gas stream. NO_x concentration in the flue gas was considered to be at 300 ppmv of which 95% was considered to be NO with rest being NO₂. The rest of flue gas consisted of water vapour: 9.45 vol%, Carbon dioxide: 12.9 vol%, Nitrogen: 72.1 vol%, Oxygen: 4.66 vol% and Argon: 0.8 vol%.

The current generation of CO₂ capture technology that uses 30% w/w MEA solvent is intolerant to flue gas with levels of SO_x and NO_x greater than 10 ppmv and to particulate content greater than 3 mg/Nm³. As a result, the implementation of CO₂ capture process requires a flue gas desulphurisation (FGD) or a caustic soda wash unit upstream. The Steam-Pro simulations did show that the limestone/lime slurry based FGD unit (98.5% efficiency) can reduce for the present case, the SO_x content of flue gas to less than 10 ppmv but due to 4% leakage of hot untreated gas into the treated gas in the stack-gas reheater, the final SO_x content upstream of the capture plant remained approximately 17 ppmv. It therefore warranted caustic soda wash prior to CO₂ absorption. 2.5% w/w caustic soda

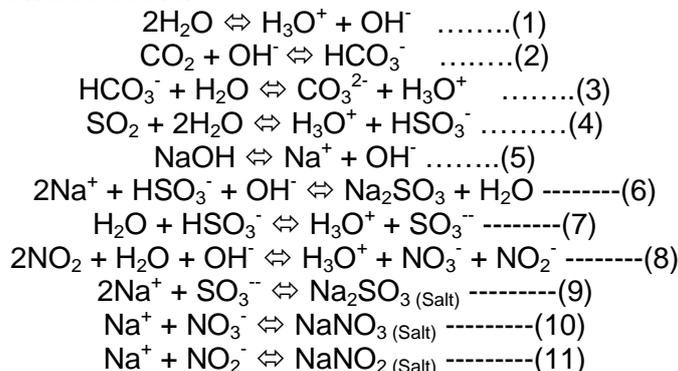
concentration was assumed in the wash water circulating within the direct contact cooler (DCC) for the exclusive purpose of bringing the SO_x content from 17 ppmv to below 10 ppmv. Since Australian power generators have no statutory requirement to have FGD unit and the caustic wash is anyway needed after FGD to bring SO_x content of flue gas within the tolerance limit of MEA solvent, direct caustic wash of flue gas in DCC column using 2.5% w/w aqueous caustic soda is also investigated as an alternative to FGD in the present study. The estimated values for concentration of MEA and its degradation products obtained in the CO₂ lean gas stream represent the theoretical vapour phase emissions of these chemicals in the treated flue gas and not the physical liquid entrainment based emissions at the plant operating condition. The later emissions are minimised in industrial practice by a Chevron type mist eliminator between the CO₂ absorption and the water wash sections, and a wire-mesh mist eliminator downstream of the water wash section. It is difficult to estimate accurately the liquid entrainment since the droplet carryover is influenced by a number of competing factors such as the design of CO₂ absorber internals, the hydrodynamics within the absorber, the impact of heat stable salts formed during CO₂ absorption on the density, viscosity and surface tension of solvent, the type of demister used in the absorber and the wash water circulation rate. Nevertheless, Veldman (1989) suggests that in an amine based CO₂ capture plant, entrainment can lead to the emission of up to 8.5 mg amine per Nm³ of treated gas whereas the Handbook from Gas Processors Suppliers' Association (2004) quotes liquid carryover from various types of mist extraction devices as 0.01 to 0.13 m³ per million m³ of gas stream. For the purposes of this study, the highest value in the range from the Handbook of Gas Processors Suppliers' Association was used to estimate physical carryover of wash water in the treated gas that leaves the wash section. From the quantity of entrained wash water and its chemical composition, the actual physical entrainment losses of MEA solvent and its degradation products were calculated. The chemical composition of the entrained wash water was considered to be same as that of the wash water circulating inside the wash section at steady state operation.

2.2 CO₂ Absorption Reactions

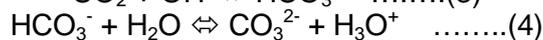
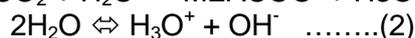
The process simulation assumed direct contact cooler (DCC) to have 3 theoretical stages, the CO₂ absorber to have 32 theoretical stages and the solvent regenerator (stripper) to have 38 theoretical stages. The direct contact cooler, absorber and the stripper were assumed to operate according to chemical rate kinetics with mass transfer considerations (Aspen-Plus Rate-Sep Models). The electrolyte NRTL model from Aspen-Plus's property data bank was used to track the ionic species generated during the CO₂ absorption/regeneration process and determine the overall physical properties of various process streams.

The chemical reactions occurring within the direct contact cooler and absorber are given below:

For Direct Contact Cooler



For the Absorber

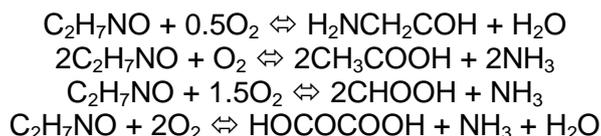


Reaction 1 is carbamate formation which is usually kinetically controlled since it is dependent on MEA concentration in solution, dissolved CO₂ concentration in solution and the absorber temperature. Reaction 3 represents dissolved CO₂ reacting with hydroxyl ions in solution at the absorber temperature. The general literature agreement is that this reaction is usually kinetically controlled <http://pubs.acs.org/doi/pdf/10.1021/ja00474a003>. Reaction 2 is ionic dissociation of water which usually proceeds to its natural equilibrium. Reactions 4 and 5 are carbonate ion formation and protonation of MEA. ASPEN Plus Simulation software providers recommend that by assuming the reactions 2, 4 and 5 as at equilibrium, the simulation results give more accurate presentation of the absorber performance. Hence, reactions 1 and 3 within the absorber were assumed to be kinetics controlled whereas the other reactions were assumed to be at equilibrium.

The vapour phase carryover of MEA in the treated gas was restricted by keeping the flue gas temperature low at the inlet to the water wash section and washing the gas with cold demineralised water. This loss can be estimated theoretically since the vapour pressure of MEA and its solubility in water at a given absorber operating temperature are the only influencing factors. MEA losses with entrained wash water from the wash tower were calculated from the chemical composition of wash water circulating within the wash tower and assuming the volume flux of entrained wash water as 0.13 m³ per million m³ of CO₂ lean gas stream.

2.3 MEA Degradation

While MEA is stable at around 120 °C, the usual reboiler temperature for industrial operations, it undergoes thermal degradation at this temperature due to reaction with the dissolved CO₂. The major degradation products resulting from these interactions are : Oxazolidone-2, 1-(2 Hydroxyethyl) imidazolidone-2 (HEIA), N-(2-Hydroxyethyl)-ethylenediamine (HEEDA), N-(2-hydroxyethyl)-diethylenetriamine (Trimer), N-(2-hydroxyethyl)-triethylenetetramine (Polymer), and Cyclic Urea of Trimer. The ethylene amine derivatives (HEEDA, Trimer and Polymer) are hard to decompose to regenerate MEA and promote plant material corrosion especially when the partial pressure of CO₂ is high. In addition to thermal degradation, MEA undergoes oxidative degradation due to presence of oxygen and other exiting impurities in the flue gas. The dissolved oxygen in aqueous MEA solution is known to form at the plant operating conditions the amino-acetaldehyde, acetic acid, formic acid, oxalic acid, glycine and other degradation products according to the following reactions (Thitakamol et al, 2007):



These acidic products react with the plant metallurgy to form organo-metallic salts that are heat stable. The extent of individual salts formed depends upon the plant operating pressure and temperature, amine concentration and the concentration of oxygen in solution. However, Thitakamol et al (2007) have shown that the formates and acetates comprise nearly 90% of the heat stable salt material. The kinetics of formation of heat stable salts during CO₂

absorption by aqueous MEA and its regeneration has been studied by Uyanga et al (2007) and these investigators recommend the following rate expression to account for the presence of heat stable salts in the amine solvent circulating between the absorber and the regenerator.

$$-R_{MEA} = K^* e^{-E/RT^*} (MEA)^{1.9} (CO_2)^{-0.3} \{ (SO_2)^{3.4} + (O_2)^{2.8} \}$$

Where,

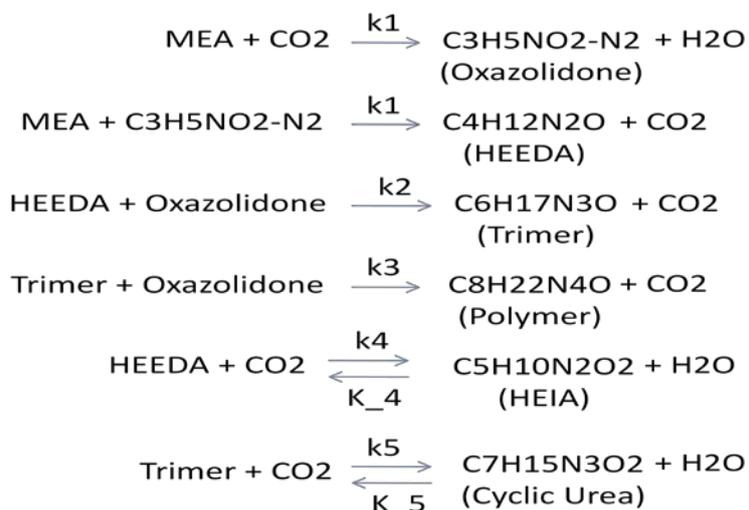
R_{MEA} = Rate of heat stable salt formation,

(MEA), (CO_2), (SO_2) and (O_2) are molar concentrations of MEA, CO_2 , SO_2 and O_2

$K = 0.00745$, $E = 45.3$, and $T = ^\circ K$, the absorber and/or stripper temperature

The above rate expression was used in the ASPEN-Plus simulation assuming the formic acid formation equilibrium reaction within the absorber and stripper to account for the oxidative degradation of circulating amine solution. The heat stable salts were therefore expressed in terms of formic acid formation.

Thermal degradation of MEA was modelled in ASPEN-Plus using the rate kinetics described by Jason Davis (2009). The chemical reactions involved during degradation are as below:



The pre-exponential constants and activation energy values associated with each of the rate constants that were taken from Jason Davis (2009) are given in Table 2.

Table 2 - Activation energy and pre-exponential constants for the thermal degradation reactions

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

It should be noted that the presence of oxidative and thermal degradation products in the lean amine solvent may have potential to affect the solvent properties such as surface tension, viscosity and density which determine the size distribution and the extent of physical carryover of solvent droplets in the treated gas.

2.4 Estimation of Degradation Product Build-Up

The MEA based post combustion CO₂ capture plants that are operating commercially, extract a slip stream from the solvent circulation loop (between 0.5 to 3 % w/w of solution) every 3 to 4 weeks and pass it through the reclamation steps to keep the concentration of solvent degradation products in the circulating solution low. This implies that in the time frame between two consecutive reclamation operations, the concentration of both oxidative and thermal degradation products in the solution keeps rising due to ongoing MEA degradation. Since the ASPEN Rate-Sep simulation package provides material and energy balance for CO₂ capture plant under the steady state operating conditions only, once the recycle stream loops are closed and converged during a plant simulation exercise, there is no direct way to estimate time based degradation of MEA solvent and build up of its degradation products that occurs in a real steady state capture plant. In order to imitate unsteady state MEA degradation in ASPEN-Plus simulation, the steady state spent amine stream leaving absorber and the steady state regenerated lean amine stream leaving stripper were duplicated as feed streams to two separate Stirred Tank Reactors (STR) in a separate Aspen-Plus simulation.

The reactor processing spent amine stream was assumed to operate at the average pressure of absorber and stripper and at the temperature of stripper inlet feed stream. This reactor accounted for the oxidative degradation reactions only. The residence time for spent amine stream in this reactor was varied to determine the build up of oxidative degradation products with time. Since these degradation products are not reversed in the stripper, it was assumed that in a real capture plant environment as MEA continues to circulate between the absorber and stripper, its oxidative degradation over time is best approximated by the extent of degradation product formation in the Stirred Tank Reactor as its residence time varies. Thus, from time, $t = 0$, to time, $t = 6$ weeks, oxidative degradation was simulated using rate expression given by Uyanga et al (2007) described above.

To model thermal degradation of MEA in Aspen-Plus, the Stirred Tank Reactor with lean amine stream leaving stripper was assumed to operate at the stripper bottom pressure and the reboiler outlet temperature. The residence time for lean amine stream in this reactor was varied to determine the build up of thermal degradation products with time. Since these degradation products are not reversed in the absorber, it was assumed that in a real capture plant environment as MEA continues to circulate between the absorber and stripper, its thermal degradation over time is best approximated by the extent of degradation product formation in the Stirred Tank Reactor as its residence time varies. Thus, from time, $t = 0$, to time, $t = 6$ weeks, thermal degradation was simulated using various rate expressions given by Jason Davis (2009) that are described above.

2.5 Initial estimate of Nitrosamine Emissions

There is very little information available in the public domain on the degradation of MEA to nitrosamine compounds due to presence of NO_x in the flue gas. Recently, Pedersen et al (2010) have investigated degradation of MEA to form nitrosamines in an Aminox rig and a high-pressure autoclave. In these experiments the authors have exposed 30 to 40 wt% MEA solution at CO₂ absorber (44 °C temperature) and stripper (120°C) conditions to a flue gas

containing 3.5 vol% CO₂, up to 14 vol% oxygen and as much as 100 ppmv NO_x. These investigators observed that NO is oxidised to NO₂ in the absorber inlet and roughly 20% of NO₂ is absorbed into the liquid phase. Their results indicate that ammonia is the primary degradation product of MEA and its production is strongly correlated with NO_x concentration in the 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 diethanolamine (DEA) – a secondary amine - that may have been present in MEA solution as an impurity or a result of NO_x induced degradation of MEA.

Strazisar et al (2003) report to have observed the presence of '**nitrosamine compounds**' at the concentration of 2.91 µmol/mL of lean MEA solution in the 800 TPD post combustion CO₂ capture plant at Trona, California. This plant has been built using Kerr McGee technology (approximately 15 to 20% w/w aqueous MEA solvent) has been in operation since the 1970's and treats a slipstream of flue gas from a coal-fired power plant. It is unclear from the publication for how long the lean MEA solvent had been in service prior to analysis; hence the extent of solvent degradation could not be determined. Also the level of purity or composition of the fresh solvent used was not reported hence the level of secondary amine contamination could not be determined also. The authors did not isolate or identify individual nitrosamine compounds and hence it cannot be unequivocally stated that the measurements made were those of nitrosamines and not an artefact of the analytical procedure. Additionally, it is unclear whether any dissolved NO₂, as a contaminant, was included in the quantification of nitrosamines which would lead to an overestimation of the analyte species.

The atmospheric emission estimates of nitrosamines are based on the information published by Strazisar et al (2003) that are related to nitrosamines formation in a PCC pilot plant. This concurs with observations of Attalla et al. (Personal Communication) where nitrosomorpholine was detected at a selected CSIRO PCC pilot plant. If this information is confirmed, the Nitrosomorpholine could be emitted to the atmosphere if formed during the capture process.

For the purpose of this study only, the Aspen-Plus process modules were adjusted to include in the process streams the presence of NDELA and Nitrosomorpholine in equal proportion, though NDELA is less volatile compared to the later compound. As a starting point, vapour phase calculations were carried out for the above nitrosamines in equal proportion at total concentration of 2.91µmol/mL of lean MEA solution. The droplet phase emissions of this nitrosamine were then calculated at 0.13 m³ liquid carryover per million m³ of gas stream.

The results have been calculated for the operating condition at the end of 3rd week of capture plant operation. One is, however, cautioned that these results should be viewed as initial estimates only. The nitroso compounds, if formed during the capture process will be of varied type with varying degree of volatility and therefore will therefore have different emission rates.

3. SIMULATION RESULTS

Figure 2 shows the process simulation flow sheet with various process streams around CO₂ absorber and stripper with their steady state flow rate, temperature and pressure values as estimated by Aspen-Plus software for the CO₂ capture plant. The flue gas from the power

plant is directly caustic washed in the direct contact cooler for SO_x/NO_x reduction prior to CO₂ absorption. The simulation results show that direct caustic wash of 1822 tonnes/hr flue gas requires 29.3 tonnes/hr of 2.5 % w/w caustic soda solution as makeup to reduce the SO_x content to below 2 ppmv. NO₂ content of flue gas is also reduced from 15 ppmv to 6 ppbv during caustic wash, however NO remains un-reacted. The direct contact cooler operates at liquid to gas ratio (L/G) of 2.6 mole per mole and re-boiler heat duty for this capture plant is 4.2 MJ/kg of CO₂. Figure 3 shows the Aspen-Plus generated process flow streams around the absorber and the water-wash tower after 3rd week of steady state operation.

Due to chemical reactions during absorption, stream G1 leaving the CO₂ absorber (ABSORBER) has 70.6°C temperature and it needs to be cooled down to 45°C to reduce the wash tower (WASH) load. This cooling load is approximately 140 MW and it is picked up by water cooled heat exchanger, HX8. This implies that in a real plant, the absorber will need to have inter-cooling capacity to reduce atmospheric emissions of MEA and its degradation products. It should be emphasized that while simulating steady state CO₂ absorption, care was taken to have zero effluent discharge from the wash tower. Circulating wash water in the wash tower was bled into the lean amine solvent stream only to the extent of maintaining water quality in the wash tower. The water wash tower was simulated as 3 equilibrium stage packed section operating at L/G ratio of 2.1 mole per mole. The results indicate that the physical plant will need at least 1 tonne/hr of makeup demineralised water to avoid building up MEA and its degradation products in the wash water. The circulating wash water has the steady state MEA concentration of 640 ppmw (0.064 % w/w) and the CO₂ lean gas leaving the wash tower has vapour phase MEA slippage of 9 ppbv.

Since flue gas at inlet to the absorber contains 9 ppbv of NO₂, formation of nitrosamines within absorber due to degradation of MEA, for example to secondary amine, diethanolamine (DEA), could be possible over time, particularly if NO is oxidised to NO₂ in the absorber inlet and NO₂ is absorbed into the liquid phase as observed by Pedersen et al (2010). Similarly, the presence of 1 ppmv SO_x in flue gas is likely to contribute towards degradation of MEA over time forming organo-sulphates due to the following reactions:

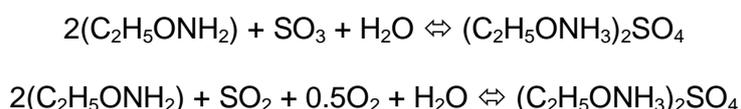


Figure 4 shows the oxidative and thermal degradation products of MEA building up in the solvent circulation loop over time during steady state CO₂ absorption. Building up of heat stable salts (represented as formic acid in this study), sulphates and other degradation products warrants periodic reclamation of solvent. Aspen-Plus simulation shows that roughly 33 tonnes/hr of circulating solvent will need to be withdrawn periodically and the reclamation unit (RECLAIM) put on stream at every 3 to 4 weeks interval. Figure 5 and 6 show vapour phase emissions of MEA and other chemicals in mg per tonne of CO₂ captured at the absorber outlet, Stream G1 and in the CO₂ Lean Stream G4, leaving the wash tower respectively as the time progresses. These results show that at both the absorber outlet and the wash tower outlet, MEA and its degradation products, NH₃, Oxazolidone, HEEDA, HEIA and nitrosamines will be present in the gas phase. The heat stable salts do not appear in the flue gas leaving absorber because not only do they have low vapour pressure but high solubility in water. Once emitted with liquid entrainment from absorber, they get washed out by the demineralised water circulating in the wash tower which further dilutes their concentration in the droplet phase. The resulting concentration in droplet (emitting from the wash tower) is very low (below ppb levels) to the point of not being within the accuracy (tolerance) limits of Aspen Plus process simulation.

The results at 0th week represent vapour phase emissions of MEA and its degradation products when the capture plant is operating at steady state with solvent completing its first circulation between absorber and stripper. It shows only MEA and ammonia emission in the gas streams (Figure 5) and represents a capture plant operating at steady state without any degradation of MEA. As solvent continues to circulate, NH₃, heat stable salts, Oxazolidone, HEEDA, HEIA, Trimer, Polymer, cyclic Urea and nitrosamines are formed with time (Figure 4) and practically all of them may be detected at the absorber outlet (in stream G1) as shown in Figure 5, however in addition to MEA only NH₃ and Nitrosomorpholine appear in the CO₂ lean gas stream, G4, leaving the water wash tower (Figure 6) at levels that could be considered noticeable. Whilst Oxazolidone, NDELA and HEIA are emitted to atmosphere, their concentrations are practically very low. The atmospheric gaseous emissions of MEA and nitrosomorpholine seem to remain constant with time but those of Oxazolidone and ammonia appear to rise with time (Figure 6). These results clearly show that cooling absorber outlet gas and washing it with a large quantity of circulating demineralised water in the wash tower minimises emissions of MEA and its degradation products to atmosphere. Table 3 below shows emissions of MEA and its degradation products in the water washed CO₂ lean gas stream leaving the wash tower at 45°C. It shows that the vapour phase emissions of heat stable salts (measured as HCOOH), NH₃ and various thermal degradation products in water washed CO₂ lean flue gas stream are practically zero but MEA emission remains practically constant at 85 mg/tonne of CO₂.

Table 3 – Vapour phase emissions of MEA and its degradation products in CO₂ lean flue gas after water-wash (mg/tonne of CO₂ Captured)

	t=0	t=1 week	t=2 week	t=3 week	t=4 week	t=5 week	t=6 week
MEA	8.53E+01						
HCOOH	0	0	0	0	0	0	0
NH ₃	0	1.21E-08	2.41E-08	3.62E-08	4.82E-08	6.03E-08	7.24E-08
OXAZOLIDONE	0	4.58E-09	8.75E-09	1.26E-08	1.61E-08	1.93E-08	2.22E-08
HEEDA	0	0	0	0	0	0	0
HEIA	0	0	0	0	0	0	0
Nitrosomorpholine	0	7.63E-03	7.63E-03	7.63E-03	7.63E-03	7.63E-03	7.63E-03
NDELA	0	1.54E-11	1.54E-11	1.54E-11	1.54E-11	1.54E-11	1.54E-11

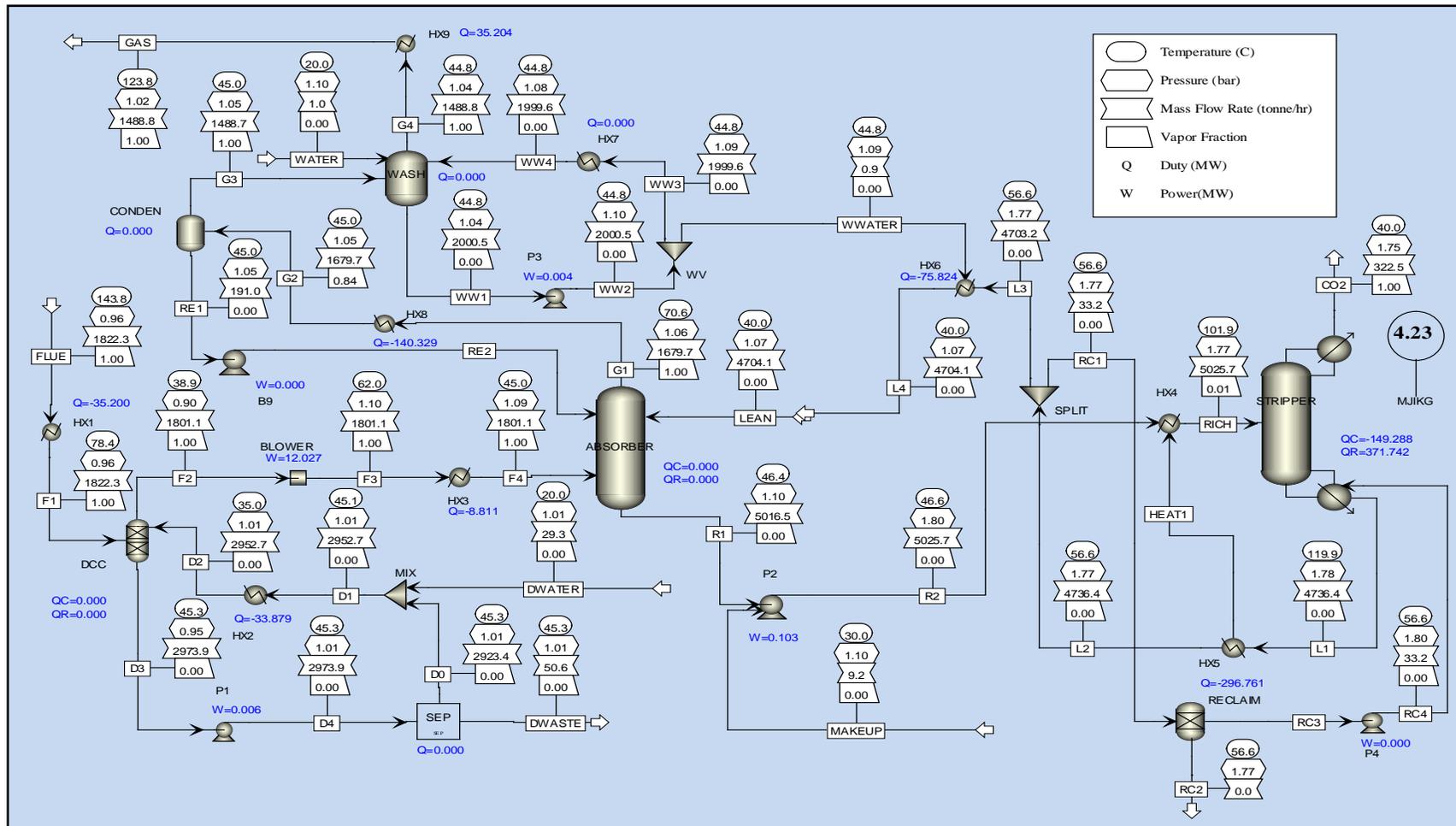


Figure 2– ASPEN process simulation flow sheet for CO₂ capture plant (direct caustic wash)

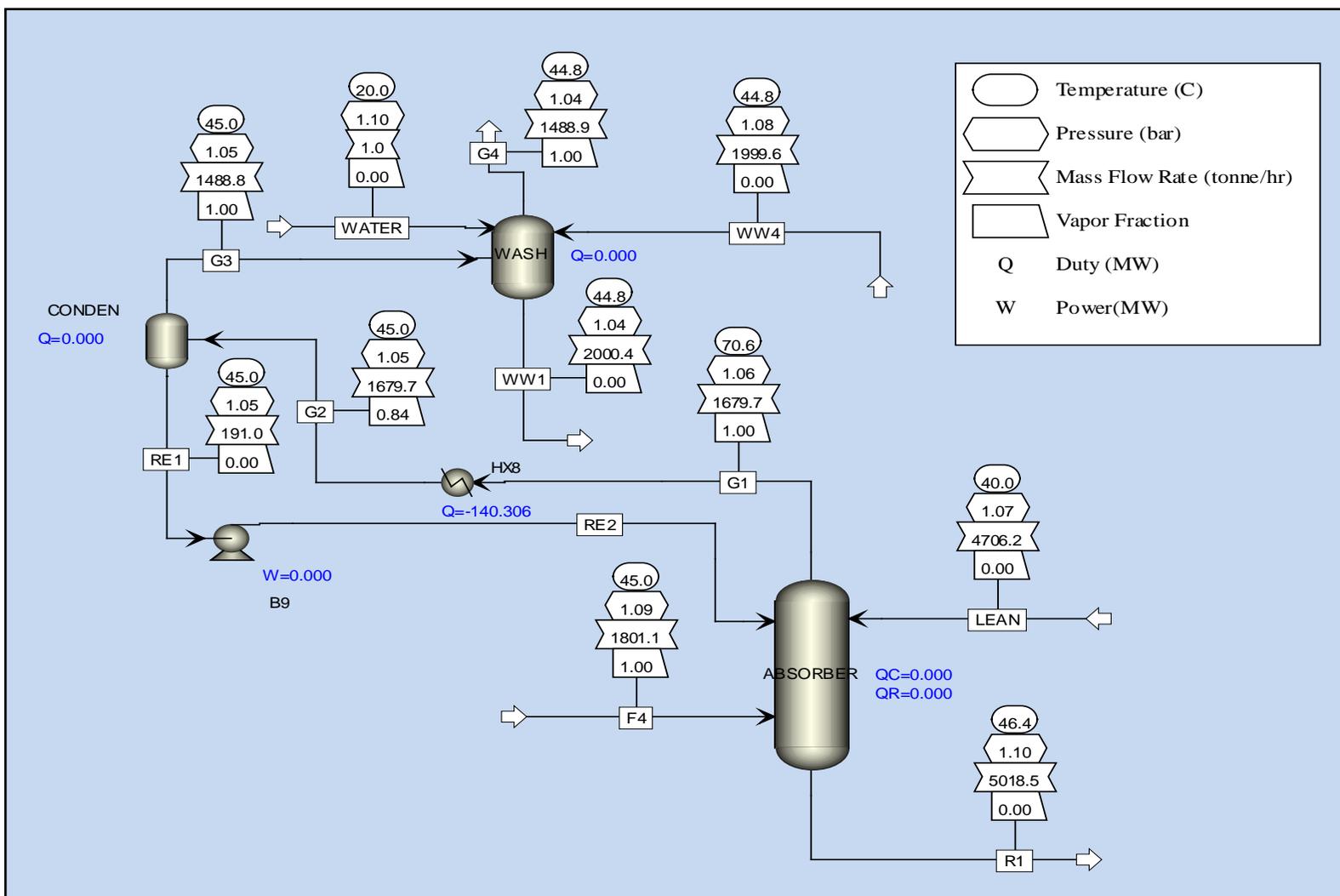


Figure 3 - Aspen-Plus simulated process flow streams around CO₂ absorber after 3rd week of steady state operation

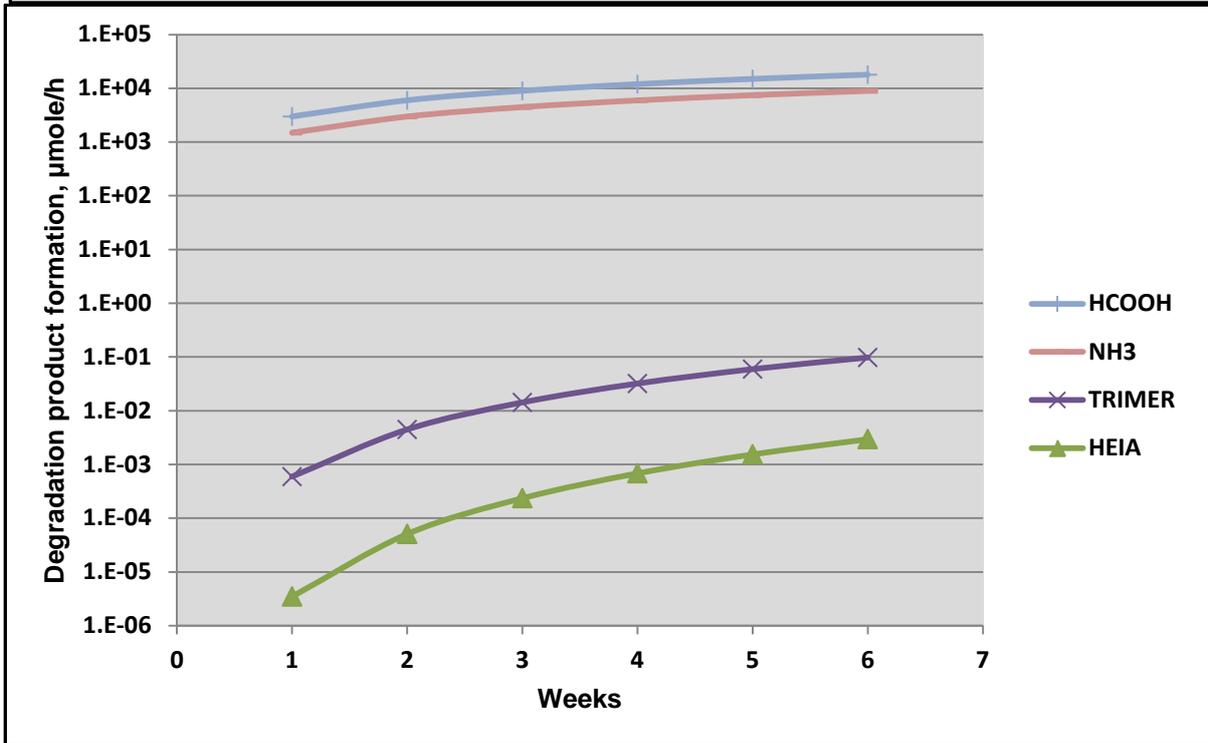
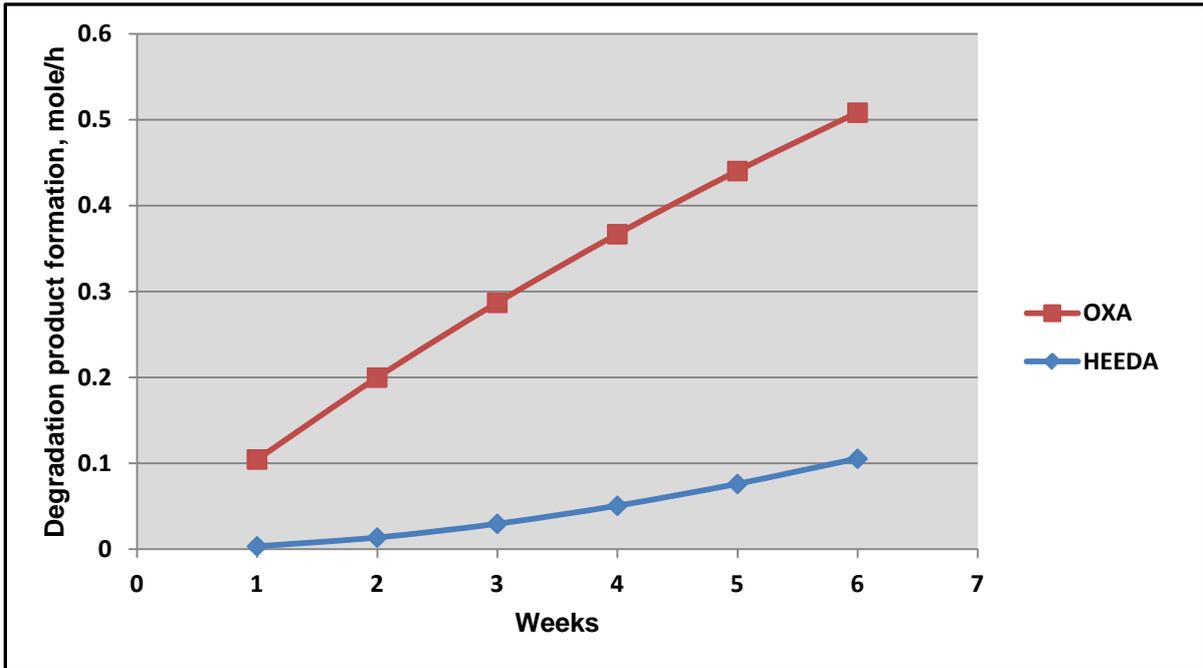


Figure 4– Aspen-Plus simulated MEA degradation product formation during CO2 absorption

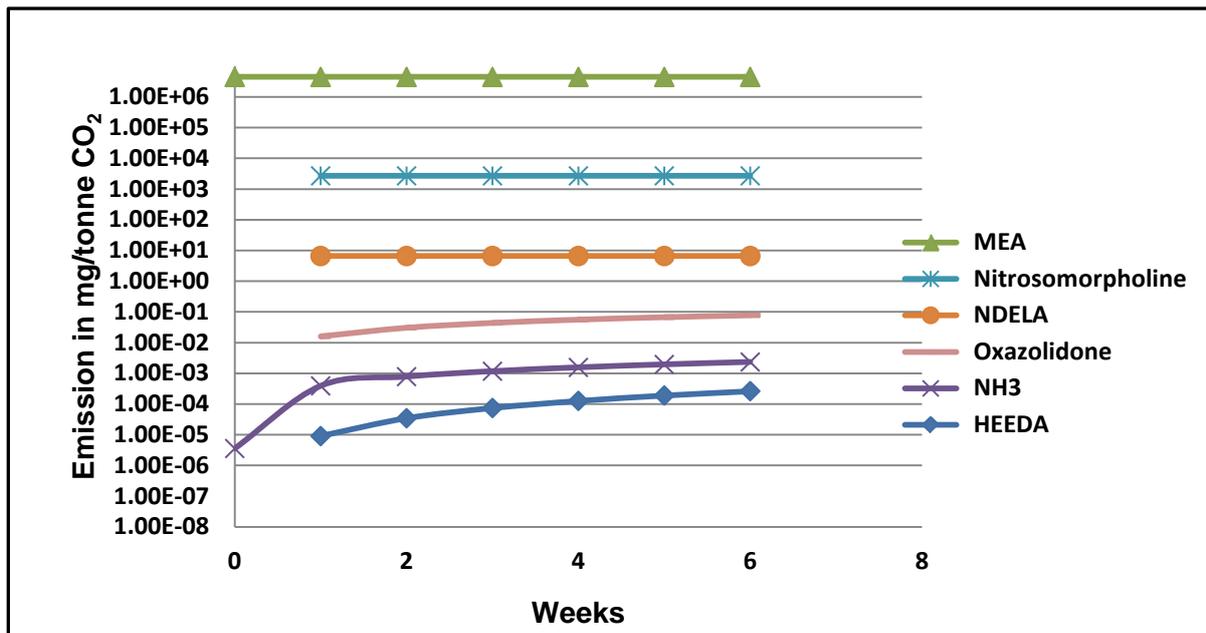


Figure 5 – Vapour phase emissions of MEA & degradation products @ absorber outlet (stream G1)

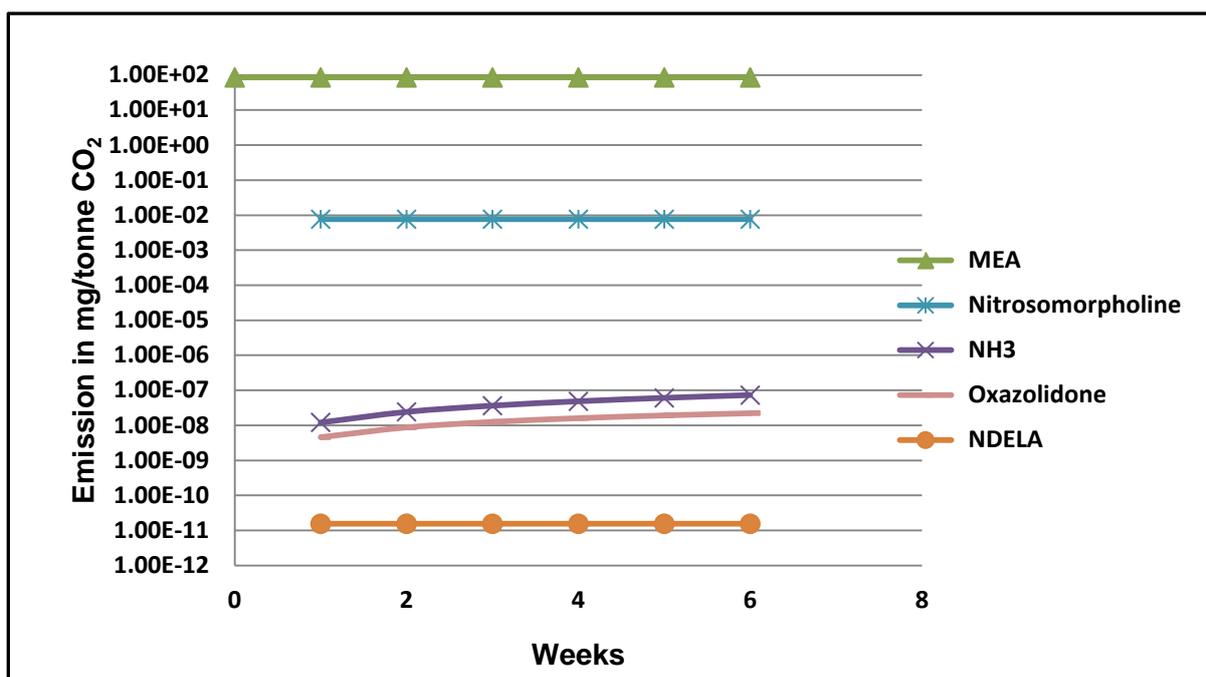


Figure 6 – degradation products @ wash tower outlet (stream G4) Vapour phase emissions of MEA &

The Aspen-Plus generated vapour phase MEA emission result is higher than the published information from Moser et al (2010) who have measured MEA emission loss in CO₂ lean flue gas under similar operating conditions as 0.6 mg/tonne of CO₂ in a post combustion capture pilot plant producing 7.2 tonnes per day of CO₂. This capture plant was linked to a lignite – fired power plant at Niederaussem, Germany. Moser et al also observed practically zero emissions of heat stable salts and thermal degradation products in CO₂ lean flue gas however NH₃ emissions were detected as ranging between 89 to 155 g per tonne of CO₂ or 27 to 47 mg/Nm³ of dry CO₂ lean flue gas. In the present study, Aspen-Plus is estimating

very low NH₃ emissions since the process model is currently devoid of rate kinetics for MEA decomposition to NH₃. Instead it uses the rate expression developed by Uyanga et al (2007) to describe the formation of heat stable salts. Moser et al (2010) also report presence of acetaldehyde (<0.2 mg/Nm³ dry gas) and acetone (0.5 to 1 mg/Nm³ dry gas) in the water washed CO₂ lean flue gas in addition to NH₃ as a result of oxidative degradation. Similarly, Aas (2009) reports various chemicals in the CO₂ lean gas at the outlet of absorber and after water wash as given in Table 4 from a post combustion CO₂ capture pilot plant that was operating at 1 tonne/hr of CO₂ production under the CASTOR/CESAR research program at Dong Energy's Esbjerg based bituminous coal firing power plant.

Table 4– Vapour phase emissions of MEA and its degradation products in CO₂ lean flue gas (CASTOR/CESAR Capture Program)

Chemicals	After Absorber (mg/Nm ³ dry)	After Water Wash (mg/Nm ³ dry)
MEA	0.7	<0.3
DEA	<0.3	<0.2
Formaldehyde	0.7	<0.1
Ammonia	25	20
Methylamine	<0.3	<0.2
Acetamide	<1.0	<1.0

The published results of Aas indicate that the pilot plant was operated in a manner such that the temperature of CO₂ lean flue gas stream leaving the water wash tower was around 45°C. Based on the pilot plant emissions data from Moser et al and Aas, the estimated concentration of several other compounds on a dry gas basis in the CO₂ 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 3. 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. Table 5 below shows the results of these calculations in terms of emissions per Nm³ of dry CO₂ lean gas leaving the Wash tower. Table 6 shows the same results in terms of emissions per tonne of product CO₂ recovered. The later presentation of atmospheric emissions results is more convenient since it directly ties the plant emissions with the CO₂ gas processing capacity of the PCC plant. It removes uncertainties associated with the percentage CO₂ recovery and any aspects of the process scale-up when determining the protocols or standards for emissions by the regulatory bodies for the benefit of technology vendors who are looking to provide the PCC-solutions.

Table 5 – Vapour phase and droplet phase atmospheric emissions of MEA and its degradation products (at the end of 3rd week)

Chemical Emissions	Chemicals Input In Stream G3		Chemicals Input In Stream G1	
	Vapour Phase	Droplet Phase	Vapour Phase	Droplet Phase
	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/Nm ³ CO ₂ dry Lean gas
MEA	2.45E-02	1.10E-01	2.63E-02	1.10E-01
NH3	1.13E-01	2.32E-03	8.56E-04	1.89E-05
HEEDA	0	0	0	0
OXAZOLIDONE	3.88E-12	2.08E-12	3.88E-12	2.09E-12
HEIA	0	0	0	0
TRIMER	0	0	0	0
CYCLIC UREA	0	0	0	0
POLYMER	0	0	0	0
DEA	1.08E-07	2.59E-05	1.05E-12	2.37E-10
FORMALDEHYDE	2.73E-01	6.16E-06	2.62E-01	5.91E-06
ACETALDEHYDE	2.98E-01	3.97E-06	2.88E-01	3.84E-06
ACETONE	3.32E-01	1.39E-05	3.12E-01	1.31E-05
METHYLAMINE	2.17E-01	6.80E-06	2.06E-01	6.46E-06
ACETAMIDE	6.99E-05	4.32E-05	1.05E-07	6.46E-08
NITROSOMORPHOLINE	2.36E-06	4.01E-07	2.36E-06	4.02E-07
NDELA	4.75E-15	8.62E-13	4.76E-15	8.63E-13

Table 6 – Vapour phase and droplet phase atmospheric emissions of MEA and its degradation products (at the end of 3rd week)

Chemical Emissions	Chemicals Input In Stream G3		Chemicals Input In Stream G1	
	Vapour Phase	Droplet Phase	Vapour Phase	Droplet Phase
	mg/tonne CO ₂	mg/tonne CO ₂	mg/tonne CO ₂	mg/tonne CO ₂
MEA	7.92E+01	3.57E+02	8.53E+01	3.58E+02
NH ₃	3.67E+02	7.52E+00	2.77E+00	6.11E-02
HEEDA	0	0	0	0
OXAZOLIDONE	1.26E-08	6.75E-09	1.26E-08	6.76E-09
HEIA	0	0	0	0
TRIMER	0	0	0	0
CYCLIC UREA	0	0	0	0
POLYMER	0	0	0	0
DEA	3.49E-04	8.39E-02	3.39E-09	7.67E-07
FORMALDEHYDE	8.85E+02	2.00E-02	8.48E+02	1.91E-02
ACETALDEHYDE	9.66E+02	1.29E-02	9.34E+02	1.24E-02
ACETONE	1.08E+03	4.50E-02	1.01E+03	4.23E-02
METHYLAMINE	7.03E+02	2.20E-02	6.68E+02	2.09E-02
ACETAMIDE	2.26E-01	1.40E-01	3.39E-04	2.09E-04
NITROSOMORPHOLINE	7.63E-03	1.30E-03	7.64E-03	1.30E-03
NDELA	1.54E-11	2.79E-09	1.54E-11	2.80E-09

These results show that the range of atmospheric emissions of MEA and its **major** degradation products in the CO₂ lean gas that leaves the water wash tower of a post combustion CO₂ capture plant that processes coal-fired power plant flue gas using 30% w/w aqueous MEA solution will be as given below in Table 7.

Table 7– Range of atmospheric emissions of MEA and its degradation products

Chemical Emissions	Minimum Per Nm ³ dry Of CO ₂ lean gas	Maximum Per Nm ³ dry Of CO ₂ lean gas	Minimum Per tonne of product CO ₂	Maximum Per tonne of product CO ₂
MEA	0.14 mg	0.14 mg	436 mg	443 mg
NH ₃	1 µg	0.12 mg	2.8 mg	374 mg
DEA	-	0.03 µg	-	84 µg
FORMALDEHYDE	0.26 mg	0.27 mg	848 mg	885 mg
ACETALDEHYDE	0.3 mg	0.3 mg	934 mg	966 mg
ACETONE	0.31 mg	0.33 mg	1.01 g	1.08 g
METHYLAMINE	0.21 mg	0.22 mg	668 mg	703 mg
ACETAMIDE	-	1.1 µg	-	0.4 mg
NITROSOMORPHOLINE	-	0.003 µg	8.9 µg	8.9 µg

It should be noted that Ammonia, DEA, Formaldehyde, Acetaldehyde, Acetone, Methylamine and Acetamide emission levels are predicted at the end of 3rd week of the capture plant steady state operation when the reclamation of the solvent is recommended to reduce the concentration of degradation products in the circulating solution.

In arriving at the above results, it was assumed that DEA which is carried over in the vapour phase at the top of absorber reacts with CO₂ when washed with circulating water.

4. DISCUSSION OF RESULTS

The determination of atmospheric emissions of harmful compounds from MEA based post combustion CO₂ capture (PCC) processes for an existing Australian coal-fired subcritical power plant was started off with an assessment of the types of MEA degradation products in PCC processes. This estimation of emission rates was determined based on formation rates found in the literature for major degradation products. In addition, the emission rates for MEA and nitrosamines as vapours have been estimated by considering their vapour pressure above the MEA solution with a certain concentration of model nitrosamine components. There has been so far only one commercially operating plant data reported in the literature that indicates nitrosamine detection at certain concentration although indirectly determined and with no individual or detailed identification of these chemicals. The emission estimates have therefore been carried out using the ASPEN process simulation software using literature based models to estimate emissions of the main degradation products. The process simulations have also provided the information related to the composition of the wash water, which determines the emission rate through droplets.

The review of process simulation results indicates that for the present case study of the Tarong coal fired power station, installation of a conventional limestone/lime based FGD (98.5% efficiency) could reduce the SO_x content of flue gas from 202 ppmv to 17 ppmv. This reduction still warrants 2.5% w/w caustic soda wash of the flue gas in Direct Contact Cooling (DCC) tower of the capture plant in order to reduce it to below 10 ppmv. Not installing the FGD and directly washing the flue gas with 2.5% w/w caustic soda results into its SO_x content dropping from 202 ppmv to 1 ppmv. Thus for the power stations that use Australian black coals, the need for FGD prior to CO₂ absorption could be easily met by 2.5% w/w caustic soda wash in the DCC tower itself because Australian black coals are low in sulphur (generally less than 1% w/w). The process simulations further show that 2.5% w/w caustic soda wash also helps in reducing the NO₂ content of flue gas from 15 ppmv to 9 ppbv which could help towards reducing the formation of various nitrosamines. The simulation results clearly indicate that emissions estimates for MEA are very much dependent on the way capture plant is operated in particular the water wash tower. High wash water circulation rate with low wash water temperature can potentially reduce MEA emissions significantly. It is important to keep dissolved MEA concentration in wash water as low as possible. The Aspen-Plus results in this study show that MEA emissions of 9 ppbv can be achieved with the wash water MEA concentration of 643 ppm and L/G ratio at 2.1 mole per mole in the wash tower. However, there is at present very little public domain experimental data available to compare the Aspen-Plus simulated wash tower performance.

4.1 Degradation Products

The detailed assessment of emissions of degradation products through Aspen-Plus was limited to using their formation predictions taken from the literature. A comparison with results from CSIRO's pilot plant operations linked to coal-fired power plants seems to

indicate that the emissions of ammonia are underestimated by the Aspen-Plus model by one order of magnitude since the model is currently devoid of the detailed kinetics of MEA decomposition to ammonia. A much better understanding must be developed for the degradation of MEA under PCC process conditions, particularly in relation to the formation of nitrosamines. This involves the identification of the major degradation products, the degradation pathways, the impact of process conditions (absorber and desorber temperature) and gas composition (CO_2 , O_2 , NO_x). As MEA undergoes thermal cycling, it is quite important to assess the effect of higher temperature on the stability of its degradation products. This study has indicated that this information is lacking. Given the complexity, it is likely that degradation products may need to be lumped to provide a simplified description of the degradation process.

Whilst the Aspen-Plus software is used to predict the vapour-liquid equilibrium and thereby determine the vapour phase atmospheric emissions of MEA and its degradation products, the physical carryover of these chemicals (droplet form) has been estimated in this study using an empirical rule proposed by the Gas Suppliers' Handbook. In practice, the extent of physical carryover of MEA and its degradation products will depend very much upon the design of absorber internals, prevailing hydrodynamics within the absorber and the influence of degradation products on foaming tendency during the counter-current gas-liquid contact (fluid properties such as surface tension and viscosity).

The design of liquid distributor, the column packing characteristics, relative velocities of two counter-currently contacting phases and the influence of physical properties of liquid (density, viscosity and surface tension) on the gas-liquid interfacial stability decide the size distribution of liquid carryover in packed towers. The droplet size distribution could vary from sub-micron to several hundred microns for CO_2 absorber. Therefore, the droplet collection efficiency of installed mist eliminators downstream of the water wash tower will determine the size distribution and mass flux of entrained liquid in the CO_2 lean gas. Prediction of this data is not possible by Aspen-Plus process simulation and it requires either a pilot plant or actual plant operational information to verify the applicability of empirical rule proposed by the Gas Suppliers' Handbook.

4.2 Evolution of degradation over time

The result of Aspen-Plus process simulations present a steady-state process condition, which is unlikely to occur when it concerns the formation of solvent degradation products, at least over the same time scale. It should be noted that the degradation products will build up over time in an operating environment of CO_2 capture. Whilst this build up is approximated in the present study by using a stirred tank reactor model with variable residence time, the basis for this approximation is the assumption that the rates for formation of MEA degradation products are smaller than the reaction rates for CO_2 with MEA. However, it should be also noted that the concentration levels of degradation products at any instance will be determined by the prevailing plant operating conditions and the plant maintenance practices. This means that the solvent regeneration process, the frequency of operating the solvent reclaimer, the solvent replenishment and the replacement of carbon filters in the lean amine circuit will all influence the formation and/or removal of degradation products. It could also be influenced by the transient operating conditions in the process plant equipment. It should be noted that the commercial technology providers use proprietary corrosion inhibitors and oxygen scavenging chemicals, the composition and working mechanisms of which are not available in the public domain and therefore the actual capture plant performance in terms of formation of solvent degradation products, their chemical identity, their concentrations in the circulating solvent and their atmospheric emissions could be somewhat different from what Aspen-Plus is predicting.

4.3 Process conditions

The results of the ASPEN process simulation indicate clearly that the temperature of the absorber and wash section (wash water inlet temperature) has a significant impact. It is very likely that higher temperatures will lead to higher emission rates since the kinetics for degradation are more favourable with increasing temperatures and so also the desorption of degradation products. This could be one of the reasons why the absorber inter-cooling strategies have become the subject of research investigations. By the same logic, it is likely that a low lean loading of the MEA solvent will result in higher emission rates for MEA from the absorber. The process modelling seems to indicate that this could be counteracted by the water wash section. An efficient design and operation of this section with low wash water inlet temperature and high internal water circulation rate has potential to lower the atmospheric MEA emission levels to asymptotic values irrespective of the initial concentration level after the absorber.

4.4 Usefulness of Aspen-Plus Simulation as emission prediction tool

Aspen-Plus process simulation software gives a steady state picture of what could be happening within a process plant. The process simulator requires as much accurate input representation of the process and plant equipment details as possible to deliver a highly reliable output, particularly if the underlying intention of using this tool is to predict vapour and droplet phase emissions. This situation is further compounded when the solvent degradation reactions are occurring simultaneously in series as well as in parallel and the stoichiometry, rate kinetics and temperature dependency of these reactions are either unknown or unreliable and information on the droplet capture equipment in terms of its efficiency with respect to the droplet size distribution and droplet flux is unknown. The results of this study have shown that Aspen-Plus has provided some characterisation and quantification of atmospheric emissions from the MEA based CO₂ capture process operation at steady state. Whilst these results may not be entirely accurate due to lacking input data for the degradation reactions, capture plant equipment details, and their operating efficiencies and associated internal hydrodynamics, they have shown that the absorber operating temperature and the wash tower operating parameters (wash water circulation rate, its temperature and the effectiveness of the demister) decide the level of atmospheric emissions.

5. CONCLUSIONS

This study shows that for a coal-fired power plant that uses Australian black coal, the need for SO₂ reduction prior to CO₂ capture in order to minimise MEA degradation can be met by 2.5% w/w caustic wash in the DCC tower of the capture plant itself. SO_x and NO₂ content of flue gas can be reduced thereby from over 200 ppmv to 1 ppmv and from 15 ppmv to 9 ppbv respectively. This study also attempts to provide an estimate of atmospheric emissions of MEA and its degradation products during the post combustion capture of CO₂ when treating flue gas stream from an Australian black coal-fired power plant. The Aspen-Plus process simulation results indicate that during the capture process the degradation products of MEA, i.e. heat stable salts, Oxazolidone-2, 1-(2 Hydroxyethyl) imidazolidone-2 (HEIA), N-(2-Hydroxyethyl)-ethylenediamine (HEEDA), N-(2-hydroxyethyl)-diethylenetriamine (Trimer), N-(2-hydroxyethyl)-triethylenetetramine (Polymer), and Cyclic Urea of Trimer are unlikely to be materially emitted to atmosphere though their concentrations may increase with time in the lean MEA solution. Whilst the concentration of degradation products in MEA circulating between the absorber and the stripper rise with time their volatility decides how much of these products and which one of them will be emitted to the atmosphere. Therefore, high boiling compounds with poor volatility such as HEEDA, HEIA and Oxazolidone will be less likely to be emitted.

The atmospheric emission estimates of nitrosamines are based on the information published by Strazisar et al (2003) that are related to nitrosamines formation in a PCC pilot plant. This concurs with observations of Attalla et al (Personal Communication) where nitrosomorpholine was detected at a selected CSIRO PCC pilot plant. If this information is confirmed, the Nitrosomorpholine could be emitted to the atmosphere if formed during the capture process. The total MEA emissions to atmosphere are likely to be around 440 mg per tonne of CO₂ captured.

When compared with CSIRO's own pilot plant measurements of ammonia emissions, the Aspen-Plus generated ammonia emission estimates are rather low since the absorption process models used in this study are currently devoid of the data on kinetics of decomposition of MEA. However, when the pilot plant observations of Moser et al (2010) and Aas (2009) are taken as the basis then total ammonia emissions to atmosphere will be in the range 2.8 to 374 mg per tonne of CO₂ captured.

Aspen-Plus process models need appropriate kinetic rate data for reliable emission estimates of other degradation products of MEA such as DEA, formaldehyde, acetaldehyde, acetone, methylamine, acetamide, nitrosamines etc. This data is currently lacking or unreliable in the open literature. The estimate of emissions of such compounds in the present study has been restricted to relying on pilot plant measurements carried out and reported by one or two public domain studies. Hence such estimates are to be treated as mere qualitative observations particularly when considering nitrosamine emissions to atmosphere. Despite the above stated inherent limitations of the present study, it conclusively proves that the absorber operating temperature and the wash tower operating parameters (wash water circulation rate, its temperature and the effectiveness of the demister) will decide the level of atmospheric emissions of MEA and its degradation products.

6. RECOMMENDATIONS FOR FUTURE WORK

The following recommendations for further work are made, based on the results of the literature review, the Aspen-Plus process simulations and a critical analysis of the overall results:

Thermodynamic models and data

Rigorous thermodynamic models are needed to describe e.g. the amine and its degradation product vapour pressure under a range of relevant process conditions, to enable process simulations to describe processes accurately. There is also a lack of data to validate the thermodynamic models. Available models are sufficient for process design purposes for a limited selection of single solvents, for example MEA, but do not yet possess the detail to provide adequate methods to be used with confidence in the assessment of emission rates.

Degradation reactions and degradation rate data

The understanding of degradation of solvents as determined by the influence of flue gas impurities (O_2 , NO_x , SO_x and CO_2), process conditions (temperatures throughout the process plant) and materials (metals) is very limited. Quantification of the reaction kinetics and stoichiometry for the formation of each degradation product including any nitroso compounds in the capture environment is the goal of this effort. A lumped approach might be necessary to cover the complexity of the degradation phenomena. Quantum chemistry modelling might provide useful insights into the preferred degradation routes. In particular additional information related to the rate of N-nitroso compounds formation is needed. This can be generated from using selected laboratory experiments, and validated by pilot plant data. For selected chemical reaction pathways, it may be possible to carry out quantum chemistry modelling to calculate the thermodynamic parameters of the degradation reactions.

Process and equipment models

Process models should be detailed enough to describe the mass transfer and reactions pertinent to the issue of atmospheric emissions from PCC processes. A rate based approach is, therefore, preferred as it provides more details regarding the local mass transfer phenomena. Results from degradation studies need to be included into the process models. The process models should be able to predict the build up of degradation product and resulting emissions as a function of time. Ideally the process and equipment models are built around a case where designs can be optimised. CFD models will be particularly useful to predict and control entrainment losses. In addition to this, the determination of the droplet size distribution and the physical and chemical characteristics of aerosols at the top of the absorber and wash section require experimental investigation. The collected information can be used to calculate the entrainment factors of droplets from the top of the absorber.

Validation of process models

Ultimately the fundamental understanding gained through the previous steps needs to be validated. Ideally a large scale pilot or demonstration plant can be utilised to measure emission rates, preferably over a period, to follow the progression of emission rates over time to take into consideration the effect of an ageing solvent. A known solvent is preferred to enable the complete analysis, without any gaps in the information underpinning the processes. The process validation should run concurrently with the development of process and equipment models and the acquisition of laboratory data on degradation and thermodynamic properties of the solvent and degradation products.

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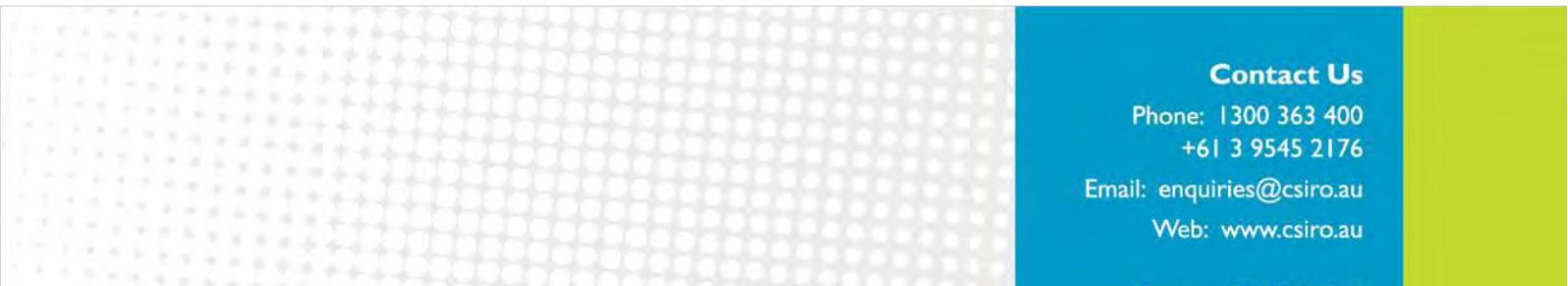
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Contact Us

Phone: 1300 363 400

+61 3 9545 2176

Email: enquiries@csiro.au

Web: www.csiro.au

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