CO_2 Capture Mongstad - Project B – Theoretical evaluation of the potential to form and emit harmful compounds

Task 1: Process Chemistry

Narendra Dave, Thong Do, Phil Jackson, Paul Feron, Merched Azzi and Moetaz Attalla.

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www.csiro.au

Enquiries should be addressed to:

Merched Azzi

Phone: 61 2 9490 5307

Email: merched.azzi@csiro.au

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Revision	Description	Issue Date
01	Draft	9 August 2010
02	Resubmitted Draft	7 September 2010
03	Final report – CCM comments addressed	14 October 2010

EXECUTIVE SUMMARY

This report describes the likely atmospheric emissions of selected amine solvents and their degradation products during a post combustion CO_2 capture process and quantifies these through ASPEN Plus process modelling. The process modelling study utilised three generic solvent compositions (given below), flue gas data typical for a gas-fired combined cycle and a range of process conditions.

Generic Solvent A	*Generic Solvent B*	*Generic Solvent C*
MEA (30 %w/w)	AMP (25 %w/w)	MDEA (25 %w/w)
Water (69 %w/w)	PZ (15 %w/w)	MEA (5 %w/w)
Heat Stable Salts (1 %w/w)	Water (60 %w/w)	Water (70 %w/w)

The vapour emissions of amine were estimated under those process conditions which resulted in the lowest reboiler duty for the post-combustion capture process. These conditions were found through an optimisation study for each generic solvent. The flue gas before and after the CO_2 absorber was reduced to the same temperature and this proved to be an important parameter. All simulations were carried out while maintaining the water balance which resulted in addition of demineralised water at temperatures above 35 ^oC. At temperatures below 35^oC the condensate in the water wash was used as the main source of wash water.

A list of expected degradation products was developed through a review of the literature. However, only for the degradation products, ammonia and heat stable salts, modelled as formic acid, formation rates were expressed quantitively and could hence be used for estimation of formation and emission rates.

No formation rates were found in the literature for nitrosamines in relation to post-combustion capture. There are several publications citing the propensity of nitrosamines to form under PCC conditions. The nitrosamine concentration in spent MEA solvent was used to estimate emissions of model components (diethyl-nitrosamine and dimethyl-nitrosamine) assuming the emission rate was governed by physical absorption. It should be stressed that there is no experimental or theoretical evidence that these particular nitrosamines (dimethyl-nitrosamine ($C_2H_6N_2O$) and diethyl-nitrosamine ($C_4H_{10}N_2O$)) will be present in a PCC process. The results related to the nitrosamine modelling should be considered hypothetical, providing a scenario output, rather than a realistic value.

Entrainment was modelled using the upper value given in a reference in which the droplet carry-over after demisters was considered proportional to the gas flow rate. The composition of the liquid carried over was taken to be that of the wash section.

The range of the specific atmospheric emissions as a result of evaporation and entrainment of amines and degradation products are given in the following table for the three generic solvents.

Specific atmospheric emission rates for the three generic solvents			
	Vapour (per tonne CO_2 captured)	**Entrainment (per tonne CO_2 captured)**	**Total (per tonne CO_2 captured)**
Solvent A			
Heat stable salts	Nil	0.1 to 0.5 mg	0.1 to 0.5 mg
Ammonia	9 mg to 2.6 g	17 mg to 0.5 g	26 mg to 3.1 g
MEA	12 mg to 11 g	9 to 47 g	21 to 58 g
Dimethyl-nitrosamine	11 to 95 g	0.4 to 1 g	12 to 96 g
Diethyl-nitrosamine	2.5 to 29 g	0.3 to 0.7 g	3 to 30 g
Solvent B			
Ammonia	3.4 mg to 1 g	8 mg to 0.3 g	12 mg to 1.3 g
AMP	0.7 g to 1.2 kg	15 to 127 g	16 g to 1.3 kg
PZ	0.8 mg to 1.5 g	0.6 to 9.5 g	0.6 to 11 g
Solvent C			
Heat stable salts	Nil	Nil	Nil
Ammonia	0.4 mg 9 g	1 mg to 0.3 g	1.4 mg to 9.3 g
MDEA	Nil	Nil	Nil
MEA	0.9 mg to 0.9 g	0.6 to 2.1 g	0.6 to 3 g
Dimethyl-nitrosamine	12 to 97 g	0.5 to 1 g	12.5 to 98 g
Diethyl-nitrosamine	0.9 to 17 g	0.2 to 0.7 g	1 to 18 g

The emission rates were quite dependent on the flue gas temperatures with the higher emission rates valid for high temperatures. The impact of the CO_2 recovery on the emission rate varied for the components under consideration.

Of the three generic solvents, Solvent B appears to have the highest specific emission rate, followed by Solvent A. Solvent C has the lowest overall specific emission rate.

This study results have been partly based on process modelling utilising information derived from public domain literature. Where data was found in the public domain it appeared to be limited to only one reference for a specific piece of information. In light of the above described significant uncertainties for estimating the overall potential releases of solvents A, B and C and their degradation products to the atmosphere, the following tasks are recommended to improve the understanding of PCC process emissions:

- Development of higher quality thermodynamic models and data for amine solvents and their degradation products including the validation.
- Identification of degradation pathways and degradation rate data, in particular any nitroso compounds through a mix of quantum chemistry modelling and laboratory experiment
- Development of dedicated process and equipment models for a better prediction of the emissions through vapour releases and droplet carry-over
- Validation of process models to provide tools useful for prediction of PCC process emissions

In addition to the vapour phase and the liquid entrainment based solvent emissions, it is possible that the fugitive emissions of these solvents may occur through the pipeline joints, valve fittings, instrumentation joints and the solvent storage vents. In a large commercial scale operation capturing million tonnes per annum of CO_2, these emissions to the surrounding atmosphere could be substantial.

1. INTRODUCTION

Previous studies have shown that amine-based CO_2 capture systems are currently the most mature and suitable for fossil fuel-fired power plants. Solvent based post combustion CO_2 capture plants that recycle solvents inside the plant, are known to lose some amount of solvent in the treated gas depending upon its vapour pressure at the operating condition of the plant and its physical carryover due to entrainment in the gas phase. This lost solvent may potentially become emissions from the plant. In addition to the solvent, various thermal and oxidative degradation products that are generated within the plant during the CO_2 absorption and solvent regeneration process may also end up in part as vapour emissions. Whilst the solvent based post combustion CO_2 capture plants have been operating at small capacity (≈ 300 TPD CO_2) around the world since early 70s, the environmental impact of the solvent and its degradation products have become of interest recently due to the perceived need to build such plants at the scale suited for reducing the CO_2 emissions from fossil fuel fired power plants.

In order to control emissions to the atmosphere from future solvent based CO_2 capture plants, it is important to optimise the plant operations at each selected component of the plant and estimate the potential emissions of degradation products along the plant before being emitted to the atmosphere. The understanding of how degradation products are formed under actual plant operations constitutes the first step towards understanding their formation mechanisms. It is generally accepted that a detailed understanding of solvent degradation mechanisms and the impact upon them of plant process parameters is essential to choose an appropriate solvent based post combustion CO_2 capture technology that is likely to cause minimal adverse impact on the environment when implemented for the greenhouse gas emission reduction purposes globally. The review of solvent based commercial technologies for post combustion CO_2 capture shows that aqueous solutions of primary, tertiary and hindered amines such as monoethanolamine (MEA), methyl-diethanolamine (MDEA) and amino-methyl-propanol (AMP) in conjunction with the reaction rate promoters such as piperazine (PZ) are used as the CO_2 solvents.

The report summarises the outcomes related to:

- Effect of process parameters on the formation and emission of potentially harmful compounds (amines, nitrosamines, alkylamines, nitramines, aldehydes)
  - Flue gas composition, CO_2 loading, DCC treatment, absorber, water wash, demister, stripper, reclaimer/reboiler, metallurgy
- Prediction of degradation products (specific or class) of H&E relevance
- Emission estimates, vapour and droplet dominated emissions
- Evaluation and ranking of generic solvents with respect to potential to emit potentially harmful compounds to air.

2. PROCESS DESCRIPTION

2.1 POST COMBUSTION CO2 CAPTURE PROCESS

In a power plant application, a continuous scrubbing system that consists of two main elements an absorber and a stripper is used to separate CO_2 from the other flue gas constituents. The configuration of the typical amine–based CO_2 capture process used during this study is described in the process flow-sheet given in Figure 1. This figure also shows all process equipment included in the process.

The CO_2 capture process releases gas to the atmosphere from the top of the absorber. The released compounds are produced as a result of complex chemical reactions occurring in the process. Some of these products continue to recycle in the plant while others are released to the atmosphere such as amines, ammonia, aldehydes and carboxylic acid.

The operating conditions of the absorber top control the amount of the 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, different parent amine and degradations products may be entrained to the atmosphere.

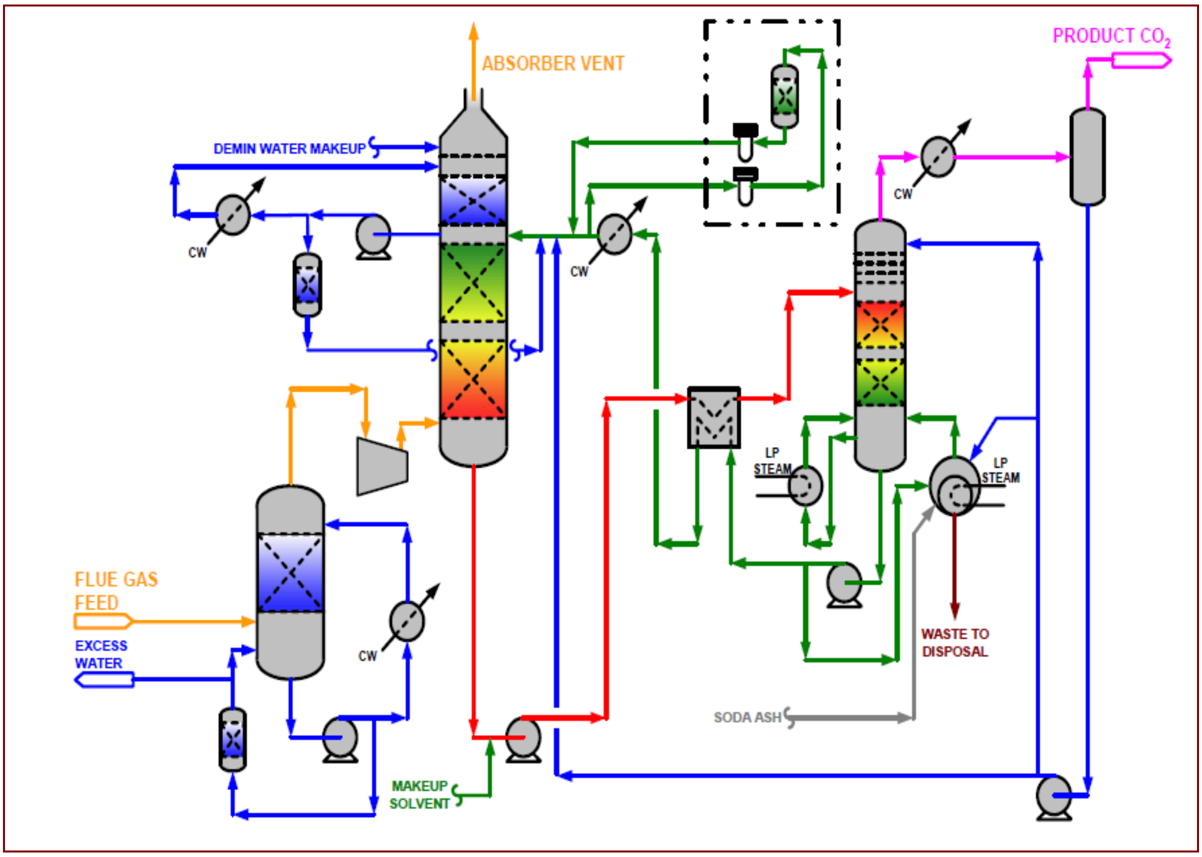


Figure 1 – An amine solvent based process flow sheet for CO_2 capture

During the absorption process the solvent undergoes both thermal and oxidative degradation over a period of time due to high temperature zones around the lean/rich exchanger and the reboiler as well as the dissolved oxygen. As these products build up in the solvent, its efficiency to capture CO_2 drops. To keep the solvent in good condition usually 0.5 to 1% of solvent is periodically taken out of the circulation and passed through a reclaimer where the degradation products are chemically bound using soda ash or caustic soda and sparging live steam through the solvent, allowing the recovery of amine from the overhead vapours. In addition, some amount of lean solvent returning to the absorber is continuously passed through an activated carbon filter (dotted line box) which adsorbs polymeric and acidic degradation products.

2.2 PROCESS INPUT PARAMETERS

The specifications of the flue gas characteristics used during this study are provided by Gassnova SF and given in Table 1. The selected flue gas parameters are generated for a typical gas fired power plant.

Table 1 – Flue Gas Specifications

Property	**Flue Gas**
Temperature to Direct Contact Cooler	120^{o}C
Pressure to Direct Contact Cooler	1.01 Bar(a)
Temperature to Absorber	20-45^{o}C
Composition (mole %)	
CO_2	3.4
N_2	76
O_2	13.8
H_2O	6.8
NO_X	3 ppmV
NH_3	2 ppmV

The flue gas flow rate is kept at 488 kg/s for the present exercise. Since the capture plants operate at steady state conditions, for higher feed gas flow rates, the process requirements such as solvent circulation rate, heating and cooling duties, blower and pump power etc change only proportionately, if identical operating conditions around the absorber and the stripper are maintained.

The chemical solvents that are planned to be used in the current study are given in Table 2.

Table 2 – Generic Solvents and Compositions

Solvent A	**Solvent B**	**Solvent C**
MEA (30 %w/w)	AMP (25 %w/w)	MDEA (25 %w/w)
Water (69 %w/w)	PZ (15 %w/w)	MEA (5 %w/w)
Heat Stable Salts (1 %w/w)	Water (60 %w/w)	Water (70 %w/w)

The capture process conditions used during the model simulations are given in Table 3. These simulations were carried out for two different rates of CO_2 capture of 70% and 90%. The absorber inlet temperature was considered at 20^{o}C, 30^{o}C and 45^{o}C. For each of the inlet temperature the reboiler temperature was considered at 100^{o}C, 110^{o}C, 120^{o}C and 130^{o}C.

Table 3 – CO_2 Capture Process Conditions

Process Condition	**Value**
CO_2 Capture	70%, 90%
Absorber Inlet Temperature (Same for liquid absorbent and flue gas)	20^{o}C, 30^{o}C, 45^{o}C
Reboiler Temperature	100^{o}C, 110^{o}C, 120^{o}C, 130^{o}C

3. SOLVENT DEGRADATION CHEMISTRY

3.1 SOLVENT DEGRADATION PATHWAYS

This section describes reaction pathways which can be, or have been, used for quantifying the emissions and degradation products (in the liquid and gas phase) as a result of the implementation of amine-based technology for the post combustion capture of CO_2. The flue gas stream originating from a fossil fuel fired power plant is a low-pressure and dilute stream that contains low concentrations of CO_2. In such cases, an aqueous alkanolamine solution is the most economical method for CO_2 absorption and separation. The range of alkanolamines studied and tested in the PCC process include:

1. Primary amines (MEA: monoethanolamine; AMP: 2-amino-2-methyl-1-propanol)
2. Secondary amines (DEA: diethanolamine; DIAP: diisopropanolamine; PZ: piperazine)
3. Tertiary amines (TEA: triethanolamine; MDEA: methyldiethanolamine;)

The primary amine monoethanolamine (MEA) is the most widely used solvent for CO_2 absorption mainly because of its high absorption capacity, reactivity with CO_2, high water solubility and low cost. However, MEA has a higher vapour pressure than most secondary and tertiary alkanolamines and degrades in the presence of O_2 (Bello and Idem, 2005). Other studies (Lepaumier, 2009; Lepaumier, 2009) have also demonstrated the impact of CO_2 on amine degradation and chemical stability.

A literature search indicates that the degradation mechanisms for different classes of amine are primarily based on distinct thermal and oxidative mechanisms (Bello and Idem, 2005). Carbamate polymerization is another degradation mechanism as reported by (Veltman, 2010) and occurs at higher temperature conditions in the presence of CO_2. This is most likely to take place in the reclaimer section of the generic PCC flow-sheet. The products formed include ethylenediamine which is a non-volatile compound.

Lepaumier (2009) compared the thermal degradation rates of ethanolamines and ethylenediamines under similar conditions of temperature and time but in the absence of CO_2.The degradation rates were found to be negligible. Thermal degradation of tertiary amines such as MDEA has also been reported (Chakma and Meisen, 1997). For a low temperature application such as the flue gas feed to a PCC plant, the effect of temperature on the formation of degradation products can be considered negligible. However, the degradation rates were substantially increased in the presence of CO_2. Degradation reactions were studied for the following primary, secondary and tertiary amines: MEA, DEA, 2-methyl-amino ethanol (MAE) and N, N, N'-trimethylethylenediamine.

The degradation of amines in the presence of O_2 leads to the formation of carboxylic acids responsible for corrosion and fouling in industrial scale unit operations. The study by Veltman (2010) assumed that ammonia (NH_3) is formed as a primary degradation product for every mole of MEA degraded. Oxidative degradation of MEA and other alkanolamines (DEA, MDEA) has been extensively reported (Meisen and Kennard, 1982). Meisen and Kennard reported the main degradation products as volatile compounds, amines, aldehydes (such as acetaldehyde and formaldehyde), and also carboxylic acids (such as formic and acetic acid etc). The oxidative degradation of tertiary amines (MDEA) gives secondary amines (DEA) together with amino-acids and carboxylic acids. Such products can end up in either the gas phase or liquid phase and may be released into the environment. The carboxylic acids are non-volatile (low vapour pressure) and will be present in the liquid phase of the solvent while the volatile products (high vapour pressure) such as MEA, ammonia, formaldehyde and acetaldehyde will appear in the vapour phase of the absorber/stripper unit operation. Table 4 gives a summary of the degradation products of primary, secondary and tertiary amines. Primary amines degrade mostly to ammonia and imidazolidinones. The secondary amines degrade to cyclic compounds such as piperazines. Tertiary amines degrade by demethylation or dealkylation to form primary and secondary amines. Secondary amines are less stable than primary and tertiary amines as they are more nucleophilic.

Table 4 - Oxidative degradation products of amines (Kennard and Meisen, 1985; Strazisar, 2003; Goff and Rochelle, 2004; Bello and Idem, 2005; Supap, 2006; Bedell, 2009; Freeman, 2009; Lepaumier, 2009, Jackson and Attalla, 2010)

Degradation Products	**Primary amines**		**Secondary amines**		**Tertiary amines**
Compound class	**MEA**	**AMP**	**DEA**	**PZ**	**MDEA**
Amines	Ammonia, ethanamine, methanamine, N-methylenethanamine, 1-propanamine		ethylenediamine		
Diamines				ethylenediamine	
Alcohols	vinyl alcohol, ethanol, 1,2-ethanediol				1,2-ethanediol
Amino Alcohols	2-(methylamino) ethanol, 2-((2-aminoethyl)amino) ethanol, 2,2'-(2-(2-hydroxyethylamino) ethylazanediyl) diethanol	2-methyl-2-(methylamino) propan-1-ol	2-aminoethanol (MEA), N,N,N-tris (hydroxyethyl) ethylenediamine, N,N,N,N-tetra (hydroxyethyl) ethylenediamine, 2,2'-(ethane-1,2-diylbis (azanediyl)) diethanol, triethanolamine (TEA), N,N-bis(hydroxyethyl) ethylenediamine, N-(hydroxyethyl) ethylenediamine		Diethanolamine, triethanolamine, 2-(methylamino) ethanol, 2-(dimethylamino)ethanol
Amides	N-(2-hydroxyethyl) formamide, N-(2-hydroxyethyl) acetamide, 2-hydroxy-N-(2-				

	hydroxyethyl) propanamide, 3-(ethyl(hydroxy) amino)-N-(2-hydroxyethyl) propanamide, 2-hydroxyethylamino-N-hydroxyethylacetamide, N-methylformamide, acetamide				
	MEA	**AMP**	**DEA**	**PZ**	**MDEA**
Aldehydes	2-aminoacetaldehyde, formaldehyde, hydroxyacetaldehyde, acetaldehyde, 2-imidazolecarboxyaldehyde, 1-methyl-2-imidazolecarboxaldehyde				
Acids	acetic acid, butyric acid, propionic acid, 2-aminosuccinic acid, 2-(2-aminoacetamido) acetic acid, oxalic acid, bicine (2-(bis(2-hydoxyethyl)amino) acetic acid), formic acid, glycolic acid, glycine (2-aminoacetic acid),		2-(bis(2-hydroxyethyl) amino) acetic acid, Acetic acid, Formic acid, Glycolic acid	Formic acid	2-(bis(2-hydroxyethyl) amino)acetic acid, Acetic acid, Formic acid, Glycolic acid

	glyoxylic acid, 5-aminopentanoic acid				
Oxazolidinones	2-oxazolidone	4,4-dimethyloxazolidin-2-one, 3,4,4-trimethyloxazolidin-2-one	Oxazolidinone, 3-hydroxyethyl-2-oxazolidinone		
Imidazolidinones	1-(2-hydroxyethyl)-2-imidazolidinone 1,3-bis(2-hydroxyethyl)-2-imidazolidin-2-one	1-(2-hydroxy-2-methylpropan-2-yl)-4,4-dimethylimidazolidin-2-one	N-(hydroxyethyl) imidazolidone, N, N-bis(hydroxyethyl) imidazolidone		
Urea Compounds	Ethylurea N,N'-di(2-hydoryethyl)urea				
Cyclic Compounds			N,N-bis(hydroxyethyl) piperazine 2,2'-(2-(piperazin-1-yl)ethylazanediyl) diethanol N-(hydroxyethyl) ethyleneimine N-(hydroxyethyl) piperazine	N-nitrosopiperazine, N,N-dinitrosopiperazine	

The degradation products associated with the generic solvents are categorised according to different compound classes. The generic solvents include MEA, AMP, PZ and MDEA. Cyclic compounds derived as degradation products from the secondary amines include piperazine derivatives and acids. Such derivates are shown to participate further in the oxidative degradation reactions to form nitrosamine compounds.

Similar to the oxidative degradation induced by O_2 and CO_2, degradation with SOx and NOx has not been extensively studied (Veltman, 2010). SOx degradation gives inorganic acids which are non-volatile, and high SOx levels are likely to result in acidification of the capture amine and associated heat-stable salt problems. NOx degradation mechanism involves the formation of nitrosamines which are an important class of compounds. These compounds are carcinogenic. Generally, nitrosamines are formed from the reaction of nitrite and secondary amines. Such formation reactions occur favourably under low pH conditions and elevated temperatures. Under such condition, nitrites forms nitrous acid (HNO_2) which after protonation and splitting to form NO^+ reacts with amines to produce nitrosamine. However, tertiary amines and quarternary ammonium compounds have also shown to yield nitrosamines (Warthesen, 1975).

The formation of nitrosamines is an important consideration for CO_2 capture in the PCC process (Attalla, 2009; Jackson and Attalla, 2010). Due to the known adverse effects on environment and human health (Wang, 2002), it will have a significant impact on the solvent selection and process configuration in a typical PCC flowsheet. Understanding the reaction mechanism and reaction pathways is critical to controlling the gas phase emissions of such compounds.

Hughes (2008) has described the mechanism of nitric oxide (NO) reaction with oxygen and subsequent formation of nitrosamines. The first product of reaction is NO_2, which reacts with NO in aqueous solution to give N_2O_3. This product is an anhydrous form of nitrous acid. During oxidative degradation of amines, NO act as a nitrosating agent in the presence of O_2. The NO reacts with O_2 to give nitrogen dioxide (NO_2) which dimerizes to give N_2O_4 and dissociates in aqueous solution to give nitrite ion (NO_2^-). The formation of carboxylic acid (from amine degradation) will also help catalyse the formation of N_2O_3. This reaction mechanism is described for low pH (<7) values. However, in the case of amine-based CO_2 capture, the pH is alkaline (pH>7), and an alternate reaction pathways for high pH values are also proposed in which oxides of nitrogen (N_2O_3) and nitrosyl group (NO^+) can initiate nitrosation.

According to Challis (1979) nitrosamines are formed under a wider range of experimental conditions and some conditions are relevant to atmospheric emissions. For the more basic amines, the maximum rates of formation of nitrosamine are in the region of pH 3-4. For neutral and alkaline conditions (pH >=7), the nitrosamine formation has been reported in the presence of formaldehyde to have slower reaction rates, however, the reaction mechanism is not well understood. Secondary amines such as piperidine, morpholine and diphenylamine are nucleophilic and reactive towards nitrosating reagents. They form nitrosamines in the presence of NO at a slow rate (Challis and Kyrtopoulos, 1979). Recent review by (Bråten, 2008) has proposed a theoretical gas-phase degradation mechanism of primary amines as well as formation of nitrosamines which has not been experimentally validated.

Recent work by Jackson and Attalla (2010) has demonstrated the formation of nitrosamines from piperazine (a secondary amine) under the post combustion CO_2 capture conditions. The formation of n-nitrosopiperazine was confirmed based on the laboratory scale experiments. The set-up includes a gas absorption apparatus. A simulated flue gas stream was entrained through an aqueous solution of piperazine (12+-0.5 pH units) and maintained at a constant temperature of 60°C using a water bath. The samples were analysed using API-MS concurrently with pH monitoring. The reaction mixture turned yellow which shows characteristics of aqueous nitrite formation. The pH of the solution remained alkaline (9.0 +-0.5) after 15 hours of operation. The nitrosation mechanism could be based on the potential of individual species such as N_2O_3, N_2O_4, HOONO and OONO radicals. However, the exact mechanism of nitrosation is unclear at this stage.

Statoil has also reported results from their work on assessment of emissions from the amine-based post combustion capture of CO_2 process. An Aminox^{TM} test rig is used to study the performance of amines and emissions of amine and degradation products to the atmosphere (Pedersen, 2010). The research direction is towards identification and understanding the mechanism of formation of potential harmful compounds from the oxidative degradation of amines in the presence of flue gas. Analytical tests conducted on samples show nitrosamines compounds being formed as a result of amine degradation. Results obtained from the Aminox^{TM} test rig indicate that nitrosamines are formed in the presence of NOx at lower rates when compared with autoclave studies.

In summary, for amine-based CO_2 capture, the presence of dissolved oxides of nitrogen has the potential to act as a nitrosating agent for reaction with amines and other intermediate degradation products (acids, aldehydes) originating from secondary amines. Such reactions can lead to the formation of n-nitrosamines, a well known class of undesired industrial and environmental pollutants.

Since amines are used for CO_2 absorption from a flue gas stream, understanding the degradation mechanisms will be complex because of the presence of other gases including CO, CO_2, SOx, NOx, O_2 and particulates. In addition, the feed (flue gas) operating conditions as well as the absorber/stripper will govern the oxidative degradation rates, degradation pathways and the products. In the next sections the steady state emissions from a PCC process based on one of the three generic solvents will be assessed using the Aspen Plus. The assessment was preceded by an analysis of the information in the literature. For the estimation of formation and emission of degradation products only those components for which quantitive data could be extracted from the literature were taken into account.

Given the significance of nitrosamine and the lack of experimental information, it becomes necessary to consider all factors in identifying, quantifying and establishing the mechanism of formation of these degradation products.

Due to the potentially harmful nature of all chemicals with N-NO and N-NO_2 functional groups, the literature covering the thermodynamic properties of those pollutants with this functionality is scarce due to the risks of conducting such research. Most open literature focuses on nitrosamine presence and detection in foodstuffs (Sen et al, 1990; ; Havery et al, 1982; Rappard et al, 1976; Scanlan et al, 1980; Ventanas andRuiz, 2006a; Ventanas and Ruiz, 2006b), cosmetics (Volmer et al, 1996a; Volmer et al, 1996b), cigarette smoke (Jansson et al, 2003; Jacob III et al, 2008; Shah et al, 2009), polluted air (Rounbehler, et al, 1980a; Krost et al, 1982; Tuazon et al,1984; Marano et al, 1982; Rounbehler et al, 1980b) and drinking waters, as a by-product of disinfection (Cheng et al, 2006; Mhlongo et al, 2009; Schreiber and Mitch, 2006). Nitramine data in the open literature is limited to their explosive properties (Leszczynski and co-workers, 2008; Ge et al, 2007; Bernstein and co-workers, 2007), with the exceptions of a few papers dealing with their detection in complex matrices (Tachon et al, 2007; Crescenzi et al, 2007; Groom et al, 2001; Gaurav et al, 2007). The relevance of this information to PCC and any nitrosamines or nitramines that might be derived from capture solvents is questionable. The body of work represents a useful guide for sampling, and useful methods of detection can be identified. For these compounds, thermodynamic data which would be required for process modelling is not available. Note that small, secondary alkylamines are too volatile to be deployed as CO_2 capture solvents at the commercial scale, and there is limited information that suggests that these molecules are either solvent- or atmospheric-chemical degradation products derived from common CO_2-capture amines. The published literature concerning nitrosamine derivatives of small, volatile amines focuses on N-nitrosodimethylamine and other nitrosoalkylamines, specifically their detection. There is some information available for the N-nitroso derivative of diethanolamine (Tunick et al, 1982; Edwards et al, 1979; Flower et al, 2006; Schothorst and Somers, 2005) due to the ubiquity of this alkanolamine in cosmetics.

The chemical mechanisms of nitrosamine formation are ill-defined. A general mechanism has been proposed for solutions at low pH (Wang *et al*, 2002), which is presented below for reference purposes only:

$$NO_2(g) \longrightarrow NO_2(aq) \xrightarrow{H_2O} HONO(aq)$$

$$HONO(aq) \xrightarrow{H^+} H_2ONO^+(aq) \longrightarrow H_2O + NO^+(aq)$$

$$NO^+(aq) + R_1R_2NH(aq) \longrightarrow R_1R_2NNO(aq) + H^+$$

Scheme 1. Mechanism of nitrosamine formation at low pH from secondary amines.

There are a number of reasons cited for the *instability* of nitrosamines derived from primary amines; Scheme 2 is a proposed mechanism for the *degradation* of primary nitrosamines at low pH (Wang *et al*, 2002). The reaction scheme follows from Scheme 1 above, however one of R_1 or R_2 in the case of a primary amine in Scheme 1 is a hydrogen atom:

$$R_1HNNO(aq) + H^+ \longrightarrow R_1HNNOH^+(aq)$$

$$R_1HNNOH^+(aq) \xrightarrow{\text{H-shift}} R_1NNOH_2^+(aq) \longrightarrow R_1NN^+ + H_2O(aq)$$

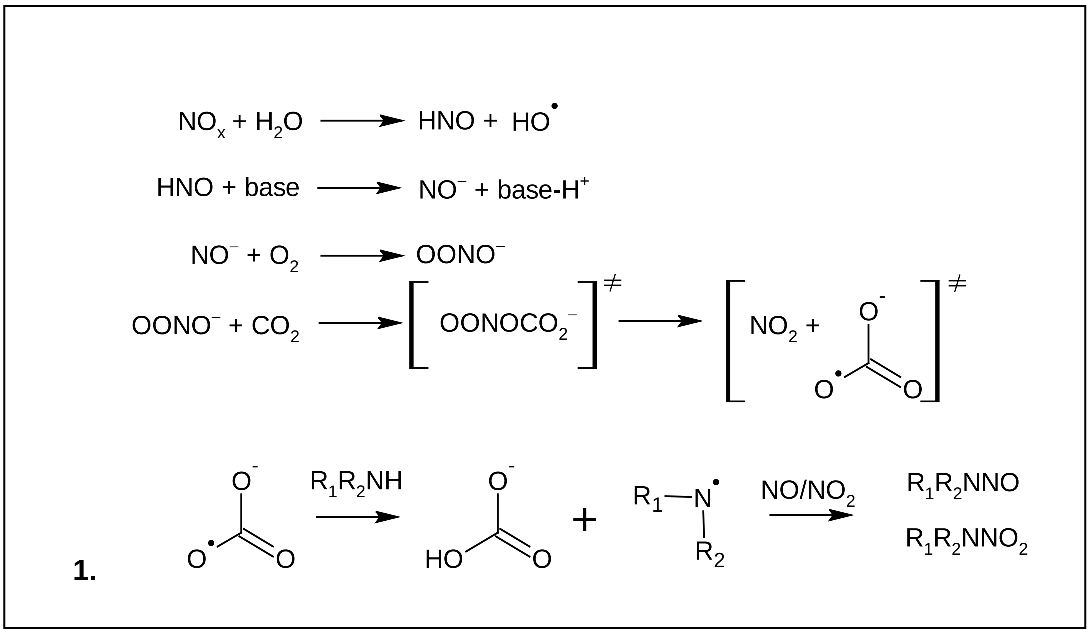
$$R_1NN^+(aq) \longrightarrow R_1^+(aq) + N_2$$

Scheme 2. Mechanism of primary amine nitrosamine decomposition at low pH.

A number of nitrogen oxides have the potential to form nitrosamines (e.g. HNO, N_2O_3, N_2O_4, NO^+, ONOO (Challis and Kyrtopolous, 1979; Hughes 2008; Hughes 1999). At neutral (physiological) pH, Goldstein and Czapski (1996) derived a rate law for the nitrosation of thiols and morpholine in oxygenated solution, which was found to be independent of the substrate being nitrosated:

$$-d[NO]/dt = 4k\,[NO]^2[O_2] \tag{1}$$

This is essentially identical to the rate law for oxidation of NO to NO_2. Reaction of O_2 with $NO^{\square}$ (generated by dissociation of nitroxyl acid, HNO) produces peroxynitrite ion, $ONOO^{\square}$. This ion reacts rapidly with CO_2 to form $ONOOCO_2^{\square}$ (Hughes, 2008). Disproportionation of the nitrosoperoxycarbonate anion yields $CO_3{\bullet}^{\square}$ + $\bullet NO_2$; the former species can react to abstract a hydrogen atom from an amine substrate to form a radical aminyl species and $HCO_3^{\square}$. Subsequent reaction with either NO or NO_2 (which are both radicals) will yield a nitrosamine or nitramine. During the disproportionation process, NO_2 could oxidise the aminyl substrate to produce an N-oxide derivative and NO. CSIRO have detected an N-oxide derivative in 15 % wt solutions of piperazine sparged with a synthetic flue gas (Jackson and Attalla, 2010). Based on this information, the most probable mechanism of nitrosamine/nitramine formation under PCC capture conditions is presented in Scheme 3.



Scheme 3. Proposed mechanism of nitrosamine formation at high pH.

SOLVENT A

Whilst MEA is stable at around 120°C, i.e. the usual reboiler temperature for industrial operations - it undergoes oxidative degradation at this temperature due to presence of NO_2 and oxygen in the flue gas and air ingress through the equipment joints. In addition, MEA undergoes thermal degradation by reacting with the dissolved CO_2 to form Oxazolidone-2, 1-(2 Hydroxyethyl) imidazolidone-2 (HEIA) and N-(2-Hydroxyethyl)-ethylenediamine (HEEDA) (Idem et al, 2007). The ethylenediamine derivative is hard to decompose to regenerate MEA and it promotes plant material corrosion especially when the partial pressure of CO_2 is high. 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:

$$C_2H_7NO + 0.5O_2 \Leftrightarrow H_2NCH_2COH + H_2O \text{ -------------(1)}$$

$$C_2H_7NO + O_2 \Leftrightarrow H_2NCH_2COOH + H_2O \text{ ----------(2)}$$

$$2C_2H_7NO + O_2 \Leftrightarrow 2CH_3COOH + NH_3 \text{ --------------(3)}$$

$$C_2H_7NO + 1.5O_2 \Leftrightarrow 2CHOOH + NH_3 \text{ ------------------(4)}$$

$$C_2H_7NO + 2O_2 \Leftrightarrow HOCOCOOH + NH_3 + H_2O \text{ ------(5)}$$

These products are more acidic than CO_2. They react with MEA and with the plant metallurgy to form heat stable salts. 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 reported that the formates and acetates comprise nearly 90% of the heat stable salt material.

The MEA degradation rate due to reaction with oxygen has been studied by Goff and Rochelle (2004) for flue gas containing 3% CO_2 and 5% oxygen in a large scale laboratory study and this data has been used by Veltman et al (2010) to calculate annual MEA loss during CO_2 capture from a 420 MW natural gas based combined cycle power plant. The kinetics of oxidation degradation and formation of heat stable salts during CO_2 absorption by aqueous MEA and its regeneration has been studied by Idem et al (2007) and these investigators recommended the following rate expression to account for the presence of heat stable salts in the amine solvent circulating between the absorber and the regenerator.

$$-R_{MEA} = K{*}e^{-E/RT}{*}(MEA)^{1.91}{*}(CO_2)^{-0.33}\{(SO_2)^{3.42} + (O_2)^{2.78}$$

Where,

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

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

K= 0.00745, E=45.3, T is the absorber and/or stripper absolute temperature

The above rate expression is valid for the following conditions:

- MEA concentration in the range 3 to 7 mol/L,
- temperature in the range of 55 to 130°C reflecting the extremes of absorber and stripper temperatures,
- O_2 concentration ranging from 6 to 100 mol%,
- SO_2 concentration ranging from 6 to 196 ppmV and,
- the total pressure up to 250 kPa.

This relationship was used in the ASPEN simulation using the formic acid and ammonia formation equilibrium reaction (4) within the absorber and stripper to account for the oxidative degradation of solvent and presence of 1% heat stable salt in the circulating amine solution. Since the flue gas for the present study does not contain SO_2, its contribution to the MEA degradation was considered as nil. To avoid the build-up of heat stable salts during solvent recirculation, ASPEN simulation was adjusted to divert around 0.7%w/w of solvent through the reclaimer.

There is very little information available in the public domain on 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 by exposing 30 to 40 wt% MEA solution at CO_2 absorber (44°C temperature) and stripper (120°C) conditions to 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. 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) nitrosamine (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. Jackson and Attalla have recently detected NDELA formation under PCC-like conditions with a synthetic flue gas containing 8000 ppm NO_x.

Strazisar et al (2003) report to have observed the presence of ‘nitrosamine compounds’ in a lean MEA solution in the 800 TPD post combustion CO_2 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 NO_2, as a contaminant, was included in the quantification of nitrosamines which would lead to an overestimation of the anolyte species.

For the purpose of this study only, the ASPEN process modules were adjusted to include the presence of dimethyl-nitrosamine ($C_2H_6N_2O$) and diethyl-nitrosamine ($C_4H_{10}N_2O$) that are available in the ASPEN library. No attempt was made to include other compounds due to the lack of available information in the literature on the nitrosamines of interest that is available in a form to be included into ASPEN. This unfortunately is a major limitation of the software and approach to this study.

It should be ***noted unequivocally*** that there is no experimental or theoretical evidence that these particular nitrosamines (dimethyl-nitrosamine ($C_2H_6N_2O$) and diethyl-nitrosamine ($C_4H_{10}N_2O$)) will be present in a PCC process. However, for the purpose of development of the ASPEN model method these two nitrosamines were simulated in the lean MEA solution and their vapour phase. As a starting point, vapour phase calculations for concentrations at 0.1, 1 and 2.91 µmol/mL of lean MEA solution were carried out.

3.3 SOLVENT B

AMP is a hindered primary amine and there is general evidence in the literature (Lepaumier et al, 2009a, 2009b) that its steric hindrance causes this amine to be more resistant to oxidative degradation in comparison with MEA (solvent A). Piperazine (PZ) is used as an absorption rate promoter that remains thermally stable even at 150°C. Since the CO_2 absorber and the stripper are usually operated at around 120°C for the post combustion capture applications, the thermal degradation of PZ does not seem to be a well studied issue at present. Nevertheless, Closmann and Rochelle (2010) and Freeman et al (2010) have very recently started to investigate both thermal and oxidative degradation of PZ during CO_2 absorption. Jackson et al (2010) report that PZ – a secondary amine - reacts slowly with NO_X in the presence of oxygen to form a nitrosamine derivative under conditions similar to those found in industrial amine based post combustion CO_2 capture processes. These investigators detected N-nitrosopiperazine, N-oxopiperazine and piperazine nitramine in the aqueous solution of 15 wt% PZ when the virgin solution was exposed to synthetic flue gas containing 12.8 vol% CO_2, 5 vol% oxygen and 0.8 vol% NO at 40°C and sampled at three hour intervals. Experiments undertaken at 700 ppm NO_x over a 15 day period have also demonstrated N-nitrosopiperazine formation (Jackson and Attalla, 2010). The results of this work, which is ongoing, are insufficiently detailed to enable the estimation of a reaction rate in dependence of for instance, the oxygen and NO_x concentration in the flue gas.

Thus, the literature survey so far indicates that there is a huge gap in the knowledge base for determining the thermal and oxidative degradation products of AMP and PZ at the operating plant conditions for post combustion capture. The kinetics of degradation products formation are not insufficiently investigated and as a result, it is impossible to predict the vapour phase levels of degradation products from a post combustion CO_2 capture plant using the ASPEN process simulator type tools. In light of this difficulty, the ASPEN simulation based estimation of vapour phase concentration in the case of Solvent B was restricted to determining such quantities for AMP, PZ and ammonia only.

3.4 SOLVENT C

Whilst thermal and oxidative degradation of MEA is well studied, MDEA degradation has been relatively less investigated. Chakma and Meisen (1977) have reported thermal degradation of 20 to 50 %w/w aqueous MDEA in the presence of dissolved CO_2 but no oxygen around. To determine the rate kinetics in a short time frame, they conducted the degradation experiments in an autoclave at 2.58 MPa partial pressure of CO_2 and in the temperature range 100 to 200°C. Thus their MDEA degradation environment was not only incomplete (lack of oxygen) but far more severe than what is encountered in a post combustion capture plant. In addition, the alkanolamine degradation products are known to occur via a number of parallel and series reactions with several intermediate transient compounds. In such a situation, it is difficult to transpose with confidence what is observed in laboratory to an industrial plant environment where solution is often cycled for weeks through absorption/regeneration steps. Nevertheless, Chakma and Meisen concluded that at 180°C, N, N-bis-(2-hydroxyethyl)-piperazine (BHEP), 2-dimethylamino ethanol (DMAE), ethylene glycol and 1- (2-hydroxyethyl)-4-methyl piperazine (HMP) were the main degradation products and these products occurred via formation of ethylene oxide (EO), diethanolamine (DEA) and DMAE according to the following equilibrium reactions:

$$\mathrm{MDEA} + CO_2 + H_2O \Leftrightarrow \mathrm{MDEAH}^+ + HCO_3^- \quad \ldots.(1)$$

$$\mathrm{MDEAH}^+ + \mathrm{MDEA} \Leftrightarrow \mathrm{DMAE} + \mathrm{EO} + \mathrm{DEA} \quad \ldots\ldots\ldots(2)$$

For the Reaction (2), Chakma and Meisen propose the rate constant, K, as 2.34E-04 sec^{-1} and the activation energy, E, as 50.9 kJ per mole.

Rooney et al (1998) have studied degradation of 30 %w/w aqueous MDEA at 82°C in the presence of both CO_2 and oxygen and determined that after 28 days of constant exposure, MDEA degraded to acetate (449 ppm), formate (249 ppm), glycolate (704 ppm) and diethanolamine (1614 ppm). No ammonia formation was detected in their experiments. These authors, however, did not determine any reaction rate constants, activation energies or stoichiometry for the degradation chemistry.

In light of the limited data available in the public domain literature on the kinetics of MDEA degradation, only the formation of 2-dimethylamino ethanol (DMAE), ethylene glycol and diethanolamine (DEA) was considered in ASPEN simulations. The degradation of MEA and the possibility of nitrosamine formation were kept in this case same as those for the Solvent A.

4. ESTIMATION OF PCC PROCESS EMISSIONS

4.1 ASSUMPTIONS AND CONSIDERATIONS FOR PROCESS SIMULATIONS

With the specifications for flue gas, CO_2 capture solvents and operating process conditions defined in section 2.2, the ASPEN process simulator (White, 2002) was used to predict the gas phase concentrations of solvents and their degradation products that may be produced during the capture process. A generic process flow sheet (Figure 1) that represents the industrial process concept based on the standard amine based post combustion capture process was adopted for the simulation. For each solvent, the available information on its degradation chemistry at the operating process conditions during CO_2 capture process was sought from the public domain literature and incorporated into the ASPEN process model where sufficient and reliable degradation data was available. The literature data on the degradation chemistry for each solvent are described further below.

The CO_2 absorber was assumed to have 3 theoretical stages whereas the solvent regenerator (stripper) was assumed to have 12 theoretical stages. Both the absorber and the stripper were assumed to operate at chemical and phase equilibrium conditions. The electrolyte NRTL model from ASPEN's property data bank was used to track the ionic species generated during the CO_2 absorption/regeneration process and determine the overall physical properties of various process streams. Where the ASPEN chemical data bank recognised the solvent degradation product but had limited physical property data for it, the "Group Theory" based predictive capability of ASPEN process simulator was used to provide the missing information. Since ammonia is present in the flue gas stream and when dissolved in water, it forms ammonium and hydroxyl ions which react with carbonate and bi-carbonate ions generated from dissolution of CO_2 in water, the reaction between ammonia and carbon dioxide in the aqueous phase was incorporated into the ASPEN process model.

For the solvents A, B and C, the process chemistry of CO_2 absorption is as below.

Solvent A

$$MEA + CO_2 + H_2O \Leftrightarrow MEACOO^- + H_3O^+ \quad .....(1)$$

$$MEACOO^- + H_2O \Leftrightarrow MEA + HCO_3^- \quad ....(2)$$

$$MEA + H_3O^+ \Leftrightarrow MEAH^+ + H_2O \quad ....(3)$$

$$CO_2 + 2H_2O \Leftrightarrow HCO_3^- + H_3O^+ \quad ....(4)$$

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \quad ....(5)$$

$$CO_2 + OH^- \Leftrightarrow HCO_3^- \quad ....(6)$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+ \quad ....(7)$$

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \quad ....(8)$$

$$NH_3 + CO_3^{2-} \Leftrightarrow NH_2COO^- + OH^- \quad ..(9)$$

NH_4HCO_3 (solid) $\Leftrightarrow NH_4^+ + HCO_3^-$ ……(10)

Reactions 1 and 6 were assumed to be kinetics controlled whereas the other reactions were at equilibrium.

Solvent B

$AMP + CO_2 + H_2O \Leftrightarrow AMPH^+ + HCO_3^-$ …..(1)

$AMPH^+ + H_2O \Leftrightarrow AMP + H_3O^+$ ………(2)

$CO_2 + 2H_2O \Leftrightarrow HCO_3^- + H_3O^+$ ……..(3)

$2H_2O \Leftrightarrow H_3O^+ + OH^-$ ……..(4)

$CO_2 + OH^- \Leftrightarrow HCO_3^-$ ……..(5)

$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$ ……..(6)

$PZ + CO_2 + H_2O \Leftrightarrow PZCOO^- + H_3O^+$ …..(7)

$PZ + H3O^+ \Leftrightarrow PZH^+ + H_2O$ …….(8)

$PZ + HCO_3^- \Leftrightarrow PZCOO^- + H_2O$ …….(9)

$PZCOO^- + H3O^+ \Leftrightarrow HPZCOO + H_2O$ --------(10)

$PZCOO^- + H_2O + CO_2 \Leftrightarrow PZCOO^{2-} + H_3O^+$ ……(11)

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$ …….(12)

$NH_3 + CO_3^{2-} \Leftrightarrow NH_2COO^- + OH^-$ …....(13)

NH_4HCO_3 (solid) $\Leftrightarrow NH_4^+ + HCO_3^-$ ……(14)

Reactions 1, 5, 7 and 11 were assumed to be kinetics controlled whereas the other reactions were at equilibrium.

Solvent C

$MDEA + CO_2 + H_2O \Leftrightarrow MDEAH^+ + HCO_3^-$ ….(1)

$MDEAH^+ + H_2O \Leftrightarrow MDEA + H_3O^+$ ………(2)

$MEA + CO_2 + H_2O \Leftrightarrow MEACOO^- + H_3O^+$ …..(3)

$MEACOO^- + H_2O \Leftrightarrow MEA + HCO_3^-$ ………(4)

$MEA + H_3O^+ \Leftrightarrow MEAH^+ + H_2O$ …….(5)

$$CO_2 + 2H_2O \Leftrightarrow HCO_3^- + H_3O^+ \quad ....(6)$$

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \quad ....(7)$$

$$CO_2 + OH^- \Leftrightarrow HCO_3^- \quad ....(8)$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+ \quad ....(9)$$

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \quad ....(10)$$

$$NH_3 + CO_3^{2-} \Leftrightarrow NH_2COO^- + OH^- \quad ..(11)$$

$$NH_4HCO_3 \text{ (solid)} \Leftrightarrow NH_4^+ + HCO_3^- \quad ......(12)$$

Reactions 1, 3 and 8 were assumed to be kinetics controlled whereas the other reactions were at equilibrium.

For each case of solvent, ASPEN process simulations were performed at varying CO_2 inlet loading to the absorber in order to determine an optimum loading with respect to the reboiler duty. At this optimum loading, the obtained values for solvent emissions represent the theoretical vapour phase loss of solvent in the treated flue gas for various plant operating conditions.

In practice, the process solvent is lost due to physical liquid entrainment in the treated gas, vapour phase carryover in the treated gas and solution degradation. In industrial practice, the physical liquid entrainment losses from the absorber are minimised by a Chevron type mist eliminator between the absorption section and the wash section, and a wire-mesh mist eliminator at the top of the absorber. Generally, it is difficult to estimate this loss accurately since it is influenced by a number of competing factors such as the design of absorber internals, hydrodynamics within the absorber, the impact of heat stable salts (formed during absorption) on the density, viscosity and surface tension of the solvent, the type of demister used in the absorber and the wash water circulation rate. In addition, at the operating temperature of the wash section, the CO_2 capture solvent and its likely degradation products are dissolved in the water droplets carried past the wire-mesh mist eliminator according to their solubility limits and hence an accurate estimate of the carried over liquid phase loss of solvent and its degradation products requires knowledge of the droplet size distribution, the droplet flux and the liquid phase chemical concentrations.

Nevertheless, Veldman et al (1989) suggest that in an amine based CO_2 capture plant, entrainment can lead to the emission of up to 8.5 mg amine per Nm^3 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 m^3 per million m^3 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 a 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.

It was assumed that the utility cooling and the process wash water is available with sufficient heat sink capacity such that the treated gas at the exit of the absorber has the temperature same as the flue gas temperature at the inlet to the absorber. The ASPEN simulation ensured that the low temperature treated gas is allowed to receive heat from the raw flue gas at 120^{o}C to obtain sufficient thermal buoyancy for release through a conventional gas exhaust chimney prior to leaving the capture plant.

In addition to the vapour phase amine loss, the following process performance parameters were obtained through the ASPEN simulations:

- Specific solvent rate
- Specific thermal energy requirement for the solvent regeneration
- Specific cooling duty
- Specific power requirement for fan and pumps.

4.2 PCC PROCESS EMISSIONS FOR SOLVENT A

Figures 2 to 10 show the main results of the ASPEN process simulations for the Solvent A (MEA -30% w/w, Water - 69% w/w and heat stable salts – 1% w/w) based post combustion CO_2 capture.

Figures 2 and 3 give the specific thermal energy requirement as a function of absorber inlet temperature for 70% and 90% removal of CO_2.

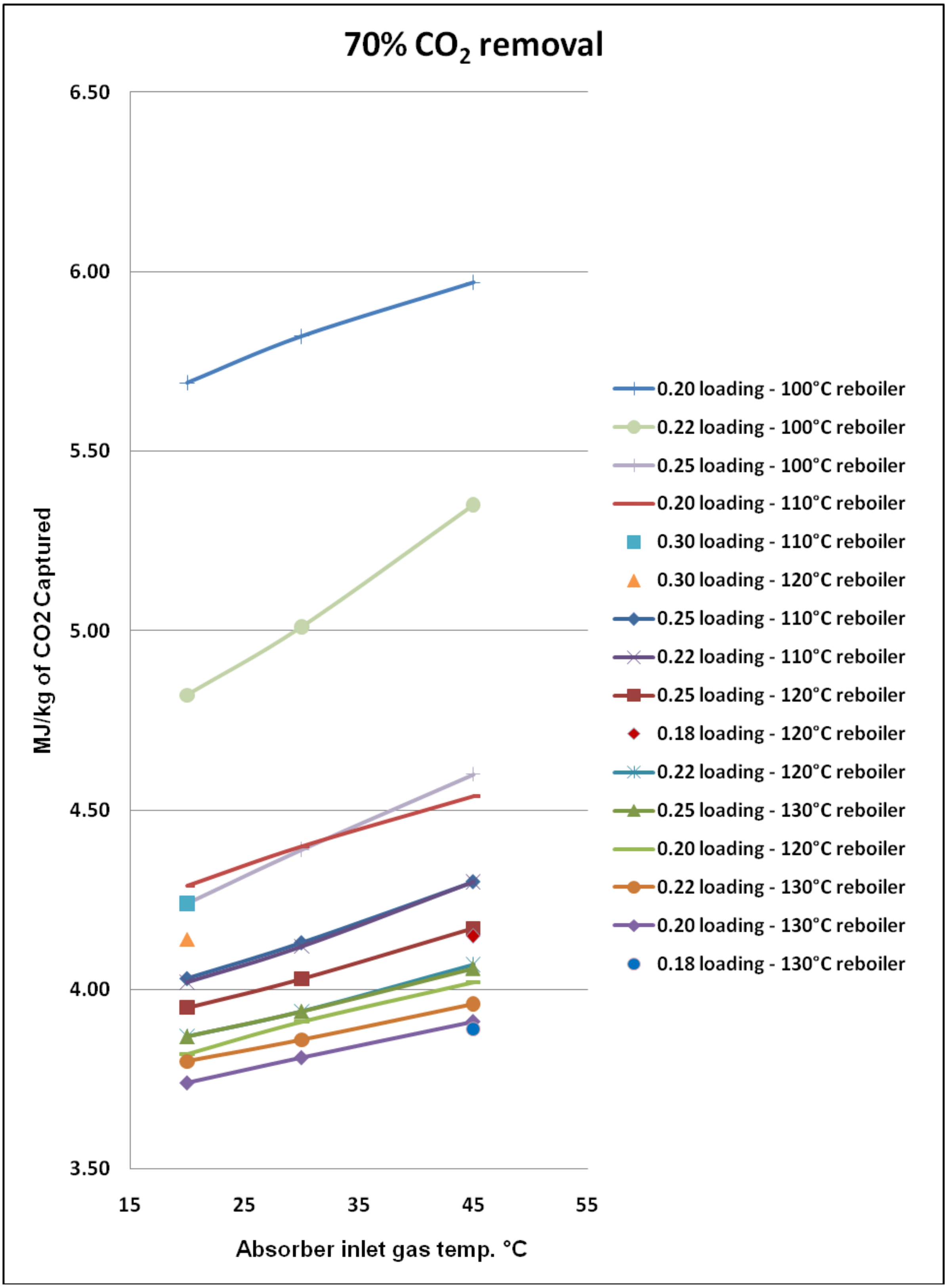


Figure 2 – Specific thermal energy requirement for 70% CO2 recovery, Solvent A

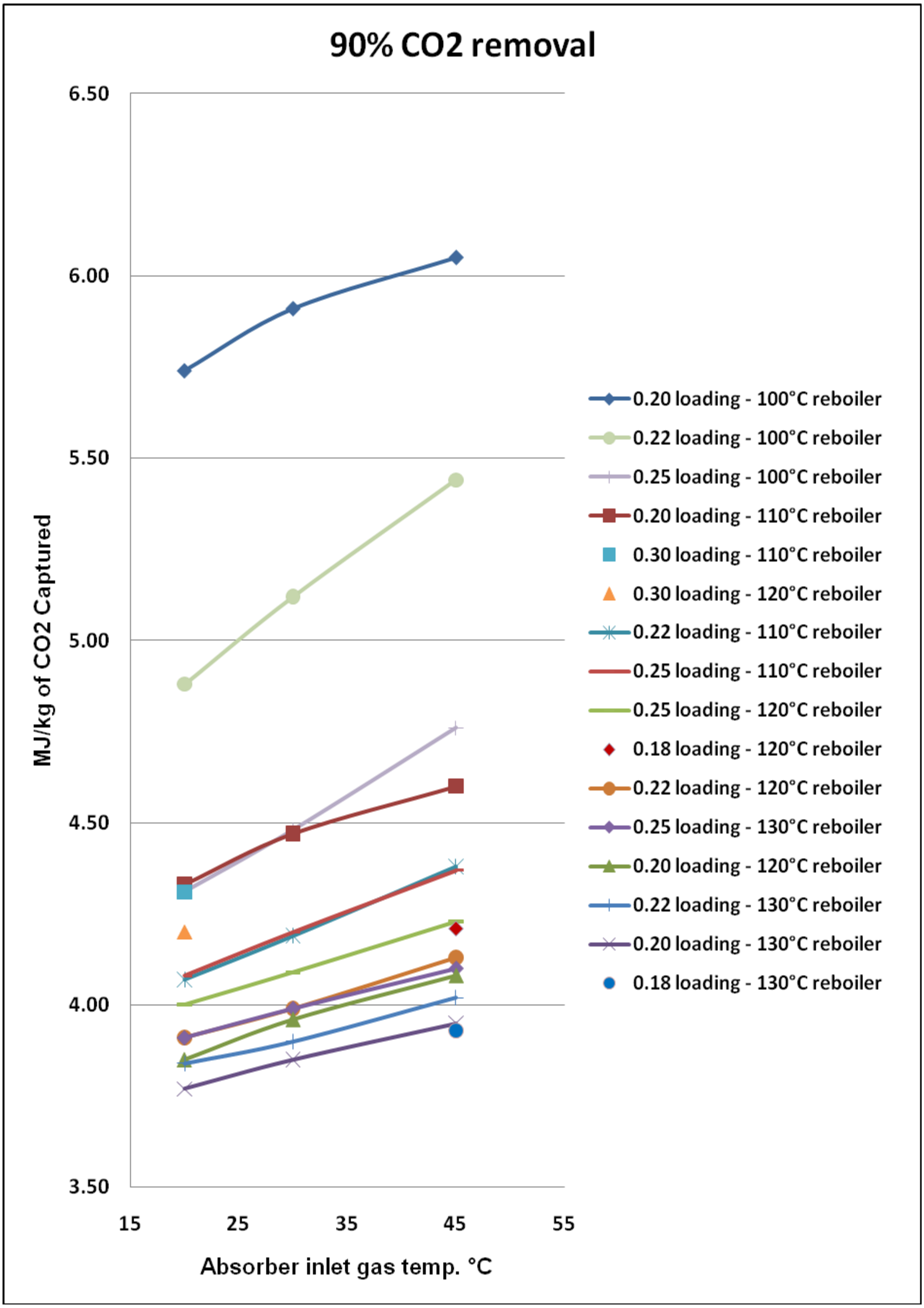


Figure 3 – Specific thermal energy requirement for 90% CO2 recovery, Solvent A

The specific thermal energy varies from 6.1 to 3.7 MJ per kg of CO_2 captured depending upon the CO_2 loading of the lean MEA solvent, flue gas temperature at the inlet of the absorber, the reboiler temperature and the extent of CO_2 recovery desired. At a given lean solvent loading the specific thermal energy requirement is lowest at the lowest gas inlet temperature as a result of the higher capacity of the solvent at lower temperature. At 70% and 90% CO_2 recovery levels, the optimum CO_2 loading of the lean MEA lies in the range 0.18 to 0.22 mole of CO_2 per mole of amine and the preferred operating value is 0.2 in terms of minimum specific thermal energy requirement for the solvent regeneration, when the reboiler operating temperature is in the range 110 to 130^{o}C. If the reboiler temperature drops to 100^{o}C, then higher loading is required to reduce the reboiler specific heat duty. Usually, in actual practice the reboiler is operated at 120^{o}C for the post combustion capture processes since exceeding the temperature above 130^{o}C causes rapid thermal degradation of the MEA solvent.

Figure 4 representing the specific solvent circulation rates further supports the above conclusion that 0.2 inlet loading is optimum in terms of reducing the solvent circulation rate to a minimum so that the plant equipment in the liquid circulation loop is most compact.

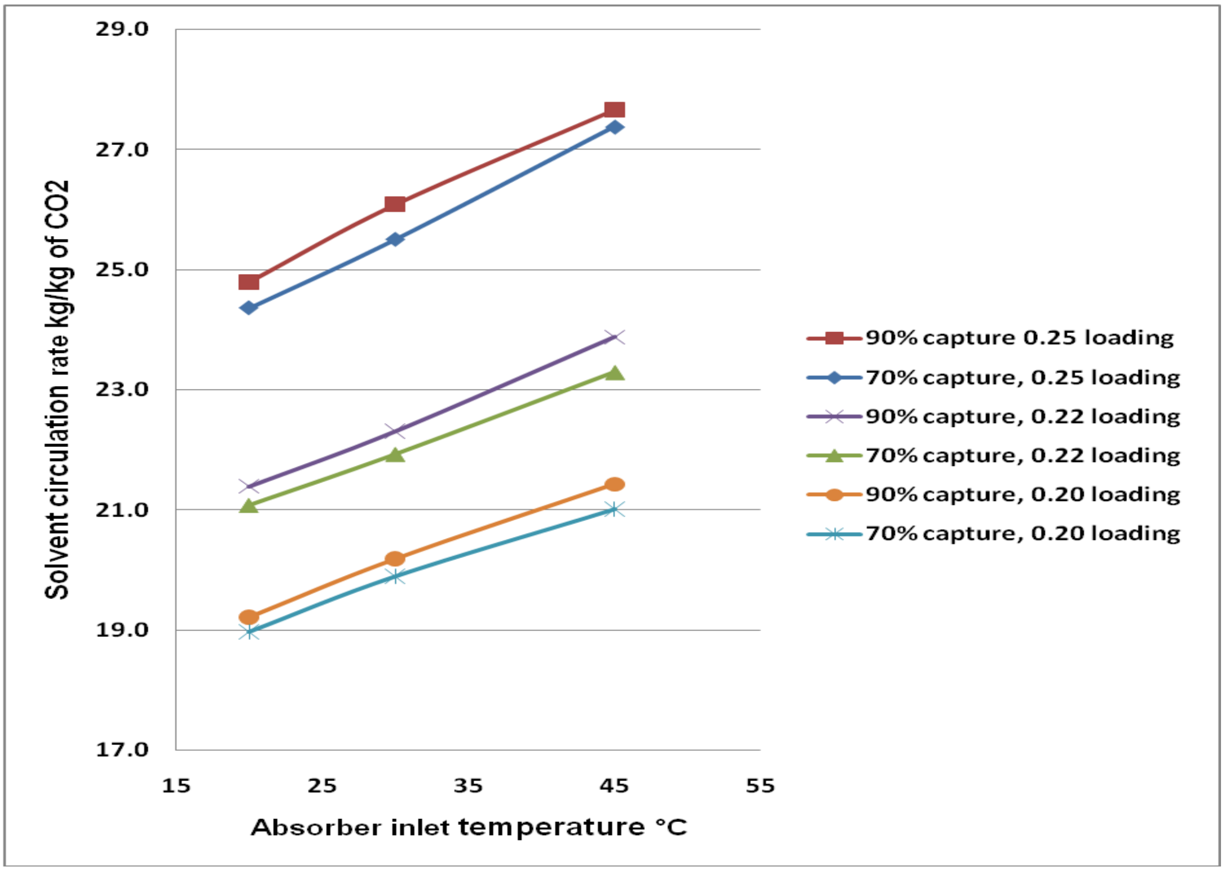


Figure 4 – Specific solvent circulation rate during CO2 capture, Solvent A

Figure 5 depicts the specific water production as a function of inlet gas temperature. It shows that when the flue gas is cooled to below 40°C prior to entering the absorber, the capture process will produce sufficient water to meet the wash water requirement to reduce the MEA emissions in the vapour phase. However, above this temperature, the process actually requires water to both cool the gas and lower the MEA emissions. It should be noted that in calculating the wash water requirement, care is taken that no excess waste water is created.

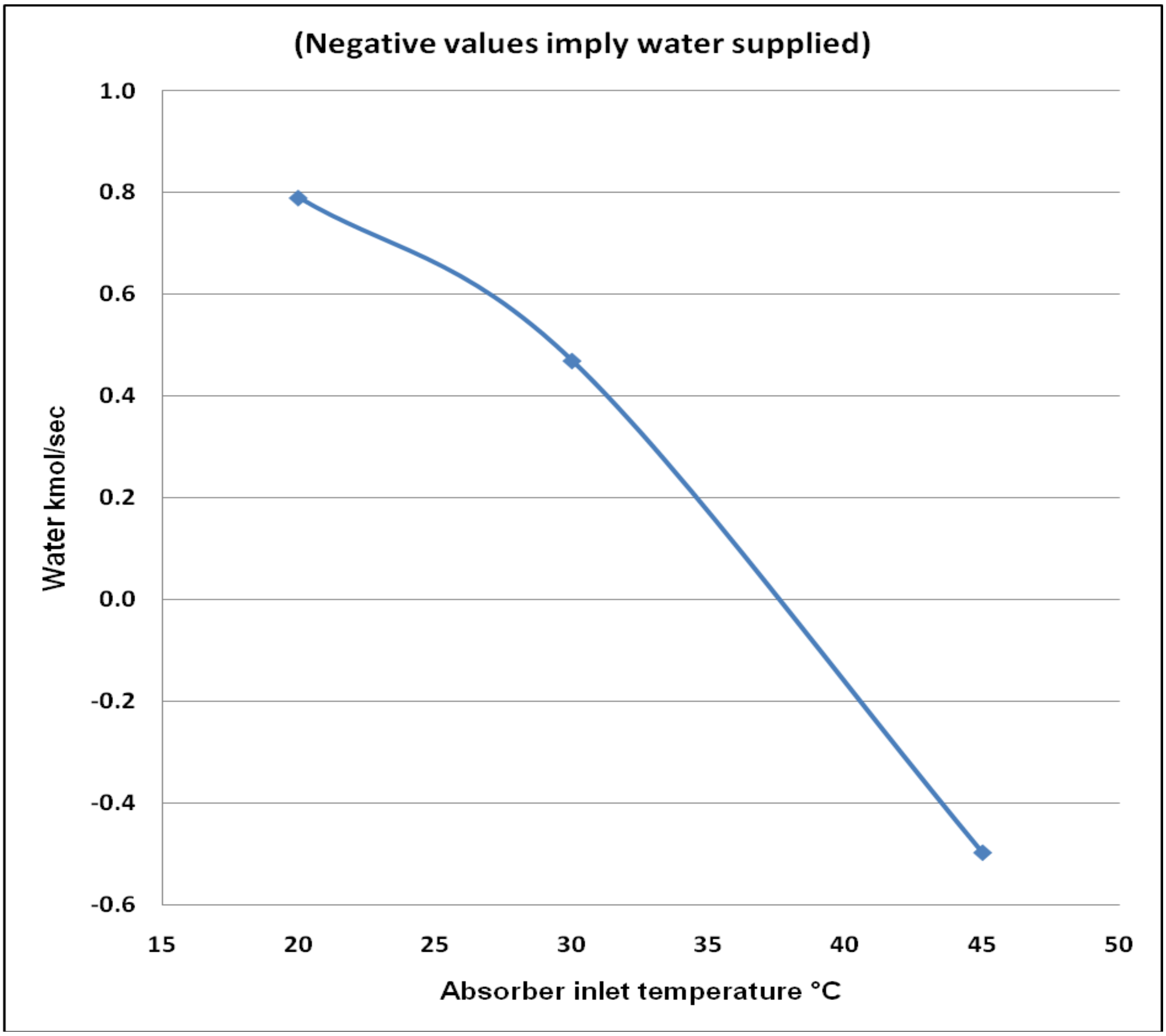


Figure 5 – Specific water consumption during CO2 capture, Solvent A

Table 5 presents values for the MEA vapour losses form from the absorber as a function of amine loading, flue gas temperature at inlet to the absorber and % CO_2 capture.

Table 5 – MEA Vapour losses from absorber as a function of CO_2 loading of Solvent A

Solvent A - Reboiler Temperature - 120°C		**20°C Absorber**		**45°C Absorber**	
	CO2 Capture (%)	**70**	**90**	**70**	**90**
CO2 Loading (mole/mole)	**Component (g/ton)**				
0.20	MEA	4.19E+02	6.11E+02	2.28E+03	3.03E+03
0.22	MEA	3.99E+02	5.63E+02	2.29E+03	2.99E+03
0.25	MEA	3.62E+02	4.82E+02	2.24E+03	2.85E+03
0.30	MEA	2.84E+02	3.35E+02	2.11E+03	2.41E+03

The results in table 5 indicate that at higher lean loading the emissions will be lower, despite the increased solvent flow rates. This is the result of the lower concentration of free MEA in the solution when the solution has a higher lean loading. Results from pilot plant experiments carried out at CSIRO's PCC pilot plant at Loy Yang Power in Victoria, Australia, indicated that the emissions from the absorber were indeed higher at low lean loadings (Feron, 2009). Hence the ASPEN Plus modelling results are in agreement with the PCC pilot plant observations.

Next table 6 presents values for the MEA emissions to the atmosphere both in the vapour form and droplets form as a function of amine loading, flue gas temperature at inlet to the absorber and % CO_2 capture required. These emissions have been calculated as g per tonne of CO_2 captured after washing the gas that leaves the absorber section with demineralised water in the wash tower. The droplet phase emissions of MEA have been calculated assuming the droplet composition same as that of the circulating wash water in the wash tower and the liquid entrainment past the demister in the wash section is 0.13 m^3 per million m^3 of treated gas as proposed by the Handbook from Gas Processors Suppliers' Association (2004).

The results in table 6 show that both the vapour phase and droplet form emissions increase with rising flue gas temperature at the inlet to the absorber and at higher level of % CO_2 captured required but remain more or less same for various amine loading conditions. This is so because the CO_2 lean flue gas temperature at the outlet of the wash tower is kept the same as at the inlet to the absorber. Furthermore the results show little impact of the lean solvent loading on the emissions, after the wash section. The process modelling results seem to indicate that the wash section is effective in reducing the effect of the higher MEA vapour at lowest lean solvent loadings. Unfortunately, within CSIRO no pilot plant results are available with an operational wash section for direct comparison of amine losses.

Table 6 – MEA emissions as a function of CO_2 loading of Solvent A

Solvent A		**Absorber Inlet Temperature - 20°C, Reboiler Temperature - 120^{o}C**					
		Vapour		**Droplet**		**Total**	
	CO_2 Capture (%)	**70**	**90**	**70**	**90**	**70**	**90**
CO_2 Loading (mole/mole)	**Component (g/tonne of CO_2)**						
0.20	MEA	1.21E-02	5.86E-02	8.63E+00	1.12E+01	8.64E+00	1.13E+01
0.22	MEA	1.21E-02	5.79E-02	8.64E+00	1.11E+01	8.65E+00	1.12E+01
0.25	MEA	1.18E-02	5.65E-02	8.54E+00	1.09E+01	8.55E+00	1.10E+01
0.30	MEA	1.17E-02	5.91E-02	8.50E+00	1.13E+01	8.51E+00	1.13E+01

Solvent A		**Absorber Inlet Temperature - 45°C, Reboiler Temperature - 120^{o}C**					
		Vapour		**Droplet**		**Total**	
	CO_2 Capture (%)	**70**	**90**	**70**	**90**	**70**	**90**
CO_2 Loading (mole/mole)	**Component (g/tonne of CO_2)**						
0.20	MEA	6.11E+00	1.11E+01	4.59E+01	4.80E+01	5.20E+01	5.91E+01
0.22	MEA	6.11E+00	1.12E+01	4.59E+01	4.82E+01	5.20E+01	5.94E+01
0.25	MEA	6.07E+00	1.13E+01	4.56E+01	4.87E+01	5.17E+01	6.00E+01
0.30	MEA	6.12E+00	1.21E+01	4.59E+01	5.22E+01	5.21E+01	6.44E+01

Figure 6 below shows the vapour phase emissions of MEA and its degradation products including the heat stable salts (as equivalent formic acid emissions) in the treated gas both before and after washing the gas with cold demineralised water. These emissions have been calculated as g per tonne of CO_2 captured and as a function of absorber inlet temperature for the case of optimum plant operating condition, i.e. CO_2 loading of 0.2 mole per mole of lean amine at inlet to the absorber and the reboiler operating at 120^{o}C.

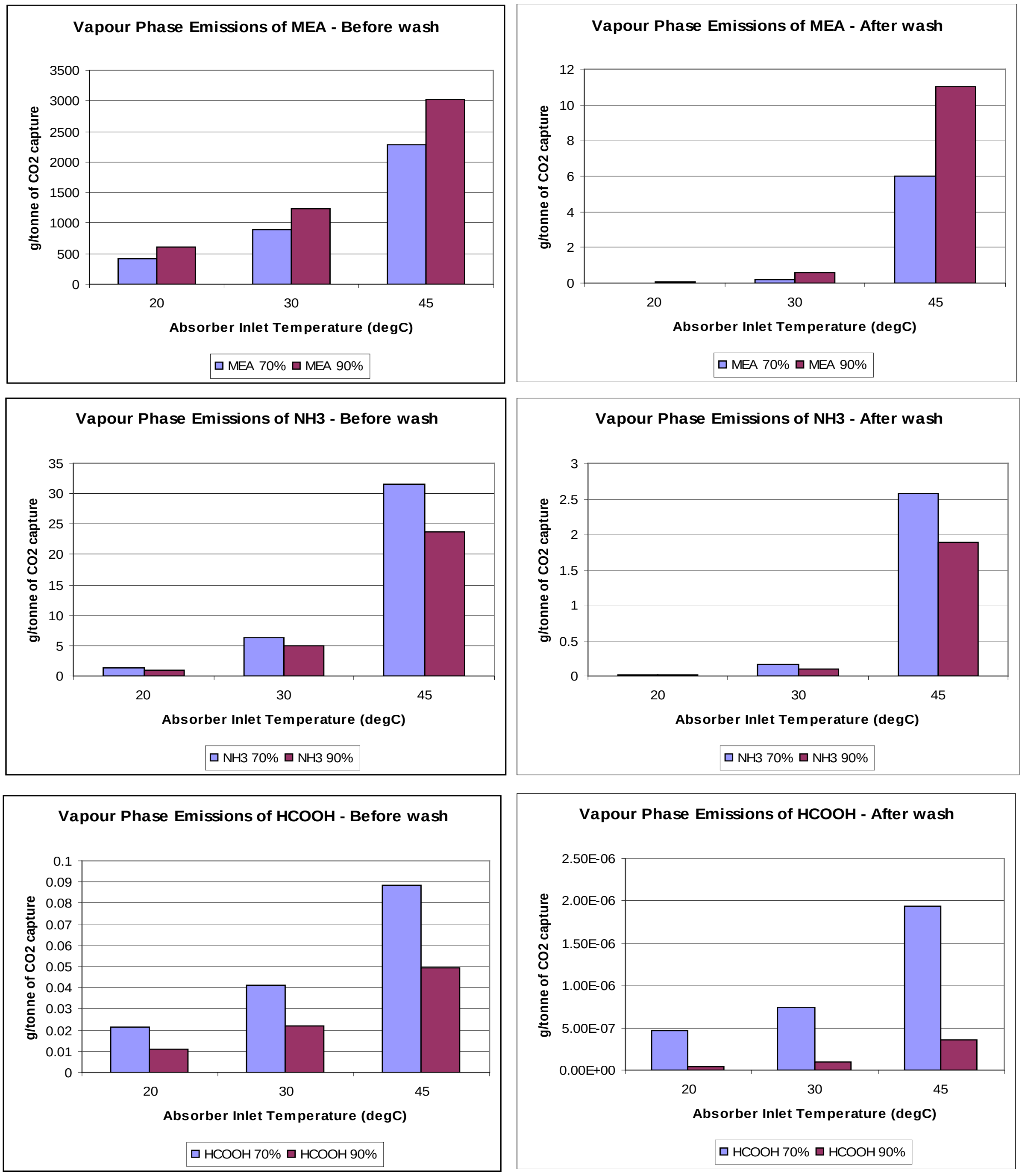


Figure 6 – Specific vapour emissions of Solvent A and its degradation products before and after wash

For the selected case, if all nitrosamines represented as dimethyl-nitrosoamine ($C_2H_6N_2O$) then we can predict the vapour phase concentration of nitrosamines as equivalent dimethylnitrosamine emissions. Similarly, by assuming diethyl-nitrosamine ($C_4H_{10}N_2O$) representing all nitrosamines, we can predict the vapour phase emissions in equivalent diethyl-nitrosamine terms. It should be stressed that these estimated values are purely based on the work by Strazisar et al (2003) and so far no similar work has been reported that indicates formation of any nitrosamine as a result of the degradation of MEA.

At the other reboiler operating temperature conditions, the emission values for MEA and its degradation products seemed to differ only marginally from the ones shown in Figures 6A.

Tables 7 and 8 below represent the emission values presented in Figures 6A and 6B as ppmV in the gas stream before and after washing with the demineralised water. These results show that MEA emission increases with the percentage CO_2 recovery desired and the absorber inlet flue gas temperature. It ranges from around 7.5 ppm by volume (0.4 kg per tonne of CO_2 captured) to as high as 65 ppm by volume (3 kg per tonne of CO_2 captured) when the treated gas is not water washed. With washing the gas, these losses are restricted to no more than 11 g per tonne of CO_2 captured, i.e. drop to well below 1 ppm by volume.

Table 7 – Specific vapour emissions of MEA and Degradation Products (70% CO_2 Capture)

Degradation Product	**Before wash (g/tonne CO_2)**	**After wash (g/tonne CO_2)**	**Before wash (ppmV)**	**After wash (ppmV)**
Absorber @ 20°C				
HCOOH	2.14E-02	4.63E-07	5.09E-04	1.13E-08
NH_3	1.34E+00	2.02E-02	8.60E-02	1.34E-03
MEA	419	0.0122	7.52E+00	2.25E-04
$C_2H_6N_2O$	1.20E+02	1.56E+01	2.39E+00	3.20E-01
$C_4H_{10}N_2O$	6.67E+01	3.64E+00	7.15E-01	4.01E-02
Absorber @ 30°C				
HCOOH	4.10E-02	7.47E-07	9.53E-04	1.79E-08
NH_3	6.38E+00	1.63E-01	4.01E-01	1.06E-02
MEA	900	0.197	1.58E+01	3.57E-03
$C_2H_6N_2O$	1.76E+02	3.36E+01	3.18E+00	6.27E-01
$C_4H_{10}N_2O$	9.95E+01	8.55E+00	1.04E+00	9.26E-02
Absorber @ 45°C				
HCOOH	8.84E-02	1.93E-06	1.97E-03	4.38E-08
NH_3	3.15E+01	2.57E+00	1.90E+00	1.58E-01
MEA	2281	6.03	3.83E+01	1.03E-01
$C_2H_6N_2O$	2.79E+02	9.53E+01	3.07E+00	1.07E+00
$C_4H_{10}N_2O$	1.62E+02	2.87E+01	1.63E+00	2.94E-01

Table 8 – Specific vapour emissions of MEA and Degradation Products (90% CO_2 Capture

Degradation Product	Before wash (g/tonne CO_2)	After wash (g/tonne CO_2)	Before wash (ppmV)	After wash (ppmV)
Absorber @ 20°C				
HCOOH	1.09E-02	4.77E-08	3.35E-04	1.51E-09
NH_3	1.00E+00	9.20E-03	8.30E-02	7.89E-04
MEA	611.5	0.05867	1.41E+01	1.40E-03
$C_2H_6N_2O$	9.36E+01	1.08E+01	1.79E+00	2.13E-01
$C_4H_{10}N_2O$	5.23E+01	2.50E+00	7.23E-01	3.57E-02
Absorber @ 30°C				
HCOOH	2.21E-02	1.02E-07	6.63E-04	3.17E-09
NH_3	4.92E+00	9.55E-02	3.98E-01	8.03E-03
MEA	1242	0.620	2.80E+01	1.45E-02
$C_2H_6N_2O$	1.35E+02	2.23E+01	2.51E+00	4.32E-01
$C_4H_{10}N_2O$	7.71E+01	5.64E+00	1.04E+00	7.91E-02
Absorber @ 45°C				
HCOOH	4.95E-02	3.53E-07	1.42E-03	1.04E-08
NH_3	2.37E+01	1.89E+00	1.83E+00	1.51E-01
MEA	3025	11.0	6.52E+01	2.44E-01
$C_2H_6N_2O$	2.12E+02	6.04E+01	3.76E+00	1.10E+00
$C_4H_{10}N_2O$	1.23E+02	1.75E+01	1.59E+00	2.32E-01

It should be emphasized here that the above loss does not include the physical entrainment related loss. However, the observations of Thitakamol et al (2007) are similar to the ASPEN results. These investigators have noted that in a well designed absorber, the MEA emissions without water wash increase from 0.11 kg per tonne of CO_2 captured at 20°C temperature of the treated gas to 0.72 kg per tonne of CO_2 captured when the treated gas temperature is 40°C. However, with water washing these emissions drop to 30 g per tonne of CO_2 captured when the treated gas temperature is 30°C.

In CSIRO's pilot plant at Loy Yang Power in Victoria, Australia, MEA concentrations in the gas exiting the absorber have been measured when the plant was operating with a 30% MEA concentration (Feron, 2009). At absorber temperatures between 40 and 55 ^{0}C and lean loadings between 0.16 and 0.27 mole CO_2/mole MEA, the MEA concentration in the exit gas from the absorber varied between 10 and 200 ppmv. The MEA concentrations as estimated in this study through ASPEN Plus are 65, 38 ppmv at 45 °C for CO_2 recovery of 90% and 70 % respectively. Hence the results from the process simulations are in good agreement with experiments. It is however not clear to what extent the measured emissions consisted of droplets.

For the ammonia emissions the concentrations during the experiments with CSIRO's pilot plant at Loy Yang Power in Victoria, Australia varied between 10 and 70 ppm when operating with a 30% MEA solution (Feron, 2007). These values are one order of magnitude higher than the emissions estimated with the degradation model built into the ASPEN Plus process simulator, as table 8 indicates levels of around 2 ppm for ammonia. This indicates that the results for the estimation of degradation products should be treated with care.

Table 9 shows the droplet emissions of MEA and its degradation products for different absorber inlet temperatures at 0.2 mole per mole CO_2 lean loading and 120°C reboiler temperature for 70% and 90% CO_2 recovery respectively. These emissions have been calculated assuming the droplet carryover past the demister in the water wash section is 0.13 m^3 per million m^3 of treated gas as proposed by the Handbook from Gas Processors Suppliers' Association (2004).

Table 9 – Entrainment emissions of MEA and Degradation Products (0.2 molar CO_2 lean loading, 120°C Reboiler Temperature)

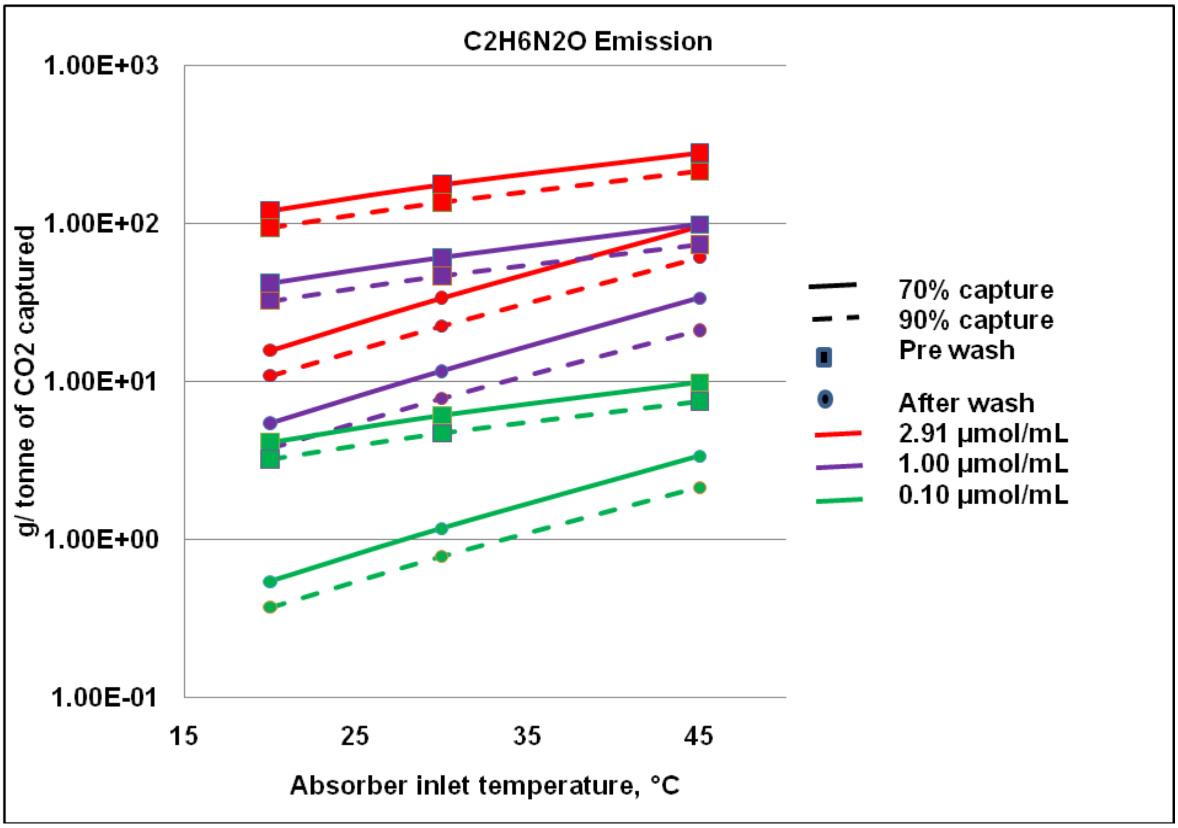
Degradation Product	**70% CO_2 Recovery (g/tonne CO_2)**	**90% CO_2 Recovery (g/tonne CO_2)**
Absorber Inlet @ 20°C		
HCOOH	1.28E-04	5.68E-05
NH_3	2.61E-02	1.71E-02
MEA	8.67E+00	1.12E+01
$C_2H_6N_2O$	6.26E-01	4.31E-01
$C_4H_{10}N_2O$	3.78E-01	2.59E-01
Absorber Inlet @ 30°C		
HCOOH	2.21E-04	1.00E-04
NH_3	1.11E-01	7.23E-02
MEA	1.70E+01	2.04E+01
$C_2H_6N_2O$	7.67E-01	5.09E-01
$C_4H_{10}N_2O$	4.91E-01	3.23E-01
Absorber Inlet @ 45°C		
HCOOH	4.78E-04	2.06E-04
NH_3	5.19E-01	3.00E-01
MEA	4.54E+01	4.75E+01
$C_2H_6N_2O$	9.96E-01	6.30E-01
$C_4H_{10}N_2O$	7.24E-01	4.41E-01

One should, however, note that in reality the concentrations of MEA in the exiting flue gas, be it as vapour or as droplet are very much dependent upon the absorber internals, absorber hydrodynamics, type of the mist eliminator used between the absorption and wash section and its efficiency, the type of wire-mesh pad used downstream of the wash section and its efficiency. It should be noted that the older designs of capture plants used dumped packings (eg Raschig rings, Intalox saddles) or bubble cap and valve type trays. These gas-liquid contact media have inherently poor flooding characteristics in which the droplet emissions could have been higher. In modern plants, it is likely that structured packings (eg Sulzer Mellapack) will normally be used. These packings have much higher flooding characteristics and therefore the actual physical entrainment related MEA emission losses may be much smaller than the old values. A number of factors such as the design of absorber internals, hydrodynamics within the absorber, the impact of heat stable salts (formed during absorption) on the density, viscosity and surface tension of the solvent, the type of demister used in the absorber and the wash water circulation rate are involved. It should be noted that the presence of 1% heat stable salts 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.

In conjunction with Figures 6A and 6B and Tables 6, 7 and 8, it can be concluded that the vapour phase and droplet emissions of MEA and its degradation products increase with the rising absorber inlet temperature. When the CO_2 lean gas is not water washed, the vapour phase emission of heat stable salts ranges from 10 to 50 mg per tonne of CO_2 captured, ammonia emission ranges between 1 to 32 g per tonne of CO_2 captured and the emission of dimethyl-nitrosamine remains in the range 120 to 280 g per tonne of CO_2 captured. Whilst the nitrosamine vapour phase emission seems high in comparison with the heat stable salts and ammonia emissions, it should be noted that it is based on the physical solubility and vapour-liquid equilibrium of 2.91 µmol/mL fixed quantity. In an industrial capture plant environment, the nitrosamines will be produced gradually over time and hence, the high values of nitrosamine concentrations in the vapour phase should be taken as representing a hypothetical worst case scenario for model development only and not a regular steady state situation. ASPEN simulations further show that, if diethyl-nitrosamine is considered instead of dimethyl-nitrosamine, then the equivalent pre-wash emission values range between 52 to 162 g per tonne of CO_2 captured. This lower emission range is in accordance with general characteristics of organic compounds, i.e. a higher molecular weight organic liquid compound (diethyl-nitrosamine) should have lower vapour pressure.

ASPEN simulations further show that when the CO_2 lean gas is water washed, the vapour phase emissions of MEA degradation products will be in the following range depending upon the flue gas temperature at the inlet to the absorber: Heat stable salts – practically nil, ammonia – 9 mg to 2.6 g per tonne of CO_2 captured, dimethyl-nitrosamine – 11 to 95 g per tonne of CO_2 captured, i.e. 200 ppbV to 1 ppmV and diethyl-nitrosamine – 2.5 to 29 g per tonne of CO_2 captured, i.e. 35 to 295 ppbV. Figures 7 and 8 show that nitrosamine in the vapour phase change proportionately when their concentration in the lean MEA changes.

Table 8 shows that over 70 to 90% CO_2 capture rate, the flue gas temperature ranging from 20 to 45°C and the reboiler temperature at 120°C, the droplet emissions of MEA and its degradation products after the treated gas is water washed remain as: heat stable salts less than 0.5 mg per tonne of CO_2 captured; ammonia less than 0.5 gm per tonne of CO_2 captured; MEA between 8.7 to 47.5 g per tonne of CO_2 captured, dimethyl-nitrosamine less than 1 g per tonne of CO_2 captured and diethyl-nitrosamine less than 0.72 g per tonne of CO_2 captured.



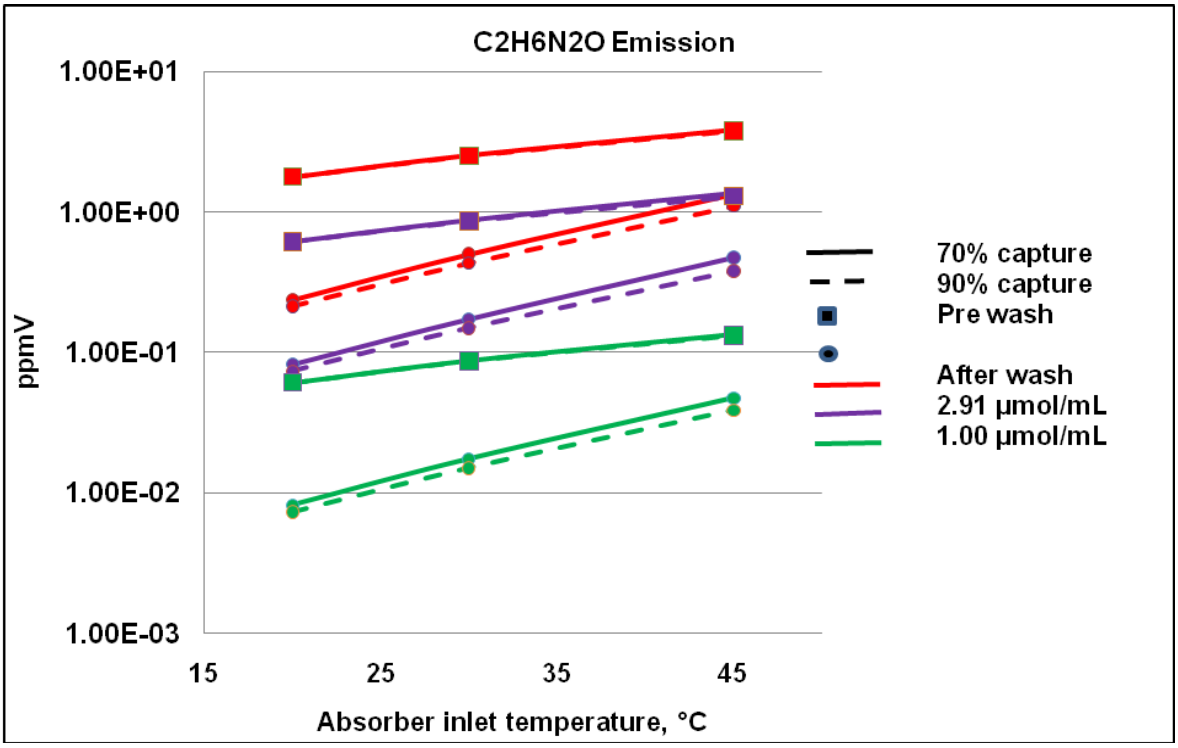


Figure 7 – Dependence of $C_2H_6N_2O$ emissions on their concentration in the solvent

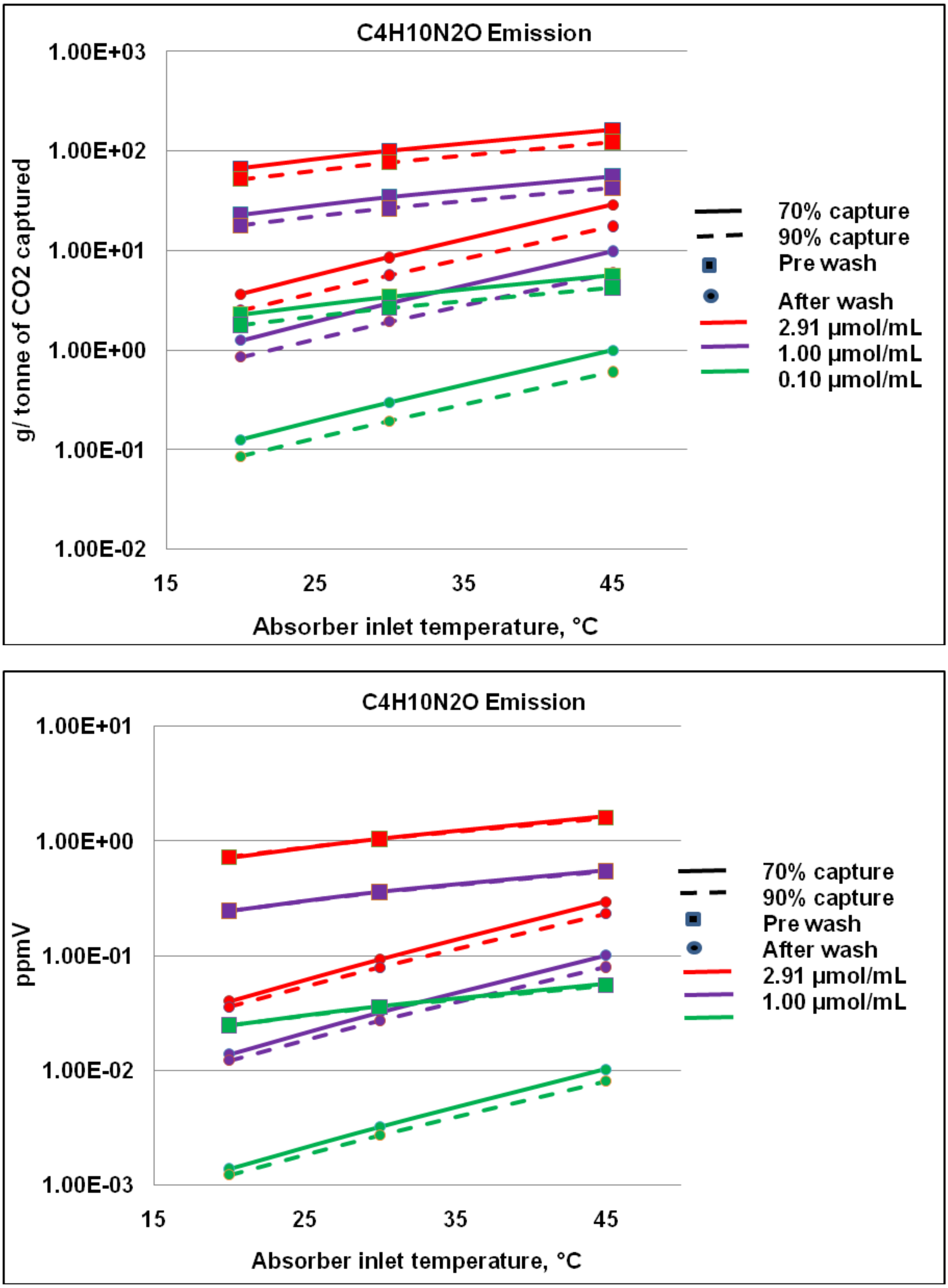


Figure 8 - Dependence of $C_4H_{10}N_2O$ emissions on their concentration in the solvent

Figures 9 and 10 show the specific cooling load involved during the aqueous MEA based post combustion capture process as applicable to Gassnova's needs for 70% and 90% CO_2 recovery rates. These results show that the minimum cooling load at 0.2 mole CO_2 per mole lean amine loading occurs around 120°C to 130°C operating range of the boiler. Obviously with higher gas temperature at the absorber inlet, the specific cooling load decreases since not much gas cooling is required when the treated gas has to have its temperature same as the feed gas.

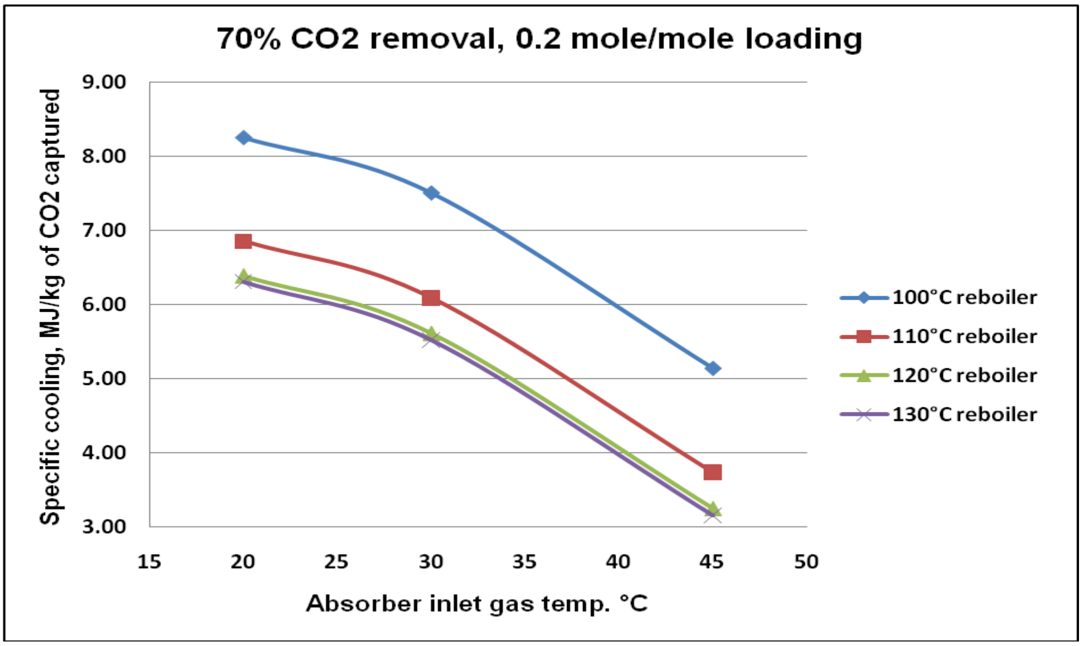


Figure 9 - Specific cooling load during CO_2 capture; Solvent A

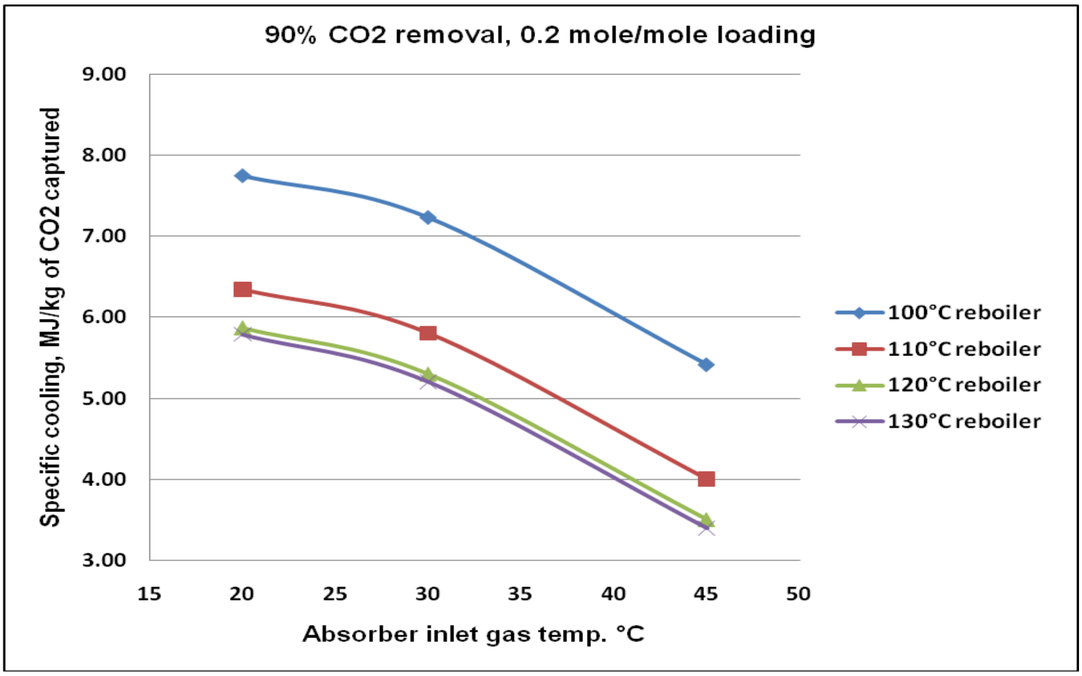


Figure 10 - Specific cooling load during CO_2 capture; Solvent A

Figures 11 and 12 show that the specific electrical power load for the aqueous MEA based post combustion capture process increases with the increasing flue gas temperature and rising reboiler temperature. It is mainly the blower electrical load that significantly contributes towards the electricity demand by the process. Once again, the specific power demand is higher when lower CO_2 recovery rate is targeted.

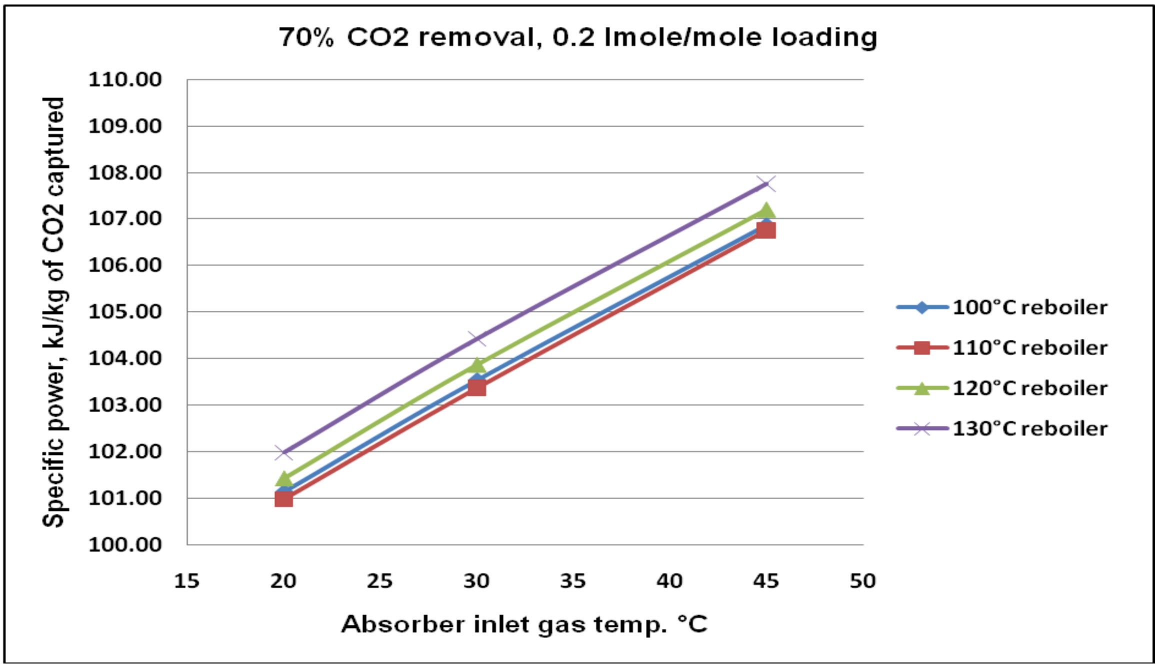


Figure 11 – Specific electrical power demand during CO_2 Capture; Solvent A

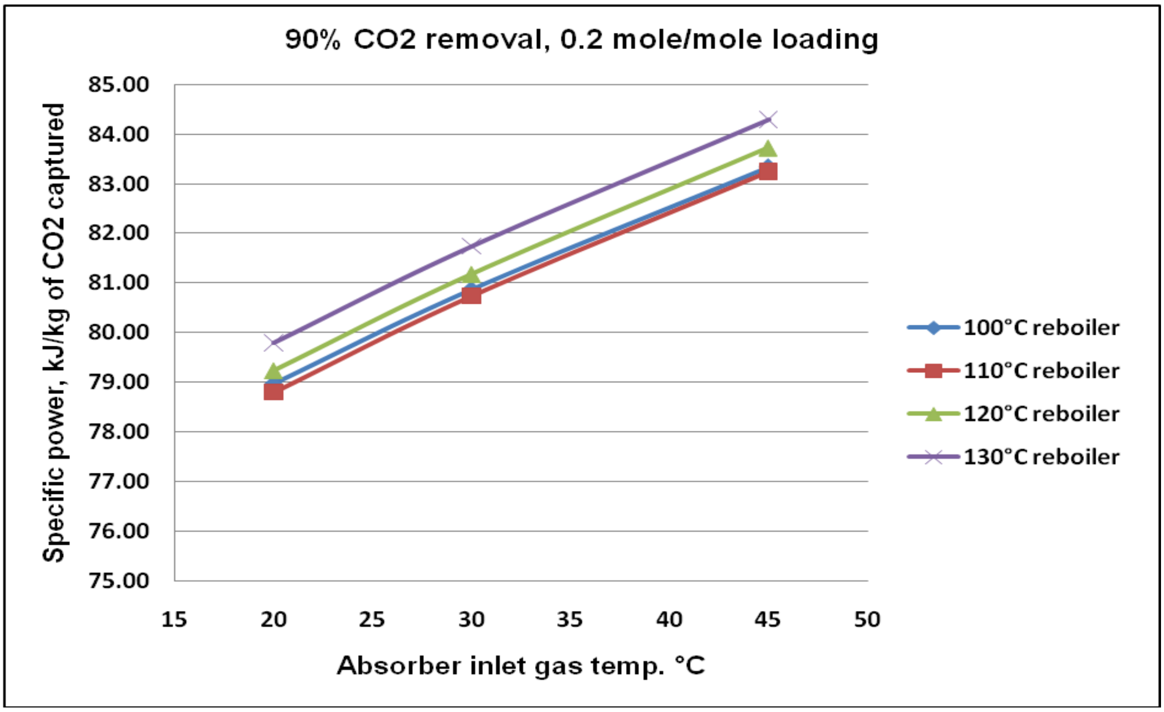


Figure 12 – Specific electrical power demand during CO_2 Capture; Solvent A

4.3 PCC PROCESS EMISSIONS FOR SOLVENT B

For AMP/PZ mixed solvent, its emissions to atmosphere both in the vapour phase and in the droplet phase were calculated after the water wash section of the absorber as a function of various CO_2 loading of the mixed solvent, % CO_2 absorption required and the flue gas temperature at the inlet to the absorber. Table 10 shows these results. As in the case for Solvent A, these emissions have been calculated as g per tonne of CO_2 captured. The droplet phase emissions calculations assume that the droplet composition is same as that of the circulating wash water in the wash tower and the liquid entrainment past the demister in the wash section is 0.13 m^3 per million m^3 of treated gas as proposed by the Handbook from Gas Processors Suppliers' Association (2004).

Table 10 – AMP/PZ emissions as a function of CO_2 loading of Solvent B

Solvent B		Absorber Inlet Temperature - 20°C, Reboiler Temperature - 120^{o}C					
		Vapour		Droplet		Total	
	CO_2 Capture (%)	70	90	70	90	70	90
CO_2 Loading (mole/mole)	Component (g/tonne of CO_2)						
0.02	AMP	7.00E-01	4.06E+00	1.48E+01	2.31E+01	1.55E+01	2.72E+01
	PZ	8.09E-03	6.26E-02	6.30E-01	1.33E+00	6.38E-01	1.40E+00
0.036	AMP	6.89E-01	3.97E+00	1.46E+01	2.28E+01	1.53E+01	2.67E+01
	PZ	8.12E-03	6.29E-02	6.36E-01	1.35E+00	6.44E-01	1.41E+00
0.05	AMP	6.80E-01	3.91E+00	1.45E+01	2.25E+01	1.52E+01	2.64E+01
	PZ	8.13E-03	6.31E-02	6.41E-01	1.36E+00	6.49E-01	1.42E+00
0.075	AMP	6.66E-01	3.80E+00	1.43E+01	2.21E+01	1.50E+01	2.59E+01
	PZ	8.15E-03	6.32E-02	6.47E-01	1.37E+00	6.55E-01	1.43E+00

Solvent B		Absorber Inlet Temperature - 45°C, Reboiler Temperature - 120^{o}C					
		Vapour		Droplet		Total	
	CO_2 Capture (%)	70	90	70	90	70	90
CO_2 Loading (mole/mole)	Component (g/tonne of CO_2)						
0.02	AMP	7.23E+02	1.22E+03	1.24E+02	1.29E+02	8.47E+02	1.34E+03
	PZ	5.94E+00	1.54E+01	6.47E+00	9.50E+00	1.24E+01	2.49E+01
0.036	AMP	7.20E+02	1.20E+03	1.23E+02	1.27E+02	8.43E+02	1.33E+03
	PZ	5.91E+00	1.53E+01	6.44E+00	9.50E+00	1.23E+01	2.48E+01
0.05	AMP	7.17E+02	1.19E+03	1.23E+02	1.26E+02	8.40E+02	1.32E+03
	PZ	5.88E+00	1.53E+01	6.41E+00	9.50E+00	1.23E+01	2.48E+01
0.075	AMP	7.11E+02	1.17E+03	1.22E+02	1.25E+02	8.34E+02	1.30E+03
	PZ	5.82E+00	1.52E+01	6.36E+00	9.47E+00	1.22E+01	2.47E+01

It shows that both the vapour phase and droplet form emissions increase with rising flue gas temperature at inlet to the absorber and higher level of % CO_2 captured required but remain more or less same for various mixed amine loading conditions. This is so because the CO_2 lean flue gas temperature at the outlet of the wash tower is kept same as at inlet to the absorber just as in the case for Solvent A.

After several ASPEN simulations, the optimum CO_2 loading at the inlet to the absorber for Solvent B was identified as 0.036 mole per mole of mixed amine. The results below are for this lean loading. Figures 13 to 19 show the solvent performance for 70% and 90% CO_2 capture at 100 to 120^{o}C reboiler operating temperature and different flue gas temperature at the inlet to the absorber. ASPEN software produced unstable results for the case of 130^{o}C reboiler temperature and hence, these results are not included.

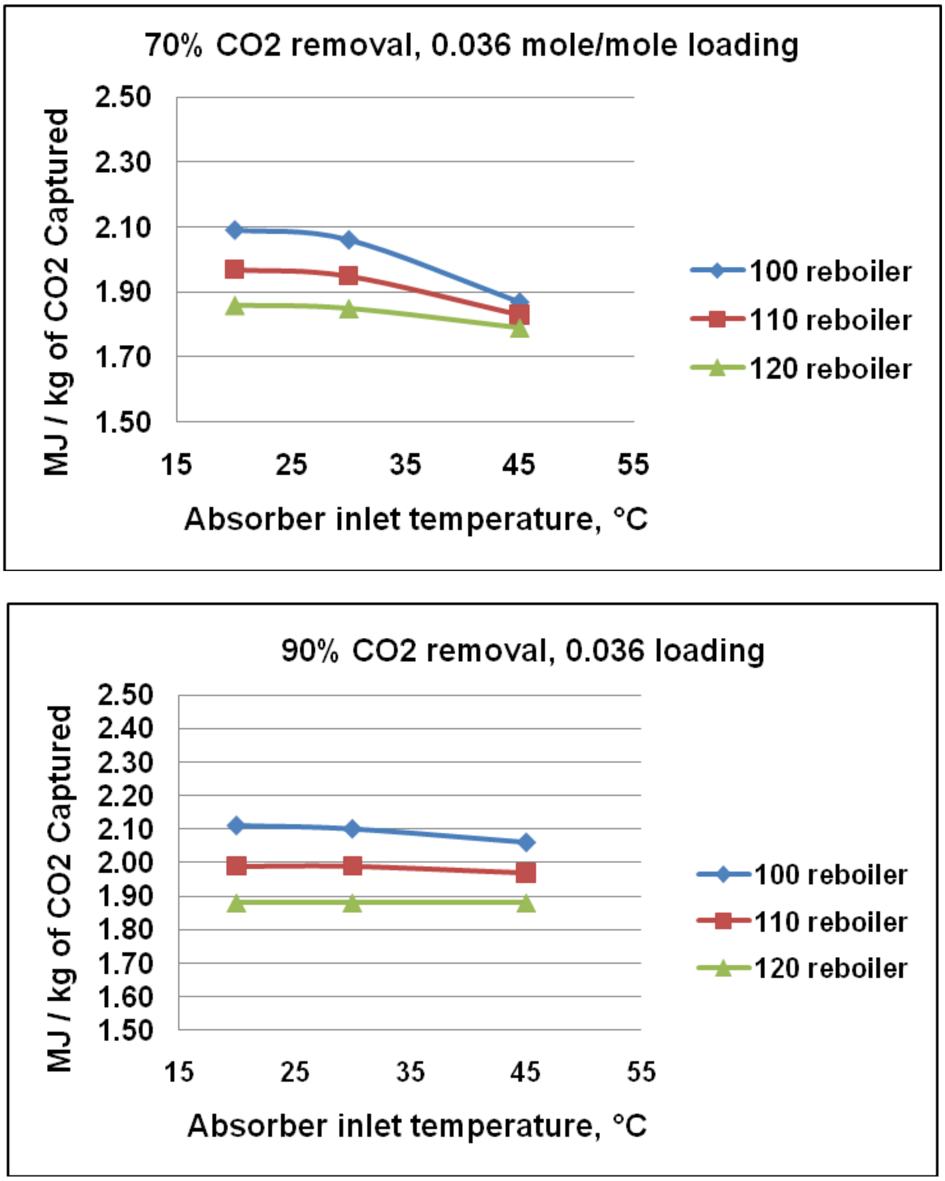


Figure 13 – Reboiler heat duty for Solvent B

As shown in Figure 13, the reboiler heat duty remains approximately between 1.8 and 2.1 MJ per kg of CO_2 captured which is substantially lower than the values observed for the Solvent A. Minimum reboiler heat duty requirement occurs around 120°C reboiler temperature for all the cases of flue gas temperatures at inlet to the absorber. There is currently little experimental data available in the open literature to verify the ASPEN generated low reboiler heat duties for Solvent B. It is generally thought the vapour liquid equilibrium data of aqueous solutions of the separate amines as used by ASPEN are adequate, but the mixture has not been assessed yet. The vapour-liquid equilibrium data measured experimentally (Puxty 2009) at 40°C and 100°C for CO_2 absorption in an aqueous solution of 1M PZ and 4M AMP mixture when compared with the ASPEN generated data for the identical conditions showed that ASPEN predicted higher values for the partial pressure of CO_2. The difference between the experimental and calculated values of the partial pressure of CO_2 was very pronounced at 100°C for all the CO_2 loadings of Solvent B. At 40°C, there was reasonable agreement between the two data sets up to 0.5 mole per mole CO_2 loading of Solvent B. However, beyond this loading there was significant divergence between the experimental and predicted values. This implies that the ASPEN simulator could be predicting CO_2 absorption relatively accurately up to the CO_2 rich solvent loading of 0.5 mole per mole but in calculating the reboiler heat duty for desorption of CO_2 at 100°C and above, it may yield lower values for it than what could be the reality. This may be the reason why ASPEN simulator produced unstable results for 130°C reboiler operating temperature. In addition, it was observed that for all cases of flue gas inlet temperature, ASPEN estimated 0.7 mole per mole equilibrium rich loading at the outlet to the absorber. Thus, the results of process modelling studies using solvent B have perhaps only limited value.

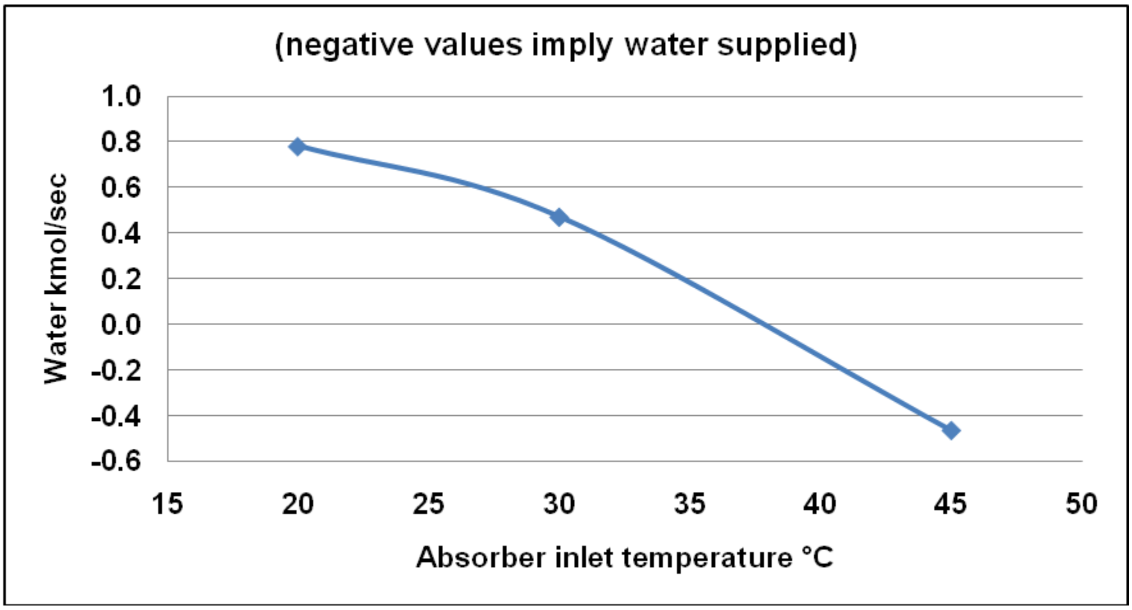


Figure 14 – Specific water consumption during capture process; Solvent B

As shown in Figure 14, when the flue gas is cooled to below 40°C prior to entering the absorber, the capture process will produce sufficient water to meet the wash water requirement to reduce the Solvent B emissions in the vapour phase. However, above this temperature, the process actually requires water to both cool the gas and lower the Solvent B emissions. It should be noted that in calculating the wash water requirement, care is taken that no excess waste water is created.

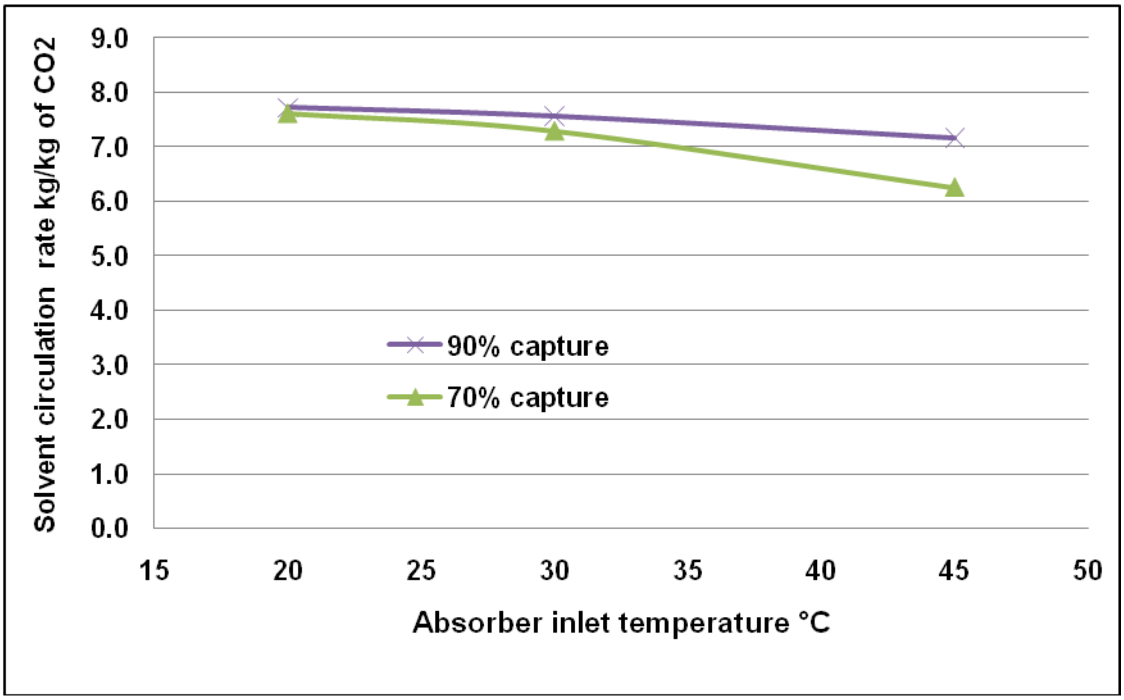
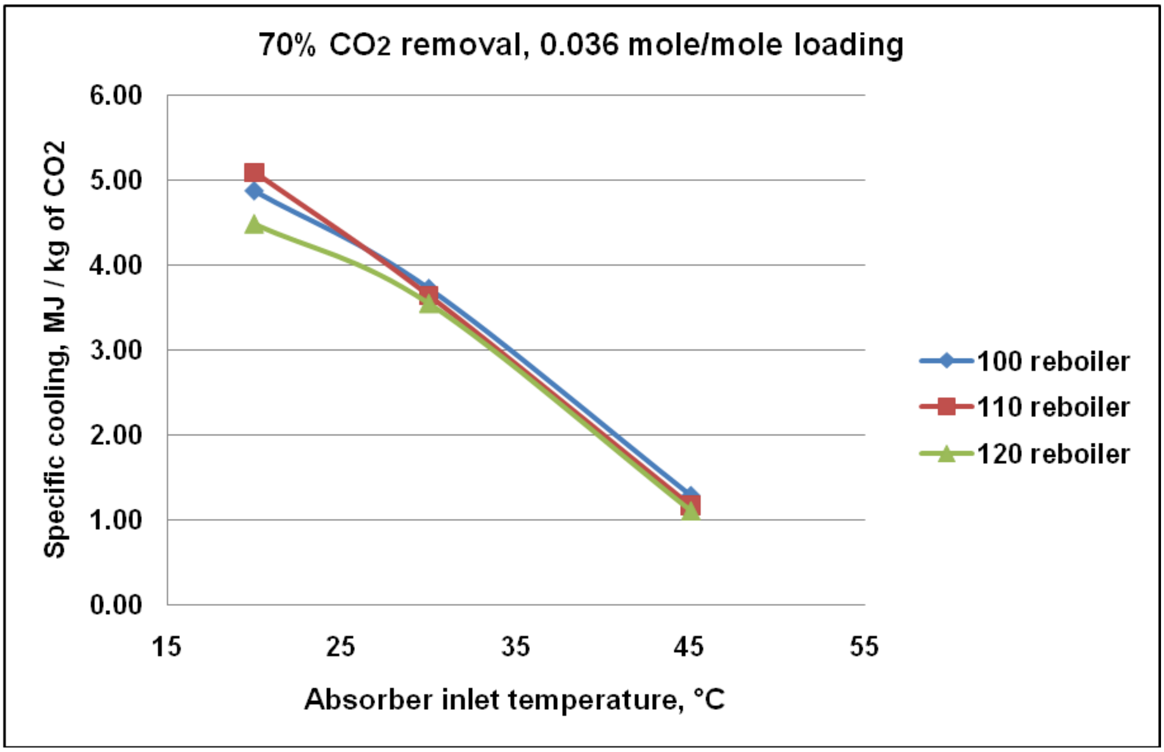


Figure 15 – Solvent circulation rate; Solvent B

Figure 15 above shows that the solvent circulation rate for 70 to 90% CO_2 capture remains in the range 6 to 8 kg of solvent per kg of CO_2 captured and it decreases as the flue gas temperature at inlet to the absorber increases. This is a very low circulation rate when compared with solvent A, but probably reasonable trend for this solvent, since the reaction rate of CO_2 absorption is expected to rise with increasing temperature and thus it may require lesser circulation rate for the same level of CO_2 recovery. However, in light of ASPEN's questionable capability to reliably predict the performance of this solvent and no independent public domain data for the solvent circulation rate for Solvent B, one should not rely on these results. Nevertheless, lower circulation rate than that for the MEA based Solvent A under equivalent conditions clearly confirms the role of piperazine as the reaction rate promoter.

Figure 16 shows that the specific cooling load for the absorption/regeneration cycle remains between 1 to 5 MJ per kg of CO_2 captured and it is consistently minimal for the reboiler operating temperature of 120^{o}C.



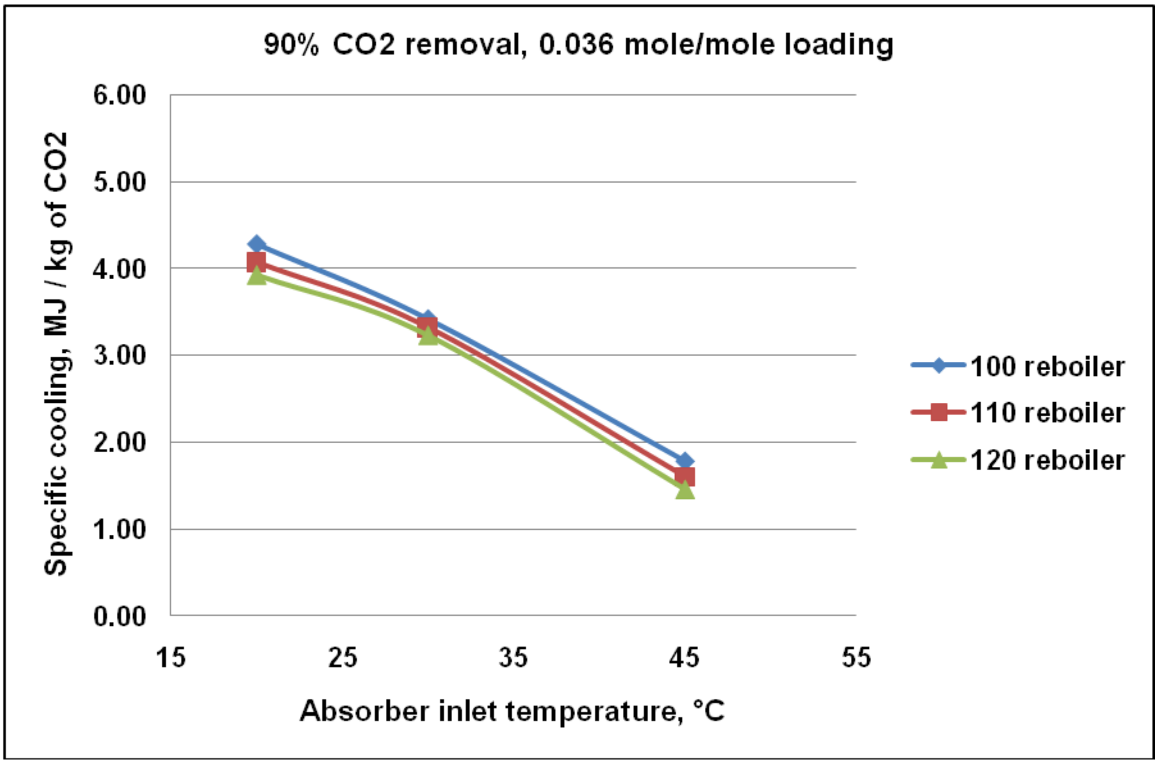
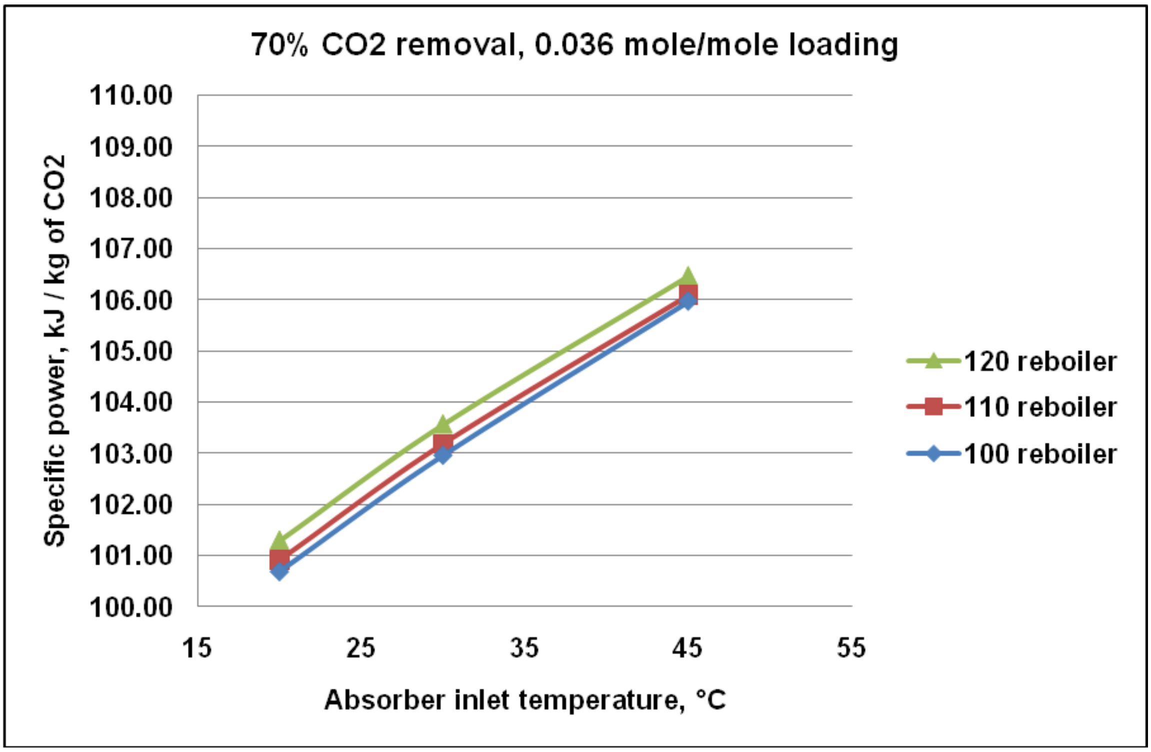


Figure 16 - Specific cooling load during CO_2 capture; Solvent B

The ASPEN simulations predict specific electrical power load during the capture process with Solvent B roughly the same as that with Solvent A (see Figures 11, 12 and 17) and the flue gas blower remains main contributor to this power load.



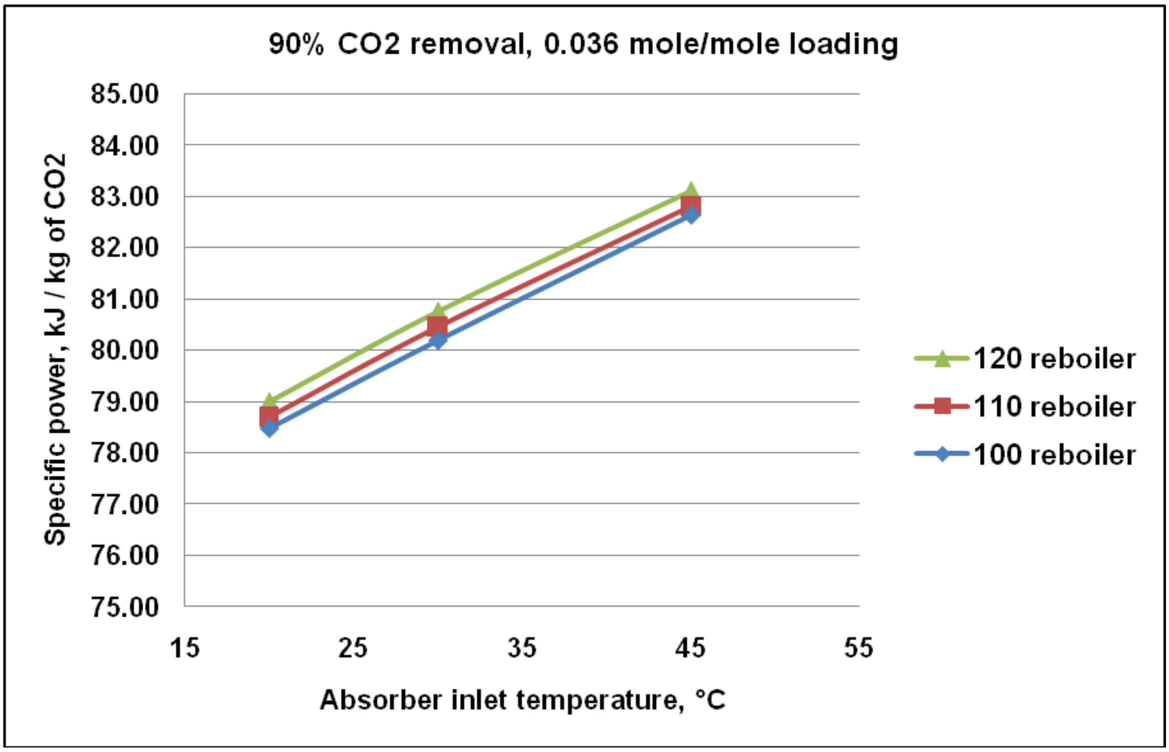


Figure 17 - Specific electrical power demand during CO_2 capture; Solvent B

Figures 18 and 19 below show the extent of the specific vapour emissions of Solvent B and its degradation products in g per tonne of CO_2 captured as well as the volumetric concentrations (ppmV). It should be noted that ammonia emission for this case is related to ammonia present in the flue gas which has not dissolved in the aqueous phase of Solvent B.

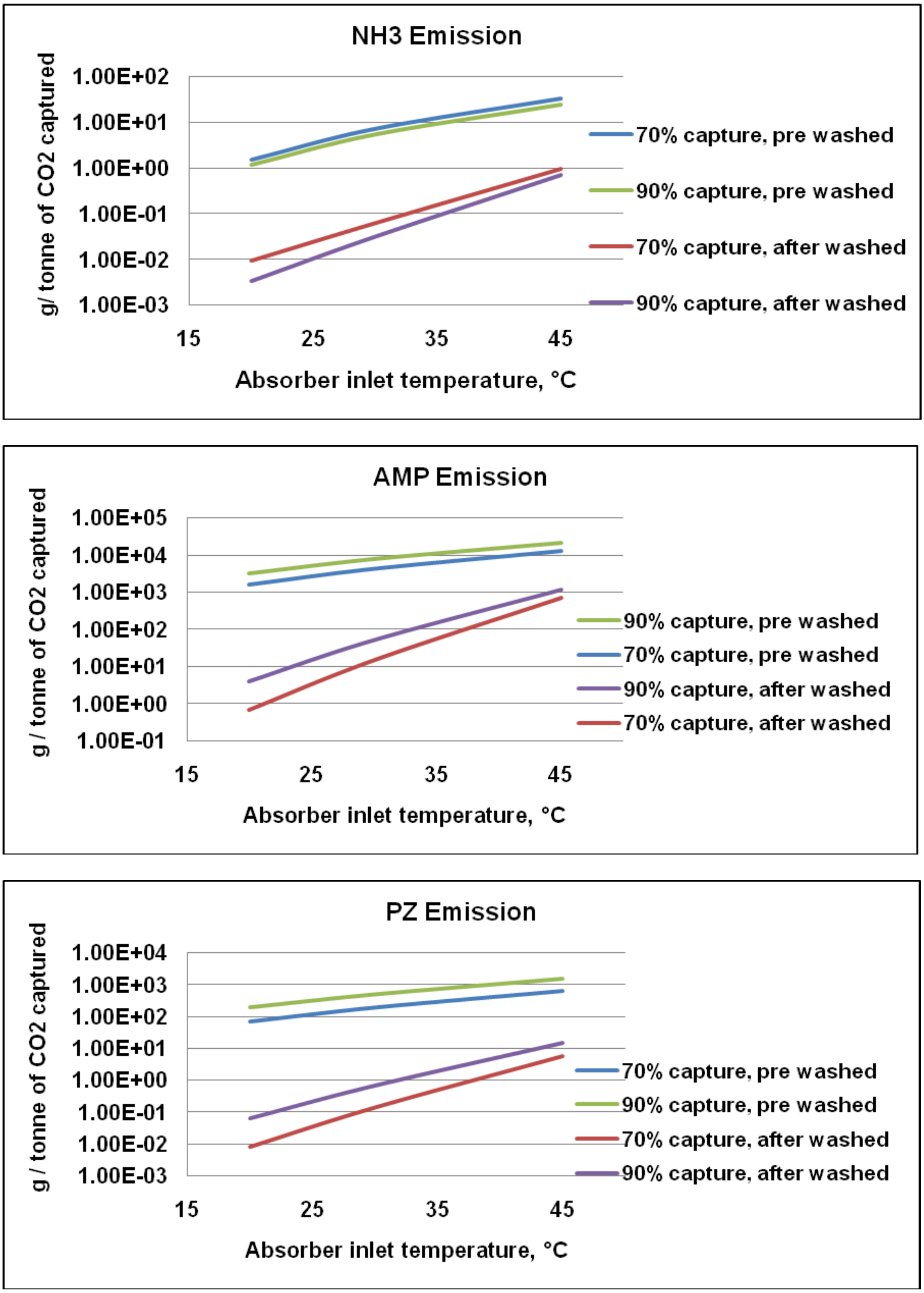


Figure 18 – Specific vapour emissions of Solvent B

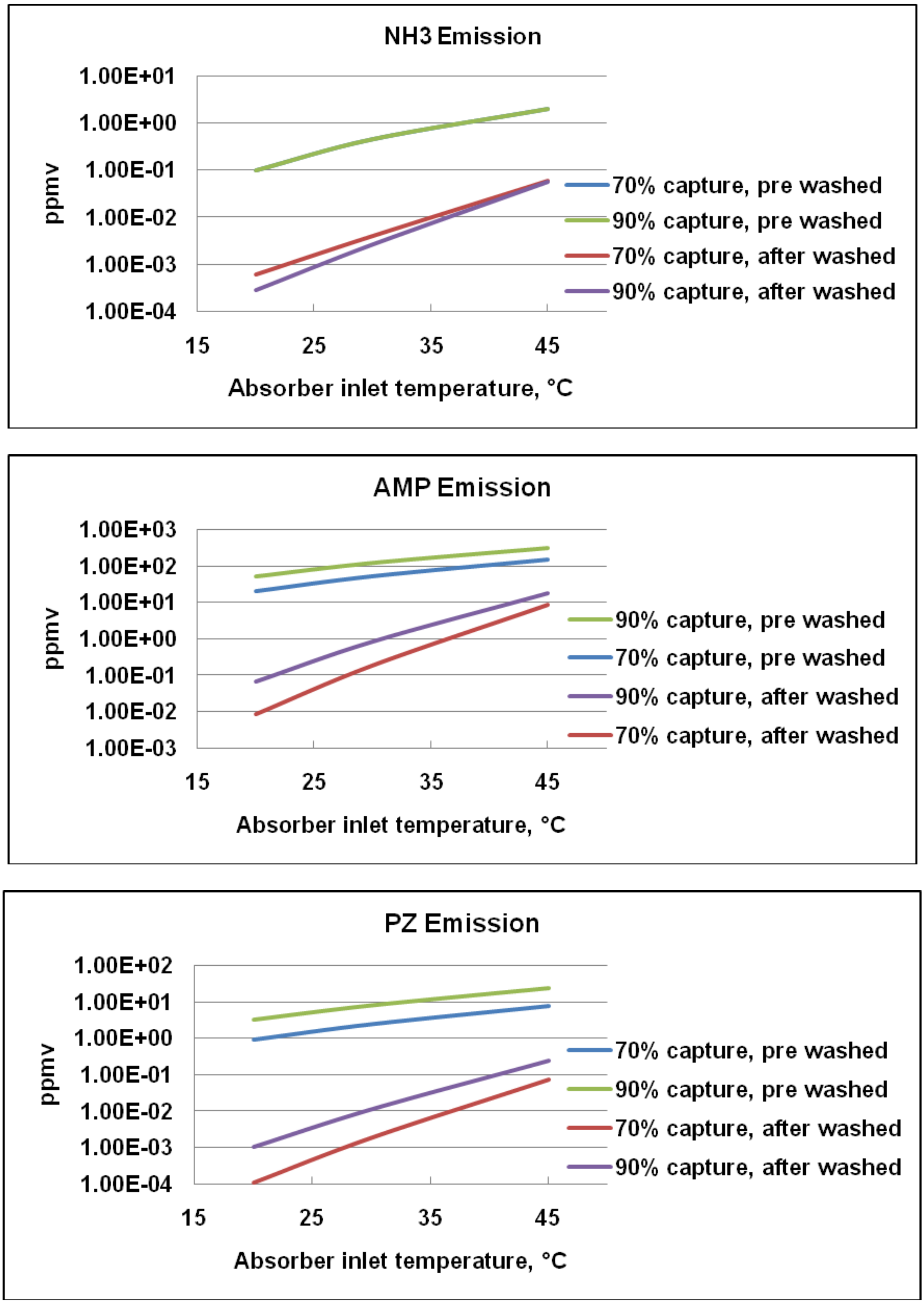


Figure 19 – Volumetric concentration for vapour emissions of Solvent B

Tables 11 and 12 below list the numerical values of these emissions for the case of reboiler operating at 120^{o}C. Both AMP and PZ emissions rise with increasing flue gas inlet temperature to the absorber. For 90% capture of CO_2, these emissions are higher than the corresponding values for 70% capture due to higher solvent circulation rate required for 90% capture. Before washing the treated gas, ammonia emissions range from 1.2 to 32 g per tonne of CO_2 captured (0.1 to 2 ppmV); AMP emissions range from 1.6 to 21 kg per tonne of CO_2 captured (19.8 to 318 ppmV) and PZ emissions range from 69 g to 1.5 kg per tonne of CO_2 captured (0.9 to 23.4 ppmV). After washing the treated gas with demineralised water and recycling the excess waste water from wash towers to the lean solvent makeup, ammonia emissions range from 0.6 to 57 ppbV; AMP emissions range from 0.7 g to 1.2 kg per tonne of CO_2 captured (8.7 ppbV to 1.8 ppmV) and PZ emissions range from 8 mg to 1.5 g per tonne of CO_2 captured (0.1 to 240 ppbV).

Table 11 – Specific vapour emissions and volumetric concentrations of AMP, PZ and Ammonia (70% CO2 Capture)

	Before Wash (g/tonne CO_2)	**After Wash (g/tonne CO_2)**	**Before Wash (ppmV)**	**After Wash (ppmV)**
Absorber Inlet @20^{o}C				
NH_3	1.53E+00	9.16E-03	9.95E-02	6.06E-04
AMP	1.60E+03	6.89E-01	1.98E+01	8.72E-03
PZ	6.94E+01	8.12E-03	8.92E-01	1.06E-04
Absorber Inlet @ 30^{o}C				
NH_3	7.15E+00	6.12E-02	4.55E-01	3.98E-03
AMP	4.31E+03	1.51E+01	5.24E+01	1.87E-01
PZ	1.94E+02	1.42E-01	2.44E+00	1.83E-03
Absorber Inlet @ 45^{o}C				
NH_3	3.23E+01	9.50E-01	1.99E+00	5.85E-02
AMP	1.32E+04	7.20E+02	1.55E+02	8.47E+00
PZ	6.55E+02	5.91E+00	7.97E+00	7.19E-02

Table 12 – Specific vapour emissions and volumetric concentrations of AMP, PZ and Ammonia (90% CO_2 Capture)

	Before Wash (g/tonne CO_2)	**After Wash (g/tonne CO_2)**	**Before Wash (ppmV)**	**After Wash (ppmV)**
Absorber Inlet @ 20^{o}C				
NH_3	1.16E+00	3.38E-03	9.71E-02	2.90E-04
AMP	3.25E+03	3.97E+00	5.19E+01	6.52E-02
PZ	1.92E+02	6.29E-02	3.18E+00	1.07E-03
Absorber Inlet@ 30^{o}C				
NH_3	5.46E+00	3.19E-02	4.47E-01	2.69E-03
AMP	7.85E+03	5.20E+01	1.23E+02	8.37E-01
PZ	4.88E+02	6.86E-01	7.91E+00	1.14E-02
Absorber Inlet@ 45^{o}C				
NH_3	2.48E+01	7.18E-01	1.96E+00	5.73E-02
AMP	2.11E+04	1.20E+03	3.18E+02	1.83E+01
PZ	1.50E+03	1.53E+01	2.34E+01	2.42E-01

There is no public domain information available to verify the reliability of the above vapour phase emission results at present. Reducing these emissions further will require more fresh demineralised water circulation in the wash tower and that could result into excess waste water which could no longer be used in the process and thus increasing the effluent treatment load for the capture plant. It should also be noted that the above results are purely ASPEN based estimates and due to limited capability of ASPEN to model CO_2 absorption/regeneration with Solvent B, these emissions could be too high in reality.

Table 13 below shows the droplet carryover emissions for AMP, PZ and ammonia. They are purely based on the assumption that droplet carryover past the demister in the water wash section of the absorber will be approximately 0.13 m^3 per million m^3 of treated gas leaving the wash section as suggested by the Handbook of Gas Suppliers' association (2004).

Table 13 – Specific entrainment emissions of AMP, PZ and Ammonia (0.036 molar CO2 lean loading, 120°C Reboiler Temperature)

	70% CO2 Recovery (g/tonne CO_2)	**90% CO2 Recovery (g/tonne CO_2)**
Absorber Inlet @ 20°C		
NH_3	0.013946	8.12E-03
AMP	1.46E+01	2.28E+01
PZ	6.36E-01	1.35E+00
Absorber Inlet @ 30°C		
NH_3	5.67E-02	3.30E-02
AMP	3.44E+01	4.74E+01
PZ	1.55E+00	2.96E+00
Absorber Inlet @ 45°C		
NH_3	3.11E-01	1.54E-01
AMP	1.23E+02	1.27E+02
PZ	6.44E+00	9.50E+00

Table 13 shows that, over 70 to 90% CO_2 capture rate, the flue gas temperature ranging from 20 to 45°C and the reboiler temperature at 120°C, the droplet emissions of ammonia, AMP and PZ after the treated gas is water washed will be as: ammonia less than 0.35 g per tonne of CO_2 captured; AMP between 14.6 to 127 g per tonne of CO_2 captured and PZ between 635 mg to 9.5 g per tonne of CO_2 captured.

4.4 PCC PROCESS EMISSIONS FOR SOLVENT C

For MDEA/MEA mixed solvent, its emissions to atmosphere both in the vapour phase and in the droplet phase were calculated after the water wash section of the absorber as a function of various CO_2 loading of the mixed solvent, % CO_2 absorption required and the flue gas temperature at the inlet to the absorber. Table 14 shows these results. As in the case for Solvent A and B, these emissions have been calculated as g per tonne of CO_2 captured. The droplet phase emissions calculations assume that the droplet composition is same as that of the circulating wash water in the wash tower and the liquid entrainment past the demister in the wash section is 0.13 m^3 per million m^3 of treated gas as proposed by the Handbook from Gas Processors Suppliers' Association (2004).

Table 14 – MDEA/MEA emissions as a function of CO_2 loading of Solvent C

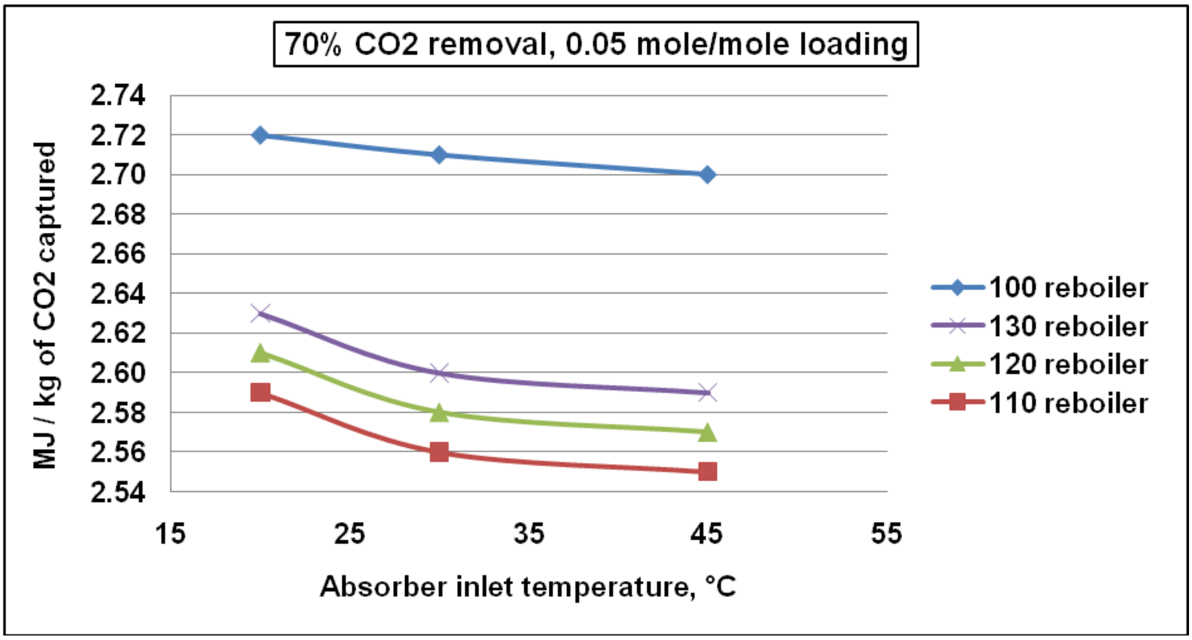
Solvent C		**Absorber Inlet Temperature - 20°C, Reboiler Temperature - 110^{o}C**					
		Vapour		**Droplet**		**Total**	
	CO_2 Capture (%)	**70**	**90**	**70**	**90**	**70**	**90**
CO_2 Loading (mole/mole)	**Component (g/tonne of CO_2)**						
0.03	MEA	8.78E-04	1.17E-02	6.20E-01	1.24E+00	6.20E-01	1.25E+00
	MDEA	0	0	0	0	0	0
0.05	MEA	9.15E-04	1.22E-02	6.34E-01	1.27E+00	6.35E-01	1.28E+00
	MDEA	0	0	0	0	0	0
0.06	MEA	9.39E-04	1.26E-02	6.42E-01	1.29E+00	6.43E-01	1.30E+00
	MDEA	0	0	0	0	0	0
0.07	MEA	9.59E-04	1.30E-02	6.49E-01	1.31E+00	6.50E-01	1.33E+00
	MDEA	0	0	0	0	0	0

Solvent C		**Absorber Inlet Temperature - 45°C, Reboiler Temperature - 110^{o}C**					
		Vapour		**Droplet**		**Total**	
	CO_2 Capture (%)	**70**	**90**	**70**	**90**	**70**	**90**
CO_2 Loading (mole/mole)	**Component (g/tonne of CO_2)**						
0.03	MEA	6.58E-02	9.32E-01	1.23E+00	2.15E+00	1.29E+00	3.08E+00
	MDEA	0	0	0	0	0	0
0.05	MEA	6.18E-02	8.76E-01	1.19E+00	2.08E+00	1.25E+00	2.95E+00
	MDEA	0	0	0	0	0	0
0.06	MEA	6.36E-02	8.92E-01	1.21E+00	2.10E+00	1.27E+00	2.99E+00
	MDEA	0	0	0	0	0	0
0.07	MEA	5.95E-02	8.40E-01	1.17E+00	2.03E+00	1.23E+00	2.87E+00
	MDEA	0	0	0	0	0	0

It shows that both the vapour phase and droplet form emissions increase with rising flue gas temperature at inlet to the absorber and higher level of % CO_2 captured required but remain more or less same for various mixed amine loading conditions. This is so because the CO_2 lean flue gas temperature at the outlet of the wash tower is kept same as at inlet to the absorber just as in the case for Solvent A.

For MDEA/MEA mixed amine solvent, the ASPEN simulations showed 0.05 mole CO_2 per mole of mixed amine as optimum inlet loading. The results below are for this loading.

Figures 20 to 26B below show the solvent performance for 70% and 90% CO_2 capture at 100 to 130^oC reboiler operating temperature and different flue gas temperature at the inlet to the absorber.



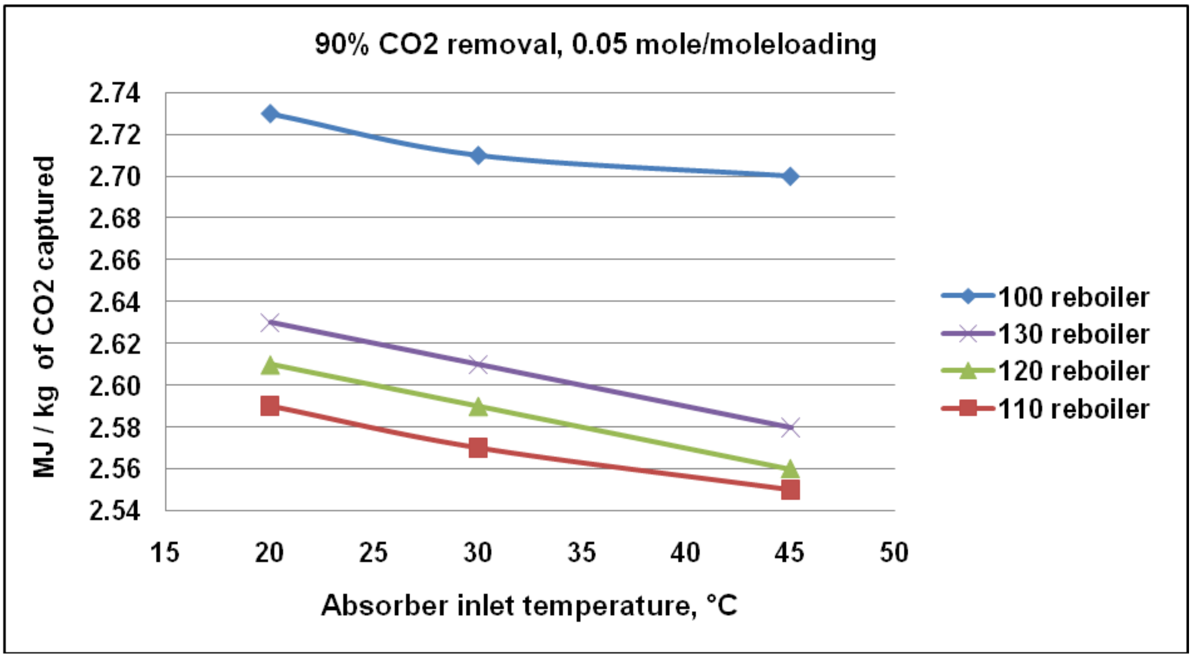


Figure 20 – Reboiler heat duty for Solvent C

The reboiler heat duty remains approximately between 2.5 and 2.8 MJ per kg of CO_2 captured which is substantially lower than the values observed for the Solvent A. Minimum reboiler heat duty requirement occurs around 110^oC reboiler temperature for all the cases of flue gas temperatures at inlet to the absorber.

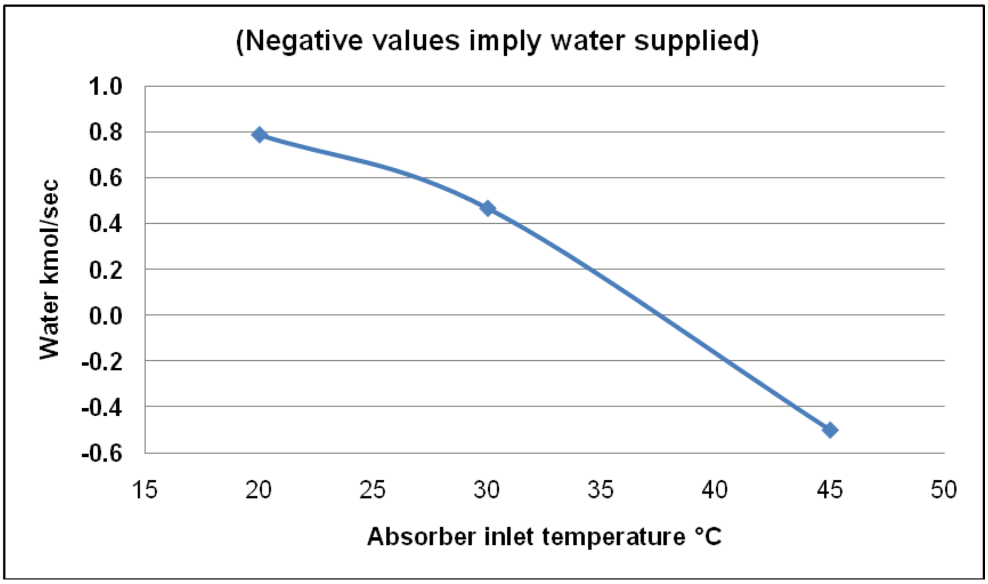


Figure 21 – Specific water consumption during capture process, Solvent C

As shown in Figure 21, when the flue gas is cooled to below 40°C prior to entering the absorber, the capture process will produce sufficient water to meet the wash water requirement to reduce the solvent emissions in the vapour phase. However, above this temperature, the process actually requires water to both cool the gas and lower the solvent emissions. It should be noted that in calculating the wash water requirement, care is taken that no excess waste water is created to increase the effluent treatment load.

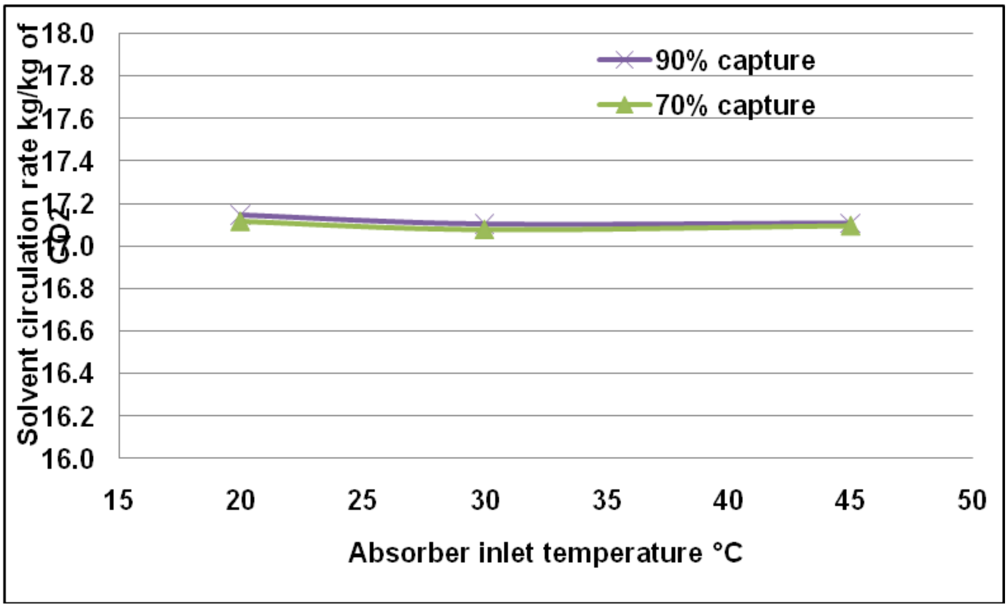
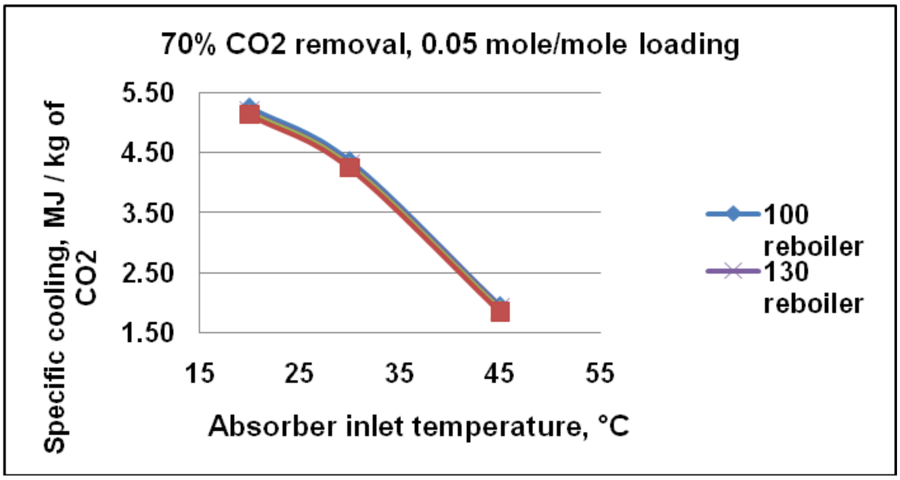


Figure 22 – Specific solvent circulation rate during capture process, Solvent C

Figure 22 above shows that the solvent circulation rate for 70 to 90% CO_2 capture remains fairly constant around 17.1 kg of solvent per kg of CO_2 captured. As shown in Figure 23 below the specific cooling load during the capture process remains roughly in the range 2 to 5.3 kJ per kg of CO_2 captured for 70 to 90% capture requirement and it is consistently minimal for the reboiler operating temperature of 110°C.



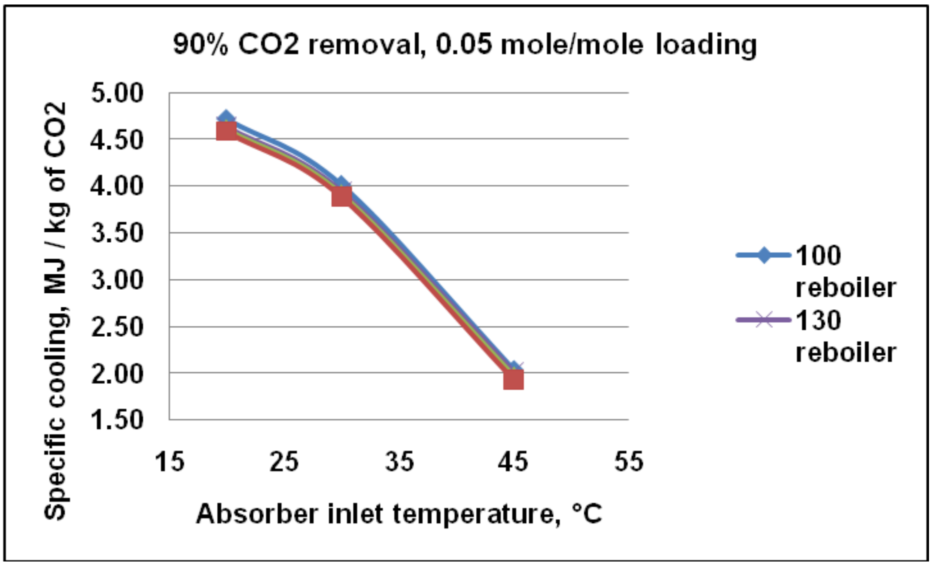
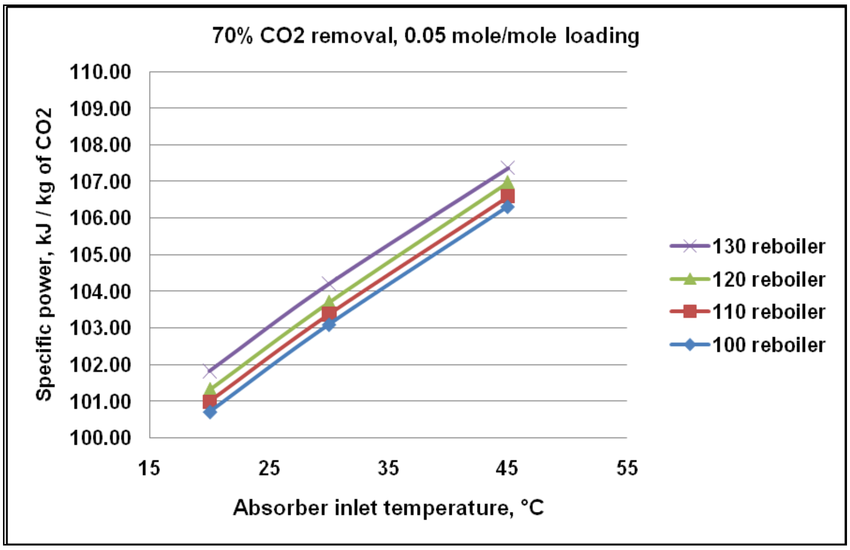


Figure 23 – Specific cooling load during capture process, Solvent C

Figure 24 below shows the specific electrical power load during capture process with Solvent C remains roughly the same as that with Solvent A and Solvent B (see Figures 11, 12, 17 and 24) and the flue gas blower remains main contributor to this power load.



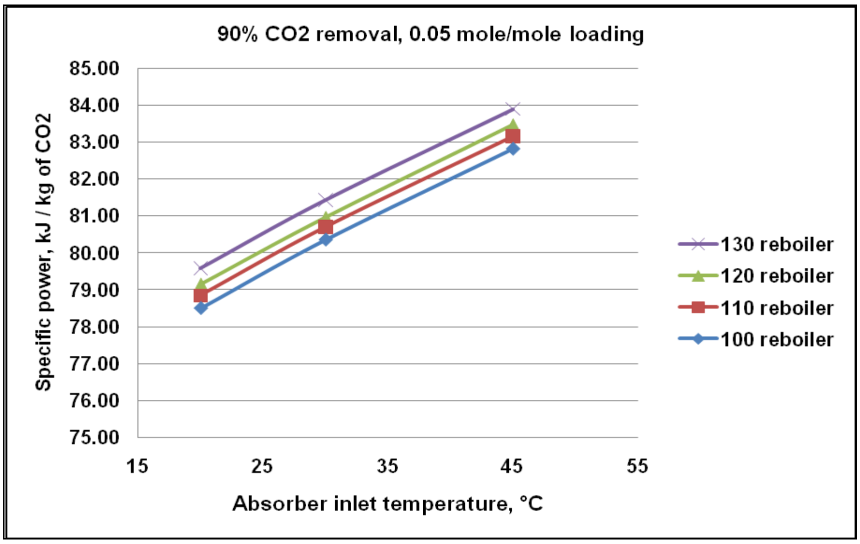


Figure 24 – Specific electrical power load during capture process, Solvent C

Figures 25/26 and 27/28 below show the extent of vapour phase emissions of Solvent C and its degradation products in g per tonne of CO_2 captured and on volumetric basis (ppmV) respectively over a range of flue gas inlet temperature to the absorber, 110^{o}C reboiler operating temperature and CO_2 loading of lean solvent at 0.05 mole per mole. It should be noted that ammonia emission for this case is related to ammonia present in the flue gas which has not dissolved in the aqueous phase of Solvent C plus that generated by the degradation of MEA as per the rate kinetics proposed by Idem et al (2007).

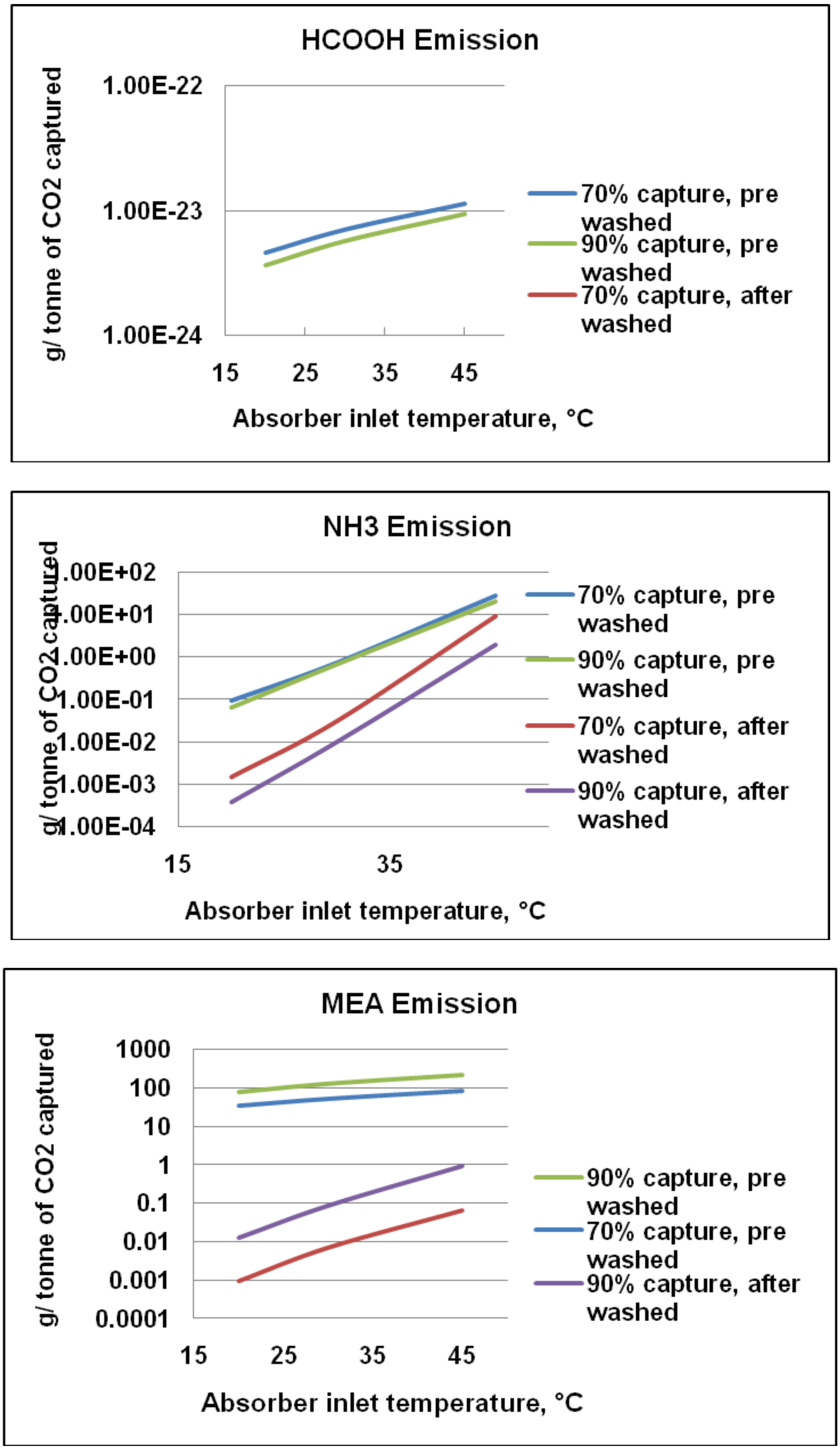
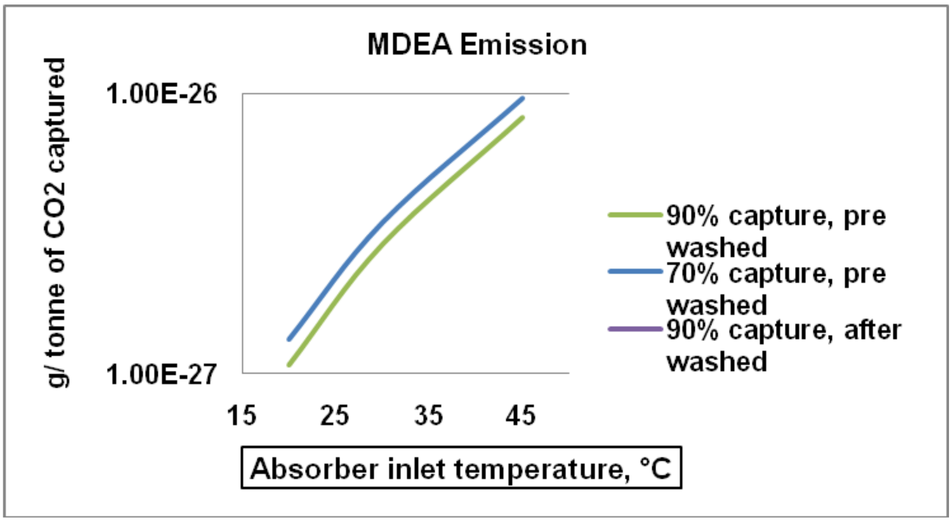
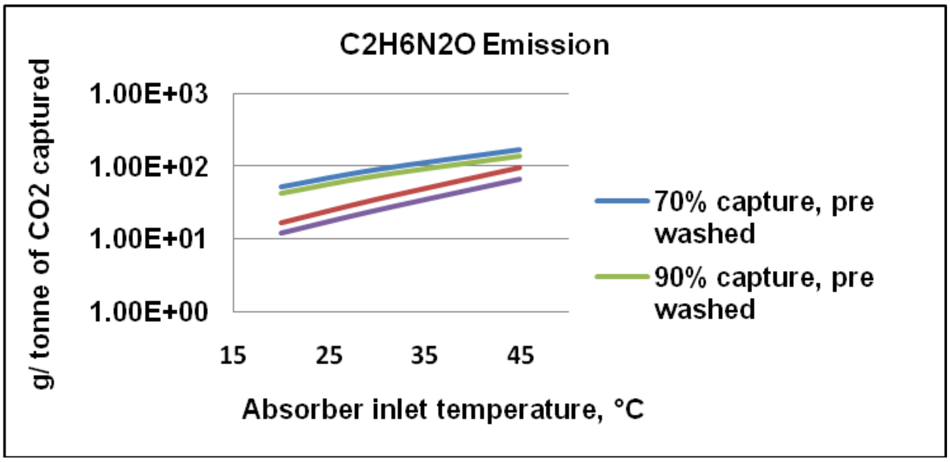


Figure 25 – Specific vapour emissions of Solvent C and its degradation products





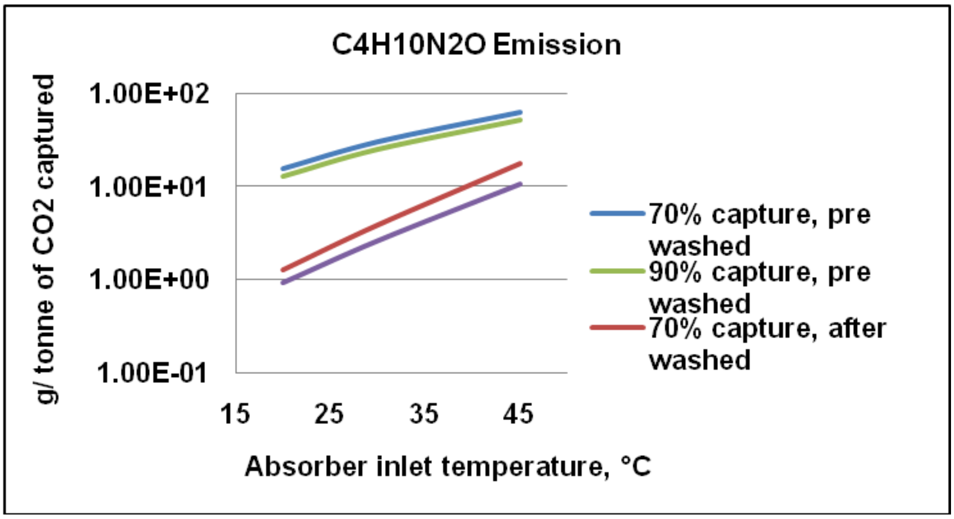
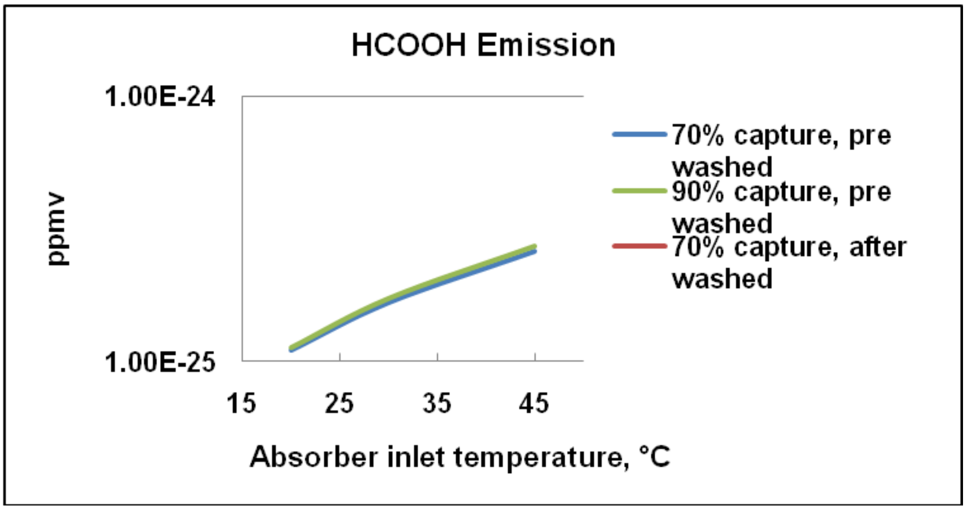
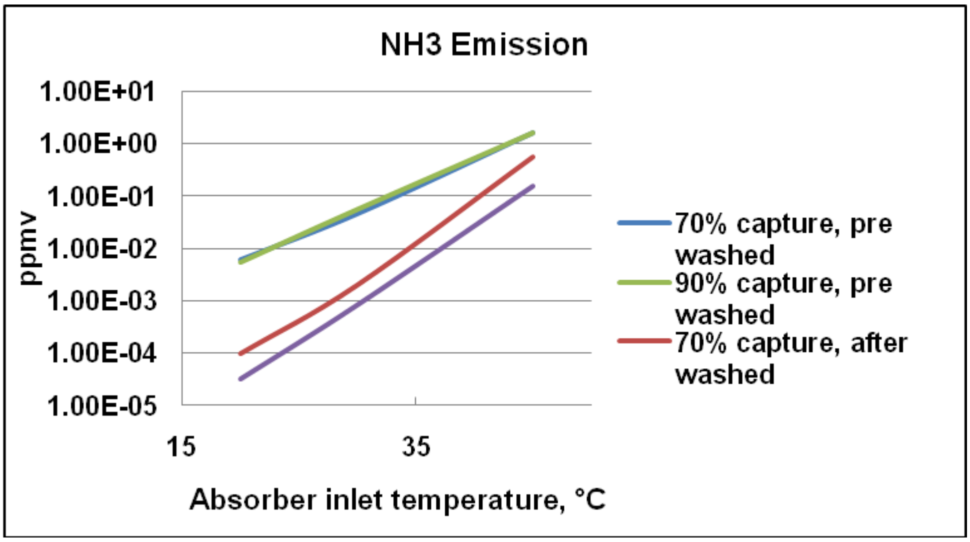


Figure 26 – Specific vapour emissions of Solvent C and its degradation products





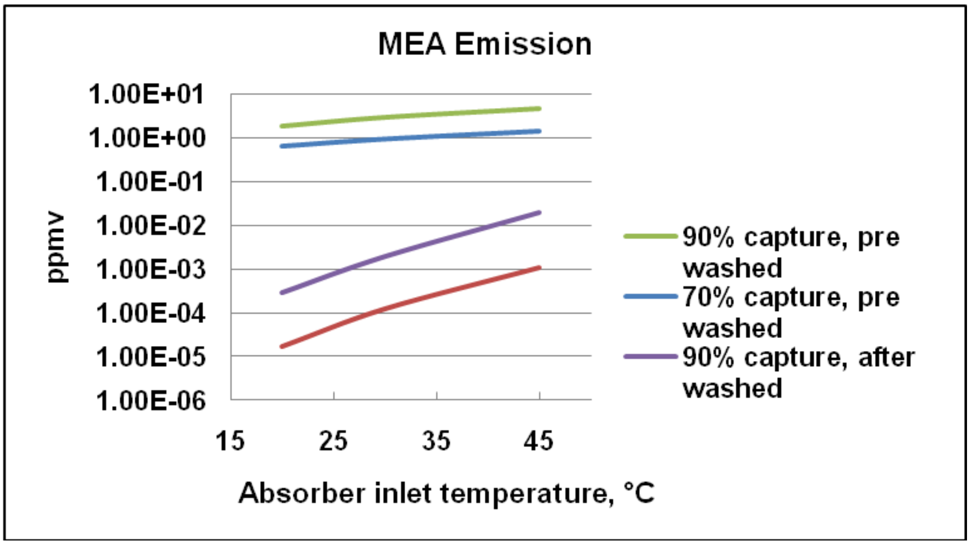


Figure 27 - Volumetric vapour concentrations of Solvent C and its degradation products

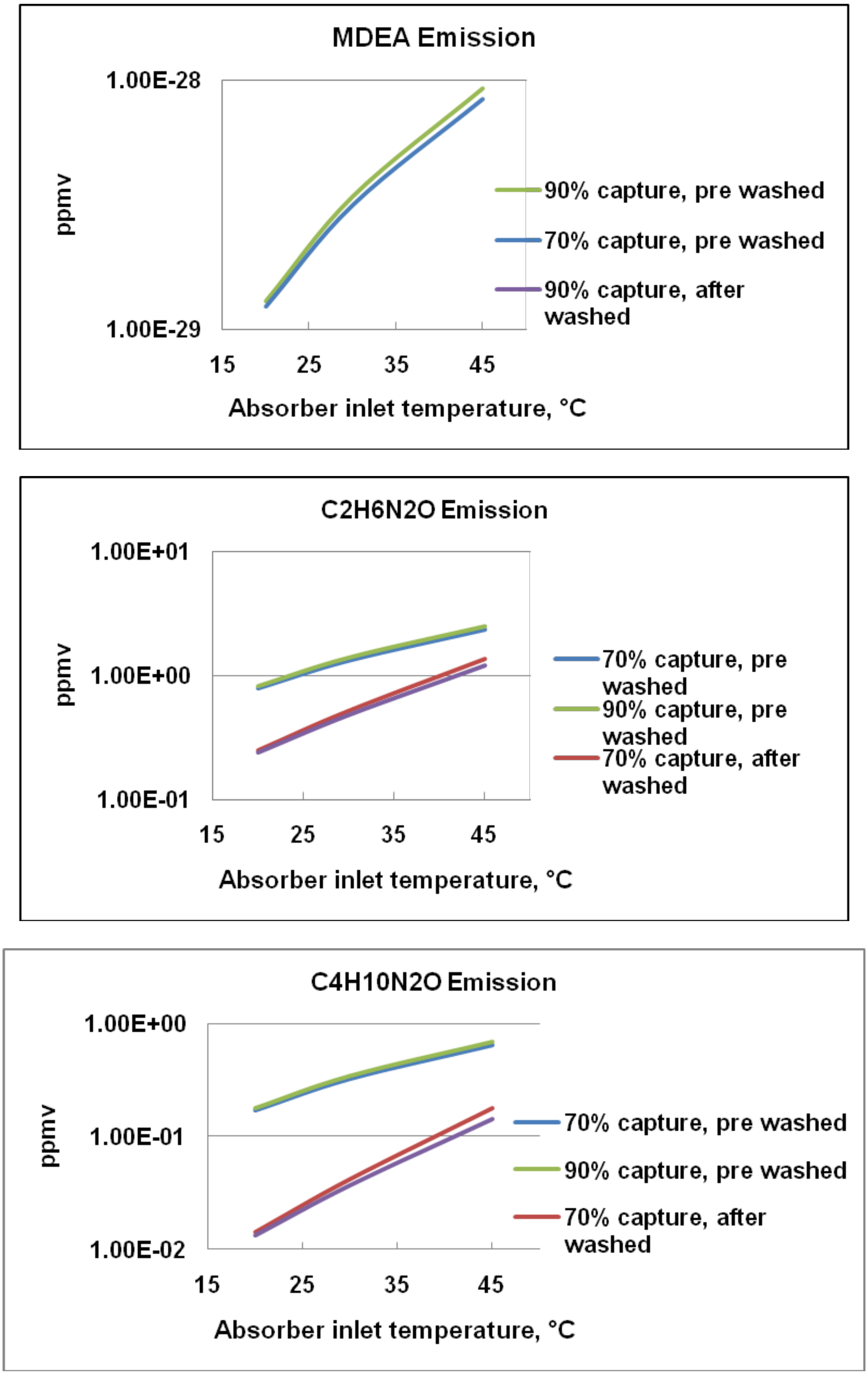


Figure 28 - Volumetric vapour concentrations of Solvent C and its degradation products

The vapour phase emissions of nitrosamines (dimethyl or diethyl forms only) were calculated assuming their concentration in the lean Solvent C to be at 2.91 µmol/mL though the basis for it is only the publication by Strazisar et al (2003). It should be noted that Srtazisar et al's observations were for 15 to 20% w/w aqueous MEA based solvent only whereas the Solvent C carries only 5% w/w MEA. Other predicted degradation products, i.e. formates (HCCOH equivalents), dimethyl-amino-ethanol (DMAE), diethanolamine (DEA) and ethylene oxide (EO) were found to be at practically negligible levels although Rooney et al (1998) have claimed to measure DEA at around 1600 ppm levels in the laboratory set-up after 28 days. One reason these degradation products are calculated by ASPEN to be at negligible levels is that it is a steady state simulator and hence, it is unable to predict the dynamic build up of such impurities which is what happens in a real plant environment.

Tables 15 and 16 list the numerical values of these emissions for the case of reboiler operating at 110^oC.

Table 15 – Specific vapour emissions of MDEA/MEA and Degradation Products (70% CO_2 Capture, 110^oC Reboiler Temperature)

Degradation Product	Before Wash (g/tonne CO_2)	After Wash (g/tonne CO_2)	Before Wash (ppmV)	After Wash (ppmV)
Absorber Inlet@ 20^oC				
HCOOH	4.55E-24	0.00E+00	1.10E-25	0.00E+00
NH_3	9.32E-02	1.47E-03	6.11E-03	9.74E-05
MEA	34.8	0.000916	6.36E-01	1.69E-05
MDEA	1.32E-27	0.00E+00	1.24E-29	0.00E+00
$C_2H_6N_2O$	5.23E+01	1.63E+01	7.88E-01	2.48E-01
$C_4H_{10}N_2O$	1.57E+01	1.27E+00	1.71E-01	1.41E-02
Absorber Inlet@ 30^oC				
HCOOH	7.03E-24	0.00E+00	1.67E-25	0.00E+00
NH_3	7.31E-01	3.07E-02	4.69E-02	1.99E-03
MEA	52.5	0.00687	9.38E-01	1.24E-04
MDEA	3.46E-27	0.00E+00	3.17E-29	0.00E+00
$C_2H_6N_2O$	8.97E+01	3.48E+01	1.32E+00	5.19E-01
$C_4H_{10}N_2O$	3.04E+01	3.85E+00	3.25E-01	4.16E-02
Absorber Inlet@ 45^oC				
HCOOH	1.14E-23	0.00E+00	2.60E-25	0.00E+00
NH_3	2.71E+01	8.96E+00	1.67E+00	5.49E-01
MEA	83.6	0.0645	1.43E+00	1.10E-03
MDEA	9.61E-27	0.00E+00	8.45E-29	0.00E+00
$C_2H_6N_2O$	1.67E+02	9.66E+01	2.36E+00	1.36E+00
$C_4H_{10}N_2O$	6.29E+01	1.74E+01	6.46E-01	1.78E-01

Table 16 – Specific vapour emissions of MDEA/MEA and Degradation Products (90% CO_2 Capture, 110 ^oC)

Degradation Product	Before Wash (g/tonne of CO_2)	After Wash (g/tonne of CO_2)	Before Wash (ppmV)	After Wash (ppmV)
Absorber Inlet@ 20^{o}C				
HCOOH	3.62E-24	0.00E+00	1.14E-25	0.00E+00
NH_3	6.37E-02	3.77E-04	5.40E-03	3.23E-05
MEA	78.2	0.0122	1.85E+00	2.92E-04
MDEA	1.07E-27	0.00E+00	1.30E-29	0.00E+00
$C_2H_6N_2O$	4.17E+01	1.20E+01	8.13E-01	2.37E-01
$C_4H_{10}N_2O$	1.26E+01	9.25E-01	1.79E-01	1.32E-02
Absorber Inlet@ 30^{o}C				
HCOOH	5.67E-24	0.00E+00	1.74E-25	0.00E+00
NH_3	6.69E-01	1.01E-02	5.54E-02	8.45E-04
MEA	130	0.0841	2.99E+00	1.97E-03
MDEA	2.89E-27	0.00E+00	3.42E-29	0.00E+00
$C_2H_6N_2O$	7.26E+01	2.46E+01	1.38E+00	4.76E-01
$C_4H_{10}N_2O$	2.50E+01	2.62E+00	3.45E-01	3.67E-02
Absorber Inlet@ 45^{o}C				
HCOOH	9.31E-24	0.00E+00	2.73E-25	0.00E+00
NH_3	2.03E+01	1.98E+00	1.60E+00	1.57E-01
MEA	219	0.905	4.83E+00	2.00E-02
MDEA	8.21E-27	0.00E+00	9.29E-29	0.00E+00
$C_2H_6N_2O$	1.36E+02	6.52E+01	2.47E+00	1.19E+00
$C_4H_{10}N_2O$	5.24E+01	1.07E+01	6.92E-01	1.41E-01

The vapour phase emissions of heat stable salts of MEA (as HCOOH) and MDEA are practically negligible compared to the emissions of MEA. Both MDEA and MEA emissions rise with increasing flue gas inlet temperature to the absorber. For 90% capture of CO_2, MEA emissions are higher than the corresponding values for 70% capture as observed in the case of Solvent A. Before washing the treated gas, ammonia emissions range from 64 mg to 27 g per tonne of CO_2 captured (5.4 ppbV to 1.7 ppmV); MEA emissions range from 35 to 219 g per tonne of CO_2 captured (0.6 to 4.8 ppmV); dimethyl-nitrosamine ($C_2H_6N_2O$) emissions range from 42 to 167 g per tonne of CO_2 captured (0.8 to 2.4 ppmV) and diethyl-nitrosamine ($C_4H_{10}N_2O$) emissions range from 13 to 63 g per tonne of CO_2 captured (170 to 690 ppbV). After washing the treated gas with demineralised water and recycling the excess waste water from wash towers to the lean solvent makeup, ammonia emissions range from 0.4 mg to 9 g per tonne of CO_2 captured (0.03 to 550 ppbV); MEA emissions range from 0.9 to 875 mg per tonne of CO_2 captured (0.02 to 19 ppbV), dimethyl-nitrosamine ($C_2H_6N_2O$) emissions range from 12 to 97 g per tonne of CO_2 captured (0.2 to 1.3 ppmV) and diethyl-nitrosamine ($C_4H_{10}N_2O$) emissions range from 0.9 to 17 g per tonne of CO_2 captured (13 to 178 ppbV). There is no public domain information available to verify the reliability of these emission results at present. Reducing these emissions further will require more fresh demineralised water circulation in the wash tower and that could result into excess waste water which could no longer be used in the process and thus increasing the effluent treatment load.

Table 17 shows the droplet emissions of Solvent C and its degradation products past the wash section in the absorber at the conditions of the vapour phase emission estimates. These values have been calculated assuming 0.13 m^3 carryover per million m^3 of treated gas leaving the wash section. Over 70 to 90% CO_2 capture rate, the flue gas temperature ranging from 20 to 45^oC and the reboiler temperature at 110^oC, the droplet emissions of ammonia, MEA, dimethyl-nitrosamine and diethyl-nitrosamine after the treated gas is water washed will be as: ammonia between 1 mg to 0.26 g per tonne of CO_2 captured; MEA between 0.6 to 2.1 g per tonne of CO_2 captured, dimethyl-nitrosamine between 0.5 to 1 g per tonne of CO_2 captured and diethyl-nitrosamine between 0.2 to 0.7 g per tonne of CO_2 captured.

Table 17 – Specific entrainment emissions of MDEA/MEA solvent and its degradation products (0.05 molar CO_2 lean loading, 110^oC Reboiler Temperature)

Degradation Product	**70% CO_2 Recovery (g/tonne CO_2)**	**90% CO_2 Recovery (g/tonne CO_2)**
Absorber Inlet@ 20^oC		
HCOOH	Nil	Nil
NH_3	1.67E-03	1.03E-03
MEA	6.34E-01	1.27E+00
MDEA	Nil	Nil
$C_2H_6N_2O$	6.56E-01	4.83E-01
$C_4H_{10}N_2O$	2.63E-01	1.90E-01
Absorber Inlet @ 30^oC		
HCOOH	Nil	Nil
NH_3	1.02E-02	7.74E-03
MEA	7.62E-01	1.52E+00
MDEA	Nil	Nil
$C_2H_6N_2O$	7.99E-01	5.65E-01
$C_4H_{10}N_2O$	3.87E-01	2.63E-01
Absorber Inlet @ 45^oC		
HCOOH	Nil	Nil
NH_3	2.64E-01	1.78E-01
MEA	1.22E+00	2.12E+00
MDEA	Nil	Nil
$C_2H_6N_2O$	1.02E+00	6.89E-01
$C_4H_{10}N_2O$	6.61E-01	4.05E-01

4.5 SUMMARY OF RESULTS FOR PCC PROCESS EMISSIONS ESTIMATES

This paragraph describes a summary of the PCC process emissions estimates for the components considered for each generic solvent.

Solvent A

ASPEN results have shown that for 70 to 90% CO_2 capture range, the optimum inlet CO_2 loading and reboiler temperature for Solvent A are 0.2 mole per mole of MEA and 120^oC respectively. At this operating condition, the reboiler heat duty is around 4 MJ per kg of CO_2.

Whilst there is enough literature information on what type of thermal and oxidative degradation products are formed when using this solvent for post combustion CO_2 capture, the reaction kinetics and stoichiometry for formation of these products is largely lacking in the public domain. There is little information on why, and to what extent the nitroso compounds are formed over time within this solvent. Due to lack of such information, ASPEN process simulations have been able to provide a very limited picture of the vapour phase emissions of Solvent A and its degradation products. Within the accuracy limits of ASPEN process simulations and its capability to duplicate in theory every aspect of a real life CO_2 capture plant environment, it can be suggested that the likely vapour phase emissions, when Solvent A is used at the process conditions specified in Table 2, will be in the following range depending upon the flue gas temperature at the inlet to the absorber: Heat stable salts – practically nil, ammonia – 9 mg to 2.6 g per tonne of CO_2 captured, MEA no more than 11 g per tonne of CO_2 captured, i.e. less than 1 ppmV.

Under the identical conditions, assuming that solvent carryover as droplets in the treated gas after the demister in the wash section of the absorber is around 0.13 m^3 per million m^3 of gas, the droplet emissions of Solvent A and its degradation products per tonne of CO_2 captured will be: Heat stable salts – 0.1 to 0.5 mg, ammonia – 17 mg to 0.5 g, MEA – 9 to 47 g.

Solvent B

For Solvent B, the ASPEN simulations have given less confident results. When compared the ASPEN generated vapour-liquid equilibrium data against the in-house data with CSIRO, it was seen that ASPEN generated partial pressure values for CO_2 differed substantially over the operating temperature range of the absorber and the solvent regenerator. Nevertheless, these results show that for 70 to 90% CO_2 capture range, the optimum inlet CO_2 loading and reboiler temperature are 0.036 mole per mole of mixed amines and 120^{o}C respectively. At this operating condition, the reboiler heat duty is around 2 MJ per kg of CO_2 and the required solvent circulation rate is less than half of that for Solvent A. This confirms the rate promoting characteristics of piperazine. Unfortunately, there is very little information on why, how and what type of thermal and oxidative degradation products are formed with this solvent in the public domain literature. Hence, ASPEN has been able to provide only a limited understanding of the likely vapour phase concentrations with the treated gas. Within the capability limits of ASPEN process simulator to model Solvent B based post combustion capture process, it is likely that when the treated gas is washed with demineralised water, the likely emissions will be: ammonia from 0.6 to 57 ppbV; AMP from 0.7 g to 1.2 kg per tonne of CO_2 captured (8.7 ppbV to 1.8 ppmV) and PZ from 8 mg to 1.5 g per tonne of CO_2 captured (0.1 to 240 ppbV). There is no public domain information available to verify the reliability of these emission results at present. Reducing these emissions further will require more fresh demineralised water circulation in the wash tower and that could result into excess waste water which could no longer be used in the process and thus increasing the effluent treatment load.

Under the identical operating condition range as for the vapour phase estimates, the droplet of Solvent B will be: Ammonia - 8 mg to 0.3 g, AMP – 15 to 127 g and PZ – 0.6 to 9.5 g.

Solvent C

For Solvent C, the ASPEN simulations show that for 70 to 90% CO_2 capture range, the optimum inlet CO_2 loading and the reboiler temperature are 0.05 mole per mole of mixed amines and 110^{o}C respectively. At this operating condition, the reboiler heat duty is around 2.8 MJ per kg of CO_2 and the required solvent circulation rate is slightly less than that for

Solvent A. Whilst there is some information available in the public domain on degradation of MEA, the information on MDEA degradation is rather confusing and practically nil. MDEA degradation has been studied in laboratory environment by Chakma and Meisen (1977) from the point of natural gas processing and so also by Rooney et al (1998). Both investigators suggest different sets of degradation products. There is no information available on formation of nitroso compounds with this solvent, but since MEA is one of the ingredients of Solvent C, it is likely that some nitroso compounds may form in real plant environment. Within the capability limits of ASPEN process simulator to model Solvent C based post combustion capture process, it is likely that when the treated gas is washed with demineralised water, the likely emissions will be: Heat stable salts – Nil; ammonia from 0.4 mg to 9 g per tonne of CO_2 captured (0.03 to 550 ppbV); MDEA – Nil; MEA from 0.9 to 875 mg per tonne of CO_2 captured (0.02 to 19 ppbV), dimethyl-nitrosamine ($C_2H_6N_2O$) from 12 to 97 g per tonne of CO_2 captured (0.2 to 1.3 ppmV) and diethyl-nitrosamine ($C_4H_{10}N_2O$) from 0.9 to 17 g per tonne of CO_2 captured (13 to 178 ppbV). There is no public domain information available to verify the reliability of these emission results at present. Reducing these emissions further will require more fresh demineralised water circulation in the wash tower and that could result into excess waste water which could no longer be used in the process and thus increasing the effluent treatment load.

Under the identical operating range of the process parameters as for the vapour phase emission estimates, the droplet emissions of Solvent C to the atmosphere per tonne of CO_2 captured will be: Heat stable salts – nil, ammonia – 1 mg to 0.3 g, MDEA – nil, MEA – 0.6 to 2.1 g, dimethyl-nitrosamine – 0.5 to 1 g and diethyl-nitrosamine – 0.2 to 0.7 g. These values are based on the upper limit of droplet carryover (0.13 m^3 per million m^3 of treated gas) suggested by the Handbook of Gas Producers' Association (2004).

4.6 GENERIC SOLVENT RANKING

Table 18 summarises the ASPEN simulations based range of emissions for generic solvents A, B, and C and their degradation products leaving the wash section of the absorber over the process conditions specified in Table 2. This range includes both the vapour losses and the entrainment losses.

Table 18 – Range of specific atmospheric emissions for the generic solvents in PCC use

	Vapour **(per tonne CO_2 captured)**	**Entrainment** **(per tonne CO_2 captured)**	**Total** **(per tonne CO_2 captured)**
Solvent A			
Heat stable salts	Nil	0.1 to 0.5 mg	0.1 to 0.5 mg
Ammonia	9 mg to 2.6 g	17 mg to 0.5 g	26 mg to 3.1 g
MEA	12 mg to 11 g	9 to 47 g	21 to 58 g
Dimethyl-nitrosamine	11 to 95 g	0.4 to 1 g	12 to 96 g
Diethyl-nitrosamine	2.5 to 29 g	0.3 to 0.7 g	3 to 30 g

Solvent B			
Ammonia	3.4 mg to 1 g	8 mg to 0.3 g	12 mg to 1.3 g
AMP	0.7 g to 1.2 kg	15 to 127 g	16 g to 1.3 kg
PZ	0.8 mg to 1.5 g	0.6 to 9.5 g	0.6 to 11 g
Solvent C			
Heat stable salts	Nil	Nil	Nil
Ammonia	0.4 mg 9 g	1 mg to 0.3 g	1.4 mg to 9.3 g
MDEA	Nil	Nil	Nil
MEA	0.9 mg to 0.9 g	0.6 to 2.1 g	0.6 to 3 g
Dimethyl-nitrosamine	12 to 97 g	0.5 to 1 g	12.5 to 98 g
Diethyl-nitrosamine	0.9 to 17 g	0.2 to 0.7 g	1 to 18 g

Not considering the nitrosamines, the bulk of emission for Solvent A is MEA entrained in the gas stream. The same is true for Solvent C but at much lower emission rates, due to the lower concentrations in solution. For Solvent B it is the vapour losses from AMP which forms the bulk of the emissions. On the whole of the three generic solvents, Solvent B appears to have the highest specific emission rate, followed by Solvent A. Solvent C has the lowest overall specific emission rate.

5. DISCUSSION

Review of procedure for estimation of emission rates from PCC process

The determination of the emission rates of harmful compounds from amine based PCC processes started off with an assessment of the nature of amine degradation products in PCC processes. This assessment has been followed by an estimation of emission rates as determined by formation rates found in the literature for the major degradation product ammonia and formate. In addition the emission rates for amines and nitrosamines as vapours have been estimated by considering their vapour pressure above the amine solution with a certain concentration of model nitrosamine components. The emission estimates have been carried out using the ASPEN Plus process simulation software equilibrium based process modelling. A literature based model was used to estimate emissions of the main degradation product ammonia. The process simulations have also provided the information related to the composition of the wash water, which determines the emission rate through droplets.

CO_2-Amine equilibrium data

The review of the process simulation results indicates that the emissions estimates for the amines are credible. The comparison with experimental data, albeit limited, indicated a good agreement with process modelling results. The thermodynamics of CO_2-amine-water systems, in particular for single amines like MEA, is comprehensively covered by the ASPEN Plus process simulator. For amine mixtures, the general process simulation results indicate that improvements in the thermodynamic models are required. This is particularly true for AMP/PZ mixtures (solvent B) where the equilibrium model used by ASPEN Plus resulted in very low values for the reboiler duty. A comparison of CO_2-AMP/PZ equilibrium data generated by ASPEN Plus with a limited dataset, available in-house, showed large differences in the CO_2 partial pressure at typical regenerator temperatures. The predicted vapour emissions from a PCC process using solvent B (AMP/PZ) were higher than for Solvent A (MEA), which is to be expected given the higher vapour pressure of both AMP and PZ at the same temperature. Hence the thermodynamic model in ASPEN Plus appears to be predicting the right tendency. Nevertheless the quality of thermodynamic modelling as determined by its ability to predict the vapour pressures of CO_2 and the amine needs to be improved.

Degradation products

The detailed assessment of emissions of degradation products through was limited to ammonia and formate, using formation predictions taken from the literature. A comparison with results from CSIRO’s pilot plant operations seems to indicate the emissions of ammonia are underestimated by the model used by one order of magnitude. A much better understanding must be developed for the degradation of amines under PCC process conditions, in particular in relation to the nitroso-compounds. 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 the solvents undergo a thermal cycling it is quite important to assess the effect of higher temperature on the stability of degradation products. This study has indicated that this information is lacking. Given the complexity it is likely that degradation products must be lumped to provide a simplified description of the degradation process.

Evolution of degradation over time

The result of the ASPEN Plus process simulation present a steady-state process condition, which is unlikely to occur where it concerns the formation of degradation, at least over the same time scale. It should be noted that the degradation products will build up over a time in an operating environment of CO_2 capture. The rates for the formation of amine degradation products are expected to be at least three others of magnitude smaller than the reaction rates for CO_2 with amines. Their concentration levels at any instance will be determined by the prevailing plant operation conditions and maintenance practices. This means that the solvent regeneration process, the frequency of operating the solvent reclaimer, solvent replenishment and replacement 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 also be noted that the commercial technology providers use proprietary corrosion inhibitors and oxidative oxygen scavenging chemicals, the composition and working mechanisms of which are not available in the public domain.

Process conditions

The results of the ASPEN Plus process simulation indicate clearly which process conditions will impact the largest on the emissions. It is clear that the temperature of the absorber and wash section (liquid entrance temperature held at the same constant level in this study) has a dominant impact. It is not surprising that higher temperatures will lead to higher emission rates as the kinetics for degradation are more favourable and desorption of reaction products is also favoured. Experimental results indicate that a low lean loading of the solvent will result in higher emission rates for the amine from the absorber. The process modelling seems to indicate that this is counteracted by the water wash section after which the amine concentration level is similar irrespective of the initial concentration level after the absorber.

Usefulness of ASPEN Plus 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 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 amine based CO_2 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, % CO_2 capture desired (solvent circulation rate and its loading), the wash tower operating parameters (wash water circulation rate, its temperature and the effectiveness of the demister) and the type of solvent used for capturing CO_2 decide the level of atmospheric emissions. In that sense, ASPEN has been able to compare the three generic solvents for CO_2 capture and rank them for environmental impact of emissions to air.

Process and equipment design

The PCC process emission estimates were derived assuming the chemical and phase equilibrium models (RADFRAC) within the ASPEN process simulator for CO_2 absorption and as such these emission estimates may need to be reassessed using the chemical rate kinetics based (RATESEP) models within the ASPEN process simulator. This will require the first steps towards the selection of equipment design parameters and specific components, such as the absorber diameter, its height, packing type and size. This has the benefit that the droplet emissions due to liquid entrainment can be assessed in more detail. These depend on the design of absorber internals and their operating efficiency, the prevailing hydrodynamics within the absorber, the gas/liquid interfacial properties and how efficiently the process plant equipment performance is controlled. The gas/liquid interfacial properties may change over time as the degradation products accumulate within the process affecting both the hydrodynamics within the absorber and as a result the extent of droplet emissions. Apart from experimental analysis in larger dedicated set-ups CFD will be useful tool to assess droplet emissions. This should include an assessment of the demister effectiveness. If the water-wash section after the CO_2 absorption section fails to operate, then the composition of droplet emissions will entirely change and be represented by the lean solvent composition. Whether such an event needs be counteracted or prevented will need to be considered in a risk assessment.

Essentials of a PCC process emission prediction method

The ASPEN Plus process simulates a steady state operation of a PCC process, providing information on its main performance parameters, such as reboiler duty, specific solvent flow rate etc. Although it is anticipated that the amine vapour losses can be adequately described, it might not be the most appropriate tool to describe the dynamics of PCC emission process emissions. Solvent degradation phenomena occur at a much slower rate than the CO_2 absorption rate, resulting in a build up of degradation products in the circulating solvent. Such degradation products can have a certain volatility which means that the total emissions are the sum of the evaporative losses as determined by the Henry coefficient of the degradation product in the solvent and the losses through droplet carry-over. Losses of non-volatile degradation products will be modelled through the droplet carry-over. Both of these effects are strongly influenced by the process and equipment design.

The process model should also include the impact of the regeneration process on the degradation product, as well as the effect of a reclaimer. Also the addition of fresh make-up solvent should be addressed. It might well be that methods to chemically transform the degradation products, separate or concentrate degradation products are included in the solvent loop and these need to be part of the model. The compounds emitted in the absorber will be fed to the wash section, where the capture of emitted compounds (either in droplets or as gaseous components) needs to be modelled accurately as well. The model will have to include the physical phenomena (droplet capture efficiency and Henry coefficient to describe absorption) and possible chemical transformations (acid-base interactions) occurring in the circulating wash-water. The next step will involve the demister section, which will remove part of the droplets carried over from the wash-section.

6. CONCLUSIONS

The study has attempted to provide an overview of a range of factors determining the emissions of PCC processes with particular reference to three generic solvents. The work utilised the ASPEN Plus process simulator to estimate the amine emissions, using information from the literature to describe ammonia emissions and providing an estimate of nitrosamines based on a literature derived equilibrium concentration in the solvent. Both evaporative emissions and droplet emissions were also considered.

The literature review of solvent degradation indicated a wide range of different degradation products which might impact negatively on the atmosphere. However, no quantitive information was found to enable modelling of the emissions of the range of degradation products. Thus no credible estimates for emissions other than amines, ammonia, formate and selected nitrosamines could be produced.

It appears that the absorber temperature is the parameter influencing emissions the most with high emissions occurring at higher temperature. The effect of solvent loading on the emissions after the wash section seems rather limited.

A limited comparison of modelling results with a limited data-set obtained from one of CSIRO’s pilot plants indicated good agreement for the amine emissions, but the predicted emissions for the major degradation product ammonia were one order of magnitude lower than the measured ones. This indicated that amine emissions can be predicted reasonably well, but for degradation products there is a need to develop more sophisticated models. A similar comparison indicated that results from the ASPEN Plus process simulator for amine mixtures need to be reviewed critically.

The comparison of emissions for the three generic solvents showed that solvent B (AMP/PZ) exhibited the highest emissions, followed by solvent A (MEA). Solvent C (MEA/MDEA) showed the lowest emission rates. These results are closely correlated with the amine vapour pressures of the different solvents.

7. RECOMMENDATIONS

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 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 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, 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 preferred as it provides more detail 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, preferable over a period, to follow the progression of emission rates over time to take into 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.

Other emissions to the atmosphere

In addition to the vapour phase and the liquid entrainment based solvent emissions, it should highlighted that the fugitive emissions of these solvents may occur through the pipeline joints, valve fittings, instrumentation joints and the solvent storage vents. In a large commercial scale operation capturing million tonnes per annum of CO_2, these emissions to the surrounding atmosphere could be substantial.

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