15 – ARPC – 03

Literature Review: Use & Environmental Impact of Amines

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Executive Summary

Process Ecology conducted an extensive literature review on the subject of amine emissions (including amine emissions and amine degradation product emissions). Two major processes which are sources of emissions were the focus of this literature review: the natural gas sweetening process and the CO_2 capture process.

For the gas sweetening process, the most common continuous losses of amine are entrainment loss, vapourization loss and degradation loss. The entrainment loss and vapourization loss will end up in the sweet gas stream and they are not released directly to air at the sweetening facility. The amine loss from degradation within the gas sweetening process will mostly end up in solid waste from regenerator, which does not significantly affect air quality.

For the amine-based CO_2 capture process, most of the amine losses will be released to air directly, without any control on the contactor overhead. Moreover, a variety of degradation products including nitrosamine (a carcinogen) will be formed in the CO_2 capture process and be released to air.

After amines are released to air, they will begin degrading to other chemical compounds. The atmospheric reactions are complex and compounds including nitrosamines can be formed. Process Ecology also conducted an environmental fugacity study through a third party company to investigate the concentration of MEA and other amines which may be released to water and soil using emission data from literature. It was shown that the amine-based CO_2 capture process has the potential to put at risk surface drinking water sources in Alberta that may be near CO_2 capture facilities.

Human health and environmental impact of amines and amine degradation products were also reviewed in this study.

Although a significant amount of literature is available, there is still a lack of real plant data and real online measurement of amine emissions for sound decisions to be made. With CO_2 capture attracting more and more attention in order to reduce GHG emissions from SAGD and other industrial plants, including power plants, it is important to fully understand and control the risk of amine emissions from this process.

The report is organized as follows:

In Section I, the amines and amine degradation products emission sources and emission rates are reviewed. Simulations using HYSYS™ and VMGSim™ are performed to investigate the amine vapourization loss from the contactor. Measurement technologies for amine emissions are also reviewed.

In Section II, the atmospheric reactions of amines and the amine partitioning in the environment are reviewed. Human health and environmental impact of amines and amine degradation products are also reviewed in this section.

In Section III, regulations on amine and amine degradation products are presented.

Section IV gives conclusions and recommendations for future work.

Section I: Quantification of Amine Emissions

1. Use of Amines in the Oil & Gas Industry

Amine is short for alkanolamine; it is widely used as an absorption agent in the natural gas processing industry to remove acid gases from produced sour gas. Another major use of amine is in the post-combustion CO_2 capture process, where amine solvent is used to remove CO_2 from flue gas. In this review study, we focused on both the gas sweetening process, and the post-combustion CO_2 capture process. There are other minor uses of amine, for example: as a corrosion inhibitor, as corrosion protection or in pH adjustment, however, these amine uses are not considered in this study due to their very low usage rate.

1.1. Gas Sweetening Process

The removal of sour gas components such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from natural gas streams is a process requirement in many parts of the hydrocarbon processing industry. This is especially true with the increasingly stringent environmental considerations and human health considerations coupled with the need to process natural gas and crude oil with increasing sulfur levels. Typical maximum levels for H_2S in pipeline transportation of natural gas are 4 ppmv [2]. The chemical solvent process, called the gas sweetening process, using the various alkanolamines (also referred to as amines), is the most widely employed gas treating process.

These processes utilize amine solvent to react with the acid gas components (H_2S and CO_2) to form a chemical compound. This compound is subsequently broken down in the regenerator to release the acid gas and regenerate the amine solvent for reuse. The alkanolamines are widely used in the natural gas processing industry. Figure 1 [2] illustrates the process flow for a typical gas treating plant employing an alkanolamine.

Gas to be processed is passed through an inlet separator to knock out any entrained liquid, and then the sour gas is introduced at the bottom of the contactor. Normally a packed or trayed tower is used and the gas is contacted counter-currently with the aqueous amine solution. The acid gas components in the gas react with the amine to form a regenerable compound. As the gas continues to pass up the contactor, more acid gases react with the amine. The sweetened gas leaves the top of the contactor. If the amine losses are excessive, a water wash section as shown in Figure 2 [2] can be added to the column to attempt to recover some of the vaporized and/or entrained amine from the gas leaving the contactor. The water wash section generally consists of three or four trays at the top of the contactor. It is recommended to install a demister pad on the vapour outlet to limit entrainment in the contactor.
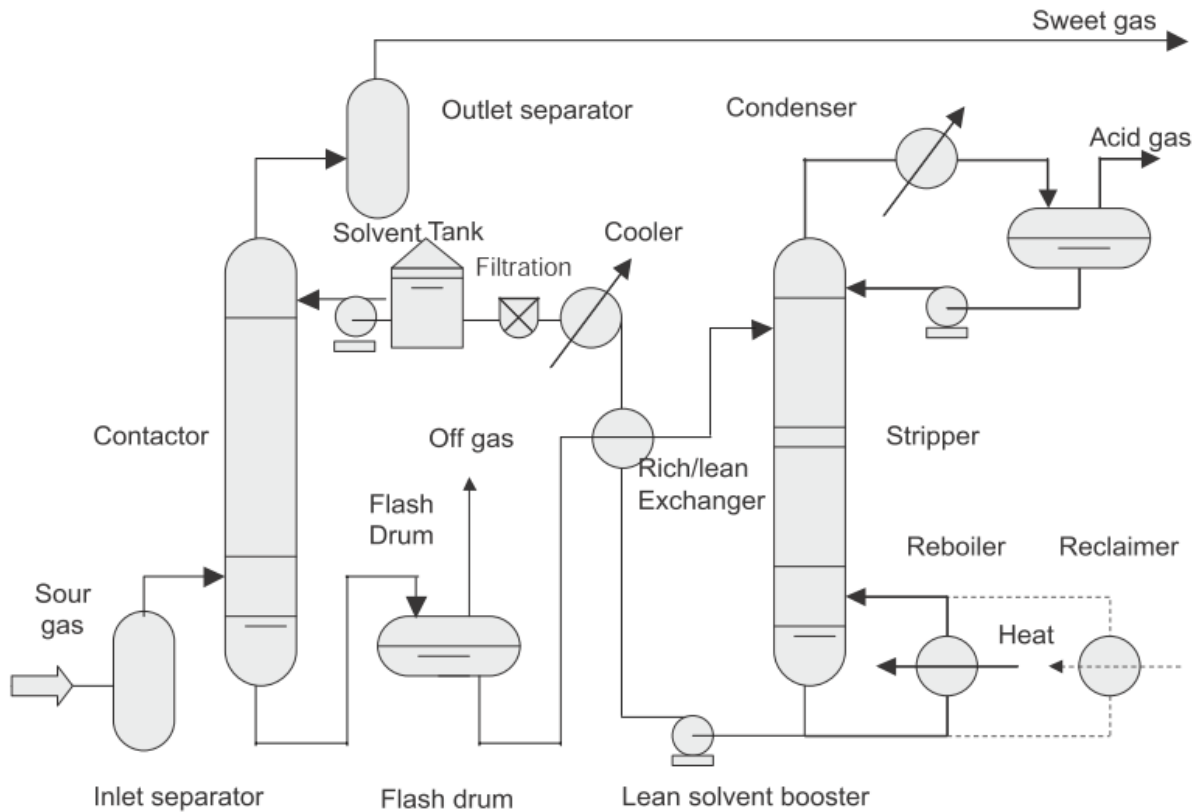
Figure 1: Typical Gas Sweetening Process by Amines [2]
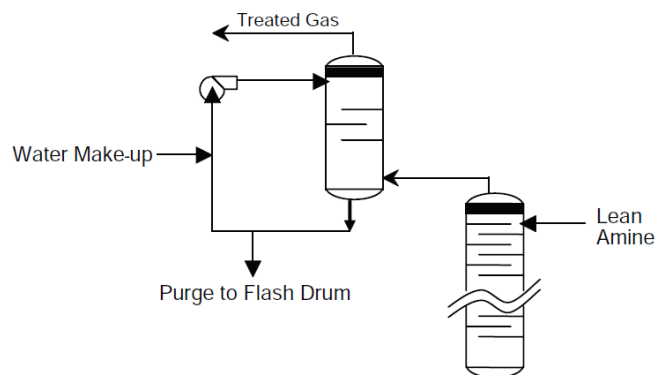
Figure 2: Typical Water Wash for Sweet Gas Leaving Amine Contactor [2]

The rich amine from the bottom of the absorber is heated by heat exchange with lean solution from the bottom of the regenerator column and is then fed to the regenerator column near the top. In units treating sour hydrocarbon gases at high pressure, it is also an option to flash the rich solution in a flash drum maintained at an intermediate pressure to remove dissolved and entrained hydrocarbons before regeneration [1].

From the flash drum, the rich amine goes to the upper portion of the regenerator. As the solution flows down the column to the reboiler, it is stripped of H_2S and CO_2. The amine solution leaves the bottom of the regenerator as lean amine. Then, the lean amine is returned to the contactor to repeat the cycle.

Chemistry in Gas Sweetening

The overall reaction between H_2S and CO_2 and primary amines is shown below [2]:

For hydrogen sulfide (H_2S) removal:

NH2 + H_2S ↔ RNH3$^+$ + HS$^-$

NH2 + HS$^-$ ↔ RNH3$^+$ + S^{--}

For carbon dioxide (CO_2) removal:

2 RH2 + CO_2 ↔ RNH3$^+$ + RNHCOO$^-$

RNH2 + CO_2 + H2O ↔ RNH3$^+$ + HCO3$^-$

RNH2 + HCO3$^-$ ↔ RNH3$^+$ + CO3$^-$

Amines used in Gas Sweetening

The GPSA Engineering Data Book [2] contains an informative section about the common amines used in the gas sweetening process. Portions of this section are shown here for clarity.

"**Monoethanolamine (MEA)** is used where there are low contactor pressures and/or stringent acid gas specifications. MEA removes both H_2S and CO_2 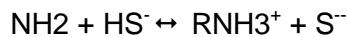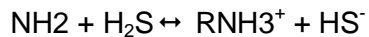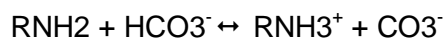from gas streams. H_2S concentrations well below 4.0 ppmv can be achieved. CO_2 concentrations as low as 100 ppmv can be obtained at low to moderate pressures. Total acid gas pick up is traditionally limited to 0.3-0.35 moles of acid gas/mole of MEA and solution concentration is usually limited to 10-20 wt%. Because MEA has the highest vapour pressure of the amines used for gas treating, solution losses through vapourization from the contactor and stripper can be high. This problem can be minimized by using a water wash.

Diethanolamine (DEA) will not treat to pipeline quality gas specifications at as low a pressure as will MEA. This amine is used to treat high pressure, high acid gas content streams having a relatively high ratio of H_2S/CO_2. The original process has been progressively improved and Total uses higher DEA solution concentrations up to 40 wt% and a high acid gas loading. The process flow scheme for conventional DEA plants resembles the MEA process. The advantages and disadvantages of DEA as compared to MEA are:

• The mole/mole loadings typically used with DEA (0.35- 0.82 mole/mole) are much higher than those normally used (0.3-0.4) for MEA.

• Because DEA does not form a significant amount of non-regenerable degradation products, a reclaimer is not usually required.

• DEA is a secondary amine and is chemically weaker than MEA, and less heat is required to strip the amine solution.

• DEA forms a regenerable compound with COS and CS2 and can be used for the partial removal of COS and CS2 without significant solution losses.

Methyldiethanolamine (MDEA) is a tertiary amine which can be used to selectively remove H_2S to pipeline specifications at moderate to high pressure. If an increased concentration of CO_2 in the residue gas may cause a problem with contract specifications or downstream processing, further treatment will be required. The H_2S/CO_2 ratio in the acid gas can be 10-15 times as great as the H_2S/CO_2 ratio in the sour gas. Some of the benefits of selective removal of H_2S include:

• Reduced solution flow rates resulting from a reduction in the amount of acid gas removed.

• Smaller amine regeneration unit.

• Higher H_2S concentrations in the acid gas resulting in reduced problems in sulfur recovery.

CO_2 hydrolyzes at a much slower rate than H_2S with MDEA. This makes possible significant selectivity of tertiary amines for H_2S. This fact is used by several companies which provide process designs using MDEA for selective removal of H_2S from gases containing both H_2S and CO_2. A feature of MDEA is that it can be partially regenerated in a simple flash. As a consequence the removal of bulk H_2S and CO_2 may be achieved with a modest heat input for regeneration."

Besides the above mentioned MEA, DEA and MDEA, there are other amine solvents like DGA or formulated/mixed amine solvents used in the gas sweetening process. Those amines are not discussed in this review study due to their relatively small usage in Alberta.

1.2. Post Combustion CO2 Capture Process

Fossil fuel combustion supplies more than 85% of energy for industrial activities, and is thus the main source of greenhouse gases (GHG) in the form of CO_2 [6]. The generally accepted goal is to limit the global temperature increase to 2°C above pre-industrial levels, which The Intergovernmental Panel on Climate Change (IPCC) has estimated would require a 50-85% emission reduction from 2000 level by 2050 [8]. Various scientific approaches have been proposed to limit the emission of CO_2, and among those approaches, it is believed that amine-based CO_2 absorption systems are the most suitable for combustion based power plants for the following reasons [17]:

(1) These systems are effective for dilute CO_2 streams (typically flue gas has 10%-12% CO_2 by volume).

(2) Amine-based systems are a proven technology which has been widely used in gas sweetening.

(3) Amine-based CO_2 capture systems can operate at normal temperatures and pressures.

(4) A major effort worldwide has been made to improve and investigate this process.
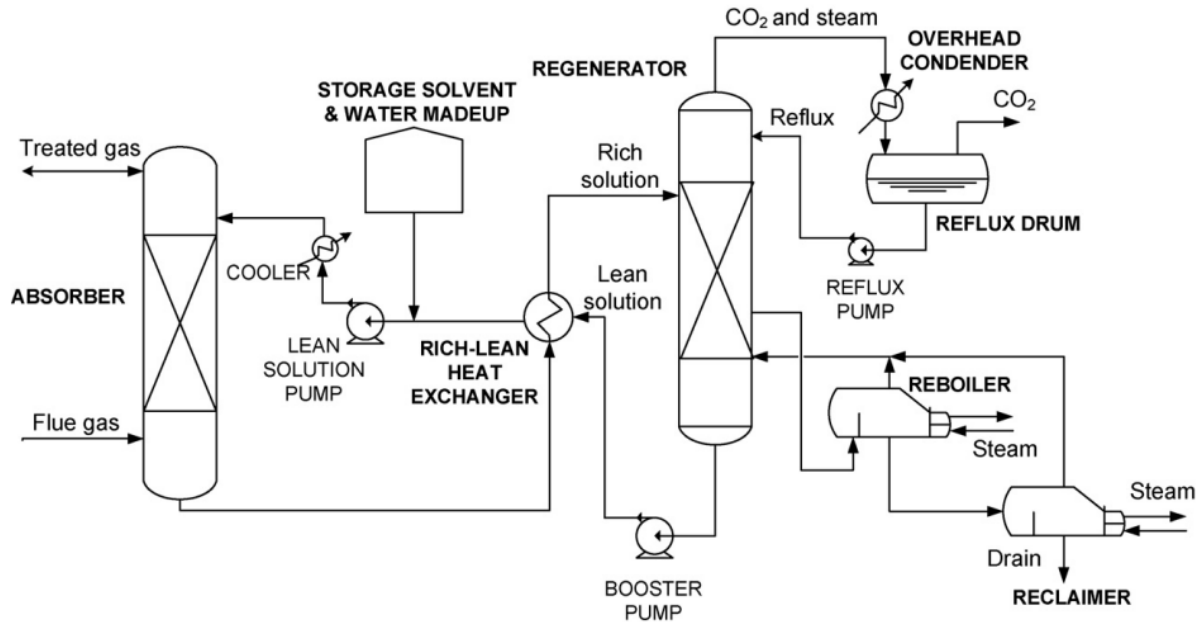
Figure 3: Typical flow diagram of solvent based CO_2 capture system [5]

Figure 3 [5] illustrates a typical configuration of the CO_2 absorption process using amine solvent. The process consists of two major sections, an absorption section where CO_2 in the flue gas is absorbed by an amine solution, and a regeneration section where the amine solution is regenerated. In the absorption section, the stream containing CO_2 is passed upward through the absorber, counter-current to the amine solvent entering the absorber at the top. Under proper conditions, CO_2 is transferred from the gas stream to the amine solvent, resulting in a treated gas with low CO_2 content passing out of the absorber top and a CO_2-rich solvent leaving the absorber at the bottom. The rich solvent is then heated in a rich-lean heat-exchanger, and enters the regenerator near the top. In the regenerator, the lean amine is regenerated from the bottom, and the captured CO_2 is released from the top. Figure 4 [28] is a 3D rendering of a solvent based CO_2 capture facility.
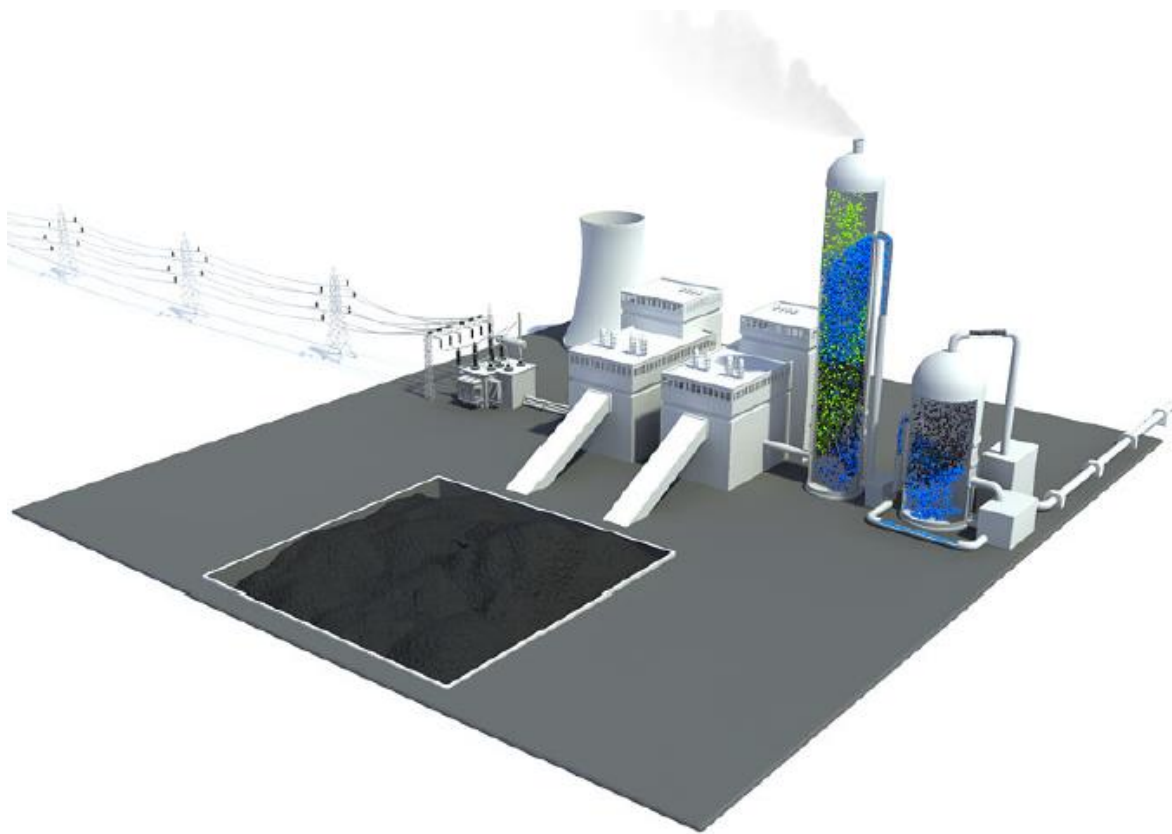
Figure 4: Illustration of a solvent based CO_2 capture facility [28]

Absorption solvent

Among various amines, monoethanolamine (MEA) is the most widely studied solvent for the removal of CO_2 from flue gases. Since MEA is the least expensive amine, the cost of solvent is expected to be the least [9]. Also, the most well-studied amine-based absorption solvent in industry is monoethanolamine (MEA). The advantages of MEA compared to other solvents are the fast reaction rate and the capability of removing even traces of CO_2 [10].

Besides MEA, sterically hindered amines are also choices for CO_2 capture. Since 1990, the Kansai Electric Power Co. (KEPCO) and Mitsubishi Heavy Industries, Ltd. (MHI) have developed patented proprietary sterically hindered amines KS-1, KS-2 and KS-3. Compared with MEA, KS-1 is claimed to require 20% less regeneration heat with less corrosion and degradation [6]. Cansolv offers two variants of its second generation CO_2 capture solvent – DC-103 and DC-103B where DC-103 favours operating cost and DC-103B favours capital cost [6]. PSR solvents developed at the University of Regina use proprietary mixtures of simple and hindered amines for CO_2 capture from flue gas. Key features claimed are lower regeneration temperature, lower solvent circulation rate and reduced degradation and corrosion [6].

In the context of this study, MEA is considered the main and most widely used solvent for post combustion CO_2 capture.

2. Emission Sources of Amines and Amine Degradation Products

2.1. Emission Sources of Amines from Gas Sweetening

In gas sweetening systems, it is necessary to add solvent during operation due to the loss of solvent. The most common ranking of solvent loss from highest to lowest is:

1) Entrainment

2) Vapourization

3) Degradation

4) Maintenance

Entrainment Loss

The majority of solvent loss is due to entrainment (from foaming, emulsions etc.). Entrainment losses are caused either by inefficient mist extraction or by foaming and subsequent carry-over of solution [11]. This problem can be minimized by the proper operation and/or proper sizing of the equipment.

Vapourization Loss

Vapourization loss mainly happens because of the exothermic absorption reaction (meaning heat is generated) in the contactor. Solvents used in gas treating, like any other liquids, have a vapour pressure that increases with temperature. In a gas sweetening system, there are three vessels where gas and liquid streams separate:

- Contactor
- Flash tank
- Regenerator Condenser

By far the largest gas stream is the one leaving the contactor. If the amine losses are excessive, a water wash section as shown in Figure 2 is typically added to the column to attempt to recover some of the vaporized and/or entrained amine from the gas leaving the contactor [2]. Solvent losses from the flash tank are usually quite small, as the amount of gas leaving this vessel is usually small when compared to the total plant stream. The amine loss from the regenerator condenser is very small, practically zero.

Maintenance Loss

The maintenance losses of amine occur during filter change outs, pump maintenance, vessel cleaning etc. The amounts of these losses are determined by the operation or repair schedule.

Degradation Loss

A portion of amine solvent may degrade into other chemical compounds in the presence of high temperature, COS etc. This is called amine degradation loss. The amine degradation in the gas sweetening process is reviewed in the next section.

2.2. Emission Sources of Amine Degradation Products from Gas Sweetening

Besides the above mentioned entrainment loss, vapourization loss and maintenance loss, another portion of amine solvent can be degraded into other chemical compounds in the gas sweetening process. This is called amine degradation.

Amine degradation happens mostly in the regenerator, especially in the bottom of the regenerator where the boiler skin temperature is high. Normally tube skin temperature should be <145°C to avoid severe amine degradation. For example, the degradation of MEA solutions increases rapidly when subjected to excessive temperatures [12].

During the operation of an amine unit, degradation occurs due to the presence of oxygen, COS and other components. Each of the degradation routes is briefly reviewed below:

Reaction with Oxygen

Amines are subject to degradation by contact with free oxygen in the feed gas. The principal mechanism involves the direct oxidation of the amines to organic acids and the indirect reaction of oxygen with H_2S to form elemental sulfur, which then reacts with amines to form dithiocarbamates, $SC(NH2)2$, and further decomposition products. A third route, whereby oxygen can degrade amines, is oxidation of H_2S to stronger acid anions such as $S2O3^{2-}$, which ties up amines as a heat stable salt. The Book 'Gas Purification' [11] states that MEA appears to be more vulnerable to oxidation than secondary and tertiary amines. Some of the degradation products cannot be reconverted to free amine by application of heat [12].

Irreversible Reaction with CO_2

Most of the commercial amines will react with carbon dioxide to form degradation products. Degradation products can reduce amine solution absorption capacity, increase solution viscosity, increase solution foaming tendency, and in some cases contribute to amine plant corrosion [11]. CO_2 degradation of amines is discussed below.

MEA: The MEA reaction with CO_2 will eventually form hydroxyethylenediamine (also known as HEED, a well-known degradation product of MEA). Although there are no detailed kinetics of the degradation reactions, it appears that high regenerator operating temperature, high equilibrium partial pressures of CO_2 and corresponding high solution loadings favour increased HEED formation [13]. In most cases, the MEA-CO_2 degradation products can be easily removed by side stream reclaiming. [13] Also, MEA can react slowly to produce a stronger base than MEA and it is more difficult to regenerate [12].

DEA: The irreversible DEA reaction with CO_2 is more complex. Study [14] stated that the reaction will initially form 3-(2-hydroxyethyl)oxazolidone-2 (HEO), then HEO will further react with other DEA to form N,N,N'-tris2-hydroxyethyl)ethyldiamine (THEED), and some of the THEED then slowly condenses itself to form N,N'-bis(2-hydroxyethyl)piperazine (BHEP). It is suggested in paper [15] that the most important measures to control DEA degradation are to keep reboiler and heat exchanger temperatures at the lowest practical level, to maximize circulation thru the reboiler, and to operate with relatively low DEA concentrations.

MDEA: Study [16] stated that there is no MDEA-CO_2 degradation product, possibly because MDEA is a tertiary amine and it cannot form a carbamate ion which can be degraded by carbon dioxide. However, a newer review paper [24] shows CO_2 induced MDEA degradation can happen and forms EG, TEA, BHEP, and other components.

Review paper [24] also listed reaction paths for degradation of MEA, DEA and MDEA by CO_2. See below, Figure 5 to Figure 7:
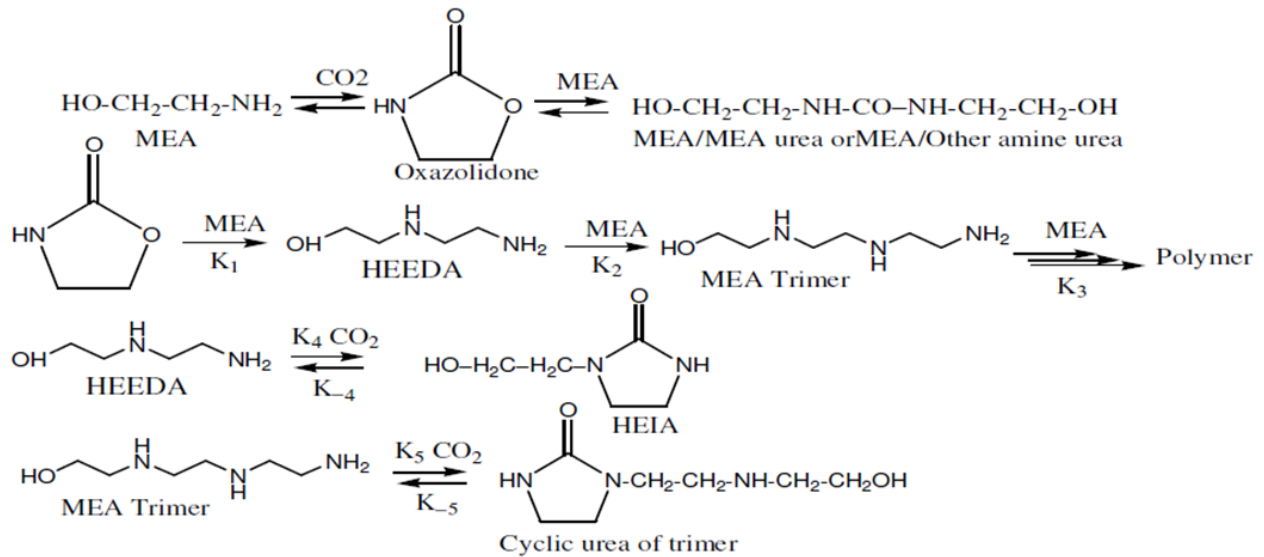
Figure 5: CO_2 induced degradation of MEA [24]
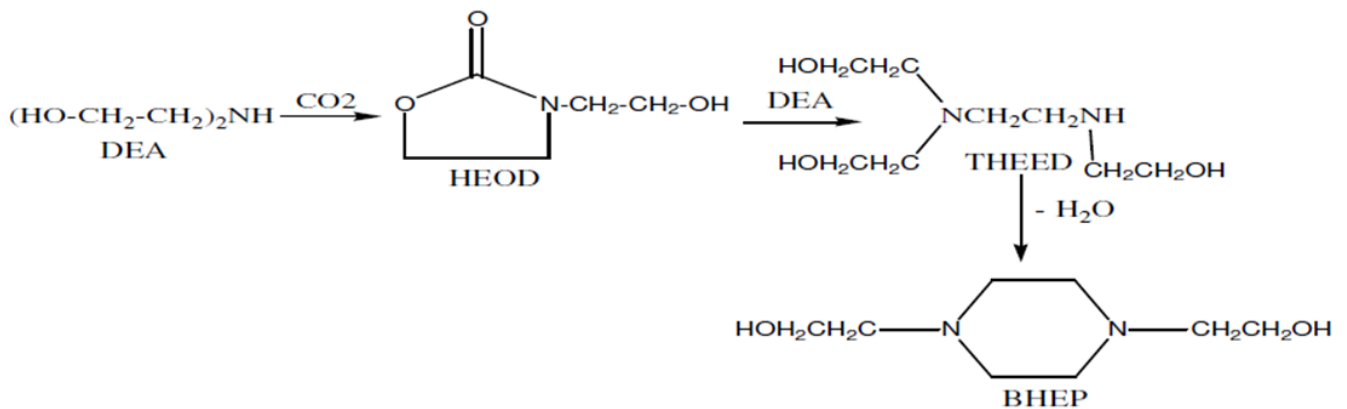
Figure 6: Reactions responsible for the degradation of DEA by CO_2 [24]
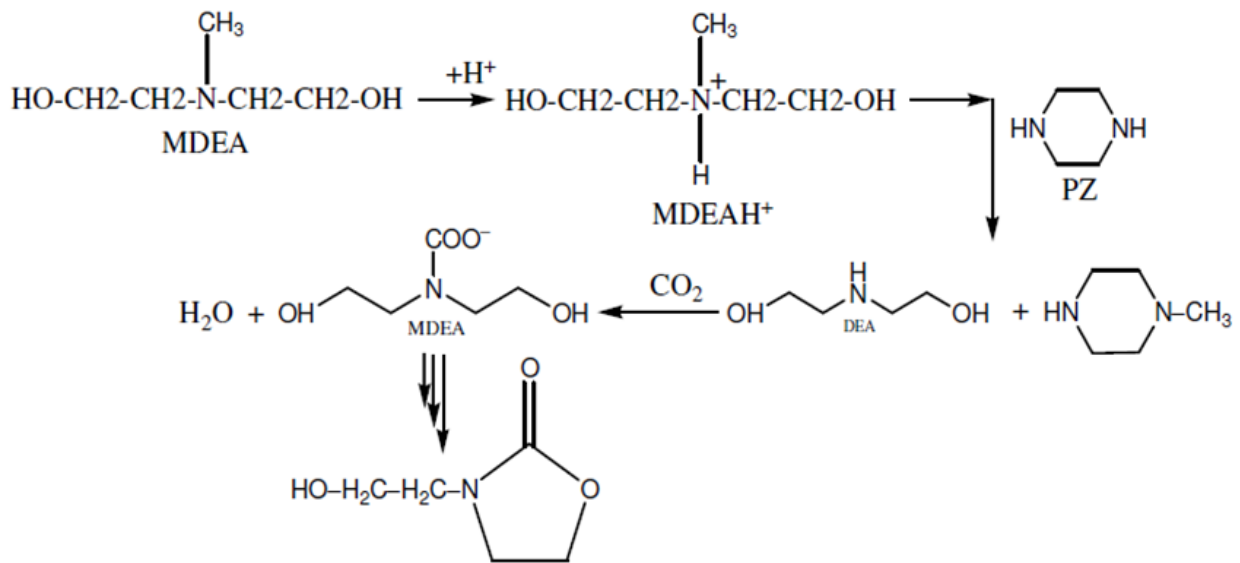
Figure 7: CO_2 induced degradation of MDEA [24]

Irreversible Reaction with COS and CS2

COS can be either present in the feed gas or can be formed by reaction between H_2S and CO_2. COS and CS2 can be removed by MEA, but the reactions are irreversible (they form heat stable salts) unless a reclaimer is used. DEA forms a regenerable compound with COS and CS2 and can be used for partial removal of COS and CS2 without significant solution loss. [2] No evidence of reaction was found with tertiary amine MDEA, and it is generally assumed that tertiary amines do not react irreversibly with COS and CS2.

An MDEA degradation study [47] in the gas sweetening process states that approximately thirty seven compounds were detected upon thermal degradation of lean MDEA. From degradation studies, the following reaction pathway for MDEA degradation (Figure 8) for some of the products is proposed:
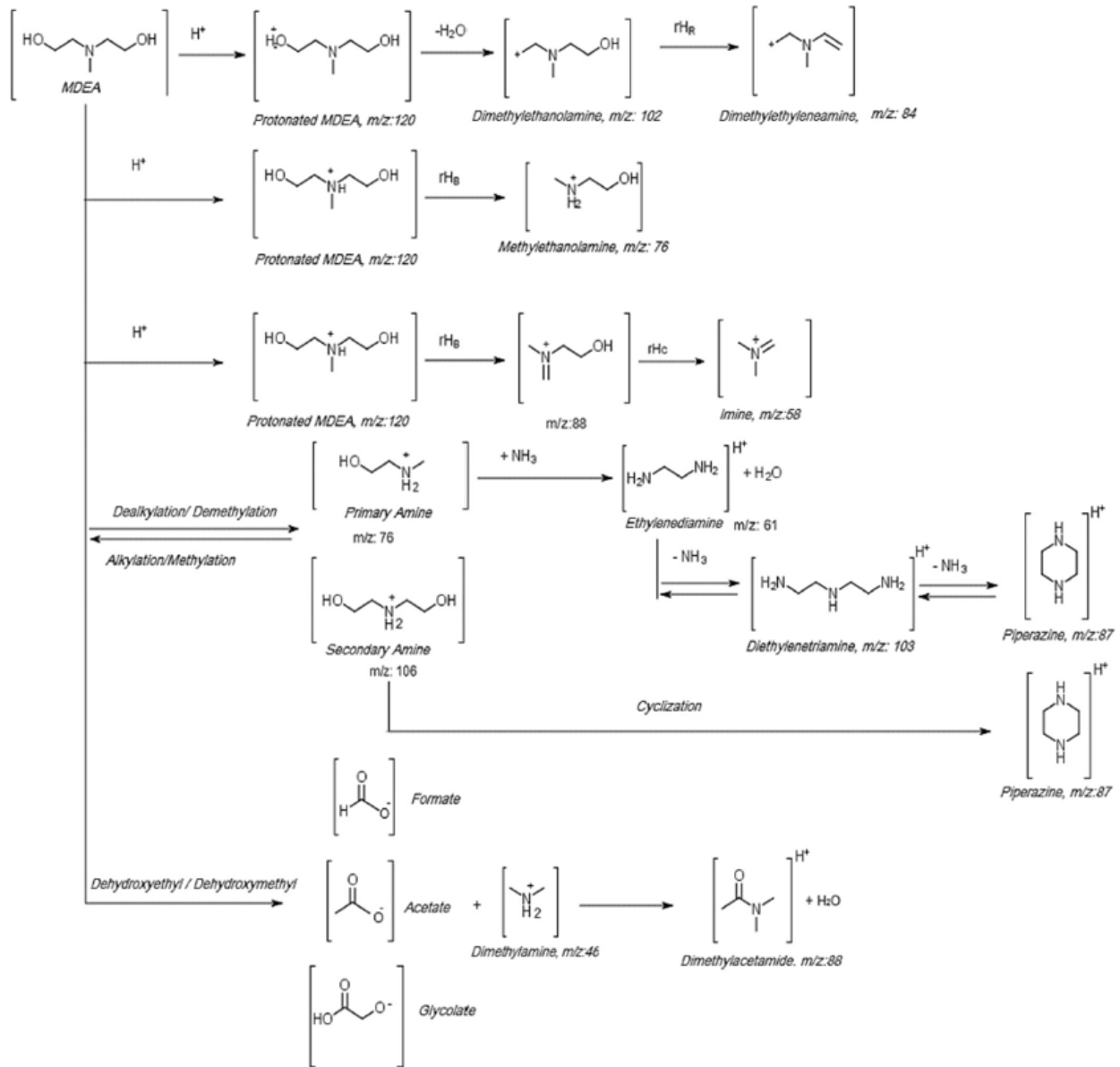
Figure 8: Predicted degradation reaction pathways of MDEA [47]

2.3. Emission Sources of Amines from Post Combustion CO2 Capture

From the environmental point of view, one of the first questions to be asked about the capture process is: will there be emissions due to the use of an amine such as MEA? The answer is yes. Similar to the natural gas sweetening process, amine emissions also happen in the solvent-based CO_2 capture process. Figure 9 [28] below shows possible emission sources of amine and amine degradation products from the CO_2 capture process.
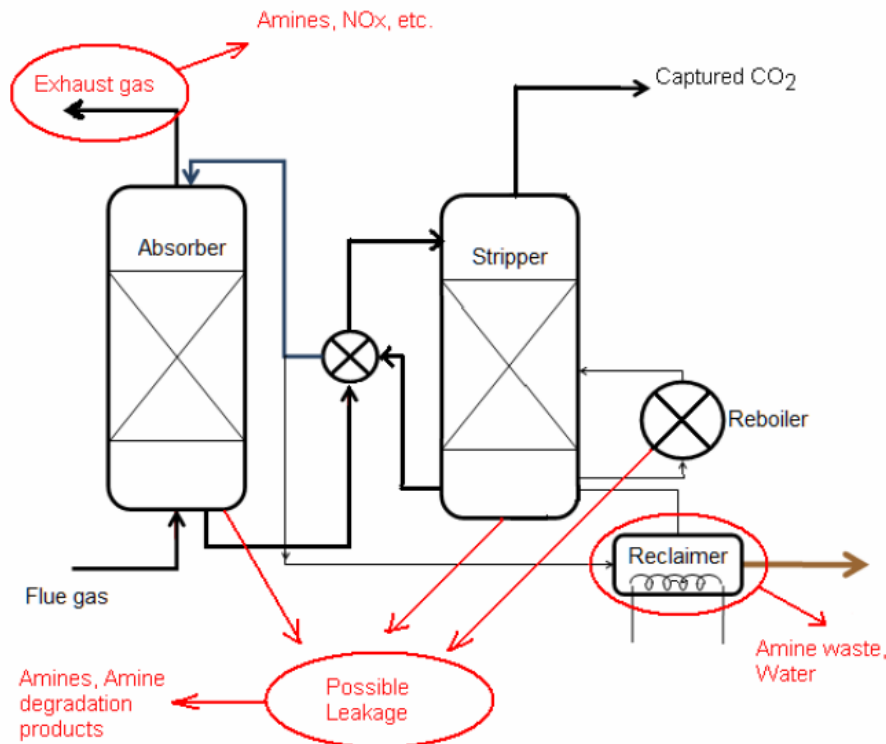
Figure 9: Possible emission sources of amine and amine degradation product from CO_2 capture [28]

Among all the points of discharge shown in Figure 9, the treated gas (being emitted locally) contains the most significant amine emission. This is one of the most significant areas where the gas sweetening process and the CO_2 capture process differ from each other.

The major loss of amine comes from the top of the absorber in the exiting treated flue gas. The emission rate greatly depends on the operating conditions of the absorber and the solvent properties (especially vapour pressure). As an example, the vapour pressure of MEA is a function of absorber temperature (it increases with increasing absorber temperature) and solvent concentration (it increases with increasing MEA concentration). Any substance with high vapour pressure tends to vaporize and leave the top of the absorber very easily with the treated gas [23]. Since MEA has the highest vapour pressure compared to DEA or MDEA, the most significant loss of MEA is through evaporation from the absorber column. However, approximately 95% of the evaporated solvent can be recovered by washing the exiting flue gas with water [25]. Study [23] stated that a water wash and/or a well-designed mist eliminator are commonly installed in the top section of the absorber to reduce such entrainment and volatility loss. Also, preliminary tests from [38] suggested that a single water wash is efficient for the removal of gaseous MEA emissions.

2.4. Emission Sources of Amine Degradation Products from Post Combustion CO2 Capture

The impurities in the gas stream to be treated are more complex in the flue gas CO2 capture process vs. the natural gas sweetening process. Solvent degradation due to the presence of high levels of oxygen, SOx, NOx and sometimes even fly ash in the flue gas causes increasing problems in long term performance. The CO_2 capture system generates several new waste products, principally ammonia gas (generated by degradation of MEA), other degradation products, and reclaimer bottoms (a potentially hazardous solid waste) [17].

One study [28] also confirmed that because of the various degradation reactions during the carbon capture process, and in the absence of engineering control measures, various degradation products are likely to be emitted. These include ammonia, acetaldehyde, acetone, and formaldehyde, together with extremely low levels of nitrosamines and nitramines.

These degradation products can cause reduction of CO_2 absorption capacity, corrosion, foaming, fouling, and an increase in viscosity [18]. Thus the degradation of amines in CO_2 capture not only causes operating problems but may also increase the operating cost and environmental concerns.

As per study [28], there are three different mechanisms for amine degradation and they take place in three different phases of the CO_2 capture process:
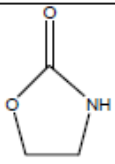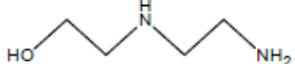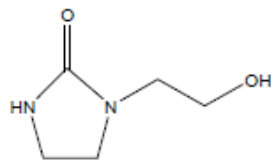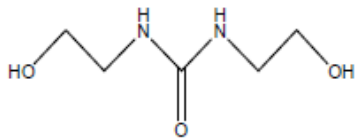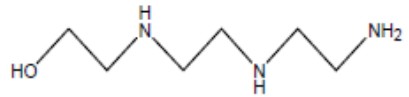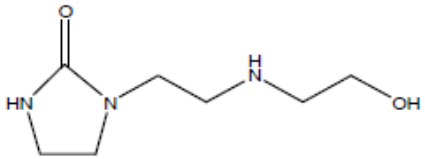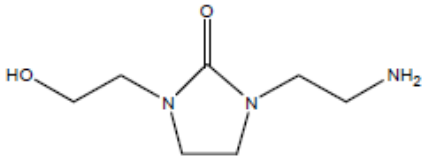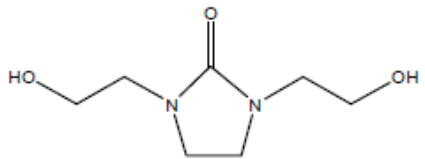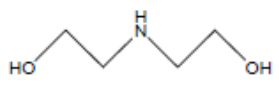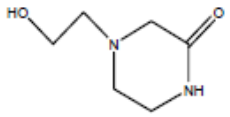
• Oxidative degradation, which mainly takes place in the absorber by the presence of oxygen, CO_2, and metal ions in the system;

• Thermal degradation, which mainly takes place in the stripper due to high temperature;

• Atmospheric degradation which occurs when amines emitted to the atmosphere degrade.

(Note: Atmospheric degradation will be reviewed in a following section of this report.)

Oxidative degradation is expected to occur in the absorber and produces products like NH3. Thermal degradation would take place as a consequence of the higher temperature in the stripper. Also, study [21] stated that MEA also reacts with acid gases, such as SO2 and NOx, and forms heat stable salts.

Below Table 1 [36] shows an example of the MEA degradation product in the presence of nitrite, in order to show the complexity of degradation reactions in the CO_2 capture process.

Table 1: MEA degradation product in the presence of nitrite [36]

Chemical Structure	Name	Abbreviation
	Oxazolidin-2-one	OZD
	N-(2-Hydroxyethyl)ethylenediamine	HEEDA
	N-(2-Hydroxyethyl)imidazolidin-2-one	HEIA
	N,N'-Bis-(2-hydroxyethyl)urea	BHEU
	N-(2-Hydroxyethyl)-diethylenetriamine	HEDETA
	N-[2-[(2-Hydroxyethyl)amino]ethyl]imidazolidin-2-one	HEAEIA
	N-(2-Aminoethyl)-N'-(2-hydroxyethyl)imidazolidin-2-one	AEHEIA
	N,N'-Bis(2-hydroxyethyl)imidazolidin-2-one	BHEI
	Diethanolamine	DEA
	N-(2-Hydroxyethyl)piperazin-3-one	HEPO

The major amine degradation routes and corresponding emissions are reviewed below:

Emissions of Ammonia

NH3 is continuously produced as a result of the oxidative degradation of MEA. Study results from [49] show that ammonia is the primary degradation product of MEA and its production is strongly correlated with NOx concentration in the flue gas. NH3 emissions increase with increasing NOx concentration in the inlet flue gas. Limiting NOx concentrations in the inlet gas can thus be an option for reducing NH3 emissions. Another study [38] discusses the origin and driving factors of the ammonia (NH3) and ethanolamine (MEA) emissions from post combustion carbon capture and shows that NH3 emission level is also closely correlated to solvent metal ion concentration. Low metal ion concentrations are required to reduce NH3 emissions.

The following options exist to abate NH3 emissions as per study [38]:

- Good solvent chemistry control (e.g. reducing metal ion concentration)
- Treated gas water wash (if necessary, multi staging)

Additionally, study [30] stated that the NH3 emission concentrations could be easily abated by using multi-stage water wash systems at the exit of absorber.

Emissions of Nitrosamine and Nitramine

In amine-based post-combustion CO_2 capture, amines can degrade to produce nitrosamines (a class of carcinogenic compounds) and nitramines (a class of potentially carcinogenic compounds). These are partly produced during the CO_2 capture process and the rest occur in the environment through photochemical oxidation.

The main reason for formation of nitrosamine and nitramines is the presence of NOx (NOx represents the species NO, NO2, N2O3 etc.). Study [20] stated that the formation of nitrosamines and nitramines in the process must be expected in the presence of NOx. It also stated that NDELA (nitrosodiethanolamine) is the main nitrosamine observed. NDELA is non-volatile but traces of two volatile nitrosamines, NDMA (nitrosodimethylamine) and NMOR (nitrosomorpholine), have also been detected in the CO_2 capture process.

A number of nitrosamines and nitramines have been reported in literature through the degradation of amines. MEA is a primary amine which in itself is unable to form a stable nitrosamine. However, experiments show that under the influence of NOx, MEA degrades to the secondary amine diethanolamine (DEA) which is then nitrosated. Study [26] stated that the formation of the secondary amine DEA from MEA has been found to increase with increased oxygen and nitrogen dioxide concentrations. Nitrosamines formed from secondary amines are the most stable.

In addition to the presence of NOx leading to the formation of nitrosamine and nitramine, study [49] stated that increasing the temperature enhances the formation of nitrosamines.

Limiting nitrogen dioxide concentrations of the feed flue gas can reduce the formation of nitrosamines and nitramines. A pre-scrubber or direct contact cooler system can be used to reduce the NOx concentration in the feed flue gas. Also, study [30] found that nitrosamine concentrations have also been found to reduce when an ultraviolet (UV) source is present within the absorber solvent. This could offer a means to abate nitrosamine emissions.

Amine Oxidative Degradation

Oxidative degradation of amines is highly undesirable for amine-based CO_2 capture as this causes operating problems like fouling and foaming, and is also responsible for equipment corrosion and an increase in the solvent's viscosity [37]. The three major driving forces of amine oxidative degradation are: 1) the presence of O2 partial pressure, 2) concentration of amine, and 3) high temperature. It is reported in [71] that oxidative degradation is accelerated by the presence of oxygen, and free metal ions. It is believed that the amine oxidative degradation is more sensitive to O2 concentration than the amine concentration. Also, the presence of acidic gases has the tendency to catalyze the oxidation of amine per study [72].

A common MEA oxidative reaction mechanism by Chi and Rochelle [34] is presented below in Figure 10:
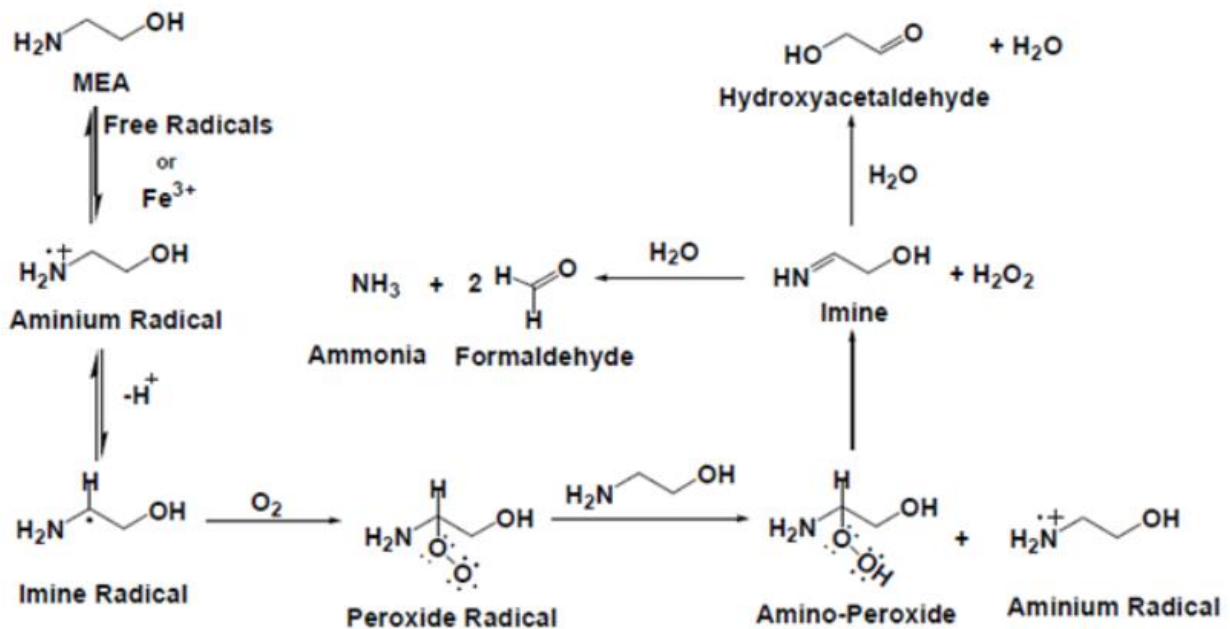
Figure 10: MEA oxidative mechanism proposed by Chi and Rochelle [34]

Furthermore, a thesis by Kali-Stella Zoannou [37] has a summary of the effect of O2 on MEA in Table 2 below.

Table 2: Effects of O2 on the MEA as reported in the literature per [37]

Authors	Parameter measured	Instrument	Observations
Supap et al. (2001)	MEA	GC-MS	Oxidation more sensitive to O_2 concentration increase than MEA concentration increase
Chi and Rochelle (2002)	NH_3 evolution	FT-IR	CO_2 presence and MEA concentration increased oxidation
Goff and Rochelle (2004)	NH_3 evolution	FT-IR	Oxidative degradation rate increased with agitation rate and CO_2 concentration
Bello and Idem (2006)	MEA	GC-MS	MEA concentration, temperature and O_2 increase the degradation rate, CO_2 loading has the opposite effect
Supap (2006)	MEA	HPLC	O_2 and MEA concentration and temperature increases cause an increase in the degradation rates
Uyanga and Idem (2007)	MEA	HPLC	CO_2 loading increase was proved to have an inhibition effect to degradation
Lepaumier et al. (2009) C	MEA	GC-MS, FT-ICR/MS, IC and NMR	20% MEA oxidation, small amounts of amino acids observed

Amine Thermal Degradation

Thermal degradation (also called carbamate polymerization) occurs in the lean/rich exchanger, regenerator and the thermal reclaiming unit, and causes MEA to form higher molecular weight products. The thermal polymerisation mechanism requires CO_2 and fairly high temperature. It is found that besides temperature, increasing the concentration of amine or CO_2 loading increases the thermal degradation [28]. As per study [20], the main thermal degradation products are oxazolidinone and higher molecular weight by-products like polyamines and cyclic amines.

Different MEA thermal degradation reactions have been proposed; refer to Figure 11 [28] and Figure 12 [35] for the mechanisms proposed in literature.
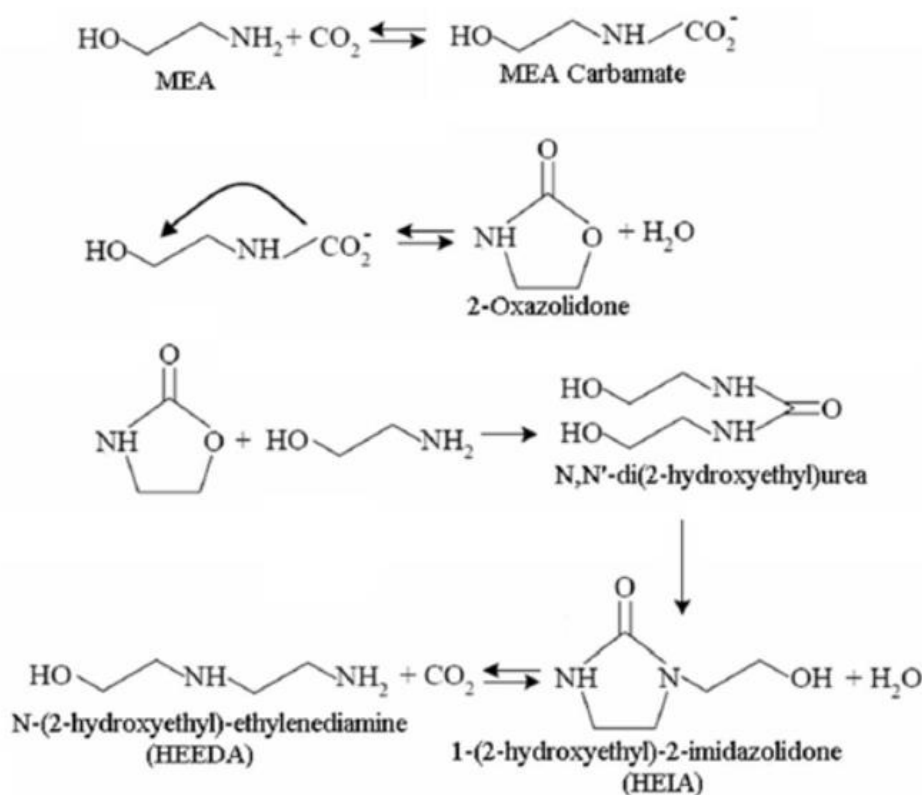
Figure 11: Possible chemical reactions taking place in thermal degradation of MEA [28]
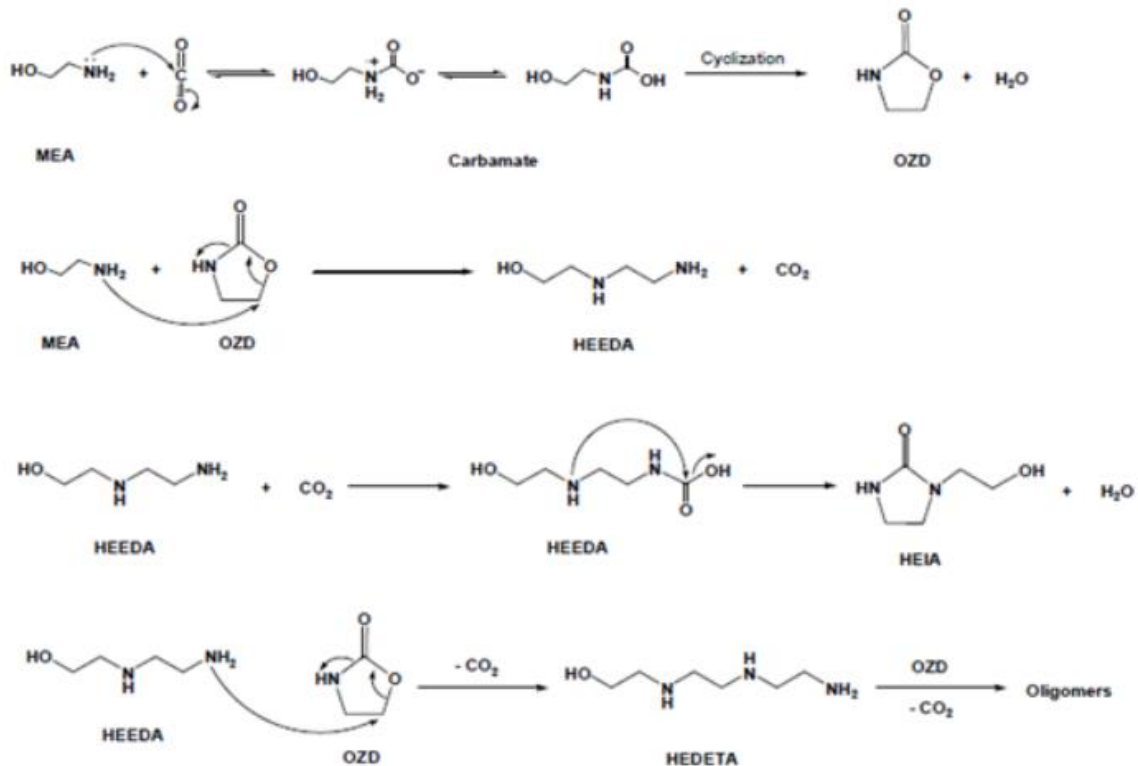
Figure 12: Carbamate polymerization mechanism in MEA thermal degradation [35]

Also, paper [35] shows a thermal urea formation mechanism:

Figure 13: Urea formation in MEA thermal degradation [35]

3. Amines and Amine Degradation Products Emission Rate Factors

3.1. Amines Emission Rate in Gas Sweetening

The most common ranking of solvent loss categories from highest to lowest is 1) entrainment due to foaming and solubility, 2) vapourization, 3) degradation and 4) maintenance. Entrainment losses from an amine absorber vary considerably depending on the mechanical design of both the upper section of the absorber and the mist elimination device. As per [11], the entrainment in a properly designed absorber should average less than 0.5 lb amine/MMSCF of treated gas, but notes that entrainment of well over 3 lb/MMSCF is not uncommon. Technical article [1] mentions that vapourization and degradation losses constitute a small portion of the overall solvent losses,

and the actual total makeup requirement losses may range from 1-3 lbs/MMSCF, dependent on the application.

Table 3 [2,61] provides a comparison of different amines. It can be seen that MEA has the highest vapour pressure and correspondingly has the highest vapourization loss.

Table 3: Comparison of Amines

Solvent Name	MEA	DEA	MDEA
Molecular Weight	61.08	105.14	119.16
Solvent Cost	Low Solvent Cost	Low Solvent Cost	High Solvent Cost
Vapour Pressure (Pa at 20 C)	53	<1	0.03
Vapourization Loss	High	Moderate	Low

Total's technical paper [12] shows typical ranges of solvent loss in the gas sweetening process:

- For MEA: 16 kg / (MSm3/d of feed gas x Mole% of acid gas)
- For DGA: 45 - 75 kg DGA / MSm3/d of feed gas if 5% acid gas
- For DGA: 70 - 100 kg DGA / MSm3/d of feed gas if 10% acid gas
- For DGA: 95 - 125 kg DGA / MSm3/d of feed gas if 15% acid gas

Another reference book "Oilfield Processing of Petroleum Volume One Natural Gas" [61] also indicated amine emission values or ranges:

- For MEA: Vapourization is 0.45 lb / MMSCF of feed gas
- For DEA, DGA, DIPA and MDEA: Vapourization is 0.02 to 0.03 lb / MMSCF of feed gas
- Entrainment loss can be 0.5 - 3 lb/MMSCF
- Overall amine consumption is 3 lb / MMSCF for MEA, 2 lb / MMSCF for DEA, DIPA and MDEA, and DGA is approximately 2.5 lb/MMSCF

John M. Campbell's July 2014 'Tip of the Month' indicates that the mechanical (entrainment) loss from the top of contactor is normally much higher than vapourization loss. It also states that amine vapourization loss from the top of the regenerator column was practically zero for all three amines.

The book "Surface Production Operations" [63] indicates that MEA losses of 1 to 3 lb/MMSCF are common and DEA losses of 1/4 to 1/2 lb/MMSCF are common.

The book "Gas Purification" [11] also indicates that the major cause of amine loss is entrainment. A properly designed absorber should average less than 0.5 lb/MMSCF of treated gas, but notes that entrainment of well over 3 lb/MMSCF is not uncommon.

Refer to Table 4 below for a summary of above amine loss data (converted to kg/e3m3).

Table 4: Summary of Literature Data for Amine Loss from Sweetening Process

Solvent	Data	Source
MEA	0.08 kg/e3m3	[12]
MEA	0.048 kg/e3m3	[61]
MEA	0.016 - 0.048 kg/e3m3	[63]
DEA	0.032 kg/e3m3	[61]
DEA	0.004 - 0.008 kg/e3m3	[63]
DGA	0.06 kg/e3m3	[12]
DGA	0.04 kg/e3m3	[61]
MDEA	0.032 kg/e3m3	[61]

Note: Data includes both entrainment and vapourization loss.

3.2. Amine Degradation Products Emission Rate in Gas Sweetening

For the quantification of amine degradation products' emission rates, technical article [1] stated that "Historically, a rule of thumb has been utilized limiting the HSS (Heat Stable Salts) to 5-10% of the amine alkalinity (for a 50 wt% amine solution, the 5-10% HSS limit corresponds to 2.5 to 5 wt% HSS as amine). However, with the increasing utilization of specialty solvents, a more conservative approach is warranted. Therefore, the HSS level should be limited to 1-2 wt. % when expressed as wt. % amine (3 wt. % maximum)."

A report by a Canadian company, CCR, [62] shows the solvent guidelines for gas sweetening process. It states that HSS should be <2.5 wt% of amines (MEA, DEA or MDEA). Also, for MEA, the formamides (MEAF) should be <3 wt% of the solution, and the HEED (hydroxyethylethylenediamine) should be <0.5 wt% of the solution. For DEA, the formamides (MEAF) should be <3 wt% of the solution, the THEED (tris-hydroxyethyl ethylenediamine) should be <1.5 wt% of the solution, and bicine (bis-(hydroxyethyl) glycine) should be <1.0 wt% of the solution. For MDEA, the MDEA fragments (compounds that are the result of DEA degradation when the MDEA molecule is broken down into simpler compounds) should be <2.5 wt% of the solution, and bicine should be <0.4 wt% of the solution.

The CCR report [62] also stated that reclaiming technologies such as a thermal reclaimer, ion exchange or vacuum distillation should be used to control degradation products. Also, one study [23] indicates the quantity of reclaimer waste varies with a ratio of slip stream to total circulation rate of process solution. A higher slip stream ratio leads to more waste produced.

3.3. Amines Emission Rates in Post Combustion CO2 Capture

Starting with an MEA mass balance in the solvent-based CO_2 capture process, the mass balance equation is shown below [31]:

Net loss of MEA = (loss in treated flue gas) + (oxidative degradation) + (heat stable salt formation – gain in the reclaimer) + (reclaimer waste) + (thermal degradation)

The released treated gas contains vapours of amine solvents. The quantities of these losses depend on the temperature of the absorber and the efficiency of the water-wash section. For instance, study [23] stated that in the case of using 30 wt% MEA solution, the emission of MEA vapour increases from 0.11 to 0.72 kg/tonne CO_2 when the temperature of the absorber rises from 20°C to 40°C without a water-wash operation. Such levels of MEA emission can substantially decrease, to about 0.03 kg/tonne CO_2 when a properly designed absorber with a well-designed water-wash section is in service. Study [25] states that approximately 95% of the evaporated solvent may be recovered by washing treated flue gas with water.

Use of MEA solvent can result in emissions of 0.1–0.8 kg MEA per tonne CO_2 captured without water-wash [71] and can be as low as 0.01–0.03 kg/tonne CO_2 captured with water-wash [5]. Typically, a CO_2-capture plant, that removes 1Mt CO_2 per year from flue gas, emits 1 – 4 ppmv MEA in the exhaust gas [17], which corresponds to 40–160 t/year. Study [74] stated the total solvent loss is about 1.6 kg solvent/tonne CO_2 for gas-fired flue gas.

Also, a paper [33] by MHI (Mitsubishi Heavy Industries) has observed that the amine emissions from the absorber, in treated flue gas, increase exponentially with the presence of SO3 in the flue gas. A measurement test [50] was done on the Esbjerg pilot plant (built in 2005, with capacity of 5000 m3/h or 1 tonnes CO_2/h), using MEA solvent with an absorption unit 34.5 m high and 1.1 m in diameter. The results from the emission measurements are: 0.7 mg MEA / Nm3 at the absorber outlet, and <0.3 mg MEA / Nm3 after water wash at the absorber outlet. The tests proved that the water wash works well in reducing the amount of MEA and formaldehyde in the emitted flue gas.

A 430 MW gas power plant at Karsto emits 1.2 million tonnes CO_2 annually without CCS [28]. With an amine based CCS, 85 percent of the CO_2 emission can be reduced. The data given below in Table 5 shows that 40 – 160 tonnes per year of amine emissions can be expected for the CO_2 capture plant at Karsto. In a first assessment of environmental consequences at Karsto [26], emissions of 1 ppmv MEA (i.e. 40 t/year) were estimated based on improved technology.

Table 5: Estimated maximum and minimum emission from Karsto 420 MW power plant [28]

	Atmospheric concentration (ppm)	Possible emissions during short periods (kg/hour)	Annual emission Ton/year
Amines emission to air	1 ~ 4	5 ~ 20	40 ~ 160

An amine emission review study [30] has a brief summary of emission values in literature; see Table 6 below.

Table 6: Reported amine emission concentration [30]

	Reported Emission Concentration (mg/Nm3)	Comments
CASTOR pilot plant	<0.1	
Niederaussem pilot plant	0.02 to 0.03	As MEA
CESAR pilot plant and theoretical studies	<0.3	As MEA. Post absorber wash sections in theoretical studies on coal fired plant. Increased emissions from natural gas fired plant (5.5 mg/Nm3) may be expected if post absorber cooling systems are not adopted.
Overview studies	0.5 to 3	As MEA (in isolation)
Mobile test facility at Longannet	1 to 4	
Anticipated emissions	3.5 to 6.8	As amine, after absorber wash systems
Laboratory conditions	8.5	
Mongstad Test Centre, Norway	1.4 to 8.2	Estimated as MEA. Reference conditions not stated. 16.3 mg/m³ as a maximum possible emission scenario
Kårstø demonstration plant	2.7 to 10.9	Estimated amine emissions

Note: For details and citation sources in above table, please refer to study [30]

In order to reduce amine emissions from CO_2 capture plants, the following technologies were ranked according to applicability and maturity in study [27]:

- An extra water wash section on top of the absorber
- High efficiency demisters and filters
- Acid wash in the final washing section on the absorber top
- UV treatment of lean amine, wash water or gaseous outlet

Pilot-plant-scale study [53] showed a glass fiber mist eliminator collected up to 95% of the entrainment that passed through the wire-mesh demister. This study also stated a two stage demister system can be used for thorough capture of the dilute amine entrainment leaving the contactor.

Toshiba [22] improved operating conditions such as the plant system and the water wash system to reduce the amount of amine emissions for a 10 tonne CO_2/day pilot plant. As a result, the latest

tests showed lower emissions of less than 1 ppm(v/v) at 2,800 hours operation. Figure 14 below shows the reduction of amine emissions by Toshiba for the 10 tonne CO_2/day pilot plant. (Note: TS-1 is the solvent name.)
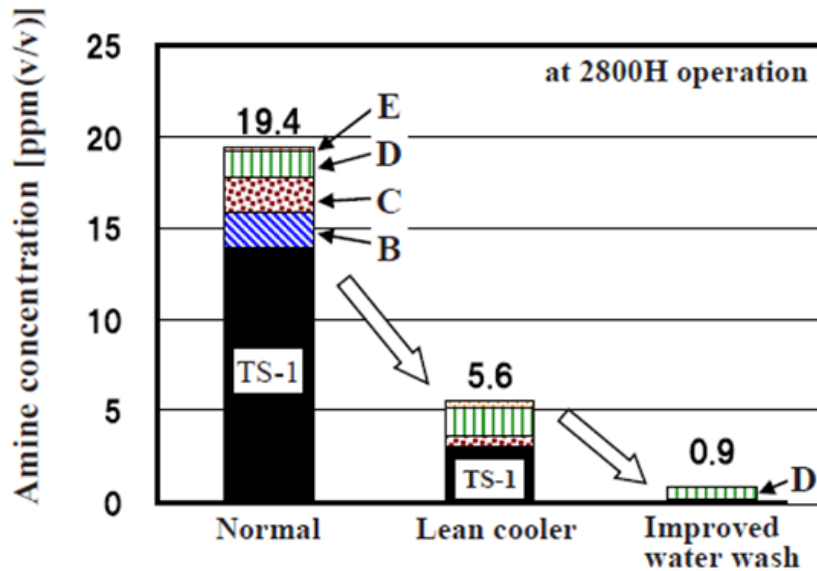
Figure 14: Reduction of amine emissions at a 10 tonne-CO_2/day pilot plant [22]

A presentation by MHI (Mitsubishi Heavy Industries) in 2010 [51] stated: "MHI introduced in 1994 an optimized packing and demister technology in the absorber column washing section. In the period 1999 to 2008, MHI installed nine commercial plants with this technology, all of them running with the proprietary KS-1 solvent. In 2003, an improved proprietary washing system was developed. They are able to reach 1 ppmv of amine emission, 1.5 ppmv of degradation products and no mist emission with this technology. Also other emission compounds are low. MHI have, however, seen the need for further reduction of amine emissions and have under development a new technology where they introduce a special reagent in the final washing stage in the top of the absorber. A liquid stream subject to waste water treatment is then produced. The target for this new technology (MHI zero amine emission system), which has been tested in pilot scale since 2009 and is expected to be commercial within two years, is to fall below 0.1 ppmv amine and 0.2 ppmv degradation products in the treated off gas." The comparison of amine emissions data using MHI technologies with time scale from 1999 is shown in Figure 15 [51] below.
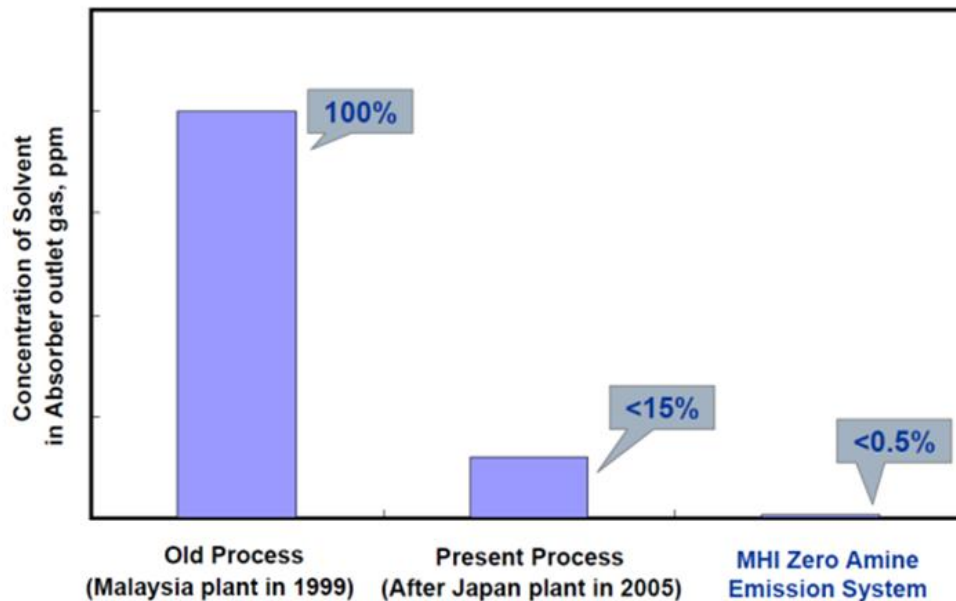
Figure 15: Amine emission improvement by Mitsubishi Heavy Industries [51]

3.4. Amine Degradation Products Emission Rate in Post Combustion CO2 Capture

Different amine degradation products such as ammonia, nitrosamine, nitramine and reclaimer waste (like HSS) are expected to be formed during the CO_2 capture process. In this section, we review the emission rates of some major degradation products.

<u>Ammonia (NH3)</u>

The NH3 emission rate will increase when MEA concentration, O2 concentration, or temperature increases. Study [19] also stated the rate was inversely affected by the increase of CO_2, H_2SO_3, and HNO3, and proposed the following kinetic rate equation for estimating NH3 emissions:

$$r_{NH_3 \text{ emission}} = \frac{k_0 e^{(-E_a/RT)} [MEA]^a [O_2]^b}{1 + k_1 [CO_2]^c + k_2 [H_2SO_3]^d + k_3 [HNO_3]^f}$$

The parameter values can be found in the detailed paper [19]. The goal of this equation is to help plant operators quickly quantify NH3 releases from the CO_2 capture system.

Another paper [31] stated that the O2 induced MEA degradation rate is 3.4×10^{-1} mol/s. Each mole of MEA degraded results in one mole of NH3 formed and therefore the NH3 formation rate equals 3.4×10^{-1} mol/s.

In one Norwegian study [56], the main emitted component is NH3 from both plants (residue fluid catalytic cracker RFCC and the combined heat and power plant CHP) at the Mongstad refinery, which presents a local eutrophication risk. However, the estimated emission amount of NH3 from Norway's CO_2 Technology Centre Mongstad (TCM) is small and is regarded as a negligible additional contribution to the environment (<1%). The highest risk was assessed to be the

exposure of the population and refinery employees to potentially carcinogenic nitrosamines and nitramines being dispersed to surrounding air and drinking water.

A UK report [30] stated "some studies showed the elevated emissions of ammonia may be expected from amine scrubber carbon capture systems that were not fitted with abatement equipment (in the order of 25 mg/Nm3). These concentrations are lower than results from other studies that suggest ammonia releases in flue gases may reach up to 250mg/Nm3."

<u>Nitrosamine and Nitramine</u>

Nitrosamine and nitramine are found to have the highest risk to human health and the environment within a CO_2 capture facility. As a primary amine, MEA in itself is unable to form a stable nitrosamine. However, MEA can degrade into a secondary amine which is then nitrosated by reaction with nitrite.

Study results [55] indicated that the order of nitrosamine formation reactivity for amines is: secondary > tertiary ≫ primary. Study [55] also demonstrated that nitrosamine accumulation in both the solvent and wash water increased linearly with NO_2 and NO concentrations in the flue gas. This linear dependence suggests that NOx reduction technologies targeting both NO and NO2 should be selected to minimize nitrosamine emission.

Study [29] reported the concentration of nitrosamines in an 800 tonne per day CO_2 capture plant is about 2.91 mol/ml of lean solution. Another study [73] reported that the emissions of both nitrosamines and nitramines may range from 5 - 47 ng/Nm3 of treated gas under pilot plant conditions operating with MEA. Like other literature data, it must be noted that these emissions can vary depending upon a number of parameters such as, but not limited to: plant size, flue gas composition and solvent.

Study [54] showed the conversion rate of nitrosamines from selected secondary amines ranged from 0.01 – 2.01% (molar formation yield).

Study [57] talked about nitrosamine formation in the amine regenerator: Nitrosamine yield was proportional to the concentration of secondary amine and was also a function of CO_2 loading and temperature. (Larger CO_2 loading leads to smaller reactivity of DEA to become nitrosamine per study [57]).

Study [31] proposed the following equation to calculate MEA degradation rate with NO2 and SO2 (since the reaction with NO2 can lead the form of nitrosamine and nitramine):

$$MEA\_deg = 2 \times f\_so2 \times SO2 + 2 \times f\_no2 \times NO2$$

where MEA_deg (mol/s) is the amount of MEA degraded, f_so2 is the reaction efficiency of SO2 with MEA (99.5%) and f_no2 is the reaction efficiency of NO2 with MEA (25%). SO2 is the amount of SO2 in flue gas (mol/s), and NO2 is the amount of NO2 in flue gas (mol/s).

Reclaimer Waste

As indicated before, the quantity of reclaimer waste depends on the ratio of slip stream to total circulation rate of amine solution. A higher slip stream ratio leads to more waste produced. Study [23] stated that a 2% slip stream generates 14.9 kg waste/tonne of CO_2 captured, while 0.5% slip stream reduces the waste to 3.7 kg/tonne of CO_2.

Study [28] indicates that a 1 million tonne per year CO_2 capture plant is expected to produce 300 to 3000 tonnes amine waste per year. The quantity of amine waste also depends on other factors such as the type of fuel, the type of amine solution, and operational conditions, but in most cases amine waste will be less than 1000 tonnes per year.

Study [31] presents the following equation to calculate the net loss of MEA due to HSS formation in reclaimer:

MEA_netloss,hss = organic acids – Na

where MEA_netloss,hss is the net MEA loss due to heat-stable-salt (HSS) formation (mol/s), organic acids is the amount of organic acids formed due to MEA reaction with SO2, NO2 and O2 (mol/s), and Na is the amount of sodium added to reclaimer to regenerate MEA (mol/s).

4. Simulation of Amine Losses from Gas Sweetening Process with HYSYS™ and VMGSim™

In order to better understand the vapourization losses of amine in the gas sweetening process, process simulators HYSYS™ and VMGSim™ were utilized to simulate typical sweetening processes using different amines (MEA, DEA and MDEA).

In a HYSYS™ simulation, the Acid Gas property package is applied and the PFD (Process Flow Diagram) is shown below:
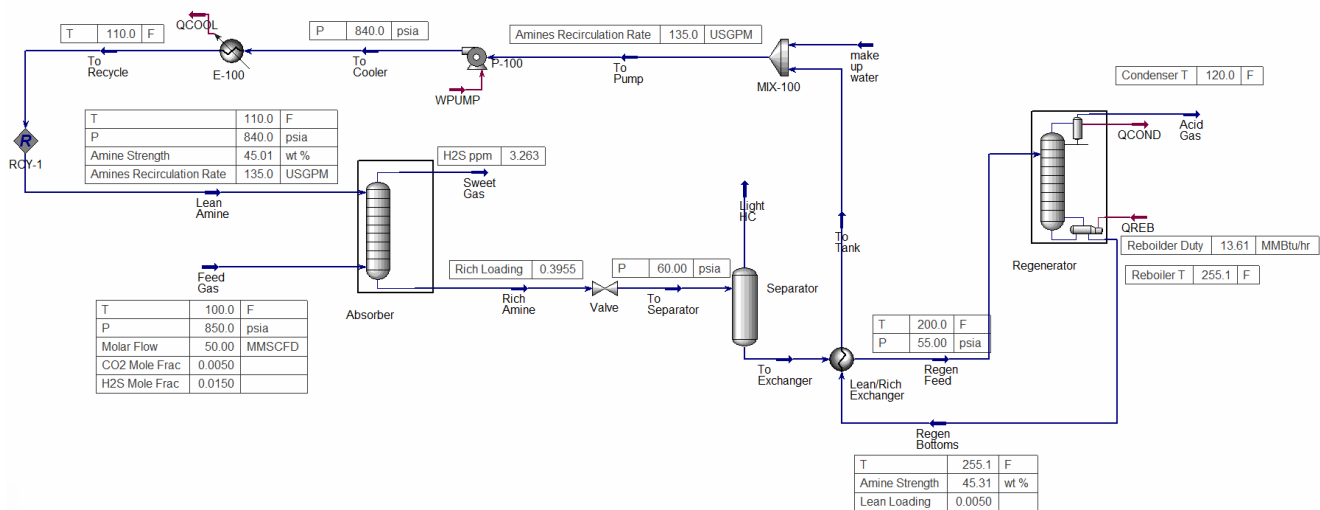
Figure 16: PFD of gas sweetening process using HYSYS™

In a VMGSim™ simulation, the amine package is applied and the PFD is shown below:
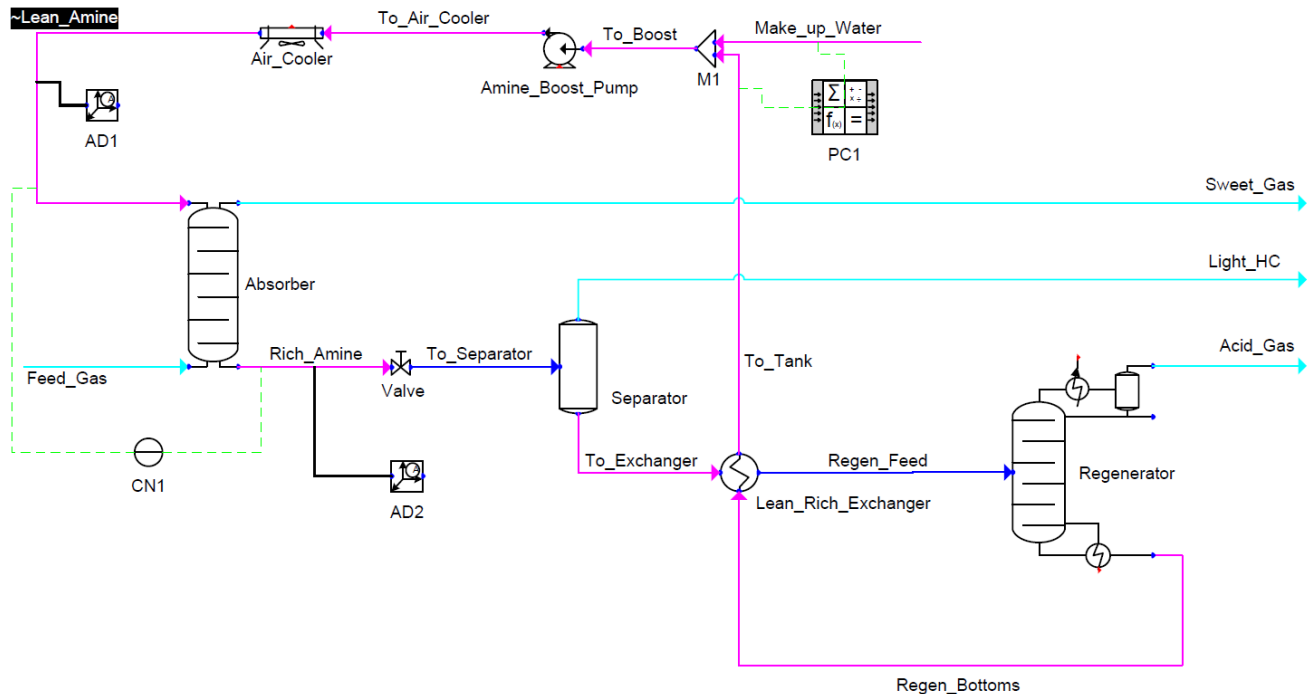
Figure 17: PFD of gas sweetening process in VMGSim™

4.1.Simulation of Gas Sweetening with MEA

In this section, the simulation of a typical gas sweetening process with MEA in both HYSYS™ and VMGSim™ is described.

The key variables configured in the simulation are:

- Inlet Sour Gas is 50 MMSCFD and contains 0.5 mol% CO_2 and 1.5 mol% H_2S.
- Lean MEA concentration is 20 wt% and circulation rate is 270 USGPM.
- The absorber has 20 physical stages and the column diameter is 5 ft.
- The absorber is operating at 100°F and 850 psia.
- The flash drum is operating at 60 psia.
- The regenerator has 20 physical stages and the diameter is 4.5 ft.
- The regenerator is operating at 30 psia, reboiler is at 254°F and condenser is at 120°F.

In this flowsheet, the rich MEA loading is 0.3 (a typical value for MEA) and the H_2S in sweet gas is below the standard 4 ppmv pipeline requirement.

From the HYSYS™ and VMGSim™ simulations, we can see that the MEA vapourization loss happens primarily in the sweet gas stream from the contactor; there is a small amount of loss from

the flash tank, and no amine is lost from the acid gas of the regenerator. The detailed amine losses are shown below in Table 7:

Table 7: Amine Vapourization Loss by Simulation (kg MEA/e3m3 inlet gas)

Location	HYSYS™	VMGSim™
Sweet Gas	0.0082	0.0019
Flash Tank	0.000016	0.000032
Acid Gas	0	0

4.2. Simulation of Gas Sweetening with DEA

In this section, a typical gas sweetening process with DEA is simulated in both HYSYS™ and VMGSim™.

The key parameters of the simulation are:

- Inlet Sour Gas is 50 MMSCFD and contains 0.5 mol% CO_2 and 1.5 mol% H_2S.
- Lean DEA concentration is 30 wt% and circulation rate is 155 USGPM.
- The absorber has 20 physical stages and the column diameter is 5 ft.
- The absorber is operating at 100 F and 850 psia.
- The flash drum is operating at 60 psia.
- The regenerator has 20 physical stages and the diameter is 3.5 ft.
- The regenerator is operating at 30 psia, reboiler is at 254 F and condenser is at 120 F.

Through the configuration of this flowsheet, the rich DEA loading of is 0.5 and the H_2S in sweet gas is below 4 ppmv pipeline requirement.

From the HYSYS™ and VMGSim™ simulations, we can see the DEA vapourization loss happens mainly in the sweet gas stream from the contactor, with a very small amount or no loss from the flash tank, and no amine loss from the acid gas of the regenerator. The detailed amine losses are shown below in Table 8:

Table 8: Amine Vapourization Loss by Simulation (kg DEA/e3m3 inlet gas)

Location	HYSYS™	VMGSim™
Sweet Gas	0.00016	0.000032
Flash Tank	0	0.00000016
Acid Gas	0	0

4.3. Simulation of Gas Sweetening with MDEA

In this section, a typical gas sweetening process with MDEA is simulated in both HYSYS™ and VMGSim™.

The key parameters of the simulation are:

- Inlet Sour Gas is 50 MMSCFD and contains 0.5 mol% CO_2 and 1.5 mol% H_2S.
- Lean MDEA concentration is 45 wt% and circulation rate is 135 USGPM.
- The absorber has 20 physical stages and the column diameter is 5 ft.
- The absorber is operating at 100 F and 850 psia.
- The flash drum is operating at 60 psia.
- The regenerator has 20 physical stages and the diameter is 3 ft.
- The regenerator is operating at 30 psia, reboiler T is at 255 F and condenser is at 120 F.

Through the configuration of this flowsheet, the rich MEA loading of is 0.4 (a typical value for MDEA) and the H_2S in sweet gas is below 4 ppmv pipeline requirement.

From the HYSYS™ and VMGSim™ simulations, we can see the MDEA vapourization loss happens mainly in the sweet gas stream from the contactor, with a very small amount or no loss from flash tank, and no amine loss from acid gas of the regenerator. The detailed amine losses are shown below in Table 9:

Table 9: Amine Vapourization Loss by Simulation (kg MDEA/e3m3 inlet gas)

Location	HYSYS™	VMGSim™
Sweet Gas	0.003248	0.000064
Flash Tank	0.0000016	0.00000032
Acid Gas	0	0

4.4. Amine Tank Emission Calculation

Amine losses can occur at amine storage tanks, mostly due to working and breathing losses. (Flashing loss is negligible since undiluted amine is not volatile in storage tanks.)

Breathing losses are caused by thermal expansion of the solution vapour in the tanks as a result of temperature increases during the daytime and seasonally. We used the EPA AP-42 (Chapter 7: Liquid Storage Tanks) method to calculate the breathing losses for an MEA tank (which contains undiluted MEA). The key inputs used in this calculation are:

- Tank diameter = 5 m, and height = 12.5 m.
- Tank is partially insulated.
- Average liquid height = 10 m.
- Tank liquid storage temperature = 30°C.
- Tank is at atmospheric pressure, and vent pressure set at 0.7 kPag and vacuum pressure set at -0.12 kPag.
- Tank liquid Reid vapour pressure (RVP) = 0.139 kPa (per HYSYS™)

Along with the vapour composition of an MEA tank, it is calculated that the yearly MEA breathing emission from this or a similar storage tank is 0.2 kg per year. This is a negligible amine emission rate. Likewise, for heavier amines like DEA or MDEA, with even lower vapour pressures, the tank breathing loss is negligible.

Working loss occurs when storage tanks of amine solution are being filled, and its emission value depends on the plant configuration and operating condition. It is generally very small and therefore not considered here.

4.5. Summary of Amine Emissions Rates

For the natural gas sweetening process, the MEA loss varies from 0.016 kg/e3m3 to 0.08 kg/e3m3; the DEA loss varies from 0.004 kg/e3m3 to 0.032 kg/e3m3; the DGA loss varies from 0.04 kg/e3m3 to 0.06 kg/e3m3; and the MDEA loss is 0.032 kg/e3m3. Gas sweetening simulations using HYSYS[TM] and VMGSim[TM] were also conducted to investigate the amine vapourization loss from the contactor. These simulations showed losses less than the overall losses reported in the literature. This is consistent with the fact that vapourization (calculated by the simulator) is a minor loss and entrainment (not calculated by the simulator) is a major loss. It is important to note that the relative magnitude of losses calculated by the simulators are in line with expected values and the trend of decreasing vapourization loss with increasing amine size (MEA < DEA < MDEA) is consistent with literature as well. The following Table 10 presents a summary of amine emissions data from the various literature as well as the data obtained from the process simulators, HYSYS[TM] and VMGSim[TM].

For CO_2 capture process, there is much scattered data from literature. The MEA loss varies from 0.01 kg/tonne CO_2 captured to 0.03 kg/tonne CO_2 captured with water wash per [5]; and varies from 0.1 kg/tonne CO_2 captured to 0.8 kg/tonne CO_2 captured without water wash per [71]. And other studies [17,30,74] showed the MEA loss varies from <0.0005 kg/tonne CO_2 captured to 1.6 kg/tonne CO_2 captured. Please see below Table 11 for a summary of amine emissions data from the various literatures.

Table 10: Summary of Literature Data and Simulation Data for Amine Loss in Gas Sweetening Process

Solvent Name	Data	Source
MEA	0.08 kg/e3m3	[12]
MEA	0.048 kg/e3m3	[61]
MEA	0.016 - 0.048 kg/e3m3	[63]
MEA	0.002 - 0.008 kg/e3m3	Simulation (Vapourization only)
DEA	0.032 kg/e3m3	[61]
DEA	0.004 – 0.008 kg/e3m3	[63]
DEA	0.000032 - 0.00016 kg/e3m3	Simulation (Vapourization only)

DGA	0.06 kg/e3m3	[12]
DGA	0.04 kg/e3m3	[61]
MDEA	0.032 kg/e3m3	[61]
MDEA	0.000064 – 0.003248 kg/e3m3	Simulation (Vapourization only)

Table 11: Summary of Literature Data for Amine Loss in CO_2 Capture Process

Solvent Name	Data	Source
MEA	0.11 - 0.72 kg/tonne CO_2 captured (without water wash)	[23] (Vapourization only)
MEA	0.03 kg/tonne CO_2 captured (with water wash)	[23] (Vapourization only)
MEA	0.1 - 0.8 kg/tonne CO_2 captured (without water wash)	[71]
MEA	0.01 - 0.03 kg/tonne CO_2 captured (with water wash)	[5]
MEA	0.04 – 0.16 kg/tonne CO_2 captured	[17]
MEA	1.6 kg/tonne CO_2 captured	[74]
MEA	< 0.0005 kg/tonne CO_2 captured	In review study [30]
MEA	0.0001 - 0.00015kg/tonne CO_2 captured	In review study [30]
MEA	<0.0015 kg/tonne CO_2 captured	In review study [30]
MEA	0.0025 - 0.015 kg/tonne CO_2 captured	In review study [30]
MEA	0.005 - 0.02 kg/tonne CO_2 captured	In review study [30]
MEA	0.0175 - 0.034 kg/tonne CO_2 captured	In review study [30]
MEA	0.0425 kg/tonne CO_2 captured	In review study [30]
MEA	0.007 - 0.041 kg/tonne CO_2 captured	In review study [30]
MEA	0.0135 - 0.0545 kg/tonne CO_2 captured	In review study [30]

Note: For citation sources in the review study [30], please refer to study [30] for details.

5. Measurement Technologies for Amine and Amine Degradation Product Emissions

There has been limited emission monitoring of amines and amine degradation products, mainly because:

a) These compounds are normally difficult to sample and analyse,
b) These compounds have the potential for formation or destruction during sampling,
c) Most instruments' detection limits are greater than the emission concentration. However, there is some experience monitoring for such substances in literature. The monitoring techniques in literature are reviewed briefly below.

FTIR (Fourier Transform Infrared Spectroscopy) is one of the technologies that has been used for monitoring amine based substances. The UK report [30] states "FTIR uses infra-red spectroscopy to create a molecular fingerprint of the sample, which is compared to an internal library to allow identification and quantification of the substances in the sample. The libraries of some FTIR manufacturers currently contain a number of amine based compounds including MEA, DEA and ammonia. The lowest detection limit (LDL) for MEA is 0.3 ppm compared to the estimated expected emission concentration of ~0.5 ppm. The LDL for DEA is 0.15 ppm compared to the estimated expected emission concentration of perhaps 0.0005 ppm. An FTIR unit can in theory be calibrated to measure nitrosamines however there is no evidence that this has been undertaken."

Also, this UK report [30] stated that a pilot carbon capture plant at Ferrybridge Power Station, Yorkshire plans to use a Tunable Diode Laser (which has a limit of detection of 1 ppmv) to monitor ammonia as an indicator compound for amine degradation emissions. That site also continually monitors for MEA using an Industrial Mass Spectrometer with a limit of detection of 0.5 ppmv.

Tedlar bags have been used for sampling amine compounds in stack emissions per report [30], then the compounds are analysed using GC-ToF-MS (Gas chromatography time of flight mass spectrometry). One of the disadvantages of the tedlar bag method is that it may leak or dilute the collected compounds.

Paper [19] uses a gas chromatograph–mass selective detector (GC–MSD, model 6890-5073) supplied by Hewlett-Packard, to analyse the condensed NH_3. Another paper [20] also uses FTIR to monitor ammonia production. Study [30] indicates that laser systems can also be used to monitor ammonia (which can be used as an indicator compound for amine emissions).

Study [32] uses a combination of technologies including a gas chromatograph-mass spectrometer instrument (GC-MS), GC with dual thermal conductivity, flame photometric detectors (TCD and FPD), and capillary electrophoresis with diode array detector (CE-DAD) to analyse emission gases.

For Norway's CO_2 Technology Center Mongstad, the following measurement schematic (Figure 18) [64] is used to monitor amine emissions.
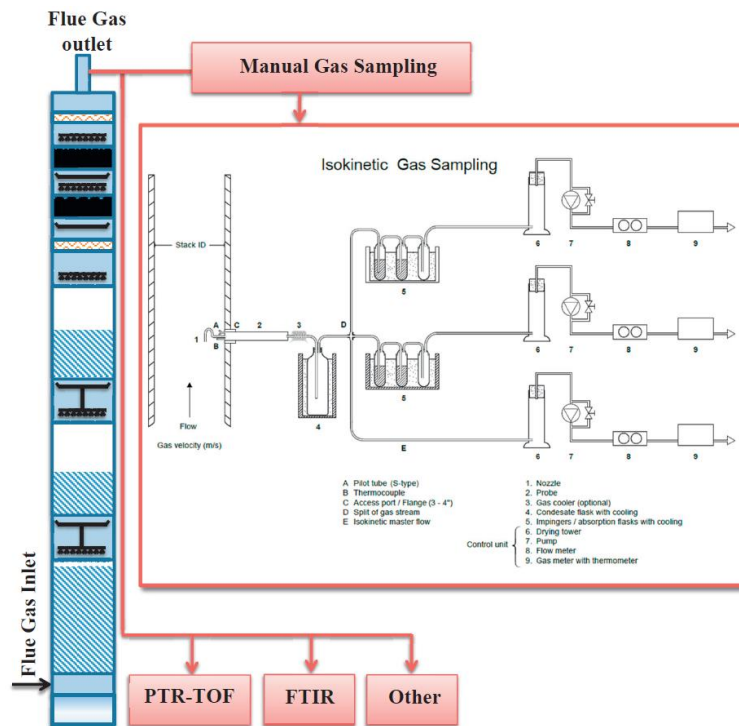
Figure 18: Emission measurement set-up at the Mongstad amine plant [64]

Details of the on-line and off-line measurement methods at Mongstad are described in [64] as follows:

"• Fourier Transform Infrared (FTIR) Spectroscopy: The FTIR is calibrated for a list of standard flue gas pollutants, including CO_2, SO2, NH3, etc., as well as solvent amines and some volatile degradation products e.g. aldehydes. The instrument is not set up for measuring alkyl amines, nitrosamines and nitramines.

• Proton Transfer Reaction Time of Flight Mass Spectrometry (PTR-ToF-MS): The PTR-ToF-MS is able to measure amines, ammonia, aldehydes, ketones, carboxylic acids, nitramines and nitrosamines which are all important target compounds in amine based CO_2 capture.

• Other: Manual isokinetic sampling technique with impingers and subsequent off-line laboratory analysis. Amines, nitrosamines, and aldehydes were analyzed using an LC MS-MS QQQ (Agilent). The condensate from the first impinger was analyzed directly on the LC MS, the acidic impinger solutions were diluted before analysis. Ammonia was analyzed on an ion chromatograph (IC)."

A Norwegian report [65] has evaluated two analytical methods: "(1) exposure of adsorbent tubes followed by thermal-desorption and analysis by gas chromatography and mass spectrometry (TD-GC/MS), and (2) exposure of impregnated filters followed by extraction and analysis by liquid chromatography and mass spectrometry on a time-of-flight instrument (IF + LC/MS)", for amine and amine degradation products measurement. Advantages and disadvantages of both methods were discussed in detail in [65].

It has been agreed in literature that nitrosamine in drinking water has a high risk to human health. The US EPA has a standard method to measure this carcinogenic compound in water: EPA Method 521:

Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS/MS). The detection limit of EPA Method 521 is shown below in Table 12 [60].

Table 12: Nitrosamine Detection Limit in EPA 521 Method [60]

Nitrosamine Component	CAS Registry Number	Detection Limit of EPA 521 Method (ng/L)
N-Nitrosodimethylamine (NDMA)	62-75-9	0.28
N-Nitrosomethylethylamine (NMEA)	10595-95-6	0.28
N-Nitrosodiethylamine (NDEA)	55-18-5	0.26
N-Nitrosodi-n-propylamine (NDPA)	621-64-7	0.32
N-Nitrosodi-n-butylamine (NDBA)	924-16-3	0.36
N-Nitrosopyrollidine (NPYR)	930-55-2	0.35
N-Nitrosopiperidine (NPIP)	100-75-4	0.66
N-Nitrosodimethylamine (NDMA)	62-75-9	0.28

Section II: Human Health and Environmental Impact of Amines and Amine Degradation Products

1. Atmospheric Chemistry of Amines

Once emitted to air from a solvent-based CO_2 capture plant, amines will start degrading to other chemical compounds. There will be a variety of degradation products and many of them will have negative impacts on human health and the environment. Study [20] identified formamide as the main gas phase photo-oxidation product of MEA, while minor amounts of the nitrosamines and nitramine can also be formed. Nitrosamines have the most significant impacts as they can cause cancer. Also, the concern with these emissions depends on the lifetime of the products: a longer life time leads to higher risk. Literature reports indicate that, in general, lifetimes of the nitrosamines and nitramine vary from 2 to 20 h, as per study [29].

The formation of nitrosamine may be controlled within the amine process as mentioned in previous sections, but cannot be controlled in atmosphere. The $^•$OH radical is the main culprit in the photo-oxidation of amines, while nitrite and $^•$Cl radicals also play a significant role. In sunlight, amines can react with atmospheric oxidants involving oxidized nitrogen compounds (photo-oxidation) to form compounds such as nitrosamines, nitramines, and amides [26]. During night time, amines can react with the atmospheric nitrate radical ($^•$NO3) to form nitramines [52].

For the conversion rate from amines to nitrosamines, study [30] mentioned that "In the US, it is reported that 3% of secondary amines and 1.8% of tertiary amines are converted to nitrosamines in laboratory chamber studies. Other US overviews have suggested a conversion ratio of amines to nitrosamines of between 10 and 30%, although this may be an overestimate due to high nitrous acid concentrations in this particular experiment. Some studies have reported worst case conversion rates of tertiary amines to nitrosamines of 2%. More recent Norwegian reaction chamber studies have found that less than 0.6% of DMA and 1.1% of N,N-Dimethylmethanamine (trimethylamine – TMA) were converted to nitrosamine." In study [26], the atmospheric conversion rates (after the release of the amines to atmosphere from the post-combustion CO_2 capture process) of MEA are assumed to be: 1% nitramines, 50% formamide, and 3% acetamide. Study [30] pointed out a nominal 10% conversion factor can be used to represent a reasonable (but highly conservative) value to predict nitrosamine and nitramine concentrations that would be generated in the atmosphere.

A worst case study [26], and a likely case study [56] were conducted for Norway's CO_2 Technology Centre Mongstad (TCM), where the 2% conversion rate to nitrosamine is used in the worst case study, and a lower conversion rate is used in the likely case study. The maximum values for the sum of nitrosamines and nitramines in both air and water are presented below in Table 13. TCM's conclusion was that the risk was acceptable after comparison with the guideline values published by Norway's NIPH (National Institute of Public Health). The Norwegian Climate and Pollution Agency granted TCM a permit in November 2011 [56] based on the likely case study.

Table 13: Maximum concentrations of sum of nitrosamine and nitramine in air and water for likely and worst case [56]

	NIPH guideline value	CHP	RFCC
Air, likely (ng/m^3)	0.3	0.0022	0.0017
Water, likely (ng/l)	4	0.023	0.027
Air, worst (ng/m^3)	0.3	0.009	0.008
Water, worst (ng/l)	4	0.52	0.63

A summary study [40] shows which compounds can be formed (see Table 14 below for Nitramine and Nitrosamine, and Table 15 for Amides). The main products of the atmospheric degradation are different amides; a number of nitrosamines and nitramines will also be formed. However, there is no quantification of how much of each compound will form, or what the relative amounts of nitrosamines and nitramines formed in the atmosphere will be.

Table 14: Nitramine and Nitrosamine compounds predicted in the theoretical study for the photo-oxidation of amines in atmosphere [40]

Registry #	Formula	Structure	Name
675141-02-3	C H2 N2 O2	O=CH—NH—N=O	Formamide, N-nitroso-
51883-27-3	C H2 N2 O3	OHC—NH—NO$_2$	Formamide, N-nitro-
64768-29-2	C H4 N2 O	H$_3$C—NH—N=O	Methanamine, N-Nitroso-
598-57-2	C H4 N2 O2	O=N—NH—CH$_3$ (with O double bond)	Methanamine, N-nitro-
598-57-2	C H4 N2 O2	O=N—NH—CH$_3$ (with O double bond)	Methanamine, N-Nitro-
62-75-9	C2 H6 N2 O	H$_3$C—N—CH$_3$ with N=O	Methanamine, N-Methyl-N-nitroso-
98033-27-3	C2 H6 N2 O2	HO—CH$_2$—CH$_2$—NH—NO	Ethanol, 2-(nitrosoamino)-
4164-28-7	C2 H6 N2 O2	Me—N—Me with NO$_2$	Methanamine, N-Methyl-N-nitro-
74386-82-6	C2 H6 N2 O3	HO—CH$_2$—CH$_2$—NH—NO$_2$	Ethanol, 2-(nitroamino)-
32818-80-7	C2 H6 N2 O3	Me—N—CH$_2$—OH with NO$_2$	Methanol, (methylnitroamino)-
42499-46-7	C3 H8 N 2O3	Me—N—CH$_2$—CH$_2$—OH with NO$_2$	Ethanol, 2-(methylnitroamino)-
26921-68-6	C3 H8 N2 O2	Me—N—CH$_2$—CH$_2$—OH with NO	Ethanol, 2-(methylnitrosoamino)-
55-18-5	C4 H10 N2 O	Et—N—Et with NO	Etanamine, N-Etyl-N-Nitroso-
7119-92-8	C4 H10 N2 O2	Et—N—Et with NO$_2$	Etanamine, N-Etyl-N-Nitro-

Table 15: Amide compounds predicted in the theoretical study for the photo-oxidation of amines in atmosphere [40]

Registry #	Formula	Structure	Name
75-12-7	C H3 N O		Formamide
60939-21-1	C2 H3 N O2		Acetamide, 2-oxo-
60-35-5	C2 H5 N O		Acetamide
123-39-7	C2 H5 N O		Formamide, N-Metyl-
598-42-5	C2 H5 N O2		Acetamide, 2-Hydroxy-
68-12-2	C3 H7 N O		Formamide, N,N-Dimetyl-
79-16-3	C3 H7 N O		Acetamide, N-Metyl-
20546-32-1	C3 H7 N O2		Formamide, N-(hydroxymethyl)-N-methyl-
127-19-5	C4 H9 N O		Acetamide, N,N-Dimetyl-
1590-50-7	C4 H9 N O2		Formamide, N-(2-hydroxyethyl)-N-methyl-
617-84-5	C5 H11 N O		Formamide, N,N-Dietyl-
17236-38-3	C5 H11 N O3		Glycolamide, N-(2-hydroxyethyl)-N-methyl-
685-91-6	C6 H13 N O		Acetamide, N,N-Dietyl-

For atmospheric reactions of MEA, refer to Figures 19, 20 and 21 below for a summary. All these figures come from study [40]. Products with lifetimes > 3 days are highlighted in boldface blue colour, and nitrosamines and nitramines formed in the atmospheric degradation of amines are highlighted in boldface red colour.
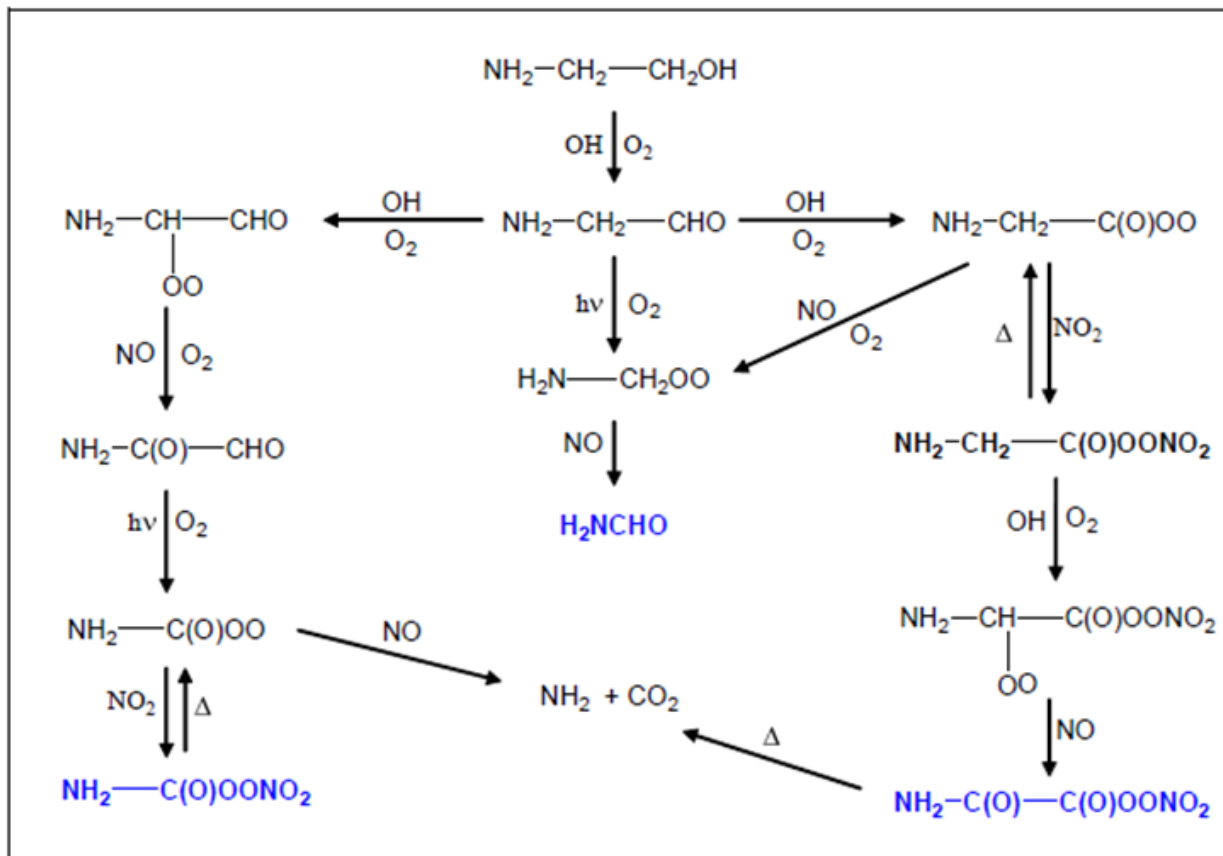
Figure 19: Atmospheric degradation of MEA following initial hydrogen abstraction at C1 [40]
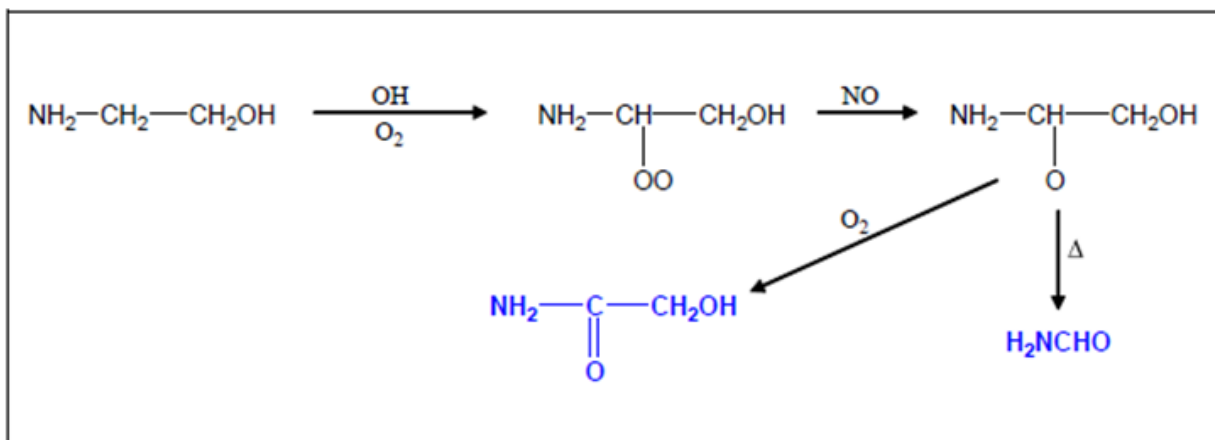
Figure 20: Atmospheric degradation of MEA following initial hydrogen abstraction at C2 [40]
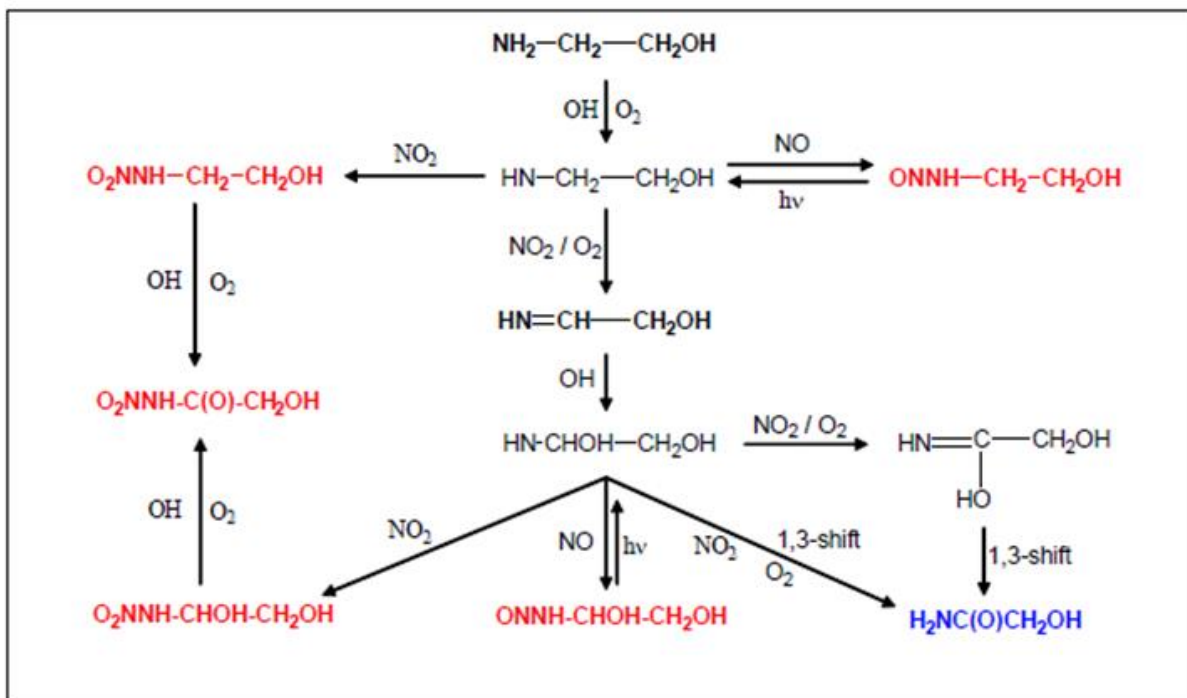
Figure 21: Atmospheric degradation of MEA following initial hydrogen abstraction from the amino group [40]

Paper [56] has a very good summary of the fate of atmospheric amines: "In short, the atmospheric photo-oxidation of MEA is dominated by reaction with the •OH radical, which may abstract a hydrogen atom from either a carbon or nitrogen atom (hydrogen abstraction from the •OH group is only a minor route). The product of major concern is the nitramine, O2NNHCH2CH2OH, resulting from hydrogen abstraction from the amino group followed by reaction with NO2. Since only around 8% of the initial MEA reaction with •OH radicals results in the formation of amino radicals that may react with both O2, NO and NO2, only a small fraction of the photo oxidized MEA ends up as nitramine. The actual yield of nitramine in the environment will depend on the local NOx conditions." Figure 22 [56] shows simplified reaction routes for MEA atmospheric degradation:
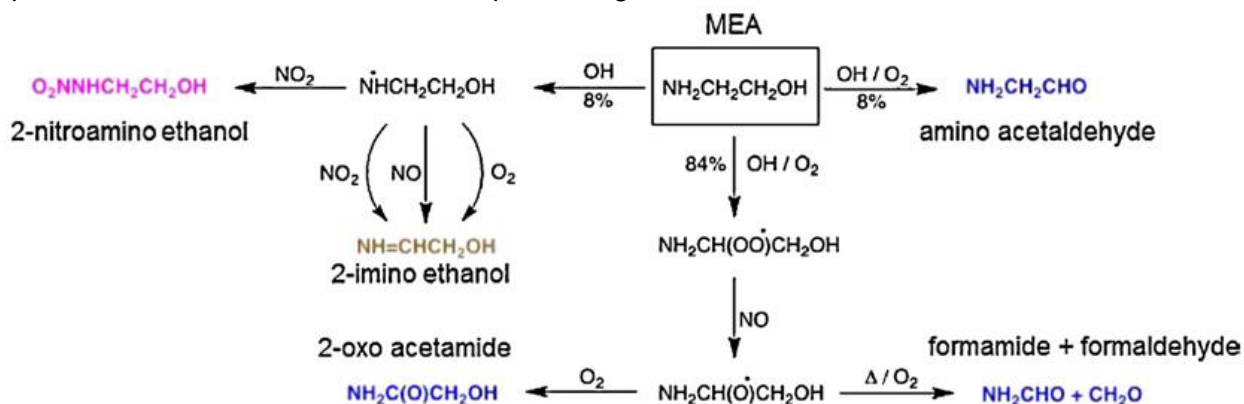
Figure 22: Simplified reaction scheme for the atmospheric photo-oxidation of MEA [56]

Study [40] also presents atmospheric reactions of MDEA, refer to Figures 23, 24 and 25.

Figure 23: The main routes to the atmospheric degradation of MDEA following initial hydrogen abstraction from one of the CH2OH groups [40]
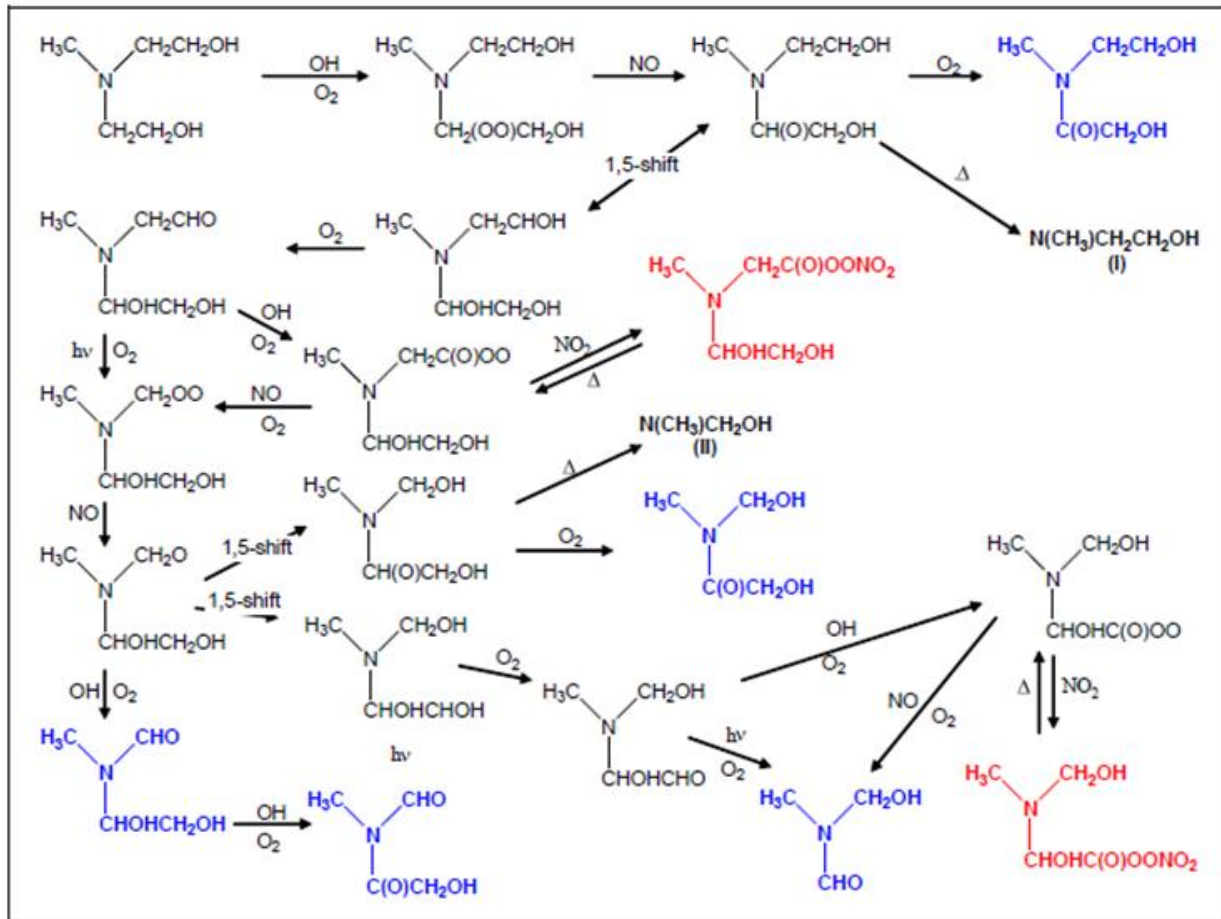
Figure 24: The main routes to the atmospheric degradation of MDEA following initial hydrogen abstraction from one of the CH2-CH2OH groups [40]
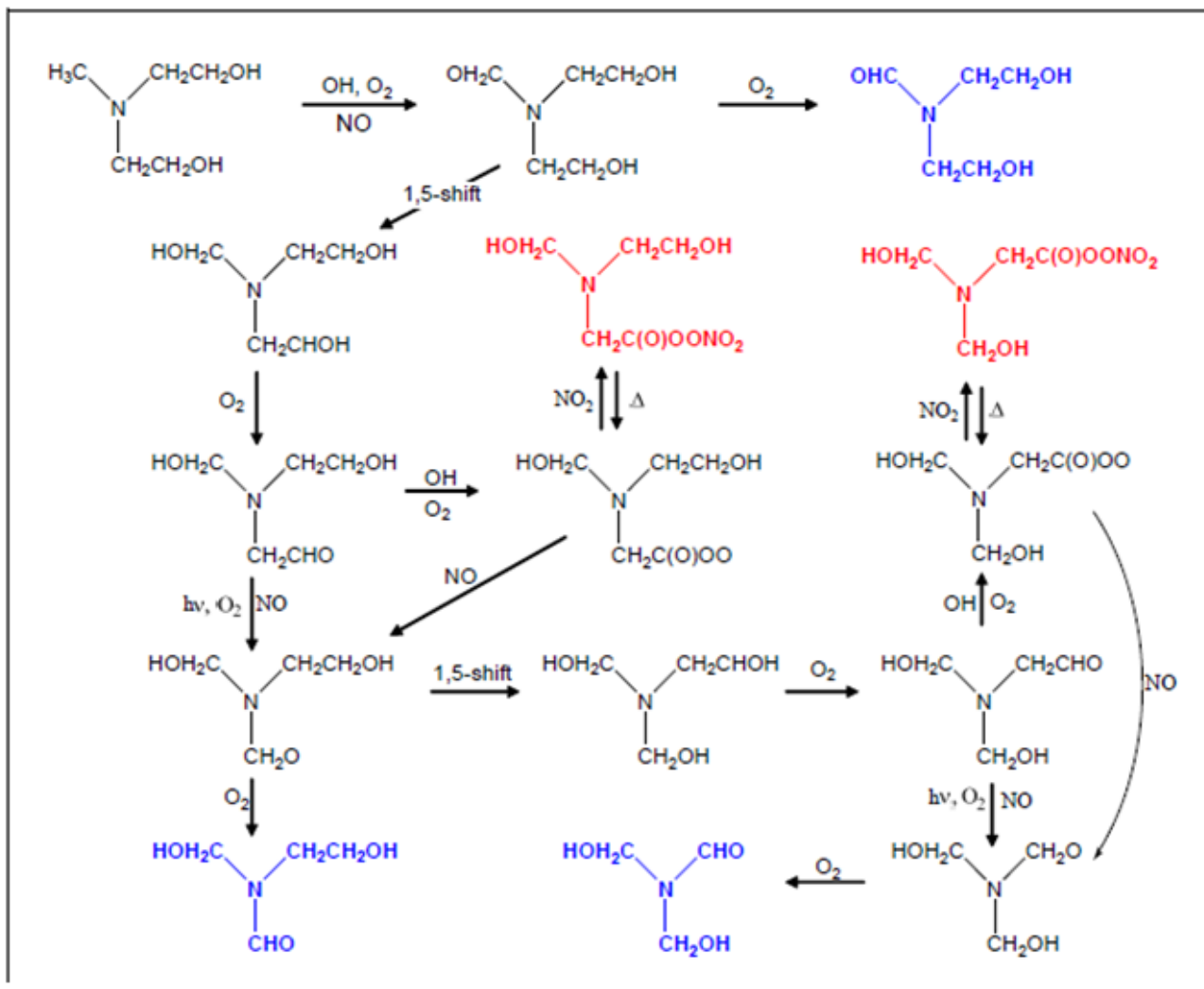
Figure 25: The main routes to the atmospheric degradation of MDEA following initial hydrogen abstraction from the CH3 group [40]

2. Amine Partitioning in the Environment (Fugacity Study)

After amine and amine degradation products are released to air, it is important to identify where these substances end up: air, earth or water. This is called partitioning in the environment, which is calculated using fugacity modelling.

One study [52] set the amine emission to 40 tonnes per year of MEA and 5 tonnes per year of diethylamine (DEYA) (which is a secondary amine) which resulted in the sum of nitrosamines and nitramines in ground-level air of 0.6 - 10 pg/m3 and in drinking water of 0.04 - 0.25 ng/L.

Another study [48] of the Mongstad CO_2 Capture plant showed that wet deposition is the major deposition mechanism (wet deposition: almost 100%), whereas dry deposition is negligible (dry deposition: 0.6% to 2%). Basically, almost all the nitrosamines and nitramines will be deposited via the wet deposition mechanism during raining hours.

Study [48] also found the peak deposition fluxes were observed in a nearby field (a few kilometres from the emission source). It should be noted that the larger the lake, the lower the predicted lake concentrations, because of the increased water volume in which the loading was diluted. Study [48] stated "The total nitramines and nitrosamines concentration in lake water (0.8 km2 for the lake in a total catchment area of 9.8 km2) was predicted to be 81.3 ng/l when considering ultimate degradation and 17.6 ng/l when the rate was taken for simple degradation to the first metabolite."
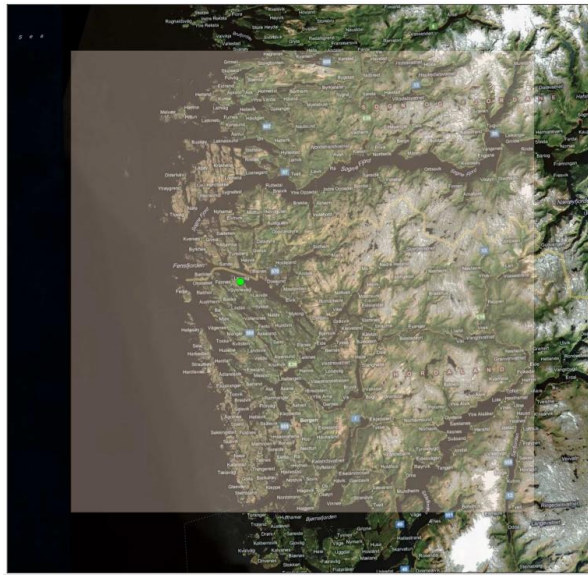
Figure 26: Area of Interest: 35 km x 35 km in study [48]

Norway's NIPH (National Institute of Public Health) has set 4 ng/l as representing a negligible lifelong risk of 1 in a million of acquiring cancer (10^{-6}), and 40 ng/l as a minimal lifelong risk of 10 in a million of acquiring cancer (10^{-5}). The result of study [48] suggested the nitrosamine and nitramine concentrations in the lake water (17.6 ng/L) will be in between acquiring cancer risks of 10^{-6} and 10^{-5}.

Fugacity Modelling in Alberta

In addition to the above studies presented in literature, an amine partitioning study was conducted using fugacity modelling through a third party environmental company (Intrinsik Environmental Sciences Inc.). This study is found in Appendix B. The emission rate of MEA was estimated by to be 11 tonnes/year based on a typical emission of 0.03 kg MEA / tonnes CO_2 captured and 1000 tonnes CO_2 captured per day for a typical SAGD development (as per one presentation from PTAC [75]). Environmental conditions used were for Alberta.

The study result showed <2% amine will be in air, <1% amine will be in sediment, approximately 70% amine will be in soil and 30% in water. Refer to Table 16 and Figure 27 below for details.

Table 16: Predicted concentration of amines in each media compartment

Chemical	Concentration			
	Air (ng/m3)	Soil (ng/g)	Water (ng/L)	Sediment (ng/g)
MEA	3.75	0.0142	189	0.000139
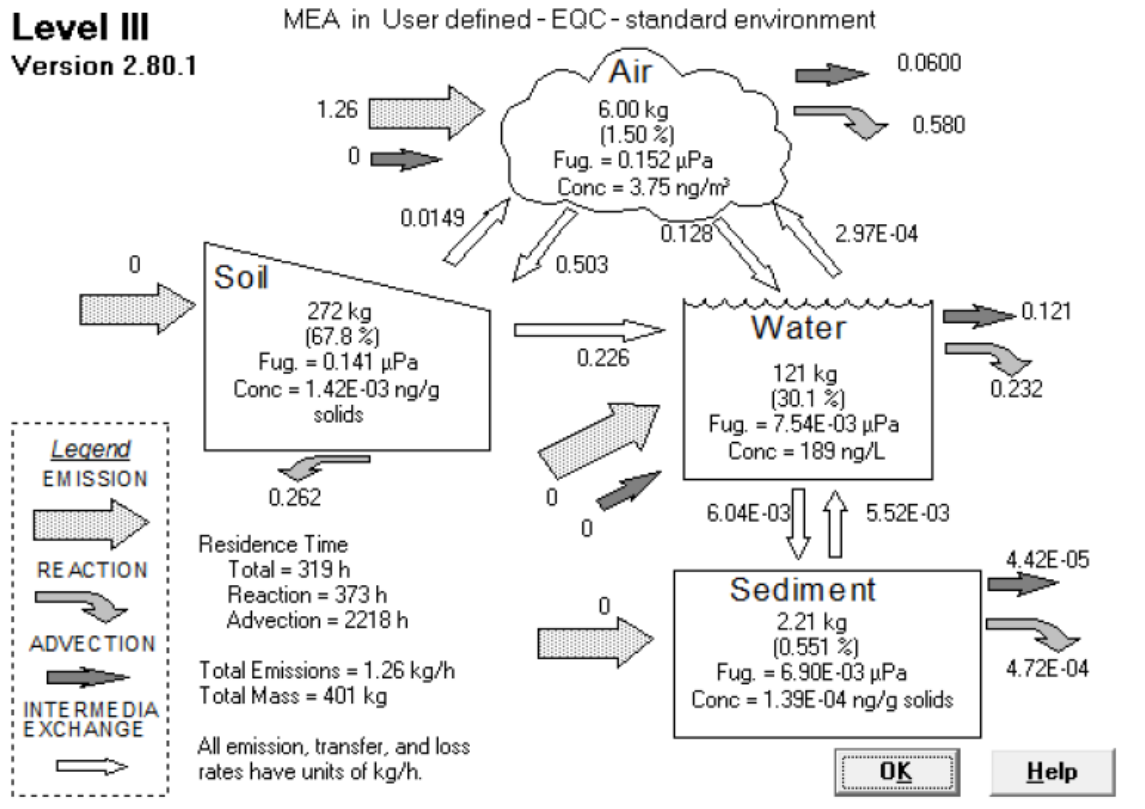
Figure 27: Fugacity Model Output for MEA

The following key values are calculated per this fugacity study:

- MEA concentration in air = 3.75 ng/m3
- MEA concentration in water = 189 ng/L

The maximum allowable MEA concentration in air set by regulation is 7.5 mg/m3 (see below Section III for details). So, based on this study, MEA in air is unlikely to pose environmental or human health impact.

However, the concentration of MEA in water has a potential risk to surface drinking water sources. From the fugacity study result, we can see that the MEA concentration in water is 189 ng/L. If we assume a conservative 2% conversion rate to nitrosamine (as per Section II, Part 1 of this report), then nitrosamine is equal to 3.78 ng/L in water. This is the same order of magnitude of some regulations (e.g. 7 ng/L per US EPA, 4 ng/L per Norway's NIPH) (see below Section III for details). This is consistent with other research indicating that water has the highest risk of contamination from amine-based emissions.

For the full detailed report (including assumptions, modelling and discussions), and fugacity models of other amines, refer to Appendix B.

3. Impact of Amines and Amine Degradation Products on Human Health and the Environment

Post combustion CO_2 capture using amine solvent is the most mature process for full-scale CO_2 capture within the next few years. The human health and environmental impact of amine emissions (including amine degradation product emissions), however, is a potential risk. Amines can react both in the process and in the atmosphere to form new substances (like carcinogenic compounds nitrosamines and nitramines) that are more harmful than the parent amine itself.

Results from a worst case study showed that the predicted concentrations of harmful compounds are at the same level of magnitude as the proposed "safety limits" (Norway), implying that risks to human health and the natural environment cannot be ruled out [39].

3.1 Human Health Impact of Amines and Amine Degradation Products

Impact of Amines

The toxicity of amines varies. The amines are all irritating to skin, and toxic at high concentrations to animals. Among the amines MEA, AMP, DEA, MDEA and PIPA, only DEA is listed as carcinogenic by NIOSH. A study [58] focused on the inhalation toxicity of DEA and TEA upon repeated exposure stated "Only DEA induced systemic toxicity at or above 150 mg/m3 (body and organ weight changes, clinical- and histo-pathological changes indicative for mild blood, liver, kidney and testicular effects). TEA appears to be less potent with respect to systemic toxicity and RT (respiratory tract) irritancy than DEA."

Another study [43] suggested that the general population, over time, should not be exposed to levels higher than 10 μg/m3 of MEA in air. Norwegian study [28] found that the maximum hourly averaged concentration will be 11μg/m3 (found within 1 km distance) when amine emissions are 160 tonne/year, which means the amine air concentration could be above the critical levels if degradation of amines is not considered. The simulations performed by the Norwegian Institute for Air Research (NILU) indicated that the maximum amine concentration in the air will be 0.1 μg/m3 when degradation of amines is considered, which is two orders of magnitude below the threshold of 10 μg/m3 of MEA, and thus should not pose a health risk

Impact of Amine Degradation Products

Literature reviews have revealed that approximately 90% of the about 300 nitrosamines tested have shown carcinogenic effects in bioassays or laboratory animals [27]. Exposure to nitrosamine has been shown to form tumours in laboratory animals, and has been linked in epidemiological studies to human cancers including pancreatic cancer and childhood brain tumours. Nitramines are also presumed to be carcinogenic, although there are little data available [52]. Nitrosamines and nitramines are thus both treated as toxic and mutagenic, and the toxicity and mutagenicity of the nitrosamines is higher than the nitramines.

Nitrosamine and nitramine contamination of drinking water around amine-based CO_2 plants can cause significant impact due to the high tendency of nitrosamine and nitramines to be absorbed in soil and water sources [29].

In the worst case study [41], the exceedance of 7 ng/l (= 0.3 mg/m2/yr) (based on US EPA's Integrated Risk Information System [76]) nitrosamines is considered harmful. Assuming the conversion of 2% of the emitted amine into nitrosamines, 24 tonnes per year is the maximum tolerable amine emissions from the plant. (See Table 17 [41] for the summary of the maximum tolerable amine emission.) Since many other assumptions were made in this study, it provided more information on prioritizing the problematic compounds rather than accurate predictions of concentrations.

Table 17: Summary of results from the worst case study [41]

Worst case run	Critical depostion flux	Maximum dep. flux (mg/m^2) ^{1}	Max. tolerable emission (t/yr)	Max. tolerable amine emiss. (t/yr)	Effect
Amines	2700 mg/m^2/yr	5.18	14400	14400	Vegetation
	300 mg/m^2/yr	5.18	1570	1570	Aquatic algae
Nitrogen ^{2}	500 mg/m^2/yr	5.18	2610	11400	Terrestrial Eutrophication
Nitros-amines	0.3 mg/m^2/yr	16.1	0.5	24	Human Health^3
	1.0 mg/m^2/yr	16.1	1.7	84	Aquatic algae
Nitramine	40 mg/m^2/yr	16.1	67	960	Human Health^3
	8.0 mg/m^2/yr	16.1	13.4	192	Aquatic Fish / Invertebrates
Formamide	960 mg/m^2/yr	16.1	1620	17800	Aquatic Invertebrates

The above worst case study comes from amine emissions for a plant capturing 1 million tonnes of CO_2 per year and a 2% assumption of conversion of amines to nitrosamines in the atmosphere. With growing knowledge of the chemistry mechanisms as well as degradation of nitrosamines and nitramines, a more 'likely case' study was developed in study [56]. The latter showed a significant decrease in risk and showed that the process will conform to Norway's NIPH guideline quality criteria as presented in Table 13 (see previous section).

Another possible degradation product is formamide, which could be hazardous to health. Liver damage can be produced by overexposure to these chemicals in man. Airborne concentrations need to be controlled and care should be taken to avoid excessive liquid contact as the chemicals are absorbed through the skin and the respiratory tract [43].

3.2 Environmental Impact of Amines and Amine Degradation Products

Since no information was found on the direct toxicity of the amines MEA, MDEA, AMP and PIPA to terrestrial plants and vegetation per study [39], the main effect of amines on the terrestrial plants and vegetation is related to eutrophication. Amines sprayed onto plants can increase plant growth and seed yield and reduce plant stress. Also, the nitrogen components (biodegraded from amines) in soil (or soil water) can benefit plant growth [28]. However, increased nitrogen load can have a negative effect on ecosystems; this effect is called eutrophication, which means the nitrogen has the potential to reduce diversity of terrestrial ecosystems [44]. Study [44] stated "Effects can be related to changes in plant species composition, plant growth (especially increased grass and herb dominance, decrease in mosses and lichens), biomass productivity, litter production, nitrogen availability, soil nutrients, soil acidification and mycorrhiza infection, which again might affect the soil fauna. Increased grass/herb dominance will probably favour grazers of invertebrates, birds and mammals, and altered competition may lead to changes in animal populations and species composition. Change in prey populations may also lead to changes in the populations of birds of prey and carnivores."

The exceedance of a critical load of 5 kg N/ha/yr may result in nitrogen eutrophication per study [41]. Based on the worst case study, refer to above Table 17; the critical load of amines can damage plants if exceeding 2700 mg/m3/yr, and that requires 14400 tonnes amine emission per year. This is many times higher than the expected maximum emissions from a typical CO_2 capture plant, so that harmful effects of amines to terrestrial plants and vegetation are therefore not expected [41]. Also, as per above Table 17, the produced toxic compounds like nitrosamines, nitramines are a much more profound problem than that of airborne nitrogen load.

As per Norway's Amine Emission Study [39], fish and algae have the most sensitive response to amine exposure, with an LOEC (Lowest Observed Effect Concentration) of 0.5 mg/L for MDEA and 0.75 mg/L for MEA, respectively. As for nitrosamines, a much lower level is expected: an LOEC of 0.025 mg/L NDMA on algae. This was the lowest effect concentration found for all compounds and test species per study [39]. For nitramines, 0.2 mg/L of CL-20 (abbreviation of the nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) on fish and 0.4 mg/L of CL-20 on invertebrates were found respectively.

For amides, report [45] pointed out that invertebrates have the most sensitive response with an exposure of 1.2 mg/liter of formamide.

For effects of amines on fauna, study [44] stated "There is also very little information on effects of relevant amines used for CO_2 removal on terrestrial free-living fauna. Laboratory experiments on animals, related to human health risks, show that all relevant amines are irritating to skin and also toxic at high concentrations with almost the same oral LD50. However, none of the amines have been reported to be carcinogenic or genotoxic. These experimental results may also apply for free-living terrestrial animals. Based on the data available it is difficult to range the amine's toxicity effect on free-living fauna. However, piperazine has been found to be highly toxic to dung beetle and partly to water invertebrates. It can also interact with nitrosating agents in vivo to form nitrosamines with possible carcinogenic risk. Thus piperazine might be the most unfavourable amine to fauna."

For effects of degradation products on vegetation, study [44] stated "Very little is known of effects on terrestrial vegetation of the degradation products amides, nitrosamines and nitramines. However, amides are known to be growth restrictive and are widely used in herbicides."

For effects of degradation products on fauna, study [44] stated "The degradation products amides, nitrosamines and nitramines are known to be toxic to mammals and soil invertebrates, and they might also affect soil microorganisms. Especially nitrosamines and nitramines are found carcinogenic to mammals."

Section III: Review of Regulations

1. Review of Regulatory Limits on Amines

Regulatory information was gathered from different authorities (both international and domestic):

- International Labour Organization Chemical Safety Card (ICSC) [66]
- US NIOSH (National Institute for Occupational Safety and Health) Pocket Guide to Chemical Hazards [67]
- US OSHA (Occupational Safety & Health Administration) Chemical Database [68]
- Alberta Occupational Health and Safety Code 2009 [69]

Table 18: Summary of Effects from [66], [67] and [68]

	MEA	DEA	MDEA
Inhalation Hazard (from ICSC [66])	Cough. Headache. Shortness of breath. Sore throat.	Redness. Pain. Severe deep burns.	Cough. Nausea. Sore throat.
Skin Hazard (from ICSC [66])	Redness. Pain. Skin burns.	-	Redness. Pain.
Eye Hazard (from ICSC [66])	Redness. Pain. Severe deep burns.	-	Redness. Pain.
Effect of short term exposure (from ICSC [66])	The substance is corrosive to the respiratory tract, skin and eyes. Corrosive on ingestion. The vapour is irritating to the eyes, skin and respiratory tract. The substance may cause effects on the central nervous system. Exposure could cause lowering of consciousness.	The substance is corrosive to the eyes.	The substance is irritating to the eyes and skin.
Effect of long term exposure (from ICSC [66])	Repeated or prolonged contact may cause skin sensitization.	Repeated or prolonged contact may cause skin sensitization. The substance may have effects on the liver and kidneys.	-

	MEA	DEA	MDEA
Immediately Dangerous to Life or Health Concentration (from NIOSH Pocket Guide [67])	30 ppm	-	-
Time Weighted Average Recommended Exposure Limit (from NIOSH Pocket Guide [67])	3 ppm (7.5 mg/m3)	3 ppm (15 mg/m3)	-
Short Term Recommended Exposure Limit (from NIOSH Pocket Guide [67])	6 ppm (15 mg/m3)	-	-
Time Weighted Average Permissible Exposure Limit (from OSHA [68])	3 ppm (8 mg/m3)	-	-
Alberta Occupational Exposure Limit - Long Term (8 hr)	3 ppm (7.5 mg/m3)	2 mg/m3	-
Alberta Occupational Exposure Limit - Short Term (15 min)	6 ppm (15 mg/m3)	-	-

Note: DEA must also be reported to Canada's NPRI if 10 tonnes/year or more were manufactured, processed or otherwise used in a facility.

2. Review of Regulatory Limits on Amine Degradation Products

As discussed in previous sections, nitrosamines are carcinogenic. Two of the most frequently investigated nitrosamines by regulatory authorities are N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) [60]. See below Figure 28 [60] for the structure of nitrosamine and structure of N-nitrosodimethylamine (NDMA).
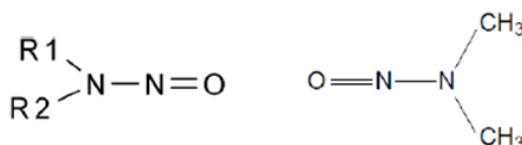

Figure 28: Structure of nitrosamine (NDEA) (left) and structure of N-nitrosodimethylamine (NDMA) (right) [60]

NDMA and NDEA are classified as Group 2A substances (probably carcinogenic to humans) by the International Agency for Research on Cancer (IARC) [60]. They are categorized as category 1B (Presumed to have carcinogenic potential for humans; largely based on animal evidence) by the European Union [60]. In the US, they are classified by the Environmental Protection Agency as a "probable human carcinogen (category B2)" under its 1986 carcinogen assessment guidelines [60].

<u>Regulations on Drinking Water Quality</u>

NDMA and other nitrosamines are among the chemicals known to cause cancer. Generally, a 10^{-5} or 10^{-6} risk level is applied to carcinogen risk assessments [60].

In Canada, the Guidelines for Canadian Drinking Water Quality [70] have set the maximum acceptable concentration (MAC) for N-nitrosodimethylamine (NDMA) in drinking water at 0.000 04 mg/L (0.04 µg/L). In the US, California [75] has set the 10^{-6} Cancer Risk level for NDEA, NDMA, and NDPA at 1 ng/L, 3 ng/L and 5 ng/L respectively. Notification levels for NDEA, NDMA, and NDPA are established at 10 ng/L to take into account the very low detection limits and their potential presence in association with drinking water treatment. Response levels are levels at which a drinking water source should be removed from service, and are set at 100 ng/L, 300 ng/L and 500 ng/L respectively. Norway's NIPH (National Institute of Public Health) set 4 ng/l as the 10^{-6} risk level, and 40 ng/l as the 10^{-5} risk level. Also, refer to Table 19 below for NDMA drinking water guideline values and associated risks from study [60].

Table 19: NDMA Drinking Water Guideline Values and Associated Risks. [60]

Authority	Concentration (ng/L)	Comment
US Environmental Protection Agency IRIS Database	0.7	10^{-6} cancer risk
Canada proposed Maximum Acceptable Concentration (MAC)	40-100	10^{-5} cancer risk
US State of California Public Health Goal	3	10^{-6} cancer risk
US EPA Regions 3 & 6 non-enforceable screening level in tap water (2007)	0.42	
World Health Organization Guideline Value	100	10^{-5} cancer risk

For the amine degradation products, information was also gathered from different organizations or authorities (both international and domestic):

- International Labour Organization Chemical Safety Card [66]
- NIOSH (National Institute for Occupational Safety and Health) Pocket Guide to Chemical Hazards [67]
- OSHA (Occupational Safety & Health Administration) Chemical Database [68]

- Alberta Occupational Health and Safety Code 2009 [69]

Table 20: Summary of Effects of Amine Degradation Products from [66], [67] and [68]

	Ammonia NH3	Amide: Formamide	Nitrosamine: NDMA (N-nitrosdimethylamine)
Inhalation Hazard (from ICSC [66])	Burning sensation. Cough. Laboured breathing. Shortness of breath. Sore throat.	Drowsiness. Headache. Nausea. Diarrhoea.	Sore throat. Cough. Nausea. Diarrhoea. Vomiting. Headache. Weakness.
Skin Hazard (from ICSC [66])	Pain. Blisters. Skin burns. ON CONTACT WITH LIQUID: FROSTBITE	Redness.	Redness. Pain.
Eye Hazard (from ICSC [66])	Pain. Severe burns. ON CONTACT WITH LIQUID: FROSTBITE.	Redness.	Pain. Redness.
Effect of short term exposure (from ICSC [66])	Rapid evapouration of the liquid may cause frostbite. The substance is corrosive to the eyes, skin and respiratory tract. Exposure could cause asphyxiation due to swelling in the throat. Inhalation may cause lung oedema, but only after initial corrosive effects on eyes and/or airways have become manifest.	The substance is moderately irritating to the eyes and skin. The substance may cause effects on the central nervous system.	The substance is irritating to the eyes, skin and respiratory tract. The substance may cause effects on the liver. This may result in jaundice. The effects may be delayed. See Notes. Medical observation is indicated.
Effect of long term exposure (from ICSC [66])	Repeated or chronic inhalation of the vapour may cause chronic inflammation of the upper respiratory tract. Lungs may be affected by repeated or prolonged exposure. This may result in chronic obstructive pulmonary disorders (COPD).	May cause toxicity to human reproduction or development.	The substance may have effects on the liver. This may result in liver function impairment and cirrhosis. This substance is probably carcinogenic to humans.

	Ammonia NH3	Amide: Formamide	Nitrosamine: NDMA (N-nitrosdimethylamine)
Immediately Dangerous to Life or Health Concentration (from NIOSH Pocket Guide [67])	300 ppm	-	no value, causes cancer
Time Weighted Average Recommended Exposure Limit (from NIOSH Pocket Guide [67])	25 ppm (18 mg/m3)	10 ppm (15 mg/m3) [skin]	no value, causes cancer
Short Term Recommended Exposure Limit (from NIOSH Pocket Guide [67])	35 ppm (27 mg/m3)	-	no value, causes cancer
Time Weighted Average Permissible Exposure Limit (from OSHA [68])	50 ppm (35 mg/m3)	-	no value, causes cancer
Alberta Occupational Exposure Limit - Long Term (8 hr)	25 ppm (17 mg/m3)	10 ppm (18 mg/m3)	-
Alberta Occupational Exposure Limit - Short Term (15 min)	35 ppm (24 mg/m3)	-	-

Section IV: Conclusions and Recommendations

Conclusions

Process Ecology conducted an extensive literature review on the subject of amine emissions (including amine emissions and amine degradation product emissions). Two major processes which are sources of emissions were the focus of this literature review: the natural gas sweetening process and the CO_2 capture process. Amine solvents are used extensively in the natural gas sweetening process to remove acid gas from produced sour gas, and amine-based solvent is considered to be the most suitable medium for the CO_2 capture process using currently best available technology.

The most common continuous losses of amine from the gas sweetening process are entrainment loss, vapourization loss and degradation loss. The amine losses from entrainment and vapourization will end up in the sweet gas stream and normally will be sent to the next processing unit (e.g., a glycol dehydrator or pipeline). In this way the amine is not released directly to air, at least not at the sweetening facility. In addition, adding a water washing section on the outlet of the absorber will reduce the amine losses to the sweet gas stream by about 90%. The amine loss from degradation within the gas sweetening process will mostly end up in the solid waste of regenerator, which likely does not affect air quality. The overall amine loss from the gas sweetening process can be 0.048 kg MEA/e3m3 gas processed, or 0.032 kg DEA or MDEA/e3m3 gas processed [61], and the "lost" amine is not released to air directly. Process Ecology also conducted gas sweetening simulations using HYSYS^{TM} and VMGSim^{TM} to investigate the amine vapourization loss from the contactor, and showed the relative magnitude of losses calculated by the simulators are in line with the trend of decreasing vapourization loss with increasing amine size (MEA < DEA < MDEA). The simulation results are in accordance with the fact that vapourization (calculated by the simulator) is a minor loss and entrainment (not calculated by the simulator) is a much larger loss. Emissions from amine storage tanks were estimated as well and the quantity of these emissions was determined to be negligible.

For the amine-based CO_2 capture process, most of the amine losses will be released to air directly, unless there is some control on the contactor overhead. Without control, the entrainment and vapourization losses will be released to air directly from the top of the absorber. The amine degradation products (largely due to the impurities in the flue gas) will also be released directly to air. Similar to the natural gas sweetening process, a water wash can help in reducing the amine and amine degradation products emissions to the air. Amine loss may be reduced to 0.03 MEA kg/tonne CO_2 captured with water wash [5]. Moreover, a variety of degradation products including nitrosamine will be formed in the CO_2 capture process (mainly in the absorber) and they will also be released to air.

After amines are released to air, they will begin degrading to other chemical compounds. The atmospheric reactions are complex and compounds including nitrosamines can be formed. A 2% conversion rate from MEA released to atmosphere to nitrosamine has been used in literature to conduct a worst case study [26]. The amines and amine degradation products can eventually end up in water in the long term, which may pose a risk to drinking water sources.

Process Ecology also conducted an environmental fugacity study through a third party company to investigate the concentration of MEA which may be released to various media, including water, using

emission data from literature. With a conservative 2% conversion rate from MEA to nitrosamine from literature, it was shown that the amine-based CO_2 capture process has the potential to put at risk surface drinking water sources in Alberta that may be near CO_2 capture facilities. Of course, some advanced emission control technologies may be able to reduce or eliminate the risk.

Human health and environmental impact of amines and amine degradation products were also reviewed in this study. Nitrosamine and nitramine degradation products are found to pose the highest risk to human health and environment for a CO_2 capture facility.

Although a significant amount of literature is available, there is still a lack of real plant data and real online measurement on the issue of amine emissions for companies and policy-makers to make sound decisions. With CO_2 capture attracting more and more attention in order to reduce GHG emissions from SAGD and other industrial plants, including power plants, it is important to fully understand and control the risk of amine emissions from this process. One report [28] recommended no commercial amine based CO_2 capture plants should be built before the knowledge gaps are filled (not expected by 2020). Also study [52] pointed out that since most CO_2 emission facilities are concentrated in the proximity of major industrial regions, it is important to realize the potential overlapping of amine emissions (including nitrosamines and nitramines emissions) in the same area.

Recommendations for further research

1. Further fill knowledge gaps, especially on amine emission rates from real plants – by measurement and modelling
2. Further develop technologies to reduce amine emissions directly to air
3. Further investigate the fate of amines when released to air
4. Establish regulations on amine and amine degradation product emissions for the CO_2 capture process once sufficient data is available.