Health and environmental impact of amine based post combustion CO$_2$ capture

Erik Gjernes$^a$*, Laila Iren Helgesen$^a$, Yolandi Maree$^b$

$^a$Gassnova SF, Dokkvegen 10, NO-3920 Porsgrunn, Norway
$^b$TCM DA, 71 Mongstad, NO-5954, Norway

Abstract

A post-combustion amine based CO$_2$ capture plant is associated with minor release of amine and amine degradation products to the atmosphere along with the treated flue gas. The possible health and environmental effect of this have been investigated extensively through the Norwegian CLIMIT-program, the CO$_2$ Technology Centre Mongstad (TCM) and the planning of a full scale capture plant at Mongstad (CCM). Based on flue gas from a combined cycle gas power plant, the capacity of TCM’s amine plant and CCM are 25 000 and 1 000 000 t/yr CO$_2$, respectively. Special attention has been given to nitrosamines and nitramines and the investigations have provided new knowledge on their formation, degradation and dispersion, going from the capture plant towards the end point in the nature. The initiatives and programmes have also included means of emission reduction as well as refining of measurements techniques. Computer models for dispersion calculation and evaluation of maximum level of components in air and drinking water are important and are part of the environmental permit for TCM. Up to now, this new knowledge has significantly reduced the risk perception for the release of amine and amine degradation products to the atmosphere.

© 2013 The Authors. Published by Elsevier Ltd.
Selection and/or peer-review under responsibility of GHGT

Keywords: CO$_2$ capture; amine; emission to air; health and environmental impact; demonstration; nitrosamine; nitramine

1. Introduction

The possible health and environmental impact of amines and amine degradation products being released to the atmosphere has received a lot of attention in Norway and a substantial amount of research has been carried out. The majority of the investigations has been financed from the Norwegian CLIMIT-program (co-founded with industry) and through the planning of the amine based CO$_2$ capture plants at

* Corresponding author. Tel.: +47 46 41 95 88
E-mail address: eg@gassnova.no.
the CO₂ Technology Centre Mongstad (TCM) and the full scale plant at Mongstad (CCM). These programs and initiatives are all sponsored by the Norwegian state. This comprehensive work has provided a better understanding of the various issues of amine release to the atmosphere and up to now this new knowledge has significantly reduced the risk perception.

The investigations have been initiated in order to obtain a knowledge base enabling a risk assessment of environment and human exposure to amines and their possible degradation products. The studies include chemistry and degradation of amines in the capture plant, emission to air and emission reduction technologies, atmospheric degradation of amines and environmental fate studies. Thus the whole chain from the capture plant to the final end point is covered. Up to now this has resulted in 55 projects executed by international as well as Norwegian institutes. The total budget exceeds 20 million euro, and the programs are in progress. The CCM activities are part of the qualification of amine technology and have the largest budget, followed by the CLIMIT-program and TCM. CLIMIT is supporting RD&D for CO₂ capture, transport and storage, and has since 2008 also built up a special research portfolio on impact of amine uses. TCM’s engagement is mainly linked to their application for a discharge permit. Impact of amine uses has also been investigated by others, but the current Norwegian initiatives are the largest and most comprehensive.

2. Investigations

An assessment from 2008 [1], based on available literature data, indicated that amine emission from capturing 1 million tons of CO₂ per year from a combined cycle gas power plant could imply a health and environmental risk. One important observation was that relevant experimental data was scarce. The possible routes of atmospheric degradation of emitted amine into nitrosamines and nitramines is an important part of an assessment, and by 2012 there are strong evidences that all major knowledge gaps in the relevant atmospheric chemistry are closed. This is the result of a focused effort on atmospheric chemistry through a series of comprehensive experimental- and theoretical investigations of amines and their degradation products. The amine chemistry in the capture plant itself has also been investigated and the degradation routes and conditions for provoking formation of substances such as nitrosamines are found. This knowledge is part of the activities for qualifying amines for CCM at Mongstad. Means of reducing emission from the absorber to the atmosphere are developed and tested. The stability of the nitrosamines and nitramines in the environment is an additional important parameter. Experimental investigations show that nitrosamines decompose more easily than nitramines in the environment and this is important for assessing the final concentration in air and drinking water. Overview of the activities can be found elsewhere [2,3,4].

2.1. Capture plant process

In an amine based capture plant the specific amine used as well as operational conditions determine candidates for emission to air. Flue gas degradation of monoethanolamine (MEA) as a function of O₂, NOₓ and temperature has been studied by Fostås et al [5]. They used a laboratory sized absorber column in combination with post treatment of solvent in an autoclave and found the amine diethanolamine (DEA) and the corresponding nitrosamine, nitrosodiethanolamine (NDLA), as well as traces of nitrosodimethylamine (NDMA), nitrosomorpholine (NMOR) and methylamine (MMA). Their methodology has been brought forward in the technology qualification amine program for CCM.

Each of the participating vendors in the qualification program for CCM will get access to a lab rig in order to test process degradation of amines according to a test protocol which have been developed by Sintef [6]. The lab rig is a compact portable unit simulating the absorber/desorber process of a normal
CO₂ capture plant. The solvent is in this rig tested through extra high level of O₂ and NOₓ in the exhaust gas and with extra high temperature in the desorber column. During the first test run by Sintef using MEA, nitrosamines were as expected, detected. By the end of 2012 four technology vendors, Mitsubishi Heavy Industries, LTD., Siemens AG, Aker Clean Carbon and Huaneng-CERI Powerspan Joint Venture will have completed this phase of the qualification program.

It is foreseen that further measures to reduce emissions from amine capture plants may be required. Amines and degradation products are expected to be found both in the gas phase and in droplet carry over from the absorber. Thus emission reduction technologies applicable for removing both gaseous components and droplets are of interest. The following technologies were ranked according to applicability and maturity [7]:

- 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

The least mature technologies have been investigated by e.g. Knuutila, Svendsen and Asif [8] who investigated UV treatment of MEA, DEA and wash water and Knudsen et al [9] who have addressed acid wash and also developed a new concept for reducing mist out of the absorber. The initiatives show that amine emission from gas power based capture in the order of ppb (parts-per-billion) is feasible.

Through the work on measuring amine and amine transformation products, sampling and analytical methods are being developed to be able to both identify and quantify nitrosamines and nitramines in process liquids and in emissions. This includes the construction of a sampling train including isokinetic sampling, sample handling, preservation, storage and transport [10] and the following analytical methods:

- a total nitrosamine analysis, a screening method for nitrosamines based on chemiluminescence, a quantitative method for analysis of both individual and groups of nitrosamines based on GC-MS [11] and a quantitative method for analysis of 5 nitramines based on LC-MS [12]. As more specific nitramines are being known and synthesized, analytical methods for a larger set of nitramines are expected to evolve. The total nitrosamine [13] analysis has very low detection limit and is suited for quantifying the unknown nitrosamines in the solvent and in emission samples. Online measurements by use of PTR-ToF-MS instruments have been used in a series of projects on atmospheric degradation, see next section, and will now be used at TCM for quantitative measurements of emissions from the CO₂ absorber unit as well as wider field measurements [14]. This instrument has limit of detection of 0.1 ppb for amines, nitrosamines and nitramines.

2.2. Atmospheric formation, destruction and dispersion

The first assessment with worst case estimates for Mongstad [1] was based on available literature data. There was e.g. no data for transformation of MEA in the atmosphere and a 2% conversion to nitrosamines was adapted from literature data on triethylamine [1]. The assessment was also based on a simplified modeling approach that e.g. assumed instantaneous conversion of amines at stack exit and no further degradation of harmful components in relation to their environmental fate. The assessment showed that amine emission from capturing 1 million ton of CO₂ per year from a combined cycle gas power plant could cause a risk to humans and the environment.

The study showed that there was little experimental data on atmospheric transformation of amines relevant for CO₂ capture as well as few data on further degradation and lifetime of the formed harmful components. In 2009 University of Oslo started their Atmospheric Degradation of Amine (ADA) program
that included experimental investigations in the European Photo Reactor, EUPHORE in Valencia, Spain. The program (2009 to 2011) has investigated and quantified the potential for forming nitrosamines and nitramines of eight amines: MEA, methyl-, dimethyl-, trimethyl-, ethyl-, diethyl, triethyl-amine and piperazine [15,16]. The various components were identified and quantified by offline analysis and adsorbents as well as by online FT-IR and PTR-ToF-MS measurements. The photolysis of nitrosamines and atmospheric lifetime of nitramines were also part of the program. By use of QSAR (Quantitative structure–activity relationship) models this comprehensive set of data provides input for theoretical modeling of other amines relevant for CO₂ capture.

Other findings were that primary amines will not form nitrosamines, however, nitramines might form from primary amines both in process and in atmosphere. The potency to form nitrosamines and nitramines has been found to be increasing in the following row for primary < secondary < tertiary amines respectively. Volatile alkylamines can also form from the alkanolamines used in the capture process and be released to atmosphere where further transition to nitrosamines and nitramines could occur [15,16].

Atmospheric transformation, destruction and dispersion has been further investigated and applied through the environmental permit for TCM and as part of CCM’s technology qualification amine program. The environmental permit for TCM, see Maree et al [17], includes limits for both the emission to air at absorber exit and the calculated yearly average of sum of nitrosamines and nitramines in the nature. These values shall not exceed 0.3 ng/m³ and 4 ng/litre for air and drinking water, respectively. This is according to recommendations from Norwegian Institute for Public Health (NIPH) [18] and based on the toxicity of the nitrosamine NDMA. The concentrations in air and drinking water are obtained by modelling atmospheric chemistry, dispersion, deposition by precipitation and degradation in fresh water with methods that were employed by Norwegian Institute for Air Research (NILU) [19,20]. The risk levels as depicted by the NIPH guidelines for nitrosamines and nitramines decreased as the NILU model developed [21]. The first sets of assumptions to the model were largely conservative in which the chemistry was assumed to happen instantaneously with no degradation of species once they are formed. These set of results were dubbed the ‘worst case’ study, but with growing knowledge on the chemistry mechanisms as well as degradation of nitrosamine and nitramine species a more ‘likely case’ study was developed [19,20]. The latter showed a significant decrease in risk and which showed that the process will conform to NIPH guideline quality criteria as presented in Table 1.

Table 1. Risk level comparison of nitrosamine and nitramine concentrations (sum) with update in dispersion model assumptions at TCM, adapted from [21]. Two flue gas sources: CHP with 3.5 % CO₂ from a combined cycle gas power plant and RFCC with 13 % CO₂ from the residue fluid catalytic cracker.

<table>
<thead>
<tr>
<th>Dispersion model case</th>
<th>NIPH guideline value</th>
<th>CHP</th>
<th>RFCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air - likely case (ng/m³)</td>
<td>0.3</td>
<td>0.0022</td>
<td>0.0017</td>
</tr>
<tr>
<td>Water - likely case (ng/l)</td>
<td>4</td>
<td>0.023</td>
<td>0.027</td>
</tr>
<tr>
<td>Air - worst case (ng/m³)</td>
<td>0.3</td>
<td>0.009</td>
<td>0.008</td>
</tr>
<tr>
<td>Water - worst case (ng/l)</td>
<td>4</td>
<td>0.52</td>
<td>0.63</td>
</tr>
</tbody>
</table>

The ‘likely case’ model and values, as presented in Table 1, accounted for degradation of nitramines and nitrosamines in both air and fresh water. Results from biodegradation studies conducted by SINTEF [22] on the nitrosamines NDELA, NDMA and nitrosopiperazine (NPz) showed significant biodegradation of these species. Nitramines, on the other hand, exhibited significant lower biodegradability [21].

CCM did during 2011 continue the study on atmospheric chemistry of amines and closed knowledge gaps related to both daytime and nighttime specific amine, nitrosamine and nitramine chemistry as well as
chemistry in the aqueous phase in the atmosphere. Table 2 indicates what has been studied and what has been found less important pathway not necessary to pursue when chemistry models were to be put up and introduced in dispersion models.

Table 2. Reaction pathways of amines, nitrosamines and nitramines studied

<table>
<thead>
<tr>
<th>Nitrosamine/Nitramine chemistry</th>
<th>Gas Phase</th>
<th>Aqueous Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation, Daytime</td>
<td>Amine +OH</td>
<td>None important</td>
</tr>
<tr>
<td>Formation, Nighttime</td>
<td>Amine+NO₃</td>
<td>None important</td>
</tr>
<tr>
<td>Destruction, Daytime</td>
<td>Nitrosamine+hv</td>
<td>None important</td>
</tr>
<tr>
<td>Destruction, Nighttime</td>
<td>None important</td>
<td>None important</td>
</tr>
</tbody>
</table>

For the most important reaction pathways all necessary data to decide reaction rates and quantities has been found through experiments and tests with the generic amines [15,16]. In this way reaction schemes with corresponding data can be included in dispersion models to enable simultaneous dispersion and chemical reaction of amines and the corresponding nitrosamines and nitramines in the atmosphere. Table 2 also shows that reactions in the aqueous phase were not found to be of importance neither for the formation or destruction of nitrosamines and nitramines. On the other hand the high solubility of capture type amines will pull the amines out of the gas phase reaction conditions in relation to degradation and they will not undergo reactions in the aqueous phase. As such partitioning of amines to the aqueous phase in the atmosphere will constitute an important loss process for capture related amines [16].

Cambridge Environmental Research Consultants (CERC) and DNV have in parallel developed two different dispersion models, ADMS- an advanced steady state gaussian plume model capable of treating simplified chemistry schemes – and Calpuff – a modified gaussian puff model with several chemistry schemes included. By introducing chemistry in dispersion models it has been shown that the maximum ambient air concentration of sum nitrosamines/nitramines can be reduced by a factor of 10 relative to the assumption of instant formation at the outlet of the stack. Simultaneous dispersion and chemical transformation is thus considerably slowing down the formation rate of nitrosamines and nitramines [23,24]. At TCM Leibniz Institute for Tropospheric Research (IfT) has been engaged to further develop dispersion modeling by use of the COSMO-MUSCAT model. NILU is currently introducing amine chemistry into WRF-Chem (Weather Research and Forecasting – Chemistry) in a CLIMIT project. Thus, several approaches for dispersion modeling with amine chemistry are currently developed in parallel.

2.3. Deposition, exposure and toxicity

Most amines and amino acids used in carbon capture are highly soluble in water. The same is expected for the corresponding nitrosamines and nitramines [25]. It is thus expected that these will dissolve in rain and fog droplets and ultimately be precipitated and end up in surface water, rivers and lakes.

The baseline studies conducted by the Norwegian Institute for Water Research (NIVA) and NILU were not able to show detectable amounts of nitramines or nitrosamines in the environment surrounding TCM at Mongstad. The surveillance activities did, however, detect amines in air, soil, moss and water [26,27]. Table 3 summarises the detection of a selection of amines in air, soil, moss and fresh water. Continuous monitoring in air, aquatic and terrestrial environments surrounding the TCM plant will be conducted on a 2 yearly basis.
Table 3. Detection of amines in air, soil, moss and fresh water as part of the baseline surveys by NIVA and NILU [26,27]. “D” refers to levels at or below detection limits that are 0.01 ng/m$^3$ for air, 1 ng/g for soil and moss and 10 ng/g for water. “S” refers to significant levels detected.

<table>
<thead>
<tr>
<th>Amine</th>
<th>Air</th>
<th>Soil</th>
<th>Moss</th>
<th>Fresh water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylamine</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>S</td>
<td>D</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>MEA</td>
<td>D</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>2-Amino-2-methylpropanol</td>
<td>D</td>
<td>D</td>
<td>S</td>
<td>D</td>
</tr>
<tr>
<td>Piperazine</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
</tr>
</tbody>
</table>

Literature reviews have revealed that approximately 90% of the about 300 nitrosamines tested have shown carcinogenic effects in bioassays or laboratory animals [18]. A genotoxic mechanism has been confirmed which implies a non-threshold approach in the risk assessment. Existing data on 23 nitrosamines which might form during carbon capture has been reviewed and IARC (International Agency for Research on Cancer) has classified 2 of them as probably carcinogenic to humans and 7 of them as possibly carcinogenic to humans. There is considerably less data on nitramines but they are suspected carcinogenic. None are however classified by IARC. Animal carcinogenicity studies have been carried out for two nitramines: methylisnitramine and dimethylisnitramine. These results indicate that dimethylisnitramine is to be considered at least 6 times less toxic than the corresponding nitrosamine, NDMA.

Due to the very limited amount of toxicity data available on nitramines a toxicity test campaign has been initiated [12]. The following five were investigated: dimethyl-, methyl-, MEA-, AMP- and piperazine-nitramine. Included in the test were acute toxicity, cytotoxicity, skin and eye corrosion, sensitization as well as genotoxicity in three different assays. Overall, the results showed very low toxicity levels. However, three out of the five tested positive on genotoxicity. The next step is to get a more quantitative evaluation of selected nitramines and rank them in relation to nitrosamines. This can give input to a more refined and less conservative toxicity evaluation than the one of today were all nitrosamines and nitramines are added and weighted equally toxic as one of the most toxic nitrosamines (NDMA).

2.4. Framework for qualifying amines for CO$_2$ capture

The knowledge gathered through the above explained studies, methods, models and procedures, will constitute a scientific framework for qualifying amines for use in CO$_2$ capture processes. This framework or toolbox is already in operation through CCM for Mongstad site.

3. Conclusion

The comprehensive investigations reported above have greatly reduced the uncertainty about health and environmental risks resulting from amine-based CO$_2$ capture. Valuable new know-how on amine technology, of high scientific and technical quality, has been generated and new sensitive methods for sampling and analysis of solvent and emissions have been developed. Atmospheric fate of emissions has been studied with regard to dispersion, transformation and degradation, and main knowledge gaps have been closed. The potential toxicity (carcinogenicity) of amine degradation products have been reviewed and tested. Finally, CCM’s technology qualification program for amines is established as a valuable toolbox and the program is currently in operation with participation of four vendors.
Acknowledgements

The authors would like to acknowledge all the institutes and researchers that have contributed to the comprehensive set of studies and the institutes and companies that have supported this financially.

References

[15] The ADA reports can be downloaded from : http://mn.uio.no/ada
[27] Tønnesen D, Dye C, Bohler T. Baseline study on air and precipitation quality for CO₂ Technology Centre Mongstad. NILU OR 73/2011.