DET NORSKE VERITAS

Executive Summary
Atmospheric Chemistry Modelling of Components from Post-Combustion Amine-Based CO_2 Capture

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Summary:

This report is the Executive Summary report of work performed by Det Norske Veritas Limited to develop a pre-existing atmospheric dispersion model called CALPUFF to perform complex chemical conversion and physical equilibria processes at the same time as dispersion calculations. It describes the objectives of each of Phase 1 and Phase 2 of this work and presents the main results, conclusions and recommendations.

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1 INTRODUCTION

1.1 Background

The CO_2 Capture Mongstad Project (CCM Project) is organised jointly by Gassnova SF and Statoil ASA with funding from the Norwegian government. This report is prepared by Det Norske Veritas Limited (DNV). Hereafter the joint clients (Gassnova SF and Statoil ASA) will be referenced as “CCM Project”, whereas the technology development process at Mongstad will be referred to as “the CCM project”.

The purpose of CCM Project is to plan and build a large scale CO_2 capture plant. The facility will be situated next to the Mongstad refinery on the Mongstad industrial site, north of Bergen on the west coast of Norway. The facility will capture CO_2 from the flue gas of a Combined Heat and Power plant (CHP), perhaps using amine-based capture technology. The design basis is the capture of approximately 1.3 million tonnes of CO_2 per year. This will then be conditioned and compressed for pipeline transport to geological storage under the Norwegian Continental Shelf.

An amine-based CO_2 capture plant may cause harmful emissions to the atmosphere. Amines and their degradation products, formed either in the process unit or after release to the atmosphere, are of particular concern to CCM Project but there is limited knowledge about the behaviour of such chemicals when released from large scale industrial processes. CCM Project has therefore launched several studies to be conducted during the capture plant development in order to improve our knowledge. One of the studies is associated with the atmospheric dispersion (and the ultimate fate) of components from post-combustion amine-based CO_2 capture. The principal pollutants of concern are: NOx (NO and NO_2), NH_3, amines, nitrosamines and nitramines, amongst others. Nitrosamines and nitramines in particular are acknowledged carcinogens. Very low environmental quality criteria have been proposed for these pollutants and hence the formation, dispersion and destruction processes of these pollutants are the main interest of this report.

The key environmental factors that determine the selection of the CO_2 capture process are:

- How much amine, nitrosamine and nitramine is released from the CO_2 capture process.
- How quickly does amine convert to nitrosamine and/ or nitramine in the environment.
- How quickly does nitrosamine and/ or nitramine decay in the environment.
- How quickly does the released gas flow, including any released or subsequently formed nitrosamine and/ or nitramine, disperse in the environment.

The magnitude of the environmental impact due to nitrosamine and/ or nitramine will be determined by the magnitude of the environmental quality criteria set by the regulator and the inter-play between the key factors above.

The overall objective of the work described in this report is to develop and demonstrate a model that is capable of assessing the environmental impacts of amines and their degradation products.

This model can then be used to help evaluate the preferred CO_2 capture process to be installed at Mongstad.

1.2 Overview of the CCM Project

The CCM project is designed to address many aspects of the Mongstad Carbon Capture and Storage project, including technology selection, detailed engineering, performance specification (including demonstrating acceptable environmental impacts) and research of basic physical and chemical processes where improvements in understanding are required.

In order to improve basic knowledge of amine chemistry in the process and in the atmosphere CCM Project commissioned many studies involving researchers and consultants.

During 2010, DNV was engaged by CCM Project to evaluate whether relatively simple air quality models could be used to satisfy the requirements of the CCM project. This activity was referred to as Call-Off 01 /1/. As part of Call-Off 01, DNV reviewed the academic reports that described amine chemistry and used an unmodified conventional Gaussian plume air dispersion model (ADMS v4) to estimate environmental impacts of nitrosamine and nitramine using various approaches and limiting assumptions.

After this work, it became clear that simple models that do not allow the definition of amine chemical transformation processes do not provide sufficient flexibility to predict the environmental impacts of amines and their degradation products with the degree of confidence required. Thus the Call-Off 01 report recommended model development work.

In April 2011, DNV began work under Call-Off 02. This was designed to address those shortcomings and was executed in two phases, which have been previously reported (Phase 1 /2/ and Phase 2 /3/).

This document provides an Executive Summary of the Phase 1 and Phase 2 work undertaken as part of Call-Off 02. Detailed results and discussion is provided in the technical reports /2, 3/ and are not repeated here.

2 PHASE 1

2.1 Objectives of Phase 1

The main objectives for Phase 1 of Call-Off 02 were to:

- Confirm the air dispersion model recommended under Call-Off 01 to be used as the basis for a development to assess how emitted substances from the carbon dioxide capture facility can be expected to behave after release to the atmosphere.
- Implement a simple amine gas phase chemistry scheme within the dispersion model.

- Demonstrate the utility of the resulting model by a site-specific emission dispersion with simple gas phase chemistry assessment.

2.2 Description of the Selected Air Dispersion Model for Development

The model selected by DNV was an open-source modified Gaussian puff dispersion model called CALPUFF Modelling System Version 6.4 (CALPUFF). CALPUFF has a number of advantages over ADMS, the dispersion modelling system used in DNV's initial investigations into the requirements of CCM Project. These are as follows:

- The time parameter is an important factor in the simulation of amine chemical reactions. ADMS is a steady-state Gaussian plume model in which the time parameter is not explicitly considered. CALPUFF is a time-varying model, in which each pollutant can be followed step by step from the source to the receptor. This capability provides a good base for a more accurate implementation of an amine chemistry model using CALPUFF.
- CALPUFF also allows for more accurate simulation of pollutant transport in complex terrain areas. Within this context, the use of 3D local area model data as meteorological input would maximise this capability.

Finally, and most importantly, CALPUFF is an open-source model written in FORTRAN. It can, therefore, be adapted to represent amine chemical processes. The CALPUFF model as modified by DNV may be referenced as “the DNV model” or “the modified CALPUFF model” below.

2.3 Brief Description of Work Performed under Phase 1

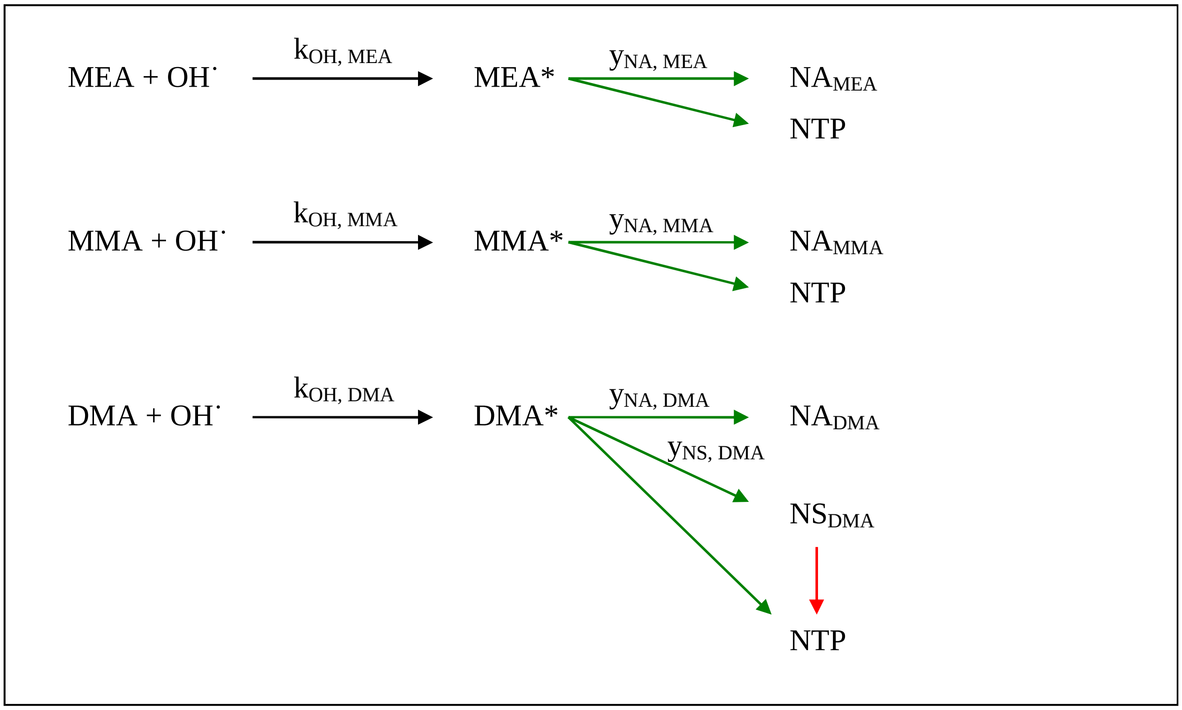
The CALPUFF model is a complex tool with 3 main executables used for different purposes, such as preparing the meteorology (CALMET), performing the dispersion calculations (CALPUFF) and post-processing the output files (CALPOST). The main CALPUFF code consists of more than 300 subroutines and functions and well over 100,000 lines of code.

The first task was to understand the code sufficiently well so as to be able to modify it to implement the new desired features with confidence whilst not impacting pre-existing calculations and calculation options.

In parallel, DNV also needed to examine the academic reports to develop a simple gas phase chemistry reaction scheme to be implemented in CALPUFF. This is shown in Figure 2.1, where MEA, MMA and DMA are three different amines (monoethanolamine, monomethylamine and dimethylamine respectively).

In Figure 2.1 and elsewhere in this report, A, NA, NS and NTP are use to represent amine, nitramine, nitrosamine and non-toxic products respectively, where NTP means “not NA and not NS”.

Figure 2.1 Phase 1 Gas Phase Amine Chemistry



Notation:
NA_x, a nitramine derived from amine x.
NS_x, a nitrosamine derived from amine x.
NTP, a non-toxic product.
$y_{p,q}$, the maximum yield of product p from amine q.

In Phase 1, the reactions were implemented as simple first order rate expressions which transformed the amine direct to the final products. That is, the rate constant and the yield percentage were combined into a single rate constant, the amine intermediate (e.g. MEA*) was not explicitly represented and the secondary reaction represented by the red arrow in Figure 2.1 was not implemented.

2.4 Key Results and Conclusions from Phase 1

DNV demonstrated that CALPUFF was capable of meeting the objectives of CCM Project by the implementation of a simple gas phase amine chemistry scheme /2/. This simple scheme made the following main simplifications and assumptions about amine chemistry in the atmosphere:

- The chemical transformation of amines in the atmosphere to harmful daughter products (nitramines or nitrosamines) is a two-stage process, depending on a number of counter-species, but the Phase 1 model made the assumption that the processes could be modelled as a one-stage process. This was accomplished by modelling the exact solution to the one-stage chemical process that produces the intermediate amine radical and applying yield factors to that radical to calculate the rate of formation of harmful products.
- Only the amine activation reaction with OH radicals was considered.

- OH radical concentration was calculated from the internal, pre-existing CALPUFF routines governing NOx and SOx chemistry.
- No facility was built-in to model the further degradation of harmful compounds into harmless ones (e.g. the red arrow in Figure 2.1 which transforms nitrosamine into non-toxic product).

The key conclusions from the Phase 1 of Call-Off 02 were as follows:

- The behaviour of the implemented simple gas phase amine chemistry in the updated CALPUFF model was concluded to be robust.
- For the case study considered, the recommended NIPH long term criterion ($0.3ng/m^3$ for the sum of nitramine plus nitrosamine) was not exceeded anywhere on the modelled grid.
- The simple gas phase amine chemistry scheme implemented makes certain assumptions that may affect the results of the analysis. However it is important to highlight that these tend to overestimate the resulting concentrations of nitrosamines and nitramines in air (that is, the assumptions are conservative).

3 PHASE 2

3.1 Objective of Phase 2

The key objectives of Phase 2 were to:

- Make higher precision predictions of the ambient air concentrations of amines and their degradation products (specifically nitrosamines and nitramines) emitted from the amine-based CO_2 capture process. It accomplished this by the inclusion of more realistic (and more complex) physical and chemical processes in the modified CALPUFF model, compared to Phase 1.
- Improve the *flexibility* of the modified CALPUFF model to represent different physical and chemical processes, and to demonstrate that the amended model gives reasonable results for different input parameters.
- Demonstrate the utility of the modified CALPUFF model through case studies.

3.2 The Phase 2 Amine Chemistry Scheme

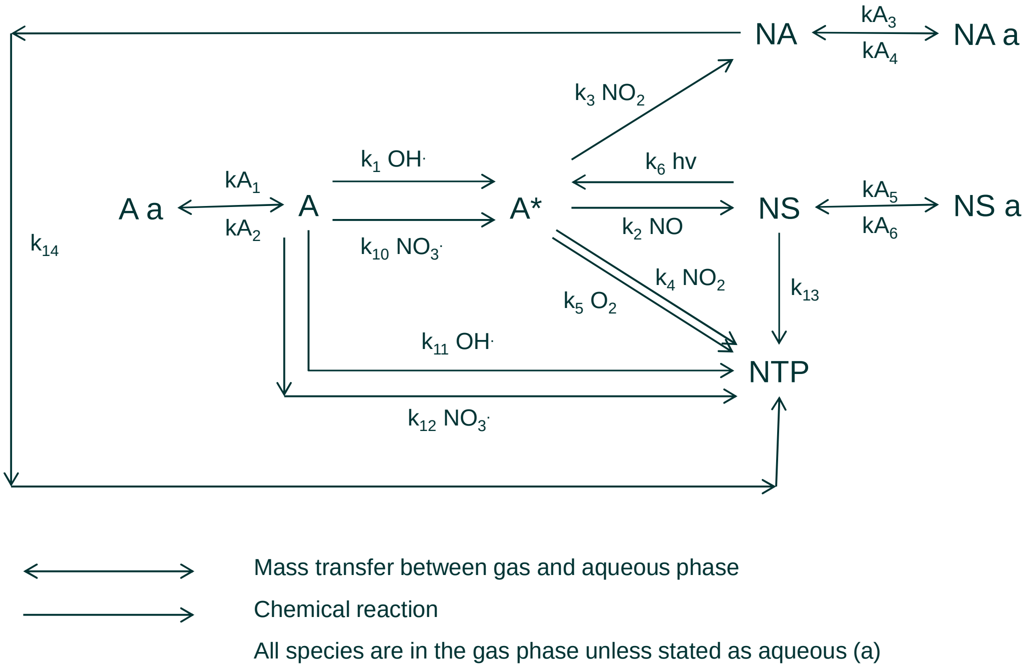
The additional chemical and physical processes to be evaluated during Phase 2 were:

- Inclusion of amine activation reactions involving reactive species in addition to $OH^{\cdot}$, such as $Cl^{\cdot}$, $NO_3^{\cdot}$, etc.. Examination of the research results showed that initiation reactions with $Cl^{\cdot}$ (and other halide radicals) were not significant, so these were not included in the Phase 2 chemistry scheme.
- Inclusion of photochemical reactions which will be slower in winter and may be absent at night.

- Inclusion of equilibria processes that transfer chemical species to a condensed aqueous phase.
- Inclusion of reactions in the aqueous phase. Examination of the research results showed that such reactions were not significant, so these reactions were not included in the Phase 2 chemistry scheme.

Figure 3.1 shows the general scheme for atmospheric amine chemistry that was incorporated into CALPUFF as part of the Phase 2 activities.

Figure 3.1 Phase 2 Generalised Amine Chemistry Scheme



In Figure 3.1:

- The emitted amine is represented by A. This may be a primary or secondary amine of any molecular mass (DNV has not yet reviewed the chemistry of tertiary amines).
- A* is the reactive intermediate formed by initial reaction of amine with the free radicals OH or NO_3.
- NA is the nitramine daughter of A.
- NS is the nitrosamine daughter of A.
- NTP is any product of amine or amine daughter product reaction that is not NA or NS.
- Any species followed by “a” is in the condensed aqueous phase.
- The symbol “hv” represents light, so k_6 is a photochemical reaction that proceeds faster when the light intensity increases.

- The radicals OH and NO_3 plus the molecules NO, NO_2 and O_2 are collectively called counter-species. They are the species that react with amine and its daughter species. The concentration of the counter species can vary with location (NO and NO_2), with light intensity (OH) or with day or night (NO_3). In the Phase 2 model the calculation of OH concentration was separated from the OH concentration model that pre-existed in CALPUFF. This provided greater control over this critical parameter.
- The scheme contains 11 chemical transformation rate constants plus 3 pairs of physical equilibria rate constants which control the gas-to-liquid phase equilibria processes for the main species of interest (A, NA and NS).

Some of the reactions shown in Figure 3.1 were included only to provide additional modelling flexibility for the future. Any of the steps can be turned off by setting the appropriate rate constant to zero.

3.3 Implementation and Validation of the Amine Chemistry Scheme

The amine chemistry scheme shown in Figure 3.1 can be represented by a system of 8 ordinary differential equations in which the variables are the concentrations of the species of interest. In order to retain the most flexible implementation possible, numerical methods were selected as the most appropriate way of solving that system of equations within the CALPUFF dispersion model.

The objective of the modified CALPUFF model is to perform both complex dispersion calculations and complex chemistry calculations simultaneously. This presents particular problems for the validation of the modified model, since the model results depend on many input variables. Whilst it may be relatively easy to develop a modified model that appears to work for specific inputs, it is not easy to demonstrate that the modified model is correct in general.

It is not usually practicable or efficient to validate a model amendment by line-by-line code verification. Instead, DNV’s approach to model development and validation was to separate the dispersion processes from the chemistry processes and to validate them separately. These validated processes were then combined together and final verification checks were performed. The model development and validation process used is summarised in Table 3.1 and is described in detail in the Phase 2 report /3/.

Table 3.1 Overview of Model Development and Validation Process

Stage	Description	Comments
MathCad Box Model of chemical and equilibrium processes. Differential equations solved numerically by several different methods.	This evaluates the effect of the Phase 2 chemical scheme using mostly constant variables (no dependence on time of day, season of year, location) and no dispersion processes.	Enabled DNV to evaluate the most robust numerical method for solving the differential equations that represent the chemical scheme.
Analytical Box Model. Reduced set of differential equations solved analytically.	This evaluates a sub-set of the Phase 2 chemical scheme using mostly constant values and no dispersion processes as described for the MathCad Box Model.	Results verified against MathCad Box Model and shown to be consistent.
FORTRAN Box Model of chemical and equilibrium processes. Differential equations solved numerically using the best numerical method selected from the work with MathCad.	Numerical differential equation solver code implemented in FORTRAN. This was written to mimic the MathCad Box Model solutions exactly.	Results verified against the MathCad Box Model and the Analytical Box Model. The results agree both quantitatively and qualitatively (trends are consistent with expectations). This agreement validates the solution of the chemical scheme differential equations that represent the Phase 2 chemical scheme (Figure 3.1) in the modified CALPUFF model.
Modified CALPUFF Model combines existing dispersion calculation with the FORTRAN Box Model of the chemical processes required by the Phase 2 chemical scheme (Figure 3.1).	The FORTRAN Box Model was modified into a FORTRAN subroutine which was then called by CALPUFF. This step completes the required chemistry capability in the modified CALPUFF model.	The CALPUFF dispersion calculations are already validated. The chemistry calculations are validated by the above checking process.

As a final check of the modified CALPUFF model, DNV included a tracer species in the emission profile for each case calculation. The tracer species has identical physical properties to the emitted amine, but does not undergo chemical reactions. This enables the following comparisons to be performed:

- The effect of dispersion without chemistry is evaluated from the concentration of the tracer.
- The effect of dispersion and chemistry together is evaluated from the concentration of amine and its degradation products (NS, NA, NTP and A*).
- An *estimate* of the effect of chemistry without dispersion can be obtained by calculating the extent of dilution from the tracer species and so the concentration of other species without dispersion can also be estimated.

These final comparisons enabled DNV to demonstrate that the modified CALPUFF model is capable of generating the complex qualitative trends that were expected by examination of the reaction scheme (Figure 3.1).

3.4 Key Results and Conclusions from Phase 2

The detailed results are presented and discussed in the Phase 2 report /3/.

DNV demonstrated that the modified CALPUFF model is capable of meeting the objectives of CCM Project through the successful implementation of a complex gas phase amine chemistry scheme and gas-liquid equilibria processes /3/. Chemistry in the aqueous phase could be easily added to this model if this is found to be justified by research results.

Case study results showed that under worst case conditions the environmental quality criterion set by NIPH could be exceeded, but compliance was shown for 2 out of the 3 case studies performed. These case studies retain a number of conservative assumptions as discussed in the Phase 2 report /3/. More work should be performed to refine the input parameters to be used in the modelling process.

Detailed examination of the results showed that dispersion process are generally faster than chemical reaction processes (the amine concentration is always close to the concentration of the tracer) and transfer of soluble amine into the aqueous phase reduces the peak concentrations of nitramine and nitrosamine observed.

A direct result of the faster relative rate of dispersion compared to the rate of chemical reaction is the rapid dilution of emitted amine and the consequent decrease in the reaction rates result in only small proportions of the source amine being converted to harmful products. The model predicts the ground level yield of harmful products as a fraction of the emitted amine present varies by location but the maximum yield is 2.2% (Case A) or 9.9% (Case B).

4 COMPARISON OF PHASE 1 AND PHASE 2 ACTIVITIES

The model developed during Phase 1 was primarily a demonstration model, designed to show the usefulness of the CALPUFF modelling system for the purpose proposed and the contractors' ability to carry out this task. The amine chemistry was modelled as a one-step reaction, which does not correctly represent the actual chemistry. It also fails to represent the counter species NO and NO_2 that take part in the second step of the chemistry. Nevertheless, Phase 1 demonstrated that CALPUFF could be adapted to represent a simplified version of the amine chemistry required.

Phase 2 was a more determined model development effort designed to represent the true chemistry in a realistic manner. The multi-step nature of the reactions leading from the source amine to harmful products was accurately reproduced in the modelling and the counter species NO, NO_2 and OH· were modelled in a way that could be controlled by the modeller without further re-programming. In addition, phase transfers between gaseous and aqueous phases were included into this version of the model, with the assumption of the presence of an abundance of water which DNV considers to be fully justified by the local environment and the nature of the emitted gas stream.

The changes between the two versions of the model are too extensive to allow comparison and explanation of the differences in results in a quantitative way, but rather the two phases of work can be regarded as essential steps in the model building process. Nevertheless, summary results of each of the four case studies performed over the two phases of Call-Off 2 are presented in Table 4.1, below. The result is quoted in terms of the peak of the sum of all the harmful species (gaseous or aqueous) as a proportion of the environmental acceptance criterion of $0.3 ng/m^3$.

Table 4.1 Summary of Case Study results for Phases 1 and 2

	Case Study	Result relative to $0.3 ng/m^3$
Phase 1	Phase 1 Base Case	c.17%
Phase 2	Case00	21%
	Case A	14%
	Case B	162%

The case studies of Phase 2 were chosen according to the following very broad principles. The reports /1/, /2/ and /3/ should be consulted for details.

- Case 00: A case study designed to mimic the base case of Phase 1.
- Case A: An optimistic case study in terms of solubility, choice of source amine and other factors.
- Case B: A pessimistic case study in terms of solubility, choice of source amine and other factors.

It is important to emphasise that the results shown in Table 4.1 are peak values. That is, the result is quoted for the geographical position at which the modelled concentrations of harmful compounds were at their greatest. The concentrations at most locations in the study area were much lower than those shown above.

Because the chemistry is represented in Phase 2 in a way that is very much more aligned with the genuine chemistry that takes place, confidence in the results of the Phase 2 model should be greater than in the Phase 1 results.

5 SUMMARY AND RECOMMENDATIONS

A general amine chemistry capability has been successfully added to the CALPUFF atmospheric dispersion modelling system. It performs chemical reactions according to the general scheme shown in Figure 3.1. DNV believe that they have demonstrated the utility of the model and have validated the modified CALPUFF model.

All reaction rates shown in this scheme are editable by the user as are the constants used in the calculation of counter species concentrations. Modifications to the way in which those calculations are made are now relatively easy to make.

The key recommendations from the study are as follows:

- The model validation process should be discussed with the regulator to ensure that results from the model will be acceptable in an assessment of environmental impacts.
- The model should be used to evaluate the impacts to the environment for real process emission parameters.
- The model results could be compared with ambient measurements of pollutant concentrations (environmental monitoring results) if available.

6 REFERENCES, ACRONYMS AND ABBREVIATIONS

6.1 References

/1/	DNV Call-Off 01, “Modelling for Atmospheric Dispersion of Components from Post-Combustion Amine-Based CO_2 Capture”, 5th October 2010.
/2/	DNV Call-Off 02, Phase 1 Report, “Atmospheric Chemistry Modelling of Components from Post-Combustion Amine-Based CO_2 Capture”, 5th October 2011.
/3/	DNV Call-Off 02, Phase 2 Report, “Atmospheric Chemistry Modelling of Components from Post-Combustion Amine-Based CO_2 Capture”, 25th May 2012.

6.2 Acronyms and Abbreviations

3D	3-Dimension(al)
A	Amine
CCM	CO_2 Capture Mongstad
DMA	Dimethylamine
DNV	Det Norske Veritas Limited
LAM	Local Area Model
MEA	Monoethanolamine
MMA	Monomethylamine
NA	Nitramine

NDMA	N-nitrosodimethlyamine
NILU	Norwegian Institute for Air Research
NIPH	Norwegian Institute of Public Health
NS	Nitrosamine
NTP	Non-Toxic products (mainly imine initially)

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