

Dear Mr Eriksen

**Full-scale carbon capture from Mongstad**

I refer to the recent discussions concerning the planning of full-scale CO<sub>2</sub> capture plant at Mongstad.

Please find enclosed a memo concerning amine-based CO<sub>2</sub> capture. This updates the assessments made in our memo of 27 September 2010. The evaluations contained in the memo have been provided by Statoil's research and development unit.

We are at your service should you have any questions about or comments on the attached memo.

Yours sincerely

Knut Georgsen  
Vice president

## Amine-based CO<sub>2</sub> capture – risk related to health effects – updated status February 2011

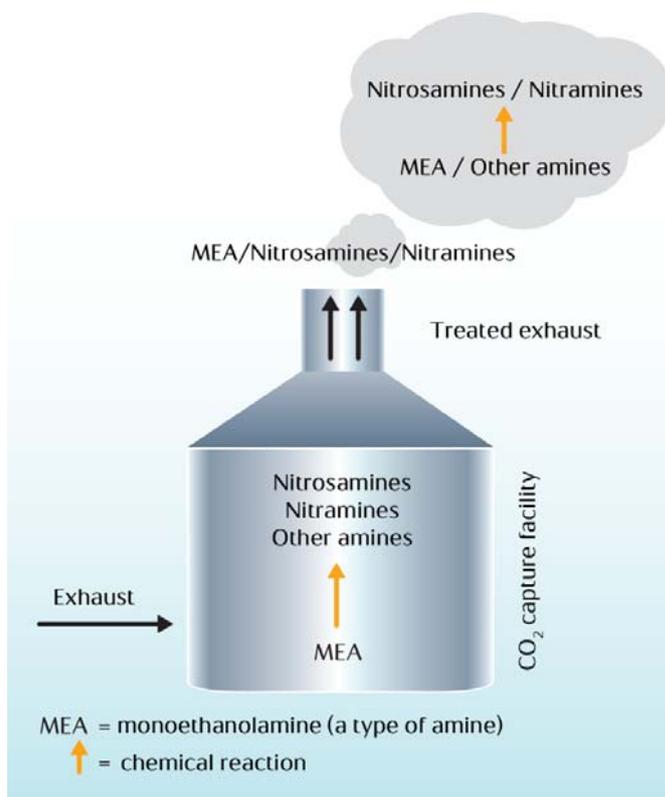
### 1 Purpose

The purpose of this memo is to provide an update concerning the risk related to health effects from amine-based CO<sub>2</sub> capture. It is an update of the memo of 27 September 2010. The update is based on knowledge acquired since September, from current R&D projects. Assessments in this memo have been provided by Statoil's research and development entity (TPD R&D).

### 2 Background

The CO<sub>2</sub> master plan for Mongstad (the Masterplan) delivered in February 2009 revealed knowledge gaps relating to the possible effects on and consequences for human health and the environment from emissions to the air of absorption chemicals and/or reaction or decomposition products. A study led by the Norwegian Institute for Air Research (NILU) identified a *theoretical* possibility for the formation of a number of reaction products, including nitrosamines and nitramines. A number of substances in this group can act as a carcinogen, depending on exposure level and duration.

The following issues have been identified, and the figure below provides an example of nitrosamine and /or nitramine formation based on the use of monoethanolamine (MEA).



MEA = monoethanolamine (a type of amine)

- MEA (or other amines) are converted during the process to nitrosamines or nitramines.
- MEA (or other amines) are converted during the process to other amines.
- Unreacted MEA (or other amines) are released together with the processed flue gases.
- Unreacted MEA (or other amines) are converted to nitrosamines or nitramines in the atmosphere after emission.
- Other amines from the process are converted to nitrosamines or nitramines in the atmosphere after emission.

### 3 R&D results

Following the work on the master plan, a number of R&D projects were initiated to learn more about the risk related to health and environmental effects. This R&D work has been based on the absorption chemical MEA. The R&D/test results (based on studies in the atmospheric gas phase) so far both confirm and disprove the theoretical studies.

- Nitrosamines are formed in the capture process through the reaction of nitrogen oxides (NO<sub>x</sub>) in the flue gases with MEA (confirms the theoretical study).
- Nitrosamines are not formed through conversion of MEA in the atmosphere (disproves the theoretical study).
- Nitramines are formed through conversion of unreacted MEA in the atmosphere (confirms the theoretical study).
- It has also been established that MEA can be converted during the absorption process to other types of amines, which can in turn react to nitrosamines and nitramines in the atmosphere.

The three first results were presented to the International Energy Agency's (IEA) greenhouse gas (GHG) seminar in February 2010, while the final result derives from tests completed in June 2010 and presented to the IEA's GHG conference in September 2010. The results are based on testing at the European PhotoReactor (EUPHORE) in Valencia, input from Aker Clean Carbon (ACC) to the emission permit application for the Technology Centre Mongstad (TCM), and experiments at Statoil's research centre.

Emission measurements were carried out in 2009 by NILU on ACC's mobile test rig in Risavika, where relatively large quantities of dimethylamines were identified. In addition, nitrosamines were identified from testing in Longannet. These findings have formed the basis for the TCM's emission permit application.

In a meeting with Statoil, ACC reported that the measurements it used as a basis for the TCM application have subsequently proved to be incorrect. Dimethylamine was not identified in later tests with MEA at Longannet and Tiller. On these grounds, ACC has provided updated emission information as the basis for the TCM's permit application.

Further experiments were conducted at EUPHORE during the second half of 2010. The purpose was to clarify atmospheric reactions for amines, nitrosamines and nitramines, with the focus on conversion and decomposition. This was intended to provide further clarification of the significance of the methylamine, dimethylamine and trimethylamine conversion products formed from the use of MEA in the capture process. The experiments were conducted in daylight and a dry atmosphere, and the results show the following outcomes for an atmosphere similar to that found in the Mongstad area.

- Nitrosamines
  - the life time of the nitrosamines is less than 1 hour in daylight
  - methylamine does not convert to nitrosamines
  - given the life time /decomposition, conversion from dimethylamine is less than 0.6%
  - given the life time /decomposition, conversion from trimethylamine is less than 1.1%

Because of the rapid decomposition, the formation and decomposition processes will work against each other. This is taken into account in the estimates above.

- Nitramines
  - the life time of nitroamines is typically three days
  - conversion from methylamine is less than 0.4%
  - conversion from dimethylamine is less than 2.5%
  - conversion from trimethylamine is less than 5%

Because of the relatively long life time of nitramines, their formation and decomposition processes will be more complex.

The significance of reactions with chlorine and of atmospheric reactions at night and in humid atmospheres remains unclear.

A literature study conducted by NILU on behalf of the CO<sub>2</sub> Capture Mongstad (CCM) project shows that very little information is available on nitramines and possible human health effects. None of the compounds are classified by the EU or mentioned in the US Environmental Protection Agency's integrated risk information system (EPA Iris), and no Norwegian tolerance limits have been established. Where a carcinogenic threat is concerned, data were only found for two nitramines which were both considered to be carcinogens. No data on possible human health effects were found for the other nitramines.

#### **4 Implications for the risk picture**

The emission permit application for the TCM represents the first quantitative risk assessment for a CO<sub>2</sub> capture plant based on amine technology which takes account of nitrosamine formation. It was submitted to the Norwegian Climate and Pollution Agency (Klif) in September 2010. The precautionary principle has been applied, and conservative estimates are used where knowledge is lacking.

The following conservative estimates were used in the dispersal and risk assessments conducted by NILU for the TCM:

- Instantaneous 10 % nitrosamine formation from the amines with nitrosamine-forming potential.
- No decomposition of nitrosamines in the atmosphere or in water.
- All nitrosamines end up in drinking water.
- Predicted tolerance limit for only one nitrosamine was used (N-Nitrosodimethylamine).

Since no Norwegian tolerance limits have been established for nitrosamines, the US figures (US EPA/Iris) have been applied together with methodology from the EU's regulation on Registration, Evaluation, Authorisation and restriction of Chemicals (Reach). The EPA's recommended water quality criterion has been utilised. No corresponding air quality criterion is specified by the EPA, so the REACH guidance of 10<sup>-6</sup> (one cancer case per one million people) as a tolerable level of risk for cancer in the general population has been applied. On the basis of this level of risk, the EPA/Iris has specified concentration limits in the air. The following predicted tolerance limits are accordingly used in the TCM's emission permit application:

- 0.07 ng/m<sup>3</sup> for nitrosamines in air.
- 0.7 ng/l for nitrosamines in drinking water.

The knowledge gained from the latest experiments in Valencia indicates that the first two assumptions are no longer valid. The life time of nitrosamines in the atmosphere is short – less than one hour. When account is taken of competing formation and decomposition processes, the experiments show the annual average conversion of nitrosamines in the atmosphere from dimethylamines and trimethylamines to be 0.6% and 1.1% respectively. This represents a substantial reduction in relation to the figures applied in the TCM's emission permit application, and means that nitrosamines in the atmosphere represent a smaller risk than assumed in the September memo. However, uncertainty persists about the conversion and life time of nitrosamines in reactions with chlorine, at night and/or in humid atmospheres.

Due to lack of information nitramines were not evaluated as thoroughly as nitrosamines in the emission permit application for the TCM. It was assumed that nitrosamines would be the dimensioning factor in relation to health and environmental effects.

However, the information from the latest experiments in Valencia shows that nitramines form to a greater extent than originally thought and are relatively stable – with a typical life time of three days. More accordingly needs to be learnt about nitramines, particularly in terms of formation, life time, and human health and environmental effects.

It is also crucial to establish what quantities of methylamines, dimethylamines and trimethylamines are released from the process based on an amine solvent, since these compounds are the precursors for the formation of nitrosamines and nitramines in the atmosphere.

Since the EUPHORE experiments address *atmospheric reactions* for amines, nitrosamines and nitramines, with the focus on conversion and decomposition, separate studies have been launched to clarify decomposition/conversion of nitrosamines and nitramines in *water*. The results will become available during 2011. Dispersal calculations also need to be performed with design parameters and emission estimates for a full-scale plant.

## 5 Summary

When the Masterplan was drawn up, theoretical calculations existed on the formation of nitrosamines/nitramines. R&D and testing have showed that these compounds are indeed formed.

The Masterplan identified the lack of information about health and environmental effects as the biggest risk in applying amine technology. At the same time, it was assumed that a substantial programme would improve knowledge in order to clarify the risk and methods for reducing it. In addition, requirements for disclosing the composition of amine solutions and for treatment methods for reducing residual emissions would document that amine technology was applicable. Combined with an assessment of the maturity of alternative technologies, this was the background for recommending a project focused on amine-based technology.

Although the latest experiments at EUPHORE have yielded positive results for nitrosamines formed in the atmosphere, uncertainty persists about the health and environmental effects of emissions from a full-scale plant related to:

- Human health and environmental effects for nitramines – lack of information on health effects and life time in the environment
- Information on the quantities of nitramines, methylamine, dimethylamine and trimethylamine released
- Formation mechanisms and reaction rates with chlorine, at night and in humid atmosphere for both nitrosamines and nitramines
- Decomposition of nitrosamines and nitramines in water
- Analysis and measurement methods.

Statoil continues to take the view that the uncertainty related to the human health effects of emissions from a full-scale plant, and thereby the risk that amine technology will not be applicable, is greater today than it was in 2009.