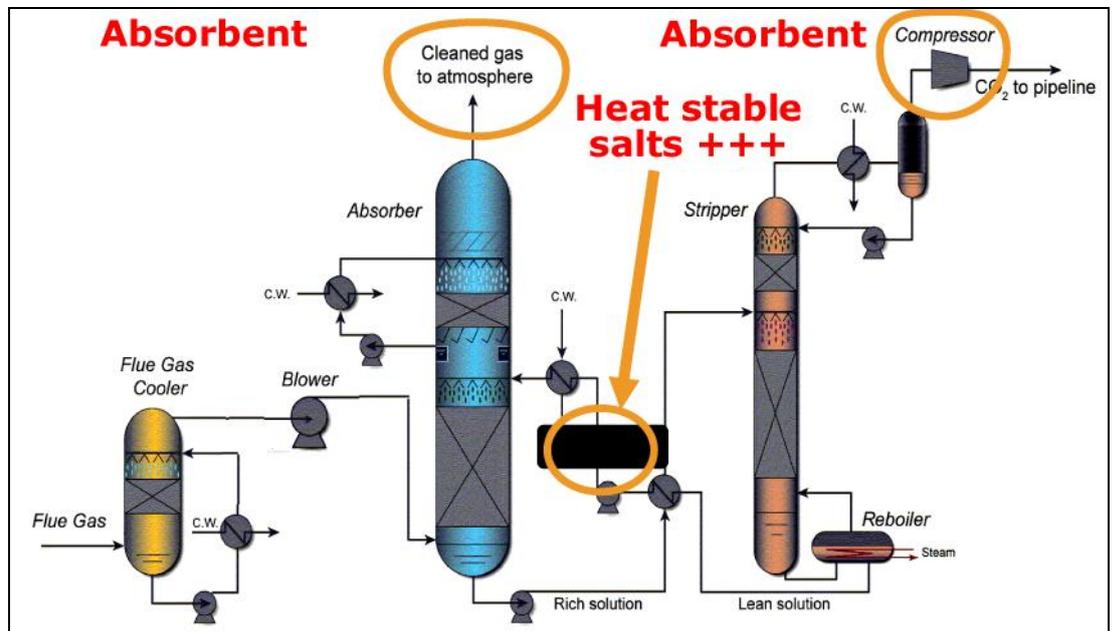


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Environmental impact of amines from CO₂ capture

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Preface

This report is based on the work that was done in connection to the expert meeting held at NILU on the 18 October 2007. The meeting came about after discussions between NILU and SFT. Both were concerned that the emissions of CO₂ capture using amines could be harmful to the environment. After a quick investigation it was found that the knowledge about these subjects were quite limited. SFT and NILU therefore sponsored a process to look into these subjects of which this report is one of the outputs.

This work and knowledge would not have been produced without the kind help and contributions from the participants and a special thanks to the persons contributing in making the presentations.

Contents

	Page
Preface	1
Summary	5
1 Introduction	9
2 Objectives of the report	9
3 The process.....	10
4 Mechanisms for deposition of amines to the environment	10
5 Toxicity of amines in the environment	11
5.1 MEA.....	11
5.2 AMP	11
5.3 Piperazine.....	11
6 Environmental evaluations of amines as a group.....	12
7 Degradation products that are likely.....	13
8 Environmental evaluation of known primary amines used for CO₂ capture.....	13
9 Reaction products from the amine process.....	14
10 Which amines have environmental effects.....	15
11 Additives to prevent corrosion and to stabilize the primary amine.	15
12 What are the main investigations necessary for an application of the use of amines.....	16
Appendix A AGENDA	21
Appendix B List of participants - Expert meeting at NILU 18/10-2007.....	41
Appendix C Description of the CO₂ capture problem and possible solutions.....	45

Summary

CO₂ capture and storage is at present a highly important issue for the Norwegian society.

There are several ways where CO₂ can be isolated and stored. There are also several ways of not producing CO₂ while producing energy.

The technology that is closest to being operational is the use of amines for CO₂ capture. The development and subsequent utilisation of this technology is considered a national effort. Furthermore, successful development of this technology is certainly also interesting from a commercial point of view. SFT and NILU have arranged an expert meeting aiming to focus on amine emissions from CO₂ capture. The presentations and summaries from the presentations are given in Appendix A.

NILU was asked by SFT to write this report from NILUs knowledge base, the content of the presentations and the discussions at the expert meeting.

NILU was also asked to give a list of activities and documentation that in NILUs point of view is important for the environmental authorities' evaluation of emission from amine based CO₂ capture plant.

For emissions to air NILU is competent to propose an activity list. For effects the suggestions must be seen as indicative and organizations that are specialized in this field should be contacted.

It is historically known that different emissions to air have caused severe environmental effects that was not foreseen and that needed to be attended to afterwards. It is therefore strongly recommended that the possible effects of the emissions are investigated either to rule them out or to redesign the process so that environmental effects are minimized.

SFT asked NILU to comment on the following topics.

- Mechanisms for deposition of amines to the environment
- Toxicity of amines in the environment
- Environmental evaluations of amines as a group
- Degradation products that are likely
- Environmental evaluation of known primary amines used for CO₂ capture
- Reaction products from the Amine process
- Which amines have environmental effects
- What are the main investigations necessary for an application of the use of amines

In Addition NILU wanted to evaluate atmospheric photochemistry, the additives for stabilizing the primary amine and the additives used to reducing corrosion.

The knowledge of emissions to air and effects of CO₂ capture with the use of amines are limited. This is most evident in the description of emissions to air. The

emissions of the primary amine are more or less known (1-5 ppm). This is known from other processes such as NO_x reduction using SCR. There are several candidates for the primary amine that can be used in the process. The different candidates will have different chemical characteristics and therefore different degradation products and impact on atmospheric photochemistry and the environment.

The fact that emissions at this stage is not well known, means that the evaluation of concentrations, deposition, load on the environment, effects of this load and the toxicity must be general. Some logical framework is put forward to be able to put limits for emissions through backwards dispersion calculations.

Most of the substances where information on effects exist is in connection to human health, this is because amines are widely used in medicine and working conditions.

It is known that amines are caustic, corrosive and smelling. It is also known that amines is a very broad group of components, some of the amines will be very reactive and therefore have the potential of causing acute effects some are less reactive and will have possibilities of causing long term effects. Acute effects are generally evaluated through short term concentrations or depositions, and the long term effects through annual averages and annual deposition loads.

Deposition of amines will be, as all air pollution, deposited through absorption of the gasses and particles on surfaces and absorption by vegetation and through precipitation. The levels of concentrations and deposition is strongly dependent on dispersion conditions, precipitation and chemical transformation.

There are different groups of amines that are known to have severe effects and that needs to be given special attention. These are nitrosamines and aromatic amines.

Emissions of amines will also contribute to the acidification of surface water and fertilization of the biota along the same lines as emissions of NO_x and NH₃. If ending up in surface water the effects on acidification will be the same as for deposition of sulphur.

There are two main degradation processes that will be active. This is the thermal oxidation degradation while the substances are within the plant and photochemical oxidation degradation after the emissions have left the chimney. The degradation processes will be dependent on the flue gas that is cleaned. The more complex the flue gases the more possibilities for different degradation products. It is known that there will be more than 50 different substances that are produced within the process. Some of these will probably be cleaned and taken out as liquid or solid waste, follow the CO₂ stream for deposition and be emitted to air. After emission these products will enter into the photochemical processes and additional components will be formed.

The additives that might be used in the process to stabilize the primary amine and prevent corrosion in the plant have a potential of creating environmental effects

and cause emissions among other things of heavy metals. It is therefore important to put emphasis on these additives.

NILU emphasises that an evaluation of the potential impact for health and the environment from a CO₂ capture plant based on amines should be mandatory. An evaluation should at least look into a theoretical exercise for establishing possible effects of the different types and quantities of amine emissions, and give a description of the different sources and sinks of the emissions. A strategy for measuring amine emissions and a surveillance network for evaluation of the environmental impacts of the emissions should be established on capture plants based on amine. The need for collecting emission data and knowledge of health and environmental impacts of these emissions should be a requirement in the emission permit to the capture plants.

Environmental impact of amines from CO₂ capture

1 Introduction

CO₂ capture and deposition is at present a highly important issue for the Norwegian society.

There are several ways where CO₂ can be isolated and deposited. There are also several ways of not producing CO₂ while producing energy.

The technology that are closest to being operational for CO₂ capture is the use of amines. The development and subsequent utilisation of this technology is considered a national effort for reducing Norwegian emissions of climate gases. Furthermore, successful development of this technology is also interesting from a commercial point of view. Several methods exist for CO₂ capture, amine capture is just one of these. SFT and NILU have arranged an expert meeting aiming at effects on the environment from amine emissions from CO₂ capture. The environmental effects of amines remain largely unknown.

To understand and quantify the environmental effects of using amines to capture CO₂ it is necessary to ensure that negative effects can be taken into consideration in the development of the capture technology. It is important for an environmental project not to cause unacceptable effects on the environment.

From the technological side the process must be designed in such a way that the maintenance and running costs are minimal. This means that the amines must be stable and reusable. There must also be a corrosion control in the process that can be obtained by additives. Additives are also used for stabilizing the primary amine. The energy consumption in running the process must be minimized.

From an environmental point of view the emissions should be non toxic and degrade into something that does not have an environmental effect.

This report is the responsibility of NILU and the views put forward builds on NILUs knowledge base, the expert meeting and the interpretation of discussions from the meeting.

2 Objectives of the report

This report shall focus on defining the knowledge base, detecting lack of knowledge and give advice on what an application for emissions to air of amines should contain. It should also give an indication on which knowledge bases that should or can be contacted.

The key bullets that will be included in the report are listed below:

- Mechanisms for deposition of amines to the environment
- Toxicity of amines in the environment
- Environmental evaluations of amines as a group
- Degradation products that are likely
- Environmental evaluation of known primary amines used for CO₂ capture
- Reaction products from the amine process
- Which amines have environmental effects
- What are the main investigations necessary for an application of the use of amines

3 The process

CO₂ capture with the use of amines can be very different with respect to emissions to air. The amine used for CO₂ capture will vary and have different possibilities of degradation and chemical reactions after the flue gas is emitted. The different amines will also probably need different additives to prevent corrosion and degradation.

Emissions to air will also be dependent on the content of other substances in the flue gas that is cleaned for CO₂. If the flue gas relatively clean the possibilities for reactions are smaller than if the flue gas contains more reactive gasses. It will also be dependent on choice of technology, the amount of flue gas that is cleaned, and to what concentration the gas is cleaned.

Emissions to air will in other words probably depend on type of process that the origin of the flue gas (coal, oil or gas fired power plant, refineries etc.), cleaning device used upfront of the CO₂ capture. The emissions will also depend on the level of capture (the emissions will be different for a 50% capture than for a 99% capture of CO₂). The emissions to air will also be strongly dependent on the primary amine and additives that are required. These emissions will have different possibilities of chemical reactions in the atmosphere after emission. This means that the toxicity of the emissions from this type of processes will be different and will therefore have different effects on the environment.

4 Mechanisms for deposition of amines to the environment

In general the deposition of gasses and particles are deposited to the environment through uptake of gasses by surfaces and through absorption of the gas or the particle in raindrops. Large particles can also be deposited through settling.

The CO₂ capture with the use of amines does not produce large particles, but locally, droplets have the potential for falling out of the plume because generally the plume will have high water vapor content and amines can cause the droplets from the plant to grow to a size that will have a settling velocity. The potential is highest close to the source for this effect. For the fallout of droplets the maximum will occur up to some hundred meters from the stack depending on local meteorology.

The amines and the additives are in general well solvable in water and the deposition through precipitation is believed to be the most important process on the regional scale. The typical maximum for deposition from a plant will be 20-100 km from the source.

5 Toxicity of amines in the environment

There are two main types of effects that have to be considered; effects occurring due to accumulation in the environment and the acute effects for human health and the environment as such. The acute effects are mainly caused by levels of concentrations in the atmosphere, gasses and particles are absorbed through the respiratory system or in the environment as such. The more chronic effects are mainly caused through deposition and long term concentrations.

There will in general be different substances that are causing the acute and chronic effects. The acute effects are in general caused by substances that react fast and are therefore effectively absorbed in the respiratory system. The chronic effects are caused by stable components that do not react easily with other substances and therefore accumulates in the environment.

From the following chapters it is shown that there are many possibilities of substances that have emissions to air. It is therefore here given only a brief description of the main known primary amines and for other substances a reference to the internet where information on toxicity is given. The information originates on the following web sites:

- <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>

Some known candidates of primary amines:

- MEA
- AMP
- Piperazine

5.1 MEA

MEA is also a main component in human cell walls and is therefore believed not to be toxic to humans. However vapour-phase MEA will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals and conflictive substances such as nitrosamines and amides can be formed.

5.2 AMP

There is less information on AMP than the other two amines mentioned here. The information is mainly from work space directives. It is known to cause liver cancer.

5.3 Piperazine

Environmental Fate/Exposure Summary:

Piperazine's production and use as an anthelmintic in human and veterinary medicine and as an intermediate for dyes, corrosion inhibitors, rubber vulcanization accelerators, insecticides, and surfactants may result in its release to the environment through various waste streams. If released to air, a vapour pressure of 0.16 mm Hg at 20 deg C indicates **piperazine** will exist solely as a vapour in the atmosphere. Vapour-phase **piperazine** will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 2.3 hours. If released to soil, **piperazine** is expected to have very high mobility **and** will exist primarily as a cation in the environment and cations generally adsorb more strongly to soils containing organic carbon and clay than their neutral counterparts. **Piperazine** may biodegrade in soil or water based on greater than 51% biodegradation measured after 28 days in an artificial river water

Vapour-phase **piperazine** is degraded in the atmosphere by reaction with photochemically produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 2.3 hours

Atmospheric Concentrations:

An ambient **piperazine** concentration of 10-60 ng/m³ in air has been reported.

URBAN/SUBURBAN: The concentrations of **piperazine** measured in submicron aerosol (less than 1-2 µm) of Pasedina, California were 0.02, 0.02, 0.05, and 0.06 µg/m³ in 1985, 1986, 1987, and 1988, respectively. **Piperazine** was not detected in supermicron aerosol (greater than 1-2 µm) samples collected during 1985, 1986, or 1988. The concentration measured in supermicron aerosol during 1987 was 0.01 µg/m³.

6 Environmental evaluations of amines as a group

The amine group in a large group of chemical substances. Some are artificially produced and some are common in nature. Amines are an important group in the environment. For instance MEA is a major part of walls in human cells.

The variety of amines has different stability in the environment. Some of the components are extremely reactive and only occur under specific conditions and others are persistent. This means that they have different potential for effects in the environment. Some are toxic and others are nontoxic and the toxicity is of cause dependent on dose. The reactive components have the potential of causing acute effects, because the amine will be absorbed more rapidly in for instance the respiratory system. The persistent amines have the potential of accumulation in the environment and therefore the potential of causing long term effects. The effects will range from nontoxic to toxic depending on the specific amine.

When released to air the amines that are reactive will enter into the photochemistry of the atmosphere. The photochemistry in the atmosphere when amines are present is not well known and will depend on the amine or combination of amine present. We know that nitros-amines are extremely

dependent on sun light and that when the sun is up, the nitros-amines are gone and when the sun sets the nitros-amines are reformed.

All amines contain nitrogen. This means that in the end the components will be available for the environment as a fertilizer. In some parts (our) of the world fertilization of the environment can be a problem. Nitrogen in surface water contributes to acidification and growth of algae and vegetation in fresh water. Added nitrogen can cause a change in the population of vegetation so that vegetation that can take advantage of nitrogen will be dominating.

Amines have in general a strong and unpleasant smell. This will of course depend on the type of amine, but can impact the quality of life for the population.

The amines used in these types of activities are solvable in water.

7 Degradation products that are likely

There are two main pathways for the occurrence of degradation products in the atmosphere. These are degradation in the reactor and production by photochemical reactions in the atmosphere after emissions. These two pathways have extreme different conditions for chemical reactions and we know that degradation products form (more than 50 have been indicated by the industry). It is likely that not all these components will have emissions to air, but some are taken out in the regeneration process and some follow the CO₂ flow for deposition. The difference in concentrations, temperature, and time of residence in the process will be parameters that will influence the degradation process. The degradation will also depend on the process producing the flue gas that is cleaned. In general a more polluted flue gas will cause a faster degeneration and more possibilities for end products.

8 Environmental evaluation of known primary amines used for CO₂ capture

From Chapter 5 it is shown that there are three known amines that are candidates for CO₂ capture. These are MEA, AMP and piperazine. It is also known that there are other amines (DEA, MDEA, DIPA) or combinations of amines that are investigated for this use.

For MEA and piperazine quite a lot of information is known. The information dates mostly back 20-30 years and the knowledge base have probably changed since then. This means that information have to be updated. Piperazine has among other things been a substance in insecticides and from this information have a potential for environmental effects. Information on MEA was mainly for medical use and on AMP little information exists. The use of these amines has clearly changed since this information was updated. This means that other types of environments and other amounts are planned to be released into the environment and this have a potential for having adverse effects.

There are mainly three paths of emissions that are leaving a CO₂ capture plant. These are the residuals taken out of the process when recycling the amine, the CO₂ taken out of the flue gas and the emissions to air. The primary amines will in different concentrations follow all these mass flows. For emission to air the flue gas is expected to have a concentration of 1-5 ppm which indicates an emission of 100-200 ton of amine a year. This is considerable and larger than the NO_x and NH₃ emissions.

The amines when deposited will probably have a fertilizing effect on the vegetation and have a potential of contributing to the acidification of surface water.

The primary amines can also have a potential toxic effect.

Amine reaction products, rate of formation, removal in the recovery process determines the concentration in the scrubber solution. Volatility of the compounds then determines the emission to air. Many of the reaction products are harmless, such as the non-volatile amine salts. Focus should be on the amine carbamates and their possible degradation products, some of which may be volatile. The naming and describing of these compounds will be an important achievement.

9 Reaction products from the amine process

There are little known on reaction products in the process, little is also known of the fate after emission. There is also a considerable uncertainty connected to the degradation processes in the reactor itself. It is known that a variety of products are possible and will to some extent be present in the emissions to air.

A theoretical study will give the most important and common reaction paths that are possible and define the different species that can be produced. It is however important to point out that it is only chemical analysis of the emissions and in the atmosphere that will give proof of the reaction rates and to what extent the different substances are produced. MEA is probably only one of several amines used in the CO₂-capture process. To characterise and quantify the amine emissions is therefore presumably a very complicated task. As an example Bello and Idem (Ind. Eng. Chem. Res., 2005, 44, 945) identified more than 30 degradation products from MEA alone.

This means that there is a variety of substances that will be present in the emissions and that will be present in different concentrations and a dedicated programme should be put into action to map and verify these components. The main bulk of work will be to identify the components present and to determine the concentrations present to enable the discussion on toxicity.

10 Which amines have environmental effects

Because of the number of components that are in the amine group it is impossible to give the toxic effects of each amine. There are several databanks that provide on line information on this and the reader is encouraged to consult the following web service.

- <http://toxnet.nlm.nih.gov/cgi-bin/sis>

Amines are in general caustic and corrosive and will therefore have a potential effect on the environment.

Nitrosamines deserve special attention. Their formation would be expected to occur in the gas phase by reaction of amines with HONO, which is formed in the dark on surfaces, by reaction of NO and NO₂ and water:



Nitrosamines are potent liver and nasal carcinogen in rats. The possible health effects of the specific nitrosamines must be clarified. Inflammation and other diseases than cancer could be of relevance.

Aromatic amines are strongly linked to human bladder cancer, and they are also suggested to induce liver, colon, pancreatic, and lung tumors.

For more explanations on the toxicity the reader is referred to appendix A, where the different toxicity is discussed or to the above mentioned web site. The recommendations are that knowledge on effects of the amines needs updating and further study.

11 Additives to prevent corrosion and to stabilize the primary amine.

The process of CO₂ capture by the use of amines is a very corrosive process and it is common to use additives to the process that prevents corrosion. Historical use of such additives is proven to have environmental effects if released to the atmosphere. Parts of the additives are metals and some heavy metals. The additive will be dependent on the type of flue gas that is cleaned and the amine in use. There is little known on the specifics of these additives because they are mainly industrial secrets.

For minimization of the loss of primary amine additives are in use. As for the additive to prevent corrosion the additive will be designed for each primary amine. The use of additive is important to lower the use of primary amine and by this reduce the cost of running the process. The specific content of the additive is not known, but additives of this kind may cause environmental effects if released into the atmosphere.

Additives are also needed for controlling foam production.

12 What are the main investigations necessary for an application of the use of amines

As described in the previous chapters there are a number of potential problems connected to the industrial use of amines for CO₂ capture. The industrial process is well known because of the use in subtracting CO₂ from produced gas in the oil industry. These processes do however not have emissions to air. SFT asked NILU to put forward a list of activities that NILU think is important for the environmental authorities' evaluation of emission from amine based CO₂-capture plant.

First some comments:

The process of CO₂ capture is a new type of industrial activity, and therefore more cautions needs to be taken in permitting emissions to air. When things have not been done before, more uncertainty on the impact exists and therefore more uncertainty on unintended effects on the environment exists. The proposed main investigations necessary are therefore more including and less excluding because we think that it is necessary to investigate the possible effects to a level that they might be ruled out. This means that the Screening phase in the EIA process must be given more emphasis. We are sure that most of the investigations are going to show that the effects on the environment are small or negliable. But this have to be shown and some of the big environmental problems have come because of not investigating possible effects. It is also necessary to put up a good surveillance network dedicated to verify the levels of concentrations and possible effects.

At the moment there are very limited possibilities of measuring the effects and verifying the impact on concentration and deposition. Therefore the main work must be based on theoretical information. This information must at a later stage be verified through measurements.

There are four main topics that are important to verity. These are

- Emissions
- Dispersion/deposition
- Degradation
- Effects

The philosophy here is to investigate the different possibilities to such an extent that they can clearly be ruled out or that they need more thorough investigations.

Emissions

The amines used for CO₂ capture are mainly unknown. The emissions of the primary amine are important to determine. This have to be monitored after the plant is put into production. In addition to the primary amine it is necessary in our view to make a theoretical evaluation of degradation products, additives for stabilization of the primary amine and for the additive to prevent corrosion. Worst case studies should be conducted for the components that are probable. This means that the maximum emission that can be produced in the flue gas should be estimated.

The theoretical estimation above is necessary because there are no similar plants that already have done the measurements so that the emissions could be estimated.

Plants using amines in the process of CO₂-capture should carry out measurements of the amine contents in the flue gas. The emissions should first be screened for the type of components that are present through a semi quantitative method that identify the components present. Then the components with a minimum of mass present should be quantified in separate analysis.

This will secure that the theoretical evaluation is valid and reduce uncertainty in the evaluation of effects on the environment.

The emissions will depend on the cleaning of the flue gas before the CO₂ is captured. The CO₂ capture process will most likely also reduce the emissions of for example NH₃. Other components might also be reduced.

Dispersion/deposition

To evaluate effects on health and the environment as such it is important to know concentrations in air with different averaging times. In addition to this, deposition needs to be evaluated. Deposition is a combination of deposition by absorption on surfaces and uptake in plants and deposition through precipitation. This is evaluated through dispersion models. The dispersion modelling techniques are well known and standard solutions. Where emissions estimates are available these must be used. If these estimates are not available the dispersion model can be used backwards so that for substances that emission estimates are not known but levels of toxicity is known the models can estimate a maximum emission and still be on an acceptable level of concentration or deposition. This way the emission permit can restrict unknown emissions and state that they are not allowed emitting more than this from the plant. This level will depend on safety factors and it will be plant dependent.

Photochemical oxidative degradation

The emissions to air will undergo chemical reactions driven by radiation from the sun. This must be evaluated theoretically. It is known that amines are influencing the already existing photochemical equilibrium in the atmosphere. This have to be evaluated and the components that can form needs to be determined. It is also necessary to determine to what extent they are formed. If some of the substances are likely to produce levels that are close to where effects may occur the limiting substance in the emissions should be identified and restrictions put on this substance to limit the photochemical production.

Determination of acceptable levels

A study must be conducted for the possible components to determine to what level the substance is used in other connections and to what extent environmental effects might occur. There will most certainly be different levels of knowledge on the different substances. A level of acceptable concentrations or depositions

should be determined from the theoretical study of the estimated emissions and the study to determine the photochemically produced substances.

Effects

There are different effects that need to be studied. Traditionally this is connected to health, effects on vegetation, soil, surface water. Depending on the levels that are estimated in the dispersion activity contributions to the sea should also be considered. Amines are also connected to foul smell.

As mentioned above amines have a corrosive and caustic effect. The process of capturing CO₂ is based on reducing the surface tension on the water droplets so that CO₂ will move from the flue gas into the drops and through this be separated from the flue gas. The flue gas that is emitted into the atmosphere is normally saturated with water vapour. Normal water will condense into cloud droplets. This is a size that does not have a settling velocity. The size of the droplet is equilibrium between the water vapour pressure and the surface tension. It is necessary to determine if the reduction is large enough to produce raindrops with a settling velocity. This rain can be smelly and corrosive and is not pleasant to encounter.

The caustic effect of amines implies that there might be acute effects from both concentrations in air and from deposition. Therefore short term concentrations and the concentration that is possible in precipitation should be investigated for human health.

Long time exposure should also be evaluated because at least some of the amines can be carcinogenic.

For vegetation the same effects must be discussed. But in addition to this the effect of fertilization must be evaluated.

For soil the deposition of the different components needs to be evaluated with respect to accumulation and degradation.

For surface water the levels of concentrations must be investigated. The levels evaluated for accumulation in organisms etc.

The flux of mass into the sea from the emissions should be evaluated to investigate potential effects.

The emissions should be evaluated for contributions to climate change. This is to give input to the developers of the technology to avoid problems if the technology is widely used.

The consumption of energy used for the CO₂ capture and the emissions that comes from the production of this energy should be estimated.

To be able to quantify concentrations measuring techniques with a sufficient detection limit and uncertainty must be developed. The measurement techniques exists for some amines but for others not. It is also important to develop good

sampling techniques and a verification of the process from sampling to concentration. It can be argued that this should not be started before the necessity is there. The argument against this is that generic methods can be developed and that this is research and the outcome is not always predictable and to be able to measure is vital to keep pace.

Appendix A

AGENDA

Agenda: Ekspertmøte Amin rensing av CO₂

- 0830: Registrering
- 0900: Innledning med etablering av mål og mening for seminaret (NILU)
- 0920: Innledning om myndighetskrav, føringer (SFT)
- 0940: Gjennomgang av prosessen og hvilke aminer er i bruk(Statoil)
- 1010: Hva vet vi om utslipp hvor store er disse og i hvilken form er de(Statoil)
- 1020: Omvandlingsprosesser i reaktoren og miljø/helsefarlige biprodukter
- 1030: Diskusjoner rundt utslipp og prosess
- 1045: Kaffe
- 1100: Transport i atmosfæren (NILU)
 - Spredning
 - Avsetning
 - Utfelling
 - Lukt
 - korrosivitet.
- 1115: Omvandling i atmosfæren etter at de slipper ut.(UIO)
- 1130: Virkninger på:
 - helse(Folkehelsa)
 - vegetasjon(
 - ferskvann(NIVA)
- 1200: Diskusjoner på effekter
- 1230: Lunch
- 1330: Måleteknikker og prøvetaking i miljø(NILU)
- 1400: Tidsløp for forskjellige prosesser
 - Prosjekter i oljeindustrien
 - Lang og kort sikt
 - Tidsaspekter for myndighetenes side
- 1420: Plenumsdiskusjon der amin rensing av CO₂ er helhetlig plan, nasjonalt løft, hva er viktig med dette oppfølging.
- Prioritering for forskjellige deltagere.
- Organisering fremover.
- Roller for de forskjellige deltagerene.

Expert meeting content

The expert meeting was divided into three sections are summarized in the following bullet points:

- Process and emissions
- Possible environmental effects
- Conclusions and way forward

The first part describes the process, and what is known on emissions and degradation products that can form in the process. The second part is concerned with the environmental effects and how government are going to handle this. This includes reactions after the emissions have left the stack, effects of concentrations, deposition both from rainfall and absorption by plants. The effects on surface water, flora and fauna, and human health were included. Also the time frames of when the different projects have their deadlines and milestones where exposed. The third part was dedicated to different strategies for the future work and how this should be organized.

Background – the underlying chemistry for amine based CO₂ capture

This chapter aims to provide a brief description of the chemistry behind the amine based CO₂ capture process. Several amines may be used for CO₂ capture (Figure 1).

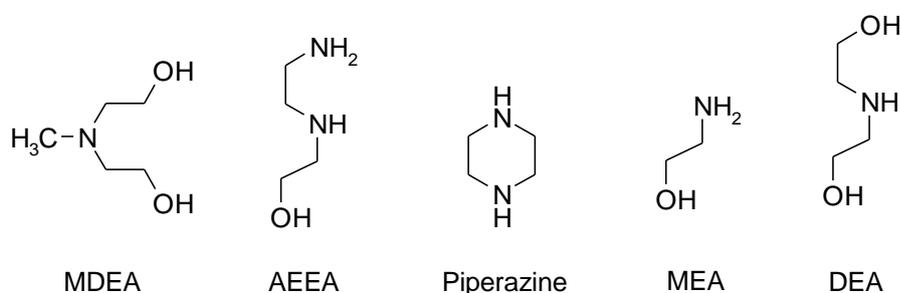


Figure 1: Some possible amines utilisable for CO₂ capture. MDEA; methyl diethanol amine, AEEA; aminoethyl ethanolamine, piperazine, MEA; mono-ethanolamine, DEA; di-ethanolamine.

The flue gas is guided through an aqueous solution containing amines, the amine then reacts with CO₂, forming a zwitterion (step 1, Figure 2). The zwitterions the transfers a proton to an un-ionised amine, forming the corresponding carbamate (step 2). The example utilises a secondary amine, tertiary amines may also be used for the same purpose.

Recycling is both environmentally and economically friendly, and the amines are recycled in the CO₂ capture (catch and release) process (Figure 2). Upon heating, the carbamate formed in step 2 (Figure 2) dissociates into the native amine and CO₂, and is available to capture a new CO₂ molecule. The released CO₂ is captured, stored, and eventually deposited.

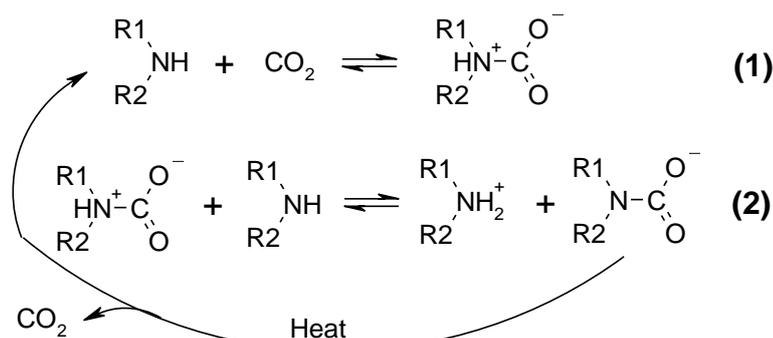


Figure 2. The chemistry behind amine based CO₂ capture.

However, the amines are not completely recycled, some is lost to the atmosphere. This loss of amines can be considerable and presumably an environmental concern, and is the major topic for the expert meeting.

Due to the poor water solubility of CO₂, an activator must also be added to the aqueous capture solution. The activators are also amines.

Summary of the presentations given at the meeting

This chapter is presented by giving a summary of the individual presentations given at the expert meeting, followed by a summary of the discussion that followed each presentation.

Introduction (Svein Knudsen, NILU)

Summary.

Amines for CO₂ capture and their effects on the environment are not a well known field. The general objective of the meeting was to provide answers to the simple questions:

- 1) What do we know?
- 2) What do we not know?
- 3) Strategy to fill the holes?

The adsorbents used for CO₂ capture should be stable and reusable, as this will be beneficial economically for the industry. However, from an environmental point of view, the word stable indicates persistence. A persistent compound has the potential of being harmful to the environment. Are the amines persistent or do they have the potential to be environmentally harmful?

To answer these questions, multi-disciplinary meetings and work-groups have the potential of being very useful. Exchange of information and information sources, experience from similar processes, enabling the identification of issues that must be known, and reasonable strategy planning are among the benefits from a multi-disciplinary team.

The question 'how to proceed' was launched, considering the following moments: time scales, ranking, emissions, modelling loads, and effects of loads. Ranking is

understood as ‘ranking of information gaps’, where these moments were mentioned: priority of the gaps, what gaps can be filled in parallel, sampling and measurement, modelling, emissions, toxicity, and effects.

Process and emissions

CO₂ capture process – general overview (Mona Lâte, StatoilHydro)

Summary.

The process is shown in Figure 3, and briefly described here. The flue gas (from the combustion) is cooled before it enters the absorber, where CO₂ is captured. The absorber is an aqueous solution containing ill- or non-defined amines (due to industrial secrecy). The amine-CO₂ complex/salt is then transferred to the stripper, where addition of heat causes dissociation of the amine-CO₂ salt, and CO₂ is released as a gas. CO₂ is collected and subsequently pumped back down into the continental shelf.

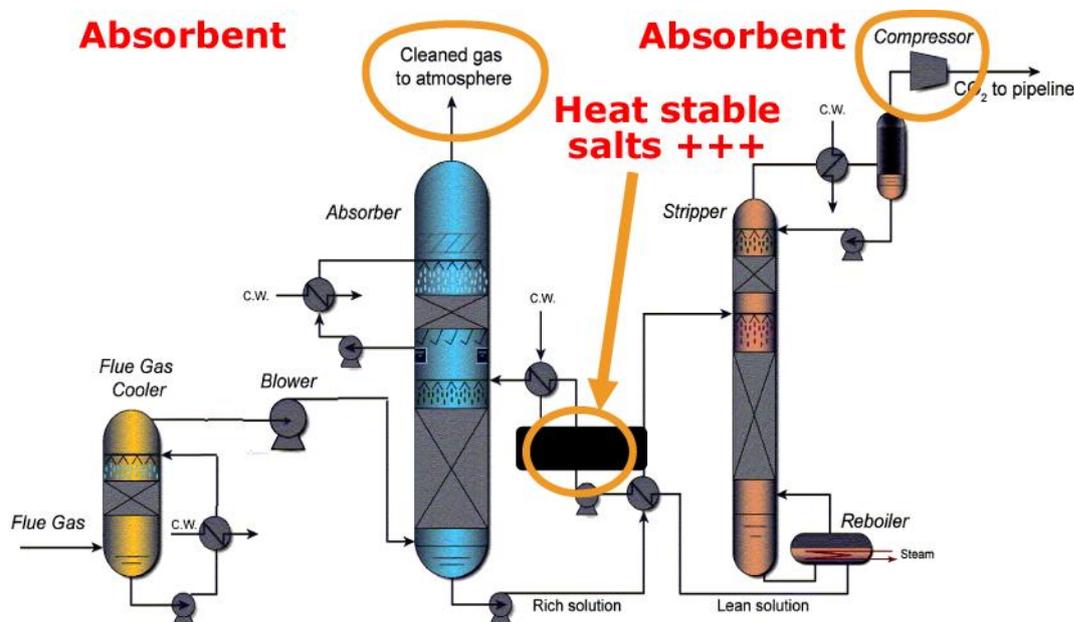


Figure 3. The CO₂ capture process.

Amine based adsorbents are coded as yellow or red, according to their noxiousness or environmental harmfulness.

Most tertiary amines (e.g. MDEA), some common activators (e.g. piperazine, AEEA), and some corrosion and foam inhibitors are coded red. Yellow coded amines include most primary and secondary amines (e.g. MEA), sterically hindered amines (e.g. Flexsorb), and some foam and corrosion inhibitors.

Statoil has established criteria for their CO₂ capture technology (Table 1)

Table 1.

Criterion	Demand
Energy efficiency	50% (included CO ₂ capture and delivered at 100 bar)
Cost of capture	Less than NOK 200/tonne CO ₂ (~US\$ 30/tonne)
CO ₂ capture	At least 80%
Emissions	Zero additional harm

These criteria are met with several challenges. Firstly, the potential chemical compounds in the discharge/emission must be identified. This will be conducted by analyses of existing pilot plants and through a prediction based on the chemical composition of the adsorbents.

CO₂ capture at Kårstø (Laila Iren Helgesen, HSE director, OED)

Summary.

The Soria Moria declaration claimed that the government wants to ensure that the recovery factor in the fields must be increased through increased research and also through the use of CO₂-injection, and to step up the efforts to reduce CO₂ emissions from the Norwegian continental shelf, e.g. through increased energy efficiency, electrification and CO₂ depositing. This led to the CO₂ capture plant at Kårstø, and a project director was engaged in April 2007. Gassnova was established in July 2007, the project organisation mobilised in August 2007, and a formal message was delivered SFT in October 2007. The project group has a mandate; it “shall make the necessary preparations for an investment decision to be made by the Norwegian government on constructing a carbon capture plant at Kårstø”. A separate project at present run by Gassco, investigate a common transport and storage solution for CO₂ from Kårstø and Mongstad.

The capture plant shall reduce CO₂ emissions from the existing gas power plant at Kårstø by 1 million tonne per year. The CO₂ capture plant must be based on post-combustion technology, and the exhaust from a gas power plant will be the CO₂ source. The project is going fast, and they want to as early as possible use (existing) qualified technology at the lowest possible risk. The CO₂ separation is obtained through utilisation of amine based technology.

The Kårstø plant has Norway’s largest generator, operating at 420 MW, and will produce 3.5 TWh, corresponding to ~3% of annual energy consumption in Norway. It is estimated that 0.6 billion cubic metres gas will be consumed annually. Furthermore, the plant aims to be Europe’s cleanest by a NO_x emission of 2 ppm and a CO₂ content in the exhaust of 4 mol %. The total CO₂ emission is calculated to 1.2 Mtonnes/yr.

The total calculated emissions from the Kårstø plant is provided in Table 2. According to the project group, these emissions are low concentrated, but large volumes give high loads. Furthermore, the emissions are spread over a vast area and the precipitation seems low, but the effect is not known.

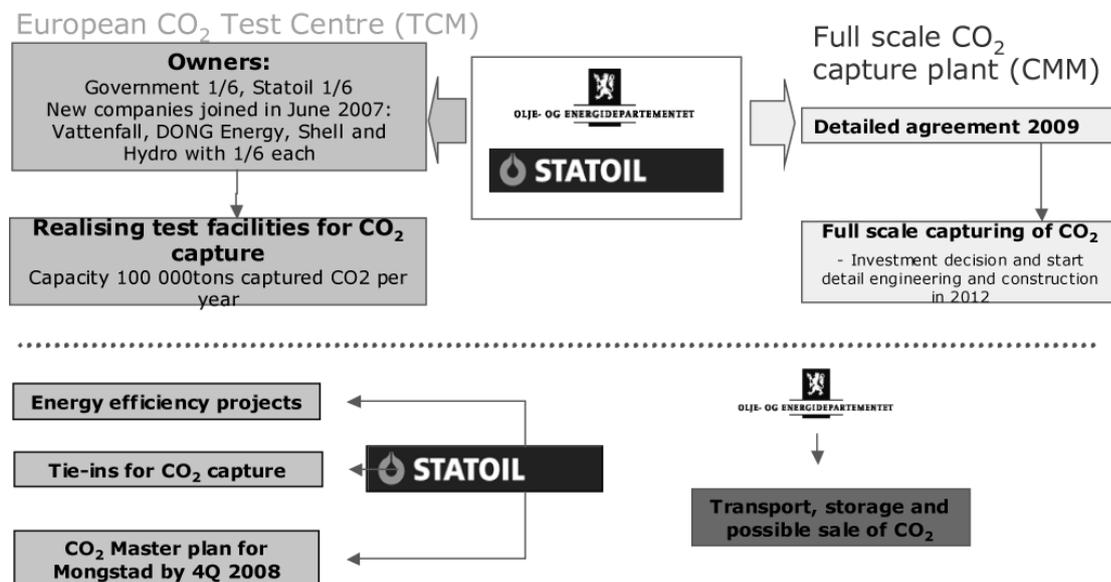
Table 2. Estimated emissions from the Kårstø plant.

Component	Emission (ppm)	Emission (kg/h)	Emission pr 8000h (tonnes/yr)
CO ₂			1,200,000
Amines to air	1-4	5-20	40-160
Acetaldehyde	0-5.5		
Trace elements	<0.2		
NO / NO _x	<2 / <0.2		
NH ₃	2-8	3-12	24-100
Degradation products		40-380	320-3,040
Excess water (pH~5.5)		0-75,000	
-estimated NH ₃ content	90-100	5.4	43
Cooling water		20,000 m ³ /h	

CO₂ capture at Mongstad (Jostein Nordland, StatoilHydro)

Summary.

A CO₂ capture plant is also planned at Mongstad. In 2006, an agreement between Statoil and the Norwegian government was reached, aiming to develop “forward looking” technology for CO₂ capture, and was given the name European CO₂ Test Centre (TCM). The owners are the Norwegian Government, Statoil, Vattenfall, DONG energy, Shell, and Hydro, all having a 1/6 ownership. A detailed organisational chart is depicted in Figure 4.

**Figure 4.** Organisational chart for the CO₂ capture project at Mongstad.

The test facility has a planned lifespan of 5 years and is designed for an annually CO₂ capture capacity of 100,000 tonnes/yr. Two different CO₂ capture technologies are tested; one is based on amines, the other on carbonate. An environmental impact assessment (EIA) will be sent to the stakeholders by the end of 2007. It is planned to submit an application for discharge permit by the end of 1Q 2008, and the plant will be started in 2010.

The CMM plant itself (see Figure 4) is a large-scale capture plant with a capacity of capturing >2M Tonnes per year, and has a life span of 25 years. The base case is amine based CO₂ capture technology. The improvement and qualification of the technology gained through TCM will be taken into account when a decision on the final concept is taken in 2012. A master plan report will be presented for the government in 1Q 2009, and will be used as a basis for negotiations. A new EIA will be submitted to the stakeholders and the government in 3Q 2011, and an application for discharge permit is planned submitted in 2012. The start up for the CMM plant is scheduled to 2014.

Transformation processes in the reactor and noxious environmental toxic by-products (Hans Aksel Hauge, GassTEK)

Summary.

Amines will be released during CO₂ capture. There are two major sources for amine discharge, from the treated flue gas and from the reclaimer (see Figure 5).

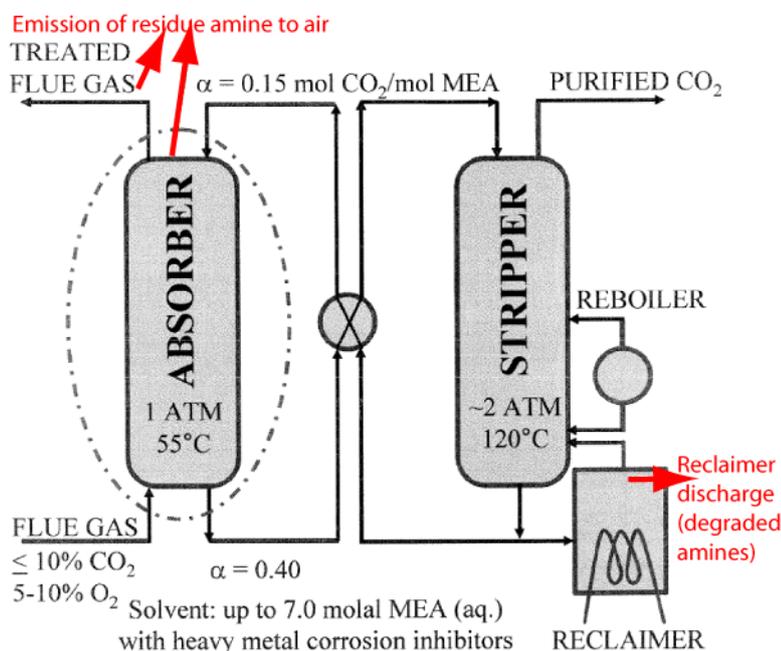


Figure 5. Sources of amine discharge in the CO₂ capture process.

The purpose of the amine reclaimer is to separate usable amines from degradation products, hence accumulation of degradation products is avoided. The reclaimer is operated either in batch mode (best efficiency) or slip stream continuous mode. There are three types of reclamation technologies: vacuum distillation, anion exchange and electro dialysis.

The vacuum distillation utilises differentiations in amine and by-product boiling points and is the only process capable to separate all kinds of by-products from the usable amines and may be operated in both batch and slip stream mode.

The amine loss occurs due to degradation, vapour losses, leaks and spills, and the total losses are estimated to be approximately 1.6 kg amine per tonne CO₂.

The generation of waste is strongly dependent on the flue gas composition and plant operating conditions, but is approximately 0.003 m³ per tonne captured CO₂.

MEA is degraded through three basic mechanisms, that is, thermal degradation, CO₂ reactions and carbamate polymerisation, and oxidative degradation.

Thermal degradation is significant above 200°C, but should not be a major route for MEA degradation as the adsorption process is operated typically at 50-55°C. However the reclaimer is operated at a slightly higher temperature and thermal degradation may occur.

Polymerisation reactions are likely to occur at the operating conditions. Various degradation products may form, including high molecular weight polymers (solids).

Alkanolamines are highly susceptible to oxidative degradation in the presence of oxygen. In the flue gas, the oxygen content is 5-10%, thus, oxidative degradation is likely to occur. It is also likely that heat stable anions are formed in the process, such as format (most likely), acetate, oxalate, glycolate, malonate, succinate, sulphate, nitrate, thiosulphate, thiocyanate, etc. These anions have higher affinity for the amines than CO₂ and will form heat stable salts (HSS) with the amines. The anion sources are amine degradation products, SO_x, and NO_x present in the flue gas.

Two different mechanisms are proposed, that is, electron abstraction and hydrogen abstraction. Both mechanisms explain the formation of NH₃ as the primary degradation product and aldehydes as secondary degradation products. Aldehydes formed in the process may undergo further oxidation to form carboxylates.

CO₂ loaded MEA is less prone to oxidation than is unloaded MEA. The reaction rates increase as the temperature and oxygen partial pressure increase, however, the degradation rate decreases as the MEA concentration increases. Degradation rates are expected to increase in this order: primary<secondary<tertiary, as primary amines react slowly with free radicals compared to the higher order amines. Sterically hindered amines are less prone to degradation than primary alkanolamines.

The flue gases may contain significant amount of SO_x, which reacts irreversibly with MEA to produce HSS. Installation of a SO_x scrubber is beneficial if flue gas is >10 ppm SO₂. However, the scrubber is not efficient towards SO₃, as 2/3 escapes the scrubber. SO₃ may form the extremely corrosive H₂SO₄ when subjected to water.

NO_x may cause corrosion and amine degradation. However, the NO_x generation can be controlled by adjusting the combustion temperature to below 1200 K. Among the NO_x, NO₂ is most harmful as it forms nitric acid (HNO₃).

The following compounds and their sources in the discharge were presented:
HSS anions: acetate, format, oxalate, glycolate, malonate, succinate, sulphate, nitrate, thiosulphate, thiocyanate, chloride, etc are present due to degradation of MEA, combustion by products (SO_x, NO_x), and contaminated additives (e.g. make up water), MEA-F, HEED, HEEU, HEI, OZD, polymers are degradation

products of MEA Aldehydes, ammonia, nitrosamines, and IZD are formed by oxidative degradation.

Cu salts, Vanadates are added as corrosion inhibitors, and EDTA and N-diethanol glycene as degradation inhibitors. Fe complexes originates from corrosion and heavy hydrocarbons from fuel or due to contamination by lubricants.

These are unfortunately only a few of the expected by-products formed in the process. For thorough and detailed discussions on the chemical composition of amine based CO₂ capture, please confer the following papers from Ind. Eng. Chem. Res.; Bello and Idem, 2005, 44, 945; Lawal and Idem, 2005, 44, 986, and Supap et al., 2006, 45, 2437.

Halten CO₂ project (HCP). Time schedule. (NN, StatoilHydro)

Summary.

The Halten project is a collaboration between the oil companies Statoil and Shell. An EIA will be completed by the end of 2Q 2008, and an application for discharge permit will be simultaneously submitted. If the test plant runs successfully, the construction of a production plant will be initiated. By January 1, 2012, a store well will be completed, and the power plant is planned to be operational by April 1, 2012, and the CO₂ capture plant ready by July 1 the same year.

NIVA: The discharge permit from SFT, what are the requirements to obtain it?
Are there other plants with CO₂ capture? -Several

CO₂-capture plants, challenges from an industrial viewpoint (Mark Claessen, Shell)

Summary.

An oral presentation without any slides was given. The amine mixtures and the solvents are industrial secrets. There are three vendors manufacturing amine solutions for CO₂-capture at present, and Shell as agreed with all of them not to reveal the content of the mixtures. However, some information about the amines was provided. Firstly, the amines are reclaimed (recycled). Secondly, an HPLC chromatogram of the mixture contained some 50 peaks. Thirdly, it was mentioned that MEA based CO₂-capture is "old-fashioned".

It is evident from the above that the emission will contain a high number (several hundred) of different amines and amine derivatives and degradation products. To characterise this very complex mixture is a challenging task.

For the time being, the different amine mixtures are scrutinised to select the most suitable vendor. The evaluation criteria include environmental impact, engineering challenges with respect to gas and liquid waste.

To obtain a discharge permit, the amines put into the process must be documented and the emissions must be specified according to the content and amount.

This information will be available as soon as a vendor has been chosen, and this will happen in 2008. There must be an information flow between the technology providers and the environmental specialists, and information about the degradation products must be shared.

Speculations regarding the content of the mixtures used for CO₂-capture. Does the mixture contain any red-labelled amines?

Governmental views

Environmental consequences of amine release from CO₂ capture plants (Fredrik Weidemann, SFT)

Summary.

SFT recommends CO₂ capture at the power plants at Tjeldbergodden, Mongstad and Hammerfest. It has already been decided that CO₂ capture must be implemented for the power plants at Mongstad and Kårstø. There are also other industry plants with large emissions of CO₂ where implementation of CO₂-capture technology should be considered, such as coal fired power plants, concrete plants, and other process industry plants.

The most appropriate technologies for CO₂ capture utilise post combustion adsorbents, either amines or carbonates. A major drawback for these technologies is that the composition of the adsorbents is either poorly defined or protected from publicity as they are industrial secrets.

The three 450 MW power plants operated by Naturkraft Kårstø AS, Industrikraft Møre AS, and Skagerak Energi AS will annually discharge 40-160, 139, and 160 tonnes of amines, respectively.

According to the Pollution Act a discharge permit application must explicitly state:

- What substances will be used and discharged
- What transformation and by-products are formed and discharged
- To what recipient(s) are the substances discharged
- How are the substances dispersed, deposited and degraded
- What degradation products are formed
- What health and environmental concerns are caused by the discharged compounds

It was further pointed out the health and environmental concerns that must be addressed, that is, ecotoxicology, persistence, bioaccumulation, genotoxicity, carcinogenicity, reproduction toxicity, chronic and acute toxicity, irritation, corrosivity, and sensitisation.

From these, a list of required toxicology data should be enclosed in the discharge permit application:

- Acute ecotoxicology (LD₅₀ or EC₅₀ for a fish species, *daphnia*, and algae)
- Degradability (e.g. hydrolysis) and bio-degradability

- Bio-accumulation ability based on log P or log D
- Acute toxicity (LD₅₀, rat)
- *In vitro* genotoxicity
- Irritation and corrosive properties
- Skin sensitisation
- Subchronic toxicity (28 days exposure)
- Reproduction toxicity (screening)

The developer has the responsibility for the environmental risk assessment elucidation. SFT has some recommendations regarding strategies for environmental (risk) assessments:

- The products, components, and reaction and degradation products, must be identified.
- (Toxicological) screening data for the components must be provided
- The amount of discharge to what recipients must be determined
- Dispersion, deposition, and relevant concentrations must be modelled
- Health and environmental risk assessments must be conducted, utilising all available information.
- External experts may be consulted

Information about all imported chemical products must be registered in the product register (PR). This information must contain an accurate description of content and composition, a classification according to relevant regulations, and available information regarding health effects, toxicity, ecotoxicity, and degradability.

Information about chemical products given to SFT in permit applications may if necessary be confidential. Authorised users within SFT may also collect data directly from the product register (PR). Based on the information provided by the applicants, SFT may conduct their own assessment of the products. SFT may submit data to external expertise for (independent) toxicological and ecotoxicological assessments. All parties involved operate under professional secrecy with respect to the PR content.

EU has adopted a new regulatory framework for chemicals called REACH. Producers and importers must register their compounds to the European Chemical Agency (ECHA). Relevant information on health and environmental effects must be reported. Additional tests (dependent on the tonnage) must be conducted. The compounds possessing the most potential harmful properties (Substances of Very High Concern) must be authorized prior to use. The end users are obliged to ensure that their use of the compounds are registered and to control that a permission for their use is granted.

Environmental and tools for analysis

Amines and CO₂ capture, dispersion, deposition and chemical modelling (Svein Knudsen, NILU)

Summary.

An important issue in predicting the environmental impact of amines is their dispersion chemical changes in the atmosphere and deposition after discharge. One strategy to obtain this is through chemical modelling, enabling the prediction of amine load at various locations.

Modelling may be conducted for dispersion and deposition at different distances and time scales. The outcome of short time dispersion modelling is the average dispersion within hours after discharge, whereas for long time dispersion modelling, dispersion is predicted for years after discharge.

Chemical modelling also implements atmospheric chemical reactions of the amines, however, to be useful, the chemical composition of the discharged amines must be known.

Furthermore, the deposition of amine pollutants (and their transformation products) may also be modelled. Dry deposition involves the adsorption to surfaces and vegetation, whereas wet deposition involves precipitation (including fog).

Status for dispersion modelling.

A model to calculate concentrations including some basic chemistry, are presently operational. There are also models available to predict depositions for specific components. However, the chemical reactions in the atmosphere of amines are poorly known and models for these reactions are at presently not operational. From the above, it is therefore necessary to develop new models or improve existing models for dispersion in the following areas:

- Models for chemical reactions in the atmosphere
- Models for dispersion for the sources in question
- Deposition algorithms and models for deposition in such models

The estimated time frames for developing these new models are 1-3 years for a new dispersion model, 1 year for a photochemical model, and 3 months for a deposition model. The modelled effects are odours as a matter of concentration, corrosion seeding and additives for corrosion prevention, such as Cu, V and other metals.

Toxicity of Amines and Nitrosamines (Marit Låg, Norwegian Institute of Public Health)

Summary.

MEA has low acute toxicity, but causes irritation to the skin, eyes, and airways.

DEA is considered slightly toxic in humans, and causes irritation. DEA reacts with nitrosating agents and nitrosamines are formed, e.g. N-nitrosodiethanolamine, a potent liver and nasal carcinogen in rats. Other amines may also cause irritation to the skin and respiratory organs.

Some aromatic amines are known to be human or animal carcinogens, e.g. 2-naphthylamine, aniline, benzidine, and azo dyes. They are activated through CYP 450 metabolism, and form DNA adducts (covalent). Aromatic amines are strongly linked to human bladder cancer, and they are also suggested to induce liver, colon, pancreatic, and lung tumors.

Several nitrosamines are mutagenic and carcinogenic, but the knowledge on human health effects is limited. Their mechanism of action is through alkylation of DNA. Nitrosamines must be bioactivated (through CYP 450 metabolism), and the metabolites are reactive towards DNA. Dimethylnitrosamine is highly carcinogenic for the liver and kidney in virtually all the mammalian species tested.

It should be elucidated whether nitrosamines are emitted or formed in the atmosphere from the relevant amines, and if so, their exposure and toxicity must be assessed.

The possible health effects of the specific nitroamines must be clarified. Inflammation and other diseases than cancer could be of relevance.

A useful database for toxicity was provided: <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>

No threshold limits for amines considering their unpleasant smell. SFT operates with risk assessments, not levels (concentrations).

Amines in removal of CO₂ – effects on vegetation (Per Arild Aarrestad, NINA)

Summary.

Amines exist as primary, secondary, and tertiary (even quaternary), and amines may be monoamines, diamines, triamines, and so on. Amines may also be aromatic (e.g. pyridine, aniline).

Amines are central in all life processes and constitute a central part in proteins (amino acids), DNA, and most eucaryotic phospholipids. In plants, amines are found in pyrrol (part of chlorophyll), histamine (amino acid, found in the hair of nettles), gramine in the grass family (involved in plant defence), and tyramine and dopamine.

MEA, also known as ethanolamine or 1-aminoethanol, is the second most abundant polar head group for phospholipids in eucarya (third in many plants after phosphatidylcholine and phosphatidylglycerol). MEA is mostly used in the industry and in agriculture, MEA is used as a neutralizer agent for anionic

emulsifiers and as an additive to herbicides and pesticides and as a growth medium.

Amines in plant cell biology are well studied. MEA as an external driver on plants and ecosystems is less studied. Anyway, MEA was reported to increase plant growth under drought stress and the use of pesticides (0.3-0.5 mg/plant). MEA exposure also increased the content in plants. MEA is biodegradable in soil to ammonia, acetate and N_2 , and increases the soil content of plant available N. Thus, the major effects of MEA exposure are probably related to nitrogen fertilisation of the habitats.

Airborne nitrogen is a threat to European biodiversity, as nitrogen is the limiting nutrient for plant growth in oligotrophic ecosystems. Increased N deposition leads to eutrophication, increased biomass production and reduced plant biodiversity. The critical load is defined below:

“The load an ecosystem can endure without significant harmful effects, according to present knowledge”, Nilsson and Grennfeldt, 1988.

The convention on long range transboundary air pollution (the Gothenburg protocol), is assessed in international working groups. The results of field and laboratory experiments and ecosystem modelling are published and are continuously updated.

From a Norwegian point of view, the critical load of arctic heathland is particularly interesting. It is estimated that a critical load of 5-10 kg N/ha/yr may result in a decline in lichens, mosses, and evergreen shrubs, whereas there might be an increase of grasses.

To conduct an environmental risk assessment of excess amine load from CO_2 capture, it is recommended the relevant literature is scrutinised. Furthermore, plant physiological experiments in greenhouse with appropriate doses of amines could be conducted, as could *in situ* spraying experiments on selected habitats vulnerable to increased N deposition, related to the critical load of the habitats.

SFT is aware of the Nitrogen load problem as both NH_3 and NO_x has been tested for exactly the same. Why is it necessary to investigate the effects of amines?

Answer (PAA): This is an important question. It is uncertain whether the N critical load model is correct.

Amines and effects in freshwater (Bente M. Wathne, NIVA)

Summary.

Regarding the effects of amines on freshwater systems, three main topics are addressed, (a) pathways in soil and water, (b) effects on freshwater, and (c) nitrogen as a nutrient.

(a) Pathways: In general, amines biodegrades rapidly and should not persist in the environment, bio-accumulate or bio-magnify. Regarding nitrogen retention, it must be elucidated how MEA enter the nitrogen cycle and the fate of MEA in the

watershed. It must also be elucidated how MEA is degraded both in soil and in water.

(b) Effects on freshwater: To predict any effects, the concentration of MEA (and other amines and nitrosamines) must be known. As some of these amines presumably are new to the ecosystems, their (unlikely) ability to bio-accumulate must be determined. It is also reasonable to determine any potential effects on drinking water quality. Finally, the effects of amines on higher organisms, such as fish, must be decided.

(c) Nitrogen as a nutrient. As for plant ecosystems, critical loads of nitrogen must be elucidated, along with their possible pH altering and eutrophication properties. EIF (environmental impact factor) application.

SFT: What is known about the effects on pH from amine deposition?

BMW: Amines will have the same effects as NH_3 and NO_3 and sulphur in the acidification process.

Measurement techniques (Christian Dye, Norbert Schmidbauer, Morten Moe, and Martin Schlabach, NILU)

Summary.

The fundamental important question ‘are there relevant emissions from amine-based CO_2 -removal?’ was raised. The answer to this is yes, based on the current (or the relevant) technology. MEA is expected to be a major component in the CO_2 -capture process, and some of the previously identified transformation products are shown in Figure 6. From the figure, at least 8 transformation products are formed from MEA alone, not counting photochemical and radical mediated transformation products. MEA is probably only one of several amines used in the CO_2 -capture process. To characterise and quantify the amine emissions is therefore presumably a very complicated task. Bello and Idem (Ind. Eng. Chem. Res., 2005, 44, 945) identified more than 30 degradation products from MEA alone.

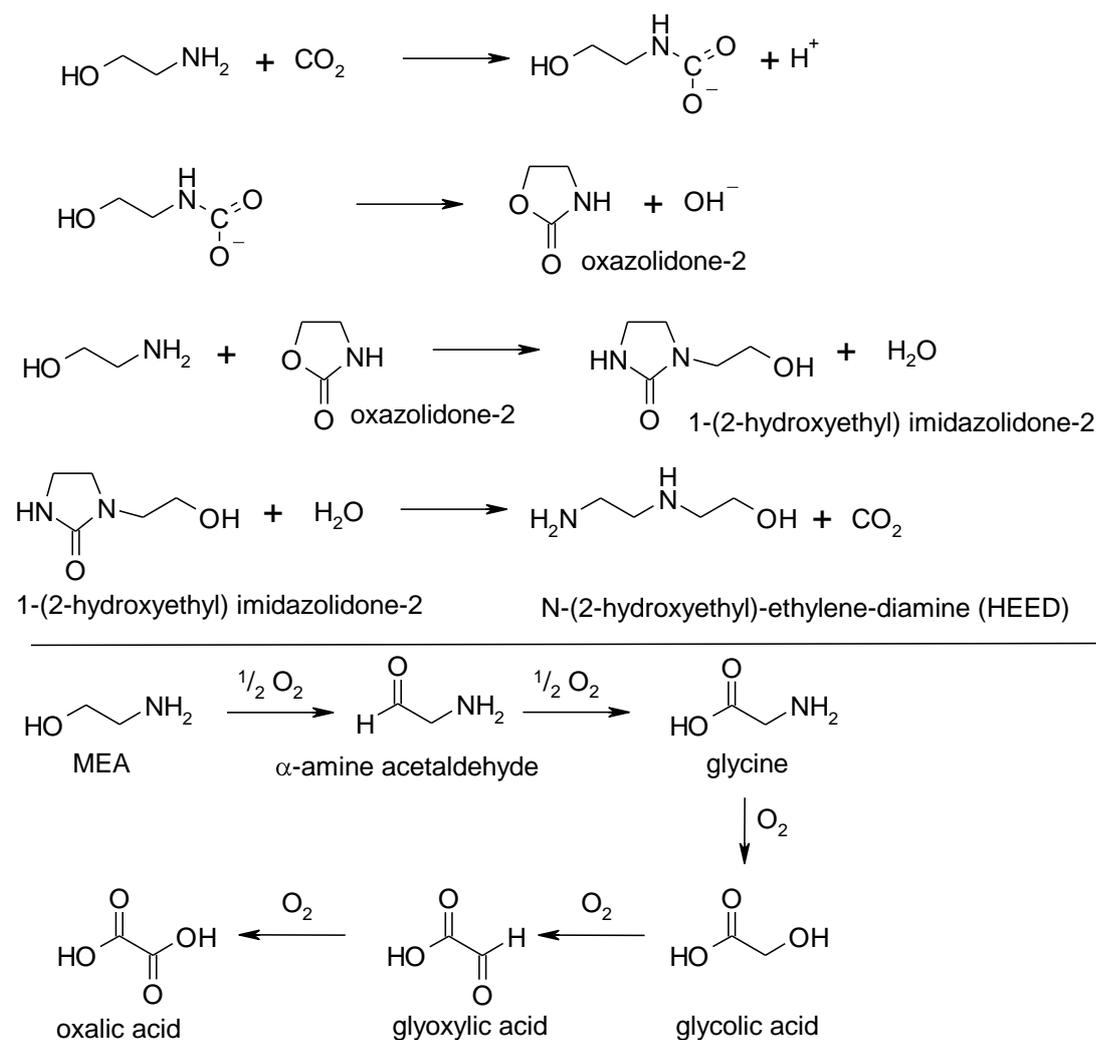


Figure 6. Some transformation products of MEA following reactions with CO_2 (top) and O_2 (bottom). The figure is from Bello and Idem, 2005).

The environmental effects of the degradation products are in most cases not known. Amines are potential fertilisers, and the oxidised degradation products are potential corrosives, allergens, and may be carcinogenic. Furthermore, the presence of additional amines may alter the local photochemical balance.

To obtain information regarding the structure of the amines and their transformation products, as well as the amounts at which they are present, a team of skilled scientists that good knowledge on reasonable sampling strategies and has access to advanced analytical equipment is an absolute necessity. NILU is experienced with sampling and analysis of emission to air, ambient air, particle and aerosol, precipitation, fog, snow cover, vegetation, soil, surface water, and other environmental sample matrices.

Furthermore, NILU has advanced equipment for the analysis of the samples, such as thermal desorption gas chromatography mass spectrometry (TD-GC-MS), suitable for non-polar organic compounds, liquid chromatography time of flight mass spectrometry (LC-TOF/MS), suitable for polar organic compounds, and liquid chromatography inductively coupled plasma mass spectrometry (LC-ICP-MS), suitable for the analysis of metals and other elements.

It was suggested that the following (pilot) investigations should be conducted:

- A general broad screening of the emitted mixture
- An investigation of the photochemical degradation of the emitted mixture
- Diurnal variation of the photochemical degradation products
- Monitoring the changes in the local photochemical processes

How can these methods be developed when it is not known which substances that are going to be measured?

These methods and the method development will be generic and will have to be finalized when the substance is known. The bulk of the work can however be done before the substance is known and this will shorten the time that is needed to measure a specific substance.

The way forward (Plenary discussion led by Svein Knudsen, NILU)

Summary.

For the CO₂ capture project, the short term is 1Q 2008, medium term 2009 and long term 2011.

In the short term, the following activities may be conducted:

- Literature and desk top exercises
- Planning of the different activities
- Deposition investigations under controlled conditions
- Screening
- Estimation of possible nitrogen loads
- Establish the infrastructure.

In the medium term, the group should:

- Establish emissions from TCM, Kårstø, and others
- Provide an overview of the photochemistry
- Establish suitable modelling tools to estimate loads
- Estimate effects and prepare evaluation programs
- Evaluate possible technical solutions for minimisation

Appendix B

List of participants - Expert meeting at NILU 18/10-2007

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Appendix C

Description of the CO₂ capture problem and possible solutions

There are primarily three technologies available for CO₂ removal from power plant emissions. A summary is given by the Intergovernmental Panel on Climate Change (<http://www.ipcc.ch/ipccreports/srccs.htm>) and include:

- A *Post-combustion* systems separate CO₂ from the flue gases produced by combustion of a primary fuel (e.g. natural gas)
- B Oxy-fuel combustion uses oxygen instead of air for combustion, producing a flue gas that is mainly H₂O and CO₂ and which is readily captured.
- C Pre-combustion systems process the primary fuel in a reactor to produce separate streams of CO₂ for storage and H₂, which is used as a fuel.

For the capture of CO₂ there are several available technologies: separation with solvents and sorbents, separation with membranes, and separation through distillation of a liquefied gas stream and refrigerated separation.

There are three commercially available absorption processes:

- 1) The Kerr-McGee/ABB Lummus Crest Process, using 15-20% w/v aqueous MEA.
- 2) The Fluor Daniel @ ECONAMINE™ process using a 30% aqueous MEA-based solution with an inhibitor to resist carbon steel corrosion and is especially tailored for oxygen-containing gas stream.
- 3) The Kansai Electric Power Co., Mitsubishi Heavy Industries, Ltd., KEPCO/MHI process. The process is based upon sterically hindered amines and three solvents (KS-1, KS-2, and KS-3) have been developed. KS-1 (its composition is unknown) was commercialised in a urea production application. In this process, low amine losses and low solvent degradation have been noted without the use of inhibitors and additives.

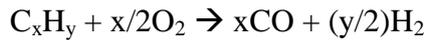
The post-combustion process is already thoroughly discussed in the present report.

The oxy-combustion strategy has several benefits. Nitrogen is removed and thus the possible generation of NO_x is avoided. The flue gas consists primarily of CO₂ and H₂O, the latter is conveniently removed from the flue gas by condensation, rendering the flue gas with a CO₂-content of 80-98%. The CO₂ is then stored after some minor cleaning steps.

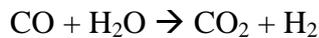
The pre-combustion strategy is a two step procedure with two different approaches for the first step; steam reforming and partial oxidation. Steam reforming relies on a catalytic transformation of the natural gas to CO and H₂ by the addition of gaseous H₂O:



In the partial oxidation, the natural gas is incompletely combusted with pure oxygen, also yielding CO and H₂:



In the second step, steam is added



CO₂ is isolated from H₂ by membrane separation.

Amine based CO₂ capture is well established and well functioning in closed systems, as those presently used and oil platforms to remove CO₂ from natural gas. However, when incorporated in a power plant where the natural gas is combusted faces some difficulties.

Firstly, in a closed system, the amines are more conveniently reclaimed as there is little emission to the atmosphere. In the open system approximately 100 tonnes of amines will be discharged annually to the atmosphere.

Secondly, the released amines have an unpleasant smell

Thirdly, the amines are heated in the reclaiming process and metals, both solids and ions will be present. The metals may act as catalysts. The heat combined with catalytic metals may lead to the formation of unprecedented by-products, such as pyridine and aniline and derivatives of these.

Fourthly, the oxygen present is prone to react with the amines, forming products one does not have to deal with in the closed systems. The health and environmental effects of the oxidised amine by-products are in most cases not known.

Fifthly, chemical reactions in the atmosphere may cause the formation of nitrosamines, a class of potentially carcinogenic compounds.

Sixthly, the discharged amines (independent on their form) may eventually deposit in areas of low nitrogen content in the soil. Most amines are converted microbiologically to plant available nitrogen in the soil, and the increased nitrogen content may enable more nitrogen demanding plants to settle in the area, with displacement of the habitat native plants as a consequence.

Seventhly, solid waste will be generated in the CO₂ capture process, e.g. carbamates. The disposal sites for the solid waste will experience a tremendous change in the nitrogen load, especially if the disposal site is placed in open air.

In conclusion, the use of amines for CO₂-capture could be precarious. However, there are commercially available technologies where amine emissions are low. From the discussion in the next section, deposition of CO₂ under the continental shelf is at present the best option to stabilise the CO₂ content in the atmosphere.

Post combustion based technology is a safe choice, as it is well established. However, the energy utilisation efficiencies may be higher for the other two combustion technologies, and they are also likely to yield less and cleaner emissions.

Mineral carbonation and industrial use of CO₂.

Instead of dispose CO₂, it can be used as a resource. One option is to convert minerals, e.g. Olivine, Serpentine, and Wallastonite to MgCO₃ and CaCO₃, the latter two could be used in concrete. However, these processes demands energy.

It is possible to convert CO₂ to e.g. urea, methanol, polycarbonates and polyurethanes. Conversion of CO₂ to biomass is an option, but is very space demanding. A 100 MW plant would require a biomass production area of 50 km² to balance the CO₂ emission.

However, at present the scale of the use of captured CO₂ in industrial processes is too small, the storage times too short and the energy balance too unfavourable for industrial uses of CO₂ to become significant as means of mitigating climate change. (http://www.ipcc.ch/pdf/special-reports/srccs/srccs_chapter7.pdf).

