# Amines Used in CO$_2$ Capture

- Health and Environmental Impacts

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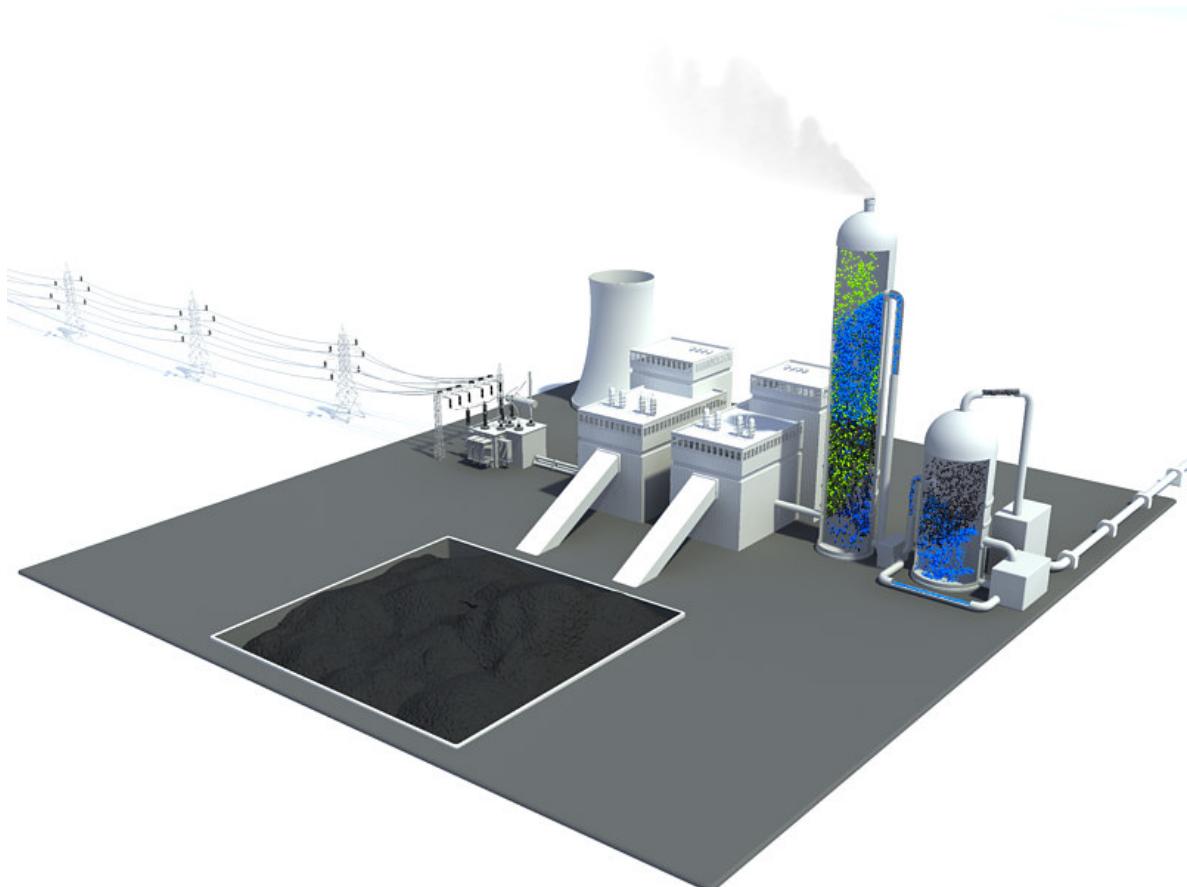
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Executive Summary

How to combat global warming

Global warming is already taking place and is one of the biggest challenges of our time. According to the Intergovernmental Panel on Climate Change (IPCC), global warming is caused by human activities and if business proceeds as usual, anthropogenic greenhouse gas (GHG) emissions will increase the average global temperature from 1.1 to 6.4 ^{o}C during the 21st century. As a consequence ecosystems may collapse and 15 to 40 percent of all species may become extinct. More draughts, floods and other extreme weather events will increase pressure on scarce food and water resources as the world population grows towards nine billion humans by 2050.

To have a reasonable chance of avoiding such dire consequences of global warming, the IPCC has recommended a 50 to 85 percent reduction of global greenhouse gas emissions from 2000 to 2050 and a peak in emissions no later than 2015. CO_2 capture and storage (CCS) is one of many solutions that are needed to achieve this ambitious emission reduction target.

Several challenges must be overcome before CCS can be deployed on a large scale. These are related to the three main areas in the CCS value chain; capture, transport and storage of CO_2. Extensive research, testing and development are ongoing within all these areas, and improvements are continuously reported.

The most mature CO_2 capture processes rely on the use of amine solvents to wash CO_2 out of a gas mixture, such as flue gas. It is well known that amines in some applications represent a health risk, but there is a lack of knowledge on health risks related to amines used for CO_2 capture. This report addresses this challenge, namely how to address the potential environmental and health risks represented by the use of amine solvents in CO_2 capture processes.

Possible environmental impacts from amines

Available literature shows that some amines and amines degradation products can have negative effects on human health (irritation, sensitization, carcinogenicity, genotoxicity). The amines can also be toxic to animals and aquatic organisms, and eutrophication and acidification in marine environments can also happen. These impacts represent a worst case scenario, and the possible impacts are, however, strongly dependent on which types of amines that are used in the CO_2 capture process and the amount of amine related emissions to air.

MEA (monoethanolamine) is today the most commonly used amine in CO_2 capture processes. MEA has a relatively high biodegradability, and MEA will in itself have no adverse effect to the human health, animals, vegetation and water organisms. The airborne emissions of nitrogen and ammonia generated from amine decomposition can however, if emitted in high concentrations, cause eutrophication and acidification. Other amines commonly used for CO_2 capture like

AMP (2-Amino-2-methylpropanol), MDEA (methyldiethanolamine) and PIPA (Piperazine) are ecotoxicological and have low biodegradability, and they will have higher environmental impact than MEA.

Once emitted to air from a CO_2 capture plant, amines will start degrading to other products. There is a variety of degradation products and most of them will not have negative environmental effects. Nitrosamines will probably be the degradation products with the most adverse environmental impacts as they can cause cancer, contaminate drinking water and have adverse effects on aquatic organisms. It is important to note that these consequences represent a worse case theoretical scenario at maximum amine emission from the CO_2 capture plant.

Recommended action to minimize environmental and health risks

An amine based capture plant will in general have several positive impacts on the environment. An amine plant will not only remove 85 to 90 percent of the CO_2, but considerable amount of other polluting components such as ashes, NO_X and SO_2 will also be removed due to required pre-treatment of the flue gas. From an environmental viewpoint the best amine plant is the one that demonstrates minimum energy requirement, high degree of CO_2 capture, minimum liquid waste, and minimum amine related emissions to air.

The available literature suggests that the environmental and health risks represented by amines in CO_2 capture *are* manageable, and most likely do *not* give reason to inhibit or slow down the wide-scale deployment of CCS. This is, however, only true if sufficient effort is given by public authorities, research communities and industry to close remaining knowledge gaps and develop proper risk management strategies. This effort should include the following activities:

1. Fill knowledge gaps

Comprehensive research is necessary to fill all knowledge gaps on environmental impacts from amines. The research should be carried out through international cooperation, and focus on the following three aspects:

- Determine the atmospheric degradation paths, precise degradation yields, and degradation products' life time in the atmosphere.

- Determine human toxicity exposure limits (both acute and chronic) as this is a prerequisite to establish safety limits.

- A simultaneous experimental and laboratory approach should be addressed for studying the ecotoxicity (both acute and chronic) to terrestrial ecology and aquatic environment.

2. Develop amines with low environmental impact

Continued research is required to develop new or improved amines, or mixture of amines, with lower energy requirements, lower emissions of amines and thereby lesser degradation products than amines used today.

3. Develop amine capture plants with minimum emissions to air

Several suppliers of amine plants are investigating measures in the design of the plant that could reduce the emissions to air. Large scale plants have not been built yet and it is the understanding within the industry and research groups that emissions could be reduced to a minimum, far less than worst case scenarios addressed in the literature. Such improvements should be tested in planned CCS demonstration projects.

4. Ensure sound amine waste handling

Research activities should be established to determine how amine waste and degradation products can be turned into harmless products. For example, it is theoretically possible to convert amines and their degradation products to biomethane, which represents a harmless and valuable source of renewable energy. The practical viability of this and other methods should be determined. Furthermore, it is important to ensure that there are capacities available at waste handling facilities for handling the large volumes of amine waste that can be expected from a global deployment of CCS.

5. Develop alternatives to amines

More research is required to find alternatives to amines that could demonstrate better performance and lower CO_2 capture cost – such as absorption based on carbonates, or other CO_2 capture concepts like adsorption, chemical looping combustion and membrane separation.

6. Establish proper regulations

Once the knowledge gaps on the environmental and health impacts of amines are filled, it is necessary to implement regulations that ensure that CO_2 capture plants are designed and operated without negative environmental impacts.

7. Use CCS demonstration programs to address risks related to amines

There are plans for building demonstration plants for CO_2 capture worldwide. All demonstration projects that are based on amine absorption should include research activities aiming at filling knowledge gaps related to environmental impacts of amines.

One example is the EU which is planning to build up to 12 CCS demonstration projects by 2015. Bellona recommends that the European Commission clearly states in their tender documents that CCS demonstration projects with amine based CO_2 capture can only receive public funding if they address research activities on environmental impact of amines. Furthermore, the tender should also state that the projects with the most comprehensive research program on impact of amines will be preferred. Prerequisites like this should be established not only in the EU, but wherever public funding is used for building large scale CO_2 capture plants.

Finally, no commercial CO_2 capture plants based on amines should be built before the knowledge gaps are filled. Commercial CCS plants are, however, not expected before 2020, and with comprehensive research programs on amines all knowledge gaps should be filled by then. The knowledge gaps on environmental impacts from amines are therefore *not* expected to delay the commercialization of CCS.

1. Introduction:

The global warming challenge

Global warming is already taking place and has become the biggest challenge of our time. According to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), global warming is caused by human activities [1] and if business proceeds as usual, anthropogenic greenhouse gas (GHG) emissions will increase the average global temperature from 1.1 to 6.4 ^{o}C during the 21st century. The global temperature is already 0.7 ^{o}C above the pre-industrial level, and a 2 ^{o}C increase is generally considered as the threshold above which dramatic and irreversible impacts will occur. Ecosystems may collapse and 15 to 40 percent of all species may become extinct. More draughts, floods and other extreme weather events will increase pressure on scarce food and water resources as the world population grows towards nine billion humans by 2050 [2,3,4].

To have a reasonable chance of avoiding such dire consequences of global warming, the IPCC has recommended a 50 to 85 percent reduction of global greenhouse gas emissions from 2000 to 2050 and a peak in emissions no later than 2015 [1].

The good news is that it *is* possible to reduce global emissions by as much as 85 percent by 2050 [5]: Energy can be generated from renewable sources and used more efficiently; fossil power can be de-carbonized by CO_2 capture and storage (CCS); and forestation management can be improved.

CO_2 capture

CCS is a technology with the potential to reduce GHG emissions while allowing continued use of fossil fuel [6-13]. The CO_2 arising from combustion of fossil fuel is captured, transported, and finally safely stored in an underground geological formation [14] as visualized in Figure 1.

CO_2 capture technologies are often classified as post-combustion, pre-combustion or oxyfuel CO_2 capture [14, 15]. In post-combustion CO_2 capture the CO_2 is separated from other flue gas components by absorption. In pre-combustion CO_2 capture, the carbon in the fuel is separated prior to combustion. In the oxyfuel process the combustion is performed with pure oxygen instead of air, leading to a flue gas consisting of only CO_2 and steam, which can easily be separated.
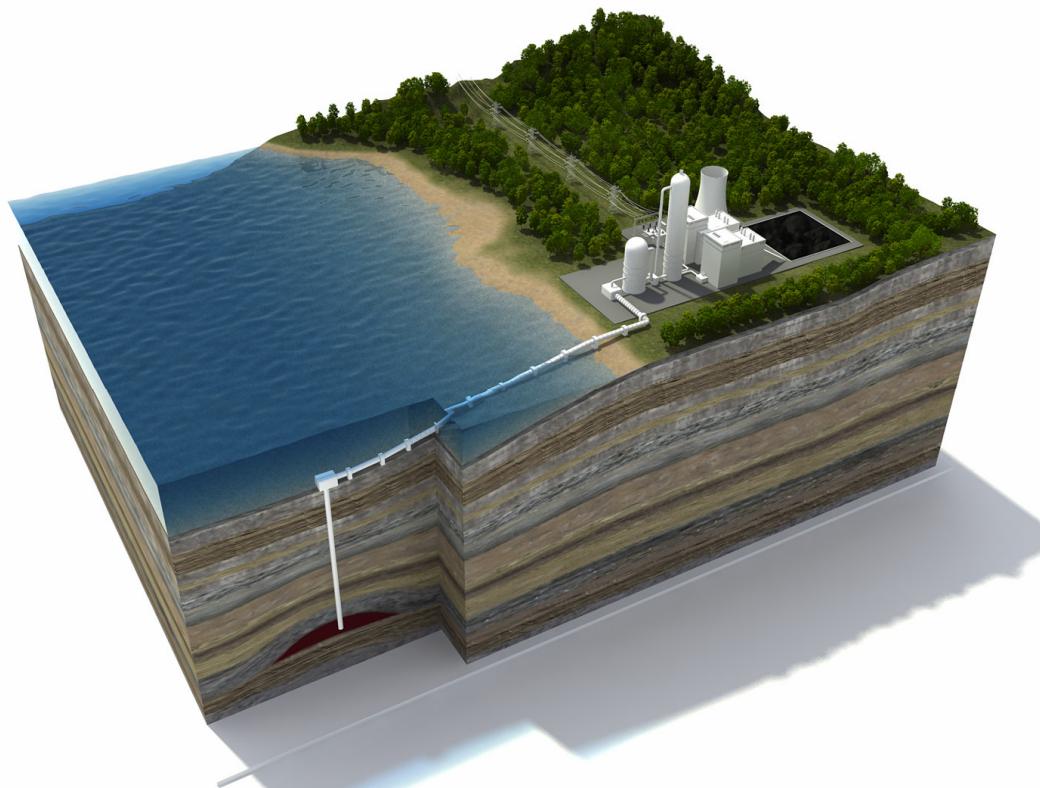
Figure 1. A schematic presentation of CO_2 capture and storage (CCS). CO_2 is captured from the flue gas coming from a coal power plant. The captured CO_2 is transported by a pipeline to a storage location where CO_2 is injected for safe storage. Typically, CO_2 will be stored more than 800 meters below the ground.
Illustration: Prosjektlab and Bellona.

Captured CO_2 is transported in pipelines or by ship to a storage site were CO_2 can be safely stored in underground geological formations called aquifers, in depleted oil and gas fields, or in deep unmineable coal beds.

CCS is not yet commercially viable and several challenges remains to be solved before this can become a reality. The most important challenges are: technological improvements to reduce the energy penalty related to CO_2 capture; establishing political and economic incentives that generates market conditions for CCS; defining regulatory framework allowing CO_2 storage; building demonstration plants to gain experience and thereby reduce cost; establishing information campaigns to inform the public and industrial and political decision makers about the potential of CCS; and technical improvements to ensure that sustainable CCS is developed.

The challenges listed above are addressed by industry and decision makers globally. Some examples are the G8 leaders that has recommended to build 20 CCS demonstration projects globally; the EU energy and climate package which has established substantial funding for CCS demonstration plants [16]; and the new Global CCS Institute (GCCSI) in Australia which is funded by 100 million Australia dollar annually by the Australian Government in order to facilitate CCS development globally [17].

According to the European Technology Platform on Zero Emission Fossil Fuel Power Plants (ETP-ZEP) CCS can become commercially available by 2020 [18]. CCS can therefore contribute to significant CO_2 emission reductions from 2020 an onwards, and by 2050 CCS can eliminate one third of global CO_2 emissions [19].

Environmental impacts of amines

The wide-scale deployment of CCS requires that health, safety and environmental risks are identified and minimized. One possible risk is related to environmental and health impacts due to the use of chemicals known as amines in some CO_2 capture processes. Questions have been raised whether amines could lead to serious health impacts for humans and ecosystems.

It is well known that amines represent a health risk, but there is a lack of knowledge on health risks related to amines used for CO_2 capture. It is necessary to perform research activities to identify the health risks. Once the risks are identified, there must be performed new studies to define how the risks can be tackled so that an amine based CO_2 capture plants can be designed and operated without any health and environmental risks.

Objective of this report

The aim of this report is to provide suggestions for how possible environmental impacts from amines can be handled. The report gives an overview of the literature available on health and environmental impacts related to amines used in CO_2 capture processes. The report also identifies the impacts that can be expected, and suggests how amines should be handled to avoid environmental and health risks. It will also be pointed out where knowledge is lacking and which new studies that needs to be performed.

Amines used in CO_2 capture are described in Section 2 of the report, and related emissions are given in Section 3. Mechanisms for degradation of amines into hazardous compounds are described in Section 4 and related health and environmental impacts are discussed in Section 5. Conclusions and recommendations for further action to minimize health and environmental risks are given in Section 6.

2. Amines used in CCS

In post-combustion CO_2 capture based on amine absorption, CO_2 is removed by a chemical absorption process that involves exposing a flue gas stream to an aqueous amine solution [20,21]. CO_2 reacts with the amines to form a soluble carbonate salt. This reaction is reversible and the CO_2 can be released by heating the solution with the carbonate salt in a separate stripping column as illustrated in Figure 2.
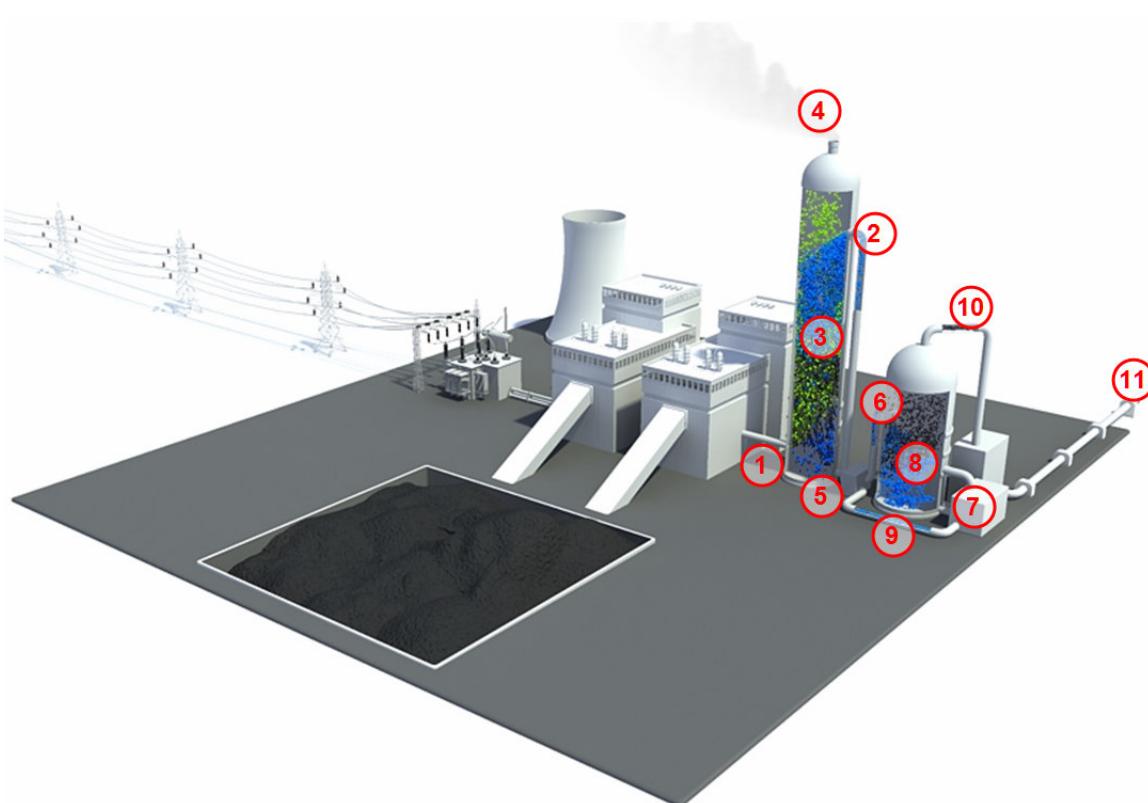
Figure 2. Post-combustion CO_2 capture based on amine absorption. The flue gas from a coal power plant enters the absorption column, also called absorber (1). CO_2 is represented by black particles and other components in the flue gas, mainly nitrogen and water vapor, is represented by green particles. A mixture of water and amine (blue particles) enters the top of the absorber (2), and the amine reacts with CO_2 inside the absorber to form carbonate salt (3). Cleaned gas will leave the top of the absorber (4), and the carbonate salt leaves the absorber (5) and is transferred to the stripper (6). Hot amine from the reboiler (7) enters the stripper, causing the carbonate salt to heat up. As a result the carbonate salt reacts to pure CO_2 and pure amine (8). The amine formed in the stripper is transferred to the reboiler where it is heated and transferred to the stripper (8) or recycled to the absorber (9). Pure CO_2 formed in the absorber (10) is compressed and transported (11) to a storage site. Illustration: Prosjektlab and Bellona.

Amine based CO_2 capture from natural gas is well known from the oil and gas industry. Similar plants are also known from the food industry where CO_2 is captured from flue gas and used in several products. The technology has also been demonstrated in pilot plants for fossil fuelled power plants, but large scale amine based CO_2 capture plants for power plants remains to be built.

Amines are chemicals that can be described as derivatives of ammonia[1] in which one or more of the hydrogen atoms has been replaced by an alkyl[2] or aryl[3] group. Amines are classified as primary, secondary, or tertiary depending on whether one, two, or three of the hydrogen atoms of ammonia have been replaced by organic functional groups. Some of the amines most commonly used in CO_2 capture are monoethanolamine (MEA), methyldiethanolamine (MDEA), 2-Amino-2-methylpropanol (AMP), Piperazine (PIPA), diglycolamine (DGA), diethanolamine (DEA), and di-isopropanolamine (DIPA). The chemical formulas of these amines are shown in Figure 3.
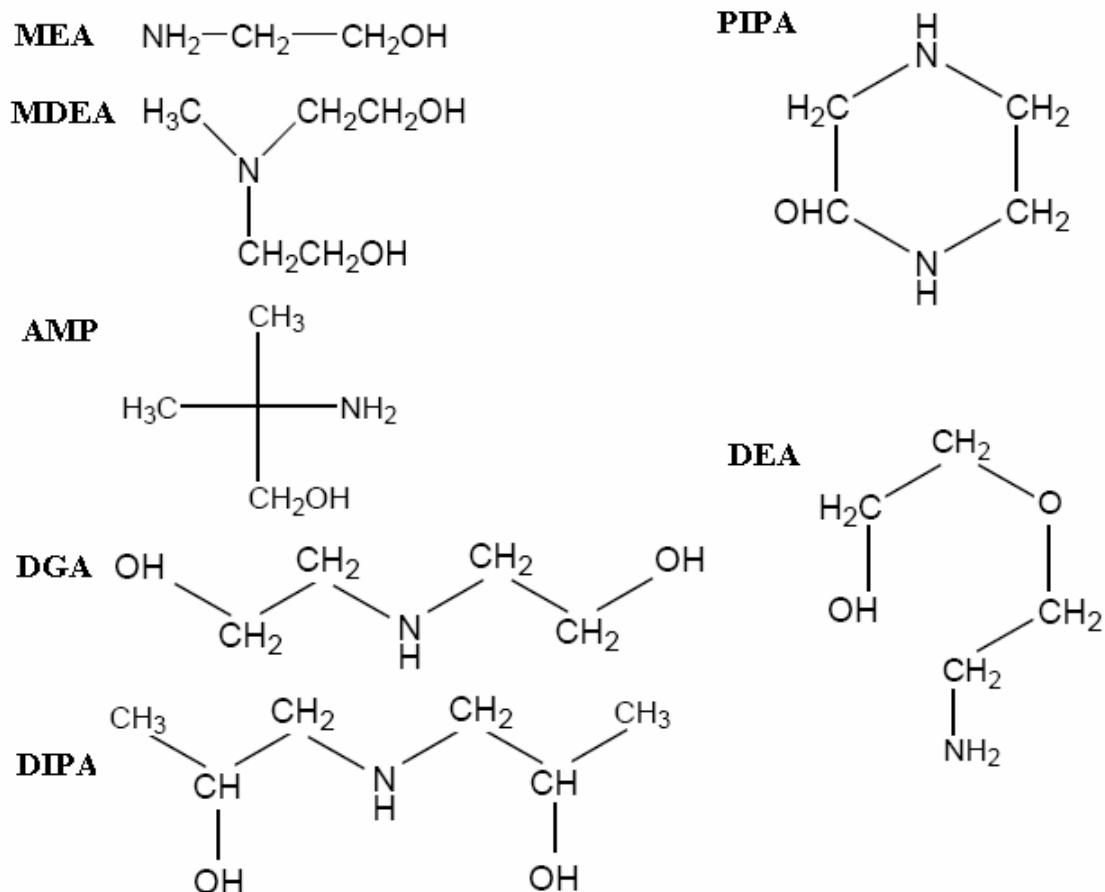
Figure 3. Chemical structures of the amines most commonly used in CO_2 capture.

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[1] Chemical formulas of Ammonia: NH_3
[2] An alkyl group are carbon and hydrogen atoms linked in a chain
[3] An aryl group are carbon and hydrogen atoms linked in a circular structure

In new technologies the solvents used for CO_2 capture are often a mixture of several different amines. This include includes MEA-piperazine blends, MDEA-piperazine blends, blends of N-methyldiethanolamine and triethylene tetramine. For several new technologies the amine mixture recipe is not known because the solvent suppliers keep it as a company secret.

The amines used for CO_2 capture are recycled, but a minor portion of the amines are either degraded or emitted to air. The emitted amines are unstable in the nature environment, and discharged amines may degrade to some dangerous substances that are toxic and represents a risk for cancer. Such degrade products includes aldehydes, amides, nitrosamines, nitramines, *cf.* Figure 4 for chemical structure. It is well known that amines and their degradation products can be dangerous to human health, animals, plant lives and the environment.
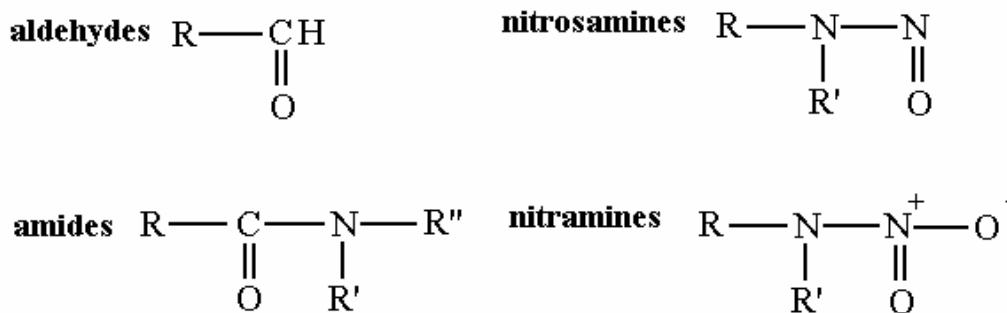
Figure 4. General chemical structures of the amine atmospheric degradation products

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3. Amine emissions

3.1. Amine emissions to the atmosphere

During the CO_2 capture process, a very small fraction of amines will escape from the absorber and be released to the atmosphere together with the cleaned exhaust gas. The amine emissions will be partly contained in water droplets generated by the scrubber and in fresh liquid droplets that are formed after the flue gas leaves the stack. The amine emissions can also be as gasses.

In Norway there exist plans for building full scale CCS at the 420 MW gas power plant at Kårstø. This plant will emit 1.2 million tonnes CO_2 annually without CCS if it is operated constantly. 85 percent of the CO_2 emissions can be reduced with CO_2 capture based on amine absorption. Estimated amine emissions from this planned CO_2 capture plant can be used as an example of how much amine emissions that can be expected from full-scale CCS plants. The data given in Table 1 shows that 40 to160 tones per year of amine emissions can be expected for the CO_2 capture plant at Kårstø [22,23,24]. The exact amine emission from full scale CO_2 capture plants will of course depend on the size of the power plant.

Table 1. Estimated maximum and minimum emission from Kårstø 420 MW power plant. [24]

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

3.2. Amine waste

The main amine waste coming from the CO_2 capture process is the waste water coming from the reclaimer. The Amine reclaimer is the unit in the process used for separating or reclaiming usable amine from its degradation products, *cf.* Figure 5. The waste includes water, amines, amine degradation products, corrosion products and other chemicals [25]. The content of amines and degradation products in the waste is uncertain and it strongly depends on which kinds of amines that are used and the type of feed gas (nature gas or flue gas) in the capture process.

A typical CO_2 capture plant with the capacity of 1 million tonnes CO_2 annually is expected to produce from 300 to 3000 tonnes amine waste annually [27]. The volume of amine waste depends on type of fuel, other cleaning processes before CO_2 capture, the type of amine used, and operational conditions, but in most cases the volume of amine waste will be less than 1000 tonnes per year.
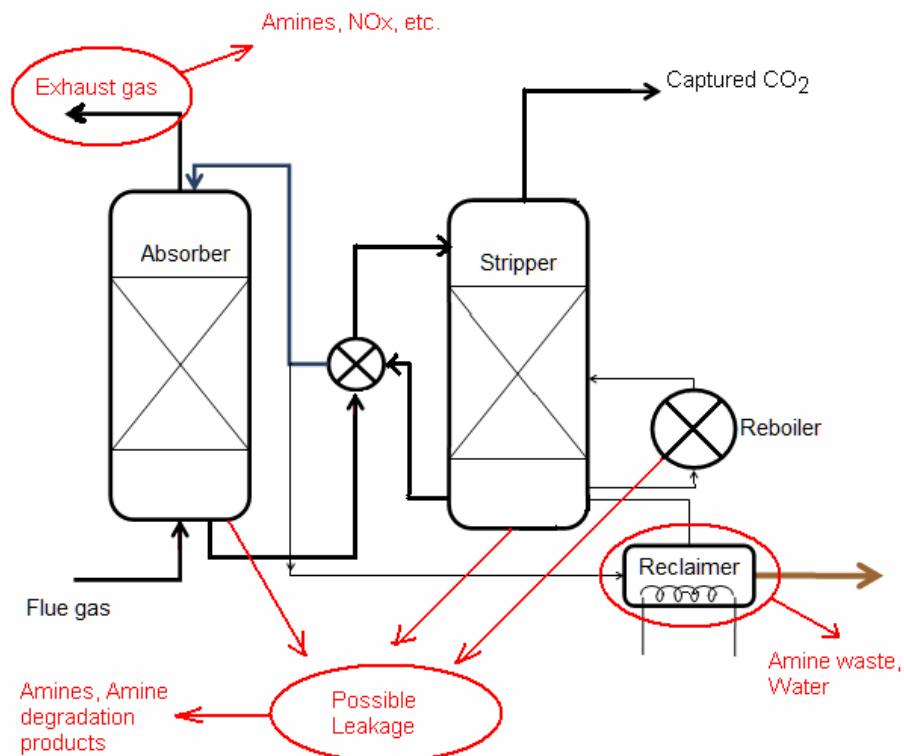
Figure 5. The possible emission sources of amines and degradation products for the CO_2 capture process. (Illustration based on reference 26.)

Amine waste is hazardous waste and must be handled in accordance with rules and regulations for hazardous waste handling. Hazardous waste shall be treated on site according to permissions or delivered to companies that have the necessary permissions to handle hazardous waste.

An example of how amine waste could look like is given in Figure 6.
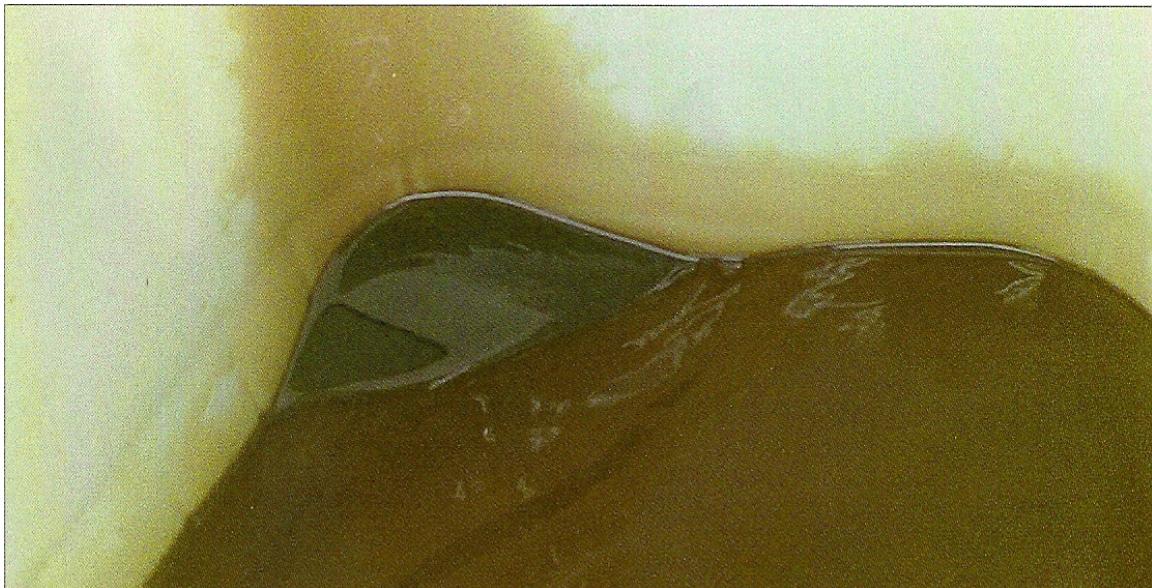
Figure 6. Picture of amine waste from a research project performed by Tel-Tek.[26]. The sticky brown liquid contains more than 90 percent amine waste and the dark brown liquid in the corner are amines in a paste-like phase [27].

3.3. Amine corrosion products and possible leakage routes

As mentioned above, corrosion products can be a source of amine waste in the CO_2 capture process. Amines and heat stable amine salts are corrosive and can take part in corrosive reactions were amine wastes are formed. Amine corrosion products will probably have lower environmental impact than the amine emissions and amine waste described in Section 3.1 and 3.2, but nevertheless studies are required to determine how amine corrosion products will influence the environment.

MEA is one of the most corrosive amines that are used for CO_2 capture. The flue gas from a fossil fuelled power plant contains a certain amount of oxygen, which can react with amines, especially MEA, to form corrosive degradation products. The blended MEA/PZ solutions are even more corrosive than MEA solutions.

The volume of amine corrosion products depends on the corrosion rate, and it is therefore important to keep the corrosion rate as low as possible. The corrosion rate increases with different factors such as concentration of PZ in the blended solution, total amine concentration, CO_2 loading, solution temperature, and dissolved oxygen content. The presence of heat-stable salts will also increase corrosion rate in both presence and absence of dissolved oxygen. Corrosion inhibitors, sodium metavanadate ($NaVO_3$) and copper carbonate ($CuCO_3$) are able to lower the corrosion rate of carbon steel to below an acceptable level of ~ 0.25 mm/year. [28].

The corrosion rate depends on the temperature, and available monitoring data shows that a relatively low corrosion will take part in the colder parts of the unit, *i.e.* the absorber inlet and outlet. On the other hand, the highest corrosion rates were always found in the hottest parts of the unit, *i.e.* at the inlet and outlet of the stripper. It is also very clear that the combination of a high temperature and high CO_2 loading give rise to a corrosive situation [29,30].

The corrosion rate, and thereby the amount of amine corrosion products, depends on the materials used in the CO_2 capture plant. If materials with low corrosion potential are selected, the volume of amine corrosion products will be minimized [31].

4. Amine degradation products

There are three different mechanisms for amine degradation and they take place at three different phases of the CO_2 capture process:

- Oxidative degradation, which mainly takes place in the absorber;
- Thermal degradation takes place mainly in the stripper process;
- Atmosphere degradation which is amines emitted to the atmosphere that degrades.

There are lots of degradation products from each of the three different amines degradation mechanisms, and the degradation products do not only depends on the degradation mechanism but also on the type amines used and the time range for the CO_2 capture process.

Literature data on amine degradation products related to CO_2 capture mainly focus on the most commonly used amines in the CO_2 capture process like MEA, AMP, MDEA, PIPA. The evaluation below of degradation products has therefore its main focus on these amines.

4.1. Oxidative degradation

Amine solvents used in CO_2 capture are subject to oxidative degradation due to the presence of oxygen or metal ions in the flue gas. The highest oxygen concentration will occur within the absorber and this is as such the most likely place for oxidative degradation of amines. Oxidative degradation requires oxygen or other oxidants and is also catalyzed by iron, and it is expected to occur in the presence of dissolved O_2 in the liquid holdup at the bottom of the absorber. Degradation products will be oxidized fragments of amines, such as ammonia, organic acids and oxidants. The degradation process will increase the amine loss and amine waste and decrease the capture capacity in the capture system.

The chemistry of oxidative degradation is complex and not fully understood. A detailed description of suggested reaction mechanisms is given below based on available literature. The suggested reaction mechanism is also visualized in Figure 7.

The amines, especially MEA, will initially react with the metal ion such as Fe^{3+}, Fe^{2+} or Cu^+ to generate the oxide radical (single electron oxidants). Without the presence of dissolved oxygen (O_2), the radical will form imines by reactions with metal ion or other oxidants. In the presence of dissolved O_2, the oxide radical will react further with the oxygen to form the peroxide radical. The peroxide radicals will further react with amine to form the imines and hydrogen peroxide. The imines will undergo different processes like hydrolysis and oxidative fragmentation to form

the final degradation products. For MEA the final degradation products will mainly be ammonia and organic acids. In addition, there will also be some intermediate products (hydroxyacetaldehyde and formaldehyde) and other oxidants after the degradation [32-37].
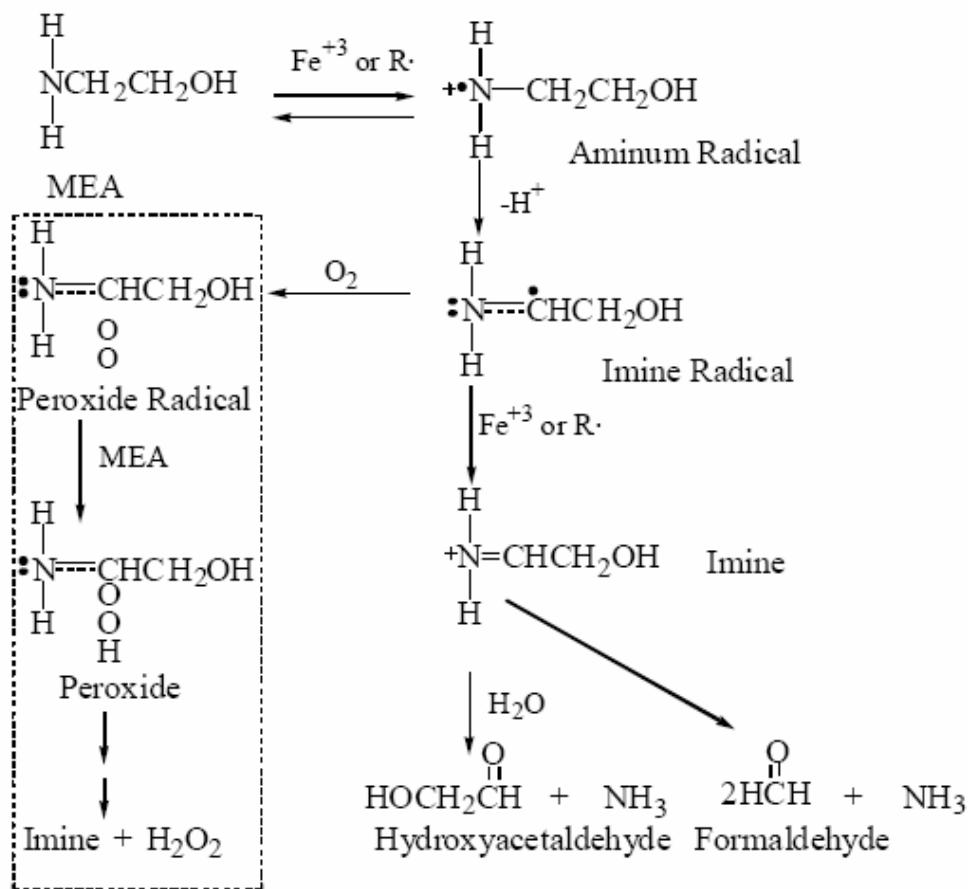
Figure 7. Possible MEA oxidative degradation reaction with and without oxygen. The imines will undergo different process like hydrolysis and oxidative fragmentation to form ammonia and organic acids which are the final degradation products.

The oxidative degradation mainly depends on the CO_2 loading, metal ion concentration and oxygen concentration. In the industrial conditions, the oxidative degradation will only occur with the present of CO_2. The CO_2 loaded amine will be easily oxidative degraded and the oxidation rate will depend on the CO_2 loading. Metal ions, especially iron, is an important catalyst in oxidation of amines. Metal ions will generate oxide radical which will increase the oxidation rate of amines.

Avoiding radical formation will limit the oxidative degradation, and it is possible to use EDTA[4] and bincine[5], which can bind stronger with metal ions, as oxidation inhibitors to reduce the

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[4] *EDTA*: ethylenediaminetetraacetic acid
[5] *Bicine*: N,N-Bis(2-hydroxyethyl)glycine - a general purpose buffer for biological research.

oxidative degradation of amines. Under specific conditions the oxidative degradation can also be controlled by the rate of mass transfer of oxygen into the amine solution, rather than the kinetics of the degradation reactions [32-37].

4.2. Thermal degradation

The high temperature and high CO_2 concentration in the reboiler and stripper are the right conditions for thermal degradation of amines. The high temperature will break the chemical bonds of amines and increase the reaction rate of amines reacting with CO_2 to form the thermal degradation production, which will also causes loss of amines in the system. Most of the thermal degradation products will be found in the bottom of reclaimer.

The thermal degradation is mainly controlled by the temperature, CO_2 loading and amines concentration. In the stripper and reboiler, the thermal degradation rate depends on both temperature and pressure. Increasing temperature or pressure will increase degradation rate, which will cause much more amine degradation products and amine lost.

CO_2 loading and amine concentration strongly influence the rate of thermal degradation. The CO_2 loading has a first order effect on the degradation rate and the amines concentration has more than first order effect on the thermal degradation.

Amines will generally react with CO_2 to form the carbonate salts. This reaction is reversible, but with high temperature, as in the stripper and reboiler, the carbonate salts will further react with amines to generate thermal degradation products. The amine will also undergo a hydrolysis process to form the final thermal degradation products.

Thermal degradation of MEA

The main thermal degradation products will obviously depend on the amine used. For MEA the final degradation products will include HEIA and HEEDA (*c.f.* Figure 8) and other polymerization products. In addition, small amount MEA-urea and other products can also be found in the degradation products. The thermal degradation products make up about 20 to 30 percent of the total MEA loss [35,37,38]
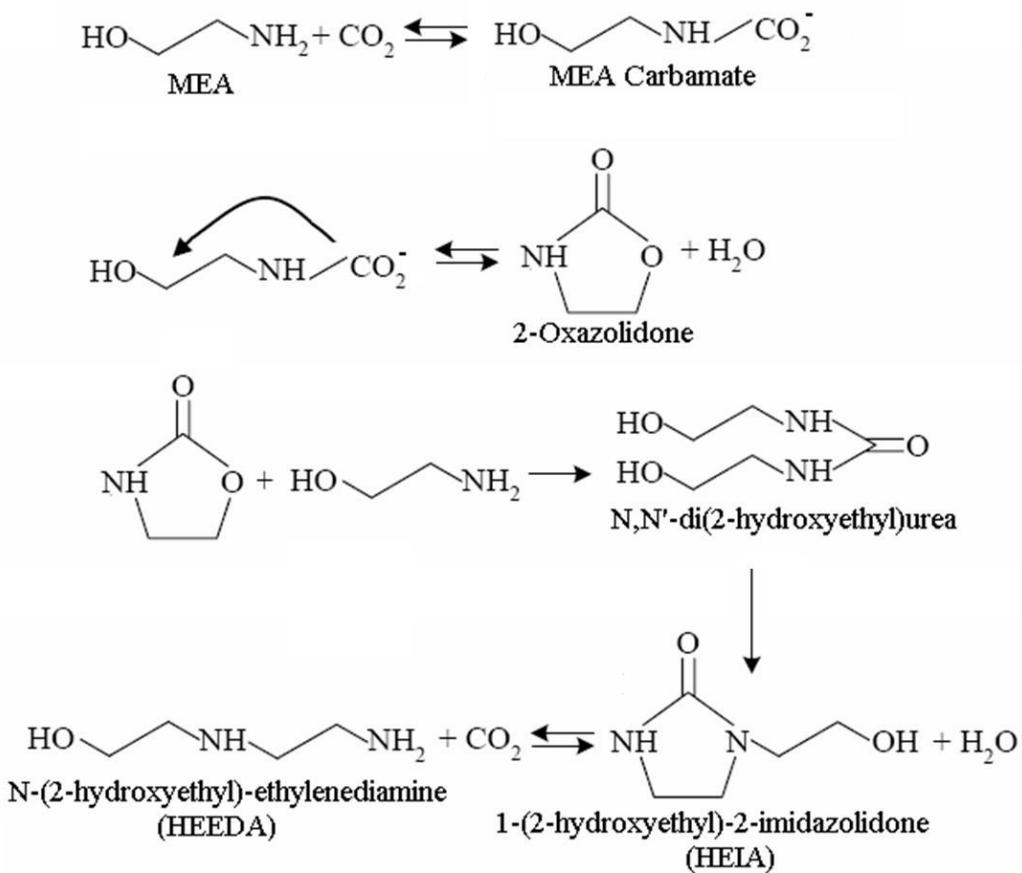
Figure 8: Possible chemical reactions taking place in thermal degradation of MEA (also called carbamate dimerization) in the CO$_2$ capture process [37,38].

Thermal degradation of MDEA, PIPA, AMP, and DGA

For MDEA, two major products identified in the Dow study were TEA and DMEA. These degradation products were formed in equal molar amount with the reaction that is consistent with the disproportionation reaction [35].

The amine PIPA seems to not undergo thermal degradations under conditions where other amines are thermally degraded. But in a blended system of MEA and PIPA, both MEA and PIPA did degrade in significant quantities. For AMP and DGA, the thermal degradation is not significant.

4.3. Atmosphere degradation

The amines emitted into the atmosphere will undergo a series of physical and chemical process, such as absorption, adsorption, photolysis and degradation. Compared to the oxidative and thermal degradation, the mechanisms and degradation pathways of atmosphere degradation are much more complex and give a much broader range of products.

In general the atmospheric degradation of amines will be initiated by reaction with OH radicals and photolysis in the day time, and normally aliphatic amines react very fast in the atmosphere with the OH radical. The OH radical abstracts the hydrogen from the CH and NH groups to generate amine radicals. Reactions with O_3 and NO_3 will furthermore initiate amines degradation in the night time. After the initiation reactions many different radicals are generated and they react further with different chemicals and radicals to form different degradation products.

The main focus in previous works on amine degradation has been on oxidative and thermal degradation and not atmospheric degradation, but recent reports from the Norwegian Institute for Air Research (NILU) and the University of Oslo (UiO) presents valuable information on atmospheric degradation mechanisms [39, 40]. MEA atmospheric degradation will form two different sets of degradation products:

1. Initial hydrogen abstraction at C1- and C2-position in MEA by OH radicals will mainly form formamide and 2-hydroxy-acetamide. Other amide and some peroxyacetyl-nitrates will also be formed.
2. Hydrogen abstraction from the amino group will lead to the formation of various amides with nitrosamines and nitramines.

The other amines used in CO_2 capture follows different atmosperic degradation pathways:

- Atmospheric degradation of AMP follow hydrogen abstraction from the -CH_2 and -CH_3 groups and gives acetamide and other amides as final products. There are also several nitrosamines and nitramines formed from hydrogen abstraction from the amino group. The expected end-product during daytime oxidation is N-nitro-formamide, and the corresponding nitrosamine, N-nitroso-formamide is expected to undergo rapid photolysis under the sun light.
- For the MDEA atmospheric degradation, the main degradation products following hydrogen abstraction from -CH_3OH groups and -CH_3 group are the amides and polyacrylonitrile(PAN)-like compounds.In addition, some nitrosamines and nitramines will form from N-based radicals coming from thermal dissociation reactions.
- For the PIPA atmospheric degradation, the main degradation products formed from the initial reaction with OH radicals are 2-Piperazinone and amides. In addition there will be formed nitrosamine and nitramine.

From the result above it is clear that the main products of the atmospheric degradation are different amides, but a number aldehydes, nitrosamines and nitramines will also be formed. The method to assess the amount of the nitrosamines and nitramines generated from atmospheric degradation is not available yet. Further experimental research is required on this area.

The chemical reactions taking part in atmospheric degradation for the different amines are given in Appendix B.

5. Health and environmental consequences

A CO_2 capture plant using amines will produce amine emissions and wastes during the whole process. Emissions of amines may occur through the cleaned exhaust gas, waste and as accidental spills. The amines and amine degradation products will enter the air, water and soil and several different environmental impacts are possible.

5.1. Atmosphere impacts

The cleaned flue gas leaving the CO_2 capture plant will contain small quantities of amines that can have environmental impacts. It is not only the amine in itself, but also its degradation products that can give environmental impacts.

5.1.1. Impact from amines

Amines emitted to the atmosphere from a CO_2 capture facility will either be adsorbed on water droplets generated by the scrubber and in fresh liquid droplets formed from the flue gas, or just enter the atmosphere as an amine gas phase. The amines will react to different degradation products in the atmosphere or form rain droplets that will come down to the earth (soil, rivers, lakes or oceans).

The toxicity of the most common amines used in CO_2 capture differs substantially. The amines are irritating to skin and toxic at high concentrations to animals. None of the amines MEA, AMP, MDEA and PIPA have been reported to be carcinogenic[6], but an indication of reproductive and developmental toxicity have been reported for MEA and PIPA [42]. PIPA has also been found highly toxic to some insect and water invertebrates [42,41] . All amines seem to be epidermal irritating, and PIPA is also found to have a sensitizing effect. Critical levels for air concentration of the amines have been established, see Table 2, and the general population should not, over time, be exposed to levels in the air higher than the concentration reported in this table. Please note that these guidelines are preliminary due to need for further research [42].

Table 2: *Critical level for inhalation exposure risk of different amines* [42].

	MEA	AMP	MDEA	PIPA
Critical amine air concentration (µg/m^3)	10	6	120	5

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[6] All toxicology terms, like carcinogenic, are well defined in Appendix A

If the degradation of the emitted amine is not addressed, the highest concentration of amines emitted from a CO_2 capture plant are found within 1 km distance. The maximum hourly averaged concentration will be 11μg/m^3 at the maximum amine emission can reach 160 ton/year. At a distance of 3 km from the capture plant the amine concentration is almost constant [42] as indicated in Table 3.

Table 3: Maximum hourly concentrations of amines in air (in μg/m3) with distance from the plant [42].

Distance from the plan (km)	1	2	3	4	5	6	8	10
Maximum amine concentration (μg/m^3)	11	6.6	4.4	3.9	5.2	5.8	5.6	4.9

The data in Table 3 indicates that the amine air concentration could be above the critical levels defined in Table 3 if degradation of amines is not addressed. Amines will form degradation products as explained in Section 4 and they will also biodegrade in the soil and water into nitrogen components available for plant growth.

The Norwegian Institute for Air Research (NILU) has performed simulations[7] that indicate that the maximum amine concentration in the air will be 0.1 µg/m^3 when degradation of amines is addressed [42]). This result is two orders of magnitude below the threshold of 10 μg/m^3 of MEA given in Table 2. Long term exposure levels of amine that can cause adverse health effects are therefore not exceeded.

On the short time scale, before the amines have started to biodegrade, the amines concentration in vicinity of the plant (see Table 3) can be close to the recommended amine concentration (see Table 2). This shows the importance of continued research on environmental effects of amines to determine possible impacts for people living close to the plant.

Then the main effect of amines on the terrestrial plants and vegetation is probably related to eutrophication, but the effect of amine emissions from the CO_2 capture plant on the ecosystems have not been be fully assessed [43,44]. There is limited information on direct toxicity of the above four amines to terrestrial plants and vegetation. Amines sprayed onto plants act as a plant bio-regulator, increasing plant growth and seed yield and reduce plant stress. Amines biodegrades in soil and soil water into nitrogen components available for plant growth. Increased nitrogen deposition leads to eutrophication, increased biomass production and reduced plant biodiversity since nitrogen is the limiting nutrient for plant growth in oligotrophic ecosystems. However, the effect of nitrogen is strongly dependent on the amount of nitrogen exposed to the plants and vegetation.

Based on the report from NILU [42], the critical load of amines to vegetation should not, over time, exceed 2700 mg/m^3/yr to avoid damage to plants. This is 10 to 100 times higher than the expected

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[7] Simulations performed by CONDE, which is the NILU in-house steady state Gaussian dispersion model.

maximum emissions from a CO_2 capture plant. Harmful effects of amines to terrestrial plants and vegetation are therefore not expected [42].

5.1.2. Impact from amine degradation products

As mentioned in Section 4, the main amine degradation products includes aldehydes, amides (mainly formamide), nitrosamines and nitramines. Environmental impacts from these components are investigated by Norwegian Institute for Air Research (NILU) [42].

The maximum air concentration of some of the degradation products that can be expected from a CO_2 capture plant are given in Table 4.

Table 4:   *Maximum hourly concentrations of amine degradation products in air (measured in $\mu g/m^3$) that can be caused by a CO_2 capture plant [42].*

Problematic Compound	Distance from plant (km)							
	1	2	3	4	5	6	8	10
Nitrosamines	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Nitramines	0.8	0.5	0.3	0.3	0.4	0.4	0.4	0.3
Formamide	1.0	0.6	0.4	0.3	0.5	0.5	0.5	0.4

One of the aldehydes that can be formed by amine degradation is the formaldehyde which is genotoxic. Formaldehyde can lead to cancer, but only in the presence of a cytotoxic component. There is no significant evidence that formaldehyde is toxic to the immune system or the reproductive system. The Norwegian Board of Health Supervision[8] has set a threshold for formaldehyde in the indoor environment at $100\,\mu g/m^3$. The concentration of formaldehyde generated from CO_2 capture process far below this threshold, and formaldehyde should not represent any health risks for humans.

Another degradation product is formamide, which could be hazardous to health. It could cause cancer and effect the reproductive ability. The risk threshold for chronic ecotoxicological effects is set to 24 μg/L as a 'Risk Factor of 50' (see appendix A for definitions). It is seen from Table 4 that expected emissions of formamide is far below this limit.

Most nitrosamines are suspected to be human carcinogens, but direct causal associations have not yet been found based on the available experimental data. Several case studies have indicated liver injury in humans from exposure to N-nitrosodimethylamine (NDMA). Corresponding to a 10^{-6} lifetime cancer risk, the value of 4 ng/m³ nitrosamines in air is used as critical level for the long term exposure of the population through inhalation. Calculations based on maximum amine

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[8] The Norwegian Board of Health Supervision is a governmental body for supervision related to health and social services. Website: http://www.helsetilsynet.no/templates/sectionpage____5499.aspx

emission from a CO_2 capture plant indicate that a long term air concentration of 2 ng/m^3 nitrosamines is possible. This is below the critical inhalation exposure limit, but it is certainly not far below. The nitrosamines are, however, rapidly decomposed by photolysis, and risk of health impacts from nitrosamines should be very small.

Amines can also degrade to nitramines, which are mutagenic and carcinogenic in rodents. But the mutagenic and carcinogenic activity of aliphatic nitramines seems in general to be much lower than those of the corresponding nitrosamines. There are however knowledge gaps related to health impacts of nitramines that needs to be filled.

There is very little knowledge available on the amines degradation products on the terrestrial vegetation. However, amides are known to be growth restrictive and are widely used in herbicides. Furthermore, the amine degradation products are in general known to be toxic to mammals and soil invertebrates, and they might also affect soil microorganisms. Especially nitrosamines and nitramines are found carcinogenic to mammals [42,45].

5.2. Water system impacts

The emissions of amines and amine degradation products from a CO_2 capture plant come into water system (rivers, lakes, oceans) by precipitation. This can cause environmental impacts not only for the water systems, but also for the marine environment.

5.2.1. Environmental impact in onshore water system

The Norwegian Institute for Water Research (NIVA) published a report on the environmental impacts of amines in water systems, and the following discussion is based on their report [46].

The lowest critical concentrations of the amines considered was found to be the MEA concentration that will have an impact on fish and algae. MEA will have a chronically impact on fishes above a critical level of 0.5 mg/liter. Algae will be chronically influenced by exposure to MEA concentrations above 0.75 mg/liter. Chronic exposure effects for invertebrates have not been identified yet according to available literature.

The highest level of toxicity from amides was found in selected invertebrates with the most sensitive effect found at a chronic exposure of 1.2 mg/liter formamide. Amide toxicity to fish and algae was often three fold higher than the lowest effect in invertebrates.

For nitrosamines, NDMA was found to have the highest toxicity effect in algae/bacteria when with a lowest observable effect at NDMA concentrations of 0.025 mg/liter. This is the lowest concentration found from all amines and amine degradation products that have an impact on living species.

An interesting point is that the chronic toxicity concentration of nitrosamines for fish and invertebrate is higher than acute toxicity concentration. This is contrary to what was expected data and suggests a shortage of sensitive chronic toxicity data for nitrosamine compounds.

The lowest concentration of nitramines that has an impact on living species was found for the compound CL-20[9] where a concentration above 0.2 mg/liter had chronically effects for fish. A critical concentration of 0.4 mg/L (also CL-20) had chronically impacts for invertebrate. Based on the available data, the toxicity concentration of nitramine are in the range from 0.2 to 6 mg/liter. This must be considered as a temporary result as long as the chronic effect for algae/bacteria has not been identified yet.

NIVA has summarized their data for acute and chronic concentrations as shown in Table 5.

Table 5. Summary of the most sensitive responses for amine emissions and main amine degradation products. The data is given as mg/liter; "⎯" indicate that data is not available yet [46].

Group	Test	MEA	AMP	MDEA	PIPA	Amides (Formamide/ Acetamide)	Nitrosamine	Nitramine
Fish	Acute	20 (NOEC)	100 (LC50)	100 (LC50)	52 (LC50)	5000 (Formamide)	5.85 (NDPA)	3.6 (RDX)
	Chronic	⊢	—	0.5	20	—	200 (NDMA)	0.2 (CL-20)
Inverte brate	Acute	83.6 (LC50)	100 (NOEC)	230 (LC50)	10 (LC50)	13 (Formamide)	7.76 (NDPA)	6.01 (RDX)
	Chronic	—	—	—	—	1.2 (Formamide)	100 (NDMA)	0.4 (CL-20)
Algae/ Bacteri a	Acute	6 (LC50)	20 (LC50)	20 (LC50)	13 (LC50)	49 (Acetamide)	—	3.2 (RDX)
	Chronic	0.75 (LOEC)	—	—	—	6600 (Acetamide)	0.025 (NDMA)	—

NOEC: No observable effect concentration
LC50: Lethal concentration at which 50% of the population are killed

NIVA has calculated the maximum annual amine emissions to avoid environmental impact to water systems. The calculations are based on a location at west coast Norway where the full scale CO_2 capture plant at Kårstø is planned. A typical annual precipitation (rainfall) of 2000 mm is assumed, and the calculation is based on the lowest MEA impact concentration on algae/bacteria which was of 0.75 g/liter (*c.f.* Table 5). It is found that the amine emissions from the plant should not exceed 1579 tonnes in order to avoid chronic toxic effects in algae. The result can be compared to the data in Table 1 where it is estimated that the CO_2 capture plant at Kårstø will annually emit 40 to 160 tonnes amine or amine degradation products. By comparing these numbers it is seen that the expected amine emissions will be at least ten times lower than the critical limit, and this simplified calculation indicate that there will be minimal risk for amine emissions having impacts on aquatic organisms [42,44].

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[9] CL-20 is the abbreviation of the nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane

It is however necessary to pay special attention to nitrosamine. If a lifetime risk of no more than one incident of cancer per 100,000 inhabitants, i.e. 10^{-5} lifetime cancer risk, is taken as an acceptable risk level, the critical nitrosamine concentration is only 7 ng/liter in precipitation. This result is based on the assumption that 2 percent nitrosamines are generated from amine atmospheric degradation and no further degradation or biodegradation happens in the atmosphere, soil and water [42]. The maximum tolerable total amine emissions from a CO_2 capture plant would then be 24 tonnes per year. This is lower than the expect amines emission from a CO_2 capture plant (see Table 1), which may threaten drinking water quality in water system close to the plant. This indicates that nitrosamines may represent a minor risk for cancer.

5.2.2. Environmental impact in marine environment

The environmental impact of amines and their degradation products in marine environment is similar, but not as severe as impacts on water systems (*c.f.* Section 5.2.1). The concentration of the amines and the degradation products will be lower in marine environment than in water systems, which is an indication of lower risk of impact. It is however still very important to assess the aquatic toxicology and biodegradation of amines in marine environments in order to prevent long term adverse effect of amine emissions.

Amines emitted to the marine environment will often undergo biodegradation where they are transferred to harmless components, but the biodegradability of different amines varies a lot as shown in Figure 9. The biodegradability of amines is represented by the purple bars in this figure, and the longer bars, the high biodegradation and thereby reduced risk of environmental impacts. The red line represents the lowest acceptable biodegradation for a chemical to be released in the marine environment and the green line represents the lower limit for chemical to be released independent of the ecotoxicity [47,48]. It can be seen from the figure that several of the amines used in CO_2 capture, like MDEA, AMP, DGA, and PIPA, have biodegradabilities below the lowest acceptable value.

In addition to the biodegradability, the ecotoxicity of amines must also be considered to assess the environmental impact in environmental systems. Ecotoxicity of the same amines as considered above are given in Figure 10. The ecotoxicity is measured as EC-50, which is the concentration where algal growth is inhibited by 50 percent. The blue line in the Figure shows the lowest acceptable value for a chemical to be released in the marine environment, and it is seen from the figure that the amines most common in CO_2 capture have values above this lowest acceptable limit.

The biodegradation and ecotoxicity results shows that not all the amines considered for CO_2 capture can be released in the marine environment. Many commonly used amines, such as MDEA, AMP and Piperazine, have very low degradability and will have a long persistence time in marine environments. On the other hand, most alkanolamines, like MEA, have a toxicity level between 10 and 1000 mg/L and a BOD level at around 25 percent, which are above the lowest acceptable

values for release of chemicals to the marine environment. MEA is therefore an acceptable amine when it comes to degradability and toxicity. Furthermore, MEA can biodegrade under aerobic and anaerobic conditions. Ammonium is formed under aerobic conditions, and ammonium, acetic acid and ethanol are the major breakdown products under anaerobic condition [49,50].

An interesting result is that the amines with amino acids group show a high biodegradability in combination with low toxicity. It should therefore be further investigated if this class of amines could be used in CO_2 capture.
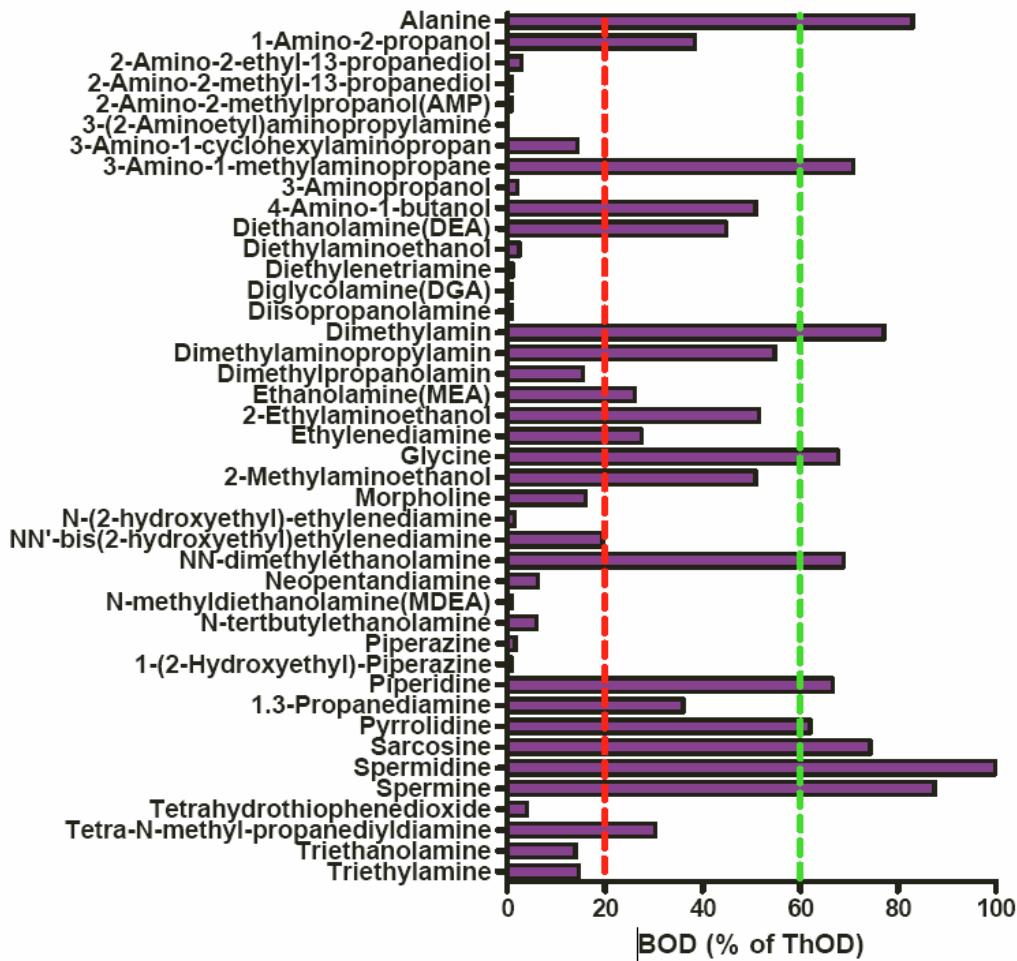
Figure 9: Biodegradability of some amines. The Biological Oxygen Demand (BOD) is a measure for biodegradation, and the purple bars are the BOD in percent degraded amine relative to the theoretical oxygen demand (ThOD) [48]. *The biodegradation results were determined according to the OECD guideline 306, "Biodegradability in seawater". The red line represents the lowest acceptable value for a chemical to be released in the marine environment and the green line represents the lower limit for chemical to be released independent of the ecotoxicity.*
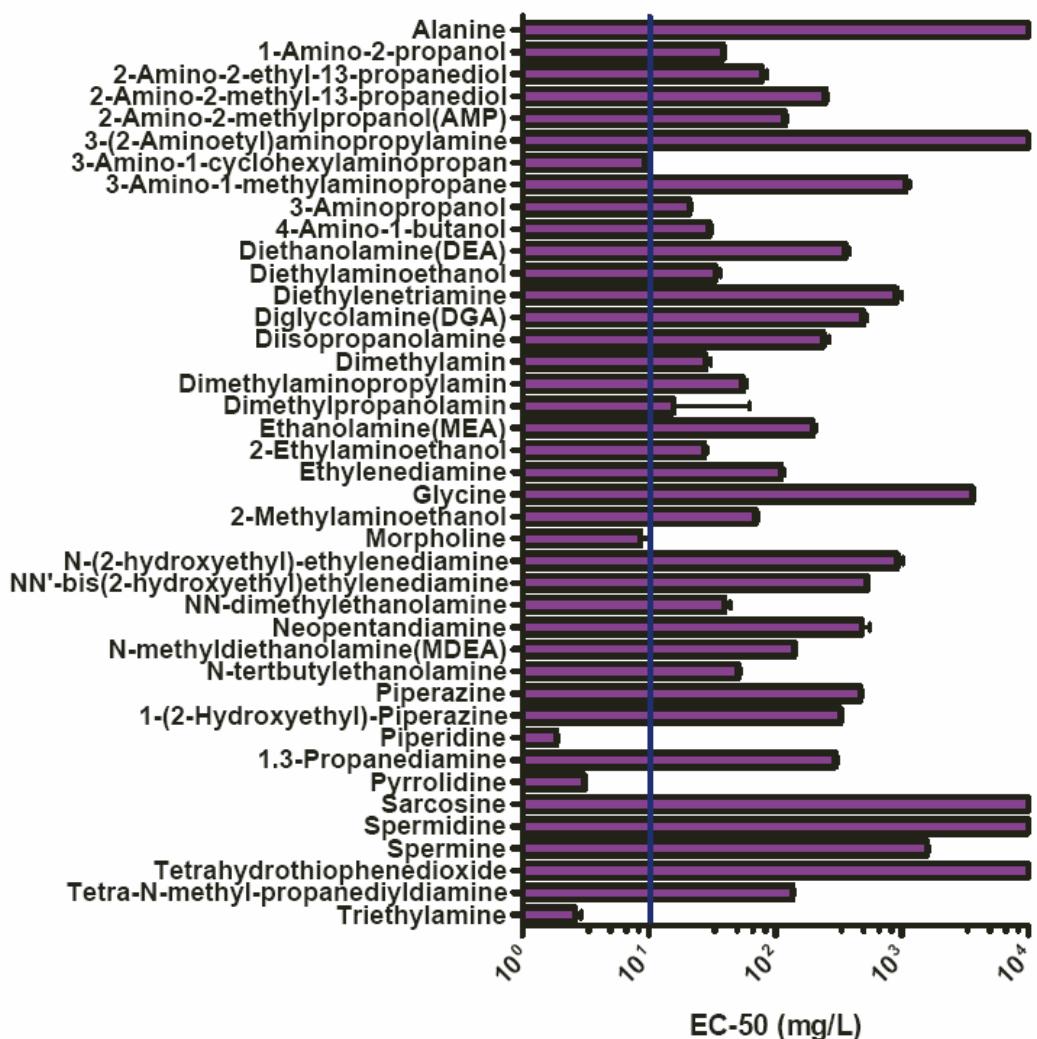
Figure 10: Ecotoxicity of some amines. Ecotoxicity is here presented as EC-50, i.e. the concentration where algal growth is inhibited by 50 percent. The results were determined by a marine phytoplankton test conducted according to ISO/DIS guideline 10253, using the alga Skeletonema Costatum [48].

There is no detailed literature available on biodegradation and ecotoxicity of amine degradation products. Evaluation of the amines degradation products' environmental impact is difficultly to asses, but it is important that future research programs focus on establishing such data.

5.3. Amine waste

Amine waste products produced in the CO_2 capture process represents an environmental risk and it should be handled thereafter. The composition of the amine waste is mainly degradation products (thermal and oxidative) from the capture process. It is clear that the amine waste is hazardous wastes, and releasing these waste products in the environment must be illegal. The environmental impact from the amine waste is still uncertain, but releasing them to environment would surely cause problems to human health and environment.

There are general regulations in place for handling hazardous waste, and amine waste products should also be handled according to these regulations. The most obvious way for handling amine waste products will be to burn the waste at officially approved hazardous waste incineration facilities.

In addition to the possibility of direct release of amine wastes to the environment, there is also the possibility of leakage of amine waste during transport. Waste release during transport can cause a much bigger environmental problem than direct emissions from the plant, because leakage during transport can bring the waste close to residential areas [27].

The cost of amine waste transport and incineration is estimated to vary from 2000 to 3500 NOK per tonne amine. Based on the results in chapter 3 it can be assumed that around 1000 tons amine waste is produced per year by a CO_2 capture plant with a capacity of 1 million tonnes CO_2 per year. By taking the high end of the cost interval above, the amine waste handling cost will be approximately 3.5 NOK/tonne CO_2, or 0.4 EUR/tonne CO_2. In the McKinsey's report on CCS economics [51], the cost of CO_2 capture and storage is estimated to around 50 to 70 per tonne CO_2, and the cost of amine waste handling is therefore less than 1 percent of total CCS cost [26,27].

6. Conclusions and recommended actions to reduce environmental and health risks

An amine based capture plant will in general have several positive impacts on the environment. An amine plant will not only remove 85 to 90 percent of the CO_2, but considerable amount of other polluting components such as ashes, NO_X and SO_2 will also be removed due to required pre-treatment of the flue gas. From an environmental viewpoint the best amine plant is the one that demonstrates minimum energy requirement, high degree of CO_2 capture, minimum liquid waste, and minimum amine related emissions to air.

Amines represent a health risk, but there is a lack of knowledge on health risks related to amines used for CO_2 capture. Available literature shows that some amines and amines degradation products can have negative effects on human health (irritation, sensitization, carcinogenicity, genotoxicity). The amines can also be toxic to animals and aquatic organisms, and eutrophication and acidification in marine environments are also possible. The impacts listed above represent worst case scenarios, and the possible impacts are strongly dependent on which types of amines that are used in the CO_2 capture process and the actual amount of amine emissions.

MEA is today the most common amine used in CO_2 capture processes. MEA have a relative high biodegradability, and MEA will in itself have no adverse effect to the human health, animals, vegetation and water organism. The airborne emissions of nitrogen and ammonia generated from amine decomposition can however cause eutrophication and acidification. Other amines commonly used for CO_2 capture like AMP, MDEA and PIPA are ecotoxicological and have low biodegradability, and they will have higher environmental impact than MEA.

Amines will start degrading to other products once they are emitted from a CO_2 capture plant. There is a variety of degradation products and most of them, like amides, nitramines and aldehydes will not have negative environmental effects. Nitrosamines will probably be the degradation products with the most adverse environmental impacts as they can cause cancer, contaminate drinking water and have adverse effects on aquatic organisms. Please note that these consequences also represent a worse case scenario at maximum amine emission from the CO_2 capture plant.

It is necessary to perform research activities to identify all the health risks related to amines. Once the risks are identified, there must be performed new studies to define how the risks can be tackled so that amine based CO_2 capture plants can be designed and operated without any health and environmental risks.

The available literature suggests that the environmental and health risks represented by amines in CO_2 capture are manageable, and most likely do *not* give reason to inhibit or slow down the wide-scale deployment of CCS. This is only true however, if sufficient effort is given to close remaining knowledge gaps and develop proper risk management strategies. This effort should include the following activities:

1. Carry out comprehensive research programs at national and international levels to fill remaining knowledge gaps on environmental impacts from amines.

2. Continued effort to identify and develop new or improved amines, or mixture of amines, that gives far less emissions of amines and degradation products than the amines used for CO_2 capture today.

3. Develop amine based CO_2 capture plants with minimum emissions to air.

4. Establish sound strategies for handling of amine waste and degradation products, such as incineration and biodegradation of waste into harmless and valuable products.

5. Develop amine-free CO_2 capture processes, such as absorption based on carbonates, or other CO_2 capture concepts like adsorption, chemical looping combustion and separation by membranes.

6. Once the knowledge gaps on environmental impacts are filled, new regulations must be adopted on national and international levels to ensure amines are used for CO_2 capture in ways that do not give any negative environmental impact.

7. Use demonstration programs to address risks related to amines by requiring that all demonstration projects based on amine absorption include research activities related to health and environmental impacts of amines.

The recommendations are discussed in detail below.

6.1. Fill knowledge gaps on environmental impacts

There is a lack of knowledge on environmental impacts of amines and their degradation products. More research is required to fill the gaps, and the research should focus on the following aspects [39,40]:

- Determine the atmospheric degradation paths, precise degradation yields, and degradation products' life time in the atmosphere.
- Human toxicity exposure limits (both acute and chronic) must be determined in order to establish safety limits.
- An experimental and simultaneous laboratory approach should be addressed for studying the ecotoxicity (both acute and chronic) to terrestrial ecology and aquatic environment.

It is important that the required research activities listed above are carried out for all amines that are considered as solvents in CO_2 capture.

In order to evaluate the amine environmental impact exact, the precise amount of amine emissions must be measured. This is challenging, and due to the amine's hydrophilic property (and the polarity of the amine) it could be difficult to analyze the amine concentration in the waste water. It is however possible to analyze primary and secondary aliphatic amines in waste water by gas chromatography-mass spectrometry [52].

With precise monitoring of amines emissions, it will be straight-forward to determine the critical limits of amine emissions and to control the real amines emission from the CO_2 capture process. New research activities should therefore focus on developing sensitive detectors that can monitor exhaust gas and waste water composition.

Several projects are ongoing to fill the knowledge gaps. Some of the most interesting experiments are performed in a large projects lead by the Norwegian Institute for Air Research (NILU) where data on amine degradation will be collected by large scale experiments in Valencia, Spain, in the world's largest laboratory for study of atmospheric chemistry [10]. Results from the experiment is expected late 2009.

6.2. Develop new and improved amines

There are research activities ongoing worldwide to develop new and improved amines, or mixtures of amines, for CO_2 capture. While the main purpose of this research undoubtedly is to reduce the energy consumption in the CO_2 capture process (and hence it's cost of operation), it is also a clear objective to minimize environmental impacts.

Ongoing research on finding more efficient amines for CO_2 capture will reduce the required volume for amines, and a secondary effect will be reduced amine emissions and amine waste. The research should also focus on finding amines that can lead to lower operating temperature in the stripper as this will reduce the rate of thermal degradation reactions. New innovations that could reduce the oxygen content in the capture process can also reduce the rate of degradation reactions [53].

Corrosion is a challenge in a CO_2 capture plant, and severe corrosion could lead to sudden and acute leaks of amine. It is therefore important to monitor and reduce the corrosion rate. By carefully monitoring corrosion, it is straight-forward to manage the risk of corrosion-induced

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[10] The NILU project is entitled "Amine Emissions to Air during Carbon Capture" and it is carried out in the EUPHORE in Valencia – the world's largest laboratory for studies of atmospheric chemistry. More information is available at the home site of one of the sponsors, the Research Council of Norway: http://www.forskningsradet.no/en/Newsarticle/Investigating+amines/1242673267486&p=

leakages. The corrosion could furthermore be lowered by using amines giving low corrosion rate or by adding corrosion inhibitors such as sodium metavanadate ($NaVO_3$) and copper carbonate ($CuCO_3$). Potential corrosion problems should also be addressed in the design phase as proactively altering the design and material of equipment can eliminate specific corrosion problem [28,29,30,31,54,55].

Finally, proper operation is very important to lower the amine emission in the CO_2 capture plant, and improved general knowledge of the complete CO_2 capture process will help reduce amine waste and amine emissions.

6.3. Develop amine plants with minimum emissions to air

Several suppliers of amine plants are investigating measures in the design of the plant that could reduce the emissions to air. Large scale CO_2 capture plant has not been built yet, and it is the understanding in the industry and research groups that emissions could be reduced to a minimum, far below the worst case scenarios addressed in the literature. Such improvements should be tested in planned CCS demonstration projects.

The possible environmental impacts of amines mentioned in this report are identified based on theoretical analysis of maximum amine emissions from a CO_2 capture plant. Technology suppliers have established comprehensive R&D programs to reduce amine emissions, and some suppliers says that the emissions will, within short time, be well below the worst case scenarios found in the literature. It has been said that amine emissions to air could be as low as less than 1 ppm. This has, however, not been documented in any scientific publications, but if such low emission rates can be achieved it will significantly reduce the risk of environmental impacts.

6.4. Ensure sound amine waste handling

Amine waste is defined as hazardous waste and it should be handled thereafter. According to regulations hazardous amine waste should be incinerated by companies officially approved for handling hazardous waste.

The technology and market for incineration of amine waste already exists. In Norway, for example, the cement producer Norcem has the capacity and license to handle 130,000 tonnes of hazardous waste per year in their hazardous waste incinerator [26,27].

In addition to incinerating amine waste it is also possible to biodegrade the waste into harmless products. Furthermore, MEA degradation products can be used to reduce NO_x emissions. Ammonia and urea are common chemicals for reducing NO_x emissions today, but these

chemicals could be replaced by MEA degradation products. This possibility could be tested in the Norcem cement kiln [26,27,56].

Another alternative is to produce biogas from amine waste. Bacterial degradation in absence of air can process amine waste into biogas which is a renewable energy source and a valuable product [26,27].

More research should be carried out with the aim to turn these alternatives into standards methods for amine waste handling. Further research on amine waste handling should also include activities on how to reduce the risk of leakage during transport of amine waste.

Finally, it is important to ensure that there are capacities available for handling the large volumes of amine waste that can be expected from a large global deployment of CCS. With all the amine based CO_2 capture plants that are planned built the coming decades it will be important to ensure that there exist hazardous waste handling facilities with sufficient capacity to handle all the amine waste.

6.5. Develop alternatives to amines

Absorption by amines is not the only option for CO_2 capture. Other possibilities like absorption by carbonates, cryogenic distillation, adsorption and membrane separation [14,21,57,58] should be further developed, and if these solutions can be further improved, they could turn out as better alternatives for CO_2 capture than absorption by amines. While the environmental risks that we are now facing with amines would then be eliminated, it is important to note that these other solutions could represent other environmental risks. It should also be noted that absorption by amines is the most mature alternative for CO_2 capture today, and this amine based technology will most likely be used in the majority of full scale CO_2 capture plants before 2020.

Zeolites [11] represent an alternative for amine based CO_2 absorption with minimized amine emissions. Zeolites can capture emitted amine and degradation products and further degrade them to harmless substances. Some Zeolites can even capture hazardous volatile nitrosamines [59]. In addition, Zeolites with proton or sodium cation can be used to further degrade volatile nitrosamines by using a ligand exchange process to separate the ethoanolamine and butyl amine from dilute amine containing waste water [60].

Using other solvents for the CO_2 absorption has been widely researched for many years. One of the most promising technologies is the "chill ammonia" process developed by Alstom where chilled ammonium bicarbonate is driving the separation process. This solvent is stable and do not degrade. The solvent is harmless to the environment, but the technology is immature and NH_3 emission to the environment represents a possible environmental risk [21].

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[11] Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents.

Cryogenic distillation separates the CO_2 at a low temperature by the relatively high triple point temperature of CO_2 (-56.6 ^{o}C). CO_2 can be separated in a pure form by partially liquefying the mixture of CO_2 and other inert gasses followed by a distillation step above the triple point temperature. This technology can only be carried out when the CO_2 concentration in the feed gas is high, and a drawback is the high energy demand for cooling the feed gas.

Physical adsorption to separate CO_2 in feed gas is widely researched and it represents a possible future alternative for CO_2 capture. The adsorbent used is a microporous solid such as silica gel, activated alumina, activated carbon and Zeolites. Some of them have been tested in laboratories and seems to work property, but further research to improve efficiency is necessary for this technology.

Membrane technology separates the feed gas streams into a permeate and a retentate stream, and this technology can be used to separate CO_2 from a feed gas with relative low CO_2 concentration. Like all the other alternatives to CO_2 capture by amine absorption, membrane CO_2 capture needs further research to increase its efficiency and solve technological challenges.

6.6. Establish proper regulations

Once the knowledge gaps on environmental impacts of amines are filled, it will be possible to design regulations for how a CO_2 capture plant can be operated without negative environmental impacts. Such new regulations should be implemented in international and national regulations for design, building and operation of CO_2 capture plants. These new regulations should be assessed by national authorities in the permitting phase of CO_2 capture projects, ensuring that only environmentally sound CO_2 capture plants are allowed built.

No commercial CO_2 capture plants based on amines should be built before the knowledge gaps on environmental impacts of amines are filled. Commercial CCS plants are, however, not expected before 2020 [51], and with comprehensive research programs on amines all knowledge gaps should be filled by then.

Possible environmental impacts from amines will most likely *not* stop or delay planned and ongoing global activities to commercialize CCS. With a comprehensive research program to fill the knowledge gaps on amines it will be possible to establish guidelines for how to build and operate amine based CO_2 capture plants. Such guidelines are a prerequisite, not a bottleneck, to ensure sustainable CO_2 capture.

6.7. Use CCS demonstration programs to address risks related to amines

At the moment there are no full scale CO_2 capture plant separating CO_2 from flue gasses from fossil fuelled power plants, but that is about to change because CCS is considered as one of the main strategies to combat global warming. The EU plans to build up to 12 demonstration projects for CCS by 2015, and the G8-leaders [12] has recommended building 20 CCS demonstration projects worldwide. This is only two of many examples of ambitious plans for building large scale CCS demonstration projects all around the world. The demonstration projects will be among the first-of-its-kind, and they will pave way for commercialization of CCS [51]. Demonstration plants for CCS will be expensive, too expensive for industrial companies to take the full bill. Public funding is required, or else the demonstration projects might not be built.

When governments invite to tenders for the CCS demonstration projects they should address the possible environmental impacts of amines in the tender documents. The tenders should demand that all CCS demonstration projects based on amine absorption should include research activities aiming at filling knowledge gaps related to environmental impacts of amines.

The EU has allocated 300 millions CO_2 emission allowances from its emission trading scheme, the EU ETS, for funding of CCS demonstration projects and innovative renewable projects. Depending on future allowance price this means that several billion euros of public funding could be available for CCS demonstration projects.

Bellona recommends that the European Commission clearly states in their tender documents that CCS demonstration projects with amine based CO_2 capture are eligible for funding only if they include research activities on the environmental impact of amines. Furthermore, the tender should also state that the projects with the most comprehensive research program on impact of amines will be preferred.

Similar prerequisites should be established not only in the EU, but wherever public funding is used for building large scale CO_2 capture plants.

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[12] G8: The Group of Eight. G8 is a forum for governments of eight nations: Canada, France, Germany, Italy, Japan, Russia, the United Kingdom, and the United States

Appendix A - Terminology

Acidification: A natural process that is used to describe the loss of nutrient bases by the process of leaching and their replacement by acidic. However, acidification is commonly associated with atmospheric pollution arising from anthropogenically derived sulfur and nitrogen such as NO_x or ammonia.

Carcinogen: It refers to any substance, radionuclide or radiation that is an agent directly involved in the promotion of cancer or in the increase of its propagation. This may be due to the ability to damage the genome or to the disruption of cellular metabolic processes.

Cytotoxicity: Cytotoxicity is the ability of being toxic to cells. Treating cells with a cytotoxic compound can result in a variety of cell fates. The cells may undergo necrosis, or the cells can activate a genetic program of controlled cell death (apoptosis).

Developmental toxicity: Any adverse effect attributable to exposure to a chemical, directed against the reproductive and/or related endocrine systems. Adverse effects include altered sexual behavior, fertility, pregnancy outcomes, and modifications in other functions that depend on reproductive integrity of system.

Ecotoxicology: The branch of toxicology concerned with the study of toxic effects, caused by natural or synthetic pollutants, to the constituents of ecosystems, animal (including human), vegetable and microbial, in an integral context

Eutrophication: Increase in chemical nutrients (compounds containing nitrogen or phosphorus) in an ecosystem. It can occur on land or in water. However, the term is often used for the resultant increase in the ecosystem's primary productivity (excessive plant growth and decay), and further effects including lack of oxygen and severe reductions in water quality, fish, and other animal populations.

Genotoxic: Describes a deleterious action on a cell's genetic material affecting its integrity. Genotoxic substances are known to be potentially mutagenic or carcinogenic, specifically those capable of causing genetic mutation and of contributing to the development of tumors.

Invertebrates: An invertebrate is an animal without a vertebral column. The group includes 95 percent of all animal species, all animals except those in the Chordate subphylum Vertebrata (fish, reptiles, amphibians, birds, and mammals).

Irritation: It is a state of inflammation or painful reaction to allergy or cell-lining damage. A stimulus or agent which induces the state of irritation is an irritant. Irritants are typically thought of as chemical agents.

Mutagenic: In biology, a mutagen is a physical or chemical agent that changes the genetic material (usually DNA) of an organism and thus increases the frequency of mutations above the natural background level. As many mutations cause cancer, mutagens are typically also carcinogens.

Reproductive toxicity: It is a hazard associated with some chemical substances which will interfere in some way with normal reproduction. It includes adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring.

Risk factor of 50: A risk factor is a variable associated with an increased risk of disease or infection. The risk factor of 50 is defined as the risk for no more than one person per 10 000 persons of exposure situation.

Sensitization: It is an example of non-associative learning in which the progressive amplification of a response follows repeated administrations of a stimulus.

Terrestrial fauna: Terrestrial animals are animals that live predominantly or entirely on land, as compared with aquatic animals, which live predominantly or entirely in the water.

Terrestrial plants: A terrestrial plant is one that grows on land. Other types of plants are aquatic (living in water), epiphytic (living on trees, but not parasitic), lithophytes (living in or on rocks) and aerial (can live hanging in air).

# Appendix B - Amines atmospheric degradation pathways

Suggested atmospheric degradation pathways for amines commonly used in CO_2 capture are given below [40]. The products highlighted in boldface are intermediate products with lifetime τOH [13] < 3 day, products highlighted in boldface blue color are final products with lifetime $\tau OH > 3$ days, and the possible nitrosamines and nitramines formed in the atmospheric degradation of amines are highlighted in boldface red color.

Atmospheric degradation of MEA
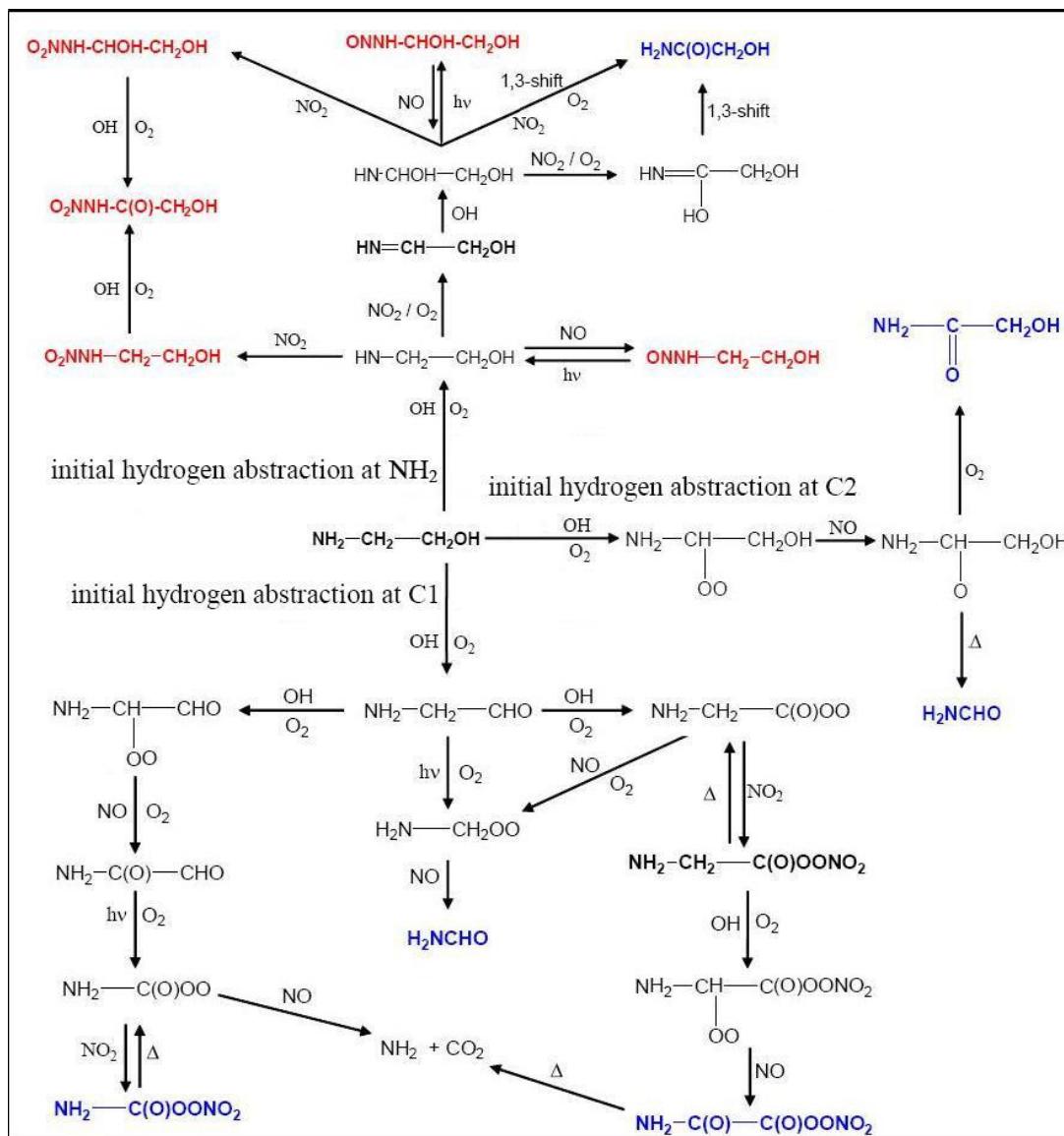
[13] τOH is a chemical's lifetime against atmospheric oxidation by the hydroxyl (OH) radical

Atmospheric degradation of AMP
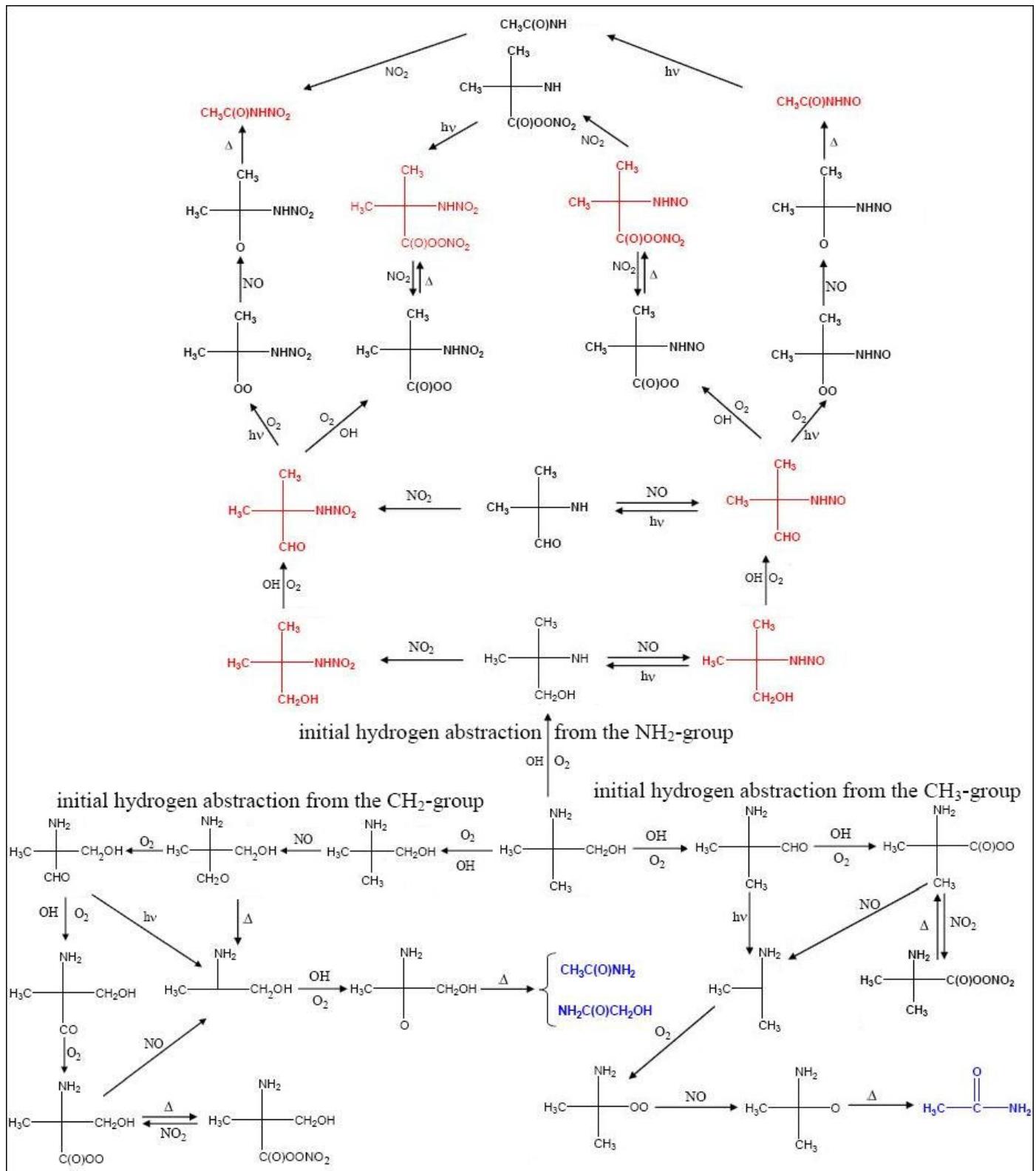
Atmospheric degradation of MDEA (1 of 2)

Atmospheric degradation of MDEA (2 of 2)

Initial hydrogen abstraction from the CH₃- group

44
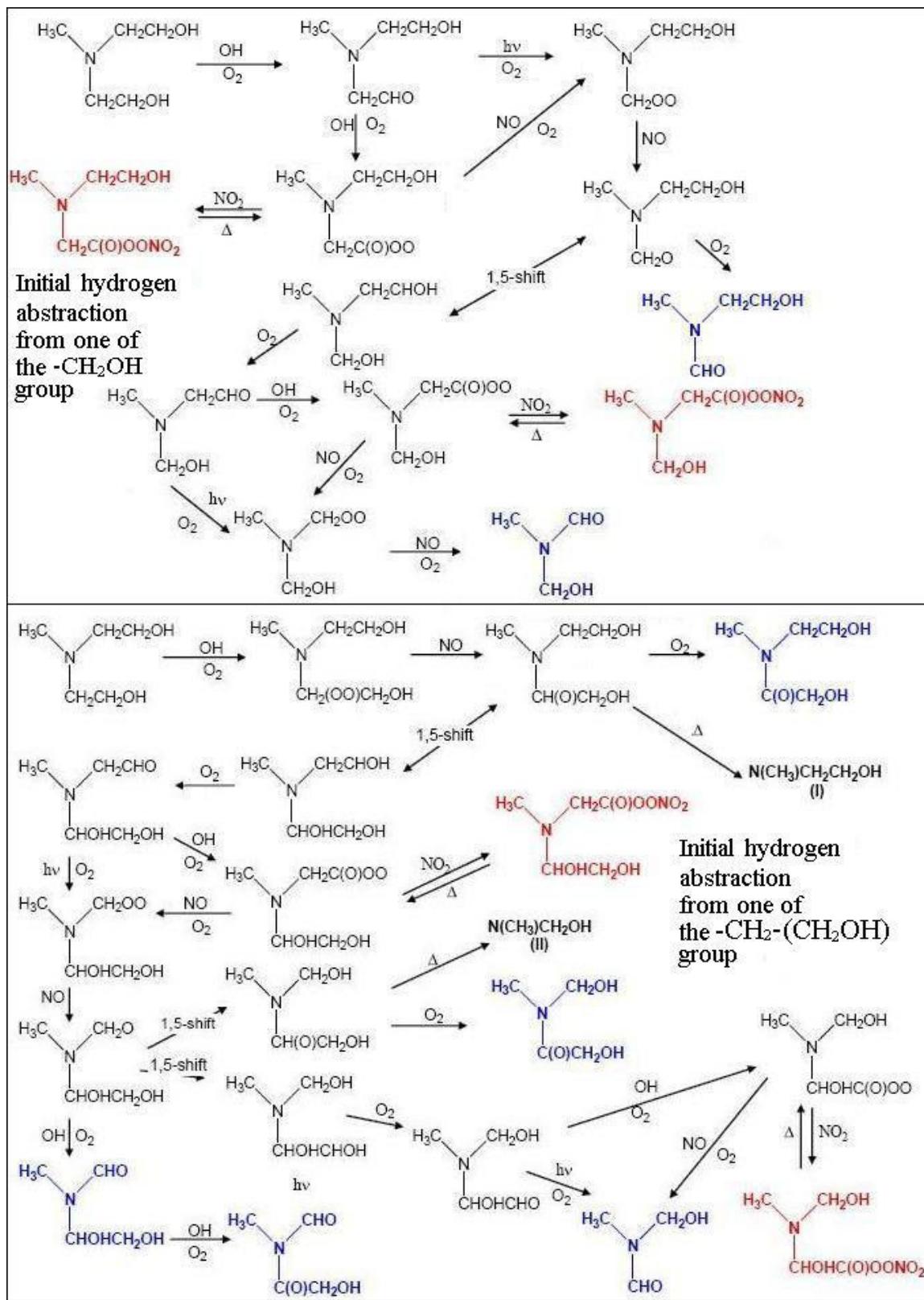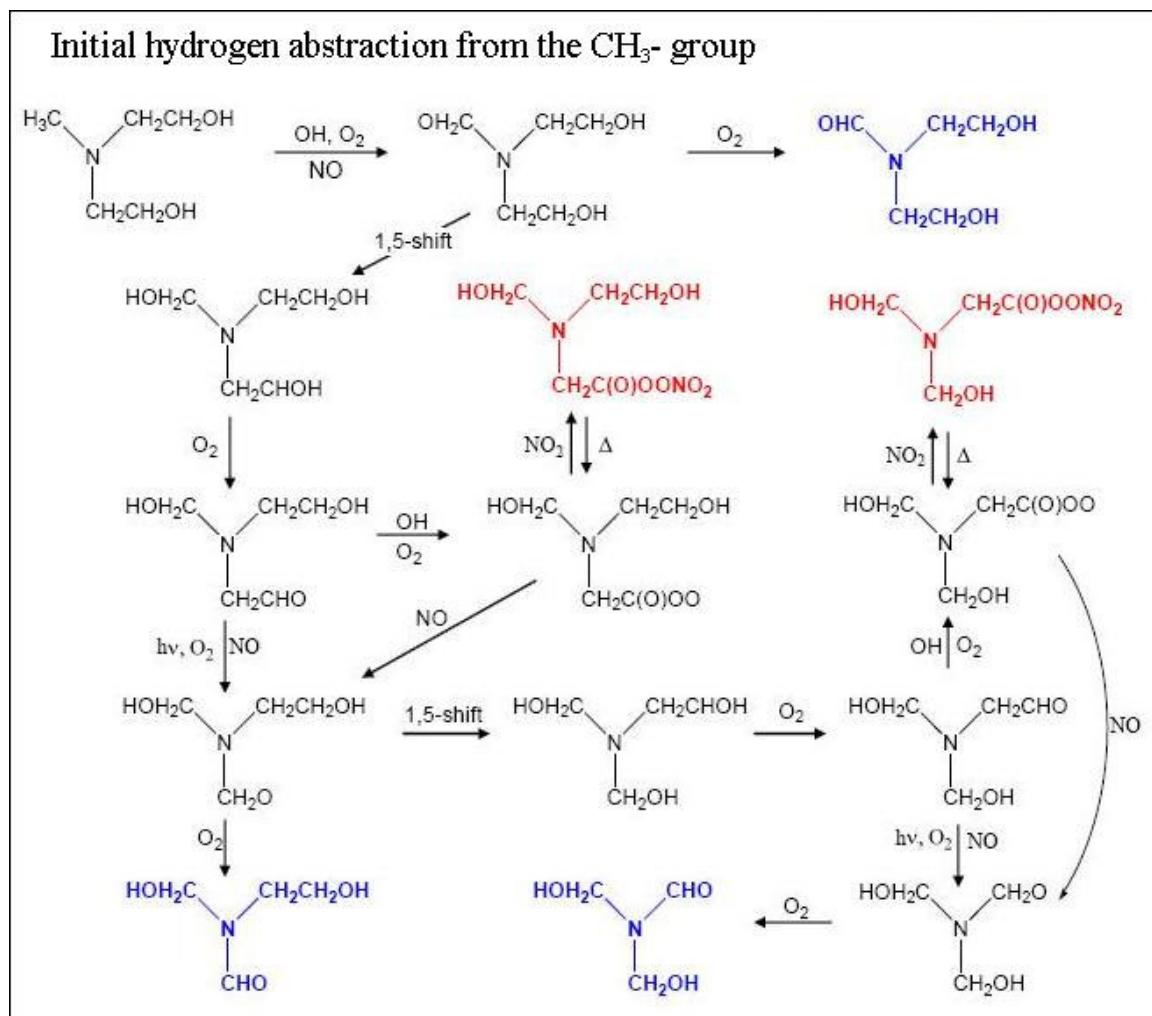
Atmospheric degradation of PIPA
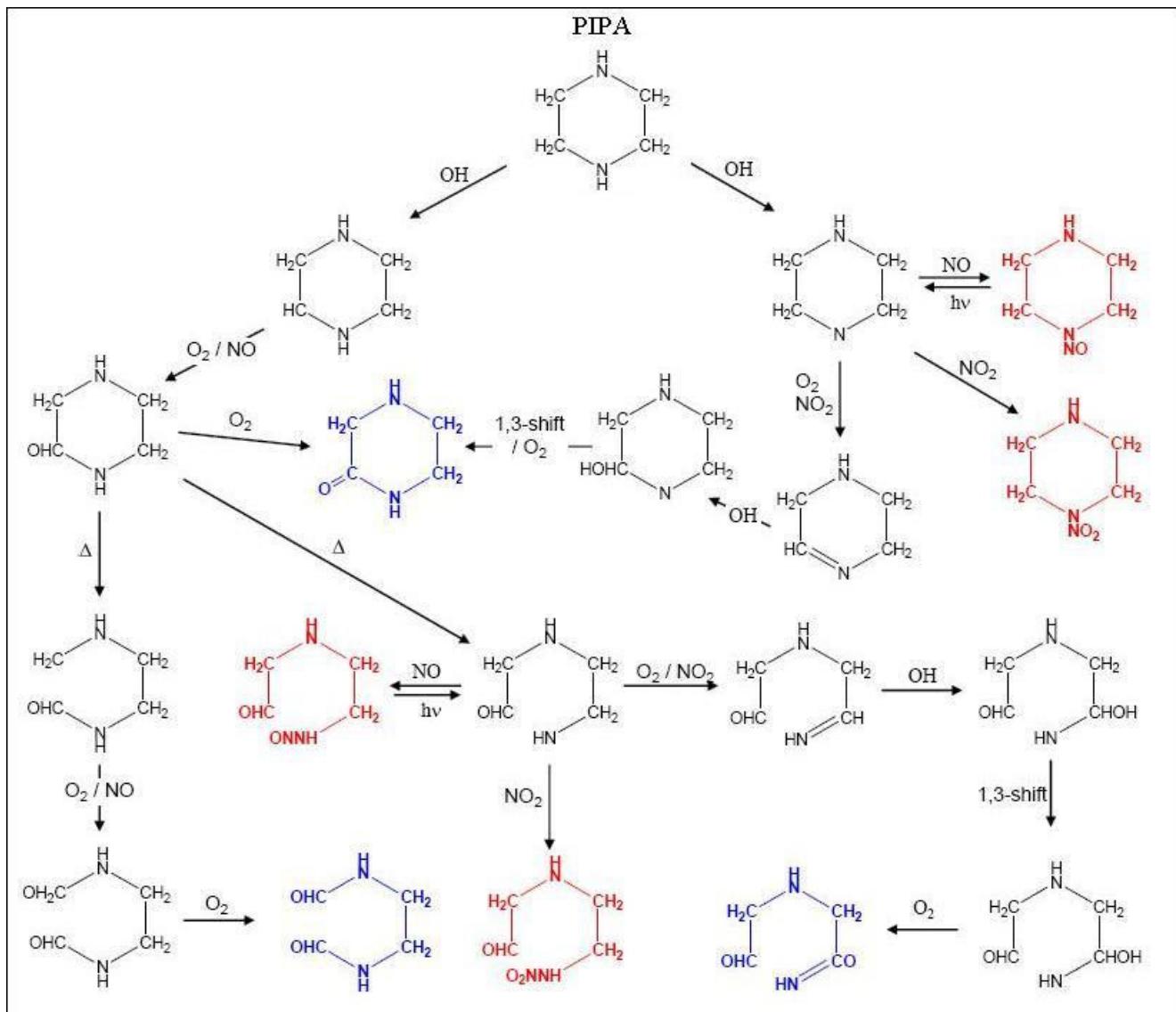
References

1   Intergovernmental Panel on Climate Change (IPCC), Climate Change 2007. Synthesis report, IPCC
     Secretariat, Geneva, Switzerland, November 2007, http://www.ipcc.ch/ipccreports/ar4-syr.htm.

2   Intergovernmental Panel on Climate Change (IPCC), Climate Change 2007, Working Group II report:
     Impacts, Adaptation and Vulnerability, IPCC Secretariat, Geneva, Switzerland, April 2007,
     http://www.ipcc.ch/ipccreports/ar4-wg2.htm.

3   Climate Change Information Kit. M. Wiliams (ed.). Published by UNEP and UNFCCC, 2002.

4   N. Stern, Stern Review: The economics of Climate Change, Cambridge University Press, October
     2006. , http://www.hm-
     treasury.gov.uk/Independent_Reviews/stern_review_economics_climate_change/sternreview_index.cf
     m

5   A. Stangeland et al, How to combat global warming. *Bellona Report*, June 2008,
     http://www.bellona.org/filearchive/fil_Bellona_CC8_Report_-_Final_version_-_30_mai.pdf

6   International Energy Agency (IEA), Energy Technology Perspectives 2006. *International Energy
     Agency, Paris*, France, 2006.

7   International Energy Agency (IEA), World Energy Outlook 2007, *OECD and International Energy
     Agency report*, Paris, France, 2007.

8   Intergovernmental Panel on Climate Change (IPCC), Climate Change 2007, Working Group III report:
     Mitigation of Climate Change, IPCC Secretariat, Geneva, Switzerland, May 2007,
     http://www.ipcc.ch/ipccreports/ar4-wg3.htm.

9   International Energy Agency (IEA), Energy Technology Perspectives 2008. *International Energy
     Agency report*, Paris, France. To be published June 2008.

10   The EU Technology Platform for Zero Emission Fossil Fuel Power Plants (ZEP), Strategic Research
     Agenda, 2006. Published online at http://www.zero-emissionplatform.eu/website/library/index.html.

11   The Future of Coal. Massachusetts Institute of Technology, 2007, http://web.mit.edu/coal/.

12   J. J. Dooley, R. T. Dahowski, C. L. Davidson, M. A. Wise, N. Gupta, S. H. Kim, E. L. Malone, Carbon
     Dioxide Capture and Storage. Report prepared by Batelle Memorial Institute, 2006,
     http://www.epa.gov/air/caaac/coaltech/2007_02_battelle.pdf.

13   J. A. Edmonds, M. A. Wise, J. J. Dooley, S. H. Kim, S. J. Smith, P. J. Runci, L. E. Clarke,
     E. L. Malone, G. M. Stokes. Global Energy Technology Strategy. Report prepared by Batelle
     Memorial Institute, 2007

14   Intergovernmental Panel on Climate Change (IPCC), Carbon Dioxide Capture and Storage, *IPCC
     report*, 2005, http://arch.rivm.nl/env/int/ipcc/pages_media/SRCCS-
     final/IPCCSpecialReportonCarbondioxideCaptureandStorage.htm.

15   Bellona Fact sheet. CO_2-capture, *Bellona publication*, February 2009,
     http://www.bellona.org/ccs/Artikler/fact_sheets_co2_co2

16   Information about the EU Energy and Climate Package is available at the Bellona CCS Web:
     http://www.bellona.org/articles/articles_2008/theEUclimate

17 Website for the Global CCS Institute (GCCSI): http://www.globalccsinstitute.com

18 The EU Technology Platform for Zero Emission Fossil Fuel Power Plants (ZEP), www.zero-emissionplatform.eu

19 Aage Stangeland, A model for the CO_2 capture potential, *International Journal of Greenhouse Gas Control*, Vol. 1, 2007, pp 418-429, http://www.bellona.org/filearchive/fil_Stangeland_-_Bellona_Paper-_Model_for_CO2_capture_potential.pdf

20 Bhurisa Thitakamol, Amornvadee Veawab, Adisorn Arroonwilas, Environmental assessment of the integration of amine-based CO_2 capture unit to coal-fired power plants for greenhouse gas mitigation, *2006 IEEE EIC Climate Change Conference*

21 Rodney J. Allam, Rune Bredesen, Enrico Drioli, Carbon dioxide separation technologies, M.Aresta (ed.), Carbon Dioxide Recovery and Utilization, Chapter 2, pp.53-120, 2003

22 A. Pedersen, L. Golmen, A. Sundfjord, T. Kroglund, Kjølevannsutslipp ved Kårstø: Konsekvenser av økt utslipp fra CO_2-fangstanlegg på Kårstø, Report no 5759-2009 from the Norwegian Institute for Water Research, February 2009. http://www.sft.no/nyheter/dokumenter/naturkraft_karsto_kjolevannsutslipp_konsekvensutredning230209.pdf

23 CO_2-håndtering på Kårstø - Fangst, transport, lagring, Report from the Norwegian Water Resources and Energy Directorate, 2007.

24 D. Borgnes and U. Ledje, CO_2-Kårstø - KU - Fagrapport konsekvenser av utslipp til luft, Report from Norsk Energi, 2009, http://sft.no/nyheter/dokumenter/naturkraft_karsto_luftutslipp_konsekvensutredning230209.pdf

25 M. H. Soma, D. Borgnes, S. Torstensen, CO_2-Kårstø - KU - Fagrapport sikkerhet, akutte utslipp og beredskap, samt avfall, report from Norsk Energi, 2009, http://sft.no/nyheter/dokumenter/naturkraft_karsto_sikkerhet_konsekvensutredning230209.pdf

26 Jon Hovland, Trygt å brenne aminavfall, *Nyhet fra CLIMIT*, juni 2009. http://www.gassnova.no/gassnova2/frontend/files/CONTENT/Climit_03_web2009.pdf

27 Preliminary results presented by Tel-Tek

28 J. Kittela, R. Idemb, D. Gelowitzb, P. Tontiwachwuthikulb, G. Parraina, A. Bonneaua, Corrosion in MEA units for CO_2 capture: pilot plant studies, *Energy Procedia 1*, 2009, pp. 791–797

29 A.Veawab, Corrosion in CO_2 capture unit for coal-fired power plant flue gas, *Greenhouse Gas Contro Technooogies*, Vol II. 2006, pp.1595-1598

30 Manjula Nainar, Amornvadee Veawab, Corrosion in CO_2 capture unit using MEA-piperazine blends, *Energy Procedia 1*, 2009, pp. 231-235

31 Sidney F. Bosen, Causes of Amine Plant Corrosion- Design Considerations, http://www.dow.com/PublishedLiterature/dh_0119/0901b80380119094.pdf?filepath=gastreating/pdfs/noreg/170-01460.pdf&fromPage=GetDoc

32 Majid Abedinzadegan Abdi, Axel Meisen, Amine Degradation: Problems: Review of Research Achievements, Recovery Techniques, http://www.engr.mun.ca/~abdi/papers/amin%20degradation-%20Conf-Tehran.pdf

33 Brian R. Strazisar, Richard R. Anderson, Curt M. White, Degradation of Monoethanolamine Used in Carbon Dioxide Capture from Flue Gas of a Coal-fired Electric Power Generating Station, http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/4b3.pdf

34 Susan Chi, Gary T. Rochelle, Oxidative Degradation of Monoethanolamine, *Ind. Eng. Chem. Res.*, 2002, 41 (17), pp 4178–4186

35   Stephen A. Bedell, Oxidative degradation mechanisms for amines in flue gas capture, *Energy Procedia 1*, 2009, pp.771-778

36   Ayanduntan O. Lawal, Raphael O. Idem, Kinetics of the Oxidative Degradation of CO_2 Loaded and Concentrated Aqueous MEA-MDEA Blends during CO_2 Absorption from Flue Gas Streams, *Ind. Eng. Chem. Res.*, 2006, 45, pp 2601-2607

37   Brian R. Strazisar, Richard R. Anderson, and Curt M. White, Degradation Pathways for Monoethanolamine in a CO_2 Capture Facility, *Energy & Fuels*, 2003, 17, pp. 1034-1039

38   Jason Davisa, Gary Rochelle, Thermal degradation of monoethanolamine at stripper conditions, *Energy Procedia 1*, 2009, pp.327-333

39   Svein Knudsen, Matthias Karl, Scott Randall, Summary Report: Amine Emissions to Air During Carbon Capture (Phase I: CO_2 and Amines Screening Study for Effects to the Environment), Report from the Norwegian Institute for Water Research, March 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=m5iQC0a%2fPqg%3d&tabid=2549&mid=5547&language=en-US

40   Hanne Birgitte Bråten, Arne Joakim Bunkan, Lihn Bache-Andreassen, Mohammad Solimannejad, Claus Jørgen Nielsen, Final report on a theoretical study on the atmospheric degradation of selected amines, report from the Norwegian Institute for Air Research (NILU), 2008, http://co2.nilu.no/LinkClick.aspx?fileticket=cCbJgoyMfrI%3d&tabid=2549&mid=5547&language=en-US

41   Per Arild Aarrestad, Jan Ove Gjershaug, Effects on terrestrial vegetation, soil and fauna of amines and possible degradation products relevant for CO_2 capture, report from the Norwegian Institute for Air Research (NILU), 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=7QAmOGCgzOg%3d&tabid=2549&mid=5547&language=en-US

42   Matthias Karl, Steve Brooks, Richard Wright, Svein Knudsen, Amines Worst Case Studies: Worst Case Studies on Amine Emissions from CO_2 Capture Plants, report from the Norwegian Institute for Air Research (NILU), 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=qNhKgZGUHjM%3d&tabid=2549&mid=5547&language=en-US

43   Marit Låg, Åshild Andreassen, Christine Instanes Birgitte Lindeman, Health effects of different amines relevant for CO_2 capture, Report from the Norwegian Institute of Public Health, February 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=nb9UzjagD7A%3d&tabid=2549&mid=5547&language=en-US

44   Matthias Karl, Amines and Rainfall Impact of Amines on Rainfall From Plume Clouds, report from the Norwegian Institute for Air Research (NILU), 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=tf1zThFvzvE%3d&tabid=2549&mid=5547&language=en-US

45   Marit Låg, Christine Instanes, Birgitte Lindeman, Åshild Andreassen, Health effects of possible degradation products of different amines relevant for the CO_2 capture, Report from the Norwegian Institute of Public Health, March 2009, http://co2.nilu.no/LinkClick.aspx?fileticket=Wr57O1TeyFk%3d&tabid=2549&mid=5547&language=en-US

46   Steven Brooks, The toxicity of selected primary amines and secondary products to aquatic organisms: A review, Report from the Norwegian Institute for Water Research, November 2008, http://co2.nilu.no/LinkClick.aspx?fileticket=zgmHr6lHBGQ%3d&tabid=2549&mid=5547&language=en-US

47   John W. Davis, Constance L. Carpenter, Environmental assessment of the alkanolamines, *Reviews of Environmental Contamination and Toxicology*, Vol. 149, 1977, pp.87-132

48   Ingvild Eide-Haugmo, Odd Gunnar Brakstad, Karl Anders Hoff, Kristin Rist Sørheim, Eirik Falck da Silva, Hallvard F. Svendsen, Environmental impact of amines, *Energy Procedia 1*, 2009, pp.1297-1304

49   Steven B. Hawthorne, Alena Kubtov, John R. Gallagher, James A. Sorensen, and David J. Miller, Persistence and Biodegradation of Monoethanolamine and 2-Propanolamine at an Abandoned Industrial Site, *Environ. Sci. Technol.*, 2005, 39 (10), 3639-3645

50   Ole Mrklas, Stuart Lunn, Angus Chu, Laboratory investigations of aerobic and anaerobic monoethanolamine biodegradation, *An Earth Odyssey*, 2001, pp. 1194-1200

51   Carbon Capture & Storage: Assessing the Economics, Report from McKinsey&Company, 2008, http://www.mckinsey.com/clientservice/ccsi/pdf/CCS_Assessing_the_Economics.pdf

52   Frank Sachet, Steffen Lenz, Heinz-Jiirgen Brauch, Analysis of primary and secondary aliphatic amines in waste water and surface water by gas chromatography-mass spectrometry after derivatization with 2,4-dinitrofluorobenzene or benzenesulfonyl chloride, *Journal of Chromatography A*, 764, 1997, pp.85-93

53   E.J. Stewart, R.A.Lanning, Reduce amine plant solvent losses: Parts 1&2, *Hydrocarbon Processing*, May 1994, pp. 67-81, and June 1994, pp. 51-54

54   Winyu Tanthapanichakoon, Amornvadee Veawab, Corrosion by Heat-stable Stalts in Amine-based CO_2 Capture Unit, Faculty of Engineering, University of Regina, Canada, http://www.netl.doe.gov/publications/proceedings/03/carbon-seq/PDFs/213.pdf

55   Olanike Lawal, Adeola Bello, and Raphael Idem, The Role of Methyl Diethanolamine (MDEA) in Preventing the Oxidative Degradation of CO_2 Loaded and Concentrated Aqueous Monoethanolamine (MEA)-MDEA Blends during CO_2 Absorption from Flue Gases, *Ind. Eng. Chem. Res.,* 2005, 44, pp.1874-1896

56   Yuan Li, Biodegradation of waste amines under anaerobic, micro-aerobic and aerobic conditions, Master Thesis, Telemark University College, 2008, http://teora.hit.no/dspace/bitstream/2282/746/1/Master_thesis.pdf

57   Jin Huang, Jian Zou, W. S. Winston Ho, Carbon Dioxide Capture Using a CO_2-Selective Facilitated Transport Membrane, *Ind. Eng. Chem. Res.*, 2008, 47 (4), pp. 1261-1267

58   Roda Bounaceur, Nancy Lape, Denis Roizard, Ce´cile Vallieres, Eric Favre, Membrane processes for post-combustion carbon dioxide capture: A parametric study, *Energy*, 31, 2006, pp 2556-2570

59   Zhengying Wu, Hongji Wang, Lili Ma, Jun Xue, Jianhua Zhu, Eliminating carcinogens in environment: Degradation of volatile nitrosamines by Zeolites Y and ZSM-5, *Microporous and Mesoporous Materials*, 109, 2008, pp.436–444

60   Frank R. Groves, JR, Amine removal from waste water by ligand exchange, *Chem. Eng. Commun.*, Vol. 31, 1984, pp.209-221