Evaluation of direct toxic impact of CO_2-capture chemicals in view of the REACH regulation.

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Commissioned by: StatoilHydro
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Synopsis:
StatoilHydro has commissioned Ostfold Research to perform a LCA (Life Cycle Assessment) of a possible future gas power plant at Tjeldbergodden, including CO_2 capture, transport and storage. StatoilHydro has evaluated the health and environmental properties of a number of possible CO_2 capture compounds and commissioned, in connection with the LCA an additional study on 8 amines in light of the REACH legislation.

The study showed that the compounds are not on the Restrictions List (Annex XVII of the REACH text) and do not fulfil the Authorisation criteria. The study also shows that although most of the studied compounds are classified as harmful to health and/or the environment, the classifications does not concern the most serious effects, f ex CMR (Carcinogenic, Mutagenic, and Toxic to Reproduction). This means that the usage of the compounds will probably not be severely restricted by REACH.

In order to get a complete overview of StatoilHydros REACH obligations and all effects of the legislation a more comprehensive study is needed. Central elements in this study would be: 1. Exposure studies 2. Mapping of degradation products, impurities and additives and 3. Assessment of Manufacturer/Importers readiness for REACH, including data gap analysis.

In the Innochem Research Project a method for calculating mixture toxicity is under development. This method could prove useful when developing exposure scenarios for carbon capture amine mixtures as required under the REACH regulation.

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(sign)	**(sign)**

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1 BACKGROUND

Statoil has commissioned a Life Cycle Analysis (LCA) Study of possible future gas power plant case at Tjeldbergodden, including CO_2 capture, transport and storage. One part of the study is an analysis of the possible consequences of the REACH regulation on CO_2 capture chemicals, degradation products, impurities and additives. Statoil have studied the environmental properties of a number of candidate compounds, most of them amines. 9 compounds and two degradation products were chosen for this study. Piperazine is an activator, and only used together with the amine MDEA.

The compounds are:

CO2 capture compounds	**CAS-no**
Mono-ethanol-amine (MEA)	141-43-5
2-Amino-2-methyl-1-propanol (AMP)	124-68-5
piperazine (PZ) (activator)	110-85-0
methyl-diethyl-amine (MDEA)	105-59-9
diisopropanolamine (DIPA)	110-97-4
diglycolamine (DGA)	929-06-6
di-ethanol-amine (DEA)	111-42-2
methylethanolamine (MMEA)	109-83-1
triethanolamine (TEA)	102-71-6
Metabolites	**CAS-no**
NH4+(aq) = ammonia dissolved in water	1336-21-6
NH3 (g) = gaseous ammonia	7664-41-7

Under the umbrella of the Norwegian Research Project Innochem research is being done to help companies fulfil their obligations according to the REACH regulation while keeping

other environmental effects to a minimum. The results of the project will be made available to the industry partners Jotun and HÅG, but also to Norwegian Industry. Ostfold research had the aim to use experience gained from, and tools developed in Innochem in the current project. One of the main results from Innochem, a method to calculate mixture toxicity in order to simplify exposure estimations in Chemical Safety Assessments, will however not be ready for use until the autumn 2008.

2 REACH AND OTHER RELEVANT LEGISLATION

REACH is the new chemicals legislation in the EC. The name says much about the content Registration (R), Evaluation (E), and Authorisation (A) of Chemicals (CH). Its aim is ambitious: All use of chemicals must be safe, no exposure to chemicals leading to harmful environmental or health effects is allowed. The responsibility for demonstrating safe use lies with the Downstream Users and manufacturers, a dramatic shift from the preceding legislation. It is important to note that REACH only concerns direct effects from chemical exposure, mostly toxic effects but also "physical" effects (f ex skin erosion from acids). The scope of the law is the whole value chain from extraction of raw material to disposal of finished product.

Combustion products are not within the scope of REACH.

REACH has many exemptions; especially in the cases where "overlap" with other legislation occur. One such example is cosmetics. The health effect of cosmetics is considered to be covered by the Cosmetics Directive and hence human health effects of cosmetic products or their ingredients are not covered by REACH, but environmental effects are. Not all "overlaps" leads to exemptions. This is the case with an industrial CO_2 capture plant. It is both covered by REACH and IPPC, the EU directive restricting polluting discharges from industry. An important element of IPPC is the granting of discharge permissions based on comparisons with Best Available Technology (BAT). REACH is more ambitious in its aim. The chemical exposure must not be harmful, irrespective of whether adequate technology is available or not.

The most important elements of REACH are the registration and the Chemical Safety Assessment. All substances that are imported into, or manufactured in the EU in amounts exceeding 1 ton/year for the specific manufacturer must be registered within a certain time frame. The registration must contain a number of specified data regarding physical-chemical properties, fate in the environment and toxicity towards human health and the environment.

The number of data required increases with increasing yearly tonnage manufactured/imported. Substances manufactured/imported in amounts exceeding 1000 tonnes/year face the toughest

data requirements and also the strictest time-line, registration must be submitted within 3,5 years after the implementation of the Directive.

The first step is pre-registration which must take place in the second half of 2008. The data requirement for pre-registration is small but the penalty for failing pre-registration is severe. If not pre-registered a compound cannot be placed on the market before a complete registration is submitted.

A Chemical Safety Report must be completed for every substance that is manufactured/imported in excess of 10 tonnes/year. The key element is a Chemical Safety Assessment (CSA). If the compound is classified as harmful to health or the environment, or are classified as PBT or vPvB then an Exposure Scenario (ES) must be calculated. Many of the compounds currently on the market have one or more classifications, many others have not undergone a full classification evaluation. Hence ES must be performed for a large number of chemicals. The key elements of an exposure scenario are:

1. Calculation of DNEL and PNEC = concentration levels considered to be “safe”, i.e. where no damage to human health (DNEL) and the environment (PNEC) occur.
2. Calculation of actual exposure levels.
3. Comparison of exposure levels with DNELs and PNECs.

An ES is based on an iterative process, i.e. steps 1-3 must be reiterated until the exposure levels are below the respective DNELs and PNECs. If the calculations show that the actual exposure levels exceed one or more DNEL and PNEC, some changes must be made and a new calculation must be made. These changes could be of a physical nature, f ex better ventilation, personal protective equipment or improvements in production equipment. It could also be introduction of more accurate data and more measurements that reduce safety factors. In the case of a carbon capture plant several possible reduction measures are possible, e.g. cleaning of the amine mix to remove degradation products, which is commonly done in plants run with MEA (monoethanolamine).

Development of the exposure scenarios require information from both manufacturer/importer (substance inherent properties) and all users down the value chain (all details regarding usage, f ex amounts used, exposure time, type of use (open/closed process), personal protective equipment, etc). Hence a close cooperation is needed between the companies in the value chain.

3 METHODOLOGY AND INPUT DATA

The goal of the analysis was to get a complete overview of the consequences of the REACH regulation on the use of certain compounds as CO2 sequestrates in a commercial CO2 capture plant.

A full analysis of consequences of REACH would consist of the following main steps:

1. **Establish Statoil Hydro's REACH obligations.**
   Does the company only fill the role as Downstream User or does it also fill the role as Manufacturer/Importer, e.g. by import the chemicals from a company outside the EU?
2. **Authorisation and restriction screening**.
   Are any of the compounds on the restriction list or fulfil the authorisation criteria?
3. **Assessment of exposure.**
   What is the extent of the exposure of the CO2 capture compound and their degradation compounds? Will the REACH demand for absolutely no harmful effects from exposure put severe restrictions on the running of the plant?
4. **Evaluation of importer or manufacturers readiness for fulfilling REACH obligations.** The most important obligation is the submission of registration but a more acute need concerns the pre-registration, which must be completed in the last 6 months of 2008. If not, the use of the compound will be treated as a new compound with all the disadvantages that this would entail.

The available information was not enough to perform all the above mentioned steps. Information is missing on:

- Identity of additives, impurities and degradation products. Concerning additives only the activator piperazine that is used together with MDEA, and the solvent Sulfolan that is used together with DIPA, are known. Concerning degradation products only NH_3 (g)/NH_4 (aq) are known. Generally commercial chemicals contain impurities, sometimes in relatively large proportions.
- Emissions of additives and their degradation products into the environment and working environment.
- Emission of impurities of capture chemicals and the degradation products of these impurities into the environment and working environment.
- Emission of capture chemicals and their degradation products into the environment.

This meant that part 3 could not be done. Part 4 could also not be done as the project did not entail contact with the manufacturers or importers of the chemicals. However by

using data from open sources it was possible to get an impression of exposure effects and data gaps for registration.

This study is based on data from the REACT Study (1), information directly from StatoilHydro and data from open sources (3, 4).

4 RESULTS AND DISCUSSION

StatoilHydro obligations
StatoilHydro does, in this context, have the role of Downstream User, as defined in REACH. Based on the information we have received we have no indication that StatoilHydro will be manufacturer or importer of CO2 capture chemicals or additives. However, if StatoilHydro will buy any of the compounds from a manufacturer outside the EU in an amount exceeding 1 ton/year the company will have to take on the duties of Importer. This would include registration and pre-registration.

As Downstream User the most important duty for StatoilHydro would be to follow the instructions given in the Safety Data Sheet, particularly the Exposure Scenario. StatoilHydro have no duty to report its intended use of the compounds to the M/I, but if this is not done then the company will have to fulfil the M/I obligations. If StatoilHydro communicates its use of the compound to the M/I, the company would most probably have to assist the M/I in the development of an Exposure Scenario (ES). Among the probable contributions from StatoilHydro would be all circumstances related to the use of the chemicals, f ex information regarding emissions, environmental fate, exposure and risk reduction measures:

- How much is emitted?
- In what compartments are the compounds emitted (ambient air, workplace air, salt water, fresh water, soil, etc)?
- How will the compounds spread and degrade in the respective compartments?
- How will human beings be exposed (how many people, how much time) either directly or indirectly, through the environment?
- What will be the effect of protective measures taken?
- How will organisms in the environment be exposed (species, concentration, etc)

Preliminary evaluation of health and environmental effects.
The study revealed that all but two (Methylethanolamine (MMEA) and diglycolamine (DGA)) of the studied amines were classified as harmful to health. Three of the compounds were classified as harmful to the environment: 2-Amino-2-methyl-1-propanol (AMP)

, NH_4^+(aq) and NH_3 (g). None of the compounds are included in the current list of restricted compounds in REACH.

Two of the compounds (MEA and TEA) are exempted from the REACH obligations as far as health effects as concerned. The reason is that these compounds are approved as cosmetic ingredients. They can be used in all rinse-off products and in stay-on products below certain concentration limits. DEA is specifically not approved in cosmetics probably due to the potential for nitrosamine formation. Based on this evidence it is not possible to generalise that secondary amines are worse than primary and tertiary amines.

We have seen the following tendencies from the available test data:

In general Piperazine is the most toxic. It is also least studied compound concerning environmental effects. Reported health effects include: immune system depression, neurotoxic effects, asthma upon workplace exposure and problems related coronary disease, asthma, bronchitis and emphysema.

Environment:

- Low bioaccumulation potential.
- When emitted, the compounds will most probably stay in the aqueous phase. Adsorption on soil and sediments will be very limited.
- Medium toxicity (R52 band, e.g. lowest toxicity 10-100 mg/l) to organisms in water.
- Biodegradability differs between the compounds, but the not readily biodegradable compounds are inherently biodegradable, i.e. no persistent compounds.
- Information on degradation products are missing.
- Data on chronic toxicity are missing.
- Data on toxicity on terrestrial organisms are missing.

Health:

- Piperazine has the highest potential for inducing negative health effects.
- Skin and eye irritation: Only in vivo animal tests are given.
- Acute and repeated dose toxicity: Few data gaps. .
- Mutagenicity/genotoxicity: In addition to Ames test some other tests have been performed.
- Carcinogenicity and reproductive toxicity. AMP and DGA have very little data, MDEA and MMEA is only slightly better.

The toxicity of the tertiary amine compounds is greatly increased if nitrosamines are formed. E.g. the reaction between TEA and Nitrite forms carcinogenic nitrosamines. Care must be taken in the design process to reduce the formation of nitrosamines in the environment and working environment.

Table 1. Overview of health and environmentally related classifications.

	Substance name	CAS-no	Risk phrases	Risk route	Environmental considerations
1	mono-ethanol-amine (MEA)	141-43-5	100 %: Xn; R20/21/22. C;R34.	Inhalation, skin contact and oral intake	Not readily biodegradable.
			Conc.>25 %: C;R20/21/22-34		
			Conc. 10-25 %: C;R34		
			Conc. 5-10 %: Xi;R36/37/38		
2	2-Amino-2-methyl-1-propanol (AMP)	124-68-5	100 %: Xi; R36/38. R52/53	Eyes and skin	
			Conc.>10 %:Xi; R36/38		Conc.>25 %:R52/53
3	piperazine (PZ)	110-85-0	C;R34, R42/43	Corrosive. Allergy sensitation inhalation og skin contact	R52/53
4	methyl-diethyl-amine (MDEA)	105-59-9	Xi; R36	Eyes.	
5	Diisopropanolamine (DIPA)	110-97-4	Xi; R36	Eyes.	
6	diglycolamine (DGA)	929-06-6	Not classified		Not classified
7	di-ethanol-amine (DEA)	111-42-2	Xn;R22-48/22	Inhalation, skin contact and oral intake.	
8	Methylethanolamine (MMEA)	109-83-1	100 %: Xn;R21/22. C;R34	Corrosive. Skin and oral intake.	
			Conc.>25 %: C;R21/22-34		
			Conc. 10-25 %: C: R34.		
			Conc.5-10 %: XI:R36/37/38		
9	triethanolamine (TEA)	102-71-6	Not classified		Not classified

Table 2. Overview of health and environmentally related classifications – degradation compounds.

	Substance name	CAS-no	Risk phrases	Risk route	Environmental considerations
1	NH_4^+(aq) = ammonia dissolved in water	1336-21-6	100 %: C; R34; N;R50.	Corrosive	R 50
			Conc.>25 %: C;N;R34-50		
			Conc. 10-25 %: C: R34.		
			Conc.5-10 %: XI:R36/37/38		
2	NH_3 (g) = gaseous ammonia	7664-41-7	R10 T;R23, C;R34	Corrosive. Inhalation.	N;R50

Authorisation screening and restriction check:

Based on the currently available information we conclude that none of the compounds fulfil the criteria for authorisation.

The investigations show that none of substances falls into any of the categories Carcinogenic (C), Mutagenic (M) or Toxic to Reproduction (R), class 1 or 2. Hence it does not fulfil the first criteria for authorisation.

The REACT study concludes that none of the studied compounds can be regarded as potentially bioaccumulating. This conclusion is hardly surprising when considering the polar nature, high water solubility and small size of the molecules. BCF measurements and calculations on some of the compounds support this conclusion. Hence we can conclude that none of the substances can be regarded as PBT (Persistent, Bioaccumulating and Toxic) or vPvB (very Persistent and very Bioaccumulating). This is the second criteria for authorisation.

The third criterion for authorisation is more general. It is formulated in Article 57 f:

"Substances - such as those having endocrine disrupting properties or those having persistent, bioaccumulative and toxic properties or very persistent and very bioaccumulative properties, which do not fulfil the criteria of points (d) or (e) - for which there is scientific evidence of probable serious effects to human health or the environment which give rise to an equivalent level of concern to those of other substances listed in points (a) to (e) and which are identified on a case-by-case basis in accordance with the procedure set out in Article 59".

RIP 4.4 (4) contains guidance on the interpretation on how to interpret and evaluate this article. The Guidance does not contain any lists of compounds or quantitative criteria. However the guidance on substances concerning persistence, bioaccumulation and toxicity contains very useful advice on the steps that should be taken to ascertain whether a compound fulfil this criterion.

The issue of endocrine disruption (ED) is much more complex since ED is not an endpoint, its effects are partially covered by the traditional categories such as Reproductive Toxicity and no test methods are currently available. However, the lists published by The Commission Working Group on Endocrine Disruption give a useful indication of ED Properties. However there is a risk for false negatives (the list does not contain all ED compounds) and false positives (not all compounds on the list are proven EDs).

From our study of the compounds inherent properties we could not find any indication of other harmful effects to human health or the environment.

Degradation products:
NH3 and NH4+ are degradation products of a number of the potential CO2 capture compounds, f ex Monoethanol amine (MEA).
Due to lack of information of degradation products no conclusions can be drawn on whether these fulfil the authorisation criteria.

Pre-registration:
The study did not involve communication with manufacturers and importers of the 9 compounds. Hence nothing is known about the status regarding pre-registration. However we expect that the pressure on pre-registration of the High Production Volume chemicals will be high. This means that the risk that these compounds will not be pre-registered is lower than for those with lower consumption.

Registration:
Most of the compounds studied are labelled as HPV (High Production Volume) compound in EUs IUCLID system. The compounds MEA, MDEA, DIPA, DGA, DEA and MMEA are HPV. TEA, Piperazine and AMP are not labelled as HPV. The amines labelled HPV are probably produced in excess of 1000 t/year. However the term HPV is related to the total amount produced, by all European manufacturers. The REACH regulations are not related to the total amount manufactured pr year but the amount imported or manufactured by the specific M/I (Manufacturer/Importer). Due to lack of data it is not possible for us to conclude what tonnage band the 8 amines will be in (1-10, 10-100, 100-1000, over 1000 tonnes/year) so it was decided to assume the > 1000 t/y tonnage band as a worst case scenario.
The study revealed large data gaps in the data available from EU official sources (IUCLID 4) when comparing with the needed registration data for compounds in the tonnage band >1000 tonnes/year. 40-60 % of the required health data is missing, whereas for environmental data

this percentage is lower 25-45 %. The main source is the official EU database IUCLID 4. However, these figures should be viewed with caution, for several reasons.

1. The companies probably have access to more data, but not published.
2. There are many exemptions from the testing requirements.
3. The data on this database has not been quality checked, very few are made under GLP conditions.
4. Much of the data comes from very old tests.
   Data on the tests are in many cases very scarce.

Hence the real extent of the data gaps is difficult to ascertain. The data must be checked by experts in the field of toxicology and ecotoxicology before the data gaps, if any, can be identified.

Chemical safety assessment:

In this study not enough data was available to make Chemical safety assessments. Exposure scenarios must be developed for most of the amines, including their degradation products. Some trends are however, clear:

1. Most of the classifications regard harm to human health. Many of these involve oral intake and skin contact. It is likely that such exposure can easily be avoided by relatively easy means. Once emitted in the environment the dilution effect probably will reduce the risk for human health damage to negligible levels. The inhalation route should also be relatively easy to handle. .
2. Few of the compounds are classified as environmentally harmful. Generally the compounds display low aquatic toxicity.
3. Two compounds (MEA and TEA) are approved for use in cosmetics and hence are exempted from all health related regulations in REACH. DEA is specifically not allowed because it will form carcinogenic compounds (nitrosamines) when reacting with certain other compounds, e.g. nitrites.

5 RECOMMENDATIONS FOR FUTURE WORK

In order to get a complete overview of the consequences of the REACH legislation it is necessary to perform an extended analysis. We recommend that the following steps be made:

a. The identity, and amounts formed, of the degradation products should be established.
b. The identity and amounts of impurities must be known.
c. The additives should be screened and investigated in the same way as the sequestering agents.

d. Exposure scenarios should be developed for the most probable candidate compounds and additives. The method for calculating mixture toxicity (developed in the Innochem project) for the purpose of simplifying development of Exposure Scenarios will be finished the autumn of 2008 and could prove a useful tool for StatoilHydro.
e. A cooperation effort with one or more suppliers should be done with the aim of making sure that the relevant Manufacturer or Importer will actually perform the REACH obligations, especially pre-registration and registration, within the specified time frames. It must also be established who should carry the costs for registration and supply missing data for registration. This is especially important for substances that have been used very little for this purpose before.

6 REFERENCES

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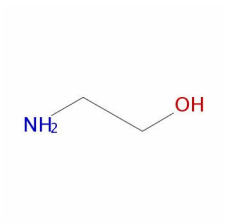
2. Solbraa, Even: "Fjerning av CO_2 i forbindelse med LNG-produksjon. Status for teknologien og utfordringer i årene framover".
3. Reach Implementation Project 3.2.1. Technical Guidance.
4. REACH Implementation Project 4.4. Guidance for the production of an Annex XIV Dossier.

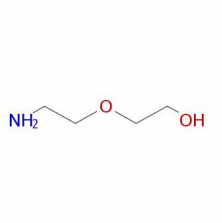
Annex 1. Evaluated candidate amine compounds.

Primary amines

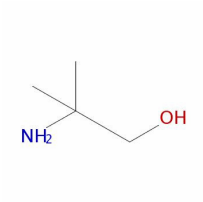
MEA



DGA

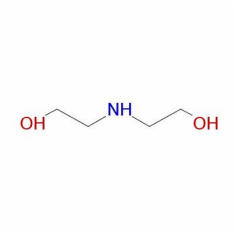


AMP

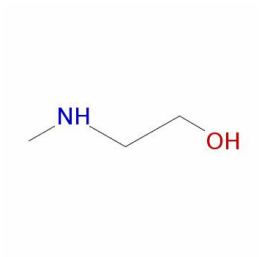


Secondary amines

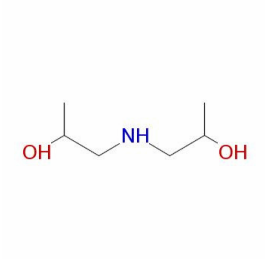
DEA



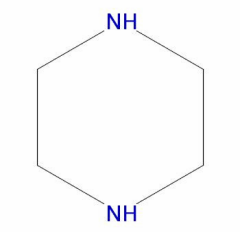
MMEA



DIPA

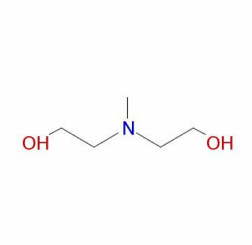


Piperazine

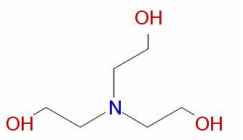


Tertiary amines

MDEA



TEA



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