ENVIRONMENTAL IMPACT OF SOLVENT SCRUBBING OF CO_2

Technical Study

Report Number: 2006/14

Date: October 2006

INTERNATIONAL ENERGY AGENCY

The International Energy Agency (IEA) was established in 1974 within the framework of the Organisation for Economic Co-operation and Development (OECD) to implement an international energy programme. The IEA fosters co-operation amongst its 26 member countries and the European Commission, and with the other countries, in order to increase energy security by improved efficiency of energy use, development of alternative energy sources and research, development and demonstration on matters of energy supply and use. This is achieved through a series of collaborative activities, organised under more than 40 Implementing Agreements. These agreements cover more than 200 individual items of research, development and demonstration. The IEA Greenhouse Gas R&D Programme is one of these Implementing Agreements.

DISCLAIMER

COPYRIGHT

ACKNOWLEDGEMENTS AND CITATIONS

This report describes research sponsored by the IEA Greenhouse Gas R&D Programme. This report was prepared by:

TNO Science and Industry
Laan van Westenenk 501
P.O. Box 342
7300 AH Apeldoorn
The Netherlands

The principal researchers were:

- René van Gijlswijk
- Paul Feron
- Hans Oonk
- J. P. Brouwer

To ensure the quality and technical integrity of the research undertaken by the IEA Greenhouse Gas R&D Programme (IEA GHG) each study is managed by an appointed IEA GHG manager. The report is also reviewed by a panel of independent technical experts before its release.

The IEA GHG manager for this report: John Davison

The expert reviewers for this report:

- Gary Rochelle, University of Texas, USA
- Edward Rubin, Carnegie Mellon University, USA
- Jan Lambrichts, Dow, EU

The report should be cited in literature as follows:

IEA Greenhouse Gas R&D Programme (IEA GHG), "Environmental impact of solvent scrubbing of CO_2", 2006/14, October 2006.

Further information or copies of the report can be obtained by contacting the IEA GHG Programme at:

IEA Greenhouse R&D Programme, Orchard Business Centre,
Stoke Orchard, Cheltenham, Glos., GL52 7RZ, UK
Tel: +44 1242 680753 Fax: +44 1242 680758
E-mail: mail@ieaghg.org
www.ieagreen.org.uk

ENVIRONMENTAL IMAPCT OF SOLVENT SCRUBBING OF CO_2

Background

Solvent scrubbing is currently the leading technology for pre and post-combustion capture of CO_2. The impacts of solvent scrubbing on the performance and costs of power plants have been studied widely but the environmental impacts are less well known. This study provides a preliminary analysis of the environmental impacts of large scale use of solvent scrubbing processes for CO_2 capture in power plants, using a Life Cycle Assessment (LCA) methodology. The study was carried out for IEA GHG by TNO Science and Industry in the Netherlands.

Study Description

Scope of the study

Environmental impacts due to the capture of CO_2 at power plants occur directly and indirectly. Direct impacts results from the avoidance of CO_2 emission to air and can also occur due to changed emissions of NO_2 and SO_x as a consequence of CO_2 capture and the emissions of solvent and its degradation products. Indirectly, an increase of environmental impact is caused by the decreased thermal efficiency, which leads to a higher fuel use, the production and transport of solvents and additives and the disposal of solvent and degradation products. The scope of the present study covers both the direct and indirect environmental impact of CO_2 capture but transport and storage of CO_2 are excluded.

Process selection

The study assesses post-combustion capture in a natural gas combined cycle plant and a pulverised coal steam cycle plant, and pre-combustion capture in a coal gasification combined cycle plant and a natural gas combined cycle plant. The study focuses on MEA solvent for post combustion capture and MDEA for pre-combustion capture. The environmental impacts of other solvents may be substantially different, so it is not possible to draw conclusions about the impacts of solvent-based CO_2 capture processes in general.

Inventory data

The first step was to quantify all of the material and energy flows for each process, including raw materials, products, emissions and wastes. TNO sent a questionnaire, followed by telephone enquiries, to a wide range of companies involved in the production and use of CO_2 capture solvents but very limited information was provided. A major reason for the poor response was commercial confidentiality, including confidential relationships between licensors and process users. The study was therefore based on information in open literature, including IEA GHG's recent studies on CO_2 capture plants.

Impact assessment

The next step, Impact Assessment, involved the translation of inventory items into environmental impacts. The widely recognized CML-LCA2 methodology was used. In this methodology, environmental impacts are quantified using nine impact categories, which are shown in table 1.

Table 1: Environmental impact categories

Impact category	Environmental issue
Abiotic Depletion	Depletion of mineral resources and depletion of energy carriers (coal, crude oil, natural gas)
Global Warming Potential	The "greenhouse effect"
Ozone Depletion Potential	Depletion of the ozone layer
Human Toxicity	Impact of toxic substances on human health, taking into account fate, exposure and effect. Calculation based on toxicological parameters
Freshwater Aquatic Ecotoxicity	Impact of toxic substances on aquatic ecosystems, taking into account fate, exposure and effect. Calculation based on eco-toxicological parameters
Terrestrial Ecotoxicity	Impact of toxic substances on terrestrial ecosystems, taking into account fate, exposure and effect. Calculation based on eco-toxicological parameters
Photochemical Ozone Creation Potential	Summer smog creation
Acidification Potential	Acidification of soils
Eutrophication	Impact of excessively high nutrient levels in soil and surface water

The contributions of each of the process inputs and outputs to each of the impact categories were calculated using substance-specific factors (equivalence factors), that express the relative severity of each substance regarding that particular environmental impact category. Toxicity data and environmental impact equivalence factors for various capture solvents were generated during this study and are included in appendices of the report. The total impacts for each environmental issue were calculated by summing the impacts of each substance.

The environmental profiles can be used to evaluate which case is preferable for each impact category. The methodology does not provide for weighting among impact categories. If one case is better for one impact category but worse for another, no unambiguous conclusion can be drawn. The environmental impacts are presented in the report as 'spider graphs', which is a normal way of presenting such information. However, caution is needed when interpreting these graphs, as there is a tendency to assume that all of the impact categories are equally important, which is not the case.

Weighting of impact categories

By applying a weighting factor to each impact category, it is possible to compare cases directly using a single parameter. TNO used a shadow price method for weighting environmental impacts. The shadow price for each environmental impact category was defined as the cost of the most expensive measures that are necessary to achieve current environmental policy goals.

Results

Capture of CO_2 reduces the thermal efficiencies of power plants. As a consequence, more fuel has to be consumed per net kWh of electricity, which results in greater environmental impacts in most categories, apart from global warming.

Pre-combustion capture plants normally have relatively low solvent consumptions and the solvent is not in contact with the atmosphere, except as a result of fugitive emissions and possible accidents, which are beyond the scope of this study. Any residual solvent contained in the scrubbed fuel gas is combusted when it is fed to the gas turbine. Pre-combustion capture processes therefore have low environmental impacts, apart from those which are due to reduced efficiency.

The flue gas emitted to the atmosphere from post-combustion capture processes will contain traces of solvent and solvent decomposition products. This study provides an initial assessment of the environmental impacts of solvent emissions, based on currently available data, but there is a high degree of uncertainty in the results due to the limited availability of data. The more stringent flue gas cleaning that is necessary prior to post-combustion capture processes, together with the capture processes themselves, result in lower emissions of acid gases (SO_X and NO_2).

Based on the shadow price evaluation, CO_2 capture substantially reduces the overall environmental impacts of power plants in all cases.

In a future scenario in which 18 Gt/y of CO_2 is captured in 2050 using post-combustion MEA scrubbing, about 30 Mt/y of MEA would be consumed. Current production of all alkanolamines is about 1 Mt/y. However, alternative solvents with much lower rates of degradation are available and under development, so future solvent consumption is likely to be substantially lower than this figure. For example, the solvent consumption is estimated to be about 5 Mt/y if KS-1 solvent was used. In addition, some of the capture of CO_2 in future is likely to be by pre-combustion capture, which would result in a further reduction in solvent consumption rates.

Expert Reviewers' Comments

The draft study report was reviewed by various external experts. IEA GHG is very grateful to those who contributed to this review. The comments from reviewers provided some significant information and helpful suggestions which contributed to the final report.

Most of the experts wanted the report to provide more detailed information on health and environmental impacts of solvents and the products of solvent degradation. In response to these comments more of the detailed data used in the report was included in appendices. Following further discussions, researchers particularly at the University of Regina provided some further information on the compositions of solvents and degradation products and their health impacts. This information is summarised in an appendix of the final report. However, it is recognised that further information is needed.

Major Conclusions

CO_2 capture reduces the thermal efficiencies of power plants. The increased fuel consumption per net kWh of electricity results in greater environmental impacts, apart from those which are due to CO_2 emissions. Some emissions to the atmosphere, particularly acid gases, will be reduced as a consequence of CO_2 capture but post combustion capture processes will emit some solvent and decomposition products, which will have environmental impacts. The decreases in thermal efficiency due to current CO_2 capture technology have been well researched, so the resulting environmental impacts are reasonably well known. However, there is a shortage of information available in the public domain to enable the other environmental impacts to be accurately quantified at present.

Recommendations

Further work to assess the environmental impacts of solvent scrubbing processes for CO_2 capture is needed. This encompasses determination of emissions to the air of solvent and its degradation products, toxicity impacts of these products, and characterization and treatment of waste streams. This will be a particularly important issue for new solvents for which environmental impacts may be less well known.

It is recommended that environmental impacts of solvent scrubbing are discussed at the next meeting of IEA GHG's CO_2 Capture Network to encourage researchers, process licensors, manufacturers and plant operators to provide more information.

Development of new CO_2 capture solvents should be focussed on those which have reduced environmental impacts.

Laan van Westenenk 501
P.O. Box 342
7300 AH Apeldoorn
The Netherlands

www.tno.nl

P +31 55 549 34 93
F +31 55 541 98 37

TNO-report

I&T-A R 2006/047

Environmental impact of solvent scrubbing of CO_2

Date	August 2006
Authors	R.N. van Gijlswijk P.H.M. Feron H. Oonk
Order no.	36129
Keywords	CO_2 capture post-combustion pre-combustion solvents environmental impact LCA shadow prices
Intended for	IEA Greenhouse Gas R&D Programme Stoke Orchard Cheltenham Gloucestershire GL52 7RZ United Kingdom

Summary

Capture and storage of CO_2 from power plants is an option by which CO_2-emissions arising from the use of fossil fuels can be reduced drastically. As such it is a promising countermeasure to climate change.

There are several ways to capture CO_2 from power plants. It appears that solvent based post- and pre-combustion capture processes are the leading option for both coal and gas based power plants. The impact of the use of these processes is well established in terms of power generation efficiency, emission reduction and cost of electricity. However, the environmental impact of the solvent processes has not yet been studied in detail.

This study evaluates the environmental impact of the introduction of solvent scrubbing of CO_2 on a large scale. To this extent, the following objectives are defined:

- Identification of the current CO_2 solvent market and the composition of the main solvents;
- Quantification of environmental impacts directly or indirectly resulting from the capture of a unit of CO_2 using solvents;
- Estimation of the potential environmental impact of large scale application of CO_2 scrubbing on a global scale;
- Identification of possibilities for the reduction of environmental impact.

In the current study the environmental impact is assessed using the Life-Cycle Assessment (LCA) framework. For the practical implementation we have selected the widely used CML-LCA2 methodology. Environmental impact assessment according to CML-LCA2 results in an environmental profile covering ten environmental issues, called impact categories (Abiotic Depletion, Global Warming Potential, Ozone Depletion Potential, Human Toxicity, Freshwater Aquatic Ecotoxicity, Terrestrial Ecotoxicity, Photochemical Ozone Creation Potential, Acidification Potential, Eutrophication).

The analysis was done for the four main options for carbon capture and their reference cases: pre- and post-combustion capture in both coal and natural gas based power plants. Within those four concepts, the effect of solvent scrubbing is evaluated using publicly available data.

Two viewpoints have been discriminated:

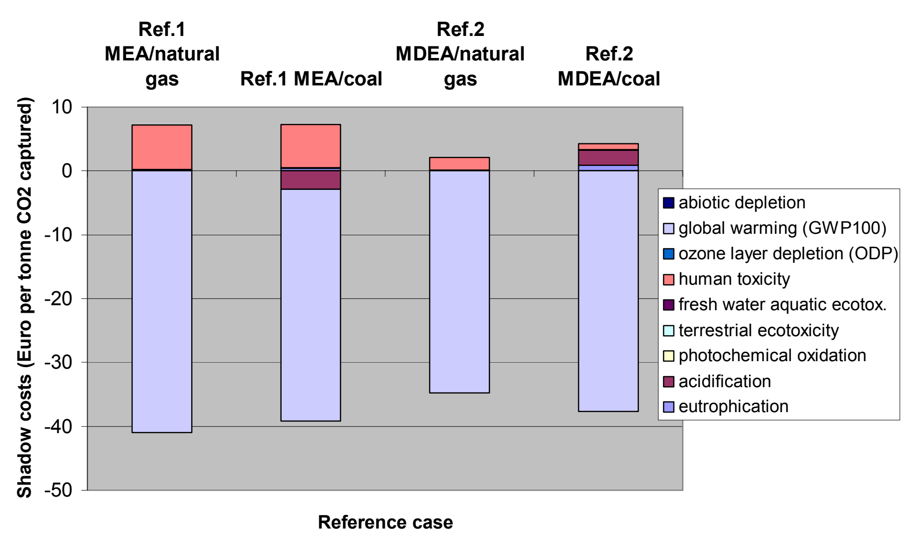
1) capture plant - the capture of a unit of CO_2, and
2) power plant - the production of a unit of electricity with or without CO_2 capture. This has led to the reference cases shown in the next table.

No.	Code	Fuel	Reference case
1	*MEA*	*Both*	*Capture of 1 tonne of CO_2 using MEA*
2	*MDEA*	*Both*	*Capture of 1 tonne of CO_2 using MDEA*
3	NGCC	Natural gas	Natural gas combined cycle power plant
4	NGCC+	Natural gas	Natural gas combined cycle power plant with MEA post combustion capture
5	POCC	Natural gas	Partial oxidation combined cycle power plant
6	POCC+	Natural gas	Partial oxidation combined cycle power plant with MDEA pre-combustion capture
7	USCPF	Pulverized coal	Ultra supercritical pulverized fuel power plant
8	USCPF+	Pulverized coal	Ultra supercritical pulverized fuel power plant with MEA post combustion capture
9	IGCC	Pulverized coal	Integrated gasification combined cycle power plant
10	IGCC+	Pulverized coal	Integrated gasification combined cycle power plant with MDEA pre-combustion capture

The cases in italic represent the first viewpoint (capture a unit of CO_2).

The method of shadow prices, as developed by TNO, is used to enable an overall analysis and comparison of environmental impacts. The shadow prices are based on the highest cost for mitigating environmental impacts.

The results shown in the next figure show that avoiding the emission of CO_2 has a net environmental benefit. The negative bars represent the net avoided CO_2 emission as a result of the capture one tonne of CO_2, the positive bars represent the additional environmental impact to accomplish this. The overall net shadow price for all options is 30 – 35 Euro/tonne CO_2 benefit.



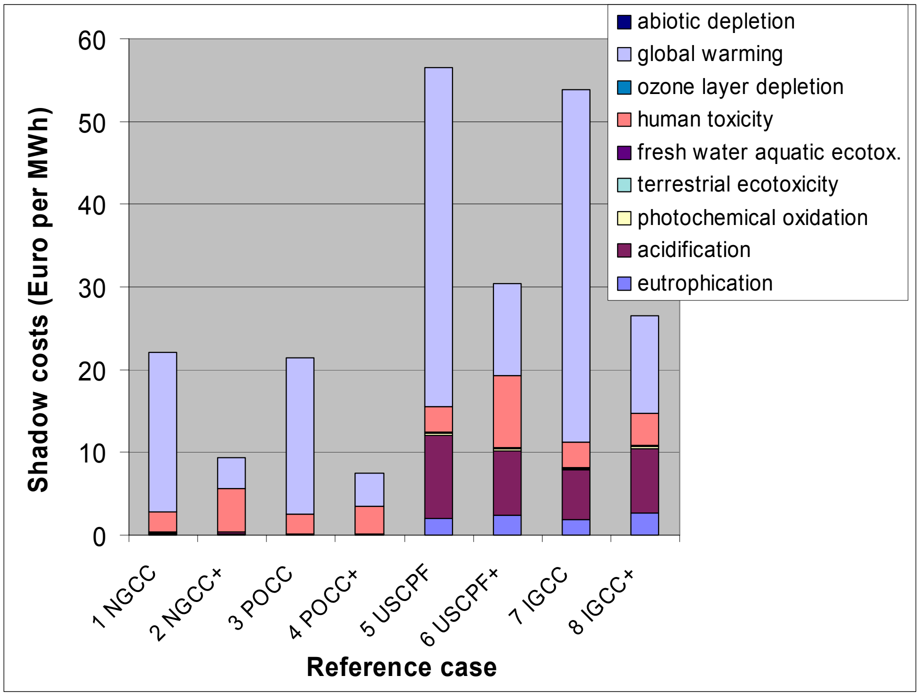
Environmental impact of reference cases 1 and 2, weighed with shadow prices method.

With the second viewpoint, results for the eight reference cases have been calculated for the generation of 1 MWh of electricity: natural gas & coal with and without post-combustion/MEA and pre-combustion/MDEA capture.

The environmental impacts for the post-combustion capture cases (NGCC and USCPF) are primarily influenced by the increased fuel use. Secondly, due to the use of a solvent, in particular as a result of production of MEA and the emission to the atmosphere, the environmental impact themes of human toxicity and terrestrial ecotoxicity show an additional increase. For post-combustion CO_2-capture from coal firing the environmental impacts themes of acidification and photochemical smog are reduced compared to the case without capture as a result of the reduced SO_2 and NO_2 emissions. As expected the environmental impact theme of global warming shows an overall decrease for all post-combustion capture cases.

The environmental impact for the two pre-combustion capture cases (POCC and IGCC) is dominated by the increased fuel use. All environmental impact themes will increase in a similar way as a result of this except, obviously, the global warming theme, which will be reduced. In case of pre-combustion capture the effects of solvent use on the environmental impact themes of human toxicity and terrestrial ecotoxicity are negligible.

Results using the method of weighing with shadow prices are shown in the next figure.



Comparison of reference cases: weighed with shadow prices.

The method of weighing with shadow prices leads to the conclusion that per MWh the natural gas reformer plant (POCC) with MDEA CO_2 capture causes the least environmental impact, closely followed by the natural gas combined cycle plant (NGCC) with MEA CO_2 capture. When compared to the natural gas fired power plants without capture, the environmental impacts are reduced by 60 – 70% as a result of CO_2 capture.

Furthermore a natural gas based plant (NGCC or POCC) without CO_2 capture has a lower impact than a coal based plant with CO_2 capture, according to the shadow price method. The higher CO_2 and SO_2 emissions in case of coal firing play an important role in this.

The method of weighing with shadow prices also shows that the highest environmental impact of all capture plants is caused by the post-combustion coal fired power plant (USCPF), although the difference with pre-combustion coal firing is small. When compared to the coal fired power plants without capture, the environmental impacts are nearly halved as a result of CO_2 capture.

Large scale deployment of CO_2 capture in power plants using MEA in 2030 and 2050 would require the alkanolamine production to increase to at least tenfold of the estimated current production, basing this on the characteristics of the FLUOR Econamine process. The resulting amount of sludge would be large, but the amounts are small compared to the fuel use, and still smaller than the consumption of limestone for SO_2-control in coal fired power plants. These sludges can also be considered to be environmentally manageable.

The following recommendations are made following the outcome of the study.
1. Development of more energy efficient solvents compared to MEA, as the impact of solvent processes for CO_2 capture is primarily related to the impact as a result of the increased fuel use. This is particularly valid for post-combustion capture where the solvent process will have the largest influence on the energy efficiency of power generation.
2. Development of solvents and solvent processes with lower emissions to the air compartment, but possibly with additional capability for removal of other flue gas components with noticeable environmental impact (SO_2 and NO_x). Reduction of the environmental impact of the solvent production process itself is also required. This is mostly relevant to post-combustion capture, as in case of pre-combustion capture the environmental impact of the solvent process on the whole is much smaller.
3. Development of alternative capture processes not requiring any additional consumables (chemicals) for CO_2-capture, with an energy-efficiency at least equivalent to the solvent processes. This is valid for both post- and pre-combustion capture.
4. More detailed studies into the environmental impacts of solvent scrubbing are needed. This encompasses e.g. determination of emissions to the air, solvent

degradation studies, characterisation of waste streams, treatment of waste streams and detailed data on solvent formulation including corrosion inhibitors. Particularly when new solvents are developed for which the environmental impacts are perhaps not known, this will become an important issue.

Table of contents

Appendices

A	Amine production processes
B	Process data
C	Environmental data solvents
D	Waste processing
E	Life Cycle Assessment methodology
F	Shadow price methodology
G	Questionnaire and accompanying letter
H	Solvent degradation and wastes
I	Toxicity potential for Monoethanolamine, Diethanolamine, Trieethanolamine, Di-isopropanolamine, Sulfolane, Methanol
J	Toxicity potential for Methyldiethanolamine and Aminomethylpropanol

1. Introduction

1.1 Capture of CO_2

Capture and storage of CO_2 from power plants and industrial plants (CCS) is an option by which CO_2-emissions arising from the use of fossil fuels can be reduced drastically. As such it is a countermeasure to climate change. The potential of this option has been mapped by the IEA Greenhouse Gas R&D Programme in a broad variety of studies dealing e.g. with the impact on generation efficiency, the methods and possibilities for long term storage, etc. The technological routes to capture CO_2 can be divided into three categories:

- Post-combustion capture

CO_2 is to be separated from a flue gas from a combustion process with air, at low pressure and low concentration.

- Pre-combustion capture

CO_2 is to be separated from a mixture with predominantly H_2 coming from a fuel conversion step, at elevated pressure and concentration.

- Denitrogenation

CO_2 is delivered in high concentration as a result of the combustion of the fuel in pure oxygen and a recycle CO_2-stream. As the denitrogenation route will produce a fairly pure CO_2-product there is no real need for CO_2-separation, as the compression and/or liquefaction will get rid of the inert gases.

As regards the development state of technologies for separation of CO_2 from power plants and industrial plant, it appears that the solvent processes are the leading option for use in both post- and pre-combustion capture. The impact of the use of these processes on the performance of the power station has been mapped in terms of power generation efficiency, emission reduction and cost of electricity [1, 2]. However, the environmental impact of the solvent processes has not yet been studied in detail. The overall impact is determined by a number of parameters, e.g. by the type of solvent (manufacturing, use and waste products) and also the scale and intensity at which the technologies are going to be applied in the future.

The use of solvents in pre-combustion capture is less intensive than the use in post-combustion capture as the specific CO_2 loads on the solvents are higher, due to the higher driving forces and the energy requirements are consequently lower. For pre-combustion capture the typical solvents are already widely applied throughout the (petro-)chemical industry in the treatment of synthesis gases after the water gas shift, either to provide H_2 or to provide CO_2 or both. These solvents can be of a chemical nature (primarily amines) or physical nature, depending on the CO_2 partial pressure. The solvents typically used in CO_2/H_2 separations are also used in natural gas treating to remove a variety of acid gases, such as CO_2, H_2S and COS. The experience coming from this market can also be utilised.

In post-combustion capture chemical solvents (mainly amines) are used, the main market being the delivery of CO_2 for food/beverage applications. The conditions are also different: oxidative in post-combustion, and reductive in pre-combustion capture. This will influence the environmental impact. As capture of CO_2 will lead to an increased use of fossil fuel reserves, it is necessary to bring the environmental impact of the solvent processes in context with the increased environmental impact of the increased fuel use. Finally, the capture and storage of CO_2 aims at the prevention of climate change. This is an environmental problem of global dimensions. Solutions to this problem will therefore need to have an impact on a global scale. It is therefore important to quantify the environmental impact of solvent processes, particularly to obtain public and regulatory acceptance of CO_2 capture and storage technology on a large scale. This issue is gaining importance with the recent initiation of several commercial scale CCS-demonstrations, e.g. in Norway [29]. Use of chemicals off-shore in Norway, hence also solvents for CO_2-separation, is governed by a “traffic light” description as indicated in table 1.1.

Table 1.1 Traffic light governing the use of chemicals offshore in Norway as a general rule.

Traffic light color	Description
Black	Chemicals that are in principle not allowed to be emitted, but approval can be given in special cases
Red	Chemicals that are potentially harmful to the environment and should therefore be phased out. Requirements in approval that these should be especially prioritized for substitution
Yellow	Chemicals that are in use but are not covered in any of the other categories. Normally approval is given without specified requirements.
Green	Chemicals that are on OSPAR’s PLONOR list (poses little or no risk), and are assessed to have no or very little negative environmental effects. Approval is given without specified requirements

A solvent like MDEA, which is widely used for natural gas treatment, is listed as a “red” chemical in Norway and could therefore be replaced by alternatives if they are available. It is clear that the environmental impact of solvent processes deserves much more attention if and when these processes are going to be used on a large scale. This study is an intended to be a starting point and intends to provide a framework for further analysis.

1.2 Study objectives

This study evaluates the environmental impact of the introduction of solvent scrubbing of CO_2 on a large scale. To this extent, the following objectives are defined:

- Identification of the current CO_2 solvent market and the composition of the main solvents;
- Quantification of environmental impacts directly or indirectly resulting from the capture of a unit of CO_2 using solvents;
- Estimation of the potential environmental impact of large scale application of CO_2 scrubbing on a global scale;
- Identification of possibilities for the reduction of environmental impact.

2. Scrubbing technology

2.1 Solvent process technologies

CO_2 Scrubbing technology is based on the use of a solvent which has a strong affinity for CO_2 relative to the other gases in which it is present. The strength of this affinity is dependent on the temperature and pressure and hence the solvents can be regenerated by raising the temperature and/or reducing the pressure. Solvent processes are widely used in the (petro-)chemical industry and the oil and gas industry, e.g. in hydrogen and ammonia production. As a result of several decades of operating experience, scrubber technology and solvent formulations have already undergone important development.

– *Physical and chemical solvents*

Scrubber solvents can be distinguished in physical and chemical solvents. In physical solvents, the equilibrium between gas and liquid phase is determined by Henry's law and as a result solvent loading is more or less linear to gas partial pressure. For chemical solvents, CO_2 reacts with specific components in the liquid phase and as a result a non-linear relation is observed, with significantly increased CO_2-loadings at low partial pressures (see figure 2.1).

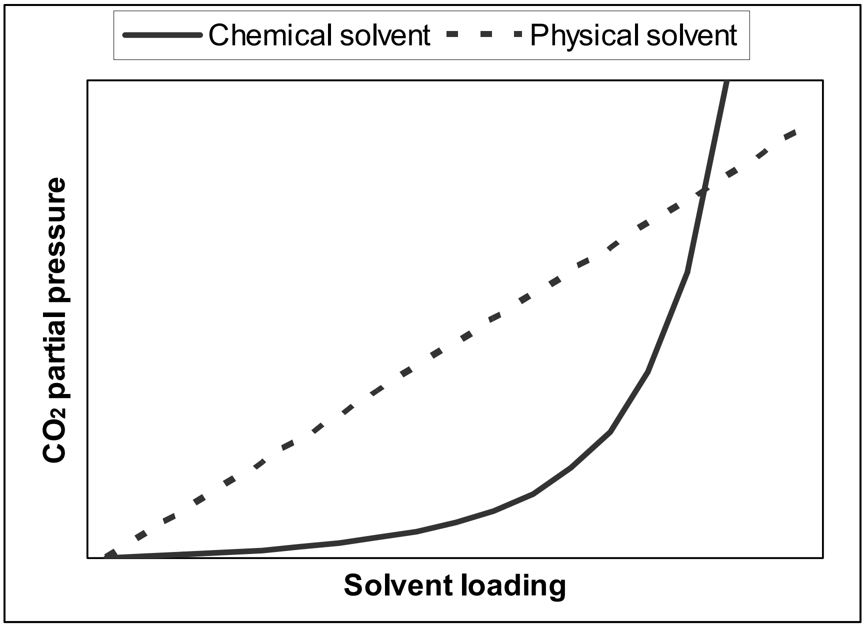


Figure 2.1 CO_2 equilibrium partial pressure for a chemical and a physical solvent.

So the type of solvent used is primarily determined by the CO_2-partial pressure in the feed gas. Typically at partial pressure levels lower than 10 bar chemical solvents are used; at partial pressure levels above 10 bar physical solvents are used.

Chemical solvents in general require a thermal regeneration process, whereas a physical solvent can be regenerated by a pressure swing.

2.2 Pre- and post-combustion capture

Two possible routes exist to remove carbon dioxide from fossil fuel based electricity generation.

In *pre-combustion* CO_2-capture, the absorption processes is used to selectively remove CO_2 from a high pressure feed gas stream in which hydrogen is the main gas component. This feed gas is obtained from a gasification process (coal) or reforming process (natural gas), which generates a synthesis gas mixture (predominantly CO and H_2). The synthesis gas mixture is then shifted by the introduction of steam to a mixture consisting of CO_2 and H_2. The partial pressure of CO_2 is much higher than in post-combustion capture, and volume flows are much smaller which allows for a more energy-efficient CO_2-separation. However due to the reforming or gasification step, overall energy loss of pre-combustion schemes is significantly increased.

In *post-combustion* capture, fossil fuels are used to generate electricity in a more conventional way. Carbon dioxide is removed from the tail-gas at relatively low partial pressures, from a relatively large volume flow and under oxidising conditions (see table 2.1).

At the moment there is no clear preference for either pre- or post-combustion technology in general terms and both approaches make sense in different situations. For retrofit applications post-combustion seems the preferred. In new projects the relatively high investment costs of post-combustion capture have to be weighed against the relatively high operating costs and efficiency loss of pre-combustion capture.

Also with regard to the use of solvent process technologies in the context of CO_2-capture it is important to distinguish between post-combustion capture and pre-combustion capture. In post-combustion capture, due to the low partial pressure of CO_2, chemical solvents are the only option. In pre-combustion capture both chemical and physical solvents are applicable. Table 2.1 gives a comparative overview of post- and pre-combustion CO_2-capture using solvents.

Table 2.1 Comparison between post-combustion and pre-combustion CO_2-capture.

	Post-combustion CO_2-capture	**Pre-combustion CO_2-capture**
Solvents	Ethanolamines (formulations) Salt solutions	Physical solvents Ethanolamines (formulations) Salt solutions
Conditions	Oxidising (O_2-atmosphere) CO_2 partial pressure: 3 -15 kPa Absorption temperature: 30 – 70 °C Desorption temperature: 100 – 120 °C	Reducing (H_2-atmosphere) CO_2 partial pressure: 200 - 2000 kPa Absorption temperature: 20 – 100 °C Desorption temperature: 20 – 120 °C (Cold methanol processes operated at temperature below 0 °C and some physical solvents are also cooled to achieve deep removal)
Flow rate	10 – 40 m^3/tonne CO_2	7 – 70 m^3/tonne CO_2
Energy[1)]	3 - 5 GJ/tonne CO_2 (thermal) 0.5 - 0.9 GJ/tonne CO_2 (electrical)	0.4 - 0.5 GJ/tonne CO_2 (electrical)

1) Refers only to energy use of the CO_2-capture itself, without compression. This does not represent the energy use of energy loss of the entire sequestration option.

In the following paragraphs post- and pre-combustion capture are described in more detail.

2.3 Post-combustion CO_2 capture

– *Process description*

The flow sheet of a chemical solvent process for post-combustion CO_2-capture is shown in figure 2.2.

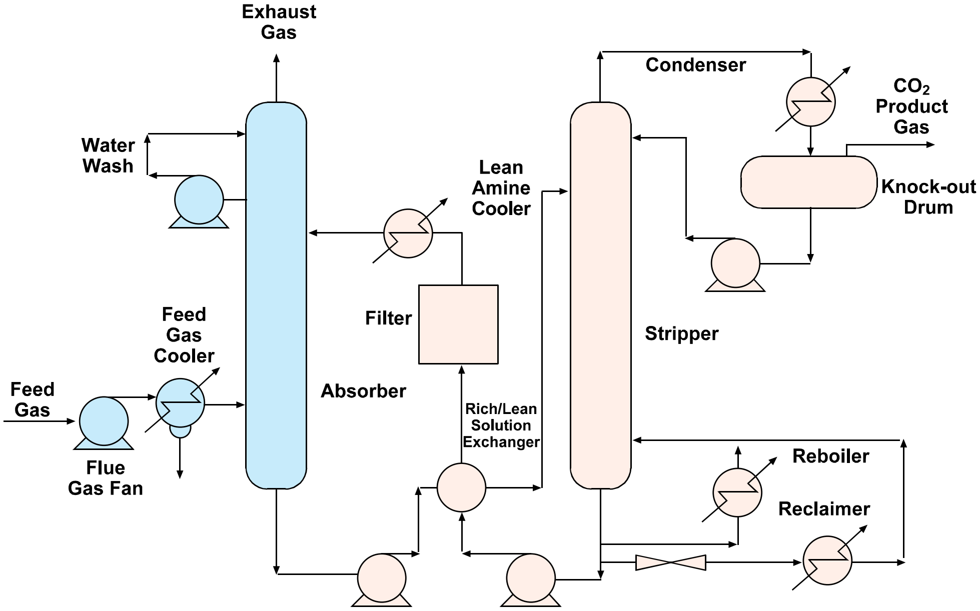


Figure 2.2 Process flow diagram for CO_2 recovery from flue gas with chemical solvent.

After cooling the flue gas, it is brought into contact with the solvent in the absorber. A blower is required to pump the gas through the absorber. At temperatures typically between 40 and 60 °C CO_2 is then bound by the chemical solvent in the absorber. After passing through the absorber the flue gas undergoes a water wash section to balance water in the system and to remove any solvent droplets or solvent vapour carried over and then leaves the absorber. It is possible to reduce CO_2 concentration in the feed gas down to very low values, as a result of the chemical reaction in the solvent, but with lower exit concentrations tending to increase the height of the absorption vessel. The “rich” solvent, which contains the chemically bound CO_2 is then pumped to the top of a stripper, via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (100 – 140 °C) and pressures not very much higher than atmospheric pressure. Heat is supplied to the reboiler to maintain the regeneration conditions. This leads to a thermal energy penalty as a result of heating up the solvent, providing the required de-sorption heat for removing the chemically bound CO_2 and for steam production which acts as a stripping gas. Steam is recovered in the condenser and fed back to the stripper, whereas the CO_2 product gas leaves the condenser. The CO_2-product is a relatively pure (> 99%) product, with water vapour being the main other component. Due to the selective nature of the chemical absorption process, the concentration of inert gases is low. The CO_2-product might contain trace components, e.g. volatile solvent decomposition products or components carried over from the flue gas. A further CO_2 purification step makes it possible to bring the CO_2-quality up to food-grade standard. The “lean” solvent, containing far less CO_2 is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level. It is possible to reduce CO_2 concentration in purified gas down to negligible values, as a result of the chemical reaction in the solvent.

– *Solvent requirements*

Since power plant flue gases are generally at atmospheric pressure, CO_2 partial pressure is very low. Also flue gas contains oxygen and other impurities; therefore an important aspect of an absorption process is in the proper choice of solvent for the given process duty. High CO_2 loading and low heat of desorption energy are essential for atmospheric flue gas CO_2 recovery. The solvents must also have low by-product formation and low decomposition rates, to maintain solvent performance and to limit the amount of waste materials produced.

Solvent degradation, either by the continuous thermal cycling of solvent or induced by the oxygen present in the flue gases is a major concern in CO_2 capture from flue gases. It will also influence the corrosion rates in the reboiler. The common method to deal with this is to incorporated oxygen scavengers and corrosion inhibitors. Solvent degradation will result in contamination of the exit gases and the formation of so-called heat-stable salts, accumulating in the solution. Also in some part of the plant the use of stainless steel is recommended to avoid corrosion. In addition to this, the use of carbon beds and filters will help in controlling these operational problems. Acid components present in the flue gas, like SO_2 and NO_2, will react with the amines in ways similar to CO_2. The CO_2 carrying capacity of the solution can be restored by adding an alkaline component e.g. sodium hydroxide. This results in a heat stable salt. The amine can be recovered thermally in the reclaimer, or by using non-thermal techniques like ion-exchange or electrodialysis.

– *Commercially available processes*

The following three solvent processes are commercially available for CO_2 capture in post-combustion systems:

- The Kerr-McGee / ABB Lummus Crest Process [3] - This process uses a 15 to 20 wt% aqueous MEA solution. The largest capacity experienced for this process is 800 tonnes/day of CO_2 utilising two parallel trains [4].
- The Fluor Daniel ® ECONAMINE ™ Process [5, 6], recently improved and now marketed as Fluor Econamine FG Plus^{SM} [7] - This process was originally acquired by Fluor Daniel Inc. from Dow Chemical Company in 1989. It is a MEA based process (30 wt% aqueous solution) with an inhibitor to resist carbon steel corrosion and is specifically tailored for oxygen containing gas streams. It has been used in many plants worldwide recovering up to 320 tonnes/day of CO_2 in a single train for use in beverage and urea production.
- The Kansai Electric Power Co., Mitsubishi Heavy Industries, Ltd. Process [8] - The process is based upon sterically hindered amines and already three solvents (KS-1, KS-2 and KS-3) have been developed. KS-1 was commercialised in a urea production application in Malaysia (200 tonnes/day CO_2) in 1999. The major benefits in this process are low heat requirements for regeneration, low amine losses and low solvent degradation without the use of inhibitors or additives.

It is evident that more suppliers with different solvent compositions will enter the market in the future, once the concept of CCS is an accepted means of reducing greenhouse gas emissions. This is of course dependent on post-combustion capture processes taking a sizeable share of this new market.

2.4 Pre-combustion CO_2 capture

2.4.1 Pre-combustion with physical solvents

– *Process description*

The process flow sheet for pre-combustion CO_2-capture for a physical solvent process is shown in figure 2.3.

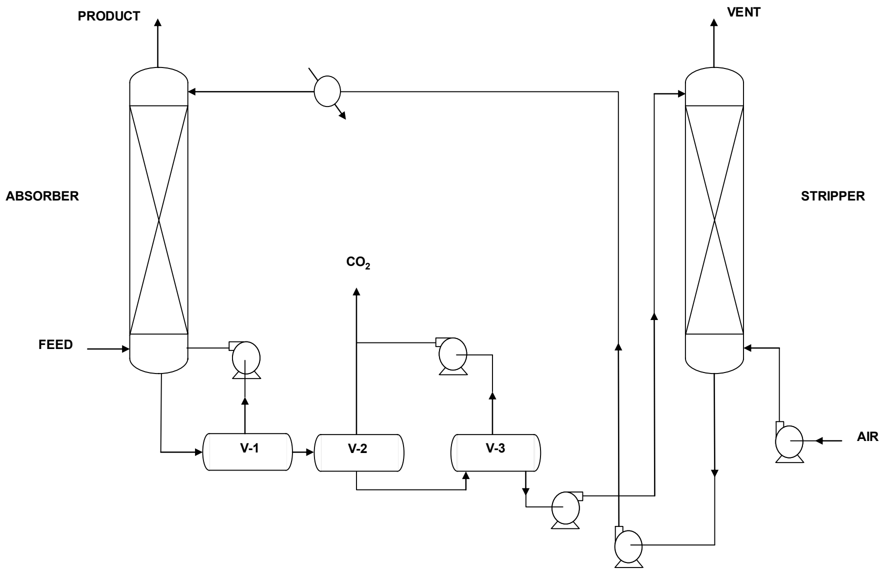


Figure 2.3 Process flow diagram for CO_2-removal from a gas mixture using a physical solvent.

The high pressure feed gas is fed into an absorber, where the gas is counter-currently contacted with the solvent. CO_2 is absorbed and is fed to a first flash-tank, where co-absorbed hydrogen and less-absorbing components are flashed off and fed back in the feed stream after recompression. In a second flash thank the pressure is reduced further and the bulk of the CO_2 is recovered. Further pressure reduction, down to vacuum pressures, will lead to deeper recovery of CO_2. Additionally an air or nitrogen stripper can be included to give very deep removal of CO_2. After regeneration the solvent will be brought up to the absorber pressure and fed back to the top of the column. The number of regeneration stages is dependent on the required CO_2-removal, but also dependent on the process economics. The re-pressurisation is the main energy requirement of this process. In pre-combustion capture a sizeable fraction of the CO_2 can be available at pressure levels higher than atmospheric, by the staged regeneration process. This will reduce the requirement for compression of CO_2.

– *Solvent requirements*

The choice of a particular physical solvent is primarily determined by the solvent loading and the selectivity. Other critical issues in the selection of physical solvents are the vapour pressure (to reduce losses), solvent stability and viscosity.

– *Commercially available processes*

The main physical solvents currently considered for pre-combustion capture are:

- Selexol (UOP, DOW) is a mixture of polyalkylene-glycoldimethylethers with low vapour pressure. It is currently used for acid gas removal from e.g. natural gas, landfill gas, ammonia synthesis gas.

- The Rectisol process (LURGI) makes use of the high acid gas solubility of methanol at low temperature. The process uses a refrigeration unit to operate at low temperature (-30 °C).
- In addition to these solvents propylene carbonate (FLUOR solvent) and N-methyl-pyrollidon (Purisol) are possible candidates, exhibiting similar performances.

2.4.2 Pre-combustion with chemical solvents

- *Process description*

In case of a chemical solvent the flow sheet will be similar to the one shown in figure 2.3, but with the addition of a thermal regeneration step for the solvent similar to the flow sheet for post-combustion CO_2-capture. Aqueous solutions of amino-alcohols have generally been used for removal of CO_2 from high pressure gas streams in natural gas treatment and other gas-processing in the (petro-)chemical industry.

- *Solvent requirements*

An overview of applicable chemical solvents for pre-combustion capture is shown in table 2.2.

Table 2.2 Chemical solvent overview for pre-combustion capture.

Type of solvent	Example
Primary amines	Monoethanolamine (MEA), Diglycolamine (DGA)
Secondary amines	Diethanolamine (DEA), Diisopropanolamine (DIPA)
Tertiary amines	Methyldiethanolamine (MDEA), Triethanolamine (TEA)
Alkaline salt solutions	Potassium carbonate

Important items in the selection of chemical solvents are the CO_2-loading capacity to result in low absorption liquid flow rates, the reaction rate as this will determine the size of the equipment and the heat requirement for regeneration, as this dominates the operating costs.

The loading capacity for chemical solvents is primarily dependent on the concentration of the active components and the achievable loading according to the thermodynamic equilibrium. For the range of alkanolamines the primary amines (MEA, DGA) will be more favourable in terms of reaction rates compared to secondary (DEA, DIPA) and tertiary (MDEA) amines. However, achievable loadings and heat requirement for regeneration will be higher for primary amines. Table 2.3 gives an overview of the characteristics of commercially available absorption liquids.

Table 2.3 Overview of characteristics of commercially available chemical solvents [9].

Solvent	MEA	DGA	DEA	DIPA	MDEA
Concentration [% mass]	< 30	< 60	< 40	< 40	< 50
Typical loading [mole/mole]	0.3	0.35	0.30-0.70	0.45	0.45
Heat of absorption [MJ/kg of CO_2]	2.0	2.0	1.5	1.5	1.3
Reaction rate at 25 °C [m^3/kmole·s]	7600	4000	1500	400	5

– *Commercially available processes*

Chemical solvents considered in pre-combustion capture are often formulated mixtures, dedicated for a specified separation tasks. Apart from the main component responsible for the acid gas loading, the mixtures might also contain activators to promote mass transfer and hence reduce column sizes. The main chemical solvent put forward in the context of pre-combustion CO_2-capture is methyldiethanolamine (MDEA), as it has a high capacity combined with a low energy requirement for regeneration, as show in table 2.3. It is offered by many suppliers, such as Dow, UOP, BASF, INEOS, Huntsman as dedicated mixtures with different trade-names. The chemical stability of MDEA in non-oxidative environments is very good and no solvent reclaiming is needed.

The use of a hybrid solvent, i.e. a mixture of physical and a chemical solvent is also possible. The Sulfinol process developed by Shell uses DIPA as the active chemical component in a mixture with sulfolane and water, both physical solvents.

2.5 Alkanolamines

Alkanolamines are mostly used in aqueous solutions as chemical solvents for acid gases. The reaction chemistry for CO_2 is dependent on the type of amine. For primary (MEA) and secondary amines (DEA) the reaction leads to the formation of a carbamate with varying degrees of stability:

Primary: $CO_2 + 2RNH_2 \rightarrow RNH_3^+ + RNHCOO^-$
Secondary: $CO_2 + 2RNH \rightarrow RNH_2^+ + RNCOO^-$

For tertiary amines (TEA, MDEA) and sterically hindered amines (AMP) the reaction leads to the formation of bicarbonate:

Tertiary: $CO_2 + RN + H_2O \rightarrow RNH^+ + HCO_3^-$
Primary/sterically hindered: $CO_2 + RNH_2 + H_2O \rightarrow RNH_3+ + HCO_3^-$

The annual production of ethanolamines, basically MEA, DEA and TEA, amounted in 1999 to 1.09 Mtonne/year [10] with half being produced in the USA,

a quarter in Western Europe and quarter in the rest of the world. These recent numbers fit in well with production figures for the United States of 0.3 Mtonne/year in 1992 and 0.45 Mtonne/year in 1995 [11].
Ethanolamines are produced for a number of uses such as:
- Surfactants (all)
- Corrosion inhibitors (DEA, TEA)
- Gas purification (all)
- Intermediates (MEA)
- Cement additives (TEA)

The production of MEA, DEA and TEA is carried out by reacting ethylene oxide and ammonia in different ratios. In this way the mixture composition can be steered. The global production mix might be MEA: 50%, DEA: 30 - 35%, TEA: 15 - 20%, but in reality the production mix is variable and equal outputs of the three amines has also been reported [11]. The process flow sheet for the production of MEA, TEA and DEA is shown in appendix A.

The fractional usage of alkanolamines for gas processing is estimated to be between 15 and 25% of the overall annual alkanolamines production, representing a world-wide usage between 150,000 and 250,000 ton. Only a negligibly small amount of amines will have been used for CO_2-removal from flue gases. Most of the amines will be used in natural gas processing and gas separation in the (petro-) chemical industry.

An estimate of the use of different amines for gas processes [12] gives the following result:
- MEA - 40%
- DEA - 31%
- MDEA - 22%
- DIPA - 5%
- DGA - 2%

The use of MEA and DEA was still widespread in 1993, but the trend in gas processing uses of alkanolamines is towards more use of MDEA-based processes. In most industrial uses MDEA is favoured over MEA and DEA because of its high loading and low heat requirement for regeneration as well as its stability in operation. It must be mentioned that MDEA is most often used in formulated mixtures in which other amines are present, usually with the function of promoting mass transfer.

2.6 Direct emissions from CO_2-scrubbing solvent processes

The direct emissions from solvent processes to the environment (air, water, soil) represent a loss of solvent and therefore there has been quite some attention to reduce these losses for economic reasons. Solvent losses throughout their use can be divided into several components [13]:

– *Mechanical*

Mechanical losses are caused by leaks in the equipment and also by accidental spills when charging or emptying the equipment. These losses will lead to pollution of the soil and if not remedied might reach the groundwater and perhaps even surface waters. These losses obviously need to be avoided at all times by good housekeeping. As many solvents are highly water-soluble the solvent components will be quickly taken up by the environment. For example, DIPA and sulfolane have been identified nearby gas processing facilities in Canada. [14].

– *Evaporation*

All solvents have a certain vapour pressure. Hence the gas stream to be treated, but also the product CO_2 will contain a certain amount of solvent. This constitutes a loss of solvent. These losses can be reduced by reducing the temperature of the solvent, thereby lowering the vapour pressure at the absorber outlet and the stripper outlet. Physical solvents are among other things selected for their low vapour pressure to reduce these losses. Chemical solvents are always used in conjunction with a water wash to absorb the evaporated solvent.

– *Entrainment*

Solvent can also be carried over in the gas stream by entrainment, i.e. droplets are formed in the absorber and carried away in the gas stream. Here also a wash section can recover the droplets carried over.

– *Degradation*

The previously described losses can be seen as losses of the original chemicals present in the solvent, whereas degradation represent losses of active component in which the solvents have undergone a chemical transformation. The degradation products might be carried away in the exit gas streams, or be caught in the carbon filter or accumulate in the reclaimer.

The pathways to degradation can be quite varied and difficult to grasp and the following degradation causes are mentioned in the literature:

- Oxidative (flue gases or air leakage)
  Degradation by oxygen is an unavoidable issue in post-combustion CO_2, because of the presence of oxygen in the flue gases. These concentrations are higher for natural gas fired combined cycles, than for pulverized coal fired plants. In pre-combustion CO_2 it might be considered not to be a problem, as the feed gases do not contain oxygen and air leakage into storage vessels etc. is the likely cause for oxidative degradation. This can of course be prevented. Oxidative degradation, which usually starts with the abstraction of hydrogen, is therefore mostly relevant in post-combustion capture. The main reaction products from oxidation are acids (acetic, formic, glycolic, oxalic).

- CO_2-induced (also promoting corrosion)
  Primary and secondary amines like MEA and DEA, respectively, will react with CO_2 by the formation of a carbamate. The carbamate can polymerise in an irreversible fashion leading to degradation. This type of degradation will increase with temperature, high amine concentrations and with a sizeable amount of CO_2 present. As MEA–solution usually contains significant CO_2-loadings after regeneration, MEA is mostly prone to this type of degradation. The main reaction products are oxazolidone and ethylene diamine which are high boiling compounds.
  Tertiary amines like MDEA and sterically hindered amines like AMP are not affected by this type of degradation as they do not form carbamates.
- Thermal (high skin temperatures)
  At high temperature (> 175 °C) the solvent degeneration will be accelerated. Therefore the amine skin temperatures of the reboiler should be limited to less than 160 °C and bulk amine temperatures should be lower than 125 °C. In this way thermal degradation can be prevented.

Solvents will have three major pathways to the environment, assuming a plant is properly maintained and operated and accidental spills and leakages are avoided:

- *Emissions via the absorber*

The emissions via the absorber are reduced by the use of a wash section on top of the absorber. The wash section which is fed with pure water will recover a large fraction of the evaporated solvent and droplets carried over. Even so the flue gas will contain solvent and solvent decomposition products (primarily NH_3). In case of post-combustion these are emissions to the air. In case of pre-combustion capture the absorber slip will be carried away with the hydrogen product to a combustor, where it will be rendered harmless. Hence only in case of post-combustion capture the emissions deserve consideration. Also in case of pre-combustion capture the feed gas streams are much smaller leading to much smaller emission. Table 2.4 gives an overview of emissions from the absorber for different post-combustion capture processes.

Table 2.4 Absorber emissions for post-combustion capture processes.

Process/study	**Absorber emission**
Fluor Econamine FG Plus^{SM} [1]	MEA: 1 ppmv
Fluor Econamine FG Plus^{SM} – natural gas fired combined cycle [15]	MEA: 0.2 ppmv NH_3: 23 ppmv
Mitsubishi Heavy Industries – natural gas fired combined cycle [16]	MEA+NH_3: 2.15 ppmv
Mitsubishi Heavy Industries – coal fired power plant [16]	MEA+NH_3: 3.44 ppmv

- *Emission via CO_2-product from stripper*

The wet CO_2-product after the condenser will also contain impurities, most likely similar to those present in the absorber outlet. The CO_2 will be further compressed, dried, transported and stored underground. In post-combustion capture the CO_2-stream is much smaller (10 – 30 times) than the flue gas stream, hence the emissions are much smaller than via the absorber. The compression and drying will furthermore lead to a large portion of the contaminants being removed.

– *Emissions via solids or sludges formed in the plant*

High boiling decomposition products, organic acids, inorganic components picked up from the feed gas and corrosion products will accumulate in the solvent and might lead to operational problems in the course of time. Other acid gases, such as SO_2, NO_2, HCl in case of flue gases from coal firing, will be picked up by solvent. They reduce the capacity of the solvent as they use up part of the alkalinity of the solvent which is then not available for CO_2. They are thermally non-regenerable. This is one of the causes for the formation of so-called heat stable salts. These and other organic acids will be neutralised by the addition of sodium hydroxide or sodium bicarbonate. A reclaimer will recover the active solvent component and produce a concentrated stream of liquid waste material. Mostly a thermal reclaimer is used, which is a small distillation column in which a large proportion of the solvent is evaporated and further used in the process. The bottom products will then be disposed off. The process flow sheet also contains a carbon filter and this filter will also contain decomposition products, mainly organic materials. The carbon will also be treated as a waste material. In pre-combustion capture the amounts of waste products formed is much less and processes based on MDEA only operate without a reclaimer. Table 2.5 gives an overview of the amount of reclaimer wastes for different post-combustion capture processes.

Table 2.5 Reclaimer waste production for post-combustion capture processes.

Process/study	**Absorber emission**
Fluor Econamine FG Plus^{SM} [1]	3.2 kg/tonne CO_2
Fluor Econamine FG Plus^{SM} – natural gas fired combined cycle [15]	1.13 kg/tonne CO_2
Mitsubishi Heavy Industries – natural gas fired combined cycle [16]	0.085 kg/tonne CO_2
Mitsubishi Heavy Industries – coal fired power plant [16]	0.086 kg/tonne CO_2

In a recent publication [28] the amount of waste produced from a solvent process based on a 30% MEA solution was estimated for 90% CO_2 capture from the flue gases of a coal fired power station. Depending on the size of the slipstream to the reclaimer, the waste produced amounted to 3.7 kg/tonne CO_2 (0.5% slipstream) or 14.9 kg/tonne CO_2 (2% slipstream). These calculated amounts are larger than given in table 2.5. The waste stream was thought to be composed of formate, acetate, thiosulphate, thiocyanate, oxalate, sulphate and an unspecified corrosion inhibitor.

In the next chapter, environmental impact of various solvent based CO_2-capture are further quantified and interpreted. Further information on solvent degradation and waste production is given in Appendix H.

3. Approach

3.1 Introduction

This study assesses the environmental impact of solvent scrubbing of CO_2 by pre-combustion and post-combustion capture using a number of solvents, applied on power plants using either natural gas or hard coal as an input. Based on technology / solvent / fuel combinations a number of scenarios are defined, further on referred to as “reference cases”. Paragraph 3.3 elaborates all reference cases, after stating the scope of the study in paragraph 3.2.
Paragraph 3.4 deals with the way the environmental impact is quantified.

3.2 Scope and system boundaries

The environmental impact of CO_2 scrubbing in power plants is not limited to the decrease of CO_2 emission of the power plant. For instance the solvents have to be produced, which leads to the consumption of energy and material. From a broader perspective, the production of electricity in a power plant fitted with CO_2 scrubbing technology has a lower efficiency, which implies that a larger amount of fuel is consumed to produce a certain amount of electricity, resulting in an increased environmental impact. An environmental Life Cycle Assessment (LCA) covers the complete chain of processes (life cycle):

- production of raw materials and energy carriers
- production process
- use phase
- demolition and waste treatment
- all intermediate transport processes

Reflected to the production of electricity in a fossil fuel based power plant, this would include:

- extraction, cleaning and delivery of fuel
- fuel preparation
- combustion
- power generation
- flue gas cleaning including CO_2 scrubbing
- treatment of residues from production
- use of the electricity produced
- (waste treatment)
- all intermediate transport processes

In this study, the use of the electricity produced is not included. Waste treatment is not relevant here (electricity is not disposed of as such). Furthermore, distribution of electricity is not regarded. In principle, the analysis is cut off at the gate of the power plant, which makes this study a “cradle to gate” life cycle assessment.

The scope of the study is visualized in figure 3.1. All activities shown in this figure are taken into account in this study.

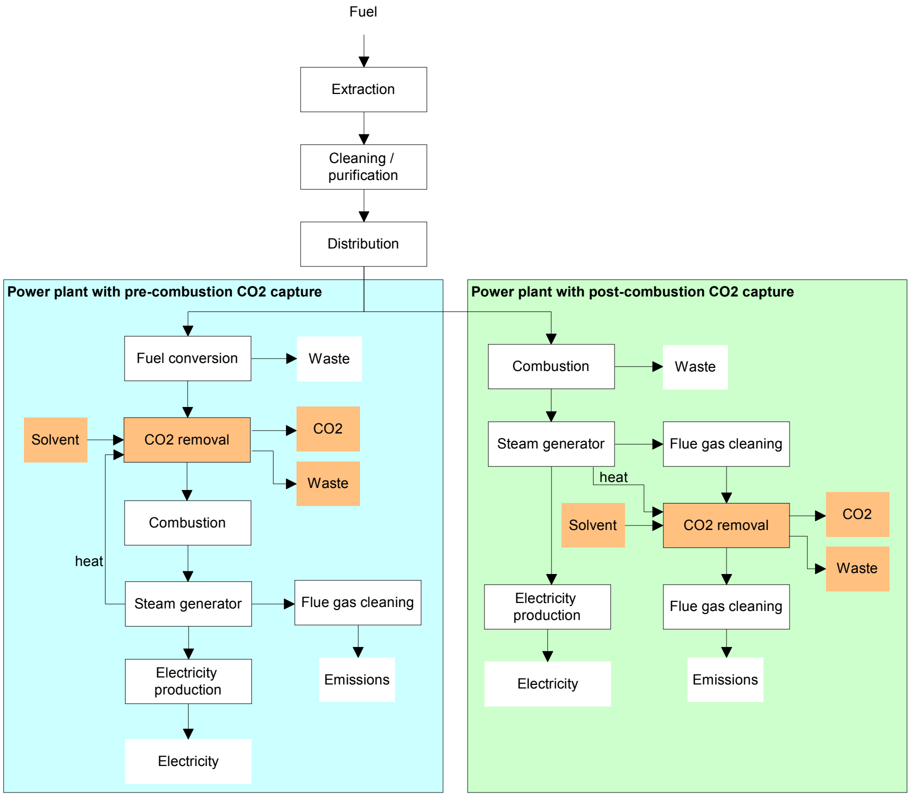


Figure 3.1 Scope of the study.

The white boxes form the life cycle of the production of electricity with natural gas or pulverized coal. The route through the left field (blue) includes reforming the fuels to hydrogen or methane, the right field (green) route indicates the direct combustion of the fuels. The orange boxes introduce capture of CO_2.

The depth of the study is usually indicated as follows:
1st order: production of the product itself
2nd order: background processes (production of raw materials, energy carriers)
3rd order: production of capital goods (machines and buildings)

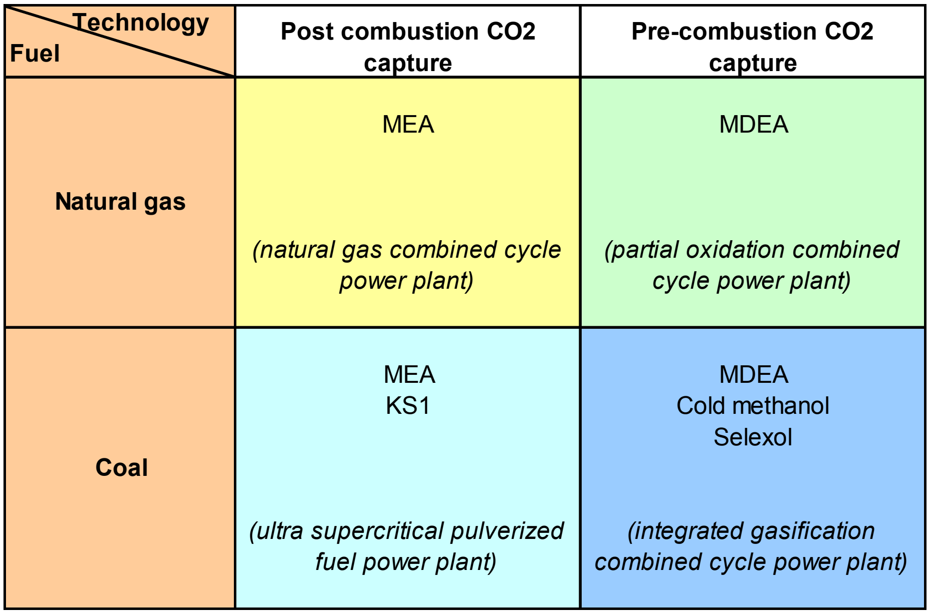
Under normal circumstances, 3rd order processes do not play a major role in the environmental impact of the system. A quick scan, based on an estimate of the amount of construction material for the extra equipment for CO_2 scrubbing, indicated that this is likely to be the case in this study. Therefore, only 1st and 2nd order processes are included in the environmental assessment.

The reference area is Western Europe. Fuel mixes for auxiliary processes as well as transport distances have been chosen to be representative for Western Europe.

3.3 Definition of reference cases

Several options are available for implementing CO_2 capture by solvent scrubbing at power plants.

Firstly, the technique can be applied on gas fired power plants and coal fired power plants, as well as on natural gas reforming plants and coal gasification plants. For each of these four applications, several solvents are suitable. Each power production / solvent combination is a possible scenario in this study. The drawing below illustrates these possibilities (see figure 3.2).



Technology **Fuel**	**Post combustion CO2 capture**	**Pre-combustion CO2 capture**
Natural gas	MEA *(natural gas combined cycle power plant)*	MDEA *(partial oxidation combined cycle power plant)*
Coal	MEA KS1 *(ultra supercritical pulverized fuel power plant)*	MDEA Cold methanol Selexol *(integrated gasification combined cycle power plant)*

Figure 3.2 Possible scenarios in this study.

Due to limited time and the limited availability of data on each solvent / technology / fuel combination, we have decided to choose one base solvent for each of the four fuel / technology combinations. Together with a non-capture case for each combination, this results in eight reference cases (see table 3.1, no. 3-10).

The environmental impact in these reference cases can be split into two major sources:

1. Electricity production
   The environmental impact of the electricity production process with or without CO_2 emission reduction.
2. Solvent scrubbing of CO_2
   A power plant with CO_2 capture has a number of differences, compared to the power plant without CO_2 capture. This includes the production of the solvent, the energy consumption of scrubber, stripper and reclaimer, the compression of CO_2 and the treatment of residues.

Two reference cases have been included to separately show the environmental impact of the capture of one tonne of CO_2: one for post-combustion capture and one for pre-combustion capture (reference case no. 1 and 2 in table 3.1).

Table 3.1 Reference cases.

No.	Code	Fuel	Reference case
1	MEA	Both	Capture of 1 tonne of CO_2 using MEA
2	MDEA	Both	Capture of 1 tonne of CO_2 using MDEA
3	NGCC	Natural gas	Natural gas combined cycle power plant
4	NGCC+	Natural gas	Natural gas combined cycle power plant with MEA post combustion capture
5	POCC	Natural gas	Partial oxidation combined cycle power plant
6	POCC+	Natural gas	Partial oxidation combined cycle power plant with MDEA pre-combustion capture
7	USCPF	Pulverized coal	Ultra supercritical pulverized fuel power plant
8	USCPF+	Pulverized coal	Ultra supercritical pulverized fuel power plant with MEA post combustion capture
9	IGCC	Pulverized coal	Integrated gasification combined cycle power plant
10	IGCC+	Pulverized coal	Integrated gasification combined cycle power plant with MDEA pre-combustion capture

As an example, the life cycle of reference case 1 is displayed in figure 3.3, accounting for the system boundaries described in paragraph 3.2.

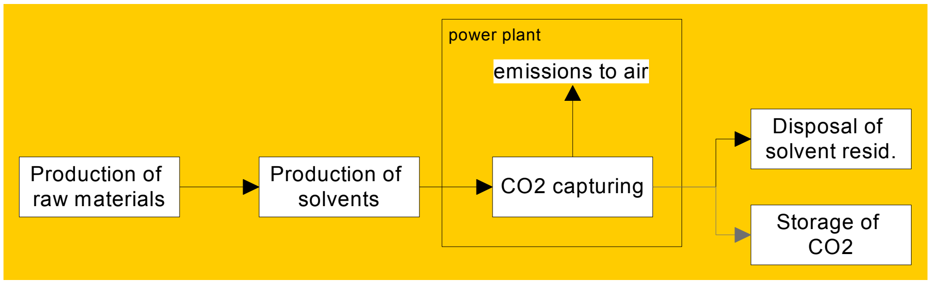


Figure 3.3 Example life cycle of reference case 1.

An example of the life cycle of reference case 4 is included as figure 3.4.

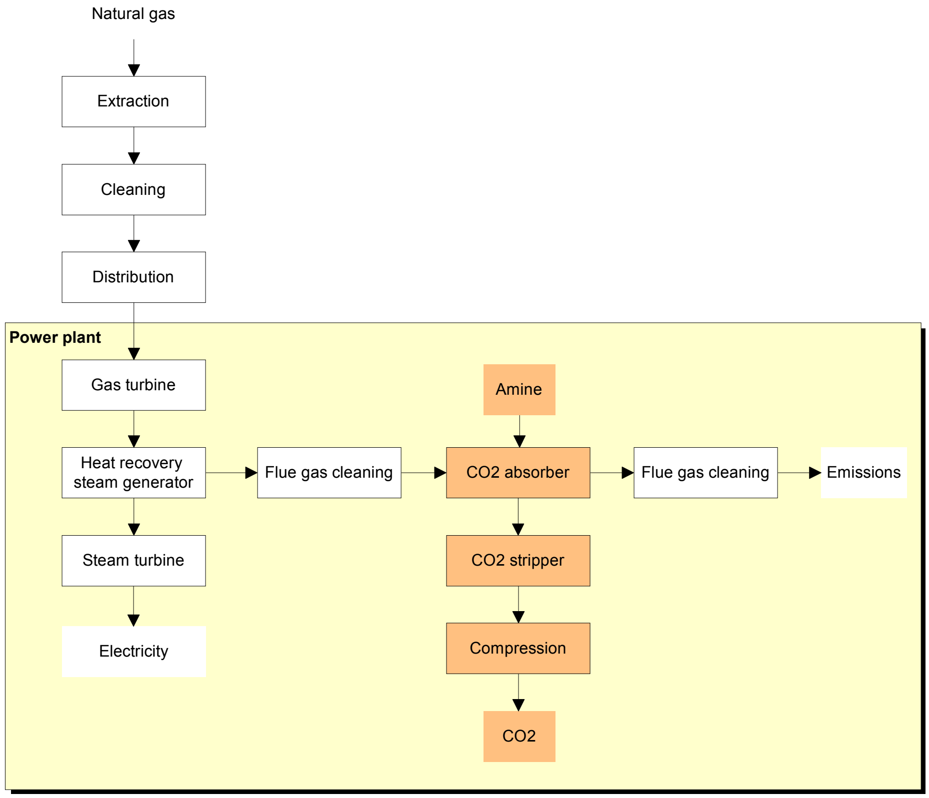


Figure 3.4 Example life cycle of reference case 4.

Each reference case has a calculation unit, in which the environmental impact is expressed. For reference cases 1 and 2 the following functional unit is used:

> *One tonne of CO_2 captured from a power plant*

For reference case 3 up to 10 inclusive, the functional unit is:

> *The production of 6.3 TWh of electricity in a natural gas or coal fired power plant, with or without solvent scrubbing of CO_2*

The amount of 6.3 TWh corresponds with a power plant with a net power output of approximately 800 MW.

Large scale deployment of solvent scrubbing of CO_2 in future may result in large environmental benefits and/or disadvantages. This study includes calculations of worldwide implementation of a combination of the reference cases described above, to an extent dictated by eventual additional future policy to stimulate further development and speeding up introduction. The two future scenarios are described in chapter 5.

3.4 Methodology of assessment of environmental impact

The evaluation of the environmental impact in this study is based on LCA, which usually consists of the following steps [17]:
- Goal and scope definition
- Inventory analysis
- Impact assessment
- Interpretation

The goal and scope definition is covered earlier in this report, mainly in paragraph 3.2. The other three steps are discussed below.
A more generic description of the steps of an LCA is available in appendix E.

Inventory analysis
The environmentally relevant data on which an LCA is based, can be divided in five categories:
IN:
- raw materials / semi-finished products
- energy

OUT:
- product(s)
- emissions
- waste

For each process, data of these five categories have to be inventoried. If the power plant is seen as one process, the following examples can be thought of:
- Raw materials/intermediate product: natural gas or pulverized coal, flue gas cleaning auxiliaries, amine based solvent
- Energy: - (all electricity and heat needs are generated internally)
- Product(s): electricity, CO_2
- Emissions: CO_2, CO, SO_2 NO_x, solvent, heat (to water)
- Waste: flue gas cleaning residues, reclaimer sludge

Obviously, each intermediate product includes a complete production chain of its own, with corresponding environmentally relevant data.

Impact assessment
The above exercise results in a gross list of inputs and outputs for each process, called *inventory table*. The next step is *characterization*. In this process, for each of

the inputs and outputs the contribution to a certain environmental issue is calculated by using substance-specific factors (equivalence factors), that express the relative severity of the substance regarding that particular environmental issue. For instance, according to the IPCC the release of one kilogramme of methane has the same effect on global warming as 21 kilogrammes of CO_2, which makes the global warming potential for methane 21 CO_2 equivalents. The characterization step results in a total equivalents figure for each environmental issue, e.g. kilogrammes CO_2 equivalents of global warming potential. The set of equivalent figures for the environmental issues is called “environmental profile”.
The final step is called *normalization*. In this procedure, the total equivalents figures are related to the scale of each environmental issue in a certain geographic reference area, e.g. Western Europe. The result is a “normalized environmental profile”.
The characterization and normalization together are called “impact assessment”.

In this study, the impact assessment has been carried out according to the widely used CML-LCA2 methodology, developed by the Institute of Environmental Sciences (CML) of the University of Leiden. The reference area chosen is Western Europe. Reference year is 1995 [17].

Impact assessment according to CML-LCA2 results in an environmental profile covering ten environmental issues, called “impact categories”, see table 3.2.

Table 3.2 Environmental impact categories.

Impact category	Environmental issue
Abiotic Depletion	Depletion of mineral resources and depletion of energy carriers (coal, crude oil, nat. gas)
Global Warming Potential	The “greenhouse effect”
Ozone Depletion Potential	Depletion of the ozone layer
Human Toxicity*	Impact of toxic substances on human health, taking into account fate, exposure and effect. Calculation based on toxicologic parameters
Freshwater Aquatic Ecotoxicity*	Impact of toxic substances on aquatic ecosystems, taking into account fate, exposure and effect. Calculation based on ecotoxicologic parameters
Terrestrial Ecotoxicity*	Impact of toxic substances on terrestric ecosystems, taking into account fate, exposure and effect. Calculation based on ecotoxicologic parameters
Photochemical Ozone Creation Potential	Summer smog creation
Acidification Potential	Acidification of the soil
Eutrophication	Impact of excessively high nutrient levels in soil and surface water

*) Because toxicity is considered to be topical when amine based solvents and their degradation products are released to air or water, a separate paragraph addresses the assessment of toxicity in this study, paragraph 3.6.

Interpretation

The environmental profiles of the cases in this study can be compared to evaluate which case is preferable from an environmental perspective. Though, comparison is allowed to be done on a *per impact category* basis. This means the methodology does not provide for weighing among impact categories. If one case has lower values for all impact categories (which is more environmentally friendly) this is not a problem. However, if a case is better on one, and worse on another impact category, no unambiguous conclusion can be drawn.

If a weight would be applied to each impact category, one was able to compare cases more easily. The "verdict" could then be based on a single indicator per case. Obviously, whichever weight is applied to each impact category, the derivation of the weight factors is a subjective procedure; the priority of each impact category can be different when a different viewpoint is taken. However, as long as the weighing method is well documented, it can be valuable for the interpretation of LCA results.

TNO has (further) developed the *shadow price method*, for weighing environmental impacts. The shadow price represents the highest acceptable cost for mitigation of one unit of environmental load. The shadow price method includes a weighing factor for each of the CML-LCA2 impact categories.

The shadow price method is grounded on policy goals for several environmental issues. All currently available mitigation measures have been put in an ascending order, i.e. starting with the cheapest one per unit of environmental load (e.g. one CO_2 equivalent of GWP): Marginal costs. When all these measures are stacked, at a certain point the policy goal can be met. The price per unit of environmental load of the last, most expensive mitigation measure taken to meet the target is called the shadow price. In figure 3.5 the construction of a shadow price is visualised.

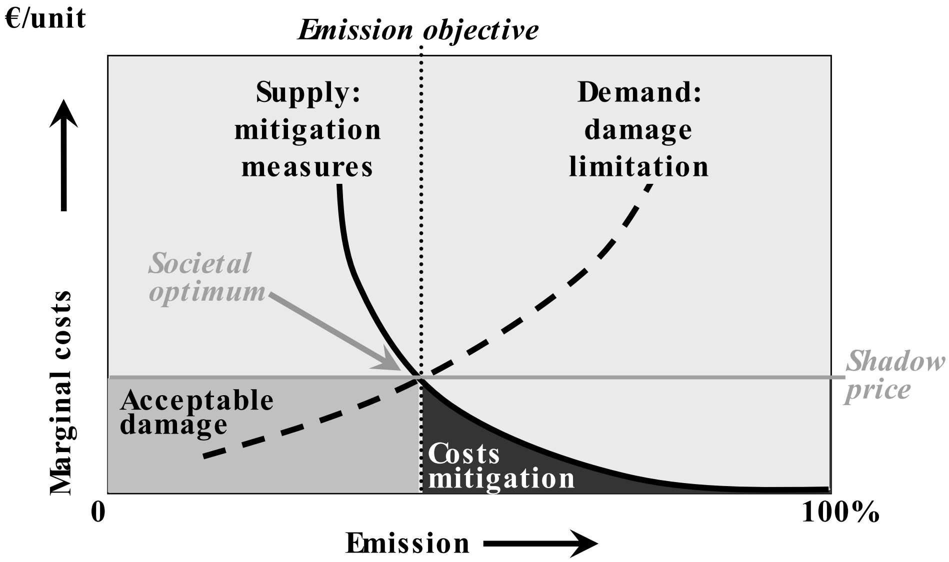


Figure 3.5 Derivation of a shadow price.

Decreasing the emission leads to increasing marginal costs (*Supply: mitigation measures*). The shadow price is the marginal cost of the most expensive measure to meet the emission objective (dashed vertical line). In that case you still accept the damage on the left side. The total costs of mitigation are represented by the area under the Supply line (black in the chart). Obviously, these would be the total costs in an optimal situation.

The shadow prices for the environmental categories of the CML-LCA2 method are presented in table 3.3 in euro per kilogram effect equivalent.

For some environmental categories, there appeared to be no legislation in the Netherlands. For example for the impact category 'abiotic depletion' shadow prices exist for energy resources, but energy is only responsible for 1% of the total antimony equivalents (Sb eq.). Energy legislation is therefore not representative for the category 'abiotic depletion' and no there is no other legislation in the Netherlands to diminish resource consumption. Without clear policy targets for an impact assessment category, is not possible to derive a level of acceptable costs. Therefore the shadow price of 'abiotic depletion' is 0 euros per kilogram antimony equivalent (see table 3.3).

Table 3.3 Environmental impact categories of CML and shadow prices.

Environmental themes	Dimension	Shadow price
Abiotic Depletion	kg Sb eq.	0 €/kg
Global Warming Potential	kg CO_2 eq.	0.05 €/kg
Ozone Depletion Potential	kg CFC-11 eq.	30 €/kg
Human Toxicity	kg 1,4 dichlorobenzene eq.	0.09 €/kg
Freshwater Aquatic Ecotoxicity	kg 1,4 dichlorobenzene eq.	0.03 €/kg
Terrestrial Ecotoxicity	kg 1,4 dichlorobenzene eq.	0.06 €/kg
Photochemical Ozone Creation Potential	kg C_2H_2 eq.	2 €/kg
Acidification Potential	kg SO_2 eq.	4 €/kg
Eutrophication	kg PO_4 eq.	9 €/kg

The shadow prices per kg effect equivalent are multiplied by the outcomes of the environmental assessment on *characterization* level. This results in a weighed environmental profile, presenting the external (prevention) costs.

By using shadow prices the external costs of increased material or energy consumption for CO_2 capture can be weighed against the costs that are saved by reducing CO_2 emissions (as can be seen in Figure 4.2).

In addition to the weighing function, shadow prices are also fit for a comparison between external costs (shadow costs) and the real costs of the production of electricity with and without CO_2 capture. This can indicate whether capture of CO_2 from power plants is an efficient measure for avoiding CO_2 emission compared to measures already being taken, in terms of euros per tonne CO_2. However, this is outside the scope of the study.

The method behind shadow prices is further explained in Appendix F.

3.5 Study methodology

The study was started by the conception of a questionnaire, addressing the major issues of both the solvent production and the solvent usage in a CO_2 capture process. The content of the questionnaire is given in Appendix G, including an explanatory cover letter. It was based on a preliminary quantification of the expected environmental impact. The list of companies to which the questionnaire was sent is given below. The list includes companies dealing with both the production issues and usage issues.

Table 3.4 List of companies to which the questionnaire was sent.

Company	Production	Use
BASF	+	+
Fluor Daniel	-	+
MHI	-	+
Huntsman	+	+
DOW Chemicals	+	+
INEOS	+	+
Shell	-	+
ABB Lummus	-	+
Air Products	+	+
UOP	-	+
CEFIC – Amine section	+	+

The responses from these companies have been limited. A number of them did not react at all, also after sending reminders. Several were approached by telephone. The main comment was that they were too busy to fill in the questionnaire. One company replied: “We regret that we have to decline the opportunity to participate in the study due to the confidential nature of the information requested and the uncontrolled publicity of the results”. Another one responded in the following way: “the information with regard to disposal and / or waste from operating plants is considered confidential between us and our customers. We are not at liberty to disclose this information even if we wanted to. As far as our own production and waste streams, I would not have access to the information directly. I am not sure the plants themselves would have the details as they are requested. It would require a study of each individual plant / unit and we would have to ask for them to develop unit specific data. We are unable to fulfill your request”.

Mitsubishi Heavy Industry was the only company willing to provide some additional data on their solvent process.

In view of this limited response, it was decided to base the study on information and data available in the open literature, although this was scattered. The analysis of the information data in the literature does allow an assessment of the environmental impact.
The type of information collected as well as the sources used in this study is described in chapter 4.

3.6 Toxicity assessment

General

Toxicity is the ability of a substance to cause adverse effects on organisms. The concentration determines whether a substance is toxic for a certain species or not. Two types of toxicity are discriminated: acute and chronic toxicity, referring to the effects due to short exposure to a high concentration and prolonged exposure to a lower concentration. Thus, besides the concentration, the duration of exposure is a relevant parameter for toxicity effects.

Toxic effects on organisms are a result of a chain of processes. First the substance is released to air, water or soil, e.g. as a result of solvent scrubbing of CO_2 (evaporation of solvent to air), or disposal of reclaimer sludges (evaporation to air, leaching of solvent with percolate that ends up in ground water or surface water). Due to continuous interaction among the compartments of the environment (air, groundwater, surface water, soil, sediment), the substance will be partly distributed from the compartment of initial release into the other compartments. The way it distributes is dependent on properties of the local environment as well as some substance-specific parameters, for instance the Henry's Law constant.

The concentration of the substance on a certain location can be predicted: Predicted Environmental Concentration (PEC). In that case, more information has to be available, for instance other sources of the substance have to be known, as well as a background concentration.

The toxic effect of a substance on organisms is usually measured as LC50, the concentration at which the substance is lethal to 50% of the individuals of a certain species (given a particular administration route). The Predicted No-Effect Concentration (PNEC) is the concentration below which no adverse effects are expected to the most sensitive species known. Where the PEC is higher than the PNEC, adverse effects may occur.

The actual concentration in the environment due to the release of, for instance, an amine to air, is not likely to be constant. Releases may be discontinuous; also, distribution through the environment takes time. Furthermore, due to decomposition, sink, accumulation in other organisms and other processes material is removed from exposure to organisms. This is called the fate of a substance. The actual exposure time is therefore influenced by biodegradation rates, sink speeds et cetera.

The above discussion is applicable to ecotoxicity. For human toxicity most of the information is valid as well. Here, also the uptake of a substance through the diet is of importance. Human toxicity is usually expressed as Threshold Limit Values (TLVs) or Acceptable Daily Intakes (ADIs).

Toxicity in Life Cycle Assessment

Modelling toxicity in Life Cycle Assessment is difficult. In the above discussion at least two parameters have been identified that are not compatible with the framework of LCA: place and time. LCA is based on a linear model; the marginal effect of an emission is considered constant, in other words every kilogramme of a substance released to the environment is accounted equally. It does not account for spatial variation such as the sensitivity of the local environment, or temporal aspects such as actual (predicted) concentrations.

Toxicity assessment in CML-LCA2 is based on the USES 2.0 multi-media fate, exposure and effect model. The LCA implementation by Huijbregts [24] tries to overcome the discrepancies between toxicology and LCA. The model accounts for

distribution of a substance among environmental compartments and multiple exposure routes, and addresses biodegradation.
For each substance, effect factors have been established for each release compartment / effect compartment combination, that represent *potential* toxicity effects of the release of 1 kg of that substance. The actual increases of environmental concentrations (as a result of distribution, degradation) have only been used to establish the ranking of potential toxicity effects among substances. The PNEC values have been taken from literature. Each potential effect is compared to a fixed reference substance, 1,4-dichlorobenzene, resulting in effect factors ("potentials") expressed as 1,4-dichlorobenzene equivalents.
For human toxicity, chronic Human Limit Values (HLVs) have been used as a basis, corresponding to an additional life-time risk of 1.10^{-6} as a result of the first mechanism occurring (genotoxic, carcinogenic, …).

Toxicity of solvents
The CML-LCA2 comes with toxicity potentials for a limited set of substances. None of the CO_2 solvents in this report were included. Therefore we have asked the author of USES-LCA2, Mark Huijbregts of Radboud University Nijmegen to calculate additional toxicity potentials for a selection of solvents [22; 23]. The results are included in appendix C.

For each solvent human- as well as ecotoxicity potentials have been calculated for a number of initial emission compartments, of which air is the most relevant for this study. As stated above, human limit values (HLVs) have been used to express human toxicity effects, and PNECs to express ecotoxicity effects. Though, for the solvents considered in this report these values are scarcely available in literature. In absence, HLVs have been derived by dividing No Observed Effect Levels (NOELs) for other mammals by a safety factor, and PNECs have been derived by dividing Lowest Observed Effect Concentrations (LOECs) or No Observed Effect Concentrations (NOECs) by a safety factor.

MDEA toxicity potentials are included for reference purposes only; release of MDEA in the POCC and IGCC plants is not assumed.

Table 3.5 presents a ranking of the freshwater aquatic ecotoxicity of the solvents considered, as well as some illustrative reference substances. Please note that these values are expressed as 1,4-dichlorobenzene equivalents, and are representative for the emission of 1 kg of substance to air.

Table 3.5 Ranking freshwater aquatic ecotoxicity potentials of solvents.

Substance (released to air)	**Freshwater Aquatic ecotoxicity potential FAETP (1,4-DCB eq.)**
Dioxins (TEQ)	*$2.1 . 10^6$*
DDT	*325*
Chromium VI	*7.7*
MEA	3.7
MDEA	1.4
TEA	1.4
AMP	1.1
1,4-Dichlorobenzene	*1*
Sulfolane	0.26
DEA	0.17
Methanol	0.0016
Benzene	*$8.4 . 10^{-5}$*
Ethene	*$1.4 . 10^{-11}$*

For human toxicity, the substances have been ranked in table 3.6. For sulfolane and MDEA no human toxicity potentials could be determined.

Table 3.6 Ranking human toxicity potentials of solvents.

Substance (released to air)	**Human Toxicity potential HTP (1,4-DCB eq.)**
Dioxins (TEQ)	*$1.9 . 10^9$*
Chromium VI	*$3.4 . 10^6$*
Ethylene oxide	*$1.4 . 10^4$*
Benzene	*$1.9 . 10^3$*
AMP	780
DEA	140
DDT	112
TEA	83
1,4-Dichlorobenzene	*1*
Ethene	*0.64*
MEA	0.64
Methanol	0.13

Large differences in ranking are visible between the tables. The human toxicity potentials of the solvents are ranked lower than their ecotoxicity potentials, compared to the reference substances. Two notes: (1) the reference substances are chosen arbitrarily; (2) the toxicity potentials are subject to large uncertainties. HLV and PNEC values from literature have an uncertainty in themselves (it is difficult to determine the no-effect point unambiguously, furthermore possibly the most

sensitive species has not been identified yet for a particular substance / compartment / administration route), and derivation from NOEC/NOEL values involves safety factors that are usually expressed in orders of magnitude.
These considerations lead to the conclusion that for most of the solvents the toxicity potentials are not significantly different if we suppose an uncertainty margin of two orders of magnitude.
How the carcinogenic nitrosamines would stack up to the substances in tables 3.5 and 3.6, is unknown. No toxicity data for chronic exposure were found.

4. Environmental impact of solvent scrubbing for CO_2 capture

4.1 Introduction

This chapter contains the results of the environmental Life Cycle Assessment of ten reference cases (see table 3.1).

Case 1 and 2 will be presented in paragraph 4.2. Cases 3 up to 10 inclusive are discussed in paragraph 4.3.

4.2 Reference cases: capture of one tonne of CO_2

4.2.1 General

This paragraph describes the environmental impact of the removal of one tonne of CO_2 in a natural gas or pulverized coal fired power plant. The life cycle is described in paragraph 2.2 and consists of the production of the solvent, transport, scrubbing, stripping, reclaiming, compression of CO_2 and treatment of reclaimer sludge. Reference cases 1 and 2 describe post-combustion and pre-combustion scrubbing, irrespective of the type of power plant in which the CO_2 removal is introduced. Because of some differences between implementation in a natural gas fired power plant and a coal fired power plant, we show both results separately.

4.2.2 Inventory data

As described in paragraph 2.4, environmentally relevant data include:
IN:
- raw materials / semi-finished products
- energy

OUT:
- product(s)
- emissions
- waste

Table 4.1 shows a number of relevant figures used in the calculations of reference case 1 and 2. Detailed inventory data is included in appendix B.

Table 4.1 Relevant data for reference cases 1 and 2.

Item	**Reference case 1 Post-combustion capture**	**Reference case 2 Pre-combustion capture**
Functional unit	1 ton of CO_2 captured	1 ton of CO_2 captured
Solvent	Monoethanolamine (MEA)	Methyl diethanol-amine (MDEA)
Amount of solvent used (gas / coal fired plant)	1.6 kg / 1.6 kg	0.012 kg / 0.012 kg
Additional fuel consumption (gas / coal fired plant)*	2948 MJ / 2630 MJ	5220 MJ / 2345 MJ
Emission of solvent to air	47 g / 14 g	Not applicable
Amount of solvent residue	3.2 kg / 3.2 kg	0.024 kg / 0.024 kg

*) The additional fuel necessary to compensate the fall of efficiency of the plant as a result of CO_2 capture; expressed in MJ calorific value. Example: whenever one tonne of CO_2 is captured in the NGCC plant with post-combustion capture, meanwhile 2.64 MWh of electricity has been produced. This would have taken less fuel in case this amount of electricity had been produced in a non-capture NGCC plant. The difference in fuel consumption is the negative side effect of the capture of one tonne of CO_2.

MEA is produced using ethylene and ammonia. MEA is distilled from a product mix (MEA, DEA, TEA). Ethylene and ammonia use is calculated using molar ratios, and amounts 284 g/kg and 734 g/kg respectively. The process itself is exothermic, however the multi-stage distillation takes approximately 5 MJ/kg product.

MDEA has methanol, ammonia and ethylene oxide as its precursors. Methanol and ammonia form monomethylamine (MMA). A two-stage reaction with ethylene oxide results in monomethylethanolamine (MMEA) and methyldiethanolamine (MDEA). Details of the production process are not available; as an approximation, the energy consumption is set to 6.6 MJ per kg MDEA. Further information on amine production processes can be found in Appendix A.

The energy for the CO_2 scrubbing process is supplied as steam, extracted from the power plant. The necessary amount of energy is derived from the cases described in [1, 2]. Reference cases 1 and 2 are derived from the differences in process data for the power plant with CO_2 removal and the power plant without CO_2 removal. This way, the additional fuel consumption as well as the changed emissions to air are expressed in the results, besides the production of solvent and treatment of reclaimer residues as a result of the capture process.

Process data for the generic production of steam, the production of MEA and the production of heat and electricity used during the production of solvents are derived from a commercially available life cycle inventory database [10].

4.2.3 Treatment of reclaimer residues

The main waste stream as a result of CO_2 capture is the reclaimer sludge. This residue stream arises during both post-combustion and pre-combustion capture, though the amounts are much smaller for the latter. The main components are water, solvent and heat stable salts.
Table 4.2 shows the composition of the reclaimer sludge of a MEA based CO_2 removal installation [1].

Table 4.2 Composition of reclaimer sludge [1].

Component	Amount
Water	33.9% vol
MEA	6000 ppm
Cr	< 2 ppm
Cu	855 ppm
Fe	129 ppm
Ni	< 2 ppm
Na	7500 ppm

Per tonne of CO_2 captured, 3.2 kg and 0.024 kg of reclaimer sludge is generated for post-combustion and pre-combustion capture, respectively (see table 4.2). For an 800 MW power plant this equals roughly 10 and 0.1 kilotonnes per year.

The composition in table 4.2 is not complete; the sum is not 100%. The composition of the remaining portion is thus unknown. To at least address the environmental impact of the full amount of reclaimer waste, it is assumed that the remaining 65% also consists of MEA.

Detailed information on current practice of treatment of reclaimer sludges is not available. The following discussion is therefore a theoretical one.

The likely treatment routes in Europe of a waste with a composition as given in table 4.2 are dependent on whether the waste is classified as hazardous or non-hazardous according to the European Commission Decision 2000/532/EC as regards the list of wastes. The reclaimer sludge with a composition as in table 4.2 is, according to the criteria, not to be regarded as hazardous waste (see evaluation in appendix D). However, the given composition is not complete (the table does not sum to 100%). Possibly unknown components would change the verdict.

Several treatment options are possible in both cases (whether the waste is hazardous or non-hazardous), see table 4.3:

Table 4.3 Treatment options of reclaimer residues (not exhaustive).

Non-hazardous waste (sludge as in table 4.2)	Remarks	Hazardous waste	Remarks
Incineration in municipal waste incinerator	See 2000/76/EC on the incineration of waste	Incineration in hazardous waste incinerator	See 94/67/EC on the incineration of hazardous waste
Landfill site for non-hazardous waste	See 1999/31/EC on the landfill of waste	Landfill site for hazardous waste	See 1999/31/EC on the landfill of waste
Co-combustion in power plant	Reuse of the sludge as an input of the power plant		

Because the waste stream has a negative calorific value, not many options are attractive. Removal of the water is not likely to result in a mechanically usable waste either.

It is not known if treatment in a wastewater treatment plant is a viable option; this depends on whether concentrations of MEA and other organic components are not toxic to the micro-organisms, and that these components can be broken down quickly enough.

In the reference cases in this study, the reclaimer residues are assumed to be treated in a waste incinerator. All organic components are assumed to be combusted. Metal compounds are partially emitted to air; the remainder ends up in the bottom ash which is landfilled. The waste incinerator model is created by TNO, and is described in appendix D.

Because incineration of wastes is not taking place on a large scale in every European country, an alternative landfill scenario is included in appendix D. Because the amount is small, the effect on the results is expected to be negligible for all reference cases.

A completely different option is the co-combustion of sludges in a coal-fired boiler. In the coal fired reference case [8] it would be possible to incinerate the sludges by feeding them back in the installation itself. Because of the small amount (0.7% m/m of the coal input for reference case 8) this is not problematic. The metallic ions in the sludge will end up in the flue gas cleaning residues. The additional environmental impact is expected to be small. Though, further research has to be done to assess the practical applicability. Fluor also suggest that the waste can be disposed of in a cement kiln, where the waste metals become agglomerated in the clinker [1].

4.2.4 Impact assessment

The impact assessment has been carried out according to the CML-LCA2 methodology (see also paragraph 3.4). Figure 4.1 shows the environmental profiles for reference cases 1 and 2. The results are presented for implementation in both a coal and natural gas based power plant. For each impact category, the highest value is set to 100%.

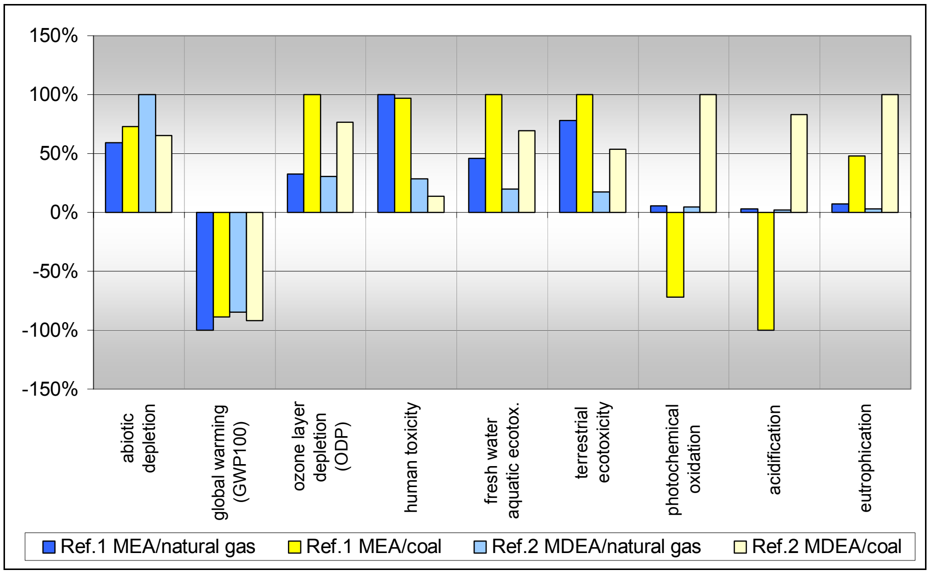


Figure 4.1 Environmental profiles of reference cases 1 and 2 for natural gas and coal.

As can be seen, the capture of one ton of CO_2 has positive and negative effects on the environment. The avoidance of the emission of CO_2 is an obvious one. Furthermore, CO_2 capture in a USCPF (MEA/coal) has positive effects on the photochemical oxidation and acidification, as is shown as negative values in figure 4.1. This is a result of removal of the remaining SO_2 in the flue gas by the stripper itself. Because figure 4.1 reflects only the *additional* environmental impact that is a result of the capture of 1 ton of CO_2, this side effect leads to negative values.

The NGCC plant with MEA has the best net CO_2 removal efficiency in figure 4.1, which can be seen in the columns for global warming. The removal of one ton of CO_2 is offset a little by the higher fuel consumption and the use and waste treatment of solvent. For the NGCC plant with MEA this offset is relatively small.

The results for abiotic depletion can be seen as a measure for fossil fuel consumption. Indeed, the most efficient system (NGCC + MEA) has the lowest additional fuel consumption. The differences seem larger than between the global warming scores; this is caused by the avoided emission of one ton of CO_2. Table 4.4 shows the absolute values for abiotic depletion and global warming potentials.

Table 4.4 Abiotic depletion and global warming scores for reference case 1 and 2.

Impact category	Reference case 1 MEA/ natural gas	Reference case 1 MEA/ coal	Reference case 2 MDEA/ natural gas	Reference case 2 MDEA/ coal
Abiotic depletion (kg Sb eq.)	1.57	1.96	2.66	1.74
Global warming (CO_2 eq.)	180	271	305	246
Net global warming (CO_2 eq.)	-820	-729	-695	-754

On basis of figure 4.1 one cannot conclude whether the capture of CO_2 has a net positive or net negative effect on the environment without weighing the different environmental impact categories. The weighing of the impact categories results in a single score, according to a fixed set of weighing factors. Figure 4.2 shows the weighed scores of figure 4.1, using the shadow prices method.

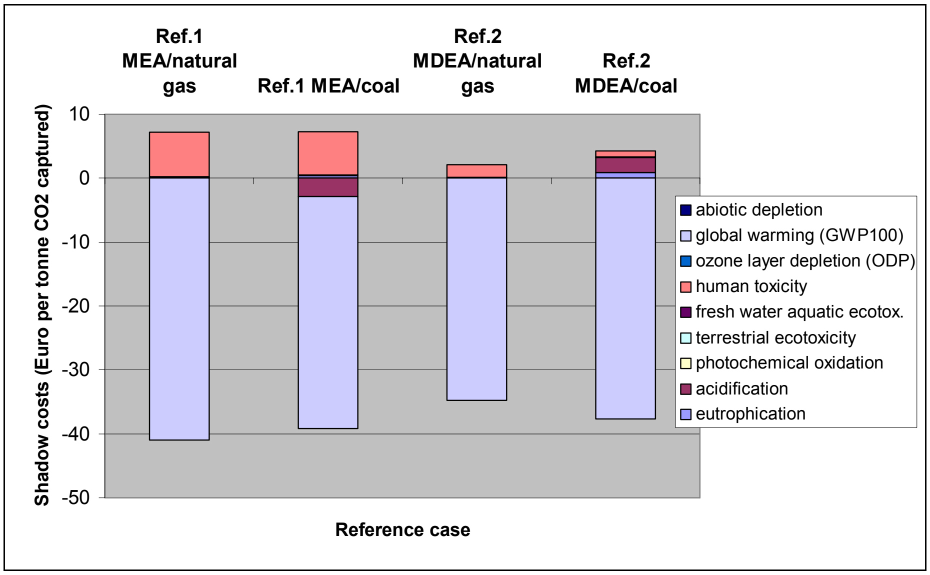


Figure 4.2 Environmental impact of reference cases 1 and 2, weighed with shadow prices method.

Based on the shadow price weighing, avoiding the emission of CO_2 has a net environmental benefit. The negative bars represent the net avoided CO_2 emission as a result of capture of one tonne of CO_2, the positive bars represent the additional environmental impact to accomplish this.

Because it is determined that abiotic depletion has no shadow price (no policy measures are carried out specifically to avoid depletion of natural resources) this impact category plays no role in figure 4.2. The impact categories global warming, human toxicity and acidification make up for almost all shadow costs. The shadow costs for human toxicity are, in this case, mainly related to the emission of solvent on the one hand (MEA cases) and emissions during the extraction and production of natural gas on the other. This way the fuel consumption penalty due to the capture of CO_2 shows in human toxicity. Acidification is caused mainly by three substances: SO_2, NO_2 and NH_3. The SO_2 and NO_2 emissions of the pulverized coal fired power plant decrease (Ref. 1 MEA/coal), while in the coal gasification plant (Ref.2 MDEA/coal) NO_x and SO_2 emissions have increased. The emission of these substances do not play a large role in natural gas fired power plants, as is confirmed by the absence of purple bars for these cases in figure 4.2.

Please note that the above results have one tonne of captured CO_2 as a unit. Paragraph 4.3 shows the results from the power production perspective: the environmental impact is calculated for the production of a MWh of electricity with and without capture of CO_2.

4.3 Reference cases: implementation of CO_2 capture in power plants

4.3.1 General

Reference cases 3 up to 10 inclusive describe direct and indirect gas- and coal fired power plants with and without CO_2 capture technology (see table 4.1). In this paragraph, the environmental impact of these cases is compared on the basis of the generation of one MWh of electricity. We have selected a number of literature sources describing power plants with a scale of approximately 800 MW, and determined the environmental burden caused by the production of one MWh.

4.3.2 Inventory data

The reference cases have been based on a study by Fluor [1] and studies carried out by Jacobs Consultancy and Foster Wheeler [19, 2].

Table 4.5 shows a number of relevant figures used in the calculations of reference cases 3-6 (natural gas based power plants). Table 4.6 shows relevant information on cases 7-10 (coal based power plants). Detailed data is included in appendix B.

Table 4.5 Relevant data for reference cases 3 up to 6.

Item	**Reference cases**			
	3 NGCC	**4 NGCC + capture**	**5 POCC**	**6 POCC + capture**
Power plant	Combined cycle	Combined cycle	Reformer	Reformer
Output	776 MW	662 MW	785 MW	694 MW
Net efficiency	55.59%	47.42%	55.88%	41.49%
Availability	7884 h/y			
Functional unit	1 MWh electricity			
Solvent	-	Monoethanolamine (MEA)	-	Methyl diethanolamine (MDEA)
Solvent consumption (kg/MWh)		0.605		0.00524
CO_2 generation (kg/MWh)	379	445	371	500
CO_2 captured (kg/MWh)	-	378	-	428
CO_2 emission to atmosphere (kg/MWh)	379	67	371	72
Emission of solvent to air (kg/MWh)		0.0178		0
Amount of solvent residue (kg/MWh)		1.21		0.0105

Table 4.6 Relevant data for reference cases 7 up to 10.

Item	**Reference cases**			
	7 USCPF	**8 USCPF + capture**	**9 IGCC**	**10 IGCC + capture**
Power plant	Pulverized coal fired	Pulverized coal fired	Coal gasification	Coal gasification
Output	758 MW	666 MW	776 MW	683 MW
Net efficiency	43.98%	34.79%	43.09%	35.04%
Availability	7884 h/y			
Functional unit	1 MWh electricity			
Solvent	-	Monoethanolamine (MEA)	-	Methyl diethanolamine (MDEA)
Solvent consumption (kg/MWh)		1.314		0.0050
CO_2 generation (kg/MWh)	739	939	771	955
CO_2 captured (kg/MWh)	-	822	-	819
CO_2 emission to atmosphere (kg/MWh)	739	117	771	136
Emission of solvent to air (kg/MWh)		0.0110		0
Amount of solvent residue (kg/MWh)		2.63		0.0100

For the production of natural gas and pulverized coal, generic environmental data from [18] is used, that represents average European production.
The inputs and outputs (raw materials, emissions and wastes) arising from the power production are derived from the literature sources mentioned [1, 2, 19].
The environmentally relevant data of CO_2 capture are described in chapter 4.2.

4.3.3 Impact assessment

Figure 4.3 shows the environmental impact of reference cases 3 up to 10 inclusive. Per impact category, the highest value is set to 100%.

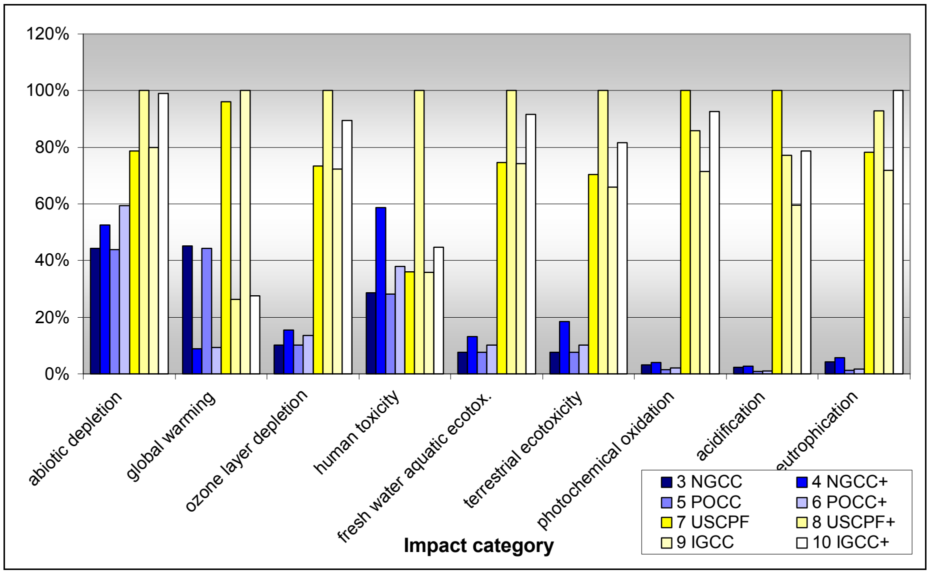


Figure 4.3 Comparison of reference scenarios 3-10 (relative per impact category).

In general, natural gas based electricity production has a lower impact on the environment than coal based electricity production. According to the CML-LCA2 calculation methodology hard coal has a higher depletion rate than natural gas, which does not correspond with actual information. However, for all other impact categories it corresponds with the current knowledge, that the CO_2 emission of direct or indirect combustion of natural gas is lower per MWh than for coal. Furthermore, emissions that influence photochemical oxidation, acidificaton and eutrophication are lower or absent for natural gas based plants (NO_x, SO_2, fine dust (PM_{10}), CO). It has to be realised that the three categories mentioned are largely influenced by the production processes of the fuels, especially for coal. This also holds for the three toxicity categories in case of the coal fed plants.
The indirect combustion plants (natural gas reformer and coal gasification) show comparable fuel consumption to direct combustion plants (see also tables 4.4 and 4.5), which translates in almost equal abiotic depletion scores. CO_2 emissions are not far off either, because of comparable CO_2 removal efficiencies.

In figures 4.4 up to 4.7 the reference cases are compared two by two: a power plant type with and without CO_2 capture. For each set, the environmental impact of the power plant without is set to 100%. The environmental impact is presented for the 9 categories as a spider-graph.

Figure 4.4 gives the environmental impact spider graph for the natural gas fired combined cycle (NGCC) without and with CO_2-capture.

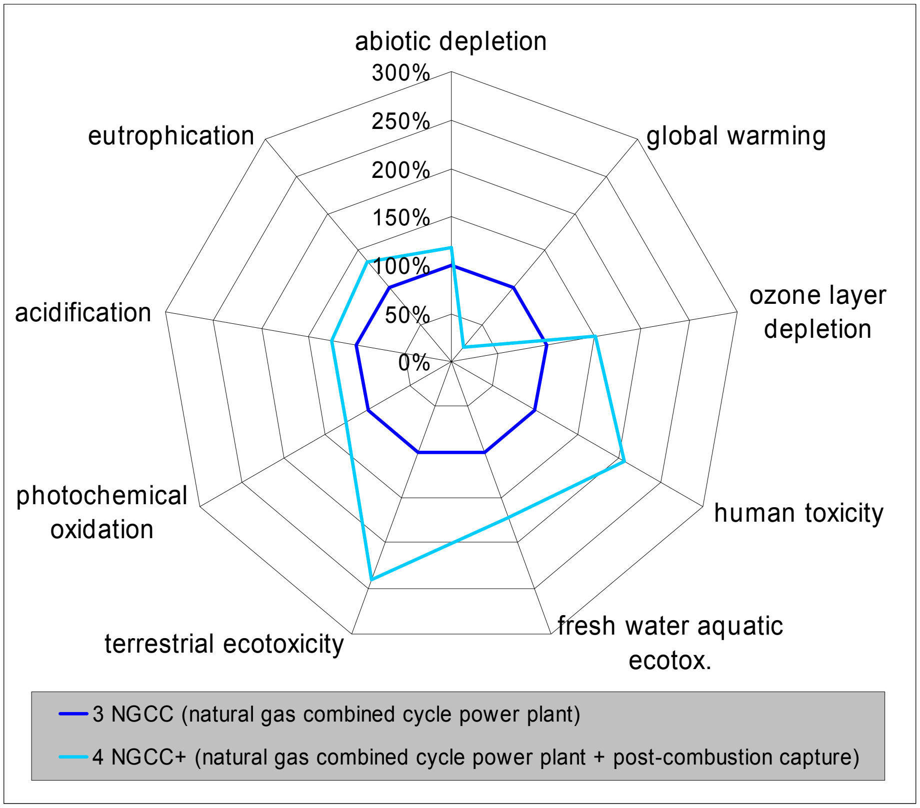


Figure 4.4 Environmental impact spider graph for NGCC.

The environmental impact for the NGCC with capture is increased for all environmental themes, except not surprisingly for the theme of global warming. The capture process for the NGCC has a significant influence on the toxicity categories. The additional impact on human toxicity and terrestrial ecotoxicity are related to the production of MEA and the emission of MEA to air (45%/55% and 60%/40%, respectively), but not on the waste production within the capture plant. The large impact on the terrestrial ecotoxicity theme is quite striking. The increase of photochemical oxidation, acidification and eutrophication is due to the higher fuel consumption. However, this is partly offset by the decrease of direct emissions of the power plant. The production of MEA also plays a role here. Ozone depletion is dominated by the production of natural gas.

Figure 4.5 gives the environmental impact spider graph for the natural gas based partial oxidation combined cycle (POCC) without and with CO_2-capture.

The very stable pattern in figure 4.5 for all impact categories but global warming indicates that the direct emissions of the plant as well as the production of MDEA do not significantly influence the results. This is linked to the low consumption of the solvent MDEA in this pre-combustion process. The solvent also is not in direct contact with the air compartment, which avoids this way of impacting upon the environment. The increase of environmental impact is to a large extent the result of the increased fuel consumption.

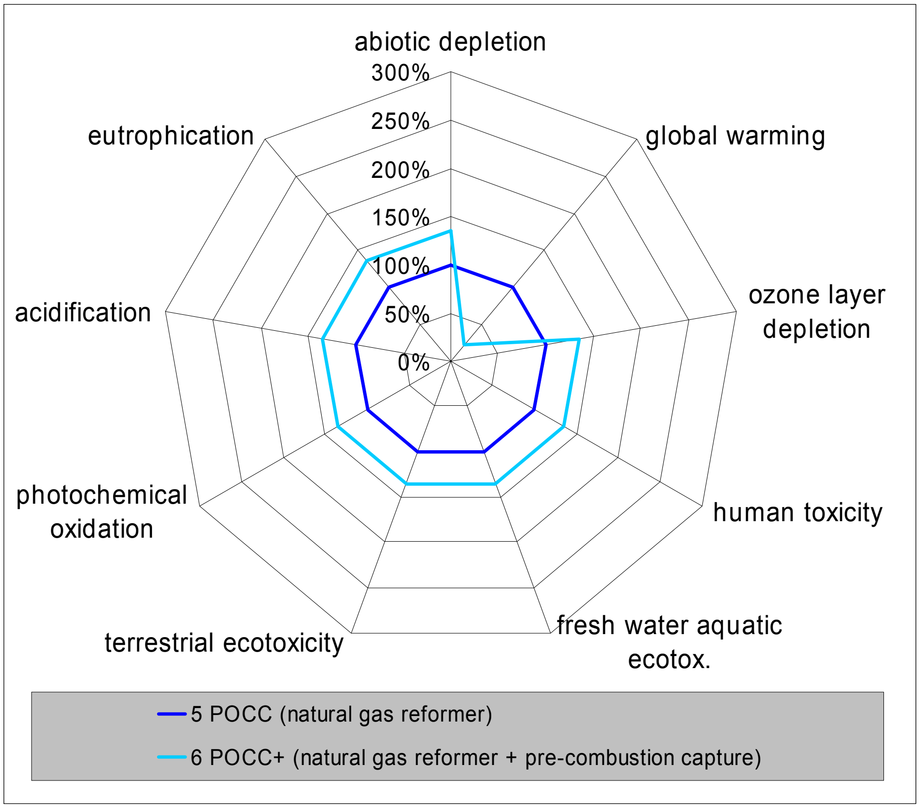


Figure 4.5 Environmental impact spider graph for POCC.

Figure 4.6 gives the environmental impact spider graph for the pulverised coal fired power plant (USCPF) without and with CO_2-capture.

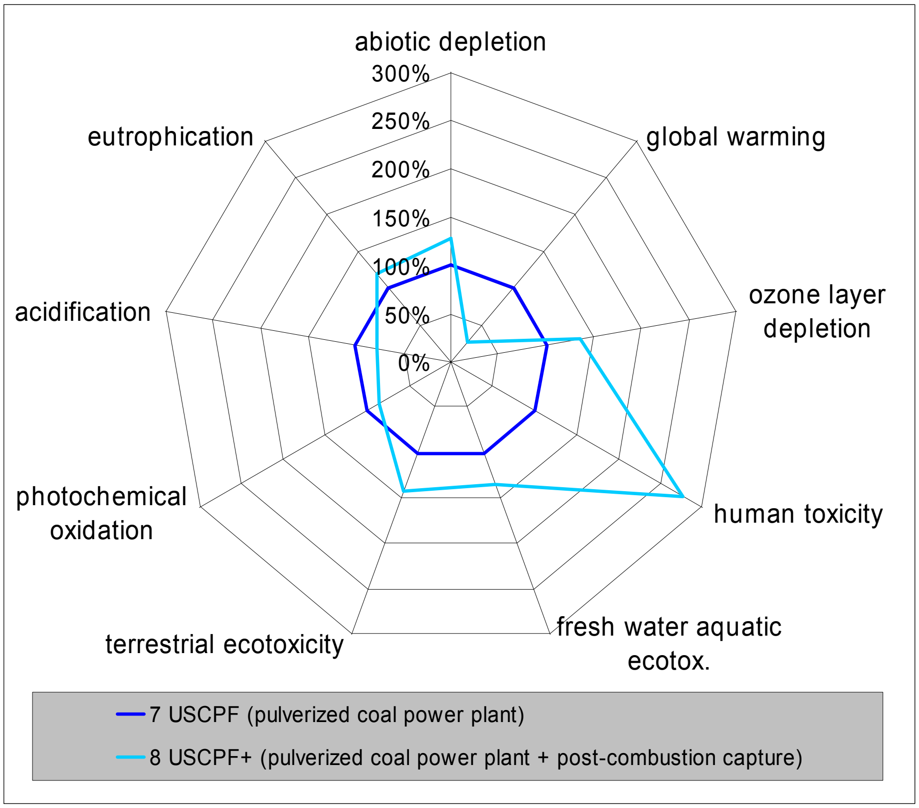


Figure 4.6 Environmental impact spider graph for USCPF.

The spider graph in figure 4.6 shows that for the direct fired power plants based on pulverized coal, the decrease of SO_2 and NO_2 emissions is clearly visible as a dent on the left side of figure 4.6 in the themes acidification and photochemical oxidation. The high impact on human toxicity is almost fully caused by the production of MEA. Although in absolute sense equal to the increase in figure 4.4 (the MEA consumption per megajoule is approximately equal) the relative increase of the score compared to a coal plant without capture is larger than for the natural gas fired combined cycle. This is directly linked to the higher CO_2 emissions per unit electricity and the higher MEA-consumption as a result of this. Other impact categories more or less reflect the increase in fuel consumption.

Figure 4.7 gives the environmental impact spider graph for the integrated gasification combined cycle (IGCC) without and with CO_2-capture.

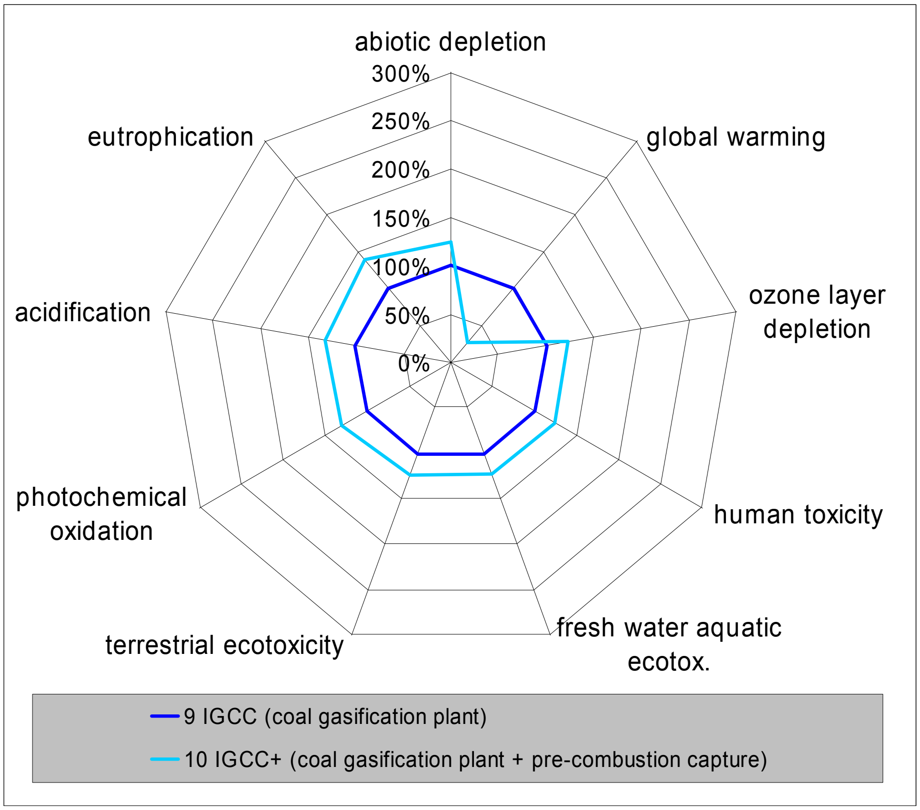


Figure 4.7 Environmental impact spider graph for IGCC.

The relatively regular increases for each impact category (but global warming) are clearly linked to the increased fuel use. It again indicates a small influence of the production of MDEA. The increase of emissions of NO_x and SO_2 in the plant fitted with pre-combustion capture leads to higher relative scores.

Weighing of the results enables comparison of the reference cases on basis of a single indicator. Figure 4.8 shows the weighed environmental profiles, expressed as shadow costs.

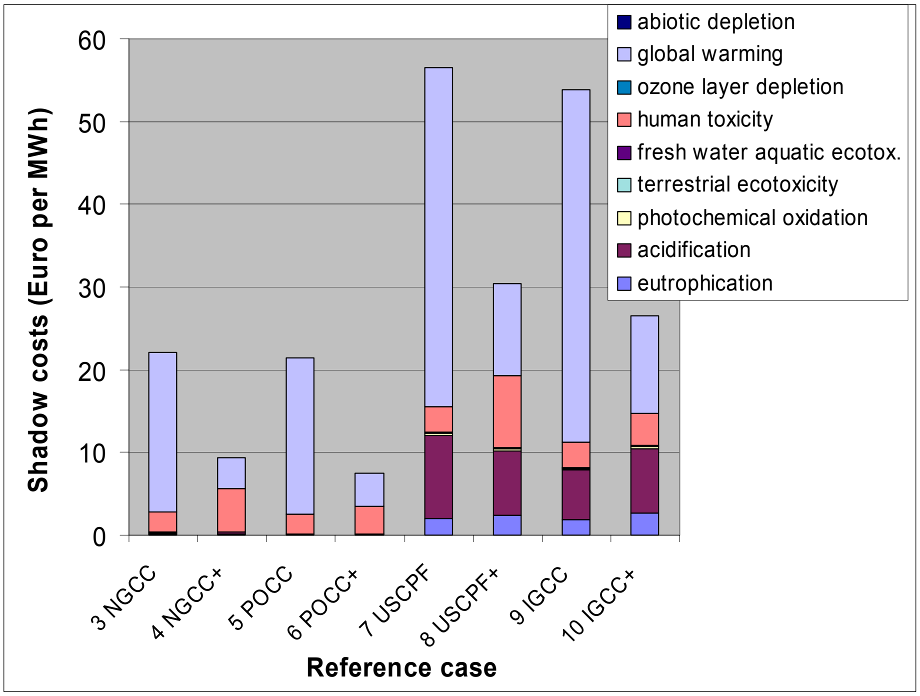


Figure 4.8 Comparison of reference cases: weighed with shadow prices.

The weighed scores show that the CO_2 emission (expressed as global warming) of the power plants is generally contributing most to the shadow costs, followed by human toxicity and acidification. In the human toxicity contributions, the effect of the production and emission of MEA can be seen (post-combustion cases). The emission of SO_2 in coal fired plants is visible as acidification. As could already be seen from figure 4.2, the CO_2 emission reduction easily compensates the additional environmental burden for CO_2-capture in all cases.

The overall lowest shadow prices are related to reference case 5, which means that, according to this weighing method, the natural gas reformer plant with pre-combustion capture causes the least environmental burden. It is, however, closely followed by the natural gas combined cycle power plant with post-combustion capture. For the natural gas cases with capture the global warming theme contribution to the shadow prices is obviously very much reduced, whereas the human toxicity theme is increased, as a result of the use of solvents. Other themes do not seem to have a significant contribution. The overall reduction in shadow prices as a result of CO_2-capture is around 60-70%, which makes it an effective measure for reducing overall environmental impact.

The highest shadow prices are for the coal fired cases, with the pulverised fuel case being the highest overall. For coal fired power plants without capture the impact of the global warming theme constitutes approximately three quarters of the shadow price, but the contributions of the acidification, human toxicity and eutrophication are also significant. For coal fired power plants with capture the situation is somewhat more complex. The impact of the global warming theme will be less, obviously through the CO_2-capture in both pre-combustion and post-combustion capture. In case of post-combustion capture the impact of the acidification theme will also be reduced (less emission of SO_2 and NO_2) but the impact of the human toxicity theme has gone up and to a lesser extent also the eutrophication theme. In case of pre-combustion capture for coal all the impact environmental themes (except global warming) is increase slightly, due to the higher fuel consumption. The overall reduction in shadow prices as a result of CO_2-capture is around 50%, which makes it an effective measure for reducing overall environmental impact.

Another conclusion that can be drawn is that the coal based plants *with* CO_2 capture still have a higher environmental impact than the natural gas based plants *without* CO_2 capture. There are two reasons for this: the inherently higher CO_2 emission of coal combustion (per unit of energy) leads to a higher CO_2 emission after capture, as the capture efficiencies are approximately equal. This puts the coal based plants at a disadvantage. The second reason is formed by the higher emissions of NO_x, SO_2 and dust, compared to natural gas based plants.

Overall it can be stated that there are two effects which are decisive in the determination of the extent of the environmental impact. First, the increased fuel use due to CO_2 capture leads to an increase in the environmental impact for all themes, except global warming. Only, the reduced emissions of SO_2 and NO_2 in post-combustion capture lead to noticeable decreases for the themes of acidification and photochemical oxidation. Secondly, the consumption of solvent will lead to an increased impact in the themes of toxicity through the atmospheric emissions. Therefore, it is clear that more energy efficient solvents and solvents whose consumption in the process is less will reduce the environmental impacts to a large extent.

5. Environmental impact of large scale deployment of CO_2 capture in power plants

5.1 Approach

For assessing the impact of a future large scale deployment of CO_2-capture in power plants, a scenario is required, describing the future development of CO_2-capture capacities and specific technologies used (pre- and post-combustion; coal and gas). The large scale deployment of CO_2-capture and storage is dependent on a range of technical, socio-economic and political factors. Setting aside political factors the most influential factors will be the cost of CO_2 capture and storage relative to a range of other options to reduce CO_2-emissions and the societal acceptance of the storage concept. Capture and storage scenarios have been developed by the International Energy Agency, using their Energy Technology Perspectives model [20]. This model makes it possible to calculate the least-cost energy system for the period 2000-2050. Two scenarios are drafted:

- a BASE-scenario, describing the use of primary energy sources and carbon dioxide emissions under no-additional policy conditions, and
- a policy scenario in which carbon dioxide emissions are taxed. In this policy scenario, global carbon dioxide emissions on longer terms are kept constant roundabout 2000-levels, which results in the stabilisation of atmospheric CO_2-concentrations at 550 ppm, consistent with recommended long-term values as defined by IPCC.

The result of the IEA-scenarios is an assessment of the amount of CO_2 being captured from either gas, coal or other (mainly industrial) sources.

5.2 IEA-scenarios

- *BASE-scenario*

The IEA has analysed the prospects for CO_2 capture and in this study the results for the BASE scenario in 2030 and 2050 will be used. This scenario is based on the World Energy Outlook 2004 Reference Scenario up to 2030 and based upon projections of e.g. energy demand for period 2030-2050. It does not take into account any CO_2-reduction policies. Table 5.1 shows the projections for the global primary energy demand, the energy source distribution and the overall annual CO_2-emissions.

Table 5.1 Global energy demand, the source distribution and the CO_2-emissions in 2000 (statistics), 2030 and 2050 (projections in BASE Scenario).

Year	**2000**	**2030**	**2050**
Energy demand	415 EJ/yr	690 EJ/yr	920 EJ/yr
- Oil	38%	33%	29%
- Coal	22%	29%	35%
- Gas	21%	21%	20%
- Others	19%	17%	14%
Total	100%	100%	100%
CO_2-emissions	25 Gt/yr	42 Gt/yr	57 Gt/yr

Annual primary energy demand, as well as CO_2 emissions, will more than double in the period 2000-2050. The BASE scenario implies a continued reliance on fossil fuels with an increasing reliance on coal, the most abundant fossil fuel, primarily driven by the expected lower costs of coal compared to the rising costs of oil and gas.

– *Policy-scenario*

Starting from the BASE scenario, a CO_2-policy scenario called GLO50 was introduced. This scenario assumes a maximum penalty of 50 US$/tonne CO_2 to be reached in 2015 in the OECD and transition economies and in 2030 in the developing countries. It furthermore assumes a certain range of performances and costs for CCS-technologies for both gas and coal fired power stations. The GLO50 scenario shows that CCS is starting to be applied around 2015, increases to around 8 GT CO_2/yr in 2030 and then increases to more than 18 GT CO_2/yr in 2050. The analysis shows that the GLO50 scenario could be consistent with a stabilisation of the atmospheric CO_2-concentration at 550 ppm. Global energy demand, the primary energy source distribution and the CO_2-emissions in 2000, 2030 and 2050 are shown in table 5.2.

Table 5.2 Global energy demand, the source distribution and the CO_2-emissions in 2000 (statistics), 2030 and 2050 (projections in GLO50 scenario).

Year	**2000**	**2030**	**2050**
Energy demand	415 EJ/yr	630 EJ/yr	850 EJ/yr
- Oil	38%	33%	28%
- Coal	22%	16%	25%
- Gas	21%	23%	22%
- Others	19%	28%	25%
Total	100%	100%	100%
CO_2-emissions	25 Gt/yr	22 Gt/yr	26 Gt/yr

– *Impact of policy on carbon dioxide capture and storage efforts*

The results in table 5.2 show a large shift towards non-fossil fuel sources (primarily renewables). The absolute coal use in 2030 has only increases slightly, but in 2050 it has more than doubled. The share of CCS on the reduction of CO_2-emissions is around 40% in 2030 but increases to nearly 60% in 2050. The study states that given the conservative estimates for competing emission reductions this scenario should be looked upon as an upper limit of the potential role of CCS.

The dominant share of CCS in the GLO50 scenario is coming from power plants rising to 80% in 2050, the remainder coming from fuel processing (natural gas treatment) and manufacturing (cement kilns). Table 5.3 gives an overview of the amounts of CO_2 captured and stored and the distribution over coal and gas fired power plants.

Table 5.3 CO_2-capture and stored according to GLO50 scenario in 2030 and 2050.

Year	2030	2050
Energy demand	630 EJ/yr	850 EJ/yr
Coal plants with capture	4.0 Gt/yr	12.4 Gt/yr
Gas fired plants with capture	2.0 Gt/yr	2.3 Gt/yr
- Others (cement, fuel processing)	2.6 Gt/yr	3.6 Gt/yr
Total CO_2 capture and stored	8.6 Gt/yr	18.3 Gt/yr
CO_2-emissions	22 Gt/yr	26 Gt/yr

5.3 Environmental impact according to IEA-scenarios

The environmental impact is modeled using the amounts of CO_2 captured and stored as determined in the IEA GLO50 scenario. Then it is assumed that the amount of CO_2 is captured by an MEA post-combustion capture process from either a coal fired or gas fired plant to determine an upper limit for the maximum environmental impact. The emitters other than power stations were taken to have an impact equal to coal fired power stations with the same emission. It has to be mentioned here that the IEA GLO50 scenario results in coal gasification plants taking the major share of power generation from coal with capture. Hence, this represents an important deviation of the IEA scenario, but as such this represents a worst case scenario for the environmental impact.

Table 5.4 gives the global amounts of solvent needed and sludges produced for the CCS-scenario in 2030 and 2050 with for reference the values for other chemicals used in power plants, i.e. limestone for SO_2-removal and NH_3 for NO_x-control.

Table 5.4 CO_2-captured and stored according to GLO50 scenario with two different post-combustion capture processes.

Year	**2030**		**2050**	
Energy demand	630 EJ/yr		850 EJ/yr	
Total CO_2 capture and stored	8.6 Gt/yr		18.3 Gt/yr	
Amount of fuel	20.9 Gt/yr		43.7 Gt/yr	
Process licensor	FLUOR	MHI	FLUOR	MHI
Amine requirement	13.8 Mt/yr	2.6 Mt/yr	29.3 Mt/yr	5.5 Mt/yr
Sludges produced	27.5 Mt/yr	0.8 Mt/yr	58.6 Mt/yr	1.7 Mt/yr
Limestone for SO_2-removal	75.2 Mt/yr		182.4 Mt/yr	
NH_3 for NO_x-control	6.5 Mt/yr		13.7 Mt/yr	

The amine requirement in 2030 and 2050 for the FLUOR Econamine FG Plus process is significant and represents a more than ten-fold increase compared to the current annual production of alkanolamines (~1 Mtonne/yr). It is however around 20% of the amount of limestone needed for SO_2-control and double the amount of ammonia needed for NO_x in 2030 and 2050. Hence it seems to be manageable use of chemicals at a power plan. The amount of sludges produced is large but represents only around 0.1% of the fuel needed. Also this can be assumed to be manageable.

The amine requirement in 2030 and 2050 for the MHI KS1 process is only 20% of the amine requirement for the FLUOR Econamine FG Plus process. Nevertheless it represents a large amount compared to the current global production of alkanolamines (maximum 2.5 – 5.5 times the current production of alkanolamines). According to the data supplied by MHI the sludge production is much less. It is assumed that the balance is lost in the absorber exhaust. This is similar to the Fluor process, but as the amine consumption is less for KS1 due to its better stability, it represents the largest loss of amines in this process.

If CCS is implemented, it is very likely that a portfolio of technologies (incorporating also pre-combustion capture and denitrogenation) will be used. Therefore the estimates for production of waste materials produced by the MEA-process, can be taken is the most pessimistic case. The implementation of other technologies is likely to result in less by-products, but will still have an increased amount of waste streams as a result of the increased fuel use.

Next the global impact of CO_2-capture compared to the situation where there is no capture was estimated. The results are shown in figure 5.1 for 2030 and figure 5.2 for 2050.

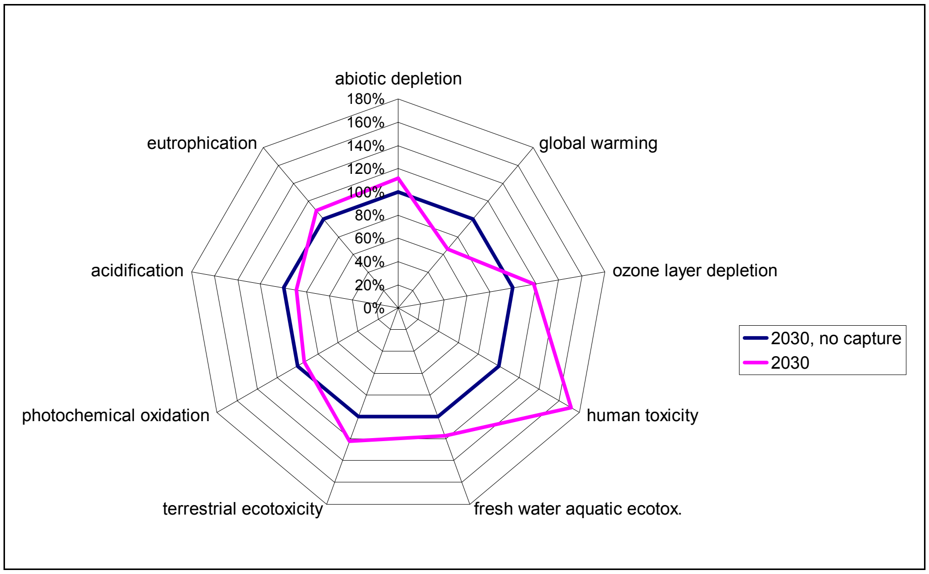


Figure 5.1 Global impact of CO_2-capture in 2030 for the relevant environmental impact categories.

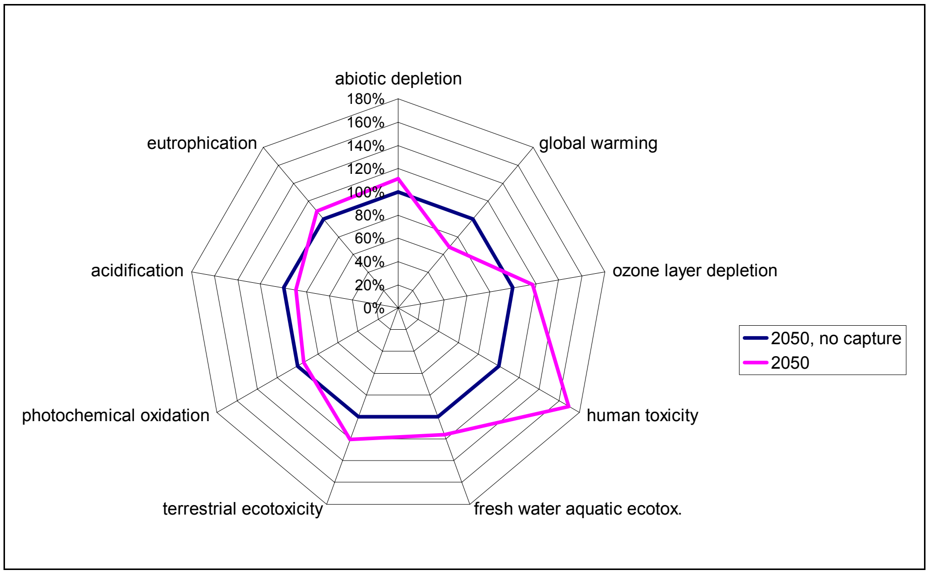


Figure 5.2 Global impact of CO_2-capture in 2050 for the relevant environmental impact categories.

The results presented are very similar because the base case is always the case without capture. It appears that CCS based on post-combustion capture using MEA leads to strongly reduced impacts on global warming, which is to be expected, because it is the objective of CCS. A number of impacts are linked strongly to the increase fuel use represented by the abiotic depletion. These impacts are eutrophication, ozone layer depletion, freshwater aquatic ecotoxicity and terrestrial ecotoxicity. The use of solvents leads to a greatly increased impact on the human ecotoxicity. However, the reduced impact on acidification and photo-chemical oxidation is one of the side benefits of CCS caused by the increased removal of trace components in flue gases (SO_2 and NO_2).

6. Conclusions and Recommendations

6.1 Conclusions

This study has evaluated the environmental impact of the large scale introduction of solvent scrubbing of CO_2 for emission reductions from power generation. To this extent, the following objectives were defined:
- Identification of the current CO_2 solvent market and the composition of the main solvents;
- Quantification of environmental impacts directly or indirectly resulting from the capture of a unit of CO_2 using solvents;
- Estimation of the potential environmental impact of large scale application of CO_2 scrubbing on a global scale;
- Identification of possibilities for the reduction of environmental impact.

The application of CO_2-capture from power plants is feasible using commercially available processes. Scenarios in this study cover pre- and post-combustion capture in both natural gas and coal based power plants.

The environmental impact of CO_2-capture has been determined throughout the complete life cycle, using the CML-LCA2 Life Cycle Assessment methodology. Two viewpoints have been discriminated: 1) capture plant - the capture of a unit of CO_2, and 2) power plant - the production of a unit of electricity with or without CO_2-capture.

Regarding the first viewpoint, the additional environmental impact as a result of capture of one tonne of CO_2 (in a power plant) is dominated by the energy consumption of the capture process and the production of solvent. In general, the natural gas based cases have an advantage here, except for the fact that MEA/coal scores better on photochemical oxidation and acidification. This is a result of additional SO_2 capture, leading to a decrease of the emission which is an environmental benefit.

Using the method of shadow price weighing, the capture of CO_2 has a net environmental benefit. In other words, the additional external costs due to the additional environmental impact are below the benefits (expressed as external costs) of the avoided CO_2 emission. The net shadow costs are 30 - 35 Euros per tonne CO_2 captured. This would have been the price to obtain an equal environmental benefit elsewhere (using other mitigation options).

With the second viewpoint in mind, eight reference cases have been calculated for the generation of 1 MWh of electricity: natural gas & coal with and without post-combustion/MEA and pre-combustion/MDEA capture.

The environmental impacts for the post-combustion capture cases (NGCC and USCPF) are influenced primarily by the increased fuel use. Due to the use of a solvent, in particular as a result of the production of MEA and the emission to the atmosphere, the environmental impact themes of human toxicity and terrestrial ecotoxicity show an additional increase. For post-combustion CO_2-capture from coal firing the environmental impact themes of acidification and photochemical smog are reduced compared to the case without capture as a result of the reduced SO_2 and NO_2 emissions.

The environmental impact for the two pre-combustion capture cases (POCC and IGCC) is dominated by the increased fuel use. All environmental impact themes will increase in a similar way as a result of this except, obviously, the global warming theme, which will be reduced. In case of pre-combustion capture the effects of solvent use on the environmental impact themes of human toxicity and terrestrial ecotoxicity are negligible.

The method of weighing with shadow prices leads to the conclusion that per MWh the natural gas reformer plant (POCC) with MDEA CO_2-capture causes the least environmental impact, closely followed by the natural gas combined cycle plant (NGCC) with MEA CO_2 capture. When compared to the natural gas fired power plants without capture, the environmental impacts are reduced by 60 – 70% as a result of CO_2-capture.

Furthermore a natural gas based plant (NGCC or POCC) without CO_2 capture has a lower impact than a coal based plant with CO_2 capture, according to the shadow price method. The higher CO_2 and SO_2 emissions in case of coal firing play an important role in this.

The method of weighing with shadow prices also shows that the highest environmental impact of all capture plants is caused by the post-combustion coal fired power plant (USCPF), although the difference with pre-combustion coal firing is small. When compared to the coal fired power plants without capture, the environmental impacts are nearly halved as a result of CO_2-capture.

Large scale deployment of CO_2-capture in power plants using MEA in 2030 and 2050 would require the alkanolamine production to increase by at least a factor 10 compared to the estimated current production, basing this on the FLUOR Econamine process. Although the amount of sludges would be large, the amounts are small compared to the fuel use and they are also still smaller than the consumption of limestone in coal firing. These sludges can also be considered to be environmentally manageable.

6.2 Recommendations

Based on the information retrieved from the literature and the analysis of this information, the reduction of the environmental impacts of CO_2-scrubbing using solvent processes can be best carried out by the following actions:

1. Development of more energy efficient solvents compared to MEA, as the impact of solvent processes for CO_2-capture is primarily related to the impact as a result of the increased fuel use. This is particularly valid for post-combustion capture where the solvent process will have the largest influence on the energy efficiency of power generation.
2. Development of solvents and solvent processes with lower emissions to the air compartment, but possibly with additional capability for removal of other flue gas components with noticeable environmental impact (SO_2 and NO_x). Reduction of the environmental impact of the solvent production process itself is also required This is mostly relevant to post-combustion capture, as in case of pre-combustion capture the environmental impact of the solvent process on the whole is much smaller.
3. Development of alternative capture processes not requiring any additional consumables (chemicals) for CO_2-capture, with an energy-efficiency at least equivalent to the solvent processes. This is valid for both post- and pre-combustion capture.

The analysis has also shown that the publicly available information on the different environmental impacts of solvent scrubbing processes is scarce. Therefore more detailed studies into these impacts involving e.g. determination of emissions to the air, solvent degradation studies, characterisation of waste streams, treatment of waste streams and data on solvent formulation, including corrosion inhibitors, is required. Particularly when new solvents are developed for which the environmental impacts are perhaps not known, this will become an important issue.

7. References

[1] Fluor, 2004: Improvement in power generation with post-combustion capture of carbon dioxide. IEA Greenhouse Gas R&D-programme report number PH4/33, November 2003, Cheltenham, UK

[2] Foster Wheeler, 2003: Potential for improvement in gasification combined cycle power generation with CO_2-capture. IEA Greenhouse Gas R&D-programme report number PH4/19, May 2003, Cheltenham, UK

[3] Barchas, R., R. Davis, 1992: The Kerr-McGee / ABB Lummus Crest Technology for the Recovery of CO_2 from Stack Gases, Energy Convers. Mgmt, 33(5-8)333-340.

[4] Arnold, D.S., D.A. Barrett, R.H. Isom, 1982: CO_2 can be produced from flue gas, Oil & Gas Journal, pp. 130-136, November 1982

[5] Sander, M.T., C. L. Mariz, 1992: The Fluor Daniel® Econamine™ FG Process : Past Experience and Present Day Focus, Energy Convers. Mgmt, 33(5-8)341-348

[6] Chapel, D., J. Ernst, C. Mariz, 1999: Recovery of CO_2 from flue gases: Commercial trends, Paper No. 340 at Canadian Society of Chemical Engineers, Saskatoon, Canada

[7] Reddy, S., J. Scherffius, S. Freguia, C. Roberts, 2003: Fluor's Econamine FG Plus^{SM} Technology: An enhanced amine-based CO_2 capture process, presented at second annual conference on carbon sequestration, Alexandria, Virginia, USA

[8] Mimura, T. K. Matsumoto, M. Iijima, S. Mitsuoka, 2001: Development and application of flue gas carbon dioxide recovery technology, Proceedings of the fifth international conference on greenhouse gas control technologies, D. Williams et. al. (eds), CSIRO publishing, Australia, pp. 138-142

[9] Chakma, A., P. Tontiwachwuthikul, 1999: Designer Solvents for Energy Efficient CO_2 Separation from Flue Gas Streams. Greenhouse Gas Control Technologies. P. Riemer, B. Eliasson, A. Wokaun (eds.), Elsevier Science, Ltd., Kidlington, United Kingdom, 35-42

[10] Hischier, R., 2003: Ecoinvent-report 8, chapter 33 - Ethanolamines pp 293-301

[11] Knaak, J.B. et. al., 1997: Toxicology of Mono-, Di-, and Triethanolamine, Reviews of environmental contamination and toxicology, Vol. 149, pp. 1-86

[12] DuPart, M.S, T.R. Bacon, D.J. Edwards, 1993: Understand corrosion in alkanolamine gas treating plants – Part 2, Hydrocarbon Processing, May 1993, pp. 8-11

[13] Stewart, E.J., Lanning, R.A., 1991: A systematic technical approach to reduce amine plant solvent losses, Laurance Reid Gas Conditioning Conference, Oklahoma

[14] Doucette, W.J., et. al. 2005: Uptake of sulfolane and diisopropanolamine (DIPA) by cattails (Typha latifolia), Microchemical Journal (81(2005)41-49

[15] Fluor/Statoil, 2005: Study and estimate for CO_2 capture facilities for the proposed 800 MW combined cycle power plant – Tjeldbergodden, Norway

[16] Email Masaki Iijima, Mitsubishi Heavy Industries, 17 June 2005

[17] Guinée, J.B. et al, 2001: Life cycle assessment - an operational guide to the ISO standard, vol. I, II and III, Institute of Environmental Sciences – University of Leiden

[18] Ecoinvent 2000 version 1.2, Swiss Centre for Life Cycle Inventories, 2005.

[19] Jacobs Consultancy, 2005: Retrofit of CO_2-capture to natural gas combined cycle power plants, IEA Greenhouse Gas R&D-programme report number 2005/1, January 2005, Cheltenham, UK.

[20] IEA, 2004: Energy Technology Analysis - Prospects for CO_2 capture and storage, IEA/OECD, Paris, France

[21] World Energy Outlook, 2004 Insights, IEA/OECD, Paris, France

[22] Huijbregts, M.A.J., 2005: Toxicity potentials for monoethanolamine, diethanolamine, triethanolamine, di-isopropylamine, sulfolane and methanol, Department of Environmental Science, Faculty of Sciences, Radboud University Nijmegen

[23] Huijbregts, M.A.J., 2005: Toxicity potentials for methyldiethanolamine and aminomethylpropanol, Department of Environmental Science, Faculty of Sciences, Radboud University Nijmegen.

[24] Huijbregts, M.A.J., 1999: Priority Assessment of Toxic Substances in the frame of LCA. Development and application of the multi-media fate, exposure and effect model USES-LCA. IDES, University of Amsterdam

[25] Ullmann's Encyclopedia of Industrial Chemistry, 2005, Wiley-VCH

[26] Kirk-Othmer Encyclopedia of Chemical Technology, 2005, Wiley-VCH

[27] Eggels, P.G. and B.L. van der Ven, 2000: Background data for the building environment, a reference database – The VLCA Database, commissioned by the Dutch Ministry for Housing, Spatial Planning and Environment, TNO-MEP report R2000/130

[28] Thitakamol, B., A. Veawab, A. Aroonwilas, Environmental impacts of absorption based CO_2 capture unit for post-combustion treatment of flue gas from coal-fired power plant, submitted to Journal of Environmental Science and Technology, July 2006

[29] Koeijer, de, G., Increased interest in degradation of amines presentation at 9th IEA GHG International CO2 Capture Network, Copenhagen, 16-6-2006

8. Authentication

Name and address of the principal:

John Davison
IEA Greenhouse Gas R&D Programme
Stoke Orchard
Cheltenham
Gloucestershire
GL52 7RZ
United Kingdom

Name and functions of the cooperators:

R.N. van Gijlswijk	-	LCA methodology, results analysis
H. Oonk	-	Reference case definition
J.P. Brouwer	-	Amine production process analysis
P.H.M. Feron	-	Amine processes, project management

Name and establishments to which part of the research was put out to contract:

Radboud University Nijmegen – Determination of toxicity potentials
Faculty of Science, Department of Environmental Science
Nijmegen, The Netherlands

Date upon which, or period in which the research took place:

1 March 2005 - 1 February 2006

Signature:	Approved by:
P.H.M. Feron Project leader	P.M. Wolfs Head of department

A Amine production processes

A.1 Production of MEA, DEA and TEA

MEA is produced by reacting 1 mole of ethylene oxide (EO) with 1 mole of ammonia (NH_3). The addition of 2 and 3 moles of EO to 1 mole of NH_3 will produce DEA and TEA, while additional EO will continue to react to produce higher EO adducts of TEA. A typical production facility will be operated in a batch mode and produce a mixture of MEA, DEA and TEA. These can be separated afterwards by distillation. MEA is the main component of the solvent. In a separate formulation process a number of substances are added (oxygen scavengers, corrosion inhibitors).

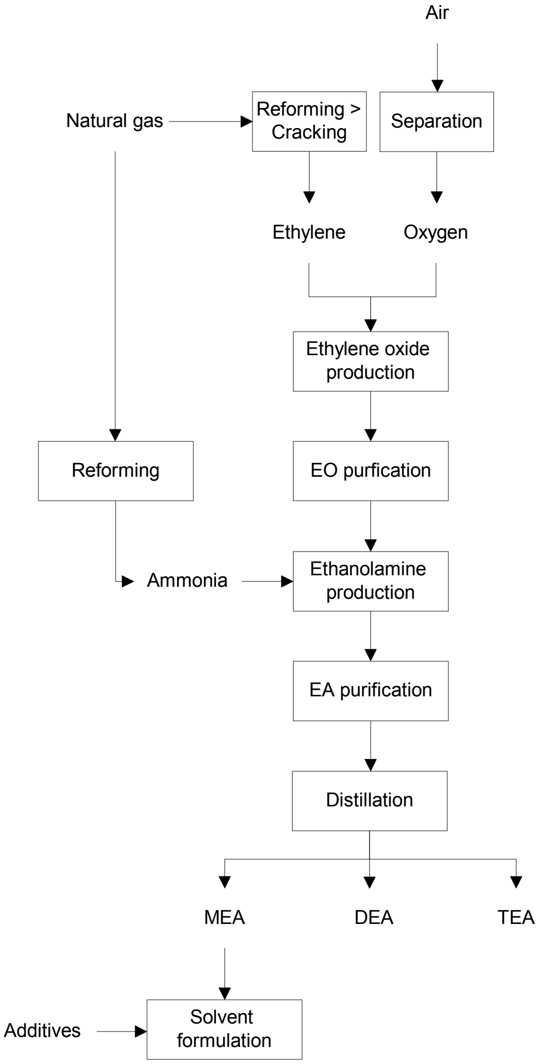


Figure A1 Overall production process for MEA, DEA and TEA.

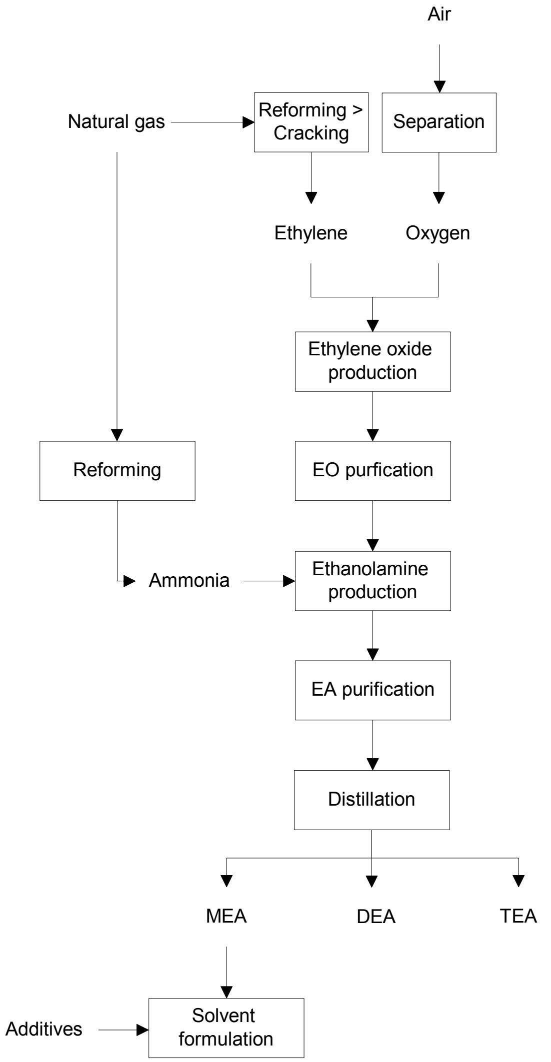


Figure A.2 Process for producing MEA, DEA and TEA from ethylene oxide and ammonia.

A.2 Production of MDEA

MDEA is produced from the reaction between mono-methylamine (MMA) and ethylene oxide. Mono-methylamine is produced from the reaction between ammonia and methanol. This yields a mixture of mono-, di- and trimethylamine, which is separated in a series of distillation columns. Unconverted reactants are recycled to the reactor.

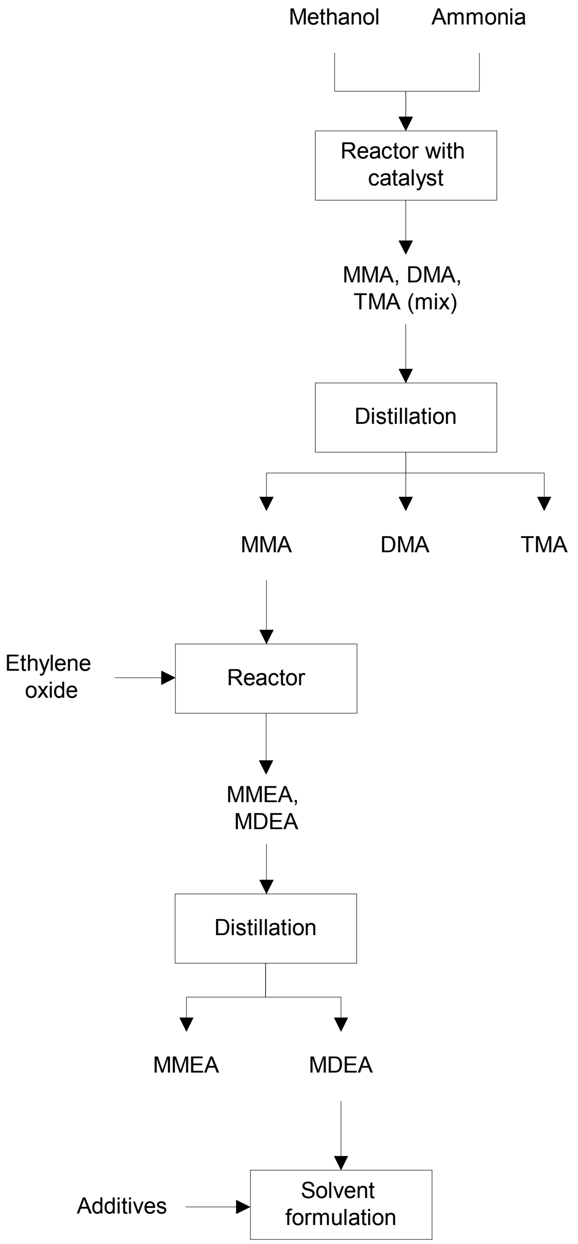
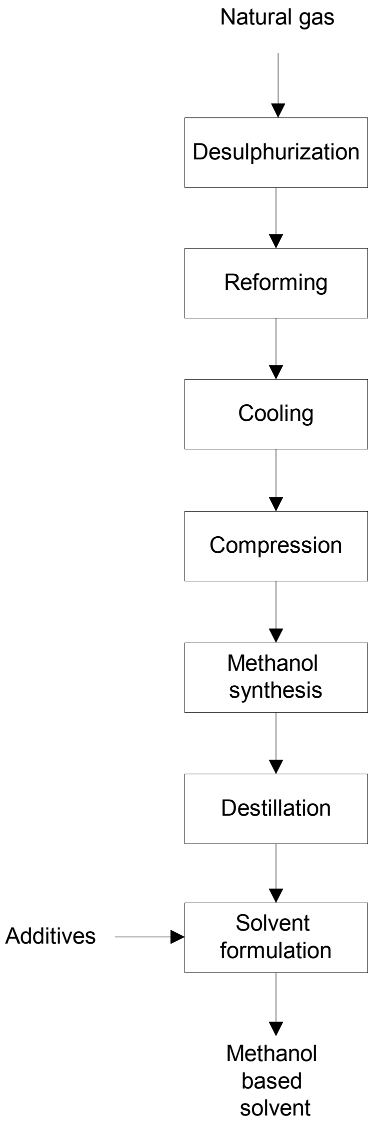


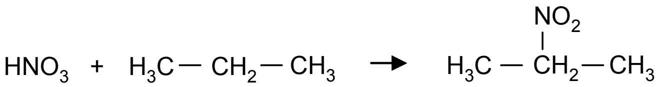
Figure A.3 Process for producing MDEA.

A.3 Production of methanol



A.4 Production of AMP

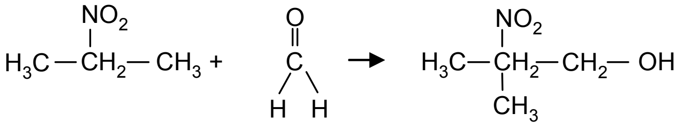
AMP (2-amino-2-methyl-1-propanol) is produced from 2-nitropropane (2-NP). This in turn is produced from the reaction between nitric acid and excess propane at 370-450°C and 8-12 bar, OR from the reaction of nitrogen peroxide (N_2O_4) with propane at 150-330°C and 9-12 bar. The reaction yields other products as well, i.e. nitromethane, nitroethane and 1-nitropropane. Selectivities and conversions are unknown. For the nitric acid route the reaction is:



$$HNO_3 + H_3C-CH_2-CH_3 \rightarrow H_3C-\overset{NO_2}{\overset{|}{CH_2}}-CH_3$$

2-nitropropane

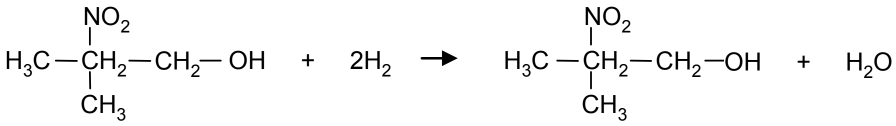
The 2-nitropropane that is recovered from the product mixture is used for a number of purposes, mainly as a solvent. For the production of AMP, the 2-NP is first converted to 2-methyl-2-nitro-1-propanol (denoted MNP here), by reaction with formaldehyde in an alkaline environment according to



$$H_3C-\overset{NO_2}{\overset{|}{CH_2}}-CH_3 + \overset{\overset{O}{\|}}{C}(H)(H) \rightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{NO_2}{\overset{|}{CH_2}}}-CH_2-OH$$

2-nitropropane *formaldehyde* *2-methyl-2-nitro-1-propanol*

This is subsequently hydrogenated to AMP in an autoclave.



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{NO_2}{\overset{|}{CH_2}}}-CH_2-OH + 2H_2 \rightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{NO_2}{\overset{|}{CH_2}}}-CH_2-OH + H_2O$$

2-methyl-2-nitro-1-propanol *AMP*

Regretfully little is known to us about the process design. The total processing route may involve the following steps:

- propane/nitric acid reactor
- separation of HNO_3, propane and 2-NP (likely the HNO_3 is virtually entirely converted; product separation may require 4 columns).
- 2-NP/formaldehyde reactor
- separation of formaldehyde, 2-NP and MNP (2 columns?)
- hydrogenation reactor
- separation of H_2, AMP, MNP (2 columns?)

The process could thus look as shown in figure 2, but it is noted that this is not based information from literature but on own considerations.

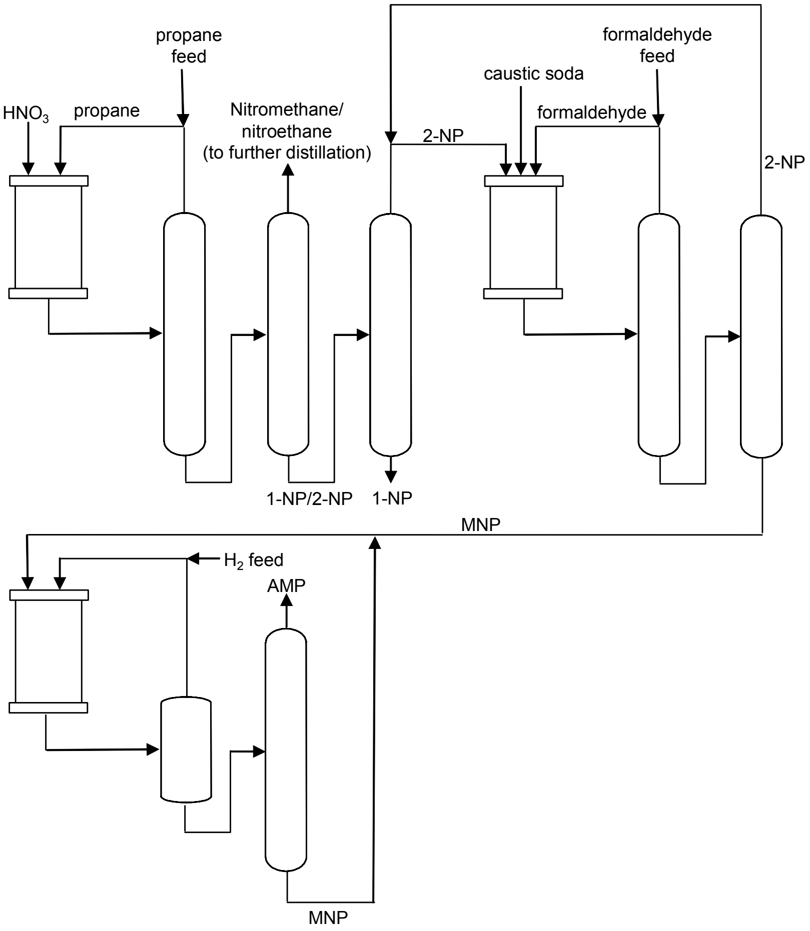


Figure 2 Simplified flowsheet for production of 2-NP, MNP and AMP (flowsheet based on own considerations, not on literature).

Further information has been requested at Angus Chemical Company (subsidiary to Dow) through their website on 6/6/2005.

B Process data

The data on solvent use and changes in gross and net power output of power plants upon CO_2-sequestration are obtained from a number of case studies. The choice of case studies is based on the availability of sufficiently detailed material and energy balances for both the reference and the capture-cases that are required as an input for LCA-calculations. This selection criterion proved to be quite strict since most reports and articles on CO_2-sequestration didn't present this degree detail. Since actions to obtain more details on these studies failed, only limited part of the vast amount of publications on capture technology could be used in this study.

B.1 Post-combustion natural gas

Most of the post-combustion cases are based on a study carried out for IEA GHG R&D-Programme by Fluor, in collaboration with Mitsui Babcock, Alstom and Imperial College London [1].
In this study the performance and costs of coal and natural gas power plants are evaluated with and without post-combustion CO_2-capture for a power plant located at the Netherlands coast and at a net power output of roundabout 700 MW_e. The capture technology considered is based on use of MEA in Fluor's Econamine FG+^{SM}-process. In general MEA (or hindered amines as KS-1) are the preferred solvent for post combustion capture, due to their relative high absorption capacities at low CO_2-partial pressures. The Econamine FG+^{SM}-process is selected in Fluor's study, since according to Fluor this process comprises several improvements. This results in considerable reduced energy consumption for capture, compared to earlier capture processes.

With respect to natural gas, two cases are elaborated:
- natural gas combined cycle without capture
- natural gas combined cycle with capture

The energy and material balances of the natural gas combined cycle plant with and without capture are presented in the tables B1 and B2.

Table B1 Energy balance of natural gas combined cycle power plants.

	Capture: none NGCC	Capture: Post-combustion NGCC + Fluor	
Summary			
Fuel fired (LHV)	1396	1396	MW
Gross output	800	740	MW
Gross efficiency	57.3	53.0	%
Losses plant			
FW pumps	16	15	MW
Losses capture			
DCC blower		20	MW
Amine pumps		3	MW
CO_2 compression		30	MW
Utility systems	8	10	MW
Total losses	**24**	**78**	**MW**
Net output	**776**	**662**	**MW**
Net efficiency	**55.6**	**47.4**	**%**
Annual net output	**6117984**	**5219208**	**MWh**

Table B2 Material balance of natural gas combined cycle power plants.

	Data per year	Capture: none NGCC	Capture: Post-combustion NGCC + Fluor EFG+	Unit
Input	Natural gas	845	845	ktonnes
	Econamine (MEA+)	0	3.2	ktonnes
	Make-up water	33.7	1067	ktonnes
	Limestone	0	0	ktonnes
	Ammonia	0	0	ktonnes
	Amine inhibitors*)	0	0	ktonnes
	Activated carbon	0	0.12	ktonnes
	Soda ash	0	0.26	ktonnes
	Miscellaneous	0	0	ktonnes
Output	CO_2	2318	348	ktonnes
	O_2	5263	5274	ktonnes
	H_2O	1847	2336	ktonnes
	N_2	27889	27872	ktonnes
	NO_2	406	341	tonnes
	SO_2	20	0	tonnes
	MEA	0	93	tonnes
	Reclaimer residues	0	6.3	ktonnes
	Waste water	33.7	1067	ktonnes

*) It is known that the Fluor EFG+ uses a proprietary inhibitor. As its composition is not known the environmental impact could not be taken into account.

B.2 Pre-combustion natural gas

The pre-combustion case for natural gas is based on a study for IEA-GHG-R&D-programme by Jacobs on CO_2-capture through partial oxidation of natural gas [19]. This study details an optimised process based in autothermal reforming of natural gas, followed by water gas shift and carbon dioxide removal. MDEA is considered the best solvent for CO_2-capture.
The reference case described by Jacobs is a standard combined cycle 800 MW_e power plant.

Table B3 Energy balance of natural gas reformer plants.

	Capture: none **POCC**	**Capture: Pre-combustion** **POCC + MDEA**	
Summary			
Fuel fired (LHV)	1405	1672	MW
Gross output	809	833	MW
Gross efficiency	57.6	49.8	%
Losses plant	**24**	**24**	
Losses capture			
- aux. consumption		159	
- power production		-43	
Total losses	**24**	**139**	**MW**
Net output	**785**	**694**	**MW**
Net efficiency	**55.9**	**41.5**	**%**
Annual net output	**6188940**	**5469919**	**MWh**

Table B4 Material balance of natural gas reformer plants.

	Data per year	Capture: none POCC	Capture: Pre-combustion POCC + MDEA	Unit
Input	Natural gas	845	1006	ktonnes
	MDEA		29	tonnes
	Make-up water			ktonnes
	Limestone			ktonnes
	Ammonia			ktonnes
	Amine inhibitors			ktonnes
	Activated carbon			ktonnes
	Soda ash			ktonnes
	Miscellaneous			ktonnes
Output	CO_2	2298	394	ktonnes
	O_2			ktonnes
	H_2O			ktonnes
	N_2			ktonnes
	NO_2			tonnes
	SO_2			tonnes
	MDEA			tonnes
	Reclaimer residues	0	57	tonnes
	Waste water			ktonnes

B.3 Post-combustion coal

Most of the post-combustion cases are based on a study carried out for IEA GHG R&D-Programme by Fluor, in collaboration with Mitsui Babcock, Alstom and Imperial College London [1].
In this study the performance and costs of coal and natural gas power plants are evaluated with and without post-combustion CO_2-capture for a power plant located at the Netherlands coast and using Australian bituminous coal or natural gas and at a net power output of roundabout 700 MW_e. The capture technology considered is based on use of MEA in Fluor's Econamine FG+^{SM}-process. In general MEA (or hindered amines as KS-1) are the preferred solvent for post combustion capture, due to their relative high adsorption capacities at low CO_2-partial pressures. The Econamine FG+^{SM}-process was selected in Fluor's study. According to Fluor this process comprises several improvements resulting in a considerable reduction energy requirement for capture, compared to earlier capture processes.

In the Fluor study detailed material and energy balances are provided for four cases:

- pulverised coal
- pulverised coal with capture

The energy and material balances of the ultra supercritical pulverized fuel plant with and without capture are presented in the tables B5 and B6.

Table B5 Energy balance of pulverized coal fired plants.

	Capture: none **USCPF**	**Capture:** **Post-combustion** **USCPF + MEA**	
Summary			
Fuel fired	1723	1913	MW
Gross output	831	827	MW
Gross efficiency	48.2	43.2	%
Losses plant			
FW pumps	34	37	MW
Draught plant	8	9	MW
Coal mills etc.	5	5	MW
ESP	2	2	MW
Miscellaneous	8	9	MW
Losses capture			
DCC blower		14	MW
Amine pumps		3	MW
CO_2 compression		60	MW
Utility systems	10	15	MW
FGD	6	7	MW
DeNOx	0.3	0.4	MW
Total losses	**73**	**161**	**MW**
Net output	**758**	**666**	**MW**
Net efficiency	**44.0**	**34.8**	**%**
Annual net output	**5973707**	**5247590**	**MWh**

Table B6 Material balance of pulverized coal fired plants.

	Data per year	Capture: none USCPF	Capture: Post-combustion USCPF + MEA	Unit
Input	Coal	1891	2099	ktonnes
	Econamine (MEA+)	0	6.9	ktonnes
	Make-up water	363	1872	ktonnes
	Limestone	50	61	ktonnes
	Ammonia	3.3	3.7	ktonnes
	Amine inhibitors*)	0	0	ktonnes
	Catalyst for denox	0	0	ktonnes
	Miscellaneous	0	0	ktonnes
Output	CO_2	4415	616	ktonnes
	O_2	1115	1474	ktonnes
	H_2O	1779	1470	ktonnes
	N_2	16126	18582	ktonnes
	NO_x as NO_2	4760	4242	tonnes
	SO_2	4760	212	tonnes
	MEA	0	58	tonnes
	Reclaimer residues	0	13.8	ktonnes
	Waste water	4.8	907	ktonnes
	Fly ash	173	189	ktonnes
	Furnace bottom ash	58	64	ktonnes
	Mill rejects	3.9	3.9	ktonnes
	Gypsum byproduct	91	111	ktonnes

*) It is known that the Fluor EFG+ uses a proprietary inhibitor. As its composition is not known the environmental impact could not be taken into account.

B.4 Pre-combustion coal

Pre-combustion cases for coal was based on a study for IEA GHG R&D-Programme by Foster-Wheeler Energy Ltd. Foster-Wheeler did this study both for Shell dry feed gasifier and Texaco's slurry feed gasifier, both in combination with a combined cycle (IGCC) for electricity production (IGCC, Integrated gasification combined cycle). The system based on the Shell's gasifier is characterised by a relative high investment, high-efficiency system (43% LHV), where the Texaco gasifier results in a relative low investment low-efficiency (38% LHV). The effect of CO_2-capture on the plant-efficiency is largest for the Shell IGCC (8,6% of LHV versus 6,5% for the Texaco IGCC). Overall a system for pre-combustion capture based on the Texaco-gasifier seems to be the lowest-cost option to produce low-CO_2 electricity. However the system based on the Shell-gasifier may be the preferred system when judged on an overall environmental impact, since per kWh_e it consumes less coal and requires less carbon dioxide to be stored. For this reason the Shell system is considered in this project.

In the Foster-Wheeler-study, a number of process variations were considered. Most of them were based on Selexol as a solvent. However one variation of the Shell-system was based on UOP/DOW Amine Guard (MDEA) as a solvent. Since no environmental data were available on Selexol, this MDEA-system is used in the LCA-comparison of capture processes. The energy and material balance of this process is given in table B7 and B8.

Table B7 Energy balance of integrated gasification combined cycle plants.

	Capture: none **IGCC**	**Capture:** **Pre-combustion** **IGCC + MDEA**	
Summary			
Fuel fired	1801	1950	MW
Gross output	910	883	MW
Gross efficiency	50.5	45.3	%
Losses plant			
ASU power consumption	100	113	MW
Process Units consumption	13	25	MW
Utility Units Consumption	1.5	2.5	MW
Offsite Islands consumption	6	9.3	MW
Power Islands Consumption	13	13	MW
Add. losses capture			
Compression		37	MW
Total losses	**134**	**200**	**MW**
Net output	**776**	**683**	**MW**
Net efficiency	**43.1**	**35.0**	**%**
Annual net output	**6117984**	**5387137**	**MWh**

Table B8 Mass balance of integrated gasification combined cycle plants.

	Data per year	**Capture: none IGCC**	**Capture: Pre-combustion IGCC + MDEA**	**Unit**
Input	Coal	1976	2153	ktonnes
	MDEA-solution	0	60	tonnes
	Make-up water	0	0	ktonnes
	Limestone	0	0	ktonnes
	Ammonia	0	0	ktonnes
	Amine inhibitors	0	0	ktonnes
	Activated carbon	0	0	ktonnes
	Miscellaneous	0	0	ktonnes
Output	CO_2	4720	730	ktonnes
	O_2	5398	5204	ktonnes
	H_2O	1632	3085	ktonnes
	N_2	30540	30580	ktonnes
	NO_2	3677	2791	tonnes
	NO_x	230	2791	tonnes
	SO_2	23	38	tonnes
	CO	1425	1169	tonnes
	Particulates	230	189	tonnes
	MDEA		0	tonnes
	Reclaimer residues	0	0.11	ktonnes
	Waste water	0.0	363	ktonnes
	Seawater (cooling)	674.1	793	ktonnes
	Slag	293.3	317	ktonnes
	Fly-ash	9.5	10	ktonnes

C Environmental data solvents

Regarding the environmental impact directly related to the solvent, three categories can be distinguished:

- impact as a result of the production of the solvent
- impact as a result of the treatment of solvent-containing residues
- direct impact of emitted solvent and decomposition products

The treatment of residues is discussed in appendix D.

Production of solvents

Monoethanolamine

Appendix A shows schemes of the production process of monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA). Environmentally relevant data have been compiled from several sources. The basis has been derived from generic MEA production process data in Ecoinvent 2000 [18], because the response of manufacturers to the questionnaires sent (see appendix G) was not satisfactory. This data set incorporated the production of the two main precursors, ethylene oxide and ammonia. Though, no distinction was made in ethylene/ammonia ratios which are different for the three products, MEA/DEA/TEA. The assumed production mix is 40%/40%/20% for MEA/DEA/TEA. At this point the data have been adapted, according to the stoichiometry for the production of 100% MEA. The production efficiency has been set to 98% for both components.
The Ecoinvent 2000 dataset does not include the energy consumption of the destillation columns for the separation of the three products. For MEA, only the first two columns (removal of water and separation of MEA from the product mix) are relevant. These have been modelled using Aspen (DSTWU model), resulting in an estimated energy consumption of 2.5 and 2.4 MJ per kg of MEA, which is assumed to be generated by combustion of natural gas.

Data for the production of the precursors ammonia and ethylene oxide as well as the production of electricity and heat are covered in the Ecoinvent 2000 database. For ammonia these are state-of-the-art technology data for Europe during the period 1995-2000, with a European average production mix of 85% steam reforming and 15% partial oxidation of heavy fuel oil. The data for ethylene oxide consists of a cross section of European plants. The literature reference describing the data has been written in 2004. For electricity and heat from natural gas European average production data has been used. The production of heat from natural gas is supposed to take place in an industrial furnace with a capacity greater than 100 kW.
The amount of electricity and heat consumed in the production of MEA is estimated.

The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water is assumed to take place in an internal waste water treatment plant (elimination efficiency of 90% for C).

Table C.1 shows the major inputs and outputs of the production of MEA.

Table C.1 Mass and energy balance production of MEA.

Input	Amount	Unit
Ammonia	0.284	kg
Ethylene oxide	0.736	kg
Cooling water	0.024	m^3
Electricity	0.333	kWh
Heat (natural gas)	2	MJ
Heat distillation (natural gas)	4.9	MJ

Output	Amount	Unit
MEA	1	kg
MEA (em. air)	1.58	g
Ethylene oxide (em. air)	1.63	g
CO_2	26.5	g
Ammonium (em. water)	3.04	g
Ethylene oxide (em. water)	1.47	g

The CO_2 emission is mainly a result of the wastewater treatment. Combustion emissions as a result of the generation of heat and electricity are not displayed here.

Methyldiethanolamine

Appendix A shows a scheme of the production process of methyldiethanolamine (MDEA). The first step is the production of monomethylamine (MMA) from ammonia and methanol. The production process is basically a multi-output process in the sense of the production of MEA (see above). The products are MMA, dimethylamine (DMA) and trimethylamine (TMA). Ecoinvent 2000 describes the production of trimethylamine (TMA) only. These data have been converted to meet the stoichiometry of the production of MMA: the input ratio of ammonia and methanol has been adapted. The mass efficiency is assumed to be 95% for both precursors. The Ecoinvent data set also lacks the energy consumption of the distillation columns. We have assumed the energy consumption of the MEA/DEA/TEA separation here: 2.5 MJ/kg MMA for the removal of reaction water and 2.4 MJ/kg for the separation of MMA.

Environmentally relevant data for the production of the precursors and energy carriers (electricity and heat from natural gas) are part of the Ecoinvent 2000 database. For ammonia, electricity and heat from natural gas these are the same average data as used in the production of MEA. As regards methanol, production data is based on generic design of natural gas steam reformer plants. Temporal representativity is unknown.

Table C.2 shows some key inputs and outputs of the production of MMA.

Table C.2 Mass and energy balance production of MMA.

Input	Amount	Unit
Ammonia	0.577	kg
Methanol	1,09	kg
Cooling water	0.024	m^3
Electricity	0.333	kWh
Heat (natural gas)	2	MJ
Heat distillation (natural gas)	4.9	MJ

Output	Amount	Unit
MMA	1	kg
Ammonia (em. air)	0.61	g
Methanol (em. air)	3.42	g
CO_2	102	g
Ammonium (em. water)	4.63	g
Methanol (em. water)	8.22	g

The CO_2 emission mentioned is not a result of the generation of heat and electricity, because those data are not displayed here.

For the production of MDEA, no real process data is available. The amount of MMA and ethylene oxide (its precursors) is calculated on basis of stoichiometry. Per kg of MDEA, 0.266 kg of MMA and 0.755 kg of ethylene oxide is required, accounting for an efficiency of 98% for both. It is assumed that the reaction is exothermic, and therefore requires no external energy source. The production data of ethylene oxide is a cross-section of European plants and is equal to these used in the production of MEA (see earlier in this appendix).

Direct impacts of emitted solvents and decomposition products
A small amount of solvent is emitted to air, as well as an unknown amount of reaction products. The environmental effect of these substances is primary related to toxicity for plants, animals and humans. In CML-LCA2 (see appendix E) impact categories that deal with toxicity are based on USES-LCA, a global nested multi-media fate, exposure and effects model [24]. Equivalence factors (*toxicity potentials*) are however available only for a limited number of substances. None of the solvents discussed in this report were included. Therefore we have asked the author of USES-LCA2, Mark Huijbregts of Radboud University Nijmegen, to calculate toxicity potentials for a selection of solvents [22; 23]. Toxicity potentials are substance-specific, quantitative representations of potential impacts per unit emission of a toxic substance.
In table C.3 toxicity potentials are presented of monoethanolamine, diethanolamine, triethanolamine, methyldiethanolamine, sulfolane, methanol and aminomethylpropanol [22; 23].
The concerning impact categories are: fresh water aquatic ecotoxicity (FAETP), terrestrial ecotoxicity (TETP) and human toxicity (HTP); the initial emission compartments are: air, fresh water, sea water, agricultural soil and industrial soil. In some occasions the human toxicity potential could not be calculated.

Table C.3 Toxicity potentials of Monoethanolamine, Diethanolamine, Triethanolamine, Sulfolane, Methanol, Aminomethylpropanol and Methyldiethanolamine (in kg 1,4-Dichlorobenzene equivalents).

Substance	**Type**	**Initial emission compartment**				
		air	**fresh water**	**sea water**	**agricultural soil**	**industrial soil**
monoethanolamine	FAETP	3.7E+00	5.7E+01	8.4E-06	6.1E+00	1.2E+01
	TETP	7.0E-01	1.0E-04	1.6E-06	2.8E+00	2.0E+00
	HTP	6.4E-01	2.1E-02	5.4E-06	3.4E+00	1.3E-02
diethanolamine	FAETP	1.7E-01	1.6E+00	4.0E-10	1.7E-01	3.4E-01
	TETP	3.1E-02	5.4E-09	7.4E-11	7.8E-02	5.8E-02
	HTP	1.4E+02	3.3E+00	6.3E-04	1.1E+03	7.3E-01
triethanolamine	FAETP	1.4E+00	1.1E+01	1.1E-10	2.5E+00	2.5E+00
	TETP	2.0E-01	2.0E-09	1.7E-11	4.2E-01	4.2E-01
	HTP	8.3E+01	3.3E+00	6.6E-04	6.1E+02	7.2E-01
methyldiethanolamine	FAETP	1.4E+00	1.2E+01	1.2E-08	2.6E+00	2.6E+00
	TETP	2.2E-01	1.1E-07	1.8E-09	4.5E-01	4.5E-01
	HTP	?	?	?	?	?
sulfolane	FAETP	2.6E-01	2.2E+00	1.5E-07	4.8E-01	4.8E-01
	TETP	3.8E-02	1.3E-06	2.2E-08	8.0E-02	8.0E-02
	HTP	?	?	?	?	?
methanol	FAETP	1.6E-03	8.4E-02	4.9E-07	8.7E-03	1.7E-02
	TETP	3.4E-04	6.7E-06	1.1E-07	4.0E-03	3.0E-03
	HTP	1.3E-01	1.2E-02	4.2E-05	1.2E+00	7.0E-03
aminomethylpropanol	FAETP	1.1E+00	2.9E+01	4.8E-05	6.2E+00	6.2E+00
	TETP	1.7E-01	4.4E-04	7.3E-06	1.0E+00	1.0E+00
	HTP	7.8E+02	4.3E+01	4.3E-02	3.4E+03	2.5E+01

The initial emission compartment, as denoted in table C.3, is (mainly) *air* in this study. If one kilogramme of MEA is released to air, this causes 3.7 kg of 1,4-dichlorobenzene equivalents of potential toxic effect in freshwater (FAETP). The potential toxic effect in soil (terrestrial ecotoxicity, TETP) and on humans is 0.7 and 0.64 kg of 1,4-dichlorobenzene.

Some remarks:

- The basis for the equivalency, 1,4-dichlorobenzene, is more or less arbitrary, and serves the purpose of obtaining an equal unit only (eq.);
- Obviously concentrations of substances in the environment are of great importance for the toxic effect in real life. Due to the linear character of LCA and the disregard of spatial differences, concentrations are not taken into account in this study. This means that the toxicity potentials as in table C.3 are mass flow based: each kg to the environment is assumed to have an equal effect.

The reports [22] and [23] are included as appendix I and appendix J.

D Waste processing

D.1 Evaluation with hazardous waste criteria

Whether a waste stream with this composition is to be treated as hazardous or non-hazardous waste, can be determined with European Commission Decision 2000/532/EC and its amendment 2001/118/EC.

The determination is based on two criteria that will have to be met both to render a waste hazardous:
- The waste has one or more of the properties as described in annex 3 to directive R91/689/EEC;
- One or more of a list of criteria (article 2 of 2001/118/EC) is met.

The following properties apply to MEA:
- H4 irritant
- H5 harmful
- H8 corrosive

The following risk phrases are applicable to MEA: (MSDS data)
R20, R34, R36, R37, R38

The following criteria of article 2 of 2001/118/EC are relevant:
- one or more substances classified as harmful at a total concentration >=25% (not applicable)
- one or more corrosive substances classified as R34 at a total concentration >=5% (not applicable)
- one or more irritant substances classified as R36, R37, R38 at a total concentration >=20% (not applicable)

Apparently the waste stream such as displayed in table D.1 is not to be classified as hazardous, on basis of the current knowledge. Though, the information in the table leaves unknown approximately 64% of the composition. Possibly one of the unknown components is relevant for the above characterization.

Assuming that recovery of (valuable) substances from the reclaimer sludge is not economically viable, two real treatment options are left: incineration and disposal on a (controlled) landfill site.

D.2 Incineration

In the 10 reference cases the reclaimer sludge is assumed to be incinerated in a municipal solid waste incinerator (MSWI). Incineration gives rise to emissions to air and water, and a number of waste streams: bottom ash, fly ash and residues of flue gas cleaning. Furthermore incineration requires some energy for handling of waste and auxiliaries. On the other hand, most incinerators are currently equipped with a combined power and heat recovery installation.

Life Cycle Assessment calculations for the MSWI have been based on a model developed by TNO, described in [27]. Some characteristics:
- technology is average Dutch situation in 1996
- flue gas cleaning is based on SCR (68%) and SNCR (32%)
- furnace is of grate type
- combustion heat is used for energy production.

Accounted for in the model are:
- Input of auxiliary materials for flue gas cleaning (NaOH, $Ca(OH)_2$, NH_3, methane and active coal)
- Energy consumption of flue gas cleaning and waste treatment
- Energy production; the amount of electricity produced equals 20% of the net calorific value of the waste; 10% of the net calorific value is converted to heat, externally applicable.
- Emissions to air and water. The amount of substances released is related to the composition of the input.

Treatment, storage or useful application of fly ashes, bottom ashes and flue gas cleaning residues is not described in the model. In this study we assume that all waste streams are landfilled. Given the composition in table D.1 the amounts of solid waste generated in the MSWI are insignificant.

Details of the MSWI model can be found in [27].

D.3 Landfill

Although there is a movement in Europe towards incineration of waste, still the larger part of the total amount of waste treated is landfilled (2002) [28]. Therefore it is interesting to see how landfilling the reclaimer sludges would influence the results. TNO report [27] contains a model of a controlled landfill site, based on the average Dutch situation in 1996. Included are, amongst others: energy input for maintenance, waste handling and leachate treatment, production and use of produced landfill gas, emissions to air, water and soil.

Due to the large amount of water in the reclaimer sludges, most certainly a mechanical or thermal dewatering process is necessary prior to acceptation on landfill sites. This is not taken into account here.

All reference cases have been recalculated using landfill instead of incineration as waste treatment of reclaimer sludges. On the level of electricity production (case 3

up to 10), hardly any differences can be seen at all. The influence is 0.6% at most, for acidification.
Case 1 and 2 represent the capture of one ton of CO_2. Even for these cases, no differences larger than 2% for a single impact category can be observed.

It is not likely that other waste treatment routes would lead to large contributions to the environmental impact of CO_2 capture. The amounts of waste are small, and the impact of treatment has proven to be small for both incineration and landfill, in relation to the impacts due to additional energy consumption, changed emission patterns and the production of the solvent.

E Life Cycle Assessment methodology

Introduction

The method of environmental Life Cycle Assessment (LCA) is seen as a suitable instrument for the evaluation of the environmental impacts of a product or an activity through its entire life cycle.

LCA is a systematic way to evaluate the environmental impacts of product system or activities by following a "cradle-to-grave" approach. The product system consists of a set of activities (processes), all focused on the fulfilment of the required function. These activities can be executed at different places and in different time periods. Therefore it is not possible to produce results, which refer to "real" environmental effects, since this requires specific locations and specific periods.

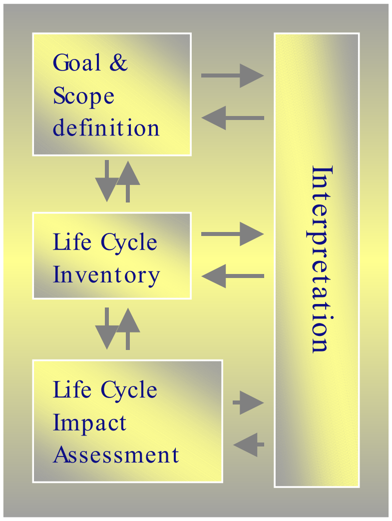
The result of a life cycle analysis is expressed in terms of "potential" effects. These potential effects are indicators for the real effects on local, regional and global level.

LCA structure

The LCA methodology is structured along a framework with four main steps or phases (ISO 14040):

1. Goal and scope definition;
2. Inventory analysis;
3. Impact assessment;
4. Interpretation.

These phases are part of an iterative process; the main flow is according to the above sequence.



1. Goal and scope definition

This deals with the clear and unambiguous formulation of the research question and the intended application of the answer that the LCA study is supposed to provide.

Important elements of the goal and scope definition are the choice of the functional unit, the selection of product alternatives to be analysed, and the definition of the reference flows for each of the alternative systems.

2. Inventory analysis

The phase is concerned with the construction of the product systems. These systems are composed of unit processes, like industrial production, waste treatment, transport and so on.

The system boundaries and flow charts of linked unit processes are drawn for each alternative product system, and quantitative input and output data for each unit process are collected, i.e. raw materials and energy use figures, as well as emissions and waste amounts. Furthermore qualitative data for representativeness, data quality etc. are collected during this phase. For those unit processes that are multifunctional, i.e. that produce more than one product; an allocation step is made: all input and output data of the unit process is allocated to each of the products, according to chosen rule (e.g. on basis of mass ratio or economic value). A final step of the inventory analysis is the aggregation of the emissions of chemicals and the extractions of natural resources over the entire product system, in such a way that a quantitative match with the system's reference flow is achieved. The result of the inventory analysis is often a long list with disparate entries, such as carbon dioxide, nitrogen oxides, chloromethane and mercury.

3. Impact assessment

This phase aims to convert and aggregate the results of the inventory analysis into environmentally relevant items. In particular, we mention here the step of characterisation, in which the inventory results are transformed into a number of contributions to environmental impact categories, such as global warming, acidification, and ecotoxicity. Optionally the characterisation results may be normalised in order to relate the results to a reference value, such as the annual global or European extent of each impacts. Finally, a weighting step may be performed, in which priority weights are assigned to the characterisation or normalisation results, and which may result into one final score for each alternative product system.

Table E.1 shows an example calculation (characterisation only).

Table 1 Example of impact assessment (characterised effect scores).

Emission	**Quantity (kg)**	**Characterisation factors (kg eq/kg)**			
		Global Warming Potential	**Photochemical ozone creation potential**	**Human toxicity**	**Acidification potential**
CO_2	220	1			
methane	3	11	0.007		
NO_x	8			0.78	0.7
N_2O	8	270			
benzene	5		0.189	3.9	
C_xH_y	5		0.377		
Characterised scores		220*1 + 3*11 + 8*270 = **2413 kg CO_2 eq**	3*0.007 + 5*0.189 + 5*0.377 = **2.851 kg C_2H_4 eq**	8*0.78 + 5*3.9 = **25.74 kg dichloro-benzene eq**	8*0.7 = **5.6 kg SO_2 eq**

4. Interpretation

During the course of the LCA, many choices and assumptions are needed. Moreover, uncertainty may be introduced with every data item. The interpretation phase deals with the meaning and robustness of the information obtained and processed in the previous phases. The interpretation may include comparisons with previously published LCA studies on similar products, uncertainty and sensitivity analyses, data checks, external comments, and much more. It is also the place in which a final judgement and decision is drawn up.

F Methodology for the assessment of shadow prices for human toxicity, ecotoxicity and abiotic depletion

A.K. van Harmelen, R.H.J. Korenromp [a], C. van Deutekom [b], T.N. Ligthart, S.M.H. van Leeuwen [c], R.N. van Gijlswijk

TNO Built Environment and Geosciences,
P.O. Box 1, NL-7300 AH Apeldoorn, the Netherlands,
email a.k.vanharmelen@mep.tno.nl

[a] now working at Adecs Oost, Zwolle;
[b] now working at Yacht;
[c] now working at ABK InnoVent, Doetinchem

(To be published)

F.1 Introduction

The lack of comparability of environmental impacts poses a problem to investors, designers and not least to environmental policy-makers. it is hard to decide which appliance is more environmentally friendly: the ozone-depleting high-efficiency fridge or the ozone-friendly but more power-hungry fridge. In such cases, environmental impacts need to be weighed. One of the methods to do this is known as the shadow price method. It uses the highest acceptable costs for mitigation measures as a weighting factor and has been operationalised for a number of impact categories in the Netherlands. For instance, the Dutch Ministry of Public Works uses the shadow price method in combination with the life cycle assessment method called CML-2 (introduced by the Leiden University Institute of Environmental Sciences) [5] in their life cycle impact assessment model DuboCalc to calculate the environmental impact of infrastructure works [2]. The advantage of using shadow prices is that different environmental impacts are translated into external costs that can be compared with each other and with the internal production costs. The danger, of course, is that certain intrinsic values are underappreciated and get lost in the total cost analysis.

Several sets of shadow prices have been assessed, mainly for near-future targets of well-documented Environmental Impact Categories (EIC) such as climate change, acidification, ozone depletion, tropospheric ozone formation and eutrophication, e.g. by the organisations CE [11], NIBE (Twin) [12] and TME [10]. Internationally, the shadow price of CO_2 is also often referred to as the price of CO_2 on the emission trading market or the marginal reduction costs of national climate policies. However, shadow prices have so far not been available for the depletion of abiotic materials (ADP) and the toxicity-related categories (human toxicity potential – HTP, marine aquatic and sediment ecotoxicity potential –

MAETP and MSETP, fresh-water aquatic and sediment ecotoxicity potential – FAETP and FSETP, or terrestrial ecotoxicity Potential – TETP). ADP relates to natural resources such as metals and fossil and nuclear fuels, the others cover pollutants including metals, pesticides, polycyclic aromatic hydrocarbons (PAHs), non-aromatic organic substances and inorganic substances.

We have developed a method to assess the actual shadow prices for these complex impact categories. This paper presents the methodology to assess the shadow prices of the human toxicity and ecotoxicity (from now on shortly referred to as toxicity) and abiotic depletion, as well as the resulting set of shadow prices.

F.2 Methodology

F.2.1 Alternative approaches

Different methods can be used to assess societal preferences for environmental quality as a basis for weighting or prioritising environmental impacts. Hofstetter [7] and Huppes et al. [9] made a distinction between **who** decides on the priority and **how** the priority or preference is assessed. As to the decision-makers, they found the government representing society most relevant for applications in a policy context. As to the way preferences are assessed, they distinguished between preferences directly assessed by statements and preferences indirectly revealed by actual, observed behaviour or market-based information. In addition to this, we – like Vogtländer [16] – think it is important to make a distinction between weighting and valuing or monetisation methods; the former use points or percentages to weigh environmental impacts, while the latter use the value in monetary terms to assess the importance of these impacts. In our view, it is an advantage to express preferences in euros, to allow measures to be prioritised in relation to production costs and other economic activities. This makes the comparison explicit, although one should evaluate qualitative differences as well. In fact, the analysis should be a basis for a discussion of priorities, rather than provide a black box answer. Table 1 presents an overview of methods to assess societal preferences, using this terminology.

Table 1 Overview of four basic approaches to weighting (%) and valuation (€) methods to assess societal preferences for environmental quality, after Huppes [9] and Pearce [14].

How [1] **Who**	**Stated** Panels, hypothetical markets (future)	**Revealed** Conventional or surrogate markets (present)
Collective policy	**Stated collective preferences** • Prevention costs/targets marginal costs (€) • Distance-to-target (%)	**Revealed collective preferences** • Prevention costs/actual marginal costs (€) [1] • Replacement costs or damage costs (€)
Private person	**Stated private preferences** • Contingent valuation (€, willingness-to-pay, willingness-to-accept compensation) • Discrete choice modelling (€) • Conjoint analysis (%)	**Revealed private preferences** • Hedonic pricing (€) • Travel cost (€)

[1] Used in this paper to monetise toxicity

Stated collective preference methods include two main categories, viz. prevention costs methods and distance-to-target methods. In a distance-to-target method, the weighting factors are deduced from environmental policy targets with respect to emissions or concentrations. The ratio between the stated future target and the present level gives the weighting factor. Prevention costs methods or averting behaviour or avoidance costs methods derive the preference from the marginal costs of meeting emission reduction targets and infer preferences from actually observed market-based information. This method has been operationalised for the Netherlands by CE under the name of 'shadow price method' [19].

This method can also be implemented for the actual marginal costs resulting from present environmental policy measures and regulations. It does not involve stated preferences but represents **revealed collective preferences**, since the market is not hypothetical but real. Although theoretically different from the stated collective preference method as implemented by CE, we do not expect the difference to be very large for short- and medium-term policy targets. The deviation from a policy target might fall within the uncertainty interval of the estimated shadow price.

Another method to monetise the revealed collective preferences is using replacement costs or damage costs, where the costs incurred to replace or repair e.g. damaged health, crops and buildings is used as the value of the environmental impact. This method is difficult to use for toxicity, where the impacts on e.g. health or ecosystems are difficult to quantify and repair.

Stated private preferences elicit preferences directly with the help of questionnaires for panels. Of the methods in this category, contingent valuation expresses preferences directly in monetary terms, whereas conjoint analysis is based upon ranking. Discrete choice modelling is a mixture of the two methods, in which the value of environmental quality is inferred from the accepted cost difference between two goods that differ in terms of one environmental quality aspect.

Revealed private preferences include hedonic pricing, where the influence of environmental factors such as noise on the market prices of e.g. houses is used as the value of the environmental impact, and the travel cost method, in which the price a consumer is willing to pay for a visit to a site (e.g. a recreational site) is regarded as the value of the environmental impact. The latter method in particular is very limited in terms of the environmental aspects included.

In the present paper, we monetise the revealed collective preferences with respect to toxicity and depletion of abiotic materials by means of the avoidance costs resulting from present policy regulations, as highlighted in black in Table 1. Besides our preference for monetary values, another reason for using actual marginal costs is that cost data on mitigation measures to meet future emission objectives are hardly available. In fact, toxicity policy and mitigation options and costs have not been elaborated to the same extent as those of e.g. acidification and climate change, where there is a long history of intense international research, policymaking and negotiations on single national equivalent emission reduction targets.

F.2.2 The concept of shadow prices

There is a demand for environmental quality or damage limitation on a virtual market for environmental quality. In this market, the willingness to pay a high price increases with the emission level of pollution, and a supply of emission mitigation measures is available that cost more per unit of reduction at higher reduction levels. If this market existed, an equilibrium price would arise at the intersection of demand and supply, as illustrated in Figure 1.

Since the environmental market is a virtual market and environmental costs are so-called external costs, the government has to set an emission target to improve the environmental quality. The price level at the intersection between the emission objective and the supply of available emission mitigation is called the shadow price, being the highest price paid by society to improve environmental quality that is still acceptable to the government. The shadow price is the extent to which total costs change as a result of a change in a limiting factor, in this case an emission objective.

The total environmental costs to society will be the costs of mitigation (the shaded area under the supply curve) plus the damage to the environment, being the remaining emissions multiplied by the price level that society is willing to pay (according to the demand curve). In market equilibrium, this is the equilibrium price.

The government will aim its emission objective at the intersection of demand and supply, since at this point the virtual environment market is in equilibrium according to society. This is known as the societal optimum. Under the assumption that the government manages to design a policy whose shadow price equals the equilibrium price, the shadow price multiplied by the remaining emissions indicates the environmental damage as perceived in (and accepted by) society. This principle is used when applying the shadow price method.

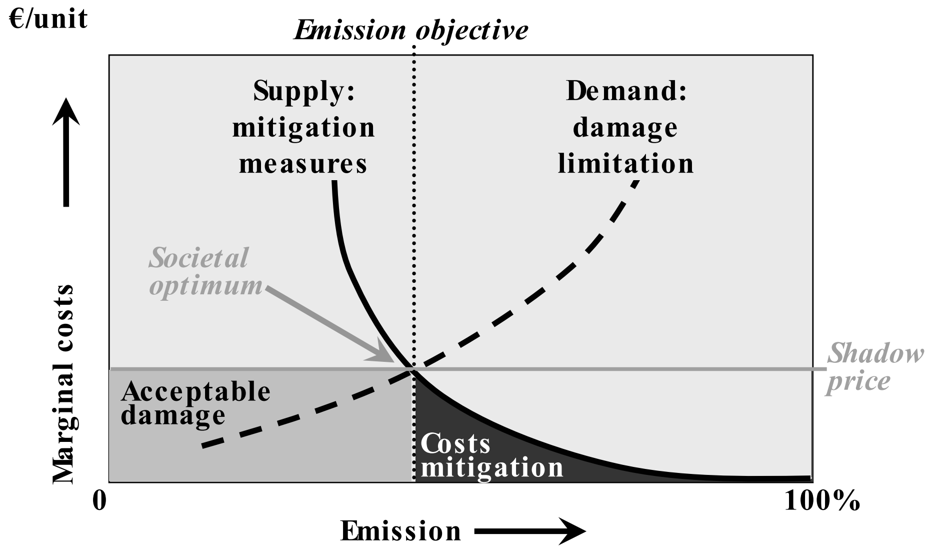


Figure 1 *In a virtual market, demand for environmental damage limitation and supply of emission mitigation by measures will result in an equilibrium price for environmental quality. If a government's emission objective crosses the equilibrium point, the shadow price is optimal and equal to the equilibrium price.*

F.2.3 Methodology for the assessment of shadow prices

We have developed a new method to assess the shadow prices of present policy regulations. For the well-known EICs such as acidification and climate change, an inventory of mitigation measures and costs derived from policy plans sufficed to assess the marginal costs of national abatement policies for a certain Environmental Impact Category. For these cases, national emission reduction cost curves and single national equivalent emission reduction targets are available, which makes the assessment of a shadow price fairly straightforward. For toxicity, the information is less clear, and no single national equivalent emission objective is available. Furthermore, the number of relevant pollutants and the data quantities are so huge that a structured approach is required. The assessment method consists of four steps:

1. Characterisation of current environmental policy for each impact category.

2. Concentrating on the most relevant substances per impact category.
3. Collection of abatement cost data by means of literature research and interviews.
4. Calculation of the shadow price based on the cost-effectiveness of abatement measures.

1. Characterisation
Since the present environmental policies and regulations determine the mitigation measures that have been taken so far, the first obvious step is to look at the areas for which regulations are currently in place with respect to the EICs under consideration. This provides the necessary context for interpreting and understanding the data collected in the next steps.

2. Concentration
We need to concentrate on a selection of relevant substances for each impact category, since the number of pollutants in combination with initial media is already exceeding 200 items. Therefore, we calculated the emissions in 1,4-dichlorobenzene equivalents (1,4-DCB) using CML-2 characterisation factors [8] and selected the most important pollutants for each EIC on the basis of three criteria:

1. share in national and sector equivalent emission in 1990;
2. historic change in equivalent emission over the 1990–2000 period;
3. present policy pressure to take measures.

The year 1990 was selected to ensure pollutants that have been greatly reduced are still included in the selection, since these pollutants are very important for the assessment of the shadow price.

We used a target group analysis of data from the Environmental Pollutant Emission Register (EPER) for the Netherlands [4] to assess which company, process or other emission source is responsible for significant reductions. This allowed us to focus and increase the effectiveness of our data collection, and to assess which important sources have been covered and which have not (yet).

3. Collection
Data were collected firstly by telephone interviews with selected companies. Although we used a very specific approach in terms of questions on reduction of pollutants, little information was collected. Hence, most of the information on measures currently available for mitigation in the EIC under consideration was collected from the relevant national and international literature.

4. Calculation
A large number of measures are available to reduce emissions of one or more pollutants. To calculate the marginal costs, the additional costs of each measure are simply divided by the additional equivalent emission reduction of all pollutants. If

pollutants contribute to more than one toxicity category, toxicity impacts need to be weighed to calculate the marginal costs. Although toxicity is expressed in 1,4-DCB equivalents in all EICs, its meaning may differ between EICs. For instance, effects in humans are not directly comparable with ecotoxicity in marine waters. We therefore developed a cost allocation method, consisting of two steps:

1. weighting the environmental impact categories;
2. allocating costs by relative contribution to the environmental impact.

The initial weight of the EIC can be varied to assess the sensitivity of the results to the assumed weight. To avoid weights being arbitrarily chosen, several so-called policy perspectives were developed to characterise the relative importance of EICs. Furthermore, an iterative procedure was established to weigh the EICs with the resulting shadow costs.

Finally, the calculated shadow prices are compared with the actual environmental expenditures reported in the annual national environment report (*Milieubalans*) [15].

F.3 Assessment of shadow prices

F.3.1 Characterisation of current environmental policy

Toxicity is an important EIC in Dutch environmental policy. The annual expenditures are € 1.8 billion (year 2000, [15]), which is more than the expenditures on climate change, acidification and eutrophication combined. Quantitative targets have been set for different compartments, either in terms of concentration limits or emission reduction targets for industrial sectors. The latter are voluntary agreements [17].

For emissions to air, explicit concentration limits have been set for many organic pollutants and heavy metals, especially for combustion processes (PAHs, volatile organic compounds or VOC, dioxins and PM_{10} i.e. particulate matter with diameters up to 10 µm). Many pesticides have been banned or have a maximum allowable concentration (MAC) value.

For emissions of toxic compounds to water, emission standards have been set for waste water discharged by companies. Furthermore, sewage treatment plants have increasingly strict concentration limits for VOCs and heavy metals.

The policy on soil has changed over the past decades. It started in the 1960s and 1970s with a campaign of rigorous soil sanitation, which has been successful. The present view is that maintaining this sanitation standard is too expensive, and that soils should only be decontaminated if this is cost-effective. This means that the highest acceptable costs, i.e. the marginal costs, are 0. Nevertheless, target MAC values have been established for heavy metals, and the use of building materials has been regulated in the context of building materials regulations (*Bouwstoffenbesluit*).

F.3.2 Depletion of abiotic materials

As regards depletion of abiotic materials, only an indicative long-term target value has been set. No objective has been formulated and the accompanying policy has not yet been developed – only an indicator is under development. Up to now, quantitative targets have been set only in waste and energy policies. The current waste policy aims to avoid dumping waste at landfills, so recycling and waste incineration with energy recovery are equally prioritised. This means that materials depletion is not the single basic goal of this policy. Energy conservation is promoted for a number of reasons, including decreasing fuel import dependency, increasing supply security, reducing greenhouse gas emissions and avoiding resource depletion. Although it is very hard to distinguish between the various goals, resource depletion does play a role. However, in terms of antimony equivalents defined according to economic reserves depletion, as in CML-2 [5], consumption of fossil fuels accounts for less than 1% of the total equivalent materials depletion. It is not possible to attach a shadow price to a material that has such a low priority in equivalent terms, which illustrates that the equivalent method is not consistent with the present policy as regards energy resources.

For all other materials, no quantitative limits are being enforced, which means that market prices reflect economic scarcity. Other environmental impacts that are not reflected in the market prices are included in the other EICs. These should not be included in the shadow price of abiotic depletion, to avoid double counting. It is therefore concluded that the best estimate of the present shadow price for depletion of abiotic materials is € 0 per Sb equivalent. In the rest of this paper, attention will be focused on the EICs involving toxicity.

F.3.3 Concentration on relevant substances and sectors

Table 2 presents the 95% percentiles of 1,4-DCB equivalent emissions of pollutant-initial medium combinations for the various EICs. To calculate the equivalent emissions, the characterisation factor for each pollutant-initial medium combination was combined with data from the Pollutant Emission Register for the Netherlands [4]. Focusing on the 95% percentile for each EIC resulted in a reduction from over 200 to 30 pollutant-initial medium combinations. In fact, only 10 so-called priority pollutants determine the 95% percentile of equivalent emissions for each EIC. The emissions are presented for the year 1990 to ensure that pollutants that have recently been substantially reduced are still included in the selection. The reduction of the priority pollutants, presented over the period 1990–

2000, is a crucial indicator of the mitigation measures that have recently been taken.
The initial medium determines the characterisation factor used, since the USES model calculates these factors on the basis of dispersion and exposure routes in combination with the toxicity of a pollutant [5]. This also explains why an emission to air can result in marine ecotoxic effects. Table 2 clearly shows that FAETP and FSETP are dominated by emissions to fresh water, TETP by emissions to soil and to a lesser extent to air, and HTP is largely determined by emissions to air. Note that MAETP and MSETP are dominated by emissions to air. This is caused by high characterisation values due to very long residence times.

The selected priority pollutants are a few heavy metals (relevant for all EICs), PAHs (for all EICs except TETP) and VOCs, benzene, dioxin and ethylene oxide (only important for HTP).

Table 2 Contributions of priority pollutants to each individual EIC (95% percentile of 1,4-dichlorobenzene equivalent emissions), presented as emission shares to each EIC for 1990, and the total and reduction over the 1990–2000 period.

Pollutant	**Initial medium**	**HTP eq**	**FAETP eq**	**MAETP eq**	**FSETP eq**	**MSETP eq**	**TETP eq**	**Reduction 1990–2000**
Chromium (III)	Agr. soil						3%	**100%**
Copper (II)	Agr. soil		11%	2%	14%	3%	1%	22%
Mercury (II)	Agr. soil						1%	**100%**
Zinc (II)	Agr. soil		2%		2%		5%	2%
Arsenic	Ind. soil						2%	-50%
Chromium (III)	Ind. soil						***49%***	-26%
Copper (II)	Ind. soil				1%			-79%
Lead (II)	Ind. soil						1%	0%
Nickel	Ind. soil		1%		1%	1%		-10%
Acrolein	Air		10%		4%		2%	***30%***
Benzene	Air	19%						***45%***
Beryllium	Air			1%				**98%**
Chromium (III)	Air						4%	59%
Chromium (VI)	Air	1%						**97%**
Dioxins	Air	1%						**95%**
Ethylene oxide	Air	3%						**93%**
Hydrogen fluoride [1]	Air			17%		7%		***47%***
Mercury (II)	Air						10%	**80%**
Nickel	Air	3%	1%	7%	1%	8%	1%	64%
Nitrogen oxides	Air	1%						20%
PAH (6 Borneff)	Air	66%						55%
Vanadium	Air	2%	9%	69%	12%	**77%**	20%	**89%**
Acrolein	Fresh wat.		***30%***		11%			-2%
Benzo[a]pyrene	Fresh wat.		14%		21%			74%
Fluoranthrene	Fresh wat.		3%		5%			54%
Copper (II)	Fresh wat.		3%	1%	4%	1%		***31%***
Nickel	Fresh wat.		3%	2%	5%	3%		***34%***
PAH (6 Borneff)	Fresh wat.	5%	11%		17%			64%
Zinc (II)	Fresh wat.		1%		2%			22%
Nickel	Mar. wat.			1%		1%		***34%***
Total		100%	100%	100%	100%	100%	100%	**77%**
Reduction 1990–2000		56%	***35%***	**76%**	***47%***	**79%**	21%	

[1] The CML-2 characterisation factors for hydrogen fluoride have been decreased by a factor 80 to correct for the incorrectly assumed long residence time.
Ind. = Industrial; Agr. = Agricultural; wat. = water; Mar. = Marine.
Shares of 25%–50%: ***bold+italic***; 50%–75%: shaded; more than 75%:**bold+shaded**.

The equivalent emission reductions for each EIC over the 1990–2000 period are presented in the bottom row of Table 2. Equivalent emissions have decreased for all EICs, although terrestrial and fresh water EICs, with a reduction of one fifth to a half, are lagging behind reductions for HTP (more than halved) and marine EICs, with a reduction of three quarters.

Obviously, a large number of mitigation measures have been implemented over the last decade. This is confirmed by the rightmost column in Table 2, which presents the equivalent emission reduction per pollutant-initial medium combination for the same period. Note that the emission reduction rate due to a measure is equal for each EIC affected; only relative contributions can differ for different EICs. Equivalent emissions to soil have not been reduced according to the EPER register. The 100% reduction in chromium and copper to agricultural soil seems more likely to be a result of a monitoring error than of a strict mitigation measure.

In the further analysis, priority is given to heavy metals (all compartments), PAHs (air and water), dioxin, hydrogen fluoride and organic compounds (air). In an additional analysis, important target groups and companies were identified to focus our data collection. For practical reasons, the results are not presented here, and the reader is referred to the project report [6].

F.3.4 Collection of marginal cost data on measures

In the previous step, a number of pollutants, sectors and companies were selected. This allowed us to interview approximately 50 companies by telephone, asking questions tailored to their specific situation in terms of emission reductions of pollutant X. In addition, we used the national [1][3][16][18] and international [13] literature on emission reduction cost curves of specific pollutants. However, international data in particular cannot be exactly fitted to the Dutch situation, since the composition of the cost curve in terms of reduction potentials may differ and the position of the emission reduction objective in the cost curve is not clear. Nevertheless, it is possible to use them as a first estimation, since marginal cost curves generally consist of a flat part and a steep part. We selected the flat part, offering the greatest potential at relatively low marginal costs. Hence, we assumed that the Dutch government has a policy that forces companies to implement the most cost-effective measures in terms of euros per 1,4-DCB equivalent avoided. If fewer measures are implemented, the prices are not very different, since this part of the cost curve is flat. If more measures are currently implemented, prices are many times higher, since these measures fall in the steep part of the cost curve, so little additional reduction is reached at high additional costs.

For the specific collection and processing of data, the reader is referred to the project report [6]. We conclude that an abundance of data is available, but in incomparable formats and often incomplete. The data, being the basis of the analysis, could be improved in terms of accuracy and scope.

F.3.5 Calculation of shadow prices using cost allocation

For each EIC, the shadow price is presented in Table 3 for different cost allocation weights. Each shadow price is based on several measures with costs of the same order. The shadow prices for marine ecotoxicity are a factor of 100 or more lower than the other shadow prices. This is partly caused by the much higher national equivalent emission for the marine EICs, due to a high characterisation factor as a result of long residence times.

The sensitivity of the shadow prices to the cost allocation based on different weights was tested by a number of examples. The composition of the weight factors was not randomly chosen, but represents a policy perspective. For instance, in the human–ecological perspective, human toxicity (HTP: weight 5) and ecotoxicity (other EICs: each weight 1) receive equal priority. Please note that the different cost allocation does not change the total costs of measures, but only the distribution of costs over the different EICs, resulting in different prices.

The results in Table 3 show that the shadow price is not very sensitive to different weights, varying by a factor a 1.5 (TETP) to 2 (HTP) or 3 (other EICs), whereas the variation between the EICs involves a factor of 10,000. Of all perspectives, the compartmental perspective with a dominant human perspective is special in terms of processing as well as interpretation.

According to the theory of revealed collective preferences, the calculated shadow prices are in themselves an assessment of the present policy perspective. Hence, if this assessment is taken as a basis for cost allocation, the method is internally consistent. This approach has been explored using iterative calculations, in which the resulting shadow price is used for the calculation of the weights for the cost allocation to calculate new shadow prices. The weights are in fact shadow costs or accepted damage, being obtained by multiplying the present national equivalent emissions by the shadow prices.

Of the selected perspectives, the human–compartmental approach gives the most consistent results, in which the proportion of damage by present emissions in EICs is similar to the weights that are being used in the cost allocation. Hence, we selected the prices according to this perspective as national shadow prices for toxicity.

Table 3 Shadow prices for EICs with cost allocation according to different weight factors [€ / 1,4-dichlorobenzene equivalent].

Perspective (weight)	**HTP**	**FAETP**	**MAETP**	**FSETP**	**MSETP**	**TETP**
	[€ / 1,4-dichlorobenzene equivalent]					
Effect oriented (1:1:1:1:1:1)	0.042	0.107	0.00027	0.067	0.00037	1.28
Human–ecological (5:1:1:1:1:1)	0.075	0.083	0.00021	0.052	0.00028	1.21
H–E marine (5:0.4:1.6:0.4:1.6:1)	0.069	0.025	0.00026	0.016	0.00035	1.18
Compartmental (4:1:1:1:1:4)	0.065	0.059	0.00018	0.037	0.00020	1.34
Human dominant (10:1:1:1:1:1)	0.083	0.065	0.00016	0.041	0.00022	1.12
CML panel [9] (16:3:4:3:4:5) [1]	0.071	0.064	0.00022	0.040	0.00029	1.55
Human–compartmental (16:1:1:1:1:4)	**0.084**	**0.040**	**0.00010**	**0.025**	**0.00014**	**1.28**

F.3.6 Discussion of environmental expenditures

The total reduction of equivalent emissions can be valued as ‘shadow reduction costs’ by multiplying by the shadow prices. These shadow reduction costs can be compared with the actual expenditures for an EIC as published in the annual national environmental report [15]. For instance, the shadow reduction costs for acidification are € 1.3 billion, using the shadow price calculated by CE [11], compared to actual expenditures of € 0.8 billion in 2000. The actual expenditures are expected to be lower, since all technological options applied are cheaper than the shadow price. The calculation is illustrated in Table 4.

A brief analysis of marginal reduction cost curves for different EICs shows that the difference between reduction costs (the area under the cost curve) and the shadow reduction costs (the area under the shadow price, being the marginal costs at the reduction objective) vary per EIC. For climate change and acidification, this difference is estimated to be of the order of a factor of 2 to 3. This factor can only partly be deduced from Table 4, however.

The shadow reduction costs for the total of toxicity EICs are approximately € 6.5 billion. This is a factor of 3.5 higher than the environmental expenditures estimated in the annual national environmental report. This leads to the conclusion that the shadow reduction costs of toxicity seems to be of the expected order of magnitude.

This is striking, since the CML characterisation factors have been developed and updated over the last decade, so the present policy is not directly based upon the most up-to-date toxicity assessments available. Nevertheless, we conclude from our shadow price assessment that present policies do not seem to greatly contradict the knowledge and application of CML toxicity characterisation factors.

---

[1] Aquatic and sediment toxicity are not distinguished and each receive half of the weight factor.

The larger the difference between the actual reduction costs and the shadow reduction costs, the steeper the marginal cost curve, indicating that marginal costs of the emission reduction options last taken, rise rapidly. This implies that the potential of relatively cheap options is becoming exhausted.

Table 4 *Overview, per EIC, of emissions, reductions and shadow prices, expressed in equivalent units, sources of shadow prices, shadow costs of these reductions and actual expenditures according to the Dutch annual environmental report Milieubalans 2000 [15].*

Environmental Impact Category	**Unit**	**Emissions 1999–2000**	**Net reduction 1990–2000**	**Shadow price**	**Source**	**Shadow reduction costs**	**Environmental expenditures [15]**
		[eq]	**[eq]**	**[€/eq]**		**[billion €]**	**[billion €]**
Climate change	kt CO_2 eq	230,000	20,000 [a]	€ 0.05	CE	€ 1.0 [a]	€ 0.4
Acidification	kt SO_2 eq	705	333	€ 4.00	CE	€ 1.3	€ 0.8
Eutrophication	kt PO_4 eq	57	20	€ 9.00	CE	€ 0.2	€ 0.5
HTP	kt DCB eq	48,018	63,726	€ 0.084	TNO	€ 5.3	
FAETP	kt DCB eq	3,269	1,705	€ 0.040	TNO	€ 0.1	
MAETP	kt DCB eq	1,286,843	3,546,718	€ 0.00010	TNO	€ 0.4	
FSETP	kt DCB eq	5,232	4,467	€ 0.025	TNO	€ 0.1	
MSETP	kt DCB eq	956,092	3,054,486	€ 0.00014	TNO	€ 0.4	
TETP	kt DCB eq	689	196	€ 1.28	TNO	€ 0.2	
Total Toxicity	kt DCB eq	2,300,142	6,671,297	€ 0.0024	TNO	€ 6.5	€ 1.8
ADP	kt Sb eq	1,7		€ 0	TNO		

[a] inland measures in 2010

F.3.7 The Dutch set of shadow prices

The total set of shadow prices for the Netherlands is presented in Table 5. Since uncertainties are quite large, we present prices rounded to 1 significant number.

Table 5 Overview of rounded shadow prices for environmental impact categories including the resulting damage costs for the Netherlands in the year 2000.

Environmental Impact Category	Equivalent unit	Shadow price [€ / kg equivalent]	Damage [billion €]	Source
Human toxicity – HTP	1,4-DCB eq	€ 0.08	4.0	TNO
Fresh water aquatic ecotoxicity – FAETP	1,4-DCB eq	€ 0.04	0.1	TNO
Marine aquatic ecotoxicity – MAETP	1,4-DCB eq	€ 0.0001	0.1	TNO
Fresh water sediment ecotoxicity – FSETP	1,4-DCB eq	€ 0.03	0.1	TNO
Marine sediment ecotoxicity – MSETP	1,4-DCB eq	€ 0.0001	0.1	TNO
Terrestrial ecotoxicity – TETP	1,4-DCB eq	€ 1.3	0.9	TNO
Abiotic depletion – ADP	Sb eq	€ 0	0.0	TNO
Climate change – GWP 100 y.	CO_2 eq	€ 0.05	11.5	CE
Photochemical oxidation – POCP	C_2H_2 eq	€ 2	0.4	CE
Acidification – AP	SO_2 eq	€ 4	2.8	CE
Eutrophication– EP	PO_4 eq	€ 9	0.5	CE
Ozone layer depletion – ODP	CFC11 eq	€ 30	0.03	CE

2The table also includes the shadow costs resulting from remaining equivalent emissions for the year 2000. According to the theory, the environmental damage is the result of the remaining emissions valued using the shadow price. The total national environmental damage for all EICs considered in this paper is € 20 billion (5% of GDP). More than half of the damage is caused by climate change, while toxicity is responsible for one quarter, which is dominated by human toxicity. This is consistent with, but not completely identical to, current expenditures, which show a larger share of toxicity. This is caused by the fact that the reductions for toxicity have already reached three quarters, leaving one quarter of the environmental burden. For climate change, the opposite is true: the largest part of the emissions still remain, resulting in high shadow costs.

To our knowledge, only one other estimation of a shadow price for total toxicity has been published, by NIBE [12]. Applying this price, € 0.048 per 1,4-DCB equivalent, to the remaining total equivalent emissions, which is in fact a very crude approach since the EICs are different, results in a total damage of € 320 billion This is a very high figure, but it should be noted that these costs refer to sustainable emission targets and not to present policies.

F.4 Conclusions & Recommendations

On the basis of the method we have developed to assess shadow prices, and our analysis of data on policy, measures and costs in the field of human toxicity, ecotoxicity and depletion of abiotic materials, it can be concluded that:

- Toxicity is an important environmental impact category (EIC).
- 1,4-dichlorobenzene equivalents according to CML-2 are useful when kept separate for each EIC.

- The resulting set of shadow prices is now complete for the EICs of CML-2, although the perspectives of present and 2010 policies differ for different EICs.
- The set of shadow prices can be used as an environmental and economic yardstick of present policies to assess environmental profiles and evaluate environmental measures in economically consistent and quantitative terms for cost-effective decision-making by companies and policymakers.

[1] Based on the research conducted, we recommend to:

- apply and evaluate the present set of shadow prices and investigate further the robustness, reliability and limitations of the present method and the data on current mitigation measures for toxicity, to improve the assessment method and the quality of the shadow prices;
- extend the present CML impact assessment method with a policy version that uses equivalents with a shorter time horizon (e.g. 100 years, like Global Warming Potentials) and addresses location-specific aspects and background concentrations, thus increasing the consistency with, and therefore the quality and usefulness for, present policy development;
- maintain and update the present set of shadow prices every few years to reflect the latest policies, in order to ensure a high quality set of shadow prices.

F.5 References

[1] Buurma et al., Zicht op gezonde teelt; Een scenariostudie voor het gewasbeschermingsbeleid na 2000, 2000

[2] Davidson, Marc. D., Ron.C.W. Wit, Weging in DuboCalc, Toepasbaarheid van de preventiemethodiek, Delft, 2003

[3] Dellink, R., en F. van der Woerd, Kosteneffectiviteit van milieuthema's. Instituut voor Milieuvraagstukken. Vrije Universiteit Amsterdam. Juli 1997.

[4] Dutch Pollutant Emission Register, data request.

[5] Guinée, J.B. et al., Life cycle assessment - an operational guide to the ISO standard, vol. I, II and III, Centrum voor Milieukunde - Universiteit Leiden, May 2001.

[6] Harmelen, drs. A.K. van, drs. ing. R.H.J. Korenromp, dr. T. Ligthart, mw. ir. S.M.H. van Leeuwen, ing. R.N. van Gijlswijk, Toxiciteit heeft z'n prijs, Schaduwprijzen voor (eco-)toxiciteit en uitputting van abiotische grondstoffen binnen **Dubo***Calc*, TNO maart 2003, to be published

[7] Hofstetter, P. Perspectives in Life Cycle Impact Assessment, A structured approach to combine models of the technosphere, ecosphere and valuesphere, Kluwer Academic Publishers, Dordrecht, the Netherlands, 1998

[8] Huijbregts, M.A.J., Priority Assessment of Toxic Substances in the frame of LCA – draft, Institute for Biodiversity and Ecosystem Dynamics, Universiteit van Amsterdam, maart 2000.

[9] Huppes, G., M.D. Davidson, J. Kuyper, L. van Oers, H.A. Udo de Haes and G. Warringa, Eco-efficient environmental policy in oil and gas production in the Netherlands, Project for NOGEPA, Den Haag, 2002/2003

[10] Jantzen, J., Duurzame groei in Nederland? Het duurzaam Nationaal Inkomen onder Paars (1990-2000), Instituut voor Toegepaste Milieu-Economie (TME), juni 2002.

[11] KPMG Sustainability en CE. Duurzame winst! De milieuwinst van de Groenregeling inzichtelijk gemaakt. September 2002. http://www.kpmg.nl/docs/bas_sustainability_advisory_services/rapport%20duurzame%20winst%20kpmg%20en%20ce.pdf

[12] NIBE Research, Duurzaam & Gezond Bouwen, juli 2002

[13] Peirce, Martin, Haydn Jones, Neil R Passant, Mike Holland, 2002, Cost Curves for the Abatement of Heavy Metal, PAH and Dioxin Emissions, AEAT/R/ENV/0159 Issue 1

[14] Pearce, D.W. and A. Howarth, Technical report on methodology: Cost-benefit analysis and policy responses, RIVM report 481505020, May 2000

[15] RIVM, National annual environment report Milieubalans 2000

[16] Vogtländer, The model of the Eco-costs / Value Ratio. A new LCA based decision support tool. Thesis Delft University of Technology, Delft.

[17] VROM, National Environmental Policy Plan - NMP4

[18] Wagemaker et al., Waterverkenningen: een strategie voor de aanpak van microverontreinigingen in communaal afvalwater, RIZA 1999.

[19] Wit, R.C.N., et al., Schaduwprijzen Prioriteringsmethodiek voor Milieumaatregelen (SPM), CE, december 1997

F.6 Acknowledgments

The research project was commissioned by the Ministry of Transport, Public Works and Water Management and supervised by a steering committee consisting of L.J.E. Duijsens (chair, Civil Engineering Division), J.W. Broers (CED, Road and Hydraulic Engineering Institute) and G. Huppes (CML). The authors would like to thank the steering committee for their valuable input and discussions throughout the project.

G Questionnaire and accompanying letter

Return address: P.O. Box 342, 7300 AH Apeldoorn The Netherlands

Laan van Westenenk 501
P.O. Box 342
7300 AH Apeldoorn
The Netherlands

www.tno.nl

T +31 55 549 34 93
F +31 55 549 32 01
info@mep.tno.nl

Subject
Questionnaire environmental impact solvent production

Date
19 April 2005

Our reference
/36129/FER

E-mail
Paul.Feron@tno.nl

Direct dialling
+31 55 549 3151

Your reference
-

Enclosure(s)
Questionnaire

Copy to
-

Dear sir/madam,

At present, one of the most challenging environmental problems is the enhanced greenhouse effect as a result of the emissions of heat trapping gases, particularly CO_2, to the atmosphere. These emissions are mainly the result of the intensive use of fossil fuels, which adds large amounts of CO_2 to the earth's atmosphere. There does not seem to be a single and simple solution to this problem and a portfolio of possible solutions is suggested. In this portfolio, capture CO_2 and subsequent storage is rapidly gaining interest as an option which could be implemented on the medium term, allowing the continued use of fossil fuels. This is important as the use of fossil fuels is increasing at a steady rate, because they are still cheap and abundant. The leading technologies for CO_2 capture are based on solvent processes and the question has been posed whether the use of the solvent processes for CO_2-capture on a large scale, would in itself not lead to severely increased environmental burdens.

TNO has been commissioned by IEA-Greenhouse Gas R&D Programme to carry out an environmental evaluation of solvent scrubbing of CO_2. To be able to make an accurate inventory of environmental impacts, we require information on the solvent production and the solvent use, i.e. information on the energy requirements, emissions etc. As your company could be a major stakeholder in this rapidly developing area, we would like to ask you to provide us with some information according to templates enclosed in this letter. Also any additional supporting information would be very welcome. The enclosed questionnaire is intended to keep the efforts within your organisation limited.

Thank you in advance for your co-operation and should you need additional information please do no hesitate to contact us!

Yours sincerely,

Paul H.M. Feron TNO Science & Industry (paul.feron@tno.nl)

René van Gijlswijk TNO Quality of Environment (r.n.vangijlswijk@mep.tno.nl)

Questionnaire environmental impact of solvent processes for CO_2-capture

TNO, the Netherlands, April 2005

Introduction

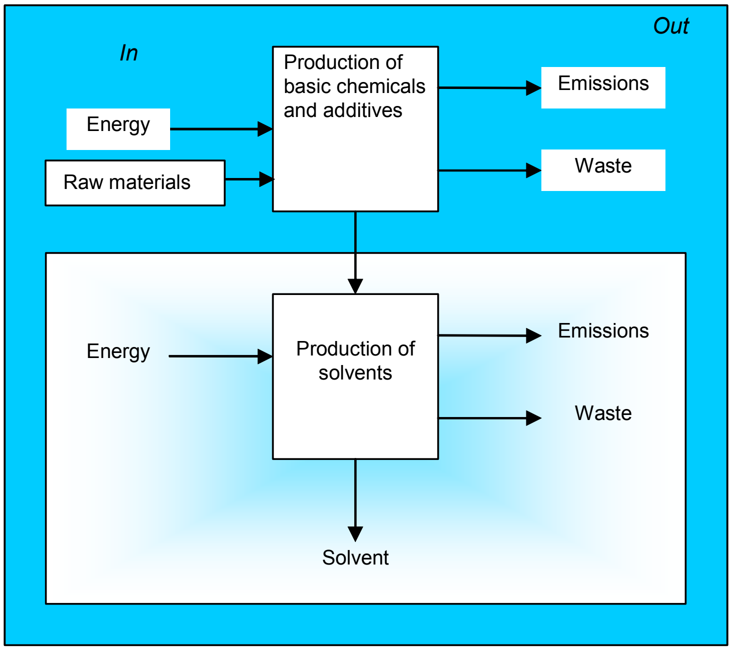
The capture of CO_2 from fossil fuel fired power plants can be realised in a so-called post-combustion operation or a pre-combustion operation. Post-combustion CO_2-capture entails separation from the flue gases from power stations. Pre-combustion CO_2-capture entails the capture of CO_2 from a converted fuel consisting of CO_2 and H_2. Both options will be considered in this study. Solvent processes are the leading processes to separate CO_2 in both capture routes. Their environmental impact both during the solvent production process as well as during their use in the capture process needs to be considered when CO_2-capture and storage is going to be employed on a large scale to prevent CO_2-emissions. This questionnaire is aimed at getting relevant data for a number of solvents and solvent processes. The next table shows an overview of the solvents and solvent processes.

Solvents for CO_2-capture.

Post-combustion	**Pre-combustion**	
Chemical solvents (in aqueous solution)	**Chemical solvents (in aqueous solution)**	**Physical solvents**
Mono-ethanolamine	Methyldiethanolamine	Methanol
Diglycolamine	Diethanolamine	Selexol
Amino-methyl-propanol	Diisopropanolamine	Propylene carbonate
Fluor Daniel Econamine FG	Piperazine	N-methylpyrrolidone
MHI KS-1 (proprietary)		
CANSOLV(proprietary)		

Generic description of production process of solvent

The diagram shown below gives a schematic overview of the production of a solvent. It is assumed that the produced solvent is ready for use for the capture of CO_2 from power plants.



From an environmental point of view each process has inputs (raw materials and fuels/electricity) and outputs (the product, emissions and waste). We ask you to provide us information on the highlighted part of the diagram: the production of the solvent itself. To make things easier and quicker for you, we have already collected information on in- and out-flows as shown in the diagram, and amounts. This may or may not make sense. Please check our suggestions, and correct if necessary. This would be of great help for our understanding. If you are not able to provide exact figures, please insert a rough figure or estimate.

Product composition
Please describe the contents of 1 kg of solvent in terms of type and concentration of the components;

- Active component (amines, solvents)
- Activators (mass transfer enhancers)
- corrosion inhibitors
- oxidative degradation inhibitors
- others

As already explained, it is assumed that the solvent is ready for use for the capture of CO_2 from power plants.

Production process
In this section we ask you to provide information about the following:

- a brief process description
- specification of utilities on your site
- processing data (subdivided into process sections whenever convenient)

We have already filled out some characteristics according to our present knowledge and estimates. This may or may not be in accordance with data from your production process. Please correct and/or add the information we have filled out. Note that we have expressed our data per kg of the active component. If it is more convenient for you, you may fill in the total energy consumption and/or emission data for your plant instead. In that case please clearly indicate the basis, i.e. the corresponding production rate of the active component and of course the proper units. The examples given are based on MEA, Selexol and MDEA and you are kindly requested to fill in the same form for other solvents you find believe are applicable.

Example: MEA

Process description:

Monoethanolamine is produced by the exothermic reaction of ammonia with ethylene oxide over a catalyst. A mixture is obtained of mono-, di- and triethanolamine. The product mixture is separated by a number of distillation columns. Unconverted reactants are recycled to the reactor.

For our inventory we would like to know the product distribution, energy usage and emissions, expressed per unit mass of MEA. For MEA a second step, dealing with the solvent formulation is also included, as the solvents are used with inhibitors to prevent oxidative degradation and corrosion.

Utilities

Gas	Caloric value:	35 MJ/Nm^3
Steam	Pressure:	5 bar
	Temperature	160°C
	Source:	Steam boiler / waste steam
Electricity	Source:	Produced on-site (combined cycle)
Cooling water	Source:	Surface water

Process data

A. Reactor and distillation section

In		suggest.	correct.
Raw materials	Ethylene oxide	1.0 kg	
	Ammonia	0.30 kg	
Utilities	Natural gas	0.06 Nm^3	Nm^3
	Electricity	0.33 kWh	kWh
	Steam	0.6 kg	kg
	Cooling water	0.04 m^3	m^3
	Fuel oil	0 kg	

Out		suggest.	correct.
Products	MEA	1.0 kg	
	DEA	0.20 kg	
	TEA	0.10 kg	
Emissions to air	Ethylene oxide	0 kg	
	Ammonia	0.002 kg	
	CO_2	0.027 kg	
	MEA	0 kg	
	DEA	0 kg	
	TEA	0 kg	
Wastes	Catalyst (type:……)	0.001 kg	

B. Formulation of solvent

In		**suggest.**	**correct.**
Raw materials	MEA	0.98 kg	
	Oxidative degradation inhibitor (type:…….)	0.01 kg	
	Corrosion inhibitor (type:…….)	0.01 kg	
Utilitities	Natural gas	0 Nm^3	
	Electricity	0.01 kWh	
	Steam	0 kg	
	Cooling water	0 m^3	

Out		**suggest.**	**correct.**
Products	MEA based solvent	1.0 kg	
Emissions			
Wastes			

Example: Selexol

Process description

Ethylene glycol is reacted with ethylene oxide over a catalyst to obtain polyethylene glycol (PEG). The product is reacted with methanol to obtain the dimethyl ether.

Utilities

Gas	Caloric value:	35 MJ/Nm^3
Steam	Pressure:	5 bar
	Temperature	150^{o}C
	Source:	Steam boiler / waste steam
Electricity	Source:	Produced on-site (combined cycle)
Cooling water	Source:	Surface water

Production of Selexol solvent (polyglycol dimethylether)

In		suggest.	correct.
Raw materials	Ethylene oxide	0.75 kg	
	Methanol?	0.20 kg	
	Water	0.05 kg	
Utilities	Natural gas	0.05 Nm^3	Nm^3
	Electricity	0.3 kWh	kWh
	Steam	? kg	kg
	Cooling water	? m^3	m^3

Out		suggest.	correct.
Products	Polyglycol DME	1.0 kg	
Emissions to air	Ethylene oxide	$1*10^{-4}$ kg	
	Methanol	$1*10^{-4}$ kg	
Emissions to water			
Wastes	Catalyst (type:….)	$1*10^{-4}$ kg	

Example: MDEA

Process description

MDEA is produced from the reaction between mono-methylamine (MMA) and ethylene oxide. Mono-methylamine is produced from the reaction between ammonia and methanol. This yields a mixture of mono-, di- and trimethylamine, which is separated in a series of distillation columns. Unconverted reactants are recycled to the reactor.

Utilities

Gas	Caloric value:	35 MJ/Nm^3
Steam	Pressure:	5 bar
	Temperature	150°C
	Source:	Steam boiler / waste steam
Electricity	Source:	Produced on-site (combined cycle)
Cooling water	Source:	Surface water

A. Step 1: Production of MMA (reaction and distillation)

In		suggest.	correct.
Raw materials	Methanol	1.5 kg	
	Ammonia	0.65 kg	
Utilities	Natural gas	0.05 Nm^3	Nm^3
	Electricity	0.33 kWh	kWh
	Steam	0.5 kg	Kg
	Cooling water	0.03 m^3	m^3

Out		suggest.	correct.
Products	MMA	1.0 kg	
	DMA	0.20 kg	
	TMA	0.105 kg	
	Water	0.85 kg	
Emissions to air	Methanol	$1*10^{-4}$ kg	
	Ammonia	$1*10^{-4}$ kg	
	MMA	0 kg	
Emissions to water			
Wastes			

Step 2: Production of MDEA

In		suggest.	correct.
Raw materials	Ethylene oxide	0.80 kg	
	MMA	0.30 kg	
Utilities	Natural gas	0 Nm^3	Nm^3
	Electricity	0.33 kWh	kWh
	Steam	0.1 kg	kg
	Cooling water	0.02 m^3	m^3

Out		suggest.	correct.
Products	MDEA	1.0 kg	
	MMEA	0.1 kg	
Emissions to air	MMA		
	Ethylene oxide		
Emissions to water			
Wastes	Catalyst (type:…..)	$1*10^{-4}$ kg	

Use of solvents

In the CO_2 capture process, solvent is lost through emissions to air and water and the CO_2-product and emissions of decomposition products to air and water. In some circumstances (particularly MEA) the solvent solutions contain degradation and corrosion inhibitors. These might end-up in the solid wastes. Please specify the decomposition products, if known, and the amount emitted to air and water.

Utilities

Gas	Caloric value:	35 MJ/Nm^3
Steam	Pressure:	5 bar
	Temperature:	150°C
	Source:	Steam boiler / waste steam
Electricity	Source:	Produced on-site (combined cycle)
Cooling water	Source:	Surface water

Use of solvent

In		suggest.	correct.
Raw materials	Solvent	1.5 kg	kg
	Activated carbon	0.075 kg	
	Sodium hydroxide	kg	
Utilities	Thermal energy	4200 kJ	kg
	Electricity	80	kWh
	Cooling water	160	m^3

Out		suggest.	correct.
Products	CO_2 captured	1000 kg	
Emissions to air	Solvent		kg
	Solvent degeneration products		kg
Emissions to water	Solvent		kg
	Solvent degeneration products		kg
Wastes	Solvent loss in CO_2		kg
	Decomposition products		
	Corrosion inhibitor		

H Solvent degradation and wastes

Solvent degradation in post-combustion CO_2 capture

The presence of oxygen in flue gases and the large volumes of flue gases being contacted with the solvent make degradation in post-combustion capture an issue of importance. Unlike other applications of solvent processes, in case of post-combustion capture a large amount of gases is more or less discharged directly into the environment and this inevitably puts a stringent limitation on the quality of the discharged gases. Beside oxygen, also impurities like SO_2 and NO_x might result in increased solvent degradation. Furthermore, the presence of metals like iron or cupper catalyses degradation reactions in the solvents.

Impact of SO_2

SO_2 is expected to react with the alkaline ethanolamine solutions in a way that is similar to the reaction with CO_2. Amine solution analysis of an operational CO_2-production plant based on MEA using a flue gas from coal firing (CO_2-content: 10-15%, O_2-content: 5-10%) indicates that more than 95% of the sulphur present in the solvent is in the sulphate form [H1]. The reaction with SO_2 results in a loss of absorption capacity for CO_2. As an example the MEA-consumption as a result of the reaction with SO_2 has been assessed using the flue gas from coal firing as given in H2. The SO_2 content in the flue gas has been taken as the parameter. It is assumed that one mole of SO_2 reacts with two mole of MEA [H1, H3] and that all of the SO_2 is removed from the flue gas.

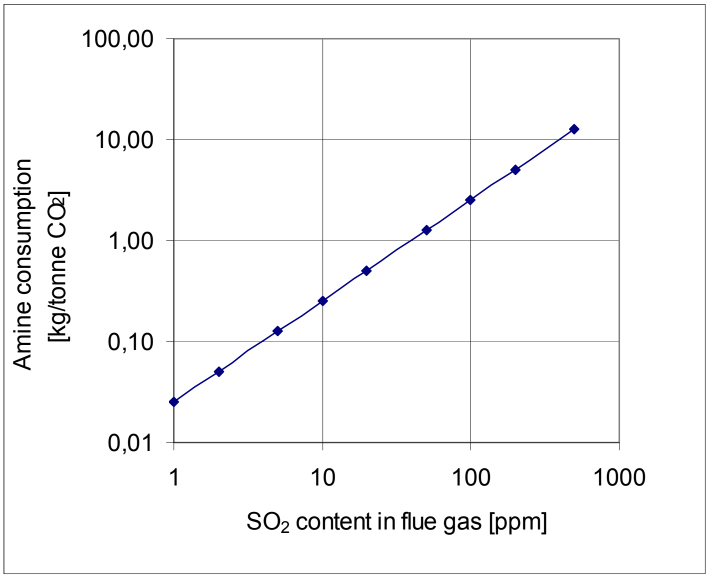


Figure H1 *Specific MEA-consumption due the reaction with SO_2 as a function of SO_2-content in the flue gas (flue gas flow rate: 710 Nm^3/s, 547 tonne CO_2/h, 85% CO_2 capture).*

The results in figure H.1 show that the consumption of MEA is around 2.5 kg MEA/tonne CO_2 at an SO_2-content of 100 ppm and 0.25 kg MEA/tonne CO_2 at a SO_2-content of 10 ppm. Bearing in mind that the MEA consumption quoted for the Fluor Econamine FG Plus^{SM} is 1.6 kg MEA/tonne CO_2, the estimates explain why the allowable is preferable below 10 ppm. However, this must be regarded as a worst case. In fact the solution can also be treated by the addition sodium carbonate or sodium hydroxide, followed by a reclaiming operation in which the MEA is made available for reuse [H1]. The SO_2 will end up as sulphate in the reclaimer bottoms product. The consumption of MEA is then replaced by an equimolar amount of alkaline salts, which have a lesser environmental impact.

Degradation of MEA solutions

The degradation of MEA in service for CO_2-separation in oxidative environments is a well-recognised issue. It usually manifests itself through darkening of the solution and the presence of ammonia in off-gases. As for instance MEA is used for life support applications (e.g. submarines), this has been investigated since the early 1950's. The complicated interactions between solvent degradation and corrosion are still not fully understood. However formulated solvents, incorporating solution stabilisers, have been developed. For instance a chelating agent (US patent 3,137,654, 16 June 1964) or a copper based salt (US patent 4,440731, 3 April 1984) are proposed to limit the corrosion of MEA-based solutions.

In H4 an overview of degradation studies as well as a detailed experimentally based analysis of MEA solution degradation is presented in situations where only oxygen is present, situations where only carbon dioxide is present and situation with the combination of both gases. The conclusion of the degradation studies overview is that previous studies have been limited as they focused on particular pathways. Therefore a more comprehensive study was needed, starting with the execution of degradation under controlled conditions. These degradation experiments have been carried out at temperatures typical of regeneration conditions but at elevated O_2 pressures (2.5 and 3.5 bar) in an effort to mimic the solvent composition after prolonged exposure to oxygen. As such the results in H4 present a catalogue of reaction mechanisms and pathways, which is useful for further research. The products found in the solutions are not only direct degradation products of MEA but also include reactions between MEA and the direct degradation products, between CO_2 or O_2 and the reaction products and between reaction products themselves. The reaction mechanisms and pathways are not only influenced by the temperature level, as might be expected, but also by the oxygen partial pressure and the MEA-concentration. The authors recognise that the addition of sodium hydroxide or carbonate to the solution, prior to a reclaiming operation might further influence the type reaction products. It is suggested here that the presences of reactive trace components in the flue gas might even lead to other degradations pathways. Some of the main conclusions of the analysis in H4 are:

- A higher MEA concentration might actually reduce degradation due to the lower O_2-solubility
- The degradation mechanisms in case of MEA for situations with O_2 only, CO_2 and the combination appear to be quite different
- The presence of CO_2 in the process leads to a lower extent of the degradation compared to the situation where only O_2 is present.

In H5 the oxidative degradation of MEA solutions was analysed using the rate evolution of NH_3 as the measuring method. Several reaction pathways were proposed allowing an estimate for the O_2 stoichiometry. Experiments were carried out at temperatures representative of absorber conditions (55 °C). Also data from other authors was analysed. It appeared that degradation by O_2 was faster with at lower CO_2-loadings and that it was likely that degradation is mass transfer limited. This allowed an estimate for the degradation of MEA-solutions for a gas stream containing 3% CO_2 and 5% O_2, which was in the range 0.29 – 0.73 kg MEA/tonne CO_2.

Solvent consumption: Plant data and manufacturer's data

The operation of several of commercial CO_2-production plants has been documented in several publications in the 1980's. Also results on solvent consumption have been presented. In H1 a solvent consumption of 3.6 kg/tonne CO_2 was the average recorded value for a process using an 18-20% MEA solution producing CO_2 from a coal fired boiler flue gas. In H6 solvent consumption varied between 1.5 kg/tonne CO_2 and 7.5 kg/tonne CO_2 for a process using a 30% MEA solution, recovering CO_2 from a flue gas from gas firing. The high values were recorded when the plant was experiencing corrosion and degradation problems, which were subsequently resolved by process improvements. It was estimated that 60% of the solvent loss was through evaporation and that through further optimisation of the washing section these losses could be reduced. These references are rather dated and recent data in the open literature show a much reduced solvent consumption of 1.6 kg/tonne CO_2 [H2].

Formation of wastes: Manufacturer's data

Several studies have been based on data supplied by Fluor. In H7, the capture of CO_2 from eleven gas turbines used in an Alaskan gas processing facility is studied for the Econamine FG^{SM} process. The amount of reclaimer waste produced is estimated to be 2.8 kg/tonne CO_2. In a more recent study [H8], based on the Econamine FG Plus^{SM} technology employed for CO_2 capture from a large combined cycle power plant, the amount of wastes produced is estimated to be 1.1 kg/tonne CO_2.

Reclaimer waste composition and emissions to air

Wastes from the reclaimer are usually aqueous sludges contain the amine itself, amine degradation products (organic salts etc.) and inorganic materials (corrosion products, flue gas components, etc.). Table H.1 shows the degradation products for the FLUOR Econamine FG Plus^{SM} process as quoted in two separate publications.

Only the results given in reference H8 give a complete description of the reclaimer waste composition. The waste production estimates in the two references are different by a factor of 2.8, which is quite a large variation.

Table H.1 Reclaimer waste composition and emissions to air from the FLUOR Econamine FG Plus^{SM}.

Reference	**H8**	**H2**
Amount	1.13 kg/tonne CO_2	3.2 kg/tonne CO_2
Composition		
MEA	15 %(wt)	6000 ppm
Water	7 % (wt)	33.9 % (vol)
MEA degradation products	75 % (wt)	-
Inorganic residues	3 % (wt)	-
Cr	-	< 2 ppm
Cu	-	855 ppm
Fe	-	129 ppm
Ni	-	< 2 ppm
Na	-	7500 ppm
Emissions to air	0.2 ppm MEA +23 ppm NH_3	1 ppm MEA

Mitsubishi Heavy Industries have also supplied data for their reclaimer waste composition and emission to the air of a capture plant using the KS-1 solvent [H9]. The composition is given in table H.2 for CO_2 capture from a flue gas from a natural gas fired combined cycle (NGCC) and from a flue gas from coal firing (USCPF).

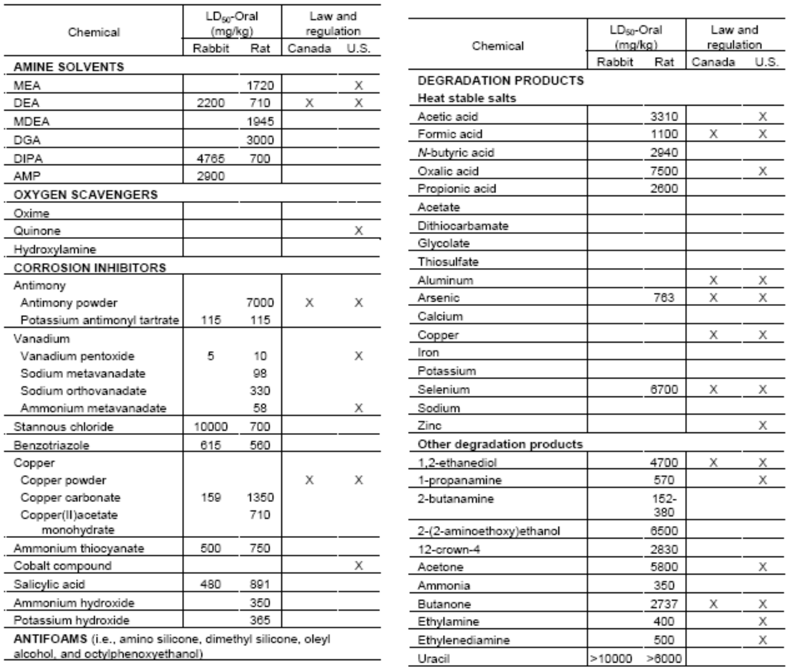
Table H.2 Reclaimer waste composition and emissions to air from MHI's KS-1 process.

Power plant	**USCPF**	**NGCC**
Amount	0.086 kg/tonne CO_2	0.085 kg/tonne CO_2
Composition		
KS-1 + water	50.0 %(wt)	50.0 %(wt)
$Na_2C_2O_4$	5.3 % (wt)	4.9 % (wt)
Na_2SO_4	15.0 % (wt)	0.0 % (wt)
$NaNO_3$	3.0 % (wt)	10.0 % (wt)
Na_2CO_3	17.0 % (wt)	10.0 % (wt)
Neutral heat stable salts	9.7 % (wt)	25.1 % (wt)
Emissions to air	3.4 ppm Amine + NH_3	2.15 ppm Amine + NH_3

In H10 et. al. the results of an investigation into the nature of compounds present in the reclaimer bottoms of a commercial CO_2 capture plant based on MEA are presented. Apart from MEA and ammonia a further 17 other organic components were found to be present. Some of these were not identified previously as MEA degradation products. Although some organic acids (acetic acid, propionic acid) were identified these were not the main components. Some reaction pathways involving these acids and MEA were, however, suggested. Nitrosamines, known carcinogenics were found in the lean solutions but not in the reclaimer bottom product. They were believed to be the result of a reaction between MEA and nitrogen oxides. Also several inorganic salts were identified. Sodium was found as expected, because sodium carbonate is added as to chemically regenerate MEA. The anions found in the reclaimer bottom were halogens (present in the fuel) and nitrate and sulphate (as a result of interaction with nitrogen en sulphur oxides present in the flue gas). The authors also point out that some of these products might have been formed due to the reclaiming process rather than the stripping process.

There is a growing interest in the assessment of the environmental impact of solvent scrubbing processes. Recent work at the University of Regina [H11] addressed this in detail compiling a list of solvents and their toxicity indices. This list also included components which are likely to be included in solvent formulations such as oxygen scavengers, corrosion inhibitors and antifoams. In addition a list of possible degradation products was given. For all chemicals it was assessed whether or not there was US or Canadian law regulating the emission control. The list is reproduced in table H.3.

Table H.3 Summary of chemicals present in CO_2 capture unit and their toxicity indices [H11].



Chemical	LD_{50}-Oral (mg/kg)		Law and regulation	
	Rabbit	Rat	Canada	U.S.
AMINE SOLVENTS				
MEA		1720		X
DEA	2200	710	X	X
MDEA		1945		
DGA		3000		
DIPA	4765	700		
AMP	2900			
OXYGEN SCAVENGERS				
Oxime				
Quinone				X
Hydroxylamine				
CORROSION INHIBITORS				
Antimony				
Antimony powder		7000	X	X
Potassium antimonyl tartrate	115	115		
Vanadium				
Vanadium pentoxide	5	10		X
Sodium metavanadate		98		
Sodium orthovanadate		330		
Ammonium metavanadate		58		X
Stannous chloride	10000	700		
Benzotriazole	615	560		
Copper				
Copper powder			X	X
Copper carbonate	159	1350		
Copper(II)acetate monohydrate		710		
Ammonium thiocyanate	500	750		
Cobalt compound				X
Salicylic acid	480	891		
Ammonium hydroxide		350		
Potassium hydroxide		365		
ANTIFOAMS (i.e., amino silicone, dimethyl silicone, oleyl alcohol, and octylphenoxyethanol)				
DEGRADATION PRODUCTS				
Heat stable salts				
Acetic acid		3310		X
Formic acid		1100	X	X
N-butyric acid		2940		
Oxalic acid		7500		X
Propionic acid		2600		
Acetate				
Dithiocarbamate				
Glycolate				
Thiosulfate				
Aluminum			X	X
Arsenic		763	X	X
Calcium				
Copper			X	X
Iron				
Potassium				
Selenium		6700	X	X
Sodium				
Zinc				X
Other degradation products				
1,2-ethanediol		4700	X	X
1-propanamine		570		X
2-butanamine		152-380		
2-(2-aminoethoxy)ethanol		6500		
12-crown-4		2830		
Acetone		5800		X
Ammonia		350		
Butanone		2737	X	X
Ethylamine		400		X
Ethylenediamine		500		X
Uracil	>10000	>6000		

In follow-up work submitted for publication [H12] the list is elaborated upon and physical solvents are also added. The draft publication also contains a list of heat stable salts found in amine treating units in refineries using MDEA or DEA. The conditions might be considered to be typical of pre-combustion capture solvent processes and lead to the presence of acetate, formate, glycolate, oxalate, sulphate, thiosulphate and thiocyanate.

The authors of H12 have also performed a case study to determine the amount of solvent waste and its composition for CO_2 capture from a coal fired power plant using a 30% MEA solution. It was assumed that the 0.5% - 2% of the solvent stream was fed to the reclaimer and that the heat stable salts amounted to 10% of the MEA concentration. The amount of waste produced from the reclaimer was calculated to be 3.7 kg/tonne CO_2 for a slip stream of 0.5% and 14.9 kg/tonne CO_2 for a slip stream of 2%. These figures are higher than those quoted by vendors [H2, H8].

References

H1 Arnold. D.S., D.A. Barrett, R.H. Isom, CO_2 production from coal-fired boiler flue gas by MEA process, presented at the 1982 Gas Conditioning Conference, Oklahoma

H2 IEA GHG R&D programme Report Number PH4/33, Improvement in power generation with post-combustion capture of CO_2, November 2004

H3 Kwong, K.V., R.E. Meissner III, S. Ahmad, C.J. Wendt, Application of amines for treating flue gas from coal-fired power plants, Environmental Progress (Vol. 10, No.3), pp. 211-215, August 1991

H4 Bello, A., R.O. Idem, Pathways for the Formation of Products of the Oxidative Degradation of CO_2-loaded Concentrated Aqueous Monoethanolamine Solutions during CO_2 Absorption from Flue Gases, Ind. Eng. Chem. 2005, 44, 945-969

H5 Goff, G.S, G.T. Rochelle, Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions, Ind. Eng. Chem. Res. 2004, 43, pp 6400-6408

H6 Pauley, C.R., P.L. Simiskey, S. Haigh, CO_2 recovery from flue gas: a case study, presented at the 1984 Gas Conditioning Conference, Oklahoma

H7 Simmonds, M., P. Hurst, M.B. Wilkinson, S. Reddy, S. Khambaty, Amine based CO_2 capture from gas turbines, paper presented at the Second Annual Conference on Carbon Sequestration, May 2003

H8 Fluor-Statoil, Study and estimate for CO_2 capture facilities for the proposed 800 MW Combined Cycle Power Plant – Tjeldbergodden, Norway, April 2005

H9 Email Masaki Iijima, Mitsubishi Heavy Industries, 17 June 2005

H10 Strazisar, B.R., R.R. Anderson, C.M. White, Degradation Pathways for Monethanolamine in a CO_2 capture facility, Energy & Fuels 2003, 17, 1034-1039

H11 Thitakamol, B., A. Veawab, A. Aroonwilas, Environmental impacts of the integration of CO_2 capture unit into coal-fired power plants, paper presented at GHGT-8, Trondheim, June 2006 (available via www.ghgt8.no)

H12 Thitakamol, B., A. Veawab, A. Aroonwilas, Environmental impacts of absorption based CO_2 capture unit for post-combustion treatment of flue gas from coal-fired power plant, submitted to Journal of Environmental Science and Technology, July 2006

I Toxicity potentials for Monoethanolamine, Diethanolamine, Triethanolamine, Di-isopropylamine, Sulfolane and Methanol

Mark A. J. Huijbregts
September 2005

Department of Environmental Science
Faculty of Sciences
Radboud University Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
Tel: +31 24 3652835
Fax: + 31 24 3653030
Email: M.Huijbregts@science.ru.nl

I.1 Introduction

Toxicity potentials are substance-specific, quantitative representations of potential impacts per unit emission of a toxic substance. In environmental life cycle assessments of products (LCAs), these potentials are used as weighting factors to determine the relative contribution of a substance to toxicity related impact categories, such as human toxicity. Huijbregts et al. (2000) calculated toxicity potentials for 181 substances with the global nested multi-media fate, exposure and effects model USES-LCA, which is based on the Uniform System for the Evaluation of Substances 2.0 (USES 2.0), developed by RIVM et al. (1998). Toxicity potentials were calculated for the six impact categories fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, fresh water sediment ecotoxicity, marine sediment ecotoxicity, terrestrial ecotoxicity and human toxicity, after initial emission to the compartments air, fresh water, seawater, industrial soil and agricultural soil, respectively. This report presents toxicity potentials for for Monoethanolamine, Diethanolamine, Triethanolamine, Di-isopropylamine, Sulfolane and Methanol, including potential impacts on the continental and global scale over an infinite time horizon.

I.2 Data input

Substance-independent data are given in Huijbregts (1999). Appendix A shows an overview of the substance-specific data used in the current calculation. Molecular weight, octanol-water partition coefficient (K_{ow}), melting point, water solubility and vapour pressure are needed as physico-chemical input parameters in USES-LCA. Experimental data were taken from US-EPA (2000). Degradation rates for all environmental compartments were derived from Quantitative Structure Activity Relationships (QSARs), following US-EPA (2000).

For the effect assessment, a Human Limit Value (HLV) or a Predicted No-Effect Concentration (PNEC), corresponding with each of the targets of protection, is required. The oral HLV of methanol was obtained from the IRIS-database (USEPA, 2005), while the oral and inhalatory HLV of diethanolamine were taken from the database of Scorecard (EDF, 2005). For monoethanolamine and triethanolamine no HLVs were found in the literature. Instead, an oral HLV of monoethanolamine was derived by dividing the chronic NOEL-value of 22 $mg.kg^{-1}.day^{-1}$ for dogs, given by Knaak et al. (1997), by a factor of 100 to account for intra- and interspecies differences. The oral HLV of triethanolamine was derived by dividing the subacute NOEL-value of 5 $mg.kg^{-1}.day^{-1}$ for rats, given by Knaak et al. (1997), by a factor of 1000 to account for intra- and interspecies differences and short exposure duration. For Diisopropylamine and Sulfolane no suitable toxicological data were found for the derivation of human HLVs.

The freshwater aquatic PNECs were derived using toxicity data from the ECOTOX database (USEPA, 2005):

- For Monoethanolamine, the LOEC of green algae (0.9 mg/l) was divided by a safety factor of 100;
- For Diethanolamine, the NOEC of the water flea (3.2 mg/l) was divided by a safety factor of 10;
- For Triethanolamine, the NOEC of the water flea (16 mg/l) was divided by a safety factor of 100
- For Di-isopropylamine, the EC50 of blue-green algae (4.2 mg/l) was divided by a safety factor of 1000;
- For Sulfolane, the LC50 for gold fish (820 mg/l) was divided by a safety factor of 1000. Note that no other toxicity values were found for this chemical;
- For Methanol, the LOEC for rainbow trout (120 mg/l) was divided by a safety factor of 20.

The PNECs for the marine aquatic environment were set equal to the PNECs derived for the freshwater environment. The PNECs for the terrestrial and sediment environment were derived using the equilibrium partitioning method.

I.3 Toxicity potentials

Table I.1 lists the toxicity potentials of Monoethanolamine, Diethanolamine, Triethanolamine, Di-isopropylamine, Sulfolane and Methanol.

Table I.1 *Toxicity potentials of Monoethanolamine, Diethanolamine, Triethanolamine, Di-isopropylamine, Sulfolane and Methanol (in kg 1,4-Dichlorobenzene equivalents).*

Substance	**Type**	**Initial emission compartment**				
		air	**fresh water**	**sea water**	**agricult. soil**	**industrial soil**
Monoethanolamine	FAETP	3.7E+00	5.7E+01	8.4E-06	6.1E+00	1.2E+01
	MAETP	3.9E-01	3.3E-02	1.1E+00	6.1E-03	1.2E-02
	FSETP	2.4E+00	3.7E+01	5.4E-06	4.0E+00	7.8E+00
	MSETP	4.8E-01	4.3E-02	1.5E+00	7.8E-03	1.5E-02
	TETP	7.0E-01	1.0E-04	1.6E-06	2.8E+00	2.0E+00
	HTP	6.4E-01	2.1E-02	5.4E-06	3.4E+00	1.3E-02
Diethanolamine	FAETP	1.7E-01	1.6E+00	4.0E-10	1.7E-01	3.4E-01
	MAETP	1.6E-02	9.3E-04	3.2E-02	1.0E-04	2.0E-04
	FSETP	1.1E-01	1.0E+00	2.6E-10	1.1E-01	2.2E-01
	MSETP	2.1E-02	1.2E-03	4.1E-02	1.3E-04	2.5E-04
	TETP	3.1E-02	5.4E-09	7.4E-11	7.8E-02	5.8E-02
	HTP	1.4E+02	3.3E+00	6.3E-04	1.1E+03	7.3E-01
Triethanolamine	FAETP	1.4E+00	1.1E+01	1.1E-10	2.5E+00	2.5E+00
	MAETP	1.2E-01	2.5E-02	2.4E-01	5.4E-03	5.4E-03
	FSETP	1.0E+00	8.6E+00	8.7E-11	1.9E+00	1.9E+00
	MSETP	1.9E-01	3.7E-02	3.7E-01	8.1E-03	8.1E-03
	TETP	2.0E-01	2.0E-09	1.7E-11	4.2E-01	4.2E-01
	HTP	8.3E+01	3.3E+00	6.6E-04	6.1E+02	7.2E-01
Di-isopropylamine	FAETP	6.3E-02	1.9E+02	1.3E-03	1.7E+01	2.1E+01
	MAETP	9.9E-02	4.6E-01	9.1E+00	6.1E-02	7.3E-02
	FSETP	4.7E-02	1.4E+02	9.9E-04	1.3E+01	1.6E+01
	MSETP	1.4E-01	6.7E-01	1.3E+01	8.8E-02	1.1E-01
	TETP	7.1E-04	4.0E-04	1.5E-05	5.1E+00	4.5E+00
	HTP	?	?	?	?	?
Sulfolane	FAETP	2.6E-01	2.2E+00	1.5E-07	4.8E-01	4.8E-01
	MAETP	2.4E-02	4.8E-03	4.8E-02	1.1E-03	1.1E-03
	FSETP	2.0E-01	1.7E+00	1.1E-07	3.7E-01	3.7E-01
	MSETP	3.6E-02	7.2E-03	7.1E-02	1.7E-03	1.7E-03
	TETP	3.8E-02	1.3E-06	2.2E-08	8.0E-02	8.0E-02
	HTP	?	?	?	?	?
Methanol	FAETP	1.6E-03	8.4E-02	4.9E-07	8.7E-03	1.7E-02
	MAETP	1.3E-03	7.5E-05	1.7E-03	3.3E-05	6.3E-05
	FSETP	1.0E-03	5.5E-02	3.2E-07	5.6E-03	1.1E-02
	MSETP	9.3E-04	8.1E-05	2.2E-03	2.6E-05	5.0E-05
	TETP	3.4E-04	6.7E-06	1.1E-07	4.0E-03	3.0E-03
	HTP	1.3E-01	1.2E-02	4.2E-05	1.2E+00	7.0E-03

FAETP = Fresh water Aquatic EcoToxicity Potential; MAETP = Marine Aquatic EcoToxicity Potential; FSETP = Fresh water Sediment EcoToxicity Potential; MSETP = Marine Sediment EcoToxicity Potential; TETP = Terrestrial EcoToxicity Potential; HTP = Human Toxicity Potential.

I.4 Literature

Environmental Defense Fund. 2005. Risk Assessment Values for Diethanolamine. Visited on 10-9-2005. www.scorecard.org

Huijbregts MAJ. 1999. Priority Assessment of Toxic Substances in the frame of LCA. Development and application of the multi-media fate, exposure and effect model USES-LCA. IDES, University of Amsterdam, Amsterdam.

Huijbregts MAJ, Thissen U, Guinée JB, Jager T, Van de Meent D, Ragas AMJ, Wegener Sleeswijk A, Reijnders L. 2000. Priority assessment of toxic substances in life cycle assessment, I: Calculation of toxicity potentials for 181 substances with the nested multi-media fate, exposure and effects model USES-LCA. Chemosphere 41: 541-573.

Knaak JB, Leung H-W, Stott WT, Busch J, Bilsky J. 1997. Toxicology of mono-, di-, and triethanolamine. Reviews of Environmental Contamination and Toxicology 149: 1-86.

RIVM, VROM, VWS, 1998. Uniform System for the Evaluation of Substances 2.0 (USES 2.0). RIVM report no. 679102044. National Institute of Public Health and the Environment (RIVM), Ministry of Housing, Spatial Planning and the Environment (VROM), Ministry of Health, Welfare and Sport (VWS), The Hague.

US-EPA, 2000. EPI Suite. Office of Pollution Prevention Toxics and Syracuse Research Corporation, United States.

US-EPA, 2005. IRIS database. RfD of Methanol. Visited on 10-9-2005. www.epa.gov/iris.

US-EPA, 2005. ECOTOX database. Toxicity data of Monoethanolamine, Diethanolamine, Triethanolamine, Di-isopropylamine, Sulfolane and Methanol. Visited on 11-9-2005. www.epa.gov/ecotox.

I.5 Substance-specific input data

Compound name	Unit	monoethanol-amine	iethanol-amine	triethanol-amine	diisopropyl-amine	sulfolane	methanol
CAS nr.	**-**	**141-43-5**	**111-42-2**	**102-71-6**	**108-18-9**	**126-33-0**	**67-56-1**
Effects assessment							
oral Human Limit Value	$mg.kg_{bw}^{-1}.d^{-1}$	0.22	0.0014	0.005			0.5
inhalation Human Limit Value	$\mu g.m^{-3}$		3				
aquatic Predicted No Effect Concentration	$ug.l^{-1}$	9	320	160	4.2	820	6000
Physico-chemical properties							
molecular weight	$g.mol^{-1}$	61.1	105.1	149.2	101.2	120.2	32.0
logKow	-	-1.31	-1.43	-1.00	1.40	-0.77	-0.77
melting point	°C	10.5	28.8	20.5	-61	27.6	-97.6
vapor pressure (25 °C)	Pa	53.9	$3.7.10^{-2}$	$4.8.10^{-4}$	$1.1.10^{4}$	$8.3.10^{-1}$	$1.7.10^{4}$
solubility (25 °C)	$mg.l^{-1}$	1.10^{6}	1.10^{6}	1.10^{6}	$1.1.10^{5}$	$4.6.10^{5}$	1.10^{6}
Henry's law constant	$Pa.m^{3}.mol^{-1}$				9.7		0.45
pKa	-	9.5	8.9	7.9			
Degradation rates							
Reaction rate in air	d	0.45	0.17	0.15	0.15	1.2	26.1
Reaction rate in surface water	d	2.3	2.3	8.7	8.7	8.7	2.3
Reaction rate in soil	d	4.6	4.6	17.3	17.3	17.3	4.6
Reaction rate in the aerobic sediment zone	d	4.6	4.6	17.3	17.3	17.3	4.6
Reaction rate in the anaerobic sediment zone	d	20.7	20.7	78.3	78.3	78.3	20.7

J Toxicity potentials for Methyldiethanolamine and Aminomethylpropanol

Mark A. J. Huijbregts

November 2005

Department of Environmental Science
Faculty of Sciences
Radboud University Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
Tel: +31 24 3652835
Fax: + 31 24 3653030
Email: M.Huijbregts@science.ru.nl

J.1 Introduction

Toxicity potentials are substance-specific, quantitative representations of potential impacts per unit emission of a toxic substance. In environmental life cycle assessments of products (LCAs), these potentials are used as weighting factors to determine the relative contribution of a substance to toxicity related impact categories, such as human toxicity. Huijbregts et al. (2000) calculated toxicity potentials for 181 substances with the global nested multi-media fate, exposure and effects model USES-LCA, which is based on the Uniform System for the Evaluation of Substances 2.0 (USES 2.0), developed by RIVM et al. (1998). Toxicity potentials were calculated for the six impact categories fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, fresh water sediment ecotoxicity, marine sediment ecotoxicity, terrestrial ecotoxicity and human toxicity, after initial emission to the compartments air, fresh water, seawater, industrial soil and agricultural soil, respectively. This report presents toxicity potentials for the aliphatic amines Methyldiethanolamine and Aminomethylpropanol, including potential impacts on the continental and global scale over an infinite time horizon.

J.2 Data input

Substance-independent data are given in Huijbregts (1999). Appendix A shows an overview of the substance-specific data used in the current calculation. Molecular weight, octanol-water partition coefficient (K_{ow}), melting point, water solubility and vapour pressure are needed as physico-chemical input parameters in USES-LCA. Data were taken from US-EPA (2000). Degradation rates for all environmental compartments were derived from Quantitative Structure Activity Relationships (QSARs), following US-EPA (2000).

For the effect assessment, a Human Limit Value (HLV) or a Predicted No-Effect Concentration (PNEC), corresponding with each of the targets of protection, is required. For Methyldiethanolamine and Aminomethylpropanol no HLVs were found in the literature. A preliminary inhalatory HLV of Aminomethylpropanol was derived by dividing the subchronic NOEC-value, corrected for discontinuous exposure duration, of 27 $\mu g.m^{-3}$ for rats (derived from Liebert, 1990) by a factor of 1000. The assessment factor of 1000 was used to account for intra- and interspecies differences and short exposure duration. The preliminary oral HLV of Aminomethylpropanol was derived by dividing the subchronic NOEL-value of 0.4 $mg.kg^{-1}.day^{-1}$ for dogs (derived from Liebert, 1990) by a factor of 1000. The assessment factor of 1000 was used to account for intra- and interspecies differences and short exposure duration. For Methyldiethanolamine, no toxicity data for mammals were found.

The freshwater aquatic PNECs were derived using ecotoxicololgical QSAR-estimates for aliphatic amines as specified by USEPA (2000):

- For Methyldiethanolamine, the estimated NOEC of green algae (15.1 mg/l) was divided by a safety factor of 100;
- For Aminomethylpropanol, the estimated NOEC of green algae (6.3 mg/l) was divided by a safety factor of 100;

The PNECs for the marine aquatic environment were set equal to the PNECs derived for the freshwater environment. The PNECs for the terrestrial and sediment environment were derived using the equilibrium partitioning method.

J.3 Toxicity potentials

Table J.1 lists the toxicity potentials of Methyldiethanolamine and Aminomethylpropanol.

Table J.1 *Toxicity potentials of Methyldiethanolamine and Aminomethylpropanol (in kg 1,4-Dichlorobenzene equivalents).*

Substance	**Type**	**Initial emission compartment**				
		air	**fresh water**	**sea water**	**agricult. soil**	**industrial soil**
Methyldiethanolamine	FAETP	1.4E+00	1.2E+01	1.2E-08	2.6E+00	2.6E+00
	MAETP	1.3E-01	2.6E-02	2.6E-01	5.7E-03	5.7E-03
	FSETP	1.1E+00	9.1E+00	9.3E-09	2.0E+00	2.0E+00
	MSETP	2.0E-01	3.9E-02	3.9E-01	8.6E-03	8.6E-03
	TETP	2.2E-01	1.1E-07	1.8E-09	4.5E-01	4.5E-01
	HTP	?	?	?	?	?
Aminomethylpropanol	FAETP	1.1E+00	2.9E+01	4.8E-05	6.2E+00	6.2E+00
	MAETP	1.3E-01	6.3E-02	6.2E-01	1.6E-02	1.6E-02
	FSETP	8.4E-01	2.2E+01	3.7E-05	4.7E+00	4.7E+00
	MSETP	1.8E-01	9.4E-02	9.3E-01	2.4E-02	2.4E-02
	TETP	1.7E-01	4.4E-04	7.3E-06	1.0E+00	1.0E+00
	HTP	7.8E+02	4.3E+01	4.3E-02	3.4E+03	2.5E+01

FAETP = Fresh water Aquatic EcoToxicity Potential; MAETP = Marine Aquatic EcoToxicity Potential; FSETP = Fresh water Sediment EcoToxicity Potential; MSETP = Marine Sediment EcoToxicity Potential; TETP = Terrestrial EcoToxicity Potential; HTP = Human Toxicity Potential.

J.4 Literature

Huijbregts MAJ. 1999. Priority Assessment of Toxic Substances in the frame of LCA. Development and application of the multi-media fate, exposure and effect model USES-LCA. IDES, University of Amsterdam, Amsterdam.

Huijbregts MAJ, Thissen U, Guinée JB, Jager T, Van de Meent D, Ragas AMJ, Wegener Sleeswijk A, Reijnders L. 2000. Priority assessment of toxic substances in life cycle assessment, I: Calculation of toxicity potentials for 181 substances with the nested multi-media fate, exposure and effects model USES-LCA. Chemosphere 41: 541-573.

Liebert, MA. 1990. Final report on the safety assessment of aminomethylpropanol and aminomethylpropanediol. Journal of the American College of Toxicology 9 (2): 203-228.

RIVM, VROM, VWS, 1998. Uniform System for the Evaluation of Substances 2.0 (USES 2.0). RIVM report no. 679102044. National Institute of Public Health and the Environment (RIVM), Ministry of Housing, Spatial Planning and the Environment (VROM), Ministry of Health, Welfare and Sport (VWS), The Hague.

US-EPA, 2000. EPI Suite. Office of Pollution Prevention Toxics and Syracuse Research Corporation, United States.

J.5 Substance-specific input data

Compound name	**Unit**	**methyldiethanol-amine**	**aminomethyl-propanol**
CAS nr.	**-**	**105-59-9**	**124-68-5**
Effects assessment			
oral Human Limit Value	$\mu g.kg_{bw}^{-1}.d^{-1}$	0.4	?
inhalation Human Limit Value	$\mu g.m^{-3}$	0.03	?
aquatic Predicted No Effect Concentration	$ug.l^{-1}$	151	63
Physico-chemical properties			
molecular weight	$g.mol^{-1}$	119.16	89.14
logKow	-	-1.50	-0.74
melting point	°C	-21	25.5
vapor pressure (25 °C)	Pa	$2.7.10^{-2}$	188
solubility (25 °C)	$mg.l^{-1}$	1.10^{6}	1.10^{6}
Degradation rates			
Reaction rate in air	d	0.17	0.63
Reaction rate in surface water	d	8.7	8.7
Reaction rate in soil	d	17.3	17.3
Reaction rate in the aerobic sediment zone	d	17.3	17.3
Reaction rate in the anaerobic sediment zone	d	78	78