

First prioritization - external costs and benefits over the life cycle of CCS cases

In-depth study of specific environmental themes in CCS chains



CATO-2 Deliverable WP4.3-D01b

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A part of CATO2 Work package 4.3 aims to find insights in the environmental impacts of carbon capture and storage chains. Certain environmental themes of Carbon Capture and Storage (CCS) technologies such as the emissions related to the production and use of solvents, waste & by-product formation, emissions to water and water consumption are relatively less investigated in the pertaining literature and have not been highlighted in existing overview studies up to now.

It is the goal of this paper to review the existing data on these aspects for CO₂ capture technologies applied on power plants. The review is based on a literature review and is provided with information from ongoing projects to indicate the current standings of knowledge on the subject.

Literature data on these specific subjects appeared to be scarce. Hence, data from field experiments (pilot and demo plants) and expert opinions on these themes are highly recommended and welcomed by the authors.

On the basis of the currently available literature, the following conclusions can be drawn:

Solvent related emissions from the CCS chain

- There is a growing awareness on the possible environmental impacts of CO₂ capture. Focus of the current research in this field is on post-combustion carbon capture using amines, which could lead to the emission of carcinogenic nitrosamines.
- Theoretical studies on the formation of nitrosamines are available. Measurements campaigns are running, but the availability of data is very limited and/or confidential.
- The emissions to air from the production process depend on the type of solvent produced and show a large variation in NH₃ emissions.
- Large amounts of waste are produced by CO₂ capture process. As a first estimate, 1 tonne per hour will be produced in an average power plant. From a technical and economic point of view, the incineration does not seem to be a large issue. Although it is important that the capacities are available to handle large waste streams when CCS is employed at large scale. The incineration of waste creates additional emissions to air for which legislation maybe needs to be adapted.

Waste and by-products from CO₂ capture

- Waste formation is of relative less interest for gas fired power plants without capture.
 Post-combustion capture can result in significant additional waste formation depending on the technology variant chosen.
- Waste formation due to volume effects can be assessed accurately with the use of the energy penalty induced by installing the CO₂ capture installation.
- Waste formation due to post combustion capture process depends on solvent selection and process configuration. Detailed data on the formation and composition of wastes from CO₂ capture technologies are not available for most of the technology variants.
- Waste formation in oxyfuel power plants is still uncertain/unknown and is not quantified in the pertaining/consulted literature.



- Waste formation in pre-combustion capture seems to be very limited compared to postcombustion capture processes, but detailed data is lacking.

Emissions to water from CO₂ capture

- Emissions to water are of relative less interest for gas fired power plants without capture.
- There is relatively modest data known to be available on emissions to water bodies due to CO₂ capture, apart from volume effects (due to energy penalty). That is, it is possible to estimate the change in emissions due to increase in primary energy demand. It is however not known what the exact effect is of CO₂ capture technologies on the composition of waste water effluent.

Water consumption from CO₂ capture

- Overall water consumption for power plants depends strongly on the energy conversion technology, process configuration and on the applied cooling technology. It can in principle be assessed with high accuracy. When equipping power plants with CO₂ capture technologies the overall water withdrawal and consumption is expected to increase due to additional cooling water demand and process water demand. This holds to a lesser extent for oxyfuel power plants for which the water balance changes due to changes in the combustion process and flue gas cleaning technologies.



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Document Change Record (this section shows the historical versions, with a short description of the updates)

Version	Nr of pages	Short description of change	Pages
01	45	First draft	

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2.1 Applicable Documents

(Applicable Documents, including their version, are documents that are the "legal" basis to the work performed)

	Title	Doc nr	Version date
AD-01	Beschikking (Subsidieverlening	ET/ED/9078040	2009.07.09
	CATO-2 programma		
	verplichtingnummer 1-6843		
AD-02	Consortium Agreement	CATO-2-CA	2009.09.07
AD-03	Program Plan	CATO2-WP0.A-	2009.09.29
	-	D.03	

2.2 Reference Documents

(Reference Documents are referred to in the document)

	Title	Doc nr	Issue/version	date
CATO-2-WP4.3-D01 part 1	First prioritization - external costs and benefits over the		01	2010.09.15
	life cycle of CCS cases; Part 1: Preliminary environmental performance assessment of CCS chains			
CATO-2-WP4.3-D01 part 3	First prioritization - external costs and benefits over the life cycle of CCS cases; Part 3: Economic valuation of environmental impacts		01	2010.09.02

2.3 Abbreviations

AMP	Aminomethylpropanol		
BAT	Best available technology		
BREF	Reference document on best available technologies		
CCS	Carbon capture and storage		
COD	Chemical oxygen demand		
DEA	Diethanolamine		
EIA	Environmental impact assessment		
EIS	Environmental impact statement		
ESP	Electrostatic precipitator		
FGD	Flue gas desulphurization		
HSS	Heat stable salt		
IEA	International Energy Agency		
IGCC	Integrated gasification combined cycle		
MDEA	Methyl diethanolamine		



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MEA	Monoethanolamine		
NGCC	Natural gas combined cycle		
PAH	Polycyclic aromatic hydrocarbon		
PC	Pulverized coal		
PCB	Polychloorbifenyl		
PM	Particulate matter		
RD&D	Research, Development & Demonstration		
REACH	Registration, Evaluation and Authorisation of CHemicals.		
SCR	Selective catalytic reduction		
TEA	Triethanolamine		
WP	Work package (CATO)		
WWT	Waste water treatment installation		



3 Introduction

A part of CATO2 Work package 4.3 aims to find insights in the environmental impacts of carbon capture and storage chains. Certain environmental themes, such as global warming potential and primary energy use are relatively well studied for CCS chains. An overview of these themes is reported in part 1 of this deliverable: Preliminary environmental performance assessment of CCS chains (CATO-2-WP4.3-D01 part 1). Other environmental aspects of CCS technologies such as the emissions related to the production and use of solvents, waste & by-product formation, emissions to water and water consumption are relatively less investigated in the pertaining literature. At least, these specific subjects have not been highlighted in existing overview studies up to now.

It is the goal of this paper to review the existing data on these aspects for CO₂ capture technologies applied on power plants. The review is based on a literature review and is provided with information from ongoing projects to indicate the current standings of knowledge on the subject.

CATO2 - WP 4.3

This report is part 2 of the first deliverable "First prioritization - external costs and benefits over the life cycle" (CATO-2-WP4.3-D01) of CCS cases of work package 4.3 "Environmental performance of CCS chains". Other parts of this deliverable are:

- Part 1: Preliminary environmental performance assessment of CCS chains (CATO-2-WP4.3-D01 part 1)
- Part 3: Economic valuation of environmental impacts (CATO-2-WP4.3-D01 part 3).

This WP aims to:

- Assess the environmental performance of CCS technologies over the complete life cycle
- Deepen the insights of all CATO2 partners in the (non-CO₂) environmental aspects of CCS in general and capture in particular by enlarging the amount of available and accessible data
- Provide input that would be required to carry out a strategic environmental impact assessment for CCS in the Netherlands.



4 Solvent related emissions from the CCS chain

4.1 Overview

In Figure 1 a schematic overview of the life cycle of power generation with CCS is given. The three main chains are the fuel chain, the solvent chain and the CO_2 chain. This report will focus on the emissions related to the solvent chain. The solvent chain of which the emissions will be discussed in the following paragraphs consists out of three parts:

- 1.1. Solvent production
- 1.2. CO_2 capture
- 1.3. Treatment of solvent waste

Solvents are both used in post- and pre-combustion capture. During the production of the solvents there will be emissions for both cases. For the CO_2 capture process only solvents used in the post combustion capture are relevant. Emissions of pre-combustion solvents are burnt during the combustion process. In the post-combustion process the solvent is used after the combustion and pollutants can be emitted.



Figure 1 Schematic overview of life cycle of power generation with CCS



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4.2 Solvent production

4.2.1 Solvents for post combustion capture

Amine based solvents used for post combustion capture are usually produced from basic chemicals like ammonia, methanol and ethylene oxide. MEA is distilled from a mixture of MEA, DEA and TEA (mono-, di- and tri-ethanolamine) and produced in a batch mode from ethylene oxide and ammonia. The solvent consists of MEA and a number of additives that function as oxygen scavengers and corrosion inhibitors.

Chilled ammonia, used in a relatively new process of chilled ammonia carbon capture, is basically just ammonia, manufactured usually by natural gas reforming.

4.2.2 Solvents for pre combustion capture

Methyl diethanolamine (MDEA) is manufactured in a way comparable to MEA: from ethylene oxide and mono-methylamine (MMA), which in turn is distilled from the reaction between ammonia and methanol, resulting in MMA, DMA and TMA (mono-, di- and tri-methylamine). Selexol is a dimethylether of polyethyleneglycol.

Table 1 shows an indication of the emissions during the production of 1 kg of solvent. For the NH_3 there is a large difference in the reported emissions. Pehnt and Henkel (2009) reported an emission about 15 times higher as van Gijlswijk et al. (2006). The emissions of the other components are in the same order of magnitude.

Table 1 Indication of all emissions due to solvent mandactuning						
	Emission from manufacturing 1 kg of solvent (mg)					
	NO _x	SO ₂	PM ₁₀	NMVOC	NH_3	Data source
Post-Combusti	on					
MEA	6300	6600	840	1700	1600	(Gijlswijk et al., 2006)
MEA	7320	8660	463	2020	23000	(Pehnt and Henkel, 2009)
Ammonia	2400	4400	720	740	14	(Ecoinvent Centre, 2007)
Pre-Combustic MDEA	n 5800	5700	620	1700	180	(Gijlswijk et al.,
Selexol	No data a	available				2006)

Table 1 Indication of air emissions due to solvent manufacturing

Note: data based on version 1.2 of (Ecoinvent Centre, 2007). Raw material ratio adapted. Added distillation step has been modelled in Aspen. (BOLK, 2008)



4.3 CO2 capture

4.3.1 Emissions to air from the CO₂ capture process

Currently, available information on solvent related emissions is scarce. Table 2 presents the emission data from post combustion CO_2 capture using amines, assigned to the various solvents as described in literature (BOLK, 2009). Key findings can be summarized as follows. Net emissions (in g/kWh) will increase for NO_x, NH₃ and possible PM₁₀ compared to power plants without CO₂ capture. The emissions of NO_x and PM₁₀ increase because of the fuel penalty. The solvent washing process will remove a part of the NO_x and PM₁₀. NO₂ reacts with the solvent, but is only a minor part (~10%) of the total NO_x. NH₃ emissions are caused by the degradation of the amine-based solvents (MEA). The emissions of SO₂ will decrease because of the solvent scrubbing step.

Though it is known that MEA itself can evaporate from the process (Gijlswijk et al., 2006) and that degradation of MEA can also lead to other emissions of volatile organic compounds, there is not information publicly available on the level of NMVOC emissions that could be generated.

		CO ₂	NO _x	SO ₂	PM ₁₀	NH_3
PC	No capture Fluor Econamine FG+ ^{1 2)}	786 114	0.37 0.45	0.25 0.009	0.042 0.072	0.0058
	MEA ^{3, 4, 5, 6)} Amines (overall)	98 105	0.65 0.55	0.0004 0.0046	0.031 0.055	0.125 0.125
NGCC	No capture Fluor Econamine FG+ ^{1, 2)}	366 54	0.09 0.11	- -	-	0.00037 0.080
	KS1 ²⁾ MEA ^{3, 4, 5, 6)} Amines (overall) ⁷⁾	63 45 49	0.18 0.11 0.12	-	-	- 0.002 0.041

Table 2 Harmonised emissions from CO₂ post combustion capture using amines (g/kWh) (BOLK, 2009)

¹⁾ (IEA GHG, 2004); ²⁾ (IEA GHG, 2004;ER, 2006); ³⁾ (EPRI, 2000;EPRI, 2002); ⁴⁾ (Rubin and Rao, 2002); ⁵⁾ (Rubin et al., 2007); ⁶⁾ (Stobbs and Clark, 2005); ⁷⁾ (Kvamsdal et al., 2007)

Experts expect that NH₃ emissions can be prevented, for example, by adding an additional acid based wash section after the absorber. Next to the capture process NH₃ emissions are produced by the de-NOx SCR unit (Koornneef et al., 2008). Prevention of NH₃ emissions can also be achieved by solvent selection (e.g. TNO Coral process (Jaspers and Allaie, 2008)).

4.3.2 Amine degradation

In Figure 2 a schematic drawing of the post combustion process is given. In yellow the locations are marked where amine emissions can leave the power plant:

- 1) The emissions to air at the top of the absorber
- 2) The residuals taken out of process when recycling the amine
- 3) The CO₂ captured from the flue gas





Figure 2 Post combustion carbon capture with marked in yellow the three main pathways where amine emissions can leave the power plant (Knudsen, 2008)

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

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

There are large numbers of degradation products from each of the three degradation routes. The degradation products not only depend from the degradation mechanism, but also from the type of amines used.

4.3.2.1 Oxidative degradation

Amine solvents can undergo an oxidative degradation because of the presence of oxygen or metal ions in the flue gas. The degradation product will be oxidized fragments of amines, such as ammonia, organic acids and oxidants. The chemistry of the oxidation process is complex and not fully understood. A possible reaction mechanism is suggested in Figure 3.





Figure 3 Possible MEA oxidative degradation reaction with and without oxygen (Bellona, 2009)

4.3.2.2 Thermal degradation

The thermal degradation of amines takes place in the reboiler and stripper where high temperatures and high CO_2 concentrations are present. Amines generally react with CO_2 to form carbamate salts. This reaction is reversible, but with high temperatures the carbamate will further react to thermal degradation products. Also a hydrolysis reaction takes place to form the final degradation products. For MEA the thermal degradation products make up about 20 to 30 percent of the total MEA loss (see Figure 4).

MDEA can degrade into TEA and DMEA. Piperazine seems not to undergo thermal degradation. In a mixture with MEA however, both components undergo degradation in significant quantities.





Figure 4 Possible thermal degradation reactions of MEA (Bellona, 2009)

Thitakamol (2007) reports concentrations of common heat stable salts found in an amine treating plant (Table 3). They are products of the reaction of the absorption solvent with acids stronger than CO_2 , such as carboxylic acids.



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Table 3 Typical concentrations of heat stable salts anions found in amine treating units (Thitakamol, 2007)

HSS type	Range	References*)	Note
	(ppmw)		
Acetate	0–1,500	Fan et al2000	DEA solution in refinery (vendor data)
	5,000	Liu and Dean-1995	MDEA solution in refinery (plant sample)
	2,406-3,789	Liu and Dean-1995	MDEA solution in refinery (plant sample)
	750–1,250	Craig and McLaughlin-1996	DEA solution in refinery (plant sample)
Formate	0–35,000	Fan et al2000	DEA solution in refinery (vendor data)
	15,000–17,000	Fan et al2000	DEA solution in refinery (vendor data)
	5,000-7,000	Fan et al2000	DEA solution in refinery (vendor data)
	25,000-30,000	Fan et al2000	DEA solution in refinery (vendor data)
	5,000–15,000	Fan et al2000	DEA solution in refinery (vendor data)
	500–11,900	Litchewski -1996	MDEA solution in refinery (plant sample)
	45,000	Liu and Dean-1995	MDEA solution in refinery (plant sample)
	10,474–57,747	Liu and Dean-1995	MDEA solution in refinery (plant sample)
Glycolate	0–150	Fan et al2000	DEA solution in refinery (vendor data)
	6,000–21,000	Craig and McLaughlin-1996	DEA solution in refinery (plant sample)
Oxalate	0–150	Fan et al2000	DEA solution in refinery (vendor data)
	100	Liu and Dean-1995	MDEA solution in refinery (plant sample)
Sulphate	0–350	Fan et al2000	DEA solution in refinery (vendor data)
	100	Liu and Dean-1995	MDEA solution in refinery (plant sample)
Thiosulphate	0–700	Fan et al2000	DEA solution in refinery (vendor data)
	600	Liu and Dean-1995	MDEA solution in refinery (plant sample)
Thiocyanate	0–3,000	Fan et al2000	DEA solution in refinery (vendor data)
	500–1,000	Fan et al2000	DEA solution in refinery (vendor data)
	2,000-3,500	Fan et al2000	DEA solution in refinery (vendor data)
	500–1,000	Fan et al2000	DEA solution in refinery (vendor data)
	1,000–3,000	Fan et al2000	DEA solution in refinery (vendor data)
	3,500	Liu and Dean-1995	MDEA solution in refinery (plant sample)
	883-21,462	Liu and Dean-1995	MDEA solution in refinery (plant sample)

*) Fan et al., 2000; Liu and Dean, 1995; Craig and McLaughlin, 1996; Litchewski, 1996



4.3.2.3 Atmosphere degradation

In 2007, the Norwegian Institute for Air Research (NILU) initiated a project to study the effects of amine emissions to the environment. The amines studied are MEA, AMP, MDEA and piperazine¹. Amines themselves are most likely of little risk, but the emissions contribute to the nitrogen load and potentially to eutrophication of the ecosystems. The amines can react with oxidized nitrogen in the atmosphere to form compounds such as nitrosamines, nitramines, aldehydes and amides. See Figure 5 for the possible reactions of MEA and Appendix A for the reaction of the other solvents. Nitrosamines are of particular concern because of their toxic and carcinogenic properties at extremely low levels. Nitramines are suspected to be carcinogenic, but less potent than nitrosamines. The suggested longer lifetime of the latter however, may lead to higher exposure values (Knudsen et al., 2009).



Figure 5 Possible atmospheric degradation of MEA (Bellona, 2009)

¹ MEA (2-aminoethanol): H₂NCH₂CH₂OH

AMP (2-amino-2-methyl-1-propanol): $(CH_3)_2C(NH_2)CH_2OH$ MDEA (2,2'-(methylimino)bis-ethanol): $CH_3N(CH_2CH_2OH)_2$ Piperazine: $HN(CH_2CH_2)_2NH$



Other results of the screening study (Knudsen et al., 2009) are:

- Atmospheric emissions modelling shows that amine emission can have impacts at both local as regional scale.
- Worst case studies for a generic full scale amine plant with conditions representing the west coast of Norway show that the predicted concentrations of photo oxidation compounds are at the same level as the proposed "safety limits", implying that risks to human health and natural environment cannot be ruled out.
- The preliminary guidelines were established for human exposure. Based on inhalation exposure risk, the general population, over time, should not be exposed to levels in the air higher than:
 - ο MEA: 10 μg/m³
 - \circ AMP: $6 \mu g/m^3$
 - MDEA: 120 µg/m³
 - Piperazine: 5 μg/m³
- It has been shown that it is highly relevant to know which precise amine is used in CCS, because each individual amine has varying effects and potential risks.
- These statements should raise concern, and highlight the necessity for further testing and analysis of amine effects in order to limit the risks or to find alternatives for their use in CCS planning.

4.3.3 Running projects on amine based post-combustion carbon capture

Recently a workshop on the "Environmental Impact of Amine Emission during Post-Combustion Capture" was organised by IEAGHG. New information on emissions was presented from projects and solvent manufacturers. The most important are listed below.

4.3.3.1 CESAR, Emission measurements at Dong's pilot plant for CO₂ capture in Esbjerg

The Cesar project aims for a breakthrough in the development of low cost post combustion CO_2 capture technology to provide economically feasible solutions for both new power plants and retrofit of existing power plants. Table 4 describes the pilot plant and flue gas conditions. Table 5 summarizes the results of the emission measurements at three locations, the in- and outlet of the absorber and after the wash section of the absorber.

Plant characteristics:	Flue gas conditions
400 MW pulverized bituminous coal	T ~ 47℃ saturate d
High dust SCR deNOx plant	<10 ppm SO ₂
3 zones cold sided ESP	<65 ppm NO _x
Wet limestone FGD (saleable gypsum)	<10 mg/nm ³ dust

Table 4 Plant characteristics and flue gas conditions



Compound	Inlet absorber (mg/Nm ³)	Outlet absorber (mg/Nm ³)	Outlet absorber after water wash (mg/Nm ³)
MEA	<0.1	0.7	<0.3
DEA	<0.2	<0.3	<0.2
Formaldehyde	<0.1	0.7	<0.1
Methylamine	<0.2	<0.3	<0.2
Acetamide	<0.6	<1.0	<1.0
Ammonia	<0.1	<23	20

Table 5 Results from Cesar project (Da Silva, 2010)

The preliminary conclusions from the CESAR project are:

- Oxidative degradation products of MEA are found in gas and liquid phase.
- The water wash reduces the amount of MEA and formaldehyde.
- The absorber reduces the amount of metals, dust and SO₂ in the flue gas leaving the absorber.

4.3.3.2 Mitsubishi Heavy industries, MHI Amine emission control technology

MHI is working on the development of the MHI Zero Amine Emission System. Test results at the R&D centre pilot plant (September 2009; solvent: KS-1, capacity: 1 t/day, feed gas: boiler) show that the emissions of amine could not be determined and that the emission of degraded amine was less than 0.2 ppm as vapour. The technology will be applied at the plant Barry Power station in Alabama with a capacity of 500 tonne CO_2 /day and is expected to be operational in 2011. Next research topics for MHI in the topic are the evaluation of the environmental effects, photogenic reaction in the air of released amine and the effect of nitrosamines into aquatic environment (Kamijo, 2010).

4.3.3.3 Fluor, Econamine FG+ Process: recent advances in emissions control

Because of an increased concern regarding amine emissions and the subsequent hypothetical formation of nitrosamines, Fluor is working on the reduction of solvent emissions into the atmosphere. After rigorous testing at the Bellingham plant (gas fired power plant, 360tonne CO_2 /day), solvent concentrations in the absorber vent were lower than 1 ppm.

A new scrubbing system has been developed by Fluor with reduced solvent emissions of 0.1 to 0.2 ppm in the vent. This process will be tested in a demonstration plant in Germany in 2011. More efficient scrubbing systems consume more power and/or reagents. Scrubbing systems should be designed to reduce the emissions to an "adequate" level, depending on the amine used, and not to an arbitrary low value. Fluor states that authorities should set target levels for emissions levels, where vendors can focus on (Reddy, 2010).

4.3.3.4 Aker Clean Carbon, emissions measurements and analysis from Mobile Carbon Capture Test facility

Aker Clean Carbon is one of the participants in the SOLVit program, which aims to develop, test and select improved solvents with low energy requirement, minimum environmental impact, low corrosion and low degradation. An advanced mobile carbon capture plant is available since 2008 for long term testing in an industrial environment. A number of emission campaigns were carried out with the following results.



Table 6 Data from emission campaigns in the SOLVit program (Graf, 2010)								
Company	NILU	SINTEF	Eurofins Miljo					
Location	Risavika, Norway	Longannet, Scotland	Longannet, Scotland					
Solvent	30 wt% MEA	30 wt% MEA	30 wt% MEA					
Flue gas	4% CO ₂	12% CO ₂	12% CO ₂					
MEA emissions	Low (ppb level)	1 to 4 mg/Nm ³	1) below detection					
			2) detected					
Ammonia	Low (< 5ppm)	~ 50 ppm	> 80 ppm					
Aldehyde	Measured	Not measured	Measured					
Amine degraded	Measured	Measured	Measured					
products								
Nitrosamines	Not measured	Not measured	Measured (sub-					
			µg/Nm³)					

The gas analysis of some compounds is challenging because of the low concentrations. Different sampling and analytical methods will give different results. Furthermore, there are uncertainties in the measurements. More campaigns, analysis and results are needed in order to conclude emission levels.

4.3.4 CO₂ capture chemicals and REACH regulation

The health and environmental properties of a number of CO_2 capture compounds have been evaluated by StatoilHydro in the light of the REACH regulation. REACH is the new chemical legislation in the EU. REACH stands for Registration, Evaluation and Authorisation of CHemicals. Industrial CO_2 capture plants are covered by REACH and the IPPC, the EU directive restricting polluting discharges from industry. An important item is the discharge permission based on the comparison with the Best Available Technologies (BAT). The current BREF (Reference Document on Best Available Techniques) for large combustion Plants (IPPC, 2006) does not contain information on solvent related emissions from CO_2 capture.

Svanes (2008) shows in his study that the selected compounds (mainly amines) and degradation products (ammonia) are not on the restricted list. Most of the compounds are classified as harmful to health and/or the environment. Using the compounds will not be severely restricted by REACH. See Appendix B for an overview of the health and environmentally related classifications of the compounds. The study did not incorporate the degradation products as nitrosamines. A more comprehensive study is recommended containing exposure studies and mapping of degradation products.



4.4 Treatment of solvent waste

Approximately 1.5 kg of solid waste per tonne of CO_2 is created by reclaiming the solvent degradation products (MEA process). An average power plant emits ca 700 tonnes of CO_2 per hour, resulting in a production of approximately one tonne of toxic waste per hour. The preferred option is to prevent the degradation of the product. An alternative option is to incinerate the waste in a waste incinerator or re-introduce the waste together with the fuel in the combustion process. From a technological point of view, no problems are expected for the last option, but current legislation may put barriers into this (BOLK, 2009).

At the moment detailed models are not available for assessing the emissions of the incineration of the residue in a hazardous waste incinerator. One study has been found which use a model of a municipal solid waste incinerator instead (Eggels et al., 2000). A calculation has been made of the emissions resulting from the incineration of solvent sludge, see Table 7. The figures are likely to be an overestimation, for hazardous waste incinerators should emit less due to stricter regulations. In another study, (van Gijlswijk et al. 2006), MEA-based post combustion capture and MDEA-based pre combustion capture result in 3.2 and 0.024 kg of reclaimer sludge per tonne of CO_2 captured.

Table 7 Indication of air emissions due to solvent residue incineration (BOLK.2008)

(, ,	
	1 kg of reclaimer sludge	Unit
NO _x	8300	mg
SO ₂	370	mg
PM_{10}	38	mg
NMVOC	270	mg
NH_3	520	mg

Bellona mentions in their study (2009) amine waste handlings costs of approximately 0.4 EUR/tonne CO_2 . It is based on estimated cost of amine waste transport and incineration of 250 to 435 EUR per tonne amine and a production of around 1000 tons of amine waste per year by a CO_2 capture plant with a capacity of 1 million tonnes CO_2 per year. In the McKinsey's report on CCS economics (2008), the cost of CO_2 capture and storage is estimated to be around 50 to 70 Euros per tonne CO_2 . The cost of amine waste handling is therefore less than 1 percent of total CCS cost. According to Bellona the technology and market for incineration of amine waste already exists. In Norway, for example, the cement producer Norcem has the capacity and license to handle 130,000 tonnes of hazardous waste per year in their hazardous waste incinerator.

Bellona (2009) mentions two possible alternatives to handle amine waste which are researched (Tel-Tek, Telemark University):

- Biodegradation of the waste into harmless products. Furthermore, MEA degradation products can be used to reduce NO_x emissions. Ammonia and urea are common chemicals for reducing NO_x emissions today, but these chemicals could be replaced by MEA degradation products.
- Production of biogas from amine waste. Bacterial degradation in absence of air can process amine waste into biogas which is a renewable energy source and a valuable product.



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

Finally, it is important to ensure that there are capacities available for handling the large volumes of amine waste that can be expected from a large global deployment of CCS. With all the amine based CO_2 capture plants that are planned to be built the coming decades it will be important to ensure that there exist hazardous waste handling facilities with sufficient capacity to handle all the amine waste (Bellona, 2009).



5.1 Introduction

Typical waste and by-products that arise from operating a power plant are highly dependent on the energy conversion process, the fuel composition and the flue gas cleaning technology configuration and performance. For a PC power plant the main typical waste and by-product streams are: gypsum (from FGD), ash (bottom and fly ash) and waste water treatment sludge/cake.

For an IGCC typical waste streams are: sulphur, slag (only in slagging gasifiers), fly ash and waste water treatment sludge/cake.

Solid waste streams from gas fired power plants are predominantly the consequence of secondary operations such as cleaning, maintenance and water cleaning. They include: used catalysts, scrap metal, used oil, packaging materials, liquids used to wash down the compressors/gas turbines, ion exchangers, and activated carbon. The water demineralization installation will also yield waste chemicals and resins that need to be disposed off. (IPPC 2006) Waste and by-product formation is typically not an environmental issue for natural gas fired power plants without CO_2 capture (IPPC 2006).

5.2 Effect of CO₂ capture

The formation of solid waste streams may change when gas fired power plants will be equipped with **post-combustion** CO_2 capture. Depending on the CO_2 capture variant, i.e. the process configuration and solvent used, several additional solid by-products may be produced. The higher oxygen concentration in the flue gas from natural gas combustion possibly results in higher oxidative degradation of solvents. MEA is for instance susceptible for this type of degradation. However, as other impurities such as SO_2 and PM are virtually not present in the flue gas, overall degradation is considerably lower compared to coal fired power plants. (Supap, Idem et al. 2009) Spent sorbent is estimated by Davidson (Davison 2007) to be between 0.2 and 1.9 kg/tonne CO_2 for gas fired power plants. The variance is explained by using various solvents, Fluor's Econamine FG+SM and MHI's KS-1 process, respectively. More information on the consumption of solvents and other resources when capturing CO_2 is provided in Appendix C Resource consumption.

Pre-combustion capture of CO_2 from advanced gas fired power plants with the use of sorbents, such as SE-WGS (sorption enhanced water gas shift) the production and disposal of the sorbent may have additional environmental impacts, this has however not been studied in detail (Jansen 2008). The production and disposal of the membranes and catalysts used in the pre-combustion concepts may also have adverse effects on the environment. Catalysts may for instance contain nickel, chromium, copper, zinc, platinum, rhodium and palladium. (Ruettinger, Ilinich et al. 2003; Harmelen, Koornneef et al. 2008)

Gas fired **oxyfuel combustion** concepts that are similar to NGCC cycles are not expected to have significant additional solid wastes. The absence of a DeNOx installation avoids the use of catalysts used for reducing NOx emissions. However, in the oxyfuel concepts that use air separation units² to produce oxygen, some typical waste streams can be: catalysts (containing

² Air separation units can be based on cryogenic air separation, pressure swing separation with adsorption and separation using membranes.



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In depth study of specific themes

biotoxic metals), (lubricating) oils, used filters and used membranes. (EIGA 2003) Oxyfuel concepts that use fuel cells can also yield waste streams. For example, the fuel cell itself contains metal oxides that may be harmful for the environment. Disposal of fuel cells would in such a case require special waste treatment.

Post-combustion - In Table 8, it is shown that in PC plants with post-combustion more ash (bottom-ash and fly-ash) is formed during combustion and is captured, collected and disposed off per kWh due to the efficiency penalty. In the post –combustion CO_2 capture unit impurities in the flue gas such as SO_x and halogen compounds react with the solvent to form heat stable salts³. These salts reduce the CO_2 binding capacity of the solvent and, moreover, are corrosive compounds that are harmful for equipment. Degradation products and other impurities are therefore separated from the solvent in a reclaimer where also solvent is recovered. Results from a study analysing the composition of reclaimer waste implicates that CO_2 capture influences the distribution of trace element emissions (Se, As, Cr, Cu, Ni, Zn and Hg) over the various waste streams from a coal fired power plant (Thitakamol, Veawab et al. 2007). The residues from the reclaimer are to be considered as hazardous waste (Strazisar, Anderson et al. 2003; Rao, Rubin et al. 2004; Thitakamol, Veawab et al. 2007) and can be in the order of several kilotonnes per year for a commercial scale power plant (Clarke, Debeljak et al. 2004), see also Table 8.

The degradation and thermal instability of MEA is widely recognized and next generation solvents are therefore the scope of RD&D programmes of CO_2 capture equipment suppliers. Doosan Babcock is one of those suppliers which states that the development of next generation solvents is aimed at, among others: lower volatality and better thermal stability of the solvent, next to less degradation and lower corrosivity (Doosan Babcock Energy 2010). This will result in lower solvent losses and less waste sludge production.

The appropriate treatment option for the reclaimer sludge is yet to be determined. It can possibly be treated in the waste water treatment installation (WWT), which means that a fraction of the sludge is emitted to the surface water and the other fraction (WWT sludge) is to be disposed of. Also incineration and landfill are considered to be options. Co-firing is an option similar to that of the optional treatment of WWT sludge (Meij, Cuperus et al. 2000). Re-introducing the sludge into the boiler will redistribute the elements of the sludge over other waste streams such as fly-ash, bottom ash and gypsum and WWT effluent and sludge. Due to limits of acceptance for the content of impurities such as mercury and other heavy metals valorisation of by-products can then become a problem (Sloss 2007).

For the coal fired PC power plants also a larger stream of solid by-product from the FGD unit, primarily gypsum, is expected due to the required improved removal efficiency and capture penalty, see Table 8.

Wen and Narula (Wen and Narula 2009) suggest that due to additional flue gas cooling, condensates become available which would add to the waste stream of the power plant. Also additional filters should be applied and disposed off. They conclude that 'power plant permits must take into account the additional wastes and emissions created by CCS' (Wen and Narula 2009)

In the chilled ammonia concept ammonium sulphate can be a by-product that is theoretically recoverable and usable as fertilizer. This is the reaction product of SO_2 in the flue gas with the ammonia solution (Yeh and Bai 1999).

³ Heat stable salt: a salt that is not capable of being regenerated by the addition of heat.



In the concept using potassium carbonate as sorbent possible new waste or by-product streams are that of nitrates, nitrites, sulphates and sulphites formed by the reaction of the sorbent with SO_2 and NO_2 (Smith, Ghosh et al. 2009). If recovered, these substances can be used as fertilizers. When using sodium carbonate, it is likely that SO_2 that still remains in the flue gas reacts to sodium sulphite, -bisulphite and -sulphate, comparable with the reaction in a sodium alkali FGD scrubbing system (cf. Koren and Bisesi 2002). These salts in solutions are liquid waste streams that should be properly treated.

Amino acids are reported by Allaie and Jaspers (2008) to be stable and show low degradation rates which would imply that also waste and by-product formation is considerably low. It should however be noted that the results of the pilot plant test are confidential for the time being and that these results cannot be verified at the moment.

Siemens has also chosen amino acid salts as the basis of their solvent. Their main arguments for this are the absence of vapour pressure, low degradation, non-toxicity, bio-degradable, nearly zero solvent slip and low environmental impact. Environmental data from field experiments are however not known to be available for Siemens' capture technology, thus data availability is also low for this solvent. (Siemens 2010)

Pre-combustion - Typical waste streams and by-products from IGCC power plants are: fly ash, bottom ash, slag and sulphur or sulphuric acid. The amount and composition of these often marketable streams depend on the gasifier and desulphurization technologies applied and on the fuel utilized (Ratafia-Brown, Manfredo et al. 2002). In Table 8, it is shown that sorbent waste increases with a factor 2 for the pre-combustion concept. Due to inaccuracy in the original data (i.e. due to rounding), this factor can be a significant overestimation, or underestimation.

Next to waste streams, the production of the marketable elemental sulphur increases per kWh. It is however uncertain whether this remains a marketable by-product in the future. For the production of slag an increase between 18% and 29% is expected in literature. This however depends on the type of gasifier technology implemented.

Oxyfuel combustion - Davidson (2003) suggest that oxyfuel combustion characteristics affect the speciation and further removal of mercury from the flue gas. Oxidized mercury is more easily captured in existing flue gas control systems. Additionally captured Hg would then end up in the waste streams of flue gas control technologies such as FGD and dust control (ESP and filters). However, some flue gas control technologies may be omitted when applying oxyfuel combustion. White et al. (2006; 2008) namely suggests a technology that removes SO₂ and NO_x in the form of sulphuric (H₂SO₄) and nitric acid (HNO₃), respectively. Both sulphuric acid as nitric acid are saleable by products. The latter substance may however react with oxidized mercury (Hg²⁺) in the flue gas rendering mercuric nitrate. This is a toxic substance and should be considered a hazardous waste. Also, the ash formation per kWh increases (see Table 8) and the composition of fly and bottom ash may change as a consequence of oxyfuel firing (Zheng and Furimsky 2003). A significant change in composition could pose problems for its qualification as usable by-product. Yan et al. (2006) also state that due to oxyfuel combustion more gaseous contaminants will be transferred to liquid, solid waste or by-product streams. Quantitative data is however not available.



Table 8 Waste streams and by products of coal fired power plants with and without CO₂ capture. From (Koornneef 2010)

Waste/by product	Technology description	Non capture g kWh ⁻¹	Capture g kWh ⁻¹	Annual increase* kt yr ⁻¹	Relative Increase (%)
Solvent waste	PC post- combustion	-	2.63 (Fluor) ^c 0.26 (MHI KS-1) ^c 2.1 (MEA) ^b	17.29 1.71 13.81	-
	IGCC pre - combustion	0.01 [°]	0.02 ^c	0.07	100%
Gypsum	PC post- combustion	9.08 ^b 15.23 ^d 13.8 ^c 53.6 (sub crit.) ^e 47.8 (super crit.) ^e	11.91 ^b 21.15 ^d 18.8-19.1 ^c 77.0 (sub crit.) ^e 70.3 (super crit.) ^e	18.61 38.92 32.87-125.57 153.84 147.93	31% 39% 36%/38% 44% 47%
Sulphur`	IGCC pre - combustion	2.78 (Shell) ^c 3.16 (GE) ^c 8.7 (GE) ^e 8.5 (CoP E-Gas) ^e 8.0 (Shell) ^e	3.48(Shell) ^c 3.81(GE) ^c 10.4 (GE) ^e 10.0 (CoP E-Gas) ^e 10.3 (Shell) ^e	4.60 4.27 11.18 9.86 15.12	25% 21% 20% 18% 29%
Bottom ash/ Fly ash	PC post- combustion	39.3 [°] 26.5/6.6 (sub crit.) ^e 24.8/6.2 (super crit.) ^e	48.9 (Fluor) ^c 48.3 (MHI KS-1) ^c 37.2/9.3 (sub crit.) ^e 35.4/8.9 (super crit.) ^e	63.12 59.17 70.35/17.75 69.69/17.75	24% 40%/41% 43%/44%
	Oxyfuel combustion	39.3°	48.0 ^c	57.20	22%
Slag	IGCC pre - combustion	44.7 (Shell)c 54.1 (GE) ^c 38.0 (GE) ^e 34.4 (CoP E-Gas) ^e 32.2 (Shell) ^e	55.8 (Shell)c 65.3 (GE) ^c 45.0 (GE) ^e 42.5 (CoP E-Gas) ^e 41.4 (Shell) ^e	72.98 73.63 46.02 53.25 60.49	25% 21% 18% 24% 29%

sub crit. = sub critical steam parameters; super crit. = super critical steam parameters indication higher generating efficiency, i.e. a lower capture penalty.

This is calculated as the difference between a 1 GW_{e net} power plant with capture with a 1 GW_{e net} power plant without capture, both with a capacity factor of 75% (6575 full load hours yr^{-1}).

^a(Odeh and Cockerill 2008)

^b(Koornneef, van Keulen et al. 2008)

d(IEA GHG 2006)

^e(DOE/NETL 2007)

6 Emissions to water from CO₂ capture

6.1 Introduction

Compounds in the liquid waste streams from power plants in general that are of interest are: active chlorine, sulphate, phosphate, bromoform⁴ (reaction product of active chlorine in salt water), chloroform (reaction product of active chlorine in fresh water) en carbohydrazide. This depends however on the cooling water conditioning technique that is applied. An alternative to chemical treatment of the cooling water to avoid organisms in the system is the application of the thermoschock treatment.(IPPC 2006)

⁽Davison 2007)

⁴ For more information see also: <u>http://www.atsdr.cdc.gov/tfacts130.html</u>



In Table 9 and Table 10 some estimated emissions from PC and IGCC power plant are presented. These emissions stem from the waste water treatment which treats sludge and waste water from, predominantly, the various (gas)cleaning processes in the power plants.

Table 9 Emission estimates for the Electrabel power plant planned to be built at the Eemshaven (Arcadis 2007)

Component	Concentration	า 👘	Annual emission	Specific emission	
	Daily	10 day			
	average	average			
	(mg/l)	(mg/l)	(tonne/yr)	g/kWh	g/ MJ primary
Particulates	30		4.8	8.00E-04	1.02E-04
COD	150		24	4.00E-03	5.11E-04
Nitrogen compounds as N	50		8	1.33E-03	1.70E-04
Sulphate	2000		320	5.33E-02	6.81E-03
Sulphite	20		3.2	5.33E-04	6.81E-05
Sulphide	0.2		0.032	5.33E-06	6.81E-07
phosphate	1		0.16	2.67E-05	3.41E-06
Fluoride	30		4.8	8.00E-04	1.02E-04
Component	(µg/l)	(µg/I)	(kg/yr)		
As	20	10	1.6	2.67E-07	3.41E-08
Cd	5	2	0.32	5.33E-08	6.81E-09
Hg	2	1	0.16	2.67E-08	3.41E-09
Cr	40	30	4.8	8.00E-07	1.02E-07
Cu	20	10	1.6	2.67E-07	3.41E-08
Ni	50	30	4.8	8.00E-07	1.02E-07
Pb	50	20	3.2	5.33E-07	6.81E-08
Zn	100	50	8	1.33E-06	1.70E-07
TI	50	40	6.4	1.07E-06	1.36E-07
	(µg/l)		(gr/yr)		
PCB	0.01		1.6	2.67E-07	3.41E-08
PAH	0.1		16	2.67E-06	3.41E-07
	(ng TEQ/I)		(mg/yr)		
Dioxin	0.01		1.6	2.67E-07	3.41E-08

Red figures show values of the detection limit. Actual values are most likely lower.

COD = Chemical oxygen demand

PAH = Polycyclic aromatic hydrocarbon

PCB = Polychloorbifenyl



Table 10 Emission estimates to water for a gas, coal, biomass and petcokes fired Shell IGCC power plant without CO_2 capture (KEMA 2006)

	Annual emission	Specific emission
Component	kg/yr	g/ kWh
Arsenic	7	9.5E-07
Cadmium	4	4.8E-07
Chromium	7	9.5E-07
Copper	7	9.5E-07
Mercury	4	4.8E-07
Molybdenum	35	4.8E-06
Nickel	14	1.9E-06
Lead	35	4.8E-06
Zinc	35	4.8E-06
Acrylate	35	4.8E-06
Sulphide	35	4.8E-06
РАН	35	4.8E-06
EOH	35	4.8E-06
dioxins/furans	0.0001	0.55.12
Component	ton/vear	9.3E-12
Component	tonycar	<i>g</i> / <i>KW</i> //
Hydrocarbons	1	1.9E-04
Phenol	0	4.8E-05
HCN	1	9.5E-05
MDEA	9	1.2E-03
Sulfolaan	18	2.4E-03
NH3	4	4.8E-04
N total	4	5.7E-04
P total	11	1.4E-03
COD	70	9.5E-03
BOD (Biochemical oxygen demand)	7	9.5E-04
Fluoride	6	7.6E-04

Based on emission performance data on page 5.37 in (KEMA 2006). Original data is given in concentration of a substance in the waste water effluent. Further assuming 80 m³/h effluent from waste water treatment facility and the most conservative assumption regarding the annual electricity generation scenario in (KEMA 2006).

BOD = Biochemical oxygen demand

COD = Chemical oxygen demand

EOH = Extractable organic halogens [only for sediments]

HCN = Hydrogen cyanide

MDEA = Methyldiethanolamine

PAH = Polycyclic aromatic hydrocarbon

PCB = Polychloorbifenyl

6.2 Effect of CO₂ capture

The effect of equipping power plants with CO_2 capture, effectively a gas cleaning process, on the emissions to water bodies is currently an underexposed subject in scientific literature.(Koornneef 2010) Cross media effects are likely as gaseous emissions are transformed into the liquid phase in several capture processes (Yan, Anheden et al. 2006). Trade-offs thus will occur when



decreasing gaseous emissions, as mass flows must balance. The quantification of this trade-off is however not possible due to lack of available data. Qualitatively some issues may however be addressed.

For example, a liquid waste stream for amine based **post-combustion** capture processes may come from the reclaimer section (Reddy, Johnson et al. 2008). Condensate waste streams are expected from the cooling sections in the CO_2 capture process, including: flue gas coolers (quench and/or water wash) and compressor intercoolers. (Wen and Narula 2009) Wen and Narula (Wen and Narula 2009) further note that more waste water may exist if an ion exchange reclaimer is used to reclaim part of the sorbent that has reacted with impurities.

Quantities and exact compositions of this waste stream are however not known to be reported in public available literature. Increased removal efficiency in emission control technologies (e.g. FGD and pre-scrubbing) and the additional reduction in the CO₂ capture process are possible processes that likely results in a shift from air emission to water or solid stream emissions. For the post-combustion process with potassium carbonate it is possible that potassium based minerals, usually fertilizers, may be discharged with the waste water if not recovered (de Meyer 2008).

For **pre-combustion** an EIA procedure may provide a direction; For an IGCC without CO_2 capture an emission of the solvents MDEA and Sulfolane of approximately 26 t yr⁻¹ is estimated (KEMA 2006), see Table 10. This may increase due to the implementation of CO_2 capture, but this is rather speculative. Yan et al. (2006) suggest that due to a change in the configuration of the flue gas cleaning system in coal fired **oxyfuel** systems contaminants may be transferred to liquid waste streams. These liquid waste streams may in turn affect overall emissions to water bodies.



7 Water consumption from CO₂ capture

7.1 Introduction

The consumption of water by power plants in the Netherlands is presented below, to give an indication of the amount of water that is currently used per kWh. The specific water withdrawal by power plants is about 140-150 l/kWh, not discerning between gas and coal fired power plants. Only 0.05 l/kWh is of this withdrawal is not used as cooling agent, but for other processes.

Table 11 Annual water withdrawal by power plants in the Netherlands in million m³ (source (CBS, PBL et al. 2010)

Year	Total consumption in NL	Specific water use	Electricity production	Total	Grou	nd water	Surface water		Тар	water	
					Total	Cooling	Total	Cooling	Salt water	Total	Cooling
	10 ⁶ m ³	l/kWh	10 ⁹ kWh	10 ⁶ m ³	1() ⁶ m ³		10 ⁶ m ³		1() ⁶ m ³
1976	13405			8590	4	2	8584	8530	•	2	0
1981	14830	183	55	10097	2	1	10093	10077	4080	2	0
1986	14543	163	57	9203	1	0	9200	9190	2645	2	0
1991	12576	141	60	8392	2	0	8387	8383	3243	4	0
1996	11661	138	59	8051	1	0	8046	8022	3784	3	0
2001	14869	177	60	10586	1	0	10583	10581	4378	2	0
2003				9175	0.6	0	9170	9170	2901	4.7	0
2004	15772			10202	0.6	0	10199	10199	3813	2.2	0
2005	14767	148	66	9794	0.8	0	9791	9791	3124	2.1	0
2006	14180	144	64	9275	0.8	0	9272	9272	3875	2.2	0
2007	14371	139	68	9392	1.6	0	9388	9388	3321	2.7	0

In Table 11, it can be seen that most of the water is withdrawn from surface water bodies. Almost all of the cooling water that is being withdrawn is led back to the surface water bodies. As this is the case, power plants do not play a significant role in the environmental theme 'desiccation'. One of the effects on the environment of using cooling water is heating of the surface water. This influences the oxygen content in the water body and may have negative effects on fish population. (CBS, PBL et al. 2010)

Cooling water discharge may also result in environmental impacts through the content of biocides in the cooling water. The cooling water is conditioned to prevent agglomeration of organisms and substances and to avoid corrosion in the power plant's cooling water circuit. (CBS, PBL et al. 2010) This is discussed in more detail in section 6.

The water requirement in a power plant can be divided into process and cooling water. The demand for cooling water supercedes the demand for process make-up water by far. Cooling water use is higher for power plants with lower efficiencies. Also a distinction should be made between power plants that use 'once through cooling' instead of cooling towers in which water



evaporates. Power plants with cooling towers have a somewhat lower efficiency as heat rejection⁵ at low temperatures is more difficult. Water withdrawal by power plants with cooling towers is in general lower per kWh; however the specific water consumption (water intake minus discharge) is significantly higher due to evaporation of cooling water.

The specific water consumption of gas fired NGCC power is in general lower compared to coal fired PCs and IGCCs as wet-scrubbing systems for gas cleaning (e.g. FGD) are not present, efficiencies are higher (less heat has to be disposed off) and more heat is discarded through the stack instead of heat rejection with cooling water (see Table 12). This also explains the lower specific water consumption of IGCCs compared to PC power plants shown in Figure 6. Roughly one third of the electricity in an IGCC is generated by the steam turbine(s) (which is cooled with water) and the remaining two third by the gas turbines. Relative more heat is rejected through the stack instead of heat discharge with the cooling water. (Ciferno 2010)

Table 12 Heat rejection in new power plants to be built in the Netherlands (KEMA 2006; KEMA 2006; KEMA 2006)

Conversion technology	Heat rejection in %		
	Cooling water	Other losses*	
NGCC	74%	26%	
PC	95%	5%	
IGCC	76%	24%	

*Includes flue gas losses.

7.2 Effect of CO₂ capture

There is insufficient information available in current open literature to draw firm conclusions on the effect on water consumption of power plants due to the application of CO_2 capture technologies. Water consumption depends heavily on process configuration and local (limiting) conditions. The limited information available suggests that the application of CO_2 capture significantly affects the specific water consumption. The water consumption is expected to increase due to the energy penalty. This implies predominantly an increase in cooling water usage. The capture system may also result in additional water demand. In Table 13, an overview is presented of several studies reporting the raw water use per kWh. The results of a recent study on water consumption of power plants with capture are shown in Figure 6.

The relative increase in water use is in most studies higher than the relative increase in primary energy. This is most distinctive for the post-combustion capture cases for which the water consumption almost doubles. This is the result of the large additional cooling requirement of the CO_2 capture process and additional demand in the scrubbing processes related to the capture plant. In Figure 6, the results are shown for power plants with evaporative cooling towers. For power plants that use 'once through cooling' water such an increase in water consumption would mean an increase in water withdrawal from and also heat rejected into surface water bodies. The exact effect would however strongly depend on the process design.

For the IGCC with pre-combustion the additional process water use is due to the additional water/steam requirement in the water gas shift (WGS) reaction (DOE/NETL 2007). The water consumption in an IGCC depends however on the gasification technology and design

⁵ Low temperature cooling agent results in a higher thermodynamic efficiency of the power plant. This efficiency is determined by the **difference** in temperature over the turbine (steam or gas).



considerations⁶. For three gasification technologies (General Electric, CononcoPhillips and Shell) and designs, the water demand and usage (consumption) is calculated in (DOE/NETL 2007). The results of that study show that differences in water demand in these three IGCCs vary approximately 11%. This variation is mainly due to the configuration of power plant with capture and then predominantly the place where the additional water/steam is added to the syngas prior to the water gas shift section. Whether the syngas is cooled with water (water quench) or steam is injected to provide the water for the WGS influences the water demand. The water *consumption* varies with about 10% and is mainly related to the origin of the water/steam required for the WGS (DOE/NETL 2007). For oxyfuel combustion the limited available data presented in Table 13 suggest an increase in water usage, although the increase is less then proportional to the increase in primary energy use. The water balance is expected to be different compared to PC power plants as the combustion process and flue gas cleaning processes applied will differ. The removal of water from the CO₂ in the first compression step is important for the oxyfuel concept. This will yield a certain amount of water which can (after treatment) be re-used in the power plant. Detailed quantitative information is however lacking in the consulted literature.



Figure 6 Specific water consumption of new coal fired power plants with evaporative cooling towers, derived from (Ciferno 2010). Note that the majority of Dutch power plants make use of once through water cooling and not of cooling towers. This would result in less water consumption but a higher water intake.

⁶ Water consumption is mostly determined by the configuration of the fuel feeding system (slurry or dry), ash handling, syngas humidifier (for WGS and for NOx mitigation in gas turbine), cooling tower (if applicable) and the condenser (Klett, Kuehn et al. 2005).



Table 13 Raw water consumption^a in conversion technologies equipped with various CO₂ capture technologies.

Conversion	Water	Water	Annual increase*	Relative	Relative
technology / CO ₂	usage no	usage with		increase in	increase in
capture technology	capture	capture		water use	primary energy
	oupturo	oupturo			
	1		3 -1		use
	l kWh '	l kWh '	million m [°] yr '	%	%
IGCC/ pre-combustion	2.57-3.12 [⊳]				
	0.6 ^c	0.9 ^c	1.97	50% ^c	16% ^c
	1.35-1.42 ^d	1.81-2.00 ^d	3.02-3.81	32-48% ^d	18-28% ^d
NGCC/ post-	1.88 ^b				
combustion	1.02 ^d	1.84 ^d	5.39	81% ^d	16% ^d
PC subcritical/ post-	4.43 ^b				
combustion	3.1 ^c				
	2.56 ^d	5.04 ^d	16.30	96% ^d	48% ^d
PC supercritical/ post-	3.94 ^b				
combustion	3.1 ^c	4.1 ^c	6.57	32% ^c	31% ^c
	2.25 ^d	4.34 ^d	13.74	93% ^d	44% ^d
Oxyfuel combustion	-	2.97-3.01 ^{e,t}	4.84-5.13	33-35% ^e	39-41% ^e
with CO ₂ removal					

This is calculated as the difference between a 1 GWe net power plant with capture with a 1 GWe net power plant without capture, both with a capacity factor of 75% (6575 full load hours yr⁻¹).

^aRaw water usage is defined as the total internal water consumption minus internal recycling.

^b(Klett, Kuehn et al. 2005) based on power plants equipped with evaporative cooling towers. Ranges for IGCC represent various gasifier technologies (GE, Shell, E-Gas).

^c(Odeh and Cockerill 2008) reflect life cycle emissions. Not specified whether figures are based on power plants with evaporative cooling tower(s) or once through cooling configuration.

^d(DOE/NETL 2007) based on power plants equipped with evaporative cooling towers. Ranges represent various gasifier technologies: GE, Shell and E-Gas. For cases from this source it is reported that 71-99% of water use is due to cooling tower water make-up.

e(DOE/NETL 2007) based on power plants equipped with evaporative cooling towers. Ranges represent variations in the purity of the oxygen supply for combustion. Compared to supercritical PC fired power plant without CO₂ capture as presented in (DOE/NETL 2007).

In regulations and guidelines in the Netherlands it is set that the water temperature of the discharge is restricted. For instance, the temperature increase due to the discharge may not be higher than 3 degrees with a maximum of 28 degrees Celsius. Also, the temperature of the discharge water should be kept below 30 degrees and the temperature difference between the cooling water and receiving water body should be kept below certain temperatures depending on the season and whether the receiving water body is salt or fresh water. In addition, limitations are present for the withdrawal of water. The withdrawal may not have significant influence on (juvenile) fishes, for instance. (CIW 2004)

When equipping power plants with CO_2 capture both the specific water withdrawal as total heat rejection most likely increases. Depending on the location and season, for instance during a drought, this may have the implication that power plants with CO₂ capture are more limited to run at full load compared to power plants not capturing CO₂; or they should be designed to cope with this limitation.



The aim of the study was to review the literature on solvent related emissions from the CO_2 capture process chain (the solvent production, the CO_2 capture process and the treatment of waste), on waste and by-product formation, on emissions to water and on water consumption from a power plant with and without CO_2 capture.

Literature data on these specific subjects appeared to be scarce. Hence, data from field experiments (pilot and demo plants) and expert opinions on these themes are highly recommended and welcomed by the authors.

On the basis of the currently available literature, the following conclusions can be drawn:

8.1 Solvent related emissions from the CCS chain

- There is a growing awareness on the possible environmental impacts of CO₂ capture. Focus of the current research in this field is on post-combustion carbon capture using amines, which could lead to the emission of carcinogenic nitrosamines.
- Theoretical studies on the formation of nitrosamines are available. Measurements campaigns are running, but the availability of data is very limited and/or confidential.
- The emissions to air from the production process depend on the type of solvent produced and show a large variation in NH_3 emissions.
- Large amounts of waste are produced by CO₂ capture process. As a first estimate, 1 tonne per hour will be produced in an average power plant. From a technical and economic point of view, the incineration does not seem to be a large issue. Although it is important that the capacities are available to handle large waste streams when CCS is employed at large scale. The incineration of waste creates additional emissions to air for which legislation maybe needs to be adapted.

8.2 Waste and by-products from CO₂ capture

- Waste formation is of relative less interest for gas fired power plants without capture. Post-combustion capture can result in significant additional waste formation depending on the technology variant chosen.
- Waste formation due to volume effects can be assessed accurately with the use of the energy penalty induced by installing the CO₂ capture installation.
- Waste formation due to post combustion capture process depends on solvent selection and process configuration. Detailed data on the formation and composition of wastes from CO₂ capture technologies are not available for most of the technology variants.
- Waste formation in oxyfuel power plants is still uncertain/unknown and is not quantified in the pertaining/consulted literature.
- Waste formation in pre-combustion capture seems to be very limited compared to postcombustion capture processes, but detailed data is lacking.



8.3 Emissions to water from CO₂ capture

- Emissions to water are of relative less interest for gas fired power plants without capture.
- There is relatively modest data known to be available on emissions to water bodies due to CO₂ capture, apart from volume effects (due to energy penalty). That is, it is possible to estimate the change in emissions due to increase in primary energy demand. It is however not known what the exact effect is of CO₂ capture technologies on the composition of waste water effluent.

8.4 Water consumption from CO₂ capture

- Overall water consumption for power plants depends strongly on the energy conversion technology, process configuration and on the applied cooling technology. It can in principle be assessed with high accuracy. When equipping power plants with CO₂ capture technologies the overall water withdrawal and consumption is expected to increase due to additional cooling water demand and process water demand. This holds to a lesser extent for oxyfuel power plants for which the water balance changes due to changes in the combustion process and flue gas cleaning technologies.



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Appendix A. Atmospheric degradation

Atmospheric degradation products of AMP, MDEA and PIPA

Atmospheric degradation of AMP











Atmospheric degradation of MDEA (2 of 2)





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In depth study of specific themes

Atmospheric degradation of PIPA





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

Table B1 Overview of health and environmentally related classifications (Svanes, 2008)



Table B2Overview of health and environmentally related classifications -
degradation compounds (Svanes, 2008)

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



Appendix C. Resource consumption

Table 1Resource consumption by energy conversion technologies equipped with and
without CO2 capture (Koornneef 2010)

Resource (process)	Technology	Source	Non capture (g kWh ⁻¹)	Capture (g kWh ⁻¹)	Annual increase ^a (kt yr ⁻¹)	Relative Increase (%)
Sorbent make-up (CO ₂ capture)	PC / post	(Odeh and Cockerill 2008) (Koornneef, van Keulen et al. 2008) (Davison 2007) (Davison 2007) (IEA GHG 2006) (DOE/NETL 2007) (DDE/NETL 2007) (NETL 2005; Jansen, Asbroek et al. 2008) (Knudsen, Vilhelmsen et al. 2006) (Knudsen, Jensen et al. 2008) (Oexmann and Kather 2009)	-	3.6 MEA 2.04 MEA 1.31 Fluor 0.13 MHI KS-1 1.31 MEA 0.37 Fluor (sub crit.) 0.33 Fluor (super crit.) 0.18 AA ^b 2.16 MEA ^c 1.26 MEA ^d 0.45 K ₂ CO ₃ /PZ ^e	23.67 13.41 8.61 0.85 8.61 2.43 2.17 1.18 14.2 8.28 2.96	-
	NGCC /post	(Odeh and Cockerill 2008) (IEA GHG 2006) (DOE/NETL 2007)	-	1.33 MEA 0.61 MEA 0.12 Fluor	8.74 4.01 0.79	-
	PFBC / post	¹ (Bryngelsson and Westermark 2009)	-	0.75 K ₂ CO ₃ [†]	4.93	-
	IGCC / pre	(Odeh and Cockerill 2008) (Davison 2007) (IEA GHG 2006)	0.02 Selexol 0.01 Selexol	0.03 Selexol 0.02 Selexol 0.005 MDEA	0.07 0.07 0.03	50% 100% -
Limestone ^g (FGD)	PC / post	(Odeh and Cockerill 2008) (Koornneef, van Keulen et al. 2008) (Davison 2007) (IEA GHG 2006) (DOE/NETL 2007)	16.9 5.6 8.4 8.4 33.6-35.9	27.2 7.5 11.4-11.6 11.6 48.2-52.7	67.72 12.49 19.72-21.04 21.04 95.99- 110.45	61% 34% 36%-38% 38% 43%-47%
Ammonia (SCR)	PC / Post	(Odeh and Cockerill 2008) (Koornneef, van Keulen et al. 2008)	0.61 0.31	0.80 0.41	1.25 0.66	31% 32%
	NGCC /post	(Odeh and Cockerill 2008)	0.20	0.23	0.20	15%

Note: sub crit. = subcritical steam parameters; super crit. = supercritical steam parameters indication higher generating efficiency, i.e. a lower capture penalty.

^aThis is calculated as the difference between a 1 GW_e power plant with capture and a 1 GW_e power plant without capture, both with a capacity factor of 75% (6575 full load hours yr¹).

^bAA= Aqueous Ammonia. Based on the assumption of 0.9 kg CO₂ captured kWh. Original value 0.2 g/kg captured (NETL 2005 ; Jansen, Asbroek et al. 2008).

[°]Based on the assumption of 0.9 kg CO₂ captured / kWh. Reported value 2.4 g/kg captured (Knudsen, Vilhelmsen et al. 2006).

^d It is reported that similar ranges were found for alternative solvents 'CASTOR 1' and 'CASTOR 2'. Based on the assumption of 0.9 kg CO₂ captured / kWh. Reported value 1.4 g/kg captured. (Knudsen, Jensen et al. 2008) ^ePiperazine promoted potassium carbonate. Based on the assumption of 0.9 kg CO₂ captured / kWh. Reported value 0.5 g/kg captured (Oexmann and Kather 2009).

Approximately 3.5% of the potassium carbonate to be replaced per year (de Meyer 2008). Based on the assumption of 0.9 kg CO₂ captured / kWh. Original value 0.83 g/kg CO₂ captured (Bryngelsson and Westermark 2009). ⁹Limestone use depends mainly on FGD efficiency and sulphur content of the fuel.