Carbon Dioxide Capture and Air Quality

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1. Introduction

Carbon dioxide (CO₂) is one of the most important greenhouse gases (GHG). The most dominant source of anthropogenic CO₂ contributing to the rise in atmospheric concentration since the industrial revolution is the combustion of fossil fuels. These emissions are expected to result in global climate change with potentially severe consequences for ecosystems and mankind. In this context, these emissions should be restrained in order to mitigate climate change.

Carbon Capture and Storage (CCS) is a technological concept to reduce the atmospheric emissions of CO₂ that result from various industrial processes, in particular from the use of fossil fuels (mainly coal and natural gas) in power generation and from combustion and process related emissions in industrial sectors. The Intergovernmental Panel on Climate Change (IPCC) regards CCS as “an option in the portfolio of mitigation actions” to combat climate change (IPCC 2005).

However, the deployment of CO₂ capture at power plants and large industrial sources may influence local and transboundary air pollution, i.e. the emission of key atmospheric emissions such as SO₂, NOₓ, NH₃, Volatile Organic Compounds (VOC), and Particulate Matter (PM₂.₅ and PM₁₀). Both positive as negative impacts on overall air quality when applying CCS are being suggested in the literature. The scientific base supporting both viewpoints is rapidly advancing.

The potential interaction between CO₂ capture and air quality targets is crucial as countries are currently developing GHG mitigation action plans. External and unwanted trade-offs regarding air quality as well as co-benefits when implementing CCS should be known before rolling out this technology on a large scale.

The goal of this chapter is to provide an overview of the existing scientific base and provide insights into ongoing and needed scientific endeavours aimed at expanding the science base. The chapter outline is as follows. We first discuss the basics of CO₂ capture, transport and storage in section 2. In section 3, we discuss the change in the direct emission profile of key atmospheric pollutants when equipping power plants with CO₂ capture. Section 4 expands on atmospheric emissions in the life cycle of CCS concepts. We provide insights in section 5 into how air quality policy and GHG reduction policy may interact in the Netherlands and the European Union. Section 6 focuses on atmospheric emissions from post-combustion CO₂
capture. We highlight in section 7 the most important findings and provide outlook on (required) research and development.

2. Carbon dioxide capture, transport and storage

2.1 CO₂ capture

The first step of the CCS chain is the capture process. A major element of this process comprises the separation of CO₂ from a gas stream. This can be the separation from produced natural gas, which often contains acid gases such as H₂S and CO₂. It also can be separated during the production of ammonia and during refining processes in the hydrocarbon industry. There is considerable less experience with removing CO₂ from flue gases at atmospheric pressure. This entails flue gases from power plants as well as industrial plants producing, for instance, steel, cement or iron. These large point sources form the largest potential for applying CO₂ capture. There are four approaches to capture CO₂ from large point sources: 1) Post-combustion capture; 2) Pre-combustion capture; 3) Oxyfuel combustion capture; 4) Capture from industrial processes.

![Diagram of CO₂ capture systems](https://www.intechopen.com)

**Fig. 1.** Simplified overview of the three CO₂ capture systems for power plants: post-, pre- and oxyfuel combustion. Grey components indicate power generation processes. Components with highlighted borders indicate processes causing a drop in generating efficiency. Components with dashed borders indicate optional processes. Note that natural gas reforming using steam is an endothermic process and therefore not a power generation process, hence the altered shading.
2.1.1 Post-combustion capture

CO₂ can be captured from the flue gas of a combustion process. This can be flue gas coming from any (pressurized) combustion in a boiler, gas turbine or industrial process yielding CO₂. Various capture mechanisms, or combinations of them, can be applied, being: phase separation, selective permeability and sorption. The last mechanism, sorption, is the most widely suggested mechanism to be used at large point sources. This mechanism encompasses chemical or physical absorption and also adsorption. In the CO₂ capture processes based on this mechanism a sorption medium, or a sorbent, is used. When these sorbents are in solution they are called solvents. The current research, development and demonstration (RD&D) focus is on using chemical and physical solvents to separate the CO₂ from the gas stream. Retrofitting existing power plants with CO₂ capture will highly likely be done with a chemical absorption based post-combustion capture technology.

The RD&D focus in post-combustion capture is mainly aimed at reducing energy requirement and capital cost through developing and adapting solvents, optimizing the required process installations and integrating the capture system with the power generation process. The application of the capture process on contaminated flue gases, e.g., flue gases from coal-fired power plants, is already commercially applied (Strazisar, Anderson et al. 2003). However, large-scale CO₂ capture as well as dealing with the contaminants in the flue gas remains a challenge.

2.1.2 Pre-combustion capture

Pre-combustion capture comprises a group of technologies that removes CO₂ before the combustion of the fuel. This requires a carbonaceous fuel to be broken down into hydrogen (H₂) and carbon monoxide (CO), i.e., syngas. To make CO₂ capture with high efficiencies possible, the syngas that is formed after steam reforming or partial oxidation/gasification has to be shifted after it is cleaned. The ‘shift reaction’, or ‘water gas shift’ (WGS) reaction, yields heat and a gas stream with high CO₂ and H₂ concentrations. The CO₂ can then be removed with chemical and physical solvents, adsorbents and membranes.

For the near-term it is expected that chemical or physical solvents (or a combination) are used for the CO₂ removal. The CO₂ removal step yields relative pure CO₂ and a gas stream with a high hydrogen and low carbon content. The latter can be used for power production in for example a (modified) gas turbine. The gas with reduced carbon content can (after further purification) also be used in the production of synfuels, the refining of hydrocarbons or for the production of chemicals. (IPCC 2005)

For solid and liquid fuels, pre-combustion CO₂ capture can be applied in an IGCC (Integrated Gasification Combined Cycle) power plant. For gas-fired power generation with pre-combustion capture other concepts are being studied (Ertesvåg, Kvamsdal et al. 2005; Kvamsdal and Mejdell 2005; IEA GHG 2006c; Kvamsdal, Jordal et al. 2007).

The technology to capture CO₂ from the syngas generated in a gasifier can be considered proven technology, is commercially available and used for several decades in other applications than for electricity production. Examples are hydrogen, ammonia and synthetic fuel production (Nexant Inc. 2006). Also, reforming and partial oxidation of (natural) gas are already widely applied, e.g., for the production of hydrogen in the ammonia production process.

The pre-combustion concept has not yet been proven in an IGCC power plant. Proving its reliability and effectiveness in power plant concepts is therefore one of the main RD&D targets. In addition, improving the efficiency of the WGS step and integration of this process with CO₂ capture is also an area of research.
2.1.3 Oxyfuel combustion

Oxyfuel combustion is based on denitrification of the combustion medium. The nitrogen is removed from the air through a cryogenic air separation unit (ASU) or with the use of membranes. Combustion thus takes place with nearly pure oxygen. The final result is a flue gas containing mainly CO$_2$ and water. The CO$_2$ is purified by removing water and impurities. The production of oxygen requires a significant amount of energy, which results in a reduction of the efficiency of the power plant. Further, the purification and the compression of the CO$_2$ stream also require energy.

The combustion with oxygen is currently applied in the glass and metallurgical industry (Buhre, Elliott et al. 2005; IPCC 2005; M. Anheden, Jinying Yan et al. 2005). Oxyfuel combustion for steam and power production using solid fuels has been at present only proven in test and pilot facilities. Oxyfuel combustion can also be applied in natural gas fired concepts. Power cycles for gaseous and solid fuels, however, vary significantly. Although there are no significant differences compared to air firing of solid fuels, the combustion process and optimal configuration of the burners are considered to be the most important hurdles to overcome. In addition, the design and configuration of the flue gas cleaning section and CO$_2$ purification section are challenges for the short-term. For the gas fired concepts, system integration and development of critical components hinder direct application on a commercial scale. Examples of critical components are the turbines and combustors for the near- and medium-term options and, additionally, the fuel reactors for the concepts in the longer term.

2.1.4 Capture from industrial processes

This group of technologies is often mentioned as the early opportunity for CCS at relative low cost. The total reduction potential due to CO$_2$ capture from these point sources is however considered to be rather limited. Examples for industrial processes are: the production of cement, iron and steel, ethylene (oxide), ammonia and hydrogen. In addition, CO$_2$ can be captured from natural gas sweetening processes and from refineries (IPCC 2005). The capture processes applied are in general the same technologies as already described above.

2.1.5 Increased primary energy use

When applying CO$_2$ capture, energy is needed to separate the CO$_2$ and compress the CO$_2$ to pressures required for transport. This energy consumption results in a reduction of the overall efficiency of for instance a power plant. This reduction is called the efficiency penalty, or energy penalty. Table 1 shows typical energy penalties for power generation concepts with CO$_2$ capture. Post-combustion CO$_2$ capture and capture using oxyfuel combustion of solid fuels show about equal increases in primary energy use. For post-combustion this increase is mainly determined by the heat requirement in the capture process. In oxyfuel combustion the separation of oxygen from the air is the main factor causing a drop in efficiency, i.e. about half of the efficiency penalty when considering a coal fired power plant (Andersson and Johnsson 2006). Both systems require significant compressor power to boost the CO$_2$ from atmospheric to transport pressures (i.e. > 100 bar). This compressor power is substantially lower in the pre-combustion technology as the CO$_2$ is removed under pressures higher than atmospheric. The required steam and the removal of chemical energy from the syngas in the process prior to CO$_2$ removal, the water gas shift reaction, contributes the most to the
increase in primary energy use. The CO₂ removal itself requires less energy in this concept. Overall, the relative increase in primary energy is the lowest for the pre-combustion capture concepts. For the gaseous fuel fired concepts, the increase in primary energy requirement is relatively lower because of the lower carbon content per unit of primary energy.

2.2 CO₂ transport
The captured CO₂ can be transported as a solid, gas, liquid and supercritical fluid. The desired phase depends on whether the CO₂ is transported by pipeline, ship, train or truck. Of these options, transport by pipeline is considered the most cost-effective one. The transport of CO₂ by pipeline in the gas phase is not favourable for projects that require the transport of significant amounts of CO₂ over considerable distances. The disadvantageous economics (large pipeline diameter) and relative high energy requirement (due to the large pressure drop) are the reasons for this (IPCC 2005; Zhang, Wang et al. 2006). Increasing the density of CO₂ by compression renders the possibility to transport the CO₂ with less infrastructural requirements and lower cost.

There is worldwide experience in transporting CO₂ using the transport media mentioned above in the oil industry for enhanced oil recovery (EOR) by injecting CO₂ into an oil field. CO₂ transport by ship is being conducted on a small scale, but is being researched as a possibility to reach offshore storage capacity or as a temporary substitute for pipelines (IEA GHG 2004; Aspelund, Molnvik et al. 2006). Transport by ship can be economically favourable when large quantities have to be transported over long distances (>1000 km) (IPCC 2005). It requires the compression and liquefaction of the CO₂.

2.3 CO₂ storage in geological formations
The last step in the CCS chain is the injection of CO₂ into geological formations. Alternatives to injection in geological formations are injection into the deep ocean and sequestration through mineral carbonation, but the current research focus is on storage in geological formations. CO₂ storage in these geological formations encompasses the injection of CO₂
into porous rocks that may hold or have held gas and or liquids. In literature, several storage media are proposed, especially: deep saline formations (aquifers); (near) empty oil reservoirs, possibly with enhanced oil recovery (EOR); (near) empty gas reservoirs, possibly with enhanced gas recovery (EGR) and deep unminable coal seams combined with enhanced coal bed methane production (ECBM). (Van Bergen, Pagnier et al. 2003; IPCC 2005) The total CO₂ storage capacity ranges between 2 and 11 Tt. It should be stressed that high uncertainties still persist regarding the estimation of storage capacity due to the use of incomplete data or simplified assumptions on geological settings, rock characteristics, and reservoir performance (Bradshaw, Bachu et al. 2006). Despite the uncertainty of these estimates, the figures suggest that there is enough storage potential to support CO₂ emissions reduction with CCS for considerable time. In practice, matching the temporal and geographical availability of sources and sinks may become a bottleneck.

3. Change in key atmospheric emissions due to CO₂ capture

Key direct atmospheric emissions of specific interest for biomass and coal fired concepts are CO₂, NOₓ, NH₃, SO₂, HCl, HF, VOC, PM, Hg, Cd, and other heavy metals. For gas fired concepts CO₂ and NOₓ are the most dominant atmospheric emissions. Equipping power plants with CO₂ capture technologies affects both the formation and fate of many of these emissions. We limited our study to three main capture systems for the removal of CO₂ depicted in Fig. 1: post-combustion, pre-combustion and oxyfuel combustion. The chemical absorption technologies that we reviewed in detail include technologies using alkanolamines, such as monoethanolamine (MEA), Fluor’s Econamine FG+ and MHI’s KS-1 solvent. Other technologies reviewed are based on absorption using chilled ammonia (NH₃), alkali salts (i.e. potassium carbonate -K₂CO₃) and amino salts. The post-combustion system can be applied to various energy conversion technologies. In this study we focus on its application to Pulverized Coal (PC), Natural Gas Combined Cycle (NGCC) and Pressurized Fluidized Bed Combustion (PFBC) power plants. The energy conversion technology that is envisaged using pre-combustion that is mainly investigated in this study is the Integrated Gasification Combined Cycle (IGCC) power plant. The energy conversion technologies using oxyfuel combustion that have been reviewed in this study more extensively are rather conventional PC and NGCC power plants. Advanced technologies briefly touched here include, for instance, chemical looping combustion.

A summary of emission factors for key atmospheric emissions reported in literature for these technologies is presented in Fig. 2. The main effects of CO₂ capture on atmospheric emissions are summarized below for the key atmospheric emissions.

3.1 Carbon dioxide

CO₂ emissions predominantly depend on the type of fuel, on the efficiency of the energy conversion and of the removal efficiency of CO₂. The removal efficiency for the oxyfuel combustion concept is found to be the highest on average (95-98%), yielding the lowest CO₂ emissions for the gas fired conversion technologies (0-60 g/kWh). Post- and pre-combustion show about equal removal efficiencies of 87-90% and 89-95%, respectively. The typically higher conversion efficiency for gasification or reforming results however in typically lower net CO₂ emissions for the pre-combustion concepts (21-97 g/kWh) compared to the post-combustion concepts (55-143 g/kWh).
3.2 Sulphur dioxide

In the coal fired power plants equipped with post-combustion CO\textsubscript{2} capture, SO\textsubscript{2} emissions are reduced significantly compared to a power plant without capture. One reason is that power plants with CO\textsubscript{2} capture should be equipped with improved flue gas desulphurization (FGD) facilities (Tzimas, Mercier et al. 2007). Furthermore, additional removal in the post-combustion capture process is expected. Koornneef et al. (2010) summarized reported values in literature and show that the minimum expected additional reduction per MJ\textsubscript{primary} compared to a power plant without CO\textsubscript{2} capture is approximately 40%; on average it is 85%.

For the amine based concept it is required to reduce the concentration of SO\textsubscript{x} in the inlet gas of the CO\textsubscript{2} capture facility as these compounds may react with the solvent, which leads to the formation of salts and solvent loss. Knudsen et al. (2006;2008) for instance reported a 40-85% uptake of total sulphur depending on the type of solvent\textsuperscript{1} used. Iijima et al. (2007) and Kishimoto et al. (2008) report that a minimum of 98% of the SO\textsubscript{2} is additionally removed\textsuperscript{2} before entering the CO\textsubscript{2} capture process. They state that then ‘almost all’ of the still remaining SO\textsubscript{2} is removed from the flue gas as salts. In literature studies additional SO\textsubscript{2} reductions of 90-99.5% are assumed (Rao and Rubin 2002;IEA GHG 2006a;Tzimas, Mercier et al. 2007;Koornneef, van Keulen et al. 2008).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig_2.png}
\caption{Atmospheric emissions of substances CO\textsubscript{2}, NO\textsubscript{x}, SO\textsubscript{2}, NH\textsubscript{3} and particulate matter for various conversion technologies with and without CO\textsubscript{2} capture, adapted from (Koornneef, Ramirez et al. 2010). Ranges indicate maximum and minimum values reported. Note that emissions are based on various fuel specifications and on the configuration and performance of the power plant and CO\textsubscript{2} capture process. ‘nr’ = ‘not reported’.
}
\end{figure}

\textsuperscript{1} During field tests MEA (monoethanolamine) and the amine based ‘Castor 1’ and ‘Castor 2’ solvents were tested. The Castor 2 solvent resulted in the 40 % uptake of sulphur compared to 80% for MEA.

\textsuperscript{2} This additional reduction succeeding the conventional FGD is achieved by the reaction of SO\textsubscript{x} with caustic soda in the flue gas cooler which cools the flue gas before it enters the absorber.
The other post-combustion technology considered here uses chilled ammonia as solvent to remove the CO\textsubscript{2} from the flue gas. Remaining SO\textsubscript{2} in the flue gas can according to Yeh and Bai (1999) react with the ammonia solution to form the recoverable ammonium sulphate. All in all, it is expected that most of the acid gases can be removed from the flue gas when a proper design of the scrubbing process is applied (Yeh and Bai 1999). However, at present no quantitative estimates for additional SO\textsubscript{2} reduction in the CO\textsubscript{2} absorption process based on chilled ammonia are available.

For oxyfuel combustion technologies the SO\textsubscript{2} emissions will generally decrease compared to conventional coal fired power plants. The reduction can be the result of several mechanisms: increased ash retention, enhanced efficiency of conventional FGD, co-injection and the possibility for new SO\textsubscript{x} removal technologies.

According to Buhre et al. (2005) and Anheden et al. (2005) the amount of SO\textsubscript{x} formation per tonne of coal combusted is essentially unchanged when applying oxyfuel combustion. However, the composition and concentration of SO\textsubscript{x} constituting SO\textsubscript{2} and SO\textsubscript{3}, does change as the flue gas stream is reduced in both volume and mass. A higher SO\textsubscript{x} concentration in the flue gas may pose equipment corrosion problems. A possible positive effect is that it also may enhance the capture efficiency of the electrostatic precipitator (ESP) (Tan, Croiset et al. 2006). Another expected positive side effect is that a higher SO\textsubscript{x} concentration may increase the removal efficiency\(^3\) of FGD technologies. Moreover, the reduced flue gas stream allows for smaller equipment. (Marin and Carty 2002; Chatel-Pelage, Marin et al. 2003; Chen, Liu et al. 2007; WRI 2007)

The issues, challenges and design considerations taken into account when designing the flue gas cleaning section for oxyfuel combustion are presented in (Yan, Anheden et al. 2006). There, possible configurations for flue gas cleaning are predominantly based on (adapted) conventional flue gas cleaning technologies. The additions compared to a conventional configuration consisting of an SCR, ESP and FGD, are a flue gas cooler (FGC) and CO\textsubscript{2} compression & purification process. The FGC is aimed to reduce the temperature, acidic substances (SO\textsubscript{2} between 93 and 97%, SO\textsubscript{3} between 58 and 78%), water content (>85%) and particulates (>90%) in the flue gas prior to compression. In the following compression & purification step additionally NO\textsubscript{x}, SO\textsubscript{2}, HCl, water and heavy metals are removed as condensate from the compressors, and with the use of an activated carbon filter and an adsorber (Burchhardt 2009; Thébault, Yan et al. 2009; Yan, Faber et al. 2009). Overall, a deep reduction of SO\textsubscript{2} and NO\textsubscript{x} emissions is expected to be possible with oxyfuel combustion, although R&D is required to better understand the behaviour of these substances in the CO\textsubscript{2} compression & purification process.

Co-injection of sulphur compounds into the underground together with the CO\textsubscript{2} is technically possible. Another possibility is the removal of sulphur compounds in condensate streams after compression of the flue gas. Both options would make the FGD section redundant. As suggested by White et al. (2008) the SO\textsubscript{2} may be recovered from the CO\textsubscript{2} stream in the form of sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) through reaction with NO\textsubscript{2}. Experiments indicate SO\textsubscript{2} conversion efficiencies between 64 and ~100% depending on process conditions (White, Torrente-Murciano et al. 2008).

\(^3\) Tests in a research facility indicate that SO\textsubscript{x} removal was improved in the case of oxygen rich combustion, which can partly be explained by longer gas residence time in the FGD (Marin and Carty 2002; Chatel-Pelage, Marin et al. 2003; Chen, Liu et al. 2007; WRI 2007).
In circulating fluidized bed boilers often limestone is injected into the furnace to control SO\textsubscript{x} emissions. In the case of oxygen firing the in-furnace desulphurization efficiency with limestone is found to be between 4 and 6 times higher compared to air firing (Buhre, Elliott et al. 2005; ZEP 2006).

The variance shown in Fig. 2 is due to parameters that may vary case by case, e.g. the sulphur content in the coal, uncontrolled SO\textsubscript{x} emission (including ash retention), removal efficiency of the FGD section, removal in CO\textsubscript{2} purification section and the degree of co-injection.

IGCC power plants have low SO\textsubscript{2} emissions, either with or without pre-combustion CO\textsubscript{2} capture. This is due to the high (typically > 99\%) removal efficiencies of sulphur compounds (H\textsubscript{2}S and COS) in the acid gas removal section and adjoined facilities. The application of pre-combustion CO\textsubscript{2} capture in an IGCC is assumed to enhance the SO\textsubscript{2} removal. The application of CO\textsubscript{2} capture is likely to result in a decrease of the emission of SO\textsubscript{2} per MJ\textsubscript{primary}, but depending on the efficiency penalty may result in an increase per kWh. Both increase and decrease per kWh have been reported in literature. The reduction per MJ\textsubscript{primary} is expected to be lower compared to the post-combustion and oxyfuel combustion technologies (see Fig. 2). With pre-combustion it is also possible to yield a stream of CO\textsubscript{2} with H\textsubscript{2}S and co-inject this into the underground. This may however complicate the transport and storage process. Also, it may be prohibited by national law and varies per country.

### 3.3 Nitrogen oxides

If an amine based solvent is used for post-combustion capture, the reduction of NO\textsubscript{x} emissions per MJ\textsubscript{primary} is expected to be small, i.e. between 0.8 and 3\%\textsuperscript{4} (Knudsen, Vilhelmsen et al. 2006; Kishimoto, Hirata et al. 2008). CO\textsubscript{2} capture requires a significant increase in primary energy use resulting in a net increase in NO\textsubscript{x} emissions per kWh. For the chilled ammonia technology, the NO\textsubscript{x} emissions are not known to be affected by the CO\textsubscript{2} absorption process. It is, therefore, likely that emissions will increase proportionally with the increase in primary energy use.

For oxyfuel combustion, in general, net NO\textsubscript{x} emissions per MJ\textsubscript{primary} are likely to decrease compared to conventional coal fired power plants. The two most important factors are that coal fired oxyfuel power plants are likely to show lower levels of NO\textsubscript{x} formation in the combustion process and that further high degree of removal of NO\textsubscript{x} in the CO\textsubscript{2} treatment train is possible.

NO\textsubscript{x} emission reduction and underlying mechanisms are fairly well understood for the oxyfuel combustion technology. NO\textsubscript{x} formation during oxyfuel combustion is found to be lower as thermal NO\textsubscript{x} formation is suppressed and fuel NO\textsubscript{x} is reduced (Croiset and Thambimuthu 2001; Buhre, Elliott et al. 2005; Tan, Croiset et al. 2006; WRI 2007). Overall, the reduction potential for NO\textsubscript{x} formation of oxyfuel combustion is according to several experiments in the range of 60-76\% (Chatel-Pelage, Marin et al. 2003; Buhre, Elliott et al. 2005; Farzan, Vecci et al. 2005; Andersson 2007; Yamada 2007). However, also no reduction has been found in some experiments (Anheden, Jinying Yan et al. 2005).

\textsuperscript{4} The main fraction of NO\textsubscript{x} is formed by NO which is expected to be unaffected by the CO\textsubscript{2} capture process. NO\textsubscript{2} fraction of NO\textsubscript{x}, which is typically about 5-10\%, may react with the solvent resulting in a reduction of NO\textsubscript{x} emission per MJ\textsubscript{primary}. However, also not all of the NO\textsubscript{2} is expected to react, i.e. only 25\% (Rao and Rubin 2002; IPCC 2005).
The final emission of NOx depends also on the flue gas treatment section. The flue gas has a high CO2 concentration, but also contains NOx, Ar, N2, O2 and SO2 when it enters the CO2 treatment train. There are several options for the treatment of the raw CO2 stream. None of them requires a DeNOx facility like SCR or SNCR5 (DOE and NETL 2007). The first option is to co-inject the NOx together with the CO2. This requires only compression and drying of the flue gas stream. The second option is to purify the CO2 with multiple auto-refrigeration flash steps. The gaseous pollutants are, in that case, separated from the CO2 stream to a high degree and vented into the atmosphere. The remaining fraction is co-injected. A DeNOx installation may be used to clean the vent stream (IEA GHG 2006b). Another concept is suggested and tested by White et al. (2006;2008) and incorporates compression of the flue gas and removal of NOx in the form of nitric acid (HNO3) through a series of reactions6. Preliminary results suggest that 48-90% of the NOx is converted to nitric acid7 and can consequently be removed from the CO2 stream.

The oxyfuel combustion variant shows no NOx emissions from gas fired power plants equipped with CO2 capture. This estimate is based on one literature source only, i.e. see (Davison 2007). This may result in an underestimation of NOx emissions. As the purity of the oxygen stream is in practice not 100%, some nitrogen may still be present in the combustion air, causing some NOx formation (IEA GHG 2006c). Whether this is co-injected or separated depends on process configuration.

During normal operation of the IGCC with pre-combustion CO2 capture, NOx will be mainly formed during the combustion of the hydrogen rich gas with air in the gas turbine. The application of CO2 capture in an IGCC will decrease the NOx emissions per MJprimary as relatively less gas is combusted in the gas turbine per unit of primary energy input. This outcome strongly depends on the assumption that the issue of NOx formation in a gas turbine fired with fuel gas with a high hydrogen content is solved by turbine manufacturers. The flame temperature is namely dependent on the gas composition and heating value. Both of these will change when applying CO2 capture. If dilution with steam or nitrogen is not applied, the flame temperature during firing of hydrogen rich fuel will increase resulting in an increase in NOx formation. Consequently, emissions per kWh can also become higher when applying CO2 capture. The uncertainty is thus higher than the range indicated in Fig. 2. This is however not quantified. (Chiesa, Lozza et al. 2005;IEA GHG 2006c;Davison 2007;DOE/NETL 2007;Tzimas, Mercier et al. 2007)

For gas fired concepts equipped with pre-combustion capture, NOx emissions are uncertain but expected to be typically higher than for conventional state-of-the-art NGCC cycles (Kvamsdal and Mejdell 2005).

Further NOx emission reduction can be achieved by adding an SCR process. A possible trade-off for SCR application is the emission of unreacted ammonia, or ammonia slip. This is especially the case when the SCR is applied on exhaust gases with low NOx concentrations. Ammonia slip from a SCR are however very small (<5 ppmv) and is assumed comparable to

5 S(N)CR = Selective (Non) Catalytic Reduction; a technology to reduce NOx emissions by converting NOx into N2 with the use of reactants, such as fun instance ammonia or urea.
6 These reactions are (taken from (White, Torrente-Murciano et al. 2008)): 2 NO2 + H2O ↔ HNO2 + HNO3 and 3 HNO2 ↔ HNO3 + 2 NO + H2O.
7 A potential by-product of this process may be mercuric nitrate (NO3)-2Hg2+ which is formed due to a reaction between the nitric acid and mercury in the flue gas. Although this substance is highly toxic it means that mercury is effectively removed from the flue gas.
normal air combustion in a pulverized coal power plant and a NGCC power plant. An optimum between NO$_x$ reduction and ammonia slip is however to be determined (Rao 2006).

3.4 Ammonia
Ammonia slip from DeNOx facilities is the main source of NH$_3$ emissions from conventional fossil fuel fired power plants without CCS. A significant increase of NH$_3$ emissions may be caused by oxidative degradation of amine based solvents that possibly will be used in post-combustion CO$_2$ capture. In the chilled ammonia technology, the unwanted emission of NH$_3$ from the CO$_2$ capture process is a serious challenge (Yeh and Bai 1999). This emission is expected to be significantly reduced by adding a water wash section at the outlet of the CO$_2$ capture process and by adaptations in the capture process (Yeh and Bai 1999; Corti and Lombardi 2004; Kozak, Petig et al. 2008). As indicated, the uncertainty regarding the estimation of NH$_3$ emissions can be considered high as the scientific literature reports a variety of values (Rao and Rubin 2002; IEA GHG 2006a; Knudsen, Jensen et al. 2008). Furthermore, new solvents and additional treatment options are possible to prevent or mitigate the emission of ammonia. The ranges shown in Fig. 2 are thus rather conservative estimates.
For oxyfuel combustion, no quantitative estimates for ammonia emissions are known to be reported.
Ammonia formed during gasification is effectively removed in the gas cleaning section in an IGCC with pre-combustion. Therefore, emissions are considered negligible.

3.5 Volatile organic compounds
No quantitative estimates for VOC emissions could be derived due to a lack of quantitative information in the pertaining literature. It is possible that VOC emissions are not significantly influenced by the post-combustion CO$_2$ capture process. In that case the VOC emissions will increase with the increase in primary energy use. However, degradation of amine based solvents may result in the emission of volatile substances, e.g. formaldehyde, acetone, acetaldehyde (Knudsen, Jensen et al. 2008). New solvents are being developed and tested that do not show these degradation products (Hopman. 2008; Knuutila, Svendsen et al. 2009).
No clear information was found on the effect of oxyfuel combustion on the formation, reduction and final emission of VOC. However, the oxygen rich conditions during combustion may have an effect on VOC formation. The fate of the formed VOC is uncertain, but it is plausible that a part of the VOCs is either co-injected or vented from the CO$_2$ purification section (Harmelen, Koornneef et al. 2008).
In IGCC power plants there are two main origins of VOC emissions: the gas turbine section and the fuel treatment section. The formation of VOC in the first is expected to be reduced due to pre-combustion CO$_2$ capture and the associated higher hydrogen content of the fuel gas. Quantitative estimates for the reduction of VOC are however not available. The emissions from the fuel treatment section are expected to remain equal per MJ$_{primary}$. VOC emission reporting for an IGCC operating in the Netherlands does not provide decisive insights into which section is the dominant source of VOC (NUON 2005; NUON 2006). The net effect of both may thus be an increase or decrease per kWh. For gas fired cycles, the replacement of natural gas with hydrogen rich fuel gas is expected to lower the emission of VOC.
3.6 Particulate matter

Often no distinction is made in the consulted literature between various sizes\(^8\) of emitted particulate matter in emission reporting. In this review, therefore also no distinction could be made between size fractions.

The high variance for post-combustion capture technologies for solid fuel fired power plants stands out in Fig. 2. The variance represents the varying assumptions in literature. On the one hand, some scholars assume a deep reduction of PM due to the application of post-combustion CO\(_2\) capture; on the other hand, other scientists assume that it will not have an effect on PM emissions. Results from an amine based post-combustion capture demonstration project however indicate a decrease in emission of particulate matter of 64-80\(^9\) per MJ\(_{\text{primary}}\) (Kishimoto, Hirata et al. 2008). Also Kozak et al. (2008) suggest a decrease with the use of chilled ammonia technology\(^{10}\). An increase in emission per MJ\(_{\text{primary}}\) is never assumed. Together with the energy penalty due to CO\(_2\) capture, PM emissions may however increase per kWh.

The low particulate matter emissions found for the oxyfuel combustion technology are partly due to the enhanced removal efficiency of the ESP\(^{11}\) that is possible during oxyfuel combustion. Particulates may also be partially co-injected with the CO\(_2\) stream. Another possibility is that particulates are vented from the CO\(_2\) treatment section. Yet another option is that PM is removed with the condensate stream that is formed when SO\(_2\) and NO\(_x\) are removed as sulphuric and nitric acid, as mentioned earlier. All together, PM emissions are estimated to be very low.

IGCC power plants are assumed to have lower PM emission factors compared to other conversion technologies and types of power plants. Pre-combustion CO\(_2\) capture has virtually no influence on the emission of PM (per MJ\(_{\text{primary}}\)) from an IGCC.

Although no quantitative estimates are available, it may be possible that PM emissions, in specific PM\(_{2.5}\) emissions, will be lower due to the enhanced capture of sulphur compounds from the syngas, which is expected to reduce the formation of sulphates, which are characterized as PM\(_{2.5}\).

3.7 Other atmospheric emissions of interest

Fig. 1 shows that the post-combustion CO\(_2\) capture process is situated after the flue gas cleaning section. Depending on the type of solvent that is used, impurities need to be removed from the flue gas in order to limit operational problems. When MEA is used, its consumption in the capture process is mainly caused by degradation by oxygen and impurities in the flue gas. Important impurities are sulphur oxides (SO\(_x\)), nitrogen dioxide (NO\(_2\)), hydrogen chloride (HCl), hydrogen fluoride (HF) and particulate matter as they react

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\(^8\) Particulate matter can be subdivided into particles with a diameter larger than 10 microns (>PM10) and smaller than 10 microns (PM10). PM10 can then be further subdivided into the size categories ‘Coarse’ (PM2.5-10) and ‘fine’ (PM2.5).

\(^9\) ‘Dust’ (not further specified as PM10 or PM2.5) emissions are reduced by 40-50% in the flue gas cooler prior to the absorption process in which another 40-60% of the particulates is removed from the flue gas.

\(^{10}\) They do not report a quantitative estimate but suggest that the flue gas cooler will result in a deep reduction of particulate matter entering the absorption process.

\(^{11}\) The efficiency of the Electrostatic Precipitator is possibly improved as a larger share of SO\(_x\) is represented by SO\(_3\) (Tan, Croiset et al. 2006).
with the MEA or cause foaming of the solvent. This may result in reduction of HF and HCl emissions. Estimates in literature vary but are as high as 90-95%.

Power plants equipped with CO\textsubscript{2} capture should thus be equipped with highly efficient flue gas desulphurization (FGD), DeNO\textsubscript{x} installations and electrostatic precipitators (ESP) and/or fabric filters to remove PM. Also, the flue gas typically requires cooling before it is processed in the CO\textsubscript{2} capture installation. In the CO\textsubscript{2} capture process also some of these substances are partially removed. The capture process is thus expected to affect (i.e. lower) the emission of these air pollutants directly and indirectly.

The consumption of solvent in the capture process is an important driver for solvent development as solvent loss deteriorates operational economics and has environmental consequences. The consumption of the solvent varies per type of solvent but is for post-combustion typically in the order of 1-2 kg/tonne CO\textsubscript{2} captured. Recent pilot plant test campaigns report solvent consumption rates for MEA at 0.3 kg/tonne captured (Moser et al. 2011). Typically, the consumption of MEA is higher compared to its alternatives. Moreover, the consumption of solvent used in IGCC with or without pre-combustion concepts can be considered very low, although an increase is expected when CO\textsubscript{2} capture is applied.

The higher oxygen concentration in the flue gas from natural gas combustion possibly results in higher oxidative degradation of solvents. MEA is to instance susceptible for this type of degradation (Supap, Idem et al. 2009). However, as other impurities such as SO\textsubscript{2} and PM are virtually not present in the flue gas, overall degradation and consumption is considerably lower compared to coal fired power plants.

For some post-combustion variants additional atmospheric emissions are expected. More specifically, the emission of solvent or degradation products of the solvent are currently of high interest (see section 6). For MEA based solvents this may be direct MEA emissions. The exact quantity of this ‘MEA slip’ (estimates range between 1 and 4 ppmv) and possible effects on the environment, including human safety, are not fully known but are intensively researched. In addition, solvent additives (e.g. corrosion inhibitors) may result in trace emissions of heavy metals (Thitakamol, Veawab et al. 2007).

For the chilled ammonia process solvent emissions may be NH\textsubscript{3} (Yeh and Bai 1999; Corti and Lombardi 2004; Kozak, Petig et al. 2008). The alkanolamine based solvents may result in the emission of VOC and NH\textsubscript{3} due to the degradation of the solvent (Strazisar, Anderson et al. 2003; Rao, Rubin et al. 2004; Knudsen, Jensen et al. 2008). Korre et al. (Korre, Nie et al. in press) report that NH\textsubscript{3} emission from using the MHI KS-1 solvent is expected to be higher than from using MEA or potassium carbonate\textsuperscript{12}. Contrarily, IEA GHG (IEA GHG 2006a) reports lower values for NH\textsubscript{3} emissions for the MHI KS-1 process compared to Fluor’s process based on MEA.

For a K\textsubscript{2}CO\textsubscript{3} based sorbent the slip into the atmosphere is considered negligible. Furthermore, this substance is considered to be less toxic to the environment (Oexmann and Kather 2009; Smith, Ghosh et al. 2009). K\textsubscript{2}CO\textsubscript{3} may however require the addition of promoters to increase the reaction rate. Some promoters, like arsenic trioxide and piperazine, are known to be toxic (Smith, Ghosh et al. 2009).

Allaie and Jaspers (Allaie and Jaspers 2008) claim that the use of amino salts does not result in ammonia formation, losses due to evaporation and virtually nihil emissions of the solvent.

\textsuperscript{12} In this case the Piperazine, an amine, is added to the potassium carbonate sorbent as an activator to increase reaction rate.
Mercury (Hg) and other heavy metals may be partially removed in the CO\textsubscript{2} capture process. Measurements on reclaimer bottoms have indicated that mercury is present in the bottoms (Strazisar, Anderson et al. 2003). A recent study however indicates that a combined process of removing mercury and CO\textsubscript{2} would not lead to significant reductions, i.e. below 15% (Cui, Aroonwilas et al. 2010).

In coal and biomass fired \textit{pre-combustion} concepts using solvents, no solvent emission to the air is expected during normal operation as any slip of the solvent would be combusted in the gas turbine or end up in the CO\textsubscript{2} stream. For this technology, \textit{co-sequestration} of H\textsubscript{2}S is a technical possibility and co-injection is common in for instance Canada (Thomas and Benson 2005).

Carbon monoxide emissions from an IGCC with capture are reduced as the WGS process is introduced, converting CO and H\textsubscript{2}O into H\textsubscript{2} and CO\textsubscript{2}. A second source of CO emissions is the pre-preparation of the fuel, i.e. storage and grinding. The latter emissions will not be directly affected by the CO\textsubscript{2} capture process, although per kWh those emissions will probably increase as more fuel has to be stored and handled per kWh.

No solvents are used in the \textit{oxyfuel} combustion system. Additional gaseous emissions per primary energy input are thus not expected. In literature it is however suggested that in oxyfuel concepts, due to higher oxygen concentrations, a larger part of elemental mercury (Hg) is converted to ionized Hg species, which will possibly result in higher capture efficiencies of Hg in flue gas cleaning sections (DeSO\textsubscript{x} and DeHg). (Marin and Carty 2002; Chatel-Pelage, Marin et al. 2003) (WRI 2007) This may be an additional benefit of CO\textsubscript{2} capture with oxyfuel combustion.

For the advanced oxyfuel concepts, chemical looping combustion\textsuperscript{13}, the loss of metal oxides to the atmosphere may be a concern. Metal oxides are used as oxygen carriers to physically separate the reduction and oxidising step in this power cycle. These metal oxides may contribute to the environmental impacts of energy supply with this concept as it might bring forward direct environmental impacts, i.e. some metals are considered toxic. Also, these oxygen carriers may bring forward environmental impacts in their life cycle, e.g. during mining, treatment and disposal.

4. Atmospheric emissions across the value chain of CCS

Life Cycle Assessment (LCA) is today one of the most used tools for evaluating the potential environmental impact of products and materials. LCA is a technique for assessing the environmental aspects and potential impacts associated with inputs and outputs of a product system. In the case of CCS, a full LCA includes the production of the fuel carrier (e.g., mining of coal), fuel transport, power production, CO\textsubscript{2} capture, CO\textsubscript{2} transport and CO\textsubscript{2} storage (see Fig. 3). Note that for most studies found in the literature, including those on CCS, emissions from the infrastructure and the extraction of raw materials other than fuel tend to be excluded since they are assumed to be relatively small in comparison to primary burdens or there is lack of data that does not allow for a reliable analysis.

\textsuperscript{13} Chemical looping concepts typically include an oxidizing reactor (OX) were a metal oxide (oxygen carrying metals that are considered are: Cu, Co, Ni, Fe and Mn) is formed through the exothermic reaction of a metal with oxygen. This is the oxygen carrier that transports the oxygen to the reduction reactor (RED). In the reduction reactor the fuel reacts (oxidizes) with the oxygen from the metal oxide (MeO).
In this section, we consider the results found by 25 studies published between 1995 and 2009. Each reviewed study typically addresses different impact categories. The focus of this section is on the atmospheric emissions of CCS during its life cycle\(^\text{14}\) and, therefore, only the following categories will be examined in detail: CO\(_2\) emissions, SOx/NOx and Particulate matter. The literature used to assess the emissions is listed in Table 2.

<table>
<thead>
<tr>
<th>Capture technology type</th>
<th>Literature sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGGC with CCS</td>
<td>(Waku, Tamura et al. 1995; Akai, Nomura et al. 1997; Lombardi 2003; Tzimas, Mercier et al. 2007; Viebahn, Nitsch et al. 2007; Weisser 2007; Odeh and Cockrell 2008; RECCS 2008; Pehnt and Henkel 2009)</td>
</tr>
<tr>
<td>Oxyfuel with CCS</td>
<td>(Viebahn, Nitsch et al. 2007; RECCS 2008; Bauer and Heck 2009; NEEDS 2009; Nie 2009; Pehnt and Henkel 2009)</td>
</tr>
</tbody>
</table>

Table 2. Literature sources used to assess the emissions of the CCS value chain.

\(^{14}\) NOx and SOx emissions lead to the formation of acid gases, which can lead to acidification, eutrophication and smog formation nd not in the consequence of a given emission. For instance, SO2 and NOx can cause acidification.
4.1 CO₂ equivalent emissions
The main goal of CCS is to reduce CO₂ emissions and consequently, Global Warming Potential (GWP). For pulverized coal-fired power plants with post-combustion capture technology using MEA a range in GWP over the life cycle of 79-275 gCO₂eq/kWh is reported (range for PC without CCS is in the range 690 to 1100 gCO₂eq/kWh). Where PCs without CCS have a share of power plant operation in life cycle GWP of about 80-95%, installing CO₂ capture decreases this share to about 43-60%. Thus, the deployment of CCS results in a pronounced increase in the share of indirect CO₂eq emissions in the complete life cycle\(^\text{15}\).

In the case of IGCCs with pre-combustion CO₂ capture, GWP values reported are in the range 110 to 181 gCO₂eq/kWh (the range for IGCCs without CCS is 666 to 870 gCO₂eq/kWh). Lignite-fired IGCCs with CCS have almost 20% less absolute emissions compared to hard coal-fired IGCCs with CCS. Installing CCS results in a reduction of about 82 to 87% for lignite-fired IGCCs with CCS relative to IGCCs without CCS, while for hard coal-fired IGCCs the relative differences are in the range of 69 to 81%.

Interestingly, hard coal-fired power plants with CCS technology are reported as having between 20% (IGCC with CCS) and 30% (PC with CCS) more GHG emissions than similar lignite-fired power plants with CCS, while without CCS technology the hard coal-fired power plants have about 10% lower emissions than lignite-fired power plants. This is due to a typically larger share of upstream emissions (e.g. fuel extraction and processing) for hard coal-fired power plants than for lignite-fired power plants. Lignite-fired power plants are often directly located at the mining site (‘mine-mouth’ operated) which results in lower transport emissions. As these upstream emissions are not reduced by CCS technology, but mainly increase due to the energy penalty, the GHG emissions from mine-mouth based power plants can be reduced further when implementing CCS.

The range in GWP for oxyfuel power plants with CCS is 25-176 gCO₂eq/kWh. The relative decrease in GWP ranges from 78% to 97%. Specifically for hard coal-fired power plants, the range in the relative difference is smaller (78% to 87%).

For NGCCs with post-combustion using MEA, the GWP are in the range 75-245 gCO₂eq/kWh, which is about 51-80% less than the values reported for NGCCs without CCS. The two studies (Späth and Mann 2004; Odeh and Cockerill 2008) reporting the lower value range (51-58%) also report about 25% indirect emissions for NGCCs without CCS technology compared to about 12-15% reported in other studies. Both studies state that in the case of NGCCs the amount of methane leakage from natural gas extraction and transport has a significant effect on life cycle GHG emissions and is more inopportune in the case with CCS due to the increase in primary energy consumption. It is, however, unclear if the other studies include this methane leakage in the reported values.

4.2 Particulate matter
PM₁₀ emissions reported for the life cycle of PC power plants with post-combustion using MEA range between 0.013 and 0.434 gPM₁₀/kWh while PM₂.₅ for the same type of plants are reported between 0.05 to 0.07 gPM₂.₅/kWh. PC plants without CCS report PM₁₀ in the

\(^{15}\) Two outliers are identified. Markevitz et al., (2009) shows a significantly smaller (23%) share of power plant operation after capture while Pehnt and Henkel (2009) showed a larger share (79%). The origin of the differences cannot be identified from the data reported.
range 0.009 to 0.35 gPM$_{10}$/kWh and PM$_{2.5}$ in the range 0.009 to 0.35 gPM$_{10}$/kWh. Contrary to the results found for GWP, no clear difference is reported for hard coal-fired and lignite-fired power plants.

Only two studies (Viebahn, Nitsch et al. 2007; RECCS 2008) report the contribution of the different part of the CCS chains. In these studies, the contribution of the PC plant with CO$_2$ capture is estimated at 33% and 45%, which is lower than the estimated contribution of a similar PC plant without CCS (60% and 65%, respectively).

The amount of studies reporting PM emissions for other CO$_2$ capture technologies is limited. One study by Odeh and Cockerill (2008) reports PM emissions for IGCCs with and without CCS technology (0.004 g/ kWh in both cases). The value is lower than those reported for PCs due to the high removal of PM in the syngas (to avoid detrimental effects in the turbine). NEEDS (2009) reports PM values for NGCCs equipped with MEA based post-combustion technology in the order of 0.005-0.006 gPM$_{10}$/kWh and 0.009-0.010 gPM$_{2.5}$/kWh (the values for a NGCC without CCS are in the range of 0.003-0.012 gPM$_{10}$/kWh and 0.007-0.008 gPM$_{2.5}$/kWh). In this case, PM emissions are mainly associated with NOx emissions (which are PM precursors) from the power plant and the winning of natural gas. Values for oxyfuel power plants with CO$_2$ capture are also reported by NEEDs (2009). For PM$_{10}$ the range reported is 0.012 to 0.025 gPM$_{10}$/kWh while for PM$_{2.5}$ this is 0.07 to 0.36 gPM$_{2.5}$/kWh.

### 4.3 NO$_x$ and SO$_x$

Table 3 shows the ranges found in the literature for the life cycle of power plants with and without CCS. The number of studies reporting specific results, particularly for IGCC and oxyfuel plants with CCS, is quite limited making it difficult to draw robust conclusions. Results for PC with post-combustion capture using MEA indicate an increase in the amount of NOx during the life cycle. The partial removal of NOx during the capture process is not large enough to offset the increase in emissions caused by the additional fuel needed to compensate the energy penalty. Literature appears less clear on the impact of post-combustion on SOx levels, with some studies showing a decrease in emissions while others indicating an increase on emissions. Koornneef et al., (2008) indicates that a decrease in both NOx and SOx emissions associated with the transport of coal can be expected since stringent regulations are anticipated to reduce sulphur content in marine fuel and to limit NOx emissions during ship transport.

In the case of NGCC plants with post-combustion MEA, SOx emissions are reported to increase over the life cycle. The level however remains well below those of PC plants due to the very low sulphur content of natural gas.

<table>
<thead>
<tr>
<th>Type of plant</th>
<th>NOx</th>
<th>SOx</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With CCS (gNOx/kWh)</td>
<td>% change</td>
</tr>
<tr>
<td>PC</td>
<td>0.58-1.39</td>
<td>+13% to +49%</td>
</tr>
<tr>
<td>IGGC</td>
<td>0.10</td>
<td>-16%</td>
</tr>
<tr>
<td>Oxyfuel</td>
<td>0.27-0.60</td>
<td>---</td>
</tr>
<tr>
<td>NGCC</td>
<td>0.13-0.30</td>
<td>-50% to +15%</td>
</tr>
</tbody>
</table>

Table 3. Emissions of SOx and NOx reported in the literature and relative change compared to a similar plant without CCS (N= number of studies).
5. Case studies – Netherlands and Europe

In this section we discuss two case studies showing the consequences of implementing CCS in the power and heat sector on non-GHG emissions that affect air quality. We consider two geographical regions: the Netherlands and the European Union.

5.1 Scenario study for the Dutch power and heat sector

The BOLK research programme was initiated by the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM) to acquire more detailed information on the synergy and/or trade-offs of GHG mitigation policies and transboundary air pollution (AP) policies (Harmelen, Koornneef et al. 2008; Horssen, Kuramochi et al. 2009). Part of that programme was aimed at assessing CCS technologies and includes scenario analyses for key atmospheric emissions (NOₓ, SO₂, PM₁₀ and NH₃) from the power sector. Three scenarios were developed and compared to the 2006 emission level (see Fig. 4):

1. Power sector emissions without CCS: No CCS is applied to the power plant sector in 2020.
2. 2020 with CCS -S1: CCS is applied to two new coal fired power plants, 1 with post-combustion and 1 with pre-combustion.
3. 2020 with CCS -S2: CCS is applied to all new coal fired power plants, 3 with post-combustion and 1 with pre-combustion.

The impact of applying CO₂ capture technologies to the power generating sector is assessed in that study for several view years (i.e. up to 2050). For the view year 2020 the scenario is based on the actual and planned power plants. CO₂ emissions from the sector are assumed to increase from 38 in 2006 to 62 Mtonne in 2020, without the introduction of CCS. In 2020, up to 24 Mtonne CO₂ could be avoided when equipping new coal fired power plants with CO₂ capture.

The results of that scenario study are shown in Fig. 4. Emissions of NOₓ, SO₂, PM₁₀ and NH₃ in the sector are estimated to increase in the reference scenario for the year 2020, due to the increase in Dutch coal fired capacity without CCS. The introduction of CCS (only post- and pre-combustion) is expected to lead to a further increase of NOₓ (up to 1.5 ktonne), PM (up to 70 tonne) and NH₃ emissions (up to 0.7 ktonne). SO₂ emissions decrease below the 2006 level. The introduction of CCS leads to a relative large increase (from 0.1 ktonne to up to 0.8 ktonne) in the overall low contribution of the power generation sector to the NH₃ emissions. For the scenario analyses, the emission data in relative old publications associated with the use of ethanolamines were used. Developments are still going on to reduce the solvent degradation and with it the emissions from solvents. With the improvement of the solvent technology, NH₃ emissions will be strongly reduced.

The additional cost of mitigating key atmospheric emissions are roughly assessed and compared to the reference scenario. The results showed that the cost mainly consist out of the increased costs for air pollution control needed to counteract the projected capacity increase of the power plant sector. The additional mitigation costs due to CCS are estimated to be small compared to those costs. The costs of NOₓ and PM₁₀ dominate the overall mitigation costs of approximately 50 million Euros per year.

The mitigation costs of NOₓ, PM₁₀ and NH₃ compared to the reference scenario are positive, because of the increase of the emissions in the CCS scenarios. Mitigation cost for SO₂ are negative due to the emission reduction of this substance in CCS equipped power plants.
Fig. 4. Emissions of NO\textsubscript{2}, SO\textsubscript{2} (ktonne/year) on left axis and of PM\textsubscript{10}, NH\textsubscript{3} (ktonne/yr) on right axis, in the Dutch power plant sector in 2020.

5.2 Scenario study for the European power and heat sector in 2030

In a study by Koornneef et al (2010) the trade-offs and synergies between climate and air quality policy objectives for the European power and heat (P&H) sector were quantified. The analysis includes assessing the impact of applying CO\textsubscript{2} capture in the European P&H sector on the emission level of key air pollutants in 2030. A model was developed with the assumption that all power plants built between 2020 and 2030 are equipped with CO\textsubscript{2} capture and that all plants built between 2010 and 2020 are retrofitted\textsuperscript{16} with CO\textsubscript{2} capture before 2030. Four scenarios were investigated: one without CCS (baseline) and three with CCS. Each one focuses on a different CO\textsubscript{2} capture system (post-combustion, oxyfuel combustion and pre-combustion).

The first scenario without climate measures was drawn entirely from the GAINS\textsuperscript{17} model developed by the IIASA (IIASA 2008). The emission levels of NECD substances in 2030 were defined by combining sector activity and emission factors for P&H plants with and without CO\textsubscript{2} capture.

In the three scenarios with CO\textsubscript{2} capture the share of power plants equipped with CO\textsubscript{2} capture technology was determined by estimating for each country the additional sector activity (in primary energy use) in the baseline scenario per combination of conversion technology and fuel for the periods 2010-2020 and 2020-2030.

\textsuperscript{16} From 2010 onwards it is more likely that the power plants will be built capture ready. In this study it was therefore assumed that only power plants built between 2010 and 2020 are retrofitted between 2020 and 2030.

\textsuperscript{17} Greenhouse gas - Air pollution Interactions and Synergies model. The GAINS model is developed to analyse trade-offs and co-benefits of strategies aimed at the reduction of air pollution and greenhouse gases on the medium-term, i.e. until 2030.
Results show a reduction in GHG emissions compared to the baseline scenario between 7% and 16% for scenarios with CCS penetration in the European power and heat sector. This comes with an increase in total primary energy use in the EU of approximately 1-5%. In the power and heat sector alone this increase is between 2% and 17%.

SO\textsubscript{2} emissions are estimated to be very low for all scenarios that include large-scale implementation of CO\textsubscript{2} capture in 2030, i.e. a reduction varying between 27% and 41%. This holds especially for the scenario with a large share of oxyfuel combustion technology. Further, it was found that NO\textsubscript{x} emissions from the P&H sector could be 15% higher in a scenario with predominantly post-combustion CO\textsubscript{2} capture compared to the baseline scenario without CCS. A reduction in NO\textsubscript{x} emissions is expected when oxyfuel combustion (-16%) or IGCC with pre-combustion CO\textsubscript{2} capture (-20%) is mainly applied.

Large-scale implementation of the post-combustion technology in 2030 may also result in significant higher NH\textsubscript{3} emissions compared to scenarios without CCS and with other CO\textsubscript{2} capture options, although uncertainty in this estimate is substantial. If these emissions are not controlled properly, NH\textsubscript{3} emissions from the P&H sector change from an insignificant contribution of 0.5% towards a possible very significant contribution of 13% of the EU total for all sectors together.

Direct particulate matter emissions are likely to be lower in the scenarios with CO\textsubscript{2} capture. The scenario with implementation of the oxyfuel combustion technology shows the largest (i.e. 59%) reduction in PM emissions in the P&H sector followed by the scenario with a significant share allocated to pre-combustion CO\textsubscript{2} capture showing a reduction of 31%. Post-combustion capture may show an increase in PM emissions due to a limited removal and a larger increase in primary energy use. The scenario with post-combustion capture resulted in PM emissions varying between 35% reduction and 26% increase. No robust conclusions could however be drawn on how CO\textsubscript{2} capture influences the emissions of various PM size categories (i.e. PM\textsubscript{2.5}, PM\textsubscript{10} and >PM\textsubscript{10}) as this is not satisfactorily addressed in pertaining literature.

6. Special highlight topic: atmospheric emissions from post-combustion capture

6.1 Solvent emissions

Due to the low partial CO\textsubscript{2} pressure in flue gases from the power sector, the use of chemical solvents is preferred in post-combustion capture. Chemical solvents seem to be the preferred option for the short-term, since this technology is relatively mature, commercially available at industrial scale (though not yet power plant scale), and post-combustion can be used to retrofit existing power stations (as end-of-pipe treatment). The disadvantages of using amines as chemical solvent are high costs for energy (energy penalty), space (due to large gas volumes) and equipment. Furthermore, amines and degradation products are found to be emitted from the stack, causing potential environmental impacts (Horssen, Kuramochi et al. 2009).

Amines can leave the power plant with the CO\textsubscript{2} captured gas to be stored in the deep underground where it is considered to have limited environmental impact. Emissions of amines to the air can take place when the residuals are taken out of process when recycling the amine at the top of the absorber (especially relevant for safety of workers) and with the cleaned flue gas at the top of the absorber where they are emitted into the atmosphere (relevant for the public and environment).
Finally, amines can degrade, e.g. into ammonia (also treated in the previous sections). The amines can also react with oxidized nitrogen in the atmosphere to form potentially harmful compounds such as nitrosamines, nitramines, aldehydes and amides. The environmental impacts are not easy to assess since there are a large number of degradation products which not only depend on the degradation mechanisms occurring in the capture process, but also on the type of amines used (Knudsen 2008).

6.2 Environmental impacts of amines

In 2007, the Norwegian Institute for Air Research (NILU) conducted a screening study to understand more about atmospheric amine chemistry and to evaluate the environmental effects of amine emissions and degradation products such as nitrosamines, nitramines, aldehydes and amides.

The amines studied are monoethanolamine (MEA), piperazine, aminomethylpropanol (AMP) and methyldiethanolamine (MDEA). Among these amines, piperazine has been through a thorough evaluation and classification in the EU system. There are several experimental studies available on MEA, but most of them were conducted during 1960s and -70s. For AMP and MDEA the toxicological data are rare. High quality inhalation studies are lacking. For piperazine and MDEA indications exist of reproductive and developmental toxicity. In addition, one study suggests similar effects of AMP. None of the amines have been reported to be carcinogenic, but this should also be evaluated further with additional studies (Låg, Andreassen et al. 2009).

Låg et al. concluded that amines themselves are most likely causing little risk to human health, but the emissions contribute to the nitrogen load and potentially to eutrophication which could have impacts on sensitive terrestrial ecosystems.

Nitrosamines (N-nitrosamines) are a large and diverse family of synthetic and naturally occurring compounds described by the formula (R1)(R2) N-N=O, where R1 and R2 is an alkyl or aryl group. Nitrosamines are typically liquids, oils or volatile solids. Nitrosamines occur in the diet, through use of tobacco, cosmetics, pharmaceutical products and agricultural chemicals. Nearly all commercially available alkylamines are generally contaminated by small quantities of their corresponding N-nitroso analogues. Industrial installations producing or using amines might be a source of nitrosamine pollution (Tricker, Spiegelhalder et al. 1989).

Exact data on concentration levels in power plants using amine based carbon capture are very sparse and very hard to find in the public literature. However, nitrosamines are considered of particular concern because of their toxic and carcinogenic properties at extremely low levels.

Nitramines are also of concern as they are suspected to be carcinogenic, though considerably less than the nitrosamines. However, the longer lifetime in the atmosphere may lead to higher exposure values. Modelling also indicates that amines lower the surface tension of water droplets, which under appropriate climatic conditions can be a trigger for rain with the potential of causing negative impacts to the local environment. 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 (Knudsen 2009).

With regard to aldehydes, Låg et al. (2009) concluded that at airborne levels for which the prevalence of sensory irritation is minimal, both in incidence and degree (<1.2 mg/m³), risks
of respiratory tract cancer are considered to be negligibly low. Acetamide may induce skin irritation. The irritating potential of the aldehydes and amides might in this context be the most relevant adverse health effect of these compounds, as the amines probably to be used in CO₂ capture also have such effects. Therefore, all these compounds have to be evaluated together with respect to irritating potential of the air around the gas plants (Marit, Instanes et al. 2009).

These statements highlight the necessity for further testing and analysis of amine effects in order to limit the risks, especially for nitrosamines and nitramines. At least as important is the measurement of amine related substances from CCS equipped power plants in order to assess the exact concentration level of specific amine related species. This is needed to assess the risks for public and workers as well as to understand the chemical formation processes as a basis for the development of countermeasures against amine effects due to CCS.

6.3 CO₂ capture solvents and regulations

The health and environmental properties of a number of CO₂ 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 CO₂ 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 CO₂ 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. The study did not incorporate the degradation products as nitrosamines. A more comprehensive study is recommended containing exposure studies and mapping of degradation products.

Based on the available literature Låg et al. (2009) suggested exposure guidelines for four amines; particularly for AMP and MDEA there are few high quality studies. The guidelines presented are therefore just indicative. The uncertainty factors were chosen in accordance with EU guidelines. Based on inhalation exposure risk, the general population, over time, should not be exposed to levels in the air higher than:

- MEA: 10 µg/m³
- AMP: 6 µg/m³
- MDEA: 120 µg/m³
- Piperazine: 5 µg/m³

Finally, it has been stated that it is highly relevant to know which precise amine is used in CCS, because each individual amine has different effects and potential risks. Furthermore, use of more than one amine infers that the exposure guidelines should be evaluated again, since amines seem to have similar adverse effects and might therefore also show additive or synergistic effects.

7. Conclusions and way forward

Depending on the applied CO₂ capture technology, trade-offs and synergies can be expected for key atmospheric emissions, being: NOₓ, SO₂, NH₃, particulate matter, Hg, HF and HCl. For
all three (pre-, post- and oxyfuel combustion) capture systems it was found that \( \text{SO}_2 \), \( \text{NO}_x \) and PM emissions are expected to be reduced or remain equal per unit of primary energy input compared to power plants without \( \text{CO}_2 \) capture. Increase in primary energy input as a result of the energy penalty for \( \text{CO}_2 \) capture may for some technologies and substances result in a net increase of emissions per kWh output. The largest increase is found for the emission of \( \text{NO}_x \) and \( \text{NH}_3 \) when equipping power plants with post-combustion capture. A decrease is expected for \( \text{SO}_2 \) emissions, which are low for all power plants with \( \text{CO}_2 \) capture.

Additional research (measurements and modelling) and regulatory efforts (norm setting) are required to cope with ‘new’ emissions from predominantly post-combustion \( \text{CO}_2 \) capture technologies. Laboratory and field experiments are necessary to obtain more precision in the estimates of emission levels, as little information exists in open literature. For this, accurate sampling and analysis methods have to be developed and validated for low concentrations.

Also, for post-combustion capture using amines it is necessary to identify and quantify the specific compounds that will be emitted or formed post-emission, where particular focus should be put on nitrosamines and nitramines. It is recommended to focus research on the determination of atmospheric degradation paths, precise degradation yields, and degradation products’ lifetime in the atmosphere. Development of models is necessary to quantify the mass fluxes and chemical interactions, and finally to integrate them in a dispersion model to quantify the load and possible environmental consequences.

Furthermore, research should be focused on the assessment of toxicity levels of these substances, as a basis for the development of both acute and chronic human toxicity exposure limits for amines and associated substances, both for workers and the public. This is needed to further compile data and information to create a relative ranking of amines with respect to potential environmental and health effects and toxicity and to find efficient ways to mitigate formation of nitrosamines and nitramines.

We recommend to set up extensive environmental monitoring programmes at currently planned \( \text{CO}_2 \) capture (demonstration) plants aimed at creating a better understanding of the formation and fate of solid, liquid and atmospheric pollutants. Emissions that should be monitored are: \( \text{SO}_x \), \( \text{NO}_x \), HF, HCl, Hg, PAH, dioxins, hydrocarbons, heavy metals, \( \text{NH}_3 \), MEA and PM. For particulate matter it is especially of interest to discern the removal efficiencies for the various sizes of particulate matter. For heavy metals it is of interest to measure to what extent the transposition occurs from atmospheric emission to waste water effluent and solid waste. Monitoring programmes should help to quantify emissions in further detail and share its knowledge with the wide research community.

Life cycle effects of implementing \( \text{CO}_2 \) capture options should not be neglected when reviewing the environmental performance of complete CCS chains, from cradle to grave. Recent studies namely indicate that for some substances (e.g. \( \text{SO}_x \)) direct (atmospheric) emissions may decrease due to \( \text{CO}_2 \) capture; but that additional life cycle emissions by up- and downstream process may result in a deterioration of the overall environmental performance of the CCS chain compared to a power plant without CCS; except for the global warming potential.

For a number of environmental impact categories no agreement exists on the exact direction (positive, negative) or the level of the life cycle impacts due to CCS deployment. The sometimes large ranges often indicate that specific regional or technical issues influence the overall environmental performance of a chain. This requires further research.

We also see a high value in screening next generation \( \text{CO}_2 \) capture technologies at an early stage on their environmental performance in order to facilitate the optimization of CCS
chains not only on its cost and GHG emission performance, but also taking into account other environmental themes.

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The atmosphere may be our most precious resource. Accordingly, the balance between its use and protection is a high priority for our civilization. While many of us would consider air pollution to be an issue that the modern world has resolved to a greater extent, it still appears to have considerable influence on the global environment. In many countries with ambitious economic growth targets the acceptable levels of air pollution have been transgressed. Serious respiratory disease related problems have been identified with both indoor and outdoor pollution throughout the world. The 25 chapters of this book deal with several air pollution issues grouped into the following sections: a) air pollution chemistry; b) air pollutant emission control; c) radioactive pollution and d) indoor air quality.

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