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EMISSIONS OF CARBON DIOXIDE CAPTURE IN POWER GENERATION WHEN USING PRECOMBUSTION CAPTURE OR OXYFUEL COMBUSTION METHODS

Master of Science thesis

Examiner: Professor Risto Raiko  
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## ABSTRACT

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Carbon dioxide capture from large point sources, such as power plants using fossil fuels, is essential for mitigating further global warming. New combustion methods are being researched to help increase the partial pressure of carbon dioxide in the flue gas of a power plant, to make carbon dioxide capture faster, cheaper and less energy intensive. The most important methods for this are gasification and combustion with pure oxygen instead of air.

Gasification of solid fuels is compatible with so called precombustion capture methods, where the carbon dioxide is removed from stream before combustion of the remaining synthesis gas. Combustion with pure oxygen, or oxyfuel combustion, reduces the amount of nitrogen in the flue gas, effectively resulting in only carbon dioxide and water vapour as the combustion product. Both methods result in higher carbon dioxide content of the gas to be treated, compared to conventional combustion with air.

Several methods exist for separating carbon dioxide from other gases. These methods are based on absorption, adsorption, membrane separation, cryogenic separation or their combination. Each capture method, as well as the two combustion methods mentioned above, has its advantages and disadvantages that concern both the capture capabilities of carbon dioxide and emissions potentially harmful not only to humans and environment, but also to related processes, such as transportation of carbon dioxide.

The emissions of different carbon dioxide capture are highly dependent on the capture process due to the different chemicals used in each method. The chemicals used are not the only possible emissions, but also thermal and chemical degradation of the chemicals may result in new, potentially thus far unpredictable compounds. The precise composition and effects of these emissions are not yet fully understood and research concerning their nature is required.

This thesis serves to show different possible emissions related to carbon dioxide capture processes and to provide this information for others, in order for them to develop measurement devices required for emission control.

## TIIVISTELMÄ

TAMPEREEN TEKNILLINEN YLIOPISTO

Ympäristö- ja energiategniikan koulutusohjelma

**SUVANTO, JUHA:** Hiilidioksidin talteenoton päästöt voimantuotannossa käytettäessä polttoa edeltävää talteenottoa tai happipolttoa

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Hiilidioksidin talteenotto suurista paikallisista lähteistä, kuten fossiilisia polttoaineita käyttävistä voimalaitoksista, on oleellista maapallon lämpenemisen hidastamiseksi. Uusia polttomenetelmiä tutkitaan, jotta hiilidioksidin osapainetta voimalaitosten savukaasuissa voidaan nostaa, mikä auttaa kehittämään nopeampia, halvempia ja vähemmän energiaa kuluttavia talteenottomenetelmiä. Tärkeimmät uudet polttomenetelmät ovat polttoaineen kaasutus ja happipolttu.

Kiinteän polttoaineen kaasutus on yhteensopiva hiilidioksidin ennen polttoa tapahtuvan talteenoton kanssa. Tässä menetelmässä hiilidioksidi erotetaan kaasutuksessa syntyvästä tuotekaasusta ennen polttokammiota. Happipoltossa käytetään hapettimena ilman sijasta lähes puhdasta happea, jolloin typen osuus savukaasuissa on huomattavasti pienempi ja savukaasut koostuvat lähinnä hiilidioksidista ja vesihöyrystä. Molemmilla menetelmillä talteenottoprosessissa käsiteltävän kaasun hiilidioksidipitoisuus on suurempi kuin tavallisessa ilmapoltossa.

Hiilidioksidin erottamiseen muista kaasuista on useita tapoja. Nämä jaetaan yleensä absorptioon, adsorptioon, huokosiin kalvoihin, kryogeniikkaan tai näiden yhdistelmiin perustuviin menetelmiin. Kullakin talteenotto- ja polttomenetelmällä on omat etunsa ja haittansa jotka vaikuttavat niin talteenottokykyyn kuin mahdollisiin päästöihin, jotka voivat vaikuttaa ihmisten ja ympäristön lisäksi myös itse talteenottoprosessiin ja siihen liittyviin osaprosesseihin, kuten hiilidioksidin kuljetukseen.

Eri talteenottotapojen päästöjen ominaisuudet riippuvat hyvin paljon prosesseista ja niissä käytettävistä kemikaaleista. Itse kemikaalien lisäksi myös niiden hajoamistuotteet ja niiden reaktiot voivat synnyttää uusia, mahdollisesti vielä tuntemattomia päästöjä. Näiden päästöjen koostumukset ja vaikutukset eivät ole vielä täysin ymmärrettyjä, joten niihin liittyvälle tutkimukselle on tarvetta.

Tämän diplomityön tarkoituksena on esittää mahdollisia päästöjä, joita voi syntyä kustakin talteenottomenetelmästä. Tätä tietoa voi hyödyntää esimerkiksi kehitettäessä mittaustekniikkaa päästöjen hallintaa varten.

## PREFACE

Work on this thesis began in September 2012 at the Department of Energy and Process Engineering, and later the Department of Chemistry and Bioengineering, at Tampere University of Technology (TUT). The thesis is part of Carbon Capture and Storage Program (CCSP), a national program that studies the application of CCS in Finland, steered by Cleen Ltd and funded by the Finnish Funding Agency for Technology and Innovation, Tekes. The thesis is part of CCSP's Work Package 4 and Task 4.1, led by Ramboll Finland Oy. The thesis was supervised by Professor Risto Raiko.

A prevalent problem concerning research of CCS emissions is the shortage of public information about the issue. Not many public research papers exist that particularly deal with CCS emissions and the potentially useful information is hidden in either thousands of more or less relevant studies or are trade secrets of companies researching and developing CCS processes. Partially because of this, it has been difficult to find the information requested by the project and my employer, eventually leading to delivering this thesis late.

Thanks are in order for my parents Maija and Olavi for financial help during the bleak first years of my studies; my sister Hilikka for support and tolerating my antics; the Student Union of Tampere University of Technology, TTYYY, for their invaluable and continued work to supervise the interests of students; and the Guild of Environmental and Energy Engineering, YKI, for all the good times spent on excursions and at the guild room, for the Donald Duck subscription and immeasurable amounts of tea. Last, my heart goes out to all my current and former neighbours at Tupsula, my home for the last ten years, who certainly have made my life more tolerable and sociable, even if it was at the expense of prolonging my student career to an inefficient mess.

Juha Suvanto

## CONTENTS

Abstract .....	ii
Tiivistelmä .....	iii
Preface .....	iv
Nomenclature .....	vii
1 Introduction .....	1
1.1 Capture methods.....	1
1.2 Storage.....	2
1.3 Emissions .....	3
1.4 Legislation in Finland .....	3
2 Oxyfuel and oxygen enrichment combustion .....	4
2.1 Cryogenic air separation .....	5
2.2 Oxygen enrichment .....	6
2.3 Chemical looping combustion.....	8
3 Precombustion capture .....	10
4 Postcombustion capture .....	12
5 Absorption-based CO <sub>2</sub> separation .....	13
5.1 Chemical solvents .....	13
5.1.1 Amines .....	14
5.1.2 Carbonates .....	17
5.1.3 Aqueous ammonia .....	18
5.1.4 Sodium hydroxide.....	18
5.1.5 Dry sorbents .....	19
5.2 Physical solvents .....	19
5.2.1 Rectisol process .....	20
5.2.2 Fluor process.....	21
5.2.3 Selexol process .....	21
6 Adsorption-based CO <sub>2</sub> separation .....	23
6.1 Zeolites .....	24
6.2 Activated carbon .....	24
6.3 Metal oxides .....	25
6.4 Layered double hydroxides .....	26
7 CO <sub>2</sub> separation with membranes .....	27
8 Cryogenic separation emissions .....	30
9 CO <sub>2</sub> purity requirements and purification .....	31
9.1 Particle removal .....	31
9.2 Flue gas condensation .....	32
9.3 NO <sub>x</sub> , SO <sub>x</sub> and mercury removal .....	32
9.4 Dehydration and removal of non-condensable gases.....	33
10 Results and discussion.....	34
10.1 Air separation .....	34
10.2 Chemical solvents .....	34

10.3 Physical solvents .....	36
10.4 Adsorbents .....	36
10.5 Membranes .....	37
11 Conclusions .....	38
References .....	39

## NOMENCLATURE

carbamate	An organic compound derived from carbamic acid ( $\text{NH}_2\text{COOH}$ ).
CCS	Carbon Capture and Storage. An umbrella term covering various methods and concepts of reducing anthropogenic carbon dioxide in the atmosphere.
CLC	Chemical Looping Combustion. A method of circulating metal oxides in order to deliver pure oxygen to a combustion chamber.
CFB	Circulating fluidized bed. In a CFB boiler the fuel and a bed material are suspended to improve combustion conditions and the bed material is recycled outside the boiler to improve heat transfer.
EIGA	European Industrial Gases Association AISBL, an international non-profit organization representing several companies producing and distributing industrial, medical and food gases
end-of-pipe	End-of-pipe technologies are additional environmental protection measures. They do not change the process itself, but reduce the environmental impact of it. For example flue gas desulfurization.
EOR	Enhanced oil recovery. A method in which $\text{CO}_2$ is pumped in oil reservoirs in order to both increase the oil yield and sequester the $\text{CO}_2$ .
EPA	United States Environmental Protection Agency.
ESP	Electrostatic precipitator, a piece of equipment to remove particles from flue gas.
FGD	Flue gas desulfurization, a process to remove $\text{SO}_x$ emissions from flue gas.
flue gas	A stream consisting of combustion products.
greenfield	A greenfield project is one with no constraints imposed by prior work.
IUPAC	International Union of Pure and Applied Chemistry, an organization representing chemists and worldwide authority in developing naming standards for chemical substances.
MOF	Metal-organic framework.
$\text{NO}_x$	A term for the two nitrogen oxides $\text{NO}$ and $\text{NO}_2$ .
permeate	A substance that has passed through a filter or a membrane.
PZ	Piperazine, $\text{C}_4\text{H}_{10}\text{N}_2$ .
retentate	A substance that has been retained in a filter or a membrane.

retrofitting	Addition of new technology or features to an old system, for example in order to improve efficiency or reduce emissions.
slurry	A thick suspension of solids in a liquid.
SO <sub>x</sub>	A term for various sulfur oxides: SO, SO <sub>2</sub> , SO <sub>3</sub> and so on.
sweetening	Removal of acid gases from a gas mixture. For example removal of CO <sub>2</sub> from natural gas.
syngas	Synthesis gas. A mixture of hydrogen and carbon dioxide, a product of gasification of a carbonaceous fuel, such as coal or oil.
WGS	Water-gas shift. A chemical reaction in which carbon monoxide reacts with water vapour to form carbon dioxide and hydrogen.

# 1 INTRODUCTION

Carbon capture and storage (CCS) is a key principle in an international attempt to mitigate global warming. The concept of CCS envelops methods decreasing the amount of carbon dioxide (CO<sub>2</sub>) released into the atmosphere and either storing the captured CO<sub>2</sub> or using it in industrial processes.

This thesis is a literary survey of recent research. It introduces existing and future CCS methods. The objective is to provide a list of possible emissions, caused by CCS methods, which may be harmful to environment, humans or CCS and related processes. The emissions are covered in conjunction with related technologies. CO<sub>2</sub> purity requirements for transportation are also discussed.

## 1.1 Capture methods

There are several methods for capturing CO<sub>2</sub>. These methods are usually divided into three categories: precombustion capture, postcombustion capture and capture with oxyfuel combustion. The main focus of this thesis is in CCS technologies relevant to oxyfuel combustion and precombustion, but postcombustion is also discussed when comparison is deemed relevant.

**Table 1.1.** Typical or estimated flue gas compositions of oxyfuel combustion, precombustion and postcombustion methods and before CO<sub>2</sub> capture (‘–’ represents no data available). (Sources: (a) Darde et al. 2009, (b) d’Alessandro et al. 2010)

Component	Oxyfuel (a)	Precombustion (b)	Postcombustion (b)
CO <sub>2</sub>	69.6 %	35.5 %	15 – 16 %
H <sub>2</sub> O	16.6 %	0.2 %	5 – 7 %
H <sub>2</sub>	–	61.5 %	–
O <sub>2</sub>	2.5 %	–	3 – 4 %
N <sub>2</sub>	8.2 %	0.25 %	70 – 75 %
SO <sub>x</sub>	0.01 %	–	< 800 ppm
NO <sub>x</sub>	0 %	–	500 ppm
H <sub>2</sub> S	–	1.1 %	–
Ar	3.1 %	–	–
CO	0 %	1.1 %	20 ppm

Precombustion capture involves converting the fuel, which may be solid, liquid or gaseous, into mostly CO<sub>2</sub> and hydrogen (H<sub>2</sub>). CO<sub>2</sub> is removed from the resulting gas and

stored, while  $H_2$  is combusted with air, resulting in mostly water vapour as the flue gas. In postcombustion capture, normal air-fired combustion methods are used and  $CO_2$  is separated from the combustion product known as flue gas. In oxyfuel combustion, the fuel is combusted with pure or almost pure oxygen, resulting in a flue gas stream of mostly  $CO_2$  and  $H_2O$ . These three umbrella methods are analysed more extensively in Chapters 2 through 4. Typical feed gas compositions for each method are presented in Table 1.1.

$CO_2$  capture methods can also be categorized by their primary means of separation into four groups. Separation by absorption can be achieved through chemical and physical solvents and is covered in Chapter 5, whereas Chapter 6 concerns adsorption-based separation. Chapter 7 deals with membrane separation. Cryogenic liquefaction of  $CO_2$  and cryogenic air separation are demonstrated in Chapter 2.

The choice of which capture method to implement is not an easy one. There are several variables that need to be taken into account. The initial costs of designing, manufacturing and installing the capture system are called capital expenditures (CAPEX) and the ongoing costs of running and maintaining the system are called operating expenditures (OPEX). High initial costs may be undesirable, because finding financiers may prove to be difficult. On the other hand, high running costs are more affected by market fluctuations and can be unpredictable. Both expenditures affect the length of the payback period. Estimating these expenditures is not necessarily easy and therefore no such rule of thumb exists as to which technology has the highest or lowest capital or operating expenditures.

Another issue to be taken into consideration, besides the economical one, is whether the power plant in question is a new greenfield project or an already existing facility. Suitability for retrofit varies depending on the desired technology. Use of space is dictated by not only the new technology being retrofitted but also the dimensions and layout of the facility. In general, postcombustion systems offer the best opportunity for retrofitting into existing power plants because they are end-of-pipe technologies.

For greenfield projects, more possibilities are available and the choice becomes more difficult as variables increase. Kanniche et al. (2010) recommend oxyfuel combustion the best capture method for pulverized coal combustion, precombustion capture by physical absorption for IGCC and amine-based postcombustion capture for NGCC. They admit their recommendations are based on a number of assumptions which are not yet demonstrated on an industrial scale.

Other reasons to prefer one technology over another may also exist. Further review of selection criteria is not covered.

## 1.2 Storage

Several suggestions for storage sites for the captured  $CO_2$  exist. Saline aquifers are underground layers of permeable rock, gravel, sand or other similar materials containing salt water which can retain  $CO_2$ . Sea sediments can similarly hold captured  $CO_2$ . In deep ocean floors the environment causes  $CO_2$  to become heavier than water and it forms pools of liquid  $CO_2$  in depressions of the bottom of the sea.

Enhanced oil recovery (EOR) is a method of pumping supercritical CO<sub>2</sub> into oil reservoirs, in order to release more crude oil from the porous rock and coincidentally sequester CO<sub>2</sub>. In a similar fashion, old natural gas reservoirs can be used to store CO<sub>2</sub>.

The importance of CO<sub>2</sub> purity of the stream being sequestered in any of the above storage sites varies. Since there is no long-term experience of CO<sub>2</sub> sequestration – only about 50 years of EOR – the long-term effects are unknown. One might think that impurities will have at least some sort of an effect on the local environment of the storage site, and that the purer CO<sub>2</sub> is the safer to store, but there is little or no research about this. Most if not all CO<sub>2</sub> purity guidelines stem from a technical viewpoint regarding such aspects as corrosion resistance of pipelines and pumping costs. Criteria for selection of a storage method lie outside the focus of this thesis.

### **1.3 Emissions**

The emissions of CCS systems can be divided into two separate categories: those harmful to environment and humans, and those harmful to the power plant and related processes. Several CCS processes are based on different chemicals, which may not necessarily be toxic themselves, but have decomposition products that have adverse health effects in the public. Amines and other chemicals containing nitrogen may turn into toxic substances. Furthermore some substances can cause mechanical failures in the varying process pressures and temperatures, such as free water in sub-zero CO<sub>2</sub> pipelines.

Prevention of these emissions is important to reduce environmental effects and maintenance costs. Recognizing possible emissions requires research, especially in how the different chemicals used in CCS react in the atmosphere.

### **1.4 Legislation in Finland**

The Finnish law prohibits geological storage of CO<sub>2</sub> inside Finland's borders for other than research purposes, but allows transport for storage in other countries. The law also imposes vague limits on the contents of the CO<sub>2</sub> stream, but is not very specific about them.

Knowledge of possible emissions caused by different CCS technologies and measuring these emissions in flue gas, CO<sub>2</sub> and byproduct streams are required to determine specific limitations for each emission species. Perhaps with increasing knowledge of the subject, especially the effects of sequestration in geological structures, the law will be changed to allow geological storage in the future.

## 2 OXYFUEL AND OXYGEN ENRICHMENT COMBUSTION

Oxygen is required in combustion of carbonaceous fuels. Conventionally ambient air, consisting primarily of oxygen (21 vol-%) and nitrogen (78 vol-%), is used in power plants as a source of oxygen. The high amount of mostly inert nitrogen in combustion air results in a large volume of flue gas, which leads to large boilers and flues. In regard to carbon dioxide capture, this excess nitrogen causes a problem, since the partial pressure of carbon dioxide in flue gas is low. Removing all or part of nitrogen from the combustion air results in smaller amounts of flue gas with higher CO<sub>2</sub> content than with regular air combustion. Using pure or “almost pure”, 95% or higher concentration (Jordal et al. 2004), oxygen to combust the fuel is called oxyfuel combustion. If nitrogen is only removed partially from the combustion air, this is called oxygen enrichment combustion.

Oxyfuel combustion has several advantages over conventional air-fired combustion. Absence of nitrogen leads to reduced amount of flue gas, which means boilers can be smaller and therefore cheaper. Heat losses to atmosphere are also reduced without the nitrogen. On the other hand, oxyfuel combustion is expensive to retrofit. With the reduced flue gas flow, existing boilers are too large, and they need to be renovated or rebuilt from scratch.

The heat transfer characteristics of combustion will change when substituting N<sub>2</sub> with CO<sub>2</sub> molecules. Because of this, new heat transfer models will need to be verified. Higher CO<sub>2</sub> content also means the heat flux to the boiler is higher, which likely leads to faster high-temperature corrosion. (Jordal et al. 2004)

Combustion in pure oxygen would result in high flame temperature, which will cause ash melting and increased NO<sub>x</sub> emissions. In order to control combustion temperature and to facilitate similar combustion conditions to existing air-fired boilers, 70–80 % of the CO<sub>2</sub>-rich flue gas needs to be returned to the boiler. With greenfield oxyfuel power plants in the future, this recycle flow can possibly be entirely avoided. CFB boilers have an extra advantage of controlling the combustion temperature through recirculation of bed material instead of flue gas. CFB boiler size and cost is easier to reduce than PC boilers. (Jordal et al. 2004)

While a 100% oxygen stream is technologically implausible to achieve, a 95% or higher purity, with 5% nitrogen, is considered sufficient for oxyfuel combustion (Buhre et al. 2005). The commercially most used method for achieving this level of purity is cryogenic air separation.

Producing pure oxygen through cryogenic distillation requires a lot of energy and has a negative impact on the net efficiency of the power plant. That is why other methods for producing oxygen are being researched. Ion transfer membranes have been proposed for

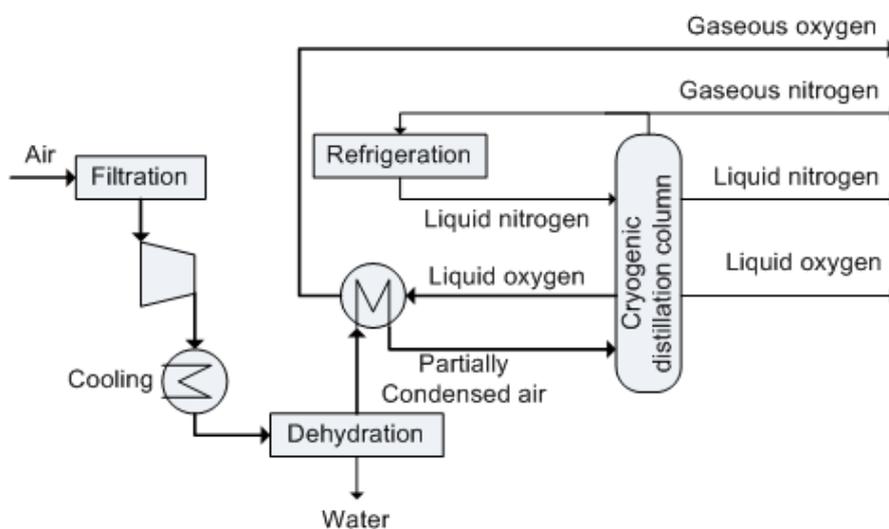
separating oxygen from gas mixtures, such as air. Low energy requirement of such membranes would make an attractive alternative for cryogenic air separation discussed in Chapter 2. Ion transfer membranes consist of mixed-metal oxide conductors. An obvious advantage of such a membrane process is that the system is driven by the constant depletion of permeated oxygen due to combustion (D'Alessandro et al. 2010). Membrane separation is discussed further in Chapter 7. Chemical looping combustion is discussed later in this chapter.

Methods similar to cryogenic air separation can be used to produce enriched oxygen. Oxygen enrichment can be considered as partial air separation, where a significant amount of nitrogen is removed, but some still remains in the combustion air. Retrofitting oxygen enrichment equipment is cheaper than oxyfuel systems, because no changes in the boiler are required and partial air separation is less energy intensive than production of pure oxygen.

Air-combusted boilers operate below atmospheric pressure to prevent CO or CO<sub>2</sub> leaking into the surroundings. The pressure difference allows air to leak into the boiler, which is not usually considered a problem. However in oxy-combustion boilers this leakage is undesired, so they must operate above atmospheric pressure, which may cause health problems due to CO and CO<sub>2</sub> leaking out.

## 2.1 Cryogenic air separation

Cryogenic air separation is based on different condensation temperatures, or boiling points, of different components of air. In atmospheric pressure the boiling point of oxygen is 90.2 K, of argon 87.3 K and of nitrogen 77.4 K. Due to different boiling points, it is possible to separate these three species from each other producing high purity streams by using a cryogenic air separation process.



*Figure 2.1. Cryogenic air separation process (adapted from Rackley 2004)*

In a simple cryogenic air separation process (Figure 2.1), air is first filtered and then compressed. The compressed air is cooled back to ambient temperature, dehydrated and fed through a heat exchanger, in which it is cooled further. Then the air is expanded through a valve, which causes it to cool even further, to a temperature where it changes into liquid phase. The liquefied air is fed into a distillation column. From the top of the column, gaseous and liquid nitrogen can be retrieved. Liquid oxygen comes out closer to the bottom of the column and is used to cool the compressed air in the heat exchanger. Part of the gaseous nitrogen stream is returned to the column after refrigeration to retain the temperature.

A modern air separation unit (ASU) may contain more distillation columns, heat exchangers and other components to separate more chemical species (such as argon) and increase the purity of the products.

Similar cryogenic distillation methods can be used to separate CO<sub>2</sub> from flue gas, but they are too expensive and energy intensive, if the gas mixtures has a low CO<sub>2</sub> fraction and is at an atmospheric pressure. On the other hand, liquefaction of CO<sub>2</sub> could be a viable option, if the pressure and CO<sub>2</sub> content are high, which is true with pre-combustion capture (Kanniche et al. 2010).

Environmental effects of cryogenic air separation units have been documented by European Industrial Gases Association (EIGA 2011). According to them, most notable emissions from an ASU are air emissions of volatile organic compounds (VOC), chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) used as refrigerants or solvents. These compounds may damage the ozone layer or promote the greenhouse effect. Identification of possible leak points is necessary to prevent these emissions. Refrigerants with less harmful potential should be considered. Other possible emissions are discharges of oil – mostly from compressors, hydraulic systems and transformers – and contaminated water. None of the emissions mentioned above should affect the purity of the oxygen used in oxyfuel combustion, and therefore neither the flue gases thereof. Same can be assumed true with cryogenic liquefaction of CO<sub>2</sub> from flue gases. (EIGA 2011)

## 2.2 Oxygen enrichment

Oxygen enrichment technologies aim to produce a stream of air with reduced nitrogen content, effectively increasing oxygen concentration. As in oxyfuel-combustion, using enriched oxygen results in a higher concentration of CO<sub>2</sub> and H<sub>2</sub>O in the flue gas due to reduced amounts of incoming nitrogen.

Oxygen enrichment has some advantages over pure oxygen production. First, production of lower purity oxygen requires less energy, because the energy intensive processes to separate the last fractions of nitrogen from air are not needed. Second, the reduced number of processes means less equipment is necessary. Therefore, compared to conventional cryogenic distillation to produce pure oxygen, both capital and operational costs of

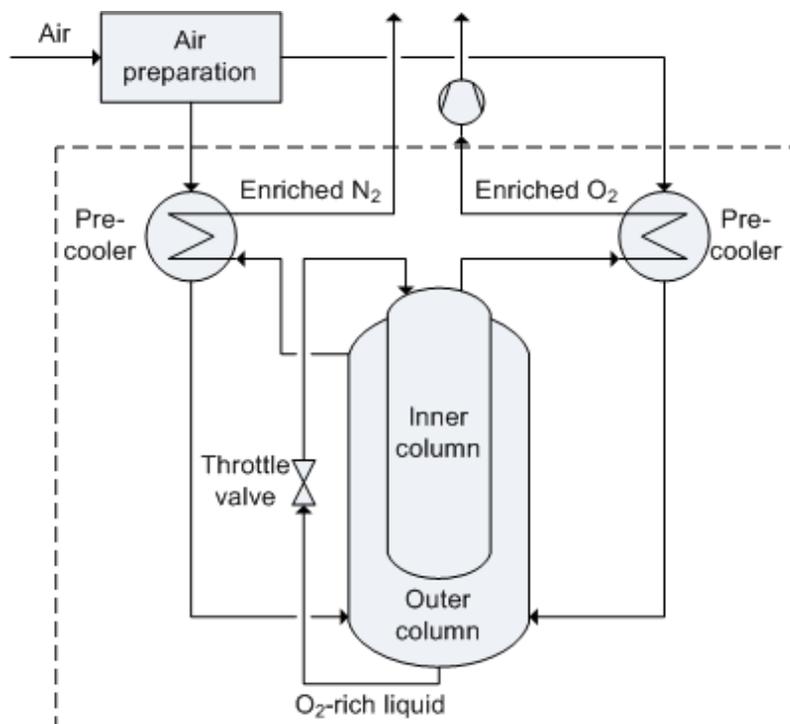
oxygen enrichment equipment are lower. Retrofitting of oxygen enrichment is easier due to smaller space requirement and better compatibility with existing boilers.

An example of an oxygen enrichment system is the Nurmia process. It is used to produce a stream with 50% oxygen and can be further improved to produce a stream with 80% oxygen. Unlike in cryogenic distillation processes, such as the Linde–Frankl Process, in the Nurmia process only the oxygen concentrate is liquefied while the nitrogen is produced in a gaseous phase. This combined with lower pressures in sub-processes results in lower energy costs. (Suhonen 2011)

The Nurmia apparatus consists of a double column, two heat exchangers, a compressor and air preparation equipment. The column and the heat exchangers are housed in a vacuum container. The Nurmia process is illustrated in Figure 2.2. The process is started with the help of liquid nitrogen.

In the Nurmia process, fresh air is first prepared by removing water, carbon dioxide and particles. This prevents water or carbon dioxide from freezing in the process and particles from disturbing it. Water can be removed by condensation or absorption. Carbon dioxide is absorbed by sodium hydroxide. Argon does not affect the process and is ignored in the preparation.

The prepared air flows into two counterflow heat exchangers, where it is cooled by streams of oxygen and nitrogen concentrates. The air then enters the outer column of a double column, where it flows upwards. The oxygen present in the air begins to condense, and an oxygen-rich liquid is formed at the bottom of the column.

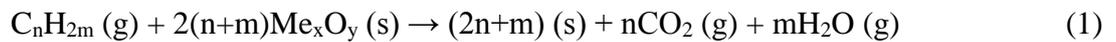


**Figure 2.2.** The Nurmia process. Dashed line represents the boundary of the vacuum (adapted from Suhonen 2011).

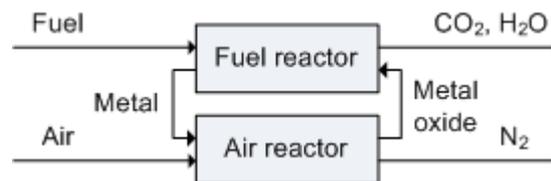
Gaseous nitrogen exits the column from the top. The nitrogen is used for pre-cooling the incoming air. The liquid oxygen exits the column from the bottom, goes through a valve where its pressure is throttled to 0.4 bars, and is then sprayed into the inner column. There is a temperature difference of approximately 4 K between the inner and outer column. This causes the oxygen condensation in the outer column, while oxygen in the inner column begins to vapourize. Gaseous low-pressure oxygen exits the column, goes through another air pre-cooler and is finally compressed to atmospheric pressure.

## 2.3 Chemical looping combustion

In chemical looping combustion (CLC), a gaseous fuel, such as natural gas or syngas, is combusted with oxygen, which is transported to the fuel with an oxygen carrier. The oxygen carrier is usually a metal oxide and it circulates between two separate reactors. The CLC process can be represented by two reactions:



In Equation 1, the metal oxide ( $\text{Me}_x\text{O}_y$ ) is reduced while the fuel ( $\text{C}_n\text{H}_{2m}$ ) is oxidized, or combusted, in the fuel reactor. In Equation 2, the reduced metal oxide ( $\text{Me}_x\text{O}_{y-1}$ ), or pure metal in some cases, is oxidized in the air reactor. See Figure 2.3 for an illustration of the overall CLC process.



**Figure 2.3.** Chemical looping combustion process (adapted from Rackley 2004).

The combustion reaction can be either exothermic (heat-releasing) or endothermic (heat-requiring). The metal oxidation reaction is always exothermic. The total amount of heat produced by these two reactions is equal to conventional combustion of the fuel.

The oxygen carrier usually consists of an active metal oxide and a support material, usually another oxide or kaolin. Additives such as starch may also be used. The choice of metal for the active oxide depends on different properties, such as high reactivity, oxygen transfer capacity and structural strength and low agglomeration. High reactivity is seen as faster reaction rates and lower dwell time in the reactors, which together mean that a smaller amount of the oxygen carrier is needed. Oxygen transfer capacity is defined by a carrier-specific oxygen ratio, or oxygen per mass of the carrier.

Oxidation and reduction enthalpies for some carriers are presented in Table 2.1 as examples. In the table, negative enthalpy means an exothermic reaction. Note that while

the reduction enthalpy may be either positive or negative, the oxidation enthalpy is always negative.

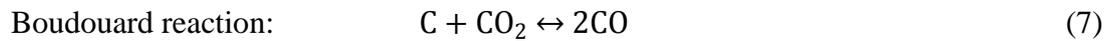
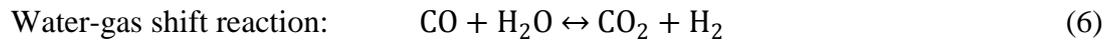
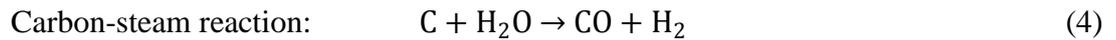
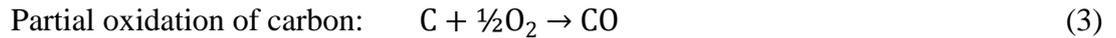
**Table 2.1.** Possible oxidation and reduction enthalpies for some oxygen carriers in chemical looping combustion of coal. (Siriwardane et al. 2009)

<b>Carrier</b>	<b>Reduction enthalpy (kJ/mol)</b>	<b>Oxidation enthalpy (kJ/mol)</b>
<b>CuO</b>	-96.5	-156
<b>NiO</b>	75.2	-327.7
<b>Fe<sub>2</sub>O<sub>3</sub></b>	79.2	-347.6
<b>Mn<sub>2</sub>O<sub>3</sub></b>	-36.1	-216.4
<b>Co<sub>3</sub>O<sub>4</sub></b>	-8.6	-243.9

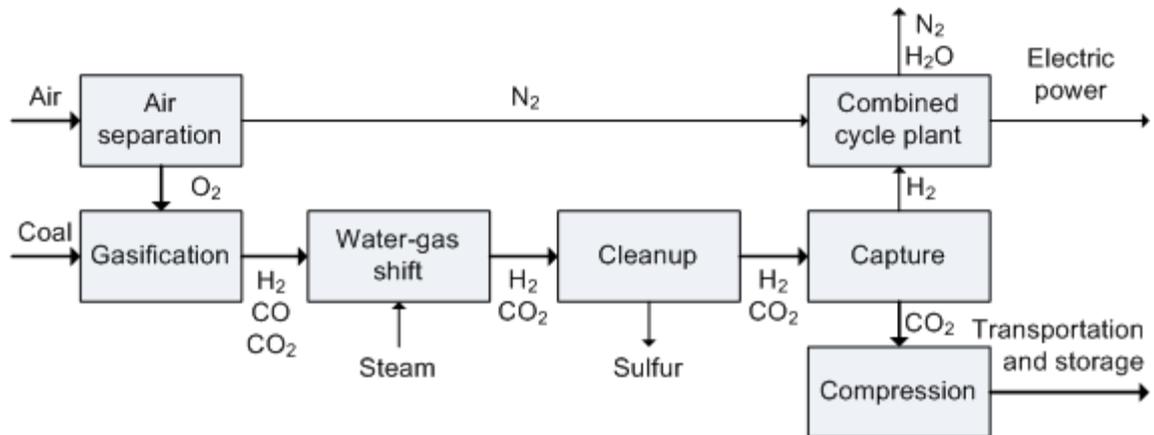
The CLC concept can also be modified to be used with syngas or hydrogen production and CO<sub>2</sub> capture. This is outside the scope of this thesis.

### 3 PRECOMBUSTION CAPTURE

In precombustion capture, also called fuel decarbonization, carbon from fuel is removed before combustion. This is achieved by gasification, a process in which the fuel is reacted at high temperatures with oxygen or steam, but without combustion. Gasification of fossil and other carbonaceous is based on the following five reactions:



The above reactions (Equations 3-6) eventually produce a synthesis gas, or syngas, containing carbon monoxide (CO) and hydrogen (H<sub>2</sub>), the concentrations of which vary depending on the original fuel used. Syngas is also a fuel and can be combusted in higher temperatures than the original fuel or used in fuel cells. Other uses for syngas besides combustion include methanol and synthetic fuel production.



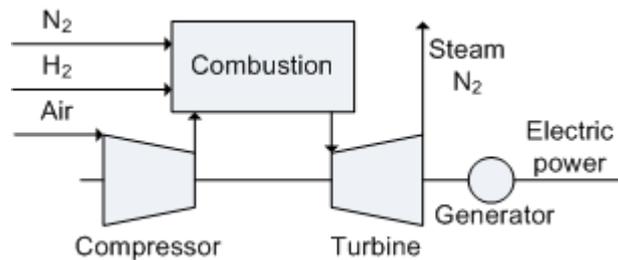
**Figure 3.1.** Process schematic of IGCC with CO<sub>2</sub> capture (adapted from Rackley).

Precombustion capture is widely accepted to be used with the integrated gasification combined cycle (IGCC) process (Figure 3.1). In an IGCC process the fuel is first gasified, using oxygen from an air separation unit. After gasification, the syngas is reacted with steam to facilitate another water-gas shift reaction to increase the amount of CO<sub>2</sub> for capture and H<sub>2</sub> for combustion. Possible sulfur compounds, such as H<sub>2</sub>S and H<sub>2</sub>SO<sub>4</sub>, are removed from the stream. Finally, the CO<sub>2</sub> and H<sub>2</sub> in the stream are separated.

The process to separate CO<sub>2</sub> and H<sub>2</sub> should be chosen based on the partial pressure of CO<sub>2</sub> in the gas mixture (Kanniche et al. 2010). Several methods for separation exist and

are based on the same principles as the ones used in postcombustion capture. These methods are described in Chapters 5–7.

The separated  $H_2$  stream is used as a fuel for a gas turbine (Figure 3.2). Fresh air is compressed and driven into the combustion chamber with the hydrogen. Nitrogen from the air separation process in Figure 3.1 can be injected to the combustion chamber or vented in the atmosphere. Combustion products – mostly steam and nitrogen – are expanded in a turbine, which provides power to the compressor and a generator for producing electricity, and exhausted.



**Figure 3.2.** Gas turbine with hydrogen combustion and optional nitrogen input (adapted from Rackley 2004).

While the  $H_2$  is combusted, the  $CO_2$  stream is purified and compressed for transportation and storage. Purification and treatment processes are described in Chapter 9.

$CO_2$  capture methods suitable for precombustion are basically the same as for postcombustion capture, even though the composition of the processed gas mixture is different.  $CO_2$  and water concentrations are higher than in postcombustion flue gas, due to reduced nitrogen content. High water content may affect some capture methods either negatively or positively, while others may be neutral to the presence of water.

Current technologies suitable for precombustion capture are limited to absorption-based separation, either with physical or chemical solvents, and  $CO_2$  liquefaction. Technologies under research include new solvents and equipment for absorption, adsorption separation, membrane separation and hybrid processes combining cryogenic and membrane technology (Rackley 2004).

## 4 POSTCOMBUSTION CAPTURE

In postcombustion capture, CO<sub>2</sub> is separated from the flue gas of a boiler. This can be achieved after a regular air-combustion boiler or an oxyfuel combustion boiler. The most relevant difference between the two combustion methods is the partial pressure of CO<sub>2</sub> present in the flue gas. Generally, postcombustion capture refers exclusively to CO<sub>2</sub> capture after a conventional air-combustion boiler, and this terminology is used in this thesis as well.

After conventional air-combustion, the CO<sub>2</sub> fraction of flue gas is much lower than after combustion with oxygen or enriched oxygen, while the N<sub>2</sub> fraction is higher. Some capture methods require a high CO<sub>2</sub> fraction and for that reason are not compatible with postcombustion capture.

The most mature and commercially available postcombustion capture technology is based on absorption of CO<sub>2</sub> in amines, as described in Chapter 5.1.1. While it may not be the most energy or cost effective method available, it is very suitable for retrofitting due to the fact that it is considered an end-of-pipe technology.

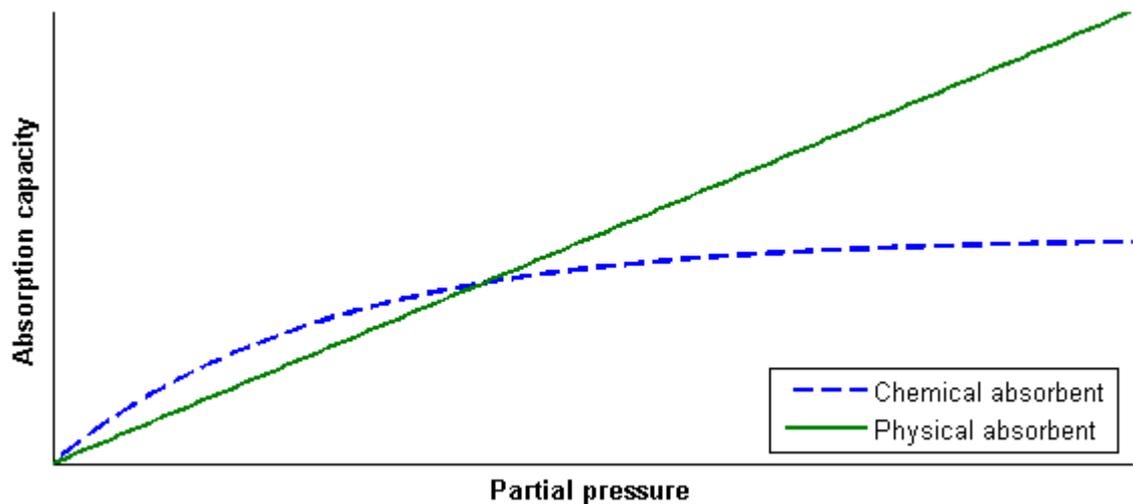
As stated earlier, cryogenic separation of CO<sub>2</sub> isn't suitable for post-combustion capture. Instead, separation with membranes is an attractive option, especially if combined with chemical absorption, but there are downsides due to dust, steam and physical degradation of the membranes (Kanniche et al. 2010).

As this thesis deals with precombustion capture and capture combined with oxyfuel combustion, postcombustion capture is not discussed further.

## 5 ABSORPTION-BASED CO<sub>2</sub> SEPARATION

Carbon dioxide can be absorbed using either physical or chemical solvents. In chemical absorption, the CO<sub>2</sub> and the solvent react reversibly to form chemical compounds from which the CO<sub>2</sub> can be recovered. In physical absorption the solvent is inert and CO<sub>2</sub> is absorbed without a reaction. (Rackley 2004)

The choice between a physical or chemical solvent should be made depending on the partial pressure of CO<sub>2</sub>. Physical solvents are more appropriate if the CO<sub>2</sub> partial pressure exceeds 8 bars, below which chemical solvents work better (Kanniche et al. 2010). See illustration in Figure 5.1.



*Figure 5.1. Absorption capacity versus partial pressure of CO<sub>2</sub> for chemical and physical solvents (adapted from Rackley 2004).*

### 5.1 Chemical solvents

Chemical absorption is based on an exothermic reaction between a sorbent and CO<sub>2</sub>. The CO<sub>2</sub> can be recovered using a reverse reaction called stripping, thus regenerating the sorbent. Usually absorption occurs at a low temperature and the regeneration process at a higher temperature, depending on the sorbent used. Chemical absorption is especially suitable if the partial pressure of CO<sub>2</sub> in the gas mixture is low (below 8 bars), as explained above. This may not necessarily be true with flue gases from oxyfuel combustion or pre-combustion.

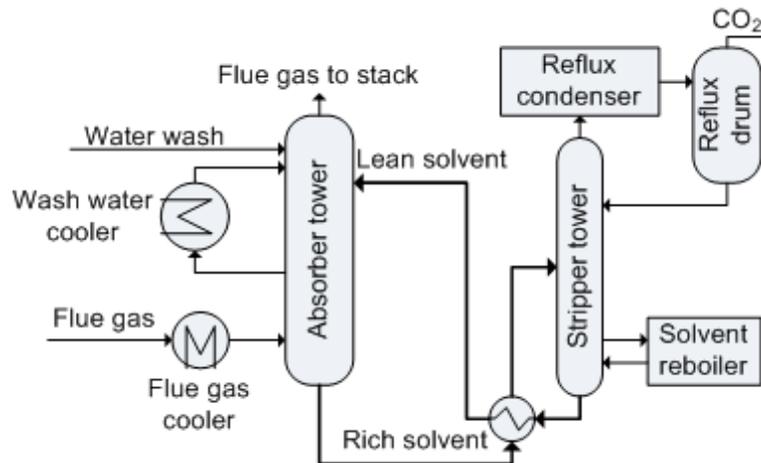
There are several chemicals suitable for CO<sub>2</sub> capture. The predominant solvents are different amines and carbonates. These – and sodium hydroxide (NaOH), aqueous or chilled ammonia and dry sorbent systems – are explained in the following subchapters.

### 5.1.1 Amines

Amines are organic compounds, in which one or more of the hydrogen atoms in ammonia ( $\text{NH}_3$ ) are substituted by organic compounds, conventionally marked in chemical formulas as R. Depending on the number of substituents replacing the hydrogen atoms of the ammonia group, amines are termed primary (chemical formula  $\text{RNH}_2$ ), secondary ( $\text{R}^1\text{R}^2\text{NH}$ ) or tertiary ( $\text{R}^1\text{R}^2\text{R}^3\text{N}$ ) amines.

Amines have been used for  $\text{CO}_2$  capture since at least the 1960s for EOR. Amine-based absorption is therefore considered a mature technology and has been studied extensively. Amines best suitable for  $\text{CO}_2$  capture are alkanolamines, which means amines containing at least one hydroxyl ( $-\text{OH}$ ) group. The hydroxyl group is considered to reduce vapour pressure and increase solubility in water, while the amino group provides alkalinity necessary to absorb  $\text{CO}_2$ . (Merikoski 2012)

Several amines are being used and researched for various  $\text{CO}_2$  capture applications. EOR is the most notable technology, but post-combustion capture has emerged since. There seems to be no reason for amine absorption not to work with oxyfuel or pre-combustion capture as well, other than the partial pressure threshold after which physical absorption becomes desirable. Primary amines are preferred when the partial pressure of  $\text{CO}_2$  is less than 1 bar, while tertiary amines are better at higher pressures, up until the threshold of 8 bars.



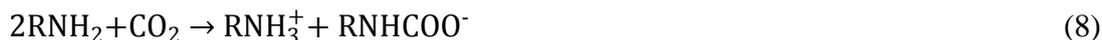
**Figure 5.2.** A typical amine-based  $\text{CO}_2$  absorption unit (adapted from Rackley 2004)

In an amine-based  $\text{CO}_2$  absorption process (Figure 5.2), flue gas is first cooled with water. Then the flue gas enters an absorber tower. In the tower, the solvent reacts with the  $\text{CO}_2$  in the flue gas. The rest of the flue gas, consisting of mostly  $\text{N}_2$  and  $\text{H}_2\text{O}$ , is washed in order to reduce solvent losses. After washing the flue gas is released to the atmosphere.

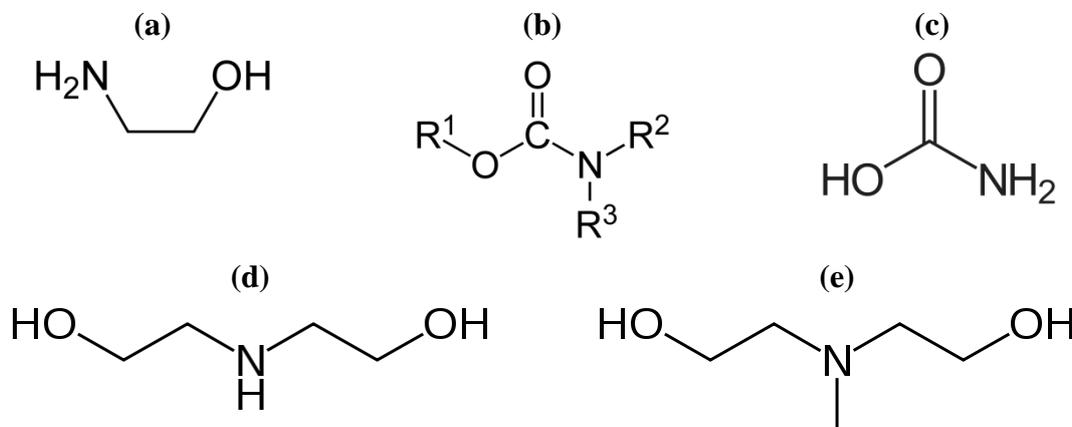
Rich solvent, which now carries most of the  $\text{CO}_2$ , goes into a stripping tower. The solvent is heated in a heat exchanger, recovering heat from recycled lean solvent. In the stripping tower, the rich solvent is heated with a reboiler, thus releasing the  $\text{CO}_2$  and regenerating the solvent. Steam and released  $\text{CO}_2$  exit the stripping tower, after which the

steam is condensed from the CO<sub>2</sub> product stream. The lean, regenerated solvent is cycled back to the absorber.

The most common amine used in CO<sub>2</sub> absorption is monoethanolamine (MEA), in which one of the hydrogen atoms is replaced by an ethanol group (Figure 5.3a). It acts as a weak base in an aqueous solution, capable of neutralizing an acidic molecule, such as CO<sub>2</sub>. When a primary amine reacts with CO<sub>2</sub>, a carbamate ion is produced (Equation 8). Secondary amines, such as diethanolamine (DEA, Figure 5.3d), react similarly to primary amines (Equation 9). Both reactions are exothermic.

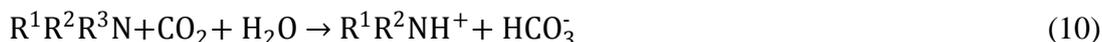


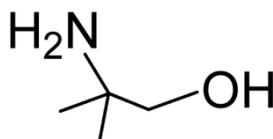
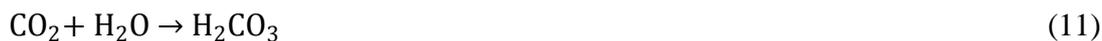
Carbamates (Figure 5.3b) are organic compounds derived from carbamic acid (NH<sub>2</sub>COOH, Figure 5.3c). Certain carbamates are used as insecticides. While most carbamate insecticides have complicated chemical structures, some simple ones exist and may pose a threat to environment, if formation and release to atmosphere occurs. An example of a relatively simple carbamate insecticide is methomyl, which may form in the presence of sulfur. Methomyl is highly toxic to humans and has low sorption affinity to soil, which may lead to serious ground and surface water contamination (Tomašević et al. 2010). Information on formation of potentially dangerous carbamates in CCS is limited and more research is required.



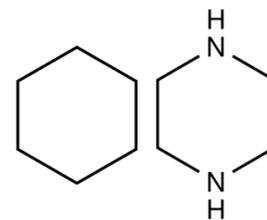
**Figure 5.3.** Structures of (a) monoethanolamine MEA, (b) carbamate, (c) carbamic acid, (d) diethanolamine DEA and (e) methyldiethanolamine MDEA.

With tertiary amines, such as methyldiethanolamine (MDEA, Figure 5.3e) CO<sub>2</sub> is absorbed by base-catalyzed hydration (Equation 10), which is exothermic. The reaction also occurs with lower amines, but its rate of reaction is so low that the contribution to CO<sub>2</sub> absorption is insignificant. Another reaction that also occurs with all three amines is the formation of carbonic acid (Equation 11), but it is also considered insignificant.





**Figure 5.4.** 2-amino-2-methyl-1-propanol (AMP).



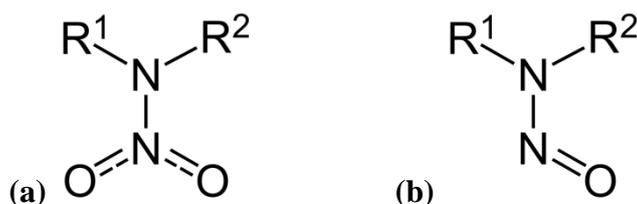
**Figure 5.5.** Cyclohexane (left) and piperazine (right).

Other relevant amines include piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP). AMP (Figure 5.4) is a sterically hindered amine. Steric hindrance means that each atom of a molecule occupies a certain amount of space, thus shaping the geometry of the molecule, with large groups preventing reactions with other groups of the molecule. Sterically hindered amines react with  $\text{CO}_2$  unlike regular amines, leading to a higher absorption capacity (per mol) and lower amine requirement. Higher selectivity for  $\text{H}_2\text{S}$  and  $\text{CO}_2$  by using sterically hindered amines has also been hypothesized. (Merikoski 2012)

Piperazine ( $\text{C}_4\text{H}_{10}\text{N}_2$ ) is a cyclohexane with two opposing carbon atoms replaced by amine groups (Figure 5.5). It is not an alkanolamine as it does not contain a hydroxyl group. Piperazine can still absorb high loads of  $\text{CO}_2$  and the absorption rate is significantly faster than of MEA, for instance. While not generally used for absorption as such, it is often used as an additive with MDEA. It is also less corrosive, less volatile and resistant to degradation by oxidation. However, it appears to have adverse health effects and long degradation time in marine ecosystems (Merikoski 2012).

Generally speaking, primary amines are more subject to degradation in the presence of  $\text{CO}_2$  compared to secondary and tertiary amines. Degradation products include formic acid ( $\text{HCOOH}$ ) and ammonia.  $\text{SO}_2$  and  $\text{NO}_2$  react with amines to form various sulfates and nitrates. Other impurities, such as  $\text{HCl}$ , may also exist in the flue gas and degrade the amines further. Amine degradation leads to a reduction in absorption capacity and introduces a need for solvent make-up and waste disposal. There is a chance these compounds, as well as the amines used themselves, can also reach the atmosphere or the  $\text{CO}_2$  product stream.

Other possible emissions caused by amine reactions are nitroamines and nitrosamines (Figure 5.6). Nitroamines ( $\text{R}^1\text{R}^2\text{N-NO}_2$ ) are amines with a nitro group ( $-\text{NO}_2$ ), while nitrosamines ( $\text{R}^1\text{R}^2\text{N-N=O}$ ) have a nitroso group ( $-\text{NO}$ ). The  $\text{R}^1$  and  $\text{R}^2$  groups can belong to the same cyclic group. Nitroamines and nitrosamines are considered carcinogenic and toxic. Their long-term effects are not well known. The reaction mechanics of how they are formed in the capture process is not known either. Furthermore, it is not well known how amines or possible degradation products react in the atmosphere.



**Figure 5.6.** Generic structures of (a) nitroamine and (b) nitrosamine.

The biodegradability of primary and secondary amines is higher than that of tertiary amines. However, sterically hindered and cyclic amines, such as AMP and PZ, are more stable and less biodegradable (Eide-Hauhmo 2012).

### 5.1.2 Carbonates

The process for CO<sub>2</sub> capture with carbonate-based absorption is similar to absorption with amines as explained in the previous subchapter (see Figure 5.2). It is based on the same chemical reaction where acid rain dissolves carbonic rocks. In the reaction carbonic acid (see Equation 11) reacts with compounds, such as calcium carbonate:



The reactions in Equations 11 and 12 remove carbon dioxide from the atmosphere and are considered a natural part of the geochemical carbon cycle. Similar reactions with different carbonates can be used to efficiently remove CO<sub>2</sub> from a flue gas stream. For example, potassium carbonate (Equation 13) and sodium carbonate (Equation 14) react with carbon dioxide and water to form potassium bicarbonate and sodium bicarbonate, respectively:



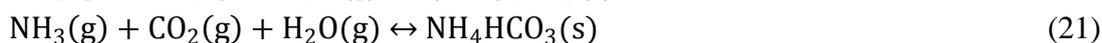
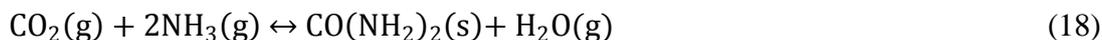
These reactions have a lower desorption energy than amine-based capture, but their reaction rate is slower. However, the reaction rate and absorption capacity can be increased with piperazine (see section 5.1.1). As an example, carbon dioxide capture by potassium bicarbonate with piperazine enhancement follows the reactions:



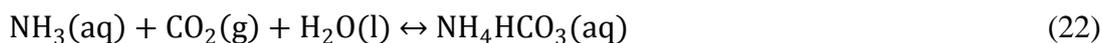
The carbamate reactions in Equations 16 and 17 dominate the CO<sub>2</sub> absorption process. These reactions require less heat for regeneration than for example when using MEA. (Rackley 2004)

### 5.1.3 Aqueous ammonia

Carbon dioxide and ammonia can react in several different ways, depending on temperature, pressure and the state of reactants. Possible products for a homogenous reaction in gas phase include urea ( $\text{CO}(\text{NH}_2)_2$ ), ammonium carbamate ( $\text{NH}_2\text{COONH}_4$ ), ammonium carbonate and ammonium bicarbonate (Equations 18-21):



The explosive limit for gaseous ammonia is 15-28 vol-%. Even though ammonia will only ignite if heated, for safety reasons only aqueous solutions of ammonia should be used. The total, reversible, reaction of carbon dioxide absorption with aqueous ammonia can be expressed as Equation 22. The actual chemical reactions involved are more complicated and are not discussed further.



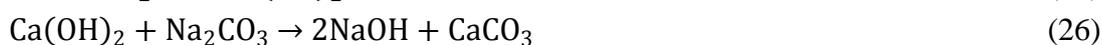
Aqueous ammonia has a higher absorption capacity for  $\text{CO}_2$  (95-99%, over 1.0  $\text{kgCO}_2/\text{kg}_{\text{solvent}}$ ) than MEA (90%, 0.36  $\text{kgCO}_2/\text{kg}_{\text{solvent}}$ ) at same temperatures and pressures (Liu et al.), which means less solvent is required.

### 5.1.4 Sodium hydroxide

Sodium hydroxide ( $\text{NaOH}$ ) can be used to absorb carbon dioxide, again based on reactions related with bicarbonates. As described before (Equation 11), water and carbon dioxide form carbonic acid. Carbonic acid reacts with sodium hydroxide to form sodium bicarbonate, which further reacts with sodium hydroxide to form sodium carbonate:



Sodium hydroxide can be regenerated with the addition of lime ( $\text{CaO}$ ). A calcium carbonate slurry is formed:



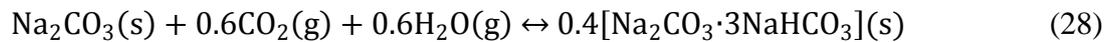
The calcium carbonate slurry is dried and calcinated back to lime, regenerating the carbon dioxide which can then be captured:



Sodium hydroxide and calcium carbonate are inexpensive and readily available chemicals, but the calcination process (Equation 27) requires a lot of energy.

### 5.1.5 Dry sorbents

Amine and carbonate slurry scrubbing processes are energy intensive and expensive due to large volumes of flue gas to be treated. An interesting alternative is the use of dry sorbents, such as sodium or potassium carbonates described in Chapter 5.1.2, in their solid form. For example, solid sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) reacts with carbon dioxide and water vapour as follows:



The product in Equation 28 is known as Wegscheider's salt or Wegscheiderite. This reaction occurs in temperatures above 70 °C, while generally alkali metal carbonates can be used at temperatures below 200 °C. The reaction is reversible so the sodium bicarbonate can be regenerated and the carbon dioxide recovered in an atmosphere of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . (Liang et al. 2004)

Other potential products from dry sodium carbonate absorption are  $\text{NaHCO}_3$  (reaction similar to Equation 14), sodium sesquicarbonate ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) and the hydrate  $\text{NaHCO}_3 \cdot \text{H}_2\text{O}$ . The last two compounds do not appear to be important for  $\text{CO}_2$  capture (Liang et al. 2004).

## 5.2 Physical solvents

Physical absorption processes use solvents which absorb acid gas components instead of reacting with them chemically. Absorption is determined by Henry's law, formulated by William Henry in 1803, which states that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. Henry's law can be expressed as an equation as follows:

$$p = k_H c \quad (29)$$

where  $c$  is the concentration of the solute,  $p$  is the partial pressure of the solute in the gas above the solution and  $k_H$  is the Henry's law constant, which depends on the solute, the solvent and the temperature. For example, the solubility of  $\text{CO}_2$  in water at 298 K is 29.41 atm·L/mol.

As can be seen from Equation 29, concentration is proportional to the partial pressure. Hence physical solvents have a linear absorption capacity, which exceeds the capacity of

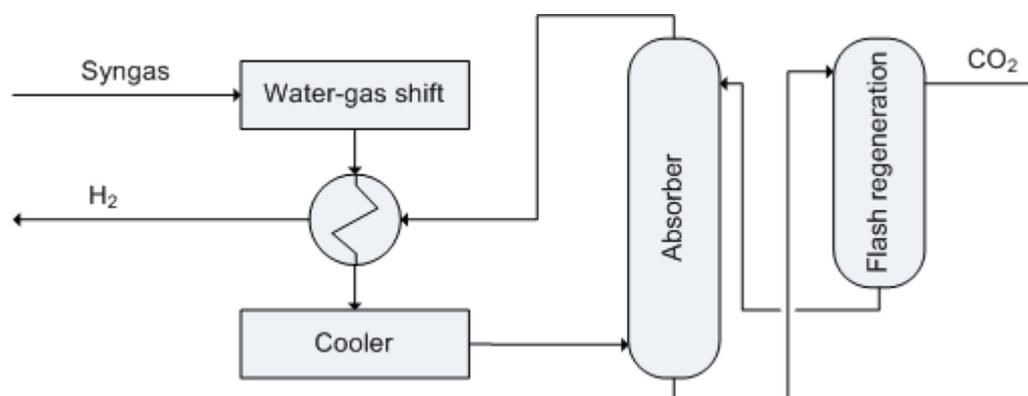
amine-based solvents at around 8 bars, as seen before in Figure 5.1 (Kanniche et al. 2010).

Requirements for a viable physical absorption process include low vapour pressure, high CO<sub>2</sub> selectivity, low viscosity, thermal and chemical stability as well as non-corrosive behavior. Low vapour pressure reduces solvent losses to the flue gas or product CO<sub>2</sub> stream. High CO<sub>2</sub> selectivity ensures better separation, leading to higher CO<sub>2</sub> capture rate and CO<sub>2</sub> purity. Thermal and chemical stability reduce solvent degradation due to high temperatures and other chemicals present in the process. Low viscosity increases absorption and desorption rates. Non-corrosive properties reduce costs of maintenance and the materials used in the equipment. (Gui et al. 2011)

The most common physical CO<sub>2</sub> capture processes are the Rectisol, Fluor and Selexol processes. They use refrigerated methanol, propylene carbonate and dimethyl ethers of polyethylene glycol as physical solvents, respectively. These processes are described in the following subchapters.

Gui and coworkers (2011) have studied other possibly suitable solvents for CO<sub>2</sub> absorption. They studied several solvents and concluded that the solubility of CO<sub>2</sub> in alcohols, ethers and ketones decreases proportionally to pressure and inversely to temperature.

### 5.2.1 Rectisol process



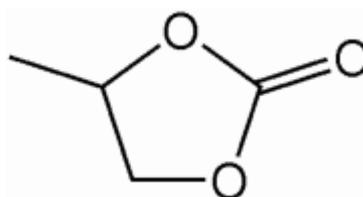
**Figure 5.7.** CO<sub>2</sub> absorption from water-gas-shifted syngas (adapted from Rackley 2004).

The Rectisol process (Figure 5.7) uses refrigerated methanol (CH<sub>3</sub>OH) and is used in syngas purification. In the process, desulfurized syngas is first water-gas-shifted and cooled. The syngas, at this point consisting of CO<sub>2</sub> and H<sub>2</sub>, then enters the absorber in which CO<sub>2</sub> is absorbed by the refrigerated methanol, which is at -10...-70 °C (Rackley 2004).

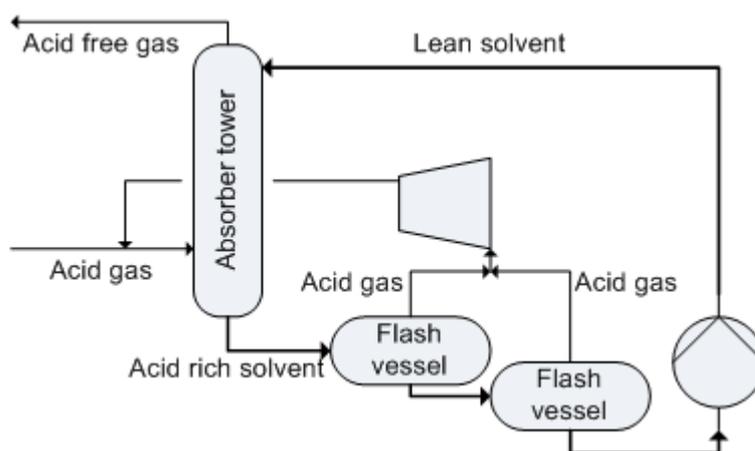
The process uses syngas, which means it is very suitable to be used in precombustion capture. It is widely configurable and can also be used to remove trace components of compounds such as hydrogen cyanide (HCN), imidogen radicals (HN) and hydrogen sulfide (H<sub>2</sub>S) from the syngas (Rackley 2004).

### 5.2.2 Fluor process

Propylene carbonate ( $C_4H_6O_3$ , Figure 5.8) is a carbonate ester derived from propylene glycol ( $C_3H_8O_2$ ). It is used in the Fluor process developed by the companies Fluor and El Paso Natural Gas Company. The Fluor process was the first physical absorption process for removing  $CO_2$  from natural gas. The process is relatively simple and can be adapted to  $CO_2$  capture from flue gas. Hydrogen sulfide ( $H_2S$ ) can be removed from the flue gas due to its high solubility in propylene carbonate. Propylene carbonate is also non-corrosive.



*Figure 5.8. Propylene carbonate*



*Figure 5.9. Illustration of the Fluor process. Solvent circulation is depicted in thicker arrows.  $CO_2$  exits the process from flash vessels. (Adapted from Rackley 2004).*

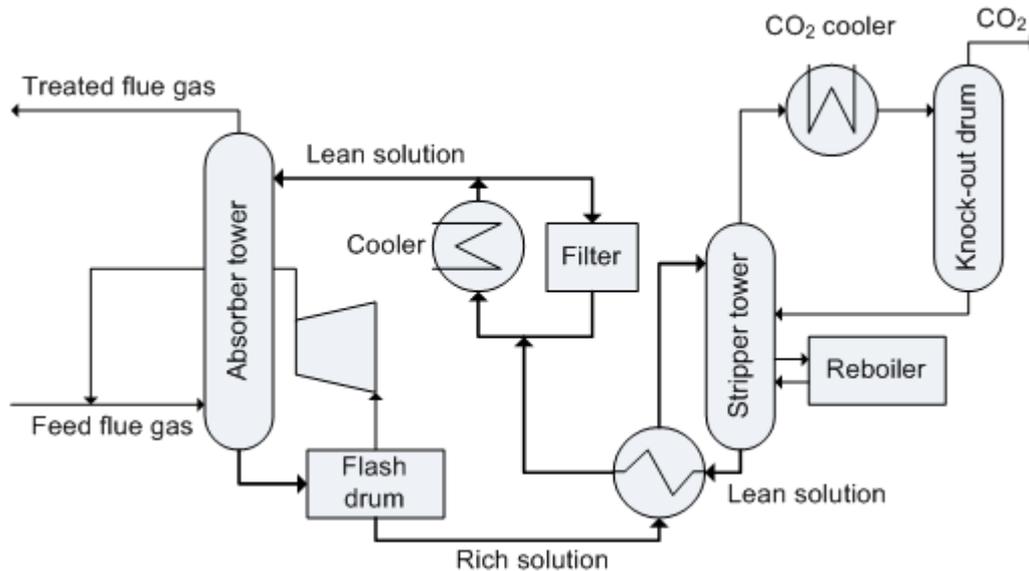
In the Fluor process (Figure 5.9) the gas mixture is fed into a high pressure absorber tower. The carbon dioxide is absorbed in propylene carbonate and the acidic solvent driven to a series of flash vessels, regenerating the solvent and releasing the  $CO_2$ . The solvent is circulated back to the absorber tower.

### 5.2.3 Selexol process

The Selexol process has been used commercially since the 1970s to remove acid gases, such as  $CO_2$ , hydrogen sulfide ( $H_2S$ ), and carbonyl sulfide ( $COS$ ), from synthetic or natural gas streams, in their own separate streams. The process can also be used to control

the dew point of hydrocarbon gases or liquefied natural gas (LNG). The ability to remove CO<sub>2</sub> is of obvious interest for CCS.

The process is based on a mixture of dimethyl ethers of polyethylene glycol. Their general chemical formula is CH<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>*n*</sub>CH<sub>3</sub>, where *n* is 3–9. Water is highly soluble in the Selexol solvent and must be avoided, which is a disadvantage. Another disadvantage of the process is the requirement for high CO<sub>2</sub> partial pressure, which on the other hand should be attainable from oxyfuel flue gas and from syngas.



**Figure 5.10.** Illustration of the Selexol process for CO<sub>2</sub> removal from natural gas. Solvent circulation depicted in thicker arrows. (Adapted from Rackley 2004).

The process itself resembles chemisorption with amines. Flue gas from the boiler goes through an absorber tower, where the CO<sub>2</sub> is absorbed in the solvent. CO<sub>2</sub> is removed from the solvent in a stripper tower.

It is probable that the various chemicals used in the Selexol solvent decompose into shorter hydrocarbons and ethers, which may react with each other or impurities in the flue gas, producing new compounds. The exact decomposition route or conditions are not known and the terminal products may vary. It is therefore recommendable to monitor the emissions of those compounds known to cause most concern in the environment and equipment, such as acids and flammable compounds, until more data is acquired.

## 6 ADSORPTION-BASED CO<sub>2</sub> SEPARATION

Adsorption is different from absorption in that the adsorbed particles, or adparticles, attach to the surface of the adsorbent either chemically, in which case the process is called chemisorption, or physically, also known as physisorption. Adsorption-based gas separation has mostly been driven by air purification applications.

There is a vast selection of different adsorbents available. Adsorbents are generally solids with a large surface area, such as zeolites, activated carbon, metal oxides and hydrotalcites. Supported amines are an interesting hybrid group using mechanics familiar from absorption technologies to adsorb the CO<sub>2</sub> on a surface. Metal-organic frameworks (MOF) are also discussed. (Choi et al. 2009)

Adsorption on a solid, while proven to produce good quality CO<sub>2</sub> for food industry, doesn't seem a viable option when processing large gas flows with high impurity content (Kanniche et al. 2010). Therefore separation by adsorption requires some auxiliary processes to remove the impurities.

In principle, the adsorbents discussed here should be applicable to oxyfuel combustion just as well as pre- or postcombustion capture. However, inherent properties of the combustion processes – such as operating pressures and temperatures, CO<sub>2</sub> concentration in the flue gas, impurity content and such – have an effect on the optimal choice of adsorbent for each combustion process. These selection criteria are not discussed in this thesis.

In general, the adsorption process involves one or more beds, in which the flue gas is contacted with the adsorbent. The CO<sub>2</sub> is then desorbed from the bed, with one of several methods depending on the adsorbent. This adsorption–desorption process can be achieved by various combinations of moving and fixed sorbent beds and exposing the sorbent and sorbate to periodically changing conditions. The change in conditions is called a 'swing'.

In temperature swing adsorption (TSA), the CO<sub>2</sub> is adsorbed at a relatively low temperature and released at a higher temperature. In the more complicated pressure swing adsorption (PSA) process, a series of low and high pressure beds are used to adsorb and desorb the CO<sub>2</sub>. Processes combining both temperature and pressure swing adsorption (TPSA) are being studied alongside other methods, such as electrothermal or electric swing adsorption (ESA), in which desorption is achieved through heating the sorbent by passing an electric current through it (Rackley 2004). Further description of these systems is outside the focus of this thesis.

Generally speaking, the most likely emission routes in an adsorption process are the CO<sub>2</sub> product stream, the exhaust stream to atmosphere and during maintenance to the environment. Most adsorbents and possible reaction products remain in particle form and can be easily removed from the streams with an ESP or a similar process. CO<sub>2</sub> emissions are not necessarily a problem if the concentrations are low, but should still be avoided.

The flue gas may contain some carbon monoxide, which could pass the adsorption process. Different adsorbents, their properties and relevant emissions are described in the following subchapters.

## 6.1 Zeolites

Zeolites are aluminosilicates containing a periodic array of  $\text{SiO}_4$  and  $\text{AlO}_4$  molecules. They are widely used as molecular sieves. Their adsorption capacity is based on the negative charge caused by the presence of aluminium atoms inside a porous silicate framework. The International Zeolite Association (IZA) recognizes 206 different framework type codes for zeolites. (IZA, 2013)

The dominant mechanism for adsorption in zeolites is physisorption, caused by the electric field, created by charge-balancing cations inside the pores and further by hydrogen bonding with silanol groups on the surface. A small fraction of  $\text{CO}_2$  is absorbed chemically into the zeolite and different carbonates or carboxylates can be formed. (Choi)

No other compounds are likely to form, so the emissions from a zeolite adsorption system are limited to the zeolite itself due to mechanical wear, leaking carbon dioxide and the possible carbonates and carboxylates, precise compositions of which depend on the zeolite used. Zeolites are resistant to degradation, but may have to be changed every so often, causing possible maintenance leaks.

## 6.2 Activated carbon

Activated carbons are porous carbonaceous particles. They can be produced from various raw materials, such as different coals, industrial byproducts, wood or biomass. They are inexpensive and can be produced in several different pore sizes, pore distributions and active surface structures, depending on the raw material and process used. Other factors related to adsorption capacity may also exist.

Producing activated carbon consists typically of two steps: carbonization and activation. In the carbonization step, the raw material is pyrolysed in an inert atmosphere to produce char, removing non-carbon elements such as hydrogen, oxygen and nitrogen. Then the char is activated, either chemically or physically, to achieve the desired porosity and surface area. In physical activation, the char is partially gasified. In chemical activation, chemicals such as  $\text{KOH}$ ,  $\text{H}_3\text{PO}_4$  and  $\text{ZnCl}_2$  are used to open micropores present in the char.

The adsorption properties of different activated carbons are highly variable, due to the variations in pore size, pore structure and surface area. In general, the  $\text{CO}_2$  adsorption properties are lower than those of zeolites in atmospheric pressures. However, at higher pressures activated carbons can exceed zeolites in adsorption capacity, possibly because of the higher surface area. Activated carbons also have lower heats of adsorption, leading to less energy intensive desorption. They are also very resistant to degradation, meaning

their adsorption capacities do not change noticeably even after several adsorption-desorption cycles. Presence of water affects the adsorption capacity negatively, due to water's competitive ability to absorb CO<sub>2</sub>. Storing activated carbons in humid conditions may reduce their adsorption capacity. Their adsorption rates are nevertheless comparable to those of zeolites.

Much like with zeolites, the only perceivable emissions from activated carbon adsorption are different particles in the product or exhaust streams and during maintenance. There is a low chance that chemicals from the char activation step still remain in the adsorbent. This may cause be problems if low-quality suppliers are used.

### 6.3 Metal oxides

Several metal oxides have basic sites capable of adsorbing acidic CO<sub>2</sub>. Suitable metal oxides tend to have a low charge-radius ratio, which means they are more ionic in nature and the basicity is higher, such as those of alkali metals and alkaline earth metals. There are also several other metal oxides that display CO<sub>2</sub> adsorption to some extent: lithium, sodium, potassium, rubidium, cesium, barium, iron, tantalum, copper, chromium and aluminium oxides. Attention should be paid to the toxicity of the oxides being used.



For example, alkaline earth metals react with CO<sub>2</sub> to form a carbonate according to Equation 30, where M represents the metal, such as Mg, Ca, Sr and Ba. The reaction in is exothermic and reversible, which allows regeneration of the metal oxide and recovery of carbon dioxide. Calcium oxide has been used this way to remove CO<sub>2</sub> in the sorption-enhanced reaction (SER) process, which produces high purity hydrogen.

Calcium oxide is considered to have an advantage over other oxides due to high availability, from precursors such as limestone or dolomite, which leads to low cost for the adsorbent. It has a higher adsorption capacity than most inorganic chemisorbents, slightly depending on the raw material from which the oxide was obtained. Degradation of CaO is fast due to pore blocking and sintering, but it stabilizes eventually to about 25% of initial adsorption capacity. Reaction kinetics of calcium oxide is slower than zeolite and activated carbon.

Magnesium oxide has a lower energy requirement for regeneration than calcium oxide, but its adsorption capacity is lower as well. Magnesium oxide functions, however, as a catalyst support due to the basicity of the oxygen atoms on the surface.

Possible emissions are likely to consist of the oxides used and the carbonates produced in the adsorption reaction.

## 6.4 Layered double hydroxides

Layered double hydroxides (LDH), also known as hydrotalcite-like compounds, are a group of compounds that consist of positively charged layers with charge-balancing anions between the layers. They are similar to hydrotalcite,  $[\text{Mg}_{3/4}\text{Al}_{1/4}(\text{OH})_2](\text{CO}_3)_{1/8} \cdot \frac{1}{2}\text{H}_2\text{O}$ , the structure of which serves as an example for the group (Rives). The general formula for LDHs is:



where  $\text{M}^{2+}$  can be for example  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$  or others;  $\text{M}^{3+}$  can be  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  or others and  $\text{A}^{m-}$  can be  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$  or others. Typically  $x$  is between 0.17 and 0.33. (Choi et al.)

The  $\text{CO}_2$  adsorption capacities of LDHs are slightly lower than those of other chemisorbents. Unlike with zeolites and activated carbon, the presence of water, whether in the feed gas or the LDH itself, is actually beneficial to adsorption capacity. Regenerability of hydrotalcite-like adsorbents is sufficient for flue gas processing even at low  $\text{CO}_2$  and high  $\text{H}_2\text{O}$  content.

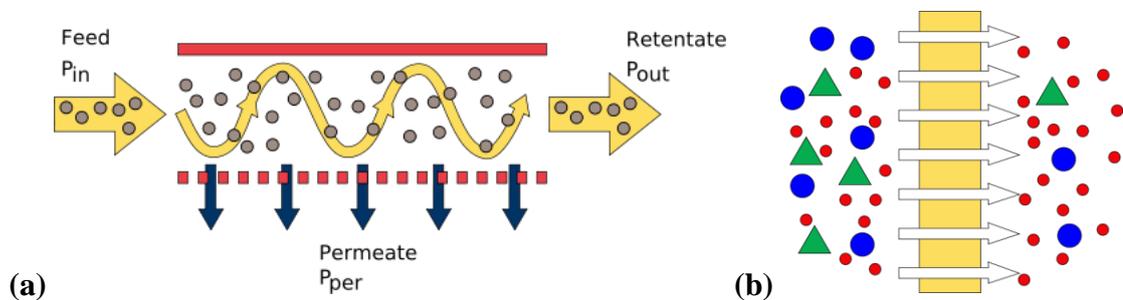
LDHs may decompose in high temperatures to other compounds. Decomposition of the LDH depends heavily on the nature of the layer cations, the interlayer anions and whether in an oxidizing, reducing or inert environment. The decomposition occurs in four stages: (i) surface dehydration, (ii) interlayer dehydration, (ii) dehydroxylation and (iv) removal of the interlayer anion. These stages occur at different temperatures and can overlap. (Rives)

The intermediate and final products of decomposition vary a lot. For hydrotalcite, the eventual decomposition product is a solid solution of  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ . For other hydrotalcite-like compounds it is reasonable to assume similar mixtures of oxides or hydroxides to form in decomposition. Some more exotic compounds may also form, such as  $\text{MgAl}_2\text{O}_4$  in the case of hydrotalcite. Due to the amount of different LDHs, an extensive list will not be provided in this thesis. Instead it is recommended that LDHs potentially compatible with  $\text{CO}_2$  adsorption are studied individually to find their decomposition routes and products.

## 7 CO<sub>2</sub> SEPARATION WITH MEMBRANES

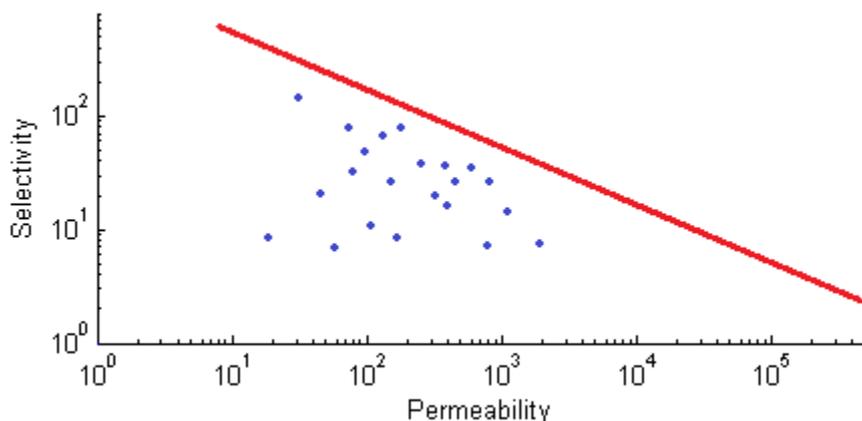
Membrane separation is an interesting choice for various reasons. Membranes are highly selective to different particle sizes, they require little or no energy to function and their configuration in power plants is very flexible compared to conventional amine absorption-desorption columns (D'Alessandro et al. 2010). For these reasons, membranes can be very efficient separating agents, particularly so if the concentration of the sorbate passing through the membrane, CO<sub>2</sub> in this case, is high. This effectively means that post-combustion capture, where the CO<sub>2</sub> concentration is low (under 15%), is not necessarily suitable for membrane capture. Instead, the higher CO<sub>2</sub> concentrations present in flue gas from oxyfuel combustion and syngas from gasification are promising for membrane separation (Choi et al. 2009).

There are two main geometric configurations for membrane separation processes. These are called cross-flow and dead-end geometries (Figure 7.1). In cross-flow geometry, the feed stream passes through the membrane, parallel to its surface. The retentate is removed from the membrane further downstream. The permeated flow is removed from the feed stream through the sides of the membrane. In dead-end geometry the feed stream direction is normal to the membrane surface. The retentate may be removed through the sides of the membrane or it may accumulate in the membrane, resulting in fouling of the membrane.



**Figure 7.1.** Cross-flow (a) and dead-end (b) geometry. In (b), triangles and large circles represent the retentate, some of which has bled through the membrane, while smaller circles represent the permeate.

The most important mechanisms in separation with membranes are diffusion and molecular sieving (D'Alessandro et al. 2010). These two mechanisms, also defined as transport factor and separation factor, are inversely related. A graphical representation known as Robeson Plot (Figure 7.2) illustrates this trade-off. An upper bound for overall membrane performance can be observed from the plot. Research will result in new membranes with increased selectivity and permeability, thus raising the upper bound.



**Figure 7.2.** An example of a Robeson Plot. The line represents the upper bound for membrane performance. The points represent different membranes.

Different membranes are usually classified as organic or inorganic depending on their constituent materials. Organic membranes may consist of materials such as cellulose, acetate or various polymers, while inorganic membranes can be made of ceramic, metals and metal oxides, molecular sieves, or metal–organic frameworks (D’Alessandro et al. 2010). Some membrane types may share properties with adsorbents described in the previous chapter.

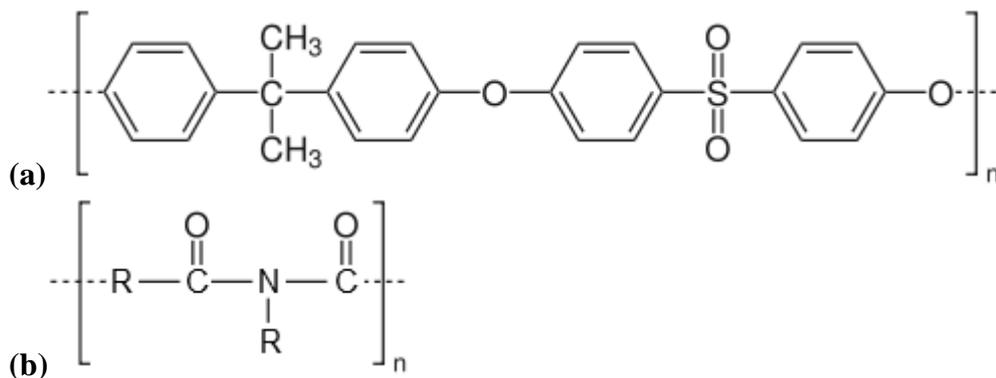
Inorganic membranes consist of either porous or non-porous materials. They have a high operation temperature which is relevant in precombustion CO<sub>2</sub> capture, in which H<sub>2</sub> and CO<sub>2</sub> are separated. In hydrogen transport membranes, CO<sub>2</sub> is retained in the membrane while H<sub>2</sub> is permeated. Hydrogen transport membranes usually consist of microporous inorganic materials, such as zeolites (see Chapter 6.1), palladium alloy tubes or ceramics.

Palladium alloy tubes are considered too expensive for CCS applications due to the thickness required for structural stability. Ceramic membranes based on perovskite oxide structures require high temperatures, above 800 °C, in order to facilitate a high hydrogen flux. (D’Alessandro et al. 2010)

Metal-organic frameworks (MOFs) are microporous crystalline solids that consist of organic ligands connecting metallic nodes forming a three-dimensional network structure. The pore diameters of MOFs are in the range of 3...20 Å. The metal nodes usually consist of one or more metal ions, such as Al<sup>3+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup> or Zn<sup>2+</sup>. The organic ligands coordinate with the metal nodes through a specific functional group such as a carboxylate or pyridyl. MOFs have several advantages over other membranes due to their unique structural properties: robustness, high chemical and thermal stability, very high internal surface area, high void volume and low density. These properties make MOFs suitable not only for gas separation, but also gas storage, ion exchange and heterogeneous catalysis. D’Alessandro and co-workers (2010) have listed several MOF configurations.

Polymeric membranes are usually based on cellulose acetate and its derivatives. They are commercially used in natural gas sweetening. Cellulose acetate membranes are not considered viable for flue gas processing due to degradation and compaction. Instead,

polysulfone and polyimide-based membranes (Figure 7.3) exhibit advantageous permeability, selectivity and thermal, chemical and plasticization resistance.



**Figure 7.3.** Repeating units of (a) polysulfone and (b) polyimide

Generally speaking, membranes used in CO<sub>2</sub> separation are inert and do not react with the compounds present in the feed gas. Instead, mechanical or thermal degradation may occur over time, especially in high temperatures. Other disadvantages include decrease in permeability over time due to fouling and particulate deposition, as well as poor efficiency at low CO<sub>2</sub> partial pressures, which requires compression for flue gas processing, creating an energy penalty.

## 8 CRYOGENIC SEPARATION EMISSIONS

Cryogenic separation of CO<sub>2</sub> from flue gas is based on the same principles as cryogenic air separation with an ASU described in Chapter 2.1. However, it is generally not considered a viable option for CO<sub>2</sub> separation from flue gas. This is due to high energy costs (Choi et al.). The same environmental concerns as for cryogenic air separation are still valid, with the added effect of various flue gas impurities resulting in formation of new compounds.

Emissions from cryogenic separation itself are limited to refrigerant leaks. The environmental effects of refrigerants are rather well known. However, the abundance of possible refrigerants makes comparing their possible effects with other compounds present in the CCS process a tedious task.

Table 8.1 lists known ozone-depleting compounds used as refrigerants. These compounds may have other environmental effects as well, depending on their decomposition products, which should be predictable based on the atoms present in each molecule. Fluorine and chlorine are very electronegative and may form compounds such as hydrofluoric or hydrochloric acid. Chlorine and bromine are corrosive and toxic. All three can form salts with especially hydrogen and sulfur, traces of which may exist in flue gas.

*Table 8.1. Types of refrigerants and their general components (EPA 2010).*

Type	Meaning	Components
CFC	chlorofluorocarbon	Cl, F, C
HCFC	hydrochlorofluorocarbon	H, Cl, F, C
HBFC	hydrobromofluorocarbon	H, Br, F, C
HFC	hydrofluorocarbon	H, F, C
HC	hydrocarbon	H, C
PFC	perfluorocarbon	F, C
Halon	–	Br, F, C, sometimes Cl and H

Other possible refrigerants include noble gases (helium, neon, argon and krypton) and other gases such as CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub>. Noble gases are inert, but they may cause asphyxiation if a large amount is released. The other gases are simple, well-known chemicals, the hazards of which have been established.

Cryogenic separation may be enhanced by including molecular sieves or other filters. They behave much like the membranes already covered in Chapter 7 and are not discussed further.

## 9 CO<sub>2</sub> PURITY REQUIREMENTS AND PURIFICATION

Purity requirements of the produced CO<sub>2</sub> stream vary depending on means of transportation and intended use. There are few published articles about the requirements, even though there are several unanswered questions in this area of CCS. The consensus seems to be that the required CO<sub>2</sub> purity is a balance between technical and economical issues.

Economically speaking, the CO<sub>2</sub> purification process would be less expensive if SO<sub>x</sub>, NO<sub>x</sub>, non-condensable gases and trace amounts of water were allowed to remain in the CO<sub>2</sub> stream. This would reduce investment costs for the plant and probably lower the energy penalty caused by CO<sub>2</sub> capture (Jordal et al. 2004). On the other hand, since impurities change the CO<sub>2</sub> stream's thermodynamic properties they may cause undesired effects in destined applications or during transportation. These effects may include corrosion and therefore material and maintenance costs, increased compression and pumping costs. Technically speaking, the purity requirements of CO<sub>2</sub> are determined by available technology, but also how the impurities might react in or affect later use or storage, and how to minimize both the CO<sub>2</sub> leakage to atmosphere and possible chemical slip to the CO<sub>2</sub> stream during the purification processes. These processes are described later in this chapter.

In conjunction with oxyfuel combustion, the flue gas is processed in five steps. First, the wet flue gas is compressed, after which it is dried. Next, the flue gas is purified. Then, the dry and purified gas is again compressed and condensed at 20 °C. Finally, the CO<sub>2</sub> is pumped to a pipeline or other transportation medium. In precombustion capture the flue gas is mostly water vapour, so these processes should be applied to the CO<sub>2</sub> product stream instead, although some processes could be unnecessary.

### 9.1 Particle removal

The first purification step after the boiler is particle removal. Particles are generally fly ash, soot or other impurities. Particles are usually removed from flue gas with, for example, a cyclone or an electrostatic precipitator (ESP). In an ESP, a strong electric field is created to charge the particles and drive them toward a collecting surface. Implementing a carbon capture process does not remove the need for an ESP, since the particles in the flue gas to be treated may influence the capture process.

Using solid sorbents for CO<sub>2</sub> capture is likely to result in particulate emissions. Even with liquid sorbents some reactions may occur which produce solid particles. These particles may exit the capture process either through the exhaust flue to atmosphere or the CO<sub>2</sub> product stream and removal should be considered, as if removing particles from flue gas.

## 9.2 Flue gas condensation

Flue gas condensation is a process in which wet flue gas is cooled to remove excess water. The condensing water vapour releases heat, which can be recovered. It also removes pollutants from the flue gas, which is particularly useful in waste incineration and biomass plants, since the fuel tends to contain impurities or moisture (Vattenfall).

As discussed before, oxyfuel combustion flue gas contains mostly carbon dioxide and water vapour. Flue gas condensation is therefore a very useful way of increasing the CO<sub>2</sub> content of the product stream.

The condensed water must be removed from the process and may contain impurities, in which case it needs to be cleaned accordingly.

The CO<sub>2</sub> stream of a precombustion facility is relatively dry and condensation is not required. In an oxyfuel combustion power plant, some water remains in the CO<sub>2</sub>-rich flue gas. In both cases, the remaining traces of water are removed by dehydration methods explained in Chapter 9.4.

## 9.3 NO<sub>x</sub>, SO<sub>x</sub> and mercury removal

Usually NO<sub>x</sub> is removed from the flue gas of air-fired power plants with a selective catalytic reduction (SCR) process. In an SCR process, a reductant such as ammonia or urea is added to the flue gas stream which is directed to a catalyst, where NO<sub>x</sub> is converted into N<sub>2</sub>. Using urea as a reductant is undesired in power plants with CCS systems, because one reaction product is CO<sub>2</sub>. Note that aqueous ammonia, as discussed in Chapter 5, is also used to capture CO<sub>2</sub>.

SO<sub>x</sub> emissions are conventionally removed with one of several methods commonly referred to as flue gas desulfurization (FGD). These methods can be classified as either throwaway or regenerable and either wet or dry processes. Most methods employ absorption as primary means of SO<sub>x</sub> removal. In throwaway processes, the used sorbent is treated as waste, while in regenerable processes the sorbent is regenerated for reuse and no waste is produced. In wet processes a slurry containing the absorbed SO<sub>2</sub> is formed and the flue gas is saturated with water, while in dry processes the waste produced is dry and the flue gas is not saturated. The most commonly used method is wet scrubbing, which uses a slurry of an alkaline sorbent, usually lime or limestone, to absorb the SO<sub>2</sub> into calcium sulfate (CaSO<sub>4</sub>). (Srivastra et al.)

Removing NO<sub>x</sub>, SO<sub>x</sub> and mercury from flue gas is relatively easy after oxyfuel combustion. The CO<sub>2</sub>-rich exhaust gas is compressed to about 15 bars for transportation purposes. Coincidentally, nitric oxide (NO) reacts with the excess oxygen into nitrous oxide (NO<sub>2</sub>) in high pressures and low temperatures:



Sulfuric acid is commercially produced using the lead chamber process. This same reaction occurs in the exhaust gas stream, where  $\text{NO}_2$  reacts with  $\text{SO}_2$  to form nitric oxide and sulfuric acid:



After all  $\text{SO}_2$  has been removed by Equations 32 and 33, the following reactions will occur and produce nitric acid ( $\text{HNO}_3$ ):



The nitric oxide produced by Equation 35 is again converted to  $\text{NO}_2$  as in Equation 32. Eventually  $\text{SO}_2$  is removed as sulfuric acid and  $\text{NO}_x$  as nitric acid. Possible traces of mercury (Hg) in the stream are also removed, since mercury reacts readily with nitric acid to form mercury(II) nitrate ( $\text{Hg}(\text{NO}_3)_2$ ). (Whitie et al. 2006)

## 9.4 Dehydration and removal of non-condensable gases

Clathrates are a group of substances, in which a certain molecule is trapped inside a cage formed by molecules of another species. The structure is called a hydrate if the cage is formed by water. Free water may form solid hydrates ( $\text{CO}_2 \cdot 6\text{H}_2\text{O}$ ) with  $\text{CO}_2$  in pipelines if the temperature drops below  $15^\circ\text{C}$  (Rackley).

These hydrates, similar to ice, may cause pressure drop or even plugs in the pipeline and are difficult to remove from the pipeline. This is especially true, if such conditions are expected to occur in the pipeline, for example in northern regions or submerged pipelines. Dehydration of the  $\text{CO}_2$  stream, or other means to prevent water from condensing, is necessary to prevent corrosion and plugging caused by hydrates. Other such means may include the injection of hydrate inhibitors, such as methanol, which is already used in the natural gas industry where hydrate formation is a well-known risk. As a general rule, there should be no more than 20 ppm by mass (or 50 ppm by volume) water in the  $\text{CO}_2$  stream. (Kanniche et al. 2010)

Dehydration also reduces corrosion caused by formation of carbonic acid ( $\text{H}_2\text{CO}_3$ ). See Table x for maximum permissible water content in  $\text{CO}_2$  pipeline transportation (300–500 ppm).

Non-condensable gases such as nitrogen, argon (Ar), excess oxygen and  $\text{NO}_x$  should be removed from the  $\text{CO}_2$  stream to improve its purity. One such way is to compress the stream into liquid state, after which the non-condensable gases can be flashed from the liquid  $\text{CO}_2$ . This should be done as a last step, since compression into liquid is necessary for pipeline transportation of  $\text{CO}_2$ .

## 10 RESULTS AND DISCUSSION

The objective of this thesis was to compile a list of possible emissions from CCS methods that might be harmful for the environment or the CCS or CO<sub>2</sub> transportation systems. An apparent shortage of research concerning these emissions was discovered. As amine absorption is the leading carbon dioxide capture method, it has been studied extensively, leaving other prospective technologies with less attention. Despite this fact the following results have been discovered.

### 10.1 Air separation

Emissions from cryogenic air separation and cryogenic separation of CO<sub>2</sub> from flue gas are mostly limited to refrigerant leaks and decomposition products of the refrigerant and possible impurities in the flue gas. Fluorine, chlorine and bromine present in various ozone-depleting refrigerants may form corrosive compounds (HF, HCl) and salts (SBr<sub>2</sub>) with other elements present in the CCS processes. All fluorides, chlorides, chlorates, bromides and bromates are suspected to cause harm to the environment or the equipment and should be monitored. Noble gases and other gaseous refrigerants may cause asphyxiation.

Using ion transfer membranes for air separation is relatively safe. In case of malfunction, such as a fire or other accident, the membrane may break or degrade, causing mechanical harm to the combustion process. Membranes themselves are inert and should pose no threat to humans or environment.

### 10.2 Chemical solvents

Due to the chemical reactions involved in chemisorption of CO<sub>2</sub>, chemical solvents can be considered to cause the most diverse spectrum of different emissions. These possible emissions depend on the specific solvents used and range from gaseous to liquids and even solids. Solid emissions, usually associated with ammonia or sodium hydroxide absorption, are relatively easy to prevent from reaching the CO<sub>2</sub> product stream, where they may cause mechanical problems to the pipelines or processes. Gaseous emissions may both enter the CO<sub>2</sub> stream as well as escape the process into atmosphere. Detection and mitigation of gaseous emissions may be difficult, but should nevertheless be possible with dedicated end-of-pipe technologies.

Primary and secondary amines react with CO<sub>2</sub> by forming carbamate compounds. These carbamates can be highly toxic. Metcalf (2000) has listed several carbamate-based insecticides. In Table 10.1, the compounds in groups (a) and (b) contain cyclic groups such as phenols and enols and can be considered less likely to form compared to the compounds in group (c), which already resemble the reaction product carbamates of CO<sub>2</sub> absorption with amines.

Carbonates are relatively stable compounds. Their CO<sub>2</sub> capture ability is based on a simple chemical reaction and none of the intermediate products should be toxic. Some carbonates are soluble water. These include lithium sodium, potassium, ammonium and some uranium carbonates. This may affect the water chemistry of the CCS process. However, most other carbonates are insoluble in water and may cause physical damage, clogging or other effects on the equipment.

Aqueous ammonia is relatively safe to use, while gaseous ammonia may explode. Precautions should be taken to avoid vapourization or phase change. Intermediate products of CO<sub>2</sub> absorption with aqueous ammonia include urea, ammonium carbamate, ammonium carbonate and ammonium bicarbonate. These compounds may find their way to the CO<sub>2</sub> product stream and, in the case of urea, atmosphere.

Sodium hydroxide based CO<sub>2</sub> capture may cause emission of solid particles such as sodium bicarbonate, sodium carbonate, calcium hydroxide or calcium carbonate. These may cause undesirable mechanical effects in the capture process or the CO<sub>2</sub> product stream.

**Table 10.1.** Trivial and IUPAC names of several carbamate-based insecticides categorized as (a) dimethylcarbamates of heterocyclic enols, (b) methylcarbamates of phenols and (c) methylcarbamates of oximes (Metcalf 2000).

<b>(a) Dimethylcarbamates of Heterocyclic Enols</b>	
<b>Trivial name</b>	<b>IUPAC name</b>
Isolan	1-isopropyl-3-methyl-5-pyrazoyl dimethylcarbamate
Dimetilan	2-dimethylcarbamoyl-3-methyl-5-pyrazolyl dimethylcarbamate
Pirimicarb	2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyl dimethylcarbamate
<b>(b) Methylcarbamates of Phenols</b>	
<b>Trivial name</b>	<b>IUPAC name</b>
Aminocarb	(4-dimethylamino-3-methyl)phenyl methylcarbamate
Bendiocarb	2,2-dimethyl-1,3-benzodioxol-4-yl methylcarbamate
BPMC	2-(1-methylpropyl)-phenyl methylcarbamate
Butacarb	3,5-di-tert-butylphenyl methylcarbamate
Carbaryl	1-naphthyl methylcarbamate
Carbofuran	2,3-dihydro-2,2-dimethylbenzofuranyl methylcarbamate
Dioxacarb	2-(1,3-dioxolan-2-yl) phenyl methylcarbamate
Ethiofencarb	2-(ethylthiomethyl) phenyl methylcarbamate
Etrofol	CPMC, 2-chlorophenyl methylcarbamate
Formetanate	3-dimethylaminomethyleneiminophenyl methylcarbamate
Isoprocarb	2-(1-methylethyl)-phenyl methylcarbamate
Metalkamate	3-(1-methylbutyl)phenyl carbamate and 3-(1-ethylpropyl)phenyl methylcarbamate

*Continued*

Table 10.1 Continued

Trivial name	IUPAC name
Methiocarb	(3,5-dimethyl-4-methylthio)phenyl methylcarbamate
Mexacarbate	(4-dimethylamino-3,5-dimethyl)phenyl methylcarbamate
MPMC	3,4-dimethylphenyl methylcarbamate
MTMC	3-methylphenyl methylcarbamate
Promecarb	3-methyl-5-(1-methylethyl)phenyl methylcarbamate
Propoxur	2-(1-methylethoxy)-phenyl methylcarbamate
TBPMC	3-tert-butylphenyl methylcarbamate
Trimethacarb	3,4,5-trimethylphenyl methylcarbamate
<b>(c) Methylcarbamates of Oximes</b>	
Trivial name	IUPAC name
Aldicarb	2-methyl-2-(methylthio)-propanal O-[(methylamino)carbonyl]oxime
Methomyl	S-methyl-N-[(methylcarbamoyl)oxy]thioacetimidate
Oxamyl	S-methyl 1-(dimethylcarbamoyl)-N-[(methylcarbamoyl)oxy] thioformimidate

### 10.3 Physical solvents

In CO<sub>2</sub> absorption with physical solvents there should be no chemical reactions between the feed gas and the sorbent, if required operating conditions are met. Therefore, in normal operation, emissions are mostly limited to leakage of the sorbent to atmosphere, the CO<sub>2</sub> stream or the working environment.

Some flue gas components other than CO<sub>2</sub> may as well be absorbed depending on the solvent's selectivity. These absorbed compounds may as well be emitted to the aforementioned environments in case they are desorbed due to a change in the surrounding pressure and temperature. Some of these compounds, such as H<sub>2</sub>S and HCN, may well be hazardous to health, so precautions should be taken during leaks and maintenance.

### 10.4 Adsorbents

Emissions caused by adsorption-based CO<sub>2</sub> capture are mostly limited to leakage of carbon dioxide into the working environment and the atmosphere. Adsorbents used in CO<sub>2</sub> capture are usually solids, which may in some circumstances unintentionally find their way into the CO<sub>2</sub> stream, where they would cause damage to either the CO<sub>2</sub> processing equipment, such as compressors, or the CO<sub>2</sub> pipelines or other transportation infrastructure.

Adsorbents will have to be regularly replaced due to degradation. It is important to prevent leakage of CO<sub>2</sub> in the working environment during maintenance. The adsorbent may become hazardous to health in case of accumulation of impurities from the fuel or

detrimental byproducts of incomplete combustion. These health hazards may desorb during maintenance due to the difference between operating and atmospheric temperature and pressure.

## 10.5 Membranes

Membranes used in CO<sub>2</sub> and oxygen separation are inert, so no chemical reactions with the feed compounds should occur when they are used correctly in proper operating conditions. Depending on membrane permeability and selectivity, geometry and other factors, such as fouling or poisoning by undesired compounds in the feed, leakage of retentate to the permeate side may occur, lowering the quality of the stream. Similarly, some of the desired permeate may not pass the membrane and may instead end up in the retentate, especially in cross-flow membranes.

Membrane emissions mostly consist of a decrease in CO<sub>2</sub> purity and CO<sub>2</sub> leakage due to poor membrane performance. Some membrane types may degrade, causing lowered performance, thus increasing emissions. Degradation may also cause mechanical damage in processes downstream from the membrane, in case of membrane erosion.

Membranes may have to be changed periodically in case of poisoning due to impurities in the feed gas. Regardless of combustion method, these possible impurities would most probably originate from the fuel being used. Care should be taken when replacing membranes, in case the impurities are hazardous to health, such as mercury or other heavy metals.

## 11 CONCLUSIONS

The aim of this literary survey was to provide information of possible emissions caused by carbon dioxide capture, when using oxyfuel combustion and gasification in conjunction with precombustion capture. There is plenty of research about carbon dioxide capture, including thermodynamic analyses, economic studies and energy requirement calculations, but published research about CCS emissions is very limited. Before important decisions about implementing CCS are made, these possible emissions should be studied to prevent unintentional environmental risks.

This thesis only covers a small amount of possible emissions originating from commercial and suggested CCS methods. Nevertheless, it should work as a starting point for development of equipment necessary for detection and measurement of these emissions.

The environmental effects of the emissions are mostly unknown, with the exception of CCS technologies using simple absorbents, such as ammonia. Effects of these various emissions to the CO<sub>2</sub> product stream are also unknown, but they can all be considered detrimental to either the processes or transportation infrastructure required. In conclusion, more published research about CCS emissions and their effects on the environment, process equipment and CO<sub>2</sub> transportation is required.

## REFERENCES

- Buhre, B., Elliott, L., Sheng, C., Gupta, R. & Wall, T. 2005. Oxy-fuel combustion technology for coal-fired power generation. *Progress in Energy and Combustion Science*, vol. 31, issue 4, pp. 283–307.
- Cho, P., Mattisson, T. & Lyngfelt, A. 2004. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. *Fuel*, vol. 83, issue 9, pp. 1215-1225. ISSN 0016-2361.
- Choi, S., Drese, J., Jones, C. 2009. Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources. *ChemSusChem*, vol. 2, issue 9, pp. 796–854.
- D'Alessandro, D., Smit, B. & Long, J. 2010. Carbon Dioxide Capture: Prospects for New Materials. *Angewandte Chemie International Edition*, vol. 49, issue 35, pp. 6058–6082.
- Eide-Haugmo, I. 2011. Environmental impacts and aspects of absorbents used for CO<sub>2</sub> capture. Norwegian University of Science and Technology, Faculty of Natural Sciences and Technology, Department of Chemical Engineering. PhD Thesis. ISBN 978-82-471-3045-2.
- EIGA. European Industrial Gases Association – AISBL. 2011. Environmental Impacts of Air Separation Units. IGC Doc 94/11/E.
- EPA. United States Environmental Protection Agency. 2010. Website, <http://www.epa.gov/ozone/geninfo/numbers.html>, accessed Feb 27<sup>th</sup> 2013.
- Gui X., Tang, Z., & Fei, W. 2011. Solubility of CO<sub>2</sub> in Alcohols, Glycols, Ethers, and Ketones at High Pressures from (288.15 to 318.15) K. *Journal of Chemical & Engineering Data*, vol. 56, issue 5, pp. 2420–2429.
- IZA. International Zeolite Association. 2013. Website, <http://www.iza-structure.org/>, accessed Feb 20<sup>th</sup> 2013.
- Jordal, K., Anheden, M., Yan, M. & Strömberg, L. 2004. Oxyfuel combustion for coal-fired power generation with CO<sub>2</sub> capture — opportunities and challenges, Proceedings of the 7th international conference on greenhouse gas control technologies, Vancouver, Canada, September 5– 9.
- Kanniche, M., Gros-Bonnivard, R., Jaud, P., Valle-Marcos, J., Amann, J. & Bouallou, C. 2010. Pre-combustion, post-combustion and oxy-combustion in thermal power plant for CO<sub>2</sub> capture. *Applied Thermal Engineering*, vol. 30, issue 1, pp. 53–62.

Liang, Y., Harrison, D., Gupta, R., Green, D. & McMichael, W. 2004. Carbon Dioxide Capture Using Dry Sodium-Based Sorbents. *Energy & Fuels*, vol. 18 issue 2, pp. 569–575.

Merikoski, R. 2012. Flue Gas Processing in Amine-Based Carbon Capture Systems. Tampere University of Technology, Faculty of Science and Environmental Engineering. Master of Science Thesis. 102 pp.

Metcalf, R. 2000. Insect Control. *Ullmann's Encyclopedia of Industrial Chemistry*

Rackley, S. 2010. Carbon Capture and Storage. Oxford, United Kingdom, Butterworth-Heinemann. 392 pp. ISBN 978-1-85617-636-1.

Rives, V. 2002. Characterisation of layered double hydroxides and their decomposition products. *Materials Chemistry and Physics*, vol. 75, issues 1–3, pp. 19–25.

Siriwardane, R., Tian, H., Richards, G., Simonyi, T. & Poston, J. 2009. Chemical-Looping Combustion of Coal with Metal Oxide Oxygen Carriers. *Energy & Fuels*, vol. 23, issue 8, pp. 3885–3892.

Suhonen, O. 2011. Energy Requirement of Nurmia Oxygen Enrichment Method. Tampere University of Technology. Preliminary study. 25 pp.

Thunder, K. & Meister, W. 2013. Pallosalama. JUKI-016. Juki Records, CD. ISRC FI-6JR-13-00001-10.

White, V. & Allam, R. 2006. Purification of oxyfuel-derived CO<sub>2</sub> for sequestration for EOR. In: Greenhouse gas control technologies. Proceedings of the eighth international conference on greenhouse gas control technologies, 19–22 June 2006, Trondheim, Norway.