



**NTNU**

**Department of Petroleum Engineering  
and Applied Geophysics**

# **Impurities in Carbon Dioxide Capture and Transport**

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## **Preface**

This thesis was written during the spring and summer of 2009. The work was done at the Department of Petroleum Engineering and Applied Geophysics at the Norwegian University of Science and Technology.

I would like to thank my supervisor Professor Jon Steinar Gudmundsson for all his help and support. Professor Gudmundsson provided me with an interesting and challenging topic. I would like to thank Aker Solutions and StatoilHydro for their input. It was inspiring to visit. I would like to thank Benjamin Pierre and Andre Strupstad. I appreciated the company and discussions we had over lunch.



## **Abstract**

Understanding the effects of impurities in carbon dioxide capture and transport is important to achieve an effective recovery of CO<sub>2</sub>. From earlier studies it appears that there is less knowledge about the effect of impurities in carbon capture and storage compared to the environmental impact of emissions and improved energy use in capture facilities. In this project the literature is searched for studies examining the effect of impurities in carbon dioxide capture and transportation up to the wellhead. Problems are identified and explanations of the underlying causes presented. The issue of water solubility in carbon dioxide is examined with the aim of determining if a higher concentration limit can be allowed in the CO<sub>2</sub> stream. Missing information is identified and commented upon.

The use of carbon dioxide capture in combination with a natural gas power plant is a relatively new concept. Most of the information is taken from experiences in scrubbing of natural gas. From the studies found it became clear that impurities will increase the degradation of amine solutions. Heat stable salts and degradation products from the degradation reactions will enhance corrosion so their concentrations must be kept under control. Due to the lack of knowledge the concentration limits recommended for impurities in CO<sub>2</sub> transport are conservative. The work shows that compression with cooling and water separation will be enough to lower the concentration of water in the CO<sub>2</sub> stream to an acceptable level to avoid hydrate and corrosion problems in pipeline transport.



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## Nomenclature

$c_e$	= Concentration in liquid phase in equilibrium with $p_L$	[kmol/m <sup>3</sup> ]
$c_i$	= Concentration at interface between gas and liquid phase	[kmol/m <sup>3</sup> ]
$c_L$	= Concentration in liquid phase	[kmol/m <sup>3</sup> ]
$C_p$	= Heat capacity	[kJ/kg.°C]
$d$	= Diameter of pipe	[m]
$\rho$	= Density	[kg/m <sup>3</sup> ]
$f$	= Friction factor	
$H$	= Henry's constant	
$K$	= Overall mass transfer coefficient	[m/s]
$k_L$	= Liquid film transfer coefficient	[m/s]
$k_p$	= Gas film transfer coefficient	[s/m]
$\Delta L$	= Length of pipeline	[m]
$N_G$	= Mass transfer rate in gas phase	[kmol/s.m <sup>2</sup> ]
$N_L$	= Mass transfer rate in liquid phase	[kmol/s.m <sup>2</sup> ]
$\Delta P$	= Pressure loss over a 100 km pipeline	[bar/100 km]
$p_e$	= Partial pressure in equilibrium with $c_L$	[N/m <sup>2</sup> ]
$p_i$	= Pressure at the interface between gas and liquid phase	[N/m <sup>2</sup> ]
$p_G$	= Pressure in gas phase	[N/m <sup>2</sup> ]
$T_{in}$	= Temperature of stream entering pipeline	[°C]
$T_{out}$	= Temperature of stream leaving pipeline	[°C]
$T_u$	= Temperature outside pipeline	[°C]
$U$	= Heat transfer coefficient	[W/m <sup>2</sup> .°C]
$u$	= Velocity	[m/s]

## Indexes (subscript)

e	= equilibrium
i	= interface
G	= Gas
L	= Liquid
p	= pressure

## Abbreviations

CCPP	= Combined Cycle Power Plant
CCS	= Carbon Capture and Storage
DCC	= Direct Contact Cooler
DEA	= Diethanolamine
DGA	= Diglycolamine
EOR	= Enhanced Oil recovery
HSS	= Heat Stable Salt
LNG	= Liquefied Natural Gas
MDEA	= Methyldiethanolamine
MEA	= Monoethanolamine
NTNU	= Norwegian University of Science and Technology
PPM	= Parts Per Million
SCR	= Selective Catalytic Reduction
TEG	= Triethylen Glycol

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# **1. Introduction**

The climate on earth is changing due to the warming effects caused by increasing levels of greenhouse gases. The increase of greenhouse gases is predominantly a result of the burning of fossil fuels. In order to prevent further climate change carbon capture and storage can provide a bridging technology for decreasing the emissions until alternative carbon neutral technologies can be developed.

Carbon capture and storage (CCS) technologies offer particular advantages in that they allow a balance between increasing demands for energy and the requirements to reduce emission. The study of CCS technologies to achieve higher efficiency is of high priority. The economical cost of CCS needs to be reduced through technological advancements.

## **1.1 Problem statement**

Contamination of the carbon dioxide phase in the capture process has not been widely investigated or reported. From previous work it has become clear that there was more unknown about impurities in carbon dioxide than about environmental emissions. Excess air is used in the combustion of natural gas. Some of the excess air will end up in the carbon dioxide phase. Most of the previous work related to this topic has been done in the field of gas sweetening. Mainly carbon dioxide and hydrogen sulfide are removed from the natural gas in the absence of other gases such as oxygen or nitrogen. The current thesis topic emerged in part from work reported by Storsæter et al. (2008) in the Natural Gas course at NTNU (Gudmundsson 2008).

Knowledge relating to gas sweetening can be applied to CO<sub>2</sub> capture from a flue gas, but with added complexity. The presence of non-condensable gases such as nitrogen will affect the pressure required for phase change from gas phase to dense phase. Oxygen from the excess air used in the power plant will give rise to new pathways for degradation and corrosion problems in the amine system. Increased concentrations of water in the super critical CO<sub>2</sub> transported could cause formation of hydrates and corrosion problems in the pipeline.

In the present thesis the effect of impurities in carbon capture and storage are investigated. The thesis will concern CO<sub>2</sub> capture, compression, drying and pipeline transportation to the wellhead. Based on known processes, the chemical components involved are to be identified and quantified as far as possible. Problems related to the impurities in the capture process

such as degradation and corrosion are investigated and explained. The issue of water solubility in carbon dioxide is examined with the aim of determining if a higher concentration limit can be allowed in the CO<sub>2</sub> stream. An attempt is made to identify what information is missing to make possible an assessment of the impurity issues in post-combustion carbon capture chains.

## **1.2 Background on carbon capture**

Capture of CO<sub>2</sub> from natural gas power plant flue gas is one of the reduction strategies to help Norway achieve its target for fossil emissions. CO<sub>2</sub> capture units can be integrated into natural gas power plants as a flue gas post treatment unit. Even though CO<sub>2</sub> capture can be technically implemented by several gas separation methods, flue gas capture into an amine solvent is the most attractive because of its maturity in gas treating services. Although CCS technology is considered mature the cost is still high. There is significant room for improvement especially in the capture system.

CCS projects involving gas and oil industry have been started in Canada, Algeria, Norway and Netherlands. More projects are planned all over the world. In Norway CO<sub>2</sub> removed from natural gas has been injected into the Utsira formation from the Sleipner platform. At the Snøhvit liquefied natural gas (LNG) project CO<sub>2</sub> is captured from the liquefaction plant and reinjected offshore. Several planned natural gas power plants, such as Mongstad and Kårstø, will have carbon capture technology to limit their emissions of CO<sub>2</sub> (Torp 2008).

## **1.3 Literature and organization**

The major source of information in this master project was anticipated to be papers and reports. A number of industrial actors were also asked if they could provide some information. Most of the information was found through searches in the NTNU library databases. In addition Google scholar was found to be a helpful tool in finding useful information about the topic in question. From the literature search it became clear that there is a lack of reports, papers and other information specific to CO<sub>2</sub> capture from natural gas power plant flue gas. Few investigations have been done into the effect of impurities in carbon capture.

The literature gathered for this project has been used throughout the text. Certain papers have been singled out and used more extensively in some chapters of the text for a better understanding of the problems caused by impurities in the capture and transport of CO<sub>2</sub>. Figures and tables are integrated into the text for easy availability.

The first chapter describes the carbon dioxide capture plant. This is followed by chapters describing the most commonly used amines in the capture process and compounds found in flue gas from gas fired power plants. A description of the main reacts for CO<sub>2</sub> capture in amine solution follows before degradation and corrosion problems are investigated in chapter six, seven and eight. Issues relating to compression and transportation are covered in chapters nine, ten and eleven. In chapter nine a simulation is done to investigate the effect of selected parameters on the capture of CO<sub>2</sub>. Chapter ten examines CO<sub>2</sub> properties and the effect of impurities on these properties. In the chapter eleven the need for additional dehydration is investigated.

## 2. Capture process

A simplified diagram of a carbon dioxide capture process can be seen in Figure 2.1. Natural gas enters a combined cycle power plant (CCPP) which emits the flue gas containing CO<sub>2</sub>. Before entering the capture and recovery step of the process the flue gas is cooled and excess water separated. The CO<sub>2</sub> reacts with an amine solution in the capture column and travels with the amine solution to the stripper. Here the CO<sub>2</sub> is released by heating the amine solution. In a last step before pipeline transport the recovered CO<sub>2</sub> is compressed and dehydrated to meet the pressure and composition requirements.

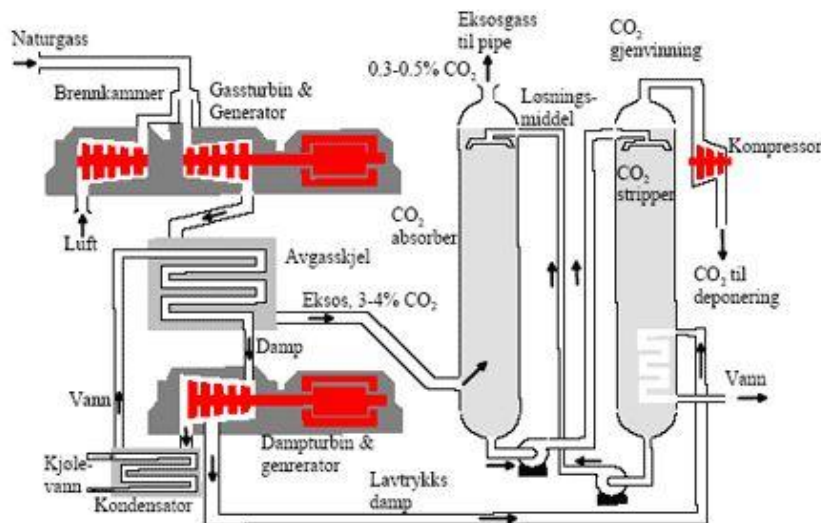


Figure 2-1 Gas-fired power plant with amine absorption from flue gas (Zero 2009)

A block flow diagram of the capture process is shown in Figure 2.2. The diagram represents the planned capture facilities at Tjeldbergodden (StatoilHydro 2005). It provides a good overview of the different steps in a capture process.

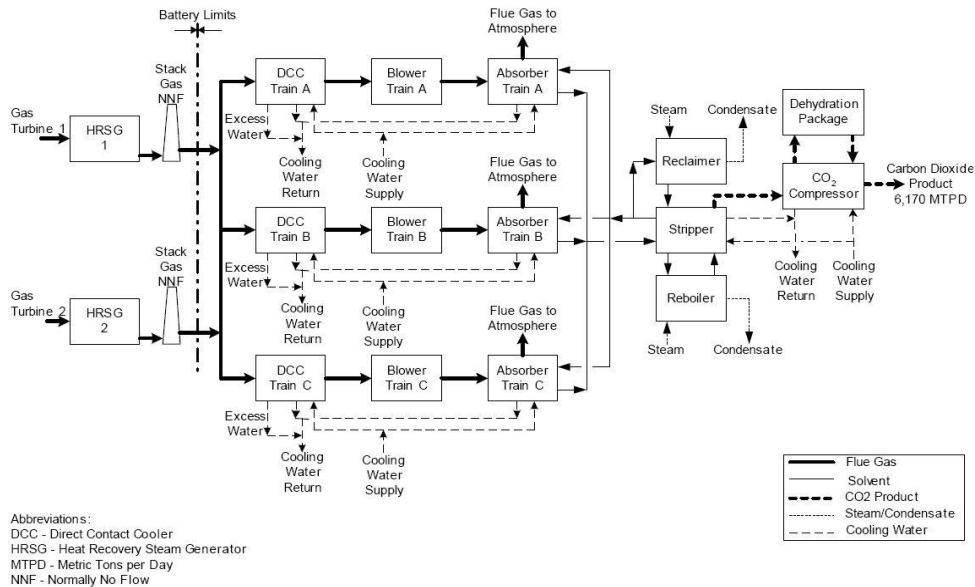


Figure 2-2 Block Flow Diagram (StatoilHydro 2005)

Contact and stripper columns are shown in Figure 2.3 (Zero 2009). The picture consists of: a contact column, a stripper column, two coolers, a heat exchanger, a condenser (reflux drum), a reclaimer and a reboiler. a direct water cooler, a blower, a water washer, two water separators, The main streams are: flue gas, treated flue gas, rich amine solution, lean amine solution and recovered CO<sub>2</sub>. In addition a direct contact cooler, blower, compression and dehydration can be seen in Figure 2.4 (StatoilHydro 2005).

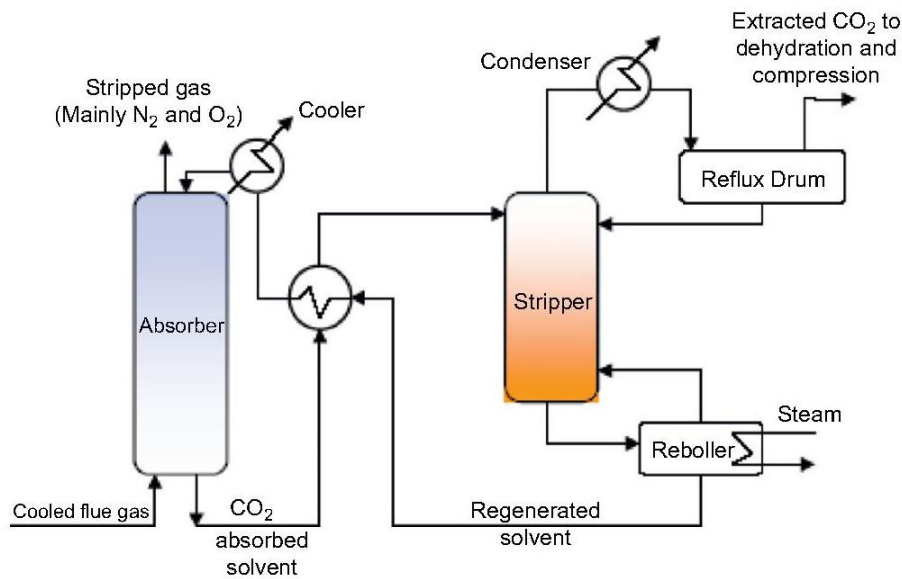


Figure 2-3 Simplified CO<sub>2</sub> capture process (Zero 2009)

A flue gas coming from a natural gas power plant is cooled by a direct water cooler. The water is separated before it enters the contact column. The flue gas flow counter current with a lean amine solution entering the column at the top. Treated flue gas will leave from the top of the contact column after passing through a water wash. A rich amine solution will leave the contact column from the bottom and pass through a heat exchanger before entering a stripper column. Heat in the stripper column to recover the CO<sub>2</sub> is provided by a reboiler. The recovered CO<sub>2</sub> leave from the top of the stripper where it passes through a reflux drum (condenser) followed by a cooler and a separator before it is ready for compression. Due to side reactions a reclaiming is used to remove degradation products. The lean amine solution leaves the stripper from the bottom and passes through the heat exchanger. Here it is cooled by the rich amine solution before passing through an additional cooler and closing the circuit by entering the contact column.

Cooling of the flue gas is required before it enters the contact column. The flue gas leaves the natural gas power plant at a too high temperature which depends of the operational conditions of the power plant. The flue gas from the heat and power plant at Mongstad exits at a temperature of 194 °C (StatoilHydro 2009). The most favorable temperature for the reaction between flue gas and amine solution is 30-50 °C (Zero 2009). To lower the temperature the flue gas passes through a direct contact cooler (DCC) where water is used to cool the flue gas down to the required temperature. A blower is situated before the contact column to overcome the pressure loss caused by the cooler (StatoilHydro 2005).

The flue gas enters at the bottom of the absorption column at close to atmospheric pressure (Zero 2009). It is close to saturated with water due to the previous direct cooling. Here it flows counter current with the lean amine solution which enters at the top of the contact column. The amine solution binds the CO<sub>2</sub> with a weak chemical bond, formed by a weak acid-base reaction (Kidnay & Parrish 2006). The reaction mechanisms will be described in Chapter 5.

The contact column contains a packing material to enlarge the contact area between the flue gas and the amine solution. There are several options how to pack the column, but packed bed absorbers are preferred to plate absorbers because of their larger contact area and lower pressure drop (Mohammad et al. 2007).

The treated flue gas exits the contact column from the top. The gas passes through a water wash scrubber before it is emitted to the atmosphere. Here entrained amine droplets are recovered and recycled back to the contact column. This is done to prevent the traces of amine from being vented to the environment. Thus, the benefit of the water wash step is twofold. First it prevents loss of amine solution saving the cost of replacing it. Secondly emission of harmful amines to the environment is limited.

Most of the nitrogen and oxygen will follow the flue gas out together with approximately 15% of the carbon dioxide. It is possible to capture close to all the CO<sub>2</sub> in the flue gas, but due to energy consideration it is common to assume that approximately 85 % of the CO<sub>2</sub> is captured (Zero 2009). The amount of carbon dioxide emitted will depend on several factors such as: selection of amine solution, temperature, pressure, contact column size, packing material and specific amine solution rate.

The rich amine solution exits the contact column at the bottom tray and the solution travels towards the heat exchanger. Here the rich solution is pre-heated by the lean amine solution coming from the stripper. The solution is heated to a temperature close to the stripper column before entering (100 – 120 °C) (Kidnay & Parrish 2006). This results in a more energy efficient process. Less heating of the rich amine solution is required to recover the CO<sub>2</sub>.

The rich amine solution enters the stripper column at the top. The stripper column is filled with a packing material to provide a larger contact area for the regeneration of the amine solution. The rich amine solution flows downward in the column. Released CO<sub>2</sub> and water vapor rises through the column. Heat to separate the CO<sub>2</sub> from the amine solution is provided

as steam at 120-140 °C in a reboiler. The stripper is operated at close to atmospheric pressure for capture of CO<sub>2</sub> from natural gas power plants (Kidnay & Parrish 2006)..

The recovered CO<sub>2</sub> leaves the stripper from the top. Before it can enter the compression and dehydration step the stream has to be cooled and excess water removed. This is achieved by passing the stream through a condenser (reflux drum), a cooler and a separator.

The amine solution can react with CO<sub>2</sub> and O<sub>2</sub> to form organic acids (Kohl and Nielsen 1997). These acids can react with the basic amine solution to form heat stable salts. The heat stable salts are not regenerated and need to be removed. If they are not removed they will accumulate in the solvent stream causing problems like corrosion and diminished absorption efficiency.

The heat stable salts can be removed in a reclaimer. For Monoethanolamine (MEA) and Diglycolamine (DGA) a semi-continuous distillation process can be used (Kidnay & Parrish 2006). The reclaimer is filled with lean amine solution. A strong base, such as sodium hydroxide, is added to the reclaimer to neutralize the heat stable salts. A slip-stream of 1-3 % of the circulating amine solution is continuously added to the reclaimer and heated to approximately 150 °C for MEA or 180 - 195°C for DGA (Kidnay & Parrish 2006). Amine vapor and water is taken off at the top and recirculated back to the amine solution. The impurities are left in the bottom of the reclaimer in the liquid phase. The cycle is briefly stopped to remove the impurities before starting all over again (Kidnay & Parrish 2006).

The lean amine solution exits the stripper at the bottom. It passes through a heat exchanger. Here it provides heat to the rich amine solution. An additional cooler is required before the lean amine stream enters the contactor from the top. This is to cool the stream down to the low temperature required in the reaction step of the capture process.

A number of pumps, heat exchangers, filter and fans are needed in addition to the described parts of the capture process. They provide the required pumping capacity, heating and cooling and removal of heat stable salts and degradation products in the process. These are not pictured in Figure 2.1, but are vital to the overall process.

The CO<sub>2</sub> products stream from the stripper needs to be compressed and dehydrated before it is ready for pipeline transport. The compressor consists of several steps. The number of steps depends on the required pressure for pipeline transport. The compressor at the proposed capture facilities at Tjeldbergodden consists of 5 steps (StatoilHydro 2005). Each compression step is followed by an air cooler and trim coolers. In the trim coolers the CO<sub>2</sub> product is cooled against sea water to 25 °C. Each cooling step is followed by knock out drums where the condensate is removed.

The CO<sub>2</sub> stream dehydration process is integrated with the compressor. One of the most common dehydration processes is absorption by triethylen glycol (TEG) (Kidnay & Parrish 2006). At an interstate pressure the CO<sub>2</sub> is sent from the compression to the dehydration step where the water level is reduced down to less than 50 ppmw. At the proposed capture process at Tjeldbergodden the interstate pressure is 39.5 kg/cm<sup>2</sup> (StatoilHydro 2005).

A detailed process flow diagram can be seen in Figure 2.4. It is the Economine FG Plus process flow diagram of the CO<sub>2</sub> capture facilities for CCPP Statoil proposes to build at Tjeldbergodden, Norway. The process flow diagram gives a detailed view of the capture process from the flue gas leaving the power plant to CO<sub>2</sub> entering the compression and dehydration step.

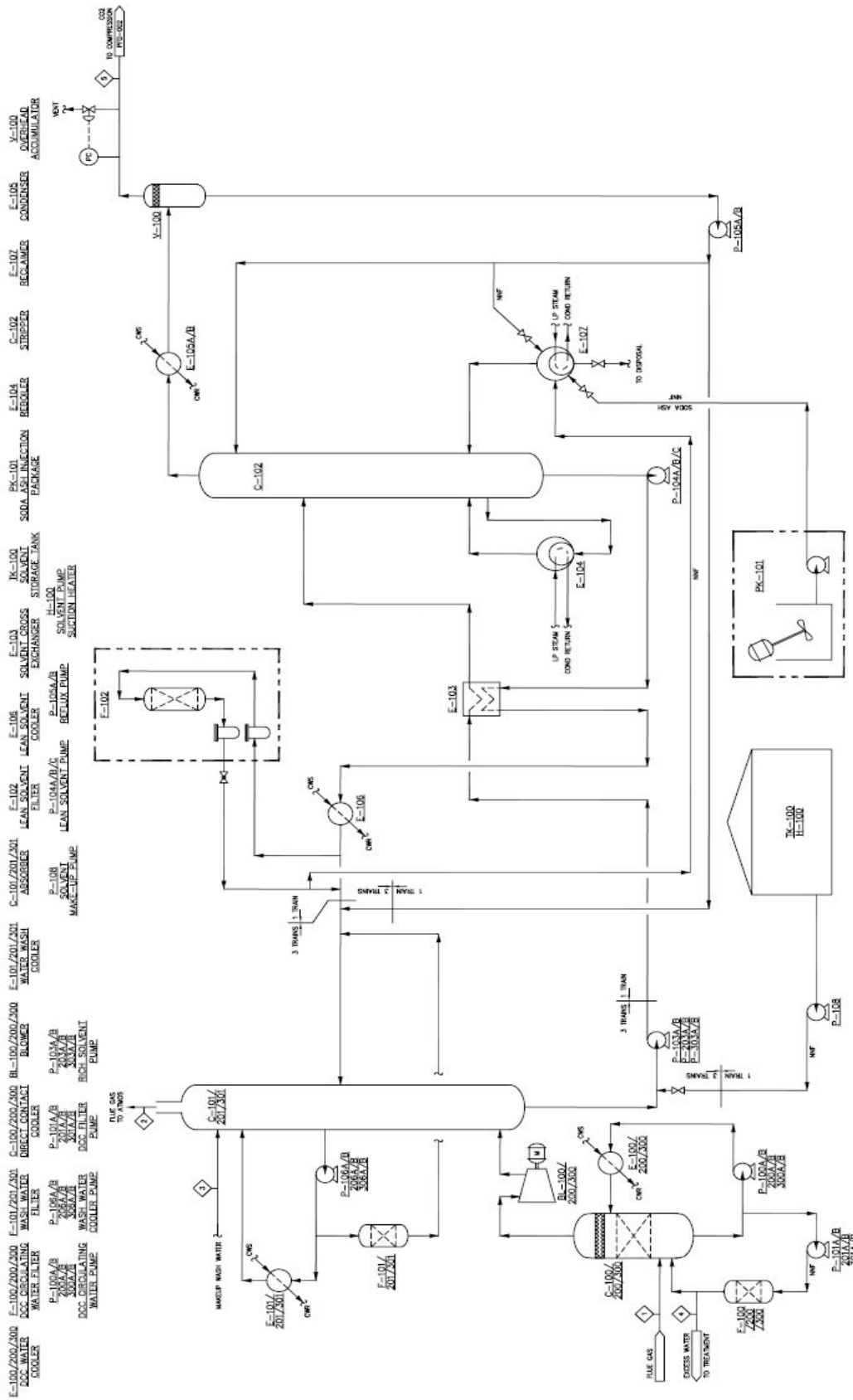


Figure 2-4 Process Flow Diagram Economine FG Plus Process Flow Diagram (StatoilHydro 2005)

### 3. Properties of amines

A number of different alkanolamines can be used in the capture of CO<sub>2</sub>. The amine selected for a process is determined by operational factors such as temperature, pressure and flue gas composition (Kohl & Nielsen 1997). The requirement of a capture process can often be met by several of the amine compounds or a mixture of them. In the end an economical analysis has to be done to choose the right amine solution for the specific case (Kohl & Nielsen 1997). In the following section a description of the most commonly used amine solutions will be given including their advantages and disadvantages.

#### *Monoethanolamine (MEA)*

MEA has been one of the most commonly used amines in the past, but is being replaced by more efficient amine solutions (Kohl & Nielsen 1997). This is especially the case for high pressure treatment of gases. However, for low pressure and low concentration of CO<sub>2</sub> MEA is still the preferred choice. This would be the case for flue gas from natural gas power plants which contain 3-4 wt% of CO<sub>2</sub> and traces of H<sub>2</sub>S.

MEA is a primary amine and the most basic of the amines described. Consequently it is the most reactive. It has a high solution capacity at low and moderate concentrations. MEA can be used in gas loadings of 0.45-0.52 mol CO<sub>2</sub>/mol MEA where the acid gas removed mainly is CO<sub>2</sub> together with traces of H<sub>2</sub>S. MEA has a high heat of reaction with CO<sub>2</sub>, 1920 kJ/kg (Kidnay & Parrish 2006).

MEA has a number of disadvantages. Its relatively high vapor pressure (0.36 mmHg at 20 °C) can cause substantial vaporization losses (Kidnay & Parrish 2006). It cannot selectively remove H<sub>2</sub>S from CO<sub>2</sub>. The high heat of reaction with CO<sub>2</sub> leads to a high energy requirement for the regeneration. Higher corrosion rates compared to other amines have been observed for concentrations over 20 wt% and high CO<sub>2</sub> loadings (Kohl & Nielsen 1997).

MEA react with Carbonyl Sulfide (COS) and Carbon disulfide (CS<sub>2</sub>) to form heat stable salts and other degradation products. The irreversible reactions are enhanced by the presence of oxygen. Among the products formed are thiosulfates. Thiosulfates are highly corrosive (Kidnay & Parrish 2006). An advantage MEA (and DGA) has over other amines is that a reclaimer can be installed in-line for intermittent removal of heat stable salts and other degradation products (Kidnay & Parrish 2006).

### *Diglycolamine (DGA)*

DGA is a primary amine. It has many similarities with MEA, but its lower vapor pressure allows it to be used in higher concentrations. Concentrations of 40-70 wt% can be used (Kidnay & Parrish 2006). This results in a need for a lower circulation rate and energy consumption compared to MEA (Kohl & Nielsen 1997). The heat of reaction with CO<sub>2</sub> is slightly higher than for MEA, 1980 kJ/kg (Kidnay & Parrish 2006).

DGA has proven efficient in purifying large volumes of gas at low pressures. It is particularly useful where the ambient temperature is high in the production of sweet gas. This has been observed at process plants in Saudi Arabia (Kohl & Nielsen 1997).

DGA can partially remove COS. Degradation products will form in reactions with CO<sub>2</sub> and COS. Steam distillation can be used to recover a large part of the DGA which would otherwise be lost (Kohl & Nielsen 1997).

### *Diethanolamine (DEA)*

DEA is a secondary amine. It is a weaker base than MEA and has a lower vapor pressure, 0.01 mmHg at 20 °C (Kohl & Nielsen 1997). The lower vapor pressure leads to less evaporation losses. The heat of reaction with CO<sub>2</sub> is lower relative to MEA, 1700 kJ/kg. Less energy will therefore be needed in the regeneration of the solution. DEA can operate at higher acid gas loadings than MEA. Typical loadings are 0.35 – 0.8 mole acid gas/mole DEA. Because of corrosion limitations the concentration range for DEA is 30 – 50 wt% (Kidnay & Parrish 2006).

DEA forms regenerable compounds with COS and CS<sub>2</sub> and can be used for their partial removal. This limits the loss of amine solution due to irreversible side reactions. However, DEA has a drawback. It undergoes irreversible side reactions with carbon dioxide. Many of the degradation products are corrosive and might make DEA a less ideal choice for gas streams with a high CO<sub>2</sub> content. Vacuum distillation might be needed to reclaim degradation products from the DEA solution (Kidnay & Parrish 2006).

### *Methyldiethanolamine (MDEA)*

MDEA can selectively absorb H<sub>2</sub>S in the presence of CO<sub>2</sub>. This is of special interest in the purification of non carbon gases where the ratio of CO<sub>2</sub> to H<sub>2</sub>S is very high. This would be the case in flue gas streams from natural gas power plants. It has been shown that MDEA can under the proper conditions reasonably well absorb H<sub>2</sub>S selectively (Kohl & Nielsen 1997).

MDEA is a tertiary amine. It has a low heat of reaction with CO<sub>2</sub>, 1420 kJ/kg, and can be used in concentrations up to 60 wt% (Kidnay & Parrish 2006). The vapor pressure is low, <0.01 mmHg at 20 °C (Dow specialty amines 2009). The loss of solution will be minimal in the contact and stripper columns. It is used for bulk removal of CO<sub>2</sub> from high-concentration gases even though the reaction kinetics is relatively slow with CO<sub>2</sub>. This is done as the energy requirements for regeneration are lower than those for other amines.

MDEA is highly resistant to thermal and chemical degradation and it is considered to be non corrosive. The resistance to degradation makes it an interesting choice for processes with O<sub>2</sub> present. It can be used alone or in combination with another amine. It has been observed that MDEA in a mixture with MEA will protect the MEA from oxidative degradation (Idem at al. 2005).

### *Sterically hindered amines*

Sterically hindered amines may or may not be alkanolamines. They are however sufficiently similar in the way they act as gas purification agents to be compared to alkanolamines. The sterically hindered amines are designed with specific molecular configuration to hinder side reactions taking place. They can be designed to specifically absorb H<sub>2</sub>S in the presence of CO<sub>2</sub> (Kohl & Nielsen 1997).

Creating a sterically hindered amine involves altering the reactivity of primary and secondary amines. A large hydrocarbon group can be attached to the nitrogen altering the structure of the amine. The introduced group will shield the nitrogen atom and hinder it from reacting with CO<sub>2</sub>. The H<sub>2</sub>S reaction will not be hindered in the same way (Kidnay & Parrish 2006).

### *Mixed amine solutions*

The practice of blending a primary or secondary amine with a tertiary amine has increased in the later years. The advantage of this is that the amine solution can be tailored to fit specific requirements. Selectivity for H<sub>2</sub>S and CO<sub>2</sub> can be adjusted. For this use the interest for MDEA has grown as a non selective solvent (Kohl & Nielsen 1997).

By mixing it with either MEA or DEA one can take advantage of the high capacity, stability and low energy requirement of the MDEA. The faster reaction rate of a primary or secondary amine would also be retained. Adding MEA or DEA to the MDEA solution has been observed to significantly increase the rate of reaction with CO<sub>2</sub> without losing the advantages of the MDEA solvent (Kohl & Nielsen 1997).

## 4. Flue gas composition

The flue gas exiting the gas power plant is made up of several different compounds. The overall composition depends on the operational conditions of the power plant. Pressure and temperature together with the natural gas composition and excess air are the most influential factors in deciding the final composition of the flue gas. Compounds found in flue gas are: Nitrogen ( $N_2$ ), Argon (Ar), Oxygen ( $O_2$ ), Carbon dioxide ( $CO_2$ ), Water ( $H_2O$ ), Sulfur oxides ( $SO_x$ ) and Nitrogen oxides ( $NO_x$ ). A brief description of the compounds will follow.

Hydrogen sulfide ( $H_2S$ ) is not considered in connection with flue gas from a natural gas power plant. At high temperature  $H_2S$  will be oxidized to other sulfur compounds as  $SO_x$  (mainly  $SO_2$  and  $SO_3$ ) (Gary & Handwerk 1984).

### *Nitrogen ( $N_2$ )*

Nitrogen is the most abundant component in the flue gas. Nitrogen is considered to be mostly inert under normal pressure and temperature conditions. The flue gas leaving a natural gas power plant consists of between 74–76 vol%  $N_2$ . At the heat and power plant at Mongstad the  $N_2$  makes up 74.8–75.1 vol% of the total flue gas stream (StatoilHydro 2009).

The source of the nitrogen in the flue gas is the excess air used in the combustion of natural gas in the power plant turbines. The excess air is used to control the temperature in the gas turbine (Bolland & Sæther 1992). All but a trace amount of the  $N_2$  will leave the capture process with the treated flue gas in the capture column. The recommended concentration limit for  $N_2$  in the pipeline transport of  $CO_2$  is <4 % (de Visser et al. 2008).

### *Oxygen ( $O_2$ )*

Oxygen is the second most abundant component in the flue gas. The concentration of oxygen in the flue gas is decided by the combustion conditions and excess air in the power turbines. This results in a relatively high amount of oxygen entering the capture process with the flue gas. Oxygen can make up as much as 13–14 vol % of the flue gas. At Mongstad the oxygen in the flue gas was measured to be 12.8–13.8 vol % (StatoilHydro 2009).

The presence of O<sub>2</sub> in the flue gas can cause several problems in the capture process. O<sub>2</sub> can react with the amine solution to form degradation products and heat stable salts in irreversible side reactions. O<sub>2</sub> and the irreversible products formed can cause and/or increase corrosion in the process (Rooney et al. 1996). Issues relating to the presence of oxygen will be investigated in following chapters. Recommending a concentration limit for O<sub>2</sub> it might be necessary with a limit as low as 50 ppm for the transport of CO<sub>2</sub> (Steeneveldt et al. 2006).

#### *Water (H<sub>2</sub>O)*

Water is the third most abundant component in flue gas from combustion of natural gas. It comes from the reaction between oxygen and methane. The amount of water in the flue gas varies with combustion conditions. In a simple case of complete combustion pure CH<sub>4</sub> and pure O<sub>2</sub> will react and produce one mole of CO<sub>2</sub> for every two moles of H<sub>2</sub>O (Speight 2007). Water will also be added to the flue gas in the direct contact cooler. The flue gas entering the contact column will be close to saturated. At Mongstad the water content in the flue gas was measured to be 6.8 – 7.7 vol % (StatoilHydro 2007). The presence of water (free water) can cause problems with corrosion and possibly hydrate formation under the right conditions. The recommended concentration limit for H<sub>2</sub>O in the pipeline transport of CO<sub>2</sub> is 500 ppm (de Visser et al. 2008).

#### *Carbon dioxide (CO<sub>2</sub>)*

CO<sub>2</sub> is the main product of the combustion and it is the fourth most abundant component of the flue gas. The amount of CO<sub>2</sub> in the flue gas is related to the composition of the natural gas and the excess air used. An excess air ratio in the range of 3 -3.5 will result in a CO<sub>2</sub> concentration in the flue gas of typically 3 - 4 vol% (Bolland & Sæther 1992). At Mongstad the carbon dioxide in the flue gas was measured to be 3.4 – 3.9 vol % (StatoilHydro 2009). The properties and the effect of impurities in the carbon dioxide stream will be discussed in Chapter 10.

CO<sub>2</sub> can cause problems in the capture process. CO<sub>2</sub> is considered a corrosive gas when it is dissolved in free water. In addition to the desired acid base reaction with the amine solution it can react to cause heat stable salts and degradation products. These products can cause and/or increase the corrosion problem in the capture process (Rooney et al. 1996).

### *Nitrogen oxides (NO<sub>x</sub>)*

NO<sub>x</sub> is the collective name for Nitric oxide (NO) and Nitrogen dioxide (NO<sub>2</sub>). It is a product of the combustion of natural gas. Natural gas does not contain any organically bound nitrogen and the molecularly bound nitrogen in the natural gas has no influence on the formation of fuel-NO. The only NO formed will be prompt-NO (EMEP/EEA 2006). NO is the primary form of NO<sub>x</sub> formed in combustion. It typically makes up 95 % of the NO<sub>x</sub> (Perry and Green 1997). In the atmosphere NO oxidizes to NO<sub>2</sub>. At Mongstad heat and power plant the NO<sub>x</sub> in the flue gas was measured to be 5 ppmv. Of the 5 ppmv the amount of NO<sub>2</sub> was 0.5 ppmv (StatoilHydro 2009).

NO<sub>x</sub> can react with amine solution and form degradation products. If need be Nitrogen oxide can be removed before the flue gas enters the absorption column. This can be done by Selective Catalytic Reduction (SCR). It is possible to lower the concentration of NO<sub>x</sub> from 25 ppm to as low as 2 ppm (Bøe 2008).

### *Sulfur oxides (SO<sub>x</sub>)*

The formation of SO<sub>x</sub> is directly related to the amount of sulfur in the fuel and relatively independent of the combustion conditions (Perry & Green 1997). It is mostly SO<sub>2</sub> and SO<sub>3</sub> that are formed. Of the SO<sub>2</sub> 1-4% oxidizes to SO<sub>3</sub>. At Mongstad the SO<sub>2</sub> in the flue gas was measured to be 0.3 ppmv. The quantity of SO<sub>3</sub> was not defined (StatoilHydro 2009).

In natural gas the sulfur content is usually insignificant (EMEP/EEA 2006). Therefore it is not necessary to remove the SO<sub>2</sub> in flue gas before it enters the contact column. It is removed along with CO<sub>2</sub> in the amine solution (StatoilHydro 2009).

### *Other components*

Several other components can be present in flue gas from natural gas combustion. Some of these are: Nitrate (NO<sub>3</sub>), Nitrous oxide (N<sub>2</sub>O), Carbon monoxide (CO), Methane (CH<sub>4</sub>), Argon (Ar), Ammonia (NH<sub>3</sub>) and particulates. The NH<sub>3</sub> does not result from any combustion process. It comes from the incomplete reaction of NH<sub>3</sub> additive in the de-nitrification process (EMEP/EEA 2006). At the heat and power plant at Mongstad the quantity of N<sub>2</sub>O is not defined. Nitrate was measured to 0.5 ppmv and Ammonia on an average 2 ppmv and maximum 5 ppmv (StatoilHydro 2009).

Carbon monoxide is an intermediate of the combustion of natural gas. In a well adjusted combustion process will be very low, a few ppm. However, if there are low temperature zones or the fuel-air ratio is out of balance, the emission of CO can be significant (Perry & Green 1997). The recommended concentration limit for CO in the pipeline transport of CO<sub>2</sub> is 2000 ppm (de Visser et al. 2008).

Traces of CH<sub>4</sub> can follow the flue gas into the capture process. The remaining CH<sub>4</sub> is the result of incomplete combustion. CH<sub>4</sub> can cause foaming of the amine solution (Kidnay & Parrish 2006). The recommended concentration limit for CH<sub>4</sub> in the pipeline transport of CO<sub>2</sub> is < 4 vol% for injection into an aquifer (de Visser et al. 2008).

Argon (Ar) is a trace gas and constitutes 0.934 vol % of the earth's atmosphere. It is a noble gas which is considered inert at normal pressure and temperature. The Argon represents roughly the same volume percent in the flue gas as in the air. At Mongstad the Ar in the flue gas was measured to be 0.9 vol % (StatoilHydro 2009). The recommended concentration limit for Ar in the pipeline transport of CO<sub>2</sub> is < 4 vol% (de Visser et al. 2008).

Particulates are formed by the incomplete combustion of natural gas. They are composed of low molecular weight hydrocarbons which were not fully combusted. They are usually less than 1 micron (micrometer) in diameter (Speight 2007). Particulates can cause foaming and scaling if not removed. The removal can be done by mechanical filters before and integrated in the capture process (Kidnay & Parrish 2006).

## 5. CO<sub>2</sub> dissolution and amine reactions

Capture of CO<sub>2</sub> in a contact column can be divided into two parts. The first part consists of the CO<sub>2</sub> moving from the flue gas phase into the amine liquid phase where it dissolves. This means that the CO<sub>2</sub> molecules must diffuse through the main body of the flue gas phase to the gas liquid interface. There it must cross the interface into the liquid side before diffusing from the interface to the bulk liquid phase. In the liquid phase the dissolved CO<sub>2</sub> can react with the amine solution in an acid-base reaction or a carbamate reaction.

### 5.1 CO<sub>2</sub> dissolution

A two-film theory is often used to describe the mass transfer in a contact column. It is a simplification of the real conditions where most of the mass transfer takes place in the turbulent region of the counter-current flow. In the two film theory it is assumed that the gas and the liquid are in equilibrium at an interface and that two thin films separate the interface from the main bodies of the gas and liquid phase (Kohl & Nielsen 1997).

The mass transfer rate in the gas phase can be written as

$$N_G = k_p(p_G - p_i) \quad (5.1)$$

where  $N_G$  (kmol/s.m<sup>2</sup>) is the rate of mass transfer in the gas phase,  $k_p$  (s/m) is the gas film transfer coefficient and  $p_G$  and  $p_i$  (N/m<sup>2</sup>) are the pressures in the bulk phase and at the interface between gas and liquid phase. (Coulson & Richardson 1990).

The mass transfer rate in the liquid phase can be written

$$N_L = k_L(c_i - c_L) \quad (5.2)$$

where  $N_L$  (kmole/m<sup>2</sup>.s) is the rate of mass transfer in the liquid phase,  $k_L$  (m/s) is the liquid film transfer coefficient and  $c_i$  and  $c_L$  (kmole/m<sup>3</sup>) are the concentrations at the interface between gas and liquid phase and liquid bulk phase.

To determine  $k_L$  and  $k_G$  the concentration and pressure at the interfacial needs to be measured. This is only possible in very special circumstances. To overcome this problem it has been found of considerable value to use two overall coefficients  $K_L$  and  $K_G$ .  $K_G$  and  $K_L$  are known as the overall gas and liquid phase mass transfer coefficients (Coulson & Richardson 1990).

Assuming that there is equilibrium between the gas and liquid phase at the interface, the mass transfer rate through the gas phase has to be equal to the mass transfer rate in the liquid phase. The mass transfer rate can then be expressed with the help of the overall gas and liquid phase mass transfer coefficients

$$N = K_G(p_G - p_e) = K_L(c_e - c_L) \quad (5.3)$$

where  $p_e$  ( $N/m^2$ ) is the partial pressure in equilibrium with the bulk concentration  $c_L$  and  $c_e$  ( $kmole/m^3$ ) is the concentration in the bulk liquid phase in equilibrium with partial pressure  $p_G$ .

Concentration  $c_e$  and pressure  $p_e$  can be determined assuming that the solution obey Henry's Law. Henry's Law states that at a constant temperature the amount of a gas dissolved in a liquid is directly proportional to the partial pressure of the gas in equilibrium with the liquid.

$$p_G = Hc_e \text{ and } p_e = Hc_L \quad (5.4)$$

$H$  is the Henry's law constant and depends on the gas and liquid and the temperature (Kohl & Nielsen 1997).

The gas film transfer coefficient  $k_p$  and liquid film transfer coefficient  $k_L$  are unknown and has to be determined through experiments. This is usually done by the manufacturers. Equation 5.5 shows the relationship between the transfer coefficients, Henry's constant and the overall mass transfer coefficients.

$$K_L = (1/k_p * H + 1/k_L)^{-1} \text{ and } K_G = (1/k_G + H/k_L)^{-1} \quad (5.5)$$

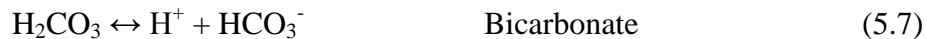
If the Henry's constant, bulk liquid concentration and bulk gas partial pressure are known, the mass transfer rate of  $CO_2$  can be determined.

## 5.2 Amine reactions

The CO<sub>2</sub> can react with the amine solution through two reactions. In a first reaction the dissolved CO<sub>2</sub> hydrolyses to form carbonic acid in reaction.



The carbonic acid reaction is followed by a slow dissociation of carbonic acid to bicarbonate.

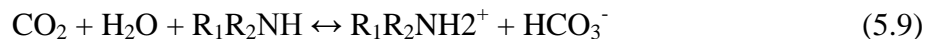


The bicarbonate then reacts with the amine in an acid-base reaction



Here R<sub>1</sub> and R<sub>2</sub> would represent hydrogen atoms if the amine was MEA. If the amine was a secondary amine R<sub>1</sub> would be a hydrogen atom and R<sub>2</sub> would be an alkyl group.

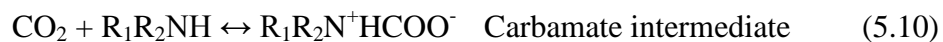
The overall reaction becomes



All amine solutions will undergo the reaction above. Due to the dissociation of carbonic acid to bicarbonate in Reaction 5.7 the overall reaction is considered to be slow (Kidnay & Parrish 2006).

The second reaction between CO<sub>2</sub> and the amine solution is only possible with primary and secondary amines. It is called a carbamate formation reaction. Tertiary amines do not have the reactive hydrogen required to undergo this reaction (Kohl & Nielsen 1997).

It starts with a reaction between CO<sub>2</sub> and the amine to form a carbamate intermediate.



The carbamate intermediate reacts with a second amine to form an amine salt.



The overall reaction becomes



The second reaction mechanism forms the amine salt of a substituted carbamic acid (Kidnay & Parrish 2006).

The reaction rate for the carbamate reaction is faster than the first reaction containing the slow dissociation of carbonic acid to bicarbonate. It can be seen from the stoichiometry of the carbamate reaction that the absorption capacity of the amine solution is limited to 0.5 mole CO<sub>2</sub> per mole amine. This is valid if the only reaction pathway is the carbamate reaction. Due to that the carbamate intermediate can undergo partial hydrolysis to bicarbonate higher loads of CO<sub>2</sub> in the amine solution can be achieved. This has been seen in some plants, but there are no studies found on the subject (Kidnay & Parrish 2006).

The two reactions affect the absorption rate of CO<sub>2</sub> differently for different amine solution. Primary and secondary amines will have similar absorption rates as they can react with CO<sub>2</sub> through the carbamate reaction. Tertiary amines lack the reactive hydrogen and therefore limited to the slow hydrolysis reaction (Kidnay & Parrish 2006).

The two mechanism discussed above are reversible. High pressures and low temperatures drive the reactions to the right leading to absorption of CO<sub>2</sub> into the amine solution. Low pressures and high temperatures will reverse the reactions driving them to the left. This provides a mechanism for the regeneration of the amine solution. CO<sub>2</sub> can be captured in the regeneration step while the amine solution can be circulated back to the absorption step (Kidnay & Parrish 2006).

The chemical reaction in the amine solution will not have a significant effect on the mass transfer rate for tertiary amines. The reaction between CO<sub>2</sub> and water is slow. The dissolved CO<sub>2</sub> molecule will diffuse well into the liquid phase before reacting with the water. Due to this the reaction will not have an appreciable effect on the overall absorption rate. It will instead be the liquid film resistant that is the controlling factor. The liquid and the gas at the interface are assumed to be in equilibrium and the mass transfer will be determined by the molecular CO<sub>2</sub> concentration gradient between the interface and the main bulk of the amine solution (Kohl & Nielsen 1997).

The chemical reaction for primary and secondary amines will have an effect on the mass transfer rate. The carbamate reaction is considered to be fast. The dissolved CO<sub>2</sub> molecules will therefore only travel a short distance before reaction occurs. The location of the reaction will therefore depend on the diffusion rate of the reactants and reaction products, the concentration of solute (CO<sub>2</sub>) at the interface and the concentration of the reactant in the bulk of the liquid. Due to the extremely small distance the solute (CO<sub>2</sub>) has to diffuse compared to the distance it would have to travel for simple physical absorption a high liquid-film coefficient is observed. In many cases the gas-film resistance becomes the controlling factor (Kohl & Nielsen 1997).

## 6. Degradation of alkanolamines

Three main types of degradation of MEA can occur in a flue gas containing oxygen. The first type is CO<sub>2</sub> degradation through a pathway called carbamate dimerization. Carbamate dimerization occurs at high temperatures in the presence of CO<sub>2</sub>. It produces high molecular weight degradation products and is expected to occur in the stripper column. The second type is oxidative degradation. Oxidative degradation need oxygen and is catalyzed by iron. It creates oxidized fragments of the solvent like organic acids and NH<sub>3</sub>. This is expected to happen in the lower part of the contact column where the concentration of dissolved O<sub>2</sub> is at its highest (Rochelle & Chi 2001). Thermal degradation is the third type of degradation. It occurs at temperatures higher than 205 °C. In the absorption and regeneration of CO<sub>2</sub> the temperature will normally not reach 205 °C, but hotspots can occur. Thermal degradation will be less significant at typical CO<sub>2</sub> capture temperatures (40-140 °C) compared to CO<sub>2</sub> and oxidative degradation (Bedell 2008).

### 6.1 Background

Few studies have been done on the degradation of alkanolamines used to absorb CO<sub>2</sub> in post combustion capture. Most studies done in this field have been aimed at understanding the degradation of the traditional gas sweetening process. These studies were usually performed in a laboratory under controlled conditions using pure gases. The complexity of degradation increases when looking at a flue gas from natural gas power plants. Flue gas contains a mixture of CO<sub>2</sub>, O<sub>2</sub>, CO, SO<sub>x</sub>, NO<sub>x</sub>, COS, CS<sub>2</sub> and particles. The effect of these components on the degradation processes of alkanolamines is poorly understood (Strazisar et al. 2003).

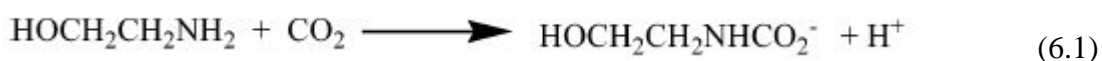
It is important to keep in mind the different conditions throughout the capture process when investigating the degradation of alkanolamines. The temperature will be different in the contact column compared to the stripper column. The concentration of the various components in the flue gas will change as the flue gas passes through the contact and stripper columns. Oxygen concentration will decrease as the carbon dioxide increases.

Monoethanolamine (MEA) is one of the most commonly used alkanolamines in post-combustion absorption of CO<sub>2</sub>. It is one of the most studied alkanolamines and therefore a natural starting point.

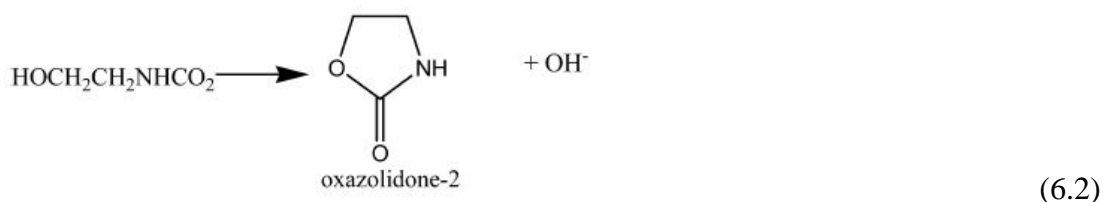
## 6.2 CO<sub>2</sub> degradation

Carbamate dimerization is a possible degradation pathway for primary and secondary alkanolamines. It is a reaction between CO<sub>2</sub> and MEA at temperatures between 40 – 140 °C (Idem & Bello 2005). This is the range of temperatures encountered in the CO<sub>2</sub> capture process. Carbamate dimerization is favored by high temperature and will therefore predominantly take place in the stripper column (Strazisar et al. 2003).

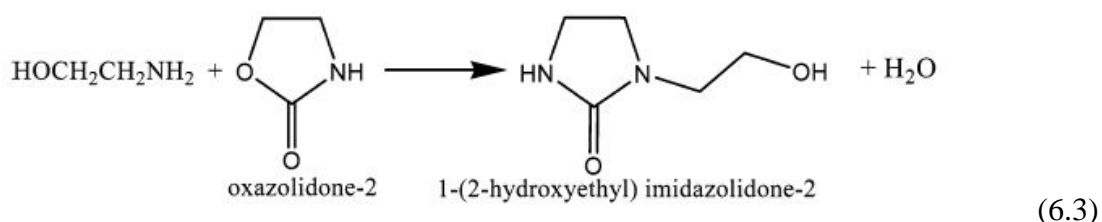
The reaction is initiated by the formation of MEA carbamate from CO<sub>2</sub> and MEA.



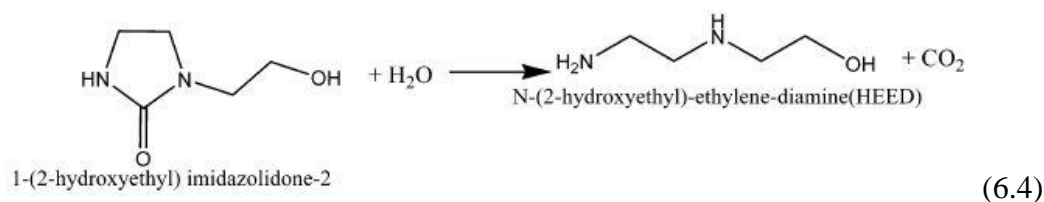
This is followed by condensation of the MEA carbamate to oxazolidone-2.



The oxazolidone-2 can react with a second MEA molecule to form the intermediate 1-(2-hydroxyethyl)-2-imidazolidone (3).



In a last step the substituted imidazolidone hydrolyzes to CO<sub>2</sub> and N-(2-hydroxyethyl)-ethylenediamine (HEED). It is possible that HEED continues to degrade in the presence of CO<sub>2</sub> to form longer substituted diamines (Idem & Bello 2005).



Studies done by Rooney et al. confirms that carbamate formation differ for primary, secondary and tertiary amines. Primary amines form carbamate more strongly than secondary amines. Tertiary amines do not form carbamate at all as they lack the reactive hydrogen (Rooney et al. 1998).

### 6.3 Oxidative degradation

Oxygen plays an important role in degradation of alkanolamines. Earlier studies have mostly focused on the gas sweetening process where oxygen is absent. Oxygen can be present in gas sweetening system if there are leaks. However, in flue gas from gas power plants there will be a significant amount of oxygen present in the gas stream. Oxygen concentration up to ~13 wt% is possible, depending on the operational conditions of the power plant. The presence of oxygen in high concentrations opens up new pathways for degradation of alkanolamines. In earlier studies experiments have been done either with CO<sub>2</sub> and alkanolamine or with O<sub>2</sub> and alkanolamine. Very few experiments have been performed to investigate degradation of CO<sub>2</sub> loaded amine solution in the presence of O<sub>2</sub>.

Ammonia and carboxylic acids have been observed as products from primary, secondary and tertiary alkanolamine degradation. They are formed by oxygen induced degradation. The suggested mechanism can be seen in Figure 6.1. In the first step MEA forms a vinyl alcohol and ammonia. The vinyl alcohol then reacts to form acetaldehyde which in turn reacts with oxygen to form acetic acid (Strazisar et al. 2003).

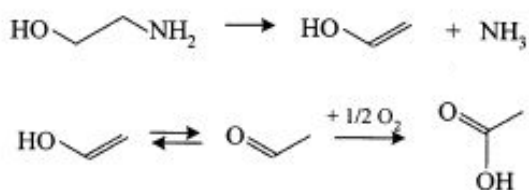


Figure 6-1 Mechanism for formation of acetic acid and ammonia (Strazisar et al. 2003)

A scheme was proposed by Rooney et al. to account for some of the observed anions compounds reported in their previous studies. The scheme can be seen in Figure 6.2. MEA is used in the scheme, but it could apply to any primary or secondary alkanolamine. No overall reaction mechanisms were proposed to account for these degradation products. This would

suggest that the products shown in the scheme are only a few of the products that can be formed by oxidative degradation (Idem & Bello 2005). Although the acid form of acetic, formic, glycolic, glyoxalic and oxalic acids are presented in the scheme, they all completely ionize to form heat-stable amine salts, such as oxalates and glyoxalates, in strong base solutions (Rooney et al. 1998).

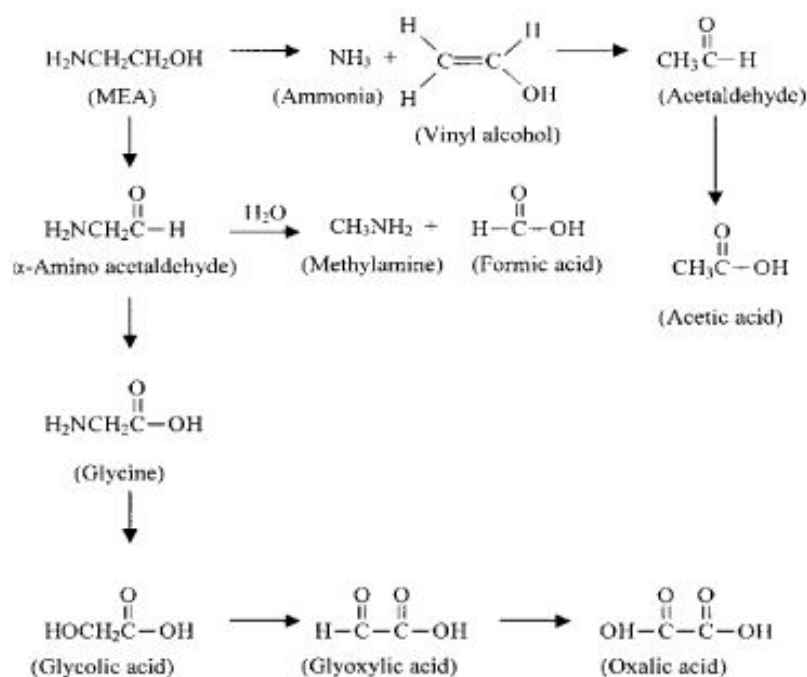


Figure 6-2 Mechanism of oxidative degradation of MEA (Rooney et al. 1998)

The presence of  $\text{CO}_2$  was found to influence the oxidative degradation of alkanolamines in studies done by Rooney et al. Both the number of compounds formed and the concentration of the products were influenced. The resistance to oxidative degradation increased in the  $\text{CO}_2$  loaded amine solution. A possible explanation for this is that the  $\text{CO}_2$  lowers the solubility of  $\text{O}_2$  in the amine solution (Rooney et al. 1998).

The possibility that MDEA can form MEA and/or DEA was also investigated by Rooney et al. Experiments revealed that DEA was formed as one of the degradation products when  $\text{O}_2$  was present. This was the case both with and without  $\text{CO}_2$ . No trace of MEA was found. The results proved that  $\text{O}_2$  plays a role in the degradation of MDEA to DEA, even at temperatures as low as  $82^\circ\text{C}$  (Rooney et al. 1998). This suggests that MDEA solutions can be susceptible to degradation by  $\text{CO}_2$  over time through the formation of DEA.

## 6.4 Thermal degradation

In 2008 Lepaumier et al. suggested a general pathway for ethanolamine degradation with CO<sub>2</sub>. The thermal degradation was done for primary and secondary amines at 140 °C. This is a slightly higher temperature than normally used in the regenerator column. However, investigation of possible benefits using a higher temperature in the regeneration step makes the study interesting (Lepaumier et al. 2008).

The pathway for ethanolamine degradation can be seen in Figure 6.3. The first step of degradation for primary and secondary amines is the formation of oxazolidinone due to carbamate ring closure. The oxazolidinone is very sensitive to nucleophilic reactions and will react with a second amine to form a dimer. In this reaction secondary amines are less stable as they are more nucleophilic than primary and tertiary amines. The dimer can be degraded to three different kinds of compounds. This depends on the R group seen in figure 3. If one R is an alkyl group, an oligomer or a cyclic compound (piperazines) will be formed. The formation of imidazolidinone will not be favored. If the R groups are hydrogen (MEA) the main product will be imidazolidinone (Lepaumier et al. 2008).

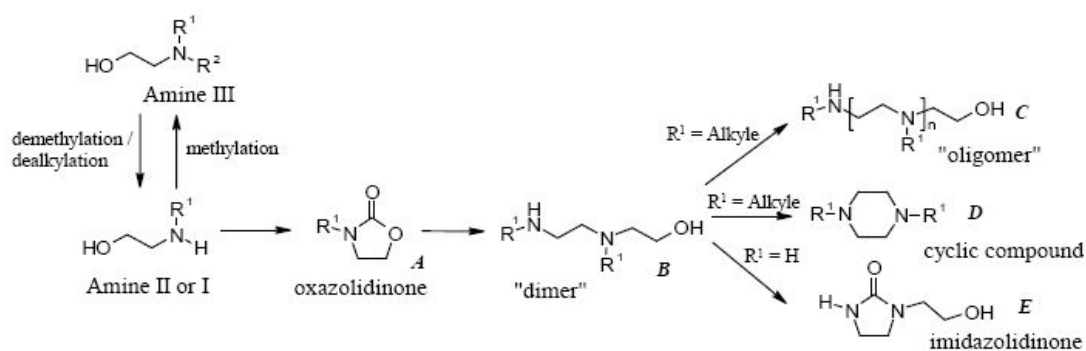


Figure 6-3 General pathways for Ethanolamines degradation with CO<sub>2</sub> (Lepaumier et al. 2008)

## 6.5 Degradation experiments

In an extensive study A. Bello and R. Idem (2005) evaluate the effects of temperature, O<sub>2</sub> partial pressure, MEA concentration and CO<sub>2</sub> loading on MEA degradation. They suggest possible pathways for the formation of degradation products under typical contact and stripper column conditions. Three systems MEA-H<sub>2</sub>O-O<sub>2</sub>, MEA-H<sub>2</sub>O-CO<sub>2</sub> and MEA-H<sub>2</sub>O-O<sub>2</sub>-CO<sub>2</sub> were used to evaluate the effects. The experimental conditions were: oxygen partial pressure 250 kPa or 350 kPa, temperature 55, 100 or 120 °C and MEA concentration 5 or 7 mol/L (Idem & Bello 2005).

The degradation of a mixture of MEA and MDEA (MEA-MDEA-H<sub>2</sub>O-O<sub>2</sub> system) was studied in a separate report. The results were compared to the oxidative degradation of MEA study. Conditions were similar in both studies.

### 6.5.1 MEA-H<sub>2</sub>O-O<sub>2</sub> system

Bello and Idem started by investigating the MEA-H<sub>2</sub>O-O<sub>2</sub> system. They observed that more degradation products were formed at the higher oxygen partial pressure (350 kPa). The additional products were assumed to be a result of further oxidation of degradation products also formed at the lower partial pressure (250 kPa). The oxygen at the lower partial pressure acted as a limiting factor for further degradation. The higher oxygen partial pressure leads to more oxygen dissolved and additional degradation products formed as observed.

The effect of temperature on the number of degradation products formed was investigated. The change in temperature from 55 °C to 100 °C and 120 °C for the two oxygen partial pressures showed that the number of degradation products formed increased with temperature. At the lower oxygen partial pressure only two compounds were common for 100 °C and 120 °C. One compound was the same for 55 °C and 120 °C. For 55 °C and 100 °C no compounds were identical. This implied that the reaction mechanisms of the degradation process changed with temperature in the MEA-H<sub>2</sub>O-O<sub>2</sub> system.

The effect of MEA concentration yielded an interesting result. The number of degradation products decreased as the MEA concentration increased for the two oxygen partial pressures. It was proposed that the higher MEA concentration caused a lower solubility of O<sub>2</sub>. The larger number of MEA molecules would compete for the relatively smaller number of O<sub>2</sub> molecules. The higher concentration of MEA could be used to lower the number of degradation products thus acting in an opposite manner to the effect of higher O<sub>2</sub> partial pressure.

### 6.5.2 MEA-H<sub>2</sub>O-CO<sub>2</sub> system

The effect of MEA concentration on the MEA-H<sub>2</sub>O-CO<sub>2</sub> was investigated. Three degradation products were found at the lower MEA concentration compared to 5 at the higher concentration. The increase in degradation products for the MEA-H<sub>2</sub>O-CO<sub>2</sub> system was opposite to the result from the MEA-H<sub>2</sub>O-O<sub>2</sub> system. This showed that in the MEA-H<sub>2</sub>O-CO<sub>2</sub> MEA concentration could not be used to reduce the total number of degradation products.

The MEA-H<sub>2</sub>O-CO<sub>2</sub> was compared to the MEA-H<sub>2</sub>O-O<sub>2</sub> system. The results showed that that a greater number of degradation products were formed in the presence of O<sub>2</sub>. This suggested that MEA is more prone to degradation in the presence of O<sub>2</sub>.

### 6.5.3 MEA-H<sub>2</sub>O-O<sub>2</sub>-CO<sub>2</sub> system

The system of MEA-H<sub>2</sub>O-O<sub>2</sub>-CO<sub>2</sub> was investigated in the same way as the previous two systems with O<sub>2</sub> and CO<sub>2</sub>. The effect of CO<sub>2</sub> was evaluated. The results yielded a rare insight into the complex workings of CO<sub>2</sub> capture by MEA in the presence of O<sub>2</sub>.

The effect of temperature was investigated for the two concentrations of MEA at the two O<sub>2</sub> partial pressures. The temperatures used were 100 °C and 120 °C, which are typical temperatures in a stripper. At the lower MEA concentration and high O<sub>2</sub> partial pressure 5 degradation products were found at 100 °C compared to two at 120 °C. No identical products were found for the different temperatures. When the MEA concentration was increased at the lower O<sub>2</sub> partial pressure 5 degradation products were found at 100 °C and two at 120 °C. This suggests that the reaction mechanisms change as the temperature change just as in the MEA-H<sub>2</sub>O-O<sub>2</sub> system.

The effect of O<sub>2</sub> partial pressure at the lower MEA concentration and 120 °C was investigated. Five degradation products were found at the lower O<sub>2</sub> partial pressure and 12 were obtained at the higher partial pressure. This suggested that an increase in O<sub>2</sub> partial pressure will increase the number of degradation products. This was the same result as for the MEA-H<sub>2</sub>O-O<sub>2</sub> system.

The effect of MEA concentration was investigated at 120 °C. The results showed that as the concentration of MEA was increased the number of degradation products increased from two products to 12 products. This suggested that an increase in MEA concentration would lead to an increase of degradation products.

Finally the effect of CO<sub>2</sub> was investigated. First the experiment was run at 100 °C for a system with and without a CO<sub>2</sub> load. The result showed that the presence of CO<sub>2</sub> in the amine solution affected the number of degradation products formed. When CO<sub>2</sub> was present five products were formed compared to eight products in the absence of CO<sub>2</sub>. The same experiment was run at 120 °C. Two degradation products were formed with CO<sub>2</sub> present and 31 products were formed in the absence of CO<sub>2</sub>. These results implied that the presence of CO<sub>2</sub> changed the mechanism for oxidative degradation in the MEA-H<sub>2</sub>O system. The result agreed with those of Rooney et al. (1998). They concluded that the addition of CO<sub>2</sub> lowers the solubility of O<sub>2</sub>.

#### *6.5.4 MEA-MDEA-H<sub>2</sub>O-O<sub>2</sub> system*

Mixing MEA and MDEA has a significant effect on the overall degradation. The presence of MDEA results in a lower number of O<sub>2</sub>, CO<sub>2</sub> or CO<sub>2</sub> and O<sub>2</sub> induced degradation products from MEA alone compared to the MEA-H<sub>2</sub>O system. However, the blend of MEA and MDEA yields and overall larger number of degradation products compared to MEA alone (Idem & Bello 2005).

The presence of MDEA together with MEA changes the reaction pathways. Experiments show that MDEA is more prone to oxidative degradation when blended with MEA. MDEA is preferentially degraded to protect the MEA. This is supported by the observation that the extent of degradation of MEA in MEA-MDEA-H<sub>2</sub>O-O<sub>2</sub> is much reduced compared to the MEA-H<sub>2</sub>O-O<sub>2</sub> system. This confirms that MDEA is preferentially degraded to protect MEA in the MEA-MDEA system (Idem & Bello 2005).

#### *6.5.5 Other effects*

Experimental results strongly support that iron is an important catalyst in MEA oxidation. The addition of 1mM iron to a 0.4 mol CO<sub>2</sub>/mol MEA resulted in the rate of oxidation increasing by a factor five. The same rate increased was seen for both ferrous and ferric concentrations. The addition of ferrous iron into a solution of MEA with no O<sub>2</sub> present resulted in no oxidation. The behavior is consistent with that ferrous iron is expected to oxidize rapidly to ferric iron in the presence of oxygen (Rochelle & Chi 2001).

Bicine have been observed to inhibit the catalytic effect of iron in oxidative degradation. Bicine is a tertiary amine. In solutions with a high pH it exists in its anion form. It is thought to be a chelating agent and it will bind the iron present in the solution. This will prevent the

iron from enhancing the oxidative corrosion. The corrosion inhibiting ability of bicine might make it an attractive compound for corrosion control at first glance, but plant corrosion experiences indicate that bicine will have the opposite (Bedell & Bosen 2004).

## 6.6 SO<sub>2</sub>, COS, NO<sub>x</sub> and CS<sub>2</sub> degradation

Carbonyl Sulfide (COS) and Carbon disulfide (CS<sub>2</sub>) reaction mechanisms with MEA and secondary alkanolamines are similar to the CO<sub>2</sub> mechanism (Sharma 1965). In a first step the reaction between MEA and COS forms an intermediate.



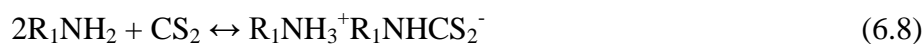
A second amine molecule is instantaneously subject to protonation.



This results in the overall reaction:



Carbon disulfide is known to induce degradation. Similar to the mechanism for COS, CS<sub>2</sub> can react with MEA to form thiocarbamates. The overall reaction is:



COS and CS<sub>2</sub> form irreversible reaction products with MEA. Some of the products formed have an effect on corrosion. To prevent corrosion problems they have to be removed to prevent accumulation in the amine solution.

Little is known about the reaction mechanism for sulfur dioxide (SO<sub>2</sub>). Most studies of degradation by sulfur compounds have been limited to COS and CS<sub>2</sub>. However, a study by Idem et al. (2006) investigated the effect trace amounts of SO<sub>2</sub> had on the degradation of MEA. They were able to demonstrate that the concentration of SO<sub>2</sub> had a clear effect on the oxidative degradation of MEA. Concentrations of 6 ppm and 11 ppm were introduced into the MEA solution. The presence of SO<sub>2</sub> was seen to induce additional oxidative degradation. Increasing the concentration of SO<sub>2</sub> in the flue gas resulted in a further increase in degradation rate (Idem et al. 2006).

Nitrosamines can form in reactions between the amine solution and nitrogen oxides. Small amounts of nitrosamines have been found in lean MEA solution 2.91  $\mu\text{mol/mL}$ . Due to their low boiling point none have been observed in the reclaimer (Strazisar et al. 2003).

Nitrosamines are carcinogens and are therefore important to keep track of in the capture process. The lack of nitrosamines in the reclaimer suggests that some may escape to the atmosphere in the absorption step. This would create health and environmental issues which would have to be investigated further.

### 6.7 Degradation compounds

Carbon dioxide, oxygen and COS will react to form contaminants as seen in previous sections. These contaminants can react further with alkanolamine molecules to form degradation products. Typical degradation products formed in different alkanolamine solutions are listed below in Table 6.1(Haws 2001).

Table 6-1 Amine degradation products (Haws 2001)

Amine		Amine degradation product	Heat stable salt
MEA	+O <sub>2</sub>	carboxylic acids	
		imidazolidone	
	+CO <sub>2</sub>	oxazolidone	OZD
		hydroxyethyl imidazolidone	HEI
		hydroxyethyl ethylenediamine	HEED
	+COS	diethanolurea	
DGA	+CO <sub>2</sub>	bis hydroxyethyl ethoxy urea	BHEEU
	+COS	bis hydroxyethyl ethoxy thiourea	
DEA	+CO <sub>2</sub>	hydroxyethyl oxazolidone	HEOD
		bis hydroxyethyl piperzine	BHEP
		tris hydroxyethyl ethylenediamine	THEED
	+COS	monoethanolamine	MEA
		hydroxyethyl imidazolidone	HEI
		bis hydroxyethyl ethylenediamine	BHEEP
DIPA	+CO <sub>2</sub>	hydroxymethyl propyl oxazolidone	HMPO
MDEA		ethylene glycol	EG
		hydroxymethyl piperzine	HMP
		diethanolamine	DEA
		triethanolamine	TEA
		Bis hydroxyethyl piperzine	BHEP

## 7. CO<sub>2</sub> Corrosion

Corrosion is one of the main concerns in the capture and transport of carbon dioxide from flue gas. It is therefore important to understand how to predict occurrence of corrosive conditions in the system. The knowledge of how corrosion occurs in the capture and transport of carbon dioxide will help understand how to combat the problem.

Carbon steel is the material of choice in many capture plants and for gas piping. It is usually the only economical choice when the pipeline transport distances are long. Certain exposed parts can be exchanged for other more corrosion resistant materials, but unprotected the corrosion rates for carbon steel can become prohibitively high. The redeeming factor for carbon steel is that the exposed steel surface can become covered in a protective layer. The layer can be corrosion products mineral scale or inhibitors.

MEA has a bad reputation for being the most corrosive of the alkanolamines used in post combustion absorption. Several investigations have shown that this is not entirely true. In the absence of acid gases there is no difference between the corrosion rates of the different alkanolamines. However, MEA and DEA form basic degradation products when reacted to CO<sub>2</sub> while MDEA as a tertiary amine does not. The degradation products can enhance the corrosion rate (DuPart et al. 1993).

### 7.1 Wet CO<sub>2</sub> corrosion

The risk of corrosion from dissolved CO<sub>2</sub> in water is primary associated with a decrease in pH. The concentration of CO<sub>2</sub> in the aqueous phase is determined by the partial pressure of CO<sub>2</sub>. The pH is in turn determined by the concentration of CO<sub>2</sub> in the water phase.

When there is free water present CO<sub>2</sub> will dissolve in the aqueous phase. In the water phase CO<sub>2</sub> will partly ionize to form a weak acid. CO<sub>2</sub> slowly dissolves in water and forms carbonic acid when partly hydrated.



The carbonic acid dissociates in two steps to form HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. How far the dissociation of carbonic acid will proceed depend on the overall pH in the aqueous phase.



The pH of the system is a result of the CO<sub>2</sub> partial pressure. The pH will decrease as the partial pressure of CO<sub>2</sub> increase in un-buffered water. In a buffered water solution the pH will increase, but the pH will still depend on the partial pressure of CO<sub>2</sub> in the same manner as for pure water (Kohl & Nielsen 1997).

There will be an equal release of alkalinity as carbon steel corrodes.



The pH of the solution will increase and when the concentration of Fe<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> reach their limit of solubility, FeCO<sub>3</sub>(s) can precipitate. The pH will stabilize when the rate of formation of FeCO<sub>3</sub> equals the corrosion rate of the steel (Dugstad 2006).



The precipitation of FeCO<sub>3</sub> is strongly dependent on CO<sub>2</sub> partial pressure and pH.

Experimental results have illustrated their influence on the precipitation. If the pH is kept constant and the CO<sub>2</sub> partial pressure is allowed to change it is seen that the solubility of Fe<sup>2+</sup> goes through a maximum at pH 5 and pH 5.5. At higher pH values the solubility of Fe<sup>2+</sup> will decrease with increasing CO<sub>2</sub> partial pressure. The opposite trend is observed for pH >6 (Dugstad 2006).

At the cathode there are three main reactions in the presence of CO<sub>2</sub>. They are as follows:



The contribution of the three different reactions depends on the temperature, concentrations, pH convection etc. The presence of CO<sub>2</sub> affects all the reactions directly or indirectly by affecting the H<sup>+</sup> concentration and the amount of un-dissociated HAc and H<sub>2</sub>CO<sub>3</sub> (Dugstad 2006).

In strong acid solutions the rate of hydrogen production proceeds according to reaction 7.6. The rate is limited by the rate which the H<sup>+</sup> can be transported to the surface from the bulk solution. Above pH 5 the contribution from reaction 7.6 is small. H<sub>2</sub>CO<sub>3</sub> contributes with

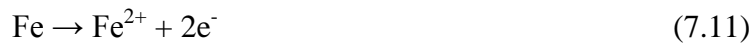
additional H<sup>+</sup> ions and allows the hydrogen evolution reaction to react at a higher rate than would be the case for a strong acid at the same pH.

For low CO<sub>2</sub> partial pressure and high pH it has been suggested that direct reduction of HCO<sub>3</sub><sup>-</sup> ion and water might be important for the cathode reaction.

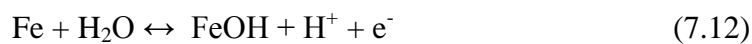


The concentration of HCO<sub>3</sub><sup>-</sup> increases with pH and is more than 300 times the H<sub>2</sub>CO<sub>3</sub> at 1 bar CO<sub>2</sub> and pH 6 (Dugstad 2006) Even though the concentration of HCO<sub>3</sub><sup>-</sup> is high the dissociation constant for bicarbonate and water is low making it a poor proton donor. This would decrease its contribution to the cathode reaction. It is however hard to experimentally determine the particular effect of the direct reduction for hydrogen evolution in reaction (7.6) and (7.7).

At the anode iron dissolves and is oxidized in an overall reaction:



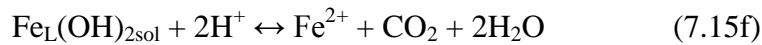
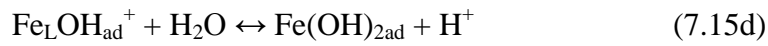
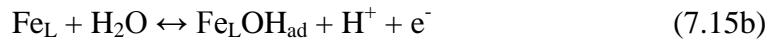
The rate of this reaction is pH dependent. For strong acids when the pH is low the proposed mechanism is:



This mechanism is often assumed to apply for CO<sub>2</sub> solutions (Dugstad 2006).

When the pH increases experimental data have indicated that the pH dependency decreases rapidly. Studies have determined that at pH>4 the anodic dissolution of iron does not depend significantly on OH<sup>-</sup> concentration, but rather by the presence of CO<sub>2</sub>.

The proposed mechanism for the anode dissolution of iron is (Dugstad 2006):



The  $\text{Fe}_L$  represents the complex  $\text{Fe-CO}_2$ . It is assumed that the complex adsorb on the electrode surface and catalyses the dissolution of iron. For  $\text{pH} > 5$  the rate determining step will be step 7.15c. For  $\text{pH} < 4$  it is postulated that the rate of this step will increase and desorption step 7.15e will become rate determining (Dugstad 2006).

For wet  $\text{CO}_2$  systems it has been seen that protective iron carbonate films can form at all temperatures. The formation is dependent on that the concentration of iron carbonate and  $\text{pH}$  are sufficiently high in the water phase. Usually a high super-saturation is needed for the formation of the protective film.

The stability and effectiveness of the iron carbonate film is dependent on the initiation of the film. If the temperature and super-saturation are high ( $> 60 \text{ }^\circ\text{C}$ ) in the bulk phase, a massive precipitation will take place. A dense iron carbonate film will form and provide good protection on most iron surfaces. If the temperature ( $< 40 \text{ }^\circ\text{C}$ ) the precipitation rate is lower and a film may never be formed. A stagnant or semi stagnant period will be needed to allow the iron carbonate to settle on the iron surface. At low precipitation rates the film created might be porous and provide very little corrosion protection. Once the protective film is created it will usually remain protective. This is true as long as the super-saturation in the bulk phase remains sufficiently high (Dugstad 1998).

## 7.2 Corrosion at high CO<sub>2</sub> pressure

Low alloy carbon steel pipes are used to transport CO<sub>2</sub> at high pressures. In most cases the CO<sub>2</sub> is dried to get rid of the free water and minimize the risk of corrosion. The drying process adds to the operational costs. A greater understanding of the corrosion mechanisms under high pressures could lead to less strict limits on the water content in CO<sub>2</sub> for pipe transport and save on handling costs.

Not much is known about what corrosion rates can be expected when transporting CO<sub>2</sub> at high pressure and at low temperatures. Some introductory experiments have been done for temperatures below 30 °C and CO<sub>2</sub> partial pressures at pressures above 30 bars. The initial results suggest that the corrosion rates are not the same as those that can be expected at lower pressures.

The corrosion rates were generally much lower at high pressure than predicted by standard CO<sub>2</sub> corrosion models. The change in CO<sub>2</sub> solubility and that liquid CO<sub>2</sub> interacts differently with water compared to gaseous CO<sub>2</sub> were proposed as possible explanations for this change. The solubility of CO<sub>2</sub> was found to be slightly lower than for lower pressures, but it was still in the same range as theoretical values (Seiersten et al. 2003).

It was found unlikely that the low corrosion rate was caused by the formation of a FeCO<sub>3</sub> in the experiments. The change of pH at a constant temperature did not lead to any significant change in concentration of iron present in the solution. It was suggested that the super saturation probably was too low for the formation of a protective FeCO<sub>3</sub> film if the mechanism is the same at high pressures as at low CO<sub>2</sub> pressures (Seiersten et al. 2003).

A change in pH from 3.1 to 5.5 did not lead to any noticeable change in corrosion rate at 5 °C and 35 or 60 bar. This result cannot be explained by standard CO<sub>2</sub> models. There was an indication that a thin film had been formed, but the experiment was not able to determine the composition of said film. It was proposed that the activity of oxygen was high enough at these high CO<sub>2</sub> pressures and would form iron oxide. High purity CO<sub>2</sub> was used in the experiments. The maximum of oxygen in solution was calculated to be 25 ppb at 72 bar CO<sub>2</sub>. At lower pressures oxygen in such amounts have no influence on the corrosion rate (Seiersten et al. 2003).

Experiments done in the supercritical region for CO<sub>2</sub> (58-95 bars) indicate that the corrosion rate is significantly lower than those predicted by models valid for lower pressures. In the high pressure region an increase in pressure has been seen to decrease the corrosion rate. This is opposite to what has been observed at low pressures. The results serve as a good indication that the corrosion mechanism at high pressures differ from the mechanism at low pressures.

The change of pH was observed to have different effects on the corrosion rate. The increase in pH generally leads to the reduction of the corrosion rate at lower pressures. In the experiments at higher pressures the results did not give a clear answer. When increasing the pH at 35 bar and 24 °C the corrosion rate was decreased by approx. 50%. Corrosion rate tests were also done for 35 bar and 44 bar at 5 °C. The pH was different for the two cases, but the corrosion rates were very similar. No clear conclusions could be had from the results, but it underlined the importance of investigating the corrosion mechanism at high pressures.

The effect of temperature was investigated at 35 bars. A clear trend was seen. The corrosion rate decreased as the temperature was reduced (Seiersten et al. 2003).

The change in pH was seen to have a surprising effect on a typical commercial inhibitor known to be effective at lower pressures. Normally an increase in pH is viewed as beneficial as the corrosion rates are expected to decrease. Experiments done with the inhibitor at lower pressures gave final corrosion rates well below 0.1 mm/year. Increasing the pH at high pressure in the presence of the inhibitor resulted in a higher corrosion rate. No explanation was found. The increased corrosion rate has no practical effects as the rates are still sufficiently low in all cases (Seiersten et al. 2003).

More data and experiments on the corrosion rate of carbon steel will be needed to be able to establish guidelines for CO<sub>2</sub> quality and allowable limits of trace impurities like O<sub>2</sub> and H<sub>2</sub>O to be determined.

### 7.3 The effect of O<sub>2</sub>

The presence of dissolved O<sub>2</sub> adds another possible pathway for iron to oxidize. At the anode iron will be oxidized to Fe<sup>2+</sup> as seen previously.

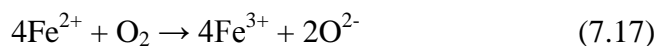


At the cathode the dissolved oxygen will react with water to form hydroxide ions.

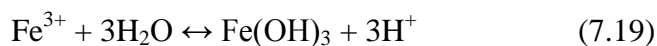
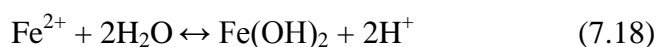


The presence of dissolved oxygen in water increases the reaction rate at the cathode. If oxygen diffusion is the controlling factor, the corrosion tends to increase as the temperature increases.

A redox reaction between O<sub>2</sub> and Fe<sup>2+</sup> also occurs in the presence of water and is important for the corrosion process.



The following multistep acid-base reactions can affect the course of the corrosion.



The availability of oxygen in solution will be limited by its solubility in water or amine solution. Products containing Fe<sup>2+</sup> will therefore be dominating.

Almost no data can be found on corrosion of carbon steel in water with CO<sub>2</sub> and trace amounts of O<sub>2</sub> in solution. Most of the data found come from gas sweetening processes for CO<sub>2</sub> and H<sub>2</sub>S in solution. The Data obtained for oxygen – carbon dioxide corrosion came from experiments done at 26 °C at atmospheric pressure. The pH of the system varied from 4.1 to 4.8. The concentration of CO<sub>2</sub> ranged from 20 to 670 ppm. The concentration of O<sub>2</sub> was 1.6, 4.3 and 8.8 ppm. The rates of corrosion were found to be roughly proportional to the concentration of dissolved O<sub>2</sub>. The corrosion rates in the presence of dissolved CO<sub>2</sub> and trace amounts of O<sub>2</sub> indicated that the corrosion caused by oxygen and carbon dioxide were independent of each other. The corrosion was however greater in the presence of both oxygen and carbon dioxide than for comparable concentrations of either gas alone (Watkins & Kincheoe 1958).

## **8. Corrosion in amine systems**

The corrosion in amine systems depend on many factors. Among them are high operating temperature, rich and lean solution loadings, solution velocity, amine solution concentration and amine type. Contaminants in the amine solution from degradation will also enhance the corrosion in the amine system.

### **8.1 Background**

In plants using alkanolamine solutions most corrosion failures are attributed to high temperatures and free acid. There are of course many other factors which influence the occurrence of corrosion. Investigating the different types of corrosion can give valuable insight into other means by which corrosion occurs. Some of the types of corrosion that can be found in alkanolamine systems are: general corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, erosion corrosion and stress corrosion cracking (DuPart et al. 1993).

General corrosion is the most common form of corrosion. General corrosion is characterized by a uniform loss of material over the exposed area. This form of corrosion is well known and can easily be measured. Unfortunately most corrosion failures are not caused by general corrosion, but localized corrosion. The localized corrosion is usually concentrated to specific areas and can go unnoticed until an unexpected failure occurs (DuPart et al. 1993).

Galvanic corrosion occurs when two dissimilar metals are coupled together through a electrolyte. In this case that electrolyte would be the loaded amine solution. An example would be a stainless steel tray held together by carbon steel bolts. Carbon steel, being the less resistant metal, would act as anodes. The bolt would corrode away in preference to the stainless steel leading to a potential catastrophic event if not discovered in time (DuPart et al. 1993).

Crevice corrosion occurs when a concentration cell forms in a small crevice between metal surfaces, or a metal and non-metal surface. The crevice corrosion is then caused by changes in acidity or by depletion of corrosion inhibitors in the crevice. It has been observed that chloride ions are effective in promoting this kind of corrosion. Crevice corrosion is found where tubes are attached to the heat exchangers tube sheet. It is especially common in the re-boiler (DuPart et al. 1993).

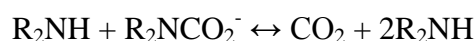
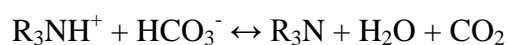
Pitting corrosion is highly concentrated to a few spots. It can be very intense and can cause penetration damage in a very short time period. The pitting corrosion occurs usually in stagnant areas and is especially promoted by halide ions. The equipment failure from this kind of corrosion is most of the time totally unexpected and sudden. Carbon steel has been found to be more resistant to pitting corrosion than stainless steel (DuPart et al. 1993).

Erosion corrosion is caused by the movement between a corrosive solution and the metal surface. The relative movement between the two results in an increased attack on the metal. Bubbles and solid particles in the liquid can help make the corrosion worse. The velocity of the corrosive liquid, the turbulence and the stability of any protective film will all affect the degree of erosion corrosion. Erosion corrosion is well-known in plumbing bends, elbows, tees, valves, pumps, blowers and impellers (DuPart et al. 1993).

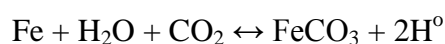
Stress corrosion cracking occurs in the presence of tensile stress and a corrosive solution. The stress can be either internal stress in the material or outside applied stress. The temperature, amine solution composition, metal composition and structure are factors that will affect the extent of stress corrosion. Results from various plants indicate that stress corrosion is more likely to occur in MEA units compared to DEA or MDEA units (DuPart et al. 1993).

## **8.2 Effects in amine systems**

A mechanism for corrosion in alkanolamine solution was suggested by Reisenfeld and Blohm. They observed that significant corrosion was caused by acid gas in the alkanolamine solution as mentioned previously. The CO<sub>2</sub> can evolve from the rich amine solution according to the following two reactions for tertiary and secondary alkanolamines.



The CO<sub>2</sub> can then react directly with the iron when there is water present as was shown earlier.



Iron carbonate is formed which have the possibility to create a protective film or be transported away. From which source the released hydrogen comes from is not seen in these

reactions. The hydrogen may come from  $H^+$ ,  $H_2CO_3$  or alkanolammonium ions (Kohl & Nielsen 1997).

In an amine system it is not the amine that is the cause of the corrosion. The acid gas  $CO_2$  captured is the cause. If carbon steel is exposed to alkanolamines under an inert gas the corrosion rates are lower than those exposed to water under the same conditions (Kohl & Nielsen 1997).

The temperature of the system has a significant effect on the corrosion rate. Observations have shown that corrosion is usually caused by the evolution of acid gases from the rich alkanolamine solution. This occurs in the regenerator, reboiler and the rich alkanolamine solution side of the rich/lean heat exchanger. Experiments have shown that the corrosion becomes more severe and the corrosion rate increases as the temperature is raised (Kohl & Nielsen 1997). The main causes for this is thought to be the increased evolution of  $CO_2$  gas and the positive effect the temperature have on degradation reactions. Temperature increases the degradation alkanolamines as discussed in Chapter 6.

The solution velocity has an effect on the corrosion rate and corrosion behavior. An increase in solution velocity will result in an increase in corrosion rate for carbon steel systems. The reasons behind this increase in corrosion rate are several. The mass transfer to and away from the corrosion site will be enhanced as a result of the steeper concentration gradient created. The products that are formed and would precipitate close to the corrosion site and possibly create a protective film at lower velocities are transported away. The higher solution rate will also have an erosion effect on the possible protective film. The protective film will deteriorate at faster under the more turbulent conditions. Even if the protective film is not completely eroded away its resistance to corrosion will be weakened and make it easier for oxidizers to diffuse to the metal surface (Veawab & Soosaiprakasham 2008).

Primary and secondary alkanolamines are more corrosive than tertiary alkanolamines. One of the reasons is that they are harder to regenerate. Primary alkanolamines have a higher heat of reaction with  $CO_2$  than secondary alkanolamines which in turn has a higher heat of reaction than tertiary solutions. The higher the heat of reaction the more energy is required to regenerate the alkanolamine solution. MDEA on the other side is easier to regenerate. The  $CO_2$  in the regenerator will come out of solution at a lower temperature than is the case for primary and secondary alkanolamines (Kidnay & Parrish 2006).

Concentration of MEA in solution will have an effect on corrosion rate of carbon steel. Experiments investigating the effect of concentration showed that increasing MEA concentration from 5.0 to 7.0 and 9.0 kmol/m<sup>3</sup> results in the increase of corrosion rate from 0.55 to 0.72 and 1.06 mmpy. This rise in corrosion rate was seen in an environment of 0.55mol/mol CO<sub>2</sub> loading and 10.13 kPa O<sub>2</sub> partial pressure at 80 °C. When the concentration of MEA is increased there will be an increase in available HCO<sub>3</sub><sup>-</sup> in the system. This will lead to a greater rate of iron dissolution and therefore a higher corrosion rate (Vewab & Soosaiprakasham 2008).

SO<sub>2</sub> in the inlet gas will form various HSS (sulfates and thiosulfates) and are reported to have an effect on corrosion. In experiments with MDEA as little as 500 ppm and 1000 ppm of SO<sub>2</sub> added has resulted in 0.5 to 0.58 mm/year corrosion to carbon steel liquid coupons. The SO<sub>2</sub> concentration should therefore be kept to a minimum and breakthrough should be avoided (Rooney et al. 1996).

An interesting observation is that the presence of dissolved oxygen generally lowers the corrosion rate in amine systems compared to those without oxygen. This happens under conditions which are beneficial for protection film growth. The thought is that the oxygen helps strengthen the protective films forming allowing them to become more efficient in preventing corrosion. This could mean that O<sub>2</sub> is needed in the system to achieve a good corrosion control under the right conditions (Veawab & Soosaiprakasham 2008).

### **8.3 The effect of heat stable salts and degradation products**

Heat stable amine salts are called heat stable because they do not regenerate in the regenerator column. Anions like oxalate, formate, thiosulfate and thiocyanate ties up the alkanolamines in the solution and lower the absorption efficiency. The ability to carry CO<sub>2</sub> is thus lowered and the solution viscosity is increased leading to additional operational costs (Haws 2001).

Degradation products are contaminants in the solution that come from the breakdown of the base amine molecule. This breakdown is often irreversible and form totally different chemical species. Examples of degradation products are ethylenediamine derivatives, which can form in the presence of CO<sub>2</sub>, O<sub>2</sub> and COS (Haws 2001).

The effects of HSS and degradation products on corrosion are not fully understood, but the common theory is that they will enhance corrosion in alkanolamine gas treating solutions. Factors that play in are the reduction of pH, chelating, increased conductivity and weaker HHS acids reacting with exposed iron as vapor.

Experiments were done by Rooney et al. 1996 to investigate the effect certain heat stable salts and metals in 50 wt% MDEA have on corrosion. The heat stable salts were oxalate, sulfate, formate, acetate and thiosulfate. The experiments were done with concentrations of 250 ppm, 500 ppm, 1000 ppm, 5000 ppm and 10000 ppm concentrations of the selected HSS. Increasing concentrations and running the experiments at two different temperatures (82°C and 121 °C) allowed them to study the impact of temperature and concentration on the corrosion rate.

The corrosivities of the various anions were seen to increase significantly as the temperature was increased. At 82 °C only oxalic acid which reacts with MDEA to form MDEA oxalate was observed to have a high corrosivity to carbon steel. At 5000 ppm it had a corrosion rate (~1mm/year) which was higher than all the other anions at 10000 ppm. Increasing the temperature to 121 °C resulted in generally much higher corrosion rates for all the anions. Acetic acid, formic acid, oxalix acid and H<sub>2</sub>SO<sub>4</sub> all showed increased corrosivities as the MDEA heat stable salt concentration increased. The sodium salts all had reduced corrosion rates compared to the MDEA heat stable salts (Rooney et al. 1996). Corrosion rates 82°C and 121 °C can be seen Figure 8.1 and Figure 8.2.

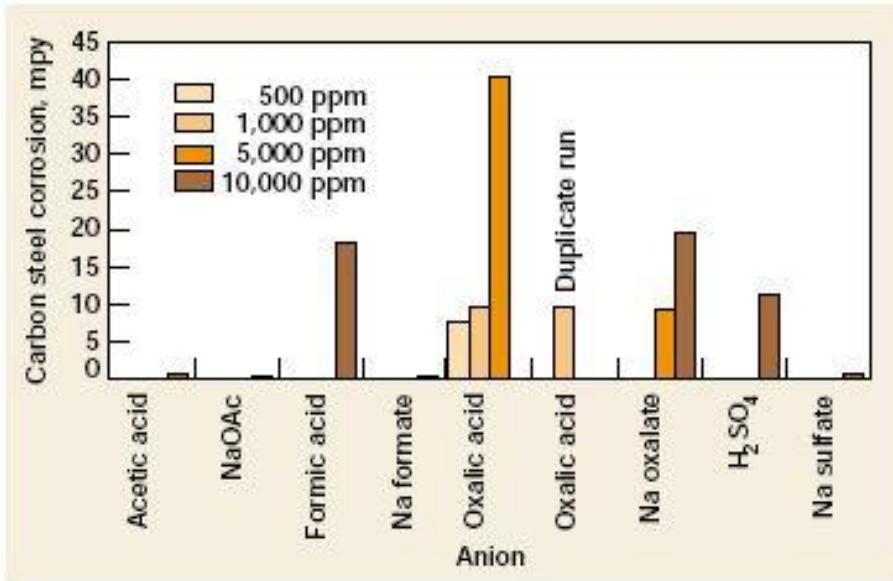


Figure 8-1 Corrosivity of various anions at 82°C to carbon steel (Rooney et al. 1996)

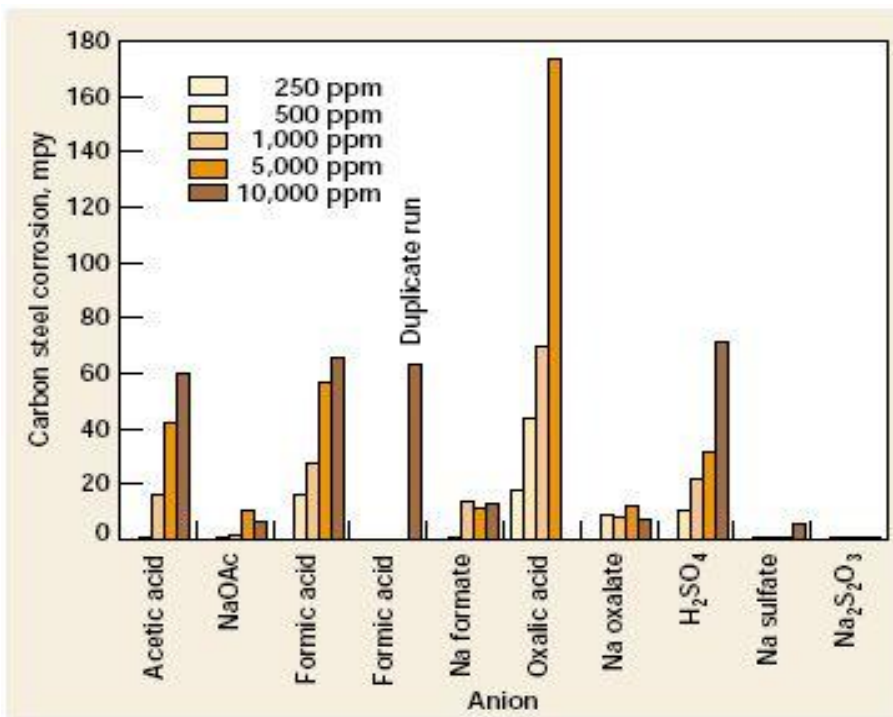


Figure 8-2 Corrosivity of various anions at 121 °C to carbon steel (Rooney et al. 1996)

Conductivity measurements were taken in 50 wt% MDEA solution to determine the effect of added anions on corrosion rate. A reasonable assumption is that a higher conductivity might result in a higher corrosion rate, but the results did not show any correlation between temperature, conductivity and corrosion. Examples of this lack of correlation are: sodium formate which has a higher conductivity than formic acid at 121 °C, but a lower corrosion rate. Sulfuric acid has a lower conductivity than sodium acetate, sodium formate and sodium thiosulfate. The corrosion rate of sulfuric acid is however significantly higher (Rooney et al. 1996).

HSS lowers the alkanolamine solutions pH. In the absorption of CO<sub>2</sub> by an alkanolamine solution an initial drop in pH is seen. This is due to the CO<sub>2</sub> being absorbed. The dip in pH will be followed by a steady decrease in pH caused by the buildup of HSS and degradation products in the solution. Increasing the concentration of HSS in the alkanolamine solution will thus result in an increase in corrosion rate.

In the experiments oxalic acid exhibited corrosion rates that could not only be explained by a lowering of pH or increasing the temperature. It had a much higher corrosion rate than the other anions in the experiments. The explanation for the high corrosion rate is thought to be the oxalic acid's ability to chelate the oxidized metal. The oxidized iron will be bound in a complex with oxalic acid dissolving protective films, which would expose new metal for further corrosion. If the chelating theory is valid several other acids should exhibit higher corrosion rates than predicted by pH alone. Based on equilibrium constants for the complexation of iron (Fe<sup>3+</sup>) and various acids like malonic acid and succinic acid this might very well be the case (Rooney et al. 1996).

Bicine is an amino acid which has been found in a great number of gas treating amine samples. It has been shown that bicine contributes to corrosion in amine systems. A theory that has been suggested is that bicine like oxalic acid forms a complex with iron (Rooney et al. 1996).

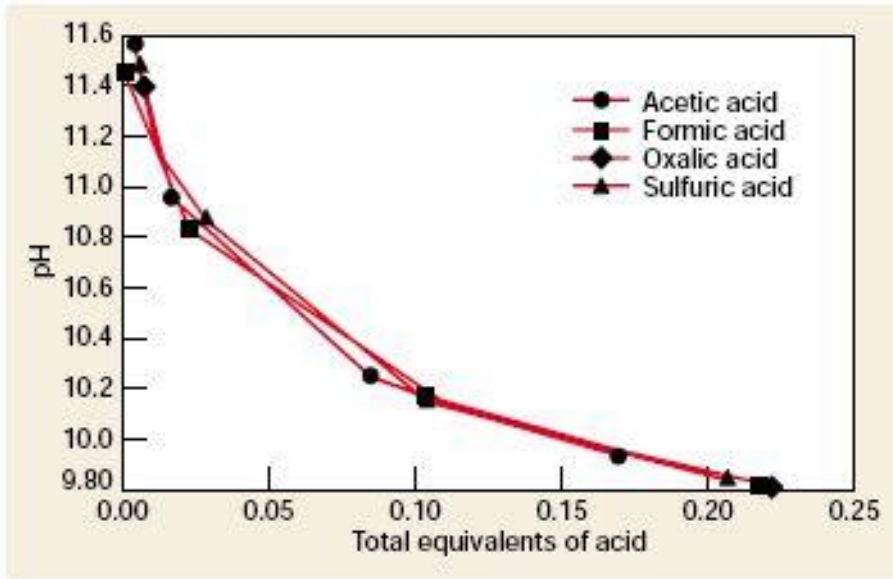


Figure 8-3 pH vs. total acid concentration for 50 wt% MDEA (Rooney et al. 1996)

The experiments performed by Rooney et al. 1996 have resulted in recommended levels for some HSS's. They recommended that the HSS level should not exceed 0.5 % of the total solution. The recommended levels for individual HSS, based on keeping the corrosion to less than 0.25 mm/year, are listed below in Table 8.1 (Rooney et al. 1996).

Table 8-1 Recommended levels of HSS (Rooney et al. 1996)

HSS	Recommended level
Oxalate	250 ppm
Formate, glycolate, malonate, sulfite and sulfate	500 ppm
Acetate	1000 ppm
Thiosulfate	10000 ppm

## 9. Simulation of capture process

A model of the post combustion absorption of CO<sub>2</sub> was created in Aspen Hysys to simulate the capture process. The effect of changing four parameters was investigated. The parameters where: amine concentration, amine flow rate, amine temperature and flue gas temperature. The capture process was in no way optimized in regards to energy consumption or CO<sub>2</sub> recovered.

### 9.1 Process flow sheet

A flow sheet was constructed describing a capture process. It illustrates the process from hot flue gas entering a direct contact cooler (DCC) to recovered CO<sub>2</sub> ready for compression. The flow sheet is shown in Figure 9.1.

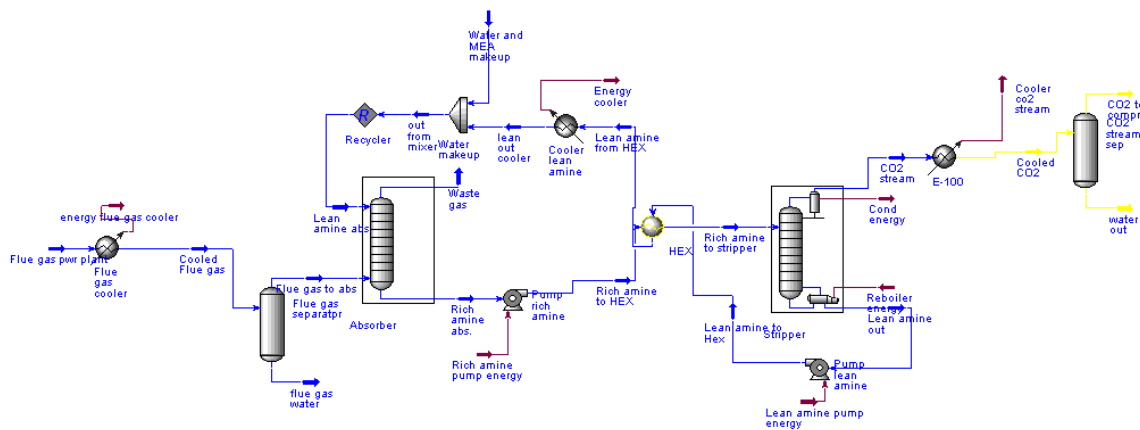


Figure 9-1 Flow sheet of a capture process

A flue gas enters the capture process at an elevated temperature. It passes through a cooler and a water separator before entering a contact column. The flue gas enters the contact column at the bottom and flows counter current with a lean amine solution entering the column at the top. Treated flue gas stream leaves the column at the top while the rich amine solution leaves from the bottom. The rich amine solution flows through a heat exchanger where it is preheated by a lean amine solution from a stripper column. The preheated rich amine solution then enters at the top of a stripper column.

Two streams leave the stripper column. From the top regenerated CO<sub>2</sub> flows through a condenser before it is cooled and condensed water removed by a separator. The lean amine solution leaves at the bottom of the stripper column through a reboiler. It passes through the

heat exchanger where it is cooled by the rich amine solution. After leaving the heat exchanger the lean amine solution passes through an additional cooler before it closes the circuit by once more entering the contact column. Makeup water is introduced through a mixer situated after the cooler to replace water lost in the contact and stripper columns.

Two pumps are used in the model. They provide the energy to overcome the pressure loss in the columns and the heat exchanger. The rich amine solution pump is also necessary to achieve the pressure at the top of the regeneration column.

## 9.2 Compositions and parameters

Compositions of flue gas and amine solution were kept simple. The flue gas from the power plant contained CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and O<sub>2</sub>. The amine solution used for capturing the CO<sub>2</sub> was made up of 20 wt% MEA and H<sub>2</sub>O. Even though the composition of the flue gas was simplified it was similar to real conditions. It entered the capture process at a 100 °C and slightly above atmospheric pressure (108.3 kPa) with a mass rate of 5000 kg/h. The flue gas parameters and composition can be seen in table 9.1 and the MEA solution parameters and composition in Table 9.2.

Table 9-1 Flue gas parameters and composition

Mass flow rate (kg/h)	5000
Pressure (kPa)	118.3
Temperature (°C) <sub>from pwr plant</sub>	100
Temperature (°C) <sub>into absorber</sub>	40
<b>Composition</b>	<b>Mass fraction</b>
Nitrogen	0.70
Carbon dioxide	0.04
Water	0.10
Oxygen	0.16

Table 9-2 MEA solution parameters and composition

<b>MEA solution flow rate and composition</b>	
Mass flow rate (kg/h)	4000
Temperature (°C)	35
Pressure (kPa)	107.3
<b>Composition</b>	<b>Mass fraction</b>
Water	0.8
MEA	0.2

The contact column was modeled as a packed column. It consisted of 10 steps. The pressure loss in the column was set to 5 kPa with the treated flue gas leaving at atmospheric pressure from the top. No water wash was connected to the top of the contact column to catch the entrained amine in the treated flue gas.

A counter current heat exchanger was selected. The lean amine solution from the stripper column was set to preheat the rich amine solution to 80 °C. The pressure loss on the rich amine side was set to 0.5 bar while no pressure loss was used for the lean amine solution side.

A stripper column was modeled as a packed column. It consisted of 15 steps. A condenser was connected to the top and a reboiler at the bottom. The pressure loss was set to 10 kPa for the stripper column and the condenser while the re-boiler had a pressure loss of 5 kPa. The temperature of the condenser was set to 82 °C with full reflux. The reboiler duty was 1,000,000 kJ/h. This resulted in the lean amine solution leaving the reboiler at an approximate temperature of 117 °C.

The system did not contain a water wash step at the top of the absorption column. Because of this some MEA was lost in the process due to evaporation. The makeup stream of water into the mixer compensated for the water loss. The loss of MEA was deemed acceptable for the purpose of this simulation.

Three coolers were used in the process. The purpose of the first cooler was to cool down the flue gas from the natural gas power plant to an acceptable temperature for the contact column. The second cooler was used to cool the lean amine solution. The purpose of the third cooler was to cool the CO<sub>2</sub> leaving the stripper column. The CO<sub>2</sub> left at an elevated temperature and had to be cooled before entering the compressor train.

### 9.3 Variables investigated

Four variables were selected and their effect on the capture process investigated. The variables selected were: amine concentration, amine flow rate, amine temperature and flue gas temperature. The amine concentration was set to 15, 20 and 30 wt%. The amine flow rate was varied between 3750, 4000 and 4250 kg/h. The amine temperature was varied between 25, 35, 40 and 50 °. The flue gas temperature was 30, 40 and 50 °C.

In a first simulation of the flow sheet the aim was to recover approximately 85% of the CO<sub>2</sub> in the flue gas. Of the captured CO<sub>2</sub> approximately 55 % was to be regenerated in the stripper column. This was achieved with typical capture process parameters described above. The flue gas temperature was 40 °C, amine solution temperature 35 °C, amine concentration 20 wt% and a circulation rate of 4000 kg/h.

Eight indicators were used to investigate the effect of the variables. The indicators were: % CO<sub>2</sub> recovered and MEA lost in the contact column, lean solution loading, mass fraction of O<sub>2</sub> and N<sub>2</sub> in the rich amine solution, % CO<sub>2</sub> recovered in the stripper column and the composition of the CO<sub>2</sub> stream leaving the capture process.

#### 9.3.1 Amine concentration

The effect of increased amine concentration was an increase in CO<sub>2</sub> captured in the contact column. The recovery rate went from 75 % for 15 wt% MEA to 90 % for 30 wt% MEA. As there was more MEA to react with CO<sub>2</sub> in solution when the concentration was increased a higher percentage of CO<sub>2</sub> was recovered. As a result of the increase in concentration more MEA was lost with the treated flue gas. The losses increased from 0.18 % to 0.23 %.

The percentage of CO<sub>2</sub> regenerated decreased as the MEA concentration increases. The reason for this was that the amount of CO<sub>2</sub> recovered increased while the re-boiler duty remained the same. More heat energy was needed to regenerate the additional CO<sub>2</sub> in the amine solution.

The concentration of N<sub>2</sub> and O<sub>2</sub> decreased slightly as the concentration of MEA increased. If the solubility of N<sub>2</sub> or O<sub>2</sub> was affected in a negative way by the MEA concentration was hard to say as the changes were small. It could however be a contributing factor.

Small changes were seen in the CO<sub>2</sub> stream composition. The mass fraction of O<sub>2</sub> and N<sub>2</sub> decreased as a result of less being transported from the contact column to the stripper as the

amine concentration was increased. Water and CO<sub>2</sub> fractions remained the same while slightly more MEA was entrained with the stream. This was caused by the increased amine concentration. All the results of changing the amine concentration can be seen in Table 9.3.

Table 9-3 Effect of amine concentration

	15 wt%	20 wt%	30 wt%
CO <sub>2</sub> recovered (%)	75.17	84.86	90.16
MEA lost (%)	0.18	0.20	0.23
Lean solution loading (mol CO <sub>2</sub> /mol MEA)	0.1747	0.1944	0.2097
O <sub>2</sub> in amine rich solvent (mass fraction)	$4.39 \cdot 10^{-6}$	$4.10 \cdot 10^{-6}$	$3.78 \cdot 10^{-6}$
N <sub>2</sub> in amine rich solvent (mass fraction)	$1.01 \cdot 10^{-5}$	$9.46 \cdot 10^{-6}$	$8.74 \cdot 10^{-6}$
CO <sub>2</sub> regenerated (%)	63.6	58.34	51.41
<b>Composition CO<sub>2</sub> stream</b>	Mass fraction		
Nitrogen	$3.08 \cdot 10^{-4}$	$2.71 \cdot 10^{-4}$	$2.13 \cdot 10^{-4}$
Water	$2.09 \cdot 10^{-2}$	$2.09 \cdot 10^{-2}$	$2.09 \cdot 10^{-2}$
Carbon dioxide	0.9786	0.9787	0.9788
Oxygen	$1.33 \cdot 10^{-4}$	$1.19 \cdot 10^{-4}$	$9.22 \cdot 10^{-5}$
MEA	$4.17 \cdot 10^{-8}$	$8.03 \cdot 10^{-8}$	$1.42 \cdot 10^{-7}$

### 9.3.2 Amine flow rate

The effect of increased flow rate was increased recovery of CO<sub>2</sub>. There was a small but noticeable increase as the flow rate increased. The reason for this was that more amine was able to come in contact with the flue gas and react. The loss of MEA decreased slightly as the circulation rate increased. This might be a result of the shorter time the MEA solution spent in the contact column. The concentration of N<sub>2</sub> and O<sub>2</sub> solved in the rich amine stream was unchanged. An insignificant change could be seen as the flow rate was increased.

The percentage of CO<sub>2</sub> regenerated in the stripper decreased. This was due to that more energy was required to heat the amine solution at the higher flow rates. The lean amine solution load increased with higher flow rates. Reason for this was that the reboiler duty was not increased. As the flow rate increased more heat was needed to regenerate the additional CO<sub>2</sub> in the stream.

There were only slight changes in the composition of the CO<sub>2</sub> stream leaving the capture process. The concentration of N<sub>2</sub> and O<sub>2</sub> did not change significantly. The amount of water in the stream remained the same as the temperature and pressure conditions did not change. The concentration of CO<sub>2</sub> remained steady at 97.8 %. The trace of MEA in the stream increased

slightly as the flow rate went up. This could be the result of the increased amount of MEA solution that passes through the stripper column. All the results of changing the amine flow rate can be seen in Table 9.4.

Table 9-4 Effect of amine flow rate

	<b>3750 kg/h</b>	<b>4000 kg/h</b>	<b>4250 kg/h</b>
CO <sub>2</sub> recovered (%)	83.37	84.86	85.92
MEA lost (%)	0.22	0.20	0.19
Lean solvent loading (mol CO <sub>2</sub> /mol MEA)	0.1860	0.1944	0.2037
O <sub>2</sub> in amine rich solvent (mass fraction)	$4.11 \cdot 10^{-6}$	$4.10 \cdot 10^{-6}$	$4.09 \cdot 10^{-6}$
N <sub>2</sub> in amine rich solvent (mass fraction)	$9.48 \cdot 10^{-6}$	$9.46 \cdot 10^{-6}$	$9.45 \cdot 10^{-6}$
CO <sub>2</sub> regenerated (%)	60.18	58.34	55.80
<b>Composition CO<sub>2</sub> stream</b>	<b>Mass fraction</b>		
Nitrogen	$2.37 \cdot 10^{-4}$	$2.71 \cdot 10^{-4}$	$2.59 \cdot 10^{-4}$
Water	$2.09 \cdot 10^{-2}$	$2.09 \cdot 10^{-2}$	$2.09 \cdot 10^{-2}$
Carbon dioxide	0.9787	0.9787	0.9787
Oxygen	$1.03 \cdot 10^{-4}$	$1.19 \cdot 10^{-4}$	$1.12 \cdot 10^{-4}$
MEA	$6.20 \cdot 10^{-8}$	$8.03 \cdot 10^{-8}$	$1.50 \cdot 10^{-7}$

### 9.3.3 Amine temperature

The change in amine temperature yielded small changes in CO<sub>2</sub> recovered and MEA lost in the contact column. For temperatures 25, 35 and 40 °C the recovery of CO<sub>2</sub> remained close to 85 %. At 50 °C a small decrease to 82.5 % was observed. The MEA lost increased with temperature from 0.14 % at 25 °C to 0.3 % at 30 °C. This was due to an increase in evaporation of the amine solution. The concentrations of N<sub>2</sub> and O<sub>2</sub> in the rich solution stream only changed significantly when the temperature is raised to 50 °C. This was most likely due to that gas solubility is a function of temperature and will decrease as the temperature increases.

Changing the amine temperature had little impact on the percentage of CO<sub>2</sub> regenerated in the stripper column. There was no significant change in CO<sub>2</sub> recovered in the rich solution stream and as the re-boiler duty was kept constant the percentage of CO<sub>2</sub> regenerated would also remain approximately the same. As a result no real change in the lean solution loading was observed.

There was little change in the composition of the CO<sub>2</sub> stream leaving the capture process. The mass fraction of H<sub>2</sub>O and CO<sub>2</sub> remained constant. The mass fraction of N<sub>2</sub> and O<sub>2</sub> indicated no real trend of either increasing or decreasing due to the temperature change. The trace of MEA decreased. All the results from varying the amine temperature are collected in Table 9.5

Table 9-5 Effect amine temperature

	25 °C	35 °C	40 °C	50 °C
CO <sub>2</sub> recovered (%)	84.74	84.86	85.01	82.49
MEA lost (%)	0.14	0.20	0.24	0.30
Lean solution loading (mol CO <sub>2</sub> /mol MEA)	0.1954	0.1944	0.1926	0.1906
O <sub>2</sub> in rich solution (mass fraction)	4.11·10 <sup>-6</sup>	4.10·10 <sup>-6</sup>	4.09·10 <sup>-6</sup>	2.81·10 <sup>-6</sup>
N <sub>2</sub> in rich solution (mass fraction)	9.48·10 <sup>-6</sup>	9.46·10 <sup>-6</sup>	9.45·10 <sup>-6</sup>	7.41·10 <sup>-6</sup>
CO <sub>2</sub> regenerated (%)	57.76	58.34	58.14	58.09
<b>Composition CO<sub>2</sub> stream</b>	Mass fraction			
Nitrogen	2.52·10 <sup>-4</sup>	2.71·10 <sup>-4</sup>	2.45·10 <sup>-4</sup>	2.53·10 <sup>-4</sup>
Water	2.09·10 <sup>-2</sup>	2.09·10 <sup>-2</sup>	2.09·10 <sup>-2</sup>	2.09·10 <sup>-2</sup>
Carbon dioxide	0.9787	0.9787	0.9787	0.9787
Oxygen	1.09·10 <sup>-4</sup>	1.19·10 <sup>-4</sup>	1.06·10 <sup>-4</sup>	1.10·10 <sup>-4</sup>
MEA	8.60·10 <sup>-8</sup>	8.03·10 <sup>-8</sup>	7.87·10 <sup>-8</sup>	6.44·10 <sup>-8</sup>

#### 9.3.4 Flue gas temperature

Increasing the flue gas temperature resulted in a lower percentage of CO<sub>2</sub> recovered. No real change was seen for 30 and 40 °C, but at 50 °C there was a significant decrease in CO<sub>2</sub> recovered. More MEA was lost as the temperature increased due to more of the solution being evaporated and entrained with the treated flue gas. The concentration of O<sub>2</sub> and N<sub>2</sub> decreased as the flue gas temperature increased.

The percentage of CO<sub>2</sub> regenerated in the stripper column remained fairly constant. As no real change in captured CO<sub>2</sub> was seen in the contact column and the re-boiler duty was kept constant this was to be expected. The slightly lower lean solution loading at 50 °C was a consequence of less CO<sub>2</sub> recovered in the contact part of the process.

The composition of the CO<sub>2</sub> stream leaving the capture process displayed small changes as the flue gas temperature was increased. The mass fraction of O<sub>2</sub> and N<sub>2</sub> reflected the decrease in concentration of these components in the amine solution from the contact column. The mass fraction of H<sub>2</sub>O and CO<sub>2</sub> mass fractions remained constant. Slightly less MEA was entrained with the CO<sub>2</sub> stream. All the results from varying the flue gas temperature can be seen Table 9.6.

Table 9-6 Effect of Flue gas temperature

	30 °C	40 °C	50 °C
CO <sub>2</sub> recovered (%)	85.48	84.86	79.06
MEA lost (%)	0.15	0.20	0.30
Lean solvent loading (mol CO <sub>2</sub> /mol MEA)	0.1938	0.1944	0.1875
O <sub>2</sub> in rich solvent (mass fraction)	$4.67 \cdot 10^{-6}$	$4.10 \cdot 10^{-6}$	$3.69 \cdot 10^{-6}$
N <sub>2</sub> in rich solvent (mass fraction)	$1.06 \cdot 10^{-5}$	$9.46 \cdot 10^{-6}$	$8.63 \cdot 10^{-6}$
CO <sub>2</sub> regenerated (%)	58.34	58.34	58.55
<b>Composition CO<sub>2</sub> stream</b>	<b>Mass fraction</b>		
Nitrogen	$2.71 \cdot 10^{-4}$	$2.71 \cdot 10^{-4}$	$2.54 \cdot 10^{-4}$
Water	$2.09 \cdot 10^{-2}$	$2.09 \cdot 10^{-2}$	$2.09 \cdot 10^{-2}$
Carbon dioxide	0.9787	0.9787	0.9787
Oxygen	$1.19 \cdot 10^{-4}$	$1.19 \cdot 10^{-4}$	$1.08 \cdot 10^{-4}$
MEA	$8.03 \cdot 10^{-8}$	$8.03 \cdot 10^{-8}$	$5.89 \cdot 10^{-8}$

#### **9.4 Other considerations**

The capture process was simplified. Heat losses and some pressure losses were neglected. The real process would contain more equipment pipes and valves which would also have heat losses and pressure losses. The amine package used for the amine absorption process puts restrictions on the compounds used. A simple system was therefore used to visualize effects of changing the chosen factors. Although the system was simple it could give a good indication of the effects the chosen parameters had on the capture process.

Aspen Hysys can be used to simulate a MEA based CO<sub>2</sub> removal process. The thermodynamic properties are calculated with Peng Robinson and Amines property package models which are available in the program. Aspen Hysys have been used for simulation of gas sweetening, dehydration by TEG and CO<sub>2</sub> capture from flue gas. As the removal processes have high energy consumption much focus has been on investigating ways to reduce this cost. It should however be of interest to investigate closer the effect of impurities on the capture process as this has an impact on the operational cost for a capture plant.

There is no option to model the irreversible side reactions that take place between the amine solution and flue gas in Aspen Hysys. As a result the percentage of recovered CO<sub>2</sub> will be higher than can be expected compared to a real capture facility. There will be no loss of amine solution due to the irreversible reactions.

## 10. Properties of pure CO<sub>2</sub>

The properties of CO<sub>2</sub> are known and have been the subject of many studies. In this section some of the important properties of CO<sub>2</sub> will be presented. The properties of pure CO<sub>2</sub> and the impact of impurities along with water and oxygen solubility will be discussed.

### 10.1 Pure CO<sub>2</sub>

The critical point of CO<sub>2</sub> is at 30.98 °C and 73.77 bar. The critical point is connected with the triple point by the saturation line. Below the saturation line the CO<sub>2</sub> will be in vapor phase and above in liquid phase. Above the critical point the pure CO<sub>2</sub> will not be able to separate into two phases. The exception would be at very low temperatures or very high pressures as can be seen in the phase diagram in Figure 10.1.

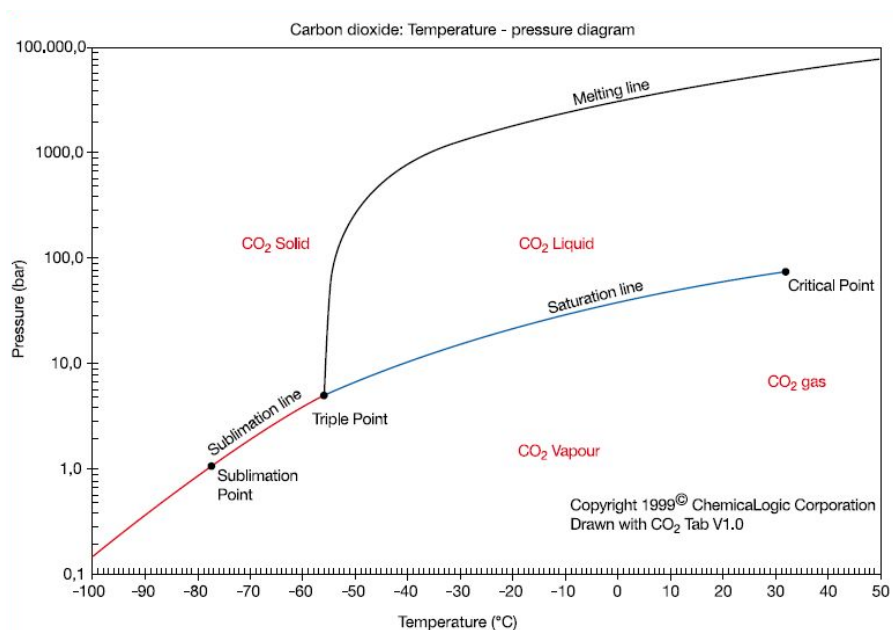


Figure 10-1 Phase diagram of CO<sub>2</sub> (Oosterkamp & Ramsen 2008)

Important to note is that pure CO<sub>2</sub> has a triple point at -56.6 °C and 5.18 bar. Below this at lower pressures and temperatures the sublimation line can be observed. No liquid will be formed in this area as the solid CO<sub>2</sub> will sublime to CO<sub>2</sub> vapor. This occurs if the pressure is decreased at constant temperature or the temperature increased at constant pressure.

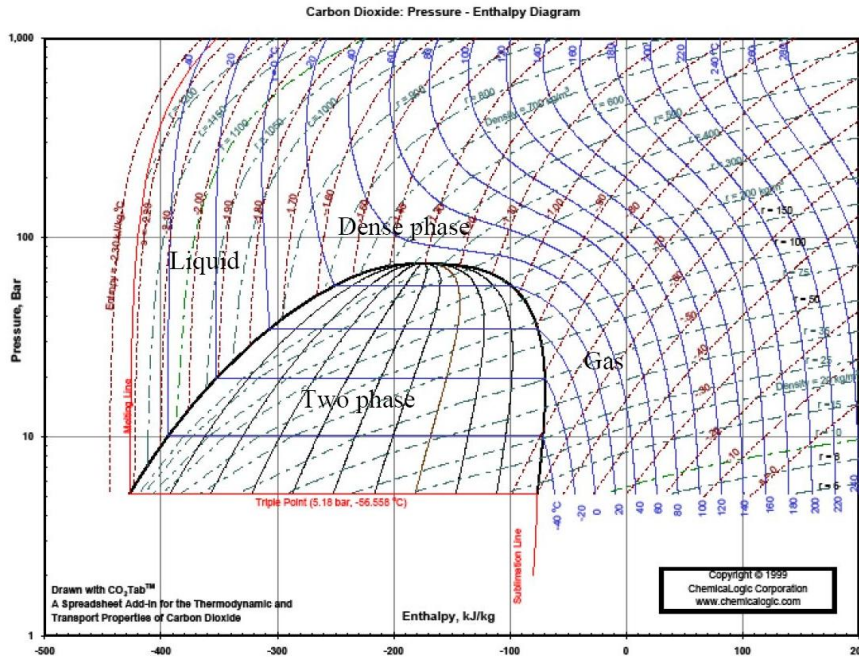


Figure 10-2 CO<sub>2</sub> Pressure-enthalpy diagram (Oosterkamp & Ramsen 2008)

The pressure-enthalpy diagram seen in Figure 10.2 can be used to track the thermodynamic path of compression and pumping. From the diagram it can be seen that less energy is needed to raise the pressure of the CO<sub>2</sub> in the dense/ liquid region compared to compression in the gas region. The isentropic lines are steeper in the dense/liquid region.

The change in temperature can be approximated for a pressure loss in the pipeline with the help of the diagram. In the liquid region the isotherms are close to vertical at low temperatures. A pressure loss would therefore result in a minimal change in temperature.

With the help of HYSYS the density and viscosity of pure CO<sub>2</sub> are presented as a function of temperature and pressure. In figure 10.3 the density of pure CO<sub>2</sub> is shown as a function of temperature and pressure.

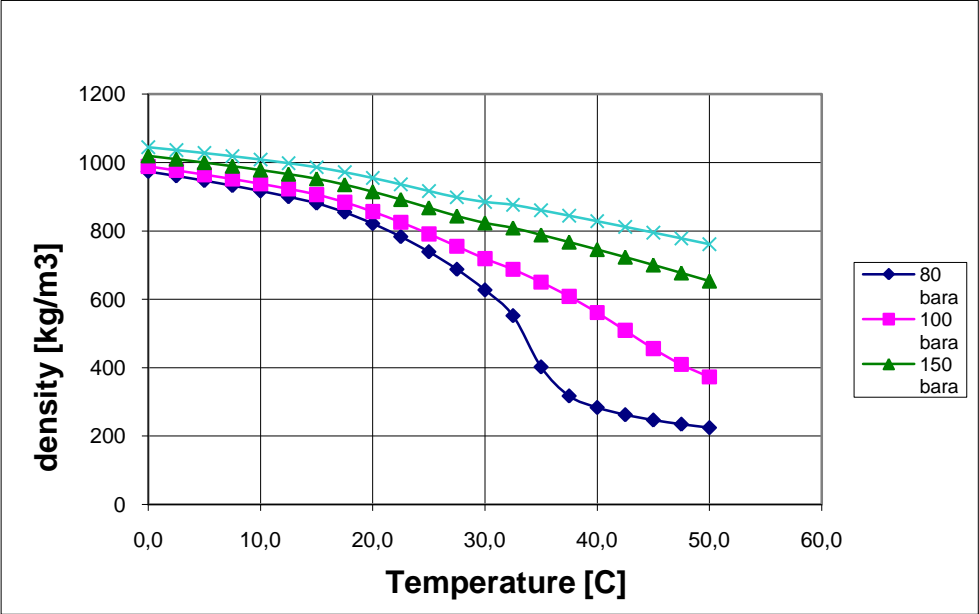


Figure 10-3 CO<sub>2</sub> density as a function of temperature and pressure

From the diagram some interesting observations can be made. The density of pure CO<sub>2</sub> has a stronger dependency on temperature compared pressure at lower temperatures. Around the critical point the density is very sensitive to small changes in temperature. The density is important when calculating the flow in the pipeline. Knowledge of the inlet temperature, ambient temperature and heat transfer is needed to achieve a correct model of the flow. The sudden change in CO<sub>2</sub> density is due to the phase change from gas phase to liquid phase.

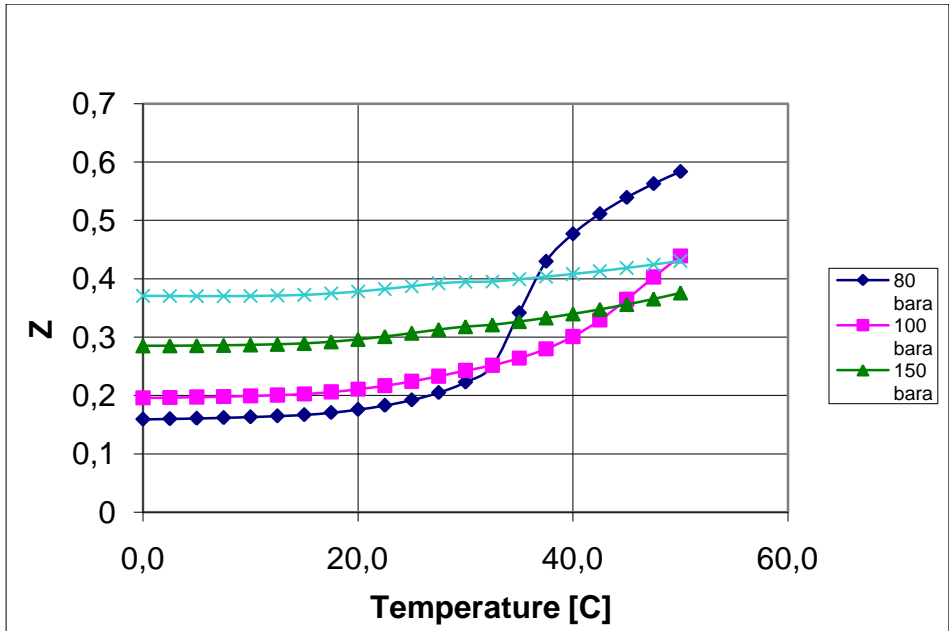


Figure 10-4 CO<sub>2</sub> Z-factor as a function of temperature and pressure

The compressibility factor at different pressures and temperatures is shown in Figure 10.4. It can clearly be seen that the ideal gas assumption does not apply to CO<sub>2</sub>. The compressibility factor is used to account for the non ideal behavior of real gas in the ideal gas equation. For an ideal gas the compressibility factor would be one independent of temperature and pressure (Oosterkamp & Ramsen 2008).

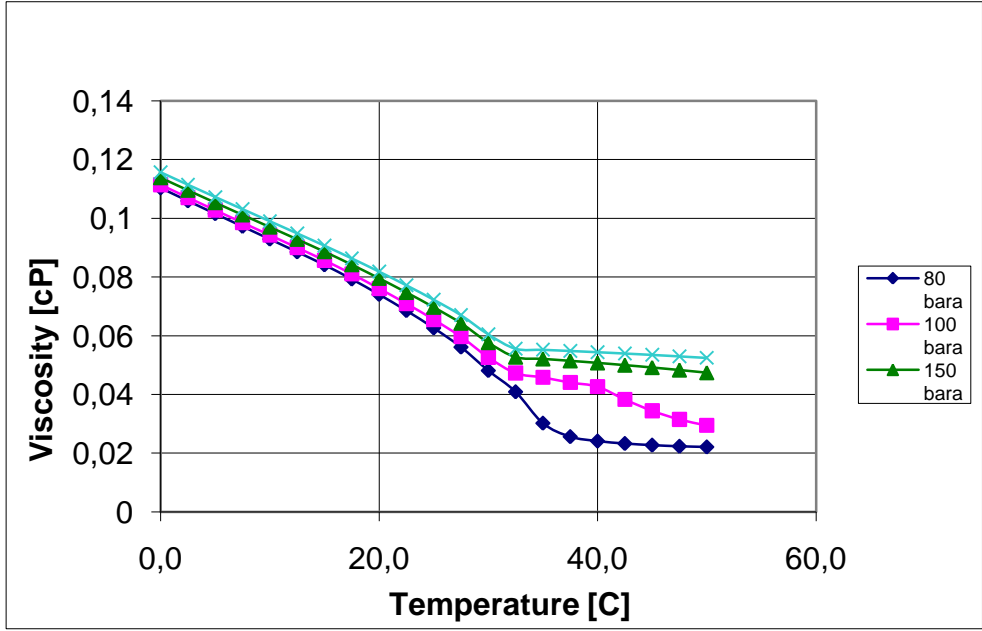


Figure 10-5 CO<sub>2</sub> viscosity as a function of temperature and pressure

It can be observed that the viscosity show a strong temperature dependency in Figure 10.5. This is especially the case close to the critical point.

## 10.2 Effect of impurities

The effect of impurities on density and viscosity are seen in Figure 10.6 and 10.7. The figures have been made by using the Hysys program. The composition used to make the diagrams is 98 mole% CO<sub>2</sub> and 2 mole% of the other component. It is important to note that the two diagrams in this section are purely for illustrational purposes and that they have not been checked against any experimental data.

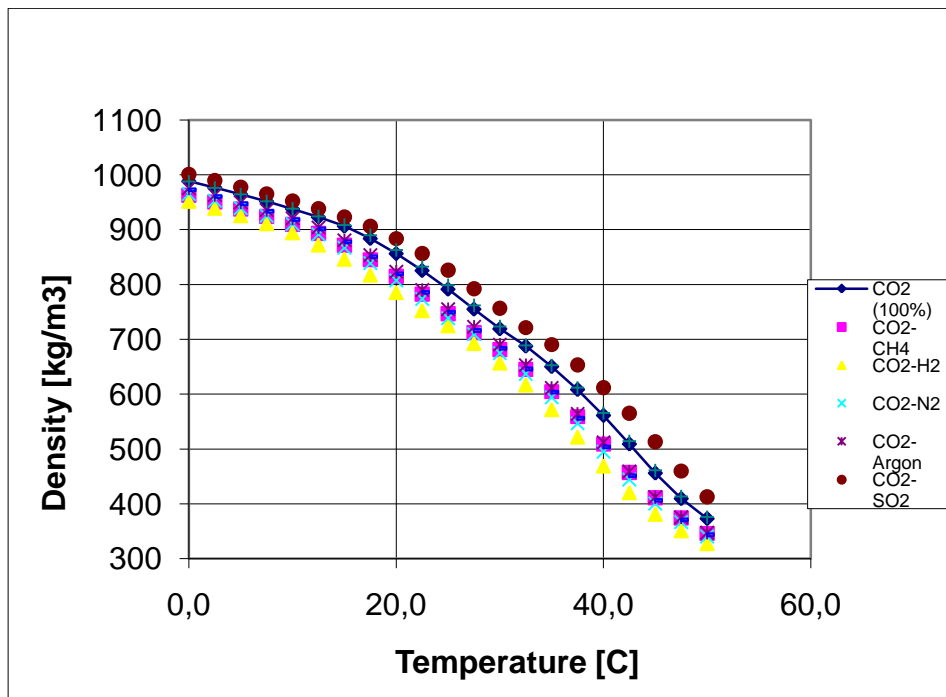


Figure 10-6 CO<sub>2</sub> density at 100 bar with changing temperature for CO<sub>2</sub> with 2 mole% of another component

The effect on CO<sub>2</sub> density when impurities are present can be seen in figure 10.6. From the diagram can be seen that only SO<sub>2</sub> will increase the density of the mixture compared to pure CO<sub>2</sub>. It can also be seen that H<sub>2</sub>S will have a minimal effect on density while H<sub>2</sub> will have significant effect.

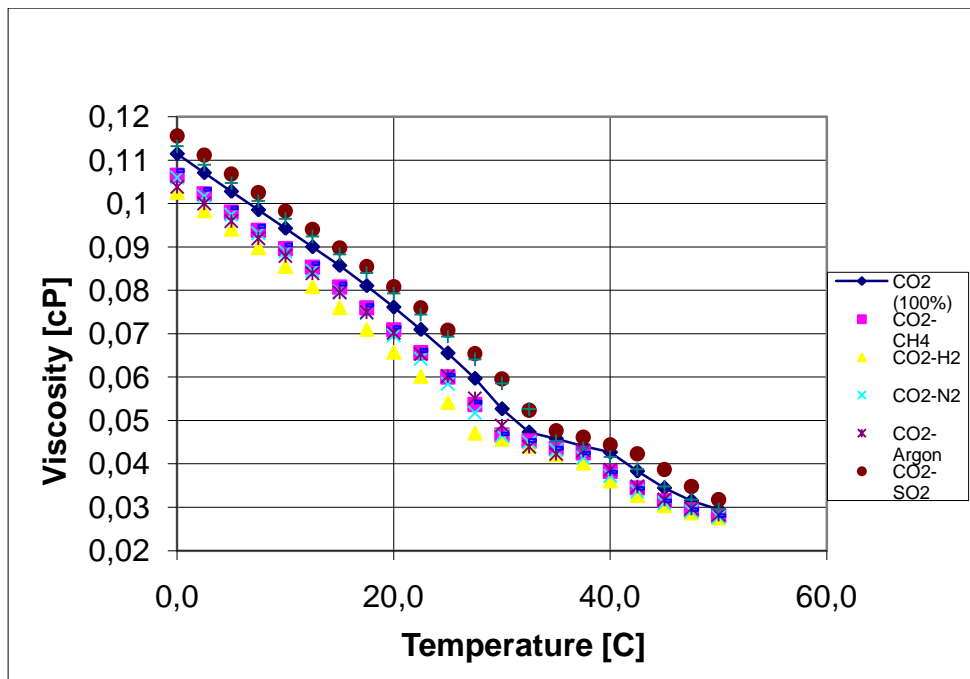


Figure 10-7 CO<sub>2</sub> viscosity at 100 bar with changing temperature for CO<sub>2</sub> with 2 mole% of the selected components

It can be seen in Figure 10.7 that H<sub>2</sub>S will have little impact on viscosity while SO<sub>2</sub> will increase viscosity slightly. All other impurities in the figure will lead to a decrease in viscosity. This indicates that impurities typically will reduce the viscosity of a dense CO<sub>2</sub> phase (Oosterkamp & Ramsen 2008).

### 10.3 Solubility of water in CO<sub>2</sub>

The solubility of water in CO<sub>2</sub> depends on temperature and pressure. The solubility will decrease as the pressure increase in the CO<sub>2</sub> gas phase until it reaches a minimum. At the minimum a phase change of CO<sub>2</sub> occurs. At the phase change the solubility of water in CO<sub>2</sub> will increase substantially. Additional pressure increase will result in an increase in solubility of water at constant temperature. This differs from supercritical natural gas where the solubility of water will decrease as the pressure increase. Important to note for possible dehydration of the CO<sub>2</sub> stream is that the minima point of the solubility curve would be the best operational point for “knocking out” water. Keeping the pressure constant and increasing the temperature will have the same effect. The water solubility in the liquid CO<sub>2</sub> will increase as shown in Figure 10.8.

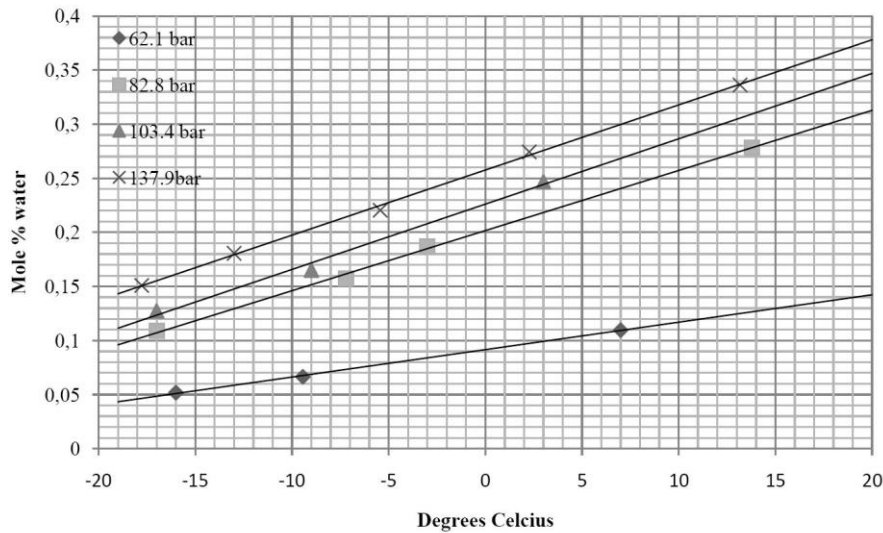


Figure 10-8 Maximum water solubility in CO<sub>2</sub> (Austegard et al. 2006)

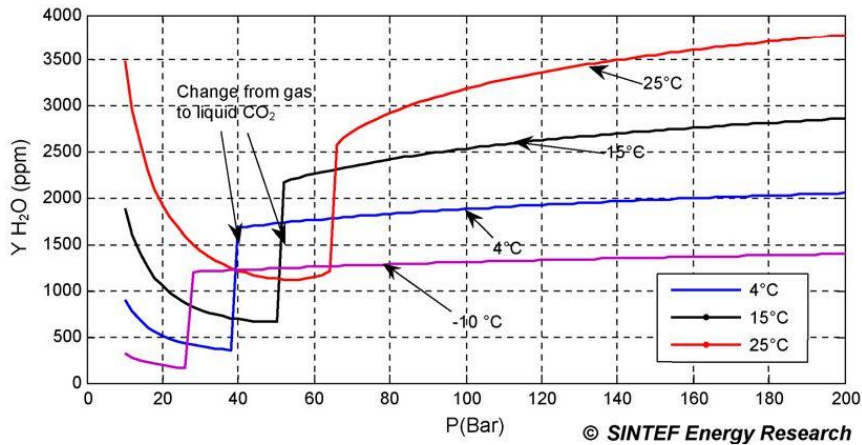


Figure 10-9 Water solubility in CO<sub>2</sub> (de Visser et al. 2008)

The water solubility dependence on temperature and pressure can be seen in Figure 10.9. It can be seen that a higher temperature leads to a higher solubility. The water solubility in gaseous CO<sub>2</sub> will decrease as the temperature is increased for a constant temperature. At the phase change between gaseous and dense CO<sub>2</sub> there is a sudden increase in water solubility which will increase slowly as the pressure continues to increase. The water solubility in dense CO<sub>2</sub> shows a weaker dependence on pressure.

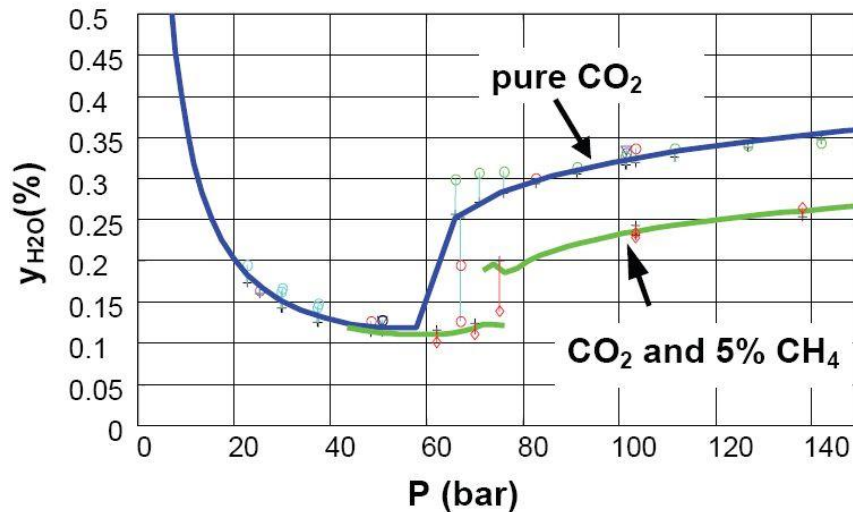


Figure 10-10 Water solubility in pure CO<sub>2</sub> and with 5% CH<sub>4</sub> (Austergard et al. 2006)

By adding 5 mole% CH<sub>4</sub> the solubility of water in CO<sub>2</sub> is lowered as can be seen in Figure 10.10. The implication of lowered water solubility in dense phase CO<sub>2</sub> can have serious consequences in pipeline transport. Water can condense out of the dense phase at an earlier time than anticipated creating two phase flow. As free water would be present in the pipeline corrosion would become a problem. The effect of other impurities on the solubility of water in dense CO<sub>2</sub> has not been found. Looking at the effect of CH<sub>4</sub> on the solubility suggests that it would be valuable to test the effect of other compounds.

#### 10.4 Hydrates

The formation of hydrate requires certain conditions. There need to be the right combination of temperature and pressure (low temperature and high pressure). Hydrate forming molecules need to be present together with a suitable amount of water. Some of the impurities that can be present in CO<sub>2</sub> that can form hydrates are CH<sub>4</sub>, N<sub>2</sub>, Ar and H<sub>2</sub>S.

The hydrate formation kinetics supercritical CO<sub>2</sub> streams are not as well known as for natural gas. Experiences in transportation of CO<sub>2</sub> at high pressures have shown that CO<sub>2</sub> hydrates can form up to temperatures of 10 °C (de Visser et al. 2008).

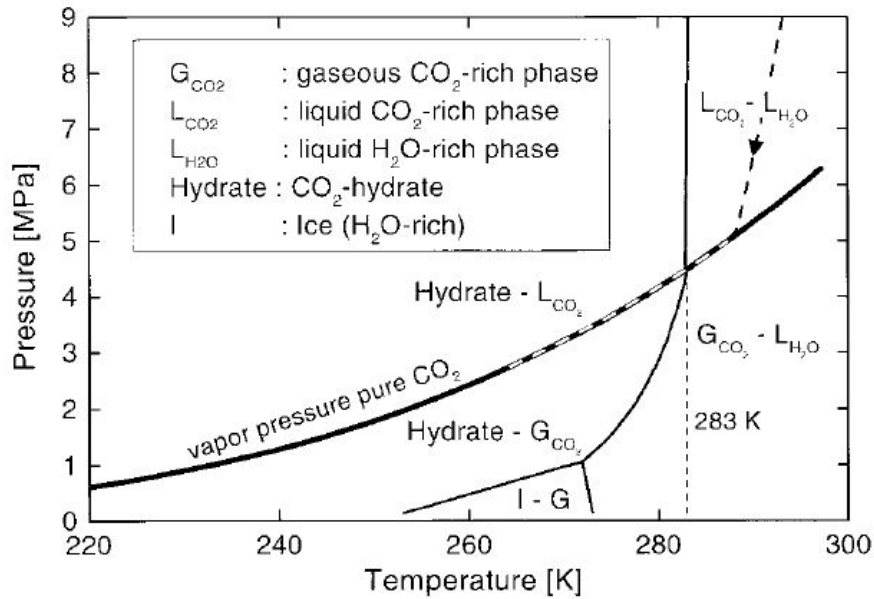


Figure 10-11 Phase equilibrium diagram for CO<sub>2</sub>/H<sub>2</sub>O (Fredenhagen & Eggers 2001)

The conditions when hydrates might form can be seen in Figure 10.11. Figure 10.11 is a phase equilibrium diagram for CO<sub>2</sub>/H<sub>2</sub>O. The phase diagram shows that hydrates will be stable below 283 K for the conditions in offshore CO<sub>2</sub> pipelines. It is important to notice that the experimental work behind this figure is based upon mixes of CO<sub>2</sub> saturated with water. The presence of free water will have an enhancing effect on the formation of hydrates.

Avoiding hydrates is important. Hydrates can build on pipeline walls. In serious cases hydrates can block the entire bore of the pipeline. It can form plugs in the pipeline potentially blocking valves and/or foul up instrumentation. During a depressurization hydrate plugs can cause structural damage to the pipeline (Oosterkamp & Ramsen 2008).

### 10.5 Oxygen solubility

Few studies have been done on the solubility of oxygen in alkanolamine/ water solutions. The most studied system is oxygen solubility in water at atmospheric pressure. It is important to get good data on the oxygen solubility in order to better predict the effect oxygen has on the degradation of alkanolamines in the CO<sub>2</sub> capture process.

Dissolved oxygen at 101.325 kPa and 20.95% oxygen in water and various generic alkanolamine solutions are presented in Figure 10.12. It can be seen that the solubility of oxygen in the various alkanolamine solution are very similar to that of oxygen in water. The

only divergence is DEA where the O<sub>2</sub> solubility decrease is more pronounced from around 55-80 °C than is the case for water and the other alkanolamines (Rooney & Daniels 1998).

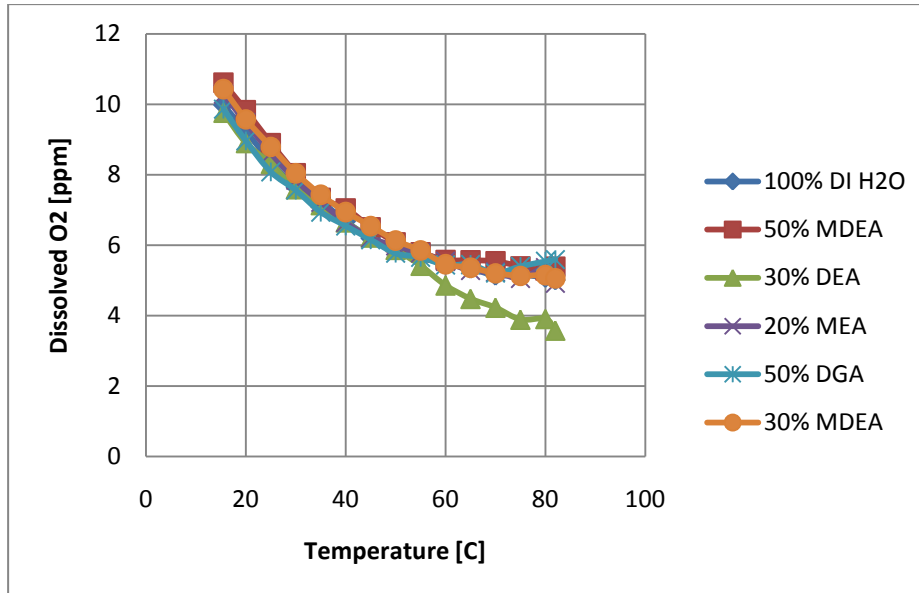


Figure 10-12 Comparison of ppm dissolved oxygen at 101.325 kPa and 20.95 % oxygen for water vs various alkanolamine/water mixtures (Rooney & Daniels 1998)

The solubility of oxygen in water decreases with temperature until it reaches a minimum at around 100 °C as can be seen in Figure 10.13 at the different pressures. The solubility of oxygen in alkanolamine solution will therefore decrease in the contact column with increasing temperature. Beyond this temperature oxygen solubility will increase again. This can have implications for the stripping step of the capture process. Here the temperature is well above 100 °C. An increase in oxygen solubility in this step can have effects on the rate of degradation of alkanolamines making predictions very hard (Rooney & Daniels 1998).

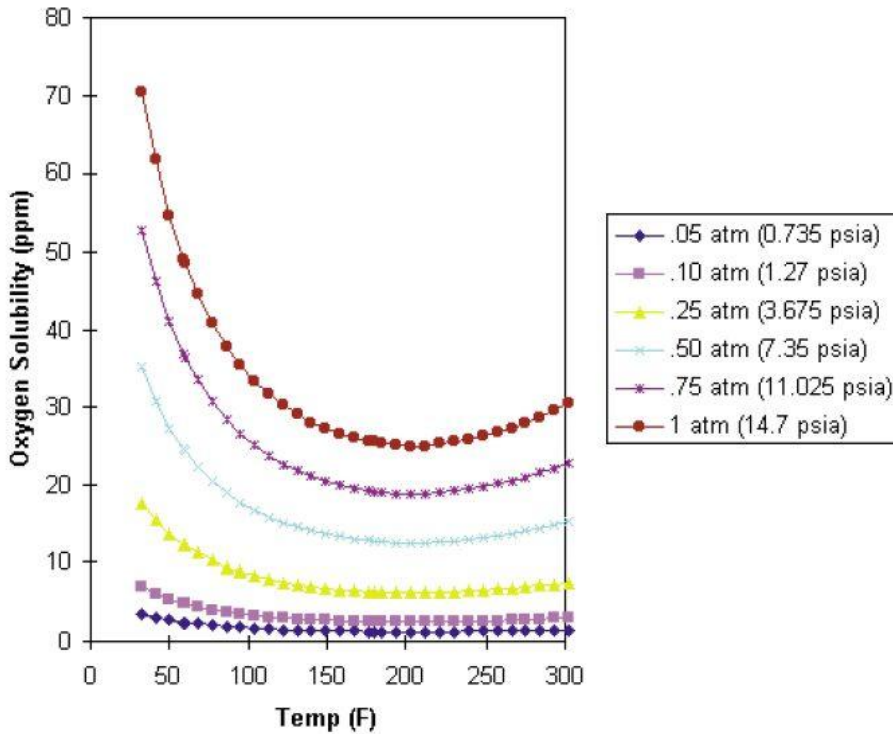


Figure 10-13 Solubility of oxygen in water at various partial pressures of oxygen (Rooney & Daniels 1998)

In the presence of salt a salting out effect is seen in the solubility of oxygen in water. This is the same effect that is seen for many other gases like helium, argon and CO<sub>2</sub>. Adding salt or increasing its concentration may have a dramatic effect on the lowering of oxygen solubility in water (Rooney & Daniels 1998).

There is not any literature on oxygen solubility in water with CO<sub>2</sub> present in the temperature range 25 – 120 °C. It is however observed that with added NaHCO<sub>3</sub> in water at temperatures from 50 – 150 °C and high pressure the solubility of oxygen will decrease. The same decrease in oxygen solubility to a minimum at 100 °C is seen as the temperature is increased followed by an increase in oxygen solubility for higher temperatures (Rooney & Daniels 1998).

## **11. Compression, dehydration and transportation**

The compression, dehydration and transport represent a significant cost in the capture of CO<sub>2</sub>. An important aspect is the amount of water (and other compounds) in the carbon dioxide stream. Present recommended limits on impurities in the CO<sub>2</sub> stream are considered very low. Less strict limits would mean considerable economical savings. A Separate regenerative dehydration step which is necessary to reach the recommended limit for water could potentially be dropped. This would leave the cooling and separation between compression steps as sufficient water removal.

To examine the concentration of water in the dense CO<sub>2</sub> stream a compressor train and a pipeline will be investigated. Using reasonable assumptions the diameter of the pipe will be calculated along with the temperature change along the pipeline. A compressor train will be modeled in Aspen Hysys investigating what concentrations of water can be expected in the dense CO<sub>2</sub> stream ready for transportation. Possible constraints will be examined and some concluding remarks put forward.

### **11.1 Transport assumptions**

A number of assumptions were made in order to calculate the pipe diameter and temperature change for a 100 km pipeline transporting dense CO<sub>2</sub>. The information is taken from various sources containing the data needed.

The diameter of the 100 km pipeline was calculated with the help of Darcy-Weisbach equation 11.1. A number of assumptions were made in order to use the equation. The pressure loss for was assumed to be 20 bar/100km. In the North Sea the pressure loss in gas pipes are 6 bar/100 km (Gudmundsson 2009). As the CO<sub>2</sub> is in dense rather than gas phase a significantly higher pressure loss of 20 bar/100 km was assumed. The density of dense CO<sub>2</sub> was set to 830 kg/m<sup>3</sup>. This was done with the help of Aspen Hysys. The density for 100 bar and 30 °C and 80 bar and 4 °C were calculated and the average was selected. The viscosity of dense CO<sub>2</sub> was found in the same manner yielding a viscosity of 0.077 mPa.s. The velocity of a dense phase liquid in pipelines is 2-4 m/s (Gudmundsson 2009). An average velocity of 3 m/s for the dense CO<sub>2</sub> was assumed. A friction factor of 0.0015 was selected.

Table 11-1 Parameters for pipe diameter calculation

$\Delta P$ [bar/100km]	20
$\Delta L$ [m]	100000
f	0.0015
$\rho$ [kg/m <sup>3</sup> ]	830
u [m/s]	3

Using the assumptions in Table 11.1 the pipe diameter was calculated with the help of the Darcy-Weisbach equation.

$$\frac{\Delta P}{\Delta L} = \frac{f}{2} \frac{1}{d} \rho u^2 \quad (11.1)$$

The calculation gave a pipe diameter of  $d=0.28\text{m}$ . Subsea pipes have a diameter of 6–20'' which convert to 0.15 – 0.51 m (Gudmundsson 2009).

The temperature of the CO<sub>2</sub> stream will change as it flows through the pipeline. The CO<sub>2</sub> stream inside the pipeline will be cooled down by the outside sea water. Assuming that the flow and temperature conditions are stable Equation 11.2 can be used for calculating the temperature drop along the pipeline. To be able to calculate the temperature at the end of a 100 km pipeline certain assumptions has to be made. The sea water outside the pipeline is assumed to be stable at 4 °C. The inlet temperature is assumed to be 30 °C. The heat transfer coefficient is between 15-25 W/m<sup>2</sup>.K for carbon steel pipes at the sea floor without insulation (Gudmundsson 2009). A value of 20 W/m<sup>2</sup>.K was assumed for the calculations. For an insulated pipeline a value of 2 W/m<sup>2</sup>.K was assumed.

The gas power plant at Kårstø is predicted to produce approximately 1.2 million tons of CO<sub>2</sub> per year (Naturkraft 2009). That means 38 kg/s of CO<sub>2</sub> is produced. The mass rate from Kårstø was assumed in the calculations.

The heat capacity of dense CO<sub>2</sub> was taken from Aspen Hysys. A heat capacity of  $C_p= 3.2$  kJ/kg.C was selected. This was the average heat capacity for the heat capacity at 100 bar and 30 °C and 80 bar and 4 °C.

Table 11-2 Parameters for temperature calculations

$T_u$ [°C]	4
$T_{in}$ [°C]	30
$U$ [W/m <sup>2</sup> .K]	20
$m$ [kg/s]	38
$C_p$ [kJ/kg.C]	3.2
$L$ [m]	100000

Using the assumption made and the result of the pipe diameter calculation the outlet temperature was calculated with Equation 11.2.

$$T_{out} = T_u + (T_{in} - T_u) \exp \left[ \frac{-U\pi d}{mC_p} L \right] \quad 11.2$$

For a pipeline without insulation the temperature will fall to seabed temperature after approximately 40 km. If an insulated pipe is used the temperature would be 13.4 °C after 100 km. The temperature is a function of distance for insulated and non insulated pipe as can be seen in Figure 11.1.

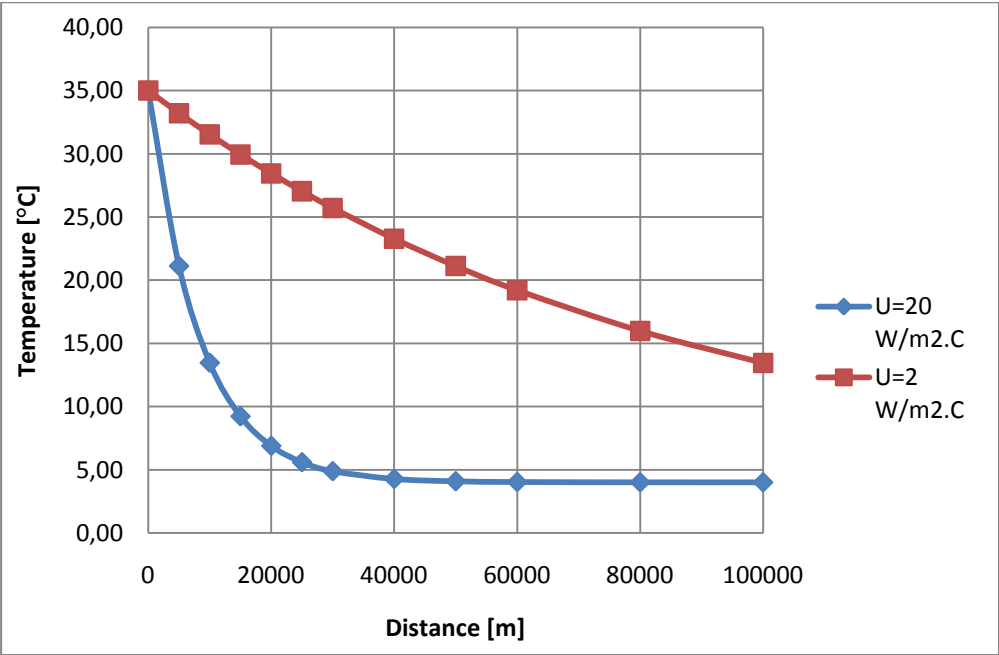


Figure 11-1 Temperature change along the pipeline for isolated and not isolated pipe

The friction factor was checked to ensure that it was a reasonable assumption in a Moody diagram. Utilizing the mass rate, diameter, density and viscosity determined earlier Reynolds number was calculated. Assuming an absolute roughness factor of 35.1  $\mu\text{m}$  for carbon steel pipes a Moody diagram could be used to check the friction factor (Gudmundsson 2009). It was determined that the stream was turbulent and that the friction factor of 0.0015 complied well with the Moody diagram.

## 11.2 Compression and separation

To avoid a phase change from dense to gas phase in the pipeline the pressure would have to stay above 50 bar at 4 °C. With an added safety of 50 % the pipeline pressure should never fall under 75 bar to avoid problems with free water.

A model of a compressor train was set up with the help of Aspen Hysys. The aim was to investigate the water concentration in a dense CO<sub>2</sub> stream after compression and water separation by cooling and separation towers. The flow sheet in Aspen Hysys consisted of a four step compression with cooling and water separation between each compressor step. The flow sheet can be seen in Figure 11.2.

The pressure of the inlet stream was 2 bar and with a composition of 98% CO<sub>2</sub> and 2 % H<sub>2</sub>O. The temperature into the first compressor was 30 °C. After each compressor step the stream was cooled down to 30 °C before entering the separator and following compressor step. The pressure drop over the cooler and separator between each of the compressors was assumed to be 1.5 bar. In other studies a lower pressure drop has been assumed, 0.5 bar, but 1.5 bar was selected in this case (Aspelund & Jordal 2007). A pressure ratio of three was selected for all four compressor steps.

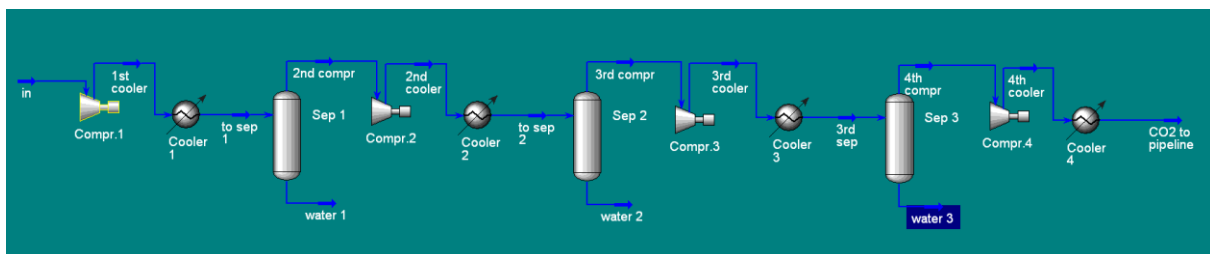


Figure 11-2 Compressor train flow sheet

The CO<sub>2</sub> stream was compressed up to 103.5 bar with the help of the compressor train modeled in Aspen Hysys. This was above the 100 bar required before transport. The pressure requirement was met. The concentration of H<sub>2</sub>O in the dense CO<sub>2</sub> stream was 743 ppm. The water concentration was also investigated for when the CO<sub>2</sub> stream was cooled to 25 °C and 35 °C between each compressor step. The concentration of H<sub>2</sub>O at 25 °C was 574 ppm and for 35 °C it was 955 ppm. The results can be seen in Table 11.3.

Table 11-3 Concentration of H<sub>2</sub>O in CO<sub>2</sub> stream

Temperature [°C]	H <sub>2</sub> O concentration [ppm]
25	574
30	743
35	955

### 11.3 Potential constraints

The danger of losing pressure in the pipeline temporary is a consideration which must be taken into account. A temporary pressure drop below 40 bar at 4 °C could lead to free water in the pipeline. At this temperature and pressure the CO<sub>2</sub> would change phase from dense to gas phase. There would be a risk of hydrates forming together with CH<sub>4</sub>, H<sub>2</sub>S and CO<sub>2</sub>. The solubility of water would decrease significantly to a level below 500 ppm (de Visser et al. 2008).

Cross-effects with CH<sub>4</sub> have been observed to have an effect on the solubility of H<sub>2</sub>O in dense CO<sub>2</sub>. Studies have shown that adding 5 % CH<sub>4</sub> to the CO<sub>2</sub> stream will lower the H<sub>2</sub>O solubility by 30 %. At 4 °C and 100 bar the solubility of water in dense CO<sub>2</sub> is 1300 ppm (de Visser et al. 2008).

Health and environmental considerations must be taken into account when determining the concentration limit of H<sub>2</sub>S and SO<sub>2</sub> in CO<sub>2</sub>. H<sub>2</sub>S is highly toxic and the current limit of 200 ppm is supportable in terms of safety and gives a reasonable safety limit (de Visser et al. 2008). For SO<sub>2</sub> potential constraints depend on its classification. This poses a particular problem. It is not clear yet if it might be regarded as industrial waste and therefore cannot be injected in reservoirs or aquifers due to legal restrictions (Aspelund & Jordal 2007).

Non condensable gases such as  $N_2$ , Ar and  $H_2$  are a potential problem in compression and transport. They will add to the energy needed to compress the  $CO_2$  stream up to the required pressure. In the case of  $N_2$  the energy requirement will go up by approximately 1 % if 1 mole% of  $N_2$  is present in the stream (Aspelund & Jordal 2006). They will also take up transport volume in the pipeline resulting in less  $CO_2$  transported. Hence, there is an added cost to compressing and transporting  $CO_2$  in the presence of non condensable gases.

#### **11.4 Concluding remarks**

Removing water in the compression train will be enough to prevent two phase flow in the pipeline. Cooling the  $CO_2$  stream to 30 °C between the four compression stages and removing the condensed water gives a water content of 750 ppm. This is low enough to avoid free water at any point in the 100 km long pipeline with sufficient safety limits. At ambient temperatures the pressure would have to sink below the point where  $CO_2$  changes phase to gas for water solubility to fall below 750 ppm.

The calculation of pipe diameter and the temperature change along the pipeline yields reasonable results. A pipe diameter of 0.28 m falls well within the limit for subsea pipes. Normally the pipe diameter for subsea pipelines up to a 100 km in length is 6-20''. The fall of temperature to 4 °C for non isolated pipe will not cause free water to form. The pressure will still be above critical pressure for  $CO_2$ . At 4 °C the solubility of  $H_2O$  in pure  $CO_2$  will still be above 1700 ppm (de Visser et al. 2008).

Although the cross-effect of impurities like  $O_2$  and non condensable gases are unknown, it is unlikely that they will have a significant impact on the solubility of water in dense  $CO_2$ . The cross-effect with  $H_2S$  has been observed to have little effect on the solubility of water in  $CO_2$ . Also, the impact on water solubility by 4 %  $CH_4$  is not a likely scenario for transportation of  $CO_2$ . The purity of  $CO_2$  will in most cases be over 99 %. Any effect impurities will have on the water solubility in dense  $CO_2$  will therefore be significantly diminished.

## 12. Discussion

The literature search showed that there are few studies done on the effect of impurities in the CO<sub>2</sub> stream. The main search tools were the extensive data bases at NTNU library, Google Scholar and SPE library. Industrial actors and people with potential knowledge were also asked to contribute information.

The lack of information is thought to be due to several factors. Although CO<sub>2</sub> capture with amine solutions is considered a mature field it has mainly been used for removing acid gas from natural gas. The capture of CO<sub>2</sub> from flue gas is in comparison relatively new and adds another level of complexity to the capture process. Components from the excess air used in combustion of the natural gas causes new forms of degradation and additional problems with corrosion. This has not been a big issue with scrubbing of natural gas and therefore few studies have been performed.

CCS has become a field of focus in the later years. It has become clear that CO<sub>2</sub> emissions from power plants need to be recovered and used or stored in some way. In light of this companies are spending a substantial amount of capital into the research and construction of capture facilities. The information gained from these projects is not going to be available to the public for some time to come.

The presence of impurities was seen to increase the extent of degradation in amine solution. Studies showed that oxygen plays an important part in this degradation. Oxygen provided additional pathways for the degradation reactions to take. It can be new pathways or reaction pathways for heat stable salts or degradation products already formed from degradation caused by CO<sub>2</sub>. Understanding what factors promote oxygen solubility in alkanolamine solutions and under what conditions can be an important way of limiting oxidative degradation. Being able to balance the need for favorable conditions in the contact column for recovery of CO<sub>2</sub> together with controlling the solubility of oxygen could be a useful means of keeping degradation low. A good scenario would be keeping the temperature low enough for good recovery of CO<sub>2</sub>, but high enough to limit the solubility of oxygen in the amine solution.

Heat stable salts and degradation products enhance the corrosion rate in the amine system. It was first thought that the amine solution itself was the cause of corrosion, but later it was observed that it is the carbon dioxide is the main cause and that the rate is enhanced by irreversible products formed. One of the reasons behind why certain degradation products

enhance corrosion is their ability to bind iron. Degradation products like Bicine and Oxalic acid has been observed to act as chelating agents. They form a complex with iron removing it from the metal surface. This allows more iron to come into solution and as a result speed up the corrosion rate.

The recommended concentration limits for impurities in the CO<sub>2</sub> stream transported by pipeline are conservative. This leads to increased cost from having to remove impurities down to a very low concentration before CO<sub>2</sub> can be transported. One of the main reasons behind these conservative recommendations is that CO<sub>2</sub> have been used for enhanced oil recovery (EOR). Here a key factor is the ability of CO<sub>2</sub> to dissolve oil at temperatures and pressure conditions of the oil reservoir (de Visser et al. 2008). Components like O<sub>2</sub>, N<sub>2</sub>, Ar, H<sub>2</sub> and CO are immiscible with oil and will increase the so called minimum miscibility pressure (MMP). If the MMP of the impure CO<sub>2</sub> is so high that it reaches the estimated reservoir fracture pressure it is unsuitable for EOR. When injecting CO<sub>2</sub> into an aquifer this would not be an issue.

Lack of knowledge keeps the impurity concentration limits low. Few studies have been made on the effect of impurities on the water solubility in CO<sub>2</sub> streams. There is a concern that allowing higher concentration limits will cause free water to form in the CO<sub>2</sub> pipeline. This would lead to potential problems with corrosion, hydrate formation and water freezing.

There is a need for more studies being done on the capture of CO<sub>2</sub> from flue gas. A better understanding of the solubility of impurities in amine solution could help limit the formation of degradation products. Investigation into which heat stable salts and degradation products enhance corrosion could help limit the problem. Understanding the mix effect of impurities in the CO<sub>2</sub> stream could help keep cost down for compression, dehydration and transport. Potentially higher concentration limits for impurities could be allowed while still avoiding problems with corrosion and hydrates in the pipeline.

### 13. Conclusions

1. An extensive literature search shows that there are few studies available on the effects of impurities in the post combustion CO<sub>2</sub> capture process. Most of the information that can be found relates to the removal of acid gases from natural gas. Little is written about the effect of oxygen in the amine process and the effects of non condensable gases on compression of CO<sub>2</sub>.
2. Impurities increase the extent of amine solution degradation. The presence of oxygen in the amine system has been observed to increase the formation of heat stable salts and degradation products. The result is amine solution lost, less CO<sub>2</sub> recovered and higher operational costs.
3. The rate of corrosion is enhanced by the heat stable salts and degradation products formed by amine solution degradation. Studies have shown that allowing degradation products to accumulate will result in a substantial increase in corrosion rate. This in turn can result in equipment failure.
4. The lack of knowledge about the effect impurities on the transportation of CO<sub>2</sub> in pipelines has resulted in conservative concentration limits. With more studies carried out and capture plants coming online the experience gained should result in less strict limits.
5. A separate dehydration step is not necessary prior to CO<sub>2</sub> transportation. The compression train with cooling and separation between compression stages will provide sufficient water removal. Only in the case of pipe rupture or sudden depressurization will there be a risk of free water forming.

## 14. References

Aspelund, A and Jordal, K.: "*Gas Conditioning-The interface between CO<sub>2</sub> capture and transport*", International Journal of Greenhouse Gas Control I, p343-354, (2007).

Austergard, A. et al.: "*Thermodynamic models for calculating mutual solubilities in H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> mixtures*", Chemical Engineering Research and Design, (2006), 781-794.

Bedell, S.A.: "*Oxidative degradation mechanism for amines in flue gas capture*", Energy Procedia, (2008).

Bedell, S.A. and Bosen, S.F.: "*The relevance of Bicine in the corrosion of amine gas treating plants*", Proceedings of the Laurance Reid gas conditioning conference, (2004).

Bolland, O. and Sæther, S.: "*New concepts for natural gas fired power plants which simplify the recovery of carbon dioxide*", Energy Convers. Mgmt, Vol 33, No. 5-8, pp 467 – 475, (1992).

Bøe, S.E.: "*Gas Fired Power Plant at Kårstø*", <http://www.ipt.ntnu.no/~jsg/undervisning/naturgass/lysark/LysarkBoee2008.pdf>, (November 2008).

Coulson, J.M. and Richardson, J.F.: "*Chemical Engineering Volume 1 (4<sup>th</sup> edition)*", Pergamon Press, Oxford England, (1990).

De Visser, E. et al.: "*Dynamis CO<sub>2</sub> quality recommendations*", International Journal of Greenhouse Gas Control 2 (2008) 478 – 484.

Dugstad, A.: "*Mechanism of protective film formation during CO<sub>2</sub> corrosion of carbon steel*", CORROSION/98, Paper No. 31, (Houston, TX: NACE, 1998).

Dugstad, A.: "*Fundamental aspects of CO<sub>2</sub> metal loss corrosion Part 1: Mechanism*", CORROSION/2006, Paper No. 06111, (Houston, TX: NACE, 2006).

DuPart, M.S., Bacon, T.R. and Edwards, D.J.: "*Understanding corrosion in alkanolamine gas treating plants Part 1&2*", Hydrocarbon Processing, (April and May 1993).

EMEP/EEA: "*Emission Inventory Guidebook*", UNECE/EMEP Task Force, (December 2006).

Fredenhagen, A. and Eggers, R.: "*The effect of hydrate formation upon the pressure release of wet carbon dioxide*", Chem.Eng.Techn. Vol. 24, (2001).

Gary, J.H. and Handwerk, G.E.: "*Petroleum Refining Technology and Economics (2nd Edition ed.)*", Marcel Dekker, Inc, (1984).

Gudmundsson, J.S.: Course in Natural Gas at NTNU, (2008). Available from:

<http://www.ipt.ntnu.no/~jsg/undervisning/naturgass/TPG4140.html>

Gudmundsson, J.S.: "*PROSESSERING AV PETROLEUM-Grunnleggende enhetsoperasjoner i produksjon av olje og gass*", (2009). Available from:

<http://www.ipt.ntnu.no/~jsg/undervisning/prosessering/kompendium/KompendiumApril2009.pdf>

Haws, R.: "*Contaminants in amine gas treating*", GPA Houston Regional Meeting, (2001).

Haws, R. and Jenkins, J.: "*Contaminant reporting in amine gas treating service*", Sulfur Recovery Symposium, (2001).

Idem, R.O. and Bello, A.: "*Pathways for the formation of products of the oxidative degradation of CO<sub>2</sub>-loaded concentrated aqueous monoethanolamine solutions during CO<sub>2</sub> absorption from flue gas*", Ind. Eng. Chem. Res., (2005), 44 (4) 945-969.

Idem, R. et al.: "*The roles of O<sub>2</sub> and SO<sub>2</sub> in the degradation of monoethanolamine during CO<sub>2</sub> absorption from industrial flue gas streams*", IEEE EIC Climate Change Technology, (2006).

Kidnay, A.J and Parrish, W.R.: "*Fundamentals of natural gas processing*", CRC Press Taylor & Francis Group, (2006)

Kohl, A. and Nielsen, R.: "*Gas Purification (5th edition)*", Gulf Publishing Company, (1997)

Lepaumier, H., Picq, D. and Carrette, P.L.: "*Degradation study of new solvents for CO<sub>2</sub> capture in post-combustion*", Energy Procedia, (2008).

Mohammad, R.M. et al.: "*CO<sub>2</sub> capture from power plants Part I. A parametric study of the technical performance based on monoethanolamine*", International Journal of Greenhouse Gas Control I, (2007), 37-46.

Naturkraft, Gasskraftverket på Kårstø, (July 2009). Available from:

[http://www.naturkraft.no/default.asp?V\\_ITEM\\_ID=454](http://www.naturkraft.no/default.asp?V_ITEM_ID=454)

Oosterkamp, A. and Ramsen, J.: "*State of the Art Overview of CO<sub>2</sub> Pipeline Transport with relevance to offshore pipelines*", Polytec, (2008).

Perry, R.H. and Green, D.W.: "*Perry's Chemical Engineers' Handbook (7<sup>th</sup> Edition)*", McGraw-Hill, (1997).

Rochelle, G.T. and Chi, S.: "*Oxidative degradation of monoethanolamine*", First National Conference on Carbon Sequestration, Washington DC, (May 14-17, 2001)

Rooney, P.C. et al.: "*Oxygen's role in alkanolamine degradation*", Hydrocarbon Processing, (July 1998), 109-113.

Rooney, P.C. et al.: "*Effect of heat stable salts on MDEA solution corrosivity: Parts 1&2*", Hydrocarbon Processing, (March 1996 and April 1997).

Rooney, P.C. and Daniels, D.D.: "*Oxygen solubility in various alkanolamine/water mixtures*", Petroleum Technology Quarterly, (Spring 1998)

Seiersten, M. et al.: "*Corrosion at high CO<sub>2</sub> pressure*", CORROSION/2003, Paper No. 03345, (Houston, TX: NACE, 2003).

Speight, J.G.: "*Natural Gas – A basic handbook*", Gulf Publishing Company, (2007).

StatoilHydro.: "*Study and Estimate for CO<sub>2</sub> Capture Facilities for the proposed 800 MW Combined Cycle Power Plant-Tjeldbergodden, Norway*", (April 2005)

StatoilHydro.: "*CO<sub>2</sub> Masterplan Mongstad*", (Downloaded March 2009).

Steeneveldt, R., Berger, B. and Torp, T.A.: "*CO<sub>2</sub> Capture and Storage Closing the Knowing-Doing gap*", Chemical Engineering research and Design, 84, (2006), 739-763.

Strazisar, B.R., Anderson, R.R. and White, C.M.: "*Degradation pathways for monoethanolamine in a CO<sub>2</sub> capture facility*", Energy & Fuels, (2003).

Torp, T.A.: "*CO<sub>2</sub> Capture and Storage – StatoilHydro's 12 years experience*", (2008). Available from:  
<http://www.ipt.ntnu.no/~jsg/undervisning/naturgass/lysark/LysarkTorp2008.pdf>

Veawab, A., Soosaiprakasham, I.R.: "*Corrosion and polarization behavior of carbon steel in MEA-based CO<sub>2</sub> capture process*", International Journal of Greenhouse gas control 2, (2008), 553-562.

Watkins, J.W., Kincheloe, G.W.: "*Corrosion of steel in water by varied ratios of dissolved gases*", *Corrosion*, 55-58, (July 1958),.

Zero, <http://www.zero.no/> (June 2009).