MASTER THESIS

CO_2 Extraction from Flue Gases for Carbon Capture and Sequestration: Technical and Economical Aspects

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Meinen Eltern zum Dank

AFFIDAVIT

I declare in lieu of oath, that I wrote this Master Thesis and
performed the associated research myself,
using only literature cited at the end of this volume.

Leonie Ebner

Leoben, October 2008

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Very special thanks to my parents for giving me the opportunity and support to study Petroleum Engineering at the Mining University of Leoben. Without them I would have never achieved my goals in the time I wanted to.
Finally, special thanks to Oliver for his unremitting support and proof-reading.

Alles Wissen und alle Vermehrung unseres Wissens endet
nicht mit einem Schlusspunkt,
sondern mit einem Fragezeichen.

Hermann Hesse

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Kurzfassung

Durch Untersuchungen an arktischen Eiskernen konnten sowohl ein Anstieg der Kohlendioxidkonzentration, der Feinstaubbelastung als auch der mittleren Temperatur in der Atmosphäre nachgewiesen werden.

Das Ziel dieser Diplomarbeit ist es Verfahren und Prozesse aufzuzeigen, die es ermöglichen Kohlendioxid aus Industrieabgasen zu separieren, um es anschließend nachhaltig sequestrieren zu können. In weiterer Folge kann damit ein Anstieg der Kohlendioxidkonzentration in der Atmosphäre durch Emissionen reduziert werden.

Die Sequestrierung kann terrestrisch oder marin erfolgen. Für die geologische Speicherung gibt es im Wesentlichen 4 verschiedene Möglichkeiten: 1) in bereits entleerten Öl- und Gaslagerstätten, 2) in salzwasserführenden Formation (Aquifer), 3) in Mineralen und 4) in nicht-abbaubaren Kohleflözen. Bei der Speicherung in den Ozeanen löst sich das Kohlendioxid entweder im Meerwasser oder es bildet Hydratseen in Tiefen über 3000m. Entscheidende Argumente für die Wahl der Sequestrierung sind die Aspekte der Gesundheit, Sicherheit und Umwelt, die gerade hier nicht außer Acht gelassen werden dürfen.

Um die Sequestrationskapazitäten optimal auszunützen, ist es sinnvoll das CO_2 nach der Verbrennung aus Industrieabgasen zu separieren. Dafür gibt es unter anderem folgende Methoden: 1) Absorption mit Monoethanolamin, 2) Druckwechsel-Adsorption, 3) Gasseperationsmembranen und 4) den Carbonation-Calcination Prozess. Diese 4 Prozesse werden hier diskutiert und mit Vor- und Nachteilen erwähnt.

Diese Separationsprozesse führen zu intensive Anlagenkosten, welche in dieser Arbeit einer wirtschaftlichen Betrachtung unterzogen werden.

Abstract

Investigations of arctic ice-cores showed an increase of carbon dioxide concentration, the particulate matter and also of the mean temperature in the atmosphere.

The objective of this thesis is to present several methods and processes to separate carbon dioxide from flue gases for sustainable sequestration. As a result the increase of carbon dioxide concentration in the atmosphere by emission can be reduced.

The sequestration can either be terrestrial or marine. There are four options for terrestrial sequestration: 1) in depleted oil and gas reservoirs, 2) in saline formations and aquifers, 3) in minerals and 4) in unminable coal seams. For marine storage the carbon dioxide either dissolves in the seawater or forms lakes of hydrates in depths below 3000m. Health, safety and environmental issues have to be considered seriously.

First of all, it is necessary to capture the carbon dioxide from the flue gas after combustion, in order to optimize the utilization of limited storage capacities. When capturing carbon dioxide the following processes will be discussed: 1) absorption using monoethanolamine, 2) pressure swing adsorption, 3) gas separation membranes and 4) the carbonation-calcination process.

These separation processes lead to intense facility costs, which undergo an economic evaluation in this thesis.

1. Introduction

Modern climate change is driven by an increase of the carbon dioxide concentration in the atmosphere. This climate change is mainly caused by combustion of fossil fuels since industrial revolution took place.

In 1997, the Kyoto Protocol was initiated to reduce the greenhouse gases. It came affect in 2005 with the first commitment period ending in 2012. Since then, more than 170 countries, which signed the protocol, have to reduce their greenhouse gas (GHG) emissions by an average of 5% below their 1990 levels. For many EU member states that results in a decrease of about 15% below their expected emissions in 2008.

This master thesis is divided into three main chapters by answering following questions:

- Where and how can carbon dioxide be stored safely?
- How can carbon dioxide be separated from flue gas?
- Is carbon capture and sequestration economical?

The fundamentals in post-combustion capture are initially described, followed by the basics and different types in carbon dioxide storage. Moreover, these storage possibilities are discussed by its safety aspects which have to be considered seriously.

The next part contains the processes adaptable for carbon dioxide capture from flue gas. Following four procedures are explained: 1) Absorption process by using monoethanolamine as absorbent, 2) pressure swing adsorption by using activated carbon, 3) gas separation membranes and 4) the carbonation-calcination process by using lime water. These processes are also discussed by three case scenarios.

Whilst discussing the three case scenarios the probable CAPEX and OPEX are estimated for a duration of 11 or 20 years by using “Que$tor” as software program.

Finally, it should be mentioned that legal regulations are not an issue in this master thesis.

1.1. Physical Properties of CO_2

Carbon dioxide is an odourless and colourless chemical compound, which appears as gas under natural condition. It is produced by all animals, plants, fungi and micro-organisms during respiration and is also needed by plants during photosynthesis. Furthermore CO_2 is generated as by-product of combustion e.g. burning of fossil fuels. Some more properties are listed in the table below.

Table 1: Properties of CO_2. [16-18]

TLV (Threshold Limit Value)	5,000 ppm
Lethal concentration	150,000 ppm
Molar mass:	44.0099 g/mol
Density:	solid: 1,600 kg/m^3 gas: 1.9767 kg/nm^3
Melting point:	-56.6 °C (at 5.3 bar)
Boiling point:	-78,5 °C
Triple point:	-56.6°C, 5.18 bar
Critical point:	31 °C, 73.8 bar (1,070.4 psi)

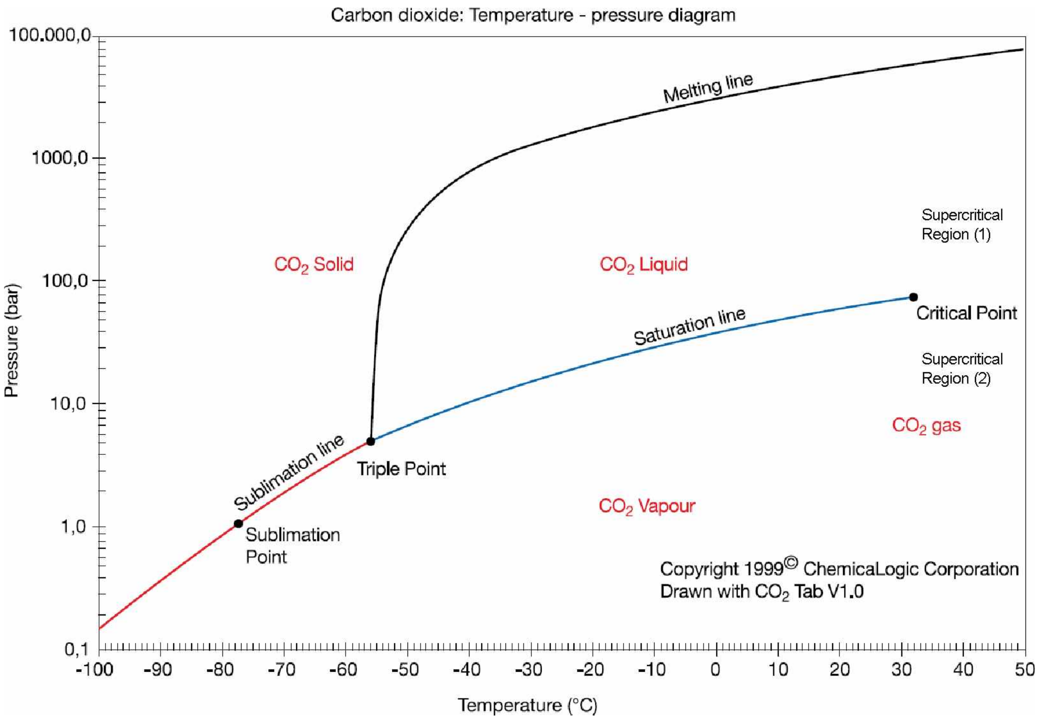

Figure 1: Phase diagram of CO_2. [1]

Figure 1 shows the phase diagram of CO_2, the critical point as well as the triple point and the equilibrium relationship of solid, liquid and vapour below its critical temperature. Above the critical temperature and pressure, the carbon dioxide is in a supercritical state, which has the characteristics of a liquid (Supercritical Region (1), shown in Figure 1). Above the critical temperature it behaves as a vapour (Supercritical Region (2) in Figure 1), which density increases with increasing pressure (Figure 2). Below the critical point a sudden discontinuity in density appears due to reaching the two-phase region.

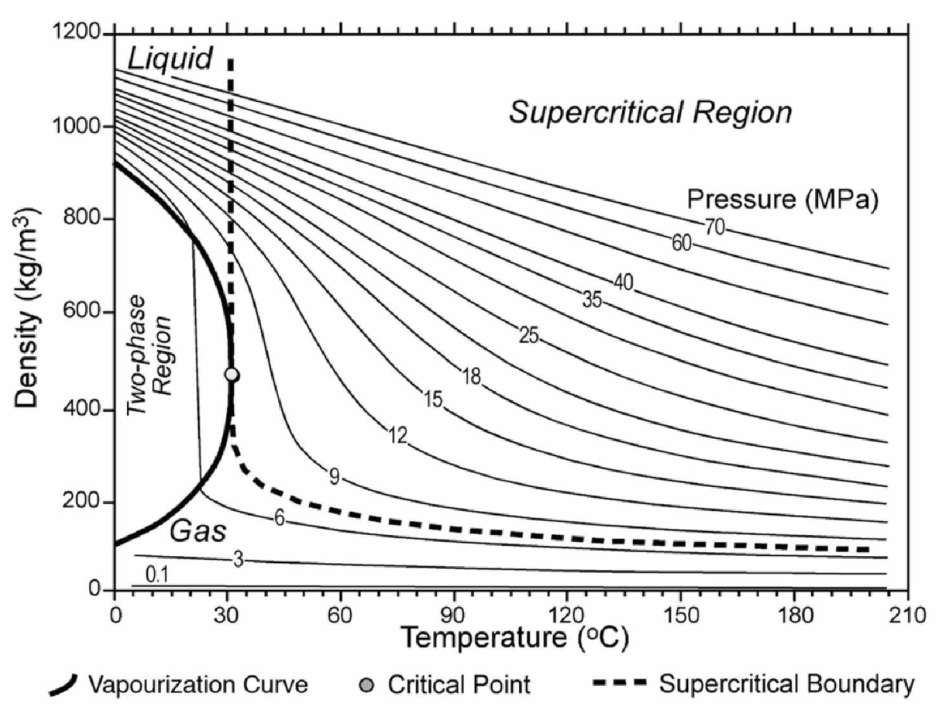

Figure 2: Density of CO_2 as a function of temperature and pressure. [1]

The viscosity of CO_2 is a function of pressure and temperature. Gas viscosity increases with increasing pressure and also with increasing temperature (Figure 3). The same discontinuity and its explanation as in the previous figure will be valid for this as well.

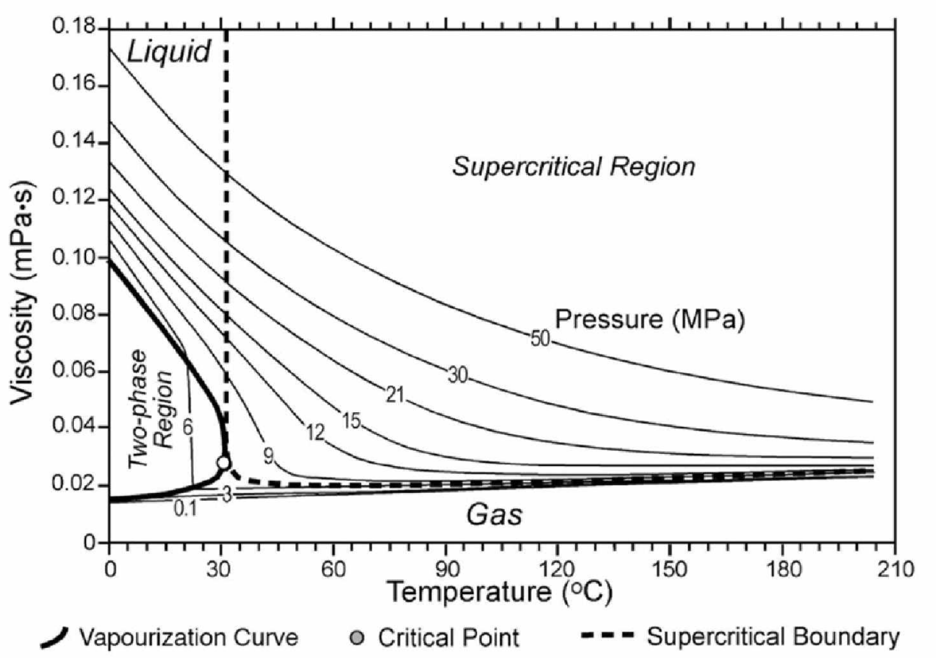

Figure 3: Viscosity of CO_2 as a function of temperature and pressure. [1]

Finally, it is necessary to mention that above an approximate depth of 500 m carbon dioxide would exist as a gas and as a liquid below that depth. Between about 500 and 2700 m depth, liquid CO_2 is lighter than sea water and tends to float upward. Below 3000 m, CO_2 is denser than sea water and tends to sink. In-between these two depths the density can vary largely depending on the temperature. Figure 4 shows this variation in comparison to the density of sea water with an average salinity of 3,5 %. It is possible that CO_2 neither rises nor falls. [1]

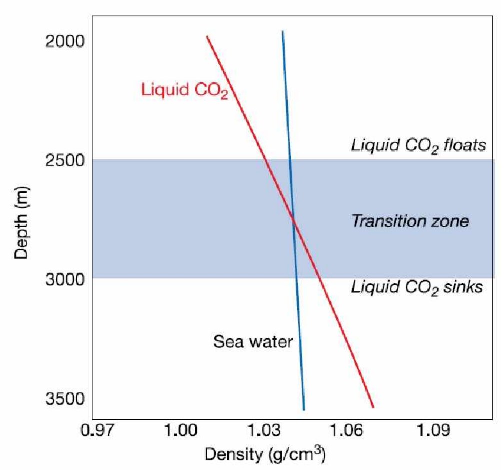

Figure 4: Density change of CO_2 in sea water. [1]

1.2. Chemical Properties of CO_2

In an aqueous solution (this may be sea water or saline water from geological formations) CO_2 forms carbonic acid, which is too unstable to be easily isolated. As shown in Figure 5, the solubility of CO_2 in water decreases with increasing temperature and increases with increasing pressure. Furthermore it has to be mentioned that the solubility of carbon dioxide in water also decreases with increasing water salinity (Figure 6). This correction factor for brine is dependent on the pressure. A discontinuity appears below 1500 psia. As shown in Figure 6 the solubility increases with increasing pressure up to 1500 psia for the salinities of 100,000 ppm and 200,000 ppm, but decreases with increasing pressure for a salinity of 35,000 ppm. For pressures higher than 1500 psia the correction factor for brine stays nearly constant.

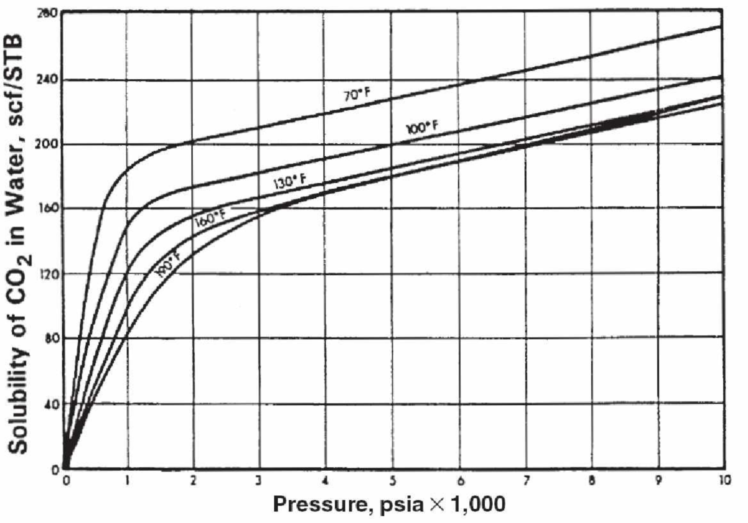

Figure 5: Solubility of CO_2 in pure water. [22]

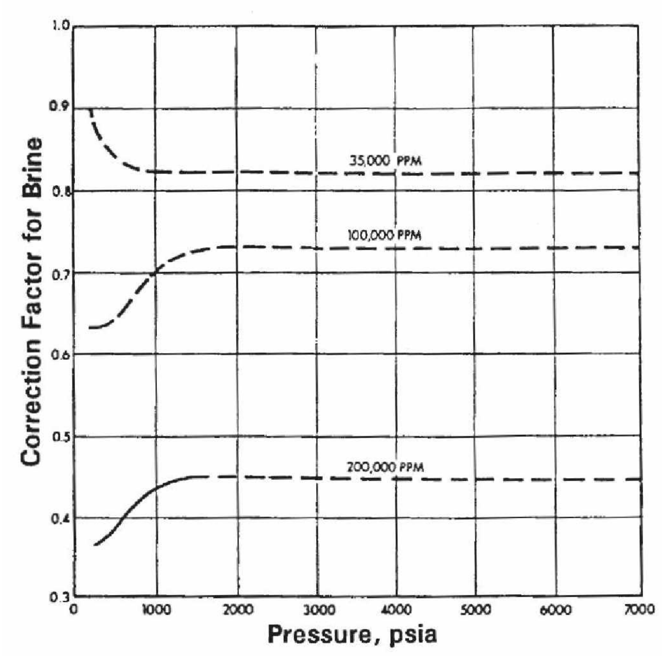

Figure 6: Correction factor for the solubility of CO_2 in brine. [22]

Example 1: Solubility of CO_2 in brine

Temperature gradient: 3°C/100m

Pressure gradient: 10bar/100m

Salinity: 100,000 ppm

Table 2: Example 1 - CO_2 Solubility in Brine.

Depth	Temperature	Pressure	Solubility in water	Corr. Factor	**Solubility in brine**
[m]	[°C; °F]	[bar; psia]	[nm^3/m^3; scf/STB]	[-]	**[nm^3/m^3; scf/STB]**
1000	30; 86	100; 1470	32.9; 185	0.73	**21.1; 131.4**
2000	60; 140	200; 2940	28.9; 162	0.75	**21.6; 121.5**
3000	90; 194	300; 4410	31.2; 175	0.75	**23,4; 131.25**

The dissolution of CO_2 in water has an important impact on the pH of the water. The dissolved carbon dioxide reacts with water to form carbonic acid (H_2CO_3), described as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Carbonic acid dissociates to form bicarbonate ions, which can further dissociate into carbonate ions. These dissociations result in a lowering of the pH.

2. Fundamentals in Carbon Capture and Sequestration

The CO_2 capture technology must to be classified into 4 basic systems:

- Capture from industrial process streams
- Oxy-fuel combustion capture
- Pre-combustion capture
- Post-combustion capture

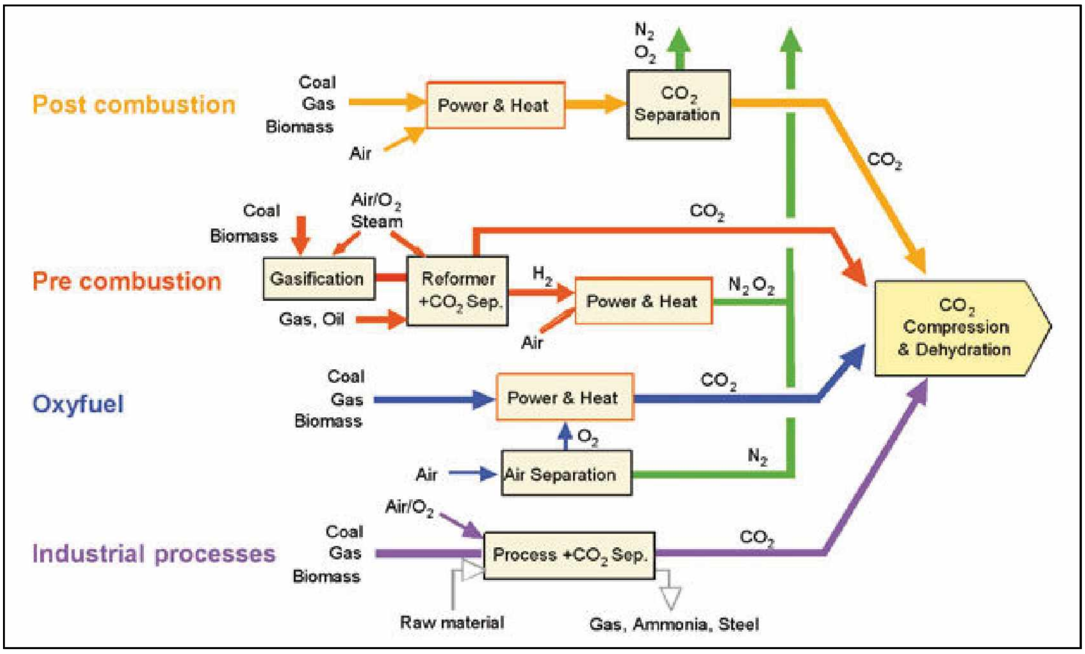

Figure 7: CO_2 capture systems. [1]

2.1. Capture from industrial process streams

In the past, CO_2 was captured from industrial process streams, only to be vented into the atmosphere as there was no need to store it. CO_2 was a by-product of purification of natural gas and production of hydrogen-containing synthesis gas (for ammonia and cement manufacturing, alcohols and synthetic liquid fuels). [1]

2.2. Oxy-fuel combustion capture

When using this capture system, almost pure oxygen is used for combustion instead of air. This will result in a flue gas, which consists mainly of CO_2 and H_2O. The water vapour is then removed by cooling and compressing the gas stream. Further treatment of the flue gas may be needed, in order to remove air pollutants and non-condensed gases (such as nitrogen) before the CO_2 is sent to storage. This process is still in the demonstration phase, which means that the technology has been built and operated at the scale of a pilot plant. Further development is necessary before the technology is ready for a full-scale system, which is economically feasible. [1]

2.3. Pre-combustion capture

The fuel has to react with oxygen or air and/or steam to become a "synthesis gas (syngas)", which consists mainly of CO (carbon monoxide) and H_2 (hydrogen). The resulting syngas is further processed into CO_2 and more H_2. This CO_2 is then commonly separated using physical or chemical absorption processes, before the combustion takes place. The remaining H_2 can now be used as a fuel for many applications, e.g. boilers, gas turbines, engines or fuel cells. [1-2]

2.4. Post-combustion capture

Post-combustion decarbonisation is the most mature, but also the most costly of these systems. Instead of venting the flue gas directly to the atmosphere, the gas is passed through equipment, which will separate most of the CO_2 by absorption, adsorption or membranes. These processes are described below. After separating the greenhouse gas from the flue gas, the remaining stream can be vented to the atmosphere. [1-3]

2.4.1. Absorption

Physical or chemical absorption are processes where one or more components of a gas mixture are extracted by contacting the gas mixture with an absorption liquid e.g. Rectisol or monoethanolamine. The solved components, here only CO_2, are transferred to the liquid phase. In physical absorption a linear dependence on gas partial pressure is assumed for the solvent capacity. In chemical absorption the solvent assumes a non-linear dependence and is higher at low partial pressures.

Physical absorption occurs faster with a cooler flue gas, but chemical absorption reacts faster with a hotter flue gas.

2.4.1.1. Physical absorption

As mentioned before, when using this kind of absorption, the CO_2 is physically absorbed and then regenerated by heating and/or pressure reduction, in which little or no energy is required. The main physical solvents are Rectisol (cold methanol) or Selexol (dimethylether of polyethylene glycol). Selexol has the ability to capture CO_2 at high pressures, with little or no compression for transport being necessary. This is an attribute, which is beneficial when using pre-combustion systems; in post-combustion processes the pressure is nearly atmospheric. Rectisol is used in a coal gasification plant in North Dakota, USA, where Rectisol captures about 5000 t/d of high quality CO_2, which is then transported via pipeline to Weyburn, Canada for EOR uses. [1, 9, 11-14]

2.4.1.2. Chemical absorption

The most common chemical solvents are amine-based solvents like monoethanol amine (MEA) or diglycolamine (DGA) – these are called primary amines. Secondary amines are for example diethanolamine (DEA) or di-isopropylamine (DIPA). Tertiary amines include triethanolamine (TEA) or methyl-diethanolamine (MDEA). A typical amine-based absorption process to capture CO_2 from flue gas is shown in the following figure:

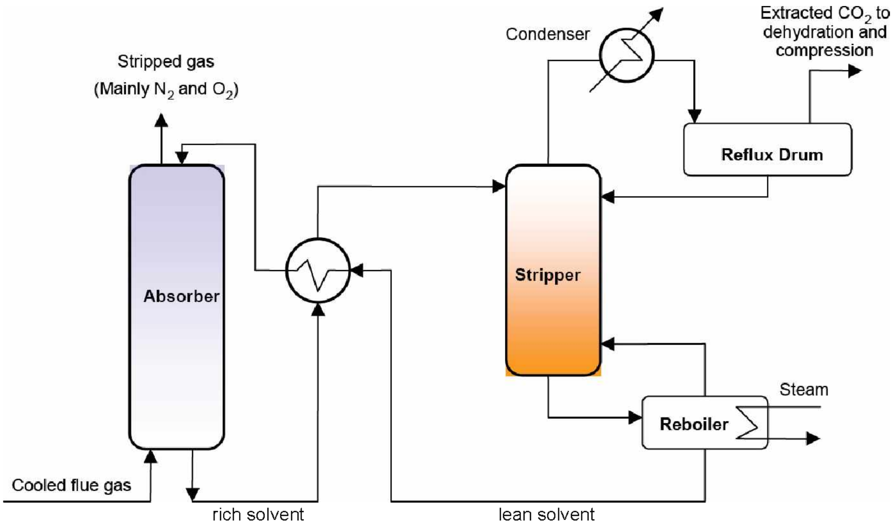

Figure 8: Principle configuration of an amine based absorption process. [9]

In Figure 8, cold flue gas flows into the absorber, where it comes into contact with a liquid solvent, which is dripping from the top. CO_2 is captured by this solvent and brought as a “rich” fluid to the stripper by passing a heat changer. The amine fluid, which is rich on CO_2, is heated up with steam in the stripper/regenerator. This increase in temperature allows the CO_2 to split up from the amines. To get a pure CO_2 stream it is necessary to pass a condenser and a reflux drum to get rid of possible water. The “lean” amine fluid is then recycled to the absorption column. The purity of the CO_2 stream by using chemical solvents can be about 98% or 99%. [1, 9, 11-14]

2.4.2. Adsorption

The difference between absorption and adsorption is that in an adsorption process the CO_2 is taken by the surface not by the volume. There are four different adsorption processes: PSA (Pressure Swing Adsorption), TSA (Temperature Swing Adsorption), VSA (Vacuum Swing Adsorption) and ESA (Electric Swing Adsorption). The most commonly used are PSA and TSA, ESA is a relatively new development that needs more experiences and is not yet commercially ready. Finally VSA is another form of PSA. The adsorption process is the same for all systems, the difference lies within the desorption process. As adsorbing materials molecular sieves (e.g. zeolites), activated carbons or a combination of both are used for capturing CO_2. They have small micropore diameters, which result in higher exposed surface area. These adsorbents have the ability to capture CO_2 from flue gases through the intermolecular forces between CO_2 and the porous surface. The desorbing process using PSA/VSA is carried out by pressure reduction (for VSA till vacuum exists) and with TSA by temperature increase. Regeneration of the solid adsorbents using ESA is accomplished by applying a low voltage across the adsorbent.

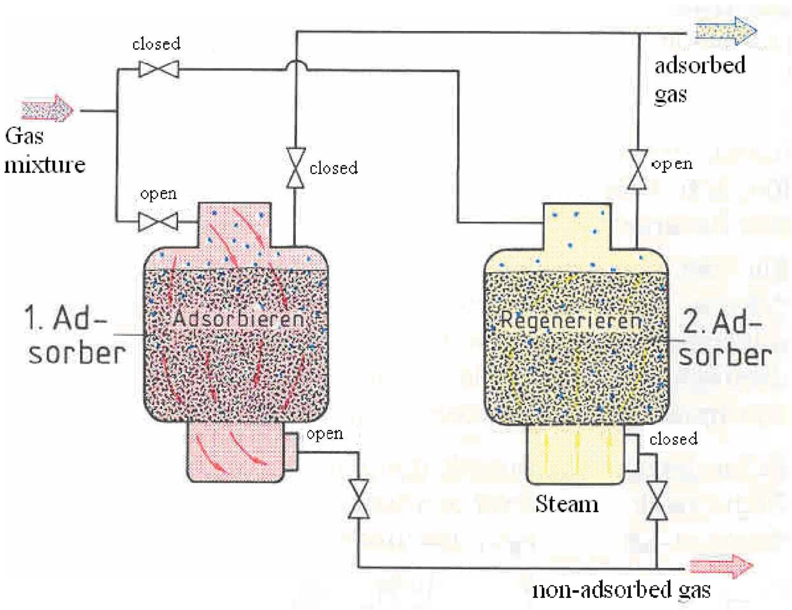

Figure 9: Adsorption process. [14]

For a continuous adsorption process it is necessary to have at least 2 sorption columns, which can switch between ad- and desorption (Figure 9). If one adsorption bed is saturated by CO_2 the flue gas stream can then be redirected to the second column. So the first column, which is saturated, can now start with its regeneration, while the adsorption procedure in the second column can start. The more adsorption capacity required the more columns will need to be installed. [1, 9, 11, 15]

2.4.3. Membranes

A membrane is a barrier film that allows a specific separation of gas mixtures through specific permeations.

Generally, there are two different types of membranes:

- Gas separation membranes
- Gas absorption membranes

2.4.3.1. Gas separation membranes

The separation of CO_2 from the flue gas relies on diffusivity of the gas molecules in the membrane. The driving force for this separation is the difference in partial pressure from one side to the other side of the membrane, as shown below in Figure 10.

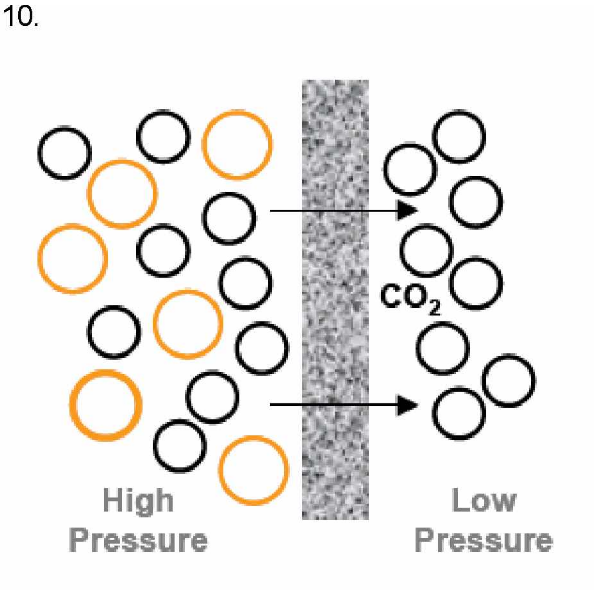

Figure 10: Principle of gas separation membranes. [9]

There are diverse types of gas separation membranes obtainable, such as ceramic, polymeric and a combination of both (hybrid). Membranes are normally structured as hollow fibre or spiral-wound modules (see Figure 26 and Figure 27 and explanations in chapter 3.3.).

The main advantages and disadvantages of the membrane compared to an absorption process are [9, 10]:

+ No separating agent is involved, that means no solvent regeneration.
+ The system is suitable for different design situations (vertically, horizontally), it is compact and lightweight.
+ Flexible in design, it allows also a multi-stage operation.
+ Can be turned down easily.
+ No make up water is required.
+ Low maintenance costs are required, because there are no moving parts.
- Sensitive to composition of flue gas.
- Sensitive to operator failures.
- Compression required for the low pressured flue gas to provide the driving force for permeation (pressure differential across the membrane).
- Separated CO_2 is needed to be compressed for further transport

2.4.3.2. Gas absorption membranes

Compared to the gas separation membranes an absorption fluid is necessary to absorb the CO_2, which diffuses through the membrane. Here the membrane has only the function to divide the gas and the liquid stream (Figure 11). Only through the liquid can the CO_2 be separated from the flue gas.

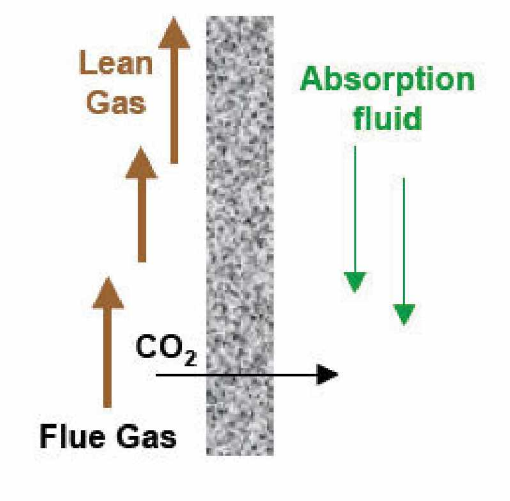

Figure 11: Principle of gas absorption membranes. [9]

For the absorption fluid all fluid types capable by an absorption process can also be used here. Furthermore, the gas absorption membrane is not sensitive to a variation of the gas flow rate, which means no flooding problems will occur. Foaming does not happen, because the gas flow does not impact the absorption liquid and there is no connective dispersion of gas and liquid. Although absorption processes are only operable in the vertical direction, gas absorption membranes can be also installed horizontally.

2.4.4. Metal oxides [8]

The final process consists of the reaction of metal oxides with carbon dioxide. This can, also be used for separation of CO_2 from flue gases. Solid metal oxides (MO) react with CO_2 to produce a metal carbonate (MCO_3). This exothermal process can be described as follows:

$$MO + CO_2 \rightarrow MCO_3$$

This reaction is also called carbonation.

The reverse process, to split the carbonate into metal oxide and carbon dioxide, is called calcination. Calcination can be achieved by heating up the carbonate beyond the calcination temperature. This calcination reaction can be represented as:

$$MCO_3 \rightarrow MO + CO_2$$

The choice of metal oxide for this process would depend on the carbonation and calcination temperature and on the reactivity of the metal oxide. Such facility equipment will consist of a carbonation reactor and a regeneration reactor.

The M in MO can for example be substituted by Ca, Zn, Mg, Ni, Cu or Pb, which are all high-purity (above 90%) metal oxides.

A metal oxide separation of CO_2 from flue gas has some important advantages:

- The separation process can take place under flue gas conditions (under high temperature). Alternatively when using absorption, adsorption or membrane separation, low temperatures and/or high pressures are required.
- Typical materials used for this reaction-based process have high equilibrium capacities, which means that they can capture a lot of CO_2 per kilo. “Under ideal conditions, MEA captures 60g of CO_2/kg, silica gel adsorbs 13.2g of CO_2/kg, and activated carbon adsorbs 88g of CO_2/kg. In contrast, a CaO-based process would capture 393g of CO_2/kg, assuming a 50% conversion of CaO over repeated cycles.” [8]
- Reaction-based separation processes are able to generate pure gas streams, because after regeneration the only gas produced is pure CO_2.

2.5. Terrestrial Storage *[1, 2, 4, 5]*

Geological sequestration of carbon dioxide presents a solution for reducing CO_2 emissions into the atmosphere. As shown in Figure 12 carbon dioxide can be stored in several ways:

- depleted oil and gas reservoirs
- saline formations(aquifer)
- minerals
- unminable coal seams

Pure carbon dioxide can also be used for enhanced oil or gas recovery, where sophisticated techniques are used to change the original properties of oil and gas. During this so called tertiary recovery the production life of a reservoir can be increased. However, enhanced oil and gas recovery will not be discussed in this thesis.

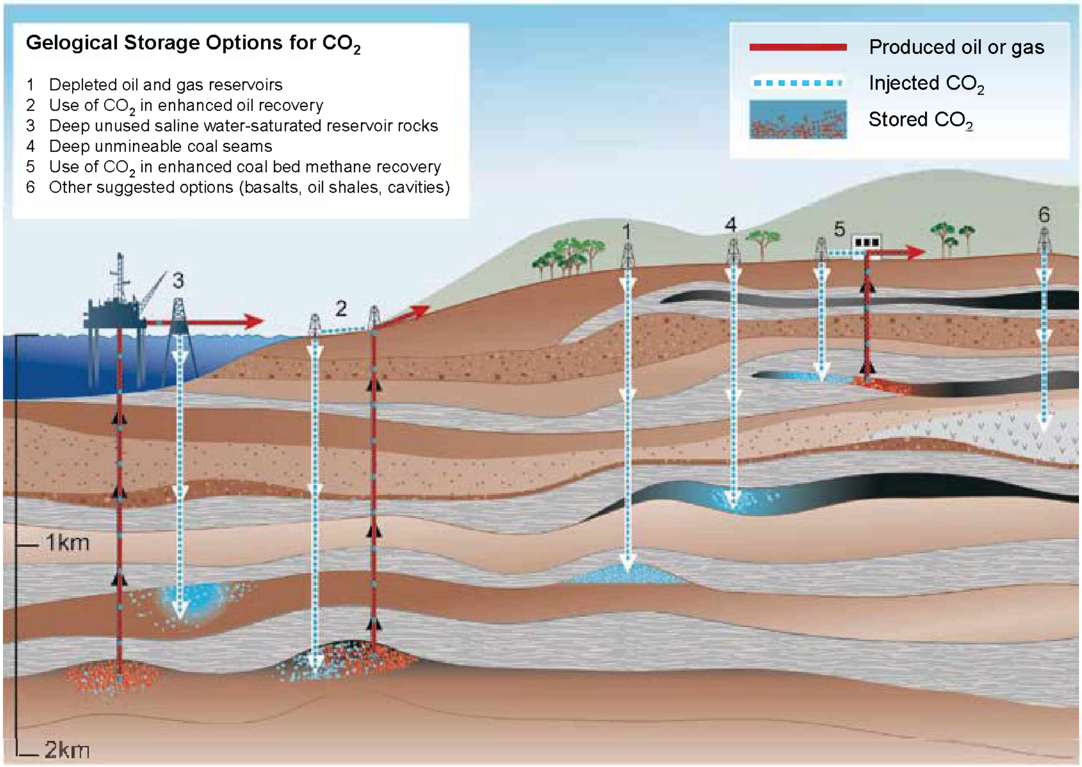

Figure 12: Ways of geological sequestration of CO_2. [1]

Of course not all options or reservoirs are feasible; it depends on local, technical, social, political and environmental conditions. If the CO_2 is injected into deep formations where high pressure exists, the carbon dioxide gas turns into a liquid or liquid-like supercritical dense phase and can move through the formation as a fluid. CO_2 has the tendency to be buoyant and will flow upwards until it reaches an impermeable layer, where the CO_2 will then be trapped below the seal rock. The most potential reservoirs are porous rock formations, which hold or have formerly held fluids. Such reservoirs are worldwide known, onshore as well as offshore. Moreover, there are also other trapping mechanisms. CO_2 molecules can dissolve in brine or fresh water, this is why saline formations (aquifers) are interesting for CO_2 sequestration. These molecules can also react with minerals to form solid carbonates (e.g. limestone) or they can be adsorbed into the pores of porous rock (e.g. coal seams).

2.5.1. Depleted Oil and Gas Reservoirs

These are formations, which hold natural gas or oil for million of years or have held it till now. Depleted gas fields demonstrate the simplest opportunity to store CO_2. They have proved their tightness over geological periods of time. This assumption is also valid for oil reservoirs. Usually there is a porous rock with a non-porous, impermeable rock structurally above it, thus creating a hydrocarbon trap. The benefits for this kind of CO_2 sequestration are the knowledge and experiences, which exist about these reservoirs. Data consisting of porosity and permeability values, the thickness of the seal rock and reservoir rock can all be available. As long as the integrity of these wells is granted only a re-completion has to be installed.

Modern reservoir simulations are able to estimate the probable CO_2 storage capacity by using the production data of the reservoir. Generally it is important to say, that the initial reservoir pressure should not be exceeded by the CO_2 injection volume.

2.5.2. Saline Formations/Aquifer

The advantage of deep saline formations (aquifers) compared to depleted oil or gas reservoirs, is the more widely geographical distribution. Regarding their common occurrence they have a vast potential for CO_2 storage capacity. Usually CO_2 is not generated in places next to depleted reservoirs, so the gas needs to be transported, which means additional costs. Saline formations are layers of porous rock that contain highly mineralized brines. A perfect formation/aquifer would have a huge pore volume, a large thickness, great permeabilites and also a good pressure communication over long distances to avoid large aquifer pressure drops during the injection. [5]

Unfortunately there is one serious disadvantage of saline aquifer storage. Relatively little information and experience are available compared to the depleted oil and gas reservoirs and also the sealing characteristics are less secure. Another, economically, drawback is that there are no existing wells drilled into saline formations.

2.5.3. Minerals

Mineral storage is another, secure method to store CO_2. Naturally occurring Mg or Ca reacts with CO_2 to form carbonates. This reaction has two major benefits: (1) Carbonates have a lower energy state than CO_2, which is why carbonatisation occurs naturally, (2) The materials are plentiful, for example like magnesium based minerals. On another side these reactions are very slow under ambient temperatures and pressure. The challenge here would be to speed up this reaction process but be economically and environmentally acceptable. That can happen, for example by reacting at higher temperatures and/or pressures. [2]

In Table 3 some earthen oxides are shown, which can react with CO_2 to form carbonates.

Table 3: Metal oxides and their carbonates. [2]

Earthen Oxide	**Percent of Crust**	**Carbonate**
CaO *Calcium oxide*	4.90	$CaCO_3$ *Calcium carbonate*
MgO Magnesium oxide	4.36	$MgCO_3$ Magnesium carbonate
Na_2O Sodium oxide	3.55	Na_2CO_3 Sodium carbonate
FeO Iron(II) oxide	3.52	$FeCO_3$ Siderite
K_2O Potassium oxide	2.80	K_2CO_3 *Potassium carbonate*
Fe_2O_3 Iron(III) oxide	2.63	$FeCO_3$ Siderite

The major earthen oxides in the crust, but which do not react to carbonates, are SiO_2 (Silicon dioxide) (~60%) and Al_2O_3 (Aluminium oxide) (~16%).

Finally it should be pointed out, that the generated carbonates are totally stable and a re-release of CO_2 into the atmosphere is not a problem. [2]

2.5.4. Coal Seams

In this section only unminable coal seams are taken into account. These are seams, which are too deep or too thin to be mined economically. Onto the pore surface of coals altering quantity of methane is adsorbed. So CO_2 sequestration into these unminable coal seams has two advantages: (1) The CO_2 can be stored and, (2) Due to this method of sequestration the methane recovery can be increased. CO_2 has a higher affinity with coal than CH_4 or N_2 (another possibility of CO_2 to mobilize CH_4). As a consequence of this higher affinity CO_2 is adsorbed onto the surface of coal by replacing the adsorbed methane. Some experiments showed that two or three molecules of CO_2 are adsorbed for one molecule of methane released.

A three times higher adsorption of CO_2 means that even if the recovered methane were to be burned and the CO_2 captured from this combustion injected again, then the coal seam can still offer a net storage in CO_2. [5]

There are also some disadvantages with this process: Coal that adsorbs CO_2 can swell, which can cause a drop in permeability. The worst case would be that no further injection of carbon dioxide is possible due to this swelling process. Moreover, like the saline aquifers also coal seams are not well understood at the moment but this can be changed in the future.

2.6. Marine Storage

Another way to sequestrate the carbon captured after combustion is in the oceans. Theoretically, the potential would be enormous. Two different models have to be classified. Firstly, the “dissolution” model where the carbon dioxide is injected at depths of 1000m or deeper, where it then dissolves in the salt water. For depths greater than 3000m the “lake” model would be present. Since the density of CO_2 is higher than seawater, in depths greater than 3000m, the carbon dioxide will sink and form a “lake” of hydrates at the sea ground or plumes (Figure 13). The CO_2 is transported to the storage site by pipelines or ships, where it is injected directly into the water column or onto the sea floor.

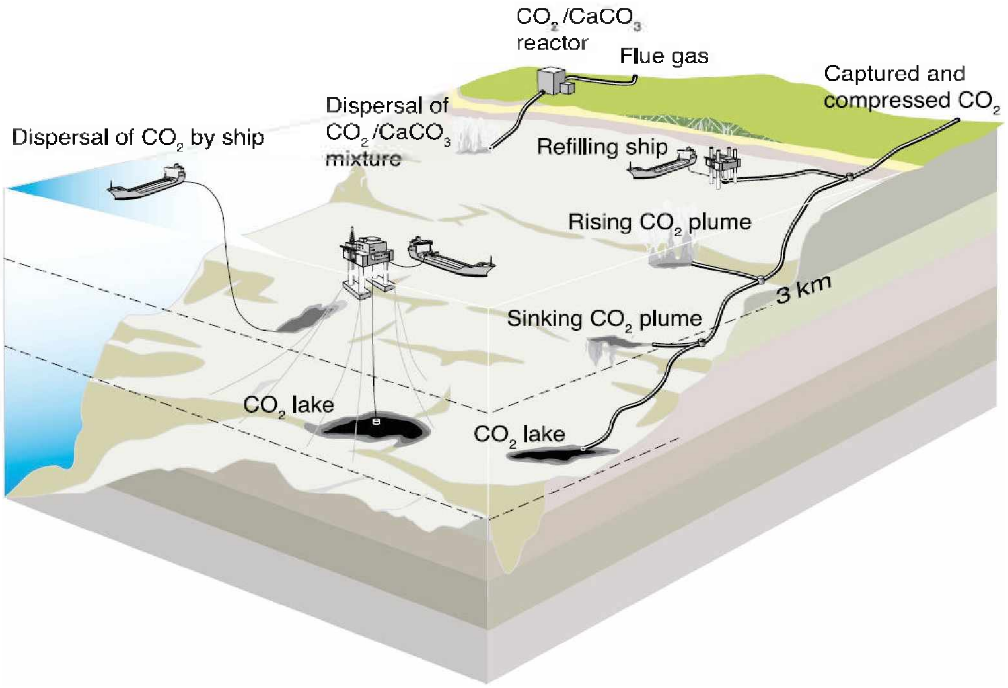

Figure 13: Methods of ocean storage. [1]

Logically, environmental damages will follow; these large CO_2 concentrations will suffocate the ocean organisms. The CO_2, which is not dissolved in water or laying as hydrates on the sea ground, can react with water to from carbonic acid H_2CO_3. So the acidity of the ocean will increase and more environmental problems will influence the plant-based and animal life in the oceans.

The main uncertainty is that it is not proven if sometime the dissolved carbon dioxide or the hydrates will move to the sea level and equilibrate with the atmosphere. Due to the climatic change an increase in the ocean temperature is predicted, which will lead to melting of the CO_2-hydrates. The carbon dioxide is no longer solid, dissolves in the sea water and reaches the ocean currents. These movements lead to a change in pressure and temperature. Sooner or later, water containing carbon dioxide will reach the ocean surface and enables the CO_2 to equilibrate with the atmosphere. So the storage would not be for eternity. Additionally, there are legal, political and social difficulties.

To sum up the ocean storage in one sentence: it is risky and totally insecure.

2.7. HSEQ – Risks in Carbon Sequestration

As mentioned above every kind of CO_2 storage has its own environmental risk potential. Generally two categories of risks are present, local risks and global risks. Should there be CO_2 leakage out of the storage formation, local danger exists for humans, ecosystems and groundwater, these are called local risks. However, global risks involve the release of CO_2, which may significantly influence the climate change.

The following section – which is divided into subterranean risks and submarine risks – should give an overview of the current knowledge, but also the lack of knowledge considering health, safety and environmental risk of carbon dioxide sequestration.

2.7.1. Subterranean Risks [6]

All the risks of CO_2 storage in subterranean reservoirs can be divided into five categories (Figure 14): [6]

- CO_2 leakage: CO_2 can migrate from the injection reservoir to other formations or may reach the atmosphere.
- CH_4 leakage: CO_2 injections in coal seams allow a sudden mobilisation and migration of CH_4, which may migrate as well to other formations or may also reach the atmosphere.
- Seismicity: CO_2 injection in geological reservoirs may cause seismic movements.
- Ground movement: Pressure changes, which are an outcome of CO_2 injection, may result in uplift of the earth surface.
- Displacement of brine: Brine can be displaced by CO_2 injection in reservoirs but also by injection in open aquifers. The brine will flow to other formations and possibly also in sweet water bearing formations.

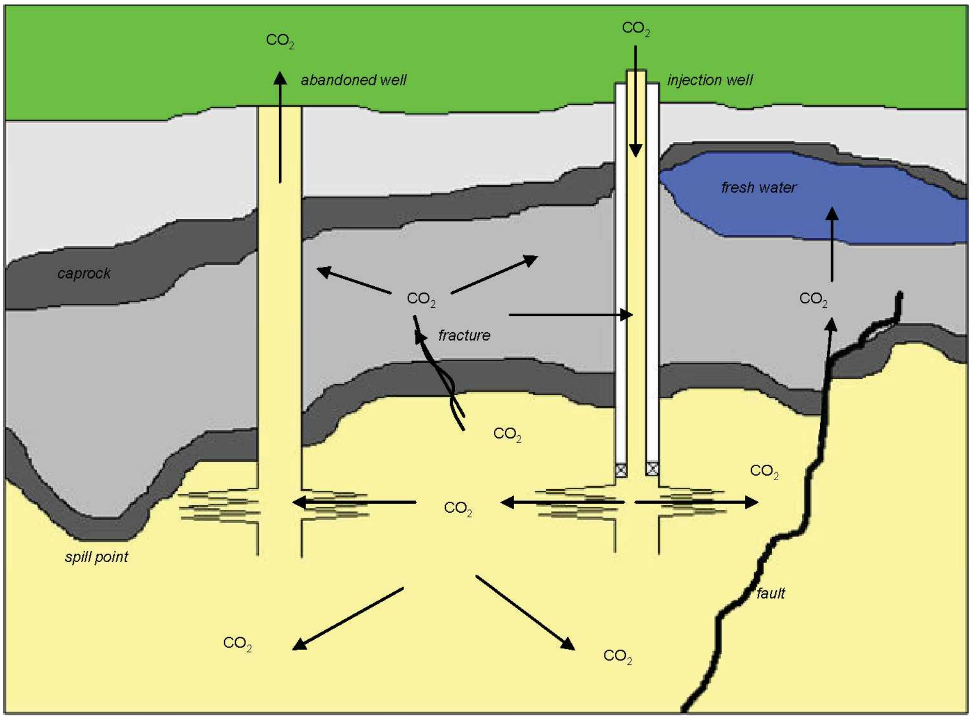

Figure 14: Risks of underground storage.

2.7.1.1. CO_2 Leakage

For every storage type, CO_2 leakage is a potential danger. As shown in the figure above, CO_2 can migrate through leaks in the cap rock or via faults to other formations or aquifers. Carbon dioxide can also escape through spill points (structurally lowest point in the reservoir, Figure 14) or dissolve in fluid. In the worst case scenario, it can leak to the atmosphere, e.g. through poor cementing (CO_2-non-resistant cement) or corrosion of abandoned wells (Figure 18).

2.7.1.1.1. CO_2 Leakage through cementation

A carbon dioxide leakage through the annulus can occur much faster than through the formation rock. It is necessary to avoid it by the use of CO_2-resistant cement. Schlumberger proposed some experiments to study the reactivity of CO_2-Water-Cement systems of Portland (non-resistant) cements and compared it with the results for a new CO_2-resistant cement. The conditions of these experiments are 90°C at 280 bars (supercritical, cp. Figure 1).

The conclusion of this experimental study on cement degradation is that Portland cement is neither resistant enough to wet supercritical CO_2 nor to CO_2-saturated water. After six months a high deterioration and a spalling effect is observed, which results in a significant pH decrease. Furthermore, dissolution occurs, which starts earlier in CO_2-saturated water than in wet supercritical CO_2. In comparison, the CO_2-resistant cement shows only a low amount of calcium carbonate precipitates in the samples. However, the value of pH is decreasing as well, like in Portland cement. This CO_2-resistant cement remains comparably inert in both wet supercritical CO_2 and CO_2-saturated water phases and shows a good stability. [26]

2.7.1.1.2. CO_2 Leakage through corrosion

Carbon dioxide corrosion results when CO_2 dissolves in water to form carbonic acid (H_2CO_3). The acid may lower the pH and sufficient quantities may promote general corrosion and/or pitting corrosion of carbon steel. The corrosion occurs by a loss of electrons from the metal. An increase in partial pressure of CO_2 results in lower pH condensate and higher rates of corrosion. Corrosion occurs in the liquid phase, often at locations where CO_2 condenses from the vapour phase. As shown in Figure 15, it is more corrosive than H_2S but less than oxygen.

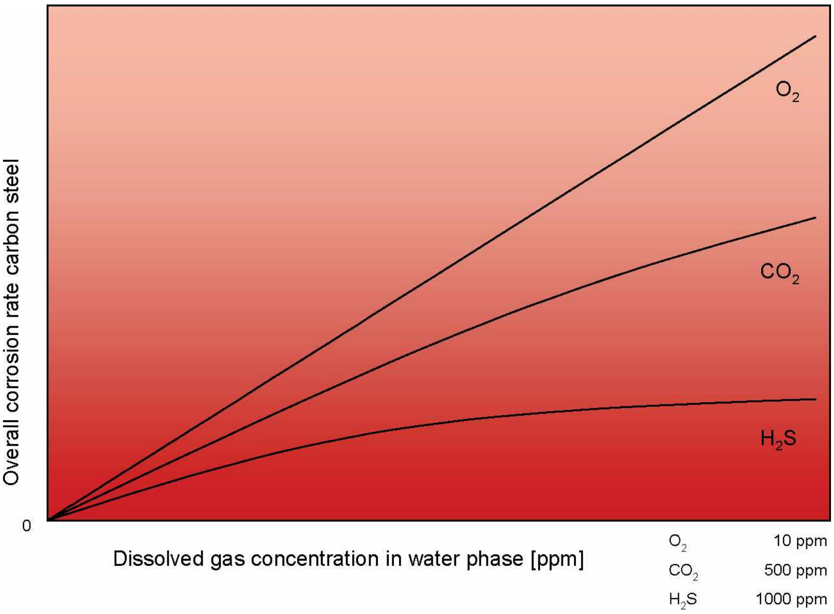

Figure 15: Corrosion rates of O_2, CO_2 and H_2O. [27]

Another issue is the corrosion on the outer tubing wall, that which is facing the formation. CO_2 is pumped with high pressure into the formation. Due to the pressure difference above the perforation, carbon dioxide is able to migrate and may reach the outer casing wall (Figure 16). Under this carbon dioxide attack, corrosion can occur, which may lead to CO_2 leakage.

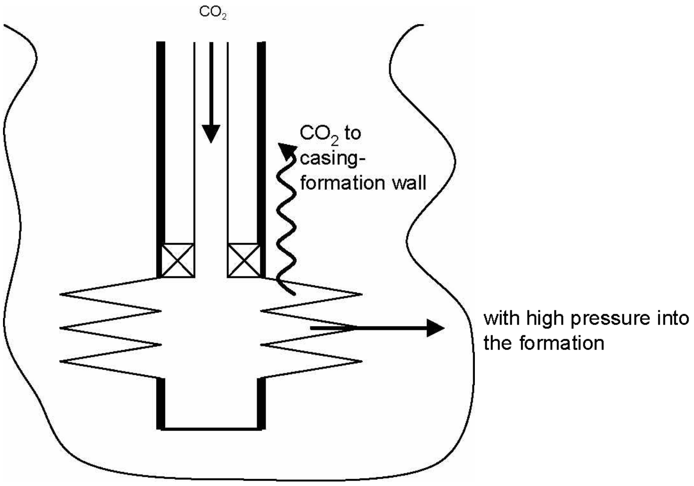

Figure 16: CO_2 corrosion on the casing.

2.7.1.1.3. CO_2 Leakage through abandoned wells

A further consideration must to be taken on old, abandoned wells which for example keep a fish, are plugged with a cement plug above and sidetracked by a new well (Figure 17). Carbon dioxide can migrate from the perforated horizon 2 to the uncased abandoned well and from there to other formations which are not able to trap carbon dioxide. Sooner or later, CO_2 will find a way to migrate to the surface.

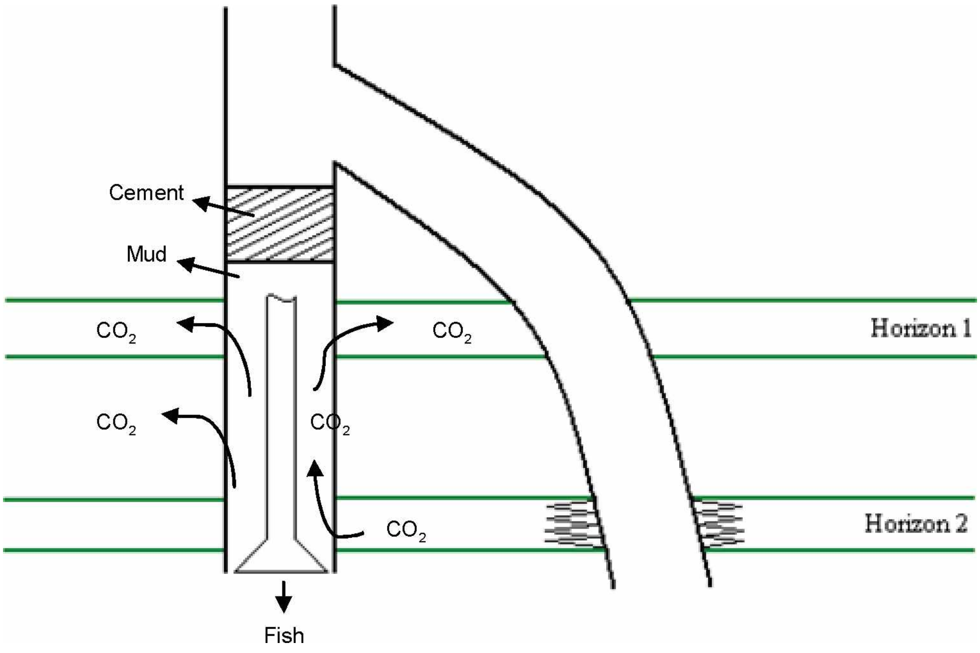

Figure 17: CO_2 leakage possibilities at sidetracked wells.

Another hazard may arise if it becomes necessary to drill through a reservoir containing the stored carbon dioxide. That will result in several drilling problems: Carbon dioxide is brought to the annulus by the mud. The carbon dioxide then dissolves in the mud thus reducing the mud weight. It is then liberated in the annulus due to pressure reduction; a pressure loss in the mud will follow. More carbon dioxide flows from the reservoir into the well, so the mud weight must be increased again. This ends in a vicious cycle, because once the maximum in mud weight will be obtained.

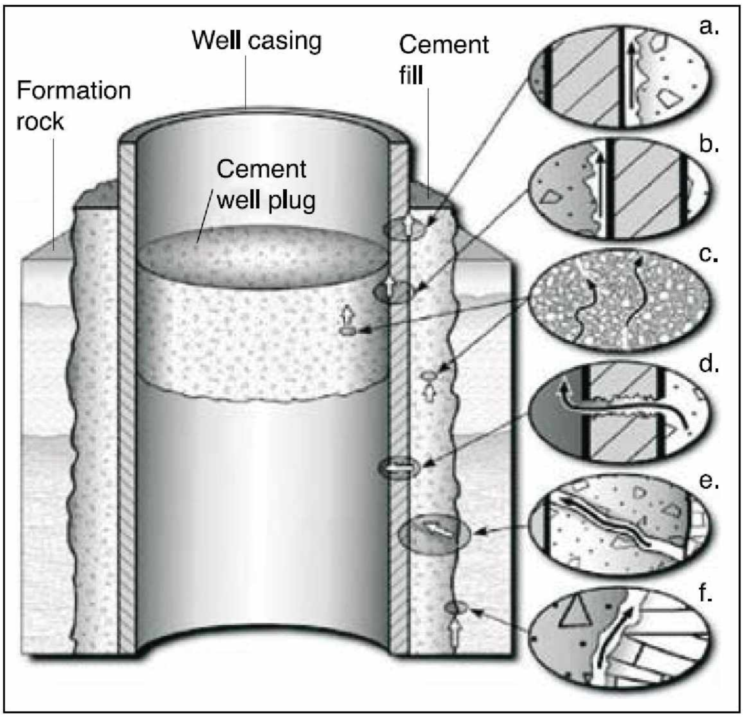

Figure 18: Possible leakage pathways in abandoned wells: (a) and (b) between casing and cement wall and plug; (c) through cement plugs; (d) through casing; (e) through cement wall; and (f) between cement wall and rock. [1]

2.7.1.1.4. Trapping mechanisms

Generally, the potential for a leakage of CO_2 depends on the sealing capacity of the cap rock and on the different trapping mechanisms. Following trapping mechanisms can retain CO_2 in reservoirs [6]:

- When injecting CO_2 in a hydrocarbon reservoir, gaseous or supercritical CO_2 will rise up due to buoyancy effects. The presence of geological traps such as low-permeable cap rock will prevent the CO_2 to migrate further; CO_2 will accumulate under the cap rock.

- CO_2 injected in deep saline aquifers might take thousands to millions of years to migrate from injection point to surface due to the extremely low flow rates encountered in these formations (hydrodynamic trapping).
- CO_2 can partly be trapped in the pore space by capillary forces (residual gas trapping).
- Since CO_2 is highly soluble in water and also dissolves in oil, solubility trapping is an important trapping mechanism. When injecting CO_2 into an aquifer, CO_2 will mainly be present as supercritical fluid before it fully dissolves. Model calculations of CO_2 injection indicate a complete dissolution taking place on a time scale ranging from 5000 to 100 000 years. When CO_2 is completely dissolved, leakage is no longer possible, since free CO_2 is not present anymore. This is provided that no CO_2 is released as a consequence of pressure and temperature changes in the reservoir.
- Dissolved CO_2 can react with silicates or carbonates to form bicarbonates or carbonate ions (ionic trapping).
- CO_2 can also react with minerals and organic matter present in the geologic formations to become part of the solid matrix, also referred to as mineral trapping. This is the most secure form of trapping. However, the extent to which injected CO_2 reacts with minerals present in either sandstone or carbonate reservoirs is considered to be low.
- In coal seams, CO_2 will be trapped by adsorption to the coal surface displacing adsorbed methane and by physical trapping in the cleats within the coal. Due to adsorption to the coal surface, less “free” CO_2 is present. Consequently, the risk of leakage in coal seams is expected to be smaller than for hydrocarbon reservoirs and deep saline aquifers, where CO_2 is predominantly present in free state in the first phase after injection.

Nevertheless these trapping mechanisms can fail and CO_2 can escape from its primary storage formation. A few situations, which lead to CO_2 leakage, are described below:

- Through the very slow but long-term expected diffusion process of CO_2 through the cap rock.
- Non-wanted man-made fractures (hydraulic fracturing), which are generated by over pressurization of the reservoir, provide new pathways for the CO_2 to follow.

- Reaction of CO_2 with the cap rock can result in high permeability zones, which cause the cap rock to dissolve. Furthermore, CO_2 can dehydrate clay shales in the cap rock and that increases again the permeability.
- Seismic action can cause a cap rock failure.
- In unminable coal seams a swelling reaction of the coal matrix can happen when CO_2 is injected and that can cause a reduction in permeability. Swelling means a volume expansion, which can induce stresses on the overlying and underlying formation. These can have the effect of faulting and possible pathways generation out of the coal seam.

2.7.1.2. CH_4 Leakage

As described in the terrestrial storage of CO_2 in coal seams, a sudden mobilisation and migration of CH_4 can occur as an effect of CO_2 injection. That's why a secure production of this methane should be planned. It is important to proclaim that CH_4 is more mobile than supercritical CO_2. Since methane is also a greenhouse gas, CH_4 leakage or emission is an important issue, which should be avoided. [6]

2.7.1.3. Seismicity

Injections of big amounts of fluid into a formation increase its pore pressure and modify the underground stress behaviour. Furthermore, fractures are created, which can cause micro seismicity and some earth tremors to occur. The potential danger here is damage to the cap rock, which is then not able to efficiently seal any more. So, the injected CO_2 can flow through these new channels upwards and might reach the atmosphere at some point. That will again result in a slow pore pressure change in the reservoir.

The probability of seismicity is assessed as low, but nevertheless, it must be totally observed. [6]

The chance of seismic occurrence can be minimised by intense and careful monitoring of the injection pressure, the in situ stresses and the pore fluid pressures. It should also be mentioned that the initial reservoir pressure should not be exceeded.

2.7.1.4. Ground movement

Like the occurrence of seismic activity also ground movements are a consequence of man-made pressure changes. This subsidence or uplift can cause damages on buildings or infrastructure and can also cause seismicity.

Generally, the mechanism of subsidence is well understood, but prediction can be very difficult. Moreover, it is not conceivable that an uplift movement can take place as a result of CO_2 injection as long as the maximum storage pressure does not exceed the initial reservoir pressure. Not only man-made pressure changes can cause subsidence, also chemical reaction between CO_2 dissolved in brine and the reservoir rock can result in dissolution of the reservoir rock (chemical compaction). In the beginning, caves can be formed under the weight of the overburden formation but later it may result in a subsidence. This chemical dissolution effect can be more dangerous in carbonate rocks with high porosity. [6]

Furthermore, subsidence can result in a casing deformation, in a casing collapse and/or in sheared casings (Figure 19). For all three situations, carbon dioxide is able to move away from its original pathway into ambient formations where the carbon dioxide can not be trapped and so might be able to migrate to the surface.

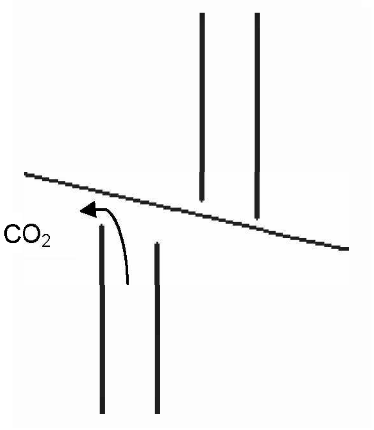

Figure 19: Shared casings due to subsidence.

2.7.1.5. Displacement of brine

As shown in Figure 14 brine can be displaced to other formations by injection of CO_2. If there are fractures or faults, which can be caused by seismicity or ground movements, the saline groundwater will migrate easily to sweet water bearing formations, where it will increase its salinity. The consequences of displacing brine are still uncertain; a rise in the water table (negative impact for depression landforms) can be possible. [6]

Monitoring is a very important element for geological storage projects. Protocols or seismic surveys can document possible CO_2 migration in the underground.

2.7.2. Submarine Risks

These potential risks can only be suggested to because there are no long term studies available. What we can be sure of, is that there is a measurable change of the ocean chemistry in the region of injection form several $GtCO_2$. Alternatively if an injection of hundreds of $GtCO_2$ takes place, the changes will be obtained for the entire ocean. Furthermore dissolved CO_2 in sea water causes an increase in the partial pressure of CO_2 and a decrease of the pH (more acidic). This effect can also cause dissolution of $CaCO_3$ in sediments or in shells of organisms. It must be noted that no controlled ecosystem tests have been made in the deep ocean, but it is expected that the degree of impacts will increase with increasing CO_2 concentrations and/or decreasing pH value. These impacts are not well understood at the moment. [1]

“In the few relevant studies conducted thus far, the public has expressed more reservations regarding ocean carbon CO_2 storage than for geological CO_2 storage.” [1]

Finally it is interesting to mention, that for example the German government would accept a maximal leakage rate of 0.01% per year that means that after 1000 years still 90% of the injected CO_2 is remained in the storage. [7]

3. Processes applied

In the following chapter, specific sorbents are chosen for the processes described in the previous part (only post-combustion). For every carbon dioxide capture process several types of sorbents can be taken into consideration but not all fit. The reasons for electing the sorbents are explained and also how the process schematic looks like by taking these sorbents.

First, the absorption process is pointed out, which is driven here by using MEA (monoethanolamine) as sorbent, followed by pressure swing adsorption, gas separation membranes and finally the carbonation-calcination process by using lime water is explained.

3.1. Monoethanolamine (MEA) – Absorption

As mentioned in chapter 2.4.1. amines are typical solvents for a chemical absorption. They are classified into three sections: primary, secondary and tertiary amines.

3.1.1. Primary Amines

Primary amines, such as MEA are classic solvents for acid gas removal. In comparison to other alkanolamines MEA is the least expensive one and has also the lowest molecular weight. Due to this low molecular weight MEA has the highest theoretical capacity for absorption of CO_2. This is only theoretical as in practice corrosion problems occur, which in turn reduce the absorption capacity. Furthermore, “MEA has the highest vapour pressure of any of the alkanolamines and high solvent carryover occurs during carbon dioxide removal from the gas stream and in the regeneration step. To reduce solvent losses, a water wash of the purified gas stream is usually required, which incurs on the additional cost of operation.” [9] Unfortunately, a contact between the aqueous MEA and impurities can result in foam. When using MEA to absorb CO_2 high rates of absorption and desorption can be reached, but greater energy requirements cause a high increase in the capture costs. Another primary amine is Diglycolamine, which is suitable like MEA for absorption of acid gas components. The reason why MEA is preferred is that MEA has higher absorption capacities than Diglycolamine.

3.1.2. Secondary Amines

Secondary amines, such as DEA or DIPA (diisopropylamine), seem to have advantages over primary amines. The energy requirements for regeneration are less compared to MEA, which result in a decrease of operating costs. However, secondary amines are unreliable if the flue gas stream contains higher CO_2 levels. This is a result of different degradation mixtures being built, which can not be regenerated by heat. This solvent waste requires the use of a reclaimer.

3.1.3. Tertiary Amines

Tertiary amines, e.g. MDEA, have again lower energy requirements for solvent regeneration than primary or secondary amines. However, tertiary amines react slower with CO_2, which means that higher circulation rates are necessary to absorb as much CO_2 as the previous groups of amines.

It is also important to mention that (aqueous) amines are not corrosive to carbon steel, but connected with carbon dioxide serious corrosion damage can occur. Inhibitors should therefore be used within all amines. The corrosion is highest when using primary amines and less when using tertiary amines.

For the applied process example MEA is used as liquid solvent because:

- least expensive alkanolamine
- highest absorption capacity
- no creation of non-reclaimable compounds
- low solvent waste
- no reclaimer-section necessary

3.1.4. Process Flow Description

After cooling the flue gas down to 50°C and compress the gas to 50 bar, it is then pumped into the absorber where it is brought into contact with the aqueous MEA (at temperatures about 40°C to 80°C). The flue gas rises from the bottom to the top whereas the MEA is injected into the absorber at the top. This is called countercurrent absorption. In the absorber column the CO_2 is captured by the aqueous MEA at the moment of contact. The CO_2-free flue gas, so called waste gas, is released from the

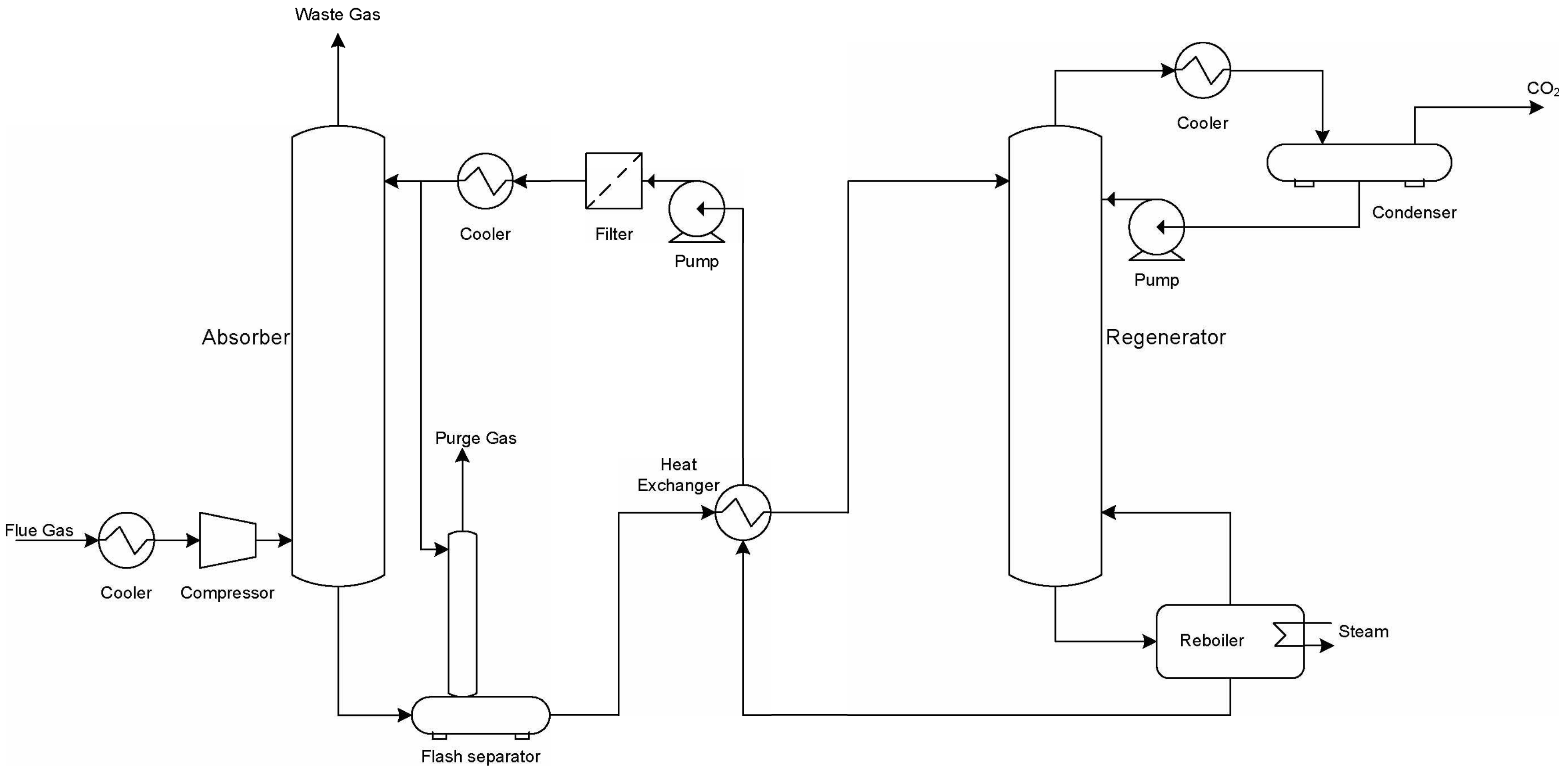

Figure 20: MEA-Absorption process.

top of the absorber and can be vented into the atmosphere. The rich MEA falls downwards and is transported to a flash separator where co-transported rest gas can be desorbed again. Afterwards the aqueous MEA, with the chemically bounded CO_2, is brought to the regenerator column (stripper) by passing a heat exchanger where it is heated up. The regeneration of the solvent takes place by heating it up to temperatures of 100°C to 140°C. The saturated MEA entering the regenerator at the top is heated up by dripping downwards and by flowing through the reboiler, where the hottest point is, so that the chemical bond with CO_2 is destroyed. The gaseous CO_2 and the generated steam rise upwards while the lean MEA cumulates at the bottom. To obtain a pure CO_2 stream it is necessary to get rid of the water, which is done by passing a cooler and a condenser and it is finally diverted back into the stripper, while the carbon dioxide is piped to a compressor for further transport. The regenerated solvent flows back to the absorber by passing the heat exchanger, a pump, a filter and finally a cooler. The filter is necessary to remove potential impurities. At this point, as the lean amine enters the absorber column once more, the circle can start again.

3.1.5. Modifications of Amine Based Processes

There are two possibilities to enlarge the absorption capacity of an amine based process, dual stream and activated.

3.1.5.1. Dual stream amine process

The difference to the in 3.1.4. described absorption process is that not the total amount of rich aqueous monoethanolamine is passing the reboiler entirely. Some is leaving the regenerator before reaching the hottest point. It is directly conducted back to the absorber to come again in contact with carbon dioxide containing flue gas (see the process flow schematic below).

This process is very energy efficient and can save about 5-10% of energy compared to the standard MEA absorption process. [29]

3.1.5.2. Activated amine process

Aqueous amine can be activated by addition of 2% of piperazine, which is acting like a catalyst; it is not taken up by the reaction but speeds up the reaction between amines and carbon dioxide. The only disadvantage is that piperazine reacts sensitive to changing pressures and temperatures.

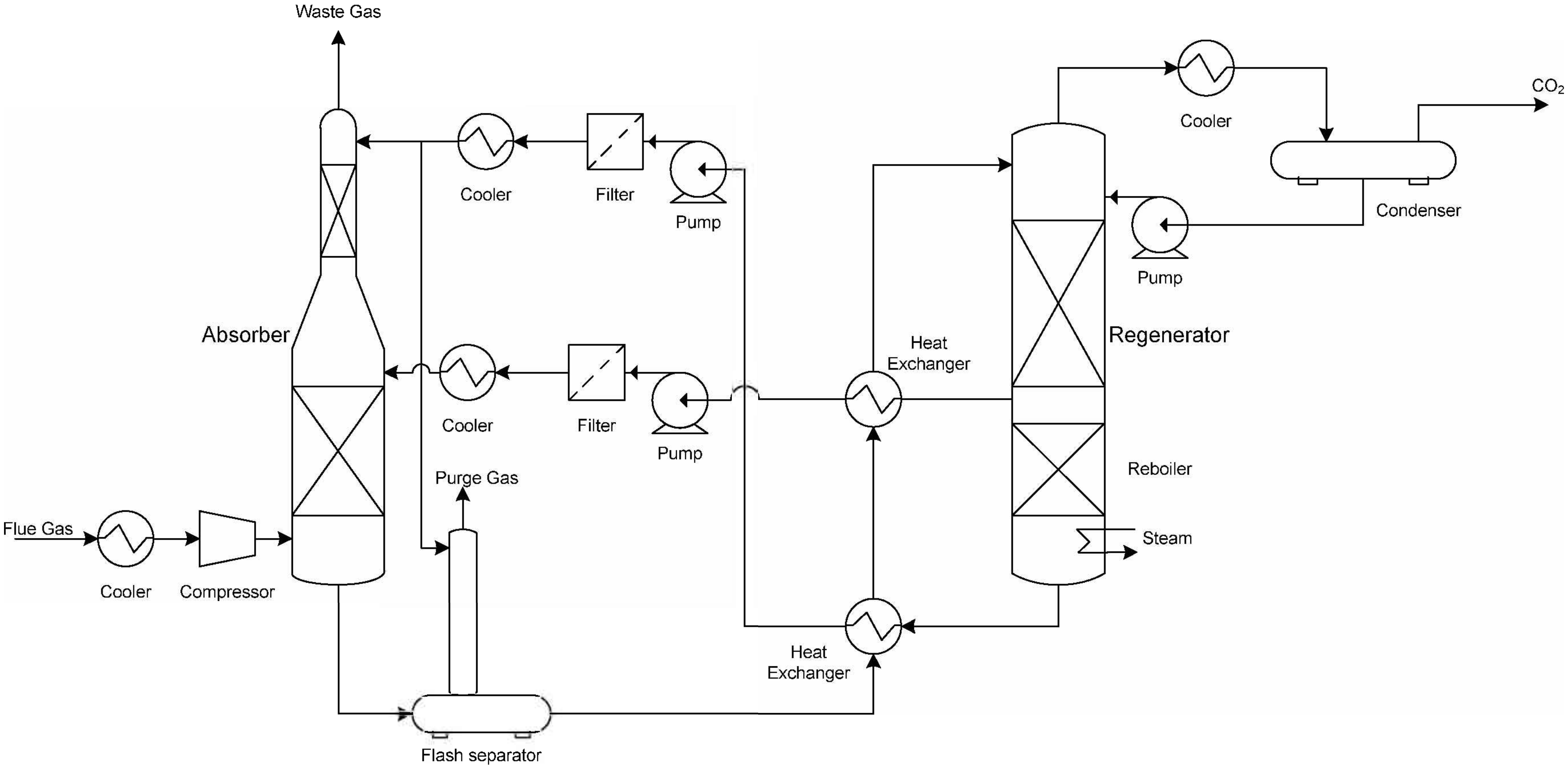

Figure 21: Typical dual-stream amine process.

3.2. Pressure Swing Adsorption

Desorbing CO_2 out of flue gas can be achieved by PSA or TSA. For VSA and ESA more research needs to be done to make these two applications commercial. In practice pressure swing adsorption is preferred over temperature swing adsorption [1]. The reason for this are the longer cycle times for sorbent regeneration, which are needed for temperature swing adsorption.

What kind of adsorbent should be taken?
Actually there are two main adsorbents: activated carbon or zeolites.

3.2.1. Activated carbon

The name “activated” means that this material has a very high surface area due to its very porous structure. One gram of activated carbon can have 300 to 2000 m^2/g and its density is about 200 to 600 kg/m^3. The size of the pores is responsible for the adsorption properties. Activated carbon can be generated out of wood, brown or mineral coal, peat or plastic material. The raw material is going to be dehydrated by distillation at temperatures of 500 °C to 900 °C. Afterwards the activation takes place (see below). Activated carbon has a wide range of usage; impregnated with other chemicals it can be used for example for gas masks to adsorb chemical toxicities. [19]

Figure 22: Activated carbon. [19]

3.2.1.1. Reactivation

Actually it is necessary to distinguish between two types of activation:

3.2.1.1.1. Physical reactivation

There is the so called *Carbonisation* where the carbon is pyrolysed (thermal decomposing) in inert atmosphere (nitrogen or argon) at temperatures of 600°C to 900°C. Or the *Oxidation* process where the raw material is exposed to oxidising temperatures about 600°C to 1200°C. Generally one of these procedures is chosen but they can also be combined. [19]

3.2.1.1.2. Chemical activation

The carbon is impregnated with acid (like phosphoric acid or sulphuric acid), with bases (e.g. sodium hydroxide) or with salts (e.g. zinc chloride) at temperatures in the range of 450°C to 900°C. Chemical activation is preferred to physical due to the lower temperatures needed and the shorter activation time. [19] Nevertheless, chemical activated carbon can not be used in every case.

3.2.1.2. Types of activated carbon

It is also important to differentiate between three different types of activated carbon, dependent on the corn size and on the inner surface area:

3.2.1.2.1. Powdered Activated Carbon (PAC)

Powdered Activated Carbon consists to 90% of corn, which is smaller than 0.18mm. Commonly it is used for cleaning of liquids (waste water, ground water, water of swimming baths, food industry and for decolouration). After the adsorption process the powered activated carbon has to be separated from the liquids by filtration. [21]

3.2.1.2.2. Granulated Activated Carbon (GAC)

Classified by CEFIC (Conseil Européen de l'industrie Chemique – European Chemistry Industry Council) granulated activated carbon should consist to 90% of particles bigger than 0.18 mm. Like powdered, the granulated activated carbon is used for purification of liquids and water treatment. The coarser grained GAC is also used for air treatment. Compared to PAC where the activated carbon is added to the liquids, using GAC a packed bed adsorption has to be installed. [21]

3.2.1.2.3. Extruded Activated Carbon (EAC)

This is the type with the biggest corn sizes. They can vary from 1,5mm up to 8mm. This type is mainly used for gas phase applications such as flue gas and waste gas treatment to get rid of toxic substances or to re-extract solvents. When using EAC a packed-bed adsorption is needed where the gas stream can pass the activated carbon bed (mostly from bottom to top). [21]

3.2.2. Zeolites

"Zeolite" is a Greek word, which means "stone that boils" and is named after a typical property; it is boiling when it is heated up (regeneration). Zeolites (Figure 23) are aluminiumsilicate minerals with a microporous structure (Figure 24), which have the ability to adsorb liquids or gases. They occur naturally but more often these are synthetic also. Typically they are used as ion-exchange beds for example for water deionisation, for creation of cleaning agents or for molecule separation.

Figure 23: Zeolite. [20]

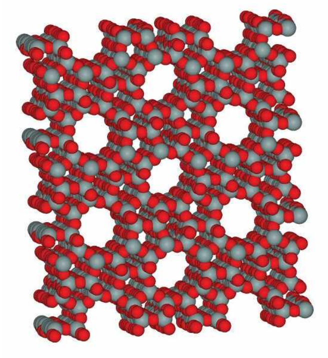

Figure 24: Micorporous structure of zeolites. [20]

If zeolites are used, a clean process can be guaranteed. Zeolites have a clear defined structure, which gives them a high mechanical stability and due to that also, a high mechanical integrity. Nevertheless, they are mostly used for temperature and not for pressure swing adsorption.

Extruded activated carbon (the activation type is not an issue here) is preferred compared to zeolites for this pressure swing adsorption process to capture CO_2 out of flue gas. EAC has lower capital expenditures than zeolites but nevertheless, the operating expenditures are expected to be higher, because activated carbon has to be renewed more often due to the rubdown of coal dust. Furthermore, another drawback for activated carbons is the lower mechanical stability compared to zeolites.

3.2.3. Process Flow Description

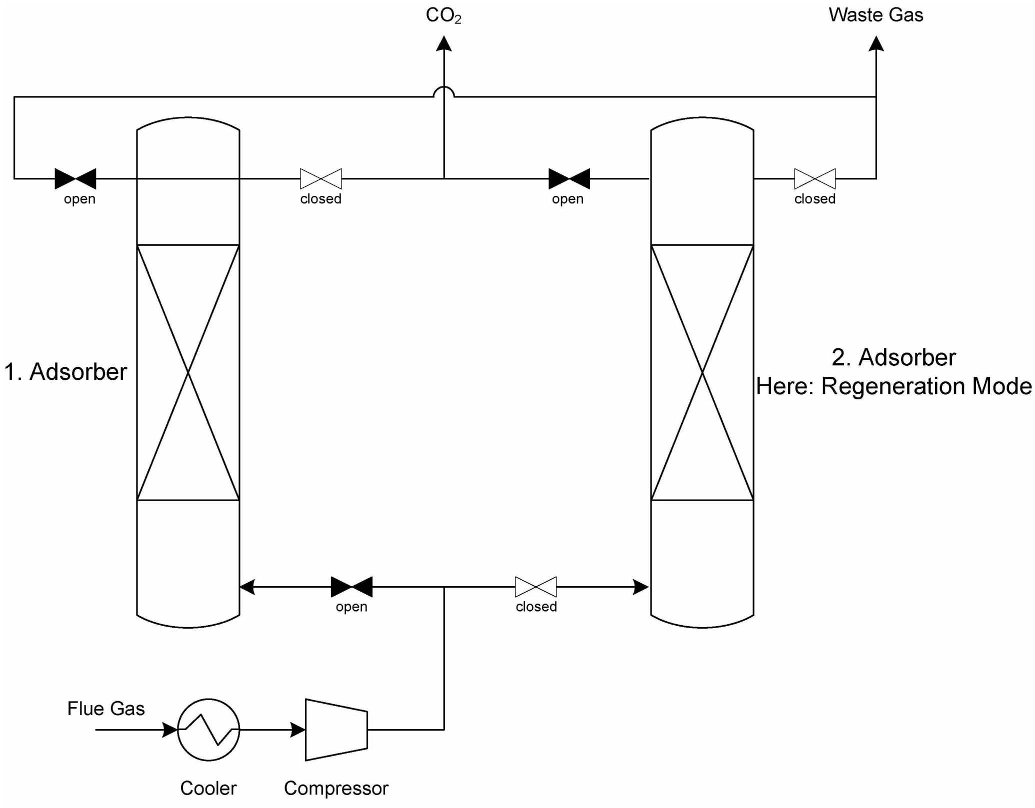

Figure 25: PSA process.

Before the flue gas reaches the adsorber column it has to be cooled and compressed up to the pressure needed in the adsorber (about 15bar). The cold, compressed flue gas enters the adsorber at the bottom and passes the activated carbon packed bed. Carbon dioxide is adsorbed by the extruded activated carbon while the waste gas leaves the adsorber at the top and is vented to the atmosphere. In order for the regeneration to take place, the valve positions change and the pressure is released into the CO_2 pipeline. The regeneration arises at atmospheric pressure; the carbon dioxide is released from the adsorption bed into the pipeline. After a defined regeneration time the valves change position and again flue gas is entering at the bottom.

3.3. Gas Separation Membrane

Using membrane technology, for capturing CO_2 out of flue gas, it is necessary to distinguish between two different types of membranes:

- Gas separation membranes
- Gas absorption membranes

Gas separation membranes are preferred in this capturing process, since they have lots of advantages compared to gas absorption membranes (see 2.4.3.).

The main selection criterion for using membranes, is the difference of partial pressures between the feed side and the permeate side. So this pressure difference influences the membrane area, which is needed to attain the required separation at given feed conditions.

As also mentioned in chapter 2.4.3. gas separation membranes can be structured as hollow fiber or spiral-wound modules. For these two modules the two most common materials are chosen and described by the following subchapters.

3.3.1. Polyimide Membranes

Polyimide membranes are hollow fiber membranes as shown in Figure 26. Using this type of membranes, the feed gas enters the membrane through the fibres. There, the carbon dioxide is transferred, due to the partial pressure difference, into the annular space where the enriched stream of CO_2 can easily be routed out. The waste gas, which can then be vented to the atmosphere, leaves the membrane at the end by flowing out of the smaller fibres.

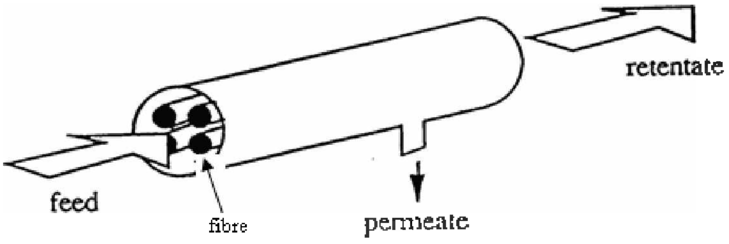

Figure 26: Hollow fiber module. [10]

Polyimides have high temperature stability and thus a good heat resistance. Furthermore, they have a low coefficient of thermal expansion. It is important to mention the low water absorption capacity of polyimides and their sensitive behaviour to water. If such membranes are used, a serious pre-treatment (cooling and water removal) must be necessary to get rid of the steam, which will condensate and can then be removed from the flue gas. Polyimides desintegrate by hydrolysis if contacted by water.

3.3.2. Cellulose Acetate Membranes

Cellulose acetate membranes are spiral-wound membranes, which act according to Figure 27. The cellulose acetate is wounded spirally around a perforated pipe. The feed gas enters the membrane section along the cross section of the membranes, it seeps through and leaves the membrane as waste gas reduced in carbon dioxide. The CO_2 is permeating to the centre of the membrane – the perforated pipe – where it can be easily removed, e.g. by a pressurized CO_2 stream.

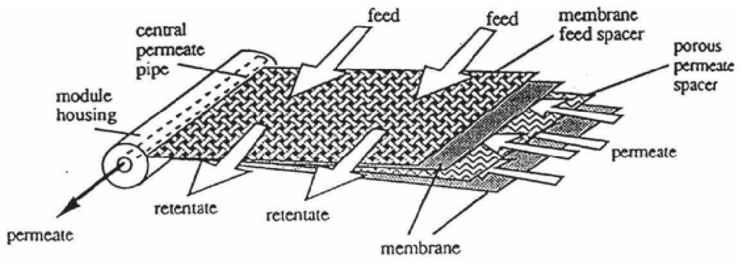

Figure 27: Spiral-wound principle. [10]

Cellulose acetate is a thermoplastic plastic, which is generated when natural occurring cellulose reacts with acetic acid. It is soluble in acetone and flame resistant to a temperature up to 300°C. At temperatures between 180 and 200°C cellulose acetate is thermoplastic deformable. Like polyimides also cellulose acetate can only absorb a low value of water vapour (maximum ~6%), just swelling a little but drying fast again. Due to the low water absorption cellulose acetate has the tendency of picking up a slight electrostatic charge. The fibers deflagrate with a blue tinted flame and by forming drops. [24]

Generally, the efficiency of the membranes and the purity of the separated stream of carbon dioxide depend on the temperature existing in the membrane. The selectivity is decreasing with increasing temperature and the permeability is increasing with increasing temperature, which should be avoided. Optimization of the process temperature is mandatory to achieve positive results!

Since cellulose acetate is not that sensitive to water as polyimide membranes, it is preferred for capturing carbon dioxide from flue gases.

3.3.3. Process Flow Description

As in the previous processes the flue gas has to be cooled here as well, down to temperatures in the range of 40-50°C. The cooling process is important to get rid of the steam, which condenses and is then piped to a water tank. Afterwards, the steam-free flue gas is transferred to a compressor where it is compressed to 40 to 50 bars to increase the partial pressure difference occurring across the membrane. Within the membrane the carbon dioxide dissolves into the membrane material and is transferred through it by the partial pressure difference. The enriched CO_2 and the waste gas can be governed in two different pipes to their next destination.

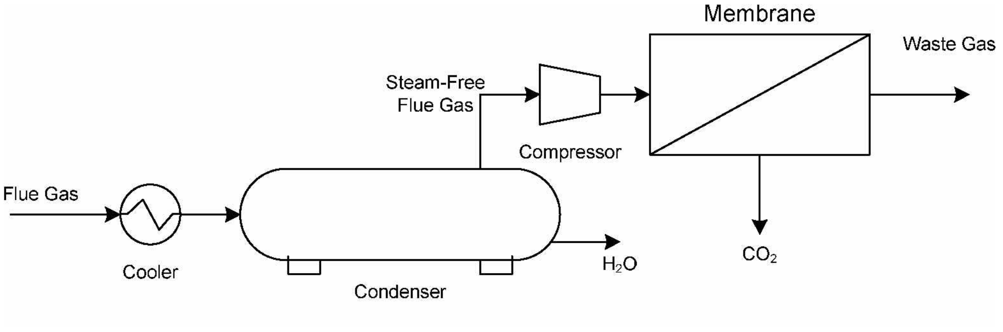

Figure 28: Membrane process.

3.4. Carbonation-Calcination Process

A carbonation-calcination capture process can occur in two totally different ways:

- as adsorption process or
- as absorption process.

The metal oxide CaO and for the carbonate $CaCO_3$ are considered due to their most frequented occurrence in the earth's crust.

For the adsorption process, calcium oxide is used instead of activated carbon or zeolites. The functionality is nearly the same: calcium oxide adsorbs carbon dioxide out of the flue gas, which results in a generation of limestone. This exotherm process can be described as followed:

$$CaO + CO_2 \rightarrow CaCO_3$$

It is a called carbonation process and can be reversed by heating up the generated limestone beyond the calcination temperature. This endotherm equation can be represented as:

$$CaCO_3 \rightarrow CaO + CO_2$$

The other possibility is to bring CaO in contact with H_2O, which react to $Ca(OH)_2$ (lime water): (exotherm)

$$CaO + H_2O \rightarrow Ca(OH)_2$$

This lime water can then be used in an absorption process to capture CO_2. (also endotherm)

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

After separating the water, the limestone can be heated up like in the adsorption process to split it into a pure stream of CO_2 and CaO. (See process flow description in 3.4.1.)

Due to process engineering causes, using lime water is chosen as favourite metal-oxide process. The reaction between lime water and carbon dioxide is easier to control, faster and has also a higher efficiency than the adsorption process. Furthermore, due to the very slow adsorptions process huge adsorber columns would be necessary, which means an increase in facility costs. Another advantage in using lime water, is the stability of liquids if storage on the surface is necessary; calcium oxide would react with the ambient air by adsorbing carbon dioxide and forming calcium carbonate.

3.4.1. Process Flow Description

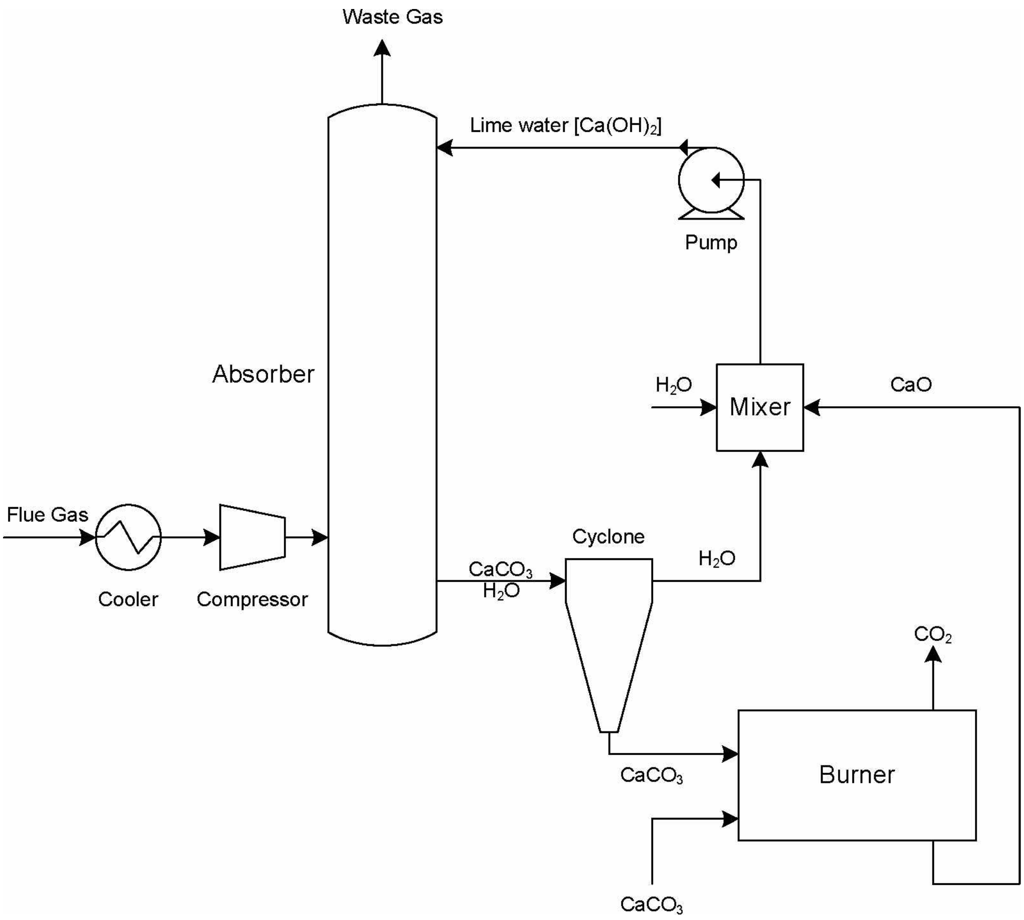

Figure 29: Carbonation-Calcination absorption process using lime water.

Before the process $CaCO_3$ is pre-treated in a burner and heated up to temperatures of 900°C to 1100 °C. The carbonate will split up at these high temperatures in a pure gas stream of CO_2 and into solid particles of CaO. At the moment when calcium oxide comes in contact with water – at atmospheric conditions – lime water is formed. This absorbent is pumped into the absorber column where it comes in contact with the countercurrent stream of flue gas, which was previously compressed before up to 50 bar. A typical absorption process takes place at temperatures of 40 °C to 50°C: the lime water adsorbs the carbon dioxide out of the flue gas by forming limestone and water. The remaining of the flue gas – the CO_2-free waste gas – is released at the top of the column to the atmosphere. The mix of water and small limestone particles is moved by circulation to the cyclone, to be separated in liquid and solid particles.

Thereafter, the water flows are mixed up again with calcium oxide, while the carbonate particles are transferred to the burner, where the circle can start again.

Some basic considerations have to be taken into account when using this type of capturing process:

- Where can the limestone be taken from? Is there a limestone mining site?
- Before the first absorption step can take place, CaO has to be gained out of limestone to generate lime water. A by-product of this energy intense process is CO_2, which also has to be stored underground.
- Material loss of CaO will occur during the process. That means again mining and burning costs and again additional CO_2.

4. Selection Criteria

In this chapter, the selection criteria of choosing the most adaptable process for capturing are discussed on the basis of three case studies. The three case studies are: a flue gas from a heater, from a gas turbine and from a blast furnace. Afterwards, some already existing projects are introduced.

For a first, quick overview about the different separation techniques, following chart can be used (Figure 30). Actually, it is designed for natural gas but can also be used (with caution) for flue gas to get an idea about the possible separation processes.

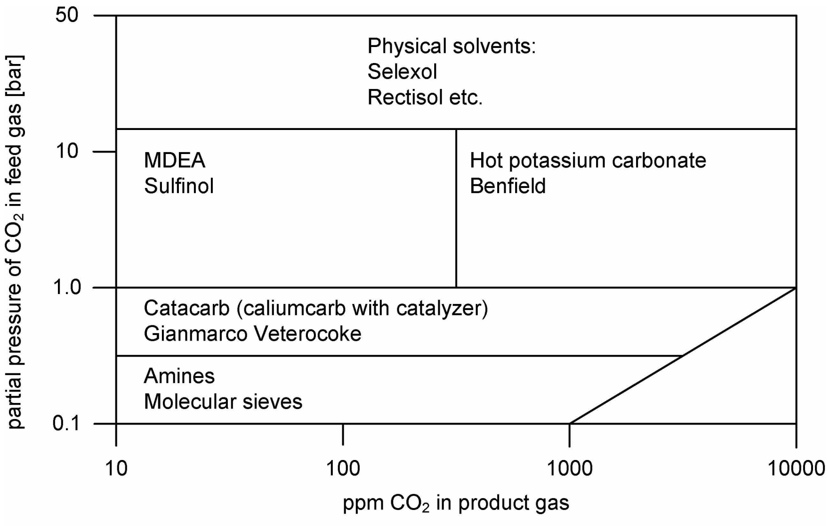

Figure 30: Quick evaluation of the right separation process. [29]

For a more detailed selection the figure above is not enough and it is compulsory to have a look on the flue gas components to select the best possible method to capture carbon dioxide out of the flue gas.

4.1. Case Studies

Case 1: flue gas from a heater; OMV Gasstation Aderklaa, Heater B-3, B-4, B-5; 24, 25, 27. September 2007 with Sensonic-5000;

Case 2: flue gas from a gas turbine; OMV Gasstation Aderklaa II, Gas turbine GT-2402 A+B; 24, 27. September 2007 with Sensonic-5000;

Case 3: flue gas from a blast furnace, VOEST Alpine, 2008.

Table 4: Flue gas data.

	Case 1: Heater	Case 2: Gas turbine	Case 3: Blast furnace
Power [MW]	600	20	300
Mode [%]	80	Normal	Normal
T [°C]	236	527	300
O_2 [%]	1.36	15.80	5
CO_2 [%]	10.94	2.87	50
CO [ppm]	<5	8	-
COrel [mg/m^3]	<5	11	-
N_2 [%]	-	-	45
NO_X [ppm]	89	53	-
NO_Xrel [mg/m^3]	182	125	-
Flue gas [m^3/day]	18,200,000	48,000	450,000

For all case studies the flue gas temperature can be neglected as selection criterion as all capture processes from the flue gas have to be cooled in the same way – down to 40-80 °C.

4.1.1. Case 1: Flue Gas from a Heater

Monoethanolamine – Absorption:

MEA will absorb CO_2 without a lot of solvent degradation if the O_2 percentages are low (1.36%). High amounts of CO_2 require a high amount of aqueous MEA. This results in a large consumption of aqueous MEA, in a high quantity of regeneration and also in a faster solvent degradation. For solvent degradation the MEA has to be replaced completely and disposed safe.

To enlarge the absorption capacity, the aqueous MEA can be activated by addition of 2% of piperazine. Further enlargement is possible if the flue gas is compressed up to values higher than 50bars before entering the absorber. This would allow the columns can have smaller dimensions and the reaction between amines and carbon dioxide would occur more quickly.

Pressure Swing Adsorption:

Flue gas from a heater has huge amounts of CO_2. A consequence of this is that the process pressure swing adsorption process will not make sense. High CO_2 volumes would require the connection of many adsorbers in series, or to have bigger adsorber beds and in turn larger adsorber columns. Shorter cycle times are required for adsorption, whilst longer cycle times are required for regeneration in order to remove all the carbon dioxide. Such a long cycle time would significantly increase energy consumption.

Gas separation membrane:

When choosing a membrane process for gas separation it is important to consider the carbon dioxide partial pressure difference. Since an increase in the CO_2 percentage results in an increase of the partial pressure of, gas separation membranes can be installed to capture carbon dioxide. To increase the rate of separation the flue gases should pass through a compressor before entering the membrane

Carbonation-Calcination:

Like pressure swing adsorption also carbonation-calcination is not compatible with high CO_2 percentage within the flue gas. An ample amount of calcium oxide is required to get a giant circulation of chemicals; this will also cause a faster solvent degradation. Mining costs will factor in order to replenish the calcium oxide.

For case 1 the monoethanolamine absorption process or the use of membranes in CO_2 separation should be considered.

4.1.2. Case 2: Flue Gas from a Gas Turbine

Monoethanolamine – Absorption:

Due to the high percentage of O_2 (15.80%) a chemical reaction between amines and oxygen can take place. First it reacts forming amine oxides and nitrogen oxides and afterwards to nitric acid. If this reaction chain occurs a complete change of the aqueous amine is necessary because nitric acid is extremely corrosive and no more carbon dioxide capture is possible.

Pressure Swing Adsorption:

Since the flue gas from the gas turbine has only a low percentage on carbon dioxide (1.36%) pressure swing adsorption would be a very useful process. The waste gas will quickly flow through the adsorption bed while the carbon dioxide is adsorbed by the activated carbon. Longer cycle times are possible and even medium dimensioned adsorber beds.

Gas separation membrane:

Gas separation membranes are not applicable for flue gas with low carbon dioxide as the partial pressure would be too low to separate the flue gas economically. A promising solution can be achieved by inserting a compressor.

Carbonation-Calcination:

This process can again be compared to the pressure swing adsorption process. Carbonation-calcination will operate very well at carbon dioxide volumes. The required quantity of lime water is low; this results in a reduction of regeneration mining costs.

For case 2 the pressure swing adsorption process or the separation by using lime water should be considered.

4.1.3. Case 3: Flue Gas from a blast furnace

Monoethanolamine – Absorption:

Due to the relatively low percentage of O_2 (5%) compared to the amount of CO_2 (50%), MEA will absorb the carbon dioxide without a lot of solvent degradation. As a consequence of the very large percentage of CO_2 present, a high amount of aqueous MEA is also necessary.

This results in a large consumption of aqueous MEA, in a great effort for regeneration and also in a faster solvent degradation. For solvent degradation the MEA has to be replaced completely and decontaminated safely.

As with case 1, an activated absorption process (using piperazine) is also an issue. A dual-stream amine absorption process (described in chapter 3.1.5.), which are processes to enlarge the absorption capacity. In this instance the flue gas should be compressed to pressures above 50 bars before entering the absorber, so that the columns can have smaller dimensions and the reaction between amines and carbon dioxide takes place in a faster way.

Pressure Swing Adsorption:

Since the flue gas from the blast furnace has a huge amount of CO_2, a pressure swing adsorption process will not work. High volume percentage of CO_2 results in the connection of many adsorbers in a series, or alternatively to have bigger adsorber beds, which result in bigger adsorber columns. Moreover, shorter cycle times for adsorption must be inducted and longer cycle times, which will significantly increase the energy consumption, for regeneration to get rid of all the carbon dioxide.

Gas separation membrane:

For the membrane process it is essential that the gas, which must be separated, is high in partial pressure. Since an increase in percentage of CO_2 results in an increase of the partial pressure of CO_2, flue gas from a blast furnace would be a good candidate.

If a quicker separation is needed a compressor can be installed, which the flue gas has to pass before entering the membrane. This compression will increase the partial pressure.

Carbonation-Calcination:

Like pressure swing adsorption also carbonation-calcination is not compatible with a high percentage of carbon dioxide in the flue gas. An ample amount of calcium oxide is required to get a giant circulation of chemicals. This will also add up in a faster solvent degradation. Unavoidable are the mining costs, which will occur if new calcium oxide is needed.

For case 3 the carbon dioxide capture by using gas separation membranes can be considered. Also the absoption by using aqueous monoethanolamine can be considered by the above mentioned reasons.

4.2. Already existing CCS Projects

Carbon capturing and geological storage is ongoing in different industrial-scale projects (project in order of 1 $MtCO_2$/yr or more): The Sleipner project in the North Sea, the Weyburn project in Canada and the In Salah project in Algeria. These 3 projects capture approximately 3 to 4 $MtCO_2$/yr, which would otherwise be released to the atmosphere. Sleipner, Weyburn and In Salah are now introduced shortly, other projects are listed in Table 5.

4.2.1. Sleipner, North Sea, Norway [1, 23]

The Sleipner field is operated by StatoilHydro in the North Sea about 250 km off the coast of Norway. Since 1996, carbon dioxide (about 9%) is immediately captured after natural gas production from Sleipner West Gas Field and stored in a saline formation more than 800 metres below the seabed. On Sleipner, CO_2 is captured by using a conventional amine process. This project was established to monitor and research the storage of carbon dioxide where the IEA Greenhouse Gas R&D Programme has cooperated to set up the monitoring and research activities. By the end of the year 2007, roughly 10 million tons have been stored with an approximate daily rate of 2,700 to 3,000 t/day. A total storage capacity of 20 million tons of carbon dioxide is expected over the lifetime of this project.

One reason why Statoil made plans to separate carbon dioxide offshore and to inject it again was the introduction of a carbon dioxide tax in 1991 by the Norwegian authorities. Today's tax comes up to around USD 50 per ton. One of the big challenges was to make the processing equipment compact enough to place it on a platform. Furthermore, StatoilHydro declares on its homepage, that the carbon dioxide will probably remain stored in the geological layer for thousands of years. The formation where the CO_2 is stored is called Utsira formation (Figure 31), which is unconsolidated sandstone filled with saline water. The reservoir is monitored continuously using seismology and other extensive models to calculate the moves of carbon dioxide in the reservoir.

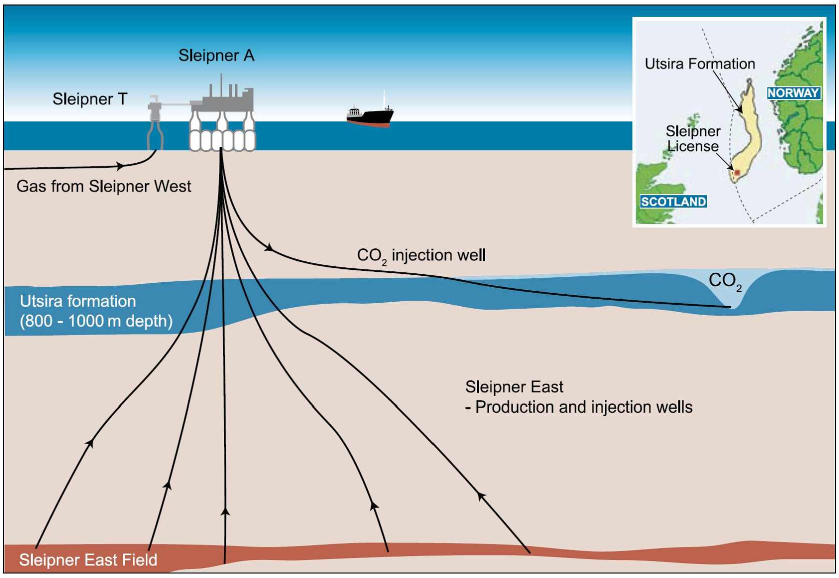

Figure 31: Simplified diagram of the Sleipner project. [1]

4.2.2. In Salah, Algerian Sahara [1, 23]

This project, a joint venture between Sonatrech, BP and StatoilHydro, is located in the central Saharan region of Algeria. As on the Sleipner project the separation of natural gas and carbon dioxide (about 10%) is also based on an amine process. The gas is delivered to European markets, while the CO_2 is re-injected into a sandstone reservoir at a depth of 1800 m, which is now depleted by gas production. The carbon dioxide injection into this 5-mD permeable reservoir started in 2004 with an approximate daily rate of 3,000 to 4,000 tCO_2/day. The total storage capacity is assumed to be around 17 $MtCO_2$.

The reservoir is an anticline with 4 gas producing wells and 3 carbon dioxide injection wells (Figure 32). The carbon dioxide is stored at the same layer as the natural gas, but in the water zone out on the flank, which is reached by long-reach horizontal wells (up to 1500 m). After the depletion of this gas reservoir it is expected that the carbon dioxide will migrate into the area of the current hydrocarbon gas.

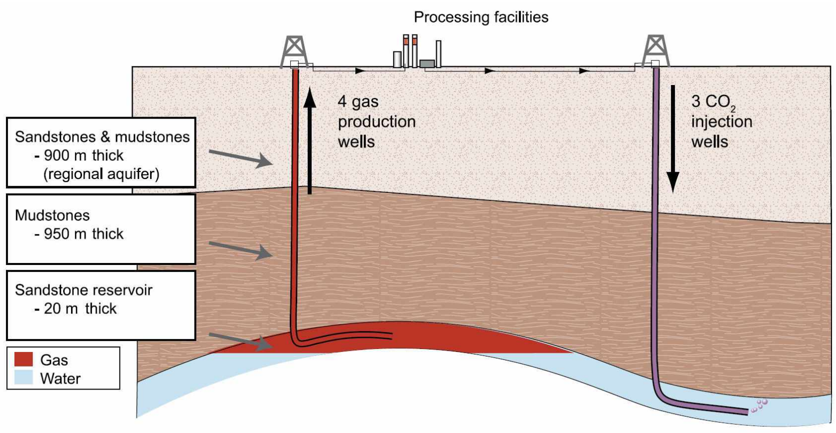

Figure 32: Schematic of the In Salah project. [1]

4.2.3. Weyburn, Canada [1, 25]

Carbon dioxide is stored in the Weyburn field, operated by EnCana, to enhance the oil recovery. The source of the CO_2 is the Dakota Gasification Company facility, located about 325 km away, in Beulah, North Dakota, USA (Figure 33). There, coal is gasified to get synthetic methane with a comparatively pure stream of carbon dioxide (~95%) as by-product. Afterwards, CO_2 is dehydrated by using physical absorption (Rectisol), compressed and piped to Weyburn instead of releasing it to the atmosphere.

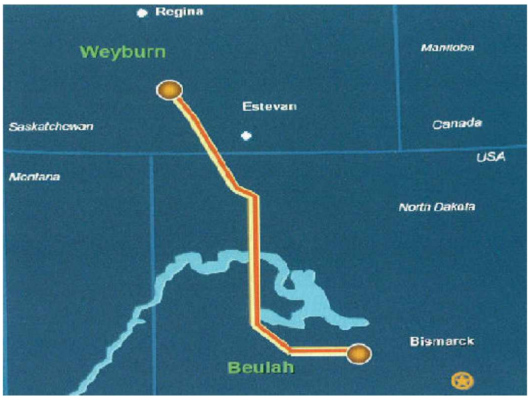

Figure 33: CO_2 pipeline from Beulah to Weyburn. [25]

Since the CO_2 injection project started in late 2000, 3,000 to 5,000 tCO_2/day are delivered. Additionally, all produced CO_2 is captured and recompressed for reinjection. The total storage capacity over the life of the CO_2-EOR project (20-25 years) is assumed to be about 20 $MtCO_2$.

The oil reservoir is a natural fractured carbonate with a thickness between 20 to 27 meters. Above the carbonate formation thick shale forms a good barrier to reservoir leakage. Furthermore, multiple high-permeability formations comprising saline water exist, in which carbon dioxide can dissolve if it reaches these zones. As in the case of Sleipner, Weyburn is also monitored by seismic surveys and the surface is also monitored to determine any potential leakage. Moreover in the Weyburn field, groundwater samples are taken and analysed as well as oil and gas samples. Finally, it can be mentioned that so far there has not been any indication of carbon dioxide leakage.

Table 5: Other existing CCS projects. [1]

Project name	**Country**	**Injection start (year)**	**Approximate average daily injection rate (tCO_2/day)**	**Total (planned) storage (tCO_2)**	**Storage reservoir type**
Weyburn	Canada	2000	3,000 to 5,000	20,000,000	EOR
In Salah	Algeria	2004	3,000 to 4,000	17,000,000	Gas field
Sleipner	Norway	1996	3,000	20,000,000	Saline formation
Snøhvit	Norway	2006	2,000	unknown	Saline formation
K12B	Netherlands	2004	100 (1,000 planned for 2006+)	8,000,000	EGR
Frio	USA	2004	177	1,600	Saline formation
Fenn Big Valley	Canada	1998	50	200	ECBM
Quinshui Basin	China	2003	30	150	ECBM
Yubari	Japan	2004	10	200	ECBM
Recopol	Poland	2003	1	10	ECBM
Gorgon (planned)	Australia	~2009	10,000	unknown	Saline formation

5. Technical Conclusion

For the sequestration of carbon dioxide, terrestrial storage variations provide much more options, certainties and information than the possibilities in marine storage. Depleted oil and gas reservoirs are most applicable due to the existing knowledge, experiences and data about the reservoir. Also the storage capacity can be estimated quite well by taking the production data. Saline formations (aquifers) are an important issue regarding their common occurrence and their huge potential in carbon dioxide storage capacity. Mineral storage is another possibility but since the according reaction is very slow under ambient conditions this process can be neglected. Finally unminable coal seams should be taken into account, as coal bed methane can be recovered and also carbon dioxide can be stored.

For every storage type plenty of health, safety and environment aspects have to be considered seriously.

As pointed out in the previous chapter the selection of which capture process is adaptable for the separation of the carbon dioxide out of flue gas, is highly dependent on the flue gas composition and consequentially the percentage of oxygen.

To sum up, for a low value of oxygen the amine based absorption process and also the use of membranes is compatible. Further, for the membranes a high partial pressure of carbon dioxide is necessary to achieve a fast and almost complete separation. An increase in partial pressure can also be maintained by a compression of the flue gas before entering the membrane. For flue gas with a high amount of oxygen it’s better to choose an adsorption or the carbonation-calcination process. An amine based process is not feasible here, because of the possibility of a chemical reaction between oxygen and amines, which results finally in a complete replacement of the aqueous amines.

Finally, it is necessary to find an appropriate average between pre-compression of the flue gas before the separation and the size of facilities. For example, the higher the pressure of the flue gas is, the smaller the dimensions for the ab-/adsorber columns to be calculated. The separation is also occurring faster.

In the end, the type of process, the selection of a sorbent, the dimensions of pre-treatment and size of the facility area are strictly dependent on the flue gas composition.

For the future, other several ways of reduction of carbon dioxide emission will become sustainable. Mainly, there are four other aspects beside carbon capture and sequestration, which have to be considered:

- Increase of energy efficiency
- Use of alternative energy
- Use of renewable energy
- Natural decrease of the CO_2 concentration

6. Economics

To understand better the capital and operating expenditures necessary for capture processes, the data from the cases described in chapter 4 are implemented in a software program called “Que$tor”. This program can be used to calculate absorption and adsorption facilities. In cases where there is a lack of economical data for existing processes the costs are estimated with “Que$tor” in order better compare the processes with each other. The estimated values are only indicative as “Que$tor” assumes a raw gas instead of a flue gas separation. In this chapter only the results of “Que$tor” are presented, the input data can be found in the appendix.

The energy required for the pre-compression of the flue gas before entering the separation facility is calculated manually by using Mollier-diagrams. When using membranes, the energy and money required for post-compression of the carbon dioxide, is also estimated by using these Mollier-charts (see 6.1. describtion by means of the first case).

6.1. Case 1: MEA vs. Membranes

As concluded in chapter 4.1.1., for case 1 MEA and membranes are preferred to PSA and carbonation-calcination. The estimation of the required energy and the related expenditures, for the compression of the flue gas is proceeded as follows:

For every component of the flue gas, the enthalpy change has to be gauged by using the different Mollier-charts, for nitrogen, oxygen and carbon dioxide (see Figure 34). The Mollier-chart should begin on the x-axis at the temperature the flue gas records after combustion. First, it has to be cooled down to 50°C and then it is compressed in three stages with two intermediate coolings. The enthalpy change for this compression is then measured and summed up. This process is completed for all components. Moreover, the power is then estimated and afterwards multiplied with the gas prize to get the operating expenditures for one year (Table 6).

The life-time of the reservoir in which carbon dioxide is injected, is assumed with 20 years.

Since it was not possible with “Que$tor” to calculate the facility equipment for membranes, those had to be estimated from pre-existing examples and compared

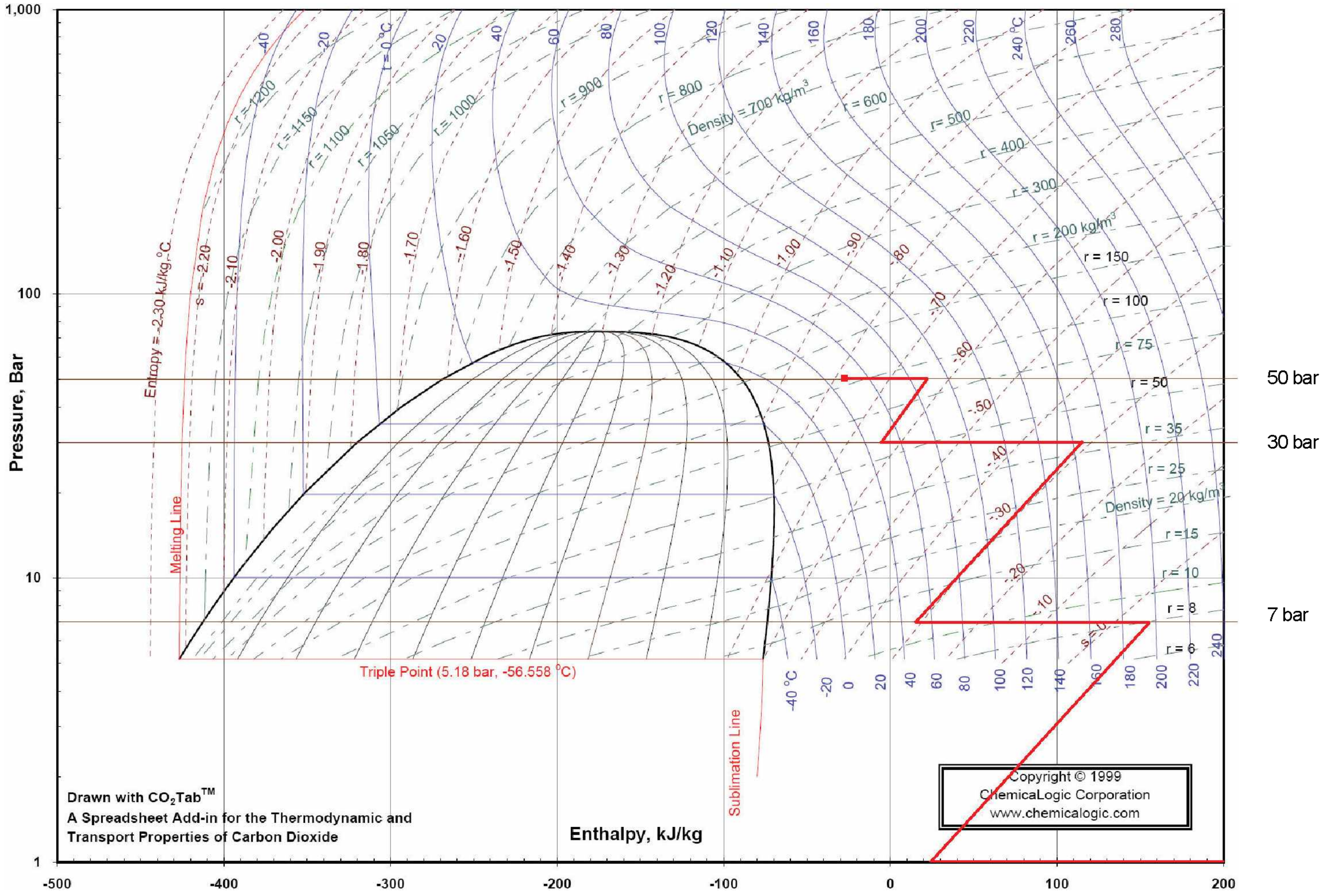

Figure 34: Mollier diagram for CO_2. [28]

then with the data given in case 1. The reference data for the membranes is taken from an OMV gas field in Kadanwari, Pakistan. There, OMV separates carbon dioxide (~10%) out of raw gas by the use of cellulose acetate membranes. Additionally, the compression costs, to transport the carbon dioxide after separation, are calculated in a similar manner to the pre-compression costs, which have been described above.

Table 6: OPEX for pre-compression - Case 1.

	%	kg/m^3	m^3/day	kg/day	kg/sec	kWs/kg	H*x_i	**MW**
N_2	87,6	1,25	15 945 200	19 931 500	230,69	454	397,7	**91,7**
O_2	1,4	1,43	254 800	364 364	4,22	402	5,6	**0,02**
CO_2	11	1,97	2 000 000	3 940 000	45,60	250	27,5	**1,25**

∑ MW	h/day	day/year	MWh/year	ct/kWh [30]	**MM€/year**
93,02	24	300	669 770	2,56	**17,146**

In the following table all costs are listed. For the pre- and post-compression, only the operating expenditures are calculated. It is assumed that the capital expenditures for the compressors are already included in the CAPEX calculated from "Que$tor" and Kadanwari.

Table 7: Total costs of MEA vs. membrane - Case 1.

	MEA		**Membrane**	
	MM€/year	*MM€ (20yrs)*	*MM€/year*	*MM€ (20yrs)*
Pre-Compression:	17,146	342,922	17,146	342,922
CAPEX *["Que$tor" and Kadanwari]* *Incl: CAPEX for pre- and post-compression*	-	135,909	-	240,000
OPEX *["Que$tor"]*	36,000	597,973	-	-
Post-Compression:	2,286	45,720	2,286	45,720
TOTAL	-	**1 122,524**	-	**628,642**

Case 1	€/tCO_2
MEA	**47,48**
Membranes	**26,60**

The total costs of the MEA absorption differs from the membrane process of about a factor of 2. This big difference results from the very low operating expenditures when membranes are used. Most of the energy costs (70-80%) required for MEA absorption is necessary for the regeneration of the rich amine solution. Since such a regeneration step is not necessary for the membranes, this part of operating expenditures can be disregarded. This is the reason that membranes are much cheaper than the absorption process.

6.2. Case 2: PSA vs. Carbonation-Calcination

To get estimated values for pressure swing adsorption, the data of case 2 has been implemented in "Que$tor" also (see Appendix). The costs for the pre-compression are again calculated as with the previous example and shown in Table 8. As seen in the table, "Que$tor" was not able to deal with the low amount of flue gas, given in case 2. To overcome this problem, the data is multiplied by a factor of 10 to assume 10 gas turbines connected together. Moreover, the life-time of the reservoir is reduced in comparison to case 1, to just 11 years. This modification was necessary to get reasonable results from the software program.

Table 8: OPEX for pre-compression - Case 2.

	%	kg/m^3	m^3/day	kg/day	kg/sec	kWs/kg	H*x_i	**MW**
N_2	81,3	1,25	390 240	487 800	5,65	320	260,16	**1,47**
O_2	15,8	1,43	75 840	108 451	1,26	290	45,82	**0,058**
CO_2	2,9	1,97	13 920	27 422	0,32	190	5,51	**0,0017**

∑ MW	h/day	day/year	MWh/year	ct/kWh [30]	**MM€/year**
1,53	10	300	4584	2,56	**0,117**

Since the carbonation-calcination process is not very popular in the industry to capture carbon dioxide out of flue gas, too little data was available to calculate capital and operating expenditures. Due to that, it is not possible to compare the pressure swing adsorption with the carbonation-calcination process. So only the costs related to PSA are listed in the following table:

Table 9: Total costs of PSA.

	PSA	
	MM€/year	*MM€ (11yrs)*
Pre-Compression:	0,117	1,291
CAPEX *["Que\$tor"]* *Incl: CAPEX for pre- and post-compression*	-	18,968
OPEX *["Que\$tor"]*	3,796	41,756
Post-Compression:	0,016	0,175
TOTAL	**-**	**62,190**

Case 2	€/tCO_2
PSA	**687,24**

Like in case 1, the capital expenditures for the pre- and post-compression are again included in the facility costs estimated from "Que\$tor". Unfortunately, this final value is not comparable to any other. It has to be considered that these capture plant is dimensioned to small for this high fixed costs. The bigger the plant, the lower the prize per one ton of captured CO_2. As with every value alluded to this chapter thus far, these should only be taken as relative values.

6.3. Case 3: MEA vs. Membranes

In this case, the life-time of the reservoir is again increased to 20 years. The pre-compression and post-compression costs are again calculated like the previous examples and listed in the table below (Table 10).

Table 10: OPEX for pre-compression - Case 3.

	%	kg/m^3	m^3/day	kg/day	kg/sec	kWs/kg	$H*x_i$	**MW**
N_2	45	1,25	202 500	253 125	2,93	454	204,3	**0,60**
O_2	5	1,43	22 500	32 175	0,37	402	20,1	**0,01**
CO_2	50	1,97	225 000	443 250	5,13	250	125	**0,64**

∑ **MW**	h/day	day/year	MWh/year	ct/kWh [30]	**MM€/year**
1,25	24	300	8981	2,56	**0,230**

For the estimation of the capital expenditures of the membranes, the reference data from Kadanwari, (OMV gas field in Pakistan) has again been taken into account. It is therefore possible to compare the MEA-absorption process with the separation by membranes.

Table 11: Total costs of MEA vs. membrane - Case 3.

	MEA		**Membrane**	
	MM€/year	*MM€ (20yrs)*	*MM€/year*	*MM€ (20yrs)*
Pre-Compression:	0,230	4,598	0,230	4,598
CAPEX *[“Que$tor” and Kadanwari]* *Incl: CAPEX for pre- and post-compression*	-	17,682	-	40,000
OPEX *[“Que$tor”]*	8,956	179,120	-	-
Post-Compression:	0,257	5,140	0,257	5,140
TOTAL	**-**	**206,540**	**-**	**49,738**

Case 3	€/tCO_2
MEA	**77,66**
Membranes	**18,70**

As with case 1, the main divergence can be detected within the operating expenditures. The aqueous amine solution has to be regenerated or renewed in defined intervals to retain the carbon dioxide capture capability. For the total sum of all expenditures using membranes costs only about one-fourth of the expenditures while using the MEA-absorption process. With this in mind, it should seriously be considered, which process is more adaptable for the several flue gas compositions.

7. Economical Conclusion

For the cost estimation a software program called “Que$tor” was used. Indicative costs attained for absorption by monoethanolamines and pressure swing adsorption could then be compared with the costs of membranes or of the carbonation-calcination process. Unfortunately, the carbonation-calcination process is not used in the industry for CO_2 capturing. Therefore, no cost information is available and the pressure swing adsorption could not be compared to this.

The comparison between MEA absorption and membranes is carried out for cases 1 and 3. In case 1, the costs for capture of carbon dioxide by membranes are about half the price than the MEA absorption. And in case 3, they are only about one-fourth of the total expenditures required for MEA absorption. The main difference is in the operating expenditures. For both types pre- and post-compression of the flue gas or the carbon dioxide is necessary. When using the membranes, an additional water separation in front of the membrane needs to be installed. Prerequisites for further pretreatment need to be considered separately. Alternatively for the MEA absorption, a regeneration step, which requires a lot of energy, has to be passed once in every cycle. Moreover, the aqueous monoethanolamines have to be replaced after some time.

For the future it will be necessary to reduce this high energy required for the regeneration of MEA and to develop the absorption and also the membrane technology. It is probably essential to develop also new absorbents with higher absorption capacity and lower energy demand during regeneration. Finally, when considering the several adsorption types, there is also room for further development.

Abbreviations

Ca	Calcium
$CaCO_3$	Calcium carbonate, limestone
CAPEX	Capital expenditures
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
Cu	Copper
DEA	diethanolamine
DGA	diglycolamine
DIPA	di-isopropylamine
ECBM	Enhanced Coal Bed Methane
EGR	Enhanced Gas Recovery
EOR	Enhanced Oil Recovery
ESA	Electric Swing Adsorption
EU	European Union
GHG	greenhouse gas
Gt	Giga tons (Giga=10^9)
H_2	Hydrogen
H_2CO_3	carbonic acid
MDEA	methyl-diethanolamine
MEA	monoethanol amine
Mg	Magnesium
N_2	Nitrogen
Ni	Nickel
OPEX	Operating expenditures
Pb	Lead (Plumbum)
pH	pondus Hydrogenii ($pH < 7$, acidic; $pH = 7$, neutral, $pH > 7$, alkaline)

PSA	Pressure Swing Adsorption
TEA	trieethanolamine
TSA	Temperature Swing Adsorption
USD	US Dollars
VSA	Vacuum Swing Adsorption
Zn	Zinc

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Appendix

A.1. Data Input in “Questor” for Case 1

Table 12: Project summary of MEA in "Que$tor" – Case 1.

ONSHORE PROJECT SUMMARY

Project name	MEA - Case 1
Region	Europe
Country	Romania
Basin	Romania Average

Procurement strategy		Currency	Rate/$
Onshore	Romania	€	1,40

Technical database	Eastern Europe

Unit set	Metric
Development type	Gas
Development concept	Wellpad group to main production facility

Overall input

Design gas production flowrate	23,70	MMsm^3/day	Reserves	120000,00	MMsm^3
Design associated liquids flowrate	0,02	Mm^3/day	Terrain	Grassland	
Water injection capacity factor	0,00		Elevation	50,00	m
Design water injection flowrate	0,00	Mm^3/day	Reservoir depth	2000,00	m
Design gas injection rate	0,00	MMsm^3/day	Reservoir pressure	170,00	bara
Condensate gas ratio	1,00	m^3/MMsm^3	Reservoir length	20,60	km
Swing factor	1,30		Reservoir width	10,30	km
Distance to operation base	100,00	km			
Distance to delivery point	100,00	km			

Fluid characteristics

Oil density @ STP	0,85	s.g.	H2S content	0,00	ppm
CO2 content	11,00	%	Gas molecular weight	43,80	
Waxy crude	No				

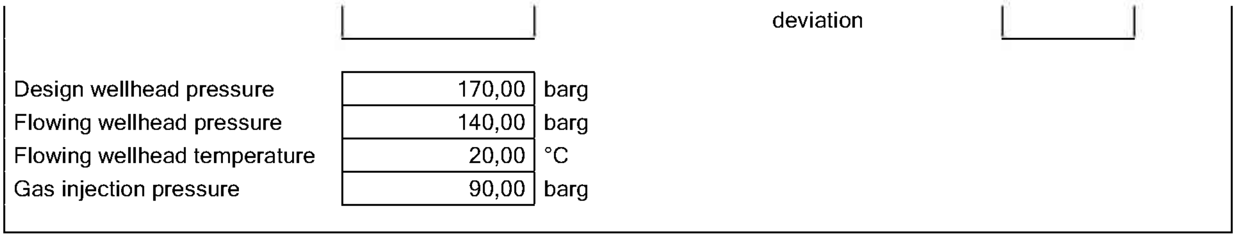
Production profile characteristics

Plateau rate	18,20	MMsm^3/day	Years to plateau	1,00	year
Productivity	850,00	MMsm^3/well	Plateau duration	18,00	year
Peak well flow	0,28	MMsm^3/day	Field life	20,00	year
Maximum drilling stepout	3,00	km	Onstream days	350,00	day

Minimum ambient temperature	-6,00	°C	Maximum ambient temperature	29,00	°C

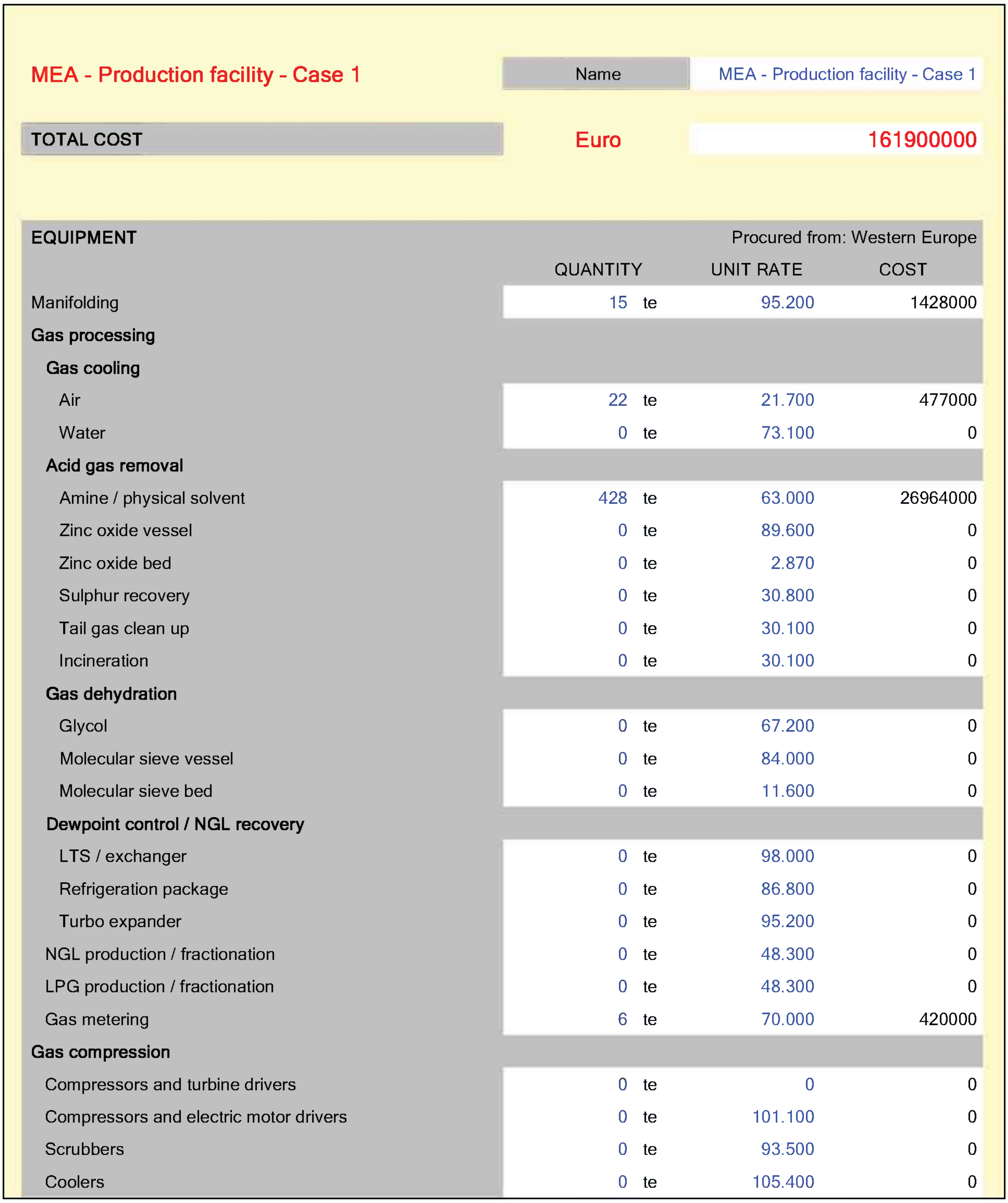
Number of wells

Production wells	10	Gas injection wells	0
Water injection wells	0	Maximum well	60,00



			deviation
Design wellhead pressure	170,00	barg	
Flowing wellhead pressure	140,00	barg	
Flowing wellhead temperature	20,00	°C	
Gas injection pressure	90,00	barg	

Table 13: Production facility costs for MEA - Case 1.



MEA - Production facility - Case 1

	Name	MEA - Production facility - Case 1		
TOTAL COST	Euro	161900000		

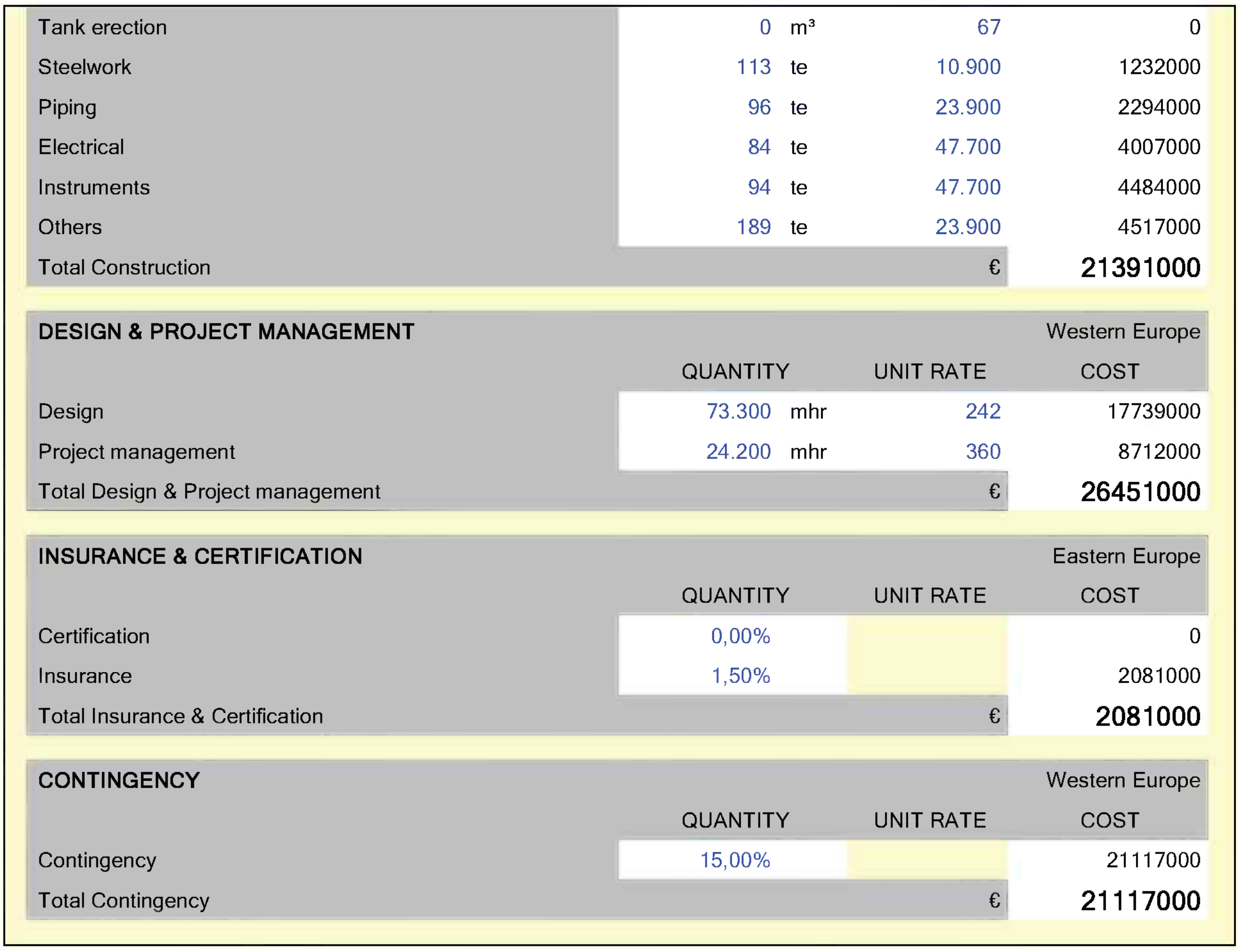
EQUIPMENT				Procured from: Western Europe
	QUANTITY		UNIT RATE	COST
Manifolding	15	te	95.200	1428000
Gas processing				
Gas cooling				
Air	22	te	21.700	477000
Water	0	te	73.100	0
Acid gas removal				
Amine / physical solvent	428	te	63.000	26964000
Zinc oxide vessel	0	te	89.600	0
Zinc oxide bed	0	te	2.870	0
Sulphur recovery	0	te	30.800	0
Tail gas clean up	0	te	30.100	0
Incineration	0	te	30.100	0
Gas dehydration				
Glycol	0	te	67.200	0
Molecular sieve vessel	0	te	84.000	0
Molecular sieve bed	0	te	11.600	0
Dewpoint control / NGL recovery				
LTS / exchanger	0	te	98.000	0
Refrigeration package	0	te	86.800	0
Turbo expander	0	te	95.200	0
NGL production / fractionation	0	te	48.300	0
LPG production / fractionation	0	te	48.300	0
Gas metering	6	te	70.000	420000
Gas compression				
Compressors and turbine drivers	0	te	0	0
Compressors and electric motor drivers	0	te	101.100	0
Scrubbers	0	te	93.500	0
Coolers	0	te	105.400	0

Water injection				
Fine filters	0	te	33.600	0
Deaerator	0	te	33.600	0
Pump turbine drive	0	te	99.400	0
Pump electric drive	0	te	82.600	0
Produced water treatment & disposal	4	te	34.300	137000
Safety	97	te	13.200	1280000
Utilities	100	te	41.300	4130000
Control and communications				6.647.000
Power				
Power generation	92	te	65.700	6044000
Power distribution	42	te	71.400	2999000
Emergency power	15	te	28.400	426000
Sub Total				50952000
Freight	5,00%			2548000
Total Equipment			€	**53500000**

MATERIALS				Procured from: Western Europe
	QUANTITY		UNIT RATE	COST
Steelwork	451	te	3.360	1515000
Piping	383	te	21.300	8158000
Electrical	84	te	32.900	2764000
Instruments	94	te	48.300	4540000
Others	189	te	15.700	2967000
Civils	7.528	m²	168	1265000
Sub Total				21209000
Freight	5,00%			1060000
Total Materials			€	**22269000**

Prefabrication				Location: Western Europe
	QUANTITY		UNIT RATE	COST
Equipment	0	te	2.550	0
Steelwork	338	te	9.700	3279000
Piping	287	te	34.300	9844000
Electrical	0	te	49.000	0
Instruments	0	te	73.500	0
Others	0	te	24.500	0
Sub Total				13123000
Load out & transport	15,00%			1968000
Total Prefabrication			€	**15091000**

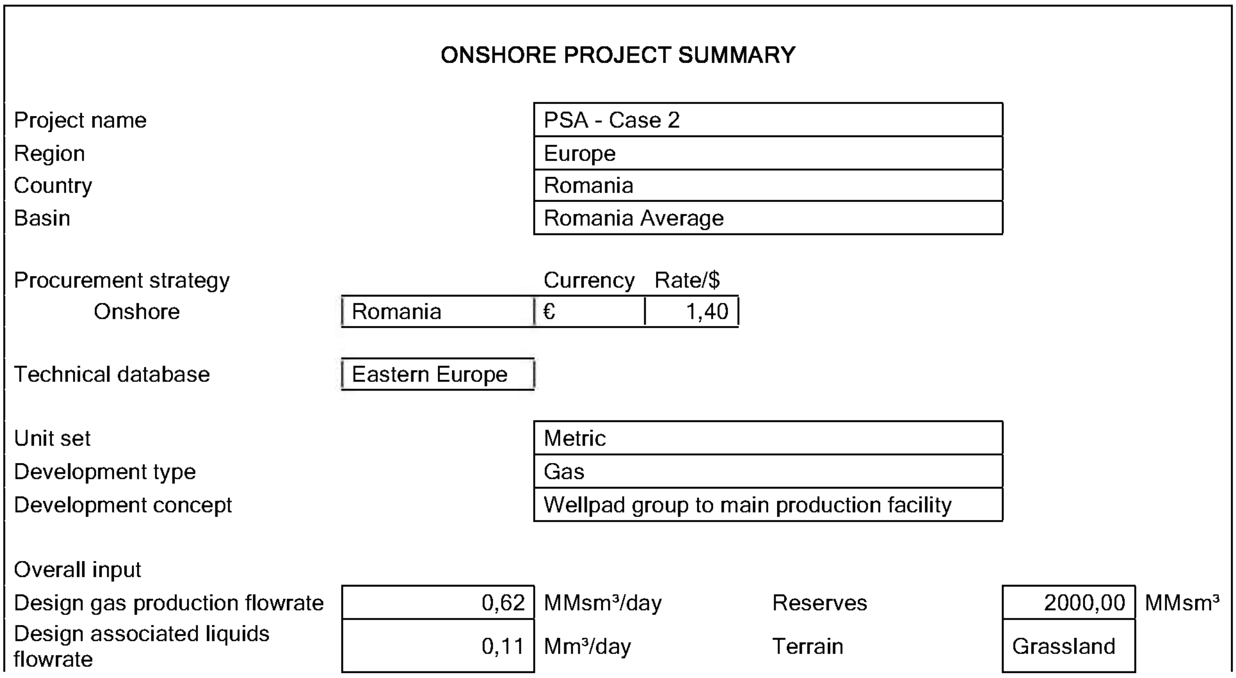
Construction				Location: Eastern Europe
	QUANTITY		UNIT RATE	COST
Site preparation	7.528	m²	66	497000
Civils	7.528	m²	236	1777000
Skid / spool erection	625	te	1.740	1088000
Equipment installation	859	te	1.740	1495000



Tank erection	0	m³	67	0
Steelwork	113	te	10.900	1232000
Piping	96	te	23.900	2294000
Electrical	84	te	47.700	4007000
Instruments	94	te	47.700	4484000
Others	189	te	23.900	4517000
Total Construction			€	**21391000**
DESIGN & PROJECT MANAGEMENT				Western Europe
	QUANTITY		UNIT RATE	COST
Design	73.300	mhr	242	17739000
Project management	24.200	mhr	360	8712000
Total Design & Project management			€	**26451000**
INSURANCE & CERTIFICATION				Eastern Europe
	QUANTITY		UNIT RATE	COST
Certification	0,00%			0
Insurance	1,50%			2081000
Total Insurance & Certification			€	**2081000**
CONTINGENCY				Western Europe
	QUANTITY		UNIT RATE	COST
Contingency	15,00%			21117000
Total Contingency			€	**21117000**

A.2. Data Input in "Questor" for Case 2

Table 14: Project summary of PSA in "Que$tor" - Case 2.

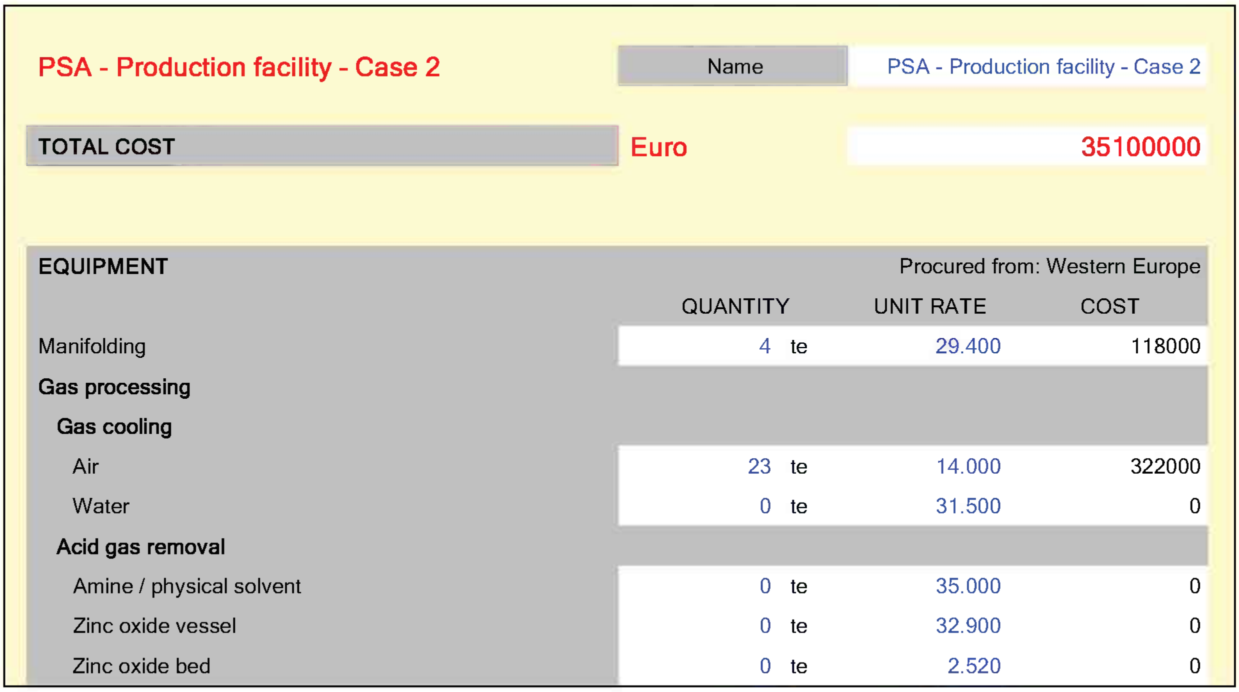


ONSHORE PROJECT SUMMARY

Project name		PSA - Case 2			
Region		Europe			
Country		Romania			
Basin		Romania Average			
Procurement strategy		Currency	Rate/$		
Onshore	Romania	€	1,40		
Technical database	Eastern Europe				
Unit set		Metric			
Development type		Gas			
Development concept		Wellpad group to main production facility			
Overall input					
Design gas production flowrate	0,62	MMsm³/day	Reserves	2000,00	MMsm³
Design associated liquids flowrate	0,11	Mm³/day	Terrain	Grassland	

Water injection capacity factor	0,00		Elevation	50,00	m
Design water injection flowrate	0,00	Mm^3/day	Reservoir depth	2000,00	m
Design gas injection rate	0,00	MMsm^3/day	Reservoir pressure	163,00	bara
Condensate gas ratio	170,00	m^3/MMsm^3	Reservoir length	2,66	km
Swing factor	1,30		Reservoir width	1,33	km
Distance to operation base	100,00	km			
Distance to delivery point	100,00	km			
Fluid characteristics					
Oil density @ STP	0,85	s.g.	H2S content	0,00	ppm
CO2 content	2,90	%	Gas molecular weight	29,10	
Waxy crude	No				
Production profile characteristics					
Plateau rate	0,48	MMsm^3/day	Years to plateau	1,00	year
Productivity	850,00	MMsm^3/well	Plateau duration	10,00	year
Peak well flow	0,28	MMsm^3/day	Field life	11,00	year
Maximum drilling stepout	3,00	km	Onstream days	350,00	day
Minimum ambient temperature	-6,00	°C	Maximum ambient temperature	29,00	°C
Number of wells					
Production wells	10		Gas injection wells	0	
Water injection wells	0		Maximum well deviation	60,00	
Design wellhead pressure	170,00	barg			
Flowing wellhead pressure	140,00	barg			
Flowing wellhead temperature	20,00	°C			
Gas injection pressure	90,00	barg			

Table 15: Production facility costs for PSA - Case 2.



PSA - Production facility - Case 2		Name	PSA - Production facility - Case 2	
TOTAL COST	Euro		35100000	
EQUIPMENT			Procured from: Western Europe	
	QUANTITY		UNIT RATE	COST
Manifolding	4	te	29.400	118000
Gas processing				
Gas cooling				
Air	23	te	14.000	322000
Water	0	te	31.500	0
Acid gas removal				
Amine / physical solvent	0	te	35.000	0
Zinc oxide vessel	0	te	32.900	0
Zinc oxide bed	0	te	2.520	0

Sulphur recovery	0	te	27.000	0
Tail gas clean up	0	te	25.900	0
Incineration	0	te	25.900	0
Gas dehydration				
Glycol	25	te	41.300	1033000
Molecular sieve vessel	0	te	31.500	0
Molecular sieve bed	0	te	10.200	0
Dewpoint control / NGL recovery				
LTS / exchanger	0	te	36.400	0
Refrigeration package	0	te	71.400	0
Turbo expander	0	te	59.500	0
NGL production / fractionation	0	te	40.600	0
LPG production / fractionation	0	te	40.600	0
Gas metering	3	te	63.000	189000
Gas compression				
Compressors and turbine drivers	0	te	0	0
Compressors and electric motor drivers	6	te	101.100	607000
Scrubbers	2	te	48.900	98000
Coolers	0	te	56.000	0
Water injection				
Fine filters	0	te	33.600	0
Deaerator	0	te	33.600	0
Pump turbine drive	0	te	99.400	0
Pump electric drive	0	te	82.600	0
Produced water treatment & disposal	5	te	34.300	172000
Safety	64	te	13.200	845000
Utilities	18	te	41.300	743000
Control and communications				3.637.000
Power				
Power generation	24	te	96.600	2318000
Power distribution	21	te	71.400	1499000
Emergency power	7	te	20.300	142000
Sub Total				11723000
Freight	5,00%			586000
Total Equipment			€	**12309000**

MATERIALS				Procured from: Western Europe
	QUANTITY		UNIT RATE	COST
Steelwork	86	te	3.360	289000
Piping	68	te	21.300	1448000
Electrical	21	te	32.900	691000
Instruments	16	te	48.300	773000
Others	41	te	15.700	644000
Civils	3.849	m²	168	647000
Sub Total				4492000
Freight	5,00%			225000

Total Materials			€	**4717000**

Prefabrication				Location: Western Europe
	QUANTITY		UNIT RATE	COST
Equipment	0	te	2.550	0
Steelwork	65	te	9.700	631000
Piping	51	te	34.300	1749000
Electrical	0	te	49.000	0
Instruments	0	te	73.500	0
Others	0	te	24.500	0
Sub Total				2380000
Load out & transport	15,00%			357000
Total Prefabrication			€	**2737000**

Construction				Location: Eastern Europe
	QUANTITY		UNIT RATE	COST
Site preparation	3.849	m²	66	254000
Civils	3.849	m²	236	908000
Skid / spool erection	116	te	1.740	202000
Equipment installation	210	te	1.740	365000
Tank erection	0	m³	67	0
Steelwork	21	te	10.900	229000
Piping	17	te	23.900	406000
Electrical	21	te	47.700	1002000
Instruments	16	te	47.700	763000
Others	41	te	23.900	980000
Total Construction			€	**5109000**

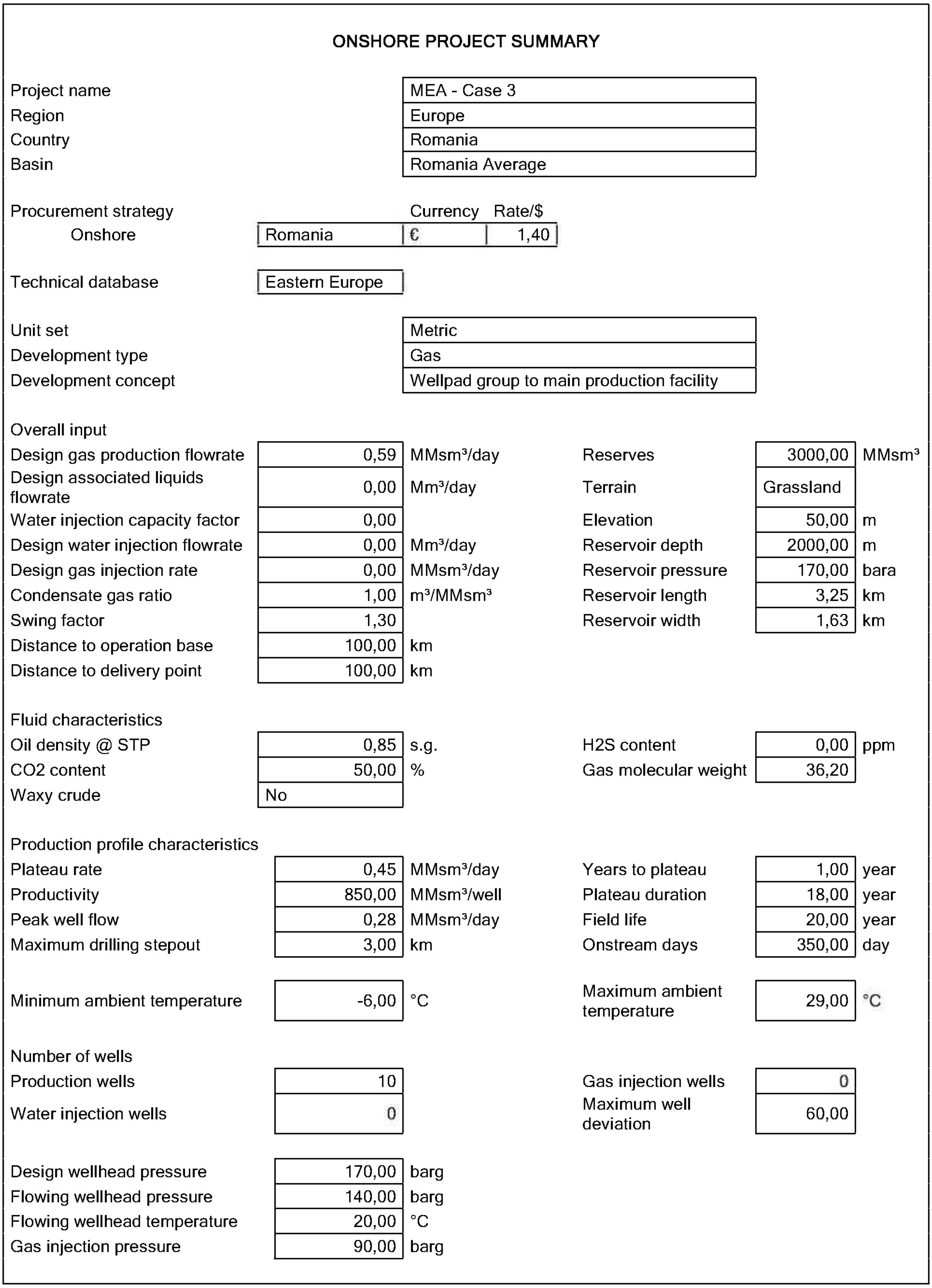
DESIGN & PROJECT MANAGEMENT				Western Europe
	QUANTITY		UNIT RATE	COST
Design	14.400	mhr	242	3485000
Project management	4.760	mhr	360	1714000
Total Design & Project management			€	**5199000**

INSURANCE & CERTIFICATION				Eastern Europe
	QUANTITY		UNIT RATE	COST
Certification	0,00%			0
Insurance	1,50%			451000
Total Insurance & Certification			€	**451000**

CONTINGENCY				Western Europe
	QUANTITY		UNIT RATE	COST
Contingency	15,00%			4578000
Total Contingency			€	**4578000**

A.3. Data Input in "Questor" for Case 3

Table 16: Project summary of MEA in "Que$tor" – Case 3.



ONSHORE PROJECT SUMMARY

Project name	MEA - Case 3
Region	Europe
Country	Romania
Basin	Romania Average

Procurement strategy		Currency	Rate/$
Onshore	Romania	€	1,40

Technical database	Eastern Europe

Unit set	Metric
Development type	Gas
Development concept	Wellpad group to main production facility

Overall input

Design gas production flowrate	0,59	MMsm³/day	Reserves	3000,00	MMsm³
Design associated liquids flowrate	0,00	Mm³/day	Terrain	Grassland	
Water injection capacity factor	0,00		Elevation	50,00	m
Design water injection flowrate	0,00	Mm³/day	Reservoir depth	2000,00	m
Design gas injection rate	0,00	MMsm³/day	Reservoir pressure	170,00	bara
Condensate gas ratio	1,00	m³/MMsm³	Reservoir length	3,25	km
Swing factor	1,30		Reservoir width	1,63	km
Distance to operation base	100,00	km			
Distance to delivery point	100,00	km			

Fluid characteristics

Oil density @ STP	0,85	s.g.	H2S content	0,00	ppm
CO2 content	50,00	%	Gas molecular weight	36,20	
Waxy crude	No				

Production profile characteristics

Plateau rate	0,45	MMsm³/day	Years to plateau	1,00	year
Productivity	850,00	MMsm³/well	Plateau duration	18,00	year
Peak well flow	0,28	MMsm³/day	Field life	20,00	year
Maximum drilling stepout	3,00	km	Onstream days	350,00	day

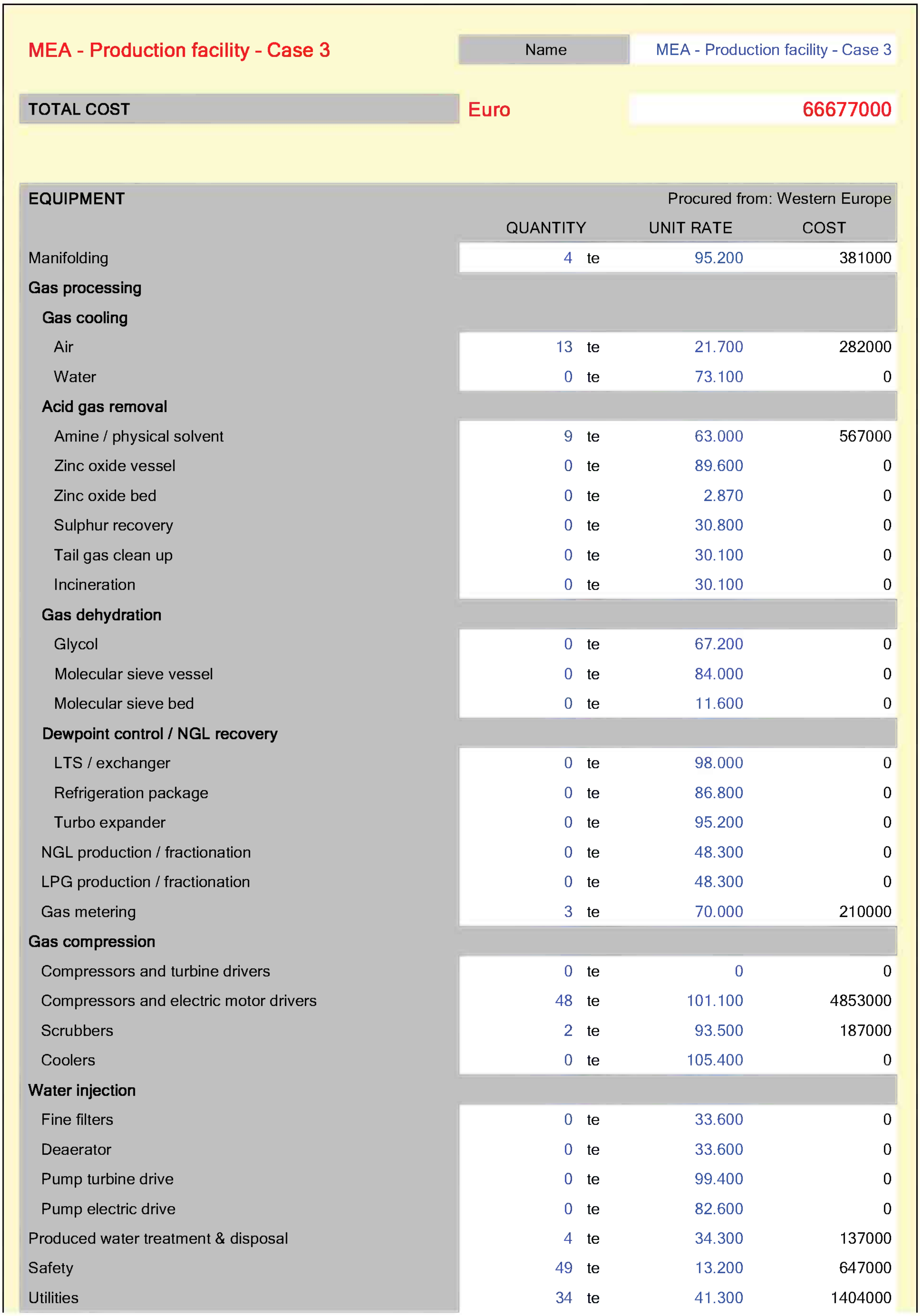
Minimum ambient temperature	-6,00	°C	Maximum ambient temperature	29,00	°C

Number of wells

Production wells	10	Gas injection wells	0
Water injection wells	0	Maximum well deviation	60,00

Design wellhead pressure	170,00	barg
Flowing wellhead pressure	140,00	barg
Flowing wellhead temperature	20,00	°C
Gas injection pressure	90,00	barg

Table 17: Production facility costs for MEA - Case 3.



MEA - Production facility - Case 3

Name	MEA - Production facility - Case 3			
TOTAL COST	Euro			66677000

EQUIPMENT			Procured from: Western Europe	
	QUANTITY		UNIT RATE	COST
Manifolding	4	te	95.200	381000
Gas processing				
Gas cooling				
Air	13	te	21.700	282000
Water	0	te	73.100	0
Acid gas removal				
Amine / physical solvent	9	te	63.000	567000
Zinc oxide vessel	0	te	89.600	0
Zinc oxide bed	0	te	2.870	0
Sulphur recovery	0	te	30.800	0
Tail gas clean up	0	te	30.100	0
Incineration	0	te	30.100	0
Gas dehydration				
Glycol	0	te	67.200	0
Molecular sieve vessel	0	te	84.000	0
Molecular sieve bed	0	te	11.600	0
Dewpoint control / NGL recovery				
LTS / exchanger	0	te	98.000	0
Refrigeration package	0	te	86.800	0
Turbo expander	0	te	95.200	0
NGL production / fractionation	0	te	48.300	0
LPG production / fractionation	0	te	48.300	0
Gas metering	3	te	70.000	210000
Gas compression				
Compressors and turbine drivers	0	te	0	0
Compressors and electric motor drivers	48	te	101.100	4853000
Scrubbers	2	te	93.500	187000
Coolers	0	te	105.400	0
Water injection				
Fine filters	0	te	33.600	0
Deaerator	0	te	33.600	0
Pump turbine drive	0	te	99.400	0
Pump electric drive	0	te	82.600	0
Produced water treatment & disposal	4	te	34.300	137000
Safety	49	te	13.200	647000
Utilities	34	te	41.300	1404000

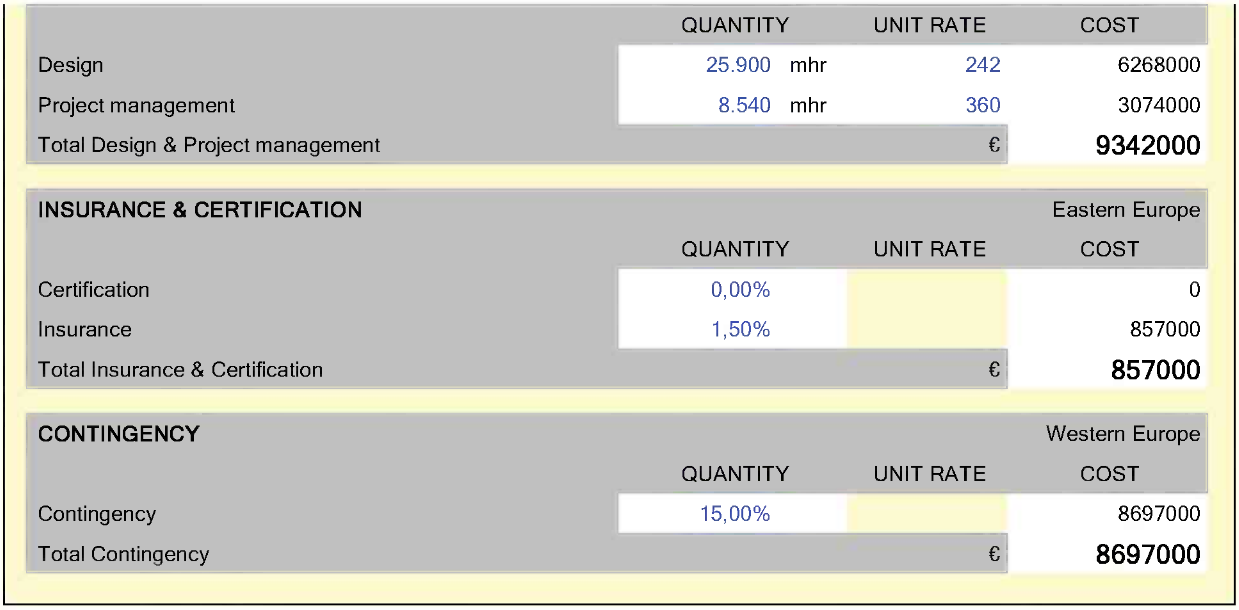
Control and communications				3.637.000
Power				
Power generation	102	te	65.300	6661000
Power distribution	57	te	71.400	4070000
Emergency power	7	te	20.900	146000
Sub Total				23182000
Freight	5,00%			1159000
Total Equipment			€	**24341000**

MATERIALS				Procured from: Western Europe
	QUANTITY		UNIT RATE	COST
Steelwork	207	te	3.360	696000
Piping	132	te	21.300	2812000
Electrical	39	te	32.900	1283000
Instruments	24	te	48.300	1159000
Others	102	te	15.700	1601000
Civils	4.271	m²	168	718000
Sub Total				8269000
Freight	5,00%			413000
Total Materials			€	**8682000**

Prefabrication				Location: Western Europe
	QUANTITY		UNIT RATE	COST
Equipment	0	te	2.550	0
Steelwork	155	te	9.700	1504000
Piping	99	te	34.300	3396000
Electrical	0	te	49.000	0
Instruments	0	te	73.500	0
Others	0	te	24.500	0
Sub Total				4900000
Load out & transport	15,00%			735000
Total Prefabrication			€	**5635000**

Construction				Location: Eastern Europe
	QUANTITY		UNIT RATE	COST
Site preparation	4.271	m²	66	282000
Civils	4.271	m²	236	1008000
Skid / spool erection	254	te	1.740	442000
Equipment installation	340	te	1.740	592000
Tank erection	0	m³	67	0
Steelwork	52	te	10.900	567000
Piping	33	te	23.900	789000
Electrical	39	te	47.700	1860000
Instruments	24	te	47.700	1145000
Others	102	te	23.900	2438000
Total Construction			€	**9123000**

DESIGN & PROJECT MANAGEMENT				Western Europe



	QUANTITY		UNIT RATE	COST
Design	25.900	mhr	242	6268000
Project management	8.540	mhr	360	3074000
Total Design & Project management			€	**9342000**

INSURANCE & CERTIFICATION			Eastern Europe
	QUANTITY	UNIT RATE	COST
Certification	0,00%		0
Insurance	1,50%		857000
Total Insurance & Certification		€	**857000**

CONTINGENCY			Western Europe
	QUANTITY	UNIT RATE	COST
Contingency	15,00%		8697000
Total Contingency		€	**8697000**