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Abstract

In the carbon capture and storage chain, capture, transport and storage set different requirements to the composition of the gas stream mainly containing CO_2. This study investigates maximum allowable concentrations of impurities in the CO_2 in order to safely transport and store it underground. Recommendations on the quality of CO_2 are given from a transport perspective mainly. Among the issues addressed are safety and toxicity limits, hydrate formation, corrosion, cross-effect of H_2S and H_2O, cross-effect of H_2O and CH_4 and free water formation. Limits set by the storage part are touched upon briefly.

EXECUTIVE SUMMARY

The integrated European project DYNAMIS investigates routes to large-scale production of hydrogen and electricity. The different steps in the CCS chain, capture, transport and storage all set different requirements to the composition of the gas stream mainly containing CO_2.[1] This study has been carried out to come up with recommendations for the composition of this stream from a transport perspective and to a certain extent also from a storage perspective.

Transport specifications for CCS streams need to be set to ensure safe transport, durability of the transport infrastructure and finally effective and efficient use of the transport capacity.

The transport of CO_2 to a storage location needs to be safe. To ensure safe transportation of CO_2 existing safety and toxicity limits are reviewed that set limitations to the concentration of compounds in the CCS stream in the event of a blow-out. The durability of the transport infrastructure is ensured by avoiding free water formation, hydrate formation and corrosion. Limits for impurities relate also to efficient transport as high level of impurities reduces available transport capacity.

The results of this study are presented in the table below. This study elaborates on the work that has been done in the European project "ENCAP" on CO_2 quality recommendations. The concentrations that have been changed with regard to the recommendations from the ENCAP project are given in bold figures. This quality recommendation covers a capture process applied to a process of co-production of electricity and hydrogen. One must be careful in applying this quality recommendation to other types of capture processes.

Table A DYNAMIS CO_2 quality recommendation

Component	Concentration	Limitation
H_2O	**500 ppm**	Technical: below solubility limit of H_2O in CO_2. No significant cross effect of H_2O and H_2S, cross effect of H_2O and CH_4 is significant but within limits for water solubility.
H_2S	**200 ppm**	Health & safety considerations
CO	**2000 ppm**	Health & safety considerations
O_2[2]	Aquifer < 4 vol%, **EOR 100 – 1000 ppm**	Technical: range for EOR, because lack of practical experiments on effects of O_2 underground.
CH_4[2]	Aquifer < 4 vol%, EOR < 2 vol%	As proposed in ENCAP project
N_2[2]	< 4 vol % (all non condensable gasses)	As proposed in ENCAP project
Ar[2]	< 4 vol % (all non condensable gasses)	As proposed in ENCAP project
H_2[2]	< 4 vol % (all non condensable gasses)	Further reduction of H_2 is recommended because of its energy content
SO_x	**100 ppm**	Health & safety considerations
NO_x	**100 ppm**	Health & safety considerations
CO_2	>95.5%	Balanced with other compounds in CO_2

Based on this study, our main conclusions are:

- The water level in CO_2 could be significantly higher than what has been agreed on in the ENCAP project, namely 500 ppm compared to 50 ppm. Under the expected transport

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[1] From this point forward, the term "CCS stream" is used when referring to the captured CO_2 volume *including* possible impurities.

[2] The concentration limit of all non-condensable gases together, which is O_2, CH_4, N_2, Ar and H_2, should not exceed 4 vol%.

conditions for a HYPOGEN type of plant (pressures, temperatures and other possible contaminants) this water level is sufficiently low and the risks for free water formation and hydrate formation are at a minimum.

- Limits for H_2S are set by safety considerations, rather than by technical limits. A concentration limit of 200 ppm for H_2S is supportable in terms of safety.
- The carbon monoxide (CO) level is set at a level of 2,000 ppm to assure safe transportation of CO_2 by pipeline.
- Oxygen (O_2) is not expected to be present in the CCS stream out of a HYPOGEN capture plant. Therefore, only a limited amount of effort is dedicated to analyse the impact of O_2 in this project. The recommended limit for O_2 has been set to 100 - 1000 ppm although there is a lack of information regarding the underground effects of O_2.
- Both levels for SO_2 and NO_2 in CO_2 are limited from a health and safety perspective and set to 100 ppm.
- The total volume of non-condensable gases (N_2, H_2, CH_4, O_2, Ar) is set to 4%. It is however recommended to limit the amount of H_2 as much as possible, because of its high energy content and market value.
- The effect of CH_4 on the solubility of water in CO_2 is significant, but not harmful for transportation of CO_2 at concentrations of CH_4 below 5% and a maximum water level of 500 ppm.

These recommendations on CO_2 quality should be treated in close connection with the limits set from a storage perspective. Although some storage issues have been mentioned briefly in this study, a parallel DYNAMIS project will do further work on specifically storage aspects.

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EXECUTIVE SUMMARY ....

1 INTRODUCTION

Background

Carbon capture and storage (CCS) is a technology that allows for the production of energy and simultaneously lowering the amount of carbon dioxide emitted during the energy production process. Carbon could also be captured from industrial processes such as ammonia production or hydrogen production. The concept of CCS is to capture CO_2 from an energy conversion process, e.g. by separation from flue gases, transport it to a storage location and store it for a long time in underground reservoirs. The captured CO_2 may also contain impurities that result from the energy conversion and/or the capture process. In this document we refer to the captured CO_2 stream including possible impurities as the “CCS stream”. The composition of the CCS stream that is to be transported should fulfil the requirements of the transport system.[3] Technically, it might not be a problem to reduce trace elements and obtain a high purity CCS stream, but these purification steps most likely lead to additional costs and energy requirements.

Aim

Today there is no composition of CCS stream that has the status of “CO_2 quality specification”. There is no consistent definition of what the composition of the CCS stream should be from the transport perspective or storage perspective. Companies that are involved in CO_2 deliveries often have an agreement with their clients on what product they trade and what product they deliver to the client. However, such logistic agreements on CO_2 compositions only show what works for a specific client. It might well be that from a pure transport perspective higher levels of impurities could be allowed than is generally given in trade specifications.

In order to come to realistic and transport relevant quality guidelines for the CCS stream from the HYPOGEN plant, it is investigated what might be maximum levels for impurities in the CCS stream. Therefore the following research question is posed:

What are the maximum concentrations of compounds in the CCS stream to safely transport it?

Because the HYPOGEN plant will be a demo plant and offers good possibilities to explore boundaries, the approach is to assess *maximum* impurity levels. Asking the question what could be maximum concentrations of impurities in CCS stream allows for systematically investigating the requirements from a transport (and storage) perspective. Based on the information on the composition of the CCS stream that leaves the capture unit and the resulting CCS stream quality guidelines the possible required purifications steps could be defined.

Scope and boundaries

The CO_2 quality requirements that are assessed for the European project ENhanced CAPture of CO_2 (ENCAP) will be used as a starting point for this assessment[4]. The work done in the ENCAP project has identified several critical aspects in the discussion on CO_2 quality. The issues regarded for transport as critical are:

- Safety and toxicity of substances present in the CO_2 stream

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[3] Storage in reservoirs or use in enhanced oil recovery will also pose CCS stream quality requirements. An additional assessment on storage CCS stream quality requirements is to be done in a separate study, also part of the DYNAMIS project. However, some important points with respect to storage will be mentioned in this report.

[4] ENCAP is European project within the Sixth Framework Programme (FP6), project website www.encapCO$_2$.org

- Avoidance of free water formation
- Avoidance of hydrate formation
- Avoidance of corrosion
- Reduction of the CO_2 volume (density)

The simultaneous presence of certain impurities in CO_2 might give rise to so-called cross-effects. The cross-effect of H_2S and H_2O and H_2O and CH_4 are investigated; other cross-effects such as O_2 and CH_4 are recommended for further research.

Transport and storage of CO_2 set different requirements to the purity of the CCS stream. This report investigates the requirements set by a *transport* perspective in the first place. It might, however, that storage in some cases may impose stricter conditions. Since there is just one CCS stream that has to go through the whole chain of capture, transportation and storage, the quality of the CCS stream will reflect the requirements for the activity (either capture, transport or storage) with most stringent quality demands.

The DYNAMIS CO_2 quality recommendation for pipeline transportation applies to CCS streams from pre-combustion and post-combustion capture processes. The most important components in the CO_2 from these types combustion processes that could possibly affect the transportation of CO_2 are covered.

Results
This document provides the quality guidelines and its background for the CCS stream from the HYPOGEN plant. The results of this assessment will be either a confirmation of the CO_2 quality as defined in the ENCAP project or, when convincing arguments exist, result in an update of the ENCAP figures. The quality guidelines as formulated in this assessment will be included in the report “Common Framework of evaluation methods and criteria” (deliverable D2.4.1. of the DYNAMIS project).

Reading guide
Chapter 2 starts with an overview on how CO_2 quality is dealt with in existing. Furthermore, this section addresses which impurities can be found in the CO_2 that leave the capture unit of a power plant.

In Chapter 3 safety and toxicity limits of compounds in the CO_2 are discussed because these relate to health, safety and environmental issues of transporting and storing CO_2. Chapter 4 considers effects of impurities on the design and operation of CO_2 transport systems. This chapter on technical limits discusses the effects of corrosion, hydrate formation and cross-effects because of the importance for the behaviour of CO_2 in the pipe.

2 BACKGROUND

2.1 Definitions of CO_2 quality

Today, there is no uniform definition of what the quality of CCS streams should be in order to safely transport and store it underground. Some guidelines such as the London Protocol (1972) include general statements about CO_2 quality. The London Protocol limits the discharge of wastes that is generated on land and disposed of at sea. Since February 2007 an amendment to the London Protocol (1996)[5] allows the storage of CO_2 into the sub sea under certain conditions. It speaks about the composition of CO_2 as ‘overwhelmingly CO_2’. The amendment states that CCS streams may contain incidental associated substances derived from the source material and the capture and sequestration processes used (International Maritime Organization, 2006), but no waste may be added to the stream. Another attempt to set requirements for the composition of CO_2 for sequestering purposes stems from Greenpeace International. Their opinion is that the qualitative description of the CO_2 condition as formulated in the London Protocol will not place sufficient control over the quality of the sequestered gas stream and therefore proposes a more stringent quantitative limit. According to Greenpeace a limit value of greater than 99.9% CO_2 by volume would be justifiable and readily achievable with existing and developing techniques (Greenpeace International, 2006).

2.2 Impurities in CCS streams

The type and level of impurities in the CCS stream depends on the fuel type, the energy conversion process and the capture process. The presence and type of impurities may differ considerably between post-combustion, pre-combustion and oxyfuel capture processes. The latter capture technology, however, is not considered to be applied to HYPOGEN concepts.

Post-combustion

Trace elements in the flue gases originate from either the fuel used or the air or oxygen feed to the system. Flue gases from coal combustion will contain CO_2, N_2, O_2 and H_2O, but also air pollutants such as SO_x, NO_x, particulates, HCl, HF, mercury, other metals and other trace organic and inorganic contaminants (IPCC, 2005). Exhaust gases from natural gas combustion processes typically contain low levels of SO_x and NO_x and higher concentrations of O_2 compared to exhaust gases from coal combustion.

Pre-combustion

Pre-combustion capture technologies remove CO_2 before the energy conversion process. For pre-combustion plants the first step is the production of a synthesis gas through gasification (coal) or reforming (gas) of the fossil fuels. Most important compounds of the synthesis gas are hydrogen and carbon monoxide. In the water gas shift reaction the CO is converted to CO_2. In a next step the CO_2 is removed from the H_2/CO_2 mixture and the hydrogen rich fuel can be used in many different applications such as boilers, furnaces and gas turbines. The captured CO_2 is not pure, but may contain trace elements such as nitrogen, oxygen, hydrogen, methane, CO and sulphur compounds like H_2S. There is no SO_x and NO_x present in captured CO_2 from pre-combustion processes. In gasification processes, oxidized compounds such as SO_2 and NO_x are not formed during the conversion of the fuel because the conversion takes place in a reducing environment.

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[5] The London Protocol of 1996 is a modernized version of the international 1972 London Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and other Matter

Figure 2-1 shows that the partial pressure of SO_2 significantly decreases when the air factor drops below 1. In coal gasification processes H_2S is formed. The concentration of H_2S may be considerable, but depends on the sulphur content of the fuel. This is the most important sulphur species to be controlled as depicted by figure 2-1.

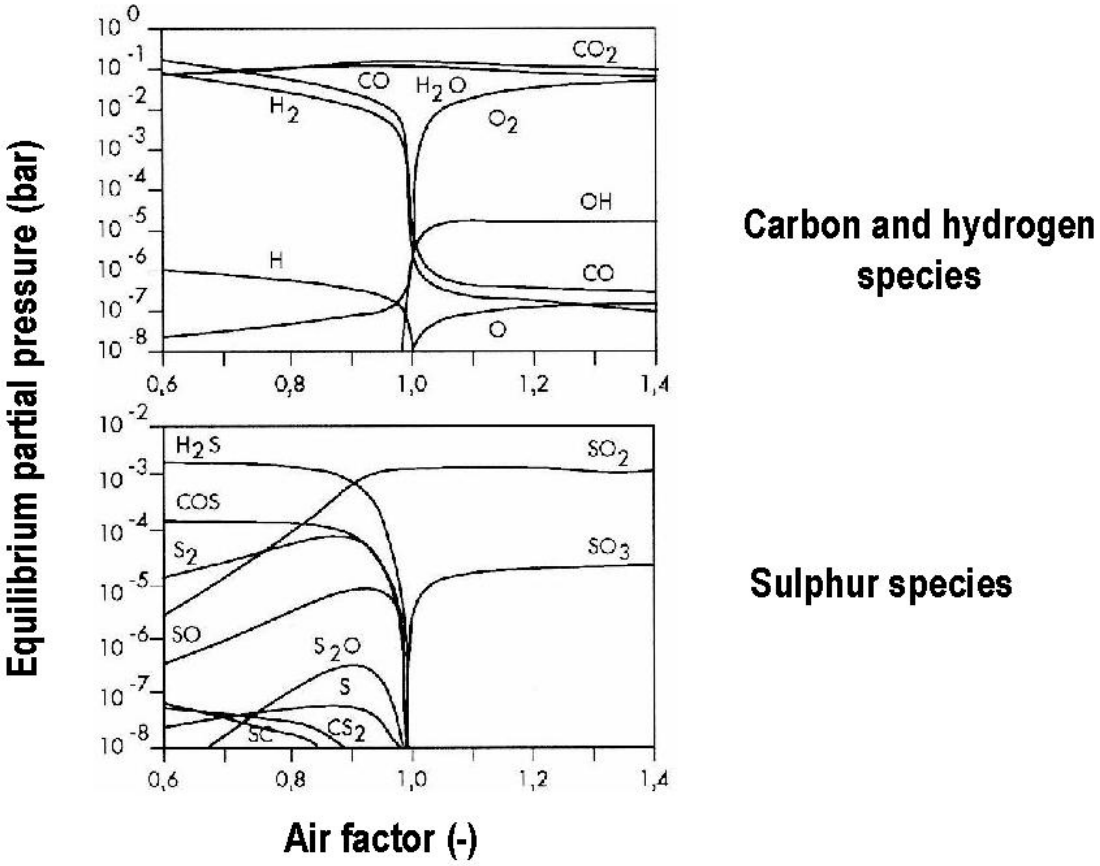

Figure 2-1 Carbon, hydrogen and sulphur species from combustion (air factor >1) and gasification (air factor < 1) according to thermodynamic equilibrium calculations (Iisa, 1992)

3 SAFETY AND TOXICITY LIMITS

3.1 Introduction

One of the prerequisites of transporting captured CO_2 is that it is done in a safe way. Safety issues associated with pipeline transport of large volumes of CO_2 mainly relate to the risks for short-term sudden leakages. CO_2 present in high concentrations may lead to suffocation. If the CO_2 contains substantial quantities of impurities this may affect the potential impacts of a pipeline leak or rupture (IPCC, 2005). Some compounds other than CO_2 that could be found in captured CO_2 are qualified as toxic substances, such CO, SO_2 and H_2S. For safe pipeline transport of CO_2 it is not sufficient to focus on the safety and toxicity limits of CO_2 only. Safety and toxicity limits for other compounds present in the CO_2 stream should be studied as well to obtain a clear view on what composition of the CCS stream actually is safe enough to transport.

In this section safety and toxicity limits of the most important compounds that might be present in captured CO_2 are addressed: H_2S, CO, SO_x, NO_x and CO_2. Existing short term exposure levels of these compounds are used as a starting point to define maximum concentration levels of these substances in CO_2 that is to be transported.

3.1.1 Method to determine maximum allowable concentration in CCS stream

The approach to define health and safety limits for CO_2 transportation uses Short Term Exposure Limits (STEL) as a reference to find maximum concentration levels for H_2S, CO, SO_x and NO_x in CO_2. Short Term Exposure Limits give the maximum amount of a compound that one can be exposed to without adverse health effects for a period of 15 minutes. See Textbox 3-1 for more information on Exposure Limits.

Exposure to CO_2 in case of a pipeline rupture is also characterized by a short-lived, but relatively strong exposure to the leaked CO_2 volume. Although STELs are not specifically defined for situations of a CO_2 pipeline rupture these limits fit best to this situation because they are defined for a short-term exposure of 15 minutes. Other reference values like emergency response planning guidelines or ceiling values e.g. show less similarity with the situation of a pipeline rupture.

To determine the maximum levels of the impurities in the CCS stream, we have to translate the STEL values of these impurities to concentrations in the CCS stream. Our approach is that the CO_2 concentration will be the limiting factor in view of safety conditions. Close to the point of a rupture, the concentration of CO_2 will exceed the STEL value. Once the CO_2 is diluted by air and its concentration has come below the STEL value (either by natural circumstances like wind, remediation action like fans or taking a safety distance into account), the concentrations of the impurities which were present in the CCS stream should also be below their STEL value. It is assumed that the dilution of all substances is proportional to that of CO_2, i.e. it is assumed that the diffusion patron of these substances is equal to that of CO_2.

The following steps have been taken:

- The existing short term exposure levels (STEL) for CO, H_2S, SO_2, and NO_2 will be used to set their maximum limit in the CCS streams.

- The maximum concentration of H_2S, CO, SO_x and NO_x in CO_2 is set to such level that the component exceeds its STEL with the same factor as CO_2 and reaches its threshold value in the dilution process at the same time as CO_2 does.
- A safety factor of 5 is applied to the maximum concentration limit to reach the recommended value - qualitatively substantiated by the following four reasons:
    - exposure limits are always subject to uncertainties and effects on the human body may differ from human to human;
    - there may be some synergy effects by the various impurities, although no evidence has been found yet on this effect;
    - similar diffusion is assumed of CO_2 and the impurities, although unlikely, this may slightly differ from substance to substance;
    - to account for potential additive effects that may arise from the various impurities involved, although no evidence has been found yet on this effect.[6]

The Occupational Exposure Limits for CO_2, CO and H_2S are discussed in the following sections to provide a knowledge base on safety and toxicity limits for those compounds that are regarded as critical in the CO_2 streams considered for the HYPOGEN plant. The Short Term Exposure Level values will serve as starting point for our setting maximum concentrations of CO, SO_x, NO_x and H_2S in CO_2 streams.

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[6] With respect to synergy effects of being exposed to a mixture of CO_2 and H_2S, no such effects have been reported (BOC Gases, Material Safety Data Sheet), but this will of course have to be investigated for all relevant compounds which could be present in the CCS stream. Such research is, however, outside the scope of this study. To compensate for these possible additive effects, a safety margin of some kind should be applied. The safety factor should be set in relation to potential additive effects due to exposure to multiple toxic compounds/air pollutants.

Textbox 3-1 Exposure limits

On a national level, quantified norms governing working conditions are established by health and safety authorities to control exposure to hazardous substances. These norms are called Occupational Exposure Limits (OEL) and set at a level at which (based on current scientific knowledge) there is no indication of risk to the health of workers exposed to it. These exposure limits are principally defined for regulating the hazardous substances in a working environment and should not per definition be applied in the same way to CO_2 pipeline transport.

National scientific institutes and scientific committees prepare health-based OELs, ideally using the concept of "no observed adverse effect levels" (NOAELs). There is no iron-cast definition of an Occupational Exposure Level, since there are scientific and legal interpretations and the latter may vary from country to country[1]. The exposure limits may rise from cases of human exposure, experiments, or epidemiological studies of exposure-response relationships. Other limits come from the results of animal studies (OSHA, 2006).

The grounds on which legal interpretations can vary include divergence in assessment methods and differing assessments on the actual risks of the chemicals themselves. In this assessment OEL-levels in European countries are addressed and compared to OEL-levels set in the United States as these are used and implemented in several other countries. Each country uses its own terms or acronyms for OELs, but most common used types of limits for airborne exposures are: Time Weighted Average (TWA), Short Term Exposure Limit (STEL) and Ceiling Limit (CL). In Table 3-1 the definitions of the occupational exposure limits are given.

Table 3-1 Definitions of commonly used exposure limits

Type of OEL	Abbreviation	Description
Time Weighted Average	TWA	The maximum average concentration of a chemical in air for a normal 8-hour working day and 40-hour week.
Short Term Exposure Limit	STEL	The maximum amount for a period of 15 minutes
Ceiling Limit	CL	The maximum amount of a toxic substance allowed to be in workroom air at any time during the day

The TWA and STEL are not absolute limits, but rather time-weighted averages measured over a time period of respectively 8 hours and 15 minutes. During this period, exposure may at times exceed the OEL, providing that such higher levels of exposure are balanced by lower levels, so that the average level for the 8-hour or 15-minute period does not exceed the OEL. The Ceiling Limit is however an absolute OEL that may not be exceeded at any time.

3.2 Exposure limits for carbon dioxide (CO_2)

Carbon dioxide, a naturally-occurring constituent of air that is essential to all life forms, is a non-toxic, inert gas and is generally regarded as not dangerous substance. The Occupational Exposure Limits assigned to CO_2 is 5,000 ppm (parts per million) and is the highest limit assigned to any substance. All countries listed in Table 3-2 have adopted the same time weighted average of 5,000 ppm. The short term exposure limit is set to 10,000 or 15,000 ppm. Limit values could have a different scope and therefore are not identical in every country.

Air contains about 300 ppm of CO_2 or 0.03%. The air we breathe out contains a few percent of CO_2. The concentration of CO_2 must be over about 2% (20,000 ppm) before most people are aware of its presence unless the odour of an associated material is present at lower concentrations. Above 2% carbon dioxide may cause a feeling of heaviness in the chest and/or more frequent and deeper respirations. As the carbon dioxide concentration climbs above a few percent, the concentration of oxygen in the air inhaled begins to be affected. At 6% carbon dioxide, for instance, the concentration of oxygen in air has decreased from 20.96 to 19.9%. OSHA has indicated that the lowest oxygen concentration for shift-long exposure[7] is 19.5%, corresponding to a carbon dioxide concentration well above 60,000 ppm (6%). Carbon dioxide concentration, not oxygen concentration, is limiting in such circumstances. The immediately dangerous to life or health concentration (IDLH) for CO_2 is defined at 40,000 ppm by the National Institute for Occupational Safety and Health (NIOSH). In Table 3-3 the effects of exposure to increasing concentrations of CO_2 are listed.

Table 3-2 Eight hour and short term exposure levels for CO_2 (source: GESTIS database, 2005)

	Limit value – eight hours		Limit value – short term	
	ppm	mg/m^3	ppm	mg/m^3
Austria	5,000	9,000	10,000	18,000
Germany	5,000	9,100	---	---
Denmark	5,000	9,000	10,000	18,000
Spain	5,000	9,150	15,000	27,400
European Union	5,000	9,000	---	---
Hungary		9,000	---	18,000
Italy	5,000	9,000	---	---
Sweden	5,000	9,000	10,000	18,000
United Kingdom	5,000	9,150	15,000	27,400
United States of America	5,000	9,000	---	---

Table 3-3 Effects and symptoms of CO_2 at various exposure concentrations (source: Safety Department Imperial College London, 2004)

CO_2 concentration		Effects and Symptoms
ppm	*Vol%*	
10,000	1%	Slight but un-noticeable increase in breathing rate
20,000	2%	Breathing becomes deeper, rate increases to 50% above normal. Prolonged exposure (several hours) may cause headache and exhaustion.
30,000	3%	Breathing becomes laboured. Hearing ability reduced, headache experienced with increase in blood pressure and pulse rate.
40-50,000	4-5%	As above. Signs of intoxication after 30 minutes exposure and slight choking sensation.
50-10,0000	5-10%	Characteristic pungent odour noticeable. Breathing very laboured leading to physical exhaustion. Headache, visual disturbance, ringing in the ears, confusion probably leading to loss of consciousness within minutes.
100,000+	10%+	Rapid loss of consciousness with risk of death from respiratory failure.

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[7] Shift-long exposure: exposure to a substance during the time of a work shift (which could be longer than 8 hours)

3.3 Exposure limits for hydrogen sulphide (H_2S)

The presence of substantial quantities of impurities, particularly H_2S, in the CCS stream that is transported could affect the potential impacts of a pipeline leak or rupture. The exposure threshold at which H_2S is immediately dangerous to life or health according to the National Institute for Occupational Safety and Health (NIOSH) is 100 ppm, compared to 40,000 ppm for CO_2.

There is limited information concerning the health effects after prolonged exposure to H_2S (Health Council of the Netherlands, 2006). It seems that H_2S causes irritation of the eyes at levels lower than 20 ppm. However, these results were obtained from research where simultaneous exposure to carbon disulfide (CS_2) was measured as well. Short term occupational exposure of H_2S might lead to lung function impairment and neurobehavioral changes. Acute effects after exposure to high concentrations include pulmonary oedema (at ca. 700 mg/m^3 and above) and “knock down” (Health Council of the Netherlands, 2006). Exposures in the range of 500-800 ppm hydrogen sulphide will lead to a rapid loss of consciousness, respiratory paralysis, coma and death (Dakota Gasification Company, 2006).

The Occupational Exposure Levels of airborne concentrations of H_2S for workers in a number of European countries are presented in Table 3-4. Exposure levels for the Netherlands are not derived from the GESTIS database, but stem from other literature sources. In the Netherlands no STEL has been defined for H_2S. The GESTIS database does not contain complete information on limit values in the United States.

Table 3-4 Eight hour and short term exposure levels for H_2S (source: GESTIS database, 2005)

Hydrogen Sulphide	Limit values – eight hours - TWA		Limit values – short term- STEL	
	ppm	mg/m^3	ppm	mg/m^3
Austria	10	15	10	15
Denmark	10	15	20	30
Spain	10	14	15	21
France	5	7	10	14
Sweden	10	14	(15)*	(20)*
Netherlands	10	14		
United Kingdom	5	7	10	14
United States of America	20 -OSHA			

* Ceiling value

3.4 Exposure limits for carbon monoxide (CO)

Carbon monoxide is a colourless odourless gas with no inherent warning properties, it may occur wherever organic or carbonaceous material is burnt in an inadequate supply of air or oxygen. When inhaled, carbon monoxide binds with haemoglobin more readily than oxygen and forms carboxyhaemoglobin. When bound to haemoglobin CO reduces the rate at which oxygen is delivered to the tissues, thereby causing hypoxia. The effects of CO depend on the percentage of carboxyhaemoglobin in the blood. In general, carboxyhaemoglobin concentrations below 2% are not associated with any significant health effects. When the concentration rises to 20 - 30% it causes neurological symptoms such as headache, dizziness, weakness, nausea, confusion, disorientation and visual disturbances. Concentrations of carboxyhaemoglobin in the blood exceeding 50% cause convulsions, respiratory arrest and death. When exposed to CO concentrations between 5000 and 10000 ppm, weak pulse, depressed respiration / respiratory failure and death can occur. Sudden death is mostly caused by effects to the heart, because the muscular tissue of this organ reacts most sensitively to the oxygen deficiency (GESTIS, 2006).

The Occupational Safety and Health Administration (OSHA) developed two permissible exposure limits (PELs) for CO exposure. Exposures may not be over 50 ppm averaged over 8 hours and may never be over 200 ppm. The NIOSH recommended a lower 8 hour average value of 35 ppm and the ACGIH has assigned CO a TWA for a normal 8-hour working of 25 ppm.

Table 3-5 Eight hour and short term exposure levels for CO (source: GESTIS database, 2005)

Carbon monoxide	Limit values – eight hours - TWA		Limit values – short term - STEL	
	ppm	mg/m^3	ppm	mg/m^3
Austria	30	33	60	66
Germany	30	35	1* - 60 ppm for 30 minutes	
Denmark	25	29	50	58
Spain	25	29		
European Union**	20	23	100	117
France	50	55		
Sweden	35	40	100 (15 min)	120
Netherlands				
United Kingdom	30	35	200	232
United States of America	50 - OSHA	55		

* 15 minutes average value, ratio of permitted short term value to the limit value
** Indicative Occupational Exposure Limit Values, proposal

3.5 Exposure limits for sulphur oxides (SO_x)

Sulphur dioxide (SO_2) is formed on burning sulphur and materials containing sulphur such as oil and coal. While it is not as deadly as H_2S, even at low concentrations SO_2 can have negative health impacts. As depicted in Table 3-6 most countries have set the 8-hour per day exposure limit to 2 ppm and the short term exposure limit to 5 ppm.

When sulphur dioxide is breathed in it can cause immediate irritation in the throat and a sensation of tightness and difficulty in breathing. People with asthma are more sensitive to these health effects and could react to concentrations of SO_2 below 1 ppm. According to Material Safety Data Sheets, burning of the nose and throat and breathing difficulties will occur at elevated concentrations and levels of 100 ppm can be considered life-threatening (IEA, 2004).

Table 3-6 Eight hour and short term exposure levels for SO_2 (source: GESTIS database, 2005)

Sulphur dioxide	Limit values – eight hours		Limit values – short term	
	ppm	mg/m^3	ppm	mg/m^3
Austria	2	5	4	10
Denmark	0.5	1.3	1	2.6
Spain	2	5.3	5	13
European Union*				
France	2	5	5	10
Sweden	2	5	(5)	(13)
Netherlands				
United Kingdom	(2)	(5.3)	(5)	(13)
United States of America	5	13		

* The UK Advisory Committee on Toxic Substances has expressed concern that, for the OELs shown in parentheses, health may not be adequately protected because of doubts that the limit was not soundly-based. These OELs were included in the published UK 2002 list and its 2003 supplement, but are omitted from the published 2005 list.

Large combustion plants

Because of its acidification and health effects, sulphur emissions from fossil fuel combustion are bound to limits. The maximum allowed SO_2 emissions are dependent on the location, type of fuel and size and type of the plant that emits the SO_2. Directive 2001/80/EC of 23 October 2001 sets limits for SO_x as SO_2 in air from combustion plants. For solid fuels this limit is set to 10 mg/Nm^3 at 15% oxygen (about 3.8 ppm), for gaseous fuels (combusted in gas turbines) this limit is set to 35 mg/Nm^3 at 3% oxygen (about 13.4 ppm) (European Commission, 2001). It shows that the air emission limit of SO_2 for solid fuels is stricter than most of the applied short term exposure limits presented in Table 3-6.

SO_3

Part of the SO_2 that is formed during combustion of fossil fuels is further oxidized to SO_3. This is a slow chemical reaction which requires temperatures above 1100 ºC. Typically less than 1% of the sulphur leaves the combustion chamber as SO_3. However, in contrast to SO_2 this small amount of SO_3 may result in cold-end corrosion when SO_3 binds to H_2O to form sulphuric acid (H_2SO_4).

Figure 3-1 shows the temperature at which sulphuric acid condensation occurs in flue gas as function of SO3 and water concentration (Backman et al., 1983).

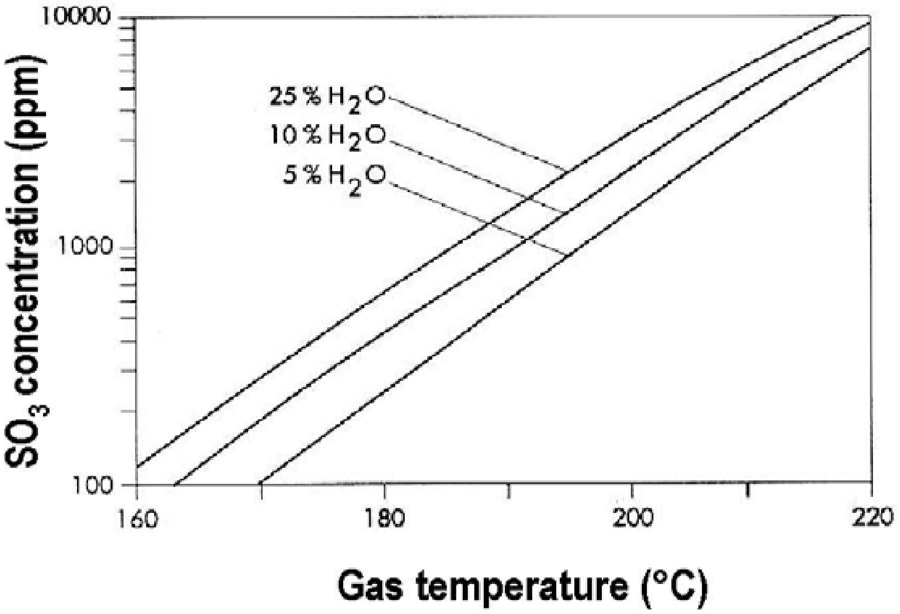

Figure 3-1 Condensation temperature of sulphuric acid in flue gas, as a function of water and SO_3 concentration (Backman et al., 1983)

3.6 Exposure limits for nitrogen oxides (NO_x)

Nitrogen oxides is a mixture of nitric oxide (NO) and nitrogen dioxide (NO_2), formed during combustion processes by the oxidation of nitrogen from combustion air. Of the NOx emissions, some 95 % or more usually is NO, whereas the fraction of NO_2 remains less than 5 % (Zevenhoven and Kilpinen, 2004). Nitrogen dioxide is a very toxic gas and exposure to it may result in unconsciousness or death. The exposure levels for nitrogen dioxide are shown in Table 3-7. No exposure levels are presented for NO, because hardly any STELs are defined for this substance. Most countries apply an 8 hour limit value of 25 ppm to NO. In this study the STEL of NO_2 will be used to define maximum concentration limits for NO_x.

Table 3-7 Eight hour and short term exposure levels for NO_2 (source: GESTIS database, 2005)

Nitrogen dioxide	Limit values – eight hours - TWA		Limit values – short term – STEL	
	ppm	mg/m^3	ppm	mg/m^3
Austria	3	6	6	12
Denmark	2	4	2	4
Spain	3	5.7	5	9.6
European Union**	0.2	-	-	-
France	-	-	3	6
Sweden	2	4	(5)	(10)
Netherlands		0,4		1
United Kingdom[1]	(3)	(5.7)	5	9.6
United States of America	-	-	5	9

[1] The UK Advisory Committee on Toxic Substances has expressed concern that, for the OELs shown in parentheses, health may not be adequately protected because of doubts that the limit was not soundly-based. These OELs were included in the published UK 2002 list and its 2003 supplement, but are omitted from the published 2005 list.

Large combustion plants

Like for SO_x emissions from large combustion plants also emission limits have been set for NO_x to reduce and control its emission to air. At 15% oxygen (gas turbines) the emission limit for SO_x as SO_2 is set to 80 mg/Nm^3 for solid fuels and to 50 mg/Nm^3 for gaseous fuels. For other combustion plants larger than 300 MW (excluding gas turbines) air emission limits for NO_x are 200 mg/Nm^3 for solid fuels.

3.7 Setting limit values for CCS streams

Table 3-8 presents the recommend maximum values of toxic substances. This recommendation is only based on health considerations. The limitations with respect to technical conditions will be discussed in the next section. It might be these limits are not strict enough and that technical limits (see chapter 4) require more stringent concentrations levels.

Based on the approach described in section 3.1.1 maximum levels of impurities are calculated. Assuming a 100% CO_2 stream, the STEL for CO_2 of 10,000 ppm is exceeded 100 times in the close vicinity of the rupture, where the air is completely replaced by the escaped CO_2. This means we have to apply this factor of 100 to the STEL of the toxic impurities (H_2S, SO_2, NO_x, CO). The resulted concentrations are tabulated in column 'Maximum (not corrected)' in Table 3-8.A safety factor of 5 is applied to get the 'Recommended maximum level'. The rationale for choosing a safety factor of 5, see section 3.1.1.

Table 3-8. Maximum and recommended level of impurities in CCS stream from health point of view

	STEL	Maximum (not corrected)	Safety factor	Recommended maximum level
	ppm	ppm		ppm
H_2S	10	1000	5	200
CO	100	10,000	5	2,000
SO_2	5	500	5	100
NO_2	5	500	5	100

4 TECHNICAL LIMITS FOR IMPURITIES

4.1 Effect of impurities on volume

Impurities in the CCS stream have two main negative effects on transport:

- Higher pressures might be required in order to avoid two-phase flow and free water formation and the consequent danger for hydrate formation and corrosion.
- The transport capacity might be reduced; as impurities occupy space and influence the compressibility of CO_2 negatively;

The pipeline capacity can be significantly reduced with increasing levels of impurities. The decrease of volumetric capacity of the pipeline is 27% for a mixture of CO_2 with 10% hydrogen (Mohitpour, 2003). From this perspective the contaminants should be limited as much as possible. Furthermore, the presence of impurities shifts the boundary of the two-phase region towards higher pressures, so that higher operating pressures are required to keep CO_2 in dense phase (IPCC, 2005).

Furthermore, the density of CO_2 is critical when transporting it, because if compressed to a liquid state with high density, a smaller pipeline diameter can be used to transport the same amount. A higher density is also favourable as it is easier to move a dense liquid than a gas (Wong, 2005). It is typical to compress CO_2 to above 73.8 bar[8] (critical pressure) so that CO_2 is always in liquid state or supercritical state, depending whether it is under or above its critical temperature of 31°C.

The volume of the CO_2 is also critical for the efficient use of storage locations. The efficiency of CO_2 storage in geological sites, defined as the amount of CO_2 stored per unit volume, increases with high CO_2 density. The presence of impurities in the CO_2 lowers the density and as a consequence lowers the storage capacity available for CO_2. The effect of impurities on the reduction of storage space is not precisely known yet; CO_2 will dissolute and react; and also the impurities may interact with the reservoir.

4.2 Effect of water in CO_2

The water content in CO_2 is critical for transport. The water content should be controlled, because of risks for corrosion and hydrate formation in the pipeline. Another consideration is that lower water levels may allow for more H_2S in the mixture before the mixture becomes corrosive. A cross-check of water and H_2S has been done to understand the trade-off between these two compounds. In this section we discuss issues related to hydrate formation and corrosion with respect to the water content in the CCS stream.

4.2.1 Hydrate formation

Hydrates are solid, crystalline compounds formed by water (“host molecules”) and small molecules (“guest molecules”). Typical guest molecules are CO_2, CH_4 and H_2S. Highly soluble gases, such as ammonia and hydrogen chloride do not form hydrates, regardless of their size.

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[8] 73.8 bar = 7.38 MPa

Hydrates form at temperatures higher than the freezing point of water and are very much like common ice in both their appearance and their properties. In a pipeline it is the accumulation of the hydrates that causes problems. These accumulations can block the line and plug and damage equipment (Carroll, 2003). The formation of hydrates requires the following three conditions:

- The right combination of temperature and pressure. Hydrate formation is favoured by low temperatures and high pressure;
- Hydrate forming molecules must be present;
- A sufficient amount of water to form the cage-like structure, but note that free water is not always required (Carroll, 2003)[9].

Hydrates can form with either gases or liquids, provided that the criteria above are met. Figure 4-1 gives the hydrate loci (combination of temperature and pressure) for several substances in natural gas. The hydrate kinetics of CCS streams is not so well known as for natural gas. Figure 4-1 is used to illustrate the hydrate formation properties of components that could also be present in CCS streams: carbon dioxide, methane and hydrogen sulphide. Although this figure gives hydrate formation in natural gas it is illustrative for the hydrate formation behaviour of CH_4, H_2S and CO_2 present in CCS streams. In this P-T diagram hydrates will form at temperatures less than the loci and at pressures higher than that of the loci (i.e. to the left and above).

The hydrogen sulphide hydrate forms at the lowest pressures and persists to the highest temperatures. The phase (P-T) diagram of H_2S and H_2O in Appendix A (Figure A-8-1) shows the hydrate formation kinetics of H_2S. When a substantial amount of H_2S is present, maintaining temperatures above 35 ºC prevents for compressor breakdown and plugging, as well as for plugging of the pipeline and injection well (Bachu, 2004).

Carbon dioxide hydrates form at pressures above 15 bar and temperatures from 0ºC (in natural gas) according to Figure 4-1. Experience with pipeline transportation of CO_2 shows that carbon dioxide hydrates appear up to temperatures of 10 ºC at current transportation pressures (Odru et al., 2006). This observation fits the pressure-temperature diagram for the system water and carbon dioxide as presented in Appendix A (Figure A-8-2).

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[9] http://members.shaw.ca/hydrate/index.htm

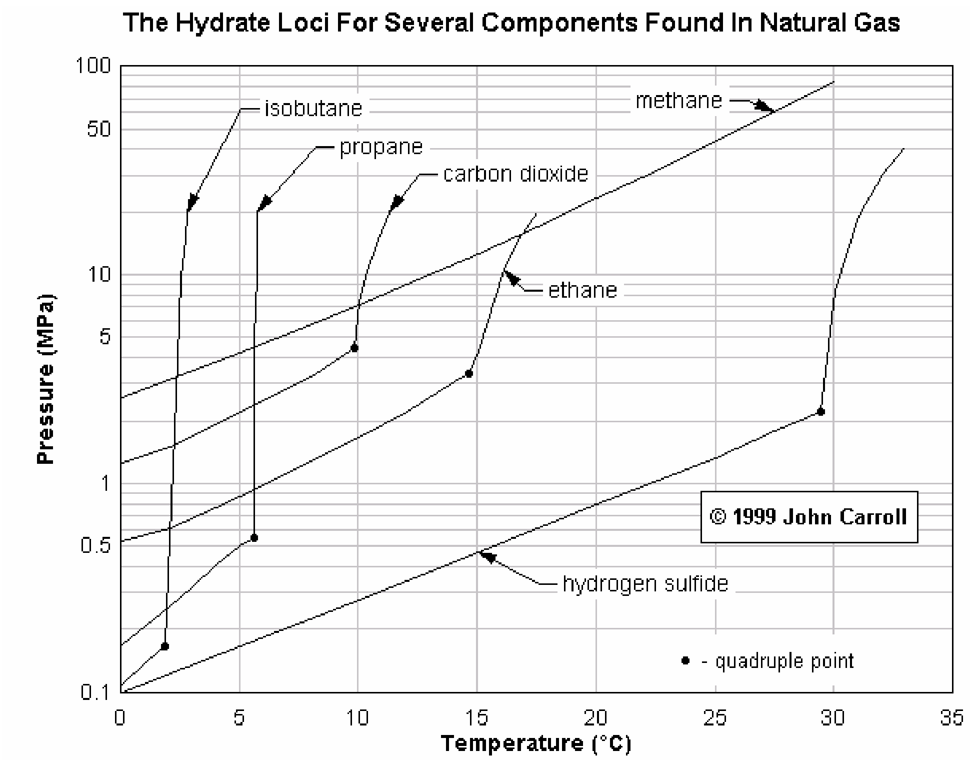

Figure 4-1 Hydrate loci for several components in natural gas (Carroll, 1999)

Although hydrate formation is a serious threat for safe pipeline operation, there are good methods to avoid them. Hydrate formation can largely be stopped by drying the CO_2 and removing the “free water” that is present. Nevertheless there is a small risk for forming of hydrates with dissolved water. Free water need not be present for hydrates to form, but certainly enhances hydrate formation (Carroll, 2003). Extra safety is built in by operating pipelines above the hydrate formation temperature, which for H_2S is 35 °C. No field reports are published that investigate the formation of hydrates with dissolved water at temperatures below the hydrate formation temperature (35 °C for H_2S). Experts, however, expect that the maximum amount of hydrates (CO_2, CH_4 and H_2S) that can be formed with dissolved water in the CCS stream will be too small to cause operational problems. This expert opinion is supported by the experience gained with acid gas injection operations in the United States, which show that gas mixtures of H_2S and CO_2 can be safely stored in the geological underground. The composition of the injected gas varies from site to site, from 95% H_2S / 5% CO_2 to 1% H_2S / 98% CO_2 (IEA GHG, 2003).
With the concentration of H_2S limited to ppm’s and a strict control of the water content it seems therefore not necessary to operate CO_2 pipelines above the H_2S hydrate formation temperature of 35 °C.

4.2.2 Corrosion

Since CO_2 dissolves in water and forms carbonic acid, which is corrosive, strict control of the water content is not only essential to prevent for hydrate formation, but also to avoid corrosion. Corrosion effects could also come from hydrogen sulphide, which forms sulphuric acid in the presence of water and from sulphur dioxide (Mohitpour et al., 2003). Even if no water is present in the CO_2, H_2S reacts with the carbon steel pipeline to form a thin film of iron sulphide on the surface of carbon steel (Wong, 2005). The iron sulphide may be dislodged at times and coat the inside surface of the stainless steel aerial coolers, thus decreasing the heat transfer efficiency. To avoid the potential problem with the heat exchanger, stainless steel can be used throughout the compressor piping if H_2S is present in the stream. A positive effect of H_2S in the CO_2 in carbon steel pipes is that it can actually allow the formation of protective compounds on the inner surfaces, increasing resistance against corrosion.

Hydrogen weakens the carbon steel, of which most CO_2 pipelines are made of, and causes it to become brittle and break. Due to the high rates the stream needs to be sufficiently dry or the pipelines need to be coated with highly corrosion resistant alloys (stainless steel) to prevent corrosion. Such solution is e.g. chosen in the Sleipner project as captured wet CO_2 needs only to be transported over a relative small distance.

In order to control corrosion effects in CO_2 pipelines, operators have several options:

- drying the CO_2 to sufficient low levels; and/or
- making use of corrosion inhibitors; and/or
- use of corrosion resistant material like stainless steel; and/or
- making use of protective coating and cathodic protection.

Corrosion rates can be in the order of mm/y when free water is present and in the order of μm/y when dry CO_2 is transported (Seiersten, 2001). Experience from existing pipelines shows that the corrosion rates are very low if the CO_2 is sufficiently dry. However, the mechanisms of the water related corrosion for CO_2 pipelines of carbon steel are not fully understood to present date (Liljemark, Personal Communication, 2006).

Drying

A typical allowable specification for water in a CO_2 pipeline with a good safety margin for avoiding corrosion is 500 ppm[10]. Other experts argue that full dehydration should be obtained, which is generally achieved through 50 ppm water content, or a concentration no more than 60% of the dew point in the worst conditions (Odru et al., 2006). In view of our analysis, this seems in most, if not all transport cases, a too stringent requirement. Figure 4-2 shows that the solubility of water into CO_2 is always higher than 500 ppm under typical transport conditions. Textbox 4-1 gives a further explanation of what is presented in Figure 4-2. The allowable water content of 500 ppm should be reconsidered when other impurities are present that lower the solubility limit, such as CH_4 and possibly also H_2S, O_2 and N_2 (IPCC, 2005). Mohitpour et al. (2003) report that water levels of 300 to 500 ppm (0.3 -0.5 kg/m^3) are accepted by industries for CO_2 transmission in carbon steel pipelines. When the CCS stream is sufficiently dry, classical carbon steel pipelines can be used to transport CO_2. Kinder Morgan (2006) claims that corrosion has not been a problem in CO_2 transportation through carbon steel pipelines, but can be a problem in oil field production.

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[10] Under typical transport conditions 500 ppm is about 0.4 kg/m^3

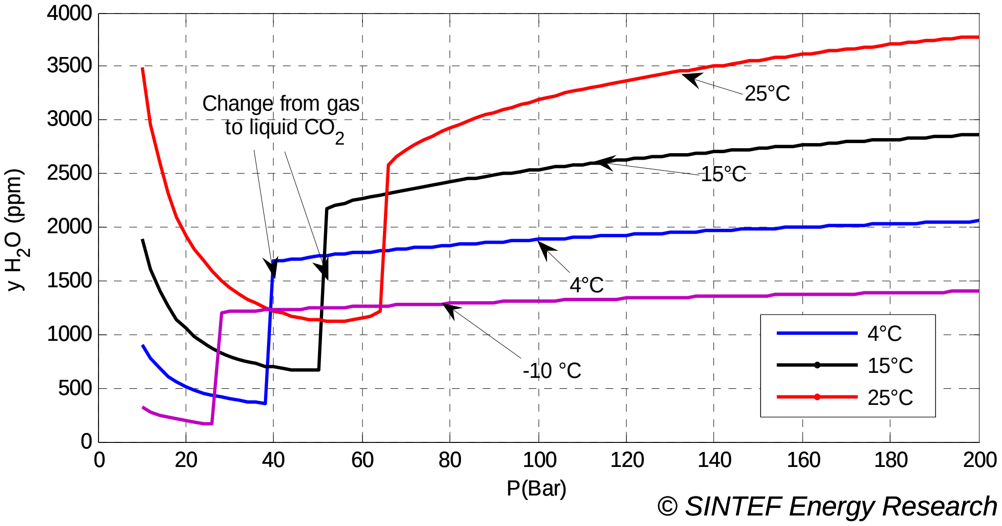

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Figure 4-2 Solubility of water in pure CO_2 as a function of pressure and temperature (Austegard et al., 2006)

Textbox 4-1 Explanation Figure 4-2 on the solubility of water in CO_2

Solubility of water in CO_2
According to Figure 4-2 the solubility of water in CO_2 reduces significantly at pressures where CO_2 changes from a liquid to gas. Furthermore, the figure also shows that the solubility of water in liquid CO_2 reduces at lower temperatures. At 120 bar the water solubility is about 1300 ppm in CO_2 at 10 ºC and about 3300 ppm in CO_2 at 25 ºC. From this it can be concluded that the water content should be controlled more strictly when CO_2 is transported at low temperatures and at relatively low pressures. At a temperature of 4 ºC, solubility is at a minimum of about 400 ppm at pressure of about 40 bar.

Corrosion inhibitors
The injection of small volumes of chemical inhibitors results in a self-healing coating in the pipeline for the protection from acids. The corrosion inhibitor increases the tolerable water limit and saves on the costs for dehydration equipment. On the other hand extra costs for the additives are needed. When dehydration is included, the metallurgy of the compressor piping can be more relaxed.

Corrosion resistant materials
A third option to mitigate internal corrosion is to use pipe materials resistant to the type of attack expected. The decisions to switch between carbon steel and stainless steel or to make all piping around the compressor of stainless steel depend on the difference in costs (Wong, 2005). It is also possible to use internal coatings and linings that isolate the corrosive fluids from the pipe wall (Mohitpour et al., 2003).

4.2.3 Combined effect of water and H_2S

It is clear that the solubility of water is critical in corrosion issues. However, the solubility of water in CO_2 might change when impurities are present and the CCS stream is not 100% pure

CO_2. The water solubility in CO_2 has been investigated in a mixture of CO_2 where also H_2S is present. In pure H_2S the solubility of H_2O is much higher compared to pure CO_2.
The project team performed modelling to the influence of H_2S impurities (at H_2S levels relevant for transporting CO_2) on the solubility of water in CO_2. This modelling results show that the effect of 200 ppm H_2S (in CO_2) on the solubility of water can be neglected (Austegard and Barrio, 2006).

4.2.4 Combined effect of water and CH_4

The impact of methane on water solubility has also been calculated and reported (Austegard and Barrio, 2006) for the recommended concentration limits, using models and parameters as adapted by Austegard et al., 2006). The results show that adding 5% CH_4 results in a decrease of water solubility of approx. 30%. In particular, at 4 °C, the solubility of a mixture of 95% CO_2 and 5% CH_4 is 1300 ppm, which is above the recommended water concentration limit.

4.3 Effect of impurities on miscibility pressure

Application of transported CO_2 in Enhanced Oil Recovery (EOR) may be an important niche market in CCS activities. It has been recognized that the minimum miscibility pressure for CO_2 in a reservoir depends on oil temperature, oil composition and CO_2 purity. The effects of compounds on the miscibility pressure of the CO_2 in oil and the effects of oxidant compounds are important issues to deal with if CO_2 is to be used in oil recovery operations.

From a storage perspective the effect that impurities in the CO_2 have on the pressure that is needed to let the oil swell in EOR operations needs to be considered. In such EOR operations pressurized CO_2 is injected in supercritical conditions into an oil field. In order to maximize the oil recovery it is best to operate the CO_2 flood as a “miscible” process. This implies that the CO_2 dissolves in the oil, which reduces the viscosity and displaces the oil, to induce an oil flow towards the production wells (IEA GHG, 2004). A key effect of such EOR operations is the ability of CO_2 to dissolve in oil at the temperatures and pressure conditions of the oil reservoir. The minimum pressure at which an injection gas (in this case CO_2) can achieve multiple-contact miscibility with the reservoir oil is called the Minimum Miscibility Pressure (MMP) (Stalkup, 1983). The MMP for an oil reservoir depends on the purity of the CO_2, the oil composition and reservoir temperature. For pure CO_2 the MMP is 74 bar at temperatures higher than 31 °C, when CO_2 becomes supercritical and the gas and liquid phase are no longer separate phases. The density of CO_2 is high enough at these conditions to be a good solvent for oils that contain a significant amount of lighter hydrocarbons. For the Weyburn oilfield (with a reservoir temperature of 59 ºC) the pure CO_2 MMP is measured at 117 and 128 bar depending on the type of experiment used (Dong et al., 2001). High temperatures of the CO_2 lower its density, which means that higher pressures are required to make CO_2 dissolve in oil.
Impurities in the CO_2 might change the minimum miscibility pressure (MMP) of the oil. The so-called “lighter” gas components such as oxygen, nitrogen, argon, hydrogen, and carbon monoxide are immiscible with oil and increase the MMP. It is claimed by SNC Lavalin Inc (SLI) that a combined total of these components of over 5%, could have a negative effect on EOR operations (IEA GHG, 2004).
Increase in MMP could lead to a decrease in oil recovery potential and overall project economics. CH_4 also increases the MMP. Results of miscibility tests at Weyburn with contaminated CO_2 show that CH_4 as a contaminant in CO_2 increases the MMP proportionally less than N_2 and CH_4 combined. N_2 and CH_4 are important contaminants in the CO_2 during injection and recycling of the CO_2. The CO_2 MMP turns out to be more sensitive to N_2 than to

CH_4 (Dong et al., 2001). If the MMP of impure CO_2 is so high that it reaches the estimated reservoir fracture pressure it is considered unsuitable for miscible CO_2 injection. CH_4 is a partly miscible component, depending on the amount of other miscible components. If the CH_4 concentration is above 3%, the MMP must be controlled. Impurities such as C_2H_6 and C_3H_8 are then left at acceptable levels (Statoil, 2004).

Other impurities in the CO_2 are acceptable or even preferred in the EOR process, because they *decrease* the MMP. Among these are H_2S, SO_2, C_2H_6 and other intermediate hydrocarbons (such as C_3 and C_4) (Lake, 1989). High concentrations of H_2S increase the miscibility of oil. Hydrogen sulphide (H_2S), which makes up 2.5% of the injection gas at Weyburn, is particularly beneficial at helping CO_2 to mix with oil. On the other hand H_2S may lead to legal barriers, especially at offshore platforms. Also public perception issues become important and should be considered.
When CO_2 with H_2S in it is stored in aquifers the effects of H_2S on the reservoir should be investigated. Knauss (2004) has conducted computer simulations and evaluated the impact of co-injecting SO_2 and H_2S present in a coal-fired flue gas stream together with CO_2 into a sandstone reservoir. The simulations show that injecting H_2S does not seem to have a large effect on the interaction between rock and water. Even relatively large amounts of H_2S should therefore not prove problematic for a CO_2 injection process. Gunter et. al. (2004) found that iron containing minerals (oxides and carbonates) react to form iron sulphide minerals when exposed to H_2S. This could reduce the permeability if the aquifer contains significant amounts of iron-containing minerals. However, changes in composition and storage potential are strongly dependent on the initial mineral phase present (Kirste et. al., 2004).
These issues will be addressed in more detail by an additional project within DYNAMIS.

4.4 Effect of oxidant compounds (O_2)

Oxygen in the CO_2 stream might have several effects, but all are related to the storage of CO_2. Currently, it is not clear what considerations have been made to allow for certain levels of oxygen in the CO_2. Because of a lack of fundamental research and development and industrial experience oxygen concentration in CO_2 that could be allowed is surrounded by much uncertainty. Statoil (2004) has defined some quality requirements for applying CO_2 to Enhanced Oil Recovery (EOR). According to those requirements, the concentration of oxidants such as O_2 should be less than 100 ppm since they react exothermally with oil and can cause overheating at the injection point. If the oil is oxidized, it will become more viscous and difficult to extract and refine. IEA GHG (2004) also mentioned this risk for oxidation of the oil in the presence of oxygen.
Another issue is that oxygen in the presence of H_2O might accelerate oxidation reactions that affect the injection equipment. Oxygen is particularly harmful because the presence of oxygen and water simultaneously could significantly increase corrosion rates in the production and downstream processing equipment. The oxygen induced corrosion effect is enhanced with the presence of H_2S, but simultaneous presence of H_2S and O_2 is not likely as H_2S is often related to pre-combustion (IGCC) process at reducing atmosphere where O_2 is not present. Praxair (2006) states that most oil operators prefer oxygen levels below 10 ppm because of reservoir safety reasons.
Other potential effects of oxygen have to do with the increased biological growth. The significance of this effect is also unknown.

For EOR operations the concentration of O_2 is generally lowered to a level of less than 100 ppm. This number however is surrounded by uncertainties since the effects of oxidation of oil and

biological growth are to a large extent unknown. Furthermore, a low concentration of oxygen is specified for meeting current pipeline operating practices, due to the corrosive nature of the oxygen.
Currently there is a lot of debate on what the CO_2 specification should be, but in the United States where EOR grade CO_2 is commonly used operational practices call for between 1 and 100 ppm oxygen. Oil field operators preferably use CO_2 with only 10 ppm O_2 in it. The limit for O_2 is only put on CO_2 for EOR storage and not for other types of CCS projects. There is concern that oxygen would cause bugs to grow or would oxidise the hydrocarbon down the well (White, 2006).

Experience with air injection as a method for enhanced oil recovery (EOR) could possibly give a knowledge base that could be transferable to CO_2 geological storage operations. The air injection process is characterized by injecting high pressure air in the reservoir to boost oil production (Stokka et al., 2005). The injected air can consist of up to 20% oxygen. When performing air injection the intention is to have oxidation and combustion taking place in the reservoir to increase the reservoir temperature and produce CO_2 that improves oil recovery. If the process is designed well the oxygen is consumed in the reservoir. There is a risk that air reaches the production well and that oxygen reacts exothermically with oil. This reaction leads to elevated temperatures may arise near the wellhead that may be harmful to the equipment. Therefore this is carefully evaluated and oxygen sensors should be placed in the producers to detect any oxygen coming to the producer and eventually shut down the well.

4.5 Effect of incondensable gases on compression work

4.5.1 Phase equilibrium

The presence of non-condensable gases affects the behaviour of CO_2. Following non-condensable gases might be present in CO_2: hydrogen (H_2), Argon (Ar), nitrogen (N_2), oxygen (O_2) and methane (CH_4). These non-condensable gases have extremely weak tendency to interact with other materials, but dilute the CO_2. The phase change becomes a more complex process compared to the normal co-existence of pure CO_2 gas and CO_2 liquid at constant pressure and temperature. The presence of non-condensable components results in increased pressure requirements for the condensation of CO_2. Austegard and Barrio (2006) show that of all non-condensable gases, hydrogen in CO_2 has the largest effect on the phase equilibrium.

Figure 4-3 shows the phase envelope for the H_2-CO_2 mixture at 5°C. The calculations conducted by Austegard and Barrio (2006) show agreement with the experimental values of Bezanehtak (2002) and indicate for instance that having 4% H_2 in the CCS stream will imply that a pressure above 80 bar will be required for full condensation of the mixture.

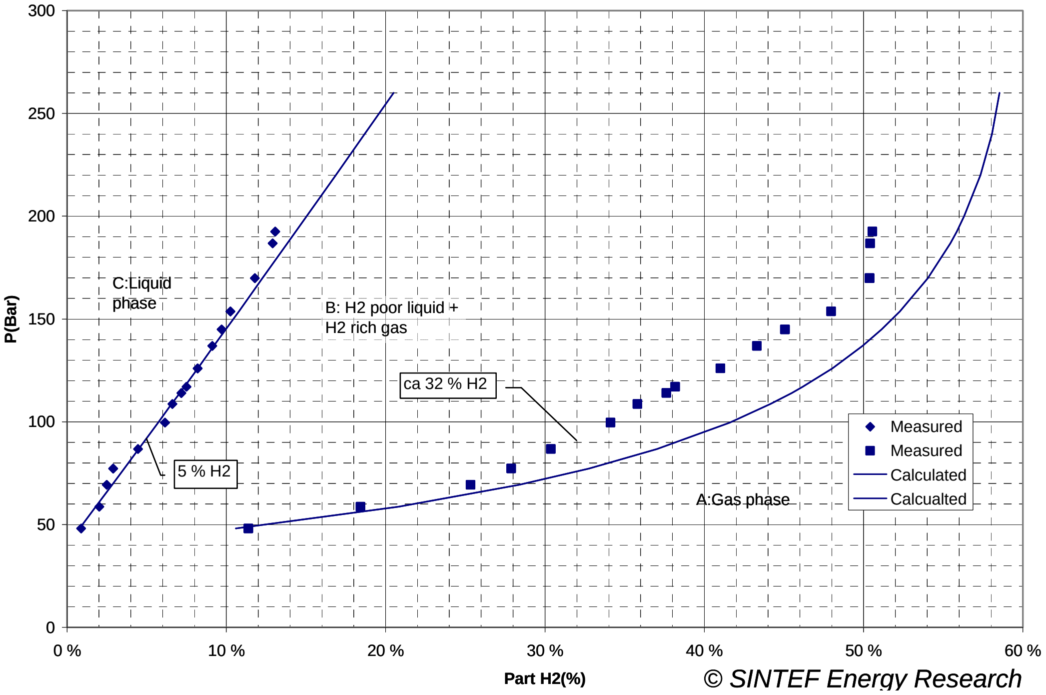


Figure 4-3 Phase envelope H_2-CO_2 at 5°C, measured values from Bezanehtak,(2002), calculations by Austegard et al. (2006).

The concentration of hydrogen in the CCS stream will - at maximum - only be a few percent. Hydrogen is a valuable gas and will be recovered for use when considerable amounts are present. In case the amount of hydrogen in CO_2 is considerable it can easily be recovered by compressing the CCS stream and flashing the hydrogen off.

4.5.2 Energy required for pressurization of impure CCS stream

Impurities present in the CO_2 will affect the required energy for compression compared to pure CO_2 mainly for two reasons:

- More substances with other compressibility characteristics need to be compressed;
- Higher pressures are required to avoid two-phase flow.

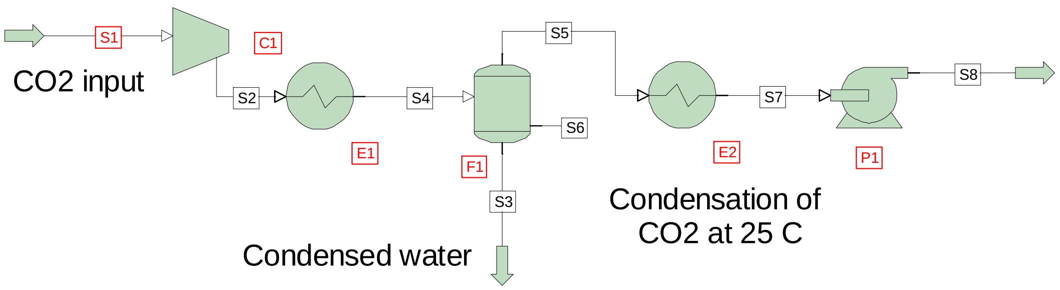
In this section we will give an indication of the required extra work for compression of contaminated CO_2 for transportation.

There are two alternatives for bringing the CCS stream to the right pressure for transportation:

- condensation by cooling and pumping;
- multi-stage compressing.

Generally, the CCS stream is compressed when it is transported at ambient temperatures through pipelines. Liquefaction is applied when the CCS stream is transported at low pressure and at low temperature by ship. Figure 4-4 shows possible conceptual lay-outs for liquefaction/pumping and compression of CO_2.

Condensation and pumping of CO2



3 Step compressor train

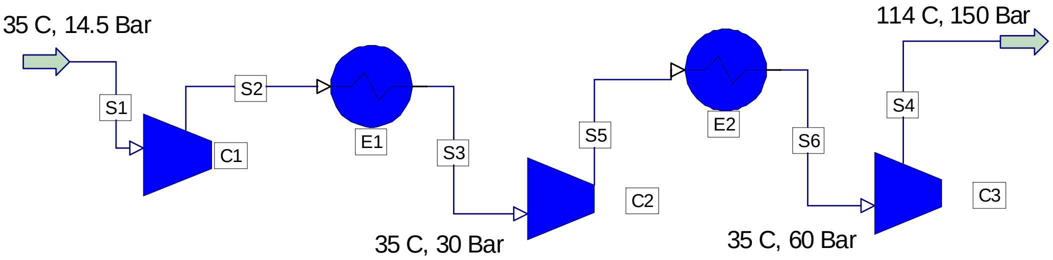


Figure 4-4 Two alternatives for pressurization: condensation and pumping of CO_2, and three-step compressing

Calculations for the compression work for a representative CCS stream from 14.5 bar to 150 bar have been conducted including small percentages of non-condensable gases. The results show that the increase in compression work is almost linearly to the concentration of inert components. The increase in compression work is approximately 2.5%, 3.5% and 4.5% for a concentration of 1% of O_2, N_2 and H_2 respectively. According to the calculations, a presence of 5% H_2 in the mixture will represent an increase of 25% of compression work (Austegard and Barrio, 2006).

5 EXISTING EXPERIENCE AND EXISTING RECOMMENDATIONS

The experience with the transport and use of CO_2 is extensive, since the chemical and oil industry already makes use of CO_2 for decades. Technical and safety procedures have been developed over time to work with this component. Transportation of CO_2 therefore is not so challenging anymore, but lessons can be learned from the compositions of the CO_2 stream that is worked with in existing projects. Two CCS projects are discussed here, the Weyburn and Sleipner project. These projects are quite different in the end use of CO_2. At Weyburn CO_2 is used for EOR operations and at Sleipner the CO_2 is injected into a deep saline aquifer for geological sequestration.

5.1 Weyburn

Since the year 2000 the Dakota Gasification company exports over 1 Mt of of high-pressure CO_2 per year to the Weyburn Oil Fields. The CO_2 is produced at the Great Plains Synfuels Plant, a coal gasification plant, and delivered by a 325 km pipeline to the Weyburn depleting oil fields to enhance the oil production of the field. The composition of the CO_2 is dictated by the Rectisol unit, using a solvent of cold methanol, at the Synfuel plant and meets the requirements for enhanced oil recovery. It produces 95% pure CO_2, without additional treatment prior to compression and transportation.

The composition of the gas carried by the pipeline at Weyburn and injected in the oil fields is presented in Table 5-1. At the Synfuels plant the CO_2 is captured using a cold methanol wash and compressed to a dense phase (Chalaturnyk and Durocher, 2005). Because of the methanol process, the solubility of water in methanol is very high, the resulting gas is very dry (water content in CO_2 is less than 20 ppm). The CO_2 injected at Weyburn has a H_2S concentration of 0.9%, which is relatively high of H_2S. Other sources of information report concentrations of 1%-5% H_2S. No extra safety measures have been taken at Weyburn to operate with high H_2S concentrations, because the pipeline crosses sparsely populated areas where these measures are not necessary.
Since the start of CO_2 injection in the Weyburn oil field there have not been real problems with corrosion from H_2S and CO_2. A combination of good material selection (stainless fibreglass is used in critical areas), the use of dry CO_2 and corrosion inhibitors has proved to be successful preventing from corrosion.

Table 5-1 Typical composition of the gas of the Weyburn EOR project (IPCC, 2005)

Component	Weyburn - EOR
CO_2	96%
H_2O	<20 ppm
H_2S	0.9% (=9000ppmv)
CO	0.1% (=1000 ppmv)
O_2	<50 ppm
CH_4	0.7%
N_2	<300 ppm
Ar (Argon)	
H_2	
Ammonia	
SO_x	
NO_x	
C_2+hydrocarbons	2.3%

5.2 Sleipner

The origin of the CO_2 that is injected in the Utsira formation is the natural gas extracted from the Sleipner West field in the Norwegian North Sea. The natural gas from the Sleipner fields contains between 4.5% and 9% CO_2. The European gas pipeline specifications limit carbon dioxide concentrations to below 2.5%. In order to meet the European specifications, carbon dioxide is stripped from the natural gas stream and injected into the Utsira formation. An amine process is used to remove the CO_2 from the natural gas stream.

Information on the composition of the gas that is injected into the Utsira formation is yet not publicly available. However, some comments could be made already without knowing the exact composition of the CO_2. The injection stream is not pure and can contain up to 150 ppm H_2S. Furthermore, the CO_2 is saturated with water (De Koeijer, 2006). H_2S present in combination with water makes the mixture very corrosive. The injection well was designed for these corrosive conditions and uses stainless steel down hole (25% Chromium duplex) and at the surface (22% Chromium duplex steel).
The non-condensable gas content is not expected to increase above 3% during normal operation, even though 5% non-condensables is stated as design basis. The carbon dioxide can contain up to 5% non-condensable gases as well. The amount of hydrocarbons (which is mainly CH_4) can vary from 0.5-2% (De Koeijer, Personal Communication, 2006).

5.3 Existing specifications

CO_2 pipeline operators have established minimum specifications for the composition of the CO_2 they transport. In Table 5-2 a typical specification of Kinder Morgan for their U.S. CO_2 pipelines is given. This specification refers to an enhanced oil recovery (EOR) project and can be regarded as a logistic agreement on how to trade the CO_2 and what type of product could be bought from the Kinder Morgan CO_2 Company. This specification is a combination of a trade definition combined with technical knowledge on what can be transported. In the right column of the table the effects that set the upper concentration limits are listed. The concentration of carbon dioxide is set at a minimum of 95% to be sure that the mixture is able to dissolve with oil and pushes the oil to the production well. A lower maximum concentration of CO_2 would imply more impurities other than CO_2 and therefore less recovery potential of oil. Another issue that should be considered is that impurities take up valuable reservoir volume and increase the storage costs of CO_2 accordingly. Nitrogen has an increasing effect on the MMP and therefore is limited to a concentration of 4%. The presence of hydrocarbons can either help or hurt the miscibility depending on molecular weight. Methane increases the MMP, but heavier hydrocarbons like propane and heavier can help. The maximum concentration is set to 5% to prevent for increasing the MMP to such levels that the CO_2 flooding does occur anymore.

The requirements of enhanced oil recovery affect the purification of CO_2 requiring removal of oxygen down to around 10 ppm (White et al., 2006). Oil operators prefer the oxygen amount to be below 10 ppm.

The maximum temperature is set at 50 ºC, which is to protect the pipeline coating. The coating will be degraded if 50 ºC is exceeded.

Table 5-2 United States Pipeline Quality Specifications (KinderMorgan, 2006)

Compound		Concentration	Minimum/maximum	Critical for
Carbon dioxide	CO_2	95%	Minimum	MMP
Nitrogen	N_2	4%	Maximum	MMP
Hydrocarbons		5%	Maximum	MMP
Water	H_2O	30 lbs/MMcf	Maximum	Corrosion
Oxygen	O_2	10 ppm	Maximum	Corrosion
Hydrogen sulphide	H_2S	10-200 ppm	Maximum	Safety
Glycol		0.3 gal/MMcf	Maximum	Operations
Temperature		50 ºC	Maximum	Materials

6 DYNAMIS QUALITY RECOMMENDATIONS

The amount of impurities in the CCS stream should be limited both from a health and safety perspective and from a technical perspective for the purpose of safe transportation of CO_2. In this chapter health and safety and technical limits to impurities in the CCS stream are combined to recommend on CCS stream quality. The table below presents the recommended maximum concentrations of impurities in the CCS stream. Figures in bold indicate concentrations of components that have been adjusted and differ from the current recommendations in the ENCAP project. The last column shows whether the concentration limit is set from a health and safety or technical perspective. The limits might be different when the storage of CO_2 asks for more stringent limits for some compounds. In this chapter, the choices for the various limits are further clarified.

Table 6-1 DYNAMIS CO_2 quality recommendations

Component	Concentration	Limitation
H_2O	**500 ppm**	Technical: below solubility limit of H_2O in CO_2. No significant cross effect of H_2O and H_2S, cross effect of H_2O and CH_4 is significant but within limits for water solubility.
H_2S	**200 ppm**	Health & safety considerations
CO	**2000 ppm**	Health & safety considerations
O_2[11]	Aquifer < 4 vol%, **EOR 100 – 1000 ppm**	Technical: range for EOR, because lack of practical experiments on effects of O_2 underground.
CH_4[11]	Aquifer < 4 vol%, EOR < 2 vol%	As proposed in ENCAP project
N_2[11]	< 4 vol % (all non condensable gasses)	As proposed in ENCAP project
Ar[11]	< 4 vol % (all non condensable gasses)	As proposed in ENCAP project
H_2[11]	< 4 vol % (all non condensable gasses)	Further reduction of H_2 is recommended because of its energy content
SO_x	**100 ppm**	Health & safety considerations
NO_x	**100 ppm**	Health & safety considerations
CO_2	>95.5%	Balanced with other compounds in CO_2

6.1 H_2O

PROPOSAL: The water content is set at an indicative figure of 500 ppm

The maximum water content should not exceed the saturation level, i.e. no free water present, to prevent for corrosion and hydrate formation. In section 4.2 we have seen that the amount of water that can dissolve in CO_2 depends on the temperature, pressure and impurities in the CO_2. In practice the allowable concentration of CO_2 might even be set at a lower level because of some additional occurrences such as the possible need for safe depressurization and cross-effects with other impurities.

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[11] The concentration limit of all non-condensable gases together should not exceed 4 vol%.

Hydrate formation occurs at low temperatures and pressures. The solubility of water at temperatures of 15 °C and 25 °C is higher than the proposed value of 500 ppm for all pressures ranging from 0 to 200 bar. The temperature of the sea water at storage depths (North Sea) is about 4 °C. At this temperature, water solubility is above the proposed 500 ppm for pressures above 40 bar. If the pressure drops below 40 bar there will be a risk for free water formation and consequently hydrate formation (Austegard and Barrio, 2006).

This particular behaviour of CO_2 should be thought of when storing CO_2 offshore, as the pressure might drop temporarily below 40 bar during pressure release procedures. Eventually, a further reduction of the water content below 500 ppm should be considered. CO_2 drying is not a large technological challenge and the additional costs might not be high.

The results of the cross-check of H_2O and H_2S (at 4°C and 100 bar) by SINTEF (Austegard and Barrio, 2006) show that the change in solubility of H_2O is negligible if 200 ppm H_2S is added to pure CO_2. Higher levels of H_2S do allow for more H_2O in the mixture, because its solubility increases. This effect however is however not significant as the solubility change is rather low and uncertainty in the calculations is relatively high.

6.2 H_2S

PROPOSAL: Increase the H_2S content from 50 ppm to 200 ppm

Health and safety considerations

H_2S is listed as a very toxic compound. The most widely recognised standards for H_2S reference an 8-hour Time-Weighted Average (TWA) of either 5 ppm or 10 ppm in air, and a 15-minute Short Term Exposure Limit (STEL) of no more than 15 ppm in air. Many monitoring programmes use instruments which set the alarms set to sound immediately if the concentration reaches 10 ppm, in which case the workers immediately have to leave the affected area.

According to the approach suggested in section 3.1.1 the concentration of H_2S in the CCS stream may not exceed 200 ppm. The figure of 200 ppm is supportable in terms of safety and gives a reasonable safety margin. In case of a blow-out the CO_2 concentration will be the limiting factor instead of H_2S. Lowering the H_2S in CO_2 limit to 100 ppm would require substantial additional investment in the AGR plant including a nitrogen wash. Further reduction of the amount of H_2S in CO_2 is expected to require a significant additional investment. Scoping calculations of Progressive Energy Ltd. indicates that the 200 ppm H_2S level is achievable without adversely affecting the design of the AGR plant or the commercial viability of a coal-fed IGCC plant (Brown, Personal Communication, 2006).

Technical

Section 4.2.1 considers hydrate formation kinetics of H_2S in CO_2. Although H_2S hydrates form up to temperatures of 35 ºC there is no direct need to operate above this temperature if H_2S concentrations are low and there is no “free” water present in the CO_2. There are no strong arguments to propose a stricter limit for H_2S than required by health and safety considerations. Expert opinion is that the maximum amount of hydrates (CO_2, CH_4 and H_2S) that can be formed with dissolved water in the CCS stream will be too small to cause operational problems. However, it is recommended to take up the issue of possible hydrate formation when only dissolved water is present in CO_2 in further research.

The water content should also be strictly controlled from the viewpoint of possible corrosion effects enhanced by H_2S. Given the available literature on this issue there are also no strong arguments to lower the maximum allowable concentration of H_2S in CO_2 below the proposed 200 ppm limit, provided that the amount of water is below its solubility limit.

Another of hydrogen sulphide is that it increases the solubility of water. Modelling results show that the effect of H_2S at the proposed concentration of 200 ppm on the solubility of water can be neglected (see section 4.2.3)

6.3 Carbon monoxide (CO)

PROPOSAL: Increase the limit for CO to 2000 ppm in CO_2.

Health and safety considerations
Using the logic explained in section 3.1.1, the limit for CO is set to a level of 2,000 ppm, including the safety factor. Applying a safety factor of 5, results in a limit of 2,000 ppm for CO. From a technical point of view and within the realistic range of CO concentrations in the CCS stream from a capture installation there is no need to limit the concentration of CO to a concentration level below 2000 ppm.

6.4 Oxygen (O_2)

PROPOSAL: The existing limit of <100 ppm might be too stringent and therefore it is proposed to set a higher limit which is yet undefined.

Within this project no strong arguments have been found that ask for the continuation of the limit for oxygen below the 100 ppm level. Since there is no evidence that 100 ppm or even lower levels are strict limits to avoid high temperatures at the wellhead and consequent occurrences. Therefore, within DYNAMIS, we suggest that the maximum concentration of O_2 in CO_2 should be more relaxed. Since there is no O_2 in the captured CO_2 for the processes that are subject of DYNAMIS, no quantitative limit for O_2 will come from DYNAMIS.

6.5 Methane (CH_4)

PROPOSAL: Aquifer < 4 vol%, EOR < 2 vol%

Transport
Methane affects the solubility of water (see section 4.2.4). The results of the cross-check of water and CH_4 for the recommended concentration limits show that the solubility of water is well above its saturation level and its recommended concentration limit for DYNAMIS of 500 ppm. The solubility of water in a mixture of 5% CH_4 and 95% CO_2 is 1300 ppm, which also supports the even more conservative proposal of a concentration limit below 4 vol% CH_4 for the aquifer case.

CO_2 storage
The aquifer and EOR case are considered separately because the consequences of CH_4 in the CO_2 mixture are different. For EOR it should be marked that CH_4 increases the miscibility pressure and makes it more difficult for the CO_2 to mix with the oil. However this effect is less

strong compared to the effect of N_2 on the miscibility pressure. Therefore the limit for CH_4 is set at less than 2 vol%.

6.6 Non-condensables (N_2, H_2, Ar)

PROPOSAL: The limits that are used in the ENCAP project will be continued at 4 vol% for all non-condensables together (including CH_4 and O_2).

Conditioning
Of these three inert components that are present in the CO_2, H_2 is the one that affects the behaviour of CO_2 most. The more hydrogen there is in the CO_2 the higher the required pressure for the total condensation of CO_2. Section 4.5.2 covers this issue. The additional compression work that is needed depends on the technology used. The additional work needed is linearly dependent on the concentration of inert components, and is approximately 2.5%, 3.5% and 4.5% for a concentration of 1% of O_2, N_2 and H_2 respectively (Austegard and Barrio, 2006).

Storage
Both hydrogen and nitrogen increase the miscibility pressure. The percent-increase of the MMP due to the percent-increase of hydrogen is 0.6%.

6.7 SO_2 and NO_2

PROPOSAL: Both SO_2 and NO_2 limits are set to 100 ppm from a health and safety perspective

Health and safety considerations
The formation of SO_2 and NO_2 is relevant in post-combustion processes (also in oxy-fuel processes, but these fall outside the scope of this study). From a health and safety perspective the maximum allowable concentration of SO_2 and NO_2 is set according to the method discussed in section 3.1.1. The limits for SO_2 and NO_2 are both set to 100 ppm.

With the knowledge that SO_2 concentrations in flue gases from coal combustion are typically around 300-5000 ppm (IPPC, 2005), the additional purification steps needed for reducing the amount of SO_2 in CO_2 to the 100 ppm level are considerable. However, purification measures removing SO_2 from the flue gas are already taken before the capture process, since amines that absorb the CO_2 to remove it from the flue gas stream, form heat-stable salts with SO_2 (and NO_2). This reaction leads to a loss of absorption capacity of the solvent and the risk of formation of solids in the solution. Commercial SO_2-removal plants will remove SO_2 up to 98-99% before the CO_2 is captured. It is generally agreed that flue gases should not contain more than 10 ppm SO_2, if amine based solvent losses are to be reduced to acceptable levels (Hendriks, 1994). Even when all SO_2 (10 ppm) in the flue gas will be captured together with the CO_2, which is not expected, the concentration of SO_2 in the CO_2 will be well below 100 ppm and not challenge the transport requirement.

Storage
The presence of SO_2 in the injected stream of CO_2 should be considered as well, because under specific conditions sulphur (S) can be oxidized, due to the lower pH created. SO_2 could give rise to strong acidification near the injection point. Xu et al., (2004) state that corrosion and well

abandonment problems caused by co-injection of SO_2 together with CO_2 will be a very significant issue.

If only minor amounts of SO_x are present in the injected gas stream this effect would be rather small. However, no limits are specified for the maximum allowable concentration of SO_x from a storage perspective and further research on this issue is recommended. The proposed concentration limit for SO_x of 100 ppm is continued.

6.8 CO_2

PROPOSAL: The concentration of CO_2 is set to >95.5%

The CO_2 content in the stream is the resultant of the presence of other impurities in the stream. Currently, there is no agreement on what the CO_2 content should be. The London Protocol says that the content of CO_2 streams should be ‘overwhelmingly’ CO_2. Greenpeace, being more conservative, claims that the CO_2 content should be 99.9%. From existing pipeline specifications it shows that the CO_2 content of the mixture that is to be transported will be >95% when all other conditions are met. This seems sufficiently high for technical reasons. Lower concentrations of CO_2 are not sought, because in that case the volume will be used less efficient. The DYNAMIS quality recommendation results in a minimum CO_2 concentration of 95.5% when all other compounds are present at maximum allowable concentrations.

6.9 Other requirements

PROPOSAL: Temperature of the CO_2 is of minor importance and should be adjusted in relation to the conditions of the capture. In case of impurities, pressure conditions may have to be adjusted to operate in a “safe region” without two phase flow. The proposal is to limit the maximum temperature CO_2 to less than **30ºC and the delivery pressure of CO_2 to (at least) 100 bar**.

Temperature

For transportation of CO_2 a small volume is preferred to efficiently use the limited capacity of pipelines. Higher density is obtained at lower temperatures and higher pressures. The compressibility and density of CO_2 are sensitive to temperature changes. Whereas the density of pure CO_2 in dense phase is 800-900 kg/m^3 at 30 °C it rapidly diminishes to 600 kg/m^3 at 40 ºC (Ecofys, 2006) CO_2 is therefore normally transported between 15 – 30 °C and 100 – 150 bar as a liquid. However, in the specification of the CO_2 product from KinderMorgan the required temperature of CO_2 is less than 50 ºC.

The critical point, where pure CO_2 changes from supercritical to liquid phase, is at 31 ºC and 73.8 bar. The density change form supercritical and liquid goes gradually, without significant changes in the behaviour of the mixture. Phase change between liquid and supercritical does not pose a problem as long as the composition of the CO_2 is sufficiently known.

During the transport in pipelines, CO_2 will fast reach the same temperature as its surroundings, which could be underground (ca 10 °C) or sea water temperature (North Sea is about 4 °C). Therefore, cooling down the CO_2 after compression is not highly necessary, but should be adjusted to the local conditions, i.e. in areas with lower temperatures and sufficient availability of low-temperature cooling water (e.g. seawater) this may be much lower than in warm areas with inland installations.

When transporting warm CO_2, heat will be transferred to the surrounding environment and might have negative effects. Existing regulation for Environmental Impact Assessments (EIA) for both natural gas and CO_2 pipelines operations deal with environmental impacts of high temperature substances that are transported. In the Netherlands, concerns are expressed on the negative effects on bulb cultivation that transporting gas with a temperature of 45 °C could have. Results of the investigation show that the eventual negative effects of heating the underground are very local and that isolation of the pipeline can significantly reduce the heat that is released to the surroundings of the pipe.
A reference position was described in which it seems environmentally acceptable in The Netherlands for the temperature of the rivers to rise as high as 27 C before remedial measures (such as no longer discharging power station cooling water into the river) are required. Thus a CO_2 delivery temperature of 30 °C was considered a reasonable starting point.

Pressure
The pressure of the CCS stream that is transported per pipeline varies along the trajectory to the storage location. The type and characteristics of the storage location or the end use of CO_2 defines the delivery pressure at the injection or end use point. Furthermore, the pressure of the CO_2 drops along the pipeline. There are several measures that can compensate the pressure drop:

- placing booster stations along the pipeline,
- increase the diameter of the pipe;
- increase the initial pressure of the CO_2 at the start of the pipeline

The optimal solution will be a trade-off between these factors (initial pressure, applying booster stations and size of pipeline) and will vary from project to project. The precise design will ultimately be economically determined.

6.10 Additional purification and conditioning

At the time of this study, a set of simulations for CCS stream composition for pre-combustion were available. For post-combustion capture such simulation data of the CO_2 composition after capture are not available. Appendix B presents the CO_2 composition of seven simulations; case 1-3 presenting CO_2 compositions resulting from pre-combustion capture applied to natural gas based processes and case 4-7 from pre-combustion applied to coal or lignite gasification processes. It turned out that for all the simulated pre-combustion processes only CO_2 was above the limit proposed in the Dynamis specification. The water content without drying is about 700 - 1000 ppm for pre-combustion processes. When the Selexol process is used there is the concentration of H_2S is well below 200 ppm. The simulations done in Dynamis work package 2 shows that the concentrations of all compounds are well in line with the DYNAMIS CO_2 quality recommendation reflecting transport requirements. Also the concentration of all non condensable gases together is well below 4% for cases 1-7. No further purification steps are needed on top of compression and drying as already applied to the outlet streams from the capture unit.

7 OVERALL CONCLUSIONS

This study has taken a step in the direction of specifying what the quality of CO_2 should be to safely transport and store it. Several critical issues in the transport of CO_2 have been covered resulting in a final recommendation on CO_2 quality for the DYNAMIS project.
The main conclusions of this task can be summarized as follows:

- The water level in CO_2 could be significantly higher than what has been agreed on in the ENCAP project, namely 500 ppm compared to 50 ppm. Under the expected transport conditions (pressures, temperatures and other possible contaminants) this level of water is sufficient low and the risks for free water and hydrate formation are at a minimum.
- Limits for H_2S are set by safety considerations, rather than by technical limits. A concentration limit of 200 ppm for H_2S is supportable in terms of safety. The cross-effect of H_2O and H_2S showed that the impact of small amounts of H_2S (200 ppm) on water solubility is negligible.
- The carbon monoxide (CO) level is set at a level of 2,000 ppm from a health and safety perspective.
- There is a lack of practical experiments on effects of oxygen (O_2) in underground reservoirs. To reflect this uncertainty, a limit range for oxygen of 100 to 1000 ppm is proposed.
- Both levels for SO_2 and NO_2 in CO_2 are limited from a health and safety perspective and amount to 100 ppm.
- The total volume for all non-condensable gases together (N_2, H_2, CH_4, O_2, Ar) is set to 4%. It is however recommended to limit the amount of H_2 as much as possible, because of its high energy content and market value.
- The effect of CH_4 on the solubility of water in CO_2 is significant, but not harmful for transportation of CO_2 at concentrations of CH_4 below 5% and a maximum water level of 500 ppm.

Comparison of the DYNAMIS CO_2 quality recommendation to several compositions of CO_2 from pre-combustion capture processes showed that further purification steps on top of compression and drying of the CO_2 are not required to comply with the transport requirements. A next step will be to also include storage requirements see whether these ask for additional purification steps. A parallel DYNAMIS project covers these issues in more detail.

Recommendations for further research
In this research the main focus has been on finding maximum allowable concentrations for impurities in the CO_2 mainly from a transport perspective. Where necessary, limitations from a storage perspective are addressed as well, but very rough. Since there is just one composition that a volume of CO_2 can get both transport and storage limitations should be considered to define the ultimate CO_2 composition to transport *and* store CO_2.

- The rather strict limits for O_2 have been questioned, because there is no good explanation why they are so strict. It could be that the limits for O_2 could be less stringent without consequences for safe transportation of CO_2.
- The possible effects of trace elements of the solvents of the capture process on pipeline transportation have not been investigated in this study. It is worth to include the trace quantities of these solvents in further work on CO_2 quality.
- The risk for hydrate formation when dissolved water is present in the CO_2 should get attention in further research. Especially, when offshore pipeline transportation of CO_2 is

considered, where temperatures will be lower and more favourable for hydrate formation, the consequences of eventual hydrate formation should be clarified.

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LIST OF ABBREVIATIONS

OEL	Occupational Exposure Level
OSHA	Occupational Safety and Health Administration
NIOSH	National Institute for Occupational Safety and Health
PEL	Permissible Exposure Limit
ACGIH	American Conference of Governmental Industrial Hygienists
ppm	parts per million
MMP	minimum miscibility pressure
EOR	Enhanced Oil Recovery
IGCC	Integrated Gasification Combined Cycle
NOAEL	no observed adverse effect level
AIHA	American Industrial Hygiene Association
IPCC	Intergovernmental Panel on Climate Change
EIA	Environmental Impact Assessments
MPa	MegaPascal
TEG	tryethylene glycol

APPENDIX A

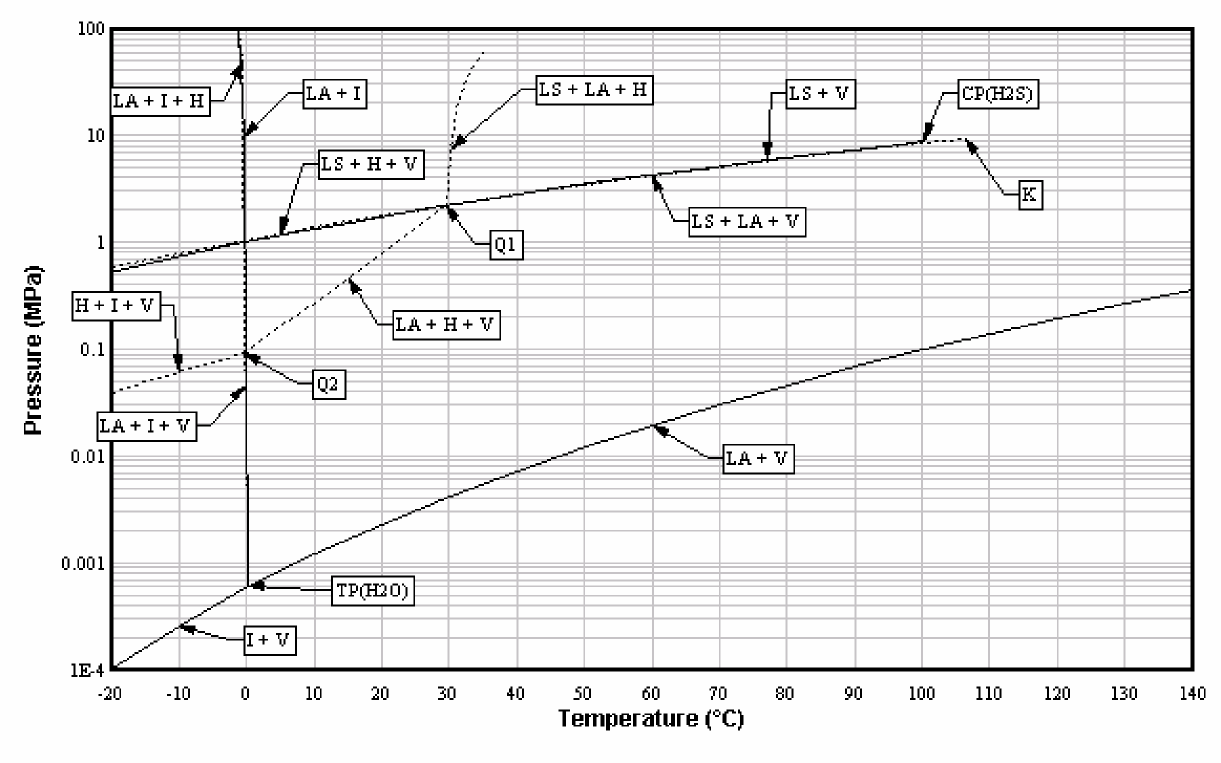

Figure A-8-1 Phase diagram of H_2S and H_2O (Carroll, 1998) With LA = aqueous liquid, LS = hydrogen sulphide-rich liquid, H = hydrate, V = vapour, I = ice, Q = quadruple point, K = three-phase critical end point, TP = triple point, and CP = pure component critical point.

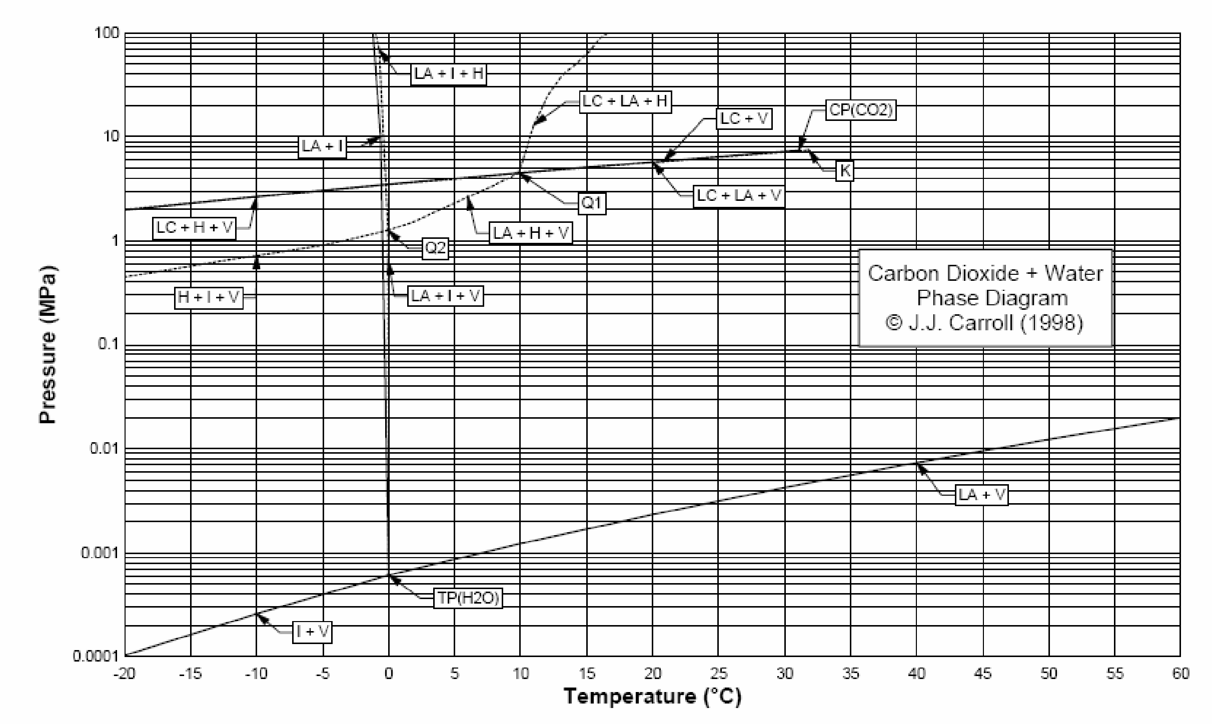

Figure A-8-2 Phase diagram of CO_2 and H_2O (Carroll, 1998)

APPENDIX B

Table 0-1 Comparison of CO_2 compositions of captured CO_2 after drying and compression to the recommendation on CO_2 quality from a transport perspective

		Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8	DYNAMIS CO_2 quality recommendation
Capture technology		PRE-COMBUSTION	PRE-COMBUSTION	PRE-COMBUSTION	PRE-COMBUSTION	PRE-COMBUSTION	PRE-COMBUSTION	PRE-COMBUSTION	PRE-COMBUSTION	
Fuel		NATURAL GAS	NATURAL GAS	NATURAL GAS	COAL	COAL	LIGNITE	LIGNITE	LIGNITE	
Process characteristics		SMR – 95% CO_2 capture	O2 ATR - 95% CO_2 capture	Air ATR – 96% CO_2 capture	Coal gasification	Coal gasification Siemens (ex. Future Energy) gasification	General Electric coal gasification	Siemens (ex. Future-Energy) gasification	British Gas Lurgi (BGL) gasification	
Capture process		Activated MDEA process (BASF)	Activated MDEA process (BASF)	Activated MDEA process (BASF)	Separate removal of H2S and CO_2, using Selexol®	Separate removal of H_2S and CO_2 using Selexol®	Separate removal of H_2S and CO_2 using Selexol®	Separate removal of H2S and CO_2 using Selexol®	Separate removal of H_2S and CO_2 using Selexol®	
Water	ppm	400	400	400	400	400	400	400	400	**500 ppm**
Carbon dioxide	vol%	99.75	99.84	99.8	98.62	98.63	99.74	98.84	99.32	**> 95 vol%**
MDEA	ppm	0	0	0	-	-	-	-	-	**Not proposed**
MEA	ppm	0.1	21	29	-	-	-	-	-	**Not proposed**
Methane	ppm	130	46	17	-	-	-	-	-	**Aquifer < 4 vol%, EOR < 2 vol%**
Hydrogen	ppm	1950	1113	1210	0.88 %vol	0.87 %vol	0.14 % vol	0.72 % vol	0.53 % vol	**< 4 vol % (all non cond. gasses)**
Carbon monoxide	ppm	4.6	15	9.7	0.11 % vol	0.11 %vol	0.01 % vol	0.08 % vol	0.01 % vol	**2000 ppm**
Nitrogen	ppm	2.4	6.3	588	0.22 % vol	0.22 %vol	0.01 % vol	0.21 % vol	50	**< 4 vol % (all non cond. gasses)**
H_2S	ppm	-	-	-	70	52	50	64	81	**200**
Ar	vol%	-	-	-	0.1 % vol	0.1 % vol	0.04 % vol	0.08 % vol	0.01 % vol	**< 4 vol % (all non cond. gasses)**
TEG	ppm	0.2	0.1	0.08						**Not proposed**
Other					0.03 % vol	0.03 % vol	0.02 % vol	0.03 % vol	0.03 % vol	
Temperature	Celsius	32.6	32.6	32.6	35	35	35	35	35	**30**
Pressure	Bar	110	110	110	110	110	110	110	110	**100**