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Author(s)		
Name	Organisation	E-mail
Luuk Buit	N.V. Nederlandse Gasunie	luuk.buit@kema.com
Mohammad Ahmad	N.V. Nederlandse Gasunie	mohammad.ahmad@kema.com
Wim Mallon	N.V. Nederlandse Gasunie	wim.mallon@kema.com
Fred Hage	Linde Gas Benelux B.V.	fred.hage@linde.com
Xiaolong Zhang	TNO	xiaolong.zhang@tno.nl
Mariëlle Koenen	TNO	marielle.koenen@tno.nl

EXECUTIVE SUMMARY

Carbon capture, transport and storage (CCS) forms a chain in which different components have to form an integrated and well-adjusted system. To accomplish this, CO₂ standards or operational preconditions have to be agreed upon. CO₂ captured in power plants or from industrial processes contains impurities. When components further down the CCS chain cannot handle CO₂ with certain impurities, the question is exactly what concentrations of impurities are acceptable.

For transport by pipeline, impurities may have an effect on:

- Thermodynamics of the mixture. This can lead to higher compression costs compared to transporting pure CO₂ or limit operational flexibility further along the transport chain, e.g. by affecting the required pressures.
- Pipeline integrity. More specifically, corrosion. CO₂ combined with free water will cause corrosion to the pipeline. Other impurities in CO₂ can add to the corrosion, as long as free water is present. For economic reasons, CO₂ pipelines will not be made of stainless steel, but carbon steel. Corrosion will have to be prevented by limiting the water concentration in CO₂.
- External safety. When CO₂ is released either accidentally or on purpose (e.g. for venting or purging reasons) the impurities contained in the CO₂ will also be released. Some impurities pose a threat to health, safety and/or the environment. It is recommended to limit these impurities in such a way that they cannot cause more harm than the CO₂ itself.

Considering these effects, some impurity limits are recommended.

Impurities in CO₂ storage

This report includes the results of an assessment of the effects of impurities in the CO₂ stream on storage. The study is based on geochemical modeling using a model called *PHREEQC* and comparison of the results with existing literature. The work focuses on the interaction between CO₂, with impurities, the formation water and the host matrix.

The data on the rock composition from a potential CO₂ storage field has been used, which is representative of a sandstone reservoir of the Cretaceous Rijnland reservoirs. These reservoirs are expected to provide a large amount of the total CO₂ storage capacity in the Netherlands.

H₂S and SO₂ (like CO₂ itself) have shown the capability to influence the pH of the formation water. However, the effect of both H₂S and SO₂ in the expected quantities appears insignificant. Minimal volume decreases of the reservoir will occur. The short term effects (<40 years) are negligible. For the longer term (>10 000 years), the volume of the reservoir could increase due to mineral precipitation by approximately 1%.

It is recommended that a number of topics should be investigated further such as NO₂ as an impurity and longer term effects, such as changes in mineral assemblage and long term pressure changes. Furthermore, different reservoir types and spatial variability of the impurities should also receive further attention.

Water in CO₂

For CCS, various specifications of the water content in CO₂ have been given in the literature. These specifications range from 40 to 500 ppm. Unfortunately, little has been published on the

rationale behind these concentration limits. The present lack of clarity on the dryness requirements is undesirable, because eventually, we must come to a water content standard for CCS that ensures cost-efficient CO₂ transport. The work presented here aims at analyzing CO₂ transport to provide some basic input for such a standard.

CO₂ captured from power plants always contains moisture. The water can be removed to a certain extent at the capture plant, but a small amount of water will remain. When the water is in solution in the CO₂, there is no problem, but free water combined with CO₂ is very acidic. The corrosive nature of wet CO₂ poses a threat to the transport system integrity. Economical considerations lead to the use of regular carbon steel, which is commonly used for most pipelines. Corrosion resistant steel would inhibit corrosion, but it would be prohibitively expensive to build CCS pipelines with this type of steel.

Using regular carbon steel requires corrosion tests to quantify the destructive effects of free water in case it is present in the CO₂. The occurrence of free water must be excluded as much as possible, since having no free water anywhere in the CO₂ transport system would be the most straightforward way of protecting it. However, drying captured CO₂ costs both money and energy and dependent on technology choice, can reduce flexibility in the CCS chain. Therefore a water concentration limit should not be more stringent than necessary.

A quick overview of the solubility of water in CO₂ is given to enable a discussion of the operational limits of the CCS transport chain.

We assumed here that the expected CO₂ characteristics in the transport network include a minimum temperature of 0 °C (onshore) or 4 °C (offshore) and a maximum temperature of over 30 °C immediately after a compressor. This leads to a water solubility of at least 1500 ppm during normal operation.

Commissioning of a CO₂ pipeline and blow down scenarios are discussed. It is recommended that the relation between the CO₂ conditions during planned blow downs and the water content should be investigated. Unplanned blow down could involve a rapid decompression and temperature drop within the pipeline, for which there are no validated models available. Therefore it is difficult to determine the right water concentration limit.

Even though in the USA, no serious problems seem to have surfaced at a water concentration of around 500 ppm in the CO₂, several research questions need to be addressed to arrive at a sound and cost efficient water concentration limit. It was found that in order for a good technical and economical basis for determining the required water concentration limit some questions remain to be answered. These include, cost data for drying installations and acceptable blow down conditions as a function of water concentration.

PROJECT SUMMARY

The CO2Europipe project aims at paving the road towards large-scale, Europe-wide infrastructure for the transport and injection of CO₂ captured from industrial sources and low-emission power plants. The project, in which key stakeholders in the field of carbon capture, transport and storage (CCTS) participate, will prepare for the optimum transition from initially small-scale, local initiatives starting around 2010 towards the large-scale CO₂ transport and storage that must be prepared to commence from 2015 to 2020, if near- to medium-term CCS is to be effectively realized. This transition, as well as the development of large-scale CO₂ infrastructure, will be studied by developing business case using a number of realistic scenarios. Business cases include the Rotterdam region, the Rhine-Ruhr/Hamburg region, an offshore pipeline from the Norwegian coast and the development of CCS in the Czech Republic and Poland.

Objectives

The project has the following objectives:

1. describe the infrastructure required for large-scale transport of CO₂, including the injection facilities at the storage sites;
2. describe the options for re-use of existing infrastructure for the transport of natural gas, that is expected to be slowly phased out in the next few decades;
3. provide advice on how to remove any organizational, financial, legal, environmental and societal hurdles to the realization of large-scale CO₂ infrastructure;
4. develop business case for a series of realistic scenarios, to study both initial CCS projects and their coalescence into larger-scale CCS infrastructure;
5. demonstrate, through the development of the business cases listed above, the need for international cooperation on CCS;
6. summarise all findings in terms of actions to be taken by EU and national governments to facilitate and optimize the development of large-scale, European CCS infrastructure.

This report

This deliverable describes the necessary input for CO₂ quality standards, by which is meant the composition of the CO₂. With adequate CO₂ quality standards, the first objective is partly met. The CO₂ composition is the characteristic influencing each and every component in the chain from capture to storage. This report provides input for a CO₂ quality standard that enables a safe, reliable and cost-efficient CCS chain.

Project partners

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N.V. Nederlandse Gasunie	Netherlands

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1 INTRODUCTION

What CO₂ composition requirements are needed for safe, reliable and cost-efficient carbon capture, transport and storage? This is the central question tackled in this report. Carbon capture, transport and storage (CCS) is an activity that involves a chain of components, each with their specific technical boundary conditions. The composition of the CO₂ is an important factor affecting the design of each of these components and vice versa. For CO₂ capture, transport and storage, respectively, the issues are depicted here with focus on CO₂ transportation.

Capture

CO₂ captured in power plants or from industrial processes contains certain concentrations of impurities. This depends on the feedstock, the type of power plant or industrial process and the capture technique (and its plant specific design) involved. The ideal situation for the CO₂ producer would be to handover the CO₂ as it is, without any conditioning, although compression at the capture plant would require some conditioning. The question is then, what concentrations of impurities are acceptable for the CCS chain components further down the chain. The stricter the impurity limit imposed on CO₂ producers, the more expensive and cumbersome their operations become. Therefore effort should be made not to impose overly strict composition or requirements. Functional requirements could be sufficient to safeguard CO₂ transport with acceptable risk levels. This effort is in the benefit of society as a whole, as it is in everyone's interest to mitigate CO₂ emissions in the most efficient way available. This requires optimising the complete CCS chain, as opposed to maximising the profit of one stakeholder or minimising the costs of one component.

Transport

In transporting CO₂ to its destination, the safety of operations is the foremost concern. For pipeline and shipping transport, acceptable risk levels have to be agreed upon. Workplace hazards, public safety and environmental hazards all have to be taken into account. To account for the risk of accidental releases of CO₂, the CO₂ stream composition needs to be carefully considered. This report does not consider the details of external safety of the CO₂ itself. The CO₂Europipe report D3.2.1 'Societal and environmental aspects' (Seebregts, 2011) addresses the risks to external safety related to CO₂ release from a leakage or rupture of a pipeline. An important aspect of external safety is integrity of the pipeline or vessel. Certain impurities can have a major impact on corrosion or other types of component degradation. System design should aim to minimise the need for maintenance on transport components to enable continuous and reliable transport.

The composition of CO₂ also determines its thermodynamic characteristics. More specifically, the phase diagram of the CO₂ depends on the types and concentrations of impurities. The most important feature of the CO₂ phase diagram, the vapour-liquid phase boundary, determines the pressure and temperature operating envelope. In the case of dense-phase transport by pipeline, the presence of impurities can lead to a higher critical density and increasing the operational pressure required, which directly adds to the transport costs.

Injection and storage

CO₂ can be stored in various types of formations: depleted gas fields, oil fields, aquifers and coal seams. For all formation types, injection of CO₂ with impurities could affect the injection well and the reservoir itself, possibly resulting in blocking CO₂ flow. To prevent this, the operator must ensure that impurity concentrations are within acceptable limits. It must be noted here that there is an extensive track record with CO₂ injection into hydrocarbon reservoirs. In many cases, sour gas (CO₂ with H₂S) has successfully been injected.

Report outline

This report starts with a discussion of the various impurities that might be present in captured CO₂. It describes the issues of each of these impurities with respect to pipeline transport and arrives at some recommendations as input for a CO₂ transport specification. A specification itself is not given within the framework of CO₂Europeipe.

The following section reports the results of an assessment of the effects of impurities in the CO₂ stream on storage. This study is based on geochemical modeling using a model called *PHREEQC* and comparison of the results to existing literature. The work focuses on the interaction between CO₂, impurities, and the formation water and the host matrix. The benefit of this work for a CO₂ transport study is that impurity limits set by the CO₂ reservoir may have an impact on the entire chain for optimisation reasons.

As water is such an important component in CO₂, a dedicated chapter discusses a water concentration limit in transported CO₂. Attention is given to the technical and economical effects resulting from limiting the maximum water concentration.

2 EFFECT OF NON-CO₂ COMPONENTS ON CO₂ PIPELINES

2.1 Introduction

CO₂ from different sources may contain non-CO₂ components which would have practical and/or potential health, safety and/or environment impacts on CO₂ transport and storage systems. Up to now there has been no commercial need to established standard for permitted levels of impurities in CO₂ for the CCS, though there are well working business specific agreements for CO₂ that is used for enhanced oil recovery (EOR) purposes (Forbes, Verma et al. 2008). The requirements for the CO₂ compositions are built into contracts between the supplier and the transporter and between the transporter and the storage operator.

An industry standard for CO₂ composition in the CCS chain will be needed in the future for large scale transport of CO₂ due to a need to accommodate a network of multiple CO₂ sources and sinks. The types and concentrations of impurities depend on the type of capture process, as shown in Table 2-1 (Thambimuthu, Soltanieh et al. 2005). It should be noted that the capture processes will probably develop over time, so the resultant CO₂ components will vary as well. Furthermore, development of CCS infrastructure could benefit from CO₂ quality standards, even if CCS infrastructure will be limited to source-sink connections. Thus making a general guideline for CO₂ composition, in which specific requirements of all possible components of the CCS network are addressed, could help large-scale CCS be developed in a cost-efficient way. On the other hand, the CCS industry should take care to avoid setting too stringent requirements.

The aim of this chapter is to review the impact of impurities in CO₂ on large scale CO₂ pipeline transmission in the CCS chain, from capture plants to the storage facilities. This may help in developing standards of the CO₂ composition requirements for large scale CCS. The discussion in this report is limited to the information obtained from published literature and geochemical modelling.

2.2 Impurities in captured CO₂

CO₂ from most capture processes contains moisture, which has to be removed to avoid corrosion and hydrate formation during transportation. Post-combustion capture (solvent scrubbing processes) produces very pure CO₂ (>99%). Many of the existing post-combustion capture plants produce high purity CO₂ for use in the food industry (IEA 2004). Pre-combustion physical solvent scrubbing processes produce CO₂ typically containing about 1-2% H₂, traces of CO, H₂S and other sulphur compounds (IEA 2003). Integrated Gasification Combined Cycle (IGCC) plants produce a combined stream of CO₂ and sulphur compounds. Oxy-fuel processes can – depending on the level of processing – produce very pure CO₂ (>99%). The capture process itself produces CO₂-rich gas that contains oxygen, nitrogen, argon, sulphur and nitrogen oxides, and various other trace impurities (see Table 2-1 (Thambimuthu, Soltanieh et al. 2005)).

An emergency shutdown of a power station could increase impurity concentrations at a particular point in the stream. Handling of these streams should be considered as part of plans

for plant upset and emergency situations. These are standard safety precautions that are in use in chemistry industry operations.

In summary, post-combustion and pre-combustion capture produce a very limited amount of impurities and - if designed for it - so can also oxy-fuel capture. Depending on the technology used, purification costs will vary.

Table 2-1 Examples of concentrations of impurities in dried CO₂, % by volume (Source data: IEA GHG, 2003; IEA GHG, 2004; IEA GHG, 2005 (Thambimuthu, Soltanieh et al. 2005)).

	SO ₂	NO	H ₂ S	H ₂	CO	CH ₄	N ₂ /Ar/O ₂	Total
Coal-Fired Plants								
Post-combustion capture	<0.01	<0.01	-	-	-	-	0.01	0.01
Pre-combustion capture (IGCC)	-	-	0.01-0.6	0.8-2.0	0.03-0.4	0.01	0.03-0.6	2.1-2.7
Oxy-fuel	0.5	0.01	-	-	-	-	3.7	4.2
Gas-Fired Plants								
Post-combustion capture	<0.01	<0.01	-	-	-	-	0.01	0.01
Pre-combustion capture	-	-	<0.01	1.0	0.04	2.0	1.3	4.4
Oxy-fuel	<0.01	<0.01	-	-	-	-	4.1	4.1

Remarks:

- a. The SO₂ concentration for oxy-fuel and the maximum H₂S concentration for pre-combustion capture are for cases where these impurities are deliberately left in the CO₂, to reduce the costs of capture. The concentrations shown in the table are based on use of coal with a sulphur content of 0.86%. The concentrations would be directly proportional to the fuel sulphur content.
- b. The oxy-fuel case includes cryogenic purification of the CO₂ to separate some of the N₂, Ar, O₂ and NO_x. Removal of this unit would increase impurity concentrations but reduce costs.
- c. For all technologies, the impurity concentrations shown in the table could be reduced at higher capture costs.

2.3 CO₂ pipeline transport experience

To date, there is significant experience with CO₂ transport. In the United States, there is about 3900 miles (6275 km) of pipelines transporting CO₂ for EOR operations. The impurity issues identified in CO₂ transport in the US could give guidance in determining safe impurity limits in CO₂ transport for CCS. The situation for CCS would, however, be quite different from the existing CO₂ transport operations, because the EOR CO₂ pipelines mostly cover sparsely populated areas and the type of safety regulations applied in the US differ from those implemented in some countries in Europe. Another important difference is the CO₂ source: in the US, the transported CO₂ is produced out of natural reservoirs, as opposed to anthropogenic CO₂. Thus, the CO₂ specifications in the US should only act as a starting point for the discussion of impurity limits for anthropogenic CO₂ relating to CCS.

One of the first CO₂ pipelines is the Canyon Reef Carriers pipeline which is constructed for CO₂ EOR and began service in 1972. The CO₂ delivered at the Canyon Reef Carriers Delivery Meter meets the following specifications (Doctor, Palmer et al. 2005):

- (a) Carbon Dioxide: >95%, mole percent.
- (b) Water: no free water.
- (c) Hydrogen Sulphide: <1500 ppmbw (= ppm by weight)

- (d) Total Sulphur: <1450 ppmbw.
- (e) Nitrogen: < 4% (mole percent).
- (f) Hydrocarbons: < 5% (mole percent).
- (g) Oxygen: <10 ppmbw.
- (h) Glycol: < $4 \times 10^{-5} \text{ L m}^{-3}$, and at no time shall such glycol be present in a liquid state at the pressure and temperature conditions of the pipeline.

Another example is the Weyburn Pipeline (EOR project in Saskatchewan, 330 km, 305-356 mm diameter). The composition of the gas carried by the pipeline is typically

CO₂ 96%,

Water less than 20 ppm

H₂S 0.9%

CH₄ 0.7%

C₂ + hydrocarbons 2.3%

CO 0.1%,

N₂ less than 300 ppm

O₂ less than 50

(UK Department of Trade and Industry, 2002)(Doctor, Palmer et al. 2005).

Three types of pipeline and impurity parameters were described in the EU CCS Guidelines (see Table 2-2)(Forbes, Verma et al. 2008). At the moment, Type I pipelines do not exist in the CO₂ EOR industry, but can be developed for a CCS project. The majority of CO₂ pipelines in the US are Type II pipelines, which have a strictly limited composition and serve multiple sources and user lines. Type III pipelines have relaxed composition requirements, which is used for transport of CO₂ mixed with high concentrations of H₂S. The Weyburn pipeline is an example of a type III pipeline. It is clear that, when pipelines with different composition requirements are to be interconnected, these requirements will have to be adjusted to the new situation.

Table 2-2 Types of pipelines and composition requirements in US (Forbes, Verma et al. 2008)

Parameter	Type i	Type II	Type III
CO ₂ —% by volume	>95%	>95%	>96%
H ₂ S—ppmbw	<10	<20	<10,000
Sulphur—ppmbw	<35	<30	-
Total hydrocarbons—% by volume	<5	<5	
CH ₄ —% by volume	-	-	<0.7
C ₂ + hydrocarbons—% by volume	-	-	<23,000
CO—% by volume	-	-	<1,000
N ₂ —% by volume/weight	<4	<4	<300
O ₂ —ppm by weight/volume	<10	<10	<50
H ₂ O —#/mmcf* or ppm by volume**	<25*	<30*	<20**

C₂ = carbon; CH₄ = methane; CO = carbon monoxide; CO₂ = carbon dioxide;

H₂O = water; H₂S = hydrogen sulfide; mmcf = millions of cubic feet;

N₂ = nitrogen; ppm = parts per million; O₂ = oxygen;

ppmbw = ppm by weight

The operation of the Canyon Reef Carriers pipeline recorded only five failures (with no injuries) during its first twelve years of operation (Gill 1985) (Hedde, Herzog et al. 2003). Two failures were explosions at compressor stations due to air (oxygen) being drawn into the suction line from the extraction plant stack line. The other failures were ruptures at the injection station that resulting from localized 'hot spots' in the tubes of the direct-fired line heater. One of them was attributed to the accumulation of corrosion products in a pipe that built up before its installation and was not removed by initial cleaning. The other two ruptures took place near support brackets where the distribution of flow through the parallel tube arrangement was not equal.

Dry carbon dioxide does not corrode the carbon-manganese steels generally used for pipelines. Schremp and Roberson did tests for X-60 carbon steel in 138 bar CO₂ containing 800 to 1000 ppm water and 600 to 800 ppm H₂S, at 3°C and 22°C (Schremp and Roberson 1975). The corrosion rate is less than 0.5 µm/year. Field experience indicates few problems with transportation of high-pressure dry CO₂ in carbon steel pipelines. The corrosion rate in a CO₂ pipeline has been reported to amount to 0.25-2.5 µm/year during 12 years operation (Gill 1985).

The water solubility in CO₂ at a given temperature decreases to a minimum as pressure is increased, and then increases when the pressure is further increased. The limit in high-pressure CO₂ (500 bar) is 5000 ppm at 75°C and 2000 ppm at 30°C (Wiebe and Gaddy 1941; Song 1988). Methane lowers the solubility limit, and H₂S, O₂ and N₂ may have the same effect.

Corrosion rates are much higher if free water is present. Hydrate may also be formed when free water is present, but only at temperatures below 12 °C and pressures below 50 bars (Carroll 1998). Corrosion and operation problems have been reported in the CO₂ project in Sacroc Unit (Newton and McClay 1977). One leak in the distribution system lateral occurred once as a result of hydro-test water remaining in a low spot in line and opening the lateral to CO₂ pressure. Corrosion rates in the supply and distribution system were monitored using corrosion couples of pipeline and 1018 steel at nine locations, the highest corrosion rate noted was 0.03 mm/year. The maximum corrosion rate in the compressor stations and dehydration system piping was 0.18 mm/year, measured using Corrosometer Probes.

Seiersten measured the corrosion rate for X65 steel in 150 to 300 hours exposure at 40°C in water equilibrated with CO₂ at 95 bar. The corrosion rate is about 0.7 mm/year, and corrosion rate was higher at lower pressures (Seiersten 2001). It is reported that 20 ppm CO₂ corrosion inhibitor can lower the corrosion rate below 0.1 mm/y at temperatures up to 30°C and CO₂ pressures up to 72 bar (Seiersten and Kongshaug 2005).

In ship transport most of the volatiles must be removed in order to avoid dry ice formation in the liquid CO₂ (Aspelund and Jordal 2007).

2.4 Preliminary recommended limits

2.4.1 Approach

For each impurity, the impact on the CO₂ transmission system is discussed, resulting in reasons to limit impurity concentrations. The focus in this discussion is on pipeline transport. Some impurities that may occur in captured CO₂ may pose a threat to the integrity of the transmission system. In case of CO₂ release, some impurities may also present a Health, Safety and Environment concern. Another effect of certain impurities is that their presence alters the thermodynamic behaviour of the CO₂. In dense phase CO₂ transport, the phase boundary of CO₂ is the lower limit for the pressure, because phase transitions are to be avoided in the pipeline. In this way the most important impurities that may be present in captured CO₂ are investigated to come to a concentration limit for CO₂ transport.

2.4.2 Impurities with HSE-risks

The first issue at hand is impurities that have an influence on external safety. The impurities contained in CO₂ are released with it when a pipeline ruptures or leakage occurs. For this reason, the impurities which pose a threat to health, safety and/or environment (HSE) need to be limited. The approach in determining these concentration limits is taken from the Dynamis project, although the results are different, because of a different safety factor (Visser 2008): when CO₂ is released, the impurities should not be more dangerous than the CO₂ itself. So the ratio between a maximum impurity limit and the CO₂ concentration is taken to be the same as the ratio of their respective short term exposure limits (STEL). To be on the safe side with the recommendations, a factor of 0.5 has been included. A simple formula results:

$$Limit_{impurity} = \frac{1}{2} \cdot Limit_{CO_2} \cdot \frac{STEL_{impurity}}{STEL_{CO_2}}$$

The STEL of CO₂ is 30 000 ppm (NIOSH 2010). Its minimum concentration in the CO₂ mixture is 95 vol%. The factor 0.5 is included to give a conservative impurity limit, because there are some uncertainties concerning interaction effects of combinations of any of the given impurities. This gives us the following preliminary impurity limit recommendations:

Table 2-3 Preliminary recommendations for impurity limits based on HSE considerations. STEL values taken from (NIOSH 2010).

Impurity	STEL	Limit in CO ₂ ***
NO ₂	5 ppm	79 ppm
CO	300 ppm*	4750 ppm
H ₂ S	15 ppm	238 ppm
SO ₂	5 ppm	79 ppm
HCN	4.7 ppm	74 ppm
COS	15 ppm**	238 ppm
NH ₃	35 ppm	553 ppm

*) STEL not found in the NIOSH database; The UK Material Safety Data Sheet (UK MSDS) for carbon monoxide was used.

***) STEL not found. BOC (BOC 1996) suggests a 15 ppm STEL, based on the STEL for hydrogen sulphide. The UK material safety data sheets for COS and H₂S (UK MSDS) indicate that COS is comparable to, but less dangerous to inhale than H₂S. Therefore we take 15 ppm as a conservative estimate for the COS STEL.

****) Note that these are *preliminary* limits and that further research and new insights will lead to adjustments.

2.4.3 Potential pipeline integrity threats

Water

Water is the most critical impurity in CO₂. A concentration of water exceeding the solubility limit for the operational envelope of the transmission system causes the occurrence of free water, i.e. condensed water. Free water in CO₂ will, of course, contain dissolved CO₂, which makes it acidic and very corrosive. Determining the right concentration limit for water is not easy, however. A discussion of this specific topic is given in section 4. A specific water concentration limit cannot be given here, because the limit needed to prevent free water depends not only on the operational envelope, but also on the concentration of other impurities.

O₂

Oxyfuel capture is the main potential source of oxygen in the CCS chain. High-concentration of O₂ is a problem with EOR/EGR because of CO₂ breakthrough, causing the produced hydrocarbons to contain a high concentration of oxygen, which adds to the product conditioning costs. At high concentrations, the fact that oxygen can also react exothermally with oil in the reservoir may become an issue (Benson, Cook et al. 2005).

Hydrocarbons

CH₄ and other hydrocarbons lower the water solubility in CO₂ (Song 1988; Heggum, Weydahl et al. 2005), thus increasing the risk of forming free water in the system. Theoretical calculations show a low critical limit for free water precipitation of approximately 1300 ppm (mole) in the case of the minimum temperature at 5 °C and the pressure of 85 bar in the pipeline (Heggum, Weydahl et al. 2005).

Normally the concentration of hydrocarbons in CO₂ is very low. For these impurities a limit of 5% for total non-condensable impurities is considered sufficient. In literature, 4% and 5% both occur, and the limit is somewhat arbitrary. A higher concentration of non-condensables is unfeasible anyway because they do not add to the CO₂ emission reduction.

H₂S

In many countries, desulphurisation is carried out in the process of power generation in coal-fired power plants. As a result, in oxyfuel and post-combustion capture, the possible concentrations of H₂S in the CO₂ are negligible. In pre-combustion CO₂, however, the H₂S concentration can be as high as 0.6% (see Table 2-1). Furthermore, wherever desulphurisation is not part of the regular power generation process, H₂S content in flue gas is expected to be substantial.

In the presence of free water, H₂S can react with oxygen to form sulphuric acid, which affects corrosion. H₂S can cause accelerated pitting corrosion of 13Cr steel and lead to cracking

(Craig 1996). However, without free water, there is no risk of corrosion by H₂S and there are existing pipeline and material codes to mitigate any effects. A limit for the H₂S concentration in CO₂ is required from a HSE point of view. In the oil and gas industry, the limit is 20 ppm (Department of Labor, 1993). In EU, the new occupational exposure limit to H₂S for short term is 10 ppm by volume (EN 2009).

SO_x and NO_x

SO_x and NO_x species in the presence of free water will form acids that corrode the materials used in separation, compression, and transmission. The effect of small amounts of SO₂ and NO_x on the CO₂ pipeline and compression system has not been well established due to lack of data. It is not clear to what degree they will lower the pH of any condensed aqueous phase in the pipeline (Sass, Monzyk et al. 2005). However, in the absence of free water, SO_x and NO_x will only be relevant with respect to external safety.

H₂

H₂ can cause cracking by diffusing into steel and influence the phase diagram of CO₂, but the concentration of H₂ in captured CO₂ is low compared to those in some natural gas pipelines. Limited data for the effect of hydrogen in CO₂ on the pipeline could be found in literature.

According to a study by NaturalHy, the safety, integrity and durability of a natural gas transmission system are not compromised when the natural gas contains up to several tens of volume percents of H₂ (NaturalHy 2010). When the total impurity concentration in CO₂ is less than 5%, hydrogen should not pose a threat to the integrity of the pipeline.

N₂

N₂ does not exist in significant amounts in pre- and post-combustion captured CO₂, but exists in oxy-fuel captured gas which is about 4% N₂ by volume. Nitrogen is a non-condensable gas that affects CO₂ storage capacity, because with more nitrogen, less storage space is available for CO₂. It has an influence on the CO₂ phase diagram similar to CH₄.

CO

CO plus CO₂ at high pressure was reported to cause stress corrosion cracking of low strength tubes and line pipe in the presence of an aqueous phase was reported by (Bowman 1975). The anodic dissolution reaction is concentrated on the very small fraction of the surface remaining free of CO. When no free water is present, CO poses no threat to the pipeline integrity. CO is toxic, though, so it is also considered above in the section on HSE impact.

Ar

Ar is an inert gas, non-condensable, which only affects the compression power, storage capacity and the phase diagram.

Glycol

A limit on glycol in CO₂ has been mentioned in the specifications for the Canyon Reef Carriers pipeline (Doctor, Palmer et al. 2005). Glycol may affect the CO₂ injection in EOR and lead to possible accumulation problems within the pipeline.

Seiersten et al. reported that the corrosion rates at high CO₂ pressures in the systems containing water/monoethylene glycol mixtures are considerably lower than predicted by corrosion models. This applies particularly at low temperatures typically for sub-sea pipelines in northern sea waters (Seiersten and Kongshaug 2005). In this report, a glycol limit is not proposed because the adverse effects of glycol are not clearly defined.

3 IMPACT OF IMPURITIES ON CO₂ STORAGE RESERVOIR

3.1 Introduction

The costs of separation and compression of CO₂ from point sources covers the largest part of the total costs of CCS (Damen, 2007 and Knauss et al., 2004). Depending on the type of capture technology (pre-combustion, oxy-fuel, or post-combustion) the captured CO₂ stream contains a number of impurities. It requires additional money and energy to increase the purity of the stream and decrease the number or level of impurities. Lowering the costs at the capture side could be accomplished by permitting a less pure CO₂ stream. Requirements on the purity of the CO₂ stream for transport by pipeline have received some attention (Visser 2008). The effects of impurities on (long term) storage are still very unclear and requirements have not been established yet.

The issue with impurities in stored CO₂ is, that during or after injection of the CO₂ mixture at the storage site, the impurities can react geochemically with reservoir fluids or matrix, which might have undesirable effects. For example, presence of oxygen may lead to overheating at the injection point due to reaction with oil if some is present. Oxygen may cause precipitation reactions and reduce the permeability of the reservoir (Aspelund and Jordal 2007). Oxygen can also stimulate the growth of certain bacteria, which affect CO₂ injection efficiency by building up biofilm and blocking the pores in reservoir. However, on the other hand, the biofilm barrier may be used to enhance the geologic sequestration of CO₂ (Mitchell, Phillips et al. 2009).

At the Ketzin storage project bacteria have been found in the subsurface (Morozova, Wandrey et al. 2010; Myrntinen, Becker et al. 2010). Bacteria are divided into aerobic and anaerobic bacteria. The former kind thrives in oxygen-containing environments. The biofilm developed as a result in the down hole may block the pores in reservoir and affect CO₂ injection efficiency. This is not an issue for permanent CO₂ storage after the injection. Oxygen is corrosive in the presence of free water. When no free water can occur, the only effect from oxygen is its impact on the mixture's phase diagram.

3.2 Current experience

Combined streams of CO₂ and sulphur compounds (primarily H₂S) are already stored, for example in Canada. Canadian acid gas is injected at 27 sites into deep saline aquifers and at 21 sites into depleted oil and gas fields. The acid gas that was generated in the process contains H₂S and CO₂. No safety or leakage incidents have been reported in 15 years since the first acid gas injection in the world started in Alberta, Canada (Benson, Cook et al. 2005). However, this option would only be considered in circumstances where the stream with a high H₂S content could be transported and stored in a safe and environmentally acceptable manner, which is not expected in Europe.

The presence of impurities in the CO₂ affects the engineering processes of capture, transport and injection, and capacity for CO₂ storage in geological media. Some impurities in the CO₂ such as SO_x, NO_x and H₂S may require classification as hazardous. Non-condensable

components in the CO₂ stream affect the compressibility of the injected CO₂ and reduce the capacity for storage.

In EOR operations, impurities affect the oil recovery because they change the solubility of CO₂ in oil. Methane and nitrogen decrease oil recovery, whereas hydrogen sulphide, propane and heavier hydrocarbons have the opposite effect (Sebastian, Wenger et al. 1985).

In the case of CO₂ storage in deep saline formations, the presence of non-condensable components affects the rate and amount of CO₂ storage through dissolution and precipitation. Experience to date with acid gas injection suggests that the effect of impurities on injectivity is not significant (Bryant and Lake 2005).

In the case of CO₂ storage in coal seams, impurities have a different effect on the storage capacity. H₂S and SO₂ have a higher affinity to coal than CO₂. If CO₂ stream containing these impurities is injected into coal beds, H₂S and SO₂ will be preferentially adsorbed and reduce the storage capacity for CO₂ (Chikatamarla and Bustin 2003). If oxygen is present, it will react irreversibly with the coal, reducing the sorption surface and the adsorption capacity. On the other hand, coal-fired flue gas (CO₂ + primarily N₂) may be used for enhanced coal-bed methane (ECBM) recovery, because CO₂ has higher sorption selectivity than N₂ and CH₄, and CO₂ can be stripped out and retained by the coal reservoir.

Research on the different aspects concerning CO₂ storage, like wellbore cement experiments or geochemical modeling on CO₂ injection in reservoirs, is mainly focused on pure CO₂. In this study, an assessment of the effects of impurities in the CO₂ stream on storage is performed, based on geochemical modeling and comparison of the results to existing literature. The work focuses on the interaction between CO₂, with impurities, the formation water and the host matrix.

3.3 Approach and assumptions

In this section the input data from the CO₂ streams and the reservoir data required for the modeling is discussed, as well as the assumptions that were made. Furthermore, the modeling code and the workflow used in this study are explained briefly.

3.3.1 CO₂ streams

Two CO₂ sources with different capture technologies have been selected for the assessment of the effect of impurities on CO₂ storage. The first is the ‘Shell Hydrogen Gasification Plant’, also referred to as Shell Pernis, with pre-combustion CO₂ capture. The stream is considered as a high quality stream with a CO₂ concentration >99 mole %. The impurities present are N₂, O₂, H₂, CO and H₂S and the highest value in the range has been taken as input for each impurity. The second source selected is a potential source with a semi-purified oxyfuel stream, containing N₂, O₂, CO, NO_x, SO₂, SO₃, H₂O and Ar. The SO₃ has been added to the SO₂ and the NO_x is assumed to be NO since the modeling software can only handle a limited number of gases. The mole concentrations of the composition of the two streams are shown in Table 3-1. In the stream from Shell Pernis some hydrocarbons are present. They are assumed to be inert and have not been included in the assessment.

Table 3-1 CO₂ stream with impurities from Shell Pernis, the Netherlands (Shell CO₂ Storage Company B.V., 2008) and from an oxyfuel scenario (purified stream) (Kather, 2009).

	Shell, pre-combustion (mole %)	Semi-purified oxyfuel (mole %)
CO₂	99.64	98.0
N₂	0.077	0.7
O₂	0.0045	0.7
H₂	0.14	-
CO	0.03	0.005
H₂S	0.00014	-
SO₂	-	0.007
NO	-	0.01
Ar	-	0.6

Three different scenarios have been investigated. The first is a baseline scenario, in which only pure CO₂ injection has been considered. The second and third are scenarios based on the impurities from the Shell Pernis and an oxyfuel source respectively. The baseline scenario will be compared to the other two scenarios to investigate the effects of the impurities in the stream.

3.3.2 Reservoir data

The data on the rock composition from a potential CO₂ storage field has been used, which is representative of a sandstone reservoir of the Cretaceous Rijnland reservoirs, i.e. a depleted natural gas field. These reservoirs are expected to provide a large amount of the total CO₂ storage capacity in the Netherlands. The rocks are dominated by quartz and contain a significant amount of clay, carbonate and other minerals like K-feldspar, glauconite and pyrite. The weight and volume percentage used for the modeling exercise are given in Table 3-2. The corresponding number of moles is in accordance to a porosity of 20% and a water saturation of 15%.

Table 3-2 Weight and volume percentage of the rock mineralogy, and corresponding number of moles in accordance to a pore volume of 1 dm³ and a water saturation of 15%.

	Reservoir composition (wt%)	Reservoir composition (vol%)	Reservoir composition (moles)
Quartz	83.0	82.8	144.4
Muscovite	1.0	0.9	0.3
Glauconite	1.0	1.0	0.2
Kaolinite	4.0	4.3	1.6
K-Feldspar	2.0	2.0	0.3
Calcite	0.5	0.5	0.5
Halite	0.2	0.2	0.4
Pyrite	0.2	0.1	0.2
Illite	8.1	8.1	2.2
Dawsonite			0.1727

Dolomite-ord

0.0089

The initial reservoir conditions are summarized in Table 3-3. The final pressure after CO₂ injection is defined as 175 bar, which is slightly below the initial pressure before gas production started. This final pressure minus the current pressure (31 bar) has been segregated into partial pressures of the different species in the CO₂ stream according to their mole concentrations.

Table 3-3 Initial reservoir conditions.

	Initial conditions
Temperature	72°C
pH	6.1
Total P	~31 bar
Water density	1.07 kg/l

3.3.3 Modelling approach

To model the effects of impurities in the CO₂ stream on (short- and long-term) storage, the software package *PHREEQC* (version 2) and geochemical llnl-database is used. *PHREEQC* computes the chemical equilibria of aqueous solutions interacting with mineral assemblages and gases (Parkhurst and Appelo, 1999).

For the modeling, batch-reaction calculations have been performed. During a batch-reaction the thermodynamic equilibrium is calculated of several phases put together in a vessel with a constant volume. In practice, when CO₂ (and impurities) is stored, injection occurs at a well from which it disperses into the reservoir. Near the injection well, the reservoir rock will be influenced by large amounts of gas flowing through, while the other end of the reservoir will only experience low gas flow. A specific location within the reservoir can be modeled with *PHREEQC* due to the homogeneous conditions within the batch of the model. In this assessment, near-well conditions are used in order to model a worst-case situation.

In the modeling assessment, partial pressures of the different gases are kept constant. This implies that when gas is dissolved in the formation water, gas is added to the system (vessel) in order to keep the partial pressure at the required value. A maximum amount of gas to be added needs to be specified in the model input. Usually, a surplus amount is used, to ensure that the availability of this gas is never the limiting factor for the reactions to take place. For CO₂ this is justified since it dissolves quickly until saturation is reached.

H₂S and SO₂ are capable of dissolution into the formation water in large amounts, while only small amounts are present in the CO₂ stream. Therefore, more precise specification of the maximum amount of these gases which can be present in the storage reservoir of the size of the reaction vessel is required. This is dependent on the dissolution rates and chemical reaction of the aqueous species, parameters which are not well known. A minimum amount of the impurities can be calculated based on the assumption of complete dispersion of the impurities over the storage reservoir, the amount of CO₂ in the vessel resulting from the CO₂-only scenario (see next section) and the ideal gas law. The number of moles of CO₂ present in the CO₂-only scenario (in solution as well as in the gas phase) multiplied by the mole % of

the impurity gives the number of moles of the impurity present in the system. In this case, dissolution of the gases would start after the total reservoir is filled and no accumulation of impurities in the formation water occurs. Accumulation of impurities would take place near the well in case H₂S and SO₂ quickly dissolve in the formation water during the injection period.

For both the Pernis (which contains H₂S) and the oxyfuel CO₂ stream (which contains SO₂) a 'no accumulation' and a '10 times accumulation' scenario for H₂S and SO₂ has been modeled.

3.3.4 Modelling workflow

For each scenario, four steps are carried out within *PHREEQC*:

- 1) The first step is the computation of the formation water (brine) composition. Measured compositions can be used, but since measurements on formation water and mineral compositions have uncertainties, together they do not give an equilibrium condition. It is assumed that the mineral assemblage is the strongest constraint. Therefore, formation water composition in equilibrium with the mineral assemblage is computed. This has been done by equilibrating pure water with surplus amounts of minerals measured in the reservoir rock and with the gases that are already present. The resulting pH of the initial formation water is 6.1.
- 2) In the next step, the computed formation water is equilibrated with the injected gases (from now on referred to as calculated formation water). This will show the short term results of injection on the pore water composition and its pH. This step is important to perform since the short term pH of the pore water can have significant effects on the injectivity due to the presence of quickly dissolving minerals and the possibility of quickly precipitating minerals.
- 3) The computed formation water (step 2) is equilibrated with the gases together with the minerals in the reservoir which are known to dissolve or precipitate quickly (calcite and anhydrite respectively) to investigate the short-term effects. Short-term is defined here as the injection period (< 40 years).
- 4) In the final stage, the computed formation water (step 2) is equilibrated with the gases and the mineral assemblage of the reservoir (final formation water) in order to study the long-term effects on the formation water and mineralogy. Long-term effects represent (near-)equilibrium conditions and is defined as >10.000 yrs.

Table 3-4 Main modeling results

Scenario	H2S	SO2	O2	pH of calculated formation water (step 2)	Short term effects; calcite dissolution (mole %), anhydrite precipitation	Short term volume change (%)	CO2 sequestered (mole %)	Sequestered in (main minerals)	Volume change (%)
1	-	-	-	4.60	Calcite -0.78%	-0.004	~7%	siderite, dolomite	-0.12
2-1	No accumulation	-	No accumulation	4.63	Calcite -0.75% No anhydrite	-0.004	~7%	siderite, dolomite	0.01
2-2	No accumulation	-	Surplus	4.56	Calcite -0.81% No anhydrite	-0.004	~0.2%	dolomite	1.01
2-3	10 times accumulation	-	Surplus	4.55	Calcite -0.83% Some anhydrite precipitation	-0.004	~0.2%	dolomite	1.01
3-1	-	No accumulation	Surplus	4.52	Calcite -0.9% No anhydrite	-0.004	~7%	siderite, dolomite	0.02
3-2	-	10 times accumulation	Surplus	2.97	Calcite -1.7% Little anhydrite precipitation	-0.007	~7%	siderite, dolomite	0.02

3.4 Modelling results

The main reactions, in which CO₂ and the different impurities are involved, as computed by *PHREEQC*, are listed in Appendix A, including their equilibrium constant at a temperature of 72°C. Appendix B shows the dissolution rates of the most common minerals. The most important modeling results are shown in Table 3-4.

3.4.1 Scenario 1 (baseline); CO₂ injection

Short term effects on formation water

Initially, injected CO₂ will partially dissolve in the formation water. As a result, the pH of the calculated formation water (step 2) decreases from 6.15 to 4.60 due to formation of carbonic acid by the following equations



Short-term effects on mineral assemblage

Since the pH of the formation water decreases due to dissolution of CO₂, some minerals, which are capable of dissolving quickly, might be affected. The model shows that a small part of the calcite can dissolve in the acid brine. This is 0.8% of the initial amount of calcite present, corresponding to a decrease in rock volume of ~0.004%. Several silicate minerals (e.g. glauconite) become highly oversaturated due to the dissolution of calcite, but since the precipitation of these minerals is very slow, this will not occur on the short term.

Long term effects on formation water and mineral assemblage

The initial mineral assemblage of the sandstone reservoir is shown in Appendix C, figure 1. In the CO₂-only scenario, the main long-term changes in mineralogical assemblage are computed to occur in the minor phases present (Appendix C, figure 2), since quartz remains at ~96 mole %. The main changes are the disappearance of illite, kaolinite, calcite and K-feldspar and the formation of diaspore, muscovite, and the carbon containing minerals siderite, dolomite and very little magnesite. The final pH of the pore water is 4.5.

Calcite dissolution occurs relatively fast and might occur in the same order of time as the equilibration of the injected gases with the formation water, as explained above. The other dissolving minerals have slower dissolution rates. Precipitation of dolomite might occur in the same order of time as calcite dissolution. However, since it requires magnesium originating from illite, which dissolves very slowly, this will not occur in the short term. The change in rock volume due to the long term mineralogical changes is a slight decrease of ~0.12%.

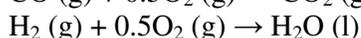
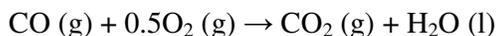
3.4.2 Scenario 2; Pre-combustion capture technology

The modeling results as computed by *PHREEQC* showed that the reactions taking place between the gases and the formation water are highly dependent on the presence or the availability of O₂. The following three scenarios have been investigated:

- 2-1) No accumulation of any impurity
- 2-2) Accumulation of O₂ (surplus amount)
- 2-3) Accumulation of H₂S (ten times) and O₂ (surplus amount)

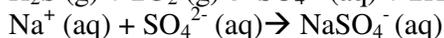
Short term effects on formation water

In the presence of O₂, CO and H₂ are favored in their conversion to CO₂ and water respectively.



All CO and H₂ would react. These reactions have hardly any effect, since they will only produce some additional CO₂ and water.

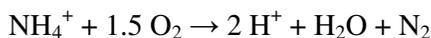
Any O₂ left is used in the model for the conversion of H₂S to SO₄²⁻ and NaSO₄⁻.



If sufficient O₂ is present to convert all of H₂S to sulphate ions, higher H₂S accumulation in the system will result in lower pH since all is computed to be converted to sulfate. If the impurities do not accumulate near the well by quick dissolution and they are evenly spread over the reservoir (scenario 2-1), the pH of the calculated formation water would be 4.63, which higher than the pH in the CO₂-only scenario. Due to the presence of insufficient O₂, additional H₂S forms from SO₄²⁻ which was already present in the aqueous phase, thereby increasing the pH. If sufficient O₂ is available the pH would be 4.56 (scenario 2-2). Ten times accumulation of the amount of H₂S in the presence of sufficient O₂ would result in a pH of 4.55 (scenario 2-3).

N₂ is computed to behave in a complex manner. It is, however, treated as an inert gas in this assessment due to the high activation energy required to break the bonds between the nitrogen atoms.

In some cases additional gaseous N₂ forms from nitrogen which was initially present in the pore water. This might be related to the pH of the formation water. In the initial formation water, some nitrogen is present as N₂ (aq) and NH₄⁺. The reaction of NH₄⁺ to N₂ is thermodynamically favorable (high equilibrium constant, see Appendix A). It would produce H⁺ and reduce the pH:



Sufficient oxygen and high pH could therefore enhance the production of additional gaseous N₂.

NO is computed to react to N₂, according to the following reaction:



As stated above, N₂ is assumed not to have any effect. Formation of O₂ however, might enhance conversion of H₂S to sulfate.

Short-term effects on mineral assemblage

Because an accumulation of H₂S can cause a significant decrease in pH on the short term, the effects on the minerals with relatively fast dissolution rates could be important. Calcite partially dissolves, dependent on the amount of H₂S present in the aqueous phase. The lower the pH of the formation water, the more calcite dissolves (Table 3-4) The calcite dissolution would buffer the pH, which increases to 4.8 – 4.9 in each scenario. Little anhydrite, which is stable at lower pH of 4-5 (Xu et al., 2007) precipitated in scenario 2-3. The amount of which is lower than the calcite dissolution, resulting in a volume decrease of ~0.005%. Anhydrite precipitation could be relatively fast (in the same order of time as calcite dissolution), thereby sequestering sulfur from the H₂S. Volume decrease due to calcite dissolution is ~0.004% and ~0.006% for scenario 2-1 and 2-2 respectively.

Long-term effects on formation water and mineral assemblage

The final mineral assemblages of the three sub scenarios as computed by *PHREEQC* are shown in Appendix C, figure 3. The mole percentage of quartz remains approximately 96% in each case. The mineral assemblages hardly differ from the CO₂-only scenario since the remaining ~4% is made up of mainly diaspore and muscovite in all cases. Compared to the CO₂-only scenario, scenario 2-2 and 2-3 more CO₂ remains in the gaseous phase. Siderite has not formed in these scenarios. Sulphur remains in the aqueous phase for each case. For scenarios 2-2 and 2-3 pyrite is converted to alunite and a significant amount of nontronite has formed at the expense of siderite, muscovite, diaspore and magnesite. Volume change is negligible in scenario 2-1. The rock volume increases by almost 1% in the other two sub scenarios. The impact of this on the rock porosity was not determined. The final pH of the formation water is 4.5 in each case.

3.4.3 Semi-purified oxy-fuel stream

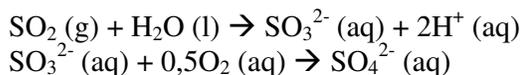
SO₂ present in the oxyfuel stream shows the tendency to completely go into dissolution. Equilibrium conditions are not limiting in the dissolution of SO₂. In contrast to H₂S, this is not dependent on the presence or availability of other impurities. The following scenarios have been investigated:

- 3-1) No accumulation of any impurity
- 3-2) Accumulation of SO₂ (ten times)

Short term effects on formation water

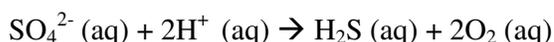
NO is computed to react to N₂ as explained in the previous section. Like for the Pernis scenario, N₂ is assumed not to have any effect due to its inert behavior. H₂ and CO will have no other effect than formation of additional water and CO₂.

SO₂ is computed to completely dissolve and react with water and oxygen to produce SO₄²⁻, thereby lowering the pH:



The more SO₂ is present in the system, the lower the pH becomes. In case the impurities do not accumulate (scenario 3-1), the initial pH of the formation water would be ~4.5. Ten times accumulation of SO₂ (scenario 3-2) would decrease the pH to a value of 3.0.

In oxygen limited conditions the SO₄²⁻ can partially be converted to H₂S by



This would (partially) buffer the pH decrease. The presence of NO and its conversion to N₂ and O₂ would create conditions in which oxygen is available, so that less sulfate would be converted to H₂S.

In both scenarios 3-1 and 3-2 sufficient oxygen is available. Conversion of SO₄²⁻ to H₂S does not occur.

Short term effects on mineral assemblage

Because an accumulation of SO₂ can cause a significant decrease in pH on the short term, the effects on the calcite dissolution and anhydrite precipitation could be significant. The model shows that in scenario 3-1 and 3-2 calcite dissolution will be 0.9 and 1.7 mole % respectively. Some anhydrite precipitation would occur in scenario 3-2. The amount is lower than the amount of calcite dissolved and the resulting volume decrease is ~0.007%. In scenario 3-1 the decrease would be ~0.004%. In both scenarios the pH of the formation water will increase due to the dissolution/precipitation reactions to a value of ~4.8.

Long term effects on formation water and mineral assemblage

The results on the modeling of the mineral assemblage can be found in Appendix C, figure 4. Like for the Pernis impurities, the final mineral assemblage computed by *PHREEQC* is close to the initial one, since the mole percentage of quartz remains ~96 mole %. The mineral assemblages hardly differ from the CO₂-only scenario since the minor mineral phases are made up of mainly diaspore and muscovite.

Also, a similar amount of carbon is stored in mineral form in these two scenarios as in the CO₂-only scenario. The sulfur remains in the aqueous phase like for the Pernis scenarios. Some pyrite has dissolved and alunite has formed. There is no difference between the two sub scenarios. Rock volume change is negligible. The final pH of the formation water is 4.5, which is the same as for the baseline scenario and the Pernis scenarios.

3.5 Discussion

3.5.1 Implications for CO₂ storage

For the Pernis and oxyfuel impurities, H₂S and SO₂ have shown the capability to influence the pH of the formation water, in addition to the CO₂. For H₂S the amount to

be dissolved and the subsequent formation of SO_4^{2-} and H^+ in the formation water largely depends on the availability of oxygen. Due to the very low concentration of H_2S in the CO_2 stream, the effect is insignificant, even if it would accumulate by a factor of 10. Higher H_2S concentrations in the CO_2 stream in combination with O_2 are unfavourable for storage capacity.

The dissolution of SO_2 and its conversion to SO_4^{2-} is independent of other impurities, but the absence of oxygen can enhance the reaction of SO_4^{2-} to H_2S , thereby reducing the pH decrease of the formation water. Due to the higher concentration of SO_2 in the oxyfuel stream, compared to the H_2S concentration, accumulation by a factor of 10 can have a significant influence on the pH of the formation water. The additional decrease in pH can have a short term effect by the quick dissolution and precipitation of calcite and anhydrite respectively. The modeling results have shown that the lower the pH of the formation water, the higher the amount of calcite dissolution. Anhydrite precipitation only occurs in the scenario with very low formation water pH (scenario 3-2). Due to the presence of calcite as cement, which glues the detrital grains, like quartz, together, the dissolution of this mineral could in principle result in improved injectivity due to enhanced porosity and permeability of the reservoir rock, although the actual effect could very well be negligible. Anhydrite precipitation would have the opposite effect. The amount of anhydrite precipitation is lower than the amount of calcite dissolution, resulting in a small volume decrease of 0.005-0.007% and thus in a slight increase in injectivity. It can be concluded that these effects are negligible as well.

Lowering the pH of the formation water would also have effects on the well integrity. Well mineralogy is sensitive to acid water. Chemical reactions might increase porosity and permeability, thereby increasing the risk of CO_2 leakage.

The long term mineral assemblage of the Pernis and oxyfuel scenarios, as computed by *PHREEQC*, is similar to the CO_2 -only scenario. Scenario 2-2 and 2-3 are the only ones which have slightly deviating assemblages. Alunite (0.12-0.13 mole %) and nontronite (0.25 mole %) have formed instead of siderite, which is present in each of the other scenarios. Pyrite has disappeared. This difference in mineralogy compared to scenario 2-1 is due to the presence of a surplus amount of oxygen and not due to H_2S . The formation of alunite and nontronite requires oxygen. The Mg, K, Al and Fe required for their formation originate from illite. In the other scenarios Mg is sequestered in magnesite and K and Al in additional muscovite and diaspore. In the absence of oxygen, pyrite and siderite are the stable, iron-bearing minerals. Since nontronite and alunite have much higher mole volumes than siderite and pyrite, the rock volume would increase by approximately 1%. This could have implications for the reservoir pressure on the long term. Whether these effects would be significant requires further research. The low pH caused by accumulation of SO_2 (scenario 3-2) does not have effects on the long term reservoir mineralogy.

In gas fields, the pore water saturation is limited compared to aquifers. In aquifers, the accumulation of H_2S and SO_2 would depend on brine advection and on diffusion rates of the aqueous species. In gas fields, advection would not take place and in case of very

low pore water saturation, diffusion would only take place on a micro scale. Since both H₂S and SO₂ could dissolve in formation water to a very high extent and presence of formation water is limited, the accumulation of these phases in gas fields depends on kinetics of the reactions. An extended literature review could give more insight into the kinetics and thus in the accumulation of H₂S and SO₂. Probably, several knowledge gaps with regard to this topic could be identified. More research would be necessary in order to be able to define maximum levels of H₂S and SO₂ in the CO₂ stream.

3.5.2 Comparison with literature

Very limited research has been performed on the modeling of impurities in CO₂ streams. Knauss et al (2005) performed a modeling study using the reactive transport code CRUNCH and Xu et al. (2007) studied the effects of H₂S and SO₂ by means of the reactive transport model TOUGHREACT. Both studies focused on aquifers for CO₂ storage. Reactive transport modeling has the advantage that fluid flow has been taken into account so that the effects of spatial variation in gaseous and aqueous species concentrations can be studied. For the modeling of geochemical effects of CO₂ injection in gas fields, fluid flow is not relevant and *PHREEQC* as a modeling tool would be adequate.

Both Knauss et al. (2005) and Xu et al. (2007) concluded in their studies that H₂S in the CO₂ stream has hardly any effect, even if it is present in high amounts. This is comparable to our results for oxygen deficient scenarios. However, *PHREEQC* has shown that H₂S could react to sulfuric acid if sufficient oxygen is present as an impurity in the CO₂ stream.

SO₂, on the other hand, was computed by the reactive transport models to have a significant effect on the pH of the formation water. According to Knauss et al. (2005) SO₂ will probably oxidize, even without much O₂ present. This is in agreement with the results of this assessment. Pyrite as well as water could provide the oxidizing conditions.

Both studies show the formation of anhydrite (CaSO₄) in the CO₂ + SO₂ scenario on the short-term in the acid region of injection due to the stability of anhydrite at lower pH (4-5) (Xu et al., 2007), where calcite has completely disappeared. In the study by Xu et al. (2007) anhydrite moved away from the injection location with time to >100 meters from the well in 100 years. Most sulfur has, however been immobilized by alunite on the long term in their study. In our study anhydrite has formed in the short term and alunite in the long term assessment and is therefore consistent with literature. In a gas field with limited pore water saturation, the anhydrite would not move away from the injection well. It would possibly dissolve again in time and be replaced by alunite, since anhydrite is not calculated to be part of the equilibrium mineral assemblage in this assessment.

3.5.3 Modeling limitations

In section 1.3 the *PHREEQC* modeling results are described in detail. This software package is based on thermodynamic equilibria; kinetics have not been taken into

account in this assessment. The reaction rates depend on several parameters, e.g. on the activation energy of the reaction. Modeling results show for example that N₂ could have a significant impact on the pH of the formation water by conversion to NO₃⁻ or NH₄⁺. However, it requires a very large amount of energy to break the bonds between the two nitrogen atoms. Kinetics of the reactions involving N₂ will most probably inhibit the formation of NO₃⁻ or NH₄⁺. In this assessment, N₂ is considered as an inert gas. For other gaseous or aqueous species, taking into account the kinetics could be important. Kinetic limitations in the models, especially concerning rate equations describing disproportionation of aqueous species has also been recognized by Xu et al. (2007).

Ionic strength is an important issue due to the presence of brine in gas fields and aquifers. It affects the activity of the aqueous species. The geochemical database used for this assessment (Ilnl-database) does not take into account ionic strength. Unfortunately, the Pitzer database which takes into account ionic strength does not contain data on every species relevant in this assessment. Since the activities of the species decreases with higher ionic strength, this assessment is a conservative approach.

Since, based on thermodynamics, H₂S and SO₂ can be dissolved to a large extent, an important question is how fast the dissolution occurs, since it affects accumulation and thus pH of the formation water near the injection well. Generally, H₂S can dissolve in water faster than SO₂, but the effects of ionic strength and high pressure and temperature conditions make it more complex. Furthermore, their dissolution depends on the competition with dissolution of other gases, which is not included in *PHREEQC*. This requires further research.

In this assessment, the final pressure after completion of the CO₂ injection has been used to investigate the short- and long-term effects on the formation water and the mineral assemblage. Since short-term was defined as the injectivity period (< 40 yrs), pressure build up from the initial (~31 bar) to the final (175 bar) value occurs, which has not been taken into account. Lower pressure would result in delay of the effects which are described for the short-term.

3.6 Further research

In this assessment, NO_x has been assumed to be NO. NO₂ on the other hand could have impact by conversion to nitric acid. This should be investigated in continued studies. Further research should focus on the *short-term effects* (injectivity period) to define maximum impurity levels based on induced injectivity changes. Acid conditions will prevail near the well and might affect its integrity. Calcite dissolution might enhance injectivity while precipitation of e.g. anhydrite might cause clogging and thus reduce injectivity. Kinetics should be included as much as possible. *Long-term effects* from changes in mineral assemblage and corresponding pressure change requires further investigation. Future research should also focus on the effects on *different reservoir types* and on the *spatial variability* (accumulation of impurities) of the effects within the reservoir.

4 WATER CONTENT OF TRANSPORTED CO₂

The work in this chapter was used to produce a paper for the GHGT conference and therefore a modified version of this chapter can be found in the Proceedings of the 10th Greenhouse Gas Technologies Conference (Buit, 2010).

4.1 Introduction

The infrastructure necessary to capture, transport and store CO₂ requires a technical specification of several CO₂ characteristics, such as pressure, temperature, and composition. One of the most important constraints on the CO₂ composition will be the water content. CCS stakeholders have published a variety of water concentration limits. A lower extreme in these specifications is 40 ppm (VROM, 2010) as specified for the Barendrecht project. In the Sacroc unit in US, specifications for dehydration allow a maximum of 50 ppm of water remaining in the dehydrated CO₂ (West 1971). The specification of the maximum of 50 ppm of water was established to assure that the CO₂ present could remain inert and not affect the material in the pipeline. CO₂ under the normal pipeline-design operating conditions can support 2500 ppm of water in solution. The drying requirements for CO₂ pipelines for EOR, operated by Kinder Morgan, is 600 ppm (Heggum, Weydahl et al. 2005). At the liquid natural gas plant at Hammerfest in Norway, the drying requirement for CO₂ is 50 ppm. In the USA, where dense phase CO₂ has been transported for decades, the water content is usually limited to about 500 ppm. In the Dynamis project, a limit of 500 ppm is recommended (Visser 2008).

Unfortunately, little has been published on the rationale behind these concentration limits. If the reason for a certain limit is given, it is just that the occurrence of free water could cause corrosion, which should be prevented. The prevention of hydrate formation is also mentioned sometimes as a reason to limit the water content. Usually it is not clear whether the given limit is lower than necessary or really sufficient to avoid free water in the pipeline. It is just an assertion that a certain limit is imposed. Known water concentration limits could have originated from an analysis of the physical processes involved in CO₂ transport, but the limit could also easily have been derived from the composition of the CO₂ source, which already supplied very dry CO₂. In the latter case, the technical limit could very well be much higher than the imposed limit.

In a business like CCS, where there is a strong emphasis on cost-efficiency, the approach in which a water concentration limit is given but not properly explained is not viable. It should be clear to all CCS stakeholders that only technical specifications are imposed and that they enable a CCS chain with minimized costs.

The present lack of clarity on the dryness requirements is undesirable, because eventually, we must come to a water content standard for CCS. The work presented here aims at analyzing CO₂ pipeline transport to provide some basic input for this standard.

4.2 Rationale for a water concentration limit

CO₂ capture processes result in captured CO₂ with some impurities. One of the impurities is water. It can be removed to a certain extent at the capture plant, but a small amount of water will remain. When the water is in solution in the CO₂, there is no problem, but free water combined with CO₂ is very acidic. The corrosive nature of wet CO₂ poses a threat to the transport system integrity, because a CO₂ pipeline will be built of carbon steel. Economical considerations dictate the use of regular carbon steel, which is commonly used for most pipelines. In theory, corrosion resistant steel could be used to prevent corrosion, but it would be prohibitively expensive to build CCS pipelines of this material.

Corrosion tests can be performed to determine what the corrosion rates would be if free water would happen to occur in a regular carbon steel CO₂ pipeline under typical transport conditions. In addition, efforts should be taken to exclude the occurrence of free water in a CO₂ pipeline as much as possible.

It is practically impossible to remove all water from the captured CO₂, although the water level can be brought down to very low levels, around dozens of parts per million. However, drying adds to the costs of CCS, both in money and energy, making it undesirable to adhere to an overly strict water content limit. The drying method chosen has a large effect on the costs; the lowest specs available (40 ppm) can be attained with a mole sieve whereas a glycol dryer costs less but is unable to reach a water content level as low. It is also important to consider the reliability and inherent protection of a drying system.

For the CO₂ producer, it is not only the capital investment in a drying installation that is important. Depending on the water concentration limit, the CO₂ producer has a certain degree of freedom in using the drying installation. When the water limit is less stringent than the level attainable by the installed drying installation, the producer can bypass part of the captured CO₂ and feed it into the transmission system directly, which would save drying costs. Furthermore, a short downtime of the drying installation can be acceptable or not, depending on the flexibility in water content allowed.

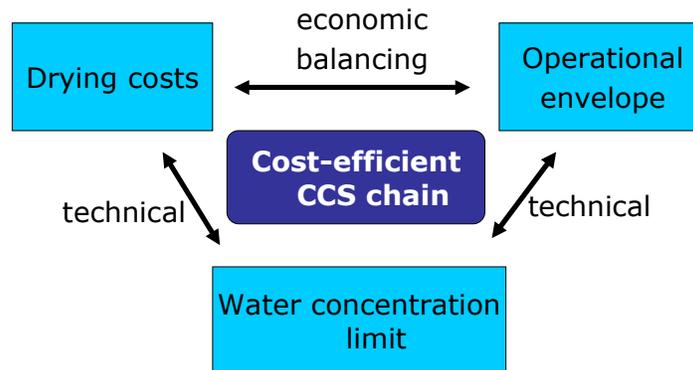


Figure 4-1 The economic and technical relations between a water concentration limit, the CO₂ drying costs and the operational envelope of the CO₂ transmission system.

In short, although technically it is no problem to dry captured CO₂ to very low water concentrations, for economical considerations it should be investigated what is the highest water content limit that can be accepted. The balancing of interests and technical and economical considerations is depicted in Figure 4-1.

4.3 Solubility of water in CO₂

The solubility of water in CO₂ depends on the CO₂ pressure, temperature and composition. In the Dynamis report, there is a convenient graph of the modelled solubility as a function of pressure. The solubility in ppm at various temperatures is given. (Visser 2008) It should be noted that there are high levels of uncertainty in the modelled results at lower temperature region where hydrates can form (Austegard et al, 2006).

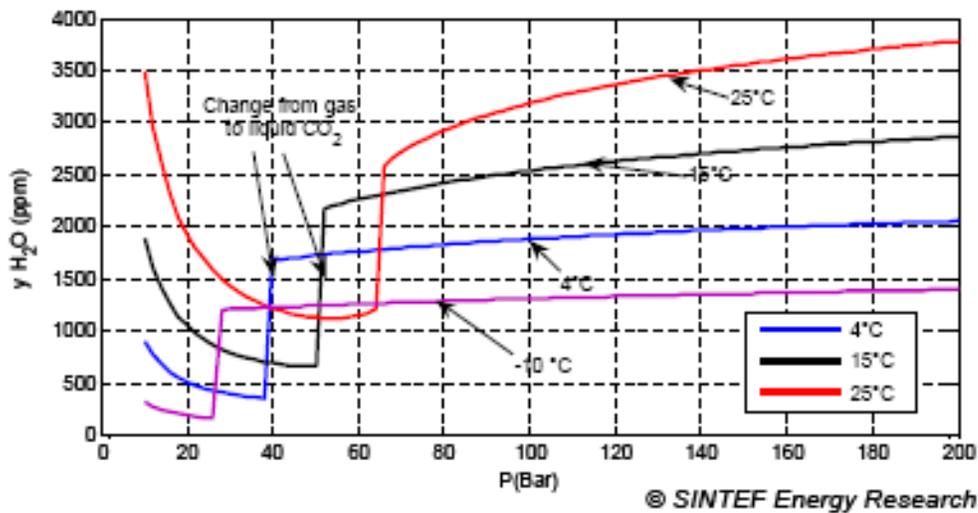


Figure 4-2 The solubility of water in CO₂ for varying temperatures as a function of pressure. Figure taken from the Dynamis report. (Visser 2008)

We see in this graph that the solubility of water decreases on the path from atmospheric pressure to the point where the phase transition from gas to liquid occurs. At the phase transition, there is a sharp increase in solubility, and with increasing pressure, the solubility increases even more. It must be noted that this graph applies to pure CO₂. Impurities might increase or decrease the water solubility.

4.4 Operational regimes

To assess how the water solubility data translate to a water concentration limit, the various possible states of a CO₂ transmission system can be evaluated. The transmission system comprises everything between the CO₂ capture site(s) and the storage reservoir(s).

4.4.1 Normal operation

First of all, we consider the situation in which the system is operating the way it was designed to operate, without interruption, with all parameters within their specifications. A dense phase CO₂ transmission system is considered to be in normal operation when there are no flow interruptions and the pressure range in the pipeline is between 85 and 150 bars in case of onshore transport and between 85 and 200 bars offshore. The lower limit is determined by the critical point of CO₂ (73,8 bars for pure CO₂, somewhat different for CO₂ with impurities (DNV, 2010)). A pressure of 85 bars ensures the CO₂ remains in the dense phase in case of a temporary shutdown. Two phase flow in the pipeline should be avoided. The upper limits of 150 and 200 bars are chosen with regard to safety and economical optimisation.

The lowest temperature that can be expected during normal operation is about 0 °C, as can be deduced from the data in the Pipe Line Rules of Thumb Handbook (McAllistor, 1998). The seawater temperature is typically around 4 °C. The maximum temperature in the transport system is found downstream of the main compressor, where CO₂ exits the final stage at above 30 °C, depending on the compressor and the required pressure. Along the pipeline the CO₂ temperature will decrease towards the ambient temperature. The operating conditions described above correspond with a water solubility of at least 1500 ppm.

4.4.2 Commissioning

When a CO₂ pipeline has been built, it must undergo hydrostatic testing before being put into use. DNV's Recommended Practice (DNV 2010) mentions that, alternatively, air, N₂ and CO₂ could be used instead of water, but this is much riskier than using water, so this is strongly discouraged. To prevent a corrosive mixture of CO₂ and water, the pipeline should be dried. This is proven technology. A stringent water concentration limit implies higher commissioning costs, so again, for the sake of cost-efficiency the required maximum water concentration should be as high as possible.

4.4.3 Blow down

A blow down of CO₂ can be intentional or the result of some incident. When the CO₂ is evacuated from the pipeline during an intentional blow down operation, e.g. for maintenance, the decrease in pressure and temperature can be controlled, enabling the pipeline operator to steer clear of free water formation. Again, the more relaxed the water concentration limit is, the more leeway the operator has in blowing down a pipeline, and the faster the blow down procedure will be carried out. A fast blow down is preferred because this will reduce downtime of the pipeline. On the other hand, if you blow down too quickly you could induce very low temperatures leading to further damage to your pipeline. Therefore from a pipeline operator / owner point of view fast blowdown is not necessarily optimal. There are other more effective strategies of reducing blowdown time.

A different case is unintended blow down, e.g. due to external damage, a valve malfunction or operational error or. In such a case, by definition, the pressure decrease is not controlled. Mitigation measures, such as a SCADA system (Supervisory Control And Data Acquisition) will have been installed in CO₂ pipeline transmission systems, but nevertheless, if there is a leakage or valve malfunction in the CO₂ pipeline, pressure and temperature could decrease rapidly. However, regarding the physics of the CO₂ outflow there is limited knowledge. Presently, there is a lack of validated models that are able to adequately describe the CO₂ conditions during outflow.

4.5 Discussion

In the process of identifying scenarios for free water formation in CO₂, we encounter several issues to be solved in order to determine the water concentration limit necessary for safe, reliable and economical CO₂ transport by pipeline.

For the correct evaluation of the economical impact of water concentration limits, cost data of suitable drying installations should be gathered.

Another research question is: What is the relation between the water concentration and acceptable blow down system design? For the most cost-efficient solution, some balancing will need to be done by comparing the economics of the blow down speeds and the corresponding downtime of the transmission system to CO₂ drying costs. It should be noted, that water content is not necessarily the only significant factor effecting blowdown.

In CO₂, free water will form when at the given CO₂ conditions, the water concentration becomes higher than the solubility. Obviously this situation will have to be avoided. But if on average, the water content is below the solubility limit, locally, e.g. in low-lying pipeline sections, the water concentration could be above the solubility limit causing condensation. Also, an upset in the CO₂ flow might give rise to free water even if the water concentration is below the solubility.

For the evaluation of the aforementioned research questions the expected impurities in the captured CO₂ should be taken into account. The same applies to research into hydrate formation, which is outside the scope of this work.

As this chapter shows, several issues have to be addressed before the best water specification can be determined. It should be noted, however, that CO₂ transport operators in the USA, to our knowledge, have not expressed any concerns about their water concentration limits, which indicates that a limit of several hundred ppm should suffice. Thorough research should indicate what the best water concentration limit is.

5 CONCLUSIONS

5.1 Impurities in CO₂ transport

The composition of CO₂ may impact CO₂ transport and injection in the following ways:

- The phase diagram varies with composition. In pipeline transport, the pressure must exceed the critical pressure to prevent two-phase flow. Another option is to transport in the gaseous phase in all circumstances. In the case of vapour-phase transport, the pressure must be kept below 40 bars, resulting in a significantly lower transport capacity than for dense phase transport.
- Corrosion of pipelines and other equipment depends on the existence of free water. This topic is discussed in more detail in section 4 of this report and conclusions are presented in section 5.3.
- Non-condensable impurities affect transport and injection capacity. Non-condensables (N₂, H₂, CH₄, O₂, Ar) affect the thermodynamics of the CO₂ mixture. More specifically, they increase the critical pressure, so for supercritical transport, a higher concentration of non-condensables requires higher transport pressures and therefore higher compression costs. For this reason, it is recommended to put the limit for non-condensable impurities at 5% by volume.
- Lastly, when CO₂ is released into the environment, the impurities may have an effect on health, safety and the environment. It is recommended that these impurities do not form a risk higher than that of the CO₂ itself. To arrive at acceptable limits of these impurities, the short term exposure limits (STEL) of the impurities are compared to that of pure CO₂. This comparison leads to a maximum impurity limit for the impurities concerned. The following formula is used:

$$Limit_{impurity} = \frac{1}{2} \cdot Limit_{CO_2} \cdot \frac{STEL_{impurity}}{STEL_{CO_2}}$$

The above considerations lead to the following recommendations of impurity limits. Note that these are recommendations only and that additional insights will lead to different values and probably to additional impurity limits.

Table 5-1 Input for impurity limits in CO₂ transport.

Impurity	Limit in CO ₂	Impurity	Limit in CO ₂
CO ₂	>95 vol%	NO ₂	75 ppm
		CO	4750 ppm
H ₂ O	no free water	H ₂ S	235 ppm
		SO ₂	75 ppm
Ar	together <5 vol%	HCN	70 ppm
CH ₄		COS	235 ppm
H ₂		NH ₃	550 ppm

N ₂			
O ₂			

5.2 Impurities in CO₂ storage

The effects of impurities on a CO₂ storage reservoir have been modelled with the software package *PHREEQC* (version 2) and the geochemical llnl-database. Different compositions of CO₂ have been modelled in several scenarios.

It was found, that a number of impurities could have an effect on storage conditions. H₂S and SO₂ (like CO₂ itself) have shown the capability to influence the pH of the formation water. However, the effect of both H₂S and SO₂ in the expected quantities appears insignificant. Minimal volume decreases of the host matrix will occur. The short term effects (<40 years) are negligible. For the longer term (>10 000 years), the volume of the matrix could increase due to mineral formations by approximately 1%. This would lead to a higher pressure in the reservoir and is something to be taken into account when determining the maximum quantity of CO₂ to be stored in a reservoir. Accumulation of H₂S and SO₂ could occur in a reservoir with low water concentrations. More research would be necessary in order to be able to define maximum levels of H₂S and SO₂ in the CO₂ stream. In particular, performance indicators need to be developed so that the results of geochemical studies can be converted into a standard.

The *PHREEQC* model is useful for calculating thermodynamic equilibria; some aspects of the modelled reactions have not been taken into account. Examples are the reaction kinetics, ionic strengths and dissolution rates. Taking these into account could give more accurate results. However, the results of the *PHREEQC* modelling can be considered conservative, so they are useful for this assessment.

A number of topics should be investigated in further research. NO₂ could have an impact on the reservoir, but this has not been considered. This study did not go into effects of impurities on injectivity. For the longer term, effects of changes in mineral assemblage should be investigated, as well as long-term pressure changes. Furthermore, different reservoir types and spatial variability of the impurities should receive attention.

5.3 Water concentration limit

In the CCS field, there have been several statements of the desired water concentration limit in CO₂, varying from 40 to over 500 ppm. While the reasoning behind these limits has been expressed in many cases, the terse explanations mostly just consisted of the assertion that the given limit is necessary to prevent the unwanted occurrence of free water at all costs. Because of the energetic and economic costs associated with drying the captured CO₂, it is worthwhile to evaluate the precise water concentration limit that is needed for a safe and reliable CO₂ transport operation.

Under normal operating conditions dense phase CO₂ can be transported containing 500 ppm water without any risk of free water formation, because the water solubility is at least 1500 ppm under these circumstances.

When a CO₂ pipeline is commissioned, it needs to be dried after hydrostatic testing. The more relaxed the water concentration limit is, the less time and money will be involved in commissioning the pipeline. Therefore, having a water concentration limit that is too stringent affects both the drying costs at the capture site and the drying during commissioning of the pipeline. Figure 5-1 describes the implications of a water concentration limit.

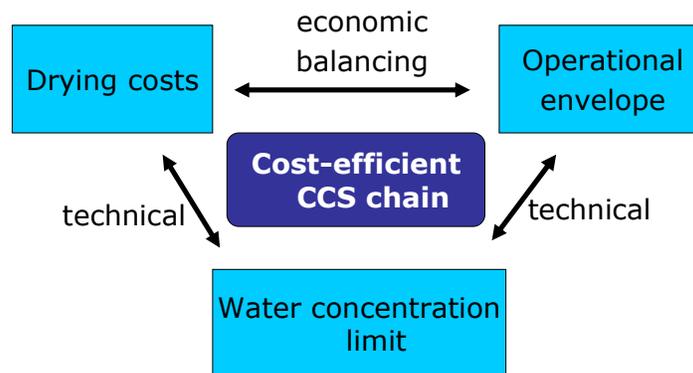


Figure 5-1 The economic and technical relations between a water concentration limit, the CO₂ drying costs and the operational envelope of the CO₂ transmission system.

In the range of water concentration limits encountered, the lower extremes of 40 and 50 ppm are probably rather conservative. In any case, a limit of 500 ppm water will prohibit free water formation during normal operation. Due to the current lack of validated models for the thermodynamics of CO₂ outflow it is not possible to assess what water content is acceptable when uncontrolled CO₂ release is taken into account. The existing US experience notwithstanding, additional analysis, both physical and economical, is needed to arrive at a water concentration limit that enables reliable and cost-efficient CO₂ transport.

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APPENDIX A. REACTIONS

Reaction	log K (at 72 °C)
N2	
$N_2 + 3H_2O = 1.5 O_2 + 2 NH_3$	-103.4
$2 O_2 + NH_3 = NO_3^- + H^+ + H_2O$	52.6
$\rightarrow N_2 + H_2O + 2.5 O_2 = 2 NO_3^- + 2 H^+$	1.8
$NH_3 + 1.0000 H^+ = NH_4^+$	8
$\rightarrow N_2 + H_2O + 2H^+ = 1.5 O_2 + NH_4^+$	-87.4
$NO_3^- + H^+ = HNO_3$	-0.8
NO	
$NO + 0.5 H_2O + 0.25 O_2 = H^+ + NO_2^-$	-1.2
$NO_2^- + H^+ + H_2O = 1.5 O_2 + NH_3$	-39.7
$2 NH_3 + 1.5 O_2 = N_2 + 3 H_2O$	100.1
$\rightarrow 2NO = N_2 + O_2$	18.3
H2S	
$H_2S = H^+ + HS^-$	-7.9
$HS^- + 2 O_2 = SO_4^{--} + H^+$	117.3
$\rightarrow H_2S + 2 O_2 = SO_4^{--} + 2H^+$	109.4
$SO_4^{--} + Na^+ = NaSO_4^-$	0.8 (25 °C)
CO	
$CO + H_2O + 0.5 O_2 = H^+ + HCO_3^-$	31.7
$HCO_3^- + H^+ = CO_2 + H_2O$	6.3
$\rightarrow CO + 0.5 O_2 = CO_2$	38.0
H2	
$H_2 + 0.5 O_2 = H_2O$	36.3
SO2	
$SO_2 (g) = SO_2 (aq)$	-0.4
$SO_2 + H_2O = 2 H^+ + SO_3^{--}$	-10
$SO_3^{--} + 0.5 O_2 = SO_4^{--}$	40.2
$\rightarrow SO_2 + H_2O + 0.5 O_2 = 2 H^+ + SO_4^{--}$	29.8
$SO_4^{--} + H^+ = HSO_4^-$	2.6
CO2	
$CO_2 + H_2O = H^+ + HCO_3^-$	-8.1
$HCO_3^- + H^+ = CO_2 + H_2O$	6.3
$\rightarrow CO_2 (g) = CO_2 (aq)$	-1.8
$HCO_3^- = CO_3^{--} + H^+$	-10.1
Ar	
$Ar (g) = Ar (aq)$	-3.1

APPENDIX B. MINERAL DISSOLUTION RATES

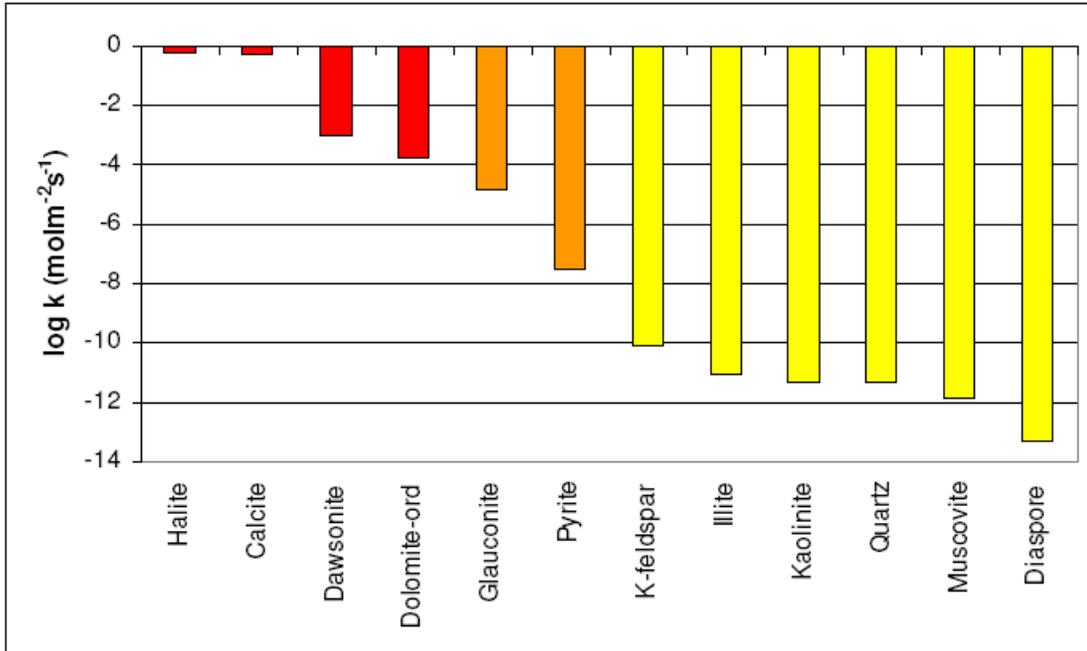


Figure 1. Dissolution rates (in log k (mol/m²/s)) of minerals under acid conditions, based on Palandri and Kharaka (2004).

APPENDIX C. CHEMICAL FORMULAE

Mineral	Chemical formula
Alunite	$KAl_3(SO_4)_2(OH)_6$
Anhydrite	$CaSO_4$
Calcite	$CaCO_3$
Dawsonite	$NaAl(CO_3)(OH)_2$
Diaspore	$AlO(OH)$
Dolomite-ord	$CaMg(CO_3)_2$
Glauconite	$(K,Na)(Fe,Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$
Illite	$K_{0.6}(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Magnesite	$MgCO_3$
Muscovite	$KAl_2Si_3O_{10}(OH)_2$
Nontronite-Mg	$Mg_{0,165}Fe_2(Si,Al)_4H_2O_{12}$
Orthoclase (K-feldspar)	$KAlSi_3O_8$
Pyrite	FeS_2
Siderite	$FeCO_3$

APPENDIX D. LONG-TERM MINERAL ASSEMBLAGES

In this appendix the initial reservoir assemblage and the assemblages calculated for the different scenarios are shown. In each case, quartz makes up approximately 96 mole %. The smaller pie diagrams show the remaining ~4 %, added to 100%.

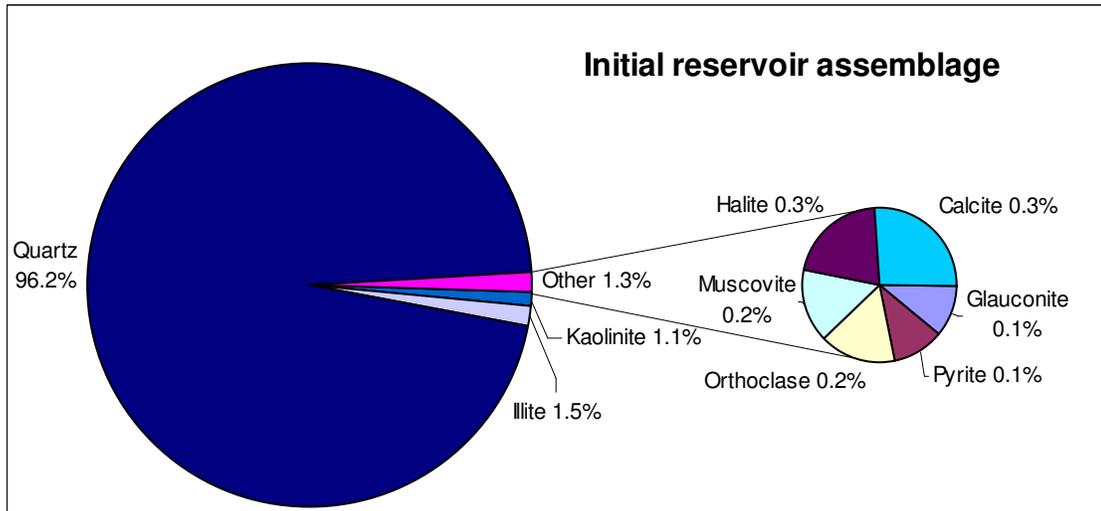


Figure 1. Initial mineral assemblage.

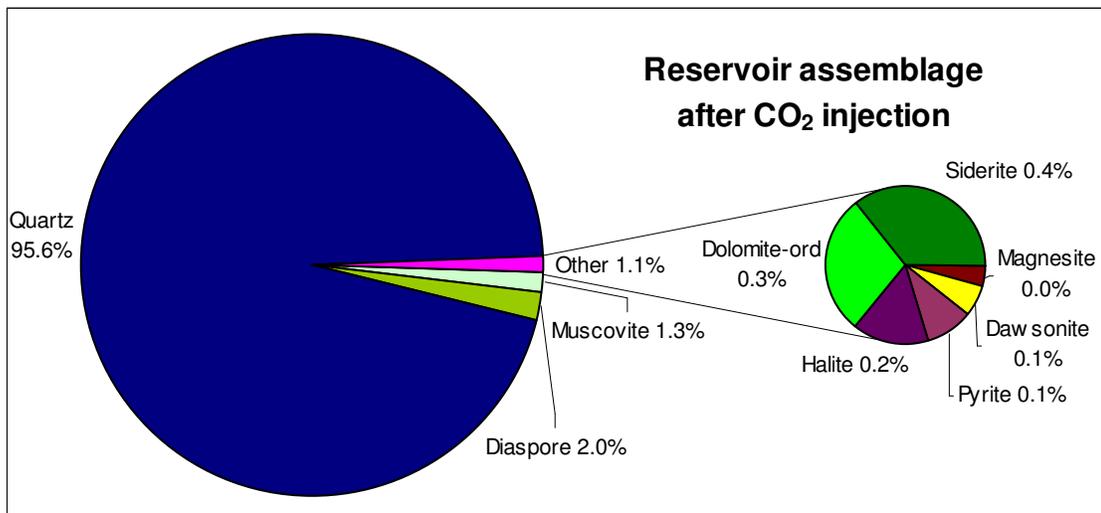


Figure 2. Mineral assemblage after CO₂ injection, pH of calculated formation water is 4.6.

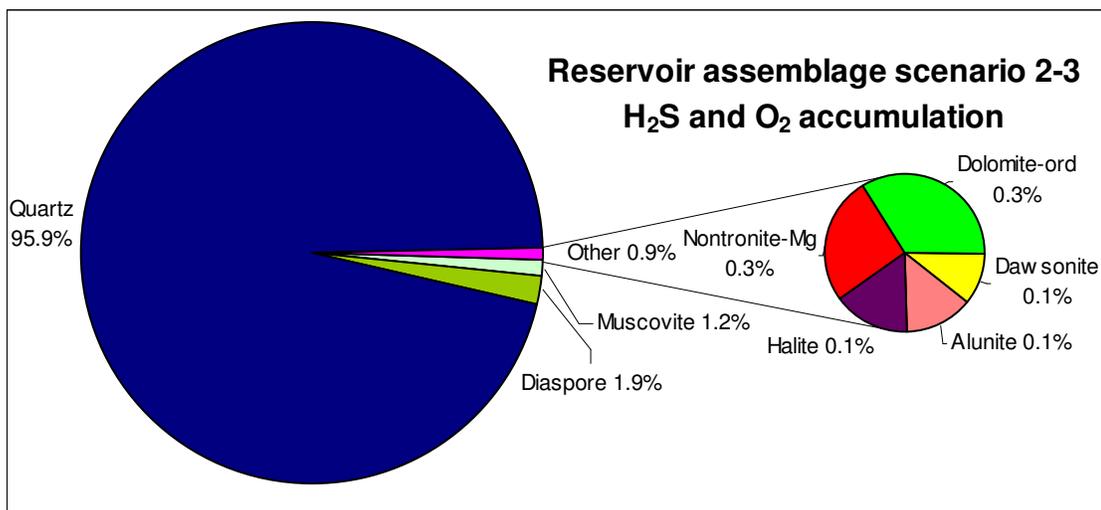
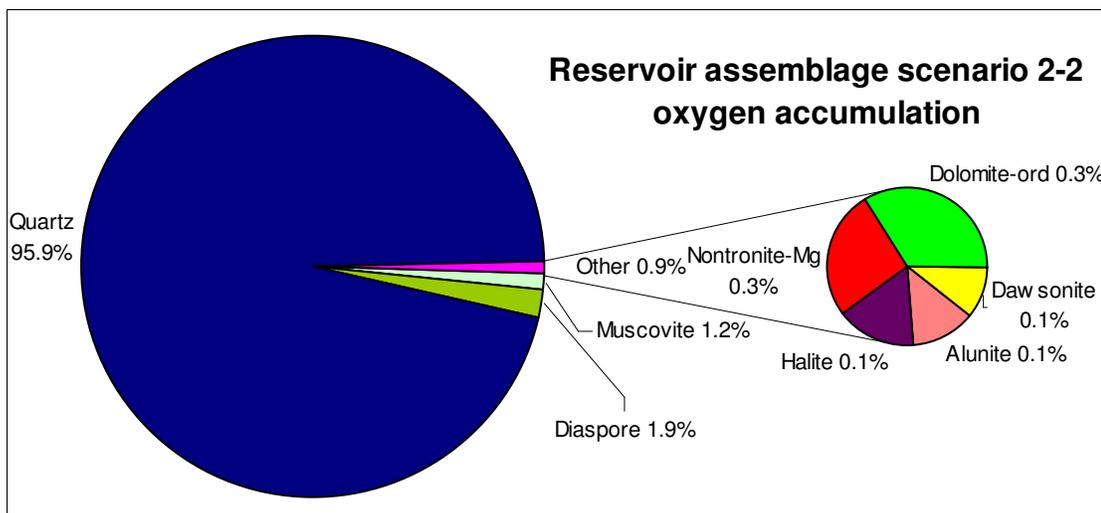
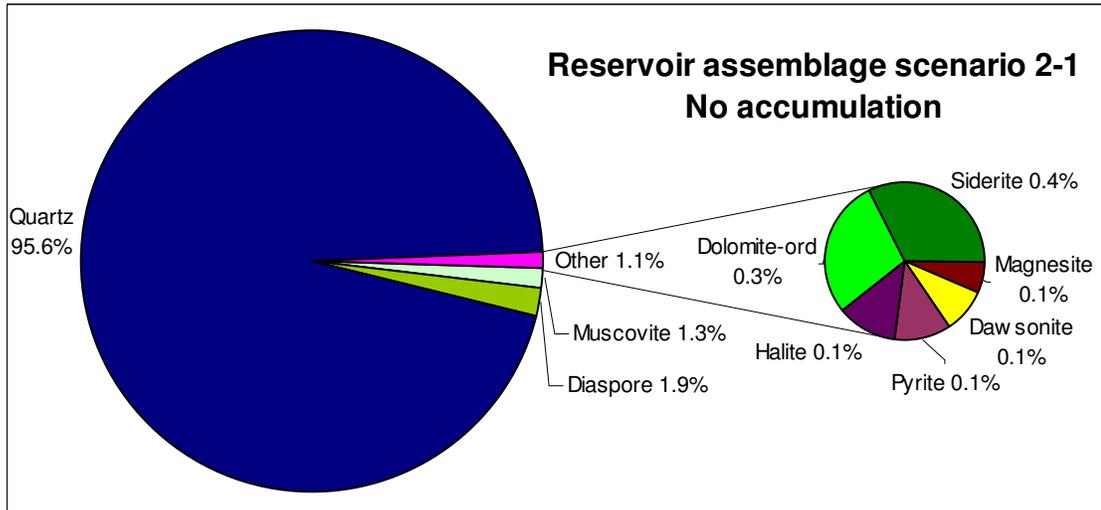


Figure 3. Mineral assemblage after injection of Shell Pernis CO₂ stream. a) No impurity accumulation,

pH of calculated formation water is 4.6. b) Oxygen accumulation, pH of calculated formation water is 4.6.
 c) H₂S and O₂ accumulation, pH of calculated formation water is 4.5.

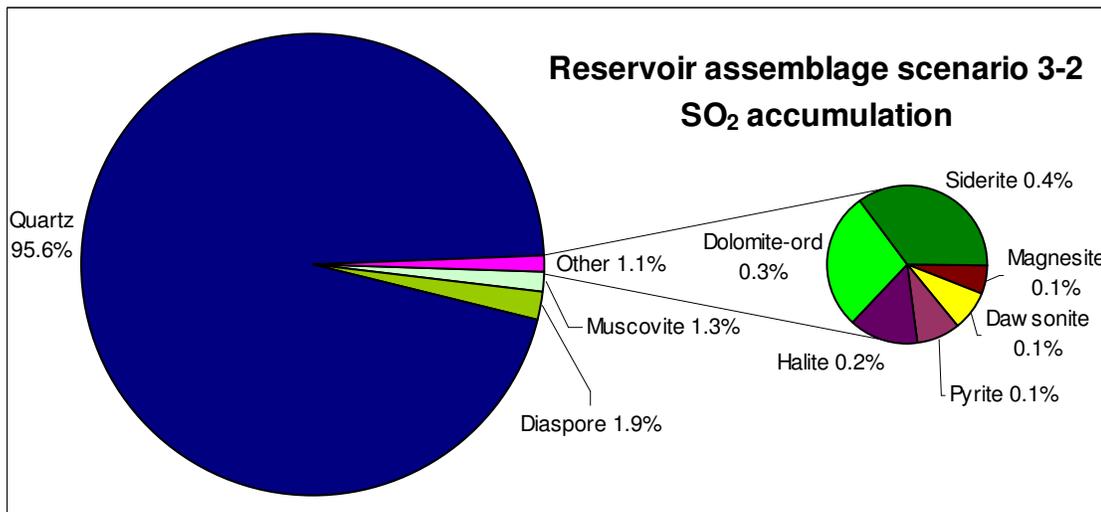
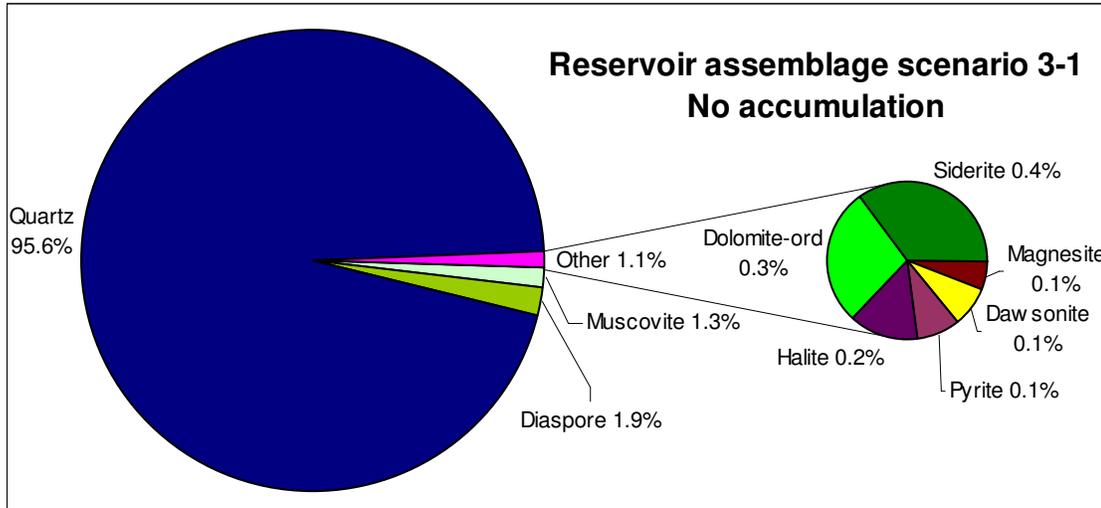


Figure 4. Mineral assemblage after injection of CO₂ stream from pre-combustion capture technology. a) No impurity accumulation, pH of calculated formation water of 4.5. b) SO₂ accumulation, pH of calculated formation water of 3.0.