
**Carbon dioxide capture,
transportation, and geological
storage — Cross Cutting Issues — CO₂
stream composition**

*Captage, transport et stockage géologique du dioxyde de carbone —
Questions transversales— Composition du flux de CO₂*





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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 265, *Carbon dioxide capture, transportation, and geological storage*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

ISO Technical Committee (TC) 265 is developing standards and technical reports related to carbon dioxide (CO₂) capture, transportation and geological storage (CCS). This technology is a technically viable solution to reduce CO₂ emissions of large stationary point sources and therefore to limit future global temperature increases. A special report by the International Panel on Climate Change (IPCC, 2005) extensively described the fundamental technical, scientific, environmental, economic and societal dimensions of CCS and its potential role in the portfolio of climate change mitigation measures.

Depending among other things on the feedstock and the CO₂ generating and capture processes, CO₂ streams captured from industrial sources or power generation contain various impurities (that is, stream components other than CO₂). The impurities differ in their concentrations but also in their physical and chemical properties. Therefore, the composition of the originally captured CO₂ stream is a key starting point in ensuring the safety and reliability of the transport and geological storage of CO₂. Compositional information may assist operators in evaluating the need for treating a CO₂ stream, based on the intended transportation options (including mixing with other CO₂ streams), usage options (EOR or other), or dedicated storage in geologic formations.

Understanding CO₂ stream composition is also important for the commerciality of CCS activities because additional purification of the CO₂ stream increases CO₂ capture costs. In addition, CO₂ stream composition is an important input factor in quantifying the amount of CO₂ stored, for the purpose of greenhouse gas emissions reporting and crediting. Because capture and purification processes are continuously evolving, it is relevant to expose the range of impurities in CO₂ streams and their concentrations, including recent publications.

This document provides up-to-date consideration of CO₂ stream quality issues for operators, regulators and stakeholders based on research results and the experience of various pilot and industrial scale CCS projects. The first part of this report summarises existing information related to CO₂ stream composition that generally results from particular capture processes. Then this report describes possible impacts and effects of the various impurities that may occur in the CO₂ stream on various downstream elements of a CCS chain, including operational aspects, potential implications for health, safety and environmental issues, and quantification of greenhouse gas emissions.

Carbon dioxide capture, transportation, and geological storage — Cross Cutting Issues — CO₂ stream composition

1 Scope

The primary aim of this document is to describe the main compositional characteristics of the CO₂ stream downstream of the capture unit, taking into account common purification options. Accordingly, this document will characterize the different types of impurities and present examples of concentrations determined in recent capture pilot projects as well as through literature review. It identifies ranges of concentrations, giving priority to in situ measurements when available.

The second aim of this document is to identify potential impacts of impurities on all components of the CCS chain, from surface installations (including transport) to the storage complex. For example, impurities can have a significant effect on the phase behaviour of CO₂ streams in relation to their concentration. Chemical effects also include the corrosion of metals. The composition of the CO₂ stream can also influence the injectivity and the storage capacity, due to physical effects (such as density or viscosity changes) and geochemical reactions in the reservoir. In case of a leakage, toxic and ecotoxic effects of impurities contained in the leaking CO₂ stream could also impact the environment surrounding the storage complex.

In order to ensure energy efficiency, proper operation of the whole CCS chain and not to affect its surrounding environment, operators usually limit the concentrations of some impurities, which can, in turn, influence the design of the capture equipment and purification steps. Such limits are case specific and cannot be described in this report; however, some examples of CO₂ stream specifications discussed in the literature are presented in [Annex A](#).

The required purity of the CO₂ stream delivered from the capture plant will to a large degree depend on the impurity levels that can be accepted and managed by the transport, injection and storage operations. The capture plant operators will therefore most probably need to purify the CO₂ stream to comply with the required transport, injection, storage specifications or with legal requirements.

Monitoring of the CO₂ stream composition plays an important role in the management of the entire CCS process. Methods of measuring the composition of the CO₂ stream and in particular the concentrations of impurities are described and other parameters relevant for monitoring at the various steps of the CCS chain are described.

The interplay between the set CO₂ stream specifications and the efficiency of the entire CCS process is also explained. Finally, the mixing of CO₂ streams coming from different sources before transport or storage is addressed, and the main benefits, risks and operational constraints are presented.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

3.1

CO₂ stream

stream consisting overwhelmingly of carbon dioxide

Note 1 to entry: The CO₂ stream typically includes impurities and may include substances added to the stream to improve performance of CCS and/or to enable CO₂ detection.

[SOURCE: ISO 27917:2017, 3.2.10]

3.2

CO₂ stream composition

concentration (generally expressed in fraction by volume) of each component of the *CO₂ stream* (3.1)

Note 1 to entry: The CO₂ stream composition is usually subject to regulatory discretion and approval. The CO₂ stream composition can also be reported as a mass concentration (e.g. mg/m³).

3.3

CO₂ purity

percentage by volume of CO₂ as a component of the *CO₂ stream* (3.1)

3.4

impurities

non-CO₂ substances present in the *CO₂ stream* (3.1) as captured or derived from source materials or the capture process, or present as a result of mixing for transportation, or added, released, or formed in conjunction with sub-surface storage and/or leakage of CO₂

Note 1 to entry: As a subset of impurities, contaminants are non-CO₂ substances whose presence in the CO₂ stream is generally unwanted.

Note 2 to entry: As a subset of impurities, additives are substances added to the stream for the purposes of managing its physical or chemical behaviour (e.g., hydrate and corrosion inhibitors), for or from interaction with equipment (e.g., lubricants), or to track its distribution in the subsurface after injection (geochemical tracers).

[SOURCE: ISO 27917:2017, 3.2.18]

3.5

non-condensable substances

chemical substances that are partially in the vapour state at pipeline operating conditions.

Note 1 to entry: O₂, N₂, Ar, H₂ and CH₄ belong to this category

[SOURCE: ISO 27913:2016, 3.18]

4 Symbols and abbreviated terms

In this report volume fractions are expressed as % (10⁻²) or ppm (10⁻⁶), in order to be in line with the original publications and the usual technical exchanges within the CCS community.

Ar	Argon
As	Arsenic
BOS	Basic Oxygen Steelmaking
°C	Degree Celsius
CCS	Carbon Dioxide Capture and Storage
Cd	Cadmium
CH ₄	Methane
CO	Carbon monoxide
CO ₂	Carbon dioxide
COS	Carbonyl sulfide
EOR	Enhanced Oil Recovery

EPA	Environmental Protection Agency
etc.	Et Cetera (Latin: And So Forth)
EU	European Union
GD	Guidance Document
GHG	Greenhouse Gas(es)
H ₂	Hydrogen
Hg	Mercury
H ₂ O	Water
H ₂ S	Hydrogen sulfide
H ₂ SO ₄	Sulfuric acid
i.e.	Id est (Latin: that is)
IEA	International Energy Agency
IEAGHG	International Energy Agency Greenhouse Gases R&D programme
IGCC	Integrated gasification combined cycle
IPCC	Intergovernmental Panel on Climate Change
K	Potassium
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
Mn	Manganese
mg	Milligram
MPa	Mega Pascal
N ₂	Nitrogen
NETL	National Energy Technology Laboratory
NH ₃	Ammonia
Ni	Nickel
Nm ³	Normal cubic meter-being a cubic meter at 101,325 kPa absolute and 273 K
NO	Nitrogen monoxide
NO ₂	Nitrogen dioxide
NO _x	Nitrogen oxides
O ₂	Oxygen
OPS	Office of Pipeline Safety

Pb	Lead
PM	Particulate Matter
ppm (= ppmv)	Parts per million (= Parts per million by volume) = 10^{-6}
Psia	Pounds per square inch absolute
Se	Selenium
SO ₂	Sulfur dioxide
SO _x	Sulfur oxides
SOP	Standard operating procedures
SRB	Sulphate Reducing Bacteria
TMEs	Trace Metal Elements
TOEs	Trace Organic Elements

5 Overview of chemical composition of CO₂ streams

5.1 Overview

In this clause available data on impurities present in CO₂ streams and the concentration ranges are described for different CO₂ sources and capture technologies. In situ measurements are emphasized.

5.1.1 Types of impurities

A number of gases could be present as impurities in the flue gas or process gas (before capture), and therefore are potentially present at the exit of the capture process. Their concentrations vary greatly from one capture technology (or process) to another, due to the various reaction pathways and to the various design options for capture and purification.

Some gases (also called “non-condensable substances”) such as Ar, O₂, and N₂ can reach several percent of the CO₂ stream at the immediate exit from the capture process, before purification and compression (IEAGHG, 2011)^[40]. The content of H₂O (condensable) can also reach several percent there. Other gases (NO_x, SO_x, H₂S, CO, and others), although present at lower concentrations, could still influence CO₂ stream behaviour.

Impurities other than gases have been reported in low concentration, (IEA-GHG, 2011)^[40], and in the case of a post-combustion capture process, solvents used in the process (e.g. amines or NH₃) and their degradation products could be present in the captured CO₂ stream. Further impurities could include particulate matter, trace metal elements (TMEs) and trace organic elements (TOEs), depending on the fuel or feedstock used. Intrinsic toxicity levels of TMEs and TOEs is often high, but concentration levels are usually very low.

When comparing data from different sites, an important difference between an industrial site and a capture pilot plant is that the latter might not include a drying-compression phase before transport. Therefore, differences in impurity concentrations could occur. When CO₂ is compressed, gases tend to dissolve in condensed water at each compression stage and are therefore removed from the CO₂ stream before transport. See also standard ISO 27913:2016^[48] on pipeline transportation systems.

5.1.2 Measurements and estimates

It is necessary to distinguish i) data that are estimates resulting from modelling from ii) measurements on the captured CO₂ stream. Published data, both measured and modelled, typically emphasize

concentrations of main impurities. Here, we focus on measurements and quote modelling estimates only where measurements are not available. However, modelling studies are also of value, because process models enable, among other things, the representation of various combinations of impurity concentrations. Other models allow predicting possible effects in other parts of the CCS chain, as will be illustrated in [Clause 6](#), e.g. for fluid density or chemical reactions.

5.1.3 Data sources

CO₂ stream composition data was compiled from existing literature by the expert group appointed by ISO/TC 265 from “WG5-Cross-cutting issues”, based on existing review reports (e.g., from international organisations or research consortia) and on results from pilot, demonstration, or commercial projects in Europe, North America, Australia, and Japan.

Note Examples of regulatory requirements, in relation with these projects, are given in Annex B.

The bulk of this document's data compilation was drawn from several review publications and reports:

- a) Anheden, et al. (2004)^[7]: summarises impurities by capture process (before condensation or purification steps),
- b) IEAGHG (2004, 2011)^{[39][40]} review reports,
- c) Farret, et al., 2012^[32]: review report of the French ClubCO₂,
- d) Porter, et al., 2015^[81]: complete review of concentrations of impurities in power plants and in the industry.

The present document draws heavily upon the above publications because they contain a significant amount of data and because they generally identify the origins of these data. Of course, other publications are also considered, as well as other ISO works, such as Table A.1 from ISO/TC 265 standard 27913:2016^[48] on pipeline transportation systems (see [Annex B](#)). References to publications lacking data source are avoided. For pre-combustion IGCC processes and for trace metals, many data encountered are unsourced.

Capture and purification processes are evolving and generally purity levels have increased. Several regulatory regimes require the CO₂ stream to consist “overwhelmingly” of CO₂. This is often approximated as a purity of at least 95 % (cf. ISO 27913:2016 on pipeline transportation systems).

Data on CO₂ stream composition are not readily at hand. The literature is not rich and is especially sparse on results from recent plants or pilot plants. Therefore, Technical Committee ISO/TC 265 addressed a data call to its member countries and to operators. Some technology suppliers could not answer the questionnaire for proprietary reasons. Original data from five capture pilots and demonstrators on power plants and one on a hydrogen production plant were collected, most of them are compared below to existing literature.

5.2 Ranges of impurity concentrations for coal fired power plants

5.2.1 Gaseous components

The composition of the CO₂ stream and thus the concentrations of the impurities varies from one capture technology to another. The flue gas from oxy-combustion is enriched in CO₂, SO_x and other minor components as a result of elimination of nitrogen from the air, and such products are then removed or captured downstream in the CO₂ purification unit. Oxy-combustion contributes to significant amounts of nitrogen, argon, and oxygen as well as oxidizing forms of sulfur and nitrogen (i.e. NO_x, SO_x) in the CO₂ stream. Post-combustion capture technologies usually produce CO₂ streams of high purity also containing oxidizing impurities such as O₂, SO_x, and NO_x. In contrast, pre-combustion capture results in impurities with reducing properties such as H₂, H₂S, or CO. However, even within a single capture technology the variability of impurity concentrations is high (up to two or three orders of magnitude; [Figure 1](#)), depending on the process itself and on the final purification steps (e.g., desulfurization equipment). Porter, et al. (2015)^[81] present a summary of ranges for impurities from

commonly considered CO₂ capture technologies for coal fired power plants. This publication references most of the previous publications, including individual results from specific plants. In [Table 1](#) below, only data referring to the final CO₂ stream (after pre-compression and purification in the case of oxy-combustion) are reported, for common capture technologies.

Note Here, post-combustion capture technologies refer essentially to chemical absorption technologies based on amine solvent. Other post-combustion technologies exist such as membrane-based CO₂ separation process. The description of capture technologies is out of scope of this document. For more detailed information see ISO/TR 27912 (2015) Carbon dioxide capture systems, technologies, equipment and processes for power and industry^[52].

**Table 1 — Ranges from common CO₂ capture technologies for coal fired power plants
(data from Porter, et al. 2015^[81])**

Impurities (ppm, unless specified differently)	Oxy-combustion with purification				Precombustion		Postcombustion	
	Double flashing		Distillation		min	max	Min	max
	Min	max	min	max				
Ar % vol	0,4	0,61	Trace	0,1	0,000 1	0,15	0,001 1	0,021
As					0,006 65	0,006 65	0,08	0,08
Benzene					0,014	0,014	0,019	0,019
CH ₃ OH					20	200		
CH ₄					0	112		
Cl					17,5	17,5	0,56	0,56
CO			10	50	0	2 000	1,2	10
H ₂					20	30 000		
H ₂ O	0	0	0	100	0,1	600	100	640
H ₂ S/COS					0,2	34 000		
Hg					0,000 584	0,000 584	0,024 9	0,024 9
N ₂ % vol	1,6	2,03	0,01	0,2	0,019 5	1	0,045	0,29
Naphthalene					0,000 8	0,000 8	0,001 2	0,001 2
NH ₃					38	38		
Ni					0,009	0,009	0,002	0,002
NO					400	400		
NO _x	0	150	5	100	400	400	20 (1,5 NO ₂)	38,8
O ₂ % vol	1,05	1,2	0,001	0,4	0	0	0,003 5	0,015
Pb					0,004 5	0,004 5	0,001	0,001
Se					0,013 5	0,013 5	0,31	0,31
SO ₂	0	4 500	0,1	50	25	25	1	67,1

NOTE "0" values are reported as such in Porter, et al. (2015); empty box indicates no available data as stated in Porter, et al. (2015).

For oxy-combustion, Porter, et al. (2015)^[81] integrated many references from previous industrial and research projects, including measurements from the industrial capture pilot at Schwarze Pumpe (Anheden, et al., 2011^[7]; White, et al., 2013^[111]). For oxy-combustion, Porter, et al.^[81] also considered raw/dehumidified CO₂ (those data are not reported in [Figure 1](#)). For oxy-combustion a pre-compression stage (15 bar to 30 bar) is usually performed before or during purification.

Further, Porter, et al.^[81] compiled detailed data on CO₂ stream composition at different steps of the capture process for the oxy-combustion pilot plant at Schwarze Pumpe: Before purification, CO₂ purity is 87 % and O₂ content is 4 %, whereas after purification by rectification CO₂ purity is 99,9 % and O₂ content is <0,001 %; SO_x concentrations decreased from <30 ppm before purification to <1 ppm after. Similarly, NO_x concentration is <350 ppm before purification and <10 ppm after purification.

Figure 1 shows the ranges of impurity concentrations for oxy-combustion that are given in Table 3 of Porter, et al. (2015)[81] after purification by double-flashing or distillation phase separation. They are compared to recent values collected by ISO/TC 265 in 2017 on the Callide demonstrator plant.

Note Also considering Spero, C. Callide Oxyfuel Project — Final Results. Global CCS Institute, April 2018. <http://decarboni.se/sites/default/files/publications/202090/cop-finalresults-publicreport-march2018.pdf>

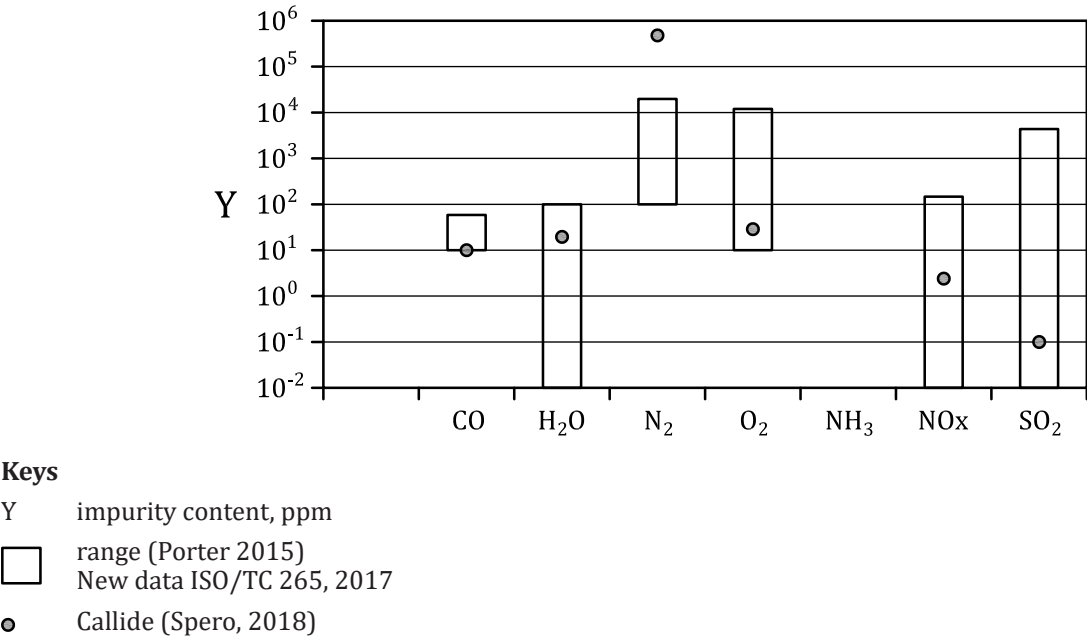
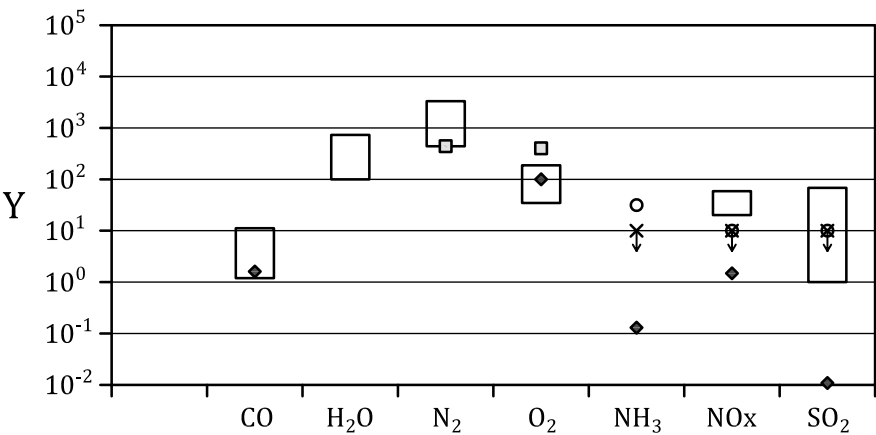


Figure 1 — Streams from oxy-combustion technology from Porter, et al., 2015[81] (bars) and recent values collected within ISO/TC 265 (symbols)

NOTE As concerns the Callide demonstrator plant, data for CO, NO₂ and SO₂ represent maximum values since measurements are below the detection limits for that specific project[15].

For post-combustion capture, Figure 2 below compares the concentration ranges according to Table 6 in Porter, et al. (2015)[81] to values recently collected within ISO/TC 265.



Keys

- Y impurity content, ppm
- range (Porter 2015)
- New data ISO/TC 265, 2017
- SECARB
- Germany
- CSIRO Loy Yang
- CSIRO Tarong

Figure 2 — Impurity concentrations for CO₂ streams from post-combustion capture from Porter, et al., 2015^[81] (bars) and recent values collected within ISO/TC 265 (symbols)

NOTE Arrows on the [Figure 2](#) represent measurements that are below the detection limits for that specific project.

These data show high variability of impurity concentrations, depending on the capture technology as well as site-specific process configurations. This variability is further discussed in [5.4.1](#).

5.2.2 Trace elements

Metallic elements in the CO₂ stream originate in the feedstock or fuel (e.g., coal). Their concentration is very low, hence they also called trace metallic elements or TMEs. IEAGHG (2011)^[40] states that mercury (Hg) can be expected to be present with pre- and post-combustion processes. Apps (2007)^[9] states that only Hg and Se are expected in high concentrations in gas phase, according to modelling results. Main values for metal concentrations are presented in [Table 2](#) below.

For mercury, only estimated values were found in the literature (IEAGHG, 2004^[39]; EC, 2011^[27]; Apps, 2007^[9]; Shah, et al., 2010^[99]). The values are very low (sometimes below the detection limits) and show high variability (see examples in [Figure 3](#) below). Given the toxicity of mercury, it is suggested that operators consider these reported concentrations with care and confirm by insitu measurements. Mercury removal from the CO₂ stream is likely during the downstream compression/drying stages, but uncertainties remain as it might be present both in the gas phase (because it is highly volatile) and in the particulate phase, adsorbed on aerosols (EC, 2011^[27]).

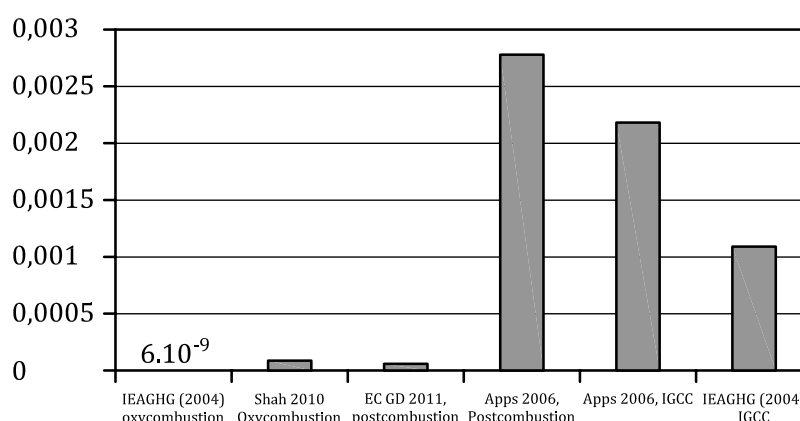


Figure 3 — Hg concentrations (ppm) in the CO₂ streams captured from coal power plants by different capture technologies estimated values, from Farret, et al. (2012)^[33]

In contrast to metals, organics generally present no direct relationship between the elemental composition of the starting material and the subsequent concentration of organics in the CO₂ stream. The concentration of organics is usually very low and depends strongly on reaction conditions during industrial processes (CO₂ generation and capture) including gaseous species, temperature, pressure, and residence time. Examples for benzene and naphthalene concentrations are given in [Table 2](#) below.

Table 2 — CO₂ impurities (trace elements) from pulverized coal with post-combustion (from Porter, et al., 2015^[81])

	MEA postcombustion plant Source EC 2011 ^[27] (estimated data)	Average values of relevant sources, including Anheden, et al., 2004 ^[2] , Apps, 2007 ^[9] , Oosterkamp & Ramsen, 2008 ^[8] , Farret, et al. 2012 ^[33]
CO ₂ % v/v	99,7	—
Hg ppm	0,000 69	0,002 8
As ppm	0,005 5	0,002 2
Se ppm	0,017	0,012 2
Mn ppm		0,03
Ni ppm		0,002
Pb ppm		0,001 1
Benzene ppm		0,019
Naphthalene ppm		0,001 2

5.2.3 Particulate matter

Particulate matter in solid or liquid form is a matter of concern in common industrial applications not specific to CCS, e.g. turbo machinery or jet engines. Particles in gas streams could considerably increase wear, e.g. in pipes or turbo machinery used for compression of gas streams for or during transport (booster stations), especially if high pressures and high fluid velocities are achieved. Particulate matter in the form of dust/particles or droplets can be present in captured CO₂ streams. For example, particulate matter might result from combustion processes or capture processes that are based on chemical looping. Post combustion capture applying amine solutions could introduce droplets into gas streams. Further downstream, corrosion products could potentially be transported within the CO₂ stream.

Note Chemical looping consists of using a metal oxide as a bed material providing the oxygen for combustion.

5.3 Ranges of impurity concentrations from industrial emitters

Various industrial facilities emit considerable amounts of CO₂. In principle two different cases can be distinguished:

- 1) Energy-intensive industries, i.e. facilities requiring heat and/or other forms of energy for processing of their materials, such as pulp and paper mills, or recycling glass fabrication. For these facilities, application of post combustion or oxy-combustion capture technologies is comparable to their application to power plants and the final CO₂ stream composition depends on the fuel, the capture and cleaning processes.
- 2) Industry with process-related emissions, i.e. facilities processing raw materials, that emit CO₂ streams of variable compositions, e.g., H₂ production, cement and lime kilns, integrated iron and steel works, and bio-gas works.

For both cases, various options for CO₂ capture exist that can be retrofitted or integrated into production processes. Some raw materials contain carbon and other elements that are released during the processing leading to a further diversification of the resulting CO₂ streams. The application of CCS in industry sectors could represent half of the emissions reductions achieved through CCS by 2050 as mentioned in IEA (2013)^[38] and GCCSI (2016)^[36].

As compared to power plants described in 4.2, fewer data are available on CO₂ stream compositions from industrial facilities. One reason is that only very recently have the first pilot plants been set up for capturing CO₂ from industrial facilities that do not remove CO₂ from the product stream as part of their overall production process.

5.3.1 Cement industry

The cement industry is globally one of the major CO₂ emitting industries. Cement production takes place on all inhabited continents in large scale plants. Cement production consists of two major steps:

- 1) calcination, traditionally in shaft furnaces, nowadays mostly in multi-stage cyclone preheaters followed by pre-calciners (e.g., CEMCAP, 2017^[18]);
- 2) clinker burning, mostly in long rotary kilns (ZEP, 2015^[114]).

The calcination process yields about 60 % of the plant's total CO₂ emissions, and energy production accounts for the remainder. The clinker burning process is typically fuelled by coal and/or refuse-derived products (animal meal, sewage sludge, etc.).

CO₂ capture strategies on a cement plant include capturing the nearly pure CO₂ stream from the calcination process, using oxy-combustion in the rotary kiln, and applying post-combustion capture processes to the mixed gas streams from the calcination process and rotary kiln. Another envisaged option is calcium looping, in which the plant's first semi-product, the burnt lime, is used as an absorbent.

CO₂ concentration in cement plant flue gas is about 15 %-30 % (e.g., CEMCAP, 2017^[18]), which is higher than in flue gases from fossil fuel power plants. The CO₂ stream composition after capture depends on where and how the CO₂ is captured as well as on the type of fuel burnt and its composition.

The cement industry is presently testing CO₂ capture in pilot plants in several countries including Norway, Belgium, the U.S., and China (e.g. LEILAC, 2016^[60], Jordal, et al., 2017^[56]). So far, measured composition data on CO₂ streams captured from these pilot plants have not been published. For reference, estimated/modelled values for CO₂ stream composition from post-combustion capture (amine scrubbing) at a cement plant are given in [Table 3](#).

Table 3 — Modelled stream composition — Cement plant
(EC, 2011^[27], quoted by Porter, et al., 2015^[81])

Substance	N ₂	H ₂ O	O ₂	Ar	CO	NO ₂	SO ₂	Se	As	Hg
Content (ppm)	893	640	35	11	1,2	0,86	<0,1	0,008 8	0,002 9	0,000 7

5.3.2 Iron and Steel industry

Pre- and post-combustion options exist for capturing CO₂ from the Blast Furnace Gas (BFG) from the iron and steel industry. There are a couple of methods as pre-combustion processing of BFG. One is chemical absorption process or physical adsorption process without extra compression. Another is pre-combustion processing of the BFG involving filtration, compression, saturation, shifting, cooling, and CO₂ separation. The resultant CO₂ stream will be similar in composition to that obtained from pre-combustion capture in coal-fired power plants (Integrated coal Gasification Combined Cycle-IGCC), e.g. the Nuon Power Station at Buggenum (Netherlands; e.g. EPRI, 2007^[30]).

In post-combustion capture from BFG the fuel is burned in a steam-raising boiler and the CO₂ is captured by amine or ammonia scrubbing or a similar process. For post-combustion capture processes, experience at power plants equipped with similar post-combustion capture facilities can provide information on resultant CO₂ stream composition.

While blast furnaces produce iron, steelmaking requires decreasing the carbon content of pig iron. The process most often used is called Basic Oxygen Steelmaking (BOS) and it liberates a CO and CO₂-rich gas called BOS gas. Flue gas of BOS gas combustion is also a candidate for CO₂ capture. A new project, 3D, funded by H2020, started in May 2019 in Dunkirk in France to demonstrate the capture technology developed by IFPE and called DMX. The main purpose is to capture CO₂ from Blast furnace flue gas.

5.3.3 H₂ production

The CO₂ stream captured at H₂ production plants based on steam methane reforming is usually of high purity (typically >99 vol % CO₂). The process of steam methane reforming is similar to the processes in pre-combustion plants; however usually the feedstock for H₂ production is natural gas instead of coal. The natural gas is typically pre-processed to remove the majority of H₂S, N₂, and CO₂ to comply with gas transportation standards and contracts. Some traces of H₂, CO, and CH₄ can remain after cryogenic physical separation process for H₂ production (as in the Cryocap project in Le Havre, France). For absorption-based process, traces of methanol and amines can be also present in the captured CO₂ stream depending on the solvents used. As an example, Table 4 shows estimated values for the CO₂ stream composition of the CCS demonstration project in Tomakomai, Japan. The CO₂ source is pressure swing adsorption (PSA) off-gas from an H₂ production unit of a petroleum refining plant, and CO₂ capture is performed by amine scrubbing.

Table 4 — Production plant, estimated value (Tomakomai, Japan)

Substance	H ₂	CH ₄	CO	N ₂	O ₂	CO ₂
Content (% v/v)	0,22	0,06	0,02	Nil	Nil	99,7

5.4 Discussion and interpretation

5.4.1 Variability among processes and industries

The reported impurity concentrations are highly variable because the impurities in the CO₂ stream are affected by many factors including the fuel and raw materials, the mode of operation of the emitter, the capture technology applied, and the purification steps.

The types of processes for CO₂ generation and CO₂ capture influence the impurity concentrations in the captured CO₂ stream, as shown above for power plants. In addition, final purification is used to manage stream composition, through desulfurization, ash/particle removal, reduction of NO_x applied to the flue

gas, stripping and/or dehydration. During compression the stream composition is sometimes further modified. However, post-capture purification steps have additional cost and demand energy; therefore, an operator might be able to optimise operations of the CO₂ stream purification in order to produce a stream of acceptable quality at reasonable cost. Operators also could consider site-specific studies for the design and economics of the CCS chain, together with risk and impact studies, in order to adapt and optimise the CO₂ stream composition (see also 8.1).

Overall, the concentrations of impurities in the captured CO₂ stream depend strongly on the intent of the operator and the concomitant design of the capture process and operational mode. The operator's intent is project-specific and related to the designated downstream part of the CCS chain, with i) technical requirements for CO₂ transportation and storage to be met and ii) legal constraints, that are often aiming at ensuring safety and avoiding environmental impacts.

To reduce capture cost, ideas have been developed in the first decade of this millennium to inject and store SO_x and NO_x together with CO₂. Later, in pilot projects, it has been considered necessary to remove SO_x, NO_x and other impurities for technical reasons. Also, the efficiency of capture processes and purification strategies has generally improved with time. For these reasons, newer processes (or capture pilot plants) usually produce CO₂ streams with higher purity. This is illustrated in Farret, et al. (2012)^[32] where results published before and after 2007 are distinguished — especially as concerns SO_x, NO_x, NH₃, H₂S. The present document reflects this tendency as many concentrations obtained in 2017 within ISO/TC 265 are lower than the ranges published earlier.

5.4.2 Compositional stability and potential chemical reactions within CO₂ streams

The initial composition of the CO₂ stream after CO₂ capture might change further downstream due to:

- i) compression and conditioning — i.e. by changing pressure and temperature conditions and thereby modifying solubility limits of the impurities in the CO₂ streams;
- ii) further purification — i.e. by an intended removal of one or more impurities;
- iii) reactions of impurities with each other;
- iv) reactions of impurities with the surroundings, e.g. pipeline walls or underground water.

These processes might also result in the formation of new phases, e.g. by condensation of acids or formation of elemental sulfur, depending on the impurities initially present. Phase equilibria between the CO₂ stream and the newly formed phases could be shifted if these newly formed phases further react with their “containment and/or surroundings” as in the corrosion of components and pipes (see 5.2.1). For example, SO₂ has the potential to deposit elemental sulfur in the presence of NO_x (Dugstad, et al., 2014^[1]). In the presence of H₂O, SO_x, NO_x, and O₂, sulfuric and/or nitric acid could form and condense. The extent of acid formation and condensation as well as the exact composition of the condensates strongly depends on the CO₂ stream composition and temperature (Soheil, et al., 2014^[95]).

If CO₂ streams of different composition are mixed, e.g. in a pipeline network, additional reactions could occur if the CO₂ streams contain impurities of more diverse chemical reactivities (see 8.1).

Predictive modelling would be desirable to predict (geo-)technically relevant reactions, so that CO₂ stream composition could be adapted if necessary. However, corresponding predictive modelling is currently hampered by a lack of data on reaction kinetics valid for the pressure and temperature conditions encountered during transport, injection, and storage. Laboratory experiments and in-situ injection experiments can help to characterize the effects of various impurities in CO₂ streams on the operation and long-term safety of CCS projects.

6 Impacts of impurities

The individual impurities can have (very) different physical and chemical properties. Accordingly, the presence of impurities in the CO₂ stream can have a range of physical, chemical, microbiological, and toxic effects, as reviewed in the following section. These effects depend on the range of impurities

present and on the impurity concentrations. As different impurities might interact, properties and impacts of individual impurities are considered not only individually but also collectively.

6.1 Physical impacts

6.1.1 Overview

Impurities can affect the thermodynamic and transport properties (collectively denoted thermophysical properties) of the CO₂ stream. By reducing the overall efficiency of the CCS technology, or by increasing the cost of the project, the physical effects of impurities can have major consequences along the CCS chain, so it is useful to assess and forecast these effects. Some of the most affected properties are listed here, together with examples relevant for practical application (Munkejord, et al., 2016^[21]):

- *Phase behaviour*. The gas-liquid equilibrium determines e.g. the highest pressure at which a two-phase state can be found, and liquid-liquid equilibrium is relevant for the system CO₂-water, since the appearance of a water-rich phase severely affects corrosion;
- *Density* is an important parameter in the dimensioning of pipelines, vessels, compressors, and pumps. It is also needed for fiscal metering, if the meters provide volume flows. In the storage reservoir an increase in the density of the injectate allows a given formation to contain a greater mass of the injectate than would otherwise be the case;
- *Speed of sound* determines the flow rate in choked flow. It is an important parameter in the dimensioning of pipelines against running ductile fracture;
- *Viscosity* is needed in calculating pressure drop in pipes, in designing processing equipment, and in subsurface reservoir flow modelling;
- *Thermal conductivity* and *heat capacity* are needed for heat-transfer calculations and heat-exchanger design.

The above properties depend to a greater or lesser extent on CO₂ stream composition. Implications for transportation and storage are described in [6.1.2](#) and [6.1.3](#), respectively.

A potential impact relates to particulate matter if present as outlined in [5.2.3](#) such as compressor fouling that might occur with particulate sizes <1 µm. Greater particle size is only tolerable in a compressor if these particles are hard and relatively dry, so that they will not agglomerate on the compressor rotor surfaces.

Various filters are used to remove particles. Particle sizes and the target particle concentrations determine filter efficiency: the smaller the particles and the lower the target concentrations, the higher the pressure drop, filter size, energy demand, and cost of particle filters. In challenging cases, progressively fine filters are usually combined in series. Porous filter materials become particle-loaded with time, requiring replacement or reactivation. Porous rocks in the subsurface also function as filters. Fluid velocities decrease radially around injection wells as particles settle out of the CO₂ stream when they slow down. Some particles such as alkaline earth oxides stick on wet grain surfaces of aquifers. They can coagulate/agglomerate as a result of reactions with brine and water to hydroxides or bicarbonates. These deposits can reduce the reservoir's permeability and injectivity. Therefore, particles are usually removed from CO₂ streams at surface installation. Filter maintenance is easier than subsurface reservoir remediation. The effect of particulate matter is not described further in this report, but [6.2.1.2](#) and [6.2.2.1](#) discuss the impact of corrosion upon injection wells, which can result in the injection of particulates into the reservoir

6.1.2 Effect on transportation (pipeline and ship transportation)

The impurities present in CO₂ streams are important for the design of CO₂ pipeline and ship transportation, as they affect, e.g. operating pressure, temperature, fluid density, safety considerations, fracture control, and cloud dispersion in the event of a release (IEAGHG, 2016^[42]). ISO 27913^[48] addresses, amongst other matters, the effect of impurities on transportation by pipeline of CO₂ streams.

In the following text and in [Table 5](#), we summarize issues concerning density, viscosity, phase behaviour, and phase equilibria."

Table 5 — Summary of physical impacts on transportation

Species/ substances	Characteristics of the species	Effect on CO ₂ stream	Potential effect/impact	Reference
Impurities in general		Globally decrease the density of the CO ₂ stream	For an equal volume flow, the quantity of CO ₂ transported will be lower, hence decreasing the efficiency of the transportation chain	Munkejord, et al., 2016 ^[71]
O ₂ , N ₂ , Ar, H ₂ ...		Higher maximum two-phase pressure	Larger propensity to ductile fracture Major leak with a widely open fracture	Munkejord, et al., 2016 ^[8071] , IEAGHG, 2011 ^[40] , Cosham, et al., 2014 ^[21] , Nordhagen, et al. 2017 ^[76]
	Non-condensable	Reduce density, increase volume, change shape of phase envelope	Increase in highest pressure of two-phase gas-liquid state	IEAGHG, 2011 ^[4640] , Mohitpour, et al., 2012 ^[69] , Porter, et al., 2015 ^[81] , Munkejord, et al., 2016 ^[71] , IEAGHG, 2016 ^[42]
H ₂ S and NOx		Deposition of elemental sulfur	Interruption to flow	Dugstad, et al. 2014 ^[2]
H ₂ O	Hydration	Hydrates formation	Interruption to flow	IEAGHG, 2016 ^[42]

6.1.2.1 Density and viscosity

The presence of impurities can influence the density and viscosity of the CO₂ stream. For pipeline transport, a high density is advantageous, since in this case mass flow rates can be higher, and pipe diameters smaller. In turn, the presence of non-condensable impurities such as Ar, N₂, or O₂ in high concentrations (e.g. from oxy-combustion) could lead to an increase in pipeline diameters for dense phase CO₂ transport, which would raise the capital cost (IEAGHG, 2016^[42]). For H₂, the effect of its low molecular weight is also significant in reducing stream density and/or requiring larger pipeline diameters (IEAGHG, 2011^[40]). A lower viscosity, as e.g. induced by Ar and/or N₂, will facilitate pipeline transport (IEAGHG, 2011^[40], Porter, et al., 2015^[81]), because the pressure drop along the pipeline decreases and less compression energy is needed. However, for fully turbulent flow, the sensitivity of pressure drop to viscosity is low.

6.1.2.2 Phase behaviour and phase equilibria

Impurities also affect CO₂ phase behaviour (Span, et al., 2013^[90], Løvseth, et al., 2016^[100]). As discussed in the review by Munkejord, et al., (2016)^[71] data are currently lacking for several relevant binary systems.

The coexistence of two fluid phases (liquid and gas) in pumps and compressors can cause hydrodynamic effects resulting in malfunction or damage of such equipment. The operation of pipes in a two-phase state requires special care. For pure CO₂, two phases can coexist in thermodynamic equilibrium along the phase boundary line in the pressure-temperature space, between the triple and the critical point. Additional components (such as impurities in the CO₂ stream) add an additional degree of freedom to the thermodynamic system and the phase boundary line widens up into a two-phase space. Thus, most impurities will increase the highest temperature and the highest pressure below which a two-phase gas-liquid state can exist. Therefore, a higher operating pressure is necessary to maintain the flow in

a single dense phase, as compared to pure CO₂, and more compression energy is also needed (Ceroni, 2014^[19]).

Note For short transport distances, two-phase conditions can also be avoided by keeping the temperature of the CO₂ stream sufficiently high, and pipes thermally insulated.

A higher maximum two-phase pressure, caused by H₂ for instance (IEAGHG, 2016^[42]), increases the risk of a ductile fracture of a pipeline. This kind of fracture can open widely causing a major leak. Use of higher-strength (e.g. thicker) pipeline can reduce this risk (Cosham, et al., 2014^[21], Nordhagen, et al., 2017^[76]).

The presence of water as a separate phase can lead to hydrate formation depending on pressure and temperature, which can cause blockages leading to dramatic flow interruptions. The inclusion of chemical inhibitors such as glycol can decrease or prevent formation of a separate water phase. (IEAGHG, 2016^[42]). However, the presence of glycol sometimes increases corrosion. The present report does not address the possible influence of impurities on hydrate formation.

H₂S and SO₂ cause negligible reduction of the solubility of water in the CO₂ stream.

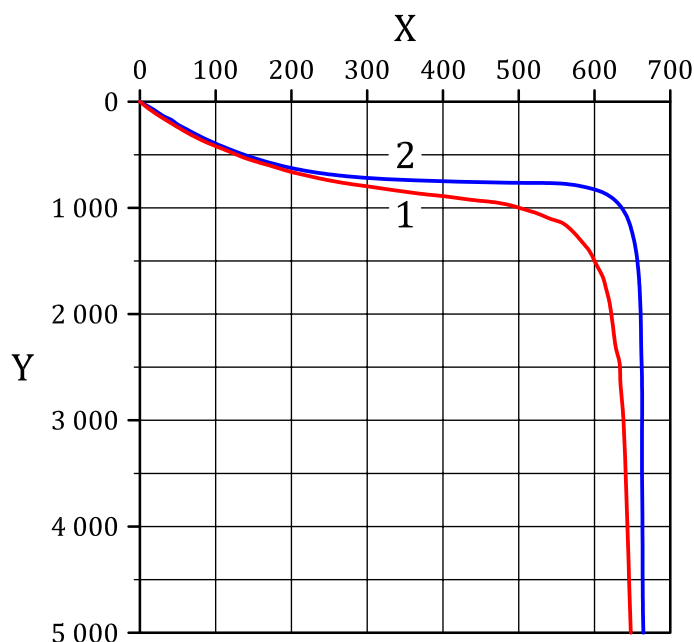
Ship transport of CO₂ is considered to be economically viable for relatively long transport distances or small volumes (e.g. Barrio, et al., 2005^[16]; Munkejord, et al., 2016^[71]). In addition, the flexibility of ships could have an advantage in early CCS deployment. Ship transport is currently considered at low (6 bar–8 bar), medium (15 bar) and high pressure (45 bar–60 bar) (Norwegian Ministry of Petroleum and Energy, 2016^[77]). From a pure ship transport point of view, low pressure (with a corresponding low temperature) is considered optimal due to the high liquid density and low gas density (Aspelund, et al., 2006^[10]). Very few studies have included the impact of CO₂ stream composition on ship transport. Engel and Kather (2018)^[29] considered the liquefaction of a pipeline CO₂ stream. They found that an increased impurity concentration lead to an increased energy demand of the liquefaction process, and to a shift from electrical to thermal energy demand for the injection. Further open technical questions related to ship transport include (a) optimal integration of the liquefaction process with the capture process, (b) the possible formation of solid CO₂ at low pressures, and (c) the implications on loading/unloading and other operational procedures.

6.1.3 Effect on geological storage

6.1.3.1 Density and buoyancy

IEAGHG (2011)^[40] have conducted a study on the effect of impurities on CO₂ stream density and storage capacity. One important finding is the existence of a minimum or a maximum storage capacity depending on the CO₂ stream composition. As already explained, the presence of non-condensable impurities results in a density lower than that of pure CO₂, leading to decreased CO₂ storage capacity and increased buoyancy in saline aquifers (Wang, 2015^[109]). The non-condensable impurities generally reduce the density of the CO₂ phase under storage conditions (Yan, et al., 2009^[113]). An example is shown in [Figure 4](#).

In contrast, inclusion of the condensable SO₂ in CO₂ streams results in a higher density than pure CO₂. However, the high solubility of SO₂ in water may generate integrity concerns in the near wellbore region (i.e. corrosion of cement and/or casing, see also [6.2](#)).



Keys

- X density [kg/m³]
Y depth [m]
1 subsurface
2 compared to pure CO₂

NOTE 1 The molar fractions of CO₂, O₂, Ar, and N₂ in (1) are 0,972 3; 0,015 9; 0,007 4 and 0,000 8, respectively.

Figure 4 — Calculated density of an assumed CO₂ stream from oxy-combustion as a function of depth for typical hydrostatic pressure and temperature gradients in the subsurface (1) compared to pure CO₂ (2)[Modified from May, et al. (2009)^[67]

The non-condensable impurities such as Ar, N₂, O₂, and H₂ generally reduce the density of CO₂ under storage conditions (Yan, et al., 2009^[113]), in special cases up to 50 % (between 800 m and 900 m depth), for low purification levels. This results in a reduction of the storage capacity, that can be greater than the molar volume fraction of the impurities. Effects of impurities in the CO₂ plume can be visualised by using “normalised storage capacities”, i.e. expressing storage capacities as a ratio between storage capacities of a pure and a mixed CO₂ stream.

Lighter elements contained in the CO₂ stream will increase its buoyancy (i.e. the density difference between the CO₂ plume and the formation water) in comparison to a pure CO₂ plume. Inferences about impacts of impurities on buoyancy and storage capacity in aquifers result from numerical simulations that calculate the effects of the CO₂ phase density on the horizontal and vertical migration of a CO₂ plume.

In depleted natural gas reservoirs, mixing of the injected CO₂ stream with residual gas will produce a CO₂-natural gas mixture with lower density and CO₂ concentration than pure CO₂, reducing CO₂ storage capacity (Schöneich, et al., 2007^[96]). The degree of mixing depends on the migration and expansion of the injected CO₂ stream in heterogeneous reservoirs (Rebscher and Oldenburg, 2004)^[84].

Overall, the discussion above about the behaviour of a CO₂ plume is mainly valid for a homogeneous porous medium (see Table 6 for the summary of physical impacts). The subsurface is not homogeneous and discontinuities strongly affect the migration of fluids (as was shown with CO₂ injection in the Utsira formation at Sleipner by Chadwick, et al., 2008)^[20]. While the density and buoyancy could be affected in a range of up to 50 % (IEAGHG, 2011)^[40], permeability in reservoir rocks usually varies over orders of magnitudes and thus, heterogeneities are likely of much greater importance in controlling the fluid migration and trapping than the effects of impurities on fluid properties.

Table 6 — Summary of physical impacts on geological storage (part 1, density and buoyancy)

Impurity	Characteristics of the impurities	Effect on CO ₂ stream	Potential effect/ impact	Recommended measure/ comment	Reference
O ₂ , N ₂ , Ar, H ₂	Non-condensable light*	Lower density	Decrease CO ₂ storage capacity, increase buoyancy in saline aquifers		Wang, 2015 ^[109] IEAGHG, 2016 ^[42]
SO ₂ , SO ₃ , NO _x	Condensable, heavy*	Increase density	Increase CO ₂ storage capacity	Usual range of this impurity is too low to affect	Talman 2015 ^[101]
Residual gas in depleted gas reservoir	CH ₄ , H ₂ S, N ₂ , CO ₂ ...	Decrease density	Change storage capacity	Significantly change CO ₂ stream composition due to high partial pressure of residual gas	Schöneich, et al., 2007 ^[96]
* Light, heavy: Molecular weight lower or higher than that of CO ₂ .					

6.1.3.2 Interfacial tension and viscosity

Non-condensable impurities such as N₂, O₂, Ar, and CH₄ will increase the plume/brine interfacial tension (IFT). Higher IFT increases the capillary pressure and improves the trapping of CO₂ bubbles by imbibing formation water.

In the presence of SO₂ the interfacial tension decreases linearly with increasing SO₂ concentration (Saraji, et al., 2014^[95]). Similar effects on the interfacial tension of CO₂/brine in the presence of another acid gas, i.e. H₂S, are reported (Shah, et al., 2008^[99]).

Literature is very scarce on the impacts of impurities on viscosity. IEAGHG (2011)^[40] note that the viscosity of dense-phase CO₂ can be lowered at pore scale by some impurities such as N₂, O₂, and Ar, affecting the migration of the CO₂ stream in the reservoir. Depending on the reservoir structure (spill point, layering, heterogeneities, etc.), changes of viscosity can lead to an increase or decrease of storage capacity.

Table 7 — Summary of physical impacts on underground storage (part 2, interfacial tension and viscosity)

Impurities	Effect on CO ₂ stream	Potential effect/ impact	Reference
SO ₂ , H ₂ S	Decrease interfacial tension	Affect storage capacity	Saraji, et al., 2014 ^[95] Shah, et al., 2008 ^[99]
N ₂ , O ₂ , Ar, CH ₄	Increase the plume interfacial tension (IFT)	Increase capillary pressure and improve residual trapping	
N ₂ , O ₂ , Ar	Decrease viscosity	Affect migration of CO ₂ plume	IEAGHG 2011 ^[40]

6.1.3.3 Phase equilibria, impurity dissolution and migration

The impact of impurities in CO₂ streams on phase equilibria has been described in 6.1.2.2 and the resulting effects will impact storage also, e.g. impurities raise the possibility of hydrate formation in the case of storage in depleted natural gas reservoirs. Formation of two CO₂-rich phases of different density could occur at storage conditions close to the critical point of CO₂. The relative permeability of these two phases will be lower compared to a homogenous fluid CO₂ phase and it could reduce their mobility. Higher injection pressures may be needed for avoiding two-phase flow within a CO₂ plume in the storage reservoir than anticipated for pure CO₂.

Following CO₂ injection, impurities are initially present in the reservoir as part of the CO₂ stream and will migrate with the CO₂ stream. While migrating, impurities partially dissolve in the formation water. The extent of impurity dissolution at a given location in the reservoir will depend on each impurity's overall solubility, dissolution kinetics, its diffusion behaviour in the CO₂ plume and the formation water and its reactivity after dissolution (e.g. Amshoff, et al. 2018^[4] & 2019^[5]). These parameters are different for each impurity. Further, each impurity's solubility and dissolution kinetics depend, e.g., on prevailing pressure and temperature conditions and on formation water composition. In general, the solubility of SO₂ in saline water is much higher than that of NO_x and O₂. In consequence, in the reservoir NO₂ (and O₂) maybe transported to greater distance from the injection well than SO₂. (IEAGHG, 2011^[40]). Thus, a detailed knowledge which impurity is present in which concentration at a given location in the storage reservoir after a certain injection period allows for a better prediction of geochemical reactions and related geotechnical consequences (see also 6.2.2). It is currently unknown whether the presence of impurities affects solubility trapping of the CO₂ plume phase, due to a lack of experimental data.

6.2 Chemical impacts

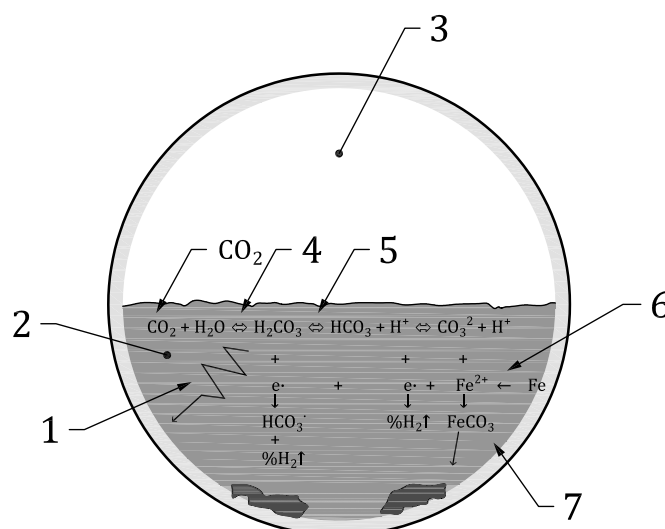
Depending on the chemical properties of each of the impurities, their presence modifies the chemical properties and in particular the reactivity of the CO₂ stream. Further, cross-chemical reactions between different impurities could also occur within the CO₂ stream leading to the formation of new impurities (such as acids) and the reduction of concentrations of other impurities. In the following, chemical impacts of impurities on the corrosion of metallic materials are described (both in surface transport equipment and in injection wells). Further subclauses deal with chemical impacts on geological storage, including interactions with the storage system, the overburden and well cements.

6.2.1 Corrosion of metallic materials

6.2.1.1 Surface transport equipment

Pipelines carrying dense phase pure, dry CO₂ are not affected by corrosion. However, impurities in the CO₂ stream might affect the corrosivity.

H₂O dissolved in the CO₂ stream is not corrosive, but free water can result in the formation of carbonic acid (H₂CO₃), which is highly corrosive (Andersson, 2008^[3]; see Figure 5). Carbon steel can suffer general or pitting corrosion, at a rate of more than 1.0mm/year in wet pure CO₂ (Mohitpour, et al., 2012^[69]). The solubility of water in a pure dense phase CO₂ stream is a function of pressure and temperature as the solubility decreases with decreasing temperature and pressure (De Visser, et al., 2008^[22]). Experimental studies with dense-phase mixtures of CO₂ and water show that the corrosion rate increases with increasing temperature. Although a protective FeCO₃ corrosion product film can form when the concentration of dissolved corrosion products becomes high, the film can fail and permit high localised corrosion rates (Dugstad, 2010^[2]).



Keys

- 1 mass transport
- 2 aqueous phase
- 3 gas
- 4 hydration
- 5 dissociation
- 6 electrochemical reactions
- 7 iron carbonate precipitation

Figure 5 — Carbon steel pipeline corrosion mechanisms (Andersson, 2008)[3]

Other components such as SO_x and NO_x can also dissolve in free water to form corrosive and acid by-products. Also, when impurities like H₂O, SO_x, NO_x, O₂, CO, and H₂S are present together in the CO₂ stream, there are a number of possible cross-chemical reactions that have the potential to form sulfuric/sulfurous acid, nitric acid, and/or elemental sulfur, which form separate phases and thereby provoke corrosion. These aqueous (acidic) phases can form at water contents of less than 100 ppm (see [Annex A](#)). The presence of amines, MeOH, EtOH, glycols, and other water-soluble components will promote the formation of an aqueous phase and reduce the concentration of water in the CO₂ at which a separate aqueous phase is formed.

Due to these interactions between various impurities and potential chemical cross-reactions, the maximum acceptable concentration of any impurity depends on the concentration of the other impurities and will be project specific (see [Annex A](#)). [Table 8](#) summarizes the effects of impurities on corrosion in case of transportation by pipeline.

Table 8 — Summary of chemical impacts — Corrosion of transport pipeline

Impurities	Characteristics of the impurity	Effects on CO ₂ stream	Potential effects/impact	Recommended measure/comment	Reference
SO _x , NO _x , O ₂ , CO and H ₂ S	Possibly react cross-chemically	Form sulfuric/sulfurous acid, nitric acid or elemental sulfur	Acid condensation triggering corrosion	Negligible when water content (or content of other impurities) is low	IEAGHG, 2011[40]
H ₂ O	Solubilization	Form H ₂ CO ₃	Corrosion and formation of protective corrosion product films (FeCO ₃)	Corrosion negligible when water content is low	Dugstad, 2010[2], De Visser, et al., 2008[22]

Table 8 (continued)

Impurities	Characteristics of the impurity	Effects on CO ₂ stream	Potential effects/impact	Recommended measure/comment	Reference
Amines, CH ₄ , Ethane, glycols, etc.	Water soluble	Form an aqueous phase and reduce the H ₂ O concentration	Corrosion	Depend on impurity concentrations	

6.2.1.2 Impact on injection wells

In the reservoir, water will dissolve in the CO₂ phase while CO₂ (and impurities) will partially dissolve into the formation water. Likewise, the impurities present in the CO₂ stream will also dissolve in the formation water.

In particular, corrosion of well equipment (casing, tubing, etc.) could occur if formation water backflow occurs when injection stops. For example, ship transport to the injection site could yield intermittent injection. Also, CO₂ injection wells connected to a large transport network will probably need to cope with a range of CO₂ arrival rates within the limits of the capture plant(s) and surface equipment, therefore causing changes in flow rate or even temporary shut off.

When injection stops, temperature increases at the bottom of the CO₂ column. When the water dissolves in the CO₂ phase and the water-enriched CO₂ phase moves upwards (by convection and diffusion), water can condense further up in the CO₂ column where the temperature is lower, so that an aqueous phase is likely to appear. Where the tubing material is exposed to such environments, pitting corrosion and cracking are likely to occur. The corrosivity of the brine and of the condensed aqueous phase depends on the amount and type of impurities and reaction products that partition to the water phases. Some impurities (SO_x, NO_x) and reaction products (H₂SO₄, HNO₃) strongly prefer the water phase while impurities like O₂ and H₂S are expected to be present in significant amounts in both phases.

6.2.2 Impacts on geological storage system

6.2.2.1 Impacts on reservoir and caprocks

Geochemical reactions of CO₂ streams with formation fluids and rocks can result in the alteration of the rock matrix by changing the abundance, type, shape, and texture of the rock-forming minerals. New minerals can form in the pore space or replace primary minerals. These reactions might be of geomechanical relevance, provided the amounts of reactants and products are sufficient. Injectivity, storage capacity, mechanical strength, and storage safety could be affected by geochemical reactions in a positive or negative way. Whether a reaction is beneficial, insignificant, or problematic for storage depends on its reaction rate and position within a storage complex: Reactions resulting in a gain of porosity could enhance permeability and injectivity of the reservoir if they occur close to wells, while such reactions could be problematic for the integrity of a caprock. On the contrary, reactions increasing the volume fraction of solid phases in the rock can reduce permeability which could be beneficial for storage safety if caprocks are affected. Moreover, such reactions might be considered positive for reservoir rocks if they are slow enough not to markedly reduce injectivity during the operation phase of a storage site but reduce plume mobility in the long term. Particulate matter in the injected CO₂ stream can also create deposits and cause pore plugging and injectivity reduction. For example, particles can coagulate by reactions with brine and water to hydroxides or bicarbonates.

Which geochemical reactions occur in a storage complex depends, among other things, on the site-specific compositions of rocks and formation water. Porous, low saline sandstone aquifers composed overwhelmingly of stable minerals, mainly quartz, are less prone to geomechanically relevant alteration than aquifers containing brines of high salinity or aquifers composed of sandstones where quartz grains are held together e.g. by clay minerals or carbonates. Arkoses or greywackes that contain feldspar or rock fragments (besides quartz grains) may be suitable reservoir rocks, however these grains are also susceptible to geochemical alteration. Reservoirs made up of carbonates or basic volcanic rocks, such as basalt, are sensitive to fast dissolution or alteration reactions, which places greater importance on the

presence of high-quality caprock. On the other hand, these rocks facilitate the conversion of free CO₂ to dissolved inorganic carbon species and solid carbonates, which will reduce the risk of leakage and the volume of the CO₂ plume. Apart from common shale and clay rich caprocks, or less abundant ignimbrites, that contain complex framework and sheet silicates of rather slow reactivity, anhydrite, rock salt, and gypsum are important caprocks that are composed of chloride, sulfate, and carbonate minerals that dissolve (and precipitate) relatively fast. These minerals are also common cement minerals within clastic sedimentary rocks. Especially, rock salt, though an excellent low permeable rock, may become a safety hazard if it is exposed to large volumes of undersaturated formation water.

CO₂ injection will provoke acidification of the formation water after its dissolution in water. Impurities add complexity to the range of possible reactions. For example, the presence of acidic gases such as SO_x (and NO_x) will further acidify the formation water particularly in the two-phase zone (formation water/CO₂ plume) due to their preferential dissolution in the formation water (e.g., Talman (2015)^[101]) and the formation of (strong) acids reactions (e.g. SO₂ → H₂SO₃, H₂SO₄).

The extent of acid formation depends on factors such as pressure, temperature, and the availability of oxidants, such as O₂ to oxidize SO₂ into H₂SO₄. NO_x are known to catalyse the reaction. Consequently, by lowering the pH value of the formation water, SO₂ and other acidic impurities will enhance dissolution of minerals there. Following any movement of the formation water, dissolved species will migrate. When the dissolved species reach the saturation limit, minerals could begin to precipitate. However, precipitation of minerals can be very slow and kinetically hindered. Thus, not all minerals expected from thermodynamics will be formed in alteration reactions. Further, dissociation of strong acids generates anions that may combine with cations dissolved in the formation water to precipitate minerals such as baryte or anhydrite. Thus, SO₂ and other acid-forming impurities (NO_x, SO_x) could have effects on the rock porosity, integrity, and injectivity as has been shown by laboratory experiments (e.g., Pearce, et al., 2015a, b^[79]; Mandalaparty, et al., 2010^[65]; Dawson, et al., 2015^[25]) and by modelling work (e.g., Azaroual, et al., 2008^[12]) for different types of reservoir rocks. Results from experimental and modelling studies have to be considered with care when employing impurity concentrations that are much higher than those currently considered in CO₂ streams (see [Clause 6](#)).

Apart from the acidification of formation waters by CO₂, SO_x and NO_x, redox reactions could occur when CO₂ streams contain redox-active impurities. Fe is a ubiquitous element, dissolved as Fe(II)-species in reduced formation waters or present in Fe(II)-containing minerals such as siderite (FeCO₃). Introduction of oxidants such as O₂ leads to the formation of Fe(III)-phases, that can replace primary iron phases, or precipitate in the pore space. Reactions of iron minerals have been investigated for CO₂ streams containing SO₂ or O₂ e.g. by Garcia, et al., 2012^[35] (for FeOOH + SO₂), Pearce, et al., 2015^[79] (for FeCO₃ + SO₂) and Waldmann, et al., 2014^[108] (for FeCO₃ + O₂). In addition, in depleted hydrocarbon reservoirs, the oxidation of light organic components may result in the formation of heavy residues that may accumulate and reduce permeability (“tar mats”). The presence of inert or non-condensable impurities in the injected CO₂ stream, such as Ar, N₂, and CH₄, will have no or negligible geochemical effects in the subsurface.

[Table 10](#) summarizes the chemical effects of impurities on a geological storage system.

6.2.2.2 Impacts on well cements

The well cements surrounding the borehole, immediately adjacent to the injection interval, may be altered by the impurities contained in the CO₂ stream. The project Puits CO₂ (2006–2010) focused on studying the impact of acid gases on wellbore cements by laboratory experiments: The kinetics of degradation was highly dependent on the medium — 6 mm/6 months in a mixture with reducing impurities (CO₂-H₂S 97 %-3 %), and 6 mm/7 weeks for a CO₂ mixture with oxidizing impurities (CO₂-NO₂-SO₂-O₂ 92,1 %-0,9 %-5 %-2 %). These conclusions differ from those obtained for pure CO₂ (Kutchko, et al., 2011^[59], Farret, et al., 2012^[32]).

More details can be found in Carroll, et al. (2016)^[17], who published a review of the various geochemical and geomechanical effects affecting wellbore integrity for CCS projects including the consequences of impurities in the CO₂ stream.

6.2.2.3 Mobilization of secondary elements

Secondary elements are not impurities of the initial CO₂ stream. They are substances that are originally present in the subsurface (reservoir, formation fluids, overburden, groundwater, soil) and can be mobilized by geochemical reactions — and then become part of the CO₂-rich phase or the aqueous phase. Among them are trace elements, such as Trace Organic Elements (TOE) and Trace Metal Elements (TME). Mobilisation of secondary elements does not create a specific risk as such. However, in case of a leakage of CO₂ or brine, overlying aquifers might be contaminated. If the storage occurs in deep saline aquifer formations containing dissolved natural gases or depleted gas reservoirs, natural gases will also mix with the CO₂ stream. In this case, natural gas components become part of the CO₂ stream that could further migrate and leak.

Some TOE and TME could also be present as impurities in the initial CO₂ stream (Table 9). However their concentration in the initial CO₂ stream is likely to be by far lower than the concentration of TOE and TME taken up from the subsurface as secondary elements as pointed out e.g. by Apps, et al. (2007) [9], Farret, et al. (2012) [32], Lions, et al., (2015) [61].

The reactions involved in the mobilization of TME and TOE and their partitioning processes are not known in detail, and both are therefore difficult to quantify. Regarding the TOE, supercritical CO₂ is a solvent and will dissolve organic matter. Regarding TME, formation water and groundwater acidification and modification of redox conditions due to CO₂ injection could influence the scavenging-release process of TME by iron oxides (Zuddas, 2009 [116]). In consequence, TME could be present in the formation water or groundwater, where they can be stabilized by formation chemical processes and will follow the water flow. A comparison of TME concentration in CO₂ streams and in formation waters is presented in Table 9.

Table 9 — Comparison of TME concentrations in CO₂ streams and formation water
[Ceroni & Farret, 2016 [33]]

	CO ₂ stream	Formation water before CO ₂ injection	Formation water after CO ₂ injection
Mn	1,2 × 10 ⁻² mg/l	3 mg/l (Kharaka, et al., 2009 [58])	18 mg/l (Kharaka, et al., 2009 [58])
Pb	2 × 10 ⁻² mg/l	2 × 10 ⁻⁵ mg/l (Zuddas, 2009 [116]) <2 × 10 ⁻⁵ mg/l (Apps, 2007 [9])	2 × 10 ⁻² mg/l (Zuddas, 2009 [116]) 10 ⁻⁴ mg/l (Apps, 2007 [9])

As concerns organic elements, in the Frio in situ injection experiment (Kharaka, et al., 2009 [58]) the values of organic carbon dissolved in the formation waters increased 20 days after the CO₂ injection by more than 2 orders of magnitude. The organic anion and BTEX concentrations of the water remained below 1 mg/l, nevertheless the authors concluded that the increase in organic matter (volatile and semi-volatile compounds) is a result of the CO₂ injection. At the Ketzin experimental site in Germany, acetate concentration in the wellbore fluids had increased nearly 20-fold 1 month after injection (Vieth, et al., 2009 [107]). In addition, laboratory leaching experiments show that the mobilization of organic matter (including BTEX) and other species by supercritical CO₂ is possible not only in oil reservoirs but also in aquifers containing no oil.

Table 10 — Summary of chemical impacts (storage)

Species/ substances	Characteristics of the species	Potential effect/impact	Recommended measure/ comment	Reference
SO _x , NO _x	Increase acidity of formation water; provide anions	Mineral dissolution and/ or precipitation affecting porosity and mechanical strength	Generally low concen- tration of these impu- rities in CO ₂ streams	Pearce 2015 [29], Talman 2015 [101], Azaroual 2008 [12], IEAGHG 2011 [40]

Table 10 (continued)

Species/ substances	Characteristics of the species	Potential effect/impact	Recommended measure/ comment	Reference
O ₂	Oxidising gas	Promotes formation of strong acids from SO _x and NO _x ; Oxidation of e.g. Fe(II) minerals		Pearce 2015 ^[79] , Waldmann, et al. 2014 ^[108]
O ₂	Oxidising gas	Oxidation of residual oil. Formation of heavy residues (tar mat) in depleted reservoir. Decrease porosity and permeability		Pearce 2015 ^[79] ,
Mobilized TMEs and TOMs by CO ₂	Potentially toxic impurity	Pollution of shallow water and subsurface water in case of leakage	Ground water treatment	Apps 2007 ^[9] , Farret, et al., 2012 ^[32] , Lions, et al., 2015 ^[61] , Kharaka, et al., 2009 ^[58]

6.3 Impacts on microbial communities in the storage complex

Overall, relatively few works deal with the impact of impure CO₂ on the deep subsurface microbial communities and biogeochemical processes.

Different studies show that the injection of high amounts of pure CO₂ in deep reservoirs impact firstly microbial communities by decreasing its activity (Morozova, et al., 2010^[70]; Wrapp, et al., 2013^[112], Santillan, et al., 2013^[94]). Then after this period of activity decrease microbes seem to acclimate to the conditions and activity increases.

Trias, et al. (2017)^[104] showed in the framework of CARBFIX project that deep ecosystems can respond quickly to injections of CO₂-charged groundwater in a basaltic storage site. The CO₂ "feed" (75 % CO₂-24,2 % H₂S-0,8 % H₂) was obtained from the purification of the geothermal gas harnessed by a nearby geothermal power plant. Injection of CO₂-charged groundwater resulted in a marked decrease (by a factor of ~ 2,5–4) in microbial richness. Ions released by basalt dissolution sustained the growth of autotrophic and heterotrophic species whose activities may have implications on mineral storage.

CO₂ can also play the role of an energy source that can be utilized by a range of different methanogenic organisms in strongly reducing environments. This process involves redox reactions which can be impacted by the presence of impurities (such as H₂S, SO_x and NO_x). However, the increase in CO₂ pressure more than doubled the rate of methanogenesis in comparison to low CO₂ pressure conditions. West, et al. (2011)^[110] examined the redox reactions involving both CO₂/CH₄ and SO₂/SO₄ redox couples. The authors show that SO₂ oxidation can be coupled to CO₂ reduction to provide sufficient energy for microbial use (particularly ~pH 3). In contrast, neither H₂S nor NO₂ half reactions produce sufficient energy for microbial use when coupled to CO₂ reduction.

Most operators in the US who inject CO₂ for EOR applications specify an O₂ limit of 10 ppm. The reason for this low level of O₂ is that the presence of even small levels of oxygen can lead to the growth of facultative aerobic species in an oil well, where the biomass they generate can be used as both a habitat and a nutrient source by sulfate-reducing bacteria (SRB). SRB obtain energy by oxidising H₂ or low molecular weight organic compounds, while reducing sulfate to H₂S. The promotion and growth of SRB can lead to the following main issues:

- Well performance can be degraded through pore plugging in the formation close to the well bore as e.g. H₂S can react with dissolved iron in formation waters to form iron sulphide, which can lead to a significant reduction in injectivity or productivity.
- When producing fluids from storage formations these can contain higher levels of H₂S, increasing their corrosivity and toxicity.

Different types of SRB grow at different temperature ranges with an upper limit of about 65 °C. Holding the reservoir temperature above this limit for deep CO₂ storage sites (e.g. cap rock at 2 500 m) could prevent this effect. However, the injection of CO₂ could provide some cooling to allow SRB growth at depth with potential implications on injectivity or corrosion.

An example of the impact of SRBs is the decrease of injectivity of the well Ktzi 201 on Ketzin site in Germany during the injection tests, studied by Zettlitzer, et al. (2010)^[115]. Here, the reservoir is located at 600 m–700 m below the surface and at a temperature of 37 °C–45 °C, therefore in the growth window of mesophilic SRB. They concluded that the black solid produced during the nitrogen lift was mainly composed of iron sulphide and that it was caused by bacterial activity (seven species of SRB have been detected in fluid samples). Organic compounds within the drilling mud and other drilling fluids were likely to be the energy source for strong proliferation of bacteria. Although in this example the organic matter that functioned as an energy sources for the microbes originated not from the CO₂ stream itself, this observation illustrates the potential role of organic impurities in CCS operations.

Table 11 summarizes the microbiological effects.

Table 11 — Summary of Microbiological effects

Species/ substances	Characteristics of the species	Effect on CO ₂ stream	CCS sys- tem/ operation	Potential effect/impact	Recommended measure/ comment	Reference
O ₂		—	Storage/ Injection	O ₂ may stimulate growth of fermenters and in turn of SRB Degrade well performance by pore plugging bacteria colony, close to the well bore. Increase corrosivity	Check microbial capabilities	

6.4 Toxic and ecotoxic effects of impurities in case of leakage

6.4.1 General statement

The cumulative effects of substances (CO₂, various impurities) are not considered in this clause.

6.4.2 Acute toxic effects

In case of an uncontrolled release (e.g., leak on a pipe), a CO₂ cloud is formed that can potentially endanger human and animal health. Possible impacts on human and animal health are toxic effects (poisoning) and the lethal effects (death). Depending on concentrations, the impurities could be more toxic than the CO₂ itself in this cloud. When a CO₂ stream escapes to the atmosphere, there will be changes in pressure, volume, temperature, and phase of each of its components and dilution with air. It is very unlikely that the composition of the "CO₂ cloud" will be the same as the composition of the "CO₂ stream". If an impurity with a toxicity threshold T for lethal effects (in ambient air) is considered, while for CO₂ the threshold for lethal effects is 10 % (see Table 12), the toxic effects of the CO₂ itself is likely to be predominant in the cloud, as compared to this impurity, as long as the concentration of the impurity within the CO₂ cloud is lower than 10 * T (= T/10 %) Therefore, if the concentration of the impurity within the CO₂ stream is greater than 10 * T it can be useful to conduct a specific study on the acute toxicity of impurities in case of accidental release of CO₂. This limit of 10 * T is only indicative, as it relies on the simple assumption that the substance behaves in the cloud like CO₂ (despite changes in temperature, pressure, or phase).

Table 12 — One-hour exposure concentration thresholds according to French regulation

Substance	CO ₂	CO	HNO ₃	H ₂ S	NH ₃	NO ₂	SO ₂
mg/m ³	196 000	3 680	2 186	521	2 380	132	1 885
ppm	100 000	2 951	779	344	3 143	64	661

NOTE 1 Lower exposure durations would give higher thresholds.

NOTE 2 Different values exist in other countries, although generally similar.

The main impurities of concern in this context are H₂S and NO₂, because these two impurities have low toxicity thresholds. H₂S is commonly present after pre-combustion capture processes. The toxicity threshold for NO₂ is about 5 times lower than that of H₂S (in ppm). Therefore, if NO₂ constitutes a large part of the NO_x species, its concentration can be close to 10 * T and a site-specific study should be considered.

Although the intrinsic toxicity of SO₂ is lower than NO₂ (toxicity threshold of SO₂ is about one order of magnitude higher in comparison to that of NO₂), SO₂ might also deserve a site-specific study, if SO_x concentration in the CO₂ stream is higher than NO_x concentrations.

Within the CO₂QUEST project, a study of the possible risks from all impurities in the CCS chain was carried out. It used a multicriteria methodology that accounted for the very different natures of the effects assessed. Results confirm that NO₂ and H₂S are the most influential impurities for acute toxicity (Mahgerefteh, et al., 2016^[64]).

For post-combustion CO₂ capture, one of the main problems associated with the process is the degradation of the amine solvents involving the formation of degradation products potentially detrimental for human and the environment. These degradation products are formed in the liquid phase of the solvent but can also be emitted with the gaseous effluents increasing the need of monitoring strategies. One of the objectives of project ANR DALMATIEN^[24] and Vial 's team was to develop new analytical methods to identify these degradation products of MEA or other amine solvents (Rey, et al., 2013^[89]). A toxic/ecotoxic study was also conducted on the degradation products from MEA. A recent published review proposes a critical analysis of the literature concerning the analytical strategies developed in the field of post-combustion capture to identify and quantify the main classes of degradation products formed, mainly amines, amides, aldehydes, nitrosamines and organic acids (Cuccia, et al., 2018^[63]). Regarding the liquid phase, the principal analytical methods involved are liquid chromatography (LC) and gas chromatography (GC) for the analysis of amines and ionic chromatography (IC) for the analysis of organic and inorganic acids. Concerning aldehydes, the most described method is derivation of the compounds with 2,4-dinitrophenylhydrazine prior to LC analysis. In order to monitor the gaseous effluents, four methods have been described: FTIR, implementation of impingers, online MS analysis and sampling on solid sorbents.

6.4.3 Chronic effects

A leakage event from the storage unit can be a leakage of the CO₂ stream itself, as a dense or gaseous buoyant phase, able to move upwards (e.g. along a fault or a well). Formation water may also leak. However, formation water with dissolved CO₂ and impurities in it may move upward toward lower-pressured formations and the surface or may move downward or laterally due to its higher density after CO₂ dissolution.

Chronic effects of impurities could arise from long-term leakage of a CO₂ stream and/or formation waters beyond the boundaries of the storage system leading e.g. to an aquifer pollution. The leakage impact could extend to surface waters, in case of connections with the initially polluted aquifer.

Two main subjects of protection can be considered:

- Human health — through the pollution of drinking water. Drinking water concentration thresholds exist, e.g. given by EU Directive 98/83/CE.

- Environment — through the pollution of underground and surface waters. Relevant concentration thresholds exist, e.g. in Annex I of EU Directive 2008/105/EC.

The concentration of a given impurity in the aquifer is not the same as the concentration in the CO₂ plume, as it depends on numerous factors including the size of the leakage and the movement and geometry of the aquifer. Several phenomena can affect its final concentration such as advection, dilution, geochemical reactions, and sorption onto rocks. These phenomena may be considered by modelling of transport and chemistry.

The CO₂QUEST project concluded that generally chronic toxicity appeared not to be a major issue for risk management of the CCS chain as compared to chemical effects, (Mahgerefteh, et al., 2016^[64]). However, this is a generic result that cannot be applied specifically to all CCS projects as such. Site-specific risk studies are carried out by operators based on detailed in situ data and detailed modelling.

7 Parameters to monitor and measurement methods

7.1 Monitoring and thresholds

Monitoring of the composition and mass flow rate of the CO₂ stream is a component of risk management that will assist in limiting impacts and minimizing risks identified in the previous clauses. Monitoring is conducted for the capture process and an overall monitoring strategy of the CO₂ stream and is implemented along the CCS chain downstream of the capture plant. The effectiveness of monitoring is improved through the definition of alert thresholds. Alert thresholds might be based either on regulatory limits, or on site-specific thresholds (operational or contractual) determined by a comprehensive risk assessment process.

A number of CO₂ specifications and recommendations for maximum acceptable impurity concentrations in the transport and storage systems have been published (see [Table 1](#) in [Annex A](#)). These specifications depend strongly on the context of each specific CCS project: country, operator, type of project, transport mode, etc. The ISO 27913:2016^[48] for CO₂ pipeline transportation systems states that “Since the maximum concentration of a single impurity will depend on the concentration of the other impurities, it is not possible due to lack of data and current understanding to state a fixed maximum concentration of a single impurity when other impurities are, or may be, present”. The present report does not provide recommendations for impurity contents.

The most referenced CO₂ quality recommendation has been suggested in the DYNAMIS project (De Visser, et al., 2008^[22]) considering CO₂ streams captured by pre-combustion capture. The National Energy Technology Laboratory (NETL) issued in 2012^[73] quality guidelines for impurity limits to be used for CCUS conceptual studies using carbon steel pipelines with the caveat that the numbers “should not be used for actual projects, which are likely to have requirements that differ”. The recommendations were based on a review of 55 CO₂ specifications found in the literature. The most recent recommendation from “The CarbonNet project” (2016)^[103] is also included in [Annex A](#).

Some international agreements, areas, and countries establish regulatory limits for CO₂ stream composition. For example, the London Protocol demands that CO₂ stream must consist “overwhelmingly of CO₂” for sub-seabed geological formation storage, which may contain incidental associated substances derived from the source material and the capture and sequestration processes. Additionally, the Protocol prohibits mixing any waste or matters into CO₂ stream for the purpose of disposal. In Japan, rules from the Ministry of Environment defined requirements for sub-seabed CO₂ storage projects, including an ordinance governing the purity of the injected CO₂. When CO₂ is captured with amine-based technology, CO₂ purity is required to be no less than 99 % in volume percentage. When the CO₂ is produced out of H₂ production process for an oil refinery, the CO₂ purity is required to be no less than 98 % in volume percentage (Japan Ministry of Environment, 2011^[55]).

7.2 Relevant parameters to monitor and measurement methods

The composition of the CO₂ stream varies in time at the capture plant outlet depending on the capture technology employed. Online continuous or semi-continuous CO₂ stream quality monitoring at the plant

outlet will identify variation. However, some demonstration projects have over several years yielded remarkably stable CO₂ product streams. Beside the impurity content, supplementary parameters useful for identifying/measuring the CO₂ stream composition include fluid state, temperature and pressure, mass flow rates, and localization of sampling points. Some measurement challenges in CCS operations arise from the physical properties of the CO₂ itself. The involvement of different processes in CCS operations and the presence of impurities in the CO₂ stream. Knowing what could be present will assist in identifying standard operating procedures for flow measurement, for sampling techniques and for analytic processes, given the different impurities that are likely to be present in the CO₂ stream. Selecting sampling points is important for monitoring CO₂ stream composition. If the pipeline is operated in dense-phase conditions, rapid depressurization would produce gaseous and solid CO₂. In this transition a partition of the impurities between the gas and the solid phases could appear and if only the gas phase is analysed this could lead to false composition results. Standard operating procedures (SOPs) will serve to ensure reliable and comparable results as SOPs provide the necessary information on measurement methods in terms of characteristics, level of validation, uncertainty, and existing alternatives. Effective application of SOPs requires that the operator performing the measurements be sufficiently knowledgeable.

7.2.1 Sampling of the CO₂ stream

One of the main challenges lies in ensuring that pressure and temperature conditions that apply to samples from the CO₂ stream are representative of the entire stream.

Physical samples of the CO₂ stream are usually taken in polytetrafluoroethylene (PTFE)-lined stainless-steel pressure vessels (generally referred to as sulfinert vessels). It is important to address the standardization of CO₂ stream sampling and analysis procedures.

7.2.2 Determining the physical properties and phase

Compared to other substances that are transported by pipeline (e.g. oil, natural gas and water) the critical point of pure CO₂ lies close to ambient temperature. This means that even small changes in pressure and temperature could lead to rapid and substantial changes in the CO₂ stream physical properties (e.g. density, compressibility). Further, when operating on or close to a phase boundary line, phase change and multiphase flow conditions can arise. Phase changes and multiphase flow occurring at measurement points will have a detrimental effect on measurement accuracy, e.g., where flowmeters are designed to operate in one specific phase only.

Operators usually choose validated equations of state describing thermodynamic properties including phase equilibria to apply to the many different CO₂ mixtures that are likely to arise in CCS schemes (see 6.1.2). Physical property modelling software packages are used to predict properties of various CO₂ mixtures. However, such models require site-specific testing and calibration as even small errors could lead to serious problems during processing and transport of CO₂. Currently, the best property models are empirical in nature, and hence cannot be more accurate than the experimental data to which they are fitted. In order to model mixtures, complete binary mixture data sets are desired, with ranges in temperature, pressure, and composition beyond what are expected for the given application. The data situation was reviewed by Munkejord, et al. (2016)^[72].

7.2.3 Flow measurement

Without knowing the phase envelope and thermophysical properties of the CO₂ stream accurately, it is difficult to perform accurate flow measurement. It is necessary to design the flow metering system for the actual physical phase it will be operating in. Accurate density measurements are necessary to allow reporting in mass CO₂ units, if the meter used measures volumetric flowrate. Flow measurement, in conjunction with the CO₂ concentration derived from sampling of the CO₂ stream, is necessary to calculate the transfer of CO₂ on a mass basis, across the CCS chain. For example, in Europe, the draft CCS Monitoring and Reporting guidelines under the EU ETS require that flow measurement be carried out within measurement uncertainty levels of 1,5 %. In order to achieve such levels, it is essential to install the correct type of flow meter at locations along the network where the flow conditions are stable and

in the single phase under which the flow meter is designed to operate. For example, gas meters are appropriate at certain locations and liquid meters at other locations along the network.

Flow measurement systems are normally calibrated, maintained, and checked at regular intervals. Flow meters are calibrated using traceable flow facilities in CO₂ under the conditions and ranges under which they will be operated. Any secondary instruments used to convert volume flow into mass flow, such as pressure, temperature, and density instruments, could also be calibrated and traceable to national standards and located as close as possible to the flow meter. Standard methods to determine the mass flow rate of the CO₂ stream, ISO 10780, ISO 5167-1, ISO 9951, ASME PTC 19.5 (Flow Measurement), ASME MFC-6-2013, are mentioned in ISO 27919-1:2018(E)^[50], Table C.2.

7.2.4 Impurity concentration measurements

Accounting of impurity concentrations in the CO₂ stream has two main applications:

- i) To manage the purity levels in the CCS chain and their possible impacts;
- ii) To determine the amount of CO₂ that is transported and stored. CO₂ is not the only component of the CO₂ stream (although it is the major one), which is important for fiscal monitoring. This issue is addressed in [Clause 8](#).

No standard measurement method exists for the determination of impurity concentrations in CO₂ as a matrix except for food grade standards: The International Society of Beverage Technologists (ISBT) Carbon Dioxide Guidelines provide a basis to identify the best available measurement methods to be applied in this context.

Moreover, the ISO 12039 method defines the performance characteristics and the calibration of automated measuring systems for the determination of CO, CO₂ and O₂ from stationary-source emissions. Standard methods for the analyses of natural gas exist, including several methods using gas chromatography, the ISO 6974 method previously mentioned, but also the ASTM D1945 method, and the ISO 19739:2004 which describes the analysis of sulfur compounds. The ISO 10715:1997 standard provides a guideline for sampling natural gas and the ISO 10723:2012 standard specifies a method of determining whether an analytical system for natural gas analysis is fit for purpose. Those methods, although they are well described and recognized, might not be directly applicable to matrices where CO₂ is the major component. According to ISO 27919-1:2018(E), Annex C, Table C2, two methods can be used to evaluate the purity of the CO₂ stream, i.e. the ISO 6974 method which describes the measurement of impurities in natural gas using gas chromatography and the US EPA method 3A which deals with CO₂ and O₂ measurements from stationary sources. Standard operating procedures for the characterization of impurities present in flue gas emitted by amine based solvent capture pilot processes have been published during the FP7-OCTAVIUS project (Fraboulet, et al., 2014)^[34].

Note Method 3a — Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources (instrumental analyzer procedure).

8 Relationship of CO₂ stream emissions and quantification

In case of emissions from anywhere in the CCS chain into the atmosphere, e.g. from a leakage or vent, GHGs present as impurities in the CO₂ stream could increase the greenhouse effect as compared to pure CO₂. The two main possible impurities that are relevant GHGs are CH₄ and N₂O, although other GHGs could be present in some cases. The Global Warming Potential (integrated over 100 years) for CH₄ is 28, for N₂O it is 298, while that of CO₂ is 1.

NOTE The influence of impurities, including GHGs in the CCS chain, on quantification and reporting is not addressed in the standard, ISO 27920¹⁾, dedicated to quantification and verification of CO₂ only.

If CH₄ is present in CO₂ streams, its concentration is typically below 100 ppm (see [Clause 5](#)).

1) Under preparation. Stage at the time of publication: ISO/DIS 27920.

However, in the particular case of EOR, CH₄ is normally present in the recycle gas stream. Measurement and quantification of CH₄ in this context might be required by regulators.

In a CO₂ stream from post-combustion capture, NO_x concentration is approximately 10 ppm-30 ppm (see [Clause 5](#)), also N₂O can be present at concentrations of about 0,1 ppm to 1 ppm. With a pre-combustion capture process (especially with a fluidized bed), nitrogen oxides are present at higher concentrations (about 300 ppm) and N₂O can form an appreciable part of these (De Soete, 2017)^[88]. If 10 ppm of N₂O were present in the CO₂ stream, the stream's global warming potential would increase by only 0,3 % as compared to pure CO₂ (because $10 \text{ ppm} \times 298 \approx 3 \times 10^{-3}$). Therefore, in non-EOR cases the impact of impurities as additional GHG emissions is probably minor as compared to the potential emissions of CO₂ itself. Additionally, this issue is also addressed in ISO 14064 (all parts)^{[45][46][47]}, especially if a Life Cycle Analysis is performed for the whole life cycle of a CCS project.

9 Integration issues

9.1 Constraints on CO₂ stream composition

It is technologically possible to treat CO₂ to near 100 % purity in the gas conditioning process. However, in most cases it is preferable to have less rigid specifications to reduce both operational and capital costs. The question is which part of the CCS chain that actually dictates the CO₂ composition.

As illustrated in [Figure 6](#), the required purity of the CO₂ stream delivered from the capture plant will to a large degree be dictated by the transport, injection and storage operators, or legal requirements. The capture plant operators will therefore most probably not be the ones to set the specifications, but may need to purify the CO₂ stream to comply with the required transport, injection, storage or utilization specifications. Impurity restrictions (bottlenecks) will be project specific and an optimization process is obviously needed where the cost of purification is balanced against the cost of for instance using more corrosion resistant materials, the cost and consequences of reduced injectivity due to possible unwanted reactions in the reservoir, purification closer to the storage or utilization sites, and the cost of down-time and repair.

What is driving the CO₂ composition?

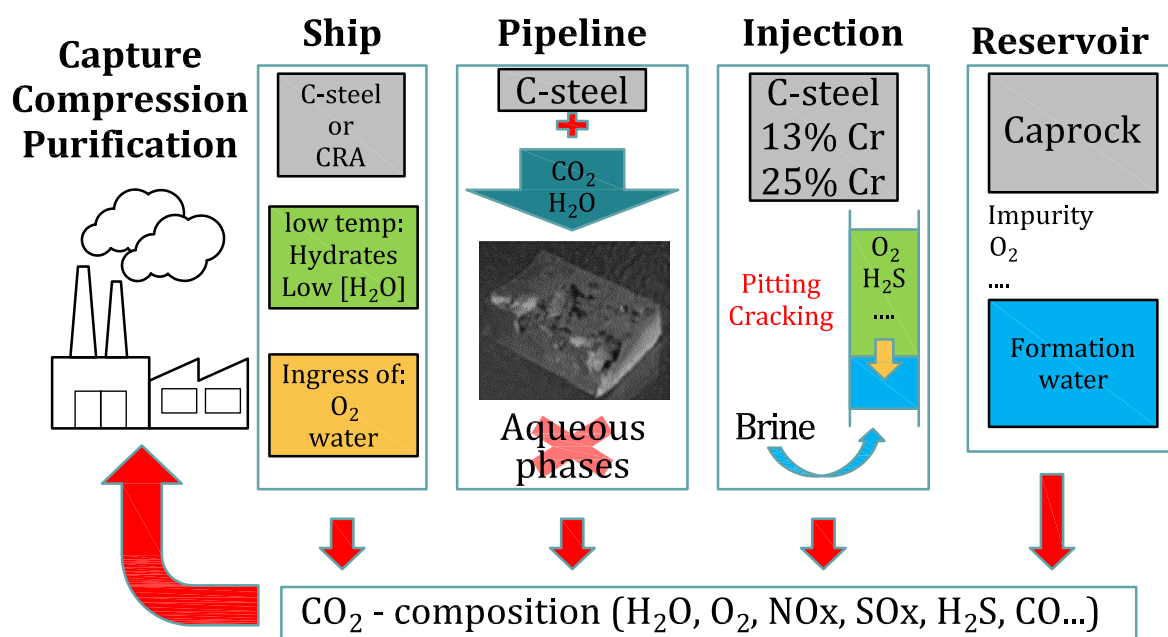


Figure 6 — Constraints on CO₂ Stream Composition

The impurity levels that can be accepted and managed by the transport, injection and storage operators will determine the composition to be delivered from the capture operator

9.2 Optimisation of CO₂ stream composition based on techno-economic assessments

Physical and chemical impacts of various impurities and combinations of impurities on the individual steps of the CCS chain have been outlined in the previous sections. If impacts of impurities in individual components of the CCS chain are known, CO₂ stream composition could be adjusted to avoid undesirable impacts. Optimisation of CO₂ stream composition along the CCS chain could ensure safety of transport, injection and storage while reducing energy consumption and costs of the CCS chain operation. This optimisation could be realized by way of various options for the technical design of the CCS chain, e.g. implementation of an additional purification step or selection of a more corrosion resistant pipe material.

To assess various transport network design options, techno-economic assessments have proven to be a valuable tool. Few studies exist that assess impacts of impurities along whole CCS chains in full complexity aiming to optimize CO₂ stream composition with the whole-chain perspective. All such studies point to the fact that such an optimisation can only be project-specific (e.g., Brunsvold, et al., 2016^[14], Porter, et al., 2015^[81], Rütters, et al., 2016^[92]). Thus, no general recommendation on optimal CO₂ stream composition can be given — as stated in [Clause 7](#). Rather, it is generally recommended to analyse cost efficiency of upstream impurity removal versus dealing with impurity impacts further downstream. Techno-economic assessments of several model CCS chains have revealed the superior cost efficiency of upstream impurity removal (Brunsvold, et al., 2016^[14]).

In addition to techno-economic considerations, ISO/TR 27918 “Life-cycle risk assessment^[53] will outline steps for taking into account the various risks as impacted by the CO₂ stream composition and/or the presence of specific impurities for a specific CCS project.

9.3 Mixing CO₂ streams before injection: Challenges in larger CCS infrastructures

Implementation of larger CCS infrastructures could be one option to reduce costs of transport and storage. Larger CCS infrastructures could include the feed-in of CO₂ streams from different sources in a common transport network (collection network with trunk line or ship transport in or without combination with pipeline transport) and/or injection of CO₂ at several storage sites (via an injection and storage hub or along the route). Large-scale infrastructure scenarios have been developed, e.g. in Europe for the North Sea area. Pipeline networks that are now in operation combine high-purity CO₂ streams from few emitters or natural CO₂ sources and involve trunk lines for CO₂ transport of short to moderate length (some examples can be found in NETL, 2012^[73]). Additional transport and storage networks are in various planning and development stages (e.g., Alberta Carbon Trunk Line Project, Canada; Norwegian Demo Project, Norway; CarbonNet Project, Australia; Porthos project, Netherlands).

Combining CO₂ streams from different sources for or during transport could bring specific benefits (e.g., dilution of a contaminant), but could also result in additional challenges in comparison to simple CCS chains. Further options for optimizing CO₂ stream composition could include arranging CO₂ stream contributions from different emitters in such a way that a highly impure CO₂ stream is combined with high purity CO₂ streams (i.e. diluted). However, such a feed-in scheme could generate an “out of specification” CO₂ slug if the flow of the purer CO₂ stream is interrupted. Of course, the high impurity CO₂ stream could be shut off, but this would potentially represent both technical and financial risks.

In general, if there are fluctuations in the flow rates of individual CO₂ streams, there will be a temporal variability of mass flow rates and composition in larger pipeline networks (e.g. Rütters, et al., 2017^[92]). For example, power plant operation will be adjusted to meet the part of the fluctuating electricity demand not covered by renewable energy sources. Other emitters might be shut down for maintenance or in case of failure. The variability both in mass flow rates and CO₂ stream composition is usually accounted for when designing and operating larger CCS infrastructures. This will involve aspects related to the mass flow rates such as pipeline capacity, and acceptable variability of flow rates for transport and injection. Further, there might be a need for temporary storage as well as injection and storage management potentially involving several injection wells and multiple storage sites.

A changing CO₂ stream composition e.g. in the trunk line with time will lead to temporal variations of thermophysical properties of the CO₂ stream with implications along the entire CCS chain (see [Clause 6](#)). In addition, the changing chemical properties of the CO₂ stream will impact reactive processes along the CCS chain (such as steel corrosion, geochemical reactions, etc.). In particular, the redox properties of CO₂ streams differ significantly depending on the capture technology. Therefore, if CO₂ streams with contrasting redox properties are fed-in in a variable manner, redox conditions in the resulting combined CO₂ stream will vary accordingly.

Furthermore, when different CO₂ streams are combined, from various emitters that differ in their composition, the spectrum of different impurities will potentially be larger than in single source-single sink CCS systems. Additional or different chemical reactions could occur within the combined CO₂ stream depending on the composition and flow rates of the combined CO₂ streams. Accordingly, some national/international regulations might impose some constraints, and a risk analysis can help to check that there are no incompatibilities among the different impurities. For instance, SO₂ and H₂S could react to form solid sulfur, or unsaturated hydrocarbons could react with NO₂ to form unstable products (see [Clause 6](#)). Specific assessments help to identify these risks in the context of modifications of mass flow rate and/or CO₂ stream composition, such as could occur during the intended or unintended (re-)start or shut-down of CO₂ emitters and CO₂ stream flows.

In comparison to simple CCS chains, larger CCS infrastructures offer a greater flexibility for coping with disturbances in the CCS chain (e.g. in CO₂ feed-in, in technical installations or in the storage) as alternative supply or transport options, and interim storage and injection sites might be available. However, setting up a large-scale infrastructure carries specific risks some of which are particularly impacted by the CO₂ stream composition. A CO₂ transport and storage infrastructure will be designed to accommodate CO₂ streams with an expected mass flow and compositions within a specified range. The future availability of CO₂ streams, both in terms of mass flow and composition, will be influenced by technological and economic developments.

10 Conclusions

Across CO₂ streams captured from power plants and industrial processes there is large variation of impurities and concentrations because the impurities depend on the fuel type or raw materials, the CO₂-generating process, the CO₂ capture process, and the final purification and compression steps. Ranges for concentrations of major impurities can be cited, even though data for usually minor impurities (such as SO_x, NO_x, CO, H₂S) and for metallic and organic trace elements are scarce and are often based on model estimates, instead of in situ measurements.

An extensive list of physical and chemical effects of these impurities has been established. These impurities can affect both surface equipment and surface and underground operations. Furthermore, some impurities can have (eco)toxic effects.

Accurate monitoring of CO₂ stream composition is important and helps to: i) ensure proper operation of CCS activities; ii) reduce risks of negative impacts; iii) ensure correct quantification of the GHG stored (or emitted); and iv) contribute to knowledge sharing among CCS stakeholders and the public.

The capture process, final purification and compression steps help to manage CO₂ stream composition. The impurity concentrations of streams depend on the aims and priorities of the operator for each specific CCS project and are influenced by legal regulations and technical requirements.

The present state of the art of identifying impurity concentrations and potential impacts confirms that management of CO₂ stream composition is a cross-cutting issue for integrated CCS projects. Mixing CO₂ streams from different origins can result in additional challenges from the technical, economic, or regulatory points of view, especially for large-scale projects.

CO₂ stream composition in CCS activities will influence the design and operation of the capture process and the final purification steps. However, it is difficult to identify thresholds for individual impurities, for two main reasons:

- First, site-specific risk studies are usually carried out by operators, taking into account data on the project and its specific environment;
- Second, interactions of impurities with each other and their surroundings might result in impacts different from those of a single impurity in a CO₂ stream.

Therefore, concentration thresholds are case-specific and subject to optimization for the entire CCS process with respect to safety and environmental protection, costs, and energy demand.

Annex A (informative)

Dense phase CO₂ corrosion

A.1 Previous experience

CO₂ is predominately transported as dense phase and sufficiently dehydrated to avoid hydrate formation. Some features of CO₂ make it more challenging to transport in pipelines than natural gas, i.e. a greater susceptibility to long-running ductile fracture propagation (Cosham, et al., 2014^[21], a greater likelihood for lower temperatures and reduced toughness due to the Joule-Thomson cooling effect (–20 °C for line venting and down to –80 °C for leakage), and a high potential corrosion rate if an aqueous phase is present.

CO₂ has been transported and used in food industry and enhanced oil recovery (EOR) for decades, mainly in USA^[43]. No serious corrosion problems have been reported in the part of the system that has been exposed to reasonably dry and pure CO₂. According to OPS (Office of Pipeline Safety) statistics, there were only 12 leak cases from CO₂ pipelines reported from 1986 through 2006 — none resulting in injuries to people^[80].

The good experience with CO₂ transport in USA is often referenced to argue that CO₂ pipeline transport will not be a big challenge for Carbon Capture and Storage (CCS). The justification for this view can be questioned as CO₂ captured from fossil-fuelled power plants and other industrial sources might give dense phase CO₂ containing impurities that have not been transported before. It is also regarded more challenging to operate CO₂ network with many point sources and to transport CO₂ to offshore storage sites.

A.2 CO₂ recommendations and specifications — A literature overview

A number of CO₂ specifications and recommendations for maximum acceptable impurity concentrations in the transport and storage systems have been published. The most cited CO₂ quality recommendation has been suggested in the DYNAMIS project^[22] The National Energy Technology Laboratory (NETL) issued in 2012^[73] and 2013^[75] Quality Guidelines giving recommendations for the impurity limits to be used for conceptual design s of studies of CCUS systems using carbon steel pipeline with the caveat: “This guideline is intended only for conceptual studies under a generic scenario and should not be used for actual projects, which are likely to have requirements that differ from the generic scenario assumed herein.”^{[73][75]} The recommendations were based on a review of 55 CO₂ specifications found in the literature^{[73][31]}. The CarbonNet Project published in 2016 a preliminary CO₂ specification for its hub-based carbon capture and storage network^[103]. Other frequently cited CO₂ specifications have been presented by IPCC^[44] and Kinder Morgan^[57].

An excerpt of the DYNAMIS, NETL and CarbonNet specifications and CO₂ specifications reported for existing pipelines are shown in [Table 1](#). The table includes potentially the most aggressive impurities (H₂O, H₂S, O₂, NO_x, SO_x, CO) from a corrosion point of view. It is clear that the recommendations vary a lot and they are quite different from the composition reported for actually transported CO₂.

The justification for many of the proposed recommendations can be questioned as the reported^[68] ^[8] CO₂ compositions presently transported in pipelines does not include flue gas impurities like for instance SO₂ and NO₂, and as concluded in a recent review^[81] hardly any lab data can be found in the literature supporting the CO₂ specifications.

Table A.1 — Impurity concentrations reported in existing pipelines^{[68][8]}, CO₂ specifications recommended by Dynamis^[22], NETL^{[73][75]}, the Australian CarbonNet project^[103] and the CO₂ specification tested in the IFE experiment^[1] described in [section A.4](#)

	Impurity levels in existing pipelines ^{[73][75]}				Published CO ₂ recommendations ^{[22][73][75][31][103]}				Testing
	Canyon Reef Carriers	Central Basin Pipeline	Cortez Pipeline	Weyburn	DYNAMIS ^[22]	NETL ^{[73][75]}	Literature review ^[81]	CarbonNet ^{[31][103]}	IFE exp. ^[1]
H ₂ O, ppmv	122	630	630	20	500	730 ^[73] / 500 ^[75]	20-650	100	122
H ₂ S, ppmv	<260	<26	20	9 000	200	100	20-13 000	100	130
CO, ppmv	—	—	—	1 000	2000	35	10-5 000	900	
O ₂ , ppmv	—	<14	—	<70	<40 000	40 000 ^[74] / 10 ^[75]	100-40 000	20 000	275
NO _x , ppmv	—	—	—		100	100	20-2 500	250	96
SO _x , ppmv	—	—	—		100	100	10-50 000	200	69

A.3 Corrosion in pure CO₂ and water

When the acceptable water content in CO₂ streams is discussed it is usually argued that no water containing phase will precipitate and cause corrosion/hydrate as long as the concentration is well below the solubility in pure CO₂. The water solubility in the pure system is >1 000 ppmv in the temperature range relevant for pipeline transport (4 °C–50 °C) and both laboratory experiments and field experience confirm very low corrosion rates for the pipelines where the water content have been specified in the range 20 ppmv to 650 ppmv.

Water precipitates when the water solubility limit is exceeded and experimental studies with dense phase CO₂ and a free water phase show that the corrosion rate increases with increasing temperature, that protective FeCO₃ corrosion product films form when the concentration of dissolved corrosion products becomes high and that the corrosion film can fail and give high localised corrosion rates. The observations seem to follow very much the trends seen at lower CO₂ partial pressure in oil and gas production. The main difference is the much higher CO₂ pressure giving typically a one-unit lower pH, a much higher solubility of corrosion products and more H⁺ ions and H₂CO₃ that can corrode the steel. The result can be extreme corrosion rates exceeding 30 mm/y when the steel is exposed to large amounts of condensed water^[2]. If only minor amounts of water precipitate, the water will be quickly supersaturated with dissolved corrosion products and a much lower corrosion rate can be expected. This mechanism is similar to Top of the Line Corrosion (TLC) in gas condensate pipelines and the corrosion rate will be limited by the availability of fresh water.

A.4 Impurities and formation of corrosive phases

When impurities like water, SO_x, NO_x, O₂, CO and H₂S are present there are a number of possible cross-chemical reactions that have the potential to form sulfuric/sulfurous acid, nitric acid and elemental sulfur. The CO₂ composition given in the last column in [Table A.1](#) was tested in a rocking autoclave system at IFE (Institute for Energy Technology)^[1]. The experiment demonstrated that H₂SO₄, HNO₃ and elemental sulfur formed (see [Figure A.1](#)) at impurity concentrations below the impurity limits given in the recommendations in [Table A.1](#).

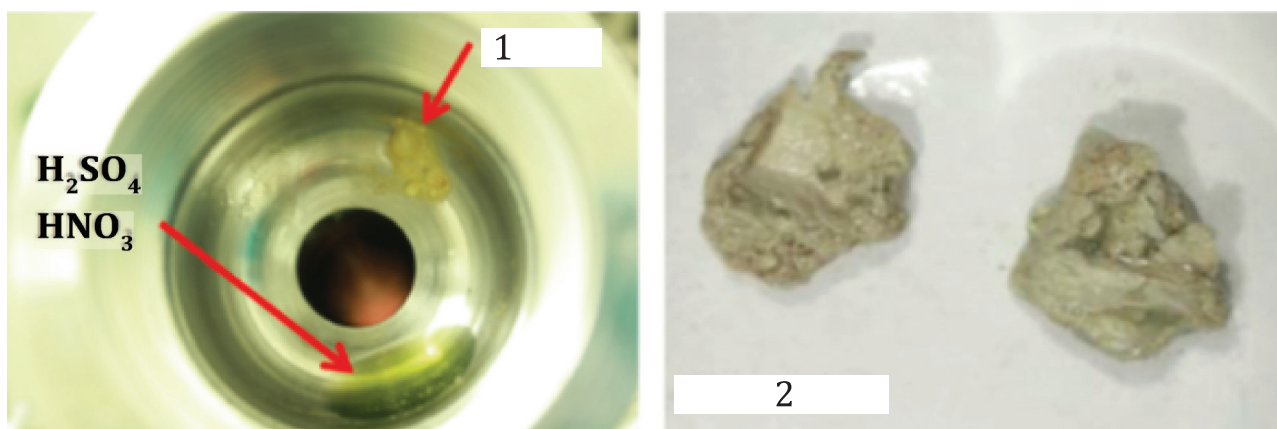


Figure A.1 — H_2SO_4 , HNO_3 and elemental sulfur formed in corrosion experiment performed at 45 °C, 100 bar and CO_2 composition as given in last column in [Table A.1](#)

A.5 Defining safe operation window for CO_2 transport

If the carbon steel surface is wetted by a water containing phase the question is not whether corrosion takes place, but at what rate. Avoiding the formation of corrosive phases and solids in the pipeline is essential for the safe operation of a CO_2 pipeline network. Precipitation of water in systems with non-reactive impurities can be predicted, but due to lack of data there are presently no publically available models that can predict precipitation of aqueous phases when reactive impurities (combinations of NO_x , SO_x , H_2S , O_2 , H_2O , CO) are present.

The lack of data was recognized in the first ISO standard for CO_2 transport that was issued in 2016^[48]. In the standard it is stated that “*Since the maximum concentration of a single impurity will depend on the concentration of the other impurities, it is not possible due to lack of data and current understanding to state a fixed maximum concentration of a single impurity when other impurities are, or may be, present*”. The standard therefore recommends consulting the most up to date research during pipeline design

A.6 Which part of the CCS chain constrains the CO_2 stream composition?

It is technologically possible to treat CO_2 to near 100 % purity in the gas conditioning process. However, in most cases it is preferable to have less rigid specifications to reduce both operational and capital costs. The point at issue for the operators is which part of the CCUS chain that dictates the CO_2 composition.

The required purity of the CO_2 stream delivered from the capture plant will to a large degree depend on the impurity levels that can be accepted and managed by the transport, injection and storage operators. The capture plant operators will therefore most probably not be the ones to set the specification but may need to purify the CO_2 stream to comply with the required transport, injection, storage or utilization specifications. Impurity restrictions (bottlenecks) will be project specific and an optimization process is obviously needed where the cost of purification is balanced against the cost of for instance using more corrosion resistant materials, the cost and consequences of reduced injectivity due to possible unwanted reactions in the reservoir, purification closer to the storage or utilization sites, and the cost of down-time and repair.

Annex B (informative)

Composition of CO₂ streams (Source ISO 27913:2016)

This section is strictly quoted from ISO 27913:2016

This annex provides essential information on the composition of CO₂ streams which is relevant for the definition of the operational envelope during the design phase. The exact composition of the CO₂ stream will depend on the CO₂ source and the installed capture technology.

Impurities in a CO₂ stream can include the following:

- oxygen (O₂);
- water (H₂O);
- nitrogen (N₂);
- hydrogen (H₂);
- sulfur oxides (SO_x);
- nitrogen oxides (NO_x);
- hydrogen sulfide (H₂S);
- hydrogen cyanide (HCN);
- carbonyl sulfide (COS);
- ammonia (NH₃);
- amines;
- aldehydes;
- particulate matter (PM).

In addition, further impurities can occur. Example CO₂ stream compositions, particularly from the power plant sector, can be found in literature^[13], but the data are extremely limited as the technology is still in development.

Impurities have impacts on the thermodynamic properties of a CO₂ stream which cannot be predicted out of the properties of pure CO₂. Furthermore, impurities can effect corrosion or generate chemical reactions. Also, properties of a CO₂ stream, like viscosity, can change.

Research to identify those impurities that can have a critical impact on the thermodynamic, chemical and other properties of the CO₂ is still taking place. Indicative levels discussed in literature are presented in summary in [Table B.1](#).

**Table B.1 — Indicative levels of main CO₂ impurities and factors driving these levels
(ISO 27913:2016, Table 1.1)**

Species	Indicative levels (volumetric composition in ppmv, unless stated as mol%)		
CO ₂	>95 mol% ^a		
H ₂ O	Corrosion, 20 to 630 ^b , Hydrate, <200 ^{c,d}		Avoiding the formation of corrosive phases and solids in the pipeline is essential for safe operation of the CO ₂ pipeline system. There are a number of possible cross-chemical reactions that have the potential to form sulfuric/sulfurous acid, nitric acid and elemental sulfur when water and SO ₂ , NO, NO ₂ , O ₂ and H ₂ S are present ^[28] , also N ₂ O, N ₂ O ₄ ^[49] . Presently, there is no publically available model that can predict which of the reactions are thermodynamically and kinetically possible and favourable when the impurities are mixed. Since the maximum concentration of a single impurity will depend on the concentration of the other impurities, it is not possible due to lack of data and current understanding to state a fixed maximum concentration of a single impurity when other impurities are, or may be, present.
H ₂	<0,75 mol% ^{e,f}	<4 % total for all non-condensable gasses, but individual contributions may also be significant	
N ₂	<2 mol% ^{f,g}		
Ar	f		
CH ₄	f,g		
CO	<0,2 mol% ^{j,k}		
O ₂	f,hNB. Downstream limitations		
H ₂ S	<200 ^{g,i,k}	Individual values, each below STEL ^m , but see Footnote n.	
SO ₂	Health and Safety <100 ^{k,l}		
NO ₂	Corrosion <50 ⁿ		

^a Industry accepted interpretation of “overwhelmingly CO₂” required by the London Convention and Protocol which came into force in February 2007.

^b The Cortez and Central Basin pipelines in the USA have 630 ppmv H₂O, but it is noted that they also have <26 ppmv of H₂S, <14 ppmv of O₂ and no SO_x or NO_x (see References ^[115] and ^[89]).

^c A figure of 250 ppm is recommended in Reference ^[115] which states “In case of a system shut-in or start-up, the risk of hydrates is low if the water content of the CO₂ stream is below 250 ppm. In situations of rapid depressurization, even a low water content level might not be sufficient to avoid hydrates.” An additional margin has been applied to recognize this. The maximum acceptable concentration will depend on the pressure/temperature operation window. It is recognized that a number of pipelines have been operated for a long time with a target water concentration of 630 ppmv without reported hydrate incidences. See also Footnote b.

^d For measures to avoid hydrate formation, see ISO 27913:2016, C.2.

^e See ISO 27913:2016, C.2 for criteria addressing hydrogen content.

^f The presence of “non-condensables”, particularly, H₂, H₂S and N₂, but also O₂, Ar, CH₄ and CO affects the decompression behaviour of the CO₂ stream^[11], and could affect shear fracture^[22].

^g The presence of “non-condensables” CH₄, N₂ and H₂S can affect the solubility of water in the CO₂ stream.

^h O₂ content to be such that it does not promote acids formation, solids formation and corrosion that adversely affect the operational integrity of the pipeline over the design lifetime, noting that a much lower level of O₂ can be required to avoid unwanted downstream impacts.

ⁱ The Weyburn pipeline has 9 000 ppmv of H₂S^[107], noting that the CO₂ is dry (<20 ppm)^[89], and that the oilfield into which the CO₂ is being injected is already sour.

^j The level of impurity required to cause CO₂-CO cracking under pipeline operating conditions is not yet known. However, it has been confirmed that in order for cracking to occur, water must be present and that the presence of O₂ enhances the susceptibility to cracking.

^k Health and safety impacts of individual impurities within the CO₂ stream are only relevant if their concentration is such that the combined toxic harmful effect of the impurities is greater than the CO₂ itself. For examples, see References ^[115] and ^[116].

^l The presence of H₂S in the CO₂ stream can promote corrosion at lower water levels than in pure CO₂^[79].

^m STEL: Short-term Exposure Limit, the acceptable average exposure over a short period of time, usually 15 minutes as long as the Time Weighted Average is not exceeded.

ⁿ There is experimental evidence that even at levels of <50 ppmv of NO_x and SO_x nitric and sulfuric acid can be formed^[25].

^o Hydrocarbon content could be limited to have a dew point such that condensation does not occur within the operational envelope (combined pressure and temperature) of the pipeline.

Table B.1 (continued)

Species	Indicative levels (volumetric composition in ppmv, unless stated as mol%)	
CO ₂	>95 mol% ^a	
Amine		The presence of amines, MeOH, EtOH, glycols and other water soluble components (e.g. HCl, NaOH, other salts) will facilitate the formation of an aqueous phase (free water) and reduce the concentration of water in the CO ₂ at which a separate aqueous phase is formed. The maximum concentrations that are acceptable will depend on the concentration of the other impurities.
Methanol		
Ethanol		
Glycol		
C ₂ +	<2,5 mol% ^o	
^a Industry accepted interpretation of “overwhelmingly CO ₂ ” required by the London Convention and Protocol which came into force in February 2007.		
^b The Cortez and Central Basin pipelines in the USA have 630 ppmv H ₂ O, but it is noted that they also have <26 ppmv of H ₂ S, <14 ppmv of O ₂ and no SO _x or NO _x (see References [115] and [89]).		
^c A figure of 250 ppm is recommended in Reference [115] which states “In case of a system shut-in or start-up, the risk of hydrates is low if the water content of the CO ₂ stream is below 250 ppm. In situations of rapid depressurization, even a low water content level might not be sufficient to avoid hydrates.” An additional margin has been applied to recognize this. The maximum acceptable concentration will depend on the pressure/temperature operation window. It is recognized that a number of pipelines have been operated for a long time with a target water concentration of 630 ppmv without reported hydrate incidences. See also Footnote b.		
^d For measures to avoid hydrate formation, see ISO 27913:2016, C.2.		
^e See ISO 27913:2016, C.2 for criteria addressing hydrogen content.		
^f The presence of “non-condensables”, particularly, H ₂ , H ₂ S and N ₂ , but also O ₂ , Ar, CH ₄ and CO affects the decompression behaviour of the CO ₂ stream[11], and could affect shear fracture[22].		
^g The presence of “non-condensables” CH ₄ , N ₂ and H ₂ S can affect the solubility of water in the CO ₂ stream.		
^h O ₂ content to be such that it does not promote acids formation, solids formation and corrosion that adversely affect the operational integrity of the pipeline over the design lifetime, noting that a much lower level of O ₂ can be required to avoid unwanted downstream impacts.		
ⁱ The Weyburn pipeline has 9 000 ppmv of H ₂ S[107], noting that the CO ₂ is dry (<20 ppm)[89], and that the oilfield into which the CO ₂ is being injected is already sour.		
^j The level of impurity required to cause CO ₂ -CO cracking under pipeline operating conditions is not yet known. However, it has been confirmed that in order for cracking to occur, water must be present and that the presence of O ₂ enhances the susceptibility to cracking.		
^k Health and safety impacts of individual impurities within the CO ₂ stream are only relevant if their concentration is such that the combined toxic harmful effect of the impurities is greater than the CO ₂ itself. For examples, see References [115] and [116].		
^l The presence of H ₂ S in the CO ₂ stream can promote corrosion at lower water levels than in pure CO ₂ [79].		
^m STEL: Short-term Exposure Limit, the acceptable average exposure over a short period of time, usually 15 minutes as long as the Time Weighted Average is not exceeded.		
ⁿ There is experimental evidence that even at levels of <50 ppmv of NO _x and SO _x nitric and sulfuric acid can be formed[75].		
^o Hydrocarbon content could be limited to have a dew point such that condensation does not occur within the operational envelope (combined pressure and temperature) of the pipeline.		

In ANSI/NACE MR0175/ISO 15156-1²⁾, the onset of Sulfur-Induced Stress Corrosion Cracking (SICC) is related to the presence of water, H₂S and the pH of the fluid being transported. If the pipeline dehydration of CO₂ stream is such that corrosion is not anticipated or no free water is formed, (thus no pH is measurable), it would then not be necessary to assess the pipeline for SICC. If the water content is such that it is likely that a water phase will be present, ISO 15156 addresses how to conduct an assessment to select an appropriate grade of steel.

2) NACE MR0175/ISO 15156-1:2001, *Petroleum and natural gas industries— Materials for use in H₂S-containing environments in oil and gas production— Part 1: General principles for selection of cracking-resistant materials.*

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