Report of the CCUS Forum Expert Group on CO₂ Specifications

'An Interoperable CO₂ Transport Network – Towards Specifications for the Transport of Impure CO₂'

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Executive Summary

The report of the CCUS Forum expert group on CO_2 specifications, supported by the Zero Emissions Platform (ZEP), complements the report on CO_2 infrastructure and provides a common understanding and clear recommendations regarding CO_2 transport specifications.

The expert group makes the following recommendations to the European Commission:

- Develop as rapidly as possible a network code and standards for a multimodal CO₂ transport network in the EU/EEA. Determining these standards and a network code will require the development of scenarios and an analysis of specific considerations for different transport modes, based on fundamental assumptions on the future European CO₂ transport network.
- Develop a strategy and clear targets for a common European CO₂ transport network. This strategy should comprise key components, including a fit-for-purpose regulatory framework for CO₂ transport with non-discriminatory, open-access, multimodal CO₂ transport infrastructure (see report on CO₂ infrastructure). Targets should cover the future size of the network by development stage, the role of each transport mode, and its precise geographical span.
- Support and prioritise research in the identified fields. In addition to providing advice on additional policy actions, the report raises several questions for which further research is requested. This includes, in a non-exhaustive way:
 - o potential interactions between several different compounds in the CO₂ stream (for example the stabilisation of aqueous phases by polar molecules);
 - prediction of phase transitions and the accompanying partitioning of the impurities into the new phases and non-equilibrium phase transition conditions, in the context of multicomponent systems;
 - o potential chemical reactions of impurities within the CO₂ stream;
 - o fundamental research on chemical reactions paths and kinetics;
 - o prediction of the mass flow and the composition in two-phase flows;
 - o dynamics of a pipeline network for CO₂ containing impurities for dense phase transport;
 - the impact of extended two-phase regions on operational procedures for pipeline transport in the dense phase;
 - o challenges resulting from solid phase formation and operational procedures for pipeline pressures above about 2 MPa for transport in gaseous states;
 - o energy-efficient technologies for heating up CO₂ streams;
 - o practical limits regarding the flexibility of mass flows into storage reservoirs;
 - o risks linked to chemical reactions that could result from the mixing of different impurities from different CO₂ streams; and
 - the design of facilities to process the landed CO₂ that could be captured from the exhaust gas of ships.

Safe transport of impure CO₂ streams is possible today. Wherever fundamental understanding of processes is incomplete, the design of transport networks follows common engineering practice: safety factors are applied to make sure that any design is on the safe side. The questions raised in this report aim at an improved design of next generation transport networks, which can be designed more economically if a better understanding of fundamental effects allows for less conservative margins. Improved theoretical understanding alone does not result in better transport networks – it has to go together with experience from practical implementation, which has to start now!

1. Introduction

a) Background

As part of the CCUS Forum, the European Commission has set up a working group on CO2 infrastructure to provide clear recommendations on how to develop and deploy sustainably a European CO₂ transport and storage infrastructure grid to reach climate neutrality by 2050. The European Commission has invited the Zero Emissions Platform (ZEP) to support and coordinate a working group of experts to complement this work and provide clear recommendations on specifications for CO₂ stream transport¹. The medium to long-term goal of the European Commission is to establish a Europe-wide network for CO₂ stream transport, which utilises all transport modes that are required for industry decarbonisation, and which helps establish a European CO₂ market. It is intended for emitters of different sizes to have undiscriminated access to this network. While pointto-point solutions directly connecting large emitters with sinks can define their own specifications for the transported CO₂ stream (with regards to pressure, temperature, impurities...) in accordance to existing national and international standards for CO₂ stream transportation, a multimodal European transport network requires an agreed international network code, which specifies characteristics for CO₂ inserted into different transport modes. Storage requirements have to be considered in case they exceed the quality requirements of the transportation infrastructure, e.g., with regard to allowable impurities. Finally, the goal is to deliver, as closely as possible, economically optimal solutions that consider the whole chain, from capture to storage.

b) Objectives

The objectives of this report and of the expert group supported by ZEP is not to establish standards competing with standards set up by standardisation bodies like the International Organization for Standardization (ISO) or the Comité Européen de Normalisation (CEN-CENELEC). The goal is to provide recommendations on the lines along which characteristics of CO₂ streams can be regulated for multimodal transport and to summarise a knowledge base on which stakeholders can negotiate a network code. It aims at providing high-level guidance for some research activities required to close identified knowledge gaps. The objective is to arrive at specifications that are based on verified knowledge. Wherever science cannot yet provide traceable and sufficiently accurate answers, specifications will have to be stricter than might be necessary, so that safety is always ensured. Costs to comply with these specifications will, as a consequence, be higher than perhaps would otherwise be necessary.

As guiding principles, the expert group has agreed on three statements:

- two-phase flow should be avoided as much as is practicable (If not everywhere and under all
 operational conditions, then at least at measuring points because, using current technology,
 it is not possible to predict the mass flow and in particular the composition in two-phase flows
 with confidence. More research work is recommended);
- the formation of corrosive phases must be avoided;
- the concentration of all impurities in a CO₂ stream should be specified to be such that their health and safety impact is always less than that of the carbon dioxide itself.

¹ ZEP is the technical adviser to the European Commission on the deployment of CCS and CCU – a European Technology and Innovation Platform (ETIP) under the Commission's Strategic Energy Technologies Plan (SET-Plan).

c) Content of this report

Chapter 2 of this report will summarise the relevant assumptions made for the development of the European CO₂ grid. Interfaces between the three principal process steps (capture, transport and storage) will be discussed. Chapter 3 introduces a new distinction that resulted from discussions within the working group: the distinction between "negotiable impurities" (for which allowable concentrations can be optimised in a way that considers the cost minimisation for the whole chain; primarily these are "non-condensable gases" such as nitrogen, argon, hydrogen or methane) and "non-negotiable impurities" (for which excessive concentrations of some impurities would create health or safety issues or could potentially damage some of the hardware associated with high investment costs). Chapter 4 summarises specific considerations for the different transport modes, including buffer storage, the infrastructure required in ports to process CO₂ captured on board of ships, and constraints resulting from injection and storage requirements. Chapter 5 summarises the resulting conclusions and recommendations on specifications for CO₂ stream transport in the European Economic Area (EEA). The report is complemented by an executive summary for policymakers.

2. Assumptions and nomenclature

a) Assumptions on the development of the European CO₂ grid

In the European Economic Area (EEA) the need to transport large amounts of CO_2 is currently being driven by individual projects in some member states linking industrial clusters to storage sites via pipeline or ship transport (*e.g.* Porthos, Aramis, Northern Lights, Greensand...). Consequently, these projects have published or announced their own minimum CO_2 stream quality specifications, reflecting the requirements of the individual storage site or transport medium. These specifications are mostly labelled as 'work in progress' and are partly conservative with respect to pipeline and reservoir integrity, reflecting knowledge gaps. On the other hand, in terms of CO_2 stream purity the requirements are usually specific, reflecting the internationally established minimum of 95 mole-%, with individual constraints on impurities. Lower requirements would presumably be aiming to unlock more sources of CO_2 by avoiding purification except where necessary for a specific technical basis.

If the EU wants to reach its climate goal of net-zero emissions by 2050 and become net-negative afterwards, a rapid increase in storage and transport volumes is going to be necessary. The first objective is to reach at least 50 million tonnes of annual injection capacity in 2030 under the European Commission proposal for a regulation 'Net-Zero Industry Act'. While it is beyond the scope of this document to make recommendations on infrastructure planning, some conditions related to CO₂ stream quality can be identified to ensure that transport capacity is not the bottleneck in the progress towards permanent CO₂ storage:

- 1. Access to infrastructure should be transparent and non-discriminatory. This is already stipulated under Directive 2009/31/EC.
- 2. Intermodality: Emission sources with no pipeline access will have to apply non-pipeline transport (NPT) solutions such as ships, barges, rail cars or trucks. These modes transport CO₂ streams discontinuously in liquid phase, usually at temperatures significantly lower than ambient. Considering the possible pipeline transportation modes "gas phase" and "dense phase", it might lead to two different pipeline sectors (emission collection and trunk lines) with two different CO₂ stream specifications. Hybrid solutions combining pipelines and NPT might also be considered.
- 3. Extension: Future interconnections between early pipeline systems connected to individual storage sites or shipping terminals are likely to improve economic efficiency as well as access.
- 4. Treatment: Overall costs along the value chain are expected to decrease when the optimal locations for CO₂ stream treatment are found.
- 5. Interoperability: Transport systems should be technically interoperable across borders.
- 6. Economic efficiency will be severely compromised if CO₂ streams from different sources cannot be blended as required without violating pipeline integrity criteria, for instance, due to inter-impurity chemical reactions.
- 7. Pipeline Operations: While designing pipeline infrastructure, consideration should be given to bidirectionality and diverse routes. Shut-ins may be necessary during e. g. maintenance and will temporarily impact transport capacity.
- 8. Climate Change: Rising ambient temperatures might affect all transport modes, i.e. pipeline and NPT. For example, maximum ground temperatures may impact transport of CO₂ streams in onshore pipelines, river barge transport capacity could significantly diminish during summer due to low water levels or the maximum travelling time of rail cars may be limited due to increased ambient temperatures raising the temperature of the CO₂ cargo.

- 9. Distances: Infrastructure is likely to be built first in Member States bordering the North Sea. CO₂ streams from Southern European and Central and Eastern Europe (CEE) countries will probably be stored separately or connected to existing infrastructure only at a later stage. Any future legal framework must accommodate transit of CO₂ through Member States.
- 10. Predictability: Lastly, the creation of CCUS value chains constitutes a "chicken and egg" situation. Investments in capture, transport and storage facilities will only be triggered if the other parts of the chain can be reasonably assumed by investors to be in place in time.

Under these assumptions the development of transport infrastructure will be impacted by CO₂ stream composition in several ways:

- 1. Predictability: The need to provide a given CO₂ stream quality can significantly impact both capital expenditure (CAPEX) and operational expenditure (OPEX) for CO₂ capture. Treatment is characterised by diminishing returns. Quantitative optimisation of the total costs of CCS would require finding a CO₂ stream purity that is not too high. Setting a purity requirement for transport infrastructure will ease risk management for today's emitters when weighing mitigation options. This still holds if the purity is not optimal, e.g. because the data used was necessarily incomplete.
- 2. Access: Among other things, non-discriminatory access also means that appropriate specifications should be set to be independent of the CO₂ stream source.
- 3. Intermodality: Batch transport of liquid CO₂ at low temperature has more stringent requirements in terms of CO₂ purity and water content than those for pipelines. Even then some trace components may still compromise reservoir integrity.
- 4. Extension: Bidirectional interconnections without treatment will only be possible if CO₂ stream quality is harmonised.
- 5. Treatment: Higher CO₂ stream purity is always beneficial for transport because it could allow a larger operational envelope, thus reducing risks associated with pipeline operational integrity. Higher CO₂ stream purity can also enable lower pressures for batch transport (e.g. by ship). However, purities that might be preferred for pipelines and storage may impose prohibitive costs on the emitters, since purity comes with additional energy requirements and higher costs. Purification technology possibly implies additional CO₂ emissions, which need to be considered over the whole value chain. There is a possibility that inter-impurity chemical reactions in pipelines may create unwanted intermediate products, e. g. water. The CO₂ stream specification must account for this. Even when this is the case, the possibility still exists when the CO₂ streams originate from diverse processes, that inlet specification limits are exceeded slightly at the exit point due to inter-impurity chemical reactions. Treatments like further drying of the CO₂ stream might be considered as an alternative to the introduction of separate limits for entries and exits but maintaining the non-corrosive nature of the CO₂ stream under all normal, transient, and upset scenarios is key.
- 6. Interoperability: Harmonised national specifications that are suitable for liquid, dense and gas phase would enable transport across borders without technical facilities except for fiscal metering of the CO₂ mass flow. It would also eliminate the need for treatment facilities at intersections involving phase changes (the need for compression/cooling or heating/throttling notwithstanding).
- 7. Economic Efficiency: Will in part be facilitated by source-independent specifications.

- o On the flipside of the accommodation of arbitrary blending, pipeline integrity must not depend on certain trace components being diluted through blending.
- o This report considers linear CCS value chains for the purpose of permanent geological storage. The expected gradual phase-in of CCU will be enabled by e. g. non-discriminatory third-party access. Beyond that no specific requirements resulting from the use of the CO₂ as a feedstock will be considered here. It is however likely that CCU applications will require high purity of CO₂ as well as the absence of catalyst poisons. Higher quality of CO₂ streams will therefore benefit usage by decreasing the need for treatment after transport, but it must be understood that this will come at significant cost to the emitting agency. Demands on CO₂ purity for catalyst-based utilisation processes are very specific; it is considered very likely that a further CO₂ purification optimised for the specific utilisation process is unavoidable.
- 8. Pipeline Operations: When designing pipeline infrastructure, consideration should be given to bidirectionality. Flow assurance is an issue and needs to be considered (see ISO/TR 27925), especially during shut-in operations, which may be necessary, e.g. during maintenance, and will temporarily impact transport capacity because the temperature and pressure of the CO₂ stream can assume any ground or water temperature. The composition of the CO₂ stream will determine the maximum saturation pressure within that temperature interval. The saturation pressure, in turn, will determine the pipeline wall thickness required to rule out Running Ductile Fractures (RDF) in dense phase pipelines. Higher CO₂ stream purity will result in lower pipeline wall thicknesses and, potentially, significantly reduced CapEx, especially if the maximum temperature is low.
- 9. Climate Change: Rising ambient temperatures might affect all transport modes, i.e. pipeline and NPT, (see above item 9). Elevated ground temperatures will result in elevated saturation pressures, requiring thicker pipeline walls, in particular when considering impurities and the effect on saturation pressures.
- 10. Distances: For long distances dense phase pipelines will usually be economically more advantageous than gas phase transport. The minimum pressure in dense phase is lower if CO₂ stream purity is higher, and allowable pressure drop is therefore higher.
- b) Interfaces between capture, transport and storage

It is generally accepted that the purity requirements for the initial transport mode are most effectively met at the capture plant. Additional purity requirements resulting from transport modes further down the transport chain (e.g. ships) may either be met at the capture plant or by post-processing in local hubs before the transport modes are changed.

Most operational CCS systems and mature projects are isolated value chains in which specifications are tailored to the planned transportation mode and stores. An EU-wide connected system for CCS could introduce several transport modes in series between capture and store and introduce interfaces in between those. The full combination of these transfers is summarised in the table below² and discussed per receiving transport mode hereafter (noting that water removal is one of the "Purification" steps):

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² Definitions of the terms used in this table can be found under 'Nomenclature'.

| То | Gas phase | Dense phase | MP shipping | LP shipping | Rail and truck |
|-------------|-------------|-------------------------|----------------|--------------|----------------|
| From | pipeline | pipeline | (14-17.5 bara) | (6.5-8 bara) | |
| Gas phase | | Fully | Purification | Purification | Not likely |
| | | compatible ³ | | | |
| Dense phase | Exceptional | | Purification | Purification | Not likely |
| MP shipping | Not likely | Fully | | Unexplored | Fully |
| | | compatible | | | compatible |
| LP shipping | Not likely | Fully | Unexplored | | Fully |
| | | compatible | | | compatible |
| HP shipping | Unexplored | Unexplored | Unexplored | Unexplored | Unexplored |

Compared to dense-phase transport, CO₂ stream transport in the gas phase is relatively energy inefficient for large-scale transport. It is an option for a collection network within an industrial cluster but not expected to be the final mode of transport towards the injection site unless in the early stages of injection into a depleted gas reservoir, or the pipelines need to pass through or close to, dense population centres. As such the transfer into a gas phase system from the other transportation modes is classified as exceptional but might be required for integrating of portions of repurposed pipelines.

A pipeline for a dense phase CO_2 stream transportation system that must be depressurised below the critical pressure for maintenance activities (e.g. valve inspection) will pass through the gas phase state as the CO_2 is boiled off inside the pipe. This rare upset condition is likely to drive CO_2 stream specifications to be similar to those for the gas phase, as the formation of a separate corrosive liquid phase during depressurisation is also an undesirable event.

CO₂ stream processing units, which feed into a dense phase pipeline, are typically based either on compression and cooling, when starting from gas phase, or based on pumping and heating of the CO₂ stream when starting from liquid phase. If no further processing is intended at the interfaces between the different transport modes (gas or dense), this implies that the CO₂ stream specification for the gas and shipping compositions must be the same as for the dense phase pipeline. This includes CO₂ stream requirements to ensure that crack growth by RDF is avoided, and also to avoid the formation of strong acids in dense phase CO₂ streams at low temperatures. The minimum pressure in dense phase can be lower if CO₂ stream purity is higher, and the allowable pressure drop is therefore higher. Compression from gas phase conditions to dense phase conditions becomes less energy intensive for low concentrations of non-condensable gases. In this case, the gaseous CO₂ stream can be compressed to an intermediate pressure and can be liquefied by heat removal at this pressure level, before an energy effective pump is used to increase the pressure to the final pipeline pressure. High concentrations of non-condensable gases increase the dew point pressure and do not allow for the application of pumps

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³ In the case where gas-phase transport allows for high concentrations of non-condensables, removal of some non-condensables might be necessary. To include emissions from small emitters, it may be advantageous to define demands for gas-phase pipelines with largely unprocessed CO₂, which then has to be processed at processing hubs downstream.

at pressures substantially below pipeline pressure (see Section 3.b). However, since the cost for additional purification may be very high, the overall economic case should be considered⁴.

Refrigeration of CO_2 streams for shipping requires significantly higher purity levels compared to those necessary for pipeline operation. Without purification⁵, impurity levels typical for various capture processes drive liquefication conditions to a combination of high pressure (25 bar) and lower temperature (< -30 °C)⁶.

Ships need to receive liquified CO₂ (LCO₂) at conditions around their lowest allowable operating pressure to manage pressure build-up during voyage as required by the IGC Code⁷:

- Venting of the cargo to maintain cargo tank pressure and temperature shall not be acceptable.
- The containment system (cargo storage tank on the ship) insulation and design pressure shall be adequate to provide a reasonable margin for the operating time and temperatures.

To meet the above requirements, a ship or barge suitable for a trade typically of 15 to 21 days is used for international shipping considering the voyage and the associated weather delays. The present ship designs do not include any conditioning equipment for managing boil-off gases at medium-pressure (operating range of roughly 14 bara to 17.5 bara); instead they rely on pressure retention. The same approach is also adopted in the development of liquid petroleum shipping⁸.

In addition to agreeing the maximum impurity levels for specific components to avoid corrosion, the level of inerts (non-condensable gases) acceptable for transfer into a ship may be specified on a combination of operating pressures and temperatures (the latter being the boiling temperature at that pressure) and accept the resulting impurity-levels of the inerts within the CO_2 stream. The transfer of refrigerated CO_2 into ships results in the reverse transfer of vapour returns. Ship pressure control during loading results in vapour return with a higher volume than that of liquid transferred, thereby creating a demand on the export terminal for a boil-off gas (BOG) system. The impurity levels of low boiling components such as H_2 , CO, NO and H_2S will be high in the vapour return gas, but predicting the actual composition in practice is difficult. Ship vapour return can introduce impurities into the liquefaction unit that handles the boil-off gas, which are unexpected and there is a risk that the accumulated levels might drive the LCO2 off spec. Specifications for liquid phase transport need to consider this possible enrichment effect; further research and some practical experience will help to avoid overly strict limitations.

⁴ Conversion from liquid phase at low temperature to dense phase at ambient temperature requires a substantial amount of heat. For the environmental assessment of the process, it is important that this heat is supplied in an efficient way.

⁵ Enrichment of low boiling impurities, such as water and SO_x, in the remaining dense phase has to be considered. The corresponding effects are not completely understood yet

⁶ Engel and Kather, 2018. Example provided by Figure 2 in <u>Improvements on the liquefaction of a pipeline CO₂ stream for ship transport</u>, 2018, https://doi.org/10.1016/j.ijggc.2018.03.010.

⁷ International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code), International Maritime Organisation.

⁸ Notaro, Gabriele and Belgaroui, Jed and Maråk, Knut and Tverrå, Roe and Burthom, Steve and Sørhaug, Erik Mathias, 2022. <u>Ceto: Technology Qualification of Low-Pressure CO₂ Ship Transport</u>, Proceedings of the 16th Greenhouse Gas Control Technologies Conference (GHGT-16), http://dx.doi.org/10.2139/ssrn.4272083.

The combined liquefaction and purification will increase costs but will also create a side stream and lower the CO₂ recovery in the liquid product. CO₂ recoveries of 96-98% have been calculated in simulation studies⁹. Moreover, the side stream has a significant CO₂ content and will most likely contain low-boiling components such as CO, CH₄, and NO that cannot be simply vented. Integration of the purification unit with the capture unit and the manufacturing complex can provide an outlet for this stream. The presence of an outlet for this stream at the harbour is key, and concepts for its effective management need to be developed.

Under the EU ETS directive each step in the CCS value chain must be monitored using a form of mass balance approach, where some of the CO_2 stream entering or leaving the installation (i.e. at the custody transfer points) is monitored using continuous measurement systems¹⁰. The loss of a few percent of CO_2 is a significant penalty. Current means to measure the mass flow (with an uncertainty of 1% to 2%) are not sufficiently accurate to determine small losses by differences between two large flows. The accuracy of mass flow measurements should be improved further. Whereas LCO_2 terminals under development aim to identify and include 'no regret' items to allow handling of LCO_2 at LP conditions in the future, the transfer of LCO_2 between two pressure levels is unexplored. A CO_2 specification for LP shipping is expected to be more stringent for water content, but data is lacking for other components.

A particular interface between transport and storage is for solid impurities (particulate matter) as these can directly impact injectivity. Stringent specifications on particulate content (total suspended solids) are very well known in well interventions and produced water re-injection schemes from oil and gas operations. The requirement can be linked to the target reservoir by the bridge theory¹¹. The removal of solids >5 micron is required even for the best reservoirs under matrix injection and more stringent requirements are typical for most reservoirs under study in the North Sea. A specification for particulate matter across the value chain is key to enforce discipline in pipeline commissioning and avoid frequent filter change-out directly upstream the offshore well.

c) Nomenclature

Relevant states of carbon dioxide (CO₂) as they are named in this report (see also Figure 2):

Gas phase

denotes states below the vapour pressure of pure CO_2 , specifically those below the pressure on the saturated vapour line of CO_2 -rich mixtures. In the context of this document, the term gas phase refers to fluid CO_2 with a density normally below 100 kg/m³. At these states, compressors have to be used to increase the pressure further. denotes states above the vapour pressure of pure CO_2 , specifically those above the pressure on the saturated liquid line of CO_2 -rich mixtures at close to ambient temperature. In the context of this document, the term dense phase refers to fluid CO_2 with a density above 500 kg/m³, whereby densities in dense phase pipeline transport will be above 750 kg/m³ in most cases. At these states, pumps can be used to increase the pressure further.

Dense phase

⁹ Deng, Roussanaly and Skaugen, 2019. Appendix B in <u>Techno-economic analyses of CO₂ liquefaction: Impact of product pressure and impurities</u>, 2019, performance of state-of-art designs is scarce, https://doi.org/10.1016/j.ijrefrig.2019.04.011.

¹⁰ Section 8.3 in EU monitoring and reporting regulation Guidance Document No.1, Version, 10 February 2022.

¹¹ The effect of solid impurities on field operations, FTC white paper.

Liquid phase denotes states on the saturated liquid line of CO₂ or of CO₂-rich mixtures in tanks of

ships or train cars (LCO₂). CO₂ or CO₂-rich mixtures in tanks are commonly transported as saturated liquid. Saturated liquid implies that there is a saturated vapour phase above the liquid, which fills the headspace of the tank. However, in general the mass of the saturated vapour is very small compared to the mass of the saturated liquid in

the tank. The density of CO₂ in the liquid phase typically exceeds 1000 kg/m³.

Vapour phase denotes states on the saturated vapour line of CO₂ or of CO₂-rich mixtures. The density

of CO_2 in the vapour phase is typically below 60 kg/m³.

Solid phase denotes solid CO₂, typically at temperatures below -54 °C. Solid CO₂ is frequently referred to as dry ice, even though dry ice technically is a compressed form of solid

CO₂. Without compression, solid CO₂ has a more snow-like appearance.

The following abbreviations and terms are used throughout the report:

- **Auto refrigeration** of CO₂ refers to the effect that the temperature of a CO₂ stream decreases as the pressure is reduced without (sufficiently large) heat input from the outside. Compared to other fluids, this effect is particularly strong in CO₂. Expansion of CO₂ can result in temperatures below -50 °C and even in the formation of solid CO₂.
- Carbon Capture and Storage (CCS) refers to the process that consists of CO₂ capture at the emitter's site, processing of the captured CO₂, transport to a storage site and injection for permanent storage in a safe geologic structure.
- Carbon Capture and Utilisation (CCU) refers to the process that consists of CO₂ capture on the emitters site, processing of the captured CO₂, transport to a utilisation site and utilisation of the CO₂ as part of a different value chain.
- CO_2 stream refers to a stream of captured CO_2 , which necessarily contains impurities. The overwhelming majority of the stream is CO_2 (at least > 95% on a molar basis).
- **Corrosion resistant alloy (CRA)** refers to highly alloyed stainless steel alloys in the context of this document.
- **Direct air capture (DAC)** refers to technologies that separate CO₂ that is contained in ambient air at low concentrations.
- **European Economic Area (EEA)** denotes the members of the European Union plus Iceland, Lichtenstein and Norway, which form a single market. Switzerland is not part of the EEA but part of the single market. The UK is neither part of the EEA nor of the single market but remains an important partner in European CCS activities.
- **Impurities** are components in a CO₂ stream other than CO₂, which are typically present at low concentration.
- **Intermodality** refers to transport schemes, in which different transport modes (e.g. pipeline transport and ship transport) interact in the sense that CO₂ is transferred from one mode to the other on its way from source to sink.
- **Interoperability** refers to the ability of transport systems developed in different countries to enable transport of CO_2 over boarders without technical or legal restrictions.
- **Joule-Thomson effect / coefficient** describes the temperature drop that results from pressure reduction without heat input from the outside.
- Linear CCS value chain refers to a value chain, where CO_2 is separated and transported to storage, without using a part of the CO_2 as, e.g., chemical feedstock, which is part of a different value chain.

- Low pressure (LP) shipping refers to ship transport of CO₂ in large vessels, which are expected to operate at tank pressures of about 7 bar and at temperatures around -50 °C. Yet no vessels operating at LP conditions have been build.
- **Liquefaction** refers to a change to the liquid phase in the context of this document; the process involves cooling to temperatures typically below -20 °C.
- Medium pressure (MP) shipping refers to ship transport of CO₂ in relatively small vessels, which typically operate at tank pressures between 13 and 18 bar and at temperatures between -35 °C and -22 °C without liquefaction system for boil-off gas, thus allowing for pressure build up during transport.
- **Network code** is a document that defines the physical parameters of a CO₂ stream to be injected into a CO₂ transport network. It is the basis, upon which commercial arrangements can be negotiated.
- Non-condensable gases are components in a CO₂ stream that, as pure fluids, cannot become liquid at the temperatures that are characteristic for processes with CO₂. Nevertheless, a liquid or dense phase CO₂ stream can contain small amounts of such non-condensable gases. Typical non-condensable gases are nitrogen, argon, oxygen, hydrogen, methane, and hydrogen, which may be found as impurities in CO₂ streams depending on the origin of the CO₂.
- Running Ductile Fraction (RDF) describes a failure mode, where a puncture of a pipeline develops into an open crack over a significant length along the pipeline. Due to the phase behaviour of CO₂, pipelines transporting CO₂ in the dense phase are particularly sensitive to RDF and need to be designed in a way that avoids this failure mode.

3. Impurities

When discussing CO₂ stream quality regarding the interoperability of infrastructure and investors predictability, a distinction can be made between two categories of impurities:

- 1. Hazardous impurities are those with an impact on health and safety or the integrity of pipelines or geological reservoirs. Established limits for each of these components are in the ppm or ppb range. Due to their possible severe impact on integrity or health and safety, the concentration of the impurities in the CO₂ stream is not subject to economic considerations and is therefore non-negotiable.
- 2. Non-condensable impurities whose partial removal becomes necessary to enable flow assurance and simply to leave more room for CO₂ in reservoirs. In summary, several percent of these components are usually considered acceptable, with a CO₂ stream minimum purity of 95 % being an internationally recognised standard. Since the effect of these impurities can be controlled by technical means and since low levels of non-condensable impurities in general reduce OPEX, CAPEX and energy demand for transport, while they increase OPEX, CAPEX and energy demand for purification, they might be subject to economical optimisation and are therefore negotiable. Examples include H₂, N₂, Ar, and CH₄.

a) Hazardous impurities

Health, Safety, and Environment (HSE) related limits cannot be subjected to economic optimisation. Many, but not all, corrosion and other phenomena related to hazardous impurities will not arise if corrosion-resistant alloys (CRA) are chosen (and others which are not found with carbon steel might be identified), but their higher cost compared to carbon steel means that this option is not normally chosen. Good Process Engineering methods should be applied at all times to produce a safe system.

Toxic components such as carbon monoxide (CO), hydrogen sulphide (H_2S), nitrogen oxides (NO_x) and sulphur oxides (SO_x) must be limited to satisfy the requirements of occupational and external safety. In case of release of a CO_2 stream, risks should be limited to that of exposure to CO_2 alone. Since most toxic components have a higher volatility than CO_2 , they will accumulate in the gas phase if a CO_2 stream is released to the environment as a multiphase flow consisting of gas and solid particles. The resulting concentrations can be calculated using appropriate models. Alternatively, all toxic molecules can conservatively be assumed to be present in the gas phase.

Corrosion of carbon steel is possible if an aqueous phase forms within the CO_2 stream. Compared to natural gas pipelines, for instance, the resulting corrosion rates are much higher because CO_2 and water will form carbonic acid in this phase. Oxygen (O_2) will also promote corrosion when dissolved. Furthermore, some combustion products like NO_x and SO_x can form the much more potent nitric and sulphuric acids. Some impurities can enable the formation of an aqueous phase, even if the water content is sufficiently low to be normally fully dissolved in CO_2 . The most prominent examples are glycols, whose use should be ruled out entirely until reliable results on applicable concentrations are available if transfer into the pipeline is possible. To a lesser extent this effect is also known from methanol and, crucially, amines. The maximum allowable impurity levels need to be determined covering the operating pressure and temperature window for the entire multimodal transport system (gas/dense phase/NPT).

CO/CO₂ stress corrosion cracking¹² is another possible phenomenon that should be avoided, and research work to define this, and examine at what level of CO this ceases to be a problem needs to be carried out.

The integrity of geological reservoirs may be compromised, for instance through caprock degradation or precipitation of iron oxides. This can be caused by the presence of O₂, NO_x or SO_x. Since water will be present underground, the use of corrosion resistant alloys (CRA) will often be necessary, for instance, in permanently wetted components. With sufficient amounts of NO_x/SO_x, especially in shutin conditions, the droplets of water may show very low pH, leading to conditions outside of the application window of super duplex and similar steels (the classic CRAs). At the present time there are no standardised tests to assess this behaviour. Limits on impurities may therefore be governed by either HSE or integrity criteria.

b) Non-condensable impurities

These impurities include hydrogen (H_2) , nitrogen (N_2) , argon (Ar) and hydrocarbons (mainly CH_4). While for any pure fluid the phase change between gas and liquid can be charted as a line in a p-T diagram, these components (on their own or in combination) lead to an envelope where both phases are present. While the thermodynamic states of saturated vapour (dashed lines) are only slightly shifted towards higher pressures even at temperatures close to the critical temperature, the pressures of saturated liquid (solid lines) can be raised substantially dependent on the concentration, especially in the case of hydrogen (Figure 1). Where possible, states within the two-phase region (between saturated vapour and saturated liquid line) should be avoided for CO_2 stream transport, at least in pipelines.

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¹²M. Gonuguntla et al., Wet CO-CO₂ stress corrosion cracking in CO₂ transport pipelines, Corrosion 2023, paper number 19052, Houston TX, AMPP 2023.

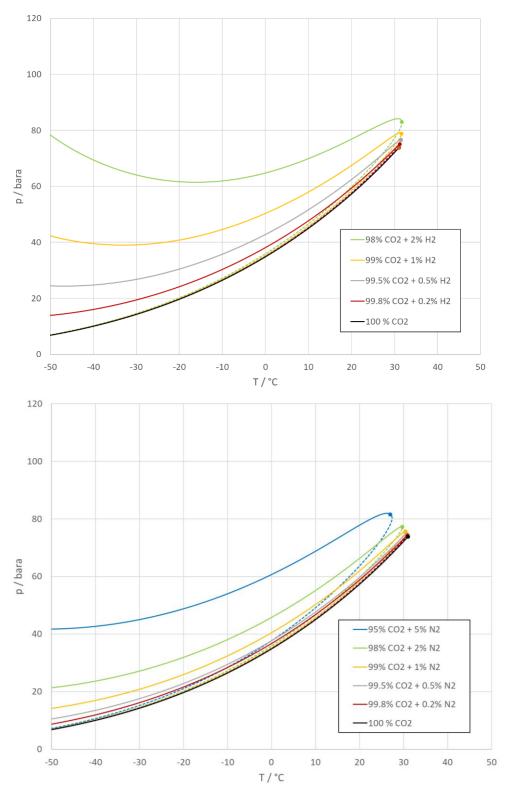


Figure 1: Influence of hydrogen and nitrogen impurities on the phase envelope of CO₂ streams, according to TREND and RefProp.

For dense phase pipeline transport, a large fraction of non-condensable results in a higher minimum pressure and thus lower allowable pressure drop and capacity. Costs for the transport of impure CO₂ may rise because it is necessary to increase the pipeline wall thickness to cater for the increased Maximum Operating Pressure, operational events caused by fluid hammer and to avoid RDF. This

impacts the CapEx depending on the saturated liquid pressure of the transport fluid. Current basis for design, accounting for RDF (DNV RP F104 13), effectively limits the pipeline diameter, and the one large-diameter pipeline may need to be replaced by parallel pipelines of smaller diameter. Standards and codes may need subsequent adaption to allow for larger diameters, and by this reduce the number of pipe strands for large clusters. For pipeline transport of gaseous CO_2 streams and geological storage non-condensable gases will simply result in lower capacity.

In the case of NPT at low temperature liquid conditions (LCO₂), limits imposed on non-condensable impurities are significantly lower than for pipeline transport or storage. This is because the Maximum Operating Pressure of tanks is directly related to the saturated liquid pressure – in the tank there is always a two-phase system, in which the state of the liquid corresponds to saturated liquid with roughly the medium composition, while the state of the gas phase above the liquid corresponds to saturated vapour at the same temperature and pressure, but with deviating composition. Wall thickness is proportional to Maximum Operating Pressure and related to CapEx. It is also limited to around 50 millimetres due to welding constraints.

Limits on non-condensable impurities for pipeline transport should consider the costs incurred for their removal during capture and/or before Non-Pipeline Transport. It should be considered that the purity requirements for shipping transport are more onerous than those for pipelines. If an intermodal spine transportation system is to be realised, then the purity of the CO₂ stream is a fundamental decision. If the CO₂ grid is designed around shipping transport then all emitters will need to comply and additional costs will be borne by them compared to a design around pipeline transport, but further processing downstream can be avoided. A CO₂ grid built around a pipeline standard would require further processing of the CO₂ stream to bring it to shipping standard, but the rest of it could be exported by pipeline. Addressing this matter as a design basis decision requires a clear vision for CO₂ stream transport and will be influenced by the route by which it is envisaged that the majority of the CO₂ will be exported and the relative costs thereof. Differences in the availability of electrical power and heat resulting from the considered processes and from local constraints may have a significant impact on the results. Energy efficiency and energy integration are important criteria for the optimisation of all elements of the CCUS chain.

¹³ DNV-RP-F104 "Design and operation of carbon dioxide pipelines, Recommended practice", Edition 2021-02 - Amended 2021-09.

4. Specific considerations

a) Dense-phase pipeline transport

For the purposes of this document dense-phase pipeline transport is defined as transport of CO_2 streams with a density above 500 kg/m³. This includes liquid states and an adjacent part of the supercritical domain, see Figure 2. This handy value is defined from a technical perspective based on the experience that for 500 kg/m³ and above, pumps can normally be used for maintaining the operational pressure.

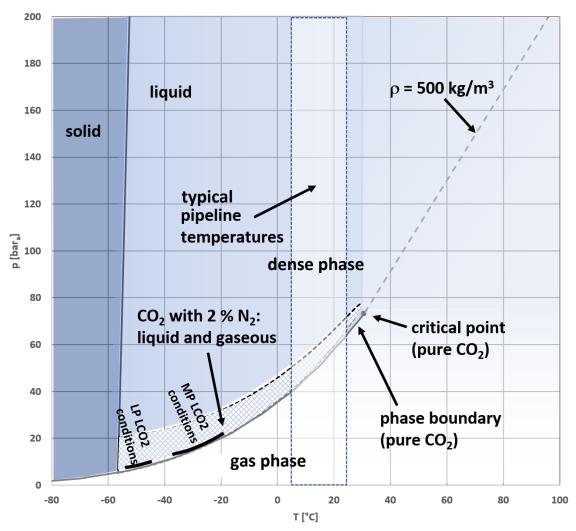


Figure 2: Phases of pure and impure CO₂

Within this range factors, like low compressibility and rotor dynamics, allow for pressurisation using pumps rather than compressors. Along with the higher pipeline capacities, the resulting comparatively low energy demand of these pumps results in lower transport costs at least over distances sufficient to make up for any increased energy demand of initial compression and cooling. Allowable pressure drops are limited by the saturated liquid pressure for the given composition and temperature.

For larger CO₂ streams high-density transport may be the only option permitted by route planning considerations due to the smaller pipeline diameters required. High-density CO₂ is a powerful solvent, and no inner pipeline coating system is currently known to maintain its integrity in this environment.

That means that surface roughness and thus pressure drop and OPEX cannot be decreased further through internal coating.

When released in an uncontrolled manner, CO_2 streams can reach temperatures of -78.5 °C and form a solid phase (below 5.2 bar), which will sublimate over time. The dynamics of the pipeline system needs to be fully considered, but the required wall thickness will usually be governed by the requirement to arrest a Running Ductile Fracture. The resulting wall thickness will largely depend on the CO_2 stream purity and, in particular, the hydrogen content. Water content for the CO_2 stream is best measured using mass spectrographs at the moment. Entries exceeding their limits can be shut off.

While high density pipeline transport is an established technology, some design or operation parameters are usually chosen conservatively based on experience without detailed quantitative knowledge of some of the underlying mechanisms. In particular further research in the following areas could lower future costs of the technology:

- The methodology for design against RDF laid out in DNV RP F104 is based on limited experimental data with modern X60 and X65 materials. Hence, the method is strictly applicable only to those materials which could be a major limiting factor. Other pipelines using other material types, for example X70 and X52, should not be designed or re-purposed by this method. Additionally, the standard *de facto* limits the pipeline diameter which can be used for dense-phase CO₂ transport. The most obvious option to overcome this situation is to enhance the scientific and technical understanding by conducting more mid-scale or full-scale tests.
- Impact of impurities on the formation of an aqueous phase, either through absorption or creation of water through chemical reactions.
- Concepts for tracking or monitoring of all relevant impurities.
- Develop and validate models to predict the formation of solids from water, hydrogen and other hydrate-building species.
- Investigate whether an aqueous phase is a necessary condition for corrosion or if it can also be facilitated by, for example, adsorption effects.
- Dynamic simulation of the pipeline grid to identify challenges from dynamic reactions and to trace impurities.

b) Gas-phase pipeline transport

Gas phase transport carries the potential for a second phase to be formed by condensation, and the impurity levels will need to be set such that this is an unlikely event. Formation of a liquid phase is undesirable because it can cause severe operational problems. For pure CO₂, the temperature-dependent vapour pressure establishes the upper pressure limit for gas phase transport. For CO₂-rich mixtures, the corresponding pressure on the saturated vapour line (the dew point) depends not only on temperature, but also on the concentration of less volatile impurities in the CO₂. The most common of these impurities is water, which can lead to the formation of a corrosive liquid phase. Thus, for the layout of gas phase pipelines it is important to limit impurities in the CO₂ stream to a level at which no condensation occurs for maximum operating pressure and minimum operating temperature. Phase equilibria for CO₂/water systems are well described, limits for allowable water contents can in principle be calculated as a function of pressure and temperature in the pipeline. For temperatures

operating below approximately 10 °C, hydrate and ice formation have to be considered when two phase formation is investigated.

However, there is a strong interaction between water and other impurities such as SO_2 , SO_3 , and NO_x , which can result in the formation of an acidic liquid phase at pressures below the dew point pressure of CO_2 containing only water. This influence, which is known as "acid dew point" in typical combustion gases, is less well described for CO_2 -rich mixtures. Initial specifications for allowable contents of combined impurities have to be conservative, potentially resulting in additional cost for CO_2 processing. Further research is recommended to derive traceable limits.

Other impurities that may lead to the formation of a second phase are traces of capture agents like amines, amine mixes or ammonia. To specify allowable concentrations for capture agents, the possible formation of a solid phase has to be considered; models allowing for an accurate description of the corresponding phase-equilibria in CO₂-rich mixtures are not yet available, as a result of which specifications have to be conservative.

In experiments, corrosion (at relatively low rates) has been observed at states at which existing models do not predict the formation of a free corrosive phase. Whether the possible formation of a liquid-like layer by adsorption on metal surfaces is the reason for these observations should be investigated further.

Non-condensable gases (such as nitrogen, argon, oxygen, methane, hydrogen) increase the pressure on the saturated vapour line and have therefore no adverse effect on allowable pipeline pressures in gas-phase transport. Still, their maximum concentration should be specified because they increase the required compression work and the volume flow in the pipeline. Except for oxygen, this limitation can be guided by purely commercial aspects; low limits may go along with increased energy consumption and CO_2 slip during processing. The allowable oxygen content can be limited to a low value as an additional safety measure against corrosion but needs to be low to avoid adverse effects in the storage media.

As explained above, the maximum operating pressure of a gas-phase pipeline is given by the pressure on the dew line, which depends on temperature. Thus, the allowable operating pressure will largely depend on the expected operating temperature – of course the effect of impurities described above must be also considered. High pressure levels reduce the relative pressure loss along the pipeline. A network-code for gas-phase CO₂ stream transport should define standard pressure-levels to allow for the development of standardised equipment.

Operating procedures, e.g. for venting of pipelines or shut-in in depressurised pipelines, and case studies for pressure-loss scenarios must consider the particularly strong Joule-Thomson effect in CO₂. Upon quasi adiabatic expansion from the gas phase, CO₂ at a pressure above about 2 MPa can form a liquid or even a solid phase. States that may result in the formation of a liquid phase are indicated in yellow in Figure 3; states that may also result in the formation of a solid phase upon expansion to less than 5.2 bar are indicated in orange. This drives the harmonisation of specified impurity levels in both gas-phase and dense-phase pipeline transport, since similar effects arise for depressurisation of dense-phase pipelines as well. However, the influence impurities have at this point is not well investigated yet. Formation of hydrates or water ice is likely and needs to be checked, based on the allowed water content, considering the effect of potentially hydrate-forming impurities as well.

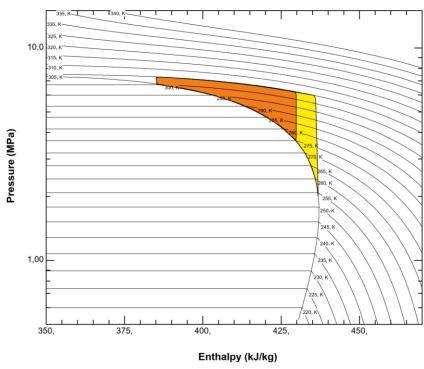


Figure 3: States relevant for gas-phase transport, at which adiabatic expansion of gaseous CO₂ leads to liquid (yellow) or for expansion pressures below 0.516 MPa even to solid (orange) formation.

In the long run, gas-phase pipes and pipelines carrying largely unprocessed CO_2 streams from small emitters to processing hubs, where the CO_2 is dried and purified for further transport, may become commercially attractive. Gas phase transport of largely unprocessed CO_2 streams results in a number of challenges that have not been properly addressed yet. This includes suitable choices for (corrosion resistant) materials, safety regulations and operational procedures avoiding the formation of a solid phase. An example of this would be where different CO_2 sources in an industrial area employ a central capture/processing facility which may be operated by an independent entity.

c) Buffer storage

Buffer storage of CO₂ streams is needed to balance intermittent with continuous flow. An example would include delivery by ship into a port and subsequent introduction into a transportation infrastructure or geological storage facility, both of which operate best under steady-state conditions. Thus, the capacity of buffer tanks has to be adapted to the size and frequency of delivered charges.

To combine high capacity with low weight and costs of buffer tanks, storage of liquid CO_2 (LCO₂) at low temperatures is technically and economically advantageous. For pressure levels and temperatures in buffer tanks the same considerations apply as for ship transport (see Section 4.d). The same is true for allowable impurities. If CO_2 is delivered to the buffer as gas phase or dense-phase stream, the low temperature liquefaction process is energy intensive, but it offers the potential for relatively simple removal of non-condensable impurities like air components. For the storage facilities themselves, experience from industrial gas companies already exists for the storage of pure CO_2 (e.g. Linde, Air Liquide). Design codes and regulations (e.g. from the European Industrial Gases Association) are available as well. For impure CO_2 , the Northern Lights project can act as an example.

No technological issues that would inhibit buffer storage of CO_2 streams are known. However, storage of CO_2 containing impurities requires consideration of some additional engineering aspects, in particular when the composition of the delivered CO_2 stream is not constant over time. In this case, e.g., tanks may need to be designed in a way that avoids "roll over"-like effects due to different densities and boiling points of different CO_2 -rich mixtures. In case the CO_2 stream leaving the buffertank needs to be heated up to pipeline or injection conditions, the energy efficiency of the process requires special attention.

d) Ship transport

As an alternative to pipeline transport, liquid CO₂ (LCO₂, liquid CO₂ at low temperature and medium to low pressure levels below 20 bar and above 5.2 bar) transport by ship is a link in the CCS chain. Ship transport requires considerable CAPEX investment for liquefaction, storage and vessels, coupled with higher liquefaction power requirements compared to the initial pipeline compression. Emitters that do not have access to local sequestration may need to access remote storage sites that are only accessible through marine routes. These could benefit most from LCO₂ transport. Ship transport of LCO₂ is also important where land or near-shore storage capacity is insufficient for delivery by pipeline, or where CO₂ stream has to be delivered to remote locations rich in renewable power as part of CCU concepts. Hence, LCO₂ transport is a key element in the CCS chain to provide flexibility and options that can minimise the total cost of carbon abatement.

A generic depiction of a CCS chain that involves LCO₂ transport is shown in Figure 4. In addition to the LCO₂ shipping vessel, the terminal requires a liquefaction system and potentially some additional treatment upstream of liquefaction. It also requires LCO₂ storage that holds the CO₂ stream cargo between loadings. Similar storage facilities may be required at the reception location to allow a moreor-less constant flow into the store.

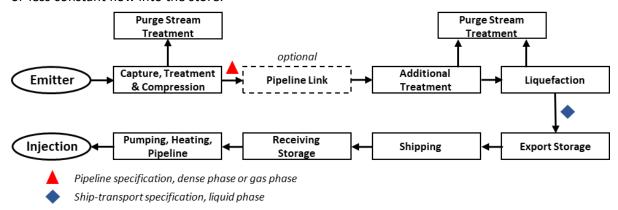


Figure 4: Generic CCS chain with LCO₂ link

Given the focus of this report on CO_2 stream specification, the different LCO_2 shipping and storage conditions that could influence CO_2 stream specification requirements need emphasising. Three potential shipping conditions have been discussed within the industry:

 High Pressure (HP): Operating at near ambient temperature and correspondingly high pressure (higher pressure than for MP & LP transport, which operate at lower temperatures).

- HP shipping can be considered a transport mode in development but is not currently the main focus of the shipping industry.
- Medium Pressure (MP): ≈13 bara, with pressure rising during the voyage up to approximately 18 bara. MP shipping is commercially available for the current LCO₂ trade. For pure CO₂ the operating temperature after loading saturated liquid at 13 bara is -32°C.
- Low Pressure (LP): ≈7 bara, with on-board refrigeration for boil-off gas (BOG) management. LP shipping is not currently commercially available. Pure CO₂ saturated at a pressure of 7 bara would operate at -49°C. On-board refrigeration would maintain this condition with limited pressure rise during the voyage.

The transport of CO_2 as boiling liquid at low temperature results in high demands on purity. Especially the concentrations of water and volatile compounds need to be maintained at very low levels. The presence of water might lead to freezing and the stabilisation of aqueous phases and hydrates, while higher levels of volatile compounds would decrease the bubble point temperature, thus the temperature in the tank at which the CO_2 stream has to be transported. The motivation for LP shipping is to achieve economies of scale by transporting larger volumes over longer distances. Minimising shipping costs might turn out to be critical to optimise the value chain and can possibly be achieved with LP LCO_2 shipping due to the lower pressure requirements. But all of this comes at the cost of even higher purity requirements of the CO_2 stream.

The following recommendations can be made:

- 1) It needs to be decided, whether a common value for water content within the CO₂ stream is specified for both LP and MP shipping, as it may have only minimal or no impact on cost or technology selection for dehydration and it would simplify the LCO₂ specification requirements.
- 2) Separate recommendations for LP and MP LCO₂ based on temperature rather than composition are made and justified as follows. Since the solubility of volatile compounds is low at LP conditions, it will be difficult to establish a composition-based allowance of volatiles that can be reliably measured and designed for. Instead, it is recommended that a *minimum temperature* for the bubble point at given pressure is specified. In case of LP shipping, this temperature should provide a reasonable margin to the triple point or phase boundary of solid CO₂. A preliminary temperature of -52°C at 7 bar could be applied; this results in a purity requirement of approximately 99.9%.
- 3) The same rationale for a temperature-based specification should be applied to MP shipping. Taking additional engineering considerations into account, a recommendation with a minimum temperature of -40 °C at 13 bar could be made. This results in a LCO₂ purity of approximately 99.5% and allows for sufficient margin for pressure build-up during transport (MP tanks usually allow for a maximum pressure of 18 to 20 bar). However, currently only tank materials for a minimum temperature of -35 °C are qualified in shipping codes. With a security margin, loading at -30 °C with 99.5% purity (with N₂ as main impurity) would result in an initial pressure of about 17.6 bar, leaving too little room for pressure build-up. Tank materials qualified for lower temperatures are urgently required.

However, the given temperature specifications are considered preliminary suggestions and are subject to further discussion. To convert measured compositions or boiling temperatures at deviating pressure into equivalent boiling temperatures at 7 bar or 13 bar, suitable algorithms need to be agreed.

e) Rail & truck transport

Today CO_2 rail transport is carried out in the liquid phase at low temperature (LCO₂). Conditions in the tank are very similar to conditions for MP shipping (see Section 4.d). Most rail tank-cars are approved for temperatures down to -40°C, corresponding to a pressure of about 13 bar at 0.5% volatile impurities, see Section 4.d. The loading temperature for pure CO_2 is normally not lower than -34°C, which corresponds to a pressure of about 12 bar. The test pressure of the tanks is at approximately 26 bar, pressure relief valves are normally set 1.3 times lower (20 bar) than the tank test-pressure. Thus, for pure CO_2 there is sufficient room for pressure build-up during transport due to heat intake. However, for CO_2 with 0.5% volatile impurities -34° C corresponds to a tank pressure of approximately 16 bar; the reserve for pressure build-up is significantly reduced. Existing tank designs are suitable for the transport of LCO_2 with impurities as discussed in Section 4.d, but the loading temperature needs to be close to the lowest approved temperature to compensate for the pressure effect of the impurities.

As far as can be ascertained, there are currently no discussions with rail tank-car operators to allow transport of CO_2 streams in the dense phase at ambient temperature. The operating pressure would need to be much too high (more than 80 bar) for an economically feasible tank car construction. Transport temperatures of -50°C or lower, which correspond to the specifications for LP ship transport, are an option but are not requested by the market today. Transport via (ISO) containers, mostly with vacuum isolation, is a viable option for smaller volumes or intermodal solutions. As long as pressure levels in the container are the same as in conventional tanks, the design of the tank has no effect on the required CO_2 stream specifications.

Whilst operating pressures, temperatures and the resulting constraints on purity are similar to those for MP ship transport, operating procedures may need to be different. Operating procedures established for the rail transport of pure CO_2 are likely to be applicable for CO_2 streams containing the specified levels of impurities as well, but they need to be reviewed for possible implications arising from the higher levels of impurities.

Collection of CO₂ streams from small emitters, in which the CO₂ contains higher concentrations of impurities, and then subjecting them to further purification at the collection hub may be an economically attractive proposition as a result of the economies of scale possible for the purification plant. However, in this case the level of impurities within the CO₂ stream whilst in the intermediate transportation stage will be a relevant issue for the construction of new rail tank-cars. Higher water and sulphur contents would result in challenges with possible corrosion of the tanks and the potential for the formation of a solid phase in the associated pipes, valves and tanks. Tank cars and appropriate operating procedures for this approach are not yet available.

Future CCS and CCU rail transport will differ from today's market mainly by increased transport volumes. This means logistics concepts will need to focus on large block trains, fast (un)loading and quick round trips. CO₂ stream transport times in the rail tank-cars will be less on average in the CCS and CCU market, but holding times will still be relevant. Transport logistics will require priority transport corridors to the CO₂ terminals, integrated infrastructure planning and support of the industry for rail-network access and efficient (un)loading stations.

Truck transport of CO_2 will be most likely to play only a minor role but may be relevant during the start-up phase and also in the long run, when it becomes necessary to collect CO_2 streams from small emitters as well. When CO_2 is transported as LCO_2 on trucks, the same considerations as for rail transport will apply. Where trucks are serving small emitters, the CO_2 stream may be transported as dense phase at ambient temperature as well. In this case bundles of high-pressure tanks with limited diameter could be used. The resulting requirements on CO_2 purity are in general similar to those discussed for dense-phase pipeline transport in Section 4.a. Tanks and operating procedures allowing for high-pressure transport of CO_2 with higher concentrations of impurities have not been developed yet.

f) Geological storage – injection

Many aspects of the injection well design and operation are driven by the properties of bulk CO₂ rather than its impurities¹⁴. Auto refrigeration of CO₂ streams in the well tubing might be an issue in lowpressure reservoirs. When injection is interrupted quickly at the top of the well, the bottom of the liquid CO₂ column will keep moving, whilst at the top of this column, some of the CO₂ will evaporate, and a gas/liquid interface will be established with relatively cold temperatures. This feature can theoretically be avoided by deploying a smooth closing procedure when the reservoir pressure is high (as in some aguifers). In highly depleted gas fields, it is anticipated that upon an interruption of the flow, the entire wellbore will reach an equilibrium between the vapour phase CO₂ and the reservoir pressure. If phase transitions take place within the tubing during shut-in, the accompanying thermal cycling will be an additional potential failure mechanism that needs further understanding to avoid. The presence of impurities (e.g., H₂ and/or N₂) results in a two-phase envelope instead of a saturation line for pure CO₂, which increases the likelihood of two-phase flow conditions being present in the wellbore; this situation should, where possible be avoided in view of the possible associated hazards and computational challenges that need to be overcome to inform the operator about the thermodynamic behaviour of the CO₂ stream. Non-condensable impurities decrease the stream density, causing the mass flux to decrease over the same pressure drop, and thus reduce the injectivity.

In the highly unlikely event of an uncontrolled CO₂ release from the well, the (sub)surface safety valve (SSV) or other barriers fitted in the well must withstand the low temperature associated with sublimation of CO₂ until near atmospheric pressure while containing the high-pressure liquid underneath.

During injection, at the well/reservoir interface, water will dissolve in the CO_2 stream resulting in the formation of carbonic acid. Continuous injection may push the formation water away from the near wellbore. However, cross flow/high permeability streaks may lead to water prevailing. This typically drives the material selection in the well to corrosion resistant alloys (CRA). The elevated CO_2 stream pressure can significantly lower the pH of condensing water to create a condition where depassivation of CRA can occur, also possibly driven by the further significant decrease in pH by the presence of SO_x and NO_x . De-passivation can cause localised corrosion and even increase the risk of

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¹⁴ A more elaborate description of these effects can be found in Sections 3 and 4 of Acevedo and Chopra, 2017, <u>Influence of Phase Behaviour in the Well Design of CO2 Injectors</u>, Energy Procedia.

cracking in these parts. Additionally, there is no general analysis of the potential for damage to the minerals in the near-wellbore zone. As indicated above, the CO_2 stream may contain water over a long time, dissolving some of the impurities (like SO_3 and SO_2). The resulting strong acids may attack the minerals in the near-wellbore zone, leading to changing environments near to the injection points which are, however, usually far away from the cap rock relevant for the integrity of the reservoir. Additionally, since the flow pattern in the reservoir may not be known to the appropriate level of granularity, the aggressive mixture of reservoir fluid and CO_2 stream may come into contact with the tubulars from the reservoir side and corrode from the outside. Due to this potential damage options, an as-simple-as-possible, damage-tolerant completion is advisable.

For CO₂ streams with typically low O₂ levels (~10 ppm-molar) this drives the selection of 25Cr to mitigate the risk of de-passivation. This constraint is particularly relevant for CO₂ storage in depleted gas fields as these would benefit from the conversion of existing production wells into injectors¹⁵. Existing wells are typically constructed from low-grade CRA such as 13Cr and some parts of the well may not be replaceable. In addition to well integrity concerns this may lead to injectivity impairment through corrosion by-products plugging the formation.

Backflow of CO₂ and formation water from the reservoir back into the well tubing cannot be ruled out. This does not only influence the lower part of the well directly in the potential water column but also shallower sections of the well which may also be in contact with this corrosive medium through convection and condensation effects. This is important for injection wells which are in intermittent service (as opposed to continuous injection). In particular those projects using direct injection from a ship will mean a situation whereby short injection periods are followed by long waiting times for the next ship to arrive. Corrosion takes place during the shut-in times, possibly all along the tubing, by small bufferless condensed water droplets. Some impurities (for example the sulphur oxides) partition preferentially from the CO₂ phase into the aqueous phase, leading to extremely low pH values. Oxygen and NO₂ do not partition strongly into the aqueous phase but they maintain an oxidative potential within the droplets which, in principle, render the mixture as very aggressive to stainless steels. Since the volume of those droplets is small, the macroscopic corrosive attack is hard to forecast, and is possibly very dependent on the location in the tubing string. An integrated computer model taking into account natural convection, solution of water from the reservoir-CO2 interface, droplet-droplet interaction and precipitation along the tubing incorporating the chemical effects would be necessary to model this situation. Since no long-term field experiences with impure CO₂ containing considerable amounts of SO₃, O₂, and/or NO₂ are available, it cannot automatically be assumed that the usual oil and gas material solutions will work. Furthermore, sufficiently standardised tests for these situations are not available, and need to be established. Intermittent service might lead to frequent thermal cycling which, due to the possibly phase transition in the CO2 case, is normally not experienced in traditional injection wells and therefore needs to be looked at in greater detail.

For well cement, a suitably well-designed Portland cement, with low permeability, will have sufficient resistance to diffusion-dominated carbonation along the axial length of the well such that it does not pose a risk for loss of isolation. Carbonic acid can degrade cement through dissolution and subsequent

¹⁵ The re-use of wells can be to limit development costs but also due to the challenges associated with drilling of new wells into highly depleted formations (underbalance drilling).

leaching of minerals from the cement, provided the cement is exposed to a considerable volume of (flowing) water, which may result in an increase in porosity and reduction in strength. Flowing water may not be found at caprock levels, especially if the seepage flow consists of humid CO_2 (the more buoyant phase) rather than of CO_2 -rich brine. Subsequent reprecipitation of carbonate minerals may occur, slowing the rate of cement degradation and in some cases, imparting self-healing properties¹⁶. It is anticipated that the extent of Portland cement degradation via bulk diffusion will be in the order of 1 - 10 m over 10,000 years¹⁷. It should also be noted that extensive mineralisation of the CO_2 will take place within this timeframe.

The risk of H_2S formation in the reservoir due to supply of nutrients for sulphur reducing bacteria or hydrogen in the feedstock that can reduce sulphur containing minerals must be considered for failure scenarios. This is not a generic requirement. For example, Rotligand reservoirs in the Southern North Sea contain minerals that acts as H_2S scavengers and will therefore limit H_2S accumulation. A CRA such as 25Cr is resistant to backflow of H_2S .

g) Geological storage – reservoir

Regarding the impact of impurities on the reservoir, three different regimes can be described: near wellbore phenomena, their impact on capacity, and their impact on the containment.

The near wellbore phenomena strongly depend on the phase behaviour of the fluid entering the reservoir. Although the conditions for the formation and dissociation of CO₂ hydrates in brines of varying salinity are well understood, there are few studies, and thus little expertise, on the effects of impurities such as CH₄, N₂, CO and H₂¹⁸. The same is true for salt precipitation, which is one of the major challenges reducing injectivity in geological storage systems. The effects of impurities are considered negligible in most studies. However, a few experimental studies suggest that SO₂ and NO₂ content can significantly increase permeability by further lowering the pH of reservoir brine with associated rock mineral dissolution, with the caveat that most studies use a large water:rock ratio that is not representative for subsurface conditions and that overestimates dissolution effects. The dissolution may counteract the effect of salt precipitation near the wellbore, especially if the reservoir

¹⁶ Wolterbeek, T.K.T., Peach, C.J., Raoof, A., Spiers, C.J. (2016), <u>Reactive transport of CO₂-rich fluids in simulated wellbore interfaces: Flow-through experiments on the 1–6 m length scale</u>, International Journal of Greenhouse Gas Control, 54(1), 96-116, https://doi.org/10.1016/j.ijggc.2016.08.034.

¹⁷ OEUK Well Decommissioning for CO₂ Storage Guidelines (Issue 1, Nov 2022) - section 3.2 & Appendix B.3 & B.4.

¹⁸ Horvat, K., Kerkar, P., Jones, K., Mahajan, D., 2012. <u>Kinetics of the Formation and Dissociation of Gas Hydrates from CO₂-CH₄ Mixtures. Energies 5(12), 2248–2262, doi:10.3390/en5072248.</u>

Eslamimanesh, A., Babaee, S., Gharagheizi, F., Javanmardi, J., Mohammadi, A. H., Richon, D., 2013. <u>Assessment of clathrate hydrate phase equilibrium data for CO₂+CH₄/N₂+water system. Fluid Phase Equilibria 349, 71–82, https://doi.org/10.1016/j.fluid.2013.03.015.</u>

Liu, J., Yan, Y., Li, S., Xu, J., Chen, g., Zhang, J., 2016. <u>Structure and Stability of Binary CH₄-CO₂ Clathrate Hydrates. Computational & Theoretical Chemistry</u> (Accepted Manuscript),

http://dx.doi.org/10.1016/j.comptc.2016.04.010.

Sadeq, D., Al-Fatlawi, O., Iglauer, S., Lebedev, M., Smith, C., Barifcani, A., 2020. <u>Hydrate Equilibrium Model for Gas Mixtures Containing Methane, Nitrogen and Carbon Dioxide</u>. OTC-30586-MS, https://doi.org/10.4043/30586-MS.

rock contains carbonates.¹⁹ To be able to interpret case studies on reactive transport effects properly it is important to consider all influencing factors and interactions; this is both a technical and a scientific challenge, which is not easily addressed using current physical and numerical modelling tools and expertise.

Impurities in the injected CO₂ stream and/or gases already present in the storage formation can affect storage capacity, although they are generally not considered in the preliminary capacity estimation. Non-condensable impurities may potentially cause a reduction in the storage capacity via two different ways:

- 1) by taking up pore space that could have been used for the CO₂, and/or
- 2) by reducing the density of the CO₂ weighted gas mixtures by decreasing the compressibility.

In an IEAGHG study²⁰ the effect of the impurities was investigated for three scenarios of gas streams in which the CO₂ purity changes from low (85%-90% mol) to medium (95%-97% mol) and high purity (> 99% mol). The impurities assumed were O₂, N₂, Ar, H₂O, NO₂, SO₂, CO, H₂ and H₂S at various concentrations in the CO₂ stream. The storage capacity for a given storage geometry was calculated using Peng-Robinson Equation of State to estimate the phase behaviour. It is found that the normalised capacity (i.e., the actual storage capacity over the nominal capacity for pure CO₂) decreases with increasing concentration of impurities, and that at a certain pressure and temperature there would be a maximum decrease in storage capacity of 60% of the nominal capacity, emphasising the relative importance of CO₂ density and compressibility of the mixture. More recent studies support this conclusion. Due to the relevance of pressure and temperature on mixture density and compressibility, the importance of impurities for storage capacity decreases with increasing depth (higher pressure and temperature)²¹.

The effects of the impurities on the dissolution of CO_2 in the brine and thus on the storage capacity have not been widely studied in the literature to date. As most high-concentration impurities under consideration in geological storage have lower solubility in water than CO_2 , the presence of these impurities would reduce the partial pressure of CO_2 and, therefore, reduce the dissolution of CO_2 in formation water. Acid impurities, such as SO_x and NO_x , would decrease the solubility of CO_2 by decreasing the pH of the formation water. However, dissolved rock minerals (carbonates) can serve as a pH buffer and weaken the effect of acid impurities on CO_2 dissolution. In one of the rare modelling studies being published the total solubility of $SO_2 + CO_2$ in water varies exponentially with respect to SO_2 concentrations, i.e., at low concentrations of SO_2 (up to 5% as a maximum case in geological storage – which is already well above limits discussed for transport) total changes in solubility of the CO_2 in water are estimated to be negligible²².

¹⁹ Aminu, M. D., Nabavi, S. A., & Manovic, V. (2018). <u>CO₂-brine-rock interactions: The effect of impurities on grain size distribution and reservoir permeability</u>. International Journal of Greenhouse Gas Control, 78, 168–176, doi:10.1016/j.ijggc.2018.08.008.

²⁰ Effects of Impurities on Geological Storage of CO₂, IEAGHG, 2011.

²¹ Neele F, Koornneef J, Poplsteinova J, Brunsvold A, Eickhof C (2017) <u>Toolbox of effects of CO₂ impurities on CO₂ transport and storage systems</u>. Energy Procedia 114:6536–6542.

²² Miri, R., Aagaard, P., & Hellevang, H. (2014). Examination of CO2–SO2 solubility in water by Saft 1. implications for CO2 transport and storage. The Journal of Physical Chemistry B, 118(34), 10214–10223, https://pubs.acs.org/doi/10.1021/jp505562j

An important but poorly understood topic is the effect of impurities on the formation and growth of gravitational instabilities in saline aquifers. It is well known that the formation of CO_2 -saturated brine fingers and their movement in aquifers from top to bottom is a long-term but important contributor to storage capacity by accelerating dissolution through convective transport. For a given Rayleigh number, dissolution of N_2 and H_2S impurities makes the system stable, while dissolved SO_2 accelerates the onset of instability.²³

The effect of impurities in the CO_2 stream on containment is related to their long-term chemical impact. In saline aquifers, during and after the storage injection, the CO_2 plume (including the impurities) tends to migrate towards the storage reservoir-caprock boundary potentially inducing geochemical reactions that may result in mineral dissolution and/or precipitation even in the cap rock formation. A low pH brine in the vicinity of the CO_2 plume may come into contact with the caprock and may cause dissolution of the caprock minerals, especially if carbonates are a part of it. If SO_2 and NO_x are present in the CO_2 stream they would form H_2SO_4 and HNO_3 in brine and promote the dissolution of rocks. H_2SO_4 may also cause precipitation but HNO_3 will not.

However, concentrations of these impurities will likely be limited to the ppm range due to concerns regarding transport. And the way from the injection point to the caprock is long. Possible chemical reactions will likely affect the vicinity of the injection site rather than the caprock – these effects have been discussed in the previous sections. As further important natural safeguard, any reactions with competent caprock (i.e., in absence of a pre-existing leak path like a conductive fault zone) are limited to the lowermost portion of the caprock (centimetre scale). This is demonstrated by modelling studies as well as by direct observations on sealing formations that have been exposed to CO_2 for over 100,000 years²⁴. The main reason for this is the slow (diffusive) transport mechanism in caprock: CO_2 and impurities can only enter the caprock through dissolution and diffusion in the formation water.

To date, no case has been reported where impurities in the CO_2 stream affected the integrity of the caprock. However, further research is recommended to understand the processes induced and/or accelerated by the impurities in the CO_2 stream on the quality of the confinement – not to guarantee the safety of confinements currently considered, which can be taken for granted based on today's knowledge, but to improve our understanding of fundamental effects, which may become relevant for the assessment of confinements that have to be explored in the future to allow for wide spread use of CCS technologies. In addition to high computational capabilities, reactive flow modelling requires a thermodynamic database completed for the reaction parameters of the impurities in brines with minerals representing the reservoir and caprock. Their coupling with geomechanical models is important for evaluating reactive effects on the quality of the confinement further.

h) Relevance of capture technologies for transport

The CO_2 capture process has a significant impact on the type and level of impurities in the CO_2 stream for storage. These impurities broadly depend on 3 variables:

 ²³ Kim, M. C., & Song, K. H. (2017). Effect of impurities on the onset and growth of gravitational instabilities in a geological CO₂ storage process: Linear and nonlinear analyses. Chemical Engineering Science, 174, 426–444.
 ²⁴ Kampman, N., Busch, A., Bertier, P., Snippe, J., Hangx, S., Pipich, V., Di, Z., Rother, G., Harrington, J.F., Evans, J.P. and Maskell, A., 2016. Observational evidence confirms modelling of the long-term integrity of CO₂-reservoir caprocks. *Nature Communications*, 7(1), p.12268.

- 1) The chemical composition of the original carbon-containing material (natural gas, coal, coke, liquid hydrocarbons, limestone, biomass, etc.). Any element in this original material (sulphur, nitrogen, chlorine, heavy metals...) may potentially end up in the CO₂ stream for storage. Waste incineration can result in high and fluctuating levels of impurities due to the inevitable, yet unpredictable fluctuations in the composition of the waste.
- 2) The process through which the original material has undergone to produce the CO₂, resulting in the diluted stream that is the feed for the capture process. Several categories can be identified:
 - Combustion, when air is used as oxidising agent. The CO₂ stream produced is mainly diluted with nitrogen, and smaller quantities of excess oxygen, water, and other impurities produced in the combustion process, such as NO_x, COS, SO₂, and SO₃. Capture strategies targeting the flue gas streams from combustion are described as post-combustion capture.
 - Oxy-fuel combustion, which uses essentially pure oxygen as the oxidising agent for the combustion. In this case, the raw flue gas stream typically contains above 70%mol CO₂. The main impurities here are excess oxygen, inert gases not completely separated from the oxygen at the Air Separation Unit (e.g., nitrogen, and argon), and water. Depending on the fuel composition, impurities produced in the combustion process (SO₂, etc.) may be present, at higher concentrations than those in the case of combustion with air.
 - Partial oxidation processes, such as steam reforming or gasification, normally found in the context of hydrogen production (e.g. to be used in hydrogenation / reduction processes, ammonia plants, 'blue' hydrogen production, or as fuel in pre-combustion capture concepts). In any of these cases, the CO₂-rich stream may contain hydrogen, nitrogen, argon, and smaller amounts of CO, methane and other light hydrocarbons, as well as sulphur compounds (e.g., H₂S) were this element to have been present in the feed material.
 - Limestone (calcium carbonate) calcination produces CO₂ and calcium oxide. This process takes place during clinker manufacturing in cement plants and requires heat, which is nearly always provided by combustion. Thus, the CO₂ produced from calcination is likely to be mixed with flue gas from combustion, which could either be based on air or on oxyfuel combustion. The main composition difference between a CO₂ stream from combustion and that from a cement/lime plant is the higher CO₂ concentration; other impurities are essentially the same.
 - Another combined situation occurs in steelmaking facilities using the Blast Furnace-Basic
 Oxygen Furnace (BF-BOF) route, where the CO₂ is generated at different points and in
 different type of processes across the plant. Impurity levels are typically a combination of
 those found in hydrogen production and in combustion processes with air, in different
 proportions depending on the particular streams targeted for capture.
 - If CO₂ is captured as part of natural gas / biogas treatment processes (gas sweetening), the CO₂ is expected to be diluted with light hydrocarbons, as well as with small quantities of sulphur compounds.
 - Finally, CO₂ can be captured from the atmosphere (DAC, Direct Air Capture), in which case typical impurities are air components and traces of capture agents.

3) The last variable affecting the type and level of impurities is the capture technology itself, which concentrates the diluted CO₂ stream in order to improve the efficiency and cost of CO₂ transport and storage. In the case of chemical (e.g., amines) or physical solvent technologies, traces of the solvent may be found in the captured CO₂ stream. If solid adsorbents (e.g., PSA, VSA, or TSA processes) are used, solid particles could be expected. Cryogenic processes will typically produce very pure CO₂ streams due to the low-temperature process requirements, which are normally stricter than those for pipeline transport or geological storage. On the other hand, CO₂ membranes, which may be used for biogas or natural gas treatment, are not very selective, so significant amounts (up to 10% mol, or even more) of other gases (for example, methane or nitrogen) have the potential to remain in the CO₂ stream.

Based on the type and level of impurities in the captured stream, the following considerations can be made on the CO₂ treatment strategy to fulfil transport and storage specifications:

- Dehydration water will always need to be removed to ppm levels, since condensation may lead to severe corrosion of the carbon steel materials. Two main types of dehydration processes are normally considered: glycol systems, which can reach water contents around 50 ppmv, and solid adsorbents (e.g., molecular sieves), which can reach levels as low as 1 ppmv. At typical transport pressure and temperature in pipelines, both dehydration concepts would be applicable. However, traces of glycols in the captured CO₂ might lead to the formation of a corrosive phase at transport conditions. Thus, glycol concentrations have to be limited to very low levels or eliminated altogether. This is particularly relevant for TEG (triethylene glycol), which is frequently used in dehydration processes for natural gas. Accurate information on phase equilibria in CO₂ containing traces of water and glycols is not yet available. Thus, limits for glycol concentrations in the CO₂ need to be chosen conservatively to date. If the CO₂ stream is to be liquefied, water levels below 10 ppmv are required, leading to the preferential use of solid adsorbents.
- Particulate removal can be readily achieved with conventional filters down to micron levels.
- Sulphur components removal there are multiple sulphur removal technologies; selection is
 normally based on the content and type of sulphur species in the CO₂ stream, together with
 the treated CO₂ stream specification. Depending on the specification level defined for the
 transport, the selection of the capture technology may be affected, potentially leading to
 higher capture costs. This is probably one of the cases where an optimum trade-off between
 cost and impurity levels can be achieved.
- Non-condensable gases (nitrogen, oxygen, argon, hydrogen, carbon monoxide, methane, etc.) at the low concentrations typically found after the capture process cannot be easily removed from the captured CO₂ stream. The carbon monoxide content should be reduced to the specified level at the capture plant due to its toxicity. Hydrogen and methane can be oxidised with catalysts, if necessary, under the addition of oxygen. On the other hand, oxygen can be removed by catalytic reaction with (added) hydrogen. An energy intensive low temperature process is required to remove nitrogen and argon. To minimise the whole-chain cost, it may transpire that it is advantageous to reduce the concentrations of nitrogen and argon to the low levels required for low temperature liquid-phase transport (ship or train / truck, buffer storage) at central hubs as part of the liquefaction process. As in the case of sulphur, very strict transport & storage specifications for the total amount of non-condensable gases or for

- individual species may rule out some in principle feasible capture technologies, potentially leading to higher capture costs.
- Finally, specification levels for minor impurities such as acids (e.g., HCl, HF, HCN), nitrogen compounds (e.g., NH₃, NO_x), or organic compounds (e.g., amines, glycols, alcohols, aldehydes, lubes, etc.) need to be established. In general, these impurities are relevant for the safety in transport; concentration limits need to be met at the capture plant. Stricter limits may be required for low temperature liquid-phase transport; to reduce concentrations further, post processing at hubs before liquefaction may be an option.
- Special consideration needs to be given for the case of mixtures of CO₂ streams from different capture processes. Mixing of varying streams can lead to compositions largely fluctuating over time. These situations present specific challenges due to potential interactions between different impurities, leading to unforeseen variations in the CO₂ stream composition. Reactions may produce additional water that could raise the CO₂ stream dew point, increasing the risk of acidic water drop-out leading to pipeline corrosion. Solids can be formed, for example by reaction of ammonia with CO₂. Both the dynamics and the chemistry of these processes and the impact of changed composition on the (acid) dew point need to be investigated further to come to optimised specifications. At this point in time, transport specifications for mixtures of CO₂ streams need to be more stringent (i.e., with lower levels for individual impurities) than if each CO₂ stream was to be transported alone, where the composition and the phase behaviour is more easily predictable.
- Purification processes generally produce purge streams, which contain some CO₂ together with the potentially hazardous impurities that have been removed. The handling of these purge streams needs to be controlled carefully, for instance, in accordance with local regulations. Concepts need to be developed to assign impurities separated at hubs downstream of the capture process (together with the associated costs) to emitters. In particular, processes for the removal of non-condensable components can be energy intensive. The energy efficiency of the whole capture and transport system needs to be considered.

i) Port infrastructure for CO₂ captured on board of ships

To decarbonise the shipping sector and to implement carbon capture onboard not only procedures and technologies for CO₂ capture and storage on board must be developed and implemented, but also infrastructure needs to be provided at the receiving ports. The amount of CO₂ that could potentially be handled is substantial: for example, the fuel traded in Rotterdam, which is the largest bunkering port in Europe, corresponds to annual CO₂ emissions of more than 30 million tonnes when it is burnt. If CCS on ship becomes a viable and widely used solution for the decarbonisation of maritime transport, ports will need to act as CO₂ hubs in the future. This will include CO₂ post-processing onshore, since CO₂ qualities delivered by ships may not be in line with demands for further transport. Global standards need to be implemented to ensure the offloading of captured CO₂, potentially with fuel, propulsion, capture-type and ship-type dependent specifications. These standards would have to cover not only pressure and temperature levels, the required purity and tolerable impurities but also the offloading procedures. These would have to be suitable for different vessels, regardless of propulsion type, fuel, size or manufacturer. Technologies and procedures required to monitor the quality of delivered CO₂ would need to be implemented. Regular off-loading of CO₂ in each port is crucial because of the increasing mass of CO₂ that would have to be moved, taking up space that would

otherwise be used for cargo. Storage capacities (possibly both for pre-processed CO_2 coming from the ships and for post-processed CO_2 waiting for further transport) have to be provided to compensate for the strongly fluctuating delivery of CO_2 . Ownership claims and responsibilities for the delivered CO_2 and for the impurities in the CO_2 stream need to be clarified.

Thus, the following aspects must be covered by international standards and codes to ensure a viable CCS chain:

- Minimum purity of CO₂ captured on board, likely to come from in different ship classes.
- Maximum concentrations of certain components, likely to be from different classes.
- Temperature and pressure levels for on-board storage and unloading.
- Definition of responsibilities for purification, ownership of the delivered CO₂ streams.

The following infrastructure would need to be provided in ports, and appropriate procedures for permitting and concepts for ownership of the infrastructure need to be established:

- Technologies for CO₂ offloading, connections for transmission: these are likely to be based on bunker vessels.
- Facilities for post-processing of CO₂ and temporary storage capacity.
- Options for further transport of the captured CO₂, either by ship or by pipeline.
- Procedures and equipment for monitoring quantity and quality of incoming CO₂.
- Heating and cooling as required by the following transport mode.

The ongoing development of technologies for CO₂ capture, purification and storage onboard of ships needs to be observed closely to deliver optimised solutions for the whole chain.

5. Conclusions and recommendations

At this stage of CCUS development, setting limits for individual impurities (or an effective sum of several impurities, which may cause similar or interdependent effects) may well be the most prominent single problem. This is mainly because the level of impurities in a CO₂ stream significantly influences each part of the value chain, and different stages of the process show conflicting requirements and different stages of technical maturity. For example, it seems reasonable that on the capture side a wide specification would lower costs and reduce effort, while on the transport and storage side an as-pure-as-possible stream would reduce many technical challenges and associated costs. It is worth considering that specifications for pipeline transport can be less stringent than for ship transport. For an optimisation of the whole value chain, more knowledge on every single step is required but – moreover – a clear political framework is essential, which defines an unambiguous vision and clear targets of a common European CO₂ transport network. However, since this industry is an emerging one and the costs and need for purification in specific environments is not fully set and understood, rules need to be set in a flexible way, where possible.

A complete picture of the quantitative description of the physical and chemical behaviour of impure CO_2 is still not available. Qualitatively, the phase behaviour of impure CO_2 mixtures is well understood for most technical impurities. There is a lack of understanding concerning the potential interactions between several different compounds in the CO_2 stream (for example the stabilisation of aqueous phases by polar molecules). For the prediction of phase transitions and the accompanying partitioning of the impurities into the new phases and non-equilibrium phase transition conditions, there is little reliable literature available for multi-component systems. This may have a direct impact on CapEx (for example for the wall thickness requirements for avoiding Running Ductile Fracture conditions) and on blowout or leakage scenarios and their safety and health considerations. More public research is required for all points listed above in order to reduce the degree of technical conservatism, which is being applied at the moment in order that project development can continue.

Chemical reactions of impurities within the CO₂ stream are hardly described and quantified in publicly available literature. This is especially important considering that chemical reactions may take place at every single step of the CCUS value chain, but of course the processes which contain a reactive CO₂ stream mixture for prolonged times may face the highest consequences. From the research already available it is obvious that the time scale for possible reactions is expected to be within the residence time for transport on ships or in pipelines – so the nature and quantity of reaction products and possibly additional phases needs to be fully understood to ensure safe, economic and reliable transport without extra security margins. Since chemical reactions might lead to the situation that certain impurity levels are exceeded during storage or transportation starting from an in-spec composition (for example by production of water during pipeline transport), a common political concept to handle this situation needs to be elaborated. Accordingly, as a final recommendation, fundamental research on chemical reactions paths and kinetics seem to be of prime importance. On that basis, safe and economic (because less conservatism has to be applied compared to thresholds defined today) impurity threshold concentrations could be worked out.

The goal to establish standards and a network code that allow for the development of a multimodal European CO₂ transport network optimised to minimise the whole chain costs will result in the need for scenario development and in specific considerations for different transport modes. Tools that are able to combine the development of European CO₂ stream transport scenarios with such a detailed

technical analysis are not yet available and need to be developed to come to cost-optimal solutions. However, the development of transport scenarios is outside of the scope of this report. This report focusses on characteristics of CO₂ streams that are relevant for different elements of the transport infrastructure.

Pipeline transport in the dense phase will most likely be the backbone of a European CO₂ transport network. Beside the overarching limitations for toxic impurities, the content of "non-condensable" gases (typically the air components nitrogen and argon, but also methane and hydrogen - for the oxygen concentration low limits apply due to concerns regarding corrosion) plays an important role. High concentrations of these gases (up to 5% in total) can be accommodated but can result in substantially more expensive pipelines and a higher energy demand than for gas phase transport. On the other hand, low impurity limits increase the cost and energy demand of purification. An optimum balance still has to be determined. The water content, the content of acid forming components, and the content of amines and glycols have to be limited strictly to avoid the formation of a corrosive second phase, but allowable limits are higher than for other transport modes. A network code needs to specify pressure levels for transport and operational procedures. Optimised operational procedures need further thought and research, mainly because throttling of CO2 in the dense phase leads to extreme temperature drops and may result in the formation of a solid phase or of a gas phase in equilibrium with a corrosive liquid phase. The dynamics of a pipeline network for CO2 containing impurities needs to be understood, as well as the impact of extended two-phase regions on operational procedures, including in particular the operation of pumps and compressors at transient states of the pipeline. Standards for the design and permitting of pipelines that do not rely on tests for every single project need to be established. For pipeline transport in general, the need to provide accurate online monitoring of impurities still is a point of concern.

Pipeline transport at gas states will become relevant to connect single medium to large emitters to hubs feeding the CO_2 into the backbone established by high-density pipelines or to make use of repurposed pipelines or in populous areas. For large amounts of CO_2 , pipeline transport at gas states is usually not attractive. High concentrations of non-condensable gases can be tolerated, but limits on water content, acid forming gases, amines and glycols need to be even stricter than for pipeline transport in the dense phase; a corrosive dense phase might be formed by condensation. The effect of acid forming gases on condensation in a CO_2 atmosphere is quantitatively not well described yet. Challenges resulting from solid phase formation and operational procedures for pipeline pressures above about 2 MPa (solid or liquid phase formation during expansion) need further consideration and, if necessary, research.

Buffer storage is an important element of all concepts including non-continuous transport modes. Storage in the dense phase under high pressure is possible and results in conditions similar to pipeline transport in the dense phase. However, for large tanks storage as liquid phase at low temperature is more suitable to limit the required wall thickness, even though the energy consumption for liquefaction at low temperature is much higher. Conditions are similar to those for ship transport. The industry has long-lasting experience with low-temperature storage of pure CO₂. However, impurities in captured CO₂ streams may result in effects that have previously not been experienced. These challenges can be handled but need to be anticipated – this requires further consideration and, if necessary, research.

Inland ship transport is relevant to collect CO₂ streams along rivers and to transport the CO₂ streams to hubs, where it can be injected into the pipeline backbone or transferred to bigger sea going ships. Sea going ships can be used to transport CO₂ to storage sites. For remote storage sites this will likely remain the preferred solution, whilst an increasing number of more favourably located storage sites will be connected to pipelines over time. Ship transport will likely be particularly relevant for a fast ramp up of CCS solutions. On board of ships, CO2 is generally transported in the liquid phase at low temperature. Small to medium ships will likely transport CO₂ as boiling liquid at medium pressure (about 13 to 18 bar at temperatures between -35 °C to -22 °C). Industrial experience with small ships carrying pure CO₂ at these conditions is available. For larger ships travelling further, transport at low pressure (7 bar at -49 °C) seems favourable. In general, liquid-phase transport at low temperature results in stricter requirements on purity than transport at ambient temperature. An effective removal of non-condensable gases during liquefaction is possible, but requires additional equipment to limit the loss of CO₂ during the process. Corresponding regulations are pending. Strict limits are required for components that might form solid phases at low temperatures (water, but also amines and glycols - allowable concentrations for amines and glycols still need further research). Overly strict limits for glycols (in particular TEG) may make dehydration processes more expensive; with regard to TEG further research is urgent. Shipping at low pressure (LP, 7 bar at -49 °C) is not yet established technology. The vicinity of LP shipping conditions to the triple-point pressure of CO₂ (5.2 bar, below this pressure solid formation would unavoidably occur) requires further thoughts and maybe research with regard to operating procedures. Ship transport necessarily includes the need to establish infrastructure in ports (CO₂ liquefaction and possibly post-processing, buffer storage, loading). Either for injection into a reservoir or further transport in pipelines, the liquid CO2 transported by ship at low temperature needs to be heated up again. While the liquefaction process necessarily is energy intensive, efficient technologies for heating up the CO₂ stream need to be promoted.

Rail and possibly truck transport will be important transport modes during the start-up phase of a CO_2 -transport network. In the long run they will be likely to be restricted to small to medium remote emitters. Rail cars and trucks usually transport pure CO_2 as a boiling liquid at low temperature and medium pressure; industrial experience for pure CO_2 is available. In general, constraints regarding CO_2 purity and operating procedures are similar to medium pressure ship transport. However, additional thoughts on operating procedures are required, e.g., to limit the amount of CO_2 that escapes as gas phase while filling the tank. Vacuum isolated containers may turn out to be an attractive alternative to classical tank cars.

Additional constraints on CO_2 characteristics may result from the **injection into geological storage sites**. Most issues related to fluctuating injection largely depend on the characteristics of CO_2 itself, rather than on impurities in the CO_2 stream. Materials for the injection pipe and flow-wetted components in the well need to be chosen in a way that they can withstand a CO_2 /brine mixture in case of a backflow. Acid forming impurities in the CO_2 increase the risk of corrosion and the threat to the cement plug closing the borehole. However, acceptable limits are engineered to be higher than for transport. In order to pose a significant threat to cement integrity, the presence of acid forming impurities in the CO_2 would have to fundamentally alter the reactive transport processes involved compared to CO_2 . None of the studies to date provide evidence or indicate that this will be the case. Thermal cycling due to fluctuating CO_2 flows and its effect on the injection facilities and the reservoir

closure to the injection point are considered critical operational issues. Further thoughts and research are recommended to determine practical limits with regard to the flexibility of mass flows into the reservoir.

On the reservoir side, impurities in the CO₂ stream may affect the near well-bore area, the capacity of the reservoir, and theoretically, its integrity. In the near well bore area, chemical reactions induced or intensified by impurities can be a challenge for the injectivity. More frequent drilling of new wells may be an economically severe management solution. The capacity of the reservoir can be significantly reduced by non-condensable gases, whereby the corresponding processes can be complex and adverse effects could result from other impurities – this needs to be considered when the capacity of reservoirs is estimated. Theoretically, chemically reacting impurities (in particular from acid-forming components like SO_x and NO_x) can be a threat to the integrity of the caprock. However, concentrations of these impurities are already restricted to the ppm level to address concerns with upstream infrastructure, and the distance from the well bore to the caprock is usually long. Possible chemical reactions are more likely to take place close to the well bore rather than at the caprock and, simply due to stoichiometry, the amount of rock that can be affected is small. Even if the caprock is affected, the key natural safeguard against any reactions with an intact caprock is that they are limited to the lowermost portion of the caprock (centimetre scale) due to the slow (diffusive) transport mechanism in caprock. To date, no cases have been identified where the caprock was weakened due to impurities on the levels anticipated for CO₂ stream transport.

The chosen **capture technology** is relevant for the impurities contained in captured CO₂, as is the **source of the CO**₂ (e.g., coal, gas, waste, biomass, cement) and the **conversion process** (e.g., combustion, gasification, fermentation, calcination). Different combinations of these three factors result in very different requirements for the processing of captured CO₂, but they cannot be reflected in different access conditions to a European CO₂ transport network. Risks can arise from chemical reactions that could result from the mixing of different impurities from different CO₂ streams and may include solid formation and the formation of an unpredicted corrosive phase. These risks are partly understood and can be circumvented by defining conservative limits for impurity concentrations, but further thoughts and research are required to deliver economically optimal limits in the long run.

 CO_2 capture from the exhaust gas of ships is a means to reduce the CO_2 emissions of marine transport. Globally, several research, development and demonstration projects address this technology. Although the technology by itself is not relevant for a European CO_2 transport network, it needs to be understood that it may turn ports into important sources of CO_2 . Regarding the characteristics of the landed CO_2 (pressure and temperature levels, impurities), global standards need to be established to allow ships to unload their CO_2 in arbitrary ports. These standards will probably not be identical to standards defined for the European transport network. Thus, ports need to be equipped not only with unloading facilities, buffer storage and connections to the transport network, but also with facilities to process further the landed CO_2 . This aspect needs further thoughts, research, and international cooperation to come to optimal solutions.

6. Sources

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