
**Carbon dioxide capture,
transportation and geological
storage — Cross cutting issues — Flow
assurance**

*Captage, transport et stockage géologique du dioxyde de carbone —
Questions transversales — Maintien de l'écoulement*

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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

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

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

Introduction

Flow assurance can be defined as an engineering discipline that is required to understand the behaviour of fluids inside vessels, pipes or porous media at flowing and at static conditions. Flow assurance provides input to design activities, such as pipeline design or risk analysis. It emerged as an engineering discipline in the oil and gas industry in the 1990s. Flow assurance analysis is delivered in the oil and gas industry by methodical numerical simulation of each pipeline and injection/production well operating case, often using flow assurance software to facilitate the analysis.

In relation to carbon dioxide capture and storage (CCS), flow assurance seeks to maintain the continuous supply of the CO₂ stream from the capture plant, through the transportation system and into the geological reservoir via injection wells. Flow assurance is required to demonstrate that all foreseeable operating modes of all components of CCS projects, planned and unplanned, are predictable, reliable and safe. It achieves this through analysis of the CO₂ stream flowing as a fluid in the various components of a CCS project's systems, from capture through to geological storage (capture, transport, injection and storage).

Some of the key issues of interest addressed by flow assurance analysis include:

- the total network or project hydraulic capacity requirements necessary for determining pipeline, injection well and reservoir operating parameters;
- management of transient operations, such as those caused by varying injection rates, varying CO₂ stream supply and during slugging, surging and start-up and shut-down operations;
- thermal management under various operational scenarios to ensure that the variations of fluid temperature are within the operating constraints of the system;
- fluid phase behaviour and physical properties as a function of CO₂ stream composition;
- hydrate management and control, resulting from Joule-Thomson effects such as pressure drop across pressure reducing valves, orifice plates and flow metering devices; and
- planned and unplanned de-pressurization of systems, such as that resulting from a pipeline rupture, well blowout or controlled venting of pipeline and equipment during maintenance activities.

Most of the above issues can be addressed by dedicated flow assurance modelling software and tools, in which both thermodynamic and hydrodynamic behaviours of fluids in technical components such as pipelines or wells are modelled. The thermodynamic properties and transport properties of fluids are closely related to their chemical composition and their associated amount or concentration. Significant differences in thermodynamic behaviour of fluid of different compositions can be observed and these differences can lead to different hydrodynamic behaviour of the flow. Therefore, fluid thermodynamic properties are a critical input to the dynamic flow models.

Existing CCS system modelling of technical components has mainly been limited to single phase CO₂. Given significant storage capacity suitable for permanent CO₂ storage exists in depleted hydrocarbon reservoirs, which can be initially at pressures where CO₂ can be subject to two-phase flow conditions, the CO₂ stream in the pipeline and injection well can be subject to two-phase flow conditions, i.e. a combination of two CO₂ phases, gas and liquid. Two-phase flow can also occur during transient operations such as opening up, closing in or depressurization of pipelines or wells. Within underground reservoirs two-phase flow is generally expected involving the injected CO₂ stream as well as formation fluids that will have to be mobilized. Facilitating unhindered flow of the CO₂ streams in CCS projects requires the inclusion of reservoir fluids (natural gas, water or crude oil) and relevant processes in the storage reservoir in the flow assurance analysis. Two-phase flow cases, such as in the examples mentioned, are a more complex challenge for flow assurance modelling compared to flow assurance in oil and gas transportation and injection/production well infrastructure.

Existing commercial software tools for flow assurance analysis are utilized for modelling the planned and unplanned operation modes for the various components of the CCS system, including the reservoir management component. These tools predict fluid behaviour and properties in the operating system. As

input, this modelling requires input data such as the CO₂ stream composition, the physical geometry of relevant infrastructure such as pipelines, injection wells and the receiving reservoir, and the operating conditions which include:

- steady-state and transient processes;
- single-phase and multiphase flow;
- pressure, temperature, phase fraction, velocity, etc., and their distribution in space and time; and
- distribution of fluid phase compositions in both time and space.

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Carbon dioxide capture, transportation and geological storage — Cross cutting issues — Flow assurance

1 Scope

This document describes and explains the physical and chemical phenomena, and the technical issues associated with flow assurance in the various components of a carbon dioxide capture and storage (CCS) system and provides information on how to achieve and manage flow assurance. The gaps in technical knowledge, limitations of the tools available and preventative and corrective measures that can be taken are also described.

This document addresses flow assurance of CO₂ streams in a CCS project, from CO₂ capture via transport by pipeline and injection well through to geological storage. It does not specifically address upstream issues associated with CO₂ sources and capture, although flow assurance will inform CO₂ capture design and operation, for example, on constraints on the presence of impurities in CO₂ streams, as there are too many different capture technologies to be treated in detail in this document.

Vessel transport and buffer storage that are considered in integrated CCS projects under development, are not covered in this document. Flow of material in the supply chain of a CO₂ source, even if delivered by a pipeline (e.g. blue hydrogen generation), and flow of gas streams within facilities generating and feeding these into a capture facility can impact flow assurance in CCS projects and networks. These are out of the scope of this document as well.

This document also examines the impact of impurities on the phase behaviour and physical properties of the CO₂ stream which in turn can ultimately affect the continuous supply of the CO₂ stream from the capture plant, through the transportation system and into the geological reservoir via injection wells.

Flow of fluids in oil reservoirs for the purpose of enhanced oil recovery is not within the scope of this document.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 27917, *Carbon dioxide capture, transportation and geological storage — Vocabulary — Cross cutting terms*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 27917 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1

carbon dioxide capture and storage network CCS network

connections of multiple CO₂ sources and storage sites

3.2

carbon dioxide capture and storage project

CCS project

either single capture-transportation-storage systems or multiple systems (networks) consisting of CO₂ capture systems, CO₂ transportation systems, and CO₂ geological storage systems

Note 1 to entry: In this document, the facilities generating a CO₂ stream are included in the considerations of flow assurance, as part of any decision or event at these facilities affecting the amount of CO₂ stream sent to the capture system, and will impact flow assurance within the CCS project.

Note 2 to entry: For more information on

- CO₂ capture systems, see ISO/TR 27912,
- CO₂ transportation systems, see ISO 27913, and
- CO₂ geological storage systems, see ISO 27914.

3.3

carbon dioxide capture and storage system

CCS system

combination of the capture, transportation and storage components considered as a single entity

3.4

component

assemblage of technical or geotechnical installations and natural features of subsurface geological systems that are separate in terms of physical space, technical disciplines, industrial practice and dominating physico-chemical processes

3.5

flow regime

type of flow pattern developed by fluid flowing through pipes

Note 1 to entry: Flow regimes depend on pressure and temperature dependent fluid properties, the diameter of the pipe, flow rates, fractions of each phase and the inclination of the pipe. Flow regimes can change with distance along a pipeline. In single phase flow, the regimes laminar and turbulent flow are distinguished.

3.6

hydraulic capacity

maximum flow rate achievable in a system for a given pressure loss

4 Abbreviated terms

BHP	bottom hole pressure
BHT	bottom hole temperature
CCS	carbon dioxide capture and storage
DHSV	down-hole safety valve
EoS	equation of state
EOR	enhanced oil recovery
HET	hydrate equilibrium temperature
MEG	mono-ethylene glycol
RFO	ready for operation

SSSV	subsurface safety valve
THMC	thermal, hydraulic, mechanical and chemical
WAG	water alternating gas

5 Overview of the necessity of flow assurance in CCS projects

5.1 General

During normal operations, CCS projects are generally designed to deliver an uninterrupted supply of a CO₂ stream:

- a) to and from the capture plant;
- b) through the transportation system, such as pipelines;
- c) into the geological storage reservoir including the injection wells and surface infrastructure; and
- d) within the storage reservoir.

Most CCS projects will be associated with fluctuating operating characteristics and conditions, i.e. varying inflow and outflow behaviours. Detailed consideration of these characteristics during the design and planning of the individual components of CCS projects need to be coupled in a way that can minimize the risk of flow interruptions of the CO₂ streams through the entire CCS project to as low as practicable. To best achieve this, the overall system fluctuations of pressure, temperature, fluid velocities and flow rates of CO₂ streams and their gradients are kept within the predefined operational ranges for these parameters at each CCS component as determined from the flow assurance modelling during the design phase of the project. The design of technical components can include means to facilitate preventive and corrective measures to achieve these operational ranges.

Notwithstanding that it would be ideal to maintain uninterrupted flow, in reality, like all industrial processes, interruptions caused by planned or unplanned events are inevitable, for example, maintenance work or unexpected equipment failure or in EOR operations injecting water and CO₂ (WAG schemes) intermittency is inherent to normal operations. Therefore, flow assurance requirements need to make provision for such fluctuations and events.

5.2 Reasons to maintain flow assurance

There are several reasons for ensuring uninterrupted flow along the entire CCS chain including:

- Technical and safety: Flow interruptions or excessive fluctuations of CO₂ stream properties (including mass flow rate, pressure and composition) increase wear of equipment and the risk of early failure due to physical or chemical effects. Chemical effects can include the formation of hydrates that can block pipes or reservoir rocks and corrode the equipment. Physical effects include vibrations, temperature effects on material integrity or mobilization of fine particles and blocking of pore throats in porous reservoir rocks. Rather sudden fluctuations of physical properties in CO₂ streams can result from phase changes or fluid dynamic effects (e.g. hydraulic hammer) that can damage infrastructure.
- Economic: Maintenance and replacement of equipment is a cost factor. A smaller than foreseen amount of CO₂ stored will reduce the income of CCS projects, e.g. from emission trading or tax credit generation as well as for transport and storage service providers. Excess CO₂ that cannot be captured, transported or stored and thus will be released to the atmosphere can result in payments for emissions. Furthermore, releasing captured CO₂ downstream is associated with unnecessary costs for the capture operation.
- Environmental: Venting of CO₂ will be counter to the purpose of climate mitigation by CCS projects and can release substances into the environment that are harmful to the human health or the

environment. The nature and concentrations of such substances depend on the capture technology. Lower than anticipated amounts of CO₂ captured, transported and stored will reduce the overall energy, resources and environmental balances of CCS projects.

5.3 Potential factors affecting flow of CO₂ streams at individual components of CCS projects

5.3.1 General

As illustrated in [Figure 1](#), the essential components of a CCS project that can impact flow of CO₂ streams are CO₂ sources, capture facilities (including purification and conditioning units), transportation infrastructure, manifolds for field distribution, injection wells and storage reservoirs.

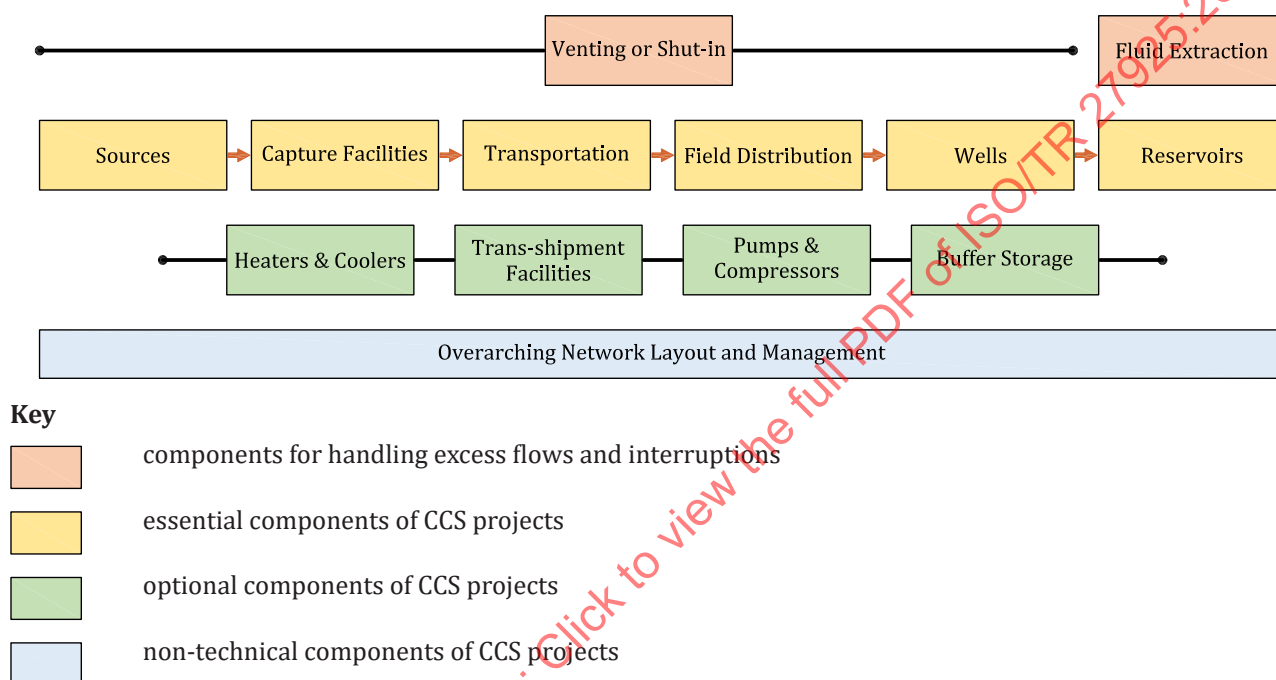


Figure 1 — Schematic overview of the components of CCS projects — CCS systems or networks

Essential components for a single source-to-sink scenario are connected by brown arrows in [Figure 1](#). Optional components and devices, that are not needed in every project, can be included at various locations within CCS projects, including trans-shipment facilities, pumps, compressors, heaters, coolers and buffer storage. Further technical components for managing flow interruptions or excess streams, likely to be installed in any CCS project, include venting or shut-in devices, e.g. safety valves along a pipeline.

Besides the technical components that impact flow assurance, management procedures will determine the overarching flow assurance within CCS projects. Flow assurance becomes a more complex issue for the overarching layout and management, for example when transportation networks connect multiple sources and sinks and facilitate alternative routing and means for transportation.

The continuous flow of CO₂ streams in CCS projects can be disturbed by flow rates above or below limits of normal operations. Counter measures can be the venting of a part of the gas streams (exhaust gas, process gas or CO₂ stream) or shut-in of equipment. Provisions for venting or shut-in can be located at multiple sites within CCS projects or within the essential components. Extraction of fluids, CO₂ stream or other formation fluids, from a storage reservoir can also be used to maintain continuous flow. For example, in the case of storage in saline aquifers, production of brine and its reinjection into other formations can be utilized for the purpose of pressure management.

Other than malperformance and failure of components, threats to flow assurance within each of the various CCS components are described in [5.3.2](#) to [5.3.8](#).

5.3.2 CO₂ sources

The CO₂ generation at the sources can vary or change for different reasons and at different timescales. The production of goods can be subject to market fluctuations that will be associated with equivalent fluctuations of industrial plants' CO₂ output. Some fluctuations can be foreseeable, such as seasonal fluctuations or planned maintenance and shut-downs. Other changes can occur on a timeline that is difficult to predict, for example, the generation of process heat can switch from coal to natural gas or hydrogen which can result in future that can lead to a permanent decrease in the generation of CO₂. This decrease and associated changes of the CO₂ concentrations in the process or flue gas stream can require changes to the capture technologies deployed. In networks of multiple sources, changes at individual sources can be levelled-out and the effects on the flow of the combined CO₂ streams can be compatible with the foreseen operational window for downstream infrastructure (see ISO/TR 27918). It is therefore necessary for the design of the various CCS components to accommodate a wide operating envelope including situations of turndown.

5.3.3 Capture facilities

The capture technologies including gas conditioning processes, determine the concentrations of impurities in CO₂ streams. The efficiency of capture processes depends on the mass flow and composition of gas streams – and their variations in time. Capture facilities and their equipment are designed to work in an optimal way within the design window of operation. Excess fluctuations of gas streams both in terms of composition and mass flow rates can lead to sub-optimal operation outside of the design window and to a reduced capture efficiency. Combining CO₂ streams from different sources and thus containing a different set of impurities can cause reactions between impurities that can result in products that can increase risks for flow assurance in downstream infrastructure, e.g. by increasing corrosion, friction, wear or deposition of products in pipelines. Thus, effort in the removal of impurities from the CO₂ stream can be required before transportation, or else combining of CO₂ streams can be prevented, if the mixture is incompatible with downstream components; see Reference [2].

5.3.4 Transportation

While the transportation of CO₂ in pipelines aims at achieving uninterrupted flow of CO₂ in a single dense phase (see ISO 27917) at ambient temperatures and high pressure, transport in vessels (road, rail, ship) are expected to be in a liquid phase at very low temperatures and moderate pressure. If physical properties of CO₂ streams in upstream and downstream infrastructure are different from that in the transportation system, installations have to be provided at either end of the transportation chain to adjust physical conditions. This equipment includes compressors, pumps, heaters and coolers. The impact of these on flow assurance depends on the technology utilized, the location of such equipment within the CCS project, and the designed range of flow rates (and CO₂ stream compositions) that these can handle.

Furthermore, the transport in vessels is inherently discontinuous, i.e. leads to intermittent transportation that requires some sort of buffering. Buffering can be achieved by pressure changes in pipelines (line packing), use of temporary stores (engineered or geological) or switching between a suitable number of vessels to ensure continuous filling and discharge of vessels, so that up- and downstream CO₂ can flow in a continuous manner. Overall, vessel transportation is more sensitive to external impacts than pipeline transportation, e.g. due to road or rail blockings, extreme water levels in rivers or off-shore storms that can interrupt shipping. Thus, additional dedicated buffers can be prudent in order to avoid interruptions, shut-ins and venting of CO₂.

5.3.5 Field distribution

In large scale storage projects, usage of several wells can facilitate CO₂ injection into reservoirs. Natural gas and oil reservoirs are usually exploited by a considerable number of wells, which can be used in active or depleted fields for CO₂ injection. A CO₂ stream arriving from distant sources has to be

distributed within the hydrocarbon fields through manifolds to the individual wells in order to fill the reservoir in an effective manner. In particular, the CO₂ demand of wells in EOR projects will be variable according to the oil production operation. For example, in WAG schemes, CO₂ is injected intermittently in individual wells. Trade-offs between optimum oil recovery and maximum CO₂ storage can be made in CO₂ EOR projects, that will be influenced by the revenues or savings from CO₂ storage and oil sale. Additional fluxes of CO₂ streams are associated with technical components for the separation of CO₂ from crude oil and formation water and recycling it to the injection wells.

Also, in aquifer storage, manifolds can be used for distributing CO₂ streams between injection wells in one or more reservoirs. Wells can be laterally spaced in one storage formation, as in the case of the Krechba storage site (Algeria), or tap reservoirs at different depths, such as in the Snøhvit field (Norwegian Continental Shelf). Benefits of using more than one well for injection into saline aquifers include the possibility to react in the case of injectivity or containment problems, the ability for switching between wells in the case of maintenance or logging in a well, or the options for pressure management and plume steering in the storage reservoir. This flexibility suits the flow assurance in the upstream components of CCS projects.

5.3.6 Injection wells

Similar to pipelines, injection wells need to maintain flow of CO₂ streams at rather constant conditions. However, the physical conditions of CO₂ streams can differ considerably from top to bottom of a well, especially if reservoir pressures are much lower, e.g. in depleted natural gas reservoirs than at the end of transportation pipelines or temperatures are much higher in the reservoirs compared to the low temperatures of liquid CO₂ in ships. Such contrasting conditions hold technical challenges for design and operation of injection infrastructure. Technical challenges include avoiding the formations of hydrates that can block flows and phase changes or thermal and/or hydraulic stresses that can impair well integrity. Corrosion or mechanical wear can lead into situations that can require monitoring (using logging), maintenance or work-overs on one or more injection wells. Wells can be out of service because of such operations for a while. Therefore, avoiding of early well workover is one of the aims for flow insurance in injection wells.

In particular, offshore CO₂-injection wells sometimes have to be operated under transient or intermittent conditions. In case of pipeline transportation, this can be due to varying CO₂ supply, and in the case of ship transportation, it can be due to the arrival of ships and the lack of buffer storages. From a study into the effect of thermal cycling in the well due to intermittent injection from ships (see Reference [3]), it was found that long intervals, low CO₂ temperatures and high injection rates lead to the highest thermal stresses in the well. Depending on the well materials and construction, those stress levels can impact well integrity showing the importance of considering thermal and mechanical stresses in the well design for cyclic injection operation.

5.3.7 Storage reservoirs

Natural rocks are heterogeneous at different scales. Sedimentary structures in the centimetre to decimetre range and beyond affect bulk hydraulic properties, such as permeability. Tectonic structures and variations of the sedimentary depositional environment in the scale of tens to thousands of metres can result in the compartmentalization of reservoirs, impacting plume migration, brine displacement, pressure build-up and injectivity of wells. The resolution of seismic images is low compared to the size of sedimentary or tectonic structures affecting fluid flow and rock samples obtained from well drilling are usually too small to be representative for a larger reservoir volume. Thus, parameters required for “precise” prediction of fluid flow in reservoirs are not available in the required resolution and full spatial coverage. Numerical models describe fluid flow in reservoirs in simplified ways, assuming generalized parameter distributions at rather coarse scales. Hence, CO₂ plumes will not spread out in natural reservoirs “exactly” as predicted by numerical models. An example of such structures that had not been resolved in seismic images before the injection of CO₂ are the shale layers within the Utsira sand at the Sleipner CCS project, that have a marked impact on the shape of the CO₂ plume within the reservoir, see Reference [4]. Thus, the uncertainties regarding actual injection rates, pressure build-up, spreading of CO₂ plumes and the displacement of formation fluids can be large and can impact the overall CO₂ uptake of a reservoir. An example of the impact of storage properties is the experience in the

Tubåen Formation storage reservoir within the Snøvit CCS project offshore Norway, see References [5] and [6]. At the given injection rates, pressure within the reservoir built up faster than anticipated requiring additional injection wells to be drilled beyond the area influenced by this premature pressure build up. During project lifetime, reservoir models generally will be updated based on operational and monitoring data to increase conformance between models and real plume behaviour and reduce uncertainties in predictions.

5.3.8 Optional components

In addition to the essential components, CO₂ streams can pass optional installations along the route of CO₂ transportation, such as trans-shipment facilities, pumps, compressors, heaters, coolers, buffer storage, venting or shut-in devices, e.g. safety valves along the CCS chain as described in Figure 1. The impact of these on flow assurance depends on the used technology, the positions within a CCS chain or network, and the specified range of flow rates and CO₂ stream compositions that these can handle.

5.4 Providing flow assurance

5.4.1 General

Assuring a stable flow of CO₂ streams through a CCS chain or network can be secured by preventative and mitigative or corrective measures. Reducing the risks of intermittent flow will likely require a project-specific balanced mix of the two approaches. Consequences of interruptions, costs, damage of reputation etc., can be criteria for the selection of measures for flow assurance.

5.4.2 Technical design

A key parameter for the appropriate design capacity for CCS projects is the expected total mass flow of a CO₂ stream and its variation over the project lifetime. High flexibility of equipment for variable flow rates is beneficial for flow assurance. In single source-sink chains, the component with the least flexibility will dictate the flexibility of the entire project to cope with fluctuations or interruptions. Redundancy of limiting components or the use of modular components can increase the flexibility of the entire project. Several units of capture facilities, pumps or injection wells can be combined for the enhancement of the overall flexibility.

Generally, storage reservoirs cannot be modified, apart from fluid extraction for pressure management or in the event injection creates, propagates or activates faults in the formation or confining layers. Thus, storage site exploration can include the surroundings (laterally and vertically) of storage formations so that additional storage volume can be tapped into if required.

Large volume buffer storage or reserve storage, e.g. in depleted fields with re-usable infrastructure, can be used for captured CO₂ that cannot be transported and stored according to the planned regular operation.

5.4.3 Operational procedures and work-flows

Where flow interruptions are unavoidable, a process for prioritising sites in CCS projects where CO₂ can be released or shut-in with the least detrimental impact can be employed. These can vary depending on the site in a CCS project where the flow is interrupted first. It is important to undertake the sequence of shut-ins and venting as well as velocities of ramp down (and up) in a manner that will minimize impacts on equipment of the entire chain. To mitigate this, as part of the preparation for such shut-down events, it is important to communicate the measurement and control technology between different components of a CCS project and the appropriate and safe response to such pre-determined and expected events. This can be challenging if different owners and operators are involved, and if addressed possibly through overarching project management.

For planned flow interruptions in CCS projects, such as those experienced during maintenance shutdowns, continuous flow, can be maintained via either use of buffer storage or availability of back up equipment to minimise variations of flow and phase behaviour of the CO₂ stream, or both.

5.4.4 Overarching project management

CCS projects can be managed as a simple source-sink system operated by a single entity. Simple source-sink systems can encounter challenges that more complex CCS networks can in principle avoid. For example, complex CCS networks would be expected to better cope with interruptions and fluctuations of flows, directing CO₂ streams through bypasses or to alternative storage sites, or obtaining CO₂ from other sources in order to maintain supply, e.g. for storage associated with EOR or if minimum flow rates are required. Ships can be very suitable to maintain such a flexibility on the CO₂ supply side as many industrial clusters of CO₂ sources are located in coastal areas, e.g. along the coast lines of the US Gulf coast, the North Sea or the Yellow Sea.

Overarching project management includes the coordination of different entities of CO₂ providers, transportation and storage operators. In the European Union, regulatory access to transportation and storage infrastructure is available to third parties where it “reasonably can be made available”, see Reference [7]. Regulators will also play a role in directing CO₂ streams, if there is a surplus of storage capacity, or expanding CO₂ transportation and storage infrastructure if additional CO₂ emitters choose to join CCS projects. Therefore, operators can be faced with requests to facilitate larger flow rates for transport and storage of CO₂ than initially planned.

Overall, the design, siting and dimensioning of CCS networks are associated with uncertainties of market developments and competing options for CO₂ sources to achieve their emission reduction or compensation. The success of renewable energy production, the substitution of fuel and processes in combination with the political targets of greenhouse gas neutrality can lead to declining needs for CCS and infrastructure can be oversized for later in its lifetime. Storage and transportation facilities can be downsized or decommissioned when CO₂ sources diminish. Thus, due to such uncertainties and the financial risks they pose on private investment, the development of transportation infrastructure and storage site exploration requires government investment to underwrite any such risks. For example, the European Union has recognized this by listing some CO₂ transport infrastructure proposals as projects of common interest for transnational energy infrastructure, that are entitled to apply for financial support from the European Union. Using these benefits in complex CCS networks can involve different legal entities and thus requires an overarching project management (in addition to the reasons mentioned in 5.4.3) comparable to the regulation of electrical power grids.

6 Fluid composition and physical properties

6.1 General

Thermal, hydraulic, mechanical and chemical processes or a combination of these processes, influence the phase behaviour and in turn the flow assurance of CO₂ streams. Nonlinear coupled formulae can be used to describe these processes. Thermodynamic and transport properties of CO₂ streams are key in modelling, designing and operating CO₂ capture, transportation and storage systems. Thus, the properties of CO₂ streams in the different systems need to be well known. Due to the complexity and multitude of possible processes and CO₂ stream phase states in multi-component and multi-phase CO₂ streams, modelling and predicting stream behaviour and flow can be challenging.

Thermodynamic properties of the CO₂ stream are of particular interest, as the critical point of pure CO₂ lies close to temperature and pressure conditions typically encountered during CO₂ transport and injection, so that two coexisting phases can be expected in different systems and at various operation conditions. Even small changes in either pressure or temperature, or both, during operation can lead to rapid and substantial changes in the physical properties of a CO₂ stream, leading to phase changes or multiphase conditions.

In the presence of impurities in the CO₂ stream, the phase boundary line widens up into a two-phase region in the pressure-temperature space and the triple point and the critical point are shifted to different temperature and pressure values. In addition to the impacts on the CO₂ stream phase state, impurities modify the CO₂ stream physical properties. The magnitude and direction of these modifications depend on the nature and the concentrations of the impurities present. In some cases, even small concentrations of impurities can lead to very pronounced changes of the properties of the

CO₂ stream. Thus, knowing and being able to predict the boundary of the two-phase region as well as the impure CO₂ stream's other physical and chemical properties is of uttermost importance for accurately designing and operating CO₂ transport, injection and storage systems.

For predicting the physical properties of pure and impure CO₂ streams, validated equations of state and physical property models are commonly used. Experimental measurements are still ongoing to qualitatively and quantitatively improve the data basis for the equations of state and property models and thus improve their applicability, accuracy and reliability for CO₂ streams of various composition.

Though the chemical composition of CO₂ streams is relevant to flow assurance, in particular due to cross-chemical reactions between different impurities potentially forming more corrosive substances, reactions with chemical substances used for capture and conditioning of CO₂ streams, and because of geochemical reactions within geological storage complexes, the focus of [Clause 6](#) is on physical properties.

6.2 CO₂ phase behaviour and thermophysical properties — Key features

The thermodynamic phase diagram in terms of pressure, P , and temperature, T , for pure CO₂ is shown in [Figure 2](#), as modified from Reference [7].

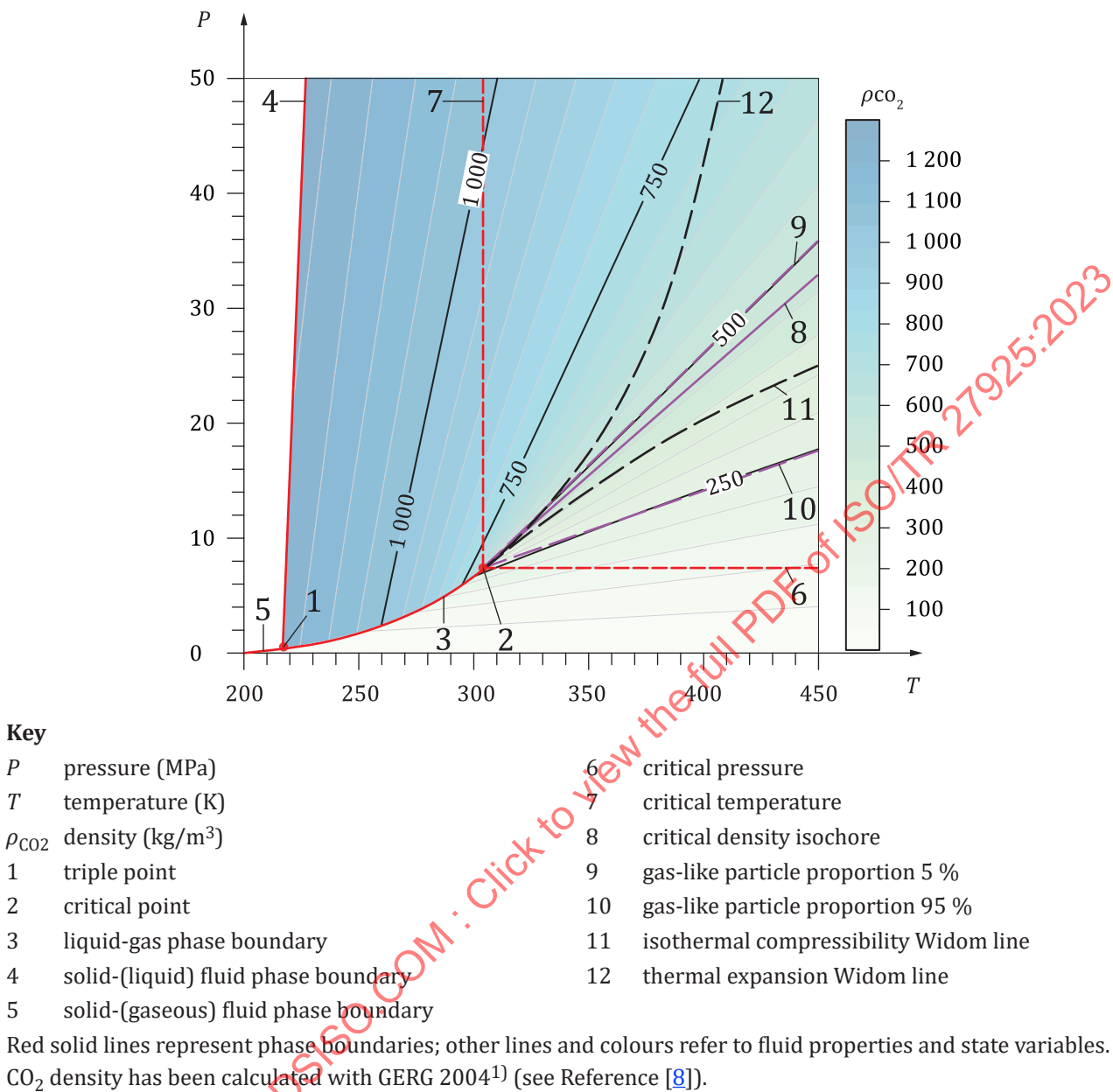


Figure 2 — Thermodynamic phase diagram for pure fluid CO₂

At temperatures below the critical temperature (and above of the triple point temperature), as the pressure increases, fluid CO₂ of low density (gas) compresses and eventually condenses into a much denser fluid (liquid), resulting in the discontinuity at the liquid-gas phase boundary in Figure 2. In thermodynamic equilibrium, the system consists of two co-existing phases – liquid and gas. The fractions of the two phases can change within technical components due to pressure, volume and temperature, *PVT*, changes.

- Fluid CO₂ in the *P-T* range between Figure 2, Key 3, 4 and 7 is often named liquid CO₂.
- Fluid CO₂ in the *P-T* range below Figure 2, Key 3, 5 and 6 is often named gaseous CO₂.
- Fluid CO₂ in the *P-T* range between Figure 2, Key 6 and 7 is often named supercritical CO₂.

1) GERG 2004 is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

- Solid CO₂ in the P - T range above [Figure 2](#), Key 4 and 5 is often named dry ice.
- Dense phase CO₂ is not a thermodynamically defined phase, but a technical term, referring to fluid CO₂ of high density. Densities characteristic for dense phase depend on the technically relevant properties in particular situations, e.g. compressibility which is relevant for pumping or turbo-compression of fluid CO₂.

Near to the critical point, the density difference between gas and liquid phase decreases and reaches zero at the critical point condition, at which the two phases become one fluid phase.

In a supercritical fluid, a gradual, monotonic transition of properties (e.g. density in [Figure 2](#)) from liquid to gaseous behaviour can be achieved by PVT changes. However, the supercritical region is not homogeneous with respect to fluid behaviour. Resulting from molecular interactions, temporal and spatial molecule association and motion, density and structure of molecular assemblages vary on a micro-scale resulting in different macroscopic fluid properties.

Near to the critical point, above of the critical pressure and temperature, a small increase in these variables will cause a large increase in the density of the supercritical CO₂. The maximum of property gradients (response functions) form curves in the supercritical fluid region, originating at the critical point, known as a Widom line. Heat capacity or isothermal compressibility are often used to define Widom lines and to distinguish gas-like and liquid-like regions in the supercritical domain. Widom lines for isothermal compressibility and thermal expansivity are shown in [Figure 2](#), see Reference [9]. Other physical properties also show large gradients with pressure or temperature near the critical point, e.g. viscosity, relative permittivity and solvent strength, which are all closely related to density. The Widom lines for these various properties vary in curvature and deviate from each other as illustrated by the two examples in [Figure 2](#), see Reference [10]. The actual location of Widom curves is dependent on the calculation model and methodology chosen, including not only the equation of state itself but also its derivatives. Different implementations of the same model can result in quite different trajectories of these curves. Therefore, it is important to understand that the trajectories of Widom curves are dependent on the physical properties of the relevant fluids.

Molecular dynamic simulations have shown that the critical isochore – the line of constant specific volume which is the reciprocal of density – coincides with the line where the proportion of gas-like particles is equal to those of liquid-like particles of a Lennard-Jones fluid – the fluid that can be adequately described by a simple model of intermolecular interactions – and local maxima of the specific isobaric heat capacity. Thus, a thermodynamic reasonable distinction of liquid and gaseous fluid behaviour can be tied to the critical density, 467 kg/m³ in case of CO₂. These simulations have also shown that corresponding proportions of gas-like particles of 5 % and 95 % would coincide with the isochores of 500 kg/m³ and 250 kg/m³, respectively, in supercritical CO₂ (see Key 9 and 10, respectively, in [Figure 2](#)).

As shown in [Figure 2](#), the pressure temperature, PT , space within the supercritical fluid region, in the transition between liquid-like and gas-like properties and behaviour, is known as the Widom area, delta, or region. Though no phase transitions will happen (at thermodynamic equilibrium) within this delta, steep gradients, minima, and maxima of properties can cause rapid changes of fluid properties resulting from variations of the state variables, P , V and T . Thus, conditions within the Widom area need consideration in the design and operation of CCS systems and their technical components. In this area, e.g. super-compressibility or latent heat can be effects to deal with in compression or heat transfer installations. At higher temperatures (and pressures), the pressure (and temperature) dependency of fluid properties declines. So much, that at pressures greater than about three times the critical pressure (22 MPa for CO₂) no “anomalous” fluid behaviour is observable and the system transforms continuously from liquid-like to vapour-like behaviour.

Other structural transitions within supercritical fluids have been observed and regions of different fluid properties have been distinguished, e.g. liquid, non-rigid liquid, vapour, ideal gas, and the transitional Widom area. Rigid and non-rigid CO₂ are distinguished by the Frenkel line, see Reference [11]. While shear waves can pass through the rigid fluid, they won't travel through the non-rigid CO₂. This behaviour can be relevant for seismic monitoring of a CO₂ plume within reservoirs, for example. As various experimental investigations and molecular dynamic simulations yield different Frenkel lines for CO₂, these are not depicted in this document which has a geotechnical focus. Further, polymorphic

phase transitions have been observed in liquid and supercritical CO₂ within pressure and temperature ranges relevant to CCS systems, see Reference [12]. Whether these recently discovered isomorphic phase transitions within fluid CO₂ are of (geo-)technical relevance, is not known at present.

The physical properties of pure CO₂ are described by equations of state (EoS), which are mathematical correlations that approximate experimentally determined fluid property data.

6.3 Modelling properties of pure CO₂

Various equations of state have been developed for pure CO₂ and these have been included or coupled to numerical process simulation tools. Some simulation tools read data from pre-calculated property tables according to local system state variables. The selection of an appropriate EoS is fundamental for obtaining reliable simulation results. In CO₂ capture, transportation and storage systems, the physical conditions of CO₂ streams can be near to the critical point of CO₂, where gradients of properties are large, uncertainties of EoS calculation results are high, and differences between various EoS matter. For example, the density of CO₂ as a function of depth, for average *p-T* conditions in the subsurface, has been calculated using various EoS (see Figure 3). Up to 500 m depth deviations of CO₂ properties from an ideal gas are low and the different EoS yield comparable density values. Between 700 m and 1 500 m depth however, the deviation between the calculation results from various EoS evidently cannot be neglected, while the density profiles of most EoS converge again towards greater depths. EoS that correspond to experimental data well are more mathematically complex than simpler EoS with larger deviations from experimental data.

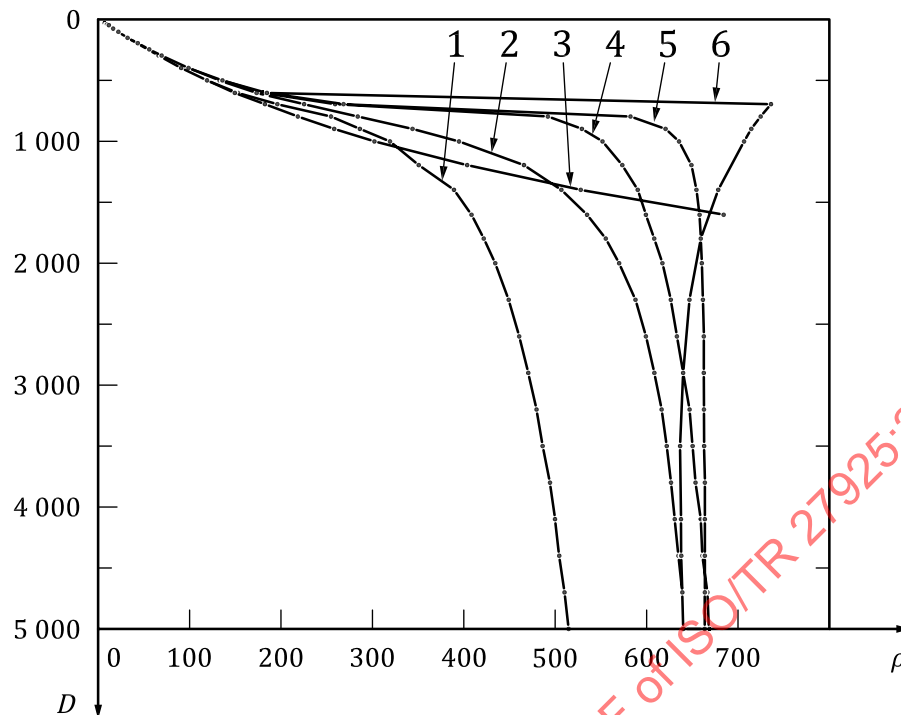
Selecting appropriate EoS will have to consider various aspects, such as:

- purity of expected CO₂ streams and validity of EoS for CO₂ stream compositions under consideration;
- *P-T*-range of validity of the EoS (calibrated against experimental data);
- expected range of physical conditions in the system under consideration;
- technically tolerable uncertainties of EoS calculations (in relation to other uncertainties);
- computational effort for solving the EoS (in relation to using calculated tables).

The equation of state model proposed in Reference [13] offers the best available prediction of pure CO₂ thermodynamic properties. It is computationally demanding and, in some situations, a less precise EoS can be sufficient for a given purpose. Separate models are needed for the computation of transport properties required by process simulation tools, see Reference [14] for viscosity.

EoS for pure CO₂ covering all conditions along a CO₂ transportation path, from source to storage reservoir, such as the Span and Wagner model, are useful for modelling of CO₂ streams in the following cases:

- where the fluid is more than 99,5 % CO₂,
- where the water dewpoint is not an issue under consideration, and
- where the behaviour of impurities in the two-phase area is not important.

**Key** D depth (m) ρ density (kg/m^3), calculated according to References [73] to [78]

1 EoS published in Reference [73]

2 EoS published in Reference [74]

3 EoS published in Reference [75]

4 EoS published in Reference [76]

5 EoS published in Reference [77]

6 EoS published in Reference [78]

NOTE The hydrostatic pressure gradient is 10 MPa/km and the temperature gradient is 30 K/km.

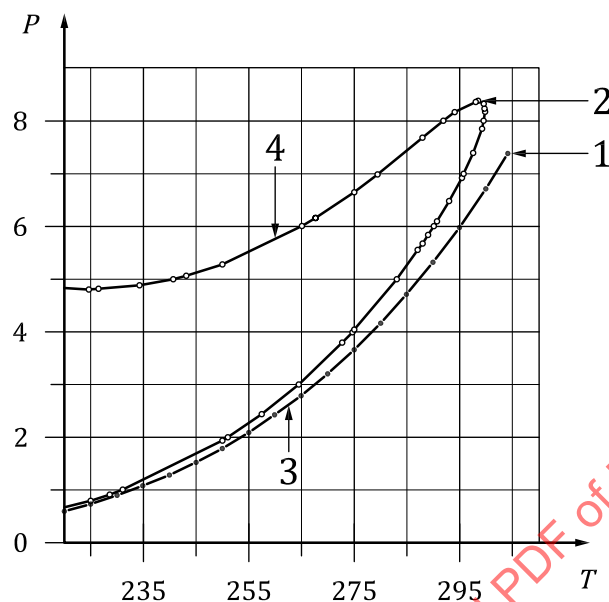
Figure 3 — CO₂ density as a function of depth, calculated with different EoS for typical pressure and temperature conditions in the subsurface

6.4 Properties of impure CO₂ — Phenomena and their modelling

Once a CO₂ stream provided for transport and storage is not pure, its phase behaviour, physical and chemical properties can differ significantly from that of pure CO₂. Therefore, appropriate thermodynamic and transport properties of impure CO₂ are needed for flow assurance analysis. As a minimum, impurities will have an impact on the operating conditions of components designed to maintain single-phase conditions, such as pipelines.

In Figure 4, the phase diagrams for thermodynamic equilibrium for pure CO₂ and a binary mixture of CO₂ and N₂ (calculated using the GERG 2004 EoS, see Reference [15]) are plotted for comparison. The equilibrium line for pure CO₂ widens to a two-phase field in P - T space in the case of the CO₂-N₂ mixture. The presence of impurities in CO₂ leads to a different critical point, compared to pure CO₂. The critical point of mixtures does not coincide with the maximum pressure and temperature of two-phase coexistence. In the example of Figure 4, the maximum pressure (cricondenbar) is about 0,05 MPa above of the pressure at the critical point, where both phase fractions are equal and the maximum temperature for two-phase coexistence is about 0,5 K above of the critical temperature of the mixture. This temperature is called cricondentherm. The shape of the two-phase region varies depending on the kind of impurities in binary mixtures. The extent of the two-phase region generally increases

with the amount of impurities. Within the two-phase region phase fractions and phase composition vary systematically, when state variables change. The amount and type of impurities present can vary significantly even for the same source, depending on the capture process operation and conditioning of the CO₂ streams. Further thermodynamic equilibria, for which the phase envelopes have been calculated, cannot always be achieved in dynamic flow situations.



Key

- P pressure (MPa)
- T temperature (K)
- 1 critical point of CO₂
- 2 critical point of a mixture of 94 % CO₂ and 6 % N₂
- 3 liquid-gas phase boundary for pure CO₂
- 4 boundary of liquid-gas coexistence field for CO₂ and N₂ mixture

Figure 4 — Example of a phase diagram for pure CO₂ and a mixture with 6 mol % of N₂

The properties of CO₂ streams with impurities typical for CCS applications have not been studied by laboratory testing to the same level of detail as for pure CO₂. The availability of binary mixture experimental data are (especially for systems with light impurities) fair to good for phase boundary conditions (i.e. bubble and dew point conditions) across the fluid range of conditions. However, what is at large scarce or missing experimental data are bubble and dew point data on multi-component CO₂ streams. The absence of such data has in turn not made possible the ability to quantify the range of uncertainty of the calculations for multi-component systems, as well as phase fractions within the two-phase region of binary and multi-component systems.

Models for mixtures of real gases for various ranges of conditions have been developed. One of the advanced EoS for CO₂-rich fluids is EOS-CG-2019, see Reference [16], including impurities relevant to CCS: H₂O, Ar, O₂, CO, CH₄, H₂, H₂S, SO₂, HCl, Cl, monoethanolamine and dimethanolamine. However, there is no universal equation of state for CO₂ streams with all kinds of mixtures of impurities, that can arise e.g. if CO₂ streams are combined in a transportation network. Also, because of limited experimental data and various multi-component mixing models included in software for calculating thermophysical properties, predictions of the properties of CO₂ streams can be subject to uncertainty and inaccuracy, especially along phase-boundaries, close to critical conditions, and within Widom areas, where the properties change rapidly. As in pure substances, Widom lines can be defined for mixtures as well. Molecular-dynamic simulations for simple binary systems (noble gases) indicate that the situation is more complex though and one or more lines can be defined, depending on the miscibility of the components, see Reference [17]. The practical relevance of these findings is still a matter of ongoing

research. These uncertainties and unknowns about supercritical fluid mixtures have to be considered during design and operation of capture, transport and storage systems for impure CO₂ streams. Eventually case-specific determinations of relevant properties of anticipated or sampled fluid mixtures can be helpful.

Some design scenarios are subject to particular uncertainties in the accuracy of property prediction and other design challenges, and can require special attention.

- The two-phase region, and phase transitions in general, present challenges for the handling of CO₂ streams as phase fractions can vary considerably within two-phase regions and from flow regimes that can be described as e.g. mist, dew, foam, a bubbling liquid, or rain in injection wells.
- The current flow assurance simulation packages have challenges to ensure stable solution in resolving phase transition under some situations.
- Estimates of pipeline running-fracture behaviour can be very sensitive to impurities in liquid or in dense phase CO₂ streams, particularly to presence of light impurities such as H₂. However, for gas phase dominated situations (i.e. early in injection into deeply depleted, low-pressure gas fields) this is less relevant.
- The density of impure CO₂ streams expected from various capture technologies is often expected to be lower than that of pure CO₂, which, in addition to the effect of dilution, will reduce storage capacities, especially in shallow reservoirs (800 m to 1 200 m in depth). Other, impurities can elevate the density of CO₂ streams.
- In situations where ice, solid CO₂ or hydrates can precipitate from CO₂ streams, EoS for fluid phases alone are not sufficient for flow assurance modelling. Phase-equilibrium algorithms can be used to predict the formation of such phases, e.g. as implemented in TREND, PVTsim or Multiflash^{TM2}, see References [18] and [19].
- The formation of a separate aqueous phase, by condensation of liquid water in a CO₂ stream can be significantly affected by the presence of very small quantities (ppm range) of polar molecules. Both phases can be mobile as a bulk two-phase mixture, but can still require attention. As soon as new phases are formed from a single-phase fluid, chemical substances fractionate between the different fluid phases and impurities can become concentrated in a minor phase. When water condenses, from a CO₂-rich phase, the accumulation of SO_x in the aqueous phase results in the formation of acids that can be corrosive. In addition to thermodynamic phase changes, new chemical substances can be formed by cross-chemical reactions between different impurities in CO₂ streams, such as strong acids, or by reactions of impurities with or in a newly formed fluid phase. If relevant, predictive modelling of such processes would require cross-chemical reaction and aqueous chemical speciation models and coupled transport simulation software, including chemical reaction kinetics.

The experimental data used for adapting the EoS parameters need to reflect the CO₂ stream composition and the *PT* conditions as closely as possible. This is pertinent where light impurities are present in the CO₂ stream, including H₂, or polar molecules, such as water.

Compressors, pumps, or pipelines are often designed for single-phase flow or homogeneous phase mixtures. It is an engineering task to attain and maintain the continuity of such flow. Two-phase flow or counter-flow of two phases, for example, by treating gas streams using solutions of liquid solvents for CO₂ capture, can exist in capture facilities, including the compression process. Two or three fluid phases will have to flow through reservoir rocks (CO₂ stream, formation water and oil). In reservoirs, in addition to fluid properties, reservoir properties also matter with respect to flow assurance, as permeability and capillary forces affect flow through porous media. Thus, chemical and reservoir engineers require further physical properties, relevant to their systems and components that are not specifically addressed in this document, but still important for the overarching flow assurance in integrated CCS projects.

2) TREND, PVTsim or MultiflashTM are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

6.5 Individual impurities

6.5.1 General

Most CO₂ streams contain multiple impurities, and CO₂ from different processes and capture technologies will have different combinations and concentrations of impurities. The number of potential chemical reactions increases with the number of impurities, and the products of these chemical reactions can cause problems such as erosion, corrosion and clogging. It is therefore important to consider the compatibility of multiple CO₂ streams, including the full range of anticipated impurities at relevant concentrations.

[Subclause 6.5](#) briefly reviews common impurities in CO₂ streams typically encountered in CCS projects; see Reference [\[20\]](#) for further details.

6.5.2 Water

Water (H₂O) is likely to be present as an impurity in most CO₂ streams from any source. Water presents few issues as vapour, but it is a significant challenge if allowed to condense as a liquid in a CCS system.

Water can cause corrosion and can form solids as either ice or CO₂ clathrate hydrates. The dew point of a water phase and the properties of that phase can be significantly affected by other impurities present in the stream.

Water content of a CO₂ stream is typically set to prevent the formation of an aqueous phase during transportation in pipelines and vessel.

6.5.3 Nitrogen and argon

Nitrogen (N₂) and argon (Ar) are both found as impurities in many CO₂ streams due to their presence in air. Nitrogen is unreactive and argon is inert. Consequently, both impurities are generally unreactive at CO₂ transport and storage conditions.

Both nitrogen and argon are lower molecular weight components than CO₂, and so tend to increase the bubble point pressure of a CO₂ stream. This can increase the minimum operating pressure of pipelines transporting dense phase CO₂ streams.

6.5.4 Hydrogen

Hydrogen (H₂) is a common impurity present in CO₂ streams from pre-combustion carbon capture, such as after steam reforming of methane or hydrogen production from hydrocarbons. Hydrogen is a very small molecule and accordingly presents unique challenges.

As with other low molecular weight non-polar components – such as nitrogen or argon – hydrogen will increase the bubble point pressure of a CO₂ stream, which will increase the minimum operating pressure of single phase/dense phase operation in a pipeline. Any gas bubbles that form, in the presence of a liquid phase, will tend to concentrate H₂ and therefore it will be at a higher partial pressure.

The two main modes where the presence of gas bubbles is likely are:

- during shutdown of a pipelines transporting dense phase CO₂ streams, where cooling of the pipeline will lead to a reduction in pipeline pressure, ultimately creating bubbles at local high points;
- during shutdown of wells, at a range of reservoir pressures where the settled out well consists of a liquid column with a small gas bubble at the top.

Hydrogen (and other components leading to an increased bubble-point pressure of the CO₂ stream) can increase the risk of running-ductile fracture in pipelines where the fluid is in a dense or liquid phase. Accordingly, this has pipeline integrity implications; see References [\[21\]](#), [\[22\]](#) and [\[23\]](#).

6.5.5 Oxygen

Oxygen (O_2) is a by-product of incomplete combustion or can result from air ingress and can accordingly be present as an impurity in CO_2 streams from many different sources.

Oxygen is lighter than CO_2 and therefore will tend to increase the bubble point pressure of a CO_2 fluid if present in sufficient concentration. It can also increase corrosion rates in the case of a free aqueous phase.

There are more significant subsurface risks associated with oxygen in some reservoirs, which can require oxygen levels to be controlled to within the ppm range. Refer to 8.3. For example:

- Oxygen can react with residual hydrocarbons in a reservoir, particularly heavy oils. At temperatures above 120 °C, low temperature oxidation (LTO) can take place and, depending on the properties of the reservoir, lead to issues associated with this exothermic reaction. In hotter reservoirs, high temperature oxidation (HTO) can take place where temperatures exceed approximately 200 °C.
- There is also experience with oxygen encouraging the growth of sulfate reducing bacteria (SRB) in some reservoirs by stimulating growth of fermenting bacteria (facultative aerobes) that provide small organic molecules which in turn can be used by SRB as a carbon and energy source. In some reservoirs, there is the possibility of issues due to the action of SRB leading to formation of biofilms that can compromise injectivity.

6.5.6 Carbon monoxide

Carbon monoxide (CO) is a product of incomplete combustion and can potentially be present as an impurity in CO_2 streams from many different sources.

Carbon monoxide is potentially toxic with significant impact on the human health. It is also lighter than CO_2 and therefore will tend to increase the bubble point pressure of a CO_2 stream if present at significant concentrations.

6.5.7 Methane and ethane

Methane and ethane are hydrocarbons most often present in a CO_2 stream where capture takes place directly from a hydrocarbon stream, for example, before combustion, such as direct capture from a hydrocarbon stream. The concentration of methane in a captured stream is typically much higher than that of ethane.

Methane and ethane tend to increase the bubble point pressure of a CO_2 stream when present at significant concentrations.

6.5.8 Propane and other aliphatic hydrocarbons

As with methane and ethane, there is the potential for heavier hydrocarbons to be present as an impurity in a CO_2 stream due to their presence in hydrocarbon fuels for combustion or within a process fluid being treated. Typically, the concentration of these heavier hydrocarbons in a CO_2 stream is much lower than that of methane or ethane.

In general, propane and heavier hydrocarbons are heavier than CO_2 , and will tend to decrease the dew point pressure (or increase the dew point temperature) of the fluid.

6.5.9 Nitrogen and sulfur oxides

Sulfur oxides (SO_x) such as SO_2 and SO_3 , and nitrogen oxides (NO_x) such as NO or NO_2 are common by-products of combustion and therefore present as impurities in many captured CO_2 streams.

Both NO_x and SO_x can be toxic with significant impact on the human respiratory system. NO_x and SO_x can react with water, even where a free liquid water phase is not present. This reaction can result in the

formation of strong acids creating a potential corrosion risk, e.g. in the pipeline, in particular after acid condensation.

Strong acids can promote alteration of wellbore cements and rocks in storage complexes, dissolution of primary minerals and the precipitation of secondary minerals in the pore space. SO_x , if present at significant level can lead to the precipitation of sulfate minerals that can reduce reservoir permeability; see Reference [20].

6.5.10 Hydrogen sulfide

Hydrogen sulfide (H_2S) is a possible impurity in gases from pre-combustion capture, natural or industrial gas streams or in gases produced by biomass fermentation.

It can be toxic and potentially harmful to humans with significant impact on the respiratory system. It can also have a detrimental impact on some storage reservoirs as a result of precipitation of sulfide minerals, such as pyrite, and subsequent loss of injectivity.

In the presence of a liquid aqueous phase, H_2S can form an acidic solution that can lead to enhanced pipeline corrosion.

6.5.11 Carbonyl sulfide

Carbonyl sulfide (COS) can be present in gases from pre-combustion capture. As with hydrogen sulfide, it can be toxic and potentially harmful to humans with significant impact on the respiratory system.

The potential impact of COS on reservoirs is not well understood. Under some conditions, it can be possible for COS to hydrolyse and create hydrogen sulfide, leading to precipitation of sulfide minerals, such as pyrite. There is little research on the behaviour of COS , and accordingly, it is not possible to rule out that COS can possibly react directly with some minerals in some other way.

6.5.12 Ammonia

Ammonia (NH_3) is a possible impurity in captured CO_2 streams, either as carryover from ammonia production or due to the use of ammonia as a solvent to capture the CO_2 itself.

Ammonia can react with CO_2 and water to create ammonium carbonate, and also with NO_x or SO_x in a similar way.

6.5.13 Amines

Amines are often used as a solvent in post combustion CO_2 capture and there is potential for traces of the solvent to be carried over into the CO_2 stream. The co-existing presence of water and certain types of amines increases the temperature at which dew point occurs compared to equivalent amounts of water in gas phase CO_2 .

6.5.14 Benzene, toluene, ethylxylene and xylene

BTEX (BTEX) are potential impurities within some captured CO_2 streams, such as from pulverised coal power plants. Benzene is the most toxic of the BTEX chemicals and potentially harmful to humans.

6.5.15 Methanol

Methanol can be used in pre-combustion carbon capture and there is potential for traces of the solvent to be carried over into the CO_2 stream. Methanol, at sufficient concentration, can form a liquid phase in an otherwise gaseous CO_2 stream.

6.5.16 Ash, dust, metals and other particulate matter

Solid particulates such as ash and dust can be carried over in the CO₂ stream from the combustion or production process, particularly from cement and lime kilns. There is experience on capture plants where trace solids from combustion have led to amine degradation, causing issues with the capture process itself. If present, solid particles can have a detrimental impact on compressors, and they also have hygroscopic characteristics concentrating humidity and possibly leading to under deposit corrosion. Alkaline ashes, reacting with H₂O and CO₂ can form solid deposits of hydroxides, bicarbonate and carbonate minerals (see also [6.6.8](#)). Particulate matter can also impact reservoir properties, especially in the near well bore environment.

6.5.17 Naphthalene

Naphthalene is a potential impurity, in very low concentration, from some sources of CO₂ including pulverised coal power plants. On its own at room temperature, naphthalene is a crystalline solid. It readily dissolves in dense phase CO₂, and it can be possible for dissolved naphthalene to precipitate due to changes in temperature and pressure.

6.5.18 Volatile organic compounds

Volatile organic compounds (VOCs) include multiple compounds: formaldehyde, acetaldehyde, dimethyl sulfide and ethanol. They can be present as impurities as waste from some processes such as biomass power plants and can also be a product from amine degradation. Some VOCs are harmful, although not acutely toxic, and can have compounding long-term health effects. As polar molecules, they can also interact with other polar impurities such as water, possibly leading to condensation of a liquid phase under some conditions when at high enough concentrations.

6.5.19 Chlorine

Chlorine (Cl₂) gas is a potential impurity within some captured CO₂ streams, such as from cement and lime kilns. It is a toxic substance and potentially harmful to humans with significant impact on the respiratory system. Chlorine is one of the most reactive chemical elements and thus is likely to react with other impurities in a CO₂ stream, e.g. promoting corrosion of iron in the presence of H₂O.

6.5.20 Hydrogen chloride, hydrogen fluoride and hydrogen cyanide

Hydrogen chloride (HCl), hydrogen fluoride (HF), and hydrogen cyanide (HCN) are sometimes present as traces in some CO₂ streams, such as from coke formation or raw syngas, post-gasification. All three compounds are toxic and will form acids in combination with water, although a free liquid water phase is required. Hydrogen cyanide is the most toxic and can induce metabolic asphyxiation in sufficient concentration.

In saline aquifers, hydrogen fluoride will form a weak acid that dissolves silicate minerals and even quartz, a main mineral in many reservoir rocks that is otherwise rather inert even to the exposure to strong acids.

6.5.21 Glycols

Glycols, such as triethylene glycol (TEG), are commonly used to dehydrate the CO₂ stream by adsorbing water. It is possible for trace amounts of glycol to be carried over into the CO₂ stream.

The co-existing presence of water and glycols increases the temperature at which dew point occurs compared to equivalent amounts of water in gas phase CO₂. In addition, present glycols like TEG will form separate liquid phase in absence of water in gas phase CO₂. This can generate an aqueous corrosive phase at water concentrations far below the solubility limits reported for pure CO₂ (see [6.6.2](#)).

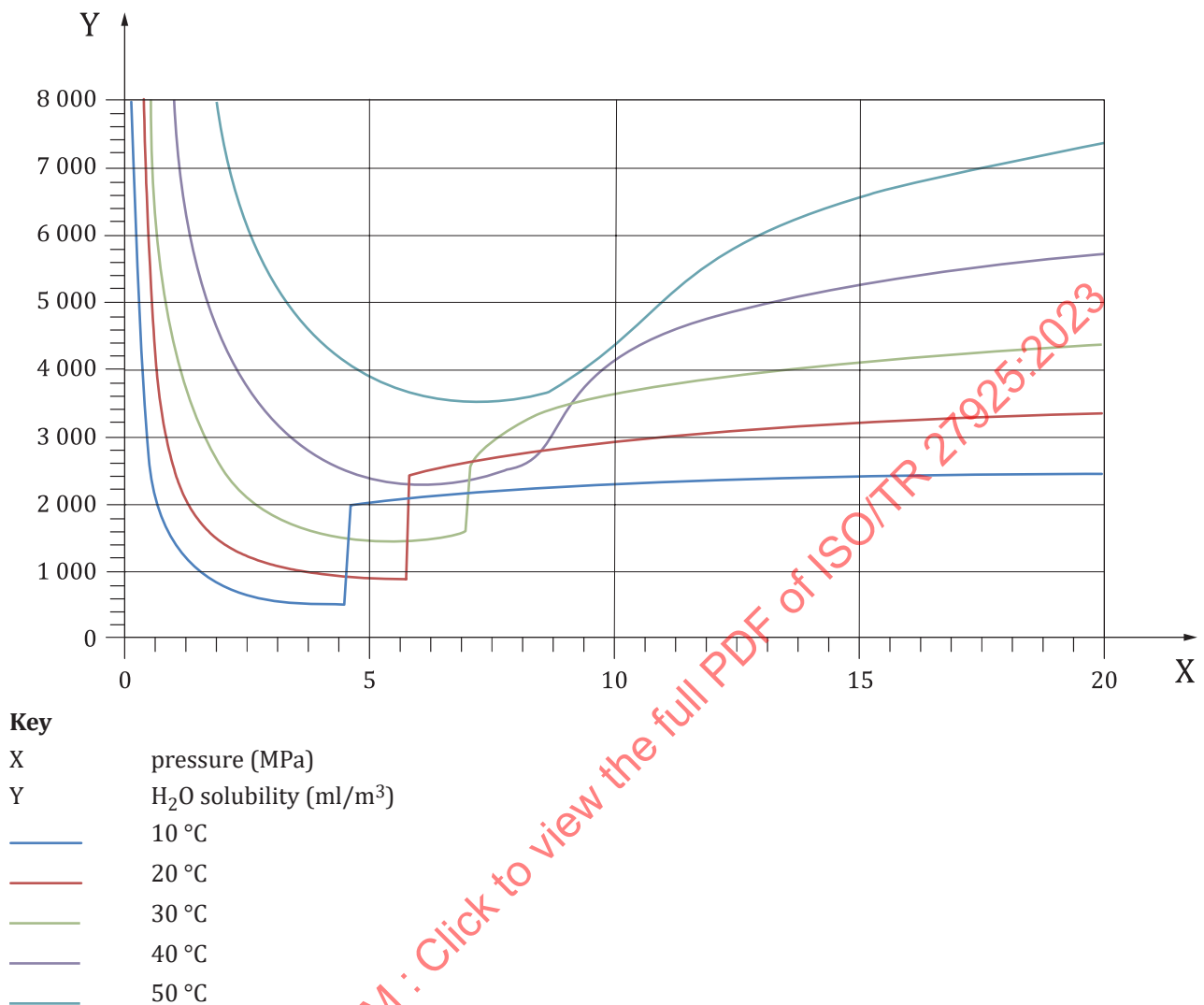
6.6 Effects of reactive impurities — Phenomena and their modelling

6.6.1 General

The co-existence of some impurities can have chemical reaction potentials under certain flow and temperature conditions, in particular, in the presence of water in the CO₂ stream. Some products from these chemical reactions can be very corrosive to pipe and well materials. Understanding and modelling these chemical reactions is important for the integrity of the transport and injection system. For a given transport and injection system, based on the CO₂ source specifications, one needs to begin with modelling the steady-state transport and injection process to quantify the distribution of various impurities in the transport and injection system, from which the chemical reaction potentials will be evaluated. Then, the corrosion process can be assessed. For transient process, the flow assurance tools can provide the predicted information on the composition variations with time and space. At the moment, it is not possible to simulate transient flow behaviour and chemical reaction of different impurities in a completely coupled way.

6.6.2 Formation of corrosive aqueous phases

Pipelines and tanks in ships are usually made of carbon steel. If the carbon steel surface is wetted by a water containing phase the question is not if corrosion will take place, but at what rate. The corrosion rate of carbon steel exposed to aqueous phases and CO₂ can be high (several mm/y) and keeping the pipeline system 'dry' is therefore essential for the safe operation of a CO₂ pipeline network. When the acceptable water contents in CO₂ streams are discussed, it is usually argued that no aqueous phase will condense and cause corrosion as long as the water concentration is well below the solubility limit. The water solubility in pure CO₂ (see [Figure 5](#)) is more than 1 000 ml/m³ in the temperature and pressure range relevant for pipeline transportation, and both laboratory experiments and field experience confirm very low corrosion rates for pipelines where the water content is in the 20 ml/m³ to 650 ml/m³ range; see References [\[24\]](#) and [\[25\]](#).



The data has been calculated with OLI software, see Reference [26]. OLI is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

Figure 5 — Water solubility in CO₂ as a function of pressure and temperature

The water solubility is strongly affected by impurities in the CO₂ stream. The change in solubility will not be very large if the impurities are inert (not undergoing chemical reactions) and non-condensable as for instance Ar, N₂, H₂ and CH₄. A much larger effect is observed when impurities are undergoing chemical reactions forming new products and phases. It has been shown experimentally that aqueous phases can form at water concentrations less than 100 ml/m³ when small amounts (<100 ml/m³) of impurities like SO₂, NO₂, H₂S and O₂ are present. These impurities can react and form elemental sulfur and strong acids giving aqueous phases with high concentrations of dissolved sulfuric acid (H₂SO₄) and nitric acid (HNO₃); see References [27] and [28]. Aqueous phases can also form more easily when salt, glycols, methanol or ethanol are present. These impurities will absorb water and generate an aqueous corrosive phase at water concentrations far below the water solubility limits reported for pure CO₂ and only water. Alkaline substances like amines and ammonia will also facilitate formation of aqueous phases, but the corrosivity will be lower as the pH will be higher.

6.6.3 CO₂ specifications

A number of CO₂ specifications for maximum impurity concentrations have been published and an excerpt showing the tentatively most reactive impurities (H₂O, H₂S, O₂, NO_x, SO_x, CO) is shown in [Table 1](#).

Table 1 — Published CO₂ specifications for maximum impurity concentrations

Component	Dynamis 2008[29] ml/m ³	NETL (for design) 2013[30] ml/m ³	CarbonNet project 2016[31] ml/m ³	Goldeneye/ Peterhead 2014 (2016)[33] ml/m ³	Northern lights 2019[34] ml/m ³	Reference experiment 25 °C 10 MPa
H ₂ O	500	500	100	50	30	122
H ₂ S	200	100	100	0,5	9	130
CO	2 000	35	900 to 5 000	10	100	0
O ₂	<40 000	10	20 000 to 50 000	1 (5)	10	275
SO _x	100	100	250 to 2 500	10	10	96
NO _x	100	100	200 to 2 000	10	10	69
Key NETL: National Energy Technology Laboratory						

The most cited CO₂ quality specification was suggested in the DYNAMIS project in 2008; see Reference [29]. Reference [30] give CO₂ stream specifications for the impurity limits to be used for conceptual design of carbon steel pipelines. These specifications were based on a review of 55 CO₂ specifications found in the literature. The Australian CarbonNet Project published in 2016 a preliminary CO₂ specification for its hub-based carbon capture and storage network; see References [31] and [32]. The limits given for the various impurities in the specifications are not only based on the risk of corrosion and formation of corrosive phases but are also based on HSE (toxicity limits) and reservoir requirements.

It is important to note that the specifications detailed in [Table 1](#) were intended to be used in actual projects without further refinement. When the specifications were published, they had not been experimentally verified. The last column in the table shows a CO₂ stream composition denoted “Reference experiment”. This composition, which is stricter than that of the Dynamis project, has been tested at IFE; see Reference [27]. Testing at 25 °C and 10 MPa showed that the impurities in the CO₂ stream reacted and formed substantial amounts of sulfuric acid, nitric acid and elemental sulfur, i.e. an environment that is highly corrosive for carbon steel. At lower temperatures, the formation of separate corrosive aqueous phases is even more likely.

[Table 1](#) shows CO₂ specifications proposed for actual CCS projects, i.e. the Peterhead in Reference [33] and Northern Lights in Reference [34]. The project specifications are much stricter than the general recommendations given in the NETL columns. Most of the low limits are a result of the capture technology giving low impurity concentrations anyway, but to achieve for instance the low O₂ content will most probably require additional cleaning steps. Material testing with CO₂ impurities can result in a need for either lower concentration specifications or introducing critical plant operating procedures including during plant upsets or recommissioning of equipment to adequately manage any threats resulting from such impurity concentrations, or both.

6.6.4 Modelling of formation of corrosive aqueous phases

Defining a safe but non-conservative operation window for a CO₂ transport network is more challenging than for a single transport line from one source to one sink. The number of possible impurity combinations and operational conditions (pressure, temperature, flow velocities) can be huge when CO₂ streams with different compositions are comingled. Due to lack of data, there are presently no publicly available models that can predict the precipitation of aqueous phases when reactive impurities are present. The lack of data was recognized in the first ISO standard for CO₂ transportation, ISO 27913. In ISO 27913, it is stated that: “Since the maximum (allowable) concentration of a single impurity will

depend on the concentration of the other impurities, it is not possible due to lack of data and current understanding to state a fixed maximum concentration of a single impurity when other impurities are, or can be, present". ISO 27913 therefore recommends referring to the most up-to-date research during pipeline design.

Experiments have shown that the concentration limits for reactions and corrosion to occur vary strongly with the type and number of impurities that are present and the prevailing temperature and pressure conditions. Certain impurity combinations are practically inert (slow reaction kinetics) even though cross-chemical reactions between them are thermodynamically possible. It is important to understand the trigger and control mechanisms for such reactions, i.e. the formation of elemental sulfur when O_2 and H_2S are present. To systematize laboratory and field data and to predict the possible formation of aqueous phases for combinations of impurities that have not been tested experimentally, it is necessary to use/develop a thermodynamic and kinetic approach for extrapolation. Such work is ongoing in the industry driven by the KDC project (Kjeller Dense phase CO_2 project, phase I, II and III) at the Institute of Energy Technology (IFE) in Norway, where a thermodynamic model of chemical reactions in dense phase CO_2 is being developed in cooperation with OLI Systems in the United States of America (see Reference [28]). For reliable simulations of reaction rates, kinetic literature data are lacking for relevant reactions at temperature and pressure ranges typically encountered during pipeline transport. A simulation attempt using and adapting kinetic literature data from atmospheric reactions and combustion processes, revealed that any H_2O in the CO_2 stream will form inorganic acids within seconds to minutes if either SO_x or NO_x or both, are available, while the oxidation of SO_2 to SO_3 and the direct oxidation of H_2SO_3 to H_2SO_4 by O_2 appear to be too slow to be of any credible threat throughout the timescale of any pipeline transport system (see Reference [2]).

6.6.5 Depressurisation and impact of reactive impurities

In CO_2 streams where the impurity levels are too low for the formation of corrosive aqueous phases, such phases can form during depressurisation via the gas phase or due to temperature changes. Below the critical temperature, depressurizing of CO_2 to the bubble-point pressure results in a two-phase gas/liquid system and impurities will partition between the two phases. Water and other reactive impurities with lower solubility in the gas phase than in the liquid CO_2 phase accumulate in the liquid CO_2 phase and a corrosive aqueous phase can form if the water solubility limit in the liquid CO_2 phase is exceeded. Corrosion after depressurisation has been demonstrated in laboratory experiments, see Reference [36]. To enable quantification and prediction of the corrosivity after depressurisation, more solubility and partitioning data for the water – dense phase CO_2 system is needed.

6.6.6 Corrosion issues in CO_2 injection wells

It is prudent to ensure CO_2 injection wells are designed with corrosion resistant alloys that are resistant to pure water and CO_2 corrosion. A challenge for wells connected to a large transport network is to ensure they can cope with a range of CO_2 arrival rates within the limits of the capture plant and surface equipment. During transient (batch wise) injection and shut in, the CO_2 stream and often highly saline formation water can occasionally mix in the bottom of the injection well and pose a potential corrosion problem particularly when impurities are present in the CO_2 stream. The impurities will partition to the water phase at this point, water will dissolve and saturate the CO_2 phase and the temperature will increase due to heat transfer from the reservoir. When the tubing material is exposed to such environments with high chloride content, pitting corrosion and different types of cracking can become a problem, see Reference [37] particularly if O_2 and H_2S are present, see Reference [38]. To avoid these problems, corrosion-resistant, highly alloyed steels can be used for the perforation and the other parts of the well tubing potentially in contact with formation water during injection stop.

6.6.7 Monitoring reactive impurities in the CO_2 stream

Routine analyses will be required to verify that the CO_2 stream compositions comply with the approved CO_2 specifications for the pipeline transportation network and the storage site. A monitoring plan including sampling procedures and instrumentation is a key component for any such verification. Recognizing and where possible, addressing the challenges of multi-phase sampling, real-time measurement techniques that are needed to enable monitoring of CO_2 compositions at strategic

locations along the pipeline network and quickly take mitigative actions in case a CO₂ source or capture plant delivers CO₂ out of specification or CO₂ out of specification is detected in the pipeline network. A challenge will be that chemical reactions and phase transitions of the CO₂ stream can lead to an increase in concentration of impurities in separate liquid and solid phases that are not represented by the samples taken from the bulk phase CO₂. Depending on the pressure and temperature (controlling the density of CO₂), the products can be lighter or heavier than the bulk CO₂ phase. The practical sampling locations will have to be evaluated for each system taking into account pressure, temperature and actual flow conditions. For example, one approach can be to sample from the top position (light components), middle position (bulk phase), and bottom position (heavy components); see Reference [26]. Understanding the kinetics of the impurity reactions and the formation of separate phases is important when monitoring data are interpreted.

6.6.8 Particle, wear and clogging

Formation of solid particles due to corrosion or redox reactions in the CO₂ stream (e.g. sulfur from H₂S, SO₂ and O₂) can have severe consequences for the pipeline, but perhaps even more so at the interface between the transport and the storage system. The particles can cause wear, clogging and reduced injectivity. The amount of sulfur that forms when e.g. 5 ml/m³ H₂S reacts and forms elemental sulfur adds up to about 3 500 kg per year in a pipeline transporting 1 billion kg of CO₂ per year. A crucial question will be how much sulfur can be dissolved in the CO₂ stream before precipitation and to which degree the corrosion products stick to the wall or become mobilised. Some products can grow on the wall for a long time and eventually spall off. Such products can form larger flakes (on the millimetre scale) while other products are more dust-like and detach easily. The safest way to minimize the impact of sulfur and corrosion products is to prevent formation of aqueous corrosive phases.

Furthermore, if an internal lining is applied, the material must be qualified for compatibility with CO₂ streams and the ability to withstand relevant pipeline decompression scenarios.

6.7 Modelling of CO₂ stream properties in commercial flow assurance tools

6.7.1 General

Modelling of CO₂ streams properties and dynamics is a reoccurring task for engineers responsible for designing and operating different components and systems in an integrated CCS project.

Chemical and process engineers for capture facilities, pipeline and flow assurance engineers for transportation, completion engineers for injection wells, and reservoir engineers for storage all have their special simulators, such as ASPEN Plus, OLGA, LedaFlow, ECLIPSE, or TOUGHII³⁾. Thermodynamic simulation tools such as MultiFlash and PVTsim Nova⁴⁾, are also used by flow assurance engineers to generate input (files) for (multiphase) flow simulation.

These dedicated software packages dealing with coupled dynamic thermal, hydraulic, mechanical and chemical (THMC) processes are well suited for individual systems or components, but often they are poorly connected to the neighbouring systems, e.g. by source and sink-terms only, or by very simple modules or tabulated values.

An overarching flow simulator for CCS networks does not exist, though. Theoretically, it can be facilitated by combining the results of simulations of the individual components of the system. Network-management approaches using simple tank- and cascade models can be a more practical way to manage flow along the entire chain including various entities and operator simulation parts of the CCS project.

All software packages, e.g. MultiFlash and PVTsim Nova, have in common, that for the simulation of THM-processes, thermodynamic properties and phase behaviour as well as transport properties

3) ASPEN Plus, OLGA, LedaFlow, ECLIPSE, or TOUGHII are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products

4) MultiFlash and PVTsim Nova are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

need to be known or calculated according to local state variables. In addition to the general physical properties described in 7.1 to 7.3 and in Reference [20], some properties of special interest to flow in pipes are described in 6.7.2 to 6.7.4, before flow assurance modelling in pipes is dealt with in detail.

6.7.2 Joule-Thomson effect

Whenever a real gas or liquid expands freely through a valve or throttling device, such that no heat is exchanged with the environment and no external work is extracted, the fluid will experience a temperature change. This is commonly referred to as the Joule-Thomson effect as expressed in [Formula \(1\)](#):

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h \quad (1)$$

where

μ_{JT} is the Joule-Thomson coefficient, expressed in °C/kPa;

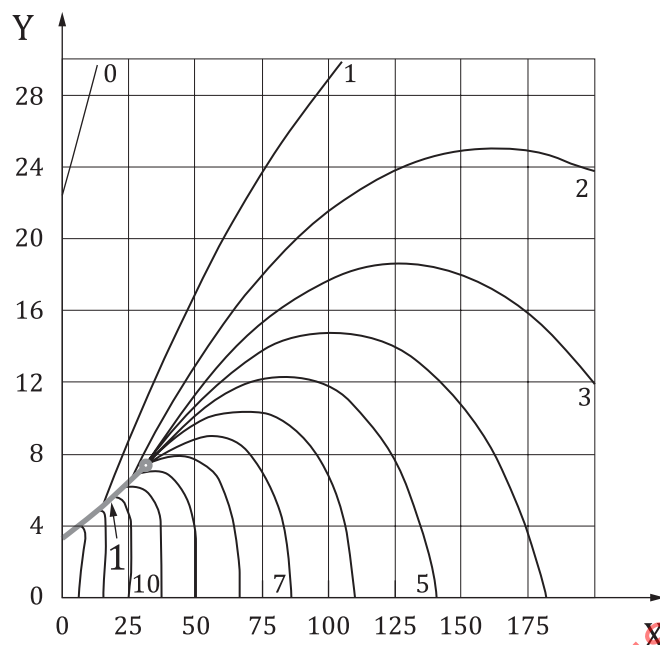
∂T is the temperature change;

∂P is the pressure change;

h is the constant enthalpy.

Provided that the gas temperature is in the region below the inversion curve (where μ_{JT} goes from positive to negative), an expansion will lead to cooling of the fluid. As ∂P is negative, by definition during an expansion, and μ_{JT} is positive below the inversion curve, ∂T must be negative for the formula to be valid.

At ambient ground or reservoir conditions, fluid CO₂ tends to have a large Joule-Thomson coefficient; see Reference [39]. Significant temperature variation can be observed in a system with large pressure variations. If pressure or temperature are increased from these ambient conditions, the Joule-Thomson coefficients decrease. Special attention to the Joule-Thomson effect in a CO₂ transport system is required at pressure and flowrate control valve locations and during pipeline depressurization and pressurization operations. The amount of cooling during isenthalpic decompression can be derived from thermodynamic diagrams, such as pressure, temperature enthalpy diagrams ([Figure 6](#)). Direct injection of CO₂ under high pressures into depleted reservoirs i.e. at low reservoir pressure at beginning of CO₂ injection, can also be problematic as in reservoirs where aqueous fluids are present, gas hydrates can form and reduce the reservoirs' injectivity.

**Key**X temperature, T (°C)Y pressure, p (MPa)

1 liquid-gas-phase boundary, ending at the critical point

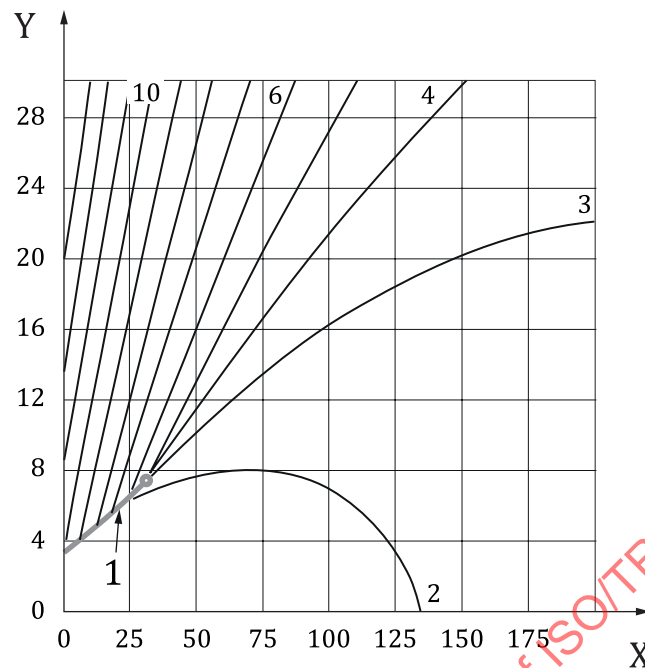
SOURCE: This figure is based on the information published in Reference [39].

Figure 6 — Joule-Thomson coefficient of CO₂ as a function of pressure and temperature

Joule-Thomson coefficients for CO₂ can become negative at low or high temperatures and at high pressure. The Joule-Thomson inversion curve encloses a p - T range within which decompression results in cooling, while outside of it, fluids heat up. Joule-Thomson coefficients and inversion curves are affected by impurities. Inversion curves for CO₂ and N₂ are published in Reference [40].

6.7.3 Viscosity

Viscosity is needed to calculate the pressure drop in pipes, in the design of processing equipment and in subsurface reservoir flow. The viscosity of CO₂ streams is proportional to pressure and inversely proportional to temperature (see Figure 7).

**Key**X temperature, T (°C)Y pressure, p (MPa)

1 liquid-gas-phase boundary, ending at the critical point

SOURCE: This figure is based on the information published in Reference [39].

Figure 7 — CO₂ viscosity (10^{-5} Pa·s) as a function of pressure and temperature

The viscosity of a CO₂ stream can be reduced, e.g. by either Ar or N₂, or both.

Viscosity is an input parameter in calculations of inlet and end-of-the-pipe pressures and to evaluate the necessity and spacing of compression stations. For fully turbulent flow (which will be the case for CO₂-transportation pipelines), the sensitivity of pressure drop to viscosity is low.

Injecting fluid CO₂ streams of high density into warm reservoirs can lead to a decrease of viscosity at typical pressures and temperatures in aquifer storage, easing flow and expansion therein.

Note that the viscosity of dense-phase CO₂ can be lowered at pore scale by some impurities such as N₂, O₂ and Ar and that lowering can affect the migration of the CO₂ stream in the reservoir. Depending on the reservoir structure (spill point, layering, heterogeneities, etc.), changes of viscosity can lead to an increase or decrease of dynamic storage capacity.

In natural gas reservoirs, the viscosity of CO₂ streams is affected by mixing with residual gases, e.g. nitrogen and methane lower the viscosity of the CO₂ streams. Given that these impurities lower the viscosity of CO₂ streams, no negative geo-mechanical impacts are expected from viscosity. Furthermore, hydrogen causes a similar effect, while such an effect is lower for oxygen and water.

However, if a fluid phase encounters and displaces another one, viscosity contrasts become important, as they impact the shape of the contact surface between the two fluids. Viscous fingering is a result of such contrasts, when CO₂ streams are injected into oil- or brine-bearing reservoirs. Depending on the reservoir geometry, viscous fingering can enhance storage efficiency. Geometry of reservoirs, their heterogeneity and the interplay between gravity and viscosity forces determines the shape of a CO₂ plume in a saline aquifer, see Reference [41]. Reservoir simulations can aid predictions about the plume shape and spill points that can be encountered by an expanding plume. If a plume comes close to a spill point, the permitted storage capacity can be reached or measures for plume steering can be taken in order to increase storage efficiency, and hence keep the CO₂ stream flowing into the reservoir. Thus, a

good knowledge of viscosities of CO₂ streams and brines under reservoir conditions is important for managing and assuring flow within saline aquifers or oil fields.

6.7.4 Flow assurance simulation for CO₂ transportation in pipes

The commercial flow assurance tools, such as OLGA and LedaFlow⁵⁾ were developed for oil and gas production and transport systems. There are three different ways to handle physical properties of fluids in these commercial flow assurance tools: table files, black oil model and composition tracking.

- Table files capture thermodynamic and property data in a look up table, with either *PT* as the independent variables, or pressure-enthalpy (*PH*). The *PH* formulation is generally better suited for modelling of CO₂ with impurities, as properties change vary rapidly in the *PT* domain near certain key areas: the bubble point, the critical point and the Widom lines.

Table files offer great flexibility for modelling of CO₂ with impurities, as the table data can be generated from any thermodynamic package. This gives the engineer the ability to select the appropriate thermodynamic package and equation of state and tune the EoS to best match the fluid properties under consideration.

It is possible, and preferable, to create very large fluid table files with very fine graduations in the *PT* or *PH* scales, which reduces rounding error where properties change rapidly. There is no inherent table size limitation in the commercial tools OLGA or LedaFlow, although there is a practical limit due to the memory available to these applications. It is possible and reasonable to build fluid table files with thousands, or tens of thousands, *PT* or *PH* datapoints.

The engineer can also consider replacing thermodynamic data in a table file with dummy data. Some specific operating cases – such as flow in a well very close to the critical point – are very unstable in the tools OLGA and LedaFlow. Use of dummy data can improve stability such that results can be generate, at the expense of the errors that have been deliberately introduced through this process.

- The black oil model, applied in some flow assurance modelling packages, is intended to simplify modelling of very complex liquid mixtures such as crude oil. Therefore, its use for CO₂ applications is considered limited and any use in CO₂ applications proceeds with caution.
- Compositional tracking is required where the composition of the fluid will change, and the model needs to consider the changes in composition. A simple example is initial start-up of a pipeline, where the CO₂ is introduced to the pipeline for the first time, and where the engineer is interested in the distribution of CO₂ throughout the pipeline over time, as it displaces the original fluid.

Compositional tracking, however, can leave very limited flexibility for thermodynamic modelling in some common commercial simulators. The equations of state that are applied to compositional tracking modules in the tools OLGA and LedaFlow are limited to a very small number with limited ability to tune these EoS.

Modelling of CO₂ streams can sometimes not be possible when using some commercial compositional tracking models developed for the hydrocarbon industry, however, they can be acceptable within acceptable uncertainty ranges for selected methods. Thus, predictions of thermodynamic and transport properties – and in turn the flow assurance modelling itself – can be subject to significant error in many operating cases of interest outside acceptable uncertainty ranges for selected models.

Despite this significant limitation with the utility of compositional tracking, they do offer improvements in numerical stability for most complex modelling cases compared with using fluid table files. For this reason, compositional tracking can be the primary technique employed for flow assurance modelling of CO₂ with impurities, with table files only used to confirm results and to deliver targeted simulations.

⁵⁾ OLGA and LedaFlow are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

As described above, a range of thermodynamic modelling approaches are available, including tuning to experimental data, where available, for modelling CO₂ streams with impurities.

Modelling two-phase reactive transport within storage formations including various fluid components, gas and aqueous phases as well as interactions with a chemically heterogeneous matrix is possible. For this, tracking of CO₂ stream composition is indispensable when CO₂ is injected into geochemically reactive or depleted natural gas reservoirs and predictions of the expansion and migration the CO₂ plumes have to be modelled. Various simulators have been developed, originally for simulations of groundwater problems in the aquatic environment. Coupled THMC simulators are available today for reservoir simulations.

Various challenges and limitations restrict the reliability of predictive simulations of such complex problems. These challenges and limitations include:

- coupling of the formulae;
- numerical and computational limitations;
- equations of state for fluid mixtures in porous media;
- adequate representation of natural heterogeneities in numerical models, varying over orders of magnitude on various length scales;
- macroscopic porosity-permeability relations, representing microscopic pore scale geometry and capillary forces in a geotechnically meaningful way;
- equations of state for two-phase mixtures;
- relating mass transfer of geochemical reactions to changes of permeability and porosity of the solid porous medium;
- uncertainties in geochemical equilibrium or reaction rate constants; especially for silicates of slow reactivity, long-term predictions are very uncertain; various databases are available, with ranges of experimental validation differing for various chemical species;
- invalid assumptions of local chemical equilibrium in reactive transport simulations;
- kinetics of dissolution/partitioning of impurities between different prevailing fluid phases.

Given these uncertainties, flow assurance evaluations in reservoirs are best performed through incorporating the results of laboratory experiments, monitoring of the CO₂ stream migration and reservoir pressures, production histories of hydrocarbon reservoirs or studies of natural analogues, in order to validate numerical simulations.

7 CO₂ pipeline transport and well injection

The main scope of the flow assurance study for a CO₂ pipeline transport and well injection system include the following:

- determining the best system configuration to comply with the requested hydraulic capacity and reservoir requirements;
- defining the allowed operating envelope of the pipeline transport and well injection system in terms of flow rate and operating conditions;
- management of transient operations, such as those caused by varying injection rates, varying CO₂ stream supply, slugging, surge, start-up and shutdown;
- thermal management under various operational scenarios to ensure that the variations of fluid temperature are within the operating constraints of the systems;
- hydrate management and control;

- planned and unplanned de-pressurization of the systems, such as that resulting from a pipeline rupture, well blowout or controlled venting of pipeline and equipment during maintenance activities, these need special attention to ensure safe operation; and
- equipment, pipeline and well integrity failure mechanisms such as corrosion, material fatigue and embrittlement.

7.1 Operation under single-phase flow conditions

7.1.1 General

The operation of a CO₂ pipeline transport and injection system under single-phase flow conditions means that the CO₂ stream is in a single-phase state (gaseous, liquid or supercritical fluid) in the whole system. The physical models to describe the thermo- and hydrodynamic behaviour of these three different fluids are identical.

The main tasks of flow assurance of CO₂ single phase flow in pipeline and well are to compute the following:

- transport and injection capacity for a given pipeline, well and storage system;
- temperature, pressure and composition distribution along the pipelines and wells;
- transient behaviour of the flow during the operation for shut-in and restart in pipeline and wells, fluid hammering, and pipeline packing.

The assessment of the transport and injection capacity is carried out to optimize the system design. It is assumed that the reservoir is available with a given injectivity, reservoir pressure and temperature. For a given transport distance, one then needs to determine the pipeline geometry (diameter, wall thickness), select the boost capacity, as well as the number of wells and the well geometry. This can be achieved by a hydraulic study of the CO₂ pipelines and wells. The complete hydraulic study of the pipeline transport and injection system normally includes hydrodynamics (pressure gradient) and heat transfer (temperature) together with the thermophysical properties which are functions of composition, temperature and pressure. The composition distribution is an important input to the fluid property quantification as well as for the assessment of flow assurance risks such as corrosion, hydrate formation, chemical reactions, etc.

The existing flow assurance tools developed for the pipeline transport and production of oil and gas have all relevant functionalities and physical models implemented that are needed for modelling of CO₂ single-phase flow in pipelines and wells, see Reference [42]. The physical models in these tools cover:

- frictional pressure drop;
- heat transfer between the CO₂ stream inside the pipe and the surroundings, including rock or soil for a buried pipeline or well (convective and conductive heat transfer);
- compositional tracking to quantify the concentration of the individual components of the CO₂ stream;
- physical properties needed to calculate the thermo- and hydrodynamic behaviour of the CO₂ stream.

In these existing flow assurance tools, the physical models for the frictional pressure gradient, heat transfer and physical properties are implemented in a coupled way, and these tools can handle both steady-state and transient flow behaviour of a CO₂ stream in a single pipe as well as in a network of pipelines and wells. These existing flow assurance tools include models for pumps, compressors and valves. As concluded in References [42] and [43], the physical models in these flow assurance tools are valid for single-phase flow of the CO₂ in a pipe. The validity of the models for pumps, compressors and valves still needs to be confirmed with dedicated operational experience or laboratory data.

The flow assurance tools include the 1996 Span and Wagner (S&W) EoS for pure CO₂, which gives an accurate prediction of the thermodynamic properties (e.g. density, heat capacity). They also include

a number of different EoSs, which have varying performance in predicting the thermodynamic properties of CO₂-rich mixtures. The uncertainties of these EoSs need to be quantified with dedicated experimental data or by comparison with reference EoSs, where available. Based on quantified uncertainties, operational window is developed with margin against phase envelope.

When using the existing flow assurance tools, some issues for close consideration include:

- the uncertainty of physical properties of CO₂-rich mixtures can be large for certain situations;
- the models for pumps, compressors and valves need further validation;
- the coupling with the flow near well-bore reservoir is handled;
- flow assurance tools do not cover the reservoir.

In 7.1.2 to 7.1.4, the pressure pulsation due to the fast closure of a valve (fluid hammer) and the issues associated with shut-in and restart are discussed in detail.

7.1.2 Fluid hammer

Any change in flow velocity in a pipeline induces a change in pressure. The sudden shutdown of a pump or closure of a valve causes fluid transients, which can involve large pressure variations (pressure waves), including local cavity formation, distributed cavitation (bubbly flow), hydraulic and structural vibrations and excessive flow oscillations. This phenomenon is called the fluid hammer effect.

Once a pressure wave is generated, it will travel towards the system boundary and then be reflected. The first pressure surge amplitude due to sudden velocity variation can be estimated by the model proposed in Reference [44]. The pressure wave propagation in the system can be simulated by using the existing flow assurance tools, see Reference [42].

In most situations, there is very little effect of the valve closing on the pressure surges until the valve is less than approximately 10 % open. This is associated with the fact that the valve opening needs to be small enough before there is any significant pressure drop across the valve and corresponding reduction in flow velocity. The fluid hammer can be mitigated by increasing the closure time of the valve and pump.

7.1.3 Shut-down of pipeline and well

Before a shut-down operation, the fluid temperature distribution along the transport and injection line depends on the flowrate and the inlet and surrounding material/fluid system temperatures. The existing flow assurance tools can be used to estimate the pressure and temperature distribution of the CO₂ stream in pipelines and wells. The CO₂ stream during normal operations is not in thermal equilibrium with the surroundings. The shut-down operation will introduce variations of the fluid temperature and pressure distribution, and in some situations, it can trigger unstable flow in the system.

The shut-down operation of a CO₂ pipeline transport and injection system can be achieved by different methods:

- closure of pipeline and well separately and at the same time, which can be carried out by:
- closure of the valve at the pump/compressor location and the wellhead valve at the same time;
- closure of the valve at the pump/compressor location, the wellhead valve and the bottom hole choke at the same time;
- closure of pipeline and well at the pump/compressor location only;
- closure of single wells without closure of the rest of the system (for multiple-well system), which can be carried out by closure of wellhead valve.

Some of the events to be avoided during pipeline shut-down and start-up operations include:

- over-pressure in the pipeline;
- pressure depletion or unstable flow in the system such that two-phase flow or back flow into the well occur.

Due to the natural geothermal gradient, an increase of the formation temperature along the well path is likely. Even under steady-state injection operation of CO₂ stream in well, thermal equilibrium between the CO₂ stream and surroundings is unlikely to be achieved. If the CO₂ injection is stopped, the temperature of the CO₂ stream in the well will increase to formation temperature. Frequent shut-in and restart operations can therefore lead to large temperature variations in the well casing material, which can cause thermo-mechanical stress on the well infrastructure, see Reference [3].

A specific issue associated with shut-in of CO₂ wells is the potential for increasing temperature and over-pressurization in the well. If shut-in of an injection well is conducted by the closure of valves and chokes at both well head and downhole, the temperature of the fluid between these two valves is likely to increase during the shut-in period. Heating of single-phase CO₂ fluid leads potentially to pressure increase due to thermal expansion. However, this pressure increase due to thermal expansion between closed valves depends on the downhole valve specification and condition. Generally, the downhole valve is specified to be partially open during shut-in, potentially relieving pressure accumulation between valves.

In wells connected to saline aquifers with an open down-hole valve, heating will not lead to a pressure increase as CO₂ can flow into the reservoir. Dissolution of CO₂ in the formation water can reduce the pressure in wells and cause formation water to enter into the injection piping. The amount of water entering the wellbore depends on the reservoir parameters near the wellbore and the injection time before shut-in. In addition, the water can also dissolve into the CO₂, and water molecules can migrate into the wellbore via a dissolution process.

In an offshore pipeline transport and well injection system, there are commonly at least three valves/chokes located at the pumping/compression stations (either offshore or onshore, or both), wellhead and downhole. Different closing procedures and protocols for such valves/chokes can have different consequences resulting in different pressure and temperature behaviour during the shut-in period. Therefore, to control such behaviour, shut-in procedures tailored to the specific system can be required. In addition, a proper procedure for partial depressurization can be needed if the pressure exceeds the pipeline or well structure integrity requirements. During the shut-in period, pressure build-up in the annulus (between casing and injection tubing) can occur in the case of well shut-down operations. Such annuli are normally filled with water/MEG or other fluids. Under offshore operational conditions, the fluid temperature in the annulus is normally close to the CO₂ stream temperature in the tubing and will be lower than the ambient temperature in the rock. During the shutdown period, the fluids in the well and annulus will be heat up. The heating process will depend on the length of the operating period of the well prior to shut-in. A long injection time is likely to result in greater cooling of the surrounding rock and in turn will result in a longer period to heat up the well fluids during the shut-in period.

If the pressure increase exceeds the maximum allowable design pressure of the casing, there will be a need to release fluid from the annulus, this can be achieved either by a service line connecting the annulus or by utilizing different fluids in the annulus, e.g. N₂. An accurate assessment of the pressure increase can be done with the temperature distribution in the annulus along the well. This local temperature distribution is important to calculate the local fluid compressibility.

7.1.4 Start-up and restart of pipeline transport and well injection

The start-up/restart procedure of a pipeline transport and well injection system needs to be established so that there is a smooth start-up without any risk of equipment integrity and reservoir formation damage. Under certain circumstances, special attention can be given to ensure that the closed in tubing head pressure during well shut-in is not higher than the injection tubing head pressure at the well head. For this purpose, systematic simulation of thermo- and hydrodynamic behaviour of the CO₂ stream in pipeline transport and well injection system by using commercial flow assurance tools for different scenarios are often performed.

Before start of injection, the fluid temperature in the well will be the same as the surrounding temperature, which is normally higher than the temperature during normal operation. After the first start-up of CO₂ injection, the cooling process of the annulus will lead to under pressure condition at the top part of the annulus. Pressure management of the annulus is an important for managing well integrity during the operational lifetime of the well. Risks to equipment can be significantly mitigated by minimising frequent shut-in and restart of the CO₂ injection operation where practical to do so.

7.2 Normal operation under two-phase flow conditions

7.2.1 General

Phases of a CO₂ pipeline transport and injection system operation mainly include:

- stable operation with relatively stable loading rate;
- transient operation with varying loading rate; and
- shut-in and restart.

Under operating pressures and temperatures within the two-phase envelope, there will be phase change (CO₂ vapour generation or condensation of gas into liquid depending on the process). The co-existence of two CO₂ fluid phases (gas and liquid phase) in the same location of the pipeline and well is called two-phase flow. The major tasks associated with the CO₂ two-phase flow in the pipeline transport and well injection are:

- maintenance of injection capacity of the given system (pipe and well geometry, reservoir condition, ambient temperature, boosting equipment etc.);
- quantification of potential transient behaviour of the flow and the corresponding mitigation method;
- identification of flow conditions that can have risks of injection capacity reduction (hydrate formation) and compromising system integrity (erosion, corrosion potential, etc.).

7.2.2 Identification of two-phase flow in the pipeline and well

Almost all existing operational CO₂-transport pipelines are operated under single-phase CO₂ conditions as well as all projects currently under development. Only a few, for example, Sleipner, have been operating their injection well with presence of two-phase flow at the upper part of the well channel. The main reason is that the current knowledge of two-phase CO₂ flow in a pipeline and well system is very limited so that the existing commercial flow assurance tools for design and operation support of transport pipeline and injection wells have not been validated for two-phase CO₂ application yet, see Reference [43], one of the main risks can be potential flow instabilities like receiving slugs of either 100 % gas or 100 % liquid where the well can swing from CO₂ production into the pipeline to uncontrolled injection with low temperatures in the top part of the well, respectively.

Two-phase CO₂ flow in the pipeline and well system can be identified using flow assurance tools if the proper physical property models are used. For pure CO₂ stream, the existing flow assurance tools have access to the best thermal dynamic models. For CO₂ streams with impurities, care is needed because the impurities can have significant impact on the phase envelope. Even though the existing flow assurance tools have not been validated for two-phase CO₂ applications, these codes can provide a reasonable prediction on the presence of two-phase CO₂ flow in the pipe and wells, see Reference [42].

Two-phase CO₂ flow can also be present in process equipment, such as valves and pumps under certain operational conditions, even though the rest of the system is operated under single phase flow conditions. The presence of bubbles in a liquid CO₂ stream in pumps and valves can lead to cavitation, and turbo compressors for gas boosting can be damaged by droplets. The flow conditions close to this equipment obtained from the flow assurance tools can be used for the selection of proper equipment.

7.2.3 State of the art of modelling two-phase CO₂ flow in pipelines and wells

The existing commercial flow assurance tools for multiphase flow in pipes and wells were developed for the application to oil and gas production and transport systems (from the bottom hole of the well to the process facilities), as well as for water and gas injection into the reservoir for the pressure support or EOR. The pipeline and well system of oil and gas production does not differ much from those for CO₂ transport and injection in terms of geometry. The differences between these two systems are the fluid types and physical properties and the flow direction.

The existing commercial flow assurance tools have all the relevant functionalities and physical models to simulate in principle all relevant CO₂ flow behaviours in pipelines and wells. These flow assurance tools have not been validated systematically for general applications of CO₂ two-phase flow in pipes and wells. There are two different issues: whether the physical models in these tools give a reasonable description of CO₂ two-phase flow behaviour and whether the numerical solver for the formula system is applicable for CO₂ two-phase flow.

As detailed in Reference [42], bubble generation is a dominant phenomenon of liquid-dominated two-phase flow of CO₂ in a near horizontal pipe and hydrodynamic slug flow has not been observed in laboratory experiments. Current flow models in existing commercial flow assurance tools do not adequately model bubble generation. In many CCS projects, CO₂ streams can contain a small amount of impurities and in turn the phase envelope of the multiphase region is very narrow in the *P-T* diagram. As a result, a small change of pressure can lead to a large mass transfer between the phases. This can cause some challenges for these flow assurance tools to resolve the equation system for two-phase CO₂ flow correctly. Therefore, simulation with existing flow assurance tools will have significant uncertainties in relation to flow regime prediction.

If the flow in pipelines and wells is unstable, the prediction uncertainties of the flow assurance tools have an impact on the flow capacity estimate and give inaccurate pressure and temperature predictions. The risks associated with transient flow behaviour can be:

- large variations of pressure and temperature in pipelines and wells, which are challenges for process equipment and introduce large thermal stress for pipeline and well materials;
- back-flow in the well bottom hole, giving formation water penetration into the well. This can lead to well material corrosion, hydrate formation, etc.;
- large variations of phase volume fraction and the flow rate of different phases at the bottom hole, which can cause damage to the formation in the near-well-bore area and impact the injectivity;
- large variations of phase volume fraction and fluid velocity at the well-head, which is a challenge for the operation of well-head choke, in particular, for a system with more than one well.

7.2.4 Shut-down and restart

Similarly, in the case of single-phase flow, the shut-down and restart procedures of the pipeline transport and injection system need to be established to avoid any risk of equipment integrity and reservoir formation damage. Current commercial flow assurance tools have not been validated for a general application of CO₂ two-phase flow in pipelines and wells, including shut-down and restart processes.

The shut-down operation of a pipeline and well system can be carried out by two different approaches: close the valve at the pumping/compressor locations only and close the valves at both ends of the pipeline. If there is a bottom hole valve in the injection well, there is also a possibility to close that valve for the shut-down operation. The closure of valves at different locations can be operated differently in terms of timing, depending on which state of the CO₂ stream in the system is favourable for both long-term shut-down and the eventual restart process. An accurate estimate of the CO₂ stream condition (temperature, pressure and phase distributions) in pipeline and well is critical for the restart operation procedure definition.

During the shut-down period, the CO₂ stream temperature in the pipeline and well will gradually develop towards thermal equilibrium with the surroundings. During this period, the fluid pressure and temperature will vary with time, at least during the initial period. There will be some flow of the CO₂ stream in the system. It can take a long time for the CO₂ stream to reach thermal equilibrium with the surroundings. When the bottom hole valve is open, there can be unstable flow during the shut-down period.

When there is stable flow during the shut-down period, the pressure, temperature, liquid-phase volume fraction and the composition of the different phases need to be estimated along the pipe with time. The main threats that can arise during stable flow regime include:

- accumulation of gaseous or liquid phase;
- formation of free water;
- hydrate formation.

For unstable flow, particularly during shut-down, the main threats that can arise include:

- corrosion potential in the well tubing due to formation water flowing back from the reservoir;
- hydrate formation;
- thermal stress in well material with pressure and temperature variations.

The restart is normally aimed at ensuring a smooth increase of the CO₂-injection rate. With the presence of a CO₂ gas column in the pipeline or well, the restart process can introduce unstable flow. If there are large pressure and temperature differences between two sides of a valve, additional pressure waves can be created due to possible phase change involving large volume changes.

7.2.5 Cavitation

Under certain conditions, a low pressure can be generated locally in a flowing fluid. If the pressure in such locations falls below the vapour pressure (or bubble-point pressure), there will be local boiling and a cloud of vapour bubbles will form. This phenomenon is known as cavitation and can cause serious problems, since the liquid flow can sweep this cloud of bubbles on into a location of higher pressure where the bubbles will collapse. This can generate pressure waves, which under certain situations have a high intensity (can be up to 400 MPa). Similarly, local temperatures can increase by as much as 800 °C, see Reference [45].

Cavitation can be a common problem in pumps and valves. For CO₂ transport and injection systems, cavitation can be a potential risk at:

- flow through valves or chokes;
- operation under two-phase flow conditions;
- transient operation, with transition from a single- to a two-phase state.

Under two-phase flow operation, due to large compressibility, the risk of cavitation in a pipe is very low.

7.3 Special operation with two-phase flow

7.3.1 Depressurization

Depressurization of CO₂ transport and injection systems can be a result of:

- planned pipeline pressure release (e.g. maintenance and repair operations) and unplanned release (e.g. pipeline rupture incident);
- well blowout.

7.3.2 Planned and un-planned pipeline pressure release

During the depressurization of CO₂ from typical pipeline operating conditions in a dense phase, the CO₂ will become cold due to the strong expansion cooling (Joule-Thomson effect). As the CO₂ expands below the triple-point pressure (5,17 bar⁶⁾), solid CO₂ (dry ice) will form.

Analyses and data sets including pressure and temperature from CO₂ pipe depressurizations have been published, see References [46], [47] and [48]. There is also documentation from the planned depressurization of a 50 km CO₂ pipeline, see Reference [49]. There are several flow assurance modellings that are currently under development that incorporate solid-CO₂ formation in various ways, however, current versions of commercial flow-assurance tools do not give satisfactory prediction of the depressurization process of a pipeline filled with a dense liquid or supercritical CO₂ stream.

The coldest temperature encountered during depressurization is that of the solid CO₂. The sublimation temperature of solid CO₂ at 1 bar is about -78 °C.

If there are restrictions downstream of the point where the CO₂ expands, the solid CO₂ can lead to blockage of the flow channel. As observed in experiments in References [47] and [50], solid CO₂, albeit in limited amounts, also forms in the pipe itself when the pressure passes the triple-point pressure.

The temperatures reached during CO₂ depressurization can be below the point where materials turn brittle. If, at the point in question, the internal pressure is still high, this can be an integrity issue. Blowdown piping and valves are typically made of stainless steel, which can withstand lower temperatures than carbon steel. Planned blowdowns are made through mainline valve vents, which can regulate the depressurization rate by varying openings. The goal is to maintain sufficient velocity to expel CO₂ vapour/dry ice/flashing liquid to atmosphere, but not vent the pipeline too quickly. The ambient temperature and wind speed/direction can influence dispersion of the vented stream.

If a pipeline is depressurized from a high point, i.e. from the gas phase, the interior of the pipeline will be significantly cooled due to the latent heat of the evaporating CO₂ liquid. This effect can be reduced by venting from the liquid instead.

For a controlled depressurization or small leakage, the mass-flow rate through the valve or hole is a governing parameter. For small release rates, the pressure drop away from the release point will be small, and the state will be similar to that of a normal operational scenario. In principle, the existing commercial flow assurance tools can handle this part of the flow if proper physical models are implemented. However, there is a need to improve the understanding and modelling of the flow behaviour across chokes and valves.

In flow-assurance tools, the predicted mass-flow rate to the surroundings depends on the valve/choke model and the minimum cross-section area. In some valve/choke models, the mass-flow rate is correlated with the pressure difference using a coefficient based on water/air single-phase flow tests from the manufacturer. These valve/choke coefficients will be different for CO₂.

A different modelling approach is to consider the flow through an orifice (restriction). The mass-release rate is governed by the flow through the orifice, and for typical pipeline operating conditions, the flow will choke, that is to say, the local flow velocity is equal to the local speed of sound. This is also called 'critical flow'. All existing models for two-phase critical flow were developed on the experimental data of steam-water system, their application for CO₂ two-phase flow has not been tested against the experimental data with CO₂-stream. For a two-phase flow state at the orifice, in order to calculate the flow rate, assumptions on the degree of flow and thermodynamic equilibrium can be made. Further work is needed here, both with respect to modelling and experiments. Both single-phase liquid or dense-phase and two-phase conditions are relevant.

In an assessment of the depressurization process, the following issues are relevant:

- mass-release rate and its variation with time; this will be different for controlled depressurization and a leak;

6) 1 bar = 0,1 MPa = 10⁵ Pa; 1 MPa = 1 N/mm²

- CO₂-stream phase state and its variation with time; phase distribution, pressure and temperature distribution.

7.3.3 Well blowout

A well blowout is characterized by a rapid discharge of CO₂. This is an undesired scenario and can involve a safety risk. High CO₂ gas concentrations near the outburst can be the case if the discharge rate is high and the surface conditions give little dispersion/diffusion of the fluid. CO₂ gas can accumulate on the ground and displace air due to a larger density.

In a blowout scenario where the back-pressure at wellhead is lower than the bubble point pressure, a rapid expansion of the well fluid due to strong evaporation of CO₂ will occur, leading to a temperature drop in the well, as the heat transfer from the surroundings would normally be insufficient to maintain the temperature. The back flow in the well (CO₂ flow from reservoir) due to the blowout can be limited via an installed down-hole-safety-valve (DHSV) design. If such valves are not in place, high flow velocities in the porous formation surrounding the well or even flashing of liquid CO₂ within the reservoir can damage the formation by loosening grains and displacing fines towards the well, which can block pore throats and reduce the reservoir permeability and well injectivity. Afterwards, well injectivity can be lower, and higher injection pressures can be needed to re-establish the planned injection rates. Solid formation material can enter the well during blow out and accumulate at the bottom of the well, which can require well work over.

7.3.4 Leakage detection

Given the impact of CO₂ on personnel and the surroundings, there is a need to evaluate the consequences of any CO₂ release from CO₂ transport and injection systems. The effects include physiological impact on humans from breathing it, the cold temperature of CO₂ expanding at atmospheric pressure, the corrosiveness of CO₂ dissolved in water, as well as the effect of CO₂ as a solvent.

Risk assessments usually start by quantifying the leakage rate in different scenarios (including blowout). The leakage rate can be quantified by using the commercial flow assurance tools if the location and the opening size are known.

The dispersion of CO₂ near the leakage locations can then be quantified. The dispersion analysis usually begins with a rupture as a worst-case scenario to determine whether this can impact the surroundings. If a leakage occurs in the pipeline, the leakage duration and dispersion can be limited by leakage detection resulting in shut-down of the source. The time for detection will depend on the size of the leakage. A small amount of impurities in CO₂-stream has little impact on the leakage process.

7.4 Other issues

7.4.1 Dry ice formation

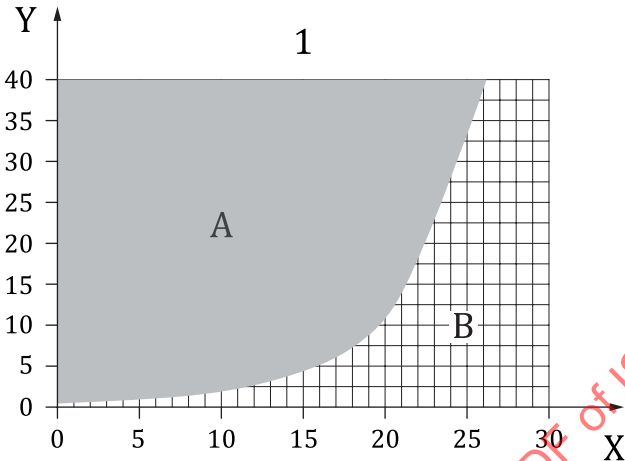
Solids can form in the CO₂ stream for different reasons and under different conditions. For a given pressure, when the temperature is below a certain limit, water ice or CO₂ hydrates can form if the water concentration is high enough. Solid CO₂ will form during depressurization from a liquid state to a pressure below the triple-point pressure. Taking account of solid CO₂ formation is needed in order to accurately predict the temperatures occurring during depressurization. Existing commercial flow assurance tools do not have models to handle the formation and sublimation of solid CO₂, although work has been done in several research codes. Remaining challenges include the prediction of the amount of solid CO₂ formed, and the degree to which it will stick to pipe walls and in valves under varying circumstances and potentially block the flow. Depressurization is discussed in [7.3.1](#).

7.4.2 Hydrates

CO₂ hydrates will form once water is present in CO₂ stream at certain pressure and temperature. Its formation can be described in terms of a HET (hydrate equilibrium temperature) curve as shown in [Figure 8](#). For a given fluid system, the hydrates can form if the pressure is larger than the pressure of

HET curve at the given temperature. The HET curve varies with fluid composition. The establishment of the HET curve for specific fluid compositions is done with dedicated experiments.

In a CO₂ transport system, the water concentration is normally low, see Reference [20] to reduce the corrosion risk of the pipeline. The HET for water of low concentration in a CO₂ stream is very low according to simulation results using the HydraFLASH⁷⁾ simulator, and much lower than expected normal operational temperatures in a pipeline system. However, hydrates can form during depressurization of a pipeline (see 7.3.1).



Key	
X	temperature, T (°C)
Y	pressure, P (MPa)
1	hydrate curve
A	hydrates
B	no hydrates

Figure 8 — Typical HET curve of hydrate formation for CO₂-H₂O system (HydraFLASH code simulation)

A large risk of hydrate formation in CO₂ transport and injection system can be observed in the downhole part of the injection well or within a reservoir. The HET curve for CO₂ saturated with water depends on the salt content in the water. Figure 9 shows an example of hydrate curves of CO₂ saturated with water with and without salt, and it can be observed that a mass fraction of 5 % of salt in the water decreases the hydrate temperature by 3 °C when compared with distilled water at 10 °C. CO₂ hydrate can form from both gaseous and liquid CO₂ in contact with water.

7) HydraFLASH is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

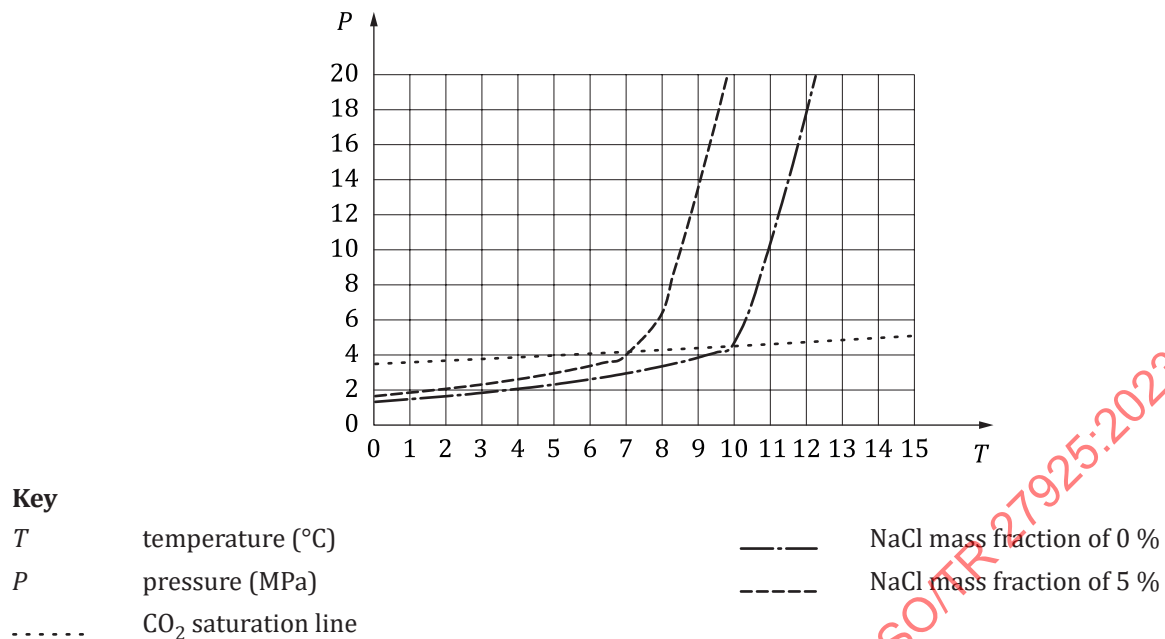


Figure 9 — Hydrate curves of CO₂ saturated with water with and without NaCl (HydraFLASH code simulation)

Possible prevention approaches for hydrate formation in CO₂ transport and injection system include:

- avoiding frequent stop/start operations, which can lead to a direct contact between CO₂ and formation water from the reservoir;
- active monitoring and control of the CO₂ stream status:
 - monitoring and controlling of temperature and humidity by downhole and wellhead sensors and heating and/or drying of the CO₂ stream prior to injection, if needed;
 - flowrate control: flowrate measurement and operation of the wellhead choke (in particular, during start-up);
 - pipeline pressure monitoring and controlling: the control of (limit) pipeline pressure during shut-down ensures low export pressure during start-up.

The formation of hydrates is promoted by high flow rates of liquid CO₂ of low temperature and by injection into depleted reservoirs with low reservoir pressure. Once hydrate is built up in the reservoir, the injectivity can be reduced. The endurance of this is related to the formation temperature in the affected injection zone. Upon hydrate formation in some (cooled) layers, the bottom hole pressure (BHP) can increase, which can lead to the requirement to reduce the injection rate.

Under an injection with reduced flowrate in the well tubing due to reduced injectivity and increasing BHP, a higher CO₂ temperature in the tubing and the reservoir is expected. This higher bottom hole temperature (BHT) of CO₂ together with heating from the reservoir can melt hydrates that were previously formed. The time of melting the hydrates depends on the re-heating process.

7.5 Ready for operation

For an offshore pipeline system, the pipeline is filled with sea water or fresh water for pressure testing after the installation. When successfully passed pressure testing, the water is removed, and the pipeline is normally filled with nitrogen gas before commissioning. The displacement of water is called dewatering, and also referred to as ready for operation (RFO). If an onshore pipeline segment between two valve stations is recommissioned after maintenance or modification (e.g. pipe replacement or tie-in), direct CO₂ injection is the only method of filling.

For carbon steel pipelines where pressure testing is performed with seawater, the dewatering operation is normally done via a train of pigs. The section between the first and the second pig is filled with fresh water to remove salt deposits and chlorides, and the rest is filled with MEG. The number of pigs varies depending on the targeted chloride concentration in MEG of the last segment of pigs and the water dew point temperature in the nitrogen-filled pipe. The final chloride concentration is normally set below a certain level based on corrosion criteria.

After the RFO, the pipeline contains N_2 at low pressure. The N_2 needs to be replaced during the first filling of CO_2 . The displacement of N_2 by CO_2 can be conducted by two ways: pigging and direct injection of CO_2 . The pigging operation for the first filling is similar to the RFO. Attention is needed to ensure the proper CO_2 flow condition. The first filling with direct CO_2 injection is more complicated. It is a challenge to estimate when all N_2 is displaced from the pipeline.

The existing commercial flow assurance tools have the functionalities to simulate the first filling process (pigging or direct injection of CO_2). The accuracy of the predicted results for such process will be similar to their prediction for the transient process of the CO_2 stream in pipeline.

8 Fluid flow in storage reservoirs

8.1 General

The ability to inject and store CO_2 in the foreseen amounts and at appropriate rates is key to the success of every CCS project. However, there are various issues that can limit injection rates and storage capacities. In addition, mitigation and corrective measures are difficult to apply in storage reservoirs, as access to the near-well area is limited and other parts of the reservoir at greater distance to the injection wells are more or less inaccessible. Therefore, it is important to consider potential disturbances of fluid flow in the reservoir and preventive measures already in the project planning to ensure flow during operation. In order to facilitate smooth and continuous injection and migration of CO_2 streams within storage reservoirs, appropriate injection schemes are needed that can consider more than one injection well for increased flexibility and robustness of operation.

Issues potentially disturbing fluid flow in storage reservoirs that can ultimately result in a (temporary) shut-down of projects can comprise, among others:

- a) a lower than expected injectivity or loss thereof;
- b) a build-up of or higher than expected reservoir pressure;
- c) an unexpected CO_2 plume migration (within the reservoir formation or the area of review/the storage complex); or
- d) either an integrity loss of the reservoir formation or containment problems, or both, i.e. leakage through the overburden or wells and their surroundings.

Issues such as these can occur due to various factors some of which can only partially be accounted for during project planning and site exploration. These factors can include, among others:

- a) uncertainties in reservoir properties (hence reservoir properties and thus either injectivity or containment other than expected/predicted, or both);
- b) the site-specific geological setting and the reservoir conditions (including P , T , composition of reservoir rocks and reservoir fluids and the rocks' natural variability and structural heterogeneity);
- c) physical and (geo-)chemical effects during injection/operation changing relevant reservoir properties;
- d) thermal effects in the reservoir rocks, the caprocks or the well due to CO_2 stream cooling or warming or injection of a CO_2 stream with a temperature different from the surrounding well and rocks that can initiate (geo-)mechanical processes in the well and the near well-bore region;

- e) drilling induced formation damage in the near well-bore reservoir rocks due to infiltration of drilling mud into the surrounding reservoir rock reducing its permeability.

To account for these inherent uncertainties and effects and to cope with potential flow disturbances, a thorough understanding of the relevant basic processes and their control factors is needed together with a robust CCS project design including appropriate preventive and corrective measures.

To verify injectivities and reservoir conditions, wells are subject to injection tests after drilling and completion after which the real injectivity is assessed. Perforations of the injection interval can be extended (e.g. for storage in multiple reservoir levels) or the reach of horizontal wells can be increased in order to overcome flow restrictions. Alternatively, additional wells can be drilled to tap the same or a different reservoir. Such measures can become necessary also if well injectivity declines with time due to an increasing skin (i.e. extra flow resistance near the well bore as compared to the pressure drop predicted by fluid dynamic simulations that results from the drilling, completion and production practices used) or processes in the reservoir limiting plume expansion. Availability of redundant wells can ensure flow when one well is out of operation or not performing as expected. Injection through more than one well will also give flexibility for plume steering and pressure management. Pressure management can also be done by brine production from the reservoir and re-injection in a geological formation different from the storage formation. Also, brine production and re-injection can be associated with specific challenges such as sand production and clogging as currently experienced at the Gorgon project. If back production of CO₂ is a foreseen corrective measure, field infrastructure prepared for reverse flow operations is needed. CO₂ back production was successfully tested at the Ketzin pilot injection site, see Reference [51].

Many large commercial CCS projects aim to inject at the CO₂ delivery temperature, i.e. the CO₂ stream temperature at the pipeline exit that depends on project specific settings and requirements. Before pipeline transport, the captured CO₂ stream is compressed and cooled to an appropriate pipeline entry temperature. During pipeline transport, the CO₂ stream reaches pipeline temperature. The fluid temperature in non-insulated pipelines is usually close to ambient (i.e. temperature of air, water body, soil or sediment depending on pipeline routing). As a result, injection temperature can show seasonal variations. At the Quest project a corresponding seasonal variation of the CO₂ bottom hole temperature has been reported that also leads to seasonal variations of injectivity; see Reference [52]. For short transport distances, insulated pipelines can be used if constant injection temperatures higher or lower than ambient are required. For example, at Sleipner the upper part of the “well” (i.e. the first 160 m) is insulated as it runs in air through one platform leg to the sea floor that is at a temperature of 6 °C, see Reference [53], while a stable wellhead temperature of 25 °C is required for injection; see Reference [54]. In the ROAD project, CO₂ transport was planned by a 22 km long insulated pipeline from Rotterdam to the P18-A platform to increase injection rates when the CO₂ is in gas phase, see Reference [55].

Injection of a CO₂ stream with a temperature different from the well and surrounding rocks can initiate geo-mechanic effects in the well and the near well-bore rocks. These can include thermal stress and fatigue which can lead to fines formation and migration and to formation damage (high skin) and potentially lower injectivity. The injection of colder CO₂ can also induce micro-fractures in the cement behind casing (which is at equilibrium with reservoir temperature prior to injection) which can impact cement integrity and hydraulic isolation between subsurface rock layers. In addition, the well construction needs to be investigated to understand the impact of the Joule-Thomson effect as the CO₂ moves from the tubing to the casing prior to entering perforations. Pressure variations within injection wells can likewise impact cement bonding and integrity, which can lead to requirements of work-over for which wells would have to be shut down (see also 7.1.2). Similarly, short-term pressure and temperature cycling, for example, due to shut-in/start-up cycles, can cause fatigue of well equipment and (near wellbore) reservoir rocks. Injecting a dense-phase CO₂ stream into a warmer reservoir can lead to a decrease of CO₂ stream viscosity at typical pressures and temperatures in storage reservoirs, in principle easing CO₂ flow and migration therein. However, field data from several projects show an inverse correlation between injectivity and bottom hole temperature pointing to a more complex set of factors controlling injectivity, see Reference [52].

If the CO₂ stream encounters and displaces another fluid phase (e.g. formation water, residual oil or natural gas), gravity forces, relative permeabilities and viscosity contrasts become important. Gravity is the primary force driving upward CO₂ migration and accumulation beneath the caprock or impermeable