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Petroleum and natural gas industries — Offshore platforms handling streams with high content of CO_2 at high pressures

Industries du pétrole et du gaz naturel — Plates-formes en mer traitant des courants à fort teneur en CO_2 à haute pression

Reference number
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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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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 67, *Materials, equipment and offshore structures for petroleum, petrochemical and natural gas industries*.

Introduction

In recent years, the oil industry has been facing challenges in developing and operating high-CO_2 content offshore fields. The CO_2-rich streams, separated from the produced natural gas, can be injected to enhance oil recovery from the reservoirs. Even in cases where the oil recovery increase is not so significant, operators have to consider the CO_2-rich stream compression and injection, in order to avoid its venting to the atmosphere.

Main concerns comprise surface safety system and material selection areas, which lack specific standards and regulations for this scenario. The commercial tools available, for instance, to model the dispersion of gases, need to be validated for CO_2 and CO_2/hydrocarbon mixtures, which have distinctive thermodynamic behaviour. This will affect the choice of materials and plant design.

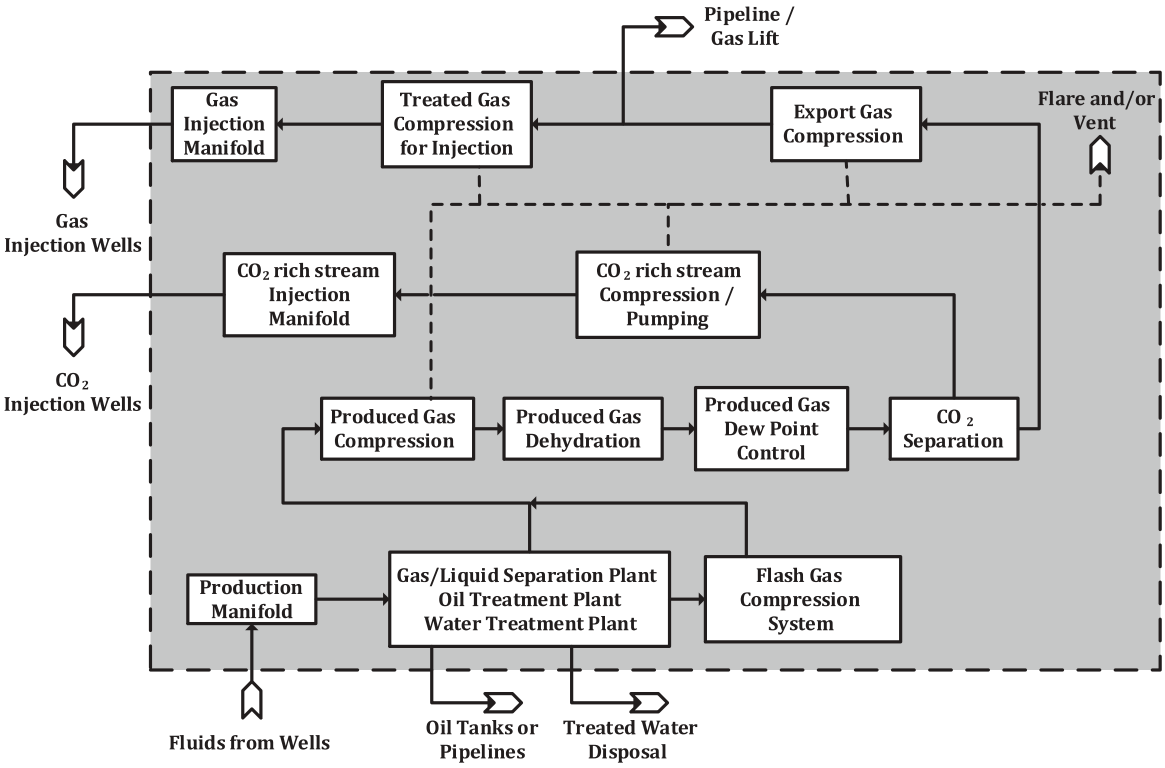
This International Standard addresses concepts and criteria for processing CO_2-rich streams, as a supplement to existing standards for offshore installations.

Petroleum and natural gas industries — Offshore platforms handling streams with high content of CO_2 at high pressures

1 Scope

This International Standard contains provisions for design of topside facilities for offshore plants handling CO_2-rich streams at high pressures; i.e. CO_2 molar concentration above 10 %. The surface systems include usual offshore process unit operations, as shown in Figure 1.

This International Standard is applicable only to topside facilities of fixed and floating oil and gas production offshore units up to the last barrier, such as an ESDV. Subsea production systems and Cryogenic CO_2 separation are not covered.



NOTE This example is within the scope of this International Standard.

Figure 1 — Example of a Process Flow Diagram (in grey zone)

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies..

ISO 13702, *Petroleum and natural gas industries — Control and mitigation of fires and explosions on offshore production installations — Requirements and guidelines*

ISO 15156 (all parts), *Petroleum and natural gas industries — Materials for use in H_2S-containing environments in oil and gas production*

ISO 21457, *Petroleum, petrochemical and natural gas industries — Materials selection and corrosion control for oil and gas production systems*

ISO 23936-1, *Petroleum, petrochemical and natural gas industries — Non-metallic materials in contact with media related to oil and gas production — Part 1: Thermoplastics*

ISO 23936-2:2011, *Petroleum, petrochemical and natural gas industries — Non-metallic materials in contact with media related to oil and gas production — Part 2: Elastomers*

API STD 521, *Pressure-relieving and Depressuring Systems, API Standard, January 2014*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
compressibility factor
Z
thermodynamic property for modifying the ideal gas law to account for the real gas behaviour

3.2
corrosion resistant alloy
CRA
alloy intended to be resistant to general and localized corrosion by oil field environments that are corrosive to carbon steels

[SOURCE: ISO 15156-1:2015, 3.6]

3.3
dense phase
fluid state (supercritical or liquid) above critical pressure

3.4
equation of state
EOS
thermodynamic equation describing the state of matter under a given set of physical conditions

3.5
free water
water not dissolved in the CO_2-rich stream

Note 1 to entry: This can be pure water, water with dissolved salts, water wet salts, water glycol mixtures or other mixtures containing water.

3.6
gas-assisted flare
flare with gas assistance system in order to increase gas net heating value

3.7
high-velocity tip flare
flare with gas exit velocities higher than 122 m/s

3.8
high-velocity vent
vent with gas exit velocities higher than 150 m/s

3.9
hydrate
solid, crystalline compound of water and light hydrocarbons or CO_2, in which the water molecules combine with the gas molecules to form a solid

3.10
CRA clad
metallic coating of CRA in which the bond between the parent metal and liner is metallurgical

3.11
low-velocity tip flare
flare with gas exit velocities lower than 122 m/s

3.12
low-velocity vent
vent with gas exit velocities lower than 150 m/s

3.13
minimum design temperature
minimum temperature below which the application limits for the materials involved are exceeded

3.14
platform
complete assembly, including structure, topsides, foundations and stationkeeping systems

[SOURCE: ISO 19900:2013, 3.35]

3.15
rapid gas decompression
RGD
depressurization
explosive decompression
rapid pressure-drop in a high pressure gas-containing system which disrupts the equilibrium between external gas pressure and the concentration of gas dissolved inside any polymer, with the result that excess gas tries to escape from the solution at points throughout the material, causing expansion

[SOURCE: ISO 23936-2:2011, 3.1.10]

3.16
supercritical phase
fluid state above critical pressure and temperature

3.17
topsides
structures and equipment placed on a supporting structure (fixed or floating) to provide some or all of a platform's functions

Note 1 to entry: For a ship-shaped floating structure, the deck is not part of the topsides.

Note 2 to entry: For a jack-up, the hull is not part of the topsides.

Note 3 to entry: A separate fabricated deck or module support frame is part of the topsides.

[SOURCE: ISO 19900:2013, 3.52]

3.18
triple point
temperature and pressure where CO_2 exists as a gas, liquid and solid simultaneously

4 Abbreviated terms

AIV	acoustically induced vibration
BLEVE	boiling liquid expanding vapour explosion
BDV	blow down valve
CH_4	methane
CO_2	carbon dioxide
CCR	central control room
CRA	corrosion resistant alloy
EERS	evacuation, escape and rescue strategy
EOS	equation of state
ESD	emergency shut down
FES	fire and explosion strategy
GDU	gas dehydration unit
H_2S	hydrogen sulfide
HC	hydrocarbon
HP	high pressure
HSE	health, safety and environment
IDLH	immediately dangerous to life or health
LP	low pressure
MMSCF	million standard cubic feet gas (60 °F and 1 atm)
NHV	net heating value
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
OSHA	Occupational Safety and Health Administration
Pa	ambient pressure
Pc	critical pressure
PEL	permissible exposure limit
PHA	Preliminary Hazard Analysis
ppmv	parts per million, volumetric basis
PR	Peng-Robinson EOS
PR-HV	Peng-Robinson EOS modified by using mixing rule of Huron-Vidal and Peneloux factor

PR-SV	Peng-Robinson-Stryjek-Vera EOS
PSV	pressure safety valve
RGD	rapid gas decompression
RO	restriction orifice
SCF	standard cubic feet
SVLE	solid-liquid-vapour equilibrium
STEL	short-term exposure limit
SRK	Soave-Redlich-Kwong EOS
Tc	critical temperature
TWA	time weighted average
v_{max}	maximum permitted velocity, expressed in m/s
Z	compressibility factor

5 Overview of CO_2-rich streams behaviour

5.1 General

In an offshore plant design, CO_2-rich streams can be handled close to or above its critical pressure (dense phase) or above its critical pressure and temperature (supercritical phase).[8] In the latter, some of its properties are similar to that of a liquid (e.g. density) and other similar to that of a gas (e.g. viscosity). The physical and thermodynamic properties of the CO_2-rich streams will have an impact on issues like hydrate formation and depressuring.

The design of a plant handling CO_2-rich streams at high pressures should be conducted using an EOS supported by experimental data in the range of operations. Examples of this approach are shown in Annex A. If experimental data are not available, data from thermodynamic based models, including readily available EOS, should be used taking into account any related uncertainties therefore allowing for sufficient safety margins.

Particular attention should be given when performing simulations near the critical point due to strong variation on stream properties and uncertainty on the description of the existing phases. For that reason, equipment normal operation envelope should avoid critical point region.

5.2 Hydrate formation

CO_2-rich streams can present a potential risk for hydrate formation similar to sweet natural gas, if water is present (as free water or in gas phase).

For high pressures, CO_2 has an inhibitor effect on hydrate formation, since an increase on the CO_2 concentration shifts the hydrate equilibrium curve towards low temperatures, as it can be seen in Annex B.

Dehydration unit design should take into account all operational conditions, including low temperatures that might occur in process systems and pipeline segments downstream from the offshore plant. Special attention should be given to the fact that CO_2 tends to increase water-holding capacity at higher pressures.

For that reason, depending on CO_2 content in the stream, it is not safe to set a water dew point specification based on higher pressure requirements only, since water condensation can occur at lower pressures (see Figure B.1).

As a first approach, a margin of 10 °C on water dew point or a reduction down to 50 % of the water saturation content should be considered.

An example of moisture content specification for Dehydration Unit is presented in Annex C.

5.3 CO_2 solid formation

Solid formation can be observed in a CO_2-rich stream depending on temperature and pressure. Low temperatures that lead to solid formation can be achieved during planned and unplanned depressuring operations, for equipment maintenance purposes and emergency conditions as well. Annex D presents phase diagram for CO_2-rich streams and discusses solid formation based on experimental and theoretical calculations.

The influence of methane content in solid formation temperature can be found in Reference [9]. The frost point is presented for a CO_2-CH_4 mixture in a wide range of concentrations, showing that increasing CH_4 content shifts the frost point curve toward lower temperatures, as shown in Annex D.

According to References [9] and [10], there is an indication that solid formed from a CO_2-rich stream in low temperature operations may be considered as composed of pure CO_2. Therefore, in the absence of experimental data and specific phase diagrams for mixtures with the solid region represented, available phase diagrams for pure CO_2 may be used as conservative approach, in order to predict the low temperatures in which solid formation is expected in an offshore plant design.

Process plant design should take into account the predicted low temperatures with additional design margin in order to specify suitable mitigation measures to avoid or deal with solid formation. More details are presented in Clause 6.

5.4 Flow metering

Design of metering systems shall take into account the peculiarities of behaviour of CO_2-rich streams. Preferably, metering systems should be located in plant sections where physical and transport properties are stable and predictable, i.e. far from critical point or phase transitions. Depending on the process, this means some meters may be designed for gas phase, while others for liquid phase.[11]

Flow computers with input for composition as well as temperature and pressure online measurements using the AGA-8 method, commonly used for natural gas, may be extended to CO_2-rich streams as long as conditions guarantee gas phase.[12] AGA-8 method also shows good predictability of supercritical phase as shown in Annex A.

Differential pressure flow meters such as orifice plates, Venturi or V-Cone are well suitable and robust, especially when working at very high pressures. Coriolis meters, being mass flow meters, are less susceptible to the variation of fluid properties or phase changes as long as no solids are formed but can be limited to operational pressures due to meter body construction.

Special care should be taken regarding changes in the CO_2-rich stream properties and potential flashing, so meter sizing and location should be properly selected.

6 Blow down, depressuring and relieving of plant and equipment

Temperature decrease observed in CO_2-rich streams during depressuring depends upon the initial and final pressures, initial temperature and stream composition.

In order to avoid brittle fracture, minimum temperatures achieved during an isenthalpic depressuring should be considered for material selection of let-down pressure devices (PSVs, BDVs, ROs) and for the entire low pressure system. Piping sections upstream the let-down pressure device can also be subjected to low temperatures and should be designed for co-incident high pressure at minimum temperature.

Apart from low temperature effects, designing relief systems of process plants (equipment or piping) should consider solid CO_2 formation, hydrate formation, adhesion and two-phase flow analysis.

Plant design should avoid operational conditions that lead to the triple point and solid formation in order to prevent plugging, piping erosion and vibration. Annex D presents examples of depressuring route in a phase diagram for CO_2-rich streams.

Designer should evaluate the following:

- control of blow down rate (such as manual assisted operations, restriction orifice or automatic control in steps);
- selection of backpressure of the blow down relief header higher than triple point and frost line. In this case proper transient studies should be carried out for a better evaluation of the whole relief system;
- avoiding pockets and minimizing bends in pipe segments downstream relief device up to main flare or vent header;
- main flare or vent header configuration to avoid potential plugging;
- use of heat tracing;
- application the full upstream pressure rating to the blow down systems in the event of risk of plugging.

For depressuring criteria, designer shall comply with API STD 521 requirements even in cases of non-flammable CO_2-rich streams.

ESD system design should consider proper installation of shutdown/isolation valves in order to limit inventory and thereby minimize trapped fluid amount and potential for incident escalation.

The risk of Rapid Gas Decompression (RGD) damages to non-metallic materials can impose limitations on the depressuring rate. This scenario should be included in the consequence analysis.

7 Flare and vent system configuration

7.1 General

Flare and Vent system design shall comply with API STD 521.

Design of CO_2-rich streams flare and vent systems shall consider the following aspects, as a minimum:

- CO_2-rich streams composition and respective minimum net heating values (NHVs);
- combustibility (flare);
- safe gas dispersion (vent);
- CO_2 solid formation (see Clause 5);
- temperature profile during depressuring (see Clause 6 and Clause 8);
- selection of metallic and non-metallic materials (see Clause 8).

7.2 System selection

Possible flare and vent system configurations are described in Table E.1.

In case of H_2S present in CO_2-rich streams, flaring should be preferred instead of venting. For flare systems, design should comply with H_2S destruction temperature, as low NHV streams have lower flame temperature. For vent systems, design shall warrant proper H_2S dispersion due to hazard and safety aspects.

Flaring gases with low NHV influences ignition stability and can cause flame extinction. Header and disposal segregation between low and high NHV releases may be considered as an option.

For streams with NHV lower than 7,5 MJ/Sm^3 (200 BTU/SCF), which corresponds approximately to a 75 % (molar) CO_2 mixture with methane, vent or gas-assisted low-velocity tip flare should be used. Minimum NHV shall be ensured in flare systems to allow flammability and combustion efficiency at the flare tip, by mixing assistance fuel gas from a reliable source to CO_2-rich streams being relieved. The capacity of assistance fuel gas should be designed for the worst-case scenario.

For streams with NHV higher than 7,5 MJ/Sm^3 (200 BTU/SCF) and lower than 28,1 MJ/Sm^3 (800 BTU/SCF), high-velocity tip flares are not recommended. The use of such tip compared with low velocity one shall be carefully evaluated. Manufacturer guarantee is required in case the high-velocity tip will be used.

For high-velocity tip flares, a typical minimum NHV gas mixture to be burned is 28,1 MJ/Sm^3 (800 BTU/SCF). This corresponds approximately to a 25 % (molar) CO_2 mixture with methane.

7.3 System configuration

7.3.1 Flare

For units dealing with CO_2-rich streams, alternative flare system for low NHV and/or low temperature may be considered in additional to typical HP and LP systems.

The ignition of CO_2-rich streams requires a high energy ignition source. Such condition can be achieved by increasing the number of pilot burners in relation to minimum requirements of pilot manufacturers' recommendations as detailed in ISO 25457.

To ensure combustion, special attention shall be given to flare tip velocities. It is important to take into account the following considerations: Low-velocity flares are those designed for and operated with an exit tip velocity lower than the maximum permitted velocity, $v_{\max}$, as determined by the Formula (1), limited to 122 m/s (400 ft/s).

$$\log_{10}\left(v_{\max}\right) = (NHV + K1) / K2 \tag{1}$$

where

$v_{\max}$ is the maximum permitted velocity, expressed in m/s;

$K1$ is the constant equal to 28,8;

$K2$ is the constant equal to 31,7;

NHV is the net heating value, expressed in MJ/Sm^3.

The method to determine the maximum permitted velocity $v_{\max}$ is shown in Reference [13].

As a rule, maximum permitted velocity calculated from Formula (1) will dictate flare tip area equivalent diameter. Effects of low temperature on flame stability can be countered by lowering velocity or adding assistance gas. Flare tip design will be dictated by flare tip suppliers and experimental evidence should be required for all critical relief scenarios and/or unproven solutions. Interaction with flare tip suppliers is recommended from the early phases of design.

Designer should evaluate noise and acoustically induced vibration (AIV) aspects.

Flare thermal design shall comply with API STD 521, following recommendations about admissible total radiation fluxes over the working areas, without the need of any heat shield in the unit.

Dispersion simulations are necessary for defining the following designing aspects: flare length, height, position and orientation due to dominant wind directions. The snuffed flare scenario should be one of those covered by dispersion studies, especially considering that low temperature releases are less likely to ignite.

7.3.2 Vent

Vent tip location shall be assessed based on dispersion studies, practical safety zones, noise, acoustically induced vibration (AIV) and thermal radiation in case of accidental ignition scenario.

Dispersion simulations, including evaluation of the CO_2 plume, are necessary for defining the following designing aspects: vent length, height, position and orientation due to dominant wind directions. The final location of the outlet orifices shall ensure that the low flow discharges be adequately dispersed.

As a general recommendation, the vent tip should be pointing 45° from the horizontal plane in the direction away from working areas. Some protection against rain may be provided.

When designing the vent system, consideration should be given to the formation of solid CO_2 due to low temperatures downstream of blow down/relief valves. If solid CO_2 formation is possible, the vent design should minimize the potential for blockage.

High-velocity vents are recommended whenever possible, in order to reduce potential CO_2 or hydrate plugging, solid adhesion and improve gas dispersion.

8 Materials

8.1 Corrosion

8.1.1 General

Internal corrosion can be a significant risk to the carbon steel piping and equipment integrity dealing with CO_2-rich streams in presence of free water. Free water combined with high CO_2 partial pressure is likely to lead to high corrosion rates. As discussed is Annexes B and C, water can be less likely to drop out from vapour phase CO_2-rich streams when compared to natural gas.

The presence of H_2S in combination with free water will have a significant effect on the corrosion rate. The possibility of oxidizing species ingress in the presence of H_2S can induce elemental sulfur deposition leading to higher corrosion rates.

Materials selection shall comply with ISO 21457. Physicochemical and corrosion models used for internal corrosion evaluation should take into account considering high CO_2 contents and high pressures.

Piping, fittings and equipment with fluids containing H_2S shall be evaluated according to ISO 15156 (all parts).

Pipe segments and other parts of the system that can have stagnant conditions (pockets) should be evaluated carefully for internal corrosion.

8.1.2 Internal corrosion control by dehydration

In general, for carbon steel piping and equipment no internal corrosion protection is required providing that free water in the CO_2-rich streams be avoided through a strict water content control procedure. This consideration should be used downstream of the dehydration system. Moisture content monitoring should be considered as part of piping and equipment design and operation.

Upset conditions and downtimes shall be taken into account. This can include dehydration system failure and dehydration off-spec when specifying critical systems where significant failure cannot be tolerated.

8.1.3 CRAs

Most of CRAs are suitable for wet CO_2-rich streams applications. The use of solid CRA or CRA clad for corrosion prevention should be considered for the dehydration system itself and the upstream facilities. Some guidelines for selecting CRAs are indicated in ISO 21457.

8.1.4 Internal corrosion protecting chemicals

Reliance on pH stabilization and injection of corrosion inhibitors can be an effective way to control CO_2-rich streams corrosion rates where free water is present. If this approach is to be adopted a qualification program is required, in order to ensure the effectiveness of this solution.

8.1.5 Internal organic coatings

Internal coating for corrosion protection is not recommended where there is a risk of damage such as detachment from the base pipe material due to RGD, erosion, installation and work-overs. Extensive corrosion rates are likely to result in sections with coating damages.[14]

8.2 Brittle fracture

If a CO_2-rich stream experiences depressuring, it can cool down rapidly because of the Joule-Thomson effect. Selected materials shall be suitable for the minimum design temperature. This applies to both parent metal and welded joints.

These materials with guaranteed low-temperature properties shall be applied to vessels, pipes, valves and fittings, including body and internals of pressure relief devices. In addition, the low temperature upstream pressure let down device in piping sections should be considered (refer to Clause 5).

8.3 Ductile fracture

Piping systems handling CO_2-rich streams are more susceptible to running ductile fractures than those for natural gas service. When a fracture initiates in a pipe with dense phase CO_2-rich stream and vapour starts to form, the decompression speed drops rapidly, keeping the pipe subjected to a high loading state. The selected piping material should resist this high loading state and thus prevent fracture propagation.

Likelihood of fracture propagation depends on piping material and thickness, on operation temperature and pressure and on the physical properties of the CO_2-rich stream.[15] A methodology for evaluating ductile fracture propagation is described in Annex G.

8.4 Lubricants

Petroleum based greases and many synthetic types of greases, used in components such as valves and pumps, can be deteriorated by CO_2-rich streams. The compatibility of the applied grease with specified CO_2-rich streams should be taken into account for the entire operating envelope of pressure and temperature.

The phase equilibrium between different kinds of lubricants and CO_2 indicates a three-phase area where two liquid phases and vapour coexist. These regions should be avoided at lubrication point. Besides, the CO_2 solubility in the lubricant reduces significantly its viscosity and can jeopardize lubrication.

There are specific lubricants and greases designed for CO_2 applications. This applies in particular to safety critical valves such as block valves, check valves and pressure relief valves where lubrication can significantly affect the ability of the valve to operate in an emergency. One possibility is to minimize the contact between lubricant and gas, so that effects will be reduced.

8.5 Non-metallic seals for CO_2 service

The materials selected shall be compatible with all states of the CO_2-rich streams. In a dense phase, CO_2-rich streams can behave as an efficient solvent and it can penetrate and saturate some non-metallic materials.

The possibility of swelling during dense phase exposure and explosive decompression damage during rapid gas decompression shall be considered for elastomer sealing. Candidate materials need also to be tested for the potential low temperature conditions that can occur during depressurization (Joule-Thomson effect).

CO_2-rich streams can cause different types of deterioration mechanisms like swelling and cracks after rapid decompression of several components, such as: O-rings, seals, gaskets and valve seats.

Non-metallic materials shall be qualified to ensure the following:

- chemical/physical compatibility with CO_2 and other chemical components in the CO_2 stream without causing significant decomposing/extraction, swelling, hardening or unacceptable negative impact on material key properties;
- resistance to full temperature range;
- ability to resist destructive decompression (RGD).

All non-metallic seals and packing elements selected shall be qualified for the intended design conditions. ISO 23936-1 and ISO 23936-2 shall be used as references. Concerning RGD evaluation for thermoplastics, ISO 23936-2 shall be used as reference, however with modified acceptance criteria: no blisters nor cracks nor holes are acceptable.

Annex H gives some tests for non-metallic materials commonly used in CO_2-rich stream applications.

9 Safety

9.1 General

Offshore units handling CO_2-rich streams at high pressures are a relatively novel process and, depending on process conditions and applied technology, complexity can be increased due to fluid dynamic properties of dense phase CO_2-rich streams. This introduces a number of new hazard management issues that should be addressed.

9.2 Impacts of the loss of containment of CO_2-rich streams

9.2.1 General

When the temperature of a CO_2-rich stream plume is below the water dew point temperature in the atmosphere into which it is being released, water vapour will condense to form a visible cloud. Otherwise, high temperature and pressure releases will take longer time to be visually perceived.

The visible cloud represents the extent of the water vapour condensation and does not represent the extent of the CO_2 plume. If a high temperature CO_2 stream is leaking (e.g. a leak from a compressor discharge), no visible cloud will be produced.

If the ambient atmosphere into which a CO_2 release flows is dry, the water vapour cloud will be smaller than on a humid day. As a result, the absence of a visible cloud should not be taken as an indication of the absence of a CO_2 leak. Otherwise, the presence of a visible cloud should not be taken as an indication of the exclusive presence of a CO_2 leak.

9.2.2 Respiratory physiological parameters

CO_2 acts both as a stimulant and as depressant on the central nervous system. Immediately after exposure to elevated CO_2 levels, physiological parameters such as ventilation rate, total volume of air inhaled and exhaled during ventilation, CO_2 partial pressure in the lungs and acidity of the blood increase. An ambient volume concentration of 3 % CO_2 results in a measurable increase in ventilation rate and volume. CO_2 at this level also cause headaches, diffuse sweating, and difficult breathing at complete rest after an exposure period of several hours.[16]

If inhaled CO_2 concentration is increased above 3 %, respiratory stimulation then increases sharply until inspired CO_2 concentration of about 10 % is reached. Between 10 % and 30 % inspired CO_2, the rate of increase in respiratory rate and volume reduces per unit of increase in inspired CO_2, until the concentration of 30 % CO_2 in oxygen is reached. At this point ventilation suddenly declines and convulsions occur.

9.2.3 Low temperature impact

The venting or release of dense phase CO_2-rich stream to atmosphere will result in a temperature drop that can be accompanied by phase changes and solid CO_2. Upon impact with adjacent structures such as equipment, instruments or electrical systems released jet can potentially cause their failure due to physical damages and/or cooling effects and be a major threat to the structural and functional integrity of nearby equipment and devices. Cooling effects are significantly more pronounced if solid CO_2 is formed during release.[18]

Furthermore, the cold jet of gas from release and entrained solids at –78 °C represents a significant hazard to personnel, since it can lead to cryogenic burns, impact injuries and severe internal injuries due to inhalation of this cold release.

9.2.4 CO_2-rich stream BLEVE

Due to the severity of the consequences of a BLEVE, it should not be disregarded during design phase. Annex F discusses the definition of BLEVE and presents a theory for prediction of CO_2-rich streams BLEVE possible occurrence. Designer should take into consideration the phenomenon (see for example Figure F.2) and avoid operational conditions into these BLEVE envelopes whenever it is possible. The possibility of CO_2 BLEVE should be taken into account depending on the amount of dense phase CO_2-rich stream similar to the impact of other volatile liquids.

The possible occurrence of a CO_2-rich stream BLEVE is based on the development of thermodynamic models considering the spinodal curves, which represents the limit-of-stability for the liquid phase during expansion,[17] as can be seen in Annex F.

In systems susceptible to BLEVE, guidance is found in Reference [18] and some areas of concern are listed as follows:

- material selection, design and inspection;
- piping and arrangement;
- piping and equipment cooling for fire protection to guarantee integrity;
- piping and equipment protection from dropped charges;
- monitoring process conditions.

9.3 Hazard identification and risk assessment and management

9.3.1 General

Hazard identification and risk assessment should be implemented using structured tools. ISO 17776 provides information about these tools and their usage in the design of petroleum and gas offshore installations. ISO 31000 provides principles and guidelines for the implementation of risk assessment and management for general use.

For reliability management and associated reliability and availability analysis and data, guidance is provided in ISO 20815, ISO/TR 12489 and ISO 14224.

9.3.2 Hazard identification

In order to determine potential damage on personnel and equipment exposed, a detailed study of the behaviour of CO_2-rich streams and all components shall be developed. In case of presence of H_2S in the stream, specific studies are also required.

For the identification of risk design scenarios the following aspects shall be considered, as a minimum:

- physiological effects of CO_2;
- pressure and expansion ratio;
- low temperature effects and solids formation;
- possibility of CO_2 stream BLEVE.

Most of the HSE issues identified in the industry were related to phase characteristics when dense phase CO_2-rich stream is depressurized, either through a planned operation or by an accidental release. The hazards that have been identified can be divided broadly into three groups:

a) piping issues, such as external and internal corrosion, hydrate formation and overstress due to free span;

b) material issues such as CO_2 solvent properties and material compatibility and effects on non-metallic material;

c) operation and engineering challenges, as follows:
    - solids formation;
    - system depressuring controlled and accidental;
    - CO_2-rich streams flammable limits;
    - low temperatures;
    - high pressures;
    - vessel ruptures/failures;
    - CO_2-rich stream BLEVE.

9.3.3 Risk assessment and management

A comprehensive risk assessment should be developed, including upset conditions, to establish control measures according to ISO 31000 guidelines. Risk management measures, once identified, should be maintained to guarantee the defined level of performance that is required.

To achieve this goal there should be a continuous management cycle in order to

- maintain an understanding of the hazards and risks,
- identify the critical risk management measures,
- define the minimum level of performance from each critical element,

- implement robust test, inspection and maintenance routines to keep the critical elements performance above defined levels,
- implement a verification process so that critical elements are likely to deliver the defined level of performance, and
- implement a review loop to ensure that any changes in the risk profile or its management are identified and feedback into the cycle is provided.

9.4 Consequence analysis

9.4.1 General

Despite the uncertainties about the accuracy and applicability of the gas dispersion models currently available for dispersion analysis for CO_2-rich streams, it is required to evaluate the consequences of incidents related to dense phase CO_2 systems' loss of containment and releasing of other hazardous stream components like H_2S.

9.4.2 CO_2 dispersion

A dispersion study is recommended to model possible CO_2-rich stream leakages behaviour in order to optimize the usage of gas detectors in open areas (quantification and location) and contribute to the development of EERS. The gas dispersion study should consider all leak scenarios identified in the PHA.

The gas dispersion study should consider, as a minimum, the following aspects:

- leak points;
- frequency of leaks;
- inventories and conditions of the released gas;
- modelling of the gas dispersion process;
- maximum and minimum CO_2 concentrations expected during unit lifetime.

9.4.3 Effects of cold CO_2 jet

A high pressure and low temperature jet of a CO_2-rich stream can compromise the integrity of adjacent structure due to the impinging force and cooling effects leading to a reduction in yield strength. Should the conditions of the jet lead to solid formation, abrasion and enhanced heat transfer increase the potential for damage and failure of the obstacles hit. Design should evaluate providing structural protection at least for critical equipment such as depressuring header and fire water main.

9.5 CO_2 detection

Process area containing equipment or piping dealing with CO_2-rich streams should be continuously monitored by gas detectors in order to immediately

- alert people of possible gas incident, and
- initiate appropriate control actions.

The provision of monitoring occupied compartment air intakes with CO_2 gas detectors interlocked with closing of dampers in ventilation ducts should be confirmed by gas dispersion analysis.

Specific safety actions on the offshore installation should begin when CO_2 gas is confirmed by two detectors in the same zone, but alarm in CCR should be triggered with gas detection by one single detector.

The following levels of CO_2 are recommended as appropriate to trigger these actions:

- 3 900 ppmv, to alert people (alarm sounds in the control room);
- 30 000 ppmv, to initiate control actions defined in the design.

The design of gas detection systems in process plants with variable concentrations of CO_2 and CH_4 mixtures may consider the possibility to detect leakages through the detection of either one of these gases. In such a way, this system can be more efficient if it is based on CH_4 detection in some cases and based on CO_2 detection in other cases. In a few cases, it should be necessary to use systems based on the detection of both gases. This evaluation should be done for maximum and minimum fluids CO_2 contents for the unit lifetime.

Depending on the process conditions, leaks from high pressure rich CO_2 streams can lead to solid CO_2 formation. In order to quantify and locate the detectors it should be considered that all leaked mass is in gaseous phase.

The final quantity and location of gas detectors, gas detection voting strategy integration into the Fire and Gas system shall comply with ISO 13702, manufacturer specifications, as well as gas dispersion study, lay out of equipment, piping and ventilation ducts.

The gas detectors should be specified to perform at low temperatures achieved during accidental release.

9.6 Strategies

Guidance provided in ISO 13702 for the control of fires and explosions on offshore facilities producing oil and gas defines the need to record results of hazard identification and risk assessment, as well as decisions taken on the measures required to reduce and control these risks. These records are named as strategies and are an essential guide for those who will operate the facility or will be engaged in any subsequent change to be introduced therein.

The FES and the EERS described in ISO 13702 should be adapted to these conditions, as well as other strategies to be developed aimed specifically at the reduction and control of risks associated with the presence of CO_2 in the fluids produced and processed.

The effects of exposure of people to atmospheres containing CO_2, considering the binomial concentration and exposure time, are reported in Annex I. Thus, the installation design should include, among its strategies, control actions to prevent and/or mitigate the potential consequences of the leakage of CO_2-rich streams.

The strategies developed should consider the different values of process variables in different areas of the facility, as well as possible variations of CO_2 content coming from the reservoir during the unit lifetime.

Although for the design of gas detection systems all leaked mass should be considered in gaseous phase, for definition of EERS it should be considered the potential of solid formation and its sublimation.

The results of the gas dispersion study support development of the FES and EERS.

Annex A
(informative)

Evaluation of EOS for CO_2-rich streams

A.1 Example of EOS verification based on experimental tests

The accuracy of an EOS selected to be used in process plant designing should be verified against experimental data for the entire range of operation (pressures, temperatures and compositions). Most EOS do not describe well the presence of water, a discussion of how to estimate water content is presented in Annex C.

Table A.1[19] presents four CO_2/HC mixtures, free of water, covering a wide range of compositions (5 % to 90 % molar of CO_2). The mixtures were synthesized in laboratory and used to provide density experimental measurement in the temperature range of 20 °C to 100 °C and pressure range of 1 700 kPa to 55 000 kPa, in order to evaluate the accuracy of Peng-Robinson EOS.[19] Phase Diagrams for the mixtures of Table A.1 calculated by Peng-Robinson EOS and are presented on Figure A.1.

Table A.1 — Synthesized mixtures (CO_2/HC)

Component	Molar composition (% molar)			
	Mixture 1	Mixture 2	Mixture 3	Mixture 4
CO_2	5,00	34,55	74,02	89,93
N_2	0,65	0,51	0,00	0,00
C_1	74,91	54,02	24,87	9,06
C_2	10,24	5,94	1,01	1,01
C_3	6,40	3,28	0,10	0,00
nC_4	2,30	1,18	0,00	0,00
nC_5	0,50	0,52	0,00	0,00
Molecular weight	22,00	28,31	36,91	41,33

Tables A.2, A.3 and A.4 present the results of experiments (compressibility factors calculated from the densities measured in the laboratory for the mixtures shown on Table A.1). The density measurements as well as the estimated compressibility factors values are based on the methodology described in A.2.

Observed errors (average and mean absolute error) of EOS predictions, for CO_2 contents in the range from 5 % to 90 % molar, represented by mixtures 1 to 4, are shown on Table A.5. In this case, the EOS mentioned in Table A.5 could lead to errors of up to 4 % in offshore plant design for the entire operational envelope.

Average error in Table A.5 is defined as the percentage deviation of the EOS predicted value when compared to the measured value (the average of estimated errors for each mixture in all range of pressure and temperature evaluated). Mean absolute error is the module of percentage deviation (the average of modules of errors for each mixture in all range of pressure and temperature evaluated).

Table A.2 — Compressibility factors (Z) for synthesized mixtures — T = 20 °C

Pressure kPa	**Temperature** 20 °C			
	Mixture 1 (5 % CO_2)	**Mixture 2** (35 % CO_2)	**Mixture 3** (74 % CO_2)	**Mixture 4** (90 % CO_2)
1 724	0,961 0	0,933 3	0,928 4	0,920 4
3 447	0,855 5	0,885 5	0,797 5	0,805 9
5 171	0,830 2	0,818 4	0,730 3	0,714 8
6 895	0,720 8	0,728 4	0,620 0	0,577 1
8 618	0,686 8	0,667 2	0,504 0	0,366 4
10 342	0,653 8	0,630 6	0,404 7	0,295 6
12 066	0,629 6	0,581 9	0,381 6	0,306 5
13 790	0,628 8	0,568 7	0,390 7	0,330 2
17 237	0,642 1	0,581 2	0,433 6	0,383 6
20 684	0,692 7	0,629 1	0,488 1	0,439 0
24 132	0,747 7	0,678 9	0,544 4	0,496 0
27 579	0,803 1	0,735 6	0,600 4	0,549 4
31 026	0,864 3	0,793 7	0,656 5	0,604 0
34 474	0,923 4	0,851 4	0,711 9	0,658 2
37 921	0,981 2	0,909 0	0,766 7	0,711 0
41 369	1,042 5	0,968 1	0,821 3	0,764 6
44 816	1,104 6	1,026 9	0,875 8	0,816 9
48 263	1,166 5	1,086 9	0,930 1	0,868 9
51 711	1,231 9	1,147 1	0,983 7	0,920 8
55 158	1,301 6	1,209 2	1,038 9	0,972 0
NOTE Mixture 4 was measured at 30 °C, since below 25 °C liquid phase would occur.				

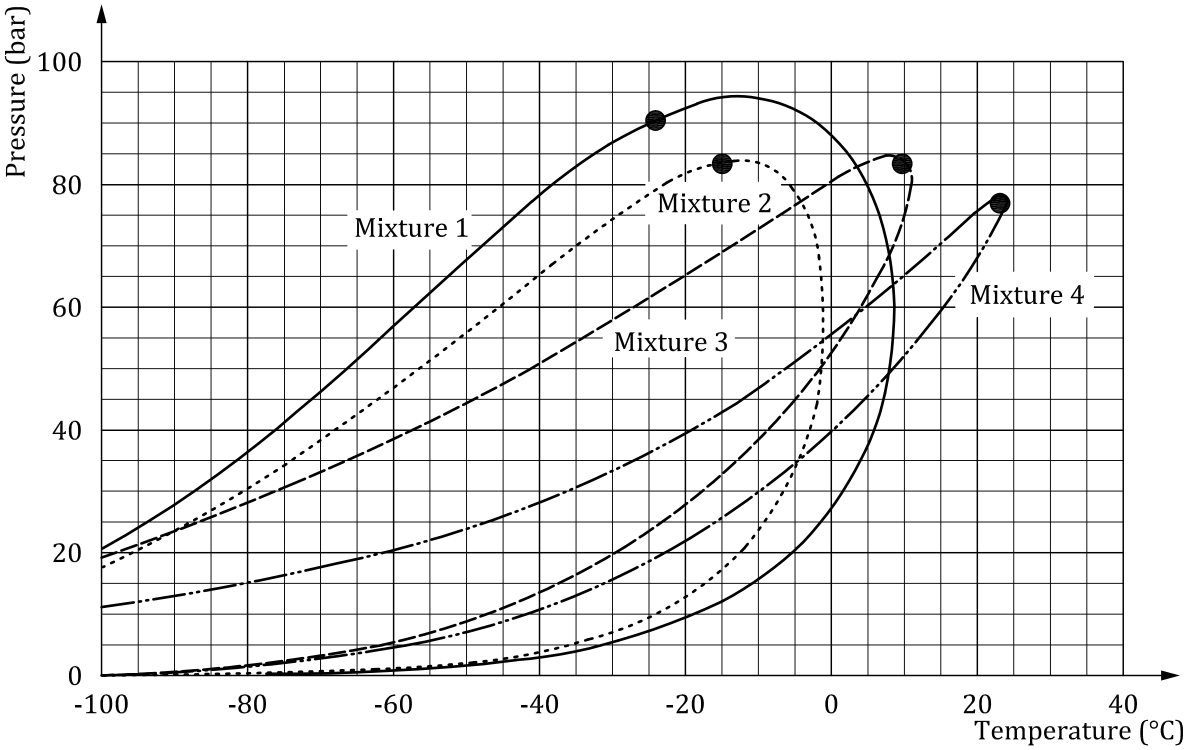


Figure A.1 — Equilibrium diagrams for CO_2/HC mixtures

Table A.3 — Compressibility factors (Z) for synthesized mixtures — T = 60 °C

Pressure kPa	**Temperature** 60 °C			
	Mixture 1 (5 % CO_2)	**Mixture 2** (35 % CO_2)	**Mixture 3** (74 % CO_2)	**Mixture 4** (90 % CO_2)
1 724	0,983 2	0,956 3	0,946 7	0,938 0
3 447	0,914 4	0,914 7	0,886 2	0,863 3
5 171	0,891 5	0,891 7	0,852 7	0,809 4
6 895	0,828 0	0,815 5	0,782 5	0,723 5
8 618	0,807 5	0,795 6	0,734 1	0,667 8
10 342	0,787 2	0,783 5	0,690 3	0,589 8
12 066	0,781 4	0,762 3	0,652 1	0,527 6
13 790	0,779 1	0,747 1	0,616 3	0,484 8
17 237	0,769 7	0,719 3	0,579 2	0,469 0
20 684	0,782 4	0,733 8	0,594 2	0,498 1
24 132	0,816 2	0,762 4	0,620 9	0,537 6
27 579	0,849 3	0,795 6	0,656 8	0,582 7
31 026	0,896 6	0,837 4	0,698 9	0,628 5
34 474	0,946 1	0,885 1	0,7454	0,675 6
37 921	0,990 5	0,929 1	0,788 4	0,722 7
41 369	1,043 1	0,978 8	0,834 7	0,770 6
44 816	1,095 4	1,028 3	0,881 4	0,817 6
48 263	1,148 1	1,077 4	0,926 7	0,865 1

Table A.3 *(continued)*

51 711	1,202 0	1,129 3	0,974 0	0,911 6
55 158	1,259 4	1,181 7	1,022 1	0,959 2

Table A.4 — Compressibility factors (*Z*) for synthesized mixtures — T = 100 °C

Pressure kPa	**Temperature** 100 °C			
	Mixture 1 (5 % CO_2)	**Mixture 2** (35 % CO_2)	**Mixture 3** (74 % CO_2)	**Mixture 4** (90 % CO_2)
1 724	0,977 8	0,992 4	0,969 2	0,971 1
3 447	0,962 1	0,965 9	0,933 2	0,904 5
5 171	0,937 3	0,932 5	0,896 4	0,860 8
6 895	0,929 8	0,916 1	0,850 5	0,821 4
8 618	0,912 5	0,887 9	0,822 6	0,783 7
10 342	0,887 9	0,854 1	0,801 4	0,748 8
12 066	0,867 5	0,840 8	0,778 3	0,720 2
13 790	0,859 7	0,825 9	0,747 8	0,686 3
17 237	0,869 4	0,827 3	0,739 1	0,653 5
20 684	0,863 3	0,825 3	0,723 7	0,641 1
24 132	0,894 8	0,847 0	0,731 0	0,643 6
27 579	0,917 2	0,869 5	0,746 1	0,664 5
31 026	0,951 2	0,890 7	0,772 9	0,695 8
34 474	0,979 4	0,923 0	0,800 9	0,728 0
37 921	1,022 9	0,965 8	0,833 6	0,763 6
41 369	1,065 4	1,004 1	0,869 1	0,802 6
44 816	1,109 6	1,039 9	0,905 0	0,841 8
48 263	1,160 1	1,088 8	0,945 7	0,882 8
51 711	1,209 6	1,131 3	0,985 5	0,923 8
55 158	1,285 1	1,180 4	1,026 3	0,964 8

Table A.5 — Errors in predictions of EOS

Component	**Average error % (mean absolute error %)**				
	PR	PR – HV	PR – SV	Sour – PR	AGA – 8
Mixture 1	+0,24 (0,34)	+1,19 (0,46)	−3,56 (0,94)	−3,57 (0,94)	−0,11 (0,98)
Mixture 2	+0,42 (0,35)	+1,08 (0,43)	−4,01 (1,01)	−3,17 (0,82)	−0,38 (1,03)
Mixture 3	+2,08 (0,46)	+2,06 (0,60)	−1,69 (0,60)	−1,38 (0,61)	+0,19 (1,42)
Mixture 4	+3,46 (0,48)	+2,83 (0,78)	−0,48 (0,64)	+0,17 (0,72)	+0,63 (1,46)

A.2 Methodology for CO_2/HC density measurement and compressibility factor (*Z*) estimation

The methods for density measurement in laboratory and compressibility factors (*Z*) calculation from experimental data are shortly described herein.

Initially, the gas sample is maintained in a pressurized bottle (600 cm^3 to 1 000 cm^3), provided with a floating piston which uses water or mercury as pressurization fluid.

The determination of the density of a mixture of hydrocarbons is performed by injecting the sample in a high pressure digital densimeter and checking the period of forced oscillation of the metal U-tube. This tube has an internal volume of 1 cm^3.

The density is related to the difference between the resonance frequencies of the filled tube and empty tube. Using another two fluids with known densities (in the present study, water and N_2), whose oscillation periods are determined under the same conditions of temperature and pressure, the mathematical parameters of this relationship are calibrated, allowing the measurement of sample density. The digital densimeter used in tests is able to work up to six significant figures.

A limitation of this method is that the mixtures should be single-phase in the conditions of the experiment; otherwise the equipment will not present stable values.

As for the compressibility factors (Z), they were estimated based on following a formula taking into account the experimental values of the variable density (ρ), see Formula (A.1).

$$Z = \frac{P.M}{\rho.R.T} \tag{A.1}$$

where

Z is the compressibility factor of gas;

P is the pressure at cell;

M is the molecular weight of gas;

ρ is the gas density;

R is the gas universal constant;

T is the temperature at cell.

A.3 Examples of EOS verification based on published data

Methods for dealing with thermodynamics of multi-component mixtures are well established. In the context of cubic equations of state, this is accomplished using the so-called “mixing rules”, whereby the parameters in the formulas of the components are combined to give a new set of parameters for the mixture.

There are available published data on literature developed in order to represent the behaviour of CO_2-rich streams and evaluate the accuracy of available EOS.

The responses of various empirical correlations for calculating the density (and hence the compressibility factor) from gas mixtures containing between 10 % and 100 % molar CO_2 were checked.[7] These results are compared with classical equations of state such as PR and SRK, and there is an indication that performances of some commercial equations are considered acceptable.

The evaluation of the predictive ability of the PR equation of state has been carried out[20] and the simulations showed good ability to reproduce the experimental data available in the literature for mixtures of gases containing H_2S, CO_2 and CH_4, free of water. In the presence of water, it is clear the need to use more complex equations of state and mixing rules.

Empirical EOS Span and Wagner[21] was developed specifically to cover the fluid region of CO_2 above the triple point. Although developed for pure carbon dioxide, the EOS can be used for CO_2 mixtures, with appropriate binary interaction coefficients. This equation is valid for equilibrium thermodynamic properties of carbon dioxide in the fluid region up to temperatures of 1 100 K and pressures up to

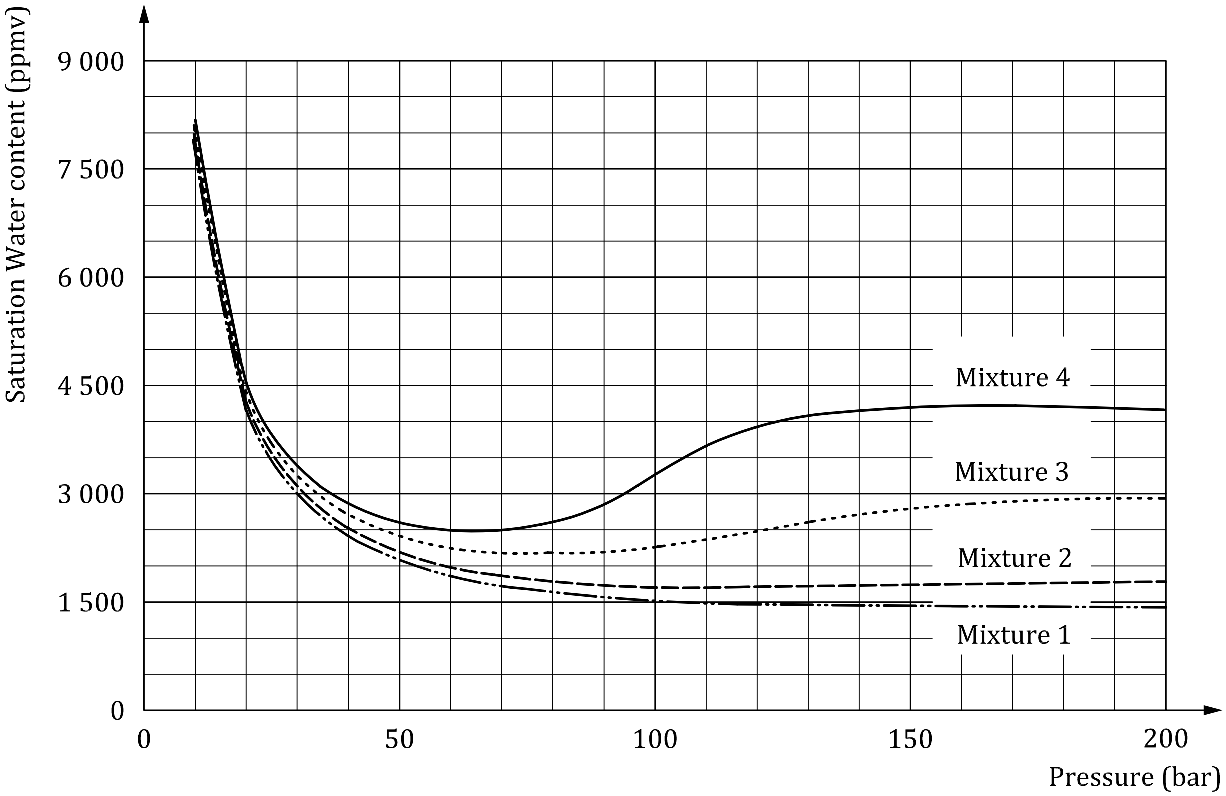
800 MPa (8 000 bar). The EOS was developed with special interest focused on the behaviour of thermal properties in the critical region and extrapolation behaviour of empirical equations of state. It is therefore able to represent thermal properties and speed of sound in the immediate vicinity of the critical point.

Annex B
(informative)

Hydrate formation

Hydrate formation will depend on variables like pressure, temperature, composition and water content.

The water content in the CO_2-rich streams is a function of pressure, temperature and composition. For CO_2-rich streams, mixture behaviour related to water content and pressure will depend on CO_2 content on the mixture, as shown in Figure B.1. The figure presents typical water content profiles with pressure predicted for the mixtures from Table A.1, at 40 °C. It can be seen that CO_2 has a higher water holding capacity than hydrocarbons and that contribution is more pronounced in supercritical conditions.



NOTE See Reference [22].

Figure B.1 — Saturation water content as a function of pressure, at 40 °C

Figure B.2 presents the hydrate stability zones for the Mixtures presented in Table A.1, predicted by the method described in Reference [23]. It can be seen that the CO_2 has an inhibitor effect on the system for pressures higher than 50 bar, since an increase in the CO_2 content shifts the hydrate equilibrium curve toward lower temperatures.

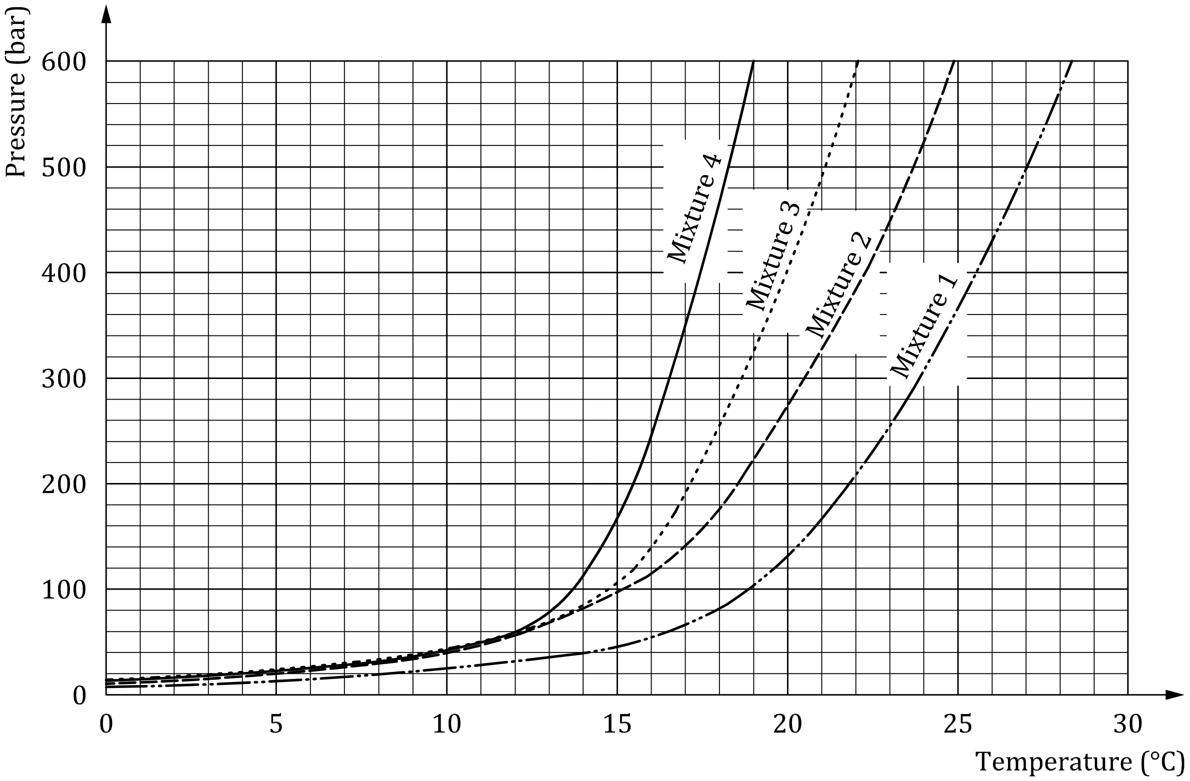
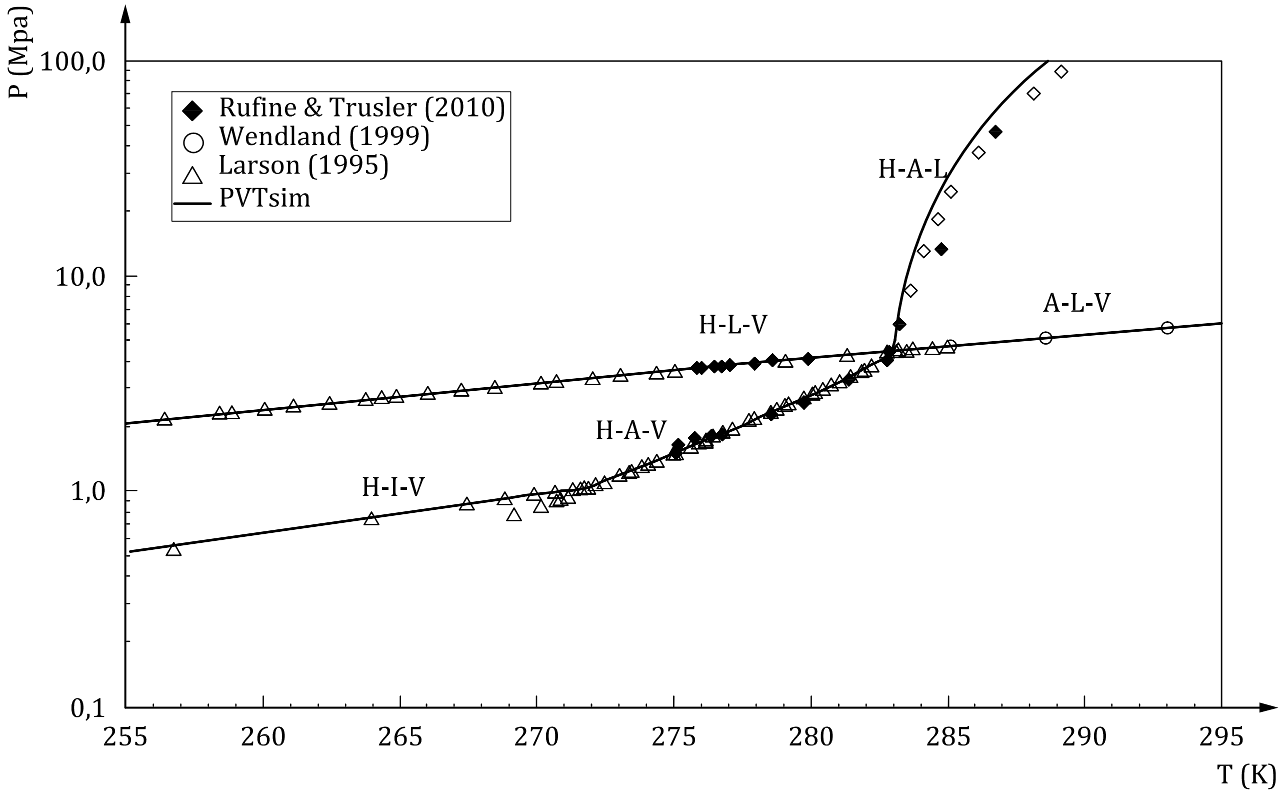


Figure B.2 — Hydrate stability zones for CO_2/HC mixtures

Figure B.3 shows the phase equilibrium curves on a P-T diagram for a CO_2-water binary system against sets of experimental data from the NIST database.[24] The predictions were based on the SRK equation of state and on the Langmuir adsorption model when there were hydrates in the equilibrium. The diagram shows the hydrate phase can exist in equilibrium with free water (aqueous) and liquid CO_2 (liquid), with free water and vapour CO_2 (vapour), with liquid and vapour and with ice (solid water) and vapour. The predictions are in good agreement with experimental data. The presented results are for saturated water systems, but hydrates can form without a free water phase, as in a dehydrated gas.



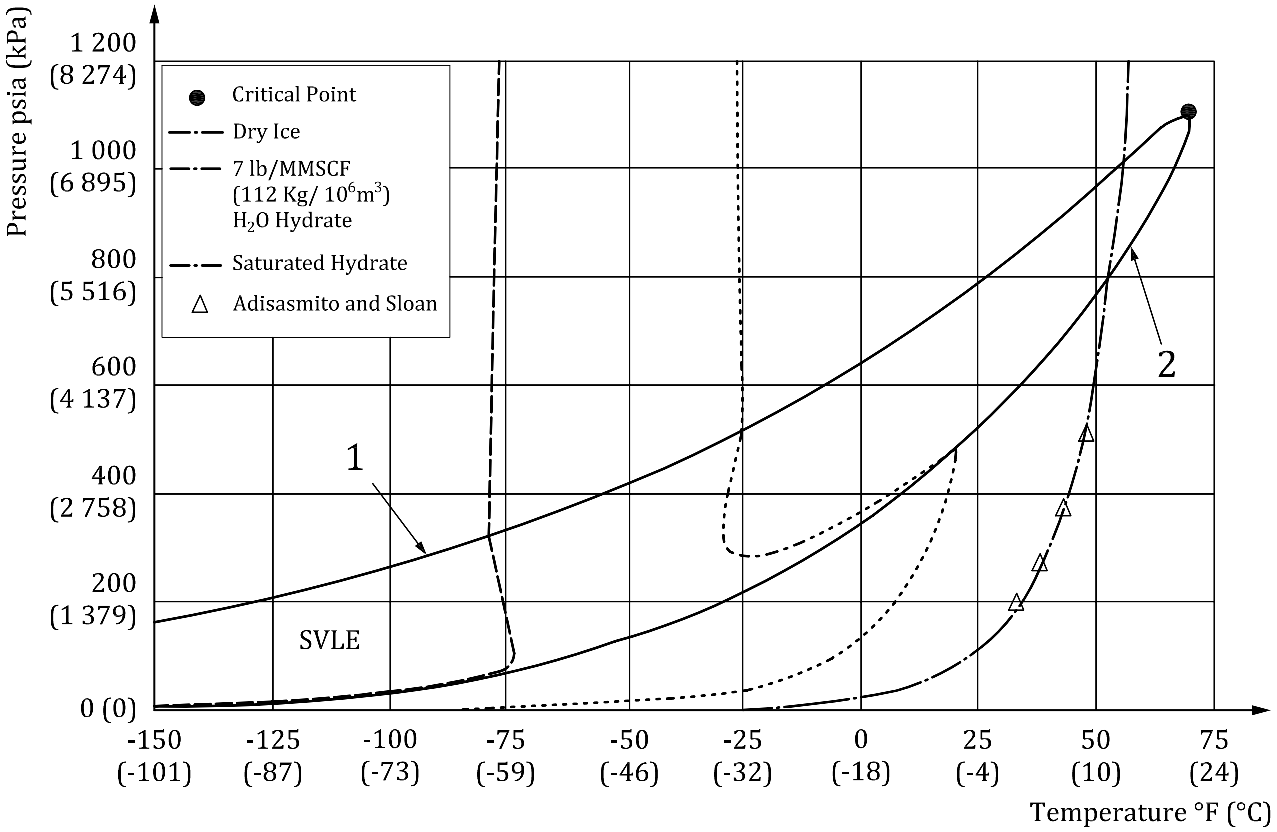
Key

H	hydrate
A	aqueous
V	vapour
L	liquid CO_2
I	ice (solid water)
◆	Rufine and Trusler[25]
○	Wendland et al.[26]
△	Larson[27]
◇	Takenouchi and Kennedy[28]
—	SRK EOS

Figure B.3 — CO_2 — Water phase diagram

As an example, Figure B.4[10] shows the phase diagram for a system containing molar concentrations of 83,15 % CO_2, 12,38 % CH_4, 1,96 % C_2H_6, 1,66 % C_3H_8, 0,37 % i-C_4H_{10} and 0,48 % n-C_4H_{10}. The diagram shows the bubble point and dew point curves (solid line), the hydrate formation curves for water saturated (dash and dot line) and dehydrated system (dot line) with 112 kg/10^6Sm^3 (7 lb/MMSCF), and the dry ice curve (solid CO_2). This solid curve is expected taking into account the high CO_2 content. It can be seen that the dehydrated system needs more severe conditions to form hydrates. Considering for example, an isobaric cooling at 400 psi (2758 kPa), the hydrates formation temperature is around 18 °F (−7,7 °C) for the dehydrated system, while it is close to 44 °F (7 °C) for the water saturated system.

Depending on the content of water and other compounds, multiple temperature zones of incipient hydrate formation at constant pressure can exist. This is particularly true for systems containing high acid gas contents. The issue is even more complex when inhibitors, such as methanol, are present, where the system can form immiscible liquid phases. Though predictions for sub-saturated systems were not experimentally validated, these predictions showed the expected physical behaviour.



Key

1 bubble point

2 dew point

NOTE See Reference [10].

Figure B.4 — Hydrate Equilibrium Curve (Saturated and Sub-Saturated Water Systems)

Annex C
(informative)

Water content specification

To design a dehydration unit, the following parameters should be taken into account:

- For feed gas: all operational envelope i.e. range of composition, operating pressure and operating temperature;
- For each end user of the dehydrated gas (see for example Figure 1): entire operational envelope i.e. range of composition, operating pressure and operating temperature.

The main purpose is to avoid the conditions for hydrate formation and corrosion.

Water content of each stream should be estimated by the following methodology:

- EOS available on commercial simulators;
- based on experiments;
- based on methods described on available references.[29]

Corrections should be applied whenever natural gas has significant amount of acid contaminant.

EXAMPLE More than 5 % of acid gas contaminant at pressures higher than 4,8 MPa.[29]

One method for water content estimative at saturation point is based on weighted average of water contribution of each component of acid gas (CO_2 and H_2S) and is described in Reference [29]. The curves with CO_2 and H_2S water contribution are represented on Figure C.1 and Figure C.2, they are based on binary data for CH_4-CO_2 and CH_4-H_2S, see Formula (C.1):

$$W = y_{\mathrm{HC}} \times W_{\mathrm{HC}} + y_{\mathrm{CO_2}} \times W_{\mathrm{CO_2}} + y_{\mathrm{H_2S}} \times W_{\mathrm{H_2S}} \tag{C.1}$$

where

W is the water content of acid gas, kg/10^6 Sm^3;

y_{HC} is the molar fraction of hydrocarbons (all components except CO_2 and H_2S);

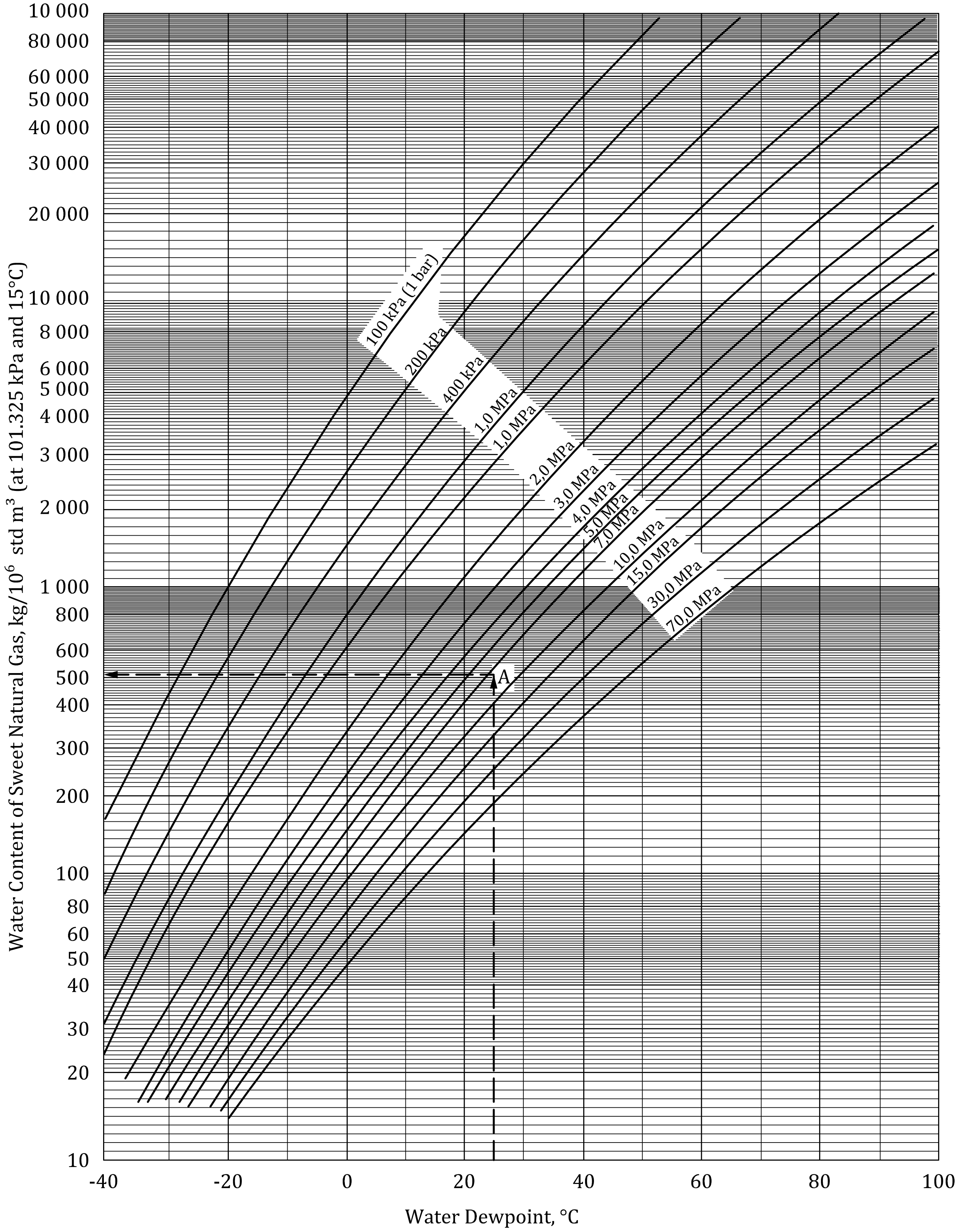
W_{HC} is the water content of sweet gas in kg/10^6 Sm^3 (from Figure C.1);

$y_{\mathrm{CO_2}}$ is the molar fraction of CO_2;

$W_{\mathrm{CO_2}}$ is the CO_2 contribution for water content in gas mixture, kg/10^6 Sm^3 (from Figure C.2);

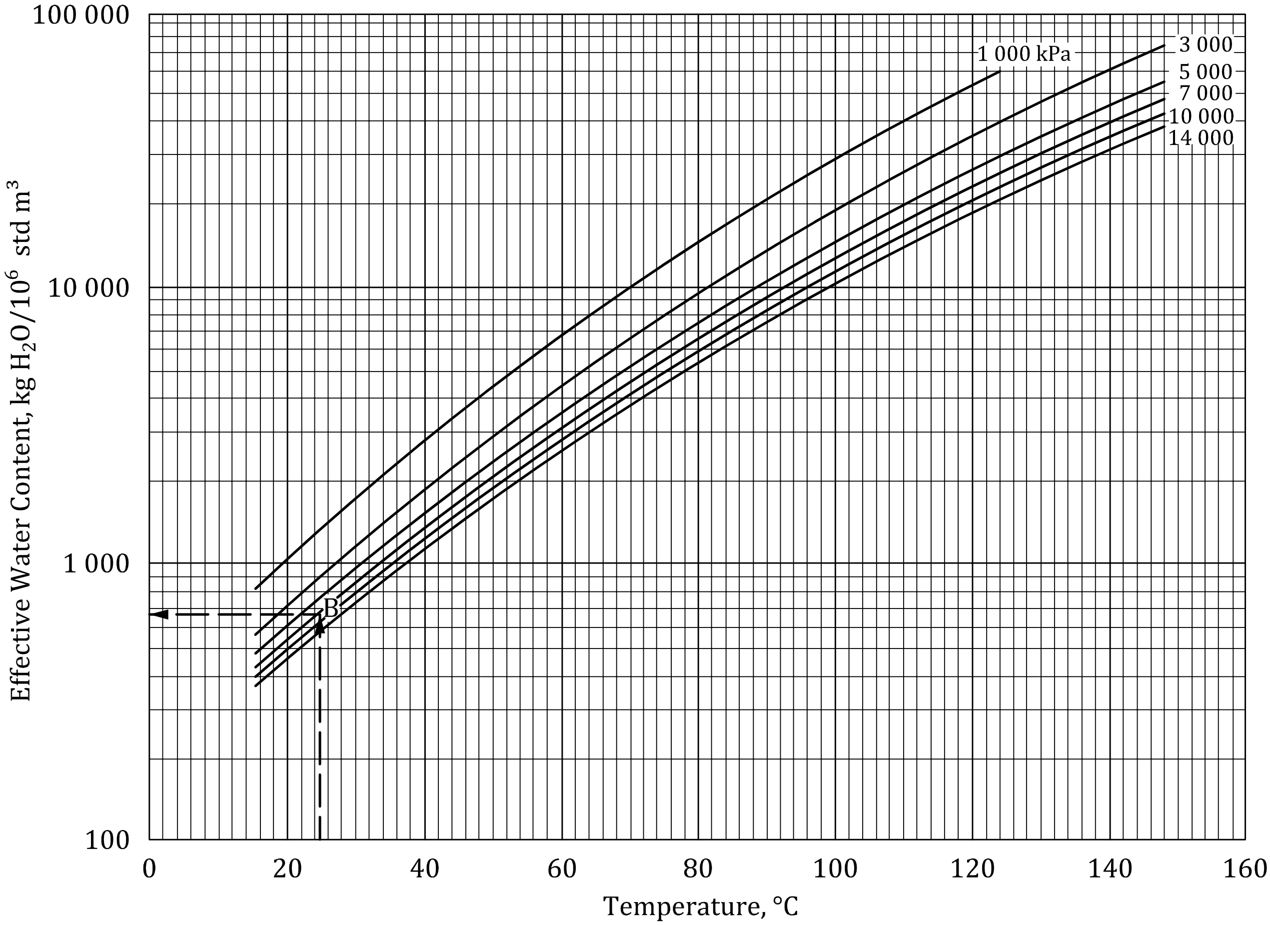
$y_{\mathrm{H_2S}}$ is the molar fraction of H_2S;

$W_{\mathrm{H_2S}}$ is the H_2S contribution for water content in gas mixture, kg/10^6 Sm^3 (from Figure C.3).



NOTE See Reference [29].

Figure C.1 — Water content of sweet gas



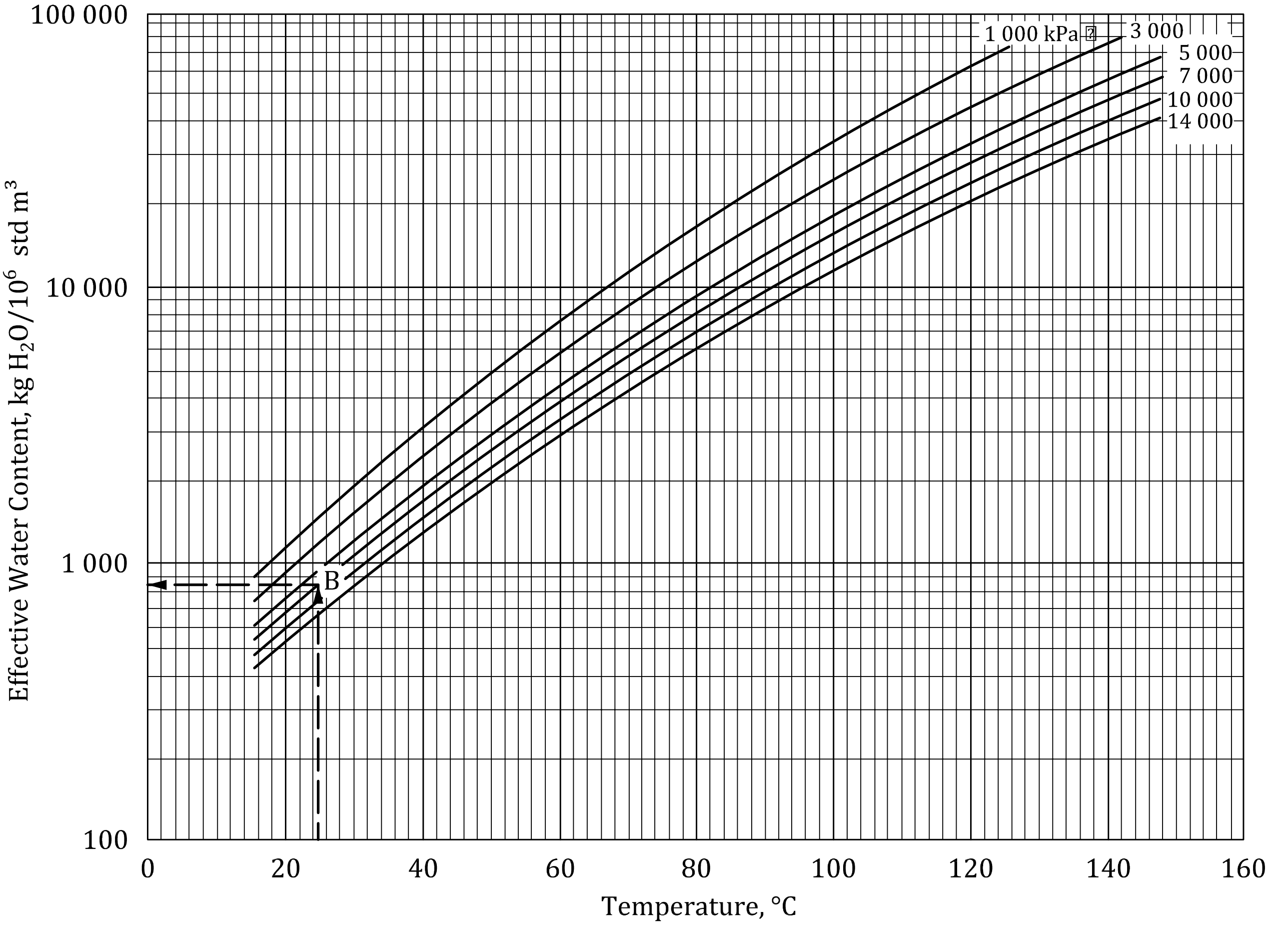
NOTE See Reference [29].

Figure C.2 — Water content contribution of CO_2

Considering the example of a CO_2-rich stream, at the inlet of a dehydration unit, with 40 % of CO_2 and 40 ppmv of H_2S, water saturated. The gas is saturated at 25 °C and a pressure of 7 000 kPa.

Water content is estimated based on the following:

- sweet gas water content from Figure C.1 (point “A”) indicates a value of 520 kg/106 Sm^3;
- CO_2 contribution is 700 kg/106 Sm^3, according to Figure C.2;
- H_2S contribution is 850 kg/106 Sm^3, according to Figure C.3;
- $W = 0{,}599\,6 \times 520 + 0{,}4 \times 700 + 0{,}004 \times 850 = 595$ kg/106 Sm^3.



NOTE See Reference [29].

Figure C.3 — Water content contribution of H_2S

As exposed in the previous example, the presence of CO_2 in natural gas increases water content because of the higher affinity of that contaminant with water.

One second method to estimate sour gas water content assumes that hydrocarbon portion of natural gas is composed of methane and water content retained by CO_2 represents 70 % of the one retained by H_2S at the same conditions.

Formula (C.2) determines the equivalent H_2S fraction:

$$Y_{H_2S,\mathrm{equivalent}} = Y_{H_2S} + 0{,}7 \times Y_{CO_2} \tag{C.2}$$

where

Y_{H_2S} is the mole percentage of H^2S in %mol;

Y_{CO_2} is the mole percentage of CO^2 in %mol.

For the previous example:

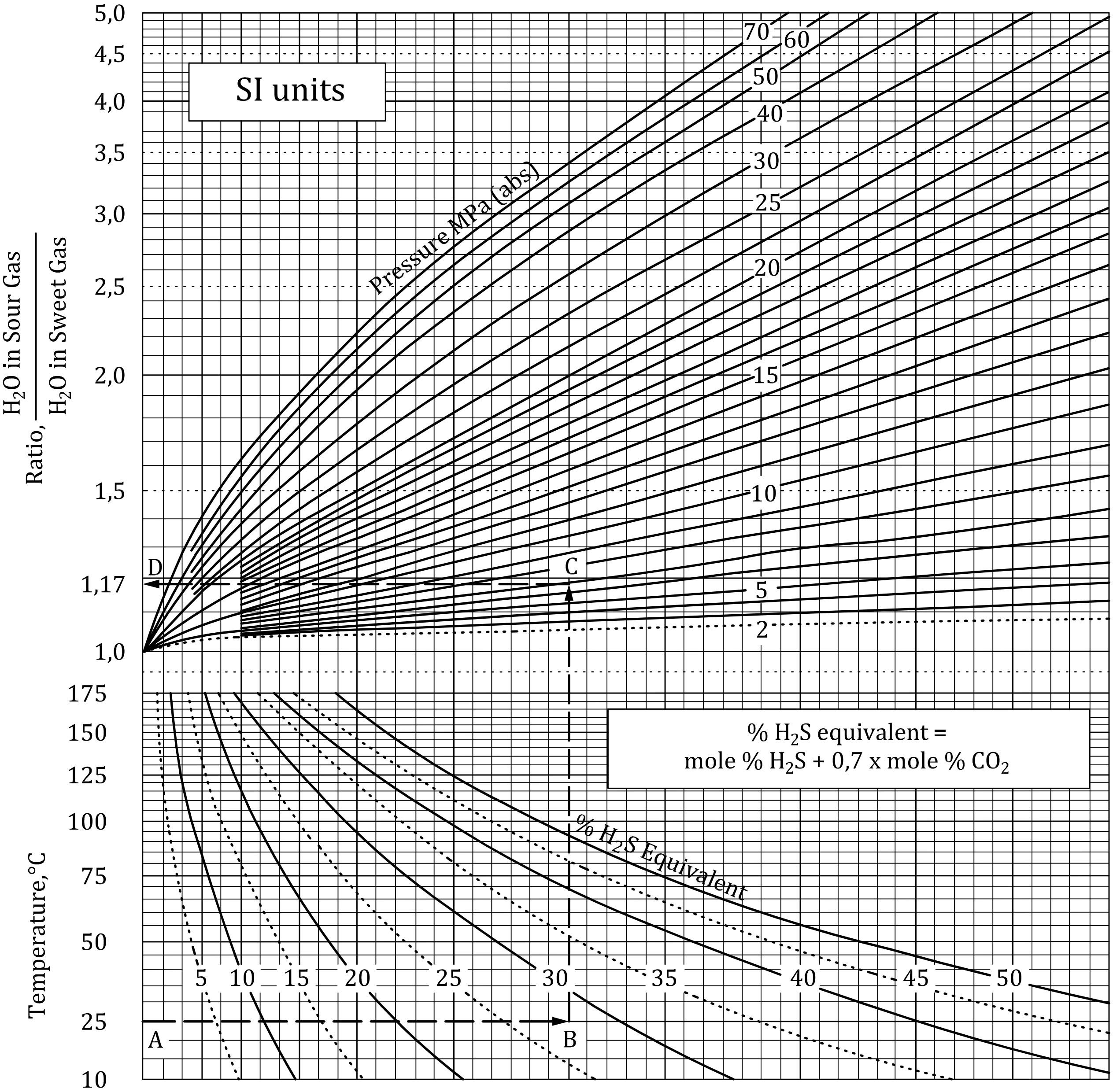
— temperature = 25 °C;

— pressure = 7 000 kPa = 7 Mpa;

- Y_{CO_2} = 40 %;
- Y_{H_2S} = 40 ppmv = 0,004 %;
- $Y_{H_2S,equivalent}$ = 0,004 + 0,7 × 40 = 28,4 %.

In Figure C.4, water content ratio = H_2O in sour gas/H_2O in sweet gas = 1,17 (path ABCD).

Water content of sour gas (40 % CO_2) = 520 × 1,17 = 608 kg/10^6 Sm^3.



NOTE See Reference [30].

Figure C.4 — Water content correction for sour gas

Designer should estimate the required water content for each end user and take the lowest value (the strictest condition). In addition, a safety margin should be applied to take into account unexpected conditions during lifetime. As a first approach, consider a 10 °C margin on final dew point or a factor of 50 % of the required water saturation content.

Some processes alter water content in gas phase and this should also be considered. If a membrane unit is selected to separate a CO_2-rich stream from a hydrocarbon stream, the permeate side will present a substantial increase in water content, due to its high permeability to water. Water content on the permeate side can be as high as 10 times higher than inlet.

Consider the following example of an offshore platform scenario, with high CO_2 produced gas, membrane separation system, gas export, gas injection and CO_2-rich stream injection into the reservoir (Figure 1).

Gas to pipeline:

— CO_2 = 3 %mol;

— P = 250 bar;

— T = 4 °C (minimum);

— Water content = 74 ppmv.

Gas to injection:

— CO_2 = 30 %mol;

— P = 250 bar;

— T = 4 °C (minimum);

— Water content = 100 ppmv.

Gas to injection:

— CO_2 = 3 %mol;

— P = 550 bar;

— T = 4 °C (minimum);

— Water content = 44 ppmv.

Therefore selected water content for Dehydration Unit design should consider the lowest value resulted from previous described analysis. See Table C.1.

Table C.1 — Recommended water content for dehydration unit outlet

Stream	Gas to pipeline 3 %mol of CO_2	CO_2 reach stream to injection, 30 %mol of CO_2	Gas to injection, 3 %mol of CO_2
Water content (ppmv)	74	100	44
Safety Margin for water dew point (%)	50	50	50
water content with Safety Margin (ppmv)	37	50	22
Is it a permeate side of a membrane?	No	Yes	No
Enrichment Factor	1	10	1
Required water content downstream GDU	37	5	22

NOTE 1 Water content with safety margin = (Water content) x (Safety Margin%)/100.

NOTE 2 Enrichment Factor only applies if the stream is a permeate side of a membrane unit for CO_2 removal. If not, Enrichment Factor = 1. It takes into account that gas water content will be increased in the permeate stream by the Enrichment Factor, i.e. Water content in permeate = (water content downstream GDU or upstream membrane unit) x (Enrichment Factor).

NOTE 3 No credit for water content reducing is taken into account for retentate (treated gas) side of the membrane.

NOTE 4 Required water content downstream GDU = (Water content with Safety Margin)/(Enrichment Factor).

For the presented example, the maximum water content for the specification of a dehydration unit should comply with the strictest condition at 5 ppmv.

Annex D
(informative)

Depressuring of CO_2-rich streams

This Annex presents considerations regarding to low temperature observed during CO_2-rich streams depressuring.

Figure D.1 presents the influence of back pressure on temperature downstream letdown pressure device for a stream containing 90 % molar CO_2 and 10 % molar CH_4 at 65 000 kPa and 40 °C, initial conditions, generated by PR EOS. It can be seen that higher backpressure has a positive impact in material selection and in solid formation prevention as well, since higher temperatures downstream relief device are achieved.

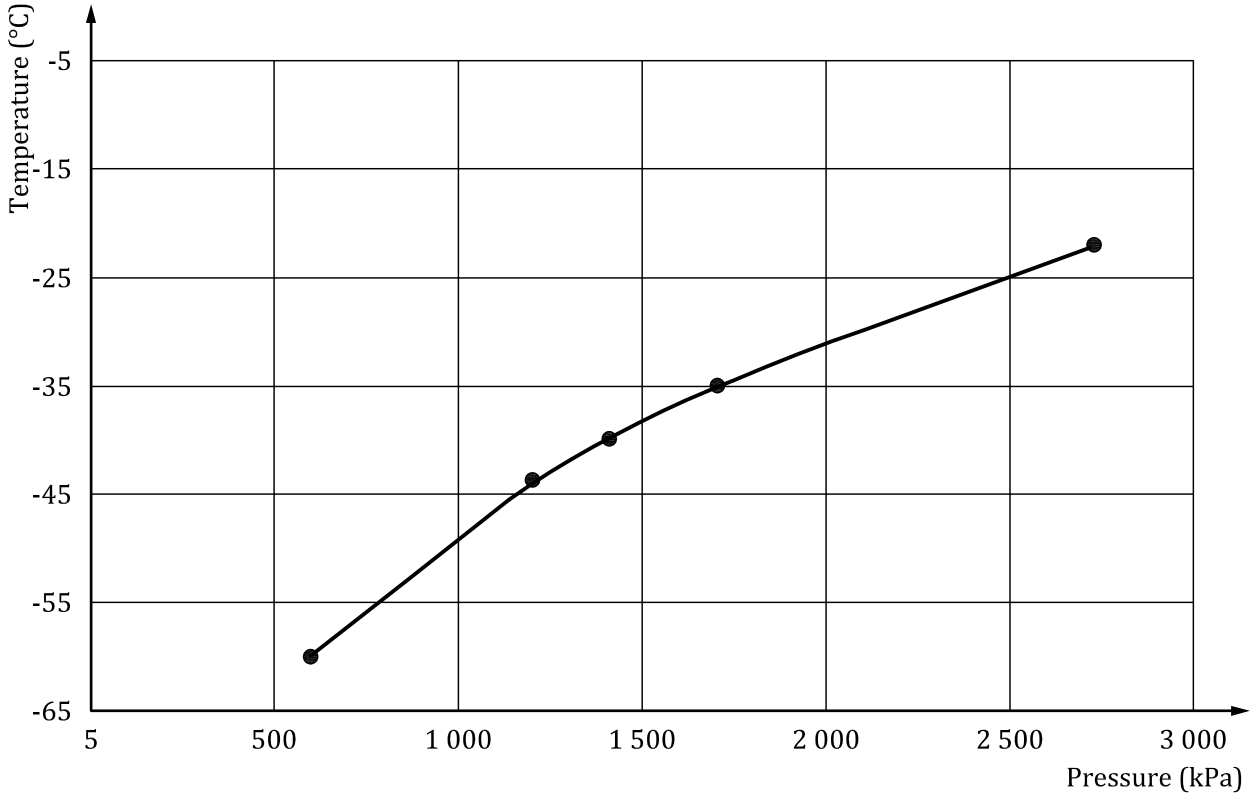


Figure D.1 — Backpressure influence on temperature downstream let-down pressure device

Additionally, Figure D.2 shows the influence of the initial temperature on the final temperature downstream letdown device for a stream containing 90 % molar CO_2 and 10 % molar CH_4 generated by PR EOS. There is no significant differences in achieved downstream temperatures for inlet pressures above 30 000 kPa and initial temperature between 0 °C and 100 °C.

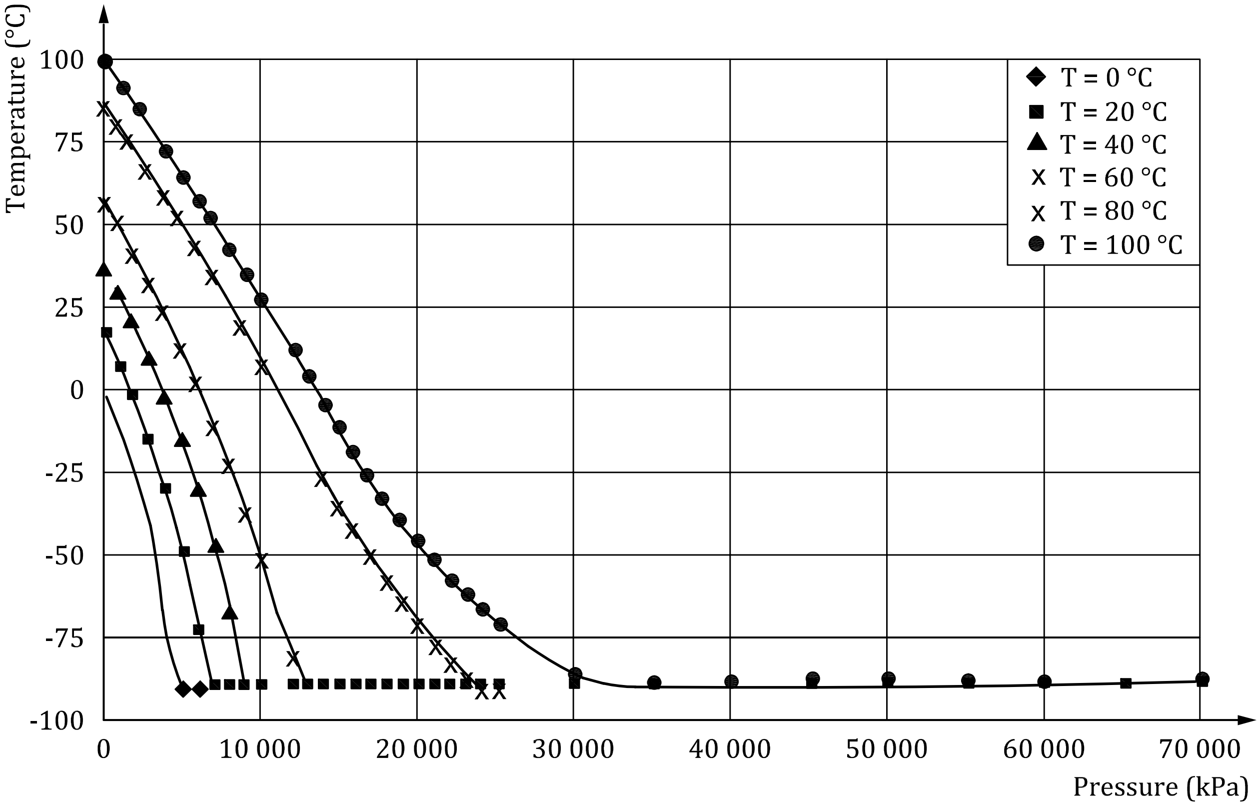


Figure D.2 — Final blow down temperature for different initial temperature and pressure of CO_2-rich stream considering 101,3 kPa backpressure on relief header

Figure D.3 shows that when the process is started from the supercritical state, the mixture can pass through a solid-liquid state, but it is also possible for the mixture to be depressured with no formation of a liquid phase at any time. Final state can be a single vapour phase or a solid-vapour mixture.

On the other hand, for the liquid state initial condition, the system first becomes a liquid-vapour two-phase system for which the Joule-Thomson effect is more pronounced (see Figure D.4). Depending on the cooling effect during the depressuring through the liquid-vapour state, the system can become exclusively vapour or solid-vapour two-phase.

Figure D.3 and Figure D.4 present the phase diagram for binary mixture of CO_2 in CH_4 obtained by PR EOS and experimental data of CO_2 solubility in light hydrocarbons.[10] SVLE represents the locus where all three phases solid-liquid-vapour coexist, whereas frost curve represents boundary between vapour and solid-vapour region and freeze curve represents the boundary of liquid and solid-liquid region.

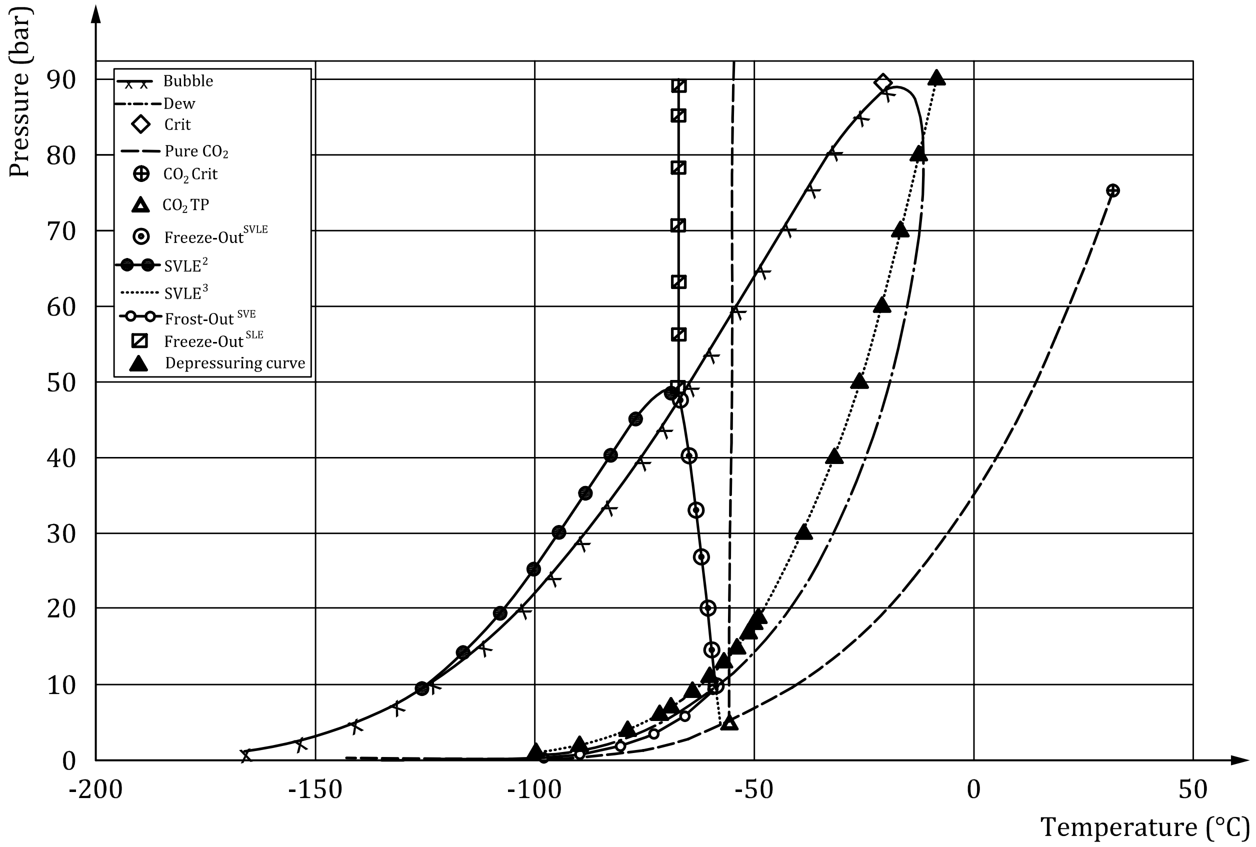


Figure D.3 — Phase diagram and depressuring route for binary mixture 50 % CO_2 and 50 % CH_4 at 65 000 kPa and 40 °C

For instance, when cooling down a system of 50 % CO_2 and balance CH_4 isobarically at pressure 4 140 kPa, the dew point is first encountered at −24,3 °C. The three phase locus is crossed at −64,3 °C and −81,2 °C. Between these temperatures, the system is a solid-vapour system. All liquid that has been formed between the dew point and upper three-phase point has frozen. Below −81,2 °C, the system is in solid-liquid equilibrium until at a lower temperature the entire system solidifies.

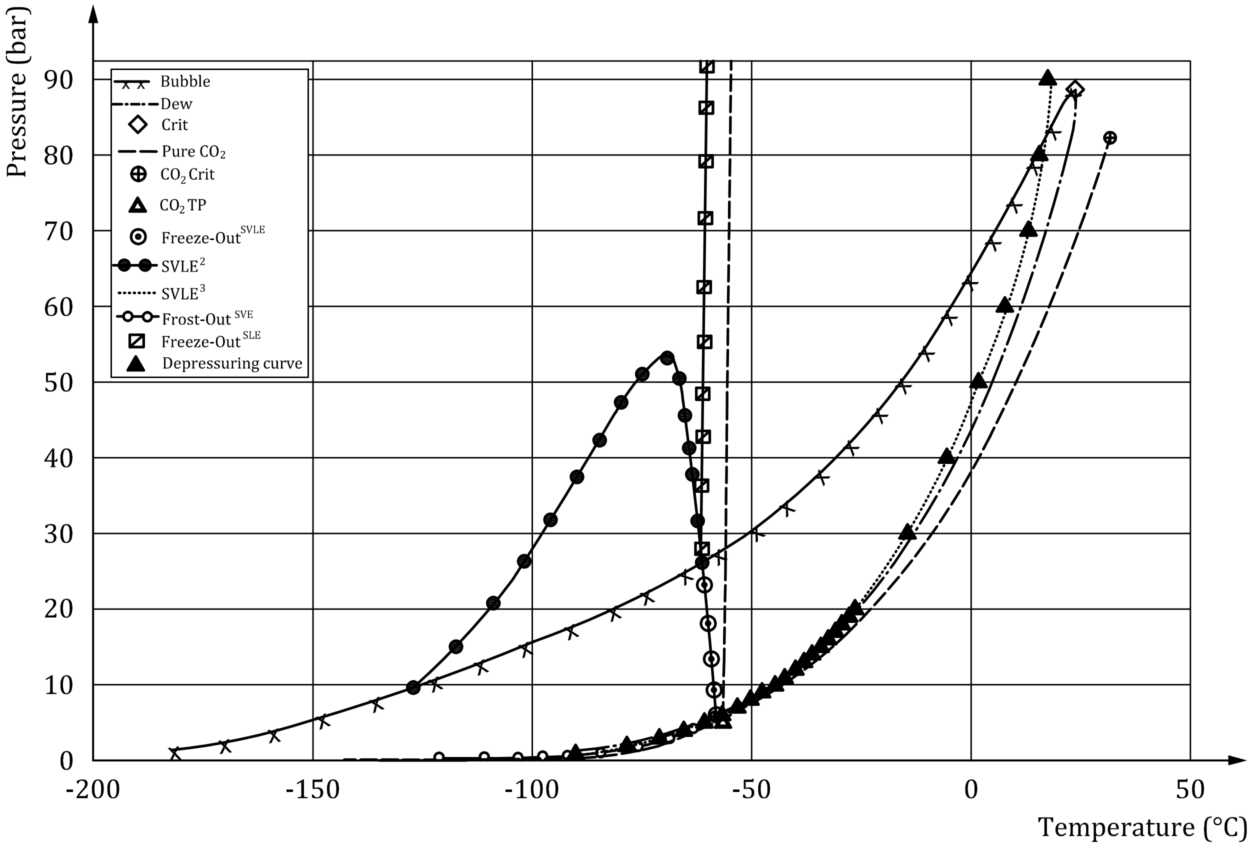


Figure D.4 — Phase diagram and depressuring route for binary mixture 90 % CO_2 and 10 % CH_4 at 65 000 kPa and 40 °C

When depressuring a stream at 65 000 kPa and 40 °C with composition equal compositions of CO_2 and CH_4, the stream is initially in a dense phase. As pressure decreases, the fluid becomes vapour and crosses the dew point curve to start forming a liquid phase. Finally, fluid reaches the 3-phase curve and starts forming a solid phase, at pressure 1 200 kPa and temperature −58 °C.

When depressuring a stream at 65 000kPa and 40 °C with composition 90 % of CO_2 and 10 % CH_4 the stream is initially is likewise in the dense phase. It can be seen that as pressure decreases the fluid becomes a liquid and then stats forming a vapour phase as it crosses the bubble point curve. Finally, it will reach the 3-phase curve and start forming a solid phase, at pressure 600 kPa and temperature −56,8 °C.

For multi-component mixture, the number of degrees of freedom increases, and therefore, the three-phase condition is not restricted to a line but a region on the pressure and temperature diagram. The solubility of CO_2 increases with the increase of ethane content in the mixture of CH_4/C_2H_6/CO_2.[31]

Annex E

(informative)

Configuration of flare and vent systems

Table E.1 indicates the required disposal system type based on the described flow/fluid discharge characteristics.

The first number on “System” column indicates the most applicable disposal system for each case. Any system type indicated may still be used.

Table E.1 — Disposal of carbon dioxide/hydrocarbon mixtures

Net heating value	Pressure header	Duration	Frequency	Flow	System[a]
NHV > 28,1 MJ/Sm^3 NHV > 800 BTU/SCF	high	continuous	operational	large	1,2
	low	continuous	operational	large	2
	high	emergency	operational	large	1,4,2
	low	emergency	operational	large	2,5
	high	continuous	eventual	large	4,1,2
	low	continuous	eventual	large	5,2
	high	emergency	eventual	large	4,1,2
	low	emergency	eventual	large	5,2
	high	continuous	operational	small	1,4,2
	low	continuous	operational	small	2,5
	high	emergency	operational	small	1,4,2
	low	emergency	operational	small	2,5
	high	continuous	eventual	small	1,4,2
	low	continuous	eventual	small	2,5
	high	emergency	eventual	small	4,1,2
	low	emergency	eventual	small	5,2

[a] Refer to net heating value of original process releases:

a) High-velocity tip flare;

b) Low-velocity tip flare;

c) Low-velocity tip gas-assisted flare;

d) High-velocity vent;

e) Low-velocity vent.

Table E.1 *(continued)*

Net heating value	Pressure header	Duration	Frequency	Flow	System[a]
7,5 MJ/Sm^3 < NHV < 28,1 MJ/Sm^3 200 BTU/SCF < NHV < 800 BTU/SCF	high	continuous	operational	large	2
	low	continuous	operational	large	2
	high	emergency	operational	large	2,4
	low	emergency	operational	large	2,5
	high	continuous	eventual	large	4,2
	low	continuous	eventual	large	5,2
	high	emergency	eventual	large	4,2
	low	emergency	eventual	large	5,2
	high	continuous	operational	small	2,4,5
	low	continuous	operational	small	2,5
	high	emergency	operational	small	2,4
	low	emergency	operational	small	2,5
	high	continuous	eventual	small	2,4
	low	continuous	eventual	small	2,5
	high	emergency	eventual	small	4,2
	low	emergency	eventual	small	5,2
NHV < 7,5 MJ/Sm^3 NHV < 200 BTU/SCF	high	continuous	operational	large	3,4
	low	continuous	operational	large	3,5
	high	emergency	operational	large	3,4
	low	emergency	operational	large	3,5
	high	continuous	eventual	large	4,3
	low	continuous	eventual	large	5,3
	high	emergency	eventual	large	4,3
	low	emergency	eventual	large	5,3
	high	continuous	operational	small	5,4,3
	low	continuous	operational	small	3,5
	high	emergency	operational	small	3,4
	low	emergency	operational	small	3,5
	high	continuous	eventual	small	3,4
	low	continuous	eventual	small	3,5
	high	emergency	eventual	small	4,3
	low	emergency	eventual	small	5,3

[a] Refer to net heating value of original process releases:

a) High-velocity tip flare;
b) Low-velocity tip flare;
c) Low-velocity tip gas-assisted flare;
d) High-velocity vent;
e) Low-velocity vent.

- Continuous or emergency duration: reliefs that last more than 15 minutes are considered as continuous duration and those that last less than 15 minutes are considered as emergency;

- Operational or eventual frequency: Operational are disposals that occur due the normal and routine operation of the installations. Non routine or abnormal situations are eventual occurrences;
- Large or small flow rates: flows over 100 000 Sm^3/d are considered as large;
- High or low pressure: the value of 5 psig upstream the flare tip or orifices at outlet of the vent is considered as the boundary between high- and low-pressure systems.

Annex F
(informative)

Boiling liquid expanding vapour explosion (BLEVE)

Boiling Liquid Expanding Vapour Explosion (BLEVE) is an explosion resulting from the failure of a container of liquid at a temperature significantly above its boiling point at normal atmospheric pressure. This rare but extremely catastrophic event can occur when a vessel containing liquid above its normal boiling point fails. It is noteworthy that the BLEVE does not cause the tank rupture. The BLEVE results from the sudden opening of the vessel which stems from flawed materials, fatigue, corrosion, poor manufacture, thermal stresses, pressure stresses, reduction in material strength due to high wall temperatures or external factors. The hazards generated by BLEVE include shock overpressures, high velocity expanding vapour and flashing liquid, fragmentation of the container, release of projectiles and release of the contained fluids.[32]

BLEVE phenomenon can be described by thermodynamics.[33] There does not yet appear to be universal agreement on the answer to the question why BLEVE occurs, but this theory shows that a physical event should occur under certain thermodynamic conditions, and this is likely to be the explanation of BLEVE.

The continuous line ABCD on Figure F.1 shows the behaviour of the substance at a constant temperature and at thermodynamic equilibrium. In the section AB, the substance is a liquid and as the volume it occupies is expanded the pressure falls dramatically and, eventually, reaches the vapour pressure of the liquid at the particular temperature at B. The liquid then starts to evaporate to become a liquid-gas mixture, and the pressure stays constant at the vapour pressure. Eventually it reaches C, where the liquid has been completely converted to gas. The pressure then drops as it is expanded further.

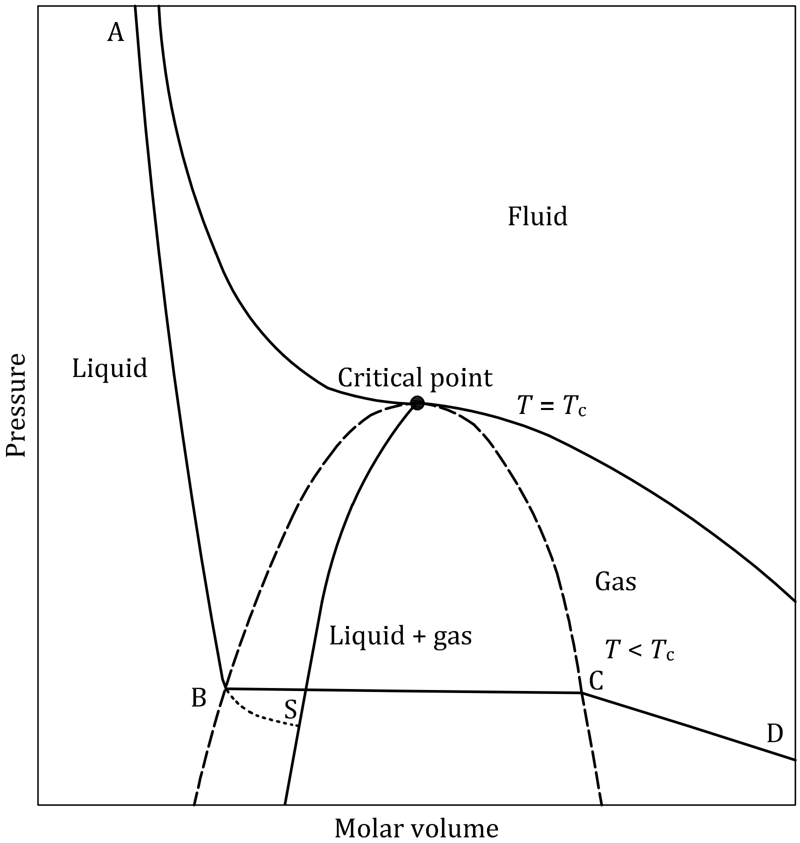


Figure F.1 — Variation of pressure with volume occupied at constant temperature and equilibrium

The variation of pressure with volume occupied at constant temperature and equilibrium is shown as solid lines: the higher at the critical temperature and the lower at a temperature below critical. The metastable situation is the dashed line BS and the spinodal curve is the dotted line.

It states that if the fall in pressure is sufficiently slow, the system moves from the metastable curve BS to the equilibrium curve BC. In the unlikely event that the point S is reached, a special and catastrophic situation arises. S is known as a spinodal point and the slope of the line at this point is zero, i.e. $(\partial p/\partial V)_T = 0$. The dotted line connects these points at different temperatures and is known as the spinodal curve, which ends at the critical point. The special nature of situations represented by points along this curve is that large density fluctuations can occur because of the insensitivity of pressure to volume.

Once the spinodal curve is reached, separation into liquid and gas will rapidly occur. The density variations develop spontaneously into liquid and gas regions. This occurs homogeneously throughout the whole liquid. The rise in pressure to the vapour pressure line BC is not large but it happens at great speed, homogeneously and at the time-scale of molecular motion. The shock to the containing vessel is significant and a BLEVE happens.[29] For a BLEVE to occur, the substance has therefore to find itself on the spinodal curve.

It is therefore possible to calculate the range of temperatures and pressures where the gas or gas mixture would reach this section of the spinodal curve following catastrophic failure. This range is represented by an envelope in temperature pressure space. The right-hand (higher temperature) boundary of this envelope represents temperature-pressure conditions where the entropy equals the critical entropy. To the right of this boundary the entropy will be above the critical entropy and therefore not subject to BLEVE. The critical point will lie on this boundary. The left-hand (lower temperature) boundary of this envelope represents temperature-pressure conditions where the entropy equals the entropy on the spinodal curve at 1 bar. To the left of this boundary the entropy will be below the spinodal entropy at 1 bar and therefore not subject to BLEVE.[33]

Figure F.2 shows the BLEVE envelop for pure CO_2, CH_4 and for two CO_2-rich streams. Dots represent critical points.[30]

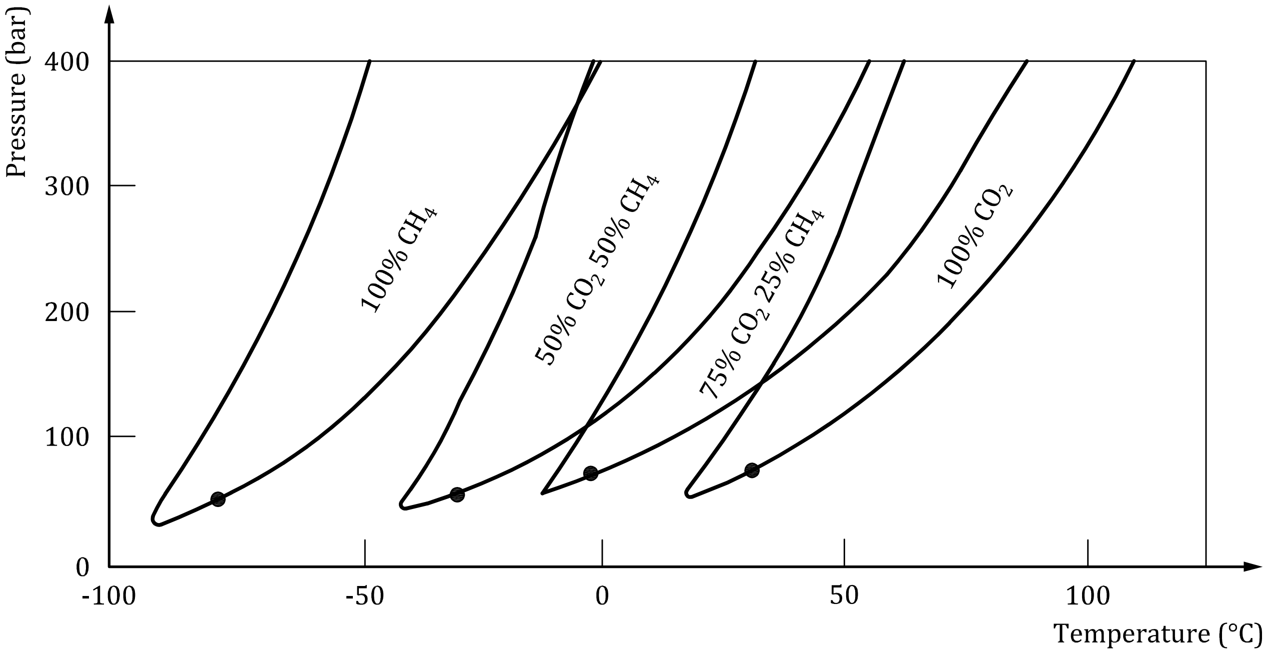


Figure F.2 — BLEVE envelope for pure methane, pure CO_2 and two mixtures of CO_2-rich streams

Annex G
(informative)

Methodology for evaluation of running ductile fracture

G.1 General

The aim of this Annex is to provide guidance for the evaluation of the probability of the propagating ductile fracture. In that case, two models have to be considered: a fracture model and a decompression model.

G.2 Propagating ductile fracture model

G.2.1 Battelle two curve model

One of the most used methods for the calculation of propagating ductile fracture is the Battelle Two Curve Method (BTC). This model combines the properties of the gas decompression, the estimation of a fracture arrest stress and the relationship between stress and fracture velocity. It was calibrated using more than 200 rupture tests in real scale from pipelines made of carbon steel API 5L X65, pressurized with air or pure natural gas. It is also based on a semi-empiric inference of two curves that describe how the fracture velocity and the gas decompression velocity change with the system pressure.

The toughness determination for the fracture interruption happens through an iterative process in order to identify the toughness that at least matches both curves to be tangent. So, this method is used to determine a minimum Charpy energy required to arrest a fracture that starts to propagate. Figure G.1 shows a scheme of this evaluation.

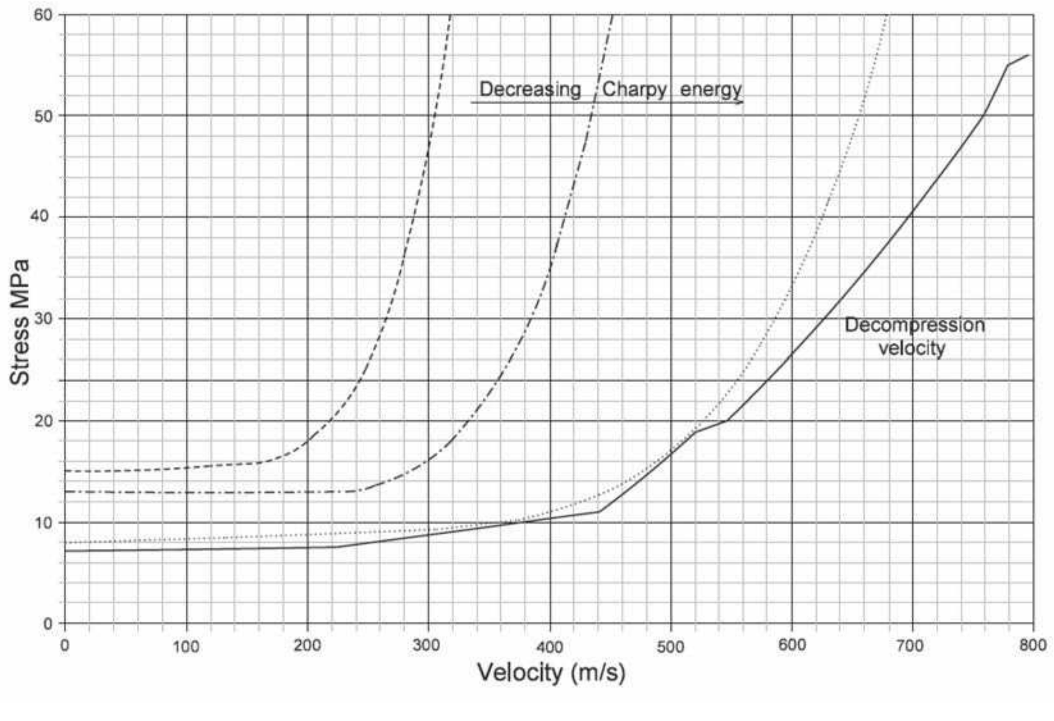


Figure G.1 — Stress–velocity relationship for fracture arrest

It has to be emphasized that this methodology is based on an extensive experimental database that was generated only for natural gas pipelines, and its applicability to CO_2 pipelines is still under investigation in some research projects.

G.2.2 Numerical models

Some numerical models are being developed in order to calculate ductile propagating fractures. It is the responsibility of the user how to apply the results, because at this moment, none of these models are consolidated, neither validated by experimental data.

G.2.3 Limitations of the fracture models

In general, simple fracture models do not consider thermal effects. In addition, they are not validated for a wide range of CO_2 content.

G.3 Decompression model

In order to determine the decompression velocity of CO_2-rich streams, a transient multiphase flow model of the fluid that considers the impact of the thermal exchanges and the friction effects of the decompression is required. This kind of model has to include a suitable EOS.

For CO_2-rich streams, there are only few experimental data for streams of interest and with pressure and temperature used in transportation line. Therefore, the accuracy of this equation for CO_2-rich streams is a critical issue. Originally, the Battelle TMC was proposed using the Benedict-Webb-Rubin-Starling (BWRS) EOS. For pure CO_2 streams Span and Wagner EOS is considered highly accurate, while GERG EOS has been proposed to describe behaviour of CO_2-rich streams. Use of Peng-Robinson EOS for this application has been reported to underestimate saturation pressure, resulting in less conservative facture prediction and control measures.[34]

Finally, it has to be emphasized that this evaluation is developed for transportation lines and this Annex gives an alternative for whom that wants to apply these criteria for piping in production facilities.

Annex H

(informative)

Non-metallic materials for use in CO_2 service

Table H.1 presents non-metallic materials commonly used in rich CO_2 stream applications. Table H.1 can be used for initial orientation purposes only. Any final decision regarding material suitability to any specific scenario should be based on testing and evaluation of specific compositions of the presented groups of materials

Table H.1 — Non-metallic materials commonly used in CO_2 applications

Category	Material type	Recommendation
Thermoplastics	Polytetrafluorethylene (PTFE)	Ageing and RGD evaluation needed for specific scenarios
	Polychlorotrifluorethylene (PCTFE)	
	Vinylidene polyfluoride (PVDF)	
	Polyamide (PA)	
	Polypropylene (PP)	
	Polyetheretherketone (PEEK)	
Elastomers	Hydrogenated nitrile butadiene rubber (HNBR)	Strongly dependent on material composition. Ageing and RGD evaluation needed for specific scenarios
	Fluorelastomer (FKM)	
	Perfluorelastomer (FFKM)	

Annex I
(informative)

CO_2 toxicology information

I.1 General

Carbon dioxide (CO_2, CAS Number 124-38-9) is the fourth most common gas in the earth's atmosphere consisting of roughly 300 ppmv or 0,03 % in volume of the clean air we breathe on a daily basis. CO_2 plays an essential role in the metabolism of the human body, along with being the most common by-product of living organisms. As a result, many individuals who have an occupational exposure to CO_2 believe it to be harmless and neglect to recognize the dangers associated with this toxic gas.

I.2 Toxicological properties of CO_2

CO_2 is commonly thought of as posing a threat to life through asphyxiation when it displaces the oxygen in air down to dangerously low levels. For CO_2 to reduce the oxygen concentration in air down to a level that is immediately dangerous to life, the CO_2 concentration would need to be in the order of 50 % (molar). Evidence shows, however, that CO_2 does create an immediate threat to life at a concentration of only 15 % in air due to the toxicological impact it has on the body when inhaled at this concentration.

In humans, CO_2 is a normal component of blood gases at low concentrations; however, at high exposure inhalation levels it is lethal. In addition, one of the most powerful stimuli known to affect the respiration is CO_2 and these results in humans being very sensitive to changes in CO_2 concentrations. The inhalation of elevated concentrations of CO_2 can increase the acidity of the blood triggering adverse effects on the respiratory, cardiovascular and central nervous systems. Depending on the CO_2 concentration inhaled and exposure duration, toxicological symptoms in humans range from headaches (in the order of 3 % for 1 hour), increased respiratory and heart rate, dizziness, muscle twitching, confusion, unconsciousness, coma and death (in the order of >15 % for 1 min).[35]

At CO_2 concentrations in excess of 50 % in air whether a person dies due to the toxicological effect of CO_2 inhalation or due to oxygen depletion is not clear and arguably immaterial. In both cases, death would be the outcome.

Exposure limits for pure CO_2 given in Table I.1 should be used as reference values for safety risk assessments.

Table I.1 — Acute health effects of high concentrations of CO_2

CO_2 ambient concentration (volume percent)	**Time**	**Effects**
17 – 30	Within 1 minute	Loss of controlled and purposeful activity, unconsciousness, convulsions, coma, death
>10 – 15	1 minute to several minutes	Dizziness, drowsiness, severe muscle twitching, unconsciousness
7 – 10	Few minutes	Unconsciousness, near unconsciousness
	1,5 minutes to 1 hour	Headache, increased heart rate, shortness of breath, dizziness, sweating, rapid breathing
NOTE See Reference [36].		

Table I.1 *(continued)*

CO_2 ambient concentration (volume percent)	Time	Effects
6	1 – 2 minutes	Hearing and visual disturbances
	<16 minutes	Headache, dyspnoea
	Several hours	Tremors
4 – 5	Within a few minutes	Headache, dizziness, increased blood pressure, uncomfortable dyspnoea
3	1 hour	Mild headache, sweating, and dyspnoea at rest
2	Several hours	Headache, dyspnoea upon mild exertion
NOTE See Reference [36].		

I.3 Carbon dioxide exposure limits

Exposure limit concentrations of carbon dioxide for occupational health and safety are often established by work regulations. The concentrations were examined to determine which concentration levels would present the greatest hazard during a worst-case release scenario.

These concentrations are stated in terms of PEL, STEL IDLH. PEL specifies airborne concentration levels under which nearly all workers can be repeatedly exposed without potential adverse effects. The STEL represents the concentration to which workers can be exposed continuously for a short period without suffering from irritation, chronic or irreversible tissue damage, or narcosis of sufficient degree to increase the likelihood of accidental injury, impaired judgment, or materially reduction in work efficiency. See Table I.2.

Table I.2 — Concentrations of concern for carbon dioxide

Exposure limit for carbon dioxide	Ambient CO_2 concentration (25 °C and 1 atm)	Exposure period
OSHA PEL[36]	5 000 ppmv	TWA concentration for 8 hour work day
NIOSH REL[37]	5 000 ppmv	TWA concentration for 10 hour work day during a 40 hour work week
HSE Long-term exposure limit[38]	5 000 ppmv	8 hour TWA reference period
NIOSH STEL[37]	30 000 ppmv	Maximum concentration for 15 minute period (maximum of 4 periods per day with at least 60 minutes between exposure periods)
HSE STEL[38]	15 000 ppmv	15 minute reference period
NIOSH IDLH[37]	40 000 ppmv	The maximum level to which a healthy individual can be exposed to a chemical for 30 minutes and escape without suffering irreversible health effects or impairing symptoms

I.4 Other health effects

I.4.1 Cryogenic burning

According to Annex D, low temperatures can be observed during depressuring of CO_2-rich streams. In these cases, calculated temperatures reached below −56 °C. In these temperatures, contact with the skin without proper protection can cause injuries within seconds because of rapid and profound cooling, leading to localized injury and cellular destruction.

The extent of the injuries caused is determined by the surface area of exposed tissue, the volume of fluid that contacts the skin and the duration of exposure time. Similar to those caused by pure CO_2, injuries can be more severe than those caused by a thermal burn, because the agent penetrates rapidly and deeply through the skin.

I.4.2 Solids aspiration

As discussed in 4.3, CO_2 solids can be formed during releases depending on the temperatures attained. In a release without obstacle, the CO_2 solids would be formed in finely divided particles. Aspiration of these solids would cause internal injuries as described in I.4.1, in addition to the effects described in Table I.1.

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