SCCS

Enabling a multi-user cross-border flexible EU-wide CO_2 transport and storage network: the impact of CO_2 stream impurities.

3rd December 2024

Presentation to SCCS Annual Conference 2024

www.progressive-energy.com

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Introduction to PEL

PROGRESSIVE ENERGY

- A low carbon energy projects company formed in 1998.
- Focused on decarbonising industry using low carbon hydrogen and carbon capture and storage technologies.
- Originator and lead developer on multiple industrial decarbonisation projects

Our projects

- Originator and lead project developer on HyNet.
- Partner alongside Essar UK in the joint venture, Vertex Hydrogen (EET), developing and building the UK’s first large scale, low carbon hydrogen production plant.
- Project management of HyDeploy – the UK’s hydrogen blending project.
- Project management of the Industrial Fuel Switching project which has conducted successful hydrogen demonstrations at Pilkington Glass, Unilever and Kelloggs.
- Originators and project managers of Peak Cluster.
- Leading partner of Grenian is a joint venture green hydrogen production development.
- Part of Bacton Energy Hub.

HyNet North West

ESSAR ENERGY TRANSITION EET

VERTEXHYDROGEN

HyDeploy

HyNet IFS
Industrial Fuel Switching

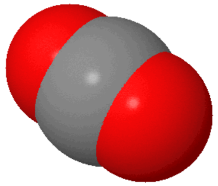
grenian hydrogen

PEAK CLUSTER

1. CO_2 and CO_2 streams
2. Gas phase CO_2 streams
3. Dense phase CO_2 streams
4. CO_2 stream specification
5. Implications for EU Network
6. Further information

1 CO_2 and CO_2 Streams

Pure CO_2



- Discovered by Joseph Black, June 11th 1754.
- Currently about 423ppm in the atmosphere – and rising.
- Does not support combustion (used as a fire suppressant).
- Heavier than air (accumulates in depressions, basements etc.)
- High J-T Coefficient (μ_{JT}): used as a refrigerant gas (R774).
- Reacts with water to form carbonic acid ($CO_2 + H_2O \leftrightarrow H_2CO_3$).
- Exhibits triple-phase behaviour.
  - Triple Point is at -56.6°C and 417barg (4.17MPa)
  - Critical Point is at 31°C and 73.8barg (7.38MPa)

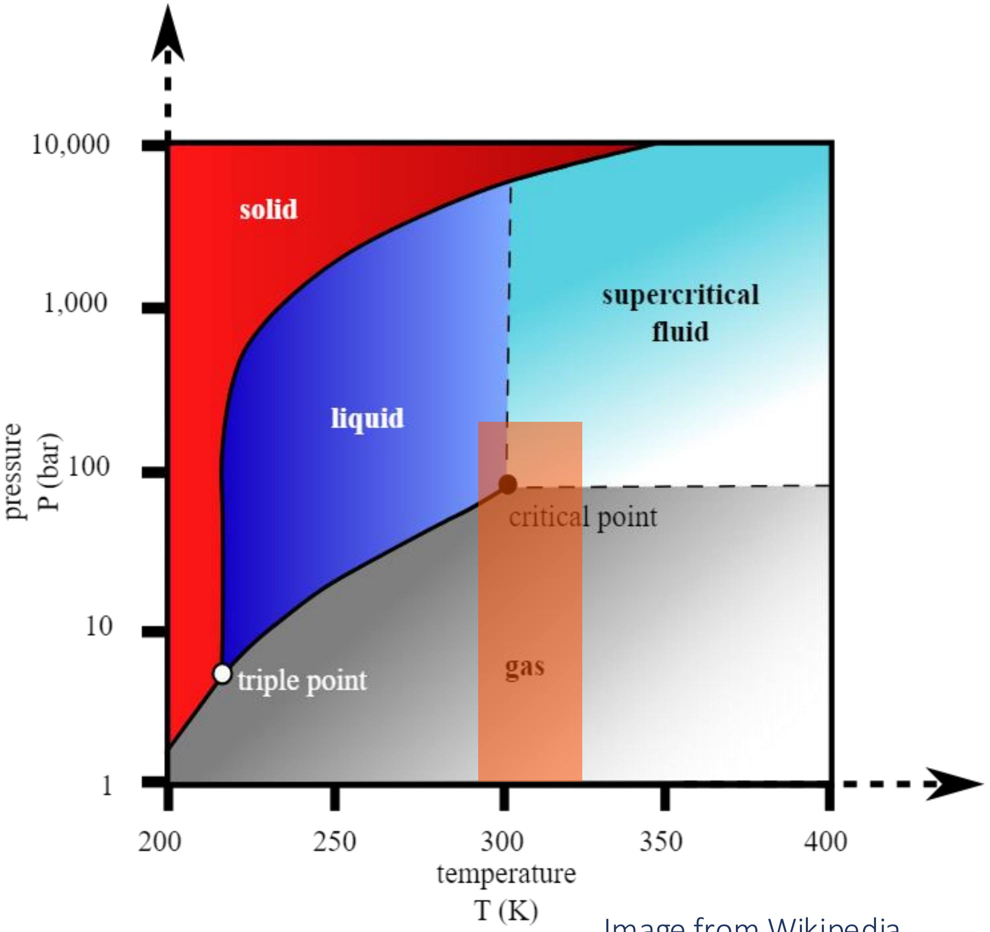
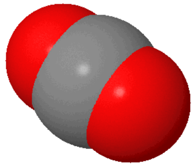
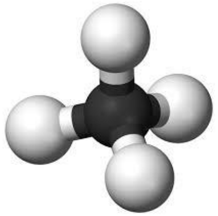


Image from Wikipedia

Note: CO_2 is very different from methane





Property	CO_2	CH_4
Density at NTP (kg/m³)	1.815	0.666
Solubility in water	Good	Poor
Explosive range (vol%)	None	4.4 – 1.7
Melting point at 1bara (°C)	Sublimes at -78.5	-161
Specific Heat Capacity J/g/°C	37.35	2.2
Toxicity	Some	None
Heat of combustion MJ/kg	None	55
kJ/mol	None	-286

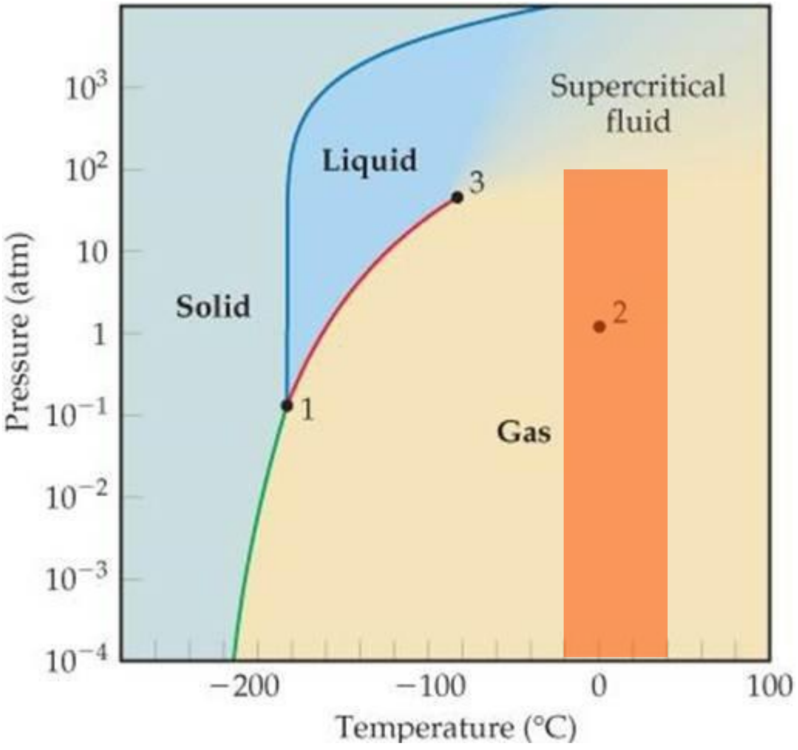


Image: Fabio Breitenschmitzer

Impure CO_2 (CO_2 stream)

- Defined at being "overwhelmingly carbon dioxide" (usually meaning >95mol% CO_2).
- Contains impurities from:
  - The process from which it has been derived.
  - The separation process.
  - Other process-derived impurities.
- Exhibits triple-phase behaviour together with a 2-phase region.
- Liquid and supercritical phase CO_2 streams are referred to as "dense phase", typically with a density of >500kg/m³. This is not a thermodynamic term.
- The Critical Point will vary depending on the impurity content
- The potential exists for the impurities to react with each another.

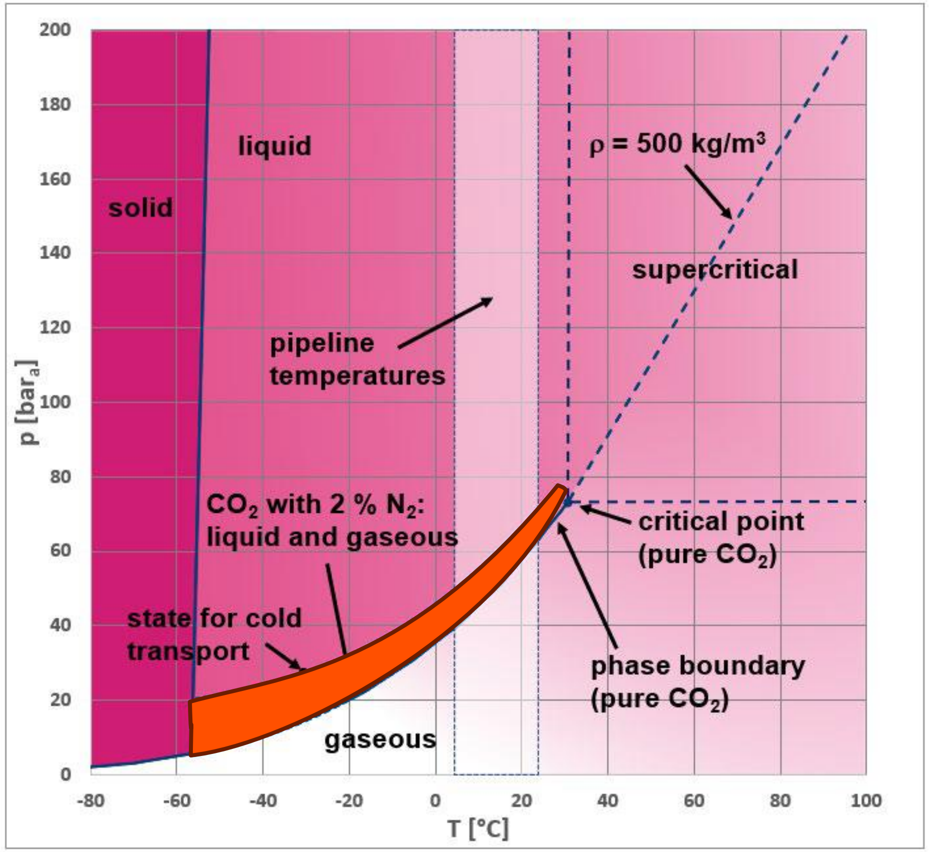


Image from 'European CO_2 Quality', Erfurth, OGE, 02.04.2024

2 Gas phase CO_2 Streams

Transport

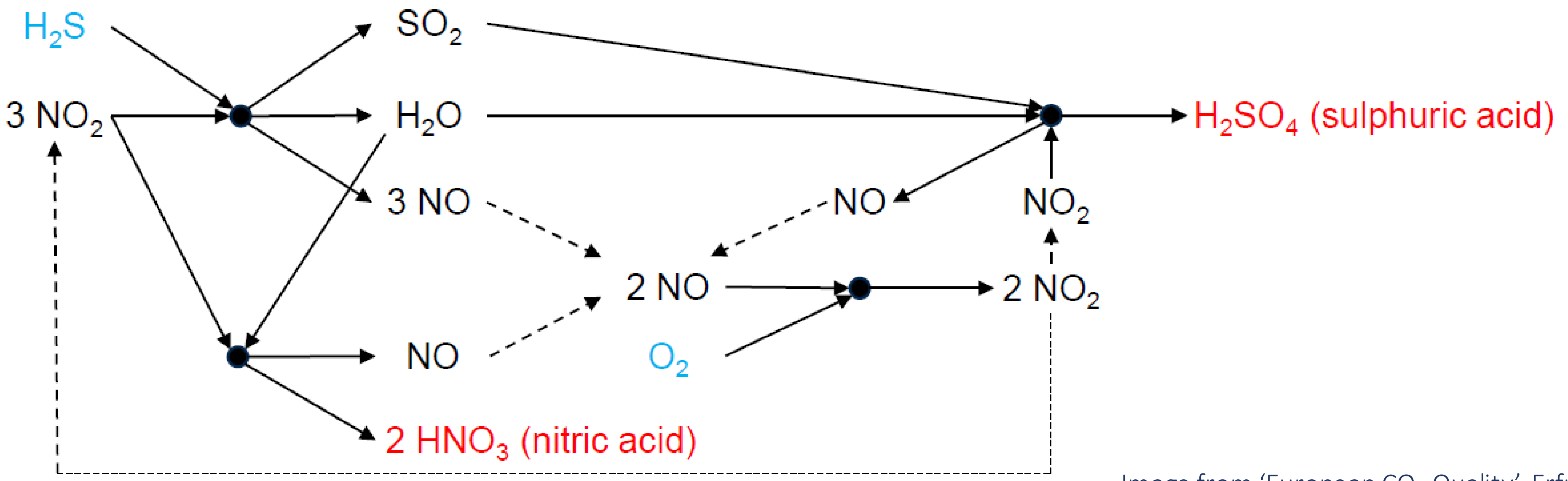
- Pipelines would be the preferred transportation method.
- Temperatures typically in the -5°to 50°C range.
- Pressures generally below 40barg (4MPa), keeping away from the 2-phase region.
- Predictable thermodynamic behaviour.
- Allowable pressure drop and thus pipeline capacity may be constrained by minimum temperature.
- Booster compressors may be needed periodically to recover pipeline pressure losses.
- Large diameter pipelines needed for high mass flows.
- Can offer low pipeline inventory in the event of failure.
- Carbon steel is the preferred material (eg. API 5L Grade X65).

Image from Rti

Image from Wikipedia

Chemistry

- Carbonic acid will corrode carbon steel at up to 10mm/year.
- CO_2 streams from **combustion** (oxidising) processes (eg. cement, lime, waste treatment, CCGTs) may contain NO, NO_2, SO_2, O_2, H_2O.
- CO_2 streams from **reforming** (reducing) processes (eg. 'blue' hydrogen production) may contain H_2, H_2S.
- The nitrogen oxide cycle can take place within a network (simplified four-step reaction mechanism):



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- CO_2 streams from **reforming** (reducing) processes (eg. 'blue' hydrogen production) may contain H_2, H_2S.
- The nitrogen oxide cycle can take place within a network (simplified four-step reaction mechanism).
- Certain impurities in the CO_2 stream can bind water, and thus enable an acidic aqueous phase even if all other impurities are within limit values. One example of this is glycols.

Health and Safety

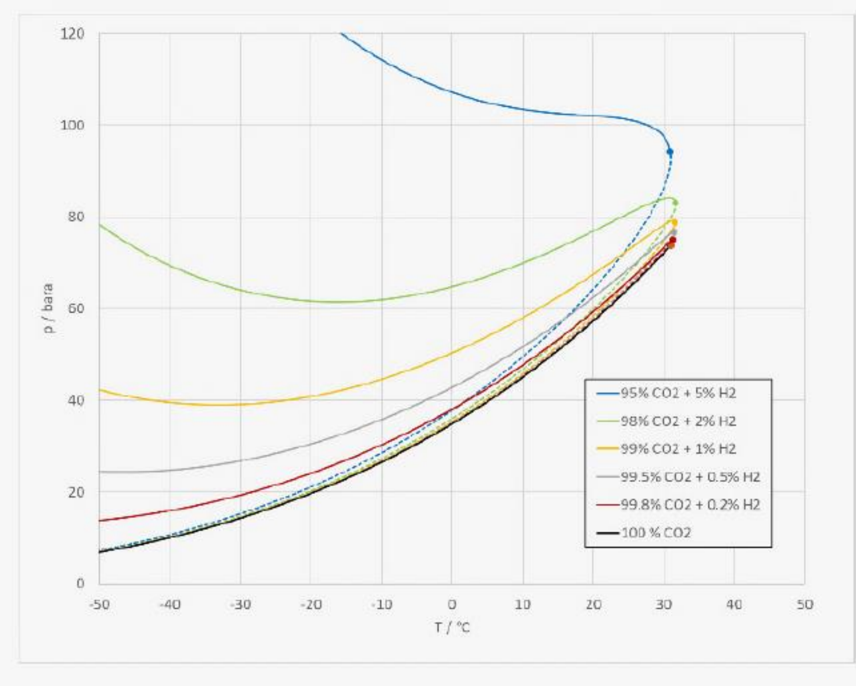
- CO_2 itself is an asphyxiant and exhibits toxic properties at higher concentrations.
- CO_2 streams may contain substances harmful to health (eg. CO, H_2S, COS, CS_2, VOCs, nitrosamines, nitramines).
- Examples:

CO	0.2 mol%
H_2S	5 ppm mol
COS	5 ppm mol
VOCs	48 mg/Nm^3 in total
Nitrosamines & nitramines	3 µg/Nm^3
Dioxins and furans	0.02 ng/Nm^3

3 Dense phase CO_2 Streams

Transport

- Would be the preferred transportation phase for remote pipelines, ships, trucks and rail.
- Temperatures typically in the 0°to 40°C range (down to -55°C for ship transport).
- Pressures generally in the 80 to 150barg (8 to 15MPa), with experience up to 200barg (20MPa)
- Important to keep away from the 2-phase region because of unpredictable thermodynamic behaviour.



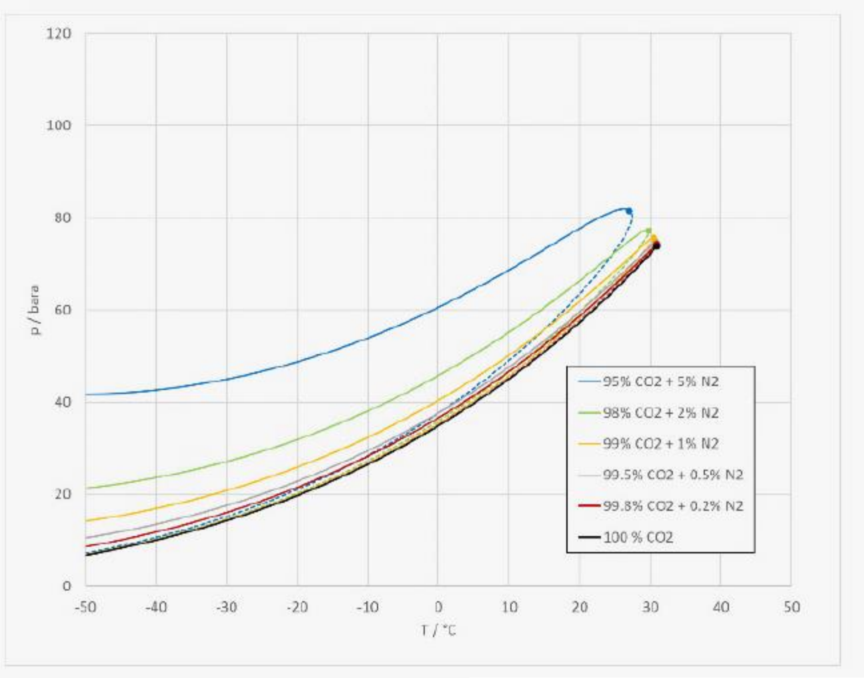


Image from ‘European CO_2 Quality’, Erfurth, OGE, 02.04.2024

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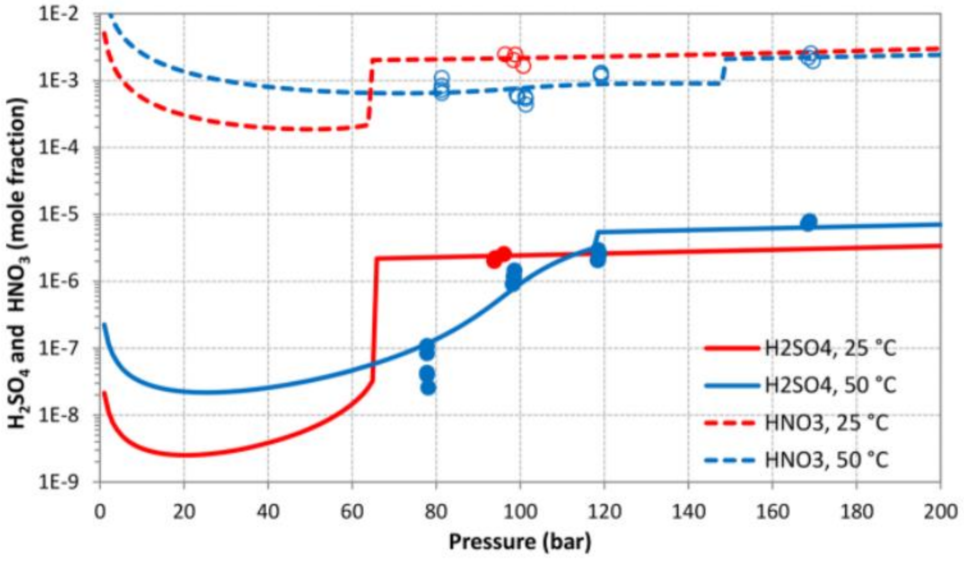
- Pressures generally in the 80 to 150barg (8 to 15MPa), with experience up to 200barg (20MPa)
- Important to keep away from the 2-phase region because of unpredictable thermodynamic behaviour.
- Pipeline failure from Running Fracture is possible.

  NB. Image is from a destructive test.

Image from "SINTEF coupled FE-CFD model for fracture-propagation control in CO_2 pipelines"

Chemistry

- The nitrogen oxide cycle can still take place (simplified four-step reaction mechanism).
- Whilst dense phase CO_2 can hold more water than gas phase,
  - Once the pipeline is depressurised and water in the CO_2 stream will drop out, form carbonic acid and corrode the carbon steel pipeline.
  - Acidic aqueous phases can form well below the saturation level, and can result in corrosion.



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  - Acidic aqueous phases can form well below the saturation level, and can result in corrosion.
- Hydrate formation needs to be avoided.

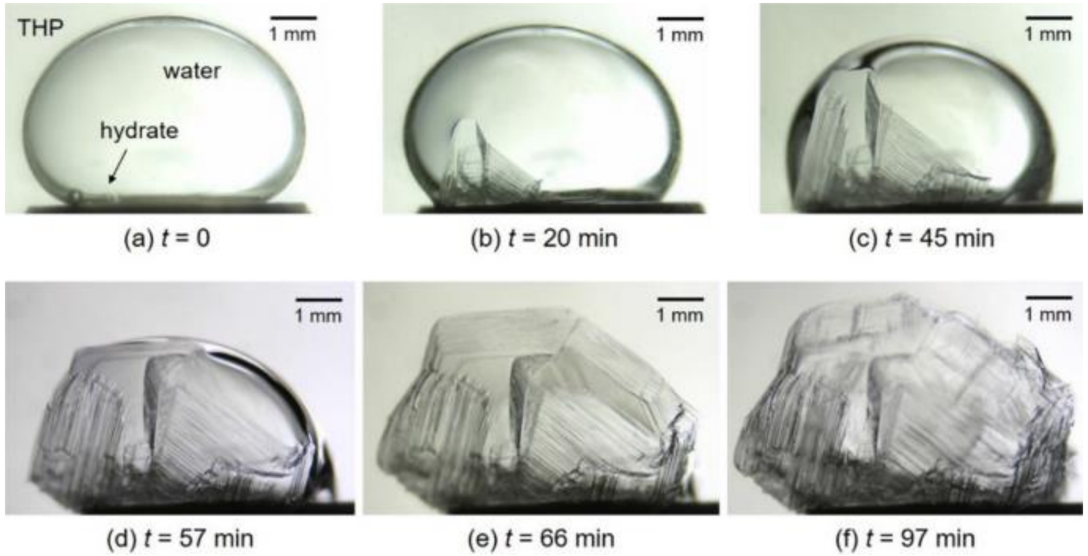

Image from 'Crystal growth of clathrate hydrate formed with H2+CO2 mixed gas and tetrahydropyran' Nature magazine, 21 May 2021

Health and Safety

- Everything described for gas phase CO_2 applies to dense phase.
- Large volumes of gas are involved in the event of a leak, for example, 1m^3 of gaseous CO_2 at 30bar (3MPa) and 10°C will expand isothermally to 37m^3. But 1m^3 of gaseous CO_2 at 130bar (13MPa) and 10°C will expand isothermally to 500m^3. The associated hazards need to be thoroughly understood.

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  - Dispersion modelling:

Image from "Hazard Analysis for Onshore and Offshore Carbon Capture Installations and Pipelines" Energy Institute, April 2024

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  - Dispersion modelling.
  - Sublimation potential.

Site of carbon dioxide pipeline rupture in Satartia, MS in February 2020. Credit: Yazoo County Emergency Management Agency

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  - Dispersion modelling.
  - Sublimation potential.
  - Fog formation.


Photo: NOAA

4 CO_2 stream specification

How to specify the maximum impurity content?

- Pure/food grade CO is expensive to produce.
- CRA pipelines are much too expensive.
- The analogy is plastic waste recycling.

Specification of impurities

- The maximum level of any impurities which have a potential health and safety impact is specified such that the over-riding hazard is that associated with the CO_2 itself.
- Oxygen is specified at the level currently expected by injection operations by petrochemical companies.
- Corrosion potential is limited by specifying levels which:
  - Avoid aqueous phase formation.
  - “Break” the nitrogen oxide cycle.
- The risk of Running Fracture is minimised by limiting the amount of those impurities which reduce the speed of sound in dense phase CO_2 (principally nitrogen).
- Some impurities are currently specified at the limit of detection.
- Some operators may wish to apply additional conservatisms, or, for example have a different perspective on the likelihood of corrosion (cost/benefit).

Specification of impurities: practical issues avoiding chemical effects

The bad guys:

- Water relatively easy to remove, eg. mol sieve (TEG is not suitable)
- NOx difficult to remove from CO_2 stream, relatively easy to remove at source eg. by SCR
- SOx difficult to remove from CO_2 stream, relatively easy to remove at source eg. low S fuel
- H_2S difficult to remove from CO_2 stream, relatively easy to remove at source eg. low S feedstock
- O_2 relatively easy to remove, eg. catalytic reaction with H_2, but expensive, and could lead to H_2 in CO_2

Specification of impurities: practical issues avoiding thermodynamic effects

The bad guys:

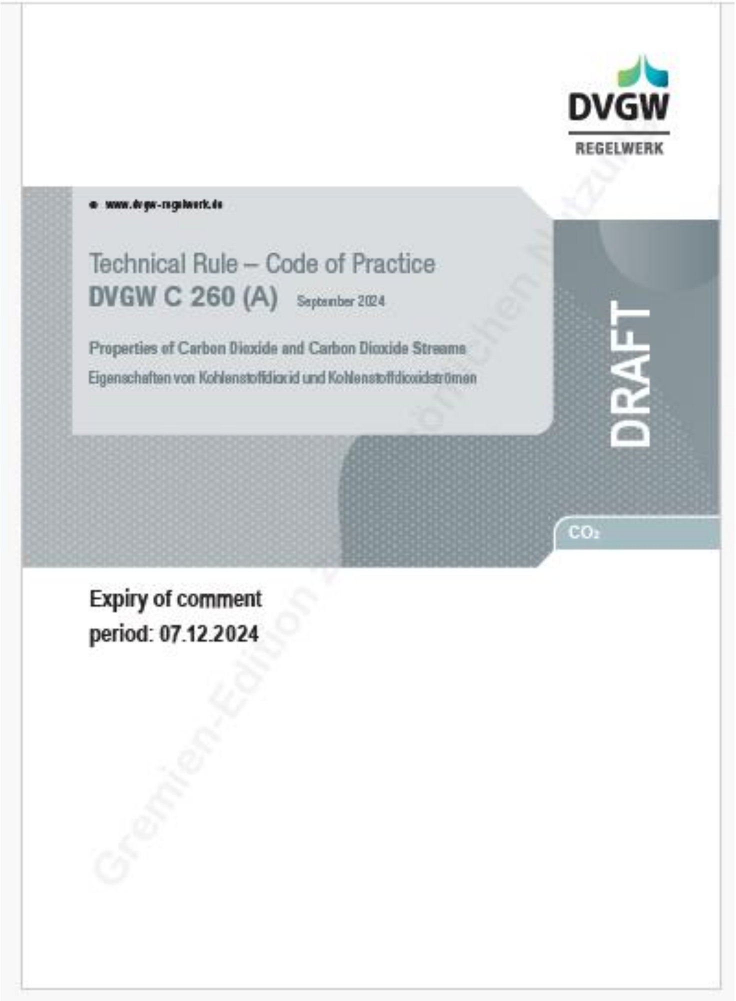
- H_2 relatively easy to remove, eg. catalytic reaction with O_2, but expensive, and leads to more H_2O in CO_2
- N_2 extremely difficult to remove from CO_2 stream, an issue for some combustion projects
- Cost thicker wall pipelines cost more, weigh more, take longer to weld, need heat treatment etc.
- Charpy (tested according to ASTM D6110) limit on toughness of steel

Note: TOUGHNESS is an indication of the capacity of a steel to absorb energy and is dependent on strength as well as ductility. Notch toughness is an indication of the capacity of a steel to absorb energy when a stress concentrator or notch is present.

5 Implications for EU Network

A trans-Europe CO_2 impurity specification

- Pipelines will cross national boundaries.
- An EU-wide infrastructure will need a single impurity specification.
- Inputs to the infrastructure will be from many diverse sources.
- Relatively little storage is available within the EU. Options include:
  - Export by ship and pipeline to Norway
  - Export by pipeline (or ship) to UK stores in North Sea
- DVGW has assembled a team of experts and produced a CO_2 stream specification for Germany
- This is being used as a basis for a CEN Standard (under TC 474)



"Potential CO2 transport network in 2050 according to scenario C1", from 'European Commission, Joint Research Center, Tumara, D., Uihlein, A. and Hidalgo Gonzalez, I., Shaping the future CO2 transport network for Europe, Publications Office of the European Union, Luxembourg, 2024, https://data.europa.eu/doi/10.2760/582433, JRC136709.

6 Further information

Further reading:

- Good Plant Design for Offshore and Onshore Carbon Capture Facilities and Pipelines, Second Edition, April 2024, available from the Energy Institute
- Hazard Analysis for Onshore and Offshore Carbon Capture Installations and Pipelines, Second Edition, April 2024, available from the Energy Institute
- "CO2CKTAILS IN A PIPELINE': THE PHASE BEHAVIOUR OF CO_2 WITH >20 IMPURITIES ", June 2021 Eduardo Luna-Ortiz, TCCS-11 - Trondheim Conference on CO2 Capture, Transport and Storage, Trondheim, Norway - June 21-23, 2021
- ISO 27913:24 "Carbon dioxide capture, transportation and geological storage – Pipeline transportation systems" October 24th 2024

Thank you

Any questions?

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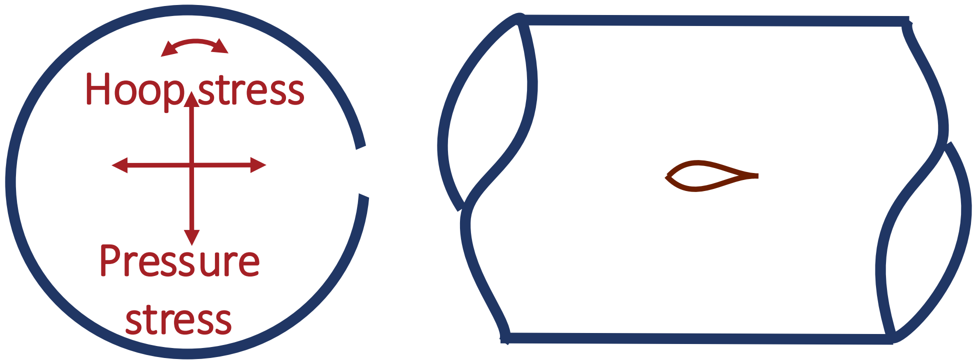
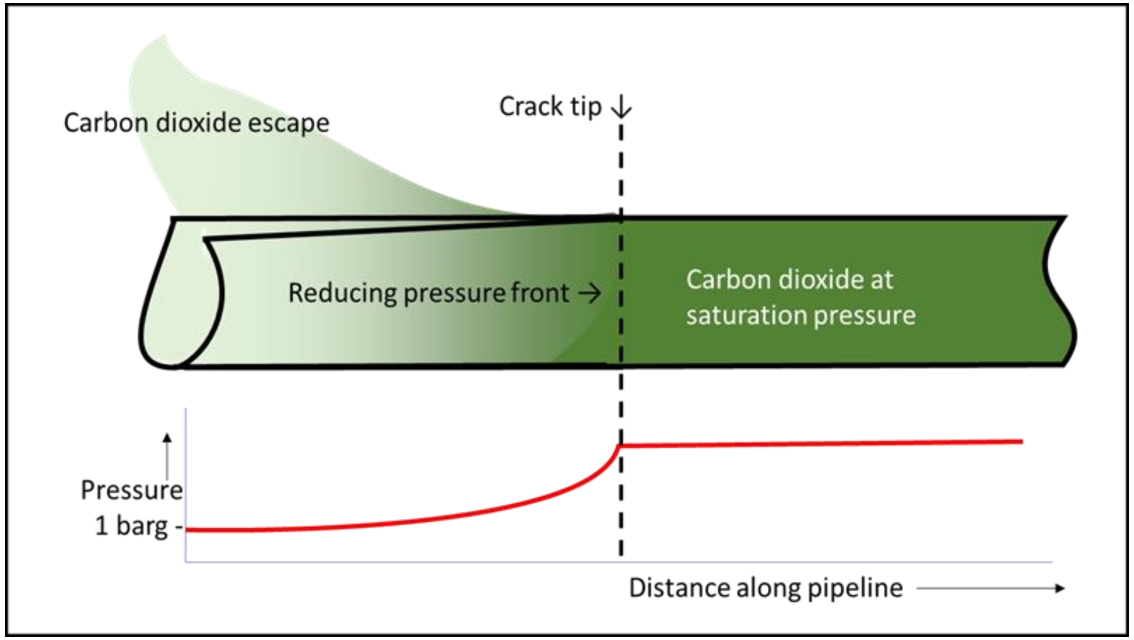
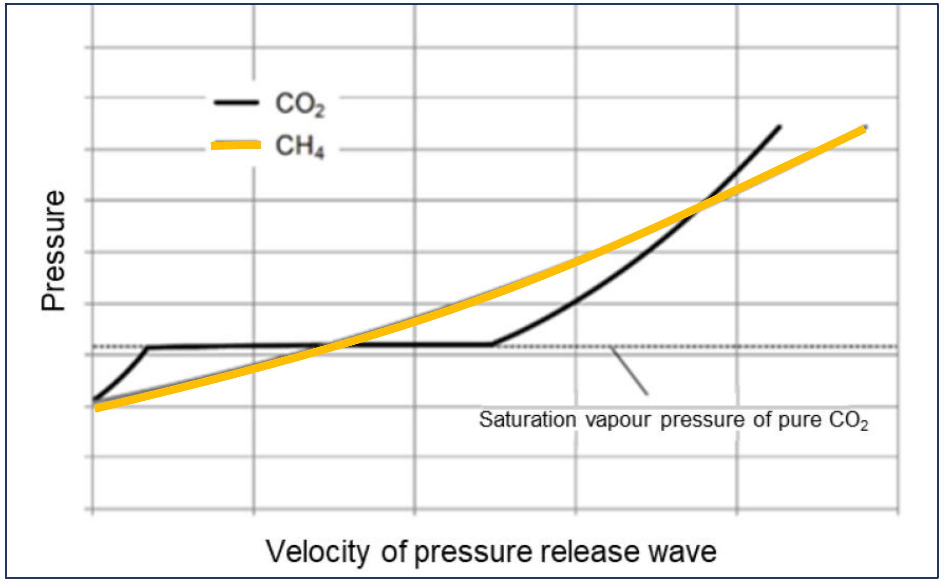
Running Fracture







Specification of impurities: principles

a) recognise that >95 mol % CO_2 in the stream is widely used industry practice;

b) recognise that the combined non-condensable content of <5 mol % is the industry practice with H_2, O_2, N_2, CH_4, Ar and CO being potential contributors;

c) set the specification such that, and with sufficient margin, hydrates or an aqueous phase are never present during any operational scenario, including transient operations (e.g., depressurisation, restart, etc.), which although infrequent and temporary will dictate the most onerous pressure/temperature conditions

d) ensure that impacts of all impurities in the CO_2 stream at all operational conditions are considered, when determining the maximum value of the saturation pressure. The minimum operation pressure shall be above the saturation pressure for that stream within the operating envelope for dense phase transport;

e) consider the impact of lighter impurity components on a refrigerated CO_2 stream, because they will remain in gaseous state when the CO_2 stream is liquid;

f) take into consideration the impact of lighter components on the potential for running ductile fracture of pipelines carrying a CO_2 stream in dense phase;

g) ensure that the impact of the level of H_2 on hydrogen-enhanced crack propagation behaviour is considered, and an increased mole-fraction of H_2 in the gas phase, and that sufficient margin to crack growth exists;

h) in the event of a release of CO_2 stream, ensure that the local hazard associated by any single impurity, is always lower, and with sufficient margin, than the hazard associated with the CO_2 itself;

i) note that during depressurization from dense phase the concentration of an impurity in the released CO_2 stream can be different due to lighter components being released from that in the original fluid, which can result in a more corrosive mixture remaining in the pipeline;

j) where there is a release to the environment, the specific hazards associated the liquid or solid phases of the components of the CO_2 stream shall be considered;

k) where an impurity might accumulate anywhere in the CCS/CCU chain, the hazard associated with this accumulation shall be considered;

l) consider the corrosion risk of induced aqueous phases in the specification for hygroscopic components that could be present as liquids in a gaseous CO_2 stream, such as glycols, amines, and methanol;

m) consider the corrosion risk in the specification for polar light components that could impact the corrosivity of an aqueous phase induced by a hygroscopic impurity;

n) note that there are possible chemical reactions within the CO_2 stream, both between the impurities and the CO_2 and between the impurities themselves. The potential impact(s) of consequential products shall be considered;

o) employ measures at source to eliminate liquids that might accumulate in a gaseous CO_2 stream and prevent the subsequent build-up of liquid in the pipeline and downstream equipment

p) keep to a practical minimum the presence of solids in a CO_2 stream;

q) consider the impact of solid particles within the CO_2 stream on equipment, e.g. and on the injection reservoir itself (if appropriate).

From ISO 27913:2024

Component	Hazard(s) in a CCS context	Units	Limit
CO_2	Asphyxiation and can acts as a toxicant at high concentrations	mol%	> 95.0
N_2 [a]	Enhances the potential for ductile fracture Occupies store pore space inefficiently	mol%	≤4.0
H_2 [a, b, c]	Enhances the potential for ductile fracture Affects the size of the multi-phase zone	mol%	≤1.0
Ar [a]	Occupies store pore space inefficiently	mol%	≤4.0
CO [a]	Health and Safety: Toxic gas	mol%	≤0.2
Methane [a]	Occupies store pore space inefficiently	mol%	≤4.0
Ethane [a]	Occupies store pore space inefficiently	mol%	≤4.0
Propane & Other Aliphatic Hydrocarbons [d]	Liquid drop-out is possible	mol%	≤0.15 in total
H_2O	Enables corrosion of carbon steel	ppm mol	≤50
O_2 [b, e]	Enables oxidation of carbon steel Enhances bacterial growth in storage strata	ppm mol	≤10
NOx (NO, NO_2) [f]	Degradation of store caprock Takes place in the production of nitric and sulfuric acid	ppm mol	≤10
SOx (SO, SO_2, SO_3) [g]	Degradation of store caprock Reactions with NO_2 can produce sulfuric acid	ppm mol	≤10
H_2S [h]	Health and Safety: Toxic gas with foul odour	ppm mol	≤5
COS	Health and Safety: Toxic gas with foul odour	ppm mol	≤100
CS_2	Health and Safety: Toxic gas with foul odour	ppm mol	≤20
NH_3	Can react to form solid ammonium carbamate	ppm mol	≤10
BTEX [i]	Health and Safety: Toxic	ppm mol	≤15 in total
Methanol	Can introduce a liquid corrosive phase	ppm mol	≤350
Solid Particulates [j, k]	Can reduce store permeability Damage to compressor components	mg/Nm^3	≤1 in total
Toxic Metal [j]	Health and Safety: Toxic	mg/Nm^3	≤0.15
VOCs [l]	Health and Safety: Toxic	mg/Nm^3	≤48 in total
Acid Forming Compounds [m]	Enables corrosion of carbon steel	mg/Nm^3	≤150 in total
Amines [n, o]	Can introduce a liquid corrosive phase	ppb mol	≤100 in total
Glycols [p]	Enables aqueous corrosion of carbon steel		NIL
Nitrosamines and Nitramines [q]	Health and Safety: Bio-toxic	$\mu g/Nm^3$	≤3 in total
Naphthalene	Health and Safety: Toxic	ppb mol	≤100
Dioxins and Furans [r]	Health and Safety: Toxic	ng/Nm^3	≤0.02 in total

Component	Notes	Units	Limit
CO_2	Dry basis	mol%	> 95,0
N_2	Total non-condensables to be < 5 mol%	mol%	See Notes.
H_2		mol%	≤ 1
Ar		mol%	See Notes.
CO		mol%	≤ 0,7
Methane		mol%	
Ethane		mol%	
Propane & Other Aliphatic Hydrocarbons	Total hydrocarbons to be < 5 mol% and a dewpoint of product with respect to hydrocarbons to be < -20 °C.	mol%	≤ 1
H_2O	The limit for water may be higher (eg.630 ppm mol) if the CO_2 stream contains vary low levels of O_2, NOx and SOx (eg. geological CO_2). See also NOTE 2.	ppm mol	≤ 630
O_2		ppm mol	≤ 10
NO_x (NO, NO_2)		ppm mol	≤ 1,5
SO_x (SO, SO_2, SO_3)		ppm mol	≤ 1
H_2S		ppm mol	≤ 55
Total sulphur		ppm mol	≤ 50
Solid Particulates		ppm wt	≤ 1
Mercury		ng/l	≤ 5
Amines		ppm wt	≤ 1
Glycols	Must not be present in a liquid state at the temperature and pressure conditions of the pipeline.	ppm mol	≤ 50
Compressor lube oil carryover		ppm wt	≤ 50 ppmw
Liquids	CO_2 stream shall be free of liquids at delivery conditions and shall not produce condensed liquids in the pipeline at pipeline temperature and pressure.		

NOTE 1 Impurities causing harm of damage to pipelines, equipment, downstream systems or reservoirs.

NOTE 2 It is possible, with a water content of 100ppm mol, for water drop-out to take place during depressurization (e.g. for maintenance). If this operation is planned, then a gas phase specification should be used to avoid aqueous phase formation.

NB. Notes for tables are not shown

Tables A1 and A2 for gas and dense phase taken from ISO 27913-24 “Carbon dioxide capture, transportation and geological storage – Pipeline transportation systems” October 24th 2024