



Applying Materials Experience from Oil and Gas Production to Carbon Capture and Storage in North East Scotland

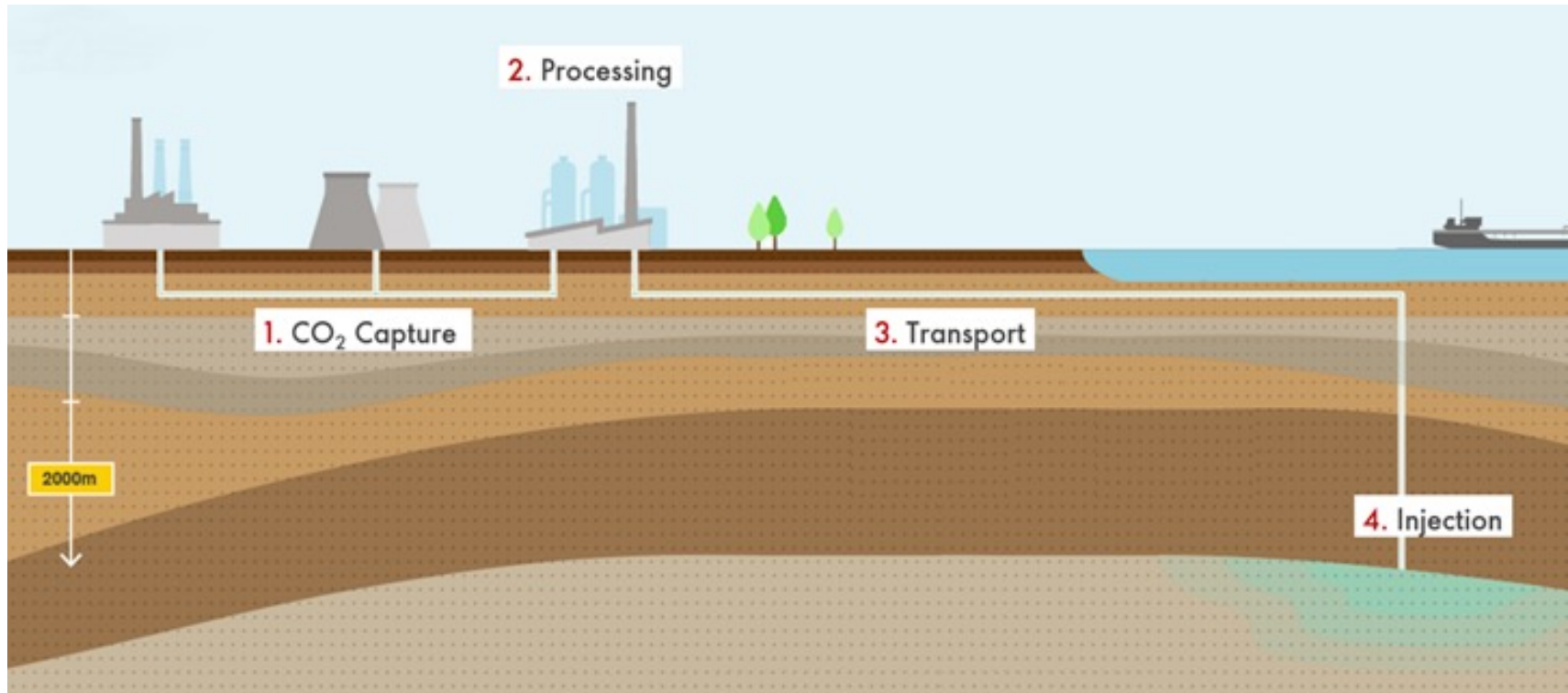
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Content

- What is CCS?
- What is dense phase CO₂?
- History of CCS in NE Scotland
- Materials & corrosion issues with CCS

What is carbon capture and storage (CCS)?



- CCUS - instead of just storing the CO₂ it is re-used in industrial processes such as plastics, concrete or biofuel manufacture



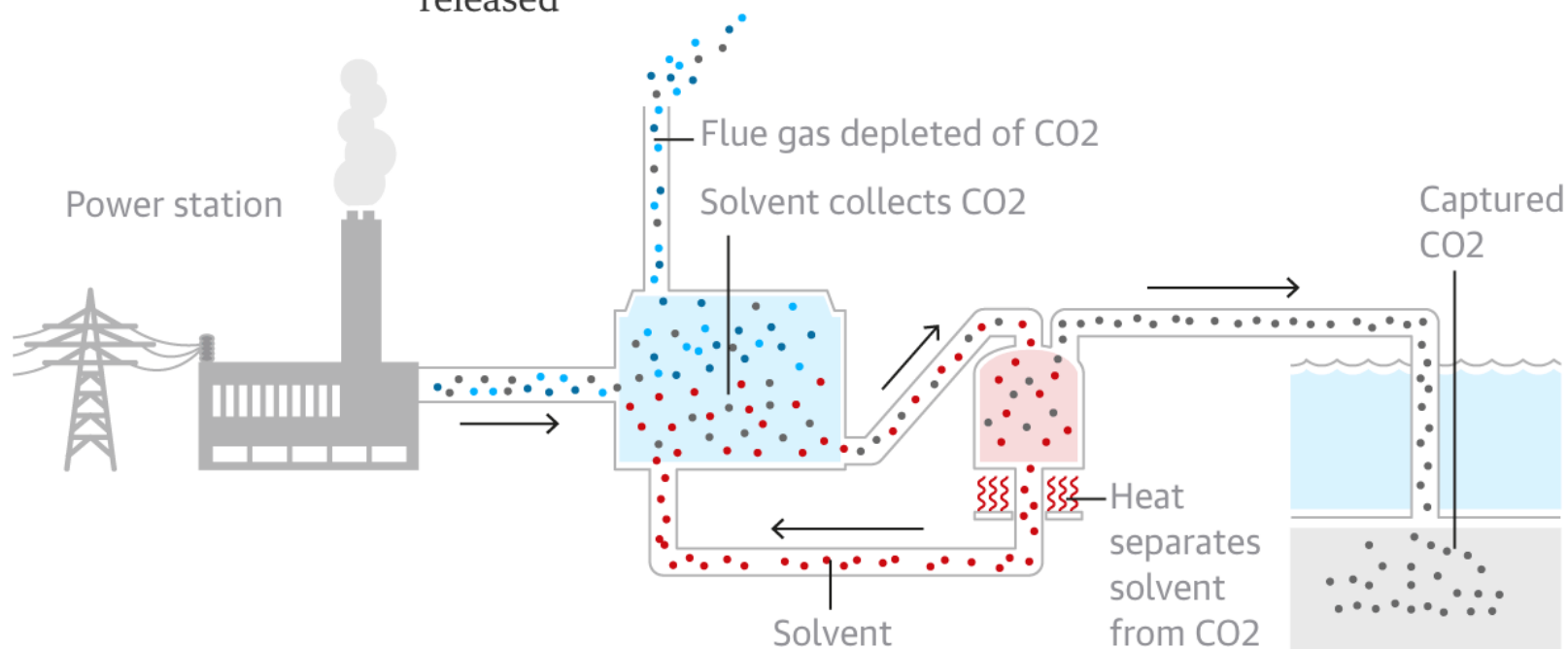
Carbon capture process

1. Power plant emissions injected into an absorber containing solvent

2. The solvent collects the CO₂ and the remaining power plant emissions are released

3. Heat is used to separate the solvent from the CO₂

4. CO₂ is stored beneath the North Sea

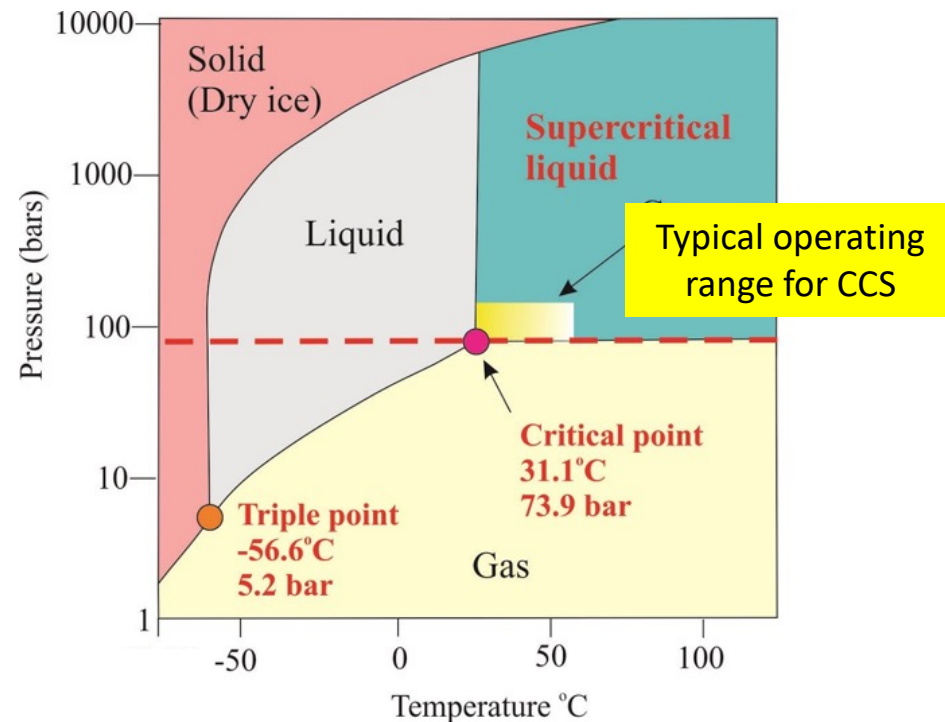


Guardian graphic. Source: Drax, C-Capture



What is dense phase CO₂

- Dense phase is a super-critical fluid state where viscosity is similar to a gas but density is closer to a liquid
- Important for pipeline transport as this means lower drag
- The critical point beyond which CO₂ exists in the super-critical phase is 31.1°C and 73.9 bar





CCS in NE Scotland

- First proposed by BP in 2005!
- Peterhead CCS project (with ConocoPhillips, Shell & SSE) to produce 'carbon-free' electricity from hydrogen
- It was proposed to convert natural gas to H₂ and CO₂ with the hydrogen used to power a 350MW power station and the CO₂ pumped via existing pipelines into the declining Miller oil field 240 km offshore for enhanced oil recovery
- Around 1.8M tonnes of carbon a year would have been taken out of the atmosphere
- In February 2007 BP announced postponement of any further investment in the project until a decision was made on whether the government would provide funding



Peterhead CCS project

BP scraps £500m Scottish carbon capture scheme

Guardian: 25th May 2007

- BP stated that the decision by the UK government to make funds available only to projects selected via a competition was a timetable which was unacceptable to BP
- The timetable would have meant that BP would have had to have kept the field mothballed which would be "uneconomic"
- BP had spent \$60M on the project
- At the time the UK government indicated that CCS should be post-combustion instead of pre-combustion
- The Miller platform is currently being removed

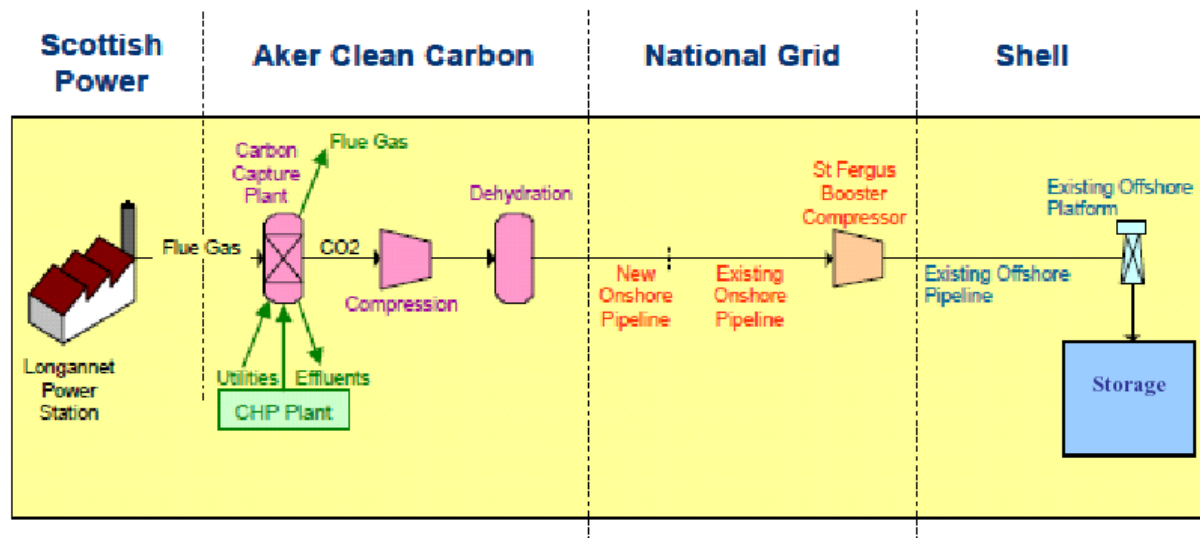


Longannet CCS project

- In 2007 the UK Government launched a competition to promote CCS which resulted in only 3 short-listed bids led by Shell, E.ON and RWE
- The competition required 20 Mt CO₂ to be injected offshore over a 10 to 15 year time-frame starting in 2014
- The UK competition offered FEED funding for 2 or possibly all 3 of the short-listed bids
- For the eventual winner it also offered up to 100% of the "incremental" Capex and Opex
- Scottish Power, National Grid and Shell Longannet project proposal became the preferred bid



Longannet project proposal



- CO₂ to be captured at Scottish Power's coal-fired Longannet Power Station west of Edinburgh
- Proposed to use redundant NG gas pipelines to transport CO₂ in vapour phase to St Fergus
- Following compression at St Fergus dense phase CO₂ transported through existing 20" pipeline to the Goldeneye offshore platform for storage



Why Longannet - Goldeneye?

- Goldeneye reservoir was due to cease production in 2012 making it available for CO₂ injection by 2014
- Offshore facilities and pipeline were reasonably new (installed 2004) and platform normally unmanned with minimum facilities and low degree of complexity
- Some new build pipeline was required including short section of dense phase line at St Fergus
- In 2011 UK government pledged £1bn to develop Longannet pilot project but the **project was cancelled in October 2011** due to the high cost estimate (£1.5 bn)
- Shell & SSE proposed a new design study for the gas-fired Peterhead station in 2012 if money was available from UK government or the EU's NER300 fund



Peterhead CCS project II

- Shell UK and SSE partnership to capture ≈ 1 Mt CO₂ per yr for 10-15 years from existing gas turbine at SSE's Peterhead Power Station
- CO₂ capture using amine based technology, compressed, cooled, and water & oxygen removed
- Dense phase CO₂ transported via new 20km tie-in from Peterhead to existing offshore 20" pipeline and injected in Goldeneye reservoir
- Re-complete existing wells with 13Cr/S13Cr tubing and accessories
- 25th November 2015:
- Goldeneye platform removed 2021



UK cancels pioneering £1bn carbon capture and storage competition



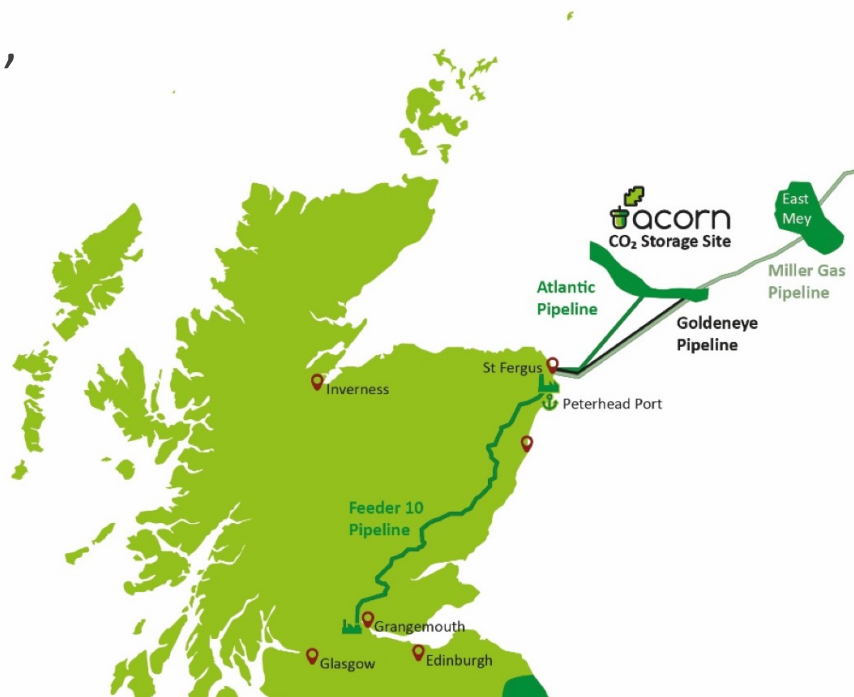
CCUS Innovation programme

- In July 2018 UK government launched CCUS Innovation programme
- UK government committed to deploy CCUS in a minimum of 2 industrial clusters by the mid-2020s, and 4 by 2030 at the latest
- Aim is to capture and store 20-30 Mt CO₂ per year by 2030
- Cluster sequencing process using CCS Infrastructure Fund of £1 bln “to provide industry with the certainty required to deploy CCUS at pace and at scale”
- First phase of evaluation of the 5 cluster submissions in November 2021 confirmed HyNet and East Coast Clusters (Teesside/Humber) as Track-1 clusters for mid-2020s with Scottish Cluster as a reserve if back-up needed
- UK government confirmed Acorn and Viking CCS systems as Track-2 clusters 20th Dec 2023 - will now assess delivery plans and carry out due diligence
- Acorn retains its status as Track-1 reserve cluster in the event that one of the Track-1 clusters encounters significant delivery challenges



Acorn project (phase 1)

- Partners:
Storegga (formerly Pale Blue Dot), Shell UK, Harbour Energy and North Sea Midstream Partners
- Capture of CO₂ from existing St Fergus industrial emitters, and removal of O₂ and water
- Compression and transport of CO₂ through onshore tie-in to Goldeneye offshore pipeline to subsea manifold
- Drilling and completion of well for CO₂ injection at Acorn South





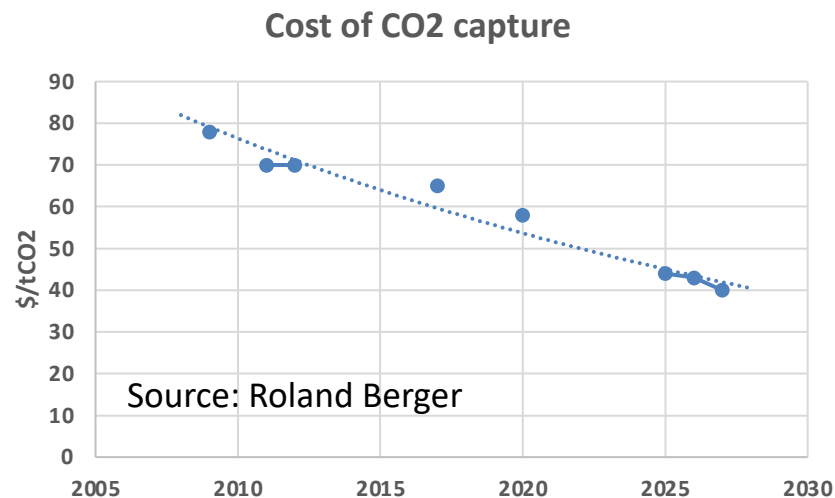
Acorn project (phase 2 options)

- CO₂ capture from new H₂ plant at St Fergus
- CO₂ capture and transport from industrial centres around Grangemouth to St Fergus via National Gas Grid Feeder 10 pipeline
- Re-use of existing Peterhead port for ship import of CO₂
- Drilling and completion of 2nd well at Acorn South and four wells at Acorn Central
- Re-use of the existing Atlantic pipeline
- International interconnection utilising the Miller Gas System pipeline



Will Acorn happen?

- High cost of CCS
- Need commitment and funding from UK government for CCS
- Chancellor's spring budget 2023 extra £20bn (over 20 years) was pledged for CCS although most likely to go to 2 clusters in England
- Key factors:
 - Impact of a new UK government within the next 12 months?
 - Scottish government net-zero ambitions?
 - Historical experience?
 - Number of Energy ministers since 2005?
 - Carbon emissions price? 88 £/tCO₂ (2024) vs current ETS 60-65 £/tCO₂
- Lack of an overall comprehensive and cohesive UK energy strategy?



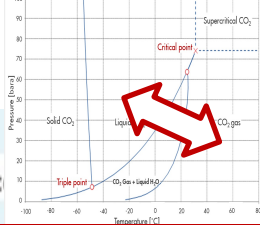


CCS materials and corrosion challenges

CO₂ Specification

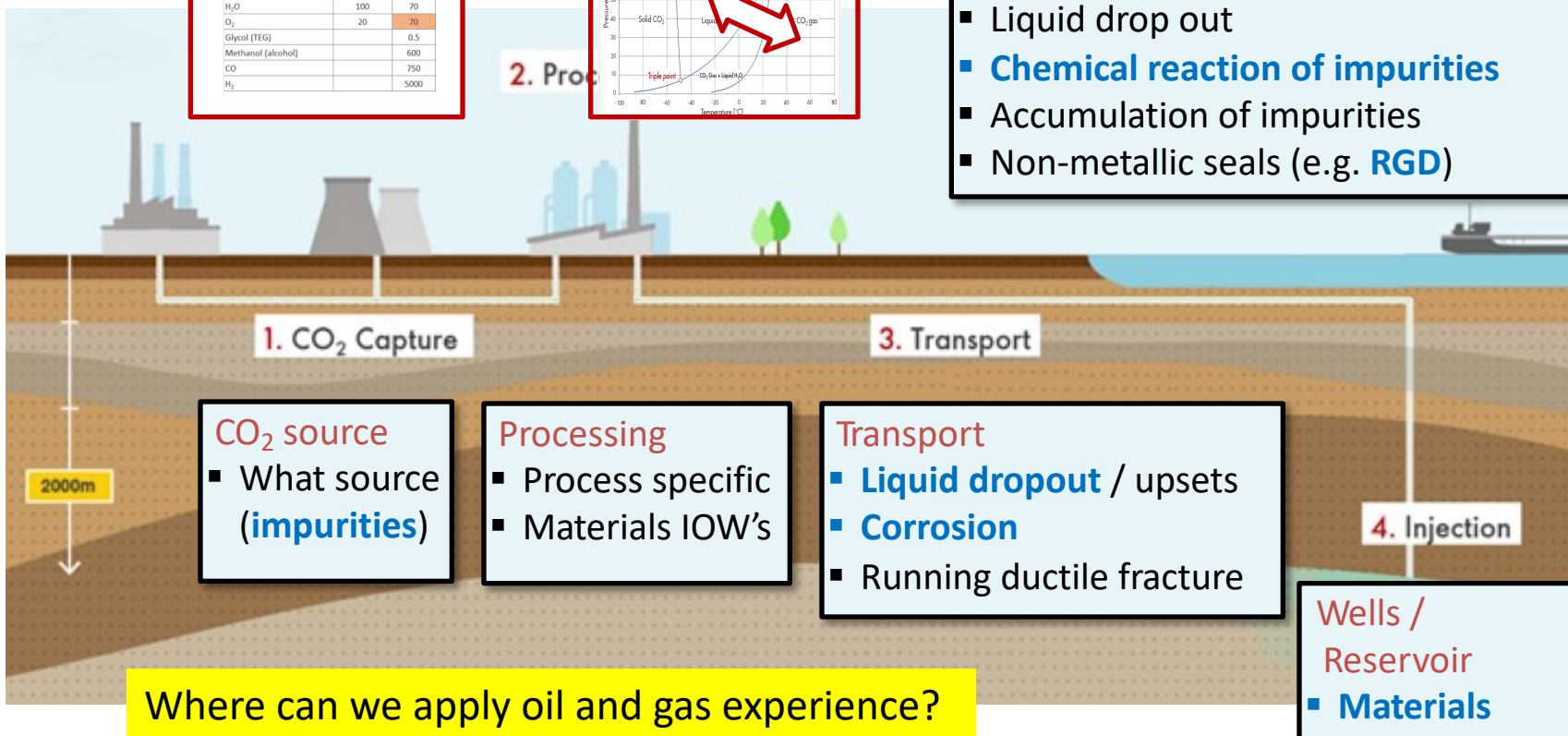
CO ₂ Spec [ppm mole]	limit for acid formation/ drop out	proposed
NO ₂	10	50
SO ₂ + H ₂ S	20	40
H ₂ S		10
H ₂ O	100	70
O ₂	20	70
Glycol (TEG)		0.5
Methanol (alcohol)		600
CO		750
H ₂		5000

Phase Behaviour



Generic challenges

- **JT Cooling** / low temp. toughness
- Liquid drop out
- **Chemical reaction of impurities**
- Accumulation of impurities
- Non-metallic seals (e.g. **RGD**)



CO₂ source

- What source (**impurities**)

Processing

- Process specific
- Materials IOW's

Transport

- **Liquid dropout** / upsets
- **Corrosion**
- Running ductile fracture

4. Injection

Wells / Reservoir

- **Materials**
- **Flowback**



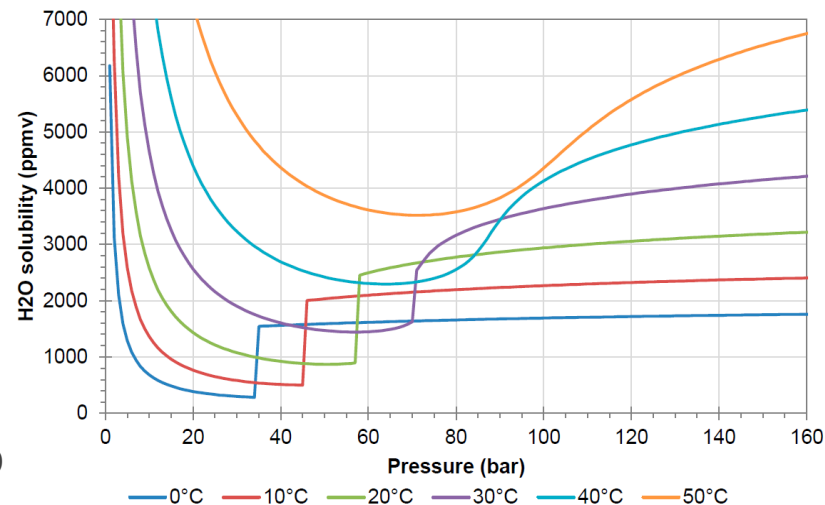
Materials selection & corrosion control

- In developing a materials selection and corrosion control strategy the following two control options exist:
 - Avoid threats that can lead to rapid failure that cannot be controlled or (timely) detected and require selection of resistant materials
 - Manage threats that can be controlled (using barriers) and/or monitored, and can be tolerated with a suitable mitigation strategy
- Threats that can lead to rapid failure include:
 - Brittle fracture due to Joule-Thompson cooling
 - Running ductile fracture
 - Hydrogen related cracking mechanisms (SSC, HE)
 - Stress corrosion cracking (CO-CO₂-H₂O SCC and Chloride SCC)
- Threats that can be controlled include:
 - CO₂ corrosion
 - Acidic corrosion from impurities



CO₂ corrosion

- Wealth of data and CO₂ corrosion prediction models developed for oil & gas sector
- Solubility of water in CO₂ depends on pressure and temperature
- When water is dissolved in dense phase CO₂ there is no corrosion
- If water drops out the CO₂ dissolves in the water to form carbonic acid and CO₂ corrosion becomes a threat
- Traditional De Waard-Milliams relationship for CO₂ corrosion rate (CR):
$$\text{Log (CR)} = 5.8 - 1710/T + 0.67 \text{ Log } (P_{\text{CO}_2})$$
- But dependence of CR on P_{CO_2} is lower at higher partial pressures in dense phase CO₂
- Correlation for dense phase CO₂ corrosion has shown that a lower factor of 0.27 instead of 0.67 can be used based on a better fit between field/lab data and model calculations

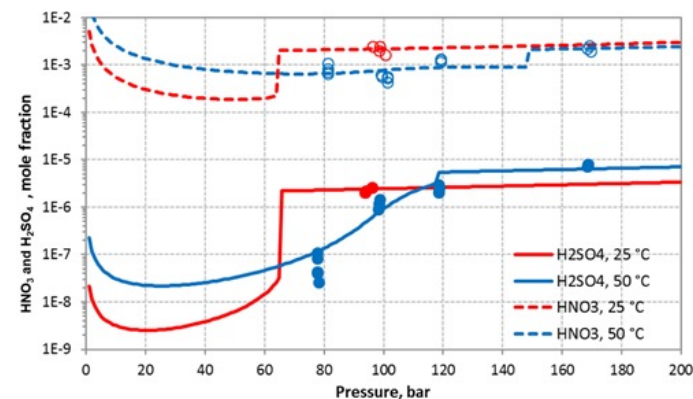
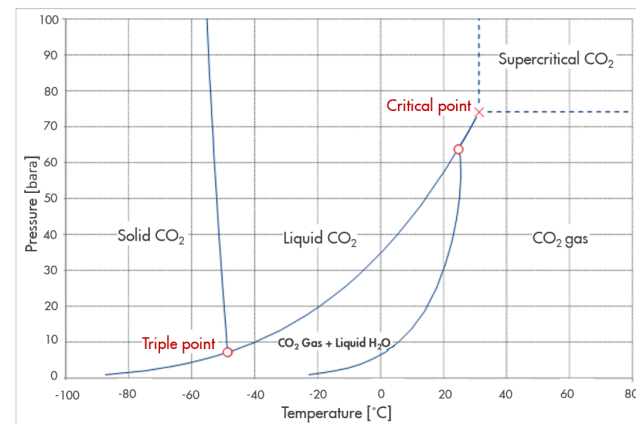


Hydrocor - Dense phase CO ₂ correlation at ~1 ms ⁻¹			
CO ₂ pressure	50 °C	20 °C	0 °C
[bar]	[mm y ⁻¹]	[mm y ⁻¹]	[mm y ⁻¹]
10	14	4	1.7
25	14	5	2
50	10	6	2.2
100	8	7	2.5



Effect of impurities

- CO₂ for storage can originate from different sources with a range of impurities such as water, O₂, SO₂, NO₂ and H₂S
- Impurities may trigger water phase below normal dewpoint and initiate shift in tendency of water to condense and create conditions for CO₂ corrosion
- Impurities can form highly corrosive liquid phases with sulphuric acid, nitric acid and elemental sulphur
- Control options for strong acids are preventing formation or avoiding drop-out
- H₂SO₄ (and also elemental sulphur) has low solubility in dense phase CO₂ so the preferred control option is preventing formation
- HNO₃ has relatively high solubility in dense phase CO₂ so the preferred option is to avoid drop out
- Important to consider transients and upset conditions when assessing process conditions and defining CO₂ specification limits





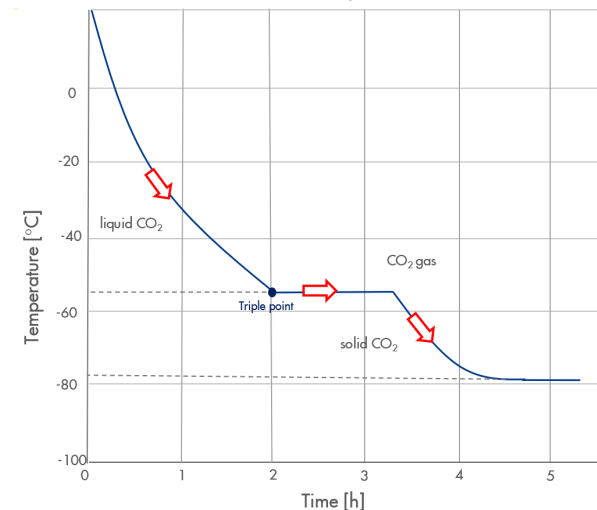
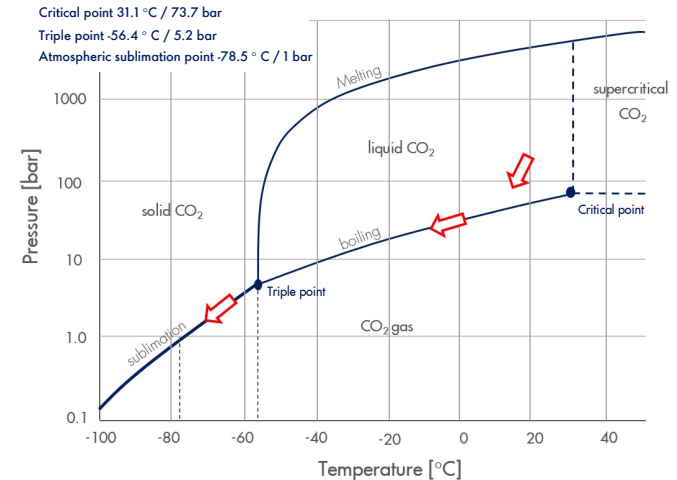
CO₂ specification limits

- Relevant impurities as well as the critical limits that impact the formation of highly corrosive reaction products were identified in studies at IFE in Norway
- Research focussed on identification of operating limits that prevent drop out of these acids and also the solubility limits of the acids that are formed
- Safe operating limits should be identified for a CCS project that avoid the drop out of acids, the risk of which significantly increases with pressure reduction especially moving from the liquid to the gas phase
- A proposed starting point for a CO₂ specification for 25°C and 100 bar is:
 - < 100 ppm mole H₂O
 - < 20 ppm H₂S + SO₂, (when there is no NO₂ this may be 60 ppm mole)
 - < 20 ppm mole O₂
 - < 10 ppm mole NO₂ - highly reactive, limits will also impact H₂SO₄ formation
- Other limits to consider are:
 - H₂S limits
 - CO for CO-CO₂-H₂O SCC
 - MeOH (can trigger formation of a water rich phase)



Low temperature brittle fracture

- Low temperature brittle fracture is a well understood phenomenon in the oil and gas sector
- Standard approaches are available to assess the risk of brittle fracture
- Important to include upset conditions like start up/shut down and blow-down scenarios where pressure drop can cause (Joule-Thompson) cooling and very low temperatures (e.g. -80°C)
- Need to define the required toughness for materials selected in the design





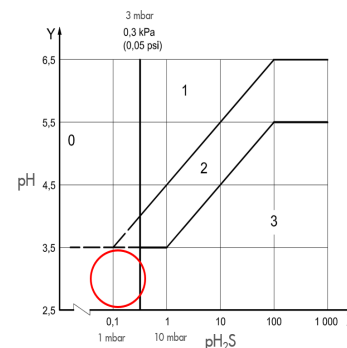
Running ductile fracture

- Many studies done to assess risk of running ductile fracture in natural gas pipelines and most commonly used method to predict pipe resistance to ductile fracture is the Battelle Two Curve Method (BTCM)
- Supercritical CO₂ make CCS pipelines susceptible to running ductile fracture especially for pipelines operating below 150 bar
- Speed of ductile fracture is function of the resistance of steel to being fractured and force trying to fracture it (i.e. the pipeline internal pressure)
 - Decompression speed of liquid CO₂ may be significantly higher than natural gas
 - As vapour forms decompression speed of the CO₂ stream drops significantly
 - During evaporation of liquid CO₂ pressure remains constant whereas CO₂ decompression wave speed reduces and the fracture will not be arrested
- To determine the risk from this type of fracture in a CO₂ pipeline a modified Battelle Two Curve model (BTCM) as outlined in ISO 27913 can be used
- More accurate predictions of pipeline resistance to running ductile fracture can be obtained from a coupled fluid-structure finite element assessment



Hydrogen related cracking mechanisms

- Hydrogen cracking related mechanisms such as hydrogen embrittlement and sulphide stress corrosion can occur when atomic hydrogen is adsorbed into steel causing embrittlement of the lattice with the potential for catastrophic cracking
- Presence of H₂S in the fluid can promote adsorption of atomic hydrogen
- Failure modes are relatively well understood from the oil and gas sector and the limits for materials are defined in industry guidance (e.g. ISO 15156)
- This allows selection and/or treatment of appropriate materials to avoid hydrogen related cracking mechanisms
- But some differences that might occur with dense phase CO₂ exposures include:
 - Water presence typically occurs at lower pressures (e.g. around 50 bar or when moving towards the gas phase)
 - At high pressure the fugacity concept seems to be different for liquid/dense phase
 - pH in water that drops out (~ pH3) will likely be lower than what is addressed by ISO 15156
- May need to select sour service materials if significant H₂S is present in the CO₂ as an impurity





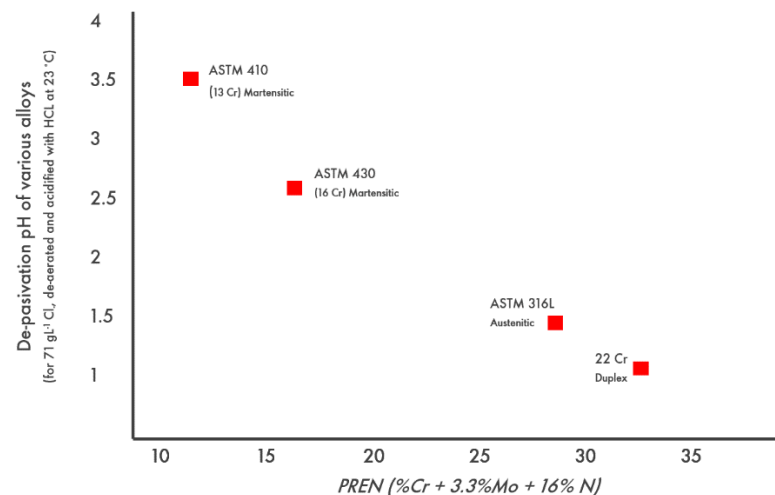
Stress corrosion cracking

- Stress corrosion cracking can occur as a consequence of the local breakdown of a passive layer typically present with corrosion resistant alloys
- SCC failure mechanisms are reasonably well understood but the specific conditions in a CCS project may create unusual circumstances that need further assessment and testing
- Specific SCC mechanism reported for carbon and low-alloy steels exposed to environments containing CO₂, carbon monoxide and water
- If sufficient water is present CO acts as an (incomplete) barrier for CO₂ corrosion and may leave a small fraction of steel exposed leading to SCC
- This form of SCC typically occurs under a very limited set of conditions but testing may be necessary if significant carbon monoxide is present in the CO₂ as an impurity



Corrosion resistant alloys

- Presence of water in CCS systems can lead to breakdown of passivity of low grade CRA such as 13Cr often used for well tubing
- High CO₂ pressure in CCS can lower pH of condensing water to create conditions where de-passivation can occur
- Well known from oil and gas experience that de-passivation can cause pitting and possible SCC
- Parameters that trigger de-passivation include pH, chloride content, temperature and presence of oxygen
- For tubulars at the bottom of injection wells in a reservoir with high salinity selection of high grade CRAs may be required
- CRA material should be selected for conditions where de-passivation does not occur under any operating scenario

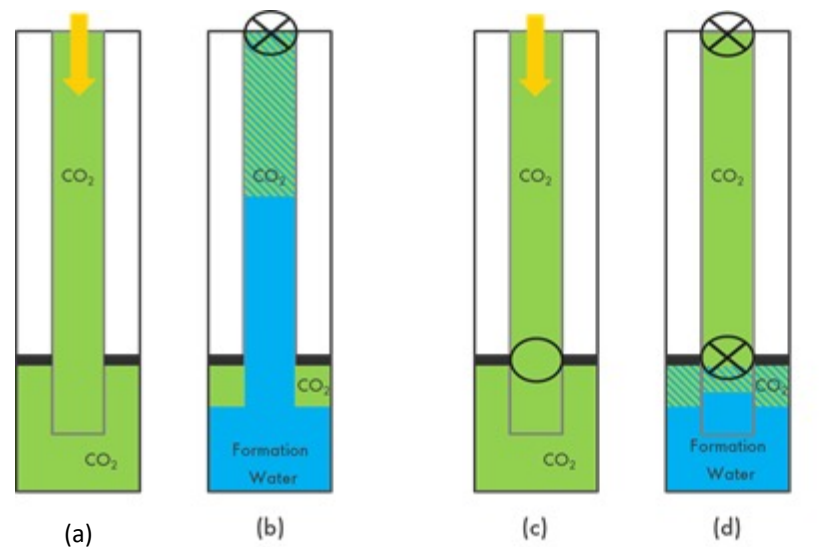


Typical values of de-passivation pH for various stainless steels



Application of downhole barrier valve

- Well design for CCS where O_2 is present can benefit from a barrier valve inserted near the bottom-hole reducing extent to which reservoir water can flow back into tubing
- Impact of the barrier valve is illustrated here
- Can be used to avoid the presence of condensing and formation water above the position where it is installed and allow lower grade CRA to be used above

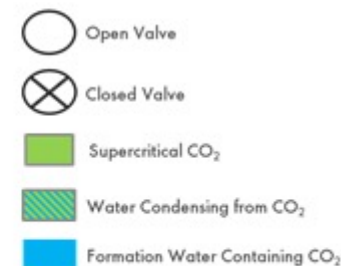


a) Injecting well without barrier valve

(b) well without barrier valve after long-term shut-in

(c) well with barrier valve under injection

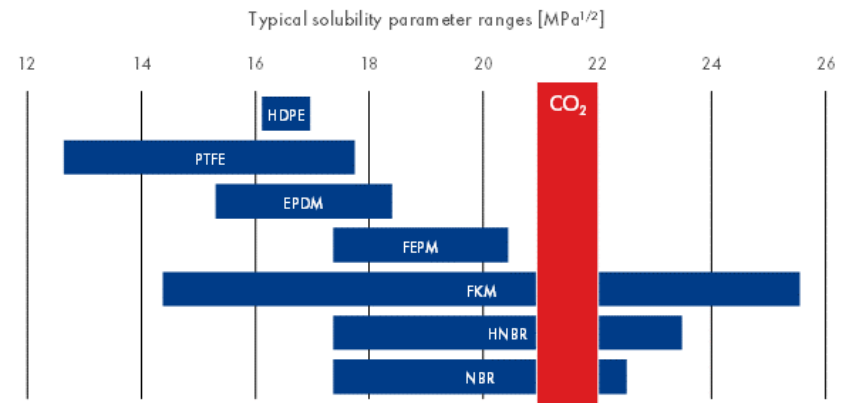
(d) well with barrier valve after long-term shut-in





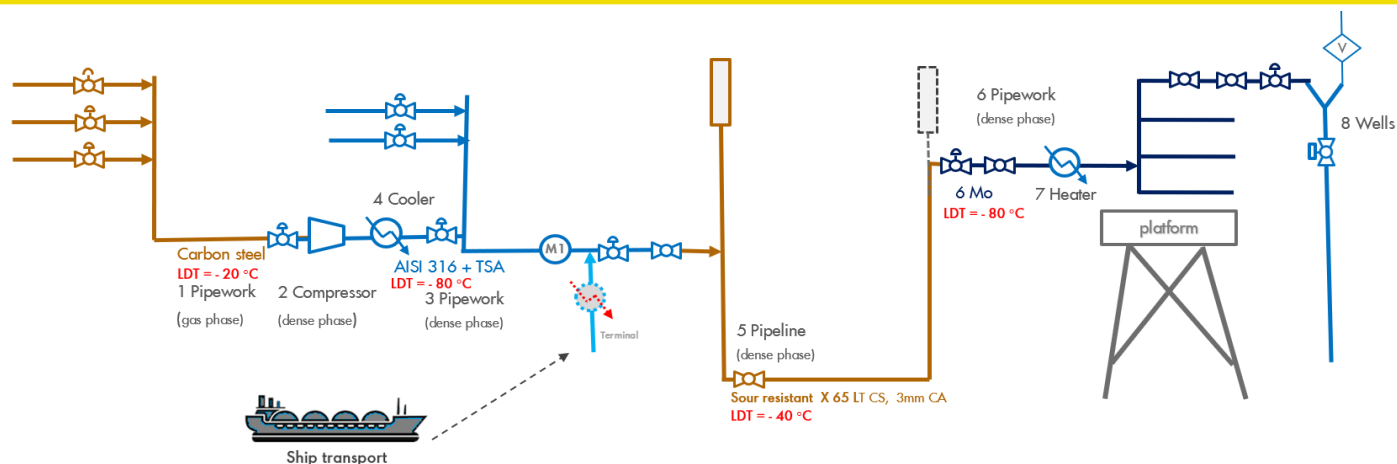
Application of non-metallics

- Dense phase CO₂ can penetrate and saturate some non-metallic materials
- Most polymers are chemically resistant to CO₂ and any interaction is mainly physical
- Significant amounts of CO₂ absorption in the polymer will result in swelling and affect properties such as strength, stiffness and resistance to permeation
- The principle of solubility parameters which was developed for interaction of polymers with hydrocarbon solvents can be used to identify the effect of CO₂ exposure on a polymer
- The potential for interaction of CO₂ and elastomers such as NBR, HNBR and FKM which can impact the RGD sensitivity is shown here
- Allows selection of alternatives





Materials selection



Component	CO2 phase	Base case material	LDT °C	Comments
Pipework	Gas	LT-CS	-25	
Compressor and coolers	Dense	AISI 316	-80	
Pipework	Dense/liquid	AISI 316 / 6 Mo SS	-80	
Storage tanks	Liquid	3.5 Ni steel	-80	
Pipeline	Dense	LT-CS + 3mm CA Sour rated?	-40	Manage pressure
Offshore pipework	Dense	6 Mo SS	-80	
Wells	Dense	L80, 13Cr, 25Cr SDSS, 6Mo SS, Nickel alloys,		Depends on LDT & flowback

- Selection driven by LDT
- Tendency to specify high alloy materials for Wells
- Take a section approach:
 - Use low alloy for top section if no water drop out
 - Bottom section dependent on where water contact is



Concluding remarks

- Materials for CCS projects need to be selected such that any degradation occurs in a controllable and detectable way and rapid degradation mechanisms are avoided
- Operating conditions including upsets that might trigger drop out of water and other corrosive liquids or cause temperature drops needs to be understood
- Impurities in the CO₂ that may lead to corrosion if drop out occurs should be managed via stringent control of the defined CO₂ specification
- Special attention is required for CRA materials in wells especially if O₂ is present in the CO₂
- Polymer materials that are exposed to CO₂ should be assessed for rapid gas decompression resistance and the potential impact of impurities
- Much data and expertise are already available from the oil and gas sector to benefit design and operation of CCS projects, although testing may be necessary to confirm suitability for the specific conditions of CCS



End

Acknowledgement:

Hans Sonke, Shell Global Solutions International B.V. NL

References:

J. Sonke, W.M. Bos, & S.J. Paterson, International Journal of Greenhouse Gas Control 114 (2022) 103601, “Materials challenges with CO₂ transport and injection for carbon capture and storage”.

J. Sonke & S.J. Paterson, AMPP 2022, San Antonio, Paper 17726, Guidance for “Materials Selection and Corrosion Control in CO₂ Transport and Injection for Carbon Capture and Storage”.

AMPP 21532-2023 "Guide for Materials Selection and Corrosion Control for CO₂ Transport and Storage"