DYNAMIC BEHAVIOR - METALLURGIC

Pipelines and equipment for transport and storage of CO_2 can be subject to several internal and external degradation mechanisms. The most relevant degradation mechanisms are wet CO_2 erosion-corrosion, soil corrosion, seawater corrosion and corrosion under insulation (CUI). Further, brittle fracture of low temperature storage vessels has been assessed. MCC has performed research study [9] on corrosion aspects to allow an optimum selection of materials of construction for pipelines and equipment in the logistical transportation system for the captured CO_2 from the emitters to an offshore storage location. A summary of that report is presented here.

Wet CO₂ corrosion-erosion

Wet CO_2 corrosion is well-known in the upstream oil and gas industry as 'sweet gas' corrosion. Corrosion of carbon steel will occur as soon as free water is present and therefore carbon steel cannot be applied in wet CO_2 . Austenitic stainless steels (TP300-series), 13 %Cr steels, and duplex stainless steels can be applied in wet CO_2 within the project specification.

However, for 13 %Cr steels and duplex stainless steels certain limitations apply to the design temperature and presence of sulphur containing components. Also, poly-ethylene (PE100) and many glass-fiber reinforced plastics (GRP) are resistant to wet CO_2 within the project specifications. Both PE100 and polyester GRP are applicable as pipeline material for wet CO_2 from the emitter to the terminal. Pressures up to 40 bar are feasible; however GRP is more suitable then PE at higher pressures. This could be an alternative for the carbon steel pipeline and the required drying equipment at the emitter.

Dry CO₂

Carbon steels can only be applied in dry CO_2 , provided that no free water phase is present. This depends on pressure, temperature and the presence of other gaseous contaminants like CO, CH₄, H₂S, SO_x, NO_x. The CO₂ is considered to be dry, provided that the water solubility is not exceeded at the operating conditions. Further, it is recommended to apply a safety factor of two, which is in line with DNV RP-J202 [10]. The water solubility is much higher in the supercritical phase compared to the liquid and gas phases. Therefore, CO₂ pipeline transport is preferably performed under supercritical conditions. Carbon steels can be applied as material of construction for dry CO₂. The corrosion rate is less than 0.01 mm/year, which can be considered as fully corrosion resistant. For pipeline transport a corrosion allowance of about 2 mm is recommended. For storage vessels continuously operating below -10 °C a corrosion allowance is not necessary.

Atmospheric corrosion or CUI

Corrosion Under Insulation is a serious threat for insulated equipment and piping especially if exposed to marine environments. CUI can occur at temperatures between -10 °C and +140 °C. Figure 11 shows a ruptured high pressure carbon steel pipe as a result of atmospheric crater-type attack under insulation (CUI). The high-pressure CO₂ pipeline (140 bara, 70 °C) ruptured at the lower elbow of a vertical line after some 20 years on-stream time. Severe corrosion only did occur at the outside of the insulated pipeline. At the inside no corrosion was observed. No coating system was applied on the carbon steel pipeline below the insulation. To avoid atmospheric corrosion a coating system has to be applied. The selected coating system should be suitable for at least corrosivity category C5-I in ISO-12944. For long term and maintenance free protection it is recommended to apply a metallic coating system like Thermal Spray Aluminium (TSA). TSA is the only protection system that offers 30 years protection in the temperature range between -100 °C and +550 °C.



Figure 11: Ruptured CO₂ pipeline (Ø 130×8 mm) due to corrosion under insulation (CUI) (source: [9]) Seawater

For offshore pipelines a coating system in conjunction with cathodic protection should be used. Equipment cooled with seawater needs to be made of titanium, however high-Mo austenitic steels could be considered, depending on the process conditions.

Soil corrosion

In order to protect buried pipelines and bottom plates of tanks an external coating system should be used in conjunction with cathodic protection. For the external coating PE-foil, asphalt bitumen or epoxy coatings can be considered.

CO₂ compressor system (rotating equipment)

For wet CO_2 conditions 13 %Cr steels or stainless steels should be used for rotating equipment.

If the CO_2 is almost free of water (< 5 ppm) then low-alloy carbon steels like AISI 4140 can be used. For interstage coolers and separators at wet CO_2 conditions, stainless steels (or cladding) should be applied. For dry conditions carbon steels can be used. It is also important whether the cooling water is present at the shell or tube side of the heat exchanger. The process conditions and materials choice should be discussed with the manufacturer of the compressor system. Interstage coolers may be designed with cooling water at the shell side. From experience it seems impossible to prevent chlorine contamination of the cooling water. Austenitic stainless steel is not resistant to chlorine contamination. Hence, duplex stainless steel will be more suitable.

Non-metallic materials

Elastomers for seals are prone to swelling and explosive decompression damage in high-pressure CO₂. EPDM, NBR, CSM and FKM are resistant in both wet and dry conditions. Many thermoplastics like PE, PP, PTFE, and PA are suitable for wet and dry CO₂. However, this is dependent on pressure and temperature (both low temperatures and elevated temperatures). PA11, PA12 and PTFE are considered suitable for application at the inner pressure sheet, which is exposed to high-pressure CO₂inside the flexible unloading hose (from the ship to the offshore unloading terminal).

Glass-fiber reinforced plastics (GRP) based on polyester, vinylester and epoxy resins can be used for both wet and dry CO₂.

However, this is dependent on pressures and especially temperatures. Polyester GRP has been used up to 40 years without problems for transport of wet CO_2 from ammonia plants to urea and CO_2 purification plants. Graphite and PTFE can be used for flange gaskets. Both poly-ethylene PE100 and polyester GRP are applicable as pipeline material for wet CO_2 from the emitter to the terminal (up to 40 bar; however higher pressures are more suitable for GRP compared to PE). This could be an alternative for the carbon steel pipeline and the required drying equipment at the emitter.

Pre-commissioning activities

Pre-commissioning activities are essential for safe and corrosion free operation of equipment and pipelines. These activities include cleaning (removal of debris), pressure testing, dewatering, drying and preservation. To avoid corrosion of carbon steel equipment and pipeline systems during commissioning, it is necessary to pay good attention to dewatering and drying before filling with CO₂. Pneumatic pressure testing is not recommended, because of the high amount of stored energy and consequent risks. However, hydrostatic testing requires the removal of water.

Rust formation on carbon and low-alloy steels may occur before commissioning. Therefore, it is recommended to apply a temporary protection system.

Integrity Management System

To ensure safe operation an Integrity Management System should be implemented. Basically, this requires the implementation of a 'plan-do-study-act' cycle as commonly used in TQM (Total Quality Management). Statistics based on the control of the water dew point is necessary. Lack of control of the water dew point increases the failure level significantly. Inspection programmes should be based on a criticality rating according to a Risk Based Inspection (RBI) philosophy. On-line corrosion monitoring of pipeline transport is strongly recommended. Standard inspections techniques can be used during equipment shutdown. Newer techniques like the INCOTEST (external measuring technique based on pulsed-EC (eddy current)) can be considered for wall thickness control of internal corrosion of e.g. storage vessels. Normally, internal inspections are required every four years. Under certain conditions and after the first inspection, it is possible to perform external on-line inspections to assess the internal condition of the pressure vessel. Thus, opening of equipment can be avoided.

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