

The Use and Validation of Fugacity in H₂S Testing, as Part of Flexible Pipe Armour Wire Qualification

Jonas Gudme, Iman Akbarzadeh and Adam Rubin
NOV Flexibles
Priorparken 480
DK-2605 Broendby
Denmark

ABSTRACT

This paper introduces permeation-based models used for the prediction of the unique environments of the flexible pipe annulus where the armour wires are placed in the flexible pipe structure. Test results are presented for SSC behavior of the armour wires in high pressure autoclaves simulating one to one the conditions of a flexible pipe annulus. The results are compared with tests executed at ambient pressure with both a partial pressure approach and with an approach based on H₂S fugacity. The difference in results are discussed in the context of the potential improvements possible with using fugacity for qualification of armour wires exposed to H₂S related degradational mechanisms.

Key words: Test method; sour service; Sulfide Stress Cracking; Hydrogen Induced Cracking, Fugacity; Flexible pipe; Annulus; H₂S; CO₂

INTRODUCTION

The recent suggestion of the H₂S fugacity as the governing parameter in Sulfide Stress Cracking (SSC) and/or Hydrogen Induced Cracking (HIC) is a change from the conventional use of partial pressure as the governing parameter.¹⁻⁴ Whereas there is still no general industry consensus on this approach the use of fugacity is already being introduced in testing programs for armour wires used in unbonded flexible pipes. Traditionally, qualification testing for carbon steels is in accordance with NACE TM-0177 executed at ambient pressure, replicating the H₂S partial pressure from the high-pressure operation condition into the ambient pressure test condition.⁵ When using a fugacity approach, it is the calculated H₂S fugacity from the high-pressure condition which is replicated in the ambient pressure testing. The use of H₂S fugacity in qualification may potentially reduce the overall conservatism related to qualification testing; thus, requiring validation before it can be applied.

The Flexible Pipe

Unbonded flexible pipes are constructed from concentric layers of polymeric and steel material. In order to preserve the flexibility of the pipe construction, the layers are not bonded together hence the phrasing unbonded flexible pipe. Figure 1 shows a typical cross section of an unbonded flexible pipe illustrating typical layers. Various types of unbonded flexible pipes may omit some of the layers. Below is a description of each of the main layers.

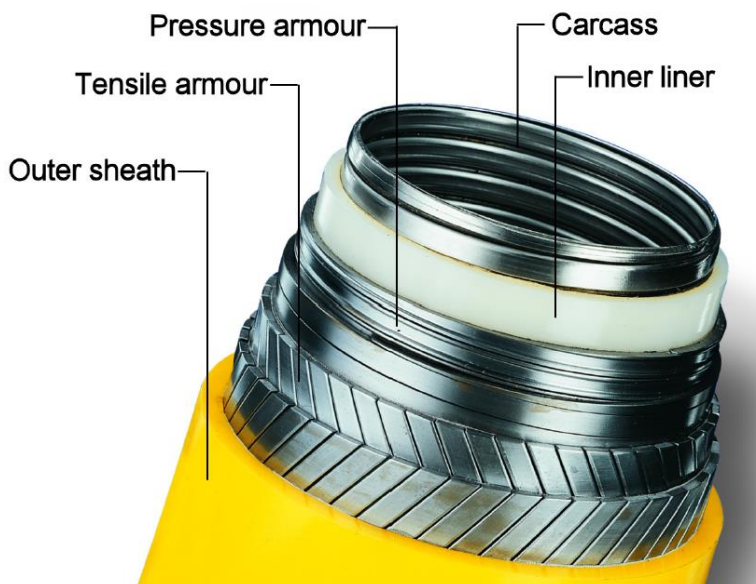


Figure 1: Main layers in a flexible pipe.

Carcass.

An interlocking layer manufactured from a stainless steel strip. The carcass prevents collapse of the inner liner and provides mechanical protection against pigging tools and abrasive particles. Selection of stainless steel grade is studied in great detail but material selection influenced by the potential adoption of a fugacity approach is outside the scope of this paper.⁶

Inner liner.

An extruded polymer layer providing internal fluid integrity. Common polymer types are Polyethylene (PE), Cross linked Polyethylene (XLPE), Polyamide 11 (PA11) and Polyvinylidene Fluoride (PVDF). The typical layer thickness ranges from 4 to 10 mm depending on pipe diameter.

Pressure armour.

Several structural layers consisting of helically wound C-shaped steel wires and/or metallic strips. The pressure armour layers provide resistance to radial loads coming primarily from the internal pressure of the bore. Typically, flexible pipes are operated at high pressures and are rated for 5,000-10,000 psi (350-700 bar).

Tensile armour.

Multiple structural layers consisting of helically wound flat steel wires. The layers are counter wound in pairs. The layers provide resistance to axial tension loads. There is typically between 30 and 80 wires parallel positioned in each layer mainly dependent on the pipe diameter.

Outer sheath.

An extruded polymer layer. Its function is to shield the pipe's steel components from the outer environment (often seawater) and to give mechanical protection.

In addition to the main layers, various polymeric tape layers are included. Anti-wear layers are incorporated in order to prevent wear and tear between the structural layers. Isolation tapes with low thermal conductivity can be applied between for example the tensile armour and outer sheath in order to obtain specific thermal insulation properties of the pipe.

The special void between the inner liner and the outer sheath is called annulus. The armour material in the annulus is protected from the high corrosive bore environment by the inner liner; however, CO₂ and H₂S will permeate through the inner liner and create a corrosive environment. The corrosiveness and H₂S level in the annulus are lower than the corresponding bore but still significant and H₂S qualification of the selected armour material grades is an essential part of flexible pipe design validation.

Annulus Environment Prediction

The annulus prediction models consist of many sub routines which have developed over the last 25 years. At its core, the model is the permeation of “small molecules” through the inner liner from the bore to the annulus. Only “small molecules” are considered since the permeation rate of bigger molecules is very slow and will not contribute to the pressure build up in the annulus. Typically, only H₂S, CO₂ and CH₄ are considered in the permeation processes. When enough pressure is built in the annulus by the permeation from the bore to the annulus, the permeation will continue through the outer sheath and out to the offshore environment into the ocean where the concentration of the diffusion species is considered infinitely low. As a result, the annulus composition will be a function of the flux into the annulus through the inner liner and flux out through the outer sheath. In order to ensure that the annulus is not over pressurized, a venting valve opening at 2 bars is implemented at the flexible pipe end fittings. Due to the water column at the end fittings the actual pressure in the annulus may be much higher (e.g. a flexible pipe positioned at 100m water depth may have 10+2 = 12 bar in the annulus).

The driving force of the permeation flux “J” has traditionally been the partial pressure difference Δp of the individual species considered, as well as the permeability coefficient Pe and the membrane thickness T:

$$J = Pe \left(\frac{p_{high} - p_{low}}{T} \right) \quad (1)$$

A system of related equations based on equation 1 above is used to calculate the steady state of the annulus where the total flux of all species into the annulus is balanced with the flux exiting the annulus through the outer sheath in combination with the flux through the venting valve.

In order to improve the accuracy of the permeation model and account for the deviations from an ideal gas law behavior, the use fugacity has been introduced to more accurately describe the activity or chemical potential of a gas. Fugacity is typically calculated as shown in Equation 2, where the partial pressure as calculated from the mole fraction x and the total pressure P, is multiplied with a fugacity coefficient φ :

$$f = x \cdot P \cdot \varphi \quad (2)$$

The fugacity coefficient φ is highly dependent on pressure, temperature and composition and is typically calculated using an equation of state (EOS) modeling software tool such as OLI, Multiflash[†], PVT-Sim[†], or similar.

When implementing fugacity as the driving factor in permeation and an annulus model, the fugacity coefficients must be calculated in the bore and annulus for all components in each iterative step which

[†] Trade name

makes the calculations computer intensive. The end effect on the calculations is significant since the driving force from the bore towards the pipe is lowered as the fugacity coefficient in the bore compared with that of the annulus is lower as a result of the high pressure in the bore. The fugacity difference (Δf) over the inner liner is thus typically lower than the corresponding partial pressure difference (Δp). For a given set of operational conditions, the permeation calculated using partial pressure thus typically yields higher predictions of H_2S in the annulus compared with calculation made with the same input data in a permeation model utilizing fugacity. This is however a massive oversimplification as the result of a permeation calculation can be highly influenced by other factors, such as temperature profile in the pipe wall cross-section, water depth and venting pressure.

The results from the permeation model are used in selecting the appropriate armour material grade in order to ensure that the selected material is resistant to the predicted H_2S level. When using the improved models based on fugacity the designer is faced with the option to base the material selection on the calculated fugacity of H_2S or the partial pressure. In order to determine the most appropriate property of the annulus, a test program has been developed in order to determine the effects.

EXPERIMENTAL PROCEDURE

In order to investigate the effect of fugacity versus partial pressure 3 sour service tests were executed. The test was conducted with a modified test procedure where both the SSC and the HIC degradation mechanisms were investigated. The test procedure is an adaptation of a 30-day SSC test heavily inspired by NACE TM-0177 and NACE TM-0316.⁵⁺⁷ The acceptance criteria were strengthened so that in addition to the SSC crack criteria also HIC type degradation in line with NACE TM-0284 was included in the acceptance criteria.⁸ The investigation for HIC cracking where done in the full length of the specimens covering both the central part of the specimens which is subjected to the full load from the 4-point bending as well as the 2 end parts with less load. A picture of the sample setup is included in figure 2. Two tests were executed at ambient pressure where the H_2S content in the test gas was varied. The third test was executed in an autoclave at 250 bar pressure. The gas mixture used was selected in order to achieve two levels of partial pressure H_2S and two levels of fugacity.

Table 1
GAS COMPOSITION IN THE THREE TESTS

Test	Total Pressure [bara]	Argon Conc. [%]	H_2S Conc. [%]	CO_2 Conc. [%]
1	1.0	0	5%	95%
2	1.0	0	1.86%	98.14%
3	250	99%	0.02%	0.975%

The pH in the ambient pressure tests was adjusted to 5.1 at the start of the test and monitored throughout the test period with an online pH metering device. It was not necessary to adjust the pH in the ambient pressure test as the pH did not drift more than 0.15 pH units. It was not possible to measure pH at 250 bar in the high pressure autoclave due to practical limitations; however, the pH in the high-pressure autoclave test 3, was comparable to the pH level in test 1 and 2 since the fugacity of CO_2 was similar in the autoclave at approximately 1 bar. The pH of the high-pressure autoclave test 3, was further checked by a calculation made in EOS software package.⁹ The test medium was the ISO 15156 solution which has: 5wt% NaCl + 0.4wt% CH_3COONa .