Impact of time of exposure on HIC testing of very high strength steel in low H_2S environments

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Abstract

The methodology for testing hydrogen induced cracking (HIC) resistance of carbon steel in mild sour service is discussed. When H_2S content is low, the use of steel grades with intermediate HIC resistance often presents many advantages, such as higher mechanical properties and economical benefits. As a counterpart, fit-for-purpose testing procedures are required in order to assess the HIC performance at the intended service conditions. With regards low H_2S environments, time of exposure is recognised as the critical testing parameter.

The environment encountered in the annular space of flexible pipelines is very often mildly severe. Due to the high confinement, pH level is higher than in bulk conditions with the same gas composition but a larger V/S ratio between the volume of electrolyte and the exposed steel surface. H_2S content in the annulus is also less than in the fluid transported in the bore of the pipeline, due to permeation through inner thermoplastic sheaths and consumption. Qualification tests of very high strength steel wires are therefore usually conducted with one month exposure at the predicted pH and P_{H2S} in the annulus, while standard testing procedures referenced in ISO 15156 specify 96 h immersion but a higher H_2S level.

In the present study, different grades of high strength steel wires were tested in environments containing as low as 100 ppmv H_2S, with exposure times varying from 96 hours and up to 1 year. For the steels grades that have been studied, it is confirmed that the actual qualification procedure consisting in 1 month exposure is appropriate to detect HIC susceptibility.

1   Introduction

Development of deep and ultra-deep water fields often requires the use of high strength and very high strength steel wires (UTS≥1000MPa) in flexible pipes in order to sustain mechanical loads [1, 2]. On the other hand, these fields are most of the time considered as containing H_2S at design stage due to the possible souring of the reservoir. Hopefully, in flexible pipe, steel wires are not in direct contact with the conveyed fluid. They are located in the annular space (see Figure 1) which is a specific medium for corrosion, less severe than the bore. These high strength steel wires need to be qualified with regards to H_2S (Sulfide Stress Cracking and Hydrogen Induced Cracking) [2]. Nevertheless, testing procedures referenced in ISO15156 are not appropriate for these high strength wires that have a low H_2S resistance. Therefore for SSC and HIC qualification, environment closer than the one encountered in flexible pipe annulus are tested:

- H_2S and CO_2 partial pressures in the annulus are calculated thanks to a dedicated permeability model [3] that considers permeation through the polymer pressure and external sheaths. Furthermore, as presented in [4], the flow rate of H_2S arriving in the annulus of flexible pipe by permeation through the polymer pressure sheath is very low. The consequence is that when the annulus is flooded, the thermodynamic equilibrium calculated thanks to the permeability model is not reached. Indeed, due to the high confinement, H_2S arriving in the annulus is partly consumed by iron sulfide precipitation. As a consequence H_2S levels in flexible pipe annulus is even lower than presented previously.
- pH is determined from long term experiments in confined environment, where the ratio between the volume of electrolyte and the surface of steel is extremely low, typically between 0.02 and 0.06 mL/cm² [5-8].
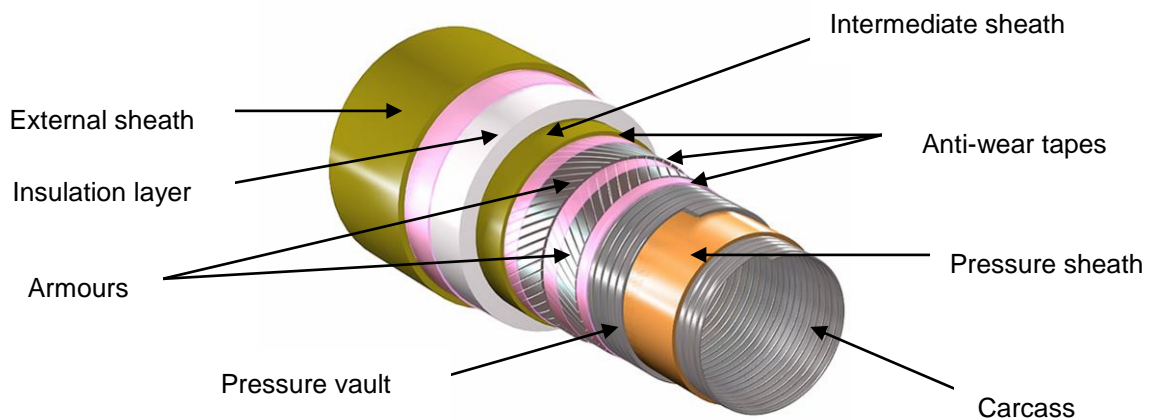
Figure 1: Example of a flexible pipeline structure

Representative environments simulating service conditions are thus characterized by relatively high pH, between 5 and 6, and P_{H2S} often below a few mbar. Fit-for-purpose tests are therefore systematically carried-out to check H_2S suitability of steel grade to target annulus environment. And since H_2S severity is extremely mild, experimental procedures have to be adapted.

The goal of this paper is to discuss methodology for HIC testing of carbon steel wire in mild sour environments. In particular, great attention will be paid to time of exposure. It is well known that high pH and low H_2S induce slow ingress of hydrogen in the steel [9, 10], thus long incubation times before HIC starts. Recent work on linepipe steels have shown that exposure periods of a few weeks were necessary at P_{H2S} below 10 mbar [11]. In this paper, exposure times from a few days and up to one year were performed, to evaluate the evolution of cracking with time, and to determine a reasonable and safe testing exposure period for qualification tests.

2 HIC experiments in low H_2S environments

2.1 Experimental methods

Tested materials

Wires of two carbon steel grades were tested, the first (A) used for sweet service and the second one (B) for mildly sour environments.

Most specimens were 120 mm long, 12 mm large and 5 mm thick. The tested surface condition was either as received (raw surface) or polished. In the as received condition, a thin layer of mixed oxide and phosphate is present due to processing conditions. The applied polishing procedure was in agreement with the HIC NACE standard TM0284 (P320 SiC grit paper). All the cutting edges of the specimens were also polished (P600 SiC grit paper). The specimens were degreased with acetone just before starting the test, otherwise they were oiled and stored in a dessicator.

Experimental procedure

The test matrix included two pH (5.5 and 6), four H_2S levels in a CO_2-H_2S mixture (100, 300, 1000 and 3000 ppm H_2S i.e. partial pressures of 0.1, 0.3, 1 and 3 mbar). The tests were run from 4 days to 1 year. In each condition 10 specimens of each grade were introduced, half as-received and half polished.

Several glass cells were used simultaneously to conduct the tests. The solution composition was 35 g/l NaCl, with $NaHCO_3$ addition to attain the target value of pH. Solutions were prepared with demineralized water and analytical grade chemicals. Gas pre-mix of the required compositions were used to saturate the solution with CO_2-H_2S mixture. The V/S ratio was 20 ml/cm^2.

After placing the specimens in the cell, the cell and the solution were de aerated separately, before introducing the solution. The gas mixture was then bubbled at a high rate for saturation and then at a lower rate to maintain the H_2S level throughout the exposure. A measurement of the sulfide concentration in the solution was performed after saturation, with a specific electrode, in order to ensure that the H_2S saturation was met. The pH was measured either continuously with a pH electrode or checked regularly. If needed, it was adjusted by addition of acidic or basic solutions.

A view of a test cell with the specimens is given in Figure 2a. An example of pH control and measurement during a one year test is provided in Figure 2b.
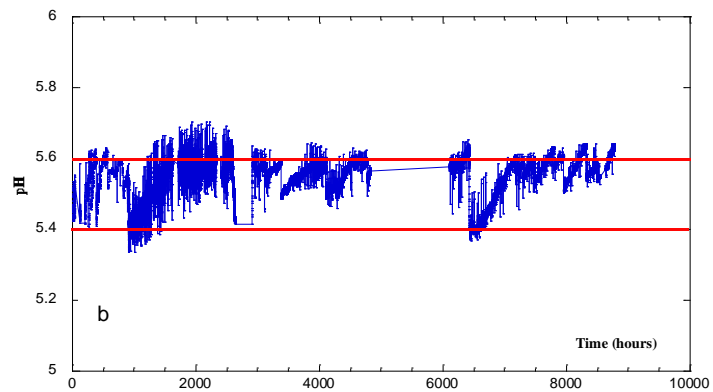
**Figure 2 a-view of a test cell with the specimens;
b-pH evolution during 1 year for a pH 5.5 test**

HIC Evaluation by ultrasonic testing

Ultrasonic inspection was applied using an immersion transducer and a 2 axis scanner. The system was calibrated according to an in-house technique. The total area of each specimen was scanned to detect the presence of internal defects. To eliminate some side-effects, a distance of 10 mm at each end of the sample was not considered for this study.

2.2 Results

2.2.1 Effect of surface condition

The impact of surface preparation is illustrated on Figure 3 for the sweet steel grade (A) tested at pH 6 and 3 mbar H_2S. This impact vanishes at long immersion times. For short tests below 1 month, cracking appears faster on polished specimens than on as received specimens. However, after 1 month exposure even if there is still more samples with HIC on polished samples, by testing enough samples, it is sufficient to detect the onset of cracking in both cases. Similar results were obtained for the mild sour grade (B).

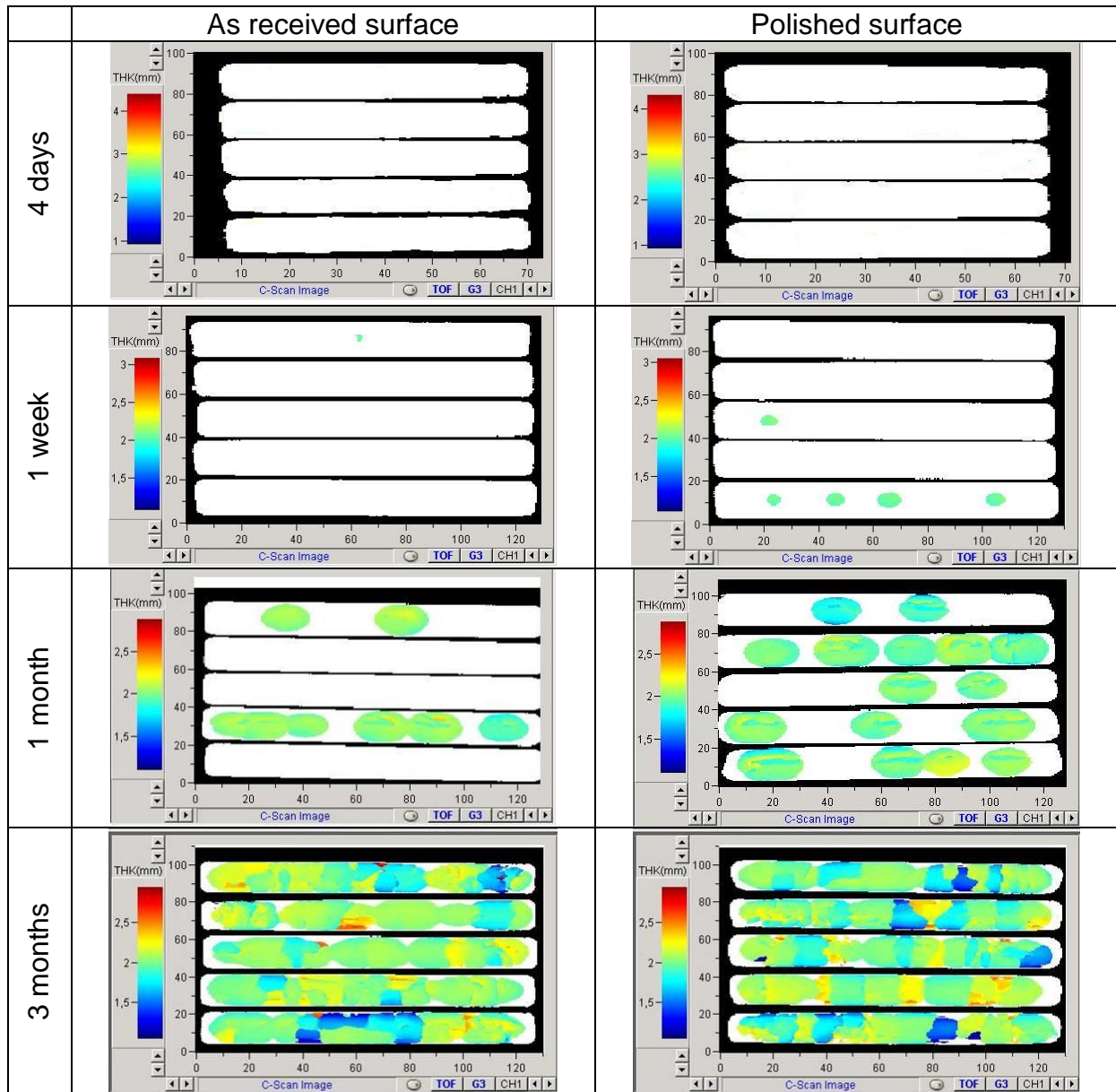|	As received surface	Polished surface
4 days		
1 week		
1 month		
3 months		

Figure 3: Evolution of HIC extent on sweet steel (A) specimens exposed at ambient temperature and pressure in a 35 g/L NaCl solution saturated with 997 mbar CO_2 + 3 mbar H_2S and at pH 6.

2.2.2 Effect of the duration of test

Figure 3 illustrates the evolution of HIC extent of sweet steel (A) exposed at pH 6 and 3 mbar H_2S, for exposure periods from 96 hours to 3 months. The results show that the usual 96 hours exposure test is clearly too short to determine the susceptibility of the steel to HIC at such low H_2S levels. In this environment, the indication obtained after one month are clear, whatever the surface condition.

The effect of even lower H_2S content is presented on Figure 4, with exposures up to 1 year. It appears that the H_2S limit for this sweet grade lies between 0.1 mbar and 0.3 mbar at pH 6.

It is particularly interesting to note that no significant evolution of HIC extent is observed between 3 months and 1 year exposure, suggesting that an equilibrium state was reached. These results also highlight some HIC resistance of this sweet steel grade at 0.1 mbar H_2S and pH 6.

This is in accordance with previous results obtained after one month exposure.

	0.1mbar H_2S raw surface	0.3mbar H_2S raw surface
3 month		
6 month		
1 year		
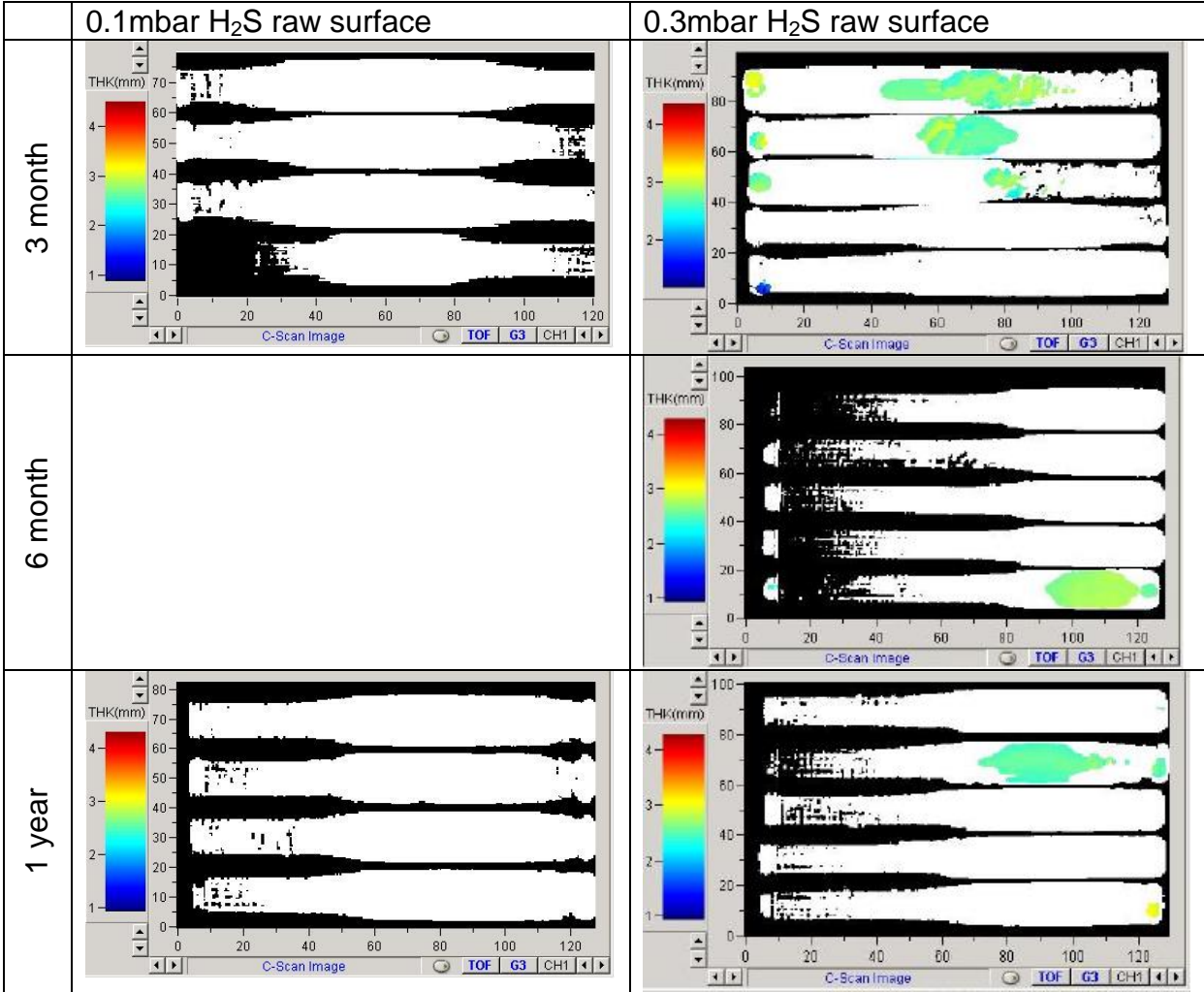
Figure 4: Evolution of HIC extent on sweet steel (A) specimens exposed at ambient temperature and pressure in a 35 g/L NaCl solution saturated with 999.7 mbar CO_2 + 0.3 mbar H_2S and with 999.9 mbar CO_2 + 0.1 mbar H_2S .

Similar tests in more severe conditions were performed with a mild sour steel grade (B), known to offer some resistance to HIC. Tests were performed at pH 5.5, where the limit of use of this steel grade is above 1 mbar of H_2S, as determined by extensive qualification tests based on 1 month exposure time. Longer tests were therefore conducted in order to check that the limits of use of this steel were not falsely influenced by too short exposure times. The results of tests at pH 5.5 and 1 mbar H_2S are presented on Figure 5, and clearly show that no HIC was detected even after 1 year immersion.

3 months	6 months	12 months
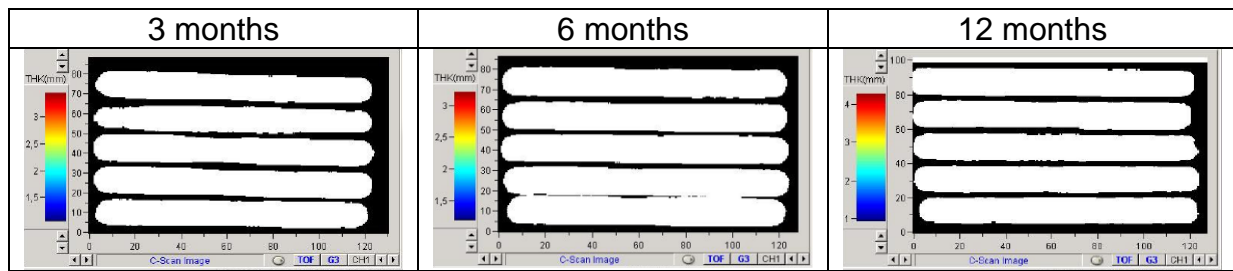
Figure 5: HIC results on a mild sour high strength carbon steel grade tested at pH 5.5 under 1 mbar H$_2$S for 3 months to 1 year

Similarly as Figure 4 showed that 0.1 mbar H$_2$S at pH 6 is included into the safe domain for the sweet grade, we can conclude that 1 mbar H$_2$S at pH 5.5 is into the safe domain of the mild sour grade. It is also confirmed that excessively long term exposures are not necessary, since all experiments show the same type of HIC response (positive or negative) after 1 month and after 1 year exposure.

It can thus be concluded from these tests that 1 month exposure time of steel armor wires offers good confidence for qualification.

3   Conclusions and perspectives

A large campaign of HIC tests has been launched on high strength and very high strength steels wires in very low severe conditions representative of flexible pipe annulus environment, i.e. H$_2$S partial pressure below a few mbar and pH above 5.

These tests have shown that there is no major impact of surface preparation of tested specimens between polished and as received surface for 1 month duration or more.

HIC tests performed at different durations between 96hours and 1 month with low H$_2$S level show that HIC damage increase with time and that a short time test is misleading as HIC has not yet appeared at 96 hours.

In order to demonstrate that 1 month testing is enough in such mild sour environment, longer duration have been tested up to 1 year. For the two steels in the different conditions tested, one month duration has been demonstrated to be sufficient. Indeed no major evolution of HIC damage has been seen between 1 month and 1 year.

One should notice that such results are probably material and environment dependent and therefore not applicable as such for other microstructures or environments. Further studies are ongoing to better understand other environment conditions and materials.

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