Development of new tests to assess sulfide stress corrosion cracking of line pipes

M. Cabrini, S. Lorenzi, T. Pastore, D. Pesenti Bucella, G. Pellegrini, A. Paggi, E. Paravicini Bagliani, P. Darcis

Semi-scale tests were performed with the aim of evaluating the influence on the resistance against SSCC of as-produced inner surface of steel pipes. The activity includes the design of tests on specimens sampled by preserving the inner surface of pipe and preliminary tests, which covers four samples taken from a commercial pipe. Two of the specimens were tested in as-produced surface conditions; the other two were heat treated in order to achieve 24 HRC hardness. Such value is above the minimum limit reported in ANSI/NACE MR0175/ISO15156-1, i.e. 22 HRC. The tests were performed in NACE solution saturated with H_2S at 25°C and 1 bar.

KEYWORDS: SSCC - LINE - PIPE STEELS - SEMI-SCALE TESTS

Introduction

Sulphide Stress Corrosion Cracking (SSCC) is an Environmental Assisted Cracking phenomenon typical of Oil & Gas Industry. The term Environmentally Assisted Cracking (EAC) means the phenomenon that takes place due to the synergistic action of the environment on a susceptible material under tensile loading[1–7]. EAC causes the formation of cracks that propagate under the combined action of stress and environment, with a risk of rupture in structural components even at loads lower than the tensile yield strength.

In Oil & Gas Industry, H_2S is often present in production fluid generally associated with high pressure of CO_2. It can affect both the risk of sweet generalized corrosion and environmental cracking. The iron sulfide corrosion products formed on carbon steel (mainly mackinawite) are poorly soluble. Small amounts of H_2S in mixture with CO_2 can stabilize the scale of carbonate, and thus their formation on the surface can slow down the dissolution rate of steel [8–10]. However, the mixed scale of iron sulfide and carbonate is conductive and can act as an effective cathodic area, changing the corrosion morphology from uniform to localized attack. As far as SSCC is concerned, H_2S increases the concentration of adsorbed hydrogen on the metal surface (Hads) and promotes its entry into the metal. In the presence of external stresses, Sulphide Stress Corrosion Cracking (SSCC) can take place on high strength steels. Its insurgence mainly depends on the H_2S partial pressure, pH and tensile strength of steels. ANSI/NACE MR0175/ISO15156-1:2015 gives requirements and recommendations for the selection and qualification of carbon and low-alloy steels, corrosion-resistant alloys, and other alloys for service in equipment used in oil and natural gas production and natural gas treatment plants in H_2S-containing environments. A limit hardness value of 22 HRC is recommended for carbon steels for sour service, but it is common practice to evaluate the SSCC resistance of materials for Oil & Gas industry by means of experimental tests.

The assessment of SSCC susceptibility of steel for pipelines is generally carried out according to NACE TM0177 by means of constant load tests on specimens sampled from components of large thickness, which show certain variability of microstructure and properties over the depth and between the external surface - subject to high cooling rates during production - and the

**M. Cabrini, S. Lorenzi,
T. Pastore D. Pesenti Bucella**
University of Bergamo, Department of Engineering and Applied Sciences, viale Marconi 5, 24044, Dalmine (Italy); CSGI - Consorzio per lo Sviluppo dei Sistemi a Grande Interfase, via della Lastruccia 3, 50019, Sesto Fiorentino, Italy; Consorzio INSTM - Via G. Giusti, 9, 50121 Firenze (ITALY)

G. Pellegrini
University of Bergamo, Department of Management, Information and Production Engineering, viale Marconi 5, 24044, Dalmine (Italy)

A. Paggi, E. Paravicini Bagliani, P. Darcis
TenarisDalmine, Dalmine S.p.A., Italy

inner one. Furthermore, surface variations of alloy chemical composition - promoted by decarburation or preferential oxidations of alloying elements, during high temperature manufacturing - should be taken into account.
In addition, an oxide layer generally forms during production, which could significantly affect the electrochemical behavior of steel and hydrogen permeation kinetics [11]. The presence of hot mill scale on the metal surface increases the corrosion potential, and in some cases can stimulate the initiation of the stress corrosion cracks [12]. Koh et al reported that cracks nucleate predominantly at nonmetallic inclusions and propagate through the steel matrix in a quasi-cleavage manner regardless of the test materials' compositions [13]. The presence of a multi-layered corrosion film consisting of iron oxides (Fe_2O_3 and Fe_3O_4) and iron sulphides (pyrrhotite, mackinawite and pyrite) was found in the correspondence of the internal surface of a failed pipeline, near the crack nucleation [14]. Residual elements, such as copper, nickel and tin, which are more noble than iron, are usually accumulated at the scale–substrate interface [15,16].
Due to this fact, it is advisable to develop easy and reliable techniques to highlight the material behavior directly on as-produced surfaces, as it can be useful to assess the actual behavior of the material in areas in direct contact with the environment. Anodic reaction of iron dissolution takes place due to hydrogen sulfide chemiadsorption on the steel surface and oxidation according to the mechanism shown by several authors, followed by the formation of mackinawite scale or its dissolution[8,17–19]. Iron sulphide (mackinawite or other complex sulphides) can re-precipitate only once Fe_{2+} e H_{S-} ions in contact with the steel surface reach supersaturation conditions. According to such mechanism, in presence of corrosion products scale on steel causes the modification of the corrosion[20] and SSCC behaviour of steel.
In view of this, the experimental activity is mainly oriented to the evaluation of the geometries of pipe samples taken directly by production by preserving the inner surface, the evaluation of suitable loading scheme and design of the loading device for bending tests to achieve uniform load and deformation condition on the inner surface of the specimen. The design of the testing procedure has been performed by numerical simulations. Experimental validation of the results has been also carried out. Preliminary tests have been carried out with the proposed methodology for examining the behavior of four samples of an experimental steel production. Two of the specimens were tested in as-received conditions and the other two were heat treated in order to achieve a hardness value of 24 HRC, to some extent above the limit reported in NACE MR 0175-12.

Development of the test methodology
The design of the methodology on pipe samples started from the evaluation of the specimen size and the loading scheme to achieve even distribution of stresses along a large area of the internal surface. Among possibilities, four point bending is the most reliable loading scheme, which grant homogeneous stress distribution along the inner surface due to constant bending moment. Actually, the curved geometry of the steel pipe specimens causes a certain inhomogeneity. Starting from this consideration, three different loading schemes were evaluated and the results were compared to four point bending: three points bending, three points bending with prismatic support and tie-rod system.
For the analysis, the material behavior of API 5L X65 steel was modeled by considering elastic modulus of 206000 MPa and yield strength of 448 MPa. The maximum tensile strength in the at the inner surface of the pipe segment was equal to the eighty percent of the yield strength. The specimen width was considered equal to twice the thickness to ensure a plane strain conditions. In view of this assumption, two-dimensional FEM model was considered.

FEM simulations
Simulations were performed for the three point bending (3PB) tests at different thickness, distance between the lower supports (span) and shape of the die (pin or prismatic) (Fig. 1). Further simulations were carried out for the four point bending (4PB) loading scheme at the same span - equal to 80 mm - between the upper die. Two different distances between the lower dies were chosen, i.e. 150 mm and 180 mm. In order to limit the forces necessary for specimen loading, the specimens' sizes were decreased from cross section size of 17x34 mm to 10x20 mm.
The 3PB loading showed the sharpest decrease of stresses moving away from the loading symmetry axis, whilst the more homogeneous stresses distribution along the inner surface was found for 4PB specimens, as expected. Tab. 1 shows the values of force and the stroke on the punch for the different loading conditions. The highest forces on the punch were calculated for 4PB loading condition. The distribution of stresses calculated by numerical simulation for the simulations with 150 mm span and for the 3PB/pin is shown in Fig. 2 and Fig. 3.

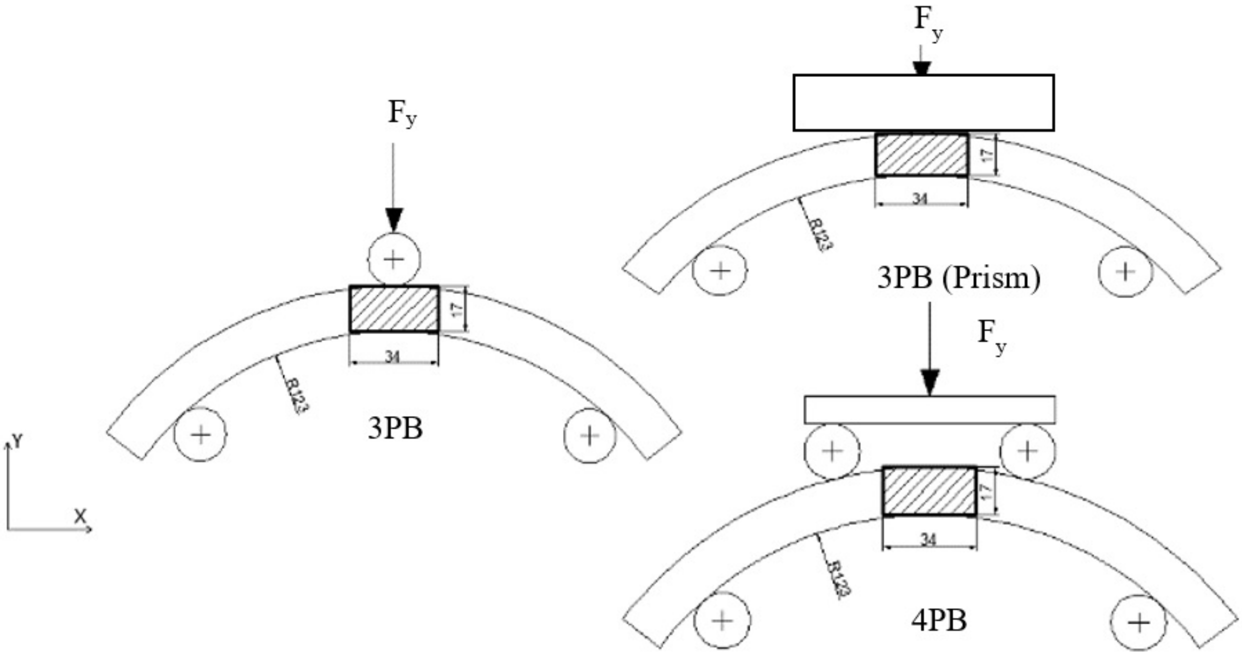

Fig. 1 – Loading devices for three point bending tests (3PB) and four points bending tests (4PB). Specimens with a thickness of 17 mm and a width of 34 mm

Tab. 1 – Results of the FEM simulations

Laoding Devices	Thickness (mm)	Span (mm)	Load element	Upper pin stroke (mm)	Fy (kN)	Gauge length° (mm)
3PB	17	150	Pin*	0.83	13	7.8
3PB	17	180	Pin*	1.68	8.8	10
3PB	17	150	Prism**	0.87	12.9	8.3
4PB	17	150-80	Pin*	1.06	18.6	24.2
4PB	17	180-80	Pin*	1.78	10.8	29.9
3PB	16	150	Pin*	0.88	11.9	7.6
3PB	10	150	Pin*	1.38	2.9	6.5
4PB	10	150-80	Pin*	1.48	4.2	13.2

* Pin Ø20 mm
** Prism 20x10 mm
° Length in which $\sigma > 95\% \sigma_{max}$

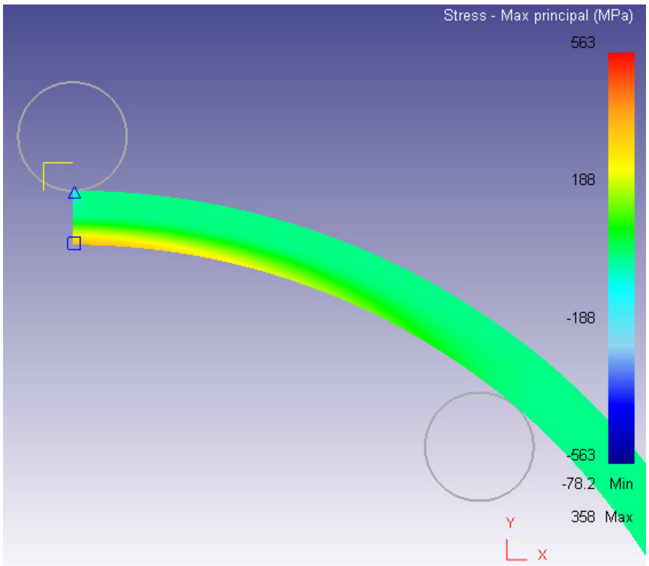

Fig. 2 – Stress distribution for the 3PB load scheme, on the specimen 10 mm thick

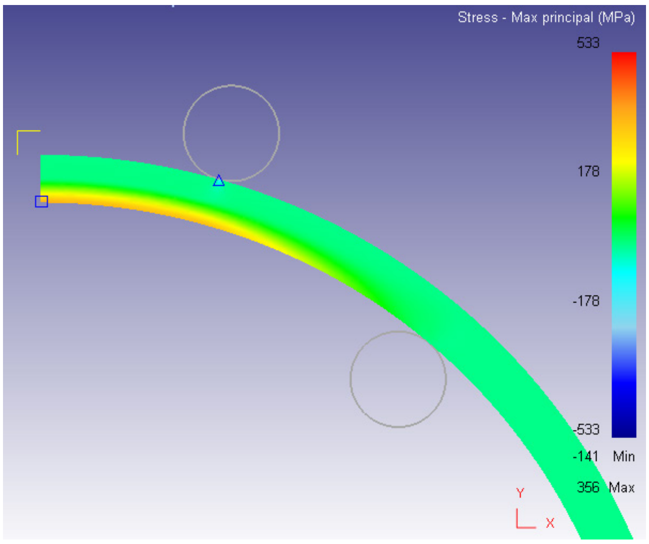

Fig. 3 – Stress distribution for the 4PB load scheme, on the specimen 10 mm thick

A loading system based on the application of tie-rod device placed in correspondence of the inner surface of the specimen was devised to overcome several limits deriving from the application of traditional loading schemes. The designed device is far more compact compared to traditional 4 point and 3 point bending devices and it permits to further reduce the dimensions of the loading device and the surfaces extension in contact with the testing solution. Fig. 4 and Fig. 5 show the design and the assembly of the loading device.

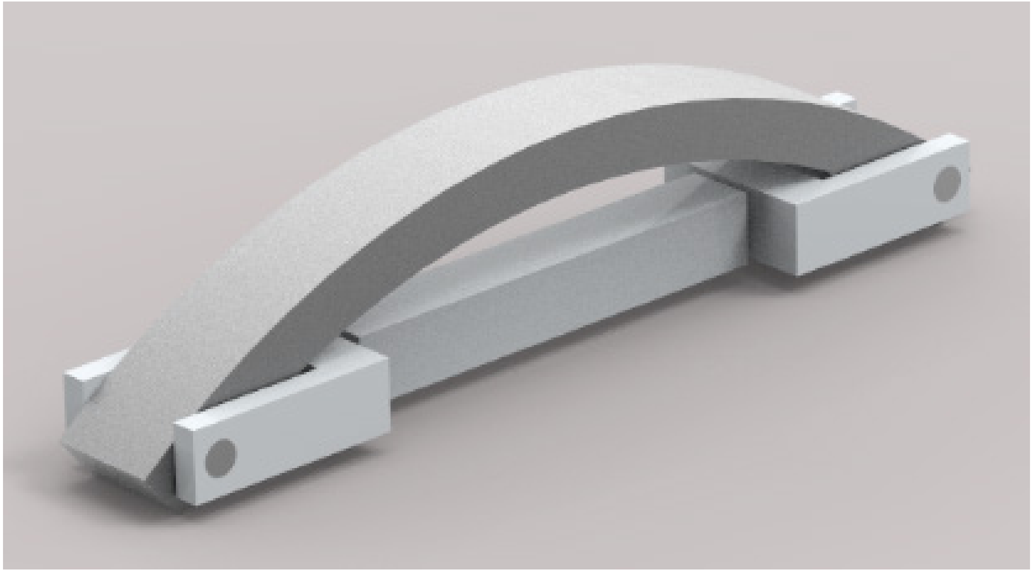

Fig. 4 – Loading device assembled before the test

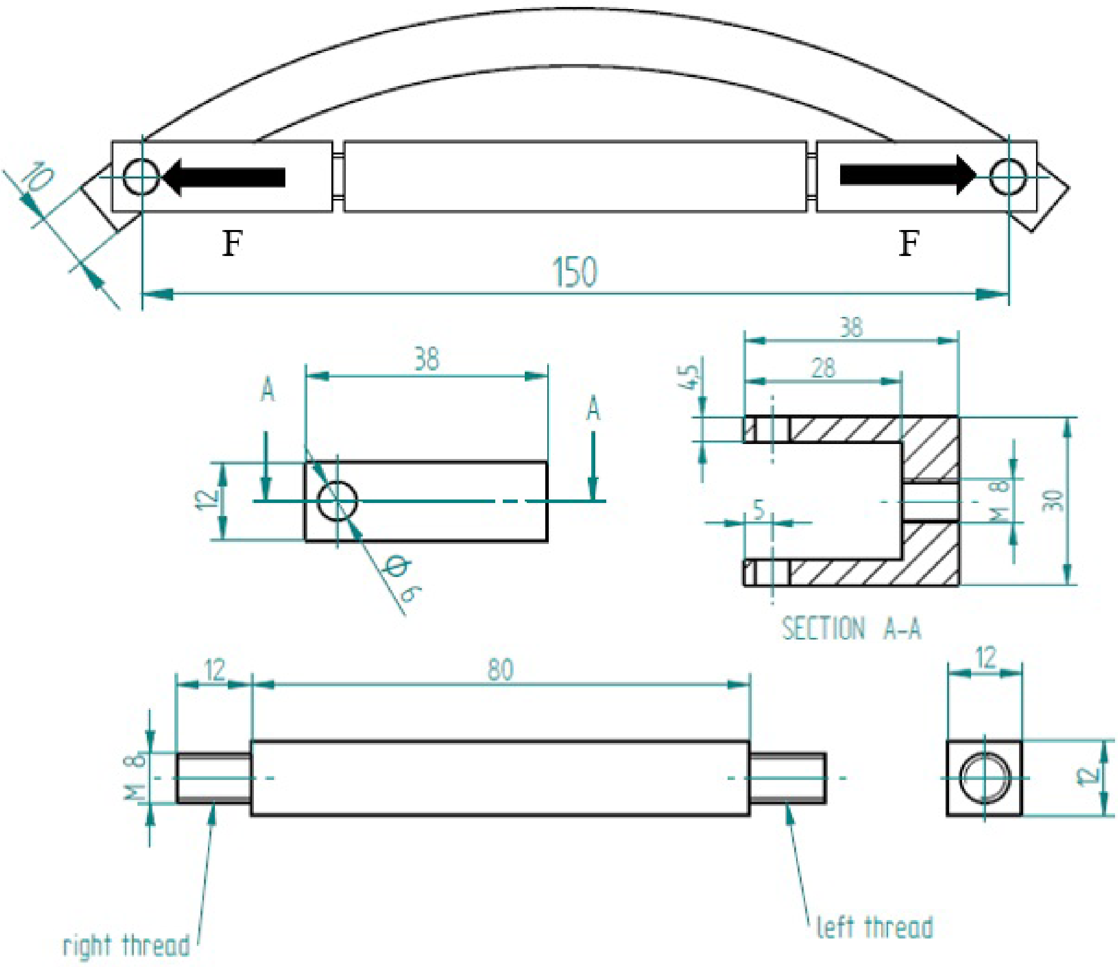

Fig. 5 – Construction drawings and loading scheme of the tie rod system at the intrados

Fig. 6 compares the stress distribution along the tensioned zones in correspondence of the inner zones of the specimen for the three loading schemes. The results refer to the simulations performed in the case of the specimen with reduced thickness (10 mm). As expected, the stresses decrease very rapidly moving away from the load axis for the 3PB scheme, whilst they are quite homogeneous for the 4PB configuration. The tie rod system allows the achievement of homogeneous tensile load at distances up to 15 mm from the symmetry axis. Under such loading case, it is possible to attain homogeneous stress distribution over a curved surface under an arc of about 30 mm. The loading device is definitely more compact compared to the others, and it is than possible to study the behavior of different conditions in the same autoclave thus accomplishing the limitation on the ratio between exposed surface to solution volume. The tie rod system ca be a reliable alternative loading device to assess the SSCC susceptibility of pipe steels with their own natural oxide scale deriving directly from the production process.

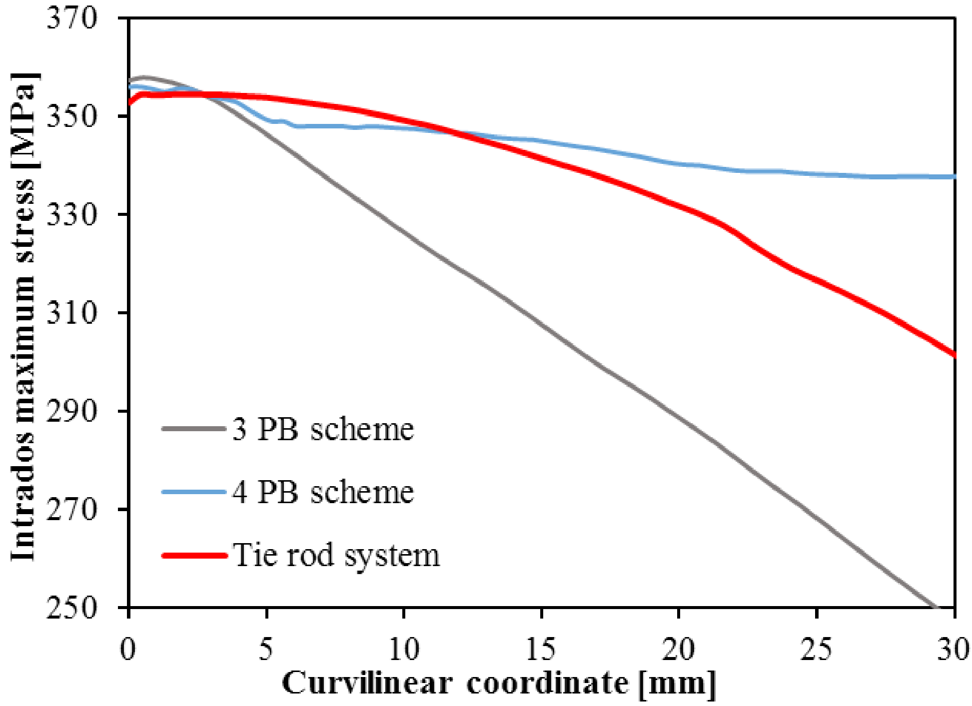

Fig. 6 – Trend of stress in the intrados area, for the tie rod system

Experimental validation

The validation of the numerical results has been performed on pipe sections taken from an experimental heat. The tests have been carried out on four specimens taken from a pipe preserving the as-produced internal surface (Fig. 7). The specimens have 20mmx10 mm cross section. Firstly, circular segments were obtained by external turning of the pipe and subsequent longitudinal cutting. The specimens were then mounted in a numerical controlled milling machine equipped with measurements transducers. The position of the actual axis of the pipe was obtained by numerical interpolation based on seven control points taken with the measuring device. The milling path was then programmed to achieve circular segments by external contouring up to a final thickness of the specimen of 10 mm, constant over the whole length of the specimen (Fig. 8). Subsequently, the 20x10 mm cross section specimens were cut and drilled to achieve the positioning of the pins at 150 mm span.

Fig. 7 – Pipe segments extracted and milled preserving the as-produced internal surface

Fig. 8 – Pipe segments after external contouring by means of peripheral milling

The hardness of the steel considered in the experimentation was 207 HV1, below the limit of 22 HRC specified by NACE MR0175/ISO 15156 for sour environments. In order to variate steel hardness, two specimens were austenitized at 920 °C for 10 minutes, followed by water quenching and tempered at 580 °C for 30 minutes. After quenching, the hardness rises up to 32 HRC (330 HV1) and decreases to 24 HRC (266 HV1) after the subsequent tempering.

Loading calibration procedure

The correlation between load and deformation at the inner and outer surface of the specimen was obtained experimentally by using an INSTRON tensile testing machine. For this purpose, loading and unloading ramps were carried out up to 8000 N. Clip gage was applied in correspondence of the most strained zones (Fig. 9). Fig. 10 shows the loading curves. The curves can be used to fix the target value to achieve at the most strained zone of the inner surface of the specimens. The value of deformation at 80% of the yield strength was taken into account for specimens loading. Practically, 0.1% of deformation measured by the clip gage at the outer surface permits to achieve about 0.20% deformation at the inner surface.

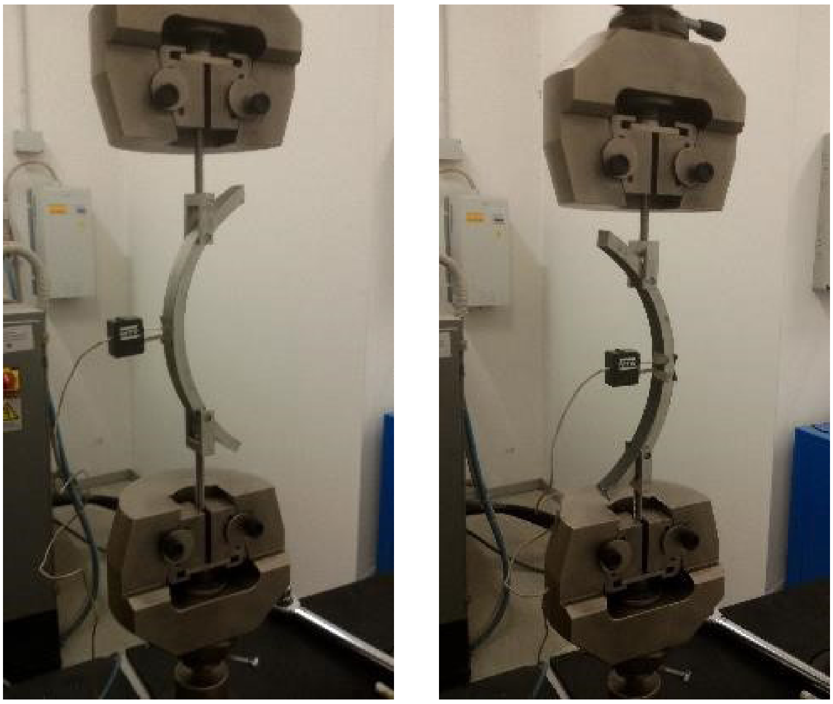

Fig. 9 – Loading and unloading ramps with an INSTRON tensile testing machine

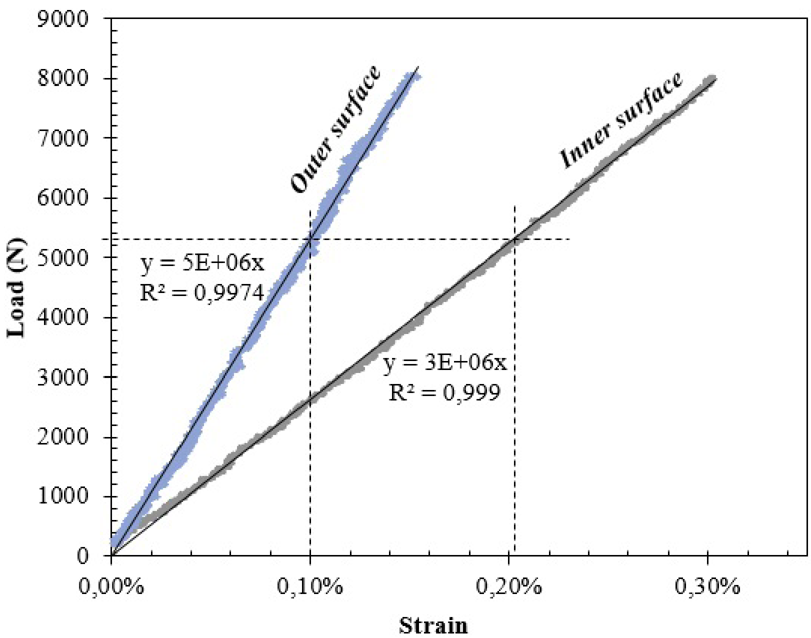

Fig. 10 –Loading ramps for the calibration of specimen loading. Correlation between deformation along the inner surface and outer surface

Specimen loading

After the calibration procedure, the loading of specimens for long-term exposure tests in sour environment was carried out by rotating the threaded sleeve, which increases its length. The device is equipped with right and left-handed threads to act as tie rod system being extended. The deformation at the inner surface is estimated by measuring the deformation at the outer surface by means of clip gage, in analogy to the calibration procedure. The loading procedure was stopped once the target deformation was reached (Fig. 11). During tests, the specimens was loaded at a compression deformation equal to -0.10% at outer surface, corresponding to a tensile stress at the inner surface equal to the 80% of the nominal tensile yield strength.

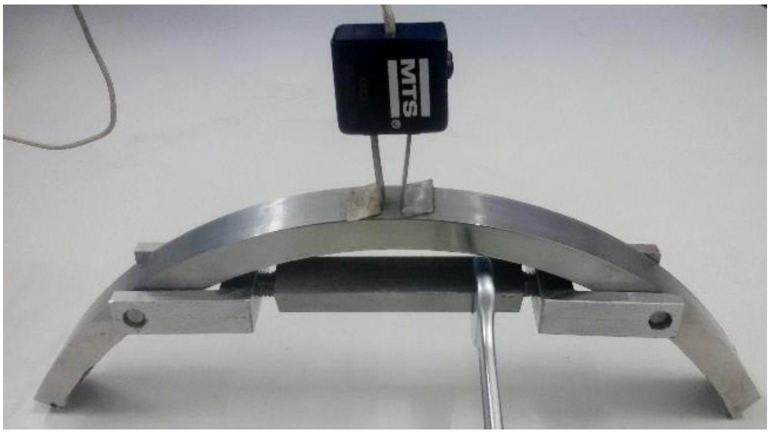

Fig. 11 – Assembly for the specimen loading by means of the tie rod system

Experimental testing

Preliminary tests were performed in Type A NACE solution (0.5% by weight of CH_3COOH and 5% by weight of NaCl, dissolved in distilled water) according to the NACE Standard TM0177-2016, deaerated with N_2 for 24 hours before the test at a temperature of 25 °C and saturated with pure H_2S at 1 bar. The nitrogen flow was then maintained for further 8 hours, before H_2S bubbling. The test duration was equal to 720 hours. The flow of H_2S was constantly maintained during test. At the end of the exposure, the solution was purged with N_2 for at least 24 hours and the specimens were then taken out from the testing chamber.

The specimens were washed with water by using non-metallic soft brush, and then they were degreased in acetone and dried at air (Fig. 12). Finally, the specimens were observed under an optical microscope up to 50x to detect the presence of SSCC cracks. No cracks were observed effect at the optical microscope denoting no relevant effect internal surface produced by manufacturing process adopted for the experimental heat considered for testing. However, further testing should be planned in order to assess conditions representative of production.

Fig. 12 – Aspect of the specimens: a) recovered at the end of the test and b) after washing

Conclusions

New methodology has been proposed for assessing the behaviour of line pipe steel to SSCC steel respect directly on as produced internal surfaces, based on the adoption of tie-rod bending test which permit to fill the gap in literature regarding such topic. Numerical simulation were performed to evaluate the best loading scheme allowing the achievement of constant loading condition on the inner surface of pipe segments obtained directly from production pipes. The system with a central tie rod was adopted in order to achieve uniform distribution of stresses along the inner surface of the pipe segment by using compact device. The suitability of the system have been demonstrated by experimental validation of the numerical results. Experimental test in sour environment have been also carried out on pipe segments obtained from an experimental heat.

REFERENCES

[1] Cabrini, M.; Lorenzi, S.; Pellegrini, S.; Pastore, T. Environmentally assisted cracking and hydrogen diffusion in traditional and high-strength pipeline steels. Corros. Rev. 2015, 33, doi:10.1515/corrrev-2015-0051.

[2] Cabrini, M.; D'Urso, G.; Pastore, T. Evaluation of the resistance to hydrogen embrittlement by the slow bending test; 2008; ISBN 9780080446356.

[3] Cabrini, M.; Pastore, T. Hydrogen diffusion and EAC of pipeline steels under cathodic protection. In Fracture of Nano and Engineering Materials and Structures - Proceedings of the 16th European Conference of Fracture; 2006; pp. 1005–1006.

[4] Cabrini, M.; Lorenzi, S.; Marcassoli, P.; Pastore, T. Hydrogen embrittlement behavior of HSLA line pipe steel under cathodic protection. Corros. Rev. 2011, 29, 261–274, doi:10.1515/CORRREV.2011.009.

[5] Cabrini, M.; Migliardi, L.; Pastore, T.; Spinelli, C. Effect of cathodic potential and strain rate on hydrogen embrittlement of HSLA steels. In Hydrogen Effects on Material Behaviour and Corrosion Deformation Interactions - Proc. of the International Conference on Hydrogen Effects on Material Behaviour and Corrosion Deformation Interactions; 2003; pp. 979–988.

[6] Barsanti, L.; Bolzoni, F. M.; Cabrini, M.; Pastore, T.; Spinelli, C. Hydrogen-embrittlement resistance of X100 steels for long-distance high-pressure pipelines; 2008; ISBN 9780080446356.

[7] Cabrini, M.; Lorenzi, S.; Marcassoli, P.; Pastore, T. Effect of hydrogen diffusion on environmental assisted cracking of pipeline steels under cathodic protection | Effetto della diffusione dell'idrogeno sui fenomeni di environmental assisted cracking di acciai per pipeline in condizioni di protezione catodi. Metall. Ital. 2008, 100.

[8] Sun, W.; Nesic, S. A Mechanistic Model of H2S Corrosion of Mild Steel. NACE Int. - Corros. Conf. Expo 2007, No.07655.

[9] Smith, S. N.; Pacheco, J. L. Prediction of corrosion in slightly sour enviroments. In Corrosion; 2002; p. Paper no. 2241.

[10] Smith, J. S.; Miller, J. D. A. Nature of Sulphides and their Corrosive Effect on Ferrous Metals: A Review. Br. Corros. J. 1975, 10, 136–143, doi:10.1179/000705975798320701.

[11] Hyodo, T.; Iino, M.; Ikeda, A.; Kimura, M.; Shimizu, M. The hydrogen permeation and hydrogen-induced cracking behaviour of line pipe in dynamic full scale tests. Corros. Sci. 1987, 27, 1077–1098, doi:10.1016/0010-938X(87)90100-4.

[12] Cabrini, M.; Lorenzi, S.; Pastore, T.; Bucella, D. P. Effect of hot mill scale on hydrogen embrittlement of high strength steels for pre-stressed concrete structures. Metals (Basel). 2018, 8, doi:10.3390/met8030158.

[13] Koh, S. U.; Yang, B. Y.; Kim, K. Y. Effect of alloying elements on the susceptibility to sulfide stress cracking of line pipe steels. Corrosion 2004, 60, 262–274, doi:10.5006/1.3287730

[14] Azevedo, C. R. F. Failure analysis of a crude oil pipeline. Eng. Fail. Anal. 2007, 14, 978–994, doi:10.1016/j.engfailanal.2006.12.001.

[15] Grabke, H. J.; Leroy, V.; Viefhaus, H. Segregation on the Surface of Steels in Heat Treatment and Oxidatio. ISIJ Int. 1995, 35, 95–113, doi:10.2355/isijinternational.35.95.

[16] Chen, R. Y.; Yuen, W. Y. D. Review of the high-temperature oxidation of iron and carbon steels in air or oxygen. Oxid. Met. 2003, 59, 433–468.

[17} Bai, P.; Zhao, H.; Zheng, S.; Chen, C. Initiation and developmental stages of steel corrosion in wet H2S environments. Corros. Sci. 2015, 93, 109–119, doi:10.1016/j.corsci.2015.01.024.

[18] Zheng, Y.; Brown, B.; Nešić, S. Electrochemical study and modeling of H2S corrosion of mild steel. Corrosion 2014, 70, doi:10.5006/0937.

[19] Veloz, M. a.; González, I. Electrochemical study of carbon steel corrosion in buffered acetic acid solutions with chlorides and H2S. Electrochim. Acta 2002, 48, 135–144, doi:10.1016/S0013-4686(02)00549-2.

[20] Choi, Y.-S.; Nesic, S.; Ling, S. Effect of H2S on the CO2 corrosion of carbon steel in acidic solutions. Electrochim. Acta 2011, 56, 1752–1760, doi:10.1016/j.electacta.2010.08.049.