ISSN 2176-5480

22nd International Congress of Mechanical Engineering (COBEM 2013)
November 3-7, 2013, Ribeirão Preto, SP, Brazil

SUSCEPTIBILITY STUDY OF STRESS CORROSION CRACKING IN FLEXIBLE PIPE TENSILE ARMORS

Paloma Pereira da Silva Coelho
Fabio de Souza Pires
GE Oil & Gas do Brasil - Rua Paulo Emidio Barbosa, 485, Quadra 6.1 (parte) - Parque Tecnológico da UFRJ, Cidade Universitária - Ilha do Fundão, Cep: 21941-615 - Rio de Janeiro, RJ – Brazil
paloma.coelho@ge.com
fabio.pires@ge.com

Paulo Pedro Kenedi
Luís Felipe Guimarães de Souza
PPEMM - Programa de Pós-Graduação em Engenharia Mecânica e Tecnologia de Materiais - CEFET/RJ - Av. Maracanã, 229 - Maracanã - RJ - CEP 20271-110 - Brazil
pkenedi@cefet-rj.br
lfelipe@cefet-rj.br

Abstract. *In Brazil, the main pipeline systems used in the processes of production, exploration and transportation in oil and gas offshore units are flexible pipes. During transportation of the fluid produced in the flexible pipes, corrosive gases such as H_2S and CO_2 permeate through the polymeric barrier layer, creating an aggressive environment in the annular space. At this location are found carbon steel structures known as flexible pipe tensile armours. The tensile armours can suffer a process of embrittlement due to the presence of free hydrogen in the annular space as a result of corrosion processes linked to the permeated gas. The presence of H_2S in the pre-salt fields coupled with the residual stresses from the manufacturing process and service, can lead to the occurrence of the phenomenon of stress corrosion cracking, which could cause the tensile armours failure. This paper aims to evaluate the flexible pipe tensile armours susceptibility to stress corrosion cracking using a slow strain-rate tests technique.*

Keywords: *stress corrosion cracking; flexible pipe; slow strain rate test*

1. INTRODUCTION

Flexible pipes systems are a fundamental part of the development of an oilfield and influence the design and specification of other system components. The pipe system to be used in a specific project is a strategic part of the business and is directly related to the subsea layout arrangement and are also related to the floating production unit used (Semi-Submersible Platforms, Floating, Production, Storage and Offloading Vessels (FPSO), etc.). The internal structure and dimensions of the flexible pipe are dependent on the design variables such as the operating depth, the severity of the fluid to be transported (high levels of H_2S and CO_2), the fluid temperature, external temperature, operation pressure cycling and others.

In some cases, the fluid conveyed across the flexible pipe consists of a multi phase mixture of liquid and gases. Certain gases in the fluid composition, such as CO_2, H_2S and CH_4 permeate through the polymeric fluid barrier reaching the pipe’s annulus. In contrast, in the case of a breach in the outer sheath, or leakage in the outer sealing system, the pipe’s annulus becomes flooded with seawater. As a result of the combination of these factors, the pipe annulus is no longer a dry environment, and it becomes, in the presence of these gases and water, an aggressive environment with pH typically ranging from 4.0 and 5.0.

The aggressive environment of the pipe annulus is related to factors such as fluid composition, polymer used in barrier pressure, internal and external temperature, operating pressure, fluid permeability among others. These factors vary with each project, presenting a great range and complexity of service environments to study in order to understand the behaviors of the materials.

Based on the information available for a specific application, a numerical model is used to predict the most probable critical environment composition of the pipe annulus that can be achieved during the service life, resulting in partial pressures for each of the risk components. The design of a flexible pipe takes into account this calculation for the selection of the most appropriate materials. The aggressive environment can lead to premature failure of the structure with loads considerably lower than expected for the dry annulus condition.

In view of the above, the objective of this study was to evaluate corrosion susceptibility of tensile armor wires in flexible pipes, simulating the effect of partial pressure of H_2S in the annular space, generating valuable test data to support flexible pipe design for such harsh environments. The methodology consisted of using a slow strain-rate tests technique according to (ASTM G129 – 00, 2006).

2. METHODOLOGY

2.1 Slow Strain Rate Technique (SSRT)

In order to establish the risk of stress corrosion in a given application, it is necessary to carry out simulation testing under representative service exposure conditions. The aim of stress corrosion testing is usually to provide information more quickly than can be obtained from service experience. The slow strain rate technique is one of the methods of loading test pieces to investigate the resistance of metallic materials to environmentally assisted cracking. (ISO 7539-1, 1995)

The slow strain rate test involves the application of very slow strain rates (typically $<10^{-4}$ s^{-1}), which are achieved by a constant extension rate on the specimen while monitoring load and extension of the specimen. The test always produces fracture of the test specimen. The results from tests conducted in the test environment are compared to corresponding test results for the same material in a control environment.

The ratios from test environment and control environment shall be utilized in evaluating the test results data for a particular extension rate as following (ASTM G129 – 00, 2006):

- Time-to-Failure Ratio (TTFR);
- Plastic Elongation Ratio (PER);
- Reduction in Area Ratio (RAR);
- Notch Tensile Strength Ratio (NTSR);
- Plane Strain Threshold Stress Intensity Factor Ratio;
- Threshold Stress Intensity Factor Ratio.

The equipment required for slow strain testing is a device which permits a selection of strain rates whilst being powerful enough to cope with the loads generated. The apparatus must allow a selection of crosshead speeds in the range 10^{-3} to 10^{-7} in/s and it should be conducted of constant extension rate in the range from 10^{-4} to $10^{-7}s^{-1}$. In accordance with (ISO 7539-1, 1995), this speed range produces a strain rate that is slow enough to allow corrosive processes to occur and fast enough to produce failure of the specimen in a reasonable period of time for materials evaluation. It should also be noted that strain rate can affect the resistance of the material (ductility, that is, reduction in area) as show in Fig. 1 from (ASTM G129 – 00, 2006).

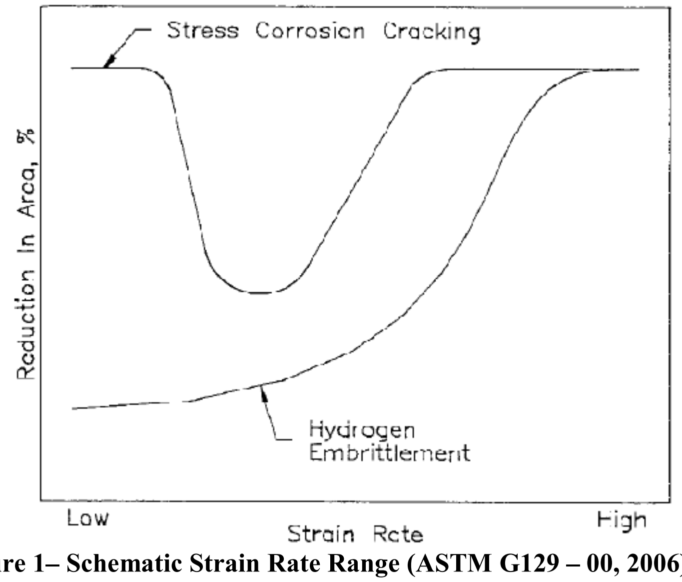

Figure 1– Schematic Strain Rate Range (ASTM G129 – 00, 2006).

For evaluating the effect of sulfide stress corrosion cracking using slow strain rate testing in aqueous media, it should be understood that H_2S dissolves to form acidic solutions, and remains as stable species in low pH (pH < 6) conditions. In operating conditions where a metallic material susceptible to the stress corrosion cracking is in an aqueous media in the presence of H_2S, a corrosion reaction occurs; on the metal surface cathodic reduction produces hydrogen some of which is adsorbed, and can diffuse as elemental atoms through the metal (Cramer, 2003).

A number of theories may explain the phenomenon of hydrogen embrittlement. These include the exertion of an internal gas pressure at inclusions, grain boundaries, surfaces of cracks, dislocations, or internal voids (Kerlins, 1987). In order to evaluate the influence of partial pressures of H_2S on tensile armors' resistance, operating in aqueous environments containing high concentrations of chlorides, a procedure was established for slow strain rate testing.

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2.2 Apparatus

The tests were performed at the Testing Laboratory of H_2S, CO_2 and Corrosivity (LAH_2S) at Brazilian National Institute of Technology (INT). The effect of corrosion against mechanical stress was evaluated by stress corrosion tests based on procedures described in ASTM G129 – 00, 2006 and NACE TM0198, 2011 standards.

A testing programme was established to evaluate the material behavior in different test environments. The material sample studied was a carbon steel tensile armor wire. The wires consisted of a carbon steel with 0.65%C produced by hot rolling with the finishing temperature being below the recristalization temperature. The tests were conducted in the air and in aqueous media containing 120,000 ppm of chloride in the form of NaCl, 0.4 g/L of sodium acetate and two H_2S partial pressures levels: media X with lower H_2S concentration and media Y with high H_2S concentration (3.3 times X media concentration).

The tests were run using a universal mechanical testing system with 100 kN load capacity, shown in Fig. 2, utilizing a slow cross-head velocity of around 10^{-4} mm/s. This velocity is in the range recommended by (ASTM G129 – 00, 2006), and according to (Parkins, 1984) is sufficient for typical corrosion cracking occurs in a reasonable period of time considering mechanical stress and corrosive environment interaction.

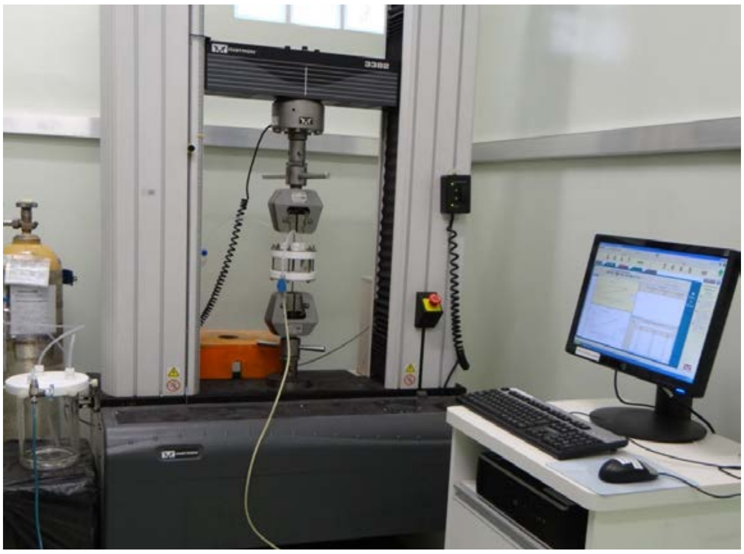

Figure 2 – Mechanical testing system and apparatus used.

2.3 Test Environment

The test programme will evaluate the material's resistance behavior under different test environments to assess the influence of H_2S partial pressure on the tensile armors of flexible pipes. Table 1 presents the test details. For each test media condition three specimens were evaluated.

Table 1 - Tests Parameters.

Test Media		pH	Slow Strain Rate [s^{-1}]	P_T [bar(a)]	Level of H_2S Partial Pressure		Test Temperature [ºC]
A	Air	N/A	2.54×10^{-4}	1	N/A		23 ± 2
B	120000 ppm Chloride + 0,4g/L Sodium Acetate	3.96	2.54×10^{-4}	1	Low	X	23 ± 2
		3.96	2.54×10^{-4}	1			
		3.96	2.54×10^{-4}	1			
C	120000 ppm Chloride + 0,4g/L Sodium Acetate	3.98	2.54×10^{-4}	1	High	Y = 3.3 X	23 ± 2
		3.96	2.54×10^{-4}	1			
		3.96	2.54×10^{-4}	1			

2.4 Teste Sample Evaluation

At the end of the tests, the samples were removed from the test machine, washed in distilled water, dehydrated with acetone and dried with hot air. After this step, the fracture surfaces of the specimen were observed. Stress corrosion susceptibility was evaluated using Stress x Strain and Stress x Strain Correct curves. In order to confirm the results of the tests and determine the type of fracture occurred, the test samples were analyzed in the fractured zone by Scanning Electron Microscope (SEM).

3. RESULTS

The Load vs Displacement curves were obtained and due to the inability to measure the real strain of the material in test solution, it was considered the displacement of the test machine cross head as the indirect measure of strain. The strain considered was $\Delta L / L_0$, where ΔL is the measured displacement of the cross head and L_0 is the effective length of gage section of the specimen.

In the course of tests it was observed that due to the severity of the test media, the material suffered little, and in some cases, no plastic deformation. In order to better quantify the plastic regime of the material and be able to compare more quality measures, a test was conducted in air to measure the true strain through the use of a clip-gauge, in order to calibrate the results obtained and, in this way, remove the effects of deformation from the set machine - grips. It is considered that the stiffness of the machine and the grips remained constant in all tests.

The ratios between the test environment and test control environment were established according to (ASTM G129 – 00, 2006) and were used to carry out a qualitative/comparative assessment of the behavior of the material related to stress corrosion cracking.

Stress vs Strain Curves and the Stress vs Strain corrected curves were obtained. In addition, as shown in Table 2, the ratios of Time-to-Failure (TTFR), Total Elongation (TER), Plastic Elongation (PER); Tensile Strength (TSR) and Maximum Tensile Stress (MTSR) were determined. The ratios of media B and C mentioned in Table 2 refer to the values obtained from the environment test condition versus the corresponding value determined in the control environment condition (media A).

To exemplify, the Eq. (1) was used in the calculation of the ratios as set out in the (ASTM G129 – 00, 2006) standard.

$$PER = \frac{E_e - E_c}{E_e} \cdot 100 \tag{1}$$

Where, in this case, *PER* corresponds to elongation in the plastic region.

Table 2 – Slow Strain Rate Test Ratio Results

Variable	Media A Ratio	Media B Ratio	Media C Ratio
Time-to-Failure Ratio (TTFR)	1.00	0.59	0.55
Total Elongation Ratio (TER)	1.00	0.69	0.59
Plastic Elongation Ratio (PER)	1.00	0.33	0.07
Tensile Strength Ratio (TSR)	1.00	0.94	0.93
Maximum Tensile Stress Ratio (MTSR)	1.00	0.97	0.97

The evaluation of slow strain rate test results is based on the decrease in the value of the ratios from unity. As show on Tab. 2, as expected, the media C with high concentration of H_2S generally presents the lower values of ratios indicating an increasing susceptibility to environmentally assisted cracking. The increasing susceptibility is most evident in the Plastic Elongation Ratio (PER).

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Figures 3 and 4 show the average curves of the total and plastic elongation results obtained in the tests conducted in the air and in the corrosion media.

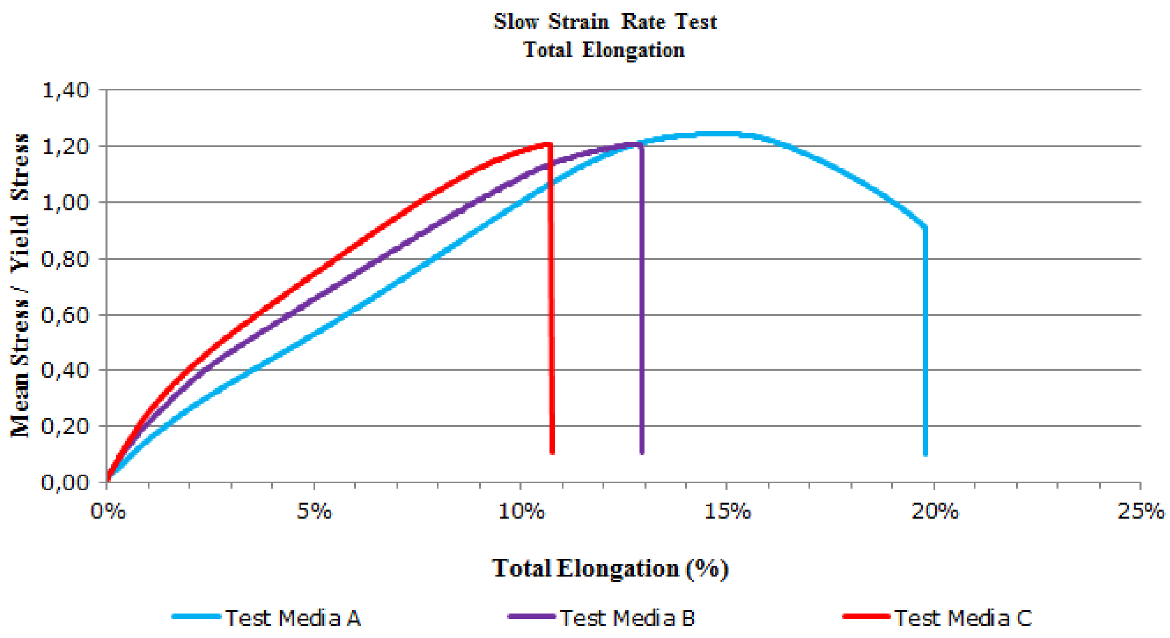

Figure 3 – Normalized Stress vs Total Elongation (%) of flexible pipe tensile armors.

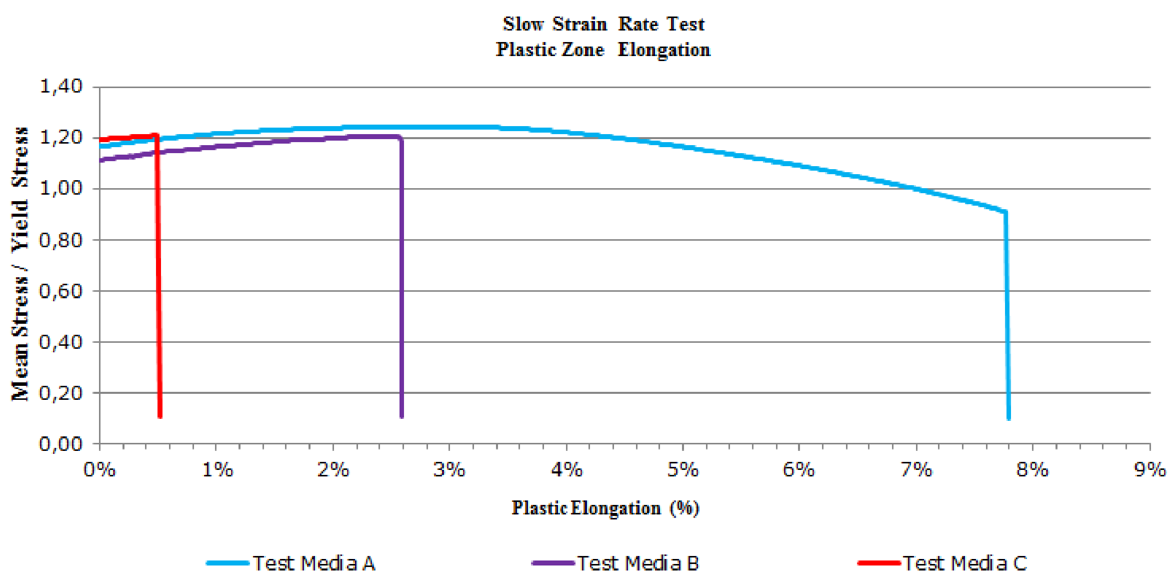

Figure 4 – Normalized Stress vs Plastic Elongation (%) of flexible pipe tensile armors

Note that the test media A (in air), used as reference, presented a superior performance when compared with the tests in media B and C. As can be seen in Table 1, the high concentration of H_2S in media C compared to that in media B had a deleterious effect.

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Figures 5 and 6 show a comparative approach between results of the total elongation and plastic elongation obtained in the tests. The corrosion media values are presented as a proportion of those from test media A.

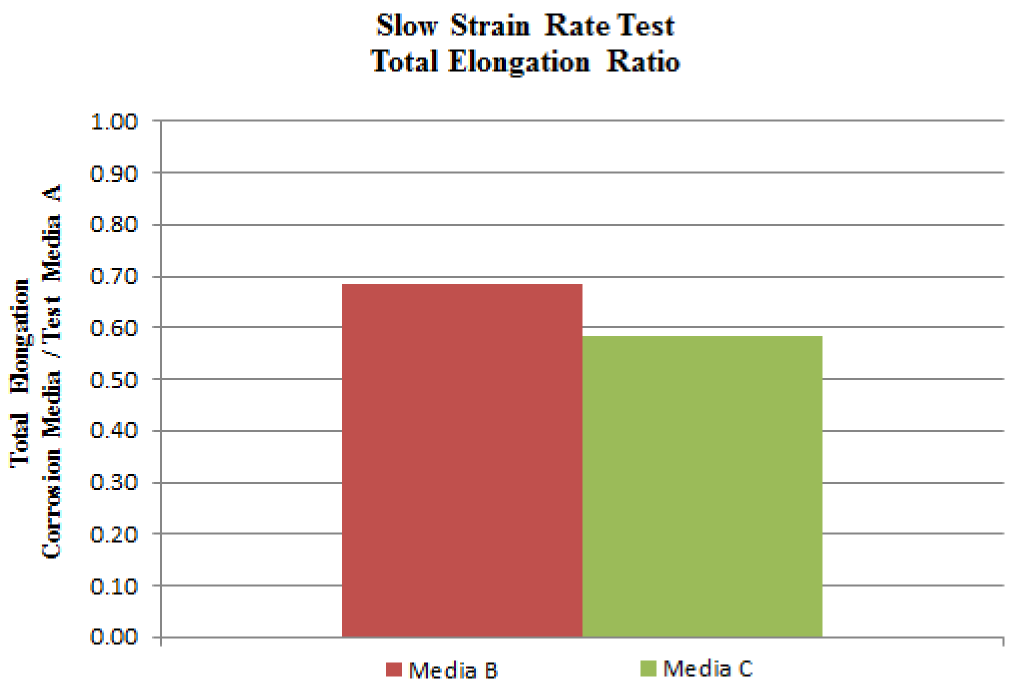

Figure 5 – Total Elongation Ratio Comparison**.**

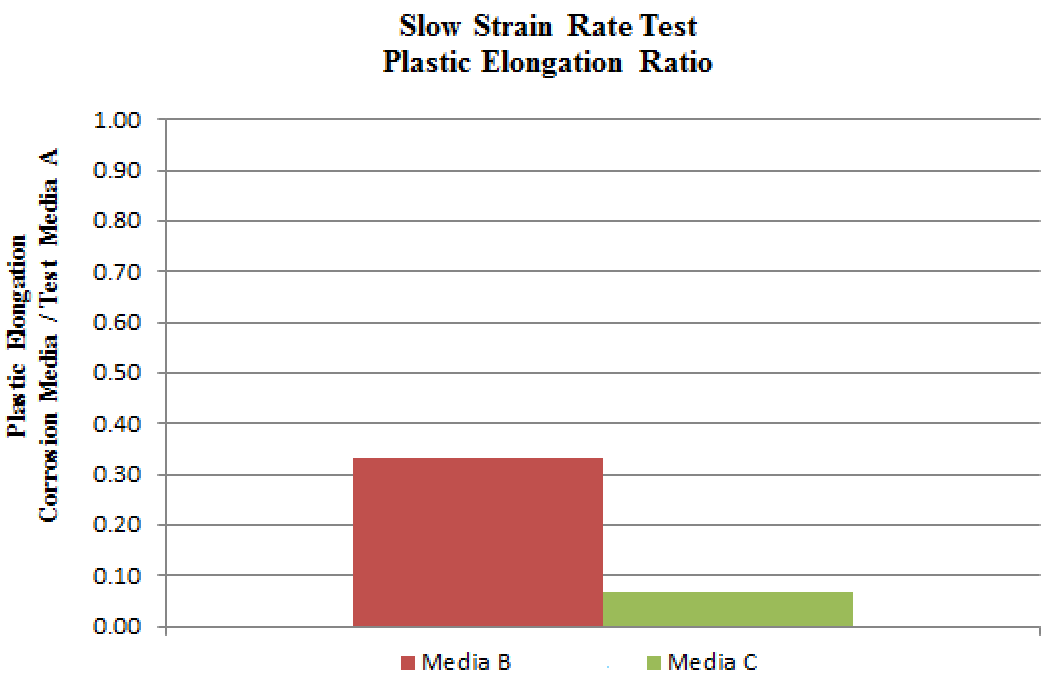

Figure 6 – Plastic Elongation Ratio Comparison.

Note, principally, in Figure 6 the huge effect of H_2S concentration in material performance, which confirms its already known deleterious effect.

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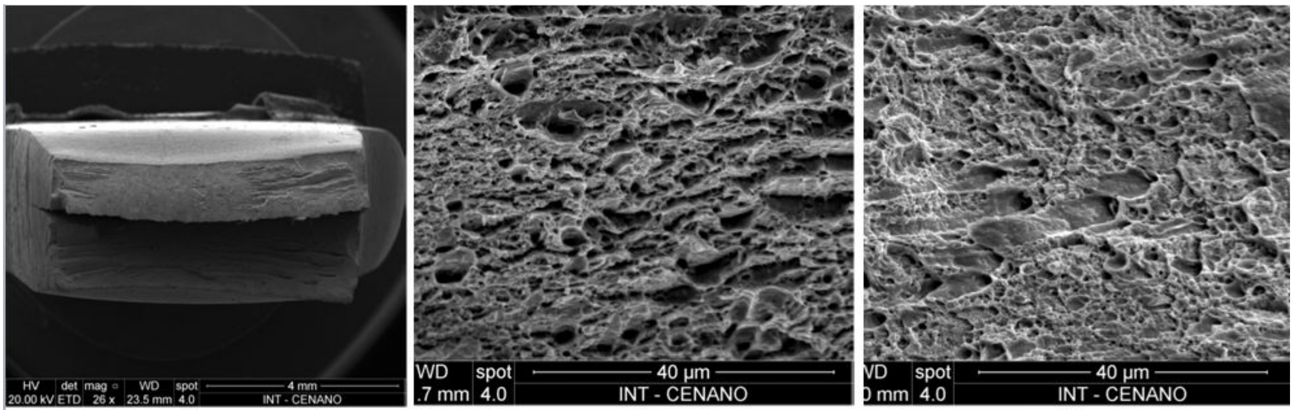
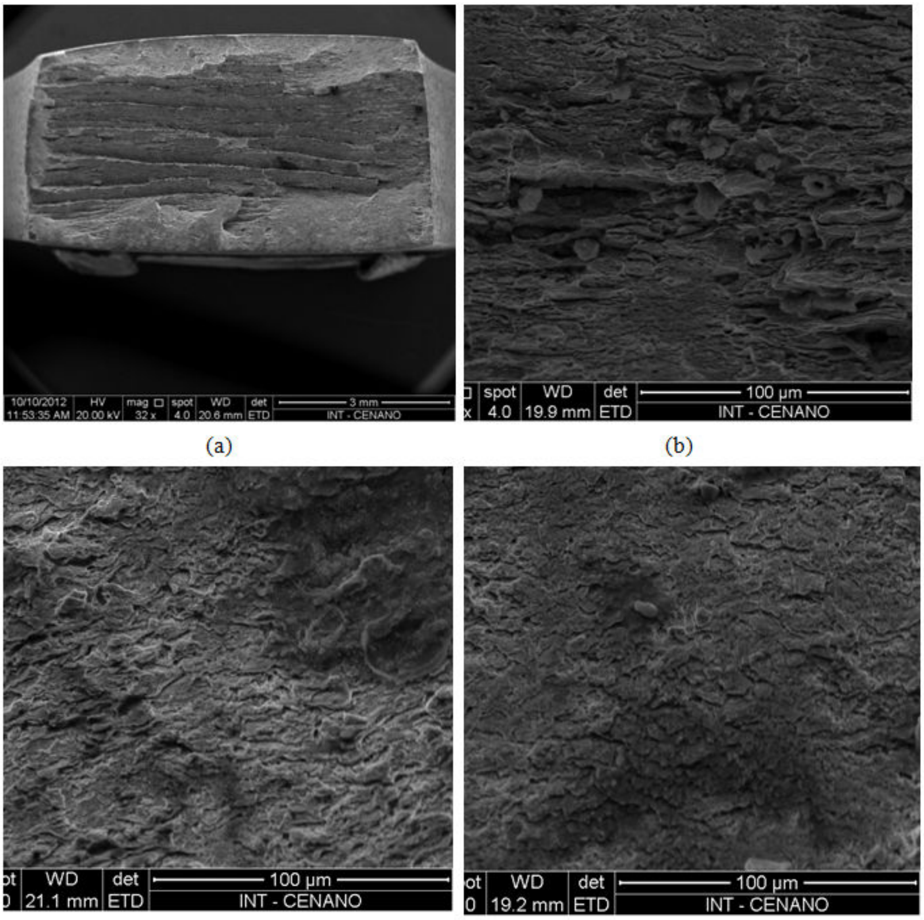
Figures 7 and 8 present typical fractures occurring in Test Media A (Air) and in Test Media B (low concentration of H_2S) respectively, focusing on the zone of transverse fracture. The macroscopic analysis of samples reveals the occurrence of significant plastic deformation (Figs. 7.a and 8.a) manifest also by area reduction. The examination of the fracture surface at higher magnification reveals the occurrence of dimples (Figs. 7.b and 7.c) typical of a ductile fracture. For the test media B the examination of the fracture surface shows a different morphology with discrete occurrences of dimples prevailing areas of quasi-cleavage mode of fracture (Figs. 8.b, 8.c and 8.d).



(a) (b) (c)

Figure 7 – Fractography of the specimens after testing in media A. (a) Macroscopic appearance, (b) Fractography from central region (ductile fracture), (c) Fractography from edge region (ductile fracture).



(c) (d)

Figure 8 – Fractography of the specimens after testing in media B (low concentration of H_2S). (a) Macroscopic appearance, (b) Fractography from central region, (c) and (d) Fractography from edge region.

ISSN 2176-5480

Figure 9 presents the fracture surface from Test Media C (high concentration of H_2S) again looking at the zone of transversal fracture. It can be observed that in this media the reduction of area (Figure 9a) is lower than in the former conditions, which correlates with the lower elongation of the sample. The surface fracture presents aspects of rupture by dimples and quasi-cleavage mechanisms (Figs. 9.b, 9.c and 9.d).

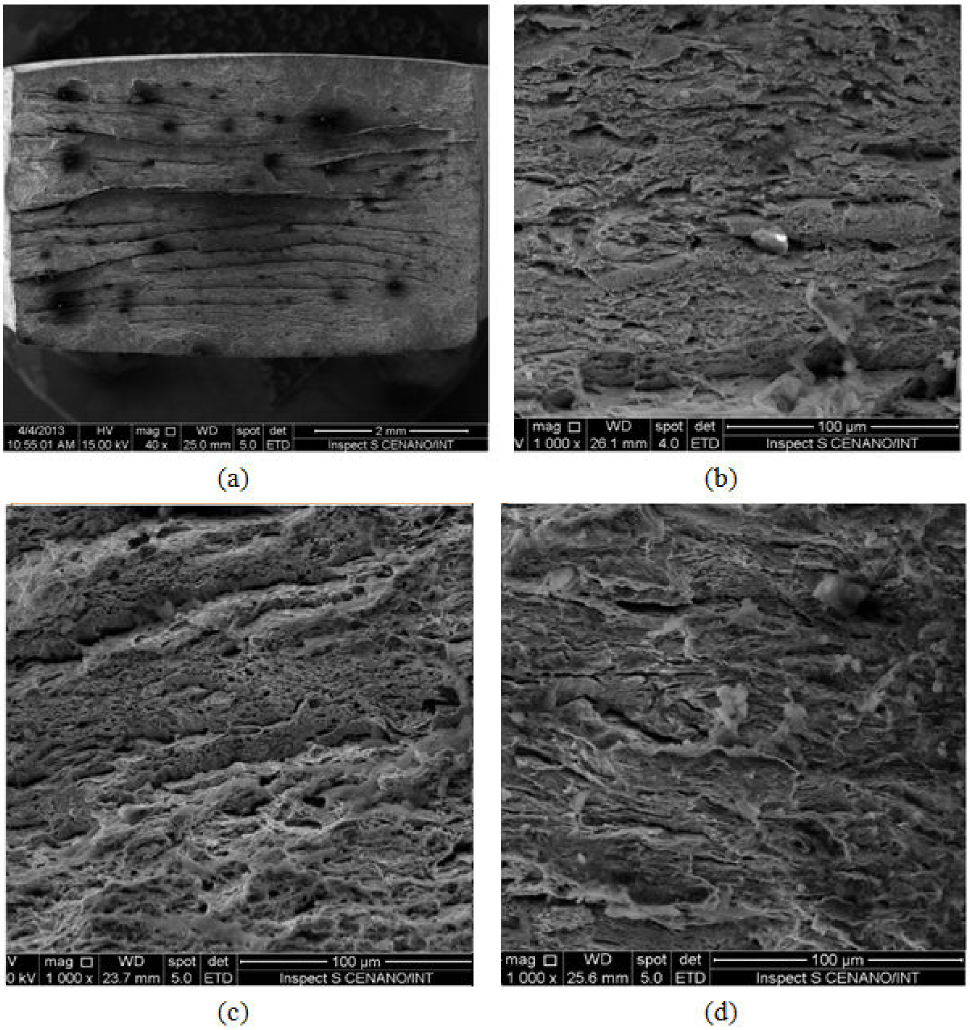


Figure 9 – Fractography of the specimens after testing in media C (high concentration of H_2S). (a) Macroscopic appearance, (b) Fractography from central region, (c) and (d) Fractography from edge region.

For all samples the macroscopic observation shows a delamination aspect of the surface fracture. This behavior can be attributed to the manufacturing process of the wires which are submitted to a severe plastic deformation under the critical temperature. The unidirectional high plastic deformation leads to a preferential orientation of the ferrite grains resulting in a layered microstructure which can deflects cracks propagating through the material (from Voort, 1987).

4. CONCLUSIONS

The macroscopic analysis of fracture surfaces indicated that all samples had aspects of low ductility with flat regions possible featuring cracking, however there was no macroscopic evidence of stress corrosion cracking. The microscopic analysis of the fracture surfaces of samples tested in a high concentration of H_2S did show signs of stress corrosion cracking, featuring secondary fracture surface cracking. Some evidence was compromised by corrosive attack of the fracture surface which occurred during the tests.

It is possible to compare the loss of ductility of the material through the plastic elongation ratio; evaluating corrosive media results against the air results, using aqueous solutions containing 120,000 ppm of chloride (Cl^- in the form of NaCl) and 0.4 g/L of sodium acetate (CH3COONA) saturated with partial pressures of H_2S. It was observed that the samples tested in a low concentration of H_2S retained only 33% of the plastic elongation ratio of that in test media A; (air) however with an increase of H_2S partial pressure the loss of plastic elongation ratio was augmented, falling to only 7% of that in test media A.

The tests carried out under plastic deformation with increasing strain rates induce a destabilization of the surface in contact with the corrosive medium and facilitates hydrogen adsorption by the material. In accordance with NACE TM 0198, 2011 criteria, the samples tested in high H_2S were classified as Class 4, with evidence of stress corrosion. The samples tested in low H_2S were classified as Class 3, with significant loss of ductility without signs of stress corrosion cracking.

5. FURTHER ACTIONS

Expand the test scope to include different H_2S partial pressures in order to identify a threshold pressure where the stress corrosion cracking starts to occur in order to determine a utilization limit for the examined material. Expand the test scope including tests at different pH levels such as 3.5 and 4.5

6. ACKNOWLEDGEMENTS

The authors would like to thank GE Oil & Gas do Brasil Technology Management and Brazilian National Institute of Technology (INT) which has been responsible for executing the experiments.

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