



24th COBEM - 2017



24th ABCM International Congress of Mechanical Engineering
December 3-8, 2017, Curitiba, PR, Brazil

COBEM-2017-0747

DEVELOPMENT OF AN EQUIPMENT TO EVALUATE THE SUSCEPTIBILITY TO HYDROGEN ASSISTED CRACKING

Guilherme Antonelli Martiniano

Danilo Eduardo Fonseca Souza

José Eduardo Silveira Leal

Sinésio Domingues Franco

Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2121, Santa Mônica, 38400-902, Uberlândia - MG
gamartiniano@gmail.com; daniloefsouza81@gmail.com; joseleal@ufu.com.br; sdf franco@ufu.br

Marcelo Torres Piza Paes

Francisco Francelino Ramos Neto

Petrobras, Centro de Pesquisas e Desenvolvimento Leopoldo Américo M. de Mello, Cidade Universitária, 21941-915, Rio de Janeiro - RJ

mtp@petrobras.com.br; fframosneto@petrobras.com.br

Abstract. *Hydrogen embrittlement of metallic materials has been a frequent problem in different industry sectors. Because it is the smallest existing atom, hydrogen diffuses into the microstructure of metallic materials, resulting in internal mechanical stresses that may eventually lead to a catastrophic failure. The most common methods available to analyze this phenomenon are time consuming and expensive. For this reason, it is desired to develop a test method that does not have such disadvantages. In this work it is presented the development of an equipment to rapidly evaluate the susceptibility to hydrogen embrittlement (SHE) of the metallic materials using the rising step load (RSL) bending test in assisted environment, which is governed by the ASTM Standard F1624. This equipment has a great advantage over the other evaluation methods of SHE, which is the shortest test time to have representative results. The validation of the infrastructure was performed by using unnotched AISI 4140 steel quenched and tempered samples, whose measured mechanical stress was compared to that returned by the RSL software and the results showed errors lower than 1 %. The tests to verify the performance of the RSL equipment were carried out on notched samples of quenched and tempered AISI 4140 steel with a hardness of 40HRC. The effect of the cathodic potential on the SHE was also evaluated. The results showed a direct relationship between the cathodic potential variation and the SHE of the sample, with stabilization of SHE at $-1.1 V_{Ag/AgCl}$. In addition, the tests showed also an increase in SHE with increasing material hardness.*

Keywords: *hydrogen embrittlement, rising step load, cathodic protection, fracture strength.*

1. INTRODUCTION

Due to the small atomic diameter and high mobility on solid materials, atomic hydrogen can easily penetrate solid materials, accumulating on small structural defects such as voids, inclusions and interstitial spaces. After reaching a critical concentration, it will start rising internal tensions on the material causing microstructural disorder that leads to embrittlement (Marina *et al.*, 2011). This phenomenon is known as hydrogen embrittlement (HE). It severely affects most of the main alloy groups depending on the environment they are in (Barnoush and Vehoff, 2011). HE has been observed on different industry sectors such as welding (Ballesteros, 2009), hot rolling (Okamoto, 2010) and electroplating (Stroe, 2006) to name a few. In oil and gas exploitation this is an issue of major concern due to the cathodic protection (Silva *et al.*, 2007), a mechanism used to prevent corrosion that ends up favoring hydrogen production and accumulation.

The Rising Step Load (RSL) is a method developed in the mid 90's by Raymond (1995) as an alternative to conventional Slow Strain Rate Tests (SSRT) to access Hydrogen Embrittlement in a faster and cheaper way through a stepwise loading in controlled environment. It consists of a four-point bend loading test using a notched sample, immersed in an electrolytic solution that provides hydrogen to permeate the sample. This method can access the susceptibility to hydrogen embrittlement (SHE) in a time frame of up to 60 hours with higher precision, or even better, as compared to traditional methods.

Based on the given premises, this article aims to present the development of an equipment for fast assessment of Hydrogen Embrittlement through RSL method as well to show its results and performance.

2. EXPERIMENTAL PROCEDURE

In this work AISI 4140 quenched and tempered steel samples with dimensions $30 \times 30 \times 200 \text{ mm}^3$ were used for validation tests in air and under cathodic protection. The notch rounding radius was $0.250 \pm 0.025 \text{ mm}$. The samples used for each purpose are shown in Fig. 1.

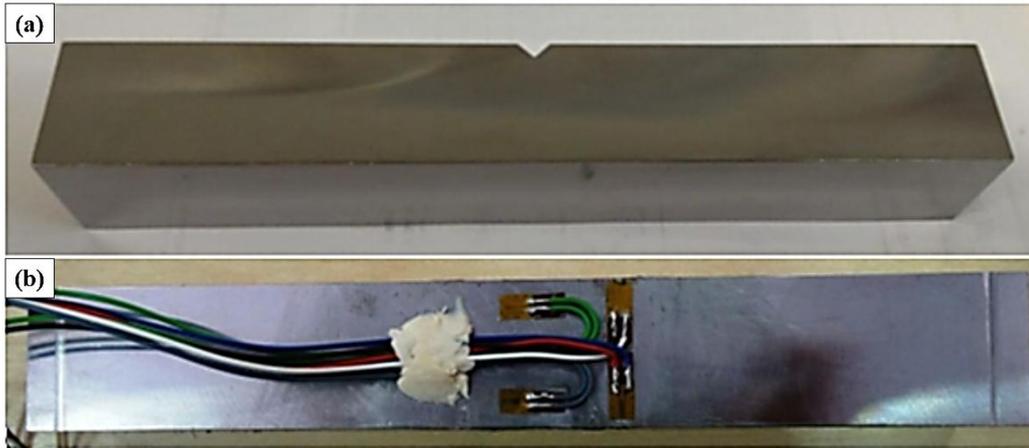


Figure 1. AISI 4140 steel samples. (a) Notched sample for hydrogen embrittlement tests. (b) Unnotched sample with strain gages for stress measurements validation

The experimental procedure is divided in two parts, the validation procedure and the hydrogen embrittlement test.

2.1. RSL validation procedure

The RSL stress measurements were validated by determining the error between the mechanical stress in an unnotched sample, calculated analytically through the Eq. (1), and the mechanical stress effectively applied to the sample, measured by using strain gages. An equipment sketch is shown in Fig. 2.

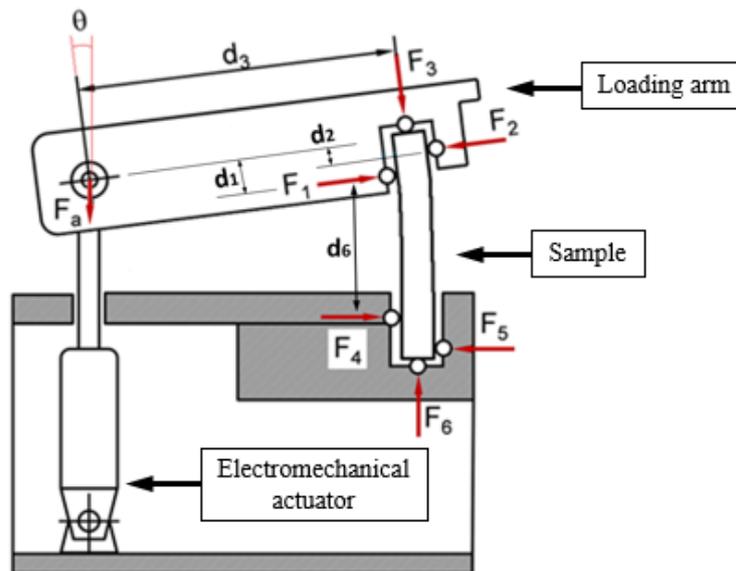


Figure 2. Sketch of the RSL equipment with illustration of the forces acting on the test body due to the application of force F_a

Additionally, all sources of uncertainty present in the test were identified and measurement uncertainty of mechanical stress (σ) was calculated by Eq. (1). For this purpose, the recommendations from the Guide to the Expression of Uncertainty in Measurement (INMETRO, 2012) were applied.

$$\sigma_{project} = F_a \left[\frac{3}{bh^2} (2d_1 \sin \theta + 2d_3 \cos \theta + d_6 \sin \theta) - \frac{\cos \theta}{bh} \right] \quad (1)$$

Where F_a is the force carried out by the actuator, d_1 is the vertical distance of the force F_l with respect to the axis of rotation of the bending arm, d_3 is the horizontal distance from the axis of rotation of the bending arm relative to the central axis of the specimen, d_6 is the vertical distance between the centers of the rollers of the loading arm and the lower support supporting the face opposite the notch of the sample, b and h represent the width and depth of the cross-section of the specimen and θ is the angle of rotation of the actuator arm, according with Fig. 2.

The validation test was conducted loading the sample by steps, in the same way that the RSL test. The applied load varied from 0.5 kN to 10.0 kN, with 20 constant load steps, where each step was incremented with 0.5 % of the maximum load and maintained for 30 seconds. The loading profile to validation test is showed in Fig. 3.

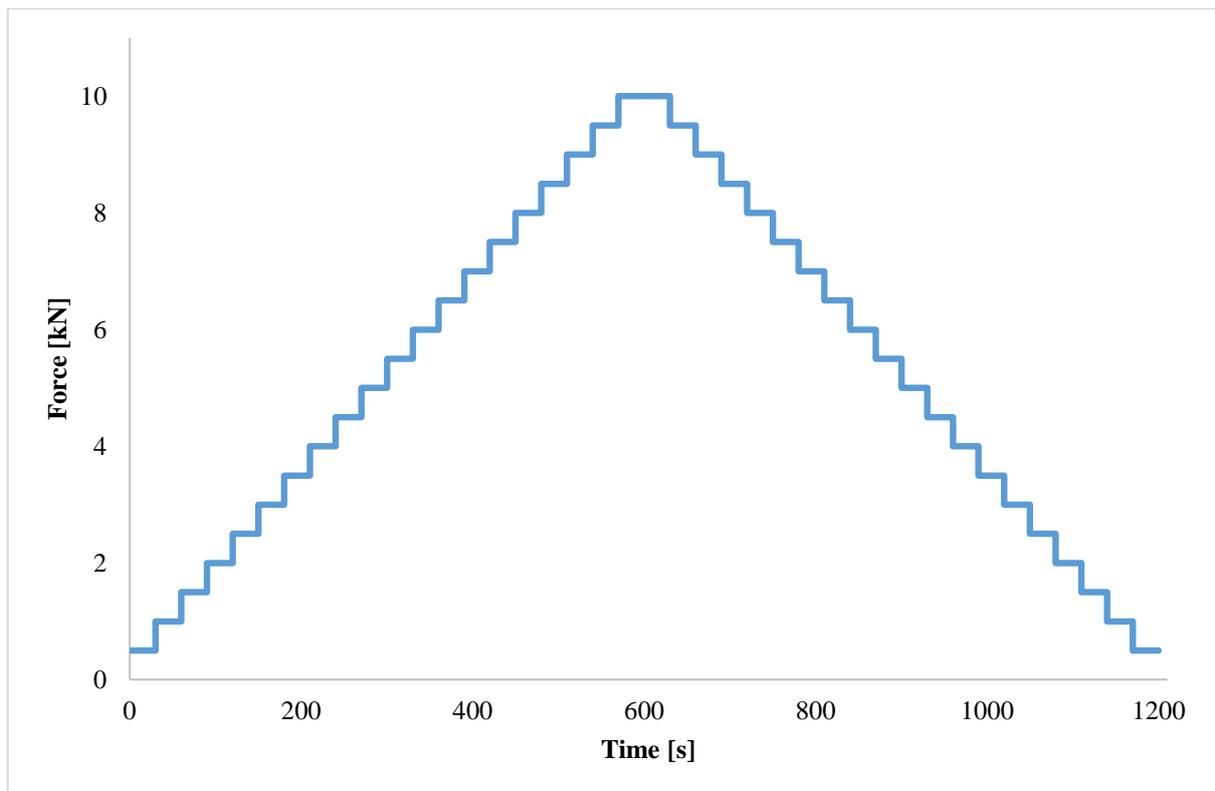


Figure 3. Loading profile for the validation test

2.2. RSL tests with hydrogen embrittlement

The RSL test is ruled by ASTM F1624 (2010), which determines how to apply the loading profiles according to the material hardness. Initially, one sample is loaded in air to rupture at a constant rate to establish the fast fracture strength (P_{FFS}). The subsequent tests are performed in a hydrogen environment at a loading profile that depends on the hardness of the samples, the loading profile for a material with hardness ranging from ≥ 33 HRC up to 45 HRC can be seen in Fig. 4. In these tests the sample is loaded by means of loading steps, which starts at a load of 5 % of the P_{FFS} , increases from 5 % to 5 % of the P_{FFS} until reaches 100 % of the P_{FFS} value. The test stops with the fracture of the sample, which is identified as a drop of 5 % of the P_{FFS} in the force applied to the sample, or if the last loading step is reached during the test. The threshold load (P_{th}), which is the load at the onset of hydrogen induced cracking, is the load corresponding to the step before the onset of crack growth for a specific loading rate.

The hydrogen embrittlement was carried out by using cathodic polarization, applying the following potentials in the sample: $-0.8 V_{Ag/AgCl}$, $-1.0 V_{Ag/AgCl}$, $-1.1 V_{Ag/AgCl}$ and $-1.2 V_{Ag/AgCl}$ in a sample immersed in a NaCl 3.5 % aqueous solution in a three-electrode configuration. Graphite was used as the counter-electrode, an Ag/AgCl electrode was used as the reference electrode and the sample were the working electrode. A picture of the three-electrode configuration adopted for the tests is can be seen at Fig. 5.

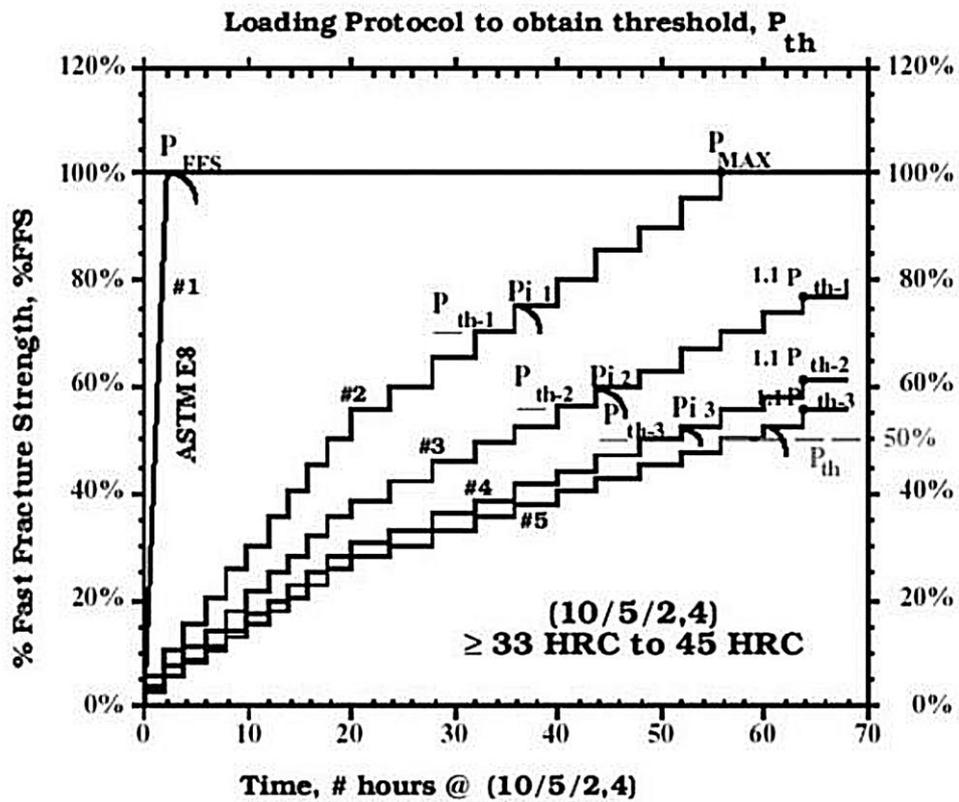


Figure 4. RSL loading profile for materials with hardness in the range ≥ 35 HRC up to 45 HRC (ASTM F1624, 2010)

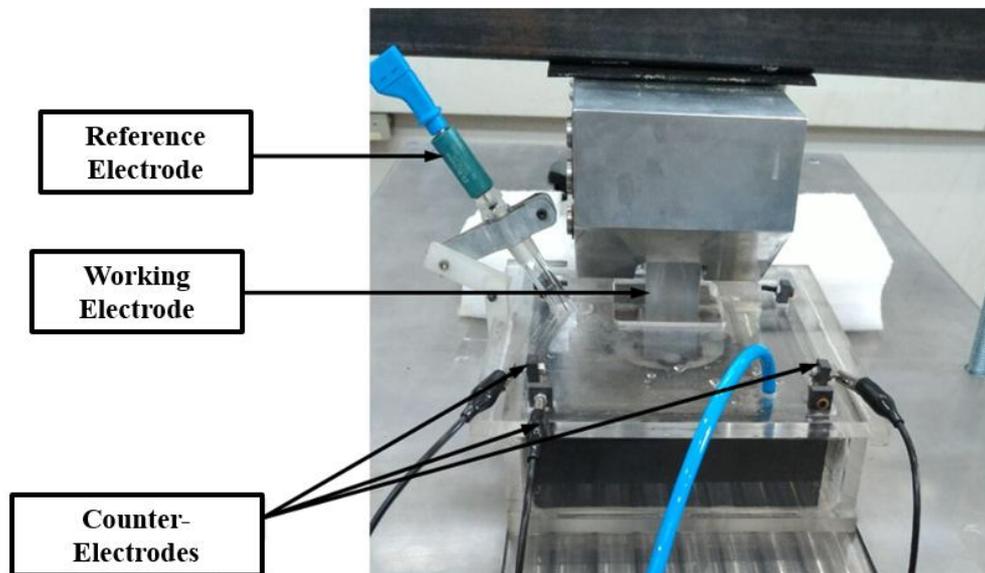


Figure 5. Three-electrode configuration adopted for the hydrogen embrittlement RSL tests

3. RESULTS AND DISCUSSION

The results obtained in the validation tests and in the RSL tests for the determination of P_{FFS} and P_{th} values are presented and discussed below. It is worth mentioning that for each test the mechanical stress equation in the sample was corrected based on the sample measured dimensions, ensuring that the measured mechanical stress value was as accurate as possible

3.1. Validation tests

The results obtained from the validation tests and expanded uncertainty can be seen in Figs. 6, 7 and 8.

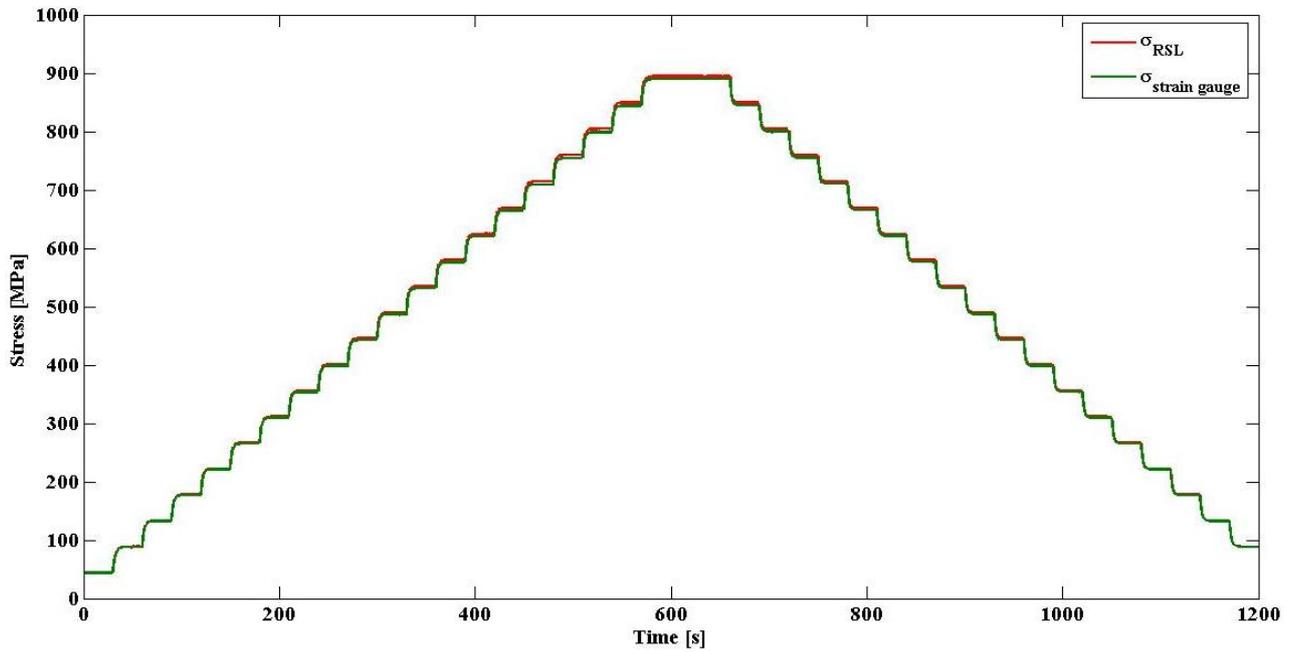


Figure 6. Analytically calculated stress (red) and experimental stress measured by using strain gages (green)

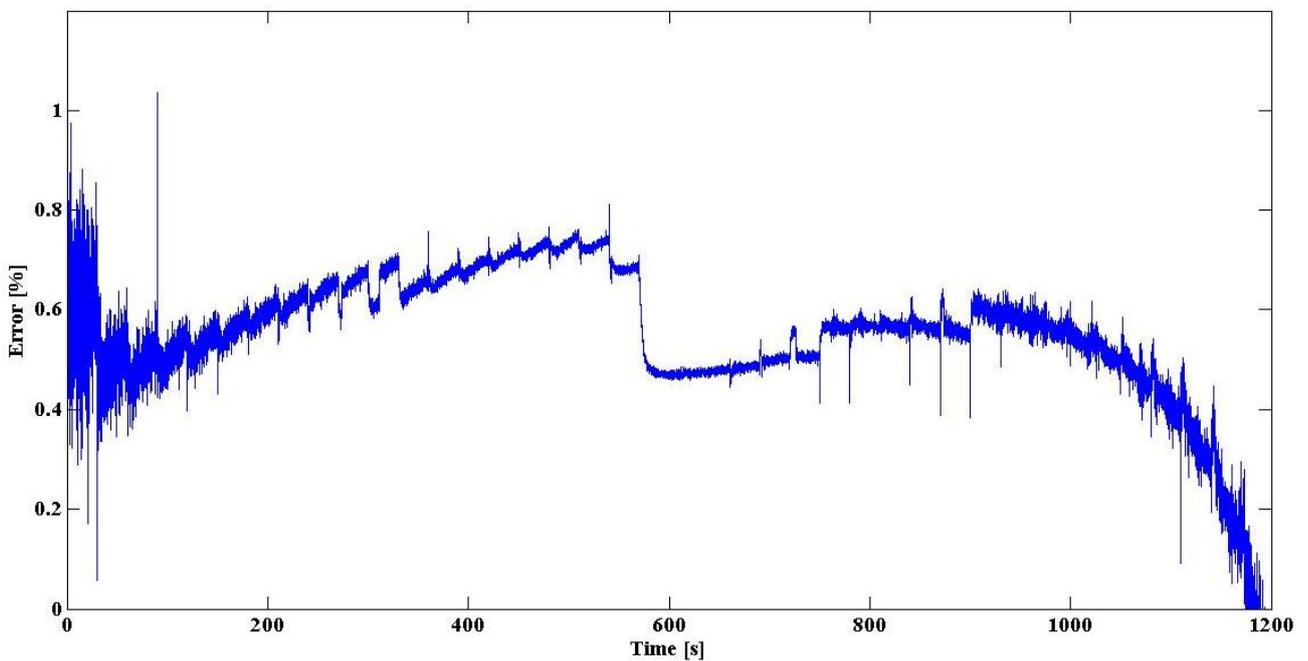


Figure 7. Error between the mechanical stress, calculated by the RSL software and the stress measured by using strain gages

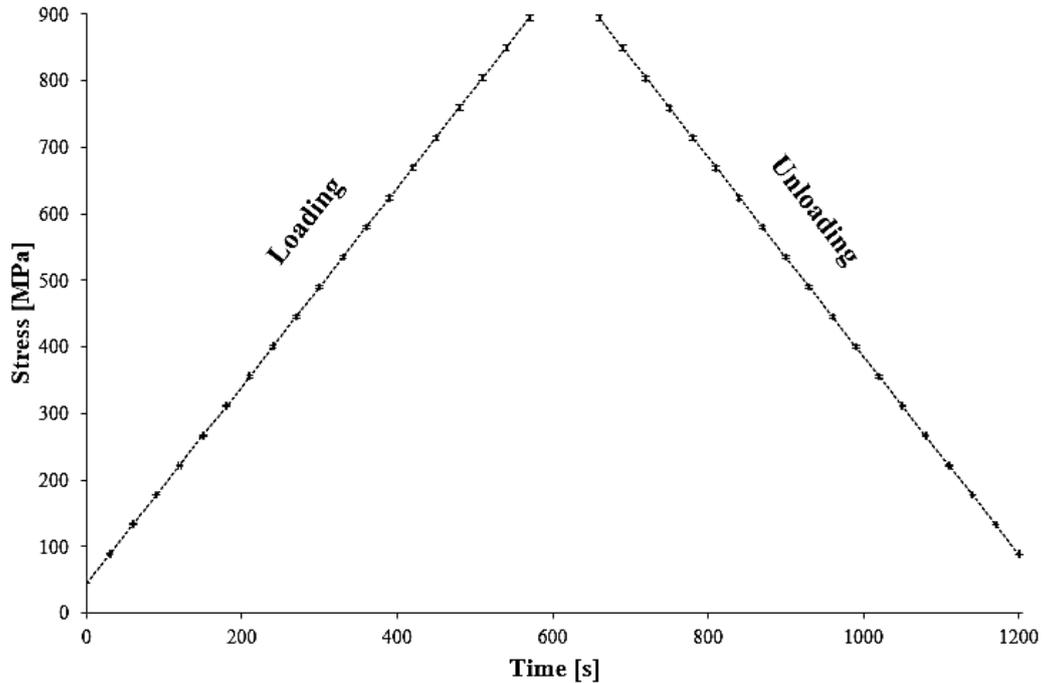


Figure 8. Mean stress measured during the validation test with the expanded uncertainties in the format of error bars

From Figs. 6 and 7, it is observed that the error between the analytical stress, calculated by using the RSL software, and the experimental one, measured using strain gages is around 0.8 % in the beginning of the test and the mean error is 0.6 %. One single point of 1 % was observed during de test but it was attributed to some signal noise or other external factor. The expanded uncertainty associated to the stress measurement by the RSL software was calculated as a function of the measurement uncertainties associated to the variables in the Eq. (1) and the result was 0.5 % of the stress calculated by the RSL software. From Fig. 8 it can be perceived that the expanded uncertainty is very low compared with the mean stress value and its value is about 0.5 % of the mean stress value at each step.

3.2. RSL tests with hydrogen embrittlement

The ASTM F1624 standard predicts only one test is sufficient for determining de P_{FFS} value. However, to enhance the representativeness of the result, four tests were realized to determine the P_{FFS} value on this work. The P_{FFS} results are shown in the Fig. 9.

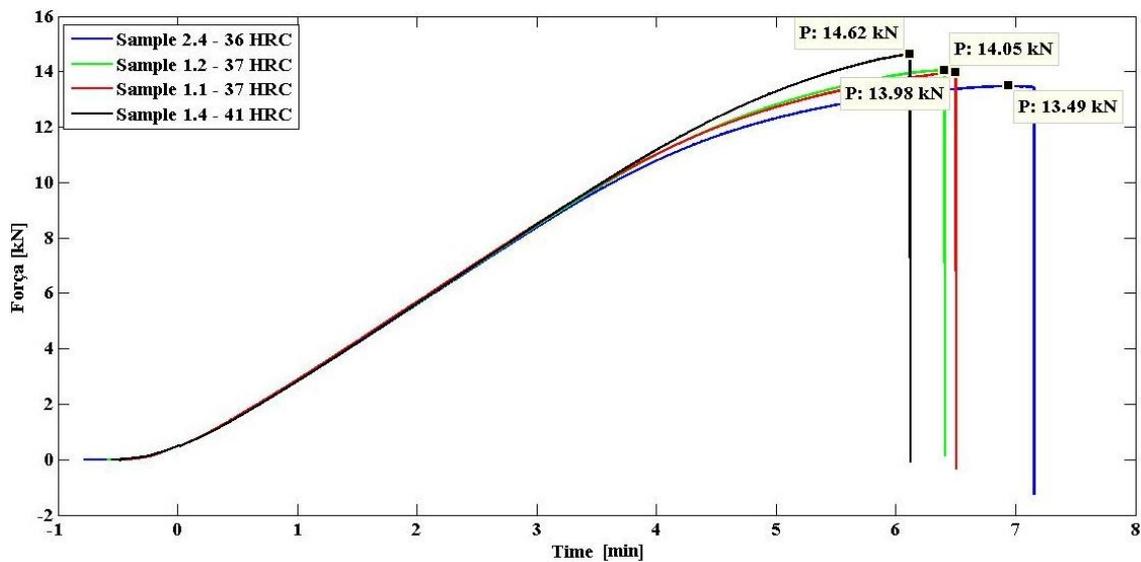


Figure 9. Fast Fracture Strength results

The P_{FFS} results in Fig. 9 show that, for lower hardness values, the FFS is lower than those for higher hardness values. However, the time to rupture is higher for the samples with lower hardness values. This happens because of the resulting effect of the stress concentration at the notch root will be lower in softer samples due to the plastic deformation. Therefore, its capacity to absorb stress will be higher, leading to a higher time to fracture.

The P_{FFS} value was obtained as the mean value of the four P_{FFS} values obtained and the result was 14.035 kN. This value was taken as the maximum reference value (P_{MAX}) for the RSL tests with hydrogenation. The RSL tests results can be seen in Figs. 10, 11 and 12.

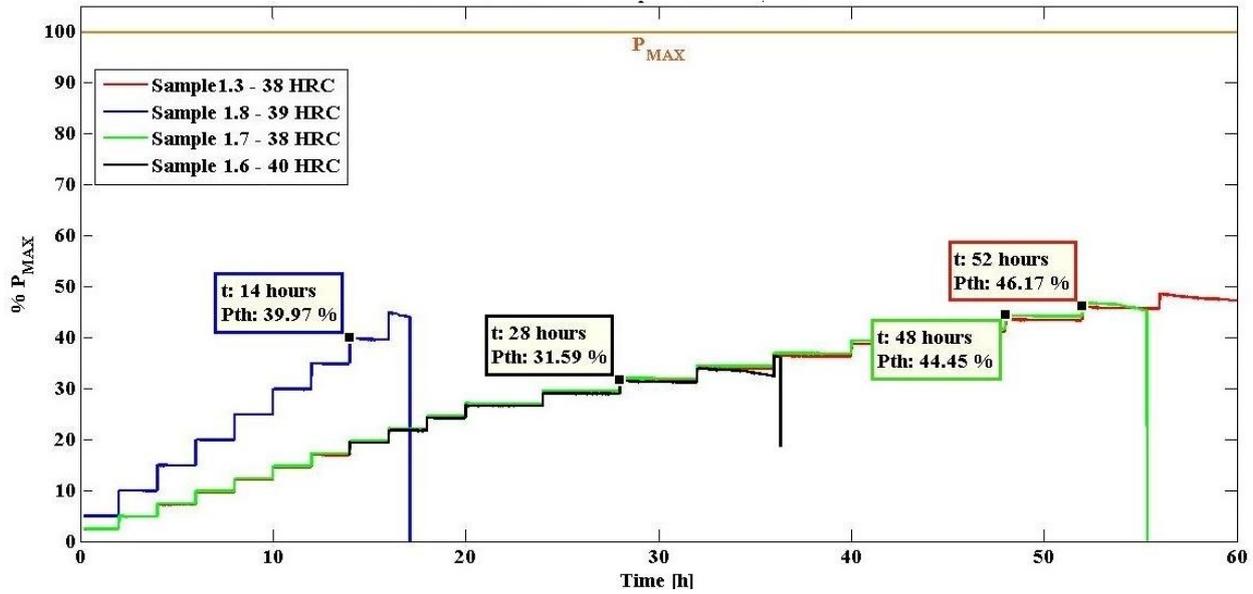


Figure 10. RSL test results for samples with different surface hardness, tested with a cathodic potential of $-1.2 V_{Ag/AgCl}$

The results in Fig. 10 show that there was a drastic reduction in the tensile strength of AISI 4140 quenched and tempered steel samples in relation to the P_{FFS} value when subjected to a potential of $-1.2 V_{Ag/AgCl}$. This reduction ranged from 57 % to 68 % of the P_{FFS} . It is also observed that the SHE is higher for the harder samples. Nanninga *et al.* (2010) identified the same behavior in samples of quenched and tempered 4037 alloy. This trend is explained by Troiano (1960), who says that this behavior is due to a combination between hydrogen and stress at the sample. The smaller plasticity at the notch root of the harder sample cannot absorb the internal tension stress introduced by hydrogen and this makes the harder sample, when hydrogenated, to break in a smaller load value than the softer sample.

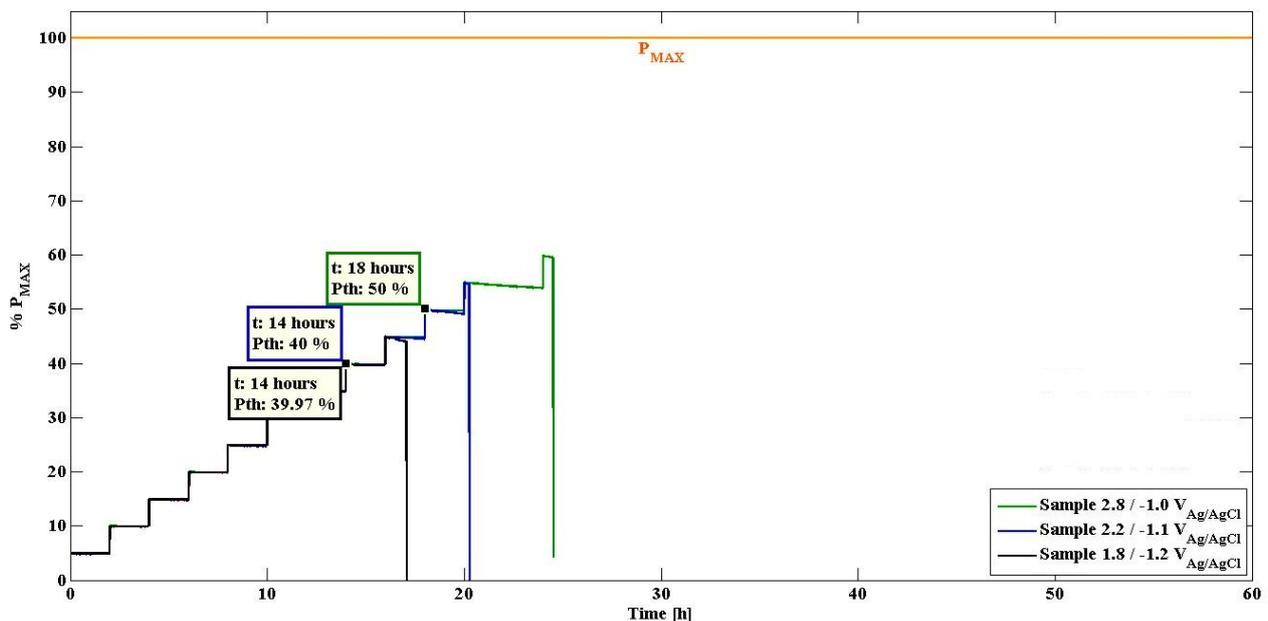


Figure 11. RSL test results for samples with surface hardness of 39 HRC, tested using different cathodic potentials

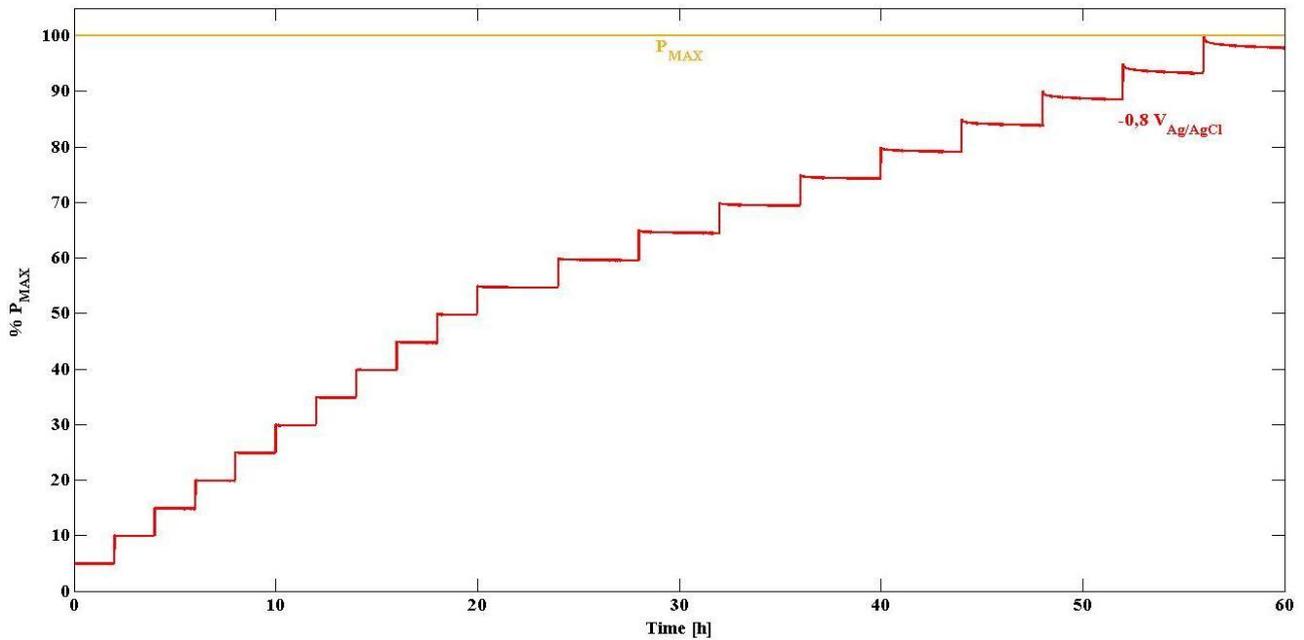


Figure 12. RSL test result for a sample with surface hardness of 40 HRC. The test was performed using a cathodic potential of $-0.8 V_{Ag/AgCl}$

The results obtained from the RSL tests, varying the cathodic potential, as shown in Figs. 11 and 12, indicate that there is a clear relation between the electric potential value applied and the SHE. For a applied cathodic potential equal to $-0.8 V_{Ag/AgCl}$ there was no evidence of HE on the sample, but, for potentials above this value, in modulus, there was a reduction in the P_{th} value due to hydrogen embrittlement. For values above $-1.1 V_{Ag/AgCl}$, there was no increase on the SHE, indicating a hydrogen saturation from this potential and beyond. Parkins *et al.* (1982) observed the same behavior in samples of high strength steel.

The stresses obtained on both tests conditions are shown on Tab. 1 below and the threshold loads and stresses in function of the sample hardness and the cathodic potential can be seen in Figs. 13 and 14.

Table 1. Tests results in all analyzed conditions

| Sample | Applied potential [$V_{Ag/AgCl}$] | Surface HRC hardness | Threshold load (P_{th}) [kN] | Threshold stress (σ_{th}) [MPa] |
|--------|--|-------------------------|-------------------------------------|---|
| 2.4 | | 36 | 13.49 | 1575.0 |
| 1.2 | FFS Tests | 37 | 14.05 | 1638.0 |
| 1.1 | | 37 | 13.98 | 1636.0 |
| 1.4 | | 41 | 14.62 | 1710.0 |
| 1.3 | | 38 | 6.48 | 748.0 |
| 1.7 | -1.2 | 38 | 6.24 | 723.2 |
| 1.8 | -1.2 | 40 | 5.61 | 651.6 |
| 1.6 | -1.2 | 39 | 4.43 | 512.3 |
| 2.2 | -1.1 | 39 | 5.61 | 647.2 |
| 2.8 | -1.0 | 39 | 7.02 | 810.5 |
| 2.7 | -0.8 | 40 | No crack was observed | |

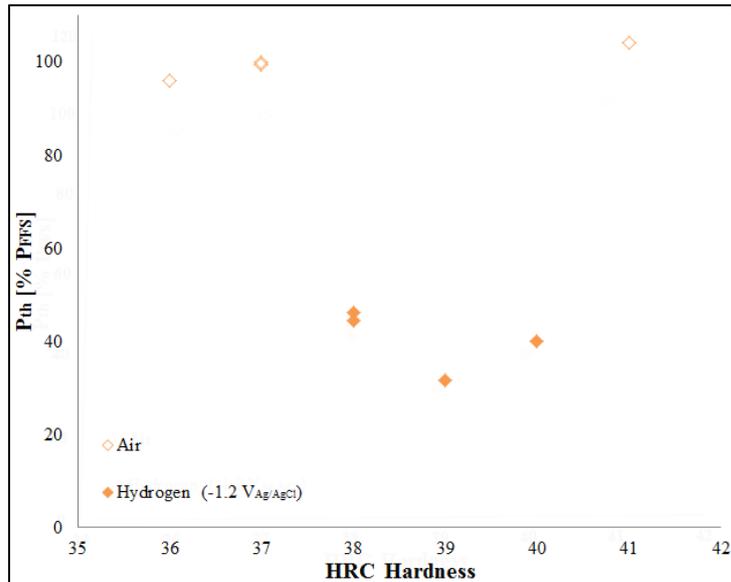


Figure 13. Variation in P_{th} as a function of the surface hardness of the samples in the RSL tests performed in air and with hydrogen at a cathodic potential of $-1.2 V_{Ag/AgCl}$. The 100 % value refers to the average P_{FFS} obtained from the outdoor tests

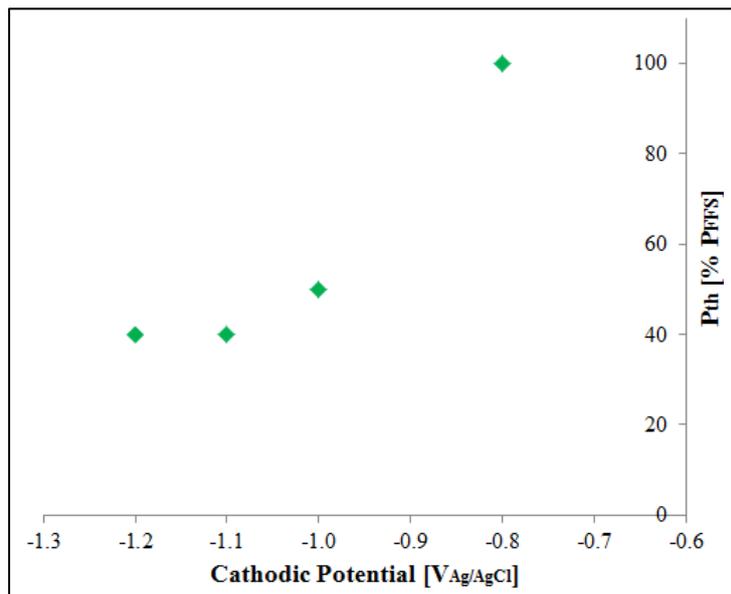


Figure 14. Relationship between the P_{th} and the cathodic potential applied during the RSL test. The 100 % value refers to the average P_{FFS} obtained from the outdoor tests

4. CONCLUSIONS

- The equipment showed an expanded uncertainty of 0.5 % of the stress calculated by the RSL software and a maximum error of 0.8 % between the stress calculated by the RSL software and the stress measured by the strain gages;
- The AISI 4140 quenched and tempered steel, with a hardness of 40 HRC, showed a high SHE when subjected to cathodic potentials of $-1.0 V_{Ag/AgCl}$ to $-1.2 V_{Ag/AgCl}$;
- When embrittled by hydrogen, the sample with the highest hardness value showed a reduction of 68 %, whereas the softer one showed a reduction of 54 % on the rupture load;

- d) It was identified that for values above $-1.1 V_{Ag/AgCl}$, in modulus, there was no increase in SFH;
- e) For the lowest cathodic potential value ($-0.8 V_{Ag/AgCl}$), no hydrogen embrittlement was observed.

5. ACKNOWLEDGEMENTS

This work was supported by CAPES-PROEX, CNPq, FAPEMIG and PETROBRAS.

6. REFERENCES

- ASTM F1624, 2010. "Standard Test Method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading Technique". American Society for Testing and Materials.
- Ballesteros, A., 2009. *Avaliação da Resistência de Juntas Soldadas Circunferenciais de Aço API 5L X-80 à Corrosão sob Tensão na presença de sulfetos e Susceptibilidade à Fragilização por Hidrogênio*. Ph.D. thesis, Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro.
- Barnoush, A. and Vehoff, H., 2010. "Recent developments in the study of hydrogen embrittlement: Hydrogen effect on dislocation nucleation". *Acta Materialia*, Vol. 58, p. 5274.
- INMETRO, 2012. "Avaliação de dados de medição - Guia para a expressão de incerteza de medição – GUM 2008" 6 Jan. 2016 < http://www.inmetro.gov.br/noticias/conteudo/iso_gum_versao_site.pdf>.
- Marina, C., Sergio, L., Paolo, M. and Tommaso, P., 2011. "Hydrogen embrittlement behaviour of HSLA linepipe steels under cathodic protection". *Corrosion Reviews*, Vol. 29 p. 261.
- Nanninga, N., Grochowski, J., Heldt, L., and Rundman, K., 2010. "Role of microstructure, composition and hardness in resisting hydrogen embrittlement of fastener grade steels". *Corrosion Science*, Vol. 52, p. 1237.
- Okamoto, M. A., 2010. *Danos causados pelo Hidrogênio em Aços para Tubos API 5L X65 e X80*. Monograph, Polytechnic School of Sao Paulo University, São Paulo.
- Parkins R.N., Elices, M., Sanchez-Galvez, V. and Caballero, L., 1982. "Environment sensitive cracking of pre-stressing steels". *Corrosion Science*, Vol. 22, p. 379.
- Raymond, L., 1995. "Rising Step Load Apparatus", *United States Patent US5505095*.
- Silva, A.G.S.G., Ponte, H.A. and Pashchuk, A., 2007, "Estudo da influência do hidrogênio permeado nas propriedades eletroquímicas do Nb / Nb₂O₅ para o desenvolvimento de um sensor". In *4th Brazilian Congress of R&D in Oil and Gas – PDPETRO2007*. Campinas, Brazil.
- Stroe, M. E., 2006, *Hydrogen Embrittlement of Ferrous Materials*. Ph. D. thesis, Université Libre de Bruxelles, Bruxelles.
- Troiano, A. R., 1960. "The role of hydrogen and other interstitials in the mechanical behavior of metals". *Metallography, Microstructure and Analysis*, Vol. 5, p. 557.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.