Rate effects on the estimation of fracture toughness by Small Punch tests in hydrogen embrittlement

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ABSTRACT

In this paper, different techniques to test notched Small Punch (SPT) samples in fracture conditions in aggressive environments are studied, based on the comparison of the micromechanisms at different rates. Pre-embrittled samples subsequently tested in air at rates conventionally employed (0.01 and 0.002 mm/s) are compared to embrittled ones tested in environment at the same rates (0.01 and 0.002 mm/s) and at a very slow rate (5E-5 mm/s). A set of samples tested in environment under a set of constant loads that produce very slow rates completes the experimental results. As a conclusion, it is recommended to test SPT notched specimens in environment at very slow rates, of around E-6 mm/s, when characterizing in Hydrogen Embrittlement (HE) scenarios, in order to allow the interaction material-environment to govern the process.

1. INTRODUCTION AND SMALL PUNCH TEST STATE OF THE ART

1.1. Introduction

A critical aspect concerning high strength steels is their resistance to Stress Corrosion Cracking (SCC) and Hydrogen Embrittlement (HE) phenomena, which lead to degradation of the mechanical properties of these steels when facing aggressive environments (1). The effect of hydrogen is especially significant in high-strength steels exposed to aqueous environments under cathodic protection (such as off-shore platforms) or those typical of H_2S presence (as in gas transport pipelines). Both phenomena, HE and SCC, are similar, resulting in brittle failures in the presence of an aggressive environment and maintained stress. Both phenomena are dependent on the crack deformation rate, and may even disappear at very high rates, while at very slow strain rates hydrogen continues to exert an embrittling effect (2).

The recommendations presented by various research groups over the last decades have been collected in the standard ISO 7539 (3). It establishes requirements concerning specimen size and solicitation rate, but does not specifically define the procedure to follow in numerous applications. Also, there are particular situations where standards cannot be followed to perform characterizations on in-service components, mostly due to the impossibility of machining specimens fitting the dimensions, or mainly the thickness required. One of those situations is usually present in the welded joints of any type of structure, or in highly stressed areas where the extraction of a certain amount of material could affect the structural integrity of the component.

To find a solution for these types of scenarios, the miniature test family was developed, which uses specimen sizes much smaller than those required by standard tests. Among these alternative techniques, the Small Punch Test (SPT) is one of the most notables. The SPT is based on punching a plane specimen of reduced dimensions, which allows parameters such as the yield stress, ultimate tensile strength and even fracture toughness of metallic materials to be estimated with high reliability (4). Over the last years some authors have proved the validity of the SPT when used in HE and SCC characterizations (5,6,7).

In order to reproduce the micromechanisms taking place in HE failures accurately, as it is imposed by standardized environmental characterizations, the test rates should be very slow, or even quasi-static (3). The ultimate research in the SPT field (7) indicates that tests performed in environment, under constant load applied to the specimen, should be a suitable option to reproduce the micromechanisms of real subcritical processes, despite the time and samples requirements are higher.

In this paper a review of all possible SPT testing techniques and a wide range of rates for its application to HE scenarios is carried out, form pre-embrittled samples tested in air at conventional rates to tests in environment at different punch rates from 0.01 mm/s up to constant load (7E-5 mm/s).

1.2. The Small Punch Test (SPT)

The Small Punch Test was first developed in the early 80's in the context of the nuclear industry (8), where the limited amount of material for surveillance programs and the difficulty in manipulating large volumes of irradiated material made it very difficult, or even impossible in some occasions, to perform conventional characterizations. The SPT allows to test in-service structures since the extraction of such a small amount of material required for SPT does not compromise the component's integrity. There is a European Code of Practice, CWA 15627, edited by CEN in 2007 (9), based on which a European Standard is in revision process (10). SPT can be considered as a quasi-non-destructive test in comparison to the components whose structural integrity want to be analyzed. It has been successfully employed in the evaluation of tensile (11) and fracture (12) properties of different materials. Because of its reduced dimensions and simplicity, this technique has been applied to characterize embrittlement situation on steels, such as the evolution of materials properties with neutron irradiation (13), the brittle-ductile transition temperature of metallic materials (14), or environmental embrittlement (5,6,7).

SPT consists of punching a plane specimen of small dimensions and deforming it until fracture. A schematic of the device used for the performance of these tests is represented in Figure 1. During the test, the force as well as the displacement made by the punch, are registered continuously, as a result obtaining curves like the ones shown in Figure 2 (7), where the following different zones can be distinguished:

- ZONE I: The beginning of the curve is the result of the superposition of two different behaviors: the indentation suffered by the specimen on the surface of contact with the punch's spherical head plus the elastic behavior as a plate of the specimen.
- ZONE II: The first convexity change in the curve is exclusively motivated by the beginning of the specimen's yielding, a point that marks the start of this second zone of generalized plate yielding of the specimen.
- ZONE III: After the second convexity change of the curve, deformations are concentrated in certain regions of the specimen and the behavior of the sample changes from plate to membrane. This zone is known as the membrane-stretching regime.

- ZONE IV: The new shape of the curve indicates the beginning of the plastic instability and the appearance of cracks that will lead to the final specimen fracture. Finally, cracks start growing, causing the collapse of the specimen once the maximum force of the test is exceeded.

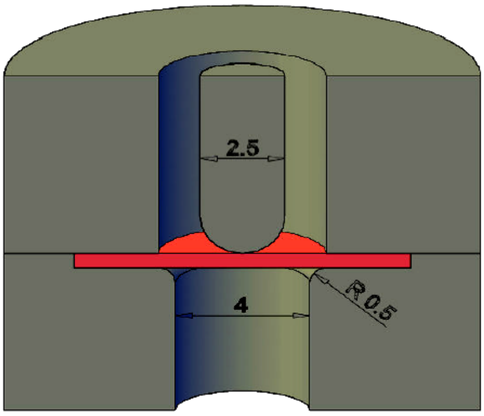

FIGURE 1. SPT DEVICE AND SAMPLE USED; DIMENSIONS IN MILIMITERS (mm).

In brittle materials or embrittlement situations, the membrane stretching (zone III) does not exist, going from a yielding plastic behavior directly to the final plastic instability. It can be observed that, while in ductile situations the specimen rupture surface has a semicircular shape and its deflection is higher (figure 2.a), in brittle scenarios the breaking typology is a star-type (figure 2.b) and the specimen deflection lower, so the energy under the curve is also lower (5).

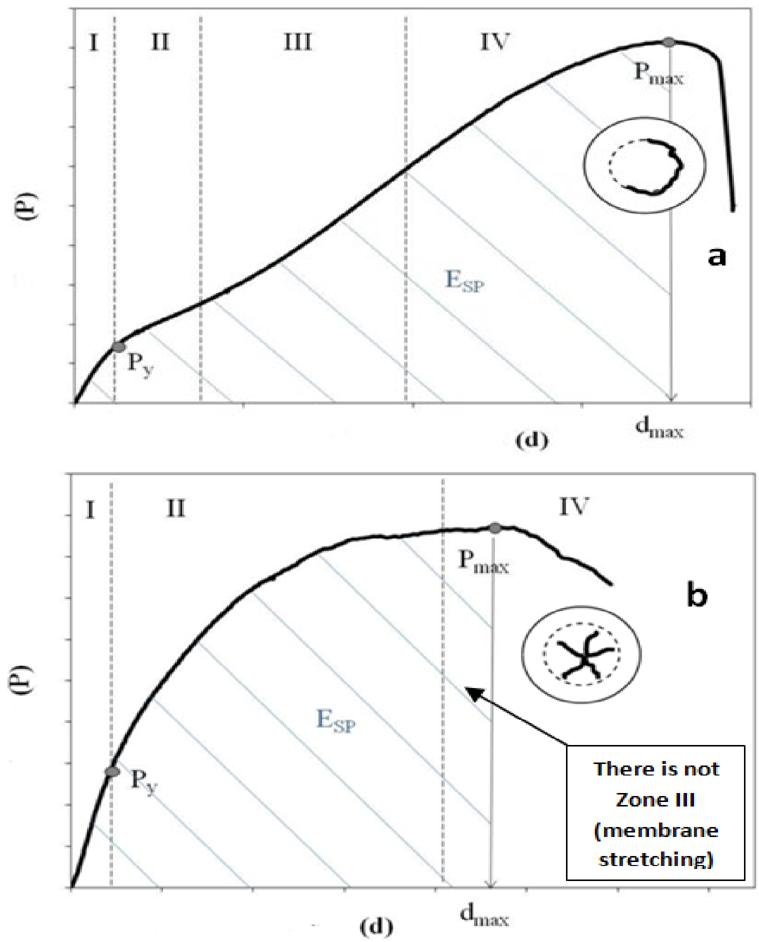

FIGURE 2. SCHEMATIC OF SPT (FORCE-DISPLACEMENT) CURVES AT CONVENTIONAL O SLOW RATES (11); a) DUCTILE MATERIALS; b) BRITTLE MATERIALS

When characterizing materials in HE situations the testing rate is an important parameter to take in account (2,7), as far as it will govern the micromechanism taking place. In environmental subcritical processes, very low rates, or even constant tests, are commonly employed (3), being the Slow Strain Rate Tests (SSRT) and the tests under constant load the most widely used for conventional characterizations. By using these testing conditions, hydrogen will have enough time not just to diffuse form reversible tramps to the new cracking areas subsequently generated during the test, but also to escape form irreversible tramps helped by plastic deformation and diffuse to the new cracking areas (15).

The ultimate research for the Small Punch test in HE characterizations (7) advises that static constant load tests, or very slow punch rates (Slow Small Punch Test, SSPT), should be used in order to allow hydrogen to cause all of its embrittling power, in the same way as advised for standardized tests. In (7) the punch displacement versus time SPT curve resulting from static load tests in environment (d-t register) was studied, resulting in the three zones shown in Figure 3.

- Zone I consists on the punch indentation and settlement.
- In zone II a quasi-constant punch rate takes place, caused by the variation on the flexibility of the system produced by an increasing cracking in the specimen in both radial and thickness directions.
- Finally, in zone III the damage level of the system is so high that the punching load cannot be supported anymore and the specimen leads to final instability and fails.

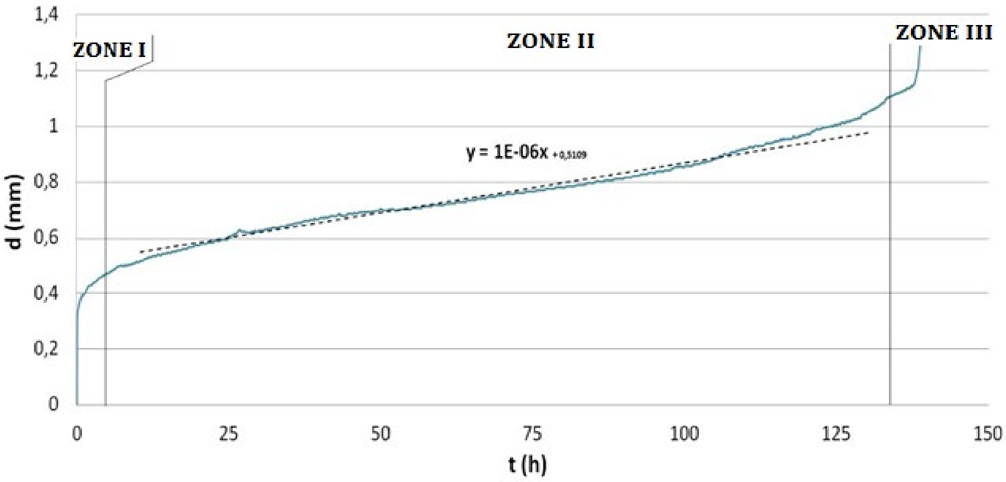

FIGURE 3. SPT (DISPLACEMENT-TIME) CURVE FOR CONSTANT LOAD TESTS IN ENVIRONMENT (7).

2. MATERIAL EMPLOYED FOR THE STUDY

The material used in this study is a Cr-Ni-Mn high-strength steel, which is employed in the manufacture of large anchor chain links for off-shore platforms. Its chemical composition is shown in Table 1, and its tempered martensite microstructure is presented in Figure 4. It is obtained by quenching and tempering processes. This steel is received in the factory in bars, which are then forged to conform the links by bending forces.

TABLE 1. CHEMICAL COMPOSITION OF THE STEEL USED (% WEIGHT).

C	Si	Mn	P	S	N	Cu	Mo	Ni
0.232	0.240	1.25	0.011	0.005	0.062	0.250	0.510	1.080
Cr	**V**	**Ti**	**Al**	**Sn**	**O**	**As**	**Sb**	**Fe**
1.050	0.100	0.002	0.016	0.011	0.0017	0.012	0.005	Rest

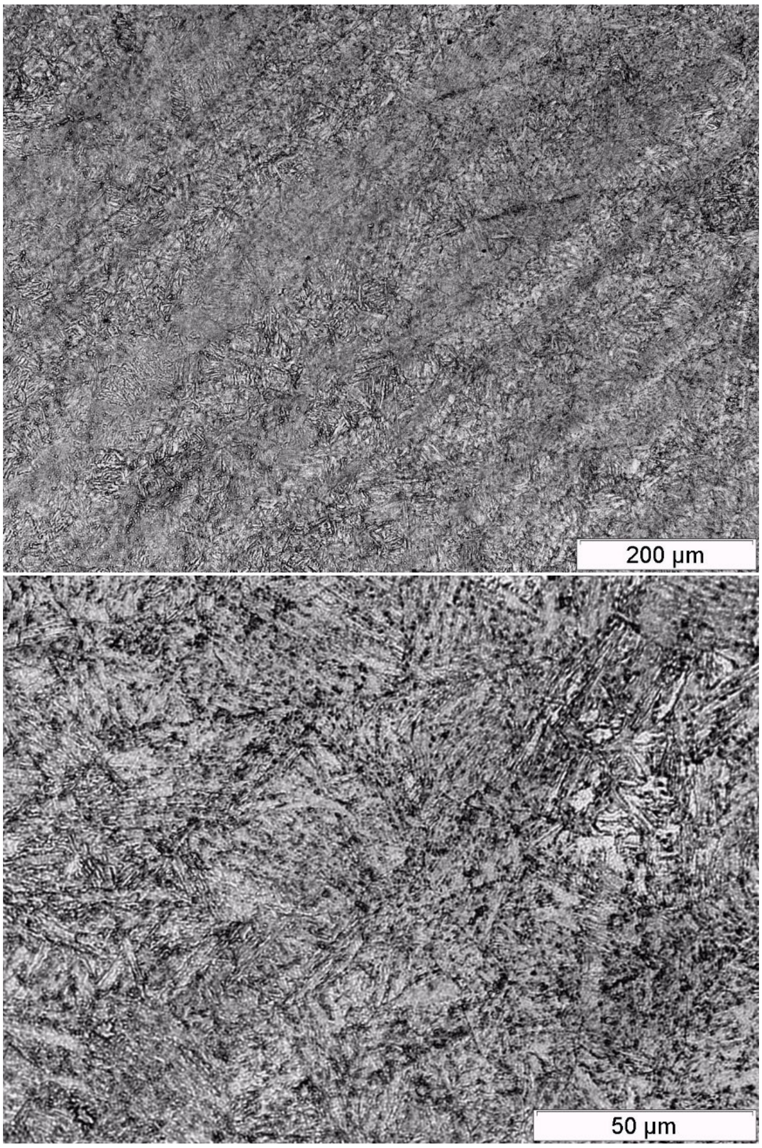

FIGURE 4. MICROSTRUCTURE OF THE STEEL USED IN THE R-L PLANE.

Standardized B=25mm thick compact specimens for fracture mechanics according to (16), and 10mmx10mmx0.5mm Small Punch notched samples according to (7,9), were obtained from a chain link for the subsequent labors. Also, in order to determine the mechanical behavior of the material as received (16,17,18) some other tensile and fracture specimens were machined to obtain the results shown in Table 2. The hydrogen content of the material as received was measured by the hot extraction technique in a Leco^{R} analyzer, obtaining the value of 0.84 ppm, shown in Table 2. Based on the results of hydrogen desorption tests performed, the diffusion coefficient for this steel was estimated of $2.3 \cdot 10^{-6}$ cm^2/s (also included in Table 2), which is in agreement with the values in the literature for the diffusion coefficient of H_2 in different types of steel (19) between 10^{-6} and 10^{-7} cm^2/s.

TABLE 2. MAIN PROPERTIES OF THE STEEL.

PARAMETER		VALUE
Yield Stress	(MPa)	920
Ultimate Stress	(MPa)	1015
Young's Modulus	(GPa)	205
Ramber-Osgood Parameters	N	14.5
	α	1.15
$J_{0.2}$	(KN/m)	821
$K_{J0.2}$	(MPa*m^1/2)	410
H_2 content as received	(ppm)	0.84
H_2 diffusion coefficient	(cm^2/s)	$2.3 \cdot 10^{-6}$

3. SIMULATION OF HYDROGEN EMBRITTLEMENT (HE)

An environmental condition known as cathodic charge (CC), or anodic polarization, has been employed in this study. It is used to protect against corrosion structures that operate in aggressive environments, or to reproduce local situations where a high amount of hydrogen is present. It causes substantial embrittlement on the steel by the action of the hydrogen going through and getting trapped in it.

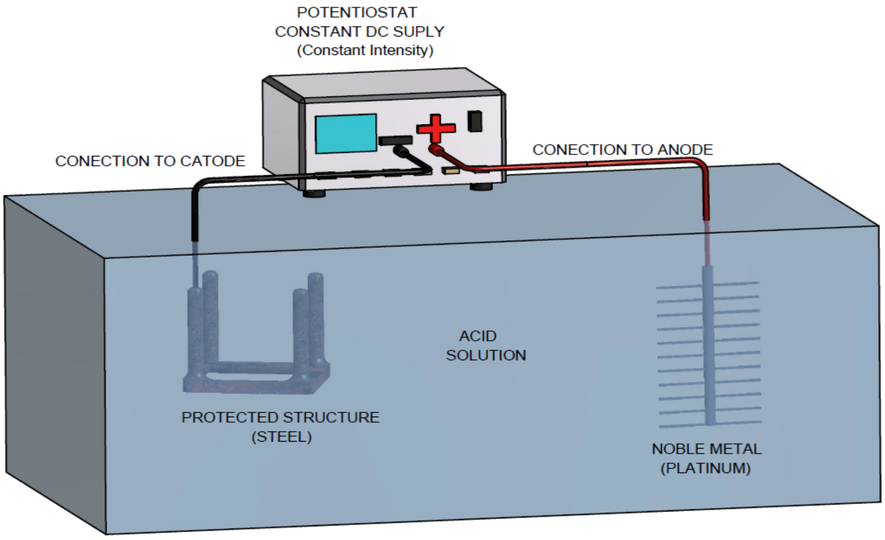

FIGURE 5. CATHODIC CHARGE METHOD. (7).

Figure 5 shows a set-up of the method used in this work (7). It consists of the interconnection, via an acid electrolyte, of a noble material (platinum in this case) and the steel, which will be protected due to the fixed current interposed (1,20,21). In this study, for the cathodic charge situations, an environmental condition in accordance (6,7,15,16) was proposed, consisting of an 1N H_2SO_4 solution in distilled water containing 10 drops of CS_2 and 10mg of As_2O_3 dissolved per liter of dissolution. The solution of As_2O_3 was prepared using Pressouyre's method (20). A platinum grid was used as an anode. The PH was controlled in the range 0.65 – 0.80 during the tests and at room temperature 20ºC - 25ºC.

An embrittlement level of 5mA/cm^2 was employed; this current density was chosen for being employed in previous works through the last decades (5,6,7,19,21) because it is a useful tool for research in hydrogen embrittlement scenarios. It is in the middle of the range (from 1 to 10 mA/cm^2) commonly used to reproduce situations of local effects of aggressive environments impossible to avoid, and sometimes to predict, that can seriously affect their structural integrity, as it introduces an significant amount of hydrogen in the material. After exposing pins for Hydrogen content analysis to this environment a period of time high enough to saturate the whole microstructure (Ø5mm pins exposed for at least 12 hours), the hydrogen content was measured, obtaining 5.45 ppm (vs 0.84 ppm as received).

4. EXPERIMENTAL METHODOLOGY

4.1. Standard fracture mechanics tests

In a first attempt fracture mechanics tests were carried out in the environmental condition described (cathodic polarization at a level of 5mA/cm^2) in order to determine the micromechanisms of fracture by SEM images, as well as the K_{IEAC} value; for this task standardized B=25mm C(T) specimens were employed; the specimens were 10% side grooved at each side. Prior to the test, the specimens were subjected to hydrogen absorption by exposing them for 48 hours to the same environment and aggressiveness conditions as the test itself. It was already employed in literature (5,6,15), and was sufficient to assure the saturation (5.45 ppm) of the whole thickness (diffusing from both sides), according to the calculations based on an estimated diffusivity of hydrogen of the material at room temperature of $2.3 \cdot 10^{-6}$ cm^2/s. Subsequently, the corresponding loading rate was applied using a slow strain rate machine. As these samples were saturated form the beginning of the mechanical load, and were tested in a continuous source of hydrogen, the hydrogen content remained constant during the whole test: 5.45 ppm.

A total of two samples were tested, each one at one of the two loading rates employed, in order study their effect; one test was performed at $6 \cdot 10^{-9}$ m/s of constant solicitation rate and another 10 times faster, at $6 \cdot 10^{-8}$ m/s, following the recommendations of the Standard ISO-7539 (3). The methodology proposed by ASTM E-1820 (16) was employed for the K_{IEAC} value calculation.

4.2. Small punch tests

The sample geometry employed for SPT, according to (7,9,10), is presented on Figure 6, it consists on a plane 10mmx10mm of section and 0.5±0.01mm of thickness including a lateral notch machined by wire electro-erosion of 0.15 mm radius. The orientation of the notches in both, SPT and C(T) samples, was the same in order to reproduce the same material orientation in both cases (Figure 6).

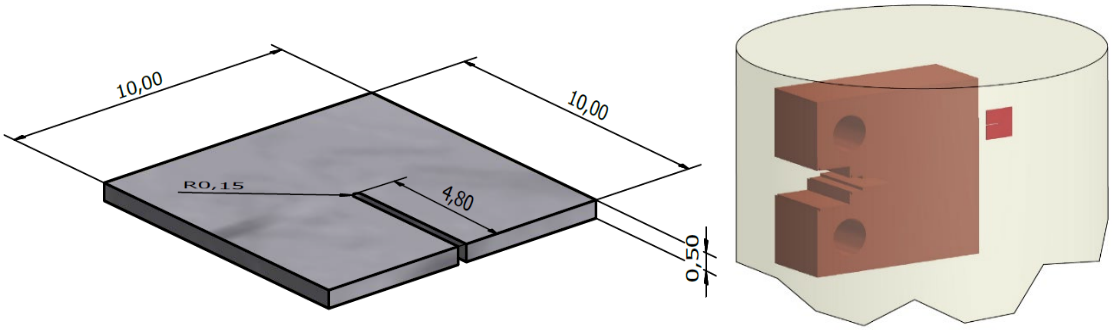

FIGURE 6. SPT NOTCHED SAMPLES EMPLOYED AND ITS ORIENTATION COMPARED TO C(T)'S ONE.

Prior to the test, the specimens were subjected to hydrogen charging by exposing them for 2 hours in the same environmental condition previously described (cathodic polarization at a level of 5mA/cm^2). This amount of time, proposed by (5,7), is higher than the requirement calculated using an estimated diffusivity of hydrogen in this steel at room temperature of $2.3 \cdot 10^{-6}$ cm^2/s; it assured a proper and complete diffusion of the hydrogen inside the material up to the saturation of the 0.5mm thick Small Punch samples (5.45 ppm). After the H_2 charge the mechanical testing was applied. Four mechanical testing conditions were employed in order to produce the different punch rates on the sample to be studied:

- Pre-embrittled samples (2h in cathodic polarization of 5mA/cm^2) were tested in air at a rate of 0.01 mm/s, which is in the range of test rates recommended by (9,10) and widely employed by authors, and at another rate five times slower, 0.002 mm/s, in order to compare their effect. For this purpose, the samples were charged (Figure 7) and, immediately extracted, dried and tested in air environment in an electric machine. A total of 8 samples were tested; 4 samples at 0.01 mm/s and 4 at 0.002 mm/s.

  As these samples were saturated of hydrogen during the pre-embrittlement, but then exposed to diffusion in air during the whole test (5 minutes for the 0.01mm/s rate and 15 minutes for the 0.002mm/s one approximately), hydrogen determination tests were carried out in order to obtain the final content. For this purpose, 8 extra SPT samples (4 for each rate) were pre-embrittled and exposed to air diffusion during the performance of the tests, in order to analyze its H_2 content just after each test end. For each rate, the average of the 4 analysis was taken as result, obtaining contents of 4.86 ppm and 4.15 ppm at the end of the tests at 0.01 mm/s and 0.002 mm/s respectively.

FIGURE 7. SPT PRE-EMBRITTLED SPECIMENS DURING ITS HYDROGEN ABSROTION.

- Embrittled samples (2h in cathodic polarization of $5mA/cm^2$) tested in continuous exposition to the environment at the conventional rate of 0.01 mm/s, and five times slower of 0.002 mm/s. As these samples were saturated form the beginning of the mechanical load, and were tested in a continuous source of hydrogen, the hydrogen content remained constant during the whole test: 5.45ppm. For this purpose, the samples were charged and tested in a device was specifically designed and built for this purpose that is presented in Figure 8; in this case, the punching is applied in the horizontal direction. Again, a total of 8 samples were tested; 4 samples at 0.01 mm/s and 4 at 0.002 mm/s.

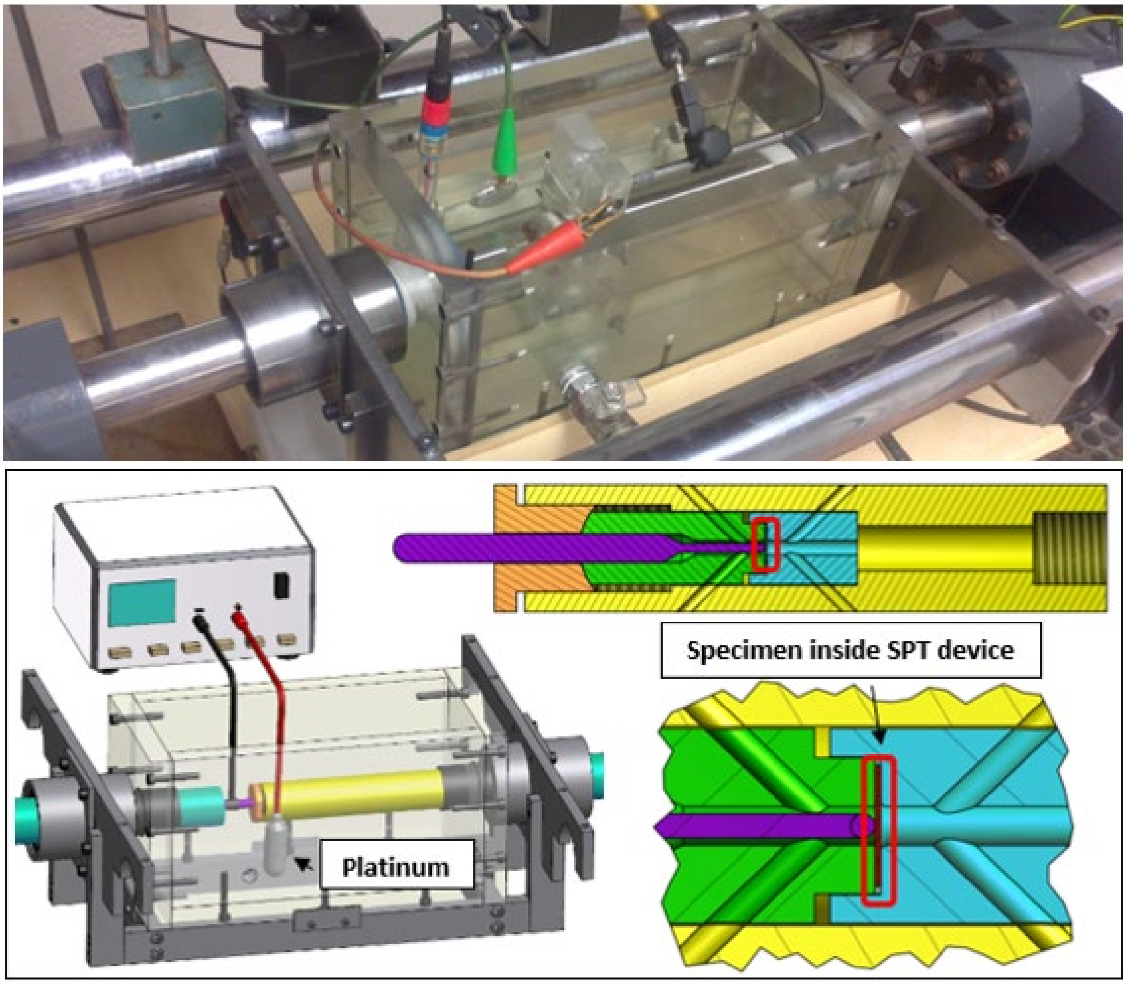

FIGURE 8. EXPERIMENTAL DEVICE FOR PERFORMING SPT TESTS IN ENVIRONMENT AT VERY SLOW RATES; REAL PICTURE DURING A TEST AND DESIGN SKETCH.

- Embrittled samples (2h in cathodic polarization of 5mA/cm^2) tested in continuous exposition to the environment at a very slow rate, 500 times slower than the conventional rate, of 5E-5 mm/s that has been previously employed by some authors (5,6,7). Also, in this case, these samples were saturated form the beginning of the mechanical load, and were tested in a continuous source of hydrogen, so the hydrogen content remained constant during the whole test: 545ppm. These tests were carried out in the device presented in Figure 8. In this case, 2 samples were tested, due to the amount of time required for each test.

- Embrittled samples (2h in cathodic polarization of 5mA/cm^2) tested in continuous exposition to the environment under constant loads. Again, these samples were saturated form the beginning of the mechanical load, and were tested in a continuous source of hydrogen, so the hydrogen content remained constant during the whole test: 5.45ppm. A set of 5 samples, one per each constant load used, were tested using decreasing imposed constant loads, which produced decreasing punch rates in the zone II of the curve, up to that load that was not enough to produce any cracking departing from the edge of the notch. After embrittling, the load was softly applied by an endless screw system on the specimen subjected to the environment. For the purpose of this test, an experimental device was designed and built, which is presented in Figure 9.

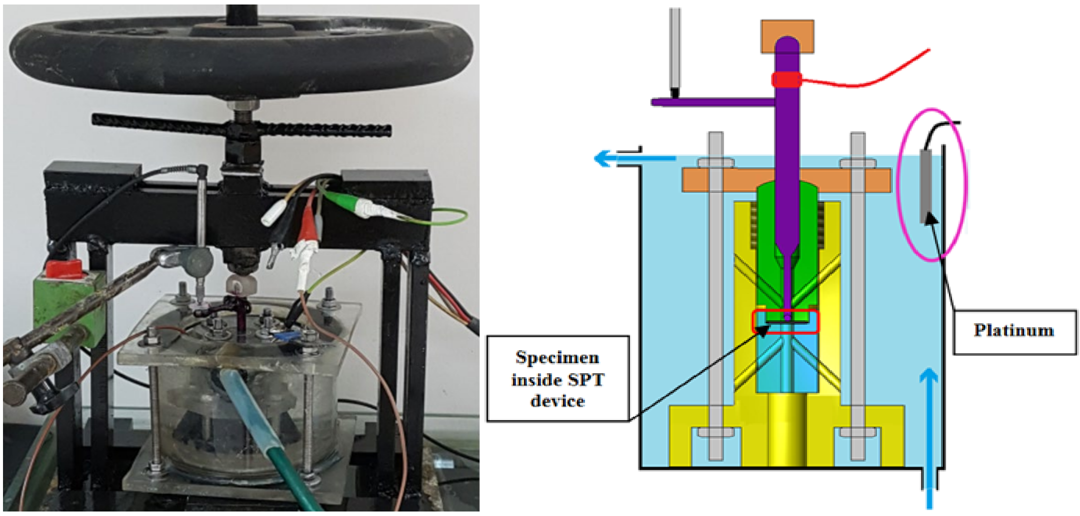

FIGURE 9. EXPERIMENTAL DEVICE FOR PERFORMING SPT TESTS IN ENVIRONMENT UNDER CONSTANT LOAD; REAL PICTURE DURING A TEST AND DESIGN SKETCH.

5. EXPERIMENTAL RESSULTS AND DISCUSSION

5.1. Standard fracture mechanics tests

Figures 10 and 11 show respectively the load-COD registers and the fractographic images obtained from the C(T) samples tested in environment. By applying the methodology exposed in ASTM E-1820 and E-399 standards (16,18), consisting of calculating the fracture toughness from the intersection of the P-COD register with a straight line having 95% of the P-COD linear-elastic slope, values of K_{IEAC}=32.62Mpa*m$^{1/2}$ and K_{IEAC}=30.08Mpa*m$^{1/2}$ were obtained from the samples tested at 6E-8 and 6E-9 m/s respectively.

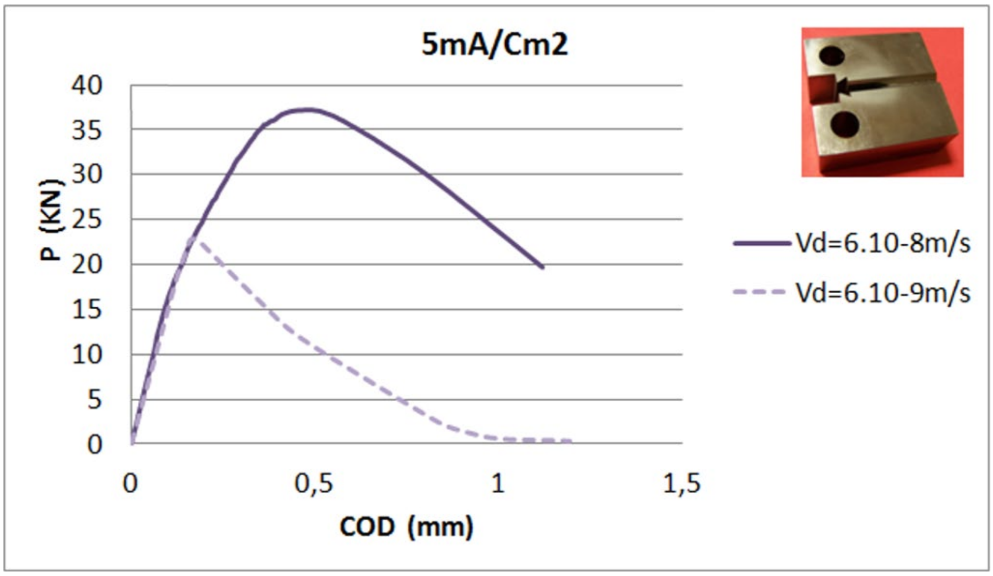

FIGURE 10. EXPERIMENTAL LOAD-COD CURVES FROM CONVENTIONAL FRACTURE MECHANICS TESTS.

The curves shape tends to lower maximum loads and COD values (lower energy) when the testing rate is slower. There is just a slight influence on the fracture toughness due to a similar crack initiation micromechanism, as presented in the fractography (Figure 11), but the sample at the lower rate develops more brittle processes during propagation, which explains such a mechanical difference between both curves. The slower the rate, the higher enough the time for hydrogen trapped in the material to get activated and diffuse to the new cracking areas, allowing all the embrittling capacity of the environment. As the methodology applied for calculating K_{IEAC} remains in the linear-elastic field, just pointing the crack initiation (without considering any propagation), the difference between these values for different testing rates is more moderate than if an elastic-plastic methodology, as the exposed in (22), for example, would have been employed.

On Figure 11, a clear environmental effect can be appreciated in the material, as a result of brittle fracture in a mixed mode of transgranularity and grain boundaries separation by cracking. It can also be observed a slightly more brittle cracked system in the most aggressive situation, where the crack initiation (transition from fatigue pre-cracking to crack propagation by environmental effects) is marked with a red line.

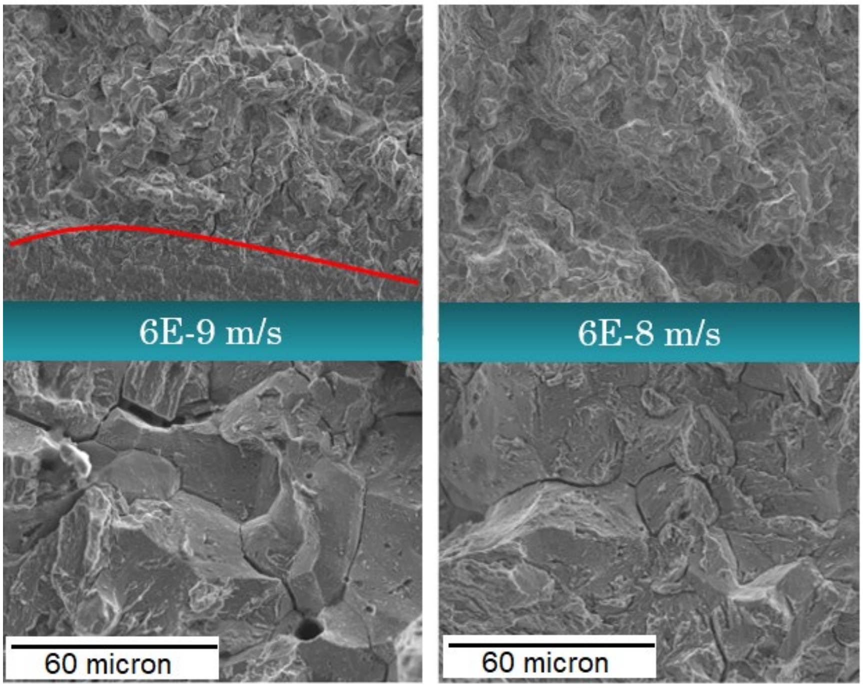

FIG 11. FRACTOGRAPHIC IMAGES FROM CONVENTIONAL FRACTURE MECHANICS TESTS.

5.2. Pre-embrittled SPT samples tested in air at 0.01 mm/s and 0.002 mm/s

Figures 12 and 13 and Table 3 present the curves, values of load and displacement and fractography form the SPT tests performed on pre-embrittled samples (2h in cathodic polarization of 5mA/cm^2) tested in air at conventional rates (0.01 and 0.002 mm/s). The register from an SPT test of the material as received is superposed for comparison (black line).

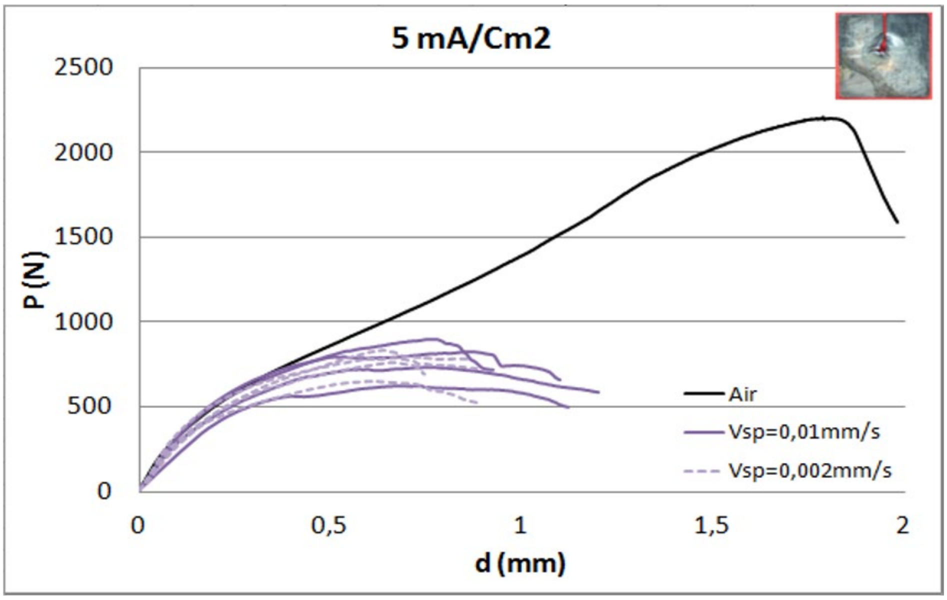

FIGURE 12. LOAD-DISPLACEMENT CURVES FROM PRE-EMBRITTLED SPT TESTED IN AIR AT CONVENTIONAL RATES. SPT AS RECEIVED TEST IS SUPPERPOSED FOR COMPARISON.

TABLE 3. VALUES OF MAXIMUM LOADS AND ITS CORRESPONDING DISPLACEMENTS FROM PRE-EMBRITTLED SPT TESTED IN AIR AT CONVENTIONAL RATES.

PRE-EMBRITTLED SPT SAMPLES TESTED IN AIR AT CONVENTIONAL RATES				
PUNCH RATE	**MAX LOAD**		**MAX LOAD DISPLACEMENT**	
0.01 mm/s	732	**768 N** (mean)	0.75	**0.77 mm** (mean)
	820		0.87	
	901		0.76	
	618		0.68	
0.002 mm/s	760	**759 N** (mean)	0.66	**0.65 mm** (mean)
	797		0.68	
	831		0.64	
	648		0.62	

As presented on Figure 12, 4 samples were used for each one of the two conditions tested (0.01mm/s in continuous line and 0.002mm/s in dashed line); this number of tests per condition was chosen in order to reduce the influence of the dispersion in the results. This dispersion is mainly caused by issues such as slight differences in the sample-tools contacts and thickness value (0.5±0.01mm) in the different tests. These samples were saturated of hydrogen during the pre-embrittlement (5.45ppm), but then exposed to diffusion in air during the whole test (5 minutes for the 0.01mm/s and 15 minutes for the 0.002mm/s approximately); hydrogen contents of 4.86 ppm and 4.15 ppm were obtained at the end of the tests for 0.01 mm/s and 0.002 mm/s respectively.

It can be observed that the exposition to the environment caused an important embrittlement in the material traduced in a loss of mechanical properties. The shape of the curve, that was the typical form a ductile material (black line) shows here a completely brittle typology. Comparing the curves from tests at 0.01 and 0.002 mm/s, as well as its fractography, a clear difference cannot be found. In Figure 13, a semi-brittle slightly transgranular fracture mode can be observed for both rates (0.01 and 0.002 mm/s), without finding any important difference between them. Compared to Figure 11, corresponding to conventional fracture mechanics tests, a much less brittle mode seems to be present in this case; any important decohesion between grain boundaries was found.

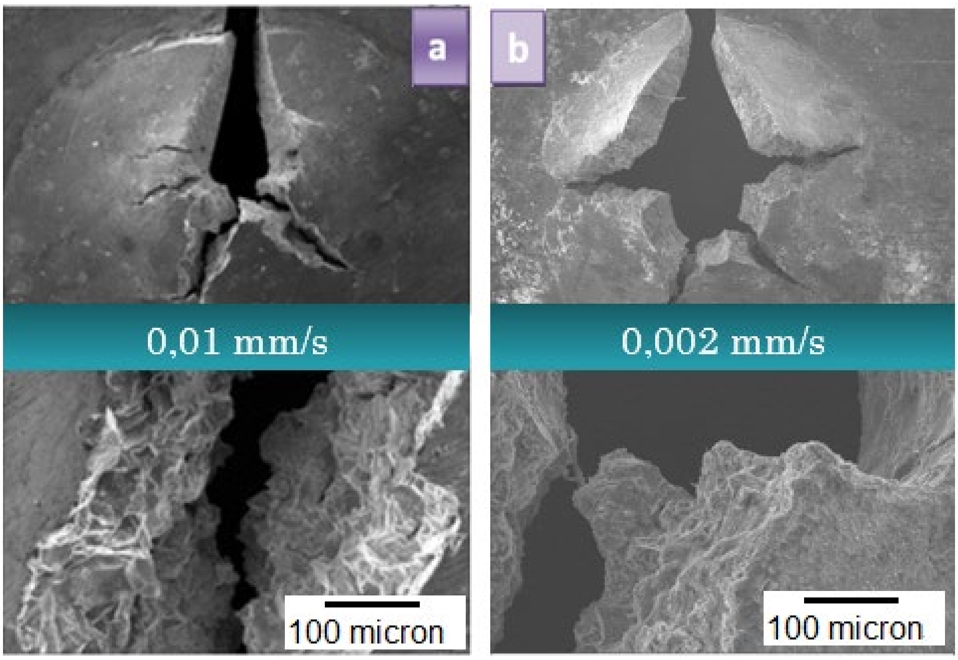

FIGURE 13. FRACTOGRAPHIC IMAGES FROM PRE-EMBRITTLED SPT TESTED IN AIR AT CONVENTIONAL RATES.

There is a competition between two effects taking place. On the one hand, the lower the punch rate is, the more time given to the trapped hydrogen to diffuse to the new cracking areas and its close zones of plasticity causing its embrittling effect. But on the other hand, the lower the rate is, the more time takes the test to be performed, so a higher quantity of hydrogen can diffuse out of the sample due to its reduces thickness (0.5mm), not being able to cause any embrittlement any more. Ergo, the profit by lowering the punch rate is compensated by the diffusion out of the sample; this dual effect will be in function of the material microstructure and hydrogen trapping net (15).

Even if is clear that the SPT pre-embrittled samples are capable of reproducing HE situations, the aforementioned fact points clearly that a more accurate way to reproduce the micromechanisms from conventional fracture mechanics tests is needed. A way to solve this situation could be performing SPT tests on samples exposed to a continuous source of hydrogen, by submerging them in the environment; in this way, a more precise study of the punch rate influence could be carried out.

5.3. Embrittled SPT samples tested in exposition to the environment at 0.01 mm/s and 0.002 mm/s

Figures 14 and 15 and Table 4 present the curves, values of load and displacement and fractography form the SPT tests performed on embrittled samples (2h in cathodic polarization of 5mA/cm^2) tested in environment at conventional rates (0.01 and 0.002 mm/s); The register form an SPT test of the material as received is superposed for comparison (black line). Again 4 samples were used for each one of the two conditions tested (0.01mm/s in continuous line and 0.002mm/s in dashed line), in order to reduce the influence of the dispersion in the results. In both cases (0.01mm/s and 0.002mm/s), as the samples were saturated form the beginning of the mechanical load, and were tested in a continuous source of hydrogen, the hydrogen content remained constant during the whole test: 5.45ppm.

In this case, the environment produced again an important embrittlement, showing the SPT curves a typical brittle shape and a decrease of properties when compared to the as received curve (black line). Despite the 0.01 mm/s SPT tested in environment curves (constant 5.45ppm) don't differ much from the SPT pre-embrittled ones (4.86ppm at the end of the test, Figure12), in this case a clearer difference between both rates (0.01 and 0.002 mm/s) can be appreciated.

Slower punch rate curves (0.002 mm/s) show a clear reduction of their mechanical properties (mainly lower maximum load and displacement) from the 0.01 mm/s ones. Also, when comparing the 0.002 mm/s curves tested in environment (constant 5.45ppm) to their homologous pre-embrittled and tested in air (4.15ppm at the end of the test), it can be observed that the maximum load and punch displacement are reduced. Thus, it can be stated that carrying out the test submerged in the environment has a clear influence.

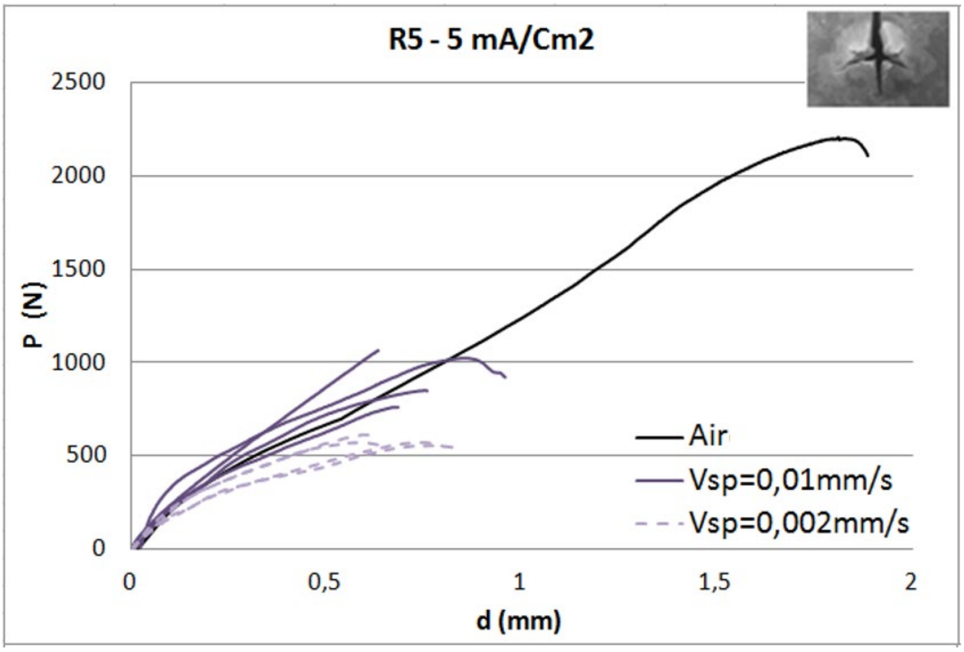

FIGURE 14. LOAD-DISPLACEMENT CURVES FROM EMBRITTLED SPT TESTED IN ENVIRONMENT AT CONVENTIONAL RATES. SPT AS RECEIVED TEST IS SUPPERPOSED FOR COMPARISON.

TABLE 4. VALUES OF MAXIMUM LOADS AND ITS CORRESPONDING DISPLACEMENTS FROM EMBRITTLED SPT TESTED IN ENVIRONMENT AT CONVENTIONAL RATES.

EMBRITTLED SPT SAMPLES TESTED IN ENVIRONMENT AT CONVENTIONAL RATES				
PUNCH RATE	**MAX LOAD**		**MAX LOAD DISPLACEMENT**	
0.01 mm/s	848	**924 N** (mean)	0.71	**0.70 mm** (mean)
	757		0.66	
	1065		0.63	
	1025		0.78	
0.002 mm/s	555	**556 N** (mean)	0.47	**0.58 mm** (mean)
	551		0.58	
	569		0.56	
	549		0.71	

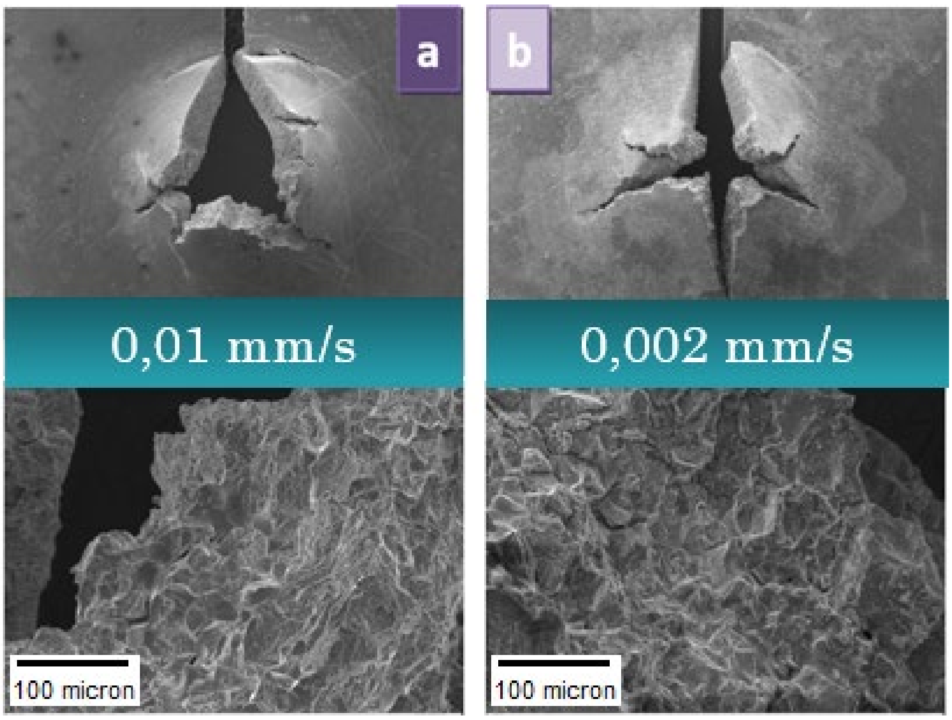

FIGURE 15. FRACTOGRAPHIC IMAGES FROM EMBRITTLED SPT TESTED IN ENVIRONMENT AT CONVENTIONAL RATES.

Regarding the fractography for this case, a combined brittle transgranular and intergranular fracture mode can be observed for both rates (0.01 and 0.002 mm/s), but slight differences can be found between them. The lower punch rate, 0.002 mm/s, shows a more brittle system that presents a slightly higher transgranularity and grain boundaries separation than 0.01 mm/s sample, and it is nearly as brittle as the one presented by fracture mechanics tests (Figure 11).

It seems that submerging the embrittled samples during the test, and reducing the punch rate in order to allow the hydrogen time enough to diffuse to the cracking plastic zones, is the way to reproduce the micromechanisms taking place during conventional fracture mechanics test accurately.

5.4. Embrittled SPT samples tested in exposition to the environment at 5E-5 mm/s

Figures 16 and 17 and Table 5 present the curves, values of load and displacement and fractography form the SPT tests performed on embrittled samples (2h in cathodic polarization of 5mA/cm^2) tested in environment at a very low rate proposed by (7) (5E-5 mm/s). The register from an SPT test of the material as received is superposed for comparison (black line). In this case, 2 samples were used for the condition tested; this was considered enough in view of the right repeatability of the results. Again, the samples were saturated form the beginning of the mechanical load and tested in a continuous source of hydrogen, the hydrogen content remained constant during the whole test: 5.45ppm.

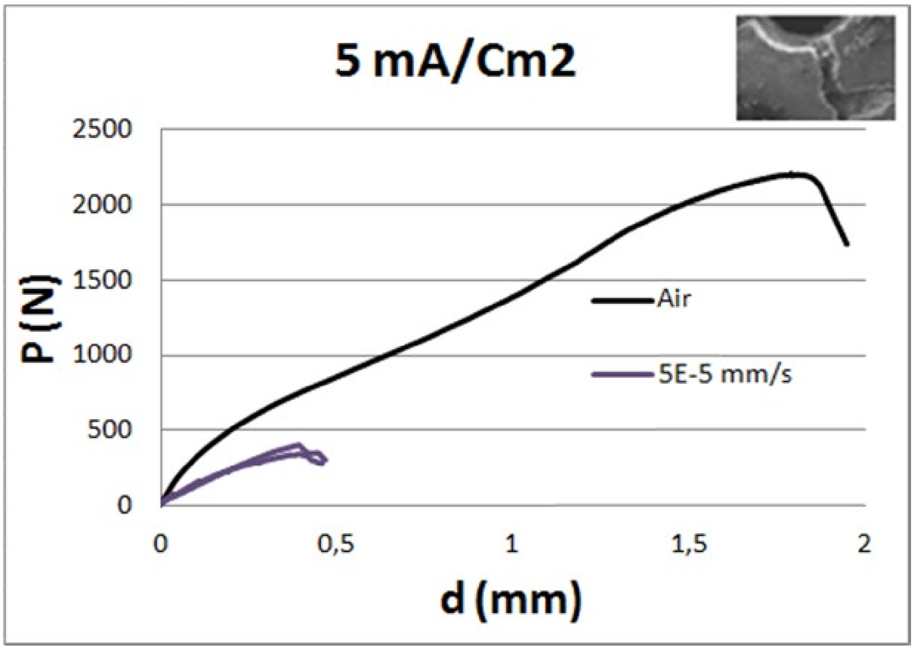

FIGURE 16. LOAD-DISPLACEMENT CURVES FROM EMBRITTLED SPT TESTED IN ENVIRONMENT AT VERY SLOW RATE. SPT AS RECEIVED TEST IS SUPPERPOSED FOR COMPARISON.

TABLE 5. VALUES OF MAXIMUM LOADS AND ITS CORRESPONDING DISPLACEMENTS FROM EMBRITTLED SPT TESTED IN ENVIRONMENT AT VERY SLOW RATE.

EMBRITTLED SPT SAMPLES TESTED IN ENVIRONMENT AT VERY SLOW RATES				
PUNCH RATE	**MAX LOAD**		**MAX LOAD DISPLACEMENT**	
5E-5 mm/s	401	**369 N** (mean)	0.37	**0.35 mm** (mean)
	337		0.33	

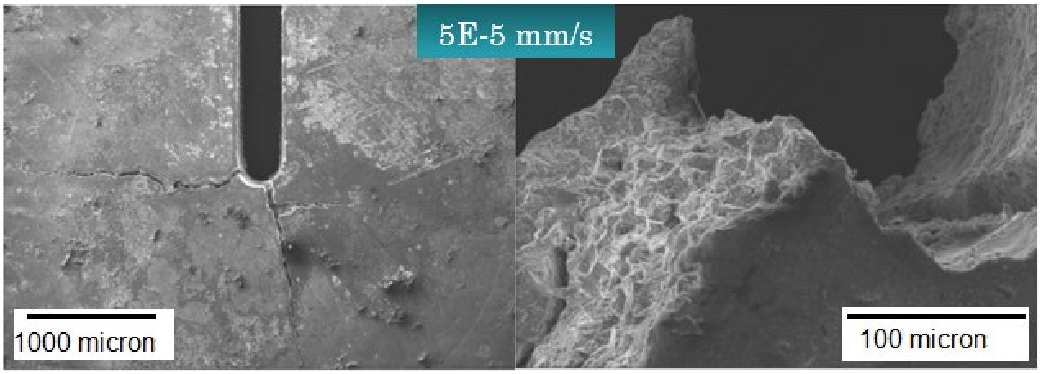

FIGURE 17. FRACTOGRAPHIC IMAGES FROM EMBRITTLED SPT TESTED IN ENVIRONMENT AT VERY SLOW RATE.

At the first look at the graphs, the mechanical response of the SPT embrittled samples tested in environment at a very low rate (5E-5 mm/s) results poorer than the samples tested in environment at conventional rates and a lot poorer than the SPT test of the material as received. The registers exhibit once more a brittle typology, that is enhanced by the very slow rate (5E-5 mm/s), which gives the hydrogen time enough to develop all of its embrittling and damaging power to the microstructure.

From the fractographic images, it can be stated that a clearly brittle pattern in a mixed mode is presented, showing transgranularity and grain boundaries separation in a similar magnitude to the one presented on conventional fracture mechanics tests on C(T) samples (Figure 11). Thus, the rate imposed by this methodology (5E-5 mm/s) can reproduce the same micromechanisms taking place during conventional fracture mechanics tests.

5.5. Embrittled SPT samples tested in exposition to the environment under constant loads

In order to study the effects for lower values of the rate, submerged SPT tests in environment under constant load had been performed after pre-embrittling 2h in cathodic polarization of 5mA/cm^2). A set of samples were tested using decreasing imposed loads, which produced decreasing punch rates in the zone II of the curve, up to the load that was not enough to produce any cracking departing from the edge of the notch. Figure 18 shows the registers displacement-time, Table 6 the values of loads and displacements in each case and Figure 19 presents the macrographic pictures of the samples tested by this methodology.

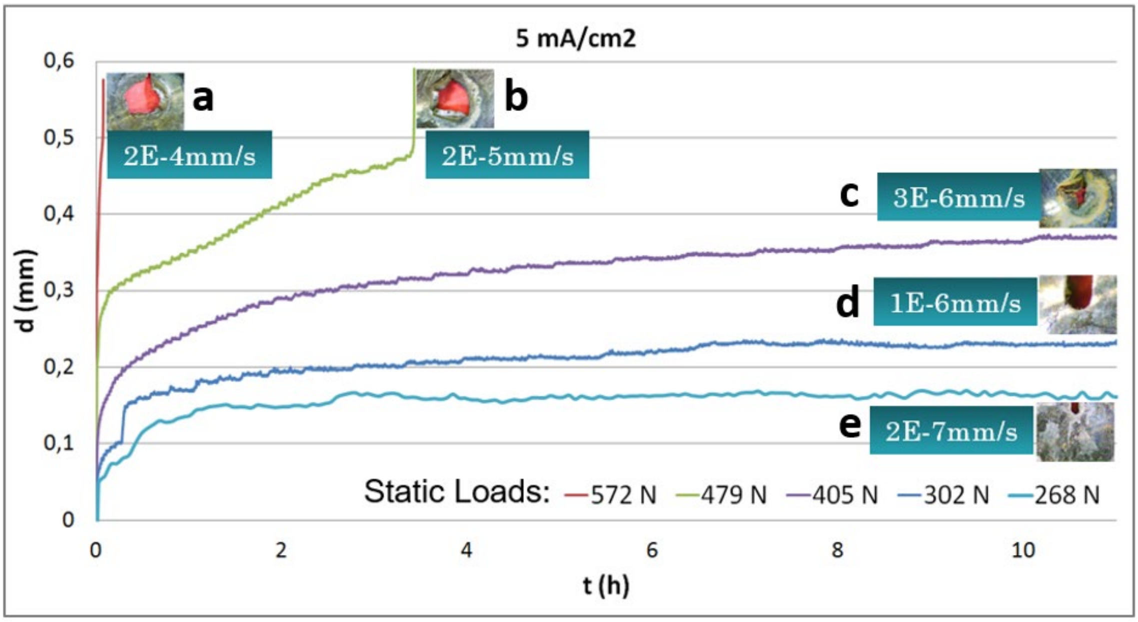

FIGURE 18. DISPLACEMENT-TIME CURVES FROM EMBRITTLED SPT SAMPLES TESTED IN ENVIRONMENT UNDER STATIC LOADS.

TABLE 6. VALUES OF MAXIMUM LOADS AND ITS CORRESPONDING DISPLACEMENTS FROM EMBRITTLED SPT TESTED IN ENVIRONMENT AT VERY SLOW RATE.

EMBRITTLED SPT SAMPLES TESTED IN ENVIRONMENT UNDER CONSTANT LOADS		
PUNCH RATE	**LOAD**	**INITIATION DISPLACEMENT**
2E-4 mm/s	572	0.31
2E-5 mm/s	479	0.30
3E-6 mm/s	405	0.29
1E-6 mm/s	302	0.15
2E-7 mm/s	**268** (lowest)	**0.11** (lowest)

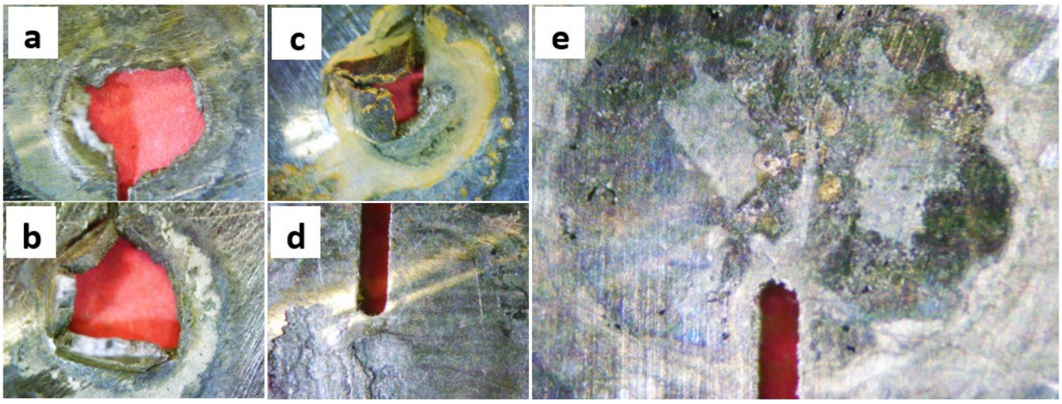

FIGURE 19. MACROGRAPHYS FROM EMBRITTLED SPT SAMPLES TESTED IN ENVIRONMENT UNDER STATIC LOADS ("e" DIDN'T DEVELOPPED MACROSCOPIC CRACKS).

The imposed loads produced a punch rate developed by the flexibility variation of the cracked sample when developing new cracking areas, due to its exposition to the combination of aggressive environment and applied load, as stated in (7).

The two highest loads ("a" and "b") produced the failure in 5 minutes and less than 4 hours developing rates around E-4 and E-5 mm/s. Samples "c" and "d" reached a quasi-stable zone II of cracks evolution, resulting this in rates in the range of E-6 mm/s; in sample "c" an important crack that drilled the sample when it collapsed can be appreciated, while in sample "d" a crack that starts from the edge of the notch was found when the test was stopped prior to the sample's collapse.

In sample "d", that developed a rate in the range of E-7 mm/s in zone II, any macroscopic crack with its onset of the edge of the notch wasn't found, although a subcritical cracking on the sample's thickness could be taking place according to the literature (7). This means that the constant load imposed must be around the threshold load for this combination of material and environment; either, a crack would have appeared if a longer time had been waited, or the imposed load is slightly under the threshold and the failure will never occur. In any case it can be concluded that the threshold takes place in rates around E-6 to E-7 mm/s

Due to the conclusion obtained from Figure 17, where the micromechanism shown seemed to be equivalent to the one presented for conventional fracture mechanics tests, no fractographic analysis were carried out. For the punch rates developed of E-6 to E-7 mm/s, hydrogen will have time enough to cause all of its embrittling capacity, so micromechanisms will be alike to those from Figure 17. This can be seen by comparing Tables 3, 4, 5 and 6, where the values of maximum loads and its corresponding punch displacements, point at which crack initiation takes place according to (5), it can be stated that the slower the punch rate is the lower these values become.

Thus, it can be stated that the static load SPT test is an appropriate methodology to reproduce HE situations. Allowing the system to be auto-cracked by the load imposed, it is assured the application of a rate slow enough to produce the HE micromechanisms present in real scenarios. On the other hand, the disadvantage of this method is the need to test several samples, up to finding the one that does not produce any cracking from the edge of the notch of the specimen.

6. CONCLUSIONS

A mechanical analysis of the curves, together with a fractographic study of the micromechanisms presented by the samples tested at different rates was carried out. Pre-embrittled SPT notched samples were tested in air at conventional rates of 0.01 and 0.002 mm/s, and embrittled samples were tested in environment from rates of 0.01 mm/s to constant load tests that reached up to E-7 mm/s. Form this study, it is concluded that:

- Very slow rates are necessary to perform SPT characterizations in environment, in order to allow the environment to reach the crack tip plasticity zones and apply all of its embrittling capacity.
- A continuous exposition of the sample to the embrittling environment, i.e. being submerged during the whole test, is required to avoid the loss of an important part of the hydrogen introduced, which is weakly trapped and can diffuse outside of the sample. This is requirement (together with slow rates) is collected in the standards (3) for conventional tests in environment, such as SSRT or K_{IEAC} tests.
- Tests at rates of 5E-5 mm/s, or lower, showed similar micromechanisms than those from conventional fracture mechanics tests on C(T) samples for the same environment.
- Constant load tests developed punch rates of around E-6 to E-7 mm/s, as a result of the system's flexibility variation assisted by the environment. Even if this technique seems suitable, it demands an excessive amount of material and time, as it needs to tests a set of samples for each environmental condition. Tests in environment at punch rates around E-6 mm/s, ergo rates 10,000 times slower than the conventionally used for SPT tests in air (9,10), seem to be a more suitable option.

As a general conclusion, to perform SPT applications to HE scenarios, it is recommended to employ embrittled notched samples tested completely submerged in the environment at a range of rates of around E-6 mm/s. By doing so, it will be assured the reproduction the micromechanisms taking place during real processes. SPT fracture characterization parameters collected in the literature such as the energy for embrittlement damage initiation, the CTOD concept or the estimation of K_{EAC} may be applied (5,6,12).

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REFERENCES

(1) HAMILTON, J.M., "The challenges of Deep-Water Artic Development", International Journal of Offshore and Polar Engineering, 21 (4), (2011), 241-247.

(2) JOHANNES REHRL, KLEMENES MRACZEK, ANDREAS PICHLER, EWALD WERNER, Mechanical properties and fracture behavior of hydrogen charged AHSS/UHSS grades at high- and low strain rate tests", Materials Science & Engineering A, 590 (2014) 360-367.

(3) ISO 7539:2011; Parts 1 to 9 "Corrosion of metals and alloys"

(4) MARTÍNEZ-PAÑEDA E., GARCÍA T.E., RODRÍGEZ C., "Fracture toughness characterization through notched small punch test specimens", Materials Science and Engineering A, vol. 657, pp. 422-430, 2016.

(5) ARROYO B., ÁLVAREZ J.A., LACALLE R., "Study of the energy for embrittlement damage initiation by SPT means. Estimation of K_{EAC} in aggressive environments and rate considerations", Theoretical and Applied Fracture Mechanics, 86 (2016), 61-68.

(6) GARCÍA T.E., ARROYO B., RODRÍGUEZ C., BELZUNCE F.J., ÁLVAREZ J.A., "Small punch test methodologies for the analysis of the hydrogen embrittlement of structural steels", Theoretical and Applied Fracture Mechanics, 86 (2016), 89-100

(7) ARROYO B., ÁLVAREZ J.A., LACALLE R., URIBE C., GARCÍA T.E., RODRÍGUEZ C., "Analysis of key factors of hydrogen environmental assisted cracking evaluation by small punch test on medium and high strength steels", Materials Science and Engineering A, 691 (2017), 180-194.

(8) MANAHAN, M.P., ARGON, A.S., HARLING, O.K., "The development of a miniaturized disk bend test for the determination of post irradiation mechanical properties", Journal of Nuclear Materials, 103 & 104, 1981, pp. 1545-1550.

(9) CWA 15627, "Small Punch test method for metallic materials, Part A: Code of practice for Small Punch creep testing, Part B: Code of practice for Small Punch testing for tensile and fracture behavior", Documents of CEN WS21, Brussels, 2007.

(10) EN Standard Working Draft WI, "Metallic materials - Small punch test method" Documents of ECISS/TC 101, AFNOR. 2018.

(11) ESKNER M., SANDSTROM R., "Mechanical property using the small punch test", Journal of Testing and Evaluation, vol 32, Nº 4, January 1995, pp. 282-289.

(12) LACALLE R., ÁLVAREZ J.A., ARROYO B., GUTIÉRREZ-SOLANA F., "Methodology for fracture toughness estimation based on the use of Small punch notched specimens and the CTOD concept", The 2nd International Conference SSTT 2012, Conference Proceedings, October 2012.

(13) FINARELLY D., ROEDIG M., CARSUGHI F., "Small Punch Tests on Austenitic and Martensitic Steels Irradiated in a Spallation Environment with 530 MeV Protons", Journal of Nuclear Materials 328, 2004, pp. 146-150.

(14) KIM M.C., OH Y.J., LEE B.S., "Evaluation of ductile-brittle transition temperature before and after neutron irradiation for RPV steels using Small Punch tests" Nuclear Engineering and Design 235, 2005, pp. 1799-1805.

(15) G.M. PRESSOUYRE, I.M. BERNSTEIN, "An example of the effect of hydrogen trapping on hydrogen embrittlement", Metallurgical transactions, vol. 12, nº A, pp. 835-844, 1981

(16) ASTM E-1820-01, "Standard Test Method for Measurement of Fracture Toughness", Annual Book of ASTM Standards, 2001.

(17) ASTM E-8-11. "*Standard test methods for testing of metallic materials*".

(18) ASTM E399-12**. "** *Standard Test Method for Linear-Elastic Plane-Strain Fracture Toughness KIc of Metallic Materials*"

(19) F. Gutiérrez-Solana, J.A. Álvarez, J. González, A. Brass, J. Chêne, L. Coudreuse, C. Renaudin, M. Astiz, J. Belzunce, “Stress corrosion cracking on weldable micro-alloyed steels”, Contract No 7210-KB/327 Final Report, EUR 17249 EN, 1992-1995.

(20) ÁLVAREZ J.A., GUTIÉRREZ-SOLANA F., "Hydrogen Induced Cracking Processes in Structural Microalloyed Steels. Characterization and Modelling", Materials Science Forum, vols. 284-286 1998, pp.303-310.

(21) ÁLVAREZ J.A., GUTIÉRREZ-SOLANA F., “An elastic-plastic fracture mechanics-based methodology to characterize cracking behavior and its applications to environmental assisted processes”, Nuclear engineering and design, vol. 188, Pp. 185-202, 1998.

(22) KUMAR V., GERMAN M., SHIH C.F., “An engineering approach to elastic-plastic solid”, Research project EPRI NP-1931, General Electric Company, NY, 1981.