Time optimization of the step loading technique in hydrogen embrittlement Small Punch Tests

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Abstract

The small punch tests consists of punching a plane small specimen until it breaks. This technique is very interesting in situations where there is a shortage of material. In recent works, it has been used with steel employed in aggressive environments, to estimate the threshold stress under which subcritical cracking will never occur. It has been presented in previous papers in combination with standard ASTM 1624, applying gradually increasing constant loads until the sample fails, to reduce the duration of the test and the results dispersión.

In the present paper, a further optimization is performed on the steps durations for SPT, simplifying the test and therefore helping to reduce the lab workload while at the same time saving costs and resources and increasing productivity. The present work is carried out on an X80 medium-strength rolled steel in hydrogen embrittlement environments under three different levels of cathodic polarization in an acid electrolyte; the chosen steel belongs to the lowest hardness range (33≤HRC<45) according to the ASTM 1624 standard. Different steps duration from 10 to 60 mintures had been analyzied, cocluding that 20-40 minutes for 1st to 10th and 11th to 20th steps respectivley are proposed as the minimum ones to reach accurate results. The proposed optimization allows to reduce the total test duration, being for sure of great interest for the metal industry as well as for the scientific comunity.

Keywords: Small Punch test, Step loading technique, ASTM F1624, Threshold stress, Hydrogen embrittlement, Test time optimization

Nomenclature

SPT	Small Punch Test
P_{th}	Threshold load ASTM F1624
σ_{th}	Threshold stress ASTM F1624
P_{FFS}	Fast Fracture Load (ASTM E8 tensile test in air)
P_{max}	Maximum load of first step sequence ASTM F1624
$P_{FFS-SPT}$	SPT Fast Fracture Load from test in air according to European Standard EN 10371
P_y	Elastic to plastic load in SPT test in air, form the test in air according to EN10371
$P_{max-SPT}$	SPT Maximum load of the first step sequence
P_{th-SPT}	SPT threshold load
σ_{th-SPT}	Threshold stress estimated by SPT
h_o	SPT sample thickness

1. Introduction

Medium and high-strength steels are widely used in the energy industry, thanks to their properties which make them able to satisfy the increasing mechanical demands. Despite their strength, these materials are strongly affected by aggresive environments, leading to EAC (Environmental Assisted Cracking), a material dettriment which can even bring to catastrophic structural failures. Some examples of applications where aggresive environments are present are marine offshore structures with cathodic protection, gas transport pipelines with presence of H_2S, or even in vehicules running with hydrogen fuel cells, a product where a very big development effort is nowadays being placed, aligned with the UE aim to stop producing passenger cars with combustión and/or hybrid engines in 2035.

To measure the fracture properties while considering the effect of adverse environments, usually ISO 7539 [1] and ASTM E1681 [2] are followed. They describe the use of slow strain tests and also tests under constant load (below which delayed failures or fractures in a certain environment will not happen). For the tests under constant load, aproximately 12 samples of cylindrical specimens are needed, meaning very long testing times (up to 10,000 h) [2]. The testing duration can be interestingly reduced (the threshold stress can be obtained withing a few days for 33HRC or harder steels with mínimum 3 samples) by following the ASTM F1624 standard [3]. It recommends using constant load steps of a certain time duration, incrementing the load in each step until the failure occurs.

In previous publications [4] the use of the incremented step loading technique described in ASTM F1624 was combined with the use of Small Punch Test (SPT). SPT is a miniature test which was originally developed to cover cases, like welded joints, where it is not feasible to obtain specimens with enough size to meet the requirements of the aforementioned standards. SPT was employed for the first time in 1980s, and since then it has already become a global alternative methodology to standard testing for médium and high strength steels characterization in aggressive environments, being published the first European SPT Standard [5] in 2021, after validating a draft document employed by research groups for nearly a decade. The combination of the step loading technique with SPT was tested in a previous publication [4], being prooved as a suitable methodology to obtain the threshold stress in hydrogen embrittlement situations. As a first approach the duration of the steps were chosen considering practical experimental purposes and diffussion properties. Therefore, as the main target of this work the step duration needs to be adjusted as the minimum one, able to ensure maximum environmental embrittelement effect, after being properly studied and justified.

2. Prior concepts

2.1. The standard ASTM F1624

ASTM F-1624 describes a fast method to obtain the threshold load of steels in aggressive environments to initiate a subcritical crack growth [3]. It consists on the application of a sequence of increasing load steps with a determined duration until the sample breaks.

This methodology, described in detail in [4] and summarized on Figure 1, firstly requires to perform a tensile test of the material in air according to ASTM E8 [6] in order to obtain the fast fracture load, P_{FFS}, which is then used to define the range of the steps to be applied. Sequences of 20 steps, of $P_{FFS}/20$ magnitude each, are carried out until the sample failure obtaining the corresponding sequence thressholds, P_{th-1}, P_{th-2}, … P_{th-n}. As many step sequences as necessary are carried out, with a minimum of three, defining the threshold load when the difference between the thresholds of two sequences, P_{th-n-1}, P_{th-n}, is less than 5%.

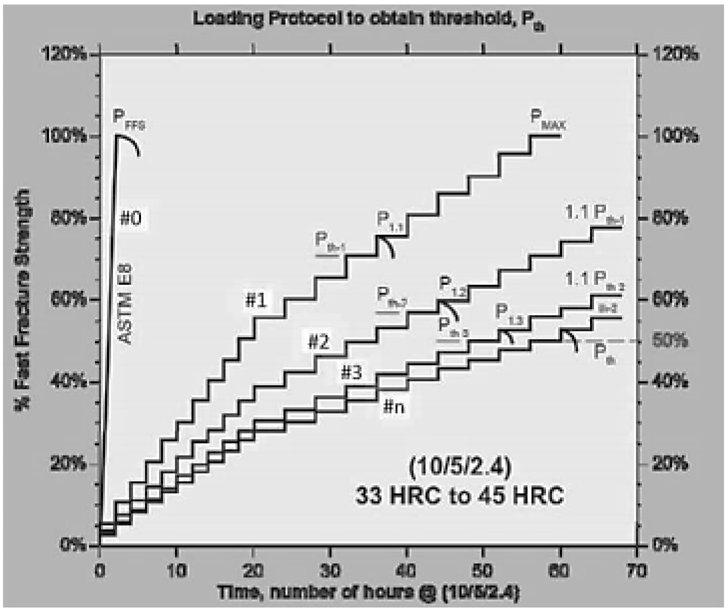

Figure 1 *Example of loading protocol to obtain the Invariant Threshold load, Pth, in 22 < HRC ≤ 45 steels [3].*

The duration of the steps is defined in function of the steel hardness, defining three levels, as indicated in Table 1. This higher environmental effect for higher mechanical properties is widely stated in literature [7]; higher step times are indicated in the softest range to allow a complete EAC effect [8].

Hardness (HRC)	**Number of steps**	**$\%P_{max}$**	**Time (h)**
≥33 to 45	10	5	2
	10	5	4
>45 to 54	10	5	1
	10	5	2
>54	20	5	1

Table 1 *Steps load profile depending on the hardness of the steel [3].*

2.2. Application of Small Punch in aggressive environment

The SPT is a miniature test (almost non-destructive, given the size of material required, normally not compromising the component or structure integrity). It was used for the first time in 1981 in the nuclear industry [9], where it was extremely hard (complex and expensive) to manipulate and characterize irradiated steel with standard test methodologies. SPT allows the option of testing in-service components extracting the miniature sample and leaving the possibility to even repair the hollow afterwards. Since 1981, several publications [10-12] have shown its effectiveness to evaluate mechanical properties like tensile, fracture and creep in various material types. It has, in fact, become an interesting alternative in the scientific comunity worldwide, and proof of it is the recent publication of the SPT European standard [5].

Thanks to its small dimensions and to the simplicity of the technique, SPT has been widely used to evaluate steel embrittlement, like in the case of neutron irradiated materials [13], in the case of brittle-ductile transition temperature of metals [14] or in hydrogen embrittlement and environmental assessments [15-21, 4].

Altough it started to be studied more than 25 years ago, another application of SPT that has been gaining interest during the last years is its application to agresive environments. In 1988, Misawa [15] simulated the conditions of on-service components in an aggressive environment. Two stainless steels were tested by immersing a specimen in an acqueous solution with high pressure and temperature. The results showed the same trend like the Slow Strain Rate Tests (SSRT), which is why the SPT technique was proposed as adequate to assess the susceptibility for embrittlement of these kind of materials. More recently, Nambu in 2007 [16] studied the effect of coating Niobium with Palladium with SPT, based on the análisis of its embrittlement. The highliht of his work was the device employed to embrittle the specimen which was in contact with a gaseous mixture at high pressure and temperature. In the last years, several publications from the Universities of Oviedo and Cantabria compared SPT in air versus SPT when permanently immersed in the aggressive solution, demostrating the feasibility of SPT to assess embrittlement in materials highly susceptible to it and emphasizing on whether the hydrogen source has been applied on one or both sides of the specimen. This work also proved that the micromechanisms developed on SPT and tensile specimens, when both embrittled in equivalent conditions, were found to be the same [4, 19-21].

To perform SPT test, a plane specimen with 0.5 mm nominal thickness and a cross section under 1 cm^2 is punched until breakage occurs. The device used for this purpose is presented in Figure 2, it was developed and built ad-hoc, consisting of a cell where the sample is embedded between two plastic matrix and punched while immersed in the aqueous solution during the complete test. The different loads corresponding to each step are applied through several weigths on the punch (gently applied), which is also coated with insulating varnish. The two rigid matrix which are embedding the specimen all around its contour, have concentric cilindrical holes in their central zone. The upper matrix hole is intended to guide the punch, while the lower matrix hole, finished with a chamfer, eases the specimen deformation along the test. The hardness of these tools, as well as the punch’s one, must be enough to assure that the geometry is not altered along the trials, therefore not lower than 55 HRC according to [5].

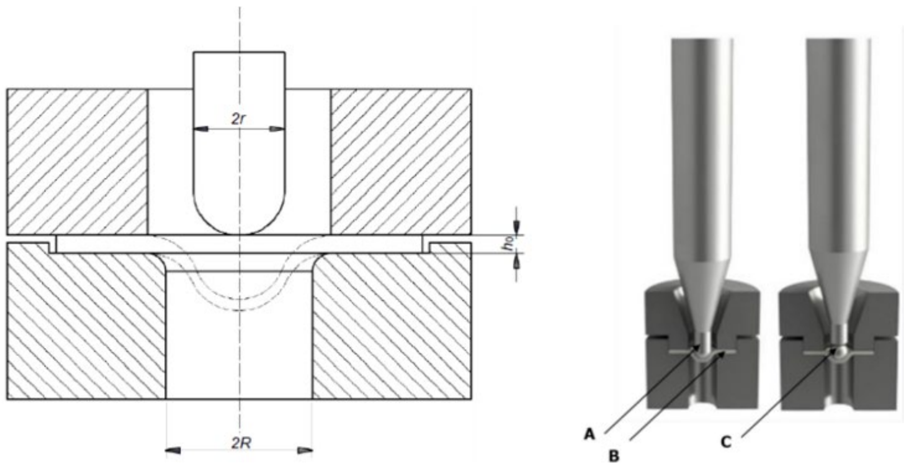

Figure 2 *SPT experimental device used in this work (left) [22]. 3D model representing A) the punch, B) the specimen, C) the punch-ball [5].*

In environmental characterizations, test rate is a relevant variable for EAC assessments [23], what affects also to SPT; the need of very slow punch rates (or even constant loads) has been demonstrated [20, 21], what gives place to realatively high testing times. Also, in order to give hydrogen enough time to diffuse from reversible traps to cracking areas generated by plastic deformation [8, 19-21, 23-25], it has been proved that the samples should be continuosly exposed to the environment during the whole test [21]. The test in air of pre-embrittled samples is then discarded, as hydrogen will not have enough time to diffuse throw the lattice if rates are to fast, or part of it will diffuse outside of the sample if they are too slow.

Previous research put their focus on interrupted SPT under constant loads, to analyze the punch displacement versus time, together with fractographic analysis and micromechanisms taking place [20], proposing the SPT technique as a simple alternative to determine the EAC instead of conventional slow strain rate tests. The last research, focused on finding a leaner SPT application to hidrogen embrittlement secenarios, pointed the step loading technique to be a suitable option to reduce the huge time demand [4]. As many aspects may still be optimized in the aforementioned methodology, the aim of the present work is to further improve it by optimizing the step time.

3. Experimental methodoloy

3.1. Material employed and embrittling environment

An X80 medium-strength rolled steel was chosen, which is commonly employed for oil&gas pipelines and has been previously used by the authors [4]. It has the ferritic-pearlitic microstructure with grain size 5-15 μm presented in Figure 3, and is 35HRC. The chemical compositon and mechanical properties in air are presented in Tables 2 and 3 respectively.

	C	Si	S	P	Mn	Ni	Cr	Mo	Cu	Al	V	Ti	Nb
X80	0.07	0.18	<0.005	<0.005	1.83	0.03	-	0.15	0.02	0.03	-	-	0.03

Table 2 *Chemical composition of X80 steel (weight %)*

	E (GPa)	σ_y (MPa)	σ_u (MPa)	e_u (%)	HRC
X80	209.9	621.3	692.9	29.6	33

Table 3 *Mechanical properties of X80 steel.*

As X80 has shown to be susceptible to hydrogen effects [4, 26], a cathodic polarization previously used by the authors [4], was chosen to produce hydrogen embrittlement on the SPT specimens in this work. In the system, shown in Figure 4, the sample works as the electrode, a platinum grid as the counter-electrode and the saturated calomel electrode as the reference.

The acid electrolyte is a solution of 1N H_2SO_4 distilled with wáter, with 10 mg of As_2O_3, prepared according to Pressouyre's method [24] with a pH between 0.65 and 0.80. All the tests were performed at room temperature (20±2°C) with continuous water agitation [1] to remove bubbles preventing any kind of local conditions or corrosion.

The polarization forces hydrogen to be absorbed by the host lattice [25]. Different hydrogen concentration levels can be simulated by different current intensity levels. Three of these aggressiveness levels were employed (1mA/cm^2, 5 mA/cm^2, and 10 mA/cm^2), starting with 10 mA/cm^2 to be able to easily observe and detect trends. After charging, hydrogen content measurements were performed on the material and are presented in Table 4. Each hydrogen content was obtained as the average of five samples values determined by the hot extraction technique by means of a Leco® RH-402 analyzer. The samples employed were pseudo-cubic pieces of an approximate weight of 1g, they were charged during 24 hours in the aforementioned conditions, and subsequently extracted from the solution, dried and cleaned using the simple acetone method according to [27]. The results show a hydrogen saturation at high intensities, as it can be observed how the contents for 10 and 5 mA/cm^2 environments are very close.

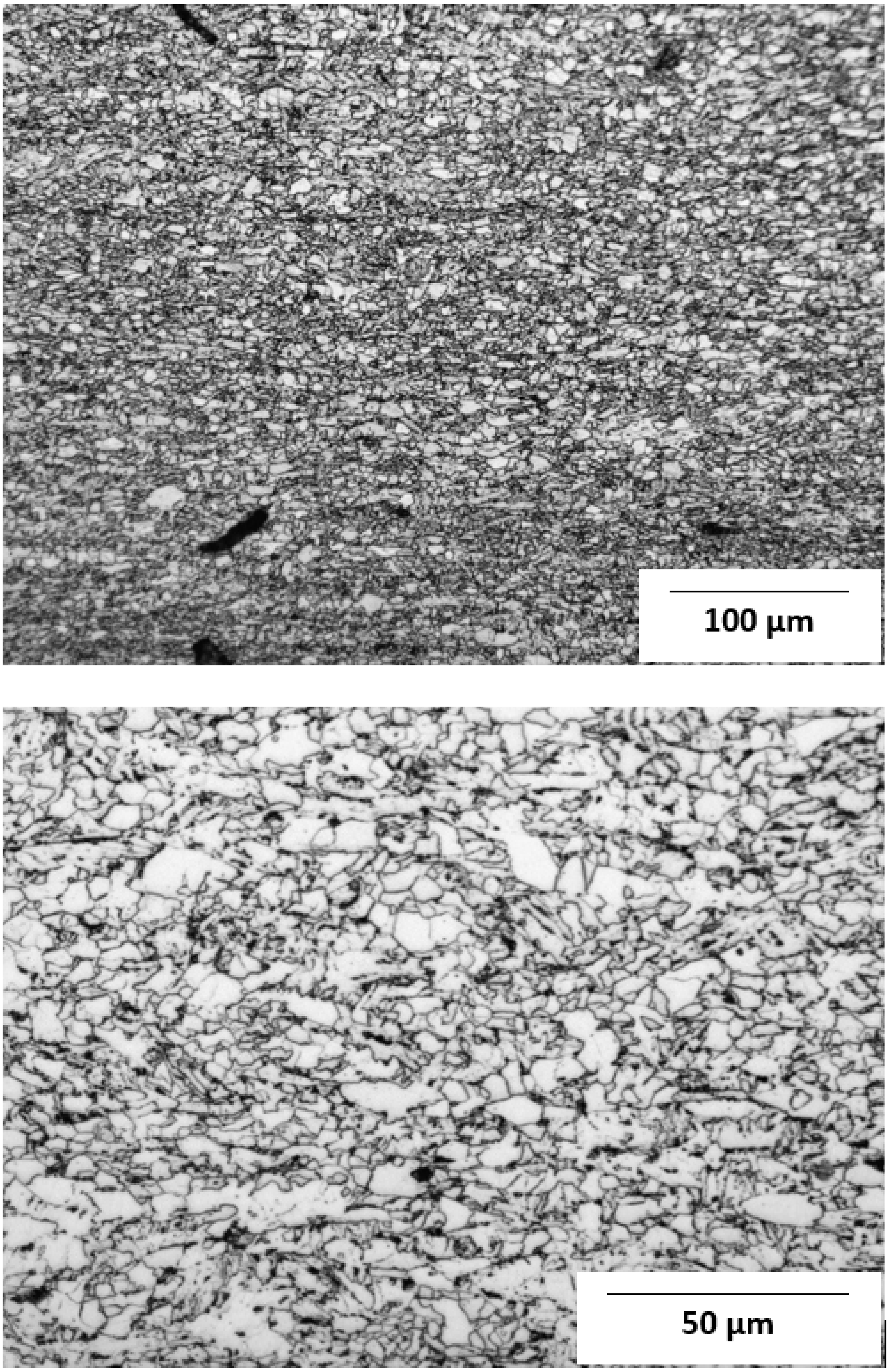

Figure 3 *Microstructure of X80 steel: x20(top) and x50 (bottom).*

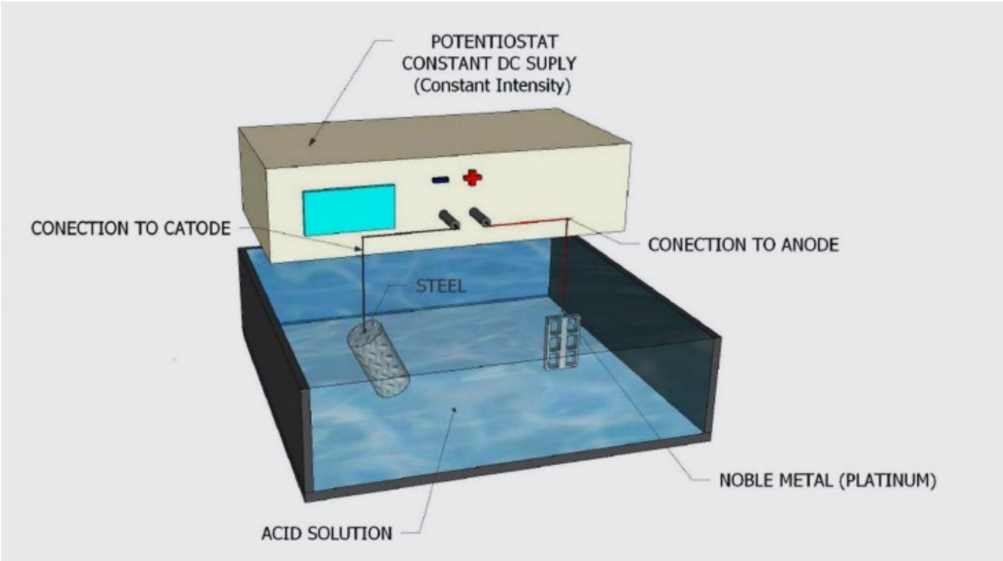

Figure 4 *Schematic of the cathodic polarization set-up employed.*

	Air (as received)	1 mA/cm^2	5 mA/cm^2	10 mA/cm^2
X80	0.89	6.20	9.79	10.1

Table 4 *Hydrogen content analisis results (ppm) [4].*

3.2. *Step time optimization proposal*

The main bases for the step loading technique applied to SPT are described in [4], which are followed in this work to optimize it. The SPT specimens employed are 0.5 ± 0.005 mm thick and have a square cross section of 10 x 10 mm^2, in accordance to [5], and commonly used in literature [4, 18-21]. SPT specimens were obtained to characterize the materials in L orientation (so perpendicularly to L direction, along which the axis of tensile specimen would be placed).

The punching tool has a hemispherical ceramic head of Ø2.5 mm, which in combination with the 45° chamfered jig results into a testing zone of Ø4 mm; it was in accordance to [5], as it was previoulsy presented in Figure 2. Figure 5 presents the experimental set-up designing and built fot the tests, in order to embrittle the sample and then apply the steps assuring to avoid impacts on the specimen. Also, to ensure the best fluid refreshement arround the specimen, air is bubbled in one of the cells corners to produe water circulation without affecting the sample. As it can be seen, the loads are applied manually by a combination of previously calibrated weights in orde to obtain the desired load.

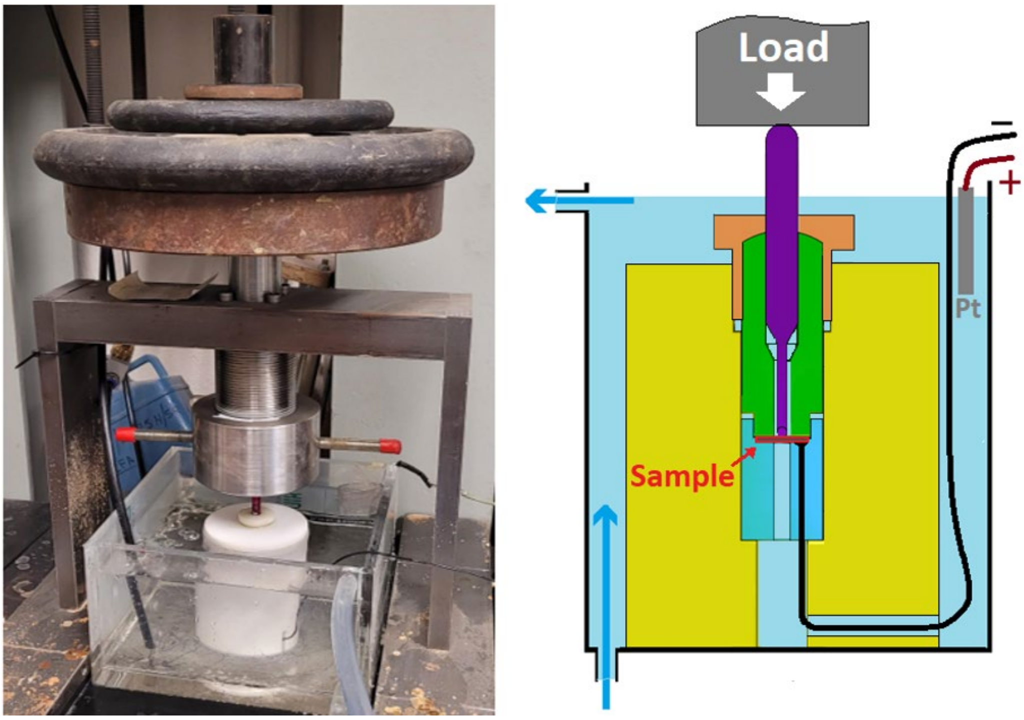

Figure 5 *Experimental set-up during a test and schematic of the device.*

From these bases, the application of the step loading technique to the Small Punch tests, which is more detailed in [4], collects the following main steps:

- A SPT test in air is performed, according to [5], to obtain $P_{FFS\text{-}SPT}$ (fast fracture load for SPT), given by the máximum load reached.

- Then, the SPT specimen is exposed to environment during two hours, in order to obtain a complete embrittlement before the mechanical testing; this time is the result of a previous research [4, 19-21] to assure saturation and steady hydrogen diffussion on an SPT sample.

- Finally, the step loads are subsequenty applied on as many samples as needed up to obtaining the thresshold (difference of two consecutive sequences thresshold loads of less than 5%). At this stage the sample is continuously inmmersed in the environment.

As a first contribution to this new technique, in the work performed in [4], steps duration of 20 and 40 minutes were chosen because this was the maximum time that allowed to perform the whole step sequence (20 steps) during a working day. In fact, when evaluated considering values of hydrogen difussivity in Steel [25] and the 0.5mm of thickness for SPT specimens, 20 and 40 minutes should be more than enough to ensure that hydrogen had diffused through the complete sample if it is considered that ASTM F1624 [3] stablishes a 2-4 hours step durations for a Ø6mm tensile specimen.
However, there is no evidence if these times allow a complete hydrogen embrittling effect, or, on the other hand, represents an excesive time loss. The optimization of the steps duration is then a very important fact, and is studied in the present work in order to find that steps duration that is the shortest that allows a complete embrittling effect, with the intend to optimize as much as possible the total test duration, while assuring enough accuracy.

In order to ahieve this, firstly the most agressive environment, 10mA/cm^2, will be studied in detail. Testing conditions with times of 10-20, 15-30, 20-40 and 30-60 minutes will be studied in order to see their impact on the thresshold load results. Then, a similar experimental campaing will be reproduced for the 5mA/cm^2 and 1mA/cm^2 conditions, trying to reduce any of the conditions if possible according to trends observed in the most aggressive condition.

4. Results and analysis

4.1. *10mA/cm^2 results*

Figure 6 shows the steps profiles obtained for the tests caried out under 10mA/cm^2 environment for the steps durations of 10-20, 15-30, 20-40 and 30-60 minutes studied. For each one of the steps durations studied, a series of several steps profiles can be appreciated (three in this case: P_{th1}, P_{th2}, P_{th3}) up to finding a convergence of two susequente profiles when resulting in thresshold loads closer than 5%, as stated by step loading methodology collected in [3]; the part of the step profiles graphed in continuous line belong to the steps that did take place, while the dashed ones correspond to the steps planned that didn't take place (the sample was already broken). Also, in each case, the SPT of the X80 material performed in air according to EN10371 is presented in the left as a comparison tool (named as FFL). On the other hand, Table 5 collects the numerical values of the corresponding threshold loads obtained, $P_{th\text{-}SPT}$.

It can be appreciated that, for all the seps durations studied, a set of three step sequences (three simples) was enough to obtain the thresshold load, $P_{th\text{-}SPT}$, fact that was also observed in the standarized tests performed on the the same material and environment according to ASTM F-1624 [3], which are detailed in the previous works [4] carried out to validate this experimental technique.

It is easy to identify on the presented results, that longer step durations mean higher difussion times, allowing a complete embrittlement of the specimen. This is in fact seen on the results, as 30-60 minutes duration test leads to the exact same resulting threshold load as in the 20-40 min duration, making evident that even longer times will lead to the same result, but if shorter times are studied it can be observed how the thresshold obtained increases as the duration is not enough for hydrogen to diffuse and assist the damage completely. The threshold load result is clearly incremented for shorter times, increasing 25% when reducing to 15-30 min the steps duration, and even further, 32%, when reducing it to 10-20 min duration steps.

These facts indicate that, for this environmental condition (10mA/cm^2), 20-40 min seems to be appropriate durations for the steel studied, while reducing these times will bring to inaccurate results. Based on it, the experimental campaigns are shortened for 5 and 1 mA/cm^2, studing just 15-30, 20-40 and 30-60 minutes steps duration. Time of 10-20 minutes is discarded as it has been seen that for 10mA/cm^2 it was not able to allow all the environmental embrittling power, then for less agressive environments, where the quantity of diffussible hydrogen is lower, this effect will be amplified.

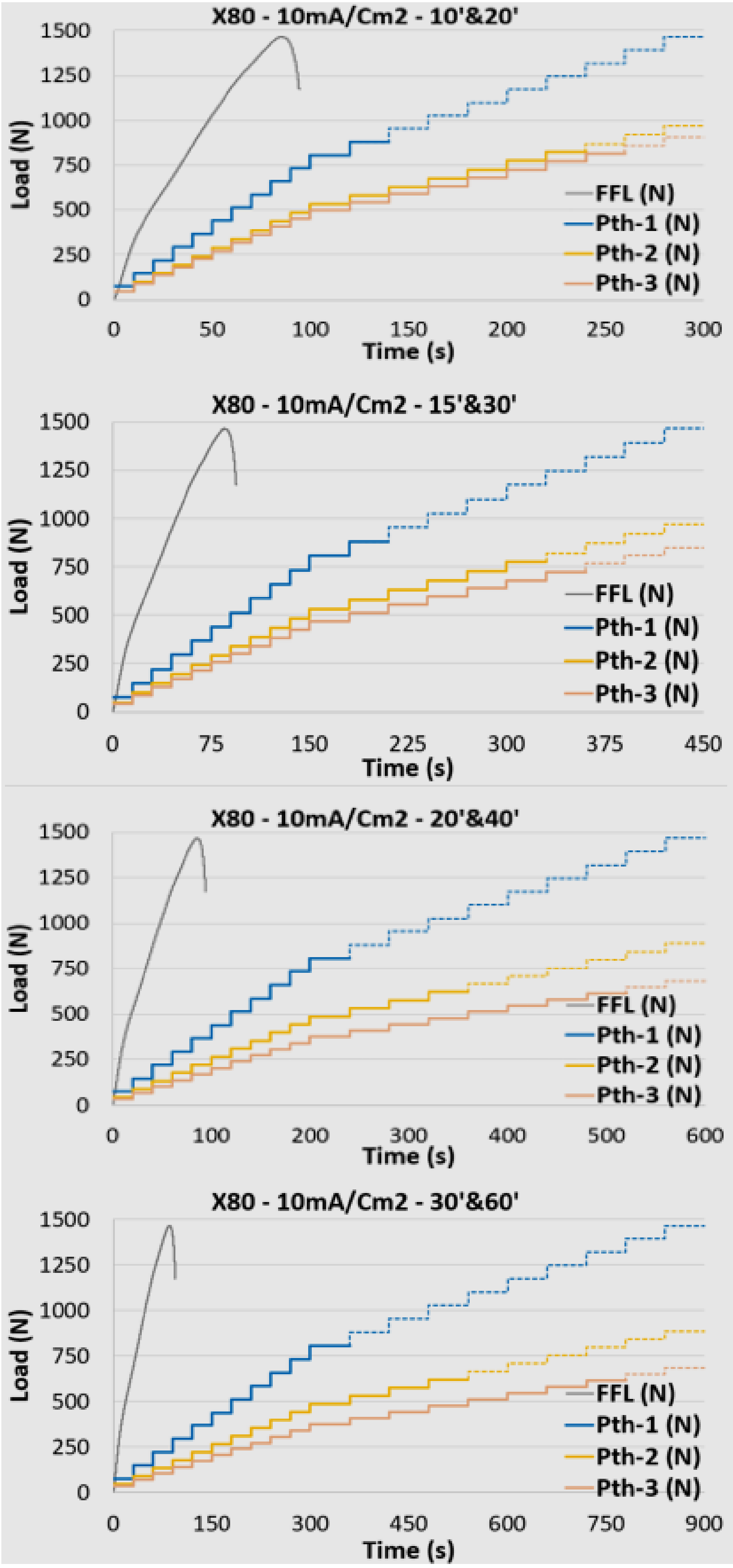

Figure 6 *Load-time resgisters of X80 steel obtained by applying the SPT loading technique when tested in a cathodic polarization environment of 10mA/cm*^{2}*; the dashed lines show the planned steps that did not take place after the specimen failure.*

	Steps time	P_{FFS} (N)	P_{th1} (N)	P_{th2} (N)	P_{th3}=P_{th} (N)	Difference
10mA/cm²	**10-20 min**	1466	880	822	**814**	+32%
	15-30 min	1466	880	774	**766**	+25%
	20-40 min	1466	806	621	**615**	-
	30-60 min	1466	806	621	**615**	-

Table 5 Fast Fracture Load, and threshold loads for all three step specimens obtained in the 10 mA/cm² environment. Pth3 is the final threshold load obtained for each of the various steps duration. The sixth column represents the percentage ratio of Pth3 (N) relative to the "20' & 40'" minutes steps duration trial.

4.2. *5mA/cm² results*

Figure 7 shows the steps profiles obtained for the tests caried out under 5mA/cm² environment for the steps durations of 15-30, 20-40 and 30-60 minutes studied. Table 6 collects the numerical values of the corresponding threshold loads obtained, P_{th-SPT}. Again, for all the seps durations studied, a set of three step sequences (three simples) was enough to obtain the thresshold load, P_{th-SPT}, as observed for the homologus standarized tests collected in [4].

The results of the 5mA/cm² environment show a similar trend to those from the 10mA/cm2 environment. When increasing the step duration to 30-60 minutes the resulting threshold load corresponds with its homologous value under 20-40 minutes steps duration. If the step duration is reduced to 15-30 minutes, the resulting threshold load is increased by 16%.

So, it can be concluded again that 20-40 min seems to be the appropriate durations for the steel studied under 5mA/cm², as reducing it will bring to inaccurate results. This makes sense as, if the steps profiles and threshold values for the 5 and 10 mA/cm² environments are compared, very close values and appareances are found, together with the fact that their hydrogen contents are also similar (9.79 and 10.10 ppm, probably near saturation) and so should be their embrittling micromechanisms.

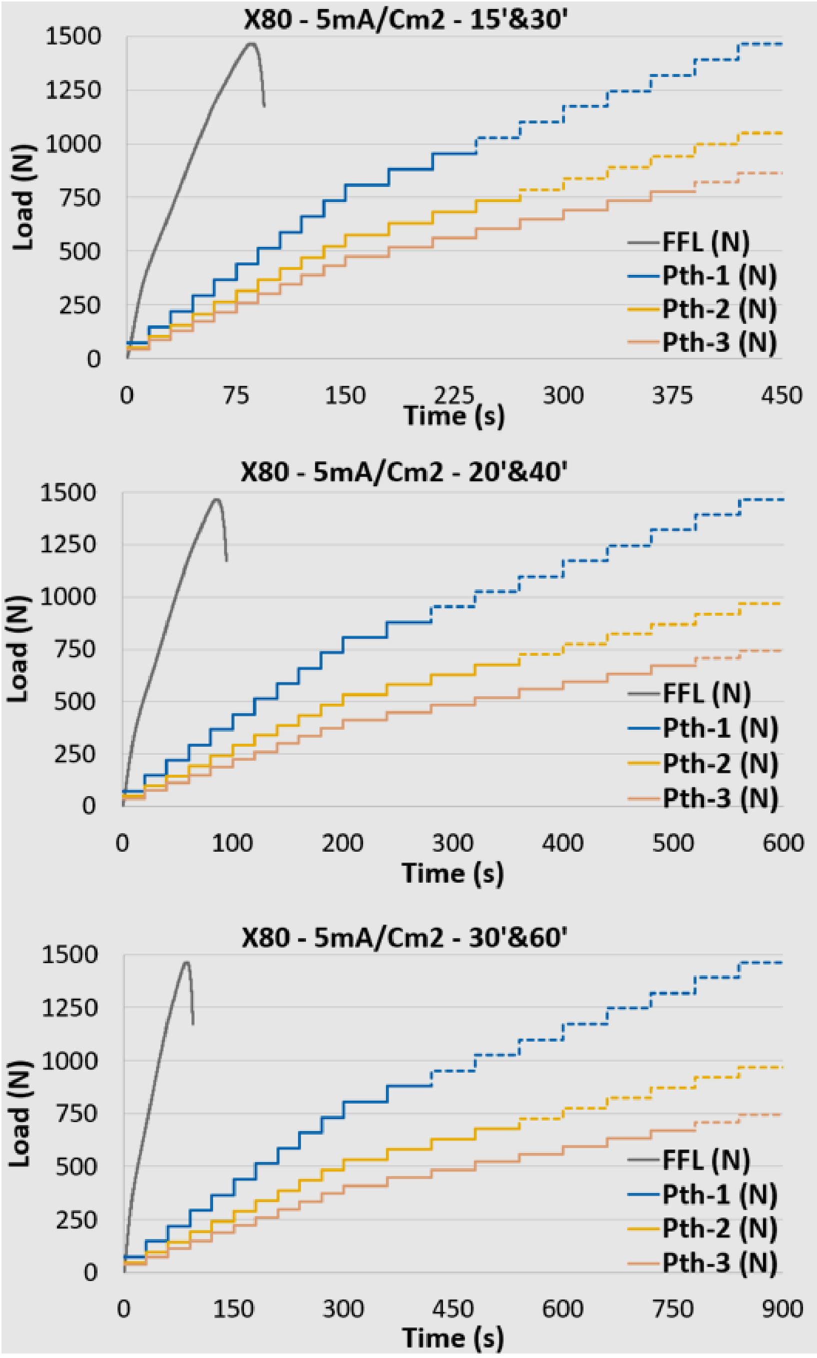

Figure 7 *Load-time resgisters of X80 steel obtained by applying the SPT loading technique when tested in a cathodic polarization environment of 5mA/cm²; the dashed lines show the planned steps that did not take place after the specimen failure.*

	Steps time	P_{FFS} (N)	P_{th1} (N)	P_{th2} (N)	P_{th3}=P_{th} (N)	Difference
5mA/cm²	**15-30 min**	1466	953	786	**778**	+16%
	20-40 min	1466	880	677	**671**	-
	30-60 min	1466	880	677	**671**	-

Table 6 Fast Fracture Load, and threshold loads for all three step specimens obtained in the 5 mA/cm² environment. Pth3 is the final threshold load obtained for each of the various steps duration. The sixth column represents the percentage ratio of Pth3 (N) relative to the “20’ & 40’” minutes steps duration trial.

4.3. *1mA/cm² results*

Figure 8 shows the steps profiles obtained for the tests caried out under 1mA/cm^2 environment for the steps durations of 15-30, 20-40 and 30-60 minutes studied. Table 7 collects the numerical values of the corresponding threshold loads obtained, P_{th-SPT}. Again, for all the seps durations studied, a set of three step sequences (three samples) was enough to obtain the thresshold load, P_{th-SPT}, as observed for the homologus standarized tests collected in [4].

In the 1 mA/cm^2 environment, similar effects as the ones presented in the previous environments can be found, altough there can be appreciated also some differences, as this condition is least agressive (6.20 ppm vs 9.79 and 10.10 ppm respectively).

In this case, when reducing the step duration to 15-30 minutes the threshold load is also increased respecting the results for 20-40 minutes, however, the ratio between P_{th} from both step durations is just 6%, which is much less than the ratios of 25% and 16% found for 10 and 5 mA/cm^2 environments (when comparing the results 15-30 and 20-40 minutes). This closer values for the 1mA/cm^2 environment respecting 5 and 10 mA/cm^2 ones is due to a lower diffusible hydrogen present in the lattice, as most of the total hydrogen absorved is stored in irreversible traps [7, 8, 24, 25]; fact related with a higer presence of microvoids (Figure 11 compared to Figures 9 and 10).

On the other hand, when increasing the steps time duration to 30-60 minutes, it can be seen that the threshold shows a very small deviation of arround 1% versus the 20-40 minutes step duration; which can therefore be assumed in the standard accuracy and considered both results the same in practice. Considering this, for 1mA/cm^2 it can be concluded again that 20-40 minutes seems to be the appropriate durations for this environment.

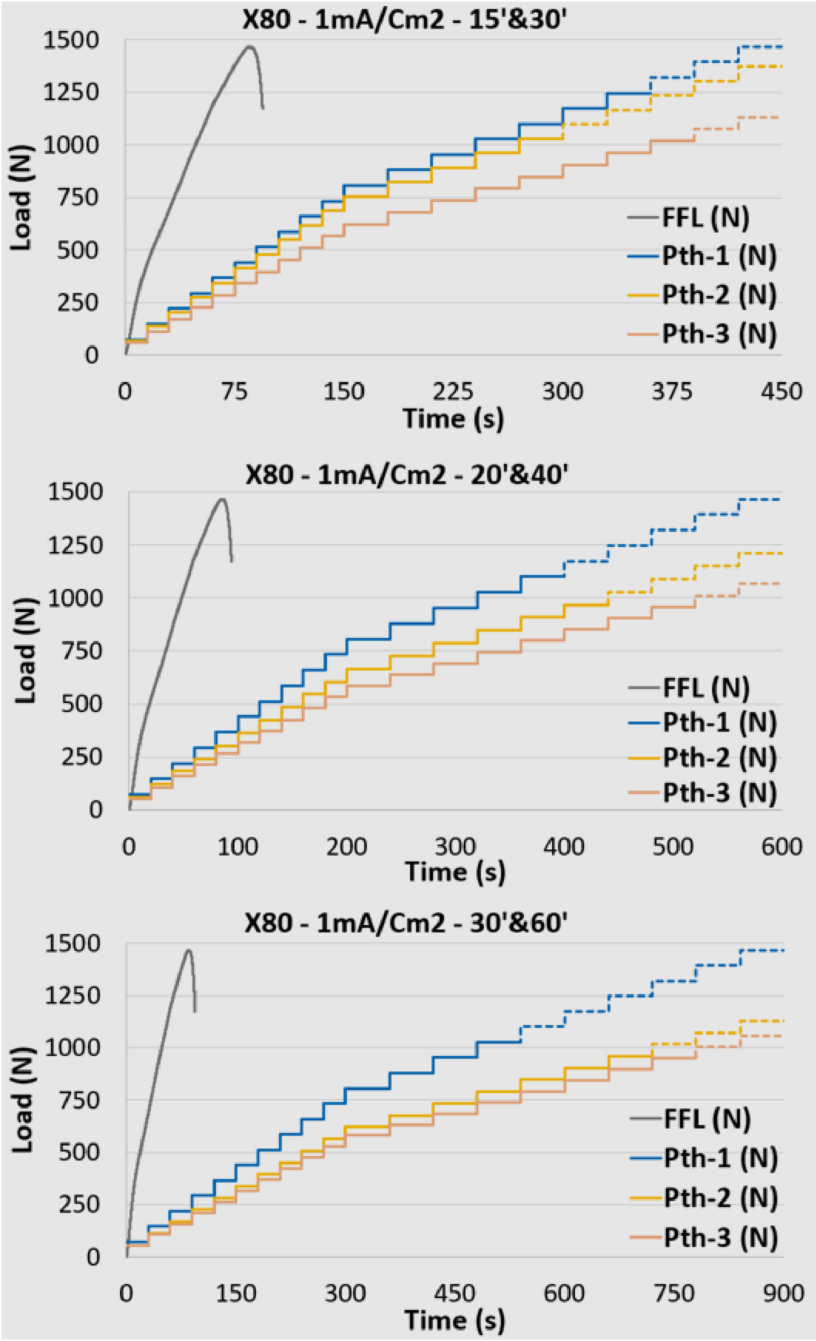

Figure 8 *Load-time resgisters of X80 steel obtained by applying the SPT loading technique when tested in a cathodic polarization environment of 1mA/cm²; the dashed lines show the planned steps that did not take place after the specimen failure.*

	Steps time	P_{FFS} (N)	P_{th1} (N)	P_{th2} (N)	P_{th3}=P_{th} (N)	Difference
	15-30 min	1466	1246	1028	**1018**	+6%
1mA/cm²	**20-40 min**	1466	1099	968	**958**	-
	30-60 min	1466	1026	959	**950**	-1%

Table 7 Fast Fracture Load, and threshold loads for all three step specimens obtained in the 1 mA/cm² environment. Pth3 is the final threshold load obtained for each of the various steps duration. The sixth column represents the percentage ratio of Pth3 (N) relative to the “20’ & 40’” minutes steps duration trial.

4.4. *Discussion*

In [4] it was concluded that the micromechanisms found in standarized tests performed according ASTM F-1624 [3] and the ones in SPT step loading tests, for 20-40 minutes time steps, were the same for homologous environmental situations in X80 steel (35 HRC). In this work, shorter and longer steps durations have been studied in order to optimize it, which numerical results have been presented in the previous epigraphs; Figures 9 to 11 display fracture surface images obtained by SEM techniques for the three environmental situations and the different steps durations studied, showing the micromechanisms obtained in each case.

The micromechanisms shown are in accordance with the numerical results in all the cases. In the most agressive envirnoment 10 mA/cm^2 (Figure 9), it can be appreciated how for the 20-40 and 30-60 minutes steps durations the micomechanisms shown are mostly the same, while for 15-30 have an slightly less brittle aspect.

For the 5 mA/cm^2 scenario, the micromechanisms found are very similar to the ones in the 10 mA/cm^2, although slightly less brittle (in Figure 10 a slightly higher presence of microvoids than the one observed in Figure 10 can be appreciated). This is in agreement with the previously exposed fact that X80 steel under 10 mA/cm^2 is very close to saturation, which implies that its behaviour under 5 mA/cm^2 will not be very different; this fact is supported also with the hydrogen content results (10.10 and 9.79 ppm) as well as the numerical ones (615 and 671N obtained as thresshold loads respectively). Again, for 5 mA/cm^2, the 20-40 and 30-60 minutes steps durations showed mainly the same micomechanisms (in some local areas the 20-40 steps durations showed a certain presence of microvoids than in 30-60 was not present, as can be seen if Figures 9 and 10 are compared, but they are of a very little relevance), while for the shortest times of 15-30 minutes those were slightly less brittle; in accordance to numerical results.

Finally, for 1mA/cm^2, the general aspect of the fracture surfaces shows a system much less embrittled than in the previous cases, showing even the microvoids presence in some cases; this is in agreement with the lower hydrogen content and the higher thresshold load result, which is closer tho the P_{FFS} than in the previous cases. Again, a slight difference can be stablished between the 15-30 minutes and the 20-40 and 30-60 ones, finding in the shortest a higher presence of microvoids than in the other ones.

Figure 9 *Fracture surfaces of X80 steel obtained by applying the SPT step loading technique when tested in a cathodic polarization environment of 10 mA/cm*^{2}*; images correspond to the sample tested under the final step protocol (the one that determines* P_{th}*).*

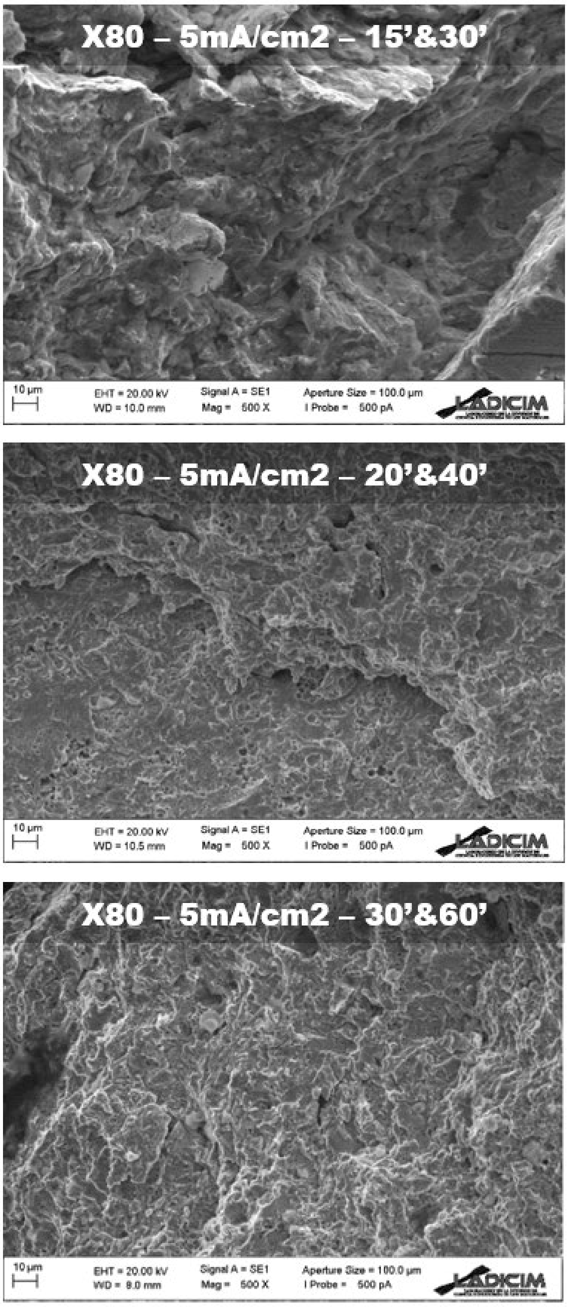

Figure 10 *Fracture surfaces of X80 steel obtained by applying the SPT step loading technique when tested in a cathodic polarization environment of 5 mA/cm*^{2}*; images correspond to the sample tested under the final step protocol (the one that determines* P_{th}*).*

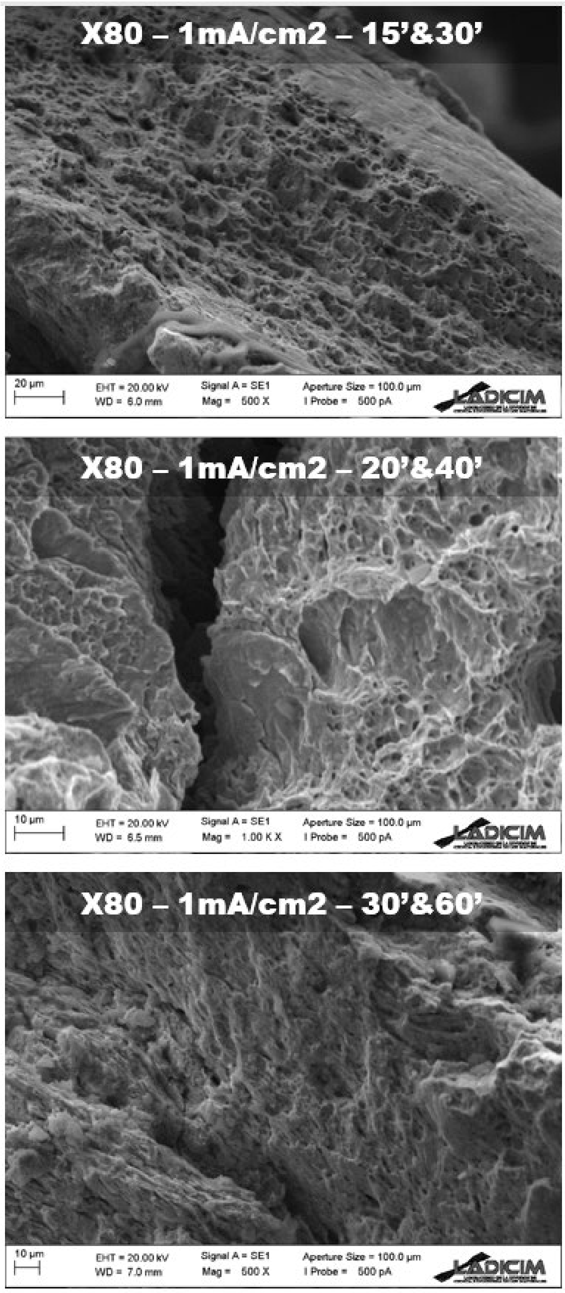

Figure 11 *Fracture surfaces of X80 steel obtained by applying the SPT step loading technique when tested in a cathodic polarization environment of 1 mA/cm^2; images correspond to the sample tested under the final step protocol (the one that determines P_{th}).*

Regarding the previous considerations, together with the nuerical results obatined, it can be stated that for ferritic pearlitic steels, which cover the $33 \leq HRC < 45$ hardness range, it seems clear that 20-40 minutes steps duration can be proposed as the most suitable to reach the required results with enough accuracy; longest times did not show any differences neither in thresshold load values nor in micromechanisms taking place, while shorter ones did, giving as a result higher threshold loads.

If taking into account difussion usual ranges of hydrogen in steel (or in iron) it can be appreciated that this time is higher than expected, fact that finds its explanation in the experimental set-up necessary to carry out SPT tests in environment (see Figure 5). While for standard tests the sample is directly inmersed in the electrolitic cell and in contact with the fluid in circulation, the SPT sample is embebed between two jigs, wich are placed inside a spile, so the fluid circulation conditions are more restrictive and make that a higher time is requiered.

It seems clear that SPT step times will allways be much higher than the theorically calculated just considering geometrical condtions of the sample, and it has been proven that 20-40 minutes steps are sufficient for 33≤HRC<45 range, which means these durations are six times smaller than the ones required for standard cylindrical specimens. This proportionality remains the same, six times, if comparing the time of 2 hours for SPT samples embrittlement usually employed [4, 19-21] to the 12 hours recommented by ASTM F-1624 for cylindrical standard specimens. It could then be stablished a proportionallity for the other hardness ranges, that will imply 10 and 20 minutes setps duration for 45≤HRC<54, and 10 minutes for the hardness case of HRC ≥54; evidently, this should be widely studied and proved experimentally.

Once the optimal step time duration is defined, this assures the obtention of an accurate threshold load. For these values to be aplicable in engineering purposes, a threshold stress needs to be dervied form the threshold load obtained; deriving stresses form SPT load results has always been one of its main issues to be solved.

There can be found different aproaches to obtain stresses from SPT loads in literature [22, 28], but in [4], the authors of the present work, recently proposed Expresion (1) for SPT when applying the step loading technique. It involves an elastic part derived form the elastic-to-plastic load, obtained as the first inflexion point form the SPT test in air (the same one used for P_{FFS} determination according to standard EN10371), P_y, and a plastic part, ($P_{th\text{-}SPT}$ - P_y), result of subtracting P_y from the thresshold load; h_0 represents the sample thickness in mm, and α a correlation coefficient.

$$\sigma_{th-SPT} = \sigma_{el-SPT} + \sigma_{pl-SPT} = \frac{3}{2\cdot\pi\cdot{h_0}^2}\cdot P_y + \frac{\alpha}{{h_0}^2}\cdot (P_{th-SPT} - P_y) \quad (1)$$

This expresión, which was derived for X80 and S420 steels in the same environments as the ones studied in this work, depends on the coefficient α, that in [4] was found to be 0.0806. However, it should be extended to the other hardness ranges, and/or environments, in order to verify this value for other materials and conditions, or propose it as a function of them.

If applying (1) to the results obtained in the present work Table 8 can be derived, where σ_{th-SPT} values are faced to σ_{th} ones obtained in the same X80 steel and environments according to ASTM F-1624 [3] (which are detailed in [4]); the elastic-to-plastic load used was P_y=121 N (obtained as the first inflexion point form the SPT test in air), the coefficient α= 0.0806 (according to [4]) and the sample thickness h_0 was taken as the real one in all the cases (between 0.495 to 0.505 mm). It can be observed how the difference between the standardized values and the SPT ones are in the ±10% accuracy usual range of SPT tests [22].

Steps time	Environment	$P_{th\text{-}SPT}$ (N)	$\sigma_{th\text{-}SPT}$ (MPa)	σ_{th} (MPa) ASTM F-1624	Difference
20-40 min	**1 mA/cm²**	958	**519**	**556**	-7%
	5 mA/cm²	671	**424**	**446**	-5%
	10 mA/cm²	615	**406**	**436**	-7%

Table 8 *Threshold stresses for obtained in the thre environments under the optimal steps times of 20-40 minutes; the values are compared from the tresshold stresses obtained in the same environments and materials from standard tests according ASTM F-1624 collected in [4].*

However, if α correlation coefficient is optimized including all X80 results (the ones presented here and the homologous from [4]) the value of α is slightly modified resulting of 0.0967 for X80 steel, which leads to think that α may be dependent on the material, or, at least, be related to the microstructure and/or mechanical properties; this fact should be deeply studied.

Finally, regarding the threshold values (loads or stresses) obtained from the aforementioned tests (collected in Table 8) together with the hydrogen contents corresponding to each situation (collected in Table 4), a trend between them can be stablished. This has already been done by the authors in [4], where a correlation that showed the resistance drop with the hydrogen content was clearly obtained. In fact, as detailed in [4], the aforementioned expression (1) was derived taking into account this embrittling effect in the plastic component of the threshold load obtained in the SPT tests, ($P_{th\text{-}SPT}$ - P_y), while it is not affecting the elasctic one, P_y, that is directly determined form the SPT in air according EN10371.

5. Conclusions and future work

In this work, the step loading technique applied to Small Punch tests has been optimized, following the main guidelienes collected in ASTM F-1624 [3] but adjusting the step durations. For a X80 steel (35 HRC) different step times have been evaluated, finding as the optimal one the application of the 1st to 11th steps of 20 minutes and 11th to 20th of 40 minutes; an optimization which is for sure of great interest for the metal industry as well as for the scientific community. In all the cases, the usually employed in litterature 2 hours embrittling time priror to the steps application was used [4, 19-21].

Compared with the recomendation of 2 and 4 hours (for the 1st to 10th and 11th to 20th steps respectively) in ASTM F1624 for 33≤HRC<45, the aforementioned 20-40 mintues steps duration resulted six times shorter. So is the embrittling time of 2 hours respecting the 12 hours recommented by ASTM F1624. It seems possible that this proportionallity will also be aplicable to the other hardness ranges considered by the standard ASTM F1624: 45≤HRC<54 and HRC ≥54.

Finally, based on the previous results, the following expression which was developped by the authors of this work in a previous one, is proposed to derive the thresshold stress form the thresshold loads obtained by SPT tests when applying the step loading technique of 20-40 minutes. It involves an elastic part derived form the elastic-to-plastic load from an SPT test in air (the same used for P_{FFS} determination), P_y, and a plastic part, ($P_{th\text{-}SPT}$ - P_y), result of subtracting P_y from the thresshold load; h_0 represents the sample thickness in mm, and α a correlation coefficient, found to be of 0.0967 in the X80 steel and environmental conditions studied.

$$\sigma_{th-SPT} = \sigma_{el-SPT} + \sigma_{pl-SPT} = \frac{3}{2\cdot\pi\cdot{h_0}^2}\cdot P_y + \frac{\alpha}{{h_0}^2}\cdot(P_{th-SPT} - P_y) \quad (1)$$

As future work, in order to further validate this promising methodology, it is essential to test steels belonging to the other hardness ranges, 45≤HRC<54 and HRC ≥54, to optimize the steps duration and the aforementioned ratio of six times shorter respecting ASTM F-1624, as well as the α correlation coefficient.

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