MATERIAL TESTING AND DESIGN RECOMMENDATIONS FOR COMPONENTS EXPOSED TO HYDROGEN ENHANCED FATIGUE – THE MATHRYCE PROJECT

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ABSTRACT

The three years European MATHRYCE project, dedicated to material testing and design recommendations for components exposed to hydrogen enhanced fatigue, started in October 2012. Its main goal is to provide an "easy" to implement methodology based on lab-scale experimental tests under hydrogen gas to assess the service life of a real scale component taking into account fatigue loading under hydrogen gas. Dedicated experimental tests will be developed for this purpose. In the present paper, the proposed approach is presented and compared to the methodologies currently developed elsewhere in the world.

NOMENCLATURE

FCV	Fuel Cell Vehicle
HE	Hydrogen Embrittlement
NDT	Non Destructive Threshold

1. INTRODUCTION

The deployment of a large hydrogen infrastructure with societal acceptance relies on the development of appropriate codes and standards to ensure safety. Indeed, the structural integrity implications of hydrogen in an energy infrastructure are profound and if unaddressed could influence the reliability, safety and economic competitiveness of this route to a sustainable future energy system [1]. While hydrogen infrastructures are gradually being built all over the world, dedicated international standards should be improved or developed to properly ensure fitness for service of pressure vessels *subject to hydrogen enhanced fatigue*. For example, high pressure compressors and pressure buffers in FCV refuelling stations experience cyclic loading due to pressure variation. The European MATHRYCE project aims to develop and provide an easy to implement vessel design and service life assessment methodology based on lab-scale tests under hydrogen gas. The project started in October 2012 and has three year timeline development. It will also foresee the cooperation of international recognized institutes around the world.

The first part of the paper is discussing how some existing codes are addressing hydrogen and fatigue issues for the design and the service life of hydrogen pressure vessels. In the second part, the proposed approach, based on the selection and further development of the most appropriate, reliable and easy to handle lab-scale fatigue test under hydrogen pressure is presented. The last part describes the experimental as well as theoretical foreseen developments to achieve this goal.

2. REVIEW OF EXISTING CODES AND STANDARDS

In this part, a non-exhaustive review of existing codes and standards for pressure vessels design, *focusing on type 1 cylinder in the presence of hydrogen* is carried out. As a reminder, there are four types of cylinders that can be used as a hydrogen storage vessel; type I (totally metallic), type II (thick metallic liner hoop-wrapped with a fibre-resin composite), type III (metallic liner fully-wrapped with a fibre-resin composite), and type IV (polymeric liner fully-wrapped with a fibre-resin composite) [2]. Standards are analysed for their limits and attention will be paid to high pressures and fatigue-based design. The focus is on seamless steel gas cylinders and fatigue loading, even though welded cylinders are admitted in some cases.

The main international standards distinguish between storage and transport applications. Table 1 gives an overview of the main international recognized standards for compressed gas *transport* applications including gaseous hydrogen. Table 2 gives an overview of the main international recognized standards for compressed gas *storage* applications including gaseous hydrogen.

Table 1: Overview of standards and codes for transport applications

Standard and code	**country**	**Volume (l)**	**Min/max P (MPa)**	**Material**	**Design Rule**	**Service life (Number of cycle)**	**Experimental fatigue verification**	**Special requirements for H_2 gas**
DOT 3AA ([5])	USA	< 450	1.0/-	Low alloy Cr-Mo steel	Prescriptive formula for minimum wall thickness	Not defined	Not required	Yes
DOT 3AAX ([5])	USA	> 450	3.5/-	Low alloy Cr-Mo steel	Prescriptive formula for minimum wall thickness	Not defined	Not required	No
ASME Section VIII, Div.3 ([7])	USA	-	-/100	Low and high alloy Cr-Mo steel, Al alloy	Prescriptive formula for minimum wall thickness or elastic-plastic analysis (according to KD-2)	Yes, depending on fracture mechanics calculations (according to KD-10)	Not required	Yes, through KD-10 article
ISO 9809-1 [3]	Inter national	From 0.5 to 150	-	Low alloy Cr-Mo steel	Prescriptive formula for minimum wall thickness	Not defined	Full scale test in a non-corrosive fluid	Yes
ISO 11120 ([4])	Inter national	From 150 to 3000	-	Low alloy Cr-Mo steel	Prescriptive formula for minimum wall thickness	Not defined	Not required	Yes
ISO/TS 15869 ([6])	Inter national	-	-	Low alloy Cr-Mo steel	Not specified. For type I ISO 9809 can be applied	N=11250 or N=5500	Full scale test in a non-corrosive fluid	Yes

Table 2: Overview of standards and codes for storage applications

Standard and code	**country**	**Volume (l)**	**Min/max P (MPa)**	**Material**	**Design Rule**	**Service life (Number of cycle)**	**Experimental fatigue verification**	**Special requirements for H_2 gas**
AD 2000-Merkblatt ([11])	Germany	-	-	Several steels, including low alloy Cr-Mo steel	Prescriptive formula for minimum wall thickness	Fatigue design based on S-N approach	Not required	Considered through a safety factor of 10 on the number of cycles
EN 13445 ([10])	EC	-	-	Several steels, including low alloy Cr-Mo steel	Prescriptive formula for minimum wall thickness	Fatigue design based on S-N approach	Not required	Not quantitatively considered
ASME Section VIII, Div. 1/2 ([12])	USA	-	-	Several steels, including low alloy Cr-Mo steel	Prescriptive formula for minimum wall thickness	Fatigue design based on S-N approach	Not required	Not quantitatively considered
ASME	USA	-	-/100	Low and high	Prescriptive formula	Yes, depending on	Not required	Yes, through

Section VIII, Div.3 ([7])				alloy Cr-Mo steel, Al alloy	for minimum wall thickness or elastic-plastic analysis (according to KD-2)	fracture mechanics calculations (according to KD-10)		KD-10 article
KHK S 0220 [8]	Japan	-	>100	JIS SCM435 Cr-Mo steel (up to 40 MPa), SUS316 and SUS3&6L	Follows the approach of ASME section VIII, Div. 3	Design life based on fatigue analysis based on S-N curves and crack growth analysis	-	-
CODAP [9]	France	-	-	Low alloy Cr-Mo steel, (UTS$\leq$950 MPa) for seamless reservoirs	Prescriptive formula for minimum wall thickness and Design by analysis	Fatigue analysis based on S-N curves		Only recommendations, such as the limit of allowed UTS for low alloy steels set to $\leq$950 MPa
ISO CD 15399 ([13])	Inter national	< 10000	15/110	Low alloy Cr-Mo steel	Not specified. For type I ISO 9809 or ISO 11120 can be applied	To be specified by the manufacturer, 15 years minimum	Full scale test in non-corrosive fluid	Yes
ISO11114-4 [14]	Inter national			Low alloy steel	Not for design. Selection of materials for Hydrogen use			

The standard ISO CD 15399 is still at a committee draft stage and the proposed approaches for evaluation of hydrogen effect in metallic material are presently under discussion in the ISO TC197/WG15. In general, standards for transportation, except ASME KD-10 [7] do not specify cylinder service life in terms of years and/or maximum number of filling cycles, while a specified life is generally defined through standards for storage applications. Only Art. KD10 [7] evaluates service life through a fracture mechanics approach taking into account hydrogen.

3. DEVELOPMENT OF THE MATHRYCE METHODOLOGY

As described previously, several methodologies are being developed around the world (e.g. USA and Japan) based on a safe-life approach or damage tolerant, including a crack growth based model. The MATHRYCE project aims at developing a European methodology to take into account hydrogen enhanced fatigue. The reasons driving this approach are now presented in the following sections.

3.1 Description of the methodology

The project aims to provide a component design and lifetime assessment methodology for high pressure hydrogen metallic components subjected to fatigue (pressure cycles), which avoids full scale tests in hydrogen, for application in design and testing standards. Thus, the approach should fulfil the following statements:

- the vessel material is subjected to fatigue under H_2 pressure,
- the mechanical properties of materials are obtained from lab-scale tests under hydrogen gas simulating or approaching actual conditions,
- the approach should be as “easy” as possible to be implemented at an industrial level,
- full scale pressure vessel testing in H_2 gas, which can be very long and expensive to be performed, should be avoided.

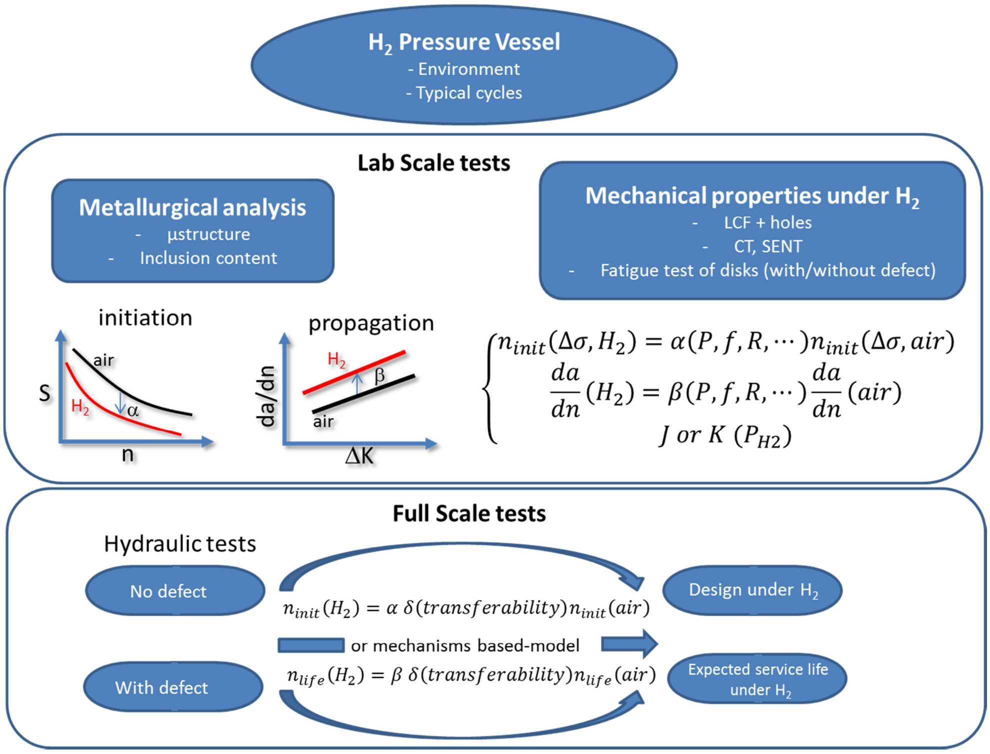

Figure 1. Sketch of the methodology to be developed

Fig. 1 schematically describes the approach. First, the most precise description of the environment and of the loading cycles under hydrogen of the component to be designed must be performed. From these data, lab-scale tests will be defined and set-up in order to understand, for a given material, how hydrogen modifies the initiation and growth of crack-like defects, such as non-metallic inclusions or surface manufacturing imperfections below the typical NDT value. Finally, the lifetime assessment will consist in combining the hydraulic cycling performance of the component with appropriate knowledge of the performance of the metallic material in hydrogen under cyclic loading.

One of the objectives is to be able to propose an approach that allows characterizing the entire hydrogen enhanced fatigue damaging process possibly using a single test and specimen. From this characterization of the performance of the material for reference cycles, the conditions for ensuring expected lifetime of a component in real life will be defined, based on iso-effect equivalence laws (parameters α and β in Fig. 1) and on mechanisms based models that could better take into account the influence of the main parameters such as hydrogen pressure, cycling frequency, stress amplitude and history, temperature, etc...

This raises the question of properly defining a reference pressure cycle. For this reason, part of the project will be dedicated to measure the influence of cycle characteristics such as cycle amplitude and cycle frequency in order to support the proper characterization for the expected service conditions during the component service life. Fig. 2 displays a simplified service life description of a buffer vessel in a hydrogen station. As shown in this figure, it includes high R ratio cycles combined with some lower R ratio cycles as well as some steps at a given pressure, corresponding to steps of low use (corresponding to nights for example). In order to take the cumulated damage obtained into account, a predictive but still conservative law must be provided starting from the appropriate lab-scale test definitions. Moreover, for type I cylinders (that are entirely metallic), the need to ensure leak before burst will have to be considered too.

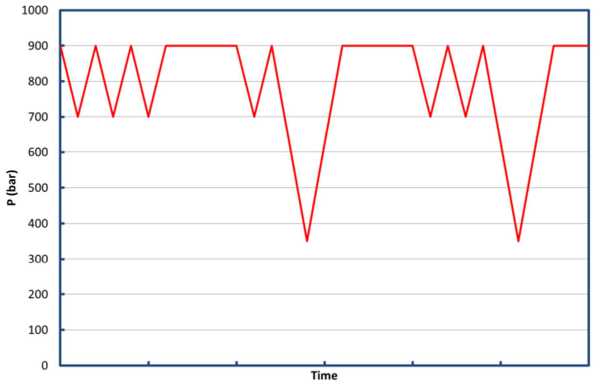

Figure 2: Example of a simplified cycling history for a hydrogen buffer in a future stationary hydrogen station for hydrogen refuelling at 700 bar and 350 bar

Moreover, temperature cycling, typically from -40°C to 85°C, may influence the crack initiation or growth promoting thermal stresses, and changing the absorption as well as diffusion kinetics. Although this parameter has been clearly identified, the preliminary developments will be based on experimental results performed at room temperature. Indeed, for most of ferritic and martensitic steels, this is the worst temperature for hydrogen embrittlement where both hydrogen absorption and diffusion are favoured.

3.2 From lab scale to full scale component

The approach should address not only the pressure vessel design, predicting the number of cycles for crack initiation but also the service-life using the data obtained on cyclic crack propagation under hydrogen and the effect of hydrogen pressure on the material toughness. To ensure a reliable and safe prediction, the transferability of the lab-scale results to a full-scale component must be carefully analysed (this is schematically identified by the δ parameter in Fig.1). This will be done by both a theoretical and an experimental approach.

Theoretical approach

Once the principal types of defects (inclusion or geometrical imperfection) in the pressure vessel will be identified, numerical simulations performed in Abaqus (Fig. 3) will give a good knowledge of the stress and strain fields ahead of it under cycling pressure. In the example shown here, a small crack 300 µm large and 300 µm depth has been simulated. In this configuration and for a pressure cycling between 90 and 70 MPa, the maximum ΔK is 5.3 MPa $m^{0.5}$. These data will guide the experimental tests definition at a lab-scale level.

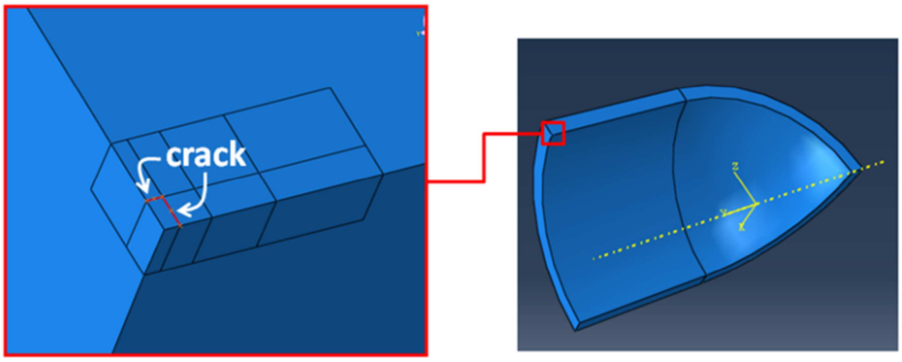

Figure 3: Example of a crack in a pressure vessel for numerical simulation

However, transferability of the results is fully linked to the way a defect or a crack is locally loaded. Indeed, the crack depth and geometry, the specimen dimensions, and the loading configuration, generally referred to as constraint effect, are known to strongly affect the toughness measurements [15]. Initiation, fatigue crack growth and toughness are not influenced in a same way by these parameters. Toughness is probably the property which is influenced the most by the constraint effects and this has to be considered in order to safely predict the service life of a component if fatigue crack growth is involved in the predictive methodology. A two-parameter approach [15] will be used to take these constraint effects into account. Although probably less affected, it is necessary to quantitatively measure how constraint can affect crack growth as well.

Validation through full scale testing under hydrogen pressure

Transferability will also be checked through experimental tests. Once the methodology will be defined, and although it should not include tests of full scale components under hydrogen pressure, the proposed rationale will be finally validated by means of fatigue tests under hydrogen pressure on full scale components. These tests will be performed in the High Pressure Gas testing Facility available at JRC (Fig. 4), allowing tests up to 90 MPa depending on the hydrogen volume involved in the experiment.

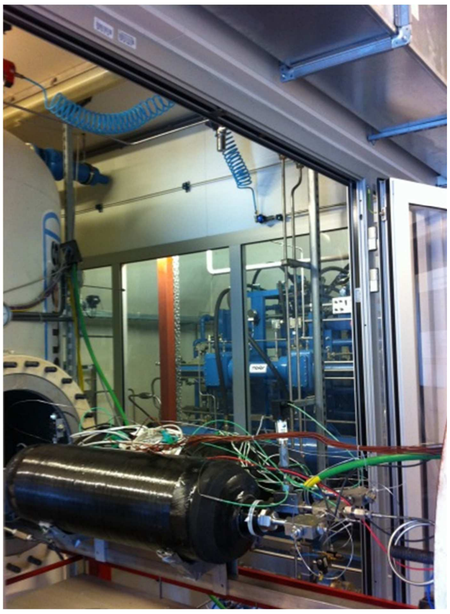

Figure 4: Experimental set-up to test pressure vessels under hydrogen cycling pressure – JRC

As noticed in a previous paragraph, it is not possible to perform the actual number of cycles within a three years project. Thus, artificial defects will be numerically designed, using the experimental results and the theoretical approach of the project in order to be able to detect crack initiation as well as crack propagation in a reasonable time compatible with the project duration.

4. EXPERIMENTAL AND THEORETICAL APPROACH

4.1 Material

As proposed, the approach should be applicable to all types of pressure vessels possibly subjected to hydrogen enhanced fatigue, thus containing metallic parts. However, in order to focus on the main aspects of the project, i.e. to propose a methodology, the developments will be dedicated to type 1 pressure vessels. They will be designed and build with a standard low alloy Cr-Mo steel type.

4.2 Experimental developments

Three types of lab-scale tests will be carried out and carefully analysed to address the fatigue of pressure vessel steels without and under hydrogen pressure. It is worth noting that ferritic steels, currently used for high pressure hydrogen components, are very sensitive to hydrogen charging conditions before or during mechanical loading. As hydrogen diffusion in these alloys is extremely rapid, it is necessary to test the material under hydrogen gas to obtain reliable results for designing a component for hydrogen pressure service.

- First, the fatigue tests on cylindrical specimens with a calibrated hole, developed by the Japanese team at Kyushu University [16], will be adapted to be processed under high pressure hydrogen (Fig. 5a). These tests provide data on both short cracks, associated to crack initiation phase and thus to initial design, and long cracks, associated to crack propagation phase and thus the assessment of the component lifetime, to propose criteria for inspection intervals. Following the initiation of a crack at the tip of a small hole in high pressure hydrogen is not straightforward. Some specific instrumentation developments are necessary to achieve this goal.

- Second, the long crack growth behaviour under cycling loadings will also be addressed using more classical fracture mechanics specimen: Compact Tensile (CT) (Fig. 5b) or Single Edge Notched Tensile (SENT) specimens. Comparison of the crack growth rates obtained with these fracture mechanics specimens and the ones obtained with low cycle fatigue specimens with a calibrated hole will confirm the obtained results.

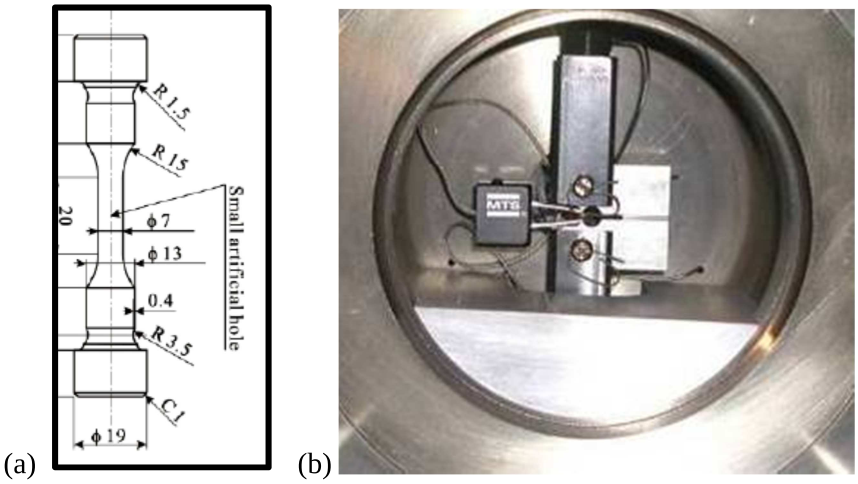

Figure 5 : (a) Fatigue test with calibrated hole [16] (b) CT specimen in the CEA experimental device under hydrogen pressure

- Third, a test based on the disk facility will be developed (Fig. 6). A disk with or without a defect (hole or small notch) will be numerically designed to obtain loading conditions close to the expected operational ones. This specimen will be loaded within the classical disk facility but under cycling pressure. In this test, differently from the standard disk test, the burst pressures under helium and hydrogen will not be compared but rather the ratio of number of cycles to initiation between these two gases. This testing methodology shall be able to detect crack initiation during the test. Both previous tests will be performed at a constant hydrogen pressure whereas this fatigue disk test could reproduce loading conditions (cycling pressure) closer to the in-service loading conditions of the component. Such a development could also help to define a test easier to handle.

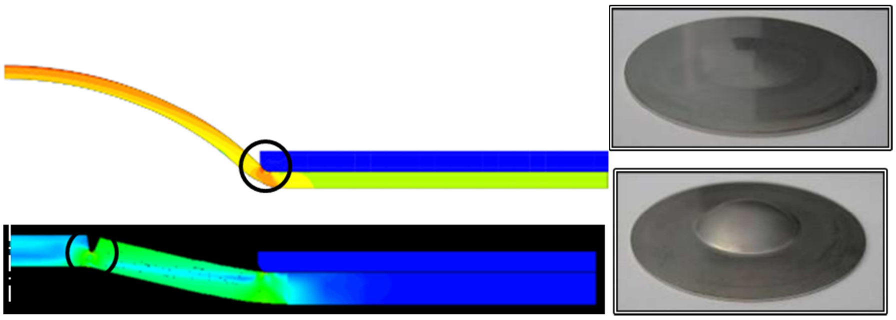

Figure 6: Preliminary simulations to define a disc tests under cycling pressure

Fig. 7 is showing the first simulations of a bi-notched disk under cyclic loading. Using this configuration, the two notches are under tensile loading. With notches, the simulations are less dependent upon the boundary conditions at clamping. However, the experimental machining of such notches with a given ratio at the tip is not straightforward. Thus both configurations, with or without defects, have advantages and drawbacks. The future simulations will help identifying the best geometry to provide a reliable and useful disk fatigue test. To do so, the cyclic stresses ahead of the notch will be compared to those obtained on the full-scale simulation (Fig. 3) and the final size and geometry of the notches will be obtained by optimisation. Finally, to properly simulate the disk test under fatigue, the material behaviour under cycling conditions will be identified, in order to take the isotropic and kinematic hardenings into account in the model.

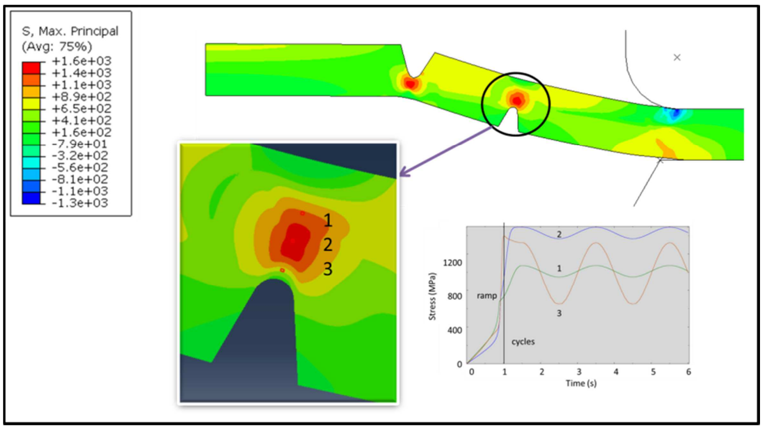

Figure 7: Cr-Mo steel bi-notched disk under pressure cycling loading between 200 and 400 bar

The experimental program will basically consist in:

- identifying the worst case conditions and finding equivalences between different types of loading conditions in order to adequately characterize the expected service ones,
- developing a relevant, and as easy as possible to handle mechanical test to determine the appropriate material characteristics for the methodology,
- validating the methodology through component testing in hydrogen.

The results obtained by the three testing methods will be systematically analysed, with the help of numerical simulations and scientific knowledge of relevant hydrogen embrittlement mechanisms, to propose the appropriate testing methods for a design methodology based on hydrogen enhanced fatigue.

4.3 Improving hydrogen enhanced fatigue knowledge

To be reliable, the methodology should be based, as much as possible, on a good knowledge of the underlying damaging mechanisms in presence of hydrogen. Although studied for years, there still is a strong lack of understanding to be able to be quantitatively predictive with mechanism based models. First, the influence of hydrogen on crack initiation and its link with the inclusion content have been very little addressed. Second, the permeation of hydrogen in the metal, including ad/absorption and diffusion coupled to the mechanical stress fields and to trapping is theoretically described. However, the involved mechanisms are very sensitive to the gas purity as well as to the material microstructure and it is not yet obvious to properly identify the real in-service or experimental conditions. Third, fatigue crack growth in ferritic and martensitic steels has been widely studied. However, the understanding is not yet strong enough to provide predictive models. As an example, the hydrogen populations involved in the damage process (lattice, trapped at the interface between inclusion and ferrite, trapped in dislocations, …) are not clearly identified. Finally, the hydrogen environment of a crack tip is dependent on the loading conditions as shown in Fig. 8.

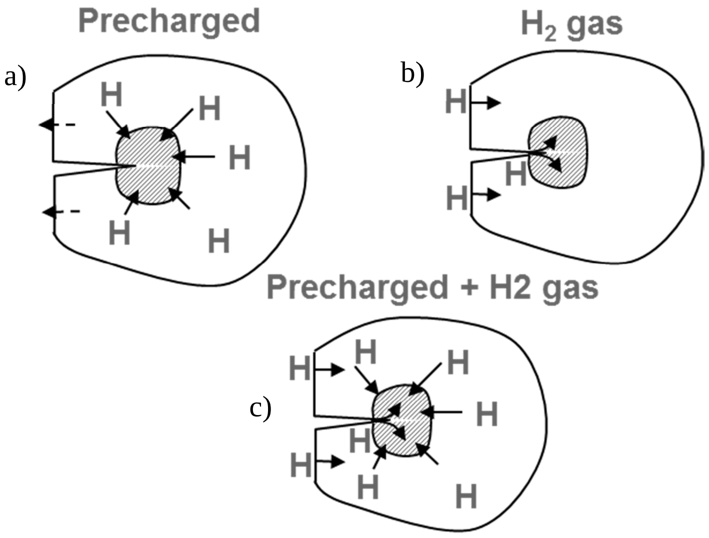

Figure 8: Hydrogen environment of a crack depending on the loading conditions [17]

The fatigue crack growth under hydrogen is sometimes modelled as a competition between the crack growth rate and the hydrogen diffusion rate in a process zone ahead of the crack, designed [18]. Thus, the hydrogen source to fill this process zone at the crack tip depends on the experimental conditions. For a pre-charged specimen, hydrogen comes from the specimen volume and is also escaping through the surface (Fig. 8a). For a specimen tested in-situ under hydrogen pressure, hydrogen reaches the process zone through the crack surface and possibly by volume diffusion from the specimen surface (Fig. 8b). Finally, considering a storage vessel in operating conditions, the material can be saturated by hydrogen due to long term exposition and hydrogen will be able to reach the process zone both from the crack tip and the surrounding specimen volume (Fig. 8c). It appears then that the quantitative experimental data may strongly differ depending on the experimental procedure. For the present project, all the tests will be performed under hydrogen pressure, including or not hydrogen precharging to saturate the material, to be as close as possible to the vessel operating conditions.

5. CONCLUSIONS

The main objectives of the MATHRYCE project are centred on the development and dissemination for standardization of a methodology for the design of hydrogen high pressure metallic vessels and for their lifetime assessment that takes into account hydrogen-enhanced fatigue. This needs to be achieved without requiring full scale component testing under hydrogen as this is not practicable considering the expected cycle lives and equipment size. The project therefore targets the justification of an approach where lifetime assessment results from combining the hydraulic cycling performance of the component with the appropriate knowledge of the performance of the metallic material in hydrogen under cyclic loading. This will be validated by comparing the lifetime prediction of a component calculated from the lab scale tests to that obtained from large scale component tests. The analysis of the results, based on numerical simulations as well as on the scientific knowledge of the possible hydrogen embrittlement mechanisms, will allow to assess or to modify the proposed design methodology. Finally statistics considerations will probably be introduced in the approach.

The main outcomes of the MATHRYCE project will be:

- The development of a reliable testing method to characterize materials exposed to hydrogen-enhanced fatigue,
- The definition of a methodology for the design of metallic components exposed to hydrogen enhanced fatigue and for the assessment of their service lifetime; this methodology being liable to be recognized for pressure equipment regulation,
- The dissemination of this methodology, as a proposed approach for standardization,
- The dissemination of prioritized recommendations for implementations in international standards.

6. ACKNOWLEDGMENTS

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