Results of the Ripple Load tests

Dissemination level: PU - Public

Hystories deliverable D4.5-0

Date: 20 October 2022

Author:

Cyriane FOURNIER [1]

[1] **Geostock, France**

Revision History

Revision	Revision date	Summary of changes
0	20 October 2022	Initial version

Checked by:

Name	Institute	Date
Bernd LODER	Montanuniversitaet Leoben	13/10/2022

Approved by:

Name	Institute	Date
Gregor MORI WP4 Leader	Montanuniversitaet Leoben	20/10/2022
Arnaud REVEILLERE Project Coordinator	Geostock	20/10/2022

TABLE OF CONTENT

1. Introduction

The objective of the WP4 of the Hystories project is to define the most qualified grades of materials for well completions of underground storage infrastructures in depleted fields and aquifers. It is also relevant to other technologies using Oil and Gas wells such as salt caverns.

To validate or not one specific grade, several static tests were conducted by Leoben University in autoclave with hydrogen under pressure, as presented in Deliverables D4.1 (protocol), 4.2 (list of steel grades), 4.3 (steel characterization) and 4.4 (first results). Nevertheless, to validate the steel grade compatibility, it was necessary to take into account their resistance to cyclic load variations that can experiences in underground storages, due to pressure and temperature variations, vibrations or elongations during injection or withdrawal of gas.

To do so, Ripple load tests, which is a cyclic load test at a stress level close to Specified Minimum Yield Strength (SMYS) were performed on specific steel grades. These tests were conducted by the French Corrosion Institute, whose report can be found in Appendix.

This report presents the experimental conditions of the Ripple load tests and the different results that were obtained.

2. Principle of the Ripple Load Tests

Assessing metallic materials suitability to hydrogen service can be a difficult task since the effects of hydrogen exposure can take long time to be visible. Ripple load tests allow to accelerate the hydrogen embrittlement phenomenon by conducting several cyclic tests within a week.

Ripple load test is a modified slow strain rate testing to assess hydrogen assisted cracking by applying tensile load cycles. A steel specimen is introduced in a pressurized chamber where the gas quality can be controlled. In this chamber, the specimen undergoes several tractions by its extremity (see schema and picture below).

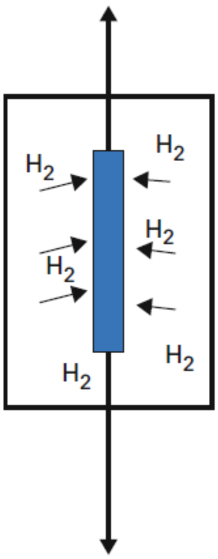


Figure 1 : Schema of the ripple load test conditions and picture of the chamber used at the French Corrosion Institute

Loading cycles were performed between 80 and 100 % of the Specified Minimum Yield Strength (SMYS) of the steel grade. The extension rate was fixed at 10^{-6} inch/s and the stress release rate at 5.10^{-6} inch/s, which allowed to perform between 114 and 295 cycles depending on the material.

An example of loading cycles is given below :

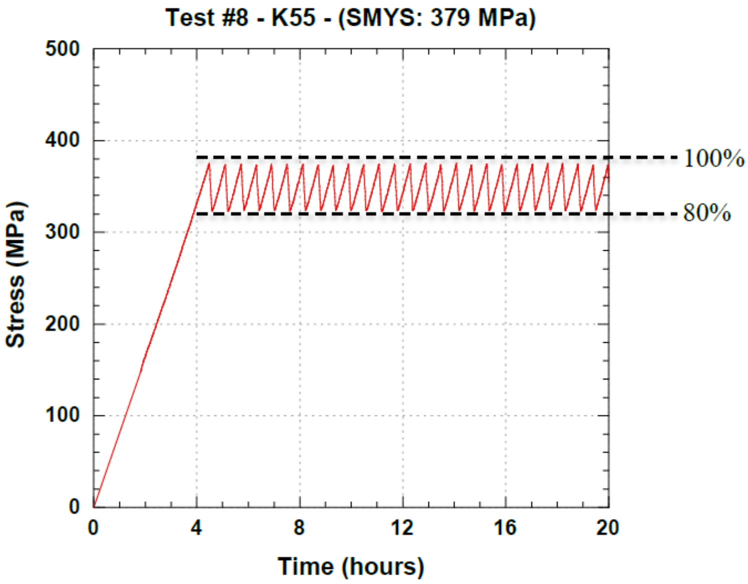


Figure 2 : Loading cycles between 100 % and 80 % of the SMYS for a K55 specimen

The whole procedure description can be read in the report from the French Corrosion Institute that is available in Appendix.

3. Specimens and test matrix

Tests were performed in a pressurized chamber containing 120 bar of hydrogen and for some specific tests 1 bar of H_2S or/and 15 bar of CO_2. It corresponds to the conditions of the static tests performed by Leoben University as defined in Deliverable D4.1.

The whole test matrix is presented here below :

Material	Partial pressures (bars)			Pre-immersion
	H_2	H_2S	CO_2	
P110	120	0	0	No
	120	1	0	No
	120	1	15	No
	120	0	0	Yes
	120	1	0	Yes
L80	120	0	0	No
	120	1	0	Yes
K55	120	0	0	No
	120	1	0	Yes
J55 Weld	120	0	0	No
	120	1	0	Yes
13%Cr	120	0	0	No
	120	1	0	Yes

When a pre-immersion is specified, the specimen was immersed during two days before the beginning of the test in a NaCl 200 g/l electrolyte with argon bubbling in the autoclave at atmospheric pressure. Therefore, conditions during this pre-immersion were deaerated.

In term of gas composition and pressure, same conditions as with Constant Load Tests were taken, but only the most extreme : with Hydrogen only (Gas A) and with Hydrogen + Carbon Dioxide + Hydrogen Sulphide (Gas D). Detailed information on the protocol for material testing are exposed in the Deliverable D4.1.

All the tests were performed at ambient temperature (23°C), which is known to be more critical for hydrogen embrittlement than higher temperatures.

During the whole test, humidity and salinity was introduced in the chamber with the presence of 15 ml of NaCl 200 g/l electrolyte at the bottom of the autoclave.

As observed in the test matrix, different steel grades were tested. The microstructure and the specified minimum yield strength of each material is presented in the table below. It is compared with the actual measured yield strength :

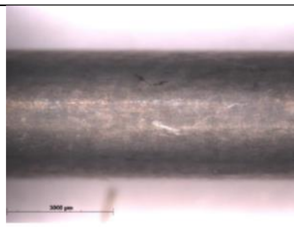
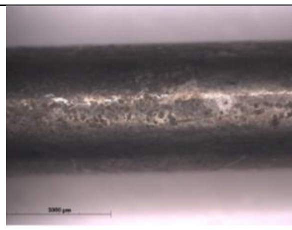
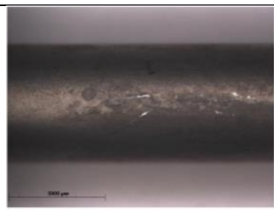
	Microstructures	SMYS (MPa)	Actual Yield Strength (MPa)
K55	Ferrite + pearlite	379	407
Welded J55	Ferrite + pearlite	379	371
L80	Tempered martensite	551	549
P110	Tempered martensite	752	894
13% Cr	Martensite	550	525

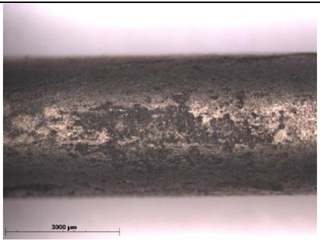
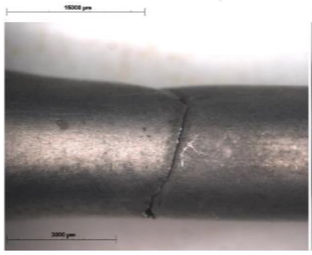
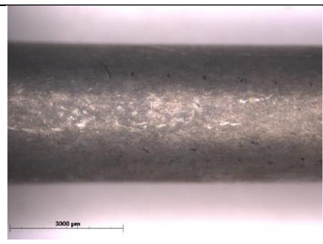
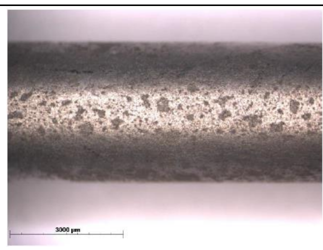
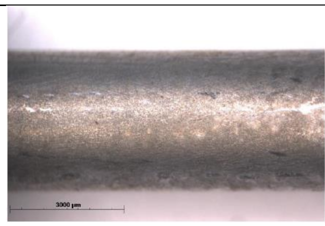
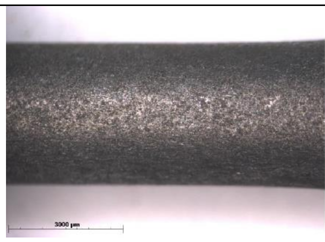
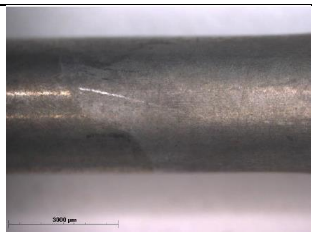
For all the steel grades, it is noticed that the actual yield strength (AYS) of the specimen is close to the theoretical Specified Minimum Yield Strength (SMYS), except for P110, where there is a difference of 142 MPa.

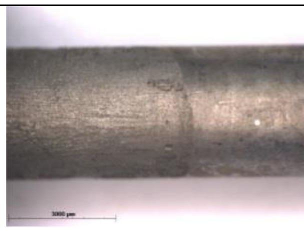
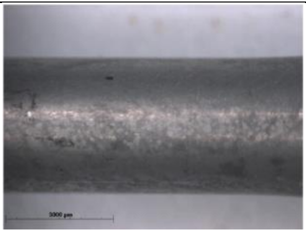
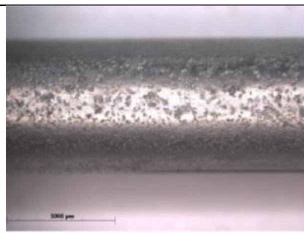
Therefore, for this material, it was decided to carry out one ripple load test between 80 and 100 % of the SMYS and another ripple load test between 80 and 100 % of AYS.

4. Experimental Results

All the results of the experiments performed by the French Corrosion Institute are available in Appendix 1, with especially the Elongation and Stress curves and post-test pictures of the specimen. Global results are summarized here below :

Test Reference	Material	Pre-immersion	Yield strength reference for ripple load tests (MPa)	Gas conditions (bars)	Number of cycles	Examination	Picture
#1	P110	No	752	120 H_2	114	No pit & no crack	
#2		No		120 H_2 + 1 H_2S	114	Pits observed & no crack	
#3		No		120 H_2 + 1 H_2S + 15 CO_2	129	No pit & no crack	No picture
#4		Yes		120 H_2	122	No pit & no crack	

#5		Yes		120 H_2 + 1 H_2S	123	Pits & localized corrosion & no crack	
#14		Yes	894	120 H_2 + 1 H_2S	2	Failure	
#6	L80	No	551	120 H_2	198	No pit & no crack	
#7		Yes		120 H_2 + 1 H_2S	192	Pits & no crack	
#8	K55	No	379	120 H_2	271	No pit & no crack	
#9		Yes		120 H_2 + 1 H_2S	279	Generalized corrosion & no crack	
#10	Welded J55	No	379	120 H_2	280	No pit & no crack	

#11		Yes		120 H_2 + 1 H_2S	295	Corrosion of the base metal & no crack	
#12	13 % Cr	No	551	120 H_2	158	No pit & no crack	
#13		Yes		120 H_2 + 1 H_2S	179	Pits & localized corrosion & no crack	

For the Ripple Load Tests performed in hydrogen environment only, there was no crack nor pitting observed at the end of the week long test on the specimen.

On the contrary, for the tests performed with hydrogen and H_2S (1 bar partial pressure), localized corrosion or pittings were observed at the end of the week long test on the specimen. This phenomenon was enhanced with the 2 days pre-immersion before the beginning of the Ripple Load Test.

To observe these localized damages, cross sections were inspected with SEM on P110 samples.

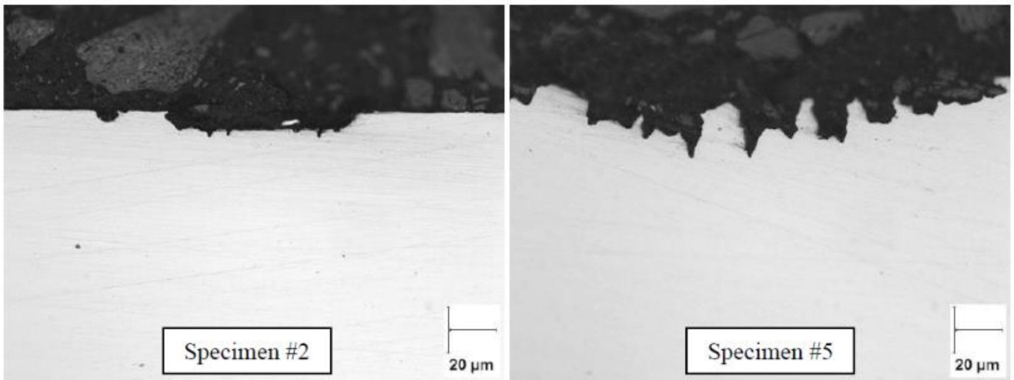


Figure 3 : Cross sections after Ripple load test on P110 sample in H2 and H2S environment. Left side without pre-immersion; right side with pre-immersion

These localized damages are similar to the one observed on P110 sample after Constant Load Test in the same environment (see picture below).

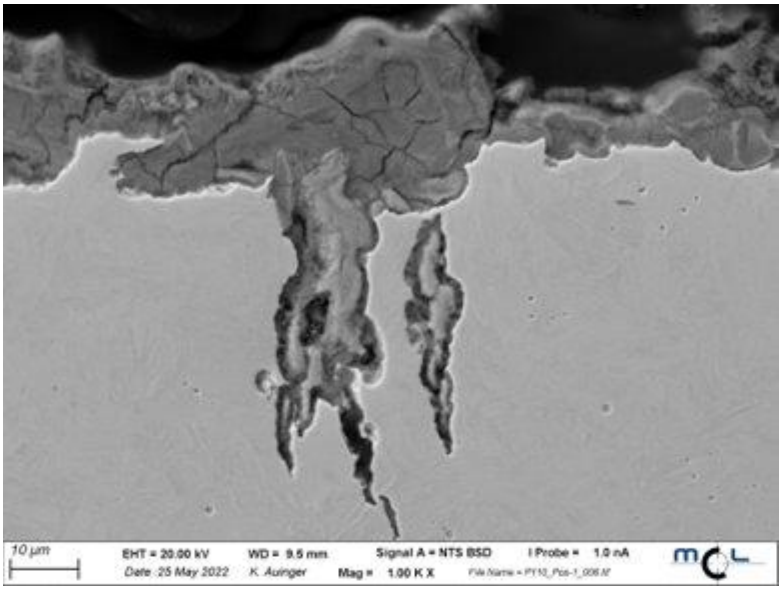


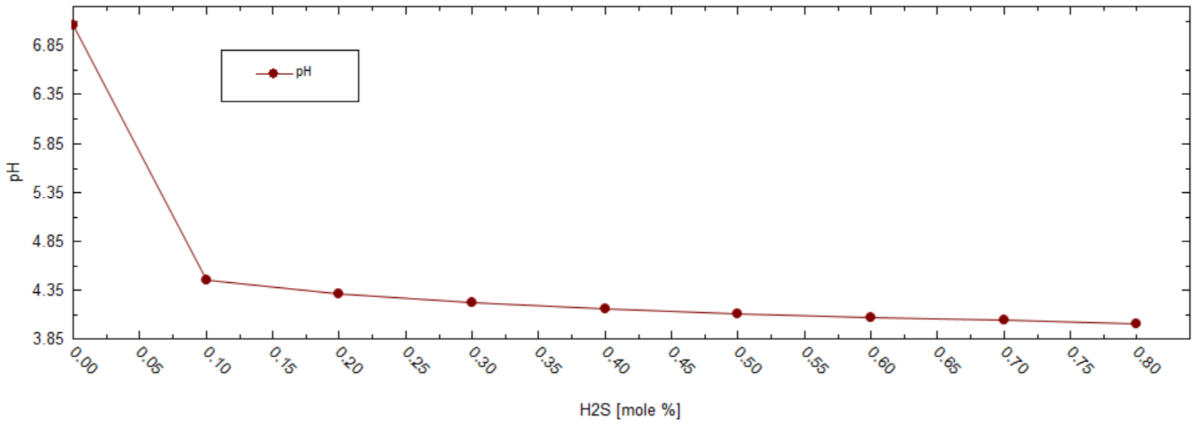
Figure 4 : Cross section of P110 after CLT at Room Temperature in Gas D with electrolyte immersion

Defects after one week of Ripple Load Tests are 30 µm long and their size is about 70 µm after one month of Constant Load Tests.

Ripple Load Test performed between 80 and 100 % of SMYS of P110 did not induce cracking, but the one performed between 80 and 100 % of AYS induced cracking after only two cycles.

5. Interpretation of the results

To explain the localized degradations that were observed with the addition of 1 bar of H_2S, simulations were performed with the software OLI (see graph below).



In a system with 120 bar of H_2 and 1 bar of H_2S, the molar percentage of H_2S is approximately 0.8 %. With such a percentage, it is observed that pH in the liquid phase can drop from 7 to 4, due to H_2S solubilisation. Presence of CO_2 in the system also involves a decrease of pH. This acid pH directly enhances corrosion and pitting phenomena.

The partial pressure of water was also calculated depending on the system (see the table below) :

Mixing of gas	Total pressure (bar)	Temperature (°C)	Salinity of electrolyte (g/L of NaCl)	pH	Partial pressure of H_2O (mbar)
H_2	120	20	200	7.03	27
H_2 + H_2S	121	20	200	3.86	24
H_2 + H_2S + CO_2	136	20	200	3.32	35

With such a partial pressure in water and in a closed system, it can be confirmed that gas was saturated in water and there was probably condensation on the steel specimen. These small droplets could explain the localized corrosion that were observed on the coupons.

Usually, Ripple load tests allow to calculate a threshold for corrosion fatigue ΔKmax, which corresponds to the maximum variations of constraints that can handle a steel grade during a specific number of cycles before cracking.

However, because there was no crack observed on most of tests, it can only be specified that the threshold is above the tested values.

The table below describes these results :

Steel grade	System	Maximum stress applied (MPa)	Ultimate Tensile Stress (MPa)	Number of cycles	Ripple load degradation (%)
L80	H_2	551	636	198	/
	$H_2 + H_2S$			192	/
K55	H_2	379	682	271	/
	$H_2 + H_2S$			279	/
Welded J55	H_2	379	593	280	/
	$H_2 + H_2S$			295	/
13% Cr	H_2	551	698	158	/
	$H_2 + H_2S$			179	/
P110	H_2	752	958	114	/
	$H_2 + H_2S$			123	/
	$H_2 + H_2S+CO_2$			129	/
	$H_2 + H_2S$	894		2	7 %

For P110, it is observed that Ripple Loading decreased the resistance of the steel before cracking by 7 %. As the reduction of area was very low (less than 5 %), instead of 60.5 % during the initial test for ultimate strength, it indicates a cracking due to hydrogen embrittlement: very fragile behaviour.

These tests helped to conclude that **P110 is not recommended for hydrogen/H_2S application when submitted to variations of constraints close to its AYS**. To make a comparison, a variation of constraints between 715 MPa and 894 MPa corresponds to a variation of pressure between 480 and 600 bar on 8-5/8'' tubing with a thickness of 9.5 mm. Most of the time, pressure considered for hydrogen storage are below these values, which indicates that this test was conservative.

These variations of constraints can also appear when elongations are observed on the tubing due to temperature variations.

For the other steel grades, **Ripple Load tests did not highlight any restrictions for hydrogen application**. **Based on these tests L80, K55, J55 welded and 13% Cr seem resistant to cracking**. Localized corrosions that were observed are due to H_2S corrosion rather than to hydrogen itself.

In a further work, it would be interesting to carry out Ripple Load tests on notches specimen to calculate a potential crack-growth rate. However, the equipment of the Corrosion French Institute was not able to monitor the localized force applied on the notch during the test. This project would require several tests to calibrate their equipment to notch specimens before launching Ripple Load Test in different conditions.

Hystories project consortium

Acknowledgment

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under grant agreement No 101007176.

This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe and Hydrogen Europe Research