



# Synthesis of the Materials and Corrosion Investigations

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Hystories deliverable D4.7-0

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# 1. Introduction

In the framework of the EU project Hystories, the possibility of hydrogen storage in old depleted gas reservoirs and natural gas storage facilities was examined throughout Europe. In the course of this project, the task of Work Package 4 (WP4) was to test the resistance of selected tubing materials to hydrogen embrittlement under relevant conditions by using autoclaves.

The final aim was to highlight the steel grades that would be the most adapted for hydrogen underground storage wells under various conditions.

To answer that problematic, several steel grades used for tubing or casing in underground storage wells were selected. They were tested in static (constant load test) and dynamic conditions (ripple load test) close to their yield strength. The conditions in the autoclaves were adapted to be representative of underground environment, with saturated humidity, high temperature and pressure, and presence of pollutant gases ( $\text{CO}_2$  and  $\text{H}_2\text{S}$ ).

Results of these tests were presented in deliverables D4.5 Ripple load tests and D4.6 Summary report on all investigated steels. Based on these results and literature information, this last deliverable of WP4 aims at synthetizing the compatibility of steels grades depending on the underground conditions.

## 2. Review of literature and existing standards for steel classification

Absorbed hydrogen can significantly reduce the ductility and the fracture toughness of a metal and cause cracking and brittle failures at stresses below the yield strength of the material. This hydrogen embrittlement (HE) can be prevented through materials selection. Therefore, materials exposed to hydrogen must be carefully selected and designed to resist hydrogen embrittlement.

Several scientific publications and material selection guidance that can be found in the literature address the compatibility of certain metals with hydrogen. These documents can be used to select the most promising metals and avoid the ones that are susceptible to HE.

ASME B31.12 Hydrogen Piping and Pipelines recommends the following metals to be considered in hydrogen gas service: Austenitic stainless steels, Aluminium alloys, Low-alloy ferritic steels and C-Mn ferritic steels, see Table 1.

On the contrary, high strength ferritic and martensitic steels, cast irons, nickel alloys are to be avoided.

Table 1: List of materials compatible with hydrogen service as per ASME 31-12.

**ASME B31.12-2019**

**Table A-2-1 Materials Compatible With Hydrogen Service**

Material	Form of Hydrogen		Notes
	Gas	Liquid	
Aluminum and aluminum alloys	Acceptable	Acceptable	...
Austenitic stainless steels with greater than 7% nickel (e.g., 304, 304L, 308, 316, 321, 347)	Acceptable	Acceptable	Beware of martensitic conversion at low temperature if stressed above yield point
Carbon steels	Acceptable	Not acceptable	Too brittle for cryogenic service
Copper and copper alloys (e.g., brass, bronze, and copper-nickel)	Acceptable	Acceptable	...
Gray, ductile, or cast iron	Not acceptable	Not acceptable	Not permitted for hydrogen service
Low-alloy steels	Acceptable	Not acceptable	Too brittle for cryogenic service
Nickel and nickel alloys (e.g., Inconel and Monel)	Not acceptable	Acceptable	Beware of susceptibility to hydrogen embrittlement
Nickel steels (e.g., 2.25%, 3.5%, 5%, and 9% Ni)	Not acceptable	Not acceptable	Beware of ductility loss
Titanium and titanium alloys	Acceptable	Acceptable	...

In the standard ISO/TR 15916: 2015, hydrogen embrittlement susceptibility of some commonly used metals is indicated. The extracted table is presented below:

Table 2: Hydrogen embrittlement susceptibility of some metals according to ISO/TR 15916.

Steel	Extremely embrittled	Severely embrittled	Slightly embrittled	Negligibly embrittled
▪ Alloy steel, 4140		X		
▪ Carbon steel				
▪ 1020			X	
▪ 1042 (normalized)			X	
▪ 1042 (quenched and tempered)		X		
▪ Maraging steel, 18Ni-250	X			
▪ Stainless Steel				
▪ A286				X
▪ 17-7PH	X			
▪ 304-ELC		X		
▪ 305		X		
▪ 310			X	
▪ 316			X	
▪ 410		X		
▪ 440C		X		
▪ Inconel 718	X			

From Table 2 it can be seen that the stainless steels A286, 310 and 316 are the least susceptible to hydrogen embrittlement. Whereas, the materials considered as extremely embrittled are maraging steel 18Ni-250, 17-7PH and Inconel 718.

Nevertheless, the standard specifies although a material may be subject to HE (even extremely embrittled), the material may still be used in hydrogen service if the service conditions allows its use (e.g. low enough stress).

In 2016, Jonathan A. Lee from the NASA published a technical report<sup>1</sup> presenting a review of experimental data on the effects of gaseous Hydrogen Environment Embrittlement (HEE) on several types of metallic materials. The results are expressed in terms of HEE index which allows to evaluate the severity of HE effects on certain materials. HEE index was measured at room temperature, in 69 MPa hydrogen pressure for stainless steels materials and at various pressures for carbon steels. HEE was classified into 4 categories: negligible, slight, severe and extreme.

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<sup>1</sup> Jonathan A. Lee Hydrogen Embrittlement NASA/TM-2016-218602 (April 2016)

This classification was based on the following results:

- NTS ratio taken from notched tensile specimens (NTS in hydrogen/NTS in Air or helium),
- and the Reduction of Area RA ratio (RA in hydrogen/RA in air or helium) and plastic elongation EL ratio ((EL) in hydrogen/(EL) in air or helium) taken from smooth specimens.

HEE index is a simple concept to evaluate the severity of HE as an initial material screening tool. In all cases, the material screening for the HEE effects is based on the decrease in the values of the HEE indexes from values of 1 (maximum HEE resistance) to 0 (minimum HEE resistance).

A simplified hydrogen embrittlement categorization is shown in the following Table 3.

Table 3: Hydrogen Environment Embrittlement categorization based on NASA/TM-2016-218602 document.

Material screening for hydrogen embrittlement based on HEE Index from NTS ratio		
H Embrittlement Category	HEE Index (NTS Ratio)	Material Screening Notes *
Negligible	1.0 - 0.97	Materials can be used in the specified hydrogen pressure & temperature range with fracture mechanics & crack growth analysis in hydrogen.
Small	0.96 - 0.90	
High	0.89 - 0.70	Cautiously use only for limited applications with detailed fracture mechanics & crack growth analysis in hydrogen.
Severe	0.69 - 0.50	Not recommended for usage at specific pressure and temperature where the HEE Index is measured.
Extreme	0.49 - 0.0	

\*Based on application at specific hydrogen pressure and temperature, where HEE Index is measured. In all categories, additional testing and fracture analysis must be performed beyond the material screening phase.

The HEE index for several different types of austenitic, ferritic, and martensitic steels is given in this technical report. Table 4 for ferritic steels is presented below:

Table 4: Extract of the HEE rating of different ferritic steels based on NASA/TM-2016-218602 document.

HEE Indexes for selected steels tested at 24 °C under high hydrogen pressure											
Alloy System	MATERIAL (HEE Tested at 24°C)	H Pressure (MPa)	Qualitative Rating for HEE	HEE Index, (Ratio H/He)			Smooth Ductility (%), in Helium or Air		Tensile Strengths, in Helium or Air (MPa)		
				NTS	EL	RA	EL	RA	NTS	YS	UTS
Ferritic Steels	A106-Gr. B	6.9	high		0.78	0.86	14	58		462	558
	A212-61T (normalized)	68.9	severe	0.68		0.60		57	765		
	A372 (class 4)	68.9	high	0.74	0.50	0.34	20	53	1378	565	813
	A372 (grade J)	24.1	severe		0.45	0.34	37	68		296	517
	A515-Gr. 70	68.9	high	0.73	0.69	0.52	42	67	730	310	448
	A516	6.9	high	0.83	0.90	0.63	19	69	758	372	537
	A517-F (T-1)	68.9	high	0.78	1.00	0.96	18	65	1557	751	813
	A533B	68.9	high	0.78	0.89	0.50	19	66	1564		820
	HY-80	68.9	high	0.81	0.86	0.85	23	70	1309	565	675
	HY-100	68.9	high	0.73	0.90	0.83	20	76	1543	668	779
	Iron (armco)	68.9	high	0.86	0.83	0.60	18	83	834	372	386
	X42	6.9	high		0.95	0.78	21	56		365	510
	X52	6.9	high	0.86	0.79	0.61	17	60	820	413	606
	X52	13.8	high		0.78	0.72	30.5	75.5		420	482
	X60	6.9	small	0.92	0.77	0.55	13	49	847	427	593
	X65	6.9	small	0.94	1.00	0.63	15	57	806	503	606
	X70	6.9	small	0.90	1.00	0.82	20	57	944	586	668
	X100	13.8	severe		0.63	0.49	20.5	78		751	882
	430F	68.9	severe	0.68	0.63	0.58	22	64	1047	496	551
	1080	6.9	severe		0.62	0.45	12	16		413	813
	1080 (Transverse)	6.9	severe		0.74	0.46	10	14		413	813
	1020	68.9	high	0.79	0.80	0.66	40	68	723	282	434
	C1025	68.9	high	0.76					730		448
	1042 (Q&T)	68.9	extreme	0.22					1626	1137	
	1042	48.2	high	0.75	0.75	0.45	29	59	1054	400	620
	4140 (Q&T)	68.9	extreme	0.25	0.19	0.19			2494	1233	1571
	4140	34.5	extreme	0.47							
	4140	68.9	extreme	0.40	0.18	0.18	14	48	2157	1233	1282
	4140 (normalized)	68.9	high	0.85					1660		930
	4340 (1652°F austen.)	34.5	extreme	0.35	0.31	0.26	12.4	54.2	2157	1302	1371

According to Jonathan A. Lee, the HEE index classification is only a qualitative material screening method based on an accelerated test in laboratory environment. It should not be used for component design without detailed fracture mechanics and design analysis for safety usage in hydrogen environment, particularly for materials that are qualitatively rated in the embrittlement category of High, Severe or Extreme.

All these different classifications are for pure hydrogen and not for hydrogen with traces of impurities as CO<sub>2</sub>, H<sub>2</sub>S or H<sub>2</sub>O.

NACE standard MR0175 / ISO 15156 is useful to classify the materials for use in H<sub>2</sub>S-containing environments. The severity of the sour environment is dependent on in situ pH and H<sub>2</sub>S partial pressure (see graph below):

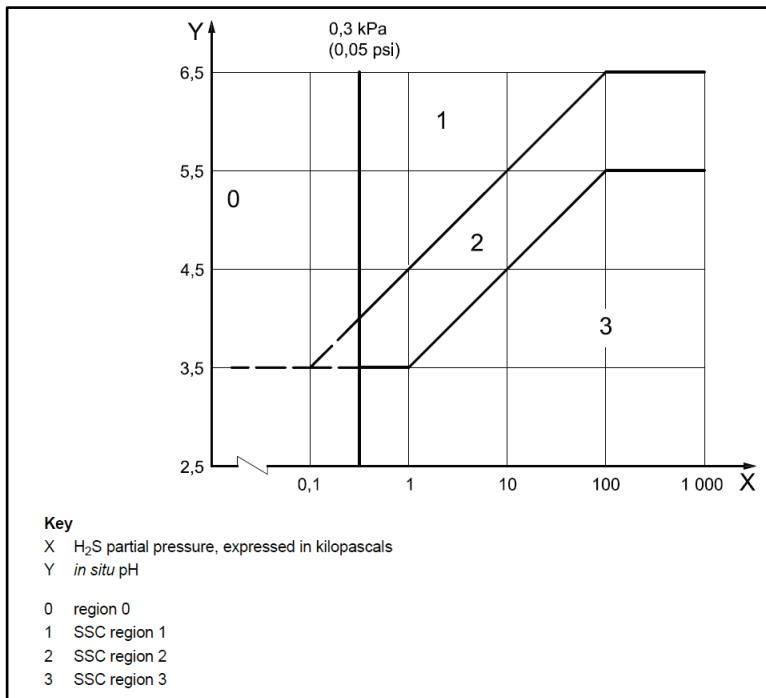


Figure 1: Severity of sour environment depending on H<sub>2</sub>S partial pressure and pH as per MR0175/ISO 15156.

In Region 0 (below 0.3 kPa of H<sub>2</sub>S), it is considered that normally no precaution for the selection of steels is required, sulphide stress cracking (SSC) and hydrogen stress cracking (HSC) can be neglected.

In Region 1, 2 or 3, risks associated to SSC and HSC cannot be neglected and specific materials should be employed. Moreover, selected material shall respect a maximum acceptable hardness value of 250 HV or 22 HRC.

Acceptable materials are listed in the Table 5 below:

Table 5: Acceptable steel grades for sour environment as per MR0175/ISO 15156

**Table A.3 — Environmental conditions for which grades of casing and tubing are acceptable**

For all temperatures	For $\geq 65^{\circ}\text{C}$ ( $150^{\circ}\text{F}$ )	For $\geq 80^{\circ}\text{C}$ ( $175^{\circ}\text{F}$ )	For $\geq 107^{\circ}\text{C}$ ( $225^{\circ}\text{F}$ )
ISO 11960 <sup>a</sup> grades: H40 J55 K55 M65 L80 type 1 C90 type 1 T95 type 1	ISO 11960 <sup>a</sup> grades: N80 type Q R95 <sup>c</sup> C110	ISO 11960 <sup>a</sup> grades: N80 P110	ISO 11960 <sup>a</sup> grade: Q125 <sup>b</sup>
Proprietary grades as described in <a href="#">A.2.2.3.3</a>	Proprietary Q&T grades with 760 MPa (110 ksi) or less maximum yield strength. Casings and tubulars made of Cr-Mo low-alloy steels as described in <a href="#">A.2.2.3.2</a> .	Proprietary Q&T grades with 965 MPa (140 ksi) or less maximum yield strength.	

Temperatures given are minimum allowable service temperatures with respect to SSC.  
Low temperature toughness (impact resistance) is not considered, equipment users shall determine requirements separately.

<sup>a</sup> For the purposes of this provision, API 5CT is equivalent to ISO 11960:2020.

<sup>b</sup> Types 1 and 2 based on Q&T, Cr-Mo chemistry to 1 036 MPa (150 ksi) maximum yield strength. C-Mn steels are not acceptable.

<sup>c</sup> In earlier editions of ISO 11960/API 5CT this grade was named C95. For the purposes of this provision, R95 and the former C95 are deemed equivalent.

It is noticed that steel grades J55, K55 or L80 type 1 are acceptable for all temperatures in sour conditions, whereas P110 is acceptable only for temperature higher than  $80^{\circ}\text{C}$ .

However, this standard is only applicable for sour environment, which is estimated to be conservative compared to gaseous hydrogen service.

Hystories laboratory tests allowed to complete the available literature and propose a steel classification for hydrogen underground application where traces of impurities are likely to appear.

# 3. Synthesis of Hystories Results

## 3.1. Reminder of the test conditions

The conditions of the tests during Hystories experiments are reminded here below. For more information, deliverable D4.1 can be consulted.

Constant Load Test:

- Tensile specimen stressed at 90 % of its measured yield strength,
- Test in autoclaves during 720 hours (one month),
- 120 bar of H<sub>2</sub> introduced, with or without 15 bar of CO<sub>2</sub> / 1 bar of H<sub>2</sub>S,
- With or without electrolyte NaCl, at salinity 1 g/l or 200 g/l,
- With or without rotation of the autoclave,
- At 20 or 120 °C.

It is underlined that for HE, worst case is considered at the lower temperature. In our case, it would be at 20 °C.

Furthermore, presence of H<sub>2</sub>S significantly increases hydrogen permeation and therefore hydrogen embrittlement. Therefore, the worst case would be in presence of H<sub>2</sub> + CO<sub>2</sub> + H<sub>2</sub>S.

Last, it was considered that presence of electrolyte with rotation also enhances hydrogen risk. Worst case was considered with 200 g/l of electrolyte in rotation.

Ripple Load Test:

- Tensile specimen stressed between 80 and 100 % of its SMYS (Specified Minimum Yield Strength),
- 5.10-6 inch/s for extension rate,
- Test in autoclaves during one week,
- 120 bar of H<sub>2</sub> introduced, with or without 15 bar of CO<sub>2</sub> / 1 bar of H<sub>2</sub>S,
- With or without pre-immersion in 200 g/l NaCl,
- Humidity introduced in the chamber with 200 g/l NaCl electrolyte in the autoclave, not in direct contact with the specimen,
- At ambient temperature, 23 °C.

## 3.2. Synthesis of the Results

### 3.2.1. Results of Constant Load Tests

Results obtained from the constant load tests are summarized in the following Table 6. For more details, please refer to deliverable D4.6.

Table 6: Summary of the results of Constant Load tests in the frame of WP4 Hystories

	Test under wet H <sub>2</sub> at RT at 1 g/l NaCl in gas phase		Test under wet H <sub>2</sub> /CO <sub>2</sub> /H <sub>2</sub> S at RT at 1 g/l NaCl in gas phase	
	Corrosion speed (mm/y)	Additional H-uptake (ppm)	Corrosion speed (mm/y)	Additional H-uptake (ppm)
K55	0.05	0.06	0.05	1.81
L80	0.05	0.11	0.2	0.73

	Test under wet H <sub>2</sub> at RT at 200 g/l NaCl in liquid phase		Test under wet H <sub>2</sub> /CO <sub>2</sub> /H <sub>2</sub> S at RT at 200 g/l NaCl in liquid phase		
	Corrosion speed (mm/y)	Additional H_uptake (ppm)	Corrosion speed (mm/y)	Additional H-uptake (ppm)	Depth of corrosion attack (μm)
20MnV5	0.22	0.33	0.18	2.56	< 5
K55	0.35	0.19	0.05	0.70	15
L80	0.05	0.01	0.2	0.37	68
P110	0.25	0.13	0.1	1.56	55
13 % Cr	0.48	0.11	0.38	6.60	< 5
316 L	NM	0.52	NM	0.61	< 5
Duplex 2205	NM	0.60	NM	2.94	Fracture
Alloy 625	NM	0.28	NM	5.73	< 5

NM: Not Measured

From these results, it was observed that corrosion speeds remain quite low in all the tests (< 0.5 mm/year), which can be considered quite low. On a same steel grade, salinity variations or presence of impurities in gas phase did not seem to have any influence on corrosion speed results. It needs to be pointed out that these measurements were taken on very small specimens and only after one month of exposure. The uncertainty is not negligible, and the above values should not be taken as reference for corrosion speed estimations. Longer exposure is recommended to determine a corrosion speed with more reliability.

On the contrary, the presence of impurities has a clear influence on hydrogen uptake inside the material. The graph below represents the increase of hydrogen uptake by adding H<sub>2</sub>S (1 bar)/CO<sub>2</sub> (15 bar) mixing at 200 g/l of NaCl.

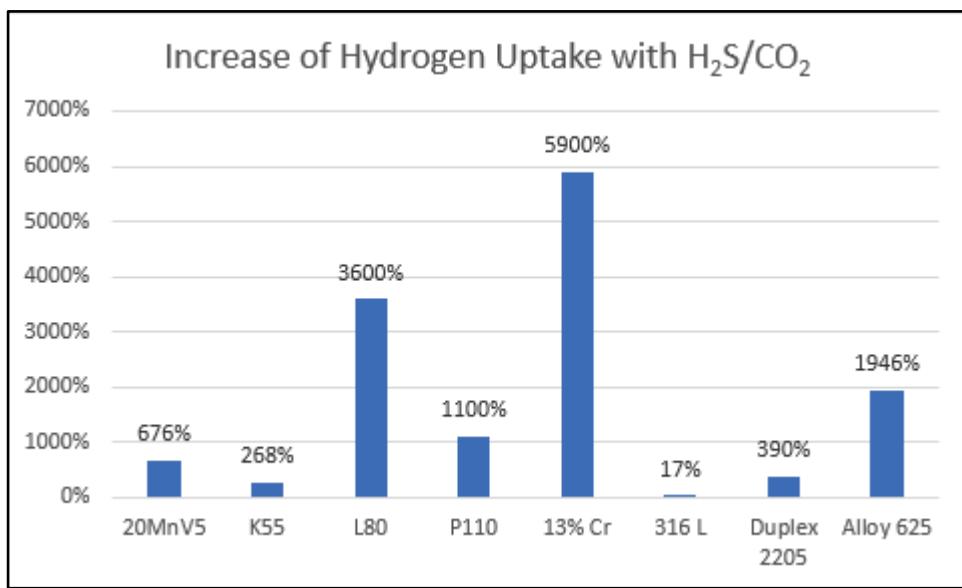


Figure 2: Increase of hydrogen uptake with  $\text{H}_2\text{S}/\text{CO}_2$  impurities compared to tests with pure hydrogen, all other test conditions being similar.

Average of the increase of hydrogen uptake from these tests was measured at about 1740 %. It is higher than the observation from Briottet (Briottet, 2018), which estimates it at +293 % with  $\text{H}_2\text{S}$  only (0.01 bar) and at +5 % with  $\text{CO}_2$  only (1 bar). It is logical to observe such a difference as the partial pressures of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  were not the same in the two different tests. Furthermore, in Briottet tests, the influence of impurities was not observed on hydrogen uptake but on crack growth rate. Nevertheless, it can be concluded from Briottet test that increase of hydrogen uptake is rather due to the presence of  $\text{H}_2\text{S}$  than  $\text{CO}_2$ .  $\text{H}_2\text{S}$  is a catalyst of hydrogen permeation.

Influence of salinity on hydrogen uptake was sometimes positive (+200 % max), sometimes negative (-60 %). Therefore, its role does not seem determinant for hydrogen uptake.

Presence of impurities have also a strong influence of the corrosion attack. No corrosion attack or fracture was noticed on steel grade specimens that were exposed to hydrogen only. However, some localized corosions/ defects were observed when  $\text{H}_2\text{S}$  and  $\text{CO}_2$  were added, these defects have been pushed until the fracture of the specimen in the case of Duplex 2205.

Impacts of hydrogen environment on welding, pre-corrosion or localized defects as notches have also been studied.

Welded J55 and K55 specimens were tested in the same conditions as other steel grades. Hardness mapping was conducted on the welded area and it appeared that measured values were higher than recommended value of 22 HRC or 250 HV for sour service. Despite these unfavourable conditions, no crack was observed during the Constant Load Tests (CLTs). The table below compares the hydrogen uptake for specimens with and without welding.

Table 7: Comparison of hydrogen uptake between base metal and welded areas during tests performed in the frame of WP4 Hystories

	Test under wet H <sub>2</sub> at RT at 200 g/l NaCl in liquid phase	Test under wet H <sub>2</sub> /CO <sub>2</sub> /H <sub>2</sub> S at RT at 200 g/l NaCl in liquid phase
	Additional H-uptake (ppm)	Additional H-uptake (ppm)
K55	0.19	0.70
Welded K55	0.65	0.95
Welded J55	0.00	1.15

A slight increase was observed on hydrogen uptake on welded specimens compared to the base metal. Nevertheless, no localized damage could be identified on SEM investigations, which tends to indicate that welded materials might increase hydrogen permeation but remain acceptable for hydrogen service, based on these results.

Pre-corroded samples were immersed in 200 g/l NaCl electrolyte with CO<sub>2</sub> at 15 bar during one week before the beginning of CLT. At the end of the experiments, a passive layer due to CO<sub>2</sub> corrosion was visible on the carbon steel specimens, however, no crack or defect was observed.

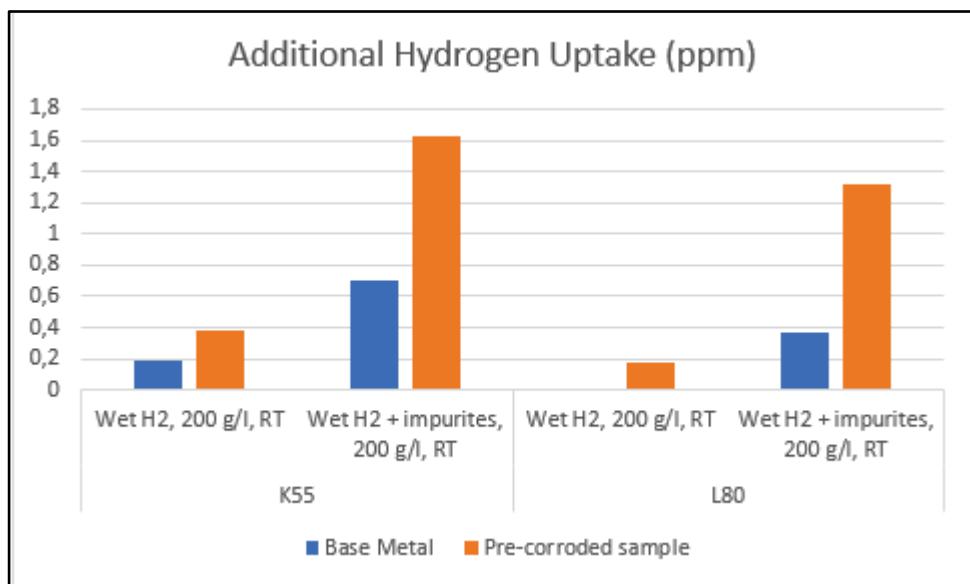


Figure 3: Comparison of hydrogen uptake between base metals and pre-corroded ones during tests performed in the frame of WP4 Hystories

On the graph, it is visible that pre-corroded samples uptake more hydrogen than the base metal. This result is surprising as it could have been presumed that the rust layer due to pre-corrosion would slowdown hydrogen permeation.

No matter what the hydrogen uptake is, microscopic evaluation did not highlight any localized defect due to pre-corrosion, and it can be concluded that rapid pre-corrosion does not seem to increase HE risk. This conclusion needs to be relative, as the specimens were pre-corroded only during one week. Steel casing or tubing that are pre-corroded due to their operation for several years are not in the same configuration at all.

Last, notches were also simulated on some specimens. A v-notch sample with 0.5 mm indentation was created, which leads to a thickness decrease of 33 % on the specimens. Even with this defect, no crack was observed after the CLT. Hydrogen uptake was not measured on the notched specimens, as the uptake is supposed to be the same of for unnotched sample, but SEM investigation revealed the presence of localized attack on the notch (see Figure 4).

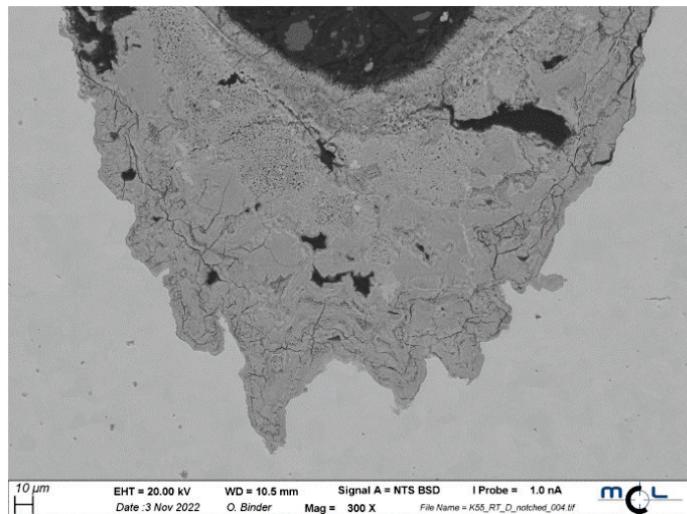


Figure 4: Cross-section of steel K55 notched at magnification 300x, with Gas D containing 200 g/l NaCl at RT

These attacks indicate some first weakness on the material that might have grown with longer exposure or in case of dynamic stress. This point highlights the fact that localized defects on the material shall be avoided to ensure the compatibility of the material for hydrogen service.

### 3.2.2. Results of Dynamic Load Tests

Results obtained from the dynamic load tests (or ripple load tests) are summarized in the following table. For more details, please refer to deliverable D4.5.

Table 8: Summary of the results of Dynamic Load tests in the frame of WP4 Hystories

	Test under wet H <sub>2</sub> at RT at 200 g/l NaCl in gas phase		Test under wet H <sub>2</sub> and H <sub>2</sub> S at RT at 200 g/l NaCl in gas phase, with pre-corrosion	
	Number of cycles	State at the end	Number of cycles	State at the end
K55	271	Not pit & no crack	279	Generalized corrosion & no crack
Welded J55	280	Not pit & no crack	295	Corrosion of the base metal & no crack
L80	198	Not pit & no crack	192	Pits visible & no crack
P110	122	Not pit & no crack	2	Failure of the specimen <sup>2</sup>
13 % Cr	158	Not pit & no crack	179	Pits, localized corrosion visible & no crack

<sup>2</sup> Test performed between 80 and 100 % of its Actual Yield Strength and not of its Specified Minimum Yield Strength.

From the 5 different specimens tested, it is observed that none of them indicate a weakness when exposed to hydrogen only. Their surfaces were still smooth with no defect after several cycles.

On the contrary, with pre-corrosion immersion and H<sub>2</sub>S addition, specimens were more sensitive and pits, localized corrosion or even fracture were noticed. P110 was the most sensitive with a fracture of the steel coupon after only 2 cycles. Once again, influence of H<sub>2</sub>S is clearly underlined.

# 4. Conclusion for Underground Application

## 4.1. Synthesis on the tested steel materials

In deliverable D4.6, based on the results of localized corrosion rates and cracking respectively, an application overview for investigated materials was presented. This table is reminded below:

Table 9: Application overview of all investigated steels

	Material	Damage	Application with H <sub>2</sub> S based on ISO 15156	Applicability in H <sub>2</sub> environment
increasing yield strength	20MnV5	no damage	Not specified	well applicable
	welded J55	no damage	Acceptable for H <sub>2</sub> S application for all temperatures	well applicable
	welded J55 pre-corroded	no damage		
	welded J55 with notch	no damage		
	K55	no damage	Acceptable for H <sub>2</sub> S application for all temperatures	well applicable
		no damage		
		some localized damage		well applicable when localized corrosion is not an issue
	welded K55	no damage	Acceptable for H <sub>2</sub> S application if hardness ≤ 22 HRC	well applicable
	L80	deep localized damage	Acceptable for H <sub>2</sub> S application for all temperatures provided that it is type 1	applicable when localized corrosion is not an issue
		some localized damage		
		some localized damage		
increasing alloy content	P110	deep localized damage	Acceptable for H <sub>2</sub> S application only if T° > 80°C	applicable at RT when no H <sub>2</sub> S is present
	quenched material	failure in H <sub>2</sub>	Not applicable	not applicable
	13%Cr	no damage	Acceptable if pH <sub>2</sub> S < 10.2 kPa	well applicable
	316L supplier 1	no damage	Acceptable if pH <sub>2</sub> S < 10.2 kPa	well applicable
	316L supplier 2	no damage		well applicable
	Duplex 2205	failure in (H <sub>2</sub> + CO <sub>2</sub> + H <sub>2</sub> S)	Acceptable if pH <sub>2</sub> S < 2 kPa	not applicable
	Alloy 625	no damage	Acceptable for H <sub>2</sub> S application for all temperatures	well applicable
	**no damage	**localized damage		**failure
	**well applicable in hydrogen environment	**applicable in hydrogen environment when localized corrosion is not an issue		**not applicable in hydrogen environment

It is proposed to complete this application review with the different classifications that were found in literature, see Table 10.

Table 10: Synthesis of the applicability of investigated steel materials based on Hystories laboratory results and bibliography.

Material	Hystories results	ASME B31-12	ISO/TR 15916	NASA/TM-2016-218602	MR0175 / ISO 15156
20MnV5	Well applicable	Acceptable as carbon steel	/	/	/
J55	Well applicable	Acceptable as carbon steel	/	/	Acceptable for H <sub>2</sub> S application for all temperatures
K55	Well applicable when localized corrosion is not an issue	Acceptable as carbon steel	/	/	Acceptable for H <sub>2</sub> S application for all temperatures
L80	Applicable when localized corrosion is not an issue	Acceptable as carbon steel	/	/	Acceptable for H <sub>2</sub> S application for all temperatures provided that it is type 1
P110	Applicable at RT when H <sub>2</sub> S is not present	Acceptable as low alloy steel	/	/	Acceptable for H <sub>2</sub> S application only if T > 80 °C
13% Cr (410)	Well applicable	/	Severely embrittled	HEE extreme	Acceptable if pH <sub>2</sub> S < 10.2 kPa
316 L	Well applicable	Acceptable	Slightly embrittled	HEE negligible	Acceptable if pH <sub>2</sub> S < 10.2 kPa
Duplex 2205	Not applicable	/	/	/	Acceptable if pH <sub>2</sub> S < 2 kPa
Alloy 625 (Inconel 625)	Well applicable	Not acceptable	/	HEE high	Acceptable for H <sub>2</sub> S application for all temperatures

From this table, it is noticed that results observed during Hystories laboratory tests are sometimes in contradiction with the assessment found in the public literature.

It is the case of Alloy 625 or 13 % Cr, results of CLT were satisfactory even in presence of H<sub>2</sub>S, whereas standards qualify them as not recommended for hydrogen application, as they could be severely embrittled.

In ISO/TR 15916, it is specified: "Although a material may be subject to hydrogen embrittlement (even extremely embrittled), the material may still be used in hydrogen service if the service conditions allows its use (e.g. low enough stress)." It is then understood that material judged as extremely embrittled are not necessarily banned for hydrogen service, but their external stresses must be cautiously checked.

On the contrary, L80 or K55 were ranked as applicable only when localized corrosion is not a problem in Hystories results, because localized attacks were noticed on these steel grades in presence of 1 bar of H<sub>2</sub>S. However, these same grades are evaluated as compatible for H<sub>2</sub>S application for all temperatures based on MR0175 / ISO 15156. It is highlighted that for Hystories tests, hydrogen sulphide concentration was significantly higher than what could be observed in underground storage conditions (usually not more than 100 ppm). Therefore, results obtained in presence of H<sub>2</sub>S in Hystories are extremely conservative. In order to clarify the application of these grades in H<sub>2</sub>/H<sub>2</sub>S environment, it would have been interesting to test also lower partial pressures of H<sub>2</sub>S in future research works.

Last, on some other cases, laboratory results and bibliography are consistent, it is the case for austenitic stainless steel that is estimated to have a negligible embrittlement with all the standards and is thus applicable for hydrogen storage applications.

## 4.2. Recommendations for underground hydrogen storage application

Concerning underground hydrogen storage, risk associated to hydrogen embrittlement will not be the same for all the environments.

It will depend on the presence of impurities in the gas, electrolyte, but also on the existence of dynamic or constant external stresses. It is proposed to distinguish here below the case of tubing and casing. As a matter of fact, hanging tubing are exposed to more vibrations or dynamic stresses than cemented casing. Moreover, most of the time, tubing is not in direct contact with water, whereas a part of the casing can be immersed in formation water.

The following chart (see Figure 5) is proposed to select a material for a hydrogen storage well depending on its environment.

This list of materials is not exhaustive and other alternatives could be proposed on case-by-case basis provided that they are hydrogen applicable or tested in the conditions of the well. A temperature below 80 °C is supposed and a maximum hydrogen partial pressure of 1 bar.

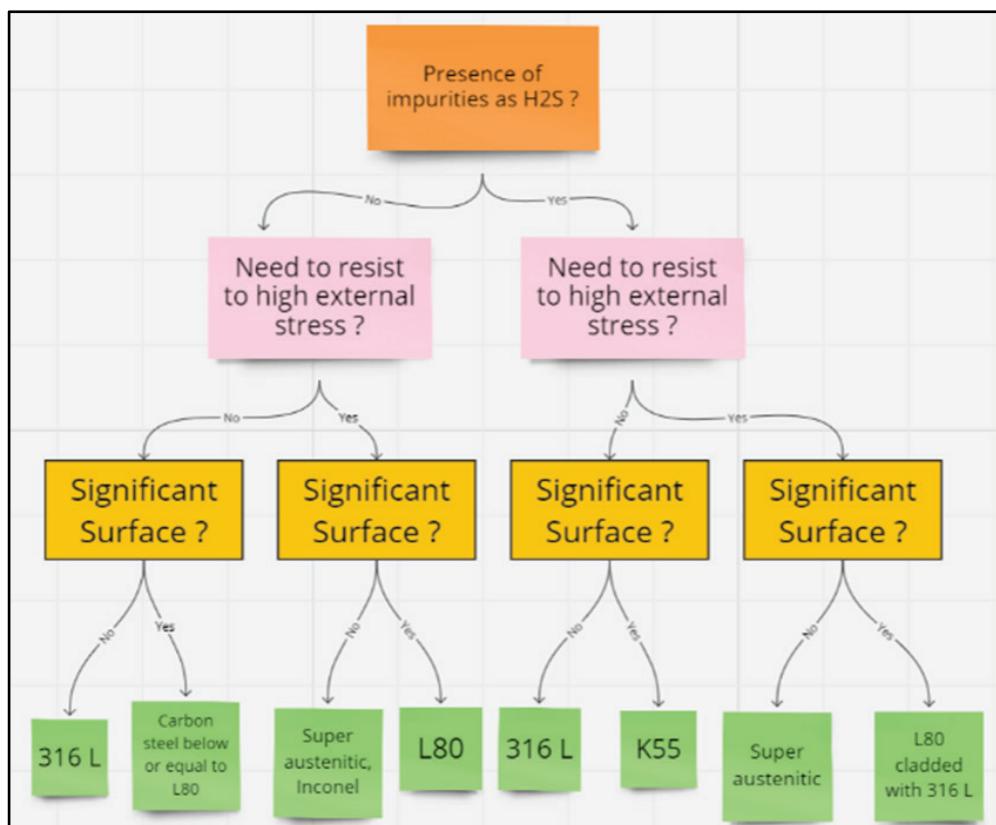


Figure 5: Proposed flowchart to select a material for wells in hydrogen environment (gas).

## Hystories project consortium



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