Session 8: Materials

Chair: Iñaki Azkarate; Panelists: Beatriz Acosta (JRC), Mathilde Weber (Air Liquide), Laurent Briotet (CEA), Chris San Marchi (SNNL)

Research Priorities Workshop – 26/27 September 2016, JRC IET Petten, Netherlands

The Focal Point on Integrated Research and Information for Hydrogen Safety

Materials

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Materials
Hydrogen effect on Materials. Ranking previous HySafe RPW. Washington DC, 2014.

Table 10. Results of voting (Materials Compatibility/Sensors)

Topic Number	Topic	Number of Votes	% of Votes Received
9.1	Reliability testing and validation of sensors for specific applications	17	22%
9.3	Sensor placement to maximize effectiveness in specific applications	16	21%
9.7	Hydrogen metals interaction studies need to be expanded to further alloys of interest, and fundamental research is still needed to understand the role of all parameters	12	15%
9.5	Complex and overbearing code requirements/limited international harmonization	11	14%
9.6	Improve understanding of embrittlement of hydrogen service candidate materials (metallic, non-metallic)	9	12%
9.8	Degradation modeling	8	10%
9.4	Reduce sensor cost and identify common performance metrics for cross-cutting applications	5	6%
9.2	Introduce testing of sensors for high concentration releases	0	0%

Materials
Hydrogen effect on Materials

1.- Hydrogen Effect on Materials

Materials are selected for industrial applications according to several factors.
In our case, the service conditions are of great importance.
Hydrogen can affect materials mainly in its mechanical properties.

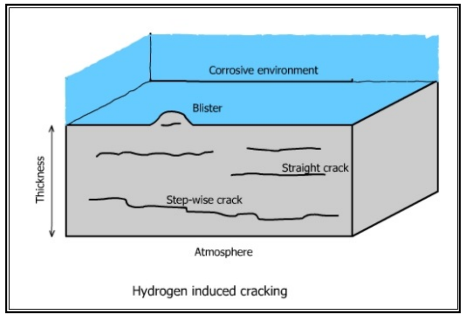
Depending of the material nature, metal or polymer, hydrogen can affect it in different ways.
In the case of metals, the main aspect responsible for the effect of hydrogen is based on the fact the Hydrogen molecule (H_2) splits into two atoms, entering the material in this atomic state and causing the deleterious effect.
This does not occur in the case of polymers, for wich the effect is more based in the permeability, diffusivity and solubility of H_2 into them.
Results can show sometimes the same kind of patterns(blisters, cracks,..) but in the most of the cases the effect is manifested in different ways.

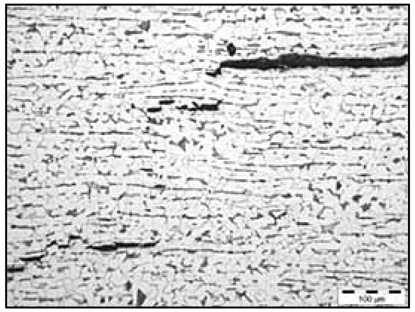
Materials
Hydrogen effect on Materials. Metals.

Types of Hydrogen Damage in Metals

1.- Hydrogen induced cracking (HIC).

Atomic hydrogen diffuses in the material and recombines in H_2 in specific sites (microcracks, inclusions,..). This H_2 can develop high pressure. In ductile materials, these pressures can deform the material producing blisters. In the case of low ductile materials, cracking can occur. It can propagate in a stepwise manner (Stepwise Cracking, SWC)



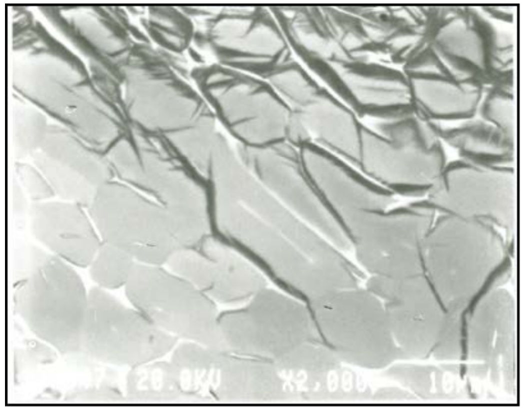



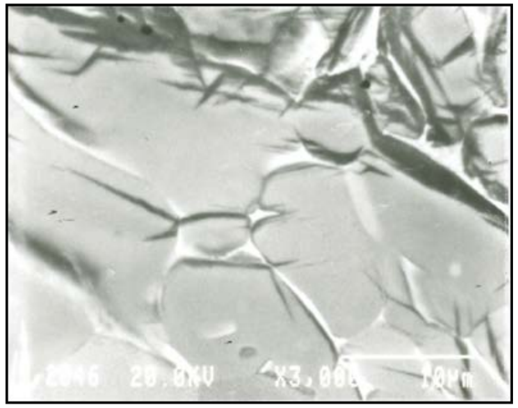
Materials
Hydrogen effect on Materials. Metals.

Types of Hydrogen Damage in Metals

2.- Hydrogen reaction.

Hydrogen can react with metallic phases forming hydrides (Ti, Zr,..) or non metallic phases (carbides) forming methane (CH4) or other compounds





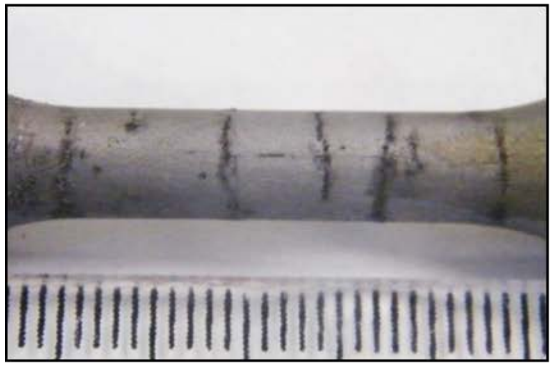
$Ti + H_2$ ----- TiH_2
$Fe_3C + 2H_2$ ----- $CH_4 + 3Fe$
$CuO + H_2$ ------ $Cu + H_2O$

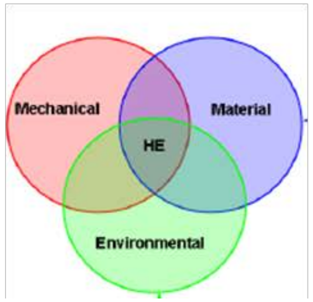
Materials
Hydrogen effect on Materials. Metals.

Types of Hydrogen Damage in Metals

3.- Hydrogen Embrittlement (HE) or Hydrogen Stress cracking (HSC).

This type of failure can take place when atomic hydrogen enters in contact with a material that is under stress (applied or residual).
In fact sometimes is considered as a type of Stress Corrosion Cracking (SCC).





Materials
Hydrogen effect on Materials. Metals.

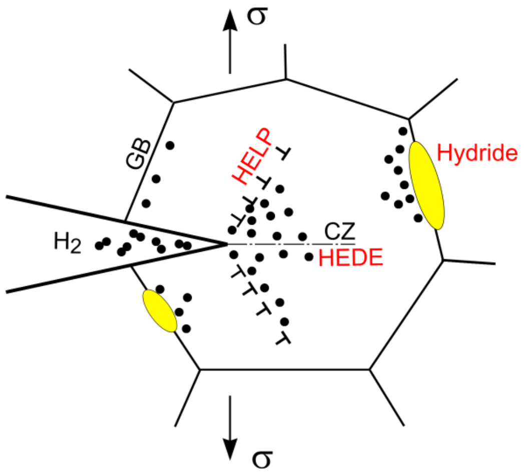
Hydrogen Embrittlement. Mechanisms.

Schematics of hydrogen embrittlement mechanisms.

HEDE: Hydrogen Enhanced Decohesion

HELP: Hydrogen Enhanced Localized Plasticity

Hydride formation and embrittlement.



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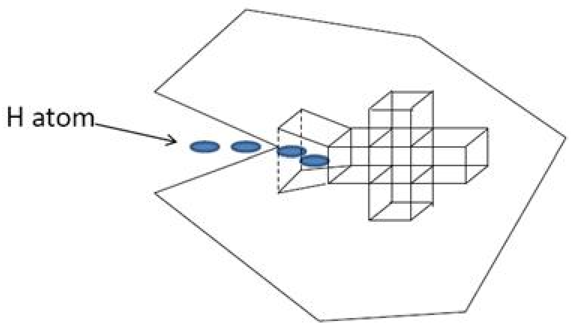
Hydrogen Embrittlement. Mechanisms.

1. HYDROGEN ENHANCED DECOHESION MECHANISM (HEDE)

The decohesion mechanism is one of the earliest mechanisms proposed for HE. This mechanism is based on the postulate that solute hydrogen decreases the forces required to separate the crystal along a crystallographic plane.
There is a decrease in atom binding forces of the metal lattice, which can result in premature brittle fracture. The brittle fracture may be in the form of either intergranular or transgranular cleavage.
The decohesion mechanism considers that there is a critical concentration of hydrogen atoms for which brittle fracture occurs.



This mechanism could be applied for intergranular fracture, where high concentration of hydrogen accumulates at grain boundaries (reaching the critical concentration for brittle fracture)

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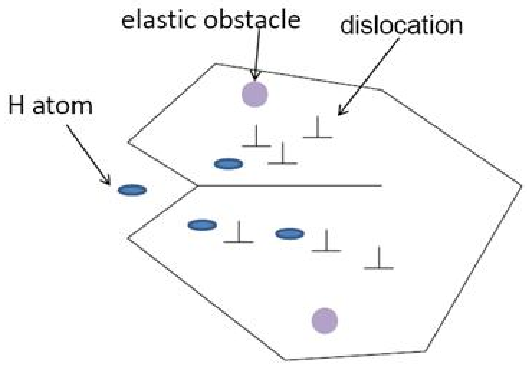
Hydrogen Embrittlement. Mechanisms.



2. HYDROGEN ENHANCED LOCALISED PLASTICITY MECHANISM (HELP)

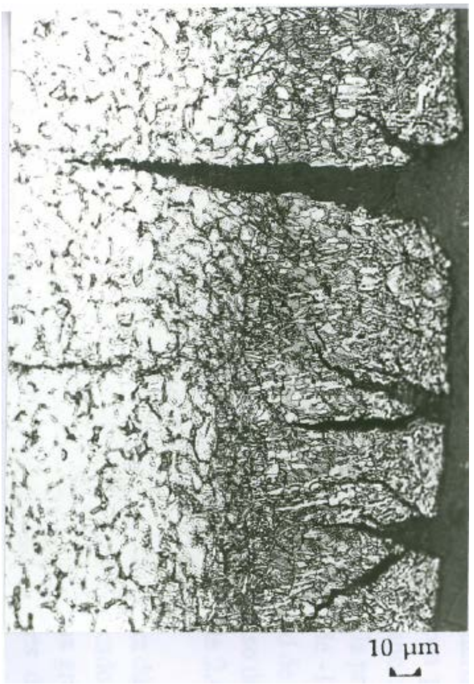
According to this model the failure occurs by locally ductile processes.
This mechanism is based on the fact that the presence of hydrogen in solid solution increases the mobility of dislocations and creates localized high deformation regions.
The reason of this increased mobility is attributed to reduction of interactions between dislocations and between dislocations and other obstacles (such as C atoms, grain boundaries) when hydrogen is present.
Dislocations thus move closer to each other, and closer to obstacles, and produce denser or more compact pile-ups when H is present.
The result of this is that microscopic regions of high deformation (where H increases the mobility of dislocations) are surrounding less ductile zones where dislocations are closely packed. The applied stress is then concentrated on these hard zones that represent only a small portion of the cross section. When the tensile stress in these small portions is higher than the ultimate tensile strength, failure occurs.
At present there is a large amount of experimental observations, by in- situ transmission electron microscopy that are supporting this mechanism. The fact that the effect of hydrogen on dislocations mobility is not dependent on the type of dislocation (edge, screw or mixed) and that it is present for different crystallographic structures, suggests that the HELP mechanism could be universal.

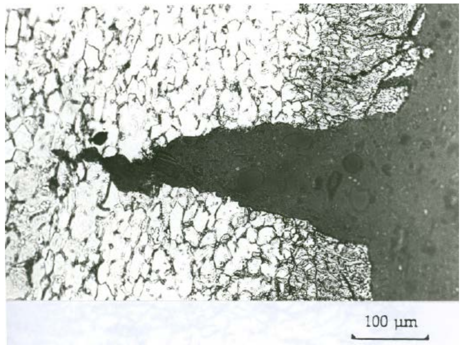
Materials
Hydrogen effect on Materials. Metals.

Hydrogen Embrittlement. Mechanisms.

3. HYDRIDE INDUCED EMBRITTLEMENT

Hydride-induced embrittlement is a second-phase mechanism that involves the nucleation and growth of an extensive hydride field ahead of a crack.
It has been observed that hydrides first nucleate in the stress field of a crack and then grow to large sizes not by the growth of individual hydrides but by the nucleation and growth of new hydrides in the stress field.
The auto-catalytic process of hydride nucleation and growth together with their brittle nature seems to be the main cause of embrittlement of V, Nb, Ti and Zr





Materials
Hydrogen effect on Materials. Polymers.

Hydrogen Embrittlement.

There are many differences between metals and polymers. The properties of polymers depend not only on their chemical structure, but on a variety of other factors. The most important of these are molecular weight (and molecular weight distribution) of polymer chains, and processing history.

For example, the degree of crystallinity of a polymer is affected by its cooling rate from the molten state. Processing techniques like extrusion can induce orientation and extension of polymer chains, influencing properties. Fillers, plasticizers, crosslinking agents, and other additives are often incorporated to modify properties. Thus tremendous variety may be associated with a single polymer.

Unlike metals, polymer properties are affected by hydrostatic pressure.

Polymers are not subject to hydrogen embrittlement in the same ways as metals. Hydrogen absorbed by polymers exists as a diatomic molecule; it does not dissociate as it is known to do in metals.

Four classes of polymers of interest based on their microstructure are considered. Two thermoplastics, and two crosslinked into networks by curing treatment.

- Semicrystalline thermoplastics
- Fully amorphous thermoplastics
- Elastomers
- Epoxies

Materials
Hydrogen effect on Materials. Polymers.

Semicrystalline thermoplastics

Chemical name	Abbreviation	Trade name(s)
High density polyethylene	HDPE	
Polyamide (nylon) Polyamide 6/Polyamide 11	PA PA6/PA11	Rilsan (PA11), Nylatron[b]
Polychlorotrifluoroethylene	PCTFE	Kel-F
Polyetheretherketone	PEEK	
Polyimide from pyromellitic dianhydride and 4,4′ diamino diphenyl ether		Vespel[c]
Polypropylene	PP	
Polytetrafluoroethylene	PTFE	Teflon

[a]Abbreviations from ASTM D1600, Standard Terminology for Abbreviated Terms Relating to Plastics.
[b]Nylatron is a family of nylon plastics typically filled with molybdenum disulfide powder.
[c]Vespel may be unfilled or may contain fillers such as PTFE, graphite, carbon fiber, or molybdenum disulfide.

Amorphous thermoplastics

Chemical name	Abbreviation	Trade name(s)
Chlorinated poly(vinyl chloride)	CPVC	
Poly(vinyl chloride)	PVC	

[a]Abbreviations from ASTM D1600, Standard Terminology for Abbreviated Terms Relating to Plastics.

Materials
Hydrogen effect on Materials. Polymers.

Elastomers

Abbreviation	Description	Trade name(s)
BR	Polybutadiene	
CR	Polychloroprene	Neoprene
EPDM	Terpolymer of ethylene, propylene, and a diene with the residual unsaturated portion of the diene in the side chain	
EPM	Copolymer of ethylene and propylene	
FKM	Fluoroelastomers of vinylidene fluoride and one or more of: hexafluoropropylene, tetrafluoroethylene, fluorinated vinyl ethers, propylene, ethylene	Viton, Tecnoflon
FMQ, FVMQ	Silicone rubbers having fluorine substituent groups on the polymer chain (fluorosilicone rubber)	
HNBR	Hydrogenated poly(butadiene-*co*-acrylonitrile)	
IIR	Poly(isobutylene-*co*-isoprene) (butyl rubber)	
MQ, VMQ, PVMQ	Silicone rubbers with varying substituents on the polymer chain (P = phenyl, V = vinyl, M = methyl). Poly(dimethyl siloxane) (PDMS) is one type of MQ	Silastic
NBR	Poly(butadiene-*co*-acrylonitrile) (nitrile rubber)	Buna N, Perbunan

[a]Abbreviations and definitions from ASTM D1418, Standard Practice for Rubber and Rubber Latices—Nomenclature.

Epoxies

Abbreviation	Description	Trade name(s)
DGEBA	Bisphenol A diglycidyl ether, also called Epichlorohydrin-bisphenol-A or epoxy resin	DER, EPON

Materials
Materials in Standards.

ISO/TR 15916

Table C.1 — Hydrogen embrittlement susceptibility of some commonly used metals[a]

Metal	Extremely embrittled	Severely embrittled	Slightly embrittled	Negligibly embrittled
Aluminium alloys				
1100				X
6061-T6				X
7075-T73				X
Be-Cu alloy 25				X
Copper, OFHC				X
Nickel 270		X		
Steel				
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			
Titanium and titanium alloys				
Titanium			X	
Ti-5Al-2.5SN (ELI)		X		
Ti-6Al-4V (annealed)		X		
Ti-6Al-4V (STA)		X		

[a] ISO 11114-4 describes test methods which allow to verify the exact sensibility of steel and metallic materials to hydrogen embrittlement.

Materials
Materials in Standards.

ISO/TR 15916

Table C.2 — Suitability of some selected materials for hydrogen service

Material	Gaseous hydrogen (GH_2) service	Liquid hydrogen (LH_2) service[b]	Remarks
METALS			
Aluminium and its alloys	S	S	Negligibly susceptible to hydrogen embrittlement.
Copper and its alloys (such as brass, bronze and copper-nickel)	S	S	Negligibly susceptible to hydrogen embrittlement.
Iron, cast, grey, ductile	NS	NS	Not permitted by relevant regulations and standards.
Nickel and its alloys (such as Inconel and Monel)	E	E	Evaluation needed. Susceptible to hydrogen embrittlement.
Steel, austenitic stainless with > 7 % nickel (such as 304, 304L, 308, 316, 321, 347)	See C.1	See C.1	May make martensitic conversion if stressed above yield point at low temperature.
Steel, carbon (such as 1020 and 1042)	See C.1	NS	Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic service.
Steel, low alloy (such as 4140)	E	NS	Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic service.
Steel, martensitic stainless (such as 410 and 440C)	E	E	Evaluation needed. Susceptible to hydrogen embrittlement.
Steel, nickel (such as 2,25; 3,5; 5 and 9 % Ni)	E	NS	Ductility lost at liquid hydrogen temperature
Titanium and its alloys	E	E	Evaluation needed. Susceptible to hydrogen embrittlement.

Materials
Materials in Standards.

ISO/TR 15916

Table C.2 — Suitability of some selected materials for hydrogen service

Material	Gaseous hydrogen (GH_2) service	Liquid hydrogen (LH_2) service[b]	Remarks
NONMETALS			
Asbestos impregnated with Polytetrafluoroethylene (PTFE)[a]	S	S	Avoid use because of carcinogenic hazard.
Chloroprene rubber (Polychloroprene[a])	S	NS	Too brittle for cryogenic service.
Polyester fibre (Dacron)	S	NS	Too brittle for cryogenic service.
Fluorocarbon rubber (Viton[a])	E	NS	Too brittle for cryogenic service.
Polyester film (Mylar)[a]	S	NS	Too brittle for cryogenic service.
Nitrile (Buna-N[a])	S	NS	Too brittle for cryogenic service.
Polyamides (nylon)	S	NS	Too brittle for cryogenic service.
Polychlorotrifluoroethylene (Kel-F[a])	S	S	
Polytetrafluoroethylene [Polytetrafluoroethylene (PTFE)[a]]	S	S	

NOTE 1 S: Suitable for use.

NOTE 2 NS: Not suitable for use.

NOTE 3 E: Evaluation needed to determine if the material is suitable for the use conditions.

[a] Polytetrafluoroethylene (PTFE), Polychloroprene, Dacron, Mylar, Viton, Buna-N and Kel-F are examples of suitable products available commercially. This information is given for the convenience of users of this Technical Report and does not constitute an endorsement by ISO of these product(s).

[b] Care should be taken that when the liquid H_2 tanks are more or less empty that the upper part could be warm. In this case, the column of GH_2 applies instead of LH_2.

Materials
Materials in Standards.

Recent Progress

- **ASME Article KD-10**: hydrogen pressure vessels
  - Fracture mechanics approach (fatigue crack growth and fracture)
- **SAE J2579**: onboard hydrogen fuel systems
  - Fatigue life approach (includes slow strain rate tensile testing)
- **CSA CHMC1**: general test methods in gaseous hydrogen (metallics)
  - Fracture, fatigue and tensile testing for metallic materials
- **CSA HPIT1**: gaseous hydrogen fuel systems for industrial trucks
  - Guidance specific to Cr-Mo pressure vessel steel with conservative design philosophy
- **ISO 11114-4**: specific to transportable gas cylinders
  - Several methods to evaluate transportable pressure vessel steels

Materials
Materials in Standards.

Current Activities

- **ASME Article KD-10**: hydrogen pressure vessels
  - Expanding scope to ASME SA-723 steels (international partnership)
- **SAE J2579**: onboard hydrogen fuel systems
  - Developing testing capability for low-temperature fatigue and coordination of testing activities through SAE and national programs
- **CSA CHMC1**: general test methods in gaseous hydrogen (metallics)
  - Evaluating fatigue-life methods by exploring parameter space (e.g., temperature, frequency, load ratio)
- **CSA CHMC2**: general test methods in gaseous hydrogen (***polymers***)
  - Committee not yet active
  - Test method development underway at US DOE National Laboratories, but limited in scope

Materials
Materials in Standards.

Gaps

- **ASME Article KD-10**: hydrogen pressure vessels
  - Available data is limited
  - Poor efficiency of fatigue crack growth testing methods
  - Fracture method is not conservative
- **SAE J2579**: onboard hydrogen fuel systems
  - Still evolving: lacks consensus on methods and metrics
  - Existing metrics are overly conservative (precludes rational basis for selection of materials)
- **CSA CHMC1**: general test methods in gaseous hydrogen (metallics)
  - Lacks internationally accepted metrics for qualification of materials
- **ISO 11114-4**: specific to transportable gas cylinders
  - Methods are not equivalent and may not be conservative (new version coming soon)
  - Does not address fatigue
  - Cannot be applied to other materials systems or components
- *No standards for hydrogen compatibility of polymer materials*

Materials
Hydrogen effect on Materials.

Main points to be discussed

1. What has been done in the last three to four years (progress)?

2. What is planned for near term research direction (working topics)?

3. What are the needs / gaps that need to be filled by future research (new directions)?

Materials
Hydrogen effect on Materials. Metals.

- **CEA. MATHRYCE project**
- **AIR LIQUIDE**
- **SNL**
- **TECNALIA**

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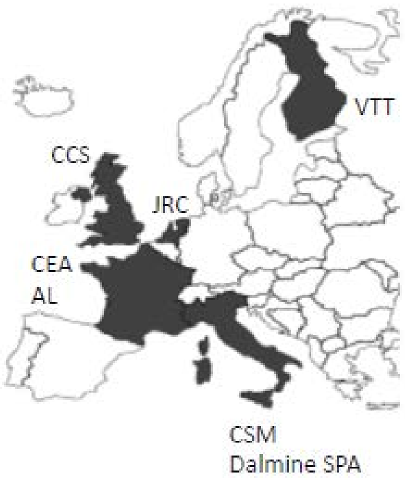
MATHRYCE

MATERIAL TESTING AND RECOMMENDATIONS
FOR HYDROGEN COMPONENTS
UNDER FATIGUE

CONSORTIUM

	Participant org. short name	Country
1	cea	France
2	AIR LIQUIDE	France
3	VTT	Finland
4	JRC EUROPEAN COMMISSION	The Netherlands
5	CCS GLOBAL	UK
6	Centro Sviluppo Materiali S.p.A.	Italy
7	Tenaris	Italy



OBJECTIVES

To provide

- an easy to implement **methodology**
- **based on lab-scale experimental tests under H_2 gas**
- to assess the service life of a **real scale component**
- taking into account **fatigue loading under H_2 gas**

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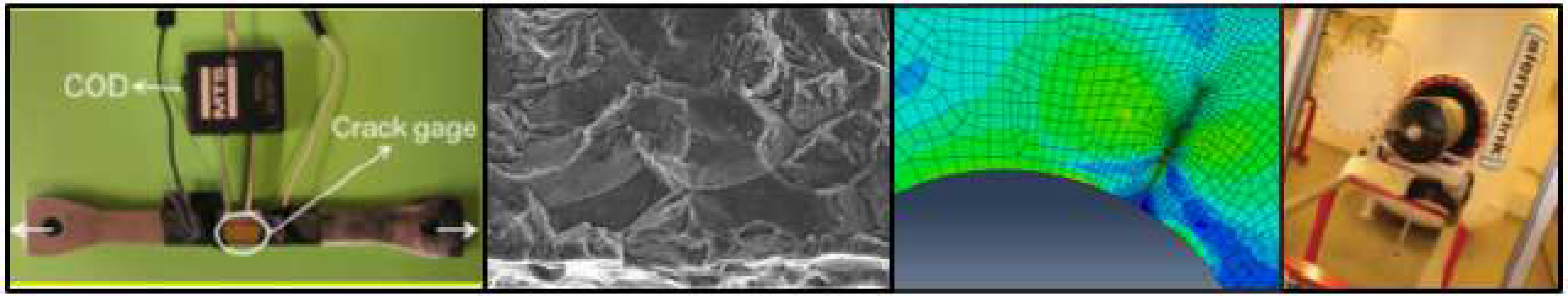
Hydrogen effect on Materials. Metals.

FINAL DISSEMINATION WORKSHOP



Hydrogen Enhanced Fatigue

Mechanisms, Modeling, Experiments and Pressure Vessel Design

www.mathryce.eu

Friday September 18, 2015

Materials
Hydrogen effect on Materials. Metals.

AGENDA

Mathryce overview	L. Briottet
Labscale – Full scale experimental comparison - Mathryce	(VTT, CSM, JRC)
Hydrogen uptake, diffusion and cracking in aqueous systems	A. Turnbull (NPL)
Fatigue characteristics of steels in presence of hydrogen	H. Matsunaga (I2CNER)
H_2 embrittlement for X70 pipeline steel in high pressure hydrogen gas	UB. Baek (KRISS)
Fatigue crack propagation in gaseous hydrogen: experiments and modelling	G. Hénaff (ENSMA)
Hydrogen induced stress cracking (HISC)	V. Olden (SINTEF)
Some issues associated with fatigue testing in high pressure hydrogen	R. Pargeter (TWI)
Proposal of fatigue-design method for steels in high-pressure gaseous hydrogen	J. Yamabe (Kyushu University)
Enhancing Fatigue Crack Growth Rate Measurements for Cr-Mo Pressure Vessel Steels in Hydrogen Gas	B. Somerday (SNL)
Codes comparison	J. Furtado / P. Bortot (AL, Tenaris)
Round table including Mathryce proposals	L. Briottet /H. Barthélémy

Materials
Hydrogen effect on Materials. Metals.
Progress

1. What has been done in the last three to four years (progress)?

Evaluation of test methods to define mechanical properties in H2 environment: toughness, fatigue, fretting fatigue (definition of specimens) and understand the most appropriate testing parameters (pressure, frequency)

- based on fracture mechanics (toughness: KIC, KIH; fatigue: da/dN vs. ΔK)

- based on non-cracked samples (fretting fatigue, disc-fatigue samples)

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Working Topics

2. What is planned for near term research direction (working topics)?

The project conclusions have been presented to ISO/TC 197, WG 15 and an annex has been provided for the current draft ISO/CD 19884 standard based on the use of a hydrogen sensitivity factor to be applied to the life of a component tested under hydraulic loading.

Materials
Hydrogen effect on Materials. Metals.
New gaps or directions

3. What are the needs / gaps that need to be filled by future research (new directions)?

A future project should validate the methodology working in different laboratories on several materials and components in view of international standardization.

Moreover, projects facilitating the increase of understanding on Fatigue Crack Initiation and Propagation of small cracks under hydrogen pressure would certainly be valuable.

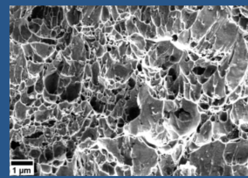
The study of the effect of hydrogen pressure on the ΔK threshold is also important.

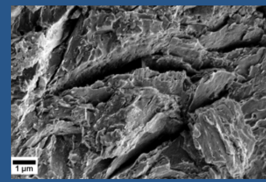
Finally, a data base providing these fatigue data for the most probable materials to be used for hydrogen pressure vessels would be very useful.

Materials
Hydrogen effect on Materials. Metals.
Progress

H_2 refuelling stations:

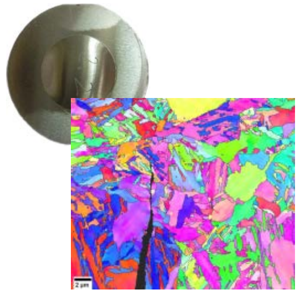
- Effect of High Pressure on selection material methods
- H_2 effect on degradation mechanisms
- Ambient Temperature (-40°+80°C)
- H_2 Charging Stations





Cr-Mo steel for buffer stations:
=>**Provide recommendations for the vessel design** based on:

- ***H_2 embrittlement,*** (KU, HYDROGENIUS, Disc test LSPM, CTE tests)
- ***H_2 enhanced fatigue*** (KU, HYDROGENIUS, MATHRYCE)



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Impact of gas impurities on material compatibility (=>mitigation strategy)
Effect of CO, O_2 and H_2O on H_2 embrittlement (Japan)

KYUSHU UNIVERSITY I²CNER

Materials
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Progress

Effect of H2 pressure on **fatigue crack propagation** of Cr-Mo steel [1]

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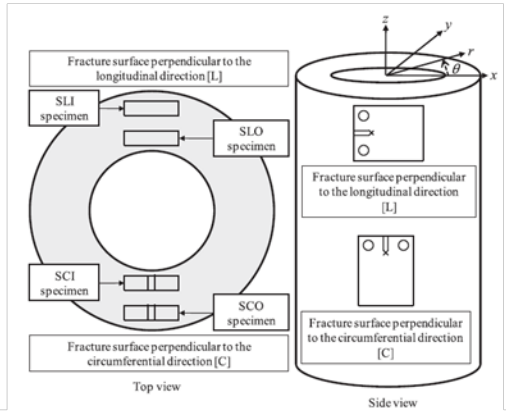
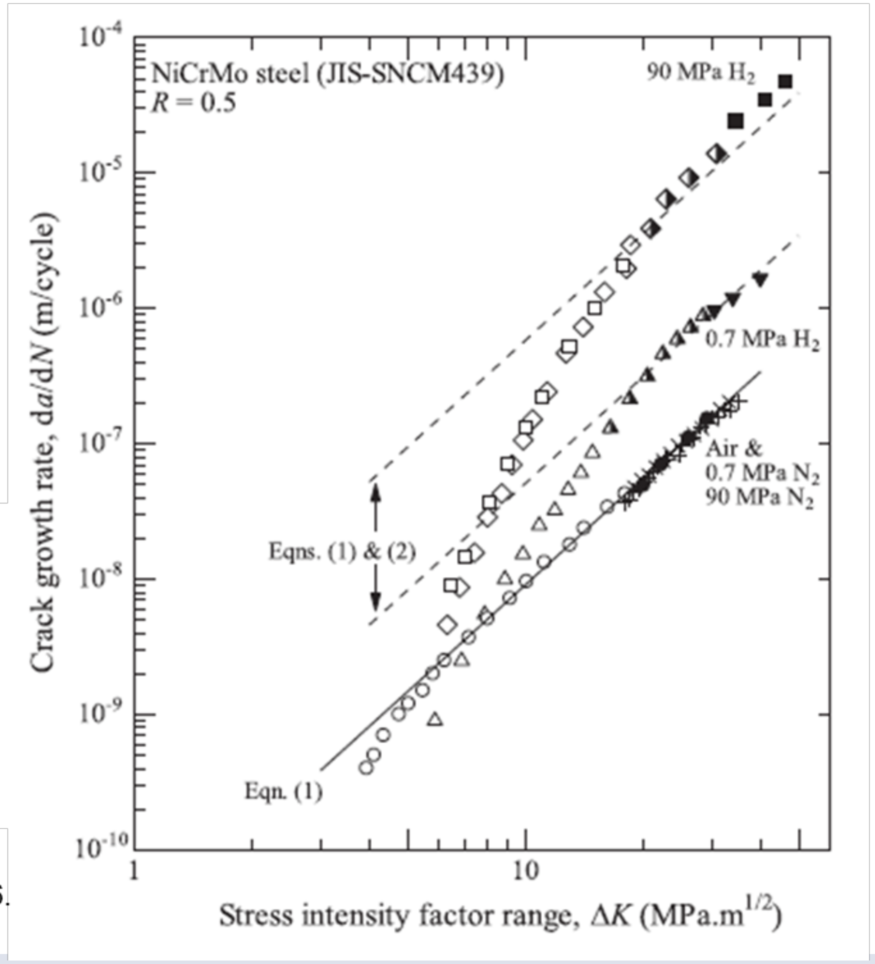
❏ sampling



Longitudinal specimens

Symbol	Environment	Frequency f (Hz)	Test type	Specimen type
□	H_2, 90 MPa	1	ΔK decreasing	SLI
▼	H_2, 0.7 MPa	1	ΔK increasing	SLI
+	N_2, 90 MPa	1	ΔK increasing	SLI
×	N_2, 0.7 MPa	1	ΔK increasing	SLI

❏ Fatigue crack propagation curves: hydrogen pressure effect



[1] A. Macadre et al.Engineering Fracture Mechanics 2011;78:3196.

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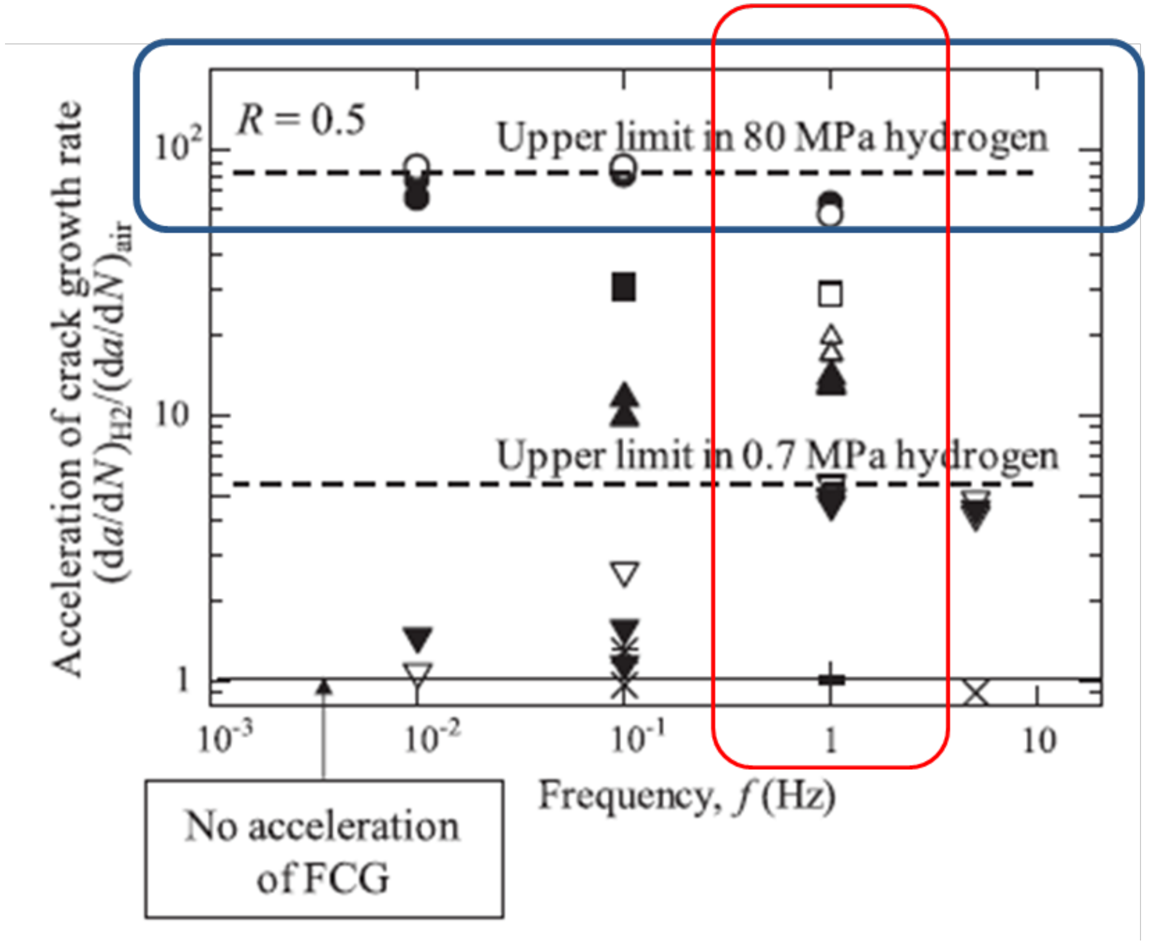
Progress

Fatigue crack propagation acceleration factor due to H2 pressure under constant ΔK



❑ testing conditions

Hydrogen atmosphere

Specimens	0.7 MPa	10 MPa	40~45 MPa	90 MPa
Circumferential (SCI, SCO)	▼	▲	■	●
Longitudinal (SLI, SLO)	▽	△	□	○

Nitrogen atmosphere

Specimens	0.7 MPa N_2	90 MPa N_2
Longitudinal (SLI, SLO)	×	+

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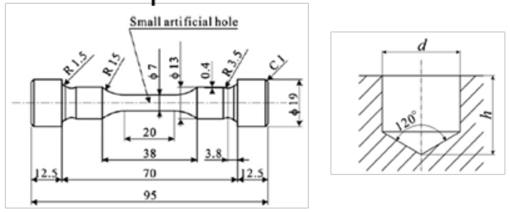
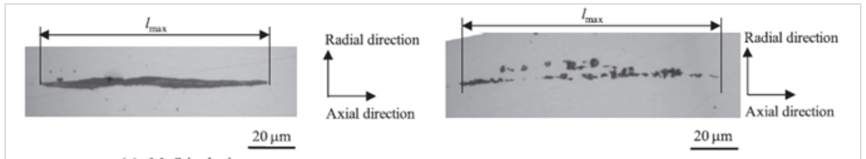
Progress

Effect of notch (artificial hole) on **fatigue crack propagation** and **SN curves** of Cr-Mo steel

❑ Sample with artificial hole



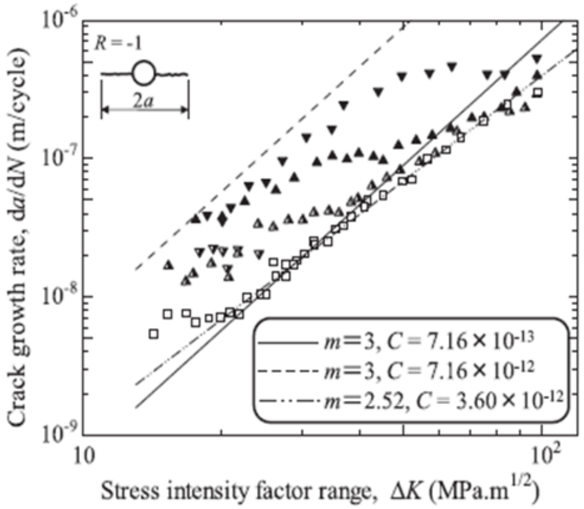
❑ inclusions



(a) MnS inclusion

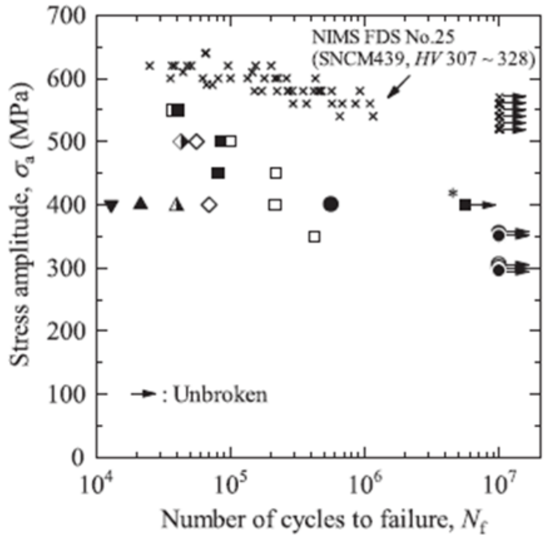
(b) Al_2O_3 inclusion cluster

❑ da/dN versus delta K curves



Symbol	Hydrogen charge	Frequency	C_H (mass ppm)
□	Uncharged	20 Hz	≤ 0.01
Δ	Immersion	20 Hz	0.16→0.07
▽	Immersion	2 Hz	0.16→0.04
▲	Gas	2 Hz	0.24→0.12
▼	Gas	0.2 Hz	0.25→0.08

❑ SN curves



Smooth

Symbol	Hydrogen charge	Frequency	C_H (mass ppm)
□	Uncharged	20 Hz	≤ 0.01
○	Uncharged	500 Hz	≤ 0.01
■	Gas	20 Hz	0.26→0.24
*■	Gas	20 Hz	0.26→0.01
●	Gas	500 Hz	0.26→0.18

Hole / Hole+precrack

Symbol	Hydrogen charge	Frequency	C_H (mass ppm)
◇	Uncharged	20 Hz	≤ 0.01
◆	Immersion	20 Hz	0.15→0.10
Δ	Immersion	2 Hz	0.16→0.07
▲	Gas	2 Hz	0.24→0.12
▼	Gas	0.2 Hz	0.25→0.08

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[1] A. Macadre et al. International Journal of Fatigue 2011;33:1608.

Materials
Hydrogen effect on Materials. Metals.
Progress

Evaluation of the effect of the level of impurities in H_2 to mitigate H2 embrittlement (CO, O_2) using molecular modelling (DFT) and tests (fretting fatigue, toughness testing) => design rules of pipes, valves, etc (in progress)

Illustrated hereafter with O_2 case

I²CNER

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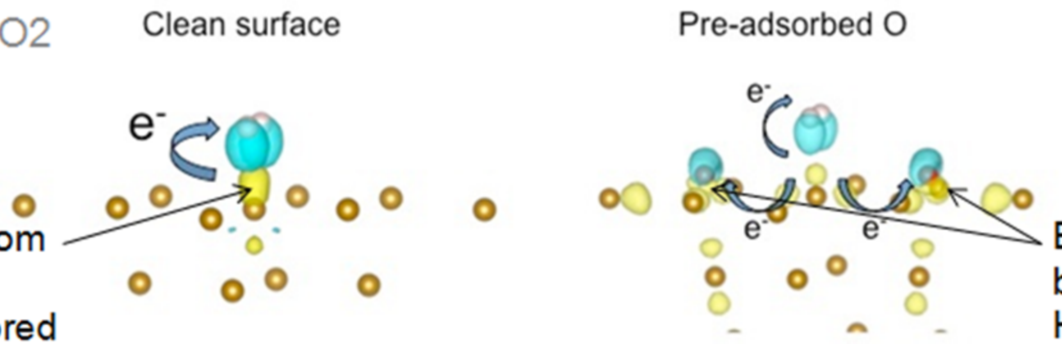
Ex: effect of O2 impurity



Electrons transfer from Fe atoms to H2 → dissociation H2 favored → HE favored

Electrons from Fe withdrawn by O atoms → dissociation H2 not favored → HE effect decreases

A. Staykov et al., *Int. J. Quant. Chem.* **114** (10), 626–635, 2014

Materials
Hydrogen effect on Materials. Metals.
Progress

Effect of oxygen on **fretting fatigue** properties of SUS 304 austenitic SS in hydrogen (1,2)

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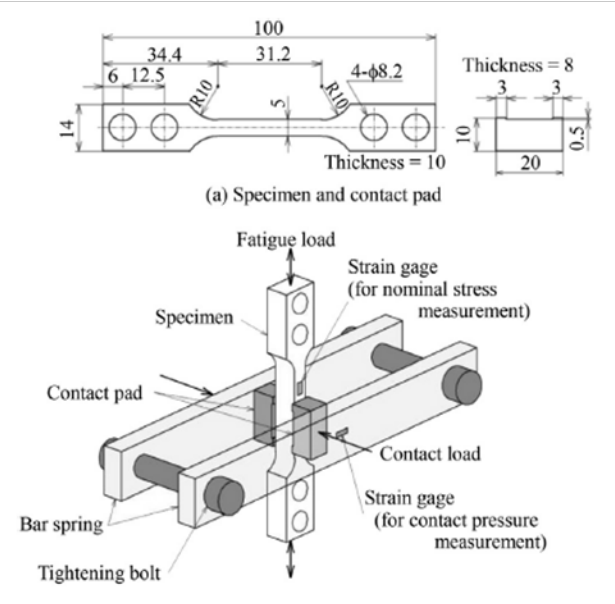
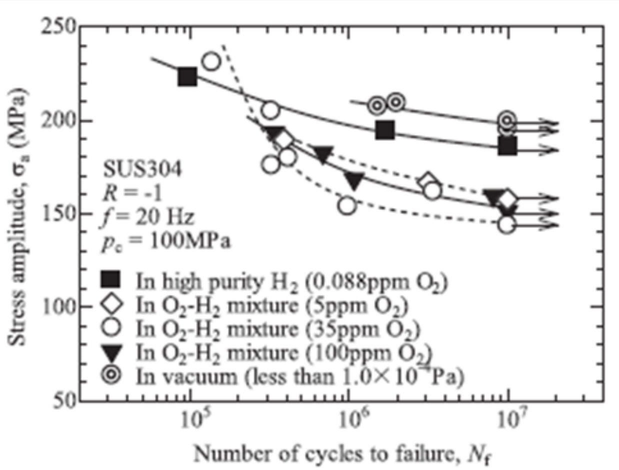
- sample and testing set-up



(a) Specimen and contact pad

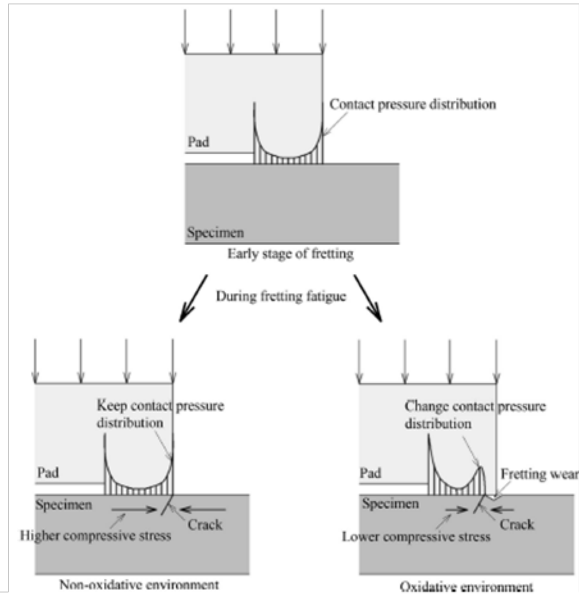
(b) Fretting fatigue test method

- SN curves: negative effect of O2 in fretting-fatigue



(a) Fretting fatigue strength in hydrogen in each environment

- Fretting-fatigue mechanism: stress distribution and surface crack position changed location due to O2

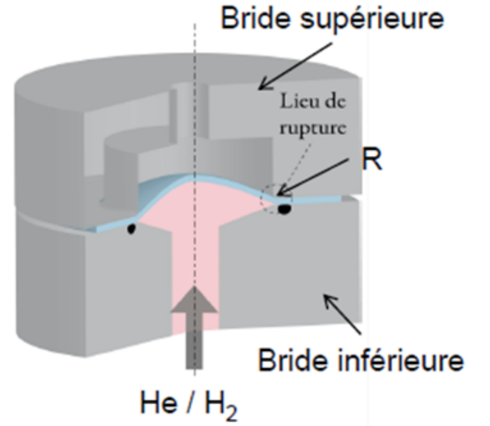


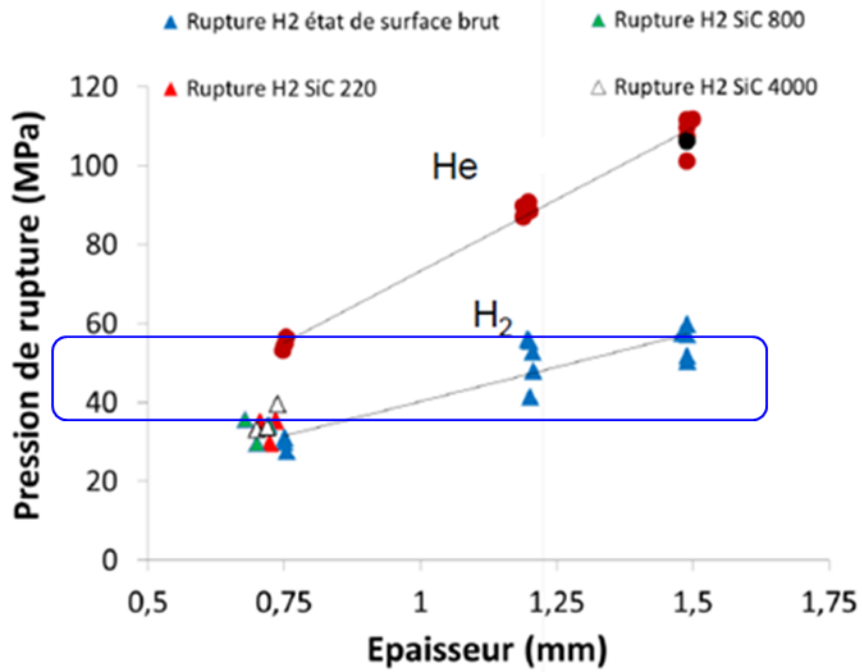
[1] Masanobu Kubota, Yutaro Adach, Yuki Shiraishi, Ryosuke Komoda, Jader Furtado, and Yoshiyuki Kondo, Effect of Hydrogen and Addition of Oxygen on Fretting Fatigue Properties, Proceedings of 2012 Hydrogen Conference, Moran, Wyoming, USA, September, 2014.
[2] Ryosuke Komoda, Masanobu Kubota and Jader Furtado, Effect of Addition of Oxygen and Water Vapor on Fretting Fatigue Properties in Hydrogen, International Journal of Hydrogen Energy (In press), 2015.

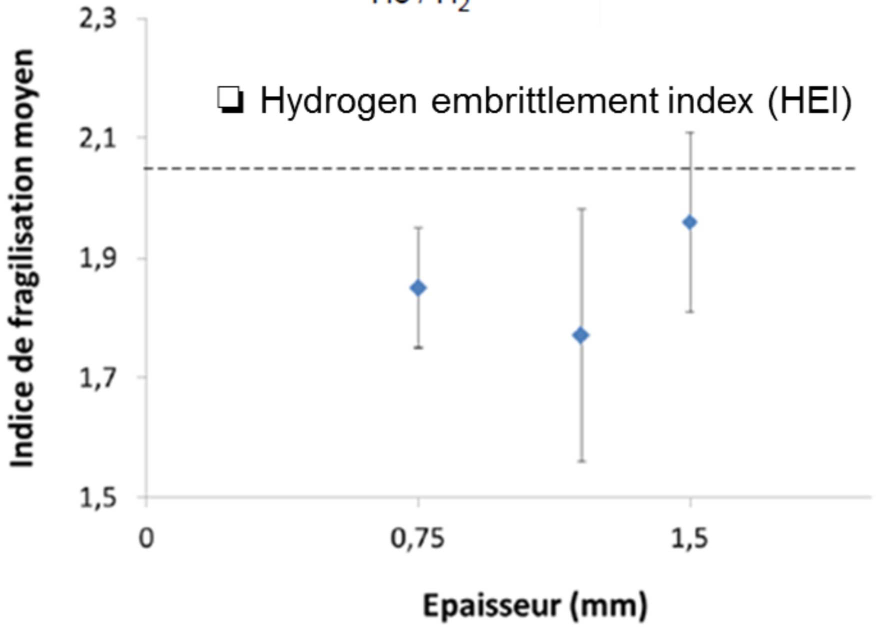
Materials
Hydrogen effect on Materials. Metals.
Progress

Evaluation of disc test (static) for high pressure applications (method A ISO 11114-4) [1]

- Thickness effect on rupture pressure and embrittling index under H2 → testing pressure extended to 50 MPa with the same testing set-up (method A ISO 11114-4)







[1] Ardon K. Analyse expérimentale et numérique de l'essai de disque de rupture: Cas de l'acier AISI 4135 testé sous hydrogène gazeux. Laboratoire des Sciences des Procédés et des Matériaux, CNRS, (UPR 3407), vol. PhD. Villetaneuse, France: Université Paris 13, Sorbonne Paris Cité, 2015. p.212.

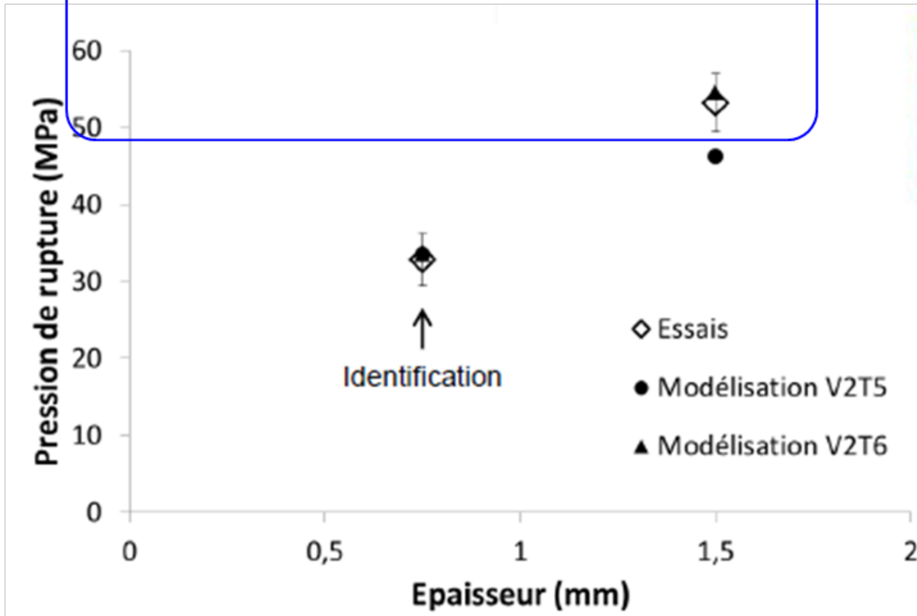
Materials
Hydrogen effect on Materials. Metals.
Progress

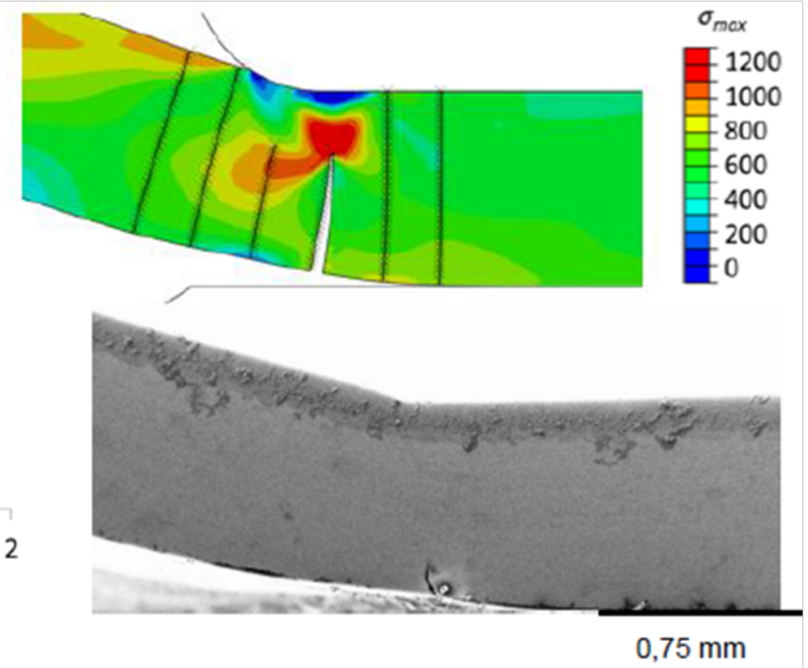
Evaluation of disc test (static) for high pressure applications (method A ISO 11114-4) [1]

- ○ Modelling

❑ Disc-rupture test results

❑ FE modelling and cracking site identification





[1] Ardon K. Analyse expérimentale et numérique de l'essai de disque de rupture: Cas de l'acier AISI 4135 testé sous hydrogène gazeux. Laboratoire des Sciences des Procédés et des Matériaux, CNRS, (UPR 3407), vol. PhD. Villetaneuse, France: Université Paris 13, Sorbonne Paris Cité, 2015. p.212.

Materials
Hydrogen effect on Materials. Metals.
New gaps or directions

Focus effort on H_2 enhanced fatigue evaluation: mechanisms under different testing samples and database increase

Continue work to update design rules and test protocols :

- Study fatigue crack initiation stage (short cracks) in terms of mechanism and early propagation rate (due to fast propagation step in hydrogen afterwards)

Continue to study scalability of fatigue testing, taking into account the effect of deep vs shallow cycles, and H_2 accelerating effect for lab (specimen) and full scale test (pressure vessel)

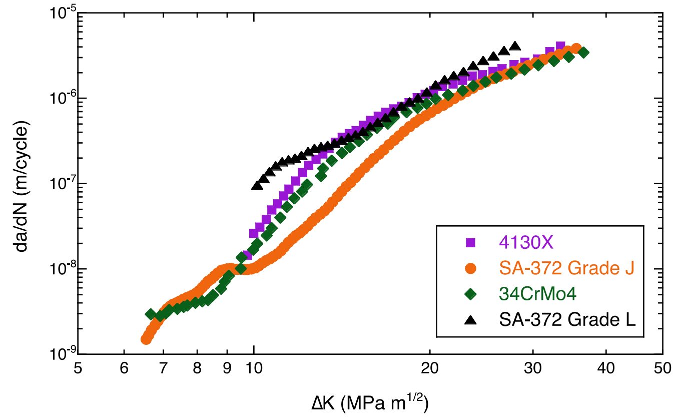
- Based on Modelling & experiments
- Need for simple & reliable methods

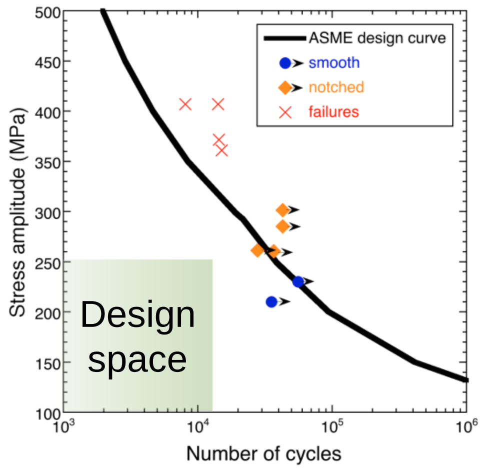
Materials
Hydrogen effect on Materials. Metals.
New gaps or directions

We need to increase our database through experiments and supported by modelling work.
Testing to evaluate fatigue crack initiation under low ΔK requires long time and modelling will help us to define key tests for model validation.
The buffer cycling pattern or conditions in terms of shallow cycles (high R=Pmin/Pmax ratio) or deep cycles (low R ratio) needs to be assessed.
Shallow cycles requires longer testing times and a correlation between shallow and deep cycles requires validation and acceptance at international levels.

Materials
Hydrogen effect on Materials. Metals.
Progress

- Sufficient fatigue crack growth data for ASME SA-372 Grade J pressure vessel steels to enable qualification (ASME KD-10)

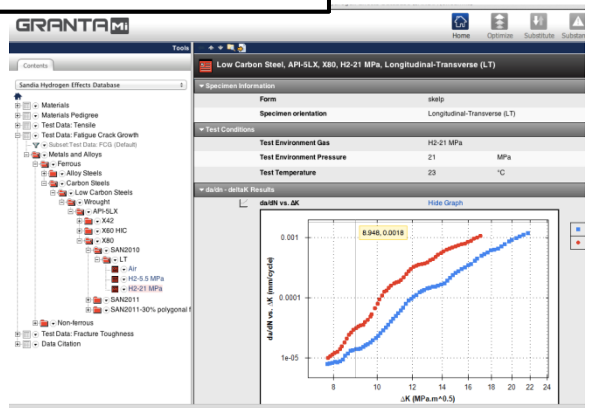




- Full-scale fatigue testing of type 1 pressure vessels with defects demonstrates suitability for low-stress pressure vessel designs

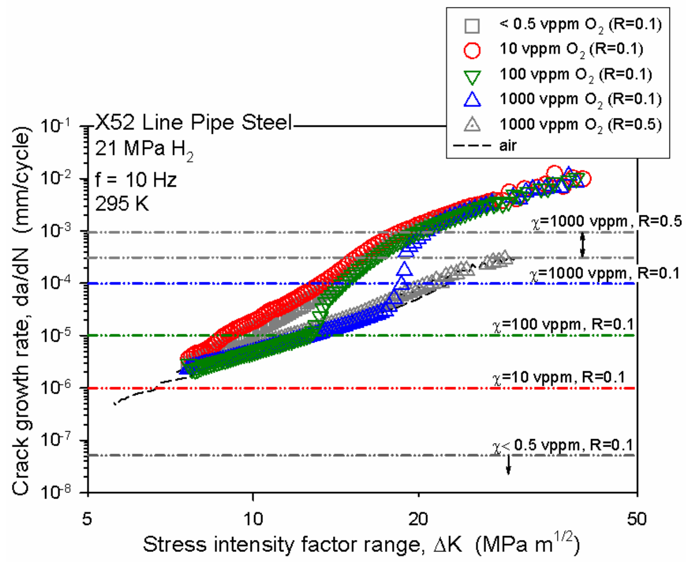
Embrittlement can be managed

- Technical Reference provides a resource (but woefully incomplete)
  - True database in development (using Granta MI)



Materials
Hydrogen effect on Materials. Metals.
Progress

- Initial work on the role of impurities in fatigue crack growth
  - Transferability to real infinite-life systems is unknown (kinetics!)



H2 pressure (MPa)	waveform	Cycles for initiation
100	sinusodial	763
100	sinusodial	860
100	triangular	1017
30	triangular	2589
30	triangular	2764
10	triangular	7136
2	triangular	18292

- Initial work on the methodology to quantify crack initiation and implement in integrity management (Mathryce program)
  - Transferability is significant challenge

Materials
Hydrogen effect on Materials. Metals.
Current activity

International partnership to evaluate high hardenability Ni-Cr-Mo pressure vessel steels

- Fatigue crack growth and fracture (ASME KD-10 design method)
- Industry partners from US, Europe and Japan

Fundamental understanding of surface effects and impurities on hydrogen embrittlement

- Fundamental work in US and Japan

Fatigue-life testing and methodology development

- US, Japan and Germany (national labs and academic institutions)
- Coordination through SAE

H2 compatibility of high-strength pipeline materials & welds

- Also considers role of residual stresses in welded materials and influence on test method

Materials
Hydrogen effect on Materials. Metals.
Gaps / Critical needs

International consensus on metrics for qualification of metals for specific applications

- Onboard vehicles (SAE, UN GTR)
- Fueling stations (storage, compression, components, etc)
- *Acceptance of low-cost materials that are "embrittled" but adequate*

Role of impurities and inhibitors

- Are impurities sufficient to "protect" system under all conditions? (H2/NG)
- Lacking impurities are effects equivalent to pure H2? (H2/synthetic NG)

LH2 storage and distribution

- Industrial technology well-developed (for large capital projects)
- May not be adequate for large-volume commercial sector (stations)

GH2 delivery and transmission

- Integrity of existing pipeline networks for pure hydrogen
- Materials in systems for pure H2 delivered to customer (residential and industrial)

Fatigue performance at low-temperature in high-pressure

- More generally design relevant data

Efficient accelerated test methodologies

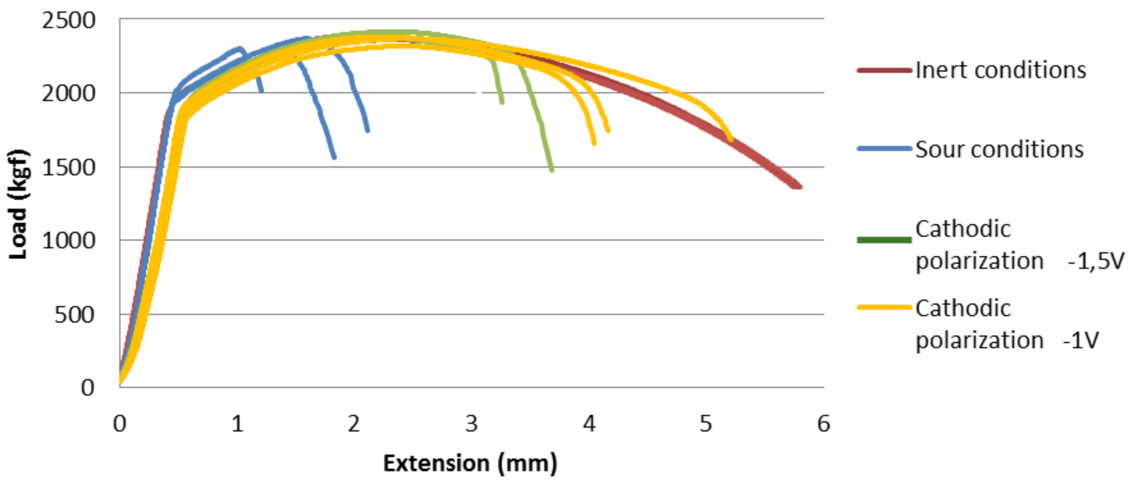
Materials
Hydrogen effect on Materials. Metals.
Progress

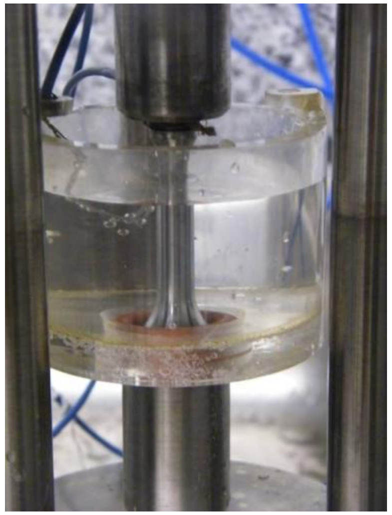
Study of the sensitivity of materials to Hydrogen Assited Stress Cracking by means of the Slow Strain Rate Testing technique (SSRT).

Material: Cr-Mo quenched and tempered low alloy steel.

Testing media: sea water (NACE TM 01 77) and four different conditions:

inert (N_2), two cathodic polarizations (-1 and -1,5V) and H_2S





Materials
Hydrogen effect on Materials. Polymers.

- **JRC**

  1. Type 4 tank liners
  2. Seals and gaskets
  3. Hoses, valves, joints
  4. Other, pipelines,..

- **Air Liquide**

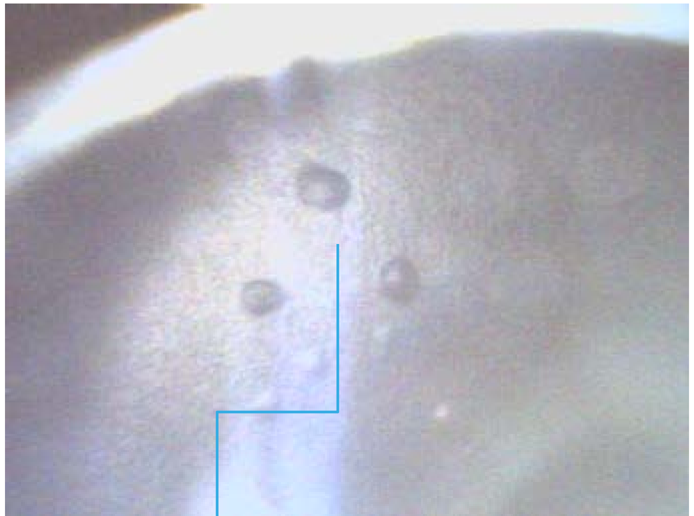
  1. Polymer liner colapse. Colline
  2. Collaboration with DoE funded projects

- **SNL**

Materials
Hydrogen effect on Materials. Polymers. Type 4 tank liners

Made of thermoplastics such as HDPE (high density polyethylene) and PA (polyamide).

Main issues: permeation, blistering, collapse (buckling), effect of low temperatures and effect of high temperatures



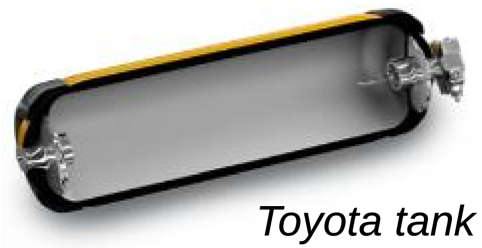
Liner blisters

Liner bucking

Materials

Hydrogen effect on Materials. Polymers. Type 4 tank liners

Progress



Toyota tank

Progress made (materials optimisation)

- **Improved liners**

  Toyota reported that PA 6* resin delivers better performance for hydrogen permeation (an order of magnitude superior to HDPE) and excellent mechanical performance, in terms of durability to withstand sudden changes in tank temperature from filling and discharging hydrogen, and shock resistance in extreme cold environment.

- **Limitation of operating conditions** (depressurisation rate) to avoid liner buckling / improved liner configuration designs as part of tanks installation/operation guidelines.

*PA 6 is a polyamide (nylon). The number describes the type and number of polymer chains in its chemical structure. The most commonly used polyamides for liners are PA 6 and PA 11. PA 6 has good mechanical properties (ductility, long term heat resistance, impact resistance at low temperature, creep resistance…) for H2 tank liner and low costs. On the other hand PA 11 is used in pipeline liners.

Materials

Hydrogen effect on Materials. Polymers. Type 4 tank liners

Working topics

On-going/near term research

- DoE project at SNNL/PNNL: Evaluation of liners (HDPE) physical properties & mechanical performance changes under High Pressure H2 exposure (static) – At near term exposure to large pressure gradient experiments (35-100-35 MPa) with/without temperature cycling (-45 – 85 °C)

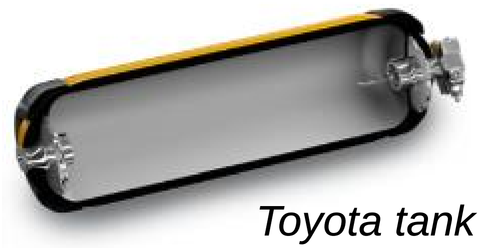
- DoE project at SNNL/PNNL: Studies on permeability, diffusivity and solubility of H2 in liners materials to understand the conditions for blister formation.

- Hexagon-Lincoln/HSECOE (DoE project ST047): Improved composite vessel for H2 cryo-compressed storage– with cryoseals for 100 bar and 80-160 K. Type 3 & type 4

Materials

Hydrogen effect on Materials. Polymers. Type 4 tank liners

New gaps or directions



Toyota tank

Knowledge gap

- **Blistering/swelling behaviour:** it has been shown that it is caused by hydrogen sorption and forms during (rapid) decompression. It depends on temperature.
- **Permeation under high pressures**: the gap in knowledge of hydrogen transport at high pressure has been partially filled in. Permeation evolution as function of pressure cycling and temperature measured, lifetime prediction possible (for how many materials?)
- **Mechanical performance with hydrogen:** HDPE elasticity modulus yield strength lower considerably under high pressure H2, while ductility increase. The evolution is not permanent, the material recovers the original characteristics after the end of exposure.

Materials

Hydrogen effect on Materials. Polymers. Type 4 tank liners

New gaps or directions

Needs/gaps for future research

☞High temperatures in tanks, the question is if polymer liners can resist higher temperatures while still performing at -40 °C (liner mechanical properties and permeability)

☞Effect of temperature excursions: exceeding the range -40 to 85 °C a number of time during tank lifetime does affect performance at end-of life?

☞Resistance to operational and accidental thermal shocks (e.g hot tank fill with very cold H2 or very fast emptied; cold tank filled in a very short time/with non-precooled H2)

☞Non-destructive methods for liners evaluation: blisters / cracks / buckling and criteria for "healthy" tank

Materials

Hydrogen effect on Materials. Polymers. Seals and gaskets

Mainly made of elastomers the main issues are material degradation/decomposition, friction/wear and pressure, thermal & chemical effects in presence of hydrogen

Subjected to 84 MPa & quick depressurisation

Before

After 3207 cycles
2-41-2 MPa H2

After test campaign with pre-cooled hydrogen

Materials

Hydrogen effect on Materials. Polymers. Seals and gaskets

Working topics / New gaps

On going/ short term research

- SNNL: Characterisation tests for polymers for gaskets, seals & O-rings (H_2 permeability, diffusivity and solubility), exposure tests to high pressure hydrogen. In 2017 evaluation of combined effects of pressure and temperature -40 °C & 100 °C is foreseen
- EPDM (ethylene propylene diene monomer) under investigation for gaskets
- Explosive decompression of O-rings and gaskets: Definition of the limits of decompression rates at certain P to minimise the damage to the system

Needs/gaps for future research

- Performance at low temperatures (loss of ductility): e.g refuelling at -40 °C but operating temperature ranges from ambient to less than 85 °C
- Thermal Fatigue / Hydrogen effect => Long term exposure & Degradation at end-of-life Methods for degradation and ageing assessment and end-of-life criteria
- Interaction of tanks materials and robust sealing concepts

Materials

Hydrogen effect on Materials. Polymers. Hoses, valves, joints

Working topics

On going/ short term research. Hoses

- NREL: Dispenser Hose Reliability Improvement (DoE project PD100). Physical & Chemical analysis of HRS hoses before and after accelerated life testing (cycling under mechanical, pressure, temperature and time stresses). First results indicates that after a number of chilled cycles (1856) leaks develop at both hose ends (dispenser and nozzle). Leaks appears to occur upon hose depresurisation, after hose gets very cold and it persists over several consecutive cycles. No clear pattern is identified yet. The amount of H2 released is small & the hose is not considered failed.
- This research continues the intention is to test additional hoses from different manufacturers
- Nanosonic, INC: Cryogenically flexible, low permeability H2 delivery hose (DoE Project PD101). Develop a flexible hose for H70 service reliable at -50 °C and 875 bar; optimised ruggedness, cost and safety, 70 fills/day and >2 years. Prototype is tested & ongoing qualification test with OEM dispenser/nozzle for safety and environmental durability. Manufacturing issue with bonding/crimping the hose and fitting solved using a innovative SiC ceramer adhesive. Deployment expected in 2017.

Materials

Hydrogen effect on Materials. Polymers. Hoses, valves, joints

Working topics

On going/ short term research.

- ORNL: Neutron scattering & X-ray scattering to investigate molecular dynamics of H2 solvated polymers and to identify microscopic properties critical to polymer performance/prediction of failure mode

Materials

Hydrogen effect on Materials. Polymers. Hoses, valves, joints

New gaps

Needs/ gaps for future research

- Harmonised methods for measuring properties of polymers at high P in H2 environment + metrics to quantify the effect of H2
- Variability in material properties depending on the supplier (for a given polymer)
- Transferability of results from laboratory scale samples to components
- Fit for purpose tests (both on samples and components): requires knowledge of operating and accidental conditions, desirable feedback from e.g. OEMs, hydrogen refuelling infrastructure operators…
- Valves, joints

Understanding the effect of long term exposures to H_2, in some cases cooled to -40 °C

Methods for degradation and ageing assessment and End-of-life criteria

- Non-metal Pipelines

At near term: add section non-metals suitable for hydrogen in ASME B31 Section 12

Conditions (accidental?) leading to liner buckling in pipelines => NDT evaluation methods

Effects of long term H2 exposure / Effect of thermal shocks (warm/cold environments)?

Materials

Hydrogen effect on Materials. Polymers. Hoses, valves, joints

New gaps or directions

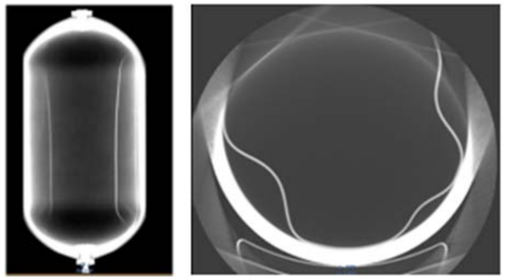
Other items for future research?

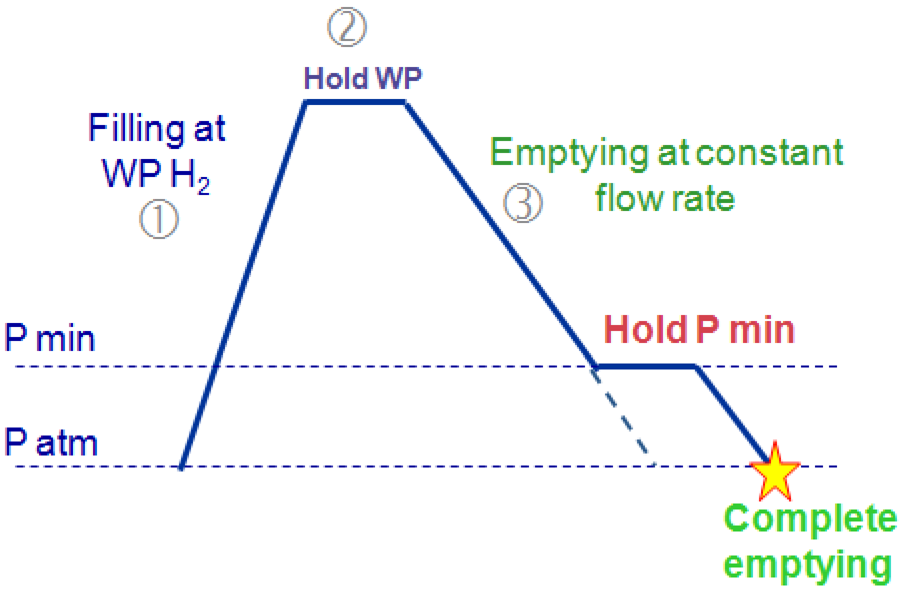
Materials for liquid hydrogen => embrittlement of elastomers at low temperatures

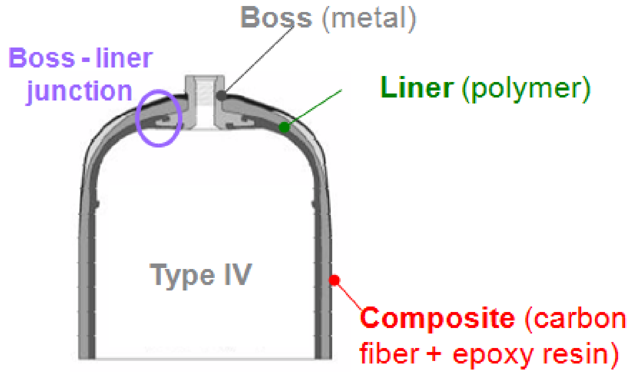
Hydrogen compatibility for materials in appliances operating at low pressure, but subjected to temperature excursions (home refuelling)

Materials
Hydrogen effect on Materials. Polymers. Colline

Study of the liner collapse of polymer liner composite pressure vessels







① Permeation rate increases with pressure

② Permeation equilibrates, with hydrogen present in porosities and absorbed in the materials

③ Trapped hydrogen desorbing, liner and composite having different permeability

⇩

Liner detaching from the composite

Materials
Hydrogen effect on Materials. Polymers. Colline

<u>Colline</u> ANR French funded project Air Liquide - CNRS (2014-2017) on polymer liner collapse during hydrogen emptying/defuelling

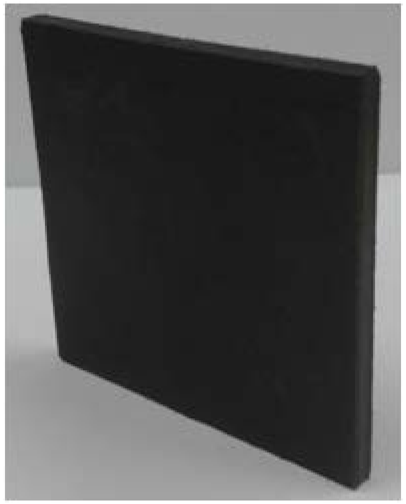
Study of initiation on specimens and pressure vessels (mostly testing)

Study of the effect further pressure cycles on pressure vessels and using modelling

Recommendations on materials, testing and operations (RPV, max flow rate, etc) of polymer liner composite pressure vessels

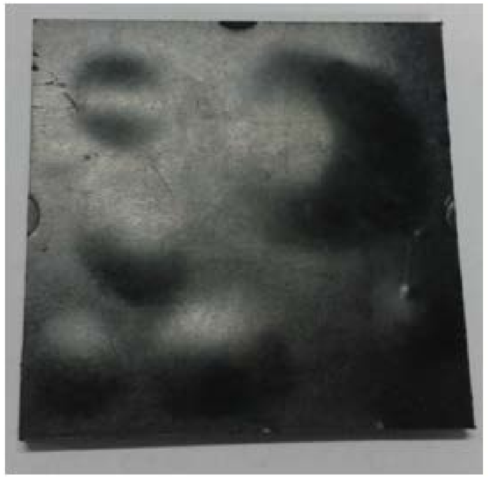
Tensile test equipment with a 350 bar H_2 chamber, temperature regulation 25 - 65°C

Bilayer specimen liner composite



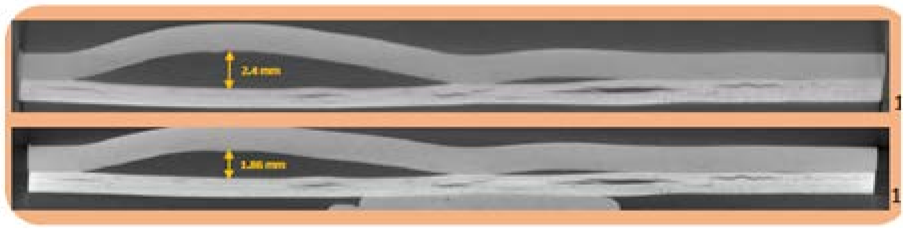
Materials
Hydrogen effect on Materials. Polymers. Colline

Pmax 350 bar
T 65°C
Flow 50 bar/min



Pmax 175 bar
T 65°C
Flow 50 bar/min

1 h after test – max gap 2.4 mm



1 month after test – max gap 1.86 mm

Initiation mechanism related to gas solubility - desorption phenomena in the materials during emptying

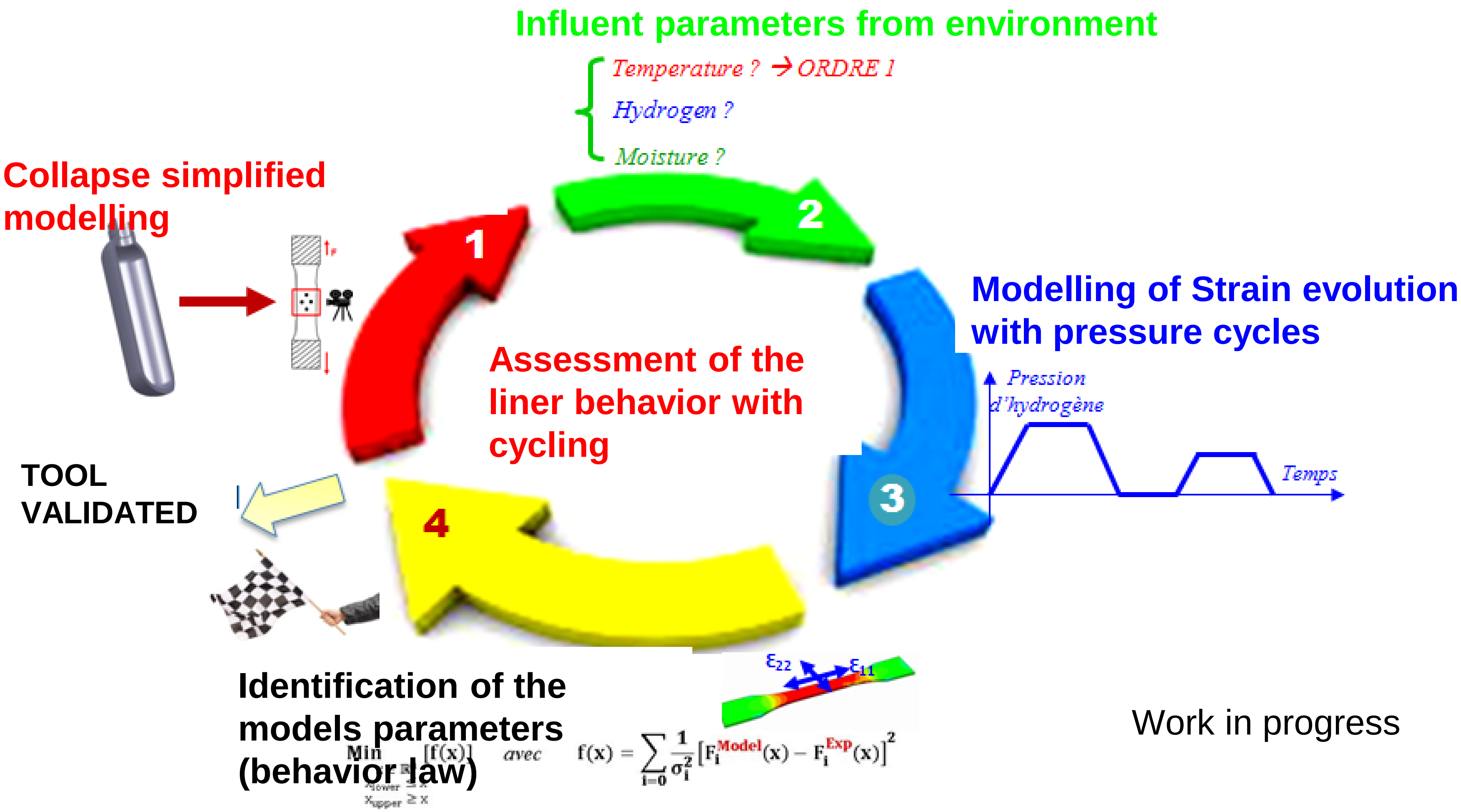
Depends thus on materials, max and min pressure, temperature and materials permeability

Impact of liner mechanical properties not studied

Some effect of mechanical load on the geometry of the collapse

Materials
Hydrogen effect on Materials. Polymers. Colline

Methodology for study of pressure cycles on liner with collapse



Work in progress

Materials
Hydrogen effect on Materials. Polymers.
Working topics / New gaps

Interaction with DOE funded project (PNNL/Ford/Sandia/ORNL) on Compatibility of Polymeric Materials Used in the Hydrogen Infrastructure

- Aim: define test protocol to select and qualify polymer materials => See Sandia presentation ?
- AL Input on materials used and operating conditions for definition of mechanical loads and testing

Need for ageing models for materials and structure considering mechanical and environmental loads (including liner collapse) to define lifetime of the components and optimize design and testing protocols

- Fitting
- Liner (including welds if any)
- Bonding materials
- Composite structure

Materials

Hydrogen effect on Materials. Polymers.

Working topics

Review of literature and analysis of gaps: SAND2013-8904

- R.R. Barth et al. "Polymers for Hydrogen Infrastructure and Vehicle Fuel Systems," October 2013, Sandia National Laboratories.

Initial observations of damage accumulation in elastomers

- Results not generalized
- Standardized methods still missing
- Selection criteria not developed

Examples
- Koga et al. Intern Autmotive Eng 2 (2011) 123
- Yamabe et al. Eng Failure Anal (2013)
- Yamabe et al. Intern J Hydrogen Energy 34 (2009) 1977
- Jaravel et al. Polym Testing 30 (2011) 811

Initial measurements of mechanical properties in low-pressure H2 environments

- High-pressure response unknown
- No standardization of methods

Examples:
- Castagnet et al. Exp Mech 52 (2011) 229
- Castagnet et al. Intern J Pressure Vessels Piping 89 (2012) 203
- Klopffer et al. Defect Diff Forum 325 (2012) 407

Materials
Hydrogen effect on Materials. Polymers.
Gaps / Critical needs

Understanding of failure modes

- Tribology
- Rapid gas decompression
- Damage accumulation and degradation due to pressure cycling
- Temperature effects in high-pressure systems

Relevant methods to evaluate hydrogen performance

- Metrics for evaluation: What is good enough?

Influence of hydrogen on fracture and fatigue

Efficient accelerated test methodologies

Session 8: Materials

Chair: Iñaki Azkarate; Panelists: Beatriz Acosta (JRC), Mathilde Weber (Air Liquide), Laurent Briotet (CEA), Chris San Marchi (SNNL)

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Thank you very much for your attention !!!!!