

Testing Hydrogen admixture for Gas Applications

Welcome to the 2nd THyGA Workshop

Presenters:	Lisa Blanchard, Laurent Briottet, CEA, Fr
Host and Moderation:	Johannes Schaffert, Gas- und Wärme-Institut Essen (GWI),
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The THyGA project has received funding from the Fuel Cells and Hydrogen Joint Undertaking under grant agreement No. 874983. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe research.



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ORGANIZATION OF TODAY'S WORKSHOP – CODE OF CONDUCT

- We are glad you could make it!
- Please keep your microphones muted when not needed
- Audience video should also be disabled during the presentations
- Calling-in per telephone is possible the number can be found in your calendar invitation





ORGANIZATION OF TODAY'S WORKSHOP – CODE OF CONDUCT

- This workshop will be interactive. Nevertheless, with 300 registered participants we need to streamline
 - the agenda and focus discussion.
- Therefore, **please feel free to make a posting in the chat any time** if you have a question and/or use the raise-hand tool, if you see it (not always the case)
- Johannes will read the questions or announce your questions and unmute your microphones so you can speak to each other in person.
- Optional (if chat function does not work): You can **send questions** to <u>schaffert@gwi-essen.de</u> and

patrick.milin@engie.com at any time.

• All questions that remain open today will not be forgotten, promised. THY_WP2_020_Presentation Webinar Materials







ORGANIZATION OF TODAY'S WORKSHOP – AGENDA

Agenda of today's THyGA Webinar on Hydrogen & Material Science	l 0h	
Welcome to the meeting, rules for today, number and spectrum of attendees	Johannes Schaffert	
Introduction by the THyGA Project	Johannes Schaffert	
Hydrogen embrittlement	Lisa Blanchard and Laurent Briottet	
Discussion on embrittlement	Johannes, Lisa, Laurent	
Hydrogen permeation and leakage	Lisa Blanchard and Laurent Briottet	
Presentation of the WP3 test on leakage	Lisa Blanchard and Laurent Briottet	
Questions and open Discussion	Johannes, Lisa, Laurent	
End of meeting	l 2h	







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THE THYGA PROJECT & CONSORTIUM

The project has been created by 9 partners to answer the Horizon 2020 call FCH-04-3-2019.

- * "Research is required to identify and verify the impacts of ... H2NG blends on the combustion characteristics ... of appliances together with the potential impacts on appliance safety, efficiency, lifetime and environmental performance (e.g. NOx emissions)."
- Low, medium and high hydrogen concentrations in natural gas should be investigated:
 - Low = <10% Vol.
 - Medium = 10-30% Vol.
 - High = 30-60% Vol.

The Project focus lies on testing. Up to 100 tests are planned, including various heating, cooking, catering, CHP, FC, ... appliances.

Project period: 2020-2022 project budget: 2,5M€. visit: <u>https://thyga-project.eu/</u>







OBJECTIVES OF THE PROJECT

- THyGA project (Testing Hydrogen Admixtures for Gas Appliances) sets out to develop and communicate a detailed understanding of the technical impact of blends of natural gas and hydrogen on end use applications, specifically in the domestic and commercial sector.
 - Screening and segmenting the portfolio of appliance technologies in the domestic and commercial sectors and assessing the impact of hydrogen admixtures.
 - Testing up to 100 commercial and residential gas appliances to provide a generic protocol that can be adapted for virtually any appliance.
- To go further, the project consortium will identify and recommend appropriate codes and standards that should be modified or adapted to answer the needs, and develop a strategy for addressing the challenges for new and existing appliances.
 - Developing a validated certification protocol for different levels of H2 in natural gas
 - Making recommendations for manufacturers, decision makers and end-users along the gas value chain for appliance design, manufacture and certification.





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STRUCTURE AND INTERACTION WITH ADVISORY PANEL





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TODAY'S WORKSHOP – SPECTRUM OF PARTICIPANTS



Distribution of registrations according to the type of organisation





Non-combustion related impact of introducing hydrogen admixture in gas network distribution

Webinar on material science, 26th of October 2020 L. Blanchard, L. Briottet

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OUTLINE

• HYDROGEN EMBRITTLEMENT (HE)

- Context and definition of HE
- Observation of HE (at room temperature and in gas environment) and mechanisms
- Materials evaluation toward HE
- Influencing factors
- Impact of HE on the materials used in gas distribution network
- Standards
- NON-EMBRITTLEMENT CONCERNS
 - Chemical compatibility
 - Permeation and leakage
- LEAKAGE TEST







BACKGROUND – DISTINCTION BETWEEN CORROSION AND HE

CORROSION *≠* **HYDROGEN EMBRITTLEMENT**

• Corrosion definition by the ISO 8044 :

"Physicochemical interaction between a metallic material and its environment that results in changes in the properties of the metal, and that may lead to significant impairment of the function of the metal, the environment or the technical system, of which these form a part."

- Can apply to:
 - Metallic materials;
 - Concrete;
 - Minerals;
 - Polymers













BACKGROUND – DISTINCTION BETWEEN CORROSION AND HE

Wet corrosion

- Electrochemical attack occuring in the presence of a fluid containing oxygen
- Electrochemical mechanism
- Metal dissolution and formation of deposit

Dry corrosion

- Chemical attack occuring in the presence of a reactif
- Absorption mechanism
- Metal dissolution and formation of a superficial oxyde layer

• Example of ferrous corrosion in aqueous medium:



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BACKGROUND – DISTINCTION BETWEEN CORROSION AND HE

CORROSION CRACKING

Corrosion of gas pipeline welds due to welding imperfections.

HYDROGEN CRACKING

Cracking in duplex stainless steel shielded metal arc (SMA) weld due to hydrogen ingress during the process



A Guide to Failure Analysis for the Oil and Gas Industry, Alber Sadek, 2016

Hydrogen Cracking of Ferritic-Austenitic Stainless Steel Weld Metal, A. J. Leonard, 2000





CONTEXT

San Francisco–Oakland Bay Bridge, 2013





SFOBB rods failure, H.E. Townsend et al., 2015

Chemical plant, 2001



Failure of piping by hydrogen attack, TG. Kim, 2002

Oil field, 2006



Garn west failure, S. Huizinga et al., 2006







HYDROGEN EMBRITTLEMENT - MECHANISMS









HIGH TEMPERATURE (400-500°C) HIGH PRESSURE (~100 BAR)

• High temperature hydrogen attack (HTHA)



API RP 941, 2016

Hydrogen reacts with the carbon in solution:

External decarburization

- Decrease in hardness and increase in ductility;
- \rightarrow Minor impact

Internal decarburization

- Formation of methane
- Accumulation in the microstructure
- Development of voids coalescence and substantial deterioration of mechanical properties

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 \rightarrow Failure







HYDROGEN INDUCED CRACKING – H₂S ENVIRONMENT

• HIC: Hydrogen Induced Cracking



whatispiping.com/sour-experiences-HIC



Detailed mechanism of surface blistering in sour environment, Crolet, 2001

Surface blistering

- I. In sour environment: H_2S facilitates hydrogen to get into the material.
- Hydrogen adsorbed into the material is recombined as H₂ gas.
- 3. Pressure accumulates in the microstructure and inducing the formation of blisters.









FORMATION OF HYDRIDES INDUCING EMBRITTLEMENT (ZR AND TI ALLOYS)

Formation of hydrides inducing embrittlement in zirconium alloy



- I. Failure of the blister in the direction normal to the applied stress
- 2. Crack propagation through the base material embrittled by the hydrides formation. Crack propagates at the interface ZrH_x / Zr
- Ductile propagation through the base metal non embrittled by hydrides formation

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HYDROGEN EMBRITTLEMENT - ~RT AND GASEOUS ENVIRONMENT

Evolution with charging conditions: time, temperature, Crystallographic environment, etc. Susceptible microstructure, grain size, Hydrogen microstructure phases, dislocation density, precipitates, etc. **Mechanical** HE failure stress or strain

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BACKGROUND - HYDROGEN ENTRY IN THE METAL







BACKGROUND - HYDROGEN TRANSPORT IN THE METAL LATTICE

1. Hydrogen diffusion and solubility



- Austenitic : ~10⁻¹⁶ m².s⁻¹ Hydrogen solubility in steels :
 - Ferritic : ~ 0,5 molH₂.m⁻³.MPa^{-1/2} Austenitic : ~ 70 molH₂.m⁻³.MPa^{-1/2}

2. Hydrogen trapping in the metal lattice



3. Influence of stress and strain

Hydrostatic stress gradient \rightarrow induces hydrogen diffusion

Hydrostatic stress \rightarrow induces higher hydrogen solubility

Dislocation \rightarrow H trapping and diffusion





BACKGROUND – DUCTILITY IN METAL

Tensile curves: comparison brittle to ductile materials









BACKGROUND – DISLOCATIONS

Dislocations:

Linear defect enabling plastic deformation in metals



J. McNally, 2013

Edge dislocation in a crystal lattice

Observation of the 3D core structure of an edge dislocation at atomic resolution.



View of an edge dislocation using transmission electronic microscope (TEM). 23 26/10/2020







HYDROGEN EMBRITTLEMENT - MECHANISMS









HYDROGEN ENHANCED DECOHESION (HEDE)

 Hydrogen weakens the atomic cohesive bond between atoms, grain boundaries, matrix/precipitates interfaces.



Hydrogen embrittlement (HE) phenomena and mechanisms, Lynch, 2011

Intergranular or cleavage features on the fracture faces



Tensile mechanical properties and fracture behaviors of nickel-based superalloy 718 in the presence of hydrogen, X. Li, 2018.







INTERACTION HYDROGEN PLASTICITY – MACROSCOPICAL OBSERVATION

Fracture surfaces of Steel-B550



Ni-Cr-Mo <steel





Identical stress concentration applied







Nagao, 2014





INTERACTION HYDROGEN PLASTICITY - DISLOCATIONS

Interaction hydrogen/dislocations

Hydrogen promotes dislocation shielding

TEM imaging



Ferreira et al., 1998 Accumulation of dislocations create high stresses in the microstructure Hydrogen promotes dislocation emission







INTERACTION HYDROGEN PLASTICITY - EMBRITTLEMENT MECHANISMS

Hydrogen Enhanced Localised Plasticity (HELP)



Adsorption Induced Dislocations Emission (AIDE) Surface mechanism Stress axis Plastic zone Small, shallow dimples Interatomic bond weakened by 0 adsorption **Voids** Alternate -slip Crack Macroscopic fracture plane Dislocation emission from crack tip

Hydrogen embrittlement (HE) phenomena and mechanisms, Lynch, 2011



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THY_WP2_020_Presentation Webinar Materials Mechanisms based on hydrogen promoting local plasticity





INTERACTION HYDROGEN VACANCIES

Hydrogen-enhanced stress-induced vacancy (HESIV)



- Tensile test in H₂ and air
- ➔ Embrittlement



→ Embrittlement





- H₂ desorption
- Decrease of vacancy density
- → No embrittlement





Nano-scale dimples on hydrogen

embrittled quasi-brittle facets

HYDROGEN EMBRITTLEMENT - DEFINITION

Hydrogen-enhanced stress-induced vacancy (HESIV)



Nagumo, 2004; Naguma, 2008; Takai 2008

X60 tested in 21 MPa H_2

(a) (b) 200nm

Neeraj, 2012



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EVALUATION OF HE- MECHANICAL TESTING







EVALUATION OF HE- MECHANICAL TESTING

CEA/LITEN equipment

In-situ testing in hydrogen gas environment









MECHANICAL TESTING – EXAMPLE/OBSERVATION

Tensile test

Evidence of X80 embrittlement in 30 MPa H_2



Fatigue crack growth rate







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INFLUENCING FACTORS - MICROSTRUCTURE



Ex: Steels

Most susceptible microstructure	Order of increasing the resistance to HE			Less susceptible microstructure	References		
Martensitic materials		Ferritic	materials	Stable austenitic alloys	(Barthelemy, 2006)		
Ferritic/perl	tic Tempered bainite			l bainite	(Brass et al., 2000)		
Martensite	Bainite	Perlite	Tempered bainite	Tempered martensite	("FD E29-649 Bouteilles à gaz transportables - fragilisation par l'hydrogène des aciers," 2016)		



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HYDROGEN EMBRITTLEMENT – HYDROGEN PARTIAL PRESSURE

Fatigue crack growth testing



- ΔK^T from which fatigue crack growth rate increases
- ΔK^T is pressure dependent
- Same increase in fatigue crack growth rate at 0,7 MPa and 90 MPa.





INFLUENCING FACTORS - IMPURITIES







INFLUENCING FACTORS – LOADING RATE

Tensile testing of a X80 at different loading rates







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INFLUENCING FACTORS – TESTING CONDITIONS

Comparison of HE susceptibility measured using different mechanical tests on a X80







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Carbon steels Stainless steels Copper and copper alloys Aluminium alloy Brass







Nguyen et al., 2020

P_{H2} = 100 bar

HYDROGEN EMBRITTLEMENT – CARBON STEELS

Tensile properties







Fractography of a X70 pipeline steel tested



100 bar gas mixture with 1% $H_2 \rightarrow P_{H2} = 1$ bar





No HE observed at P_H = 1bar HE observed at P_H = 100bar: No necking, development of secondary cracks, quasi-cleavage





HYDROGEN EMBRITTLEMENT – CARBON STEELS







STAINLESS STEELS

Tensile testing on ferritic and austenitic stainless steels in He and H₂ gas environments (0,4 \times 10⁻⁴ mm.s⁻¹)







ALUMINIUM ALLOYS

Formation of stable oxide film in all reducing environments

 \rightarrow impedes hydrogen ingress



FCC microstructure



 \rightarrow low hydrogen diffusion properties

Al alloys in dry hydrogen are not susceptible to HE



Hydrogen embrittlement and aging of natural gas distribution network in the presence of hydrogen



• Objective: To evaluate the effect of hydrogen embrittlement on five alloys identified according to their propensity to be present on the gas network and the potentiality of their mechanical properties to be affected by hydrogen.

• Description of the test:

- Embrittlement testing
- Among the five alloys
 - Brass CW617N and brass CW614N
 - Zamak (pressure regulator)
 - Copper (tubing)
- Three gas blends were used for the test: natural gas (NG), NG+6%vol.H₂, NG+ 20%vol.H₂

Conclusions:

- Brass CW617N, brass CW614N, copper and zamak : no significant susceptibility to HE
- Zamak, copper and brass CW617N : no hydrogen susceptibility
- Brass CW614N: low hydrogen effect, but stayed non-significant and do not constitute a risk in terms of security in the service conditions.







STANDARDS

Existing standards for hydrogen storage and transport (high pressure):

ISO 11114-4: "Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 4: Tests methods for selecting metallic materials resistant to hydrogen embrittlement"

ASME B31.12-2019: "Hydrogen piping and pipelines"

ASME BPVC: Section VIII – "Rules for construction of pressure vessels division 3 –Alternative rules for construction of high pressure vessels"







HYDROGEN EMBRITTLEMENT – CONCLUSION AND QUESTIONS

- HE is a concerned for many industries;
- Different proposed mechanisms but no link between mechanism and components design-life prediction;
- Susceptibility of main alloys used in gas distribution network:

Carbon steels > Ferritic stainless steels > Austenitic stainless steel ~ Aluminium ~ Brass ~ Copper

 In the context of gas distribution network: P_{H2} < 1.03 bar; limited mechanical loading, limited stress concentration ?

 \rightarrow No high HE susceptibility is expected in those conditions







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CHEMICAL COMPATIBILITY

 Corrosion or selective dissolution at room temperature in dry hydrogen gas environment.

In dry hydrogen environment, hydrogen is not a concern for corrosion of metallic materials

 \rightarrow Focus on polymers (Polyethylen (PE))



충 THyGA



CHEMICAL COMPATIBILITY OF PE

Testing of resistance to hydrogen exposure of PE







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HYDROGEN PERMEATION AND LEAKAGE









HYDROGEN PERMEATION IN PE – NATURALHY PROJECT

• NATURALHY : Blending Hydrogen into Natural Gas Pipeline Networks: A Review of Key Issues

Permeation on main materials used on the US gas network distribution (~4 bar) and service (~200mbar)



Increase of gas loss with the hydrogen content Incubation time for methane to permeate – not for hydrogen Economical point of view H gas losses at low operating pressure not problem





HYDROGEN LEAKAGE PROPERTIES

- Hydrogen leakage is a concern
- Leak characteristics of hydrogen, methane and propane (Leader et al., 2001).

	Hydrogen, H ₂	Methane, CH_4	Propane,	Helium, He
			C_3H_8	
Density, Kg,m ⁻³	0.0838	0.6512	1.870	0.1634
Viscosity, g.cm ⁻¹ .s ^{-1×} 10 ⁻⁵	8.9	11.7	8.0	19.6
Relative flow rates,				
volumetric:				I
Subsonic flow	1	0.77	1.11	I
• Laminar flow	1	0.35	0.21	
• Turbulent flow	1	0.34	0.20	
Sonic flow				





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TIGHTNESS TEST OF GAS NETWORK DISTRIBUTION COMPONENTS

 Objective: To evaluate the tightness of the components located on the gas line within the building from Germany, Denmark, Belgium and France to the mixture CH₄ + H₂.







TIGHTNESS TEST OF GAS NETWORK DISTRIBUTION COMPONENTS

Static testing
Measure of the pressure
drop within closed lines
(several months)Dynamic testing
Measure of the gas flow in each
line alternatively to impose a
constant pressure
(several hours)

- Test parameters:
 - Gas mixture: 40%CH₄ + 60%H₂
 - Temperature: RT
 - Pressure: 30 mbar

DGC (Danish gas technology centre)

• BDR Therma group

Components sourcing

- Electrolux
- GWI (Gas- und Wärme-Institut Essen) (Germany)
- DVGW.EBI (German Technical and Scientific Association for Gas and Water)





TIGHTNESS TEST PRESENTATION OF THE LINES AND COMPONENTS

Electrolux and DGC line



Materials in the Electrolux gas circuit: Aluminium (burner, pipe, pressure regulator) Brass (gas thermostat) Aluminized iron (manifold) Materials in the DGC: Iron, copper, brass

GWI, DVGW.EBI and DGC line



Materials in the line: Steel, stainless steel, copper, brass



THY WP2 020 Presentation Webinar Materials





TIGHTNESS TEST OF GAS NETWORK DISTRIBUTION COMPONENTS

GWI, DVGW.EBI and DGC lines





Gas meters tubing and valves made of steel, copper, brass and stainless steel.





TIGHTNESS TEST OF GAS NETWORK DISTRIBUTION COMPONENTS

GWI, DVGW.EBI and DGC lines



Gas meter, tubing, pressure valves made of steel, copper, brass and stainless steel.







QUESTIONS

Thank you for your attention

Link to THyGA project:

https://thyga-project.eu/

Link to the state of the art on the "Non-combustion impact of hydrogen admixture material compatibility":

https://thyga-project.eu/deliverable-d2-4-non-combustionrelated-impact-of-hydrogen-admixture-material-compatibility/

