Compatibility of hydrogen with different materials

European Hydrogen Train the Trainer Programme for Responders

Compatibility of hydrogen with different materials

Content

1. Interaction of hydrogen with metals
2. Interaction of hydrogen with polymeric materials
3. Limitation of hydrogen permeation
4. A new standard for polymer hydrogen application compatibility

Objectives of the lecture

1. Explain the mechanisms of hydrogen interaction with metallic and polymeric materials;
2. Establish effect of hydrogen embrittlement on safety of hydrogen storage systems;
3. Define the hydrogen permeation phenomena;
4. Point out the safe permeation rate for hydrogen storages on-board of passenger cars and buses.

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Interaction of hydrogen with metals (1/3)

- Hydrogen has: 1) a very small sized atoms and 2) a low viscosity.
- Hydrogen can be easily absorbed by different materials (including those used for hydrogen storage). This, in turn, leads to the degradation of their mechanical properties, which may result in **unwanted hydrogen leaks** and **structural failures**.
- The correct selection of suitable materials for hydrogen storage is a crucial safety measure.
- Affect piping, walls of storage vessels, filling connectors, valves, fittings, etc.
- Silent movie showing hydrogen bubbles emerging from steel, at defects and other locations (Delft University, 1950).

https://www.youtube.com/watch?v=bv9ApdzalHM

Source: Google free images

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Interaction of hydrogen with metals (2/3)

The compatibility of hydrogen with metallic materials is affected by chemical interactions and physical effects, which include:

- **Corrosion** (dry corrosion (at high temperatures, **hydrogen attack**), wet corrosion (most common, caused by moisture), corrosion caused by impurities in a gas

Hydrogen itself is a non-corrosive gas.

- **Hydrogen Embrittlement (HE)**
- **Embrittlement at low temperatures (‘cold embrittlement’)**
- **Violent reactions** (e.g. ignition)

Source: Barthelemy H. Hydrogen storage technologies, compatibility of materials with hydrogen, a presentation to Joint European Summer School for fuel cell and hydrogen technology, August 2011, Viterbo, Italy.

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Interaction of hydrogen with metals (3/3)

Video of hydrogen crack arrest

(SINTEF experiment)

https://www.youtube.com/watch?v=Pu34W8jmkss&list=PLlphoM9ggM3Rf-Npmdq0S3WrCSpx0U4SL&index=6&t=2s

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Hydrogen Embrittlement (HE)

- Embrittlement is a **loss of a metal ductility**. Due to hydrogen ad-/absorption a material becomes brittle and can fracture.
- **HE** (an entry of hydrogen into a material) occurs at lower temperatures (nearly ambient).
- HE negatively affects three basic systems: production, transportation/storage and use.
- At higher temperatures (above 200 °C) **hydrogen attack** takes place.
- Hydrogen can be either in atomic or in molecular form.
- No clear mechanism of HE. Several mechanisms suggested:

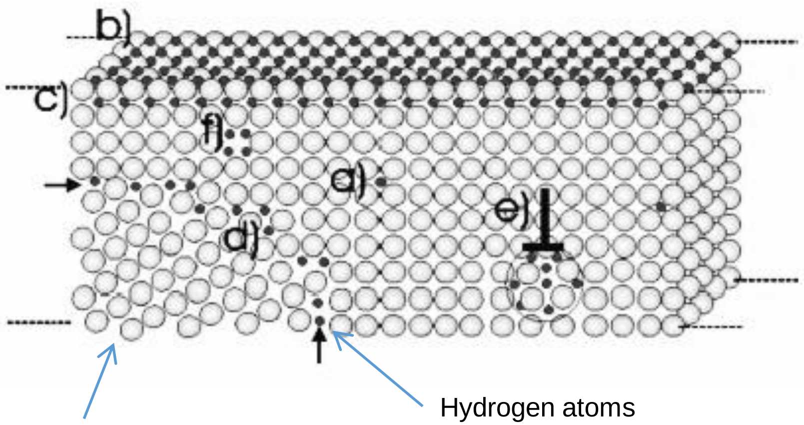
a) Formation of hydrogen solution in a metal lattice

b) Hydrogen adsorption on the surface and c) on the subsurface of a metal

d, e, f) Hydrogen accumulation in structure defects

(grain boundaries, vacancies dislocations)

Hydrogen can form compounds within a metal lattice (metal hydrides or methane).



Source: Barnoush, A (2011) Hydrogen embrittlement.

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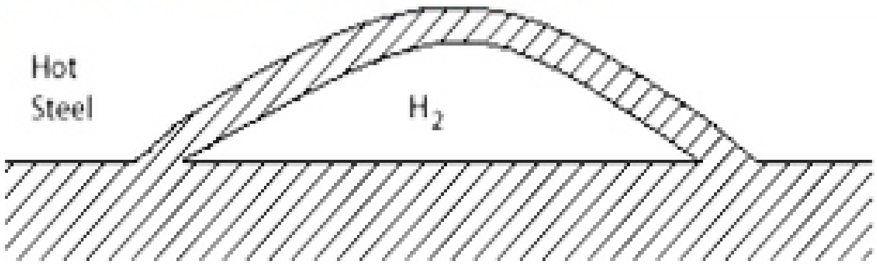
Sources and categories of HE

High strength steels are susceptible to HE the most.

Hydrogen can enter a material via several routes:

- **Manufacturing** operations (welding, electroplating, pickling etc).
- As a **by-product** of wet **corrosion** of a metal.
- **Surface treatment** (e.g. cathode protection of a metal against corrosion).
- **Adsorption** on a metal surface.



There are three categories of HE

- **Environmental HE** - occurs when the material is being subjected to a hydrogen atmosphere, e.g. in storage tanks.
- **Internal Reversible HE** - occurs when hydrogen enters the metal during its processing; may lead to the structural failure of a material that never has been exposed to hydrogen before.
- **Hydrogen reaction embrittlement** - occurs at higher temperatures when hydrogen chemically reacts with a constituent of the metal to form a new microstructural element or phase such as a hydride or to generate gas bubbles also known as **blistering**.

Source: Barthelemy, H (2006). Compatibility of metallic materials with hydrogen. Teaching Materials of the 1st European Summer School on Hydrogen Safety, 15-24 August 2006.

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Factors affecting HE in steels

Material:

- Microstructure
- Chemical composition
- Heat treatment and mechanical properties
- Welding
- Cold working (strain hardening)
- Non-metallic inclusions

Environment:

- Hydrogen purity
- Hydrogen partial pressure
- Temperature
- Stress and deformation
- Exposure time

Design and surface conditions:

- Stress level
- Stress concentration
- Surface defects

Source: Barthelemy, H (2006). Compatibility of metallic materials with hydrogen. Teaching Materials of the 1st European Summer School on Hydrogen Safety, 15-24 August 2006.

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Suitability of materials for hydrogen service

- A material **should not be used** unless data are available to prove that it is suitable for the planned service conditions. In case of any doubt the material can be subjected to HE susceptibility testing (e.g. ISO 11114-4).
- *ISO/TR 15916:2015 Basic considerations for the safety of hydrogen systems.*
- **Metals** that **can be used without any precautions**: brass and copper alloys (e.g. beryllium copper CuBe); aluminium and its alloys.
- **Materials highly sensitive to HE**: nickel and high content nickel alloys; titanium and its alloys
- Many materials can be safely used under controlled conditions (e.g. limited stress, absence of surface defects, etc.)

Source: Barthelemy, H (2006). Compatibility of metallic materials with hydrogen. Teaching Materials of the 1st European Summer School on Hydrogen Safety, 15-24 August 2006.

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Incidents and accidents caused by HE

- The material affected by HE may fail prematurely and sometimes in catastrophic way when stress is applied.

Some examples:

- Pipe failure at a hydrogen production plant (steam methane reformer;1996; rupture occurred in a 24-inch diameter stainless steel pipe; escaping high-pressure gas caused an energy release and subsequent fire; fire was extinguished within 10 minutes by fire-fighters; cause: cracking of the pipe due to corrosion caused by alkaline - KOH) [1]).
- Explosion of hydrogen gas caused by the breakage of external gas duct at space rocket testing facility (laboratory, May 16, 1991; Kakuda, Miyagi, Japan; cause: nickel alloy of the exhaust gas duct welding became brittle after 132 tests of high-pressure and high-temperature hydrogen gas combustion over 5 years [2]).

Sources:
[1] H2 Incidents, H2 Incident Reporting and Lessons Learned (database). Available from: http://www.h2incidents.org/ [2] JST Failure Knowledge database (http://www.sozogaku.com/fkd/en/cfen/CC1200114.html)

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Mitigation of HE and hydrogen attack

- Reduction of corrosion rate (use of inhibitors or surface coatings).
- Dry conditions during welding process.
- Use of a pure gas.
- Use of a clean steel (deoxidized).
- Selection of materials (addition of: vanadium V to ferritic steels; rare earth elements to ferritic steels; nickel, carbon and manganese to austenitic steels).
- Alloying with chromium, molybdenum, tungsten.
- Heat treatment (baking) to remove absorbed hydrogen.
- Minimization of residual stresses.

Source: Barthelemy, H (2006). Compatibility of metallic materials with hydrogen. Teaching Materials of the 1st European Summer School on Hydrogen Safety, 15-24 August 2006.

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Polymers and hydrogen

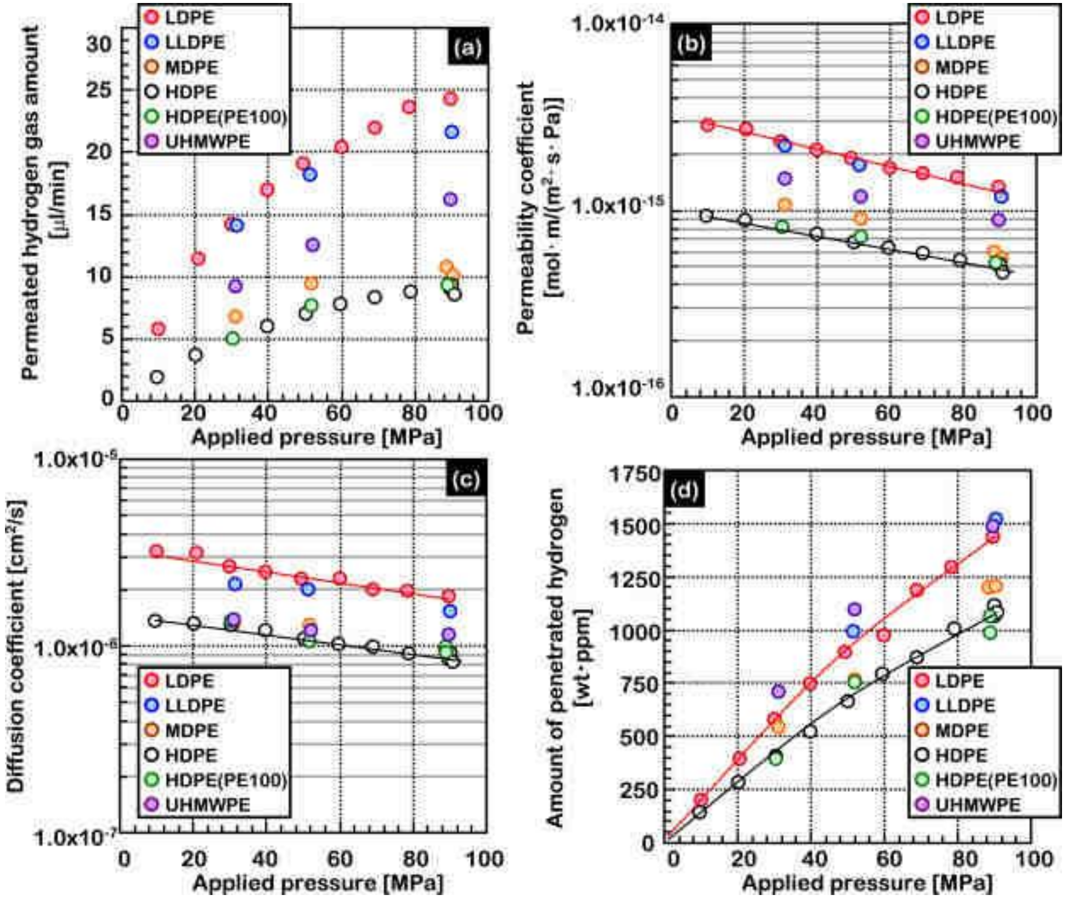
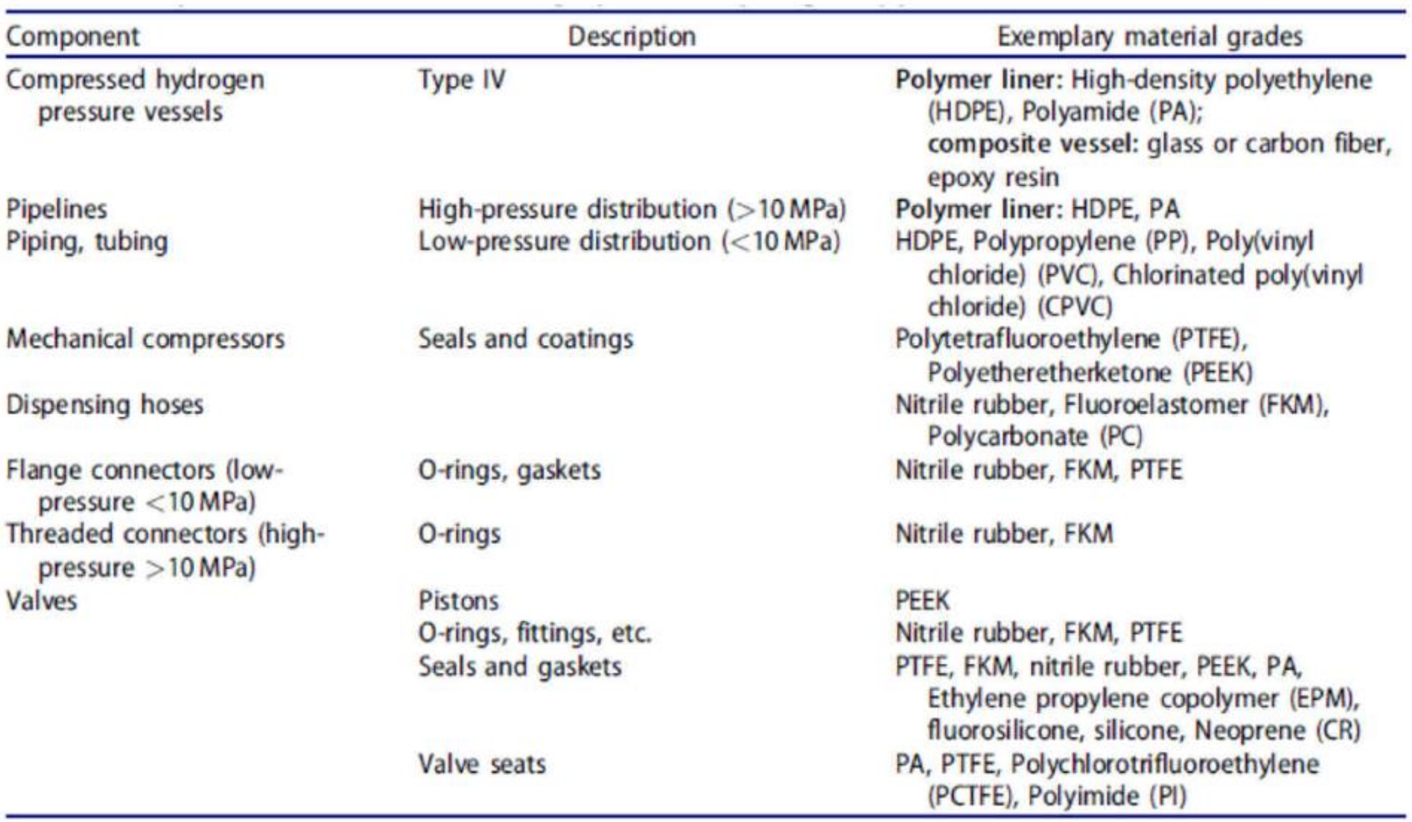


Figure: Comparaison of PE liner materials/H_2 (Type IV Tank)

Source: J.S. Jang & N.K. Chung, Pressure Vessels and Piping Conf. (2020)

Table : Example of Polymers for exposure to H_2 at high pressure



Component	Description	Exemplary material grades
Compressed hydrogen pressure vessels	Type IV	**Polymer liner:** High-density polyethylene (HDPE), Polyamide (PA); **composite vessel:** glass or carbon fiber, epoxy resin
Pipelines	High-pressure distribution (>10 MPa)	**Polymer liner:** HDPE, PA
Piping, tubing	Low-pressure distribution (<10 MPa)	HDPE, Polypropylene (PP), Poly(vinyl chloride) (PVC), Chlorinated poly(vinyl chloride) (CPVC)
Mechanical compressors	Seals and coatings	Polytetrafluoroethylene (PTFE), Polyetheretherketone (PEEK)
Dispensing hoses		Nitrile rubber, Fluoroelastomer (FKM), Polycarbonate (PC)
Flange connectors (low-pressure <10 MPa)	O-rings, gaskets	Nitrile rubber, FKM, PTFE
Threaded connectors (high-pressure >10 MPa)	O-rings	Nitrile rubber, FKM
Valves	Pistons	PEEK
	O-rings, fittings, etc.	Nitrile rubber, FKM, PTFE
	Seals and gaskets	PTFE, FKM, nitrile rubber, PEEK, PA, Ethylene propylene copolymer (EPM), fluorosilicone, silicone, Neoprene (CR)
	Valve seats	PA, PTFE, Polychlorotrifluoroethylene (PCTFE), Polyimide (PI)

H2@Scale program of the U.S. Department of Energy (DOE) Fuel Cell Technologies Office

Source: W. Balasooriya et al., Polym. Reviews (2021), N. Menan et al., Proc. ASME (2016), R.R. Barth et al., Sandia Nat. Lab. (2013)

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Interaction of hydrogen with polymeric materials

- Polymeric liners for type IV tanks.
- PEMFC systems (Gasket failure in a PEMFC – see Husar et al. J Power Sources, 2007, p. 85-91).
- Swelling of polymers as a result of gas (or liquid) absorption; lead to change of an object dimensions (e.g. O-rings); hardness and strength are reduced; cracking may occur.
- ‘Blistering’ effects.
- Presence of impurities in the gas, which are not compatible with polymeric materials.
- In case of the fire polymeric materials ignite relatively easy; materials degrade and mechanical strength significantly reduces and this may lead to rupture.
- Type III and IV tanks without protections (TPRD) cannot withstand fire for longer than 12 minutes.
- **Permeation of hydrogen** through polymers is common.

Source: Husar, A, Serra, M, Kunusch, C. Journal of Power Sources, 2007, p. 85-91.

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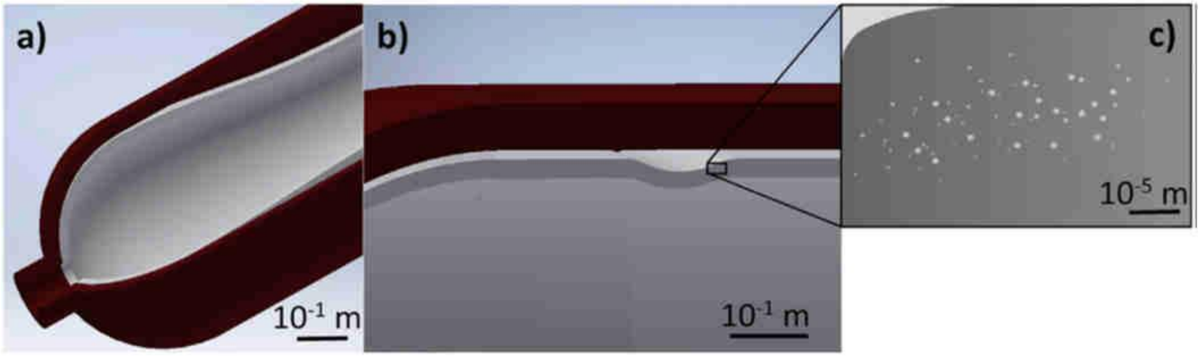
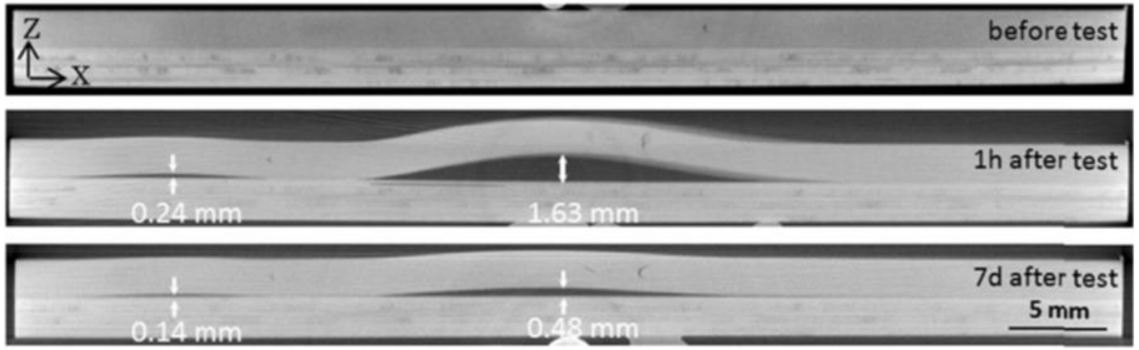
Composite liner degrdation

- ***Liner and liner/composite interface behaviors in tank structure under use conditions***

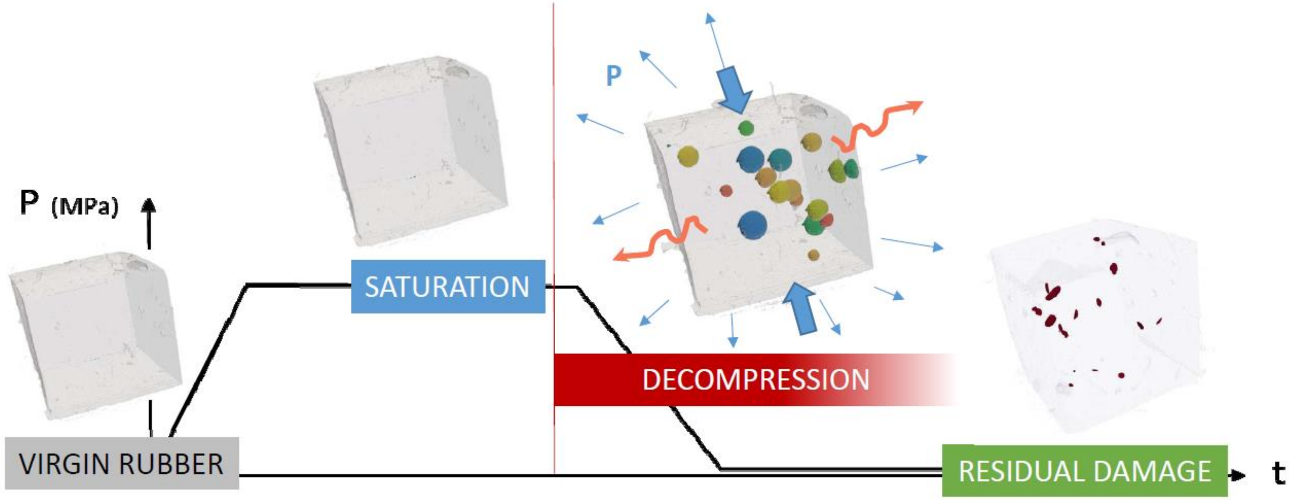


M. Melnichuk et al., Intern. J. Hydrogen Energy (2020)



J. Pepin et al., Intern. J. Hydrogen Energy (2018)

- ***Rubber: blistering with H_2***



Source: S. Castagnet et al., Polymeris H2 day (2021)

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Permeation of hydrogen

- Hydrogen has the smallest size of atoms/molecules and is characterised by the highest diffusivity.
- **Permeation** is a movement of particles (atoms, molecules or ions) through or into a permeable substance. A diffusion of hydrogen occurs "through the walls or interstices of a container vessel, piping or interface material" [SAE J2578, 2009]. For cGH_2 system it results in a slow release of hydrogen.
- Hydrogen permeates: metals in atomic form, polymeric materials – in molecular form.
- Permeation is negligible for storage containers with metallic liners (types I, II, and III) and may pose a **safety issue** for vessels with **polymeric liners** (type IV **and V**).
- **Aluminium** has a low permeability **2.84×10^{-27}** mol/s/m/MPa$^{1/2}$ (Korinko et al., 2001), while a **polymer** (e.g. Noryl) has a permeability of **5.55×10^{-15}** mol/s/m/MPa$^{1/2}$ (Stodilka et al., 2000), i.e. 12 orders of magnitude higher.

Sources: Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II. Available from: www.bookboon.com, free download e-book

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Permeation rate

Permeation rate of hydrogen through a particular material (J in mol/s/m^2) depends on: the material nature, temperature (T in K), reservoir pressure (p_r in MPa) and the reservoir wall thickness (l in m)

$$J = P_0 \exp(-E_0 / RT) \frac{\sqrt{p_r}}{l}$$

Parameters dependent of the nature of the material:
P_0 - pre-exponential factor (mol/s/m/MPa$^{1/2}$);
E_0 - activation energy (J/mol)

The higher the storage pressure the higher is the permeation rate.

The permeation from on-board hydrogen storage is a safety issue for enclosures (example: a FC vehicle parked in a garage). Hydrogen can accumulate over time, producing a flammable mixture with air. As a result of permeation in sealed enclosures without ventilation, the lower flammability limit (LFL) of 4 vol. % of hydrogen in air can be reached within a long period of time.

Three main phenomena will affect the dispersion of permeated hydrogen: **buoyancy, diffusion, and ventilation**.

Sources:
Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II. Available from: www.bookboon.com, free download e-book
Adams, P, Bengaouer, A, Cariteau, B, Molkov, V and Venetsanos, AG (2011). Allowable hydrogen permeation rate from road vehicles. International Journal of Hydrogen Energy. Vol. 36, pp. 2742-2749.

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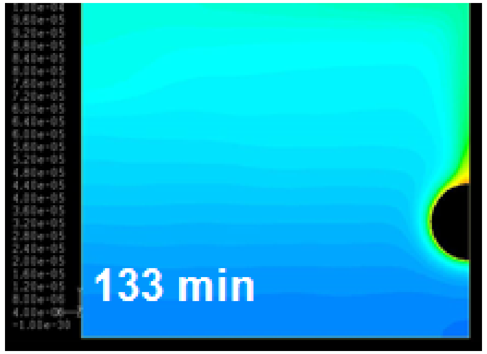
Permeated hydrogen distribution (in an enclosure)

CFD modelling proved that **hydrogen is distributed uniformly in a garage-type enclosure** (the perfect mixing of hydrogen with air).

- Permeation rate J=1.14 NmL/hr/L of tank volume (which is below the allowable by the European Law (Commission Regulation, 2010) permeation rate limit of **6 NmL/hr/L** (at 20 ^{o}C).
- Typical garage size: $L \times W \times H$=5×3×2.2 m (V=33 m^3); still air.
- Storage tank size: L=0.672 m, D=0.505 m, hemisphere at each end (V=0.2 m^3). Floor clearance : 0.5 m.
- Temperature: 298 K.
- Time to reach LFL of 4 vol. % in the **closed** garage with chosen tank and permeation rate will be **240 days**.
- Time for hydrogen diffusion through the height of the garage is **0.7 days**



No areas of 100% hydrogen

Maximum concentration at 133 min: tank top - 8.2×10^{-3} vol.%;

ceiling - 3.5×10^{-3} vol.%.

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The maximum allowable permeation rate

$$Q_{perm}^{max} = \frac{Q_a \cdot C_{\%}}{100 - C_{\%}} \cdot \frac{60 \cdot 10^6}{V \cdot f_a \cdot f_t}$$

Based on perfect mixing equation

where $C_{\%}$ - concentration of hydrogen in air, vol. %;
Q_a and Q_g - air flow and hydrogen gas leakage rate, respectively, m^3/min;
V – water capacity of hydrogen storage, L;
f_a – aging factor, taken to be 2, for unknown aging effects;
f_t – test temperature factor (3.5 at test temperature 20^{o}C, 4.7 – 15^{o}C).

Does dispersion of permeated hydrogen lead to a perfect mixing in a garage? As a result of a permeation-induced leak, hydrogen releases in very small amounts, equally along the surface of a storage vessel.

Sources:
Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II. Available from: www.bookboon.com, free download e-book
Adams, P, Bengaouer, A, Cariteau, B, Molkov, V and Venetsanos, AG (2011). Allowable hydrogen permeation rate from road vehicles. International Journal of Hydrogen Energy. Vol. 36, pp. 2742-2749.

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Regulated permeation rate of hydrogen (1/2)

Minimum Testing Temperature (^oC)	**Maximum allowable permeation rate (mL/hr/L)**	
	Passenger car	City bus
15	**6.0**	**3.7**
20	**8.0**	**5.0**

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Regulated permeation rate of hydrogen (2/2)

The following assumptions have been made (Adams et al., 2011):

- The allowable permeation rate is specified in NmL/hr/L water capacity.
- Permeated hydrogen can be considered to disperse homogeneously.
- Worst-credible natural ventilation rate for a domestic garage is 0.03 ACH (air change per hour) .
- Maximum permitted hydrogen concentration is 1 vol. % , i.e. ¼ of LFL.
- Maximum long term material temperature is 55 ^{o}C.
- New container, with a factor of 2 to convert from the worst case end of life condition.
- For a test conducted at a temperature of 20 ^{o}C, a factor of 3.5 is used to convert from the maximum prolonged material temperature to the test temperature (factor 4.7 at temperature 15 ^{o}C).

With this level of permeation rate the hydrogen dispersion in typical garage is not a problem!

For comparison:

- ❖ Japan Automotive Research Institute: **5** NmL/hr/L (15 ^{o}C).
- ❖ Society of Automotive Engineers J2579, end of life, 55 ^{o}C: **150** NmL/min/vehicle
- ❖ ISO/TS15869:2009 at end of life (20 ^{o}C): **75** NmL/min/container

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New standard for polymer hydrogen application compatibility

- A new standard called “CHMC 2 – Test Methods for Evaluating Material Compatibility in Compressed Hydrogen Applications – Polymers” has been created and published (August 2019) by ANSI / CSA.
- The results of these tests are intended to provide a basic comparison of polymer materials performance in applications utilizing compressed hydrogen.
- The first test is the hydrogen permeation where the issue is to show if the polymer is unable to contain hydrogen through the material.
- The second test is the physical stability to check if the polymer is unable to maintain dimensions (swelling or shrinking) and/or mass.
- The third test is a rapid cycling test where the issue is material degradation (extrusion, cracks or blisters) due to hydrogen exposure.
- the last critical test is material contamination test where the issue is materials release constituents causing impurity of the hydrogen.

Hydrogen storage

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