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BASICS OF HYDROGEN SAFETY FOR FIRST RESPONDERS

Lecture. Safety of hydrogen storage

FCH

FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

Content

- Hydrogen storage options
- Compressed hydrogen storage
  - Types of CGH_2 storage vessels
  - On-board hydrogen storage
  - Pressure relief devices (TPRDs)
  - Consequences of catastrophic failure of high-pressure hydrogen storage
  - Fire resistance rating (FRR) of hydrogen tanks
  - Safety strategies for inherently safer high-pressure hydrogen storage
  - CGH_2 storage: potential hazards and safety issues
- Interaction of hydrogen with different materials (metallic and polymeric)
- Limitation of hydrogen permeation
- Liquefied and cryo-compressed hydrogen storage
- Solid storage of hydrogen

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Objectives of the lecture

- Understand how hydrogen is stored and appreciate the challenges associated with different types of storages;
- Distinguish between various storage options of hydrogen: compressed gas, liquefied and storage in solids;
- Recognise different types of storage vessels currently in use to store compressed hydrogen;
- Name the main components of on-board hydrogen storage;
- Explain the working principle of a PRD fitted onto hydrogen storage and make a comparison with PRDs used in storage of other fuels (CNG, LPG, etc.);
- Learn the main aspects of storage tank testing in general and bonfire test protocols in particular;
- Explain the causes, which may lead to a catastrophic failure of high-pressure hydrogen storage vessel and to describe its consequences;
- Identify factors affecting the fire-resistance rating of hydrogen tanks;
- Define safety strategies for inherently safer compressed hydrogen storage;
- Understand the main safety and technical issues associated with compressed hydrogen storage;
- Explain the mechanisms of hydrogen interaction with metallic and polymeric materials;
- Establish effect of hydrogen embrittlement on safety of hydrogen storage systems;
- Define the hydrogen permeation phenomena;
- Point out the safe permeation rate for hydrogen storages on-board of passenger cars and buses;
- Identify safety concerns associated with liquefied hydrogen storage and storage of hydrogen in various solid materials.

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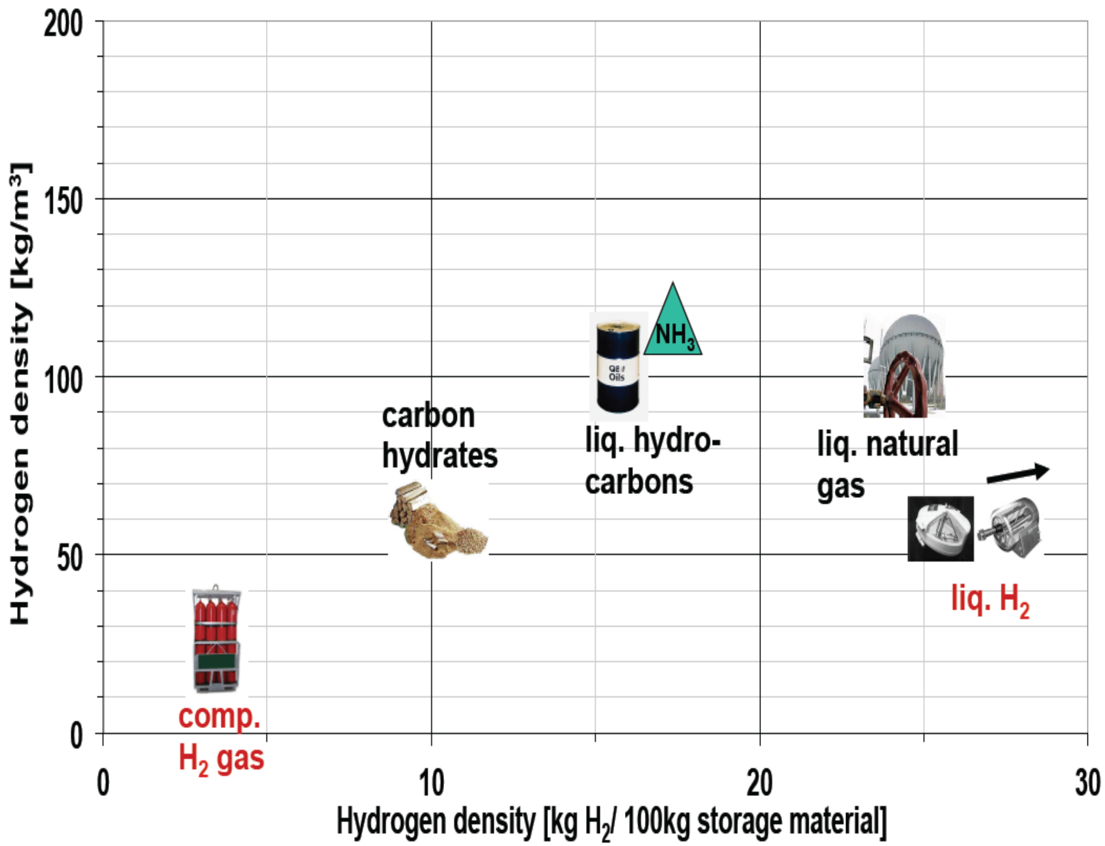
Hydrogen density



Source: Andreas Zuttel, H2FC Technical School, 2014

- Hydrogen is the lightest gas with a low normal density 0.09 g/L (at 288 K and 1 bar)
- Hydrogen has a **high energy content by weight** and **low energy content by volume**
- **Volumetric** and **gravimetric** densities describe hydrogen storage
- Challenge – to develop safe, reliable, compact , light-weight, and cost-effective hydrogen storage technology

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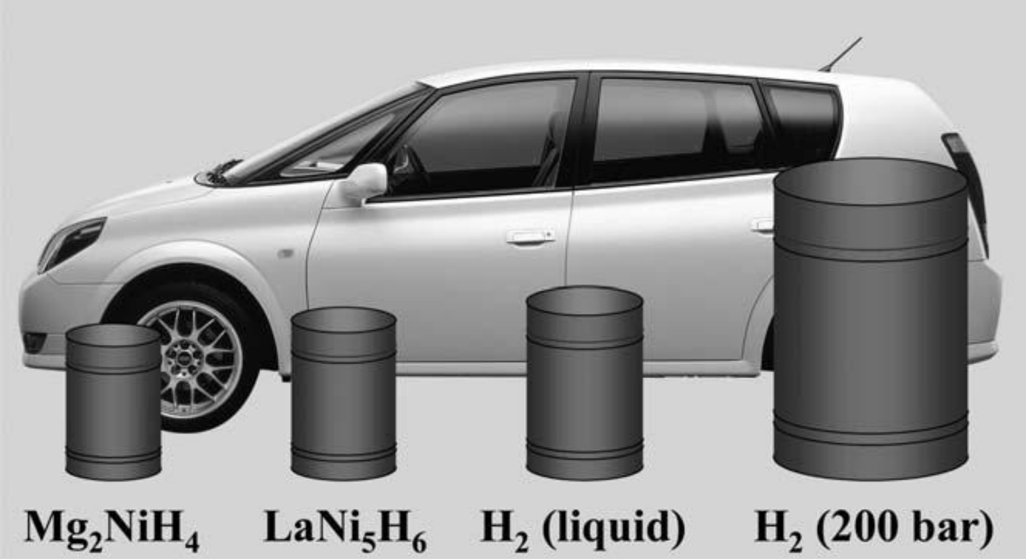
Volumetric and gravimetric capacities



Source: Risø Energy Report 3, 2004

- **Volumetric and gravimetric** capacities/densities are used to describe gas storage approaches. Hydrogen research activities moving towards increasing both capacities.
- **Cryo-compressed storage** of hydrogen is the only technology that is close to revised 2015 DOE targets for volumetric and gravimetric efficiency

Problem: difficult to store large quantities of hydrogen under atmospheric pressure and ambient temperature without taking up significant amount of space (need for large tanks). Critical for use in vehicles: size and weight constraints for achieving sufficient driving range (500+ km). To increase volumetric density **gaseous hydrogen (GH_2) is compressed to high pressures (p).**

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Compressed gaseous (CGH_2) storage

- For industrial or laboratory uses CGH_2 stored in **metal cylinders** at pressures of 15-20 MPa.
- For on-board storage CGH_2 typically compressed to 35 (buses) or 70 MPa (cars).
- The cylinders are designed for maximum working pressure with a minimum wall thickness.
- At refuelling stations CGH_2 pressurised in stages (up to 100 MPa).

Three different pressure levels at refuelling station with gaseous storage: low-pressure storage (**'cigar' tanks**, p=4.5 MPa); medium-pressure storage (**a group of cylinders**, p=20-50 MPa) and high-pressure storage (**composite cylinders**, p=70-100 MPa)
Example: Linde hydrogen refuelling station

Note: pressure, p. Units: MPa or Pa, bar. 1MPa =10 bar; 1MPa = 10^6 Pa

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Nominal Working Pressure

- **Nominal Working Pressure (NWP)** is a gauge pressure, which characterises typical operation of a system. For CGH_2 containers *NWP is a settled pressure of compressed gas in fully filled container at a uniform temperature of 15 °C* (definition).
- On prototype FC vehicles hydrogen is typically stored at NWP of 35 MPa or 70 MPa, with maximum fuelling pressures of 125% of NWP (43.8 MPa or 87.5 MPa, respectively). Burst pressure is 2.25 of NWP.
- Most commonly hydrogen is dispensed at pressures up to 125% of NWP
- During the normal (re-)fuelling process, the pressure inside the container may rise up to 25% above the NWP as adiabatic compression of the gas causes heating within the containers. As the container cools down after refuelling, the pressure drops. By definition, the settled pressure of the system will be equal to the NWP when the container is at 15 °C.

Source: GTR, Proposal for a global technical regulation (gtr) on hydrogen fuelled vehicles, 2013

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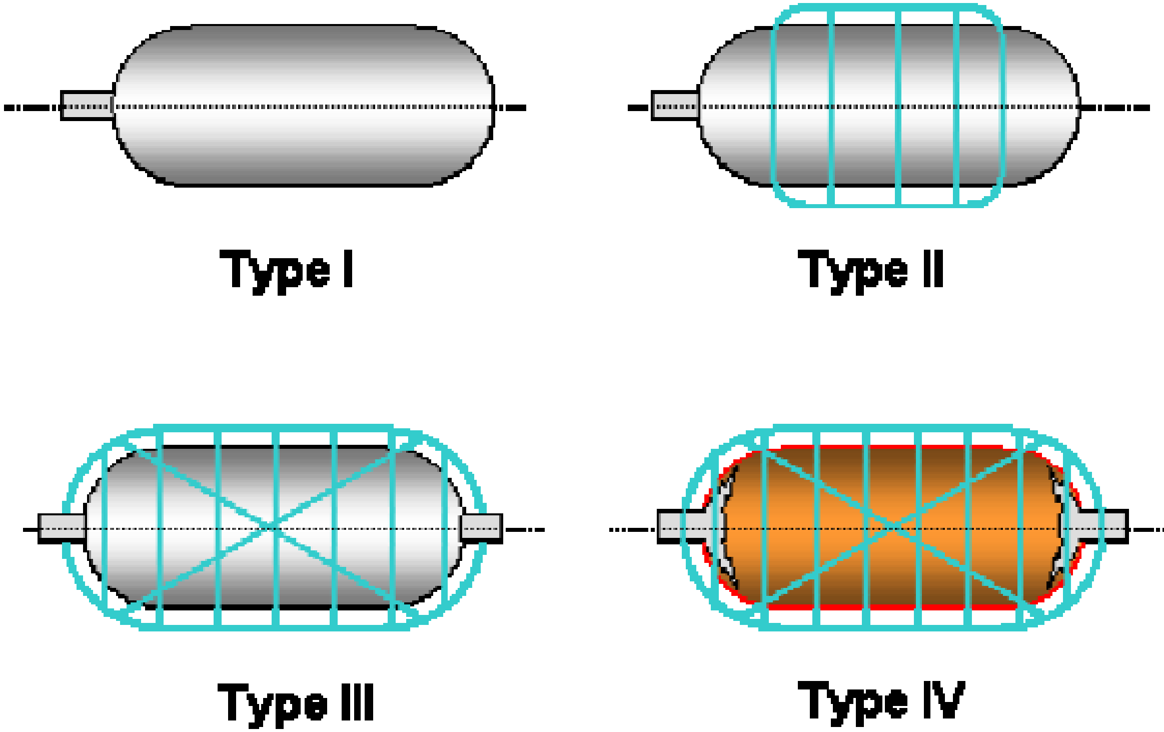
Tanks for CGH_2 storage



4 types of vessels

Type I: made of **metal**

Type II: metallic vessel hoop-wrapped with **fibre resin composite**

Type III: **metallic liners** fully-wrapped with **fibre resin composite**

Type IV: polymeric liner fully wrapped with **fibre resin composite**

Materials for CGH_2 storage vessels

Hydrogen is prone to leakage due the small size of its molecules!

Storage tanks have **at least two layers.** The thickness of the walls depends on the pressure to be applied.

Materials:

- **for liners** - metals (steel or aluminium); plastics (high density polyethylene (HDPE) or polyamide).
- **for wrapping** - carbon reinforced epoxy resin, aramid fibres, etc.
- Metals must <u>not</u> allow hydrogen permeation or be subjected to hydrogen embrittlement (especially when their use involve extensive pressure and temperature cycling)

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Type I and II vessels

Type I vessel

- seamless containers made of steel or aluminium;
- very heavy vessels with thick walls;
- steels susceptible to hydrogen embrittlement;
- designed for pressures not higher than 25MPa;
- used in natural gas vehicles;
- relatively cheap storage option for stationary applications

Type II vessel

- seamless metallic vessels;
- hoop-wrapped with fibre resin;
- very heavy vessels;
- can withstand pressures up to 45-80 MPa;
- used as high pressures buffers at hydrogen filling stations;
- cost is competitive due to a low number of fibres

Not suitable for automotive applications due to the weight and volume constrains

Sources: Barthelemy, H (2007). Teaching materials of the 2nd European Summer School on Hydrogen Safety, 30 July-8 August 2007, Belfast, UK.

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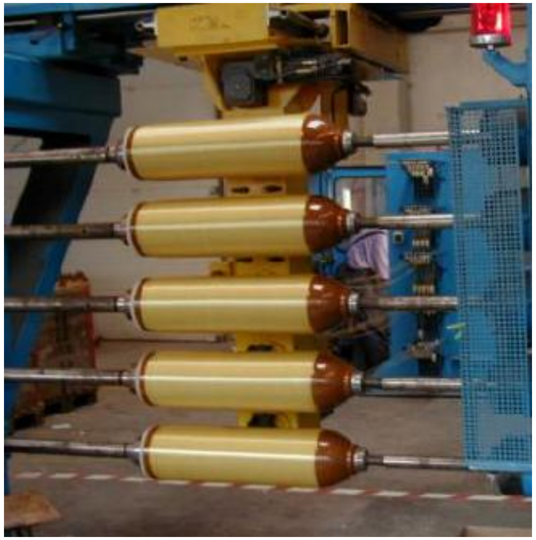
Type III and IV vessels

Containers are lighter in weight; thinner walls compared to type I and II vessels

Type III vessel

- Seamless or welded aluminium liners
- Fully wrapped with fibre resin composite
- Less affected by hydrogen embrittlement

Type IV vessel



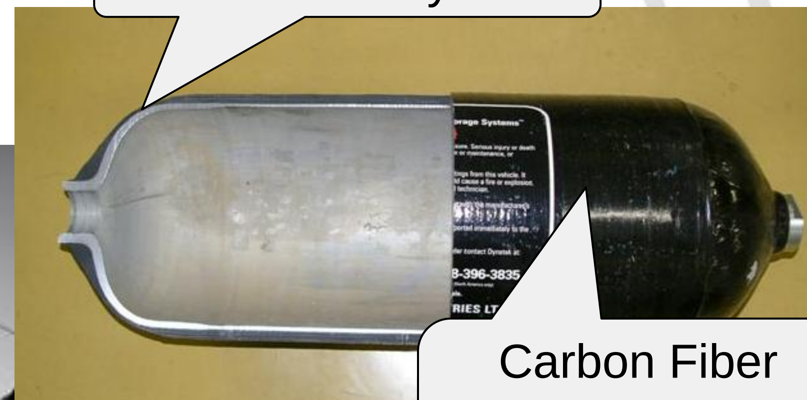
- Non-metallic (plastic) liners wrapped with fibre/epoxy matrix
- Metallic bosses are in place for shut-off valves installation
- Fibre wrapping provides strength required
- Although the cylinders are lighter than all-metal liners they are more expensive
- NWP = 70 MPa
- Disadvantage: hydrogen permeation through the liner

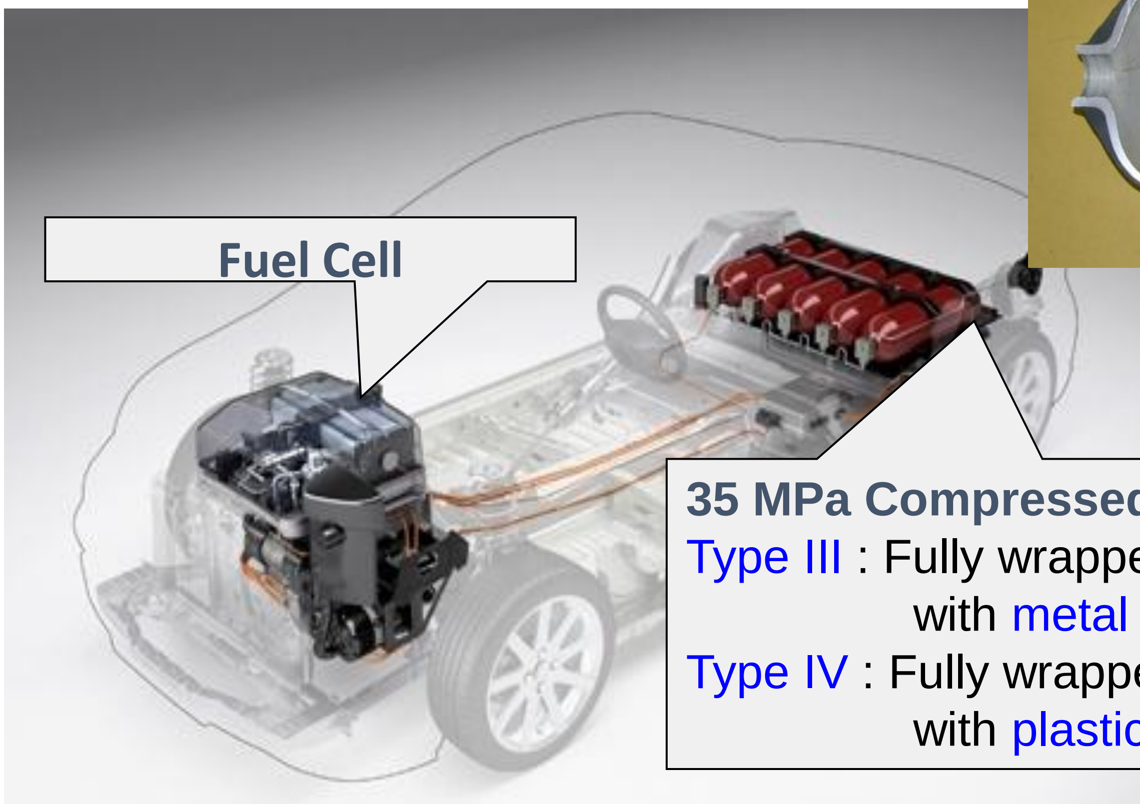
Source: Barthelemy, H (2007). Teaching materials of the 2^{nd} European Summer School on Hydrogen Safety, 30 July-8 August 2007, Belfast, UK.

On-board hydrogen storage

The **key functions:**

- to receive hydrogen during fuelling;
- to contain hydrogen until needed;
- to release hydrogen to FC system for use in powering the vehicle.





35 MPa Compressed Hydrogen Tanks

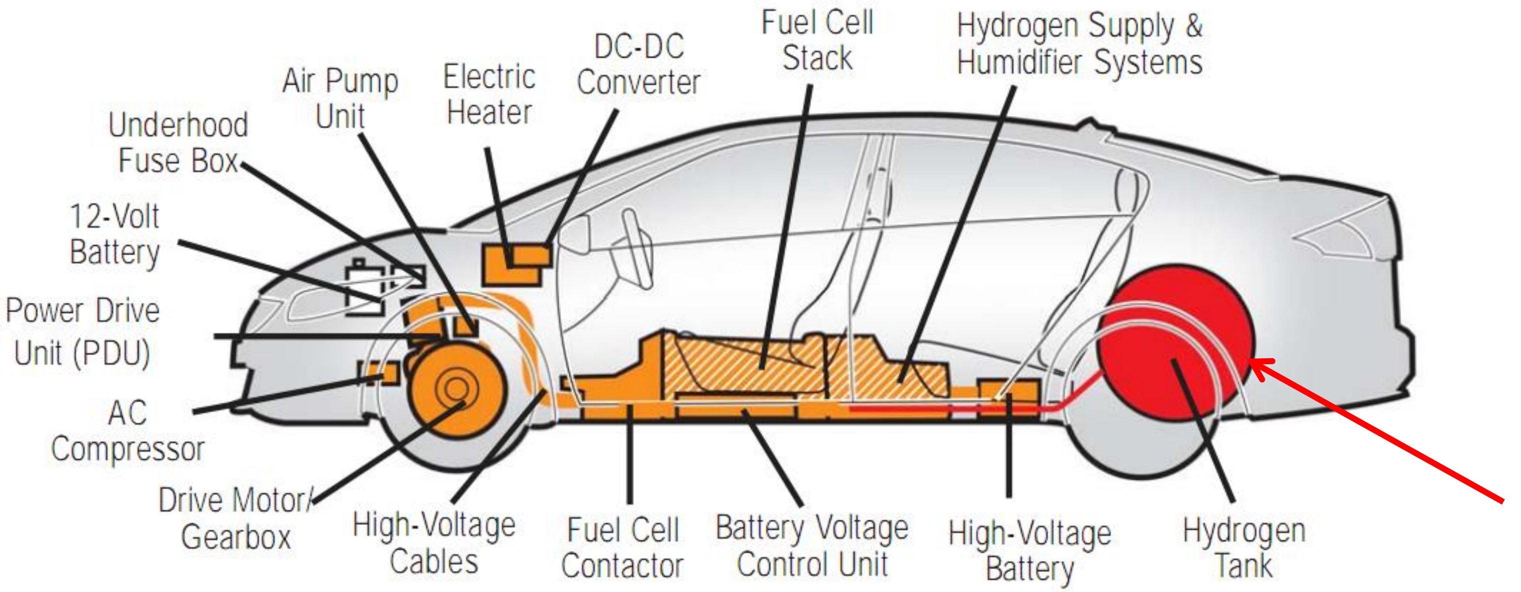
Type III : Fully wrapped composite tanks with metal liners

Type IV : Fully wrapped composite tanks with plastic liners

Source: Tomioka, J (2011) The 4th International Conference on Hydrogen Safety September 18th, 2011

On-board hydrogen storage tanks (1/2)

- **FC car** (up to 6 kg hydrogen):



Source: [Honda Emergency Response Guide. Honda Fuel Cell Vehicle]

It could be more than one tank (e.g. [Toyota Mirai FCV] has two 70 MPa tanks)

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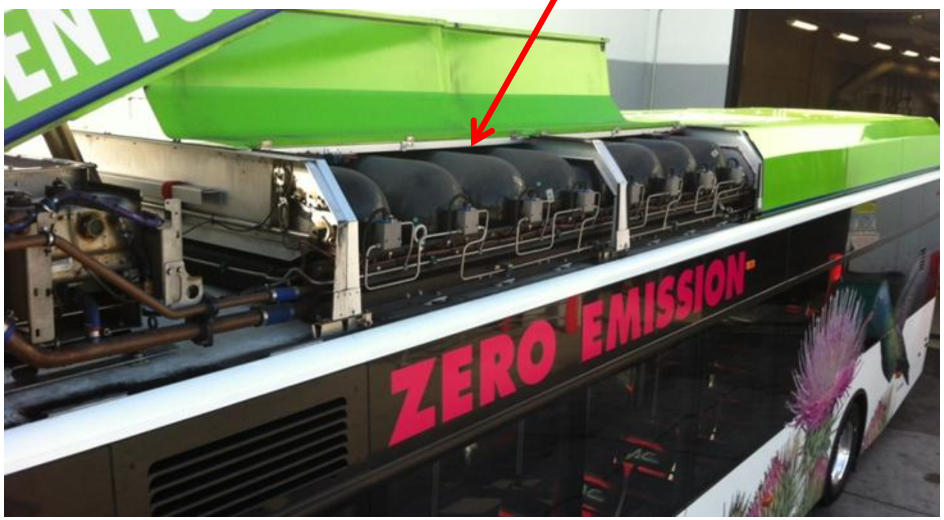
On-board hydrogen storage tanks (2/2)

- **FC bus** (up to 50 kg hydrogen)
- Several tanks located on the bus roof
- Advantages of FC buses compared to the conventional ones are **lower concentration of greenhouse gases**; **increased energy efficiency and a quieter operation.**



Photos: courtesy of National HFC FR training, USA

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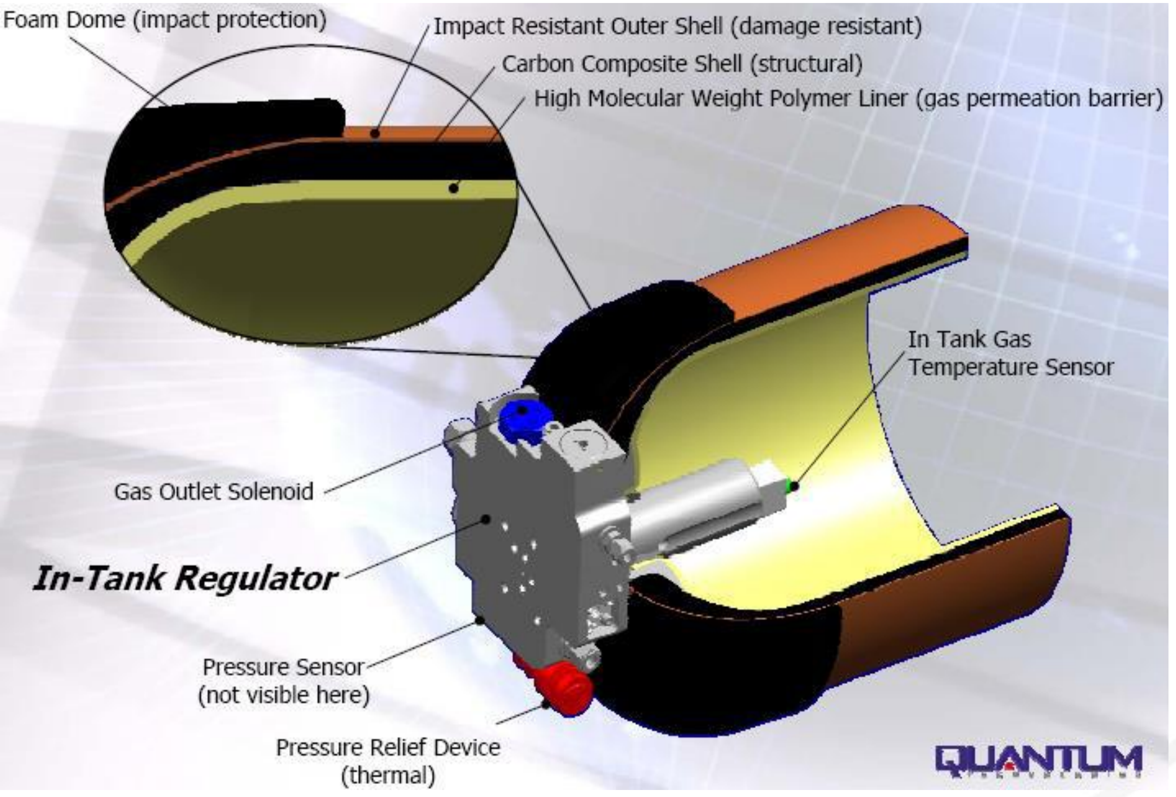
Type IV tank for GH_2 storage

Type IV tank for storage of compressed gaseous hydrogen, Quantum Technologies

- Impact resistant **foam dome** (light-weight, energy absorbing, cost-competitive).
- Impact resistant **outer shell** (bullet-proof, cut/abrasion resistance
- **CFRP shell** (light-weight, corrosion resistant, fatigue/creep, relaxation resistant),
- **Polymer liner** (light-weight, corrosion resistant, permeation barrier, cost-competitive)



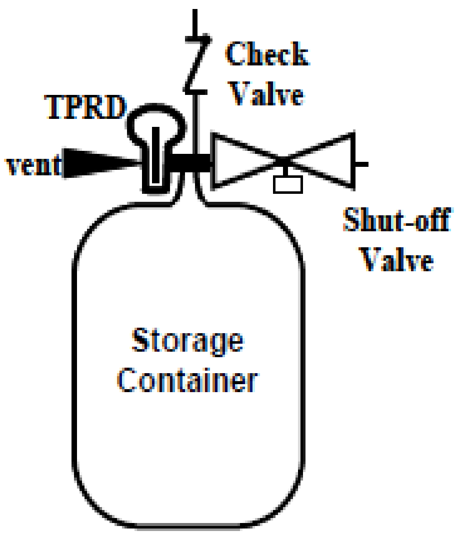
Cross section of Quantum hydrogen storage tank wall

Source: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/04_warner_quantum.pdf

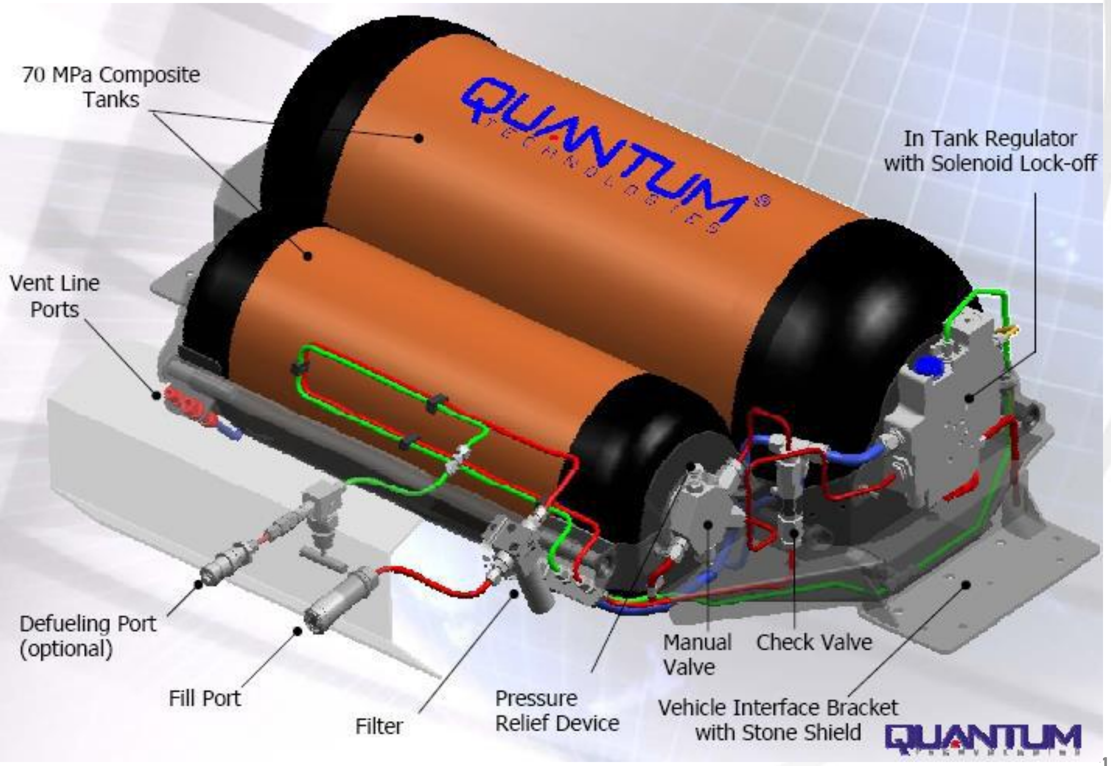
Composite type IV tank

Typical components:

- container/vessel
- check valve
- shut-off valve
- thermally activated pressure release device (**TPRD**)



- *Permeation* is specific to type IV vessels. Permeation rate should not be higher than **6 ml/hr/L** (at 20^{o}C) – EU regulation
- Hydrogen diffusion through polymeric material
- Hydrogen accumulates between the liner and CFRP forming a 'blister'.
- May cause partial or full collapse of the liner (if p of accumulated hydrogen becomes higher than internal pressure the liner)
- Development of special polymers



Source: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/04_warner_quantum.pdf

Issues with CGH_2 storage

Technical issues

- **Large volumes of tanks required**

5 kg - estimated amount of hydrogen an FC car needs for 500-km driving range
The densities of gaseous hydrogen at room temperature: 23 g/L (at 35MPa, room temp.); 39 g/L (at 70MPa, room temp.). To store 5 kg of hydrogen on-board of a FCH vehicle **minimum volumes** of 217 L and 128 L will be required to accommodate 35 MPa and 70 MPa, respectively. In reality the volumes should be even larger.

- **Heavy weights** (e.g. 66 kg when empty). The weight of hydrogen stored is *ca.* 1% of a tank weight . It drops even lower than 1% at pressures above 35MPa (higher pressures need thicker cylinder walls).
- **High costs**

Safety issues

- **Loss of containment/rupture**
- **Interaction of hydrogen with materials used for liners (metals or plastics)**
- **Heating effects during refilling**
- **Filling orientation**

Source: Klebanoff, L (Ed) (2012). Hydrogen storage technology: Materials and applications. Boca Raton: CRC Press. Taylor&Francis.

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Pressure relief devices (PRDs)

- In the event of a fire, **thermally activated pressure relief device (TPRD)** provides a controlled release of the CGH_2 from a high pressure storage container before its walls are weakened by high temperatures leading to a hazardous rupture.
- **TPRDs vent the entire contents of the container rapidly.** They do not reseal or allow re-pressurization of the container. Video of reclosing TPRD in action.
- Storage containers and TPRDs that have been subjected to a fire are expected to be removed from service and destroyed [1].
- PRDs are designed according to codes and standards. PRDs should be manufactured, installed, operated, maintained, inspected, and repaired according to laws and rules of local jurisdictions [2].
- On-board hydrogen storage **must be fitted with PRDs/TPRDs** according to the European Commission Regulation (EU) No 406/2010.

Sources:
[1] GTR, Proposal for a global technical regulation (gtr) on hydrogen fuelled vehicles, 2013
[2] Malek M.A. Pressure relief devices ASME and API code simplified. McGraw Hill, New York, 2006.

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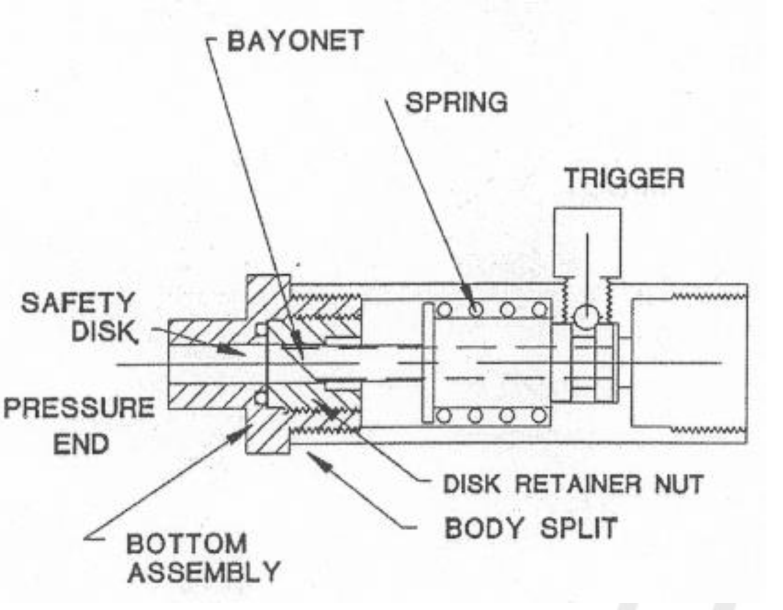
How TPRDs work

- PRDs are designed to open when pressure or temperature reaches a certain limit. TPRDs open if temperature is above 108-110ºC.
- Hydrogen tanks should be protected with **non-reclosing** TPRDs
- A **glass bulb PRD:** bulb is hollow and contains liquid. Upon heating the bulb breaks down; frees the poppet to move to the left. This opens the O-ring seal and vents the gas through the radial ports.
- A **bayonet PRD:** upon reaching its triggering temperature (*ca.*124 °C) the trigger melts and allows the ball bearing to move and release the spring, which punctures the safety disk with a bayonet. The content of the storage tanks is released through the hollow bayonet.



PRD before (left) and after activation (right)

[A bayonet PRD used in CNG buses](Mirada) (Mirada)

Glass bulb PRD (Rotarex)

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Why and how TPRDs fail

TPRD failures:
Type 1: a TPRD fails to vent properly.
Type 2: a premature activation of a TPRD.

- PRDs can be blocked during incident/accident.
- PRDs can become corroded or otherwise damaged such that they relieve pressure when they should not be

Let's watch the videos:
http://depts.washington.edu/vehfire/begin.html

- LA, CNG bus on fire
- Holland, CNG bus in fire

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Global Technical Regulations (GTR) 2013

- A PRD shall be a **non-reclosing** and a **thermally activated** device.
- A PRD shall be **directly installed** into the opening of a container, or at least one container in a container assembly, or into an opening in a valve assembled into the container, in such a manner that **it shall discharge the hydrogen into an atmospheric outlet that vents to the outside of the vehicle.**
- It shall not be possible to isolate the PRD from the container protected by the PRD, due to the normal operation or failure of another component.
- The hydrogen gas discharge from PRD shall not be directed:
  - towards exposed electrical terminals, exposed electrical switches or other ignition sources;
  - into or towards the vehicle passenger or luggage compartments;
  - into or towards any vehicle wheel housing;
  - forward from the vehicle, or horizontally from the back or sides of the vehicle.

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Source: GTR, Proposal for a global technical regulation (gtr) on hydrogen fuelled vehicles, 2013.

Testing of hydrogen tanks

GTR 2013

Tests applicable to all types of tanks:

- Hydrostatic **burst test**: the pressure at which the tank bursts, typically more than twice of the working pressure.
- **Leak-before-break** test: the fuel tank shall fail by leakage or shall exceed the number of filling cycles (11,250)
- **Bonfire** test: the fuel tank shall vent through the non-reclosing TPRD; the fuel tank shall not fail when exposed to a bonfire of 20 minutes duration.
- **Penetration** test: the fuel tank shall not rupture when an armour piercing bullet or impactor with a diameter of 7.62 mm or greater fully penetrates its wall.

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RCS relevant to fire tests

Table 1. Selected RCS applicable to fire tests of high pressure hydrogen storage tanks

RCS	Title	Country	Year
SAE J2578	General fuel cell vehicle safety	U.S.	2002 2009 re-published
SAE J2579	Fuel systems in fuel cell and other hydrogen vehicles	U.S.	2008 2009 re-published
JARI S001	Technical standard for containers of compressed hydrogen vehicle fuel devices	Japan	2004
ISO 15869	Gaseous hydrogen and hydrogen blends - Land vehicle fuel tanks (Technical Specification)	International	2009
EU regulation 406/2010	Implementing EC Regulation 79/2009 on type-approval of hydrogen-powered motor vehicles	EU	2010
GTR 2013	Proposal for a Global Technical Regulation (GTR) on hydrogen and fuel cell vehicles. (ECE/TRANS/WP. 29/GRSP/2013/41).	International	2013

GTR fire tests

- A hydrogen storage container fitted with a TPRD, a check valve, a shut-off valve and any additional features including vent line(s) and vent line covering(s) and any shielding affixed directly to the container (such as thermal wraps and coverings/barriers over TPRD(s)).
- A hydrogen storage system is pressurized to a nominal working pressure (NWP) and exposed to fire.
- A high-pressure container shall vent through a TPRD in a controlled manner without a hazardous rupture.

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Fire test procedure (1/3)

Table 2. A summary of conditions for a test started as a localized fire (GTR, 2013)

Test method	Method 1, generic installation test (without protective devices, only thermal shielding) Method 2 for specific vehicle installation (includes protective devices and other vehicle components)
Pressure in the container	100% of nominal working pressure (NWP)
Medium in the container	Compressed hydrogen/compressed air can be used if agreed in certain regions/countries
Distance from the container to the fire source	100 mm
Fire source	LPG burners configured to produce uniform minimum temperature
Fire source length	1.65 m
Number and the location of thermocouples (TCs)	Minimum 5 TCs covering the length of the container up to 1.65 m maximum. At least 2 TCs are in localized area and at least 3 TCs equally spaced no more than 0.5 m apart in the remaining area
Position of TCs	25±10mm from outside surface of the container along its longitudinal axis
Additional TCs	At TPRD sensing point or at any other location
Wind shields	To ensure uniform heating

Fire test procedure (2/3)

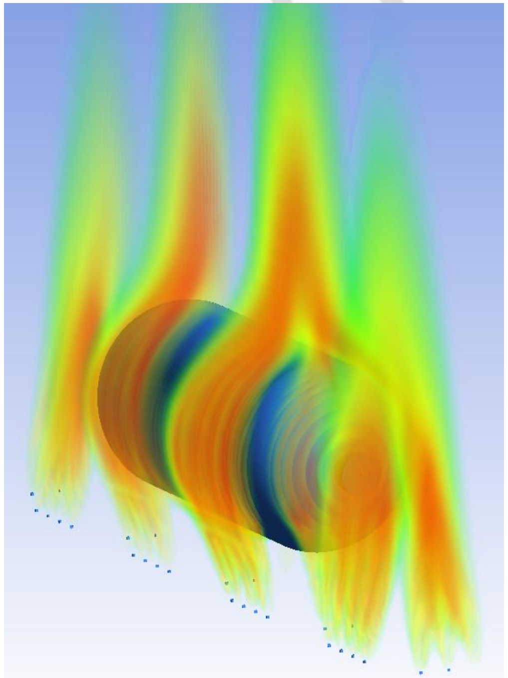
Table 2. A summary of conditions for a test started as a localized fire (contd.) (GTR, 2013)

Length and width of localised fire	250±50 mm and the width encompasses the entire diameter of the tank
Localized fire exposure area	Area furthest from TPRD(s) – generic installation (Method 1)
	The most vulnerable area should be identified for specific vehicle installation (Method 2). This area, furthest from TPRDs, positioned directly over the fire source
T_{min} of TCs in localized area	**600 °C** - from 3 to 10 mins of fire exposure.
Start of engulfing fire	Main burner is ignited at 10 mins of the test and fire source is extended to 1.65 m. After 12 mins of exposure the temperature should be increased to at least 800 °C
T_{min} of TCs within engulfing region	**800 °C** – from 12 mins until release of hydrogen via TPRD(s)
Duration of the test	Test continues until the **system vents through a TPRD** and the **pressure falls to less than 1 MPa.** The venting shall be continuous (without interruption), and a **storage system shall not rupture**. **An additional release through a leakage** (not including release through a TPRD) that results **in a flame with length greater than 0.5 m** beyond the perimeter of the applied flame **shall not occur.**

Engulfing fire test: GTR (1/2)

Table 3. A position of a container above the fire

Container length	Number of TPRDs	Position of a container
≤1.65 m	1	Horizontal; centrally above the fire source
>1.65 m	1 PRD at one end of a container	Horizontal; above the fire source that commences at the opposite end of a container
>1.65 m	>1 PRD along the length of a container	Horizontal; centrally above the fire source, centre of which is located midway between those PRDs that are separated by the greatest horizontal distance



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Engulfing fire test: GTR (2/2)

Table 4. A summary of conditions for engulfing fire test

Medium in the container	Compressed hydrogen at 100% of NWP
Fire source length	1.65 m
Number of TCs	Minimum 3 TCs suspended in the flame approx. 25 mm below the bottom of the container
Distance to the fire source	100 mm
Metallic shielding	To prevent direct flame impingement on a container valves, fittings, or PRDs. Metallic shielding should not be in direct contact with fittings
Fire protection of TCs	Metallic shielding or TCs may be inserted into blocks of metal measuring less than 25 mm×25mm×25mm
T_{min} of TCs	Within **5 minutes** after fire is ignited, an average flame temperature should not be less than **590 °C** (determined by the average of two TCs recording the highest temperatures over 60 seconds interval)
Measurements	Temperatures of TCs and a container pressure shall be recorded every 30 seconds during the test
Duration of the test	Until container fully vents (pressure falls below 0.7MPa)

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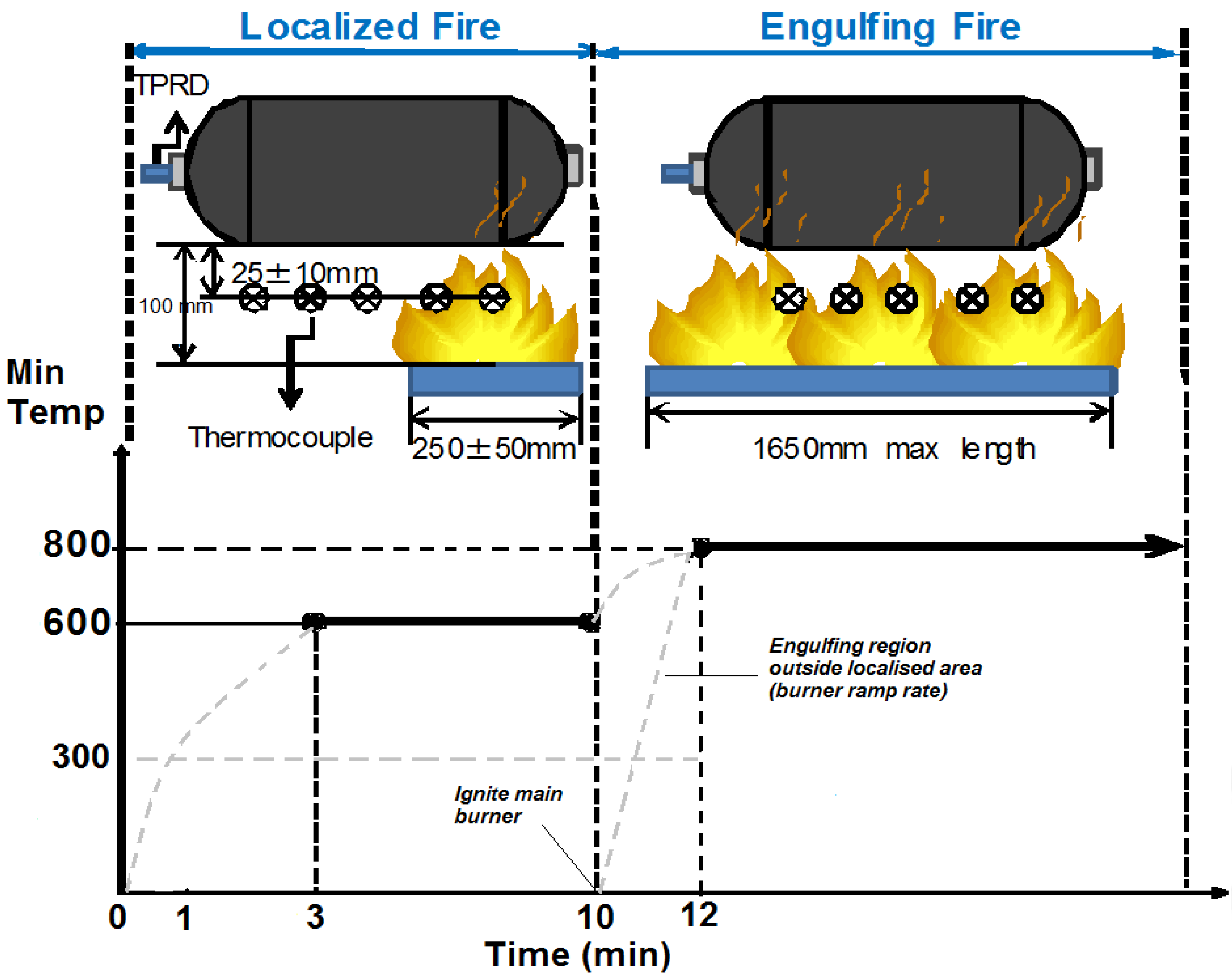
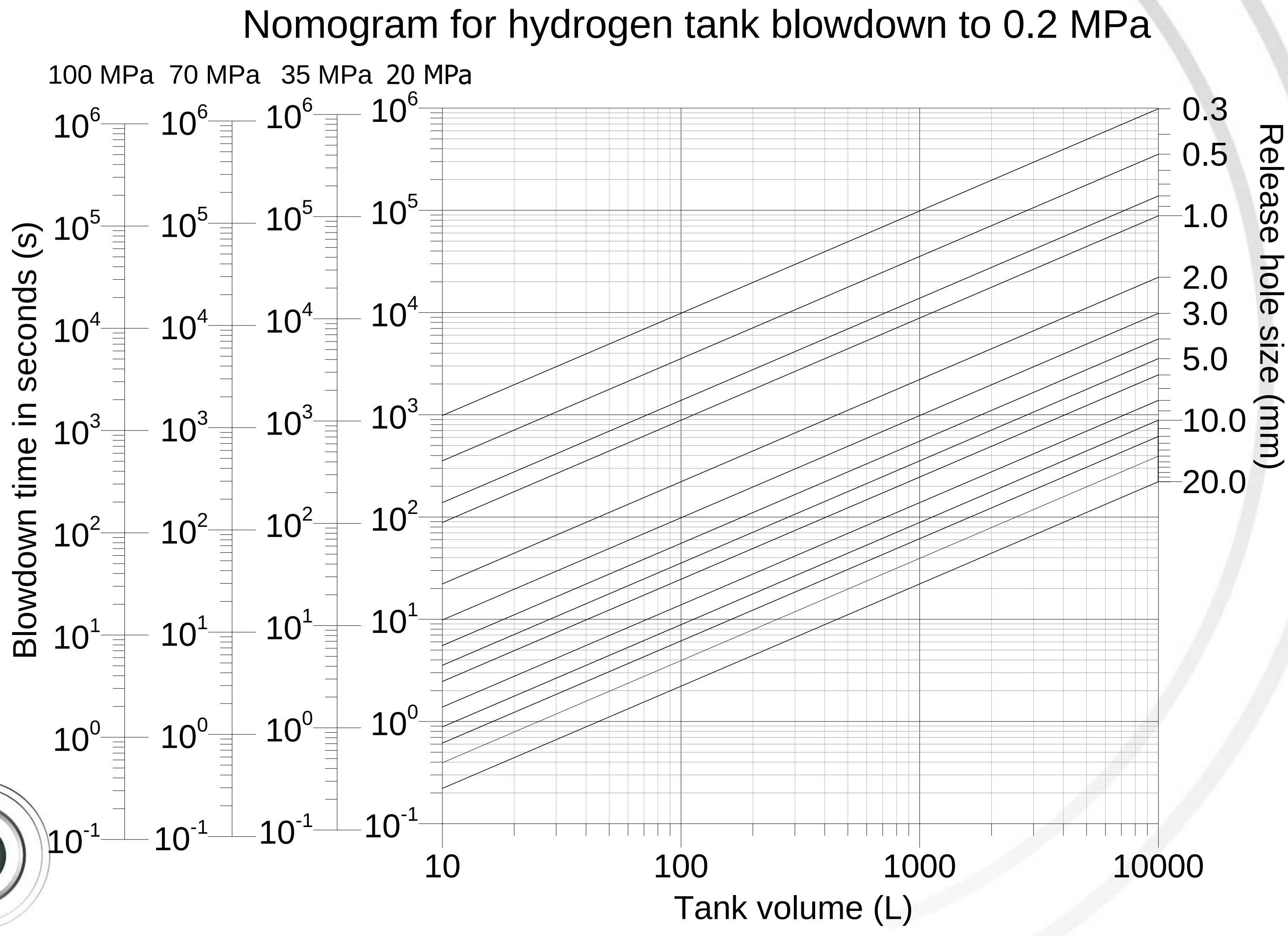
Fire test procedure (3/3)



Blow-down of hydrogen storage tank



Fire test protocols: GTR - 2013

	Localized fire region	Time period, min	Engulfing fire region (outside the localized fire region)
Action T_{min} T_{max}	**Ignite burners** Not specified <900°C	**0-1** - -	**No burner operation** Not specified Not specified
Action T_{min} T_{max}	**Increase temperature and stabilize fire for start of localized fire exposure** >**300°C** <900°C	**1-3** - -	**No burner operation** Not specified Not specified
Action T_{min} T_{max}	**Localized fire exposure continues** 1-minute rolling average >**600°C** 1-minute rolling average <900°C	**3-10**	**No burner operation** Not specified Not specified
Action T_{min} T_{max}	**Increase temperature** 1-minute rolling average >600°C 1-minute rolling average <1100°C	**10-11**	**Main burner ignited at 10 mins** Not specified Not specified
Action T_{min} T_{max}	**Increase temperature and stabilize fire for start of engulfing fire exposure** 1-minute rolling average >600°C 1-minute rolling average <1100°C	**11-12**	**Increase temperature and stabilize fire for start of engulfing fire exposure** > 300°C <1100°C
Action T_{min} T_{max}	**Engulfing fire exposure continues** 1-minute rolling average >**800°C** 1-minute rolling average <1100°C	**12 – end of the test**	**Engulfing fire exposure continues** 1-minute rolling average >800°C 1-minute rolling average <1100°C

Results of the fire test

- The arrangement of the fire should be recorded in sufficient detail to ensure the rate of heat input to the test article is reproducible.
- The results include:
- the elapsed time from ignition of the fire to the start of venting through the TPRD(s), and
- the maximum pressure and time of evacuation until a pressure of less than 1MPa/0.7MPa is reached.
- TCs temperatures and a container pressure should be recorded at intervals of every 10 sec/30 sec or less during the test.
- Any failure to maintain specified minimum or maximum temperatures invalidates the test results.
- Any failure or inconsistency of fire source should invalidate the test results.

GTR should include fire test without a TPRD and provide information on Fire Resistance Rating (FRR) for public and firemen safety.

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Effects of fire on high pressure storage tanks

- Maximum temperatures measured on the composite surface: (750-850 ^{o}C)
- The cylinder was leaking across its entire surface with slightly more leakages towards its ends.
- The epoxy resin disappeared but the carbon fibres did not burn.
- The release of hydrogen through an orifice with a diameter of 0.5 mm and opening within 90 seconds prevented the studied 36 L cylinder from bursting.

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Source: Ruban, S, et al (2012). Fire risk on high-pressure full composite cylinders for automotive applications. International Journal of Hydrogen Energy, Vol. 37, pp. 17630-17638.

Catastrophic failure of storage tank in a fire (1/2)

- Experiment sponsored by the Motor Vehicle Fire Research Institute (MVFRI) and operated by Southwest Research Institute (SWRI), USA [1].
- Storage pressure about **35 MPa**, no pressure relief device (PRD), propane burner (perforated piping in a wind-barrier pan). Only **1.64 kg** of hydrogen (Zalosh, 2007) [2].
- **Type IV tank tests:** 72.4 L (*LxD*=84x41 cm) **stand-alone tank**, high-density polyethylene liner, carbon fibre structural layer, and fiberglass outer layer. Heat Release rate **(HRR)= 370 kW**, P=34.3 MPa. Fire resistance rating (FRR) = **6 min 27 s**
- **Type III tank tests:** 88 L tank **under a typical SUV** (Sports Utility Vehicle, *LxW*=4.5x1.8 m), 28 cm above the ground. **HRR=265 kW (GTR 2013 issue)**, P=31.8 MPa. FRR = **12 min 18 s.**

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Sources: [1] Weyandt, N (2006). Vehicle bonfire to induce catastrophic failure of a 5000-psig hydrogen cylinder installed on a typical SUV, Motor Vehicle Fire Research Institute. Report. December, 2006. Available from: www.mvfri.org
[2] Zalosh, R (2007). Blast waves and fireballs generated by hydrogen fuel tank rupture during fire exposure. Proceedings on the 5th Seminar on Fire and Explosion Hazard, Edinburgh, UK, 23-27 April 2007, pp. 2154-2161.

Catastrophic failure of storage tank in a fire (2/2)

Test observations:

- **The internal cylinder temperature and pressure increased only marginally (due to a low thermal conductivity of CFRP)** from 27ºC to 39ºC and from 34.5 MPa to 35.7 MPa during final period between 6 min and 6 min 27 s of fire exposure, which culminated in a catastrophic rupture of type IV tank.
- **Burning of tank composite layers** started in ***45 s*** (Type IV) and ***20 s*** (Type III) – black soot appearance.
- Flame penetrated the vehicle (SUV) interior after about 4 minutes of exposure fire.

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Bonfire test: type IV tank (no PRD)

“Fire resistance” is 1-6 minutes.

No combustion contribution to the blast.

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Blast waves (TPRD blocked)

Type IV (stand-alone). Measured peak pressures varied from **300 kPa at 1.9 m**, to **41 kPa at 6.5 m**. The highest pressures were in a direction perpendicular to the tank longitudinal axis.

Type III (under SUV). **140 kPa at 1.2 m** (SUV absorbs energy?), **12 kPa at 15 m**. Blast pressures were higher in a direction parallel to the fuel tank longitudinal axis.

Please note: pressure effects on people (Barry, 2003):
- 10.3-20 kPa - people are knocked down;
- 13.8 kPa - possible fatality by being projected against obstacles;
- 34 kPa - eardrum rupture;
- 35 kPa - 15% probability of fatality;
- 54 kPa - fatal head injury;

> 83 kPa - severe injury or death (about 5 m)

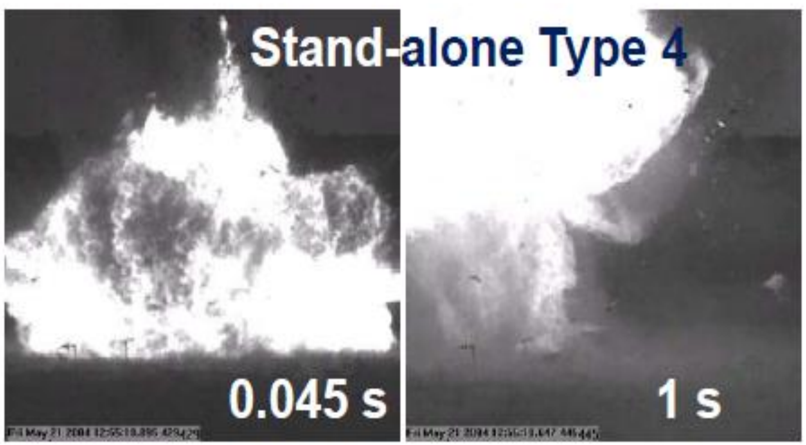
http://www.mvfri.org/Contracts/Final%20Reports/CNGandH2VehicleFuelTankPaper.pdf.

Note: Energy stored in a tank is proportional to PxV (larger tanks has more hazardous potential through the blast wave in case of rupture)

Source: Zalosh, R (2007). Blast waves and fireballs generated by hydrogen fuel tank rupture during fire exposure. Proceedings on the 5th Seminar on Fire and Explosion Hazard, Edinburgh, UK, 23-27 April 2007, pp. 2154-2161.

Fireball

- Type IV: a fireball is **7.7 m** in diameter (45 ms after thank rupture). Fireball is lifted in 1 s (see Figs. below, left).
- Type III: a fireball is **24 m** in diameter.
- Simple correlation (Zalosh, 2007) gives 9.4 m for 1.64 kg of hydrogen.
- Fireball duration is about 4.5 s in both cases (IR video), and twice less by high-speed visible range cameras.
- Correlation (Zalosh, 2007) gives 0.6 s duration (does not work!)
- **Heat flux** (Type III) measured at a distance of **15.2 m** in peak spikes were **210-300 kW/m^2** (NOTE: about 35 kW/m^2 - 1% fatality in 10



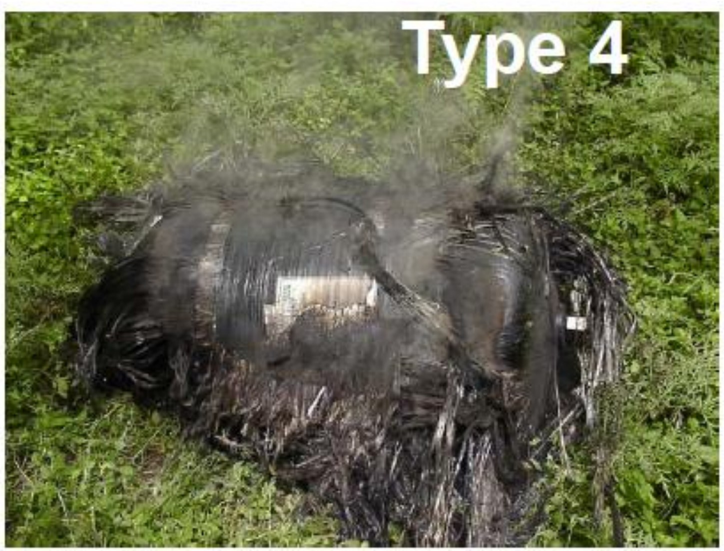
Type 3 under SUV

Source: Zalosh, R (2007). Blast waves and fireballs generated by hydrogen fuel tank rupture during fire exposure. Proceedings on the 5th Seminar on Fire and Explosion Hazard, Edinburgh, UK, 23-27 April 2007, pp. 2154-2161.

Projectiles

- Type IV (stand-alone): the largest tank projectile fragment was the 14 kg top half of the tank found **82 m away** from the original tank location.
- Type III (SUV test): a large tank fragment found **41 m** from the SUV. Fragment projectiles from the SUV were found at distances up to **107 m**. It is possible that undiscovered fragments may have travelled even further.
- A car could act as a "missile" (**22 m** displacement!)
- EU Regulations 2010: "Hydrogen components …must not **project beyond** the outline of the vehicle".

Source: Zalosh, R (2007). Blast waves and fireballs generated by hydrogen fuel tank rupture during fire exposure. Proceedings on the 5th Seminar on Fire and Explosion Hazard, Edinburgh, UK, 23-27 April 2007, pp. 2154-2161.



HyResponse

Fire resistance of storage vessels

Fire test, CNG tank not equipped with a PRD

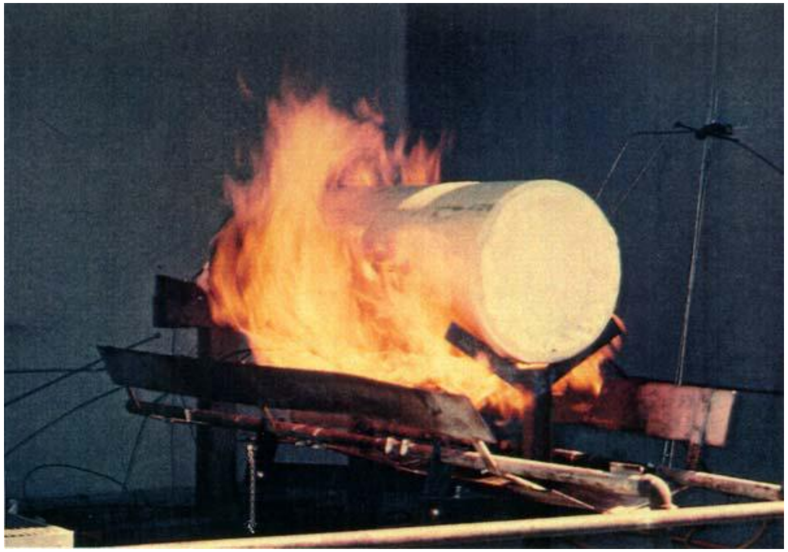
- Current level of **fire resistance rating (FRR)** for hydrogen storage tanks remains low: it ranges from **3.5 to 12 minutes (recent research at UU demonstrated FRR more than 1 hr 50 mins)**.
- Due to the relatively large orifice diameter (4-6 mm) of a TPRD the **length of a flame** produced is too high (**from 10 to 15 m**) and a **hazard distance** is around **50 m**.

- **Unacceptable for life safety and property protection!**

European regulations require that on-board storage passes a bonfire test. However, there is **no requirements to FRR** of a tank to inform the public and firemen.

HyResponse

Fire protection of hydrogen storage tanks



- A composite tank coated with a sprayed ceramic insulating material (Gambone and Wong, 2007).

- A composite tank wrapped with a ceramic blanket (Gambone and Wong, 2007). Intact after having been exposed to an intense **localized fire for 45 minutes**.

Source: Gambone, L.R. and Wong, J.Y., Fire Protection Strategy for Compressed Hydrogen-Powered Vehicles, ICHS2, 2007).

HyResponse

Fire protection of hydrogen storage tanks

Concept of thermal insulation

- Protective encapsulation not only imparts fire resistance but also provides an additional level of impact protection (Gambone and Wong, 2007).
- This may allow tank designers to reduce the amount of reinforcing composite material which could reduce the cost and weight of storage systems.

Source: Gambone, L.R. and Wong, J.Y., Fire Protection Strategy for Compressed Hydrogen-Powered Vehicles, ICHS2, 2007).

HyResponse

Safety strategies for inherently safer design

- With one layer of **intumescent paint applied to** Type IV tank an **increase of the FRR by an order of magnitude!**
- There is an urgent need to demonstrate increased fire resistance of Type III and IV tanks used by car manufacturers (if OEMs say there is “no safety problems” – they have to demonstrate actual **fire resistance rating** of their on-board storage to the general public – “to pass” bonfire test is not enough!)

HyResponse

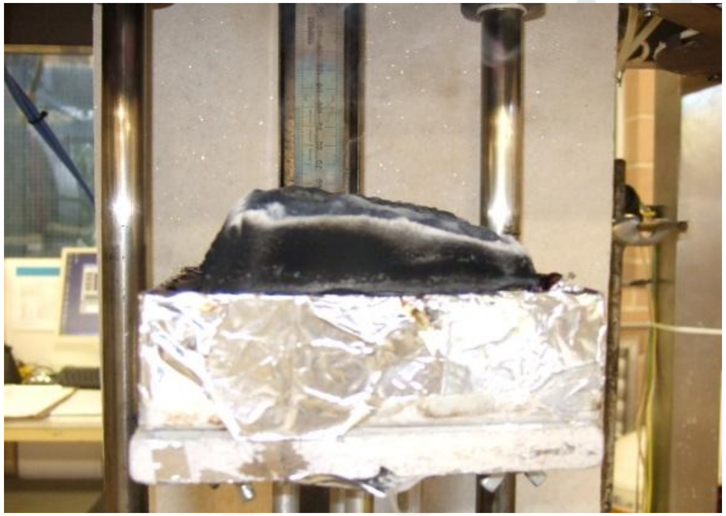
Intumescence

- Intumescence is a versatile method for providing reaction and resistance to fire to materials

- When heating beyond a critical temperature, **the intumescent material begins to swell** and then to expand forming an insulative coating limiting heat and mass transfer

- A multi component system- essentially consists of **a char former** (e.g. pentaerythritol); **acidic component** (e.g. ammonium polyphosphate); a **spumific/blowing agent** (e.g. melamine)

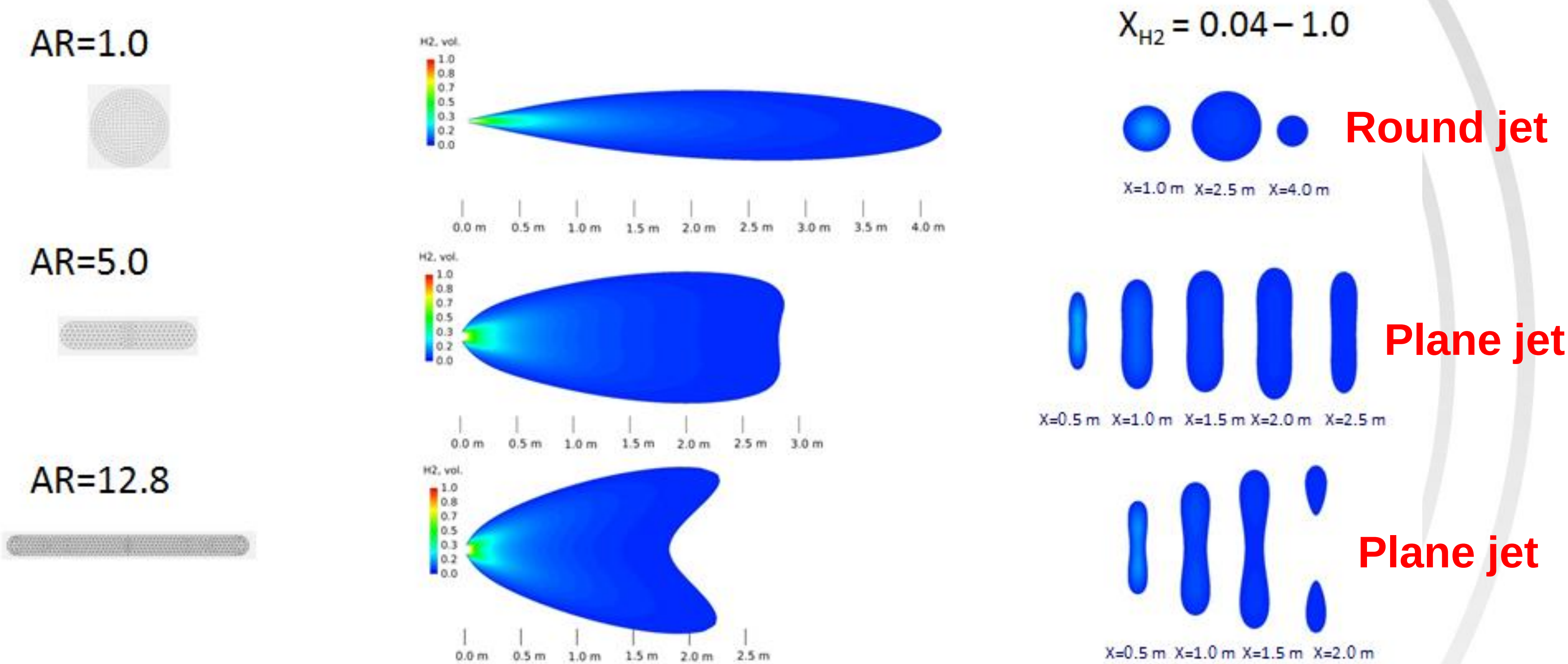
Intumescent coating **before** the fire exposure



Intumescent coating **after** the fire exposure

HyResponse

PRDs with plane nozzles



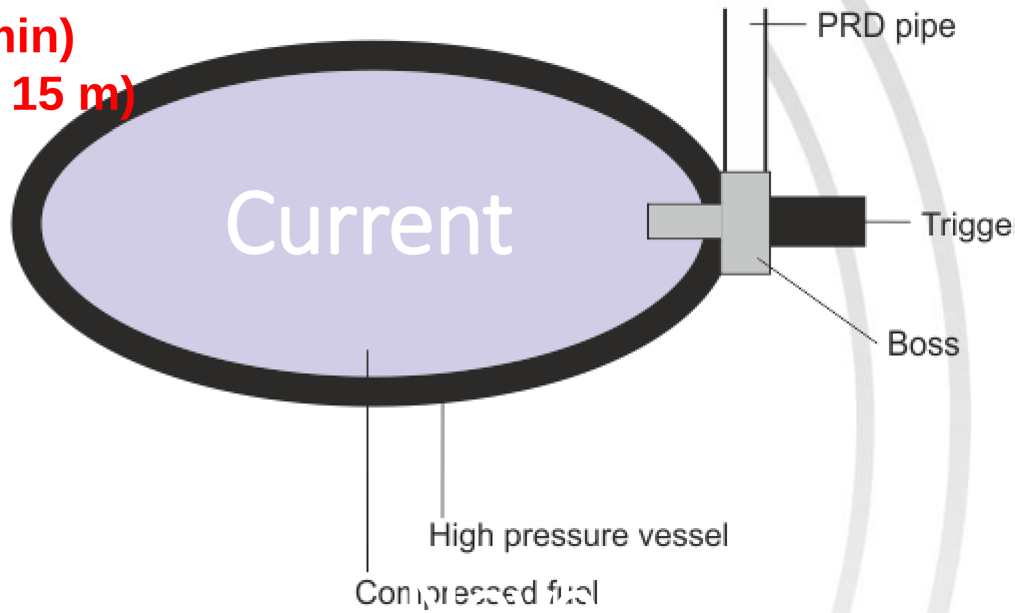
Reduced size of flammable envelope; reduced jet fire length; faster hydrogen concentration decay

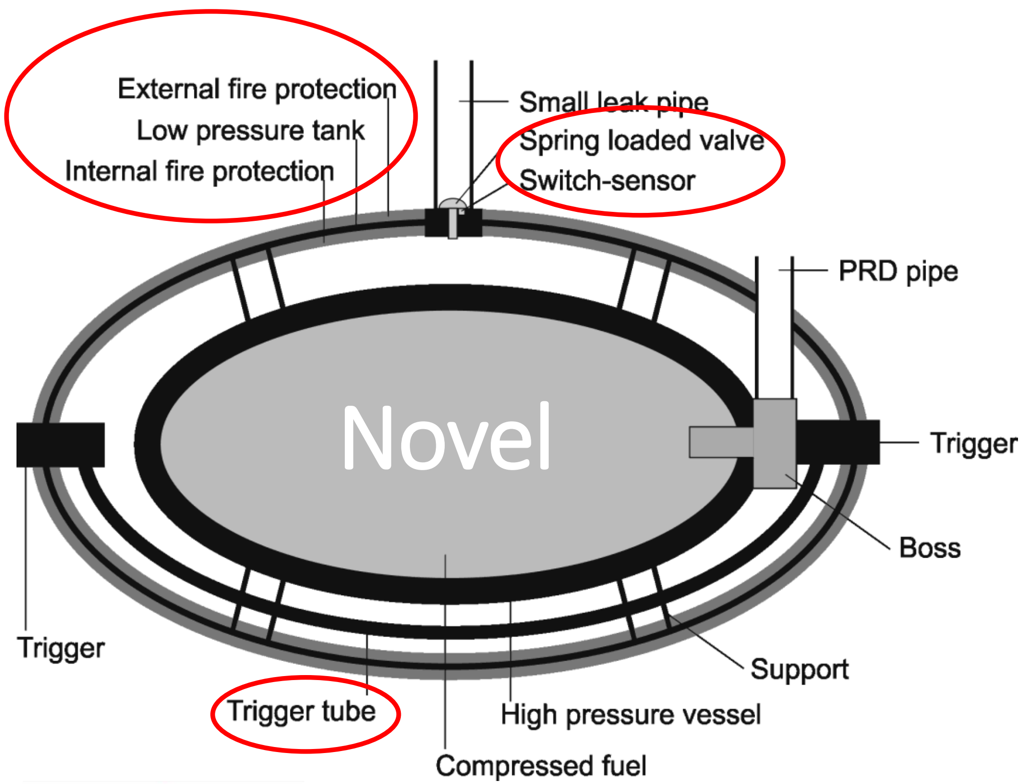
Source: Makarov, D, and Molkov, V. (2013). Plane hydrogen jets. International Journal of Hydrogen Energy, Vol. 38, no. 19, pp. 8068–8083.

HyResponse

Storage tank with three fire resistant layers

Fire resistance: **1-2 hour (instead of 5 min)**
Flame length: **less than 1 m (instead of 15 m)**
Automated **control of tank aging**





Work-in-progress at Ulster

Potential hazards of on-board GH_2 storage (1/3)

- **Difficulty in identification of hydrogen release**: it is odourless, colourless and tasteless gas. Odorants cannot be used.
- Hydrogen can cause **embrittlement** of metals, leading to cracks formation/propagation and hydrogen leak. This may result in the decrease of a material's strength and consequently in the container's fracture.
- **Accumulation of hydrogen** over time in enclosures such as a garage or mechanical workshop, a vehicle passenger compartment. **Asphyxiation** might occur due to displacement of air with hydrogen.
- Formation of hydrogen-oxygen or hydrogen-air **flammable mixtures**. The intake of flammable mixture into a building ventilation system may lead to deflagration or even to detonation.

HyResponse

Potential hazards of on-board GH_2 storage (2/3)

- High pressure hydrogen **jets may cut bare skin** (Hammer, 1989).
- **Overpressure and impulse** (eardrum damage, tank rupture, flying debris, shattered glass etc).
- **Pressure peaking phenomenon** (a garage collapse in 1 sec).
- Hydrogen **ignites easily** (minimum ignition energy for hydrogen combustion is 0.017 mJ, which is 10 times lower compared to other fuels). A static spark can ignite hydrogen.
- Hydrogen **flames are invisible** in the daylight.

Source: Hammer, W (1989). Occupational Safety Management and Engineering, 4th edition, Prentice Hall, Englewood Cliffs, New Jersey, 1989, ISBN 0-13-629379-4, chapter 19.

HyResponse

Potential hazards of on-board GH_2 storage (3/3)

- Hydrogen burns rapidly and does not produce smoke. Flash fire, jet fire.
- An external fire, heat or thermal radiation can cause a mechanical rupture of a tank. Fire resistance **up to 12 minutes** (publicly available) before catastrophic failure.
- In case of TPRD malfunction a worst-case scenario: **a rupture (catastrophic failure) of hydrogen storage tank, producing fireball, blast waves and burning projectiles.**
- Video: CNG tank bonfire, no PRD

HyResponse

Source: Zalosh, R (2007). Blast waves and fireballs generated by hydrogen fuel tank rupture during fire exposure. Proceedings on the 5th Seminar on Fire and Explosion Hazard, Edinburgh, UK, 23-27 April 2007, pp. 2154-2161.

Interaction of hydrogen with metals (1/2)

- Hydrogen has: 1) a very small size of 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).

Source: Google free images

HyResponse

Interaction of hydrogen with metals (2/2)

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.

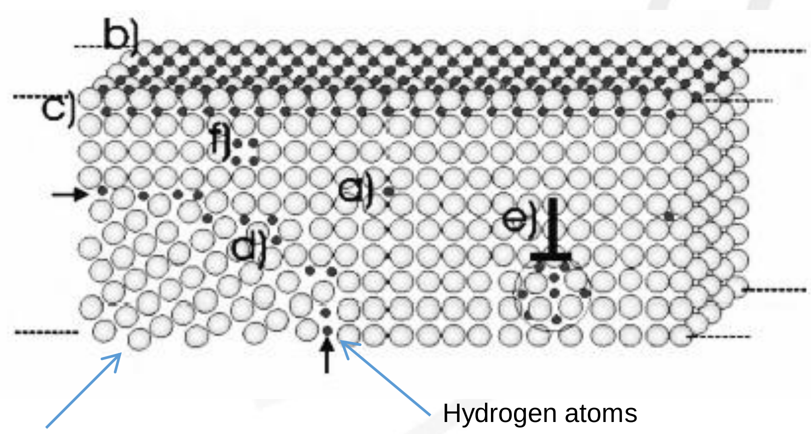
- **Hydrogen Embrittlement (HE)**
- **Embrittlement at low temperatures ('cold embrittlement')**
- **Violent reactions** (e.g. ignition)

Video of hydrogen crack arrest (SINTEF experiment)

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.

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 ^{o}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.

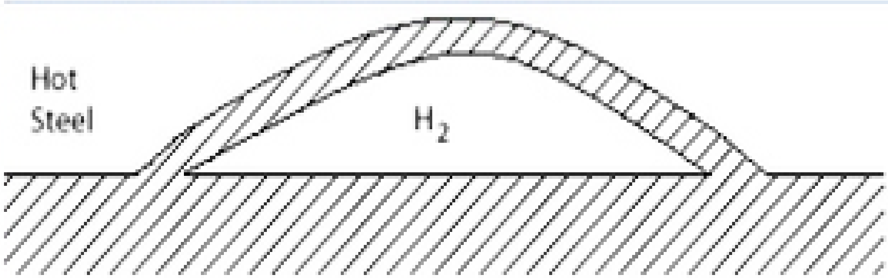
HyResponse

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.

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

HyResponse

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.

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 15916:2004 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.

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)

HyResponse

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.

HyResponse

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.

Interaction of hydrogen with polymeric materials

- Polymeric liners for type IV tanks.
- PEM FC systems (Gasket failure in a PEM FC) [1].
- 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 cannot withstand fire for longer than 12 minutes.
- **Permeation of hydrogen** through polymers is common.

HyResponse

Source: [1] Husar, A, Serra, M, Kunusch, C. Journal of Power Sources, 2007, p. 85-91.

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 <u>negligible</u> for storage containers with <u>metallic liners</u> (types I, II, and III) and may pose a **safety issue** for vessels with **polymeric liners** (type IV).
- **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 taken from:
Molkov, V (2012). Fundamentals of hydrogen safety engineering, Part I and Part II. Available from: www.bookboon.com, free download e-book

HyResponse

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.

HyResponse

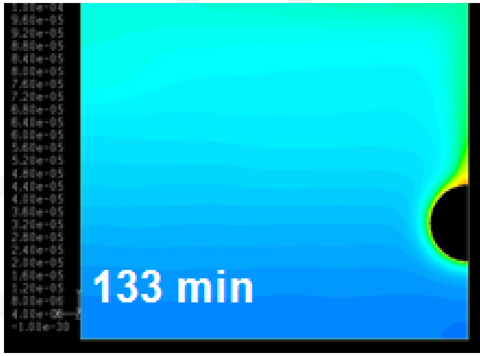
Permeated hydrogen distribution (in an enclosure)

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 ^oC).
- 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 leads 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

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

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 °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 °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 °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 °C).
- ❖Society of Automotive Engineers J2579, end of life, 55 °C: **150** NmL/min/vehicle
- ❖ISO/TS15869:2009 at end of life (20 °C): **75** NmL/min/container

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Liquefied hydrogen (LH_2) storage (1/2)

- Tanks for LH_2 can store more hydrogen compared to those for GH_2: volumetric capacity of LH_2 0.070 kg/L as opposed to 0.030 kg/L for GH_2 tanks at 70 MPa.
- LH_2 stored at low (**cryogenic**) **temperatures** -253 ºC and near-ambient pressure (0.6 MPa).
- **Sufficient** level of tanks **insulation** needed to prevent the release of evaporated gas.
- Major industrial gas suppliers have cryogenic tanker delivery lorries.
- Hydrogen refuelling stations and airspace applications (higher energy density than GH_2).

Issues:

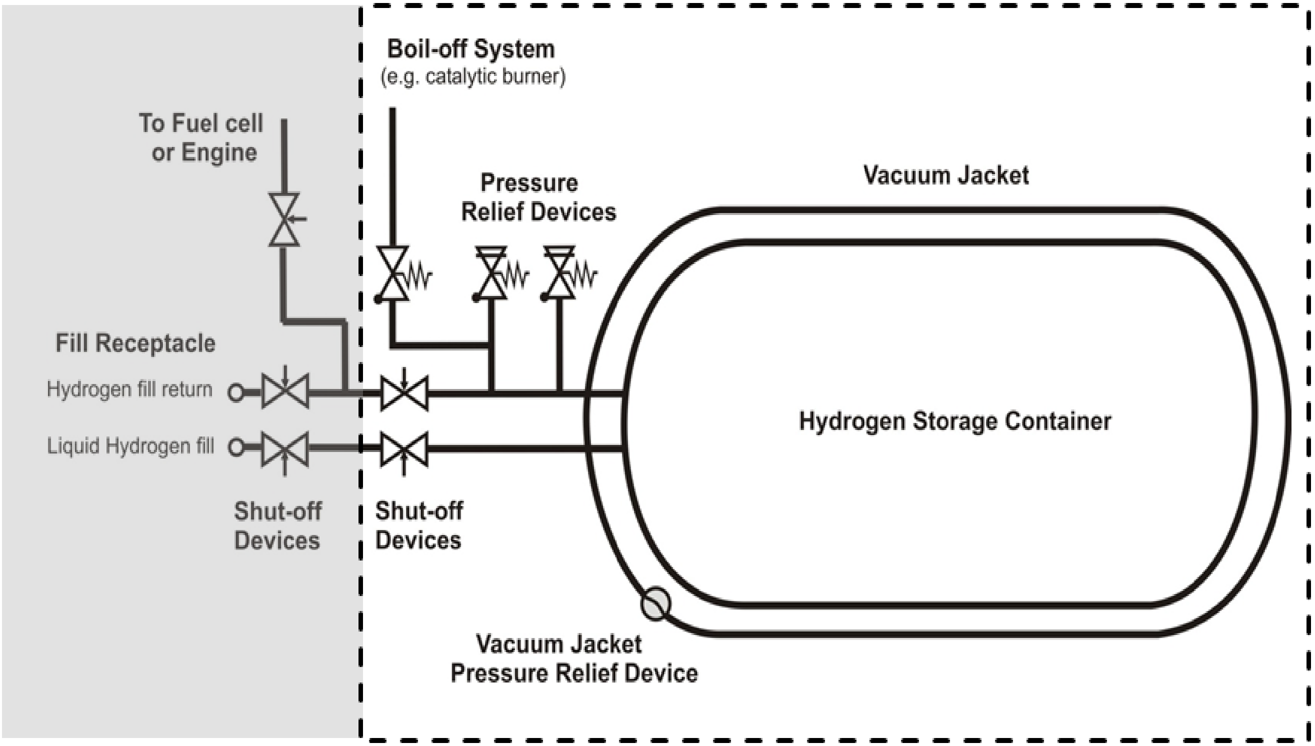
- Boil-off phenomenon (rate of 0.3-3% per day).
- High level of energy required for liquefaction (about 30% of heating value of hydrogen)
- Volume, weight and costs of tanks
- Video of LH_2 spillage: **cryogenic burns**

Liquefied hydrogen (LH_2) storage (2/2)

Components of LH_2 storage:

- LH_2 **storage container**
- **Shut-off** devices
- A **boil-off system**
- **PRDs**
- The interconnecting **piping** (if any) and **fittings** between the above components

Double-walled vacuum insulated vessel (light-weight steel alloys)



Source: GTR, Proposal for a global technical regulation (gtr) on hydrogen fuelled vehicles, 2013.

HyResponse

Safety issues of LH_2 storage

- **Loss of containment:** damage of the external tank walls can lead to the disruption of vacuum, causing heating and subsequent pressure rise inside the vessel.
- Condensed air may form an **oxygen enriched atmospheres** in the vicinity of LH_2 storage (risk of explosion if external wall tank is damaged)
- **Boil-off** losses: concerns when vehicles parked for a long time (pressure builds up until boil-off valves open.
- Boil-off/evaporation can be caused by:
  - *Ortho-para H_2 conversion*: conversion of ortho- to para-hydrogen is an exothermic reaction. If the unconverted normal hydrogen is placed in a storage vessel, the heat of conversion will be released within the container, which leads to the evaporation of the liquid.
  - *Residual thermal leaks*: the heat leakage losses are proportional to the ratio of surface area to the volume of the storage vessel. The shape of cryogenic vessel should be spherical since it has the least surface to volume ratio. A big cause of heat leaks in cryogenic storage is through the support struts in the vessel.
  - *Sloshing*: a motion of LH_2 in a vessel due to acceleration or deceleration, which occurs during its transportation by tankers . Some of the impact energy of the liquid against the vessel is converted to thermal energy.
  - *Flashing:* occurs when LH_2 at a high pressure is transferred from trucks and rail cars to a low pressure vessel
- **Ice formation**: low temperatures may result in ice build-up on storage elements (e.g. valves, dewars) leading to an excessive exterior pressures, and to possible rupture of the vessel.

HyResponse

LH_2 releases

- In case of a LH_2 leak or spill, a hydrogen cloud will be formed; could flows horizontally for some distance or even downward, depending on the terrain and weather condition.
- **Volume ratio of LH_2 to GH_2: 848**
- Videos of LH_2 spill outdoor: east sta; west sta
- **Solid deposits** (in HSL experiments) formed by condensed air and LH_2. May be enriched with oxygen (possible explosion-in HSL large scale experiments one secondary explosion occurred).
- **Ignition of LH_2 vapour cloud**: ignitions occurred in 10 of the 14 tests undertaken by HSL.

Solid deposit formation, HSL experiment, UK [1]

LH_2 vapour cloud ignition, HSL experiment, UK [2]

HyResponse

Sources:
[1] Royle M, Willougby D, 2012. Releases of unignited liquid hydrogen, Buxton: Health and Safety Laboratory.
[2] Hall J, Willoughby DB, Hooker P, 2013. Ignited Releases of Liquid Hydrogen, Buxton: Health and Safety Laboratory.

Cryo-compressed hydrogen storage

- Combines storage of hydrogen at **cryogenic temperatures** in a **vessel** that can be **pressurised** (e.g. to 35 MPa)
- Developed by Lawrence Livermore National Laboratory (LLNL) and BMW Group.
- Liquid hydrogen or cold compressed hydrogen can be stored.

Advantages:

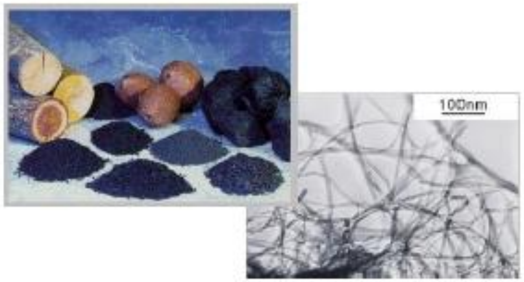
- higher hydrogen density compared to LH_2 and GH_2 storage options
- potential improvement in weight, volume and overall costs of tanks
- radically lower theoretical burst energy of cryogenic hydrogen.

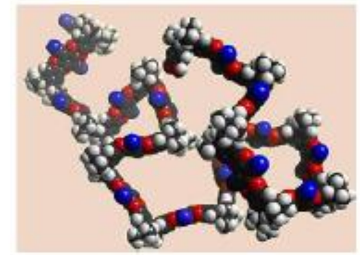
At R&D stage.

Source: Argonne National Laboratory Report , 2009 (ANL/09-33)

HyResponse

Options for solid storage of hydrogen





Overview of physical and chemical storage options

Carbon and HSA materials

- Activated carbon
- Nanotubes and graphite nanofibres
- Buckyballs
- Zeolites
- Metal organic frameworks (MOF)
- Clathrate hydrates

Rechargeable hydrides

- Alloys and intermetallic compounds
- Complex compounds
- Nanocrystals

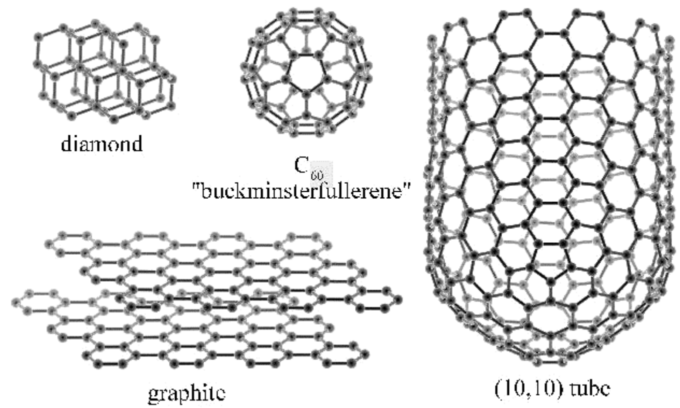
HSA- high surface area

Chemical hydrides (hydrolysis)

- Encapsulated sodium hydride (NaH)
- Lithium, calcium magnesium hydrides
- Complex hydrides $LiALH_4$; $NaAlH_4$

Chemical hydrides (thermal decomp.)

- Aluminium hydride
- Ammonia borozane



Chemical hydrides: $NaBH_4 + 4\,H_2O \rightarrow NaOH + H_3BO_3 + 4\,H_2$

$$3\,NaAlH_4 \rightarrow Na_3AlH_6 + 2\,Al + 3\,H_2$$

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Source: Mays, T. H2FC Technical School, 2014

Safety issues of solid storage options

- Very early R&D stage
- Many potential options: rechargeable hydrides, chemical hydrides (H_2O& thermally reactive), carbon and other HSA materials.
- Most-developed option: metal hydrides (potential for > 8 wt.% H_2 and > 90 kg/m^3 hydrogen-storage capacities at 10-60 bar).

Technical issues:
Weight, lower desorption temperatures, recharge time and pressure, high costs, cyclic life, container compatibility and optimisation.

Safety concerns:

- Pyrophoric materials: can react spontaneously in air (vigorous reaction, heating, ignition)
- Stability (many hydrides oxidize or react with water)
- Toxicity (e.g. metal hydrides are toxic to humans)
- Heat management (cooling required as materials release heat upon hydrogen uptake)
- Risk of dust cloud explosions (even for non-pyrophoric compounds)

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