

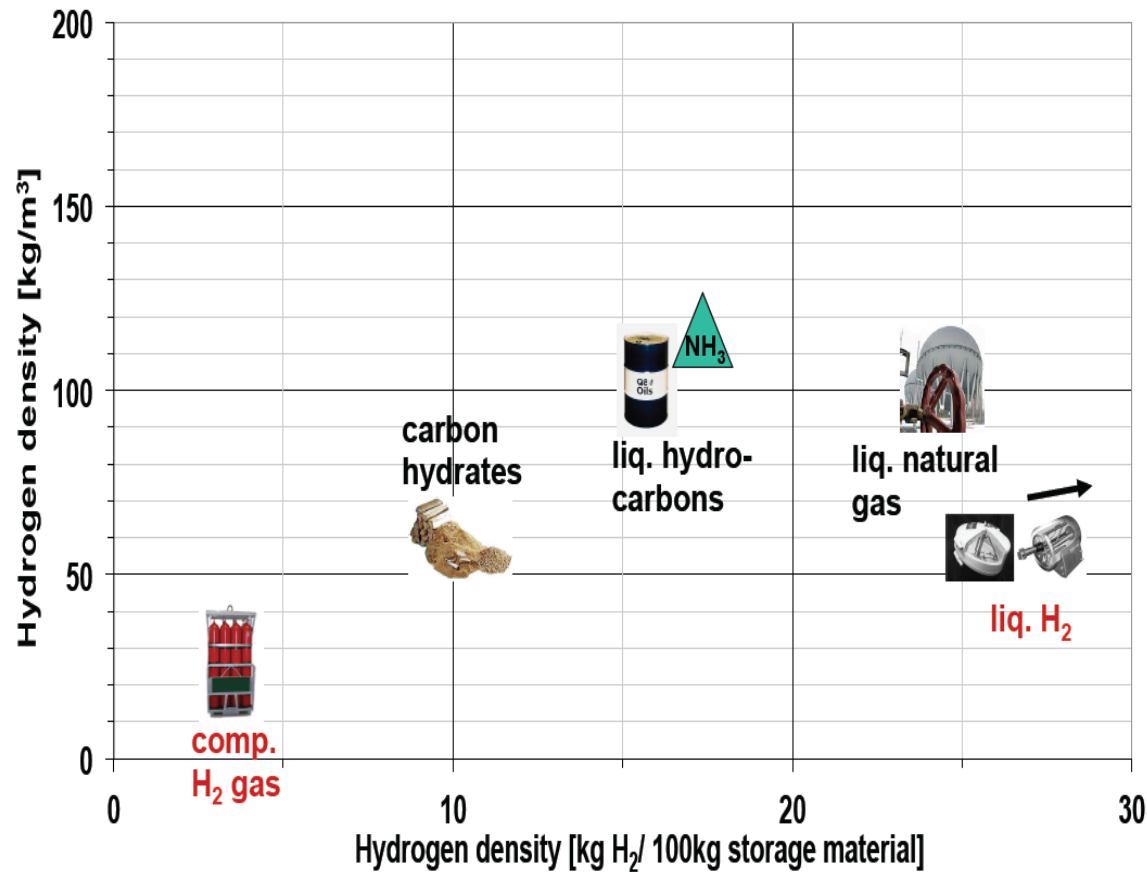
# Hydrogen storage



1. Hydrogen storage options
2. Compressed hydrogen storage
  - 2.1 Types of compressed gaseous hydrogen (CGH<sub>2</sub>) storage vessels
  - 2.2 On-board hydrogen storage
  - 2.3 Pressure relief devices (TPRDs)
  - 2.4 Consequences of catastrophic failure of high-pressure hydrogen storage
  - 2.5 Fire resistance rating (FRR) of hydrogen tanks
  - 2.6 Safety strategies for inherently safer high-pressure hydrogen storage
  - 2.7 CGH<sub>2</sub> storage: potential hazards and safety issues
3. Interaction of hydrogen with different materials (metallic and polymeric)
4. Limitation of hydrogen permeation
5. Liquefied and cryo-compressed hydrogen storage
6. Solid storage of hydrogen

1. Understand how hydrogen is stored and appreciate the challenges associated with different types of storages;
2. Distinguish between various storage options of hydrogen: compressed gas, liquefied and storage in solids;
3. Recognise different types of storage vessels currently in use to store compressed hydrogen;
4. Name the main components of on-board hydrogen storage;
5. Explain the working principle of a TPRD fitted onto hydrogen storage and make a comparison with TPRDs used in storage of other fuels (CNG, LPG, etc.);
6. Learn the main aspects of storage tank testing in general and bonfire test protocols in particular;
7. Explain the causes, which may lead to a catastrophic failure of high-pressure hydrogen storage vessel and its consequences;

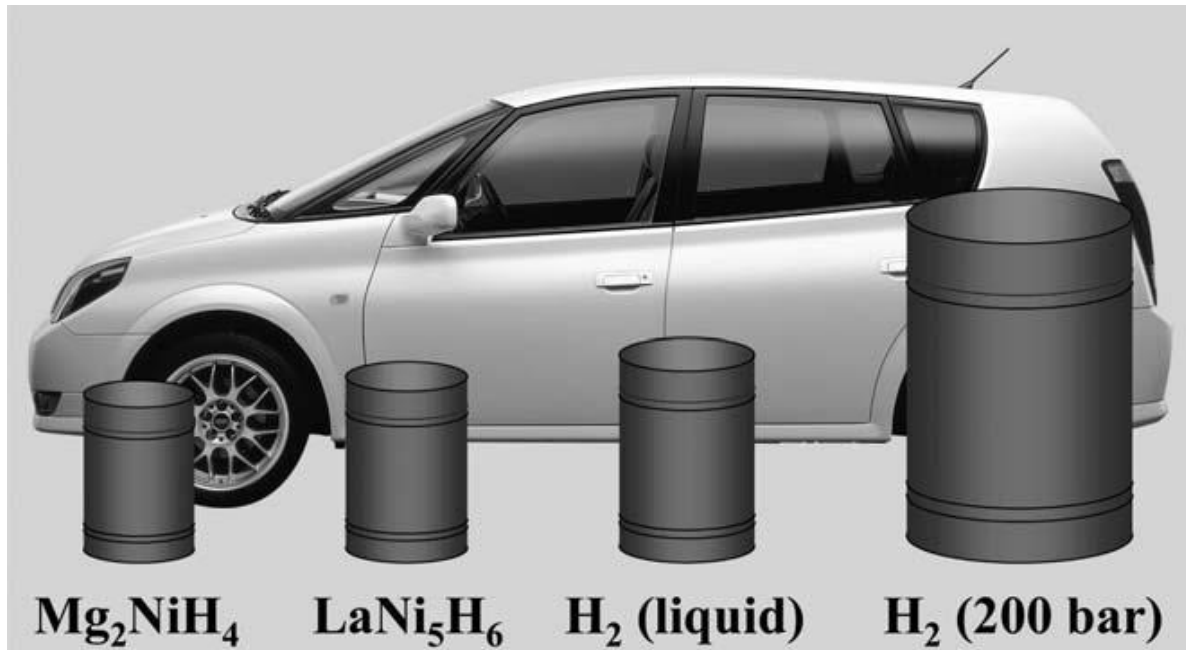
8. Identify factors affecting the fire-resistance rating of hydrogen tanks;
9. Define safety strategies for inherently safer compressed hydrogen storage;
10. Understand the main safety and technical issues associated with compressed hydrogen storage;
11. Explain the mechanisms of hydrogen interaction with metallic and polymeric materials;
12. Establish effect of hydrogen embrittlement on safety of hydrogen storage systems;
13. Define the hydrogen permeation phenomena;
14. Point out the safe permeation rate for hydrogen storages on-board of passenger cars and buses;
15. Identify safety concerns associated with liquefied hydrogen storage and storage of hydrogen in various solid materials.



- 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

## Hydrogen storage

### Volumetric and gravimetric capacities



Source: Risø Energy Report 3, 2004

**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).**

- **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

## Hydrogen storage

### Compressed gaseous (CGH<sub>2</sub>) storage

- For **industrial** or **laboratory** uses CGH<sub>2</sub> stored in **metal cylinders** at pressures of **15-20 MPa**.
- For **on-board** storage CGH<sub>2</sub> 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<sub>2</sub> pressurised in stages (up to **100 MPa**).



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

*Example:* Linde hydrogen refuelling station

**Note:** 1MPa =10 bar; 1MPa =  $10^6$  Pa

<https://www.youtube.com/watch?v=Pjh639S2dek>

- ❖ **Nominal Working Pressure (NWP)** is a gauge pressure, which characterises typical operation of a system. For  $\text{CGH}_2$  containers *NWP is a settled pressure of compressed gas in fully filled container at a uniform temperature of 15 °C* (definition).
- ❖ FC vehicles onboard 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)**.
- ❖ 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**.

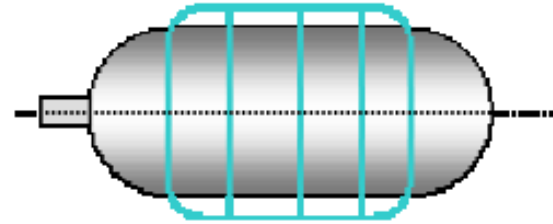


## Hydrogen storage

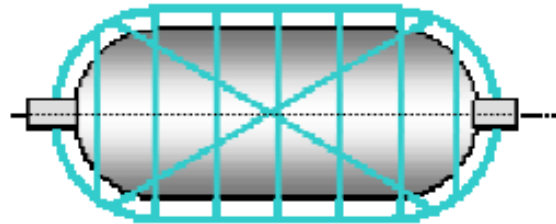
### Tanks for $\text{CGH}_2$ storage



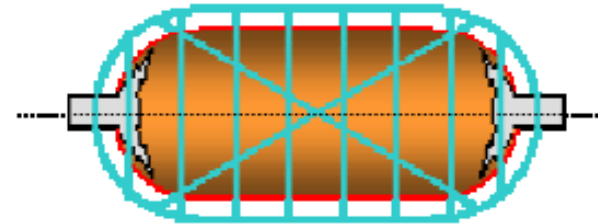
**Type I**



**Type II**



**Type III**



**Type IV**

#### 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

In 2014 the first prototype of **type V** tank was produced. It is an all-composite vessel without a liner.

**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), etc.
- **for wrapping** – thermoset or thermoplastic resin, aramid fibres, etc.
- Metals must not allow hydrogen permeation or be subjected to hydrogen embrittlement (especially when their use involve extensive pressure and temperature cycling)

### 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 constraints**

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

## Hydrogen storage

### 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



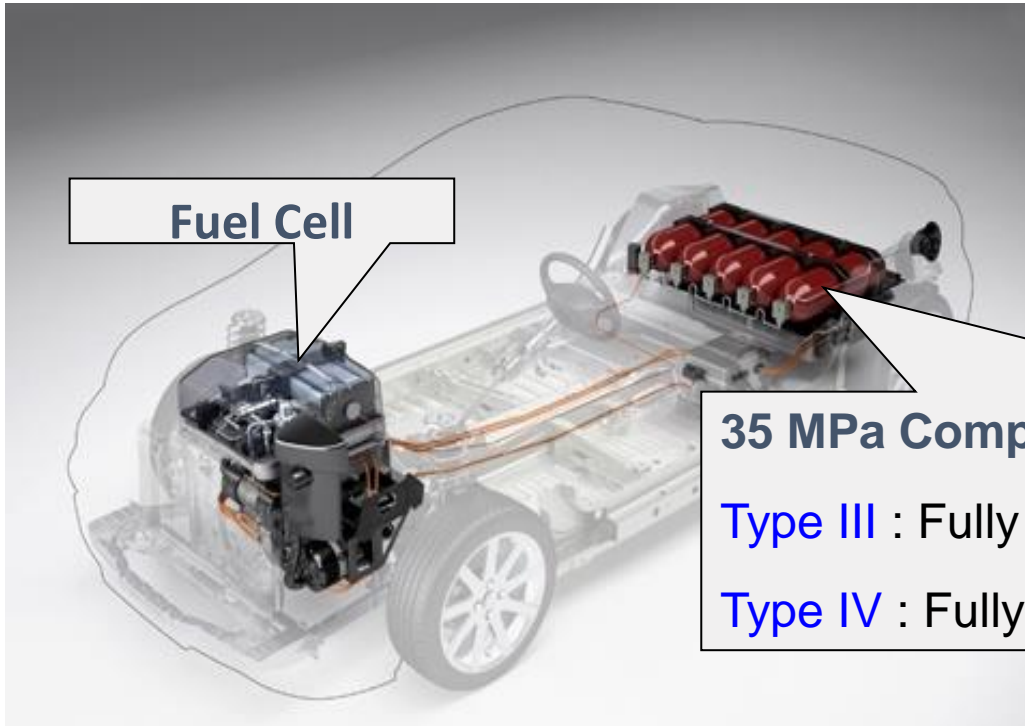
- **Non-metallic (plastic) liners** wrapped with fibre/polymer matrix
- Metallic bosses are in place for shut-off valves installation
- Fibre wrapping provides **strength** required
- Although the cylinders are lighter than all-metal liners they are **more expensive**
- NWP = **70 MPa**
- Disadvantage: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

## Hydrogen storage

### 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

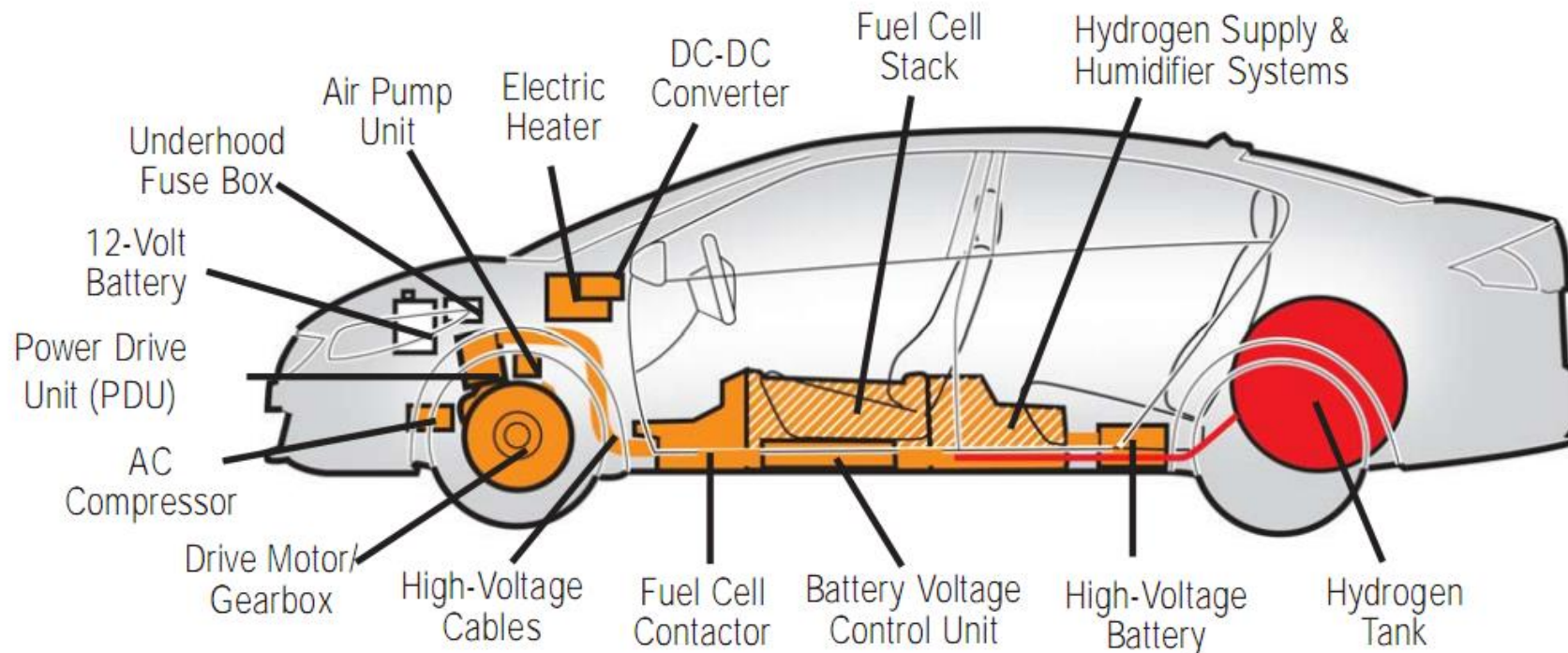
**Type III** : Fully wrapped composite tanks with **metal liners**

**Type IV** : Fully wrapped composite tanks with **plastic liners**

## Hydrogen storage

### 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)

- **FC bus** (typically 25 kg hydrogen, 600 L hydrogen at 70 MPa)
- 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.**



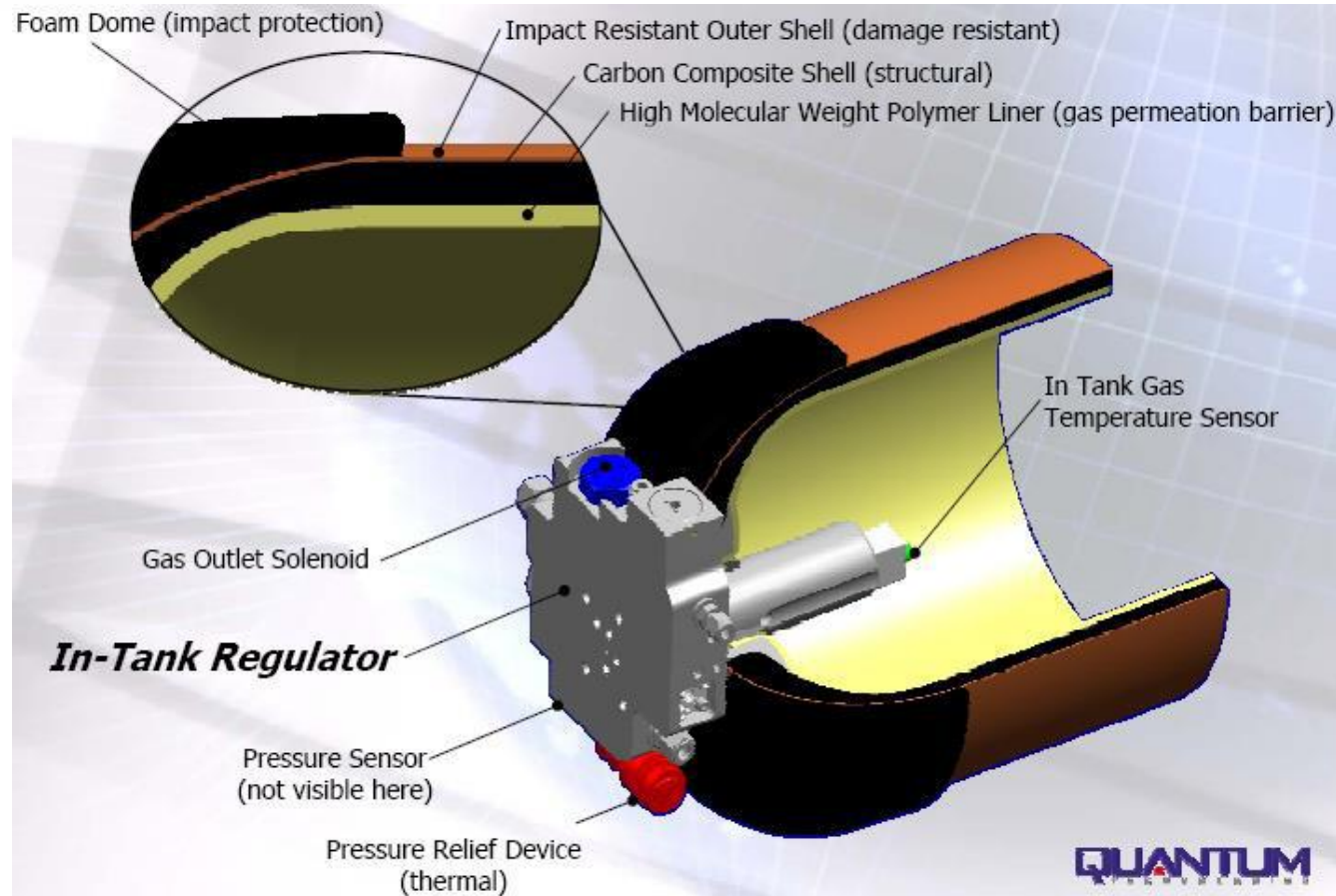
Source: Tim Mays, H2FC Technical School , 2014



Photos: courtesy of National HFC FR training, USA

## Hydrogen storage

### Type IV tank for GH<sub>2</sub> storage



Cross section of Quantum hydrogen storage tank wall

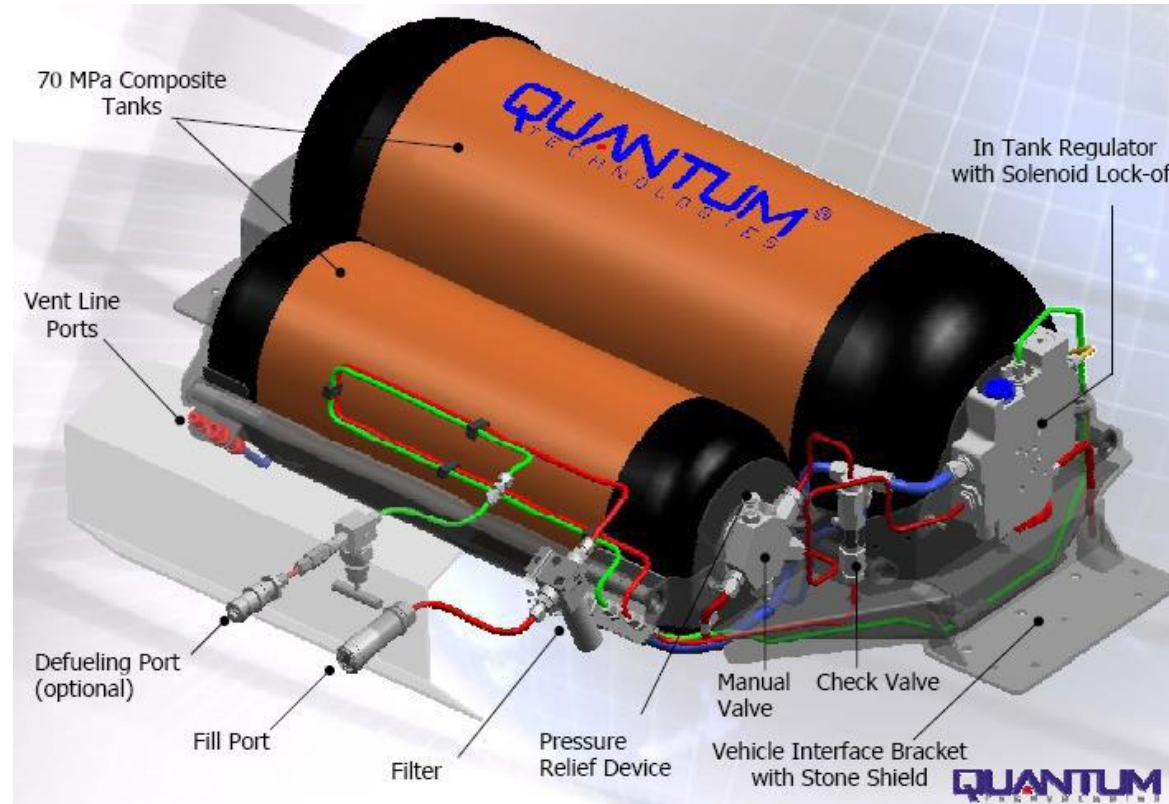
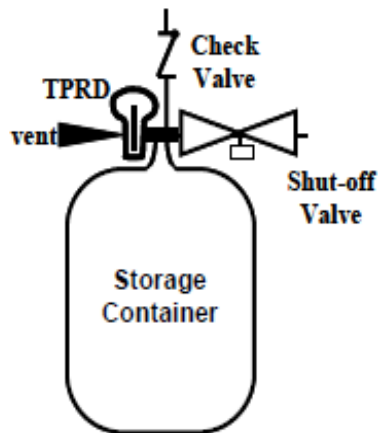
Source: [http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/04\\_warner\\_quantum.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/04_warner_quantum.pdf)



## Hydrogen storage Composite type IV tank

### Typical components:

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



Source: [http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/04\\_warner\\_quantum.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/04_warner_quantum.pdf)

- *Permeation* is specific to type IV vessels. Permeation rate should not be higher than **6 ml/hr/L** (at 20°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

### 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**

- **In the event of a fire, thermally activated pressure relief device (TPRD)** provides a controlled release of the  $\text{CGH}_2$  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.
- 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.

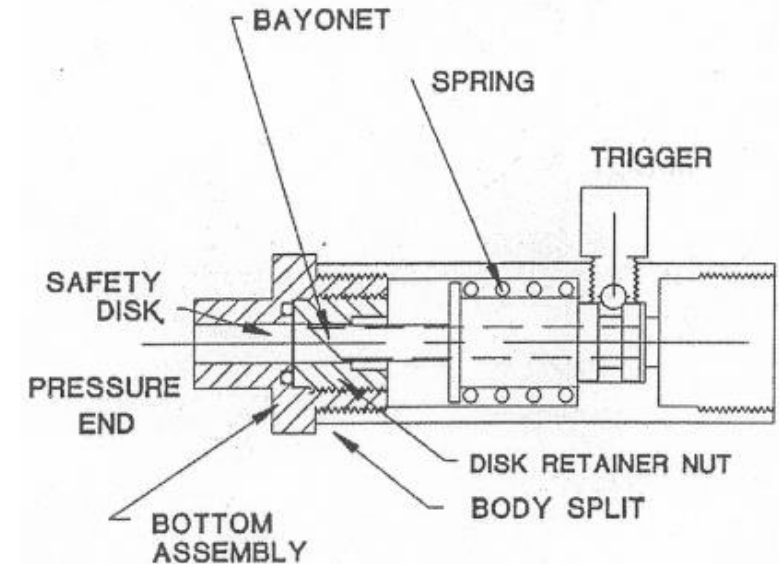
Sources:

[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.

### How TPRDs work

- PRDs are designed to open when pressure or temperature reaches a certain limit. TPRDs open if temperature is above **108-110°C**.
- 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)



[Glass bulb PRD](#) (Rotarex)



## Hydrogen storage

### Why and how TPRDs fail

#### **TPRD failures:**

Type 1: a TPRD fails to vent properly.

Type 2: a premature activation of a TPRD.

Type 3: a TPRD fails to be activated.

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

Useful link: <http://depts.washington.edu/vehfire/begin.html>

CNG bus on fire videos:

<https://www.youtube.com/watch?v=vHf2o9oVY24>

<https://www.youtube.com/watch?v=lvuDiZkHJUo>

- 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 TPRD from the container protected by the PRD, due to the normal operation or failure of another component.
- The hydrogen gas discharge from TPRD 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.

#### 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.

**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
<b>EU regulation 406/2010</b>	Implementing EC Regulation 79/2009 on type-approval of hydrogen-powered motor vehicles	EU	2010
<b>GTR 2013</b>	Proposal for a Global Technical Regulation (GTR) on hydrogen and fuel cell vehicles. (ECE/TRANS/WP. 29/GRSP/2013/41).	International	2013
<b>GTR Number 13</b>	The United Nations Economic Commission for Europe Global Technical Regulation (GTR) Number 13 (Global Technical Regulation on Hydrogen and Fuel Cell Vehicles)	North America, Japan, Korea, EU	2017



- 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.

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

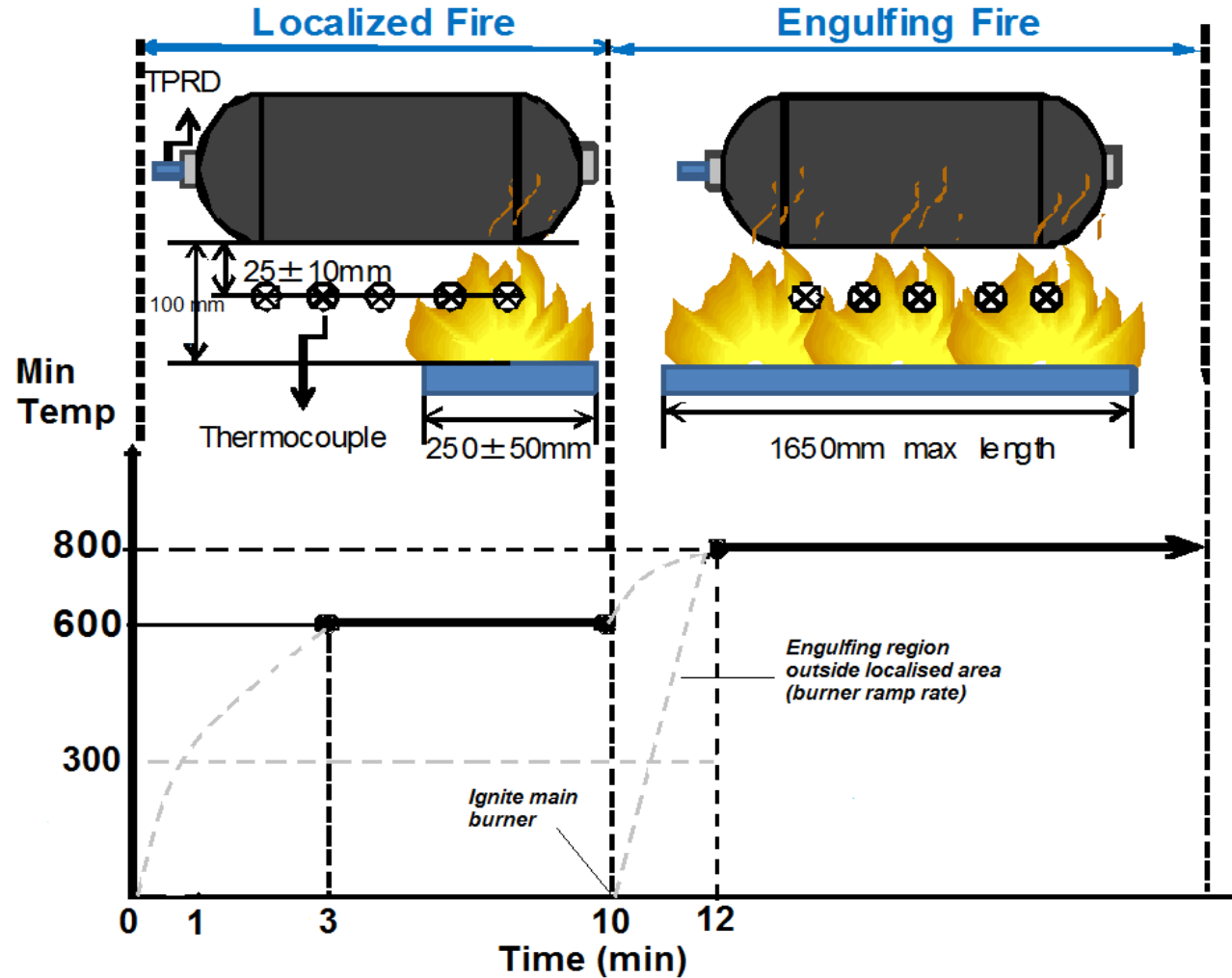
<b>Test method</b>	Method 1, generic installation test (without protective devices, only thermal shielding) Method 2 for specific vehicle installation (includes protective devices and other vehicle components)
<b>Pressure in the container</b>	100% of nominal working pressure (NWP)
<b>Medium in the container</b>	Compressed hydrogen/compressed air can be used if agreed in certain regions/countries
<b>Distance from the container to the fire source</b>	100 mm
<b>Fire source</b>	LPG burners configured to produce uniform minimum temperature
<b>Fire source length</b>	1.65 m
<b>Fire source width</b>	Encompass the entire diameter (width) of the storage system
<b>Number and the location of thermocouples (TCs)</b>	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
<b>Position of TCs</b>	25±10mm from outside surface of the container along its longitudinal axis
<b>Additional TCs</b>	At TPRD sensing point or at any other location
<b>Wind shields</b>	To ensure uniform heating

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

<b>Length and width of localised fire</b>	250±50 mm and the width encompasses the entire diameter of the tank
<b>Localized fire exposure area</b>	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
<b>T<sub>min</sub> of TCs in localized area</b>	<b>From 600 to 900 °C</b> - from 3 to 10 mins of fire exposure
<b>T<sub>max</sub> of TCs in localized area</b>	<b>From 800 to 1100 °C</b> - from 12mins until release of hydrogen via TPRD(s)
<b>Start of engulfing fire</b>	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
<b>T<sub>min</sub> of TCs within engulfing region</b>	<b>800 °C</b> – from 12 mins until release of hydrogen via TPRD(s)
<b>Duration of the test</b>	Test continues until the <b>system vents through a TPRD</b> and the <b>pressure falls to less than 1 MPa</b> . The venting shall be continuous (without interruption), and a <b>storage system shall not rupture</b> . 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 <b>shall not occur</b> .

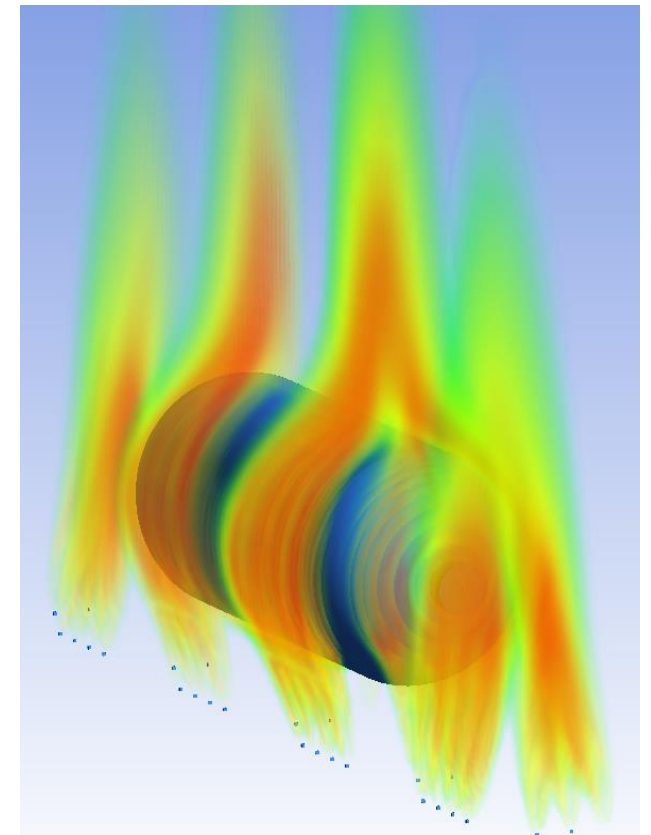
## Hydrogen storage

### Fire test procedure (3/3)



**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



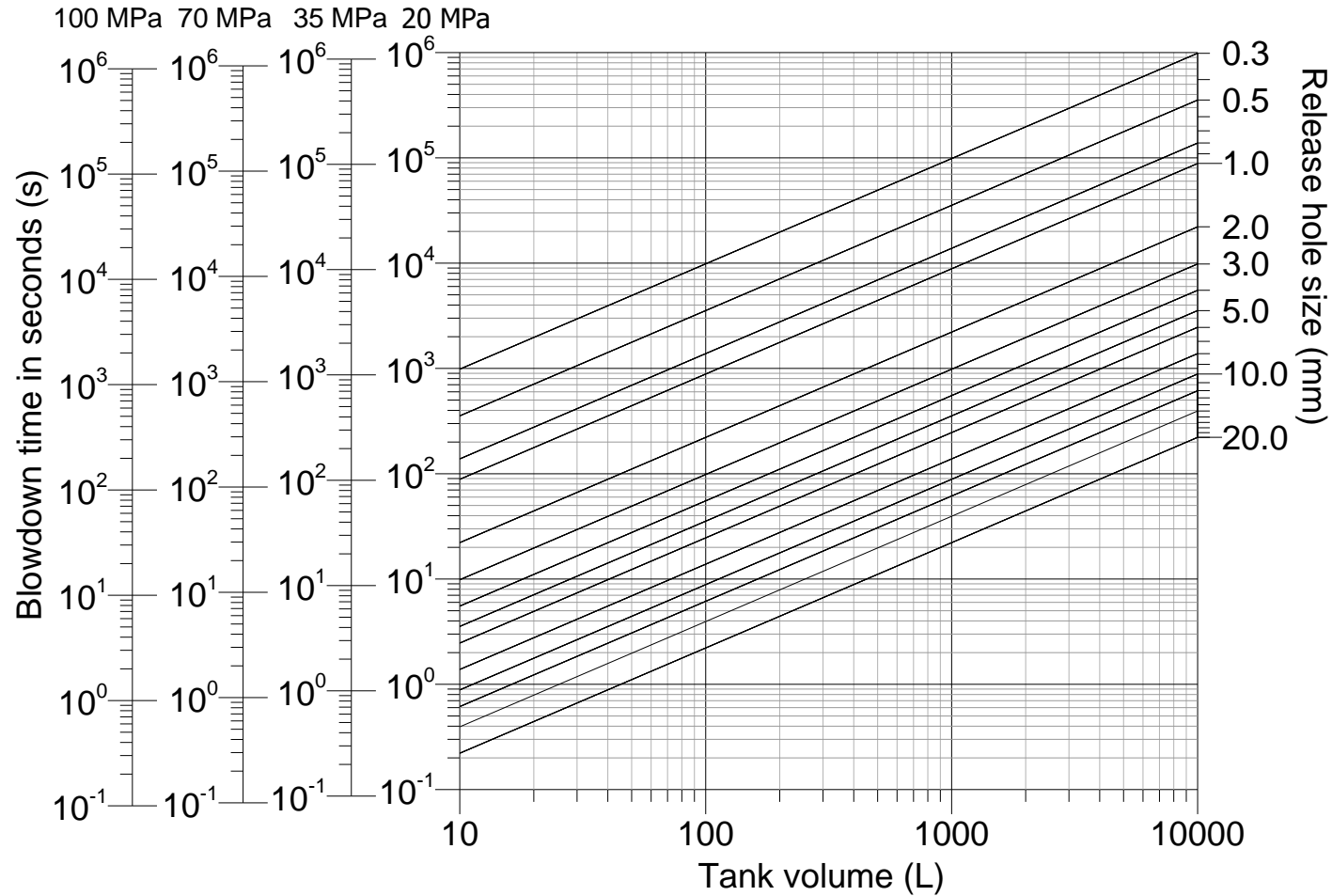
**Table 4. A summary of conditions for engulfing fire test**

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

# Hydrogen storage

## Blow-down of hydrogen storage tank

Nomogram for hydrogen tank blowdown to 0.2 MPa



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



- 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.
- Compliance to thermal requirements begins 1 minute after entering the period with constant minimum and maximum limits and is based on a 1- minute rolling average of each thermocouple.
- 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.**

## Hydrogen storage

### Effects of fire on high pressure storage tanks

- Maximum temperatures measured on the composite surface: (750-850 °C)
- The cylinders rupture in a fire, where TPRD is absent or does not activate.
- The polymer 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.

#### Engulfing bonfire test



#### A wall of the composite tank after the fire



#### Results of the leak test after the fire



### 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 ( $L \times D = 84 \times 41$  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,  $L \times W = 4.5 \times 1.8$  m), 28 cm above the ground. **HRR=265 kW (GTR 2013 issue)**,  $P = 31.8$  MPa. **FRR = 12 min 18 s.**

Sources: [1] Weyandt, N (2006). Vehicle bonfire to induce catastrophic failure of a 5000-psi hydrogen cylinder installed on a typical SUV, Motor Vehicle Fire Research Institute. Report. December, 2006. Available from: [www.mvfri.org](http://www.mvfri.org)

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

#### Test observations:

- **The internal cylinder temperature and pressure increased only marginally (due to a low thermal conductivity of CFRP)** from 27°C to 39°C 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.

## Hydrogen storage

### Bonfire test: type IV tank (no TPRD)

**“Fire resistance” is 1-6 minutes.  
No combustion contribution to  
the blast.**

<https://www.youtube.com/watch?v=n-Jh5kPdvTE&list=PLlphoM9ggM3Rf-Npmdq0S3WrCSpx0U4SL&index=9>





## Hydrogen storage

### 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, 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):**

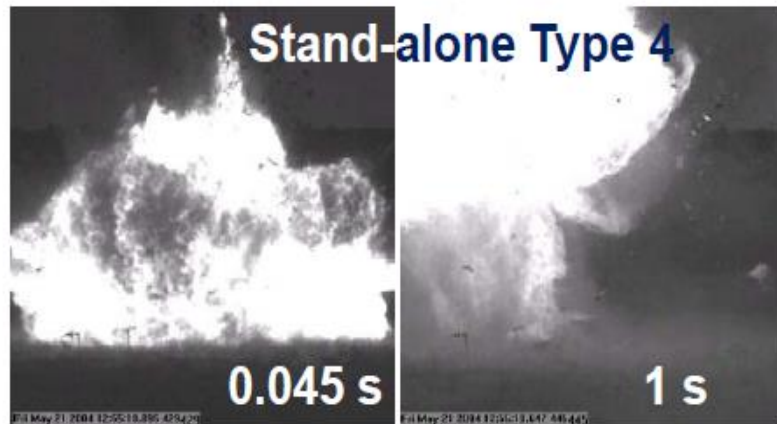
- 10.3-20 kPa - people are knocked down;
- 13.8 kPa - possible fatality by being projected against obstacles;
- 34 kPa - eardrum rupture;
- 35 kPa - 15% probability of fatality;
- 54 kPa - fatal head injury;

**> 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  $P \times V$  (larger tanks has more hazardous potential through the blast wave in case of rupture)

### Fireball

- Type IV: a fireball is **7.7 m in diameter** (45 ms after tank 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<sup>2</sup>** (NOTE: about 35 kW/m<sup>2</sup> - 1% fatality in 10 seconds).



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

- 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”.





## Hydrogen storage

### Fire resistance of storage vessels



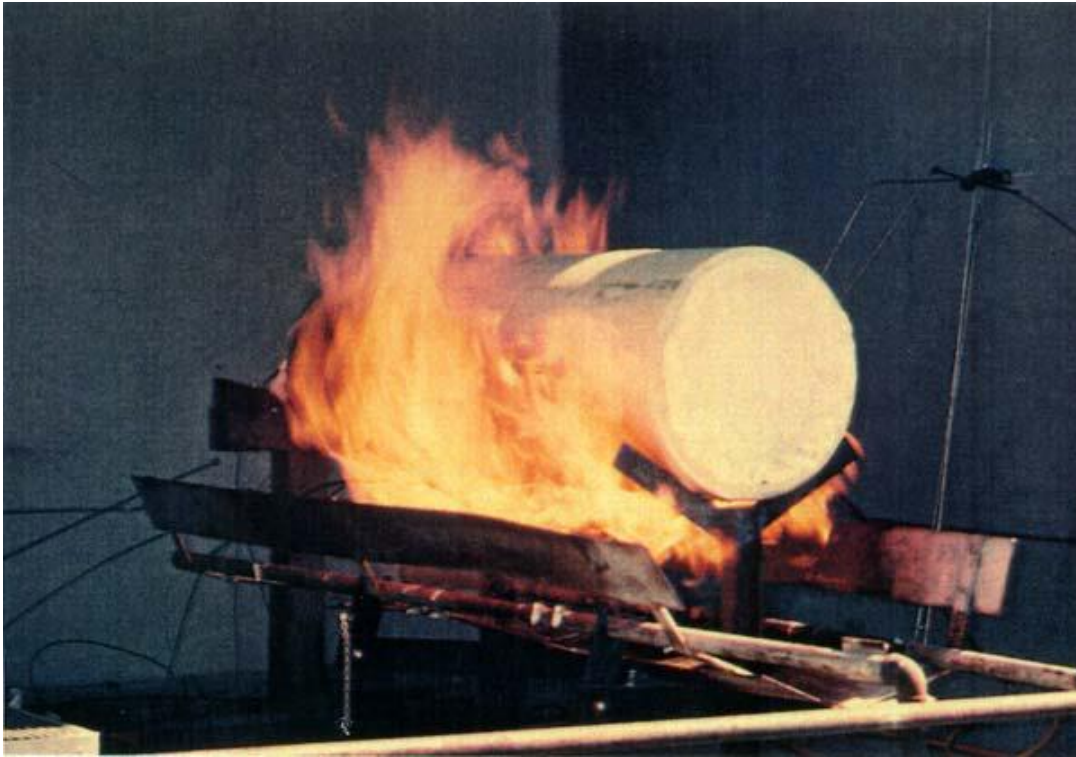
[Fire test, CNG tank not equipped with a PRD](#)

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.

- 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!**

## Hydrogen storage

### 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).

#### 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.



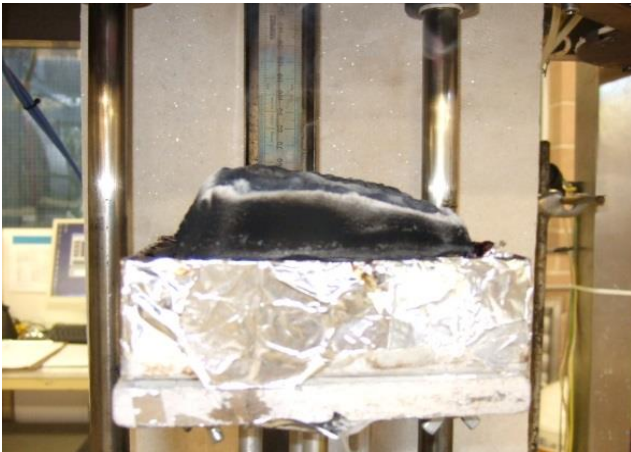
- With one layer of **intumescent paint applied to** Type IV tank an **increase of the FRR by an order of magnitude!**
- There is an urgent need to demonstrate increased fire resistance of Type III and IV tanks used by car manufacturers (if OEMs say there is “no safety problems” – they have to demonstrate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

## Hydrogen storage

### Intumescence



Intumescent coating **before** the fire exposure

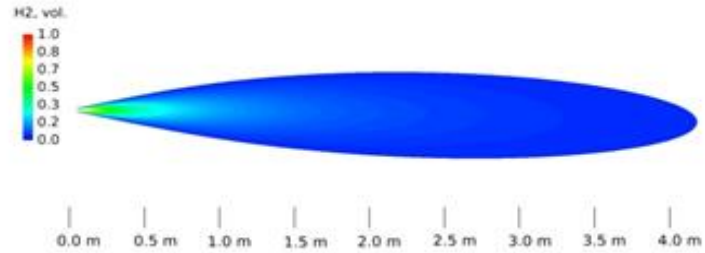


Intumescent coating **after** the fire exposure

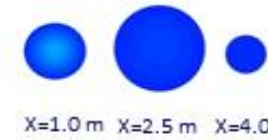
- Intumescence is a versatile method for providing reaction and resistance to fire to materials
- When heating beyond a critical temperature, **the intumescent material begins to swell** and then to expand forming an insulative coating limiting heat and mass transfer
- A multi component system- essentially consists of **a char former** (e.g. pentaerythritol); **acidic component** (e.g. ammonium polyphosphate); a **spumific/blowing agent** (e.g. melamine)

## Hydrogen storage TPRDs with plane nozzles

AR=1.0

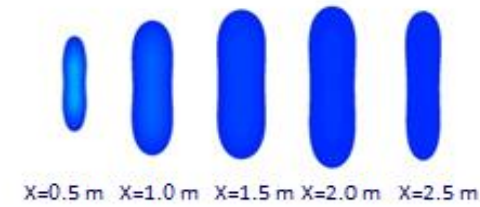
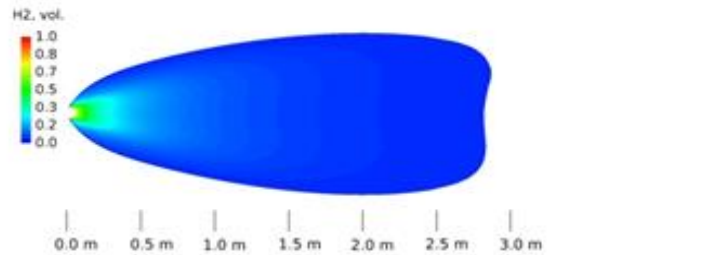


$X_{H_2} = 0.04 - 1.0$



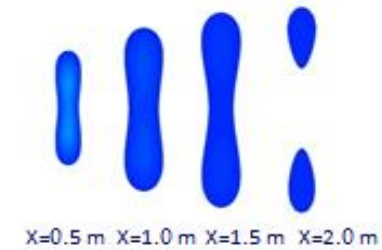
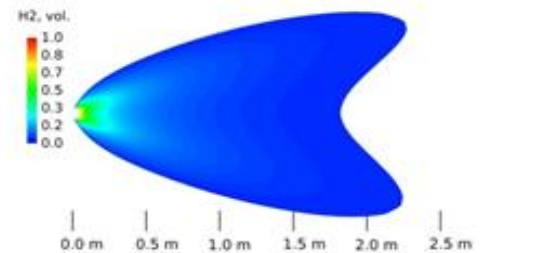
Round jet

AR=5.0



Plane jet

AR=12.8



Plane jet

**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.

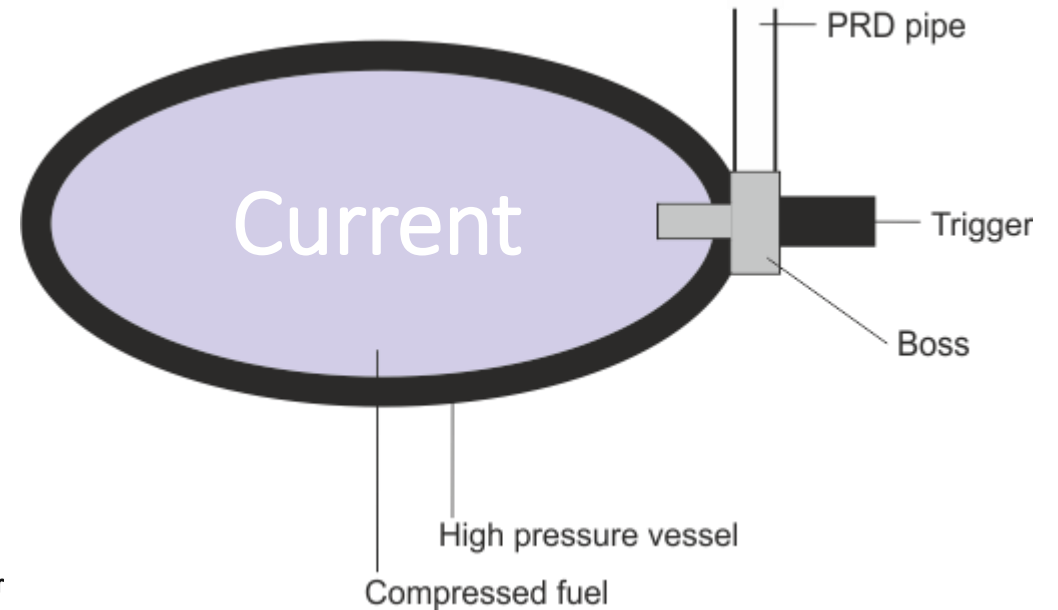
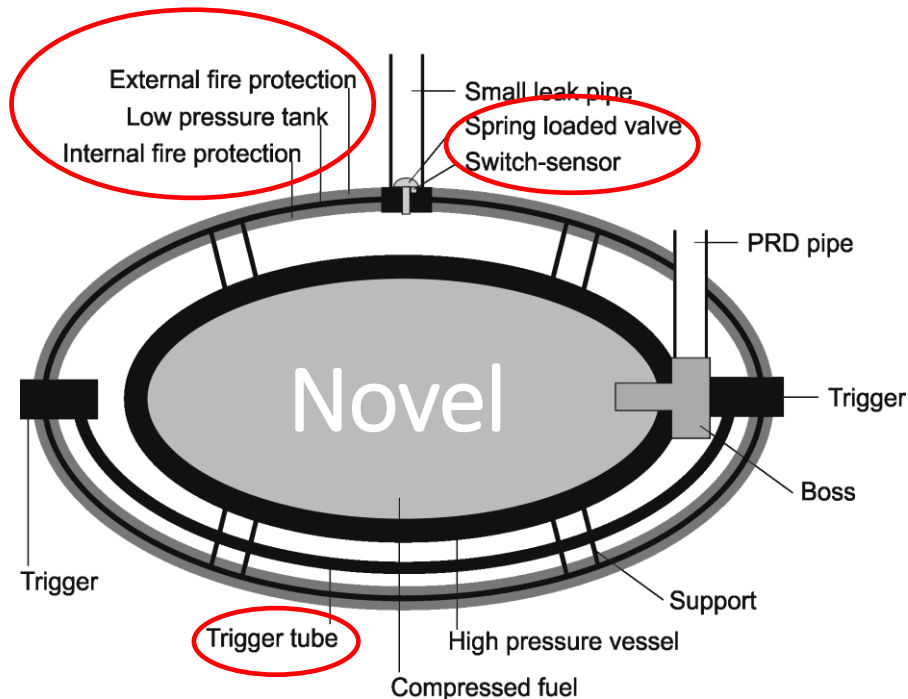
## Hydrogen storage

### 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**

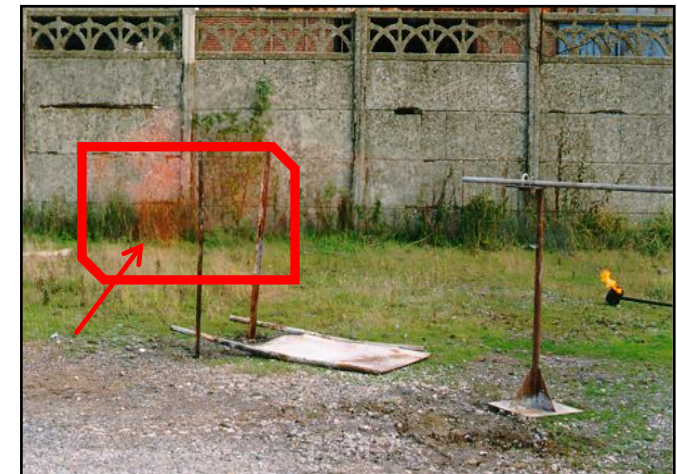


Work-in-progress at Ulster

- **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.



- 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.



- 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 TPRD](#)



<https://www.youtube.com/watch?v=dzeqGxlssk8&list=PLlphoM9ggM3Rf-Npmdq0S3WrCSpx0U4SL&index=8>

- Tanks for LH<sub>2</sub> can store more hydrogen compared to those for GH<sub>2</sub>: volumetric capacity of LH<sub>2</sub> 0.070 kg/L as opposed to 0.030 kg/L for GH<sub>2</sub> tanks at 70 MPa.
- LH<sub>2</sub> stored at low (**cryogenic**) **temperatures** -253 °C 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<sub>2</sub>).

#### 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

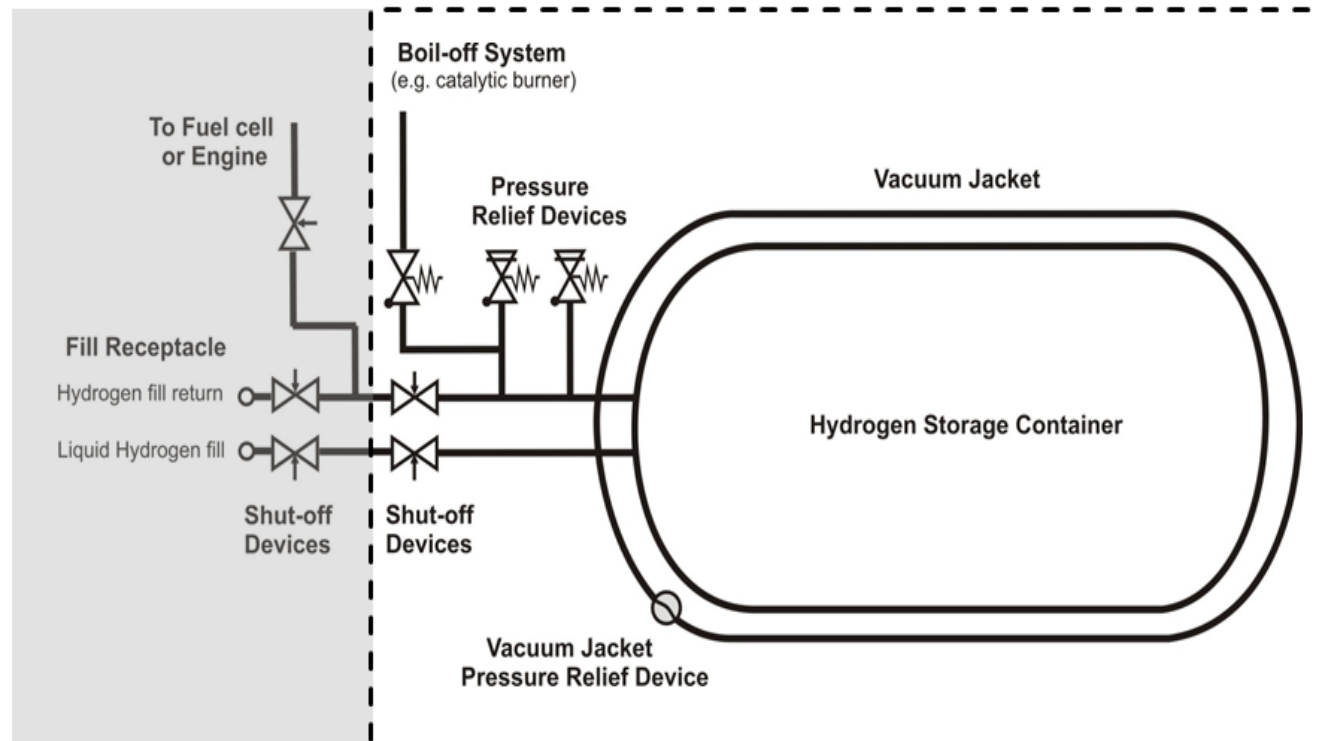
## Hydrogen storage

### Liquefied hydrogen (LH<sub>2</sub>) storage (2/2)

Components of LH<sub>2</sub> storage:

- LH<sub>2</sub> storage container
- Shut-off devices
- A boil-off system
- TPRDs
- The interconnecting piping (if any) and fittings between the above components

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



- **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<sub>2</sub> 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).
- **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.

- Boil-off/evaporation can be caused by:
  - *Ortho-para H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> at a high pressure is transferred from trucks and rail cars to a low pressure vessel

- In case of a LH<sub>2</sub> leak or spill, a hydrogen cloud will be formed; could flow horizontally for some distance or even downward, depending on the terrain and weather condition.
- **Volume ratio of LH<sub>2</sub> to GH<sub>2</sub>: 848**
- **Solid deposits** (in HSL experiments) formed by condensed air and LH<sub>2</sub>. May be enriched with oxygen (possible explosion-in HSL large scale experiments one secondary explosion occurred).
- **Ignition of LH<sub>2</sub> vapour cloud**: ignitions occurred in 10 of the 14 tests undertaken by HSL.



Solid deposit formation, HSL experiment, UK [1]



LH<sub>2</sub> vapour cloud ignition, HSL experiment, UK [2]

Sources:

[1] Royle M, Willoughby 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.





Hydrogen storage

**LH<sub>2</sub> releases (2/2)**

Videos of LH<sub>2</sub> spill outdoor

[https://www.youtube.com/watch?v=pD\\_OrWVJaW4&list=PLlphoM9ggM3Rf-Npmdq0S3WrCSpx0U4SL&index=11](https://www.youtube.com/watch?v=pD_OrWVJaW4&list=PLlphoM9ggM3Rf-Npmdq0S3WrCSpx0U4SL&index=11)





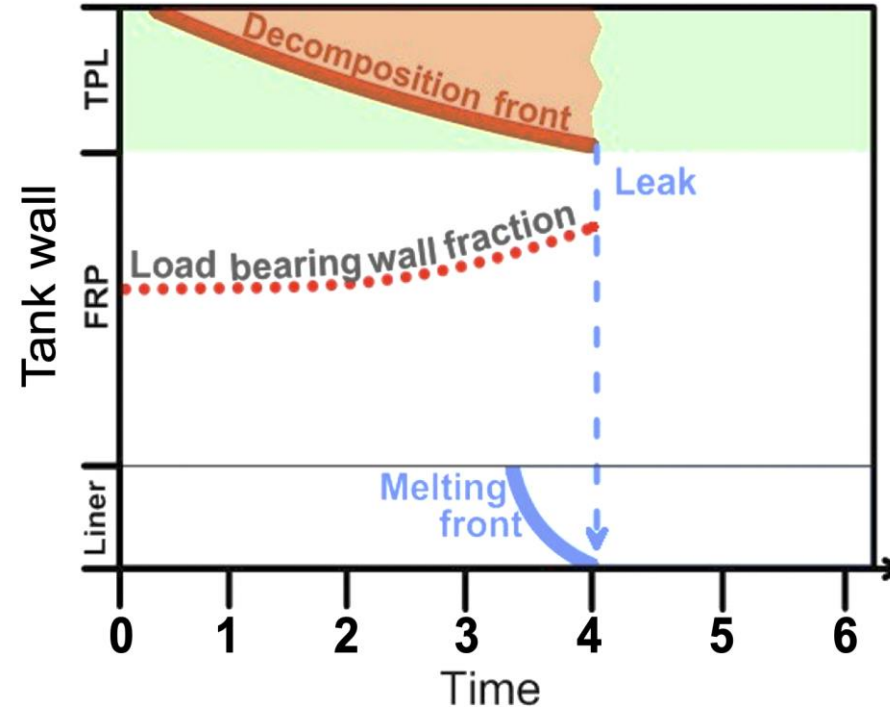
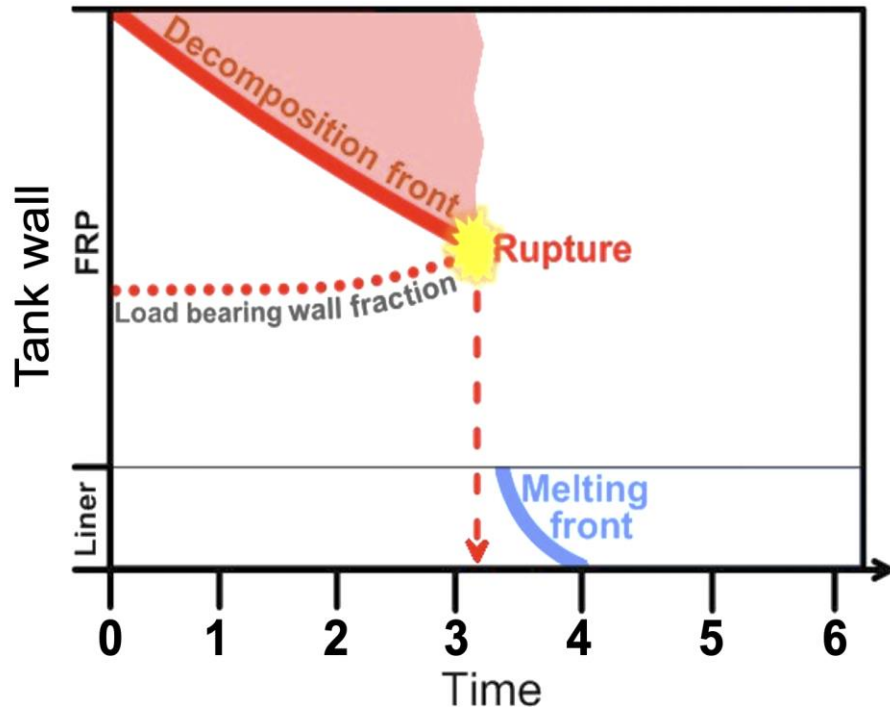
## Hydrogen storage

### 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:**

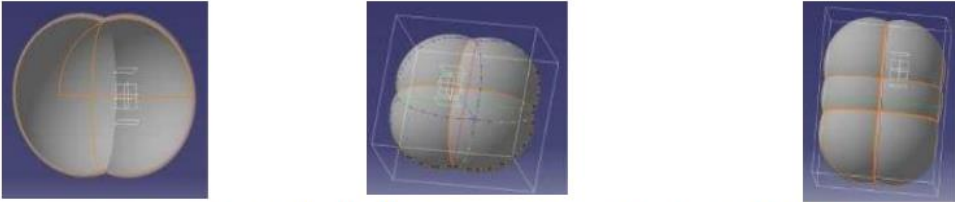

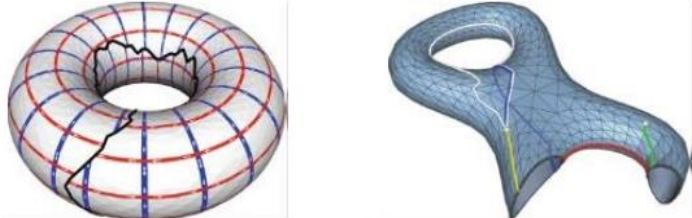
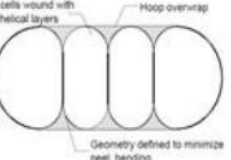

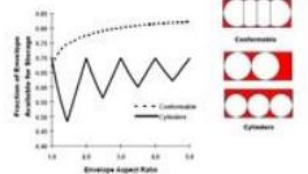
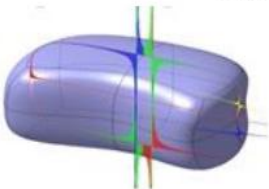

- higher hydrogen density compared to LH<sub>2</sub> and GH<sub>2</sub> storage options
- potential improvement in weight, volume and overall costs of tanks
- radically lower theoretical burst energy of cryogenic hydrogen.



Ulster's IP:  
International (PCT)  
Application No  
PCT/EP2018/053384

- Two composites with different thermal properties. External composite “TPL” has lower thermal conductivity, the internal part of wall composite “FRP” has higher thermal conductivity.
- Once the liner is melted, hydrogen starts to leak through tank wall safely as insignificant leak and the internal pressure reduces before the composite wall loses its load-bearing ability.

## Hydrogen storage Novel storage techniques

 <p>Conformable Tanks : Delft University of Technology, The Netherlands</p>		
 <p>Freie Berlin University</p>	 <p>Conformable Tank : DLR, Germany</p>	
 <p>Individual cells wound with hoop and helical layers</p> <p>Hoop overlap</p> <p>Geometry defined to minimize peel, bending</p>	 <p>THIOKOL</p>	 <p>Pressure of Hydrogen</p> <p>Envelope Aspect Ratio</p> <p>Conformable</p> <p>Cylindrical</p>
<p>Conformable Tanks : Thiokol Propulsion</p>		
 <p>Conformable tank : Hype project</p>	 <p>Conformable tubes : Copernic Project</p>	



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# Hy Responder

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FUEL CELLS AND HYDROGEN  
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