



HyResponse

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LECTURE - Safety of hydrogen storage

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Contents

Introduction	3
Objectives of the lecture.....	3
Hydrogen storage options	4
Compressed gaseous hydrogen storage	5
Types of cGH ₂ storage vessels.....	6
On-board hydrogen storage	8
Pressure Relief Devices	11
Testing of cGH ₂ tanks.....	13
Consequences of catastrophic failure of high-pressure hydrogen storage (blast waves, fireballs, projectiles)	17
Fire resistance rating of hydrogen tanks	18
Safety strategies for inherently safer high-pressure hydrogen storage	19
Potential hazards and safety issues associated with cGH ₂ : summary	20
Interaction of hydrogen with different materials.....	21
Interaction of hydrogen with metallic materials	21
Interaction of hydrogen with polymeric materials.....	25
Limitation of hydrogen permeation.....	26
Liquefied and cryo-compressed hydrogen storage	28
Solid storage of hydrogen	31
Summary	31
References	33

Introduction

Hydrogen is typically stored and transported in two forms: as a compressed hydrogen gas or as a cryogenic liquid. The most common way to store hydrogen is in metal or composite cylinders/tanks of different sizes and capacities. Sometimes they can be connected into a bundle or gathered onto a basket for transportation. Due to a small size of its molecules hydrogen is prone to leak easily through some materials, cracks, or poor joints of the storage tanks, as opposed to other common gases at equivalent pressures. Although hydrogen is generally non-corrosive and does not react with the materials used for storage containers, at certain temperature and pressure conditions it can diffuse into a metal lattice causing a phenomenon known as 'hydrogen embrittlement.' In addition, in case of fires, the composite materials used for storage vessels may degrade and a loss of hydrogen containment may occur. In the worst case scenario, this may lead to a catastrophic rupture of a hydrogen storage tank, generating a blast wave followed by a fireball and flying projectiles/missiles. For this reason, hydrogen storage equipment must be designed and maintained to high safety standards to ensure the integrity of the container.

The present lecture gives an overview of hydrogen storage options and also addresses the main safety and technical issues associated with them. It also covers the topics of hydrogen interaction with different types of materials and hydrogen permeation, which are extremely relevant to hydrogen storage technologies. It should be mentioned that the topic of hydrogen storage is vast; thus this lecture is mainly focused on high-pressure hydrogen storage systems as this technology is most common and wide-spread. The phenomena such as unignited releases, fires and explosions will be discussed in the subsequent lectures.

Objectives of the lecture

By the end of this lecture first responders will be able to:

- 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 the 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.

Hydrogen storage options

Hydrogen storage is an enabling technology across the entire range of FCH applications, from on-board vehicles to stationary and portable power generation [1]. There is no universal solution for hydrogen storage. Instead, the solution must be carefully selected to address specific system requirements. For example, the space and weight are critical factors for FC passenger vehicles, whereas weight can be a desirable attribute for FC forklifts or marine applications. For space applications NASA has been utilising liquid hydrogen for years [2].

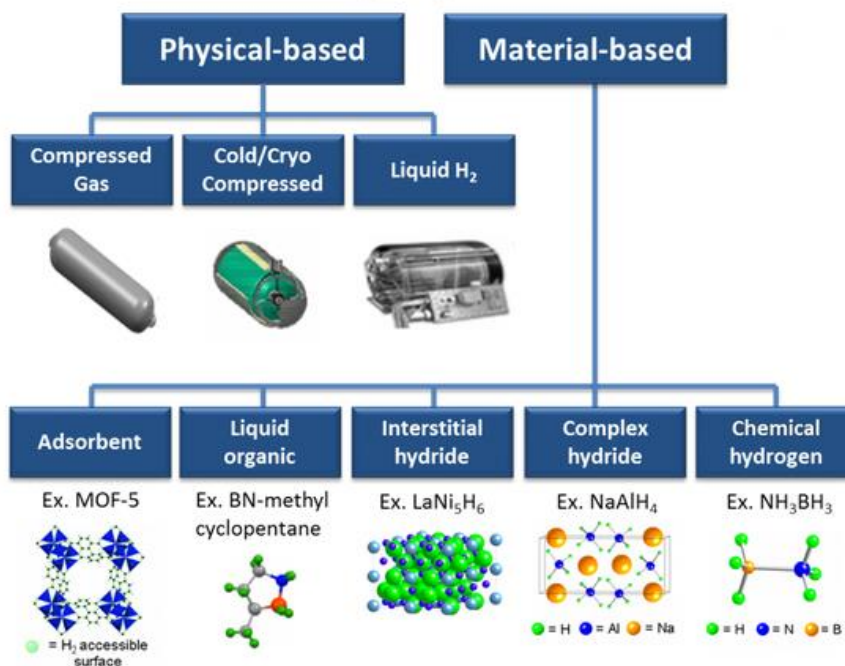
Hydrogen is the lightest gas with a low normal density of 0.09 g/L (at 288 K and 1 bar). As it follows from Table 1 it has very high energy content per mass of any fuel (about three times more than petrol). However, due to its low density, hydrogen has very low energy content per unit volume (about four times less than petrol). As a result, storing hydrogen, particularly within the size and weight constraints of a vehicle, represents a challenge [3]. The research is underway to develop safe, reliable, compact, light-weight, and cost-effective hydrogen storage technology.

Volumetric and *gravimetric capacities* (densities) are two terms often used when describing gas storage approaches. In the case of hydrogen, research activities are geared towards increasing both capacities, i.e. higher both volumetric and gravimetric capacities are desirable. As it is shown in Table 1 there is more energy in 1 kg of hydrogen than in one 1 kg of petrol. However, it is also evident that the same mass of hydrogen occupies a larger volume. Hydrogen is not a liquid at ambient temperature and, therefore, to store the amounts sufficient for a certain driving range on a vehicle (above 500 km) it is necessary to either compress it to very high pressures (for example to 700 bar for automotive applications), or to cool it significantly to obtain a liquid form. These extremes of pressure and temperature present safety challenges for the materials used and in the event of a loss of containment.

Table 1. Energy content by weight and by volume for hydrogen and other common fuels [4].

	Hydrogen	Natural gas	Petrol
Energy content per unit mass	2.8 times more than petrol	~1.2 times more than petrol	43 MJ/kg
Energy content per unit volume	4 times less than petrol	1.5 times less than petrol	120 MJ/Gallon

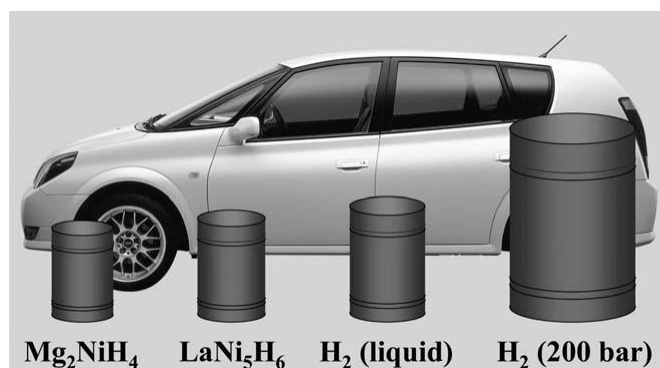
Hydrogen can be stored *physically* as a compressed gas (cGH₂) or as a cryogenic liquid (LH₂). The gaseous hydrogen storage systems typically require compressed gas vessels, i.e. tanks (to withstand up to 700 bar pressure). Storage of hydrogen as a liquid requires extremely low temperatures because its boiling point at 1 atm pressure is -253°C. The LH₂ storage is commonly used for bulk hydrogen storage and transportation (please refer to Lecture 'Introduction to FCH applications and hydrogen safety'). Hydrogen can also be stored in *materials*: on the surfaces of solids (by adsorption) or within solids (by absorption) [1]. An overview of hydrogen storage options is given in Figure 1.



Source: US Department of Energy (DoE): <http://energy.gov/eere/fuelcells/hydrogen-storage>

Figure 1. An overview of hydrogen storage technologies.

Figure 2 [5, 6] illustrates the volumetric densities achieved or expected to be achieved for the various storage options in on-board vehicle applications. The US DOE has set targets in their research programme [7] for each of the parameters so that research can be discontinued if it appears that one of the targets cannot be reached.



Source: Risø Energy Report 3, 2004.

Figure 2. The volume occupied by 4 kg of hydrogen stored in different ways, relative to the size of a car.

Compressed gaseous hydrogen storage

Currently, the most common way of storing hydrogen is as a compressed gas in metal cylinders at different pressures. As it was shown in previous lectures many FC applications use hydrogen at higher pressures. In addition to this, the hydrogen compression process increases its volumetric density. Hydrogen for industrial or laboratory use is typically compressed to pressures of 15-20 MPa (150-200 bar). In FC vehicles, hydrogen pressurised to 35-70 MPa is stored in on-board storage

tanks. At hydrogen refuelling stations gaseous hydrogen is pressurised (up to 100 MPa) in stages and stored in banks of containers. For examples, three different pressure levels at a refuelling station with gaseous storage can be used: low-pressure storage (in 'cigar' tanks, $p=4.5$ MPa); medium-pressure storage (in a group of cylinders, $p=20-50$ MPa) and high-pressure storage (in composite cylinders, $p=70-100$ MPa). The major concerns related to cGH_2 are: the large amount of energy needed for the compression; the stress on the containers' materials caused by repeated cycling from low to high pressures; the inherent safety issues for the use of such high pressures in pressurised vessels; the high weights and additional costs to design such vessels. Other issues such as hydrogen permeation and embrittlement should be considered as well. Thus, the containers used to store cGH_2 must be made of robust materials and must withstand high pressures without a loss of containment. The design and manufacture, transportation and use of vessels suitable for pressurised hydrogen storage are regulated by government agencies. The designed hydrogen storage vessels (as well as the materials they are made of) should comply with the requirements of RCS developed by ISO, CGA, ASME, and other organisations (more detailed information on relevant RCS is available in the Lecture 'Regulations, codes and standards for First Responders').

The following definition will be useful to know:

Nominal Working Pressure (NWP) is a gauge pressure, which characterises typical operation of a system. For cGH_2 tanks the NWP is a settled pressure of compressed gas in a fully filled container at a uniform temperature of 15 °C [8]. Hydrogen on-board of FC vehicles is typically stored at the NWP of 35 MPa or 70 MPa, with maximum filling 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 a normal (re-)filling 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 refilling, the pressure drops. By definition mentioned above, the settled pressure of the system will be equal to the NWP when the container is at 15 °C.

Types of cGH_2 storage vessels

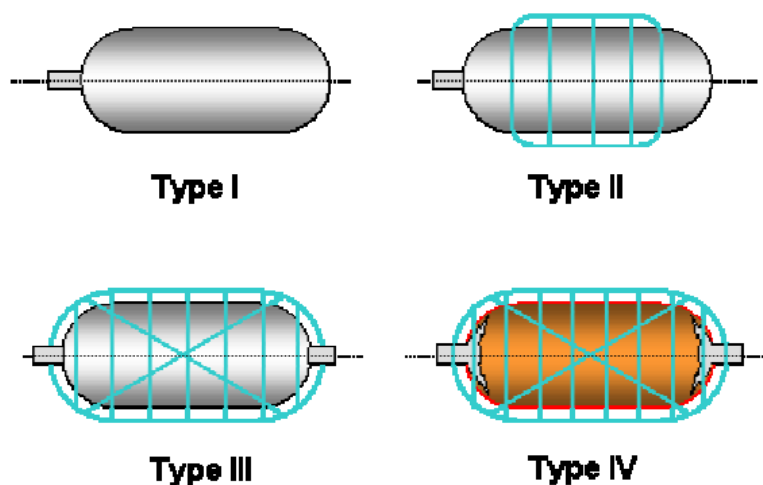
Due to a number of unique hydrogen properties (please see the Lecture 'Hydrogen properties relevant to safety') hydrogen should be compatible with the materials the walls of the storage tanks are made of. Four types of vessels have been developed and used for hydrogen transportation and storage:

- Type I: made of metal seamless metallic container
- Type II: seamless metallic container 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 [9]. The schematic representations of the vessels types used for cGH_2 are shown in Figure 3.

The pressure, at which hydrogen will be stored at, mainly affects the thickness of the storage container walls, the size/weight of the containers, the choice of materials, and the costs. Usually, three types of materials are used for design and manufacturing of hydrogen storage tanks: metals (aluminium or steel), polymers (high-density polyethylene or polyamide) and carbon fibres. Metals should neither allow hydrogen permeation nor be subjected to hydrogen embrittlement, especially if they are to undergo an extensive pressure/temperature cycling during their life-time. The hydrogen tanks are designed for a maximum working pressure, with the minimum wall thickness dictated by

the metal's tensile strength [9]. Although the design of hydrogen tanks have been improved in the recent years, particularly through the application of light-weight materials such as polymers and aluminium, the issues of large volumes and heavy weights still remain. For example, the mass of hydrogen stored in a metal cylinder is only about 1% of its total mass [11].



Source: Barthelemy, 2009 [10].

Figure 3. Types of hydrogen tanks used for compressed gaseous hydrogen storage [10].

Type I vessels are seamless containers made of steel or aluminium. They are very heavy, with thick walls. Type I tanks designed for pressures not higher than 25 MPa. Type I vessels used in CNG vehicles and can be considered as a relatively cheap storage option for some stationary applications. Type II vessels have seamless metallic tanks hoop-wrapped with fibre resin. They are also very heavy and can withstand pressures up to 45-80 MPa. These tanks can be used as high pressure buffers at hydrogen refuelling stations. Their cost is competitive due to a relatively low number of fibres used (Figure 3). Both type I and type II vessels are not suitable for automotive applications due to heavy weights and large sizes.

Types III and IV vessels are usually lighter and have thinner walls compared to types I and II containers. Type III vessels with NWP of 35 MPa have seamless or welded aluminium liners fully wrapped with fibre resin composite. The materials used are less affected by hydrogen embrittlement. Type IV vessels with NWP of 70 MPa are made of non-metallic (i.e. plastic) liners in a fibre/epoxy matrix. Metallic bosses are also available for shut-off valves installation. The fibre wrapping around the polymeric liner provides the required level of strength to contain pressurised hydrogen, while the liner mainly acts as a permeation barrier [11]. Although these cylinders are lighter than those containing all-metal liners they are more expensive. The disadvantage of type IV tanks is a possibility of hydrogen permeation through the polymeric liner. Currently, these types of tanks are preferably used for automotive applications (forklifts, cars, buses, etc.).

The examples of storage vessels, which can be found at stationary applications include: a bundles or a basket of cylinders, fixed tube bundles or tube trailer used to deliver hydrogen to refuelling stations (Figure 4).



Source: AirLiquide Image Bank

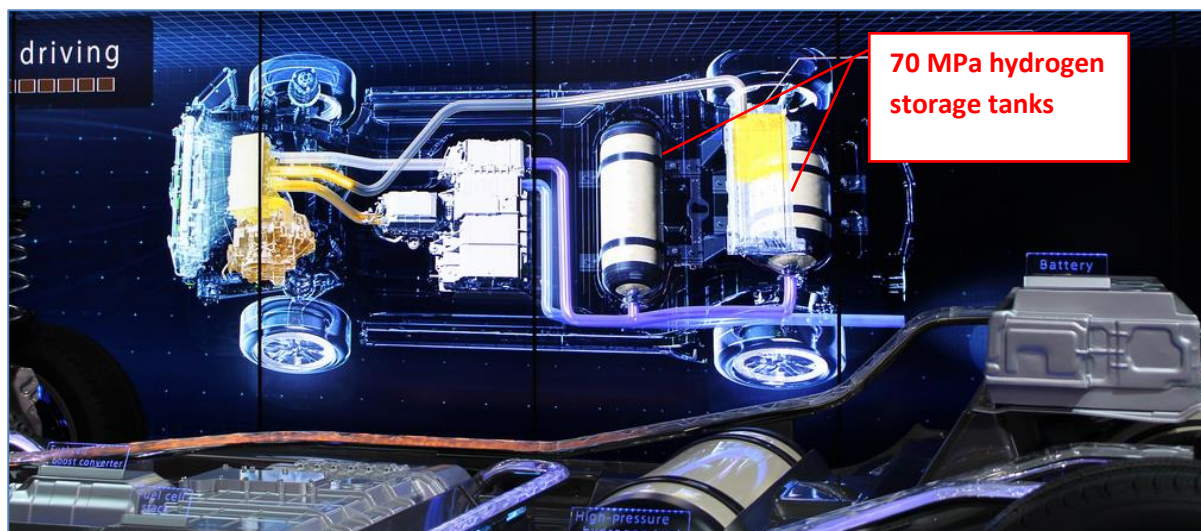
Figure 4. The examples of hydrogen storage vessels common for stationary applications:
(a) fixed bundle of cylinders, (b) a basket of cylinders.

On-board hydrogen storage

As mentioned earlier, the most suitable vessels to store hydrogen on-board of vehicles are Type III and Type IV. These technologies are also widely used for storage of other gases (e.g. natural gas or air), but the main difference is the need for much higher pressures in the on-board hydrogen storage: 35 to 70 MPa for hydrogen compared to 20 MPa for natural gas. Hydrogen storage systems installed on-board should perform the following functions:

- to receive hydrogen during (re-)fuelling;
- to contain hydrogen until needed;
- to release hydrogen to FC system to power the vehicle.

Currently, FC vehicles use tanks that store cGH_2 . The on-board storage of LH_2 is not used in any vehicles at the present time [4]. The on-board hydrogen system usually contains: a single or several cGH_2 storage tank(s), a refueling receptacle, and hydrogen fuel lines. The tanks are usually located in the rear of the vehicle. Each tank is equipped with its own, thermally activated pressure relief device (TPRD). In case of fire, TPRDs will release hydrogen either individually or they can be routed to a single vent location. The direction of hydrogen release from TPRD is vertically downwards or at slight angle, when a car is normal position, with four wheels on the ground [4, 8]. The hydrogen fuel lines contain hydrogen at much lower pressures (from ambient to about 0.7 MPa) than in the tanks. The lines are made of stainless steel compatible with hydrogen. An example of a FC vehicle, Toyota Mirai, and its hydrogen storage tanks (70 MPa) are shown on Figure 5. More detail about this car can be found on: <http://www.toyota.com/mirai/fcv.html>



(a)



(b)

Source: Google Images, loyalty free.

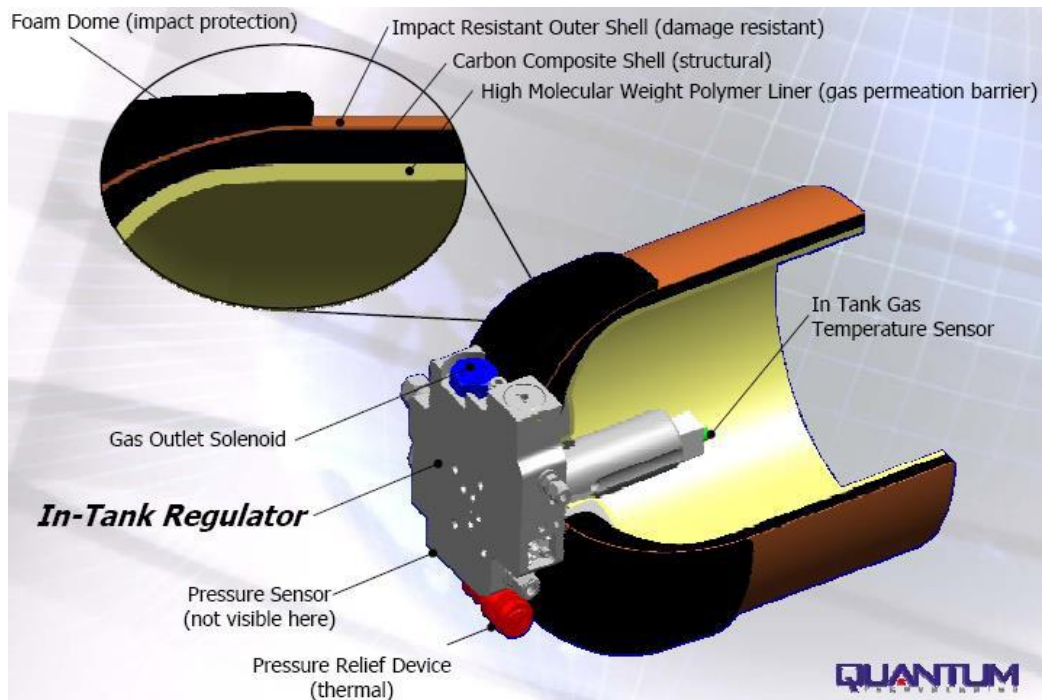
Figure 5. (a) Main components of Toyota Mirai FC vehicle, and (b) its hydrogen storage tank.

Today's light-duty passenger FCVs typically store up to 6 kg of hydrogen on-board needed to provide a driving range in the region of 400-500 km [4]. Similar to CNG buses, the hydrogen fuelled buses store hydrogen on the roof in several tanks. The fuel cell stack is usually located in the rear engine compartment of the bus. Up to 50 kg of hydrogen can be stored on-board of a FC bus. Not only car manufacturers like Toyota or Honda produce hydrogen storage tanks, but also companies such as Lincoln Composites, Dynatek Industries, Quantum Technologies and others.

A cross-section of Type IV tanks produced by Quantum Technologies is shown in Figure 6. The tank has:

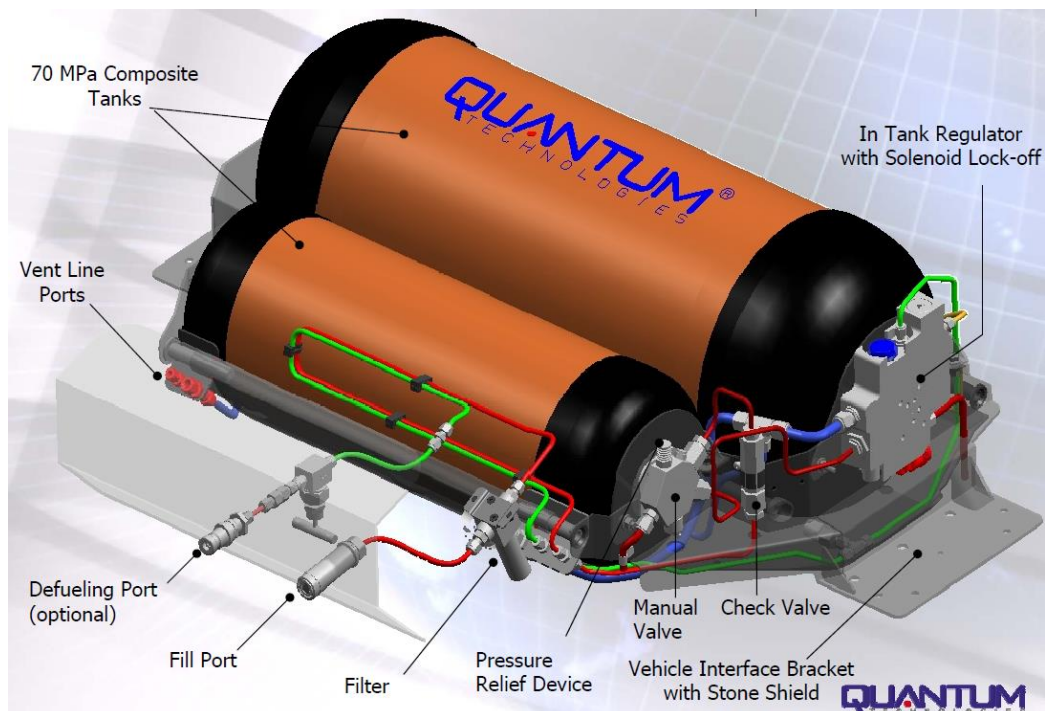
- an impact resistant foam dome, which is light-weight, energy absorbing, and cost-competitive;
- an impact resistant outer shell, which is bullet-proof and provides the tank with cut/abrasion resistance;
- a Carbon Fibre Reinforced Plastic (CFRP) shell, which is light-weight, corrosion-, fatigue-, creep-, and relaxation-resistant;
- a polymeric liner, which is light-weight, corrosion resistant and serves as a permeation barrier.

A general view of the Quantum Technologies 70 MPa composite tanks with the key safety and communication features are shown in Figure 7. These tanks are extremely robust and much stronger than petrol tanks which can be made of plastic.



Source: Warner, 2005 [12]

Figure 6. A cross-section of a Quantum hydrogen tank wall with integrated fuel storage systems [12].



Source: Source: Warner, 2005 [12]

Figure 7. Type IV compressed gaseous hydrogen storage tank by Quantum Technologies [12].

The main issue for the type IV tanks is hydrogen permeation through the polymeric liner. According to the EU regulation the permeation rate of hydrogen (at 20 °C) for a FC car should not exceed 6 Nml/hr/L to avoid formation of flammable composition in a worst credible scenario of a private garage with ventilation rate 0.03 air-changes per hour (ACH) [13]. The permeation phenomenon will

be discussed further in this lecture. Hydrogen permeation through the polymeric liner can lead to its accumulation in the space between the liner and CFRP forming a 'blister'. This may cause a partial or full collapse of the liner, when the pressure of the accumulated hydrogen becomes higher than the internal pressure of the liner (e.g. during tank depressurisation). Therefore the development of specialised polymers is much needed to address this problem.

Pressure Relief Devices

The main safety feature of the hydrogen storage systems (both for automotive and stationary applications) is pressure relief devices (PRDs). The definition of a *Pressure Relief Device* (PRD) is as follows: a PRD is a safety device that protects against a failure of a storage vessel by releasing some or the entire tank content in the event of high temperatures, high pressures or a combination of both [14]. In the event of a fire, *Thermally Activated Pressure Relief Device* (TPRD) provides a controlled release of the gaseous hydrogen GH_2 from a high pressure storage container before its walls are weakened by high temperatures, leading to a *catastrophic rupture*. TPRDs vent the entire contents of the container rapidly. They do not reseal or allow re-pressurization of the container for hydrogen systems.

Hydrogen storage vessels and their TPRDs that have been subjected to a fire are expected to be removed from service and destroyed [8]. 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 [15]. According to the European Commission Regulation (EU) No 406/2010, the on-board hydrogen storage must be fitted with PRDs/TPRDs [13].

The 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 the non-reclosing TPRDs (Please note that CNG vehicles usually equipped with reclosing PRDs). There are many types of PRDs available on the market. The most common ones include a fusible metal plug, a glass bulb or a bayonet (Figure 8). A fusible metal plug inside the PRD melts, when temperatures are higher than 110 °C, opening and venting the entire content of the tank. A glass bulb in a PRD (Figure 8a) 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 (Figure 8b) upon reaching its triggering temperature (*ca.* 124 °C) 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.

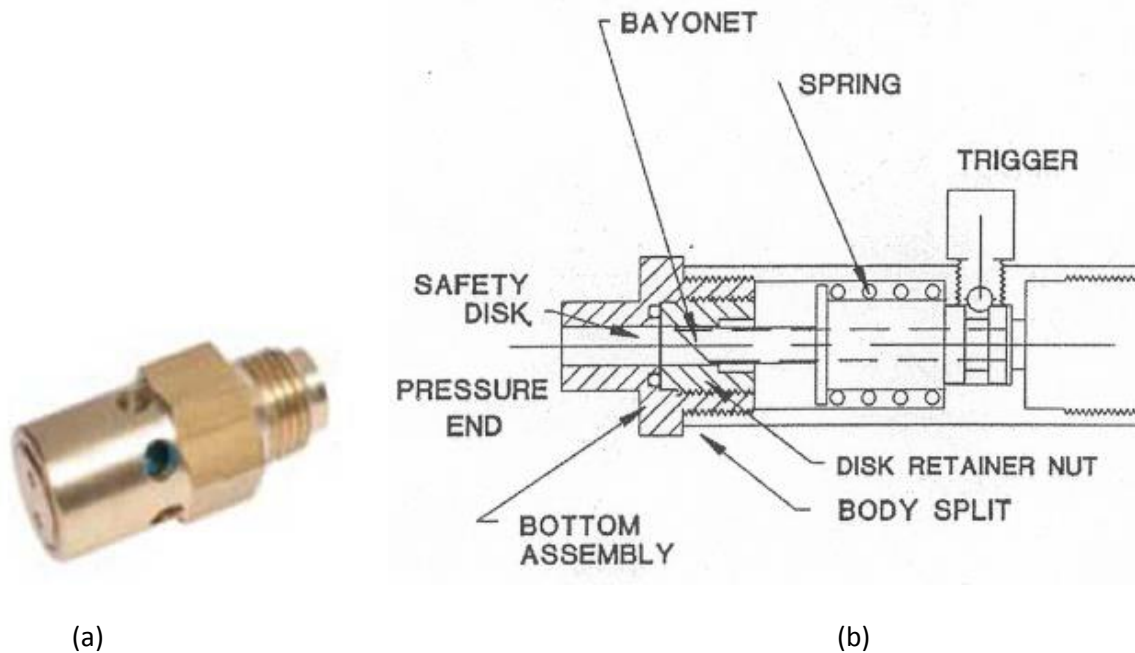


Figure 8. Glass bulb (a) and bayonet (b) types of PRDs.

Without a PRD, overheating of the storage tank may result in its catastrophic failure, releasing the flammable gas and the large amount of stored mechanical energy due to the compression. 'Even without the chemical energy from gas flammability, the mechanical release of pressure can cause the tank to break its restraints, pierce any containment provided by the vehicle body and fly great distances. With the PRD in place, the controlled release may result in an intense flame for a short time (until pressure in the tank is relieved), but the overall risk is likely to be reduced' [16].

Unfortunately, even when PRDs are installed they might fail in two different modes: either by a premature activation or by failing to vent properly. The reasons for PRDs failures are different. PRDs can be blocked by dirt, stones or ice and thus fail to act when necessary. They can become corroded or otherwise damaged such that they relieve pressure when they should not be. The videos recorded by the Southwest Research Institute during the tests when PRDs failed to open both on CNG and hydrogen storage tanks can be found here: <http://depts.washington.edu/vehfire/begin.html>

According to Global Technical Regulations (GTR) on Hydrogen-Fuelled Vehicles (2013), a PRD should be a 'non-reclosing and a thermally activated device. It should 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' [8].

Also as per requirements of the GTR [8] the discharge of hydrogen gas 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;

- towards any class 0 component;
- forwards from the vehicle, or horizontally from the back or sides of the vehicle [8].

The direction of a TPRD hydrogen release is indicated on Figure 9 [4].

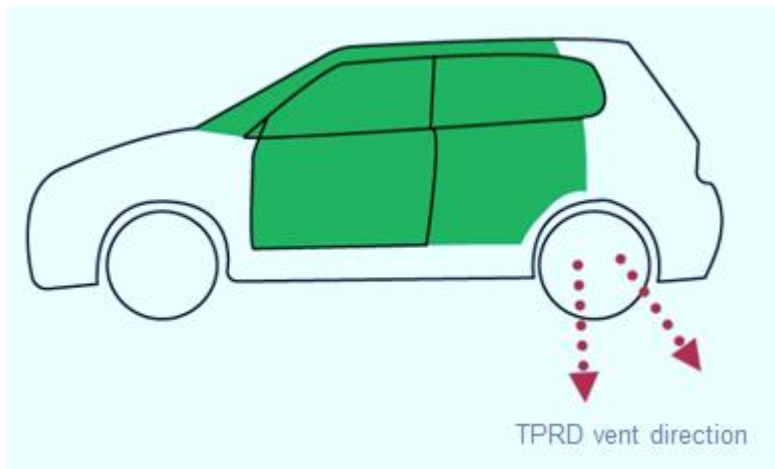


Figure 9. Possible directions of hydrogen release in case of TPRD activation in a FC car [4].

Testing of cGH₂ tanks

All types of vessels for storage of cGH₂ should be designed, manufactured, tested, and maintained in accordance with relevant codes and standards. The testing is carried out on national and international (GTR) level. The examples of some types of test include [4, 8]:

- Bonfire test. The tank shall vent through the non-reclosing TPRD and shall not fail when exposed to a bonfire of 20 minutes duration. The conditions of this test will be discussed in the current lecture in detail.
- Hydrostatic burst test. The pressure, at which the tank bursts, typically more than 2.25 times of the working pressure.
- Ambient pressure cycling test. Hydrogen tanks shall not fail before reaching 11,250 fill cycles (representing a 15-year life of use in commercial heavy-duty vehicles).
- Penetration test. The tank shall not rupture when an armour piercing bullet or an impactor with a diameter of 7.62 mm or greater fully penetrates its wall.
- Leak-before-break test. The tank shall fail by leakage or shall exceed the number of filling cycles (11,250).

The goal of all the tests is that the tanks vent and do not rupture [4].

Let us consider the *bonfire test* in detail as it has high relevance to first responders. The selected RCS relevant to bonfire test are indicated in Table 2.

Table 2. Selected RCS applicable to bonfire 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	Global Technical Regulation (GTR) on hydrogen and fuel cell vehicles. (ECE/TRANS/WP.29/GRSP/2013/41).	International	2013

The latest version of the GTR [8] requires that hydrogen storage container is 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 pressurised to the NWP and exposed to fire, for 10 minutes in a localised fire (i.e. when only portion of the tank exposed to flames) and then progressing to an engulfing fire stage. A high-pressure container shall vent through a TPRD in a controlled manner (to pressures below 1 MPa) without a rupture. In case, if the need to empty the content of hydrogen tank arises, the PRD will release gas off the vehicle, towards the ground and most likely producing violent hydrogen flame for a short period of time. The tank systems typically release hydrogen (blow-down) within a few minutes [4, 8].

The procedures for the bonfire test (both in localized and in engulfing region) are depicted in Figure 10. More details about the test conditions and protocols are given in Tables 3-6.

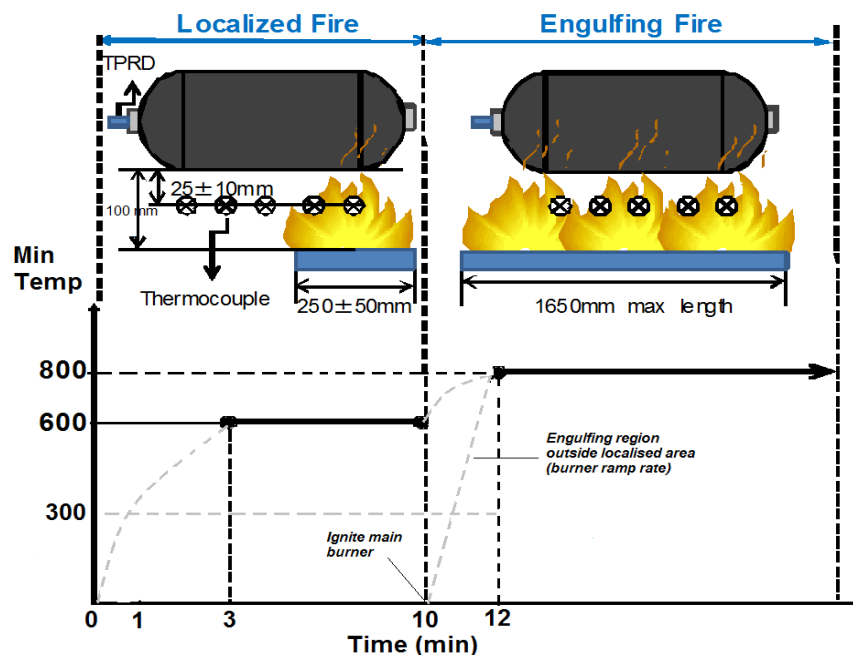


Figure 10. The bonfire test progression in time.

Table 3. A summary of conditions for a test started as a localized fire, GTR [8].

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
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.

Table 4 details how the hydrogen tank should be positioned for the engulfing stage of bonfire test depending on its size and the number of TPRDs.

Table 4. A position of a container above the fire [8].

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 5. Protocols for the bonfire test as stated in GTR [8].

	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

The container may also be subjected to engulfing fire (without localised stage) when no shielding components attached to it. The summary of the conditions for the engulfing fire test is given in Table 6. The list of actions and set temperatures for localised/engulfed regions of the bonfire test are indicated in Table 6. 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 thermocouples' (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. The results of the test include:

- the elapsed time from ignition of the fire to the start of venting through the TPRD(s);

- the maximum pressure and time of evacuation until a pressure of less than 1MPa/0.7MPa is reached.

Unfortunately, the GTR do not include bonfire testing of tanks without TPRDs, which can give the valuable results on *fire resistance rating* of the tanks.

Table 6. A summary of conditions for engulfing fire test [8].

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 container valves, fittings, or PRDs. Metallic shielding should not be in direct contact with fittings
Arrangement of TCs	Thermocouples may be attached to steel cubes up to 25 mm on a side
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)

Consequences of catastrophic failure of high-pressure hydrogen storage (blast waves, fireballs, projectiles)

What happens if TRPD fails to activate? The studies carried out at the Southwest Research Institute, USA [17, 18] demonstrated that the catastrophic rupture of the tank will occur. Two types of tanks (type III and type IV), not equipped with TPRDs, pressurised to about 35 MPa and containing only 1.64 kg of hydrogen were tested. The fire was created by a propane burner. Type IV (with high-density polyethylene liner, carbon fibre structural layer, and fiberglass outer layer) tank, 72.4 L in capacity and with dimensions of L x D=84 x 41 cm was tested stand-alone. The Heat Release rate (HRR) for the fire was 370 kW. Pressure inside the vessel P was at 34.3 MPa. Type III tank (with capacity of 88 L and L x W=4.5 x 1.8 m) was placed under a typical Sports Utility Vehicle (SUV), 28 cm above the ground. HRR=265 kW, P=31.8 MPa. The internal cylinder temperature and pressure increased only marginally (due to a low thermal conductivity of CFRP), from 27 to 39 °C and from 34.5 to 35.7 MPa, during the final period between 6 min and 6 min 27 s of fire exposure, which culminated in a catastrophic rupture of Type IV tank. The reason for this is not pressure increase but degradation of the outer shell of the tank. The burning of tank composite layers started in 45 s for Type IV and 20 s for Type III, gauged by the appearance of black soot. The failure time, after fire initiation (i.e. fire resistance) was measured as 6 min 27 s for Type IV and 12 min 18 s for Type III tank. It was observed that the flame entered the SUV interior just after 4 minutes! Therefore, if the passengers are inside the vehicle, their successful escape or rescue would have had to be accomplished within this short period of time [17].

For Type IV (stand-alone) tank, the measured peak pressures from the *blast wave* varied from 300 kPa at 1.9 m, to 41 kPa at 6.5 m. The highest pressure was in a direction perpendicular to the tank longitudinal axis. It is worth mentioning here that pressures above 83 kPa lead to severe injuries or death [19]. For Type III tank (under the SUV) the peak pressures were lower: 140 kPa at 1.2 m and 12 kPa at 15 m. Nevertheless this level is sufficient to knock people down (from 10 to 20 kPa) [19]. Also please note, that the energy stored in a tank is proportional to PV (where P – pressure; V – volume). The larger tanks and at higher pressures have more hazardous potential through the blast wave in case of the tank rupture [17].

The size of the *fireballs* produced were 7.7 m in diameter at 45 ms after the tank rupture of Type IV, and 24 m in diameter for Type III tank. The fireballs were lifted in 1 s. The fireball duration was about 4.5 s in both cases (recorded by IR video), and twice less if recorded by high-speed visible range cameras. The heat flux peak values measured in case of Type III tank test at a distance of 15.2 m were equal 210-300 kW/m² (Please note that about 35 kW/m² heat flux leads to 1% fatality in 10 seconds) [17].

In case of Type IV tank (stand-alone test) the largest tank *projectile* fragment was the 14 kg top half of the tank found 82 m away from the original tank location. As for Type III tank test (SUV test) a large tank fragment was found 41 m away from the SUV. The fragment projectiles from the SUV were found at distances up to 107 m. It is possible that undiscovered fragments may have travelled even further [17]. Also, a car could be considered as a “missile” itself (up to 22 m displacement!) according to the experiments reported by Weyandt, 2006 [18]. Under no circumstances should the firefighters attempt to remove a burning hydrogen tank from a vehicle. A new methodology was developed at Ulster that allows the determination of the hazard distances for two general cases: harm to humans and damage to buildings if high pressure hydrogen tank catastrophically fails [19, 20]. This new approach will be discussed in the lecture dedicated to hydrogen deflagrations, detonations and blast waves.

Fire resistance rating of hydrogen tanks

There is an urgent need to demonstrate an increased *fire resistance* of Type III and IV tanks used by car manufacturers. For example, current level of fire resistance for Type IV hydrogen storage tanks remains low: it ranges from 3.5 to 6.5 minutes. Even if a TPRD installed, 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 for the members of the public could be around 50 m [21]. This makes a self-evacuation or any rescue operations at an accident scene extremely difficult or sometime impossible.

The work carried out by Ruban et al (2012) was focused on the effects of fire on composite Type IV hydrogen storage vessels, usually fitted on FC vehicles [22]. The aim of this study was to investigate the behaviour of an unprotected composite cylinder in a response to a fire attack in order to design an appropriate protection for it and to reduce the length of any potential hydrogen flame [22]. A series of tests were performed on a 36 L cylinder at a pressure of 70 MPa. The time period from the fire exposure to the bursting of this cylinder (i.e. the burst delay) was measured. The effects of the fire type (localised or global) and the pressure in the tank during the exposure were studied. It was concluded that without any thermal protection, in the case of the studied cylinder, the orifice diameter could be decreased by a factor 10 compared to current practices, allowing the flame length and consequently the safety distance to be decreased by the same factor of 10 [22]. The work

evaluated the relationship between the designs of the TPRD i.e. reduced diameter versus the thermal resistance of the tank.

Gambone and Wong [23], and then Webster [24] studied several thermal protection techniques for composite tanks. The tested solutions included a spray of ceramic insulation materials on its outer surface, a wrapping with a ceramic blanket, a protective encapsulation, various intumescent paints, etc. Authors [23, 24] did not aim to analyse total fire resistance of the tanks, though Webster reached fire duration 30 min without thermally protected tank rupture [24]. The thermal insulation may not only impart fire resistance but also provide an additional level of an impact protection. This, in turn, may allow tank designers to reduce the amount of reinforcing composite materials needed, which could reduce the cost and weight of storage systems [23].

Safety strategies for inherently safer high-pressure hydrogen storage

The improvement of *fire resistance rating* of hydrogen storage tanks is the topic of an ongoing research at Ulster University, HySafer, funded by UK EPSRC. The idea is to improve the fire resistance of composite hydrogen storage tanks by applying a coating of an *intumescent* paint. The intumescence is a versatile method for providing materials with a reaction and resistance to fire. When heated beyond a critical temperature, the intumescent material begins to swell and expand, forming an insulation coating and limiting heat and mass transfer. An intumescent paint/coating is a multi-component system that essentially consists of *a char former* (e.g. pentaerythritol); an acidic component (e.g. ammonium polyphosphate); *a spumific/blowing agent* (e.g. melamine). Preliminary simulations of research student at Ulster demonstrated that even with one layer of an intumescent paint (in the range 7-20 mm) applied to Type IV tank its fire resistance rating increases by an order of a magnitude.

As it was mentioned previously many applications using hydrogen as an energy carrier require its storage, in gaseous form, at pressures up to 100 MPa. Due to such high pressures the required hazard distances can be quite large. Therefore, to reduce the costs of the required systems and infrastructure, there is a need to develop innovative engineering systems that can allow these distances to be safely reduced, when considering both unignited hydrogen releases and jet fires. For example, a correctly designed and installed PRD should produce a jet fire with the shortest possible flame length or, in case of unignited release, a flammable cloud with the smallest dimensions. In order to achieve this, a plane nozzle flow is considered to be a realistic scenario to investigate leaks from high-pressure equipment cracks, fittings, connections, etc. The results of the CFD study carried out at Ulster University (HySAFER) indicated that the reduction of hazard distances is possible through the use of *plane nozzle* TPRDs [25]. There is a lack of experimental data when considering hydrogen jets emanating from plane nozzles. The model introduced by Makarov and Molkov [25] aimed to numerically predict the behaviour and structure of highly under-expanded hydrogen jets emanating from round nozzles and plane nozzles with different aspect ratios (ARs) [25]. This allowed understanding of hydrogen concentration decay and predicting at what point the hydrogen concentration in air drops below the LFL of 4 vol. %. During this study the simulations were carried out on non-reacting under-expanded hydrogen jets emanating from a high-pressure hydrogen storage at pressure 400 bar from three different nozzles – round nozzle with internal diameter 1 mm, plane nozzle with AR=5.0, and plane nozzle with AR=12.8 with all nozzles having the same cross-sectional area. This work investigated the subsequent differences in the structure of the jets produced. The results from the simulations undertaken revealed that the longest flammable

envelope was produced by the round nozzle jet, reaching around 4.1 m downstream. In contrast, the plane nozzle jets produced much shorter flammable envelopes: the plane nozzle with AR = 5.0 reached 2.8 m downstream and the plane nozzle with AR = 12.8 reached 2.3 m downstream. For AR=12.8 flammable envelop shortened 1.8 times compared to circular nozzle where AR=1 (Figure 11). Hydrogen jet fires were studied by Mogi and Horiguchi using the described above experimental setup [26]; the shortest jet fire – 1 m - was again produced by the plane nozzle with AR=12.8, while the round nozzle resulted in jet fire about 2.0 m length.

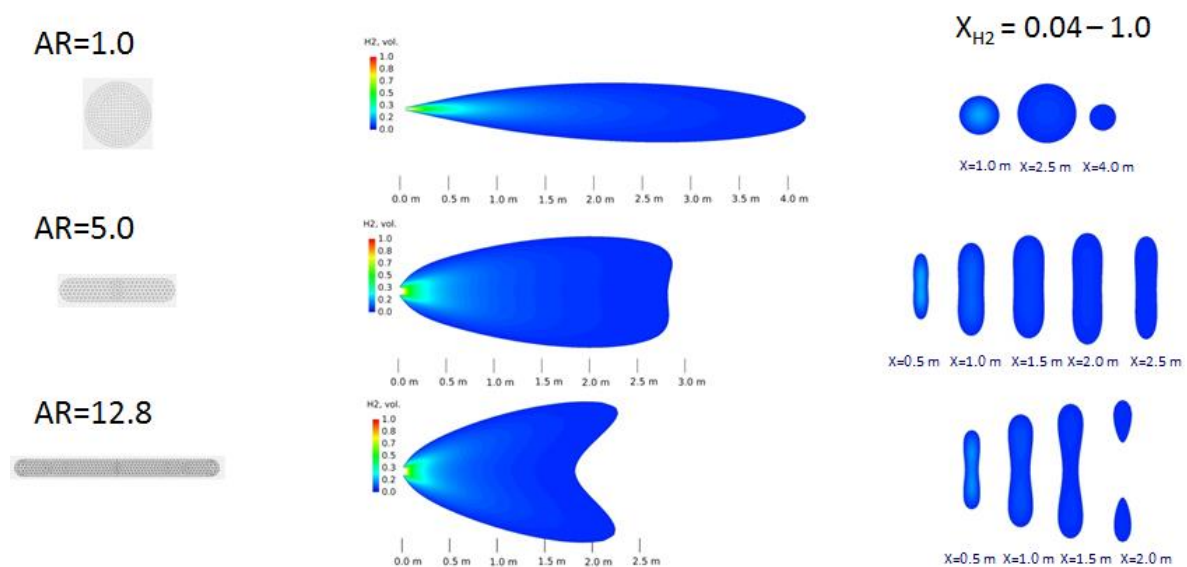


Figure 11. Distribution of hydrogen volume fraction (0.04 – 1.0 range) along the minor axis for round and plane nozzles [25].

Potential hazards and safety issues associated with cGH₂: summary

The potential hazards associated with the on-board storage of compressed gaseous hydrogen include:

- Difficulty in identification of hydrogen release as the gas is odourless, colourless and tasteless. The odorants cannot be added to hydrogen.
- Hydrogen can cause *embrittlement* of metals. This may result in the decrease of material strength and consequently in container's fracture, leading to a hydrogen leak.
- Accumulation of hydrogen, over a long period of time, in enclosures such as a garage or mechanical workshop, vehicle passenger compartments. *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 a deflagration or even to a detonation.
- High pressure hydrogen jets may cut bare skin [27].
- An overpressure and impulse can lead to: people's eardrum damage, tank rupture, flying debris, shattered glass, etc.
- *Pressure peaking phenomenon* may lead to a garage collapse in just one second (will be discussed in the following lectures).
- Hydrogen can be ignited easily as its MIE is 0.017 mJ (which is 10 times lower compared to other fuels). A static spark can ignite hydrogen released.

- When pure hydrogen is burning its flames are invisible in the daylight.
- Hydrogen burns rapidly and does not produce smoke.
- An external fire, heat or thermal radiation can cause a mechanical rupture of a tank due to the thermal decomposition of the polymeric and composite materials. The current value of fire resistance (publicly available) is up to 12 minutes before the catastrophic failure may occur.
- In case of a TPRD malfunction, a worst-case scenario is possible: a rupture (i.e. a catastrophic failure) of hydrogen storage tank, producing fireball, blast waves and burning projectiles.

Interaction of hydrogen with different materials

The topic of hydrogen interaction and compatibility with different materials is vast. In this section of the lecture two different aspects will be considered: the interaction of hydrogen with metallic and polymeric materials, i.e. with the materials, which are primarily used for the storage vessels. Due to the small size of its molecules and atoms, hydrogen can be easily absorbed by different materials including those used for hydrogen storage. This, in turn, leads to the degradation of the materials mechanical properties, which may result in unwanted hydrogen leaks and structural failures.

The aim here is to provide First Responders with sufficient knowledge to make relevant decisions. The interaction of hydrogen with the materials is pertinent to all FCH applications. However, in addition to being compatible with hydrogen the materials used for storage are often subjected to high pressures, low temperatures, and cyclic or static loading, thus they must be selected accordingly. The selection of materials compatible with hydrogen is addressed in ISO standards applicable to FCH technologies (lecture on RCS).

‘Hydrogen has a low viscosity and small atoms that can be absorbed into materials, so leaks and embrittlement of certain materials are possible, which can result in structural failure’ [3]. Mechanical degradation of structural materials under the influence of hydrogen is a serious problem and caused many incidents/accidents during production, storage, transportation and use [28]. The correct selection of suitable materials for the components is a crucial for safety of hydrogen storage systems. This relates to piping, walls of storage vessels, filling connectors, valves, fittings, etc. The silent movie produced in 1950s by Delft University illustrates how hydrogen bubbles emerge from steel at defects and other locations (<https://www.youtube.com/watch?v=bv9ApdzalHM>).

Interaction of hydrogen with metallic materials

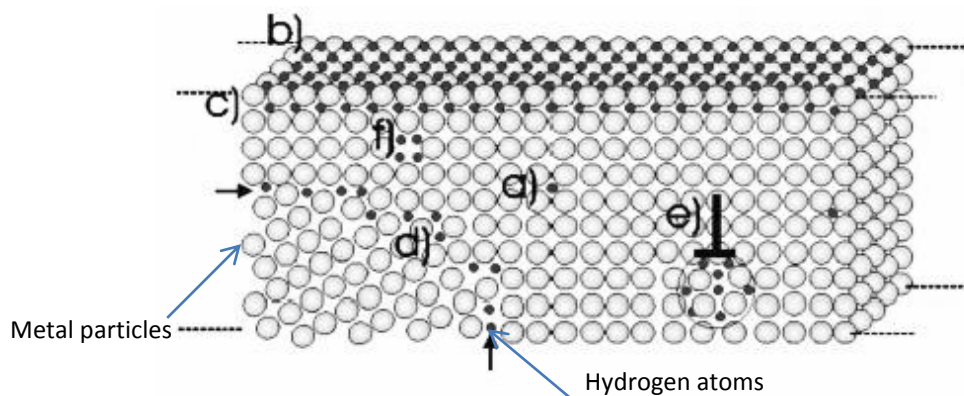
The compatibility of hydrogen with metals is affected by chemical interactions and physical effects, which include:

- Corrosion: dry corrosion (at high temperatures, *hydrogen attack*); wet corrosion (most common, caused by moisture); corrosion caused by impurities in a gas.
- Hydrogen embrittlement (HE)
- Embrittlement at low temperatures (‘cold embrittlement’)
- Violent reactions (e.g. ignition)

Dry corrosion is a chemical reaction between a dry gas and a metal, which eventually may lead a reduction of a cylinder wall thickness [29]. This type of corrosion is not very common, because its rate is very low at ambient temperature. However, at high temperatures hydrogen can react with some metals, forming hydrides for example. In general, wet corrosion can occur in a hydrogen storage vessel following the water entry. Please note that hydrogen is a non-corrosive gas and

cannot even in wet conditions cause this type of corrosion. At low temperatures some metals can become more brittle. This is due to a change from ductile to brittle behaviour mode when the temperature is lower than a “nil-ductility” temperature, which is sometimes considerably higher than that of the cryogen. It represents a problem for installations exposed to periodic temperature cycles. Several accidents involving a cryogenic storage tank were caused by cold embrittlement.

The phenomena of hydrogen embrittlement (HE) and hydrogen attack will be discussed in more details further. Embrittlement is a process, by which various metals, mainly high-strength steels, become brittle (i.e. lose their ductility) and crack after being exposed to hydrogen [3]. It is caused by ingress of either molecular or atomic hydrogen into a metal lattice. It occurs at relatively low temperatures (e.g. at ambient). Hydrogen attack happens at higher temperatures, above 200 °C. The exact mechanism of HE is not clear. Several mechanistic routes are suggested as shown on Figure 12: (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 such as grain boundaries, and vacancies dislocations. Also, hydrogen can form compounds within a metal lattice such as metal hydrides or methane [30].



Source: Barnoush, A (2011) [30]

Figure 12. Suggested routes for hydrogen entry into metal/metal defects [30].

High-strength steels are most sensitive to the HE. The sources for the HE include:

- Some operations of steel manufacturing such as welding, electroplating, pickling, etc.
- Hydrogen formed as a by-product of wet corrosion of a metal.
- Metal surface treatments (e.g. cathode protection of metal against corrosion).
- Adsorption on a metal surface.

HE is categorised as follows [31]:

- Environmental HE - occurs when a material is being exposed to a hydrogen atmosphere, e.g. in storage tanks.
- Internal reversible HE - occurs when hydrogen enters a metal during its processing. This type of HE may lead to a structural failure of a material that has never been exposed to hydrogen before.
- Hydrogen reaction embrittlement - occurs at higher temperatures, when hydrogen chemically reacts with a constituent of a metal, forming a new microstructural element or phase such as a hydride or to generate gas bubbles also known as *blistering* (see Figure 13).

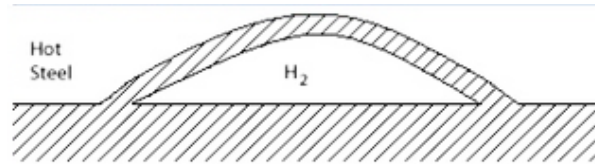


Figure 13. Formation of a blister caused by hydrogen reaction embrittlement.

A whole range of factors influence the level of HE process [31]:

- 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

The evaluation and selection of materials suitable for hydrogen service should be done well in advance of their use for FCH applications. A material should not be used unless the 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). As per standard ISO/TR 15916: 2004 HE is possible for any metal [32]. However, some metals can be used without any precautions. For example, brass and copper alloys (e.g. beryllium copper CuBe); aluminium and its alloys. On the contrary, metals that are highly sensitive to HE include: nickel and high content nickel alloys; titanium and its alloys. As for steels, the susceptibility to HE may depend on several factors outlined above. Many materials can be safely used under controlled conditions (e.g. limited stress, absence of surface defects, etc.) [32].

As it was mentioned earlier inadequate choice of materials will lead to incidents or serious accidents. If a material is affected by HE it may fail prematurely and sometimes in catastrophic manner when stress is applied. There are several examples of incidents associated with an incorrect selection of a material [28].

1. [A pipe failure at a hydrogen production plant.](#) The incident occurred in 1996. 'A pipe rupture occurred in a steam methane reformer (SMR) process that produces hydrogen and exports steam. The rupture occurred in a 24-inch diameter stainless steel (SS) pipe used to allow the process gas flow to bypass the high-temperature shift converter (HTS) during start-up. When the pipe ruptured,

process gas contained in process equipment located upstream and downstream of the break vented into the SMR plant yard area. The vented process gas was a mixture of hydrogen, carbon monoxide, carbon dioxide, steam, and methane at 550 psig and 650 deg F (38 bar and 343°C). The escaping high-pressure gas caused an energy release and subsequent fire. The fire was confined within the SMR plant, but equipment located near the pipe failure was damaged. The SMR plant distributed control system (DCS) worked properly to automatically shut down the process, thereby limiting the amount of process gas that escaped. Emergency response services were provided on the scene by the local county fire department within minutes of the incident and the fire was extinguished within 10 minutes. There were no injuries and no releases of any acutely hazardous materials covered by the Risk Management Prevention Plan (RMPP), EPA CERCLA, and SARA Title III regulations [28].

Metallurgical examination of the failed pipe segment revealed cracking on the pipe interior. The cracks were the result of stress corrosion cracking (SCC) of SS, caused by the presence of caustic (potassium hydroxide). The most likely source of the caustic was small amounts of potassium promoter normally present in the SMR catalyst. The section of the HTS bypass piping where the rupture occurred was normally cool and non-flowing. The piping layout allowed water and potassium hydroxide condensed from the process gas stream to collect in a low point. The SS material of construction of the bypass piping was susceptible to SCC from the concentrated caustic solution collecting in the bypass piping' [<https://h2tools.org/lessons/pipe-failure-hydrogen-production-plant>]. Materials incompatibility was one of the causes of the incident. As a result 'The SS 24-inch pipe that failed was replaced with 1-1/4 Cr 1/2 Mo alloy pipe that is corrosion-resistant to SCC. A revised HTS bypass piping layout was installed to prevent the hazardous conditions that lead to the failure. A detailed hazard review and evaluation of all of the materials of construction in the hydrogen plant process gas system led to preventively changing several other pieces of piping and equipment items in the SMR process to 1-1/4 Cr 1/2 Mo'[<https://h2tools.org/lessons/pipe-failure-hydrogen-production-plant>] [28].

2. [An explosion of hydrogen gas caused by the breakage of external gas duct at a space rocket testing facility.](#) An incident happened in a laboratory, on May 16, 1991 in Kakuda, Miyagi, Japan. 'An explosion occurred at testing equipment of a fuel-feeding system for a space rocket engine. During testing of a 42 MPa high-pressure hydrogen gas flow system, an exhaust gas duct outlet was damaged; hydrogen blew out and exploded. It seemed that the cause of this accident was deterioration of the exhaust gas duct outlet by thermal stress. High-pressure hydrogen was flowing during the test, and burned not in the burner (a gas generator), but in a silencer tower after flowing through the exhaust gas duct. This explosion was caused by the damage of that duct' [<http://www.sozogaku.com/fkd/en/cfen/CC1200114.html>]. The main reason for this accident is that 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 [28].

Mitigation measures for HE and hydrogen attack are:

- 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 [31].

Interaction of hydrogen with polymeric materials

As it was mentioned earlier, the polymeric materials are increasingly being used for the liners and wrapping of hydrogen storage vessels. For the wrapping of composite tanks (Type III and IV) glass, aramide or carbon fibres can be used [29]. These fibres are characterized by their tensile modulus, tensile strength and elongation [29]. Polymers are also present in some fuel cells as a material for membranes. Please read about an incident occurred on a PEM FC [33]. Two phenomena often associated with polymeric materials used in FCH applications: a *permeation* of hydrogen through the materials and the *degradation of the mechanical properties* of the polymers. From material point of view, hydrogen storage represents quite a challenge. The materials used for hydrogen storage must be light in weight but also should be able to withstand extremely high pressures whilst maintaining their integrity. There are several unwanted effects of hydrogen on polymeric materials:

1. A *swelling* of polymers, which occurs due to a gas (or a liquid) ab-/adsorption. This can lead to an unacceptable increase of components' dimensions (especially for O-rings) or to a formation of cracks related to a sudden outgassing when the partial pressure is decreased [9]. The significant level of swelling can be obscured by 'leaching out' of plasticisers and fillers frequently used in polymeric materials. Other important effects such as changes in a polymer mechanical strength and hardness should also be considered. According to standards a swelling of more than 15% in normal service conditions is marked as 'NR' (not recommended); a swelling less than this is marked as 'A' (acceptable) provided other risks are acceptable. Hydrogen gas under pressure may lead to swelling of several polymers used in liners of the tanks.
2. Relatively large amounts of hydrogen can dissolve in a polymeric material, thus a polymer exposure to hydrogen can cause not only swelling but also a *blistering*, similar to the one shown on Figure 13.
3. If gaseous hydrogen contains a certain type of *impurities*, which are not compatible with the polymeric materials, this may lead to a deterioration of mechanical properties and eventually to a rupture of a component. This risk should be considered depending on the hydrogen source.
4. *Risk of fire*. Hydrogen is a flammable gas and in case of a fire polymeric materials ignite relatively easy. As a result of that materials degrade and mechanical strength significantly reduces and this eventually may lead to a rupture. Type III and IV tanks cannot withstand fire for longer than 6 - 12 minutes (typically). That is why tanks are usually fitted with PRDs capable of venting the hydrogen within this time, thus resulting in long jet fires.
5. Hydrogen *permeation*. Barthelemy stated that permeation of hydrogen through the polymeric liner is one of the main issues for the hydrogen high pressure vessels along with the HE [29]. Permeation is discussed in the following section of this lecture.

Limitation of hydrogen permeation

Permeation is an inherent phenomenon for all gases, which are in contact with polymers, and is the result of the hydrogen gas dissolution and diffusion in the polymer matrix. Due to a small size of its molecules hydrogen diffusion and thus the permeation are enhanced [29].

According to SAE J2578 (2009), permeation for cGH₂ systems could be defined as a diffusion of gas through the walls or interstices of a container vessel, piping or interface material [34]. It is worth noting that hydrogen in atomic form permeates metals, whilst for polymers permeation occurs in molecular form [21]. Current Type IV storage containers use a polymer liner, for example made of high-density polyethylene, typically overwrapped with carbon fibres set in a resin matrix. Other fibres such as glass or aramid may also be used, but most automotive systems use carbon fibre. The wrapping around the container varies in thickness, depending on the stress distribution. Type III or Type IV containers are used for most automotive applications.

The *permeation rate* through a particular material is described by Eq. (1), where J , is permeation rate (mol/s/m²), T is material temperature (K), p_r is reservoir pressure (MPa), l is the reservoir wall thickness (m), P_0 is pre-exponential factor or permeability coefficient (mol/s/m/MPa^{1/2}) and E_0 –is activation energy (J/mol):

$$J = P_0 \exp(-E_0 / RT) \frac{\sqrt{P_r}}{l} \quad (1).$$

Pre-exponential factor and activation energy both depend on the nature of material. The higher the storage pressure the higher is the permeation rate. The permeation rate also increases when the wall thickness is reduced. Three main phenomena will affect the dispersion of permeated hydrogen: buoyancy, diffusion, and ventilation.

For metallic containers (i.e. Type I and Type II) or containers with metallic liners (i.e. Type III), the permeation rate is considered to be negligible. However, hydrogen permeation is an issue for containers with polymeric liners (i.e. Type IV containers). For example, at 293 K, aluminium has a low permeability 2.84×10^{-27} mol/s/m/MPa^{1/2}, while a polymer like Noryl has a permeability of 5.55×10^{-15} mol/s/m/MPa^{1/2}, i.e. 12 orders of magnitude larger [21].

The economic and technological viability of on-board hydrogen tanks depends amongst other things on their gravimetric and volumetric capacity as mentioned earlier in this lecture. The gravimetric capacity is currently improved using high pressures for cGH₂ storage, which dictates choice of light-weight, non-metallic Type III and Type IV tanks. However, as it was just described, Type IV tanks are characterised by a strong permeability.

Permeation may be categorised as a long-term slow hydrogen release from a cGH₂ system. Controlling the permeation has long been recognised as a key enabler in the development of hydrogen storage technologies [35]. The permeation from on-board hydrogen tanks is a safety issue for enclosures as hydrogen can accumulate over a period of time to create a flammable mixture with air. In sealed enclosures without ventilation the LFL of 4 vol. % of hydrogen in air can be reached as a result of permeation over quite a long time. In order to estimate the time for reaching LFL locally, e.g. under the garage ceiling, or homogeneously throughout the garage, it is important to know how hydrogen will be distributed in the enclosure.

The formation of a flammable mixture is a major safety concern for indoor use of FCH systems. There are two safety questions: *How safe is the permeation of hydrogen through a polymeric liner used in an on-board storage and its dispersion in a garage? Is natural ventilation sufficient to eliminate potential hazard of flammable hydrogen-air mixture formation?* The distribution of permeated hydrogen within an enclosure such as the garage, when LFL of hydrogen in air (4 vol. %) is reached, is important to define the *maximum allowable permeation rate* for FC vehicles equipped with cGH_2 tanks on-board [21].

Let us consider the dispersion of permeated hydrogen from a storage tank in a typical garage with adiabatic walls and still air. The following parameters were considered: storage tank size: $L=0.672$ m, $D=0.505$ m, hemisphere at each end ($V=0.2$ m³); permeation rate J equal to 1.14 NmL/hr/L of tank volume (below the allowable by the European Law [13] permeation rate limit of 6 NmL/hr/L (at 20 °C); typical garage size $L \times W \times H=5 \times 3 \times 2.2$ m (volume $V=33$ m³); still air; floor clearance of 0.5 m; temperature of 298 Analytical solution demonstrated that the time to reach LFL of 4 vol. % in the closed garage with chosen tank and permeation rate will be 240 days. On the other hand, time for hydrogen diffusion through the height of the garage is 62051 s or 0.7 day, which means that permeated hydrogen will make a uniform mixture across the considered garage height.

CFD study with the view to investigate the uniformity of permeated hydrogen dispersion in a garage-like enclosure was also carried out [36]. Numerical simulations were performed based on an original approach of a hydrogen mass source term introduction in the hydrogen conservation equation in control volumes around the tank surface. The permeation leak was simulated as a volumetric release of hydrogen in a thin layer of control volumes around the tanks surface of 1.87 m². CFD simulations indicated a negligible stratification of hydrogen. It is shown that the maximum hydrogen concentration in an enclosure is always on the top surface of the tank and it never reaches 100 vol. %. Both the analytical analysis and numerical simulations have demonstrated that diffusion and buoyancy contributions to the hydrogen transport from the tank surface are balanced within 1 minute from the beginning of the process. The quasi-steady state conditions within the enclosure with approximately linear distribution of hydrogen from the top to the bottom are established in about 1 hour for the considered permeation rates. For example, the maximum concentration of hydrogen at time of 133 min on the tank top surface was 8.2×10^{-3} vol. % (Figure 14). The observed difference in hydrogen concentration between the ceiling and the floor is about 3×10^{-3} vol. % and this difference conserves with time. Both values are significantly lower that LFL of 4 vol. %.

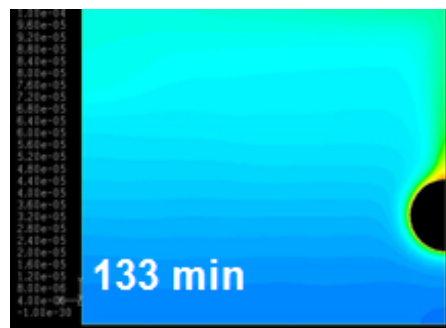


Figure 14. A snapshot of permeated hydrogen dispersion in a garage-like enclosure [36].

As a result of a permeation-induced leak, hydrogen releases in very small amounts, and spreads equally along the surface of a storage vessel. Due to a practically uniform dispersion of hydrogen permeated through the walls of the polymeric liner of the on-board storage tank on a FC vehicle parked in a garage, the perfect mixing of hydrogen and air is considered. Based on this the maximum allowable permeation rate can be calculated as [21, 37]:

$$Q_{perm}^{max} = \frac{Q_a \cdot C_{\%}}{100 - C_{\%}} \cdot \frac{60 \cdot 10^6}{V \cdot f_a \cdot f_t}, \quad (2)$$

where $C_{\%}$ - concentration of hydrogen in air, vol. %;

Q_a and Q_g - air flow and hydrogen gas leakage rate, respectively, m³/min;

V – water capacity of hydrogen storage, L;

f_a – aging safety factor, taken to be 2, for unknown aging effects;

f_t – test temperature safety factor (3.5 for tests at temperature 20 °C, and 4.7 for tests at 15 °C).

The values of maximum allowable permeation rate for a passenger car and a city bus are calculated and presented in Table 7, taking into account the following:

- The 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 air change per hour (ACH).
- Maximum permitted hydrogen concentration is 1 vol. %, i.e. ¼ of LFL.
- Maximum long term material temperature is 55 °C.

Table 7. The calculated safe permeation rates 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

With the levels of permeation rate indicated in Table 7 the hydrogen dispersion in typical garage would not represent a problem. These allowable permeation rates are regulated by the European Law [13]. Different limits on hydrogen permeation rate are accepted elsewhere. For example, please compare the following levels:

- 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.

Liquefied and cryo-compressed hydrogen storage

Storage tanks for LH₂ can hold more hydrogen compared to those for GH₂: volumetric capacity of LH₂ is 0.070 kg/L as opposed to 0.030 kg/L for GH₂ tanks at 70 MPa. However, a significant amount of energy (around 30% of the energy contained in hydrogen) is required for liquefaction. Hydrogen may

be liquefied for a simplified transport or storage. All of the major industrial gas suppliers have cryogenic delivery tankers. LH₂ is used at hydrogen refuelling stations and in airspace applications.

As you may already know from previous lecture, the normal boiling temperature of hydrogen is extremely low: 20.3 K (-253 °C). The volume expansion ratio of LH₂ to GH₂ is 848. LH₂ stored at low (cryogenic) temperatures and at pressures of around 0.6 MPa. An appropriate and sufficient level of tanks insulation is needed to prevent the release of evaporated gas. The costs of materials suitable for LH₂ storage tanks as well as the volumes and weights of tanks are significantly higher than those for GH₂.

The LH₂ storage tank is a dewar, double-walled, vacuum-insulated vessel made of lightweight steel alloys. There is no permeation, as the double-walled tank retains vacuum between the walls. The LH₂ storage has a major challenge. The inherent heat input from the environment may lead to warming and boiling of LH₂ inside the tank. When the pressure in the storage vessel remains constant the vapours produced from boiling of LH₂ are called boil-off. These vapours can be released through venting. The boil-off (evaporation of LH₂) can be caused by the following factors:

- *Ortho- para-hydrogen 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 LH₂ 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 LH₂ at a high pressure is transferred from trucks and rail cars to a low pressure vessel.

The main components of on-board LH₂ tank are shown on Figure 15. They include:

- LH₂ storage container
- Shut-off devices
- A boil-off system
- Pressure Relief Devices (PRDs)
- The interconnecting piping (if any) and fittings between the above mentioned components.

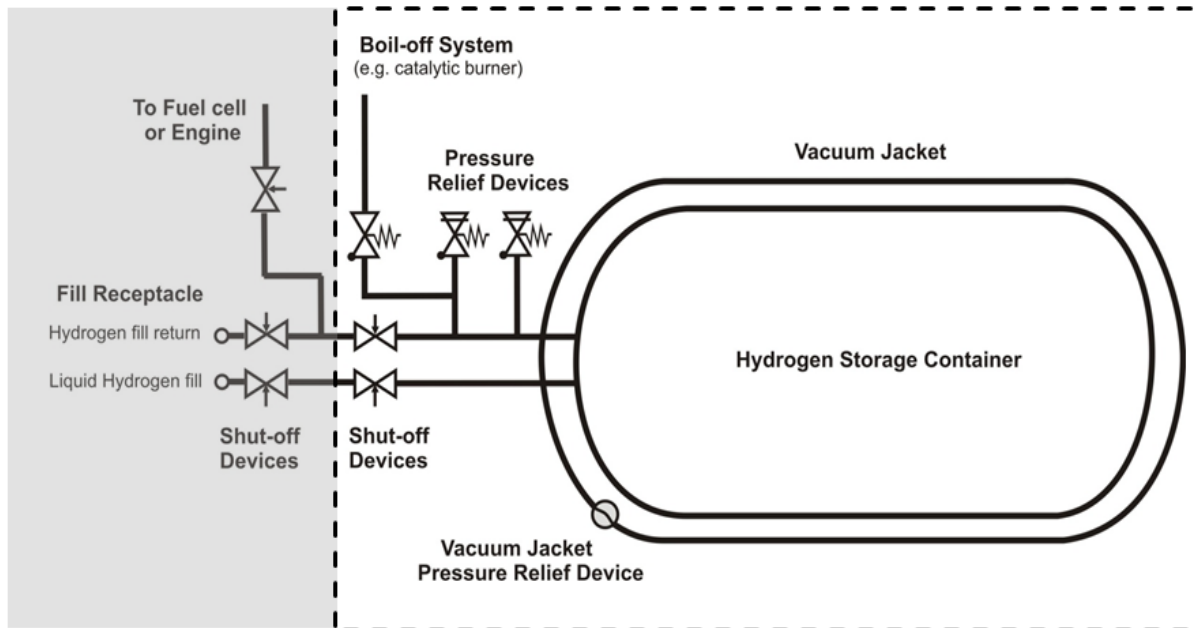


Figure 15. A schematic representation of LH₂ storage system [8].

Some safety issues associated with LH₂ storage are discussed below:

1. A loss of LH₂ containment. A damage of the external tank walls can lead to the disruption of vacuum, causing heating and subsequent pressure rise inside the vessel. This should be avoided wherever possible.
2. Formation of oxygen-enriched atmospheres. The condensed air may form oxygen enriched atmospheres in the vicinity of LH₂ storage. The solid deposits formed by condensed air and LH₂ could be enriched with oxygen. This poses a risk of explosion if the external wall tank is damaged. The mechanism is considered as a possible reason for a powerful secondary explosion occurred during large-scale LH₂ release experiments at HSL [38].
3. The boil-off. It raises concerns when vehicles are parked for a long time as the pressure build-up is possible until the boil-off valves open.
4. Ice formation. Low temperatures may result in ice build-up on the storage elements (e.g. valves, dewars) leading to an excessive exterior pressures, and to a possible rupture of the vessel.

In case of a LH₂ leak or spill, a hydrogen cloud will be formed. This cloud may flow horizontally for some distance or even downward, depending on the terrain and weather condition. The ignition of LH₂ vapour cloud is possible. For examples, recent experiments carried out at HSL (UK) found that the ignitions occurred in 10 of the 14 tests [39].

Cryo-compressed storage combines storage of hydrogen at cryogenic temperatures in a vessel that can be pressurised (e.g. to 35 MPa), as opposed to current LH₂ vessels which employ near-ambient pressures. Liquid hydrogen or cold compressed hydrogen can be stored. This technology, which is still at R&D stage, was developed by Lawrence Livermore National Laboratory (LLNL) and BMW Group. It has the following advantages:

- higher hydrogen density compared to LH₂ and GH₂ storage options;
- potential improvement in weight, volume and overall costs of tanks;
- significantly lower theoretical energy of cryogenic hydrogen associated with tank rupture;

- lower evaporative losses than liquid hydrogen tanks, and are much lighter than metal hydrides.

Solid storage of hydrogen

In the introductory lecture it was highlighted that hydrogen can also be stored either chemically or physically in certain materials (Table 8). There are several mechanisms known for storing hydrogen in materials: absorption, adsorption or chemical reaction. This technology, is currently at R&D stage, does not require high pressures or low temperatures. In contrast to cGH_2 and LH_2 storage options, the accidental loss of confinement may only happen if the materials are heated leading to a release of hydrogen [40].

Table 8. A range of materials used for storage of hydrogen in solids.

Carbon and High Surface Area materials	Chemical hydrides (hydrolysis)	Rechargeable hydrides	Chemical hydrides (thermal decomposition)
<ul style="list-style-type: none"> • Activated carbon • Nanotubes and graphite nanofibres • Buckyballs • Zeolites • Metal organic frameworks (MOF) • Clathrate hydrates 	<ul style="list-style-type: none"> • Encapsulated sodium hydride (NaH) • Lithium, calcium magnesium hydrides • Complex hydrides $LiAlH_4$; $NaAlH_4$ 	<ul style="list-style-type: none"> • Alloys and intermetallic compounds • Complex compounds • Nanocrystals 	<ul style="list-style-type: none"> • Aluminium hydride • Ammonia borozane

As you can see there are many options: rechargeable hydrides, chemical hydrides, carbon and other High Surface Area (HSA) materials. The most developed option is metal hydrides (potential for > 8 wt. % H_2 and > 90 kg/m^3 hydrogen-storage capacities at 10-60 bar). Hazards and safety issues associated with solid storages are indicated below:

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

There are also some technical and other issues such as: weight, lower desorption temperatures, recharge time and pressure, high costs, cyclic life, container compatibility and optimisation.

Summary

This lecture addressed different hydrogen storage options – compressed, liquefied and in solid materials, as well as hazards and safety issues associated with them. A close attention was paid to

the most common method of storing hydrogen in high-pressure storage tanks. The different types of hydrogen storage vessels and their main components have been considered. The topics relevant to First Responders such as consequences of a catastrophic rupture of the vessels and fire resistance rating of hydrogen storage tanks were discussed in details. This lecture also covered the topics of hydrogen interaction/compatibility with different materials, hydrogen embrittlement and hydrogen permeation. The measures on the reduction of hydrogen embrittlement and limitation of hydrogen permeation were discussed as well.

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