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HyTrEc 2
Hydrogen Transport Economy for the North Sea Region

HySKILLS

HYDROGEN STORAGE AND SAFETY

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UNIVERSITETET I TROMSØ

FROM ADVERTISEMENT AT ABERDEEN INTERNATIONAL AIRPORT

INTRODUCTION

Hydrogen is typically stored and transported in two forms:

- As a compressed hydrogen gas
- Or as a cryogenic liquid.

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.

For this reason, hydrogen storage equipment must be designed and maintained to high safety standards to ensure the integrity of the container.

OBJECTIVES

In this lecture I will give an overview of hydrogen storage options and the main safety and technical issues associated with them.

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.

LEARNING OUTCOMES

By the end of this lecture you will be able to:

Understand how hydrogen is stored and appreciate the challenges associated with different types of storages;

Recognise the 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.);

Understand the main safety and technical issues associated with compressed hydrogen storage;

Establish effect of hydrogen embrittlement on safety of hydrogen storage systems;

Identify safety concerns associated with liquefied hydrogen storage and storage of hydrogen in various solid materials.

HYDROGEN STORAGE OPTIONS

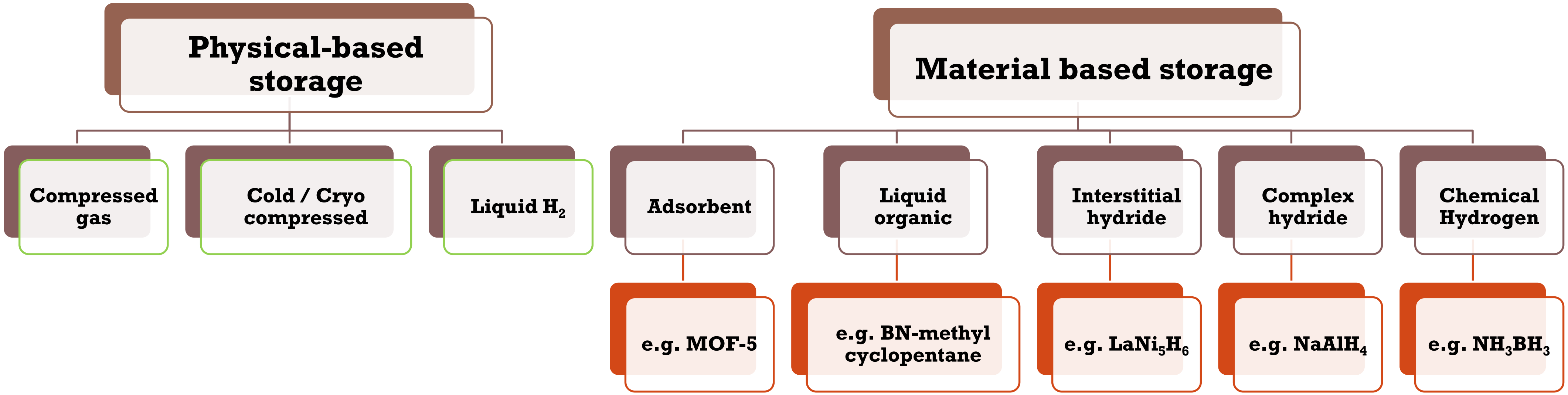
Hydrogen storage is an enabling technology across the entire range of Fuel Cell and Hydrogen (FCH) applications, from on-board vehicles to stationary and portable power generation.

There is no universal solution for hydrogen storage. Instead, the solution must be carefully selected to address specific system requirements.

ENERGY CONTENT BY WEIGHT AND BY VOLUME FOR HYDROGEN AND OTHER COMMON FUELS

	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 STORAGE TECHNOLOGIES



COMPRESSED GASEOUS HYDROGEN STORAGE CGH2

The most common way of storing hydrogen is as a compressed gas in metal cylinders at different pressures.

	Pascal	Bar
	Pa	bar
1 Pa	$\equiv 1\ N/m^2$	10^{-5}
1 bar	10^5	$\equiv 10^6\ dyn/cm^2$

MAJOR CONCERNS RELATED TO CGH2

- 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.
- Hydrogen permeation and embrittlement.

IMPORTANT TERM: NOMINAL WORKING PRESSURE (NWP)

Nominal Working Pressure (NWP) is a gauge pressure, which characterises typical operation of a system.

For cGH2 tanks the NWP is a settled pressure of compressed gas in a fully filled container at a uniform temperature of 15 °C.

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.

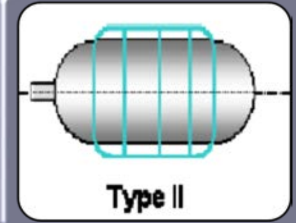
During a normal (re-)filling process, the pressure inside the container may rise up to 25% above the NWP as adiabatic compression of the gas causes heating within the containers. As the container cools down after refilling, the pressure drops. By definition mentioned above, the settled pressure of the system will be equal to the NWP when the container is at 15 °C.

TYPES OF HYDROGEN STORAGE TANKS

Type I: made of metal seamless metallic container

Large storage capacity in terms of volume, but allows for 1% to 2% hydrogen storage compared to the cylinder mass.

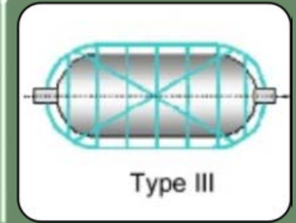
Standard ASME Section VIII, Division 1 tanks maximum pressure of 3,000 psi (200 Bar). ASME Section VIII Division 2 or 3 can have pressures up to and beyond 15,000 psi (1,000 Bar).



Type II: seamless metallic container hoop-wrapped with fibre resin composite.

CFRP Layer

4500 PSI (300 Bar)



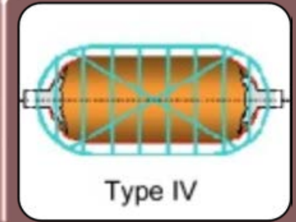
Type III: metallic liners fully-wrapped with fibre resin composite

CFRP Layer

10000 PSI (700 Bar)

Non load bearing

Lightweight



Type IV: polymeric liner fully wrapped with fibre resin composite

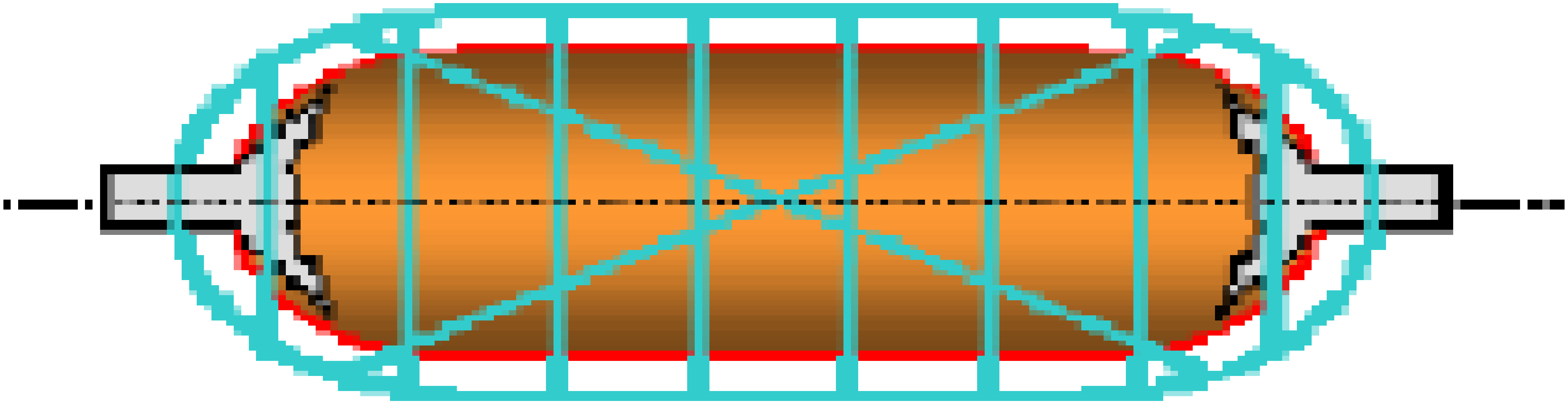
Plastic liner, CFRP Layer

10000 PSI (700 Bar)

Non load bearing

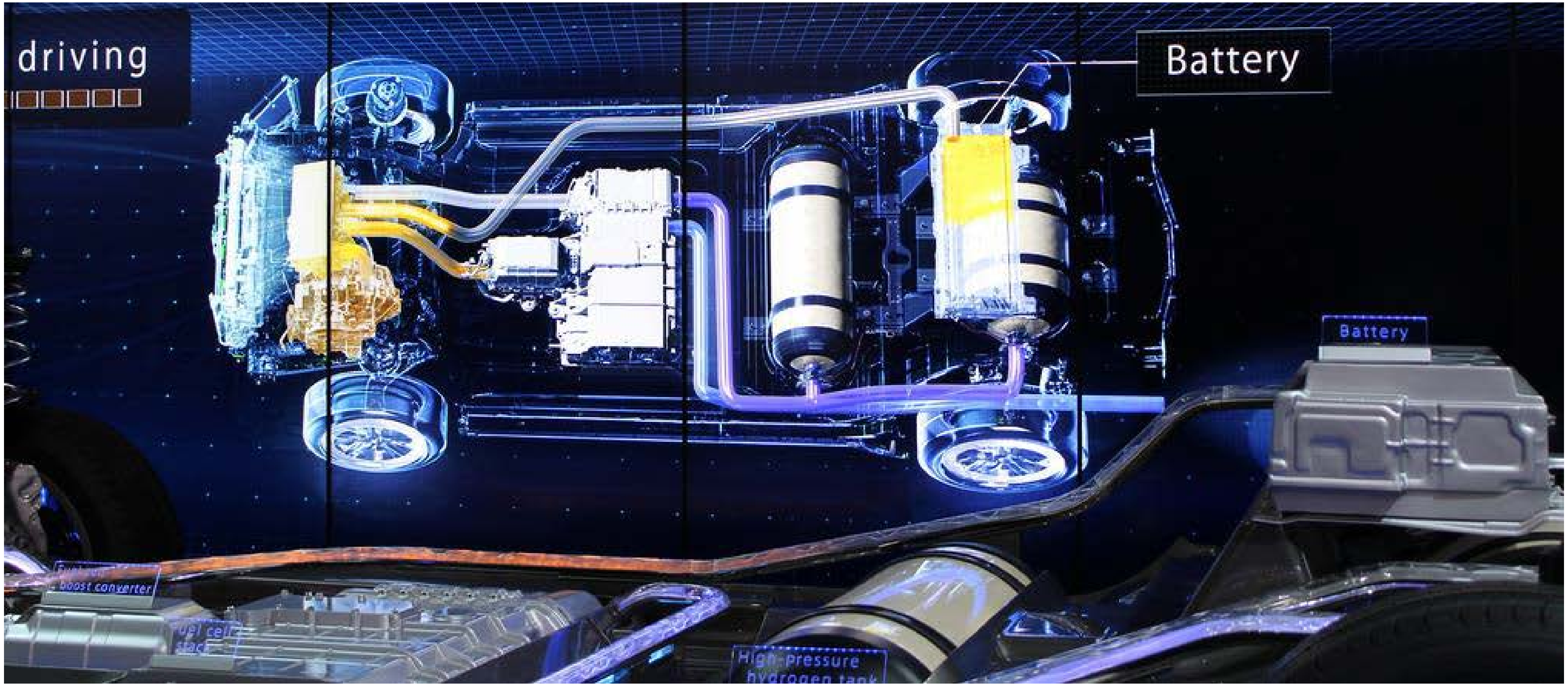
Lightweight

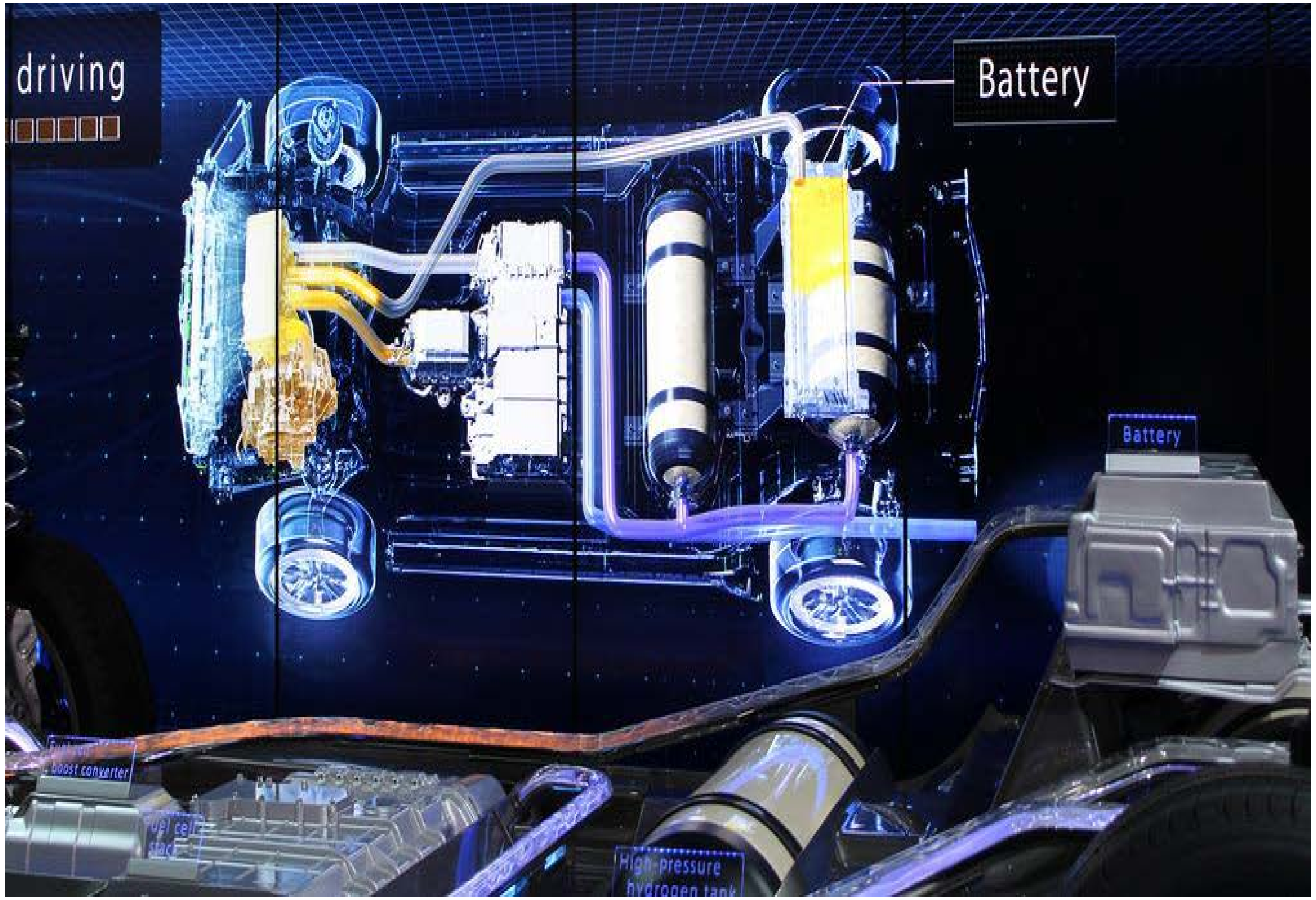
HYDROGEN STORAGE VESSELS FOR STATIONARY APPLICATIONS



Type IV

ON-BOARD HYDROGEN STORAGE





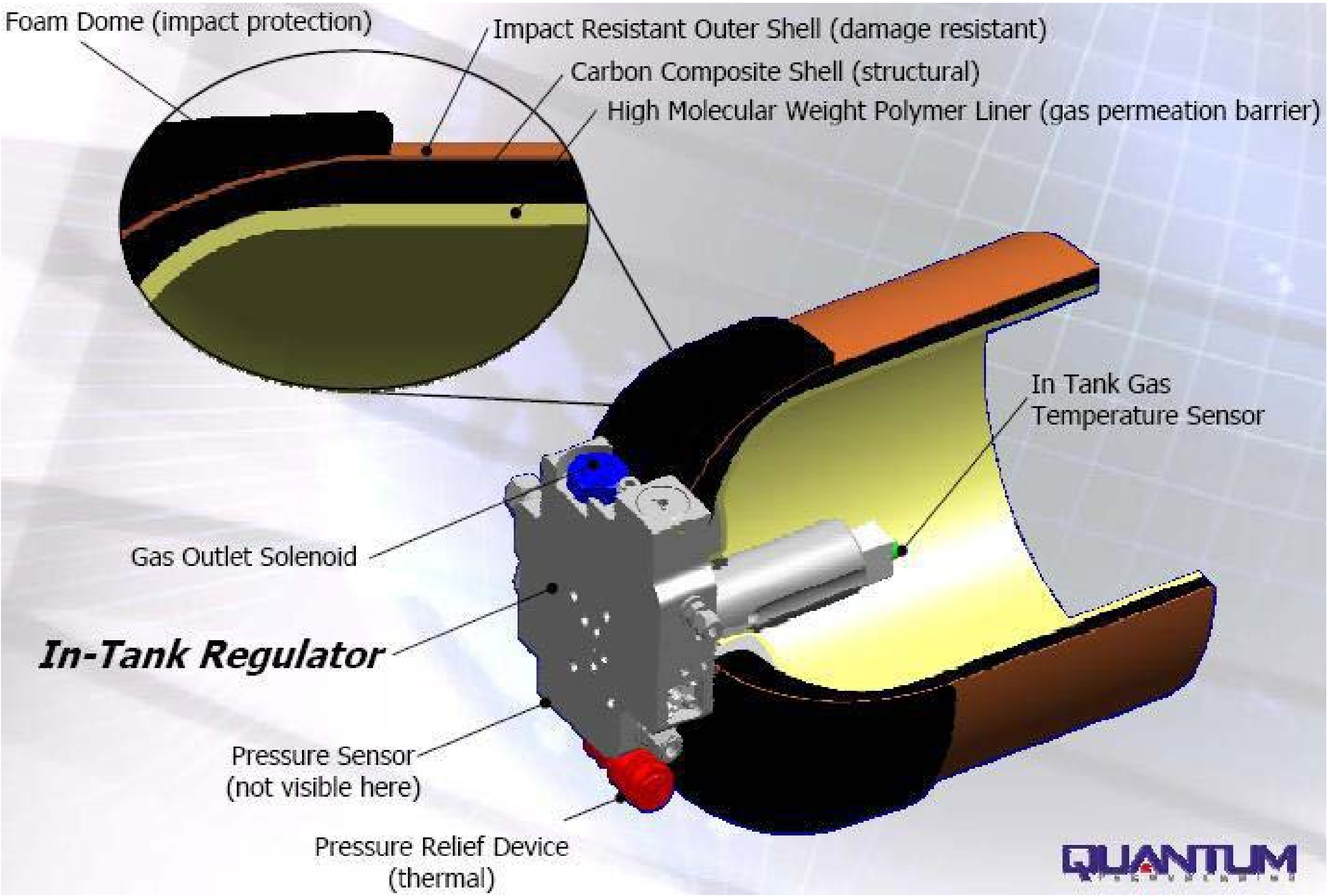
Source: Warner, 2005

TYPE IV CGH2 STORAGE TANK WITH THE KEY SAFETY AND COMMUNICATION FEATURES

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

A CROSS-SECTION OF A QUANTUM HYDROGEN TANK WALL WITH INTEGRATED FUEL STORAGE SYSTEMS

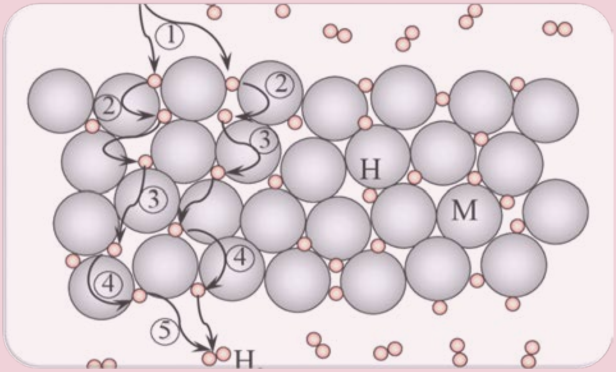
SOURCE: WARNER, 2005



- 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.

HYDROGEN EMBRITTLEMENT (HE)

Also known as **hydrogen-assisted cracking** or **hydrogen-induced cracking** (**HIC**).



Hydrogen atoms are small and can permeate solid metals. Once absorbed, hydrogen lowers the stress required for cracks in the metal to initiate and propagate, resulting in embrittlement.

HOW TO STOP HYDROGEN EMBRITTLEMENT?

Hydrogen factors

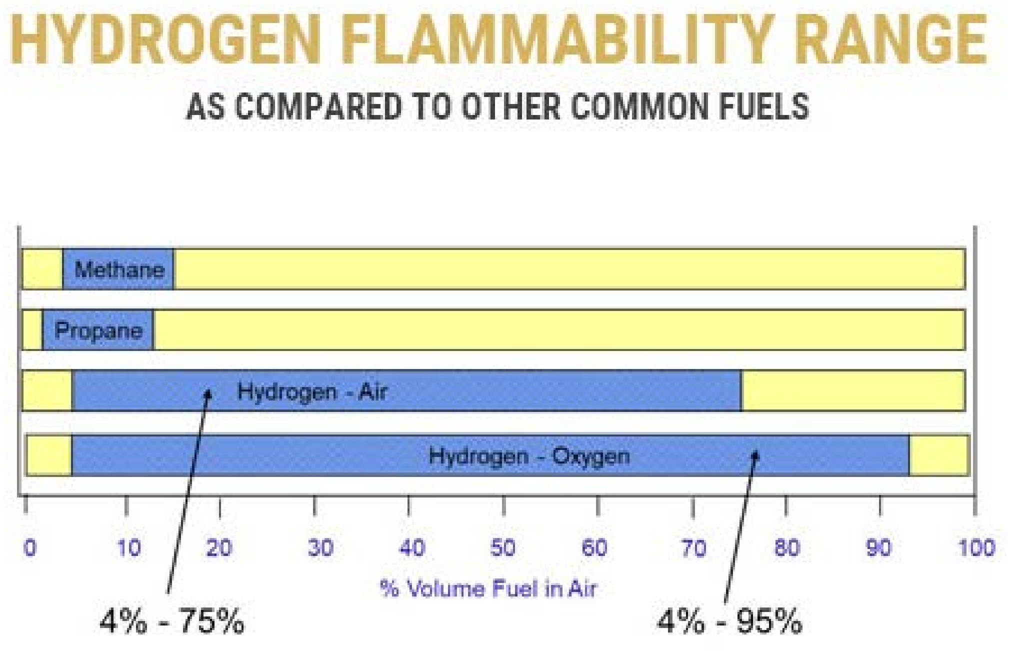
- Include factors such as the pressure, temperature, and purity of the gas.

Stress factors

- Include externally applied stresses, such as maximum applied stress, number of cycles, stress risers, etc.
- They also have internal residual stresses developed during processes such as fabrication, welding, or heat treating.

Material factors

- Primarily involve selecting a material with excellent hydrogen resistance at your operating pressure and temperature



HYDROGEN PERMEATION THROUGH THE POLYMERIC LINER

- This is the main issue for the type IV.
- According to the EU regulation the permeation rate of hydrogen (at 20 ^{o}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].
- 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).

PRD WITH FUSE METAL AND POPPET

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.

According to the European Commission Regulation (EU) No 406/2010, the on-board hydrogen storage must be fitted with PRDs/TPRDs.

The PRDs are designed to open when pressure or temperature reaches a certain limit. TPRDs open if temperature is above 108-110 oC. Hydrogen tanks should be protected with the non-reclosing TPRDs (Please note that CNG vehicles usually equipped with reclosing PRDs).

PRD TRIGGERING

Hydrogen vehicle containers require PRDs primarily to protect against impinging fires.

Modern composite tanks are good thermal insulators, and they weaken at high temperatures.

Fuel pressure is not expected to increase significantly during an impinging fire. A container may not be filled with hydrogen at the time of the fire.

PRDs can be triggered by pressure, temperature, or a combination.

Most hydrogen and CNG vehicle containers are protected by temperature activated PRDs.

TWO TYPES OF PRD FAILURES

Type 1 failures — Are when a PRD should vent but does not.

- Type 1 failures are usually associated with blockage by dirt or ice.
- PRDs are the final safety device. Type 1 failures are very hazardous.

Type 2 failures — Are when a PRD should not vent but does.

- Type 2 failures can arise from impact, ice formation, or worn PRD components.

TYPES OF PRDS

PRDs are made for diverse fluids, conditions, and flow passage sizes.

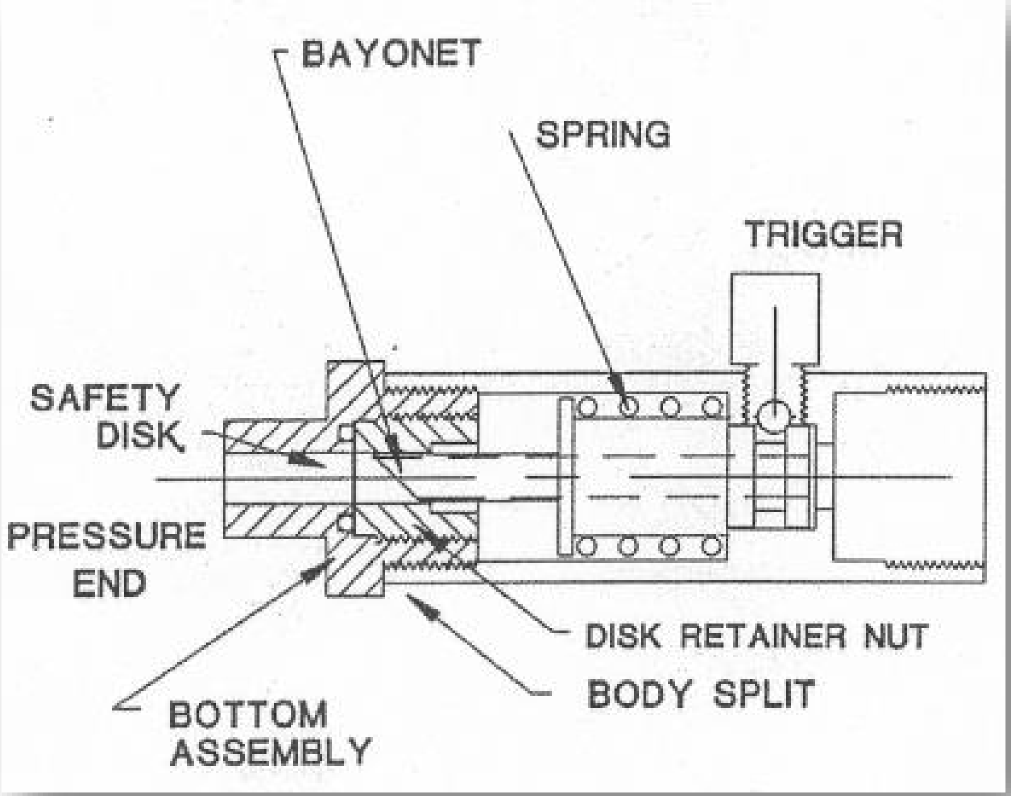
The two main categories are:

- Reclosable and
- Nonreclosable.

Reclosable PRDs can be reused, but they are not used for hydrogen vehicle containers because:

- They do not vent fully,
- They restrict the flow rate, and - they are pressure activated.

BAYONET PRD



A bayonet PRD 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. Response time is reduced if fuse metal is directly exposed to hot gas.

A Mirada bayonet PRD is shown.

Gas vents from right to left through the hollow bayonet.

PRD WITH FUSE METAL AND POPPET

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.

A fusible metal plug inside the PRD melts, when temperatures are higher than 110 oC, opening and venting the entire content of the tank.

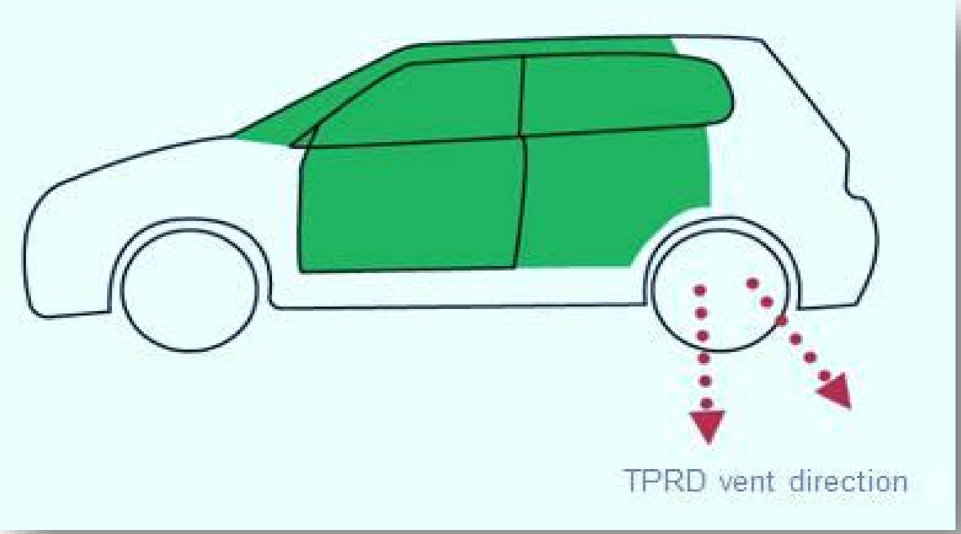
GLOBAL TECHNICAL REGULATIONS (GTR) ON HYDROGEN-FUELLED VEHICLES (2013) RELEVANT TO PRD

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'

(GTR) ON HYDROGEN-FUELLED VEHICLES (2013)



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].

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 goal of all the tests is that the tanks vent and do not rupture [*US DoE, US Department of Energy (2008)*].

EXAMPLES OF SOME TYPES OF CGH2 CYLINDER TESTS

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).

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 republished
SAE J2579	Fuel systems in fuel cell and other hydrogen vehicles	U.S.	2008 2009 republished
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

POTENTIAL HAZARDS AND SAFETY ISSUES ASSOCIATED WITH CGH2: SUMMARY

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.

An overpressure and impulse can lead to: people's eardrum damage, tank rupture, flying debris, shattered glass, etc.

POTENTIAL HAZARDS AND SAFETY ISSUES ASSOCIATED WITH CGH2: SUMMARY

Pressure peaking phenomenon may lead to a garage collapse in just one second.

Hydrogen can be ignited easily as its MIE (Minimum ignition energy) 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.

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.

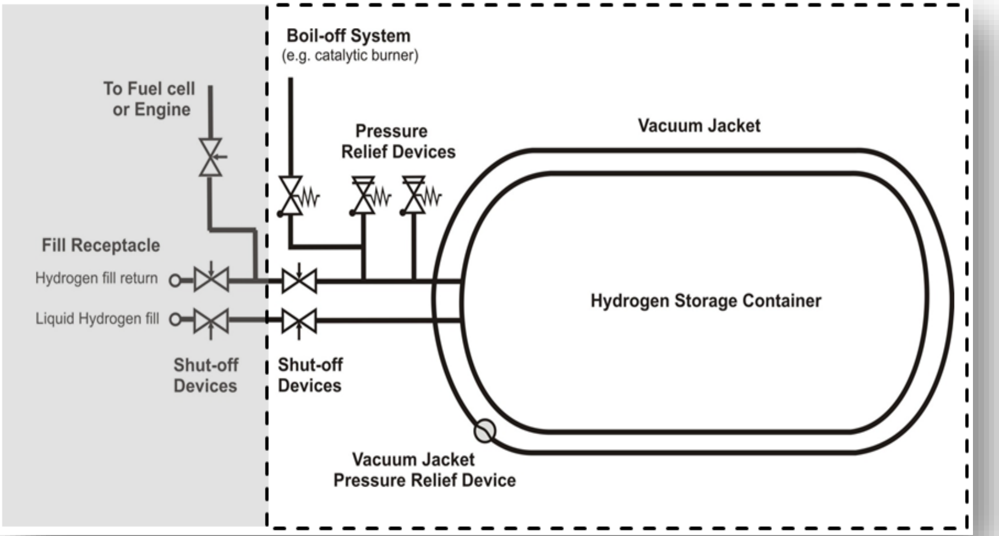
The normal boiling temperature of hydrogen is extremely low: 20.3 K (-253 oC).

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.

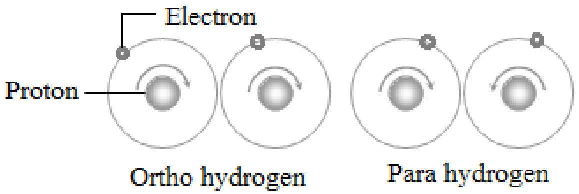
THE LH2 STORAGE TANK



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)

***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.**

SOME SAFETY ISSUES ASSOCIATED WITH LH2 STORAGE

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.***

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]***

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.***

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.***

CRYO-COMPRESSED STORAGE

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 rapture;
- Lower evaporative losses than liquid hydrogen tanks, and are much lighter than metal hydrides.

SOLID STORAGE OF HYDROGEN

Carbon and High Surface Area materials.

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

Chemical hydrides (hydrolysis)

- Encapsulated sodium hydride (NaH)
- Lithium, calcium magnesium hydrides
- Complex hydrides LiALH4; NaAlH4

Rechargeable hydrides

- Alloys and intermetallic compounds
- Complex compounds
- Nanocrystals

Chemical hydrides (thermal decomposition)

- Aluminium hydride
- Ammonia borozane

HAZARDS AND SAFETY ISSUES ASSOCIATED WITH SOLID STORAGES

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.*
Technical and other issues such as:	*weight, lower desorption temperatures, recharge time and pressure, high costs, cyclic life, container compatibility and optimisation.*

FINAL REMARKS AND 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 measures on the reduction of hydrogen embrittlement and limitation of hydrogen permeation were briefly discussed.

ACKNOWLEDGEMENT

- The lecturer wishs to acknowledge contributions to this lecture from the following sources:
  - Erasmus + HySkills project: Information on Hydrogen storage was adapted from the Hydrogen Storage VET module developed through HySkills.
  - EU HyResponse project: Useful information was adapted from HyResponse Lecture: "Safety of hydrogen storage", Compiled by S. Tretsiakova-McNally; reviewed by D. Makarov (Ulster University), chromeextension://efaidnbmnnnibpcajpcglclefindmkaj/http://www.hyresponse.eu/files/Lectures/Safety_of_hydrogen_storage_notes.pdf

Thank you

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