European Train the Trainer Programme for Responders

Lecture 5

Safety of liquefied hydrogen

LEVEL I

Firefighter

The information contained in this lecture is targeted at the level of Firefighter and above.

This topic is also available at level II and IV

This lecture is part of a training material package with materials at levels I – IV : Firefighter, crew commander, incident commander and specialist officer. Please see the lecture introduction regarding competence and learning expectations

Note: these materials are the property of the HyResponder Consortium and should be acknowledged accordingly, the outputs of PRESLHY have been used as a basis

FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

Disclaimer

Acknowledgments

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Summary

For various applications of hydrogen where volume is an essential issue, liquified hydrogen (LH_2) is a necessary for the sake of volume reduction. However, there are also other situations where the liquid state represents a reasonable and economic solution for storage and distribution of large amounts of hydrogen depending on the end-user's requirements. Furthermore, LH_2 has the advantage of extreme cleanliness making it appropriate in many industrial applications. Major drawback is the enormous energy input required to liquefy the hydrogen gas, which has a significant impact on the economy of handling LH_2.

The hazards associated with the presence and operation of LH_2 containing systems are subject of safety and risk assessments. Essential part of such accident sequence analyses is the simulation of the physical phenomena which occur in connection with the inadvertent release of LH_2 into the environment by computation models. The behaviour of cryogenic pool propagation and vaporization on either a liquid or a solid ground as well as potential pool burning is principally well understood. Furthermore, state-of-the-art computer models have been developed and validated against respective experimental data. There are, however, still open questions which require further efforts to extent the still poor experimental data basis.

This lecture is based on the Deliverable 6.1 – Handbook of hydrogen safety: Chapter on LH2 safety – of Pre-normative REsearch for Safe use of Liquid Hydrogen (PRESLHY) project. The experimental and theoretical investigation of the characteristics of liquid hydrogen, its favourable and unfavourable properties, as well as the lessons learnt from accidents have led to a set of codes, standards, regulations, and guidelines, which resulted in a high level of safety achieved today. This applies to both LH_2 production and the methods of mobile or stationary LH_2 storage and transportation/distribution, and its application in both science and industries.

Keywords

Liquefied hydrogen, cryogenic release, accidental spill, combustion, liquid hydrogen technology

Table of contents

1. Target audience

The information contained in this lecture is targeted at LEVEL 1: Firefighter. Lectures are also available at levels II, III and IV: crew commander, incident commander and specialist officer.

The role description, competence level and learning expectations assumed at crew commander level are described below.

1.1 Roll description: Firefighter

A firefighter is responsible and expected to be capable of carrying out operations safely in personnel protective equipment including breathing apparatus using equipment provided, like vehicles, ladders, hose, extinguishers, communication and rescue tools, under any climatic conditions in areas and to emergency situations which can be reasonably anticipated as requiring a response.

1.2 Competence level: Firefighter

Trained in the safe and correct use of PPE, BA and other equipment which it is expected they will operate first responders must be supported by appropriate knowledge and practice. Behaviours that will keep them and other colleagues safe should be described by Standard Operating Procedures (SOP). Practiced ability to dynamically assess risk to self and others safety is required.

1.3 Prior learning: Firefighter

EQF 2 Basic factual knowledge of a field of work or study. Basic cognitive and practical skills required to use relevant information in order to carry out tasks and to solve routine problems using simple rules and tools. Work or study under supervision with some autonomy.

2. Introduction and objectives

The use of liquified hydrogen (LH_2) in practical applications is of great interest due to the higher energy density of LH_2 in comparison with that of compressed gaseous hydrogen (cGH_2). LH_2 is typically used as a concentrated form of hydrogen storage. As for any gas, storing it as liquid takes less space than storing it as a gas. The density of LH_2 is only 70.8 kg m^{-3} at standard pressure and boiling temperature (1 atm, 20.3 K). LH_2 requires cryogenic storage technology such as special thermally insulated containers and requires special handling common to all cryogenic fuels, which bring potential risks for LH_2 generation, transportation and application.

The aim of this lecture is to provide responders with sufficient knowledge and the potential hazards of LH_2, helping responders to understand the properties and behaviour of LH_2.

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

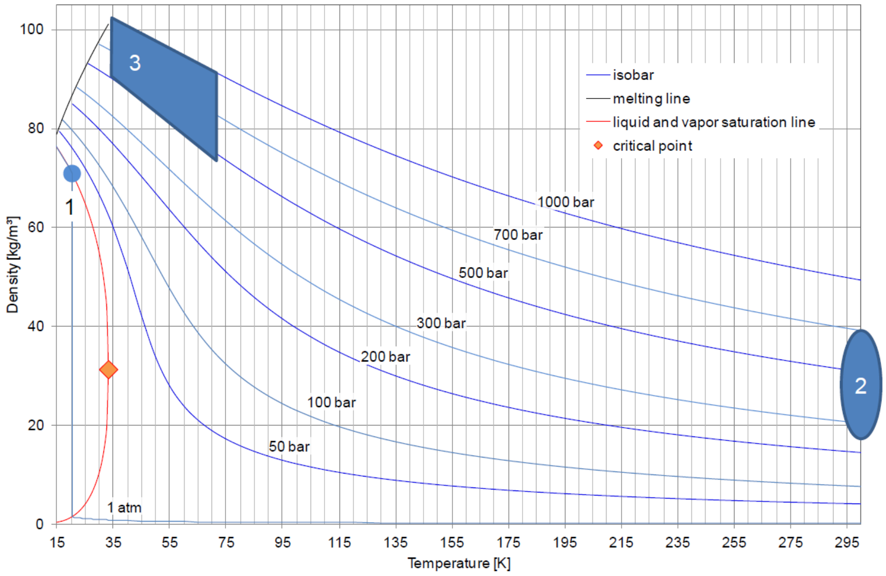
- Understand the properties, in terms of physical and chemical, of LH_2;

- Know the hazards of cryogenic hydrogen;
- Recognise the release and combustion of cryogenic hydrogen and the thermal and pressure hazards;
- Be familiar with the technologies of LH_2 generation, storage, and transport.
- Identify the risk and hazard of LH_2 pertinent to responders.

3. Liquid hydrogen properties

3.1 Physical properties

Liquid hydrogen (LH_2) is the liquid state of the element hydrogen. To exist as a liquid, hydrogen must be cooled below its critical point of 33 K. However, for it to be in a fully liquid state at atmospheric pressure, hydrogen needs to be cooled to 20.28 K (−252.87 °C) [1]. The triple point of hydrogen is at 13.81 K [1] and 7.042 kPa [2]. Liquid hydrogen also has a much higher specific energy than gasoline, natural gas, or diesel. Liquid hydrogen is typically used as a concentrated form of hydrogen storage. As for any gas, storing it as liquid takes less space than storing it as a gas at normal temperature and pressure. However, the liquid density is very low compared to other common fuels. Once liquefied, it can be maintained as a liquid in pressurized and thermally insulated containers. The density of liquid hydrogen is only 70.99 g/L (at 20 K), a relative density of just 0.07 (Figure 1). The energy density of hydrogen is very high; 1 kg of hydrogen contains approximately 2.5 times more energy than 1 kg of natural gas. Although the specific energy is more than twice that of other fuels, this gives it a remarkably low volumetric energy density, many folds lower. The main properties of LH_2 are summarised in Table 1.



1 - liquid @ ~20 K; 2 - pressurised gas @ ~300 K; 3 - cryogenic compressed gas

Figure 1. Density of hydrogen in the low temperature range as a function of pressure [3].

3.2 Chemical properties

Hydrogen is able to react chemically with most other elements. In connection with oxygen, hydrogen is highly flammable over a wide range of concentrations. It burns in a non-luminous hot flame to water vapor liberating the chemically bound energy as heat (gross heat of combustion: 286 kJ/mol). A stoichiometric hydrogen-air mixture contains 29.5 vol% of hydrogen. The flammability range is of 4–75 vol% of concentration in air, up to 95 vol% in oxygen, and widens with increasing temperatures. The lower flammability limit (LFL) as the minimum amount of fuel that supports combustion, is usually the more important limit for low-rate releases, since it will be reached first in a continuous leakage. Most importantly, the cloud with > 4% hydrogen concentration may cover longer distances and larger area from the releases point.

A weak spark or the electrostatic discharge by a human body, which is in the range of 10 mJ, would suffice for an ignition; this is, however, no different from other burnable gases. The minimum ignition energy is even further decreasing with increasing temperature, pressure, or oxygen contents. Measurements at cryogenic temperatures have been provided recently [6].

4. Liquid hydrogen hazards

Liquid hydrogen requires cryogenic storage technology such as special thermally insulated containers and requires special handling common to all cryogenic fuels. This is similar to, but more severe than liquid oxygen. Even with thermally insulated containers it is difficult to keep such a low temperature, and the hydrogen will gradually leak away. It also shares many of the same safety issues as other forms of hydrogen, as well as being cold enough to liquefy, or even solidify atmospheric oxygen, which can be an explosion hazard.

In order to define the different hazardous scenarios and associated consequences, LH_2 storage is considered only. Table 1 summarizes these events, with initial causes and potential final consequences.

Table 1. Description of potential hazardous events.

Feared events	Main conditions	Consequences
1 - Burst of the storage at working pressure (P_W) (impinging fire / fragment)	100% gaseous H_2 - 10 bar - type I vessel	Overpressure and fragments
2 - Accidental event on storage with liquid H_2 (fire case) at $2P_W$	Burst of LH_2 storage Flash fire	"BLEVE" with thermal effects
3 - Failure on the storage (breech or perforation)	10 bar, rapid liquid H_2 spreading and evaporation on ground	Pool vaporization and cryogenic cloud formation with overpressure effects in case of flammable cloud ignition
4 - Leak on the pipe between storage and pump	10 bar, liquid * diphasic pressurized release * and/or H_2 liquid pool, vaporization forming a flammable cloud	Liquid hydrogen jet and potential rainout forming a LH_2 pool on the ground and overpressure effects due to flammable mixture ignition
5 - Leak on the pipe between pump and atm. vaporizer	1000 bar, liquid * diphasic pressurized release but behaving like a high pressure gaseous jet	Certainly nearly-gaseous high pressure jet behaviour with overpressure effects due to ignition
6 - Burst of the storage at rupture pressure (P_R)	100% gaseous - 10 bar, type I	Overpressure and fragments

Note: BLEVE – boiling liquid expanding vapour explosion.

Regarding scenarios previously summarized, it can be highlighted that some of them are specific of liquid hydrogen, and other are gaseous feared events are already described, or similar.

4.1 Physiological problems with cryogenic hydrogen

Hydrogen is classified as non-toxic and non-acid, non-carcinogenous, being a simple asphyxiant with no threshold limit value (TLV) or LD50 (lethal dose 50%) value established [7].

Vaporization of released liquid hydrogen affects the composition of the atmosphere, particularly in (partially) confined areas, carrying the risk of asphyxiation. The enormous liquid/ambient expansion ratio combined with condensation of O_2 from the ambient air and burning of flammable H_2-air mixtures leads to a significant dilution of the local atmosphere. An oxygen volume fraction of less than 19.5% is considered by NASA to be dangerous to humans; less than 8% will be lethal within minutes (Table 2). Alarm levels are generally set at 19% of oxygen.

Table 2. Impact on humans by an atmosphere with decreasing oxygen contents.

Oxygen contents in air (%)	Symptoms
~21 – 19	None
~19 – 15	Reduced reaction times, no visible effects
~15 – 12	Heavy breathing, rapid heart beat, impaired attention or coordination
~12 – 10	Dizziness, faulty judgement, poor muscular coordination, rapid fatigue, lips slightly bluish
~10 – 8	Nausea, vomiting, inability to move, loss of consciousness followed by death
~8 – 6	Brain damage after 4–8 min, death within 8 min
< 6	Coma after 40 s, respiratory failure, death

Direct contact with liquid hydrogen or with surfaces at very low temperature causes cryogenic "burns" similar to thermal burns. Living tissue will freeze except for very brief contact periods where the temperature difference between cryogen and skin is still high (film boiling regime) and heat transfer small. The freezing of skin onto a cold surface can lead to severe damage upon removal. Prolonged skin exposure to cold hydrogen may result in frostbite. A symptom is short-lived local pain. Frozen tissues are painless and appear waxy, with a pale whitish or yellowish color. Thawing of the frozen tissue can cause intense pain. Shock may also occur. Prolonged inhalation of cold vapor or gas may cause serious lung damage. Particularly eyes are sensitive to cold. A longer exposure to cold temperatures after a large spill lowers the body temperature resulting in hypothermia, organ dysfunction, and respiratory depression [5].

There are no significant environmental hazards associated with the accidental discharge of liquid hydrogen due to its non-toxic character.

4.2 Immediate ignition of pressurised LH_2 release

Immediate ignition of a LH_2 high pressure jet seems to be similar to a gaseous hydrogen high pressure jet, with overpressure effects due to ignition.

5. Liquid hydrogen technology

5.1 Liquid hydrogen production process and infrastructures

One of the challenges in building a hydrogen economy is the establishment of an efficient production and supply infrastructure. Large scale distribution favours the relatively dense liquid phase LH_2, but liquefaction still suffers from low energy efficiencies. Historically, LH_2 was mainly used as a rocket fuel, where the low efficiency in the production did not matter. A major program of hydrogen liquefaction was started in the USA within space programs leading to the design and construction of large-scale liquefaction plants.

5.2 Liquid hydrogen storage and transport

5.2.1 Liquid hydrogen storage

Liquid hydrogen storages are already existing for professional for long time ago. But up to now there is no liquid hydrogen storage in public domain. Storage tanks for LH_2 can hold more hydrogen compared to those for GH_2: volumetric capacity of LH_2 is 0.070 kg/L as opposed to 0.030 kg/L for GH_2 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. LH_2 is used at hydrogen refuelling stations and in airspace applications.

The main components of on-board LH_2 tank are shown on Figure 2. They include:

- LH_2 storage container,
- Shut-off devices,
- A boil-off system,
- Thermal-activated Pressure Relief Devices (TPRDs),
- The interconnecting piping (if any) and fittings between the above-mentioned components.

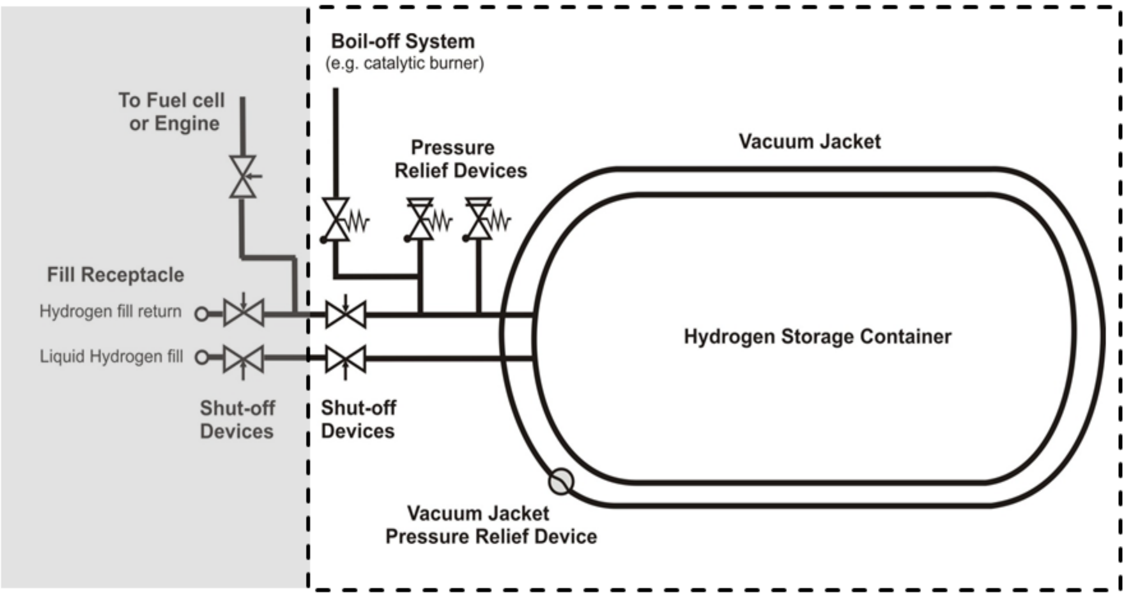


Figure 2. A schematic representation of LH_2 storage system from Ref. [8]

These storages can be in vertical or horizontal position. Cryogenic fixed storage has a volume from 10 m^3 to 300 m^3 with an internal pressure around 12 bar.

Figure 3. Horizontal and vertical liquid hydrogen storages. (Source Air Liquide).

In most of the cases, LH$_2$ storages are aerial. Nevertheless, it exists few cases of underground LH$_2$ storages, buried or vault as illustrated and defined in Figure 4.

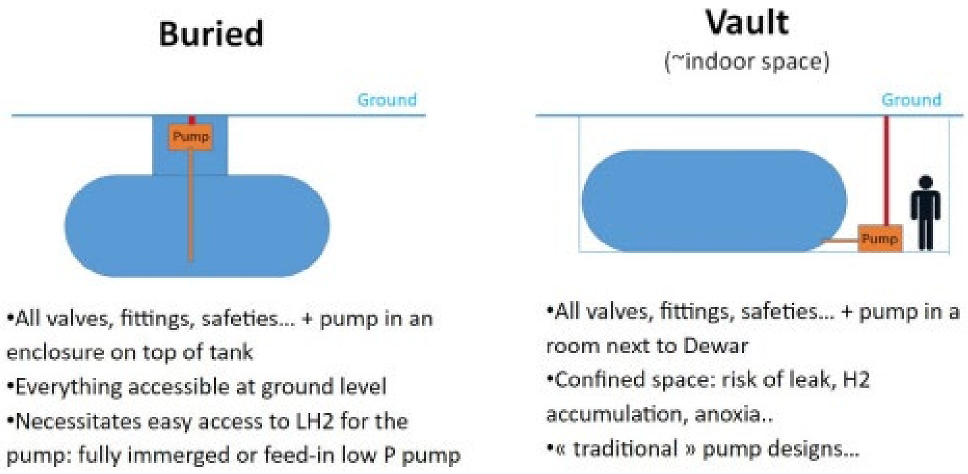


Figure 4. The two main possible designs for underground LH$_2$ storages.

5.2.2 Cryostat for stationary applications

Cryogenic vessels have been commonly used for more than 70 years for the storage and transportation of liquid hydrogen.

5.3 Liquid hydrogen refuelling station

Basically, as shown in Figure 5, a LH$_2$-based refueling station consists of:

- a LH$_2$ tank (around 20 m^3 - 1000 kg-H$_2$) with a maximal operating pressure of 10.3 bar,
- an insulated process line from the bottom of the storage to the LH$_2$ pump, driving LH$_2$ from the storage tank to a vaporizer; this device allows to pump LH$_2$ up to 1000 bar,
- a heater (named VAP: hot oil, electric in order to heat up hydrogen at 1000 bar),

- 1000 bar gaseous buffers (few m^3); these buffers are generally bundles of type I or II (i.e. metallic cylinders or long metallic tube).

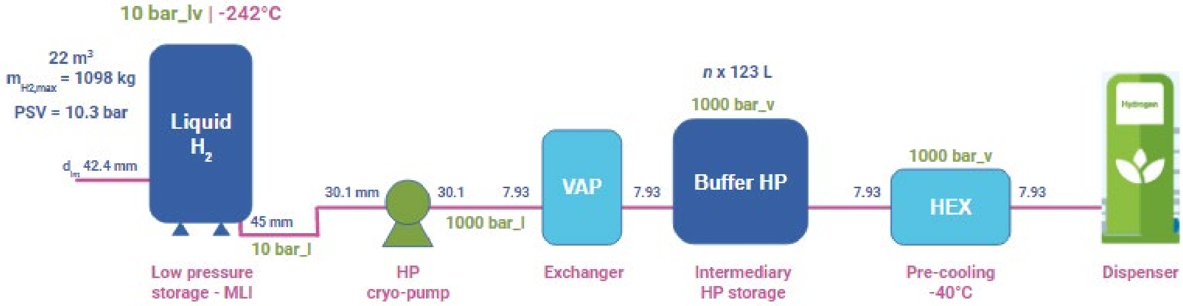


Figure 5. Simplified sketch of a liquid hydrogen refuelling station.

All the other parts (e. g. dispenser, filling hose et al.) of the refueling station are similar to classical gaseous refueling station (see comparison in Figure 6).

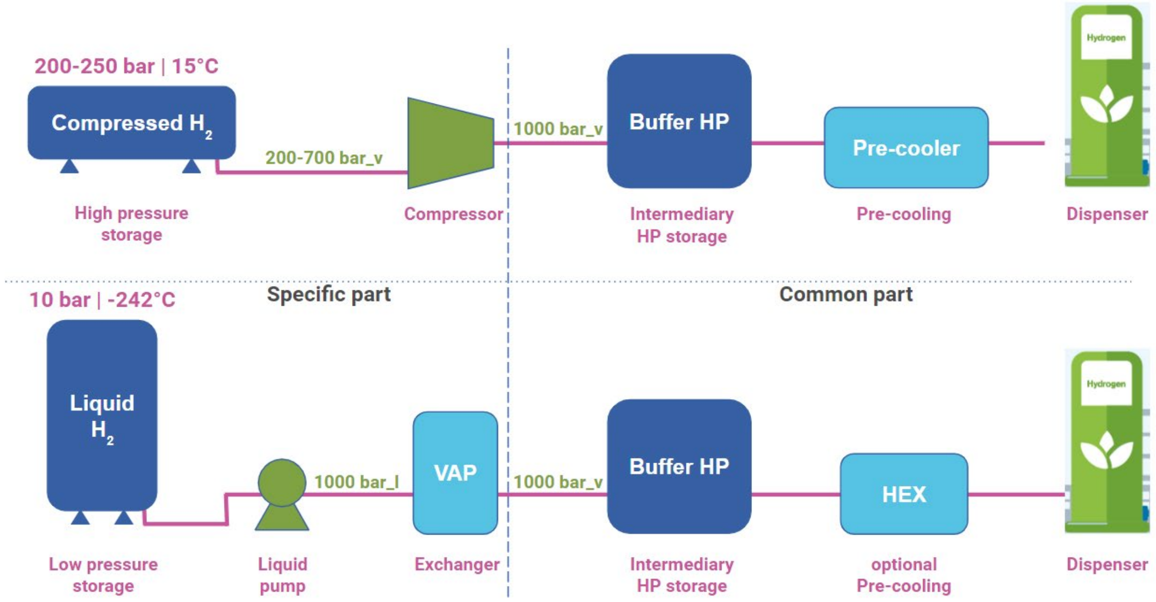


Figure 6. Simplified comparison between gaseous and liquid hydrogen refuelling stations. Top: gaseous HRS, bottom liquid HRS.

The LH_2 tank is delivered by a LH_2 truck. This LH_2 truck is composed of a 40 m^3 horizontal tank operating between 1 and 12 bar (inventory: 4 t-H_2). The connection between the storage and the truck is done by a flexible transfer line. The transfer is performed without a pump. A small vaporizer is present on the trailer to produce a pressure build-up in the truck tank and allow the transfer of liquid hydrogen in the stationary vertical storage.

More concretely below the Linde Liquid hydrogen refuelling station installed at Oakland (US) (see Figure 7).

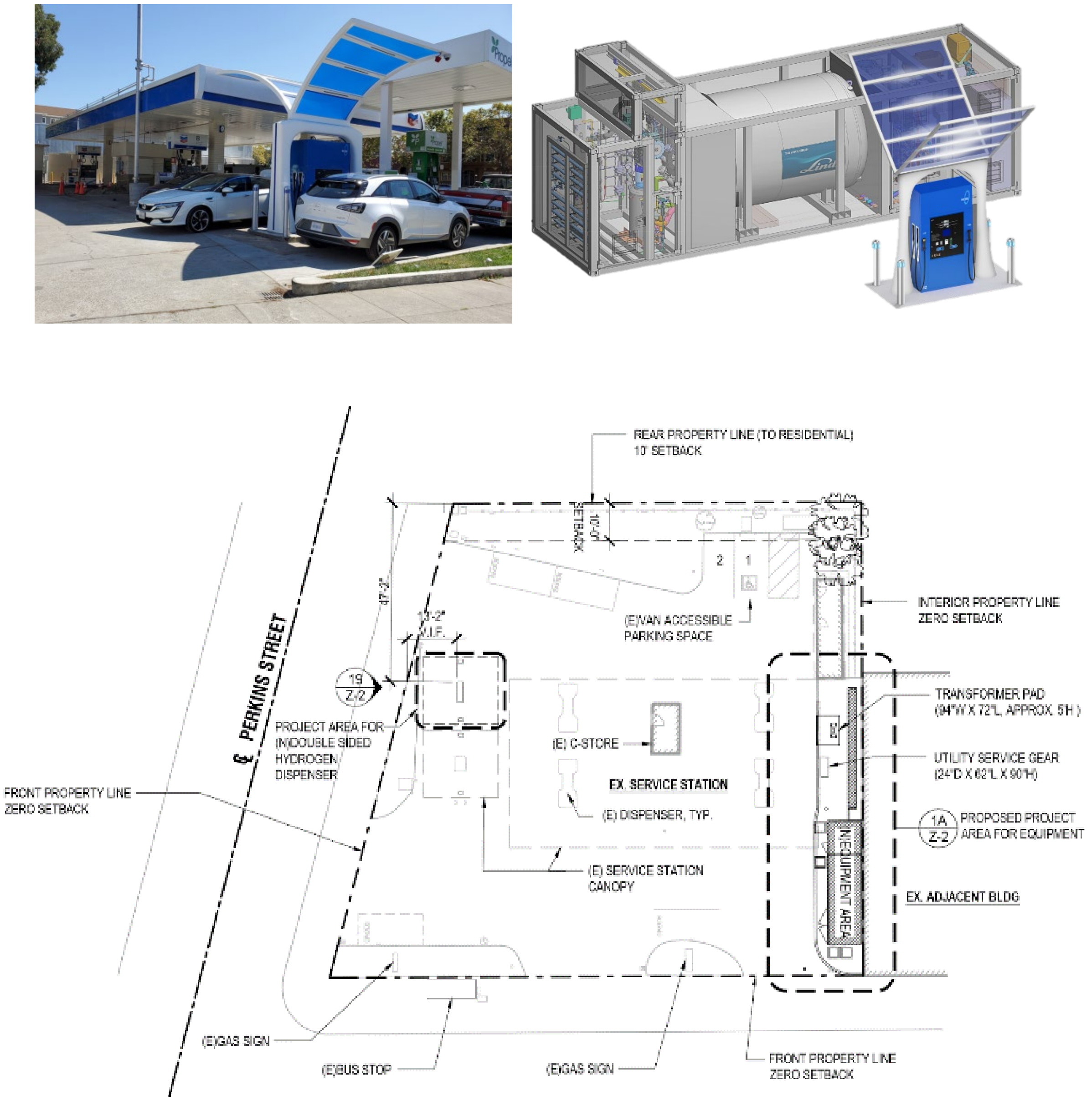


Figure 7. Linde LHRS and layout in Oakland. (Sources: Linde)

In France, a safety distance of 20 m between public domain and liquid hydrogen source is required. Safety features on liquid refuelling stations are almost the same as for a gaseous refuelling station (see Table 3).

Table 3. Safety features for gaseous/liquefied HRS.

What	Where	For what
Qualified and validated hose and fittings	Process and dispenser	Avoid accidental leakages
Periodic replacement of the hose	Dispenser	Avoid accidental leakages
H_2 detection	Inside the process container Inside the dispenser	Activate warning, and shut-off valves if required in case of accidental leakage
Flame (UV/IR) detector	In the process container Outside, close to the dispenser	Activate warning, and shut-off valves if required in case of accidental ignited release
Automatic shut-off valve	Several between H_2 storage and dispenser	Limit H_2 inventory in case of accidental release
Process pressure monitoring	General	Detect abnormal pressure drop due to leak or piping rupture
Naturally ventilated confined spaces	Process container Dispenser	Avoid to reach flammable limits of H_2-air mixture in case of accidental release
Forced ventilation	Process container for some models	Avoid to reach flammable limits of H_2-air mixture in case of accidental release if natural ventilation not possible or not efficient enough
ATEX certified equipment	In confined spaces where leaks can occur (i.e. skids and dispenser)	Avoid ignition sources
Hose grounded	Dispenser	Prevent sparks caused by static electricity during refuelling
Automatic leak test before filling	General	Avoid accidental leakages
Flow restrictors	General	Limit flowrate in case of release or piping rupture
Automatic closing time	General	Close H_2 feeding valves in case of hose rupture or leak
Hose break-away device	Dispenser	Avoid major leak by closing feeding flexible in case of tearing by forgetting to disconnect the vehicle
Shock protection (bollard)	Dispenser	Protect the dispenser from major mechanical aggression by vehicle accidental stamping and avoid catastrophic leak
Emergency punch stop	Few meters from the dispenser	Close H_2 feeding valves in case of emergency

Conductive (grounded) concrete slab	Dispenser	Prevent sparks caused by static electricity during refuelling

5.3.1 Buses

Most buses carry the hydrogen as compressed gas. There are, however, a few examples where the hydrogen was stored in liquid form.

6. Liquid hydrogen hazards and associated risk for Responders

Health hazards associated with the release of liquefied hydrogen are outlined below.

- Contact with liquid hydrogen or its splashes on the skin or in the eyes can cause serious cold burns by *frostbite or hypothermia.*
- *Cryogenic burns* can also result from contact of unprotected parts of human body with either cold fluids or cold surfaces.
- Inhalation of cold hydrogen vapours may cause *respiratory discomfort* and can result in *asphyxiation*.
- Direct physical contact with LH_2, cold vapours or cold equipment can cause serious *tissue damage.* Momentary contact with a small amount of the liquid may not pose as great a danger of a burn because a protective film of evaporating gaseous hydrogen may form. Danger of freezing occurs when large amounts are spilled, and exposure is extensive[1].
- Personnel should not touch cold metal parts and they should wear *protective clothing*. They also need to protect the affected area with a loose cover.
- *Cardiac malfunctions* are likely when the internal body temperature drops to 27°C or lower, and death may result when the internal body temperature drops lower than 15°C.
- *Asphyxiation* is also possible if liquefied hydrogen released and vaporised indoors.

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[1] Effect of liquid nitrogen: https://www.youtube.com/watch?v=F9dhZJQk80A&feature=youtu.be&t=291

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