

# Ensuring Safety in Liquid Hydrogen Operations: Understanding Hazards and Mitigating Risks

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This paper investigates essential safety measures for handling liquid hydrogen (LH<sub>2</sub>) in the process industry, emphasizing its cryogenic properties, flammability risks, and material compatibility. Liquid hydrogen is stored at extremely low temperatures (−253°C), poses challenges such as thermal contraction, material embrittlement, and increased leakage risk due to low viscosity and high permeability. Leaks result in rapid vaporization, forming highly flammable clouds with a wide flammability range (4-75% in air), leading to explosion hazards if ignition sources are present. The high expansion ratio upon vaporization can cause significant pressure buildup, risking vessel or pipeline rupture. Mitigation strategies include selecting appropriate materials, as many common materials become brittle or fail under cryogenic conditions. Austenitic stainless steels and nickel-based alloys are preferred for their toughness and corrosion resistance, while cryogenic polymers offer flexibility and chemical inertness. Regular monitoring and proactive maintenance using non-destructive testing (NDT) techniques, such as ultrasonic inspection and acoustic emission monitoring, are crucial for detecting material degradation and ensuring safe operation. Moreover, effective hydrogen leak detection systems must integrate automated safety mechanisms like rapid shutdown valves and ventilation controls to prevent explosive scenarios. Proper relief devices and strategic vent outlet placement are necessary to manage pressure and ensure safe gas dispersion, leveraging hydrogen's buoyancy to avoid flammable pockets at ground level.

In conclusion, understanding liquid hydrogen's behaviour under operational conditions and implementing robust safety protocols are critical for minimizing risks and ensuring safe, efficient operations in the process industry, protecting personnel, equipment, and the environment.

## 1. Introduction

Liquid hydrogen represents one of the most efficient solutions for storing and transporting large quantities of this energy carrier, widely studied for the transition to a low-carbon economy. Due to its high energy density and potential applications in strategic sectors such as transportation and industry, many countries are investing in this technology, developing specific regulations and directives to promote its adoption.

For large-scale applications, such as in the energy and transportation sectors, low-temperature storage is one of the most promising methods. This approach compensates for hydrogen's very low density by drastically reducing its volume and increasing its energy density. However, maintaining ultra-cryogenic temperatures poses significant process safety challenges (that will be analysed in the next chapters, together with preventive and protective measures), which can be categorized as follows:

Cryogenic Challenges:

- **Material Fragility:** at such low temperatures, many conventional materials become brittle and can break. The use of special alloys resistant to extreme cold is essential.
- **Cold Burns:** direct contact with liquid hydrogen or extremely cold surfaces can cause severe cryogenic burns to skin and tissues.
- **Volumetric Expansion:** during heating and the transition from liquid to gas, hydrogen increases in volume by about 850 times, creating the risk of high pressures in tanks if not properly managed.

#### Leaks and Dispersion:

- **Boil-off Effect:** even with efficient insulation, some liquid hydrogen inevitably evaporates, increasing pressure in tanks that must be managed with safe venting systems. The resulting gaseous hydrogen can increase risks related to material embrittlement and leaks.

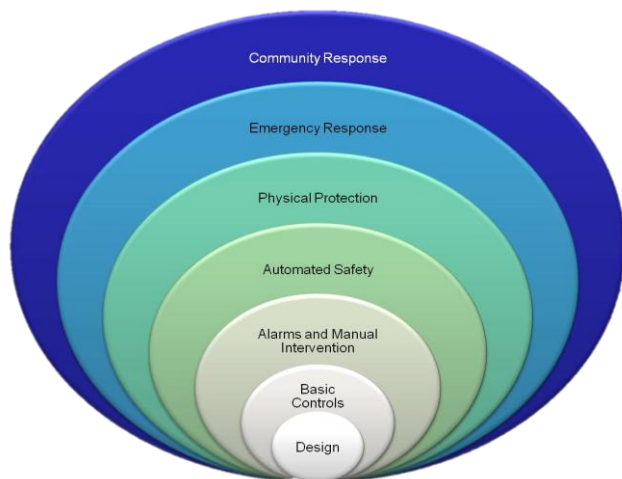
#### Low Technological Maturity:

- **Reliability of Safety Systems:** as an evolving technology, some monitoring, leak detection, and containment systems may not yet be sufficiently tested on a large scale.
- **Non-standardized Emergency Procedures:** globally, there are still few universally adopted protocols for managing emergencies related to large liquid hydrogen storage.

The main hazards associated with hydrogen systems can be listed and prioritized as follow (ISO/TR 15916:2015): flammability (thermal effects, pressure effects, easy ignitability of some mixtures), small size of the molecule (low viscosity, high diffusion rate, high buoyancy), asphyxiation hazards if oxygen is replaced. Regarding the environmental effects, the impact of hydrogen gas escaping into the atmosphere, e.g., due to boil-off gas from liquid storage, is minimal. Under atmospheric conditions, the thermal translational velocity of molecular hydrogen exceeds the escape velocity of the earth. As hydrogen ascends to the upper atmosphere, it will either oxidize to form water, react with pollutants, or escape into space.

## 2. Design

The design of an industrial plant generally represents the first protective barrier against the hazards associated with any chemical or physical process (*Figure 1*). A well-conceived design can prevent accidents, reduce risks through the adoption of appropriate technical solutions, the integration of control systems, the selection of materials capable of withstanding extreme conditions and strategic facility placement based on risk assessments (Carluccio et al., 2024).



*Figure 1. Onion model for Process Safety*

near known points of discontinuity (flanged joints, valves, etc.) but also through the material itself. This process can degenerate into the formation of cracks due to lattice distortion caused by the diffusion of hydrogen atoms into the metal, a phenomenon known as Hydrogen Embrittlement, which exhibits its greatest aggressiveness in the storage of gaseous hydrogen.

As reported in the Technical Reference ISO/TR 15916:2015, the selection of a material that is suitable for use in a hydrogen system involves several factors, including the following:

- compatibility with adjoining materials (matching properties under changes in temperature and pressure, for example, and the effect of such changes on the material's shape and dimensions)
  - transition from ductile to brittle behaviour as function of temperature
  - modes of plastic deformation, particularly certain unconventional modes encountered at very low temperature
  - effects of metallurgical instability and phase transformations in the crystalline structure on mechanical and elastic properties
- compatibility with the conditions of use (effects of temperature and pressure, for example, on ductility, and expansion/contraction; property changes associated with changes in operating conditions).

The suitability of some commonly used materials is reported in the Table 1 below, where:

The design must meet numerous safety requirements: storing liquid hydrogen at extremely low temperatures without compromising structural integrity is one of the main challenges faced by many researchers working on the ecological transition and beyond. In addition to thermal effects (e.g., low temperature ductility, thermal contraction), mechanical stresses and corrosion contribute to the alteration of the storage system's properties, increasing the risk of leaks. The inherently insidious nature of hydrogen makes it particularly prone to localized leaks not only

S: Suitable for use

NS: Not suitable for use

E: Evaluation is needed to determine if the material is suitable for the use conditions

Furthermore, care should be taken when tanks containing liquid H<sub>2</sub> are almost empty, since the upper part could be worm. In this case, the column of Gaseous hydrogen service applies instead of Liquid hydrogen service

*Table 1. Suitability of some selected materials for liquid hydrogen service (Table C.2 ISO/TR 15916:2015)*

Material	Gaseous hydrogen service	Liquid hydrogen service	Remarks
<b>METALS</b>			
Aluminium and its alloys	S	S	Negligibly susceptible to hydrogen embrittlement
Copper and its alloys	S	S	Negligibly susceptible to hydrogen embrittlement
Iron, cast, grey, ductile	NS	NS	Not permitted by relevant regulations and standards
Nickel and its alloys	E	E	Evaluation needed. Susceptible to hydrogen embrittlement
Steel, austenitic stainless with > 7% nickel (304, 304L, 308, 316, 321, 347)	E	E	May make martensitic conversion if stressed above yield point at low temperature
Steel, carbon (such as 1020 and 1042)	E	NS	Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic services
Steel, low alloy (such as 4140)	E	NS	Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic services
Steel, martensitic stainless (such as 410 and 440C)	E	E	Evaluation needed. Susceptible to hydrogen embrittlement
Steel, nickel (such as 2,25; 3,5; 5 and 9 % Ni)	E	NS	Ductility lost at liquid hydrogen temperature
Titanium and its alloys	E	E	Evaluation needed. Susceptible to hydrogen embrittlement
<b>NONMETALS</b>			
Asbestos impregnated with Polytetrafluoroethylene (PTFE)	S	S	Avoid use because of carcinogenic hazard
Chloroprene rubber (Polychloroprene)	S	NS	Too brittle for cryogenic services
Polyester fibre (Dacron)	S	NS	Too brittle for cryogenic services
Fluorocarbon rubber (Viton)	E	NS	Too brittle for cryogenic services
Polyester film (Mylar)	S	NS	Too brittle for cryogenic services
Nitrile (Buna-N)	S	NS	Too brittle for cryogenic services
Polyamides (nylon)	S	NS	Too brittle for cryogenic services
Polychlorotrifluoroethylene (Kel-F)	S	S	
Polytetrafluoroethylene (PTFE)	S	S	

Furthermore, conducting non-destructive testing (NDT) on equipment containing liquid hydrogen is crucial: NDT helps identify potential defects and weaknesses in materials and welds without causing damage, ensuring the integrity and reliability of the equipment. This is particularly important for cryogenic systems, as any failure could lead to catastrophic leaks and consequent fire / explosion scenarios. By adhering to international guidelines, such as ISO 21010, ISO 21012, ISO 21028-1 for requirements specific for design, construction, type and production testing, and marking requirements for cryogenic vessels, as well as standards like ISO 17636-1 and ISO 17636-2 for radiographic testing of fusion-welded joints, and ASME BPVC Section V for various NDT methods, safety risks are minimized, ensuring protection of both personnel and the environment.

### 3. Instrumentation and controls

Together with the proper design of the system, instrumentation and control systems are crucial for managing the operation and safety of hydrogen facilities. Instrumentation allows for the continuous monitoring and measurement of various process parameters, while control systems ensure that the process stays within safe and optimal limits. Together, these systems are fundamental for both the efficient functioning and safety of hydrogen systems.

To ensure safety, hydrogen facilities should be equipped with a range of control and safety devices. A reliable warning system is essential to detect abnormal conditions, malfunctions, or potential failures. This system should include both visible and audible alerts and be designed with redundancy to prevent complete failure due to a single malfunction.

Additionally, safety features within the system should automatically intervene to reduce risks identified by the warning system. Manual controls should be limited by automatic devices to prevent operating outside safe

parameters. The instrumentation, software, and computers used for safety should be independent from those used for regular operations and must include enough redundancy to avoid system failures.

Furthermore, various technologies are available for hydrogen gas detection; hydrogen detectors are typically installed above potential leak points and areas where hydrogen may accumulate, such as the highest point in a room or at the intake of ventilation ducts. Infrared (IR) cameras can image heat across a wide field of view. Ultraviolet (UV) detection is specifically used to identify hydrogen flames, but careful collimation of the sensor's field of view is necessary, since these detectors can be easily triggered by sunlight or welding activities.

Continued advancements in monitoring techniques and the development of robust fail-safe protocols are critical to improving the safety and reliability of hydrogen systems.

### 3.1 Liquid Hydrogen Behaviour

Liquid hydrogen, due to its extremely low boiling point, rapidly transitions from a liquid to gas when exposed to normal temperatures or spilled in an ambient environment. This rapid vaporization can result in high pressures if the hydrogen is confined, posing significant risks. Additionally, the low temperature of liquid hydrogen causes most gases, with the exception of helium, to condense into a solid form upon contact. The solidified gases can obstruct pipes, valves, and orifices, creating blockages that disrupt system operations. A process known as cryopumping can exacerbate this issue: as the gases condense, their volume decreases, potentially creating a vacuum that draws in even more gas. Prolonged leaks can lead to large accumulations of solidified gases, displacing liquid hydrogen and, when the system is eventually warmed for maintenance, causing the frozen materials to re-gasify. This could result in dangerous pressure buildup from reactive mixtures. Furthermore, gases trapped within the system could transfer heat into the liquid hydrogen, leading to increased evaporation and pressure rise.

Outside of the liquid hydrogen system, un-insulated pipes and vessels can condense gases such as air on their outer surfaces. This liquid and solid condensate, resembling water, can lead to oxygen enrichment due to the higher boiling point of oxygen (90 K) compared to nitrogen (77 K). If oxygen comes into contact with combustible materials, combustion risks arise, even with materials that are not typically considered flammable.

The vaporization of liquid hydrogen also causes rapid condensation of atmospheric humidity, resulting in a visible white cloud of condensed water. However, caution is needed when interpreting this cloud as an indicator of the hydrogen/air mixture. While some sources suggest that the extent of the water cloud correlates with the hydrogen/air mixture's spread, this is an unreliable and rough guide. The actual extent of the flammable hydrogen/air mixture could be larger than the visible water cloud, underscoring the complexity of assessing the true risks in such scenarios.

In terms of process safety, these phenomena highlight the importance of designing systems to prevent leaks, carefully controlling temperature and pressure, and ensuring proper insulation of components to minimize condensation-related hazards. Additionally, close attention must be paid to the potential for oxygen enrichment and the handling of condensed gases, as these factors can contribute significantly to fire and explosion risks.

### 3.2 Hydrogen gas detection

Given the limitations of human sensory perception, alternative methods are required for hydrogen detection. Various commercially available detection technologies can identify hydrogen presence, many of which are suitable for integration into automated warning and operational control systems. Strategic placement of hydrogen detectors includes areas prone to leaks or spills, routinely disconnected hydrogen connections, locations where hydrogen accumulation is possible, building air intake ducts if hydrogen ingress is a concern, and exhaust ducts where hydrogen release may occur.

Key criteria for selecting hydrogen sensors include accuracy, reliability, cross-sensitivity, maintainability, calibration requirements, zero drift, detection limits (both upper and lower), response time, recovery characteristics, operational methodology (active or passive), and system compatibility. In addition to stationary detection systems, operators should also be equipped with portable hydrogen detectors for real-time monitoring around hydrogen-handling facilities. A commonly established alarm threshold is 1% hydrogen (volume fraction) in air, corresponding to approximately 25% of the lower flammability limit (LFL). This threshold generally ensures sufficient response time for appropriate safety measures, such as system shutdown, personnel evacuation, or other necessary interventions, with the possibility of an earlier warning if required.

### 3.3 Fire detection

In the absence of impurities, a hydrogen-air flame exhibits minimal emissivity within the visible spectrum, rendering it nearly imperceptible to the human eye under daylight conditions. Additionally, its thermal radiation output is low, further complicating detection via conventional sensory means. Given these properties, the implementation of dedicated hydrogen flame detection systems is critical in environments where hydrogen leaks, spills, or hazardous accumulations may occur. The selection of a hydrogen flame detection system should

consider detection range, susceptibility to false alarms, response time, and spectral sensitivity to ensure accurate and timely identification of hydrogen flames.

To enhance safety in hydrogen-handling facilities, personnel should use portable hydrogen flame detectors for real-time monitoring. While basic methods like straw brooms can provide preliminary detection, they are unreliable in high-risk environments. In large-scale facilities, delayed detection of turbulent hydrogen jet fires may endanger personnel by obstructing evacuation routes.

### 3.4 Ventilation

Ventilation systems for confined spaces must be designed to effectively control hydrogen accumulation and migration, ensuring the maintenance of concentrations below the lower flammability limit while accounting for variations in pressure and temperature. In scenarios where hydrogen originates externally, ventilation must prevent ingress unless deactivation is specifically controlled.

To mitigate ignition hazards, confined spaces designated for hydrogen storage or processing must incorporate active or passive ventilation systems coupled with hydrogen detection mechanisms. Mechanical ventilation should either be interlocked with hydrogen detection or activated preventively before hydrogen introduction and remain operational until complete removal. Emergency shutdown procedures should not disable ventilation unless the hydrogen source is external. Additionally, the presence of suspended ceilings and inverted pockets should be minimized or adequately ventilated. All ventilation system components must conform to explosion-proof standards, ensuring that mechanical failures do not generate ignition sources.

## 4. Venting systems

In liquid hydrogen systems, when liquid hydrogen turns to gas, the rapid increase in volume can over-pressurize containment structures, like storage vessels, and cause them to burst. This hazard is managed using pressure relief devices in critical areas, such as between valves, where hydrogen could get trapped. Without proper relief, a catastrophic failure could occur, resulting in explosions or flying debris. For this reason, hydrogen venting systems are a critical part of every hydrogen system and must be included as part of the hazard review.

When hydrogen mixes with air, deflagrations can create pressures up to eight times the initial pressure, while detonations can create pressures up to 20 times higher due to reflected shock waves. Traditional pressure relief systems, like rupture disks, can't protect against detonations because these waves move faster than the speed of sound, meaning relief systems don't react quickly enough. These systems are only effective against slower deflagrations.

The discharged hydrogen should be directed away from people and equipment to reduce fire risk (several incidents occurred in the past due to improper geometry of the vent: onboard storage systems should include pressure relief devices with fire-resistant ratings since an ignition could occur during the venting, and any enclosure housing the hydrogen system must be able to handle or vent pressure in case of accidental release). If multiple relief devices are connected, their operation should not interfere with each other. Redundancy in the form of both relief valves and rupture disks is common to ensure reliability. Furthermore, pipes and supports must be designed considering seismic and wind conditions since an incorrect design could cause catastrophic damage; also, LH<sub>2</sub> requires a warning sign to never spray water on the vent stack (NFPA 2, 2023).

## 5. Training and awareness

A hydrogen facility or system comprises various operations essential for its effective functioning, involving not only the system's components and equipment but also the personnel responsible for these tasks, specialized tools, and personal protective equipment (PPE) to ensure safety. Human error is the leading cause of accidents in hydrogen systems; the initiation and severity of accidents may not be solely linked to system operators but may also stem from broader organizational knowledge of hydrogen and its applications. Understanding the limitations of the system's design, operational and maintenance needs, and potential hazards to personnel and the public is critical for all stakeholders. The safe operation of hydrogen systems is a collective responsibility that requires clear communication, specialized training, and strong organizational control. Personnel should receive training appropriate to their roles and responsibilities. When managing large hydrogen quantities, collaboration with local communities and emergency responders is crucial.

A robust safety training program is necessary to address human capabilities and limitations, aiming to prevent accidents and minimize their impact. All individuals engaged with hydrogen systems, including operators, technicians, engineers, and administrators, must be well-versed in the chemical, physical, and hazardous properties of hydrogen in the context of their specific duties. Operators should be proficient in handling the equipment and systems under their responsibility, with training covering emergency responses to events such as unignited releases, fires, deflagrations, or detonations. Furthermore, personnel should be trained in

evacuation procedures and first-aid for cold and cryogenic injuries from hydrogen exposure. Refresher training should occur regularly, with annual reviews of the program to ensure its alignment with the latest safety practices and standards.

## 6. Conclusion

Hydrogen systems, like all energy carriers, have intrinsic hazards due to the nature of the substance. As such, these systems must incorporate built-in safety features to prevent and mitigate potential risks. Inherent safety must guarantee a holistic approach, ensuring all the risks related to the LH<sub>2</sub> system to be identified and properly managed: this typically include proper selection of the material to be used for the equipment, fail-safe design (e.g., multiple protective measures such as redundant safety components as pressure-relief devices), automatic and passive safety operations further enhancing the system's reliability, including remote monitoring of critical parameters and the ability to remotely operate the system, Furthermore, the awareness of personnel involved is of paramount importance: they shall be trained to conduct normal operations as well as for any abnormal condition. From a process safety management (PSM) perspective, systematic hazard identification and risk assessment are essential for ensuring the safety of hydrogen systems. HAZOP studies and ATEX analyses play crucial roles in this process. Both methodologies are key tools in identifying, evaluating, and managing process safety risks, helping to prevent hazardous events before they occur. Proper implementation of these safety analyses, alongside robust PSM systems, is essential for minimizing risks and ensuring the safe operation of liquid hydrogen facilities.

### Nomenclature

ASME – American Society of Mechanical Engineers

ATEX – Atmosphères Explosibles

GH<sub>2</sub> – Gaseous Hydrogen

HAZOP – Hazard and Operability

IR – Infrared

ISO – International Organization for Standardization

LH<sub>2</sub> – Liquid Hydrogen

NDT – Non-Destructive Testing

NFPA – National Fire Protection Association

PSM – Process Safety Management

PTFE – Polytetrafluoroethylene

TR – Technical Report

UV – Ultraviolet

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