Hydrogen Innovation Initiative

Engineering considerations for cryogenic hydrogen applications

An introductory primer for engineers

February 2025

Introduction to the Hydrogen Innovation Initiative

The Hydrogen Innovation Initiative (HII) was established with support from Innovate UK and its Industrial Advisory Board to make hydrogen work for the UK. HII is a trusted group of organisations bringing together industry, government, and academia to create an investible, globally competitive hydrogen technology and services sector, here in the UK. Our vision is for UK technology powering the global hydrogen economy – transforming UK industry into a net zero powerhouse.

We are supporting UK companies in bringing innovative products and services to market that will be an integral part of the fast-growing global hydrogen economy.

Working together, we can future-proof the UK's domestic hydrogen supply chains by helping improve export prospects and upskilling the workforce, allowing UK businesses to compete in the global hydrogen economy.

HII's partners include the Advanced Propulsion Centre, the Aerospace Technology Institute, the Catapult Network, Glass Futures, the National Physical Laboratory, the Net Zero Technology Centre and TWI.

Acknowledgements

This report, and the work it describes, was undertaken through collaboration between the Health and Safety Executive (HSE), the High Value Manufacturing Catapult and the Connected Places Catapult, as a part of the Hydrogen Innovation Initiative (HII). HII would like to thank Element Digital Engineering (formerly Filton Systems Engineering) for their contribution to the report in Appendix A.

Disclaimer

The contents of this report, including any opinions and/or conclusions expressed or recommendations made, do not supersede current HSE policy or guidance.

CATAPULT High Value Manufacturing

CATAPULT Connected Places

RESEARCH AND CONSULTANCY FROM HSE

Contents

Introduction to the Hydrogen Innovation Initiative		3
Acknowledgements		3
Disclaimer		3
1	Introduction	6
2	Properties of hydrogen	7
3	Cryogenic hydrogen safety considerations	9
3.1	Hazards	11
3.1.1	Gas dispersion	11
3.1.2	Cryogenic gas dispersion	11
3.1.3	Pool formation	11
3.1.4	Ignition	11
3.2	Ignition consequences	12
3.2.1	Jet fire	12
3.2.2	Explosion	12
3.2.3	Pool fire	12
3.3	Pressure system hazards	13
3.3.1	Pressurisation through warming	13
3.3.2	BLEVE	13
3.4	Cryogenic hazards	14
3.4.1	Condensing air or water	14
3.4.2	Blocked pipes	14
3.4.3	Liquid air exposed pipes	14
3.4.4	Cascading events (fire suppression systems)	14
3.4.5	Cold surface burns	14
3.4.6	Hypothermia	14
3.4.7	Phase change	14
3.5	Hydrogen-specific hazards	15
3.5.1	Embrittlement	15
3.5.2	Permeation	15

4 Design considerations 16
4.1 System level design 16
4.1.1 Regulations, codes of practice and standards 16
4.1.2 Specific design considerations for cryogenic hydrogen systems 18
4.2 Component level design 22
4.2.1 Storage tanks 22
4.2.2 Insulation 22
4.2.3 Valves 24
5 Material considerations 25
5.1 The impact of cryogenic hydrogen on material properties 25
5.1.1 How materials are affected by hydrogen 25
5.1.2 How materials are affected by cryogenic temperatures 27
5.2 Material compatibility for application in hydrogen environments 27
5.3 Materials testing requirements 30
5.3.1 Testing pyramid 30
5.3.2 Testing for metallic materials 31
5.3.3 Testing for polymers and composites 31
6 Manufacturing considerations 32
6.1 Shaping and forming 32
6.2 Joining 33
6.3 Post processing 33
7 References 36
Appendix A – Illustrative case study: element digital engineering 42
Appendix B – Regulations and approved codes of practice 49

1 Introduction

With growing commitments from governments and corporations around the globe to reduce carbon emissions, there is an increasing interest in cryogenic hydrogen as a replacement for traditional fossil fuels. This document seeks to provide an introductory primer to the engineering considerations required in the use of cryogenic hydrogen.

This document is split into the following sections:

- **Properties of hydrogen** - A comparison of various states of hydrogen with traditional fossil fuels.
- **Cryogenic hydrogen safety considerations** - A categorisation and summarisation of the behaviour and safety implications of cryogenic hydrogen.
- **Design considerations** - An overview of high-level and component-level design considerations, along with a list of key regulations.
- **Material considerations** - An overview of the effect of cryogenic hydrogen on materials, a list of suitable materials, and suggestions for material compatibility testing.
- **Manufacturing considerations** - An overview of the effect of manufacturing processes on the suitability of materials for cryogenic hydrogen service.

An illustrative example of liquid hydrogen facility design is provided in Appendix A, alongside an overview of regulations and approved codes of practice (ACOPs) in Appendix B.

2 Properties of hydrogen

This section compares hydrogen with conventional fossil fuels to form a foundation which will be built upon in the upcoming sections to facilitate the safe design of cryogenic hydrogen systems.

At standard atmospheric conditions, hydrogen is a colourless, odourless, buoyant gas that burns readily in air. Due to the high energy density of hydrogen by mass and the fact that it combusts with air without releasing carbon emissions, hydrogen has been identified as having the potential to be an important energy vector for the future. A key issue surrounding the use of hydrogen is that, despite it having a high energy density by mass, its energy density by volume is far lower than other common fuels (Table 1), making it relatively inefficient to store and transport. To solve this technical challenge, hydrogen is often stored in compressed, cryogenically compressed and liquid forms. There are not universally defined parameters for these terms, so for the sake of this report:

- **"Gaseous hydrogen"** is gaseous, at or below atmospheric pressure and has a temperature above 123 K
- **"Compressed hydrogen"** is gaseous, has a pressure above atmospheric pressure and a temperature above 123 K
- **"Cryo-compressed hydrogen"** is gaseous, has a pressure above atmospheric pressure and a temperature between 20 K and 123 K
- **"Liquid hydrogen"** refers to any hydrogen that is in the liquid phase irrespective of pressure and temperature
- **"Cryogenic hydrogen"** refers to both cryo-compressed and liquid hydrogen

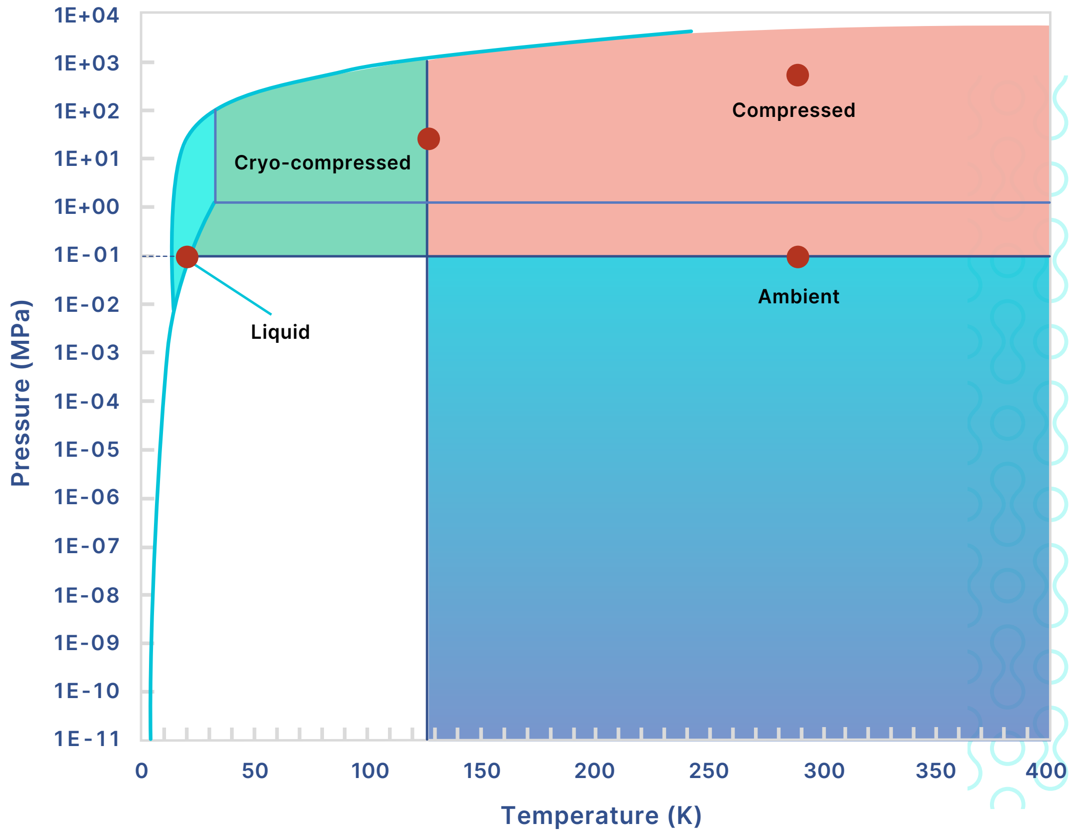


Figure 1. Phase diagram of hydrogen showing the categories of hydrogen for this document. Cryogenic hydrogen is defined as anything colder than 123 K.

These categories are shown on the hydrogen phase diagram (Figure 1). For ease of comparison, Table 1 shows common storage conditions that are representative of hydrogen in each of the above states: compressed hydrogen at 288 K and 100 MPa, cryo-compressed at 123 K and 30 MPa, liquid hydrogen (LH_2) at 20 K and ambient gaseous hydrogen at standard temperature and pressure.

Table 1. Physical properties of various fuels

	Melting point (K)	**Boiling point (K)**	**Energy density by volume (MJ/m^3)**	**Energy density by mass (MJ/kg)**	**Viscosity (Pa·s) (10^{-6})**	**Density (kg/m^3)**
Methane	90.7 [1]	111.2 [1]	36.6 [2]	55.6 [2]	11.0 [1]	0.668 [1]
Air	63.3 [1] (N_2), 54.8 [1] (O_2)	77.4 [1] (N_2), 90.2 [1] (O_2)	-	-	18.2 [1]	1.20 [1]
LPG propane	85.2 [1]	231.2 [1]	19719.0 [2]	46.6 [2]	8.0 [1]	507 [1]
Kerosene[1]	263.7 [1]	489.1 [1]	32303.5 [3]	43.1 [3]	2031 [1]	749.5 [1]
Marine Fuel Oil[1]	334.1 [4]	704.9 [4]	36064.6 [2]	42.68 [2]	9680.4 [5]	845 [5]
Hydrogen	14.1 [6]	20.2 [6]	11.9 [2]	119.96 [2]	8.9 [7]	0.084 [8]
Compressed hydrogen (100 MPa)	-	14.0 – 34.4 [6]	5928.4 [2]	119.96 [2]	12.3 [7]	49.42 [8]
Cryogenic compressed hydrogen (123 K, 30 MPa)	-	33.1 [6]	5167.9 [2]	119.96 [2]	7.56 [7]	43.08 [8]
Liquid hydrogen (20 K)	14.1 [6]	20.15 [6]	7078.4 [2]	119.96 [2]	38.4 [7]	70.85 [8]

---

[1] Fuels are mixtures of different hydrocarbons. Propane, dodecane and octacosane have been chosen in some cases to represent each fuel type for ease of comparison

Table 2. Combustion properties of various fuels

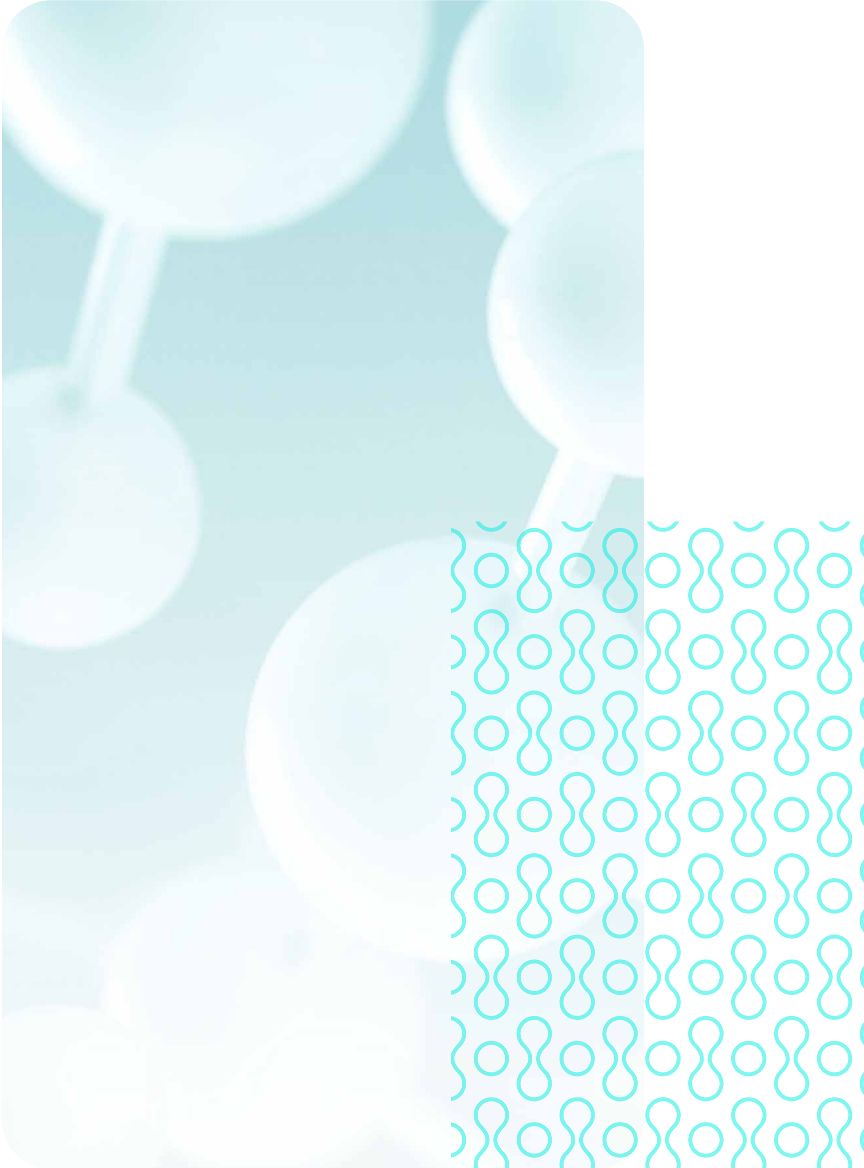
	MIE (air mixture) (mJ)	LFL in air (%)	UFL in air (%)	Auto ignition temperature (K)
Methane	0.28 [9]	5.0 [10]	17.0 [11] [12]	868 [11] [12]
LPG propane[1]	0.25 [9]	1.8 [10]	8.9 [10]	743 [11] [12]
Kerosene[1]	40 (at 325.15 K) [13]	0.7 [14]	5 [14]	483 [11] [14]
Marine Fuel Oil[1]	-	0.7 [5]	5 [5]	-
Hydrogen	0.017 [13]	4.1 [10]	72.5 [10]	773 [11] [12]
Liquid hydrogen (20 K)	>0.05[2]	7.7[3][15]	66.7[2]* [15]	773 [11] [12]

3 Cryogenic hydrogen safety considerations

This section gives an overview of some of the key safety considerations when dealing with cryogenic hydrogen. This is not a comprehensive list intended to be applicable to all cryogenic and liquid hydrogen applications. The hazards broadly fit into four categories:

- Flammability hazards (including ignition consequences)
- Pressure hazards
- Cryogenic hazards
- Hydrogen-specific hazards

These are briefly expanded in the following sections regarding hazards of liquid hydrogen and its evaporation to gaseous hydrogen.

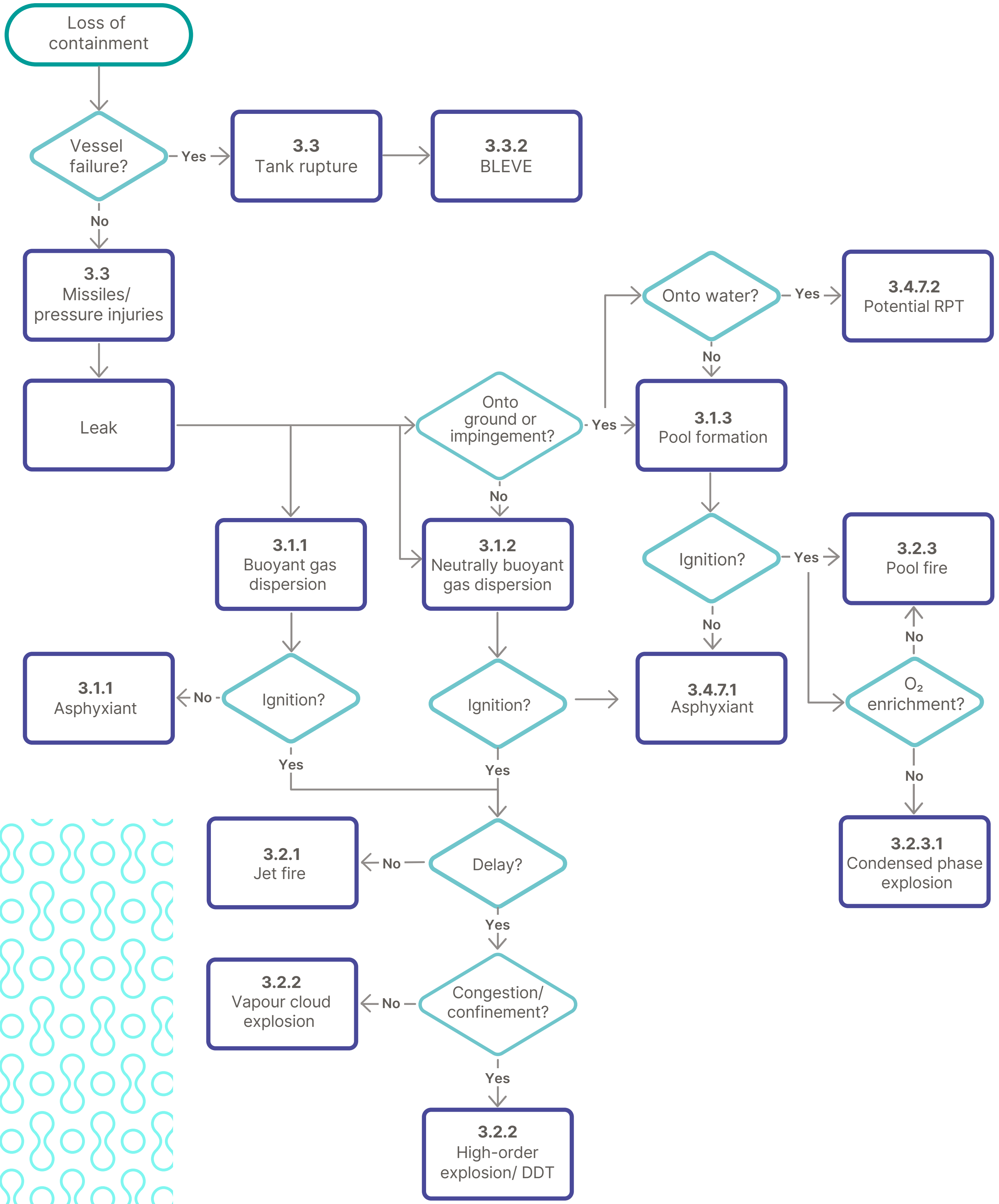


---

[2] based on MIE for cold hydrogen at -120°C

[3] for hydrogen just above point of vaporisation

Figure 2. Flow diagram for a loss of containment event with a liquid hydrogen system



3.1 Hazards

Whilst hydrogen is like other flammable gases, it exhibits some key behavioural differences, particularly at cryogenic temperatures, that need to be considered.

3.1.1 Gas dispersion

Hydrogen gas has a very high diffusivity in air (0.611 cm^2.s^{-1} at standard conditions) [16], meaning that leaks can quickly form a mixture with the surrounding air. The low density of hydrogen at standard conditions means that it is buoyant. High concentrations of hydrogen also pose asphyxiation risk, particularly in enclosed spaces.

3.1.2 Cryogenic gas dispersion

Cold hydrogen is less buoyant than at standard temperature (hydrogen at 22 K has the same density as air at 288 K). This means that a cold hydrogen vapour cloud could stay at low levels and so be more difficult to disperse, and potentially cause a greater hazard than hydrogen at normal temperatures. Cryogenic hydrogen will rapidly cool the surrounding air, and other materials it might impinge upon, both of which could potentially liquify the surround air.

3.1.3 Pool formation

Liquid hydrogen can form pools when it comes into contact with sufficiently cooled surfaces such as the ground or other bodies. In addition to this, cryogenic hydrogen can condense the nitrogen and oxygen in the ambient air. In a confined space, this will result in an oxygen depleted atmosphere. As oxygen condenses at a higher temperature than nitrogen, the condensate may become oxygen enriched. An oxygen rich condensate poses a greater explosion risk if in contact with a flammable substance when compared to a mixture of gaseous air and the same flammable substance.

3.1.4 Ignition

Since hydrogen rapidly diffuses in air, readily forming flammable clouds, ignition mechanisms for hydrogen-air mixtures should be considered.

3.1.4.1 Minimum ignition energy and flammable limits

Hydrogen has a minimum ignition energy (MIE) in air of 0.017 mJ at standard atmospheric conditions [17]. For comparison, the MIE of methane is an order of magnitude greater at 0.28 mJ.

Hydrogen has a very broad flammability limit (FL), which means that it forms flammable mixtures with air across a wide range of concentrations. Gaseous hydrogen at standard atmospheric conditions has a flammability range of 4.1 - 72.5% by volume in air. For comparison, the flammability ranges of methane and kerosene are 5.0 - 17.0% and 0.7 - 5.0% respectively. The flammability limits of liquid hydrogen are narrower when compared to gaseous hydrogen: between 7.7 and 66.7% by volume in air.

3.1.4.2 Auto-ignition

Hydrogen has an auto-ignition temperature of 773 K, which is relatively high compared to other common fuels such as kerosene vapour at 483 K and propane at 743 K.

3.1.4.3 Electrostatics

Hydrogen can be ignited by very small electrostatic discharges due to the low ignition energy (0.017 mJ). Hydrogen does not hold a charge, however two-phase flow in electrically insulated pipework can induce a charge on pipework. The formation of solid condensates from air may also result in electrostatic charges that could result in ignition [18]. Electrostatic discharges from the human body can typically be around 10 mJ and so they are easily capable of causing ignitions in hydrogen-air atmospheres.

3.1.4.4 Shock ignition

Shockwaves can ignite flammable hydrogen-air atmospheres by:

- A shock moving through a flammable cloud of hydrogen can cause compression and ignition at the shock front, potentially resulting in a detonation.
- A shock caused by a high-pressure release of hydrogen can also cause ignition behind the shock front, as the shock can heat air to above the autoignition temperature, resulting in an ignition once a flammable mixture is reached.

3.1.4.5 Spontaneous ignition

Out of 676 hydrogen incidents, a statistical review found that 419 (60%) had unidentified ignition sources [Yang et al, 2021]. Most of these incidents originated as high-pressure hydrogen leaks, with several ignition mechanisms posited as possibilities, but with no clear evidence of an ignition source [19].

3.2 Ignition consequences

Hydrogen ignites relatively easily, but the consequences of an ignition can vary with other compounding factors such as ignition delay and turbulence.

3.2.1 Jet fire

Jet fires are caused when a continuous release of hydrogen is ignited.

- The maximum ignition distance is the maximum horizontal distance between the point of hydrogen release and the ignition source to ignite a hydrogen jet fire. This maximum distance increases as hydrogen release temperature decreases, and mass flow rate of hydrogen increases.
- Jet flame length increases as hydrogen release temperature decreases and as mass flow rate increases [20].
- The heat flux of jet fires also increases as hydrogen release temperature decreases and as mass flow rate increases [20].

3.2.1.1 Pale flame

Hydrogen burns with a very pale flame and does not produce smoke; therefore hydrogen jet fires can be hard to detect visually.

3.2.1.2 Low radiance

Hydrogen flames emit little infrared radiation, increasing the likelihood of someone coming into contact with a hydrogen flame without first detecting the heat from it. The hazard associated with this phenomenon is further compounded by the low visible light emittance.

A large proportion of the radiance of hydrogen flames is in the UV range, meaning that people can suffer sunburn-like effects from standing close to a hydrogen fire.

3.2.1.3 Heat

The primary hazard associated with hydrogen jet fires are burns sustained from coming into contact with the flame.

3.2.2 Explosion

Explosions can result from a delayed ignition of a hydrogen leak and can vary widely in severity, and therefore damage potential, based on various factors. Explosions can result in extreme heat, pressure and noise, which can cause significant injuries and damage to structures.

3.2.2.1 Vapour cloud explosions

Vapour cloud explosions occur when a leak of hydrogen gas accumulates and mixes with air and then is subsequently ignited. Factors such as the level of turbulence, which can be influenced by the geometry of the space into which hydrogen has been released, can result in higher order deflagrations (where a flame is propagating at subsonic speeds). Other factors affecting the flame speed of the explosion include hydrogen concentration and level of oxygen enrichment; higher levels of oxygen enrichment and fuel/air mixtures close to stoichiometric ratios (29.5 vol% H_2) will result in higher order explosions.

3.2.2.2 Detonation

Detonations are very energetic events, where combustion is propagated through a supersonic shock front. These shock waves are accompanied by exothermic releases, meaning detonations can be damaging both through overpressures and through strong heating.

3.2.2.3 DDT

Deflagration to Detonation Transition (DDT) is a phenomenon where a flame propagating at subsonic speeds (deflagration) quickly transitions to a detonation, where the flame becomes propagated by a shockwave travelling at supersonic speeds and at substantial overpressures. DDTs are most likely to occur in congested or confined environments. The detonation concentration limits of hydrogen are 18.3% to 59% in air at atmospheric pressure.

3.2.3 Pool fire

Liquid hydrogen releases can form pools on surfaces, which, when ignited, burn with a pale flame.

3.2.3.1 Condensed phase

Liquid hydrogen can form mixtures with solid, oxygen enriched air, forming a detonable slurry on surfaces. These condensed phase deposits can form after prolonged exposure to liquid hydrogen, where the surface cools sufficiently to support a condensed phase mixture. These mixtures can detonate through usual ignition mechanisms, including mechanical shock, thermal initiation and electrostatics [18].

3.3 Pressure system hazards

Liquid and cryogenic hydrogen systems share common hazards with other pressure systems. These include the force from a release of compressed liquid or gas and the impact from debris which may be ejected by the pressurised release.

3.3.1 Pressurisation through warming

Cryogenic hydrogen naturally tends to warm over time as heat ingresses into the fluid. This will lead to over-pressurisation if not actively managed through cooling systems and venting, or the use of pressure relief devices in case of emergency.

Liquid hydrogen systems are particularly susceptible since a phase change has an associated expansion ratio of 1:848.

3.3.2 BLEVE

In the case of liquid hydrogen storage, Boiling Liquid Expanding Vapour Explosions (BLEVEs) are a hazard. These can occur when the hydrogen is stored above its boiling point at standard atmospheric pressure but is kept as a liquid due to high pressure. Upon loss of containment, the drop in pressure results in the almost instantaneous boiling of the hydrogen, known as flashing. This is an extremely energetic process to the extent that it can be classed as an explosion without ignition.

As hydrogen is a flammable gas, there is the added possibility of the BLEVE igniting if there is a suitable ignition source present. Anecdotal evidence suggest the shock from the expansion of gas or the heating effect from friction between the gas and containment material can ignite hydrogen BLEVEs, as can external ignition sources i.e. heat or ESDs (electrostatic discharges) [21].

3.4 Cryogenic hazards

Hydrogen stored at cryogenic temperatures shares hazards common to other cryogenic fluids.

3.4.1 Condensing air or water

As the temperature of cryogenic/ liquid hydrogen is lower than the melting point of water and can be below the boiling and melting point of nitrogen and oxygen, the effects of ice and condensed air in a cryogenic system must be considered.

3.4.2 Blocked pipes

Cryogenic temperatures could lead to the blockage of pipes with water or condensed air. This can result in over-pressurisation.

3.4.3 Liquid air exposed pipes

Air can condense on exposed cryogenic pipework, which could result in liquid air dripping from the pipes. Contact with liquid air can result in cold burns or cause spontaneous ignition in surfaces such as asphalt.

3.4.4 Cascading events (fire suppression systems)

Water from fire suppression systems will quickly freeze when in contact with cryogenic hydrogen. This can result in blockages in pipework, vents, etc., which can lead to over pressurisation of the system and subsequent loss of containment. Spraying water on pressure relief systems is likely to cause them to stop functioning correctly, due to ice formation.

3.4.5 Cold surface burns

Due to the extremely low temperature of liquid hydrogen, contact with pipework can result in cold surface burns and frostbite. Boil-off gas from liquid hydrogen is also cold enough to cause severe cold burns, and inhalation can cause lung damage.

3.4.6 Hypothermia

Pipework containing liquid hydrogen, or releases of liquid hydrogen can cool the surrounding area, which could result in hypothermia given a long enough exposure time. Confined areas containing liquid hydrogen can drop to temperatures capable of causing hypothermia.

3.4.7 Phase change

As liquid hydrogen is stored close to its boiling point, it will boil readily if not actively cooled. This can result in over-pressurisation of pressure systems (see section 3.3.1) as well as those described in this section.

3.4.7.1 Asphyxiation

Liquid hydrogen has a liquid-gas expansion ratio of 1:848, meaning that consideration should be given to the asphyxiation risk, due to the potential for a small amount of liquid hydrogen (LH_2) to displace a relatively large amount of oxygen. Gaseous hydrogen also poses an asphyxiation risk in the event of a leak. Confined, non-ventilated spaces will pose the greatest asphyxiation risk in the event of a liquid or gaseous cryogenic hydrogen leak.

3.4.7.2 Rapid Phase Transition (RPT) explosion

RPT explosions occur when liquid hydrogen comes into contact with a body of water, which can facilitate rapid heating of the hydrogen. The heating causes very quick boiling of the hydrogen, causing it to expand rapidly in an explosion. RPT have not definitively been observed in LH_2 but has been seen in liquified natural gas (LNG) spills onto water. These RPT events with LNG spills into water have been observed to be relatively unpredictable, with the degree of turbulence in the water and cryogen contact velocity being important factors as to whether an RPT occurs or not [21]. It is assumed that the same principle could apply to LH_2, although the probability has been predicted to be much lower, and the predicted consequence of an LH_2 RPT is also less than LNG RPT explosion [22]. It should be noted that relatively few spills of LH_2 onto water have ever occurred. Whilst LH_2 RPTs have not been observed, injection of LH_2 into water does generate overpressures in the mbar range, and the resulting gas clouds above the water have been observed to consistently self-ignite, causing significant and damaging blasts [23].

3.5 Hydrogen-specific hazards

Some risks posed by hydrogen are relatively uncommon in other substances, which are primarily due to the uniquely small molecule size.

3.5.1 Embrittlement

Hydrogen embrittlement is an effect where the properties of metals in contact with hydrogen deteriorate because of their exposure. Hydrogen embrittlement causes a reduction in ductility, tensile strength and fracture toughness, and increases the propagation rate of fatigue cracking. This effect should be considered when dealing with pressure systems containing hydrogen. For applications involving cryogenic and liquid hydrogen, the effects of temperature on mechanical properties, including ductile-brittle transition temperature (DBTT) of the material should be considered in parallel to the embrittling effects of the hydrogen. This is discussed in Section 5.

3.5.2 Permeation

Hydrogen is a small molecule which can permeate through materials, joints and seals. Some materials are more susceptible to permeation than others. This can depend on the material itself, in addition to treatments, coatings and manufacturing techniques. NASA have provided data for hydrogen permeation through a number of materials; however, the list is far from exhaustive [24].

4 Design considerations

There are a wide range of applications which may use cryogenic hydrogen and the guidance may change depending on the context of use. As such, this section only serves as an overview for the considerations and regulations that will apply to many applications of cryogenic hydrogen. The documents referenced in this section will not be sufficient to cover all hazards for all scenarios involving cryogenic hydrogen.

This section is split into two parts: the first covers high-level regulations, codes, and standards as well as hazard mitigation considerations, termed ‘system level design’. The second part focuses on common components (tanks, insulation, and valves) in more specific detail, termed ‘component level design’. An illustrative example of the design of a cryogenic hydrogen system that has addressed some of these design considerations is shown in Appendix A.

4.1 System level design

System level design involves identifying potential hazards and risks of an assembly or construction holistically, then devising solutions that eliminate, substitute, control or mitigate the risks until they are as low as reasonably practicable (ALARP).

A list of regulations applicable to cryogenic hydrogen systems is in section 4.1.1 and supplemented with summaries and associated Approved Codes of Practice (ACOP) in Appendix B. A non-exhaustive list of design considerations for cryogenic hydrogen systems is in section 4.1.2, broken down into three hazard categories: pressure systems, flammable gases, and cryogenic temperatures.

4.1.1 Regulations, codes of practice and standards

The guidance for designing cryogenic hydrogen systems can be categorised into three levels: regulations, approved codes of practice, and codes and standards.

Regulations are mandatory and set out the responsibilities of duty holders when undertaking certain activities. These responsibilities vary depending on the circumstance but could include ensuring a suitable risk assessment has been conducted for certain activities. Some regulations that are relevant to cryogenic systems are:

- ATEX.
- Carriage of Dangerous Goods and Use of Transportable Pressure Equipment Regulations (CDG).
- The Control of Major Accident Hazards (COMAH).
- The Control of Substances Hazardous to Health (COSHH).
- The Dangerous Substances and Explosive Atmospheres Regulations (DSEAR).
- Land Use Planning (LUP).
- Pressure Equipment Regulations (PER).
- Pressure Systems Safety Regulations (PSSR).
- The Provision and Use of Work Equipment Regulations (PUWER).

Other regulations may apply depending on the specific use-case. A summary of each regulation, along with references, are included in Appendix B.

The second level are Approved Codes of Practice (ACOP). HSE and others produce ACOP which contain advice on the practical application of the regulations. It should be noted however that ACOP guidance document is not legally binding, so alternate methods of compliance can be used. However, these Codes have a special legal status: in the event of prosecution for a breach of health and safety law, if it is proved that the relevant provisions of the Code were not followed, proof of an alternate method of compliance must be shown. There may be some industry specific hazards and processes which are not covered in ACOPs. Relevant ACOPs for regulations pertinent to cryogenic hydrogen systems are listed in Appendix A.

At the third level there are various codes and standards that provide relevant guidance, published by bodies such as the International Organisation for Standardisation (ISO), the British Stands Institution (BSI), ASTM International, the National Fire Protection Association (NFPA), the Institution of Gas Engineers and Managers (IGEM) and the European Industrial Gases Association (EIGA). These cover a wide range of potential applications and vary in technical depth from more general standards to do with the use of hydrogen and hydrogen systems, down to specific use cases. Industries such as maritime or aviation may have independent codes and standards for the use of liquid and cryogenic hydrogen. It is recommended to search relevant organisations for guidance relating to more specific applications. The following is a list of some applicable codes and standards.

- ISO/TR 15916:2015 – Basic considerations for the safety of hydrogen systems [25].
- ISO 26142:2010 – Hydrogen detection apparatus — Stationary applications [26].
- ISO 20088-1:2016 – Determination of the resistance to cryogenic spillage of insulation materials — Part 1: Liquid phase [27].
- ISO 20088-2:2020 – Determination of the resistance to cryogenic spill of insulation materials — Part 2: Vapour exposure [28].
- ISO 20088-3:2018 – Determination of the resistance to cryogenic spillage of insulation materials — Part 3: Jet release [29].
- ISO/DIS 11326 – Ships and marine technology — Test procedures for liquid hydrogen storage tank of hydrogen ships [30].
- ISO/AWI 13985 – Liquid hydrogen — Land vehicle fuel tanks [31].
- ISO/AWI 13984 – Liquid Hydrogen Land Vehicle Fuelling Protocol [32].
- ISO 13984:1999 – Liquid hydrogen — Land vehicle fuelling system interface [33].
- ISO/TC 67/SC 9 – Production, transport and storage facilities for cryogenic liquefied gases [34].
- NFPA 2: Hydrogen Technologies Code [35].
- NFPA 55: Compressed Gases and Cryogenic Fluids Code [36].
- CP46: The storage of cryogenic flammable fluids. 2016 – BCGA [37].
- CP36: Cryogenic liquid storage at users' premises. Revision 2: 2013 - BCGA [38].
- BS 5429:1976 – Code of practice for safe operation of small-scale storage facilities for cryogenic liquids [39].
- EIGA_Doc_06/19_Safety_in_Storage_Handling_and_Distribution_of_Liquid_Hydrogen [40].
- AIR8466 (WIP) Hydrogen Fuelling of Aircraft, in both gaseous and liquid form – SAE International (Currently work in progress) [41].
- EI Model code of safe practice Part 15: Area classification for installations handling flammable fluids [42].
- IGEM/H/1 – Reference Standard for low pressure hydrogen utilisation [43].

4.1.2 Specific design considerations for cryogenic hydrogen systems

This section discusses safe cryogenic hydrogen system design by considering how to manage the three broad categories of safety hazards: pressure systems, flammable gas and cryogenic temperatures. While not exhaustive, these considerations and their interactions can help inform hazard identification, risk assessment and control measures. Specific applications of cryogenic hydrogen may require additional design considerations.

4.1.2.1 Pressure systems

Liquid hydrogen (LH$_2$) systems will incur a level of boil-off which will lead to an increase of pressure in the system over time. Additionally, ancillary compressed gaseous hydrogen systems may also be present, such as hydrogen liquefier feeds or purging systems. This pressure must be controlled through suitable engineering means.

Safety relief valves are required on any section of a liquid hydrogen system that can isolate or trap LH$_2$, including during emergency or maintenance situations. They should be designed with consideration for all components they are protecting [44] and positioned so that the vented hydrogen is directed away from possible ignition sources. Example solutions are high-level vents [45], flaring, or hydrogen recovery. This is depicted as a sketch in figure 3. Pressure relief devices and associated venting pipework should also be designed such that moisture cannot collect, freeze, or interfere with proper operation [46]. For further detail on valve design for liquid hydrogen systems, see section 4.2.3.

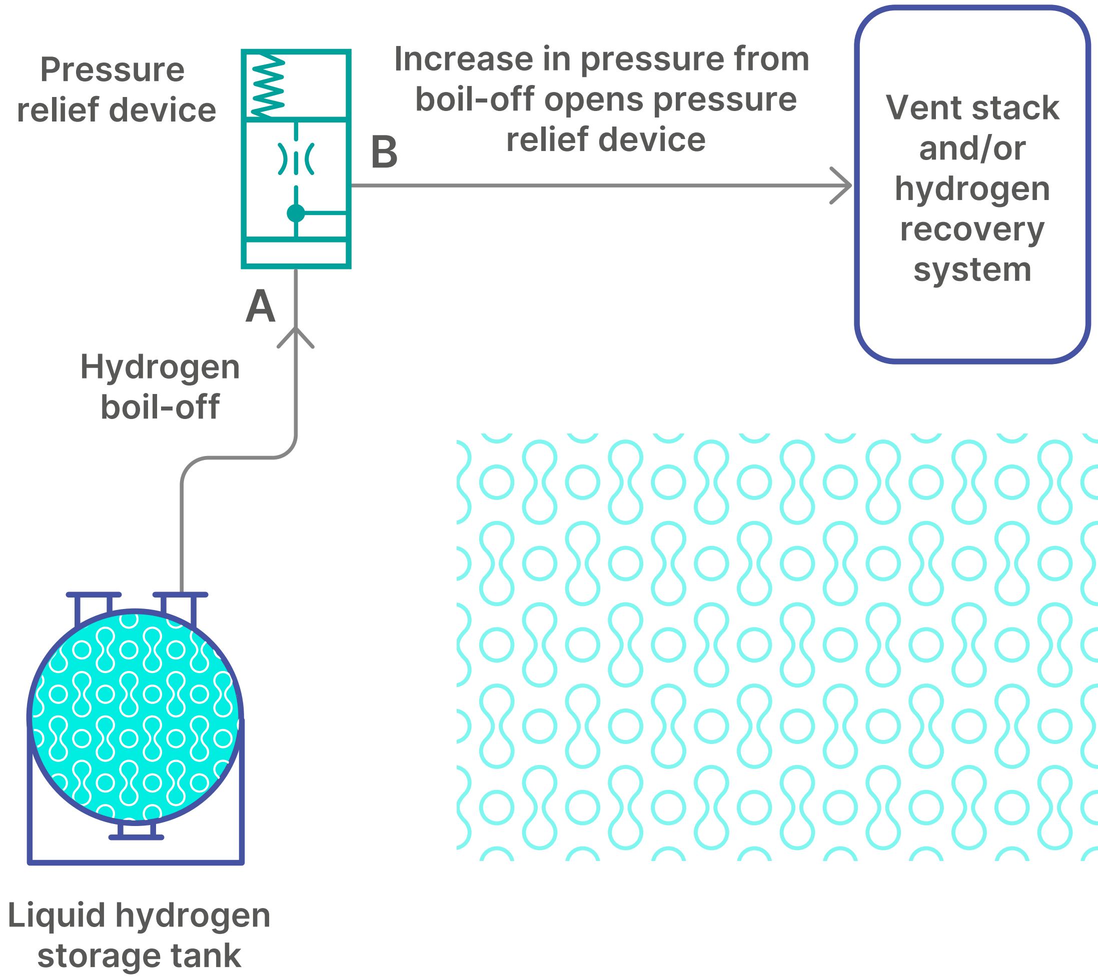


Figure 3. Example of a pressure relief device used to vent boil-off from an isolated hydrogen storage tank to a hydrogen recovery system or vent stack.

4.1.2.2 Preventing the formation of explosive atmospheres

Purging

As with any flammable gas, a hydrogen system should be purged of oxygen with an inert gas to prevent the formation of a flammable atmosphere [47]. The potential phase change of the inerting gas must also be considered with cryogenic systems as gases such as nitrogen can freeze and cause blockages in the pipework, potentially leading to over pressurisation. Helium gas can be used as an inerting gas; however, it is more typical to use a two-stage purge: nitrogen to remove the oxygen, then ambient gaseous hydrogen to remove the nitrogen.

Leak prevention

Leak paths can be minimised by reducing the number of joints to a practicable minimum. The use of welded joints is often preferable in many applications as the likelihood of leaks occurring is reduced [48]. Any tubing, fittings and equipment should be rated for the pressure, temperature, process fluid (hydrogen) and environment of operation. This involves consideration of any mechanical, chemical, or atmospheric properties that could cause degradation of the system resulting in leaks.

Ventilation

Ventilation should be used to allow the dispersal of hydrogen gas from a spill of liquid hydrogen. Facility design may employ natural ventilation if it is sufficiently open to the atmosphere, however, if the system is located indoors or in a confined space, active ventilation may be required. The active ventilation system may have requirements to meet the appropriate Safety Integrity Level or to be safe for installation in an explosive atmosphere. Regardless of these requirements for the specific use-case, common faults such as power failure should be considered at the design stage of any active safety system.

4.1.2.3 Preventing ignitions

Leak detection

Leak detection is required to identify an escape of hydrogen as soon as possible. This enables isolation or other corrective actions to be taken, halting the uncontrolled release. There are several options for detecting leaks [49]:

- Point gas detectors can monitor the presence of hydrogen gas in an environment. Care should be taken in positioning point sensors to provide suitable coverage of the area. Gaseous hydrogen at ambient temperature is lighter than air and will rise from a leak source. Cryogenic hydrogen, however, may initially remain closer to the ground.
- Mass balances keep track of the mass of hydrogen entering and leaving the system.
- Ultrasonic gas leak detectors listen for the sound of leaking gas. They are particularly useful for detecting high pressure leaks in outdoor environments as they are not impacted by wind.
- Leak detection tape changes colour when in the presence of hydrogen. It can be wrapped around connection points to help maintenance teams identify leaks quickly.
- Pressure measurements can identify a leak if there is an unexpected drop in pressure.

Controlling ignition sources

Sources of ignition should be removed from areas that have been determined to potentially contain a flammable atmosphere, which will be determined by a hazardous area classification or similar process using industry-relevant standard such as:

- BS EN IEC 60079-10-1:2021 Explosive atmospheres – Classification of areas. Explosive gas atmospheres.
- ICG Code IA104E 2016 International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk.
- RTCA DO-160G environmental Conditions and Test Procedures for Airborne Equipment.

This includes electrical equipment and sources of static such as mechanical equipment or clothing. Any equipment, including Personal Protective Equipment (PPE), should be suitably rated for the zone of use.

Managing liquid air as an oxidiser

At liquid hydrogen temperatures, air can condense on the outer surface of uninsulated pipe sections. Liquid air is an oxidiser and therefore has the potential to exacerbate any ignition events. Concrete is preferred over bitumen-containing surfaces, such as asphalt, as liquid air can escalate the severity of a fire through oxidation of the asphalt. Other materials that are incompatible with oxidisers, such as some greases, should also be avoided on cryogenic hydrogen systems.

Pool management

Depending on the storage conditions and leak geometry, pools of a mixture of liquid hydrogen, liquid components of air, and solid components of air can form from an uncontrolled release of liquid hydrogen. The flow of pools should be considered and controlled, potentially with bunds, to protect sensitive area such as drains. Bunds have a trade-off, however, in that they can increase the retention time of a pool, prolonging the hazard. Unless required for other reasons, areas that could be subject to pooling should be as unobstructed as possible. The ground surface should also be considered. Gravel, for instance, has been found to encourage the formation of a detonable mixture of hydrogen and condensed components of air [34].

The use of water (or other comparatively warm substance) to clear hydrogen pools should be carefully considered prior to initiation. While seemingly unlikely, rapid phase transitions (RPTs) have not been ruled out because of spraying water on hydrogen pools, which could have serious consequences. Water would increase the vaporisation rate of the pool, reducing the duration that vapour is produced for. However, this could also create a larger and hazard above the pool potentially resulting in a more severe ignition event. The balance of risks should be considered before taking this action.

4.1.2.4 Mitigating ignitions

Managing jet fires

When ignited, hydrogen burns with a clear flame which is barely visible in daylight and emits significantly less heat than hydrocarbon fires [50]. Systems for detecting and monitoring hydrogen fires including thermal imaging cameras or UV/IR flame detectors can be implemented, however the low radiance of hydrogen flames can make some of these methods difficult, especially in certain environments.

Using water to distinguish a hydrogen fire is often avoided for two reasons: a cloud of unburnt hydrogen could form and ignite, causing a vapour cloud explosion; and water can freeze in the presence of the low temperatures of the cryogenic hydrogen, blocking pipes and potentially escalating the situation. Typically, a jet fire is considered less hazardous than a delayed ignition of a hydrogen cloud [51], so current industry practice for hydrogen fires is to isolate the source (for example, by closing a valve) and then letting the remaining hydrogen burn out. In some circumstances water could be used to cool the surrounding areas to prevent the spread of fire, however the utmost of caution should be used to avoid blocking vent lines with ice. Additionally, vegetation and flammable material should be kept away from the surrounding area to minimise the chance of the fire spreading to adjacent areas.

Mitigating vapour cloud explosions

Vapour cloud explosions (VCEs) can occur if an uncontrolled release of cryogenic hydrogen has a delayed ignition. This can result in significant damage from the pressure and thermal effects of the explosion.

Congestion and confinement can increase the severity of an explosion by orders of magnitude, potentially even resulting in a detonation. As such, the area around a cryogenic hydrogen facility should be clear of congestion and confinement as far as practicable. This includes not only the facility, but also anywhere that a hydrogen cloud could travel to, given that cryogenic hydrogen has a propensity to remain closer to ground level for longer. The dispersion from hydrogen vents and hydrogen leaks should be predicted with various realistic weather conditions to enable suitable controls for the VCE risk.

If after all other preventative and mitigative controls are applied there is still an evident risk of significant explosions, the stability, robustness and location of the surrounding equipment and structures should be such to withstand the blast effects to mitigate the impact of an explosion. This includes the exclusion of items that could generate missiles such as untethered equipment, loose fixings, glass, pebbles etc. Noise also poses a risk of injury to those nearby and should be included in explosion assessments.

4.1.2.5 Cryogenic temperatures

Ideally, systems and components in liquid hydrogen systems should be maintained at cryogenic temperatures to avoid temperature cycling and reduce the risk of thermal fatigue or cracking caused by repeated thermal stresses [52]. Further to this, the coefficient of thermal expansion (CTE) mismatches needs to be accounted for when designing integrating components. Where it cannot be avoided, supports for piping and other components should be designed to allow for movement caused by temperature changes [45].

Hydrogen also has large mobility in metals that is many orders of magnitude higher than other interstitially dissolved atoms [53]. This can eventually lead to premature failure of components through localised ductile rupture [54]. Keeping systems at cooler temperatures reduces hydrogen's mobility which can minimise the risk of component failure through this mechanism. To maintain these temperatures, insulation is required which is discussed in section 4.2.2.

Any uninsulated pipes containing cold gaseous hydrogen could lead to ice or condensed air formation. Where possible, these pipes should be equipped with collection trays to capture any ice melt or liquid air. Pipes without collection trays should not be placed overhead due to the hazard of falling ice or liquid air droplets [45].

As a last layer of protection, cryogenic PPE should be used to prevent cryogenic burns and frostbite if skin comes into contact with extremely cold materials or an escape of liquid hydrogen. This could include an unslotted helmet if liquid air could form above head-height. This should also be compatible with the other hazards associated with the cryogenic hydrogen facility, such as those posed by flammable gases or manual handling.

4.2 Component level design

This section will explore design considerations of a selection of the key components in typical liquid hydrogen system: storage tanks, insulation, and valves. A universal requirement for any component in cryogenic hydrogen service is material compatibility, which is expanded upon in section 5.

4.2.1 Storage tanks

Liquid hydrogen storage tanks contain both liquid and gaseous hydrogen. Cryogenic storage tanks hold hydrogen at < 200 bar: compressed gaseous hydrogen tanks typically operate at pressures of 200-1000 bar and cryo-compressed hydrogen tanks operate at a minimum pressure of 300 bar [55]. Design methods are described in ISO 21009-1 - cryogenic vessels - static vacuum insulated vessels, part 1: design, fabrication, inspection and test [56], and ISO 21009-2, cryogenic vessels, static vacuum insulated vessels - part 2 operational requirements [57]. A NASA review from 2006 provides detail into key design issues and potential solutions for liquid hydrogen cryogenic storage tank structures for aircraft applications [58].

There are five types of high-pressure vessel classifications [59]:

- **Type I:** pressure vessel made of metal (commonly used for hydrogen gas storage at 150-300 bar)
- **Type II:** pressure vessel made of thick metallic liner hoop wrapped with a fibre-resin composite (typically used for high pressure stationary applications)
- **Type III:** pressure vessel made of a metallic liner fully wrapped with a fibre-resin composite (typically used for portable applications)
- **Type IV:** pressure vessel made of polymeric liner fully wrapped with a fibre-resin composite. The port is metallic and integrated in the structure (typically used for portable applications)
- **Type V:** composite vessel with no liner. These tanks are not commercially available but offer the potential for increasing the gravimetric and volumetric density of hydrogen storage

To minimise heat transfer due to geometric factors, the ideal tank shape for a nonintegral tank is spherical. The curved surfaces reduce heat loss due to the low surface area-to-volume ratio, but they also present manufacturing challenges. In practice, a cylindrical vessel with rounded ends is often selected for nonintegral applications, which reduces the technical complexity for manufacturing and allows better space utilisation.

Temperature differences of up to 300 °C could occur from the inside to the outside of the tank. This requires insulation to reduce heat flow into the tank. In addition, there is a requirement to shield and isolate the system from atmospheric gases to prevent solidification, as all gases but helium can solidify or condense on the surface of the tank, obstructing lines or causing corrosive effects.

In components that operate within a wide temperature range, consideration needs to be given to the relative coefficients of thermal expansion (CTE) of contacting materials. In such situations the materials can become highly stressed during operation which could compromise the integrity of a component. Consequently, CTE mismatches need to be accounted for when designing storage tank components and insulation jackets [60].

Tank materials must also be selected to have suitable mechanical properties from room temperature down to cryogenic temperatures. This is discussed in section 5.

4.2.2 Insulation

There are broadly three categories of insulation which can be used to minimise heat transfer through cryogenic tanks. These are foams, vacuums, and Multi-Layer Insulation (MLI).

Foams

Foam insulation layers can be both on the inside and the outside of a cryogenic tank and are typically applied by spraying, though preformed sheets can also be used. Foams can be rigid or flexible and are typically made from polymers, such as polyurethane or polyisocyanurate, though glass foams also exist, such as perlite or other silica-based foams [12]. Foam-based insulations are lightweight and have low mass density. The use of foams is well established and low in cost, as well as being compatible with most materials. However, they offer low resistance to thermal radiation [61] and can be easily damaged. Aerogels, which are open-celled, mesoporous solid foams are becoming more widely used due to the ability to tailor the balance between structural and thermal properties. These are however less well established [62].

Vacuum

Vacuums can be used to insulate, either in the form of jackets around the vessel, or as a layer between wall of the inner and outer vessels. Maintaining a sufficiently low vacuum pressure can be a challenge in such systems. When used between the walls of a vessel, relative coefficients of thermal expansion between layers of the vessel need to be carefully considered.

The use of vacuum insulation is well established and has near zero thermal conductivity. However, radiation heat transfer is still possible, and a heavier and costlier tank design is usually required. Furthermore, loss of the vacuum leads to catastrophic failure of the insulation system [60].

Vacuum jacketed pipelines are also well established for cryogenic systems. They consist of two layers of pipe, one running concentrically within the other, and a low-pressure vacuum maintained between the two. The inner pipe is called the core, and carries the liquid hydrogen, while the outer pipe is the insulating jacket which also provides the structural strength for the pipeline. Such systems can be expensive, and vulnerable to external loading. Jacket design should consider thermal flexibility of the inner line and allow the jacket to follow its natural thermal displacement. The vacuum jacket is also required to have a dedicated pressure-relief system. Other design considerations for vacuum jackets include the spacing of bellows expansion joints, as well as structural support between the two pipes by using spacers in the annulus [45].

Multilayer Insulation

Multilayer insulation (MLI) is thermal insulation composed of multiple layers of thin sheets; typically plastic sheets coated in metal. While it offers good insulation to thermal conductivity, it is particularly effective at insulating thermal radiation [13]. Consequently, it is usually used in combination with vacuum systems though layers should be spaced to allow vacuum between the layers. MLIs are a well-established technology, having been used in aerospace for decades, and have a low cost.

4.2.3 Valves

Due to evaporation of liquid hydrogen, tanks and other components must be designed to allow “boil-off” through a relief valve to maintain an appropriate pressure. Cryogenic valves need to be specifically designed to withstand extreme temperature changes, as well high pressures [63]. To protect against very low temperatures, valves can be jacketed to provide insulation and prevent condensation, which can cause corrosion. Complex designs and use of compressing components, such as springs, need careful design solutions to prevent seizure. At low temperatures sealing faces and the packing assembly will become less elastic. This can lead to a freezing of the stem (or bonnet) mechanism. Cryogenic valves are therefore fitted with extended stems to increase the distance between the packing and the liquid hydrogen and ensure that the actuating assembly is kept above freezing [64].

For cryogenic valves, consideration should be given to any sealants and lubricants used in the mechanism of the valve, as hydrogen is a very small molecule and is prone to leaking, while lubricants are likely to have a specific temperature window in which they operate effectively [65]. Furthermore, seating faces within the valve should be assessed for contact wearing, as temperature can change the tribology of coupling materials [66]. Teflon or polychlorotrifluoroethylene (PTFCE) are commonly used for valve seats in liquid hydrogen system due to their compatibility at temperature. A review of the use and behaviour of elastomers at cryogenic temperatures by Robbins et al. discusses options to use elastomers O-rings that would otherwise be used as a static seal at room temperature, however all offer disadvantages relating to either high cost, poor performance or complexity[67].

5 Material considerations

In the design process, the selection of materials begins with identifying and prioritising critical design criteria, as discussed in Section 4. Since the performance of a component relies on a combination of properties, it is crucial to employ multi-criteria decision making and effective testing strategies to evaluate the suitability of materials in various environments. The key categories of material compatibility with cryogenic hydrogen are:

1. **How the material is affected by hydrogen.** For example, most metals are susceptible to hydrogen embrittlement, whereas polymers and composites are affected by gaseous hydrogen permeation and diffusion.
2. **How the material is affected by cryogenic temperatures.** Both metals and polymers experience a significant loss in ductility, and some may even become brittle. Material failure can lead to unwanted leaks and even structural failure.

Though this report focuses on cryogenic applications, it is important to highlight that as hydrogen moves through a system, the physical state may change (for example, liquid to gas) thereby imposing additional material requirements.

There is limited availability of material property data for cryogenic hydrogen applications. The current knowledge (as of 2024) is summarised in section 5.2 and known testing methodologies are proposed in section 5.3.

5.1 The impact of cryogenic hydrogen on material properties

Due to the extreme environment of cryogenic applications, significant focus must be allocated to the understanding of specific material properties that may otherwise not often be required in engineering design and material selection. The sections below highlight a selection of critical material properties specific to cryogenic hydrogen, including hydrogen embrittlement susceptibility, ductile-to-brittle transition temperature, and coefficient of thermal expansion.

5.1.1 How materials are affected by hydrogen

5.1.1.1 Hydrogen embrittlement

One of the primary considerations for materials implemented in hydrogen applications is the effect of Hydrogen Embrittlement (HE), which is a complex and potentially detrimental phenomenon affecting the mechanical integrity of materials, particularly certain metals. It occurs in metals when atomic hydrogen enters the metal lattice and interacts with the metal's microstructure, internal defects such as inclusions, porosity or cracks, or hydride forming elements. As hydrogen accumulates, it significantly reduces the material's ductility, toughness and increases the propagation rate of fatigue cracking, rendering it more susceptible to sudden and catastrophic fractures, even under relatively low stress conditions, below its yield strength. The mobility of hydrogen within a metal to cause these effects is impacted by density dislocation. This mechanism is shown in Figure 4.

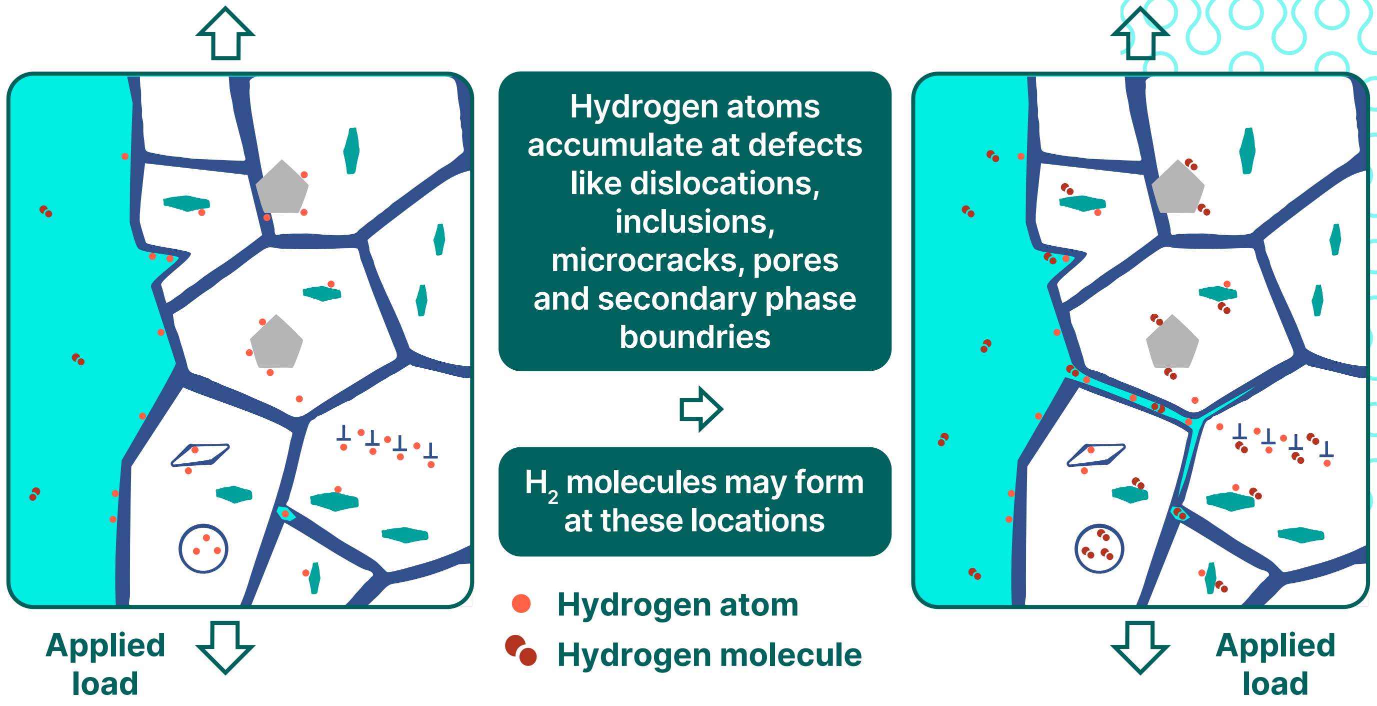


Figure 4. Schematic depicting the hydrogen infiltration that leads to metal embrittlement.

It is worth noting that the exact mechanisms of embrittlement and their relative contributions can vary depending on the type of material, environmental conditions, and stress state of the material, either from internal or externally applied stresses. Although there is a limited amount of research on hydrogen embrittlement at cryogenic temperatures, there are numerous resources available for general information on hydrogen embrittlement [52] [53] [54].

5.1.1.2 Hydrogen permeation

Though polymers are not susceptible to the same embrittlement mechanisms as metals, they are affected by permeation of hydrogen molecules into the polymer structure. Hydrogen absorbed on the polymer surface is present as hydrogen molecules rather than as dissociated hydrogen atoms, and permeation rate is dependent on the storage pressure differential to ambient pressure [48]. Hydrogen molecules that permeate into the polymer can interact with the polymer chains and cause a plasticising effect, reducing the material's strength and increasing its toughness [49]. The polymer may become more brittle and prone to cracking or fracturing under mechanical stress. Hydrogen permeation can also cause dimensional changes in the polymer, potentially leading to swelling or contraction. The effect may be reversible under operating conditions that do not cause plastic deformation, and where a time allowance has been made for the material to degas. This expansion and degas phenomena should be considered in the maintenance and repair of joints, and the impact on overall shape and size stability.

When fibre-reinforced polymeric composites are used to contain hydrogen, interconnected microcracks, the opening of which can be accelerated by hydrogen permeation, can create a pathway for leaks. Additionally, if microcrack networks contain liquid hydrogen and the laminate undergoes thermal cycling, the liquid hydrogen may boil within the laminate, resulting in delamination damage [51].

To mitigate the effects of hydrogen permeation, strategies can be explored such as selecting hydrogen-resistant polymers, incorporating barrier layers, and applying coatings to reduce hydrogen diffusion.

Cryogenic temperatures (below -123°C) [46], can, however, have a beneficial effect of slowing diffusion processes of hydrogen in materials. The reduced availability of thermal energy at low temperatures hinders atomic motion and results in slower diffusion rates through the material compared to higher temperatures.

5.1.2 How materials are affected by cryogenic temperatures

The specific behaviour of materials at cryogenic temperatures can vary depending on the composition, microstructure, and specific conditions of the material. Therefore, comprehensive testing, characterisation, and understanding of the materials' behaviour at cryogenic temperatures, as well as other service conditions, are crucial for safe and reliable performance in cryogenic applications.

5.1.2.1 Ductile-to-Brittle Transition Temperature

When metals and polymers are used at cryogenic temperatures, they exhibit several unique behaviours and characteristics due to the significant decrease in temperature. The most significant effect at cryogenic temperatures is the decreased ductility and increased brittleness, specifically due to the critical ductile-to-brittle transition temperature (DBTT).

At temperatures above the DBTT, the material's fracture behaviour is more ductile, meaning it can undergo plastic deformation and energy absorption before ultimately failing. Below the DBTT, the material becomes more brittle, with reduced ability to deform plastically before fracture. The transition temperature depends on factors such as composition, microstructure, and loading conditions. Metals that have a Face Centred Cubic (FCC) atomic structure do not exhibit a DBTT.

The combination of cryogenic temperatures and hydrogen exposure can accelerate the shift from ductile to brittle behaviour in materials, effectively increasing the DBTT. This means that materials that might exhibit ductile behaviour at higher temperatures could become brittle and prone to sudden fracture when exposed to cryogenic temperatures and hydrogen.

5.1.2.2 Coefficient of Thermal Expansion

Cryogenic hydrogen can have a notable impact on the coefficient of thermal expansion (CTE) of components, especially those made from combinations of different materials or polymer-based composites. The CTE is a material-specific measure of how much a material expands or contracts in response to changes in temperature. CTE mismatch can occur when two materials with different CTEs are brought into contact or assembled together, which can lead to thermal stress, dimensional changes, and leakage and seal failure in a cryogenic system. CTE mismatch between materials must be carefully accounted for when selecting materials and designing systems, as described in Section 4.

5.2 Material compatibility for application in hydrogen environments

In the case of fibre-reinforced polymer composites, the coefficient of thermal expansion (CTE) of the matrix resin and its compatibility with the reinforcing fibre play a crucial role in cryogenic applications. The primary failure modes observed in polymer-based composites used in cryogenic hydrogen storage vessels are matrix cracking, debonding of the fibre/matrix interface, delamination, and fibre rupture [50].

Based on the mechanisms described in the previous section, it is clear when selecting a material for cryogenic hydrogen applications the susceptibility to hydrogen degradation and their mechanical characteristics at design temperatures, must be considered. The known compatibility of materials in cryogenic environments have been summarised in Table 3[45] [68].

Materials databases mainly consist of mechanical properties and physical constants, which are usually obtained by testing materials in the following environmental conditions:

- High pressure gaseous hydrogen.
- Hydrogen pre-charged condition via electrochemical process.
- Liquid nitrogen or liquid helium cooled condition.
- Atmospheric liquid hydrogen condition.

The availability and scope of publicly available material databases are still very limited in terms of environmental conditions, breadth, and reproducibility of testing, especially for cryogenic hydrogen applications. The most complete sources of available information are:

- The Technical Database for Hydrogen Compatibility of Materials established by Sandia's National Laboratories [69].
- Cryogenic materials properties established by National Institute of Standards and Technology [70].

Table 3. Common materials for in-service applications in gaseous (GH_2) and liquid (LH_2) hydrogen environments a tick denotes suitable material, a cross denotes an unsuitable material, and question mark denotes where further evaluation is required [45] [68].

Material	GH_2	LH_2	Remarks
Metallic materials			
Aluminium and its alloys	✓	✓	Negligible susceptibility to HE. GH_2: subject to certain conditions [45]
Cooper and its alloys (brass, bronze and copper-nickel)	✓	✓	Negligible susceptibility to HE
Iron, cast, grey and ductile	⊗	⊗	Not permitted by relevant codes and standards
Nickel and its alloys (e.g., Inconel and Monel)	?	?	Evaluation needed. Susceptible to HE. **GH_2:** Susceptible to HE, to be used under controlled conditions **LH_2:** Mechanical properties of Ni alloy needed to be evaluated at service conditions

Material	GH_2	LH_2	Remarks
Metallic materials			
Austenitic stainless with > 7% nickel (e.g., 304, 304L, 308, 316, 316L, 321, 347)	✓	✓	Negligible susceptibility to HE
Steels, low/mid carbon (e.g., 1020 and 1042)	?	⊗	Evaluation needed. Susceptible to HE. High DBTT for cryogenic service
Steel, low alloy (e.g., 4140)	?	⊗	Evaluation needed. Susceptible to HE **GH_2:** Susceptible to HE **LH_2:** Brittle at LH_2 service conditions
Steel, high alloy	⊗	⊗	Susceptible to HE (GH_2) and brittle at LH_2 conditions
Martensitic stainless steel (e.g., 410 and 440C)	?	?	Evaluation needed. Susceptible to HE
Steel, nickel (e.g., 2.25%, 3.5%, 5% and 9% Ni))	?	⊗	Lost ductility at LH_2 temperature
Titanium and its alloys	?	?	Evaluation needed. Susceptible to HE **GH_2:** Suitability dependent upon alloy composition **LH_2:** Mechanical properties of Ti alloys needed to be evaluated at service conditions
Non-metallic materials			
Polychlorotrifluoroethylene (PTFCE)	✓	✓	
Chloroprene rubber	✓	⊗	Too brittle at LH_2 temperature
Polyester fibre (Dacron)	✓	⊗	Too brittle at LH_2 temperature
Nitrile rubber	✓	⊗	Too brittle at LH_2 temperature
Polyester film	✓	⊗	Too brittle at LH_2 temperature
Fluorocarbon rubber	?	⊗	Too brittle at LH_2 temperature
Polyamides (Nylon)	✓	⊗	Too brittle at LH_2 temperature
FRP composites	?	?	Evaluation needed across combinations of fibres and matrix materials

5.3 Materials testing requirements

5.3.1 Testing Pyramid

Due to the limited availability of relevant material databases, significant testing needs to be undertaken. The performance of materials, including those in extreme environments, can be established progressively through a structured program of analysis and a sequence of experimental tests. These tests are carried out using specimens of different sizes and levels of complexity. This structured approach is commonly referred to as the Pyramid of Testing. The level of complexity, along with the associated costs and time requirements, increases as testing progresses up the testing pyramid. Material properties extracted from tests conducted at lower tiers can serve as a basis for establishing specifications and design limits for larger scales and more intricate components, flowing into system level requirements.

This structured approach may be extended to consider temperature and hydrogen related effects in isolation first, and then consider the combination of these conditions when necessary. This may give rise to a more economical test regime, employing liquid nitrogen and liquid helium cryogens, ahead of employing liquid hydrogen. This structured approach to understand performance properties of materials, components and systems allows a performance-based approach to assurance and regulation. Guidance on the application of this methodology in the context of composite materials is provided by European Union Safety Aviation Agency (EASA) [71]. Global capability for cryogenic and hydrogen materials testing has been compiled by the National Physical Laboratory (NPL) and the Aerospace Technology Institute's (ATI) Hydrogen Capability Network, highlighting capability in Europe and the USA [72].

5.3.2 Testing for metallic materials

There are a wide range of testing methods that can be selected for characterising the different properties of metals depending on the intended applications and service conditions. However, the most common tests relevant to cryogenic fracture toughness, hydrogen embrittlement and permeability, with standards widely accepted, are listed as below:

- Impact toughness Charpy V-notch (CVN) testing (ASTM E23, ISO 148-1 or EN 10045-1).
- Slow Strain Rate Testing (SSRT) with notched specimen (ASTM F1624).
- Fracture Toughness Testing (ASTM E1820; ASTM E399).
- Hydrogen Permeation Testing (ASTM G148; ISO 17081:2014 (EN)).
- Sustained Load Testing (SLT) (ASTM F519).
- Slow strain rate testing for environmentally assisted cracking (ASTM F1940, G129).
- Cryogenic testing of metals:

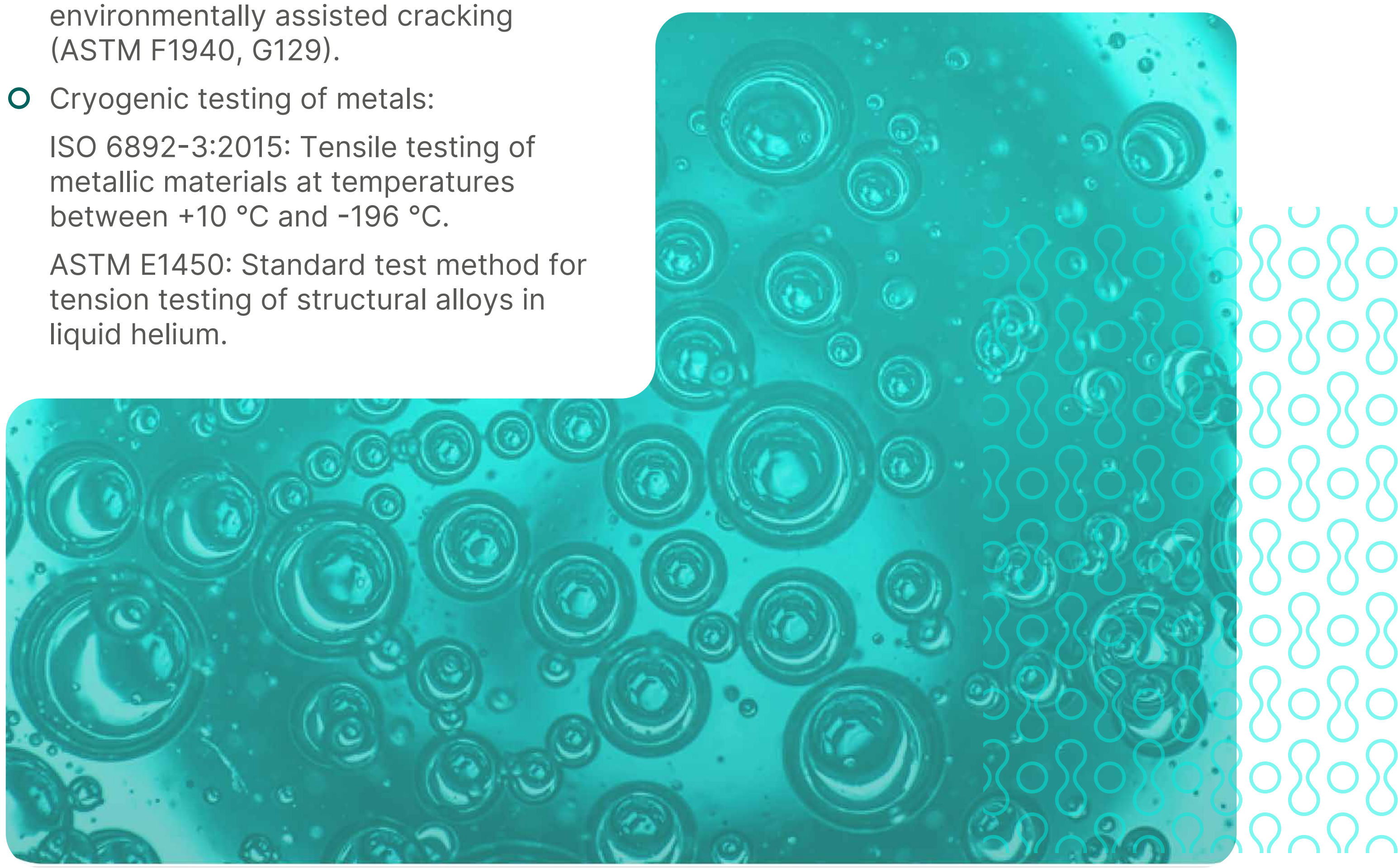
  ISO 6892-3:2015: Tensile testing of metallic materials at temperatures between +10 °C and -196 °C.

  ASTM E1450: Standard test method for tension testing of structural alloys in liquid helium.

5.3.3 Testing for polymers and composites

The testing of polymers is conducted in accordance with relevant standards, with specimens exposed to hydrogen environments as described previously. Mechanical testing for polymers and fibre reinforced polymer composites at cryogenic temperatures with hydrogen environment is still in its infancy.
At the time of writing there are no defined standards for testing at these temperatures, however requirements for cryogenic mechanical testing of fibre-reinforced polymer matrix composites have been compiled by NPL [73].

Composite material testing can be challenging given the potentially complex material response, and the implications of small-scale test results on large scale applications can be missed. For this reason, a testing pyramid approach is often used where the complexity of the testing is incrementally increased.



6 Manufacturing considerations

Following on from the design of a system and the down selection of appropriate materials for the application, it will also be necessary to consider how the method of manufacture of individual components could influence their integrity and durability in the service environment. This is imperative when referring to metals, as the microstructure and internal defects can be strongly affected by the manufacturing process.

Two of the main considerations for manufacturing metallic components are to minimise the residual stresses in tension state and prevent any harmful changes to the microstructure. Any degree of residual stress within a material will support hydrogen diffusion through the material, as well as be superimposed onto the externally applied stress on a component, promoting earlier failure. Similarly, processes which have the potential to introduce defects, such as inclusions, porosity or cracks, will influence the hydrogen mobility in the material or potentially lower the cryogenic properties of the material, such as fracture toughness and fatigue durability.

Additionally, other adverse changes to microstructure can reduce the ductility of the material, such as from induced phase transformations. For instance, when austenitic stainless steel, such as grade 316 stainless steel, is subject to severe cold plastic deformation the beneficial austenite microstructure can be transformed into brittle martensite.

With polymer and composite materials, measures can be taken during manufacturing to limit the introduction of defects into the material or limit the altering of material properties. However, improper curing of resins and fibre misalignments can occur in composite manufacturing, causing porosity. Similarly, errors in carbon dispersion and weak knit lines can impart defects into polymer materials.

6.1 Shaping and forming

Commonly used processes to create the shape of a component include:

- **For metals:** casting, forging, rolling, pressing, stamping, subtractive or additive manufacture.
- **For polymers:** injection moulding, rotational moulding, blow moulding, compression moulding, extrusion, vacuum forming, calendaring.
- **For composites:** weaving, braiding, hand or spray lay-up, filament winding, automated fibre placement, resin transfer moulding, resin film infusion.

For metallics the influence on the microstructure will be determined by factors such as temperature and cooling rates, the amount of working and strain rates. This will determine the phases present and the size and shape of the grains. As described in the section on materials, the mechanisms of hydrogen induced degradation are highly complex and the role of interactions between the hydrogen atoms and the crystallographic features, including dislocations and vacancies, is still to be fully established. It is however known that the method of manufacture does influence the density of these dislocations.

Another consideration, in the context of metallic materials, is that not all forming processes are compatible with all alloy systems. For example, aluminium alloy 2195 is commonly used for cryogenic applications in the space sector but this alloy is only available as wrought plate or billet, as it is not suited to casting or additive manufacturing. This may limit the choices available to manufacture components.

With certain thermoplastic materials the degree of crystallinity may be dictated by differential cooling rates in processes such as injection moulding, this being influenced by cross section thickness and tool heating/cooling procedures.

Evidence suggests that increasing the crystalline content of material such as polyetheretherketone (PEEK), can reduce fracture toughness [74]. Conversely high crystallinity can act as a barrier to hydrogen permeation [75].

With composite materials the level of consolidation achieved between the fibres and the resin will be influenced by a combination of the material system and the forming process. For example, filament winding of a pressure vessel could be performed with either tow-preg material or by wet winding. With the latter more commonly able to achieve a lower void content in the composite, while the former would typically have a higher fibre volume fraction.

The amount of cross linking in the epoxy resin can be determined by factors such as temperature, moisture content, hold time and pressures. Highly cross-linked epoxies may exhibit lower impact toughness but provide higher permeability resistance. The addition of fillers, multi-walled carbon nanotubes, and toughening agents like core-shell rubber particles has been shown to enhance the tensile strengths and improve impact and microcracking resistance of epoxy resins at cryogenic temperatures [76].

6.2 Joining

As mechanical or bolted joints can create additional leak paths or introduce multiple materials that may cause problems with differential thermal expansion/contraction, they are generally to be minimised within hydrogen systems with preference for fully penetrating welded joints.

Mechanical joints, where required, need to be prepared with appropriate tolerances and suitable gaskets/sealing materials that are compatible with liquid and gaseous hydrogen, within the pressure and temperature range of the service environment.

The welding of certain steels is known to produce microstructures that are particularly susceptible to hydrogen embrittlement, this combined with high residual stresses of certain joints can lead to catastrophic failure. Selection of the most appropriate joint configuration, welding procedure and post weld heat treatment is required to avoid this issue.

The acceptance criteria for defects and joint alignment may be influenced by the service temperature and criticality of the application, this in turn would guide the selection of the most appropriate joining method. As an example, research from NASA [77] indicates that friction stir welding (FSW) is preferable to fusion welding processes for the joining of thin aluminium plate sections of LH_2 storage tanks, as the process provides superior joint efficiency.

Guidance on such matters can be found in relevant standards including:

- BS-ISO 20421 “Cryogenic vessels – large transportable vacuum-insulated vessels part 1.”

This also recommends suitable procedures for the inspection and testing of the fabrication.

6.3 Post processing

Heat treatment processes such as solution annealing or tempering, if applied correctly, can transform undesirable microstructures, eliminate residual stress and reduce dislocation density, thus providing the optimum microstructures to avoid issues with LH_2. Alloy specific considerations create more complexity here, but guidance within the relevant standards can help to make informed decisions.

Within ISO20421-1 Cryogenic vessels – large transportable vacuum-insulated vessels part 1 [78], it is stated that for austenitic steels “heat treatment of cold formed heads should be performed for liquid hydrogen service…” Whereas for aluminium alloys “Cold-formed ends…do not normally require post-forming heat treatment.”

Some manufacturing process can add hydrogen into the material, including welding. Electroplating for example can introduce hydrogen into a steel surface, but such phenomena are well documented and measures can be taken to minimise their effect.

One important aspect when considering a LH_2 application is the need for rigorous and thorough cleaning of the components. Any residual contaminants such as grease and oils may freeze at the cryogenic temperatures causing blockages or restrictions. Particulate contamination may prevent gasket or joints from sealing correctly leading to leaks of liquid or gaseous hydrogen. Established international standards such as CGA G4.1 Cleaning of Equipment for Oxygen Service [79] could be used to provide suitable cleaning procedures and acceptance levels.

Table 4 provides an overview of some of the known issues with several generic manufacturing processes, and the potential impact this could have on performance and properties in relation to hydrogen and cryogenic service. These potential impacts are currently theoretically based on the principles and mechanisms of hydrogen induced degradation discussed in earlier sections and require further investigation to be qualified.

Table 4. Overview of known issues with several generic manufacturing processes, and the potential impact for use with LH_2.

Manufacturing process	**Common impacts of manufacturing process on surface, microstructure and defects**	**Potential impact when exposed to hydrogen and cryogenic service**
Welding/joining, in particular fusion welding **(Solid-state welding/ joining process is favourable)**	Cracks Porosity Heat affected zone (HAZ) Localised high level of tensile stress	Reduced fracture and fatigue properties Increased hydrogen transport kinetics and potential for hydrogen accumulation at dislocations
Casting	Porosity Coarse microstructure Undesired carbides in ductile castings Non-uniform residual stress	Increased hydrogen trapping potential Reduced fracture toughness
Forging	Fine equiaxed microstructure	Generally beneficial, but may lead to increased absorbed hydrogen content
Cold working	High dislocation density Martensite transformation due to severe cold deformation	Increased maximum absorbed content by hydrogen accumulation at dislocations

Manufacturing process	Common impacts of manufacturing process on surface, microstructure and defects	Potential impact when exposed to hydrogen and cryogenic service
Additive manufacturing	Microcracks Porosity High level residual stress High surface roughness Anisotropic grain structure	Increased hydrogen transport kinetics and potential for hydrogen accumulation at dislocations and porosity Anisotropic mechanical properties including fracture toughness
Surface engineering	Electrical plating could generate hydrogen within the coating Tensile/compressive residual stress Modified microstructure Reduced surface roughness	Surface engineering processes may be beneficial to increase hydrogen embrittlement resistance when used to apply a compressive residual stress on the component's surface
Surface finishing	Remove surface defects Reduce surface roughness Generate surface residual stress	Smooth surface increases fatigue strength Lack of data on the effect of hydrogen embrittlement at cryogenic
Powder metallurgical processes	Prior particle boundary (PPB) Porosities Micro-voids Micro-segregations of impurities Reduced yield strength due to uncontrolled grain growth	PPBs and voids may act as hydrogen trapping sites and reduced toughness of the matrix
Machining	Machining can deform the subsurface of a material, changing the stress state and potentially introducing defects	Surface roughness impacts adsorption rate of hydrogen onto metal surface. Joint and seal integrity is determined by machining tolerances and surface roughness

7 References

[1] National Institute of Standards and Technology, "Thermophysical Properties of Fluid Systems," US Department of Commerce, [Online]. Available: https://webbook.nist.gov/chemistry/fluid/. [Accessed 07 July 2023].

[2] HydrogenTools, "Lower and Higher Heating Values of Fuels," [Online]. Available: https://h2tools.org/hyarc/calculator-tools/lower-and-higher-heating-values-fuels. [Accessed 07 July 2023].

[3] K. Annamalai and I. K. Puri, "Combustion Science and Engineering," CRC Press, no. ISBN 978-0-8493-2071-2, p. 851, 2006.

[4] W. (. Haynes, "CRC Handbook of Chemistry and Physics. 95th Edition," CRC Press LLC, Boca Raton, 2014.

[5] bp, "Safety Data Sheet BP Marine Fuel Oil IF 40," 02 12 2021. [Online]. Available: https://www.bp.com/content/dam/bp/country-sites/en_au/australia/home/products-services/data-sheets/bp-marine-fuel-oil-if-40.pdf#:~:text=Prevention%20P201%20-%20Obtain%20special%20instructions%20before%20use.,-%20Keep%20away%20from%20flames%20and%20hot%20s. [Accessed 07 July 2023].

[6] N. I. o. S. a. Technology, "Thermophysical Properties of Hydrogen," US Department of Commerce, [Online]. Available: https://webbook.nist.gov/cgi/fluid.cgi?ID=C1333740&Action=Page. [Accessed 07 July 2023].

[7] HydrogenTools, "Hydrogen Viscosity at Different Temperatures and Pressures," [Online]. Available: https://h2tools.org/hyarc/hydrogen-data/hydrogen-viscosity-different-temperatures-and-pressures. [Accessed 07 July 2023].

[8] HydrogenTools, "Hydrogen Density at different temperatures and pressures," [Online]. Available: https://h2tools.org/hyarc/hydrogen-data/hydrogen-density-different-temperatures-and-pressures. [Accessed 07 July 2023].

[9] H. Haase, "Electrostatic Hazards, Their Evaluation and Control," Verlag, Chemie, Weinheim., 1977.

[10] The Engineering ToolBox, "Gases - Explosion and Flammability Concentration Limits," [Online]. Available: https://www.engineeringtoolbox.com/explosive-concentration-limits-d_423.html. [Accessed 07 July 2023].

[11] PubChem, National Library of Medicine, [Online]. Available: https://pubchem.ncbi.nlm.nih.gov/. [Accessed 07 July 2023].

[12] T. E. ToolBox, "Fuels and Chemicals – Autoignition Temperatures," [Online]. Available: https://www.engineeringtoolbox.com/fuels-ignition-temperatures-d_171.html. [Accessed 07 July 2023].

[13] J. Z. P. B. S. C. J. S. S.P.M. Bane, "Experimental investigation of spark ignition energy in kerosene, hexane and hydrogen," California Institute of Technology.

[14] INCHEM, "Kerosene (EC232-366-4)," 2021. [Online]. Available: https://www.inchem.org/documents/icsc/icsc/eics0663.htm. [Accessed 07 July 2023].

[15] e. a. Eichert H., “Gefährdungspotential bei einem verstärkten Wasserstoffeinsatz. Study for the Büro für Technikfolgenabschätzung des Deutschen Bundestags,” Deutsches Zentrum für Luft- und Raumfahrt (DLR), 1992.

[16] D. B. Verfondern K., “ Pool spreading and vaporization of liquid hydrogen.,” Int J Hydrogen Energy, vol. 32, no. 13, pp. 2106-2117, 2007.

[17] C. P. D. C. P. H. M. K. S. C. K. Lyons, “Theory and analysis of ignition with specific conditions related to cryoegnic hydrogen: Project Deliverable; PRESLHY,” 28 02 2020. [Online]. Available: https://hysafe.info/wp-content/uploads/sites/3/2020/02/200127-WP4_D4_1_Theory-of-cryogenic-hydrogen-V1.2.pdf. [Accessed 21 06 2024].

[18] G. Atkinson, “Experimental and analyses on condensed phases; Deliverable D4.8; PRESLHY,” Fuel Cells and Hydrogen Joint Undertaking, Grant 779613, 2020.

[19] S. H. G.R. Astbury, “Spontaneous ignition of hydrogen leaks: A review of postulated mechanisms,” International Journal of Hydrogen Energy, vol. 32, no. 13, pp. 2178-2185, 2007.

[20] E. S. H. Pratikash P. Panda, “Ignition and flame characteristics of cryogenic hydrogen releases,” International Journal of Hydrogen Energy, vol. 42, no. 1, pp. 775-785, 2017.

[21] L.-H. A., “A review of large-scale LNG spills: experiments and modeling.,” J Hazard Mater, pp. 119-140, 2006.

[22] E. &. O. L. &. S. H. &. R. G. &. U. F. &. P. N. Aursand, “Risk and Consequences of Rapid Phase Transition for Liquid Hydrogen,” 2020.

[23] K. v. W. e. al., “Experimental Investigation into the Consequences of Release,” Chemical Engineering Transactions, vol. 90, pp. 541-546, 2022.

[24] NASA, “Permeability Data for Aerospace Applications,” 1 March 1968. [Online]. Available: https://ntrs.nasa.gov/citations/19690004779. [Accessed 12 July 2023].

[25] ISO, “ISO/TR 15916:2015 - Basic considerations for the safety of hydrogen systems,” December 2015. [Online]. Available: https://www.iso.org/standard/56546.html. [Accessed 07 July 2023].

[26] ISO, “ISO 26142:2010 Hydrogen detection apparatus — Stationary applications,” June 2010. [Online]. Available: https://www.iso.org/standard/52319.html. [Accessed 07 July 2023].

[27] ISO, “ISO 20088-1:2016 Determination of the resistance to cryogenic spillage of insulation materials — Part 1: Liquid phase,” September 2016. [Online]. Available: https://www.iso.org/standard/67009.html. [Accessed 07 July 2023].

[28] ISO, “ISO 20088-2:2020 Determination of the resistance to cryogenic spill of insulation materials — Part 2: Vapour exposure,” January 2020. [Online]. Available: https://www.iso.org/standard/67010.html. [Accessed 07 July 2023].

[29] ISO, “ISO 20088-3:2018 Determination of the resistance to cryogenic spillage of insulation materials — Part 3: Jet release,” November 2018. [Online]. Available: https://www.iso.org/standard/67011.html. [Accessed 07 July 2023].

[30] ISO, “ISO/DIS 11326 Ships and marine technology — Test procedures for liquid hydrogen storage tank of hydrogen ships,” Under Development. [Online]. Available: https://www.iso.org/standard/83810.html. [Accessed 07 July 2023].

[31] ISO, “ISO/AWI 13985:2006 Liquid hydrogen — Land vehicle fuel tanks,” November 2006. [Online]. Available: https://www.iso.org/standard/39892.html. [Accessed 07 July 2023].

[32] ISO, “ISO/AWI 13984 Liquid Hydrogen Land Vehicle Fueling Protocol,” (under development). [Online]. Available: https://www.iso.org/standard/86295.html. [Accessed 07 July 2023].

[33] ISO, “ISO 13984:1999 Liquid hydrogen — Land vehicle fuelling system interface,” March 1999. [Online]. Available: https://www.iso.org/standard/23570.html. [Accessed 07 July 2023].

[34] ISO, “ISO/TC 67/SC 9 Production, transport and storage facilities for cryogenic liquefied gases,” 2015. [Online]. Available: https://www.iso.org/committee/5749612.html. [Accessed 07 July 2023].

[35] “NFPA 2 Hydrogen Technologies Code,” National Fire Protection Association, 2023.

[36] NFPA, “NFPA 55 Compressed Gases and Cryogenic Fluids Code,” 2023.

[37] BCGA, “CP46 The storage of cryogenic flammable fluids.,” 2016. [Online]. Available: https://bcga.co.uk/publications/cp46-the-storage-of-cryogenic-flammable-fluids-2016/. [Accessed 07 July 2023].

[38] BCGA, “CP36 Cryogenic liquid storage at users’ premises. Revision 2: 2013,” 2013. [Online]. Available: https://bcga.co.uk/publications/cp36-cryogenic-liquid-storage-at-users-premises-revision-2-2013/. [Accessed 07 July 2023].

[39] BSI, “BS 5429:1976 Code Of Practice For Safe Operation Of Small-Scale Storage Facilities For Cryogenic Liquids (British Standard)”.

[40] “Safety in Storage, Handling and Distribution of Liquid Hydrogen,” EIGA, 2019.

[41] SAE, “AIR8466 Hydrogen Fueling of Aircraft, in both gaseous and liquid form,” (WIP).

[42] Energy Institute, “EI Model code of safe practice Part 15: Area classification for installations handling flammable fluids,” Energy Institute Publications, 978 1 78725 441 1, 2024.

[43] IGEM, “IGEM/H/1 - Reference Standard for low pressure hydrogen utilisation,” Institution of Gas Engineers and Managers, 2023.

[44] NASA, “Safety Standard for Hydrogen and Hydrogen Systems: Guidelines for Hydrogen System Design,” 1997.

[45] Lloyds Register, “Guidance Notes for Liquid Hydrogen Systems,” 2023. [Online]. Available: https://www.lr.org/en/knowledge/lloyds-register-rules/guidance-notes/guidance-notes-for-liquid-hydrogen-systems/. [Accessed 17 July 2023].

[46] HydrogenTools, “Liquid System Pressure Relief,” [Online]. Available: https://h2tools.org/bestpractices/liquid-system-pressure-relief. [Accessed 22 June 2023].

[47] HydrogenTools, “Purging,” [Online]. Available: https://h2tools.org/bestpractices/purging. [Accessed 03 01 2024].

[48] Energy Institute, “Area classification for installations handling flammable fluids,” Model code of safe practice, vol. Part 15, no. 4th edition.

[49] Connected Places Catapult, “Zero Emission Flight Infrastructure – Hydrogen Infrastructure Options for Airports: Supplementary Report,” 2023.

[50] W. M. Rattigan, “Hazards of Liquid Hydrogen,” Health and Safety Executive, 2010.

[51] P. X. M. X. M. J. LI. Zhiyong, “Study on the Harm Effect of Liquid Hydrogen Release by Consequence Modeling,” International Journal of Hydrogen Energy, vol. 37, no. 22, pp. 17624-17629, 2012.

[52] ScienceDirect, “Thermal Fatiue - an overview,” [Online]. Available: https://www.sciencedirect.com/topics/materials-science/thermal-fatigue. [Accessed 03 01 2024].

[53] K. W. Kehr, “Theory of the diffusion of hydrogen in metals,” Topics in Applied Physics, vol. 28, 2005.

[54] P. S. N. A. Y. Liang, “On the effect of hydrogen on plastic instabilities in metals,” Acta Materialia, vol. 51, no. 9, pp. 2717-2730, 2003.

[55] H. Barthelemy, M. Weber and F. Barbier, “Hydrogen storage: Recent improvements and Industrial Perspectives,” International Journal of Hydrogen Energy, vol. 42, pp. 7254-7262, 2017.

[56] International Standards Organisation, “ISO 21009-1:2022 – Cryogenic vessels — Static vacuum-insulated vessels — Part 1: Design, fabrication, inspection and tests,” 2022.

[57] International Standards Organisation, “ISO 21009-2:2015 – Cryogenic vessels — Static vacuum insulated vessels — Part 2: Operational requirements,” 2015.

[58] NASA, “NASA/TM - 2006-214346 – Review of Current State of the Art and Key Design Issues With Potential Solutions for Liquid Hydrogen Cryogenic Storage Tank Structures for Aircraft Applications,” 10 2006. [Online]. Available: https://ntrs.nasa.gov/api/citations/20060056194/downloads/20060056194.pdf. [Accessed 03 01 2024].

[59] H. Barthelemy, “Hydrogen Storage – Industrial prospectives,” International Journal of hydrogen energy, vol. 37, pp. 17364-17372, 2012.

[60] J. Z. G. S. M. A. Sbodh K. Mital, “Review of Current State of the Art and Key Design Issues With Potential Solutions for Liquid Hydrogen Cryogenic Storage Tank Structures for Aircraft Apllications,” NASA, 2006.

[61] M. M. L. Glicksman, “Radiation heat transfer in foam insulation,” International Journal of Heat and Mass Transfer, vol. 30, no. 1, pp. 187-197, 1978.

[62] J. Fesmire, “Aerogel-Baed Insulation Materials for Cryogenic Applications,” IOP Conf. Ser.: Mater. Sci. Eng., vol. 011288, p. 502, 2019.

[63] ISO, ISO 21011:2008 Cryogenic Vessels, Valves for cryogenic service, 2008.

[64] Pegler and Louden, “Installation, Operating and Maintenance Instructions, Stem Assumpy Supplement,” Worcester Controls.

[65] SLB, “How It Works: Cryogenic Valves,” [Online]. Available: https://www.slb.com/resource-library/article/valve-insights/how-it-works-cryogenic-valves. [Accessed 04 01 2024].

[66] Z. W. L. G. L. T. T. M. T. W. Q. W. Mingkun XU, “Tribological properties of PTFE-based fabric composites at cryogenic temperature,” Friction, vol. 12, pp. 245-257, 2023.

[67] D. W. R. H. R.F Robbins, “The Application and Behavior of Elastomers at Cryogenic Temperatures,” in Advances in Cryogenic Engineering, New York, 1967.

[68] D. I. Azkarate, “Materials Compatibility with Hydrogen,” in Safety of Hydrogen Systems, Sevilla, Spain, 2014.

[69] Sandia National Laboratories, “Technical Reference for Hydrogen Compatibility of Materials,” [Online]. Available: https://www.sandia.gov/matlstechref/. [Accessed 12 July 2023].

[70] National Institute of Standards and Technology, “Properties of Solid Materials from Cryogenic-to-room-temperatures,” [Online]. Available: https://trc.nist.gov/cryogenics/materials/materialproperties.htm. [Accessed 12 July 2023].

[71] EASA, “Easy Access Rules for Acceptable Means of Compliance for Airworthiness of Products, Parts and Appliances (AMC-20),” EASA, 16 March 2021. [Online]. Available: https://www.easa.europa.eu/en/document-library/easy-access-rules/online-publications/easy-access-rules-acceptable-means?page=20. [Accessed Janruary 2024].

[72] M. G. N. S. P. M. H. E. S. Giannis, “International landscape on cryogenic and hydrogen materials testing,” September 2024. [Online]. Available: https://www.npl.co.uk/getattachment/national-challenges/environment/Hydrogen-programme/Latest-research-on-hydrogen-infrastructure/International-landscape-on-cryogenic-and-hydrogen-materials-testing.pdf.aspx?lang=en-GB. [Accessed 05 10 2024].

[73] R. S. M. G. N.S Perez, “NPL Report MAT 102,” 03 2022. [Online]. Available: https://eprintspublications.npl.co.uk/9464/1/MAT102.pdf. [Accessed 03 06 2023].

[74] D. M. R.A. Chivers, “The effect of molecular weight and crystallinity on the mechanical properties of injection moulded poly(aryl-ether-ether-ketone) resin,,” Polymer, vol. 35, no. 1, pp. 110-116, 1994.

[75] H. K. e. al., “High-pressure hydrogen permeability model for crystalline polymers,” International Journal of Hydrogen Energy, vol. 48, no. 2, pp. 723-739, 2023.

[76] D. C. e. al., “A Review of the Polymer for Cryogenic Application: Methods, Mechanisms and Perspectives,” Polymers, vol. 13, no. 3, p. 320, 2021.

[77] G. Henson, “Materials for Launch Vehicle Structures,” in Aerospac Materials and Applications, Westlake, OhioAerospace Materials and Applications, American Institute of Aeronatics and Astronautics, 2018.

[78] International Standards Orgnaisation, ISO 20421-1:2019 Cryogenic vessels — Large transportable vacuum-insulated vessels — Part 1: Design, fabrication, inspection and testing, 2019.

[79] C. G. Association, CGA G-4.1, Cleaning of Equipment for Oxygen Service, 2018.

[80] HSE, “Carriage of Dangerous Goods Manual,” [Online]. Available: https://www.hse.gov.uk/cdg/manual/index.htm. [Accessed 03 06 2024].

[81] HSE, “Control of Major Accident Hazards (COMAH),” [Online]. Available: https://www.hse.gov.uk/comah/. [Accessed 09 June 2023].

[82] HSE, “The Control of Major Accident Hazards Regulations 2015: Guidance on Regulations,” 2015.

[83] HSE, “COSHH basics,” [Online]. Available: https://www.hse.gov.uk/coshh/basics/index.htm. [Accessed 09 June 2023].

[84] HSE, “Control of Substances Hazardous to Health Regulations 2002 (as amended) Approved Code of Practice and Guidance,” 2013.

[85] HSE, “ATEX and explosive atmospheres,” [Online]. Available: https://www.hse.gov.uk/fireandexplosion/atex.htm#whatatex. [Accessed 09 June 2023].

[86] HSE, “Dangerous Substances and Explosive Atmospheres Regulations 2002. Approved Code of Practice and guidance,” 2013.

[87] HSE, “HSE’s land use planning methodology,” [Online]. Available: https://www.hse.gov.uk/landuseplanning/methodology.htm. [Accessed 22 06 2023].

[88] HSE, “Pressure Equipment (Safety) Regulations 2016,” [Online]. Available: https://www.hse.gov.uk/pressure-systems/pesr.htm. [Accessed 09 June 2023].

[89] HSE, “Pressure Systems Safety Regulations 2000 (PSSR),” [Online]. Available: https://www.hse.gov.uk/pressure-systems/pssr.htm. [Accessed 09 June 2023].

[90] HSE, “Safety of Pressure Systems Regulations 2000 Approved Code of Practice and guidance,” 2014.

[91] HSE, “PUWER: The Provision and Use of Work Equipment Regulations 1998,” [Online]. Available: https://books.hse.gov.uk/PUWER. [Accessed 09 June 2023].

[92] HSE, “Safe use of work equipment Approved Code of Practice and guidance,” 2014.

Appendix A – Illustrative case study: Element Digital Engineering

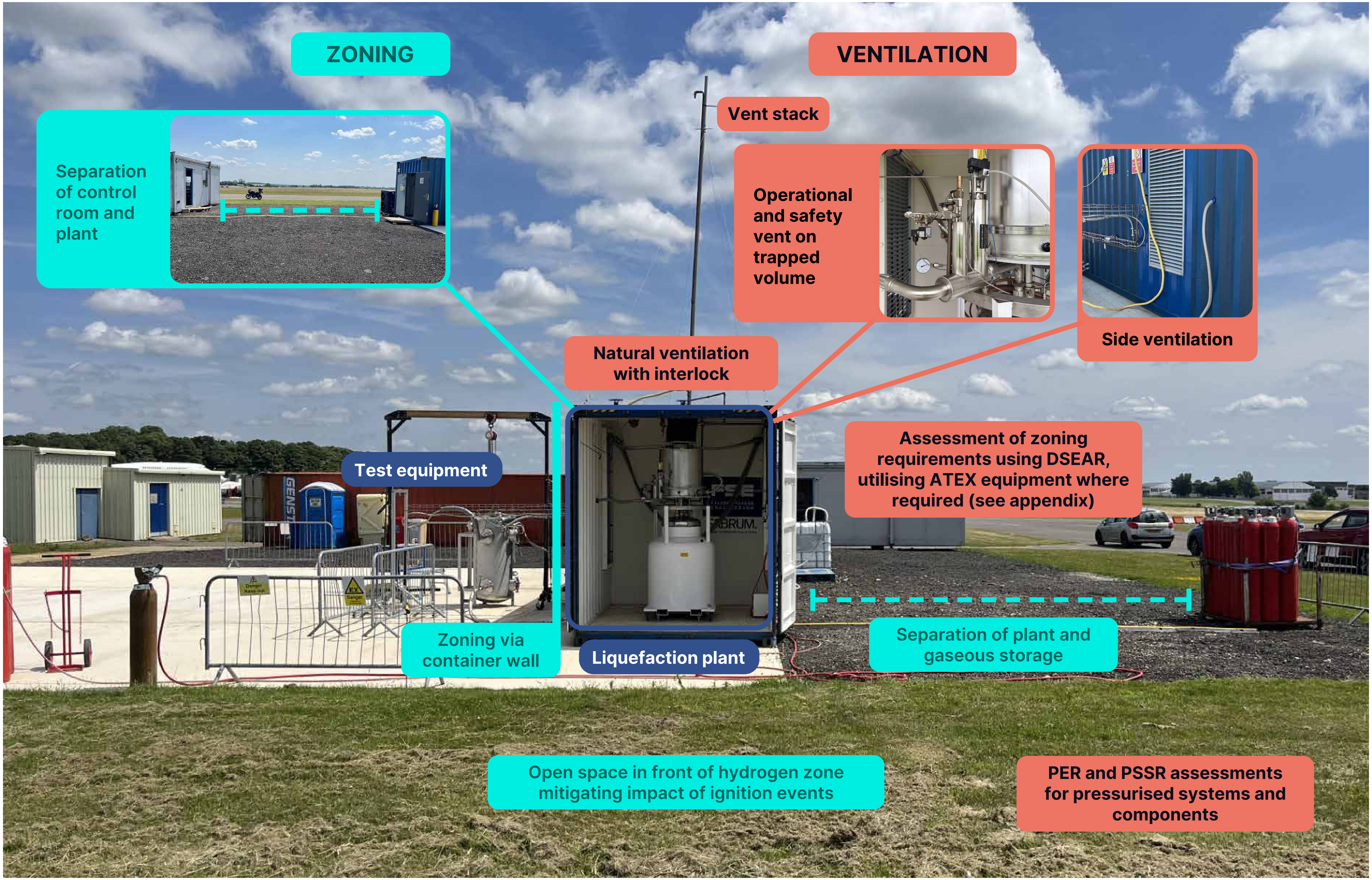
This section provides a high-level overview of design features a liquid hydrogen system. Filton Systems Engineering have contributed to this by providing examples of design considerations for their liquid hydrogen facility, covering flammability hazards, cryogenic hazards, and pressure hazards.

Element Digital Engineering (formerly Filton Systems Engineering) own and operate a hot and cold fuel test facility out of Cotswold Airport which opened in 2021. It was upgraded in 2022 to include a hydrogen liquefier and to support both cryogenic & gaseous fuel testing.

The hydrogen liquefaction plant consists of a 250L storage Dewar capable of storing approximately 16kg of LH_2, two cryocoolers with a liquefaction capacity of up to 15kg/day, and a test area and equipment including pressurisation/control and vacuum test tanks. The system is capable of achieving approximately 18K, however the actual liquefaction temperature is dependent on the operating pressure (typically around 24K at a nominal 1.5barg).

Disclaimer: HSE have not reviewed the detailed design and calculations for FSE’s facility and therefore cannot endorse the approach taken. It is not a comprehensive review of all considerations needed for a safe liquid hydrogen system but is an example liquid hydrogen system which considers aspects of design covered in this report.

Example cryogenic and pressure hazard design features



ZONING

Separation of control room and plant

VENTILATION

Vent stack

Operational and safety vent on trapped volume

Side ventilation

Natural ventilation with interlock

Test equipment

Assessment of zoning requirements using DSEAR, utilising ATEX equipment where required (see appendix)

Zoning via container wall

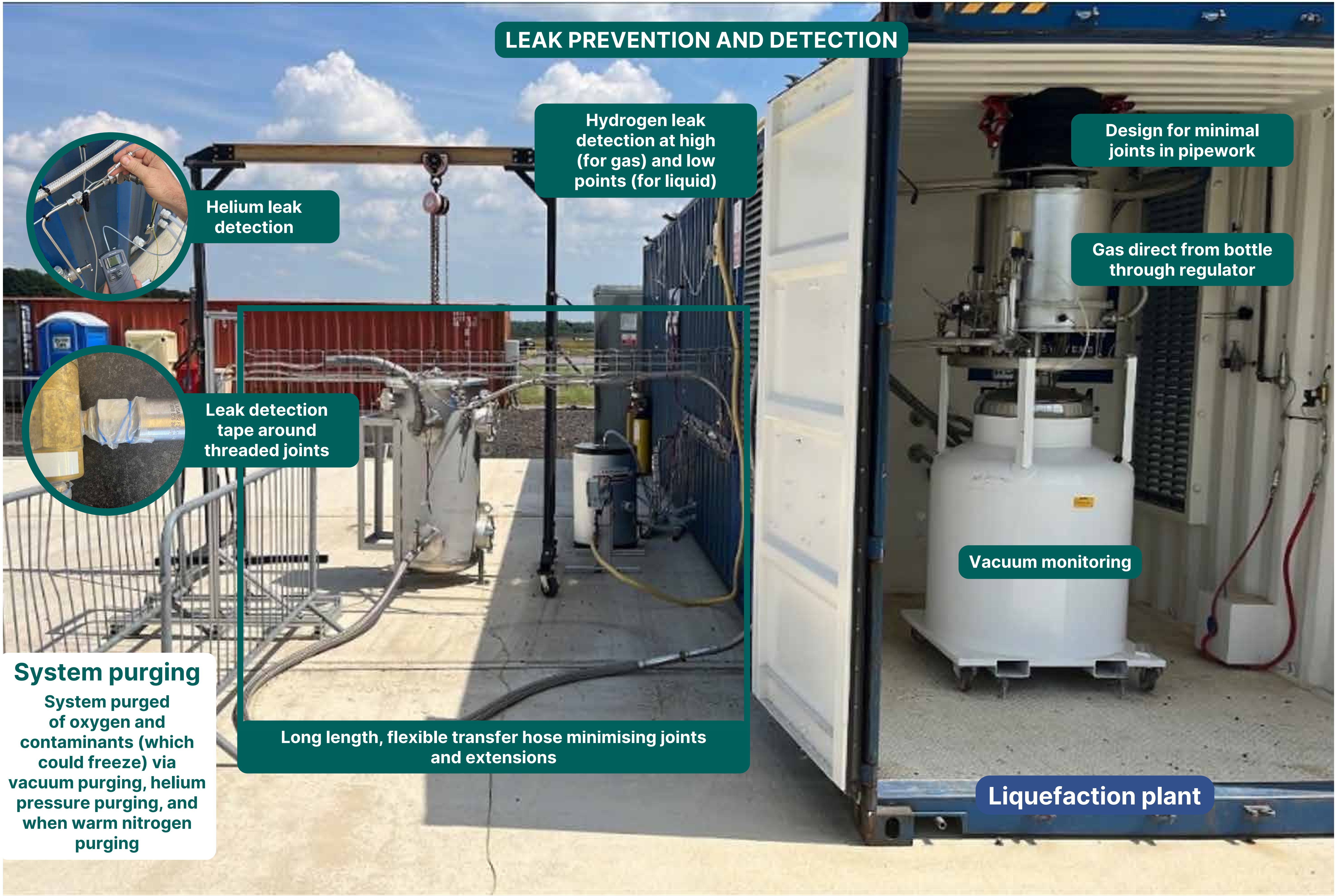
Liquefaction plant

Separation of plant and gaseous storage

Open space in front of hydrogen zone mitigating impact of ignition events

PER and PSSR assessments for pressurised systems and components

LEAK PREVENTION AND DETECTION



Helium leak detection

Hydrogen leak detection at high (for gas) and low points (for liquid)

Design for minimal joints in pipework

Gas direct from bottle through regulator

Leak detection tape around threaded joints

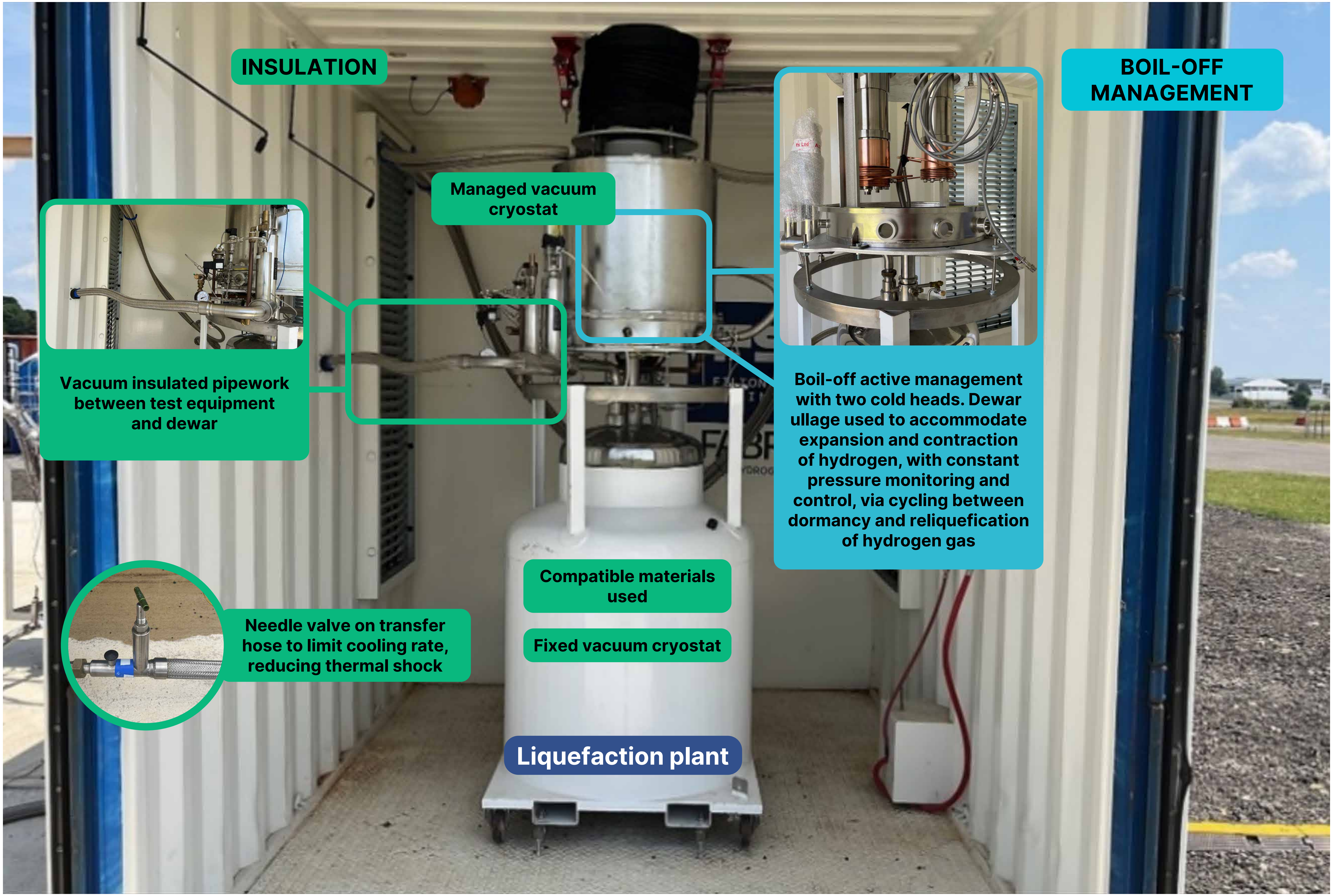
Vacuum monitoring

Long length, flexible transfer hose minimising joints and extensions

System purging

System purged of oxygen and contaminants (which could freeze) via vacuum purging, helium pressure purging, and when warm nitrogen purging

Liquefaction plant



INSULATION

Managed vacuum cryostat

BOIL-OFF MANAGEMENT

Vacuum insulated pipework between test equipment and dewar

Boil-off active management with two cold heads. Dewar ullage used to accommodate expansion and contraction of hydrogen, with constant pressure monitoring and control, via cycling between dormancy and reliquefication of hydrogen gas

Compatible materials used

Needle valve on transfer hose to limit cooling rate, reducing thermal shock

Fixed vacuum cryostat

Liquefaction plant

Appendix B – Regulations and Approved Codes Of Practice

Table 5 contains details of the relevant regulations that are applicable to liquid hydrogen systems, alongside details of the associated ACOPs (where applicable).

Table 5. Regulations and ACOP relevant to liquid hydrogen systems.

Regulation	Description	Related ACOP
ATEX	The name given to two European Directives for controlling explosive atmospheres; Directive 99/92/EC (also known as ATEX 137 or the ATEX Workplace Directive) and Directive 2014/34/EU (also known as ATEX 114 or the ATEX Equipment Directive).	See DSEAR ACOP
Carriage of Dangerous Goods and Use of Transportable Pressure Equipment Regulations (CDG)	Responsibilities covered under CDG include suitable containment of the dangerous goods, proper labelling, marking and documentation for the containers and vehicles and appropriate driver training, including handling procedures and emergency response actions [80].	None available
The Control of Major Accident Hazards (COMAH)	Ensures businesses take all necessary measures to prevent major accidents involving dangerous substances [81]. These regulations aim to prevent major accidents involving dangerous substances, and to limit the environmental harm and harm to people in case of an accident. It establishes requirements for risk assessment, emergency planning, and public consultation. Operators are responsible for developing safety reports, establishing control measures, and notifying authorities of any major accidents or incidents. A site with less than 5 tonnes of hydrogen will be under the threshold amount, a site between 5 and 50 tonnes will be classed as a lower tier site and a site with above 50 tonnes will be classed as an upper tier site. The different tiers translate to different levels of safety obligation. It should be noted that these limits relate to the total amount of hazardous material on a site, with each material having been assigned an upper and lower limit.	The Control of Major Accident Hazards Regulations 2015: Guidance on regulations [82]
The Control of Substances Hazardous to Health (COSHH)	Requires employers to adequately control exposure to materials in the workplace that cause ill health [83]. Substances Hazardous to Health are defined as: chemicals, products containing chemicals, fumes, dusts, vapours, mists, nanotechnology, gases and asphyxiating gases, biological agents and pathogens. Lead, asbestos and radioactive materials are not covered under COSHH as they have their own separate regulations. Under COSHH, employers have a legal obligation to assess the risks associated with the use of hazardous substances in the workplace. Control measures, ensuring adequate training, exposure level monitoring and emergency planning are all responsibilities covered under COSHH. The main hazards of hydrogen covered under COSHH are that it is a simple asphyxiant and extremely flammable.	The Control of Substances Hazardous to Health Regulations 2002 (as amended). Approved Code of Practice and Guidance [84]
The Dangerous Substances and Explosive Atmospheres Regulations (DSEAR)	Puts into effect the requirements of directive 99/92/EC and place duties on employers to eliminate or control the risks from dangerous substances [85] which can cause harm through fires, explosions or the corrosion of metal. This covers the control of substances which can cause harm through fires, explosions or the corrosion of metal. As hydrogen is a flammable substance and therefore falls under the scope of DSEAR. DSEAR places legal duties on employers and other duty holders to manage the risks associated with hazardous substances and explosive atmospheres. Key responsibilities include hazardous area classification, ensuring adequate training and competence and providing control measures. When dealing with hydrogen, the following control measures must be implemented, listed in priority order: ○ Reduce the quantity to a minimum. ○ Avoid or minimise a release. ○ Control releases at the source. ○ Prevent the formation of a dangerous atmosphere. ○ Collect, contain and remove any releases to a safe area. ○ Avoid ignition sources. ○ Avoid adverse conditions that could lead to danger. ○ Keep incompatible substances apart. Mitigation measures are also required to reduce harm in the event of a dangerous event. Listed in priority order: ○ Reduce the number of employees exposed. ○ Provide explosion and corrosion resistant plant. ○ Provide explosion suppression or relief equipment. ○ Control or minimise the spread of fires or explosions. ○ Provide suitable personal protective equipment.	Dangerous Substances and Explosive Atmospheres Regulations 2002. Approved Code of Practice and guidance [86]

Land Use Planning (LUP)	Guidance on Land Use Planning can be found on the HSE website. This covers the safety implications of major accident hazard sites and how this relates to the surrounding community. The responsibility of land use planning now lies with local planning authorities, with guidance from HSE. Facilities with more than 2 tonnes of hydrogen will require permission from the local planning authority [87].	None available
Pressure Equipment Regulations (PER)	These regulations cover the design, manufacture and conformity assessment of pressure equipment and assemblies with maximum operating pressures above 0.5 bar. As hydrogen is generally stored at pressure, the pressure equipment used will be subject to PER [88].	None available

Pressure Systems Safety Regulations (PSSR)	Regulations to prevent serious injury as a result of the failure of a pressure system [89]. This covers pressure systems containing a 'relevant fluid', where a pressure system is defined as:
	○ a system comprising one or more pressure vessels of rigid construction, any associated pipework and protective devices
	○ the pipework with its protective devices to which a transportable pressure receptacle is, or is intended to be, connected
	○ a pipeline and its protective devices
	○ and a 'relevant fluid' is defined as:
	  ○ steam at any pressure
	  ○ compressed or liquified gas, including air, at a pressure greater than 0.5 bar above atmospheric pressure; pressurised hot water above 110 °C
	  ○ a gas dissolved under pressure in a solvent (acetylene)
	The responsibilities covered under PSSR are given to the owners, operators and managers of pressure systems. These responsibilities surround the use, inspection and maintenance of pressure systems to ensure safe operation. As hydrogen is considered to be a relevant fluid, pressure systems containing hydrogen will be covered under PSSR.	

The Provision and Use of Work Equipment Regulations (PUWER)	These regulations apply to anyone coming into contact with equipment or machinery at work, including employers, employees, suppliers etc. Under PUWER, it must be ensured that the equipment used with hydrogen is suitable, taking into account the hazardous properties, such as low MIE and flammability. Inspection and maintenance should be carried out where necessary through the life of any equipment to ensure long term suitability [91].	Safe use of work equipment Approved Code of Practice and guidance [92]

Hydrogen
Innovation
Initiative

Get in touch:

Hydrogen Innovation Initiative
iCentrum Innovation Birmingham
Holt Street
Birmingham
B7 4BP

www.hydrogeninnovation.co.uk

HII partners:

ADVANCED PROPULSION CENTRE UK
AEROSPACE TECHNOLOGY INSTITUTE
CATAPULT Compound Semiconductor Applications
CATAPULT Connected Places
CATAPULT Digital
CATAPULT Energy Systems
CATAPULT High Value Manufacturing
CATAPULT Offshore Renewable Energy
CATAPULT Satellite Applications
Glass Futures
NPL National Physical Laboratory
Net Zero Technology Centre Technology Driving Transition
TWI