DECARBONIZATION SERIES
WHITE PAPER

GCT
Gas Cleaning & Energy Solutions

Introduction to Hydrogen Gas Safety
Part I: Industrial Storage

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December 2022

Abstract

Although many different types of facilities use hydrogen, nearly all are likely to contain a gasified storage system in some form or another. The main hazards with hydrogen storage and handling are specific to the physical and chemical properties innate with hydrogen including a wide flammability range, low ignition energy, low molar mass, and small molecular size. These parameters affect not only the construction of a storage system, but the way in which it is operated, and the equipment needed to support it. A safe and robust industrial system can be achieved through a combination of thoughtful engineering design, redundant sensors and detection systems, along with adhesion to proper operating procedures.

Introduction

With rapidly growing demand, multiple means of production, and countless potential applications in chemical processing and energy, hydrogen has undoubtably become a key commodity for a decarbonized future [1]. As its applications grow more diverse, it is imperative to implement the best technology and practices to ensure the safe storage and use of hydrogen. In any type of application, the need for a storage system is evident, whether it be as a gas, cryogenic liquid, or even in solid-bound form as a metal hydride, each has associated advantages and disadvantages. Currently, the most common form of storage is simply in the gaseous form which leads to the discussion of how to safely design such a system. Advances in material science, hydrogen leakage detection systems, storage and transfer control systems, and refinement of operating procedures all lead to a safer operating system.

This white paper provides a review of standards, best practices, and the most up-to-date technologies to design a safe gaseous hydrogen system in an industrial setting. First, the design of the storage vessel itself is studied including details regarding the surrounding area and recommended venting and purging procedures. A review of some relevant leak detection technologies and the potential odorization of hydrogen will be considered to ensure safe and efficient operation of a system. Lastly, the design of piping systems for safe transport of hydrogen from a storage tank is reviewed.

The content of this white paper is shared for information purposes only and should by no means be used as the basis for design and engineering. The strictest standards should be followed from the National Fire Protection Association (NFPA), the Compressed Gas Association (CGA), the Environmental Protection Agency (EPA), as well as any local agencies. As safety standards continue to change, the most up-to-date standards (along with local or state regulations) should be routinely reviewed and applied as part of a formal safety engineering procedure.

Storage Vessels

A challenge when dealing with a gaseous hydrogen storage system is the high pressure typically needed when compared to other gases. Due to its low molar mass, to store an equivalent mass of hydrogen at a given temperature and volume, the pressure must be 16 times higher than that of an oxygen storage system. In industrial applications, composite-reinforced pressure vessels are not economically feasible; for this reason, metallic vessels are used allowing for usual operating pressures between 20-30 MPa. This type of container leads to relatively poor mass storage efficiency where the mass of the stored hydrogen is only about 1 % of the mass of the operational container [2].

The design of a hydrogen storage vessel and the ancillary instrumentation used is primarily based on explosion prevention and protection, while the material of construction is based primarily on hydrogen quality, environmental conditions, operating conditions, and in particular the potential for embrittlement.

Many potential explosion protection and prevention strategies can be used, including deflagration prevention by oxidant concentration reduction or predeflagration detection and control of ignition sources. The reader can refer to NFPA 68 and 69 standards for a complete list and detailed implementation strategies.

Depending on the nature of the hydrogen generation system, contaminants could lead to differing material selections. For example, if hydrogen is produced via electrolysis with NaOH or KOH as an electrolyte catalyst, caustic vapor could contaminate the storage tank if there is insufficient mist elimination leading to the need for a more corrosion-resistant material.

Due primarily to its small atomic size, hydrogen has the ability to damage materials that are in direct contact through a process called hydrogen embrittlement. Although the mechanism by which hydrogen causes embrittlement is not fully understood, the general understanding is that hydrogen atoms can diffuse easily (due to their small size) into the microstructure of the metal and cause it to become more brittle, lowering the stress required for cracks in the metal to initiate and propagate. This also causes a loss of ductility of metals and is likely the defining characteristic when choosing a material for a hydrogen storage system. To mitigate this effect, austenitic (300 series) stainless steels are recommended as they are relatively immune to high pressure hydrogen embrittlement (316 being the preferred grade). Carbon and alloy steels can also be used for low-pressure hydrogen vessels (<20 MPa working pressure) above 29 °C. However, grey, ductile, or cast irons and plastic should not be used for the purposes of storing gaseous hydrogen [3] [4]. A complete list of acceptable materials for hydrogen service can be found in The American Society for Mechanical Engineers (ASME) B31.12.

Purge Systems

In addition to a rugged storage system, proper pressure-relief and purge systems should also be in place in the case of over pressurization or for maintenance purposes. A pressure relief valve made of 300 series stainless steel, carbon steel, or bronze should be located on the storage tank with a vent stack to atmosphere; refer to ASME B31.12 for detailed information on material selection and CGA G-5.5 for detailed information on vent stack design. Vent stacks should be placed a minimum of 3 m (10 ft) above grade, 0.6 m (2 ft) above adjacent equipment, or 1.5 m (5 ft) above rooftops, away from personnel areas, ignition sources, air intakes, or building openings/overhangs [5]. The vent stack design (height, pipe size, location and discharge direction) should be engineered to follow NFPA 2 and CGA G-5.5 and meet the specific relief pressure and relief valve size on the storage vessel. The engineered vent stack may be higher than the minimum height above grade, equipment, and rooftops. As hydrogen gas is lighter than air, the risk of asphyxiation is minimized if these protocols are followed.

Hydrogen has a lower flammability limit (LFL) of 4 vol% in air and an ignition energy of 0.019 mJ, approximately 10 times lower than that of common hydrocarbons, increasing the risk for explosions [6] [7]. There are varying opinions on the efficacy of an inert gas dilution to prevent autoignition or using a flame arrestor to inhibit backwards propagation of a flame in the event of venting. The use of either or both is acceptable though not required. Dilution of pure hydrogen to below 25 % of its lower flammability limit (1 vol% hydrogen in air) results in an unrealistic volume of inert gas to be used that itself has safety considerations for storage, however, a purge of the vent stack volume itself before venting could help in ensuring safe exit of the gas and would require far less volume of inert gas to be stored at the facility.

When the system is being taken offline for maintenance or decommissioning, the system should be purged with an inert gas (e.g., nitrogen) after depressurization such that the final mixture in the system is non-flammable [5]. This can be done by purging the system with 5 vessel volumes of inert gas (to reduce the hydrogen concentration to below 1%) or by continuous purging until appropriate concentration is confirmed with the use of a hydrogen detector designed for use with an inert gas background [8].

Containment Area

A gaseous hydrogen storage tank or vessel can be installed in a variety of ways, each with benefits and drawbacks. Common to an industrial setting would be an aboveground outdoor bulk storage tank. "Aboveground" identifies the setting for fixed installation vertical or horizontal tanks above or below grade with no backfill. "Outdoor" defines the tank area without overhead cover. An overhead cover is permissible so long as less than 25% of the perimeter is enclosed by walls, this is classified as weather protection. An area with overhead cover and greater than 25% of the perimeter enclosed by walls would qualify the containment area as "indoor". "Bulk" identifies the quantity of store gaseous hydrogen being greater than 141.6 Nm^3 (5000 scf) [5].

Requirements for indoor storage areas differ vastly and are dependent on the volume and pressure of hydrogen being stored, the nature of its use, and the size and design of the indoor structure. Details regarding indoor storage will not be covered in this white paper (for details, the reader can refer to NFPA 2 and NFPA 55).

A hydrogen storage system requires sufficient spacing from any potentially hazardous exposures. These distances depend not only on the hazards themselves, but also on the pressure and amount of hydrogen being stored, as well as the minimum pipe size in the system. Distances may also be reduced with the use of a non-combustible fire-rated barrier interrupting the line of sight between hazards with a maximum of 2 sides at 90° angles or 3 sides at 135° angles (see Figure 1 for details). The reader can refer to NFPA 2 and OSHA 1910.103 for detailed descriptions of distances to hazardous exposures [5].

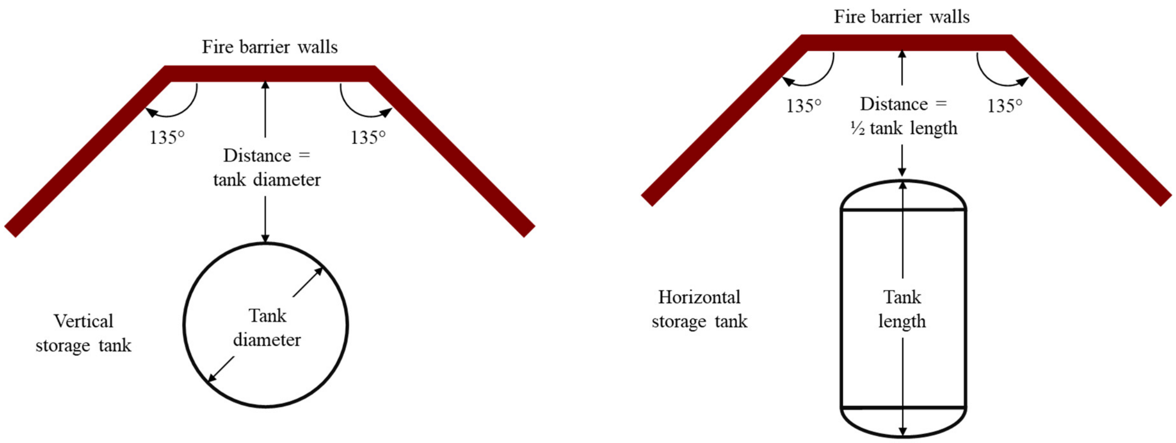

Figure 1: Design requirements for a non-combustible fire barrier around a hydrogen storage tank [5]

A storage tank, connected piping, valves, fittings, and use areas should also be protected from potential vehicular damage by installing guard posts or bollards. Posts should be constructed of steel with a minimum diameter of 102 mm (4 in) and filled with concrete. Spacing between posts should be kept to a maximum of 1.2 m (4 ft) between each other and a minimum of 0.9 m (3 ft) from the tank. The footing is required to be a minimum of 0.9 m (3 ft) deep and 380 mm (15 in) diameter. The posts should have a minimum height of 0.9 m (3 ft) [5]. Where the compressed gas vessel is located in an area that is open to the public, the storage and use area should be fenced and locked with access restricted to supplier and user personnel only. Although not necessary to fence a vessel if it is in a user secure area and not accessible by the public, fencing may still be used for security based on personnel access patterns [9].

Figure 2: Bollards protecting a compressed gas storage tank from potential vehicular damage [10]

Hazard identification signs should be mounted on stationary aboveground tanks and containers and on entrances to locations where they are stored. In addition, the area where a hydrogen system is located is required to be permanently placarded as follows:

WARNING: HYDROGEN – FLAMABLE GAS –
NO SMOKING - NO OPEN FLAMES

"No smoking" signs should also be posted within 7.6 m (25 ft) of outdoor storage areas and inside rooms where hydrogen may be stored [9].

All electrical equipment including control valves, sensors, compressors, and PLCs also need to comply with minimum distance requirements to hydrogen storage systems unless specifically designed and rated for explosive atmospheres. NFPA 70 (NEC or National Electrical Code) describes electrical classification areas. Class 1 electrical classification areas are those areas where flammable gases may be present in a quantity sufficient to ignite. This Class is then subdivided based on the hazard level of the area. Division 1 is defined as an area where ignitable concentrations can exist under normal operating conditions, whereas Division 2 is defined as an area where ignitable concentrations would only occur in accidental rupture or abnormal operation. Electrical equipment used in this area should either explicitly list approval for Class 1, Group B (hydrogen) atmospheres, be purged or ventilated in accordance with NFPA 496, or be intrinsically safe. Refer to Table 1 and Figure 3 for details [11].

Table 1: Electrical area classification around Class 1, Group B (hydrogen) systems [11]

Location	Distance Measured Spherically from the Source	Electrical Area Classification
Hydrogen Vent Outlet	Within 1 m	Class 1 Division 1
	Between 1 m to 4.6 m	Class 1 Division 2
Hydrogen Storage Equipment	Inside Vessel	Class 1 Division 1
	Within 4.6 m	Class 1 Division 2

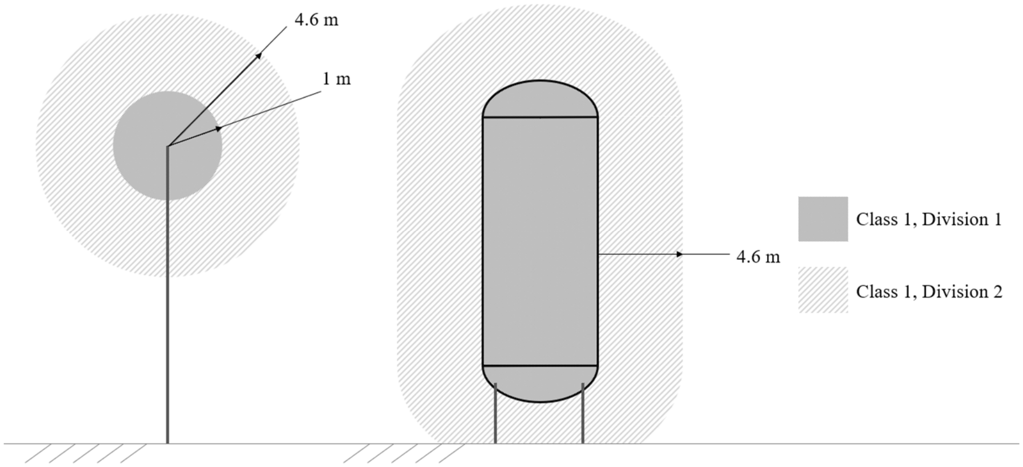

Figure 3: Electrical area classification in area around a hydrogen vent stack (left) or storage tank (right) [11]

Leak Sensor Types and Efficacy

Detecting leaks is not only important to minimize hydrogen losses, but due to its wide flammability limit range and low ignition energy, an accumulation of hydrogen from a leak could cause a fire or an explosion, especially indoors. Various types of hydrogen sensors and leak detector technologies exist, and while none of them provide perfect detection, a combination of different technologies along with routine inspections is the best way to ensure safe operation.

NFPA requirements call for the detection of gaseous hydrogen inside hydrogen equipment enclosures (HEE) that include hydrogen generation, compression, or processing equipment. This detection must be linked to the mechanical ventilation system and initiate ventilation at a rate of 0.0051 $m^3/sec/m^2$ (1 $scf/min/ft^2$) of floor area in the enclosure when the hydrogen concentration is measured at a minimum of 0.4 vol%. Alternatively, mechanical ventilation can be continuously running and not be linked with the hydrogen detection system. The detection system must also be linked to the emergency shutdown system (ESS); detection of hydrogen at 1 vol % (25% of its LFL) or higher must result in the activation of the ESS [5]. There are no other requirements for hydrogen detection from NFPA, however, standards vary from country to country and state to state; care should be taken to ensure local norms and standards are being followed.

Point detectors are useful to be placed in indoor locations or near storage areas where hydrogen can accumulate. A good rule of thumb is to place this type of sensor in the highest draft-free location in the room 30 cm (12 in) or more below the ceiling to avoid elevated temperatures [5]. These sensors can also be used outdoors when combined with hydrophobic screens to protect from rain. It is important to note that the point sensors do not measure hydrogen concentration over an area, only at the point of the sensor, as they rely on diffusion of hydrogen towards the sensor. In outdoor and well-ventilated areas, hydrogen concentration is likely to be diluted by air and may not adequately identify a leak; for this reason, it is recommended that point sensors be placed as close as possible to potential leak sources in these situations. Most point sensors also require routine calibration with standard gas mixtures.

Commonly found types of hydrogen point sensors include:

- Electrochemical
- Metal Oxide (MOX)
- “Pellistor” or Catalytic Bead
- Thermal Conductivity

In addition to point detectors, fixed ultrasonic leak detectors can help identify leaks in high-pressure systems (usually above 7 bar) by identifying anomalies in ultrasonic sound waves attributed to gas leaks. These sensors usually have a spherical radius in which they can detect leaks and can be useful for outdoor storage tanks, short pipelines, or use areas. As background noise can affect the performance of these detectors; care should be taken to ensure appropriate placement.

To pinpoint the leak source more accurately and to detect leakages that fixed sensors may miss, operators should perform routine inspections with handheld sensors. Many types are commercially available, including handheld versions of the above-mentioned sensors, usually equipped with vacuum pumps to get an accurate measurement of hydrogen in the area the device is pointed towards. Portable ultrasonic leak detectors are also available and provide audio-visual feedback when nearing the source of a leak. Thermal imaging can detect leaks based on temperature differences between the leaking gas and its immediate surroundings. This method can be used from moving vehicles, helicopters, or portable handheld systems and is capable of inspecting several miles or hundreds of miles of pipeline per day [12].

In addition to area detection and routine inspections, the use of a visual indicator can be beneficial to identify leaks more easily. Commercially available hydrogen detection tapes wrapped around joints and fittings change color when in contact with diatomic gaseous hydrogen. This can be especially useful during commissioning or in areas that may experience high levels of vibration increasing the possibility for a leak. Special care should be taken as some detection tapes may show a false positive if they come in contact with hydrogen sulfide.

In the case of a hydrogen fire, a flame camera or sensor with an audiovisual alarm can notify personnel of a problem area and trigger emergency shutdown and/or evacuation procedures. Hydrogen flames are often invisible or difficult to see with the human eye, especially in daylight or artificial light. Flame cameras designed for hydrogen flame detection monitor radiation emitted by the flame in the ultraviolet (UV) and infrared (IR) spectral bands. These cameras are appropriate for indoor or outdoor use and multiple cameras can be strategically installed to ensure full visual coverage over the area in which hydrogen is being stored and transported. These cameras usually have a wide field of view (~130°) and a range of less than 20 m (65 ft).

Figure 4: Common leak detectors used in hydrogen systems. Catalytic bead point sensor (top left [13]), ultrasonic area leak detector (top middle) [14], handheld electrochemical sensor with pump (top right) [15], handheld ultrasonic leak detector (bottom left) [16], handheld thermal imaging leak detector (bottom middle) [17], UV/IR flame camera (bottom right) [18]

Odorization Potential

Because hydrogen is an odorless gas, adding an odorant into a gas stream will make the gas smell and can allow for humans to detect the presence of the gas even at concentrations well below flammability levels in order to ensure their own safety and potentially help identify possible leaks. Odorants allow for the detection of leaks in positions where it may be difficult to place detectors. Commonly used with hydrocarbons for the past century, odorizers allow for an early warning system before flammable levels are reached [6]. Gas odorization is, in most countries, a legal or regulatory requirement that specifies that natural gas in air must be readily detectable by odor at a concentration of 20 - 25 % of the LFL, however, there are no regulations for the use of an odorant in hydrogen systems [19]. As a safety measure it can still be beneficial to introduce an odorant in certain industrial situations.

Odorant selection is strongly based on the density and vapor pressure of the gas being odorized. Ideal odorants should have certain physical and functional properties including [20]:

- Low odor detection threshold
- Suitable detection intensity
- Little or no olfactory fatigue
- Distinguishable from smells of daily life

- Characteristically unpleasant
- Low boiling point
- Low corrosivity
- Low toxicity

Some odorization compounds are used by themselves (such as tetrahydrothiophene), but most use a mixture of various compounds including sulfides and mercaptans. Ethylmercaptan is the main compound used in most odorants for natural gas and liquid propane leak detection due to its extremely low odor threshold, although tetrahydrothiophene is also often used [21]. The type of odorant that is chosen to be used in hydrogen systems should be carefully reviewed as many sulfur-based odorants, although unharmful in thermal based applications, can cause serious degradation of fuel cell performance or damage in semiconductor applications. [22]. Of the odorants that are compatible with fuel cells, 5-ethylidene-2-norbornene, although promising with regards to all other functional properties, does not produce a characteristically unpleasant smell and can be referred to as "fruity" and should not be used. [23].

Piping Systems

Piping for gaseous hydrogen systems is permissible to be installed aboveground or underground. Underground usage must utilize a welded construction for all connections and have no valves, unwelded mechanical joints, or connections installed underground. The piping should be installed on sufficient compacted bedding of at least 150 mm (6 in) and be separated from other pipes horizontally by at least 2 pipe diameters but need not exceed 230 mm (9 in), and vertically by a minimum of 150 mm (6 in) of compacted bedding material. Thorough soil testing should be conducted to determine if cathodic protection is required for the underground piping. Aboveground installations should use either threaded or tube fitting connections for less than 1 in nominal pipe; for greater than 1 in nominal diameter pipe, flanged inlet and outlet connections can be used, however, welded or high temperature brazed connections are preferred [5] [24]. All segments of piping should be protected from potential over-pressurization by incorporating strategically placed pressure relief valves.

The material selection of piping is similar to that of storage tanks; important considerations include hydrogen quality, operating and environmental conditions, and potential for embrittlement. Austenitic stainless steels are recommended for product piping, tubing, valves, and fittings; when available, austenitic steels should be used in the annealed condition. Carbon steel usage should be limited to low pressure applications with temperatures above 29 °C. Grey, ductile, or malleable cast iron should not be used for piping, tubing, valves or fittings. Plastic piping and tubing should not be used except under controlled laboratory applications with low flow pressure [24]. Detailed material selection and design considerations for hydrogen piping systems can be found in ASME B31.12.

Due to the highly explosive nature of hydrogen and the extremely small ignition energy, the elimination of any sources of sparks is important. All parts of the piping system should be sufficiently grounded, and continuity across piping should be ensured. For this reason, plastic hoses should only be used where rigid piping is not practical and should have electrical continuity through the length of the hose or make use of a bonding strap.

Hydrogen piping should be labeled with the name of the gas and the direction of flow. If a piping system is used to convey more than one gas at various times, the piping should be marked accordingly [5]. See Figure 5 for detailed label placement instructions.

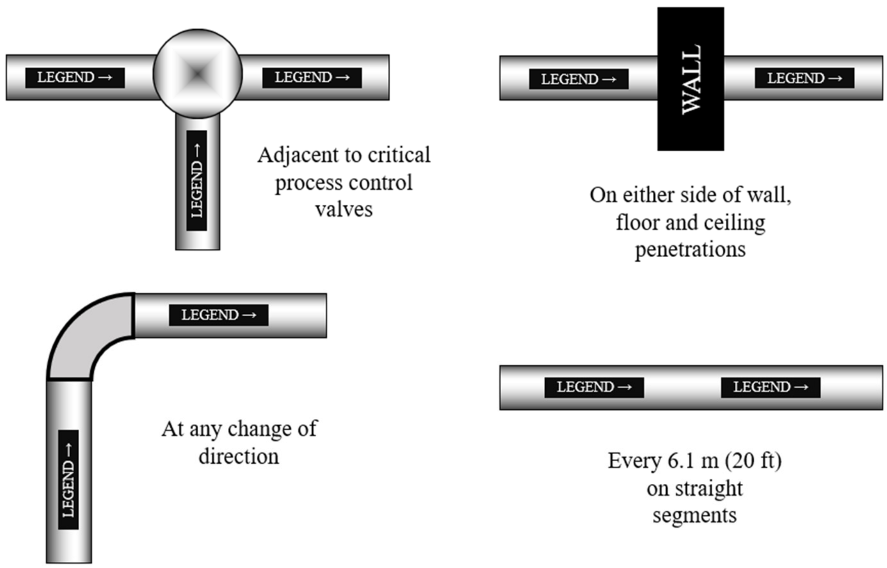

Figure 5: Position of label markers on hydrogen piping systems

Conclusion

The safety considerations and design criteria for implementing a gaseous hydrogen storage system must be evaluated on a case-by-case basis formed on the specific use of the system as well as the operating and environmental conditions. Industrial storage vessels are commonly metallic in construction with no composite reinforcement. The design of such a vessel should consider explosion protection and prevention along with the possibility of embrittlement. The vessel should be equipped with a pressure relief system for operational emergencies, and in the case of maintenance shutdown, the vessel should be fully purged with an inert gas until the final mixture inside the container is non-flammable. The area around a storage vessel and vent stack is also important. Adequate distance to hazards and electrical systems must be maintained, and electrical equipment used must have appropriate safety ratings for the location in which they are used. These distances may potentially be reduced with the use of a rated firewall.

There are also many ways of detecting possible leaks for the purposes of explosion prevention or to ensure efficient operation of a storage or piping system, among them, the use of point, area, or handheld sensors, or even the potential for odorization of the hydrogen gas. Aboveground and underground piping design should be based on environmental and operating conditions as well as the possibility for hydrogen embrittlement.

It is important to note that the standards and technologies identified in this paper only account for a small representation of the extensive information and practices available to draw upon when designing a system. The strictest standards should be followed from the National Fire Protection Association, the Compressed Gas Association, the Environmental Protection Agency as well as any local agencies. Detailed technical information regarding hydrogen sensors or leak sensors should be taken directly from their respective suppliers, and experimental technologies should be used only in addition to redundant backup proven technologies. Personnel should be professionally trained to perform routine maintenance and inspections, while properly documenting findings.

This paper is for information purposes only and should by no means be used as the basis for design and engineering. As safety standards continue to change based on the growing understanding of hydrogen systems, the most up-to-date standards should be routinely reviewed and followed.

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