Module Hydrogen Safety, Risks, Standards & Regulation

Acceptable performance in this module will be the satisfactory achievement of the standards set out in this part of the Module Specification. All sections of the statement of standards are mandatory and cannot be altered.

Content

OUTCOME 1 State the current Health and Safety legislation covering employers and employees.

The content of this module is designed to allow the learners to work safely within a hydrogen environment/workplace. This is underpinned by the learner gaining knowledge of the relevant legislation, roles/responsibilities and requirements of Common Law in the interpretation of current legislation. Learners will also be required to carry out a risk assessment and complete pro-forma documentation. The study of legislation should include an awareness of the purpose and application of the Management of Health and Safety at Work Regulations 1999 (EU); and, specific regulations, industry standards, legislative requirements, codes of practice, manufacturers' recommendations and specifications, and environmental requirements.

General health and safety principles

There are many generic hazards which can arise during the examination and sampling procedure. There are also specific hazards relevant to certain goods. You must take a proactive approach to protect your own safety and that of other people working with you or for whom you are responsible. Further, you must also make sure that you do not expose others to greater risks either through contamination of the goods or, because of your own action, by leaving the goods in a dangerous state.

Health and safety procedures

Good health and safety practices are everyone's responsibility. National legislation will dictate how your health and safety policies are implemented. However, as a guide, every system should include:
a stated policy on individual and corporate responsibility for safety.

- a set of risk assessments for the locations and the work being done, identifying hazards and countermeasures.
- safe working practice guides giving specific recommendations about safe procedures for completing the work.
- an accident reporting procedure which allows lessons to be learnt and fed back into the risk assessments and safe working practice guides.
- regular reviews to ensure that the risk assessments and safe working practice guides are kept up to date (at least annually — or following any change affecting health and safety).

When working in dangerous environments it is good practice to work in teams of at least two. You may also operate a 'buddy' system where two officers are responsible for each other's safety. Basic first-aid training given to all staff will enable them to give swift help to any colleague in difficulties.

Risk assessments

Risk assessments may cover either a location or a procedure. They should cover all the possible hazards and countermeasures. You should conduct risk assessments for each location where sampling takes place. A risk assessment is a process to manage and control health and safety by:

- identifying the hazard.
- evaluating the risk.
- introducing preventive and protective measures to reduce or eliminate the risk.
- reviewing the control measures to make sure they are still appropriate.

Copies of risk assessments should be available to anyone entering or working in the area and should be reviewed annually or when any change affecting the location or procedure occurs. Generic risk assessments may be used as a basis for local risk assessments. More information about a risk assessment is given in Outcome 3. However, your national administration may use different forms or procedures, but the principle remains the same.

Safe working practice guides

You should agree standard safe working practices with managers and/or health and safety experts for particular locations and procedures e. g. working in or on:

- freezers
- top of road/rail tankers or other bulk containers
- bulk grain handling
- traders' premises (i.e., unfamiliar locations)
- areas where cranes and fork-lift trucks are operating
- container terminals
- roll-on/roll-off terminals
- rail terminals

Safe working practices may cover such aspects as:

- personal protective equipment to be used
- notification of the operator
- making sure a colleague or operator is always present to ensure your safety
- procedures for access to the location
- sampling equipment
- Sampling procedures

Safety and warning signs

Signs and labels are provided to protect your health and safety and that of the people working with and around you. You must observe the signs at all times and take any precautions. European directives have been adopted to standardise safety and warning signs. However, existing signs may not match the new designs. If it is not clear what a sign means you should seek advice from the person responsible for health and safety at your location, whether it is a port, quayside, warehouse or on board a vessel or aircraft.

The United Nations has introduced international hazard warning signs for goods transport and they are used all over the world. This section therefore gives an overview of the types of signs used and of their general meaning.

Prohibition signs

A prohibition sign means that the action or activity indicated is prohibited. You must always obey these signs. Some show just a symbol, others have explanatory text beneath.

No Pedestrian access

Not Drinking Water

No smoking

Failure to obey these signs could put yourself and others at risk of injury or death.

Warning signs

Warning signs are intended to alert you to possible hazards. The hazard may be intermittent or permanent. The sign is there to remind you of the possible danger. You must consider the hazard and take the necessary precautions. The first sign above gives a general warning — text may be added to spell out a hazard which is not covered by the recognised symbols, or it may warn of a range of hazards.

Mandatory signs

Mandatory signs indicate a specific safety measure that you must take before you enter the designated area or proceed with your tasks. Failure to observe these signs could put you at risk of immediate injury and/or long-term health problems. If the correct equipment is not available you must not carry on.

			
Eye Protection	Head Protection	Ear Protection	High Visibility Clothing

Safety signs

As well as the Prohibition, Warning and Mandatory Signs they will be a variety of safety signs including emergency exit signs in case of fire, First Aid signs and Firefighting equipment signs.

		
First Aid Kit	Eye Wash	Fire Extinguisher

As in the previous cases, the sign may contain text. You should familiarise yourself with the location of these signs before you start work. Safe fire exits and procedures should be included in the risk assessment and safe working practice guides.

Further information on this subject can be found on the Europa website at: https://echa.europa.eu/-/updated-interactive-guide-on-safety-data-sheets-and-exposure-scenarios-available.

Employer's responsibilities

Under health and safety law employers are responsible for managing health and safety risks in their businesses. The following provides a broad outline of how the law applies to employers. Don't forget, employees and the self-employed have important responsibilities too

It is an employer's duty to protect the health, safety and welfare of their employees and other people who might be affected by their work activities. Employers must do whatever is reasonably practicable to achieve this. This means making sure that workers and others are protected from any risks arising from work activities.

- Assess risks.

Employers have duties under health and safety law to assess risks in the workplace. This means identifying work activities that could cause injury or illness and taking action to eliminate the hazard, or if this isn’t possible, control the risk.

- Provide information about risks.

Employers must give workers information about the risks in their workplace and how they are protected, also instruct and train them on how to deal with the risks.

- Consult employees.

Employers must consult employees on health and safety issues. Consultation must be either direct or through a safety representative that is either elected by the workforce or appointed by a trade union.

- Provide health and safety information.

Employers have a legal duty to display the approved poster in a prominent position in each workplace or to provide each worker with a copy of the approved leaflet.

- Workers - reporting a health and safety issue

Emergency procedures and incident management requirements and procedures.

Facility personnel who are expected to take offensive action in the event of a hydrogen release must be trained to respond appropriately to protect people and property. Training should be based on the specific system in place and should be coordinated with any facility-wide Emergency Response Plan(s). An emergency action plan that describes incident procedures should be the basis for such training. The emergency action plan should include:

- Evacuation procedures, description of exit routes, and identification of staging areas for non-responding personnel
- An alarm system or other means for notifying employees, such as a public address system, should be identified.

- An alarm system (consisting of both audible and visible alarms) with distinctive signals used for each type of emergency is preferred.
- Practice drills should occur periodically to ensure that employees are familiar with the alarms and know instinctively how to respond. The meanings of the various signals should be posted in all operational areas.
- Procedures for employees who oversee critical operations during an incident
- Actions to be taken by personnel who initially respond to hydrogen leaks, spills, fires, and transportation emergencies
- Location of emergency response equipment
- Appropriate fire suppression response
- Establishing security
- Procedures to account for all employees after emergency evacuation is completed
- Procedures for employees performing medical and rescue activities
- The preferred means for reporting fires and other emergencies (including emergency phone numbers)
- Establishing and maintaining communications
- Preparing for possible media coverage
- Contact information for persons who can provide additional information or explanation of duties covered by this plan.

Hazardous areas, hazards associated with working in a hazardous area, requirements for working in a designated hazardous area, workplace situations that could be classified as a hazardous area, hazards associated with gas supply work environment and hydrogen characteristics

Hydrogen Reaction terminology

One molecule of hydrogen dissociates into two atoms (H2 → 2H) when an energy equal to or greater than the dissociation energy (i.e., the amount of energy required to break the bond that holds together the atoms in the molecule) is supplied.

- Hydrogen has the smallest size of atoms/molecules and is characterised by the highest diffusivity.
- Permeation is a movement of particles (atoms, molecules or ions) through or into a permeable substance.

- A diffusion of hydrogen occurs "through the walls or interstices of a container vessel, piping or interface material" For cGH2 system it results in a slow release of hydrogen.
- Hydrogen permeates metals in atomic form, polymeric materials – in molecular form.
- Permeation is negligible for storage containers with metallic liners (types I, II, and III) and may pose a safety issue for vessels with polymeric liners (type IV and V). Permeation rate of hydrogen through a particular material (J in mol/s/m2) depends on the material nature, temperature (T in K), reservoir pressure (pr in MPa) and the reservoir wall thickness (l in m)

$$J = P_0 \exp(-E_0 / RT) \frac{\sqrt{p_r}}{l}$$

Parameters dependent of the nature of the material:
P_0 - pre-exponential factor (mol/s/m/MPa$^{1/2}$);
E_0 - activation energy (J/mol)

- The higher the storage pressure the higher is the permeation rate. The permeation from on-board hydrogen storage is a safety issue for enclosures (example: a FC vehicle parked in a garage).
- Hydrogen can accumulate over time, producing a flammable mixture with air. As a result of permeation in sealed enclosures without ventilation, the lower flammability limit (LFL) of 4 vol. % of hydrogen in air can be reached within a long period of time.
- Three main phenomena will affect the dispersion of permeated hydrogen: buoyancy, diffusion, and ventilation.

Hazards of hydrogen

Analyses of accidents indicate the following factors are of primary importance in causing system failures:

(a) Mechanical failure of the containment vessel, piping, or auxiliary components (brittle failure, hydrogen embrittlement, or freeze-up)

(b) Reaction of the fluid with a contaminant (such as air in a hydrogen system

(c) Failure of a safety device to operate properly

(d) Operational error

Analyses of accidents have shown that the response, through design or operating procedures, to a failure should be such that a single failure does not lead to a series of failures or a chain reaction of failures, such as, any failure must be restricted to a local event; otherwise, the hazard and potential for damage is greatly enhanced Ignition.

Fires and explosions have occurred in various components of hydrogen systems as a result of a variety of ignition sources. Ignition sources have included mechanical sparks from rapidly closing valves, electrostatic discharges in ungrounded particulate filters, sparks from electrical equipment, welding and cutting operations, catalyst particles, and lightning strikes near the vent stack. A potential fire hazard always exists when hydrogen is present.

Green Hydrogen (GH2) diffuses rapidly with air turbulence increasing the rate of GH2 dispersion. Evaporation can rapidly occur in a liquid hydrogen (LH2) spill, resulting in a flammable mixture forming over a considerable distance. Although ignition sources may not be present at the leak or spill location, fire could occur if the movement of the flammable mixture causes it to reach an ignition source. Example: Observation alone is not a reliable technique for detecting pure hydrogen-air fires or assessing their severity. A fire resulted from an accident in which a small leak developed. The equipment was shut down and the flame appeared to diminish; however, molten metal drippings from the equipment indicated a more severe fire was in progress. A deflagration could result if a mixture within flammability limits is ignited at a single point.

Hydrogen Safety: Hydrogen Flame Prop Demonstration

Physiological Hazards

Personnel present during leaks, fires, or explosions of hydrogen systems can incur several types of injury. Asphyxiation is a hazard when someone enters a region where hydrogen or a purge gas has displaced the air, diluting the oxygen below 19.5 percent by volume.

Blast waves from explosions will cause injury as a result of overpressure at a given location or a combination of overpressure and duration at a given location

The radiant heat that reaches and is absorbed by a person from a GH2-air flame is directly proportional to a variety of factors including exposure time, burning rate, heat of combustion, size of the burning surface, and atmospheric conditions (especially water vapor).

Cryogenic burns result from contact with cold fluids or cold vessel surfaces.

Exposure to large LH2 spills could result in hypothermia if proper precautions are not taken.

Collisions During Transportation. Damage to hydrogen transportation systems (road, rail, air, and water) can cause spills and leaks that may result in fires and explosions. Most of the incidents during transportation occurred outside of industrial facilities. Seventy-one percent of the hydrogen releases did not lead to an ignition. The relatively few ignitions may be due to a lack of ignition sources or the rapid dispersal of hydrogen into the atmosphere. In any event, the accident data provide further incentive to transport, transfer, and store hydrogen outdoors, away from occupied areas

Common causes of hydrogen accidents and ignition.

General. The hazards associated with the use of hydrogen can be characterized as physiological (frostbite, respiratory ailment, and asphyxiation), physical (phase changes, component failures, and embrittlement), and chemical (ignition and burning). A combination of hazards occurs in most instances. The primary hazard associated with any form of hydrogen is inadvertently producing a flammable or detonable mixture, leading to a fire or detonation. Safety will be improved when the designers and operational personnel are aware of the specific hazards associated with the handling and use of hydrogen.

Leaks

Leaks can occur within a system or to the surroundings. Hazards can arise by air or contaminants leaking into a cold hydrogen system. Leaks are usually caused by deformed seals or gaskets, valve misalignment, or failures of flanges or equipment. A leak may cause further failures of construction materials. For leaks involving LH2, vaporisation of cold vapor hydrogen to the atmosphere may provide a warning because moisture condenses and forms a fog. Undetected hydrogen leaks can lead to fires and explosions.

Hydrogen Dispersion

A property of hydrogen that tends to limit the horizontal spread of combustible mixtures from a hydrogen spill is its buoyancy. Although saturated hydrogen is heavier than air at the temperatures existing after evaporation from a spill, it quickly becomes lighter than air, making the cloud positively buoyant. The dispersion of the cloud is affected by wind speed and wind direction and can be influenced by atmospheric turbulence and nearby structures. Although condensing moisture is an indication of cold hydrogen, the fog shape does not give an accurate description of the hydrogen cloud location. The use of dikes or barricades around hydrogen storage facilities should be carefully examined because it is preferred to disperse any leaked or spilled LH2 or SLH2 as rapidly as possible. Dikes or berms generally should not be used unless their purpose is to limit or contain the spread of a liquid spill because of nearby buildings, ignition sources, etc. However, such confinement may delay the dispersion of any spilled liquid by limiting the evaporation rate and could affect a combustion event that might occur.

Storage Vessel Failure

The release of GH2 or LH2 may result in ignition and combustion, causing fires and explosions. Damage may extend over considerably wider areas than the storage locations because of hydrogen cloud movement. Vessel failure may be started by material failure, excessive pressure caused by heat leak, or failure of the pressure-relief system.

Vent and exhaust system accidents are attributed to inadequate ventilation and the inadvertent entry of air into the vent. Backflow of air can be prevented with suitable vent stack designs, provision of makeup air (or adequate supply of inert gas as the situation demands), check valves, or molecular seals.

Purging

Pipes and vessels should be purged with an inert gas before and after using hydrogen in the equipment. Nitrogen may be used if the temperature of the system is above 80 K (-316 °F), whereas helium should be used if the temperature is below 80 K (-316 °F). Alternatively, a GH2 purge may be used to warm the system to 80 K (-316 °F) and then switch to a nitrogen purge if the system is below 80 K (-316 °F); however, some condensation of the GH2 may occur if the system contains LH2. Residual pockets of hydrogen or the purge gas will remain in the enclosure if the purging rate, duration, or extent of mixing is too low.

Example: A dangerous purging practice that led to an explosion occurred when only a portion of a hydrogen system was isolated to reduce the purge time and volume. Complete isolation usually cannot be ensured because of the propensity of hydrogen to leak.

Vaporisation System Failure

Pipe valving in vaporisation systems may fail, causing injury from low-temperature exposures. Ignition of the hydrogen may occur, resulting in damage from fires and explosions.

Condensation of Air

An uninsulated line containing LH2 or cold hydrogen gas, such as a vent line, can be sufficiently cold (less than 90 K (-298 °F) at 101.3 kPa (14.7 psia)) to condense air on the outside of the pipe. The condensed air, which can be enriched in oxygen to about 50 percent, must not be allowed to contact sensitive material or equipment. Materials not suitable for low temperatures, such as carbon steel, can become embrittled and fail. Moving parts and electronic equipment can be adversely affected. Condensed air must not be permitted to drip onto combustible materials such as tar and asphalt (an explosive mixture can be created).

Hydrogen Embrittlement

Containment systems may fail, and the subsequent spills and leaks will create hazards when the mechanical properties of metallic and non-metallic materials degrade from hydrogen embrittlement. Hydrogen embrittlement is a long-term effect and occurs from continued use of a hydrogen system. Especially, piping and vessel ruptures caused by materials problems including hydrogen embrittlement, stress corrosion, and weld failures. Most of the damage was incurred by ignition of the hydrogen following the rupture. All repairs and modifications to piping and equipment that handles hydrogen must be carefully engineered and tested.

Types of accidents and their consequences

One of the specific characteristics of accidents involving hydrogen is the seriousness of their consequences as illustrated by the table below:

Consequences	On a sample comprising 213 cases with known consequences	
	Nb of cases	%
Deaths	25	12
Serious injuries	28	13
Injuries (including serious ones)	70	33
Internal material damage	183	86
External material damage	17	8
Internal operating losses	89	42
ß Evacuated population	8	3,8

Figure 1 ttps://www.aria.developpement-durable.gouv.fr/wp-content/files_mf/SY_hydrogen_GB_2009.pdf

25 mortal accidents involving hydrogen including 5 French accidents, constitute 12 % of the studied sample. Accidents with and without serious injury respectively account for 13 and 33 % of the studied sample. However, it must be noted that the human consequences for hydrogen-related accidents mainly target employees of disaster sites. Rescue workers and the general public are only rarely affected. Thus, all mortal accidents whose deaths are detailed concern employees. These facts are related to the accident typology involving hydrogen, as well as the rapid kinetics of the underlying phenomena: 84% of the studied events include fires and/or explosions. The remaining 16% concern non-ignited H2 leaks, runaway reactions without explosion or corrosion detected prior to accident.

The following table lists the main sectors of activity concerned by accidents involving hydrogen

Activities	On a 215 cases sample	
	Nb of cases	%
Chemical sector*	84	39
Refining / petrochemical industry*	47	22
Transport, packaging and storage	35	16
Metallurgy / metal works	17	7,9
Waste treatment / recycling	8	3,7
Nuclear industry	5	2,3

* excluding transport, packaging and storage

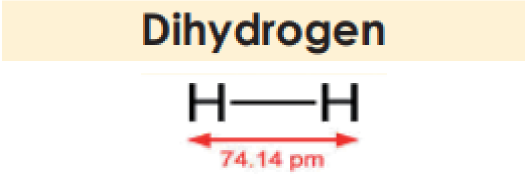
Figure 2 ttps://www.aria.developpement-durable.gouv.fr/wp-content/files_mf/SY_hydrogen_GB_2009.pdf

One of the above listened accidents happened in Saint-Fons (69), in 1988, grinding operations were scheduled on a tank having stored sulphuric acid. All operation procedures were properly carried out. Nevertheless, a deflagration occurred inside the tank at the start of the operation. Casualties include one death and two cases of serious injury. The tank was partly destroyed. The explosion occurred due to the presence of hydrogen (100 g) in a dead area where no measurements were taken. The hydrogen resulted from the corrosion of the iron tank under the action of sulphuric acid.

Two types of activities can be identified:

- activities where hydrogen is either produced or used such as chemical, refining, transport, packaging, nuclear industry,
- activities where hydrogen is accidentally produced like metallurgy and metal works, sanitation, waste treatment and recycling.

Dihydrogen is gaseous at room temperature and pressure. It cannot be detected by humans as it is colourless, odourless and non-toxic and is found in trace quantities in the atmosphere. The main physics-chemical properties of hydrogen give rise to specific risks discussed later.



Formula	H2
Molar mass	2,016 g/mol
Mass per vol. of gaz (20°C/1 atm)	0,08342 kg/Nm³
Water solubility (vol/vol at 15,6°C)	0,019
Boiling point (1 atm)	-252,8 °C
Mass per vol. of liquid at boiling point	70,96 kg/m³

Figure 3ttps://www.aria.developpement-durable.gouv.fr/wp-content/files_mf/SY_hydrogen_GB_2009.pdf

These include:

- low molar mass and small size giving it a high tendency to leak,
- extreme flammability and low ignition energy,
- ability to embrittle metals and alloys by altering their mechanical properties,
- violent reactions with certain compounds due to its reducing properties.

Combustion terminologies

Combustion, or burning, is a chemical process that involves releasing energy from a fuel and air mixture. In the case of hydrogen combustion, liquid or gaseous hydrogen is burned in a modified gas-turbine engine to generate thrust. This process is identical to traditional internal combustion, except hydrogen replaces its fossil fuel counterpart.

Consisting of a fixed cylinder and one or more moving pistons, a spark ignition engine works in the following way:

- During the intake process, fuel is mixed with air and introduced into the cylinder.
- The piston then compresses the fuel-air mixture, which is ignited by a spark.
- Ignition results in combustion. The expanding combustion gases drive the piston, which rotates the crankshaft.
- This rotational motion turns the wheels, in the case of automobiles.

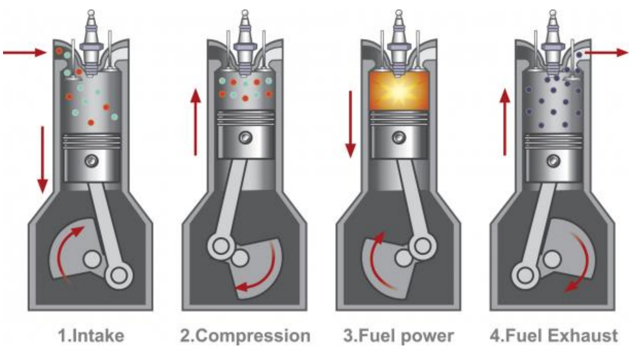


Figure 4 https://www.airbus.com/en/newsroom/stories/2020-11-hydrogen-combustion-explained#:~:text=Consisting%20of%20a%20fixed%20cylinder,Ignition%20results%20in%20combustion.

Hydrogen has many unique properties that make it suitable for combustion, including the following:

- Wide flammability range: Hydrogen can be combusted via a wide range of fuel-air mixtures. In fact, hydrogen can run on a "lean" mixture, which means the amount of fuel is less than the amount needed for combustion with a given amount of air. This results in greater fuel economy and a final combustion temperature that is generally lower, which reduces the number of pollutants, such as NOx, emitted via the exhaust.
- High auto-ignition temperature: Hydrogen's high auto-ignition temperature enables higher compression ratios in a hydrogen engine compared to a hydrocarbon engine.
- A higher compression ratio results in greater thermal efficiency, or less energy loss during combustion.

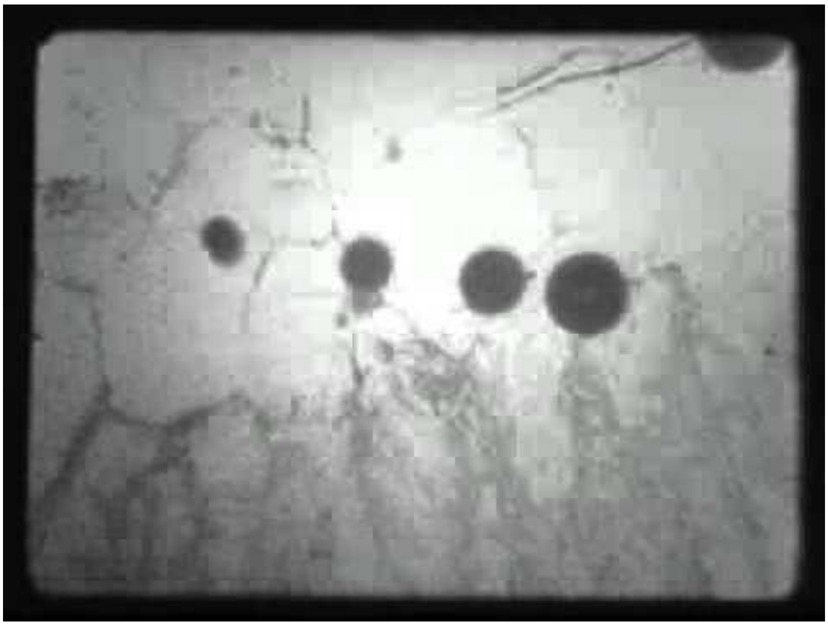
Hydrogen compatibility

- Hydrogen has a very small sized atoms and a low viscosity.
- Hydrogen can be easily absorbed by different materials (including those used for hydrogen storage). This, in turn, leads to the degradation of their mechanical properties, which may result in unwanted hydrogen leaks and structural failures.
- The correct selection of suitable materials for hydrogen storage is a crucial safety measure.
- Affect piping, walls of storage vessels, filling connectors, valves, fittings, etc.

The compatibility of hydrogen with metallic materials is affected by chemical interactions and physical effects, which include:

- Corrosion (dry corrosion (at high temperatures, hydrogen attack), wet corrosion (most common, caused by moisture), corrosion caused by impurities in a gas Hydrogen itself is a non-corrosive gas.

The Silent movie showing hydrogen bubbles emerging from steel, at defects and other locations.



Hydrogen Embrittlement (HE)

- Embrittlement at low temperatures ('cold embrittlement')
- Embrittlement is a loss of a metal ductility. Due to hydrogen ad-/absorption a material becomes brittle and can fracture.
- HE (an entry of hydrogen into a material) occurs at lower temperatures (nearly ambient).
- HE negatively affects three basic systems: production, transportation/storage and use.
- At higher temperatures (above 200 oC) hydrogen attack takes place.
- Hydrogen can be either in atomic or in molecular form.
- No clear mechanism of HE. Several mechanisms suggested:
    i. Formation of hydrogen solution in a metal lattice
    ii. Hydrogen adsorption on the surface, and on the subsurface of a metal
    iii. Hydrogen accumulation in structure defects (grain boundaries, vacancies dislocations) Hydrogen can form compounds within a metal lattice (metal hydrides or methane).

High strength steels are susceptible to HE the most. Hydrogen can enter a material via several routes:

- Manufacturing operations (welding, electroplating, pickling etc).
- As a by-product of wet corrosion of a metal.
- Surface treatment (e.g., cathode protection of a metal against corrosion).

- Adsorption on a metal surface.

HE occurs when the material is being subjected to a hydrogen atmosphere, e.g., in storage tanks:

- Internal Reversible HE - occurs when hydrogen enters the metal during its processing; may lead to the structural failure of a material that never has been exposed to hydrogen before.
- Hydrogen reaction embrittlement - occurs at higher temperatures when hydrogen chemically reacts with a constituent of the metal to form a new microstructural element or phase such as a hydride or to generate gas bubbles also known as blistering.

A material should not be used unless data are available to prove that it is suitable for the planned service conditions. In case of any doubt the material can be subjected to HE susceptibility testing (e.g., ISO 11114-4).

- ISO/TR 15916:2015 Basic considerations for the safety of hydrogen systems.
- Metals that can be used without any precautions: brass and copper alloys (e.g., beryllium copper Cube); aluminium and its alloys.
- Materials highly sensitive to HE: nickel and high content nickel alloys; titanium and its alloys
- Many materials can be safely used under controlled conditions (e.g., limited stress, absence of surface defects, etc.)
- The material affected by HE may fail prematurely and sometimes in catastrophic way when stress is applied.

Safe storage procedures and purpose - Why Hydrogen Storage is Important

Hydrogen storage is important if it is to form part of the future renewable energy mix. With international efforts to reduce emissions and the use of carbon-based fuels, hydrogen fuel cells could help create a greener solution to our power generation needs, including powering anything from small electronic devices to vehicles, aircraft and even whole buildings.

Another advantage of hydrogen as an energy source is that it can be obtained by electrolysis from electricity produced from surplus renewables, at the same time allowing hydrogen to fulfil a corresponding energy demand. Alternatively, hydrogen can be stored in large quantities for extended periods of time. Unlike with batteries, this energy is not lost over time and can therefore be produced and stored on an industrial scale as part of a green energy mix. This stored hydrogen can then be retrieved as a back-up energy supply when needed.

Hydrogen can also be used as a complementary fuel source alongside batteries in the transport sector. The hydrogen system provides the bulk of the energy storage, and a small capacity battery will act as a buffer to provide regenerative braking, meet any sudden increased power demands and increase the lifetime of hydrogen fuel cells by reacting to load changes. This complementary fuel method is already in use for some commercially available vehicles, such as the Honda FCX Clarity hydrogen car. Of course, hydrogen fuel cells have already been used safely for decades to provide clean power for forklifts that need to operate cleanly in indoor environments.

Hydrogen storage is important if it is to be part of our future clean energy solutions, yet more research and infrastructure improvements are required in order for hydrogen to realise its full potential.

Hydrogen can be stored in three different ways:

1. As a gas under high pressures
2. In liquid form under cryogenic temperatures
3. On the surface of or within solid and liquid materials

Each of these storage techniques has its own requirements and challenges, as shown below:

Compressed gas

Hydrogen can be compressed and stored in a gaseous form under high pressures. This requires storage tanks to have pressures of 350-700 bar or 5000-10,000 psi.

Cryogenic Liquid Storage

Hydrogen can be stored cryogenically in a liquid form. Low temperatures are required to stop the liquid hydrogen from boiling off back into a gas, which occurs at -252.8°C. Liquid hydrogen has a higher energy density than gaseous hydrogen but getting it down to the required temperatures can be costly. In addition, storage tanks and facilities for cryogenic liquid hydrogen storage must be insulated to prevent evaporation should any heat be carried into the liquid hydrogen due to conduction, convection or radiation. Despite these challenges, liquid hydrogen is in demand for applications requiring high levels of purity and it can be found being used in space travel.

Combined Cold-and-Cryo-Compressed Hydrogen

The storage methods of compression and cryogenic cooling used above can also be combined to create a further development of hydrogen storage. In this instance, the hydrogen is cooled before being compressed. This creates a higher energy density than with compressed hydrogen but, as with cryogenic liquid storage, also requires more energy use to achieve.

The energy used for these different types of hydrogen storage equal 9-12% of the energy made available for compression (from 1 to 350 or 700 bar) and around 30% for liquefaction. The energy use varies depending on the exact method, quantities and external conditions; however, work is underway to find more economic methods of storage with a lower required energy input.

Materials-Based Hydrogen Storage

As well as being compressed as a gas or stored as a liquid, hydrogen can be stored using materials. There are three types of hydrogen storage materials; those that use adsorption to store hydrogen on the surface of the material; those that use absorption to store the hydrogen within the material; and hydride storage, which uses a combination of solid materials and liquid.

- In adsorption, hydrogen molecules or atoms attach to the surface of the material. In this method, the hydrogen attaches itself to materials with high surface areas, including microporous organometallic framework compounds (metal-organic frameworks (MOFs)), microporous crystalline aluminosilicates (zeolites) or microscopically small carbon nanotubes.
- Hydrogen adsorption to materials in powder form can achieve high densities of volumetric storage due to the increased surface area for the sorbent. In absorption, hydrogen is dissociated into hydrogen atoms that are incorporated into the internal solid lattice framework of a material.
- Hydride storage, the third of these material storage systems for hydrogen, can use the reaction of hydrogen-containing materials with water or other liquid compounds, like alcohols. This method to store hydrogen, also known as 'chemical hydrogen storage,' sees the hydrogen effectively stored in both the material and the liquid.
- Metal hydride storage systems work by the hydrogen forming an interstitial compound with elemental metals such as palladium, magnesium, and lanthanum, intermetallic compounds, light metals like aluminium, or some alloys. These metal hydrides adsorb molecular hydrogen onto their surface and then incorporate them in elemental form into the metallic lattice with heat output. They can be released again with heat output and these hydrides can absorb large volumes of gas, with palladium, for example, able to absorb volumes of hydrogen 900 times that of its own.

Hydrogen can also be chemically bound with a liquid organic hydrogen carrier. These chemical compounds have a high capacity for hydrogen absorption and include the carbazole derivative N-ethyl carbazole and toluene.

These material-based methods allow large amounts of hydrogen to be stored by materials of smaller volume, at lower pressure, and in temperatures close to room temperature. Materials based storage can allow for volumetric storage densities greater than those for liquid hydrogen. However, materials-based storage is still in development as the cost of charging and discharging and processing hydrogen is still deemed to be too high as well as time-consuming.

Underground Hydrogen Storage

Salt caverns, exhausted oil and gas fields or aquifers can all provide underground hydrogen storage on an industrial scale. Such underground storage sites have been used for natural gas and crude oil for years, where they were held to balance supply or demand fluctuations or in preparation for a crisis.

Cavern storage is the most expensive of the options, but also the most suitable for hydrogen storage. Operational experience of cavern-based hydrogen storage is currently limited to a few locations in Europe and the USA. The most common of these are depleted underground natural gas stores, which are used as hydrogen reservoirs for surplus renewable energy.

Gas Grid Hydrogen Storage

As an alternative for underground cavern storage, surplus hydrogen can be fed into the public natural gas network to create hydrogen enriched natural gas (HENG).

Hydrogen-enriched town gas or coke-oven gas, with a hydrogen content over of 50% volume, was distributed to homes in Germany, the USA and Britain via gas pipelines into the 20 Century. The infrastructure used at the time still exists, although it was later modified to carry natural gas.

While it is generally accepted that gas with 10% hydrogen content could be introduced into the existing natural gas system without causing a negative impact on end users or pipeline infrastructure, a number of critical components have been deemed unsuitable for use at these levels of hydrogen concentration.

Despite this drawback, it is felt that large quantities of hydrogen gas could be stored in this manner by using much of the existing natural gas networks in industrial nations and then directly converted back into electricity via hydrogen fuel cells.

OUTCOME 2 Prepare to handle hydrogen gas

PERSONNEL TRAINING

- Hydrogen Handling Training. Personnel handling hydrogen or designing equipment for hydrogen systems must become familiar with the physical, chemical, and specific hazardous properties of GH2, LH2, and SLH2. Training should include detailed safety programs that recognize human capabilities and limitations. The goal of the safety program is to eliminate accidents and to minimize the severity of accidents that occur.
- Designer Training. Personnel involved in equipment design and operations planning must be trained to carefully adhere to accepted standards and guidelines and comply with the regulatory codes.
- Operator Certification. Operators must be certified for handling GH2, LH2, and SLH2, as appropriate, and in the emergency procedures for spills and leaks. Operators must be kept informed of any changes in safety procedures and facility operations
- Hazard Communication Program - develop, implement, and maintain at the workplace a written hazard communications program for their workplaces.
- Annual Review. Each installation will annually review all operations being performed at the installation to ensure that the safety training program is working effectively and to identify and enter into the program all potentially hazardous jobs in addition to jobs designated mandatory. Employee safety committees, employee representatives, and other interested groups should be provided an opportunity to assist in the identification process

Use of inherent safety features

Regardless of quantity, all hydrogen systems and operations must be devoid of hazards by providing adequate ventilation, designing and operating to prevent leakage, and eliminating potential ignition sources. Further, barriers or safeguards should be provided to minimize risks and control failures.

Safety Systems

Safety systems should be installed to detect and counteract or control the possible effects of such hazards as vessel failures, leaks and spills, embrittlement, collisions during transportation, vaporisation system failures, ignitions, fires and explosions, cloud dispersions, and the exposure of personnel to cryogenic or flame temperatures.

Safe Interface

- A safe interface must be maintained under normal and emergency conditions so at least two failures occur before hazardous events could lead to personal injury, loss of life, or major equipment or property damage.
- Warning systems should be installed to detect abnormal conditions, measure malfunctions, and indicate incipient failures. Warning system data transmissions with visible and audible signals should have sufficient redundancy to prevent any single-point failure from disabling the system.
- Flow Controls. Safety valving and flow regulation should be installed to adequately respond for protection of personnel and equipment during hydrogen storage, handling, and use.
- Safety Features - System and equipment safety features should be installed to automatically control the equipment required to reduce the hazards suggested by the triggering of the caution and warning systems. Manual controls within the systems should be constrained by automatic limiting devices to prevent over-ranging.

FAIL-SAFE DESIGN

- Certification. The equipment, power, and other system services shall be verified for safe performance in the design and normal operational regimes through certification.
- Fail-Safe Design. Any failure from which potentially hazardous conditions are a risk shall cause the system to revert to conditions that will be safest for personnel and with the lowest property damage potential.
- Redundant Safety. Redundant safety features shall be designed to prevent a hazardous condition when a component fails.

Safety Review

All plans, designs, and operations associated with hydrogen use must be subject to an independent, safety review

- Safety reviews should be conducted on effects of fluid properties, training, escape and rescue, fire detection, and firefighting.
- Operating Procedures. Operating procedures for normal and emergency conditions shall be established and reviewed as appropriate
- Hazards Analysis. Hazards analyses must be performed to identify conditions that may cause injury, death, or property damage.

- Mishap Reporting. Reporting, investigating, and documenting the occurrences, causes, and corrective action required for mishaps, incidents, test failures, and mission failures shall follow established basic policy procedures and guidelines

Working safely with gases and refrigerants

Relevant safety standards and legislation in the EU A standard is a document that establishes important requirements for a specific system, product or process. Standards aim to reduce costs, increase performance and improve safety. Standards are developed through a process of sharing knowledge and building consensus among technical experts. They are usually voluntary. However, additional laws and regulations may refer to standards and therefore make compliance with them compulsory.

Legislation	Year	Title	Scope	Relevant harmonised standards*
Directive 94/9/EC[5] Directive 2014/34/EU[6]	1994 2014	ATEX 'Equipment' Directive: equipment and protective systems intended for use in potentially explosive atmospheres Recast to react on Regulation (EU) No. 765/2008, entering into force Apr 20, 2016	- equipment (both electrical and mechanical) being used in potentially explosive atmospheres - defines product categories and characteristics products must meet in order to be installed in potentially explosive atmospheres - dedicated to manufacturers and distributors	EN 1127-1 EN 13463-1, -5, -6 EN 14797 EN 14986 EN 15198 EN 15233 EN 60079-0, -15, -20-1
Directive 97/23/EC[7]	1997	Pressure Equipment Directive (PED)	- pressure equipment and assemblies with internal pressure higher than 0.5 bar - harmonisation of national law regarding design, manufacture and conformity assessment of pressure equipment - more restrictive in regard with flammable refrigerants	EN 378-2 EN ISO 4126 EN 12178 EN 12263 EN 12284 EN 13136 EN 14276-1, -2
Directive 1999/34/EC[8]	1999	Product Liability Directive	- liability of defective products	
Directive 1999/92/EC[9]	1999	ATEX 'Workplace' Directive: occupational health and safety in potentially explosive atmospheres	- protection for workers in potentially explosive atmospheres - classification of working areas where explosive atmospheres exist into zones - dedicated to machine owners	
Directive 2006/95/EC[10]	2006	Low Voltage Directive (LVD)	- applying to any 'electrical equipment' designed for use with a voltage rating of between 50 and 1,000 V for A/C and between 75 and 1,500 V for D/C	EN 60204 EN 60335-1, -2-24, -2-34, -2-40
Directive 2006/42/EC[11]	2006	Machinery Safety Directive (MSD)	- machinery and similar equipment, safety components - risk reduction through integration of safety into design, production, maintenance, dismantling etc. of machines	EN 378-2 EN 1012 EN 1127-2 EN 60204-1 EN 60335-1,-2-40

Source: http://www.newapproach.org/Directives/DirectiveList.asp

A variety of standards address technical aspects of RAC equipment. Some also include environmental requirements (e.g., EN 378). The growing use of technologies associated with natural refrigerants has continuously led to the development of related standards in recent years. Most standards are independent from the refrigerant, yet some define rules regarding specific refrigerants.

When it comes to safety, standards may include the following:

- Safety classification of refrigerants (flammability, toxicity).
- Occupancy types, refrigerant charge size limits and room sizes.
- Safe design and
- Testing of components and pipes (e.g., pressures),
- Testing of assemblies (systems).
- Electrical safety, ignition sources.
- Installation areas, positioning, pipework, mechanical ventilation, gas detection.
- Instructions, manuals, name plates.
- Servicing, maintenance and refrigeration handling practices. The most relevant of these aspects are highlighted in detail in the following sections.

Working with flammable refrigerants

When working with flammable refrigerants, design features and operational practices must be established to minimise risks. Knowledge of the properties of the various refrigerants is required. Raising the awareness of practices for safe handling and storage of flammable refrigerants and appropriate system designs are measures that can prevent possible accidents. Precautions need to be taken to prevent the occurrence of leakages and to prevent a dangerous degree of released refrigerant. In the case of flammable refrigerants, potential ignition sources must be eliminated.

Electrolysis system safety

"Hydrogen and oxygen both have distinct hazards. Those hazards can be amplified if a fault enables them to mix within an electrolysis system"

A tragic example of these increased hazards occurred at a research facility in Korea, where an alkaline water electrolyser was set up to generate hydrogen. Hereby an oxygen permeated the hydrogen storage tank, creating a high-pressure combustible mixture. The tank exploded with the power of 50 kg of TNT. It caused two fatalities, six injuries, and over $30 million in damage.

Combined risks of hydrogen and oxygen

To understand and mitigate the hazards of electrolysis systems, we must consider the inherent risks of hydrogen. Hydrogen is easily combustible. It has one of the widest flammability ranges of any fuel and will ignite at anywhere between 4% and 75% concentration in air. It's much easier to create a combustible mixture of hydrogen compared to other fuels like propane, which will only ignite at 2-10% concentration in air.

Hydrogen also has an extremely low ignition energy, meaning it takes little effort to start a combustion reaction. Hydrogen needs as little as 0.02 mJ of energy to ignite in air, making it 14.5 times easier to ignite than propane, which requires at least 0.29 mJ. Electrolysis systems have many Balance of Plant components and processes that could easily become ignition sources.

If H2 and O2 mix unintentionally, the results can be deadly. In pure oxygen, hydrogen becomes even easier to ignite and will combust with significantly more energy. Increased oxygen concentrations also increase the severity of an energetic explosion which releases a blast of energy through a pressure wave.

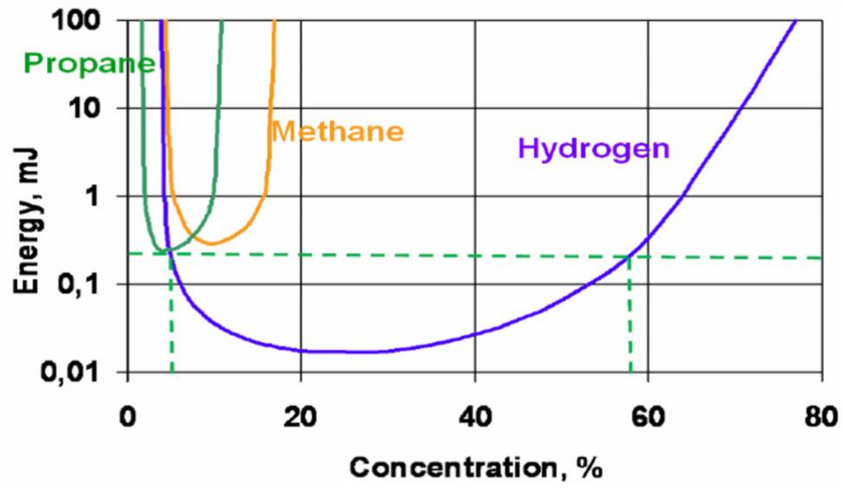


Figure 5 A graph illustrating the wide range of combustible concentrations and low ignition energy required for hydrogen compared to propane and methane - Image courtesy of Hy Response.

The risks and advantages of electrolysis systems

Electrolysers are tricky because, by function, hydrogen is in close proximity to high electrical current loads. Typically, electrical components must be ‘electrically classified’ for safe use around hydrogen when a leak is possible. However, it is not possible to electrically classify an electrolyser. The stack is always a potential ignition source if a combustible gas mixture forms during operation. Fortunately, electrolysis systems have their advantages too. Several inherent design factors help mitigate the risk of combustion.

Many electrolysis applications put their H2 to work right away. That means limited fuel is available beyond the small amount in the output process lines. As soon as the power is cut, hydrogen and oxygen production rapidly halt. Since there is limited stored H2 and production can be stopped quickly, there’s less risk of forming a combustible mixture.

Furthermore, many electrolysis systems vent their oxygen into the air at ambient pressure. Ambient air is a much less dangerous oxidizer than pure, pressurized oxygen.

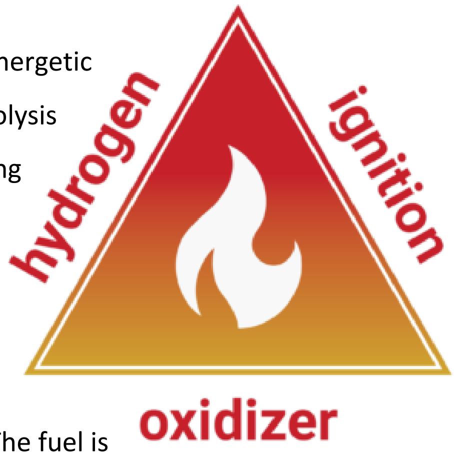
Last, in most applications, mechanical ventilation around the electrolyser stack and balance of plant functions will sweep away any small hydrogen leaks before they reach combustible mixture concentrations. These features can prevent a combustion event by never letting a combustible mixture form in the first place.

System integrations

Electrolysis equipment has inherent risks based on system integration. An electrolyser may be safely engineered by the manufacturer, but what happens when it’s installed in various applications or powered by unique electrical devices? Will vents and failsafe measures still work correctly?

A contributing factor to the Korean electrolyser incident (mentioned above) was likely using the device outside the manufacturer’s design limits. Because the alkaline water system was not run at proper power levels, cell membrane degradation allowed oxygen to permeate to the hydrogen side of the electrolyser. Even this relatively simple operational mistake had significant consequences.

Electrolyser system safety strategies



How can electrolysis system designers and users avoid the energetic consequences of combustion? A common approach to electrolysis safety begins with the fire triangle, a simple illustration featuring three factors necessary for combustion:

- **fuel**
- **ignition source**, and
- **oxidizer**.

Eliminating just one side of the triangle will prevent combustion. The fuel is hydrogen, and the oxidizer is oxygen — either in ambient air (21% O2) or pure oxygen. The goal is to anticipate ignition sources, but because the required ignition energy is so low, it can’t reasonably rule them out. Even a small static spark is enough for combustion.

The first defence is to keep the hydrogen away from the oxidizer — avoiding unintentional mixing. Thus, at first considering potential electrolysis system failure modes that can create unintentional mixing. It then explores mitigation strategies, including:

- **Leak prevention:** Prevent external leaks from mixing hydrogen with ambient air and prevent internal leakage from one part of the system to the other.
- **Ventilation:** Install mechanical ventilation fans to sweep the electrolyser enclosure and reduce hydrogen accumulation.
- **Venting and disposal:** Evaluate concentrations for all operational modes and create procedures for venting O2 and H2 during system start up, operation, and shutdown.
- **Purging:** Purge H2 systems with nitrogen or other inert gases before and after use (optional).
- **Detection:** Use personal monitors, leak sniffers, imaging cameras, and fixed H2 Incorporate detection into procedures and automated safety controls.
- **Safety planning:** Provide regular training to all personnel who work around hydrogen or electrolysis systems. Develop clear plans for maintenance, operation, and emergencies.

Hydrogen Gas Detection Technology

Hydrogen is an odourless, colourless, and tasteless gas. Industry, therefore, relies on hydrogen gas detectors to detect leaks. IGD has two technologies suitable for detecting hydrogen: pellitory sensors and electrochemical sensors.

Pellistor

Pellistor, or catalytic bead, sensors rely on the use of a catalyst that causes flammable gas within the sensor to ignite at a much lower temperature than usual. When combustion occurs, heat is produced in proportion to the amount of flammable gas present. The concentration of flammable gases can then be derived from this measurement and expressed as a percentage of the lower explosive limit

Pictured: TOC-750 safe area addressable gas detector

Pellistor sensors are typically used as a general “catch-all” technology for flammable gas detection. Pellistors respond to any flammable gas, measuring 0-100% LEL *(Lower Explosive Limit - it is the defined minimum concentration of gases and vapours suspended in the air that allows for ignition in the presence of an energy source)*. Since a 4% concentration of hydrogen is explosive, this corresponds to 100% LEL.

Electrochemical

Electrochemical sensors work by reacting the target gas – in this case, hydrogen – with an electrolyte, which produces a current in proportion to the amount of gas present. This allows for much more sensitive hydrogen gas detection compared to pellistor sensors. For example, 25% LEL equates to 1% hydrogen concentration, or 10,000 ppm. IGD electrochemical gas detectors offer sensitivity in the ranges of 0-1000 ppm to 0-40,000ppm. However, the downside of this extreme sensitivity is that electrochemical sensors can be destroyed on exposure to levels exceeding their measurement range, requiring them to be replaced. IGD electrochemical hydrogen detectors are ideally suited to applications where detection of hydrogen at low levels is critical.

Other Detection Technologies

Several other gas detection technologies exist; however, these are not recommended for hydrogen detection.

- **Infrared** sensors are unable to detect hydrogen since diatomic molecules like hydrogen don't absorb infrared radiation.
- **Semiconductor** gas detectors can be used to detect hydrogen; however, these sensors also typically respond to a wide range of other gases and vapours. The likelihood of false alarms means that semiconductor sensors are not advised for these applications.
- **Thermal conductivity** is another viable technology, though low sensitivity and selectivity render them poor for hydrogen detection applications.

Portable Hydrogen Gas Detectors

Finally, there are portable hydrogen monitors for added personal safety and leak identification. These can either be as a single gas monitor at 0-1000ppm to help identify leaks in equipment. Alternatively, there is a variety of gas monitor for confined space works.

OUTCOME 3 Perform a risk assessment exercise within a given hydrogen environment.

What is a Risk Assessment?

A Risk Assessment is simply a careful examination of what, in your line of work, could cause harm to people so that you may weigh up whether you have taken enough precautions or need to do more to prevent harm. The aim is to ensure that no one gets hurt or becomes ill, as accidents and sickness can ruin lives and affects your business if output is lost, machinery is damaged, insurance costs increase or result in going to court.

You are legally required to assess the risks present in your workplace. Some assessments of the relationship between hazard and risk are very precise, based on numerical assignments of values which are calculated from detailed considerations of engineering and other disciplines.

The important things you need to decide are whether a hazard is significant and whether you have it covered by satisfactory precautions to ensure the risk is minimised. This needs to be checked when you assess the risks. For example, electricity can kill but the risk of it doing so in an office setting is unlikely, provided that 'live' components are insulated and metal casings properly earthed.

5 step approach to hazard identification and risk assessment

Step 1: Look for Hazards

Walk around your workplace and look for what could reasonably be expected to cause harm, not the trivial things but rather concentrate on significant hazards. Also ask your employees what they think and if they've noticed anything that you may not find immediately obvious.

Step 2: Decide who might be harmed, and how

This can include young workers, trainees, non-language fit, cleaners, visitors, contractors, maintenance workers, members of the public or people you share your workplace with.

Step 3: Evaluate the risks and decide if current precautions are adequate or need improvement

When considering whether current precautions are adequate also consider if the remaining risk is tolerable or intolerable. If it's intolerable than you need to re-evaluate the precautions and improve until the remaining risk is minimised. The real aim is to minimise risk and to do so you may need to add further precautions.

Step 4: Record your findings

If you have more than five employees you must record the 'Significant findings' of your assessment, this means writing down the significant hazards and conclusions.

An example of this may be: 'Electrical installations: insulation and earthing regularly checked and working as intended. The employees must also be informed of these findings.

Step 5: Review your assessment and revise it if necessary

Your business will inevitably evolve, and as new equipment and procedures are introduced so too will new risks. When a significant change has been made, update the Risk Assessment as necessary. Do not do this for every trivial change.

In general, if there is little knowledge and understanding of risks and the components of the risks associated with the use of a particular technology, the safe design, use and operation of equipment will have many uncertainties associated with it. This leads to a riskier situation. However, if those involved attain a greater knowledge and understanding of the issue, then a much higher level of certainty in the safe design, use and operation will be achieved. This ultimately leads to a reduced level of risk

For the case of flammable refrigerants, such an assessment must include:

- Hazardous properties of the substance.
- Risk of exposure to individuals.
- rob ability of an explosive atmosphere to occur and to persist.
- Probability of ignition sources to exist and to trigger.
- Necessary action in the event of a fire or explosion and the degree of expected effects.
- There are several methods for risk assessments available, as well as standards that may be directly or broadly applicable to the situation or equipment under consideration.

Temporary flammable zone and safe working area Certain locations should be marked as 'temporary flammable zone' when working on systems with flammable refrigerants. This temporary zone should range from about half a metre radius from the system to a distance appropriate in relation to the maximum amount of refrigerant which could be released during the working procedure. The 'safe working area' begins three metres away from the system. No ignition sources should exist in a two-metre radius; a gas detector should be used to be aware of HC concentration in the air before and after work is carried out. Tools used in temporary flammable zones must be suitable to work with in potentially explosive atmospheres

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https://www.youtube.com/watch?v=xyANahuhGs0&ab_channel=HealthandSafetyExecutive

GUIDANCE ON LEARNING AND TEACHING APPROACHES FOR THIS MODULE

This module is to be delivered using a variety of learning and teaching approaches such as structured lessons with formative and summative assessments, in addition to practical demonstration of safe handling of hydrogen, where possible. Support material particularly that of the interactive activities should be fully utilised during the delivery of all HySkills modules.

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