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**REPORT ON ASSESSMENT OF HYDROGEN SAFETY & SECURITY
(S&S) AND HYDROGEN REGULATIONS**

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The European Commission is supporting the Coordination Action "HyLights" and the Integrated Project "Roads2HyCom" in the field of Hydrogen and Fuel Cells. The two projects support the Commission in the monitoring and coordination of ongoing activities of the HFP, and provide input to the HFP for the planning and preparation of future research and demonstration activities within an integrated EU strategy.

The two projects are complementary and are working in close coordination. HyLights focuses on the preparation of the large scale demonstration for transport applications, while Roads2HyCom focuses on identifying opportunities for research activities relative to the needs of industrial stakeholders and Hydrogen Communities that could contribute to the early adoption of hydrogen as a universal energy vector.

Further information on the projects and their partners is available on the project web-sites www.roads2hy.com and www.hylights.org



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1. Introduction

Work Task 1.5 in the Roads2HyCom project is directed towards assessment of the safety and security aspects of new hydrogen technologies.

More specific the following tasks will be dealt with in WT1.5:

- Mapping of standards and safety regulations for hydrogen in Europe
- Impact of new hydrogen technologies on the safety of the specific technologies as well as for production, distribution and storage.

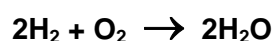
After a short introduction to hydrogen, in which the chemical and physical properties relevant for safety are highlighted, an overview of the most commonly used safety assessment methods is given in Chapter 2, as well as their characteristics and the field of application. Then the most suitable methods for use within the context of this handbook are discussed. In Chapter 3 typical values for the parameters required for a safety assessment of the various hydrogen technologies are given. Chapter 4 deals with the material aspects and failure mechanisms of hydrogen installations. Regulations, standards and codes of practice applicable to hydrogen installations are summarised in Chapter 5.

1.1 Introduction to hydrogen

Hydrogen is the lightest of all elements. At ambient temperature and pressure, hydrogen is a gas with a density of 0.089 kg/m³. Its density is about 13 times lower than the density of air, which makes hydrogen buoyant in air. If released in a contained environment it will rise and accumulation in the upper region of the container. Hydrogen rises more rapidly than other flammable gases like methane, propane, or gasoline vapour. In open environments hydrogen will quickly disperse into the atmosphere.

Chemical properties

The molecular weight of hydrogen is 2.016. Hydrogen undergoes oxidation by the reaction:



This reaction produces 238 kJ/mol of heat. Hydrogen as a fuel has an energy density of 119 MJ/kg, corresponding to 10.7 MJ/Nm³ in the gaseous state and to 1700 MJ/m³ in the liquid state. The main physical and chemical properties of hydrogen are summarized in the table below:



Table 1: Physical parameters of hydrogen

Property	Unit	Value
Molecular weight		2.016
Critical temperature	K	33.25
Critical pressure	kg/cm ²	13.2
Density (gas)	15 °C, 1 atm 0 °C, 1 atm	g/Nm ³ 84.09 89.98
Density (liquid)	kg/m ³	70.8
Boiling point	K	20.28
LHV	MJ/kg	119.93
HHV	MJ/kg	141.86
Energy density (gas)	MJ/Nm ³	10.7
Energy density (liquid)	MJ/m ³	1700

Hydrogen is highly flammable and very easily ignited. Hydrogen is fundamentally a reducing agent but is not very reactive with many compounds. However it reacts violently (or even explosively) with compounds like halogens and oxidising agents. Mixtures of hydrogen and organic vapours can ignite or explode upon contact with finely divided Rany nickel, palladium or platinum in the presence of oxygen.

Because of the small size of the atoms, hydrogen is also a very mobile compound. It diffuses easily into materials and endorses high requirements for sealing of pressurised hydrogen containers.



2. Methodology

2.1 General methods for safety or risk assessments

When tasked with the safety assessment of a product, technology or process various parameters should be considered. The choice of the most suitable assessment method will depend on these considerations. The following should be taken into account:

- What is the target group (personnel, customers, the general public, other equipment) that might suffer adverse consequences (domino effects)?
- In which stage of development is a process (design, engineering, construction, commissioning, operation, maintenance, decommissioning)?
- What type of regulations apply (e.g. prescribed techniques, specific norms and criteria, probabilistic or deterministic assessments)?
- Is a quantitative or qualitative assessment required?
- Are we considering undesired events (accidents) or safety during regular use (operational and workers safety)?
- What is the purpose of the assessment, e.g. is it selecting a safe location for a process (unit), or selecting the safest process from a range of alternatives (relative ranking), or assessing safety in comparison to other processes or techniques (benchmarking)?
- What are the input data requirements and how much data is available at the time of assessment; i.e. is the technology new (which means limited data is available), or is the technique tried and tested and has safety relevant data been collected?

In Table 2 the most commonly used assessment methods are summarised, together with an evaluation of the various characteristics discussed above. The assessment methods are ranked from early stages of design, where many (process, equipment, instrumentation) parameters are still unknown, to a mature, site specific situations in which all these parameters have been assigned, the environment of the system is known and where data are available (and required) for safety assessments.

The most commonly used safety assessment methods are described below. Other methods do exist, but they are usually a variation or combinations of (elements of) the methods mentioned below.



Table 2: Safety assessment methods and their characteristics

method	target	process stage	Qualitative /quantitative	Accident / operational safety	Benchmarking / relative ranking	Data requirements
Inherent safety assessment	People, both on and off-site	Early design	Qualitative	Accident and operational	Relative	Low
F&EI (Dow Fire and Explosion Index)	People, both on and off-site	Early design	Semi quantitative	Accident	Ranking and benchmarking	Low - medium
FMEA (Failure Mode and Effect Analysis)	Usually: people and equipment on site	Early-engineering	Qualitative / semi quantitative	Accident	Ranking	Medium
HAZOP (Hazard and Operability study), What-if analysis	Usually: people and equipment on site	Detailed engineering, operation, maintenance / modification	Qualitative / semi quantitative	Accident	Ranking	Medium - high
Fault and Effect Trees Analysis (including Risk graph and LOPA)	People and equipment, on and off-site	Following FMEA / HAZOP	Quantitative	Accident	Ranking	High
Quantitative Risk Assessment (QRA) including probability assessments and effect calculations.	Usually: general public (external)	After FMEA / HAZOP / fault and effect trees	Quantitative	Accident	Ranking and benchmarking	Very high



2.1.1 Inherent safety assessment

An Inherent Safety Assessment should be the starting point for the development of each process. Such an assessment is aimed at:

- Replacing dangerous components with less dangerous components (“substitution”);
- Minimising volumes of dangerous substances used, generated (also intermediates) and stored during and after the process (“intensification”);
- Choosing the least hazardous process conditions (reduce pressure, temperature as close to ambient as possible) (“moderation”);
- Make the process as simple as possible, since more can go wrong with complex systems (“simplification”).

The data required at this stage are general hazard data on the substances used and some knowledge on the various processes that will be or have been applied to make the product. It will give a (qualitative) ranking of the safety of the various options.

2.1.2 Dow Fire and Explosion Index (F&EI)¹

The Dow F&EI is an easy to use methodology to assess the risk of a process at the conceptual phase of a process. The substance and process parameters are read from tables. Depending on the value of the parameters penalties or credits (process hazard factors) are assigned. The main attributes of the F&EI are:

- Material Factor (MF)
- General Process Hazards Factor (F1)
- Special Process Hazards Factor (F2)
- Process Unit Hazards Factor ($F3 = F1 + F2$)
- Fire & Explosion Index ($F\&EI = F3 \times MF$) (see Table 3)
- Effect Distance (Effect Distance = $F\&EI / 4$).

The F&EI can be used at an early stage of process design. Only a small quantity of data is required. It also gives a value (degree of hazard) that allows some kind of benchmarking. Therefore it is very suitable for comparing the safety aspects of various (hydrogen) technologies, because only a little information is required on the way in which the technology has been implemented from the perspective of equipment and instrumentation.

¹ Dow's Fire & Explosion index – hazard Classification Guide. American Institute of Chemical Engineers, NY 1993.



Table 3: Dow fire and Explosion Index degree of Hazard

F&EI	Degree of hazard
1 - 60	Light
61 -96	Moderate
97 - 127	Intermediate
128 - 158	Heavy
> 158	Severe

2.1.3 Failure Mode Effect Analysis (FMEA)

The Failure Mode Effect and (Criticality) Analysis (FME(C)A) is mostly applied on the components (subsystems) of an installation. A team of experts guided by an independent facilitator over the course of several sessions analyse the possible deviations from the intended use of the system, component or part under study.

The deviations have to be considered with respect to possible causes, effects / consequences, and safeguards. The criticality refers to the ranking of the deviations with respect to severity and likelihood. Depending on the findings recommendations for improvement are proposed by the experts.

For an FMEA specific information on equipment and instrumentation is required. This implementation specific aspect plus the qualitative nature of the method make it less suitable for a general safety assessment and comparison of the various hydrogen technologies.

The methodology is widely explained in several references^{2, 3}.

2.1.4 Hazard and Operability Study (HAZOP) and What-if Analysis

A HAZOP is applied after the detailed engineering phase of a new (or modified) project, or at regular intervals for existing installations (typically 5 years). It is executed in a number of sessions by a team of experts guided by a facilitator and, if needed, assisted by a scribe.

The analysis makes use of key words to be applied on specific points (nodes) in the process.

The key words are, for example, “no”, “more”, “less”, “reverse”, “other than”, etc and are applied on the process parameters such as flow, temperature, pressure, phase, etc.

Information on equipment, instrumentation and process parameters is required for a HAZOP (e.g. Processed & Instrumentation Diagram (P&ID)). Also, operator actions

² IEC-812

³ Methods for determining and processing probabilities – CPR 12E. Committee for the Prevention of disasters, 2nd ed. 1997. “Red book”.



have to be taken into account in the analysis. This may be assessed by a What-If Analysis.

The What-If Analysis is mostly applied on a procedure consisting of several steps but it can also be applied on P&IDs. When applied on P&IDs, the ‘What if’ questions can be prepared in advance. When applied on procedures it may be carried as part of the HAZOP or only for a specific situation, for example a sampling procedure. For each step it is analysed whether certain deviations may occur, their causes, consequences and any safeguards to prevent the deviation. A risk ranking of each deviation may be applied. The What-If Analysis is usually more direct and easier to complete than a HAZOP. It is more like an FMEA.

As with an FMEA, for a HAZOP and What-If Analysis specific information on the process and the way it is implemented is required. Hence these methods are not very suitable for a general safety assessment and comparison of the various hydrogen technologies.

2.1.5 Fault and effect trees

Fault and effect trees are graphical ways to present results of safety analyses. An example of a fault and effect tree is given in Figure 1.

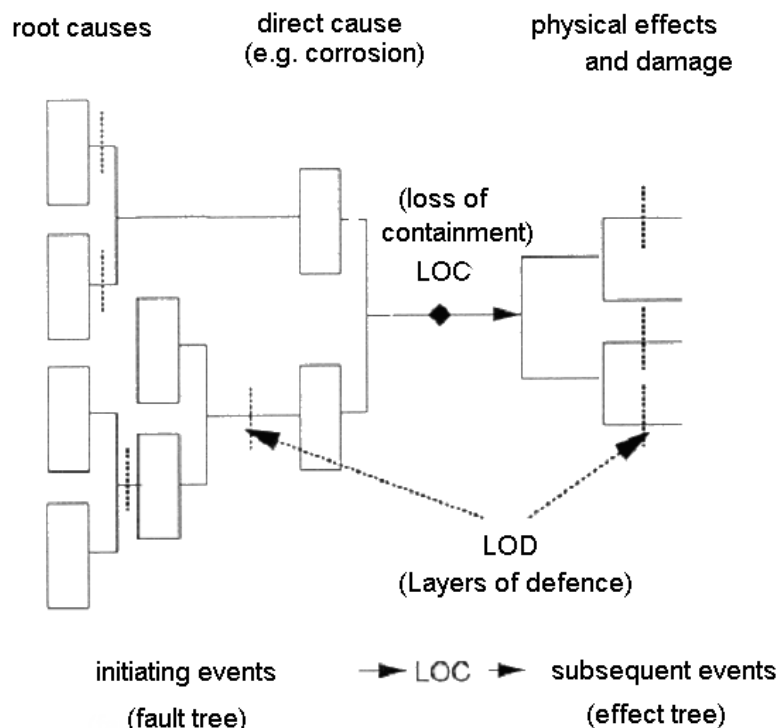


Figure 1: Fault and effect tree



The starting point is the identification of a Loss of Containment situation (LOC), which is the result of a hazard being released. Events leading to an LOC are called initiating events and are displayed in a fault tree (left half of Figure 1). Events in the fault tree directly leading to the LOC are called direct causes. Further to the left are underlying events (causing event further to the right). Farthest to the left in the fault tree are root causes.

Central to the analysis of a fault tree is the use of OR and AND gates between events. Two independent events that may cause another undesired event which contributes to the LOC these are indicated with an OR gate. If a certain event can only be caused if two (or more) other events occur at the same time, then an AND gate is used.

Events following an LOC are called subsequent events and are displayed in an effect tree (right half of Figure 1). At the end of an effect tree all the possible effects (damage) are shown. Sometimes layers of defence or barriers are shown. Barriers prevent an event causing another event (e.g. a fire wall preventing a small fire causing a larger fire in a nearby building).

Often frequencies or probabilities are assigned to the various events in fault and effect trees. Events, LOC scenarios and potential effects are often derived from FMEA or HAZOP studies, preceding the fault and effect tree analysis.

As with FMEA, HAZOP or What-If Analysis, specific information on the process and how it is implemented is required, even more so if event frequencies and probabilities need to be assessed. Hence this method is not very suitable for a safety assessment for various hydrogen technologies as intended in this handbook.

2.1.6 Quantitative Risk Assessment (QRA)

In a Quantitative Risk Assessment (QRA) all accident (or LOC) scenarios are fully quantified and the results are compared to risk acceptance criteria. If risk acceptance criteria are met no safety measures (or Layers of Defence (LODs)) are required. If risk criteria are not met measures need to be taken. Such measure can be preventive (i.e. LODs in the fault tree of Figure 1) or mitigative (LODs in the event tree of Figure 1).

Which scenarios should be taken into account and how event frequencies and probabilities should be evaluated could be the result of a HAZOP – fault / effect tree - chain of analysis, or they could be prescribed by regulations. Risk acceptance criteria might be a result of company policy (often the case if effects stay within the boundaries of the site) or may be set by regulators (which is usually the case if effects extend beyond site boundaries - the domain of external safety). In the HyApproval project's "Handbook for Hydrogen Refuelling Station Approval" contains an example of risk acceptance criteria that might be applicable⁴.

⁴ The HyApproval "Handbook for Hydrogen Refuelling Station Approval"
http://www.hyapproval.org/Publications/Deliverables_and_Reports/HyApproval_D2_2_Final_Handbook_V2.0.pdf
Chapter 12 of this Handbook contains an example of risk acceptance criteria



QRAs are very time consuming and frequently the exclusive competence of specialists making use of sophisticated computer programs. With such programmes the various phenomena that play a role during the development of an accident scenario are assessed in a quantitative way: the accidental release of hydrogen, the subsequent dispersion through the atmosphere, possible accumulation, ignition phenomena, explosion effects (pressure waves and heat radiation) and finally consequences for human beings in the vicinity and damage to structures. The HySafe project's Biennial Report on Hydrogen Safety, June 2007, Chapter III describes these phenomena in more detail⁵.

Even more than with fault tree analysis, situation specific information is required for a QRA, often including local regulations. Therefore a QRA is not at all suitable for an objective comparison of the safety of various hydrogen technologies. However, in order to have the implementation of a certain technology approved in a particular environmental setting such a QRA might be required.

A more extensive description of a QRA is given in Chapter IV of the HySafe Biennial Report on Hydrogen Safety, June 2007⁶.

An actual example of a QRA of a Hydrogen Refilling Station was worked out by the HyApproval project⁷.

in Appendix IV of the HyApproval project.

If the safety risks, resulting from a QRA, exceed the risk acceptance criteria safety measures are required. Examples of safety measures are also given in the Chapter V of the HySafe Biennial Report on Hydrogen Safety, June 2007⁸.

⁵ HySafe Project "Biennial Report on Hydrogen Safety", June 2007
Chapter III: Accidental Phenomena and Consequences
http://www.hysafe.org/download/1198/BRHS_Chap3_V1p2.pdf

⁶ HySafe Project "Biennial Report on Hydrogen Safety", June 2007
Chapter IV: Risk Assessment
http://www.hysafe.org/download/1199/BRHS_Chap4_V1p2.pdf

⁷ The HyApproval "Handbook for Hydrogen Refuelling Station Approval"
Appendix IV of this Handbook will contain an example of risk acceptance criteria
<http://www.hyapproval.org/>

⁸ HySafe Project "Biennial Report on Hydrogen Safety", June 2007
Chapter V: Hydrogen Safety Barriers and Safety Measures
http://www.hysafe.org/download/1200/BRHS_Chap5_V1p2.pdf



2.2 Hydrogen Safety Assessment - discussion and conclusion

As will be clear from the above section, for a general safety assessment and comparison of various hydrogen technologies, as intended here, only methods near the top of the list in Table 2, say the top two, will be suitable. Of course, once the technology has been implemented and the actual design and construction stage of an installation is reached one or more of the methods further down the list may or will become important. A technology evaluated to be relatively “unsafe” in an early general safety assessment may become the preferred choice, depending on the local situation and (additional) safety measures taken.

Focussing on the first two methods it will be clear that **quantities** of dangerous substances (hydrogen and in some cases other chemicals used in the process, e.g. methane) and the operational conditions, like **pressure** and **temperature** are important. On the basis of these parameters it is possible to calculate the extent of the damage (effect or safety distance) if such a quantity were to be released inadvertently. Such calculations will be shown below, using “typical” values of the parameters for each hydrogen technology.

Calculation of the F&EI also requires quantity, pressure and temperature data. In addition some more detail regarding the process itself is required. An advantage of the F&EI is its wide acceptance. Hence a comparison with other (chemical) processes may be possible. It should be noted, however, that F&EI was designed for use with relatively large process installations. As a matter of fact the method is not recommended for use with quantities below approximately 454 litres of combustible material. Many, especially non-industrial, hydrogen units will contain less material. Nonetheless by a consistent application of the F&EI method the results can give a relative ranking of the safety of the various methods.

In Chapter 3 some “typical” values of the relevant parameters for a general safety assessment of a number of hydrogen systems are given. As the number of hydrogen applications is still limited and most hydrogen applications are still in the development phase it is difficult to find such “typical” values. Hence the lists are neither complete nor universally applicable.

2.3 Safety in the hydrogen chain

For a general safety assessment of a technology the whole chain from production, through distribution and storage to end-use technology should be taken into account. Hence, after assessing the safety of the separate technologies, the safety of the complete hydrogen chain, of which these technologies form a part, should be assessed.

The safety of the chain is determined by the weakest link in the chain. By evaluating the hydrogen chains it may appear that certain end-user technologies that on their own are less safe than other end-user technologies, may become the preferred choice as this disadvantage is off-set by safer technologies earlier in the chain, e.g. by a safer production of hydrogen or by less transport.

An illustration of a hydrogen chain is presented in Figure 2.

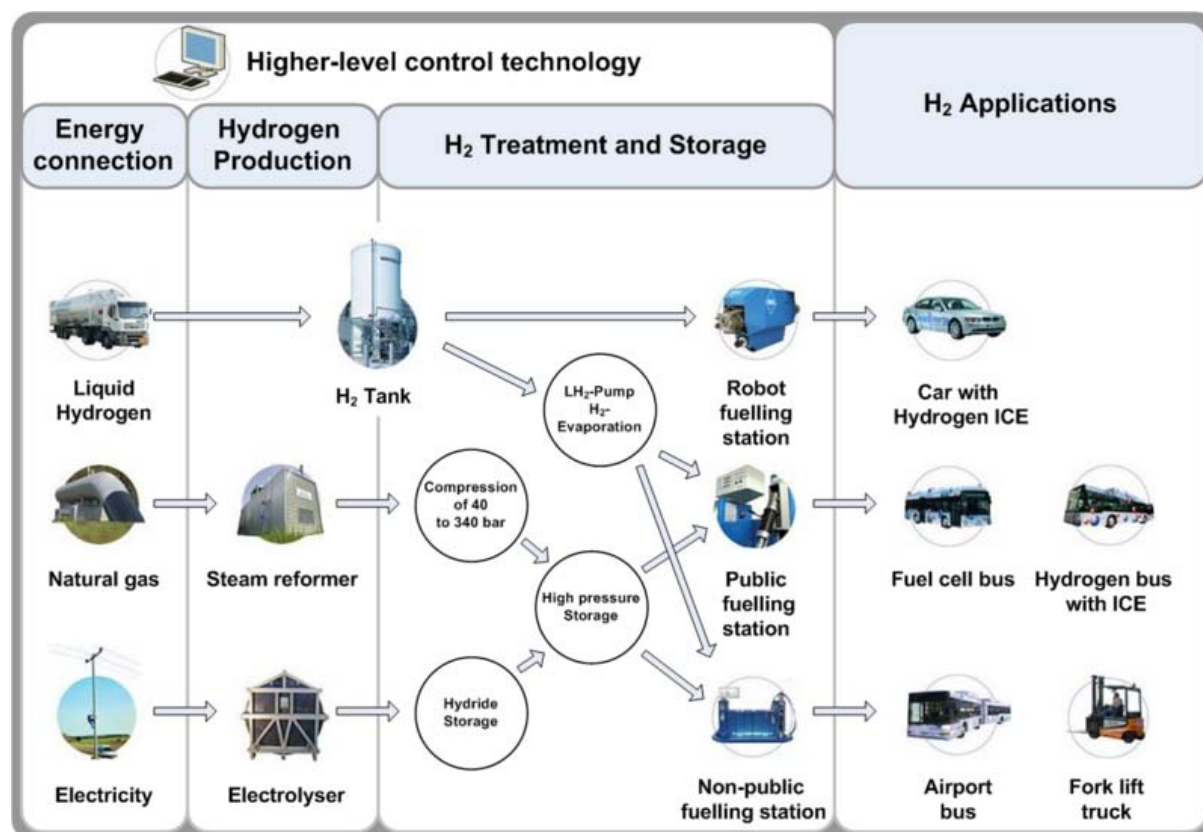


Figure 2: Example of a hydrogen chain (Contribution ET-Germany)

2.4 Identification of maximum credible accidents with Hydrogen

In order to calculate effect distances it is necessary to know how the dangerous material was released. In other words we need to assume a Loss Of Containment (LOC) scenario. Typically release will occur as a result of a leak. Although leaks may come in various shapes and sizes, some guidelines on leak sizes can be found in the “Dutch guidelines for quantitative Risk Assessment” (usually referred to as the “purple book”)⁹. Using this guideline the following leaks (and installations) should be considered:

- For stationary vessels (e.g. storage tanks, gas cylinders, reformers):
 - Instantaneous release of the complete inventory (catastrophic failure);
 - Continuous constant release of complete inventory in 10 min;
 - Continuous release through a hole of 10 mm diameter.
- For connecting pipes:
 - Release through both ends of a pipe in case of full rupture (leak size = pipe diameter);

⁹ “Guideline for quantitative risk assessment” – CPR 18E / PGS 3, Committee for the Prevention of disasters; see http://www.vrom.nl/get.asp?file=Docs/milieu/200602_PGS3.pdf



- Release through a hole 1/10 of pipe diameter with a maximum of 50 mm;
- For road tankers:
 - Instantaneous release of the complete inventory;
 - Release through both ends of a hose or loading arm in case of full rupture (leak size = pipe diameter);
 - Release through a hole 1/10 of hose or loading arm diameter with a maximum of 50 mm;

The instantaneous release scenarios should be considered a worst case, or maximum credible accident (MCA).

Applying the above scenarios to hydrogen results in the following:

- Adverse effects will only take place if the escaped gas is ignited.
- Instantaneous release of the complete contents of a vessel with compressed gaseous hydrogen will lead to the formation of a vapour cloud (i.e. a cloud with a mixture of hydrogen and air), which, if ignited, will cause a fire ball. If the cloud is not ignited immediately and unobstructed dispersion of the hydrogen in free air is possible, this cloud will dilute to harmless (un-ignitable) concentrations after some time. In confined areas, however, dangerous hydrogen accumulations may be formed. When ignited, this might result in explosions with accompanying overpressures.
- In the case of catastrophic failure of a cryogenic liquid hydrogen vessel or pipe a pool of liquid hydrogen may be formed. Only part of the released material will form a vapour cloud. The exact amount will depend on circumstances.
- A calculation with TNO's software EFFECTS shows that in the case of an instantaneous release of all the liquid hydrogen from a cryogenic tank at -252°C, 50% of the material will instantaneously vaporise. The liquid pool will evaporate quickly afterwards and a (short lived) pool fire may occur.
- A release of compressed gaseous hydrogen through a hole of some size will cause a jet fire, if ignited. If un-ignited the same scenarios as in the case of instantaneous release may be possible. Released material through holes in cryogenic vessels will evaporate quickly and, unless accumulation of hydrogen takes place, no adverse effects are expected.

Therefore two effect distances are relevant:

- Size of a fire ball in the case of (delayed) ignition of a vapour cloud;
- Size of a jet fire in the case of direct ignition following release of pressurised gaseous hydrogen from a hole in a vessel or a pipe.

These calculations will need to be carried out for all isolatable systems in an installation.



Explosion overpressures are dependent on confinement conditions (and thus site dependent) and therefore cannot be used for a general safety assessment.

In Chapter 3 some typical values of relevant parameters for a general, elemental safety assessment are given for a number hydrogen systems. Of course in individual circumstances values may very well be different.

2.5 Determination of consequence classes for hydrogen

Effect distances will determine how far from the accident location undesirable consequences may be suffered. The actual consequences, however, will depend on:

- The presence of persons or other targets (such as buildings that may be damaged) within the effect distance
- The environmental conditions (like confinement, ventilation, presence of ignition sources)
- The mitigation measures that may be present (like fire walls, fire extinguishers, evacuation plans, etc)

Often the consequences that may be the result of an accident are divided into a limited number of consequence classes. An example of such a set of consequence classes is shown in Table 4. With increasing severity of the consequence classes the willingness to accept such a consequence will diminish and more and/or better safety and security measures will (have to) be taken.

Table 4: Consequence classes

Consequence Class	Plant personnel	Assets	Reputation	Downtime
1	First aid / first aid treatment (e.g. minor cuts and burns)	No damage	No impact	< 1 hr
2	Minor injury / medical treatment required / lost time injury < 5 days	Minor damage	Slight impact	1 hr – 1 day
3	Major injury / extensive injuries / lost time injury > 5 days (e.g. broken bones, major strains, permanent disability)	Considerable damage	Considerable impact	1day – 2 weeks
4	Fatality within workforce	Major damage	National impact	2 weeks–6 months
5	Multiple fatalities or third party	Total loss	International impact	> 6 months



3. Relevant parameters for safety of hydrogen systems

In this chapter, where possible, “typical” values for the parameters that are required for a general (basic) safety assessment are given for the various hydrogen technologies.

Roads2HyCom has categorised hydrogen related technologies according to stage along the energy chain, as shown in Table 5. These categories are used in Chapter 3.

Table 5: Categories of Hydrogen technologies to be used in the safety evaluation

Categories of Hydrogen Technologies	Specific technology to be studied
Production of Hydrogen	Steam reforming Electrolyser Biological systems Gasification Thermo-chemical water splitting Photo-electrochemical systems
Storage of Hydrogen	Compressed Liquid Materials based / absorption Chemical
Transport of Hydrogen	Pipelines Road –rail tankers (g or l) Ships
Transport applications / primary drives	Fuel cell Combustion engine Electric / hybrid drives On board production
Stationary applications	
Portable/mobile applications	



3.1 Primary energy sources for generation of hydrogen

In Table 6 a few safety (and environmental) aspects are shown for the primary energy sources for the production of hydrogen.

Table 6: Safety and environmental aspects of primary energy sources for hydrogen

Primary Energy Sources	Hazardous substances	Special Risks / Remarks
Wind energy	None	Mechanical impact by broken-off rotating blades
Biogas	CH ₄ / CO ₂	Fermentation of biological substances (manure, sewage sludge, household rubbish)
Solar Energy	Not applicable	
Liquid Biofuel		
Nuclear Energy		Radioactivity: e.g.: radioactive waste
Hydrocarbons (coal, oil, natural gas)	Carbon (also containing Sulphur)	The formation of CO ₂ when burnt, is a main disadvantage.
Hydro electrics		Environmental damage. The energy extracted from the water depends on the volume and on the difference in height between the source and the water's outflow.
Biological systems		



3.2 Production, storage and transport of hydrogen

In Section 2.2 it was shown that **quantities** of dangerous substances (hydrogen and in some cases other chemicals used in the process, e.g. methane) and the operational conditions, like **pressure** and **temperature** are essential requirements for a safety assessment. In the case of an incident, *the quantity released* is important. Typical incidents that are often considered are: instantaneous release of the complete contents of a unit and release of the amount present in a blocked-in system as a result of a pipe rupture. In the tables below these parameters are shown for the most common hydrogen production (Table 7), transport (Table 8, Table 9) and storage (Table 10).

Explanation of some of the table headings:

- Hazardous substance: In addition to hydrogen, other hazardous materials may be present
- Capacity is optional
- Max Amount: in kg, litres:
 - 1) Total amount present in that unit
 - 2) The maximum amount that may be spilled in the event of complete failure of that unit (usually the maximum amount present)
 - 3) The maximum amount that may be spilled in the event of a pipe rupture (taking into account the working of safety valves and shut-off valves)
- The maximum (or working) pressure in that unit
- The maximum (or working) temperature in that unit
- The maximum diameter of pipes connected to the unit



Table 7: Input data for safety assessment of Hydrogen production systems

See text above for further explanation.

Hydrogen Production System	Hazardous substances	Capacity [Nm ³ /h]	Max amounts (1, 2, 3)	Pressure [MPa]	Temperature [°C]	Max. Ø of pipes connected to the unit
Steam reforming:						
Pre- converter	Natural gas, steam, CO ₂ , CO, H ₂	100 Nm ³ /h	1= 40 l 2=>40 l 3=	1-4 MPa	700 – 900 °C	6 mm
Converter	CO ₂ , CO, H ₂		1= 2= 3=	3-4 MPa	250°- 400 °C	
Pressure Swing Adsorber (PSA)	CO ₂ , H ₂		1= 2= 3=	3 MPa	5°- 50 °C	
Electrolysis	H ₂ , O ₂ , KOH	130 Nm ³ /h	1=~10 l 2= 3=	3 MPa		



Table 8: Input data for safety assessment of Hydrogen transportation systems

See text above for further explanation.

Hydrogen Transportation System	Hazardous substances	Length pipeline (1, 2, 3)	Pressure [MPa]	Temperature	Max. Ø of pipes connected to the unit
Pipelines – CGH ₂	Hydrogen	45 km, section might be 10 km.	>10Mpa		100 mm inside
Chemische Werke Hüls	CH ₂	203 km long	1, 1-2, 3 MPa	Room temp.	10-45 mm
Air Products Texas	CH ₂	121 km long	3,5 MPa	Room temp.	200mm
Pipelines – LH ₂	Hydrogen	Longest 300 m, no real transport option			
Tube trailers – CGH ₂ 40 ton truck	Hydrogen	1=400 kg (total) 2= 20 kg (= 1 tube) 3=	20 MPa – 30Mpa	Room temp.	Tube: length 10 m, diameter 30 cm. Pipes connected: 12 mm
Cryogenic liquid hydrogen trailers – LH ₂	Hydrogen	1= 3,000 kg 2= 3=	0-45 psig	-253° C	Fill / discharge: 1 inch Purge 1 inch



Table 9: Additional information on hydrogen transport systems

Hydrogen transport systems	Application/ Remarks
Pipelines – CGH ₂	Transport: material: carbon steel and (no stainless steel) To be considered: <ul style="list-style-type: none"> ◦ Limited infrastructure of suitable pipelines ◦ Energy to move hydrogen through a pipeline (comparison to natural gas)
Pipelines – LH ₂	Possible for transport applications?
Tube trailers – CGH ₂ 40 ton truck (racks with multiple cylinders)	Short-distance road transport (factor energy cost to be considered) How many tubes on one truck
Cryogenic liquid hydrogen tankers – LH ₂	Long distance road transport by super-insulated, cryogenic, over-the-road tankers. (Liquefaction costs to be considered)



Table 10: Input data for safety assessment of H2 storage systems – see text above for further explanation.

Hydrogen Storage System	Hazardous substances	Amount (1, 2, 3)	Pressure [MPa]	Temperature	Max. Ø of pipes connected to the unit
Cryogenic tank	Hydrogen	1 = 500 – 50000 Litre	Max 10 bar	-253 °C	1 inch
Bundles of cylinders	Hydrogen	1 = 50 litre per cylinder	200 bar	Ambient	21,8 mm (Din 477) 6 mm



3.3 Hydrogen applications

In this section, safety aspects of a number of hydrogen applications are given.

Hydrogen refuelling stations

Refuelling takes place through a dispenser. Important for the safety assessment is the volume (1) of hydrogen that can escape in case of a rupture of the hose. An important parameter for this is the time until the safety valve closes.

Table 11: Input data for safety assessment of Hydrogen refuelling systems

See Section 3.2 for further explanation.

Hydrogen refuelling system	Hazardous substances	Amount (1)	Pressure [MPa]	Temperature	Max. Ø of pipes connected to the unit
Liquid hydrogen Airport Munich	Hydrogen	Max 15 litres = 1 kg	3 bar	- 253 °C	12 mm
Compressed gaseous hydro- gen	Hydrogen	max. 0.5kg	250 bar 350 bar 700 bar	-40-60 °C	12 mm (Weh TK25) 4mm
		<5 l(0.1 kg at 250 bar)			21.8 mm



Hydrogen fuel tanks

Table 12: Input data for safety assessment of Hydrogen fuel tanks

See paragraph 3.2 for further explanation.

Hydrogen transport applications	Hazardous substances	Amount (1,2,3)	Pressure [MPa]	Temperature	Max. Ø of pipes connected to the unit
Hydrogen storage on board of H ₂ driven cars H ₂ driven buses H ₂ driven motor bicycles H ₂ driven trucks H ₂ driven aircrafts	Hydrogen	1= 5 kg 2= 5 kg 3=	200 – 875 bar	-40 - 85 °C	4 till 12 mm
	Hydrogen	1= 45 kg (9 tanks of 210 litre)	350 bar	15 °C	12 mm
		5 l (0,15 kg)	350 bar		
	Hydrogen	1= 45 kg (9 tanks of 210 litre)	350 bar	15 °C	12 mm
	LH2	12000 kg	10 bar	-253 °C	1 inch
Energy supply through Fuel cells PEM buses & cars ICE Hybrid systems	Hydrogen	1,2,3, less than 200 gr 100gr	0.5	100 °C	~0,5 –2 inches ?
	Hydrogen	Less than fuel cell applications		125 – 600 °C	~ 1 inch
	Hydrogen	Like fuel cells 10% hydrogen, 90 % natural gas	350 bar		



Other applications

Table 13: Input data for safety assessment of various Hydrogen applications

See paragraph 3.2 for further explanation.

Hydrogen applications	Hazardous substances	Amount (1,2,3)	Pressure [MPa]	Temperature	Max. Ø of pipes connected to the unit
H ₂ Back-up power (UPS = uninterrupted power supply)	Hydrogen	6 cylinders of 50 litre	200 bar	Ambient	6 mm
H ₂ Remote power	Hydrogen	6 cylinders of 50 litre	200 bar	Ambient	6 mm
H ₂ driven portable electronic devices	Hydrogen	1 l (25 mg)	Fuel cell 200-300 mbar		



4. Material aspects of hydrogen systems

4.1 General considerations

The design of new equipment is based on the so-called guideline or code development cycle (see Figure 3). For each new application, certain requirements are drawn up. This leads to a choice of certain types of materials. This is translated into requirements for these materials. For example, they must have a certain purity, tensile strength, or a certain thickness. Classically, the guidelines and codes (like API, ASTM, ASME, NEN, ISO, DIN) are only established after a new application is developed. First, one thinks of a new application. Next, one considers appropriate materials to build it from. Finally one agrees to fix the requirements in certain guidelines. Often, one then enters into a new cycle, because the application may have changed or a new application has been thought of, requiring other materials and improved guidelines.

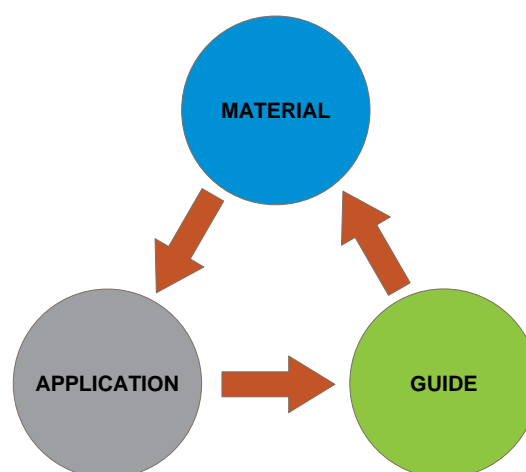


Figure 3: Guideline or code development cycle

Also for hydrogen applications codes or guidelines are present (as well as standards and regulations - see Chapter 5 for details), and they advise that materials to be used should, for example, be able to resist high pressures, or the cryogenic temperatures associated with hydrogen. Further more, safety measures (e.g. release valves) are specified. The question of which material is actually suitable for use with hydrogen is not answered in the codes; this is left up to the user to decide.

Unfortunately, answering this last question is far from trivial. This is due to the fact that handling of hydrogen can be associated with:

- High pressures
- Cryogenic temperatures



- Hydrogen induced steel embrittlement
- Hydrogen induced crack growth in steels
- Slow hydrogen leakage through polymer liners

The first two issues are adequately handled in the guidelines, but the last three are not. This means that equipment built according to the guidelines, is not necessarily safe. For safe operation, one also needs a very careful choice of material, and knowledge about this subject thus has to be searched elsewhere. This knowledge is publicly available in hydrogen manuals like the one maintained by EIGA and the one maintained by NASA.

The guidelines therefore serve as absolute minimum requirements for operation of a hydrogen application: an application that does not conform to the guidelines is sure to be unsafe in some respect. The problem is that other issues, like the hydrogen induced steel embrittlement, cannot be detected without destroying (part of) the equipment. This makes it difficult, if not impossible, to create a test or requirement that defines a “safe level of operation” for any given steel in any given hydrogen application built according to the guidelines. Instead, one has to rely on previous experience or on regularly updated manuals, such as those mentioned above.

An outline of the different hydrogen-material interactions is given below. Other points discussed include the degradation mechanisms due to interaction with hydrogen; the problem of hydrogen leakage due to diffusion and permeation; two widely available manuals on the use of hydrogen and, finally, a summary of the status quo in terms of known facts and gaps in knowledge.

4.1.1 Degradation mechanisms

For the shift to a hydrogen economy, it is likely that in the early transition stages the existing infrastructure is used to transport hydrogen. Therefore, this section considers the materials used in the already present natural gas infrastructure. The natural gas infrastructure consists of main ducts are made out of steel, local pipes made out of polymer materials and finally, copper pipes used in people’s homes. The possible effect of gaseous hydrogen on each of these three types of materials is discussed below.

In general, in the discussion below, no specific steel or material grades are recommended. This is for the following reason: the current document, once prepared, will not be updated. New experience in using alloys for hydrogen applications is, on the other hand, constantly being generated. This means that if a certain grade was recommended in this document, it is likely that this would be superseded by better grades developed in the future. Any material grade mentioned below should therefore be seen as an example only. But upon applying the knowledge in real, practical systems one must always check for the recommendations in the currently existing guidelines, which are regularly updated. Examples of such updated guidelines are the NASA Safety standard for hydrogen and hydrogen systems, and the EIGA Gaseous Hydrogen stations document.



Degradation of steels

Several degradation mechanisms are known for hydrogen originating from the gas phase and hydrogen formed by electrochemical loading. The discussion below is largely based on the papers by Hirth et al.¹⁰.

Degradation of steels: Hydrogen embrittlement

Hydrogen can make steels brittle at ambient temperatures. This is possible if the hydrogen molecules can dissociate on the steel surface, and if subsequently the hydrogen atoms formed can diffuse into the bulk of the steel. The mechanism of hydrogen embrittlement is up until now unclear. On one hand, hydrogen is suspected to decrease the atomic bonds in the iron lattice (decohesion theory), on the other hand it is suspected to cause an increased local plastic deformation. The consequence then may be a lowered fracture toughness and crack growth resistance, thus leading to a higher probability of fracture. The measure of embrittlement depends on the hydrogen concentration, the type of steel, and the microstructure of the steel.

Most literature, however, states that the influence of hydrogen at normal surrounding conditions (-20 to +50°C) is minimal. This apparent contradiction is caused by the fact that the usual oxide on a steel surface prevents the hydrogen from dissociating and diffusing into the bulk of the steel. This is not necessarily due to the oxide skin being a physical barrier for the hydrogen molecule, but more due to the blocking of the catalytic activity of a clean (non-oxidised) metal surface.

This notwithstanding, there are also experiments with direct evidence for embrittlement occurring in the case of a clean surface. In practice, a clean metal surface can be present when through a mechanical load local plastic deformation occurs. This is possible, if in the presence of crack-shaped defect, the yield limit of the material is locally exceeded as a consequence of (low frequency) changing loads of sufficient size. This is, amongst others, researched in the European NaturalHy project, with numerous experiments on crack growth under industrial conditions being performed at TNO. A very thorough review of the theories behind, and the effects of hydrogen embrittlement is presented in Deliverable 6 of that project. Changing loads can amongst others arise through a change in hydrogen pressure, a change in temperature or by a physical load. Much research on this topic has also been performed by the HySafe project.

Another problem arises when ultra pure hydrogen is being used (say, better than 4.0, i.e. >99,99 vol% purity). This high purity is sometimes required to prevent poisoning of fuel cells. But, as a side effect, it may also cause a deterioration of the oxide scale on the steel, thus allowing hydrogen diffusion into the steel. Less pure hydrogen can contain enough traces of oxygen, carbon monoxide or water to maintain a good oxide scale, but with ultra pure

¹⁰ J. P. Hirth, Effect of hydrogen on the properties of iron and steel, Metallurgical Transactions A 11 (1980) 861-890
J. P. Hirth and H. H. Johnson, Hydrogen problems in energy related technology, Corrosion-NACE 32 (1976) 3-26



hydrogen this is not necessarily the case. Not all trace impurities help in preventing hydrogen embrittlement, hydrogen sulphide for one increases the attack.

Hydrogen embrittlement is divided into three categories, hydrogen environment embrittlement (HEE), hydrogen stress cracking (HSC) and loss in tensile ductility. These are somewhat related, and the categories are not mutually exclusive. HEH is usually associated with gaseous hydrogen, while HSC is associated with hydrogen from other sources. The attack is found (under at least some conditions) amongst others steels, Ni-base alloys, metastable stainless steels, titanium alloys, carbon and low alloy steels.

In conclusion, if there are mechanical loads and/or ultra pure hydrogen present, then hydrogen can enter into a steel at room temperature. This in turn causes a weakening of the steel, which makes it more likely to fail. Care should therefore be taken to choose an appropriate material with the right dimensions, and to avoid mechanical loads. From a practical point of view, it is thus far not possible to assess whether a material is brittle or not by means of non-destructive testing. However, cracks formed due to hydrogen embrittlement can be detected using the standard non-destructive testing techniques, like for example acoustic emission.

Degradation of steels: Blistering

In electrolysis conditions, atomic hydrogen can enter the steel, and then locally recombine at a defect. This then causes a local very high pressure of di-hydrogen, ultimately causing the formation of a blister. This kind of degradation is most frequently observed when the alloy is charged with hydrogen under electrolytic conditions.

Degradation of steels: Hydrogen attack

At high temperatures, gaseous hydrogen can attack carbon and low alloy steels. Hydrogen is thought to react with carbon in the steel to form methane. This results in decarburisation and the formation of fissures, thus leading to premature failure. This kind of degradation mechanism can be mitigated by the use of steels with stronger carbide formers.

Degradation of steels: other mechanisms

Other degradation mechanisms relevant for this review include micro-perforation by high pressure hydrogen (found in compressors), and hydride formation (found for several elements including titanium).



Polymer material degradation

Research towards the physical interaction between hydrogen and polymer materials is not known. In the 1970s and 80s Brown¹¹ performed research towards the influence of helium, nitrogen, argon, oxygen, and water on the mechanical behaviour of some polymer materials (PE, PP, PMMA, PS, PET). The findings of this study are that some effects are noticeable until about 100°C above the boiling point of each gas. The boiling point of hydrogen is -253°C. So, based on the research by Brown it can be expected that hydrogen at normal surrounding conditions will have no physical interaction with polymer materials to the extent that it will cause a measurable deterioration in properties.

Chemical attack by hydrogen is also unlikely. Unsaturated hydrocarbons can be hydrogenated in a catalytic process, in which the unsaturated bond is converted into a saturated one. However, the typical materials used for hydrogen transport (PE, PVC) do not contain carbon-carbon double bonds that can be saturated. There is no further literature known in which there is reported increased polymer material degradation due to hydrogen.

In conclusion, increased degradation due to hydrogen is unlikely, but hard evidence from literature is missing.

Degradation of copper

Hydrogen embrittlement of technically pure copper is only known to occur if the alloy contains oxygen (in the form of copper oxides). This form of degradation is not very likely because ducts of copper are usually produced from oxygen-free copper. Other forms of hydrogen embrittlement are not known. Further more, copper is usually only applied at low pressures and low temperatures, thus reducing the risk of material degradation.

Other degradation mechanisms

In many hydrogen storage tanks, a combination of carbon fibre reinforcement with a hydrogen impermeable liner is used. Depending on the application, the liner may be metallic or made from a polymer.

In case the liner is metallic, a problem can arise due to the difference in thermal expansion coefficient of the metal and the carbon fibre. This is because a change in the temperature of the tank (due to filling and emptying, or due to radiation from the sun or outside weather conditions) will cause the materials to expand and shrink repeatedly. If the liner and the reinforcement do not expand at the same rate, the liner may separate from the reinforcement. This results in a weakening of the storage tank and may cause a leak in due time.

In the case the liner is made from a polymer material, the difference in thermal expansion coefficient is less, but the barrier against hydrogen permeation is also lower (as discussed below).

¹¹ N. Brown, Mechanical behaviour in gaseous environments, in Failure of Plastics, eds. W. Brostow and R. D. Corneliussen, Hanser, Munich, (1986) 287-304.



4.1.2 The problem of permeation and diffusion

Permeation through polymer materials

Due to the small size of hydrogen molecules, diffusion of molecular hydrogen through polymer materials is relatively fast. This means that, when tubes from ordinary polymer materials are used in confined, non-ventilated spaces, hydrogen can slowly seep through the wall of the tube and accumulate in the surrounding space. This is a risk that is especially clear for insulated and/or buried tubes and inside closed rooms and closets, where the hydrogen can build up. In a later stage it can then ignite or even explode.

A typical permeation rate for one kilometre of transport tube with an outer diameter of 110 mm, wall thickness of 10 mm, made out of HDPE, filled with 10 bar hydrogen is 70 litres per 24 hours. The higher the hydrogen pressure inside the tubing and the thinner the wall thickness, the higher the permeation rate will be (see also Section 4.6). In comparison, the permeation values for natural gas are 10-50 times lower than for hydrogen.

Of course by using different materials or coatings the diffusivity barrier across the tube can be made larger. However, the natural gas pipeline system, which is currently the most likely candidate to be used for hydrogen transport, is already in place, and the materials used in the end sections are often polymers (like PE100 or HDPE, PVC-CPE, and MDPE). However, the tubing inside houses is usually made from copper.

As for the case of mobile applications of hydrogen, often carbon fibre reinforced hydrogen storage tanks are used. These tanks contain a liner as a diffusion barrier to the hydrogen. This liner can be either metallic or polymeric in form. As described above, thermal cycling of such liner / reinforcement combinations can cause premature failure of such storage tanks.

In addition to the problem of diffusion through polymer tube walls, there is the problem of sealing. Connections between different pieces of tubing (which be polymer material, but can also be steel) will need to have better seals than the ones conventionally used for natural gas. Otherwise the hydrogen will leak out through the seal, yielding similar risks as for the case of hydrogen diffusion through the polymer tube wall.

In conclusion, some permeation of molecular hydrogen will take place when using polymer materials. The safety risk will strongly depend on the possibility that hydrogen can accumulate, i.e. by being trapped in closed spaces.

Diffusion through steels

Diffusion of hydrogen through steels is in general not a significant problem, since hydrogen diffusion through steels is much slower than through polymer materials. Problems are only expected to occur at possible defects, connections and flanges, where defective seals can facilitate a hydrogen leakage. It is important to note that,



unlike with polymer materials, molecular hydrogen first has to split up into hydrogen atoms before it can diffuse into a steel.

Diffusion through copper

Diffusion through copper is not a significant problem, since copper is only used at low pressure and the diffusion rate constant of hydrogen in copper is small. Problems are only expected to occur at possible defects, connections and flanges, where defective seals can facilitate hydrogen leakage.

Leakage from connections

The general recommendation to prevent leakage from connections in tubes or pipes is that all connections should be welded. The use of flanged or threaded connections should be kept to a minimum, since they can act as a source for hydrogen leakage. The use of compression fittings is not recommended. For more detailed information, please refer to the EIGA guidelines.

4.1.3 Industrial experience and manuals

Despite the warnings listed above, hydrogen in general can be safely handled. There is ample industrial experience in handling it. This knowledge is present in the form of best practices in different (engineering) companies, not as much in government directives that require the use of material X under circumstance Y (see e.g. <http://www.fuelcellstandards.com>). The only question is how to translate this already present knowledge into failsafe equipment and to apply it also on smaller scales with non-expert users.

As for designing and building hydrogen-containing equipment, specialist knowledge is needed. A lot of this knowledge is collected in the NASA Safety standard for hydrogen and hydrogen systems, including recommendations on which materials are to be used for gaseous and liquid hydrogen, guidelines and engineering practices. In addition to the NASA guidelines, the EIGA Gaseous Hydrogen stations guidelines can also prove useful.

4.1.4 Conclusions, gaps and recommendations

Hydrogen has been safely used under industrial circumstances for more than a century. There is good knowledge available on the influence of hydrogen on many materials. The current standards do not specify the use of certain materials for use with hydrogen, they are written on a more general level. However, recommendations about which materials to use are collected in the NASA safety standard for hydrogen and hydrogen systems and in the EIGA Gaseous Hydrogen stations guidelines. It is important to take care that, once the guidelines are mature, these are also translated into layman's terms (keeping in mind that expert supervision is always needed).

Some materials, like certain steels, can be adversely affected by hydrogen, which may lead to premature failure. This can be prevented by avoiding certain types of steels, by avoiding or minimising cyclic mechanical loads, by changing the temperature and/or pressure, and by selectively introducing other species in the gas



stream. A major challenge here is also to detect hydrogen embrittlement using non-destructive techniques. Cracks and defects (due to hydrogen embrittlement) can be detected using standard non-destructive testing techniques like acoustic emission. However, the brittleness of the material can not be assessed without taking out a piece of the material. This requires further research.

Other materials, like polymers, allow the permeation of hydrogen. This can cause the accumulation of hydrogen in closed spaces. Care should therefore be taken to prevent the accumulation of hydrogen, either by restricting hydrogen permeation or by applying active ventilation.

Whereas there is a lot of information on the degradation of steels due to hydrogen, very little information is available about the degradation of polymers due to hydrogen. Degradation seems unlikely, but more research should be valuable to validate this hypothesis. An important recommendation is therefore that more research is needed in the field of polymer degradation by hydrogen.

Further more, in storage tanks which consist of carbon fibre reinforcement combined with a hydrogen impermeable liner, serious problems can arise due to the difference in the thermal expansion coefficient. More research is also needed in this field to counteract this problem.

Of course, apart from degradation due to hydrogen, and permeation, one also needs to address the effects of temperature and pressure when selecting a suitable material for use with hydrogen. Storage can take place at cryogenic temperatures and high pressures, while production can be associated with high temperatures and high pressures. This sets extra requirements on the materials to be used.

Lastly, there is a tendency to move to high pressure (350 bar), cryogenic (20K) storage of hydrogen. Very little experience in the materials behaviour under these conditions is available. More research is therefore also needed in this field to ensure safe operation.



4.2 Material aspects of Hydrogen safety & security in Hydrogen production systems

Depending on the hydrogen production system, different problems may apply. Electrolysis units may encounter blistering, while syngas-based systems (biogas, liquid bio fuel, coal etc) are more prone to hydrogen embrittlement. All of the units will include a pressurisation unit, so high pressure regulations apply.

4.3 Material aspects of Hydrogen safety & security in large scale Hydrogen Storage and Distribution systems

In large scale hydrogen storage and distribution systems, the main problems come from hydrogen embrittlement and from leakages (or permeation). In case of gaseous or sorbed hydrogen, the storage is at room temperature. For liquid hydrogen, cryogenic temperatures are used, and the encasing materials should be able to withstand the low temperature, and possible degradation by hydrogen.

In distribution systems, failure is often through (accidental) external tampering, because of digging activities near pipelines. The pipeline can be directly damaged, or the soil bed on which it rests can be removed, which locally increases the stresses in the pipeline. Both can cause a much faster deterioration.

4.4 Material aspects of hydrogen safety & security in professional applications

Low purity applications like internal combustion engines (ICE) pose less of a risk towards hydrogen embrittlement. High purity applications, particularly fuel cells, pose a greater risk towards hydrogen embrittlement. Stationary objects with less changing loads pose a lesser threat than moving objects, which experience recurring cyclic loads.

4.5 Material aspects of hydrogen safety & security in small (non-professional) scale Hydrogen Production, Storage, Distribution and Application systems

Non-professional hydrogen systems will always have to be designed by professionals. Aside from the need for this equipment to be fool and vandal proof, there is the problem of tampering with the equipment. For example, someone may want to repair damage to the equipment himself or herself, rather than relying on a (more expensive) contractor, or he or she may want to change something in the setup. This is, in principle, unsafe, and should therefore be discouraged. The situation here is similar to the natural gas system, where only qualified people are allowed to change or repair an existing setup.



4.6 Chapter Appendix

The steady state permeation rate of hydrogen gas through a wall can be calculated as follows:

$$\frac{F}{A} = \frac{P * p}{d}$$

Where F is the flow of hydrogen in cm^3/day , A is the wall area (m^2), P is the permeation coefficient ($\text{cm}^3 \text{ mm}/(\text{m}^2 \text{ day atm})$), p is the difference in hydrogen pressure over the wall (atm), and d is the wall thickness (mm). The formula clearly shows that for large hydrogen pressures and small wall thicknesses, a lot of permeation will take place.

The permeation coefficient is specific for each gas / material combination. In general the permeation coefficient decreases with decreasing temperature. Some typical values are listed in Table 14. Please note that in general the permeation coefficient for hydrogen is at least ten times higher than for methane, using a comparable material.

Table 14: Permeation coefficient for a number of polymers

Gas	Polymer material	Permeation coefficient ($\text{cm}^3 \cdot \text{mm}/\text{m}^2 \cdot \text{day} \cdot \text{atm}$)	Temperature (C)
Hydrogen	LDPE	640	25
Hydrogen	PP	2700	20
Hydrogen	uPVC (u-unmodified)	110	25
Hydrogen	pPVC (p-plasticized)	110-250	27
Methane	LDPE	192	25
Methane	HDPE	25	25
Methane	uPVC	1.8	25



5. Regulations, standards and codes of practice affecting design, installation, operation & maintenance of hydrogen installations

5.1 Introduction

Existing hydrogen installations have been built to a number of different codes & standards, primarily based on national and local specific requirements. Some codes and standards applied have been derived from experiences with the CNG industry. Hydrogen specific international codes and standards (e.g. ISO) are presently still under development.

The purpose of regulations, standards and codes is to ensure safe and reliable design and operation of a product or facility.

Authorities, e.g. local, national, or international governments, provide compelling legal *regulations* to protect the public, workers, and the environment from dangers. A European Community Directives is an example of a regulation. This is a collective legislative act requiring member states to achieve a particular result without dictating the means of achieving that result. In addition to the EC directives the European countries typically have their own more prescriptive regulations for manufacturing, operation and maintenance of hydrogen installations.

Codes (also referred to as codes of practise) and standards serve as *guidelines* developed by interested parties to support free exchange of goods and services, and to promote safety and common understanding. Interested parties are typically companies and associations. While *standards* are developed by standardisation organisations through a thorough development processes involving workgroups consisting of a wide range of interested parties, *codes* may be developed by a few or only a single company or association. Because of the more rigorous development process standards generally have a wider acceptance than codes.

The notion “Code” is unfortunately used differently in USA, where it refers to a standard or collection of rules made binding by a local or national government. This document adheres to the European definition.

Unlike regulations, standards and codes are not legal documents, yet standards may be included or referred to in regulations and through the regulation be made legally binding. In this case the standard is said to be harmonised with the regulation and becomes a harmonised standard. CEN and CENELEC, the European counterparts to the international standardisation organisations ISO and IEC, have adopted international standards and harmonised these with a range of the European directives. The reason for the parallel structure is that the European standards can have a legal force in Europe as opposed to the international standards. References of Harmonised European Standards for European directives can be found on the European Commissions web pages:

http://ec.europa.eu/enterprise/newapproach/standardization/harmstds/index_en.html



In addition to the European and international standardisation bodies there are national bodies such as the US National Fire Protection Association, NFPA, which are relevant for the construction and operation of hydrogen installations. Some national bodies have adopted standards from other national or international bodies, thus a standard may have different ID numbers or codes in different countries. An overview of the international work on standardisation of hydrogen related equipment and technologies is shown in Figure 4.

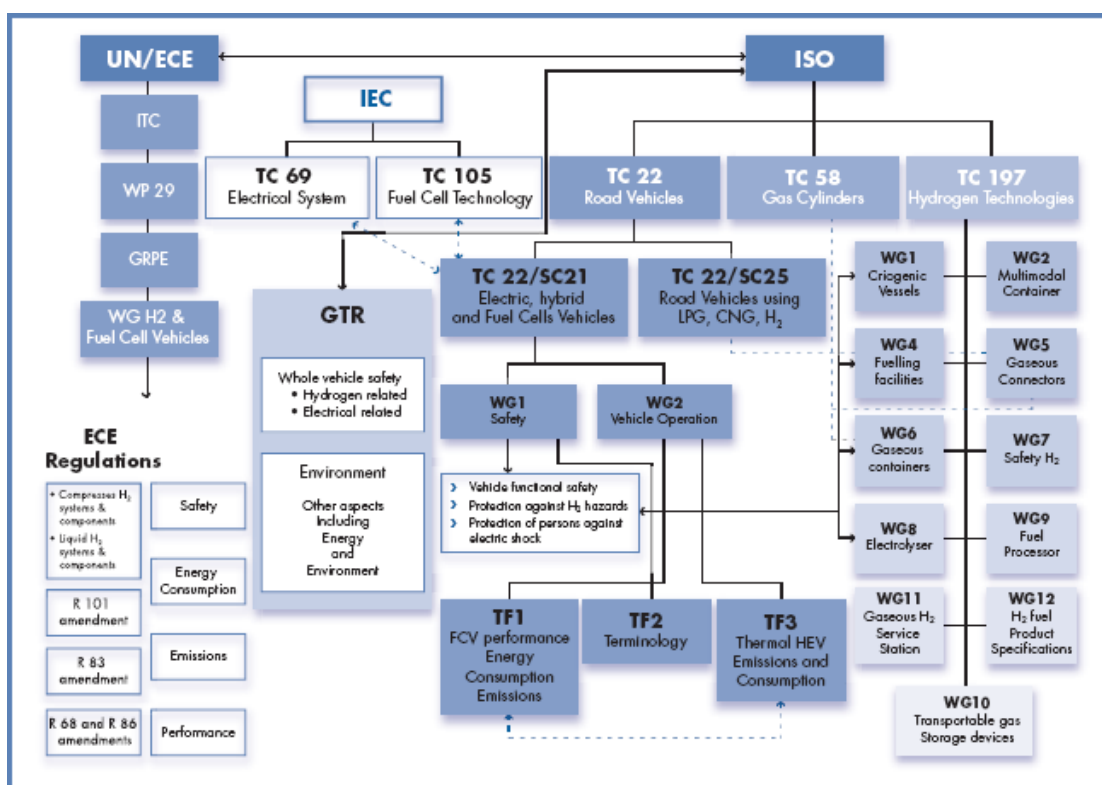


Figure 4: Overview of the international work on standardisation of hydrogen equipment and technologies.

(Source: “Introducing Hydrogen as an energy carrier” by the European Commission)

In this chapter the EU regulations and the European (CEN, CENELEC) and International (ISO, IEC) standards will be discussed together with the most commonly used codes (EIGA, NFPA, etc.) and national standards. The intention of this chapter is to give an overview of relevant regulations, standards and codes affecting design, installation, operation and maintenance of hydrogen installations. Some of these regulations, standards and codes are exclusively aimed at hydrogen installations and some are of a much more general nature. Examples of the latter are the Pressure Equipment Directive (PED), Transportable Pressure Equipment Directive, (TPED), the ATEX Product Directive (also known as ATEX 95 and ATEX 100) and the ATEX User Directive (also known as ATEX 137). It is also important to distinguish between the regulation of entire systems and the regulation of system parts as exemplified by the ATEX directives, where the product directive regulates the design and manufacturing process of equipment developed for use in explosive atmospheres in



order to ensure proper quality standards, while the user directive is focusing on risk to the health and life of workers at a facility where explosive atmospheres may be present.

5.2 Directives, Standards and Codes of practice

5.2.1 General remarks

ISO has issued a technical report, ISO/TR 15916:2004, which is a guideline for the use of hydrogen in its gaseous and liquid forms. The report identifies the basic safety concerns and risks, and describes the properties of hydrogen that are relevant to safety. Currently ISO is also developing a **technical specification ISO/TS 20012 on gaseous hydrogen service stations**.

Several standards are developed for explosion prevention and protection. Part 1 of EN 1127 covers the basic concepts and methodology. The determination of explosion limits and auto ignition temperatures of gases and vapours are covered by EN 1839 and EN 14522, and the determination of explosion pressure, and the rate of explosion pressure rise are covered by EN 13673 part 1 and 2. The general principles for a leak detection system is covered by EN 13160 part 1. Performance requirements and test methods of stationary hydrogen detection apparatus designed to measure and monitor hydrogen concentrations are covered by ISO 26142.

Equipment for use in potentially explosive atmospheres is covered by both the European and the international standardisation organisations. CEN covers the non-electrical equipment with part 1 of the standard EN 13463, and has developed terms and definitions for equipment and protective systems intended for use in explosive atmospheres, EN 13237. Electrical apparatus to be placed in an explosive atmosphere is covered by the international standard IEC 60079 and the equivalent CENELEC standard EN 60079. The 60079 standards are divided in several parts, where the most relevant parts cover general requirements – part 0, classification of hazardous areas – part 10, electrical installations in hazardous areas (other than mines) – part 14, inspection and maintenance of electrical installations in hazardous areas (other than mines) – part 17, and repair and overhaul for apparatus used in potentially explosive atmospheres (other than mines or explosives) – part 19. A wide range of equipment specific ATEX harmonised standards and a list of all standards related to the ATEX product directive, sorted on equipment can be found through the following links:

<http://ec.europa.eu/enterprise/newapproach/standardization/harmstds/reflist/atex.html>
<http://www.newapproach.org/Directives/ProductFamilies.asp?94/9/EC>

The CEN standard EN ISO 4126 (based on ISO 4126) is a standard harmonised with the PED, and covers a variety of safety devices for protection against excessive pressure. A wide range of equipment specific PED harmonised standards and a list of all standards related to the pressure directive, sorted on equipment or materials type can be found through the following links:

<http://ec.europa.eu/enterprise/newapproach/standardization/harmstds/reflist/equippre.html>
<http://www.newapproach.org/Directives/ProductFamilies.asp?97/23/EC>



The classification of areas where explosive atmosphere may occur are also covered in the EIGA code IGC 134/05 which was developed to facilitate and harmonize the interpretation and implementation of the required assessments according to the ATEX user directive.

The TPED applies to the equipment used to transport gases, compressed or liquefied. In the case of transport by rail the RID is applicable. The ADR is applicable when transported by road when the tanks or tank containers have a total capacity exceeding 3000 litres.

When dealing with gaseous or liquefied hydrogen under pressure the PED is applicable. The ATEX directives are applicable due to the potentially explosive atmosphere.

Several European standards covering cryogenic vessels are harmonized with PED. EN 1252 on materials, EN 1626 on valves for cryogenic service, EN 1797 on gas/material compatibility, and EN 13648 on safety devices for protection against excessive pressure.

5.2.2 Directives, Standards and Codes of practice tables - Overview

This paragraph contains a list of directives and standards applicable to hydrogen installations.

European Directives

67/548/EEC

- ***Title:* Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances**
- *Relevance to:* Dangerous substances
- *Status:* Published. **Amended seven times and latest by the Council Directive 92/32/EEC of 30 April 1992.**
- *Application:* **The directive deals with notification of substances, exchange of information on notified substances, and assessment of potential risk to man and the environment of notified substances, as well as classification, packaging and labelling. Not applicable for carriage of substances.**

73/23/EEC – Low Voltage Directive, LVD

- *Title:* Council Directive 73/23/EEC of 19 February 1973 on the harmonisation of the laws of Member States relating to electrical equipment designed for use within certain voltage limits.
- *Relevance to:* General safety, Equipment certification and conformity
- *Status:* Published
- *Application:* Applies to electrical equipment designed for use with a voltage rating of between 50 and 1 000 v for alternating current and between 75 and 1 500 v for direct current. **Not applicable to electrical equipment for use in**



an explosive atmosphere. The directives scope include protection against hazards from electrical equipment and correct marking of electrical equipment and packaging thereof.

80/779/EEC

- **Title: Council Directive 80/779/EEC of 15 July 1980 on air quality limit values and guide values for sulphur dioxide and suspended particulates**
- *Relevance to:* Environmental protection, Sulphur dioxide
- *Status:* Published
- *Application:* Fix limit values and guide values for sulphur dioxide and suspended particulates in the atmosphere and the conditions for their application in order to improve the protection of human health and the environment.

89/336/EEC – Electromagnetic Compatibility Directive, EMC

- *Title:* Council Directive 89/336/EEC of 3 May 1989 on the approximation of the laws of the Member States relating to electromagnetic compatibility
- *Relevance to:* General safety, Equipment certification and conformity
- *Status:* Published
- *Application:* Applies to apparatus liable to cause electromagnetic disturbance or the performance of which is liable to be affected by such disturbance. Apparatus includes all electrical and electronic appliances together with equipment and installations containing electrical and/or electronic components. The directives scope includes protection against electromagnetic disturbance from electrical apparatus and certification of such equipment.

89/391/EEC

- **Title: Council Directive 89/391/EEC of 12 June 1989 on the introduction of measures to encourage improvements in the safety and health of workers at work**
- *Relevance to:* Safety of workers at work, General
- *Status:* Published
- *Application:* To introduce measures to encourage improvements in the safety and health of workers at work. It contains general principles concerning the prevention of occupational risks, the protection of safety and health, the elimination of risk and accident factors, the informing, consultation, balanced participation in accordance with national laws and/or practices and training of workers and their representatives, as well as general guidelines for the implementation of the said principles. It shall apply to all sectors of activity, both public and private. A worker is any person employed by an employer, including trainees and apprentices but excluding domestic servants.



89/654/EEC

- **Title: Council Directive 89/654/EEC of 30 November 1989 concerning the minimum safety and health requirements for the workplace (first individual directive within the meaning of Article 16 (1) of Directive 89/391/EEC)**
- *Relevance to:* Safety of workers at work, HSE
- *Status:* Published
- *Application:* Protection of workers from risks to their safety and health at the workplace. It shall apply to all sectors of activity, both public and private. A worker is any person employed by an employer, including trainees and apprentices but excluding domestic servants.

89/655/EEC

- **Title: Council Directive 89/655/EEC of 30 November 1989 concerning the minimum safety and health requirements for the use of work equipment by workers at work (second individual Directive within the meaning of Article 16 (1) of Directive 89/391/EEC)**
- *Relevance to:* Safety of workers at work, Work equipment
- *Status:* Published
- *Application:* Protection of workers from risks to their safety and health due to the use of work equipment at work. It shall apply to all sectors of activity, both public and private. A worker is any person employed by an employer, including trainees and apprentices but excluding domestic servants.

91/271/EEC

- **Title: Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment**
- *Relevance to:* Environmental protection, Waste water
- *Status:* Published
- *Application:* Concerns the collection, treatment and discharge of urban waste water and the treatment and discharge of waste water from certain industrial sectors.

93/68/EEC – CE Marking Directive

- *Title:* Council Directive 93/68/EEC of 22 July 1993 amending Directives – among others – EMC and LVD. The initial Machinery Directive, directive 89/392/EEC, was also amended, but this was later amended by the directive 98/37/EC.
- *Relevance to:* General safety, Equipment certification
- *Status:* Published
- *Application:* Added two Annexes to the LVD regarding CE conformity marking and international production control. Amendments to Annex I of the EMC regarding CE conformity marking.



94/9/EC – ATEX Product Directive (also known as ATEX 95 and ATEX 100)

- *Title:* Directive 94/9/EC of the European Parliament and of the Council of 23 March 1994 on the approximation of the laws of Member States concerning equipment and protective systems intended for use in potentially explosive atmospheres.
- *Relevance to:* Equipment certification, Explosive atmosphere
- *Status:* Published
- *Application:* Applies to equipment and protective systems intended for use in potentially explosive atmospheres. Such equipment and systems also include safety devices, controlling devices and regulating devices intended for use outside potentially explosive atmospheres but required for or contributing to the safe functioning of equipment and protective systems with respect to the risks of explosion.

94/55/EC – ADR

- *Title:* **Council Directive 94/55/EC of 21 November 1994 on the approximation of the laws of the Member States with regard to the transport of dangerous goods by road**
- *Relevance to:* Hydrogen supply, Transportation
- *Status:* Published
- *Application:* **applicable to hydrogen transport.**

96/49/EC – RID

- *Title:* **Council Directive 96/49/EC of 23 July 1996 on the approximation of the laws of the Member States with regard to the transport of dangerous goods by rail**
- *Relevance to:* Hydrogen supply, Transportation
- *Status:* Published
- *Application:* **applicable to hydrogen transport.**

97/23/EC – Pressure Equipment Directive, PED

- *Title:* Directive 97/23/EC of the European Parliament and of the Council of 29 May 1997 on the approximation of the laws of the Member States concerning pressure equipment.
- *Relevance to:* Pressure equipment, Fixed
- *Status:* Published
- *Application:* Applies to the design, manufacture and conformity assessment of pressure equipment and assemblies with a maximum allowable pressure PS greater than 0.5 bar. Pressure equipment includes vessels, piping, safety accessories and pressure accessories.

98/24/EC

- *Title:* **Council Directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at**



work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)

- *Relevance to:* Safety of workers at work, Chemical agents
- *Status:* Published
- *Application:* Protection of workers from risks to their safety and health arising, or likely to arise, from the effects of chemical agents that are present at the workplace or as a result of any work activity involving chemical agents. It shall apply to all sectors of activity, both public and private. A worker is any person employed by an employer, including trainees and apprentices but excluding domestic servants.

98/37/EC – Machinery Directive, MD

- *Title:* Directive 98/37/EC of the European Parliament and of the Council of 22 June 1998 on the approximation of the laws of the Member States relating to machinery.
- *Relevance to:* General safety, Equipment certification and conformity
- *Status:* Published
- *Application:* Applies to machinery and lays down the essential health and safety requirements therefore. It shall also apply to safety components placed on the market separately. Machinery is an assembly of linked parts or components, at least one of which moves, joined together for a specific application. Safety component should fulfil a safety function when in use and the failure or malfunctioning of which endangers the safety or health of exposed persons.

1999/36/EC – Transportable Pressure Equipment Directive, TPED

- *Title:* Council Directive 1999/36/EC of 29 April 1999 on transportable pressure equipment
- *Relevance to:* Pressure equipment, Transportable
- *Status:* Published
- *Application:* Enhance safety with regards to transportable pressure equipment approved for inland transport of dangerous goods by road and by rail and to ensure the free movement of such equipment within the EU, including placing on the market and repeated putting into service and repeated use aspects. The term “transportable pressure equipment” shall include receptacles and tanks used for the transport of Class 2 substances in accordance with the Annexes to the RID and ADR treaties. Class 2 substances include gases, compressed, liquefied or dissolved under pressure. The ADR and RID treaties are covering the transport of dangerous goods by road and rail respectively. *However ADR shall not apply to substances of Class 2 in tanks or tank containers of a total capacity exceeding 3000 litres and deeply refrigerated liquefied gases.*

1999/92/EC – ATEX User Directive (also known as ATEX 137)

- *Title:* Directive 1999/92/EC of the European Parliament and of the Council of 16 December 1999 on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres.



(15th individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)

- *Relevance to:* Safety of workers at work, Explosive atmosphere
- *Status:* Published
- *Application:* Protection of workers potentially at risk from explosive atmospheres. It shall apply to all sectors of activity, both public and private. A worker is any person employed by an employer, including trainees and apprentices but excluding domestic servants.

ISO standards, drafts, reports and specifications

ISO 11114-1

- *Title:* Transportable gas cylinders - Compatibility of cylinder and valve materials with gas contents – Part 1: Metallic materials
- *Relevance to:* Hydrogen supply, gaseous transport
- *Status:* Published standard
- *Application:* Guidance in the selection and evaluation of compatibility between metallic gas cylinder and valve materials, and the gas content. Seamless and welded gas cylinders used to contain compressed, liquefied and dissolved gases, are considered.

ISO 11114-4

- *Title:* Transportable gas cylinders - Compatibility of cylinder and valve materials with gas contents – Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement
- *Relevance to:* Hydrogen supply, gaseous transport
- *Status:* Published standard
- *Application:* Applies to seamless steel gas cylinders and specifies test methods and the evaluation of results from these tests in order to qualify steels suitable for use in the manufacture of gas cylinders (up to 3 000 l) for hydrogen and other embrittling gases.

ISO 13984:1999

- *Title:* Liquid hydrogen – Land vehicle fuelling system interface
- *Relevance to:* Dispensing facilities, Liquid hydrogen
- *Status:* Published standard
- *Application:* Applies to the design and installation of liquid hydrogen fuelling and dispensing systems, and specifies the characteristics of liquid hydrogen refuelling and dispensing systems on land vehicles of all types in order to reduce the risk of fire and explosion during the refuelling procedure and thus to provide a reasonable level of protection from loss of life and property.
- *Corresponding standards:* SAE J2783 (under development)

ISO 13985:2006

- *Title:* Liquid hydrogen – Land vehicle fuel tanks



- *Relevance to:* On-board hydrogen storage, Liquid hydrogen
- *Status:* Published standard
- *Application:* specifies the construction requirements for refillable fuel tanks for liquid hydrogen used in land vehicles as well as the testing methods required to ensure that a reasonable level of protection from loss of life and property resulting from fire and explosion is provided.

ISO/DIS 15869

- *Title:* Gaseous hydrogen and hydrogen blends – Land vehicle fuel tanks
- *Relevance to:* On-board hydrogen storage, Gaseous hydrogen
- *Status:* Under development
- *Application:* This International Standard specifies the requirements for light-weight refillable fuel tanks intended for the onboard storage of high pressure compressed gaseous hydrogen or hydrogen blends on land vehicles. This International Standard is not intended as a specification for fuel tanks used for solid or liquid hydride hydrogen storage applications.

ISO/TR 15916:2004

- *Title:* Basic considerations for safety of hydrogen systems
- *Relevance to:* General safety
- *Status:* Published standard
- *Application:* Providing guidelines for the use of hydrogen in its gaseous and liquid forms. It identifies the basic safety concerns and risks, and describes the properties of hydrogen that are relevant to safety.

ISO 16110-1

- *Title:* Hydrogen generators using fuel processing technologies – Part 1: Safety
- *Relevance to:* Hydrogen supply, fossil fuels
- *Status:* Under development
- *Application:* Applies to hydrogen generation systems with a capacity less than 400 m³/h at 0 °C and 101,325 kPa, which convert fossil or biomass fuel to a hydrogen rich stream of composition and conditions suitable for e.g. a hydrogen compression, storage and delivery system.

ISO/CD 16110-2

- *Title:* Hydrogen generators using fuel processing technologies – Part 2: Procedures to determine efficiency
- *Relevance to:* Hydrogen supply, fossil fuels
- *Status:* Under development
- *Application:* covers operational and environmental aspects of the performance of hydrogen generators described in ISO 16110-1.



ISO 17268:2006

- *Title:* Compressed hydrogen surface vehicle refuelling connection devices.
- *Relevance to:* Dispensing facilities, Compressed gas
- *Status:* Published standard
- *Application:* Applies to design, safety and operation verification of Compressed Hydrogen Surface Vehicle, CHSV, refuelling connection devices. Applies to nozzles and receptacles which (1) prevent hydrogen fuelled vehicles from being refuelled by dispenser stations with working pressures higher than the vehicle; (2) allow hydrogen vehicles to be refuelled by dispenser stations with working pressures equal to or lower than the vehicle fuel system working pressure; (3) prevent hydrogen fuelled vehicles from being refuelled by other compressed gases dispensing stations; and (4) prevent other gaseous fuelled vehicles from being refuelled by hydrogen dispensing stations.
- *Corresponding standards:* SEA J2600 (published standard)

ISO/TS 20012

- *Title:* Gaseous Hydrogen – Service Stations
- *Relevance to:* General safety
- *Status:* Under development
- *Application:* Applies to non-residential, pure hydrogen refuelling stations, and will address separation distances.

ISO/DIS 22734-1

- *Title:* Hydrogen generators using water electrolysis process – Part 1: Industrial and commercial applications
- *Relevance to:* Hydrogen supply, electrolysis
- *Status:* Under development (Draft International Standard)
- *Application:* This standard defines the construction, safety and performance requirements of integrated, packaged hydrogen gas generation appliances using electrochemical reactions to electrolyse water to produce hydrogen and oxygen gas.

ISO/CD 22734-2

- *Title:* Hydrogen generators using water electrolysis process – Part 2: Residential applications
- *Relevance to:* Hydrogen supply, electrolysis
- *Status:* Under development
- *Application:* As part 1, for residential applications

ISO 26142

- *Title:* Hydrogen detector
- *Relevance to:* General safety
- *Status:* Under development



- *Application:* Defines the performance requirements and test methods of stationary hydrogen detection apparatus that is designed to measure and monitor hydrogen concentrations.

CEN standards

EN 1127-1:1997

- *Title:* Explosive atmospheres – Explosion prevention and protection – Part 1: Basic concepts and methodology
- *Relevance to:* Protection systems
- *Status:* Published standard

EN 1252-1:1998

- *Title:* Cryogenic vessels – Materials – Part 1: Toughness requirements for temperatures below – 80 C
- *Relevance to:* On-board hydrogen storage, Liquid hydrogen
- *Status:* Published standard

EN 1626:1999

- *Title:* Cryogenic vessels – Valves for cryogenic service
- *Relevance to:* On-board hydrogen storage, Liquid hydrogen
- *Status:* Published standard

EN 1797

- *Title:* Cryogenic vessels – Gas/material compatibility
- *Relevance to:* On-board hydrogen storage, Liquid hydrogen
- *Status:* Published standard

EN 1839:2003

- *Title:* Determination of explosion limits of gases and vapours
- *Relevance to:* Risk assessment
- *Status:* Published standard

EN 4126-1, 2, 3, 4, 5, 6, 7

- *Title:* Safety devices for protection against excessive pressure
- *Relevance to:* Non-electrical equipment
- *Status:* Published standard

EN 13160-1:2003

- *Title:* Leak detection systems – Part 1: General principles
- *Relevance to:* Detection systems



- *Status:* Published standard

EN 13237:2003

- *Title:* Potentially explosive atmospheres – Terms and definitions for equipment and protective systems intended for use in potentially explosive atmospheres
- *Relevance to:* Protective systems
- *Status:* Published standard

EN 13463:2001

- *Title:* Non-electrical equipment for potentially explosive atmospheres – Part 1: Basic method and requirements
- *Relevance to:* Non-electrical equipment and installations
- *Status:* Published standard

EN 13648-1, 2, 3

- *Title:* Cryogenic vessels – Safety devices for protection against excessive pressure
- *Relevance to:* Non-electrical equipment, Liquid hydrogen
- *Status:* Published standard

EN 13673-1:2003

- *Title:* Determination of maximum explosion pressure and the maximum rate of pressure rise of gases and vapours – Part 1: Determination of the maximum explosion pressure
- *Relevance to:* Risk assessment
- *Status:* Published standard

EN 13673-2:2005

- *Title:* Determination of maximum explosion pressure and the maximum rate of pressure rise of gases and vapours – Part 2: Determination of the maximum rate of explosion pressure rise
- *Relevance to:* Risk assessment
- *Status:* Published standard

EN 14522:2005

- *Title:* Determination of the auto ignition temperature of gases and vapours
- *Relevance to:* Risk assessment
- *Status:* Published standard



IEC standards

IEC 60079-0

- *Title:* Electrical apparatus for explosive gas atmospheres - Part 0: General requirements
- *Relevance to:* Electrical equipment and installations
- *Status:* Published standard
- *Application:* Specification of general requirements for construction, testing and marking of electrical apparatus and components intended for use in explosive gas atmospheres. Electrical apparatus complying with this standard is intended for use in hazardous areas in which explosive gas atmospheres, caused by mixtures of air and gases, vapours or mists, exist under normal atmospheric conditions.
- *Corresponding standards:* EN 60079-0 by CENELEC (published standard)

IEC 60079-10

- *Title:* Electrical apparatus for explosive gas atmospheres – Part 10 : Classification of hazardous areas
- *Relevance to:* Electrical equipment and installations
- *Status:* Published standard
- *Application:* Classification of hazardous areas where flammable gas or vapour risks may arise, in order to permit the proper selection and installation of apparatus for use in such hazardous areas.
- *Corresponding standards:* EN 60079-10 by CENELEC (published standard)

IEC 60079-14

- *Title:* Electrical apparatus for explosive gas atmospheres - Part 14: Electrical installations in hazardous areas (other than mines)
- *Relevance to:* Electrical equipment and installations
- *Status:* Published standard
- *Application:* Specification of requirements for the design, selection and erection of electrical installations in explosive gas atmospheres. These requirements are in addition to the requirements for installations in non-hazardous areas. Applies to all electrical equipment and installations in hazardous areas, and at all voltages.
- *Corresponding standards:* EN 60079-14 by CENELEC (published standard)

IEC 60079-17

- *Title:* Electrical apparatus for explosive gas atmospheres - Part 17: Inspection and maintenance of electrical installations in hazardous areas (other than mines)
- *Relevance to:* Electrical equipment and installations
- *Status:* Published standard



- *Application:* Intended to be applied by users, and covers factors directly related to the inspection and maintenance of electrical installations within hazardous areas only.
- *Corresponding standards:* EN 60079-17 by CENELEC (published standard)

IEC 60079-19

- *Title:* Electrical apparatus for explosive gas atmospheres - Part 19: Equipment repair, overhaul and reclamation
- *Relevance to:* Electrical equipment and installations
- *Status:* Published standard
- *Application:* Gives instructions, principally of a technical nature, on the repair, overhaul, reclamation and modification of a certified equipment designed for use in explosive atmospheres.
- *Corresponding standards:* EN 60079-18 by CENELEC (published standard)

CENELEC standards

EN 60079 – Part 1, 10, 14, 17, 19

- *Title:* Electrical apparatus for explosive gas atmospheres

See corresponding IEC standards

EIGA standards

IGC 06/02

- *Title:* Safety in storage, handling and distribution of liquid hydrogen
- *Relevance to:* Hydrogen storage, Liquid hydrogen
- *Status:* Published code of practice
- *Application:* Describes certain rules and precautions related to liquid hydrogen. The code includes (1) features for layout and design e.g. safety distances and suitable mechanical and electrical equipment, (2) notices, instructions and customer information in order to facilitate control of an emergency, (3) testing, operations and maintenance of equipment, (4) training and protection of personnel.

IGC 15/06

- *Title:* Gaseous hydrogen stations
- *Relevance to:* Hydrogen storage, Gaseous hydrogen
- *Status:* Published code of practice
- *Application:* The code shall serve as a guidance of designers and operators of gaseous hydrogen stations and reflect the best practices currently available. It includes issues such as safety of personnel, operations instructions, protection, and emergency situations.



IGC 23/00

- *Title:* Safety training of employees
- *Relevance to:* Safety of workers at work, General
- *Status:* Published code of practice
- *Application:* **Serve as a guideline for training program for employees dealing with industrial gases such as hydrogen. The guideline includes a safety training checklist and information about hazards related to the various gases.**

IGC 75/07

- *Title:* Determination of safety distances
- *Relevance to:* General safety, Risk management and mitigation
- *Status:* Published code of practice, Revision of IGC 75/01
- *Application:* Establishing basic principles for calculating appropriate safety distances for the industrial gas industry. It is intended to be an aid to writing and revising codes and practices which involve specifying separation distances for safe equipment layout. It shall apply to equipment required for the storage and processing of industrial, medical and speciality gases.

IGC 121/04

- *Title:* Hydrogen transportation pipelines
- *Relevance to:* Dispensing facilities, Compressed gas
- *Status:* Published code of practice
- *Application:* Contains a summary of current industrial practices related to metallic transmission and distribution piping systems carrying pure hydrogen and hydrogen mixtures.

IGC 122/00

- *Title:* Environmental impacts of hydrogen plants
- *Relevance to:* Environmental protection, Operation
- *Status:* Published code of practice
- *Application:* Concentrates on environmental impacts of hydrogen and carbon monoxide production, and shall provide a guideline for identifying and reducing the environmental impacts of such facilities. This document is relevant for sites which produce hydrogen by electrolysis or chemical processes and covers principal impacts and impacts due to compression, desulphurising, reforming, maintenance and storage.

IGC 134/05

- *Title:* Potentially explosive atmosphere – EU directive 1999/92/EC
- *Relevance to:* Safety of workers at work, Explosive atmosphere
- *Status:* Published code of practice



- *Application:* To facilitate and harmonize the interpretation and implementation of the required assessments and specifically classification of areas where explosive atmosphere may occur according to the ATEX user directive

IGC 137/06

- *Title:* Environmental aspects of decommissioning
- *Relevance to:* Environmental protection, Decommissioning
- *Status:* Published code of practice
- *Application:* Providing guidance to identification and management of environmental risks associated with decommissioning.

NFPA standards

NFPA 50A – Superseded by NFPA 55

- *Title:* Standard for Gaseous Hydrogen Systems at Consumer Sites
- *Relevance to:* Hydrogen storage, Gaseous hydrogen
- *Status:* Published standard
- *Application:* Present requirements for designing systems including container locations, safety devices, marking, piping, venting, and other components.

NFPA 50B – Superseded by NFPA 55

- *Title:* Standard for Liquefied Hydrogen Systems at Consumer Sites
- *Relevance to:* Hydrogen storage, Liquid hydrogen
- *Status:* Published standard
- *Application:* Present requirements for designing systems including container locations, safety devices, marking, piping, venting, and other components.

NFPA 52

- *Title:* Vehicular Fuel Systems Code, 2006 Edition
- *Relevance to:* Hydrogen fuelled engines
- *Status:* Published standard
- *Application:* Presents the latest fire safety rules for hydrogen as well as CNG and LNG fuel systems on all vehicle types plus their respective compression, storage, and dispensing systems.

NFPA 55

- *Title:* Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks
- *Relevance to:* Hydrogen storage, Gaseous and Liquid hydrogen
- *Status:* Published standard
- *Application:* Present requirements for designing systems including container locations, safety devices, marking, piping, venting, and other components. Incorporates the standards NFPA 50A and NFPA 50B.



NFPA 221

- *Title:* Standard for High challenge Fire Walls, Fire Walls, and Fire Barrier Walls
- *Relevance to:* General safety
- *Status:* Published standard
- *Application:* Addressing the requirements for fire walls and fire barriers.

Other standards and codes

CGA G-5.4

- *Title:* Hydrogen Piping at Consumer Locations
- *Relevance to:* Hydrogen supply, Pipeline interface
- *Status:* Published standard
- *Application:* Serve as a guide for materials and components selection to assist in installing a safe and effective hydrogen supply system at a customer's site. It covers the system criteria, cleaning, installation, testing, operation, maintenance and repair.

CGA G-5.5

- *Title:* Hydrogen Vent System
- *Relevance to:* General safety
- *Status:* Published standard
- *Application:* Presents design guidelines for hydrogen vent systems for gaseous and liquid hydrogen installations at consumer sites, and provides recommendations for their safe operation. Intended to be a useful reference for personnel who design, install, and maintain hydrogen vent systems.

CGA H-3

- *Title:* Cryogenic Hydrogen Storage
- *Relevance to:* Hydrogen storage, Liquid hydrogen
- *Status:* Published standard
- *Application:* Contains the suggested minimum design and performance requirements for shop-fabricated, vacuum-insulated cryogenic tanks (vertical and horizontal) intended for aboveground storage of liquid hydrogen.

ASME B31.3

- *Title:* Process piping
- *Relevance to:* Hydrogen supply, Pipeline interface
- *Status:* Published standard
- *Application:* Contains requirements for piping covering materials and components, design, fabrication, assembly, erection, examination, inspection, and testing. This Code applies to piping for all fluids including cryogenic fluids.



ASME B31.12

- *Title:* Hydrogen piping and pipelines
- *Relevance to:* Hydrogen supply, Pipeline interface
- *Status:* Under development
- *Application:* Contains requirements specific to hydrogen service in power, process, transportation, distribution, commercial and residential applications.



6. Appendix A – Hydrogen Accidents

6.1 Release of Hydrogen

The most common accidental release of hydrogen will be through leaks, holes, cracks and through broken or ruptured lines and hoses.

Gaseous hydrogen will form jets as a result of a positive pressure difference between the container and the environment. If released in an open space hydrogen will disperse into the air and rise to higher levels due to its buoyant nature. The dispersion and shape of the gas cloud formed depends on many factors such as, density differences, atmospheric conditions (e.g. turbulence) and the topography.

The release of hydrogen in obstructed areas does not allow free dispersion of the cloud. When gaseous hydrogen is released in closed areas, accumulation of the hydrogen poses a threat by forming a flammable mixture with air. Local geometry and ventilation systems in hydrogen plants will affect the dispersion mechanism of hydrogen (gaseous or liquid) in confined areas.

Liquid hydrogen has a boiling point well below the ambient temperature of air. Thus the release of LH₂ results in the spontaneous vaporization of a certain fraction of the liquid. Depending on local conditions and the thermodynamic state of the cryogen a two-phase flow will develop. Another effect of releasing LH₂ into the atmosphere is condensation and solidification of moisture present in the atmosphere. In a closed area the condensation of moisture may provide a warning sign of a hydrogen leak due to the formation of a fog. The phenomena that may occur after release of LH₂ into the environment are shown in the Figure 5.

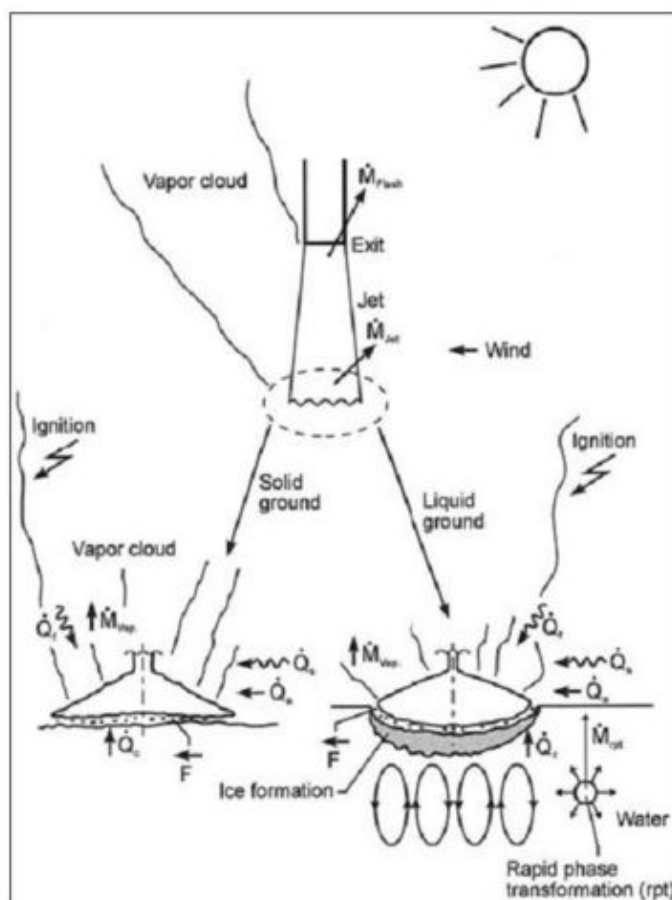


Figure 5: Physical phenomena occurring upon the release of cryogenic liquid

6.2 Causes of Hydrogen Ignition

Hydrogen is a highly flammable gas that reacts violently with halogens and oxidising agents. There are various sources for ignition of flammable mixtures of hydrogen. When ignited, parts of the combustible mixture are heated to temperatures high enough to cause adjacent uncombusted layers to react also, producing a flame that propagates throughout the mixture.

Hydrogen has a very low ignition energy, 0.017 mJ. With such a low ignition energy it is often difficult to determine the exact cause of the ignition. Some of the important causes of ignition are described below.

- **Electrostatic Electricity**

Insulating and non-conducting materials can be charged by static electricity. Hydrogen is extremely prone to ignition due to the accumulated charge on these materials. The maximum tolerable charge transferred for hydrogen is 10 nC, which is a very small quantity. A preventive measure for this includes the restriction on the size of the chargeable surface.



- **Electric Spark**

An electrical spark is produced as a discontinuous electric discharge across a gap (between two electrodes for example) when the voltage exceeds the breakdown voltage. A typical electrical spark of an ignition system can be divided into three zones, namely, breakdown phase, arc phase and glow phase. The efficiency of the electrical to thermal energy conversion of a gas decreases from breakdown to the glow phase due to the heat losses to the electrodes. For the initiation of the flame on the gas shortly after the breakdown, the chemical reaction should produce enough energy to overcome heat losses and the ignition kernel should grow beyond a critical size. The critical size is typically two times larger than the laminar flame thickness.

- **Auto-Ignition**

When a substance spontaneously ignites in a normal atmosphere without any external source of heat it is said to have auto-ignited. Auto-ignition is the result of exothermic energy of the oxidation reactions that self-accelerate at certain conditions to release a high amount of heat. The auto-ignition limit of a mixture depends on its composition, the size of the container, wall properties and internal flow conditions. Pressure has less effect on the auto-ignition limit than the temperature. The auto-ignition temperature of a stoichiometric hydrogen-air mixture under atmospheric conditions is 585°C.

- **Mechanical Friction and Impact**

Hydrogen has a high probability of ignition due to mechanical rubbing and impacts. It can be ignited due to the hot spots near the point of contact or due to the burning metal particles (sparks) produced. The ignition ability of the sparks depends on various factors such as size, material, velocity of motion, number of sparks, etc.

- **Ignition by Explosive**

An explosive is a powerful source of ignition. Although no data has been found in the literature about the minimum amount of explosive required for igniting a fuel-air mixture, a number of experimental and theoretical studies help in determining the amount. The mass of explosive required to initiate an unconfined detonation in a hydrogen-air mixture is very much less than that required for less reactive fuel/air mixtures. The minimum amount of tetryl required for initiating an unconfined detonation in various highly detonable fuel-air mixtures is given in the table below. For all the fuels listed below, except acetylene, the most detonable mixture lies within a stoichiometry range of between 1.1 and 1.3. For acetylene the value for the most detonable mixture is 2.05.



Table 15: Minimum amount of tetryl required for initiating an unconfined detonation

Fuel	Mass of tetryl (g)
Hydrogen	0.8
Methane	16000
Propane	37
Ethylene	5.2
Acetylene	0.4

- **Ignition by Open Flame and Hot Surface**

Open flames and hot surfaces are another sources of hydrogen ignition. With hot surfaces the hydrogen-oxidant mixture is ignited when a sufficiently large volume of the mixture reaches the auto-ignition temperature. This happens when the hot surface is at a temperature well above the auto-ignition temperature. The ignition behaviour of the flammable mixture depends on various factors, such as, the mixture concentration, ambient temperature, size and shape of hot surface, degree of confinement around the surface, convection currents across the surface and the material of surface. The hydrogen-air mixture is ignited at the temperatures of 640-930°C. Catalytic surfaces dramatically reduced the required surface temperature for ignition.

6.3 Accident Consequences

Hydrogen leakages and ignition affect the surrounding environment. The surrounding environment includes 'targets', such as human beings, buildings, adjacent equipment and so on. The effects following a release and the subsequent consequences for the target groups will depend on the accident scenario. For instance, direct ignition of pressurised hydrogen following a release from a hole will cause a jet fire aimed in a certain direction, potentially causing burns or fire. Delayed ignition of a confined mixture of hydrogen and air may cause an explosion or deflagration, with (additional) pressure effects. The major consequences of such accidents are briefly described below. Of course safety will be improved if the professionals dealing with hydrogen are aware of the hazards and their consequences.

- **Pressure Waves and Pressure Loads**

Chemical explosions are usually exothermal oxidation reactions. In such explosions the combustion energy is carried away by a blast wave uniformly distributed in all directions. The form of this wave changes according to the combustion processes (slow deflagration or fast turbulent flame or



detonation). The main features of the pressure wave are overpressure and pressure increase or decrease rate. The characteristic shape of the pressure-time function for detonation shock wave and deflagration pressure wave are shown in Figure 6. The hazard level after the explosion will depend upon these parameters. Thermal radiations and throw of debris are the typical consequences.

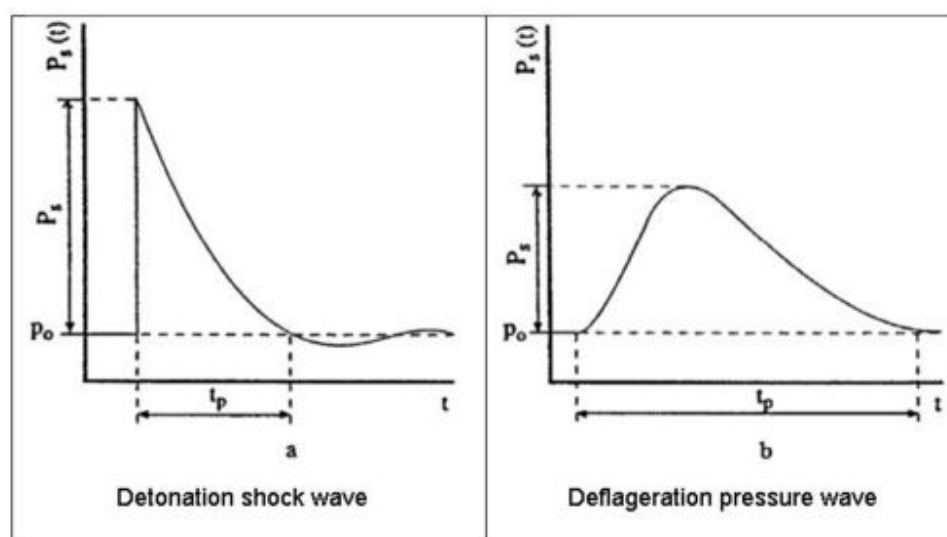


Figure 6: Characteristic shape of pressure-time function

Physical explosions (for example the bursting of pressure vessels) also create shock waves. This can occur due to expansion of the fluid due to excess heating. The destruction level will be high for higher liquid density. For the flammable liquids a fireball will be produced. Missiles and projectiles may be emitted from a physical explosion and may cause injuries, fatalities or damage at considerable distances depending on the explosion energy liberated. The explosions with major obstructions in their path are the most dangerous.

- **Interaction of Blast Wave with Structure and Structural Response**

When a blast wave produces an impact on a structure the consequences are a change in pressure, air movement, thermal radiations, flying missiles, etc. The hazard level depends on the distance between the structure and the blast centre. At close distances the structure is loaded with a high intensity pressure load over a localized region, whereas at greater distances the load intensity decreases but the load is distributed over a large surface area. The load due to the gas explosion is considered to be a dynamic load due to its short overpressure duration.

The interaction can be divided into two phases: defraction loading and drag loading. Defraction loading is characterized by direct and reflected pressure forces. The major pressure differences are developed from the edges of the structure. During the drag phase strong transient winds flow. The drag forces mainly affect smaller structures such as pipe work.



The blast wave produces dynamic loads on the structure. The response of the structure to these loads depends on its mass and stiffness. Detonations tend to excite the high natural frequencies of a building, whereas deflagrations are more effective for the lower frequencies.

- **Heat Radiation**

Hydrogen flame radiates significantly less infra-red radiations (heat, mainly due to water vapour bands) and virtually no visible radiations (light). Thus hydrogen burns with a pale blue almost invisible flame. But the flame also emits some amount of ultra-violet radiations. The lower radiation from a hydrogen flame makes the flame itself hotter than a hydrocarbon flame, and objects engulfed by a hydrogen flame tend to heat faster. However, the lower radiation of heat from the flame means that less heat is radiated to objects or people outside the flame. The consequence of the almost invisible hydrogen flame is that the human physical perception of the heat from a hydrogen fire does not occur until direct contact with the combustion gases. This problem is often resolved by throwing a dry fire extinguisher or dust into the air that will cause the flame to emit visible radiation.

- **Physiological Impact**

Skin contact with liquid hydrogen may cause severe cold burns. Prolonged skin exposure to cold hydrogen may result in frostbite. Small flashes or exposure to liquid hydrogen may damage the eye tissues. On inhaling the cold gas lungs may be damaged or breathing problems may arise. Prolonged exposure of the entire body to the cold can result in hypothermia.

Hydrogen is not poisonous, but as with any gas (except oxygen) a risk of asphyxiation exists, mainly in confined areas, as a result of oxygen depletion. Oxygen depletion may be a result of consumption in hydrogen combustion or condensation on very cold surfaces like liquid hydrogen pools. As a remedy the alarm levels are precisely set for 19% oxygen.

Direct exposure to the shock wave created due to an explosion may cause severe damages, especially in the lungs and inner ear. Indirect blast effects include effects generated by missiles and body translation.

Hydrogen fires may have inverse effects on human beings in two regions: at elevated air temperature and heat radiation. Below 70°C no severe effects can be found. Physiological responses at different elevated temperature are given in the table below.



Table 16: Physiological responses at different elevated temperature

Temperature (°C)	Effects and symptoms
127	Difficult breathing
140	Tolerance time 5 minutes
149	Mouth breathing difficult
160	Rapid unbearable pain with dry skin
182	Irreversible injury in 30 seconds
203	Respiratory systems tolerance time less than 4 minutes with wet skin

Above 150°C heat radiation is dominant. Depending on exposure time and radiation level consequences may vary from just pain, to severe (second and third degree) burns. Besides the infrared content hydrogen combustion produces UV radiation capable of sunburn-like effects. Hydrogen fires are difficult to see during daylight and due to the optical properties, the heat of smaller flames is felt late.

6.4 References

- Hysafe
Biennial Report on Hydrogen Safety
Version 1.0, June 2007



7. Appendix B – Hydrogen Safety Measures

7.1 Leak prevention measures

7.1.1 Safety procedures and training

Following proper (e.g. inherently safe) design and construction of the installation, maintenance and safety procedures and use of trained personnel are probably the most important preventive safety measures. Procedures and training methods are available in the chemical industries using hydrogen. Similar procedures have to be developed for the future hydrogen community.

People handling hydrogen or designing the systems for hydrogen should be familiar with the basic chemical, physical and hazardous properties of hydrogen. They should be also aware of human capabilities and limitations. The training should address the ignition sources, ignition prevention, materials to be used in a hydrogen system, transport and loading precautions. The system designers should be trained in the accepted standards and codes. The operators should have the knowledge of emergency safety procedures. The trained staff should always be kept informed of any changes in safety procedures.

In addition to the training of professionals who deal with hydrogen, it is also important to train the public, who are going to use the appliances based on hydrogen regarding the basic properties of hydrogen.

7.2 Measures preventing accumulation and ignition

If, despite all leak prevention measures, an accidental release of hydrogen occurs it is important to prevent any escalation, i.e. to minimise the amount that escapes, to prevent formation of a combustible/explosive atmosphere and to make sure ignition cannot occur. Some measures to achieve this are given below.

7.2.1 Ventilation

Ventilation is useful for preventing the formation of explosive atmospheres when hydrogen is dealt with in a confined space. The basic principle of ventilation is to bring fresh outside air inside the room and remove the inside air. The main advantages of using ventilation in hydrogen systems are:

- It prevents the accumulation of explosive gas inside the room
- It dilutes the explosive gas by bringing fresh air in
- It limits the resident time of explosive atmospheres



Ventilation can be of two types, forced (mechanical) and natural. Selection of the appropriate type depends on many factors. Natural ventilation functions due to temperature differences, winds and draughts. Hydrogen buoyancy and diffusion characteristics should be taken into account while selecting the size of openings and their positions. Although it is a cheaper option than the mechanical ventilation, it is less controllable and is affected by weather conditions at the openings. On the other hand mechanical ventilation can give constant and controlled flow. The main concern in mechanical ventilation is the sizing. It can be sized based on the previous experiences, based on calculations or based on hydrogen leak detection sensitivity. The main disadvantage of this type of ventilation is that the gas cloud and air will be more turbulent. In this case if the gas cloud is ignited then the explosions will be more severe. Using a combination of natural and mechanical ventilation can be a solution in some cases.

7.2.2 Inerting

Inerting is defined as the replacement of a sufficient proportion of oxygen contained in a gaseous atmosphere by an inert gas, to avoid the ignition of atmosphere. It is an important method for preventing the formation of an explosive atmosphere. However, it can be dangerous for the workers due to the asphyxiating property of inert gas. The main inerting methods include:

- Pressure swing method
- Volume swing method
- Flow-through method
- Displacement method

The inert state of the system should be properly controlled in order to make it safe.

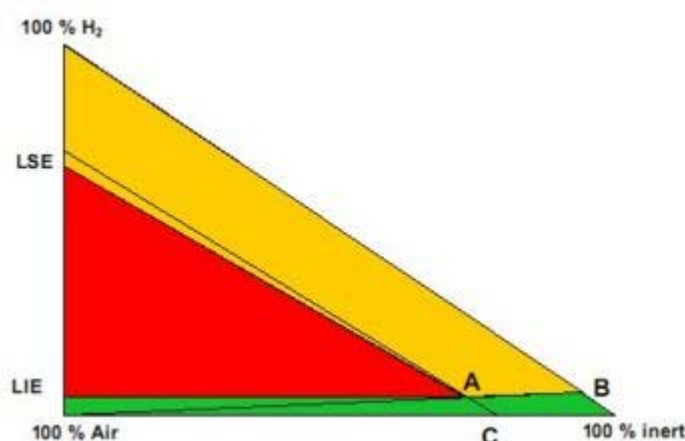


Figure 7: Schematic of Hydrogen-Air-Inert mixtures



The conditions of a hydrogenated atmosphere to be inert can be derived from the triangular diagram representing the hydrogen-air-inert mixtures (see Figure 7). The three coloured zones in the diagram represent:

- **Red zone** corresponds to the explosion area
- **Orange zone** corresponds to the mixtures which are not explosive but which may explode if they are mixed with air. They are relative inert.
- **Green zone** corresponds to mixtures which are not explosive and which will not explode if they are mixed with air. They are absolute inert.

7.2.3 Recombiners

A recombiner is a device that promotes the recombination of hydrogen and oxygen to form water. It serves to avoid, remove or, at least, slow down the formation of flammable mixtures formed due to leakage of hydrogen.

Recombiners can be classified as active and passive devices. Active recombiners use heat to initiate conversion. Passive recombiners use the property of hydrogen that, in the presence of catalysts like platinum and palladium, reacts with oxygen at low temperatures in an exothermic reaction. While using recombiners appropriate measures should be taken to keep the system temperatures below the self-ignition temperature. At present the two main application fields of recombiners are batteries and nuclear reactors.

7.2.4 Control of ignition sources

Electrical equipment, hot surfaces, open flames and static electricity are the possible ways of ignition of hydrogen and propagation of the flame. By controlling these sources explosions can be avoided.

7.3 Detection Measures / automatic shut down system

7.3.1 Detection of hydrogen leaks

A major hazard that may result from an unwanted release of hydrogen is the build up of an explosive atmosphere, in particular because of the relatively high flammability and low ignition energy of hydrogen. Thus appropriate detection measures should always be taken into consideration.

A sensor should be compatible with other safety equipments such as fire detection and suppression units. The sensing unit should not be an ignition source. The number and distribution of detection points depends mainly on the possible leak rate, amount of ventilation and area size. The detection system should include audible and visual alarms. Maintenance of the sensors is very important as it helps to keep the performance of the sensor at a high level. The main criteria for selecting a hydrogen sensor are listed below.



- Response time
- Detection range
- Durability
- Calibration / Maintenance
- Cross sensitivity
- Area coverage

Various types of hydrogen sensors are available today and are used depending on the operating conditions. The electrochemical, catalytic and thermal conductivity sensors are mainly used in the industries where hydrogen presents a risk. The semi-conductor-based sensor is most often used in research laboratories, whereas the MEMS (micro-electro-mechanic system) are used in the aeronautic and spatial industries. Some of the new emerging new technologies are palladium wire network, surface acoustic wave sensor, fibre optic with palladium micro mirror, etc. Different types of sensors used for detecting gaseous hydrogen and their short description is given in the table below.

Table 17: Hydrogen gas detectors

Type of de-tector	Description
Catalytic	A palladium and/or platinum catalyst is used to facilitate the combustion of hydrogen with oxygen. A sensing element detects the heat of combustion.
Electro-chemical	Liquid or solid electrolytes surrounding a sensing electrode and a counter electrode. Reaction with hydrogen product produces a current. The hydrogen gas must flow through a gas permeable membrane to reach the electrolyte.
Semi-conducting oxide	Hydrogen gas reacts with chemisorbed oxygen in a semiconductor material, such as tin oxide, and changes the resistance of the material.
Thermal conductivity	The rate of heat conduction from a heat source into the surrounding environment is dependent on the thermal conductivity of that environment.
Mass spectrometer	The gas is ionized and then accelerated through an electric field along a curved path. The amount of curvature induced by the electric field is dependent on the mass of the particle and is used to separate the particles by mass. A detector is placed in the path of the desired gas to be measured.
Sonic	Leaking gas can produce acoustical emissions in the range of 30 to 100 kHz, with 40 kHz being the most common.
Optical	The differences in the refractive index of various gases can be used for detection in sensors using optical interferometry.
Glow plugs	Glow plugs are not a true gas detection technique. When a combustible gas mixture exists, the glow plug ignites the mixture and then the fire is detected with heat sensors.



7.3.2 Detection of hydrogen flames

Hydrogen burns with a pale blue flame and does not emit visible light or smoke. Hydrogen flames emit significantly less heat. Thus it is difficult to detect the flames by human perception. Therefore hydrogen fire detectors are necessary. Special imaging systems are required for determining the size and location of the flame. Many times it is difficult to differentiate hydrogen related signals from parasitic signals. Thus to prevent false alarms human analysis may be advantageous. The hydrogen fire detectors should possess following main characteristics.

- Detect hydrogen flame at sufficient distance
- Detect small flames

Several types of detectors can be used, some of them being thermal detectors, some UV and some IR light detectors. A selection of available typical fire detectors, along with a short description, is given in a table below.

Table 18: Hydrogen fire detectors

Type of detector	Description
Temperature sensor	Thermocouple or resistance temperature device (RTD) that detects the heat of the fire.
Heat sensitive cable	Wire or fibre-optic based cable that changes resistance or optical properties if any portion of the cable is exposed to high temperatures or is burned through.
Optical	Ultra-violet, mid/near-infrared, and thermal infrared detectors for the detection of radiation emitted by the hydrogen flame. Infrared detectors must be optimized for hydrogen flame emissions that are not the same as hydrocarbon fires.
Thermal conductivity	The rate of heat conduction from a heat source into the surrounding environment is dependent on the thermal conductivity of that environment.
Broadband imaging	Thermal or mid-infrared imaging systems effectively image hydrogen flames but require an operator to interpret the image for detection of fire.
Narrow band imaging	Band-pass filters centred around the 950, 1100, and 1400 nm peaks can produce adequate images with low-cost silicon CCD cameras, image converter tubes, and vidicon systems. The filters must be carefully selected to block unwanted solar background while optimizing the imaging band for atmospheric transmission of the hydrogen fire radiation.
Broom / dust	Putting flammable objects or dust particles into a hydrogen flame will cause the flame to emit in the visible spectrum. Corn straw brooms, dirt, and dry fire extinguishers have been used for this purpose.



7.4 Mitigation measures

In case of fires the supply of hydrogen should be shut off as soon as possible. Hydrogen fires are not extinguished because of the danger of re-ignition or explosion. Adjacent metal surfaces should however be cooled with water or other means, as they can be the possible sources of re-ignition.

Water can be used as a fire extinguisher. Small fires can be extinguished with dry chemical extinguishers or with carbon dioxide, nitrogen, and steam.

7.4.1 Explosion venting of equipment and buildings

Venting of deflagrations is recognized as the most widespread and cost-effective explosion mitigation strategy. Various guidelines describing the venting of deflagrations are available.

7.4.2 Active inerting, suppression and isolating systems

Inerting, as described before, is used to dilute an explosive atmosphere to prevent ignition. In situations where no human activity is involved all of the air can be replaced by an inert gas. Typical inert gases are nitrogen, carbon-dioxide and some special mixtures, for example Inergen (mainly Ar and N₂, some CO₂), Argonite (Ar, N₂).

A chemical suppression or isolation system may also be used in quenching the flame. But they pose more challenges. The flames may propagate faster because of turbulence created by suppression systems. In isolation systems, early detection of fire and fast isolation is necessary.

7.4.3 Water based protection systems

Water can be used to extinguish the fire. Water spray systems can be provided for hydrogen storage containers, grouped piping and pumps where a potential fire hazard exists. The system should deliver a uniform spray pattern over 100% of the surface of the container, pump and adjacent piping. Deluge systems can also be used as a secondary fire protection.

7.4.4 Passive measures

These include soft barriers (use of polyethylene sheets to prevent the gas from entering in specific regions), barricades, fire walls, etc.

Barricades protect the uncontrolled areas from the consequences of failure of the hydrogen system. They also protect the hydrogen system from the hazards of nearby operations. They are intended as protective devices to arrest fragments or attenuate blast waves. The pressure vessels, piping and other components, used for both hydrogen systems and other systems, should be designed in such a way that they do not produce shrapnel. Instead the system leaks before the rupture. Barricades are more effective against fragments than in reducing overpressures. Thus it should be placed in a direct line of sight between the source of fragments and



the facility to be protected. The most common type of barricades include earthworks and earthworks behind retaining walls. Barricades reduce peak pressures and impulses behind the barricades. However blast waves can reform under some circumstances. Barricades should not cause excessive confinement that might lead to detonation rather than simply burning the escaping hydrogen.

Impoundment areas and shields should be used for diverting spills in order to control the extent of liquid and vapour travel caused by spills.

7.4.5 Emergency response measures

Hydrogen fires are not easy to extinguish. An effective emergency response requires the intended emergency response organisation to be prepared. Thus proper emergency response planning should be done.

To some extent, the emergency response measures adopted for the hydrogen technology may be similar to those used for other gaseous fuels. The emergency response plan should be based on the systematic identification of hazards, followed by an evaluation of the risk management. The aim should be to minimise the risk to people.

Communication is a key element in any emergency response plan. Effective communication involves explaining the technical measures, being organized, defining the procedures and training the emergency response team, all as part of the overall strategy. If communication fails, an effective emergency response is not possible.

7.4.6 Safety distance

A very effective way to prevent damage or harm from an accident is to observe a safe distance from the potential accident location. As will be clear from the above section, what a safe distance is will depend on the type of target (human beings, buildings, other installations) and its characteristics. It will also depend on the accident scenario that may occur. If no hydrogen can accumulate, an explosion will not take place. If accumulation can take place the accumulated volume will be important. Also hydrogen kept at higher pressure will give longer jet fires, when a leak occurs. All these factors will need to be considered when determining a safety distance. Nonetheless, below some safety distances that have been reported are reproduced. They should however only be used as a guideline, unless one is sure that the conditions and parameters used to calculate these distances are representative for one's own situation.



Gaseous Hydrogen (GH₂) Systems

The order of preference for the location of a GH₂ system are given in the table below.

Table 19: Order of preference for location of GH₂ system

Nature of location	GH ₂ Volume (m ³)		
	Less than 85	85 to 425	Over 425
Outdoors	I	I	I
In separate building	II	II	II
In special room	III	III	Not permitted
Inside buildings, but not in a special room and exposed to other occupancies	IV	Not permitted	Not permitted

Note: The location of GH₂ storage, as determined by the maximum total quantity of GH₂, shall be in the order of preference indicated by Roman numerals with I indicating the most preferred and IV the least preferred location.

As an other example, the safety distances for a GH₂ system with volume 85m³ or less located inside a building are tabulated below.

Table 20: Safety distances for a GH₂ system (85m³ or less volume located inside a building)

Distance from...	Distance (m)
Stored flammable materials	6.1
Open flames, electrical equipments or other sources of ignition	7.6
Ventilation intakes and air conditioning equipment	15.2
Other flammable gas storage	15.2
Concentrations of people	7.6
Another GH ₂ system of 85 m ³ or less	At least 15.2



Non-propellant Liquid Hydrogen (LH₂) Systems

The order of preference for locations of a non-propellant LH₂ system are given in the table below.

Table 21: Order of preference for location of non-propellant LH₂ system

Nature of location	LH ₂ Volume (litre)			
	150 to 189	190 to 1136	1137 to 2271	More than 2271
Outdoors	I	I	I	I
In separate building	II	II	II	Not permitted
In special room	III	III	Not permitted	Not permitted
Inside buildings, but not in a special room and exposed to other occupancies	IV	Not permitted	Not permitted	Not permitted

Note: The location of GH₂ storage, as determined by the maximum total quantity of GH₂, shall be in the order of preference indicated by Roman numerals with I indicating the most preferred and IV the least preferred location.

The safety distances for a LH₂ system (150 to 189 litres) housed inside building, not located in special rooms, and exposed to other occupancies are tabulated below.

Table 22 Safety distances for a LH₂ system (150 to 189 liters located inside a building)

Distance from...	Distance (m)
Flammable liquids and readily combustible materials	6.1
Ordinary electrical equipment and other sources of ignition including process equipment or analytical equipment	7.6
Air intakes, air conditioning equipment, or air compressor intakes	15.2
Storage of other flammable gases or storage of oxidizing gases	15.2
Welding, cutting operations and smoking	Prohibited

Propellant Liquid Hydrogen System

While deciding the location and safety distance of a propellant LH₂ system compatibility of LH₂ with other chemicals used and their volume should be considered. A chemical is said to be compatible with LH₂ if on storing them together the probability and magnitude of effects of accident are not high.



7.5 References

- Hysafe
Biennial Report on Hydrogen Safety
Version 1.0, June 2007
- NASA
Safety Standard for Hydrogen and Hydrogen Systems
Version NSS 1740.16