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## Basic considerations for the safety of hydrogen systems

*Considérations fondamentales pour la sécurité des systèmes à l'hydrogène*



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# Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.



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ISO/TR 15916 was prepared by Technical Committee ISO/TC 197, *Hydrogen technologies*.



 

# Introduction

Generally the public is not familiar with industrial hydrogen systems, nor does it have any experience with the new hydrogen systems under development today. The focus of this Technical Report is on the new energy applications. The intent is to provide, those unfamiliar with the technology, a basis upon which to understand the safety issues. This document concerns itself with applications that derive their utility from the chemical reactions of hydrogen and does not apply to applications based on nuclear processes.

Traditionally, hydrogen has been used extensively in the petrochemical and chemical industries and in smaller quantities in the electronics, steel-producing, glass-making, and food hydrogenation industries. In energy applications, the only significant use of hydrogen has appeared in space programmes. This is about to change, given the promise that hydrogen brings as an efficient energy carrier and an energetic fuel with minimal environmental impact. Systems are being developed that produce hydrogen from primary energy sources such as sunlight, wind power, biomass, hydro and fossil fuels, for use in energy applications for home and office heating, generation of electricity, and transportation.

The safe use of hydrogen as a fuel is a primary ISO goal as it seeks to facilitate the rapid emergence of these hydrogen technologies. A key element in the safe use of hydrogen is understanding its unique safety-related properties and that there are acceptable engineering approaches to controlling the risks associated with the use of hydrogen. This Technical Report describes the hazards associated with the use and presence of hydrogen, discusses the properties of hydrogen relevant to safety, and provides a general discussion of approaches taken to mitigate hydrogen hazards. The aim of this Technical Report is to promote the acceptance of hydrogen technologies by providing key information to regulators and by educating the general public on hydrogen safety issues.



The development of International Standards to eliminate barriers to international trade and to simplify the arduous regulatory process by providing hydrogen-specific standards to allow early implementation for rapidly emerging technologies was among the needs identified in the ISO/TC 197 Business Plan. This Technical Report is one of many documents that have been developed, or are in the process of being developed, by ISO as a response to the needs described in the ISO/TC 197 Business Plan. Detailed safety requirements associated with specific hydrogen applications are treated in separate International Standards. This Technical Report provides an informative reference for those separate standards as a common, consistent source of safety-related hydrogen information. This should result in a reduction in duplication and possible inconsistencies in these separate standards.

The considerations presented in this Technical Report are broad, general, and attempt to cover all aspects of hydrogen safety. The degree to which these guidelines are applied will vary according to the specifics of the application (such as the conditions and quantity of hydrogen involved, and the way in which the hydrogen is used). Industrial users may find large portions of the guidelines, presented herein, applicable for their operations. It is not expected that the general public will be required to apply this degree of knowledge to safely operate a hydrogen appliance. It is anticipated that good appliance design, coupled with appropriate care in installation, will reduce the degree of safety considerations to levels that are deemed acceptable by the public for common appliances in use today. The manufacturers of hydrogen appliances will need to consider these guidelines to tailor sufficient specific information for the operation of their appliances, in the environment in which they are to be used, and for the audience that will use them. Readers are encouraged to keep these points in mind as they consider the information presented in this document. Hydrogen has been safely used in many different applications over many years. Adherence to the principles presented in this Technical Report can lead to a continuation of the successful use of hydrogen.

# Basic considerations for the safety of hydrogen systems

## 1 Scope

This Technical Report provides 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. Detailed safety requirements associated with specific hydrogen applications are treated in separate International Standards.

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11114–4:— [1)], *Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement*



ISO 14687:1999/Cor 1:2001, *Hydrogen fuel — Product specification*



## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in Annex E apply.

## 4 Overview of hydrogen applications

### 4.1 Basic hydrogen infrastructure

#### 4.1.1 Categories of infrastructure

Conceptually, the purpose of hydrogen applications can be categorized as the

a) production,

b) storage and transport, and

c) use of hydrogen.

Some applications may involve all three categories.

#### 4.1.2 Production

The primary means of bulk production of hydrogen today involves chemical processes such as steam reforming of natural gas, displacement of hydrogen from acids by metals, and electrolysis of water. In the

1) To be published.

 

future, photochemical processes and genetically tailored plants may also become practical means of producing hydrogen.

Different means of hydrogen production are used for special applications. For example, some applications seek to minimize storage or hazards by supplying hydrogen (or oxygen with hydrogen as a byproduct) on demand. Several electrolyser technologies are under development for this purpose. Ultra-pure research-grade hydrogen and oxygen outputs are possible from these systems.

### 4.1.3 Storage and transport

#### 4.1.3.1 General

Hydrogen that is produced at a site for use elsewhere has to be processed into a state which can be readily stored and transported to consumer applications. Compared to conventional fuels, hydrogen's low density under ambient conditions and its low boiling point make it difficult for storage of sufficient quantities to suit typical applications. Proven methods of increasing hydrogen storage density include handling hydrogen as a pressurized gas or a refrigerated liquid, and using ground transport, water transport or piping for delivery. Only very small quantities of hydrogen are permitted for transport by commercial aircraft. Piping of hydrogen is used in industrial settings. In the past, hydrogen had widespread use as a component of “town gas” that was piped to street lighting. Today hydrogen is not commonly distributed in piping for commercial or public applications. This may change with more widespread use of hydrogen.

#### 4.1.3.2 Gaseous storage and transport

Where small to intermediate quantities of hydrogen are required, gaseous hydrogen is compressed and stored in high-pressure containers. Conventional storage tanks of aluminium and steel are routinely used to contain hydrogen at pressures up to 40 MPa [2]. Tube trailers, designed for highway service, transport quantities in the range of 300 000 litres to 500 000 litres.



#### 4.1.3.3 Liquid storage and transport

Another approach to hydrogen storage is to condense the hydrogen into a liquid or slush (solid hydrogen mixed with the liquid). This requires chilling the hydrogen to cryogenic temperatures (about 20 K) to form a liquid and below 14 K to form slush hydrogen. At present, slush hydrogen has only been considered as an aerospace propellant and the economics for production do not favour its more extensive use. To maintain the hydrogen as a cryogenic fluid in storage, exposure to ambient-level heat has to be minimized or excessive loss of hydrogen will result. This isolation from heat is best accomplished using a vacuum-jacketed container, not unlike a thermos bottle. No isolation is perfect, and without capture and reliquefaction, the slow loss of hydrogen to the atmosphere has to be accepted unless the usage rate exceeds the boiling rate, or alternatively a boil-off management system is adopted. Transport of liquid hydrogen is accomplished in vacuum-jacketed containers by truck, railcar or tanker, and upon delivery it is transferred to vacuum-jacketed cryogenic storage vessels at point-of-use sites. Storage systems as large as 3 700 000 litres are in use for aerospace applications. However, cryogenic liquid hydrogen cannot be stored indefinitely unless it is refrigerated, which is not economical for most applications. Liquid hydrogen is either used or eventually lost to the environment.

#### 4.1.3.4 Other storage options

Chemical compounds rich in hydrogen bonds, hydrogen mixed with other fuels, hydrides, and materials with high surface adsorption of hydrogen may find applications in hydrogen storage systems (see Annex D). A device called a reformer can be used to obtain the hydrogen from a storage compound. Where these systems use chemicals other than hydrogen, special safety considerations unique to the materials should be applied in

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2) Throughout this Technical Report there are frequent references to pressures in units of kilopascals (kPa) and megapascals (MPa) and temperatures in units of kelvin (K) with values that may be unfamiliar. To help readers relate to the values of these units, conditions familiar to all are noted here. Atmospheric pressure at sea level is 101,3 kPa or 0,1 MPa (14,7 psia), and the freezing point temperature of water is 273,15 K (0 °C or 32 °F).

 

addition to the considerations for hydrogen. Such considerations are beyond the scope of this Technical Report.

#### 4.1.3.5 Vehicular storage systems

The volume of hydrogen and the mass of containment vessels for high-pressure gaseous systems or cryogenic systems are challenges for vehicular fuel storage design. To reduce the volume and mass of fuel tanks proposed for hydrogen-powered vehicles, lightweight composite materials are being developed. At present, containment pressures of 35 MPa are being used with fuel-cell vehicles. Technologies for higher containment pressures of up to 70 MPa, using composite materials, are being developed.

### 4.1.4 Hydrogen use applications

Hydrogen use applications include fuel cells, internal combustion engines, turbines, rocket thrusters, and all applications that use these components.

A variety of energy applications based upon electrolysers and hydrogen fuel cell systems will soon be commercially available. These range from small portable systems designed to replace standard batteries such as “D” cells to 1 kW, 10 kW, and larger systems designed for remote or distributed energy systems necessary to power homes, remote villages, or augment the power grid. Portable systems typically rely on a hydrogen supply that is replaced or recharged. Larger systems are envisioned with integrated renewable energy sources such as wind power systems or photovoltaic systems. These systems are both producers and consumers of hydrogen, as they convert electricity to hydrogen, store the energy in a storage media, and then convert it back to electricity when it is needed. This is done with an electrolyser that converts the renewable energy into hydrogen. The hydrogen is processed for storage and used with a fuel cell or a combined heat-and power-generating unit to produce electricity on demand. Such systems may be further integrated to capture waste heat for heating or industrial processes. These applications consist of a component that performs the primary function and components that control, make safe, supply hydrogen, store hydrogen, or otherwise support the primary function.



## 4.2 Typical hydrogen system components

### 4.2.1 General

In a generic hydrogen system, there are primary and auxiliary components integral to hydrogen safety. Examples of components that perform primary functions are the rocket thrusters within rocket motors for aerospace applications, the cell stacks within fuel cells for energy applications, the internal combustion engines for transportation applications, and the catalytic converters within cooking stoves for residential use.

Auxiliary components that provide essential support for primary functions may possess all or some of the following:

a) hydrogen storage or a source of hydrogen, and oxidizer storage or a source of oxidizer;

b) fluid delivery lines to connect hydrogen and oxidizer to the reaction system;

c) flow controls;

d) pressure-relief systems that are incorporated into the design of components a), b) and c);

e) detection components.

### 4.2.2 Storage vessels

The design and function of storage vessels and their components should reflect the type of service, such as either high-pressure gaseous vessels or cryogenic liquid vessels. Quantities greater than 7 500 litres under standard conditions are usually located outdoors or in specially designed structures. Vessel construction should meet specific national code requirements for pressure vessels. Storage vessels that contain cryogenic hydrogen use special insulation or vacuum jacketing. Vacuum needs to be maintained with vacuum pumps.

### 4.2.3 Fluid delivery lines, piping, joints and seals

Piping and seals need to be suitable for hydrogen over the life of the system. Stainless-steel lines are commonly used. Hydrogen permeates most materials and will readily leak through any small breach in a system. Hence, welded joints are preferred where leaks cannot be tolerated. Where a joint or a seal may require periodic opening, some form of hydrogen gas or flame detection is desirable, if permeation or a leak could lead to a flammable mixture.

### 4.2.4 Flow controls

A variety of components are used to control the flow of hydrogen within the system. Valves, check valves and regulators are the most common mechanical components. These may be manually operated or remotely controlled using electric or pneumatic actuators. Actuators need to be specifically designed so as not to be a source of ignition for released hydrogen. Check valves are used to prevent unwanted back flow. Regulators control the pressure of fluids within a system. Controls also include fluid sensors such as pressure gauges, flow meters, liquid level indicators, and other control systems.

### 4.2.5 Pressure-relief systems

Vessels and piping that confine or potentially may confine hydrogen should be protected against overpressurization with a pressure-relief system. Examples of circumstances that may lead to overpressurization by a hydrogen system are fire or failure of a regulator, which releases high-pressure hydrogen into a part of the system designed for a lower pressure. The pressure-relief system typically uses pressure-relief valves and burst (rupture) disks to direct overly pressurized hydrogen to a vent system. A pressure-relief valve possesses a spring-loaded seal that opens when a set pressure is exceeded. A burst disk is a similar device except pressure relief occurs upon rupture of a pressure-sensitive diaphragm. This device is usually used in parallel with a pressure-relief valve as a fail-safe path for overpressurization. The burst disk must be replaced if it is ruptured. Even the evacuated spaces in vacuum-jacketed lines in a cryogenic system need to be protected from failures that could introduce high-pressure hydrogen.



### 4.2.6 Detection components

Outside of the hydrogen system, the control system can monitor the presence of hydrogen gas or hydrogen fire. A variety of technologies are available to detect hydrogen gas. Hydrogen detectors are typically placed above a probable leak point where hydrogen may accumulate, and at the intake of ventilation ducts. Infrared (IR) cameras can image heat over a wide field of view. Ultraviolet (UV) detection is used to specifically detect hydrogen flame, but careful collimation of the sensor's field of view is required because sunlight or welding activities can readily trigger these detectors.

### 4.2.7 Other components

Hydrogen systems can use catalytic converters and “getters” in order to remove unwanted or excess hydrogen. Filters can be used to remove impurities from hydrogen in the system or from auxiliary systems. For example, the proton exchange membrane (PEM) stacks used in electrolysis and fuel cells require pristine water that is carefully filtered and deionized. Heat exchangers, coolers and radiators may be required in hydrogen systems.

### 4.2.8 Considerations for conditions external to the system

Inherent in all hydrogen designs are

a) considerations for the conditions in which the system is operated,

b) fail-safe operation that accounts for potential modes of failure, and

c) long-term plans, which cover the operational life of the system.

For example, fixed-hydrogen systems must be located according to specific requirements found in national safety standards. These standards identify specific construction and materials requirements for structures, based on the quantity of hydrogen, whether it is gaseous or liquid, and the desired location for the hydrogen storage. Hydrogen designs should account for all possible circumstances anticipated during the life of their operation, and the designs should place the system in a safe state for all reasonable failure modes.

### 4.3 Hydrogen fuel

Hydrogen fuel possesses impurities left by the production process or introduced during storage and post-production handling. The quantity and type of impurities may adversely affect hydrogen-consuming systems; hence, ISO 14687:1999/Cor 1:2001 was published to specify the quality characteristics of hydrogen fuel to ensure uniformity of hydrogen fuel products produced for vehicular, appliance, or other fuelling applications. This specification classifies hydrogen fuel according to three types, I, II and III, for gaseous, liquid, and slush hydrogen, respectively. Type I is further divided into Grades A, B and C, which specify increasing levels of purity. The cost of storage and handling increases with a reduction in the impurities. ISO 14687:1999/Cor 1:2001 specifies impurity levels for water ($H_2O$), total hydrocarbon (THC), oxygen ($O_2$), argon (Ar), nitrogen ($N_2$), helium (He), carbon dioxide ($CO_2$), carbon monoxide (CO), mercury (Hg), sulfur (S), and permanent particulates.

### 4.4 Environmental effects

The environmental effects arising from the use of hydrogen systems are anticipated to be benign. With very few exceptions, pure water is the only reaction product. The exception is air-breathing systems that combust hydrogen at high temperatures and can create nitrogen oxides ($NO_x$). PEM fuel cells and electrolysers produce only water, and some electrolyser–fuel cell systems can capture most of the water produced for re-use. This formation of water from hydrogen/oxygen reactions is well known by the outdoor observers of NASA Space Shuttle launches, who have, when the wind is right, experienced rain out of a clear blue sky. At some future point, if hydrogen-powered transport becomes the dominant transportation means, then areas with high usage such as in cities may experience an elevation in humidity, or hydrogen-powered vehicles may be required to condense and capture the water emissions. This elimination of pollutants (such as CO, $CO_2$ and $NO_x$) as a reaction byproduct is one of the primary benefits from using hydrogen systems.



## 5 Safety considerations for the use of gaseous and liquid hydrogen

### 5.1 General

The unique properties of hydrogen, which make it valuable as an energy carrier or fuel, require proper design and operation in order to avoid the inadvertent creation of hazards.

The combination of hydrogen behaviour and the particular attributes of a hydrogen system determine the nature of the potential hazards that the operators face. For instance, whether the system operates with high-pressure hydrogen or operates at cryogenic temperatures defines the nature of the potential hazards.

The primary hazards and issues associated with hydrogen systems can be categorized and prioritized as follows:

a) combustion;

b) pressure;

c) low temperature;

d) hydrogen embrittlement;

e) exposure.

This list simply stresses where concern should be focussed in the design and operation of hydrogen systems. Exposure is placed last because of the realization that any of the first four hazards can result in consequences that far overshadow the consequences of exposure. Note this list does not detail specific hazards, or the possibility that different elements within the list can act together to form an overall hazard. These hazards and issues should be considered when evaluating hydrogen hazards.

Because the operation of hydrogen systems may involve many people, the effort should be considered a team effort. Anyone involved with the use of hydrogen should be familiar with the safety-related properties of hydrogen and the hazards associated with those properties.

## 5.2 Hazards involved as a consequence of the properties of hydrogen

### 5.2.1 General

A discussion of the correspondence between hydrogen properties and their associated potential hazards provides insight into safety issues. While the concern for combustion hazards is common to all hydrogen systems, the way these hazards manifest themselves arises from whether the hydrogen is used as a liquid or a gas.

Some general safety-related properties of gaseous and liquid hydrogen are discussed below. Additional information on hydrogen's general safety-related properties as a gas and a liquid are summarized in Clause 6 and some selected property data is tabulated in Annex A.

### 5.2.2 Gaseous hydrogen



Gaseous hydrogen has neither a characteristic colour nor odour. It forms the smallest, lightest molecule of any gas. As a result, gaseous hydrogen better permeates through materials, passes through smaller leak paths, diffuses more rapidly in surrounding media, and has greater buoyancy than other gases. The consequences, arising from these properties, are that released hydrogen rapidly rises and diffuses, but if confined, it can accumulate in high spots.

Hydrogen vessels and piping systems require good seals, and leaks are always a concern. Furthermore, hydrogen leaks are difficult to detect with unaided senses, if they do not make an audible noise. It has been demonstrated that hydrogen can permeate slowly through confined materials. The permeation rate varies for different kinds of materials. For metals such as steel, at ambient temperature, the rate is extremely low with insignificant quantities permeating over very long periods of time. Some caution should be observed with polymeric materials, which allow greater permeation and thus significant quantities of hydrogen can accumulate, if the flow enters into a small unventilated volume. Hydrogen gas dissolved in a liquid can permeate into adjoining vessel materials.

Because of hydrogen's low density at ambient conditions, it is typical to store and transport gaseous hydrogen at elevated pressures.

### 5.2.3 Liquid hydrogen

Liquid hydrogen appears clear with a slight blue tinge. It possesses an extremely low boiling point, a low density, a low heat capacity, and a large volumetric expansion when heated to a gas.

Liquid hydrogen with its low boiling point of 20,3 K will rapidly boil or flash to a gas if exposed or spilled into an ambient temperature environment (300 K). Warming liquid hydrogen to an ambient temperature gas can lead to very high pressures, when it is confined.

Another consequence of liquid hydrogen's low temperature is that, with the exception of helium, all gases will be condensed and solidified should they be exposed to it. Leaks of air, nitrogen or other gases past valve seals, into direct exposure with liquid hydrogen can lead to several hazards. The solidified gases can plug pipes and orifices and jam valves. The reduction in volume of the condensing gases may create a vacuum that can draw in yet more gases, in a process known as cryopumping. Should the leak persist for long periods, large quantities of material can accumulate displacing the liquid hydrogen. At some point, should the system be warmed for maintenance, these frozen materials will re-gasify possibly resulting in high pressures or combustible mixtures.

Outside of the liquid hydrogen system, un-insulated pipes and vessels containing liquid hydrogen can condense gases such as air into solid and liquid forms on their outer surfaces. The liquid condensate flows and looks like liquid water. Should the oxygen component within liquid air come in contact with combustible materials, fire and explosion hazards can occur.

## 5.3 Factors involved in combustion hazards

### 5.3.1 Aspects of combustion

The principle hazard presented by hydrogen systems is the uncontrolled combustion of accidentally released hydrogen. This holds true because of the high potential for leaks and formation of combustible mixtures, the ease of ignition of these mixtures, and the potential for high-energy releases that can occur as a fire or an explosion.

For hydrogen to combust, two additional elements need to be present: an oxidizer such as air and a source of ignition. Each of the factors necessary for combustion (a fuel, an oxidizer and an ignition source) can be represented on one of the three sides of a triangle, a concept known as a fire triangle. Mixtures of hydrogen and oxidizers are flammable over a wide range of concentrations, pressures and temperatures. Mixtures are readily ignitable near stoichiometry. A variety of common physical processes (open flames, hot surfaces, friction, etc.) can act as sources of ignition, including static sparks that are below the threshold of human sensation. Because of the ease of ignition of hydrogen/oxidizer mixtures, most methods for the reduction in risk of hydrogen combustion rely on separation of hydrogen from the oxidizers.



There are several modes of hydrogen combustion: fire at a point source, deflagration and detonation. Each can present potential hazards and they are dependent on the circumstances of how the hydrogen is exposed to an oxidizer. In standard terrestrial applications, air is an omnipresent oxidizer. Electrolysers and some fuel-cell systems may have the potential to mix pure or enriched oxygen with hydrogen.



Basic hydrogen combustion data are provided in Annex B.



### 5.3.2 Fires

A source of hydrogen, for example a leak, when surrounded by an oxidizer such as air, can be ignited to produce a fire much in the same fashion as a Bunsen burner. Depending on the rate of release of hydrogen from the source, fires can manifest themselves with outputs ranging from that of a small candle to large high-pressure jet engines. If a fire occurs in a sealed region, a pressure rise will occur. In contrast to hydrocarbon fuels such as gasoline, which generate most of their radiation as visible light and heat, the hydrogen flame radiates significantly less heat, is practically invisible, and emits ultraviolet radiation, which can cause something similar to sunburn. Light passing through the thermal gradients in the flame sometimes casts a shadow.

When the fire triangle is satisfied, a hydrogen fire is possible. The heat released by an uncontrolled hydrogen fire can be very destructive to its surroundings. In a sealed region, hydrogen/air fires can result in a pressure increase as much as 8 times the initial pressure for a stoichiometric mixture. Aside from the release of energy and hot gases, there are several other consequences of these properties from a safety perspective. First, hydrogen combustion is almost visually imperceptible under artificial light or daylight. Equally important is that the human physical perception of heat does not occur until there is direct contact with the combustion gases. Operations in proximity to hydrogen flames should also consider UV exposure. Thus, without detection equipment, the first indication of a possible flame is usually the hissing noise of the gas leak and perhaps the shadows from the thermal gradients of the flame.

### 5.3.3 Explosions

#### 5.3.3.1 General

When hydrogen and an oxidizer are allowed to form a mixture prior to ignition, the ensuing flame will move rapidly throughout the combustible region. The flame can combust by two different processes: deflagration or detonation. To our physical senses, both processes can be perceived as an explosion. The shock wave and hot product gases impinging upon the surroundings outside of the combustible region can also be referred to as a blast wave. There is no combustion in the blast wave, but it physically displaces the surrounding (non-reacting) gases and loose material (shrapnel). To our physical senses, the blast wave is indistinguishable from the deflagration and detonation processes.

#### 5.3.3.2 Gaseous deflagration

A deflagration is a flame that propagates through a combustible medium at a rate less than the speed of sound within the un-combusted media. The criteria for flammability are the same as those for fire. The presence of confining surfaces such as pipe or vessel walls can elevate the pressure and can promote an increase in the speed of the flame to hundreds of metres per second in a process known as flame acceleration. If the flame reaches high speed and encounters turbulence, the deflagration process can transform into a detonation. This is called a deflagration-to-detonation transition (DDT).

#### 5.3.3.3 Gaseous detonation

The detonation process differs from deflagration in that a shock wave is integral to the combustion process. Detonations propagate at a rate greater than the speed of sound within the un-combusted media, typically 1 500 m/s to 2 000 m/s, and they also produce high pressures. As a more energetic process, detonation requires a richer hydrogen-oxidizer mixture and sources of ignition with significantly more energy than is needed for fire or deflagration. For example, in the open, a highly explosive charge is required to initiate a detonation in hydrogen-air mixtures. However, the presence of confining surfaces can act to expand the range of mixtures that are detonable and significantly reduce the ignition energy necessary for detonation. Detonations that impinge on surfaces are reflected such that the superposition of the incident and reflected pressure waves are cumulative, producing greater pressures of 2 to 3 times the incident shock pressure.



#### 5.3.3.4 Liquid- or condensed-phase detonation

Solid oxidizer mixed in liquid hydrogen can be made to detonate with a yield similar to that of explosives. For this form of combustion to occur, the mixture needs to be subjected to an initiation source with an energy equivalent to a highly explosive charge. There is a lack of well-developed information characterizing this process.



#### 5.3.3.5 Safety considerations

Safety considerations that arise from the gaseous hydrogen deflagration and detonation behaviour include understanding

- whether system failures can lead to hydrogen-oxidizer mixtures,
- the influence of confinement both within and outside of the system, and
- the consequences of formation of high pressures, high temperatures and rapid propagation of flame fronts.

The conditions necessary for liquid-phase detonation are not typically found in standard equipment. Deflagrations of gaseous hydrogen-air mixtures can produce pressures as much as 8 times the initial pressure. Detonation of hydrogen-air mixtures can produce pressures as much as 16 times the initial pressure and with reflection, pressures 50 times the initial pressure. One important consideration is that the relief systems, designed to protect hydrogen systems from overpressure, rely on sensing the build-up of pressure. Because detonation waves move faster than the speed of sound, relief systems do not sense the approaching wave and cannot react in time to protect the system from the rapid pressure rise.

## 5.4 Factors involved in pressure hazards

### 5.4.1 General

Many hydrogen applications contain hydrogen in a gaseous form under high pressure or as a cryogenic liquid. In both of these forms, hydrogen presents several pressure-related hazards, primarily overpressure that should be addressed in the design and operation of a hydrogen component or system.

 

### 5.4.2 Gaseous hydrogen

Gaseous hydrogen can be compressed to very high pressures. Under such pressures, the hydrogen has considerable potential (stored) energy. The release of this energy can generate a blast wave depending on the energy release rate.

### 5.4.3 Liquid hydrogen

A sudden increase in volume is associated with the phase change of liquid hydrogen to gaseous hydrogen, and still another gradual volume increase occurs for gaseous hydrogen that is allowed to warm from liquid temperature to ambient temperature.

### 5.4.4 Safety considerations

In a liquid hydrogen system, the increase of volume for the phase change of liquid hydrogen to gaseous hydrogen and the expansion of heated gas can overpressurize, in a matter of seconds, containment structures such as a storage vessel or piping to the point of bursting. This type of hazard is commonly addressed by the use of relief devices in all parts of a hydrogen system where liquid or cold gaseous hydrogen can be trapped, such as between two valves. Inadequate relief can lead to catastrophic failure of the component, resulting in a blast wave and/or high velocity shrapnel.

The location of a compressed gas storage vessel at a safe distance from personnel and other facilities should also be considered essential, as a consequence of this hazard.

## 5.5 Factors involved in temperature hazards



Many materials experience a reduction in size and a drastic decrease in their ductility, as well as a decrease in their specific heat when they are cooled to liquid hydrogen temperatures.



Care should be taken to ensure that structural materials retain sufficient toughness, and that the system design accounts for the shrinkage of materials. The consequence of material failure in a hydrogen system is the release of hydrogen either internal to the system (through a valve seat, for example), or external to the system (through seals, for example).

## 5.6 Factors involved in hydrogen embrittlement hazards

### 5.6.1 Hydrogen embrittlement

Materials used in vessels or other components can undergo a significant loss of their structural strength when exposed to hydrogen. This phenomenon is known as hydrogen embrittlement, and occurs when hydrogen or hydrogen compounds permeate into the lattice structure of the material. At the atomic level, for embrittlement to occur, hydrogen molecules must first dissociate into atoms before they can diffuse into the metallic structure. At temperatures close to ambient, a number of metallic materials are susceptible to hydrogen embrittlement, particularly those with a body-centred cubic crystal lattice structure. This is a particular problem with many ferritic steels if they are subjected to mechanical stresses. The process takes place on freshly generated metallic surfaces that are likely to form on surface defects or other stress raisers as a result of stress-induced local plastic deformation processes. Impurities such as hydrogen sulfide dissociate into atomic hydrogen even more easily than molecular hydrogen.

Failure to address embrittlement concerns can result in catastrophic failure of containment structures (such as a Bourdon tube in a pressure gauge, or a storage vessel). Hydrogen embrittlement is counteracted by proper design and selection of materials (see Annex C).

### 5.6.2 Hydrogen attack

At temperatures above 200 °C, many low-alloyed structural steels can suffer from another hydrogen-related embrittlement phenomenon known as hydrogen attack. It is a non-reversible degradation of the steel microstructure caused by a chemical reaction between diffusing hydrogen and the carbide particles in the