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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

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

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[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 steel, resulting in the formation of methane. Severity of the hydrogen attack increases with increasing temperature and pressure.

5.7 Health hazards

5.7.1 Cold burns

Direct skin contact with cold gas or liquid hydrogen can lead to numbness, a whitish colouring of the skin, and to frost bite. An additional consideration is that prolonged exposure of the entire body to cold can result in hypothermia. Personnel should not touch cold metal parts and they should wear protective clothing.

5.7.2 High temperature burns

Direct or near-direct contact with combusting hydrogen and hot product gases can result in severe burns. The flame temperature of a stoichiometric hydrogen/air mixture is 2 323 K. The hazard of exposure to this high temperature is compounded by the physical characteristics of hydrogen combustion in air. Hydrogen flames in air are difficult to see in daylight. Moreover, because of the low flame emissivity, or the characteristic that little infrared radiation is produced by the combustion, the personnel do not sense the heat even when they are in close proximity to the flame.

5.7.3 UV-exposure burns

Hydrogen combustion produces UV radiation capable of sunburn-like effects. Personnel working in proximity to hydrogen combustion sources such as flare stacks should wear appropriate personnel protective clothing/equipment to protect the face, eyes and skin.

5.7.4 Asphyxiation

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.

Smoke inhalation, one of the major causes of injury and a primary consequence of a fire, is considered less serious in the case of hydrogen, because the sole combustion product is water vapour. However, secondary fires can produce smoke or other combustion products that present a health hazard.

5.8 Team approach and training needed for the safe use of hydrogen

The primary cause of accidents with hydrogen systems is due to human error (see 7.1.2). The basis for an accident and the extent of its consequences may lie not only with a system's immediate operators, but may be due in part to how hydrogen and its particular applications are viewed by all personnel in an organization. The limitations of a particular hydrogen system design, its operation and maintenance requirements, and the potential for exposure of the personnel and the public to hazards should be appropriately understood by all.

Safe handling of hydrogen and hydrogen systems is a team effort requiring effective communications, training, and organizational control. Individuals at all levels should receive training consistent with their involvement and responsibility. When large quantities of hydrogen are handled, it may be necessary to coordinate the activity with the surrounding community, including fire fighters and community emergency response planners. Measures taken by prudent organizations are described in Clause 7.

6 Basic properties of hydrogen

6.1 General properties

6.1.1 Atomic and molecular properties

Hydrogen, named from the Latin words hydro (water) and genes (forming), is the simplest and most abundant element in the universe. Atomic hydrogen can possess any of three possible atomic weights or isotopes:

protium, deuterium or tritium. Protium, with an atomic mass equal to 1, is the most common isotope. As a pure substance, hydrogen exists as a molecule, designated H_2, in which two hydrogen atoms have formed a covalent bond. There are two molecular forms: orthohydrogen and parahydrogen. Bulk hydrogen, whether in gaseous or liquid form, is a mixture of ortho-hydrogen and parahydrogen in which the temperature determines the equilibrium quantities of each form. At normal temperature and pressure (NTP), parahydrogen makes up 25 % of the total mixture. This mixture is known as normal hydrogen. At lower temperatures, equilibrium favours the existence of more parahydrogen, with liquid hydrogen at 20 K composed of 99,8 % parahydrogen.

This apparent complexity of different isotopes and molecular states has little effect on most non-nuclear-energy safety considerations. Deuterium is found only in trace quantities in nature, and tritium is produced in nuclear reactors. The chemistry of hydrogen, and in particular the combustion chemistry, is little altered by the different atomic and molecular forms. Non-nuclear energy applications typically use thermophysical data that applies to normal hydrogen (protium). The only exception occurs for cryogenic applications such as liquid hydrogen storage, in which heat is an important parameter. The larger property differences between orthohydrogen and parahydrogen occur in those properties for which heat is important (such as enthalpy, specific heat capacity and thermal conductivity), whereas other properties of orthohydrogen, such as density, vary little from parahydrogen properties.

NOTE If concentrated, the heavier atomic weights of deuterium and tritium result in different physical properties, and their radioactivity may be a safety concern.

6.1.2 Appearance and general characteristics

Gaseous hydrogen is flammable, non-toxic and non-corrosive. It is colourless, odourless, tasteless, and does not support life (asphyxiant). Liquid hydrogen is transparent with a light blue tint and non-corrosive.

6.1.3 Phase properties

The behaviour of hydrogen is dominated by the low temperatures at which transitions between gas, liquid, and solid phases occur. The highest temperature, at which a vapour can be liquefied, the critical temperature, is approximately 33 K for hydrogen. The normal boiling point (NBP) is 20,3 K at an absolute pressure of 101,323 kPa. The triple point, which is the condition under which all three phases can coexist, is 13,8 K at an absolute pressure of 7,2 kPa (a sub-atmospheric pressure). These temperatures are all far below the freezing point of water and even below the freezing point of air.

6.2 Selected thermophysical properties

6.2.1 General

Selected hydrogen engineering data for the gaseous and liquid phases are presented in 6.2 in order to give sufficient background to understand hydrogen safety issues. Some numerical data are tabulated in Annex A. Also selected data on other gases are provided in Annex A for comparison.

6.2.2 Selected thermophysical properties of gaseous hydrogen

6.2.2.1 Dispersion

Hydrogen possesses high buoyancy and greater diffusivity than other gases. Under ambient conditions, hydrogen has a density of 0,083 8 kg/m^3 and a specific gravity of 0,069 6 (air = 1). Therefore, hydrogen is approximately 14 times less dense than air, making it the lightest of all gases. Note that the density of any gas is inversely proportional to temperature; for example, cooling a gas makes it denser. The small size of the hydrogen molecule gives it diffusivity greater than that of helium and approximately three times that of nitrogen in air at ambient conditions. Gaseous hydrogen also readily diffuses into solids.

In the case of gaseous hydrogen leaks, its high buoyancy affects gas motion considerably more than its high diffusivity. However, the effects of wind can dominate diffusion and buoyancy. The buoyancy of hydrogen when it is allowed to rise will create convection currents. As a consequence of these properties, hydrogen gas readily disperses and forms ignitable mixtures with air. In an unconfined atmosphere, these mixtures quickly dilute to a level below the lower flammability limit. Caution should be noted in applying these observations when hydrogen vapours at cryogenic temperatures are released. Hydrogen vapours at temperatures of 23 K or lower are denser than NTP air and, until they warm, can settle into low-lying areas.

6.2.2.2 Viscosity

The low viscosity of hydrogen, in combination with its small size, is a key reason for the likelihood of hydrogen gas leaking through porous materials, fittings or seals.

6.2.2.3 Gaseous heat capacity, thermal conductivity and the Joule-Thomson coefficient

On a molar basis, the heat capacity of hydrogen is similar to that of other diatomic gases despite its low molecular mass. The thermal conductivity of hydrogen is significantly higher than that of other gases. Contrary to the behaviour of many gases, which cool when expanded across an orifice at ambient temperatures, the expansion of hydrogen produces heat. This kind of expansion commonly occurs in systems that release hydrogen at elevated pressure to the atmosphere through a vent. This temperature rise, characterized by the Joule-Thomson coefficient, is not sufficient to cause ignition.

6.2.3 Selected thermophysical properties of cryogenic liquid hydrogen

6.2.3.1 Density and thermal expansion

Liquid parahydrogen at its NBP has a density of 70,78 kg/m^3. The corresponding specific gravity is 0,071 0 ($H_2O = 1$) or approximately 14 times less dense than water.

With the addition of heat, the volume of liquid hydrogen expands significantly more than what we expect based on our experience with water. This property is indicated by the coefficient of thermal expansion, which at NBP is 23 times that of water for ambient conditions. The significance for safety arises when cryogenic storage vessels have insufficient ullage space to accommodate expansion of the liquid. This can lead to an overpressurization of the vessel or entrainment of the liquid into transfer and vent lines.

6.2.3.2 Equivalent volume of gas

A considerable 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 the NBP to NTP. The ratio of the final volume to the initial volume for the phase change from liquid hydrogen to gaseous hydrogen and expansion of heated gas is 845. This total volume increase can result in a final pressure of 172 MPa (25 000 psia) starting with an initial pressure of 0,101 MPa (14,7 psia) if the gaseous hydrogen is completely confined in a fixed volume.

6.2.3.3 Heat capacity

The specific heat at constant pressure of liquid parahydrogen (9,688 kJ/kg·K) is more than double that of water and greater than 5 times that of liquid oxygen at its NBP.

6.2.3.4 Ortho-para conversion

The process of hydrogen liquefaction should not only remove sensible and latent energies, but it should remove the energy released by the ortho-para state conversion. The heat of conversion is 715,8 kJ/kg, which is 1,5 times the heat of vaporization. This is an exothermic process that is very slow and can take several days to complete. The liquefaction process can be accelerated with the use of a paramagnetic catalyst.

6.3 Basic combustion properties

6.3.1 Selected combustion properties of hydrogen

Hydrogen-oxidizer mixtures can combust either as a fire at a fixed point, a deflagration, or a detonation. Flammability limits and ignition energy are two primary variables used to characterize the circumstances under which fire and deflagration occur. Detonation limits are determined from measurements of detonation cell sizes. Some hydrogen combustion data are given in Annex B. Selected combustion data for several common fuels are also given in Annex B for comparison purposes.

6.3.2 Flammability limits that apply to fire and deflagration

Hydrogen, by itself in bulk, does not undergo a chemical reaction when exposed to an ignition source. For combustion to occur, hydrogen has to be mixed with sufficient quantities of oxidizer to form a flammable mixture. An optimum, or so-called stoichiometric mixture, provides the exact ratio of reactants such that all the fuel and oxidizer components of the reactants can combust completely to produce reaction products and heat. For example, two hydrogen molecules react with one oxygen molecule to produce two molecules of water. On a volumetric basis, this is a mixture that is approximately 66,66 % hydrogen and 33,33 % oxygen. Non-stoichiometric mixtures that are fuel-rich (more fuel than necessary for an optimum reaction) or fuel-lean (less fuel than necessary for an optimum reaction) can also support combustion, but not all the reactants are used. For a given set of reactants and specific conditions (for example, temperature and pressure), combustion is limited to a specific range of mixture compositions.

Flammability limits are a convenient means for conveying the range of fuel/oxidizer mixture compositions capable of supporting combustion. They are expressed as a lower flammability limit (LFL) for the minimum amount of fuel that supports combustion, and an upper flammability limit (UFL) for the maximum amount of fuel that supports combustion, and are commonly expressed on a volume fraction (percentage) basis. The flammability limits for hydrogen in air under ambient conditions are shown in Table B.3 ranging from 4 % to 75 % volume fraction. In comparison to more common fuels such as gasoline, this is a very broad range.

Specialized combustion data should be consulted for hydrogen introduced into harsh or low-pressure environments, environments containing chemicals or environments altered by the failure of the hydrogen system. A variety of factors including temperature, pressure, diluents, strength of ignition sources, flow, distance between adjacent confining surfaces and direction of flame propagation can alter the flammability limits. This is illustrated by the effects of natural convection, which expand the flammability limits for upward-propagating hydrogen combustion and decrease the flammability for downward-propagating hydrogen combustion in hydrogen/air mixtures. In this instance, the buoyancy-induced upward velocity of the hot, burnt gases retards a downward-propagating flame, but promotes an upward-propagating flame.

Cool surfaces remove energy from flames and ignition sources, such that if the surfaces are sufficiently close, combustion cannot continue or be initiated. Hydrogen flames entering such regions are said to be arrested or quenched, such as in a flame arrestor. The quenching gap in NTP air is 0,064 cm.

6.3.3 Ignition energy and minimum ignition energy as applied to fire and deflagration

A variety of processes, including flames, electrical sparks, fused wires, incendiaries, hot surfaces, heating, rapid adiabatic compression, shock waves and catalytic materials, can be sources of ignition for hydrogen/oxidizer mixtures. All of these processes heat a portion of the combustible mixture to its auto-ignition temperature (AIT) such that adjacent uncombusted layers also react. The result is a flame that propagates throughout the mixture. For a given combustible mixture and ignition type, there is a minimum energy below which ignition does not occur. This is known as the minimum ignition energy (MIE), and it is typically measured using spark-discharge apparatus.

The MIE varies with the composition of the mixture. Less energy is necessary to ignite a mixture nearer to its stoichiometric composition. Over the flammable range of hydrogen/air mixtures, the MIE varies by almost three orders of magnitude and can be as low as 0,017 mJ. However, for practical purposes, the MIE remains substantially constant over a hydrogen concentration range of 25 % to 35 %. In addition to the mixture composition, other factors such as the initial gas pressure and temperature can influence the MIE. Since most ignition sources generate more than 10 mJ, all fuels listed in Table B.2 would be ignited if their fuel/air ratio exceeds the lower flammability limit. Powerful ignition sources capable of forming shocks, such as high-energy spark discharges and explosives, can directly initiate detonations.

6.3.4 Deflagration

A flame that relies on heat-transfer and mass-transfer mechanisms to combust and move into regions of unburnt mixtures is known as a deflagration. In a stationary mixture in the open with no confinement, the flame will propagate with laminar or “smooth flow” at a rate of 2,7 m/s. Confinement, as found between walls, within pipes and ducts, traps the expanding reaction products and produces a bulk flow, which in turn propels the flame front more rapidly into the unburnt mixture. With the creation of a bulk flow, surfaces adjacent to the flame and obstacles can increase the mixing of unburnt mixture and the flame, thereby increasing the rate of combustion. This process can accelerate the flame speed to hundreds of metres per second with an attendant formation of considerable overpressures, reaching several hundred kilopascals. At high velocities, turbulence created by obstacles to flow can lead to the formation of shock waves capable of initiating a detonation. This process is known as a deflagration to detonation transition (DDT). The maximum propagation velocity of a deflagrative burning flame in a turbulent flow field is limited to the speed of sound in the unburnt gas mixture (975 m/s for a stoichiometric hydrogen/air mixture).

Beyond the flammability limit and the ignition energy data, it is difficult to quantify effects that produce flame acceleration. Confinement is necessary and, with initial conditions such as those near-stoichiometric mixtures and strong initiation sources, rapid deflagrations at the verge of transition to a detonation can occur within one metre of travel. Testing for specific scenarios is required to determine the potential for deflagration or even for detonation.

6.3.5 Detonation

6.3.5.1 General

A detonation is characterized by the auto-ignition of a shock-compressed gas. It propagates at supersonic velocities of 1 500 m/s to 2 000 m/s relative to the supporting unburnt mixture with an attendant pressure rise in the range of 1,5 MPa to 2 MPa. The detonation process does not consist of a single uniform shock wave, but possesses many little detonation cells.

6.3.5.2 Detonation limits

The measured widths of these detonation cells depend on the mixture concentration and the degree of confinement. This dimension can be related to the critical energy necessary to initiate a detonation and to the critical dimension below which a detonation cannot occur. Data for hydrogen/air detonations are shown in Annex B. Cell width data vary not only with mixture concentration, but also with a variety of other factors including pressure, the presence of diluents, and temperature. With knowledge of mixture concentration and cell width, the general approach to evaluating the limits of detonation is to determine if credible sources of initiation above the critical energy for initiation of detonation are possible. System confinements are evaluated to see if dimensions are sufficient to permit detonation. In unconfined mixtures, a direct initiation of a detonation is very unlikely because the minimum energy for a direct ignition is on the order of 1 kJ, which is typical of solid explosives.

Compared to fire and deflagration, the detonation process requires near-stoichiometric mixtures and stronger initiation sources. Detonation cell data is used to quantify detonation limits, rather than the composition limits because an increase in the initiation energy leads to broader detonation limits.

7 Mitigation and control of risks

7.1 General mitigation and control of risk

7.1.1 General

There are general principles, guidelines and recommended practices that are essential for the safe use of hydrogen. While a given hydrogen application has the potential to be unique, priorities can be discerned in the application of these general principles based on the experience and lessons learned from mishaps involving hydrogen described in 7.1.2. Perspective on how an understanding of hydrogen hazards can be approached is provided in 7.1.3 and general guidelines on how to minimize hazards is provided in 7.1.4. More specific information has been organized into sections covering hydrogen design, flammability and explosion, detection, facilities, operations, and recommendations for organizations.

The degree to which any of these principles should be applied will vary according to the need. Hydrogen systems developed for use by the public should possess inherent design features that foster safety with minimum requirements for oversight and training. Hydrogen systems used in industrial settings may require all of the considerations presented.

7.1.2 Lessons learned from past experience

The lessons learned from past experiences provide valuable insight into the priorities that should be established for the application of recommended practices and guidelines. A 1974 study of 96 mishaps involving hydrogen identified and categorized the causal factors. A summary of the results is provided below with an assessment of the percentages involved. More than one factor may have been involved in some mishaps, consequently the percentage shown for these categories totals more than 100 %.

Several categories based on human error were identified. Operational and work area deficiencies were found responsible for 26 % of the mishaps. These mishaps were attributed to inadequate working conditions during installation, maintenance, fabrication, and cleaning; and the lack of training, specific instructions, or both. Procedural deficiencies were found responsible for 25 % of mishaps. This category included the failure to follow established procedures, or to prepare proper procedures. Design deficiencies were found responsible for 22 % of the mishaps. Here inadequate component or system designs, including failure to specify safety devices and omission of other essential information, failure to determine stress and fatigue, errors in material selection (such as clerical errors in drawings and specifications) were described as the causes. Planning deficiencies identified as limited planning, such as failure to prepare test plans or to prepare hazard studies, attributed to 14 % of the mishaps.

Other categories identified included malfunctions, material failures, material incompatibility, and contamination. Malfunctions, defined as anomalies that occurred, such as components in the system that failed to function as intended, attributed to 8 % of the mishaps. Material failures, attributed to 3 % of the mishaps, included the failure of materials and components as a result of stresses that had been considered within the design limits. Material incompatibility, such as incompatible materials either brought together by accident or designed into the system, attributed to 3 % of the mishaps. The use of contaminated materials attributed to 1 % of the mishaps.

The first four categories account for 87 % of the mishaps. Of these, the first and second categories account for 51 % and involve operational procedures. The third and fourth categories account for 36 % and involve design and planning. Thus, these four categories account for a major share of the mishaps and involve human errors. Although not shown in the above numbers, valves were involved in 20 % of the mishaps, and systems contaminated with air were involved in 21 % of the mishaps.

The above statistics suggest two primary goals in the design and operation of a hydrogen system:

a) minimize the possibility for human error, and

b) have a system that is capable of remaining safe in the event of a human error.

7.1.3 Addressing hazards

A variety of options are available for addressing hazards: eliminate, prevent, avoid, control, and ignore. Examples of each option are provided below.

The preferred choice for dealing with a hazard is to eliminate the hazard, but (as is the case with hydrogen) this is not always possible. The properties of hydrogen that make it valuable as a fuel also make it hazardous. This option might be illustrated by choosing to use an inert gas whenever possible rather than using hydrogen (eliminate the hazard by eliminating the hydrogen).

If a hazard cannot be eliminated, then perhaps it can be prevented. The use of a material that is not susceptible to hydrogen embrittlement, for example, will prevent a hydrogen embrittlement hazard. In this example, in comparison with the example above, the hydrogen is still used, but a material that is subject to embrittlement is not used.

An option that is available if a hazard cannot be eliminated or prevented is to avoid the hazard as much as possible. For example, limit the exposure of people to the hazard by both limiting the time of exposure and the number of people that will be exposed.

The option that is often the only one that is practical is to control a hazard. This involves controlling the elements of the hazard rather than eliminating, preventing, or avoiding them. This might involve, for example, limiting the pressure or flowrate that is used in an operation.

If the consequences of a hazard are such that they are insignificant or that they can be tolerated, then an option that is available is to accept the hazard. This option usually involves a careful examination of the hazard and its consequences in order to justify the decision that it can be accepted.

7.1.4 Minimizing the severity of the consequences of hazards

An important principle underlying safe hydrogen use is to seek designs and operations that minimize the severity of the consequences of a potential mishap. This can be accomplished in several ways, such as the following:

- minimize the quantity of hydrogen that is stored and involved in an operation;
- isolate hydrogen from oxidizers, hazardous materials and dangerous equipment;
- separate people and facilities from the potential effects of fire, explosion, or detonation originating from the failure of hydrogen equipment or storage systems;
- elevate hydrogen systems or vent them above other facilities;
- prevent hydrogen/oxidizer mixtures from accumulating in confined spaces (under the eaves of roofs, in equipment shacks or cabinets, or within equipment covers or cowlings);
- minimize personnel exposure by limiting the number of people exposed, the time that the personnel are exposed, the use of personal protective equipment, the use of alarms and warning devices (including hydrogen and fire detectors), and area control around a hydrogen system;
- practice good housekeeping, such as keeping access and evacuation routes clear and keeping weeds and other debris away from hydrogen systems;
- observe safe operational requirements, such as working in pairs (“buddy system”, see E.11) when operating in a hazardous situation.

7.2 Mitigation of design risks

7.2.1 Design for inherent safety

Just as hydrogen has inherent hazards (hazards that are part of the essential nature of hydrogen), a hydrogen system or facility should have inherent safety features (safety is an essential characteristic that must be built-in). Typical inherent safety features include fail-safe design, automatic safety operation, caution devices, and warning devices.

A fail-safe design involves measures such as redundant safety features (for example, pressure-relief devices), back-up critical components and systems, fail-safe position for valves and similar components (for example, valves should automatically go to the safe position in the event of a power failure); and single-fault or dual-fault tolerance as needed, depending on the consequence of the hazard.

Automatic safety design includes features such as remote monitoring of critical information, remote operation, and automatic limiting of operating conditions (for example, pressure or flowrate) or automatic operation of appropriate equipment if hydrogen is detected. This would include such operations as: closing shutoff valves, turning ventilation on or off as appropriate, and initiating appropriate shutdown operations.

A hydrogen system should include caution and warning devices as necessary to alert personnel in the event of any abnormal condition, malfunction or failure. Such devices should provide the personnel with adequate time to respond to the event.

7.2.2 Considerations in the selection of suitable construction material

7.2.2.1 General

Materials that are suitable for hydrogen service and the conditions to which they will be exposed should be used. Materials that are in contact with other materials should be compatible with each other, as well as with hydrogen and the use conditions.

Material considerations for a hydrogen system will involve both metals and non-metals (such as polymers and composites). Some of the considerations that are involved in selecting a material include: temperature effects, hydrogen embrittlement effects, permeability and porosity, and compatibility of dissimilar metals when used together.

7.2.2.2 Low-temperature design considerations

The low-temperature toughness behaviour of metallic materials is closely controlled by their lattice structure. Metals and alloys with a face-centred cubic structure, as with austenitic steels and many aluminium, copper and nickel alloys, exhibit only a moderate decrease of their toughness at cryogenic temperatures. Adequate fibre-reinforced composite materials and laminated structures employing glass, polyamide, or carbon can also be used to give satisfactory behaviour in cryogenic service.

The design of equipment for low-temperature service should account for the stress caused in components by thermal expansion or contraction. There are quite large differences in the total linear contraction between various materials, with polymers having considerably larger contractions than metals. Proper design should accommodate the thermal expansion of the different materials involved.

The condensation and solidification of contaminants within a cryogenic system or on cold external surfaces of the containment structure may not be acceptable to design criteria. Within a system, contaminants should always be minimized. External surfaces can be insulated using vacuum jacketing or insulators. Care should be taken where insulators made from flammable foam or other flammable material may be directly exposed to condensed liquid air. Oxygen enrichment can increase the flammability and even lead to the formation of shock-sensitive compounds.

When use conditions provide the potential for unprotected human exposure, insulation should be used to protect against cryogenic burn (frostbite).

7.2.2.3 Embrittlement and hydrogen attack

In general, the susceptibility to hydrogen embrittlement can be reduced by the following actions:

- restricting the hardness, and therefore the strength level of the material used, to a safe value;
- lowering the level of applied stress;
- minimizing residual stresses, for example by stress-relieving weldments and by normalizing or fully annealing cold-worked materials;
- avoiding or minimizing cold plastic deformation from operations such as cold bending or forming;
- avoiding situations that can lead to local fatigue in components that are subjected to frequent load cycles, since hydrogen is known to significantly accelerate a possible initiation and propagation of fatigue cracks in a structure;

- using austenitic stainless steels, which in general are less susceptible to hydrogen embrittlement and are commonly used as structural materials for hydrogen equipment because of their excellent toughness behaviour at cryogenic temperatures;
- using the test methods specified in ISO 11114-4 to select metallic material resistant to hydrogen embrittlement.

Practical engineering solutions for avoiding hydrogen attack should also be considered. They involve the use of low-alloyed steels containing carbide stabilizers to reduce the reactivity of carbon with the absorbed hydrogen.

7.2.2.4 Non-metallic materials

The application of non-metallic materials (rubber or plastic) as sealants has a long history of use in hydrogen service. Most polymers cause no problems in connection with hydrogen. However, hydrogen can diffuse through these materials much more easily than through metals. The amounts usually are not sufficient to create ignitable mixtures outside the vessel, but they can cause a loss of gas over a long period of time, or they could spoil an insulation vacuum.

Proper care should be exercised in the selection of organic materials used as sealant for high-pressure hydrogen service. The permeation of hydrogen into these materials over an extended period of time, followed by rapid depressurization, can result in mechanical failure or shredding of the seals.

Fibre-reinforced polymers (FRPs) are becoming more and more important as materials for pressure vessels. A metal liner is usually placed inside the vessel to hold the hydrogen so that the FRP material is not in direct contact with hydrogen.

7.2.3 Considerations for vessels and components

The following guidelines apply to both gaseous and liquid hydrogen systems, unless only one is specified. Hydrogen storage vessels (containers) should be

- designed, fabricated, and tested in accordance with appropriate pressure vessel standards and codes,
- constructed of appropriate materials,
- insulated with appropriate thermal insulation (especially liquid-hydrogen storage containers),
- equipped with a shutoff valve on the discharge port, as close to the vessel as possible,
- equipped with a pressure control system (especially liquid-hydrogen storage vessels),
- equipped with an approved vent system,
- equipped with pressure-relief devices to prevent overpressure,
- located in accordance with appropriate quantity-distance standards,
- legibly marked with the name “Hydrogen” or “Liquid Hydrogen — Flammable Gas” for gaseous or liquid containers as appropriate or in the appropriate national language.

Liquid hydrogen tanks that are emptied and allowed to return to ambient conditions should be checked for the accumulation of impurities such as oxygen and nitrogen. This may be accomplished as a part of regular maintenance practice. Near-stoichiometric mixtures of oxygen particulate in liquid hydrogen have the potential to detonate. Oxygen particulate in cryogenic hydrogen gas can deflagrate. Solid air in a liquid hydrogen piping system can plug lines and orifices, and can interfere with the operation of valves and other equipment. Oxygen accumulation in stored hydrogen should not exceed 2 % volume fraction when the mixture is allowed to warm to a gaseous state in the confinement.

7.2.4 Prevention of overpressure

The potential exists for developing pressures that could exceed the containment capability of a hydrogen system, especially those involving liquid hydrogen, because of the volume increase as a result of a liquid-to-gas phase change. This hazard is commonly addressed by the use of pressure-relief devices.

7.2.5 Considerations for piping, joints and connections

Some general considerations for gaseous and liquid hydrogen piping include the following:

- design, fabricate, and test in accordance with approved standards;
- construct with appropriate materials;
- have appropriate flexibility (such as expansion joints, loops and offsets);
- locate in accordance with appropriate standards;
- do not locate beneath electrical power lines;
- avoid buried lines wherever possible. If lines are to be buried, consider the effects of galvanic corrosion, the difficulty in conducting a visual inspection for line integrity, and the possibility that a leak can take a path to an unforeseeable location, resulting in an accumulation and an explosion hazard. Leak checks are difficult to perform on buried lines, with the exception of pressure-decay techniques;
- galvanic corrosion can occur, particularly when moisture is present, with dissimilar metals and should be considered in socket-type piping joints. The more corrosive (less noble) material will preferentially corrode and should be used for the female part.
- use appropriate supports, guides and anchors;
- use appropriate pressure-relief devices;
- insulate with appropriate thermal insulation (especially piping for liquid hydrogen and cold gaseous hydrogen);
- label as to contents and direction of flow.

Welding or brazing are the preferred methods for making piping joints; however, flanged, threaded, socket, slip or compression fittings may be used depending on operating conditions. Gaskets and thread sealants are suitable for gaseous hydrogen service. Some types of joints, gaskets, and sealants are not suitable for use at low temperatures. A bayonet joint is typically used for joints in liquid hydrogen piping, where frequent connection and disconnection (such as in fill lines) are necessary. If this is not possible, hydrogen gas or fire detectors should monitor the regions around the joints. Soft-solder (low melting point) joints should not be used for hydrogen service.

Non-metallic lines can function adequately for short-term use, if adequate ventilation and hydrogen detection are provided.

7.2.6 Cleaning considerations

A hydrogen system, including its components, should be designed and installed to allow it to be cleaned, and to be effectively maintained clean. Effective cleaning should remove grease, oil, and other organic materials as well as particles of scale, rust, dirt, weld splatter and weld flux. The compatibility of a cleaning agent with all construction materials should be established prior to its use. Common cleaning methods include steam or hot water cleaning, mechanical descaling, vapour degreasing, solvent degreasing (washing), detergent degreasing (alkaline washing), acid cleaning (pickling) and purging. A cleaning procedure should be established and reviewed for effectiveness and safety concerns.

7.2.7 Component considerations

7.2.7.1 General

A hydrogen system commonly involves a considerable number of components, such as valves, pressure-relief devices, pressure regulators, check valves, filters, instrumentation and pumps. These components are important elements of the system and they can be crucial for the safety of the system.

The components in a hydrogen system should be fabricated of materials, including soft goods such as seats and seals, that are compatible with the operating conditions, such as temperature and pressure, and with each other if more than one material is involved.

7.2.7.2 Pressure-relief devices

Pressure-relief devices should be installed in any volume in which liquid hydrogen or cold gaseous hydrogen could be trapped, to prevent overpressure from expansion of the liquid hydrogen or cold gaseous hydrogen. A low-pressure system supplied by a regulator connected to a high-pressure source should be protected from overpressure by a relief device, unless the low-pressure system is designed for the maximum pressure of the source.

Relief devices should be set to limit the pressure so that it does not exceed the maximum allowable working pressure of the system that they are protecting. The relief devices should be sized for adequate flow capacity for the most extreme conditions that could be encountered. Hydrogen released from the discharge port (the outlet) of relief devices should not impinge upon other components or personnel. Should multiple relief devices be routed and manifolded to a common vent, care should be taken to ensure that the operation of one device does not restrict flow or influence the opening pressure of other relief devices. Redundancy in both number and type of relief devices (such as relief valve and rupture disk) is commonly used.

Shutoff valves should not be installed between a relief device and the volume that it is protecting.

7.2.7.3 Valves

Cryogenic globe or globe-type valves are recommended for liquid hydrogen service, but plug or ball-type valves may be used. Ball valves used in liquid hydrogen service should have provisions to prevent trapping liquid in the ball when the valve is closed. A valve for liquid hydrogen service is usually an extended-stem design and is commonly insulated with a vacuum jacket.

7.2.7.4 Filters

Filters are useful for reducing hazards associated with contamination, especially from solid particles, and in liquid hydrogen systems from solid particles that could include oxygen. The primary purpose of a filter is to collect impurities in a hydrogen system. Some recommendations concerning filters include the following.

- Filters should be accessible and capable of being isolated for cleaning.
- Filters should not be cleaned by back-flushing through the system.
- Filters should be cleaned or replaced periodically or whenever the pressure drop across the filter reaches a specified value.
- The quantity and location of filters should be determined as required to minimize impurities in a system (refill or re-supply lines are primary locations for filters).

7.2.7.5 Instrumentation and controls

Instrumentation provides a means to communicate with physical processes to obtain quantitative measurements of the behaviour or state of a process. Controls provide a means to maintain or change the behaviour or state of a process. These are essential elements of a hydrogen system for both the operation of the system and for the safety of the system. The system should have adequate instrumentation and controls to ensure that the operation is within acceptable limits.

7.3 Mitigation of flammability and explosion risks

7.3.1 General

Hydrogen/air and hydrogen/oxygen mixtures are readily ignited over a wide range of mixture compositions, pressures and temperatures. Near-stoichiometric mixtures at ambient pressures are so sensitive that designers, safety evaluators, and others should assume an ignition source would be present even when stringent measures to remove ignition sources have been taken.

7.3.2 Prevention of unwanted hydrogen/oxidizer mixtures

The prevention of the formation of an unwanted hydrogen/oxidizer mixture is a key part of preventing fire, deflagration or detonation. This is done by keeping the hydrogen and an oxidizer such as air separate. The following are some of the techniques to be used in order to achieve this goal.

- **Purging**: A system should be purged with an inert gas to remove air before admitting hydrogen into the system, and the system should be purged of hydrogen before opening it to air.

- **Leak-free system**: A system that is to contain hydrogen should be leak tested and be leak-free prior to admitting hydrogen. Periodic leak tests should be performed and any leaks that are found should be repaired.

- **Disposal**: Hydrogen that is vented to the atmosphere should be done so through vent systems that are properly designed and located.

- **Ventilation**: An enclosed space such as a room or building in which hydrogen could accumulate should be provided with adequate ventilation to prevent the formation of a combustible mixture.

- **Maintain positive pressure**: Hydrogen systems, especially liquid hydrogen systems, should be kept at a positive pressure in order to prevent air from the exterior of the system from entering.

- **Periodic warm-up of liquid hydrogen systems**: Liquid storage vessels should be periodically warmed sufficiently for impurities such as air to be vaporized and purged from the system.

- **Filters**: A filter may be used in a liquid hydrogen system to capture impurities that could include solid air. Such filters should be periodically isolated, warmed, and purged to remove any such impurities.

7.3.3 Ignition

7.3.3.1 Electrical sources of ignition

Another key to preventing fire, deflagration, or detonation is to eliminate ignition sources. The energy required to ignite a hydrogen/oxidizer mixture is very small. Consequently, many electrical, thermal and mechanical sources of ignition are possible.

The following phenomena are to be considered as potential electrical sources of ignition.

- **Charge accumulation leading to static discharge**: Static charge is caused by the accumulation of electrons on a surface, and occurs based on a material's electrical conductivity and dielectric strength parameters. The relative rates of charge accumulation and of charge dissipation, within the flowing fluid, determine the amount of charge accumulation. This effect is very small for pure flowing hydrogen, whether as a gas or liquid, but solid particles in the flow could greatly increase the build-up of an electric charge. The type of frozen gas or particle (oxygen, carbon dioxide, nitrogen, hydrogen, sand, metal, oxide flakes from the walls of pipes, etc.) could be important. The potential for static electricity generation can be a specific problem for metal hydride systems, where small hydride particles can be suspended in the flowing hydrogen. The use of a non-metallic filter to trap particles can increase the problem and can produce from 10 to 200 times more charge than a system with no filter. The large surface area of filters allows static charge to accumulate more readily.

- **Static discharge**: Discharges of static electricity can produce high temperatures, often sufficient to cause a material to reach its ignition temperature. For example, friction of one material rubbing against another, such as with clothing fabrics or with two-phase flow, can cause accumulation of electrostatic charges.

- **Electric arc**: Electric arcs can provide the energy to ignite a combustible hydrogen/air or hydrogen/oxygen mixture. Normal sources include switches, electric motors, portable phones, pagers and radios.

- **Lightning discharge**: Lightning strikes and their potential electrical fields can result during the approach and passing of a storm system.

- **Electrical charge generated by equipment operation**: Equipment that can generate electrical charges includes compressors, generators, vehicles and other construction equipment.

- **Electrical short circuits**: Short circuits or other electrical equipment failures can produce arcs and sparks.

- **Grounding**: Grounding methods should be evaluated to minimize the risk of static discharge and the potential for lightning strikes in outdoor environments. Materials selected for use in hydrogen environments should be evaluated for their ability to discharge static electricity. Insulative materials such as wood, paper, and some fabrics will typically form a conductive layer that can prevent static build-up by absorbing water from the air in environments where the relative humidity is greater than 50 %. Recommended practices for grounding methods to prevent static discharges can be found in various national and International Standards that cover the installation of electrical equipment in hazardous environments.

Electrical equipment selected for use in hydrogen environments can also be a source of sparks or heat generation, and care should be taken to follow the appropriate national and International Electrical Standards for installation.

7.3.3.2 Mechanical sources of ignition

Phenomena to be considered as potential mechanical sources of ignition are

- mechanical impact and/or friction and galling,

- metal fracture or tensile rupture, and

- mechanical vibration and repeated flexing.

7.3.3.3 Thermal sources of ignition

The following phenomena are to be considered as potential thermal sources of ignition:

- open flames and/or hot surfaces (for example, welding and cigarette smoking by personnel);

- exhausts (for example, combustion engines and exhaust stacks);

- explosive charges (for example, charges as used in construction, fireworks or pyrotechnic devices);

- catalysts and reactive chemical materials: High temperatures can result from the interaction of hydrogen with catalysts or other chemical reactants. Some applications that use such materials include recombining hydrogen emitted from lead-acid batteries to produce water and hydrogen detection instruments;

- resonance ignition from repeated shock waves that can occur in a flowing system;
- heating by high-velocity jets, as might occur from an exhaust stack;
- shock waves and/or fragments, as might occur from the rupture of a tank or vessel.

7.3.4 Deflagration and detonation

The potential for deflagration and detonation should be assessed in hydrogen designs, facilities and operations. Strategies to minimize the potential for flame acceleration or detonation include

- avoiding confinement where flammable hydrogen mixtures might form,
- using flame arrestors, small orifices, or channels to prevent deflagration and detonation from propagating within a system,
- using diluents and water spray systems to retard flame acceleration.

NOTE Hydrogen/air flames are difficult to quench and can burn around the droplets in heavy sprays of water.

If the potential for deflagration and detonation cannot be eliminated, then hydrogen system design and operations should take into account the possibility of their occurrence. This includes designs with sufficient strength to withstand the high pressures or remote operation in order to protect facilities and personnel.

7.3.5 Oxygen enrichment

While liquid hydrogen is usually transferred in vacuum insulated lines, cold hydrogen flowing through tubes which are not sufficiently thermally insulated can easily cool the system below 90 K so that condensed air with an oxygen content of up to 52 % is present. This oxygen-enriched condensate enhances the flammability of materials and makes materials combustible that normally are not. If a line cannot be insulated, the area underneath should be free of any organic material. This includes bituminous road covers and similar material. This is of particular concern when transferring large quantities of hydrogen.

7.4 Detection considerations

7.4.1 Hydrogen gas detection

Because of the limitations of the human senses, other means are needed to detect hydrogen. A variety of methods and detector types are commercially available to detect the presence of hydrogen. Many of these detectors are suitable for use in automatic warning and operating systems.

It is recommended that hydrogen detectors be used wherever hydrogen is used. Some suggested locations for hydrogen detectors include the following:

- locations where hydrogen leaks or spills are possible;
- at hydrogen connections that are routinely separated (for example, hydrogen refuelling ports);
- locations where hydrogen could accumulate;
- in building air intake ducts, if hydrogen could be carried into the building;
- in building exhaust ducts, if hydrogen could be released inside the building.

Some important factors to consider in the selection of a hydrogen sensor are

- accuracy,

- reliability,
- maintainability,
- calibration,
- detection limits (high and low),
- response time,
- point or area coverage, and
- compatibility with the system.

Hydrogen system operators should have a portable hydrogen detector available for their use in and around a hydrogen system. A commonly used concentration level for alarm is 1 % hydrogen (volume fraction) in air, which is equivalent to 25 % of the lower flammability limit. This level normally should provide adequate time to respond in an appropriate manner, such as system shutdown, evacuation of personnel, or other measures as necessary.

7.4.2 Fire detection

In the absence of impurities, a hydrogen/air flame is almost invisible to the human eye during daylight. Also, the emissivity of a hydrogen flame is low. Thus, a hydrogen flame is difficult to see or to feel. As a consequence of these two characteristics of a hydrogen flame, it is recommended that means be provided for detecting the presence of a hydrogen flame in all areas in which leaks, spills, or hazardous accumulations of hydrogen may occur. A variety of methods and detector types are available for the detection of a hydrogen flame.

Some important factors for consideration in the selection of a hydrogen flame detector are the following:

- detection distance and area covered;
- susceptibility to false alarms from sources such as the sun, lightning, welding, lighting sources and background flare stacks;
- response time;
- sensitivity to appropriate radiation spectrum.

Hydrogen system operators should have a portable hydrogen flame detector available for their use in and around a hydrogen system. A common straw broom extended into regions suspected of flame can be successfully used as a detector. Caution should be observed when solely relying on portable flame detectors for protection around large hydrogen facilities. These detectors may fail to detect in time large burning leaks of hydrogen coupled with turbulent wind flow that can engulf personnel and cut off a safe path of retreat.

7.5 Considerations for facilities

7.5.1 General

The commissioning of facilities that use hydrogen requires the same level of consideration for design and safety as does the design of hydrogen components and systems.

7.5.2 Locations

Keeping a hydrogen facility or system far enough away from people and other facilities can minimize the effects of an event such as a fire, deflagration or detonation. Suitable separation distances also provide protection for hydrogen facilities from incidents at other nearby facilities. The separation distance requirements, also commonly referred to as the quantity-distance (Q-D) requirements, are determined as a function of the quantity of hydrogen involved. Generally, the larger the quantity of hydrogen involved, the greater are the recommended separation distances. Under some circumstances, small quantities of hydrogen may be stored and used in a room or building, but generally outdoor storage and use is recommended. The separation distance can be determined for the potential hydrogen events or for the potential events at other facilities, whichever requires the greater distance.

Some important factors in determining the Q-D for a hydrogen facility include

- the most probable event that could occur, which would involve parameters such as the
    - quantity of hydrogen involved,
    - condition of the hydrogen (gas, liquid, pressure, temperature, etc.),
    - effects of possible combustible cloud migration prior to its ignition, and
    - presence of other fuels or oxidizers,
- protection afforded by shielding, barricading or other means,
- the type of activities involved at the hydrogen facility (propulsion testing, for example).

7.5.3 Exclusion areas

An area of appropriate size around a hydrogen facility, especially hydrogen storage areas, should be controlled. This control should include

- limiting access to necessary authorized personnel, who should meet the necessary training requirements, and are properly clothed and equipped,
- approved equipment (meeting specified requirements, such as the elimination or control of ignition sources),
- approved operations (which are consistent with the requirements for safety of the personnel and reducing risks to adjacent facilities),
- providing signs in controlled areas with appropriate warnings so that personnel are aware of the potential hazard in the area,
- considering the use of appropriate fencing to control access to critical areas.

A method for keeping track of personnel entering and leaving a controlled area should also be considered. This should restrict the number of personnel within the exclusion area at the same time.

7.5.4 Dikes, impoundments and barricades

A dike or impoundment can be used to contain a liquid hydrogen spill, to limit it from spreading into an undesired area. The use of crushed stone in an impoundment area can provide added surface area for a greater vaporization rate. An impoundment area can limit the vaporization rate, which could possibly produce a smaller combustible cloud, but could also result in a longer time needed to vaporize the spilled liquid.

A barricade can be used to protect a hydrogen facility from shrapnel and fragments from other nearby facilities or to protect nearby facilities from shrapnel and fragments that could result from an explosion at a hydrogen facility. Earth mounds and blast mats are common types of barricade. Barricades can also include physical barriers to protect hydrogen facilities or systems from motor vehicles. Quantity-distance requirements for a hydrogen facility can be reduced by the use of barricades to reduce the shrapnel and fragment hazard.

Barricades and dikes or other retaining devices around hydrogen facilities or systems should only be used with great care, because of the enhanced detonation effects associated with confinement.

7.5.5 Safety control equipment

A hydrogen facility or system should be equipped with a variety of safety control equipment, such as:

- **Warning system**: A warning system should be installed to detect abnormal conditions, malfunctions, and to indicate incipient failures. Warning system data transmissions with visible and audible signals should have sufficient redundancy to prevent any single-point failure from disabling the system.
- **Flow control**: Safety valves and flow regulation should be installed to adequately respond for the protection of personnel and equipment during hydrogen storage, handling and use.
- **Safety features**: System and equipment safety features should be installed to automatically control the equipment required to reduce the hazards suggested by the caution and warning systems. Manual controls within a system should be constrained by automatic limiting devices to prevent over-ranging.

Any instrumentation, software and computer used for safety control should

a) be independent of similar equipment for normal operations, and

b) have sufficiency redundancy to prevent any single-point failure from disabling the equipment.

An inert gas subsystem is needed for various purging operations. Hydrogen equipment should be purged with an inert gas before and after using hydrogen in the equipment. Air in a system should be purged with an inert gas prior to introducing hydrogen into it, and hydrogen should be purged from a system with an inert gas before opening the system and admitting air. Caution should be exercised if carbon dioxide is used as a purge gas. It may be difficult to remove all carbon dioxide from the system low points where the gas can accumulate.

Common purging techniques include

- evacuation and backfill,
- pressurizing and venting, and
- flow-through.

The selection of the proper purging technique requires an evaluation of the equipment to be purged. Important purge parameters include flowrate, duration, mixing and dilution. The inert-gas subsystem should be protected by a suitable means against contamination with hydrogen.

7.5.6 Disposal of hydrogen

Hydrogen should always be disposed of according to an approved method. Hydrogen is commonly disposed of by venting to the atmosphere through a vent (where the hydrogen is not burned) or a flare system (in which the hydrogen is ignited at the release point and burned). The release point for venting should be above the highest point of the immediate surroundings and away from electrical lines or other potential ignition sources. Flaring is preferred for larger quantities of gaseous hydrogen. Site-specific conditions and hydrogen vent rates are two factors involved in determining which system is appropriate. Flaring is generally used for vent rates greater than about 0,23 kg/s, or for any quantity that cannot be disposed of safely by venting.

Disposal factors that should be considered are

- the quantity of hydrogen that could exist in a combustible cloud,
- the extent of the combustible cloud,

- thermal radiation from a flame (from a flare system or a vent system fire), and
- site conditions such as size of the exclusion area, building locations, personnel control and weather.

The back-flow of air into a vent system should be prevented. Water should never be sprayed so that it can enter a liquid-hydrogen vent system that gets sufficiently cold to freeze the water, because the ice could plug the vent system.

A vent system should be equipped with a purge system to extinguish a vent-system fire, as well as to purge air or hydrogen from the vent system. Hydrogen being vented from a vent system is often ignited by lightning or other mechanisms, producing a flame that is difficult to detect visually. The size of the flame is a function of the hydrogen vent rate.

The thermal radiation from a flare system should be evaluated and appropriate separation distances applied to protect the personnel.

Vents on roofs should be located such that hydrogen does not enter building air intakes.

7.5.7 Buildings

Design of buildings and rooms in which hydrogen is stored or used should address safety issues such as the following, in order to minimize the hydrogen hazards:

- construction of non-combustible materials;
- no spaces where hydrogen can accumulate;
- no sources of ignition;
- pressure relief for all potential explosion overpressure;
- adequate ventilation;
- appropriate use of hydrogen detectors.

7.5.8 Ventilation

Considerations for ventilation should appropriately address the scenarios of

a) a hydrogen presence inside a confined space, and

b) a migration of hydrogen into a confined space from a source outside the confined space.

In the first scenario, a ventilation system should remove hydrogen from the confined space. In the second scenario, the ventilation system should not introduce hydrogen into a confined space, unless it is shutdown.

Hydrogen leaks or spills, in a non-ventilated confined space, can readily form ignitable gas mixtures. Consequently, confined spaces containing equipment for handling or storing of hydrogen should always have an active or passive ventilation system. The confined space should have hydrogen detectors to detect the presence of hydrogen and to avoid the build-up of a flammable mixture.

The following are some other considerations for ventilation systems.

- Ventilation should be established prior to hydrogen being introduced into a confined space and continue until hydrogen is removed from the confined space.
- Ventilation should not be shut off as a function of an emergency shutdown procedure unless the source of hydrogen is outside the confined space.

- Suspended ceilings and inverted pockets in confined spaces should be avoided or adequate ventilation of these spaces should be ensured.
- Electrical equipment in the ventilation system should meet appropriate provisions for operation in a combustible environment.

7.5.9 Electrical components

Careful consideration should be given to any electrical apparatus or wiring that is in close proximity (approximately 1 m) to locations where an ignitable hydrogen/air mixture can exist in the following situations:

- under normal operating conditions (for example, a filling port);
- because of frequent repairs, maintenance operations or leaks;
- because of hydrogen release as a result of a breakdown, or faulty operation of equipment, or processes that might also cause simultaneous failure of electrical equipment.

Under these conditions, electrical equipment and wiring should be

- approved for use in a hydrogen environment,
- intrinsically safe for use in a hydrogen environment, or
- placed in an approved enclosure that is purged with an inert gas.

Also, electrical equipment and wiring should operate at an exposed surface temperature of less than the ignition temperature of a hydrogen/air mixture. Explosion-proof equipment should be used in all locations described above unless it can be shown that it is not necessary, or required by local, regional or national codes.

Electrical equipment and wiring located between about 1 m and 8 m from a location as described above, or within a distance of about 5 m from a gaseous hydrogen storage vessel or 8 m from a liquid hydrogen storage vessel, should also be carefully considered, but their requirements are somewhat less stringent than the closer locations described above. Electrical equipment located at a distance greater than 1 m as described above should not produce sparks, arcs or other ignition mechanisms.

Lightning protection should be provided for hydrogen equipment.

Hydrogen equipment should be electrically bonded, especially across joints with a polymer seal, and grounded. Mobile hydrogen equipment should be electrically grounded prior to being connected to other hydrogen equipment. Static charges and spark generation should be avoided.

7.5.10 Alarms and warning devices

Warning systems should be installed to provide an alarm in the event of a potentially hazardous situation, with sufficient time to enable safe shutdown of the hydrogen system.

The warning system should provide an audible or a visible alarm, or both.

Some system alarm/warning conditions are

- pressure (high or low, as appropriate),
- hydrogen in a building ventilation intake,
- flare flameout,

- loss of vacuum insulation,
- valve position (open or closed, as appropriate),
- pump speed (high or low, as appropriate),
- filter differential pressure,
- hydrogen leak, and
- fire.

7.5.11 Fire protection and fire fighting

A fire protection subsystem should be considered for a hydrogen facility or system. Fire protection measures may include

- process shutdown system (either automatic or manual),
- sprinkler system,
- deluge system, and
- dry-chemical or halon extinguishing system.

Small fires may be extinguished by dry-chemical extinguishers, carbon-dioxide extinguishers, nitrogen or steam.

Normally a hydrogen fire is not extinguished until the hydrogen source has been isolated, because of the danger of ignition of a large combustible cloud that could develop from unburned hydrogen.

Water may be used to cool equipment adjacent to a hydrogen fire.

7.6 Considerations for operations

7.6.1 General

A hydrogen facility or system typically involves a number of operations that are performed during its normal functioning. These operations involve not only the equipment and components of the system, but also the personnel that perform the operations, special equipment needed to perform the operations, and personal protective equipment needed to protect the personnel performing the operations. In addition to the normal operations involved with a hydrogen facility or system, there are emergency operations that may be required in the event of a failure or a mishap.

7.6.2 Personal protective equipment

Personnel performing operations at a hydrogen facility or system can reduce the possible consequences of a hazard by using appropriate protective equipment. Some of the conditions for which personnel should be protected include: exposure to cryogenic temperatures, flame temperatures, thermal radiation from a hydrogen flame, and oxygen-deficient atmospheres of hydrogen or inert purge gases such as nitrogen and helium.

Procedures that are established for operations involving hydrogen should describe the personal protective equipment (PPE) that is needed for the operations to be performed. Some general guidelines for PPE that should be considered beneficial in working with hydrogen are summarized below. These guidelines do not address PPE that should be considered when involved in other activities such as working on electrical circuits or performing a cleaning or decontamination operation.

Here are some specific recommendations for PPE.

- Eye protection should be worn (for example, a complete face shield should be worn when connecting and disconnecting lines or components).
- Properly insulated gloves should be worn when handling anything that comes in contact with liquid hydrogen or cold gaseous hydrogen. The gloves should fit loosely, remove easily, and not have large cuffs.
- Full-length trousers, preferably without cuffs, should be worn with the legs kept on the outside of boots or work shoes.
- Closed-toe shoes should be worn (open or porous shoes should not be worn).
- Clothing made of ordinary cotton, flame-retardant cotton or Nomex® should be worn. Avoid wearing clothing made of nylon or other synthetics, silk or wool because these materials can produce static electricity charges that can ignite flammable mixtures. Nomex® material provides good anti-static qualities and provides some fire protection. Synthetic material (clothing) can melt and stick to the flesh, causing greater burn damage. Any clothing sprayed or splashed with hydrogen should be removed until they are completely free of hydrogen gas.
- Gauntlet gloves, tight clothing, or clothing that holds or traps liquid against the body should be avoided.
- Hearing protection should be worn if the hydrogen facility or system involves equipment that creates loud noise.
- Hard hats should be worn if the hydrogen facility or system involves any danger from falling objects.
- Self-contained breathing equipment should be worn when working in a confined space that may have an oxygen-deficient atmosphere.
- Portable hydrogen- and fire-detection equipment should be used to warn of hydrogen leaks and fires.
- Personnel should ground themselves before touching or using a tool on a hydrogen system.

The use of spark-proof tools is often recommended; however, the energy required for ignition of a flammable hydrogen/air mixture is so small that even spark-proof tools can cause an ignition. Consequently, all tools should be used with caution to prevent slipping, glancing blows or dropping, all of which can cause sparks.

7.6.3 Cool-down

The cool-down of a liquid hydrogen system from NTP to its operating temperature (NBP) is a process that should be conducted in accordance with an approved procedure, such that the process proceeds in a controlled manner. The cool-down process can involve several techniques such as liquid flow, cold gas flow, liquid soak, and pre-cooling with liquid nitrogen.

The cool-down process can result in large temperature gradients, both circumferential and radial, which can create large stresses in the containment structure or components such as valves. Also, cool-down can result in large thermal contraction (especially in a long line), which can create large stresses in the line. Non-uniform cooling can result when two-phase flow occurs. Stratified flow can result in large circumferential temperature gradients, which in turn create high stresses in a pipe. Stratified or wave flow (usually associated with low flowrates) can result in pipe bowing, which is produced when the bottom part of a pipe contracts more than the top part, because the bottom part is cooled by the liquid and the top part is cooled by the gas.

The cool-down process generally results in the generation of a large quantity of gas that needs to be handled safely. The system should be designed to accommodate the large gas flow that is needed to achieve the cool-down of a system.

7.6.4 Transportation

Hydrogen should be transported in accordance with applicable local and national regulations and laws that govern the transport of a hazardous (flammable) substance. Permits, as required, should be obtained for the transport of hydrogen. Transport personnel should be trained in handling emergencies that might arise while the transport vehicle is on the road. Flares normally used for highway vehicular accident identification or warning should not be used in close proximity to vehicles transporting hydrogen.

7.6.5 Storage and transfer operations

The following are some general guidelines for storage and transfer operations.

- Do not overfill a liquid storage vessel.
- Do not overpressurize any part of the system.
- Avoid thermal cycling of a pressure-relief system.
- Warm and purge liquid hydrogen vessels periodically to keep the accumulated oxygen content in the vessel to less than 2 %.
- Electrically ground mobile and stationary systems before making any other connections.
- Be alert for leaks and discontinue operations if a leak or fire occurs.
- Do not cool down a liquid hydrogen storage vessel too rapidly.
- Examine systems for corrosion or other damage.
- Keep the area around a hydrogen system clean.
- Cancel or discontinue operations during an electrical storm, or whenever one is approaching.
- Keep storage and transfer areas clear of non-essential personnel and equipment.
- Remove sources of ignition from operational areas.
- Use a “buddy system” (see E.11).
- Use items such as barricades, warning signs and ropes to establish access control to an operational area.

7.6.6 Operating procedures

Approved procedures and checklists should be followed in all operations involving a hydrogen system. Procedures and checklists should be developed by knowledgeable personnel, reviewed and approved by appropriate personnel prior to their use. Procedures and checklists are important elements in the safe operation of a hydrogen system. These documents should provide information that includes instructions on steps to take in the event of a leak or other abnormal event, and how to use special equipment (such as personal protective equipment and monitoring equipment). Procedures and checklists should be reviewed periodically to verify their effectiveness.

Procedures should be established for the following operations: cleaning, cool-down, operating, purging, storage (especially filling), hydrogen transfer, leak checks, modifications, repairs, maintenance and decommissioning.

7.6.7 Safety procedures

7.6.7.1 General

The safety of personnel at and near a hydrogen facility should be carefully reviewed, and emergency procedures developed at the earliest planning and design stages. Advance planning for a variety of emergencies, such as fires and explosions, should be undertaken so the first priority is the reduction of risk to life.

Consideration should be given to the development and training in emergency procedures for events that might occur. This should include events such as

- hydrogen leak (controllable leak and uncontrollable leak),
- hydrogen fire,
- hydrogen explosion,
- excessive pressure,
- hydrogen contamination (with an oxidizer or an inert gas),
- line rupture,
- liquid hydrogen spill,
- combustible cloud migration,
- electrical fire,
- failure of critical equipment, and
- inability to vent a cold gaseous or liquid hydrogen system.

7.6.7.2 Emergency procedures

Considerations that emergency procedures should address are the following:

- emergency escape procedures and emergency escape-route assignments;
- procedures to be followed by employees who remain to operate critical systems before they evacuate;
- procedures to account for all employees after an emergency evacuation has been completed;
- rescue and medical duties for those employees who are to perform them;
- the preferred means of reporting fires and other emergencies;
- names and regular job titles of persons responsible for providing further information or explanation of duties under the emergency plan;
- actions to be taken by the initial-response personnel;
- appropriate fire-suppression response;
- establishing and maintaining communications;
- appropriate medical response;

- requesting outside assistance;
- establishing security;
- possible media coverage;
- salvage and restoration operations;
- establishing a command post with a pre-designated line of authority;
- hazardous-material inventory (including materials such as asbestos).

An emergency alarm system should be established to alert personnel that an emergency situation exists. Emergency procedures should be reviewed periodically to ensure that the procedures are relevant and up-to-date. Safety and fire-fighting personnel should be involved in the development of emergency procedures and in emergency drills.

7.6.7.3 Fire-fighting procedures

Hydrogen fires should not be extinguished before the gas supply is interrupted. Otherwise, unburned gas may create explosive mixtures. Water spraying may be necessary to keep facilities cool.

7.6.7.4 Liquid spill procedures

In case of a liquid spill, the flow should be interrupted by closing valves further upstream. Measures in the vicinity of the spill site should not be taken, and the area near it should be evacuated until a reasonable time has elapsed for the liquid to evaporate and for the gas to disperse to concentrations below the flammability range. The use of dikes or other retaining devices should only be done with great care because of the enhanced detonation effects associated with confinement.

Vaporized liquid hydrogen will rapidly condense to water in air, forming a white cloud of condensed water. Note that some sources of hydrogen safety-related information will claim that the extension of the cloud of condensed water is a rough guide for the extension of the flammable hydrogen/air gas mixture cloud. This should by no means be taken as a basis for safety measures. The condensed water cloud is heavier than hydrogen and the hydrogen diffuses more rapidly than water vapour in air, making it likely that the extent of the hydrogen gas cloud will be greater than the apparent water vapour cloud.

7.7 Recommended practices for organizations

7.7.1 General

Organizations involved in the use of hydrogen should establish and enforce such policies and procedures as are needed to ensure that hydrogen is used in a safe manner. Organizational policies and procedures should address issues such as safety responsibility, risk and risk management, and applicable codes, standards, and regulations that apply to the organization's operations. It is desirable that a safety culture be established among the organization's personnel to promote thinking about safety at all times, especially as it performs its duties. An emphasis on safety in working with hydrogen should come from the highest level of the organization, as an indication of its importance to the organization.

7.7.2 Control through organizational policies and procedures

Upper management of an organization should establish organizational policies and procedures by which a programme or project involving hydrogen is directed, conducted, controlled, monitored and evaluated. Upper management also should provide controls, guidance and oversight of such a programme or project to ensure that proper planning, monitoring, reporting, evaluation and assessment of the programme or project is achieved. Appropriate organizational policies and procedures should be established to provide “conception to grave” control over a hydrogen facility, system or product.

An organization may use documents such as this Technical Report as a basis or support of its policies and procedures to ensure that hydrogen is used safely.

7.7.3 Use of approved procedures and checklists

Procedures and checklists should be prepared and used for all operations involving a hydrogen system. Inadequate procedures and failure to follow procedures have been common factors in many hydrogen mishaps.

7.7.4 Conduct appropriate reviews

Reviews, such as design reviews, safety reviews, hazard analyses, and operational reviews, provide valuable verifications when conducted by an experienced team of qualified personnel.

7.7.5 Approved maintenance and quality control programmes

Maintenance and quality control programmes should be used to ensure that a hydrogen system is installed and kept in a safe condition through inspections and replacement of components, both as needed and according to a routine schedule.

7.7.6 Personnel training

A detailed safety-training programme that recognizes human capabilities and limitations should be required of all personnel involved with the use of hydrogen. A primary goal of the safety-training programme is to eliminate accidents and to minimize the severity of any accidents that do occur.

All personnel involved with the use of hydrogen (including operators, technicians, engineers, designers and administrators) should be familiar with the physical, chemical, and hazardous properties of hydrogen pertaining to the applications with which they are involved. Personnel involved in activities such as equipment design and operations planning should be trained to carefully adhere to accepted standards and guidelines, and to comply with appropriate regulatory codes and requirements. Operators should be trained in the proper use of the specific equipment and systems that they are involved in operating. They should be certified as capable of operating specific equipment and systems.

Operators should be trained in how to respond to emergencies involving their equipment and systems. Training should include the actions to be taken in the event of an emergency, such as a fire or an explosion. Personnel should be trained to assist in the safe and orderly emergency evacuation of personnel. Training should include preventative and first-aid procedures for emergency care of injuries, including procedures for cold and cryogenic injuries where cold gaseous hydrogen or liquid hydrogen is involved.

Refresher training of personnel should be given at periodic intervals (such as annually). Also, the safety-training programme should be reviewed periodically to ensure that the training programme is relevant and up-to-date.

7.7.7 Hazard assessment

Hydrogen is typically classified as a hazardous material based on its flammability properties. When working with hydrogen, various safety aspects should be evaluated to ensure that the design and implementation of a system adequately addresses these safety aspects. An excellent method of addressing all safety aspects is the use of hazard assessments. A hazard assessment identifies hazards and operational deficiencies in the process or procedure being studied and in particular evaluates the response of the system to deviations from the intent of the design. The procedure for performing a hazard assessment consists of generating a document that lists the deviations with their causes, consequences, safeguards and recommendations. The best method for generating a hazard assessment document is to bring together several experts with various backgrounds in a series of structured, facilitated, “brainstorming” sessions. The aerospace industry, petrochemical industry, and chemical societies are excellent sources for examples and procedures for performing a hazard assessment.

Annex A
(informative)

Hydrogen properties

Table A.1 provides selected safety-related physical and thermophysical properties of normal and parahydrogen.

Table A.1 — Selected safety-related physical and thermophysical properties of normal and parahydrogen

Property [a]	**Normal hydrogen**	**Parahydrogen**
Properties at normal temperature and pressure (NTP)		
Temperature, K	293,15	293,15
Pressure (absolute), kPa	101,325	101,325
Density, kg/m^3	0,083 76	0,083 76
Specific heat at constant pressure (c_p), kJ/kg·K	14,33	14,89
Specific heat ratio (c_p/c_V)	1,416	1,383
Enthalpy, kJ/kg	4 129,1	4 097,7
Internal energy, kJ/kg	2 919,5	2 888,0
Entropy, kJ/kg·K	70,251	64,437
Velocity of sound, m/s	1 294	1 294
Viscosity, µPa·s	8,81	8,81
Thermal conductivity, mW/m·K	183,8	191,4
Heat of conversion from normal to parahydrogen at 300 K, kJ/kg	27,56	—
Volume expansivity, K^{-1}	0,003 33	0,003 33
Properties at critical point (CP)		
Temperature, K	33,19	32,976
Pressure (absolute), kPa	1 315	1 292,8
Density, kg/m^3	30,12	31,43
Latent heat of vaporization, kJ/kg	0	0
Specific heat at constant pressure (c_p), kJ/kg·K	Very large	Very large
Specific heat ratio (c_p/c_V)	Large	Large
Enthalpy, kJ/kg	577,4	38,5
Internal energy, kJ/kg	—	2,8
Entropy, kJ/kg·K	27,07	17,6
Velocity of sound, m/s	—	350
Viscosity, µPa·s	(3,5)	3,5
Thermal conductivity, mW/m·K	Anomalously large	Anomalously large
Properties at normal boiling point (NBP)		
Temperature (K)	20,930	20,268
Pressure (absolute), kPa	101,325	101,325
Density, kg/m^3	1,331 (V) 70,96 (L)	1,338 (V) 70,78 (L)
Latent heat of vaporization, kJ/kg	446,0	445,6
Specific heat at constant pressure (c_p), kJ/kg·K	12,20 (V) 9,772 (L)	12,15 (V) 9,688 (L)
Specific heat ratio (c_p/c_V)	1,683 (V) 1,698 (L)	1,869 (V) 1,688 (L)

Table A.1 (*continued*)

Property [a]	Normal hydrogen	Parahydrogen
Enthalpy, kJ/kg	717,98 (V) 272,0 (L)	189,3 (V) – 256,3 (L)
Internal energy, kJ/kg	641,9 (V) 270,7 (L)	113,6 (V) – 257,7 (L)
Entropy, kJ/kg·K	39,16 (V) 17,32 (L)	29,97 (V) 7,976 (L)
Velocity of sound, m/s	357 (V) 1 101 (L)	355 (V) 1 093 (L)
Viscosity, µPa·s	1,1 (V) 13,2 (L)	1,1 (V) 13,2 (L)
Thermal conductivity, mW/m·K	16,9 (V) 99,0 (L)	16,9 (V) 99,0 (L)
Volume expansivity, K^{-1}	0,064 2 (V) 0,016 4 (L)	0,064 2 (V) 0,016 4 (L)
Heat of conversion from normal to parahydrogen, kJ/kg	527,14	—
Properties at triple point (TP)		
Temperature, K	13,957	13,803
Pressure, kPa	7,205	7,042
Density, kg/m^3	0,129 8 (V) 77,21 (L) 86,71 (S)	0,125 6 (V) 77,021 (L) 86,50 (S)
Specific heat at constant pressure (c_p), kJ/kg·K	10,53 (V) 6,563 (L) — (S)	10,52 (V) 6,513 (L) — (S)
Specific heat ratio, c_p/c_V	1,695 (V) 1,388 (L) — (S)	1,693 (V) 1,382 (L) — (S)
Latent heat of vaporization, kJ/kg	452,0	449,2
Latent heat of fusion, kJ/kg	58,09	58,29
Latent heat of sublimation, kJ/kg		507,39
Enthalpy, kJ/kg	669,67 (V) 217,6 (L) 159,5 (S)	140,3 (V) – 308,9 (L) – 367,2 (S)
Internal Energy, kJ/kg	612,52 (V) 215,8 (L) 157,7 (S)	84,23 (V) – 309,0 (L) – 367,3 (S)
Entropy, kJ/kg·K	46,4 (V) 14,2 (L) 10,1 (S)	37,52 (V) 4,961 (L) 0,739 (S)
Velocity of sound, m/s	307 (V) 1 282 (L) — (S)	305 (V) 1 273 (L) — (S)
Viscosity, µPa·s	0,74 (V) 26,0 (L) — (S)	0,74 (V) 26,0 (L) — (S)
Thermal conductivity, mW/m·K	12,4 (V) 73,0 (L) 900 (S)	12,4 (V) 73,0 (L) 900 (S)
Volume expansivity, K^{-1}	0,075 2 (V) 0,010 2 (L)	0,075 2 (V) 0,010 2 (L) 0,004 94 (S)

Table A.1 (*continued*)

Property [a]	Normal hydrogen	Parahydrogen
Other properties		
Molecular mass	2,015 94	2,015 94
Equivalent volume gas at NTP/volume liquid NBP	847,1	845,1
Equivalent volume gas at CP/volume liquid NBP	2,357	2,252
Equivalent volume gas at NBP/volume liquid at NBP	53,30	52,91
Equivalent volume gas at TP/volume liquid NBP	546,3	563,8
Equivalent volume liquid at TP/volume liquid NBP	0,919 0	0,919 0
Equivalent volume solid at TP/volume liquid NBP	0,818 4	0,818 1
Pressure required to maintain NBP liquid density in NTP GH_2 (fixed volume, no venting), MPa		172 [b]
Joule-Thomson maximum inversion temperature, K		200
Diffusion coefficient in NTP air, cm^2/s		0,61
Diffusion velocity in NTP air, cm/s		$\leqslant$ 2,0
Buoyant velocity in NTP air, m/s		1,2 to 9
Vaporization rate (steady state) of liquid pool without burning, mm/s		0,42 to 0,83

NOTE 1 (L): Liquid phase.
NOTE 2 (S): Solid phase.
NOTE 3 (V): Vapour phase.
NOTE 4 c_V: Specific heat at constant volume, kJ/kg·K.
NOTE 5 Numbers in parentheses are estimates.

[a] Unless specified otherwise, source of data is reference [9].
[b] Calculated value.

A.1 Comparison with other common gases

Table A.2 provides some safety-related thermophysical properties of gaseous hydrogen and other common gases for comparison purposes.

Table A.2 — Thermophysical properties of common gases

Gas	Density at 20 °C and 100 kPa kg/m^3	Viscosity at 20 °C and 100 kPa µPa·s	Diffusion coefficient in air cm^2/s	Lower heating value MJ/kg
Hydrogen (H_2)	0,082 7	8,814	0,61	119,93
Helium (He)	0,164 0	19,609	0,57	0,00
Methane (CH_4)	0,659 4	11,023	0,16	50,02
Nitrogen (N_2)	1,149 6	17,637	0,20	0,00

A.2 Comparison with other liquefied gases

Table A.3 provides some safety-related cryogenic properties of liquid hydrogen and other liquefied gases at their normal boiling point for comparison purposes.

Table A.3 — Selected properties of some cryogenic fluids at their normal boiling point

Liquefied gas	Boiling temperature K	Liquid density kg/m^3	Gas density kg/m^3	Heat of vaporization J/g
Hydrogen (H_2)	20,3	70,8	1,34	454,6
Helium (He)	4,2	125,0	16,89	20,6
Methane (CH_4)	111,6	422,5	1,82	510,4
Nitrogen (N_2)	77,3	808,6	4,53	198,6

Annex B
(informative)

Hydrogen combustion data

B.1 Safety-related combustion properties

Table B.1 provides selected safety-related combustion properties of parahydrogen.

Table B.1 — Safety-related combustion properties of parahydrogen

Property	Value [a]
Heat of combustion, kJ/g	119,93 (low) 141,86 (high)
Flammability limits, vol fraction, %	4,0 to 75 (in NTP air) [b] 4,1 to 94 (in NTP oxygen) [b, c]
Detonability limits, vol fraction, %	18,3 to 59 (in NTP air) [b] 15 to 90 (in NTP oxygen) [b, c]
Stoichiometric composition in air, vol fraction, %	29,53
Ignition energy (minimum) for ignition in air, mJ	0,017
Auto-ignition temperature, K	858 [d]
Ignition temperature (hot air jet), K	943
Flame temperature in air, K	2 318
Thermal energy radiated from flame to surroundings, %	17 to 25
Burning speed in NTP air, m/s	2,65 to 3,25
Deflagration propagation speed in a stoichiometric H_2/air mixture, m/s	975
Detonation propagation speed in NTP air, m/s	1 480 to 2 150
Maximum experimental safe gap in NTP air, cm	0,008
Quenching gap in NTP air, cm	0,064
Detonation induction distance (L/D) in NTP air	~ 100
Limiting oxygen index, vol fraction, %	5,0
Burning rate of spilled liquid pool, mm/s	0,5 to 1,1
Energy of explosion (theoretical explosive yield), g TNT/g H_2 g TNT/kJ H_2 kg TNT/m^3 NTP GH_2 g TNT/cm^3 NBP LH_2	~ 24 ~ 0,17 [e] 2,02 1,71

NOTE 1 NTP: normal temperature and pressure (293,15 K and 101,325 kPa).

NOTE 2 NBP: normal boiling point (20,268 K and 101,325 kPa).

NOTE 3 TNT: trinitrotoluene, symmetrical (explosive energy = 4 602 J/g TNT).

[a] Unless specified otherwise, source of data is reference [9].

[b] The values are ones commonly given. It is recommended that they be used only as a guide. These properties are a function of many variables that are to be evaluated to determine their values for a specific application.

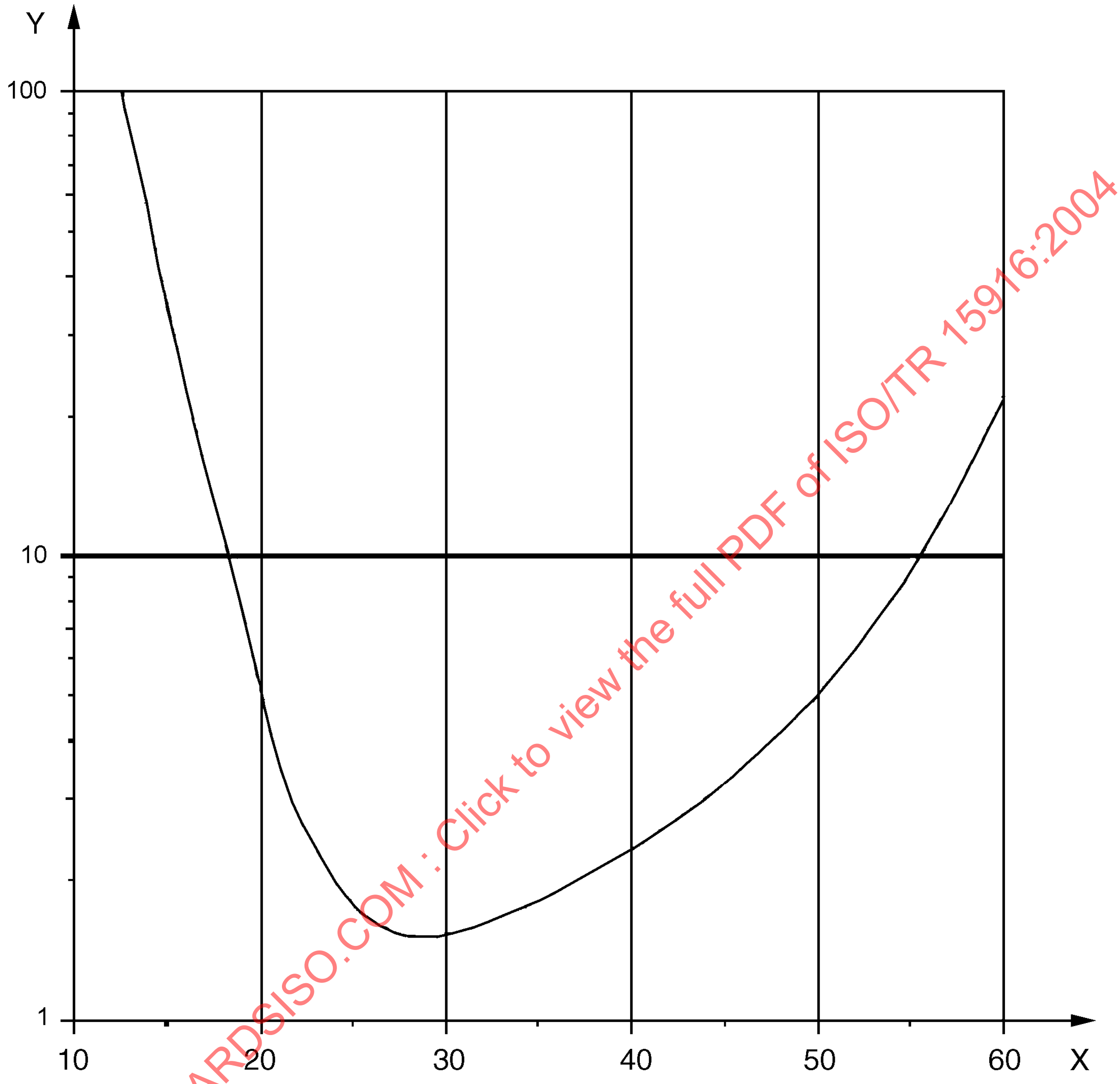
[c] Source of data is reference [8].

[d] Different values have been reported for the autoignition temperature of hydrogen in air ranging from 773 K to 858 K. This variation may be due to the influence of different materials used to contain hydrogen in test apparatus. See reference c above for the source of data.

[e] Based on high heat of combustion.

B.2 Detonation cell widths for hydrogen/air mixtures

Figure B.1 shows detonation cell widths for hydrogen/air mixtures.



Key

X hydrogen concentration, volume fraction (%)

Y detonation cell width, cm

Figure B.1 — Detonation cell widths for hydrogen/air mixtures at 101,3 kPa (14,7 psia) [10]

B.3 Comparison of hydrogen with other common fuels

Table B.2 compares the ignition and combustion properties of hydrogen and other common fuels.

Table B.2 — Ignition and combustion properties for air mixtures at 25 °C and 101,3 kPa for several common fuels

Fuel	Lower flammability limit % vol. fraction	Lower detonation limit % vol. fraction	Stoichiometric mixture % vol. fraction	Upper detonation limit % vol. fraction	Upper flammability limit % vol. fraction	Minimum ignition energy mJ	Auto-ignition temperature °C	Laminar burning velocity cm/s
Hydrogen (H_2)	4,0	18,3	29,5	59,0	75,0	0,017	585	270
Methanol (CH_3OH)	6,0	Not available	12,3	Not available	36,5	0,174	385	48
Methane (CH_4)	5,3	6,3	9,5	13,5	17,0	0,274	537	37
Propane (C_3H_8)	1,7	3,1	4,0	9,2	10,9	0,240	450	47
Gasoline [a] (C_8H_{18})	1,0	1,1	1,9	3,3	6,0	0,240	215	30

NOTE The data in Table 2 are not well-defined physical properties but are determined according to certain standard procedures. Therefore, the data serve for a comparison between common flammable gases only. They should not simply be adopted for the design of installations or components, or for the definition of safety requirements.

[a] The values are given for octane; gasoline may have a different composition depending on its production source.

Annex C
(informative)

Material data

C.1 Material selection criteria

Hydrogen components and hydrogen systems commonly involve a wide variety of material, both metals and non-metals (such as polymers). Each material that is involved (for example, seats, seals, adhesives, lubricants, electrical insulation, springs, bolts and piping) should be carefully evaluated for its use in the design, operating, and emergency conditions to which it will be exposed.

The selection of a material that is suitable for use in a hydrogen system involves several factors. Some considerations involved in the choice of a material to be used in a hydrogen system include the following:

- compatibility with hydrogen (with concerns such as hydrogen embrittlement, hydrogen attack, hydriding, porosity, permeation and diffusion);
- compatibility with adjoining materials (matching properties under changes in temperature and pressure, for example, and the effect of such changes on the material's shape and dimensions);
- compatibility with the conditions of use (effects of temperature and pressure, for example, on ductility, and expansion/contraction; property changes associated with changes in operating conditions);
- compatibility with the surrounding environment or exposure (for example, a corrosive environment or high temperature from a hydrogen fire or fire from nearby materials);
- toxicity (the use of a material that is toxic in any way, such as during fabrication, should be considered only when absolutely necessary);
- failure mode (for example, brittle rapid rupture versus ductile slow separation);
- ability to fabricate into the desired form (for example, machining, welding and bending);
- economics;
- availability.

Most of these considerations are common for the selection of a material for any purpose. However, the first one is unique to hydrogen, and the next two are important for liquid hydrogen applications, because of the low temperature involved (20 K). A brief discussion of these first three considerations is given below.

C.2 Hydrogen embrittlement

Hydrogen embrittlement is a serious concern for metals exposed to hydrogen. Hydrogen embrittlement can cause a significant deterioration in the mechanical properties of metals. Hydrogen embrittlement involves a large number of variables such as the temperature and pressure of the environment; the purity, concentration and exposure time of the hydrogen; and the stress state, physical and mechanical properties, microstructure, surface conditions, and the nature of any crack front in the material. The susceptibility to hydrogen embrittlement of some commonly used metals is summarized in Table C.1.

Although a material may be subject to hydrogen embrittlement (even extremely embrittled), the material may still be used in hydrogen service. For example, compressed gas cylinders that have been used successfully for many years for the storage and transport of compressed hydrogen gas are commonly made of alloy steel 4130X.

Table C.1 — Hydrogen embrittlement susceptibility of some commonly used metals

Metal	Extremely embrittled	Severely embrittled	Slightly embrittled	Negligibly embrittled
Aluminium alloys				
1100				X
6061-T6				X
7075-T73				X
Be-Cu alloy 25			X	
Copper, OFHC				X
Nickel 270		X		
Steel				
Alloy steel, 4140	X			
Carbon steel				
1020		X		
1042 (normalized)		X		
1042 (quenched & tempered)	X			
Maraging steel, 18Ni-250	X			
Stainless steel				
A286				X
17-7PH	X			
304 ELC			X	
305			X	
310				X
316				X
410	X			
440C	X			
Inconel 718	X			
Titanium and titanium alloys				
Titanium			X	
Ti-5Al-2.5SN (ELI)		X		
Ti-6Al-4V (annealed)		X		
Ti-6Al-4V (STA)		X		

C.3 Low temperature effects

C.3.1 General

The selection of a structural material for use in liquid hydrogen service is based primarily on the mechanical properties of the material, such as yield and tensile strengths, ductility, impact strength and notch insensitivity. The material should have certain minimum values for these properties over the entire temperature range of operation, with appropriate consideration for emergency conditions such as a hydrogen fire. The material should be metallurgically stable, so that phase changes in the crystalline structure do not occur with time or repeated thermal cycling.

The choice of a material for use at liquid hydrogen temperature of 20 K involves material behaviour considerations such as the following:

- transition from ductile to brittle behaviour as a function of temperature;
- modes of plastic deformation, particularly certain unconventional modes encountered at very low temperatures;
- effects of metallurgical instability and phase transformations in the crystalline structure on mechanical and elastic properties.

Two of the primary considerations in the selection of a material for liquid hydrogen service are low-temperature ductility (low-temperature embrittlement) and thermal contraction.

C.3.2 Low-temperature embrittlement

Many materials change from ductile to brittle behaviour as their temperature is lowered. This change in behaviour can occur at temperatures much higher than cryogenic temperatures.

The results of the Charpy impact test as a function of temperature can be used as an indication of the ductile-to-brittle transition behaviour of a material. Another indication of the ductile-to-brittle behaviour of a material can be obtained by the relationship of the yield and tensile strengths of a material as a function of temperature. If the yield strength of a material approaches the tensile strength of the material as the temperature decreases, then the material will become increasingly brittle.

Generally, a material that has a ductile-to-brittle transition temperature above 20 K should not be used with liquid hydrogen, unless its use is given careful consideration and thorough analysis. Most polymers become brittle at temperatures much higher than liquid hydrogen temperature, and consequently, their use in liquid hydrogen systems is generally avoided.

C.3.3 Thermal contraction

Materials generally have a positive expansion coefficient, that is, the material will expand as its temperature rises (however there are a few exceptions to this). The temperature span from ambient to liquid hydrogen temperature is about 280 K. Such a large temperature decrease can result in significant thermal contraction in most materials. It is necessary to account for this contraction in the use of a material at liquid hydrogen temperature. The thermal expansion coefficient itself is a function of temperature.

Typical values for thermal contraction for a temperature change from an ambient to a cryogenic temperature are as follows:

- about 0,3 % in iron-based alloys;
- slightly over 0,4 % in aluminium;
- well over 1 % in many plastics.

The use of a plastics material between two metal surfaces (for example, seals) would have to accommodate the approximately 0,6 % more contraction that the plastic would experience compared to the metal.

C.4 Material suitability for hydrogen service

A material should be evaluated carefully before it is used for hydrogen service. A material should not be used for hydrogen service unless data are available to show that the material is suitable for the intended service conditions. Materials that have been used successfully with hydrogen should be preferred over materials with little or no history of use with hydrogen. The suitability of some commonly used materials for use with hydrogen is shown in Table C.2, which is provided as a guideline and for informative purposes only.

Table C.2 — Suitability of some selected materials for hydrogen service

Material	Gaseous hydrogen (GH_2) service	Liquid hydrogen (LH_2) service	Remarks
METALS			
Aluminium and its alloys	S	S	Negligibly susceptible to hydrogen embrittlement.
Copper and its alloys (such as brass, bronze and copper-nickel)	S	S	Negligibly susceptible to hydrogen embrittlement.
Iron, cast, grey, ductile	NS	NS	Not permitted by relevant codes and standards.
Nickel and its alloys (such as Inconel and Monel)	E	E	Evaluation needed. Susceptible to hydrogen embrittlement.
Steel, austenitic stainless with > 7 % nickel (such as 304, 304L, 308, 316, 321, 347)	S	S	May make martensitic conversion if stressed above yield point at low temperature.
Steel, carbon (such as 1020 and 1042)	E	NS	Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic service.
Steel, low alloy (such as 4140)	E	NS	Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic service.
Steel, martensitic stainless (such as 410 and 440C)	E	E	Evaluation needed. Susceptible to hydrogen embrittlement.
Steel, nickel (such as 2,25; 3,5; 5 and 9 % Ni)	E	NS	Ductility lost at liquid hydrogen temperature
Titanium and its alloys	E	E	Evaluation needed. Susceptible to hydrogen embrittlement.

Table C.2 (*continued*)

NONMETALS			
Asbestos impregnated with Teflon [a]	S	S	Avoid use because of carcinogenic hazard.
Chloroprene rubber (Neoprene [a])	S	NS	Too brittle for cryogenic service.
Polyester fibre (Dacron)	S	NS	Too brittle for cryogenic service.
Fluorocarbon rubber (Viton [a])	E	NS	Too brittle for cryogenic service.
Polyester film (Mylar) [a]	S	NS	Too brittle for cryogenic service.
Nitrile (Buna-N [a])	S	NS	Too brittle for cryogenic service.
Polyamides (nylon)	S	NS	Too brittle for cryogenic service.
Polychlorotrifluoroethylene (Kel-F [a])	S	S	
Polytetrafluoroethylene (Teflon [a])	S	S	

NOTE 1 S: Suitable for use.

NOTE 2 NS: Not suitable for use.

NOTE 3 E: Evaluation needed to determine if the material is suitable for the use conditions.

[a] Teflon, Neoprene, Dacron, Mylar, Viton, Buna-N and Kel-F are examples of suitable products available commercially. This information is given for the convenience of users of this Technical Report and does not constitute an endorsement by ISO of these product(s).

Annex D
(informative)

Hydrogen-storing compounds

D.1 General

Hydrogen storage and transport systems can make use of chemical compounds containing hydrogen to improve the energy density for hydrogen storage and to avoid high pressure or low-temperature hydrogen storage requirements. These chemical compounds are energetic materials with their own safety considerations, and should be handled accordingly. In addition, the interaction of chemical compounds with hydrogen systems should be considered.

A variety of chemical compounds using different physical mechanisms for hydrogen storage are under investigation. These include common liquid fuels, metal hydrides, liquid organic hydrides, and newer materials such as fullerenes, carbon-fibre nanotubes and glass microspheres. Some of the liquid fuels considered include methanol, methylcyclohexane (MCH), ammonia, gasoline and hydrazine. Hydride systems may use metal alloys, catalysts and liquid slurries. The safety considerations are presented in general terms because of the great physical differences in these chemical compounds and the systems that use them, the lack of hazards characterization of the more novel materials, and the potential for new as yet undefined systems. Specifics for chemical compounds in common use can be found in material safety data sheets (MSDS) and in safety literature.

D.2 Basic safety considerations for chemical compounds

Basic safety considerations include accounting for physical and combustion properties, handling and toxicity issues, and any special concerns. As a minimum, the following safety information, along with the supplier’s MSDS, should be accounted for in the system design and conveyed to those at potential risk of exposure:

a) general description of common or special hazards;

b) physical properties;

c) combustion properties in air;

d) material compatibility;

e) handling information;

f) toxicity;

g) fire fighting.

Annex E
(informative)

Terms and definitions

This Technical Report is addressed to a very broad audience, including many people who have non-technical backgrounds. Consequently, it is possible that readers might encounter terms in this document with which they are unfamiliar because the document is of necessity technical in its content. To address this possibility, an extended vocabulary of terms with their definitions that are used in this Technical Report is provided below. This vocabulary is intended to make this Technical Report as user-friendly and understandable as possible, and to give a clear intent of the meaning of many of the terms used herein.

E.1
ambient conditions
international standard atmospheric conditions at sea level (288 K temperature and 101,323 kPa absolute pressure), or local surrounding conditions characterized by the temperature and pressure at a particular location, such as a city or facility

E.2
annealing
heat treatment process used to soften hard steel so that it can be machined or cold-worked

E.3
arrested flame
combustion process which is stopped or flame which is put out

E.4
auto-ignition
autogeneous ignition
spontaneous ignition
phenomenon in which a mixture of gases, vapours, mists, dusts or sprays ignites spontaneously with no external ignition source

E.5
auto-ignition temperature
AIT
lowest temperature at which **auto-ignition** (E.4) occurs

E.6
backfill
process by which a desired gas is used to replace an undesired gas in a system volume

NOTE Typically the undesired gas is first removed by evacuation with a vacuum pump, then the desired gas is put in.

E.7
back-flow
flow of a fluid in the direction opposite to the normal flow direction

NOTE This term is used to describe the entry (diffusion) of atmospheric air into a hydrogen vent line.

E.8
ball valve
valve that functions with a ported sphere in a housing

NOTE 1 On-off flow control is achieved by rotation of the sphere 90°.

NOTE 2 Diverter ball valves are available for split-flow and other special applications.