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## **Basic considerations for the safety of hydrogen systems**

*Considérations fondamentales pour la sécurité des systèmes à 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 3.

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is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.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 Technical Report 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 has any experience with the new hydrogen systems under development today. The focus of this document is on the new energy applications. The intent is to provide those unfamiliar with the technology a basis upon which to understand 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 programs. 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, hydroelectric, and fossil fuels; for hydrogen use in energy applications for the home and office heating, generation of electricity; and for 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 document 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 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 ISO 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.

## Basic considerations for the safety of hydrogen systems

### 1 Scope

This Technical Report provides guidelines for the use of hydrogen in its gaseous and liquefied 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 ISO standards.

**NOTE** 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 currently in use today. The manufacturers of hydrogen appliances will need to consider these guidelines to tailor sufficient specific information for the operation of their appliance, in the environment in which it is to be used, and for the audience that must use it. 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 document can lead to a continuation of the successful use of hydrogen.

### 2 Normative references

The following normative documents contain provisions that, referenced in this text, constitute provisions of this Technical Report. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this Technical Report are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 11114-4:—<sup>1)</sup> *Transportable gas cylinders — Compatibility of cylinders and valve materials with gas contents — Part 4: Test methods for hydrogen compatibility with metals*

ISO 14687: 1999/Cor 1:2001 *Hydrogen fuel – Product Specification*

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1) To be published.



### **3 Terms and definitions**

This Technical Report is addressed to a very broad audience, including many that are non-technical in their background. Consequently, it is possible that a reader might encounter terms in the document with which he or she is unfamiliar because the document is of necessity technical in its content. To address this possibility an extended glossary of terms, with definitions, that are used in this technical report is provided in Annex E. This glossary is intended to make the report as user friendly and understandable as possible, and to give a clear intent of the meaning of many of the terms used.

### **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: (1) production, (2) storage and transport, and (3) use of hydrogen. Some applications may involve all three categories. The following discussion introduces the basics of hydrogen infrastructure.

##### **4.1.2 Production**

The primary means of bulk production of hydrogen today involve chemical processes such as steam reforming of natural gas, displacement of hydrogen from acids by metals, and electrolysis of water. In the 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 and the hydrogen is a byproduct) on demand. Proton Exchange Membrane (PEM) electrolyzers 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 is to be processed into a state that 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 temperature 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. 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 in the liquid). This requires chilling the hydrogen to cryogenic temperatures (about 20 K) to form a liquid and below 14 K to form hydrogen slush. At present, slush hydrogen has only been considered as an aerospace propellant and the economics for production do not favour its use. To maintain the hydrogen as a cryogenic fluid in storage, exposure to ambient-level heat is 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 reliquification, slow loss of hydrogen to the atmosphere is to be accepted unless the use rate exceeds the boiling rate, or alternatively a boil off management system is adopted. Transport of liquefied 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 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 in most applications. Liquefied 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 application in hydrogen storage systems (See Annex D). A device called a reformer can be used to obtain the hydrogen from the storage compound. Where these systems use chemicals other than hydrogen, special safety considerations unique to the materials should be applied in addition to the considerations for hydrogen and such considerations are beyond the scope of this document.

#### 4.1.3.5 Vehicular storage systems

The volume of hydrogen and weight of containment vessels for high-pressure gaseous systems or cryogenic systems are challenges for vehicular fuel storage design. To reduce the volume and weight 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 by applying 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 electrolyzers 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 storage media, and then convert it back to electricity when it is needed. This is done with an electrolyzer that converts the renewable energy into hydrogen. The hydrogen is processed for storage and used with a fuel cell 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 those components that control, make safe, supply hydrogen, store hydrogen, or otherwise support the primary function.

## 4.2 Typical hydrogen system components

### 4.2.1 Basic hydrogen components

A description of a generic hydrogen system is presented to help the reader identify components integral to discussion on hydrogen safety. Examples of components that perform primary functions include for aerospace applications the rocket thrusters within rocket motors, for energy applications the cell stacks within fuel cells, for transportation applications the internal combustion engine, and for residential use the catalytic converter within a cook stove. Ancillary components that provide essential support for the primary function 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) Controls; and
- d) Pressure relief system [which will be incorporated in the design of components a), b), and c)].

Characteristics of note for hydrogen components are described below to further clarify their function.

### 4.2.2 Storage vessels

The design and function of storage vessels and their components should reflect the type of service typically as, either high-pressure gaseous vessels or cryogenic liquid vessels. Quantities greater than 7,500 litres under standard conditions are usually located outside 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 is to be maintained with vacuum pumps.

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

Piping and seals are 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 Controls

A variety of components are used to control the flow of hydrogen within the system. The most common mechanical components are valves, check valves and regulators. These may be manual or controlled remotely using electric or pneumatic actuators. Actuators are to be specifically designed so 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 the control system.

### 4.2.5 Pressure relief components

Vessels and piping that confine or potentially may confine hydrogen should be protected against overpressurization with a pressure relief system. Examples of circumstances that might 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 relief system typically uses relief valves and burst (rupture) disks to direct overly pressurized hydrogen to the vent system. A relief valve possesses a spring-loaded seal that opens when a set pressure is exceeded. A burst disk is a similar device except relief occurs upon rupture of a pressure sensitive diaphragm. It is usually used in parallel with the relief valve as a failsafe path for over pressurization. The burst disk is to be replaced if it is engaged. Even the

evacuated spaces in vacuum-jacketed lines in a cryogenic system are to be protected from a failure that could introduce high-pressure hydrogen.

#### 4.2.6 Detection components

Outside of the hydrogen system the control system may monitor for hydrogen fire or gas. A variety of technologies are available to detect hydrogen gas. Hydrogen detectors are typically placed above a likely 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 may use catalytic converters and getters to remove unwanted or excess hydrogen. Filters may be used to remove impurities from hydrogen in the system or from ancillary systems that are involved. For example, the 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: (1) considerations for the conditions in which the system is operated, (2) failsafe operation that accounts for potential modes of failure, and (3) long-term plans, which cover the operational life of the system. For example, fixed-hydrogen systems are to be located or sited 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 hydrogen storage. Hydrogen designs are to account for all possible circumstances anticipated during the life of their operation and the designs are to 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 that specify increasing purity level. The cost of storage and handling increases with a reduction in impurities. ISO 14687:1999/Cor 1:2001 specifies impurity levels for water (H<sub>2</sub>O), total hydrocarbon (THC), oxygen (O<sub>2</sub>), argon, nitrogen (N<sub>2</sub>), helium, carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), mercury, sulphur, and permanent particulates.

### 4.4 Environmental effects

The environmental effects arising from the use of hydrogen systems are anticipated to be benign. Pure H<sub>2</sub>O, with very minor exceptions, is the only reaction product. The exception being air-breathing systems that combust hydrogen at high temperatures can create nitrogen oxides (NO<sub>x</sub>). PEM fuel cells and electrolyzers will produce only water and some electrolyzer-fuel cell systems may capture most of the water produced for reuse. This formation of water from hydrogen/oxygen reactions is well known by 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 H<sub>2</sub>O emissions. This elimination of pollutants (such as CO, CO<sub>2</sub>, and NO<sub>x</sub>) as a byproduct of reaction is a primary benefit from using hydrogen systems.

## 5 Safety considerations for the use of hydrogen in its gaseous and liquefied forms

### 5.1 Overview

An overview of the safety considerations necessary to avoid hazards and successfully use hydrogen is presented in this clause. The unique properties of hydrogen that make it valuable as an energy carrier or fuel require proper design and operation 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 face the operators. For instance, whether the system operates with high-pressure hydrogen or operates at cryogenic temperatures, defines the nature of potential hazards. The term hazard is used often in connection with safety, so for clarity a definition is provided. Hazards are events or conditions that can result in exposure to harm or loss. This includes injury or death, damage to property, equipment or the environment, delay or failure of mission, and interruption of business.

The primary hazards and issues associated with hydrogen systems can be categorized and prioritized in order of concern 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. Health is placed last because the realization of any of the first four concerns can result in consequences that far overshadow the concerns 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 its properties

#### 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 are common to all hydrogen systems, the way these hazards manifest themselves arises from how the hydrogen is used as a liquid or 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 selected property data are tabulated in Annex A.

## 5.2.2 Gaseous hydrogen

Gaseous hydrogen has neither a characteristic colour nor odor. 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, will 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 our unaided senses if they do not make an audible noise. It has been demonstrated that hydrogen can move slowly through confined materials. This rate varies for different kinds of materials. For metals such as steel, at ambient temperature, the rate is extremely low with insignificant quantities moving over very long periods of time. Some caution should be observed with polymeric materials, which allow a greater movement that can accumulate significant quantities of hydrogen, if the flow enters into a small unventilated volume. Hydrogen gas dissolved in liquids will permeate into adjoining vessel materials. Because of gaseous hydrogen's low density under ambient conditions, it is typically stored and transported 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, 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 in an ambient temperature environment (300 K). Warming liquid hydrogen to an ambient temperature gas can lead to very high pressures should it be 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 these temperatures. Leaks of air, nitrogen, or other gases past valve seals into direct exposure with the 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 can 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 uninsulated pipes and vessels containing liquid hydrogen can condense gases such as air into solid and liquid forms on the outer surfaces. The liquid condensate flows, and looks like liquid water. Should the oxygen component within liquid air contact combustible materials fire and explosion hazards can result.

## 5.3 Factors involved with combustion hazards

### 5.3.1 Aspects of combustion

The principle hazard presented by hydrogen systems is uncontrolled combustion of accidentally released hydrogen. This is held to be 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 release that may occur as fire or explosion.

For hydrogen to combust, two additional elements are to be present: an oxidizer such as air and a source of ignition. Each factor necessary for combustion, a fuel, an oxidizer, and an ignition source, can represent one of the three sides of a triangle, a concept known as the 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 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 are dependent on the circumstances of how the hydrogen is exposed to an oxidizer. In

standard terrestrial applications, air is an omnipresent oxidizer. Electrolyzers and some fuel-cell systems may have the potential to mix pure or enriched oxygen with hydrogen.

Basic hydrogen combustion data is provided in Annex B.

### 5.3.2 Fire

A source of hydrogen, for example a leak, when surrounded by an oxidizer such as air can be ignited much in the same fashion as a Bunsen burner to produce a fire. 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 jets. 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 and practically no radiation in the visible range, but significant radiation in the ultraviolet range. 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 fire 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, from a safety perspective there are several other consequences of these properties. First, hydrogen combustion is almost visually imperceptible under artificial light or daylight. Equally important is that human physical perception of heat doesn't occur until direct contact with the combustion gases. Operations in proximity to hydrogen flames should also consider UV exposure. 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 Explosion

#### 5.3.3.1 General

When hydrogen and 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, either process may be perceived as an explosion. Shock waves 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 materials (shrapnel). To our physical senses the blast 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 in the uncombusted 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 meters per second in a process known as flame acceleration. If the flame reaches high speed and encounters turbulence, the deflagration process may transition 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 uncombusted media, typically 1500 m/s to 2000 m/s and 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 high 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 for detonation. Detonations that impinge on surfaces are reflected such that the superposition of the incident and reflected pressure waves are additive, producing greater pressures 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 high explosives. For this form of combustion to occur, the mixture is to be subjected to an initiation source with an energy equivalent to a high explosive charge. There is no well-developed body of information characterizing this process.

#### 5.3.3.5 Safety considerations for deflagration and detonation

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 for 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 reflections, pressures 50 times the initial pressure can form. One important consideration is that the relief systems designed to protect hydrogen systems from overpressure rely on sensing the buildup of pressure. Because detonation waves move faster than the speed of sound, relief systems do not sense the approach wave and cannot react in time protect their system from the rapid pressure rise.

### 5.4 Factors involved in pressure hazards

#### 5.4.1 General

Many hydrogen applications contain hydrogen in 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 considerable increase in volume is associated with the phase change of liquid hydrogen to gaseous hydrogen, and still another volume increase occurs for gaseous hydrogen that is warmed from liquid temperature to ambient temperature.

#### 5.4.4 Safety considerations

In a liquid hydrogen system the ratio of the final volume to the initial volume for this phase change and expansion of heated gas is 845. Confinement of this total volume increase can result in a final pressure of 172 MPa (25 000 psia). A pressure of this magnitude may overpressurize containment structure 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 any part 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 a safe distance from personnel and other facilities should be considered essential as a consequence of this hazard.

## 5.5 Factors involved in temperature hazard

Many materials experience a reduction in size, a drastic decrease of 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 shrinkage of materials. The consequence of failure of these materials in hydrogen service 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 hazard

### 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 are to 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 centered 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 at surface defects or other stress raisers as a result of stress induced local plastic deformation processes. Impurities like hydrogen sulphide dissociate into atomic hydrogen even more easily than molecular hydrogen.

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

### 5.6.2 Hydrogen attack

At temperatures above 473 °C, many low-alloyed structural steels may 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 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 2323 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 and because of their low emissivity, or characteristic that little infrared radiation is produced by the combustion, cannot be sensed as heat by personnel 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 safe use of hydrogen

The primary cause of accidents with hydrogen systems is due to human error (see Clause 7.1.2). The basis for an accident and the extent of its consequences may not lie only with a system's immediate operators, but may be due in part to how hydrogen and its particular application are viewed by all personnel in an extended organization. The limitations of a particular hydrogen system design, its operation and maintenance requirements, and the potential for exposure of personnel and the public to hazards should be understood as needed 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 either of three possible atomic weights or isotopes: protium, deuterium and 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<sub>2</sub>, in which two hydrogen atoms have formed a covalent bond. There are two molecular forms: orthohydrogen in which the spin states of the two hydrogen nuclei are parallel (both with the same spin) and parahydrogen in which the spin states are antiparallel (with opposite spins). Bulk hydrogen, whether in gaseous or liquid form, is a mixture of orthohydrogen and parahydrogen in which the temperature determines 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 affect on most non-nuclear energy safety considerations. Deuterium (D<sub>2</sub>) is found only in trace quantities in nature and tritium (T<sub>2</sub>) 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 will typically use thermophysical data that applies to normal hydrogen (protium). The only exception occurs for cryogenic applications where heat is an important parameter such as liquid hydrogen storage. The larger property differences between ortho- and parahydrogen occur in those properties

where 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 will result in different physical properties and their radioactivity may be a safety concern.

### 6.1.2 Appearance and general characteristics

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

### 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 subatmospheric pressure). These temperatures are less than a tenth of the ambient temperature “shirt-sleeve” environment with which we are familiar.

## 6.2 Selected thermophysical properties

### 6.2.1 General

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

### 6.2.2 Selected thermophysical properties of gaseous hydrogen

#### 6.2.2.1 Dispersion of hydrogen

Hydrogen possesses high buoyancy and greater diffusivity than other gases. Under ambient conditions, hydrogen has a density of 0,0838 kg/m<sup>3</sup> and a specific gravity of 0,0696 (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, i.e. cooling a gas makes it more dense. The small size of the hydrogen molecule gives it a 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 and 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 Joule-Thomson coefficient

On a molar basis the heat capacity of hydrogen is similar to that of other diatomic gases despite its low molecular weight. 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 heating. 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<sup>3</sup>. The corresponding specific gravity is 0,0710 (H<sub>2</sub>O = 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 volume increase occurs for gaseous hydrogen that is warmed from the NBP to NTP. The ratio of the final volume to the initial volume for this process 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/kgK, 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

The ignition and combustion properties for hydrogen are discussed in clause 6.3. Hydrogen-oxidizer mixtures can combust either as a fire at a fixed point, 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 size. Some hydrogen combustion data is given in Annex B. Selected combustion data for several common fuels is 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 is 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 percentage by volume basis. The flammability limits for hydrogen in air under ambient conditions are shown in Table B.3 ranging from 4 % to 75 % by volume. In comparison to more common fuels such as gasoline, this is a very broad range.

Specialized combustion data should be consulted for hydrogen introduced to 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, the distance between adjacent confining surfaces, and the 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 autoignition 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- 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 2,7 m/s. Confinement, as found between walls, within pipes, and ducts, traps the expanding

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

### **6.3.5 Detonation**

#### **6.3.5.1 General**

A detonation is characterized by the autoignition of a shock-compressed gas. It propagates at supersonic velocities of 1500 m/s to 2000 m/s relative to the supporting unburned 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 form. Data for hydrogen/air detonations is 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 energy 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 in the order of 1 kJ, which is typical of solid explosives.

Compared to the fire and deflagration processes, 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**

General principles, guidelines, and recommended practices that are essential for the safe hydrogen use are described in this clause. 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 will 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 percentage involved. More than one factor may have been involved in some mishaps; consequently, the total percentage shown for these categories sums to 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 cause. 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. Materials 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 was found at fault for 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 people making mistakes. 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: (1) minimize the possibility for human error, and (2) 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 one 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 to the maximum possible extent. For example, limit the exposure of people to the hazard by both the times that they can be exposed and the number of people that can 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 flow rate 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 to justify the decision that it can be accepted.

#### **7.1.4 Minimize the severity of the consequences of a hazard**

An important principle underlying safe hydrogen use is to seek designs and operations that minimize the severity of the consequences of a 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 failure of hydrogen equipment or storage systems;
- Elevate hydrogen systems or venting 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 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 keep weeds and other debris away from hydrogen systems; and,
- Observe safe operational requirements such as the use of the buddy system when working 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 is 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- or dual-fault tolerant 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 flow rate) 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 such caution and warning devices as necessary to alert personnel in the event of any abnormal condition, malfunction, or failure. Such devices should provide personnel adequate time to respond to the event.

## 7.2.2 Considerations in the selection of suitable materials of construction

### 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 nonmetals (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-centered 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 may also be used to give satisfactory behaviour in cryogenic service.

The design of equipment for low temperature service should account for the stress set up 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 may be insulated using vacuum jacketing or insulators. Care should be taken where insulators made from a flammable foam or other flammable material can be directly exposed to condensed liquid air. Oxygen enrichment can increase flammability and even lead to the formation of shock-sensitive compounds.

When use conditions permit 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:

- 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 by e. g. stress-relieving weldments and by normalizing or fully annealing cold-worked material;
- 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 that 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; and
- 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 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 Nonmetallic materials

The application of nonmetallic materials 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 easier 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.

Fibre-reinforced polymers (FRP's) 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 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 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, and
- Legibly marked with the name "Hydrogen" or "Liquefied Hydrogen — Flammable Gas" for gaseous or liquid containers as appropriate.

Liquid hydrogen tanks that are frequently filled and emptied should be regularly checked for the accumulation of impurities such as oxygen and nitrogen. 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 may interfere with the operation of valves and other equipment. Oxygen accumulation in stored hydrogen should not exceed 2 % by volume 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 one 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 of 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 where 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 may 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,
- Have appropriate supports, guides, and anchors for the use conditions,
- Have pressure relief devices as appropriate,
- Insulate with appropriate thermal insulation (especially liquid hydrogen and cold gaseous hydrogen piping), and
- Label as to contents and flow direction.

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 of these 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 in 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 effectively maintain the system 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 may be crucial in 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 types 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 solid particles, and, in liquid hydrogen systems, 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 resupply 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 operation of the system and for safety of the system. The system should have adequate instrumentation and controls to ensure that 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 will 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 a fire, deflagration, or detonation. This is done by keeping hydrogen and an oxidizer such as air separate. Some of the aspects of achieving this goal include the following:

- 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 free of leakage 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 to prevent air from the exterior of the system from entering.
- Periodic warm-up of liquid hydrogen systems: Liquid storage vessels should be 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 part of preventing a fire, deflagration, or detonation is to eliminate ignition sources that might ignite a combustible hydrogen/oxidizer mixture. 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 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, nitrogen, hydrogen, sand, metal, oxide flakes from the walls of pipes, etc.) could be important. The potential for static electricity generation may 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 against another such as with clothing fabrics or that might occur with two-phase flow causes 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 the potential fields can result during the approach and passing of a storm.
- 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 equipment failure 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 discharge 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

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

- 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: Examples include welding and cigarette smoking by personnel.
- Exhaust: Examples include combustion engines and exhaust stacks.

- Explosive charges: 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: Repeated shock waves 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 with a system; and
- Using diluents and water spray systems to retard flame acceleration. Note that hydrogen/air flames are difficult to quench and can burn around the droplets in heavy water sprays.

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 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. Where 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 Hydrogen and fire detection

### 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 where hydrogen is used. Some suggested locations for hydrogen detectors include:

- Locations where hydrogen leakage or a spill is possible,
- At hydrogen connections that are routinely separated (hydrogen refuelling ports, for example),

- Locations where hydrogen could accumulate,
- In building air intake ducts if hydrogen could be carried into the building, and
- 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 by volume 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 during daylight to the human eye. 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 should 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:

- 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, and
- 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 do the design of hydrogen components and systems.

### 7.5.2 Site

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

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

- The most credible event that could occur, which would involve parameters like 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, and
- The type of activities involved at the hydrogen facility (propulsion testing, for example).

### 7.5.3 Exclusion areas

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

- Limiting access to necessary, authorized personnel (who should meet necessary training requirements, and are properly clothed and equipped);
- Approved equipment (meeting specified requirements, such as elimination or control of ignition sources);
- Approved operations (which are to be consistent with the requirements of safety to personnel and reducing risks to adjacent facilities);
- Controlled areas should be placarded with appropriate warnings so that personnel will be aware of the potential hazard in the area; and
- Consideration given to 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 control how many personnel are within the exclusion area at the same time.

#### 7.5.4 Dikes, impoundments, and barricades

A dike or impoundment may 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 may limit the vaporization rate, which could possibly produce a smaller combustible cloud but could also result in a longer time to vaporize the spilled liquid.

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

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

#### 7.5.5 Control safety equipment

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

- Warning system: A warning system should be installed to detect abnormal conditions, malfunctions, and indicate incipient failures. Warning system data transmissions with visible and audible signals should have sufficient redundancy to prevent any single-point failure from disabling the system.
- Flow control: Safety valving and flow regulation should be installed to adequately respond for protection of personnel and equipment during hydrogen storage, handling, and use.
- Safety features: System and equipment safety features should be installed to automatically control the equipment required to reduce the hazards suggested by the 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 as safety control equipment should be (1) independent of similar equipment for normal operations, and (2) 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.

Common purging techniques include the following:

- 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: rate, duration, mixing, and dilution. The inert gas subsystem should be protected by a suitable means against contamination with hydrogen.

### 7.5.6 Hydrogen disposal

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 include:

- The quantity of hydrogen that could exist in a combustible cloud,
- The extent of the combustible cloud,
- Thermal radiation from a flame (from an flare system, or from a vent system fire), and
- Site conditions such as size of 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 vent system could be plugged by the ice.

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 distance applied to protect personnel.

Vents on a roof 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 to minimize the hydrogen hazards involved.

- Constructed of noncombustible materials,
- No spaces where hydrogen could accumulate;
- No sources of ignition,
- Pressure relief for a potential explosion overpressure,
- Adequate ventilation, and
- Hydrogen detectors.

### 7.5.8 Ventilation

Considerations for ventilation should address, as appropriate, the scenarios of (1) a hydrogen presence inside a confined space, and (2) a migration into a confined space of hydrogen 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 could introduce hydrogen into the 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 hydrogen should always have an active or passive ventilation system. The confined space should have hydrogen detection device(s) to detect the presence of hydrogen and to avoid the build up of a flammable mixture.

Considerations for ventilation systems include:

- 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 ensured.
- Electrical equipment in the ventilation system should meet appropriate provisions for operation in a combustible environment as appropriate.

### 7.5.9 Electrical

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:

- Under normal operating conditions (such as a fill port),
- Frequently because of repair or maintenance operations or leakage, or
- Because of a 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 a location as 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 of a location as described above, or within a distance of about 5 m of a gaseous hydrogen storage vessel or 8 m of a liquid hydrogen storage vessel, should be considered carefully also, but their requirements are somewhat less stringent than the closer location described above.

Electrical equipment located at a distance greater than 1 m as described above should not produce sparks, arcs, or other ignition mechanism.

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 its 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 a safe shutdown of the hydrogen system.

The warning system should provide audible, visible, or both alarms.

Some system alarm/warning conditions are as follows:

- 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 considerations**

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

- 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, and 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 by 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, are the 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 temperature, flame temperature, 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.

Some specific recommendations for PPE are:

- Eye protection should be worn. 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 and remove easily, but 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<sup>®</sup> 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<sup>®</sup> 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 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 a 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, that 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) that 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 creates high stress in a pipe. Stratified or wave flow (usually associated with a low flow rate) 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 liquid and the top part is cooled by gas.

The cool down process generally results in the generation of a large quantity of gas that is to be handled safely. The system should be designed to accommodate the large gas flow that is needed to achieve 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 General storage and transfer operations**

Some general guidelines for storage and transfer operations include the following:

- Do not overfill a liquid storage vessel
- Do not over-pressurize 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 in an electrical storm, or as 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”.
- 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 and approved by appropriate personnel prior to their use. By providing written instructions that are carefully reviewed and approved, procedures and checklists are important elements in the safe operation of a hydrogen system. These documents can provide information that includes instructions on steps to take in the event of a leak or other event, and special equipment (such as personal protective equipment and monitoring equipment) that is needed. Procedures and checklists should be reviewed periodically to verify their effectiveness.

Among those operations for which procedures should be established are the following: cleaning, cool down, operating, purging, storage (especially fill), hydrogen transfer, leak checks, modifications, repairs, maintenance, and decommissioning.

### 7.6.7 Emergency 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 includes events listed below:

- 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
- Inability to vent a cold gaseous or liquid hydrogen system

#### **7.6.7.2 Considerations for emergency procedures**

Considerations that emergency procedures should address:

- Emergency escape procedures and emergency escape route assignments,
- Procedures to be followed by employees that remain to operate critical facility or system operations before they evacuate,
- Procedures to account for all employees after 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 for further information or explanation of duties under the emergency plan,
- Actions by initially responding personnel,
- Appropriate fire suppression response,
- Establish and maintain communications,
- Appropriate medical response,
- Summoning outside assistance,
- Establishing security,
- Possible media coverage,
- Salvage and restoration operations,
- Establish a command post with a pre-designated line of authority, and
- Hazardous material inventory (including materials such as asbestos).

An emergency alarm system should be established to alerting 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 considerations

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 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 confinements.

The vaporization of liquid hydrogen will rapidly condense 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 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 its personnel to promote thinking about safety at all times, especially as they perform their 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 program or project involving hydrogen is directed, conducted, controlled, monitored, and evaluated. Upper management also should provide controls, guidance, and oversight of such a program or project to ensure that proper planning, monitoring, reporting, evaluation, and assessment of the program 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 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 checks when conducted by an experienced team of qualified personnel.

### **7.7.5 Follow approved maintenance and quality control programs**

Maintenance and quality control programs 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 on a routine schedule.

### **7.7.6 Personnel training**

A detailed safety-training program 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 program 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 as pertains 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 program should be reviewed periodically to ensure that the training program is relevant and up-to-date.

### **7.7.7 Hazards analysis**

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 a hazard assessment. The hazard assessment identifies hazards and operational deficiencies in the process or procedure studied and in particular evaluates the response of the system to deviations from the design intent. 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 the hazards assessment document is to bring together several experts with varying 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 data

#### A.1 Selected hydrogen properties data

Selected safety-related physical and thermophysical properties of normal and parahydrogen are given in Table A.1.

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

Property <sup>a</sup>	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 <sup>3</sup>	0,08376	0,08376
Specific heat at constant pressure (C <sub>p</sub> ), kJ/kg· K	14,33	14,89
Specific heat ratio (C <sub>p</sub> /C <sub>v</sub> )	1,416	1,383
Enthalpy, kJ/kg	4129,1	4097,7
Internal energy, kJ/kg	2919,5	2888,0
Entropy, kJ/kg· K	70,251	64,437
Velocity of sound, m/s	1294	1294
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 <sup>-1</sup>	0,00333	0,00333
Properties at critical point (CP)		
Temperature, K	33,19	32,976
Pressure (absolute), kPa	1315	1292,8
Density, kg/m <sup>3</sup>	30,12	31,43
Latent heat of vaporization, kJ/kg	0	0
Specific heat at constant pressure (C <sub>p</sub> ), kJ/kg· K	Very large	Very large
Specific heat ratio (C <sub>p</sub> /C <sub>v</sub> )	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 <sup>3</sup>	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 <sub>p</sub> ), kJ/kg· K	12,20 (V) 9,772 (L)	12,15 (V) 9,688 (L)

Property <sup>a</sup>	Normal hydrogen	Parahydrogen
Specific heat ratio ( $C_p/C_v$ )	1,683 (V) 1,698 (L)	1,869 (V) 1,688 (L)
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) 1101 (L)	355 (V) 1093 (L)
Viscosity, $\mu\text{Pa}\cdot\text{s}$	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, $\text{K}^{-1}$	0,0642 (V) 0,0164 (L)	0,0642 (V) 0,0164 (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, $\text{kg}/\text{m}^3$	0,1298 (V) 77,21 (L) 86,71 (S)	0,1256 (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) 1282 (L) — (S)	305 (V) 1273 (L) — (S)
Viscosity, $\mu\text{Pa}\cdot\text{s}$	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, $\text{K}^{-1}$	0,0752 (V) 0,0102 (L)	0,0752 (V) 0,0102 (L) 0,00494 (S)

Property <sup>a</sup>	Normal hydrogen	Parahydrogen
Other properties		
Molecular weight	2,01594	2,01594
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	0,9190	0,9190
Equivalent volume solid at TP/volume liquid NBP	0,8184	0,8181
Pressure required to maintain NBP liquid density in NTP GH <sub>2</sub> (fixed volume, no venting), MPa		172 <sup>b</sup>
Joule-Thomson maximum inversion temperature, K		200
Diffusion coefficient in NTP air, cm <sup>2</sup> /s		0,61
Diffusion velocity in NTP air, cm/s		≤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 <sub>v</sub> : Specific heat at constant volume, kJ/kg· K		
NOTE 5 Numbers in parentheses are estimates		
<p><sup>a</sup> Unless specified otherwise source of data is: McCarty, R. D., Hord, J., and Roder, H. M., Selected properties of hydrogen (engineering design data), U.S. Department of commerce, National Bureau of Standards, Washington, DC, NBS Monograph 168, February 1981.</p> <p><sup>b</sup> Calculated value.</p>		

## A.2 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 gases**

Gas	Density at 20°C and 100 kPa kg/m <sup>3</sup>	Viscosity at 20°C and 100 kPa μPa.s	Diffusion coefficient in air cm <sup>2</sup> /s	Lower heating value MJ/kg
Hydrogen (H <sub>2</sub> )	0,0827	8,814	0,61	119,93
Helium (He)	0,1640	19,609	0,57	0,00
Methane (CH <sub>4</sub> )	0,6594	11,023	0,16	50,02
Nitrogen (N <sub>2</sub> )	1,1496	17,637	0,20	0,00

## Comparison with other liquefied gases

Table A.3 lists the safety related cryogenic properties of liquefied 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 <sup>3</sup>	Gas density kg/m <sup>3</sup>	Heat of vaporization J/g
Hydrogen (H <sub>2</sub> )	20,3	70,8	1,34	454,6
Helium (He)	4,2	125,0	16,89	20,6
Methane (CH <sub>4</sub> )	111,6	422,5	1,82	510,4
Nitrogen (N <sub>2</sub> )	77,3	808,6	4,53	198,6

## Annex B (informative)

### Hydrogen combustion data

#### B.1 Safety-related combustion properties

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

**Table B.1 — Selected safety-related combustion properties of parahydrogen**

Property	Value <sup>a</sup>
Heat of combustion, kJ/g	119,93 (low) 141,86 (high)
Flammability limits, vol %	4,0 to 75 (in NTP air) <sup>b</sup> 4,1 to 94 (in NTP oxygen) <sup>b,c</sup>
Detonability limits, vol %	18,3 to 59 (in NTP air) <sup>b</sup> 15 to 90 (in NTP oxygen) <sup>b,c</sup>
Stoichiometric composition in air, vol %	29,53
Ignition energy (minimum) for ignition in air, mJ	0,017
Autoignition temperature (K)	858
Ignition temperature (hot air jet), K	943
Flame temperature in air, K	2318
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 <sub>2</sub> /air mixture, m/s	975
Detonation propagation speed in NTP air, m/s	1480 to 2150
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 %	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 <sub>2</sub> g TNT/kJ H <sub>2</sub> kg TNT/m <sup>3</sup> NTP GH <sub>2</sub> g TNT/cm <sup>3</sup> NBP LH <sub>2</sub>	~24 ~0,17 <sup>d</sup> 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 = 4602 J/g TNT)
<sup>a</sup> Unless specified otherwise source of data is: McCarty, R. D., Hord, J., and Roder, H. M., <i>Selected properties of hydrogen (engineering design data)</i> , U.S. Department of commerce, National Bureau of Standards, Washington, DC, NBS Monograph 168, February 1981.	
<sup>b</sup> 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.	
<sup>c</sup> Source of data is: Benz, F. J., C. V. Bishop, and M. D. Pedley. <i>Ignition and Thermal Hazards of Selected Aerospace Fluids: Overview, Data, and Procedures</i> . NASA White Sands Test Facility, Las Cruces, NM, RD-WSTF-0001, October 14, 1988.	
<sup>d</sup> Based on high heat of combustion	



### B.2 Detonation cell widths for hydrogen/air mixtures

Detonation cell widths for hydrogen/air mixtures are shown in Figure B.1

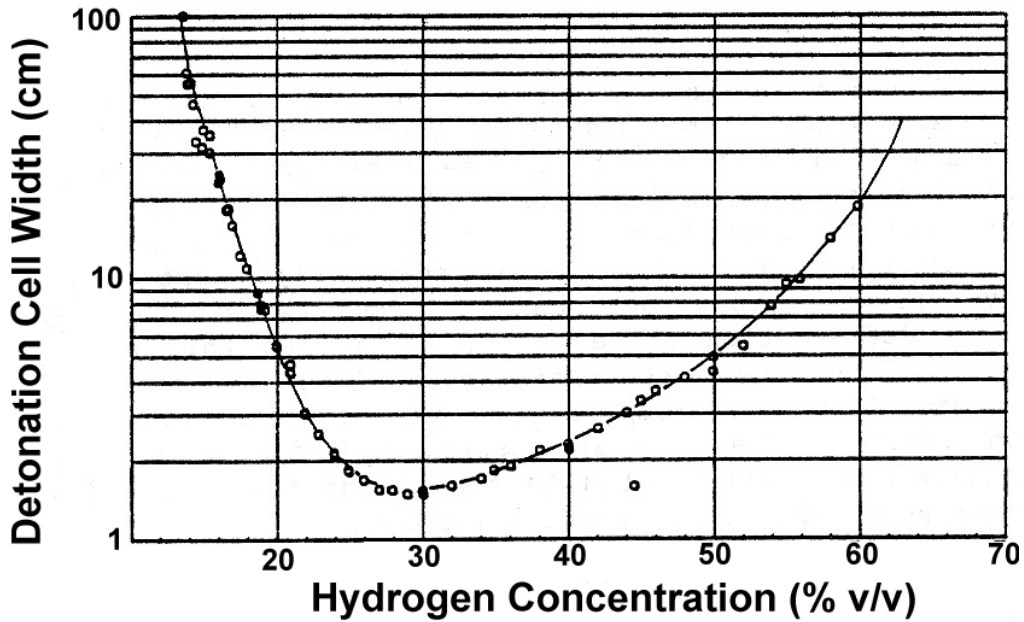


Figure B.1 — Detonation Cell Widths for Hydrogen-Air Mixtures at 101,3 kPa (14,7 psia) (Benz. et. al.)

### 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 % by volume	Lower detonation limit % by volume	Stoichiometric mixture % by volume	Upper detonation limit % by volume	Upper flammability limit % by volume	Minimum ignition energy mJ	Auto-ignition temperature °C	Laminar burning velocity cm/s
Hydrogen (H <sub>2</sub> )	4,0	18,3	29,5	59,0	75,0	0,017	520	270
Methanol (CH <sub>3</sub> OH)	6,0	Not available	12,3	Not available	36,5	0,174	385	48
Methane (CH <sub>4</sub> )	5,3	6,3	9,5	13,5	17,0	0,274	630	37
Propane (C <sub>3</sub> H <sub>8</sub> )	1,7	3,1	4,0	9,2	10,9	0,240	450	47
Gasoline <sup>a</sup> (C <sub>8</sub> H <sub>18</sub> )	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.

<sup>a</sup> The values are given for Octane; gasoline may have a different composition depending on its production source.

## Annex C (informative)

### Materials data

#### C.1 Material selection criteria

Hydrogen components and hydrogen systems commonly involve a wide variety of materials, both metals and non-metals (such as polymers). Each material that is involved (such as for 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 use conditions (effects of temperature and pressure, for example, on ductility, and expansion/contraction; property changes associated with changes in the operating conditions),
- Compatibility with the surrounding environment or exposure (such as, 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 (brittle rapid rupture versus ductile slow separation, for example),
- Ability to fabricate into the desired form (machining, welding, and bending for examples)
- Economics, and
- 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 a 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

The selection of a structural material for use in LH<sub>2</sub> service is based primarily on the mechanical properties (such as yield and tensile strength, ductility, impact strength, and notch insensitivity) of the material. The material should have certain minimum values of 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 LH<sub>2</sub> temperature, 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, and
- 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 LH<sub>2</sub> service are low-temperature ductility (low-temperature embrittlement) and thermal contraction.

### C.3.1 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 ductile-to-brittle transition behaviour of a material. Another indication of the ductile or 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 becomes increasingly brittle.

Generally, a material that has a ductile-to-brittle transition temperature above 20 K should not be used with LH<sub>2</sub> unless its use is given careful consideration and thorough analysis. Most polymers become brittle at temperatures much higher than LH<sub>2</sub> temperature and, consequently, their use in LH<sub>2</sub> systems are generally avoided.

### C.3.2 Thermal contraction

Materials generally have a positive expansion coefficient; that is, the material will expand as its temperature rises (there are a few exceptions to this, however). The temperature span from ambient to LH<sub>2</sub> temperature is about 280 K. Such a large temperature decrease can result in a significant thermal contraction in most materials. It is necessary to account for this contraction in the use of the material at LH<sub>2</sub> temperature. The thermal expansion coefficient itself is a function of temperature.

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

- About 0.3 % in iron-based alloys,
- Slightly over 0.4 % in aluminium, and
- Well over 1 % in many plastics.

The use of a plastic material between two metal surfaces (such as a seal), for example, would have to accommodate the approximately 0.6% more contraction that the plastic would experience than the metal.

## C.4 Material suitability for hydrogen service

A material should be evaluated carefully before it is used in hydrogen service. A material should not be used in hydrogen service unless data is 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	GH <sub>2</sub> service	LH <sub>2</sub> service	Remarks
<b>METALS</b>			
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 LH <sub>2</sub> temperature
Titanium and its alloys	E	E	Evaluation needed. Susceptible to hydrogen embrittlement.
<b>NONMETALS</b>			
Asbestos impregnated with Teflon	S	S	Avoid use because of carcinogenic hazard.
Chloroprene rubber (Neoprene)	S	NS	Too brittle for cryogenic service.
Dacron	S	NS	Too brittle for cryogenic service.
Fluorocarbon rubber (Viton)	E	NS	Too brittle for cryogenic service.
Mylar	S	NS	Too brittle for cryogenic service.
Nitrile (Buna-N)	S	NS	Too brittle for cryogenic service.
Polyamides (Nylon)	S	NS	Too brittle for cryogenic service.
Polychlorotrifluoroethylene (Kel-F)	S	S	
Polytetrafluoroethylene (Teflon)	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.			

## Annex D (informative)

### Hydrogen-storing compounds

#### D.1 General

Hydrogen storage and transport systems may 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, interaction of chemical compounds with the hydrogen system 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 the 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
- a) Physical properties
- b) Combustion properties in air
- c) Material compatibility
- d) Handling information
- e) Toxicity
- f) Fire fighting

## Annex E (informative)

### Terms and definitions

For the purposes of this Technical Report, the following terms and definitions apply.

#### **E.1 AIT (autoignition temperature)**

the lowest temperature at which a material will spontaneously ignite without addition of additional energy such as from an ignition source (see autoignition)

#### **E.2 ambient conditions**

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

#### **E.2 annealing**

annealing is a heat treatment process that is used to soften hard steel so that it may be machined or cold-worked

#### **E.3 arrested**

the combustion process is stopped or the flame is put out

#### **E.4 autoignition**

the phenomenon in which a mixture of gases, vapours, mists, dusts, or sprays ignites spontaneously with no external ignition source. It is also called "autogeneous ignition" and "spontaneous ignition"

#### **E.5 backfill**

a process by which a desired gas is used to replace an undesired gas in a system volume. Typically the undesired gas is first removed by evacuation with a vacuum pump, then the desired gas is put in

#### **E.6 back-flow**

the flow of a fluid in the opposite direction as the normal flow direction. This term is used to describe the entry (diffusion) of atmospheric air into a hydrogen vent line

#### **E.7 ball valve**

the ball valve functions as a ported sphere in a housing. On-off flow control is achieved by rotation of the sphere 90 degrees. They are available as diverter ball valves for split-flow and other applications

#### **E.8 blast wave**

an intense pressure wave set in motion by the shock waves and hot product gases of a hydrogen deflagration or detonation that impinges upon the surroundings, typically air

#### **E.9 Bourdon-tube**

a thin-wall, curved tube, that is closed at one end and the other end is attached to a pressure source. Pressure changes cause a change in the curvature of the tube. This change in curvature is used to indicate the pressure in the system

**E.10 buddy system**

a system used in hazardous operations where one person performs a necessary task while another person located in a safe area observes. The observer is fully prepared (clothing, training, etc.) to effect rescue of the primary person from the hazardous area in the event of incapacitation

**E.11 buoyancy**

refers to the vertical force exerted on a body of less dense hydrogen gas by the surrounding heavier static gas, typically air

**E.12 catalytic converter**

a catalyst that is used for converting orthohydrogen to parahydrogen in a liquefaction process so that the liquid hydrogen produced is mostly parahydrogen. Some commonly used catalysts in this conversion process are: (1) hydrous ferric oxide, (2) chromic oxide on alumina particles, and (3) nickel-based compounds

**E.13 check valve**

a check valve operates on differential pressure and allows flow in one direction only

**E.14 code**

as used in this Technical Report, code refers to regulations, requirements, and standards that have been made binding and mandatory compliance is mandated by a local or national government

**E.15 collimate, collimation**

to make parallel; to line up in a straight line.

**E.16 combustion**

a reaction process [including burning or fire, deflagration, or detonation] by which hydrogen gas, liquid, or solid is oxidized producing hot product gases, heat, ultraviolet radiation, and possibly pressure waves when confined

**E.17 component**

any part of a complete item or system

**E.18 confined space**

A space not normally occupied by personnel. It has limited or restricted openings for entry and exit, may lack adequate ventilation, and may contain or produce "dangerous air contamination"; therefore, it may not be safe for entry.

**E.19 confinement**

physical restriction sufficient to influence the combustion process

**E.20 convection current**

the unforced motion or circulation of a fluid involving the transport of mass from one location to another (see natural convection)

**E.21 cryogenic**

a condition involving a very low temperature (below the atmospheric boiling point of about 120 K)

**E.22 cryopump, cryopumping**

a process that consists of a surface cooled to a temperature of less than 120 K so that gases and vapours condense at this surface. This process is used as a vacuum pump

**E.23 deflagration**

a flame or chemical reaction moving through a flammable mixture at a rate less than the speed of sound in the unburned mixture. Deflagrations are characterized by velocities in the hundreds of meters per second and where confinement acts on the flame, elevated pressures



**E.24 deflagration-to-detonation-transition (DDT)**

an event, often caused by turbulence, in which a deflagration initiates a detonation

**E.25 deluge system**

a water spray system that is used to keep equipment, especially hydrogen storage vessels, cool in the event of a fire

**E.26 detonation**

an exothermic chemical reaction coupled to a shock wave that propagates through a detonable mixture or media. The thermal energy of the reaction sustains the shock wave, and the shock wave compresses unreacted material producing the high temperatures necessary to drive the reaction. The detonation process is characterized by a propagation speed that is greater than the speed of sound in the unburned mixture

**E.27 detonation cell**

the fundamental mechanism for energy release within a detonation. The spatial arrangement of the shock front and acoustic waves moving behind and transverse to the shock front define a cellular region of combustion that is observed experimentally as a “fish-scale” shaped track on sooted foils exposed to the detonation. The width of this diamond shape is denoted the cell size and this length can be empirically related to formulas that can predict the energy required to directly initiate detonation and the physical dimensions of structures that prohibit detonation

**E.28 detonation limits**

the upper and lower detonation limits are the maximum and minimum concentrations of a gas, vapour, mists, spray, or dust in air or oxygen for stable detonations to occur. The limits are controlled by the size and geometry of the environment, the concentration of the fuel, as well as the means by which ignition occurs. Detonation limit is sometimes used as a synonym for Explosive Limit

**E.29 deuterium**

an isotope of hydrogen, denoted “D<sub>2</sub>”, possessing one neutron and one proton in the nucleus

**E.30 diffuse**

the flux of a fluid through another material (for examples, the motion of hydrogen gas through air; or the movement of hydrogen gas through the wall of a rubber hose). The diffusion coefficient is the mass of material diffusing across a unit area in unit time at a unit concentration gradient

**E.31 diluent**

an inert component within a gas mixture that reduces the concentration of the remaining (active) materials

**E.32 ductile, ductility**

the ductility of a material is indicated by the percentage elongation to failure or the reduction in cross-sectional area of a specimen in a simple tensile test. Materials that have an elongation of greater than 5 % at failure are considered to be ductile while those with less than 5 % are considered to be brittle. Materials may make a ductile-to-brittle transition at low temperatures

**E.33 electrolysis**

a process in which electric current is used to promote a chemical reaction, i.e. in the case of water, the separation of hydrogen from oxygen

**E.34 electrolyzer**

a device that performs electrolysis

**E.35 emergency**

an unintended circumstance bearing clear and present danger to personnel or property, which requires an immediate response

**E.36 emissivity**

the relative amount of radiant heat emitted by a surface when compared to a black body at the same temperature. The emissivity of hydrogen/air combustion is small compared to other familiar sources of heat such as a wood fire

**E.37 enthalpy**

a thermodynamic function of a material that is equivalent to the sum of the internal energy and the product of the pressure and the volume. Enthalpy is a term used in lieu of “total heat” or “heat content”.

**E.38 entrainment**

a process wherein the flow of a gas pulls or draws along liquid droplets with the gas flow. This is of special concern in the vent system for a liquid hydrogen storage vessel and is most likely to occur with rapid vent rates. It is undesirable because of (1) the considerable volume expansion of the liquid, which would have an effect on the vent rate, including the vent capability of relief devices, and (2) the loss of the liquid product that occurs

**E.39 explosion**

the rapid equilibrium of pressure between the region of energy release (system) and its surroundings. Explosions may occur through mechanical failure of vessels containing high-pressure fluids (which includes a gas) or through rapid chemical reactions producing large volumes of hot gases (see detonation limit)

**E.40 facility**

a group of buildings or equipment used for specific operations at one geographic location

**E.41 fail-safe**

the ability to sustain a failure without causing loss of equipment, injury to personnel, or loss of operating time

**E.42 fatigue**

the gradual deterioration of a material that is subjected to repeated loading and unloading (see load cycle)

**E.43 fault tolerant, dual**

a system or design in which the failure of two elements to perform as intended does not cause an entire system or design to function unpredictably or catastrophically; that is, it will continue to function as intended. The faults may be in related areas or function completely independently

**E.44 fault tolerant, single**

a system or design in which the failure of a single element to perform as intended does not cause an entire system or design to function unpredictably or catastrophically; that is, it will continue to function as intended

**E.45 fire**

a rapid chemical reaction that produces heat and light; sustained burning as manifested by any or all of the following: light, flame, heat, and smoke; a stationary flame with the flammable mixture fed into the reaction zone. Hydrogen flames are nearly invisible in daylight and without smoke unless other materials are entrained in the flames

**E.46 fire triangle**

a concept aid showing the requirements for combustion. It depicting fuel, oxidizer, and an ignition source as the three sides of a triangle where should any one side not be present, combustion cannot occur

**E.47 flame**

the zone of burning gasses and fine suspended matter associated with the combustion of a substance; a hot, usually luminous burning of gas or vapour. A flame may be stationary with the flammable mixture fed into the reaction zone, or a flame may propagate through the flammable mixture, as in a deflagration (see deflagration)

**E.48 flame front**

region of burning or chemical reaction, typically several millimetres across, that separates burned and unburned regions

**E.49 flammable, flammability**

the degree to which a material is easily ignited in an oxidizing atmosphere. The concentration of a fuel in an oxidizer below which a burning reaction cannot be sustained (see flammability limit)

**E.50 flammability limit, lower flammability limit (LFL), upper flammability limit (UFL)**

the lower (LFL) and upper (UFL) vapour concentrations (usually reported as percent by volume) of fuel in a flammable mixture that will ignite and propagate a flame. These limits are functions of temperature, pressure, diluents, and ignition energy

**E.51 flare flameout**

the extinguishment of the hydrogen flame of a hydrogen flare system resulting in hydrogen being vented unburned to the atmosphere. This process may also be referred to as "blow off"

**E.52 fuel cell**

a device that produces electricity from a chemical reaction between an electrolyte or oxidizer and a fuel such as hydrogen

**E.53 galling**

the damaging or breaking the surface where two parts rub together, creating heat and wear (which produces loose particles). Galling is generally encountered when identical or similar hardness materials are in sliding or rotating contact with each other. The potential for galling increases with materials of similar chemical composition and hardness

**E.54 getter**

a getter is a substance that takes up gas at very low pressures by using a sorption process. A primary use of a getter is to improve or maintain a vacuum in a closed system

**E.55 globe valve**

globe valves derive their name from the globular shaped cavity through which flow passes. The globe valve is considered as a general-purpose valve for on-off control and flow modulation. It has a linear characteristic in terms of percent flow versus percent open. There are three major valves in the "globe" family: globe, angle, and Y. They are all characterized by a closure member (generally, a plug or a tapered plug) that travels in a line perpendicular to the valve seat. They differ primarily in the orientation of the seat to the direction of flow. These valves use a plug to shut off flow at the valve seat and to control flow through the body passages. The plug is attached to a valve stem that protrudes through the bonnet. The bonnet retains pressure in the valve body and contains the packing that prevents leakage of process media along the valve stem. Because the plug is positioned by linear motion of the valve plug stem, these valves are also referred to as sliding-stem valves

**E.56 guideline**

a consensus document that originates from any one of a number of different professional organizations to provide technical information about safe practices and procedures

**E.57 hardness**

a composite property of a material. It includes yield strength, work hardening, true tensile strength, modulus of elasticity, and others. It involves resistance to local penetration, to scratching, to machining, to wear or abrasion, and to yielding

**E.58 hazard**

existing, or potential, condition that can result in, or contribute to, damage to people, property or the environment

**E.59 heat and mass transfer mechanism**

flames in deflagrations propagate by a process in which radiation, hot gas, and chemically active species move into adjacent regions of the unburned gas

**E.60 hydride**

a compound containing hydrogen and another element. These compounds are being investigated as potential storage media for hydrogen

**E.61 hydrogen embrittlement**

the deleterious changes in the physical properties of metals that hydrogen can produce

**E.62 ignite, ignition**

to cause to burn; to catch fire. The raising of a substance to its ignition point (the minimum temperature at which a substance will continue to burn without additional application of external heat

**E.63 ignition energy**

the energy required to initiate flame propagation through a flammable mixture. The minimum ignition energy is the minimum energy required to ignite a particular flammable mixture at a specified temperature and pressure

**E.64 Joule-Thomson coefficient**

the cooling or heating that occurs when a highly compressed gas is allowed to expand in such a way that no external work is done is known as the Joule-Thomson effect. If the Joule-Thomson coefficient is positive, an expanding gas will be cooled; if it is negative the expanding gas will be heated

**E.65 laminar flow**

the flow of fluid particles in paths that are parallel to the axis of the pipe and without any radial flow components

**E.66 load cycle**

the repeated loading and unloading of a material such that it undergoes repeated stressing. For example, the repeated pressurization and depressurization of a storage vessel (see fatigue)

**E.67 maximum allowable working pressure (MAWP)**

the maximum gage pressure permissible in a storage vessel (at its top) or piping system for a designated temperature. The MAWP is the basis for the pressure setting of the pressure relieving devices protecting the vessel or piping system. It may also be the maximum allowable operating pressure rating of pressure vessels manufactured in accordance with national pressure vessel codes

**E.68 metal fracture**

the straining of a metallic material to the extent that it breaks or fails in either a ductile or brittle behaviour

**E.69 MIE (minimum ignition energy)**

the minimum energy required to ignite a flammable mixture under given conditions of temperature, pressure, and diluents present (see ignition energy)

**E.70 molecular weight**

the total weight of atoms within a molecule

**E.71 natural convection**

the motion of fluid particles caused by buoyancy forces that arise when a hot body creates temperature and density gradients within a fluid

**E.72 NBP (normal boiling point)**

the temperature at which a liquid boils at normal atmospheric pressure (101,325 kPa absolute)

**E.73 NO<sub>x</sub> compound**

any compound of nitrogen with oxygen produced by high temperature combustion of fuels with air

**E.74 NTP (normal temperature and pressure)**

a temperature and absolute pressure of 293,15 K and 101,325 kPa

**E.75 Orthohydrogen**

a hydrogen molecule in which the rotation of the nuclear spin of the individual atoms in the molecule is in the same direction (parallel)

**E.76 Overpressure**

the pressure in a blast wave above atmospheric pressure, or a pressure within a containment structure that exceeds the maximum allowable working pressure of the containment structure

**E.77 Parahydrogen**

a hydrogen molecule in which the rotation of the nuclear spin of the individual atoms in the molecule is in the opposite direction (antiparallel)

**E.78 Permeate, permeability**

to spread or flow throughout, or to pass through the openings or interstices of a material. That is, to diffuse through, or throughout. Permeability is the rate of diffusion of a pressurized gas through a porous material

**E.79 Photovoltaic**

A device able to produce an electric potential upon exposure to electromagnetic radiation (includes solar radiation)

**E.80 plastic deformation**

the permanent deformation that occurs in elastic materials when the material is strained beyond its elastic limit

**E.81 pressure regulator**

a device that is used to regulate the pressure in a system to a set value. The regulator converts a variable high pressure input to a constant lower pressure output

**E.82 pressure relief device**

a basic safety device used to prevent the pressure within a system from exceeding the MAWP. This device is installed so that excessive pressure within the containment structure may be relieved before damage to the containment structure can occur. A relief valve is typically a spring loaded valve that will open at a set pressure. A rupture disk contains a membrane that is designed to rupture at a set pressure

**E.83 protium**

the hydrogen isotope with one proton and the most common constituent of molecular hydrogen

**E.84 proton exchange membrane (PEM)**

the name designation for fuel cell and electrolyzer technologies based on a permeable Teflon membrane. The Teflon membrane, a key aspect of this technology, selectively permits hydrogen ions to move in fuel cells or electrolyzers

**E.85 purge**

a process used to remove impurities. For example, before hydrogen is admitted to a system, the air that is in the system should be removed to avoid the formation of a combustible mixture within the system

**E.86 Q-D (quantity distance)**

quantity of flammable or explosive material and distance separation relationships that provide defined types of protection. These relationships are based on levels of risk considered acceptable for the stipulated exposures and are tabulated in appropriate Q-D tables. Relationships include separation distances for safe operations between facilities,

roadways, etc. and total quantities of energetic materials that can interact in a given location. This approach to safety is commonly used for hydrogen in aerospace and military applications

**E.87 Quench**

to terminate a chemical reaction or propagation of a flame

**E.88 quenching distance**

the gap dimension required to prevent the propagation of an open flame through a flammable fuel/air mixture

**E.89 quenching gap**

the quenching gap is defined as the spark gap between two flat parallel-plate electrodes at which ignition of a combustible fuel/air mixture is suppressed; smaller gaps totally suppress spark ignition. The quenching gap is the passage gap dimension requirement to prevent propagation of an open flame through a flammable fuel/air mixture that fills the passage

**E.90 redundancy**

the use of more than one independent means to accomplish a given function

**E.91 reformer**

a device for supplying hydrogen from other fuels

**E.92 resonance ignition**

ignition of a combustible mixture as a result of repeated shock waves that can occur during flow in a piping system. Acoustic oscillations within a resonant cavity can cause a rapid temperature rise. This rise is more rapid and reaches higher values if particles are present or gas velocities are high

**E.93 risk**

exposure to the chance of injury or loss as applies to safety. It is a function of the possible frequency of occurrence of an undesired event, of the potential severity of resulting consequences, and of the uncertainties associated with the frequency and severity

**E.94 shock wave**

a large amplitude compression wave in which there is a rapid and great change in density, pressure and particle velocity as caused by a violent collision, explosion, or impact. The subsequent transmission of energy moves as a wave at velocities greater than the speed of sound relative to the undisturbed material

**E.95 soft goods**

non-metallic materials such as polymers, coatings, and lubricants. In a valve, for example, soft goods would refer to items such as the seals, possibly the seat, and o-rings

**E.96 specific gravity**

the ratio of the density of a material to the density of a standard material such as water

**E.97 specific heat capacity**

the specific heat (also called specific heat capacity and heat capacity) of a substance is defined as the amount of heat (energy) required to change the temperature of a unit mass of the substance by one degree while the pressure is held constant, or while the volume is held constant

**E.98 standard**

a generally agreed upon set of criteria specifically designed to define a safe product, practice, mechanism, arrangement, process or environment based on currently available scientific and experimental knowledge concerning the subject or scope of the standard

**E.99 stoichiometric mixture**

the mixture of reactants in a chemical reaction that optimizes production of reaction products

**E.100 stratified flow**

flow of a fluid through a tube or pipe in which the liquid phase of the fluid flows along the bottom of the tube or pipe with little interference with the vapour phase that is flowing above the liquid phase. This type of flow occurs when the vapour flow rate is relatively low

**E.101 stress**

The internal force per unit of area developed within a body when the body is subjected to a system of external forces, or a non-uniform temperature change

**E.102 system**

An assembly of components to which hydrogen is delivered, stored, or used. A system may include components such as: storage vessels, piping, valves, pressure relief devices, pumps, vacuum subsystem, expansion joints, and gages. A system could refer to a new site, a new facility at a site, or a new installation at a facility

**E.103 tensile rupture**

the state that is reached when a material is subjected to an increasing tensile load and deforms (stretches) until the material fractures (ruptures)

**E.104 thermal conductivity**

the thermal conductivity of a material is defined as the heat-transfer rate per unit area of the material divided by the temperature gradient causing the heat transfer. Thermal conductivity is usually temperature dependent; that is, it varies with temperature

**E.105 thermal radiation**

the electromagnetic radiation emanating from materials as a consequence of their temperature. From the human perspective this is heat radiation

**E.106 tritium ( $T_3$ )**

an isotope of hydrogen with two neutrons and mass number three

**E.107 turbulence**

flow conditions where radial components or eddies exist together with the fluid motion parallel to the pipe axis

**E.108 ullage space**

the amount a storage vessel lacks of being full of liquid, usually a minimum of 10 % of the vessel volume

**E.109 UV (ultraviolet radiation)**

ultraviolet radiation is emitted when hydrogen combusts in air or oxygen

**E.110 Vacuum jacket**

the use of a vacuum for thermal insulation involves a double wall construction technique in which the space between the two walls is evacuated, resulting in a vacuum between the inner wall and the outer wall. The outer wall is commonly referred to as the vacuum jacket

**E.111 Viscosity**

the resistance of a fluid to shear motion — its internal friction

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