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Basic considerations for the safety of hydrogen systems

Considérations fondamentales pour la sécurité des systèmes à l'hydrogène

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 197, *Hydrogen technologies.*

This second edition cancels and replaces the first edition (ISO/TR 15916:2004), which has been technically revised.

Introduction

The focus of this Technical Report is on the relatively new hydrogen energy applications. The intent is to provide, those unfamiliar with the technology, a basis upon which to understand the safety issues. This Technical Report 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 first significant use of hydrogen has appeared in space programmes. This is changing, given the promise that hydrogen brings as an efficient energy carrier and a fuel with minimal environmental impact. Systems are being developed that produce hydrogen using variety of energy sources and feedstocks such as sunlight, wind, biomass, hydro power and fossil fuels, for use in energy applications for home and office heating, generation of electricity and transportation.

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

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

The considerations presented in this Technical Report are broad, general, and attempt to address most 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. The manufacturers of hydrogen appliances will need to consider these guidelines to tailor sufficient specific information for the operation of their appliances, in the environment in which they are to be used, and for the audience that will use them. Readers are encouraged to keep these points in mind as they consider the information presented in this Technical Report. Hydrogen has been safely used in many different applications over many years. Adherence to the principles presented in this Technical Report can lead to a continuation of the safe and sustainable use of hydrogen.

Basic considerations for the safety of hydrogen systems

1 Scope

This Technical Report provides guidelines for the use of hydrogen in its gaseous and liquid forms as well as its storage in either of these or other forms (hydrides). It identifies the basic safety concerns, hazards and risks, and describes the properties of hydrogen that are relevant to safety. Detailed safety requirements associated with specific hydrogen applications are treated in separate International Standards.

“Hydrogen” in this paper means normal hydrogen ($^1H_2$), not deuterium ($^2H_2$) or tritium ($^3H_2$).

2 Normative references

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

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

ISO 11119 (all parts), *Gas cylinders — Refillable composite gas cylinders and tubes — Design, construction and testing*

ISO 14687 (all parts), *Hydrogen fuel — Product specification*

ISO 16110 (all parts), *Hydrogen generators using fuel processing technologies*

ISO 16111, *Transportable gas storage devices — Hydrogen absorbed in reversible metal hydride*

ISO 17268, *Gaseous hydrogen land vehicle refuelling connection devices*

ISO 19880-1[1)], *Gaseous hydrogen — Fueling stations — Part 1: General requirements*

ISO 19881[2)], *Gaseous hydrogen — Land and vehicle fuel tanks*

ISO 19884[3)], *Gaseous hydrogen — Cylinders and tubes for stationary storage*

ISO 22734 (all parts), *Hydrogen generators using water electrolysis process*

ISO 26142, *Hydrogen detection apparatus — Stationary applications*

3 Terms and definitions

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

3.1
ambient conditions
AIT
local surrounding conditions characterized by the temperature and pressure at a particular location, such as a city or facility

Note 1 to entry: See *normal temperature and pressure* (3.71).

---

1) Under development.

2) Under development.

3) Under development.

3.2
annealing
heat treatment process used to soften hard steel so that it can be machined or cold-worked

3.3
arrested flame
combustion process which is stopped or flame which is put out

3.4
auto-ignition
Ignition which does not require external ignition energy because the thermal energy of the molecules alone is enough to overcome the activation threshold for combustion initiation

3.5
auto-ignition temperature
lowest temperature at which *auto-ignition* (3.4) occurs; 858 K for hydrogen

3.6
backfill
process by which a desired gas is used to replace an undesired gas in a system volume

Note 1 to entry: Typically, the undesired gas is first removed by evacuation with a vacuum pump, then the desired gas is put in.

3.7
back-flow
flow of a fluid in the direction opposite to the normal flow direction

Note 1 to entry: This term is used to describe the entry (diffusion) of atmospheric air into a hydrogen vent line.

3.8
ball valve
valve that functions with a ported sphere in a housing

Note 1 to entry: On-off flow control is achieved by rotation of the sphere 90°.

Note 2 to entry: Diverter ball valves are available for split-flow and other special applications.

3.9
blast wave
intense pressure wave set in motion by the *shock waves* (3.94) and/or hot product gases of a fast *deflagration* (3.22) or *detonation* (3.25) that impinges upon the surroundings, typically air

3.10
bourdon tube
thin-wall curved tube that is closed at one end and attached to a pressure source at the other end

Note 1 to entry: Pressure changes cause a change in the curvature of the Bourdon tube that is used to indicate the pressure in the system.

3.11
buoyancy
vertical force exerted on a body of less dense gas by the surrounding heavier static gas, typically air

3.12
catalytic converter
catalyst that is used for converting ortho-hydrogen to para-hydrogen in a liquefaction process so that the liquid hydrogen produced is mostly para-hydrogen

Note 1 to entry: Some commonly used catalysts in this conversion process are hydrous ferric oxide, chromic oxide on alumina particles, and nickel-based compounds.

3.13
check valve
valve that operates on differential pressure and allows flow in one direction only

3.14
collimate
make parallel or line up in a straight line

3.15
combustion
reaction process by which a flammable substance is oxidized, producing hot product gases, heat, radiation, and possibly pressure waves

Note 1 to entry: An *explosion* (3.38) in the sense of this Technical Report is a combustion process.

3.16
component
any part of a complete item or system

3.17
confined space
space not normally occupied by personnel

Note 1 to entry: Confined space 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.

3.18
confinement
physical restriction, sufficient to influence the combustion process or to facilitate the accumulation of hydrogen

3.19
convection current
motion or circulation of a fluid involving the transport of mass from one location to another driven by temperature dependent density gradients

Note 1 to entry: See *natural convection* (3.68).

3.20
cryogenic
condition involving very low temperatures in the vicinity of the *normal boiling point* (3.69)

3.21
cryopumping
process that consists of cooling a surface to a temperature of less than 120 K so that gases and vapours condense on the surface

Note 1 to entry: This process, though usually undesirable in the context here, is also used as a vacuum pump.

3.22
deflagration
combustion process in which a flame or chemical reaction moves through a flammable mixture at a rate less than the speed of sound in the unburned mixture

Note 1 to entry: Fast deflagrations are characterized by velocities in the hundreds of metres per second, and their effects to not differ much from those of a *detonation* (3.25).

Note 2 to entry: Laminar deflagration waves are characterized by velocities in the several metres per second and do not cause significant over pressures in the open.

3.23
deflagration-to-detonation-transition
DDT

event, often caused by turbulence, in which a *deflagration* (3.22) initiates a *detonation* (3.25)

3.24
deluge system

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

3.25
detonation

shock stabilized combustion process resulting in a combustion phenomenon propagating faster than the speed of sound

Note 1 to entry: A detonation is an explosion, but the reverse is not true.

Note 2 to entry: 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.

3.26
detonation cell

fundamental part of the mechanism for energy release within a *detonation* (3.25)

Note 1 to entry: The spatial arrangement of the shock front and acoustic waves moving behind and transverse to the shock front defines a cellular region of combustion that is observed experimentally as a “fish-scale” shaped track on sooted foils exposed to the detonation.

Note 2 to entry: The width of this diamond shape denotes the cell size, and its length can be empirically related to the formulae that can predict the energy required to directly initiate detonation and the physical dimensions of the structures that prohibit detonation.

3.27
detonation limits

maximum and minimum concentrations of a gas, vapour, mist, spray or dust, in air or oxygen, for stable *detonation* (3.25) to occur

Note 1 to entry: The limits are in reality controlled not only by the concentration of the mixture but also by the size and geometry of the environment as well as the means by which ignition occurs. There is no standard procedure for their determination.

Note 2 to entry: See *flammability limits* (3.47)

3.28
deuterium
D or ^{2}H

isotope of hydrogen having a nucleus containing one neutron and one proton

3.29
diffusion

flux of a fluid through another fluid or material due to concentration gradient

EXAMPLE The motion of hydrogen gas through air, or the movement of hydrogen gas through the wall of a rubber hose.

Note 1 to entry: The diffusion coefficient is the mass of material diffusing across a unit of area in a unit of time at a unit concentration gradient.

3.30
diluent

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

3.31
dual-fault-tolerant
system design in which the failure of two elements to perform as intended does not cause an entire system to function unpredictably or catastrophically

Note 1 to entry: The faults may be in two related areas or two areas which function completely independently, and the system should continue to function as intended.

3.32
ductility
<of a material> percentage elongation to failure or the reduction in cross-sectional area of a specimen in a simple tensile test

Note 1 to entry: Materials may make a ductile-to-brittle transition at low temperatures.

3.33
electrolyser
device that performs *electrolysis* (3.34)

3.34
electrolysis
process in which electric current is used to promote a chemical reaction

Note 1 to entry: In the case of water, an example is the separation of hydrogen from oxygen.

3.35
emergency
unintended circumstance, bearing clear and present danger to personnel or property, which requires an immediate response

3.36
emissivity
relative amount of radiant heat emitted by a surface when compared to a black body at the same temperature

Note 1 to entry: The emissivity of a hydrogen/air combustion is small compared to other familiar sources of heat, such as a wood fire.

3.37
enthalpy
thermodynamic property of a material that is equivalent to the sum of the internal energy and the product of the pressure and the volume

3.38
explosion
self-sustained combustion of a gas mixture releasing heat, and hot combustion products when the rate of reaction in a reacting mixture increases with time until either the fuel or oxidizer is consumed or nearly so

Note 1 to entry: This definition excludes pressure sources not related to chemical reactions (like burst of a pressure vessel, BLEVE, etc.).

Note 2 to entry: There is neither a standard terminology nor another generally acknowledged definition for the term “explosion”, but different sources give different definitions, some of them not even requiring that combustion takes place.

Note 3 to entry: When hydrogen and an oxidizer (air) are allowed to form a mixture prior to ignition (premixed mixture), after ignition, the ensuing chemical reaction (combustion wave) will propagate through the flammable region. The resulting combustion process releases heat. The resulting dilatation of the products, if fast enough, can cause a pressure wave to propagate from the source. See References [9] and [11] in the Bibliography for more information.

3.39
facility
group of buildings or equipment used for specific operations at one geographic location

3.40
fail-safe
ability to sustain a failure without causing loss of equipment, injury to personnel, or loss of operating time

3.41
fatigue
gradual deterioration of a material that is subjected to repeated loading and unloading

Note 1 to entry: See *load cycle* (3.62).

3.42
fire
sustained burning of a fuel jet as manifested by any or all of the following: light, flame, heat, and smoke

3.43
fire triangle
visual concept showing the requirements for combustion depicting a fuel, an oxidizer and an ignition source as the three sides of a triangle, where combustion cannot occur if any one side is not present

3.44
flame
zone of combustion of a gas or vapour from which light and heat are emitted

Note 1 to entry: 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* (3.22).

Note 2 to entry: Unlike hydrocarbon flames, hydrogen flames are weakly radiating. They radiate in the near UV (faint blue) and in the near IR (reddish). Only if particles are entrained into the flow from the surroundings will the flame thermally radiate producing a yellow color. Because hydrogen weakly radiate in the near UV and IR, they are often difficult to see in the daylight.

3.45
flame front
region of burning or chemical reaction (typically from fractions to several millimetres across) that separates burned and unburned regions

3.46
flammability
degree to which a material is ignitable in an oxidizing atmosphere

3.47
flammability limits
explosion limits
lower (LFL) and upper (UFL) concentration thresholds of fuel gas in a flammable mixture at a given temperature and pressure that will sustain propagation of a combustion wave

Note 1 to entry: These limits are functions of temperature, pressure, diluents, fluid dynamics, and ignition energy.

Note 2 to entry: These limits are usually expressed as percent (volume fraction of fuel gas).

Note 3 to entry: The values given in this paper (see Table B.1) are determined according to standardized procedures. The measurement of the "Explosion limits" as defined e.g. in Reference [5] in the Bibliography leads essentially to the same results as that of the "Flammability limit" in this paper, as e.g. Reference [6] in the Bibliography.

3.48
flare flameout blow off
extinguishment of the hydrogen flame of a hydrogen flare system, resulting in unburned hydrogen being vented to the atmosphere

3.49
fuel cell
electrochemical device that converts the chemical energy of a fuel and oxidant, both externally supplied, to electrical energy and by-products, including heat

3.50
galling
damaging or breaking of the surface where two parts rub together, creating heat and wear, which in turn produce loose particles

Note 1 to entry: Galling is generally encountered when materials of identical or similar hardness are in sliding or rotating contact with each other.

Note 2 to entry: The potential for galling increases with materials of similar chemical composition and hardness.

3.51
getter
substance that takes up gas at very low pressures by a sorption process

Note 1 to entry: A primary use of a getter is to improve or maintain a vacuum in a closed system.

3.52
guideline
consensual document that originates from any one of a number of different professional organizations and provides technical information about safe practices and procedures

3.53
hardness
composite property of a material involving resistance to indentation, deformation, and/or abrasion

Note 1 to entry: It is measured as yield strength, work hardening, true tensile strength, modulus of elasticity, and other material characteristics.

3.54
hazard
potential source of harm

Note 1 to entry: The term hazard can be qualified in order to define its origin or the nature of the expected harm (e.g. electric shock hazard, crushing hazard, cutting hazard, toxic hazard, fire hazard, drowning hazard).

3.55
hydride
compound containing hydrogen and another element

Note 1 to entry: Several metal hydrides are being investigated as potential storage media for hydrogen.

3.56
hydrogen embrittlement
deleterious changes in the ductility properties of a metal that exposure to hydrogen can produce

3.57
ignite
to cause to burn or to catch fire

Note 1 to entry: The process involves 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).

3.58
ignition energy
energy required to initiate a flame in a flammable mixture; function of the mixture concentration

Note 1 to entry: See also *minimum ignition energy* (3.65).

3.59
Joule-Thomson coefficient
coefficient relating the change of temperature to that of pressure in the *Joule-Thomson process* (3.60)

Note 1 to entry: If the Joule-Thomson coefficient is positive, an expanding gas will be cooled and if it is negative, the expanding gas will be heated. For hydrogen, it is negative above 200 K (inversion temperature).

3.60
Joule-Thomson process
cooling or heating that occurs when a highly compressed gas is allowed to expand in such a way the enthalpy remains constant; scientifically known as isenthalpic expansion

3.61
laminar flow
fluid particles moving along smooth paths in thin layers with one layer gliding smoothly over an adjacent layers (only a molecular interchange of momentum)

3.62
load cycle
repeated loading and unloading of a material such that it undergoes repeated stress

Note 1 to entry: See *fatigue* (3.41).

EXAMPLE Repeated pressurization and depressurization of a storage vessel.

3.63
maximum allowable working pressure
MAWP
maximum gauge pressure permissible in a storage vessel or piping system for a designated temperature

Note 1 to entry: The MAWP is the basis for the pressure setting of the pressure-relief devices protecting the vessel or piping system.

Note 2 to entry: The MAWP may also be the maximum allowable operating pressure rating of pressure vessels manufactured in accordance with national pressure vessel regulations and standards.

Note 3 to entry: This pressure may be called by different names depending on the system and the source of the regulation.

3.64
metal fracture
straining of a metallic material to the extent that it breaks or fails in a ductile-to-brittle behaviour

3.65
minimum ignition energy
MIE
while the *ignition energy* (3.58) of a given combination of gases depends on the concentration of the mixture, the minimum ignition energy is the absolute minimum of this function

Note 1 to entry: The concentration at which the MIE is found is always more or less close to the stoichiometric concentration, but usually deviates systematically from it.

3.66
molecular mass
total mass of the atoms within a molecule

3.67

most easily ignitable mixture

MEIM

mixture of a fuel gas and an oxidizer which has the lowest ignition energy [see *minimum ignition energy* (3.65)] as function of the concentration

3.68

natural convection

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

3.69

normal boiling point

NBP

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

3.70

normal hydrogen

75 % ortho and 25 % para hydrogen

3.71

normal temperature and pressure

NTP

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

Note 1 to entry: Always check the source of the data to make sure that it does not consider 273,15 K or 288,15 K as “normal”.

3.72

NOx compound

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

3.73

ortho-hydrogen

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

Note 1 to entry: See *para-hydrogen* (3.76).

3.74

overpressure

<in a blast wave> pressure above atmospheric pressure

3.75

overpressure

<within a containment structure> pressure that exceeds the maximum allowable working pressure of the containment structure

3.76

para-hydrogen

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

Note 1 to entry: See *ortho-hydrogen* (3.73).

3.77

PEM fuel cell

polymer electrolyte fuel cell

proton exchange membrane fuel cell

fuel cell (3.49) that employs a solid positive-ion-exchange resin membrane as the electrolyte

3.78
permeability
rate of diffusion of a pressurized gas through a porous material

3.79
permeation
flow of a fluid (gas) through another (usually solid) material by diffusion without a defect or opening of the latter

Note 1 to entry: To be distinguished from leak flow which is not based on diffusion.

3.80
photovoltaic system
device able to produce an electrical potential upon exposure to electromagnetic radiation, including solar radiation

3.81
plastic deformation
permanent deformation that occurs in elastic materials when the material is strained beyond its elastic limit

3.82
pressure regulator
device that is used in a system to regulate the pressure to a set value

Note 1 to entry: The regulator converts a variable high-pressure input to a constant lower-pressure output.

3.83
pressure-relief device
basic safety device used to prevent the pressure within a system from exceeding the MAWP (3.63)

Note 1 to entry: This device is installed so that excessive pressure within the containment structure can be relieved before damage to the containment structure occurs.

Note 2 to entry: A pressure-relief device is a spring-loaded or other valve that will open at a set pressure or temperature, or a rupture disk that contains a membrane designed to rupture at a set pressure.

3.84
Protium
Symbol H
hydrogen isotope with one proton

Note 1 to entry: Protium is the most common constituent of molecular hydrogen.

3.85
purge
process used to remove impurities

Note 1 to entry: For example, before admitting hydrogen to a system, the air in the system is removed to avoid the formation of a combustible mixture within the system.

3.86
quench
terminate a chemical reaction or the propagation of a flame

3.87
quenching distance
gap dimension required to prevent the propagation of an open flame through a flammable fuel/air mixture

3.88
quenching gap

<between electrodes> spark gap between two flat parallel-plate electrodes at which ignition of a combustible fuel/air mixture is suppressed

Note 1 to entry: Smaller spark gaps between electrodes totally suppress spark ignition.

3.89
quenching gap

<in a passage> passage gap dimension required to prevent propagation of an open flame through a flammable fuel/air mixture that fills the passage

3.90
redundancy

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

3.91
reformer

device for supplying hydrogen from other fuels by stripping the hydrogen atoms from the molecules

3.92
resonance ignition

ignition of a combustible mixture as a result of repeated *shock waves* (3.94) that can occur during flow in a piping system

Note 1 to entry: Acoustic oscillations within a resonant cavity can cause a rapid temperature rise, the rate of which is more rapid and reaches higher values if particles are present or gas velocities are high.

3.93
risk

product of the damage which will be caused by a potential accident and its probability

3.94
shock wave

large-amplitude compression wave in which there is a rapid and great change in density, pressure, and particle velocity

Note 1 to entry: A shock wave can be 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.

3.95
single-fault-tolerant

system design in which the failure of a single element to perform as intended does not cause an entire system to function unpredictably or catastrophically

Note 1 to entry: The system should continue to function as intended.

3.96
soft goods

non-metallic material

EXAMPLE Polymers, coatings, or lubricants.

Note 1 to entry: For example, in a valve, the term soft goods would refer to items such as the seals, possibly the seat, and the O-rings.

3.97
specific gravity

ratio of the density of a material to the density of a standard material such as water (for liquids) or air (for gases)

3.98
specific heat capacity
ratio of the heat (energy) required to change the temperature of a unit mass of a substance by a certain temperature difference and the latter, frequently given under important boundary conditions such that either the pressure is held constant, or the volume is held constant

3.99
standard
generally agreed-upon set of criteria specifically designed to define a product, practice, mechanism, arrangement, process or environment based on currently available scientific and experimental knowledge concerning the relevant subject or scope; basic concept for the free trade of goods and services

3.100
stoichiometric mixture
mixture of reactants in a chemical reaction that optimizes production of the reaction products

3.101
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

Note 1 to entry: This type of flow occurs when the vapour flow rate is relatively low.

3.102
stress
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

3.103
system
assembly of components in which hydrogen is delivered, stored, or used

Note 1 to entry: A system can include components such as storage vessels, piping, valves, pressure-relief devices, pumps, vacuum subsystems, expansion joints, and gauges.

Note 2 to entry: A system can refer to a new site, a new facility at a site, or a new installation at a facility.

3.104
thermal conductivity
heat-transfer rate per unit area of a material divided by the temperature gradient causing the heat transfer

Note 1 to entry: Thermal conductivity is usually temperature-dependent, that is, it varies with temperature.

3.105
thermal radiation
electromagnetic radiation emanating from a material as a consequence of its temperature

Note 1 to entry: From the human perspective, this is heat radiation.

3.106
tritium
T or 3H
isotope of hydrogen having two neutrons and a mass number of three

3.107
turbulence
flow condition in which radial components or eddies exist together with the fluid motion

3.108
ullage space
volume which a storage vessel lacks of being full of liquid

Note 1 to entry: The ullage space is important for the safe operation of the vessel and usually given in the applicable regulations or standards.

3.109
vacuum-jacketed
thermally insulated using 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

Note 1 to entry: The outer wall of the double-wall construction is commonly referred to as the vacuum jacket.

3.110
viscosity
resistance of a fluid to shear motion (its internal friction)

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 following:

- production;
- storage and transport;
- use of hydrogen.

Some applications may involve all three categories.

4.1.2 Production

Hydrogen is a very abundant element, and numerous are the processes that can be used to extract the element from its compounds. Large amounts of hydrogen are produced in the chemical industry as by-product. Dedicated hydrogen production is usually done by reformation of natural gas [see ISO 16110 (all parts)]. Other processes include electrolysis of water [see ISO 22734 (all parts)], displacement of hydrogen from acids by metals, dehydrogenation of chemicals, processing of waste, etc. In the future, photochemical processes and genetically tailored plants or microorganisms may also become practical means of producing hydrogen.

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

4.1.3 Storage and transport

4.1.3.1 General

Hydrogen that is produced at a site for use elsewhere has to be processed into a state which can be readily stored and transported to consumer applications. Compared to conventional fuels, hydrogen’s low density under ambient conditions and its low boiling point make it difficult for storage of sufficient quantities to suit typical applications. Proven methods of increasing hydrogen storage density include handling hydrogen as a pressurized gas or a refrigerated liquid, and using ground transport, water transport, or piping for delivery. Only very small quantities of hydrogen are permitted for transport by commercial aircraft. In the past, hydrogen had widespread use as a component of “town gas” that was frequently used in kitchens. Today, there are some hydrogen pipelines and pipeline networks in certain areas for the chemical industry.

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 or increasingly compound materials [Composite Overwrapped Pressure Vessels (COPV)] are routinely used to contain hydrogen at pressures up to 40 MPa, with increases up to 70 MPa intended. Tube or cylinder trailers are designed for road service transport quantities in the range of 300 kg or more.

4.1.3.3 Liquid storage and transport

Another approach to hydrogen storage is to condense the gas into a liquid. This requires cooling the hydrogen to temperatures close to its normal boiling point of 20 K. To maintain the hydrogen as a cryogenic fluid in storage, transfer of heat from ambient to the liquid has to be minimized to avoid excessive loss of hydrogen due to boil off. This isolation from heat transfer is best accomplished using a vacuum-jacketed container, like a thermos bottle. No isolation is perfect, and without capture and reliquefaction the slow loss of hydrogen (about 1 % per day) to the atmosphere has to be accepted when the tank is left to itself. For large scale storage tanks this loss drops considerably to under 0,03 % per day (i.e. 1 % per month).

Transport of liquid hydrogen is accomplished in vacuum-jacketed containers by truck, railcar, or tanker, and upon delivery, it is transferred to vacuum-jacketed cryogenic storage vessels at point-of-use sites.

4.1.3.4 Other storage options

The density of liquid hydrogen is even exceeded by that of slush (mixture of liquid and solid hydrogen at the triple point temperature of 13,8 K). The disadvantage is that the creation of such a mixture requires even more energy than simple liquefaction and that it can be stable only if the triple point pressure of some 7,2 kPa is maintained. At present, slush hydrogen has only been considered as an aerospace propellant. The economics for production do not favour its more extensive use.

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

A comparatively new way to store hydrogen is to do it as a supercritical fluid just above the critical point ("cryo-compressed"). This preserves some of the advantage of liquid storage (high density), but avoids the problems associated with handling two phases. The thermal insulation of such a tank does not have to be as elaborate as for liquid storage since the content of the tank is allowed to warm up to a certain degree.

4.1.3.5 Vehicular storage systems

The volume of hydrogen and the mass of containment vessels for high-pressure gaseous systems or cryogenic systems are challenges for vehicular fuel storage design. To reduce the volume and mass of fuel tanks proposed for hydrogen-powered vehicles, lightweight composite materials are being developed. In order to achieve a range acceptable to customers, most car makers use pressure cylinders with a maximum nominal pressure of 70 MPa (twice the maximum pressure for natural gas cylinders used onboard vehicles). The resulting safety requirements for production, approval, and operation of cylinders like this are discussed extensively in ISO 19881.

4.1.4 Hydrogen use applications

Hydrogen end use applications include fuel cells, combustion reciprocating and turbine engines, turbines, rocket thrusters, burners, and all applications that use these components. A variety of energy applications based upon electrolysers and hydrogen fuel cell systems will soon be commercially available. These applications range from small portable systems designed to replace standard batteries of 1 kW to 10 kW to larger systems (kWs to MWs in size) designed to supplement the power grid or designed for remote or distributed energy systems necessary to power homes or remote villages. Portable systems typically rely on a hydrogen supply that is replaced or recharged.

Larger systems are envisioned to match the variable energy input from renewable sources (wind, sun) with equally variable customer demand. Electricity is not easily stored but can be efficiently converted into hydrogen by electrolysers. These systems are both producers and consumers of hydrogen, as they convert excess amounts of electricity to stored chemical energy as hydrogen, store this energy in a suitable device, and then either convert it back to electricity when it is needed or use it as fuel. Re-conversion to power can be done with a fuel cell, a gas turbine, reciprocating ICE or a combined heat and power-generating unit to produce electricity (and heat) on demand. Such systems can be further integrated and used to stabilize power grids and to capture waste heat for heating or industrial processes.

4.2 Typical hydrogen system components

4.2.1 General

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

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

- hydrogen storage or a source of hydrogen, and oxidizer storage or a source of oxidizer;
- fluid delivery lines to connect hydrogen and oxidizer to the reaction system;
- flow controls;
- pressure-relief systems that are incorporated into the design of the above mentioned components;
- detection components.

4.2.2 Storage vessels

The design, function, and applied construction materials of storage vessels and their components should reflect the type of service, e.g. high-pressure gaseous vessels or cryogenic liquid vessels. Large quantities should preferably be located outdoors or in specially designed structures. Vessel construction should consider the state of the technology. Storage vessels that contain cryogenic hydrogen use special insulation or vacuum jacketing. Care should be taken that boil-off is released via suitable devices, purged or managed appropriately, and that the fire resistance of the vessel is known.

4.2.3 Fluid delivery lines, piping, joints, and seals

Hydrogen as the smallest molecule has a high tendency for diffusion and permeation. It will also feature a high flow rate in case of a leak somewhere in the system. Piping and seals need to be suitable for hydrogen use over the life of the system. Hence, welded joints are preferred where leaks cannot be tolerated. Where a joint or a seal may require periodic opening, care should be taken to prevent the formation of ignitable mixtures and the presence of ignition sources.

4.2.4 Flow controls

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

4.2.5 Pressure-relief systems

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

4.2.6 Detection components

Outside of the hydrogen system, the control system can monitor the presence of hydrogen gas or hydrogen fire. A variety of technologies are available to detect hydrogen gas. Hydrogen detectors are typically placed above a probable leak point and where hydrogen may accumulate, which is usually at the highest point of a room, or at the intake of ventilation ducts. Cross sensitivity of the sensors should be taken into account. 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. ISO 26142 defines the requirements applicable to hydrogen detection apparatus used in stationary applications.

4.2.7 Other components

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

4.2.8 Considerations for conditions external to the system

Inherent in all hydrogen designs are the following:

- considerations for the conditions in which the system is operated (e.g. indoor or outdoor);
- fail-safe operation and passive safety measures that account for potential modes of failure;
- long-term plans which cover the operational life of the system.

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

4.3 Hydrogen fuel

Hydrogen fuel can possess impurities left by the production process or introduced during storage and post-production handling. The quantity and type of impurities might adversely affect hydrogen-consuming systems. Which impurities are tolerable and to which extent depends on the nature of the consumption system. ISO 14687 was developed to specify the quality characteristics of hydrogen fuel to ensure uniformity of hydrogen fuel products produced for various applications.

4.4 Environmental effects

The environmental effects arising from the use of hydrogen systems are anticipated to be benign. With very few exceptions, pure water is the only reaction product. One notable exception is air-breathing systems that combust hydrogen at high temperatures and can create nitrogen oxides (NO_x). Good choice of the operating point, however, can reduce these emissions to levels far below the limits possible for hydrocarbon combustion without requiring after treatment technologies. In addition, a carefully constructed hydrogen combustion strategy that enables conventional NO_x after treatment technologies can further reduce NO_x emissions to near zero values. If appropriate, low-temperature catalytic oxidation can eliminate NO_x production entirely.

The effects of hydrogen gas escaping into the atmosphere (e.g. boil-off gas from liquid storage) are negligible. Indeed, under atmospheric conditions, the thermal translational velocity of molecular hydrogen is greater than the escape velocity of the earth. As hydrogen is transported to the upper atmosphere, it will either oxidize to water or react with pollutants or escape into space. This is why there is so little hydrogen free in the atmosphere.

5 Basic properties of hydrogen

5.1 General properties

5.1.1 Atomic and molecular properties

Hydrogen, named from the Greek words *hydro* (water) and *genes* (generate), is the simplest and most abundant element in the universe. Atomic hydrogen can possess any of three possible atomic weights or isotopes: protium, deuterium, or tritium. Protium, with an atomic mass equal to 1, is the most common isotope. Tritium is radioactive (decay by β emission, with 12,3 year half-life). As a pure substance, hydrogen exists as a molecule, designated H_2, in which two hydrogen atoms have formed a covalent bond. There are two molecular forms: ortho-hydrogen (with parallel arrangement of the nuclear spin of the two atoms) and para-hydrogen (antiparallel). Bulk hydrogen, in particular in its gaseous form, is a mixture of ortho-hydrogen and para-hydrogen in which the temperature determines the equilibrium quantities of each form. At normal temperature and pressure (NTP), para-hydrogen makes up 25 % of the total mixture. This mixture is known as normal hydrogen. At lower temperatures, equilibrium favours the existence of the less energetic para-hydrogen, with liquid hydrogen at 20 K composed of 99,8 % para-hydrogen.

This apparent complexity of different isotopes and molecular states has little effect on safety considerations. Deuterium is found only in small quantities in nature, and tritium is produced mainly by irradiation of materials in nuclear reactors. The chemistry of hydrogen, and in particular the combustion chemistry, is little altered by the different atomic and molecular forms. Non-nuclear energy applications typically use material data that applies to normal hydrogen (2 protium atoms arranged in 75 % as ortho-hydrogen and 25 % as para-hydrogen molecules). The only exception occurs for cryogenic applications such as liquid or cryo-compressed hydrogen storage, in which heat is an important parameter. The larger property differences between ortho-hydrogen and para-hydrogen occur in those properties for which heat is important (such as enthalpy, specific heat capacity, and thermal conductivity), whereas other properties of ortho-hydrogen, such as density, vary little from para-hydrogen properties.

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

5.1.2 Appearance and general characteristics

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

5.2 Selected thermophysical properties

5.2.1 General

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

5.2.2 Selected thermophysical properties of gaseous hydrogen

5.2.2.1 Dispersion

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

In the case of gaseous hydrogen leaks, the effects of fluid dynamics (such as wind, momentum, or buoyancy controlled flows) can dominate molecular diffusion. The buoyancy of hydrogen when it is allowed to rise will create convection currents. As a consequence of these properties, hydrogen gas has a tendency to disperse and diffuse and form ignitable mixtures with air. In an unconfined atmosphere, these mixtures ultimately dilute to a level below the lower flammability limit (LFL). But it should not be taken for granted that this will necessarily happen very quickly; boundary conditions can have a strong effect. Caution should also be used in applying these observations when hydrogen vapours at cryogenic temperatures are released. Hydrogen vapours at temperatures of 23 K or lower are denser than NTP air. Usually, the condensation of atmospheric humidity will also add water to the mixture cloud (making it visible), making it even denser.

5.2.2.2 Viscosity

The low viscosity of hydrogen, an effect of the small size of the molecule, causes a comparatively high flow rate if the gas leaks through porous materials, fittings, or seals. This negative effect is to a certain extent offset by the low energy density of the gas in comparison with methane or other hydrocarbon gases.

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

On a molar basis, the heat capacity of hydrogen is similar to that of other diatomic gases despite its low molecular mass. The thermal conductivity of hydrogen is significantly higher than that of other gases.

In a Joule-Thomson process (isenthalpic expansion) starting at ambient temperature, the temperature of hydrogen will not drop but rise. This temperature rise, however, is not sufficient to cause ignition.

5.2.3 Selected thermophysical properties of cryogenic liquid hydrogen

5.2.3.1 Density and thermal expansion

Liquid para-hydrogen at its normal boiling point (NBP) has a density of 70,78 kg/m^3. The corresponding specific gravity is 0,071 (the specific gravity of water is 1). This means that liquid hydrogen is 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 open space to accommodate expansion of the liquid. This can lead to an over pressurization of the vessel or entrainment of the liquid into transfer and vent lines.

5.2.3.2 Equivalent volume of gas

A considerable increase in volume is associated with the phase change of liquid hydrogen to gaseous hydrogen, and still another gradual volume increase occurs for gaseous hydrogen that is allowed to warm from the NBP to NTP. The ratio of the final volume to the initial volume for the phase change from liquid hydrogen to gaseous hydrogen and expansion of heated gas is 847. For systems where the volume is fixed, this phase change and associated temperature rise to NBP from NTP will result in a pressure of 177 MPa.

5.2.3.3 Heat capacity

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

5.2.3.4 Ortho-para conversion

The process of hydrogen liquefaction should not only remove sensible and latent heat, 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.

5.3 Basic combustion properties

5.3.1 General remark on safety characteristics

The safety relevant properties of flammable gases, including hydrogen, are frequently discussed in terms of characteristics like flammability limits or ignition energies. It should be kept in mind that these characteristics are not scientifically well-defined properties of the gas itself (like density, viscosity, molecular mass, etc.). They depend strongly on the measurement procedure. They are only comparable if measured according to exactly the same procedure. This is reflected by the fact that there are now three standardized ways to measure the lower flammability limit of hydrogen in air mixtures, giving results between 3,6 % and 4,2 % (two in Reference [5], one in Reference [6] of the Bibliography). Since, in this context, we are most often concerned with behaviour under atmospheric conditions (NTP), the pressure and temperature is usually taken to be ambient (~20 °C, and 0,101 MPa), so flammability limits are commonly used to describe the mixture space of interest. In case of doubt, refer to the applicable standards (see Reference [5] or [6] in the Bibliography).

Flammability of hydrogen/air mixtures is also a function of flame propagation direction, for example, downward propagating flames have a lean limit on the order of 9 %, whereas upward propagating flames have a lean limit on the order of 4 % (see Reference [10] in the Bibliography).

Detonation limits are ambiguously defined in the literature. The value at which a detonation can occur is a strong function of geometry, fluid dynamics, and mixture ratio. The value commonly reported as the lower detonation limit of 18 % should not be taken even as a rough guide. The combustion literature provides examples of detonations occurring as low as 11 % and possibly lower. There is no standard measurement procedure for this property, unlike for flammability limits.

5.3.2 Selected combustion properties of hydrogen

Combustion occurs in three different physical processes, namely:

a) as a non-premixed flame;

b) as a premixed flame propagating as a deflagration wave (a subsonic process);

c) as a premixed flame coupled with a shock wave propagating as a detonation wave (a supersonic process).

A deflagration wave is a subsonic process where the pressure change across the flame is negligible. A detonation is a supersonic process, which has very significant pressure rise across the front (10 times or more). Deflagration waves propagate by the diffusion of heat and chemical radicals in front of the wave to ignite the mixture whereas detonations propagate by adiabatic shock heating. Under suitable fluid dynamic conditions, a deflagration wave can accelerate to near the speed of sound and can even transition to a detonation wave (known as a deflagration to detonation transition, or DDT). In these cases, a fast deflagration wave can create a spherically propagating audible sound wave similar to that created by a detonation wave.

Flammability limits, ignition energy, and auto ignition temperature are primary variables used to characterize the circumstances under which combustion can occur. Detonation limits correlate with detonation cell sizes. Some hydrogen combustion data are given in Annex B. Selected combustion data for several common fuels are also given in Annex B for comparison purposes.

5.3.3 Explosions

When hydrogen and an oxidizer (air) are allowed to form a mixture within the flammability limits prior to ignition (premixed mixture), after ignition, the ensuing chemical reaction (combustion) may propagate through the combustible region. The resulting combustion process releases heat. The resulting expansion of the products, if fast enough, can cause a pressure wave to propagate from the source. For the purposes of this Technical Report, an “Explosion” is defined to be a self-sustained combustion of a gas mixture releasing heat, and hot combustion products.

In common language, the term “Explosion” frequently also includes other processes that generate a rapid release of energy that causes a blast, for example, the burst of a vessel due to overpressure. Care should be taken to distinguish the phenomena from each other.

5.3.4 Deflagration

The process that a flame relies on chemical reactions associated with complex heat and mass-transfer mechanisms that propagates subsonically into regions of unburnt mixtures is known as a deflagration. The concentration, pressure, and temperature of the unburnt medium have to be inside the flammability limits. In a stationary mixture in the open with no confinement, the flame will propagate with laminar or “smooth flow” at a burning velocity into the unburnt mixture in the order of 2 m/s to 3 m/s (which is about 10 times faster than for hydrocarbon flames). For hydrogen-air mixtures, the visible propagation velocity can be higher than the burning velocity. This can be caused by the expansion of hot combustion products behind the flame adding a convection velocity to the flame propagation velocity. For example, if a tube is open on one end filled with premixed gases and ignited on the open end then the flame propagation speed will NOT be affected by the expanding gasses. However, for the same tube configuration and igniting it at the closed end, the flame will accelerate due to the expanding gases behind the flame at the closed end of the tube.

Confinement, as found between walls, within pipes and ducts, can trap the expanding reaction products and produce 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 ahead of the flame can increase the mixing of unburnt mixture and the flame, thereby increasing the burning rate. This process can accelerate the flame to hundreds of metres per second with an attendant formation of considerable overpressures, reaching several hundred kPa. The maximum propagation velocity of a deflagration wave in a turbulent flow field is limited to the speed of sound in the unburnt gas mixture (975 m/s for a stoichiometric ratio hydrogen/air mixture under NTP). Flow turbulence and various flame front instabilities, e.g. due to confinement and obstacles, can even accelerate the flame up to deflagration to detonation transition (DDT).

Some deflagrations proceed so slowly that they hardly create a pressure wave. For practical purposes and in order to remain in the framework of existing standardization, “explosion” in this paper will be any combustion reaction which happens in a mixture which has a pressure, temperature, and concentration within its flammability limits.

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

5.3.5 Detonation

5.3.5.1 General

Detonation differs from deflagration in that there is a leading shock wave, which is coupled with the combustion wave. Detonations of gas mixtures propagate at a rate greater than the speed of sound within the un-combusted media, typically 1,500 m/s to 2,000 m/s with an attendant pressure rise in the range of 1,5 MPa to 2 MPa starting from atmospheric pressure (0,1 MPa). The detonation wave front does not consist of a single uniform shock wave, but possesses many transverse waves generating a cell structure. The width of detonation cells depends on mixture composition, pressure and temperature of the gas mixture. For a given fuel and oxidizer, usually the cell widths are smallest for mixtures close to stoichiometric ratio mixture composition. The fine structure of real detonation front is very complicated and difficult to simulate at even moderate scales.

The direct initiation of a detonation requires a hydrogen-oxidizer mixture closer to the stoichiometric ratio composition and sources of ignition with significantly more energy than is needed for deflagration. For example, in the open, a rather strong explosive charge is required for direct initiation of a detonation in hydrogen-air mixtures.

5.3.5.2 Detonation limits

Compared to deflagration, the direct initiation of a detonation process requires mixtures closer to the stoichiometric ratio and stronger initiation sources. Detonability limits are therefore always within the flammability limits. But whether a detonation is able to propagate depends not only on the mixture concentration but also on the relationship between the size of the detonation cell and the geometrical boundary conditions as well as on the turbulence level of the reacting fluids. The widths of detonation cells depend on the mixture composition and other parameters. Cell width data vary not only with mixture concentration, but also with other factors including pressure, the presence of diluents, and temperature. With knowledge of mixture concentration and cell width, the general approach for evaluating the limits of detonation is to determine if sources with sufficient energy for direct initiation above the critical energy for initiation of detonation are possible. An increase in the initiation energy leads to broader detonation limits. Geometrical characteristics, in particular degree of congestion (blockage ratio) and confinement, are evaluated to see if a detonation can be induced after a phase of flame acceleration. So it is not possible to give simple composition figures as condition for detonability of a mixture. There is no standard procedure for the determination of detonation limits.

5.3.6 Flammability limits

Hydrogen, by itself in bulk, does not undergo a chemical reaction when exposed to an ignition source. For combustion to occur, hydrogen has to be mixed with sufficient quantities of an oxidizer to form a flammable mixture. The greatest part of the discussion in this paper here is about combustion of premixed gas clouds.

An optimum, or stoichiometric ratio 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 of two parts of hydrogen (67 %) with one part of pure oxygen. For a mixture of hydrogen with air, where additional nitrogen is present, the stoichiometric ratio mixture is 29,5 % hydrogen.

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 consumed. For a given set of reactants and specific conditions (for example, temperature and pressure), combustion is limited to a specific range of mixture compositions, the boundaries of this combustible mixture are the flammability limits.

Flammability limits are a convenient means for conveying the range of fuel/oxidizer mixture compositions, temperature and pressure ranges capable of supporting combustion (propagating flames). They are expressed as a lower flammability limit (LFL) for the minimum percentage of fuel that supports combustion for a given pressure and temperature and an upper flammability limit (UFL) for the maximum percentage of fuel that supports combustion for a given pressure and temperature. In the safety literature, these limits are commonly expressed as the mixture fraction on a volume fraction (percentage) basis. The flammability limits for hydrogen in air under ambient conditions are shown in B.3. In comparison to more common fuels such as methane or propane, this is a very broad range because the upper limit is much higher than these other fuels.

Specialized combustion data should be consulted for hydrogen introduced into high or low-pressure environments, environments containing chemicals or environments altered by the failure of the hydrogen system. A variety of factors including temperature, pressure, diluents, strength of ignition sources, flow, distance between adjacent confining surfaces, and direction of flame propagation can alter the flammability limits. This is illustrated by the effects of natural convection, which expand the flammability limits for upward-propagating hydrogen combustion and decrease the flammability limits for downward-propagating hydrogen combustion in hydrogen/air mixtures under NTP. In this instance, the buoyancy-induced upward velocity of the hot, burnt gases retards a downward-propagating flame, but promotes an upward-propagating flame. The presence of atmospheric humidity, lubricants, or other hydrocarbons can also give the mixture properties, which differ considerably from those of an undiluted hydrogen-air mixture.

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 arrested or quenched, such as in a flame arrestor. The quenching gap for a stoichiometric mixture of hydrogen and air and at NTP is 0,64 mm and decreases with increase of pressure and temperature.

For more information on “Flammability limits”, see 3.48.

5.3.7 Ignition energy and minimum ignition energy as applied to deflagration

A variety of processes, including flames, electrical sparks, fused wires, incendiaries, hot surfaces (including catalysts), heating, rapid adiabatic compression, or shock waves can be sources of ignition for hydrogen/oxidizer mixtures. The result is a flame that propagates throughout the mixture. For a given combustible mixture and ignition type, there is a concentration dependent minimum energy below which ignition does not occur. This is known as the ignition energy, and it is typically measured in a standardized apparatus.

The ignition energy varies with the composition of the mixture. It becomes infinite at the flammability limits. Somewhere between these limits, the ignition energy has a minimum, usually at a concentration a bit lower than the stoichiometric one (for fuel gases lighter than air). The most easily ignitable mixture (MEIM) for hydrogen can be found in the range between 22 % and 26 % (see Reference [1] in the Bibliography). Over the flammability range (a given pressure and temperature) of hydrogen/air mixtures, the ignition energy varies by almost three orders of magnitude and can be as low as 0,017 mJ for the most easily ignitable mixture (minimum ignition energy, or MIE). In addition to the mixture composition, other factors such as the spark gap, the initial gas pressure, and temperature can influence the ignition energy. 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. Note that the use of spark free tools is not an absolute guarantee that no spark will occur.

Even these tools might convey enough energy to a material or a material combination to create a hot spot or to rip off a burning particle.

6 Safety considerations for the use of gaseous and liquid hydrogen

6.1 General

The properties of hydrogen, which make it valuable as an energy carrier or fuel, require proper design and operation in order to avoid the realization of a hazard just as it is the case for any energy carrier.

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

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

- flammability:
    - thermal effects;
    - pressure effects;
    - easy ignitability of some mixtures;
- small size of the molecule:
    - low viscosity;
    - high diffusion rate;
    - high buoyancy;
- interactions with materials (embrittlement of certain metals);
- asphyxiation hazard if oxygen is replaced;
- hazards associated with the storage procedure:
    - elevated storage pressure for gas;
    - low temperature for cryogenic liquid;
    - others for other methods, like metal hydrides.

This list simply stresses where concern should be focused in the design and operation of hydrogen systems. Note that 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.

Some of the above mentioned properties can either increase or reduce the hazard of a certain situation, depending on the circumstances. The high diffusivity of hydrogen gas means that a mixture cloud will expand quickly in all directions (including downward) and can reach ignition sources, if there are any. At the same time, it may dilute and become unreactive if accumulation of hydrogen is excluded.

While the rapid diffusion of hydrogen may dilute a cloud of escaped gas this should not be taken as automatically granted. Under most conditions, a release of hydrogen will result in a fluid dynamic motion that will dominate the transport and keep the hydrogen from diffusing away from the jet. In the case of a buoyancy-driven flow, the ensuing fluid dynamics will form a rapidly rising turbulent plume that will dominate the diffusion process. Likewise, in a release of hydrogen from a pressure vessel where the pressure is greater than 0,2 MPa (two atmospheres) the issuing jet will be a result of a chocked flow and again the fluid dynamics will dominate the molecular diffusion and buoyancy effects of hydrogen.

6.2 Hazards involved as a consequence of the properties of hydrogen

6.2.1 General

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

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 5 and some selected property data are tabulated in Annex A.

6.2.2 Gaseous hydrogen

Gaseous hydrogen has neither a characteristic colour nor odour. It forms the smallest, lightest molecule of any gas (about 14 times lighter than air). 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 has a tendency to rise and diffuse, but if confined, it can accumulate in high spots and reach ignition sources located there (e.g. ceiling lights).

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

Because of hydrogen's low density at ambient conditions, it is typical to store and transport gaseous hydrogen at elevated pressures or as a liquid. Another option for storage is the use of chemical compounds like hydrides.

6.2.3 Liquid hydrogen

Liquid hydrogen appears clear with a slight blue tinge. It possesses an extremely low boiling point (20,3 K), a low density for a liquid (about 70 kg/m^3), a low heat capacity, and a large volumetric expansion when heated to a gas as it is common for most cryogenic liquids (ratio of gas/liquid volume is about 850).

Liquid hydrogen with its low boiling point will rapidly boil or flash to a gas if exposed or spilled into a normal temperature environment. Warming liquid hydrogen to ambient temperature gas can lead to very high pressures when it is confined.

Another consequence of liquid hydrogen's low temperature is that, with the exception of helium, all gases will be condensed and solidified should they be exposed to it. Leaks of air, nitrogen, or other gases into direct exposure with liquid hydrogen can lead to several hazards. The solidified gases can plug pipes and orifices and jam valves. In a process known as cryopumping, the reduction in volume of the condensing gases could create a vacuum that can draw in even more gas. 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 of reactive mixtures. On the other hand, these other gases might also carry heat into the liquid hydrogen and cause enhanced evaporation or pressure rise.

Outside of the liquid hydrogen system, un-insulated pipes and vessels containing liquid hydrogen can condense gases such as air into solid and liquid forms on their outer surfaces. The liquid condensate flows and looks like liquid water. Since oxygen has a higher boiling point (90 K) than nitrogen (77 K), oxygen enrichment is possible. Should the oxygen component within liquid air come in contact with combustible materials, combustion hazards can occur even with materials which are commonly not considered as flammable.

6.3 Factors involved in combustion hazards

6.3.1 Aspects of combustion

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

For hydrogen to combust, two additional elements need to be present: an oxidizer such as air and a source of ignition. Each of the factors necessary for combustion (a fuel, an oxidizer, and an ignition source) can be represented on one of the three sides of a triangle, a concept known as a fire triangle. A fire is possible only when all three sides of the triangle are there. Mixtures of hydrogen and oxidizers are flammable over a wide range of concentrations, pressures, and temperatures. Mixtures near stoichiometry are particularly ignitable. 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. Even ignition without an artificially provided energy source is possible under certain conditions of sudden release into an oxidizing atmosphere (unplanned ignition of sudden hydrogen release into piping with air could occur at storage pressures as low as 0,2 to 0,3 MPa). Because of the ease of ignition of hydrogen/oxidizer mixtures, most methods for the reduction in risk of hydrogen combustion rely on separation of hydrogen from the oxidizers (primary explosion protection measure: prevent the formation of reactive mixtures).

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

Basic hydrogen combustion data are provided in Annex B.

6.3.2 Non-premixed combustion processes

A source of hydrogen, for example a leak, when surrounded by an oxidizer such as air, can be ignited to produce a flame much in the same fashion as a burner. Depending on the rate of release of hydrogen from the source, this combustion process can manifest itself with outputs ranging from that of an invisible microflame through a small candle to large high-pressure jet fires with flame length of 10 m to 15 m. 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 less heat and is practically invisible in broad daylight. Most of the emission is around 311 nm. Chemiluminescence around 350 nm has also been measured. This radiation is just outside the visible range near ultraviolet (UV) spectrum. Light passing through the thermal gradients in the flame or hot products flow sometimes casts a flickering light/dark pattern.

For the human senses, these characteristics make detection of small hydrogen flames difficult compared to hydrocarbon flames. Thus, without suitable detection equipment, the first indication of a small flame is likely to be the hissing noise of the gas leak and perhaps the intermittent shadows from the thermal gradients of the flame.

6.3.3 Explosions

6.3.3.1 General

An explosion may be manifested through a deflagration or a detonation. If the deflagration is fast enough, it may produce a blast wave similar to a detonation. Only the noise of a detonation is a perceivable sharper bang than that of a deflagration. The initiation of a deflagration needs much less ignition energy than the direct initiation of a detonation.

The shock wave and hot product gases impinging upon the surroundings outside of the combustible region can also be referred to as a blast wave. There is no combustion in the blast wave, but it physically displaces the surrounding (non-reacting) gases and loose material (shrapnel).

6.3.3.2 Deflagration-to-Detonation Transition

The presence of confining surfaces and obstacles such as pipes, vessels, and enclosure walls can significantly elevate the flame speed and increase it to hundreds of metres per second in a process known as flame acceleration (slow/fast deflagration). If the flame reaches a high enough speed and encounters turbulence and flame instabilities, the deflagration process can transform into a detonation. This is called a deflagration-to-detonation transition (DDT).

6.3.3.3 Detonation

Detonations that impinge on surfaces are reflected. The reflected pressure waves typically produce greater peak pressures of 2 to 3 times the incident shock pressure. Detonations of non confined gas clouds have a tendency to occur more easily with increasing cloud size.

6.3.3.4 Safety considerations

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

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

Deflagrations of gaseous hydrogen-air mixtures can produce pressures as much as 8 times the initial pressure, even more in special geometries. Detonation of hydrogen-air mixtures can produce pressures as much as 20 times the initial pressure (for very short durations even more) and with reflection, pressures 50 times the initial pressure. One important consideration is that the relief systems, designed to protect hydrogen systems from overpressure, rely on sensing the build-up of pressure. Because detonation waves move faster than the speed of sound, relief systems do not sense the approaching detonation wave and cannot react in time to protect the system from the rapid pressure rise. Rupture disks, relief panels, etc. are only useful against combustion phenomena progressing slower than the speed of sound (deflagrations, not detonations).

6.4 Factors involved in pressure hazards

6.4.1 General

Many hydrogen applications contain hydrogen in a gaseous form under high pressure or as a cryogenic liquid. In both of these forms, hydrogen presents several pressure-related hazards. Pressure effects are characteristic and could be hazardous for scenarios involving unignited release in a vented enclosure, initial stage of a jet fire, deflagrations, and detonations. The two most relevant pressure effects that should be addressed in the design and operation of a hydrogen component or system are quasi-static overpressure and dynamic pressure effects on structural elements. Suitable distances between hydrogen storages and working or public areas can be an appropriate measure of mitigation.

Handling and storage of hydrogen in commercial settings is the topic of other International Standards such as ISO 19880-1 that covers the requirements applicable to gaseous hydrogen fuelling stations.

6.4.2 Gaseous storage

Gaseous hydrogen can be compressed to very high pressures. Under such pressures, the hydrogen has considerable potential (stored) energy, like any other gas. The release of this energy can generate strong pressure effects depending on the release rate, even without a subsequent combustion. Attention needs to be given to the flow rate of hydrogen release (unintentional or intentional) in enclosures (see Reference [14] in the Bibliography for details).

6.4.3 Liquid hydrogen

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

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

6.5 Factors involved in low temperature hazards

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

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

6.6 Factors involved in hydrogen embrittlement hazards

6.6.1 Hydrogen embrittlement

Some metallic materials used in vessels or other components can undergo a significant loss of their ductility 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 first have to dissociate into atoms before they can diffuse into the metallic structure. At temperatures close to ambient, a number of metallic materials are susceptible to hydrogen embrittlement, particularly those with a body-centred cubic crystal lattice structure. This is a particular problem with many ferritic steels if they are subjected to mechanical stresses. The process takes place on freshly generated metallic surfaces that are likely to form on surface defects or other stress concentrations and as a result of stress-induced local plastic deformation processes. Impurities such as hydrogen sulphide dissociate into atomic hydrogen even more easily than molecular hydrogen. High tensile strength steels are frequently found to be more susceptible to embrittlement than are low tensile strength steels.

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

6.6.2 Hydrogen attack

Already at temperatures above 200 °C, many low-alloyed structural steels can suffer from another hydrogen-related embrittlement phenomenon known as hydrogen attack. It is a non-reversible degradation of the steel microstructure caused by a chemical reaction between diffusing hydrogen and the carbon in the steel, resulting in the formation of methane. Severity of the hydrogen attack increases with increasing temperature and pressure.

6.7 Health hazards

6.7.1 Cold burns

Direct skin contact with cold gas, liquid hydrogen, or metallic parts cooled by them 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.

6.7.2 High temperature burns

Direct contact with combusting hydrogen or hot post flame gases resulting from combustion of hydrogen will cause severe burns. The flame temperature of a stoichiometric hydrogen/air mixture is about 2 300 K, similar to that of other flames. Hydrogen flames in air are difficult to see in daylight. Due to the low radiative heat transfer of hydrogen flames, personnel near a hydrogen flame might not sense the proximity of the flame.

6.7.3 Asphyxiation

Hydrogen is not poisonous, but does not support metabolism either. 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.

6.8 Team approach and education/training needed for the safe use of hydrogen

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

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

7 Mitigation and control of hazards and risks

7.1 General mitigation and control of hazards and risk

7.1.1 General

There are general principles, guidelines, and recommended practices that are essential for the safe use of hydrogen. While there are many different hydrogen applications, priorities can be discerned in the application of these general principles based on the experience and lessons learned from incidents 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 system design, flammability, detection, facilities, operations, and recommendations for organizations.

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

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.

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 study of mishaps involving hydrogen (see Reference [4] in the Bibliography) identified and categorized the causal factors. A summary of the results is provided below with an assessment of the percentages involved. More than one factor may have been involved in some mishaps, consequently the percentage shown for these categories totals more than 100 %.

Several categories based on human error were identified. Operational and work area deficiencies were found responsible for 26 % of the mishaps. These mishaps were attributed to inadequate working conditions during installation, maintenance, fabrication, and cleaning; and the lack of training, specific instructions, or both. Procedural deficiencies were found responsible for 25 % of the mishaps. This category included the failure to follow established procedures, or to prepare proper procedures. Design deficiencies were found responsible for 22 % of the mishaps. Here inadequate component or system designs, including failure to specify safety devices and omission of other essential information, failure to determine stress and fatigue, errors in material selection (such as clerical errors in drawings and specifications) were described as the causes. Planning deficiencies identified as limited planning, such as failure to prepare test plans or to prepare hazard studies, were responsible for 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, were responsible for 8 % of the mishaps. Material failures, responsible for 3 % of the mishaps, included the failure of materials and components as a result of stresses that had been considered within the design limits. Material incompatibility, such as incompatible materials either brought together by accident or designed into the system, was responsible for 3 % of the mishaps. The use of contaminated materials was responsible 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 human errors. Although not shown in the above numbers, valves were involved in 20 % of the mishaps, and systems contaminated with air were involved in 21 % of the mishaps.

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

— minimize the possibility for human error;

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

More recent experience on hydrogen accidents and incidents has been compiled in databases accessible via the Internet. Most important among them are Hydrogen Incident and Accident Database (HIAD) by HySafe and h2incidents.org by the US DoE.

7.1.3 Addressing hazards

The first step is identifying that a hazard exists and which consequences it may have. A variety of options are available for addressing them: eliminate, prevent, avoid, mitigate, or accept. Examples of each option are provided below.

The preferred choice for dealing with a hazard is to eliminate it. This option might be illustrated by choosing to use an inert gas whenever possible.

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

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

The option that is often the only one that is practical is to mitigate a hazard. This involves controlling the elements of the hazard including the consequences 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 in order to justify the decision that it can be accepted.

7.1.4 Minimizing the severity of the consequences of hazards

An important principle underlying safe hydrogen use is to seek designs and operations that minimize the severity of the consequences of a potential mishap. This can be accomplished in several ways, such as the following (note that not all of these measures are necessary for all hydrogen applications):

— minimize the quantity of hydrogen that is stored and involved in an operation;

— minimize pipeline diameter and operational pressure to satisfy technological requirements to mass flow rate where applicable;

— isolate hydrogen from oxidizers, hazardous materials, and dangerous equipment;

— identify and, if possible, separate or eliminate potential ignition sources;

— separate people and facilities from the potential effects of unignited releases, fire, deflagration, or detonation originating from the failure of hydrogen equipment or storage systems;

— elevate hydrogen systems and vent them above other facilities;

— prevent hydrogen/oxidizer mixtures from accumulating in confined spaces (under the eaves of roofs, in equipment shacks or cabinets, or within equipment covers or cowlings);

— minimize personnel exposure by limiting the number of people exposed, the time that the personnel are exposed;

— use of alarms and warning devices (including hydrogen and fire detectors), and area control around a hydrogen system;

— use of personal protective equipment;

— practice good housekeeping, such as keeping access and evacuation routes clear and keeping weeds and other debris away from hydrogen systems;

— observe safe operational requirements, such as working in pairs when operating in a hazardous situation.

7.2 Mitigation of design hazards and risks

7.2.1 Inherently safer design

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

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

Automatic safety design includes features such as remote monitoring of critical information, remote operation, and automatic limiting of operating conditions (for example, pressure or 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 caution and warning devices as necessary to alert personnel in the event of any abnormal condition, malfunction or failure. Such devices should provide the personnel with adequate time to respond to the event. As part of these considerations, fire resistance of main components like storage vessels should be known and available to prepare a safety plan to manage potential incident/accident.

7.2.2 Considerations in the selection of suitable construction material

7.2.2.1 General

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

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

7.2.2.2 Low-temperature design considerations

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

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

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

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

7.2.2.3 Embrittlement and hydrogen attack

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

- restricting the strength level of the material used to the necessary limit;
- lowering the level of applied stress;
- minimizing residual stresses, for example, by stress-relieving weldments;
- normalizing or fully annealing cold-worked materials;
- avoiding or minimizing cold plastic deformation from operations such as cold bending or forming;
- avoiding situations that can lead to local fatigue in components that are subjected to frequent load cycles, since hydrogen is known to significantly accelerate a possible initiation and propagation of fatigue cracks in a structure;
- using austenitic stainless steels, which in general are less susceptible to hydrogen embrittlement and are commonly used as structural materials for hydrogen equipment because of their excellent toughness behaviour at cryogenic temperatures;
- using the test methods specified in ISO 11114-4 to select metallic material resistant to hydrogen embrittlement.

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

7.2.2.4 Non-metallic materials

The application of non-metallic materials (rubber or plastic) as sealants has a long history of use in hydrogen service. Polymers usually cause no problems in connection with hydrogen in terms of chemistry or physics (embrittlement as in the case of metals cannot happen since they have no lattice). However, hydrogen can diffuse through these materials (without damaging them) much more easily than through metals. The amounts usually are not sufficient to create ignitable mixtures outside the vessel, but they can cause a loss of gas over a long period of time, or they could spoil an insulation vacuum.

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

Fibre-reinforced polymers (FRPs) are becoming more and more important as materials for pressure vessels. A liner (usually another polymer, sometimes metal) is usually placed inside the vessel to hold the hydrogen so that the FRP material is not in direct contact with hydrogen. Details on cylinder design are given in the various parts of ISO 11119 for transportable applications, ISO 19881 for onboard applications and ISO 19884 for stationary applications. The fire resistance of such materials may be low in comparison to metals, but they have to pass the appropriate qualifying tests.

7.2.3 Considerations for vessels and components

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

- designed, fabricated, and tested in accordance with appropriate pressure vessel standards and regulations,
- constructed of appropriate materials,

- reduce flow rate, pressure, diameter to a minimum required by technological needs,
- 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 designed to conform with fire resistance of a vessel and to exclude its structural failure during the release,
- located in accordance with appropriate regulations, and
- legibly marked with the name “Hydrogen” or “Liquid Hydrogen — Flammable Gas” for gaseous or liquid containers as appropriate or similar.

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

7.2.4 Prevention of overpressure

In liquid hydrogen storage systems in particular, there exists the potential for developing pressures that could exceed the containment capability because of the volume increase as a result of a liquid-to-gas phase change, if this happens in an uncontrolled way. 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 regulations and standards;
- construct with appropriate materials;
- have appropriate flexibility (such as expansion joints, loops and offsets);
- locate in accordance with appropriate standards;
- do not locate beneath electrical power lines;
- if lines are to be buried, consider the effects of galvanic corrosion, the difficulty in conducting a visual inspection for line integrity, and the possibility that a leak can take a path to an unforeseeable location, resulting in an accumulation and an explosion hazard. Leak checks are difficult to perform on buried lines, with the exception of pressure-decay techniques;
- galvanic corrosion can occur with dissimilar metals, particularly when moisture is present, and should be considered in socket-type piping joints. The more corrosive (less noble) material will preferentially corrode and should be used for the female part;
- use appropriate supports, guides and anchors;
- use appropriate pressure-relief devices;
- insulate with appropriate thermal insulation (especially piping for liquid hydrogen and cold gaseous hydrogen);

— label as to contents and direction of flow.

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

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

7.2.6 Cleaning considerations

Cleaning a hydrogen system and keeping it clean is of importance if either the hydrogen may carry traces of other materials into the system or if the purity of the hydrogen is of particular importance for the reliability of the system.

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

7.2.7 Component considerations

7.2.7.1 General

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

The components in a hydrogen system, including soft goods such as seats and seals, should be fabricated of materials 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

Appropriate pressure-relief devices should be installed in any volume which contains hydrogen or in which it could be trapped, to prevent overpressure.

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. Possible effects, like cooling, by the gas flow itself should be considered. Hydrogen released from the discharge port (the outlet) of relief devices should not impinge upon other components or personnel; the possibility of ignition of the gas should be considered. Should multiple relief devices be routed and manifolded to a common vent, care should be taken to ensure that the operation of one device does not restrict flow or influence the opening pressure of other relief devices. Redundancy in both number and type of relief devices (such as relief valve and rupture disk) is commonly used.

Shutoff valves should not be installed in such a way that they can block the path between a relief device and the volume that it is protecting.

Onboard storage systems should be equipped with pressure relief devices, the parameters of which should be in compliance with a fire resistance rating of the onboard storage. If the hydrogen system as a whole is contained in another enclosure, the latter should be able to withstand or to vent overpressure if an accidental release would take place.

7.2.7.3 Filters

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

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

7.2.7.4 Instrumentation and controls

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

7.3 Prevention and mitigation of fire and explosion hazards and 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 easily ignited. Therefore, designers, safety evaluators, and others should assume an ignition source is 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 known as “primary explosion protection”. It is a key part of any safety system. This is done by keeping the hydrogen and an oxidizer such as air separate. The following are some of the techniques to be used in order to achieve this goal.

Purging: A system should be purged with an inert gas, when dealing with liquid hydrogen helium has to be used, to remove air before admitting hydrogen into the system and the system should be purged of hydrogen before opening it to air.

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

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

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

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

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

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

7.3.3 Ignition

7.3.3.1 Electrical sources of ignition

Another key to preventing fire, deflagration, or detonation is to eliminate ignition sources ("secondary explosion protection"). Many electrical, thermal, and mechanical sources of ignition are possible. In some cases, for example, at sudden release of gas from a high pressure system, it may be difficult or impossible to find out where exactly the energy came from.

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

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

Static discharge: Discharges of static electricity can produce high temperatures, often sufficient to cause a material to reach its ignition temperature.

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

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

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

Electrical short circuits: Short circuits or other electrical equipment failures can produce high surface temperatures, arcs and sparks.

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. Insulation materials such as wood, paper, and some fabrics will typically form a conductive layer that can prevent static build-up by absorbing water from the air in environments where the relative humidity is greater than 50 %. Recommended practices for grounding methods to prevent static discharges can be found in various national and international standards that cover the installation of electrical equipment in hazardous environments.

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

7.3.3.2 Mechanical sources of ignition

Phenomena to be considered as potential mechanical sources of ignition are the following:

- mechanical impact and/or friction and galling;
- metal fracture;
- mechanical vibration and repeated flexing.

7.3.3.3 Thermal sources of ignition

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

- open flames and/or hot surfaces (for example, welding and cigarette smoking by personnel);
- exhausts (for example, combustion engines and exhaust stacks);
- explosive charges (for example, charges as used in construction, fireworks or pyrotechnic devices);
- catalysts and reactive chemical materials: High temperatures can result from the interaction of hydrogen with catalysts or other chemical reactants. Some applications that use such materials include recombining hydrogen emitted from lead-acid batteries to produce water and hydrogen detection instruments;
- heating by high-velocity jets, as might occur from the rupture of a tank or vessel;
- shock waves and/or fragments, as might occur from the rupture of a tank or vessel;
- reflected or repeated acoustic and shock waves that can occur in a flowing system.

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 premixing of the reactants, for flame acceleration or detonation include the following:

- avoiding confinement and congestion where flammable hydrogen mixtures might form;
- using flame arrestors, small orifices, or channels to prevent deflagration and detonation from propagating within a system;
- using diluents, like steam or CO_2, or oxygen depletion techniques where possible to retard flame acceleration;
- reduce size of a system where possible to narrow detonability limits.

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

7.3.5 Oxygen enrichment

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

7.4 Detection considerations

7.4.1 Hydrogen gas detection

Because of the limitations of the human senses, other means are needed to detect hydrogen. A variety of methods and detector types are commercially available to detect the presence of hydrogen. Many of these detectors are suitable for use in automatic warning and operating systems. See ISO 26142 for details concerning stationary systems.

It is recommended that hydrogen detectors be used wherever hydrogen is used. Possible cross-sensitivities should be considered. Some suggested locations for hydrogen detectors include the following:

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

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

- accuracy;
- reliability;
- cross sensitivity;
- maintainability;
- calibration;
- zero drift;
- detection limits (high and low);
- response time;
- recovering or non-recovering in time;
- active or passive techniques with and without energy supply;
- compatibility with the system.

Apart from the stationary detection system, hydrogen system operators should also have a portable hydrogen detector available for their use in and around a hydrogen system. A commonly used concentration level for main alarm is 1 % hydrogen (volume fraction) in air, which is equivalent to approximately 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. A warning may be given earlier.

7.4.2 Fire detection

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

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

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

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

7.5 Considerations for facilities

7.5.1 General

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

This Technical Report deals with measures for the technical safety of facilities, not their security against attacks from the outside.

7.5.2 Locations

Keeping a hydrogen facility or system far enough away from people and other facilities can minimize the effects of an event such as a fire, deflagration, or detonation. Suitable separation distances also provide protection for hydrogen facilities from incidents at other nearby facilities. Generally, for a given pressure range, the larger the quantity of hydrogen involved, the greater are the recommended separation distances. Under some circumstances, small quantities of hydrogen may be stored and used in a room or building, but generally outdoor storage is recommended. The separation distance can be determined for the potential hydrogen events or for the potential events at other facilities, whichever requires the greater distance. Safe design and operation of a facility, however, should not be replaced by wider separation distances.

Some important factors in determining the suitable layout for a hydrogen facility include the following:

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

7.5.3 Exclusion areas

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

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

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

7.5.4 Protecting barricades

If there is a certain non-vanishing probability for the burst of hydrogen system parts a barricade can be used to protect other nearby facilities from shrapnel and fragments that could result from an explosion at a hydrogen facility. The same holds if a potential burst of systems in the neighbourhood makes it necessary to protect a hydrogen facility. Earth mounds and blast mats are common types of barricade. Barricades can also include physical barriers to protect hydrogen facilities or systems from motor vehicles.

Barricades or other retaining devices around hydrogen facilities or systems should only be used with great care, because of the increased chance for premixing leading to enhanced detonation effects associated with confinement.

Barricades can also include physical barriers to protect hydrogen facilities or systems from motor vehicles.

7.5.5 Safety control 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 to indicate incipient failures. Warning system data transmissions with visible and audible signals should have sufficient redundancy to prevent any single-point failure from disabling the system.

Flow control: Safety valves and flow regulation devices should be installed to adequately respond for the protection of personnel and equipment during hydrogen storage, handling, and use.

Safety features: System and equipment safety features should be installed to automatically control the equipment required to reduce the hazards suggested by the caution and warning systems. Manual controls within a system should be constrained by automatic limiting devices to prevent over-ranging.

Any instrumentation, software, and computer used for safety control should

- be independent of similar equipment for normal operations, and
- have sufficiency redundancy to prevent any single-point failure from disabling the equipment.

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

Common purging techniques include the following:

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

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

7.5.6 Disposal of hydrogen

Hydrogen should always be disposed of according to an approved method. Intentional disposal of hydrogen is commonly done 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. The ignition of a pre-mixed gas mixture should be avoided.

Disposal factors that should be considered are the following:

- the quantity and concentration of hydrogen that could exist in a combustible cloud;
- the extent of the combustible cloud;
- thermal radiation from a flame (from a flare system or a vent system fire);
- site conditions such as size of the exclusion area, building locations, personnel control, and weather.

The back-flow of air into a vent system should be prevented. Water should never be sprayed so that it can enter a liquid-hydrogen vent system that gets sufficiently cold to freeze the water, because the ice could plug the vent system. It may be useful to add inert gas to a vent to limit ingress of air when hydrogen is not flowing.

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 product of hydrogen mass flow rate and leak diameter.

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

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

Venting wet hydrogen may need to consider freeze-protection.

7.5.7 Buildings

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

- use of non-combustible materials;
- no spaces where hydrogen can accumulate;
- minimize sources of ignition;

- pressure relief systems to mitigate deflagrations by venting technique;
- adequate ventilation;
- appropriate use of hydrogen detectors.

7.5.8 Ventilation

Considerations for ventilation should appropriately address the scenarios of

- a hydrogen presence inside a confined space, and
- a migration of hydrogen into a confined space from a source outside the confined space.

In the first scenario, a ventilation system should remove hydrogen from the confined space or at least keep its concentration below the appropriate lower flammability limit (the flammability limits are functions of pressure and temperature which will deviate from those obtained under ambient conditions). In the second scenario, the ventilation system should not introduce hydrogen into a confined space, unless it is shut down.

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

The following are some other considerations for ventilation systems.

- Depending on geometrical configuration and amount of natural (or unforced) ventilation, mechanical (or forced) ventilation could be either interlocked with hydrogen detection or be established prior to hydrogen being introduced into a confined space and continue until hydrogen is removed from the confined space.
- Ventilation should not be shut off as a function of an emergency shutdown procedure unless the source of hydrogen is outside the confined space.
- Suspended ceilings and inverted pockets in confined spaces should be avoided or adequate ventilation of these spaces should be ensured.
- Electrical equipment in the ventilation system should meet appropriate provisions for operation in a combustible environment.
- The design of the ventilator should be such that even in case of a failure it cannot generate mechanical sparks by the movement of the parts relative to each other.

7.5.9 Electrical components

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

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

Under these conditions, electrical equipment and wiring should be

- approved for use in a hydrogen environment,
- intrinsically safe for use in a hydrogen environment, or

— placed in an approved enclosure that is purged with an inert gas.

Explosion-proof equipment should be used in all locations described above unless it can be shown that it is not necessary.

Electrical equipment and wiring located close to locations as described above or to a hydrogen storage vessel should also be carefully considered, but their requirements are somewhat less stringent than the closer locations described above.

Lightning protection should be provided for hydrogen equipment.

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

7.5.10 Alarms and warning devices

Warning systems should be installed to provide an alarm in the event of a potentially hazardous situation, with sufficient time to enable safe shutdown of the hydrogen system and evacuation of people when applicable. Hazardous situations are not restricted to the escape of flammable gas.

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

Some system alarm/warning conditions are the following:

— 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;

— fire.

Which systems are to be used should be decided on the basis of the conditions on site.

7.5.11 Fire protection and fire fighting

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

— process shutdown system (automatic and/or manual);

— sprinkler system;

— deluge system;

— dry-chemical extinguishing system.

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

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

If possible, system components around a flame may be cooled with water to prevent mechanical failure due to decreased strength at elevated temperatures.

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. Dangerous behaviour such as smoking should not be allowed In addition to the normal operations involved with a hydrogen facility or system, there are emergency operations that may be required in the event of a failure or a mishap.

7.6.2 Operating procedures

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

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

Procedures should be easily accessible for everybody who might need them. It is recommended to have the current version on display in the room where the work is done.

7.6.3 Personal protective equipment

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

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.

Necessary or mandatory parts of PPE have to be selected on the basis of the conditions onsite. Here are some specific recommendations for PPE in connection with hydrogen systems.

- Eye protection should be worn if appropriate (for example, a complete face shield should be worn when connecting and disconnecting lines or components or goggles during handling of cryogenic liquids).
- Properly insulated gloves should be worn when handling anything that comes in contact with liquid hydrogen or cold gaseous hydrogen. The gloves should fit loosely, remove easily, and not have large cuffs.
- Full-length trousers, preferably without cuffs, should be worn with the legs kept on the outside of boots or work shoes. Flame-retardant aramid-fibre clothing is commonly used in industry.

- Closed-toe shoes should be worn (open or porous shoes should not be worn).
- Clothing made of ordinary cotton, flame-retardant cotton or antistatic material 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. Synthetic material (clothing) can melt and stick to the flesh, causing greater burn damage. Any clothing sprayed or splashed with hydrogen should be removed until they are completely free of hydrogen gas.
- Gauntlet gloves, tight clothing, or clothing that holds or traps (pockets) liquid against the body should be avoided.
- Hearing protection should be worn if the hydrogen facility or system involves equipment that creates loud noise.
- Hard hats should be worn if the hydrogen facility or system involves any danger from falling objects.
- Self-contained breathing equipment should be worn when working in a confined space that may have an oxygen-deficient atmosphere.
- Portable hydrogen and fire-detection equipment should be used to warn of hydrogen leaks and fires.
- Personnel should ground themselves before touching or using a tool on a hydrogen system if any hydrogen is or is suspected to be in the area.

7.6.4 Cool-down

The cool-down of a liquid hydrogen system from ambient conditions to its operating temperature (at or near NBP) is a process that should be conducted by trained employees 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. Operating instructions should be carefully followed.

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

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

7.6.5 Transportation

Hydrogen should be transported as it is appropriate for a hazardous (flammable, pressurized) substance. 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.

7.6.6 Storage and transfer operations

The following are some general guidelines for storage and transfer operations. Detailed procedures are dependent on local and application specific boundary conditions.

- Always take the locally prevailing conditions into account, including company procedures or manufacturer instructions.

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

7.6.7 Safety procedures

7.6.7.1 General

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

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

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

7.6.7.2 Emergency procedures

Considerations that emergency procedures should address are the following:

- emergency escape procedures and emergency escape-route assignments;
- procedures to be followed by employees who remain to operate critical systems before they evacuate;
- procedures to account for all personnel after an emergency evacuation has been completed;
- rescue and medical duties for those employees who are to perform them;
- the preferred means of reporting fires and other emergencies;
- names and regular job titles of persons responsible for providing further information or explanation of duties under the emergency plan;
- actions to be taken by the initial-response personnel;
- appropriate fire-suppression response;
- establishing and maintaining communications;
- appropriate medical response;
- requesting outside assistance;
- possible media coverage;
- salvage and restoration operations;
- establishing a command post with a pre-designated line of authority;
- hazardous material inventory.

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

When a company or an institute has a general alarm and emergency system, the provisions for the hydrogen systems should be integrated in it.

7.6.7.3 Fire-fighting procedures

Hydrogen flames should not be extinguished before the gas supply is interrupted. Otherwise, unburnt gas may create premixed explosive flammable mixtures which if ignited could lead to significant hazardous situation. Water spraying may be necessary to keep adjacent facilities cool to prevent mechanical failure of heated components.

7.6.7.4 Liquid spill procedures

In case of a liquid spill, the flow should be interrupted by closing valves further upstream. Measures in the vicinity of the spill site should not be taken, and the area near it should be evacuated until a reasonable time has elapsed for the liquid to evaporate and for the gas to disperse to concentrations below the flammability range.

Vaporized liquid hydrogen will rapidly cause condensation of atmospheric humidity, forming a white cloud of condensed water. Note that some sources of hydrogen safety-related information will claim that the extension of the cloud of condensed water is a rough guide for the extension of the flammable hydrogen/air gas mixture cloud. This should by no means be taken as a basis for safety measures. The visible water cloud is, at best, only a very rough guide for the extension of the hydrogen/air mixture cloud and the hydrogen/air mixture may be larger than the visible water 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 they are needed to ensure that hydrogen is used in a safe manner. Organizational policies and procedures should address issues such as safety responsibility, hazards and risk management, and applicable standards, and regulations that apply to the organization’s operations. It is desirable that a safety culture be established among the organization’s personnel to promote thinking about safety at all times, especially as it performs its duties. An emphasis on safety in working with hydrogen should come from the highest level of the organization, as an indication of its importance to the organization.

If the organization has a quality management system, it is recommended that the policies and procedures related to the safe use of hydrogen be integrated into it.

7.7.2 Control through organizational policies and procedures

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

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

7.7.3 Use of approved procedures and checklists

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

7.7.4 Conduct appropriate reviews

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

7.7.5 Approved maintenance and quality control programmes

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

7.7.6 Personnel education/training

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

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

Training should include the actions to be taken in the event of an emergency, such an unignited release, a fire or a deflagration or detonation. Personnel should be trained to assist in the safe and orderly emergency evacuation of personnel. Training should include preventative and first-aid procedures for emergency care of injuries, including procedures for cold and cryogenic injuries where cold gaseous hydrogen or liquid hydrogen is involved.

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

7.7.7 Hazard and operability assessment

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

Annex A
(informative)

Hydrogen properties

A.1 General

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

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

Property[a]	**Normal hydrogen**	**Parahydrogen**
Properties at normal temperature and pressure (NTP)		
Temperature, K	293,15	
Pressure (absolute), kPa	101,325	
Density, kg/m^3	0,083 76	0,083 76
Specific heat at constant pressure (c_p), kJ/kg·K	14,33	14,89
Specific heat ratio (c_p/c_V)	1,416	1,383
Enthalpy, kJ/kg	4 129,1	4 097,7
Internal energy, kJ/kg	2 919,5	2 888,0
Entropy, kJ/kg·K	70,251	64,437
Velocity of sound,·m/s	1 294	1 294
Viscosity, µPa·s	8,81	8,81
Thermal conductivity, mW/m·K	183,8	191,4
Volume expansivity, K^{-1}	0,003 33	0,003 33
Heat of conversion from normal to para-hydrogen at 300 K, kJ/kg	27,56	
Properties at critical point (CP)		
Latent heat of vaporization, kJ/kg	—	
Temperature, K	33,19	32,976
Pressure (absolute), kPa	1 315	1 292,8
Density, kg/m^3	30,12	31,43
Specific heat at constant pressure (c_p), kJ/kg·K	Very large	Very large
Specific heat ratio (c_p/c_V)	Large	Large
Enthalpy, kJ/kg	577,4	38,5
Internal energy, kJ/kg	[data not available]	2,8
Entropy, kJ/kg·K	27,07	17,6
Velocity of sound, m/s	[data not available]	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	

Table A.1 *(continued)*

Property[a]	Normal hydrogen	Parahydrogen
Density, kg/m^3	1,331 (V) 70,96 (L)	1,338 (V) 70,78 (L)
Latent heat of vaporization, kJ/kg	446,0	445,6
Specific heat at constant pressure (c_p), kJ/kg·K	12,20 (V) 9,772 (L)	12,15 (V) 9,688 (L)
Specific heat ratio (c_p/c_V)	1,683 (V) 1,698 (L)	1,869 (V) 1,688 (L)
Enthalpy, kJ/kg	717,98 (V) 272,0 (L)	189,3 (V) -256,3 (L)
Internal energy, kJ/kg	641,9 (V) 270,7 (L)	113,6 (V) -257,7 (L)
Entropy, kJ/kg·K	39,16 (V) 17,32 (L)	29,97 (V) 7,976 (L)
Velocity of sound, m/s	357 (V) 1 101 (L)	355 (V) 1 093 (L)
Viscosity, µPa·s	1,1 (V) 13,2 (L)	1,1 (V) 13,2 (L)
Thermal conductivity, mW/m·K	16,9 (V) 99,0 (L)	16,9 (V) 99,0 (L)
Volume expansivity, K^{-1}	0,064 2 (V) 0,016 4 (L)	0,064 2 (V) 0,016 4 (L)
Heat of conversion from normal to para-hydrogen, kJ/kg	527,14	
Properties at triple point (TP)		
Temperature, K	13,957	13,803
Pressure, kPa	7,205	7,042
Density, kg/m^3	0,129 8 (V) 77,21 (L) 86,71 (S)	0,125 6 (V) 77,021 (L) 86,50 (S)
Specific heat at constant pressure (c_p), kJ/kg·K	10,53 (V) 6,563 (L) — (S)	10,52 (V) 6,513 (L) — (S)
Specific heat ratio, c_p/c_V	1,695 (V) 1,388 (L) — (S)	1,693 (V) 1,382 (L) — (S)
Latent heat of vaporization, kJ/kg	452,0	449,2
Latent heat of fusion, kJ/kg	58,09	58,29
Latent heat of sublimation, kJ/kg		507,39
Enthalpy, kJ/kg	669,67 (V) 217,6 (L) 159,5 (S)	140,3 (V) -308,9 (L) -367,2 (S)
Internal Energy, kJ/kg	612,52 (V) 215,8 (L) 157,7 (S)	84,23 (V) -309,0 (L) -367,3 (S)

Table A.1 *(continued)*

Property[a]	Normal hydrogen	Parahydrogen
Entropy, kJ/kg·K	46,4 (V) 14,2 (L) 10,1 (S)	37,52 (V) 4,961 (L) 0,739 (S)
Velocity of sound, m/s	307 (V) 1 282 (L) — (S)	305 (V) 1 273 (L) — (S)
Viscosity, µPa·s	0,74 (V) 26,0 (L)	0,74 (V) 26,0 (L)
Thermal conductivity, mW/m·K	12,4 (V) 73,0 (L) 900 (S)	12,4 (V) 73,0 (L) 900 (S)
Volume expansivity, K^{-1}	0,075 2 (V) 0,010 2 (L)	0,075 2 (V) 0,010 2 (L) 0,004 94 (S)
Other properties		
Molecular mass	2,015 94	2,015 94
Equivalent volume gas at NTP/volume liquid NBP	847,1	845,1
Equivalent volume gas at CP/volume liquid NBP	2,357	2,252
Equivalent volume gas at NBP/volume liquid at NBP	53,30	52,91
Equivalent volume gas at TP/volume liquid NBP	546,3	563,8
Equivalent volume liquid at TP/volume liquid NBP	0,919 0	0,919 0
Equivalent volume solid at TP/volume liquid NBP	0,818 4	0,818 1
Pressure required to maintain NBP liquid density in NTP GH_2 (fixed volume, no venting), MPa	172[b]	
Joule-Thomson maximum inversion temperature, K	200	
Diffusion coefficient in NTP air, 10^{-4} m^2/s	0,61	

NOTE 1 (L): Liquid phase.

NOTE 2 (S): Solid phase.

NOTE 3 (V): Vapour phase.

NOTE 4 c_V: Specific heat at constant volume, kJ/kg·K.

NOTE 5 Numbers in parentheses are estimates.

[a] Unless specified otherwise, source of data is Reference [9] in the Bibliography.

[b] Calculated value.

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 common gases

Gas	Density at 20 °C and 100 kPa kg/m^3	Viscosity at 20 °C and 100 kPa µPa·s	Diffusion coefficient in air 10^{-4}·m^2/s	Lower heating value MJ/kg
Hydrogen (H_2)	0,082 7	8,814	0,61	119,93
Helium (He)	0,164 0	19,609	0,57	n/a
Methane (CH_4)	0,659 4	11,023	0,16	50,02
Nitrogen (N_2)	1,149 6	17,637	0,20	n/a

A.3 Comparison with other liquefied gases

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

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

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

Annex B
(informative)

Hydrogen combustion data

B.1 Safety-related combustion properties

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

Table B.1 — Safety-related combustion properties of normal hydrogen

Property	Value[a]
Heating value, kJ/g	119,93 (lower) 141,86 (higher)
Flammability limits, vol fraction, %	3,6 to 76,6 (in NTP air,[5] Method T) 4,2 ... 77,0 (in NTP air,[5] method B) 3,75 ... 75,1 (in NTP air,[6]) 4,1 ... 94 (in NTP oxygen)[c]
Stoichiometric concentration in air, vol fraction, %	29,53
Ignition energy (minimum) for ignition in air, mJ	0,017
Concentration at which the minimum ignition energy is found, vol fraction, %	22 to 26
Auto-ignition temperature, K	858[d]
Ignition temperature (hot air jet), K	943
Stoichiometric Flame temperature in air, K	2 318
Thermal energy radiated from flame to surroundings, %	17 to 25
Maximum laminar burning speed in NTP air, m/s	2,65 to 3,25
Maximum deflagration propagation speed in a stoichiometric NTP H_2/air mixture, m/s	975
Detonation propagation speed in NTP air, m/s	1 480 to 2 150
Maximum experimental safe gap in NTP air, mm	0,08
Quenching gap stoichiometric mixture in NTP air, mm	0,64
Limiting oxygen index, vol fraction, %	5,0
Burning rate of spilled liquid pool, mm/s	0,5 to 1,1

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

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

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

[a] Unless specified otherwise, source of data is Reference [9] in the Bibliography.

[b] The values are ones commonly given. It is recommended that they be used only as a guide. These properties are a function of many variables that are to be evaluated to determine their values for a specific application. In particular, they are hardly useful for evaluating a realistic accident situation.

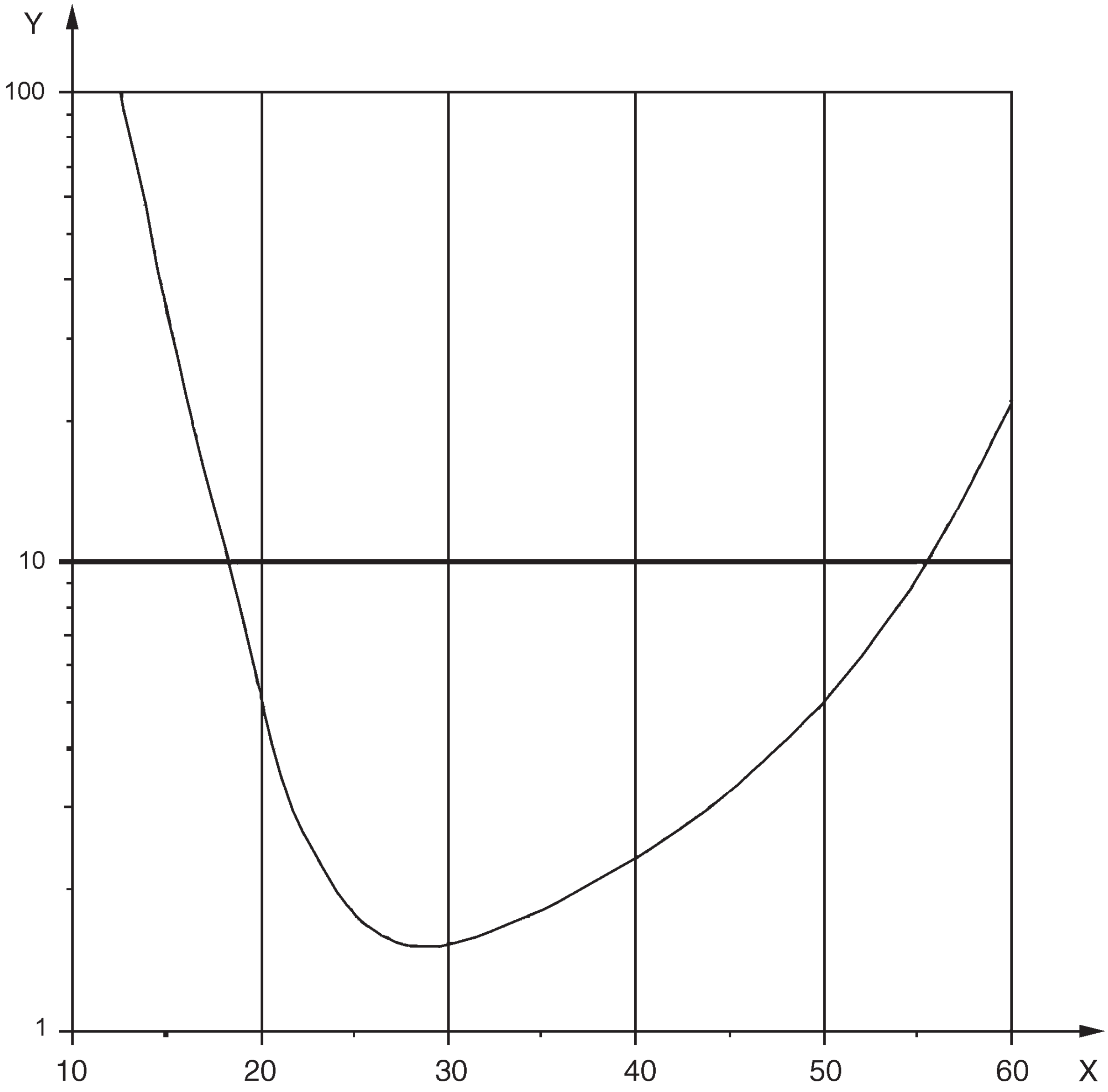
[c] Source of data is Reference [8] in the Bibliography.

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

[e] Based on high heat of combustion.

B.2 Detonation cell widths for hydrogen/air mixtures

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



Key

X hydrogen concentration, volume fraction (%)

Y detonation cell width, cm

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

B.3 Comparison of hydrogen with other common fuels

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

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

Fuel	**Lower flammability limit** % vol. fraction	**Stoichiometric mixture** % vol. fraction	**Upper flammability limit** % vol. fraction	**Minimum ignition energy** mJ	**Auto-ignition temperature** K	**Laminar burning velocity** m/s
Hydrogen (H_2) (see Table B1)	4	29,5	77	0,017	858	2,70
Methanol (CH_3OH)	6,0	12,3	36,5	0,174	658	0,48
Methane (CH_4)	5,3	9,5	17,0	0,274	810	0,37
Propane (C_3H_8)	1,7	4,0	10,9	0,240	723	0,47
Gasoline[a] (C_8H_{18})	1,0	1,9	6,0	0,240	488	0,30

Annex C
(informative)

Material data

C.1 Material selection criteria

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

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

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

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

C.2 Hydrogen embrittlement

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

Although a material may be subject to hydrogen embrittlement (even extremely embrittled), the material may still be used in hydrogen service if the service conditions allows its use (e.g. low enough stress).

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

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 and 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		

[a] ISO 11114-4 describes test methods which allow to verify the exact sensibility of steel and metallic materials to hydrogen embrittlement.

C.3 Low temperature effects on metals

C.3.1 General

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

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

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

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

C.3.2 Low-temperature embrittlement

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

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

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

C.3.3 Thermal contraction

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

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

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

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

C.4 Material suitability for hydrogen service

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

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

Material	**Gaseous hydrogen** (GH_2) **service**	**Liquid hydrogen** (LH_2) **service**[b]	**Remarks**
METALS			
Aluminium and its alloys	S	S	Negligibly susceptible to hydrogen embrittlement.
Copper and its alloys (such as brass, bronze and copper-nickel)	S	S	Negligibly susceptible to hydrogen embrittlement.
Iron, cast, grey, ductile	NS	NS	Not permitted by relevant regulations 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)	See C.1	See C.1	May make martensitic conversion if stressed above yield point at low temperature.
Steel, carbon (such as 1020 and 1042)	See C.1	NS	Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic service.
Steel, low alloy (such as 4140)	E	NS	Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic service.
Steel, martensitic stainless (such as 410 and 440C)	E	E	Evaluation needed. Susceptible to hydrogen embrittlement.
Steel, nickel (such as 2,25; 3,5; 5 and 9 % Ni)	E	NS	Ductility lost at liquid hydrogen temperature
Titanium and its alloys	E	E	Evaluation needed. Susceptible to hydrogen embrittlement.
NONMETALS			
Asbestos impregnated with Polytetrafluoroethylene (PTFE)[a]	S	S	Avoid use because of carcinogenic hazard.
Chloroprene rubber (Polychloroprene[a])	S	NS	Too brittle for cryogenic service.
Polyester fibre (Dacron)	S	NS	Too brittle for cryogenic service.
Fluorocarbon rubber (Viton[a])	E	NS	Too brittle for cryogenic service.
Polyester film (Mylar)[a]	S	NS	Too brittle for cryogenic service.
Nitrile (Buna-N[a])	S	NS	Too brittle for cryogenic service.
Polyamides (nylon)	S	NS	Too brittle for cryogenic service.
Polychlorotrifluoroethylene (Kel-F[a])	S	S	
Polytetrafluoroethylene [Polytetrafluoroethylene (PTFE)[a]]	S	S	

NOTE 1 S: Suitable for use.

NOTE 2 NS: Not suitable for use.

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

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

[b] Care should be taken that when the liquid H_2 tanks are more or less empty that the upper part could be warm. In this case, the column of GH_2 applies instead of LH_2.

Annex D
(informative)

Other storage options

D.1 General

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

A variety of chemical compounds using different physical mechanisms for hydrogen storage are under investigation. These include common liquid fuels, metal hydrides (see ISO 16111), liquid organic hydrides, and newer materials such as fullerenes, carbon-fibre nanotubes and glass microspheres. Some of the liquid fuels considered include methanol, methylcyclohexane (MCH), ammonia, gasoline, and hydrazine. Hydride systems may use metal alloys, catalysts, and liquid slurries. The safety considerations are presented in general terms because of the great physical differences in these chemical compounds and the systems that use them, the lack of hazards characterization of the more novel materials, and the potential for new as yet undefined systems. Specifics for chemical compounds in common use can be found in material safety data sheets (MSDS) and in safety literature.

D.2 Basic safety considerations for chemical compounds

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

- general description of common or special hazards;
- physical properties;
- combustion properties in air;
- material compatibility;
- handling information;
- toxicity;
- firefighting.

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