HARARE

Deliverable 6.1

Safe use of hydrogen for lab and pilot scale

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DISSEMINATION LEVEL: PUBLIC

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1 INTRODUCTION

1.1 Purpose of the document

The purpose of this document is to supply necessary information for safe handling of hydrogen for lab and pilot scale applications of HARARE project. When hydrogen is oxidized with oxygen, the only by-product is water vapor, making it an ideal energy carrier and oxidizing agent for a green environmentally friendly and sustainable economy. Hydrogen is however commonly viewed as a highly dangerous substance because of past accidents that are frequently incorrectly ascribed to the presence of hydrogen, e.g., the well know Hindenburg accident. When handled safely, hydrogen poses no more, although some slightly different, risks than natural gas, while some other fuels, like liquid petroleum gas (LPG / commonly referred to as propane, although it is usually a variable mixture of propane and butane), can in fact be more dangerous because they are heavier than air and therefore easily concentrate and accumulate in basements, enclosed spaces and even move into and along drains or sewers, creating hazards in unexpected locations.

1.2 Structure

This document is structured as follows:

- Section 1 is an introduction chapter describing the main purpose of the deliverable.
- Section 2 describes the properties of hydrogen, its risks and hazards.
- Section 3 describes the storage and delivery of hydrogen.
- Section 4 gives information about material selection.
- Section 5 gives detailed information about safety from different aspects.
- Section 6 describes piping systems for hydrogen flow trains.
- Section 7 briefly discusses other components such as vents, instrumentation, atmospheric monitoring.

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2 PROPERTIES OF HYDROGEN

2.1 General

Hydrogen is a flammable, non-toxic, colourless, odourless, tasteless gas at ambient conditions. It is the lightest element and the lightest gas. It is significantly lighter than air (its relative density to air is 0.07), so that it rises quickly and diffuse rapidly when released into the atmosphere.

Due to its very small molecular size, it can diffuse rapidly through some porous materials or components that are considered gas tight with other gases. It is highly flammable and requires very little energy to ignite. Leaks disperses upwards very rapidly, from the point of release a sabre-like combustible area pointing towards the sky with fast mixing below lower explosive limit (LEL).

The formation of a combustible and drifting cloud is not expected – and the chance of an explosion is quite low. The auto ignition temperature of a hydrogen air mixtures is 572°C, versus 632°C for methane.

The speed of sound in hydrogen is 1290 m/s (at 1.013 bar(a) & 15°C) versus 466 m/s in CH_4. A high-volume pressurized leak is thus very loud. Hydrogen is unusual in that it has a negative Joule-Thomson effect, i.e., it heats up slightly when depressurized, but (from 200 bar) not to a high enough temperature to present any hazards or risks. Hydrogen is not an ideal gas and deviates significantly from the equation of state of an ideal gas ($PV = nRT$). [Deviations from the Ideal Gas Law (purdue.edu)]

2.2 Hazards

Hydrogen is extremely flammable in air with a very wide flammability range from approximately 4 to 75% (vol/vol). In oxygen the flammability range is even broader, from 5% to 93%.

Confined mixtures of hydrogen and air / or oxygen explode violently. Confined hydrogen clouds are highly unlikely to occur outdoors but could occur within poorly ventilated buildings or rooms or e.g., in fume cupboards when the extraction is not running or within an enclosed experimental setup.

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Hydrogen burns in air with an almost invisible, very hot and pale blue flame that emits very little radiation so that it gives very little warning of its presence. Shimmering and the movement of the hot gases are usually visible. Hydrogen flames can typically only be extinguished by isolating the hydrogen source.

FIGURE 1: AN ALMOST INVISIBLE HYDROGEN FLAME BURNING IN AIR

At high concentrations hydrogen is an asphyxiant as it displaces the oxygen in air. This is however unlikely to occur in a lab or pilot plant environment as it requires a large quantity of hydrogen to escape within a small enclosed or confined space. The flammability risk is significantly higher than the risk of asphyxiation. Refer to Table 1 for the symptoms and effects associated with oxygen depletion.

NOTE: A person can survive 3 weeks without food, 3 days without water but less than 3 minutes without oxygen!

TABLE 1: EFFECTS OF OXYGEN DEPLETION

O_2 (Vol %)	Effects and Symptoms
18 - 21	No discernible symptoms
11 – 18	Reduced physical and intellectual performance, without being aware of this!
8 – 11	Fainting within a few minutes without prior warning
6 – 8	Fainting very quickly, can be resuscitated if removed immediately
0 - 6	Immediate fainting. Brain damage even if rescued.

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2.2 Risks

High pressure hydrogen leaks from large storage vessels, cylinders or distribution piping can disperse quickly and create a potentially flammable cloud over a relatively large distance under the right ambient conditions.

The ignition energy of hydrogen is extremely low, so that leaks ignite very easily. The ignition energy is almost 15 times lower than that of methane.

A pressurized hydrogen leak will usually ignite due to an electrostatic charge or by the ignition of impurities in the hydrogen or the pipeline, resulting in a long jet flame that turns upwards quite quickly. If this hot flame impacts an adjacent storage vessel, a catastrophic failure can occur very quickly.

Even controlled or intentional (e.g., a safety valve lifting) venting via a chimney can ignite very easily.

An explosion of an enclosed flammable cloud will result in catastrophic destruction in the vicinity of the explosion.

FIGURE 2: HYDROGEN EXPLOSION IN A COMPRESSOR BUILDING

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FIGURE 3: FRAGMENTS OF A HYDROGEN CYLINDER THAT RUPTURED AFTER THE INGRESS OF OXYGEN INTO THE HIGH-PRESSURE HYDROGEN CAUSED AN EXPLOSION

Potential ignition sources:

- Flames, including cutting and welding flames as well as sparks
- Direct fired space heating and process heating equipment
- Cigarettes, matches, lighters, etc.
- Portable electronic devices like mobile phones, cameras, torches, etc.
- Hot surfaces
- Mechanical equipment
- Electrical equipment, lights and heating
- Sparks from friction heating or impact, e.g., use of non-spark-free tools
- Sparks from electrical equipment, electrostatic discharge
- Stray currents from electrical equipment
- Lightning strikes
- Vehicle’s ignition systems, electrical systems, etc.

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3 STORAGE AND DELIVERY

Hydrogen is typically delivered as a compressed gas in high pressure cylinders (200 or 300 bar) or high-pressure cylinder bundles (200 or 300 bar) for lab and pilot scale. For larger industrial applications the delivery is usually in pressurized tube trailers (typically at 200 bar, but also up to 500 bar in containerized high pressure composite tubes) from which an on-site 50 bar buffer storage vessel is filled, or as a cryogenic liquid at – 253°C (at 1 bar (g)).

3.1 Cylinder handling

A standard 200 bar 50-liter cylinder weights up to 80 kg (depending on the gas within) and can pose a serious risk if it were to fall over. As a result, cylinders should always be **well secured** and may only be transported with the cylinder valve closed and the cylinder cap in place. Hydrogen cylinders should be stored in a well ventilated and locked location that is specifically intended for storing combustible gases, as per local regulations.

First decrease the setpoint of the pressure regulator (by turning the adjustment screw / spring anti-clockwise / out), then open the cylinder valve very slowly. Slowly increase the operating pressure downstream of the pressure regulator by screwing the adjustment screw / spring of the regulator inwards. Always ensure that the selected outlet pressure does not exceed the maximum operating pressure of the downstream equipment.

The equipment downstream of the pressure regulator should be protected by a safety relief valve that is designed to safely vent the full flow that can pass through the pressure regulator at the maximum supply pressure in the event of a pressure regulator failure. This safety relief valve must be vented to a safe location. The outlet location of this vent line is considered to be an explosive zone and must be appropriately located and signposted. Verify that the system is depressurized before disconnecting hoses or regulators.

When opening a depressurized hose or connection, a small amount of hydrogen will still escape, posing a potential ignition risk!

Always open cylinder valves (all gases, not just hydrogen!) very slowly. Too rapid opening causes adiabatic compression (of any gas) and temperatures can reach 800°C. This can be fatal with oxygen!

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FIGURE 4: INDIVIDUAL CYLINDERS, A CYLINDER BUNDLE AND A CRYOGENIC STORAGE TANK

FIGURE 5: A 200 BAR HYDROGEN TUBE TRAILER AND A HIGH PRESSURE 500 BAR COMPOSITE TUBE TRAILER

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4 MATERIAL SELECTION

Due to its very small molecular size, hydrogen will leak through seals, joints and rubber / synthetic pipes. Verify what the regulations are in your country / location for the types of joints, materials and connections when working with hydrogen e.g., in Germany TRBS 2152 Part 2, Avoidance or limitation of hazardous explosive atmosphere - *auf Dauer technisch dicht (*permanently technically leak tight*)*.

Threaded connections should be avoided whenever possible or kept to an absolute minimum. Joints should be checked with a leak test spray regularly. Remember that this test must be performed when the system is pressurized and in service, else no leak will be detected!

Ensure that all gaskets, seals and lubricants are hydrogen compatible as hydrocarbons are cracked over time and purged out of the material. Clean work and a very thorough purging of pipelines prior to start-up is essential. Any dirt will eventually accumulate in control valve seats and other dead ends.

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5 SAFETY

5.1 Training

Anyone working with hydrogen or hydrogen containing equipment must be properly trained on the hazards, safe use and handling of hydrogen, including the safe handling of cylinders. The training shall include at least the following: potential hazards, site safety regulations, emergency procedures, use of firefighting equipment as well as the use of protective clothing and equipment. This training must be documented. Refresher training should take place annually and must also be correctly documented.

5.2 Personal protective equipment (PPE)

Flame retardant and anti-static clothing (ideally overalls), long sleeves and gloves should be worn when working with or close to hydrogen areas. This is absolutely critical in ATEX zones or areas where an explosive composition or gas mixture could or may be expected to occur (which is by definition an ATEX or Ex-Zone!). Avoid wearing synthetic clothing when working with hydrogen.

Safety shoes should be worn when handling, moving, or transporting cylinders and cylinder bundles, or any other heavy equipment. Eye protection must be worn when working with pressurized gases or on any equipment, piping or hoses that contain or could potentially contain pressurized gases.

It is recommended that ear protection be worn, especially when intentional hydrogen combustion (e.g., hydrogen fired burners) is taking place or may be expected to occur. This is because a small flash-back may occur that results in a non-hazardous, although still extremely loud, explosion occurring within a partially confined space.

5.3 Ambient monitoring

If local conditions require it or if in a confined space, hydrogen specific ambient monitoring should be worn whenever working with hydrogen or when in the vicinity of piping and systems containing hydrogen. This is especially critical in confined or potentially confined spaces. It is always better to err on the side of caution rather than take unnecessary risks.

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5.4 Equipment and tools

Only anti-static tools may be used when working on or close to hydrogen containing piping or systems. Remember that even the smallest electrostatic discharge can ignite a flammable cloud of hydrogen.

5.5 Explosive atmospheres / Explosive zones

The precise definition of an explosive atmosphere or explosive zone will depend upon local regulations, guidelines and standards. In general, it concerns the presence or potential presence of an explosive mixture of air and a dangerous substance (in the case of hydrogen, a gas, but it could also be a vapor, mist, dust or fibre) that could ignite and burn or explode, depending on the ambient conditions. The level or severity of the zone will depend on the frequency or likelihood as well as the duration of it being present or occurring. Local regulations must be understood and shall always be strictly implemented and adhered to.

5.6 Fire protection

A hydrogen fire can typically only be extinguished by isolating the source. If a flame is extinguished, beware of reignition of the still escaping hydrogen! Keep hydrogen away from all sources of ignition – no smoking or open flames. Prevent static discharges. Only explosion proof electrical installations and equipment (e.g. ATEX in the EU) may be used within a hazardous or potentially hazardous area (explosive zone). No hot work is allowed, unless if the equipment and atmosphere is free of hydrogen. If appropriate, the piping and / or equipment must be purged with an inert gas and the hydrogen content verified before any hot work is allowed to commence. All equipment must be grounded. Keep the area where hydrogen is stored and worked with free combustible materials.

5.7 Safety reviews / Risk assessments

A well-documented risk assessment, safety review or HAZOP must be performed prior to the start of all tests, trials or work that does not follow an already verified and approved working procedure. If in doubt, rather err on the safe side and review the proposed work once again and involve at least one, ideally more, colleagues or participants with a technical background who also understand the potential risks and hazards. Always ask the question "what are we doing differently compared to what we have done in the past or usually do" is always a good starting point for the risk assessment.

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6 PIPING SYSTEMS

All pipe and component connections must be "permanently technically leak tight" (German TRBS (*Technical rules for Operational Safety*) 2152 Part 2, Avoidance or limitation of hazardous explosive atmosphere - auf Dauer technisch dicht) in order to avoid ATEX / EX Zones. In the EU plant components are considered to be permanently technically leak tight if they are designed in such a way that they remain technically tight due to their construction or their technical tightness is constantly ensured by maintenance and monitoring. Examples are welded plant components, tongue and groove flanges as well as special seal types, e.g., double-acting mechanical seals.

IVSS Infoblatt Dichtheit von Anlagenteilen und Verbindungen (bgrci.de) provides some details and explanations, in German. These are based on German regulations and may not apply in some other regions or countries. Please ensure that local regulations related to explosive atmospheres are understood and complied with.

Refer to the paragraph above on "Materials Selection" for additional information. At low pressure and open pipe ends there is a risk of sucking air back into the hydrogen pipe due to a high gas velocity in conjunction with its low density.

In low flow or no flow vertical pipes, hydrogen's low-density results in it escaping upwards and air being sucked back into the pipes. As a result, explosion or detonation proof designs (this is however not relevant to laboratory or pilot scale system piping sizes) as well as flame back arrestors and buoyancy seals are required. Prior to service, all piping must be purged with an inert gas in order to remove all traces of oxygen.

Before a hydrogen system is opened it must be depressurized, and whenever possible, be purged with an inert gas. The system should be designed so that it can be safely and easily purged with an inert gas. Escaping hydrogen gas can and will ignite quickly and easily! Hydrogen systems should always be operated with and maintained under a positive pressure to prevent the ingress of air. Regularly check all connections for leak tightness.

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7 COMPONENTS

Ensure that all components are approved for hydrogen service at the expected temperatures and pressures. Refer to the paragraph above on “Materials Selection” for additional information. Do not use cast iron or cast fittings or components. Also take into account any impurities or contaminants that may be present, e.g., when ammonia is expected to be present, do not use copper and copper /tin- /zinc-based alloys.

7.1 Vents

Simple vent stacks / chimneys ensure the safe release of hydrogen, a flare is not required. Venting to a safe location at a height that takes the prevailing wind direction, surrounding buildings and the expected dispersion cloud “*geometry*” into account is essential.

7.2 System design

Include the ability to purge piping and flexible hoses with an inert gas into a safe place! Suitable check valves as well as manual shut-off valves on purge lines – never rely on check valves only! If possible, avoid mixing different gas types. Minimize or, better still, eliminate interconnections to other gases or materials. Explosion protection document (or similar) and approval by an accredited body and / or local authorities may be required. Explosive zones (Ex, ATEX, etc.) will exist in areas where leaks can occur (e.g., a safety valve that is improperly vented) or will occur and cannot be prevented using technical measures (e.g., when hoses are disconnected).

7.3 Instrumentation and routine monitoring / Maintenance

This would depend on the complexity of the process / installation as well as what and how it must be controlled. The appropriate instrumentation and required monitoring as well as their maintenance should become clear when performing the risk assessment of the intended process.

7.4 Documentation

All processes must be documented and readily available at the point of use, e.g., start-up, operation, shut-down, maintenance, etc. The risk assessment(s) and any decision-making steps must also be documented and stored on site in a safe location.

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8 DOCUMENTATION

Below is a list of some of the documents that are available on-line, some of which have been used as a guideline for this document while others provide more background information about the future of the green hydrogen economy.

EIGA Doc 15/21 Gaseous hydrogen installations

EIGA Doc 23.07/18 Safety training leaflet 07 Hydrogen

EIGA Doc 100/20 Hydrogen cylinders and transport vessels

EIGA Doc 121/14 Hydrogen pipeline systems

EIGA Doc 211/17 Hydrogen vent systems for customer applications

IGC Document 134/12/E Potentially explosive atmospheres EU Directive 1999/92/EC

Home | Linde Hydrogen

Hydrogen-Insights-2021.pdf (hydrogencouncil.com)

Path-to-Hydrogen-Competitiveness_Full-Study-1.pdf (hydrogencouncil.com)

Shell hydrogen study

www.energietage.de

INFUB - 11th European Conference on Industrial Furnaces and Boilers, INFUB-11 Power-to-gas and the consequences: impact of higher hydrogen concentrations in natural gas on industrial combustion processes, Jörg Leicher et al. 18518N_H2_Subs_abschluss_korr.pdf (gwi-essen.de)

A hydrogen strategy for a climate-neutral Europe, 08.07.2020 hydrogen_strategy.pdf (europa.eu)

Hydrogen infrastructure – the pillar of energy transition Siemens Energy · Technical document · DIN A4 portrait – Template (siemens-energy.com)

Bibliography | Hydrogen Tools (h2tools.org)

HySafe - Safety of Hydrogen as an Energy Carrier

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