Hydrogen H_2

Safety, Risks and Hazards (Risk Assessment)

Prof. Thorsten Schneiders
TH Köln – Cologne University of Applied Sciences
GIZ cooperation training sessions on Green Hydrogen and its Derivatives
12th of April 2023

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Hydrogen H_2 Safety, Risks and Harzards

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Establish	**Safety**
Use	**Risk Assessment & Management**
To avoid and impede	**Risks and Harzards**

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Establish	**Safety**
Use	**Risk Assessment & Management**
To avoid and impede	~~**Risks and Harzards**~~

Hydrogen is as safe as any other energy carrier when you know ist special properties and consider them in design and operations of the technology

Thomas Jordan, Hysafe, KIT, FVEE conference 2021

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Overview

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- Is hydrogen dangerous?
- Hydrogen properties
- Hydrogen safety challenges
- Risk Assessment, risk management, and safety concepts
- Organizations and information sources
- Site visit: Shell 10 MW electrolyzer

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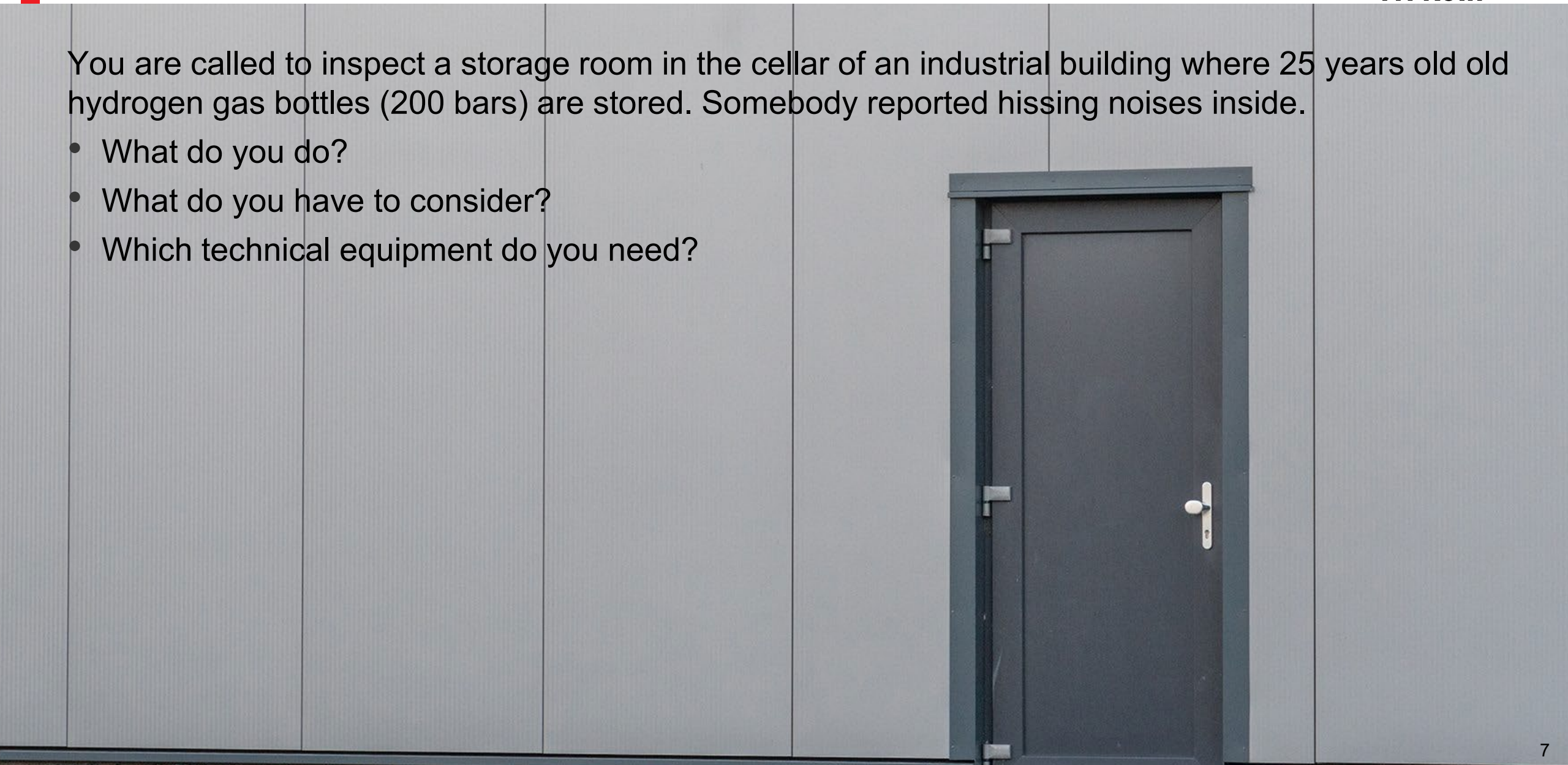
Is hydrogen dangerous?

On-site inspection of a gas storage room

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You are called to inspect a storage room in the cellar of an industrial building where 25 years old old hydrogen gas bottles (200 bars) are stored. Somebody reported hissing noises inside.

- What do you do?
- What do you have to consider?
- Which technical equipment do you need?



On-site inspection of a gas storage room

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- What do you have to consider?
- Which technical equipment do you need?



What is expecting you behind that door?

Can you sense hydrogen?

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A)	Can you see hydrogen?	Yes	No
B)	Can you smell hydrogen?	Yes	No
C)	Can you taste hydrogen?	Yes	No
D)	Can you hear hydrogen?	Yes	No

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Is hydrogen dangerous?

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A)	Is hydrogen toxic?	Yes	No
B)	Is hydrogen inflammable?	Yes	No
C)	Is Hydrogen explosive?	Yes	No
D)	Can hydrogen escape from old gas bottles?	Yes	No

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Unfortunately, humans do not have good gas sensing

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Can you see hydrogen?	No
Can you smell hydrogen?	No
Can you taste hydrogen?	No
Can you hear hydrogen?	No

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Hydrogen has some properties that may make it dangerous when not handled properly

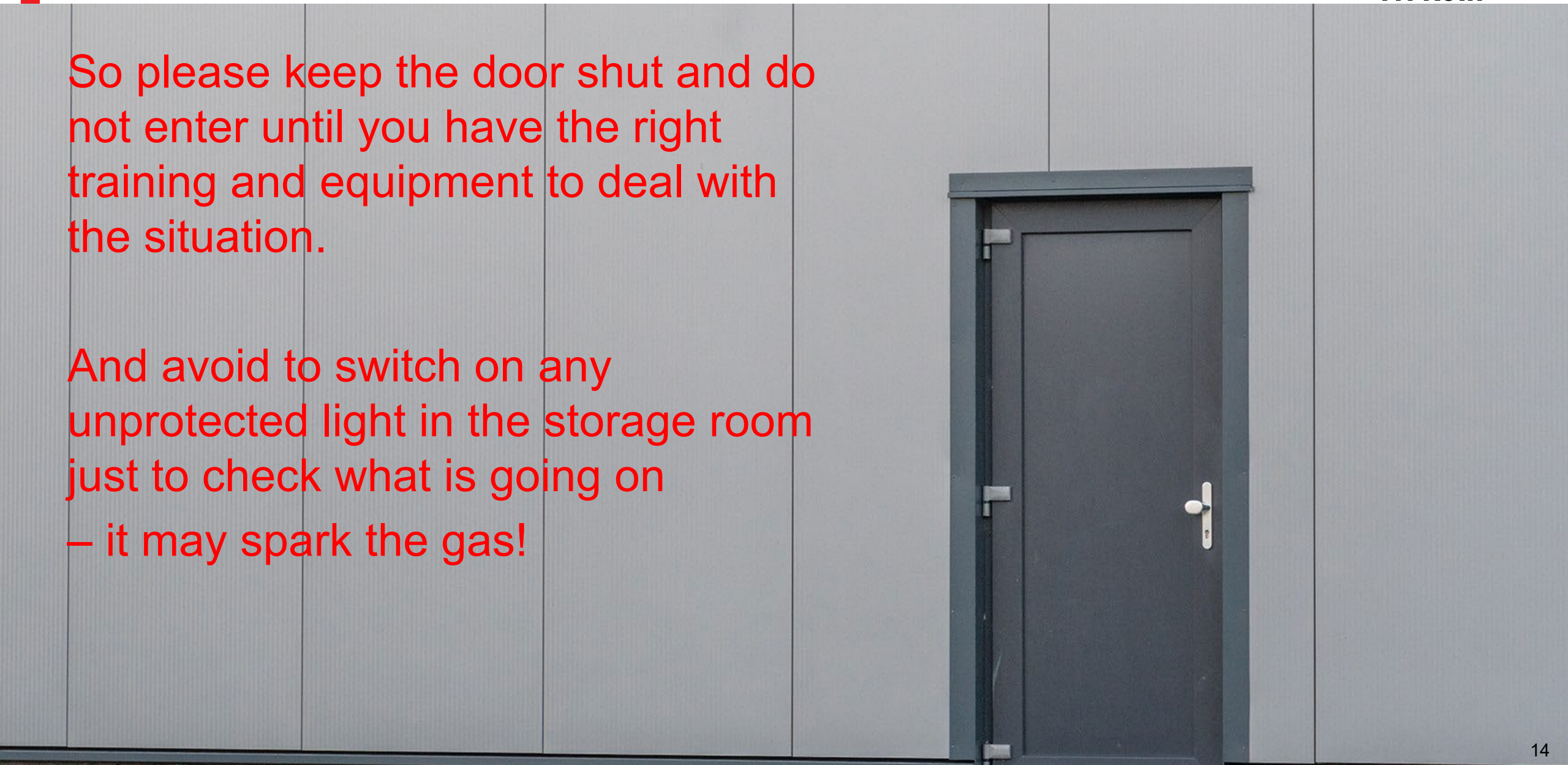
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Is hydrogen toxic?		No
Is hydrogen inflammable?	Yes	
Is Hydrogen explosive?	Yes	
Is hydrogen able to escape from old gas bottles?	Yes	..but hissing would mean major leakage

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On-site inspection of gas storage room

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So please keep the door shut and do not enter until you have the right training and equipment to deal with the situation.

And avoid to switch on any unprotected light in the storage room just to check what is going on – it may spark the gas!

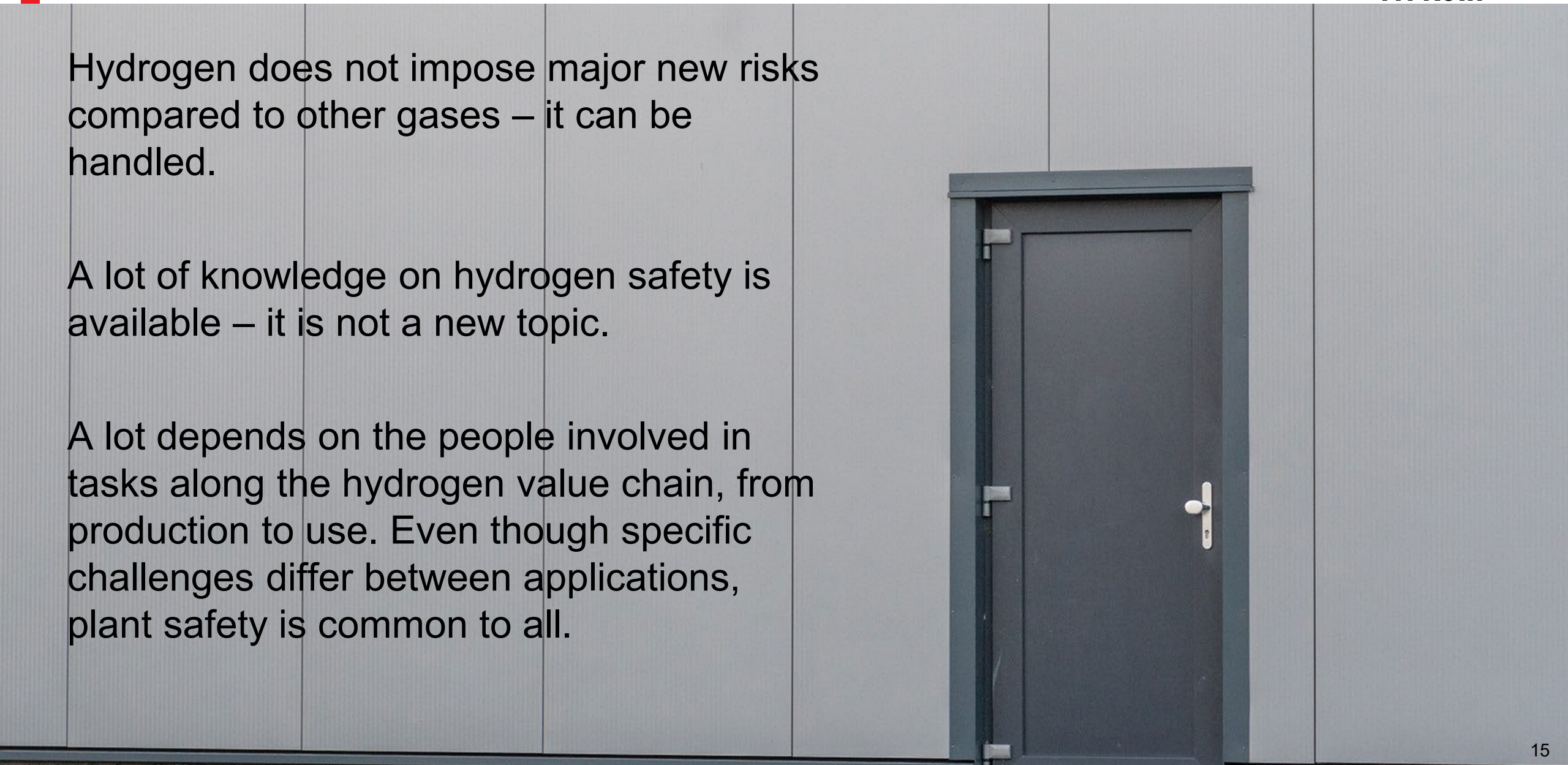
Hydrogen safety is possible and accessible

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Hydrogen does not impose major new risks compared to other gases – it can be handled.

A lot of knowledge on hydrogen safety is available – it is not a new topic.

A lot depends on the people involved in tasks along the hydrogen value chain, from production to use. Even though specific challenges differ between applications, plant safety is common to all.



Any questions or comments?





Hydrogen properties

Hydrogen properties in comparison

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	Hydrogen Gas	Natural Gas	Gasoline
Color	No	No	Yes
Toxicity	None	Some	High
Odor	Odorless	Yes (mercaptan)	Yes (benzene)
Buoyancy *Relative to **Air***	14X Lighter	2X Lighter	3.75X Heavier
Energy by Weight	2.8X > Gasoline	~1.2X > Gasoline	43 MJ/kg
Energy by Volume	4X < Gasoline	1.5X < Gasoline	120 MJ/Gallon

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Source: Hydrogen Safety Panel, 2018]

Gas properties in comparison

Hydrogen H_2 and natural gas CH_4 have different properties relevant for applications

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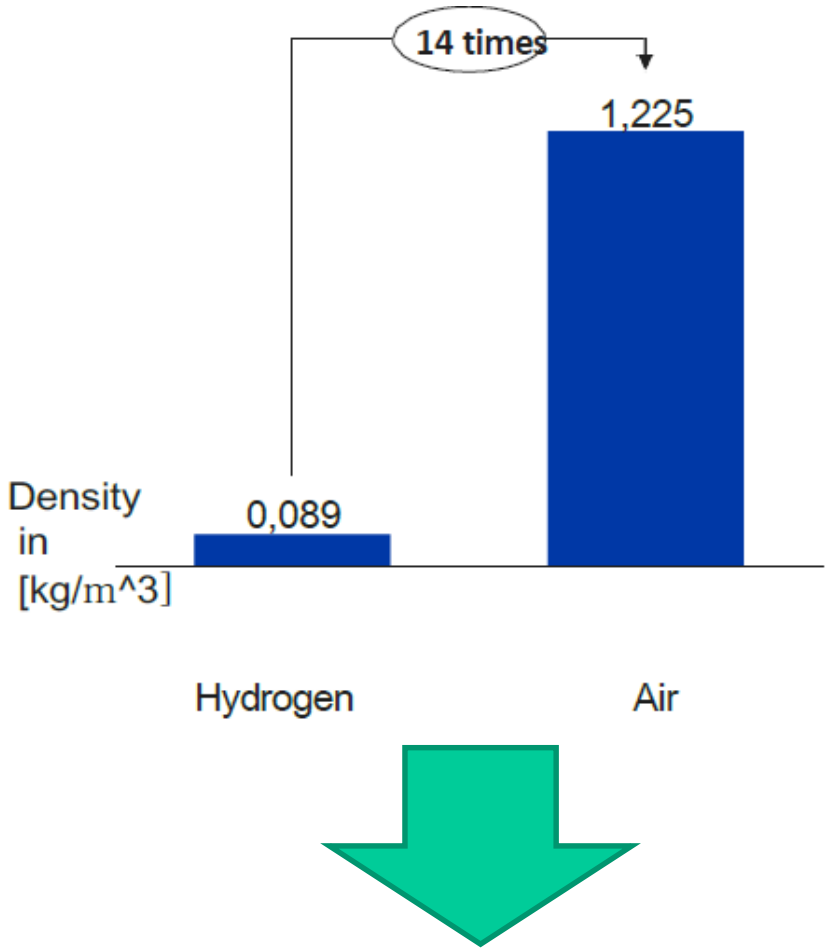
	Hydrogen H_2	Methane CH_4
Density	0.0899 kg/Nm³	0.7175 kg/Nm³
Volumetric energy density	3.0 kWh/Nm³	9.97 kWh/Nm³
Gravimetric energy density	33.3 kWh/kg	13.8 kWh/kg
Calorific value	120.0 kJ/kg	50 kJ/kg
Calorific value	143 MJ/kg 11.7 MJ/m³	55.5 MJ/kg 39.9 MJ/Nm³
Lower Wobbe index	Wi = 40.90 MJ/m³	Wi = 48.17 MJ/m³
Upper Wobbe index	Ws = 48.34 MJ/m³	Ws = 53.45 MJ/m³
Relative density in relation to air	0.0695	0,56

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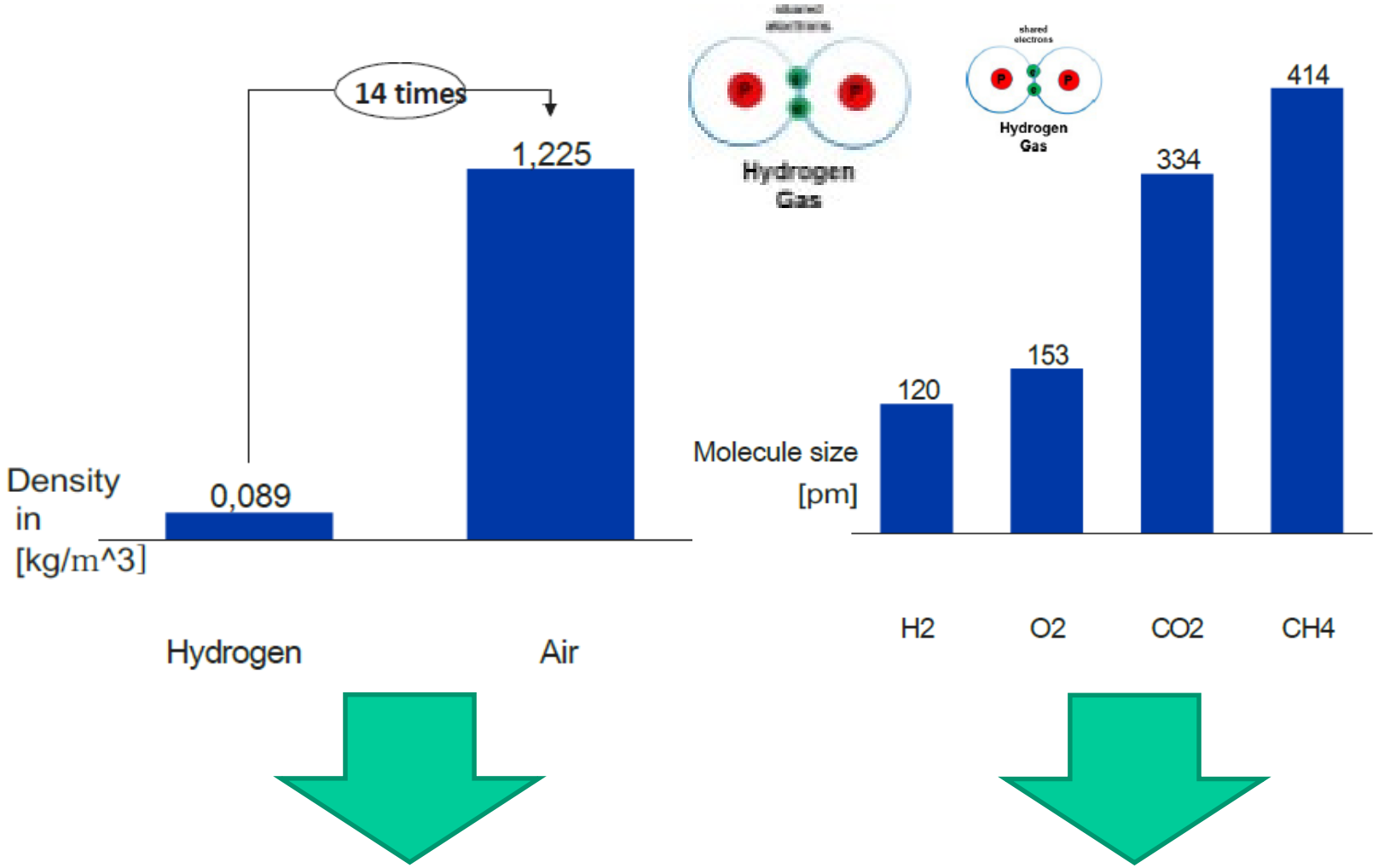
Hydrogen properties



Hydrogen gas will
always float up in the air

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Hydrogen properties



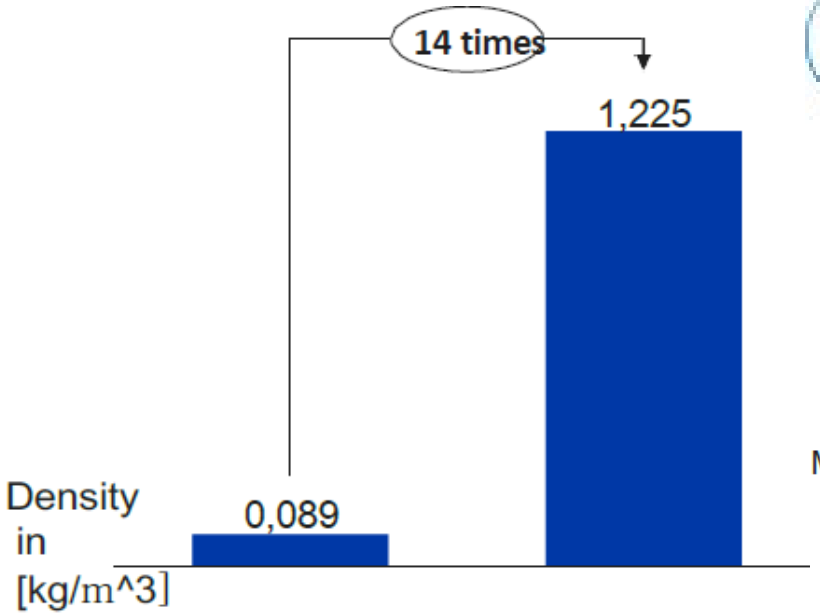
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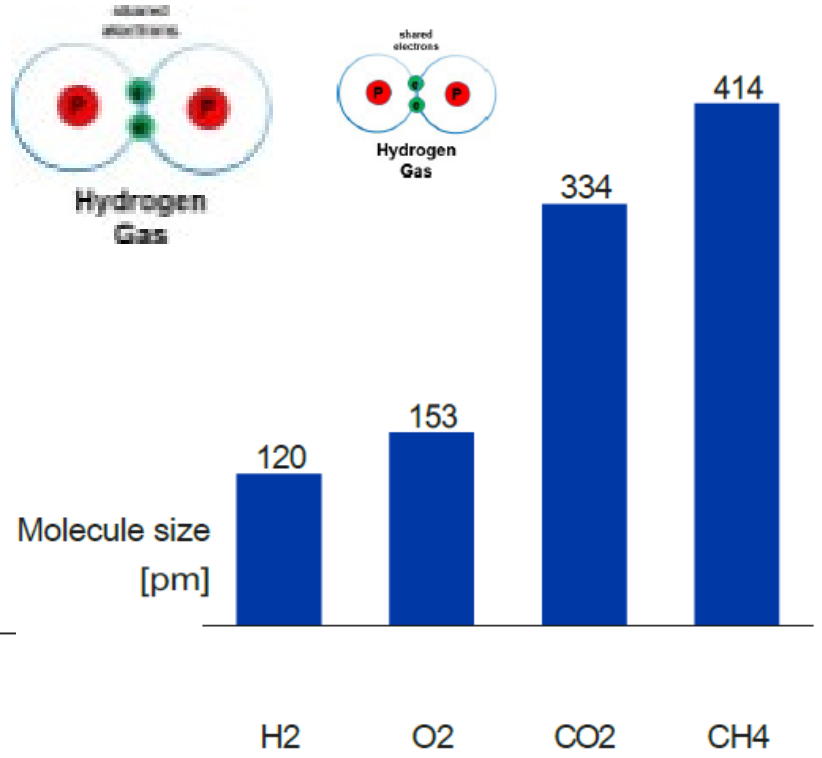
Hydrogen has a very small molecule size that allows it to permeate materials and easily react with metals

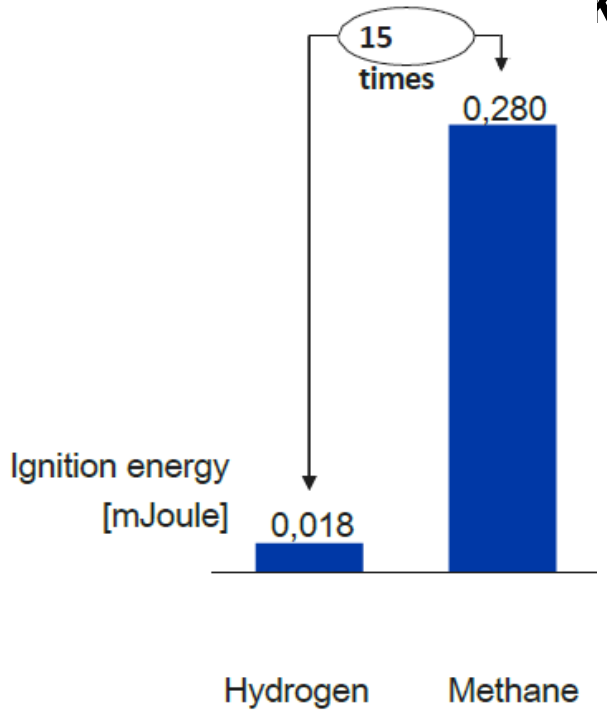
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Hydrogen properties

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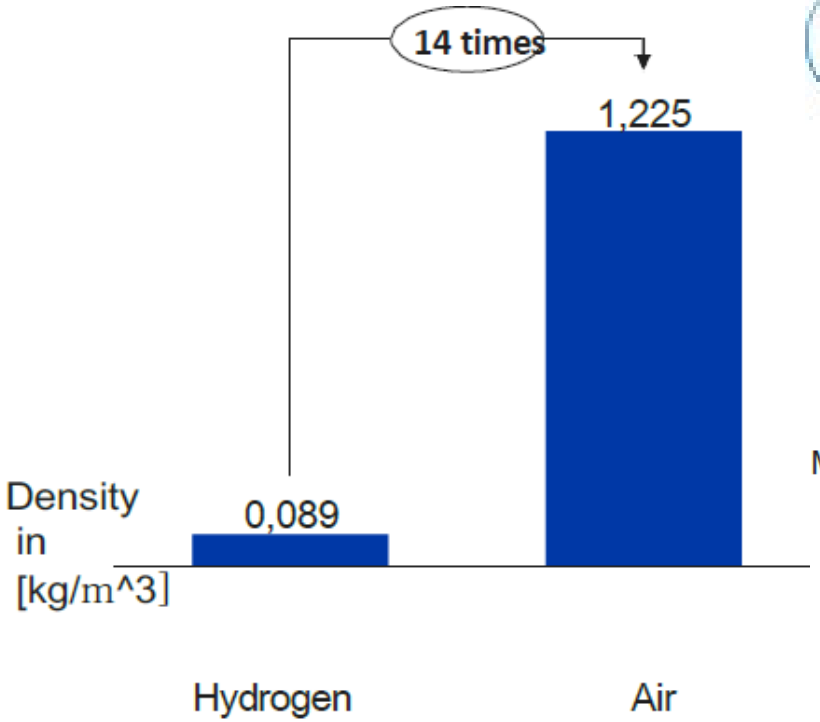
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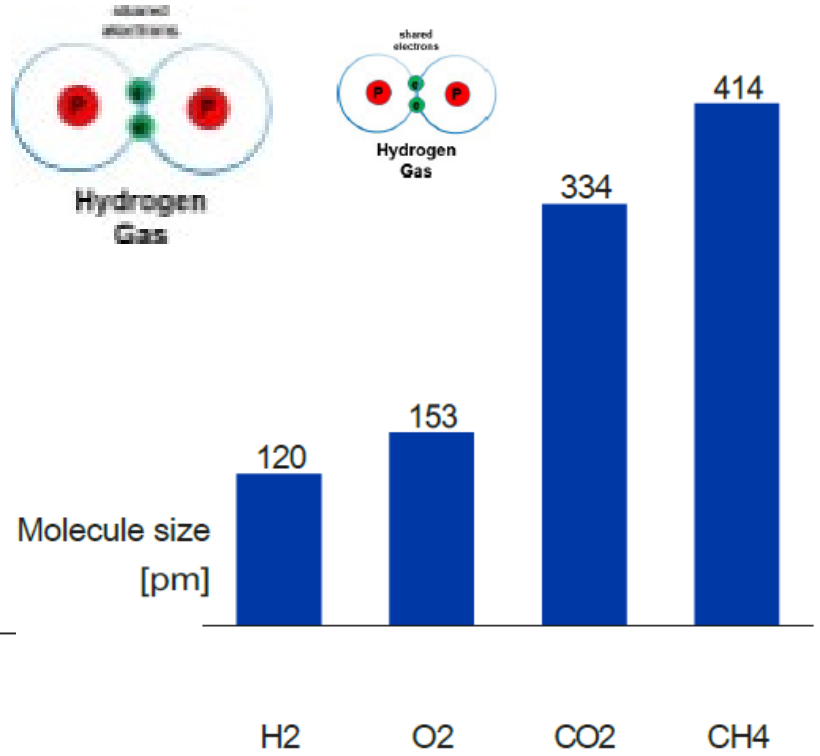
Hydrogen gas requires a much smaller iginition energy than methane, a tiny spark may be enough

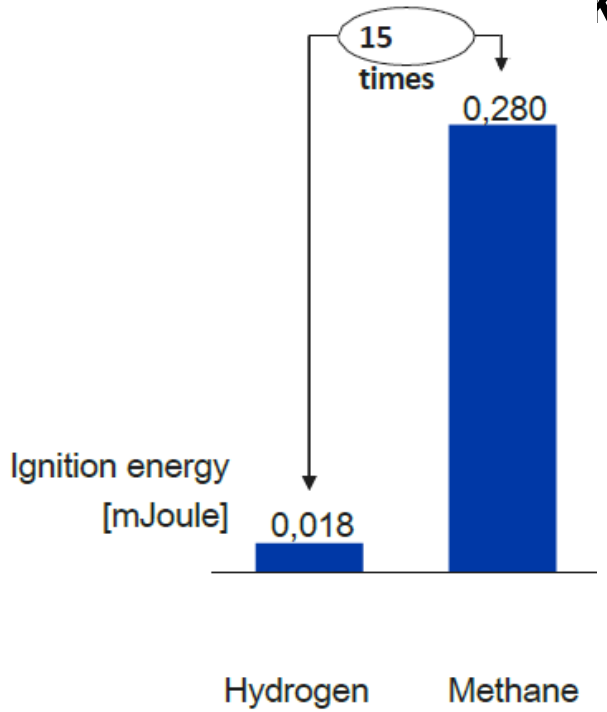
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Hydrogen properties

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- Hydrogen has the highest gravimetric energy density of all energy carriers, but compared to natural gas, however, only about one third of the volumetric energy density
- Hydrogen-air mixtures can be produced with very low energy expenditure can be ignited with only 10% required for the ignition of a gasoline-air mixture.
- Wide flammability limit hydrogen: 4% - 75% [volume% in air]
- Flame speed of hydrogen is 7 times higher than methane.

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Pros and cons of hydrogen as a fuel for combustion

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Advantages of hydrogen include:

- like methane it is not poisonous, (just asphyxiating and explosive);
- it has quite a high spontaneous ignition temperature (SIT) of 650^{o}C – it needs a spark to ignite
- it has very wide flammability limits (3–70% H_2 in air mixture) – it is easier to maintain a flame
- it burns to water vapour, thus eliminating CO_2 emissions
- it burns with a much higher flame speed (300 cm/s) than methane (30 cm/s), thus stabilizing the flame.

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Disadvantages include:

- higher flame speed increases flame temperature locally, which can generate high levels of NOx
- the wide flammability limits require consideration in the safety assessments;
- hydrogen has a different Wobbe Index from methane, to be taken into account in design and
- hydrogen has a different combustion air requirement index, CARI (a measurement of the combustion air required for a gas), compared with methane.

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Hydrogen burners for high-temperature

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- Higher flame temperatures increase thermal NOx-production from ambient air N2
  - Compenstation required (flue gas circulation
- Different compostion of flue gases (e.g. vapor, NOx)
  - High condensate content
  - High flame temperatures increase Nox concentrations (thermal NOx)
- Changed heat transfer and heat release
- Flameback/flashback due to higher flame speeds

- In the mid-term, hydrogen availability will be limited. Therefore new burner systems need to have a high flexibilty for diffenrent fuels and mixtuers of hydrogen and natural gas

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Key Take-Aways: H_2 properties

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- Hydrogen has special properties to be considered
- Low density lets it float up in the air
- Samall molecules may pass through materials and sealings
- Low iginition energy and wide limits of flammbility may lead to risky hydrogen –air mixtures that can easily be ignited.

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Any questions or comments?





Hydrogen safety challenges

H2 has no odour, no colour, may explode or burn unseen

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Odourless and colourless
Hydrogen has no smell and no colour, so is undetectable for humans. With methane, this issue is mitigated by adding odorants, and research is in progress to determine whether this will also be possible with hydrogen.
Gas and leak detectors are essential.

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[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

Hydrogen is odourless, colourless and even tasteless

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- People cannot perceive hydrogen, as it is colorless and odourless
  - It has not yet been sufficiently investigated whether hydrogen can be added some odorants (like natural gas with sulphuric smell) as this would spoil the hydrogen purity
- Gas and leakage detection has to be used
- Gas leakages are mostly soundless, only major leakages can be detected by the human ear

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EXPLOSION
Unlike actual explosives, pure hydrogen cannot explode. The risk comes when it hits the air. For hydrogen to cause an explosion, oxygen needs to be present, and its volumetric concentration needs to be between 4 % and 77 % by volume in air, the Lower and Upper Explosion Levels (LEL and UEL). But if hydrogen is allowed to escape, even a static spark from clothing would be enough to set off an explosion.
Explosion protection is important

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[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

Hydrogen may lead to explosions

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- Hydrogen may be explosive
  - low ignition energy
  - Wide flammability limit: 4% - 75% [volume% in air] and explosion limit
  - Addition of lubricants may decrease ignition temperature
- Equipment in explosion-protected (EX)-areas needs to be certified ,like Ex-protected electronics (e.g. lights, switches, tools)
- Ex-areas are defined depending on the risk of explosive mixtures
- Forced ventilations (e.g. fans, automatic window openers) can reduce explosioin risk.
- A higher inert gas concentration (nitrogen) must be achieved when repair work is carried out on plant components

[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

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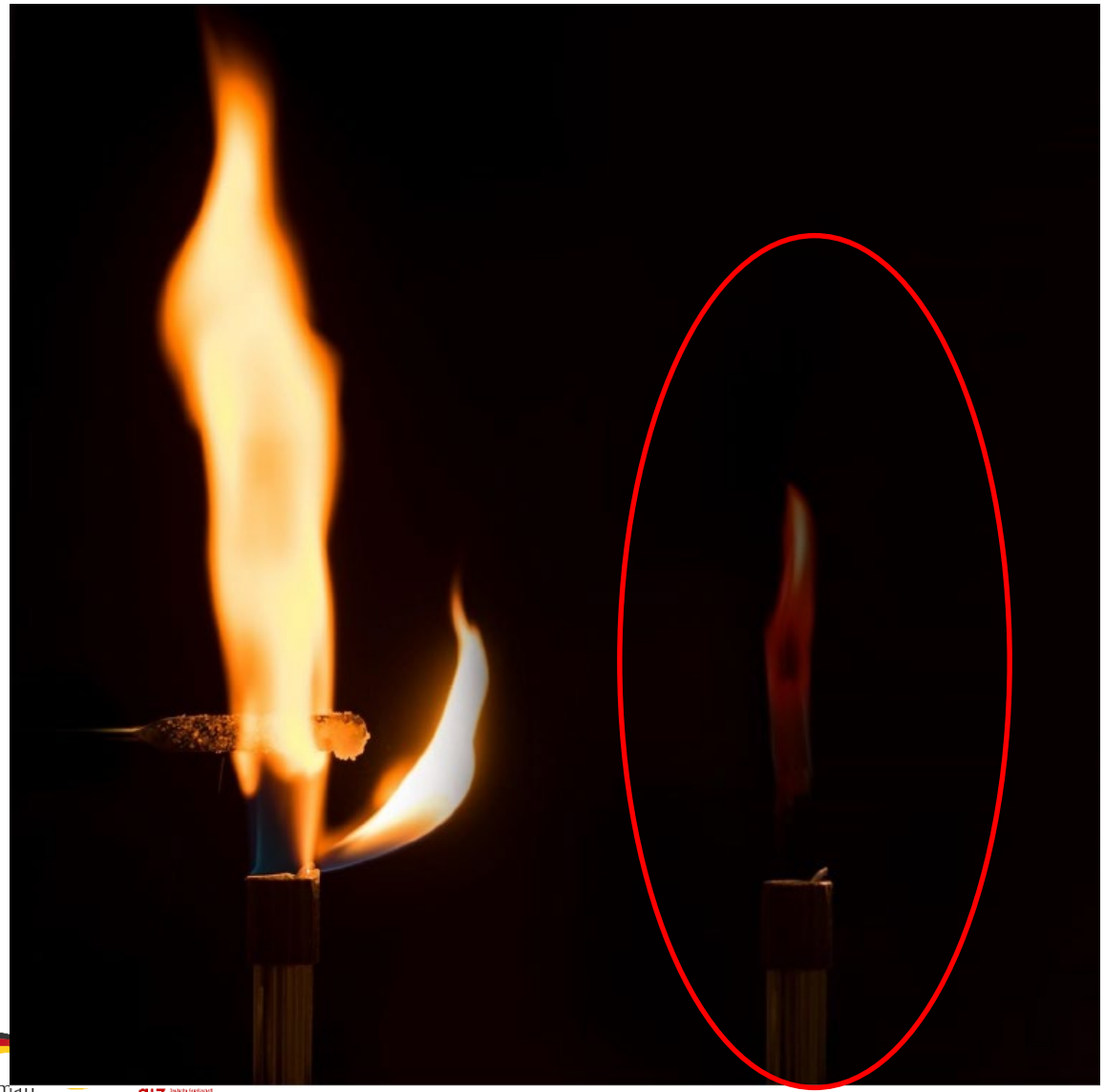


INVISIBLE FLAME
Hydrogen burns with a very pale flame that is invisible in daylight. Because it emits little of the infrared radiation that humans perceive as heat, it cannot be sensed as heat (and is also less likely to ignite objects in the vicinity). A hydrogen flame does however emit substantial ultraviolet radiation.
Special UV detectors are therefore required to alert to the presence of hydrogen flames.

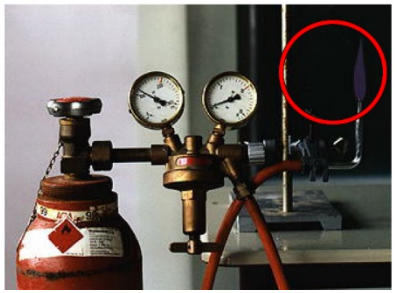
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[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

Pure hydrogen has an “invisible“ flame

No traditional look of a fire when hydrogen is burning



- A pure hydrogen flame is barely visible in daylight, at night the flame is visible
  - Other substances burining with hydrogen may produce visible flame
- A pure hydrogen flame hardly emits any heat (infrared radiation (IR)) but considerable ultraviolet radiation
  - Objects in the vicinity hardly catch fire
  - No sens of heat, but rather sunburn-like feeling
- Usage of UV-flame detection required instead of the usual IR-detectors



[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

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Leaks must be detected, permeation has to be avoided

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LEAKS

Owing to its small molecules and low viscosity, hydrogen can leak from pipelines and other structures more easily than denser gases. In fact, when it leaks from a pipe at sufficiently high pressure, hydrogen can even self-ignite.

As well as pipelines engineered to hydrogen-ready specifications, regular inspection is imperative to detect leak points at joints and along pipelines. Fixed leak detectors add another layer of safety.

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[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

Leakage

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- Due to ist low molecule size and low viscosity, hydrogen can qucikly escape from pressurized gas lines and containers
- In addition to the correct design and construction, maintence and regular plant inspections are necessary to ensure safety
- Stationary gas measurement technology and early warning systems support safe operations

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[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

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PERMEATION

Hydrogen can easily permeate materials and in some cases embrittle them.

For this reason, stainless steel and composite materials are typically used for storage tanks.

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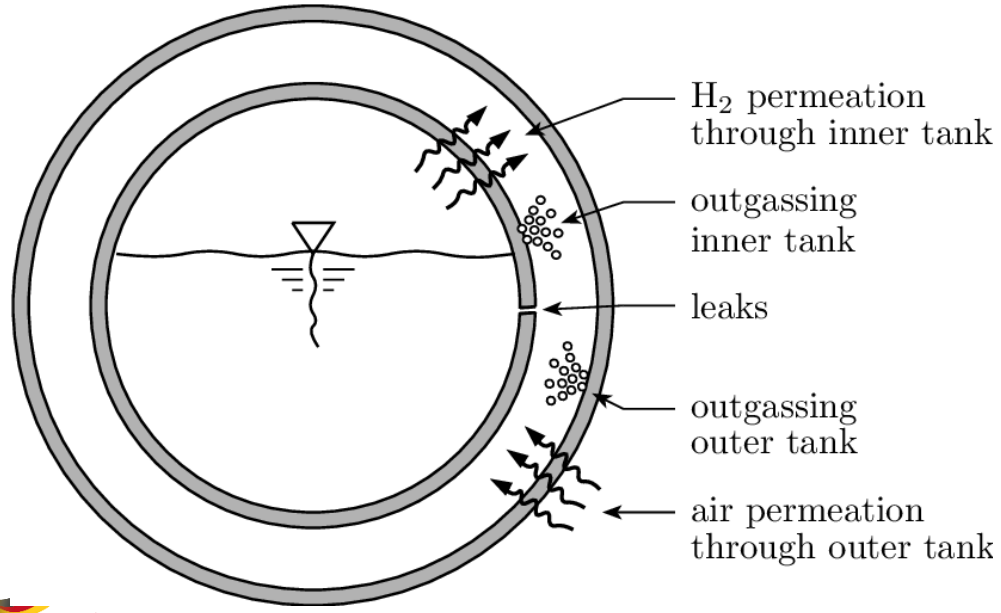
[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

Permeation

The small hydrogen moelcules can easily travel through wieder metal structures

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Permeationskoeffizienten von verschiedenen Polymeren					
Gas / Rohrwerkstoff	O_2 Sauerstoff	N_2 Stickstoff	H_2 Wasserstoff	CO_2 Kohlendioxid	H_2O Wasserdampf
PE	8 - 19	2-6	25-55	32-75	0,5 – 1,5
PP	5	5	65	14	1,1
PVC	0.4	0,04	10	0,9	6,5
PVDF	0.7	0,2	3	< 1,0	5.2
Wasserdampfdurchlässigkeit in g/ (m^2 * d)					
Gasdurchlässigkeit in cm^3 / (m^2 * d * bar)					



- Hydrogen is the smallest of all molecules and can easily pass through materials
  - To penetrate these
  - Lead to embrittlement
  - However, hydrogen has been safely stored, transported and used for centuries
- Proper selection, handling and maintenace of materials is critical
- However,…
  - …very old pressuried steel gas bottles were found whcih still contained
  - …the permeation of hydrogen form the tank of a fuel cell car in a garage would require more than 200 days to reach a critical mixture in the air-tight garage

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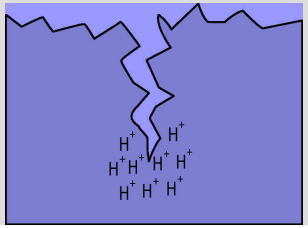
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EMBRITTLEMENT

Hydrogen embrittlement occurs due to the diffusion of hydrogen in the microstructure of metal piping or infrastructures. In combination with mechanical stress, the hydrogen creates hairline cracks that grow progressively larger over time

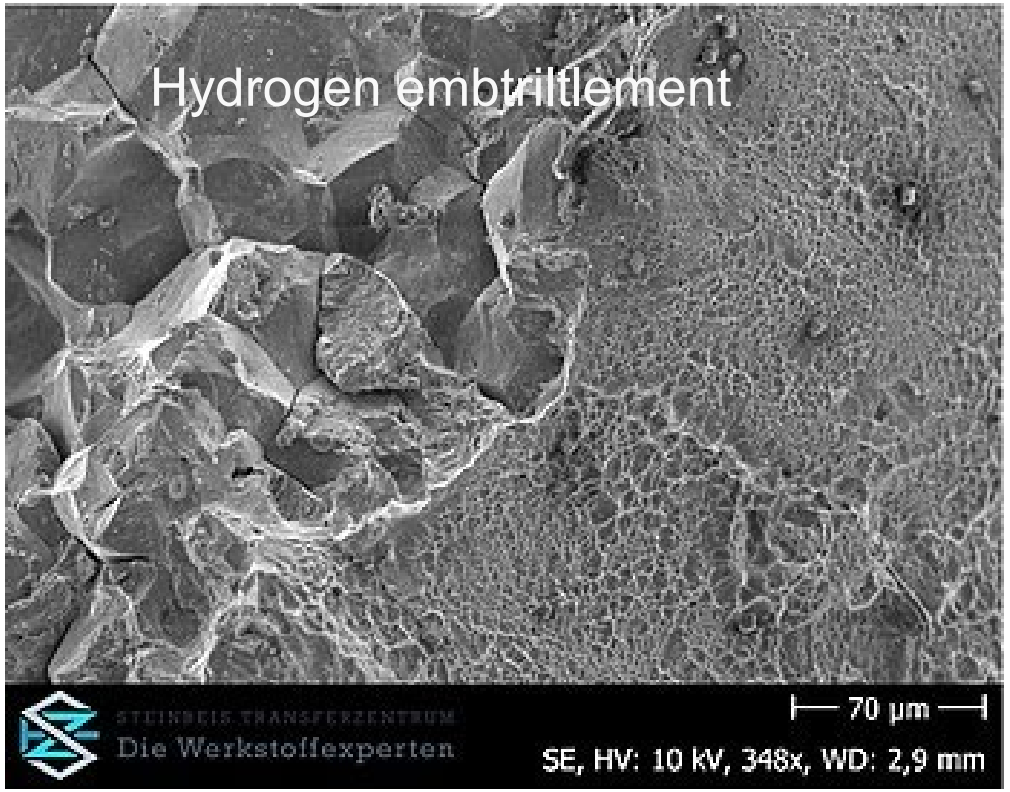
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Embrittlement may corrode steel gas pipes

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Brittleness caused by hydrogen leads to cracks in tubes



Crack in steel tube due to embrittlement



- Hydrogen embrittlement is the brittleness of material due to the influence of hydrogen
  - It occurs due to the diffusion and dissolution of hydrogen in the microstructure of metal piping or infrastructures
- In combination with mechanical stress, the hydrogen creates hairline cracks that grow progressively larger over time
- Increasing the Ni percentage (up to 10%) or Ti and decreasing the C percentage in the material reduces the chance of hydrogen embrittlement
  - These atoms occupy critical locations in the crystal structure of austenitic stainless steel stabilizing the microstructure

[Source: demaco-cryogenics]

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Gas pockets require detection and ventilation, CO alarms have to be adjusted

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GAS POCKETS

Like ammonia and methane, hydrogen is less dense than air and forms gas pockets below indoor ceilings when leaking.The presence of hydrogen will not be perceived at ground level, even when dangerous amounts are accumulating beneath the ceiling.

When hydrogen and methane are mixed, hydrogen can form gas pockets above methane.

Hydrogen detectors are therefore typically placed at the top, with methane detectors below that level.

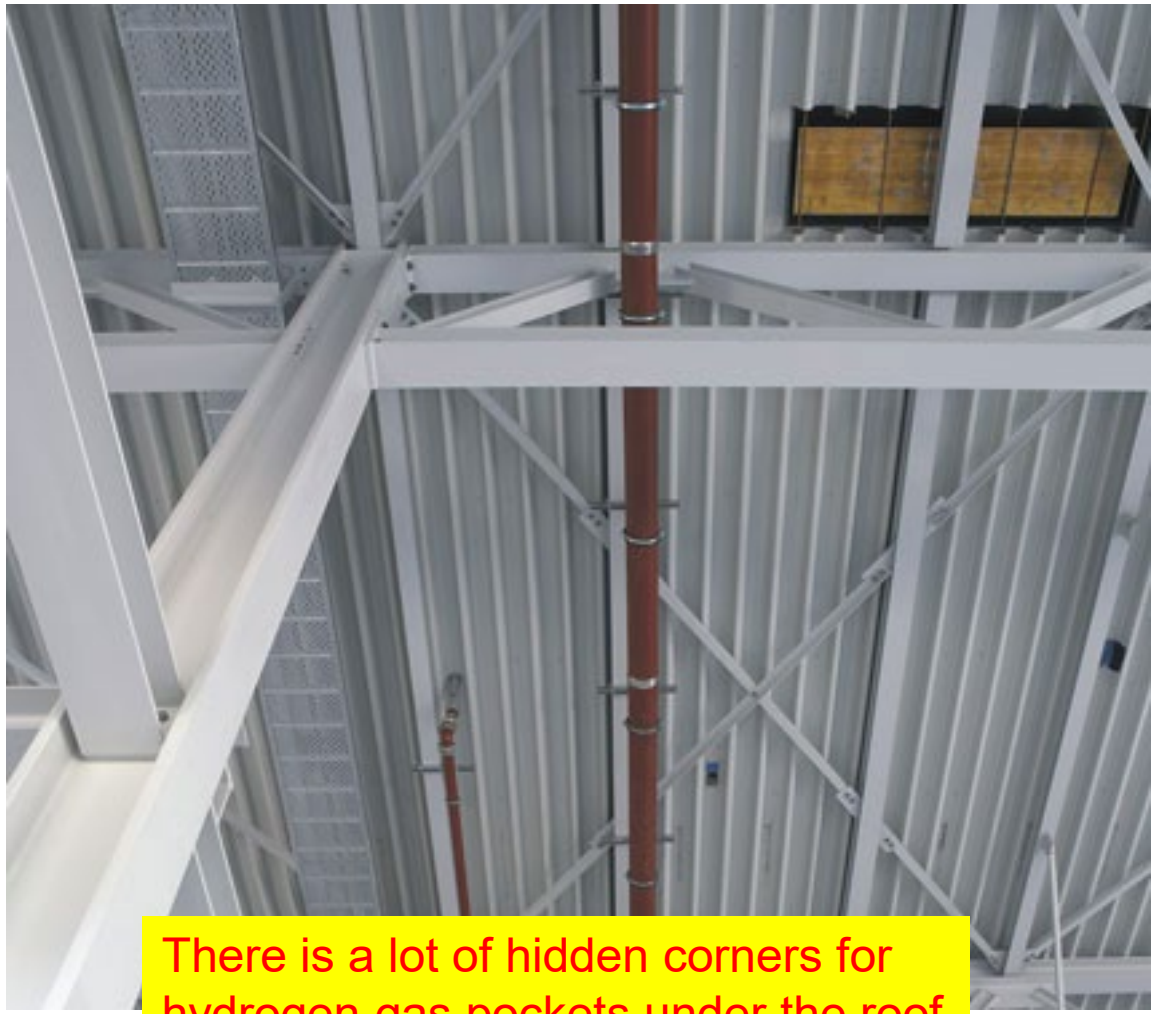
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[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

Gas pockets

Hydrogen may escape from tanks and build up gas pockets under the roof

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There is a lot of hidden corners for hydrogen gas pockets under the roof

- Ammonia, methane and hydrogen have a lower density than air and rise up
- In event of leaks, these gases form gas clouds below the ceiling
  - Therefore, gas measurement technology is usually installed at the top
- Pure hydrogen or methane-hydrogene mixtures form clouds above methane
  - Detectors for hydrogen should be installed at the highes spots, methane detection sould be installed below
  - Alternatively, CatEx sensors should be useed

https://www.youtube.com/watch?v=d49TzVF1gmY

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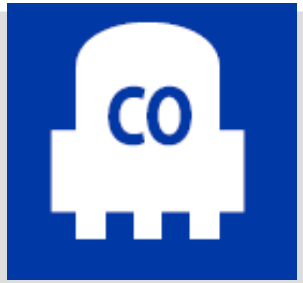
Gas pockets require detection and ventilation, CO alarms have to be adjusted

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GAS POCKETS

Like ammonia and methane, hydrogen is less dense than air and forms gas pockets below indoor ceilings when leaking.The presence of hydrogen will not be perceived at ground level, even when dangerous amounts are accumulating beneath the ceiling.
When hydrogen and methane are mixed, hydrogen can form gas pockets above methane.
Hydrogen detectors are therefore typically placed at the top, with methane detectors below that level.



CO ALARMS

Carbon monoxide (CO) sensors are cross-sensitive to hydrogen.
If used near possible hydrogen exposure, **CO sensors** should be compensated for hydrogen so that cross-sensitivity and false alarms are reduced to a minimum.

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[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

Key Take-Aways: H_2 safety issues

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Hydrogen safety issues include:

- Odourless and tasteless
- Risk of explosions
- Invisible flame
- Leaks
- Permeation
- Embrittlement
- Gas pockets
- CO alarms

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Key Take-Aways: H_2 safety issues

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Hydrogen safety issues include:

- Odourless and tasteless
- Risk of explosions
- Invisible flame
- Leaks
- Permeation
- Embrittlement
- Gas pockets
- CO alarms

Measures
Use detectors
Use detectors
Use detectors
Use detectors
Check materials
Change materials
Use detectors
Adjust detectors

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Any questions or comments?



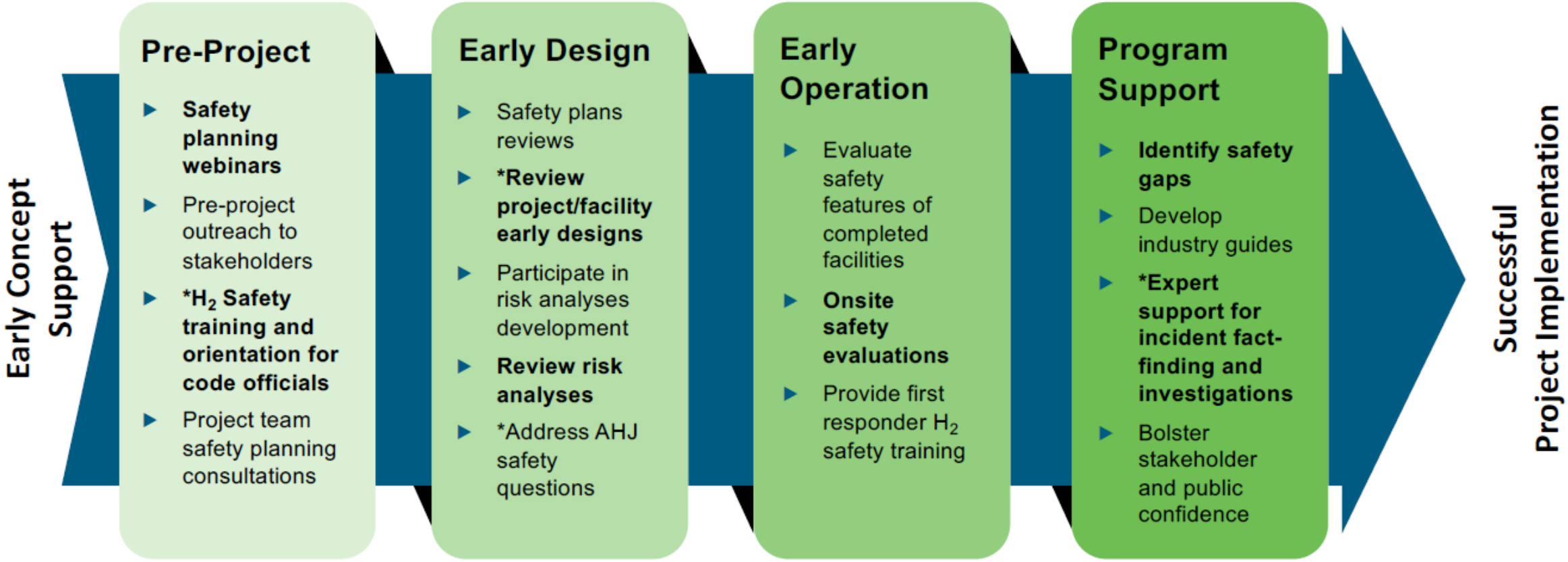
Risk Assessment, risk management, and safety concepts



Measures for safe implementation of hydrogen technologies

Every project step requires simultaneous development of safety aspects

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* Support for AHJ and code officials can bridge the gap for inexperienced staff, facilitate faster approvals, support a greater confidence in project safety and provide more technically justified safety features or alternate means and methods

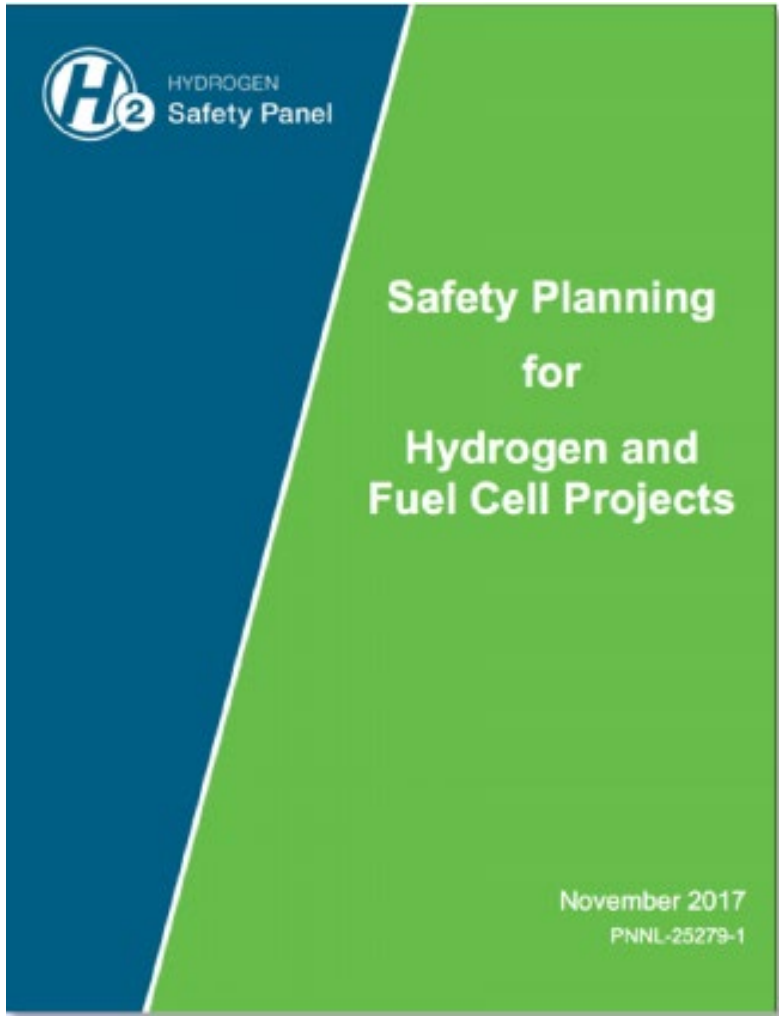
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[Source: Hydrogen Safety Panel,, 2018]

Guidance for safety planning of hydrogen projects

Safety planning should be integral part of design and operation of an H_2 system

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URL: https://h2tools.org/hsp/reviews

- Safety planning guidelines are available in the internet – even for free – others require registration or membership at the respective organization
- The HSP guideline “Safety Planning for Hydrogen and Fel Cell projects” was originally developed by the HSP for the U.S. Department of Energy in 2005
  - It provides information on safety practices for hydrogen and fuel cell projects
- The project safety planning process is meant to help identify risks and avoid potential hydrogen and related incidents.
- This document can aid in generating a good safety plan that will serve as a guide for the safe conduct of all work related to the development and operation of hydrogen and fuel cell equipment.

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[Source: Hydrogen Safety Panel,, 2018]

Analyzing the hazards

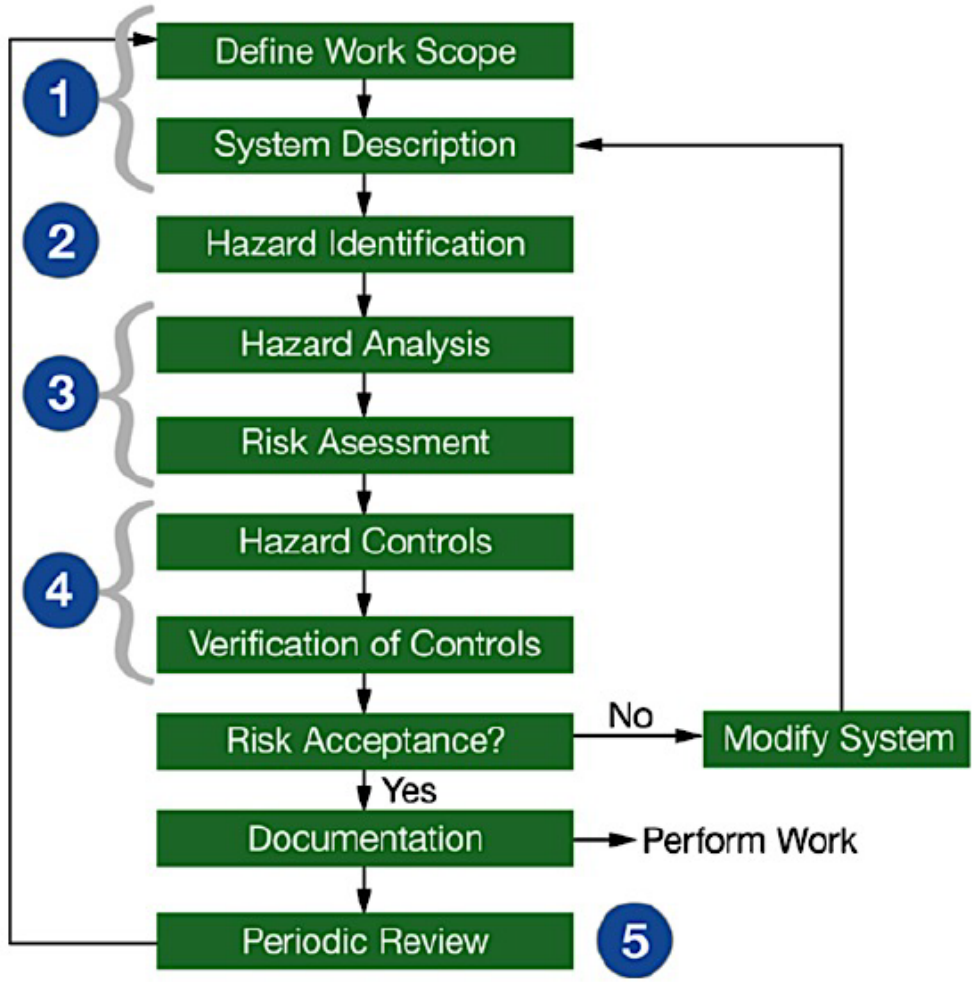
Hazard analysis can reveal facility design problems and unsafe hydrogen operations

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Hazard Analysis and Risk Assessment Steps

1. Define the scope of work
2. Identify hazards
3. Evaluate the impact of the hazards on
   a) the environment and public
   b) the facility and institution
   c) the equipment and personnel
4. Assess the likelihood and severity of each hazard
5. Resolve hazards
6. Follow up actively with periodic review of work scope and hazards

See https://h2tools.org/bestpractices/safety_planning/hazard_and_risk, and https://h2tools.org/sites/default/files/h2_snapshot_v2i2.pdf



[Source: Hydrogen Safety Panel,, 2018]

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Risk management

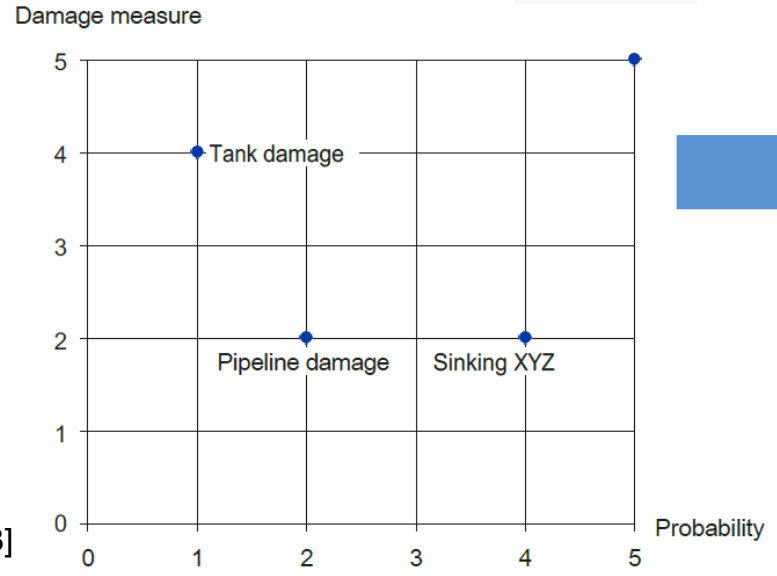
Risk evaluation is a standardized procedure

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Probability of the Entrance		Severity of the damage				
		Negligible	Low	Ernst	Fatal	Disaster
		1	2	3	4	5
Very likely	5	5	10	15	20	25
Probably	4	4	8	12	16	20
Possible	3	3	6	9	12	15
unlikely	2	2	4	6	8	10
impossible	1	1	2	3	4	5

Risk matrix

High
Medi
Low



	Scenario	Measure
1	Tank damage XYZ	Measure XYZ
2	Pipeline damage in XYZ	Measure ABC
3	DEF drop	Measure OPQ

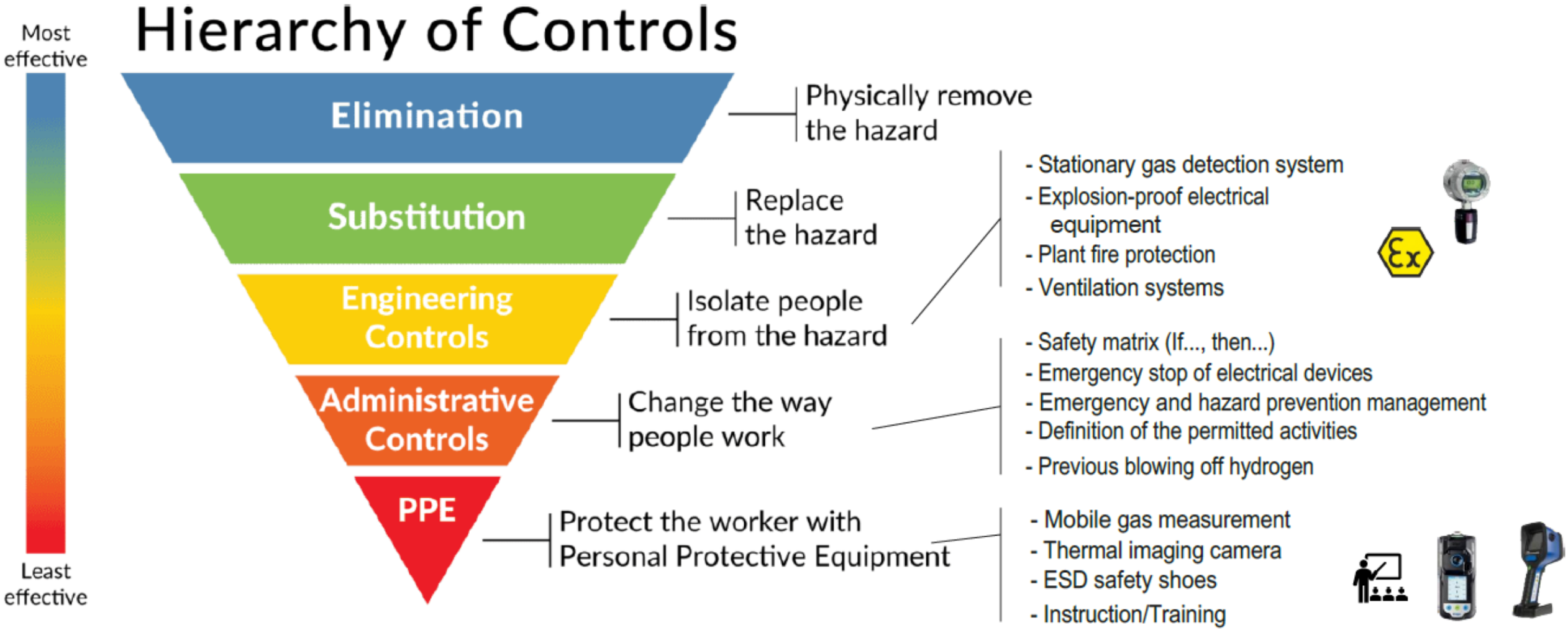
[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

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Risk minimization

Hierarchy of controls for selection of protective measures

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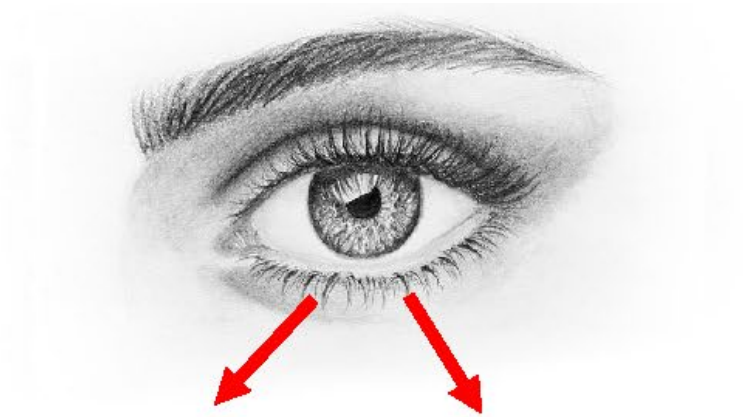
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[Source: Hydrogen: How to meet the safety challenges, Draeger 2023]

Gas detection

Sensors substitute human senses

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Open Path Gas Detector



Flame detectors



Gas Camera









Toxic Gas Detector



Flammable IR Gas Detector



Flammable Catalytic Gas Detector





UGLD

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[Source: Dräger: - Hydrogen: how to meet the safety challenge, 2018]

Detection technology for hydrogen (1)

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Dräger PointGard 2200
Flammable Gas Detector



Dräger Flame 2700
(Multi-IR) Flame Detector

CATALYTIC BEAD SENSOR (CATEX)

- CatEx sensors detect flammable gases and vapours such as hydrogen below their lower explosive limit (100% LEL). They have good long-term stability and a fast response time. They are mainly used for continuous area monitoring of the ambient air.

FLAME DETECTORS

- Hydrogen flames radiate energy mainly in the UV band, so UV flame detectors excel at fast detection of hydrogen flames. As they are susceptible to false alarms from other UV sources, they are best suited to locations that do not contain other potential UV sources i.e., indoor applications. For hydrogen flame detection UV sensors are often combined with an IR sensor in one device. This offers better (but not full) false alarm immunity capability than just UV detection alone. Multi Infrared (MIR) is another option for hydrogen flame detection. Although standard IR devices cannot detect hydrogen, MIR devices use a combination of IR sensor filters and software analysis to detect flames and reduce false alarms. Specific MIR devices have been explicitly designed to detect the low-level radiation from hydrogen flames using unique sets of IR filters.

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[Source: Dräger: - Hydrogen: how to meet the safety challenge, 2018]

Detection technology for hydrogen (1)

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Dräger Polytron(R) 8900 UGLD
Ultrasonic Leak Detector

ULTRASONIC GAS LEAK DETECTION

- Ultrasonic detectors “listen” to high-pressure leaks, and can detect even small leaks very fast. They serve as early warning area monitors: they respond earlier than conventional gas detectors because they register the sound of leaking gas instead of measuring the concentration of accumulated gas clouds.



Dräger X-am® 8000
Multi Gas Detector

ELECTROCHEMICAL SENSOR (EC)

- EC sensors are a good choice when selective measurements of hydrogen on ppm concentration level are required. They offer advantages such as fast response, high accuracy, great stability and a long service life. This technology is useful for point leak detection and personal air monitoring.

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[Source: Dräger: - Hydrogen: how to meet the safety challenge, 2018]

Key Take-Aways: H_2 safety concept

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Suitable concepts for hydrogen safety are available, even for free

- Think of safety at any process step
- Analyze hazards
- Use know-how from previous projects and the guideline s derived from them
- Apply risk management
- Use appropriate tools like detectors to mitigate risks

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Any questions or comments?





Organizations and information sources

Hysafe

International Association for Hydrogen Safety



Useful Wiki on hydrogen:
http://www.hysafe.net/wiki/BRHS/BRHS

International Assoiation for Hydrogen Safety: hysafe.info
EC Network for Hydrogen Safety: hysafe.net

- The association is the **focal point** for all hydrogen safety related issues. It has been founded as an international **nonprofit** institution by the European Commission co-funded network of excellence.
- The association **facilitates** the networking for the further development and dissemination of **knowledge** and for the **coordination of research** activities in the field of hydrogen safety. So it supports cost effective hydrogen safety research, enables innovative technologies and engineering, and provides education and training on a professional level.
- Based on its leading position in hydrogen safety research and development, HySafe determines the **state-of-the-art** in hydrogen safety and continuously develops further the associated strategic research agenda.

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Center for Hydrogen Safety

www.aiche.org/chs

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A timely partnership to enable broader impact and sustainability of significant safety resources

Pacific Northwest NATIONAL LABORATORY

AIChE

A not-for-profit membership organization within AIChE

CENTER FOR Hydrogen SAFETY

Promotes the safe operation, handling, and use of hydrogen across all applications by providing

- Diverse accredited education and outreach resources, including training for first responders
- Global hydrogen safety conferences
- Greater accessibility to the PNNL Hydrogen Safety Panel for industry, state, and government agencies
- Leadership in addressing safety gaps

HYDROGEN Safety Panel

HYDROGEN Emergency Response Training Resources

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Hydrogen Safety Panel (US)

h2tools.org

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Hydrogen Safety Panel (HSP)

- Identify Safety-Related Technical Data Gaps
- Review Safety Plans and Project Designs
- Perform Safety Evaluation Site Visits
- Provide Technical Oversight for Other Program Areas

Hydrogen Tools *Web Portal* (http://h2tools.org)

- Hydrogen Facts, Training, Forums, HyARC Tools
- Hydrogen Lessons Learned, Best Practices, Workspaces

hsp

Emergency Response Training Resources

- Online Awareness Training
- Operations-Level Classroom/Hands-On Training
- National Hydrogen and Fuel Cell Emergency Response Training Resource



- Free source with several helpful documents, based on US standards and market conditions: lessons learnt form US infrastructure and projects
- Consider different metric systems (ft³, BTU, gallons etc.)
- Website also covers „lessons learnt“ from incidents (h2tool.org/lessons)

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Hydrogen Safety Guide

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To read on:

Source: HYPOS Hydrogen Safety Guide, 2021

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Hydrogen safety standards

Getting an overview is for free, but standards are subject to charges

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Safety instructions.
13 - Handling hydrogen.

1. Preliminary note

The safe handling of hydrogen requires knowledge of its properties and appropriate safety measures. Corresponding experience and recommendations from practice are compiled in these safety instructions. They are not intended to replace binding safety regulations, but to supplement them.

2. Features

Physical properties

Hydrogen is the lightest of all gases (density 84 g/m^3 at 15° C and 1 bar). Hydrogen escaping into the atmosphere therefore immediately flows upwards and can accumulate under the ceiling of the room, under roof vaults or similar.

Hydrogen is either stored in gaseous form at ambient temperature at high pressures (up to 300 bar) in gas cylinders or tanks, or it is stored virtually pressureless as cryogenic liquefied hydrogen (LH_2) transported or stored in insulated containers. When hydrogen is expanded (e.g. from 175 to 1 bar), a small temperature increase (from 20° C to 25° C) can be observed - in contrast to other gases. This temperature rise is not sufficient to allow outflowing hydrogen to be "self" ignition, since the ignition temperature is approx. 600° C.

Liquid hydrogen (LH_2) is a very light liquid (density of 70 g/liter). LH_2 evaporates very quickly in air.
In the process, approx. 750 liters of gaseous hydrogen are produced from 1 liter of LH_2. Immediately after evaporation, the gaseous hydrogen is still very cold and is somewhat heavier than air. For this reason, it initially spreads out almost horizontally. However, it warms up quickly.

Its density becomes progressively lower and it then flows upwards.

At the temperature of the liquid water (-253° C at 1.013 bar), all liquids and gases - except helium - are solid. Therefore, all other substances must be reliably kept out of LH_2 systems. For example, a mixture of solid air and LH_2 would have explosive-like properties.
The low temperature of the liquid water causes atmospheric air to condense on the outside of non-insulated plant components. The liquid air can become enriched with oxygen due to partial evaporation of the nitrogen and - if it drips onto combustible materials (wood, asphalt) - cause an explosion risk.

Warning of flammable substances

Chemical properties

Hydrogen burns with oxygen or air to form water. This property determines the vast majority of applications.
The technical objectives can be very different (reduction of chemical compounds, binding of oxygen, generation of heat, generation of high-purity water vapor, etc.). Hydrogen can also react with other oxidants (e.g. chlorine or nitrous oxide). When hydrogen is mixed with an oxidant and then ignited the combustion can be explosive. If this process takes place in an enclosed space, in addition to the development of heat, there is a rapid increase in pressure, which can have a destructive effect.

The concentration range in which hydrogen forms an explosive mixture with air at normal pressure and temperature is extremely large compared with other flammable gases (lower explosion limit - LEL 4 % by volume, upper explosion limit - LEL 75.6 % by volume).
This is not necessarily a safety disadvantage of hydrogen. For example, propane (LEL 2.1% by volume) is much more likely to result in an explosive atmosphere when emitted into the air than hydrogen. On the other hand, when air enters a gas system, hydrogen is more cri- tical because the explosive mixture is is already reached at 24.4% by volume air (OEG 75.6% by volume H_2), while with propane an explosion hazard would only arise at 90.5% by volume air (OEG 9.5% by volume propane).

Hydrogen/air mixtures are ignited by ignition sources with very low energy. The minimum ignition energy of hydrogen is 0.019 mJ, which is a power of ten lower than that of propane. For example, rust particles entrained in a fast-flowing stream of hydrogen can produce an ignitable spark by electrostatic charging or by impact with an obstacle. Because this ignition source often cannot be recognized or detected, hydrogen has been wrongly "suspected" of being self-igniting.

A hydrogen flame is very pale and hardly visible in bright daylight. You can detect a suspected hydrogen flame by, for example, placing paper in the

Safety instructions. 13 - Handling hydrogen. Page 1

- An extensive set of standards regarding hydrogen have been developed
  - Techncial guidleines by companies
  - Formal legally binding regulations from technical regulations (commercially available)

Useful overview at Department of Energy / US

- https://www.energy.gov/eere/fuelcells/safety-codes-and-standards

Code & Standards database (listing only, standards are commercially available)

- https://h2tools.org/fuel-cell-codes-and-standards?search_api_fulltext=

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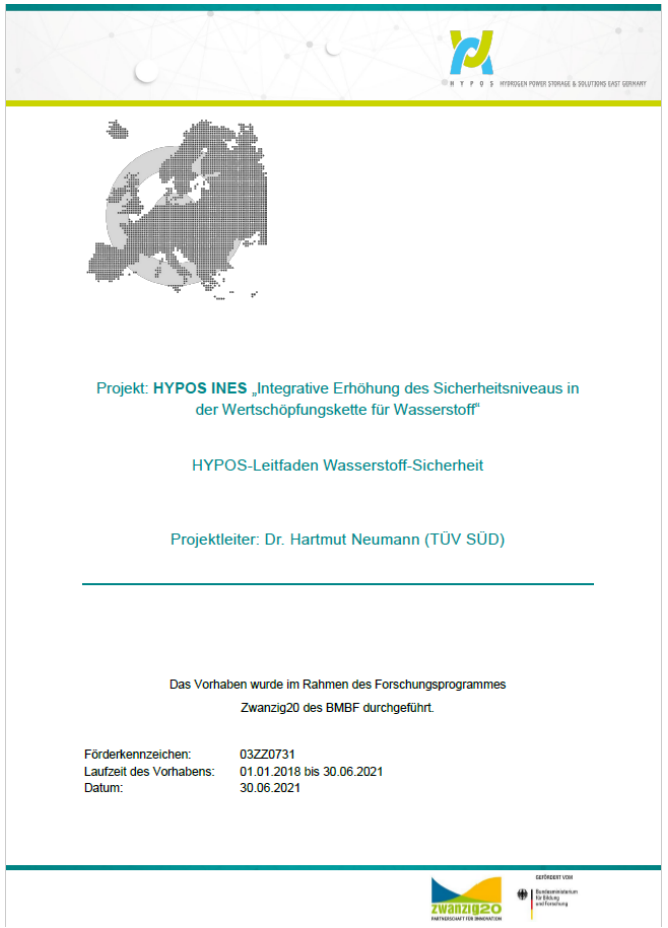
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HYPOR PROJECT - HYDROGEN POWER STORAGE & SOLUTIONS EAST GERMANY

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H Y P O S

www.hypos-eastgermany.de



Projekt: **HYPOS INES** „Integrative Erhöhung des Sicherheitsniveaus in der Wertschöpfungskette für Wasserstoff"

HYPOS-Leitfaden Wasserstoff-Sicherheit

Projektleiter: Dr. Hartmut Neumann (TÜV SÜD)

Das Vorhaben wurde im Rahmen des Forschungsprogrammes Zwanzig20 des BMBF durchgeführt.

Förderkennzeichen:	03ZZ0731
Laufzeit des Vorhabens:	01.01.2018 bis 30.06.2021
Datum:	30.06.2021

- Hypos is a publicly funded hydrogen network undertaking resarch to build up competences and carry out implementation projects in Eastern Germany
- One of the outcomes is a hydrogen saftey guide

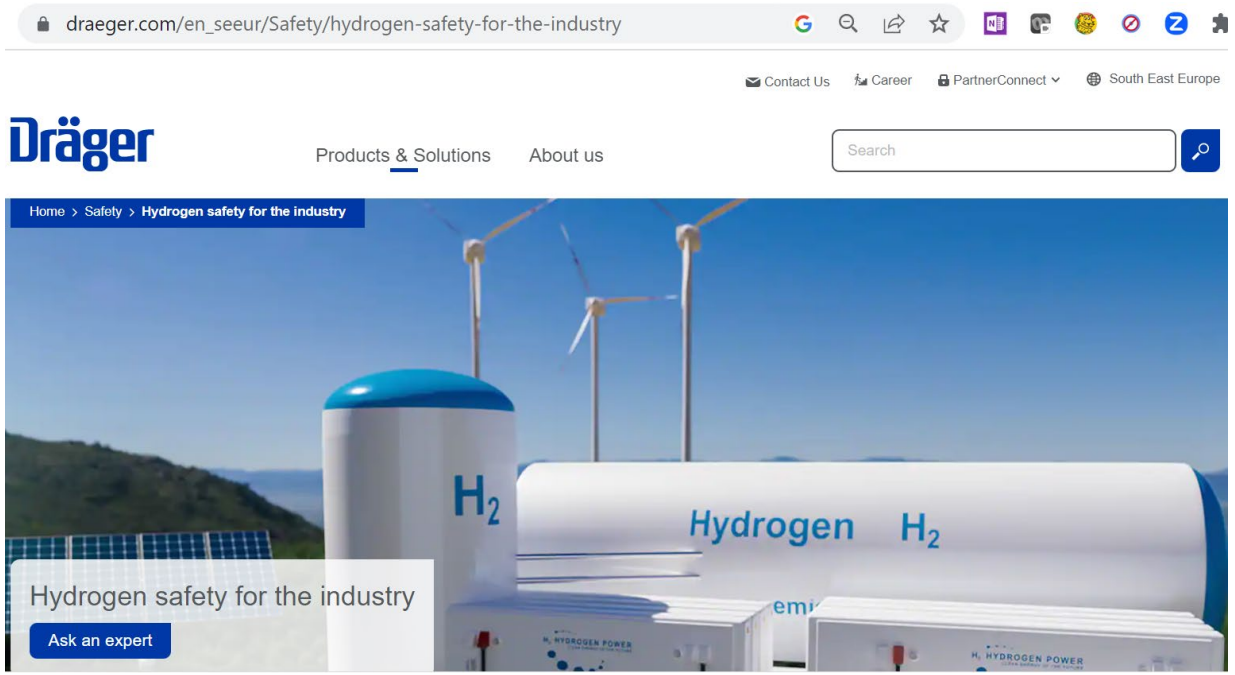
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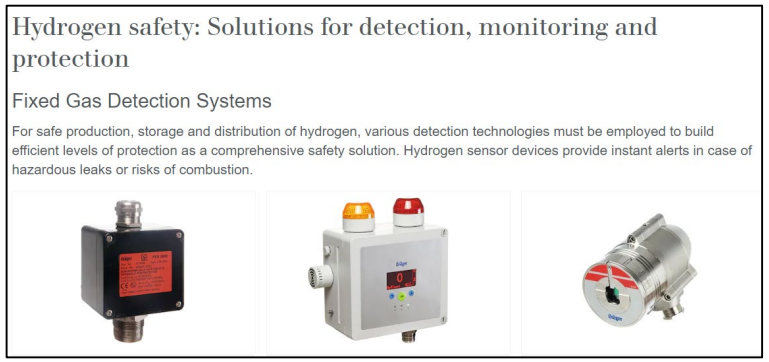
Gas equipment suppliers

Commercial interest to sell safety equipment

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- Gas equipment suppliers like **Draeger** offer information and the equipment for hydrogen safety
  - https://www.draeger.com/en_seeur/Safety/hydrogen-safety-for-the-industry







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Key Take-Aways: organizations and information sources

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- Since decades, technical regulations have been established for hydrogen safety, e.g. for chemical industry
- Additional standards were developed for Hydrogen vehicles
- An overview can be found for free, but standards are subject to charge
- Associations like Hydrogen Safety Panel (US) or HySafe (EU) provide valuable information for free

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Any questions or comments?



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Site visit:
Shell 10 MW electrolyzer
in Wesseling near Cologne/Germany

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Site visit: Shell 10 MW electrolyzer

Shell refinery in Cologne – industrial location for electrolyzer

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Site visit: Shell 10 MW eletrolyzer

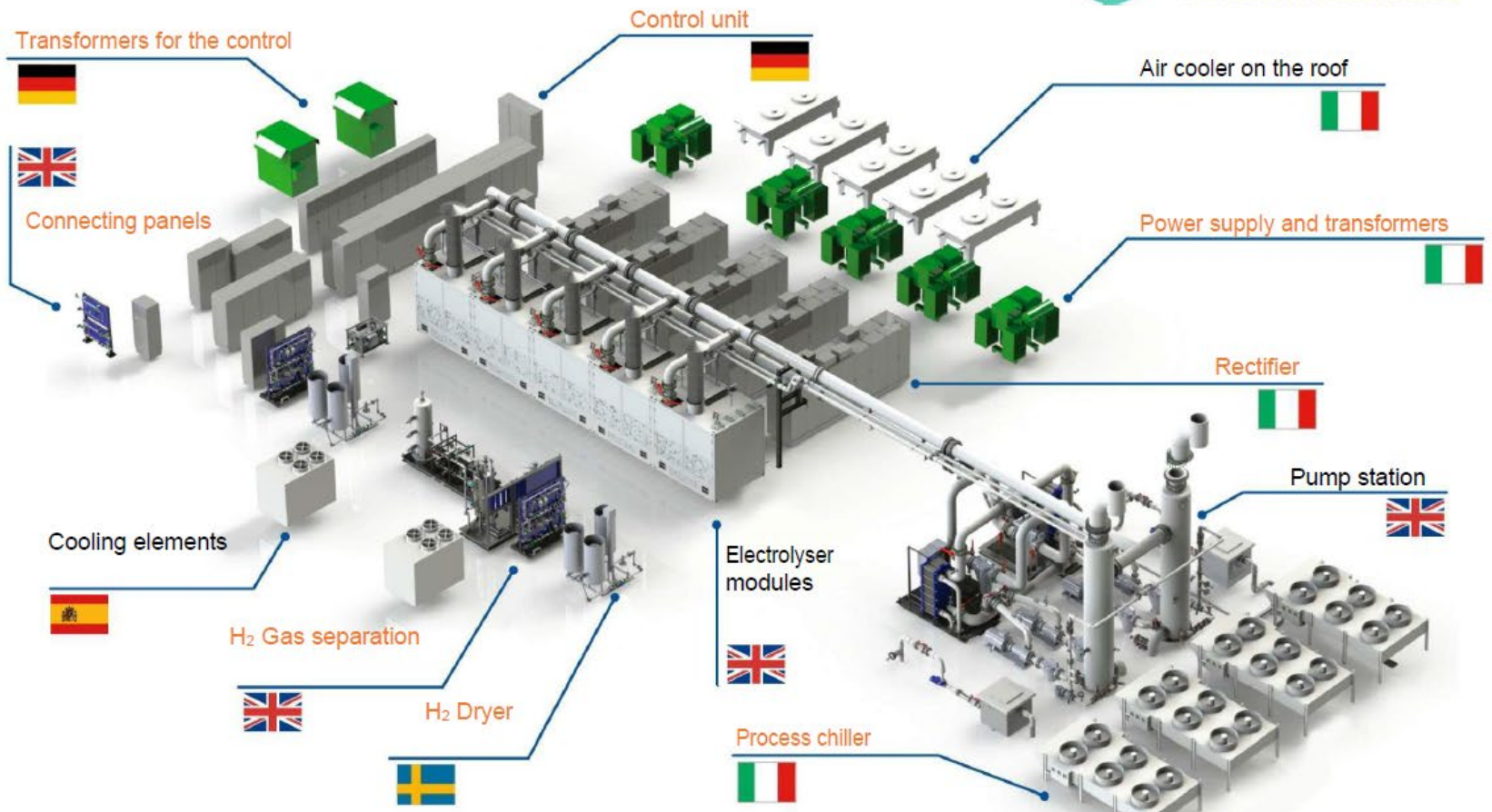
Plant layout and components

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Construction of the largest PEM electrolyzer in Europe

REFHYNE
CLEAN REFINERY HYDROGEN FOR EUROPE

- 10 MW power
- Production capacity up to 1,300 tons of green hydrogen
- The first PEM electrolyzer on an industrial scale
- Pilot plant for the next expansion stage of 100 MW



ITM POWER Energy Storage | Clean Fuel
SINTEF
sphera
elementenergy

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Site visit: Shell 10 MW electrolyzer

Air view of electrolysis plant

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Site visit: Shell 10 MW electrolyzer

Publicly supported project REFHYNE

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Site visit: Shell 10 MW electrolyzer

Connection to water and hydrogen infrastructure at refinery site

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Pipes connecting electrolyzer with water supply and hydrogen infrastructure on site



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Site visit: Shell 10 MW eletrolyzer

Can you spot the unsafe problem?



Site visit: Shell 10 MW eletrolyzer

Can you spot the unsafe problem?



Site visit: Shell

H2 Venturi roof

- Electrolyzers are operated in containers that are kept below atmospheric pressure
- Gases from inside of containers are ventilated below roof where they are diluted with ambient air flow
- Venturi flow provdes high ambient air flow





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Any questions or comments?



Conclusions:

H_2 safety to go



[Quelle: Tchibo]

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Key takeaways: Hydrogen Safety

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- Hydrogen is not more unsafe than other energy carriers, but hydrogen safety needs to consider ist special properties and the resulting safety challenges
  - Consider: hydrogen is flammable, has a much larger explosion range compared to natural gas, and has a very low ignition energy.
- Hydrogen safety issues are known, hydrogen safety standards are available and proven in practice

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Key takeaways: Hydrogen Safety

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One last leasson learnt:

Be aware that hydrogen safety is a full-time job. Somebody must take over the role a Health & Safety manager and be extensively trained for the job.

All people on site must be trained and equipped to assure hydrogen safety.

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Checkpoint 1: Hydrogen Properties

Which of the following statements concerning the properties of hydrogen is correct?

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A)	**Compared to natural gas, hydrogen is less reactive and easier to handle**
B)	**Hydrogen can easily form dangerous mixtures with air**
C)	**Hydrogen is more difficult to ignite than natural gas**
D)	**When getting in contact with oxygen, hydrogen will immediately explode**

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Checkpoint 2: Hydrogen Safety Challenges

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Which of the following statements concerning the safety challenges of hydrogen is correct?

A)	Hydrogen has a specific smell that can be detected by trained dogs
B)	Hydrogen flames are very hot and always visible, and may easily ignite surrounding materials
C)	It is not possible to avoid leakage of hydrogen in gas pipes
D)	Hydrogen may corrode existing steel gas pipes in the gas infrastructure

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Checkpoint 1: Hydrogen Properties

Which of the following statements concerning the properties of hydrogen is correct?

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Checkpoint 2: Hydrogen Safety Challenges

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Which of the following statements concerning the safety challenges of hydrogen is correct?

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B)	**Hydrogen flames are very hot and always visible, and may easily ignite surrounding materials**
C)	**It is impossible to avoid leakage of hydrogen in gas pipes**
D)	**Hydrogen may corrode existing steel gas pipes in the gas infrastructure**

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Any questions or comments?



Thank you!

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Prof. Dr. Thorsten Schneiders

Professor for Energy Storage

Head of Virtual Institute Smart Energy

TH Köln
Cologne University of Applied Sciences
Betzdorfer Str. 2
50679 Köln

T +49 221 8275 2335
M +49 160 938 16530
thorsten.schneiders@th-koeln.de

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Backup

Additional slides

Important parameters for gases

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Source: Breton, Handbook of Gas Utilization Technology
scf = standard cubic feet

Parameter	Meaning
Calorific value H_i Index i = "inferior	The calorific value H_i (formerly: lower calorific value H_u , unit: kJ/kg) is the maximum amount of heat that can be used in combustion *without* condensation of the water vapor contained in the exhaust gas: H_i is related to the amount of fuel used.
Calorific value H_s Index s = "superior“	The calorific value H_s (unit: kJ/kg) is the maximum amount of heat that can be utilized during combustion of a combustion in which condensation of the water vapor contained in the exhaust gas occurs. In heating technology ("condensing boiler"), the calorific value H_s includes the calorific value H_i plus the energy released by condensation of the resulting water vapor (the heat of condensation).
Standard state	For the sake of standardization, the properties of gases are referred to the standard state: 101,325 Pa = 101,325 N/m² =1,013.25 mbar, 0°C = 273.15 K; 1 Nm³ = 1 m³ at standard conditions
Conversion	1 kWh/Nm³ = 3.6 MJ/Nm³ = 3.6 10^6 J/Nm³ 1 Btu/scf = 0.03525 MJ/Nm³ (1 Btu = 1.05506 kJ : British thermal unit) 100,000 Pa = 100,000 N/m² = 1000 hPa = 100 kPa = 1.000 bar

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Wobbe index

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Source: Cerbe, Fundamentals of Gas Technology

Parameter	Meaning
Definition	**Wobbe index** is a measure of energy delivery of a burner and essential parameter for assessing the interchangeability of gases. The Wobbe index is the quotient of the calorific value (H_s), or heating value (H_i) and the square root of the relative density.
Comparability	Fuel gases with the same Wobbe index result in the same heat load in the burner at the same nozzle pressure. The burner nozzle does not need to be replaced in this case.
Upper Wobbe index Ws	$W_s = \frac{H_s}{\sqrt{\frac{\varrho}{\varrho 0}}}$ The upper Wobbe index is the quotient of the calorific value (H_s) and the square root of the relative density.
Lower Wobbe index Wi	$W_i = \frac{H_i}{\sqrt{\frac{\varrho}{\varrho 0}}}$ The lower Wobbe index is the quotient of the heating value (H_i) and the square root of the relative density.
Relative density	$d = \frac{\rho}{\rho_0}$ The relative density is the ratio of the density ρ of a fuel gas to the density ρ_0 of dry air under the same pressure and temperature conditions.

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Further parameters of gas technology

Technology
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Source: Cerbe, Fundamentals of Gas Technology

Designation	Description
Air number λ	Air number (air ratio) indicates the ratio of supplied to theoretically required air flow for combustion
Flame speed	Propagation rate of the combustion reaction
Ignition temperature	Minimum temperature for initiation of the combustion process
Ignition energy	Energy to be supplied for fuel-air mixture to ignite
Ignition delay time	Delay time between ignition and combustion
Ignition limits	Concentration limits for the fuel-air mixture (too rich/too lean): heat released must be sufficient to maintain minimum temperature for ignition
Methane number	In gas engines: knock resistance during combustion of gas mixtures, comparable to the octane number The lower the methane number, the lower the knock resistance, which increases the risk of spontaneous ignition and engine knock. The higher the methane number, the more resistant the gas mixture is to knocking.

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