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Risks, their occurrence and their prevention through the implementation of hydrogen in the energy-intensive industry

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Hydrogen shows great promise for reduction the CO₂-emission of production in energy-intensive processes. Due to the immense amount of energy required to melt raw materials, for example in glass and aluminum production, switching from natural gas to (green) hydrogen or mixing the two fuels would significantly impact decarbonization and emissions. However, there are plant and process risks associated with the implementation of hydrogen that need to be considered. This applies to hydrogen storage, hydrogen distribution, and the melting furnace. It is also unclear whether and to what extent hydrogen affects the quality of the product.

Against this backdrop, the question arises about how the decarbonization of energy-intensive processes requires attention on the plant and process side. To summarize the existing knowledge, the use of hydrogen in the energy-intensive industry, differences to the current state of the art and risks are first shown. A literature review on hydrogen damage, its mechanisms, and phenomena is carried out to explain the interaction between hydrogen and certain materials. In the next step, material databases and experimental test results for materials relevant to such industries will be used to compile assessments of their compatibility. To ensure the safety of people, machines, and products in the event of a fault, measurement options for hydrogen leaks are discussed and their operating conditions, advantages, and disadvantages are described. Finally, recommendations for the glass industry are given to ensure plant and process safety as well as economic efficiency.

Keywords: hydrogen embrittlement, process safety, preventive and corrective maintenance, energy-intensive process, layered leak monitoring, hydrogen compatibility

1. Use in Energy-Intensive Industry

Natural gas is primary used as fuel for the melting furnaces (Destatis 2024) in energy-intensive industries such as glass, aluminum, or steel production. An alternative fuel is needed for two reasons: Firstly, because of the associated carbon dioxide (CO₂) emissions (European Parliament 2023), and secondly, to free ourselves from geopolitical dependencies (European Consilium 2023). (Green) Hydrogen (H₂) is to be used as a substitute. Combustion with oxygen releases water and energy, reducing CO₂ emissions. If the H₂ is not produced from natural gas by steam reforming or methane pyrolysis, for example, but by water electrolysis or the Kværner process, natural gas can be avoided.

1.1 Plant infrastructure for hydrogen utilization

When converting from natural gas to H₂, the glass industry is considering two approaches to process planning: a costly new build of an entire plant or an attempt to recycle existing plant components for the use of H₂. The latter has economic and environmental advantages and should contribute to CO₂ reduction. Various characteristics of the plant components used in natural gas applications determine whether they are also suitable for H₂ applications. These include, for example, the material of a component, the design of the operating points of actuators and the measurement methods of sensors, to name but a few. This study aims to provide an overview of some of the general discussions on fuel switching for energy intensive

industries. An evaluation of component evaluation criteria and the implementation of a safety and risk management analysis is essential for any industrial operator. It should also be noted that additional system components may be required for H₂ applications.

1.2 Differences between natural gas and hydrogen

Switching from natural gas to hydrogen as a fuel cannot be done without further ado. These two gases have different properties. If these are not taken into account, there may be risks for the system and process.

Natural gas can be present in various mixing ratios. It primarily consists of methane (up to 99 %) and can also be mixed with ethane, propane, ethene, and butane.

H₂ is flammable and explosive in a larger range when mixed with air. (4 to 77 vol% for H₂, 5.3 to 18 vol% for methane (CH₄)). In the event of a leak, an explosive gas mixture with hydrogen may form sooner or exist for longer. The minimum ignition energy is 0.017 mJ for H₂ and 0.274 mJ for CH₄. Explosive gas mixtures made from hydrogen require only a fraction of the energy that would be required for an explosive gas mixture with natural gas to cause a detonation or explosion. The flame speed of 2.7 m/s for H₂ is significantly higher than that of 0.37 m/s for CH₄. This needs to be considered when designing the new burner or when evaluating the existing natural gas burner being used. The energy content (higher heating value) of H₂ is 3.54 kWh/m³, whereas CH₄ has an energy content (higher heating value) of 11.1 kWh/m³. For the

same amount of energy, many times more is needed than if natural gas were used.

1.3 Hazard potentials of gaseous compressed hydrogen

Due to its physical and chemical properties, as well as its storage form, H₂ can pose certain risks for both plants and people. H₂ is colorless and odorless gas. -However, H₂ cannot be detected by the human senses. H₂ is the smallest and lightest molecule and can penetrate materials more efficiently, follow leakage paths, and spread more quickly in the environment (relevant in enclosed rooms). For this reason, pipe or hose connections, such as threaded connections, welds, flanges and couplings, should be checked for leaks. If there is a leak, H₂ and air will mix. This means that two of the three required criteria of the fire triangle are fulfilled, see Figure 1.

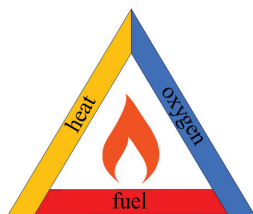


Fig. 1: Fire Triangle. Three necessary conditions for a fire to occur.

The ignition energy, the third requirement, can be generated by static charge, friction due to the leakage, or an external source (hot surface, spark, fire). Due to the wide range of mixing ratios of H₂ and air, which constitute an explosive gas mixture, leaks are considered a significant safety risk.

2. Methodology

To minimise the risks of hydrogen ignition, it is recommended that the methodological approach is based on EN 1127-1:2019-10 'Explosive atmospheres - Explosion prevention and protection - Part 1: Basic concepts and methodology'. Risk reduction is achieved primarily by prevention and secondarily protection. Prevention can be achieved by substitution, reduction of amount of substances capable of forming explosive atmospheres or inerting. Leakage of flammable/combustible substances can be avoided or reduced by design and construction, or dilution by ventilation can be achieved. The following relevant EU directives and European/international standards must be observed and applied regarding explosion protection (see Table 1).

Table 1: key guidance documents for preparation of an explosion protection concept

Directive/Standard	Name
2014/34/EU (ATEX 114)	Directive on the harmonisation of the laws of the Member States relating to equipment and protective systems intended for use in potentially explosive atmospheres.
2012/18/EU	Control of major-accident hazards involving dangerous substances

Table 1 continued: key guidance documents for preparation of an explosion protection concept

Directive/Standard	Name
1999/92/EC (ATEX 137)	Directive on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres
89/391/EEC	Directive on the introduction of measures to encourage improvements in the safety and health of workers at work
EN 1127-1:2019-10	Explosive atmospheres - Explosion prevention and protection
EN 60079-10-1:2022-02	Explosive atmospheres - Part 10-1: Classification of areas - Explosive gas atmospheres
EN 61511-1:2019-02	Functional safety - Safety instrumented systems for the process industry sector
ISO/TR 15916:2015-12	Basic considerations for the safety of hydrogen systems
ISO 26142:2010-06	Hydrogen detection apparatus - Stationary applications
EIGA 15/21	Gaseous Hydrogen Installation
EIGA 121/14	Hydrogen Pipeline Systems

In addition, national standards, regulations or laws may contain supplementary information and requirements. In Germany, for example, the rules and regulations of the German Social Accident Insurance (DGUV), Technical Rules for Operational Safety (TRBS) and Technical Rules for Hazardous Substances (TRGS) must also be observed. Due to national, plant and process-specific characteristics, the explosion protection concept and safety and risk management should be developed for each application by specialised personnel.

3. Influence of Hydrogen on Metallic Plant Components

H₂ has been used in industry for over a century, so safer handling can be expected in the sectors and transferred to energy-intensive sectors. However, for economic reasons, existing systems (designed for natural gas) are now repeatedly being considered for operation with H₂ (Retrofit). One problem that can arise with this approach is hydrogen embrittlement (HE). This describes processes in which metallic components of the system develop cracks and damage (up to complete failure) when exposed to H₂. The fear is that the materials used to date are unsuitable for pure H₂ applications, resulting in a safety risk for the system and process during operation. To understand the problem of HE, the entry into the material, mechanisms that can lead to loss of ductility, and phenomena that indicate HE are described.

3.1. Entry of hydrogen into a material

Damage due to interactions between the material and the H₂ hydrogen can occur with various components made of different materials between delivery/storage, plant and furnace. The materials relevant to the glass industry are metals, polymers and Ceramics. Ceramics, which are being analysed by another research group as part of an EU project, are not covered in this study.

The process of H₂ absorption in metals involves various intermediate steps. According to Vehoff, the process is shown schematically in Figure 2.

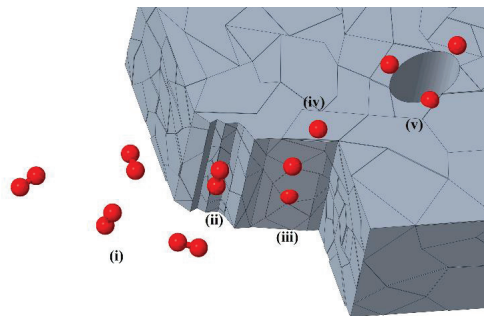


Fig. 2: Process of H_2 penetration into a material according to Vehoff (1997).

The process includes:

- (i) H_2 gas transport takes place as a molecule.
- (ii) The H_2 molecule is adsorbed on the surface.
- (iii) Dissociative H_2 chemisorption takes place.
- (iv) Atomic hydrogen enters the material atomically through absorption.
- (v) The atomic hydrogen is trapped between the metal atoms by diffusion and subsequent occupation of the metal lattice.

This causes various defects in the lattice, which build up and lead to material failure. Figure 3 shows possible H_2 -occupied areas.

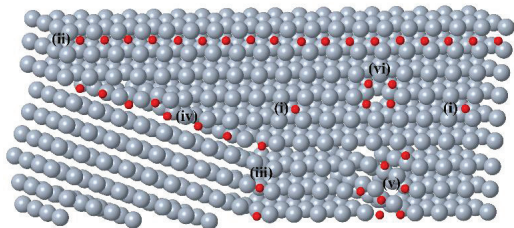


Fig. 3 Possible areas for deposition of atomic hydrogen in the lattice structure based on Pundt (2004).

Possible accumulation sites for hydrogen in the atomic lattice are:

- (i) interstitial lattice sites,
- (ii) present at open volume defects (e.g., outer surfaces and inner surfaces in pores),
- (iii) internal cracks,
- (iv) grain boundaries or phase boundaries,
- (v) dilatation field of dislocations and
- (vi) in vacancies.

Different factors can enhance or mitigate HE if H_2 is trapped in the metal lattice structure. Important variables influencing HE occurrence are stress and intensity, H_2 content, pressure, temperature, strain rate, and alloy strength, purity, and structure. Other influencing factors are ambient pressure, purity, exposure time to H_2 , and surface condition. A critical combination of material, manufacturing, and coating-related factors can lead to severe cracks and material failure. Several

explanations for cracks and material failure have been attempted, as no approach can comprehensively describe the processes. The currently recognized mechanisms that are used as explanatory approaches are summarized and described below.

3.2 Mechanisms of hydrogen embrittlement

Natural gas is currently still used in energy-intensive sectors and in areas of public life. The use of hydrogen as an alternative fuel is being considered in many areas. For economic reasons, attempts are being made to maintain the existing gas infrastructure and convert it to hydrogen. As different materials are used depending on the application, the following two chapters first discuss possible mechanisms that can lead to premature material failure. Various materials are then evaluated for their hydrogen compatibility using material databases and publications.

3.2.1 Hydride-induced embrittlement

In 1969, Westlake proposed a mechanism based on the formation and fracture of hydrides at crack tips (Westlake 1969). Failure begins with H_2 diffusion into areas of increased hydrostatic stress ahead of cracks. This triggers and enlarges a hydride phase, which leads to fracture of the hydride when a critical size is reached. As a result, the crack propagation is interrupted at the interface between the hydride and the matrix. The occurrence of a hydride mechanism depends on temperature and strain-rate conditions where H_2 has time to diffuse ahead of crack tips. Additionally, the process can only occur at temperatures where the hydride phase remains stable and brittle (Birnbbaum 1983). When H_2 exists as a solute, HE is not evident, and tensile specimens may undergo significant plastic deformation before the nucleation of hydrides and subsequent brittle fracture.

3.2.2 Hydrogen-enhanced decohesion or hydrogen-induced decohesion

In 1926, Pfeil proposed a decohesion theory suggesting that H_2 diminishes cohesion across cubic cleavage planes and grain boundaries (Pfeil 1926). In the following years, decohesion theory was used as a basis so that a quantitative selection of further developments is available as an explanation (Orani 1970, Gangloff 2003, Troiano 2016). Decoherence is commonly described as a simple, stepwise separation of atoms once a critical crack tip displacement is reached, corresponding to about half the distance between the atoms. However, the separation of atoms at the crack tips is restricted by nearby atoms. Therefore, the separation process could be more intricate and involve slight lateral movements of the atoms to reach the critical crack tip displacement (Knott 2013). Decoherence could be accompanied by some dislocation activity, which increases stresses at the decohesion sites. However, this activity should be limited to prevent continuous atomically sharp crack tips blunting. Decoherence due to high H_2 concentrations can occur at various locations, including by adsorbed H_2 at the atomically sharp crack tips, in areas where dislocation shielding effects lead to maximum tensile stress, locations of maximum hydrostatic stress, and particle-matrix interfaces in front of the cracks (Lynch 2013). Extremely high elastic stresses are likely needed to generate high H_2 concentrations in the interstitial lattice sites in front of the crack tips, which leads to decohesion. Along the grain boundaries, decohesion could occur at or in front of the crack tips because H_2 is trapped at specific locations. This could be due to a

weakening of the bonds caused by both H_2 and metalloid impurities accumulation. For both internal HE and environmental HE, the diffusion of H_2 at the mentioned locations is a factor that should not be neglected. An exception is when environmental HE occurs solely due to H_2 adsorption at the tips of external cracks (Lynch 2012, Nagao et al. 2018, Wasim et al. 2021, Dwivedi and Vishwakarma 2018).

3.2.3 Hydrogen-enhanced localized plasticity

That hydrogen-assisted cracking arises from H_2 dissolved in the material because it supports the movement of dislocations was initially proposed by Beachem and is based partly on fractographic observations (Beachem 1972). From the 1980s onwards, the idea of Hydrogen-enhanced localized plasticity was adopted and further developed (Robertson et al. 2009). The proposed theory is that H_2 accumulates near crack tips due to hydrostatic stresses or because H_2 intrudes at these sites. The deformation due to the H_2 is concentrated around the crack tips as the dissolved H_2 promotes dislocation activity. Accordingly, subcritical crack growth occurs due to a more localized microvoid coalescence process than in an inert environment. Both internal HE and environmental HE require H_2 to diffuse into localized areas in front of the crack tips to use the Hydrogen-enhanced localized plasticity mechanism as an explanation. Depending on whether there are locally high H_2 concentrations inside the grain or near grain boundaries, the crack paths can be transgranular or intergranular (Lynch 2012, Dwivedi and Vishwakarma 2018, Barrera et al. 2018).

3.2.4 Adsorption-induced dislocation emission

Lynch proposes in 1986 the adsorption-induced decohesion mechanism, which states that hydrogen-assisted cracking can also result from H_2 adsorption at the crack tip (Lynch 1986). Metals for which HE has been demonstrated include aluminum, nickel, titanium alloys, and magnesium in aqueous or H_2 environments. Lynch investigated crack propagation metallographically and fractographically and identified a localized plastic flow and Hydrogen-assisted microvoid coalescence process as a possible cause of that environmentally assisted cracking. Accordingly, adsorption is the cause of the emission of dislocations from the crack tips. This leads to a tendency for cracks to coalesce with voids in front of the cracks. Lynch has also observed HE mechanisms in aluminum alloy 7075, high-strength steels, and titanium, which involve local sliding processes triggered by adsorption (Lynch 1988). Work and modeling in some materials support the Adsorption-induced dislocation emission mechanism (Barrera et al. 2018, Pundt and Kirchheim 2006, Kuk et al. 1987, Song and Curtin 2013).

3.2.5 Hydrogen-enhanced strain-induced vacancy formation mechanism

The Hydrogen-enhanced strain-induced vacancy formation theory states that H_2 increases the density and clustering of voids. Initially, voids coalesce into microvoids, which can coalesce into larger voids. According to Nagumo, who initially proposed the theory in 2004, this reduces resistance to ductile crack growth (Nagumo 2004). Evidence of this was observed in H_2 -loaded samples, which were tested using tensile testing and fracture toughness testing. Hydrogen-enhanced strain-induced vacancy formation mechanism had predicted, and it proved, that the H_2 -charged samples had a higher pore density than the uncharged samples after the same fatigue cycles.

In experiments in a H_2 atmosphere at high pressure and high temperature, McLellan et al. find that the density of vacancies in iron is greatly increased compared to thermal equilibrium. This is seen as an indication that iron- H_2 interactions reduce the formation energy of vacancies (McLellan and Xu 1997). Using positron emission spectroscopy Sakaki et al. observe the hydrogen-induced increase in vacancy formation during the deformation process (Barrera et al. 2018, Sakaki et al. 2006).

3.2.6 Hydrogen-assisted microvoid coalescence

The merger of microvoids plays an important role in some models, including hydrogen-assisted microvoid coalescence. This mechanism describes the processes of cavity nucleation, cavity growth, cavity coalescence, crack expansion, and fracture. Local plastic deformations due to the action of H_2 and the associated dislocation movement of the material lead to crack propagation in the direction of the existing cavities. As evidence of the effect of H_2 , a brittle intergranular fracture can be observed at the edge of the sample. In addition, in some experiments, fish eyes containing Hydrogen-assisted microvoid coalescence shear pits were found near the fracture (Pradhan et al. 2012, Dwivedi and Vishwakarma 2018, Venezuela et al. 2018).

Based on the number of mechanisms published and discussed, some of which put forward contradictory arguments, it is clear that no model can fully explain the mechanisms. Even if experimental evidence is still pending for some situations, the consensus is that several microscopic mechanisms may work together to cause a macroscopic brittle fracture. Different combinations of mechanisms can be explained depending on the material or experimental conditions.

4. Hydrogen Compatibility with Materials

If the retrofit approach is not pursued, preventive attention can be paid to the choice of materials when building the hydrogen infrastructure. The following article first briefly lists evaluation criteria that can be used to assess hydrogen compatibility and then presents an initial assessment of hydrogen compatibility for materials that can be used in energy-intensive processes.

4.1 Evaluation criteria

To assess the suitability of a material for use with H_2 , material parameters need to be defined and compared between H_2 and atmospheric applications. These parameters include tensile properties (smooth and notched), fracture mechanics (fracture toughness and threshold stress intensity factor), fatigue (low and high cycle fatigue, fatigue crack growth rate, creep, fracture toughness), composition and microstructure (material composition, microstructure) and manufacturing.

4.2 Ferritic steels

Among other things, a reduction in tensile ductility and additional aggravation of the problem due to stress concentrations (Hoover et al. 1981, Raymond et al. 1988), reduction in fracture toughness (Thompson and Moody 1994, Cialone and Holbrook 1985, Louthan et al. 1986), increased susceptibility to crack propagation under static loading and under given metallurgical conditions (Raymond et al. 1988, Thompson and Moody 1994, Loginow and Phelps 1975), and accelerated growth of fatigue cracks were observed (Walter and Chandler 1976).

4.3 Austenitic steels

Austenitic steels are not a homogeneous group, and no general statement can be made about them. Some derivatives, such as A286, 216, 316, or 22-13-5 (Nitronic 50), have little or no susceptibility to HE. Other 300 series austenitic steels such as 304, 305, 321, and other nitrogen-hardened stainless alloys such as 21-6-9 are unsuitable for H₂ applications (Lee and Woods 2016). Some studies attribute this to the nickel content. At a nickel concentration between 10 and 30 %, the strain-induced martensitic transformations are reduced and thus the resistance to H₂-hydrogen assisted fractures is increased (Caskey Jr. 1983).

4.4 Martensitic steels

A combination of high strength, high toughness, and corrosion resistance characterizes martensitic stainless steels. Few reports deal with H₂-assisted fracture of precipitation-strengthened martensitic Fe-Cr-Ni stainless steels under the influence of compressed H₂. The findings indicate that martensitic steels are very susceptible to environmental HE: significant loss of area reduction observed (Murray et al. 1987) and reduction in fracture toughness observed (Caskey Jr. 1983).

4.5 Nickel and Nickel alloys

Pure nickel and its alloys that are not within the range shown in chapter 3.3 are highly to HE. Despite good properties in terms of high-temperature strength, oxidation, and hot corrosion resistance, pure nickel is highly embrittled by H₂ (Caskey Jr. 1983, Jewett et al. 1973, Chandler and Walter 1974). In binary alloys and nickel-rich alloy systems, an intense HE process is also observed (Lee 2012, Morea and Wu 1984, Cooper 1976).

4.6 Titanium-based alloys

The extant findings indicate that titanium is not compatible with H₂ applications. Although titanium generally exhibits good corrosion resistance, HE could not be confirmed concerning under the test conditions carried out in the publications (Fritzemeier and Jacinto 1989, Wille and Davis 1981, Tal-Gutelmacher and Eliezer 2005, Christ et al. 2003).

4.7 Copper and copper alloys

It has been established that copper and copper alloys are not susceptible to environmental HE under normal condition, Ellis et al. 1993, Louthan and Caskey Jr. 1976). However, an exception occurs when oxygen or copper oxide remains, and the material is used at higher temperatures (above 375 °C). In the presence of H₂, the gases may react to form water vapor. This reaction can induce fractures or form bubbles, reducing the material's fracture toughness and ductility.

4.8 Aluminum and aluminum alloys

Examining the available test results for aluminum in a H₂ atmosphere reveals no observable deterioration in mechanical properties. However, a specification that is limited by the presence of moisture in the H₂ atmosphere has been identified. Manufacturing defects can occur during the production process, but these are considered to be instances of internal HE. Under the test conditions described in the publications, no environmental HE has been observed (Jewett et al. 1973, Chandler and Walter 1974).

4.9 Polymers

In contrast to metals, polymers are not prone to HE. The absorbed H₂ does not dissociate and is present in the polymer as a diatomic molecule. However, it has been demonstrated that H₂ can exert an influence on the properties of the polymer. It can be hypothesized that H₂ behaves inertly in conjunction with most polymers. However, the effects of H₂ at high pressures are a subject of ongoing investigation, as certain gases (e.g., CO₂) have been observed to exert a plasticizing effect on polymer properties (Lorge et al. 1999). It has been demonstrated that polymers can dissolve substantial quantities of H₂. However, it is important to note that high-pressure H₂ applications can potentially induce damage to polymer materials, manifesting as either bubble formation or swelling (Lee and Woods 2016, Barth 2013).

5. Layered Monitoring Hydrogen Releases

If hydrogen is released despite preventive measures, the effects can be minimised by technical measures. A H₂ leak can be detected at various stages using different methods. Implementing a combination of monitoring strategies, tailored to the quantity of escaping H₂ and its interaction with the surrounding environment, facilitates the identification of the fault in its early stages, thereby minimizing the resultant effects. The layered monitoring of a hydrogen leak is described below.

5.1 Leak detection layer

Monitoring potential connections or predetermined breaking points directly, can ascertain a H₂ gas leak's location. Another way to detect and locate a leak is to use acoustic sensors. However, it should be noted that no definitive statements can be made regarding the concentration or the quantity of leakage.

5.1.1 Detection tape

The detection tape is a simple method of monitoring instruments, vulnerable joints or possible predetermined breaking points. The tape is applied to encompasses the area to be monitored. In the event of gas leakage, the presence of H₂ molecules prompts a reaction with the color pigments within the tape, gradually transforming the tape's color (illustration see Fig. 4). The primary advantage of this method is characterized by its durability, cost-effectiveness and ease of use for personnel. However, it should be noted that the efficacy of the tape is contingent upon personnel conducting regular checks of the system.

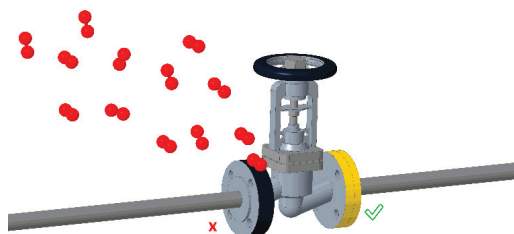


Fig. 4: Illustration of detection tape.

5.1.2 Gas leak detection spray

A comparable approach involves using a gas leak detection spray, predicated on the leak test. In this method, pressurized test specimens are immersed in a solution, and the presence of bubbles indicates a leak. The advantages and disadvantages of this method are analogous to those of the detection tape. In addition, it must be noted that the gas leak detection spray may penetrate the gas pipe at certain parts of the system, specific process parameters or due to improper handling.

5.1.3 Ultrasonic leak monitoring

An alternative method of detecting a leak and ascertaining its location is to utilize ultrasonic sensors. These sensors can detect the ultrasonic signature of a particular gas in the event of a leak (illustration see Fig. 5). A key benefit of this approach is its integration with higher-level control and regulation systems, enabling the immediate detection of leaks as they occur. Furthermore, a single sensor can be utilized to monitor entire parts of the system within a specified intake radius. However, it should be noted that this method is associated with higher costs associated with purchase and maintenance, and its implementation is contingent upon a comprehensive safety concept for the system. Due to interference factors, ultrasonic sensors should be calibrated on site to minimise false alarms.

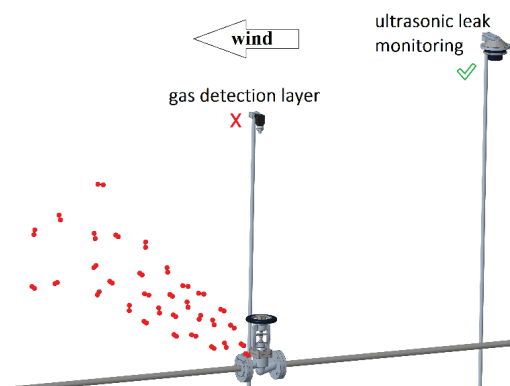


Fig. 5: Schematic illustration of ultrasonic monitoring based on Lee et al. (2024).

5.2 Gas detection layer

Unlike the leak detection layer, the gas detection layer is capable of providing a quantitative assessment of the concentration of the resulting gas mixture at the installation site. In the event of a leak, hydrogen spreads in all directions without external influence (wind) and rises due to its density. In enclosed spaces it can accumulate under the ceiling and form a flammable gas mixture. Depending on the location (proximity to the gas pipe) and taking into account the influencing factors (indoor or outdoor application), the gas detection layer reacts at different speeds, in the worst case not at all. Conclusions as to the location of the leak are limited.

5.2.1 Catalytic hydrogen sensors

Catalytic H_2 sensors comprise a platinum or palladium coil that serves as a catalyst (illustration see Fig. 6). These sensors use a combustible gas (H_2) near to ambient oxygen, resulting in the release of heat that is directly proportional to the quantity of H_2 present. This reaction instigates a change in the electrical

resistance of the platinum coil, thereby facilitating the determination of the concentration. A wire mesh at the sensor input functions as a flame arrester. These sensors are notable for their robustness, cost-effectiveness, linear sensor response depending on the gas concentration, and ease of calibration. However, they exhibit low selectivity (i.e., activation by other flammable gases) and low sensitivity in the percentage range.

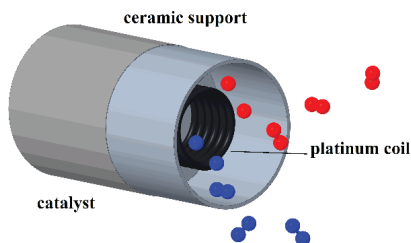


Fig. 6: Example of catalytic sensor based on Ivanov et al. (2022)

5.2.2 Electrochemical hydrogen sensors

The principle of the electrochemical H_2 sensor is based on three electrodes, a membrane, and a liquid electrolyte. The gas flows into the sensor and through the membrane, which is only passable for the gas but not for the liquid electrolyte. Upon reaching the working electrode, a chemical reaction ensues, involving either oxidation or reduction, depending on the gas species. This reaction leads to the flow of electrons from the sensing electrode to the counter electrode or vice versa. The electron flow thus generates a current proportional to the gas concentration. The current is then amplified, and the electronics measure the output variable according to calibration. A notable advantage of this technology is its ability to detect even low concentrations (ppm), and the sensors are straightforward to install and maintain. However, these sensors are also characterized by a low selectivity. Additionally, their service life is limited, and external influences such as moisture can falsify the measurement result.

5.3 Fire Detection Layer

Flame sensors can be utilized in a worst-case scenario of ignition. While a H_2 flame is barely or not at all visible to the human eye, flame sensors utilize infrared or a combination of infrared and ultraviolet detectors. An alarm is triggered if a sensor detects an emission corresponding to the configured wavelength. The primary advantage of this approach is that it enables the safe detection of a H_2 flame from a distance. However, most detectors lack a 360° all-around view function and only respond at specific distances. Besides, the sensors are susceptible to obstruction by water, dirt, ice, and grime, which can impede their functionality. Ultraviolet and infrared sensors also have a cross sensitivity to certain interferences (other ultraviolet and infrared sources, reflection or technical applications)

6. Recommendations for the Energy-Intensive Industry

A plethora of databases, standards, guidelines, and rules for the design of proper H_2 plants have now been developed to ensure and optimize safety. These are to be regarded as supplements to the prevailing standards, guidelines, regulations, and legal stipulations concerning safety precautions for individuals,

materials, components, systems, and the environment in the context of flammable gases.

A pivotal component in the design of H₂ systems is ISO/TR 15916:2015, entitled "Basic considerations for the safety of hydrogen systems".

When selecting materials, databases such as "Technical Reference for Hydrogen - Compatibility of Materials" (Marchi and Somerday 2012) and "Hydrogen Embrittlement" (Lee and Woods 2016) can help with the pre-selection of materials for H₂ system components. The ISO/TR 15916:2015 annex also lists some materials and their compatibility for H₂ applications. The system should be designed to meet the requirements for storage or production, conditioning, and use of H₂, considering product's quality and quantity.

To minimize or avoid the accumulation of H₂ into an explosive atmosphere, it is recommended the DIN EN 1127-1:2019-10, "Explosive atmospheres - Explosion prevention and protection - Part 1: Basic concepts and methodology". The German TRGS 722 "Avoidance or restriction of hazardous explosive atmospheres" contains additional details and concepts, for example, "technically permanently tight" designed connection points.

To ensure the effective management of H₂ releases, it is important to implement a monitoring system at multiple escalation stages. In open-air applications, the primary concerns are leak detection and fire detection, as the reliability of gas detection is compromised due to the potential for falsified measured values. H₂ Detection tape at joints is recommended to facilitate the detection of the most minor leaks during personal inspections. Also, the deployment of sensors should be tailored to the system's spatial requirements, dimensions, and exhaust air capabilities. Acoustic sensors, or inline measurement technology such as differential pressure sensors, are practical tools for detecting leaks. The gas detection layer can be employed in conjunction with or as a substitute for acoustic sensors for system components that are not susceptible to external influences, such as wind. The use of these sensors must be in accordance with the stipulations outlined in ISO 26142:2010-06, H₂ detection Apparatus - Stationary applications.

7. Conclusion

In conclusion, this study provides only an overview of the current challenges of fuel switching in energy-intensive industries. It does not claim to be exhaustive with regard to potential risks, their occurrence and avoidance and the standards listed. The directives and standards listed in Chapter 2 can be used as key guidance documents for system operators and contractors. Each industrial operator must have a safety and risk management system in place for its specific application, which must be carried out by specialised personnel.

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References

- Destatis (2024). Industry, manufacturing - Importance of energy-intensive industries in Germany. Federal Statistical Office (Destatis). <https://www.destatis.de/DE/Themen/Branchen-Unternehmen/Industrie-Verarbeitendes-Gewerbe/produktionsindex-energieintensive-branchen.html> (accessed August 16, 2024).
- European Parliament (2023). Climate Change: The Greenhouse Gases Causing Global Warming. European Parliament. <https://www.europarl.europa.eu/topics/en/article/20230316STO77629/climate-change-the-greenhouse-gases-causing-global-warming>. (accessed August 20, 2024).
- European Consilium (2023). Where Does the EU's Gas Come from? European Consilium. <https://www.consilium.europa.eu/en/infographics/eu-gas-supply/>. (accessed August 20, 2024).
- Vehoff, H. (1997). Hydrogen Related Material Problems. In H. Wipf, *Hydrogen in Metals III: Properties and Applications*, pp. 215–278. Springer.
- Pundt, A. (2004). Hydrogen in Nano-Sized Metals. *Advanced Engineering Materials* 6, No. 1–2, pp. 11–21.
- Westlake, D. G. (1969). Generalized model for hydrogen embrittlement. *ASM (Amer. Soc. Metals), Trans. Quart.* 62, No. 4, pp. 1000–1006.
- Birbaum, H. K. (1983). Mechanisms of Hydrogen Related Fracture of Metals. In R. M. Latanision and J. R. Pickens, *Atomistics of Fracture*, pp. 733–769. Springer.
- Pfeil, L. B. (1926). The Effect of Occluded Hydrogen on the Tensile Strength of Iron. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* 112, No. 760, pp. 182–195.
- Oriani, R. A. (1970). The diffusion and trapping of hydrogen in steel. *Acta Metallurgica* 18, No. 1, pp. 147–157.
- Gangloff, R. P. (2003). Hydrogen Assisted Cracking of High Strength Alloys. In I. Milne, R. O. Ritchie and B. Karihaloo, *Comprehensive structural integrity* 6, pp. 31–101. Elsevier Science.
- Troiano, A. R. (2016). The Role of Hydrogen and Other Interstitials in the Mechanical Behavior of Metals. *Metallography, Microstructure, and Analysis* 5, No. 6, pp. 557–569.
- Knott, J. (2013). Fracture Toughness and Hydrogen-Assisted Crack Growth in Engineering Alloys. *Hydrogen Effects in Materials*, pp. 385–408.
- Lynch, S. P. (2012). Hydrogen Embrittlement Phenomena and Mechanisms. *Corrosion Reviews* 30, No. 3–4, pp. 105–123.
- Nagao, A., M. Daddamia, B. P. Somerday, P. Sofronis, and R. O. Ritchie, (2018). Hydrogen-Enhanced-Plasticity Mediated Decohesion for Hydrogen-Induced Intergranular and "Quasi-Cleavage" Fracture of Lath Martensitic Steels. *Journal of the Mechanics and Physics of Solids* 112, pp. 403–430.
- Wasim, M., M. B. Djukic, and T. D. Ngo (2021). Influence of Hydrogen-Enhanced Plasticity and Decohesion Mechanisms of Hydrogen Embrittlement on the Fracture Resistance of Steel. *Engineering Failure Analysis* 123, pp. 105312.
- Dwivedi, S. K., and M. Vishwakarma (2018). Hydrogen Embrittlement in Different Materials: A Review. *International Journal of Hydrogen Energy* 43, No. 46, pp. 21603–21616.
- Beachem, C. D. (1972). A New Model for Hydrogen-Assisted Cracking (Hydrogen "Embrittlement"). *Metallurgical Transactions* 3, No. 2, pp. 441–455.
- Robertson, I. M., H. K. Birbaum and P. Sofronis (2009). Hydrogen effects on plasticity. *Dislocations in solids*, 15, 249–293.
- Barrera, O., D. Bombac, Y., Chen, T. D. Daff, E. Galindo-Nava, P. Gong, D. Haley, R. Horton, I. Katzarov, J. R. Kermode, C. Liverani, M. Stopher and F. Sweeney (2018). Understanding and Mitigating Hydrogen Embrittlement of Steels: A Review of Experimental, Modelling and Design Progress from Atomistic to Continuum. *Journal of Materials Science* 53, No. 9, pp. 6251–6290.
- Lynch, S. P. (1986). A Fractographic Study of Hydrogen-Assisted Cracking and Liquid-Metal Embrittlement in Nickel. *Journal of Materials Science* 21, No. 2, pp. 692–704.
- Lynch, S. P. (1988). Environmentally Assisted Cracking: Overview of Evidence for an Adsorption-Induced Localised-Slip Process. *Acta Metallurgica* 36, No. 10, pp. 2639–2661.

- Pundt, A. and R. Kirchheim (2006). Hydrogen in metals: Microstructural Aspects. *Annual Review of Materials Research* 36, No. 1, pp 555–608
- Kuk, Y., P. J. Silverman, and H. Q. Nguyen (1987). Adsorbate-Induced Reconstruction in the Ni(110)-H System', *Physical Review Letters* 59, No. 13, pp 1452–1455
- Song, J. and W. A. Curtin (2013). Atomic Mechanism and Prediction of Hydrogen Embrittlement in Iron. *Nature Materials* 12, No. 2, pp 145–151
- Nagumo, M. (2004). Hydrogen related failure of steels - A new aspect. *Materials Science and Technology* 20, pp 940–950
- McLellan, R. B. and Z. R. Xu (1997). Hydrogen-Induced Vacancies in the Iron Lattice. *Scripta Materialia* 36, No. 10, pp 1201–1205
- Sakaki, K., T. Kawase, M. Hirato., M. Mizuno, H. Araki, Y. Shirai, and M. Nagumo (2006). The Effect of Hydrogen on Vacancy Generation in Iron by Plastic Deformation, *Scripta Materialia* 55, No. 11, pp 1031–1034
- Pradhan, P. K., P. R. Dash, P. S. Robi, and S. K. Roy (2012). Micro Void Coalescence of Ductile Fracture in Mild Steel during Tensile Straining. *Fracture and Structural Integrity* 6, No 19, pp 51–60
- Venezuela, J., Q. Zhou, Q. Liu, H. Li, M. Zhang, M. S. Dargusch, and A. Atrons (2018). The Influence of Microstructure on the Hydrogen Embrittlement Susceptibility of Martensitic Advanced High Strength Steels. *Materials Today Communications* 17, pp. 1–14
- Hoover, W. R., S. L. Robinson, R. E. Stoltz, and J. R. Spingarn (1981). Hydrogen Compatibility of Structural Materials for Energy Storage and Transmission. No. 81, 29598. NASA STI/Recon, Livermore, CA
- Raymond, L., H. J. Cialone, and J. H. Holbrook (1988). Sensitivity of Steels to Degradation in Gaseous Hydrogen. *Hydrogen embrittlement: prevention and control*. PA 19428-2959, pp 134–152. ASTM International
- Thompson, A. and N. R. Moody (1994). Hydrogen Effects in Metals. Minerals, Metals and Materials Soc
- Cialone, H. J. and J. H. Holbrook (1985). Effects of Gaseous Hydrogen on Fatigue Crack Growth in Pipeline Steel. *Metallurgical Transactions A* 16, No. 1, pp 115–122
- Louthan, M. R., I. L. May, and G. F. Van der Voort (1986). Welding, Failure Analysis and Metallography. ASM International
- Loginow, A. W. and E. H. Phelps (1975). Steels for Seamless Hydrogen Pressure Vessels. *Corrosion* 31:11, pp 404–412
- Walter, R. J. and W. T. Chandler (1976). Cyclic-Load Crack Growth in ASME SA-105 Grade II Steel in High-Pressure Hydrogen at Ambient Temperature. *Effect of hydrogen on behavior of materials*. 750907, pp 273–186
- Lee, J. A. and S. Woods (2016). Hydrogen Embrittlement. NASA/TM-2016–218602
- Caskey Jr., G. R. (1983). Hydrogen Compatibility Handbook for Stainless Steels. *DP-1643*. Du Pont de Nemours
- Murray, G. T., J. P. Bouffard, and D. Briggs (1987). Retardation of Hydrogen Embrittlement of 17-4ph Stainless Steels by Nonmetallic Surface Layers. *Metallurgical Transactions A* 18, No. 1, pp 162–164
- Jewett, R. P., R. J. Walter, W. T. Chandler, and R. P. Frohberg (1973). Hydrogen Environment Embrittlement of Metals. NASA-CR-2163. NASA. Washington, D.C.
- Chandler, W. T. and R. J. Walter (1974). Testing to determine the effect of high-pressure hydrogen environments on the mechanical properties of metals. In L. Raymond, *Hydrogen embrittlement testing*. Pp 170–197. ASTM International.
- Lee, J. A. (2012). Hydrogen embrittlement of nickel, cobalt and iron-based superalloys. in R. P. Gangloff and B. P. Somerday, *Gaseous Hydrogen Embrittlement of Materials in Energy Technologies 2*, pp 624–667. Woodhead Publishing
- Morea, S. F. and S. T. Wu (1984). *Advanced High Pressure O2/H2' Technology*. Proceedings of a Conference Held at George C. Marshall Space Flight Center, (Vol. 2372). NASA-CP-2372. NASA. Washington, D.C
- Cooper, R. A. (1976). Low cycle fatigue life of two nickel-base casting alloys in a hydrogen environment. In A.W. Thompson and I.M. Bernstein, *Effect of hydrogen on behavior of materials*. NAS8-27980. pp. 589–601. AIME
- Fritzemeier, L. G. and M. A. Jacinto (1989). Hydrogen Environment Effects on Beryllium and Titanium Aluminides. In N.R. Moody and A.W. Thompson, *Hydrogen Effects on Material Behavior*, pp. 533–542. TMS
- Wille, G. W. and J. W. Davis (1981). Hydrogen in titanium alloys. DOE/ET/52039-2. McDonnell Douglas Astronautics Co., St. Louis, MO
- Tal-Gutelmacher, E. and D. Eliezer (2005). Hydrogen Cracking in Titanium-Based Alloys. *Journal of Alloys and Compounds* 404–406, pp 621–625
- Christ, H. J., A. Senemmar, M. Decker and K. Prüssner (2003). Effect of Hydrogen on Mechanical Properties of β -Titanium Alloys. *Sadhana* 28, No. 3, pp 453–465
- Ellis, D. L., A. K. Misra, and R. L. Dreshfield (1993). Effect of Hydrogen Exposure on a Cu-8 Cr-4 Nb Alloy for Rocket Motor Applications. NASA-TM-106429. NASA. Washington, D.C
- Louthan, M. R. and G. R. Caskey Jr. (1976). Hydrogen transport and embrittlement in structural metals. *International Journal of Hydrogen Energy* 1, No. 3, pp 291–305
- Lorge, O., B. J. Briscoe, and P. Dang (1999). Gas Induced Damage in Poly(Vinylidene Fluoride) Exposed to Decompression. *Polymer* 40, No. 11, pp 2981–2991
- Barth, R. R., K. L. Simmons, and C. W. San Marchi (2013). Polymers for Hydrogen Infrastructure and Vehicle Fuel Systems. SAND2013-8904. Sandia National Lab. Livermore, CA
- Lee, J. H., Y. Kim, I. Kim, S. B. Hong, and H. S. Yun (2024). Comparative Analysis of Ultrasonic and Traditional Gas-Leak Detection Systems in the Process Industries: A Monte Carlo Approach. *Processes* 12, No. 1, pp 67
- Ivanov, I. I., A. M. Baranov, D. N. Spirjakin, S. Akbari, S. M. Mironov, H. Karami, and G. B. Gharehpetian (2022). Expanding Catalytic Sensor Capabilities to Combustible Gas Mixtures Monitoring', *Measurement* 194, 111103
- Marchi, C. S. and B. Somerday (2012). Technical Reference for Hydrogen Compatibility of Materials. SAND2012-7321. Sandia National Laboratories. Livermore, CA