hydrogen

MDPI

Communication

Instances of Safety-Related Advances in Hydrogen as Regards Its Gaseous Transport and Buffer Storage and Its Solid-State Storage †

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† This paper is dedicated to the late Professor Akira Ueno at Ritsumeikan University (Japan).

Abstract: As part of the ongoing transition from fossil fuels to renewable energies, advances are particularly expected in terms of safe and cost-effective solutions. Publicising instances of such advances and emphasising global safety considerations constitute the rationale for this communication. Knowing that high-strength steels can prove economically relevant in the foreseeable future for transporting hydrogen in pipelines by limiting the pipe wall thickness required to withstand high pressure, one advance relates to a bench designed to assess the safe transport or renewable-energy-related buffer storage of hydrogen gas. That bench has been implemented at the technology readiness level TRL 6 to test initially intact, damaged, or pre-notched 500 mm-long pipe sections with nominal diameters ranging from 300 to 900 mm in order to appropriately validate or question the use of reputedly satisfactory predictive models in terms of hydrogen embrittlement and potential corollary failure. The other advance discussed herein relates to the reactivation of a previously fruitful applied research into safe mass solid-state hydrogen storage by magnesium hydride through a new public–private partnership. This latest development comes at a time when markets have started driving the hydrogen economy, bearing in mind that phase-change materials make it possible to level out heat transfers during the absorption/melting and solidification/desorption cycles and to attain an overall energy efficiency of up to 80% for MgH_2-based compacts doped with expanded natural graphite.

Keywords: safety concerns; hydrogen transport; buffer storage; solid-state storage; metal hydrides

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1. Introduction

Hydrogen has the highest gravimetric density of all fuels and therefore plays a pivotal role as an energy vector in the ongoing transition from fossil fuels to renewable energies. However, hydrogen has a low volumetric density which, so far, makes transporting or storing it difficult and expensive [1]. More generally, all alternative fuels, like hydrogen, have to prove their technical maturity and economic interest while the regulatory framework is still missing in most countries [2]; this is the reason why any achievement of safe and cost-effective improvements is worth mentioning.

Section 2 of this paper serves as a reminder of the safety considerations, codes, and standards as well as of the lessons learnt in relation to hydrogen. This section serves as an introduction for the following sections, which describe two instances of advances that are both committed to improving safety [3,4] and, therefore, fall within the global search for environmentally friendly energy solutions that are safe by design [5–7]. These instances relate to two essential sectors of the hydrogen infrastructure, namely transport and storage.

As regards hydrogen gas transport, the underlying rationale for identifying and qualifying new materials for pipelines stems from the limited amount of hydrogen in 'hythane', a methane–hydrogen fuel that is a gas mixture generally composed of 20 vol% H_2 and 80 vol% CH_4 which has been given its own name, and that existing natural-gas pipelines can transport [8,9]. Although large-diameter pipelines constitute the most economical way to transport hydrogen in large amounts, comprehensive cost analyses have yet to be carried out to determine whether existing pipelines could be repurposed by coating their inner wall with a protective layer or whether new pipelines should be built [10–12]. In the latter case, higher-grade steels such as X80 can be used to limit the pipe wall thickness required to withstand high pressure, thereby reducing the overall cost [13]. The greater the technological readiness of this approach, the higher the appropriate level of technical testing resources required to validate or question the results obtained from predictive damage and fracture codes; innovation in that matter has to do with the need to test structures that are more complex than the modelled structures used for finite-element analysis.

In another area of development, solid-state storage, which involves storing hydrogen in solid materials such as metal hydrides, chemical hydrides, or adsorbents, offers high volumetric energy densities and improved safety compared to gaseous or liquid storage [1,14–17]. Magnesium hydride (MgH_2), with its high hydrogen storage capacity, relatively lower cost, good reversibility, abundant natural reserves, and environmental friendliness, has been the subject of extensive research over the past decade [4,10,18,19]. Noticeably, whereas McPhy-Energy produced fairly reactive MgH_2-based pellets very early on [20], better conditions for the development of mass applications seem to be emerging now [4] and, therefore, offer the opportunity to benefit directly from the improvements achieved in the meantime.

2. Safety, Codes, and Standards

The two instances of advances mentioned in this paper deal with safety issues in opposite ways, the first one having been specifically developed to address the challenges in the transport or buffer storage of hydrogen gas, while the second one has, instead, been developed to avoid storing hydrogen in a gaseous state.

2.1. Safety Considerations about Hydrogen Gas

Hydrogen used for energy appliances is colourless, odourless, tasteless, non-toxic, non-poisonous, and non-corrosive. However, compared to conventional hydrocarbons, hydrogen has certain particularities that must be taken into account in safety studies:

- Because of its wide flammability range from 4 to 75 mol% at ambient pressure and temperature (Figure 1), hydrogen is classified as an extremely flammable gas in accordance with Classification, Labelling and Packaging Regulation (EC) No 1272/2008 of 16 December 2008 [21];
- Hydrogen ignites very readily when close to stoichiometric conditions, where a minimum ignition energy (MIE) in air is observed at just 17 μJ [22] (Figure 2)—for comparison, an electrostatic discharge just felt by a person is around 1000 μJ—and the MIE decreases in pure oxygen to 1.2 μJ [23]. This characteristic is reflected by the IIC gas subgroup for equipment used in potentially explosive atmospheres (ATEX) in accordance with EU legislation (Directive 2014/34/EU) [24];
- The burning velocity of hydrogen in air at stoichiometric ambient conditions is $2.37\ \mathrm{m{\cdot}s^{-1}}$ [25] and can even increase up to $3.5\ \mathrm{m{\cdot}s^{-1}}$ at a concentration of 40.1% [26]. Related to its fast chemical kinetics and high diffusivity, this burning velocity is higher than that of other hydrocarbon fuel–air mixtures and results in a greater chance for a transition of the combustion mode from deflagration to detonation;
- Due to its small-sized molecule, hydrogen leaks are more likely to occur than with other inflammable gases. Furthermore, due to its low viscosity, the volume flow rate is then nearly three times higher compared, for instance, with methane [27];

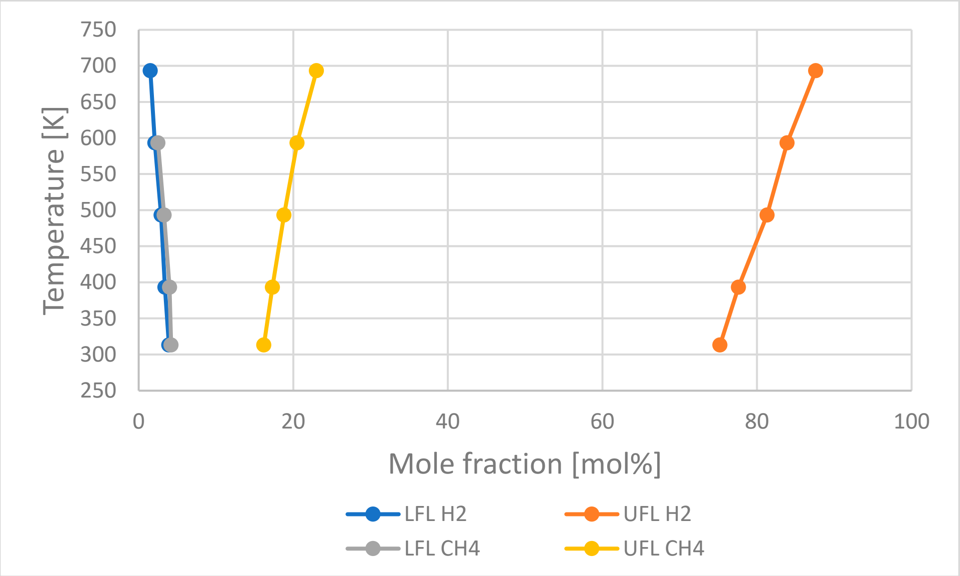


Figure 1. Influence of temperature on the lower (LFL) and upper (UFL) flammability limits for hydrogen and methane, respectively [28].

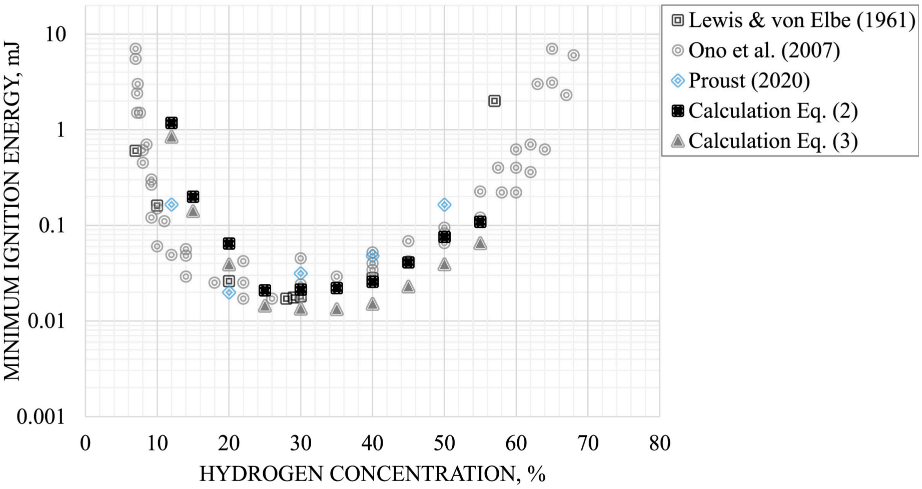
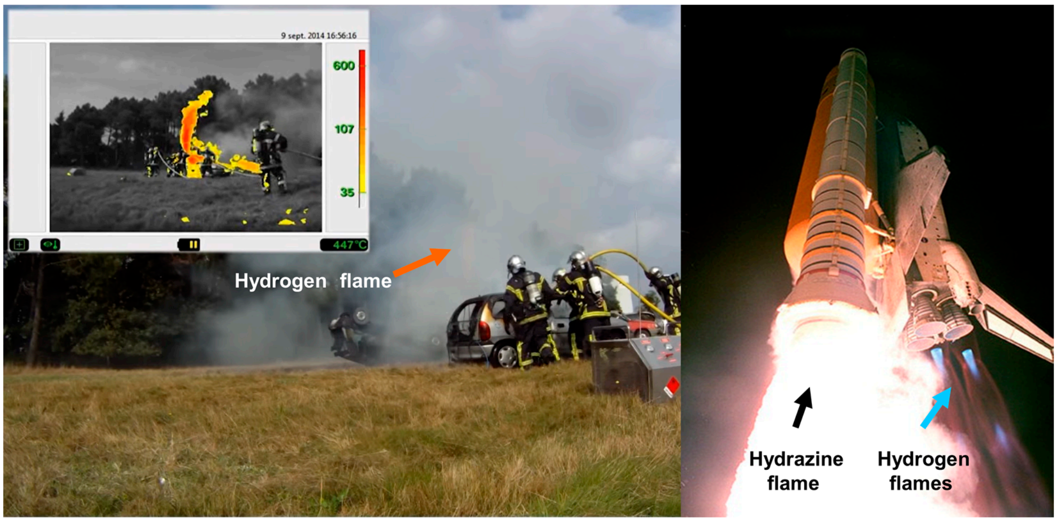


Figure 2. MIE calculated (Equations (2) and (3) [22]) and experimental [22,29,30] as a function of hydrogen concentration in air [31].

- At ambient conditions, hydrogen is about 8 times lighter than natural gas and 14 times lighter than air. While released in an open environment, it will typically rise and disperse rapidly. This is a safety advantage in an outside environment, for instance, with a subsonic or vertically orientated leak, but it has to be carefully taken into account in a confined space by a pertinent leak detection system and a ventilation assuring sufficient air dilution at the leak source;
- A jet fire of hydrogen generates a pale blue flame almost invisible in daylight (Figure 3a). However, its visibility can be increased if particles are entrained in the flame (e.g., dust) and hydrogen flames are also visible at night, as shown in Figure 3b. In air, a premixed stoichiometric blend can lead to a flame temperature of 2403 K [25];



(**a**) (**b**)

Figure 3. Visibility of hydrogen flames: (**a**) light-duty vehicle burn test [32]; (**b**) space shuttle launch [33].

- The dominant energy emission occurs in the mid-infrared, where the peak irradiance is more than one thousand times greater than the peak measured in the ultraviolet. Thermal radiation is therefore very limited and unconventional UV detection is required [33];
- According to different experiences with hydrogen at concentrations below 10 vol% in air [34], the explosion resembles a flash fire with nearly no pressure rise. At higher concentrations, deflagration is observed where the flame speed is subsonic, and the maximum pressure peak is reached at 8 bar (800 kPa) in air and 10 bar in pure oxygen [35]. At supersonic flame speeds, detonation occurs and can be observed at ranges in excess of 12.5 vol% of hydrogen, where explosion pressures 15–20 times greater than the initial pressure can occur at the detonation front depending on the concentration and turbulence conditions in the environment. The most violent reaction occurs when hydrogen is near its stoichiometric value of 29.5 vol% in air. Table 1 summarises the main differences between deflagration and detonation;

Table 1. Main differences between deflagration and detonation.

	Deflagration	**Detonation**
Speed of flame propagation	Subsonic, e.g., never exceeding the level of 10 m·s^{-1} for lean hydrogen-air mixtures in a smooth 10 mm-thick channel	Supersonic, e.g., for stoichiometric hydrogen—air mixtures: 1600 to 2000 m·s^{-1}
Mechanism of propagation	The flame front propagates by transferring heat and mass to the unburnt hydrogen–air mixture ahead of the front	Powerful pressure wave compressing the unburnt gas ahead of the wave up to a temperature above the auto-ignition temperature
Protection by venting	Effective explosion protection	Ineffective protection

- Various embrittlement mechanisms such as hydrogen-induced cracking or blistering are also possible with hydrogen depending both on the metal, alloy, or composite selection and on the process parameters (temperature and pressure typically), so that the choice of the material constitutes a point of vigilance when designing containers or pipelines (Section 3).

Because of the complex process of establishing regulations, they often lag behind innovation. However, the normative framework governing hydrogen safety has benefitted from dynamic updates in recent years. These updates have been driven by committees such as ISO Technical Committee 197, which focuses on standardisation in the field of systems and devices for the production, storage, transport, measurement, and use of hydrogen. In Europe, CEN/TC 268 Working Group 5 deals specifically with hydrogen technology applications in support of Directive 2014/94/EU and its planned revision under the 'Fit for 55' package, as requested by the European Commission. In addition, CEN-CENELEC Joint Technical Committee 6 is responsible for devices and connections related to the production, storage, transport, distribution, measurement, and use of hydrogen from renewable and other energy sources.

2.2. Lessons Learnt with Hydrogen

To correctly address the risks, the specific characteristics of hydrogen shall be taken into account in risk analyses. A prudent step before any risk analysis is to look at potential lessons learnt from hydrogen regarding the process previously implemented during its lifecycle. There are only two hydrogen-specific free databases in the world:

- The Hydrogen Incident and Accident Database 2.0 (HIAD) [36] with 706 incidents;
- The Hydrogen Lessons Learned Reporting Tool [37] with 221 incidents.

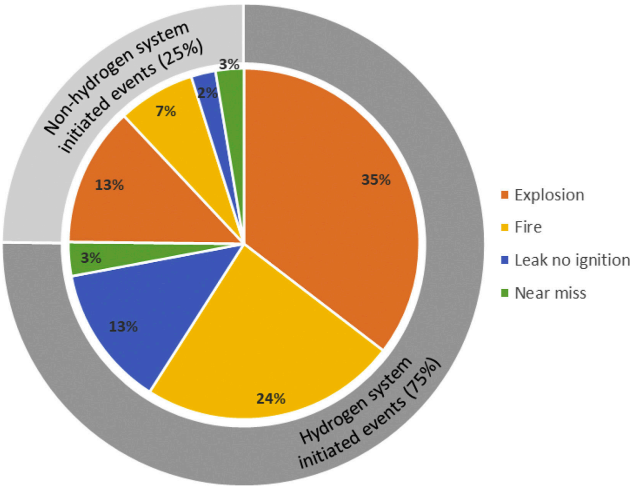


Figure 4. Analysis of the HIAD database in percentages of the events initiated by hydrogen or non-hydrogen systems (outer circle) and those related to different consequences (the inner circle) [38].

Additionally, there are some non-specific free databases such as the French database Accident Reporting Information Analysis [39], maintained by the Bureau for Analysis of Industrial Risks and Pollutions (BARPI), which reports 955 incidents with hydrogen, therein mainly involved as a chemical product and not as an energy carrier. As well, there is the Japanese one, the High Pressure Gas Safety Act Database [40], which presents a compilation of statistics on accidents, with a focus on accidents resulting in injury or death, especially those having occurred at manufacturing plants for high pressure gas. Some further databases are described by Campari et al. [41].

The HIAD 2.0 analysis of Wen et al. [38] states that 'about half of the incidents were related to [organisational] and management factors. Material/manufacturing errors are the second main cause with a share of 35%. Other main factors include individual and human factors (29%), system design errors (27%) and job factors (14%). Only 11% of the incidents were related to installation errors. An important message from this analysis is that the "soft factors" play just as big a role in the causes of incidents as technical factors' (Figure 4).

A similar conclusion has been drawn by BARPI for incidents involving hydrogen in the chemical, petrochemical, refining, and nuclear industries, as well as in transport (Table 2). Indeed, an analysis shows that, in over 70% of the cases, the organisational and human factor played a predominant role in the root causes for these accidents to occur. BARPI therefore stressed that constant vigilance must be exercised at all levels—management, field operatives, subcontractors—bearing in mind that in the presence of hydrogen, the risk of ignition is permanent [42]. It can be noted that, owing to the typology of the accidents and to the fast kinetics of the associated phenomena, the human consequences of these accidents mainly concern the employees of the damaged sites, with the first responders and the public being rarely affected. For example, whenever the status of the victims was provided, the fatal outcomes turned out to concern employees (the five cases recorded for France were all linked to maintenance work).

Table 2. Severity of the accidents (consequences and frequency) [42].

Consequence	Number of Accidents	% *
Fatal outcome·s	25	12
Serious injuries	28	13
Injuries (serious ones included)	70	33
Onsite damage	183	86
Offsite damage	17	8
Operating losses	89	42
Population evacuation	8	3.8

* Out of 213 accidents where consequences are known, as collected until 2010 by BARPI.

3. Transport and High-Capacity Buffer Storage of Hydrogen Gas

In this first instance, the whole implementation of an innovative test bench has been carried out to address the safety issues raised by the use of hydrogen gas.

The materials for the transport of hydrogen gas are subject to numerous studies. By limiting the pipe wall thickness required to withstand high pressure, high-strength steels can prove economically relevant for safely transporting large hydrogen gas quantities over a long distance in pipelines, although this gas raises specific constraints [13]:

- In many circumstances, hydrogen gas can weaken metallic materials, notably high-strength steels containing ferritic phases;
- The volumetric density of hydrogen gas being much lower than that of natural gas, the pressure has to be increased in order to deliver the same amount of energy, whereas, thanks to the higher compressibility factor of hydrogen, its pressure drop in a pipeline over a long distance is significantly lower than that of natural gas.

The renewable-energy-related high-capacity buffer storage of hydrogen shall also be considered because it induces more severe constraints than its transport in terms of cycling. This buffer storage allows the conversion of excess electricity into hydrogen to compensate for the intermittency inherent to both photovoltaic panels and windfarms, as the stored gas can be reinjected at the appropriate times either into the electricity network (after reconversion) or into the gas one (by methanation), or, of course, be directly used as a clean fuel (green hydrogen).

Addressing these concerns has led to assessing the case of the high-strength X80 steel. This has been engaged in a collaborative way with ENGIE Lab CRIGEN (Stains, France) and CEA-LITEN (Grenoble, France) [43,44]. The test bench herein presented entered that collaborative way and has been designed for carrying out tests on defect-bearing pipe sections under hydrogen that should help in quantifying the impact of hydrogen on their failure pressure and lifespan. Two subsequent phases have been followed:

- Validation phase: the main objective was to demonstrate the capacity of the implemented bench to test a selection of representative pipe sections under cyclic loading at a low frequency (40 s per cycle typically). The possibility to test under monotonic loading was also to be demonstrated;

- Operational phase: a series of bursting tests under monotonic loading has been implemented on pre-notched pipe sections. The pressurised medium was pure hydrogen, which corresponds to a 'worst-case' scenario, for the effect to be as significant as possible. In each case, a reference test has been carried out under nitrogen pressure for comparison with the results obtained under hydrogen. SEM observations were carried out initially to determine the fragile or brittle nature of the fractures.

  These two phases are detailed below.

3.1. Validation Phase

The test bench co-owned by the French National Centre for Scientific Research and ENGIE has been implemented for several purposes, the first two ones being of prime interest for safety considerations:

- To validate defect failure assessment models by comparing their numerical results with the experimental ones obtained on the test bench;
- To study the stability or instability of internal as well as external defects on hydrogen pipelines, considering the fact that, in highly populated areas such as Western Europe, the most frequent incidents on natural-gas pipelines are due to mechanical damage in relation to third-party aggressions [45]. Internal corrosion-type defects are in the minority, or even non-existent, due to the non-corrosive qualities of the transported gas, but there may be occurrences of internal defects at the girth welds (Figure 5c);
- To validate the transferability of the fracture-mechanics results obtained on laboratory specimens to a real structure;
- To possibly serve as an instrumented hydrogen reservoir to be coupled, for instance, with an electrolyser, as in the case of a renewable-energy-related buffer storage.

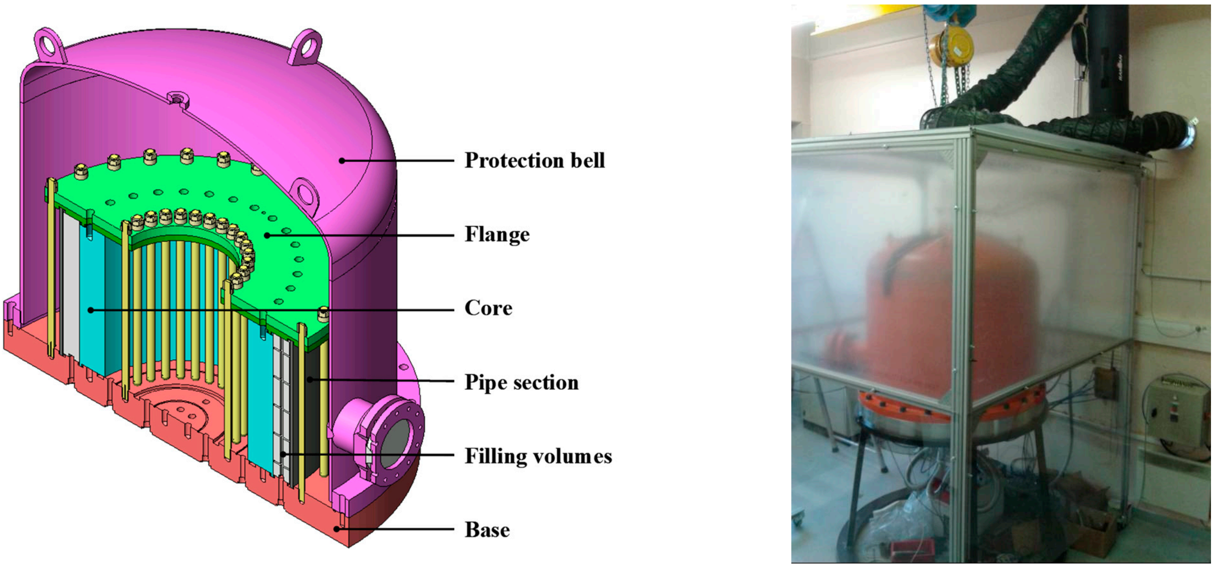
(**a**) (**b**) (**c**) (**d**)

Figure 5. Types of defects on pipelines: (**a**) dents; (**b**) gouges; (**c**) welding defects; (**d**) corrosion.

More particularly, the test bench has been designed and implemented for reproducing real operating conditions in terms of:

- The presence of idealised or realistic defects identical to those identified by the industrial partner (Figure 5);
- The same gas/defect interactions as for a distribution pipeline;
- The bi-axial stress state in the pipeline section.

In comparison with usual laboratory tests, compliance with the above conditions was deemed to mean that the test bench would best reproduce the real operating conditions of a gas transport pipeline. It is in this regard that it has been implemented as a complementary means of investigation compared to those available at ENGIE and CEA-LITEN. The technical requirements included specifications for monotonic burst testing up to 300 bar or cyclic burst testing between 40 and 100 bar, in hydrogen or nitrogen, and the test cell (Figure 6) was itself designed to test 500 mm-long pipe sections that adhere to ISO 6708 'Diamètre Nominal' (DN) and U.S. Nominal Pipe Size (NPS) DN 900/NPS 36 (Ø 914.4 mm), DN 600/NPS 24 (Ø 609.6 mm), or DN 300/NPS 12 (Ø 323.9 mm). Coupled with the representative operating conditions mentioned above, these dimensions are large enough for the test bench to be considered as at the TRL 6 level in terms of technological readiness. In particular, the sections to be tested are long enough to include two pipe ends connected by a circumferential weld (Figure 5c).



(**a**) (**b**)

Figure 6. (**a**) 3D cross-section of the test cell; (**b**) mobile hood and air-extraction duct surrounding the test cell during testing under hydrogen.

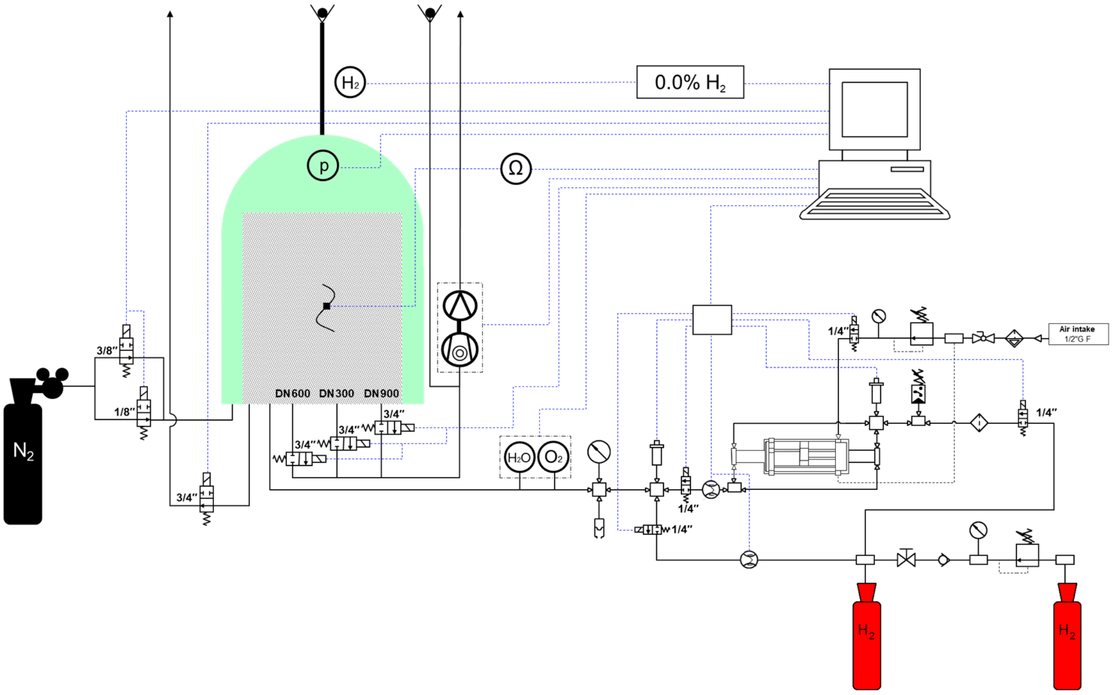


Figure 7. Overall diagram of the test bench.

The operating conditions are in accordance with the main diagram shown in Figure 7; a controllable valve has been added to integrate any refilling of the buffer cylinder into the pilot program, so that cycling is not interrupted even in the event of micro-leakage. Compared with cyclic loadings where the compressor is used to its full capacity, monotonic loadings could have given rise to elevated pressure increments at the output of the compressor (irrespective of the accuracy of the setpoint); a throttle valve, a pressure sensor, and a buffer tank (refillable H_2 cylinder) have consequently been added and typically allow reducing the pressure increments to 0.4 bar, which is consistent with the expected pressure-ramp accuracy.

The purity required to evaluate any embrittlement effect (less than 1 ppm mol O_2 and less than 3 ppm mol H_2O) can be satisfied through the use of the commercial high-quality 'Alphagaz 2' hydrogen gas (Air Liquide, Paris, France), which contains less than 0.1 ppm mol O_2 and less than 0.5 ppm mol H_2O.

The description and the characteristics of the ATEX zones, as imposed by explosive-atmosphere-related safety rules, for the room hosting the test bench (the control computer is located outside this room) were established during the zoning; the internal volume of the protective bell (filled with nitrogen gas until the pipe section bursts) and its upper vent fall within Zone 1, while its external volume inside the mobile hood equipped with a continuously operating air-extraction duct (Figure 6b) falls within Zone 2. The possibility of performing tests with CH_4–H_2 or N_2–H_2 mixtures would not derogate from these provisions. Filling volumes are placed between the pipe-section wall and the test-cell core in order to reduce the volume of hydrogen as much as possible (Figure 6a) for both safety and operating reasons, the free volume being only intended for the occasional installation of severely dented pipe sections (Figure 5a).

The most salient constraint regarding the test-bench specifications was to ensure a bi-axial stress state in the pipe section. The possibility of introducing axial stresses (typically up to 21.5 MPa for 100 bar applied in a DN 300 pipe) has nevertheless been validated by clamping both ends of thick-walled pipe sections, where 'thick-walled pipe' refers to a 7.7 mm wall thickness for a DN 300 pipe as compared to a 4.2 mm for a 'thin-walled pipe'; both pipe sections shall, however, be considered as 'thin-walled' cylinders in terms of high-pressure containment (ratio between the outer and inner diameters below 1.1). The introduction of axial stresses aims at replicating real operating conditions, namely no axial stresses (the length of the pipe section can decrease freely as a result of the increase in internal pressure) or constrained axial deformations (clamped pipe section) for replicating above-ground and underground pipelines, respectively.

3.2. Experimental Phase

For low-strength steels, prevailing contentions [46] posit that embrittlement under static load would be the result of the synergetic action of shear localisation and decohesion mechanisms, but could be intergranular under a cyclic load. Fractographic evidence indeed suggests that hydrogen-assisted transgranular fracture under static loading is induced by void or microcrack initiation through decohesion at the internal interface (precipitate/inclusion or phase boundaries) ahead of a crack/notch accompanied by shear localisation leading to the linking of the void/microcrack with the tip of the crack.

For high-strength steels such as X80, modelling has to take into account their ferritic-pearlitic microstructure. A thorough study dealing with the hydrogen embrittlement susceptibility of the X80 steel had previously been performed [47] and the respective involvement of different hydrogen populations (adsorbed, diffusible, or trapped) on the associated embrittlement mechanisms has been addressed through tensile testing at various strain rates and hydrogen pressures. Changes in gas (hydrogen or nitrogen) during loading have also been imposed in order to be able to discriminate amongst the potential hydrogen embrittlement mechanisms proposed in the literature. The results of these tests have shown that hydrogen induces several kinds of damage including decohesion along ferrite/pearlite interfaces and microcrack initiations on the external surface.

Several other studies have been performed; one of them (Figure 8) showed a dramatic effect of hydrogen on the elongation for two different strain rates, as compared to tests in air and in nitrogen gas at the same gas pressure of 300 bar [48].

Defects in the microstructure, particularly precipitates, as well as dislocations are known to act as trap sites for hydrogen, but the hydrogen effect on mechanical properties may also be reinforced in the presence of highly triaxial stress states. It was therefore decided to test unclamped DN 300 pipe sections with a notch sized for an anticipated failure at 67 ± 15 bar under monotonic loading with a ramp of 0.1 bar$\cdot$s^{-1}. The external notch was machined at an equal distance from both ends and was oriented in the longitudinal direction of the pipe section. Pre-notched pipe sections were also equipped in their external part with several type CEA-06-125UT-350 'rosettes' (Vishay Measurements Group France, Chartres, France), each with two strain gauges set at 90°. The conditions for the proper diffusion of hydrogen before testing were also specified; they set the minimum exposure time to 12 h under slight overpressure. All tests were successfully performed and resulted in ruptures with full opening of the pipe section (Figure 9).

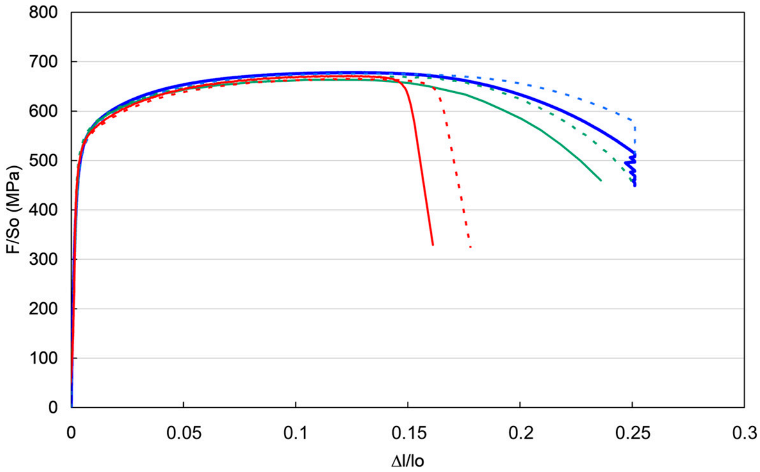


Figure 8. Hydrogen impact on tensile properties (red curves) as compared to air (blue curves) and nitrogen gas (green curves).

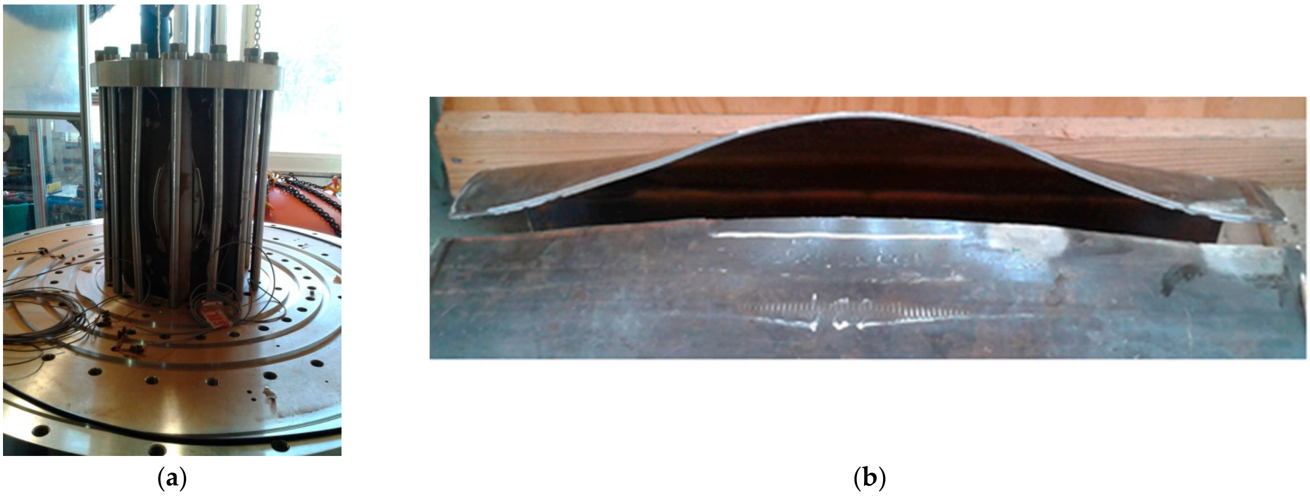

(**a**) (**b**)

Figure 9. Burst DN 300 pipe section still mounted on the test cell (**a**) and removed (**b**).

Fractographic investigations usually focus on the characterisation of either the ductile or brittle mode of rupture; however, both modes were observed on every tested pipe section. This dual behaviour is relevant with the strong texture that exists in the API 5L X80 steel, where the orientation of the ferritic–pearlitic microstructure is reinforced by rolling at the elaboration stage; this illustrates the kind of differences that may arise between a real structure and the modelled structures used for finite-element analyses, the apparent validity of damage and fracture codes being based on numerical-simulation results that are deemed correct when they are reproducible, regardless of the correctness of the modelled structure at the appropriate level. In this perspective, due to the difficulty, for modelling purposes, of taking into account too many aspects, such as the fact that large-sized pipes are longitudinally welded, the implemented test bench holds importance in its ability to assess their actual relevance. Similarly, with regard to future qualification standards, the test bench can provide guidance on the relevant mechanical tests to be applied in the field of hydrogen gas transport and buffer storage.

4. Safe Mass Storage in the Solid State

As already mentioned, the present instance inherently deals with safety issues from the outset, as it relates to an alternative way to store hydrogen. Indeed, solid-state storage eliminates the safety problems associated with hydrogen gas.

Between the production and uses of hydrogen, one of the main bottlenecks in its clean-energy-based chain is related to the distribution and consequently to the mass storage of this light element. Concerns to be addressed include:

1. Keeping physical or chemical operations as simple as possible for long-time operations;
2. Making kinetics fast enough to anticipate production and delivery that are both mostly intermittent;
3. Safe modes of management.

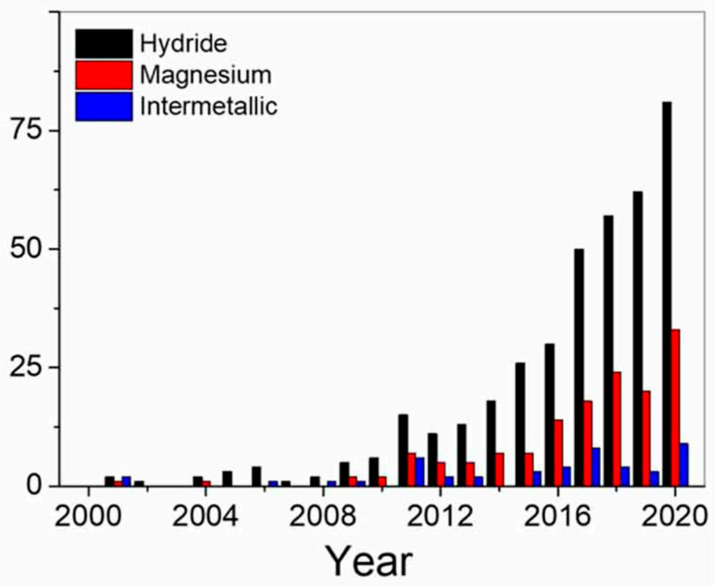


Figure 10. Number of scientific reviews per year published along the 20 past years dealing with hydrides (black), intermetallic systems (blue), or, more specifically, magnesium-based hydrides only (red) (source Scopus) [49].

In terms of densification, the comparison between molecular hydrogen either as a liquid at 20.4 K or as a gas under a pressure of 700 bar and a solid atomic form such as MgH_2 leads to figures of merit of 71, 42, and 106 $kg \cdot m^{-3}$, respectively. Incidentally, many other solid forms are actively considered, with wide panels of specific performances within reach: e.g., d-metal-based metals and alloys, complex metal hydrides (alanates and boranates), nano-carbonaceous adsorbers, molecular organic frameworks, and liquid organic hydrogen carriers [1]. As shown in Figure 10, during the past two decades, there was a huge increase in published reviews dealing with hydrogen storage, about 40% of them being, however, specifically dedicated to magnesium-based systems.

Compared to the many metals and alloys able to absorb hydrogen reversibly, magnesium exhibits very interesting advantages as well as some drawbacks. It is the seventh most abundant element in the Earth's crust and its extractive and refinement metallurgies are well developed. Consequently, it is not so expensive compared to aluminium. Also, recycling Mg by-products is rather easy since it is a bio-compatible element. It forms a mono-element hydride MgH_2 that will not be subject to disproportionation during adsorption/desorption cycles. Furthermore, the maximum hydrogen uptake is amongst the best for a solid-state metal hydrogen carrier, namely 7.6 wt%.

However, two main drawbacks have appeared when handling the reaction $Mg + H_2 \leftrightarrow MgH_2$:

1. The reaction is particularly slow, even when starting from raw powdered samples;
2. Active reaction takes place at over 300 °C but, interestingly, under a few bars of hydrogen pressure.

Considering the first point, the kinetics can be promptly accelerated by mechanical treatment of the metal particles. Since Mg is a ductile metal, the well-known method to promote a reactive material is to use the high-energy ball-milling technology, which can be applied to the pre-hydrogenated particles, as they exhibit the same fragile character as ceramics. The ball-milling treatment leads to reducing the size of the particles, which themselves contain nanometre-sized crystallites, to a few micrometres. Thanks to this mechanical treatment, the specific surface for the hydrogenation reaction is considerably increased and many defects (such as nucleation centres to form MgH_2) are distributed in the structure. Moreover, additives of many types, such as metal, alloys, oxides, halides, or alanates, which work as catalysts when introduced during the ball-milling operation, are proving to be markedly efficient in terms of hydrogenation/dehydrogenation kinetics. However, the ball-milling method is of limited value for the purpose of mass production, due also to energy, manpower, and safety (highly pyrophoric powders) concerns. With respect to the latter, good manufacturing practices are required; the metallic transfer unit must be filled with Ar gas prior to introducing the ball-milled powders when transferring them to the subsequent operations—which are also carried out under inert atmosphere—of blending with expanded natural graphite (ENG) and of pressing into the final compact. However, the final MgH_2-based compacts are outstandingly unreactive under air, even in contact with a flame, since the dissociation pressure is as low as 10^{-6} bar at room temperature.

Alternative routes have been found by using severe plastic deformation (SPD) techniques [50], enabling to develop the conditions required for a rapid nucleation in bulk Mg-based materials. SPD techniques indeed result in multiplying the crystal defects such as dislocations and twins, densifying the grain boundary network, and eventually delivering an ultrafine-grained structure. The main in-lab techniques used for demonstration are high-pressure torsion [51,52], equal-channel angular pressing [53,54], multiple cold rolling, accumulative roll bonding [55,56], and fast forging [57,58]. Once again, energy efficiency will be the key to effective implementation on a very large scale. Advantageously, when processing bulk materials through the SPD route, there is no pyrophoric effect as in the case of ball milling.

The second main drawback mentioned above proves critical for the low-temperature metal hydrides based on d-transition metals since they can reversibly store around 2 wt% H_2 at a moderate temperature and mostly work under a maximum hydrogen pressure of a few tens of bars. The enthalpy of reaction of H_2 with Mg to form MgH_2, $\Delta H \sim -74\ kJ \cdot mol_{H2}{}^{-1}$, leads to exothermic absorption and endothermic desorption. It corresponds to a third of the heat of combustion of hydrogen, which is ~33 $kWh \cdot kg_{H2}{}^{-1}$. This means that the thermal part of the energy must be managed and better integrated throughout the process, using appropriate materials and tanks. In this respect, the combined use of ENG-doped MgH_2-based compacts with an ancillary tank containing a phase-change material (PCM) allows increasing the total storage performance up to an 80% energy efficiency [59–62].

To obtain such results, one the hand, the level of doping with ENG has to markedly improve the conductivity of the MgH_2-based compacts and, on the other hand, the melting temperature of the PCM must be adjusted between the absorption and desorption temperatures of the compacts, as shown in Figure 11. In such a configuration, ideal absorption can be achieved at 10 bar with a temperature maintained down to 340 °C, while desorption achieved at almost 310 °C leads to delivering a pressure of about 2 bar.

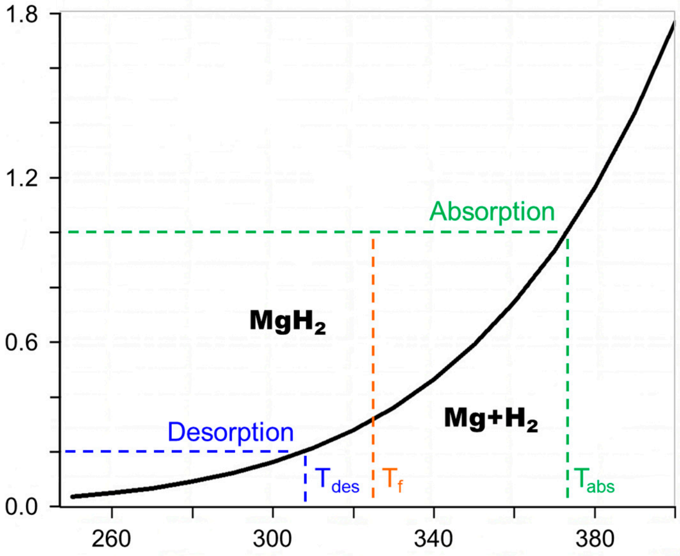


Figure 11. Equilibrium diagram of the system Mg + H_2 ↔ MgH_2 showing a melting temperature T_f of the PCM intermediate between the absorption (T_{abs}) and desorption (T_{des}) temperatures of the compacts.

Interestingly, autonomous mass storage units can be optimised with the heat of the absorption transferred for melting the PCM and then automatically re-used when solidifying the PCM to desorb the MgH_2 compacts [20,63].

The MgH_2 compacts have been tested up to ~7500 adsorption/desorption cycles without significant loss of either the maximum H-uptake or of the kinetics of the reactions. By doing so, elementary tanks (~100 kg_{MgH2}:~15 kg_{H2}) can be assembled into large containers to eventually form storage units ranging from one hundred kilowatts to tens of megawatts.

Alongside these performances and capacities, research and development activities should pay attention to the potential permeation of hydrogen with regard to all the shells and other items of equipment involved in this technology, for their safest use. Also, the different walls and pipes, and the ancillary equipment of the tanks, having to withstand hydrogen gas pressure, mechanical efforts, and temperature variations, either separately or concomitantly, need to be analysed in terms of potential hydrogen embrittlement [64].

Industries that need large quantities of hydrogen, such as the steel, cement, chemical, or glass industries, as well as large refuelling stations, will eventually be able to use large solid-state hydrogen storage units operating on site and supplied with green hydrogen (renewably sourced) in complete safety (pressure < 15 bar) [4].

5. Conclusions

In addition to a reminder of the safety considerations about hydrogen, the two instances of safety-related advances presented herein deal with opposite, yet constructive, approaches.

On the one hand, an innovative test bench has been implemented at the appropriate TRL 6 level to directly address the challenges in the transport as well as in the high-capacity buffer storage of hydrogen gas. Having been designed to test structures that are more complex than the modelled structures used for finite-element analyses, this bench can be used to validate or question the use of reputedly satisfactory predictive models in terms of hydrogen embrittlement and potential corollary failure. It can also provide guidance on the relevant mechanical tests to be applied in the fields of hydrogen gas transport and buffer storage that will require adequate qualification standards.

On the other hand, solid-state storage eliminates from the outset the safety problems associated with gaseous hydrogen, but also covers another area of development that had hitherto hindered the clear emergence of solutions such as the one initiated by McPhy-Energy a decade ago with MgH_2-based prototype tanks operating with an overall energy efficiency of up to 80%, where phase-change materials make it possible to level out heat transfers during the absorption/melting and solidification/desorption cycles. In addition to more favourable market conditions, the new public–private partnership developing this solution has been granted the European Inventor Award 2023 [65].

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