

HYDROGEN STORAGE: RECENT IMPROVEMENTS AND INDUSTRIAL PERSPECTIVES

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ABSTRACT (UP TO 300 WORDS)

Efficient storage of hydrogen is crucial for the success of hydrogen energy markets. Hydrogen can be stored either as a compressed gas, a refrigerated liquefied gas, a cryo-compressed gas or in hydrides. This paper gives an overview of compressed hydrogen storage technologies focusing on high pressure storage tanks in metal and in composite materials. It details specific issues and constraints related to the materials and structure behavior in hydrogen and conditions representative of hydrogen energy uses. This paper is an update of the 2019 version that was presented in Australia. It especially covers recent progress made regarding regulations, codes and standards for the design, manufacturing, periodic inspection and plastic materials' evaluation of compressed hydrogen storage.

1.0 INTRODUCTION

Hydrogen is used worldwide for industrial applications (heat treatment of metals, glass industry, etc.). It is stored and transported in compressed form. In the last few years, deployment and investments in hydrogen have accelerated rapidly in response to government commitments to deep decarbonisation, establishing hydrogen as a key component in the energy transition [1]. The development of hydrogen as a reliable energy vector is strongly connected to the performance and the level of safety of the components of the supply chain. In this respect, achieving an efficient and reliable storage is crucial to address hydrogen energy markets:

- Fuel for vehicles: light duty vehicles and heavy duty vehicles such buses, trucks, trains, aeronautics and ships powered with hydrogen and a fuel cell or a combustion engine that requires autonomy, volume savings and/or lightweight. Fuelling infrastructures requires high pressure buffer driven by pressure cycle lifetime.
- Stationary applications: power generator for residential, buffers for hydrogen refuelling stations (Figures 1 and 2). For this application, the choice of the storage solution is driven by of the storage cost and pressure cycle life.
- Transport of large quantity of hydrogen in trailers (Figure 3) equipped with composite tubes or multi element gas containers (pressure vessels manifolded together and assembled in a frame)

Hydrogen can be stored either as a compressed gas, a refrigerated liquefied gas, a cryo-compressed gas or in hydrides [2]. This paper gives an overview of compressed hydrogen storage technologies focusing on high pressure storage tanks in metal and in composite materials for pressure range from 200 bar to 1100 bar. In case of footprint constraints, volume savings and lightweight needs, composite pressure vessels are preferred (i.e. on-board storage in vehicles, hydrogen trailers, in some case hydrogen refuelling stations buffers).



Figure 1. Hydrogen refuelling station in Les Loges en Josas (France).



Figure 2. Buffers for hydrogen refuelling stations (vertical Type II cylinders and horizontal Type I tubes).



Figure 3. Hydrogen trailer in Long Beach (USA).

2.0 OVERVIEW OF COMPRESSED HYDROGEN STORAGE TECHNOLOGIES

Hydrogen can be stored in four types of pressure vessels as presented in Figure 4. The pressure vessels are generally cylinders but they can also be polymorph or toroid. Metallic pressure vessels are designated as Type I. Type II pressure vessels consist in a thick metallic liner with a fibre resin composite hoop wrapped on the cylindrical part. The fully composites materials based pressure vessels (designated by COPV) are made of a plastic or metallic liner wrapped with carbon fibres embedded in a polymer matrix (filament winding). When the liner contributes to the mechanical resistance (more than 5%), the COPV is of Type III (mostly metal liner). Otherwise, the COPV is of Type IV (mainly polymer liner or seldom extremely thin metal liner).

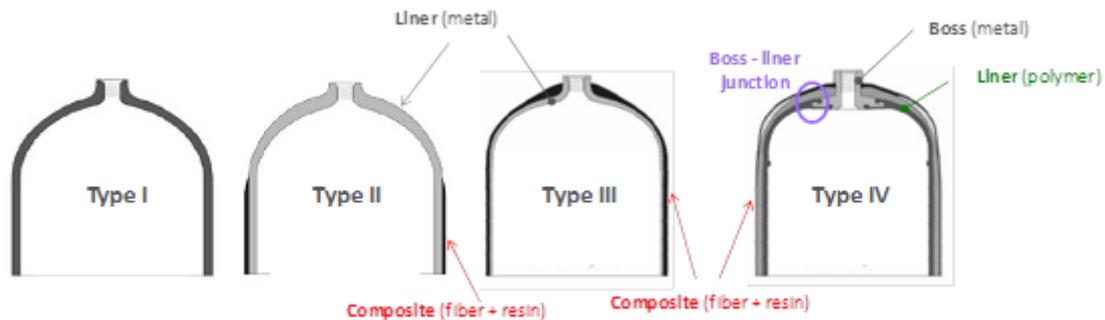


Figure 4. Representation of Type I, II, III and IV COPV [2].

Finally, Type V is used to designate pressure vessels without liner made of thermoset or thermoplastic composite matrix. They can be manufactured using different processes: welding of domes or winded structure (in the latter case, a possible design is to have the liner and the composite matrix made of the same thermoplastic). Type V COPV have been used for more than 20 years.

In 2017, some concerns have been raised regarding Type V COPV due to incidents reported after some cylinders burst into a fire. In 2019, the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR 2019) [3] set up a restriction for Type V COPV with regards to the method of manufacturing. Type V manufactured from two parts joined together are not allowed to be manufactured anymore. This restriction has also been introduced into the current revision of EN 12245 [4]. This manufacturing technique was mainly used for low pressure gases such as LPG.

2.1 SOME HISTORY & KEY CHARACTERISTICS

The development of metallic pressure vessels was led by industrial needs in the end of the 19th century in particular to store carbon dioxide for beverages. Hydrogen storage at 120 bar in wrought iron vessels is reported in about 1880 for military use. Pressure vessels made of seamless steels manufactured by drawing and forming of plates (Lane & Taunton British patent) or tubes (Mannesman German Patent) were developed in parallel in late 1880s. Until the 1960s, the working pressure was 150 bar. It was then increased to 200 bar and then to 300 bar. High pressure composites pressure vessels were introduced in the 1960s in the USA for military and space applications (aluminium or polymer liner with glass fibre wrapping). The first application for the civil market was breathable apparatus for firefighters in the 1970s. From the 1980s these pressure vessels started to be used for diving, fuel storage (compressed natural gas) and leisure applications (paintball) with a more extended material mix. The most common working pressure is ranging from 250 bar (compressed natural gas) to 300 bar (oxygen and air for breathing apparatus). Recently (21st century) 350 bar to 700 bar COPV were developed and approved for hydrogen energy applications. Moreover, regulations, codes and standards have been set up for both industrial gases and fuel gas storages. More recently, cylinders without liners i.e. Type V (already existing for low pressure

applications such as LPG) are being investigated for high pressure applications. The market share of composites pressure vessels remains quite small compared to metallic pressure vessels due to their higher cost (about 30 000 000 COPV in the world). The choice of the storage is based on the final application, which requires a compromise between technical performance and cost competitiveness. For industrial applications, hydrogen is stored from 200 to 300 bar in metallic Type I cylinders which have poor mass storage efficiency (about 1 wt% of hydrogen stored), that can be far from targets fixed for Hydrogen Energy applications. As an example, the USA Department of Energy target weight efficiency for on-board storage in vehicles is set at 5.5 wt% of hydrogen stored in a system in 2020 [5]. Currently, the most mature technology to reach such target is COPV made of carbon fibre composite with a working pressure of 700 bar. Table 1 presents the main feature of the different type of pressure vessels.

Table 1. Key characteristics of compressed gas storage pressure vessels.

	Technology maturity	Cost performance	Weight performance
Type I	Pressure limited to 500 bar	++	-
Type II	Pressure not limited	+	0
Type III	For $P \leq 450$ bar – (difficulty to pass pressure cycling requirements for 700bar, [6])	-	+
Type IV	For $P \leq 1100$ bar – First commercial series – liner behaviour in gas to be further studied	-	++
Type V	Very limited experience for high pressures, mostly for low pressures	-	++

2.2 DESIGN & MANUFACTURING

The most common materials used to manufacture pressure vessels are:

- For metallic parts: aluminium alloy 6061 or 7060, steels (stainless or Chrome Molybdenum steels)
- For polymer parts: polyethylene or polyamide based polymers
- For composite: glass, aramid or carbon fibre embedded in a resin. The fibre characteristics are given in Table 2. Carbon fibres are preferred for pressure higher than 350 bar. In the same way, various resins can be used (polyester, epoxy, phenol, etc.). Epoxy resins are preferred based on their good mechanical properties, stability and compatibility with filament winding process. Pre-impregnated fibres are available. For cost reasons, fibre impregnation just before the filament winding is most often preferred.

Table 2. Range of fibre mechanical properties.

Fibre type	Tensile modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
Glass	~ 70-90	~ 3300-4800	~ 5
Aramid	~ 40-200	~ 3500	~ 1-9
Carbon	~ 230-600	~ 3500-6500	~ 0.7-2.2

For all pressure vessels, the design shall take into account the application, test pressure, external environment (potential mechanical impacts, chemical degradation, integration, etc.), the cycling life and the safety coefficient defined both for stationary or transportable applications. Materials choices shall also take into account failure modes and operating conditions as it will be discussed in next section. For example, Figure 5(a) gives the main stresses considered for metallic cylinders/liners (note that domes are generally oversized). The composite wrapping is designed using finite element analysis with

respect to static conditions.

Type I pressure vessels and metallic liners can be manufactured from three different processes as shown in Figure 5(b):

- from plates by deep-drawing to form the shape,
- from billets: the billets is first heated to carry out drawing,
- from tubes: with closing of the ends.

The neck is then formed by hot-spinning. The neck is machined in the excess of metal coming from the spinning step. Heat treatment is then applied to have the desired mechanical properties.

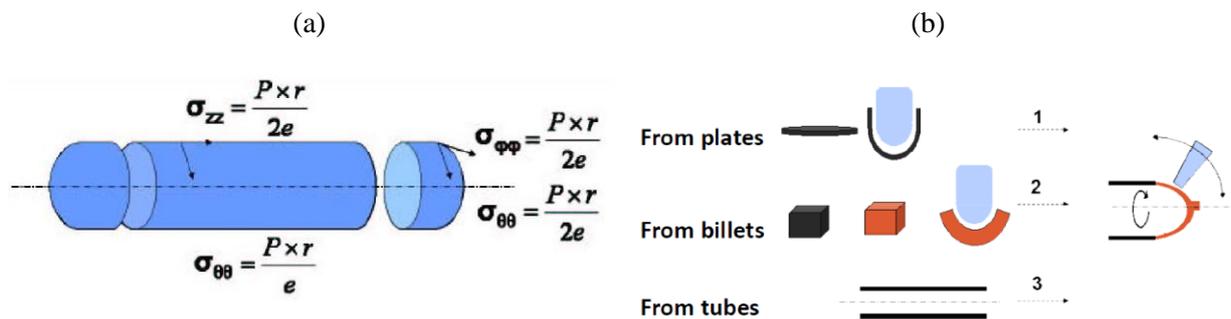


Figure 5(a). Stress Calculation in metallic pressure vessels.

Figure 5(b). Manufacturing of metallic pressure vessels from plates, billets and tubes.

Polymer liners of Type IV COPV can be obtained by rotomolding, blow molding or by welding injected domes to an extruded tube of polymer. Metallic parts (boss(es)) can be inserted in the domes during the forming process or glued to the liner in a second step.

For composite pressure vessels, the composite is obtained by filament winding of the fiber embedded in the resin (either by wet winding or by using pre-impregnated fibers). The composite is wrapped using a circumferential angle (hoop) for Type II COPV and a combination of circumferential, helical and polar angles for Types III and IV COPV as illustrated in Figure 6. The curing of the resin of the composite is finally carried out by UV exposure and more typically by curing in an oven.

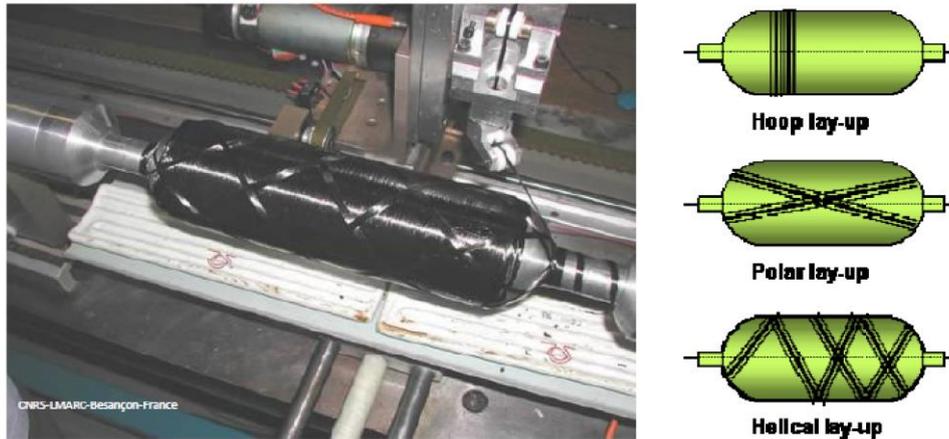


Figure 6. Manufacturing principle of the composite wrapping.

For each technology, quality controls of the materials and of manufacturing steps are performed and monitored. The pressure vessel final control is a proof test, typically at 1.5 times the working pressure. Development of non destructive testing technique such as acoustic emission are of interest for manufacturing quality insurance.

3.0 MATERIALS ISSUES & R&D CHALLENGES

The compatibility of hydrogen with the materials chosen and the impact of operating conditions on the materials and the structure have to be assessed. The whole lifecycle of the pressure vessel has to be considered: storage, transportation, use (emptying, handling, etc.), filling steps including gas quality management, periodic inspection and maintenance. The objective is to prevent the risk of failure by burst or leak in service and to guarantee the performance.

3.1 METALLIC PARTS (PRESSURE VESSEL, LINER AND BOSS)

In general, metallic materials and in particular steels, in contact with hydrogen are affected by hydrogen embrittlement (HE), with consequent degradation of mechanical properties and premature crack. It results from H atoms diffusion inside the microstructure and trapped by materials defects, such as dislocations and second phases particles. The hydrogen transport by dislocations depends on the stress and can lead to combined hydrogen-assisted cracking damages like stress-sensitive hydrogen cracking and hydrogen-enhanced fatigue. Major efforts have been performed by the industry and academia in mitigating this problem through a better understanding of the HE mechanisms, the improvement of alloys manufacturing and ultrasonic examination, components assembling, and appropriated mechanical testing [6]. Regarding to the latter issue, different testing methods exist to assess fracture toughness properties of metallic materials in gaseous hydrogen (K_{IEAC}): ASTM 1681 [7], ASTM 1820 [8] and methods B and C of ISO 11114-4 [9] and ANSI/CSA [10]. An experimental study is on-going to assess the different methods and evaluate the need for international harmonization of testing methods [6].

Another testing method is to check the sensitivity to hydrogen embrittlement for a given material, by using a disc membrane under gas pressure (method A of ISO 11114-4 [9]). Discs are burst separately under helium and hydrogen. An embrittling ratio “burst pressure in helium divided by burst pressure in hydrogen” is calculated. The lower the ratio, the less susceptible the steel will be to hydrogen embrittlement. Using the existing test benches leads to hydrogen rupture pressures in the range of 300 bar. Recent research work has showed that the disc test may be used at higher pressure with increased

disc thickness, up to 500 bar [11].

When subjected to cycling conditions, hydrogen pressure vessels are affected by hydrogen-enhanced fatigue (HEF). This damage mode may occur when fatigue conditions are met, i.e. under pressure cycling, and then diffusible hydrogen (not permanently trapped) tends to accelerate the crack growth by enhancing dislocations generation or lowering the atomic cohesion of metallic elements in the steel. The European project Mathryce (FCH-JU, 2013-2016) has given some recommendations on how to perform lab-scale tests [12], either to assess Fracture Mechanics parameters under hydrogen, or to get a HEF safety factor on the number of cycles to failure between air and hydrogen [12] [13]. Some results of this project are shown in Figures 7 and 8.

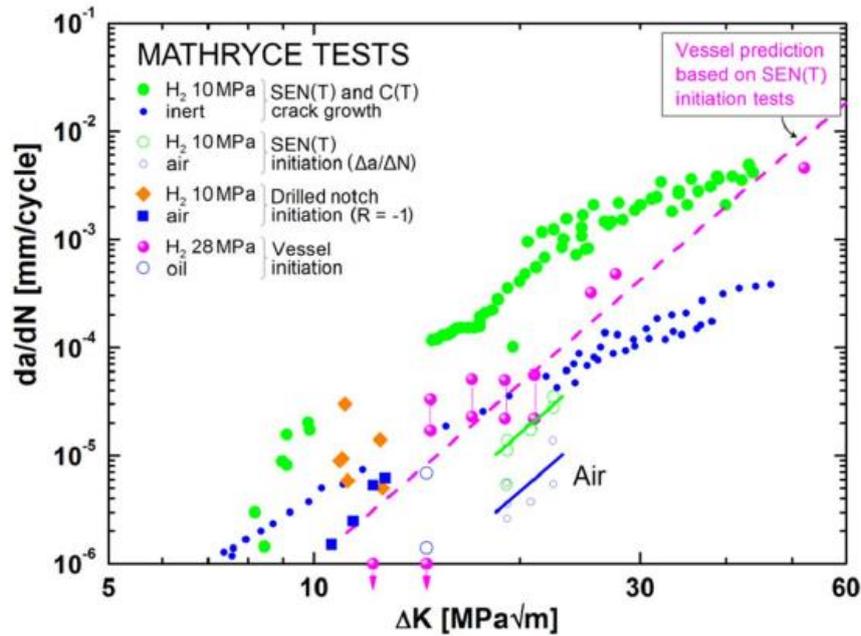


Figure 7. Compilation of different test data transformed to average crack growth rate estimates.

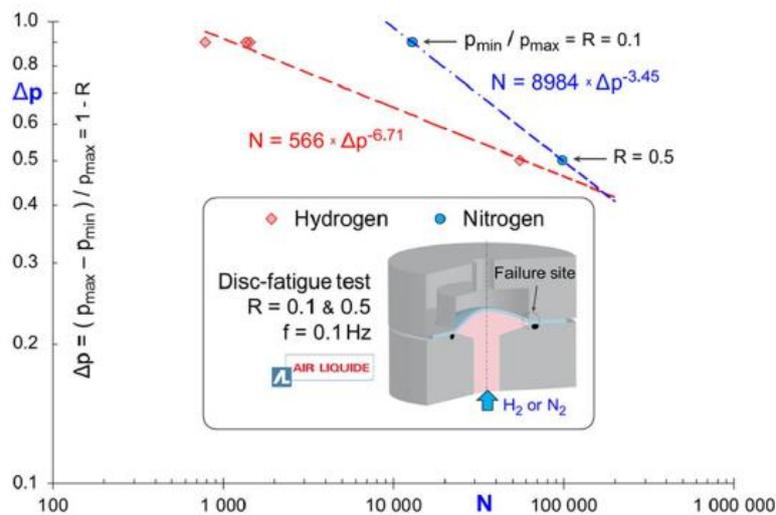


Figure 8. Results of disc-fatigue tests. Correlation between loading ratio and number of cycles to failure.

It has to be noted that hydrogen buffers in hydrogen refuelling stations are subject to shallow pressure cycles with high R-ratio ($R=P_{min}/P_{max}$) compared to full pressure cycles (deep cycles with low R-ratio). Tests have been performed on Type I, Type II and Type III cylinders to identify the relation between pressure cycle amplitude and number of cycles to failure for different cylinder designs. Cylinders were pressure cycled from 20 to 450 bar, from 20 to 390 bar, from 20 to 300 bar and from 150 to 300 bar [14]. The tests performed confirmed the validity of the formula proposed in EN 17533 [15] for the shallow and deep cycles, that is:

$$n_{eq} = \sum_i n_i \left(\frac{\Delta P_i}{\Delta P_{max}} \right)^3$$

with:

n_{eq} = number of shallow cycles equivalent to number of full cycles required in a given standard.

ΔP_i = variation of pressure during a given actual (shallow) pressure cycle

n_i = number of (shallow) pressure cycle corresponding to ΔP_i

ΔP_{max} = pressure amplitude during the (full) cycle tests as specified in the reference standard

3.2 POLYMER PARTS (LINERS OF TYPE IV PRESSURE VESSELS)

A high purity of hydrogen is required to guarantee performance and reliability of fuel cells. The standard EN 17124 [16] set these hydrogen specifications in terms of maximum quantity of impurities admitted. The standard being under revision, Table 3 presents the last quantity of impurities proposed in the draft revised standard [17]. This standard has been prepared under Mandate M/533 given to CEN by the European Commission and the European Free Trade Association [18]. So far, among the species listed in Table 3, water has been identified as the main compound that could degas from a polymer liner. The content of water in a polymer depends on its chemical nature. Thermal gravimetric analysis have evidenced that polyethylene water uptake can be neglected while the water uptake of polyamide is of several weight percent (the weight percent depends on the polyamide grade). Such water content in the polymer liner could lead to the implementation of additional drying steps of COPV prior to gas filling to respect the 5 ppm specification.

Table 3. Concentration of impurities in hydrogen listed in FprEN 17124:2021[17].

Individual contaminant	Maximum concentration of individual contaminant
Water (H ₂ O)	5 µmol/mol
Total hydrocarbons (THC) ^a (Excluding Methane)	2 µmol/mol
Methane (CH ₄)	100 µmol/mol
Oxygen (O ₂)	5 µmol/mol
Helium (He)	300 µmol/mol
Nitrogen (N ₂)	300 µmol/mol
Argon (Ar)	300 µmol/mol
Carbon dioxide (CO ₂)	2 µmol/mol
Carbon monoxide (CO) ^b	0,2 µmol/mol
Total sulfur compounds (H ₂ S basis)	0,004 µmol/mol
Formaldehyde (HCHO) ^b	0,2 µmol/mol
Formic acid (HCOOH) ^b	0,2 µmol/mol
Ammonia (NH ₃)	0,1 µmol/mol
Halogenated compounds ^c (Halogenate ion basis)	0,05 µmol/mol
Maximum particulates concentration	1 mg/kg
<p>^a Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (µmolC/mol).</p> <p>^b Total of CO, HCHO, HCOOH shall not exceed 0,2 µmol/mol</p> <p>^c All halogenated compounds which could potentially be in the hydrogen gas (for example, hydrogen chloride (HCl), and organic halides (R-X)) should be determined according to the hydrogen quality assurance discussed in Clause 5 of FprEN 17124:2021 [17] and the sum shall be less than 0,05 µmol /mol).</p>	

The permeation of gases is an inherent phenomenon for all gases in contact with polymers. It is the result of gas molecules dissolution and diffusion in the polymer matrix [19]. Because hydrogen is a small molecule, the permeability is enhanced. For safety reasons, permeation maximum allowable rates are defined in standards and regulations.

Quick emptying of COPV may in some cases lead to a deformation of the liner when pressure is released, as depicted in Figure 9. It is attributed to the diffusion of hydrogen through materials and accumulation at the interfaces, voids and in materials (solubility). The occurrence of the deformation depends on the

maximum pressure in the cylinder and on the pressure maintained in the cylinder at the end of emptying. Residual pressure valves use thus appears mandatory. To define unloading flow rate, it is also necessary to take into account emptying speed. Further tests are needed to propose recommendations on operating conditions and assess the effect of liner deformation on cylinder lifetime (does it lead to an increased risk of leakage?). Such question tackles multidisciplinary fields by coupling diffusion mechanisms to mechanics [20].

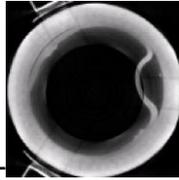


Figure 9. X-ray tomography of a polymer liner with permanent deformation after an emptying.

During filling and emptying, the structure and in particular the polymer liner and the boss liner junction are subjected respectively to high (65 or 85°C, depending on standards) and low temperatures (-40 to -60°C, depending on standards). Materials need to be selected accordingly to avoid materials degradation and thus leak risk.

3.3 COMPOSITE PARTS (TYPES II, III AND IV)

3.3.1 COMPOSITE AGEING

The resin of the composite plays a key role in the ageing process of the composite. Damage accumulation (i.e. fibre breaks) in a specimen of composite accelerates at temperature close to the glass transition temperature of the resin of the composite during sustained load tests. It results from the evolution of load transfer properties of the resin in case of fibres damage. In particular, a minimum difference of 30°C between the maximum operating temperature and the glass transition temperature has been proposed [21].

3.3.2 MECHANICAL IMPACTS

Regarding the composite wrapping, damage accumulation can result from pressure loads & environment impact in operation [20] and accidental mechanical impacts. In the scope of hydrogen energy markets, COPV can be subjected to a broad range of impacts either usual or accidental (car accident, fall or impact during handling and transportation of transportable COPV). Damage mechanisms occurring in such composites are fibre breakages, delamination and matrix cracking.

Damage resulting from a mechanical impact (e.g. a stone projected on a COPV of an hydrogen trailer or a damage created on a portable COPV dropped on the floor), its evolution under typical in-service loadings (monotonic pressurization, filling/emptying cycles,...) and the corresponding loss of performance are not well described for COPV as only a few studies tackle the consequence of impact on the residual lifetime of composite materials obtained by filament winding [22][23][24][25]. In addition, it is observed that a surface impact creates damage in the thickness of the composite as illustrated in Figure 10 [23] and can even damage the liner as illustrated in Figure 11 for Type III COPV.

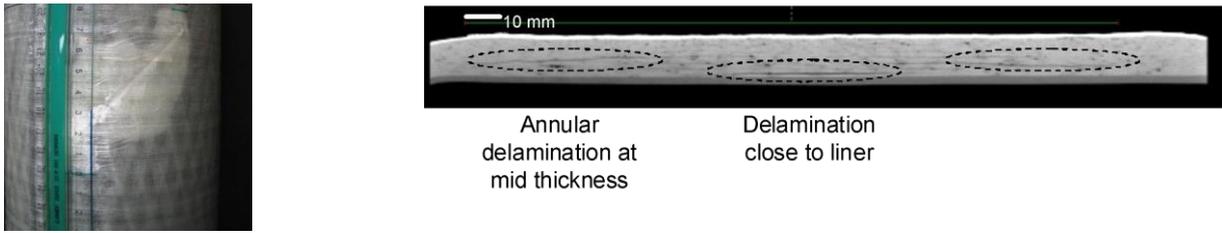


Figure 10. (a) illustration of the external surface composite damage and (b) in the thickness of the composite by XRay CT Scan for a mechanical impact with angular impactor [25].

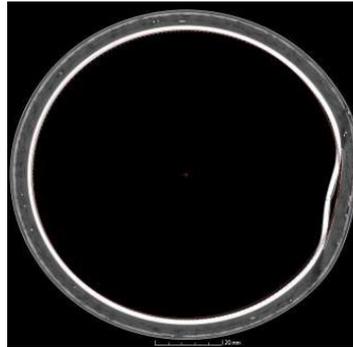


Figure 11. Deformation of a metallic liner after subjected to a mechanical impact on the external surface of the COPV.

A deeper understanding of how the different damage mechanisms appearing inside the thick composite overwrap affect the residual burst pressure and fatigue resistance of the vessel is required. An approach is to establish a relationship between impact energy and burst pressure reduction or number of cycles to failure reduction, in order to obtain a critical damage which can be defined as the point where the loss of performance starts to decrease [26] [27]. This approach may be used to define the rejection criteria to be applied during inspection of COPV, whatever the non destructive techniques (NDT) used.

Periodic inspection of COPV is required by regulations. Currently, periodic inspection consists of a visual inspection (internal and external) and a hydraulic proof test. As an alternative to hydraulic proof test which gives poor information on the real damage level in COPV (as illustrated in Figures 7 and 8), NDT providing more information on damage level are under development.

In the European project HyPactor (FCH-JU 2014-2017), up to 100 pressure vessels of various sizes (from 36 to 513 L) and service pressures (from 250 to 950 bar) have been impacted, inspected, cycled and/or burst in order to investigate the link between impact, observable damage and residual performance [28]. Many NDT have been tested. Acoustic emission is particularly studied [29] [30] and proposals of standards are under development (ISO/TS 19016 [31] for Modal Acoustic Emission and ISO/DIS 23876 [32] for Acoustic Emission).

Another inspection development axis is the in-service monitoring of COPV, aiming to follow-up specific parameters such as temperature, strain, or acoustic waves and analysing any deviation to a reference state. Monitoring could be performed permanently or on demand, depending on the integration level of the system.

3.3 FIRE RESISTANCE

Bonfire tests were carried out on different COPV, mostly with a polymer liner. The time to burst and

pressure at time to burst have been evaluated. At time to burst, the pressure in COPV increases by less than 10% [33] [34]. The increase of pressure is thus not responsible for the burst of COPV, as observed in metallic pressure vessels. The knowledge of the degradation of the composite materials in fire has been developed by different projects and fire protection strategies proposed [34] [35] [36]. Results of fire tests carried out on pressurised cylinders with polymer liner and without any protection allowed exploring their behaviour. It was confirmed that below a certain pressure level, in an engulfing fire, the failure mode switches from burst to leak through the body [33]. This is due to a competition between on one side the degradation of the composite material, which leads to a burst when the pressure can no longer be contained; and on the other side the heat transfer to the liner, which leads it to melt and create a pathway for the gas to exit through the cylinder. A potential path of research could be to design a pressure vessel for which the only failure mode in fire is a leak, by increasing the thermal conductivity while limiting the loss of strength of the composite layup. Still, so far the leak through the cylinder body is not fully mastered and cannot be guaranteed in all fire conditions, so the use of a pressure relief system is mandatory when burst must be avoided. If needed by the safety strategy, Temperature Pressure Relief Device (TPRD) could be combined with fire resistant materials such as intumescent paint to delay time to burst and allow smaller TPRD diameter if requested by the application [36].

3.4 WORKING TOPICS ON HYDROGEN STORAGE TECHNOLOGIES

There is a need for an agreement on periodic requalification procedures and desire for development of effective in-service continuous monitoring of the composite structure. Degradation mechanisms of high pressure gaseous hydrogen storage vessels under extreme conditions (fire, blast, etc.) needs also to be investigated.

Since the weight is not the important issue for buffers used in hydrogen refuelling stations, solutions to have Types I and II vessels from 850 to 1100 bar are being investigated leading to challenges on how to conduct hydrogen fatigue tests at such pressure.

For metal liners, work is being performed to improve the database of tests to include more steel grades, harmonize the test methods to characterize metal components for use in hydrogen and to evaluate fatigue life by taking also into account the degrading mechanism of materials/components in contact with high pressure hydrogen. In order to mitigate the risk of hydrogen embrittlement, multi-layered pressure storage are being developed.

For plastic liners, temperature limits (especially during filling and emptying cycles) have to be taken into consideration as they have impact on the degradation/ageing of the material. In addition, the behaviour in hydrogen (solubility, decompression, blistering and collapse) needs to be assessed. Therefore, the hydrogen storage industry needs to have a standard for hydrogen compatibility of polymers with harmonized material test method at sample and cylinder level to select liner materials that are compatible with service conditions [37].

For composite structure, the lack of effective non-destructive examinations techniques for composites applicable at the manufacturing stage and in service is complicated to develop. Trials have been performed demonstrating that calibration phases and standardization of methods are essential [38].

For Types III and IV vessels, currently, burst ratio considers exclusively static fatigue (creep strength). Cyclic fatigue is tested under the focus of functionality not of degradation that is detectable in statistics. The worst case degradation in service has to be based on residual strength tests of storage units in service. If the sketched approach for the worst case degradation is globally successful, the life time issue could be solved more easily. If it is partly successful, it will become necessary to look in detail on the issue of artificial ageing processes: possibly causing level and kind of degradation adequate to in-service degradation.

The priorities identified during the Research Priority Workshop on Hydrogen Safety in Buxton (United Kingdom) in 2018 were the following [39]:

- To have ageing models considering mechanical loads and all influencing operating parameters, including liner collapse (this will also assist improvement of test protocols defining material selection criteria to qualify hydrogen cylinder design);
- To be able to model the damages induced by impacts on high-pressure tanks;
- To have new solutions for smart and reliable fire detection and protection systems (TPRD, protections, fire detections, heat conduction to promote liner melting, etc.);
- To understand the effect of overheating on the structural performance and lifetime of the whole storage systems in case of extreme hot filling scenarios, and other temperature excursions.

4.0 PROGRESS MADE IN STANDARDIZATION

Progress has been made over the past years and more recently to develop storage for hydrogen storage at both European and international levels.

For design standards, EN 17533 [15] which covers the cylinders and tubes used as stationary vessels was published in 2020. This standard gives requirement for manufacturing stationary vessels but also requirements for using existing approvals given to transportable vessels in order to use them as stationary vessels. The KD-10 method (taken from ASME) was introduced, allowing to take into account hydrogen influence on design. An accelerating factor of 5 for fatigue life in hydrogen service is given in the draft standard [12][15]. The previous Vienna Agreement with ISO/FDIS 19884 was withdrawn since at ISO level, the final vote failed. For trailers, the European standard EN 17339 [40] was published in 2020 and the standard was accepted to be referenced in ADR 2023 for fully wrapped transportable composite cylinders and tubes for hydrogen service that are permanently mounted in a frame (such as trailer or bundle) with adapted safety factor, allowing to reduce the quantity of carbon fiber per cylinder or tube, based on the result of HyCOMP (FCH-JU, 2011-2014) [21].

At ISO level, a work have been initiated within ISO/TC 58 “Gas cylinders”, Subcommittee 3 “Cylinder design” in order to publish a Technical Report to justify the unneccessity of having the note concerning the service life testing in the UN Model Regulations for COPV with a design life longer than 15 years [41].

For compatibility standards, a revised version of ISO 11114-4 (testing methods for determining hydrogen compatibility of steels) was published in 2017 [9]. In addition, a new standard ISO/DIS 11114-5 [37] is under development for evaluating the compatibility of plastic liner materials with gases, in particular compatibility with hydrogen. In addition, the revision of ISO 11114-2 [42] is on-going and will include also the typical liner materials.

For non-destructive examinations, the technical specification ISO/TS 19016 (Modal Acoustic Emission for periodic inspection and testing of composite cylinders) was published in 2019 [31]. This technical specification is under revision to change the status to an international standard. Another standard is under development for Acoustic Emission at ISO level (ISO/DIS 23876 [32]). Such technologies allow to not dismount the composite cylinders when they are assemble in a trailer or as bundles. These technologies could also be useful for the inspection of buffers. However, in Europe, the Pressure Equipment Directive [43] does not cover the periodic inspection of buffers. Such examination is covered by national rules and sometimes the requirements are not fully adapted to the

new applications (e.g. requirements in terms of pressure, humidity). Work will be needed to adapt existing rules to the new needs.

At European Industrial Gases Association, a document has been published to provide a method to establish pictures for the visual inspection at time of filling or periodic inspection of composite pressure vessels [27].

5.0 RECYCLING

Managing the end of life of the composite pressure vessels is a topic to address as composite materials recycling is under development. EIGA proposed a guideline on the management of wastes of composite cylinders [44]. Some on-going developments are investigated for the use of thermoplastic matrix instead of thermoset resins which will facilitate the recycling of composite cylinders.

The ongoing THOR (FCH-JU 2019-2021) project (Thermoplastic Hydrogen tanks Optimised and Recyclable) [45] is centred around the development of thermoplastic composite cylinder to compensate the state-of-the-art composite tanks that suffer from some limitations (reliability, performance and cost targets, refuelling/emptying time, weight and volume, durability, life-cycle cost and recyclability).

The academic research works undertaken on the recycling of composites relate to primarily those with thermoset matrix, as they constitute more than 90% of the current market. Many technological solutions were developed, based on either mechanical (e.g. crushing), thermal (e.g. pyrolysis), chemical (e.g. solvolysis) or biological (e.g. composting) treatments. Nevertheless, to date, except for carbon fibres reinforced composites, none of these solutions passed the stage of the industrial pilot, for economic reasons mainly.

Despite regulation tightening, more than 90% of these materials is left to landfills.

Concerning the end-of-life and the management of the production scraps, composites with thermoplastic matrix offer an undeniable advantage compared to thermoset ones. Their fusible nature makes it possible to imagine unprecedented ways of recycling. In terms of revalorization of the material, the re-granulation for plastic injection, or the treatment by the Thermosaïc® process constitute the most interesting opportunity. The interest of this project is to test the feasibility of recycling with the Thermosaïc® process, by integrating the problems of thinning the shreds, to guarantee optimized mechanical performances of the produced panels. Challenging work will concern the development of strategies making it possible to produce shreds having a geometry compatible with this process.

The expected innovation of the THOR project concerning recycling are:

- Thermomechanical recycling of carbon fibre composite in a semi-finished product in the form of panels with high mechanical properties;
- Delamination/crushing of large thickness containing carbon fibres composite into fine thickness fragments.

6.0 CONCLUSION

In order to store hydrogen, compressed storage is the most mature technology. Hydrogen energy applications have triggered the development of high pressure compressed storage in composite pressure vessels based on carbon fibre. Challenges remain to improve the durability while still ensuring the safety of cylinders in service over periods of 20 years and more for high pressure storage (up to 1100 bar). Therefore, the impact of operating and accidental conditions on the materials and on the structure has been studied to propose when needed recommendations to regulations, codes and standards and to the industry regarding design and operation of COPV. Non Destructive Technique have to be further

investigated for manufacturing quality control and periodic inspection to assess whether the cylinder is still fit for service.

Regarding metallic pressure vessels, high pressure service led to R&D work on damage mechanisms and testing methods for materials selection. Progress has also been done on hydrogen enhanced fatigue.

Regulations, codes and standards are evolving in order to support the hydrogen mobility markets.

It is to be noted that there is a renewed interest for the use of liquefied hydrogen for storing, transport or even as a fuel.

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