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.

REFERENCES

COPV: Composite Overwrapped Pressure Vessels
FCH-JU: Fuel Cell and Hydrogen Joint Undertaking
HEF: Hydrogen Enhanced Fatigue
HE : Hydrogen Embrittlement
ISO : International Standardization Organisation
NDT: Non Destructive Technique

1. INTRODUCTION

Hydrogen is used worldwide for industrial applications (heat treatment of metals, glass industry, etc). It is stored and transported in compressed form. More recently, new applications have emerged in the field of energy. 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 transportation: buses, cars, scooters or other vehicles 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: back-up power supply, power supply to off-grid area, power generator for...
residential. For this application, the cost of hydrogen supply is the main parameter as well as pressure cycle life.

- Portable applications: portable back-up power supply or power generator.
- Transport of large quantity of hydrogen in trailers equipped with composite tubes or multi element gas containers

Hydrogen can be stored either as a compressed gas, a refrigerated liquefied gas, a cryo-compressed gas or in hydrides [1]. 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 20 MPa to 110 MPa. 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).

2. **OVERVIEW OF COMPRESSED HYDROGEN STORAGE TECHNOLOGIES**

Hydrogen can be stored in four types of pressure vessels as presented in Figure 1. The pressure vessels are generally cylinders but they can also be polymorph or toroid. Metallic pressure vessels are known as type I. Type II pressure vessels consist in a thick metallic liner hoop wrapped on the cylindrical part with a fiber resin composite. 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 1. Representation of type I, II, III and IV COPV [2]](image)

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 12 MPa 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 15 MPa. It was then increased to 20 MPa and then to 30 MPa. 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 firemen 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 25 MPa (compressed natural gas) to 30 MPa (oxygen and air for breathing apparatus). More recently (21st century) 35 MPa to 70 MPa 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. 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 at 20 to 30 MPa 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 [3]. Currently, the most mature technology to reach such target is COPV made of carbon fibre composite with a 70 MPa working pressure. The Table I presents the main feature of the different type of pressure vessels.

Table 1. Key characteristics of compressed gas storage pressure vessels

<table>
<thead>
<tr>
<th></th>
<th>Technology maturity</th>
<th>Cost performance</th>
<th>Weight performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>Pressure limited to 50 MPa</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Type II</td>
<td>Pressure not limited</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Type III</td>
<td>For P ≤ 45 MPa – (difficulty to pass pressure cycling requirements for 70 MPa, [4])</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Type IV</td>
<td>For P ≤ 110 MPa – First commercial series – liner behaviour in gas to be further studied</td>
<td>-</td>
<td>++</td>
</tr>
</tbody>
</table>

2.2 Design & manufacturing

Most common materials are:

- metallic parts: aluminium 6061 or 7060, steel (stainless steel or Chrome Molybdene)
- polymer parts: polyethylene or polyamide based polymers

- composite: glass, aramid or carbon fibre embedded in epoxy resin. The fibre characteristics are given in Table 2. Carbon fibres are preferred for 35 MPa and more applications. 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 commercially available. For cost reasons, fibre impregnation just before the filament winding is most often preferred.

Table 2. Range of fibre mechanical properties

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>Tensile modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>~ 70-90</td>
<td>~ 3300-4800</td>
<td>~ 5</td>
</tr>
<tr>
<td>Aramid</td>
<td>~ 40-200</td>
<td>~ 3500</td>
<td>~ 1.9</td>
</tr>
<tr>
<td>Carbon</td>
<td>~ 230-600</td>
<td>~ 3500-6500</td>
<td>~ 0.7-2.2</td>
</tr>
</tbody>
</table>

For all pressure vessels, the design shall take into account the service, test pressures, the external stresses (like mechanical impacts, chemical, integration, etc), the cycling life, the lifetime and the
safety coefficient defined both for static and dynamic conditions. Materials choices shall also take into account failure modes and operating conditions as it will be discussed in next section. For example, Figure 2a gives the main stresses considered for metallic cylinders/liners (note that domes are generally overdesigned). The composite wrapping is designed using finite element analysis with respect to static conditions.

Type I pressure vessels and type II and III liners can be manufactured from three different processes as shown in Figure 2b: from plates by deep-drawing to form the shape, from billets: the billets is first heated to carry out drawing, from tubes. The neck is then formed by hot-spinning. The ports are machined in the excess of metal coming from the spinning step. Heat treatments are then applied to have the desired mechanical properties.

![Figure 2. (a) stress calculation in metallic pressure vessels. (b) manufacturing of metallic pressure vessels from plates, billets and tubes](image)

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

For composites 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 pressure vessels and a combination of circumferential, helical and polar angles for type III and IV pressure vessels as illustrated in Figure 3. The curing of the resin of the composite is finally carried out by UV exposure and more typically by curing in an oven.
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 is of interest for manufacturing quality insurance.

3 MATERIALS ISSUES & R&D CHALLENGES

The compatibility of the gas 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 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 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 is stress dependent and can lead to a 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, components assembling, and appropriated mechanical testing [4]. Regarding to the latter issue, different testing methods exist to assess fracture toughness properties of metallic materials in gaseous hydrogen (KIHAC): ASTM 1681 [5], ASTM 1820 [6] and methods B and C of ISO 11114-4 [7] and ANSI/CSA [8]. An experimental study is ongoing to assess the different methods and evaluate the need for international harmonization of testing methods [4].
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 [7]). 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 30 MPa. Recent research work has showed that the disc test may be used at higher pressure with increased disc thickness, up to 50 MPa [9].

When subject 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, 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 [10] [11]. Some results of this project are shown in Figures 4 and 5.

![Figure 4. Compilation of different test data transformed to average crack growth rate estimates.](image)
It has to be noted that hydrogen buffers in hydrogen refuelling stations are subject to shallow pressure cycles with high R-ratio ($R = \frac{P_{\text{min}}}{P_{\text{max}}}$) compared to full pressure cycles (deep cycles with low R-ratio). Tests have been performed on Type 1, and composite cylinders Type 2 and 3 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 [12]. The tests performed confirmed the validity of the formula proposed in ISO/CD 19884 for the shallow and deep cycles, that is:

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

with:

- $n_{eq}$ = number of shallow cycles equivalent to number of full cycles required in a given standard.
- $\Delta P_i$ = variation of pressure during a given actual (shallow) pressure cycle
- $n_i$ = number of (shallow) pressure cycle corresponding to $\Delta P_i$
- $\Delta P_{\text{max}}$ = pressure amplitude during the (full) cycle tests as specified in the reference standard

### 3.2 Polymer parts (liner of type IV pressure vessels)

A high purity of hydrogen is required to guarantee performance and reliability of fuel cells. The standard ISO 14687-2 set these hydrogen specifications in terms of maximum quantity of impurities admitted (see Table 3). 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 ISO 14687-2 [13]

<table>
<thead>
<tr>
<th>Component</th>
<th>Target concentration of impurities (µmol/mol)</th>
<th>Component</th>
<th>Target concentration of impurities (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inert gases (Nitrogen + Argon)</td>
<td>100</td>
<td>Total sulphured components</td>
<td>0.004</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5</td>
<td>Ammonia</td>
<td>0.1</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>2</td>
<td>Formaldehyde</td>
<td>0.01</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.2</td>
<td>Formic acid</td>
<td>0.2</td>
</tr>
<tr>
<td>Total hydrocarbons</td>
<td>2</td>
<td>Total halogenated compounds</td>
<td>0.05</td>
</tr>
<tr>
<td>Water</td>
<td>5</td>
<td>Helium</td>
<td>300</td>
</tr>
</tbody>
</table>

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 [14]. 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 6. It can be 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. Emptying speed also has an effect to consider then defining unloading flow rate. 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 [15].

![Figure 6. X-Ray tomography of a polymer liner COPV with permanent deformation after an emptying](image)

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 have to be chosen 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 [16].

3.3.2 Mechanical Impacts

Regarding the composite wrapping, damage accumulation can result from pressure loads & environment impact in operation [17] 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 [17][18][19][20]. In addition, it is observed that a surface impact creates damage in the thickness of the composite as illustrated in Figure 7 [20] and can even damage the liner as illustrated in Figure 8 for type III COPV.

![Figure 7. (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 [20].](image)
Figure 8. 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 [21][22].

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), non destructive techniques (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 [23]. Many NDT have been tested. Acoustic emission is particularly studied [24][25] and a proposal of standard is under construction (ISO/DIS 19016).

3.3 Fire resistance

Bonfire tests were carried out on different COPV, mostly with a polymer liner. 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% [26][27]. 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 [27][28][29]. 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 [27]. 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 could be combined with fire resistant materials such as intumescent painting to delay time to burst and allow smaller diameter Temperature Pressure Relief Device if requested by the
application [29].

4 RECYCLING

Managing the end of life of the composites cylinder is a topic to address as composite materials recycling is under development. EIGA recently proposed a guideline on the management of wastes of composites cylinders [30].

5 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 70 MPa). 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 Techniques 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 (up to 110 MPa) led to Research & Development work on damage mechanisms and testing methods for materials selection. Progress has also been done on hydrogen enhanced fatigue.

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