Hydrogen high pressure tanks storages: overview and new trends due to H_2 Energy specifications and constraints

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ABSTRACT:

The topic of this paper is to give an historical and technical overview of hydrogen pressure tanks and to detail the specific issues and constraints of hydrogen energy uses. Hydrogen, as an industrial gas, is stored since the beginning of the last century in seamless steel cylinders. At the end of the 60s. tubes also made of seamless steels were used ; specific attention was paid to hydrogen embrittlement in the 70s. Aluminum cylinders were also used for hydrogen storage since the end of the 60s, but their cost was higher compared to steel cylinders and smaller water capacity. To further increase the service pressure of hydrogen tanks or to slightly decrease the weight, metallic cylinders can be hoop-wrapped. Then, with specific developments for space or military applications, fully-wrapped tanks started to be developed in the 80s. Because of their low weight, they started to be used in for portable applications: for vehicles (on-board storages of natural gas), for leisure applications (paint-ball) etc… These fully-wrapped composite tanks, named types III and IV are now developed for hydrogen energy storage; the requested pressure is very high (from 700 to 850 bar) leads to specific issues which are discussed. Each technology is described in term of materials, manufacturing technologies and approval tests. The specific issues due to very high pressure are depicted.

KEYWORDS : overview – pressure vessels – hydrogen storage.

Introduction

The following 4 types of high pressure vessels are classified (see Figure 1):

- Type I: pressure vessel made of metal
- Type II: pressure vessel made of a thick metallic liner hoop wrapped with a fiber-resin composite.
- Type III: pressure vessel made of a metallic liner fully-wrapped with a fiber-resin composite.
- Type IV: pressure vessel made of polymeric liner fully-wrapped with a fiber-resin composite. The port is metallic and integrated in the structure (boss).

The pressure vessels are generally cylinders, but composite vessels can also be polymorph or toroid.

Hydrogen can be stored in the four types of pressure vessels. The choice of the storage is based on the final application which requires a compromise between technical performances and cost-competitiveness. H_2 as industrial gas is stored in type I tanks, the pressure of which is from 150 to 300 bar (usually 200 bar). These are the most spread high pressure vessels today and are the cheapest. When only higher pressures are required – mainly for stationary applications – the type II tanks are preferred. Type III and type IV vessels are intended for portable applications, for which weight savings is essential. However these vessels are much more expensive. Technical performances will be presented in the last paragraph of this paper.

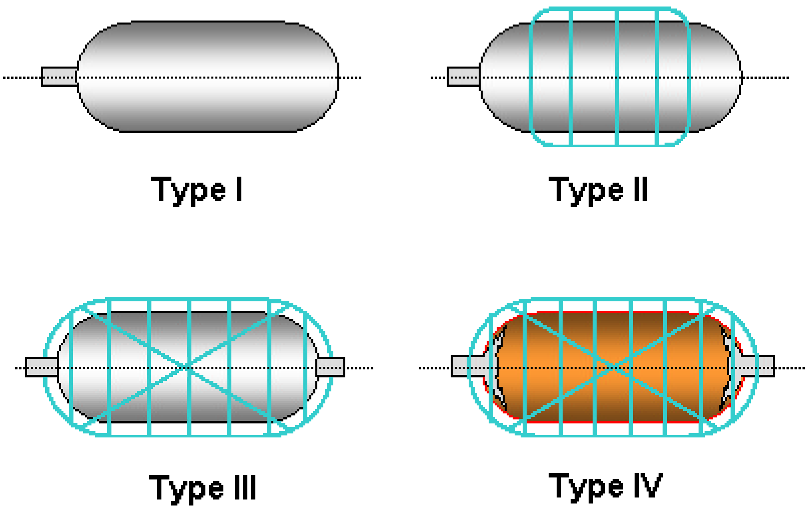


Figure 1 : schematic representation of the 4 pressure vessel types

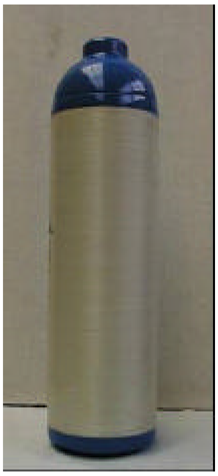
			
Type I cylinder	Type II vessel	Type III or IV vessel	Toroid composite vessel

Figure 2 : pressure vessels pictures

Some history

The oldest pressure vessel type is the type I, when made of steel. It was introduced in the 19th century between 1870 and 1880. It was lead to the development of a new industry at that time: the industrial gas business. More particularly, it seems to be first linked to the high consumption of carbon dioxide for beverage, with the necessity to store it safely, in the liquid state and in high quantities. The probable date of such storage for carbon dioxide seems to be 1874. Note that low pressure vessels (<20 bar) were already used in the mid 19th century: they were made of copper, generally low capacity and used for the very first breathable apparatus; but they cannot not be qualified as high pressure vessels. Regarding the hydrogen, it was mainly used during the last 19s century for military observation balloons in Asia and in Africa (around 1880). It was stored in 120 bar pressure vessels in wrought iron vessels in 1880; of course, these cylinders were very heavy (500 kg of steel were needed to store 25Nm^3 of hydrogen), but they seem to be the first to be able to transport safely hydrogen at high pressure. Vessels made with seamless steel were introduced in 1885, manufactured by drawing and forming of plates (Lane & Taunton British patent) with a special development for making the neck. Meanwhile, the manufacturing of high pressure cylinder from seamless tubes was developed (Mannesmann German patent). High pressure cylinders manufactured from billets were also perfected in the late 1880s.
At the beginning of the 20th century, the three main processes – still used today for industrial gas cylinders production, especially for hydrogen storage – were existing. Only the wrought iron first process was given

up. Of course, some improvements were then performed during the 20th century. These improvements concerned the end closing, the materials, the thermal treatments etc… For example, the aluminum type I cylinders were introduced in after the First World War. The motivation was to have a non magnetic storage for sub-marines. Their use was only really spread after 1960.
Until the 60s, the service pressure of these storages was 150 bar. From 1960, the service pressure was increased up to 200 bar. Today both 200 and 300 bar cylinders are co-existing for industrial gases.
It is interesting to note that the core processes developed in the 19th century for type I vessels are still used today.

High pressure composite vessels were introduced more than 70 years after and were especially developed for space and military applications, for which technical performances – especially weight – was a very important criteria. The experimentation of composite vessels started in the 50s but the first high pressure vessels used for space and military applications started actually in the 60s in the US (rocket motors and other pressure vessels for space shuttles, sonar equipment etc…). The market of these new high pressure vessels was very low in the 60s and the production was not regular at that time: manufactured batches could count from about ten to a few hundreds vessels (no series production). They were made of a metallic or polymeric liner wrapped with glass fiber composite. The civil market started to be penetrated in the first 70s and was linked to the will to increase the market of these high tech products. When compared to the type I conventional vessels for industrial gases, the cost of these composite vessels and the lack of regulation for composite vessels slowed down this penetration. For example, in the late 70s, 100 000 cycles were requested by the ASME code for pressure vessels – what composites tanks could not fulfill. As a consequence, for each model and each application, the composite vessels had to obtain a special authorization and their lifetime was limited. However, the first important civil market in the 70s was the breathable apparatus for firemen. From 80s on, these composite vessels started to be used for skin diving, fuel storage (mainly natural gas) and leisure applications (like paint-ball). The storage pressures were conventional: from 100 to 300 bar.
Many improvements were also performed since the first developments: for example, weight has decreased, cycling performance has increased by using thin liners with adequate mechanical properties, and other fibers than glass (kevlar, carbon). Moreover the regulation was set up for both industrial gases and fuel gas storages.
Except for very specific applications (military) and type II for H_2 trailers since 90s, the composite vessels were not used for hydrogen storage as industrial gas, because of their high cost. Hydrogen started to be stored in composite vessel when the potential use of hydrogen as an energy carrier began.

Design and manufacturing

For all pressure vessels, the design shall take into account the service and test pressures, the external stresses which are specific to the use (like impacts, aggressive media, vibrations, temperature of service, weight of connectors etc…), the real lifetime (cycling) and the safety coefficients defined for both static and dynamic conditions. The failure modes like plastic deformation, buckling, creeping, fatigue etc… for metals, delaminations, fiber ruptures, cracks, ageing etc… for composites are also taken into account for the design. All these parameters define the mechanical design and the choice of the materials. The materials shall also be compatible with the gas when in contact. It is important to note that metallic vessels and composite vessels are very different:

- The metal is isotropic, the composite is anisotropic: the mechanical properties are concentrated in the fiber direction for the composite.
- The failure modes are different.
- The ageing is different.

For example, Figure 3 gives the main strains which are generally considered for metallic pressure vessels. In general, the domes are over designed. That is why the type II vessels, with their hoop reinforcement on the only the cylindrical part of thick liners, can easily withstand higher pressures.

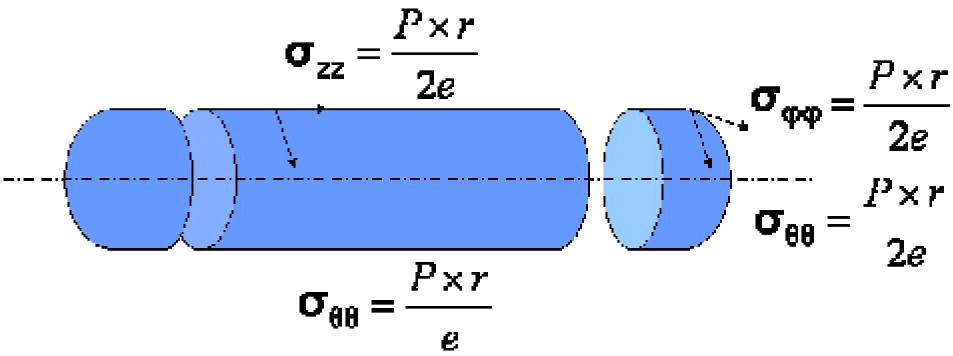


Figure 3 : main strains considered for the metallic pressure vessels design (type I and metallic liner)

For the composite wrapping, an analytical and simplified calculation is generally performed to have a first estimation of the lay-up design. Then a complete study with a finite elements software is necessary for a correct and optimized design (which should be coherent with the filament winding machine code).

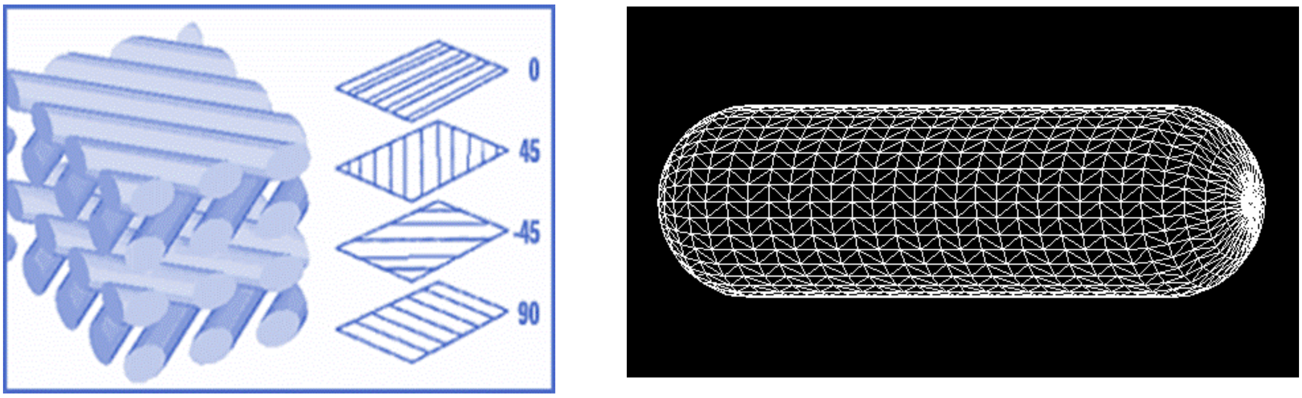


Figure 4: multi-layered element & vessel meshes example

Type I vessels can be manufactured from 3 different processes (see Figure 5 for the principles):

- **From plates**: the process consists in deep-drawing metallic plated to form the shape (this step can be performed many times to have the desired diameter and thickness); the neck is formed by hot-spinning and the port is machined in the excess of metal coming from the spinning step. A one port cylinder is thus obtained. The heat treatments are then applied to have the desired mechanical properties.
- **From billets**: the billet is firstly heated to allow the drawing to be performed. The process is then similar to the previous one.
- **From tubes**: Tubes are purchased and in general the original thickness is kept for the hoop. The domes are formed by hot spinning and a 1 or a 2 ports cylinder can be obtained. The process is then similar to the first one.

For each technology, quality controls of the materials used and of each step of manufacturing is performed and traced. The liners of type II and type III vessels can be manufactured in the same ways.

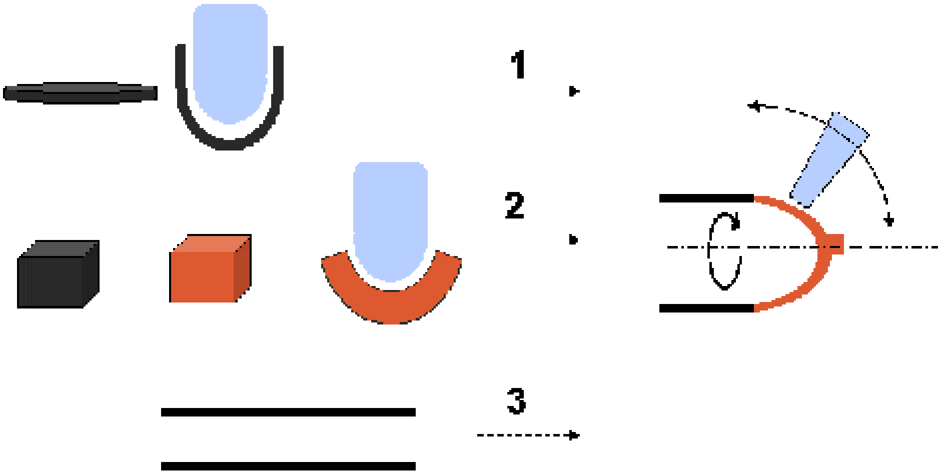
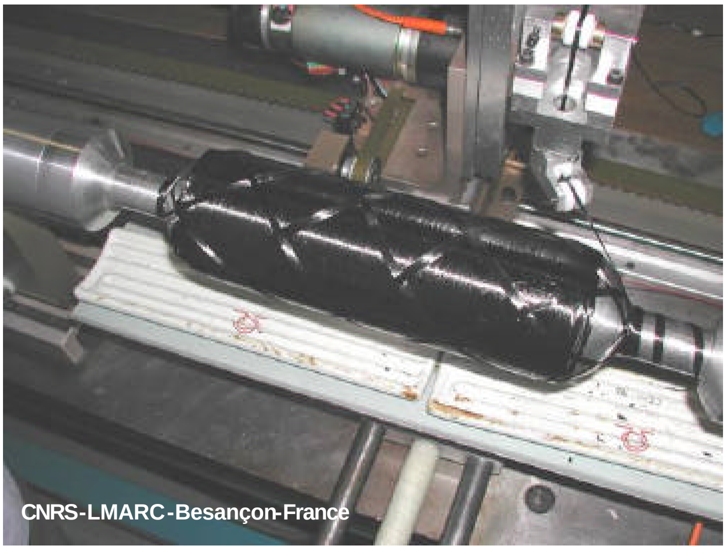


Figure 5 : principle of metallic tank manufacturing processes
(1 : from plates / 2 : from billets / 3 : from tubes)

The polymeric liners can be made by:

- **From the polymer or the monomers** by the rotomolding process: the polymer (or the monomers) is introduced in a mold the shape of which is the final liner shape. The liner is made by heating and then cooling the mold while rotating (the fusion temperature or the polymerisation temperature have to be reached). It can be one or two port liner. The metallic bosses are introduced during the rotomolding step or stick on the liner before wrapping.
- **From tubes:** polymeric tubes (made by extrusion blow molding) and domes (equipped with the metallic boss) are purchased at the desired diameter. Both shapes are welded to form the liner.

For all composite vessels, the metallic or the polymeric liner is then hoop-wrapped or fully wrapped with the composite with a **filament winding machine**. For cylinder vessels, 3 wrappings are possible: hoop, polar and helical (see Figure 6). Types II are only hoop-wrapped. Type III and IV vessels are generally a combination of hoop and polar wrapping – but a combination of the 3 wrapping can be considered. Many vessels can be wrapped in the same winding machine if it is equipped for many winding heads. Once the liner is wrapped, the resin must be cured. The curing is generally performed in ovens with the resin appropriate heat treatment.



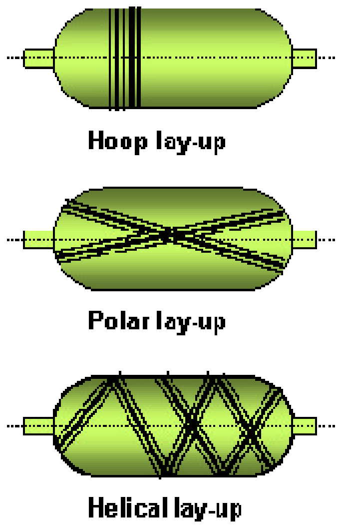


Figure 6 : winding machine and the 3 winding possibilities.

Materials suitable for hydrogen high pressure vessels

From a material compatibility point of view, the main issues for the hydrogen high pressure vessels are:

- the risk of hydrogen **embrittlement** of the steel : this phenomena leads to a premature crack of the steel due to H atom dissolution and trap (stress corrosion cracking). The main risk is the burst of the tank. A lot of efforts on H_2 gas pressure embrittlement understanding and prevention rules were conducted in the 70s and 80s after many accidents occurred with steel pressure vessels. The prevention rules based on 200 bar cylinders were then defined.
  The parameters which influence the embrittlement behavior of the pressure vessel are:
  - H_2 purity, storage pressure, temperature, stresses and strain and time of exposure (environment effects)
  - Microstructure, chemical composition, inclusion, mechanical properties and welding quality (steel properties).
  - Stress levels, stress concentration, surface defects (design quality)

  The first high pressure steel vessels were made of soft steel (carbon content < 0,25%) and for a long time, only this steel was authorized for pressure vessels. Today and since the 50s, thanks to the steel metallurgy development, various compositions are suitable. Table 1 presents the conventional steels used for type I and type II vessels in the gas industry. By extrapolation, the same requirements are defined for type III vessel steel liners. It is important also to note that if the metallic boss of type IV is made of steel, the same requirements are also required. For more information on the risk of hydrogen embrittlement of steels, please see the H. Barthelemy paper in WHEC 16 proceedings.

Type of steel	*Note*
Normalized and carbon steels	Embrittlement to be assessed if Rm>950 MPa.
Stainless steels	Some of them can be sensible to embrittlement (ex. : 304)
Quenched and tempered steels	**More used** (ex.: 34CrMo4); Embrittlement to be assessed if Rm>950 MPa.

Table 1 : steels acceptable for hydrogen pressure storage (ISO 11114-1)

- the **permeation** rate through the polymeric liner. The permeation is specific of type IV vessels and is an inherent phenomenon for all gases in contact with polymers. It is the result of the H_2 gas dissolution and diffusion in the polymer matrix. It had been identified at the beginning of composite vessels development and low permeable polymers are one topic of research.
  Because H_2 is a small molecule, the diffusion and thus the permeation are enhanced. For safety reason, the permeation shall be lower to a certain rate. This leads to the development of special polymers which are suitable for hydrogen liners. In 2006, polyethylene and polyamide (specific semi-crystalline grades) are the most used liners for hydrogen energy type IV tanks.

No specific issue brought by hydrogen gas is met with aluminium alloys (except if presence of mercury). The aluminium alloy grades used for the high pressure vessels are 6061 and 7000. They are not specific to H_2 and are used for the types I, II and III vessels and also for the metallic boss of type IV tanks.

Either glass, aramide or carbon fibers can be used for composite tanks wrapping. These fibers are characterized by their tensile modulus, tensile strength and elongation. Table 2 gives the usual ranges of these mechanical properties for each category of fiber. Hydrogen is stored in very high pressure vessels when used for hydrogen energy applications (service pressure = 350 bar). As a consequence, from a mechanical point of view, carbon fiber is preferred. In the same way, various resins can be used (polyester, epoxy, phenolic etc…). But, for pressure vessels, due to its good mechanical properties and good stability, the most used is the epoxy resin. Pre-impregnated fibers are commercially available, but expensive. Thus, mainly for cost reasons, the fiber is impregnated just before the winding step.

Fiber category	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

Table 2 : range of fiber mechanical properties

To conclude, when compared to the storage of other gases, hydrogen requires special attention for the choice of the steel for types I, II and III tanks & for the polymer choice for type IV tanks. A material test is generally requested to prove that the embrittlement is low: tensile test, disc test, fracture mechanism tests. A full permeation measurement is required on one vessel to prove that the permeation is below a specified rate (1 cm^3/l/h in 2005). A measurement on a sample alone could also be sufficient to assess the permeation rate.

Tests approval & regulation

With the use of high pressure vessels came also some accidents, as it often occurs with all new technology. These accidents forced the authorities to impose the first pressure cylinder regulation in 1895. Type I vessels approval tests were defined mainly based at the beginning on the experience of boilers.

Today the cylinders used to transport gases (including hydrogen) are regulated. In Europe, this is covered by the Transportable Pressure equipment Directive (TPED) which relies on the ADR/RID and the standards developed by the CEN TC 23. At international level a similar regulation is being prepared by the United Nations; this regulation will rely on ISO standards prepared by ISO TC 58.
For hydrogen stations, the cylinders and tanks used as buffers shall follow in Europe the Pressure equipment Directive (PED) in North America the ASME code. Some exemption for composite cylinders is under discussion and in other countries the applicable pressure vessels codes.
For hydrogen tanks used on vehicles, there is not yet any regulation in place but the exemption given use often the standard under preparation with ISO TC 197 (ISO DIS 15869).

New trends due to hydrogen energy

Today industrial hydrogen is delivered as a function of the customer consumption. The supply modes are presented in Table 3. In this paragraph, we will then only consider pressure storages in vessels.

Consumption (Nm^3/h)	*Type of supply*
< 100 Nm^3/h	200 or 300 bar cylinders
From 1 to several hundreds Nm^3/h	200 or 300 bar trailers – 20K liquid tank – small on site production (electrolyser/reforming etc…)
A few thousands Nm^3/h	Pipelines – on-site production.

Table 3: industrial hydrogen conventional delivery in 2006

Compared to industrial gas, hydrogen energy has brought new constraints for pressure vessels and this, mainly for the transportation field. Before entering into details for pressure vessels dedicated to hydrogen energy, it is important to remind the main hydrogen energy applications. They are listed below and are depending on the fuel cell development (PEMFC mainly):

- fuel for transportation : buses, cars, scooters, other leisure vehicles. These vehicles can be powered by a fuel cell or by an internal combustion engine fuelled with H_2. Use in boats is also considered.
  For this application, the main constraint at the moment is the weight and volume savings. As a consequence, when pressure storage is considered, only types III and IV could the cost of the storage system is also important.
- Stationary applications: back-up power supply or power generator for residential.
  For this application, the cost of hydrogen supplied is the main parameter.
- Portable applications: portable back-up power supply, portable power generators, electronics (computers, mobile phones etc…).
  Weight and volume savings are primordial.

The performances which are generally used to compare the pressure vessels are Cm and Cv defined as:

- Cm: weight performance: mass of H2 stored divided by the mass of the vessel (%wt)
- Cv: volume performance: mass of H2 stored divided by the external volume of the vessel (g/l)
- cost

The safety requirements are of course the same for all of them. Figure 7 shows the technical performances as a function of service pressure for the today technology of type III and type IV vessels. The performances are given with 10% of incertitude. Note that the Cm for type I and type II vessels are respectively 1 and 1,5 % at 200 bar (the weigh is ~60-70kg to store $10Nm^3$ of hydrogen).

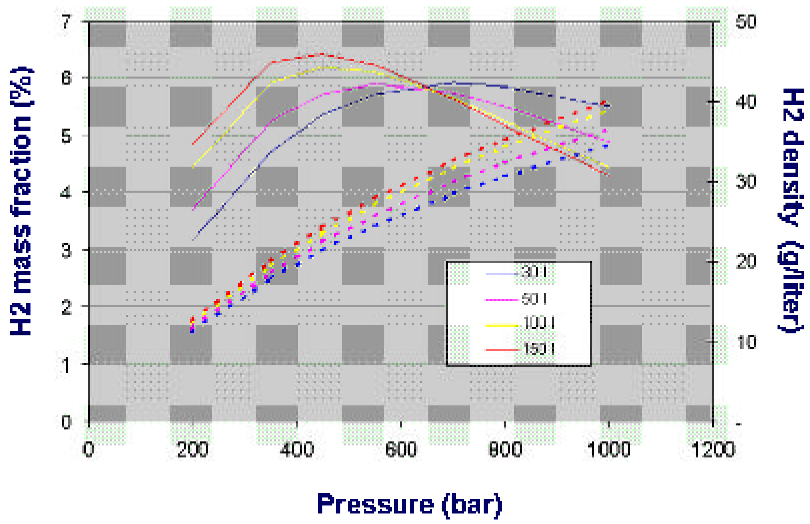


Figure 7: Cm and Cv as a function of the pressure (types III and IV)

The general features for type I vessels and that they are heavy (Cm ~1% max) and pressure limited. Indeed, to have high service pressures of type I tanks, the thickness of the wall shall be increased. But, heat treatment during the manufacturing cannot be as efficient as on thinner walls: the very high pressure walls will have strong material properties heterogeneity through the thickness. It generally reaches the point where steels are very sensible to hydrogen embrittlement and thus defect growth unpredictable. This has resulted in restriction for 350 bar all metallic vessel use in Europe. As a consequence, for higher-pressure applications (700 bar refuelling pressure) type I technology, shall definitely be avoided to reach an appropriate safety level. For on board storages in vehicles, both the weight and the pressure limit will restrict their use. On the other hand, they are the cheapest high pressure vessels. Thus, when no space or weight savings are required, they are the more competitive and technological sufficient supply mode. It is the case for stationary applications like back-up power supply or power generator. An example of this application is given in Figure 8.

Figure 8 : stationary fuel cell power supply equipped with conventional 200 bar type I vessels (Axane technology)

Type II vessels are still heavy (no significant improvement compared to type I), but they can easily withstand very high pressures. Due to their weight, they are not a solution for on board hydrogen storage. But they have other uses in the hydrogen energy. For example, they are used as high pressure buffers in hydrogen fast filling stations. 450 and 800 bar type II buffers are used today for the demonstration and the deployment of H_2 fuel stations. Because few fibers are needed, they remain cost competitive for such applications. An example of fast filling station is given in Figure 9.

Figure 9 : fast filling station with type II buffers

Type III and type IV tanks are one of the most suitable solutions today for on-board storages. These technologies are widely used for other gases (air, natural gas), but the main difference for on-board hydrogen is the need of very high pressures: 350 to 700 bar for H_2 instead of 200 bar for natural gas or 300 bar for breathable apparatus. This pressure increase meets technological issues.
However, even at very high pressures, these storages do not fulfill the automotive industry requirements in term of technical performances and cost. The Department of Energy in the US (DoE) gives the requirements of Table 4 for the whole on-board storage system (that is including valves, pressure regulators, pipes etc… from the vessel itself up to the fuel cell or the thermal engine). It is clear that these requirements won't be achieved with today technology. For a car system and a 700 bar pressure storage, the weight performance at the moment seems to be 5-6% at the vessel level (not system). From a pure technical point of view, maybe a change in the fiber type could allow to reach these values (for example by using a very high performance carbon fiber ; a prototype 700 bar vessel have reached 11% weight performance by using very high cost materials in 2001). But the cost will highly increase. One other solution could be to re-define the safety coefficient. At the moment for carbon fiber composite vessels, it is equal to 2.25. The proposal would be to decrease it, especially for 700 bar on board storage. This would allow both to save weight and volume and to decrease the cost. Some initial studies have been undertaken on that topic both in North America and in Europe.

	2005	*2010*	*2015*
System gravimetric density (kWh/kg)	1,5	2	3
(%wt)	4,5	6	9
System volumetric density (kWh/l)	1,2	1,5	2,7
(kgH_2/100l)	3,6	4,5	8,1

Table 4: DoE requirements for transportation

With the usual design, 350 bar type III and type IV tanks seem to be commercially available in 2005. They are used in FC or IC H2 powered buses for which 350 bar seems sufficient. For cars, due to the low energetic density of hydrogen and specific car constraints – mainly room and autonomy equivalent to gasoline cars – higher pressures are required. A consensus seems to agree for the 700 bar (10 000 psi). Very high pressure composite tanks started to be developed a few years ago and they are not fully available from a commercial point of view. Testing and development are still on going ; it is expected that the increasing interest for hydrogen energy, and the first large scale demo and commercial application will open the market, allowing the manufacturers to increase their efforts for more reliable and cost effective solutions in the coming years.

At the moment, In Europe, information concerning the high pressure composite vessels developments can be found in the European integrated project: STORHY. In this project, work in on going on 700 bar tank technical performances improvement, on increasing the wrapping step in the production cycle and on very new vessel design to decrease cost. In North America, In DoE programs, developments are also on going of vessel and manufacturing cost improvements.

For small portable applications (computers etc…), no pressure storage is considered at the moment.

Conclusion

The main features (state-of-the-art) of the 4 pressure vessels are summarized in Table 5.

Type I	*Type II*	*Type III*	*Type IV*
Technology mature : **++** Pressure limited to 300 bar (⇒ density : -) Cost performance : **++** Weight performance : -	Technology mature : **+** Pressure not limited (⇒ density : **+**) Cost performance : **+** Weight performance : **0**	Technology mature for P=350 bar; 700 bar under development. Cost performance : - Weight performance : **+**	Technology mature for P=350 bar; 700 bar under development. Cost performance : - Weight performance : **+**

Table 5 : main features for H_2 pressure vessel types in 2006

Each pressure vessel type can be used in the hydrogen energy supply chain. This depends mainly on the application type of the fuel cell. The main developments today concern type III and type IV at very high pressure. Even with the today design, some improvement has to be performed for the 700 bar pressure in order to fulfil the hydrogen energy standards. It is important to underline that these standards are still under discussion.

Acknowledgment

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