H2 HIGH PRESSURE ON-BOARD STORAGE CONSIDERING SAFETY ISSUES

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ABSTRACT

The present paper reviews the state-of-the-art of integrated structural integrity monitoring systems applicable to hydrogen on-board applications. Storage safety and costs are key issues for the success of the hydrogen technology considered for replacing the conventional fuel systems in transport applications. An in-service health monitoring procedure for high pressure vessels would contribute to minimize the risks associated to high pressure hydrogen storage and to improve the public acceptance. Such monitoring system would also enable a reduction on design burst criteria, enabling savings in material costs and weight. This paper reviews safety and maintenance requirements based on present standards for high pressure vessels. A state-of-the-art of storage media and materials for onboard storage tank is presented as well as of current European programmes on hydrogen storage technologies for transport applications including design, safety and system reliability. A technological road map is proposed for the development and validation of a prototype, within the framework of the Portuguese EDEN project. To ensure safety, an exhaustive test procedure is proposed. Furthermore, requirements of a safety on-board monitoring system is defined for filament wound hydrogen tanks.

1.0 INTRODUCTION

Hydrogen can be stored in a wide variety of ways, each of them with specific advantages and disadvantages. The overall criteria for choosing a storage method should be safety and ease of use [1]. Storing hydrogen by way of Metal Hydride Tanks, Compressed Hydrogen, Liquid Hydrogen, Carbon Nanotubes, Glass Microsphere, Liquid Carrier or Chemical Storage are the main possibilities being studied and developed at the moment [2-5].

Hydrogen storage at high pressure has the main objective of achieving interesting energy densities (above 0,75kWh/litre which is the recognized value at 350 bar). However, as each additional cubic meter compressed into the same space requires 35 standard atmospheres, i.e. 35 bar, of added pressure, compressing the gas is expensive and so the storage of hydrogen by this method requires optimization and R&D. Structural reliability and strong validation procedures are of major importance when developing this type of storage in high-performance composite vessels. The path is being defined as to go up to 700 bar of operating pressure, and composite materials of fibre-polymer basis, by way of their stiffness-to-weight and strength-to-weight favourable ratios, are in the front row of that development.

In Europe and United States of America, a several number of projects and programs have been conducted in this particular area of hydrogen storage in the last years. Table 1 presents some of the most relevant research projects/programs (or even proprietary pre-commercial works) led in compressed storage of gaseous hydrogen. It presents also some related projects once they treat of standards or procedures that are to be accounted in the design and development of such tanks.

Table 1 – R&D main current or/and former projects/programmes in compressed storage of gaseous hydrogen

Project Acronym	Description	Project Leader
Institutional R&D Financed Programs		
StorHy	Research on storage technologies (gaseous, liquid, solid), focusing on automotive applications	Magna Steyer, AT
HySafe	contribute to common understanding and approaches for addressing hydrogen safety issues, including harmonisation of testing methods, benchmarking and identification of best practices	EC, JRC-IE
Hymosses	Hydrogen in mobile and stationary devices - safe and effective storage solution	University of Stuttgart, DE
DoE Hydrogen Program	Storage of hydrogen (or its precursors) on vehicles within the distribution system	DoE – EERE, USA
	Technical validation of systems in real-world environments	
	Safety assurance and facilitation of the development of model codes and standards for domestic and international production, distribution, storage, and utilization of hydrogen	
Industrial (or pre-commercial) Developments		
Trishield$^{\text{TM}}$	Hydrogen storage tank	Quantum
***	Low Cost, High Efficiency, High Pressure Hydrogen Storage	Quantum
Tuffshell™	10,000 psi Composite Hydrogen Fuel Tank	Lincoln Composites
COPV’s	Composite Over-wrapped Pressure Vessels for high and low pressure cryogenic storage of hydrogen	HyperComp Engineering Inc., USA
CH2-ISS	Development of a Compressed Hydrogen Gas Integrated Storage System for Fuel Cell Vehicles	Lincoln Composites, USA
***	Advanced Light Weight Fuel Storage Systems$^{\text{TM}}$	Dynetek Industries Ltd.
***	Lightweight composite tanks	Lawrence Livermore National Laboratory, USA

Simultaneously to the development of new prototypes, techniques and devices for the reliable storage of H2 there are several technical committees and forums drafting new procedures and standards in order to guarantee an increasingly efficient and safe implementation of H2 based technologies in our societies. One interesting and important issue to account for is certainly the harmonization of all the disperse standards and procedures that are being drafted. The most relevant committees and associations interested and acting in this area are then, EIGA – European Industrial Gases Association, CEN – European Committee for Standardization, ISO – International Standards Organization (TC197 "Hydrogen Technologies"), NFPA – National Fire Protection Association (USA), ASME – American Society of Mechanical Engineers (USA), CGA – Compressed Gas Association, UNECE – United Nations Economic Commission for Europe and IEC – International Electrotechnical Commission. Some of these entities are more deeply dedicated to on-board automotive CGH2 storage as others relate to every relevant safety and regulatory issues on hydrogen's usage.

The sensor technology has grown in last years. Vehicles that in the 80s were using 4 sensors are nowadays using up to 1500 [6]. The main driver of this evolution was safety. For high-pressure H2 storage the safety issues are also important criteria. A monitoring system can also enable savings on material costs, due to a reduction of burst ratio factor from 2.35 to 1.8, according to the last proposal for a new draft regulation from UNECE GRPE informal group "Hydrogen/Fuel Cell Vehicles" [7]. Material costs are considered the primary cost drivers, with the carbon fibres representing 40- 80% of the total cost. The use of a monitoring system may represent significant opportunities for cost-reduction. The development of a structural health monitoring system for high-pressure storage has been considered in some projects like ZEM [8] for all-composite CNG tanks using embedded long-gage interferometric sensors for on-line monitoring during tank refuelling. Optical fibre sensors are good candidates for the development of an on-line health monitoring procedure due to the intrinsic properties of the optical fibre like low dimensions, insensitivity to electromagnetic interferences, etc. Among the different optical fibre sensors, the fibre Bragg grating (FBG) seem to be a good candidate as it provides direct absolute strain measurements and thanks to its multiplexing capacity. The feasibility of using FBG sensors for the strain imaging of the tank using sensor arrays to locate and assess damage to composite parts has already been studied [9-13] as well as the use of piezoelectric sensors [14] for impact damage detection on composite overwrapped pressure vessels.

Within the EDEN project [15], designed to develop a Portuguese supporting platform for the arising hydrogen economy, fixing the main abilities and know-how for the production, management, logistics and implementation of hydrogen based systems, the thematic of hydrogen storage systems is considered as a specific task. It is proposed to develop a prototype of a pressure vessel for gas storage at high and very high pressure, and also capable to continuously measure the damage evolution and the automatic detection of critical functioning. In this paper are presented the aspects that have been considered for its execution.

2.0 VESSELS FOR HIGH-PRESSURE H2 STORAGE

In the case of gaseous storage, current available technology (with commercial products for 350 bar pressure storage) is around five times less energydense than gasoline or diesel fuels – that is to say, storing hydrogen uses five times the space per unit energy. So, there is a need for ever increasing pressures, and the current aim is for 700 bar in fibre-reinforced composite tanks, which would give acceptable road vehicle autonomy. This requires material and design improvements in order to ensure tank integrity. High-strength fibres need to be developed and liners made impermeable to hydrogen. Safety and certification issues are paramount.

Lastly, it is important to standardise peripheral equipment such as safety sensors, fuel station flow meters, and 700 bar dispensers and nozzles for rapid refuelling [16]. Today's state-of-the-art for hydrogen storage includes 35 MPa (350 bar) and 70 MPa (700 bar) compressed gas tanks and cryogenic liquid hydrogen tanks for on-board hydrogen storage. Carbon fibre-reinforced compressed hydrogen gas tanks are being developed by several private and funded R&D programmes (as seen in table 1). Such tanks are already in use in prototype hydrogen-powered vehicles. Two alternative types of inner liners are typically used: the aluminium (type III storage pressure vessels according to EIHP classification [17]) and the high molecular weight polymer ones (type IV storage pressure vessels). The application of such materials comes from the necessity of guarantee permeability of the inner liner to the hydrogen molecules and low weight. The use of certain steels proved to be potentially dangerous given the embrittlement tendency of those materials in contact with hydrogen [18]. While the inner liner gives the main geometry and volume capacity, a structural outer shell is placed over the liner (*vide* Figure 1). The most relevant prototypes were made with carbon fibre-epoxy systems and produced by filament winding technique which allows the precise placement of the fibres' tow over the liner surface, optimizing, in this way, its global structural ability.

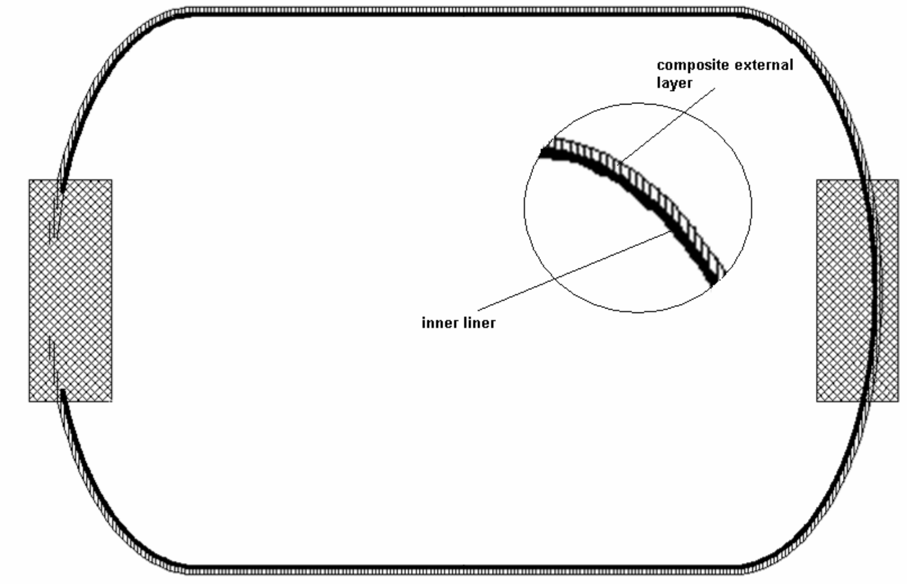

Figure 1 – scheme of the composite vessel layers

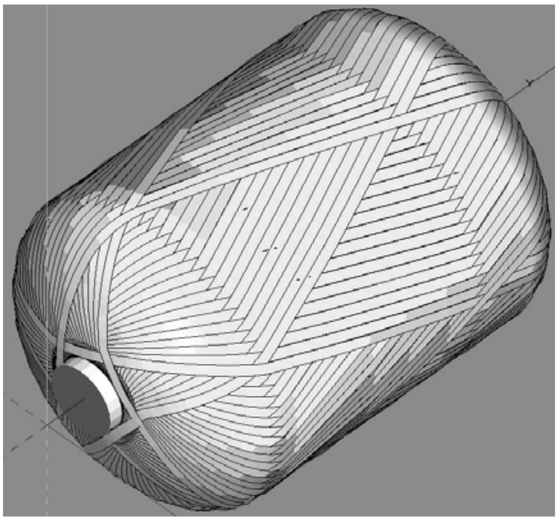

Figure 2. CAD model of first filament winding layer (EDEN project)

Figure 3. 26 litres vessel prototype after short-term hydrostatic pressure test at 320 bar [15]

Figures 2 and 3 show one CAD model of the first layer of the carbon patterned outer shell and a small vessel prototype after completion of filament winding, respectively. The main considerations in the design of compressed hydrogen gas tanks involve high pressure capacity, weight, volume, conformability, cyclic use and cost. The cost of high-pressure compressed gas tanks is essentially dictated by the cost of the carbon fibre that must be used for light-weight structural reinforcement. In order to improve savings in material, maintaining high levels of safety and confidence, it is necessary to go further in the specific knowledge of fibres’ interaction at a layer level (interactions between layers and even within one same layer), once the three-dimensional real winding pattern introduces specific mechanical loading conditions (such as shear stresses, for example). That certainly is a key challenge for the near future of high-pressure vessels commercial diffusion. The Portuguese project EDEN, besides the main drive on sensor technologies for health monitoring, is complimentarily placed aside of other task dedicated to the numerical modelling of filament winding specificities that become important when thinking of these type of vessels and their future massive utilization. The sensors are supposed to be embedded within the composite layer during filament winding process. Compatibility of sensors technologies with this manufacturing process need to be studied. The reliability of the sensors after their embedment for different manufacturing parameters will be analysed along the project. Additionally, test procedures of increasing demands are being developed and included in the main standards reference drafts, implemented by several technical committees dedicated to these issues of hydrogen tank storage safety. Presently, the most relevant prototypes are being certified under a various and redundant number of standards and certificatory institutions around the world, given the lack of harmonisation at a global scale (either in terms of geographic means and in number of relevant parameters to account for) of the reference standards, codes of practice and legislation.

3.0 SAFETY AND MAINTENANCE REQUIREMENTS

Only a small number of hydrogen technologies, systems and components are in operation and many are in the pre-commercial development phase and still proprietary. As such, only limited data are available on the operational and safety aspects of these technologies. Lack of technical data for underground and above ground storage, certainly results in undesired over dimensioning. Insurance rates are tied to current codes and standards [19]. Requirements for off-board bulk storage are generally less restrictive than on-board requirements; for example, there may be no or less restrictive weight requirements, but there may be volume or "footprint" requirements.

Two main efforts shall be held by the various working groups of these research programmes aiming to successfully base the hydrogen economy: the confident, gradual and consensual development of harmonized codes and standards around the world and the effective analysis of the life-cycle and efficiency of hydrogen based energy systems, particularly in what comes to storage issues.

Applicable procedures and standards for hydrogen storage systems and interface technologies will facilitate implementation/commercialization and assure safety and public acceptance [20]. Standardized hardware and operating procedures, and applicable codes and standards, are required. As for an example, two recent prototypes for hydrogen pressurized storage felt the necessity of pass such a wide range of tests as follows [21]:

- Hydrostatic Burst
- Extreme Temperature Cycle
- Ambient Cycle
- Acid Environment
- Bonfire
- Gunfire Penetration
- Flaw Tolerance
- Accelerated Stress
- Drop Test
- Permeation
- Hydrogen Cycle
- Softening Temperature
- Tensile Properties
- Resin Shear
- Boss End Material

Moreover, they needed (at least for marketing and commercial purposes) to accomplish a great number of standards as shown in table 2. This reinforces the relevance of the costs of exhaustive testing campaigns and, therefore, of their harmonisation in an adequate way, as stated in section 2. Some of the standards refer to the same testing procedures, differing mainly in their regional legal applicability but others refer to the same region and the main difference is then the applying committee.

Table 2. Standards accomplished for the certification of DynetekTM vessel prototype [22]

Standard / Organization	Region
ISO 11439	International
NGV 2	USA / Japan / Mexico / Argentina
KHK	Japan
FMVSS 304	USA
TÜV	Germany
NFPA 52	USA
DRIRE	France
CSA B51	Canada / Australia / Hungary / UK
BUREAU VERITAS	Argentina
ISO 15869 INTERNATIONAL	(draft)
EIHP	(draft)
ECE R110	Europe

Within the Portuguese EDEN Project, several standards and drafts will be analyzed, in order to evaluate their coherence and applicability to the arising national platform for H_2 economy. The result of that study will be integrated in the project practices and final outputs.

4.0 ON-LINE MONITORING SYSTEM

Concerning the health monitoring procedure, at the end of EDEN project, a methodology for filament winding pressure vessels based on embedded sensors will be proposed. Storage at higher pressures implies increased risks that must be specially considered in the automobile industry. Economical and energetic development based on hydrogen will imply the safety certification of storage. Conventional methods of periodic non destructive inspection (NDI) have contributed to increased reliability and safety of these devices. However, periodic inspections represent additional operating cost. In this operation the device must be dissembled and reassembled several times, promoting this way damage of the parts. The main limitation of these NDI methods is that they don't assure that damage won't occur between inspections. A structural integrity system will be developed to allow at any moment the evaluation of safety conditions, improving reliability and safety and reducing operating costs.

Sensors embedment on composite materials during production will allow the development of structural integrity monitoring methods that exceed all the limitation of conventional NDI technologies. The application of FBG sensors seems to be the more appropriated for this application compared to conventional electronic technologies for monitoring local strains. Temperature and strain sensing capabilities, associated to cost and the ability to embed the sensors in the structural component during manufacturing, enable this new attractive monitoring applications. Composite materials processing and the small dimensions of optical fibres enable the embedment of a net of sensors with small impact on mechanical properties. In a first approach, the compatibility of composite manufacturing technologies with the embedment of sensors will be studied, in terms of sensitivity variation of the sensor and fragility of the host material. Contrarily to other sensors, as piezoelectric, several optical sensors can be printed in a same fibre, avoiding this way large cablings that induce defects on the material. On the other side, optical fibre sensors are immune to electromagnetic interferences, contrarily to piezoelectric and conventional strain gauges. In addition, many piezoelectric sensors or strain gauges can not stand the high temperatures of filament winging process when using thermoplastic composites. However, piezoelectric effect based sensors won't be discarded in this study considering that it is necessary to determine which are the most appropriate sensors considering their intrusivity, sensitivity, integrity and reliability.

A multisensing solution is needed that is capable to be able to assure the tank in-service integrity from the measurement of physical sizes such as, for example, strain, temperature, hydrogen presence. Acoustic emission (AE) testing is commonly used (ASTM E2191-02) for in complement to hydro-proof testing permitting a higher confidence in safety of cylinders [23]. Studies in the field of AE testing applied to type III and IV pressure vessels underlined that AE seem to be an appropriate and efficient method of quality control, especially for Type III cylinders [23]. They also demonstrated the potential of AE for detection of critical flaws, delamination and impact damages during in-service pressure testing of Type IV cylinders [24].

Within the framework of EDEN project, the proposed solution for in-service monitoring will be based on measurements of strain and temperature, and also AE for detection and localization of damage and its severity determination. Two types of sensors are considered: optical fibres based and piezoelectric effect based sensors. The sensors are embedded in composite materials at manufacturing. The proposed health monitoring concept will take into account the effectiveness of continuous monitoring. Aspects such as the effectiveness of real-time availability of the data provided by the sensors and their interpretation will be considered.

5.0 SUMMARY

It is believed that an energy economy based on hydrogen (produced from renewable energy sources), with fuel cells as energy conversion technology could resolve the major concerns about security of energy supply, source diversification and reduction of greenhouse gas emissions. However, before reaching the objective of such energy system, some fundamental issues must still be considered such as the hydrogen storage safety.

The next step for H2 storage will be directed to meet safety, percent weight, energy density, and specific energy goals of 6% hydrogen by weight. EDEN project will intend to answer to some of these considerations by thee optimization of filament winding manufacturing process and the implementation of a health monitoring procedure.

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