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COMPOSITE 700 BAR-VESSEL FOR ON-BOARD COMPRESSED GASEOUS HYDROGEN STORAGE

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SUMMARY

Hydrogen storage is the key to enable an extensive use of hydrogen as an energy carrier. None of the current technologies are able to satisfy all car manufacturers' specifications. The French Atomic Energy Comission (CEA) has, since 1998, been involved in the development of innovative materials and processes dedicated to the manufacturing of full composite 10,000-psi vessels for on-board storage of gaseous H_2, and the present paper reviews the most recent technical and scientific achievements, comparing them to state-of-the-art CGH2 storage systems.

Keywords: Composite Pressure Vessel Hydrogen Storage

HYDROGEN STORAGE TARGETS

A large amount of research and development is still required to cut costs and improve the volumetric performance, reliability and durability of composite pressure vessels for hydrogen storage. Various European and French projects aim at developing robust, safe, efficient and cost-competitive on-board storage systems for compressed gaseous hydrogen (CGH2). The targets formulated by the European Union (EU) and the Department of Energy (DOE) in order to obtain progression in the development of lightweight tanks in fuel cell vehicles (FCV) are summarized in table 1.

Table 1: Requirements for on-board H_2 storage systems

Storage Parameter	**Units**	**2010 target**	**2015 target**
Driving range	**km**	**400-600**	**400-600**
Hydrogen storage mass	**kg**	**4 - 10**	**4 – 10**
Gravimetric capacity (specific energy)	kWh/kg	2	3
Gravimetric energy density	Mass %	6	9
System Weigth (for 4 kg H_2)	**kg**	**67**	**45**
Volumetric capacity	kWh/L	1.5	2.7
Volumetric Energy density	H_2 kg / 100L	4.5	8.1
System Volume (for 4 kg H_2)	**L**	**89**	**50**
Energy Storage system cost	$/kWh	4	2
System cost (for 4 kg H_2)$^{(1\ H_2\ kg \approx 33.33\ kWh)}$	**$**	**534**	**267**
Operating temperature	**°C**	**-40 to +85**	
Operating pressure		**1 to 700 bar**	
Refuelling rate	H_2 kg / min	1.2	2
Refuelling time (for 4 kg H_2)	**min**	**3'20**	**2'**
Life cycle (1/4 tank to full)	cycles	1000	1500
Safety requirements for 700 bar vessel		**EIHP II**	
Minimum Burst pressure (2.35 SF)	bar	> 1645	
Life cycle (from 20 to 875 bar)	cycle	> 15000	
Permeation rate	(H_2 Ncm^3/h/L)	< 1	
Recyclability	According to End-Of-Life Vehicle Directive 2000/53C		

Considering the gravimetric and volumetric density as well as safety requirements, full composite vessels are conceivable for an on-board hydrogen storage up to 70 MPa. Presently, research and development efforts are focused on containers with either metallic (steel or aluminum) or plastic (thermoplastic or thermoset) liners - vessels denoted respectively type-III and type-IV. According to state-of-the-art and STORHY [1] results, type-III containers suffer from a limited cycling resistance. It is not conceivable that car use be reduced to a few hundred fuel refillings (which is currently the case for FCV prototypes with 700-bar type-III vessels). So far, only type-IV vessels have demonstrated their ability to withstand the 15,000 cycles from 2 to 87.5 MPa required by EIHP II [2] and ISO-15869 [3] for a 70-MPa nominal operating pressure. Type-IV containers are thus promising candidates for high-pressure gaseous hydrogen storage, provided that they satisfy the required hydrogen tightness. The EIHP II draft is a regulation applied to compressed gaseous hydrogen systems and to specific components of motor vehicles utilizing compressed gaseous H_2. This draft is to a large extent based on the CNG regulation where vessel safety factors are overdesigned, particularly with regard to burst.

At the present time, new regulation drafts are under discussion. Compared to the initial draft, based on EIHP II or ISO 15869 / TC197, safety factors (presented in table 2) are being lowered for several reasons. The burst safety factor for type-IV carbon fiber vessels demonstrates a 15% decrease from 2.35 (EIHP II) to 2.00 (ISO 15869 DIS 3), resulting in a diminution of carbon and vessel masses and a lowering of the vessel cost for 10,000-psi (70-MPa) type-IV gaseous H_2 vessels from around 8 to 11 %. The safety factor in pressure cycling tests has been reduced by 25% from 15,000 cycles to 11,250 cycles as it was deemed to be overdesigned with regard to the standard service life of a vehicle. Today, type-III vessels are able to run for a few hundred cycles from ≈300 psi (2 MPa) to 12,500 psi (87.5 MPa), whereas type-IV vessels have proven to withstand 15,000 cycles during cycling tests at ambient temperature (demonstrated in the European STORHY project 2004-2008 concerning CEA technology in full-scale vessels). A decrease of safety factors is expected also with regard to the H_2 permeation rate value for type-IV vessels where the permeation rate displays an increase of 200% or 280% from 1 N cm^3 H_2/h/L to 2 or 2.8 N cm^3 H_2/h/L. The liner thickness can be reduced, rendering it possible to increase the H_2 volume. The permeation rate of the liner used within the CEA has been measured to be 20-fold (or even 40- or 56-fold, depending on standards) the minimal rate. Consequently, the liner thickness can be reduced to improve mass and volumetric storage densities.

Table 2: Safety Factor Evolution

	Type-III or type-IV Carbon Fiber Composite Vessels		
	Burst pressure	Pressure Cycling	H_2 Permeation rate (type-IV)
EIHP II 12b.	2.35 x Nominal Pressure (164.5 MPa @ 70 MPa)	> 15,000 cycles (from 2 MPa to 87.5 MPa)	< 1 N cm^3 H_2 / h / L internal volume
ISO 15869.3	2.25 x Nominal Pressure if NP < 35 MPa (157.5 @ 70 MPa) 2.00 x Nominal Pressure if NP > 35 MPa (140 MPa @ 70 MPa)	11,250 cycles (from 2 MPa to 87.5 MPa)	< 2 N cm^3 H_2 / h / L internal volume @ 35 MPa < 2.8 N cm^3 H_2 / h / L internal volume @ 70 MPa

As shown in table 3, it is only the type-IV technology that satisfies all design criteria (burst, pressure cycling, H_2 permeation), and so far, no solution fulfils the gravimetric, volumetric and cost targets (respectively 6% mass, 1,5 kWh/L and 4 \$/kWh). It is today possible to meat the gravimetric requirement (5,4% in 2008 and 6% as the target for 2010). On the other hand, the cost target is very far from reach (13 \$/kWh estimated in 2008 and 4 \$/kWh the target for 2010). Unless carbon fiber and manufacturing costs drop considerably, it seems unattainable. Furthermore, the 2010 volumetric target of 1.5 kWh/L cannot be met at 700 bar and a 33.33 kWh/H_2 kg fuel cell engine efficiency. Indeed, the maximum value is 1.33 kWh/L – and this only if the vessel wall thickness is considered to be zero! The target value of 1.5 kWh/L should be attainable for a nominal pressure of approximately 980 bar (14,000 psi) and/or for a fuel cell engine efficiency of around 50 kWh/H_2 kg.

Table 3: State-of-the-art On-board High Pressure Vessels for Gaseous H_2

Manufacturer	**Lincoln composites (US)**	**Quantum technologies (US)**	**Dynetek (Canada, Germany)**		**Ullit (France)**	**Faber (Italy)**	**Luxfer (UK)**
	Tuffshell®	Trishield®	Dynecell®				
Type	IV	IV	III		IV	III	III
Nominal Pressure (bar)	700	700	350	700	700	700	345
Liner Material	PE	PE	Alu		PA6	Steel	Alu
Composite Fiber	GF + CF	CF	CF		CF	CF	CF
Gravimetric Rate (%)	3.9 to 5.3	2.5	3.6	5.2	5.4	/	3.4
Volumetric rate (kWh/L)	0.75 to 0.8	0.8	0.5	/	0.66	/	0.66
Burst Pressure (bar)	1,750	1,650	830	1,900	>1,645	/	/
Number of Cycles from 20 to 875 bar	/	/	/	/	>15,000	/	/
H_2 Permeation rate (N cm3 / h / L)	/	/	/	/	< 0.05	/	/
Vessel Cost Estimation (\$/KWh) for 100,000 vessels/year	/	/	/	/	≈13	/	/
Sources	*Lincoln Composites Web Site*	*DOE report 2004/2005*	*Dynetek, Storhy Web Site*		*Storhy Web Site*	*Faber Web SIte*	*Luxfer Web Site*

METHODOLOGY

Carbon fibers are widely used along with epoxy-type matrices for the fabrication of high-pressure vessels. The conception process of such architectures involves computation (design validation, stress distribution, process simulation and finite elements analysis) in addition to real material and structure characterizations (mechanical testing, micrography, hydraulic vessel testing…). The common methodology for vessel development follows four steps: material, design, process and performance. As shown in figure 1, the optimization phase consists in cycling through the steps to reach the target by minimizing the value of the cost and maximizing volumetric and mass densities.

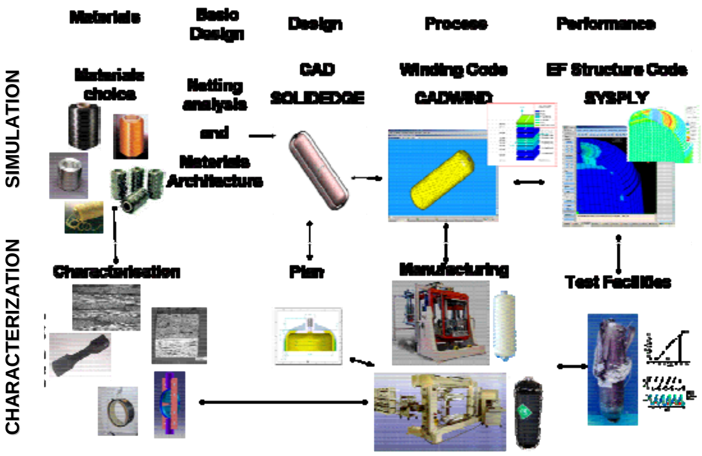


Figure 1: A synopsis of composite shell design.

The CEA has at its disposal in-depth real material characterization methods, enhanced numerical tools (design and process simulation) and *in-situ* smart monitoring techniques (embedded CFO sensors) to improve the design process of high-performance full composite vessels based on thermoplastic or thermoset liner materials.

MATERIALS

Considering gravimetric and volumetric densities, as well as safety requirements, type-IV vessels are the most promising candidates for on-board hydrogen storage. They display no fatigue issues, the H_2 leakage is far below standards, and they exhibit decent weight performances. Vessels fabricated by the CEA-ULLIT have demonstrated abilities to withstand 15,000 cycles from 20 to 875 bar, as required by EIHP II for a nominal operating pressure of 700 bar. Moreover, the CEA is involved in the development of innovative materials as well as materials for composite filament winding (thermoplastic and thermoset matrices) and also fabricates different material types of liners (based either on thermoplastics and thermosets).

Since 1998, the CEA has been down several paths in order to develop a polymer with elevated hydrogen barrier properties capable of fulfilling the requirements for the maximum leakage rate. Among the various studies carried out, the potential of multi-layered systems, nanoclay-polymer blends, inner coatings and technical polymers was assessed. Finally, within the French POLYSTOCK project, the CEA developed, with its partners AIR LIQUIDE and ULLIT, a polyamide-6 (PA-6)-based polymer. A specific formulation was chosen based on the best compromise for permeation, mechanical strength, elasticity and processability. Since this polymer was sensitive to thermal oxidation, the CEA created an innovative 1-step reactive rotational molding process [4][5] starting directly from liquid monomers or precursors (figures 2 and 3). The mold was considered to be a chemical synthesis reactor in which the polymerization and the shaping/molding occurred simultaneously. The polymerization takes place at between 150 and 180°C and lasted from 30 to 90 min depending on the size of the pieces and eventually on the number of layers.

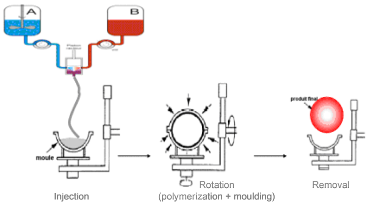


Figure 2: Reactive rotomolding

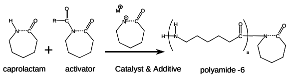
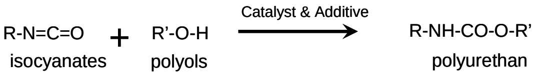


Figure 3: Anionic polymerization of PA-6

Figure 4: A PA-6 liner obtained by reactive rotomolding

Due to thermomechanical and processing limitations, the CEA has also investigated the potential of thermosets for fabricating liners. This was done within the French HYBOU project. A specific polyurethane (PU) formula was designed in partnership with RAIGI, and the corresponding reactive material, widely used for insulation, foams, coatings and moldings, was put through a crosslinking reaction which led to an irreversible, infusible and insoluble 3D-network. Figure 5 displays the scheme for this thermosetting reaction, which could be conducted at room temperature in 5 to 15 minutes depending on the size of the pieces. Figure 6 presents a photo of the PU liner.



$$\underset{\text{isocyanates}}{\text{R-N=C=O}} + \underset{\text{polyols}}{\text{R'-O-H}} \xrightarrow{\text{Catalyst \& Additive}} \underset{\text{polyurethan}}{\text{R-NH-CO-O-R'}}$$

Figure 5: Thermosetting reaction of polyurethanes

Figure 6: Reactive rotomolded PU liner

The hydrogen permeation behavior of the obtained materials has been extensively studied and was found to depend strongly on the pressure and the temperature. Relations between macromolecular architectures and H_2 permeation have been defined and are presented in figure 7.

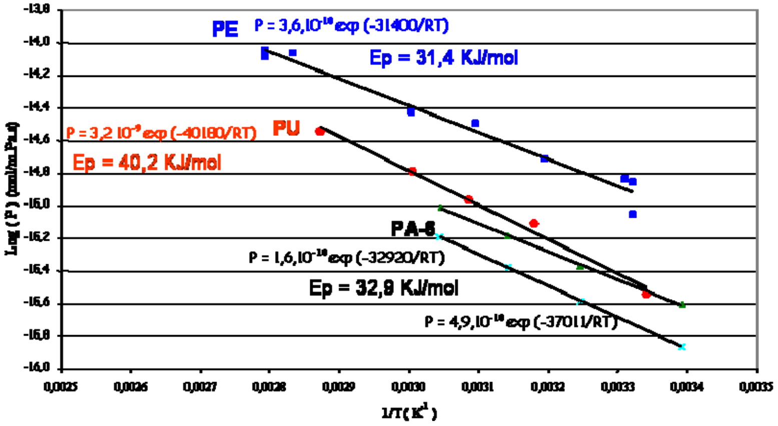


Figure 7: The temperature dependency of the H_2 permeation for PE, PU, PA-6.

While the hydrogen tightness is linked to the liner, the pressure resistance arises from a carbon fiber reinforced composite structure. In order to minimize the mass of carbon fiber, the composite architecture has to be well designed.

DESIGN

The design of a composite vessel, portrayed in figure 8, is extremely specific as it should take into account boss, liner and composite materials, liner manufacturing process specifications as well as constraints for the filament winding process. The composite architecture has to be optimized in order to approach the predefined target as closely as possible. Moreover, the design should take into account the service and test pressures, the external stresses, which are specific to the use (and dependent on, for instance, impact, aggressive media, temperature etc…). For the particular case of type-IV vessels, the main composite design test is that of the burst pressure.

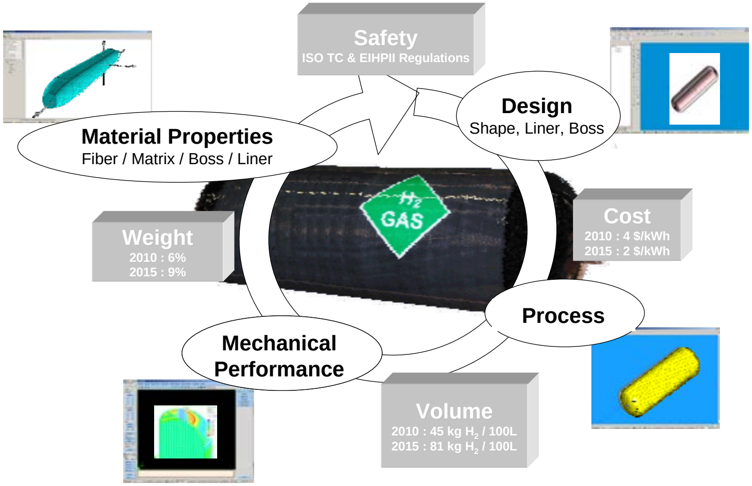


Figure 8: The global methodology for vessel design.

The first design of a container can be basic since it is possible to start with a simple and robust composite architecture of the vessel, compatible with an industrial manufacturing. The definition of the dome shape, the boss thickness, as well as the thickness and angles of the composites can be obtained analytically [6]. For the filament winding, the dome is represented by the cylindrical part of the container forming the spherical or elliptical shell ends of the vessel. Basically, the outlines of a pressure vessel dome are geodesic, which means that the fiber is placed along the shortest distance between the beginning of the dome (end of cylinder) and the external neck of the boss. The design of the shape depends on two conditions: that the filament stress be identical at each point of the dome and that the main load on the surface of revolution undergo reaction in the direction of the filament. If these conditions are met, the fibers should have no reason to slip and all supportive loads should go through the axis of the vessel.

The geodesic shape is currently considered to be the optimal deformed shape of the dome, and this point should be verified during vessel tests or FEM analysis. Geodesic dome contours may also be calculated with a simple procedure for predicting stresses in a fiber-reinforced composite by neglecting the contribution of the resin system, a method known as netting analysis. This technique applies principles of static equilibrium without considering the strain compatibility. The analysis of filament-wound structures also assumes that filaments display no bending or shearing stiffness and that they carry only the axial tensile loads. However, even when such theoretical flaws are present, netting analysis is useful for sizing and predicting failure in simple structures such as cylinder vessels.

In a second step, the FE tools are used to simulate the mechanical behavior for an architecture defined by a Filament Winding simulation. For burst, the quadratic interaction failure criterion in stress and strain space is recommended for unidirectional and multidirectional composite materials, and the first ply failure can be determined with for instance the energetic Tsaï-Wu criterion. However, this approach is far too conservative when designing a lightweight vessel. The burst pressure evaluation can also be estimated by the ultimate failure of a laminate with a very time-consuming ply-by-ply iterative procedure. Nevertheless, the simplest alternative is to consider the maximum stress and strain criteria by taking into account conservative mechanical property values. This method has led to good burst evaluation results for other vessel applications and is therefore often used. However, the range of fiber mechanical properties, especially with regard to strength, is too large either within a spool or from one spool to another, forcing the designer to consider the lower strength properties, which can be 20% lower than the announced strength. Thus, with appropriate criteria, the mechanical performances of the vessel can be evaluated by FE codes and optimized by modifying the composite architecture. The new architectures have to be realistic and can be evaluated by using results from process filament winding simulations.

PROCESS AND MECHANICAL BEHAVIOR SIMULATIONS

Based on filament winding process simulation (demonstrated in figure 9), the ply material thickness and the fiber angle can be computed at each point of the vessel's composite laminate structure. The pattern type can be chosen so as to minimize bridge and cross effects. Consequently, the level of processability of the design can be evaluated and the design can be modified if necessary. By using the outputs of the process simulation as inputs for the FE composite codes, it is possible to simulate the mechanical behavior of the composite structure. Therefore, with appropriate criteria, the mechanical performances of the vessel can be evaluated and an optimization can be run on the composite architecture. An FE code such as the SYSPLY code dedicated for composite structure, can be used to obtain ply-by-ply mechanical evaluations, as shown in figure 10.

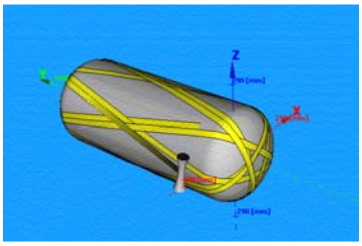


Figure 9: A filament winding simulation

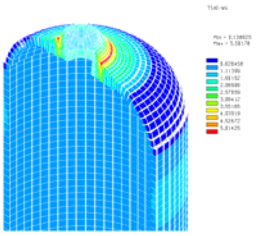


Figure 10: The Tsai-Wu criterion

PROCESS, VESSEL CHARACTERIZATION AND PERFORMANCE

The fabrication and characterization of demonstration vessels represent main issues of project development. All the CEA designs are validated in full-scale 700-bar H_2 cylinders. Through liner polymer syntheses and formulation knowledge, reactive roto-molding and filament process capabilities, design and simulation methodologies, the CEA has together with its French industrial partner ULLIT, developed and fabricated the only 700-bar vessel with a PA6 liner capable of meeting the EIHP 2 test criteria with regard to burst (>1,645 bar), permeation (<< 1 $Ncm^3/h/L$) and cycling (>15,000 cycles). The vessel was developed within the European STORHY project and was tested by an independent academic partner (WRUT). Figure 11 displays a schematic of the process and characterization of the vessel.

Figure 11: A schematic of the process and characterization of a type-IV H_2 vessel.

The average thickness of the composite was approximately 20 mm using the T700 fiber from SOFICAR / TORAY - today considered an optimal fiber. The global mass of the 37-L vessel (for a volume of water at 700 bar) was 28 kg. General technical data are presented in table 4.

Table 4: Technical data for the 700-bar type-IV H_2 vessel developed by CEA–ULLIT.

Vessel mass	28 kg
Internal volume	37 L @ 700 bar (1.5 kg H_2, around 150 km FCV range)
Mass storage capacity	1.5 kg H_2 => Gravimetric Storage Density = 5,4%
Volume storage capacity	Overall volume= 70 L => Volumetric Storage Density =2 kg H_2 / 100 L (0.66 kWh/L)
Liner	Rotomolded patented PA6
Operating Pressure	700 bar
Boss	1’1/8
Cost	Estimated at 650 $ for 100,000 / year => 13 $/KWh
Burst pressure	Measured within STORHY project > 1645 bar (>2.35 OP)
Proof pressure	1050 bar (1.5 OP)
Leaking rate	<< 1 N cm3/L/ hr (measured within STORHY project < 0.05 N cm3/L/hr)
Fatigue test	> 15000 cycles from 20 to 875 bar (1 cycle/min within STORHY project)

In order to evaluate the mechanical behavior of the container, STORHY cycling tests were performed in accordance with the Draft ECE [2]. All experiments were realized at ambient temperature with the use of a hydraulic fatigue test bench from the Wroclaw University of Technology. Cycles of 20 to 875 bar were carried out at an average rate of 1 cycle per minute, and the tested objects were free from any built-in defects. Prior to the tests, the containers were fully equipped with a large number of sensors to record the various types of mechanical behavior. The sensor types ranged from conventional strain and stress gauges to optical fibers with Bragg gratings (FBG). Acoustic emission (AE) sensors were also applied in order to monitor fiber and/or matrix breakage and to obtain correlations with other signals.

All experiments were realized at ambient temperature with the use of a hydraulic set-up in WRUT (figure 12). Prior to the tests, the vessels were filled with a non-corrosive working fluid, i.e., oil.

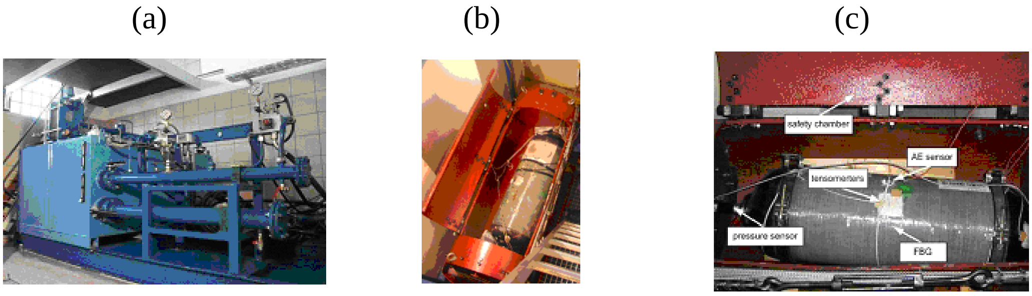

(a) (b) (c)

Figure 12: (a) The hydraulic cycling apparatus, (b) the safety chamber and (c) the fully equipped vessel prior to testing.

The CEA vessel was cycled 15,000 times and results demonstrated that its integrity remained unchanged since no detectable defects were recorded. The gauges showed no significant increase in the maximum value of the strain, nor did the acoustic sensors register any worrying events. The type-IV vessel developed by the CEA thus appeared stable with regard to cycling. Furthermore, the FBG and strain gauges registered consistent strain values during the cyclic pressurizations.

Figure 13 portrays pressure and acoustic signals during selected moments of the experiments. At the beginning of the test (i.e., after 50 cycles), acoustic events were observed to take place for high and low values of the pressure (2 peaks). The first peak referred to the composite layer arrangement in high pressure ranges, whereas the second was produced by the delamination process, which occurred between the carbon and the protective glass layer. After 1,700 or 15,000 cycles, only the peak in the low-pressure range remained, thus demonstrating the stability and fatigue resistance of the container.

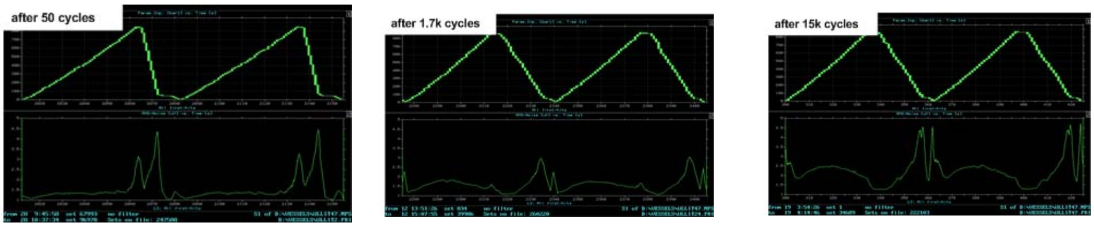

(a) (b) (c)

Figure 13: Graphs of pressure (upper) and RMS of the acoustic signals (lower) during pressurization after (a) 50 cycles, (b) 1,700 cycles and (c) 15,000 cycles.

Burst tests were also performed in accordance with draft regulations [2]. All experiments were realized at ambient temperature with the use of an air-driven hydraulic pump from WRUT (figure 14). Prior to the tests, the vessels were filled with water and degassed. A handful of polymer-liner-based vessels, developed by the CEA, were tested at the WRUT burst test facility.


(a) (b) (c)

Figure 14: (a) A hydraulic burst pump, and (b,c) vessels after bursting, depending on the composite winding architecture.

A first pressurization, with a maximum value of 1050 bar, was performed as a proof test and in order to calibrate the gauges. The rate of pressurization was 2 bar/s and the rate of depressurization was 10 bar/s (between 1050 bar and 100 bar) and 2 bar/s (from 100 bar to 20 bar). Subsequently, the pressure was increased a second time, at an average rate of 4 bar/s, until rupture occurred. The maximum burst pressure was found to be greater than the minimum required value of 1645 bar (standard safety ratio of 2.35). Contrary to the cycling test, a progressive damaging of the container was recorded during the burst test. Signals from the acoustic emission sensors are presented in figure 15. As can be seen, the increase in the intensity of the acoustic signals was basically proportional to the increase in pressure, thus attesting to the degradation of the composite structure.

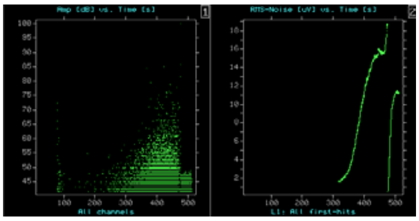


Figure 15: Acoustic signals during the burst test of a vessel with a polymeric liner.

MATERIAL SYNERGIES, SENSORS AND PERSPECTIVES

The CEA continues to work on improving vessel performances, integrating material synergy functionalities and sensors (table 5) for an intelligent structure manufacturing and monitoring. Nevertheless, development and progress are still necessary, particularly in terms of really understanding the behavior of polymer materials and thick composite structures over long-term use, of determining the influence of process parameters on materials and a vessel's initial performance and durability, and of comprehending the true safety and reliability and of novel materials, new computer tools and concepts. Already planned future work includes a new vessel concept, the durability of high-pressure vessel constituents and smart monitoring.

Table 5: Sensor evaluation for composite pressure vessels.

	Product	**Advantage**	**Disadvantage**	**Tempe-rature**	**Strain**	**Stress**	**Press-ure**	**Material Indice**
Optical Fiber		Intrusiveness Multi-parameter Precision Absolute measure	Cost Process	+	+	+	+	+
Acoustic emission		Multi-parameter Localization	Measure analyses Discontinued measure Bonding	+	+	+	+	
Strain gauge		Cost Process	Mono-parameter Surface measure Bonding		+	+		

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