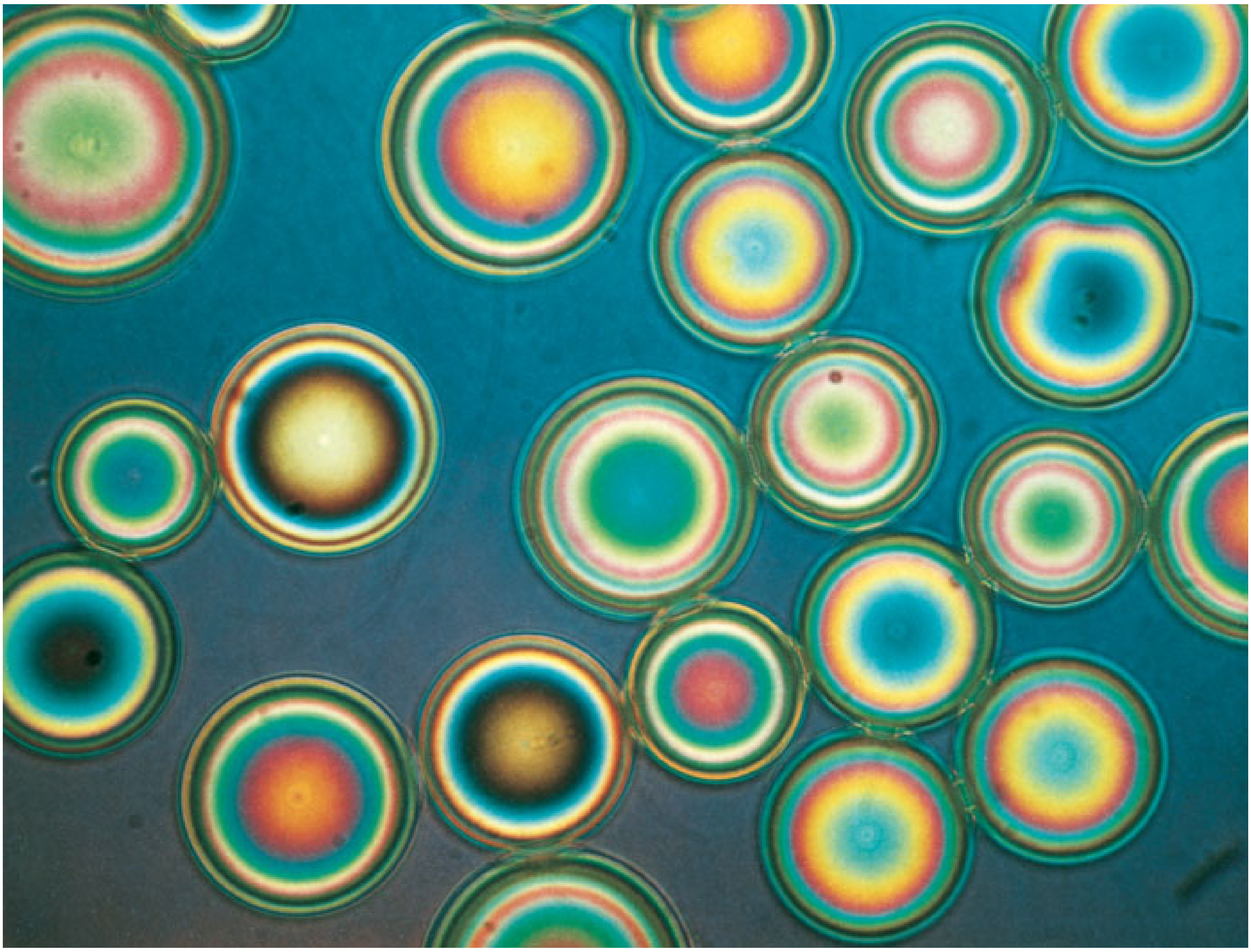
III. ENERGY STORAGE
electricity and hydrogen on demand

Storage is still the Achilles' heal of the energy industry. The CEA is working on the different aspects of energy storage as part of its research and development programme. The anticipated emergence of hydrogen as an important energy carrier opens up new horizons in energy storage, transmission and application. And this is especially true in the supply of fuel cells, as these provide highly efficient electricity generation. In most cases, such electricity would no longer have to be stored in batteries, particularly in electric vehicles. At this stage, innovative solutions are required for the storage of hydrogen itself.
Nevertheless, storage batteries, especially those based on *lithium*, are improving their own performance capacities, and this is an area which the CEA is actively investigating. For certain applications, such as portable equipment, it may be worthwhile using hydrogen-powered fuel cells, possibly manufactured *in situ* from a hydrocarbon, to back up and charge a storage battery.

HYDROGEN STORAGE



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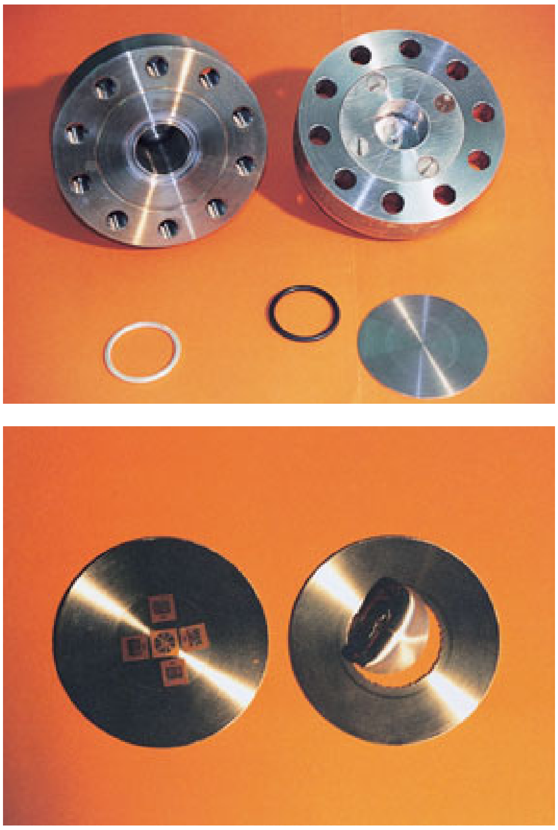
The high pressure storage of hydrogen in microballoons, developed by the CEA during experiments on power lasers, is one of the techniques which may be used in the future. Above: interferometric control of the geometric characteristics of microballoons, with an average diameter of 500 µm and a thickness of 5 µm.

How to stock hydrogen safely and efficiently?

Due to its restrictive physico-chemical properties, hydrogen must be handled extremely carefully if it is to be used safely. Hydrogen storage presents specific problems, for which solutions already exist or are coming to light. The CEA is drawing on its experience to develop each one of these solutions and assess its safety. Of all the safety studies carried out on systems implementing hydrogen-powered fuel cells, those concerning hydrogen storage are the most crucial. This work is proceeding alongside essential standardisation efforts.

The hydrogen storage issue is contingent on the constraints inherent in the (immediate) use of the gas, such as purity, quantity, operating throughput and temperature, thermomechanical environment, etc. Nevertheless, it is generally characterised by the need to take hydrogen's properties into consideration, such as its explosiveness and flammability as well as the hydrogen (H) atom's radius, which is the smallest in existence. The first point has a bearing on *safety-security* studies and their validation, the second impacts *the choice of storage concept*. Indeed, the small size of the molecules (H_2) facilitates their diffusion through metallic and non-metallic materials, thereby generating permeation(1) leaks, altering mechanical properties through interaction with flaws (embrittlement) and accelerating corrosion and stress corrosion cracking. *Low pressure* techniques are being looked into, in view of reducing these risks which are directly linked to the pressure of the gas. These techniques may use solid compounds, such as **hydrides**, to **absorb** the hydrogen, or carbonaceous tubular structures, the size of a nanometer (1 nm = 10^{-9} m), which trap the hydrogen. These solutions do have drawbacks in terms of cost, weight, feasibility and availability. This explains why *high pressure* storage is also being explored, the focus being on optimising and fully understanding the material that serves as a barrier to the gas.



To measure the embrittlement of a material by hydrogen, it is placed in a cell (top), in the shape of a disc with built-in control instruments (bottom left), and breakage tests are then conducted (split disc, bottom right).

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High pressure storage

Research into the high pressure storage of hydrogen is mainly conducted on materials which are in direct contact with the gas. Specific technical objectives, such as low solubility and permeation and a limited propensity to embrittlement and corrosion, are associated with the standard specifications for materials used for pressurised tanks (cost, weight, forming, assembly, fatigue(2), creep(3), etc.). The CEA (Atomic Energy Commission), which has many years' experience in the safe of high pressure storage (several hundred bars) of hydrogen and its isotopes(4), has attained a certain degree of competence regarding the behaviour of many metallic and non-metallic materials in the presence of hydrogen. As a result, austenitic(5) steels and a number of aluminium alloys have been selected as, when they are processed in the correct conditions, it is guaranteed that they can be used safely. However, these metallic materials produce relatively expensive storage tanks with a low mass storage capacity (ratio of the mass of stored gas to the tank mass), of around 2 to 3%.

One way of improving this capacity is to maintain a thin metallic material in contact with the gas (bladder) and to guarantee its mechanical resistance and a satisfactory degree of tightness by using a polymer envelope, reinforced with carbon fibre. This solution provides a mass storage capacity of around 5%. A breakthrough is possible thanks to current research into the replacement of

(1) The passing of a gaseous flow through a solid wall.
(2) Behaviour of a material when subjected to periodic thermomechanical stress.
(3) Deformation of a material when subjected to a constant level of stress, over time.
(4) Atoms of the same chemical element, exhibiting nuclei of varying masses; for example, ^{1}H (hydrogen), ^{2}H (deuterium), ^{3}H (tritium).
(5) A type of steel with a specific microstructure (cubic, centered face).

Prototype of a multi layer polymer tank, for hydrogen storage.

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the metallic bladder by a "multi layer" polymer type material, the different **formulations** of which provide permeation and mechanical resistance characteristics compatible with storage tank operation. With this technique, mass storage capacities of 5 to 10% are plausible, along with a significant reduction in costs. At the same time, the CEA is working on proving that it is safe to use this type of tank in a standard pressurised storage tank environment.

Another high pressure storage technique is being taken into consideration: glass microballoons. As part of the development of targets for physics experiments on a power laser (programme connected with the future Méga-Joule laser), the CEA's research teams are putting the finishing touches to microballoons with a diameter of around 1 mm and a thickness of a few dozen micrometers (1 µm = 10^{-6} m), capable of withstanding very high pressure (several hundred bars). These hollow balloons are filled by high temperature permeation (400 °C). The gas can then be released by breaking the glass or heating. Research is focused on optimising their geometric and mechanical characteristics. This "futuristic" solution should not be ruled out as it presents certain advantages with regard to safety. Indeed, all the gas is enclosed within millions of microballoons, reducing the risk of explosion.

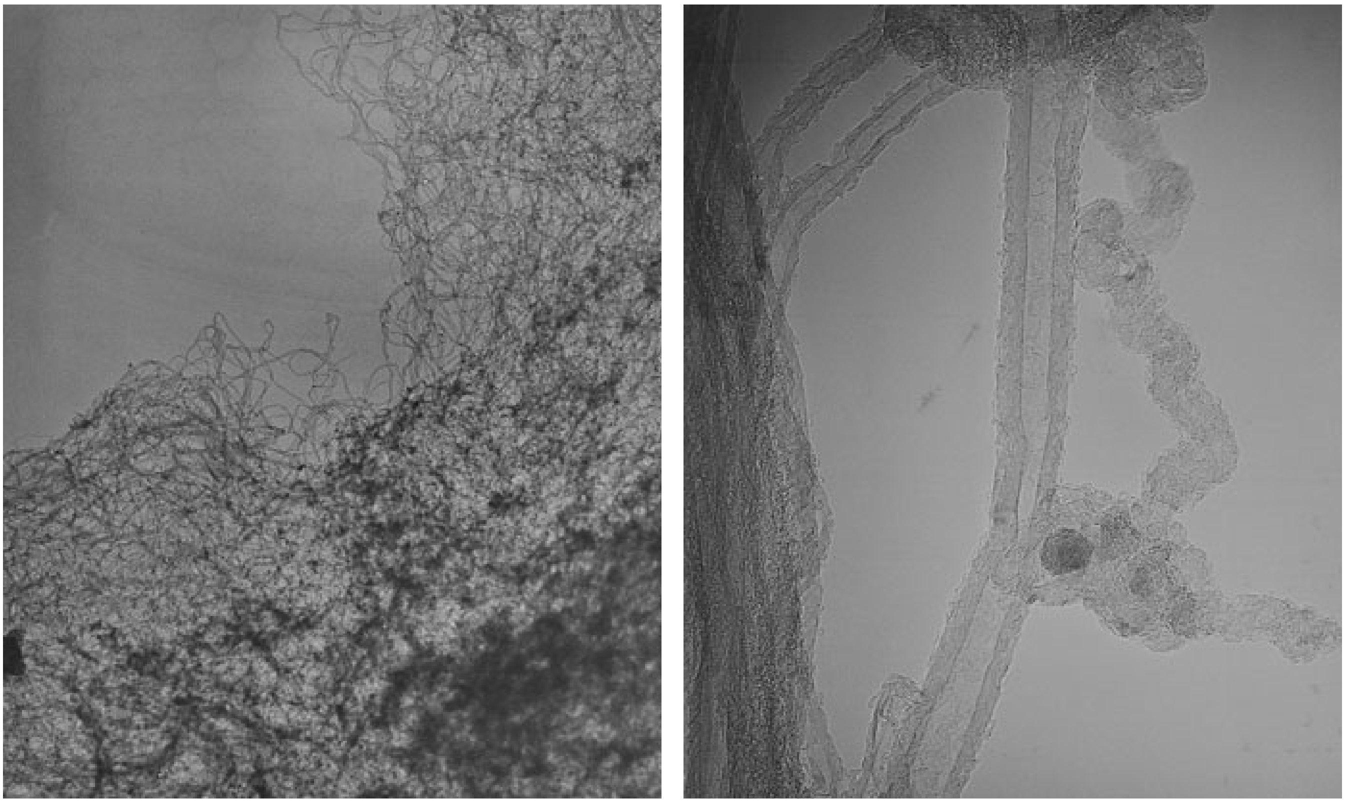
This rapid overview of high pressure storage would not be complete if it did not touch upon the inconvenient drop in overall energy efficiency caused by compressing the gas, an energy consuming operation. The technology used to manipulate gas under high pressure must also be taken into consideration, and a number of shortcomings in the approval procedures for this type of hydrogen tank must be rectified.

Low pressure storage

An alternative to the use of gas pressurised tanks consists in storing hydrogen in the form of metal hydrides. These compounds, which are obtained through the direct reaction of certain metals or metal alloys to hydrogen, are capable of absorbing the hydrogen and restoring it when required. A lot of research has been done into these materials over several years, and a very wide range of performance measurements is now available (see table). Of course, the criteria for selecting a metal hydride for storing hydrogen are contingent upon the intended application (mobile: transport, portable equipment..., stationary or fixed) and its environment (thermal...). Above all, these materials must have a high mass absorption capacity (ratio of the mass of hydrogen stored to the mass of metal used), rapid **absorption/desorption** kinetics, a low equilibrium pressure at room temperature (lower than atmospheric pressure) in order to prevent leaks and guarantee containment integrity, and a low degree of sensitivity to impurities in the hydrogen stored.

	magnesium hydride	palladium hydride	titanium-iron hydride	magnesium-nickel hydride	zirconium-manganese hydride	lanthanum-nickel hydride
mass absorption capacity (%)	7.6	0.72	1.86	3.6	1.77	1.5
balance pressure at 20 °C (bar)	10^{-6}	$8.2 \cdot 10^{-3}$	4.1	10^{-5}	10^{-3}	1.8
temperature for 1 bar (°C)	279	147	- 8	255	167	15
degree of sensitivity to impurities in hydrogen	highly sensitive to oxygen and water	sensitive to carbone monoxide	highly sensitive to oxygen, water and carbone monoxide	relatively low sensitivity	sensitive to sulphur dioxide	sensitive to oxygen, water and carbone monoxide
absorption/desorption kinetics	very slow	fast	fast	average	very fast	very fast

Table. Performance analysis of the main families of metal hydrides studied for hydrogen storage.



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Electron microscopy images, transmitted from carbon nanotubes developed by high temperature catalytic decomposition.
Left : an overall view (x 6 000); right: a close-up view of a nanotube (x 150 000).

There are two very considerable advantages to this type of storage: it is safe, as the pressure implemented remains low and it is compact, as most metal hydrides have high volume absorption capacities (ratio of the volume of hydrogen stored to the volume of metal used). For example, it is possible to store the equivalent of a 7-litre hydrogen tank (7 000 cm^3), filled at atmospheric pressure, in a small palladium cube of 27 cm^3, under a hydrogen pressure that is ten times lower. Nevertheless, this type of storage has a major drawback: a low mass absorption capacity, usually between 1 and 2%, which falls well short of the minimum 6% capacity recommended for mobile applications. Moreover, costs are relatively high, being around 20 Euro/kg of material. Only magnesium hydride has a high mass absorption capacity (around 7%), but its use is limited by very slow absorption/desorption kinetics, which are incompatible with most of the targeted applications.

A lot of research is currently being conducted at the CEA and throughout the world into optimising the performance of metal hydrides in hydrogen storage. There are two possible approaches, depending on the material's properties. The first approach involves the development of alloys from standard inter-metallic compound families (compounds derived mainly from zirconium-manganese $ZrMn_2$ and lanthanum-nickel $LaNi_5$ alloys) containing substituents that allow an increase in the mass absorption capacity and limit sensitivity to hydrogen impurities, without reducing absorption/desorption kinetics. The second approach focuses on elaborating the magnesium (and its derivatives) in such a way as to considerably increase its absorption/desorption kinetics. The implementation of nano-divided structures(6) is being explored as part of this research programme. When the reactive surface of these structures is increased, exchanges between the gas and the solid are facilitated. Considerable progress is being made as a result of this work.

The 1991 discovery of the carbon nanotube by Japanese scientist Sumio Iijima opened up new possibilities with respect to the development of safe, reliable hydrogen storage devices. These materials, made up of graphite planes organised into concentric tubes with a nanometric diameter, seem to possess exceptional hydrogen absorption properties (mass absorption capacities ranging from 0 to 65% according to the author). These results must, however, be considered with caution, in view of the fact that they are very disparate and that most of the mechanisms involved in hydrogen absorption are not fully understood. Right now, research into this subject is branching off in all direc-

(6) The characteristic dimensions of these structures' geometry are close to the nanometer.

tions, both in terms of developing procedures for improving production yields (ratio of the quantity of synthesised nanotubes to the quantity of carbon initially used) and the purity of the material obtained, and advancing theories to explain these carbonaceous nano-structures' amazing ability to store hydrogen. The crucial issue now, besides confirming these properties, is the feasibility of mass producing these materials in the future, bearing in mind that today's production is limited to a few grams for laboratory testing. A small prototype will be developed by 2002.

Towards more multi-purpose solutions

It is clear that the ideal method of storing hydrogen does not yet exist and that each of the techniques described above is suitable for certain types of application, according to its performance level. Whereas high pressure storage has significant advantages with respect to mobile applications, storage in the form of metal hydrides guarantees a good level of safety and a high degree of modularity for stationary applications. Finally, the potential for improvement in this area remains high. While pressurised storage is now seen as a fully fledged solution from a technological point of view, storage in carbonaceous nanostructures and, to a lesser extent, in the form of metal hydrides, is receiving unflagging attention which should, in the long run, produce a storage technique that is both safe and efficient, for the widest possible range of applications.

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Hydrogen storage safety: tests and standards

The automobile industry is evaluating the best way of approaching the imminent technological revolution, in order to meet the challenge of environmental protection. As the year 2020 approaches, the traditional internal combustion engine is gradually being superseded by the electric engine. At present, the possibility of marketing these future vehicles is, to a large extent, contingent upon the use of a **reformer** that converts a **hydrocarbon** such as **methane** into hydrogen, which is then used to supply a fuel cell. As far as technological complexity and cost considerations are concerned, the high pressure storage of hydrogen in vehicles is a suitable alternative to solutions based on reforming.

Nevertheless, a recent European survey showed that the public still has a negative opinion of hydrogen. The survey confirms that psychological barriers to hydrogen do exist, and that they are an impediment to the more widespread use of this gas.

Air Liquide and the CEA: co-operating closely

Air Liquide, world leader in the field of industrial and medical gases, has, over the last fifteen years or so, been developing its activities in the energy sector (vapour and energy) as part of the extended range of services available to its industrial customers. So, when Renault launched the Fever project in 1994 (to fit the Laguna with a PEMFC cell and a liquid hydrogen tank), it was only natural for Air Liquide to be involved in the design and development of the liquid hydrogen tank, and in deliberations concerning hydrogen supply logistics.

Today, the development of this technology, which involves globally optimising the fuel cell system, is a crucial issue which will enable Air Liquide to develop its *hydrogen and energy* offer. The global optimisation of the fuel system, both in terms of performance and cost, requires a wide variety of skills. In view of this, the CEA and Air Liquide agreed, over two years ago, to join forces with PSA on the Hydro-Gen project (Partner/Berlingo fitted with a fuel cell). The CEA's Technological Research Division in Grenoble, and Air Liquide's Advanced Techniques Division in Sassenage, Isère, aim through their research to understand, improve and model the behaviour of these fuel cells. The geographic proximity and the complementarity of these two teams, as well as the results obtained so far, are key factors in the successful development of this new sector.

Michel Mouliney
Air Liquide

Risk assessment tests

As for the CEA, it has fully committed itself to two European projects, Hydro-Gen and the Euro Quebec Hydrogen Pilot Project, which address the issue of safely storing gaseous hydrogen in large bottles inside road vehicles, at a pressure of 700 bars. The partnership between Air Liquide, Ineris (National Industrial Environment and Risks Institute), PSA Peugeot Citroën and the CEA should result in the development of a demonstration prototype incorporating five 25-litre bottles, measuring 20 cm in diameter and 1 metre in length, capable of independently powering the vehicle over a distance of 500 km (see box). Composites Aquitaine, an industrial company specialising in pressure vessels made out of composite materials, the Aquitaine Department of Industry, Research and the Environment (Drire) and CEA teams in Grenoble, Valduc and at the Cesta have had to work together closely on assessing the risks involved in using this prototype. Over twenty bottles, designed and developed especially for the occasion, underwent a variety of tests. After the usual cer-

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14 m drop test on a high pressure hydrogen tank at the CEA/Cesta's external testing ground.

tification tests such as cycling(1) and hydraulic bursting, even more spectacular tests were conceived. These included dropping the tanks from a height of several metres, head-on crashes between vehicles, and fire.

The results obtained at the end of 2000, on completion of these tests and simulation studies, will provide a basis on which to calculate the risks involved in the large-scale use of hydrogen on the road network. It should be noted that the first bottles tested performed very well in all the standard, mandatory tests. These promising results should further the progress of hydrogen storage techniques, and make the very idea of this type of storage more acceptable. The European automobile industry, which appreciates the efforts made in this field, is keen to support any new work undertaken in connection with these two projects.

Standardisation activities

The CEA is participating actively in the preparation of future international standards. The development of these standards is absolutely necessary to the widespread diffusion of technologies related to the production, transportation, storage and numerous applications of hydrogen. Indeed, these standards are a guarantee for the user, in terms of quality and safety. They are also an essential starting point for the drawing up of regulations. The International Standard Organisation (ISO) therefore created, in 1990, a technical committee (no. 197) to fill the gap in standards in the "hydrogen technologies" field. Thanks to this work, the first two ISO standards were published in 1999. The first one concerns liquid hydrogen filling systems, and the second one deals with the purity of the hydrogen fuel, especially with respect to its use in fuel cells.

The CEA is taking an active part in the work done by this technical committee, within the framework of two work groups going under the headings of "gaseous hydrogen – fuel systems for vehicles" and "gaseous hydrogen – fuel tanks for vehicles". Moreover, a French standard has been created as a result of research conducted at the CEA into the embrittlement of metals by hydrogen.

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(1) Test which consists in successively increasing and decreasing pressure in order to validate the bottles' mechanical resistance to fatigue.