New energy, new hazards? The hydrogen scenario

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1 Introduction

For the last ten years and more, INERIS has acquired a practical experience on hydrogen safety. Among others, the following experimental topics have been dealt with :

- confined hydrogen explosion,
- liquid hydrogen leak and subsequent dispersion in air phenomenon,
- hydrogen jet release, dispersion and inflammation,
- measurement of hydrogen concentration in air-hydrogen atmospheres,
- pressurised hydrogen tank testing.

In parallel risk assessment have been carried out on hydrogen-related equipment (reformers, electrolysers ...).

This long lasting experience is now invested in hydrogen technologies. In this field, INERIS is involved in several European and national projects as well as in standardisation working groups focussing on the safe handling of hydrogen

2 New energy

2.1 Hydrogen as a new "energy carrier" ?

Hydrogen based economy and associated energy converters fuel cell systems are said to be a part of the response to increasingly worrying ecological and economical issues embodied by either global warming or the depletion of fossil energy sources.

Indeed, hydrogen shows many benefits in the field of air pollutant as its combustion reduces pollutant and greenhouse gas emissions (carbon dioxide...)[1]. Besides, energy conversion yields seem to be better and finally it allows fossil fuels dependant economy to rely on other energy loops. Hydrogen can virtually be produced from a wide variety of domestic sources. It can also provide a storage medium for intermittent and seasonal peak energy needs.

Hydrogen can be used as an energy carrier for many traditional technologies such as cars (direct combustion engines using hydrogen or hydrogen based mixtures, fuel cell systems), electrical plants, systems to provide heat and electricity for buildings, remote power unit systems, backup systems... .

Hydrogen technologies are under test across Europe (stationary power units, boats, city buses, cars...). Different challenges are being faced : technological, hydrogen production, hydrogen storage,... . Along with public acceptance, authorities agreement for demonstration projects is sometimes difficult to obtain for these new technologies (imported technologies are not CE marked, no straight forward applicable regulation...). Regulation and standardisation will therefore have to make their way to ease hydrogen technologies implementation.

To answer some of potential public fears, this paper will compare hydrogen hazards with more conventional fuels. We will then discuss hazards related to fuel cell systems. All together, we will try to evaluate if **there is any new hazard to be expected along with hydrogen technologies development.** Finally, we will present existing regulations and standardisation expectations prior to briefly discuss social acceptance aspects.

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[1] US Department of Energy, Energy Efficiency and Renewable Energy, *http://www.eere.energy.gov*

2.2 What is a fuel cell ?

Fuel cells are the core of the hydrogen economy. A fuel cell is an electrochemical energy converter in which hydrogen is combined with oxygen (from air supplied to the system) to produce water and electricity, emitting neither pollutants nor excessive noise. The expected theoretical efficiencies are varying according to the technology used but are higher than those of conventional combustion processes. This means that in the long term,fuel cells will probably be an alternative energy converter.

Any fuel containing an atom of hydrogen (methanol, gasoline, natural gas, biogas, and so on) can be used as fuel in a cell.

Different types of fuel cell have been develop d so far. All of them can run with hydrogen. Proton exchange membrane fuel cells (PEMFC) are more than any other technologies expected to be commonly found (cars,h ome generator..).

Figure 1 gives a schematic view of flows within a fuel cell as well as its working conditions.

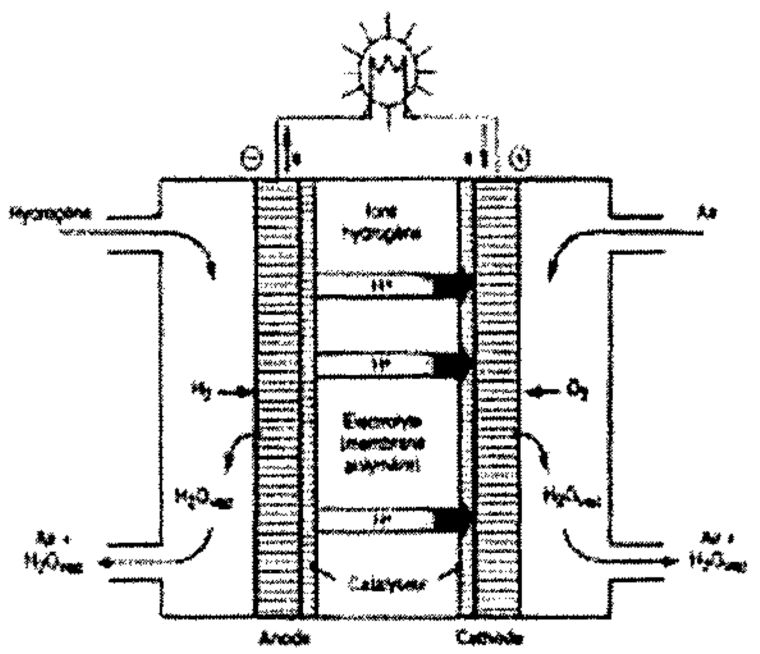

Figure 1.S chematic view oj flows and working conditions of a fuel cell[2].

Hydrogen is supplied either from a storage system where it may be in the form of a cryogenic liquid, hydrides or compressed gas, or from a production system within the installation itself: for example by electrolysis of water, hydrocarbon cracking,v apour reforming of methanol, and so on.

The operating principle is simple: the cell consists of an assembly of elementary units each constituted by a cathode chamber and an anode chamber separated by two electrodes that channel the electrons, with an intermediate electrolyte which may be solid or liquid according to the type of cell. The atom of hydrogen, under the effect of a catalyst, breaks down into a proton and an electron. Protons enter the electrolyte, while the electrons are collected and passed through the external electric circuit before returning to the cathode, where they recombine with protons and oxygen to form a molecule of water. Besides water (by-product of the reaction), electric current and heat are collected at the output, in varying proportions according to the chosen operating point, which is particularly valuable in fixed combined generation applications.

[2] Source : R. GALLEY & C. GATIGNOL, "Les perspectives offertes par la technologie de la pile à combustible", Report of the "Office Parlementaire des choix scientifiques et technologiques", France, p. 30,2 001.

3 The hydrogen scenario

We have seen that hydrogen goes along with fuel cells. In the following paragraphs we will try to identify specific safety issues related to its use in a gaseous form.

General considerations

Gaseous hydrogen is a highly flammable, colourless, odourless and non toxic gas. It is the lightest of all gases.

The following table 1 offers a comparison of hydrogen safety characteristics with the ones ofp ropane, methane and gasoline.

Table 1. Comparison ofhydrogen safety characteristics with more conventionalfuels[3]..

Property	Unit	Hydrogen	Methane	Propane	Gasoline
Molecular weight	kg/kmol	2.016	16.043	44.10	
Heat of combustion (high)	kJ/g	141.86	55.53	50.41	
Limits of flamability in air (LFL - UFL) Downward propagating	vol%	4.0-75.0	5.3-15.0	2.1-9.5	1 – 7.8
Limits of detonability in air (LDL – UDL)	vol%	18.3-59.0	6.3-13.5	3.1-7[4]	1.1-3.3
Stochiometric composition in air	vol%	29.53	9.48	4.03	1.8
Minimum Ignition Energy in air (MIE)	mJ	0.02	0.29	0.26	0.24
Maximal Experimental Safety Gap at NTP (MESG)	cm	0.008	0.12	NA	0.074
Auto-Ignition temperature	°K	858	813	760	228 - 471
Buoyency	W/r to air	0.07	0.55	1.52	3.4-4.0
Diffusion coefficient in NTP-air	cm^2/s	0.61	0.16	0.12	0.12
Diffusion velocity in NTP-air	cm/s	≤ 2.0	≤ 0.51	N.A.	
Burning velocity in NTP air	cm/s	265-325	37-45	N.A.	0.42
Energy of explosion NTP	$g\ TNT/m^3$	2.02	7.03	20.3	44.22
Toxicity		non toxic (asphyxiant)	non toxic (asphyxiant)	non toxic (asphyxiant)	toxic

We will now discuss these safety characteristics in the light of accidental phenomenon.

Hydrogen dispersion

In similar release conditions (diameter and pressure), hydrogen is expected to mix with air and disperse more rapidly than other fuels, driving down more quickly its concentration in air in unconfined space. Its low molecular weight drives this property : higher jet speed and higher diffusion coefficient.

[3] sources : "Investigation on safety, regulations and acceptability of hydrogen", Euro-Quebec Hydro-Hydrogen Pilot Project (EQHHPP), November 1993.

C.E. Thomas, "Direct Hydrogen fueled proton exchange membrane fuel cell system for transportation applications - Hydrogen Vehicle Safety Report", Direct Technologies Inc., prepared by Ford Motor Company for DOE, May 1997.

[4] source : J.L. Alcock, "Compilation of existing safety data on hydrogen and comparative fuels", EIHP 2 Project, Shell Global Solutions, May 2001.

On the other hand, its higher leak flow (3 times the volumetric one of propane or methane in turbulent conditions)[5], its diffusion in air ability (4 times the one of propane or methane) and its buoyancy tends to make hydrogen more hazardous in confined spaces than other fuels.

Flammability

Lower flammability limit is a key safety factor **for vapour and gases knowing how easy it is to ignite an explosive atmosphere.** Hydrogen MIE is 10 times lower than conventional fuels (17µJ[6]). At stoechiometric conditions the weakest static electricity discharge (brush discharge) is entitled to ignite the mixture. At LFL,M IE of methane is comparable to the one of hydrogen.

Experience shows that hydrogen air-mixture ignites most of the time[7].

Ability to ignite makes hydrogen very large flammability range less of interest since we would expect it to ignite before reaching high concentration values. Ability to ignite would also tend to minimise explosive atmosphere volume and therefore associated effects. **However, if hydrogen accumulates above LFL in a confined space, it is more likely to ignite.**

Hydrogen auto-ignition temperature (858°K) is slightly higher than the one of other fuels. Auto-ignition is not a usual cause of hydrogen ignition[8].

Formation ofan explosive atmosphere

We have seen that hydrogen disperses more rapidly in air. This propriety enhances formation of large explosive atmosphere in confined spaces. We will now consider high pressure leaks[9] in open spaces without obstacle.

The following table 3 compares explosive atmospheres volumes for different gases at different leaking pressure and diameter.

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[5] See note 3

[6] One has to bear in mind that spark discharges of the human body has an energy level of about 10 mJ.

[7] Reference : C.E. Thomas, "Direct Hydrogen fueled proton exchange membrane fuel cell system for transportation applications - Hydrogen Vehicle Safety Report", Direct Technologies Inc., prepared by Ford Motor Company for DOE, May 1997.

[8] See note 7.

[9] Current hydrogen mobile technologies favour high pressure storage of hydrogen.

Table 3. Comparison of explosive volumes at similar leaking conditions for hydrogen, methane & propane (Explojet/INERIS software).

		Propane				Methane				Hydrogen			
		Leak diameter (mm)				Leak diameter (mm)				Leak diameter (mm)			
Pressure		1	2	4	10	1	2	4	10	1	2	4	10[10]
10 bar	Distance to LFL (m)	0,46	0,92	1,84	4,6	0,38	0,64	1,3	3,2	1,1	2,2	4,4	11
	Flammable mass of fuel (kg)	0,00005	0,0004	0,003	0,046	0,00001	0,0001	0,0008	0,012	0,000056	0,00045	0,0036	0,056
	Explosible volume (m^3)[11]	0,0008	0,006	0,05	0,78	0,0003	0,002	0,0017	0,26	0,011	0,09	0,72	11,2
250 bar	Distance to LFL (m)					1,6	3,2	6,4	16	5,5	11	22	54
	Flammable mass of fuel (kg)					0,0015	0,012	0,1	1,5	0,007	0,056	0,46	6,79
	Explosible volume (m^3)					0,033	0,26	2,1	32,5	1,4	11,2	90	1360

The following observations can be made:

- at a given pressure, whatever the gaz, distance to LFL doubles when leaking diamater also doubles. At the same time, explosible mass or explosible volume are multiplied about 10 times,
- in any situations, methane leads to smaller explosive atmospheres volumes,
- in any situations, hydrogen leads to much larger explosible volumes,
- whatever the pressure, hydrogen leads to explosible volumes about 40 times higher than the ones with methane,
- at the same leaking pressure, hydrogen and propane lead to the same explosible mass. Explosible volume is somehow very different due to hydrogen low molecular weight.

Table 4. Explosible volumes of hydrogen / air formed for different leaking diameters at 700 bar (Explojet/INERIS software).

		Leak diameter (mm)		
Pressure (bar)		1	2	4
700	Distance to LFL (m)	9,1	18,2	36,4
	Flammable mass of fuel (kg)	0,0318	0,255	2,04
	Explosible volume (m^3)	6,39	51,1	409

Combustion regime

Hydrogen burning velocity is far greater than the one of other fuels. Generally speaking, likelihood to transit from deflagration (DDT) to detonation regime is in relation with this burning velocity.

However, past accidents have shown that few DDT have been observed. In open spaces, deflagration is the combustion regime to be expected unless a very energetic source (explosives) ignites the detonable mixture[12].

[10] For this specific case, figures given by PHAST 6.1 (DNV) are half of those given by Explojet.

[11] Explosible volume is given between LFL and UFL

[12] Reference : L.C. Cadwallader and J.S. Herring , "Safety issues with hydrogen as a vehicle fuel", Idaho National Engineering and Environmental Laboratory, September 1999.

Pressure effects

Damageable pressure effects accompany explosion phenomenon. Because of its speed of pressure rise hydrogen explosion induced pressure effects are expected to be more severe than for other gases even though volumetric energy release is lower than the one of other studied fuels.

This quick evaluation shows that hydrogen has a different behaviour than conventional fuels. Hazardous or safe potential of hydrogen is to be revealed by the technology and the context of use.

Therefore, we now propose a risk evaluation overview of a PEMFC.

4 Risk analysis of Proton Exchange Membrane Fuel Cell systems

4.1 Critical events related to the core of the cell

Whatever technology is used, the core of the cell consists of an assembly of elementary units in which an electrochemical reaction takes place between a fuel (hydrogen) and an oxydant (usually oxygen from the air). The core of the cell remains unchanged over time. In non degraded mode, hydrogen and oxygen never come into direct contact.

Hydrogen leakage and release : formation of an explosive atmosphere

Leakage (accidental situation) can be distinguished from normal release. Normal release is caused by chronic purging[13] of the core (PEMFC). Purged hydrogen is then released into air. In confined spaces, one has to pay attention nott o progressively enrich the air with hydrogen until it reaches its LFL (high speed release and homogeneous mixing or stratification and further mixing phenomenon). In unconfined spaces no explosive atmosphere is to be expected unless at the point of hydrogen release. The volume of this explosive atmosphere is driven by the flow and the release diameter at operating pressure. Premixing below LFL prior to release is a possible safety solution.

Along with chronic purging, chronic leakage is to be evaluated. Indeed, hydrogen diffusion ability makes it difficult to confine. As a consequence, minor chronic leaks have to be expected.

Hydrogen accidental leakage in PEMFC encompasses a wide range of situations:

- purge malfunction : purging becomes permanent leading to more hydrogen to be released into the outside air,
- membrane puncture can lead to an equivalent situation as well as to form an explosible mixture within the stack. This latest situation is not critical mainly because of reduced volume and the presence of catalyst that would favour moderated hydrogen combustion,
- core, manifold and piping leakage,
- reverse electrolysis of the cells… .

In PEMFC, membrane rupture is a noticeable situation with the potential to lead to large leaks. Membrane rupture can be induced by :

- inappropriate pressure balance between each side of the membrane side,
- excessive local temperature (lack of humidification, inhomogeneous or insufficient cooling …),
- membrane ageing.

[13] Hydrogen purging drives away excessive nitrogen (nitrogen from the air side permeates through the membrane to the hydrogen side) and water on the cathode side.

Any of the above situations can lead to the formation of local (open spaces) and extensive explosive atmosphere (confined spaces).

Severity of the above situations depends on the studied fuel cell. Possible consequences whatever minor or severe the leak is have to be quantified. As such, for each system, one should put figures on :

- the maximum leakage rate and associated maximum explosive volume,
- chronic purge induced explosive atmosphere in open air and ventilated confined space,
- the chronic leakage flow of hydrogen.

Electrical hazards

Beside hydrogen leaks and associated explosive atmosphere, electrical hazard is a prevalent risk due to the presence of high voltage.

4.2 Basic safety principles

General safety principles

Enforcement of safety principles requires first of all to avoid the hazard (replacement), then to reduce/control its potential and finally to set safety distances with potential targets. Users should also be informed about risks of the equipment.

Control of hydrogen risk

Above principles apply to fuel cell systems. Control of hydrogen hazards goes through:

- reduction/avoidance of chronic release of hydrogen by appropriate design,
- minimising the size of explosive atmosphere in case of leakage or release (operating pressure, pipe size, maximum hydrogen flow[14]...),
- avoidance / limitation of confinement in design and use of the system (open space or controlled ventilation),
- control of ignition sources (appropriate electrical equipment, physical segregation between electrical and hydrogen parts,...),
- early detection of leak and leak interruption before reaching a hazardous situation,
- enforcement of state of the art technical safety principles (redundancy of critical equipment, fail safe system,...)
- regular checks and maintenance,
- end-user information.

Complete control of hydrogen leakage is not realistic. However driving down leakage situation to acceptable level of risk should be the main objective.

Under construction IEC standards (IEC TC 105) suggest among others leaking tests to be undertaken.

This brief evaluation shows that this new technology brings along risks that can be overcome with traditional approaches and safety measures.

[14] Maximum hydrogen flow is to be balanced with maximum fuel cell stack hydrogen consumption.

5 Regulations and standards related to fuel cell systems

It goes without saying that since fuel cell systems are made up of a variety of equipment, such as compressor, storage tanks, electrical systems,... that many existing regulations and standards can be applied.

Specific regulations and standards are under construction in Europe and at the international level. On legal and standardisation point of view, stationary applications have to be distinguished from mobile applications.

5.1 Standardisation

An **ISO**[15] **technical committee** - **TC 197** - "Hydrogen Technologies" was set up in 1990 to prepare standards for systems and devices involved in producing, storing, transporting, measuring and using hydrogen. Its 7th working group has prepared a standard on the "Basic requirements for the safety of hydrogen systems"

An **IEC**[16] **technical committee** - **TC 105** - "Technologies of fuel cells" was set up in 1996 to prepare standards for fuel cell technologies for both stationary and mobile applications. Its 3rd group focusses on the safety of stationnary fuel cell systems.

In North America, organisations such as the National Hydrogen Association (NHA), the Canadian Hydrogen Association, the National Fire Protection Association (NFPA), the American National Standards Institute (ANSI), and the American Society for Mechanical Engineers (ASME) are working to draw up codes,s tandards and guides concerning the construction and use of fuel cell systems.

In Europe, there is no specific standard for stationary fuel cell systems. A technical committee has been created within the CEN[17]/CENELEC[18] and covers residential fuel cells with a power up to 70 kW.

5.2 Regulations

In Europe existing directives among others can be applied to stationnary fuel cell systems for CE marking.

Three of these directives appear to be applicable in every cases :

- Machine Directive 98/37/EC[19]
- Low voltage Directive 73/23/EEC
- Electromagnetic Compatibility Directive 89/336/EEC, 92/31/EC, 98/13/EC.

Today, there is no regulation, neither for fuel cell vehicles nor for mobile hydrogen storage.

European Directive 70/156/CE "type-approval of motor vehicles and their trailers" does not include hydrogen vehicle type-approval.

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[15] ISO: International Standards Organisation

[16] IEC: International Electrotechnical Commission

[17] CEN : Comité européen de normalisation

[18] CENELEC : Comité européen de normalisation électronique

[19] Its worth indicating that ATEX 94/9/EC is applied as part of the machine directive expectations

To overcome this barrier, UNECE[20] rules relative to onboard hydrogen storage are under construction.H owever,t hese later rules do not cover the use of a fuel cell in a vehicle.

Meanwhile future dedicated regulations, a manufacturer can apply for a prototype approval of its vehicle.

6 Social acceptance of hydrogen

For lay people, the use of hydrogen induces hazardous meanings (explosion).

However, development of hydrogen use will not take off without the public (potential users) onboard.

Social brake is not a dead end. Studies conducted in Germany came to the conclusion that **social acceptance of hydrogen can be overcome by raising public awareness[21].**

This communication action could consist in:

1. offering to the public information about hydrogen technologies (through schools and the mass media) ;
2. developing public tests, pilot projects and demonstrations, and these should be accompanied with explanatory measures in order to introduce the information ;
3. advertising upon safety approaches ;
4. stressing environmental advantages of hydrogen.

Conclusion

Hydrogen economy adresses some of today's environmental issues. As such, it is entitled to become one of tomorrow's new energy carrier. If so, hydrogen is supposed to offer the same services at an equivalent price as today's fuel with equivalent level of safety.

Comparative safety studies require not only to focus on the product itself, but also on supporting technologies as well as on context of use (confined environnement).

It is obvious that hydrogen has different properties than today's fuel. Some of them tend to make it safer (it disperses more rapidly in open space) and some other more hazardous (potentially strong pressure effects) in foreseen context of use. However, it does not bring along risks than can be overcome with traditional approaches and safety measures.

Fuel cell systems do not appear to put public safety at stakes. High pressure storage could be more critical and require special attention from industrial, standardisation and regulatory bodies.

Hydrogen technologies developers seem to have learned from other energy carriers errors in the sense that safety studies are intrinsequely part of the development. On going standardisation work pushes towards an appropriate and homogeneous level of safety in order to avoid any preliminary accident that could geopardise hydrogen future use in everyday life. However, the use of hydrogen will inevitably lead to accidental situation as other fuels would.

Thus, in comparing hydrogen with current energy technologies, one should not be blind on hazards related to the use of gasoline for instance. Gasoline has not the same propension as hydrogen to

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[20] United Nations Economic Commission for Europe

[21] Ludwig-Bôlkow-Systemtechnik GmbH and Ludwig-Maximilians-Universitàt München, "The acceptance of hydrogentechnologies",http://www.hydrogen.org/accepth2/.

explode but it takes fire. Statistics show that gazoline fire sets by car accidents counts for 1%[22] of fatalities on the road. Would hydrogen be responsible for 1% fatalities in case of car accidents ? One has to come to turn with the reality of today's fuel in their context of use. **Comparative studies should pay attention not to underestimate risks of usual fuels because of their everyday usage and overestimate risks of hydrogen.** Hydrogen requires to be better known through experimental / demonstration projects.

Still, acceptance relies on expected users : the public. **Pragmatic safety studies are one thing public acceptance is another one.** If hydrogen is an appropriate solution, it has to take the public onboard to erase the fear of the unknown.

[22] Information given by Laboratoire d'Accidentologie et de Biomécanique PSA Peugeot Citroen Renault - France