TABLE OF CONTENTS

P	REAMBL	E	2
1	HYDR	OGEN GENERALITIES	3
Ī		sical and Chemical Properties	3 3 3 3 3
		ses of the Life Cycle of Hydrogen	3
	1.2.1	On Site Production	3
	1.2.2	Storage	3
	1.2.3	Distribution	4
	1.3 Use		
	1.3.1	In an Isolated Site	5 5
	1.3.2	Backup Electrical Power Supply	5
	1.3.3	Supply of Forklifts, Trans-pallets	6
	1.3.4	Hydrogen Powered Traction Systems	6
	1.3.5	Station for Hydrogen Vehicles	7
	1.3.6	Presentation of a Fuel Cell	7
2	HAZA	RDS AND PHENOMENA ASSOCIATED WITH HYDROGEN	9
	2.1 Pres	sentation of Hazards Associated with Hydrogen	9
	2.1.1	Risk of Asphyxia (Anoxia)	9
	2.1.2	Thermal Hazard	9
	2.1.3	Explosive Hazard Presented by Hydrogen	10
	2.1.4	Cryogenic and Vaporization Hazards	12
	2.2 Cor	relations between Phenomena and Hazards Associated with Hydrogen	12
	2.2.1	Inventory of Phenomena	12
		ry of Possible Scenarios	13
		essment of Technologies	15
	2.3.1	Presentation of Different Storage Methods	15
	2.3.2	Behavior of Storage Media in Case of Accident	15
3	INTER	VENTION PROCEDURES	17
	3.1 Gen	eral Rules for Interventions	17
	3.1.1	Clothing	17
	3.1.2	5	17
	3.1.3		17
	3.1.4	Chronology of the Response	17
		cue of Persons	18
	3.3 Fire		20
	3.3.1	Fire in the Electrical Section of an H ₂ Production Installation	20
	3.3.2	Fire Threatening an H ₂ Installation or H ₂ Storage	21
	3.3.3	Flaming H ₂ Leak	22
	3.4 Hyc	Irogen Leak	23
	NINEV T. T	Definitions.	
	NNEX I: I	Abbreviations and Acronyms	

ANNEX II: Abbreviations and Acronyms ANNEX III: Summary Table, Decision Trees ANNEX IV: To Go Further . . . ANNEX V: Notes and References, Bibliography

PREAMBLE

The present document reflects the state of knowledge concerning the technology and the use of hydrogen as an energy source in France.

Fire departments are likely to be confronted more often with the hazards generated by hydrogen. The use of hydrogen is more and more common and new methods of storage are appearing.

The purpose of this document is to offer fire departments a risk analysis, in particular for those relating to new high-pressure storage methods and new uses of hydrogen and to define global intervention strategies intended to reduce or prevent these hazards in a sustainable manner.

These technologies are in constant evolution and updates will be necessary in the future.

In addition, the information fire departments have is vital to the proper progress of rescue operations.

It is strongly recommended that Regional Environmental Planning departments and industrial personnel indicate to the fire and rescue departments the installation of projects employing hydrogen.

The technical terms used in this note are defined in a glossary in Annex I.

Lastly, it is important to note that this Operational Information Note does not question risk analyses performed:

- on a fixed storage facility (cf. "Study of Hazards"), or
- on the Transport of Dangerous Materials TDM

<u>1 HYDROGEN GENERALITIES</u>

1.1 Physical and Chemical Properties

Hydrogen is the lightest gas. In a non-confined environment, hydrogen has a tendency, therefore, to rise and to be rapidly diluted in air, which can be considered as a factor of safety.

Hydrogen is inflammable. Its flame is very difficult to detect, it dissipates little radiant heat, and it is colorless, odorless, non-toxic, and almost invisible.

Mixed with oxygen from the air (or another oxidizer), hydrogen produces an explosive atmosphere.

Hydrogen/air mixtures under certain conditions (cf. 2.1.2 Thermal Hazard) ignite under the action of ignition sources containing little energy: a simple static electricity phenomenon, for example, could suffice to cause ignition.

1.2 Phases of the Life Cycle of Hydrogen

Hydrogen is an energy vector, so it must be fabricated before being stored and used.

The two new main uses of hydrogen are:

- the fuel cell (notably for electric or hybrid vehicles), internal combustion engines, gas turbines for the production of electricity;
- the new co-generation systems for producing energy (electricity and heat).

1.2.1 On Site Production

The growing recourse to renewable energy sources is leading today to the development of electrolysis.

The reaction of the decomposition of water by electrolysis can be written as follows:

$$\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{H}_{2} + \frac{1}{2}\mathrm{O}_{2}$$

This reaction requires electrical energy to be supplied and heat is released from it.

1.2.2 Storage

Hydrogen can be stored in the form of liquid, gas, or hydride.

1.2.2.1 Liquid Form

In order to be stored in liquid form, the temperature of hydrogen must be lowered below its boiling temperature at atmospheric pressure. This means that liquid hydrogen is stored at -250° C.

At this temperature, it is essential to use appropriate individual protective equipment (gloves and cryogenic apron, safety glasses - cf. paragraph 2.1.4 Cryogenic and Vaporization Hazards).

1.2.2.2 Gaseous Form

In order to increase the quantity of hydrogen which can be stored in a tank, it is compressed by increasing the pressure.

The pressure in the tanks can vary from several tens to several hundreds of bars.

1.2.2.3 Hydride Form

Another method of storing hydrogen is based on the formation of solid metal hydrides. At the current time, the main technique used for this purpose consists of "trapping" hydrogen as a hydride within solid magnesium metal (MgH₂).



This technology allows the hazard associated with storing significant quantities of hydrogen to be minimized.

A "tablet" of 43g contains 0.5 m³ of hydrogen.

There are other research projects underway for storing hydrogen in the solid form using different methods.

1.2.3 Distribution

Depending upon the final use and the quantities required, hydrogen can be transported:

- by road, rail or water,
- stored in gas bottles, in "cigars," in tanks, or
- pressurized or as a cryogenic liquid.

When it is stored in a pressurized bottle, hydrogen can be identified by:

- the top of the bottle having a red color (inflammable), or
- the banana-shaped label on which information concerning the gas and the • producer are listed.



When it is transported by truck, tanker-truck, or transport barge, hydrogen is identified by the following plate "Danger" and the pictogram "Danger":

Pressurized Hydrogen

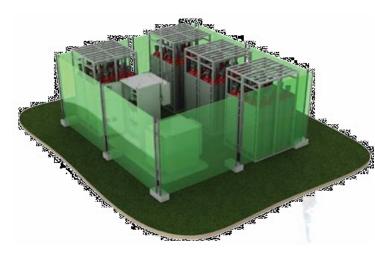


Hydrogen is also transported by pipework (gas pipeline). Northern Europe is crossed by a large pipeline network of several thousands of kilometers.

1.3 Uses

1.3.1 In an Isolated Site

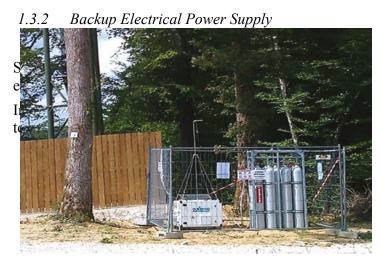
Autonomous, clean electricity generation for temporary or permanent power for isolated sites such as telecommunications antennas, video surveillance, signaling, lighting, measurement sensors.



Rated voltage 230 V (AC) Rated power 2.75 kVA / 230 V (AC) Maximum power 5 kW Battery capacity 150 Ah at 48 V Battery life 1h at 2 kVA

Rated voltage 220 V (AC) / 50 Hz Rated power 2 kVA Maximum power: - 6 kVA for 10 s; - 4.5 kVA for 30 min









Rated voltage +/- 24 V or +/- 48 V or +/- 80 V (DC). Rated power 1.5 to 3 kVA/ 24 V or 10 kVA / 48 V or 14 kVA/80 V (DC).

1.3.4 Hydrogen Powered Traction Systems

Hydrogen powered traction systems can be used for all the traction needs of a vehicle and deliver maximum power which can vary from 50 to 120 kVA for current models.

These systems are adapted to all types of uses, whether for open road or urban traffic. Their efficiency varies with the load (weight of vehicle). They operate optimally between 10% and 30% of the maximum load, and are therefore well suited to the urban traffic cycle.

Hydrogen consumption of a light vehicle varies from 0.8 to 1.2 kg/100 km. This requires carrying between 2 and 6 kg of hydrogen depending upon the type of vehicle and use considered.

Pressurized gas storage constitutes a simple solution. This technology is currently used for natural gas at 200 bars and concerns about 1.5 million vehicles worldwide.

The storage pressure of hydrogen is increasing. Where it was once 350 bars, it is now generally 700 bars. The tanks are composed of an aluminum or polymer liner reinforced by a filamentary winding of carbon fibers and epoxy resin.



Figure 1: Hydrogen bus -25 to 40 kg of H₂

Diagram1:Illustration of an H_2 car

The development of the hydrogen subsidiary in the automotive industry will have to begin by fleet vehicle use, forklifts, and public transportation, and then spread to individuals. This will translate into the development of service stations dedicated to refueling vehicles.

1.3.5 Station for Hydrogen Vehicles

A hydrogen filling station consists of using the technology related to the distribution of gaseous hydrogen so as to fill the hydrogen tanks of vehicles under conditions as simple as those for gasoline or diesel.

The filling pressure can attain 700 bars (allowing the fill to be made in 3 to 5 minutes for a car and 10 for a large truck).

The safety standards used in the industry are applied to these stations.



Figure 2: Filling of a car with H₂

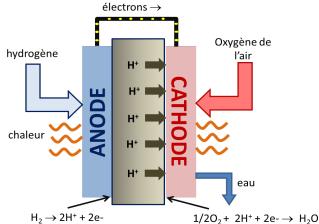


Figure 3:Filling station of a hydrogen powered forklift truck

1.3.6 Presentation of a Fuel Cell

The principle is quite simple: an electrochemically controlled oxy-reduction reaction occurs between hydrogen and oxygen with the simultaneous production of electricity and heat according to the chemical reaction:

 $2H_2+O_2\to 2H_2O$ at the anode $H_2\to 2H^++2e^-$ at the cathode O_2+2 $H^++2e^-\to H_2O$



$1/20_{2}$ +	2H' +	$2e \rightarrow$

Original	Translation	
Electrons	Electrons	
Hydrogène	Hydrogen	
Chaleur	Heat	
ANODE	ANODE	
CATHODE	CATHODE	
Oxygène de l'air	Oxygen from air	

eau water

Supply of gaseous fluids: at the cathode, the cell is supplied with O_2 from the air under a pressure which varies, depending upon the manufacturer, from several hundred millibars to 1.5 bar.

The cell is supplied with H_2 from a regulating system which imposes the desired flow rate under a pressure equal to the cathode pressure.

Elimination of the water produced: the flow rate of air at the cathode drains the water produced by the reaction and passes through a separator at the outlet of the cell. This water can be stored to serve miscellaneous functions or directly discharged to the exterior.

Elimination of heat: the thermal energy produced in the cell is of the same order of magnitude as the electric power and must be removed to avoid overheating.

2 HAZARDS AND PHENOMENA ASSOCIATED WITH HYDROGEN

2.1 Presentation of Hazards Associated with Hydrogen

Hydrogen is a colorless, odorless, non-toxic and non-corrosive gas capable of generating a risk of asphyxia (anoxia), a thermal hazard, and an explosive hazard.

2.1.1 Risk of Asphyxia (Anoxia)

As for all gases, the increase in the concentration of hydrogen leads to the decrease in the proportion of oxygen, which can lead to asphyxia (anoxia).

The risk of asphyxia occurs essentially in confined environments.

Hydrogen is a very light gas (density: 0.066); it has a tendency therefore, to rise⁵ and to be rapidly diluted in air in an open environment.

It should be noted, therefore, that if the conditions are ripe for the risk of asphyxia (anoxia), the explosion hazard will be preponderant.

2.1.2 Thermal Hazard

The combustion reaction of hydrogen in air corresponds to the following balance equation:

$$H_2 + \frac{1}{2} O_2 + 2 N_2 \rightarrow H_2 O + 2 N_2$$

Hydrogen is an extremely inflammable gas under normal temperature and pressure conditions.⁶ It is characterized by the following data.⁷

Properties	Associated data
Lower Flammability Limit (LFL)	4%
Upper flammability Limit (UFL)	75%

^{1:} Flammability characteristics of hydrogen

The essential characteristics of hydrogen are a very wide range of flammability and a very low ignition energy.

It should be specified that a simple static electricity discharge is sufficient to ignite hydrogen. It is important therefore, to note that the probability of ignition of hydrogen is very great.⁸

The resulting flame from the combustion of hydrogen in air is almost invisible and with a temperature of 2000° C.¹⁰

The hydrogen flame radiates¹¹ little. This property thus limits the risk of propagation in the case of a fire. This can be illustrated by the thermal fluxes released during the combustion of a hydrogen leak in a pipe (following table).

			diate combu laming leak		Dela	yed comb (fire-ball	
Scenario of a pipework leak	Tank pressure (bar)	Long dur	ation therm (kW/m²)	Short-term thermal effects			
		3 kW/m ²	5 kW/m ²	8 kW/m²	SEI ¹⁴	SEL ¹⁵	SELS ¹⁵
		The	distances are in	n m	The	e distances ar	e in m
Hose from an articulated trailer		7.2	7.2	7.2	7	6.4	6.4
0.1 mm	200	0.2	0.2	0.2	0.4	0.4	0.4
0.2 mm		0.5	0.4	0.4	0.9	0.8	0.8
4 mm		11	9	8	17.6	16	16
0.1 mm	525	0.4	0.3	0.3	0.8	0.7	0.7
0.2 mm		0.7	0.6	0.6	1.5	1.3	1.3
2.3 mm		9	7.9	7	17	15	15
4 mm		17	15	13	29	26	26
5.16 mm		22	19	17	37	34	34
0.1 mm	450	0.2	0.2	0.2	0.7	0.6	0.6
0.2 mm		0.3	0.3	0.3	1.5	1.2	1.2
4 mm		16	14	12	27	24	24
5.16 mm		21	18	16	35	31	31
0.1 mm	700	0.2	0.2	0.2	0.8	0.8	0.8
0.2 mm		0.8	0.4	0.4	1.72	1.5	1.5
2.3 mm		10	9	8	19	18	18
4 mm		19	17	15	33	30	30

*Table 2: Thermal flux correlations and distances during the combustion of a hydrogen leak in a pipe as a function of the diameter of the leak and the tank pressure*¹²

2.1.3 Explosive Hazard Presented by Hydrogen

The explosive range of hydrogen is very wide if you consider that the limits of flammability are similar $\frac{16}{16}$ to the explosive limits.

The speed of propagation of the flame allows the nature of the energetic regime of the explosion to be determined:

- either the deflagration: the flame front moves at a subsonic speed; the newly released gases are thus compressed by the expansion of the volume. A continual increase of the pressure in the gas cloud is observed;
- or the detonation: the speed of propagation of the flame is supersonic. The formation of a shock wave is observed.

The hydrogen flame propagates much more rapidly than the usual fuels (CNG, LPG): the risk of detonation cannot, therefore, be ignored.

			Delayed combustion (fire-ball)				
Scenario of a	Tank pressure	Length of flame	Effects of over-pressure (mbar)				
pipework leak	(bar)	(m)	20	50 (SEI)	140 (SEL)	200 (SELS)	
				The dista	nces are in m		
Hose from an articulated trailer			13.1	8.2			
0.1 mm	200	0.2	0.5				
0.2 mm		0.4	1	0.5			
4 mm		7	20	10	6	5	
0.1 mm	525	0.4	1	0.5			
0.2 mm		0.8	2	1			
2.3 mm		7	18	9	6	5	
4 mm		12	32	16	9	8	
5.16 mm		15	42	21	12	10	
0.1 mm	450	0.3	0.8	0.4			
0.2 mm		0.7	1.4	0.7			
4 mm		11	30	15	9	7	
5.16 mm		14	38	19	11	9	
0.1 mm	700	0.5	1	0.5			
0.2 mm		0.8	2	1			
2.3 mm	,	8	22	11	6	5	
4 mm		14	38	19	11	9	

*Table 3: Thermal flux correlations and distances during the combustion of a hydrogen cloud following a leak in a pipe as a function of the diameter of the leak and the tank pressure*¹²

- The diameters 0.1 and 0.2 mm correspond to an accidental leak (failure) of an item of equipment;
- The diameter of 2.3 mm corresponds to the diameter of an H4 rack;
- The diameter of 4 mm corresponds to the diameter of a gas hose (see Annex I).

2.1.4 Cryogenic and Vaporization Hazards

The liquid state being the most favorable for storage and transport, hydrogen is maintained at -252.8°C (i.e., 20.35°K) under a pressure of between 1 and 10 bars.

In this state it is comparable to a cryogenic liquid.

Three dangers are associated with hydrogen in the cryogenic liquid state. They concern:

- the ability to be extremely cold (cryogenic hazard)
- the ability of very small quantities of liquid to occupy very large volumes when passing to the gaseous state (vaporization hazard).
- its temperature being lower than the air condensation point, leading to the enrichment of oxygen in non-insulated zones in contact with liquid hydrogen (see dangers of liquid oxygen).

- Cryogenic hazard: cryogenic liquids are able to cause effects on the skin similar to thermal burns.

- Vaporization hazard: in the case of a leak, a liter of liquid hydrogen vaporizes to form 780 liters of gas, which can lead to a risk of anoxia in a confined environment.

2.2 Correlations between Phenomena and Hazards Associated with Hydrogen

2.2.1 Inventory of Phenomena

The incidents or accidents likely to produce the hazards mentioned previously concerning hydrogen can be inventoried within the matrix shown on the following page.

2.2.1.1 Phenomena Associated with the Bursting of a Tank

The sizing of the thermal effects, of over-pressure, and ejection in the framework of implementing zoning can be modeled using tools usually employed by managers of mobile chemical intervention cells.

2.2.1.2 Phenomena Associated with a Leak

The consequences²¹ of a hydrogen leak occurring on a pipe or on a storage chamber mainly depend on three factors: the flow rate of the leak (see Annex IV), confinement, and the presence of an ignition source.

The noise generated by a hydrogen leak is—because of the size of the molecules, the pressure, and its escape speed—very great (see Annex IV). Thus an open rack, whose orifice at the exit to the hose measures 4 mm, produces a sound of 130dB, under a pressure of 200 bars.

Translation
Two types of accidents
Shattering of a tank
Generating elements
Because of the container (jacket)
Ex. no.1: mechanical sagging of the jacket
Ex. no.2: excessive corrosion of the jacket
Because of the content (hydrogen)
Ex. no.3: increase of internal pressure caused by heating (fire close to tank)
Ex. no.4: increase of internal pressure caused by filling
Consequences
Pressure wave
Fire-ball
Projection of fragments
Leak on a tank or a pipe
Low flow-rate leak
In a confined environment
Accumulation of hydrogen
Combustion of the pre-mixture
Fire
Detonation
In open air
Dispersion of hydrogen
No combustion
High flow-rate leak
Immediate combustion
Flaming jet
Dispersion
Combustion of the pre-mixture
Fire
Detonation

2.3 Assessment of Technologies

2.3.1 Presentation of Different Storage Methods

Hydrogen can be stored at high pressure in casings complying with the following characteristics: $\frac{23}{2}$

Composition	Designation	Storage pressure (bars)	Bursting pressure (bars)	Volume of chamber (expressed as water—liters)	Volume of hydrogen content (m ³)	Weight of hydrogen content (kg)
Composite material Type III	Bottle 74 liters	350	595	74	20	1.8
	Rack H4 B142	525	578	568	207.5	18.7
Composite material	Bottle 80 liters	700	770	80	35.8	3.2
Type IV	Rack H4 B142	700	770	568	254.1	22.8
	B142	700	770	142	63.5	5.7
	B 20 liters	200	380	20	3.3	0.3
Steel	B50 liters	200	380	50	8.4	0.75
Туре І	Rack V9 B50	200	380	450	75.2	6.76
	Rack V18 B50	200	380	900	150.4	13.5

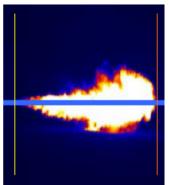
 Table 2: Comparison between steel and composite material bottles (non-exhaustive examples)

2.3.2 Behavior of Storage Media in Case of Accident

Not all bottles are equipped with thermal fuses (device intended to favor the emptying of the content gas). This is why, when in doubt, it must systematically be considered that such devices are absent during the intervention while taking into account the potential danger of an untimely triggering of a fuse (thermal flux).

The fuse triggers at a temperature of between 100° and 120°C. It allows the bottle to be rapidly emptied in the case of heating and the risk of bursting to be avoided.





Photos taken during a vertical and a horizontal leak

In a normal configuration, the discharge can occur vertically or

horizontally. Despite this, the diameter of the orifice is not uniform and does not allow the length of the flame to be determined.

For bottles without equipment, and in case of accident, a loss of seal will be noticed, or indeed bursting.

3 INTERVENTION PROCEDURES

For all interventions, the standard operating procedures (SOP) apply.

Thus, the operations of

- Reconnaissance
- Life-saving
- Establishments
- Attack
- Protection
- Removal of material
- Surveillance

remain pertinent, in particular for operations related to a fire, but proceed in different ways depending on the type of intervention.

With regard to the analysis of the response, the elementary operations of the SOP are to be performed according to the basic actions defined below.

These points are to be treated or ignored. The conclusions of the analysis of the area where the intervention will take place will allow a decision to be made concerning which of the following basic actions will be taken, in what order, and if certain actions can be performed simultaneously.

3.1 General Rules for Interventions

3.1.1 Clothing

The wearing of a complete fire suit and isolating breathing apparatus (ARI) is obligatory.

3.1.2 Weather Conditions on the Day

Whatever the incident to which the fire department must respond, knowledge of the weather conditions is extremely important for the emergency operations commander.

3.1.3 Parking of Emergency Vehicles

The weather conditions and the configuration of the land determine how the fire trucks should be parked so that they are outside the exclusion zone.

The engagement of the first fire trucks and the modification of the exclusion zone during the action etc. are events likely not to comply with this recommendation.

3.1.4 Chronology of the Response

The emergency operations commander must take his (her) necessary distance to identify the priority hazard to take into account at each phase of the response and thus to adapt his (her) tactics.

The chronology which follows incorporates the principles of the standard operating procedure while integrating the particularities of the specific installation where hydrogen is used as an electrical energy source (fuel cell, forklift, automobile, etc.)

For responses following a leak (on fire or not), the emergency operations commander must take into account the audible phenomena (see 2.2.1.2 Phenomena Associated with a Leak).

3.2 Rescue of Persons

The responses can be assembled according to the following four operational situations:

- incident or accident to a person not directly linked to an H_2 energy production installation
- faintness or fainting due at oxygen starvation (anoxia) following an H_2 leak in a confined environment;
- electrocution by contact with the installation <u>following damage or malfunction;</u>
- burning following a hydrogen leak (immediate or delayed combustion).

Apart from the difficulty of recognizing an electrical hazard or an H_2 leak (odorless and colorless), these hazards are to be feared in the following priority.

SOP	Acts or elementary actions	Objectives:
	Identify	 Make contact with the safety manager of the installation to obtain clarifications concerning the incident; Take into account the risk of an H₂ explosion in confined premises; Take into account the risk of anoxia in confined premises.
Reconnaissance	Forbid	 Forbid windward progression and imperatively establish an exclusion zone at 50 m; Ban non-ATEX electrical or electronic apparatus in the exclusion zone (cell phones, beepers, walkie-talkies, etc.).
	Inspect	- Cut off external power sources in the building.
Rescue		 If confined premises and H₂ leak: wearing of isolating breathing apparatus (ARI) obligatory; evacuate the victim outside of the exclusion zone as rapidly as possible. If risk of victim electrocuted: use emergency electrical hazard equipment to remove the victim; avoid any contact between the rescuers and the electrical elements.
Establishment/ Attack	Intervene	 Confirm or re-define the exclusion zone first (50m); Perform measurements with an explosimeter (from the top to the bottom of the installation or storage system).
Protection Intervene		 Actions with a risk of anoxia: close the H₂ supply valves; ventilate the premises favoring natural drawing (do not use electrical or machine means of smoke removal). Actions with an electrical hazard Actuate the emergency stop pushbutton (timeout of 20 min with presence of current remaining).
Removal Surveillance		 The surveillance phase ceases as soon as you are assured of the following: the level of oxygen in the premise is normal (about 20%); the absence of ATEX by explosimeter measurements; the electrical installation is secured and taken in charge by a technician.

3.3 Fire

The responses can be organized according to the following three operational situations:

- Fire in the electrical section of an H₂ production installation
- Fire threatening an H_2 installation or H_2 storage
- Flaming H₂ leak

SOP	Acts or elementary actions	Objectives			
		- Make contact with the safety manager of the installation to obtain clarifications concerning the incident;			
		-Take into account the "low voltage" hazards.			
Reconnaissance	Forbid	- Forbid windward progression and imperatively establish an exclusion zone at 50 m;			
	TOTOR	- Ban non-ATEX electrical or electronic apparatus in the exclusion zone.			
	Inspect	- Cut off external power sources in the building.			
Rescue		See 3.2 Rescue of Persons			
		- Confirm or re-define the exclusion zone first (noise of pressurized H ₂ leak, explosimeter measurements, etc.);			
Establishment/ Attack		 Proceed to extinguish the fire depending on its virulence: → with a powder or CO₂ extinguisher at a distance > 1 m; → with variable flow-rate nozzles (LDV) with diffused pulsed attack jet at a distance > 3 m. 			
	Intervene	(Actuate the emergency stop pushbutton for the installation (timeout of 20 min with presence of residual current);			
Protection	Isolate	- Take account of the direction of flow of the extinguishment water during the timeout phase of the installation (electrical hazard);			
		- Close the H ₂ supply valves;			
		- Ensure that the premises are ventilated by natural drawing (oper existing outlets).			
Removal		- Look for hot spots or measure the temperature on the H_2 storage using appropriate means such as an infrared camera or a pyrometer;			
Surveillance		- The surveillance phase ends as soon as it is noted that the extinguishment actions seem to be effective.			

3.3.1 Fire in the Electrical Section of an H₂ Production Installation

SOP	Acts or elementary actions	Objectives
	Identify	- Make contact with the safety manager of the installation to obtain clarifications concerning the incident;
Reconnaissance		- Take account of the explosion hazard for the H_2 tanks subject to fire with projections (several tens of meters for bottles to several hundreds for semi-trailers).
Reconnaissance	Forbid	 Forbid windward progression and imperatively establish an exclusion zone at 50 m; Ban non-ATEX electrical or electronic apparatus in the exclusion
	Inspect	 - Data holi-ATEX electrical of electronic apparatus in the exclusion zone. - Cut off external power sources in the building;
Rescue	mspeet	See 3.2 Rescue of Persons
	_	- Confirm or re-define the exclusion zone first (tanks or installation directly threatened by the flames);
		- Proceed to extinguish the fire sites;
	Intervene Isolate	- Ensure the preventive cooling of the installations and H_2 storage using the following means:
Establishment/ Attack		 → setting up hoses with "peacock tail" type nozzles; → direct spraying in JDA of the H₂ tanks by means of at least a variable flow-rate (LDV) 250 liter/min nozzle (avoid directing the jets onto the pipework); → or putting in place "sensitive point defense" protective system on open air installations (power bay, etc.) used during FDF maneuvers.
		(Actuate the emergency stop pushbutton for the installation (timeout of 20 min with presence of residual current);
Protection		- Close the H ₂ supply valves;
		- Ensure that the premises are ventilated by natural drawing (open existing outlets).
		- Look for hot spots or measure the temperature on the H_2 storage using appropriate means such as an infrared camera or a pyrometer;
Removal Surveillance		 The surveillance phase ceases as soon as you are assured that: → the extinguishment actions seem to be effective; → the water projected onto the H₂ storage flows off without evaporating on contact.

N.B.: Actuating the emergency stop pushbutton during the *Protection* phase allows sources of electrical ignition, intrinsic to the installation implicated, to be eliminated.

3.3.3 Flaming H₂ Leak

SOP	Acts or elementary actions	y Objectives	
		- Make contact with the safety manager of the installation to obtain clarifications concerning the incident;	
	Identify	- Take account of the dispersion of H_2 in the premises before ignition (possibility of delayed ignition of an H_2 cloud, of type UVCE).	
		- Forbid windward progression and imperatively establish an exclusion zone at 50 m;	
Reconnaissance	Forbid	- Ban non-ATEX electrical or electronic apparatus in the exclusion zone;	
Reconnuissance		- Ban extinguishing a flaming leak;	
		- Forbid actions on the electrical circuit of the installation in the presence of an H_2 leak.	
		- Cut off external power sources in the building;	
	Inspect	- Confirm the presence of a flaming leak and its length by means of suitable equipment such as an infrared camera (flame difficult to see over its length);	
		- Be attentive to the significant noise coming from a flaming gas leak.	
Rescue		See 3.2 Rescue of Persons	
		- Refine the exclusion zone (explosimeter measurements, information on the type of incident);	
Establishment/ Attack		- Put a water curtain in place to prevent any propagation;	
Анаск		- If need be, provide preventive cooling of nearby installations and H_2 storage.	
	Tuto more a	- Close the H ₂ supply valves;	
Protection	emoval	- Ensure that the premises are ventilated by natural drawing (open existing outlets).	
		- Look for hot spots or measure the temperature on the H_2 storage using appropriate means such as an infrared camera or a pyrometer;	
Removal Surveillance		- Take explosimeter measurements in confined premises especially at hot spots;	
		- Actuate the emergency stop pushbutton for the installation (timeout of 20 min with presence of residual current).	

N.B.: Actuating the emergency stop pushbutton during the *Removal* phase allows sources of electrical ignition, intrinsic to the installation implicated, to be eliminated.

3.4 Hydrogen Leak

Hazards generated by an H_2 leak are characterized by the state (liquid or gas) of the storage and the duration of the leak (several tens of minutes to several hours).

The following hazards can arise:

- \rightarrow risk of anoxia (see 3.2)
- → risk of burning by cold in the presence of liquid H_2 (-253°C)
- \rightarrow risk of combustion (see 3.3.3)
- → risk of explosion of an H_2/air mixture in the flammability range (4% to 75%)

SOP	Acts or elementary actions	Objectives			
	Identify	- Make contact with the safety manager of the installation to obtain clarifications concerning the incident (state of H_2 , evaluation of emptying time, etc.);			
-		- Take the risk of explosion into account.			
Reconnaissance		- Forbid windward progression and imperatively establish an exclusion zone at 50 m;			
	Forbid	- Ban non-ATEX electrical or electronic apparatus in the exclusion zone;			
		- Forbid actions on the electrical circuit of the installation in the presence of an H_2 . leak.			
	Inspect	- Cut off external power sources in the building.			
Rescue		See 3.2 Rescue of Persons			
Establishment/		- Refine the safety perimeter with measurements from an explosimeter (from the top to the bottom of the installation);			
Attack/ Protection		- Ensure that the premises are ventilated by natural drawing (open existing outlets);			
	Intervene	- Close the H ₂ supply valves.			
Isolate Removal Surveillance		 The surveillance phase ceases as soon as you are assured that any risk of explosion is removed (complete draining of the tank, or draining into the open air in an area, secured and monitored by the operator, effective ventilation of the premises, etc.); Actuate the emergency stop pushbutton for the installation (timeout of 20 min with presence of residual current). 			

N.B.: Actuating the emergency stop pushbutton during the *Removal* phase allows sources of electrical ignition, intrinsic to the installation implicated, to be eliminated.

ANNEX I

DEFINITIONS

Response zone

Zone which groups together the exclusion zone, the area monitored, the support zone, and any location where fire department operations are taking place.

Lyre

- Interconnection hose: these are rigid pipes, generally of steel, which allow gas systems to be interconnected, such as racks or expansion panels.
- Expansion lyre: these are the shape of the pipework and are designed to absorb thermal variations due to external conditions. They are found in the form of a semicircle, a "U," or an *omega*.

Rack

A rack is a group in a structure of several interconnected bottles. Examples:

- a "V9 B50" rack corresponds to 9 bottles of 50 liters (water) grouped together vertically,
- An "H20 B100" rack corresponds to 20 bottles of 100 liters (water) grouped together horizontally,

Liner

A bottle is made in 2 parts: the packing and the liner. The packaging ensures mechanical resistance while the liner essentially (or integrally) ensures the seal of the bottle.

Buffer

English term for designating a buffering capacity. It is used here to designate the highpressure, compressed storage which is available in hydrogen service stations. Their capacities can vary from 500L to 2000L (water) for pressures going from 450 to 700 bar.

ANNEX II

ABBREVIATIONS AND ACRONYMS

ARI	Appareil respiratoire isolant (isolating breathing apparatus)
ATEX	Atmosphere explosive
COS	Commandant des opérations de secours (emergency operations commander)
DREAL	Directions régionales de l'environnement, de l'aménagement et du logement (Regional Directorates for the Environment, Layout and Lodgings)
FDF	Feux de forêts (forest fires)
GNV	Gaz natural pour vehicles (natural gas for vehicles)
JDA	Jet diffusé d'attaque (diffused attack jet)
Κ	degree Kelvin
kVA	kilo volt ampere – unit of power ($P = VxI$)
LDV	Lance à débit variable (variable flow-rate nozzle)
LFL	Lower flammability limit
LPG	Liquid petroleum gas
SEI	Seuil des effets létaux (irreversible effects threshold)
SEL	Seuil des effets létaux (lethal effects threshold)
SELS	Seuil des effets létaux (significant lethal effects threshold)
SOP	Standard operating procedures
TMD	Transport de marchandises dangereuses (transport of dangerous merchandise)
UFL	Upper flammability limit
UVCE	Unconfined vapor cloud explosion

Bursting scenario: hydrogen tube trailer 2m³ **Rack V9 - V18** Rack H4 B142 Rack H4 B142 Compressed Buffer 2m³ Buffer 1m³ **Bottle 74** Bottle 201 **Bottle 801 Bottle 501 B**50 Type of bottle (bar) \sum V M Π Π Ι Γ Γ Η Γ pressure (bar) Tank pressure Burst (bar) SEI [m] 13.2 ∞ ∞ Short-term thermal effects SEL [m] S --SELS [m] S -1 -1 20 [m] Effects of over-pressure (mbar) 50 [m] 140 [m] ∞ ∞ 200 [m] ∞

SUMMARY TABLES, DECISION TREES

ANNEX III

Rack H4 B142 700 93.4 h 15 h 56	Rack H4 B142 525 85.85 h 13.74 h 52	Buffer 2m ³ 450 288.02 h 46.08 h	Buffer 1m ³ 450 144 h 23.04 h	74 L bottle 350 10 h 2 h 6	Compressed hydrogen tube trailer200213 h34.08 h	Rack V18 B50 200 96 h 921 min	Rack V9 B50 200 48 h 461 min	50 L bottle 200 320 min 52 min	20 L bottle 200 128 min 21 min	(bar) 0.1 mm 0.25 mm 1 mi	
56 11 min	52 10 min			6						1 mm 2.3 mm	Draining time
				6							Draini
				23 sec	8 min	4 min	2 min	12 sec	5 sec	4 mm 3	time
		6.2	3.1 min							5.3 mm	
		2.1 min	1 min							9.1 mm	

ANNEX IV

TO GO FURTHER...

Physical and Chemical Characteristics of Hydrogen

Designation	Value	Observations		
Critical temperature	-240°C (or 33.15°K)	These are the coordinates of the critical point		
Critical pressure	12.98 bar	These are the coordinates of the critical point		
Temperature at triple point	-259.3°C (or 13.85°K)	These are the coordinates of the triple point		
Pressure at triple point	0.0072 bar	These are the coordinates of the triple point		
Melting point	-259°C (or 14.15°K)			
Boiling point	-252.8°C (or 20.35°K)	at 1.012 har		
Density of the liquid phase	70.973 Kg/m ³	at 1.013 bar		
Density of the gaseous phase	1.312 Kg/m^3			

Flammability Characteristics of Hydrogen

Properties	Associated data
Lower flammability limit (LFL)	4% volume in air
Upper flammability limit (UFL)	75% volume in air
Minimum ignition energy	20µJ
Auto-ignition temperature	585°C

Data¹ Characterizing the Combustion of Hydrogen

Properties	Associated data
Lower calorific power	$10,800 \text{ kJ/m}^3$
Upper calorific power	12,770 kJ/m ³
Stoichiometric mixture in air (% vol)	29.53%

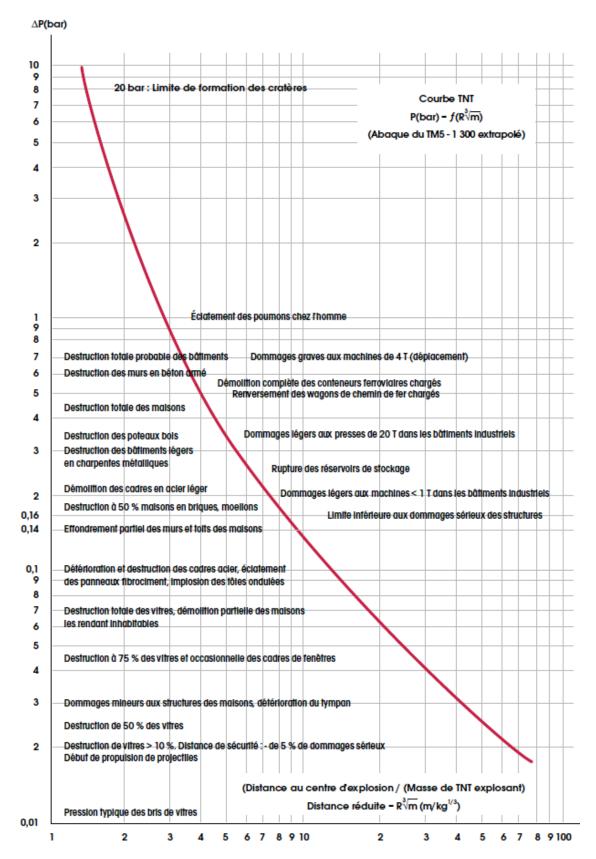
It should therefore be noted that the combustion can occur when the concentration of hydrogen in air is between 4% and 75%. The associated oxy-reduction reaction will be complete when the mixture is in stoichiometric proportions.

Reference Values Relative to the Threshold for Overpressure Effects

Level of overpressure	20 mbar	50 mbar	140 mbar	200 mbar	300 mbar
Effects on structures	Threshold for significant destruction of windows	Threshold for slight damage to structures	certails damage to	Threshold for domino effects	Threshold for very serious damage to structures
Effects on man	Threshold for indirect effects by breakage of windows on man	Threshold for irreversible effects defined by significant danger to human life	effects defined by	Threshold for lethal effects defined by very grave danger to human life	

¹ In *sheet no.2.1 - les données Basic sur hydrogen (Hydrogen database)*, March 2001, Association Française de Hydrogen (French Hydrogen Association) (AFH2).

TNT Equivalent Curves



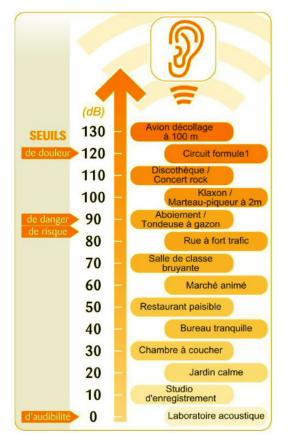
Original	Translation
ΔP(bar)	∆P(bar)
20 bar : Limite de formation des cratères	20 bar : Limit of formation of craters
Courbe TNT	TNT Curves
$P(bar) - f(R^{3}\sqrt{m})$	$P(bar) - f(R^{3}\sqrt{m})$
(Abaque du TM5 – 1 300 extrapolé)	(Graph of TM5 - 1,300 extrapolated)
Eclatement des poumons chez l'homme	Bursting of lungs in man
Destruction totale probable des bâtiments	Probable total destruction of buildings Serious damage to machinery of 4T
Dommages graves aux machines de 4 T (déplacement)	(displacement)
Destruction totale des maisons	Total destruction of houses
Démolition complète des conteneurs	Complete demolition of loaded railcars
ferroviaires chargés	complete demontion of folded functions
Renversement des wagons de chemin de fer	Overturning of loaded railcars
chargés	o vortaining of roaded functions
Destruction des poteaux bols	Destruction of poles
Destruction des bâtiments légers en	Destruction of light buildings with metal
charpentes métalliques	frames
Dommages légers aux presses de 20 T dans	Light damage to 20T presses in industrial
les bâtiments industries	buildings
Rupture des réservoirs de stockage	Rupture of storage tanks
Dommages légers aux machines < 1 T dans	Light damage to 1T machinery in industrial
les bâtiments industries	buildings
Limite inférieure aux dommages sérieux des	Lower limit of serious damage to structures
structures	
Démolition des cadres en acier léger	Demolition of light steel frames
Destruction à 50% maisons en briques,	Destruction of 50% of houses made of
moellons	bricks or cinder blocks
Effondrement partiel des murs et toits des maisons	Partial collapse of walls and roofs of houses
Détérioration et destruction des cadres acier,	Deterioration and destruction of steel
éclatement des panneaux fibrociment,	frames, bursting of fibro-cement panels,
implosion des tôles ondulées	implosion of corrugated iron
Destruction totale des vitres, démolition	Total destruction of windows, partial
partielle des maisons les rendant	demolition of houses rendering them
inhabitables	uninhabitable
Destruction a 75% des vitres et	Destruction of 75% of windows and
occasionnelle des cadres de fenêtres	occasionally of window frames
Dommages mineurs aux structures des	Minor damage to house structures,
maisons, détérioration du tympan	deterioration of eardrums
Destruction de 50% des vitres	Destruction of 50% of windows
Destruction de vitres $> 10\%$. Distance de	Destruction of windows $> 10\%$. Safety
sécurité : - de %% de dommages sérieux	distance: from 5% of serious damage
début de propulsion de projectiles	Start of propulsion of projectiles
Distance au centre d'explosion/ (Masse de	Distance to center of explosion (weight of
TNT explosant)	TNT exploding)
Distance réduite - $P(bar) - f(R^{3/m})$	Reduced distance - $P(bar) - f(R^{3}/\overline{m})$
Pression typique des bris de vitres	Typical window breaking pressures

<u>Speed of Combustion of Different Combustible Gases in Stoichiometric Proportions</u> with Air

Combustible natural gas	Maximum speed of laminar combustion
Hydrogen	3.5 m/s
Methane	0.45 m/s
Butane	0.5 m/s
Acetylene	1.58 m/s

The hydrogen flame propagates seven times more rapidly than that of natural gas: the risk of detonation cannot therefore be ignored.

Leak – Acoustical Hazard



- An open framework at 200 bars, equipped with a lyre outlet orifice of 4 mm produces a noise of 130 dB;

- During tests performed by the Air Liquide company on a pipe of 5mm at a pressure of 700 bars, the values measured extended from 100 to 140 dB (the pressure falling very rapidly to 150 bars).

- In terms of personal protection and for installations, automatic safety systems detect leaks as of the lowest pressures.

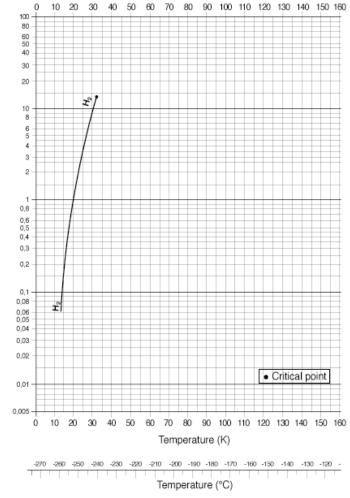
Leaks reaching 50 to 60 dB do not present any risk for persons close by unless in the "confined space" configuration.

Source	bruitpa	rif.fr
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Original	Translation
SEUILS	THRESHOLDS
(dB)	(dB)
De doubleur	Pain
De danger	Hazard
De risque	Risk
D'audibilité	Audibility
Avion décollage a 100 m	Aircraft taking off at 100 m
Circuit formule1	Formula 1 circuit
Discothèque / Concert rock	Nightclub/Rock Concert
Klaxon / Marteau-piqueur a 2m	Klaxon/Pneumatic drill at 2 m
Aboiement / Tondeuse à gazon	Barking/Lawnmower

Rue à fort trafic	High-traffic street
Salle de classe bruyante	Noisy classroom
Marché animé	Animated market
Restaurant paisible	Peaceful restaurant
Bureau tranquille	Quiet office
Chambre à coucher	Bedroom
Jardin calme	Calm garden
Studio d'enregistrement	Recording studio
Laboratoire acoustique	Acoustics laboratory

Cryogenics Information



Identification of the saturated vapor pressure of hydrogen.

Hydrogen can therefore be assimilated under certain conditions to a cryogenic liquid. In fact it can be considered as a liquefied gas conserved in the liquid state at low temperature.

Cryogenic liquids are able to cause effects on the skin similar to thermal burns.

Original	Translation	
Vapour Pressure	Vapor Pressure	
(bar or 0.1 MPa)	(bar or 0.1 MPa)	
Critical point	Critical point	
Temperature (K)	Temperature (K)	
Temperature (°C)	Temperature (°C)	

Low Flow-Rate Leak

Generally associated with a seal failure, the low flow rate is likely to cause the progressive accumulation of hydrogen.

In a confined and/or poorly ventilated space, this environment allows a pre-mixture to be created which can produce a deflagration or even an explosion.

Vapour Pressure (bar or 0.1 MPa)

In the open air, the high coefficient of diffusion of hydrogen generally allows a rapid dispersion of the fuel.

High Flow-Rate Leak

Mainly associated with a rupture of piping fed by a pressurized tank with a failure of the safety devices, the high flow rate generally allows a jet of hydrogen to be created. The combustion²² of a jet of hydrogen therefore leads to the creation of a flaming branch.

Symptoms Related to the Decrease in the Atmospheric Concentration of Oxygen

Atmospheric concentration of oxygen at normal atmospheric pressure	Symptoms observed
	Lowering of night vision
17%	Increase of the quantity of air inhaled
	Acceleration of cardiac rhythm
16%	Vertigo
15%	Attention, judgment, and coordination problems
	Episodes of apnea
	Tiredness
	Loss of motor control
	Strong perturbations of judgement and muscular coordination
12%	Loss of consciousness
	Irreversible cerebral lesions
	Inability to move
10%	Nausea
	Vomiting
	Irregular breathing
6%	Convulsive movements
	Death in 5 to 8 minutes

The risk of asphyxia comes primarily in confined environments: hydrogen is in fact a very small molecule with a high diffusion coefficient in air.² It has a tendency, therefore, to rise³ and to be rapidly diluted in air in an unconfined environment.

It should be noted therefore that if the conditions are ripe for the appearance of the risk of asphyxia (anoxia), the appearance of the explosion hazard is very great. This probability is mainly due to the low energy of ignition of hydrogen.

² The diffusion coefficient of hydrogen in air is 0.61 cm²/s while that of natural gas is 0.16 cm²/s In *sheet no.2.1 - les données Basic sur hydrogen (Hydrogen database)*, March 2001, Association Française de Hydrogen (French Hydrogen Association) (AFH2).

³ Gaseous hydrogen has a density of 0.07. It is therefore much lighter than air (d=1).

	HYDROGEN	METHANE
PCS (kJ/kg)	141,860	51,990
Gas density at 273K (kg/Nm ³)	0.08988	0.6512
Specific heat (Cp) 293K (J/kg K)	14,266	2237
Specific heat (Cv) 293K (J/kg K)	10,300	1714
Thermal conductivity of the gas (W/(mK))	0.1897	0.0328
Boiling point (at 1013 mbar abs.) (K)	20.268	111.6
Critical temperature (K)	33.30	190.5
Auto-ignition temperature in air (K)	858	813
Flame temperature in air (K)	2,318	2,148
Flammability limits in air (% vol)	4-75	5.3 - 15
Detonation limits in air (% vol)	13-65	6.3 - 13.5
Minimum ignition energy (J)	20	290
Theoretical explosive energy (kg of TNT/m ³ of gas)	2.02	7.03
Detonation overpressure (stoichiometric mixture) (bars)	14.7	16.8
Diffusion coefficient in air (cm/s)	0.61	0.16
Flame speed in air (cm/s)	260	38
Detonation speed in air (km/s)	2.0	1.8
Stoichiometric mixture in air (% vol)	29.53	9.48

Comparative Table H2 "C CH4

Tests Performed

In the case of bottles equipped with thermal fuses and those currently being tested²⁴ by the Air Liquide company on composite material bottles, the bursting of bottles occurs 5 minutes after being exposed to fire (Type B100 bottle filled to 525 bars or 700 bars).

On the other hand, a B100 type bottle filled to a pressure less than 350 bars did not burst but leaked.

The same tests showed that the opening of the thermal fuse of the valve/regulator in a rack composed of 4 bottles of type B142, caused:²⁵

- either rapid combustion of the discharged hydrogen characterized by a flame of 10 to 12 m and a thermal flux of 3 kW/m² at 5.5 m, or
- a delayed combustion of an explosive volume by the pre-mixture of hydrogen and air characterized by an over-pressure of 200 mbar visible at 11 m or an over-pressure of 50 mbar visible at 4.5 m.

In a rack composed of 4 bottles of type B152 at 525 bar, a leak of 0.1 mm on a pipe linking the valve/regulator to one of the chambers created an explosive atmosphere comprising 6.0% to 8.5% of hydrogen.

The fire resulting from the ignition of the pre-mixture led at the rack to:

- an over-pressure of 1 to 2 bar,
 a fire-ball (see table p.25) at the outlet to the rack.

ANNEX V

NOTES AND REFERENCES, BIBLIOGRAPHY

- <u>1</u> Safety Data Sheet AL067A Relative to Hydrogen, July 2005, AIR LIQUIDE.
- <u>2</u> Anoxia is the significant decrease in the quantity of oxygen distributed by the blood to the tissues.
- <u>3</u> *Guide d'intervention face au risque chimique (Chemical Hazards Intervention Guide)*, page 258, edition 2008, FNSPF.
- <u>4</u> The coefficient of diffusion of hydrogen in air is 0.61 cm²/s while that for natural gas is 0.16cm²/s. Cf. *Fiche no.2.1 les données de base sur l'hydrogène (*Hydrogen Database) March 2001, Association Française de l'Hydrogène (AFH2).
- 5 Gaseous hydrogen has a density of 0.07. It is therefore much lighter than air (d=1).
- $\underline{6}$ The normal temperature and pressure conditions are given at 273.15°K and 1 atm.
- <u>7</u> Sheet *n*°7.1 Hydrogen Memorandum, June 2001, INERIS.
- 8 An inherent analytical study of 499 accidents or incidents involving hydrogen has shown that only 10% of leaks have not given rise to combustion. *Sheet no.2.1 les données de base sur l'hydrogène (*Hydrogen Database) March 2009, Association Française de l'Hydrogène (AFH2).
- <u>9</u> Sheet *no.2.1 les données de base sur l'hydrogène (*Hydrogen Database) March 2001, Association Française de l'Hydrogène (AFH2).
- 10 The flame temperature of hydrogen in air at 300°K (i.e., 26.85°C) is 2318°K (i.e., 2044.85°C) while that of natural gas is 2148°K (i.e., 1874.85°C). Cf. *Fiche no.2.1 les données de base sur l'hydrogène (*Hydrogen Database) March 2001, Association Française de l'Hydrogène (AFH2).
- 11 Report of a debate *INERIS Associations relatif à l'hydrogène*, October 2008, INERIS.
- 12 Properties of Hydrogen, AIR LIQUIDE (by Simon JALLAIS).
- 13 Seuil des Effets Létaux (Irreversible Effects Threshold) (Decree of 29 September 2005).
- 14 Seuil des Effets Létaux (Irreversible Effects Threshold) (Decree of 29 September 2005).
- 15 Seuil des Effets Létaux (Irreversible Effects Threshold) (Decree of 20 September 2005).
- <u>16</u> *Guide d'intervention face au risque chimique (Chemical Hazards Intervention Guide)*, page 241, edition 2008, FNSPF.
- Guide to the Methods of Evaluation of the Effects of an Explosion of a Gas in the Open Air (page 10/166), July 2009, INERIS & Sheet no. 1 Flammability and Explosivity of Hydrogen, June 2001, INERIS.
- 18 Decree of 29 September 2005 Relative to the Evaluation of the Intensity of Effects and the Gravity of the Consequences of Potential Accidents in Studies of the Dangers of Classified Installations Subject to Authorization.
- <u>19</u> Sheet *no.7.1 Hydrogen Memorandum*, June 2001, INERIS.
- 20 Guide to the Methods of Evaluation of the Effects of an Explosion of a Gas in the Open Air (page 22/166), July 2009, INERIS.
- 21 Sheet no.7.2. les données de base sur l'hydrogène (Hydrogen Database) March 2009, Association Française de l'Hydrogène (AFH2).
- 22 Combustion can occur spontaneously because of the low ignition energy.
- 23 Rack of Bottles H4-142 Logistics 700 bars for H2 Energy, January 2013, AIR LIQUIDE (by VERGHADE).
- 24 *R&D Safety of Hyperbaric Composite Storages, 2013*, AIR LIQUIDE (by Sidonie RUBAN and Lucas BUSTAMANTE).

25 Rack of Bottles H4-142 – Logistics 700 bars for H2 Energy, January 2013, AIR LIQUIDE (by VERGHADE).