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BSc Thesis

Guidelines for the safe operation of a hydrogen-based fuel cell laboratory

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Abstract

Hydrogen, compared to other fuels we use nowadays, has very different properties and behavior. Laboratories working with this fuel must apply extreme caution and follow strict safety guidelines for successful use. This B.Sc. thesis is presenting a set of safety guidelines for the design of a hydrogen-based fuel cell laboratory in order to minimize the risks of human and property casualties. In this document we will do a comparison between hydrogen and other common fuels, discuss hydrogen properties, safety concerns, standards, and introduce safety vulnerability detection methods. This document can be used in the basic stages of a laboratory design and also as material for university courses in order to help students understand hydrogen safety concerns.

Keywords: *hydrogen, safety, laboratory, event tree analysis, leakage, fire, explosion, embrittlement, ventilation, cryogenic, electrolyzer, storage, piping, lab, design, operation.*

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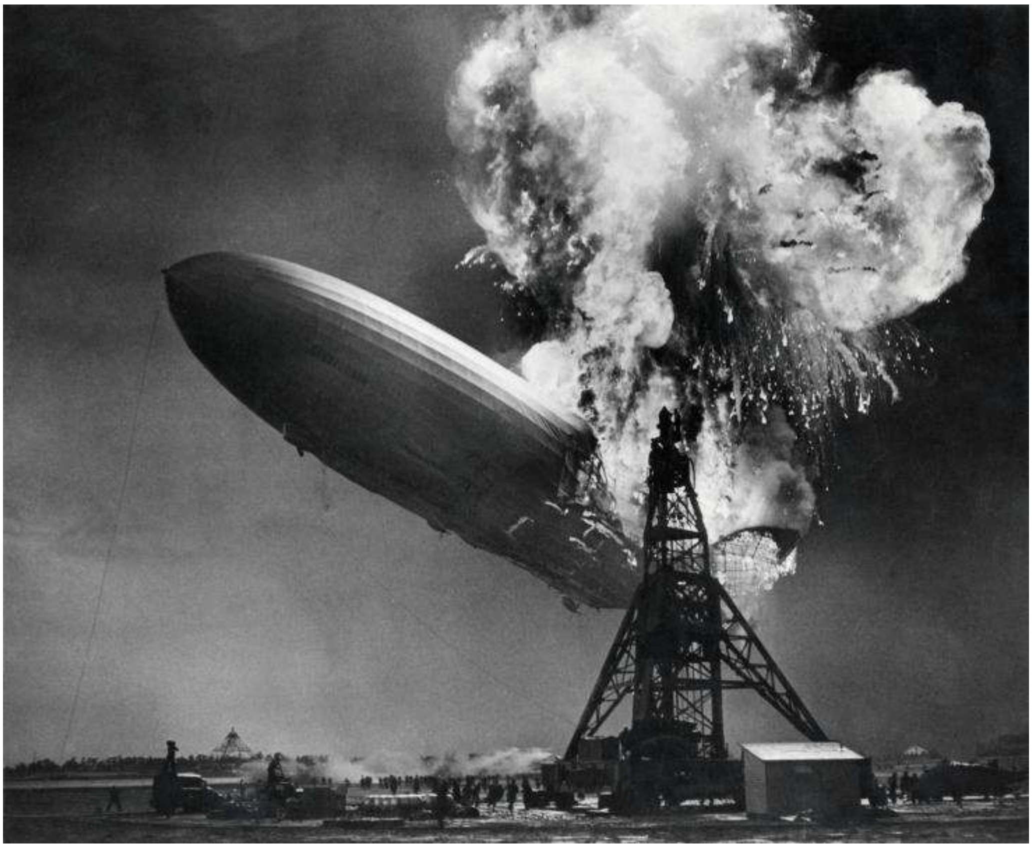

Figure 1 - The stern of the Hindenburg begins to fall (www.airships.net)

Researches on hydrogen safety has started many years ago. The importance of this concept arose when many tragic accidents occurred and caused immense casualties. Of example we can refer to accidents in the aerospace and power plant sectors. Although hydrogen is known as a very hazardous gas, it is no less or more dangerous than other fuels we use nowadays. The Hindenburg incident is a good example for a misinterpretation of hydrogen. This incident took place in Lakehurst, New Jersey (USA) on May 6 1937. A massive balloon (240 tons) filled with hydrogen gas caught on fire and left 36 people dead. Lots of researches have been done on the cause of the incident and most have come to the conclusion that the fire was started by an electricity jump. As mentioned in [1] the cause of this incident was a lightning. This incident gave hydrogen a misleading reputation. Hydrogen was used to keep the airship buoyant and was initially blamed for the disaster, but an investigation in 1990s by Addison Bain provided evidence that the airship's fabric envelope was coated with some reactive material similar to solid rocket fuel. This material was easily ignitable by an electrical discharge. The builder of Hindenburg, the Zeppelin Company has confirmed the flammable coating was to be blamed for the fire [2].

The safe and successful use of hydrogen depends on the knowing of and adhering to the latest knowledge, technology and regulations for the design and operation of facilities and systems. Engineers and all the staff working with hydrogen must undergo periodic trainings in order to achieve the latest knowledge and skills. Safety must be considered in all engineering stages including design, construction, operation and maintenance [3]. The safe practice in the production, storage and usage of hydrogen is very important to the global acceptance of fuel cells and hydrogen technologies. A catastrophic disaster could highly damage people’s perception of this fuel [4].

Industry has developed new safety designs and equipment because hydrogen’s properties and behavior are different than the fuels we use now. In chapter 2, we will review some of the basic hydrogen properties and do a comparison between some common fuels and hydrogen. This will help the reader understand hydrogen behavior and its safety concerns.

In chapter 3 we will discuss safety considerations in a hydrogen laboratory by introducing some safety standards and codes used for designing a lab, methods for safety vulnerability identification, and qualification of risks. In chapter 3.5 we will also talk about the different safety aspects in a lab and explain safety systems and methodologies to mitigate safety concerns.

This document can be used as a basic guide for understanding hydrogen safety in laboratory design. The designer can use this guide for the initial design stages but should not rely solely on the information provided in this document. This guide can also be used as material for fundamental university courses to help students understand hydrogen safety concerns.

2 Hydrogen Properties and Behaviors

2.1 Basic Hydrogen Properties

In order to be able to properly design and operate a hydrogen facility, we need to understand the properties of hydrogen first. In the next subsections we will explain how some of this properties can positively or negatively affect the safety aspects of a laboratory.

Table 1 - Hydrogen Properties[1]

Properties	Notes	Values	Units
Autoignition temperature[2]	[a]	500	°C
		932	°F
Boiling point (1 atm)	[b]	-252,9	°C
		-423,2	°F
Density (NTP[3]**)**	[b]	0,08375	kg/m^3
		0,005229	lb/ft^3
Diffusion coefficient in air (NTP)	[a]	0,610	cm^2/s
		6.57×10^{-4}	ft^2/s
Enthalpy (NTP)	[b]	3858,1	kJ/kg
		1659,8	Btu/lb
Entropy	[b]	53,14	J/g-K
		12,70	Btu/lb-°R
Flame temperature in air	[a]	2045	°C
		3713	°F
Flammable range in air	[a]	4.0 - 75.0	vol%
Ignition energy in air	[c]	2×10^{-5}	J
		1.9×10^{-8}	Btu
Internal Energy (NTP)	[b]	2648,3	kJ/kg
		1139,3	Btu/lb
Molecular weight	[b]	2,02	

[1] Reference state: Internal Energy U=0 at 273.16 K for saturated liquid and Entropy S=0 at 273.16 K for saturated liquid

[2] The autoignition temperature depends on hydrogen concentration (minimum at stoichiometric combustion conditions), pressure, and even the surface characteristics of the vessel. Reported figures range from 932-1085 F according to source [a].

[3] NTP (normal temperature and pressure) = 20 C (68 F) and 1 atm

Properties	Notes	Values	Units
Specific gravity (air = 1) (NTP)	[c]	0,0696	
Specific volume (NTP)	[b]	11,94	m^3/kg
		191,3	ft^3/lb
Specific heat at constant pressure, C_p (NTP)	[b]	14,29	J/g-K
		3,415	Btu/lb-^oR
Specific heat at constant volume, C_v (NTP)	[b]	10,16	J/g-K
		2,428	Btu/lb-^oR
Thermal conductivity (NTP)	[b]	0,1825	W/m-K
		0,1054	Btu/ft-h-^oR
Viscosity (NTP)	[b]	8.813×10^{-5}	g/cm-sec
		5.922×10^{-6}	lb/ft-sec

Sources:
[a] National Aeronautical and Space Administration, Safety Standard for Hydrogen and Hydrogen Systems (NSS 1740.16), 1997.
[b] NIST Chemistry WebBook. http://webbook.nist.gov/chemistry/
[c] "Hydrogen Fuel Cell Engines and Related Technologies. Module 1: Hydrogen Properties." U.S. DOE. 2001, http://www.eere.energy.gov/hydrogenandfuelcells/tech_validation/pdfs/fcm01r0.pdf.
[d] https://www.h2tools.org/bestpractices/design/properties

2.2 Hydrogen Compared to other Fuels

Hydrogen gas is no more or less dangerous than other flammable gasses, it simply has different properties which some of them provide safety benefits. However, like gasoline and natural gas, hydrogen is flammable and can behave dangerously and must be handled responsibly. For this purpose some guidelines must be applied and the users must understand the behavior of hydrogen. Some of the most notable differences between hydrogen and other common fuels is listed below:

2.2.1 Density and Diffusivity

Diffusivity as defined by Fick's law is as follows:

$$J = -D\frac{d\phi}{dx} \tag{2-1}$$

Where:

J = Diffusion flux, the amount of substance that flows through a unit area per unit time. $\left[\frac{mole}{m^2.s}\right]$

D = The diffusion coefficient. $\left[\frac{m^2}{s}\right]$

$d\phi$ = Change in concentration of substance. $\left[\frac{mole}{m^3}\right]$

dx = Change in length. $[m]$

Hydrogen spreads about 3.8 times faster than natural gas (see Table 2), which means that when released, it spreads quickly into the room and does not form flammable cloud thanks to the low fuel concentration and the high diffusion rate. The lower flammability limit (LFL) volume of hydrogen in air is about 4%.

Table 2 - Diffusion coefficient for gasses in air at different temperatures and atmospheric pressure (www.engineeringtoolbox.com)

Name	Formula	**0 °C**	**20 °C**	**100 °C**	**200 °C**	**300 °C**	**400 °C**
Methane	CH4		0.21	0.321	0.485	0.678	0.899
Carbon monoxide	CO		0.208	0.315	0.475	0.662	0.875
Carbon dioxide	CO2		0.16	0.252	0.39	0.549	0.728
Hydrogen	H2	0.668	**0.756**	1.153	1.747	2.444	3.238
Water vapor	H2O	0.219	0.242	0.399	0.638	0.873	1.135
Helium	He	0.617	0.697	1.057	1.594	2.221	2.933

Also hydrogen has a density of $0.0838\ \frac{kg}{m^3}$ at natural temperature and pressure (NTP) which is far below the density of air ($1.205\ \frac{kg}{m^3}$) at equal conditions. Therefore this gas is positively buoyant over almost the whole temperature of its gaseous state. This spontaneous rise by physic laws gives us an advantage compared to other fuels in discarding the unwanted gas. By designing a proper roof or ventilation we can prevent the accumulation of hydrogen very easily. Since hydrogen is the lightest element in the universe it is very hard to confine hydrogen. Industry uses these properties in the design of hydrogen labs to help hydrogen escape up and away from the user in case of an unexpected release [2, 3].

Caution should be taken in working with hydrogen in cryogenic temperatures. Hydrogen vapors in this temperature are denser than air at NTP. The low temperature hydrogen will cause the humidity in air to condense and add water to the mixture cloud making it visible and augmenting the molecular mass of the mixture even more [3] (see section 3.5.5 for more details).

2.2.2 Expansion Ratio

The expansion of hydrogen with the addition of heat at NBP[1], is about 23 times the expansion of water at ambient conditions [3]. The safety concern is when liquid hydrogen stored in a vessel hasn't got enough space to expand and results in an over pressurization of the tank or a leakage. When hydrogen changes phase from liquid to gas a great volume change occurs. Also as it warms up from NBP to NTP[2] another instance of volume growth follows. The ratio of the final to initial volume of liquid hydrogen heated from NBP to NTP is 847. This volume change can cause a pressure rise of about 177MPa (starting from 0.101 MPa) if the liquid is in a closed vessel [3].

2.2.3 Odor, Color and Taste

Hydrogen is odorless, colorless and tasteless. So it is not easily detectable by human senses. Also, by the tendency of hydrogen to rise quickly, a leakage in a confined space would result in a hydrogen accumulation beneath the roof and away from humans' sense range. Comparing with natural gas, both fuels are odorless, colorless and tasteless, but in case of natural gas it is possible to add a sulfur-containing odorant, called mercaptan, to make it detectable by human senses. The use of such odorants in hydrogen would result in the contamination of fuel cells and the PEM (Proton Exchange Membrane) therefore it is not possible [2].

2.2.4 Flame Heat Radiation

Hydrogen compared to hydrocarbon fuels has lower radiant heat, meaning that the heat emitted from the flame to the surrounding is much less than carbon based fuels. The flame from burning hydrogen is just as hot as hydrocarbon fuels but has lower heat emission due to the absence of carbon and the presence of heat absorbing water vapor. This greatly reduces the risk of initiating secondary fires and has a significant impact for the public and rescue workers [2].

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[1] Normal Boiling Point (also called atmospheric boiling point).

[2] Normal Temperature and Pressure (20C and 1 atm).

2.2.5 Combustion

Hydrogen's buoyancy, diffusivity and small molecular size make it difficult to create a combustible situation. For combustion to occur, and adequate concentration of hydrogen, the right amount of oxidizer and a source of ignition energy must be present. Compared to other fuels, hydrogen has a wider flammability range (4-74 %). See Table 3 and Figure 2 for a comparison of different fuels.

Table 3- Combustion properties of fuels

	Hydrogen	**Gasoline Vapor**	**Natural Gas**
Flammability Limits in air (volume ratio)	4-74 %	1.4-7.6 %	5.3-15 %
Ignition Energy $(\boldsymbol{mJ})$	0.02	0.20	0.29
Flame Temperature in air $(°\boldsymbol{C})$	2045	2197	1875
Stoichiometric Mixture in air	29 %	2 %	9 %

However at low concentrations (below 10%) the ignition energy for hydrogen is very high, making hydrogen practically harder to ignite close to the LFL[1]. If the hydrogen concentration augments to the

[1] Lower Flammability Limit

stoichiometric (most easily ignited in air) mixture of 29% (see Table 3) the ignition energy drops much lower than natural gas (about 1/15) making the mixture very easily combustible [2].

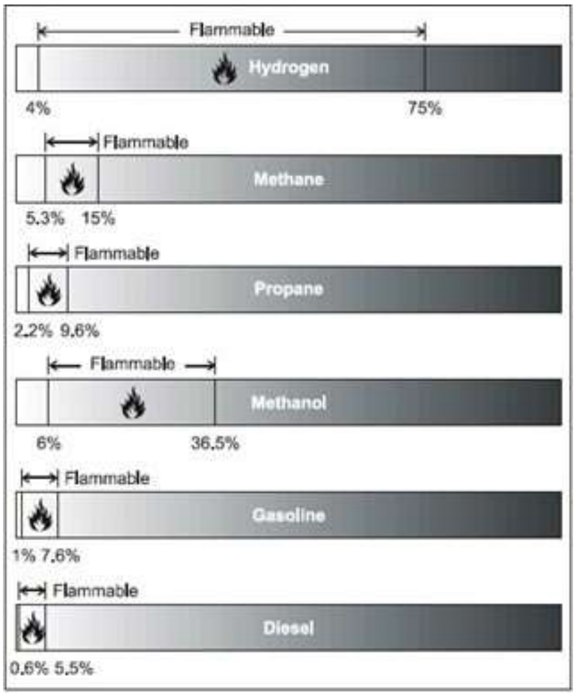

Figure 2 - Flammability range of different fuels [1]

Fires produced from hydrogen are safer than gasoline fires. Since hydrogen tends to move upwards quickly, if the reservoir of a fuel cell based car catches on fire the flames tend to move up and away from the car. But in a gasoline car the fire will quickly take over the whole vehicle. See Figure 3, Figure 4 and Figure 5 for a simulation of two cars catching on fire. The car on the left is powered by hydrogen and the one on the right by gasoline. As you can see in Figure 4 the fire from the hydrogen powered car tends to rise upwards and away from the vehicle. After about one minute, you can see that the fire has taken over the whole vehicle on the right side of the figure but the hydrogen powered car is still unharmed [5].

Figure 3 – Simulation time: 0 min, 0 sec - Hydrogen powered vehicle on the left. Gasoline powered vehicle on the right. (Fuel Leak Simulation Dr. Michael R. Swain)

Figure 4 - Simulation time: 0 min, 3 sec – Ignition begins, Hydrogen powered vehicle on the left. Gasoline powered vehicle on the right. (Fuel Leak Simulation Dr. Michael R. Swain)

Figure 5 - Simulation Time: 1 min, 0 sec - Hydrogen flow is subsiding, view of gasoline vehicle begins to enlarge. (Fuel Leak Simulation Dr. Michael R. Swain)

The energy released from burning hydrogen is more than gasoline, but this energy is released in shorter period of time. A reservoir of liquid hydrogen will burn with a velocity of about 3-6 cm/min and a reservoir of liquid methane will burn with a velocity of about 0.3-1.2 cm/min and gasoline will burn with a velocity of about 0.2-0.9 cm/min. Hydrogen will burn much faster than other fuels [1].

2.2.6 Explosion

If a tank contains only hydrogen (without any oxidizer) explosion can't occur. An oxidizer such as oxygen (at least 10%) or air (at least 41%) must be present. Hydrogen can cause explosion in a concentration range of 18.3-59%. Although this range is wide, it is still less dangerous than gasoline. Because gasoline's explosive concentration ranges from 1.1-3.3% making it potential to explosions at low concentrations. Also, because of its tendency to rise quickly, hydrogen is less likely to form a combustible cloud in open atmosphere. In contrast, heavier gasses such as propane and gasoline hover over the ground creating a greater danger of explosion.

2.2.7 Asphyxiation

Besides oxygen, any gas can cause asphyxiation. In most cases hydrogen's diffusivity and buoyancy allows it to spread quickly and be unlikely to cause asphyxiation.

3 Laboratory Safety Considerations

3.1 Standards and Codes

Every laboratory designer should be aware of the latest standards and codes. Codes and standards help dictate safe building and installation practices. Today, hydrogen components must follow strict guidelines and undergo third party testing for safety and structural integrity. In this document we will include some of the most important considerations according to safety standards including:

1- ASME B31.12[1]: This standard has been published for use in designing hydrogen piping systems. It takes into consideration both current steel specifications and chemical compositions [6].
2- ANSI/AIHA/ASSE Z9.5: Laboratory Ventilation and Decommissioning Package establishes minimum control requirements for the ventilation and decommissioning of laboratories. It also establishes best practices for laboratory ventilation systems to protect personnel from overexposure to harmful or potentially harmful airborne contaminants generated within the laboratory and decommissioning [7].
3- NFPA 2[2]: This code provides fundamental safeguards for the generation, installation, storage, piping, use, and handling of hydrogen in compressed gas (GH2) form or cryogenic liquid (LH2) form [8].
4- NFPA 13[3]: This standard shall provide the minimum requirements for the design and installation of automatic fire sprinkler systems and exposure protection sprinkler systems covered within this standard. This standard is written with the assumption that the sprinkler system shall be designed to protect against a single fire originating within the building. The purpose of this standard shall be to provide a reason-able degree of protection for life and property from fire through standardization of design, installation, and testing requirements for sprinkler systems, including private fire service mains, based on sound engineering principles, test data, and field experience [9].
5- NFPA 45[4]: The purpose of this standard shall be to provide basic requirements for the protection of life and property through prevention and control of fires and explosions involving the use of chemicals in laboratory-scale operations. This standard is designed to control hazards and protect personnel from the toxic, corrosive, or other harmful effects of chemicals to which personnel might be exposed as a result of fire or explosion. The goal of this standard shall be to achieve a comprehensive laboratory fire prevention and protection program to prevent injury or death to occupants and emergency response personnel [10].

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[1] Code for Hydrogen Piping and Pipelines
[2] Hydrogen Technologies Code
[3] Standard for The Installation of Sprinkler Systems – National Fire Protection Association
[4] Standard on Fire Protection for Laboratories Using Chemicals – National Fire Protection Association

6- NFPA 55[1]: This standard is applied to installation, storage, use and handling of compressed gasses and cryogenic fluids in cylinders, containers, equipment and tanks in all occupancies. The purpose of this code shall be to provide safeguards for installation, use and storage of compressed gasses and cryogenic fluids in portable and stationary storage equipment [11].

7- NFPA 91[2]: This standard provides minimum requirements for the design, construction, installation, operation, testing, and maintenance of exhaust systems for air conveying vapors, gases, mists, and particulate solids as they relate to fire and/or explosion prevention except as modified by other NFPA standards [12].

3.2 Safety Aspects

A good safety plan will consider both primary and secondary failure modes. Secondary failure modes are those that come about as a result of other kinds of failure. Every hidden failure or potential hazard should be identified and planned ahead for. Every threat that could cause property damage and human casualties should be identified, eliminated or mitigated. Safety of all the following should be ensured:

Personnel: Any threat that endangers the life and safety of human life, either to the public and personnel must be mitigated or eliminated.

Equipment: Damage to property should be minimized or totally eliminated. Damaged equipment can be both the result of a failure or the cause of it. If an equipment fails, it can in turn damage other properties and cause more casualties. Therefore it is critical to minimize the damage to the equipment.

Business Interruption: Although not so much for laboratories, the prevention of business interruption in a commercial institution is essential to the safety plan. A proper safety plan will consider emergency solutions to keep providing a service or product.

Environment: Any aspect of a natural or built environment that could be damaged due to a failure should be identified and analyzed. A qualification of any failure potential to cause environmental damage is mandatory.

[1] Compressed Gases and Cryogenic Fluids Code

[2] Standard for Exhaust Systems for Air Conveying of Vapors, Gases, Mists, and Particulate Solids

3.3 Identification of Safety Vulnerabilities

There are several industrial methods for ISV. The ISV should be done on the early stages of the project. It should help the project team identify potential threats and safety issues, discover ways to lower the probability of an incident, and mitigate the consequences.

The ISV should consider:

- The potential hazards of the operation
- Previous incidents and near-misses
- Engineering and administrative controls applicable to the hazards and their interrelationships, e.g. the use of hydrogen sensors and emergency shutdown capabilities.
- Mechanisms and consequences of failure of engineering and administrative controls
- A qualitative evaluation of a range of the possible safety and health effects resulting from failure of controls
- Facility location

The ISV should be conducted by a group of people with enough expertise in all aspect of the work performed. One of the team members should have experience and knowledge specific to the set of process, equipment and facility being evaluated. Also a member of the team must be knowledgeable in the ISV method being used.

Several methods have been put introduced. Some of them are listed in Table 4 [4]. In the subsequent chapter we will discuss the “Event Tree Analysis” method.

Table 4 - A list of ISV methods

Method	Description	References
FMEA Failure Modes and Effects Analysis	Modes and Effects Analysis The FMEA process has these elements: • Identify top level hazards and events • Identify related equipment, components, and processes • Identify potential failure modes and effects o Identify designs that provide inherent safety • Identify potential prevention and mitigation corrective action	• http://www.fmeainfocentre.com/ a non-commercial web-based inventory dedicated to the promotion of FMEA • Government documents, including MIL-STD-882C and MILSTD-1629A • NASA Scientific and Technical Information http://www.sti.nasa.gov/ • A discussion and worked example can be found in *Guidelines for Hazard Evaluation Procedures*, *Second Edition with Worked Examples*, Center for Chemical Process Safety, American Institute of Chemical Engineers, 1992
"What If" Analysis	A speculative process where questions of the form "What if … (hardware, software, instrumentation, or operators) (fail, breach, break, lose functionality, reverse, etc.)..?" are formulated and reviewed.	A discussion and worked example can be found in *Guidelines for Hazard Evaluation Procedures*, *Second Edition with Worked Examples*, Center for Chemical Process Safety, American Institute of Chemical Engineers, 1992.
HAZOP Hazard and Operability Analysis	Systematically evaluates the impact of deviations using project information.	An extensive description and worked example of the HAZOP procedure can be found in *Guidelines for Hazard Evaluation Procedures*, *Second Edition with Worked Examples*, Center for Chemical Process Safety, American Institute of Chemical Engineers, 1992.
Checklist Analysis	Method evaluates the project against existing guidelines using a series of checklists. This technique is most often used to evaluate a specific design, equipment or process for which an organization has a significant amount of experience.	• A discussion and worked example can be found in *Guidelines for Hazard Evaluation Procedures*, *Second Edition with Worked Examples,* Center for Chemical Process Safety, American Institute of Chemical Engineers, 1992. • Risk-based decision-making guidelines, United States Coast Guard (http://www.uscg.mil/hq/gm/risk/e-guidelines/RBDM/html/vol3/02/v3-02-cont.htm)
Fault Tree Analysis	Fault Tree Analysis is a deductive (top-down) method used for identification and analysis of conditions and factors that can result in the occurrence of a specific failure or undesirable event. This method addresses multiple failures, events, and conditions.	A discussion and worked example can be found in *Guidelines for Hazard Evaluation Procedures*, *Second Edition with Worked Examples,* Center for Chemical Process Safety, American Institute of Chemical Engineers, 1992.

Method	Description	References
Event Tree Analysis	This method is an inductive approach used to identify and quantify a set of possible outcomes. The analysis starts with an initiating event or initial condition and includes the identification of a set of success and failure events that are combined to produce various outcomes. This method identifies the spectrum and severity of possible outcomes and determines their likelihood.	A discussion and worked example can be found in *Guidelines for Hazard Evaluation Procedures*, *Second Edition with Worked Examples,* Center for Chemical Process Safety, American Institute of Chemical Engineers, 1992.
Probabilistic Risk Assessment	A Probabilistic Risk Assessment (PRA) is an organized process for answering the following three questions: 1- What can go wrong? 2- How likely is it to happen? 3- What are the consequences?	A detailed description of this method can be found in *Guidelines for Chemical Process Quantitative Risk Analysis*, Center for Chemical Process Safety, American Institute of Chemical Engineers, 2000.
Others	Other methods or combinations of methods, including those developed by the project team's organization, may be used.	See *Guidelines for Hazard Evaluation Procedures*, *Second Edition with Worked Examples,* Center for Chemical Process Safety, American Institute of Chemical Engineers, 1992.

3.3.1 The Event Tree Analysis Method (ETA)

This ISV method includes the identification of every effective factor in the occurrence of an incident. The ETA is a standard method for analyzing incidents in industry. It mainly includes the following steps:

1- Indicating the type of the occurred incident
2- Identifying critical factors which can be effective in analyzing the incident
3- Drawing the event tree and using it to compare critical factors and the occurrence of the incident.
4- Evaluating and analyzing the results of the incidents.

3.3.2 ETA Application

The critical factors can be very effective in analyzing an incident. In this section we will demonstrate an example of how to use the Event Tree Analysis method using the critical factors of a hydrogen leakage.

When a *quick combustion* happens, the combustible cloud of hydrogen burns with oxygen in a very short period of time. The combustion of a layer of the cloud causes the other layers to burn until the fire reaches the core layer of the cloud, which by then, the whole fuel catches on fire (in a fireball form). This type of fire can move long distances until it takes over the whole place. In contrast when the combustion takes some time to occur, the hydrogen cloud will have enough time to mix properly with oxygen and therefore the combustion will end quickly. The difference between these two is that, since the fireball is produced quicker, it will burn all combustible layers if a proper ignition source exists.

So if hydrogen is well-mixed with air, a quick combustion will occur. This quick combustion will cause an initial pressure increase. In this state, it is possible that the air-fuel ratio is stoichiometric. This in turn causes the flame to diffuse quickly and produces a flame wave. In this conditions, the initial flames will disperse quickly and the pressure will increase greatly. When the explosion wave is spread, a *sudden combustion* occurs. Gas mixtures in a confined space will explode, which is also called as *CVCE: Confined Vapor Cloud Explosion*. If we have an unconfined space Flash fire will occur. Flash fire is a sudden intense fire caused by ignition of a flammable gas. It has a very high temperature and a short duration [1].

The application of ETA in hydrogen leakage incidents has been demonstrated in Figure 6.

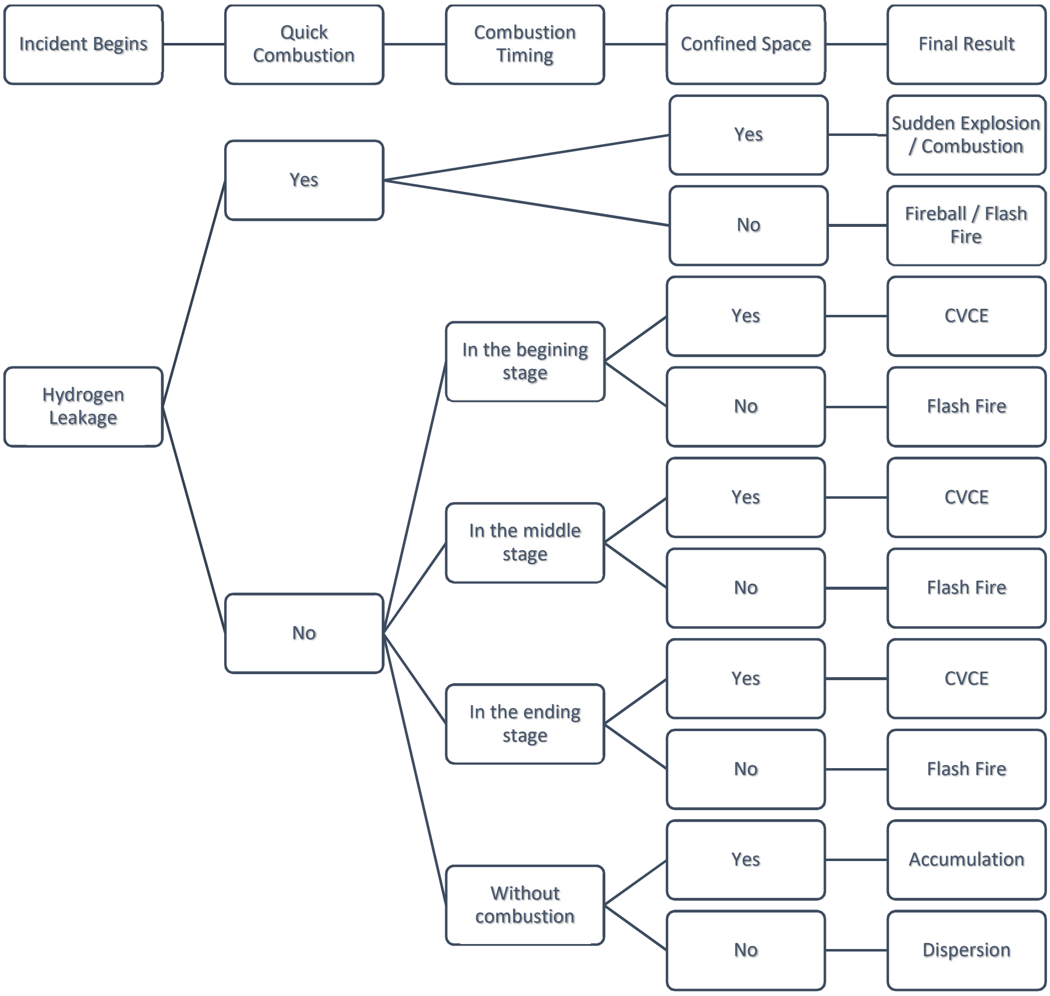

Figure 6 - An example of an ETA hierarchy

3.4 Risk-Binning Matrix

After identifying the safety vulnerabilities, it is important to able to classify these risks. Each vulnerability can be assigned a qualitative risk using a frequency-consequence matrix as shown in Figure 7. Highest consequences are usually assigned to events that could reasonably result in an unintended release of hazardous material, destruction of equipment, and/or injury to people [4].

		Frequency			
		Beyond Extremely Unlikely	Extremely Unlikely	Unlikely	Anticipated
Consequence	High	10	7	4	1
	Moderate		8	5	2
	Low		9	6	3
	Negligible	12	11		

Negligible Risk	Lower Risk	Moderate Risk	Higher Risk

Figure 7 - Risk binning matrix, Frequency/consequence criteria

The frequency criteria used for risk-binning is as follows:

Table 5 - Frequency criteria for risk-binning

Acronym	**Description**	**Frequency Level**
A	Anticipated, Expected	$> 1E - 2/year$
U	Unlikely	$1E - 4 < f \leq 1E - 2/year$
EU	Extremely Unlikely	$1E - 6 < f \leq 1E - 4/year$
BEU	Beyond Extremely Unlikely	$\leq 1E - 6/year$

The consequence criteria mostly concerns property damage, production loss, and human injuries.

Table 6 - Consequence criteria for risk-binning

Consequence Level	Impact on Populace	Impact on Property/Operation
High (H)	Prompt Facilities Acute injuries – immediately life threatening Permanent disability	Damage > $50 million Production loss in excess of 1 week
Moderate (M)	Serious injuries Non-permanent disability Hospitalization required	$\$100{,}000 \leq Damage \leq \$50\ million$ Equipment destroyed Critical damage Production loss less than 1 week
Low (L)	Minor Injuries No hospitalization	$Damage \leq \$100{,}000$ Repairable damage Significant operational down-time Minor impact on surroundings
Negligible (N)	Negligible injuries	Minor repairs to equipment required Minimal operational down-time No impact on surroundings

3.5 Laboratory Safety Considerations

The following sections will discuss safety considerations according to hydrogen properties debated in chapter 2.

3.5.1 Leakage and Unignited Release

3.5.1.1 Leak Detection

Leak detection can be achieved by providing hydrogen detecting sensors in the lab. A secondary option is monitoring the piping's pressure and flow rate for changes that would signify a leakage present in the room. The leak detection system should be able to automatically shut off the main hydrogen valve and start the ventilation systems (such as fans and fume hoods). The system should also set off alarms and visual lightings to alert the personnel. A proper system should detect hydrogen concentration with a sensitivity of plus or minus 0.25% by volume of hydrogen in air (2,500 ppm). The response time should be 1 second at a concentration of 1% volume. A detection range of at least 1% by volume (10,000 ppm) is mandatory [11, 8].

The hydrogen sensors should be positioned properly to make sure the leaked hydrogen reaches them. The best locations for installing sensors are close to the critical locations where leakage may occur (immediately above where hydrogen flow is concentrated) and where hydrogen may accumulate. In a rare condition when permanent detection systems are not installed, portable leak detectors (such as thermal imaging cameras) must be available [11, 8].

3.5.1.2 Temperature increase

Leakage from high pressure tanks can cause free expansion. The Joule-Thomson effect describes the temperature change of a real gas or liquid when it is forced through a valve or porous plug. At room temperature, all gases except *hydrogen, helium* and *neon* cool upon expansion according to the Joule-Thomson effect. For hydrogen, the immediate effect after a leakage is an increase in the average temperature of the gas. To emphasize the importance of this temperature rise, imagine if the whole tank (about 5 kilograms of hydrogen) empties through the leak. The specific heat of hydrogen (14.29 J/g.k at NTP) is about 15 times greater than the specific heat of air (1.005 J/g.k). So this leak will result in a temperature rise of 10° to 20° C depending on the size of the lab. In a confined space, this could be the source of an explosion [1].

To calculate the temperature of hydrogen being released, we need to know the Joule-Thomson coefficient.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_{H(enthalpy)} \tag{3-1}$$

Where In equation (3-1) :

∂T is the temperature change $[K]$

∂P is the pressure change [Pa]

P is the pressure and μ_{JT} is the Joule-Thomson coefficient. The inversion temperature is the temperature where the Joule-Thomson coefficient equals 0. The maximum inversion temperature of hydrogen is 210K which happens at low pressures. If the pressure increases the inversion temperature drops to 202K in atmospheric and 125K in 5000 psi pressure. In the case of hydrogen, the Joule-Thomson coefficient for all pressures greater than 7400 psi is negative. This means that a leak from a hydrogen tank results in a temperature increase. If this temperature rise is high enough, the hydrogen cloud auto ignites on fire [1]. In such conditions we must use fundamental thermodynamic relations for the Joule-Thomson coefficient:

$$\mu_{JT} = \frac{[T\left(\frac{\partial v}{\partial T}\right) - v]}{C_p^{idea\ \ gas} - \int_0^p \left[T\left(\frac{\partial^2 v}{\partial T^2}\right)_P\right] dp} \tag{3-2}$$

In which v is the molar volume and $C_p^{ideal\ gas}$ is the specific heat in constant pressure for ideal gas.

Other equations of state have been introduced for calculating the Joule-Thomson coefficient. This coefficient has been calculated equal to -0.05 K/bar for a temperature of 25° C pressure of 5000 psi and a temperature of 33°C pressure of 10000 psi [1].

3.5.1.3 Under-expanded turbulent jet

In a laboratory, hydrogen might be stored at a pressure up to 100 MPa. Unscheduled release at such pressure creates a highly *under-expanded turbulent jet* in which the pressure at the nozzle exit is above atmospheric pressure. This turbulent jet behaves differently from *expanded jets* in which the pressure at the nozzle exit is equal to atmospheric pressure. The majority of leaks and unintended releases from hydrogen cylinders will be in the form of an under-expanded jet. See Figure 8.

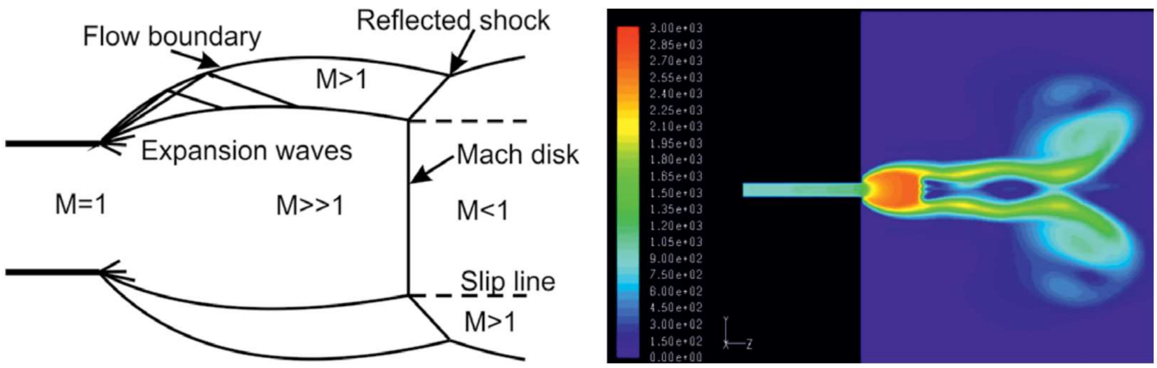

Figure 8 - Schematic presentation of an under-expanded jet (Left) and an initial stage of under-expanded jet release (Right) (See [3, p. 67] for reference)

In an under expanded jet the pressure at the nozzle exit has not fully dropped to the atmospheric. At high pressures the velocity at the nozzle exit remains locally sonic (M=1). The expansion down to atmospheric pressure takes place outside the nozzle. The critical pressure ratio for sonic (choked) flow of compressible gas is about 1.9 at STP ($\gamma = 1.405$) and 1.89 at NTP ($\gamma = 1.390$) [3, p. 67].

Equation (3-3) can be used to estimate the pressure at the leak (nozzle) exit by the storage pressure.

$$\frac{P_{Reservoir}}{P_{Nozzle\ exit}} = \left(\frac{\gamma + 1}{2}\right)^{\gamma(\gamma-1)} \qquad (3\text{-}3)$$

3.5.2 Fire Protection

Fire protection is mandatory in every facility design specially research labs. The fire produced by burning hydrogen is invisible and has no smoke. It and can only be seen in low light and if the surrounding air contains some sulfur or excess humidity. Also this kind of fire can't be extinguished by water [1]. Since hydrogen disperses really quick, fire from hydrogen can only exist around leaks. For larger leaks, a larger amount of air must be available for combustion to occur. If a leak catches on fire, the length of the flame is at most 500 times the diameter of the leak. Therefore, if for example the leak is 1mm wide, the flame length will be at most 0.5 meters [1].

To minimize the risks of fire and to mitigate the damages caused, we need to take into consideration the following factors:

- **The use of emergency shutoff valves:** The most effective way to extinguish a hydrogen fire is to shutoff the source or supply. Therefore emergency shutoff valves should be considered in the design of the supply piping. These shutoff valves must be activated automatically in accordance with sensors and alarms.
- **Fire extinguishers:** Depending on the quantity of the hydrogen being stored or used and the arrangement of the laboratory, consideration should be given to the installation of automatic sprinklers (See NFPA 13) or some other kind of fire extinguishing system. The designer can refer to the NFPA 45 standard to find an alternative fire extinguisher.
- **Fire detection:** The installation and use of fire detection systems and alarms is mandatory. The designer should consult with the AHJ[1] for special requirements according to local laws for buildings and fire codes.
- **Use of non-sparking equipment and hand tools:** As we discussed in chapter 2.2.5, If hydrogen concentration augments to the stoichiometric mixture of 29% the ignition energy drops lower than the ignition energy of natural gas (about $1/15$) making the mixture easily combustible. Every lab equipment should be made in such a way to avoid producing sparks which are potential to starting a fire in case of leakage. Use of metallic tools such as hammers can be the initial cause of a fire. Other potential risks are electrical equipment that could cause a spark such as fans and lightings.
- **Handling and storage:** Handling paths and storage amounts of hydrogen in liquid and gas form should be minimized. Storage spaces should not be close to combustible material or dry plants (closer than 4.6 meters). The fire from hydrogen tends to go upwards and has a low heat radiation flame, therefore it has lower chances of spreading horizontally. But if a combustible object in proximity catches on fire it will initiate a hydrocarbon fire which in turn has smoke, a higher heat radiation and a higher chance of spreading. To avoid such consequences it is suggested not to place any green space around the laboratory. For further safety concerns about storage see section 3.5.4
- **Smoking area controls:** No-Smoking signs should be installed wherever there is a risk of fire (such as in the proximity of cylinders and storage).

3.5.3 Explosion Protection

Laboratories should be explosion proof. We must consider using explosion resistant walls or barricades around the lab. The amount of hydrogen must be limited in experiments and equipment must be accessible by a remote control from afar. The experiments must be conducted in a detached or isolated building or if not possible, outdoors. A proper ventilation will reduce the chances of explosion. As we will

[1] Authority Having Jurisdiction

discuss in an example in chapter 3.3.2, explosion is more likely to occure in confined spaces. It is important to consider enough explosion venting around the building on outside walls. Also it is recommended to use blow-off panels[1] on the perimeter walls [13].

3.5.4 Electrolyzers , Storage and Piping

It is recommended to minimize storage compartments by using an electrolyzer to produce the required hydrogen. The electrolyzer should be synced with the hydrogen detection system to be shut down as soon as hydrogen leakage is detected in the room. It is important to make sure that the room where the electrolyzer is installed is explosion proof. See section 3.5.3 for explosion safety. The oxygen exhausted form the electrolyzer should be safely vented outside.

In case storage is necessary, the following criteria should be met:

- Cylinders should be handled by trained personnel only.
- Cylinders should be stored outside the lab in a safe location far from direct sunlight. They should be secured from tipping over by safety restraints.
- Cylinders should not be installed under electrical equipment and power lines.
- Every cylinder must be equipped with a pressure regulator designed for hydrogen.
- Every cylinder must be equipped with two gauges showing the outlet and cylinder pressures.
- Supply lines must have a manual shutoff valve to allow isolation of equipment in case of an emergency.
- Excess flow valves or flow restrictors should be used to control maximum flow.
- If a cylinder is not in use it should NOT be stored inside the lab.
- Cylinders stored outdoors should NOT be installed within 10 feet of windows, doors, or other building openings.
- Cylinders should not be stored closer than 50 feet to ventilation intakes.
- The storage area must have 25% of its perimeter directly open to atmosphere. (Not blocked by walls, fences are okay)
- Storage areas should be clear of vegetation and combustible materials for at least 15 feet.
- Storage areas should be covered from vehicle damage.
- “NO SMOKING” signs must be posted in the storage areas (no smoking allowed for at least 25 feet away).

[1] Blowout panels, also called blow-off panels are used in enclosures, buildings or vehicles where a sudden overpressure may occur.

- Storage areas should be easily accessible by personnel, at the same time, be away from public and safe from physical damage [13, 11, 14].

Safety considerations concerning piping and delivery are as follows: (For cryogenic liquids special considerations should be taken into account. See chapter 3.5.5)

- Piping systems for the delivery of hydrogen should be installed by a person qualified by specific training.
- Manual shutoff valves must be located near each point of use.
- The shutoff valve should be easy to access and away from potential hazards.
- Delivery lines should be kept as short as possible.
- A main shutoff system should be available (away from potential hazards and points of use).
- Piping should be designed for a pressure greater than the maximum possible pressure during abnormal conditions.
- Piping systems must not be used for gases that they are not designed for.
- In case plastic piping is being used, tests should be conducted to make sure the material is not permeable by hydrogen.
- Each and every portion of a piping system should have uninterruptible pressure relief.
- Every part of the system that can be isolated must have adequate pressure relief.
- Pressure relief should be piped to a safe discharge outside or fume hood exhaust.
- All shutoff valves should be clearly marked and labeled.
- At each discharge point and along the piping, the hydrogen line must be labeled regularly at short intervals along its path [13, 11, 14].

3.5.5 Cryogenic Liquid[1]

As mentioned in chapter 2.2.2, if warmed, cryogenic liquids can create over pressurization. In case of leakage, they can expand and form a noticeable volume of combustible cloud. Liquid hydrogen is usually transferred through vacuumed and well insulated pipelines. A failure to well-insulate the lines will cause the surrounding air to condense with an oxygen content of up to 52%. The liquid condensate looks like liquid water and it highly enhances the flammability of combustible materials. It may also turn noncombustible materials to combustible. Another concern of hydrogen at low temperatures is that every substance (except helium) will be condensed and solidified when exposed to it. This effect might plug the pipelines, orifices and valves. Also in a process called cryo-pumping the condensed substance can cause a vacuum drawing in more gas (e.g. and oxidizer like air). If the systems is later warmed for maintenance this might cause over pressurization, fire, and explosion. In case hydrogen is being stored and transferred in cryogenic form, it is important to make the following considerations.

[1] A liquid with a boiling point below -150 centigrade.

- Ventilation should be adequate to handle even the largest anticipated leakage from a cryogenic tank. A proper ventilation will keep the combustible cloud mixture from reaching the flammability range discussed in chapter 2.2.5.
- Liquid confinement should be prevented at all cost. Block all drains and floor openings to prevent the leaked liquid be stuck and accumulated.
- Electrical equipment and switches must be safe from the touch of liquid leakage. For equipment that are potential to be exposed to liquid hydrogen, special considerations should be taken into account.
- Storage at such low temperatures will cause condensation of the surrounding air. In this case the condensed air must not be in touch with combustible materials.
- To dispose liquid hydrogen, firstly totally vaporize it and then vent it safely.
- Special piping requirements apply to cryogenic liquids. Such low temperatures in grounded piping can cause the floor to freeze, therefore all transfer lines must be well insulated. If a specific line can't be insulated, the area beneath must be clear of any kind of combustibles. Also contraction of materials must be considered. The liquid causes metals to become brittle and easily breakable. Special material selection must be taken into account.
- The design pressure should be well above 150% of the maximum pressure relief.
- Pressure relief should be enough to prevent rupture [3, 13, 10, 11].

3.5.6 Embrittlement

Hydrogen easily can deteriorate metals. Even though hydrogen is non-corrosive, if absorbed by steel it will brittle the metal and cause failure. This effect is called "Hydrogen Embrittlement" and it involves many factors such as the environment temperature and pressure, the purity, concentration, and exposure time of hydrogen. Other factors include the stress points, physical and mechanical properties, micro structure, surface conditions, and etc. Most of the problems arise when welding (by causing thermal stress points) and improper material is used [3].

Material Selection depends on mechanical properties of the material (s_{yield} , s_{ut}, ductility, impact strength, notch sensitivity). The selected material must have a minimum value for each of the mentioned properties over the whole operation temperature. Also we must consider emergency situations where the temperature and pressure rise or drop out of the operation range. The material must be resistant to phase change in the crystalline structure, so that with repeated thermal cycles or time it stays stable [3].

3.5.7 Ventilation

A critical factor in the design of every laboratory is the ventilation system. A proper ventilation system will keep the hydrogen condensation about 25% of the lower flammability limit (4% as discussed in chapter 2.2.5). In other words the hydrogen concentration should not exceed 1% by volume in the laboratory. The air exchange rate should be 0.3 m^2 per minute for every square meter of solid floor space [13].

It is important that the ventilation systems do not shutdown as a function of emergency shutdowns. All ventilation systems should be spark proof. The air intake must be positioned properly to not take in hydrogen from another exhaust and recirculate it in the lab. The exhaust points must not be allowed to recirculate in the lab. Since hydrogen is lighter than air, the exhaust from fume hoods and special exhaust systems should be discharged above the roof. Fans should be selected to meet the requirements for fire, explosion.

4 Conclusion

Gathering all the information we discussed, a proper lab should have all these qualities:

1- Installation of proper hydrogen sensors or monitoring pressure in the piping for leakage detection.
2- Leak detection system must be able to shut off the main supply valve.
3- Leak detection system must be able to turn on the ventilation system.
4- Installation of alarms and visual lightings to alert the personnel.
5- Hydrogen detection system must be able to detect hydrogen concentration with sensitivity of plus or minus 0.25% by volume of hydrogen in air (2,500 ppm).
6- The hydrogen detection system must have a response time of 1 second at a concentration of 1% by volume (10,000 ppm).
7- The hydrogen sensors should be positioned properly to make sure the leaked hydrogen reaches them.
8- In a condition where permanent detection systems are not installed, portable leak detectors (such as thermal imaging cameras) must be available.
9- Emergency shutoff valves must be installed.
10- Shutoff valves must be activated automatically in accordance with sensors and alarms.
11- Fire detections sensors must be installed.
12- Fire detection alarms must be installed.
13- Depending on the quantity of the hydrogen being stored or used and the arrangement of the laboratory, consideration should be given to the installation of automatic sprinklers or some other kind of fire extinguishing system.
14- Use of non-sparking equipment and hand tools is mandatory.
15- Handling paths and storage amounts of hydrogen must be minimized.
16- No plants or combustive materials must be located near storage spaces.
17- No Smoking signs must be installed in the proximity of cylinders and storage.
18- Laboratories should be explosion proof.
19- Explosion resistant walls or barricades must be installed around the lab.
20- The experiments must be conducted in a detached or isolated building or if not possible, outdoors.
21- Consider enough explosion venting around the building on outside walls.
22- It is recommended to use blow-off panels on the perimeter walls.
23- It is recommended to minimize storage compartments by using an electrolyzer to produce the required hydrogen.
24- The electrolyzer should be synced with the hydrogen detection system to be shut down as soon as hydrogen leakage is detected in the room.
25- Make sure that the room where the electrolyzer is installed is explosion proof.
26- The oxygen exhausted form the electrolyzer should be safely vented outside.
27- Cylinders should be handled by trained personnel only.

28- Cylinders should be stored outside the lab in a safe location far from direct sunlight. They should be secured from tipping over by safety restraints.
29- Cylinders should not be installed under electrical equipment and power lines.
30- Every cylinder must be equipped with a pressure regulator designed for hydrogen.
31- Every cylinder must be equipped with two gauges showing the outlet and cylinder pressures.
32- Supply lines must have a manual shutoff valve to allow isolation of equipment in case of an emergency.
33- Excess flow valves or flow restrictors should be used to control maximum flow.
34- If a cylinder is not in use it should NOT be stored inside the lab.
35- Cylinders stored outdoors should NOT be installed within 10 feet of windows, doors, or other building openings.
36- Cylinders should not be stored closer than 50 feet to ventilation intakes.
37- The storage area must have 25% of its perimeter directly open to atmosphere. (Not blocked by walls, fences are okay)
38- Storage areas should be clear of vegetation and combustible materials for at least 15 feet.
39- Storage areas should be covered from vehicle damage.
40- Storage areas should be easily accessible by personnel, at the same time, be away from public and safe from physical damage.
41- Piping systems for the delivery of hydrogen should be installed by a person qualified by specific training.
42- Manual shutoff valves must be located near each point of use.
43- The shutoff valve should be easy to access and away from potential hazards.
44- Delivery lines should be kept as short as possible.
45- A main shutoff system should be available (away from potential hazards and points of use).
46- Piping should be designed for a pressure greater than the maximum possible pressure during abnormal conditions.
47- Piping systems must not be used for gases that they are not designed for.
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50- Every part of the system that can be isolated must have adequate pressure relief.
51- Pressure relief should be piped to a safe discharge outside or fume hood exhaust.
52- All shutoff valves should be clearly marked and labeled.
53- At each discharge point and along the piping, the hydrogen line must be labeled regularly at short intervals along its path.
54- Ventilation should be adequate to handle even the largest anticipated leakage from a cryogenic tank.
55- A proper ventilation will keep the combustible cloud mixture from reaching the flammability range.

56- Liquid confinement should be prevented at all cost. Block all drains and floor openings to prevent the leaked liquid be stuck and accumulated.
57- Electrical equipment and switches must be safe from the touch of liquid leakage. For equipment that are potential to be exposed to liquid hydrogen, special considerations should be taken into account.
58- Storage at such low temperatures will cause condensation of the surrounding air. In this case the condensed air must not be in touch with combustible materials.
59- To dispose liquid hydrogen, firstly totally vaporize it and then vent it safely.
60- Special piping requirements apply to cryogenic liquids. Such low temperatures in grounded piping can cause the floor to freeze, therefore all transfer lines must be well insulated. If a specific line can't be insulated, the area beneath must be clear of any kind of combustibles. Also contraction of materials must be considered. The liquid causes metals to become brittle and easily breakable. Special material selection must be taken into account.
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62- Pressure relief should be enough to prevent rupture.
63- Material selection depends on mechanical properties of the material (s_{yield} , s_{ut}, ductility, impact strength, notch sensitivity). The selected material must have a minimum value for each of the mentioned properties over the whole operation temperature.
64- Consider emergency situations where the temperature and pressure rise or drop out of the operation range.
65- The material must be resistant to phase change in the crystalline structure, so that with repeated thermal cycles or time it stays stable.
66- A proper ventilation system will keep the hydrogen condensation about 25% of the lower flammability limit.
67- The hydrogen concentration should not exceed 1% by volume in the laboratory.
68- The air exchange rate should be 0.3 m^2 per minute for every square meter of solid floor space.
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70- All ventilation systems should be spark proof.
71- The air intake must be positioned properly to not take in hydrogen from another exhaust and recirculate it in the lab.
72- The exhaust points must not be allowed to recirculate the exhaust air in the lab.
73- The exhaust from fume hoods and special exhaust systems should be discharged above the roof
74- Fans should be selected to meet the requirements for fire, explosion.

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