Hydrogen: Analyzing Its Hazards

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Representative Hydrogen Regulation Publishers

- NFPA
- API
- IBC
- IFC
- IEC
- IMC
- IFGC
- EIGA
- CGA
- ASME
- FM Global
- OSHA

The goal of this paper is to review hazard identification techniques available to evaluate the hazards and risks associated with a hydrogen system. In the previous paper of this series, an historical and future view of hydrogen was provided. This paper provides the reader with an overview of techniques used for evaluating the hazards of hydrogen production and consumption.

Regulatory Requirements and Framework

As discussed previously, hydrogen has been used as an energy source for more than 50 years. Due to significant concerns surrounding the flammable hazards of hydrogen, a wide range of global regulatory regimes have been built around it, with the intent of mitigating the potential for accidental releases that could result in catastrophic explosions.

Careful consideration should be made about which standards or codes apply to a particular application, as well as any jurisdiction and regional/national requirements. The standards listed in Table 1 below, while most often applied, do not represent an exhaustive list of all available codes/standards related to hydrogen; individual code review and consideration is warranted for each application.

Defining Process Hazards Analysis (PHA) Scope

When performing a PHA on any system, defining the scope and boundaries of the analysis is a necessary first step. Will the scope address only the system equipment, or the utilities as well as production and compression/storage equipment? Depending on the scope boundaries, it may be helpful to consider whether any upstream consequences at the starting node or downstream consequences at the ending node will also be considered. For example, in an electrolyzer-based system, utilities such as a high voltage supply to the cell stack, chilled water, de-ionized (DI) water, and others may also be associated with the process being analyzed. If those utilities are not considered, some hazardous scenarios may be missed.

Table 1. Some Well-known Hydrogen-related Codes and Standards

Source	Standard	Description	Applicability
NFPA	2	Hydrogen Technologies Code	Liquid and gaseous systems with >95% hydrogen by volume.
	55	Compressed Gases and Cryogenic Fluids Code	Systems with compressed/cryogenic flammable gases and liquids, including hydrogen.
	70	National Electrical Code	Applies to all electrical installations, with special provisions for classified areas.
	496	Standard for Purged and Pressurized Enclosures for Electrical Equipment	Applies to electrical equipment in classified areas.
	497	Recommended Practice for the Classification of Flammable Liquids, Gases or Vapors and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas	Used to classify hazardous areas for use with electrical equipment.
	2112	Standard on Flame-Resistant Clothing for Protection of Industrial Personnel Against Short-Duration Thermal Exposures from Fire	Recommended for use in installations with flammable/ combustible gases or liquids.
API	RP 520	Recommended Practice for Sizing, Selection, and Installation of Pressure Relieving Devices	Applies to all pressure relief devices for overpressure protection.
	RP 521	Recommended Practice for Pressure-Relieving and Depressurizing Systems	Applies to all pressure relief systems.
IBC	-	International Building Code	Applies to all occupied buildings. Which sections apply are based on building classification. Special requirements for hydrogen occupancies are only required if hydrogen exceeds Maximum Allowable Quantity (MAQ)
IFC	-	International Fire Code	General fire protection code requirements. Special requirements for hydrogen occupancies are only required if hydrogen exceeds MAQ.
IEC	60079-10-1	International Electrotechnical Commission	Explosive atmospheres – classification of areas

Source	Standard	Description	Applicability
IMC	-	International Mechanical Code	General requirements for mechanical systems used to control building environments, including exhaust and ventilation systems. Specific requirements are called out for hazardous gases.
IFGC	-	International Fuel Gas Code	Minimum requirements for fuel gas systems and gas fired appliances. Chapter 7 requirements for gaseous hydrogen apply at >95% hydrogen by volume.
EIGA	IGC Doc 121/04/E	Hydrogen Transportation Pipelines	RAGAGEP document on hydrogen transport and distribution pipelines. Not considered a regulatory requirement in the US.
CGA	G-5.4	Standard for Hydrogen Piping Systems at User Locations	Hydrogen piping. (Minimum hydrogen content not specified, but NFPA 2 is referenced, which cites >95% by volume).
	G-5.5	Standard for Hydrogen Vent Systems	
	G-5.6	Hydrogen Pipeline Systems	
ASME	B31.3	Process Piping	All process piping systems including gas systems.
	B31.12	Hydrogen Piping and Pipelines	Piping and pipelines with hydrogen content. Minimum content is not specified for piping, cited as >10% by volume for pipelines. Hazards cited include protection against partial hydrogen content, so it should be used even at low hydrogen concentrations.
	BPVC	Section VIII Pressure Vessels	All vessels operating at pressure above atmospheric pressure.
FM Global	5-1	Electrical Equipment in Hazardous (Classified) Locations	Any electrical equipment within an area deemed classified based on HAC study.
	7-32	Ignitable Liquid Operations	Applies to the portion of the system that includes liquid hydrogen.
	7-77	Testing of Engines and Accessory Equipment	Engine/turbine testing systems.
	7-91	Hydrogen	Hydrogen supply and delivery systems and protections. No hydrogen concentration specified.
OSHA	29 CFR 1910.103	Hydrogen	Hydrogen delivery systems (storage, piping, equipment). No hydrogen concentration specified.
	29 CFR 1910.119	Process safety management of highly hazardous chemicals	Applies when stored hazardous materials at a site (including hydrogen) exceed 10,000 lbs.

Another important aspect is the detail level and accuracy of the facility drawings that are provided to the PHA team. Since multiple new technologies are being developed quickly, the drawing set used to analyze the hazards during the PHA may not be the most accurate version available or may even be outdated. This can result in incomplete or incorrect analysis. It is preferable to perform a PHA at different stages of a capital project lifecycle. By performing an initial high level PHA using techniques such as HAZID (Hazard Identification) at the 30% design stage and performing a HAZOP (Hazard and Operability Study) and LOPA (Layers of Protection Analysis) at the 60% and 90% design stages, costly design changes can be identified much earlier, with the end result of an inherently safer design for the facility processing systems.

Performing the PHA

Once the scope boundaries and key assumptions have been defined, a PHA can be planned and conducted. Numerous published tools and techniques are available to perform a PHA effectively on a hydrogen system, however, one key point to consider is the experience level of the team conducting the PHA. There are many new organizations and new technologies in the hydrogen and hydrogen carrier space, but organizations new to hydrogen processes may not possess enough experience or have enough data available for the team to perform an effective PHA. Therefore, additional pre-work for a hydrogen-based PHA may be warranted compared to other processes. An overview of steps to follow in conducting an effective PHA is illustrated in Figure 1 below.

Figure 1. An Overview of Steps to Follow for an Effective PHA

(Courtesy : OSHA Academy)

Key nuances are discussed below:

1. *Understanding of the key applicable codes and standards:* Table 1 is a good starting reference for hydrogen management, but as new standards and technology are constantly evolving, the related hazards must be further understood. Therefore, it is vital to consult the latest editions of these standards, and if possible, to participate in the input or development of these standards, so they are more applicable for various applications. One of the first items for a PHA facilitator may be to verify if and to which standards/codes the system is built. This will allow the facilitator to help the team focus on the subject matter being reviewed. Having this clarified early on helps minimize disruption and confusion during a PHA. For example, if a specific distance requirement exists in one standard vs. another, the team may not know how to analyze the hazards of a hydrogen release. Similarly, if the area classification is performed to NFPA vs. IEC standards, the requirements may be completely different. This could affect the list of possible safeguards or protection layers and hence the mitigated risk profile for the scenario.

2. *Understanding of PHA techniques and selection:* As described above, there are various techniques that can be deployed to perform a PHA, with the most standard ones being HAZID, HAZOP and What-If. In some cases, a checklist type analysis may be performed if the system has been well understood and a detailed checklist has been developed. Similarly, a more quantitative analysis like LOPA may be required to determine Safety Integrity Level (SIL) targets. In other cases, a more detailed analysis may be required for certain scenarios using Failure Modes and Effects Analysis (FMEA) or Fault Tree Analysis (FTA). Note, to perform a more detailed analysis, failure rate data on components may be needed. Note that such data might not be available for electrolyzer membranes and similar components. A typical electrolyzer operation is shown in Figure 2.

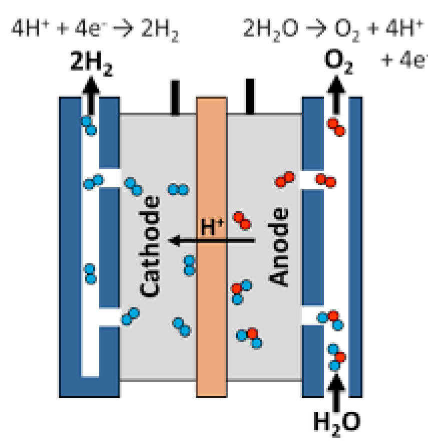

Figure 2. Typical Electrolyzer Operation (Courtesy: Department of Energy)

3. *Understanding the risk tolerance criteria:* Each end user and/or site will have different risk tolerance criteria, which should be developed ahead of time, understood, and explained to the team at the start of PHA meetings. Traditional PHA studies have risk matrices developed and confirmed to use in the PHAs. However, with smaller operators or end users with small electrolyzer type applications, this may not be as well defined. Without defined risk tolerance criteria, PHA recommendations may

be high-level and hard to prioritize. Therefore, it is generally best if a basic risk matrix is developed, which considers high level consequences and likelihoods based on industry guidelines from Center for Chemical Process Safety (CCPS) and others.

4. *Understanding the various available protections (prevention and mitigations):* For electrolyzer-based systems, significant safety protections that can help prevent a release are built into the system. If a release occurs in such systems, depending on the location, detection and ventilation system may be appropriate mitigations. Considering that the purpose of a PHA is to identify safeguards or protection layers that prevent an accidental release, an early detection and an effective ventilation system might be able to keep the concentrations below 25% LFL (Lower Flammability Limit) and hence prevent the possibility of a large-scale Vapor Cloud Explosion (VCE). Similarly, if there are Safety Instrumented Functions (SIFs) used to prevent a release or initiate a shutdown of the electrolyzer, such mechanisms should be carefully studied and understood by the facilitator before commencing the PHA.
5. *Understanding of previous incidents and Management of Change (MOCs):* A previous incident list on similar systems can be very helpful in aligning the team on the hazards of such a system. A compiled set of data for these incidents may not exist for the facility, but online and intra-company research, as well as information from vendors, can be helpful in preparing such a list. In addition, MOCs on an operating system should also be reviewed to cover any changes that have been made to the system.
6. *Understanding of siting risks:* During a PHA, a full facility siting study is not performed, but can be reviewed if available. A subsequent paper in this series will discuss siting risks in more detail. However, for PHAs, siting risks should be considered in order to study the impact to various receptors (people outside, within buildings, environment, equipment, etc.), which helps confirm which safeguards/protection layers should be allocated to different scenarios. For example, an HVAC ventilation system (designed correctly) may be a valid protection layer for an indoor release, but such a protection layer may not be appropriate for outdoor releases. Or mitigative safeguards (e.g., deflagration vent panels) may be considered as PHA recommendations if the facility siting analysis indicates damage to walls of the building from an internal hydrogen explosion.

Example of an Electrolyzer PHA

Table 2 on the following page shows an example chart of hazards and associated mitigations for Proton Exchange Membranes PEM and Alkaline type electrolyzers. This is not an exclusive list, but it focuses on high consequence/high risk scenarios. A detailed PHA would also consider operability and other hazards associated with the system in addition to the types of hazards described in the chart.

As described above, a PHA is an important and effective technique used to identify hazards in hydrogen systems. Since technologies are quickly developing and organizations new to hydrogen hazards are coming on board every day, there is a further emphasis on the need for well-executed PHAs. When done properly, and not to simply fulfill a requirement, a PHA can help identify both screening level and more detailed analysis that may be needed to identify and protect against the significant flammable and explosion risk scenarios associated with hydrogen. The next paper in this series will discuss the various material related concerns that are relevant to hydrogen-based systems.

Table 2. High-Level PHA of PEM and Alkaline Electrolyzer

TABLE 1. PEM and alkaline electrolyzer hazards and mitigation using a hazard and operability study or process hazard analysis

Hazard scenario ID	Initiating cause or secondary consequence	Detailed consequence	Non-independent protection layer (IPL) safeguards and other primary control/ containment measures	Possible IPL safeguards
1	Blocked electrolyzer H_2 line Vent valve does not open More H_2 supplied than needed Power supply high amperage (current controller failure)	Potential high pressure in line and at the electrolyzer. Possible overpressure and pipe rupture with release of H_2. Possible ignition and fire/explosion with possible injury to personnel.	1) Vented deflagration panels	1) Relief valve 2) High pressure shutdown of the electrolyzer 3) Increase the speed of heat, ventilation and air conditioning (HVAC) system
2	Loss of deionized water supply	Loss of H_2 generation and possible overheating of the cell stack. Potential damage to the cell stack and release of H_2, which can lead to ignition, fire/explosion and injury to personnel. The consequence of this scenario is limited to the volume of H_2 stored in piping and vessels since H_2 generation has been stopped.	1) Vented deflagration panels	1) Level switch shuts down the electrolyzer 2) Water flow switch shuts down the electrolyzer 3) Resistivity sensor shuts down the electrolyzer 4) Increase the speed of HVAC system 5) Cell stack temperature shuts down the electrolyzer
3	Loss of chilled water supply	Possible overheating of the cell stack or the power supply box. Potential damage to the cell stack and release of H_2, which can lead to potential ignition, fire/explosion and injury to personnel.	1) Vented deflagration panels	1) Cell stack temperature shuts down the electrolyzer 2) Increase the speed of HVAC system
4	Loss of chilled water supply	Possible overheating of the cell stack. H_2 possibly sent into the oxygen lines and released, which can lead to potential ignition, fire/explosion and injury to personnel.	1) Vented deflagration panels	1) Cell stack temperature shuts down the electrolyzer 2) Increase the speed of HVAC system
5	Pressure control valve at the oxygen separator fails to open	Possible increased pressure at the oxygen separator. Possible overpressure and release of oxygen. This could increase the likelihood of flammability, upon any other release of flammable material. Possible ignition, fire/explosion and injury to personnel.		1) Relief valve at the separator 2) High pressure alarm
6	Drains on H_2 separator left closed	Possible to send wet H_2 downstream to users with impact downstream.		1) Dew point monitoring alarms
7	Reverse flow from H_2 to oxygen side (through membrane diffusion, short at the cell stack or in the vent lines)	Possible contamination of the oxygen line. Possible overpressure of the oxygen line. Possible ignition, fire/explosion and injury to personnel.		1) Combustible gas sensor shuts down the electrolyzer
8	Air ingress into the H_2 vent line	Possible ignition in the vent piping causing the vent to rupture and injure personnel.	1) Vent design is per NFPA 2 standards	
9	Exchanger tube leak at the chiller	Possible to send H_2 in the closed loop chiller line and piping. Possible downstream impact with overpressure in piping.		1) Combustible gas sensor in the chiller lines with action to shut down the electrolyzer
10	Temperature/level control valve failure at the water tank	Possible overheating water in the tank. Loss of water in the cell stack and cell stack damage. Possible leak of H_2 with possible		1) Cell stack temperature shuts down the electrolyzer 2) Increase the speed of HVAC system
11	Loss of fan at the exchanger in power cabinet	Possible overheating of the power cabinet. Possible to increase temperature of the power supply unit, damage the inverter and other electronics. Possible damage to the equipment with impact to electrolyzer performance.		
12	Water tank overfilled	Possible to send water to the oxygen stack. Possible freezing of the oxygen vent stack, preventing vent oxygen when needed. Possible damage and operational issue.	1) Heat tracing in the oxygen vent line 2) Water drain at the oxygen vent	1) High level switch in the water tank
13	Water carryover into the H_2 vent	Possible to send water to the H_2 stack. Possible freezing of the H_2 vent stack, preventing the H_2 to vent when needed. Possible overpressure of the H_2 lines with possible ignition, fire/explosion and injury to personnel.	1) Heat tracing in the H_2 vent line 2) Water drain at H_2 vent stack 3) Vented deflagration panels	1) Increase the speed of HVAC system
14	H_2 embrittlement	Potential for failure of pressure swing adsorption (PSA) piping components. Possible release of H_2, which can lead to ignition, fire/explosion and injury to personnel.	1) Vented deflagration panels	1) Increase the speed of HVAC system
15	Improper purging of H_2 lines	Potential for failure of PSA piping components. Possible release of H_2, which can lead to ignition, fire/explosion and injury to personnel.	1) Vented deflagration panels	1) Increase the speed of HVAC system
16	Loss of nitrogen flow to anolyte/catholyte tank before startup	Possible formation of explosive mixture in electrolyzer. Possible ignition, fire/explosion and injury to personnel.	1) Vented deflagration panels	1) Low nitrogen alarms 2) Backup nitrogen purge 3) Low nitrogen shutdown of the electrolyzer
17	Loss of cooling water to the anolyte/catholyte coolers	Possible higher diffusion, leading to the formation of explosive mixture in electrolyzer. Possible ignition, fire/explosion and injury to personnel.	1) Vented deflagration panels	1) High temperature alarms at the anolyte/catholyte piping 2) High/high temperature shutdown of the electrolyzer
18	High cell voltage	Possible higher diffusion, leading to formation of explosive mixture in electrolyzer. Possible ignition, fire/explosion and injury to personnel.	1) Vented deflagration panels	1) High temperature alarms at the cell stack 2) High/high temperature shutdown of the electrolyzer
19	High level in anolyte/catholyte header tank	Possible damage to cell diaphragm, leading to explosive mixture in multiple cells. Possible ignition, fire/explosion and injury to personnel.	1) Vented deflagration panels	1) High level alarms at the anolyte/catholyte water tank 2) High level at anolyte/catholyte water tank shuts down the electrolyzer