Process Hazard Analysis of Alternate Hydrogen Production Methods

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by

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DECLARATION

I hereby declare that the project report titled 'Process Hazard Analysis of

Alternate Hydrogen Production Methods' submitted by Leon John DAlmeida,

for the award of the degree of Professional Master's Program in Chemical

Engineering to Purdue University, is a record of work carried out by me under the

supervision of academic mentors (Dr. Ray Mentzer & Dr. William R. Clark) and

industrial mentors (Mr. Edward Marszal, Mr. David Moore & Mrs. Rebecca

Peterson).

Further, I declare that the work reported in this project report has not been

submitted and will not be submitted, either partially or in full, for the award of any

other degree or diploma in this institute or any other institute or university.

Signature of candidate

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"Success is often the result of taking a wrong step in the right direction"

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Abbreviations

| BoP | Balance of Plant | | | |
|----------|---|--|--|--|
| CAGR | Compound Annual Growth Rate | | | |
| CL | Concentration Layer | | | |
| CSB | Central Board of Investigations | | | |
| ESTA | Employee Safety Training Assessment | | | |
| FMEA | Failure Mode and Effects Analysis | | | |
| GDL | Gas Diffusion Layer | | | |
| HAZID | Hazard Identification | | | |
| HAZOP | Hazard & Operability Study | | | |
| HER | Hydrogen Evolution Reaction | | | |
| HT-PEMFC | High Temperature Proton Exchange Membrane Fuel Cell | | | |
| LT-PEMFC | Low Temperature Proton Exchange Membrane Fuel Cell | | | |
| MEA | Membrane Electrode Assembly | | | |
| OER | Oxygen Evolution Layer | | | |
| OSHA | Occupational Safety and Health Administration | | | |
| P & ID | Piping & Instrumentation Diagram | | | |
| PAFC | Phosphoric Acid Fuel Cells | | | |
| PBI | Polybenzimidazole | | | |
| PEM | Proton Exchange Membrane | | | |
| PFD | Process Flow Diagram | | | |
| PFSA | Perfluorosulfonic acid | | | |
| PHA | Process Hazard Assessment | | | |
| PI | Polyimides | | | |
| PPE | Personal Protective Equipment | | | |
| QRA | Qualitative Risk Assessment | | | |
| SCSRs | Self-Contained Self-Rescuers | | | |
| SOEC | Solid Oxide Electrolytic Cell | | | |
| SOP | Standard Operating Procedure | | | |
| SPE | Solid Polymer Electrolyte | | | |
| SPEEK | Sulfonated Polyether Ether Ketone | | | |
| WHA | Workplace Hazard Assessment | | | |

Literature Review

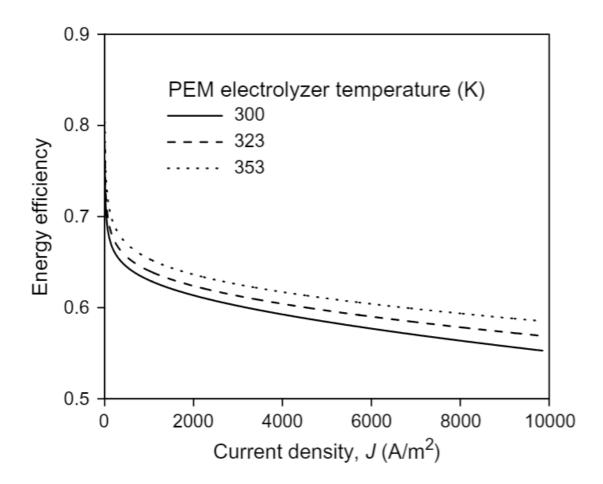
At present, majority of global hydrogen production (96%) comes from fossil fuels, whereas only 4% is produced through water electrolysis. Fossil fuel-based hydrogen production results in lower purity and higher greenhouse gas emissions. In order to address the depletion of fossil fuels and the environmental impact of hydrogen production, water electrolysis powered by renewable energy sources is considered a promising alternative. This research project focuses on Proton Exchange Membrane (PEM). PEM electrolyzers offer advantages like high current density, compactness, and fast response. PEM & SOEC have been introduced to generate H₂ energy. PEM is currently available for production, whereas SOEC is still undergoing research. Generally specifications for each electrolyzer model are provided by the manufacturers and vendors as per their requirements. Water electrolysis cannot be exploited for hydrogen production, as a part of it is lost due to "heat". In order to overcome the issues faced by Alkaline electrolyzer, PEM electrolyzer has been developed. Due to the expensive catalyst materials like platinum, rhodium and other precious metals used in their production, reducing the cost while maintaining high efficiency is a significant challenge for all electrolyzers [1]. High production cost raises its market value and results in slow development. Investigations have been carried out by researchers to understand the relationship of current ripple formation between thristorbased and classic chopper rectifiers and have reached a conclusion that the current ripple need to be as small as possible in order to optimize energy consumption. Analysis was performed on the large rectifiers on the impedance vs frequency to evaluate the challenges faced, such as power quality and control. In order to improve the Hydrogen flow rate, it is vital to control the current passing through the rectifier [2]. Water electrolysis provides an effective alternative fuel to cope with the decline in fossil fuels. Electricity generated via power grid is not an ideal source to supply electrolyzers, since most of the electricity is generated by fossil-fueled power plants (i.e., coal and natural gas-fired power station) results in greenhouse gas emissions (e.g. CO₂, CO).

Energy storage (such as Hydrogen buffer storage) helps to regulate consumption and production. Based on PEM stack electrical needs, energy can be supplied to the PEM electrolyzers via variety of AC-DC converters. The stack voltage, which ranges from few to hundreds of volts, depends heavily on the rated power of the device, where current varies between rates of ten to

thousands of amps (Or, in the watt to megawatt range). Different requirements and specifications must be considered prior to selecting a suitable AC-DC converter for Electrolyzer application [4]. To avoid cases of power switch failures and current ripple reduction, design of the step-down DC-DC converter is recommended. In order to enhance power quality, we can combine rectifier and DC chopper to avoid the use of bulky active and passive filters. It is anticipated that the use of hydrogen technologies will also expand into other industries, such as transportation, mobility, electrical micro-grids, and even residential applications. In order to do so, efforts must be intensified on enhancing characteristics of hydrogen-based systems, such as effectiveness, start-up speed, etc. The advancement in Hydrogen technology focuses on improving existing electrolyzers, making it more effective, lightweight, and long-lasting. For this reason, research is currently being done on improving the stack technology (which is primarily based on Proton Exchange Membrane), whose size depends on the electrolyzer's power, that improves performance of the stack [5]. One of the many solutions is to combine the renewable energies (e.g. wind, solar etc.) so that it can meet the entire energy requirements of the world, as the single source of renewable energy is not sufficient to meet the growing demand [6].

The colour spectrum of the hydrogen can change over time with advancement in technology [8]. Most investigations on PEM electrolysis focus on improving catalysts and PEM electrolytes. However, current research and literature lacks detailed thermodynamic and electrochemical modeling analyses on PEM electrolytic hydrogen production, which is essential for better understanding of its working mechanisms and design optimization [7]. From Fig. 1, we can deduce an inverse relationship between energy efficiency and membrane thickness. Thicker electrolyte membrane has higher ohmic over-potential, and higher operating potential, that result in lower energy efficiency.





Hydrogen has so far been handled safely for many years and used in a number of applications, including but not limited to aerospace technology, chemical processing, food, and electronics industries. In the past, safety precautions for using the earliest forms of energy (such as wood) were created through trial and error [9]. The new energy systems should include safety planning as a fundamental component of its design and operation that includes identifying hazards, assessing risks by taking into account the likelihoods and ramifications of incidents related to those hazards, and minimizing risks. At present PEM electrolyzers are the most common type of units that are used in commercial settings. The focus of this study will be on hazard and risk analysis in order to determine level of risk and need for safeguard in hydrogen generation systems. Hazard and Operability (HAZOP) study is the particular Process Hazard Analysis (PHA) technique used for hazard and risk analysis in the hydrogen generation system. Prior to conducting a HAZOP study, a failure analysis is created in order to identify possible failures to

set up process deviation. The fundamental idea behind a HAZOP study is to thoroughly describe the process and create a (Process Hazard Analysis) PHA on the basis of consequence indexed to determine what the causes and effects of these deviations may be [10]. Numerous studies on the various risks associated with H₂ use have been carried out, with a focus on hydrogen fueling stations, unintended release of H₂ and H₂ jet flames; that helped in carefully building systems for analysis based on the prototype system [22]. It has been observed by several researchers that if electro-osmotic drag prevails over back diffusion, the anode will dry out while cathode will remain hydrated at high current densities, whereas it is opposite at low current densities since Hydrogen gas will diffuse back to the anode causing an explosive reaction [24].

Introduction

The main focus of this project is to develop a series of hazardous scenarios that should be considered when implementing PEM that includes a discussion of causes, consequences, and typical safeguards. This information was developed and presented through the technique and documentation style of HAZOP.

Hydrogen: Hydrogen is considered as an efficient fuel. Since it is chemically bonding with most of the elements, it has been used as an industrial chemical for many years. Hydrogen is used in automobiles to combine with Oxygen in fuel cells to produce electricity and to power the engine [11]. Though Hydrogen can be produced in different forms, this project will focus only on electrolysis process. Since it is not freely available in nature it is produced from other alternative sources of energy [13]. Unlike carbon-based fuels, hydrogen produces no harmful by-products when burned. The combination of hydrogen and oxygen in fuel cells only produces electricity, heat and clean water [11].

Electrolysis: Hydrogen exists in gaseous form at standard temperature and pressure (273K and 1013 hPa) and is available in the atmosphere at 29.534 vol% as an element. Electrolysis is one of the methods to extract hydrogen from water by using electricity. It produces carbon free hydrogen from nuclear and renewable sources. PEM technology efficiency ranges from 50% to 80% [16]. This reaction takes place in a device called an electrolytic cell. Electrolyzers size ranges from small unit-size and are suitable for small-scale decentralized hydrogen production to large centralized manufacturing plants that can be directly connected to greenhouse gas-free renewable and other forms of power generation. Similar to a fuel cell, electrolyzers consists of a membrane that separates the anode and cathode from mixing. Due to differences in the types of electrolyte materials that they contain and the ionic species they conduct, electrolyzers operate in different ways [13]. During two partial reactions cracking occurs at the two electrodes of the electrolytic cell; the cathode (-) and the anode (+). In practice, electrolytic devices consist of several interconnected electrolytic cells, also called stacks. When the voltage is switched on, electrolysis reaction takes place. Between the two partial reactions, charge equalization occurs in the form of conduction of the ion through the electrolyte. In addition, a membrane is required

to separate the two reactions and prevent product gases from mixing or reacting. The type of electrolyte and the ionic charge differ in different electrolysis techniques [19].

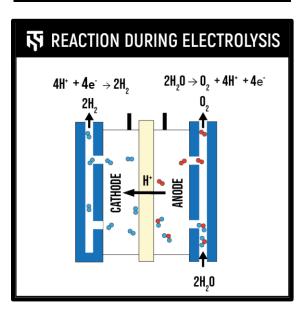


Fig 2. Electrolysis Process in PEM

Market: Proton Exchange membrane Market size was valued at around USD 8.29 billion in 2023 and is expected to reach a value of approximate USD 32 billion by 2032, at a CAGR (Compound Annual Growth Rate) of 17% over the forecast period of 2023 to 2030 as referred in fig 3. This indicates a positive outlook for the market, driven by increasing demand for clean energy solutions and advancements in fuel cell technology. The main drive is the growing demand for electric vehicles. PEM market provides several opportunities for expansion in the coming years. It is one of the key opportunities in the development of new materials and manufacturing process that can reduce costs and improve the performance of the fuel cell. In terms of revenue, automotive held the largest market share of 29% [19]. It is anticipated that the growing popularity of medium, commercial, light, and heavy-duty cars will increase demand for PEM fuel cell. Due to its high power density and capability to operate in chilly conditions it enables a wide range of stationary applications. In 2022, the high temperature market segment had the largest market share recorded. The utility of High-Temperature Proton Exchange Membrane Fuel Cells (HT-PEMFC) in terms of system requirement changes constantly and is typically operated in hybrid mode alongside a battery. Buildings that use combined heat and power can benefit from the HT-PEMFC systems that runs on natural gas which requires a

suitable controller and system for operating in a desirable situation. HT-PEMFC can operate at temperatures ranging from 120°C to 200°C. The Low-Temperature Proton Exchange Membrane Fuel Cell (LT-PEMFC) can operate at temperatures ranging from 60°C to 80°C. Perfluorosulfonic acid (also known as Nafion) is typically used as the membrane in LT-PEMFCs. The LT-PEMFC operates at temperatures lower than 100°C because Nafion is sensitive to change in its internal moisture level [20].

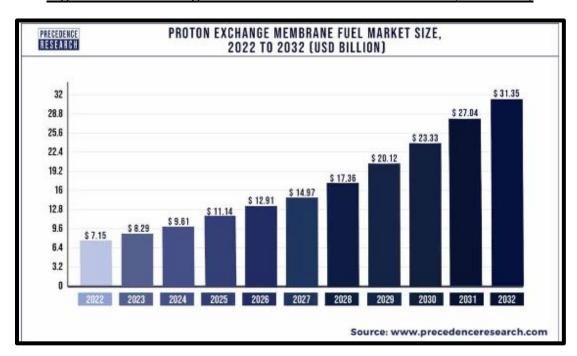


Fig 3. Proton Exchange Membrane Global Market Growth (2023-2032)

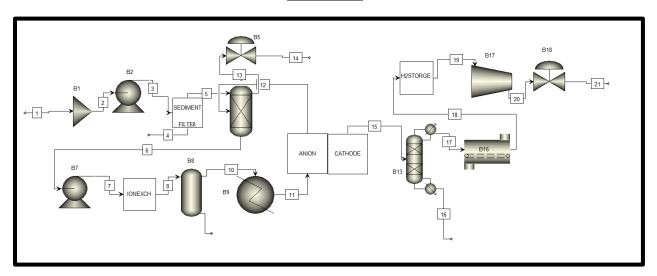
Process

The pretreated feed is first sent to the mixer. Since water may contain suspended particles, it needs to be mixed well before sending it to the sediment filter for filtration. Hence the main purpose of the mixer is to ensure efficiency of the sediment filter by preventing any coagulation of the sediments. The pretreated feed is pumped to the filter and main purpose of the pump is to maintain a steady and consistent flow, allowing the filter to capture and remove larger particles before sending the water to the separator. The pretreated feed is then sent to the sediment filter for filtration and extraction of any solids (sediments). After the filtration process the treated water is sent to the H_2O-O_2 separator for removal of O_2 to which the O_2 is vented out and water

is drained downstream. Hydrogen and Oxygen are highly flammable gases, and the main purpose is to keep them separated to reduce the risk of any potential fire/explosions. The water is then pumped to the ion exchanger to remove ions as water accumulation in the membrane can cause scaling or fouling on the surface of the PEM over time, by removing these ions we can extend the membrane life. The water is then heated by an electric heater inserted into the main water tank to ensure the proper process temperature during stack operations. By electrolysis process H₂ is obtained at the cathode and the mixed stream (O₂-H₂0) is obtained at the anode. Assuming the process is not a full 100% conversion, the mixed stream is vented back to the separator and H₂ is sent to the extractor for drying or removal of moisture. After extracting the moisture from the product stream, it is sent to a 2-bed dryer for absorption and regeneration from which water is drained out. Once the moisture is completely drained out from the product stream it is then sent to the buffer storage to maintain the balance between consumption and production. The product stream is then pumped out to the gas export pipeline under high pressure. If there is still moisture content in the product stream then it is sent back to the extractor to repeat the same process to prevent any explosive reaction in the buffer storage. Meanwhile the dryer can act as a regenerator to generate the H₂ gas and send it to the buffer storage. The main purpose why moisture content should be removed is to prevent any corrosion, maintain the storage structural integrity, as there will be a risk in pressure fluctuations due to the temperature changes and could cause unwanted reactions and result in releasing the undesirable byproducts [14].

Fig 4. Archetype Process Flow Diagram For H2 Production Using Proton Exchange

Membrane



Proton Exchange Membrane (PEM): The "Membrane Electrode Assembly (MEA)" is an important part of the PEM that includes the membrane, the catalyst layers, and the gas diffusion layer (GDL). The electrolyte can either be fluorinated, sulfonic acid or polymer membrane. Water is electrolyzed using a Proton Exchange Membrane (PEM) in a cell with a Solid Polymer Electrolyte (SPE) that separates the product gases, conducts protons, and insulates the electrodes from electricity. In terms of power supply, a commercial AC/DC converter will supply power to the electrolyzer from the electrical power grid to which a commercial DC/DC step-down converter is inserted to properly reduce the stack voltage as hydrogen flow is proportional to the electrical current supplied. This converter enables continuous voltage output regulation over a sufficiently wide range. The ability of PEM electrolysis to function at high current densities is one of its biggest advantages. At times energy is uncaptured due to sudden spike in the energy input, especially for high dynamic energy sources such as wind and solar and can operate at high current densities lowering the operation cost [16]. PEMs are frequently used to produce hydrogen and generate electricity hence it is a dual function provider. Due to high ionic conductivity and good mechanical strength membranes like Nafion and Nafion-based are used but has its drawbacks such as lengthy synthesis process and poor proton conductivity at high temperatures. PEM electrolyzers have advantages of being able to operate at high voltage and current densities while producing hydrogen gas that is up to 99.995% pure. The Oxygen Evolution Reaction (OER) begins when hydrogen ions move from the anode to the cathode through the PEM as a result of electrolysis. When hydrogen ions are reduced at the cathode, one hydrogen (H₂) molecule is released, and this initiates the Hydrogen Evolution Reaction (HER) as shown in fig 5. [18].

Fig 5. Overall Electrolysis Reaction

| Reactions | | | | |
|--|--|--|--|--|
| Anode $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$ | | | | |
| Cathode | $2H++2e^-\rightarrow H_2$ | | | |
| Overall | $2H_2O \rightarrow H_2 + \frac{1}{2}O_2$ | | | |

Parameters Affecting the Membrane-Based Electrolysis: The first parameter to be considered is the "operating temperature" in which a typical Nafion-based membrane serves as the main element of the membrane electrode in a PEM electrolysis process. This process can typically run at temperatures ranging from 31°C to 91°C approximately. Due to Nafion membrane's inability to withstand operating temperatures above the specified range, it results in mechanical degradation and a loss of ionic conductivity, because the electrochemical reaction has faster kinetics at higher operating temperatures. The second parameter is the "concentration" in which the amount of hydrogen produced and the rate of the reaction, that are strongly influenced by electrolyte concentration. A greater concentration in the electrolyte boosts the solution's ionic conductivity, which encourages hydrogen evolution reactions and boosts yield. The membrane, electrodes, gasket, current collector, bipolar plates, and other parts of the MEA can deteriorate due to an excessive electrolyte concentration, which in turn affects the hydrogen yield. Concentrated electrolytes, whether acidic or alkaline, have corrosive properties that can harm the pump, the tubes, thermocouples and other heating elements [18].

One of the variables that can affect the kinetics of the electrolyte is the flowrate in the electrolysis reaction because the membrane functions as the electrolyzer's central component. The electrolyzer has improved in many areas over past ten years, but the effects of different operating parameters are still being studied. Notably, kinetic and thermodynamic relationships have not yet been used to pinpoint the primary limiting factors. However, a faster electrolyte flowrate may act as a bottleneck, reducing the rate of ionization in a HER or OER instead of necessarily increasing the rate of hydrogen production. In order to achieve an optimal hydrogen yield, a good balance must be maintained between an optimal electrolyte flowrate and other parameters [18].

To achieve optimum performance it is necessary to hydrate the PEM. At times challenges can be faced such as the excess water in the stack either due to malfunction or rupture or more flow can fill the pores hindering the diffusion of Hydrogen to the cathode and decreases the efficiency of the catalyst, making it difficult to transport oxygen to the catalyst layer. The overall effect is referred to as 'GDL/CL flooding'. Oxygen mass transport is limited due to accumulation of water in the membrane. Whereas it has quite the opposite effect when the diffusion occurs

backwards, this can result in the drying phenomenon and poor performance. Another factor that can affect the performance of the membrane is due to the sharp increase in electrical resistance of the membrane which results in degradation of membrane life with increase in ohmic losses. Hence, a proper balance is maintained between water removal and production which is also necessary to maintain current densities. Drying condition are such that active sites on that catalyst are hindered by the sulfonic ion bonds increasing its activation polarization, in addition to degradation of the membrane (delamination). Therefore, maintaining high PEM water content is essential to ensure high ionic conductivity and also can use capillary transport to move water through the GDL [24].

Membranes

Nafion: Perfluorosulfonic acid (PFSA) membranes like Nafion are well-known and frequently used in PEM fuel cells and electrolyzers. Because of its excellent physicochemical qualities and good ionic conductivity, Nafion performs well and is currently favored. One of its main drawbacks is its high fuel permeability which causes "PEM fuel cell systems to lose a lot of fuel and perform less efficiently". Ion crossovers are another factor that lowers the hydrogen yield in PEM electrolyzers. Since membrane production cost is high, there have been multiple methods to address this shortcoming such as inorganic fillers, acid doping, and introduction of various polymer backbones into the Nafion membrane. More effective hydrogen synthesis can be achieved by running an electrolyzer cell at a higher temperature that results in the rise in ionic conductivity and decline in anode and cathode activation. At Higher temperatures PEM fuel cell performance is enhanced with increase in Hydrogen production at the expense of the fuel cell durability [18].

Polybenzimidazole (PBI): The term "Polybenzimidazole" (PBI) refers to the structure of aromatic heterocyclic polymers that contains multiple benzimidazole units. PBI membranes have a few advantages over Nafion membranes, such as better chemical stability, greater tensile strength and a specific affinity for "Polyaryletherketone" and a few other polymers. These qualities have led to extensive research into the use of "Polybenzimidazole-based (PBI-based)" membranes in fuel cells, water electrolysis, and flow batteries. Hybrid Membrane Synthesis is

one of the methods to help improve the PBI by focusing on the low conductivity to make it a good substitute. Combination with Sulfonated Polyether Ether Ketone (SPEEK), Sulfonated Polysulfone, or Sulfonated partially Fluorinated Arylene Polyether to create ion cross-linked structures are some of the notable examples [18].

Polyimide: Polyimides (PIs) are another group of promising polymers that are used for PEMs. PI's are aromatic and contain imide heterocyclic structure in the main backbone chain as depicted in Fig. 6. PI finds applications in many other fields owing to its superior thermal, mechanical and chemical stability at higher temperature in addition to its film forming ability. These characteristics are required for fuel cell membranes, therefore, with little modification, sulfonated PI's are abundantly used as PEMFCs [18].

Process Hazard Analysis

Balance of Plant: To cut costs and gain market share quickly, the developed system is made up of commercially available components that make up the Balance of Plant (BoP) around the electrolysis stack. BoP involves the following subsystems that are Heat Management Subsystems, Water Management Subsystems, Power Conditioning Subsystems and Control Subsystems [14].

Risk Analysis: By taking into account variables like likelihood and severity, risk assessment process aids in identifying hazards and quantifying the risks connected to those hazards. HAZOP, FMEA, HAZID, QRA, and other techniques are available for conducting risk assessments for specific systems to which the main focus will be on the HAZOP. Electrolyzers are subject to the same rules. Due to the presence of flammable gases, oxygen, electricity, high-pressure, high-temperature, and the potential release of gases beyond the recommended concentration, electrolyzers are considered as complex systems. If proper precautions are not taken, all these characteristics may result in fatal incidents [15].

HAZOP Study & FMEA (Failure Mode Analysis): One methodology that is frequently used by industries for assessing risk is conducting operability study (HAZOP). HAZOP offers a methodical way to assess the electrolyzer system's design and spot potential hazards that might have gone unnoticed during the general design stage. HAZOP is carried out following the first

design, that is, after the first P&ID (Piping and Instrumentation Diagram); the full system layout with all existing components is defined. Several sessions of HAZOP are held where a core team of individuals with the necessary skills come together to brainstorm. A HAZOP moderator with knowledge of the HAZOP method and a scribe who tracks progress should lead the sessions. Depending on the complexity, a system is divided into a number of nodes, and each node's hazards are identified using standardized guide terms and process parameters (consequences and causes) [15]. The analysis of the accident scenarios starts with investigating the parameters that result from the operation. FMEA is another brainstorming technique for identifying risks associated with the failure modes of system components. With both approaches, the effects and likelihood of accidents are qualitatively evaluated. Some of the derivation parameters in the HAZOP are temperature, pressure, voltage, and the chemical composition, more and less were used as indicators describing consequences and causes [22].

Nodes are integral part of the HAZOP and must be characterized to offer more understanding on the archetype PFD. The nodes are divided into four pathways in this process, node 1 which includes the pretreated feed all the way to the separator to separate water and Oxygen thus leading to the second node that is Oxygen vent. Node 3 is the water drained from the separator all the way to the PEM stack and finally node 4 is the electrolysis process to the H₂ gas export pipeline.

Definitions:

Hazard: Refers to a potentially harmful source. Deviations from the intended design or operation may be dangerous. HAZOP studies concentrate on hazards, and it should be noted that a single hazard may have the potential to cause various types of harm to the personnel and process safety. (Reference to the HAZOP worksheet).

Harm: Refers to physical harm or harm to people's health, environment, or property. The result of a hazard occurring is harm, which can take many different forms, including threats to user or patient safety, worker safety, business risks, regulatory risks, environmental threats, etc.

Risk: A combination of likelihood and severity. Since the core methodology does not call for the identification (also known as rating) of the probability or severity of harm, "risk" is not

always expressly identified in HAZOP studies. But if it's necessary, risk assessment teams may decide to rate these elements in order to more precisely quantify and rank risks.

Risk Severity Rankings: Using an ordinal scale is one of the most popular ways to describe risk severity. This is due to the fact that it is frequently challenging to precisely estimate the potential harm. A ranking system from least to most severe is known as an ordinal scale. The rating on the scale can be broken into the following: 1 = Negligible: The risk is so negligible that it can be disregarded by the team. 2 = Low: The risk is negligible and can be controlled by following standard procedures. 3 = Medium: The risk is significant, but it can be controlled or mitigated with additional measures. 4 = High: The risk is serious and demands immediate attention. 5 = Maximum: The risk is significant and requires attention. Depending on the viewpoint from which it is measured, the Risk Severity varies. The ordinal scale could be quantified using percentages, time, or cost overruns. This could lead to overlap. Risk Severity is influenced by a number of factors. For example, the size of the project may have an impact on the risk level. Project complexity can also influence the risk severity [23].

Explosion and Fire Safety: Combustible, oxidant, and ignition are the three elements needed for combustion, which are commonly represented by the fire triangle. All three of these substances can be found together in an Electrolyzer. Avoiding ignition sources is the most common practice. Due to hydrogen's low ignition energy, this is challenging. A hydrogen-air mixture can be ignited with just a static spark. In order to identify potential leak sources (during normal operation as well as failure modes), the system design should be reviewed by a team of experienced engineers as part of the assessment of explosion and fire safety. The failure modes and the internal characteristics of the systems are analyzed by FMEA and HAZOP [15].

Practices to Reduce the Risk of Explosion: The electrolysis course at WHA (Workplace Hazard Assessment) starts by looking into the possible electrolysis system failure modes. After that, it looks into various mitigation measures, such as: Prevent internal leakage from one area of the system to another and external leaks from combining hydrogen with outside air. Installation of mechanical ventilation fans will help to ventilate the electrolyzer enclosure and prevent hydrogen buildup. In order to properly vent O₂ and H₂ during system startup, operation, and shutdown, it is important to measure concentrations for all operational modes. Before and after

use, purge H_2 systems with nitrogen or other inert gases (optional). Use personal monitors, leak detectors, imaging cameras, and fixed H_2 gas detectors [21].

OSHA Regulations: (OSHA) Occupational Safety and Health Administration were created to ensure that safety protocols are setup to protect the workers and to provide different EPA level of protection, as listed in the table below [25].

Table 1: OSHA EPA Levels of Protection

| Level | Type of Suit | Equipment | Protection Provided | Application | Limitation |
|-------|---|--|---|---|---|
| A | Vapor Protective Suit | Chemical resistant gloves, chemical resistant boots, Two way radio communication | Skin, eye, respiratory | Chemical that has high level of hazards to respiratory, skin and eyes. Operations in poor ventilated areas | Integration without loss of performance must resist permeation. |
| В | Liquid Splash Protective Suit | Same as A | Same as A, less skin protection | Medium risk to skin, Hazards related to liquid contact. | Same as A |
| С | Support Function Protective Garment | Full Face piece, air purifying, canister equipped respirator | Same as B, less respiratory protection | Unknown Air contaminants, no affect to skin. | Same as B but airborne concentration must be less than IDLH levels, Atmosphere must contain at least 19.5% O2 concentration. |
| D | Coveralls, Safety boots, glasses or chemical splash goggles | Gloves, face shield | Minimal skin protection, no respiratory protection | No known hazards except for splashes, potential for inhalation or direct contact to chemicals. | Atmosphere must contain at least 19.5% O2 conc. , should not be worn in hot zones |

Workplace Hazard Assessment (WHA): It is essential to recognize that hazards are not necessarily present outside, but also inside the workplace. For this reason OSHA recommends that employers conduct inspection, testing and preventive measures all in the form of an 'SOP' and if hazards are identified 'PPE' and 'safety practices' need to be implemented. The next process will be to fill out a form to which "ESTA' will assign a particular training depending on the area and type of work the employee is carrying out [27].

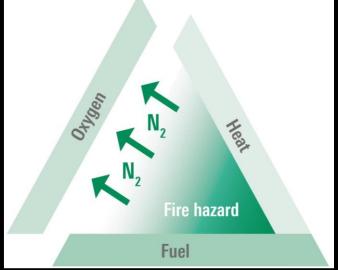
Preventive Measures

Break the Fire Triangle: The main three components required to start the fire are: oxygen, heat energy or fuel which are dependent on each other. Flammability of the materials is directly proportional to oxygen concentration. We can use Oxygen sensors to continuously monitor concentration levels in the observed areas. Uniformity is maintained in the observed areas by purging with Nitrogen due to its ability to reduce Oxygen concentration levels. Nitrogen can either be pumped from some external source or can be generated by membrane technology or activated carbon. This shall help reduce the oxygen and toxic concentration that can help people enter the affected area for a quick and fast repair by following the OSHA regulations [26].

Fire Triangle



Principle to break the fire triangle



Risk on Nitrogen Purging: Anything above the safety threshold concentration can prove to be harmful. Despite the gas being used for purging and tank blanketing, Nitrogen is a hazardous gas and must be handled with care. Exposure to high concentrations can lead to choking, physical and mental impairment and dizziness. According to the OSHA safety recommendation employees must work in workplace with O₂ concentrations ranging from 19.5% to 24%. All personnel are trained on the use of PPE but recommendations such as MineARC are already in place to monitor hazardous gases, including Nitrogen to which they are either fixed or are portable (e.g Aura-PT). SCSRs are also provided to provide safe escape from hazardous areas as they provide 30 to 70 minutes of breathable air in case of emergency response [29].

Inference

The introduction of safeguards in the process doesn't mean that the process is completely safe. The hazards might be caused due to off specification, pressure and temperature fluctuations, tank ruptures, valve malfunctions etc. To prevent incidents from recurring, "Central Board of Investigations (CSB)" urges companies to revise "Standard Operating Procedures (SOP)" to make the operation "easy to do the right and hard to do the wrong" method. This can be done by regular system checking, setting up monitoring levels (flow rate, gas release, and level), alarms in the areas that are prone to be affected and valves connected to drain hazardous material away from personnel. Regular updates to evaluate and strengthen process safety culture should be implemented by adapting appropriate practice guidance published by the Center for Chemical Process Safety and to set up robust safety management system to handle reactive chemicals by identifying, evaluating and controlling.

Conclusion

Presently Hydrogen is relishing its unprecedented momentum. The extensive and independent research determines the future of hydrogen and its crucial role. The decrease in fossil fuel reserves raises concerns to meet growing energy demand. By taking this into consideration, most researchers are now focusing on developing and relying on non-conventional resources that have emerged recently. Though there are multiple challenges such as cost, lack of differentiation, lack of hydrogen market, limited infrastructure, energy losses and policy effects that can hinder the efforts, still it is necessary to develop the non-conventional resources to sustain. There is also an unprecedented increase in the fuel cell market as noticed in a research conducted by Globaldata, that is not only related to PEM electrolyzers but also for other fuel cells, such as Phosphoric Acid Fuel Cell (PAFC). Researches are still being done on both low and high temperature PEM. Among the categories of PEM, the hydrocarbon-based has highest performance than other bio-inspired PEM. Enhancements to the PEM are considered on the basis of mechanical strength, proton conductivity and simple performance boost on membrane, electrodes or the whole membrane electrode assembly. Although sufficient research has been conducted on the PEM and its process; it can be further explored in areas such as leakage severity which will require specification and data of each equipment, pipeline and tubing. Also implement changes in the HAZOP study by implementing the design, operating conditions and by developing a safety mechanism to deal with security breach such as cyberattacks. All in all, "safety practices and hazard analysis" plays a vital role in the advancement of PEM electrolyzer that results in higher hydrogen yield.

Appendix

Table 2. Hydrogen Type & Production Methods

| Hydrogen Type | Source | Method |
|-----------------|--|---|
| Grey Hydrogen | Fossil Fuels (Natural Gas / Coal) | Pyrolysis, Gasification, Coal Gasification, Steam Reforming, Membrane Reactors, Partial Oxidation, CO2 Dry Reforming |
| Blue Hydrogen | Fossil Fuels (Natural Gas / Coal) with CO2 Sequestration | Coal Gasification, Steam Reforming, Membrane Reactors |
| Green Hydrogen | Hydrogen Produced from Electricity of Renewables | Electrolysis |
| Black Hydrogen | Bituminous Coal | Coal Gasification |
| Brown Hydrogen | Lignite | Coal Gasification |
| Red Hydrogen | Water | High-temperature Catalytic Splitting of Water using High Temperature |
| Pink Hydrogen | Water and Nuclear Power | Electrolysis |
| Yellow Hydrogen | Water and Solar Power | Electrolysis |

Fig 6. Nafion Membrane

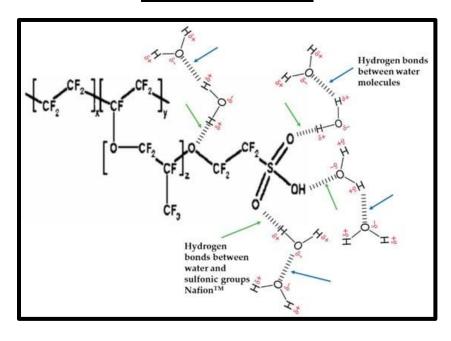


Fig 7. Polybenzimidazole Membrane

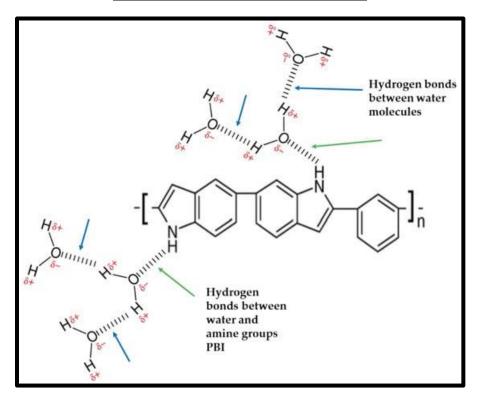


Fig 8. Sulfonated Poly Arylene Ether Ketone (SPEEK) Membrane

Fig 9. Polyimide Membrane

<u>Table 3: Comparison of LT-PEMs based on thickness, water uptake, In-Exchange Capacity (IEC), Proton Conductivity and Power Density</u>

| Sl No. | Membrane | Operating Condition | | | Thickness (µm) | Water Uptake (%) |
|-----------|---------------------------|-----------------------------|------------------|-------------------------------------|-------------------|------------------------|
| | | Pressure (atm) (*MPa) | Temperature (°C) | Relative humidity (RH) (%) | | |
| 1 | Nafion | 1 | 25 | - | 183 | 33 |
| 2 | BPSH-BPS | - | 80 | - | - | 60 |
| 3 | BisAF-BPSH | - | 80 | - | 150 | 71 |
| 4 | Nafion 117-Ce | - | 60 | 70 | - | 26.4 |
| 5 | Nafion+CeO2 | 1 | 90 | 100 | 35 | |
| 6 | Nafion+CeO2 | 1 | 70 | 100 | 160 | 25.9 |
| 7 | SPEEK | 1 | 25 | | 300 | 600 |
| 8 | SPEEK/BPO4 | 1 | 25 | 100 | 200 | 116 |
| 9 | SPEEK | - | 25 | 100 | 82 | 120 |
| 10 | SPEEK/PSSA-g- PVDF | - | 65 | 50 | 50 | 35 |
| 11 | AP6FSPEEK | | 80 | 100 | - | 69.3 |
| 12 | SPEEK/NIM-SiO2 | 0.1* | 60 | 100 | 110 – 130 | 52.6 |
| 13 | C-SPAKES/Im- MOF-801-4 | - | 90 | 100 | - | 12.5 |
| 14 | SPAES50 | 1 | 30 | 45 | 20 | 27.2 |

1atm=0.1Mpa

| Sl. No | Membrane | Conductivity (mS/cm) | IEC (meq/g) (*mmol.gm) | Power density (mW/cm^2) |
|-----------|-----------------------|----------------------|------------------------------|-------------------------|
| 1 | Nafion | 35 | 0.93 | 126.04 |
| 2 | BPSH-BPS | 95 | 1.28 | - |
| 3 | BisAF-BPSH | 130 | 1.6 | - |
| 4 | Nafion 117-Ce | - | 0.89* | 433 |
| 5 | Nafion+CeO2 | 88.3 - | | - |
| 6 | Nafion+CeO2 | 176 | 0.84* | 120 |
| 7 | SPEEK | 10 | 1.95 | - |
| 8 | SPEEK/BPO4 | 6.1 | - | - |
| 9 | SPEEK | 16.8 | 2.3 | - |
| 10 | SPEEK/PSSA-g-PVDF | 720 | - | 470.52 |
| 11 | AP6FSPEEK | 87 | 1.65* | - |
| 12 | SPEEK/NIM-SiO2 | 220 | 1.73* | 92.8 |
| 13 | C-SPAKES/Im-MOF-801-4 | 66 | 0.68* | 15.5 |
| 14 | SPAES50 | 112.3 | 1.89 | - |

Table 4: Summary of Hydrogen Production By Water Splitting Technologies along with the types of diaphragm/membrane used, advantages, disadvantages, and efficiencies

| Water Splitting Technologies | Advantages | Disadvantages | Efficiency |
|---|---|--|------------|
| Alkaline Type of diaphragm: porous inorganic (asbestos, ceramic, cement) | Well established technology Economical, Very durable Operates at low temperature (30–80 °C) Inexpensive electro catalyst | High concentration corrosive electrolytes Limited current density (below 400 mA/cm2), Low operating pressure Low energy efficiency, Low gas purity | 60-80% |
| Solid oxide Types of membranes: oxygen ion ceramic electrolyte membrane, YSZ | Dual-function fuel cell and Electrolyzer Superior ionic conductivity Ultrapure hydrogen Excellent efficiency | Very high operating temperature (500–850 °C), Energy intensive process and not economical, Low durability (stability and degradation)Still immature technology—lab scale | 90 – ~100% |
| PEM Type of membranes: Nafion, PBI, SPEEK, polyethylene High hydrogen purity (up to 99.995%), High current density, High voltage efficiency, Dynamic operation | | High-cost catalysts, Mildly durable Costly membrane, More expensive stack materials compared to alkaline Partially established technology | 55 – 70% |
| AEM Types of membranes: A201 membrane, Selenion AMV, A901 membrane | Lower cost of catalysts Inexpensive stack components -(Nickel- based) | Low ionic conductivity Early stage of development Low power efficiency Low membrane stability Large Ohmic resistance loss Large catalyst loading | 50-70% |
| Acid-alkaline amphoteric Types of membranes: bipolar membrane, acid- doped PBI-based membranes, Nafion Reduced energy consumption, Reduced over potential, Hydroger production four times that of alkaline electrolysis | | Increased membrane resistance Need to use bipolar ion-exchange membrane, Need to use both acidic and alkaline electrolytes | ~100% |
| Microbial, Types of membranes: SPAES * / polyimide, SPEEK, SPEEK/PES, Nafion, AMI-7001, bipolar membranes, charge- mosaic membranes, microporous membranes | Requires only a low external voltage Uses organic materials | Still under development High internal resistance Complicated design Low rates of hydrogen production Fabrication and operational costs are high | 60–70% |
| Photo electrochemical Types of membranes: polyamide, Nafion based membrane | Direct solar to hydrogen conversion Simpler setup | Low conversion factor Low hydrogen production Still at infancy stage | <10% |

Table 5. Pipeline Material

| Pipeline Number | Material | Stream | Exit | Entry |
|--------------------|-------------------------|--------|-------------------------------|--------------------------------|
| 1 | Pretreated Feed (water) | Liquid | Reservoir/storage tank | Mixer |
| 2 | Water (Mixed) | Liquid | Mixer | Pump |
| 3 | Water (Pretreated Feed) | Liquid | Pump | Sediment Filter |
| 4 | Sediment (solids) | Mixed | Sediment Filter | Waste |
| 5 | Water | Liquid | Sediment Filter | Pump |
| 6 | Water (Treated) | Liquid | Separator | Pump |
| 7 | Water (Treated) | Liquid | Pump | Ion Exchanger |
| 8 | Water (Treated) | Liquid | Ion Exchanger | Carbon Filter |
| 9 | Carbon | Mixed | Carbon Filter | - |
| 10 | Water | Liquid | Carbon Filter | Heat Exchanger |
| 11 | Water (Heated) | Liquid | Heat Exchanger | Anion Electrode (PEM stack) |
| 12 | Water+O2 (Mix Stream) | Mixed | Anion Electrode (PEM Stack) | Separator |
| 13 | O2 | Vapor | Separator | Control Valve |
| 14 | O2 | Vapor | Control Valve | - |
| 15 | H2+H2O | Mix | Cathode Electrode (PEM Stack) | Extractor |
| 16 | Н2О | Liquid | Extractor | - |
| 17 | H2 | Vapor | Extractor | Dryer |
| 18 | H2 | Vapor | Dryer | Extractor |
| 19 | H2 | Vapor | Storage Tank | Compressor |
| 20 | H2 | Vapor | Compressor | Control Valve |
| 21 | H2 | Vapor | Control valve | Exit Pipeline |

Table 6. Equipment

| Sl No. | Equipment Number | Name | |
|--------|------------------|-------------------|--|
| 1 | B1 | Mixer | |
| 2 | B2 | Pump | |
| 3 | В3 | Sediment Filter | |
| 4 | В4 | Extractor | |
| 5 | B5 | Control Valve | |
| 6 | В6 | Ion Exchanger | |
| 7 | В7 | Control Valve | |
| 8 | В8 | Carbon Filter | |
| 9 | В9 | Heat Exchanger | |
| 10 | B10 | Anion Electrode | |
| 11 | B11 | Cathode Electrode | |
| 12 | B12 | PEM Stack | |
| 13 | B13 | Extractor | |
| 14 | B14 | - | |
| 15 | B15 | Dryer | |
| 16 | B16 | H2 Storage | |
| 17 | B17 | Compressor | |
| 18 | B18 | Control Valve | |

Table 7. Failure Mode Analysis

| Sl No. | FMEA failure mode | | | |
|--------|---|---|--|--|
| 1 | Hydrogen embrittlement Open/close failure of automatic val- | | | |
| 2 | Cholride stress corrosion cracking | nolride stress corrosion cracking Open/close failure of control valve | | |
| 3 | Corrosion | Open/Close failure of check valve | | |
| 4 | Fatigue Pressure indicator failure | | | |
| 5 | Loosening of threaded joints | Temperature indicator failure | | |
| 6 | Weld Defect | Safety valve failure | | |
| 7 | Defect Filter clogging | | | |
| 8 | Deterioration of sealing material Filter damage | | | |
| 9 | Gland leakage | Start/stop failure | | |
| 10 | Seat leakage | Voltage indicator failure | | |
| 11 | Damage of Nafion membrane | | | |

Fig 10. HAZOP Methodology

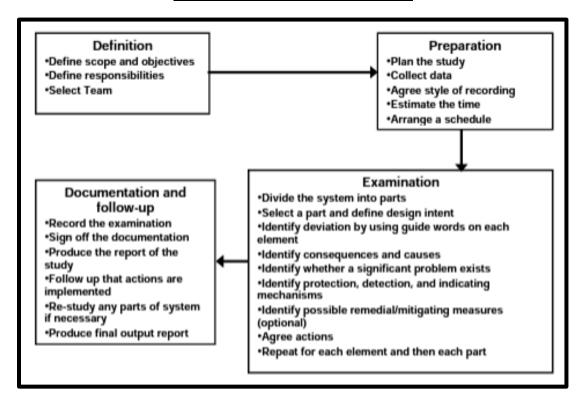


Fig 11. Generic Severity Rating Scale

Severity Rating Scale

| Rating | Description | Definition (Severity of Effect) | | |
|--------|---------------------|---|--|--|
| 10 | Dangerously high | Failure could injure the customer or an employee. | | |
| 9 | Extremely high | Failure would create noncompliance with federal regulations. | | |
| 8 | Very high | Failure renders the unit inoperable or unfit for use. | | |
| 7 | High | Failure causes a high degree of customer dis- satisfaction. | | |
| 6 | Moderate | Failure results in a subsystem or partial mal- function of the product. | | |
| 5 | Low | Failure creates enough of a performance loss to cause the customer to complain. | | |
| 4 | Very Low | Failure can be overcome with modifications to the customer's process or product, but there is minor performance loss. | | |
| 3 | Minor | Failure would create a minor nuisance to the customer, but the customer can overcome it without performance loss. | | |
| 2 | Very Minor | Failure may not be readily apparent to the cus- tomer, but would have minor effects on the customer's process or product. | | |
| 1 | None | Failure would not be noticeable to the customer and would not affect the customer's process or product. | | |

Table 8. HAZOP Worksheet

PHA Worksheets

| Node 1: (Liquid Stream) Reservoir, Mixer, Pump, sediment Filter, H2O-O2 sep |
|---|
|---|

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------------------|---|--|---|---|--------------------|
| 1.1. High Pressure | 1.1.1. Potential overpressure at the separator. Potential loss of mechanical integrity. Potential rupture of the separator resulting in large release of gas and liquid to which can cause fire upon contact to an ignition source. | above the equipment | 6. install a spill back to the low pressure separator | 2 | |
| | | | Operator response to high pressure alarm | | |
| | | | Install a pressure gauge on the upstream and on the separator | | |
| | | | High Integrity Pressure Protection Systems | | |
| | | 1.1.1.2. External fire in the vicinity of the separator | 5. High pressure shutdown | | |
| | | | 4. Install a thermal expansion relief on the valved section | | |
| | | | Install a pressure gauge on the upstream and on the separator | | |
| | | | Operator response to high pressure alarm | | |

| 1.2. Low Pressure | 1.2.1. Potential loss of light and intermediate components lost to the gas phase in the separator resulting in less liquid. | 1.2.1.1. Pipeline leak or rupture | 9. operator response to low pressure alarm 8. low flow shutdown 7. Low pressure shutdown | 2 | |
|--------------------------|---|---|--|---|--|
| | | 1.2.1.2. Fitting and flanges leakage | 9. operator response to low pressure alarm 8. low flow shutdown 7. Low pressure shutdown | | |
| | | 1.2.1.3. control valve failure | 9. operator response to low pressure alarm 8. low flow shutdown | | |
| | | | low pressure shutdown lo. increase backup pump | | |
| | | 1.2.1.4. increase in pumping capacity | low flow shutdown Low pressure shutdown | | |
| | | | operator response to low pressure alarm revision on the design | | |
| | | | specification on the pump | | |
| 1.3. High Temperature | 1.3.1. High pressure builds up in the transfer line and separator. | 1.3.1.1. Cooler failure | Operator response to high temperature alarm 15. release pressure relief valve | 2 | |
| | | | 14. Regular system checking | | |

k is the second continuous con

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|--|---|---|---|--------------------|
| | | | 13. Install temperature sensor and alarm | | |
| | inter | 1.3.1.2. High intermediate storage | 16. Operator response to high temperature alarm | | |
| | | temperature | 15. release pressure relief valve | | |
| | | | 14. Regular system checking | | |
| | | | 13. Install temperature sensor and alarm | | |
| | | 1.3.1.3. Pressure indicator failure | 16. Operator response to high temperature alarm | | |
| | 1.3.2. Difficult to control the 1.3.2.1. | | 15. release pressure relief valve | | |
| | | | 14. Regular system checking | | |
| | | | 13. Install temperature sensor and alarm | | |
| | | 16. Operator response to high temperature alarm | 2 | | |
| | | controller fallace | 15. release pressure relief valve | | |
| | | | 14. Regular system checking | | |
| | | | 13. Install temperature sensor and alarm | | |
| | | | 17. An automatic shutdown of the reactor when its temperature increases abnormally. | | |

| 1.4. Low Temperature | 1.4.1. Water sump and drain line freeze up. | 1.4.1.2. Winter freeze | 17. An automatic shutdown of the reactor when its temperature increases abnormally. 20. Operator response to low temperature alarm 19. supply enough energy 13. Install temperature sensor and alarm 18. Install temperature transmitter 17. An automatic shutdown of the reactor when its temperature increases abnormally. 20. Operator response to low temperature alarm 19. supply enough energy 13. Install temperature sensor and alarm 18. Install temperature sensor and alarm | 2 | |
|-------------------------|---|---|---|---|--------------------|
| Deviation | Consequence | Cause 1.4.1.3. Heating element dysfunction 1.4.1.4. Excessive heat transfer | Safeguard 17. An automatic shutdown of the reactor when its temperature increases abnormally. 20. Operator response to low temperature alarm 13. Install temperature sensor and alarm 18. Install temperature transmitter 17. An automatic shutdown of the reactor when its temperature increases abnormally. 20. Operator response to low temperature alarm 13. Install temperature sensor and alarm 14. Install temperature transmitter | L | PHA Recommendation |

| 1.5. High Level | 1.5.1. Potential overfill of the separator will leak into the O2 export pipeline. Potential for offspec product. | 1.5.1.1. Liquid outlet is closed | 25. Install a backup drain 24. High level Shutdown 14. Regular system checking 23. Operator response to high level alarm 22. Monitor the flow rate | 2 | |
|--------------------|--|--|--|---|--|
| | | 1.5.1.2. Blockage in | 24. High level Shutdown | | |
| | | vapor stream | 14. Regular system checking | | |
| | | | 23. Operator response to high level alarm | | |
| | | | 22. Monitor the flow rate | | |
| | | 1.5.1.3. Failure of shutdown | 14. Regular system checking | | |
| | | valve | 23. Operator response to high level alarm | | |
| | | | 22. Monitor the flow rate | | |
| | | | 26. Install a secondary backup valve/pump/route | | |
| | | 1.5.1.4. Too high flow rate of recycle for mixer | 23. Operator response to high level alarm | | |
| | | | 24. High level Shutdown | | |
| | | | 14. Regular system checking | | |
| | | | 21. Monitor the flow rate of recycle | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-------------------|--|---|---|---|---|
| 1.6. Low Level | 1.6.1. Potential for loss of mechanical integrity. Potential for rupture of vessel or associated | 1.6.1.1. Valve is partially closed | 31. Install a level indicator and controller | 2 | Interlock to be configured to stop transfer pump on desired |
| | piping. | | 28. low level shutdown | | equipment |
| | | | 27. Operator response to low level alarm | | |
| | | | 30. install a backup valve | | |
| | | 1.6.1.2. Pipeline is partly blocked | 32. install a backup pathway or a secondary route | | |
| | | | 14. Regular system checking | | |
| | | | 29. monitor the flow rate | | |
| | | | 28. low level shutdown | | |
| | | | 27. Operator response to low level alarm | | |
| | | | 31. Install a level indicator and controller | | |
| | | 1.6.1.3. Pump is not in full | 14. Regular system checking | | |
| | | operation | 29. monitor the flow rate | | |
| | | | 28. low level shutdown | | |
| | | | 31. Install a level indicator and controller | | |
| | | | 27. Operator response to low level alarm | | |
| | | 1.6.1.4. Too low flow rate of recycle for mixer | 27. Operator response to low level alarm | | |
| | | and the second | 14. Regular system checking | | |
| | | | 21. Monitor the flow rate of recycle | | |

h

| valve failure separator 36. Operator response to high flow alarm | 34. install independent level transmitter 33. Install automatic pump shutdown 1.7.1.2. Control 37. Monitor the flow into the | 14. Regular system checking 35. Install high level indicator | 1.7.1. The mixture is not properly separated. Decrease product quality. Decrease efficiency of sediment filter. 1.7.1. The mixture is not properly pump pump malfunctions 37. Monitor the flow into the separator 36. Operator response to high flow alarm |
|---|--|---|---|
|---|--|---|---|

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|-------------|---------------------------------|---|---|--------------------|
| | | | 14. Regular system checking | | |
| | | | 35. Install high level indicator | | |
| | | | 34. install independent level transmitter | | |
| | | | 33. Install automatic pump shutdown | | |
| | | 1.7.1.3. level control fails | 37. Monitor the flow into the separator | | |
| | | | 36. Operator response to high flow alarm | | |
| | | | 14. Regular system checking | | |
| | | | 35. Install high level indicator | | |
| | | | 34. install independent level transmitter | | |
| | | | 33. Install automatic pump shutdown | | |

| 1.8. Low | 1.8.1. Low supply of mixture, rate | | 41. Monitor the flow rate of the | 2 | |
|----------|------------------------------------|-----------------|----------------------------------|---|--|
| Flow | of reaction decrease | leakage | recycle for mixer | | |
| | | | 39. operator response to low | | |
| | | | flow alarm | | |
| | | | 40. install low flow indicator | | |
| | | | 14. Regular system checking | | |
| | | | 38. Monitor the flow out of the | | |
| | | | separator | | |
| | | | 42. Material loss | | |
| | | 1.8.1.2. Flange | 41. Monitor the flow rate of the | | |
| | | leakage | recycle for mixer | | |
| | | | 39. operator response to low | | |
| | | | flow alarm | | |
| | | | 40. install low flow indicator | | |
| | | | 14. Regular system checking | | |
| | | | 38. Monitor the flow out of the | | |
| | | | separator | | |
| | | | 42. Material loss | | |
| | | 1.8.1.3. Pump | 41. Monitor the flow rate of the | | |
| | | malfunction | recycle for mixer | | |
| | | | 39. operator response to low | | |
| | | | flow alarm | | |
| | | | 40. install low flow indicator | | |
| | | | 14. Regular system checking | | |
| | | | 38. Monitor the flow out of the | | |
| | | | | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|----------------------|---|-----------------------------------|--|---|--------------------|
| | | | separator 42. Material loss | | |
| | | 1.8.1.4. Level control fails | 41. Monitor the flow rate of the recycle for mixer | | |
| | | | 39. operator response to low flow alarm | | |
| | | | 40. install low flow indicator | | |
| | | | 14. Regular system checking | | |
| | | | 38. Monitor the flow out of the separator | | |
| 1.9. No Flow | 1.9.1. Loss of feed to the separator. Pump overheats. Potential discharge outside | 1.9.1.1. Supply tank is empty | 45. ensure good communication with intermediate storage operator | 2 | |
| | | 1.9.1.2. Pumps | 14. Regular system checking | | |
| | | fail to run | 43. Operator response to low flow alarm | | |
| | | 1 | 47. Check design specification (revision needed) | | |
| | | | 46. Install a low level alarm | | |
| | | 1.9.1.3. Pipeline is fractured | 14. Regular system checking | | |
| | | is fractured | 43. Operator response to low flow alarm | | |
| | | | 46. Install a low level alarm | | |
| | | 1.9.1.4. Valve is closed | 49. Install a backup route to redirect the flow | | |
| | | | 43. Operator response to low flow alarm | | |
| | | | 14. Regular system checking | | |
| 1.10. Composition | 1.10.1. Contaminated water, decrease in efficiency of the separator, product not achieved | 1.10.1.1. pipeline fracture | 48. Constant water quality checking | 2 | |
| | | | 14. Regular system checking | | |

Node 2: (Vapor Stream) O2 vented out from the extractor

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|---|--|--|---|---|-----------------------|
| 2.1. High Pressure 2.1.1. Poor Separation, Potential pressure equilibrium from separator to the gas export line, potential over pressurization of discharge piping, rupture of tubes, potential loss of mechanical integrity, potential fire and explosion, oxygen rich environment affect the PPE, potential internal damage to the compressor. | equilibrium from separator to the gas export line, potential over pressurization of discharge piping, | 2.1.1.1. utility malfunction | 51. Install a pressure relief valve | | |
| | | 3. Operator response to high pressure alarm | | | |
| | | 50. Install a pressure gauge | 8 | | |
| | | 2.1.1.2. Pressure indicator fails | 5. High pressure shutdown | 8 | |
| | | 3. Operator response to high pressure alarm | | | |
| | | 51. Install a pressure relief valve | | | |
| | | 2.1.1.3. Inadvertent closure of SIS valve downstream | | | |
| | | | 53. Gas detection alarm | | |
| | | | 5. High pressure shutdown | | |
| | | | 3. Operator response to high pressure alarm | 8 | |
| | | | 51. Install a pressure relief valve | 9 | |

| 2.2. Low Pressure | 2.2.1. Potential vacuum conditions, potential valve damage, commercial issue with asset damage. | 2.2.1.1. Shutdown valve fails | 3. Operator response to high pressure alarm |
|----------------------|---|---|--|
| | | | 5. High pressure shutdown |
| | | 2.2.1.2. Level indicator fails affecting the control valve | 3. Operator response to high pressure alarm |
| | | contoi vaive | 5. High pressure shutdown |
| | | 2.2.1.3. Inadvertent closure of shutdown valve | 60. Automated low pressure shutdown upstream of the separator |
| | | | 3. Operator response to high pressure alarm |
| | | | 5. High pressure shutdown |

h

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|-------------|-----------------------------|--|---|--|
| | | | 126. Oxygen gas detectors | T | 11. Consider vented deflagration panels. |
| | | | 58. install thermal expansion relief valve | | |
| | | | 16. Operator response to high temperature alarm | | |
| | | | 55. High temperature shutdown | | |
| | | 2.3.1.2. Utility failure | 126. Oxygen gas detectors | | |
| | | | 58. install thermal expansion relief valve | | |
| | | | 16. Operator response to high temperature alarm | | |
| | | | 55. High temperature shutdown | | |
| | | | 127. Secondary backup cooler | | |

| 2.4. Low Temperature | 2.4.1. Pipeline will freeze up. Decrease in flow out. O ₂ vapor concentration increases. | 2.4.1.1. Winter freeze | 20. Operator response to low temperature alarm 59. Install temperature indicator | |
|-------------------------|--|--|---|--|
| 2.5. High Level | 2.5.1. Potential overfills of the separator with liquid flow to the gas export pipeline. | 2.5.1.1. Blockage at the outlet stream | 14. Regular system checking 23. Operator response to high level alarm 62. Install level controller 61. Install level indicator | |
| 2.6. Low Level | 2.6.1. Potential for gas blow by into the separator causing overpressure. Potential loss of mechanical integrity. Potential rupture of vessel or associated piping. Potential fire/explosion | 2.6.1.1. inlet stream leakage | 126. Oxygen gas detectors 14. Regular system checking 63. Fit low level alarm 27. Operator response to low | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-------------------|---|---|---|---|-----------------------|
| | | | level alarm | Г | |
| | | 2.6.1.2. faulty level control measurement | 14. Regular system checking | | |
| | | measurement | 27. Operator response to low level alarm | | |
| 2.7. High Flow | 2.7.1. Potential accumulation of vapor resulting in overpressure of separator, potential rupture of vessel resulting in release of vapor potential fire/explosion | 2.7.1.1. failure of flow indicator controller causing | 14. Regular system checking | | |
| | | the flow valve to open | 15. release pressure relief valve | | |
| | | | 3. Operator response to high pressure alarm | | |
| | | | 5. High pressure shutdown | | |
| 2.8. Low Flow | 2.8.1. No credible safety hazard identified | 2.8.1.1. No additional causes | | | |
| 2.9. No Flow | 2.9.1. O2 cannot be vented. Separator will over pressurize and rupture due to no means of release. O2 mixes back with H2 causing | 2.9.1.1. Blockage at the gas export line and the | 66. install pressure relief valve | | |
| | explosion | separator outlet | 67. Install a secondary backup route to vent out the gas | | |
| | | | 65. install flow controller | | |
| | | | 64. Install flow indicator | 3 | |
| | | | 14. Regular system checking | 3 | |

| 2.10 | 2.10.1 D | 2 10 1 1 | 14 D 1 | |
|-------------|---|---------------------|----------------------|--|
| 2.10. | 2.10.1. Potential of large flammable gas and | 2.10.1.1. | 14. Regular system | |
| Composition | liquid release to atmosphere, potential significant | Introduction of gas | checking | |
| | commercial and environmental impacts | into the liquid | | |
| | | stream due to | 57. Install fans for | |
| | | rupture | dilution of | |
| | | • | flammable gas | |
| | | | | |
| | | | 53. Gas detection | |
| | | | alarm | |
| | | | | |
| | | | 56. valves and | |
| | | | piping made of | |
| | | | elastomers due to | |
| | | | low ignition | |
| | | | temperature | |
| | | | | |

Node 3: (Liquid Stream) Separator, Pump, Ion Exchange Filter, Absorber, Heat Exchanger, Proton Exchange Membrane Stack.

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------------------|--|---------------------------------------|---|---|---|
| 3.1. High Pressure | 3.1.1. Potential deadheading of pumps resulting in pump damage due to overheating. Commercial issue with asset | 3.1.1.1. Flooding | 5. High pressure shutdown | 2 | 6. In case of water spill Firefighters' protective clothing gloves, helmet, |
| | damage. Poor Separation. Flooding/leakage hazards. Potential fire/explosion. Transfer line subjected to full pump delivery or surge pressure. Burst and release of gases to surroundings. Potential contamination of the oxygen-water line with possible overpressure. 3.1.1.2. Isolation valve closed in error level controller valve failure | | 68. Install flow indicator to provide spillback to the separator | | running or bunker coat, running or bunker pants. Protects against heat, hot water, and some particles. |
| | | | 16. Operator response to high temperature alarm | | |
| | | Isolation valve closed in error or | 16. Operator response to high temperature alarm | | |
| | | AND THE PROPERTY OF THE PARTY OF | 5. High pressure shutdown | | |
| | | | 14. Regular system checking | | |
| | | 3.1.1.3. Valve failure | 68. Install flow indicator to provide spillback to the separator | | |
| | | | 16. Operator response to high temperature alarm | | |
| | | | 5. High pressure shutdown | | |
| | | | 14. Regular system checking | | |
| | | | | 68. Install flow indicator to provide spillback to the separator | |

| 1 1 | 3.1.1.4. Pump | 16. Operator response to | |
|-----|-------------------|-------------------------------|--|
| | Failure | high temperature alarm | |
| | | | |
| | | 5. High pressure shutdown | |
| | | | |
| | | 14. Regular system | |
| | | checking | |
| | | | |
| | | 68. Install flow indicator to | |
| | | provide spillback to the | |
| | | separator | |
| | 3.1.1.5. Flow | 16.0 | |
| | | 16. Operator response to | |
| | indicator failure | high temperature alarm | |
| | | 5. High pressure shutdown | |
| | | 3. High pressure shutdown | |
| | | 14. Regular system | |
| | | checking | |
| | | | |
| | | 68. Install flow indicator to | |
| | | provide spillback to the | |
| | | separator | |
| | | • | |
| | 3.1.1.6. | 16. Operator response to | |
| | Shutdown valve | high temperature alarm | |
| | inadvertent | | |
| | closure | 5. High pressure shutdown | |
| | | | |
| | | 14. Regular system | |
| | | checking | |
| | | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|-------------|-------------------------------------|--|---|--------------------|
| | | | 68. Install flow indicator to provide spillback to the separator | | |
| | | 3.1.1.7. O2/H20 pipeline rupture | 14. Regular system checking | | |
| | | | 133. Combustible gas sensor shuts down the Electrolyzer | | |

| 3.2. Low | 3.2.1. Potential pump cavitation | 3.2.1.1. | 70. Install pressure | 2 | |
|-------------|---|--------------------------------|---------------------------|---|--|
| Pressure | resulting in pump damage. | Unstable | indicator and controller | | |
| | Commercial issue with asset damage. Product cannot be | condition | 43. Operator response to | | |
| | removed. Not achieved desired | | low flow alarm | | |
| | operations. | | 69. Low pressure shutdown | | |
| | | 1 | 70. Install pressure | | |
| | | pump capacity | indicator and controller | | |
| | | | 43. Operator response to | | |
| | | | low flow alarm | | |
| | | | 69. Low pressure shutdown | | |
| | | 3.2.1.3. Failure | 70. Install pressure | | |
| | | of shutdown valve | indicator and controller | | |
| | | | 43. Operator response to | | |
| | | | low flow alarm | | |
| | | | 69. Low pressure shutdown | | |
| | | 3.2.1.4. Valve | 70. Install pressure | | |
| | | blocked in pump suction | indicator and controller | | |
| | | | 43. Operator response to | | |
| | | | low flow alarm | | |
| | | | 69. Low pressure shutdown | | |
| 3.3. High | 3.3.1. Difficult to remove excess | 3.3.1.1. | 20. Operator response to | 2 | |
| Temperature | heat | Temperature control failure | low temperature alarm | | individual air suction blower to heat exchanger should be |
| | | | 59. Install temperature | | stopped on High Temperature. |
| | | | indicator | | |
| | | | 18. Install temperature | | |
| | | | transmitter | | |
| | 3.3.2. difficult to control reaction, | 3.3.2.1. Failure | 14. Regular system | 2 | |
| | Lower yield, Increase production cost | in cooler | checking | | |
| | | | 20. Operator response to | | |
| | | | low temperature alarm | | |
| | | | 59. Install temperature | | |
| | | | indicator | | |
| | | | 18. Install temperature | | |
| | | | transmitter | | |
| | | 3.3.2.2. | 14. Regular system | | |
| | l | L | | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-------------------------|--|---|--|---|--------------------|
| | | Superheated steam supply | checking 20. Operator response to | | |
| | | | low temperature alarm | | |
| | | | 59. Install temperature indicator | | |
| | | | 18. Install temperature transmitter | | |
| 3.4. Low Temperature | 3.4.1. Poor separation | 3.4.1.1. Heating system malfunction | 20. Operator response to low temperature alarm | 2 | |
| | | maranetton | 14. Regular system checking | | |
| | | | 72. Increase heat duty of heating | | |
| | | | 71. Monitor the temperature of the tank | | |
| 3.5. High Level | 3.5.1. Accumulation in the equipment, flooding/leaking | 3.5.1.1. Excessive feed | 22. Monitor the flow rate | 2 | |
| | hazards | | 62. Install level controller | | |
| | | | 74. install level indicator | | |
| | | | 23. Operator response to high level alarm | | |
| | | | 64. Install flow indicator | | |
| | | 3.5.1.2. Flow level controller failed | 14. Regular system checking | | |
| | | 3.5.1.3. Blockage in | 22. Monitor the flow rate | | |
| | | vapor stream | 23. Operator response to high level alarm | | |
| | | | 14. Regular system checking | | |
| | | | 75. Monitor the level | | |

h

| 3.6. Low | 3.6.1. Increase production cost, | _ | 78. Install monitoring | 2 | |
|----------|----------------------------------|---------------|-----------------------------|---|--|
| Level | backflow of material | malfunction | system | | |
| | | | 27. 0 | | |
| | | | 27. Operator response to | | |
| | | | low level alarm | | |
| | | | 26. Install a secondary | | |
| | | | backup valve/pump/route | | |
| | | | varve pump/route | | |
| | | | 77. Fast repair of the pipe | | |
| | | | leaking | | |
| | | | | | |
| | | | 76. Regular pipe cleaning | | |
| | | | | | |
| | | 3.6.1.2. Pipe | 78. Install monitoring | | |
| | | blockage | system | | |
| | | | | | |
| | | | 27. Operator response to | | |
| | | | | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|-------------|---------------------------|-----------------------------|-----|--------------------|
| | | | low level alarm | П | |
| | | | 26. Install a secondary | 1 | |
| | | | backup valve/pump/route | | |
| | | | 77. Fast repair of the pipe | | |
| | | | leaking | | |
| | | | 76. Regular pipe cleaning | 1 | |
| | | 3.6.1.3. Pipe | 78. Install monitoring | 1 | |
| | | leaking | system | | |
| | | | 27. Operator response to | 1 | |
| | | | low level alarm | | |
| | | | 26. Install a secondary | 1 | |
| | | | backup valve/pump/route | | |
| | | | 77. Fast repair of the pipe | 1 | |
| | | | leaking | | |
| | | | 76. Regular pipe cleaning | 1 | |
| | | 3.6.1.4. level | 78. Install monitoring | 1 | |
| | | controller malfunction | system | | |
| | | marrunction | 27. Operator response to | 1 | |
| | | | low level alarm | | |
| | | | 26. Install a secondary | 1 | |
| | | | backup valve/pump/route | | |
| | | | 77. Fast repair of the pipe | 1 | |
| | | | leaking | | |
| | | | 76. Regular pipe cleaning | 1 | |
| | | | 79. Increase the feed flow | 1 I | |

| Flow heating process, more | 3.7.1. Difficult to control the | 3.7.1.1. failure in | 5. High pressure shutdown | 2 | 2. Interlock to be configured |
|----------------------------|--|---|---|---|---|
| | heating process, more reactants go to the reactor, incomplete | operation monitor | 81. Install control valve | | to stop feeding system on High difference in weight. |
| | reaction, pump damage, commercial issue with asset damage. | | 36. Operator response to high flow alarm | | |
| | | 14. Regular system checking | | | |
| | | 80. Install high flow detector and alarm | | | |
| | 3.7.1.2. More flow | 7. Low pressure shutdown | | | |
| | | in the stream | 5. High pressure shutdown | | |
| | | | 81. Install control valve | | |
| | | | 36. Operator response to high flow alarm | | |
| | | | 14. Regular system checking | | |
| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
| | | | 80. Install high flow detector and alarm | | |
| | | 3.7.1.3. low | 7. Low pressure shutdown | | |
| | | pressure in the export pipeline due | 5. High pressure shutdown | | |
| | | to a leak or rupture | 81. Install control valve | | |
| | | | 36. Operator response to high flow alarm | | |
| | | | 14. Regular system | | |

checking

80. Install high flow detector and alarm

| 3.8. Low Flow | 3.8.1. Waste time and energy, increase production cost, rate of | 3.8.1.1. Pump | 22. Monitor the flow rate | 2 |
|--|--|--------------------------|--|---|
| reaction decrease, decrease product concentration, and | reaction decrease, decrease product concentration, and | martunction | 14. Regular system checking | |
| | pump cavitation. | | 39. operator response to low flow alarm | |
| | | | 78. Install monitoring system | |
| | | | 82. change the leaking pipe | |
| | | | 77. Fast repair of the pipe leaking | |
| | | | 76. Regular pipe cleaning | |
| | | 3.8.1.2. pipe | 22. Monitor the flow rate | |
| | | blockage | 14. Regular system checking | |
| | | | 39. operator response to low flow alarm | |
| | | | 78. Install monitoring system | |
| | | | 82. change the leaking pipe | |
| | | | 77. Fast repair of the pipe leaking | |
| | | | 76. Regular pipe cleaning | |
| | | 3.8.1.3. pipe leaking | 22. Monitor the flow rate | |
| | | reaking | 14. Regular system checking | |
| | | | 39. operator response to low flow alarm | |
| | | | 78. Install monitoring system | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|-------------|-----------------------------------|---|---|--------------------|
| | | | 82. change the leaking pipe | | |
| | | | 77. Fast repair of the pipe leaking | | |
| | | | 76. Regular pipe cleaning | | |
| | | 3.8.1.4. Low supply of mixture | 22. Monitor the flow rate | | |
| | | supply of mixture | 14. Regular system checking | | |
| | | | 39. operator response to low flow alarm | | |
| | | | 78. Install monitoring system | | |
| | | | 82. change the leaking pipe | | |
| | | | 77. Fast repair of the pipe leaking | | |
| | | | 76. Regular pipe cleaning | | |

| | | | | _ | |
|-----------------|--|----------------------------|---|---|--|
| 3.9. No Flow | 3.9.1. No steam or air supply, waste time, cost and energy, no supply of feed and product. | 3.9.1.1. Pump failure | 43. Operator response to low flow alarm | 2 | |
| | supply of feed and product. | | 73. Install backup pump | | |
| | | | 14. Regular system checking | | |
| | | | 85. install control valve | | |
| | | 3.9.1.2. Pipe rupture | 43. Operator response to low flow alarm | | |
| | | | 73. Install backup pump | | |
| | | | 14. Regular system checking | | |
| | | | 85. install control valve | | |
| | | 3.9.1.3. Cooler failure | 43. Operator response to low flow alarm | | |
| | | | 73. Install backup pump | | |
| | | | 14. Regular system checking | | |
| | | | 85. install control valve | | |
| | | 3.9.1.4. valve is closed | 43. Operator response to low flow alarm | | |
| | | | 73. Install backup pump | | |
| | | | 14. Regular system checking | | |
| | | | 85. install control valve | | |
| | | 3.9.1.5. Pipe | 43. Operator response to | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|----------------------|--|------------------------------|--|---|---|
| | | blockage to PEM | low flow alarm | | |
| | | | 73. Install backup pump | | |
| | | | 14. Regular system checking | | |
| | | | 85. install control valve | | |
| | | | 86. secondary backup route to the PEM | | |
| 3.10. Composition | 3.10.1. Potential export pump cavitation, potential pump damage, commercial issue with | 3.10.1.1. Poor separation | 14. Regular system checking | 2 | |
| | asset damage, contamination at the absorber or the deionizer | | 43. Operator response to low flow alarm | | |
| | | | 69. Low pressure shutdown | | |
| | | 3.10.1.2. NPSH is too low | 14. Regular system checking | | |
| | | | 43. Operator response to low flow alarm | | |
| | | | 69. Low pressure shutdown | | |
| | | 3.10.1.3. Deionizer fails | 84. automated shutdown to the operation. | | |
| | | | 83. secondary route or a backup | | |
| | | | 14. Regular system checking | | |
| 3.11. Electrical | 3.11.1. Poor separation, loss of feed to the equipment. | 3.11.1.1. Mixer failure | 87. Check on agitation | 2 | |
| loss | recu to the equipment. | | 14. Regular system checking | | |
| | | 3.11.1.2. Pump failure | 88. operator response to alarm | | |
| | | | 14. Regular system checking | | |
| | | | 84. automated shutdown to the operation. | | |
| | 3.11.2. Static Charge generation | 3.11.2.1. Over- voltage | 135. Consider a backup DC-DC rectifier | 2 | Consider providing Human static discharge point near the rectifier or electrical subsystems and SOP to incorporate the same |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------------------|---|---|---|---|--|
| 4.1. High Pressure | 4.1.1. Potential hydrogen release, potential fire/explosion, PEM stack fails, Potential | 4.1.1.1. Valve closed and pump failure | 14. Regular system checking | 2 | 7. Consider revision of API standard RP 520 (Recommended Practice for Sizing, Selection, and Installation of |
| | spillback to the PEM stack due to over pressurization, potential | | 128. Hydrogen Gas detection alarm | | Pressure Relieving Devices) or NFPA 497 (Recommended Practice for the Classification of Flammable |
| | loss of mechanical integrity, potential rupture, potential internal damage to dryer, poor | | 53. Gas detection alarm | | Liquids, Gases or Vapors and of Hazardous (Classified) Locations for |
| | separation. Possible to send wet H2 downstream to users with impact downstream. | | 3. Operator response to high pressure alarm | | Electrical Installations in Chemical Process Areas) mainly used to classify hazardous areas. |
| | | | 5. High pressure shutdown | | Consider adding vented deflagration panels Consider vent design as per NFPA 2 standards |
| | | | 89. Install pressure relief valve | | |
| | | 4.1.1.2. Inadvertent closure to the SIS valve | 128. Hydrogen Gas detection alarm | | |
| | | | 14. Regular system checking | | |
| | | | 53. Gas detection alarm | | |
| | | | 3. Operator response to high pressure alarm | | |
| | | | 5. High pressure shutdown | | |
| | | | 89. Install pressure relief valve | | |

k is the contraction of the c

| 4.1.1.3. Pressure | 128. Hydrogen Gas | |
|---------------------|--------------------------------|--|
| indicator failure | detection alarm | |
| | 14. Regular system | |
| | checking | |
| | | |
| | 53. Gas detection | |
| | alarm | |
| | 3. Operator | |
| | response to high | |
| | pressure alarm | |
| | 5. High pressure | |
| | shutdown | |
| | | |
| | 89. Install pressure | |
| | relief valve | |
| 4.1.1.4. Steam | 128. Hydrogen Gas | |
| utility malfunction | detection alarm | |
| | 01 T | |
| | 91. Lower the reboiler duty | |
| | leooner daty | |
| | 90. Install pressure | |
| | gauge | |
| | | |

| | 14. Regular system | |
|--------------------|----------------------|--|
| | checking | |
| | | |
| | 53. Gas detection | |
| | alarm | |
| | | |
| | 3. Operator | |
| | response to high | |
| | pressure alarm | |
| | prosume unum | |
| | 5. High pressure | |
| | shutdown | |
| | siidtdowii | |
| | 90 Install pressure | |
| | 89. Install pressure | |
| | relief valve | |
| 4.1.1.5. Loss of | 120 Hudenson Co. | |
| I . | 128. Hydrogen Gas | |
| containment from | detection alarm | |
| Hydrogen storage | 110 P | |
| tank | 119. Pressure | |
| | switch to shut down | |
| | the compressor | |
| | | |
| | 118. Combustible | |
| | gas detector | |
| | | |
| | 117. Pressure relief | |
| | valve on Hydrogen | |
| | Compressor | |
| | | |
| | 116. Pressure | |
| | Indicator on | |
| | discharge line | |
| | | |
| | 115. Install a | |
| | pressure and | |
| | pressure Switch on | |
| | I- I | |
| | Hydrogen | |
| | compressor. | |
| 4116 P-! | 120 Tuestell | |
| 4.1.1.6. Drains on | 130. Install | |
| H2 separator left | pressure controller | |
| closed | and indicator | |
| | | |
| | 129. Install a | |
| | secondary drain as | |
| | backup | |
| | <u> </u> | |

| 4.2. Low | 4.2.1. Product cannot be | 4211 Increase | 9. operator response to | 2 | |
|----------|---------------------------------|---------------|--------------------------|---|--|
| Pressure | removed, undesirable operations | pumping | low pressure alarm | 2 | |
| riessure | removed, undesirable operations | capacity | low pressure ararin | | |
| | | capacity | 14. Regular system | | |
| | | | checking | | |
| | | | | | |
| | | | 93. Install low pressure | | |
| | | | alarm along with the | | |
| | | | PIC | | |
| | | | | | |
| | | | 92. Install pressure | | |
| | | | controller | | |
| | | | | | |
| | | | 73. Install backup | | |
| | | | pump | | |
| | | 4212 Unetable | 14. Regular system | | |
| | | condition | checking | | |
| | | condition | circuing | | |
| | | | 53. Gas detection | | |
| | | | alarm | | |
| | | | | | |
| | | | 3. Operator response to | | |
| | | | high pressure alarm | | |
| | | | | | |
| | | | 5. High pressure | | |
| | | | | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|-------------|-------|--|---|--------------------|
| | | | shutdown 89. Install pressure relief valve | | |

| 4.3. High Temperature | 4.3.1. Difficult to remove excessive heat, steam become superheated, difficult to control reaction, accumulation in column, membrane becomes dehydrated reducing the efficiency of the PEM stack - Delamination, catalyst degradation. | 4.3.1.1. Furnace malfunction | 122. Increase the speed of the HVAC system 17. An automatic shutdown of the reactor when its temperature increases abnormally. 16. Operator response to high temperature alarm 14. Regular system checking 13. Install temperature sensor and alarm | 2 | |
|--------------------------|--|--|---|---|--|
| | | 4.3.1.2. Temperature control failure | 131. Consider an explosion vent 17. An automatic shutdown of the reactor when its temperature increases abnormally. 16. Operator response to high temperature alarm 14. Regular system checking 13. Install temperature sensor and alarm | | |
| | | 4.3.1.3. failure in cooler | 17. An automatic shutdown of the reactor when its temperature increases abnormally. 16. Operator response to high temperature alarm 14. Regular system checking 13. Install temperature sensor and alarm | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|-------------|--|---|---|--------------------|
| | | 4.3.1.6. temperature controller malfunction | 17. An automatic shutdown of the reactor when its temperature increases abnormally. | | |
| | | | 16. Operator response to high temperature alarm | | |
| | | | 14. Regular system checking | | |
| | | | 13. Install temperature sensor and alarm | | |

| 4.4. Low Temperature | [16] A. | 4.4.1.1. Malfunction steam utility | 102. Install TIC 101. adjust inlet flow temperature 100. Monitor the temperature 20. Operator response to low temperature alarm 14. Regular system checking 97. Increase reboiler duty | | |
|-------------------------|---|--|---|--|--|
| | | 4.4.1.2. Too low heat duty of reboiler | 96. Temperature probe in reboiler 102. Install TIC 100. Monitor the | | |
| | | | 20. Operator response to low temperature alarm 14. Regular system checking | | |
| | | | 96. Temperature probe in reboiler 99. Increase heat duty of reboiler | | |
| | | | 98. Thermocouple of each stage | | |
| | | 4.4.1.3. Furnace failure | 102. Install TIC 100. Monitor the temperature 20. Operator response to low temperature alarm 14. Regular system | | |
| | | | 96. Temperature probe in reboiler | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|-------------|---|--|---|--------------------|
| | | | 99. Increase heat duty of reboiler | | |
| | | | 98. Thermocouple of each stage | | |
| | | 4.4.1.4. Low | 102. Install TIC | | |
| | | power supply | 100. Monitor the temperature | | |
| | | | 20. Operator response to low temperature alarm | | |
| | | | 14. Regular system checking | | |
| | | | 96. Temperature probe in reboiler | | |
| | | | 99. Increase heat duty of reboiler | | |
| | | | 98. Thermocouple of each stage | | |
| | | 4.4.1.5. | 102. Install TIC | | |
| | | Excessive heat transfer by cooler | 100. Monitor the temperature | | |
| | | | 20. Operator response to low temperature alarm | | |
| | | | 14. Regular system checking | | |
| | | | 96. Temperature probe in reboiler | | |
| | | | 99. Increase heat duty of reboiler | | |
| | | | 98. Thermocouple of each stage | | |

| 4.5. High Level | 4.5.1. Potential overfills of the dryer, storage tank, PEM stack. Potential for off spec product, potential fire/explosion. | 4.5.1.1. Failure of level controller | 66. install pressure relief valve | f 5. Consider Flame/fire retardant coveralls normal worn as an undergarment. |
|--------------------|---|--|---|--|
| | | controller | 14. Regular system checking Provides pro flash fires. Also can con the IFC fire | Provides protection from flash fires. |
| | | | | Also can consider reviewing the IFC fire code (General fire protection code |
| | | | 24. High level Shutdown | requirements. Special requirements for hydrogen |
| | | 4.5.1.2. Valve is closed | 66. install pressure relief valve | occupancies are only required if hydrogen exceeds MAQ (maximum |
| | | | 14. Regular system checking | allowable quantity)). |
| | | | 23. Operator response to high level alarm | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------|-------------|---|---|---|--------------------|
| | | | 24. High level Shutdown | | |
| | | 4.5.1.3. Failure of shutdown valve | 66. install pressure relief valve | | |
| | | Tarve | 14. Regular system checking | | |
| | | | 23. Operator response to high level alarm | | |
| | | | 24. High level Shutdown | | |
| | | 4.5.1.4. Convective transfer caused | 66. install pressure relief valve | | |
| | | by pressure gradient | 14. Regular system checking | | |
| | | | 23. Operator response to high level alarm | | |
| | | | 24. High level Shutdown | | |
| | | 4.5.1.5. Back diffusion of water from the | 66. install pressure relief valve | | |
| | | cathode to anode | 14. Regular system checking | | |
| | | | 23. Operator response to high level alarm | | |
| | | | 24. High level Shutdown | | |
| | | 4.5.1.6. Electro- osmotic drag from the anode | 66. install pressure relief valve | | |
| | | to cathode | 14. Regular system checking | | |
| | | | 23. Operator response to high level alarm | | |
| | | | 24. High level Shutdown | | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-------------------|--|--|--|---|--|
| 4.6. Low Level | 4.6.1. Potential for gas blow by to the cathode, potential overpressure at the PEM stack, potential for loss mechanical integrity, potential for rupture of vessel, potential release of flammable material, potential fire/explosion. | 4.6.1.1. Failure of level controller | Regular system checking Parular system checking To Operator response to low level alarm Install a secondary drain to reroute Install a pressure relief valve | | 8. Consider revising the SOP by implementing the IEC 60079-10-1 that is the international electro technical commission (applied mainly in explosive atmosphere - classification of areas) and EIGA with standard IGC Doc 121/04/E by performing ITPM - Inspection, Testing and |
| | | 4.6.1.2. Valve is too much open | 27. Operator response to low level alarm 103. Install a secondary drain to reroute 51. Install a pressure relief valve | | preventive measures (applied for mainly Hydrogen transportation pipelines using RAGAGEP document on hydrogen transport and distribution pipelines) |
| 4.7. High Flow | 4.7.1. Difficult to control the heating process, more reactants go to the reactor, incomplete reaction, increase production cost | 4.7.1.1. Failure in operation monitor | 36. Operator response to high flow alarm 14. Regular system checking 80. Install high flow detector and alarm | | 10. Consider revision of FM global with standard 7-91 for Hydrogen with is applied for Hydrogen supply and delivery systems and protections. No hydrogen concentration specified. or OSHA - 29 CFR 1910.103 |
| | | 4.7.1.2. More flow in one stream than the other | 36. Operator response to high flow alarm 80. Install high flow detector and alarm 14. Regular system checking 81. Install control valve | | |
| | | 4.7.1.3. valve is open too much | 105. Gas detection alarm in case of rupture 51. Install a pressure relief valve 80. Install high flow detector and alarm 36. Operator response to high flow alarm 14. Regular system checking 104. Install secondary backup valve | | |

| 4.8. Low Flow | 4.8.1. Increase production cost, waste time and energy, low supply of mixture, decrease product concentration, combustion of hot vapors with hazard to and loss of life. Possible formation of explosive | 4.8.1.1. Pump malfunction | 39. Operator response to low flow alarm 107. install a secondary pump 106. install secondary pipeline 14. Regular system checking | | 11. Consider vented deflagration panels. |
|------------------|--|---|--|---|--|
| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
| | mixture in Electrolyzer. Possible ignition, fire/explosion and injury to personnel. | | 76. Regular pipe cleaning | | |
| | | e/explosion and injury to 4.8.1.2. Pipe | 14. Regular system checking | | |
| | | | 27. Operator response to low level alarm | | |
| | | | 103. Install a secondary drain to reroute | | |
| | | | 51. Install a pressure relief valve | | |
| | | | 78. Install monitoring system | | |
| | | | 53. Gas detection alarm | | |
| | | | 14. Regular system checking | | |
| | | | 27. Operator response to low level alarm | | |
| | | | 103. Install a secondary drain to reroute | | |
| | | | 51. Install a pressure relief valve | | |
| | | 4.8.1.4. Loss of Nitrogen flow to anolyte/catholyte | 125. Low nitrogen shutdown of the Electrolyzer | | |
| | | tank before startup | 124. backup Nitrogen purge 123. Low nitrogen alarm | | |

| 4.9. No Flow | 4.9.1. No steam, H2 gas supply, waste time, cost and energy, potential fire/explosion due to pressure buildup in the storage tank for H2 gas. | 4.9.1.1. Pump failure | 81. Install control valve | |
|-----------------|--|--------------------------|---|--|
| | | | 108. Install a secondary backup route | |
| | | | 43. Operator response to low flow alarm | |
| | | | 14. Regular system checking | |
| | | | 73. Install backup pump | |
| | | 4.9.1.2. Pump rupture | 109. Install alarm | |
| | | | 81. Install control valve | |
| | | | 108. Install a secondary backup route | |
| | | | 43. Operator response to low flow alarm | |
| | | | 14. Regular system checking | |
| | | | 73. Install backup pump | |
| | | 4.9.1.3. Valve is closed | 3. Operator response to high pressure alarm | |
| | | | 14. Regular system checking | |
| | | | 30. install a backup valve | |

| Deviation | Consequence | Cause | Safeguard | L | PHA Recommendation |
|-----------------------------|--|--|---|---|--|
| | | | 110. Install a secondary tank connected to the primary storage tank to vent out the gas to reduce pressure buildup | | |
| 4.10. Composition | 4.10.1. Potential inflow of O2 to the H2 gas pipeline, Potential fire/ explosion. | 4.10.1.1. membrane has reached its end user | 105. Gas detection alarm in case of rupture 111. Stop operation | | |
| | | | 14. Regular system checking | | |
| 4.11. Electrical loss | 4.11.1. Loss of feed to the dryer, | 4.11.1.1. Pump failure | 113. Secondary backup system if AC-DC fails can shift to DC-DC rectifier | 3 | 9. Consider revision of the SOP for source FM Global with standard 5-1 for electrical equipment in Hazardous Equipment in Hazardous (classified) locations (applied mainly for any electrical equipment within an area deemed classified based on HAC study - Hazardous area classification) |
| | | 4.11.1.2. Dryer failure | 73. Install backup pump | | |
| | | | 14. Regular system checking | | |
| | | | 112. reroute the gas flow | | |
| | | | 111. Stop operation | | |
| | | | 84. automated shutdown to the operation. | | |
| | | | 114. Install secondary column | | |
| 4.12. High Cell Voltage | 4.12.1. Possible higher diffusion leading to formation of explosive | 4.12.1.1. DC- DC rectifier malfunction | 121. High temperature shutdown of the Electrolyzer | 3 | 11. Consider vented deflagration panels. |
| | mixture in Electrolyzer, possible ignition, fire/explosion and injury to personnel | maranetton | 120. High temperature alarms at the cell stack. | | |
| Additional work Po | 4.13.1. Possible to send water to the H2 stack. Possible freezing of the H2 vent stack, preventing the H2 to vent when reached. Possible overpressure of the H2 lines with possible ignition fire/explosion and injury to personnel. | 4.13.1.1. Water carryover into the H2 vent | 132. Set up water drain at H2 vent stack | 2 | 12. Consider setting up heat tracing in the H2 vent line. |
| | | | 122. Increase the speed of the HVAC system | | Consider vented deflagration panels. |
| 4.14. Maintenance | 4.14.1. Reduced lifetime of tank may cause damage. Hydrogen leakage to process area leading to fire or explosion. | 4.14.1.1. Hydrogen embrittlement Phenomenon | 134. Venting system installation 118. Combustible gas detector | 3 | 13. Replace tank material with stainless steel. |

Citation:

- 1. Burin Yodwong, Damien Guilbert, Matheepot Phattanasak, Wattana Kaewmanee, Melika Hinaje and Gianpaolo Vitale, AC-DC Converters for Electrolyzer Applications: State of the Art and Future Challenges, 2020.
- 2. Solanki, J.; Wallmeier, P.; Böcker, J.; Averberg, A.; Fröhleke, N. High-current variable-voltage rectifiers: State of the art topologies. IET Power Electron. 2015, 8, 1068–1080.
- 3. Buttler, A.; Spliethoff, H. Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review. Renew. Sustain. Energy Rev. 2018, 82, 2440–2454.
- 4. Hiva Kumar, S.; Himabindu, V. Hydrogen production by PEM water electrolysis—A review. Mater. Sci. Energy Technol. 2019, 2, 442–454.
- 5. Julio José Caparrós Mancera 1, Francisca Segura Manzano 1, José Manuel Andújar 1, Francisco José Vivas 1 and Antonio José Calderón, An Optimized Balance of Plant for a Medium-Size PEM Electrolyzer: Design, Control and Physical Implementation.
- 6. Ogawa, T.; Takeuchi, M.; Kajikawa, Y. Analysis of trends and emerging technologies in water electrolysis research based on a computational method: A comparison with fuel cell research. Sustainability 2018, 10, 478.
- 7. Meng Ni, Michael K.H. Leung *, Dennis Y.C. Leung, Energy and exergy analysis of hydrogen production by a proton exchange membrane (PEM) electrolyzer plant.
- 8. https://www.nationalgrid.com/stories/energy-explained/hydrogen-colour-spectrum.
- 9. Kirchsteiger, C., Vetere Arellano, A.L., Funnemark, E., Towards Establishing an International Incidents and Accidents Database (HIAD), Journal of Loss and Prevention in the Process Industries, 20, 2007, pp. 98-107.
- 10. Muhammad Nanda Faria, Asep Handaya Saputra, Process Hazard Analysis of Hydrogen Generation System with Electrolysis Process.
- 11. https://www.airproducts.com/industries/hydrogen-energy/hydrogen-basics
- 12. https://www.nrel.gov/research/eds-hydrogen.html

- 13. https://www.energy.gov/eere/fuelcells/hydrogen-production-electrolysis
- 14. N. Briguglio, G. Brunaccini, S. Siracusano, N. Randazzo, G. Dispenza, M. Ferraro, R. Ornelas, A.S. Arico, V. Antonucci, Design and testing of a compact PEM electrolyzer system.
- 15. https://hydrogentechworld.com/electrolyser-safety-through-certification#:~:text=A%20Hazards%20and%20operability%20study,during%20the%20general%20design%20phase.
- 16. Agata Godula-Jopek, Hydrogen Production: by Electrolysis.
- 17. Carmo, M; Fritz D; Mergel J; Stolten D (2013). "A comprehensive review on PEM water electrolysis". International Journal of Hydrogen Energy. 38 (12): 4901–4934.

- 18. Mohd Fadhzir Ahmad Kamaroddin, Nordin Sabli, Tuan Amran Tuan Abdullah ,Shamsul Izhar Siajam, Luqman Chuah Abdullah, Aishah Abdul Jalil and Arshad Ahmad, Membrane-Based Electrolysis for Hydrogen Production: A Review.
- 19. https://ptx-hub.org/water-electrolysis-explained/#:~:text=The%20basic%20principle%20of%20electrolysis,(%2B)%20%E2%8 0%93%20in%20the%20electrolysis%20cell.
- 20. https://www.precedenceresearch.com/proton-exchange-membrane-fuel-cells-market#:~:text=The%20global%20proton%20exchange%20membrane,highest%20market%20share%20in%202022.
- 21. https://wha-international.com/wha-enhances-electrolysis-system-safety/#:~:text=Electrolysis%20system%20safety%20safety%20safety%20surce%2C%20and%20approach%20to%20electrolysis%20safety,%2C%20ignition%20source%2C%20and%20oxidizer.
- 22. Naoya KASAI, The qualitative risk assessment of an electrolytic hydrogen generation system.
- 23. https://www.eclipsesuite.com/risk-severity/#:~:text=1%20%3D%20Negligible%3A%20The%20Risk%20is,requires%20immediate%20attention%20and%20action.
- 24. P.K. Bhattacharya, Water flooding in the proton exchange membrane fuel cell.
- 25. https://www.osha.gov/sites/default/files/publications/all_about_OSHA.pdf
- 26. https://www.wagnergroup.com/en/knowledge/knowledge-portal/fire-preventionoxygen-reduction-systems.html
- 27. https://ehs.uconn.edu/workplace-hazard-assessment-wha/
- 28. https://minearc.com/nitrogen-hazard-in-focus/#:~:text=If%20a%20continuous%20flow%20of,lightheaded%20and%20ultimately%2C%20lose%20consciousness.
- 29. Katerine A. Lemos, PhD. U.S. Chemical Safety and Hazard Investigation Board, AB Speciality Silicones, September 24, 2021, investigation report, pg 50-51.