Institute for Sustainable Process Technology

Enabling Safe Green Hydrogen Production on Industrial Scale

A Process Safety Study

Foreword

Dear Reader,

The production of hydrogen through electrolysis has been carried out at an industrial scale for more than a hundred years. One would think that there are only a few things we lack in our knowledge about the technology. In practice though, we find that when we try to scale-up and install an electrolyser system we quickly run into many unknowns. Especially when we want to scale up our technology and drive up its' productivity, while also dealing with power that may vary, unknowns appear – and many of them in relation to safety. And safe operation is crucial. For all.

In ISPT we shape partnerships with people from industry who are confronted with this kind of questions in their daily practice. When we bring them around the table, they find they have peers who run into the same challenges, and are in pursuit of answers, insights and best practices. This always leads to deep conversations and brings new insights, solutions and value to all involved. And the good news is, in ISPT, when we learn from working together, we write it down and share it with a broad audience, so you, our reader, can learn too.

The report you find in front of you is an excellent example of this kind of collaborative and open work. With our partners, both users and developers of electrolysers, we looked at approaches to do risk assessments. Our partners realized that a thorough understanding of the process safety risks for water electrolysers is essential to come to safe designs and operating practices. This is what they learned by working together. And now you can learn about them too! I hope this report will be as useful for you as the learning experience of our partners has been to them. And if you have any questions, feel free to reach out - we are here for you.

Happy reading, and safe operations!

- Dr. Ir. Andreas ten Cate
Program Director ISPT

Summary

Enabling Safe Green Hydrogen Production on Industrial Scale

The project ‘Safety Standardisation of Green Hydrogen Electrolyser Systems’ pertains to hydrogen produced on an industrial scale using renewable energy at Alkaline Water Electrolyser (AWE) and Proton Exchange Membrane (PEM) water electrolysis plants. This project is a follow up to the ISPT project ‘Safety Aspects of Green Hydrogen Production on Industrial Scale’ which mapped the basic safety aspects of green hydrogen production. This project is a deep dive and describes a process safety study based on generic hazard scenarios for hydrogen electrolysers that can be used by OEMs and operator owners for their plant-specific process risk assessments. Also, ATEX regulations have been reviewed. Standardisation is required to align industry and authorities for safe implementation and operation of electrolyser plants.

This report

In this public report, the key findings of a process safety study on water electrolysis is presented. The results of this project have been presented to the Dutch normalisation institute (NEN) and is used for the development of a dedicated National Technical Agreement (NTA). This report is successor of the first report ‘Safety Aspects of Green Hydrogen Production on Industrial Scale’. It is the result of a more than two-year long project involving extensive cooperation with safety experts from Battolyser Systems, Equinor, Green Hydrogen Systems, HyCC, ISPT, John Cockerill, NEN, Ørsted, Plug Power, RHDHV, RWE, Shell, TNO, VoltH2, Yara. The project was managed and executed by the Institute for Sustainable Process Technology (ISPT).

The scenarios

Discussions with project partners revealed that there are so many variations of the two main technologies covered in this report (AWE and PEM) that the generic process hazard scenarios developed can be used as a basis for plant-specific risk assessments, but cannot replace them. The generic hazard scenarios describe the risk of in-equipment explosions due to the unwanted presence of both hydrogen and oxygen, and the release of hydrogen into the indoor or outdoor atmosphere. This report only briefly deals with the release of oxygen. The studies do not cover other hazards related to water electrolysis such as the release of lye or occupational hazards such as contact with electrical parts.

Safety Studies

The causes for fire and explosion scenarios could be related to the following categories:

- Design aspects
- Membrane manufacturing and maintenance
- Degradation of cell and stack components
- Process control failures

The safety studies have been building on the bow ties which were developed during the previous ISPT project. The bow ties are helpful tools in discussions on threats, barriers and consequences between. The safety studies reveal that the risks associated with water electrolysis plants can be

reduced to an acceptable level if existing risk assessment and risk reduction methodologies currently applied at (petro)chemical plants are applied to water electrolysis plants. An effective Process Safety Management (PSM) system is considered essential. This includes inherent safe design, HAZOP and LOPA assessments, and (instrumental) safeguarding methods (SIL). Plant-specific details are important to define the required safety measures e.g. the presence of other (occupied) buildings, installations or people, available vs. required safety distances, etc.

The detection of excessive hydrogen and oxygen concentrations inside equipment is an important safety measure for reducing risk. The studies show that there are scenarios involving both PEM and AWE technologies that develop so rapidly that gas analysers are too slow and do not provide effective safeguards. Plant-specific risk assessments should therefore give particular consideration to the speed with which scenarios develop. Another important finding was that hydrogen (and oxygen) may accumulate in equipment other than major process equipment such as, for example, cooling circuits due to internal leakages. To detect deviating gas concentrations inside equipment it is preferable to locate sensors close to the stack. No suitable sample conditioning or sensors, however, are currently available to measure inside a two phase (gas/liquid) flow.

Calculations of crossover due to pinholes show that locally high concentrations in the stack header may be diluted with gas from other cells. This dilution reduces the likelihood of or even prevents propagation of fire and/or explosions to downstream equipment. Electrolysers are expected to run on intermittent renewable energy with load variation. Switching between low and normal load is not expected to directly influence the safety of electrolyser systems. However, higher occurrences of start-up and shutdown are expected to result in accelerated membrane degradation i.e. shorter cell component lifespans. Monitoring membrane degradation is important to identify and prevent hazardous gas compositions developing. Direct membrane monitoring is not possible, however (slow) changes in process parameter trends such as plant output, plant efficiency, increased cell and stack voltages, and gas concentrations may be indications of degraded membranes. Trend analysis is therefore important. Cell voltage monitoring may help in predicting the condition of the cells. In addition, maintenance programmes should pay attention to this aspect of electrolyser safety.

ATEX

ATEX regulations are important for assessing the risk of gas explosions and fires and for zoning purposes regarding area classification. Release calculations from a hole in equipment show that the tendency of hydrogen to rise (buoyancy) at a release is influenced to a major extent by emission direction, hole diameter, and pressure. Upward flow may only start at some distance from the release location. This causes significant different zoning for area classification.

The Netherlands utilises NPR7910-1 to this end. A review of NPR7910-1 revealed that it should not be used for hydrogen because it is based on much heavier, organic vapours. For example, the shapes and dimensions of hazardous zones described in the NPR differ signficantly from those for hydrogen. The European standard IEC60079 – 10-1 should be used instead of this NPR. Other ATEX-related aspects such as ventilation, preventing the accumulation of flammable substances, etc. also apply to hydrogen. Ventilation, whether (induced) forced or natural, may only be effective for leaks subject to the ATEX regulations, yet may be insufficient to prevent the formation of a flammable cloud in the event of major leaks (accidents).

Gas detectors can be an important safeguard for detecting increased concentrations of hydrogen and oxygen. The optimum position of gas detectors in rooms and buildings very much depends on the local situation.

Next steps

The standardisation of electrolysers will continue internationally with updating ISO22734, other norms e.g. by DNV JT301 and nationally with the NTA8221 – "Process safety for the production of hydrogen by electrolysis" and the PGS40 – Hydrogen production. It is important that alignment between industry and authorities will continue and best practices will be shared.

List of Abbreviations

AEM	Anion Exchange Membrane (electrolyser)
ALARP	As Low As Reasonably Practicable
ATEX	Atmosphères Explosibles
AWE	Alkaline Water Electrolysis
BBP	Bipolar Plate
BoP	Balance of Plant
CVM	Cell Voltage Monitoring
CFD	Computational Fluid Dynamics (modelling/simulations)
CCPS	Center for Chemical Process Safety, American Institute of Chemical Engineers AIChe
DDT	Deflagration to Detonation Transition
EU	European Union
G/L	Gas/Liquid
GW	GigaWatt
HAZOP	Hazard and Operability (study)
HAZID	Hazard Identification (study)
HSE	Health, Safety and Environment
ISPT	Institute for Sustainable Process Technology
KO	Knock-out (vessel)
LFL	Lower Flammability Limit
LO	Locked Open
LOC	Loss of Containment
LOPA	Layers of Protection Analysis
MOC	Management of Change
NFPA	National Fire Protection Association
OEM	Original Equipment Manufacturer
QRA	Quantitative Risk Analysis
PEM(WE)	Proton Exchange Membrane (Water Electrolysis)
PFD[1]	Probability of Failure on Demand
PFD[1]	Process Flow Diagram
PGS	Publicatiereeks Gevaarlijke Stoffen [series of publications on hazardous substances]
PSM	Process Safety Management
PSSR	Pre-Start-up Safety Review
PTL	Porous Transport Layer
QRA	Quantitative Risk Assessment
RFNBO	Renewable Fuel of Non-Biological Origin
SIL	Safety Integrity Level
SIS	Safety Instrumented System
SMS	Safety Management System
SOE	Solid Oxide Electrolysis
TNT	model: pressure (wave) calculations based on explosion of TriNitroToluene (TNT)
UFL	Upper Flammability Limit
WP	Work Package

1 PFD is used for both Probability of Failure on Demand and Process Flow Diagram. These abbreviations are common in the process industry and what exactly is meant is clear from the context it is used.

Definitions

- Diaphragm, membrane and cell separator: all are used to indicate the separation between the anode side and cathode side inside cells for AWE as well as for PEM
- Probability of Failure on Demand (PFD): is a measure of the availability of a safety function. It expresses the probability that a system might fail to function according to its design when it needs to.
- Different names are used for comparable aspects in the various types of risk assessments such as bow tie, HAZID/HAZOP and LOPA. This report uses the terms 'Threat', 'Cause' and 'Initiating event' for events that cause scenarios to develop. Secondly, the terms 'Barrier', 'Safeguard' and '(Independent) Protection Layer' are applied to methods aimed at or means for the prevention or mitigation of hazardous scenarios.
- Definitions in bow tie analyses:
  - Hazard: anything with the potential to cause harm that is part of normal operations i.e. a desired situation.
  - Top Event: unwanted situation due to a loss of control of a hazard.

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1. Introduction

The project 'Safety Standardisation of Green Hydrogen Electrolyser Systems' concerns hydrogen produced using renewable energy at an industrial scale utilising Alkaline Water Electrolyser (AWE) and Proton Exchange Membrane (PEM) electrolysis plants. This project is a follow up to the ISPT project 'Safety Aspects of Green Hydrogen Production on Industrial Scale' (2023) which inventoried the basic safety aspects of green hydrogen production [1]. The report describes the results of a process safety study for standardisation. Standardisation is required to align industry and authorities for safe implementation and operation of electrolyser plants. The standardisation aspects are covered in a second report, 'Enabling Safe Green Hydrogen Production – Needs for Standardisation'.

Background

The green hydrogen production using electrolysis is scaling up rapidly as it is essential if the EU wishes to achieve its climate goals. Since green hydrogen production facilities typically produce hydrogen and oxygen in their electrolysers, fire and explosion hazards accompany the large-scale implementation of electrolysis, in addition to other, familiar hazards, pertaining to chemical and industrial processes.

Electrolysis for hydrogen production is not a new technology. However, large-scale green hydrogen production using intermittent renewable electricity generated by wind and the sun is a new application of this existing technology. In addition, the current AWE and PEM technologies are being further developed. Other (new) technologies such as Solid Oxide Electrolysis (SOE) lie outside this project's scope. The renewable electricity used to drive the reaction that produces hydrogen is not always available. The power supply's intermittent nature means that the electrolysers will operate at varying electrical loads and may suffer frequent starts and stops. Pending technology specifics, both load variation when outside operating limits and start/stops potentially affect the degradation of the equipment and potentially increase the likelihood of events that initiate hazardous scenarios.

Focus of this Report

This report provides information for risk assessments to be done in the life cycle of water electrolysis plants. This includes a basic set of generic hazards scenarios, design considerations and risk prevention and reduction options to be considered in process safety studies for the design and operation of AWE and PEM electrolysers. The report focuses on fire and explosion hazards and is based on the design for a GigaWatt large-scale production plant [2]. Electrolyser products and systems offered by suppliers in the market can differ in scale, technology and design. The hazard scenarios are however generic and can be applied to all AWE and PEM plants. The current ATEX guideline in the Netherlands NPR7910-1 was reviewed with regard to its applicability to hydrogen. The detection of hazardous concentrations of hydrogen (and oxygen) is an important aspect with regard to preventing fires and explosions.

Target Audience

The target audience for this report includes companies involved in developing designs and technology for as well as owning and operating green hydrogen production facilities, representatives of authorities involved in the permitting process for green hydrogen production facilities, and financials, security firms and knowledge groups to whom safe, green hydrogen production is relevant. This also includes organisations involved in aligning best practices and creating guidelines and/or standards.

This report

In this public report, the key findings of a process safety study on water electrolysis is presented. This report is successor of the first report 'Safety Aspects of Green Hydrogen Production on Industrial Scale'. It is the result of a more than two-year long project involving extensive cooperation with safety experts from Battolyser Systems, Equinor, Green Hydrogen Systems, HyCC, ISPT, John Cockerill, NEN, Ørsted, Plug Power, RHDHV, RWE, Shell, TNO, VoltH2, Yara. The project was managed by the Institute for Sustainable Process Technology (ISPT).

The results of this project have been presented to the Dutch normalisation institute (NEN) and are used for the development of the NTA8221 – "Process safety for the production of hydrogen by electrolysis" and the PGS40 – Hydrogen production.

Report Contents

Chapter 2 describes the scope of the electrolysers subject to the safety studies whereas Chapter 3 provides a brief description of AWE and PEM electrolyser systems. Chapter 4 describes the applied approach, methods and data for this project. Chapters 5 and 6 report the results of the safety studies of the abovementioned subjects. Chapter 7 and 8 describes ATEX and detection aspects. Chapter 9 describes options for (further) risk reduction. Key findings are provided in Chapter 10. In the Annex 1 and 2 the detailed results of the process safety study can be found.

2. Scope Description

2.1 Industrial scale

The project's scope is limited to hydrogen produced at an industrial scale using AWE and PEM electrolysers that utilise renewable energy. The definition of when hydrogen can be termed 'green' was determined by EU standards for green hydrogen (RFNBO). In this project's context, the term 'industrial scale' refers to hydrogen plants with a capacity ≥ 10 MW. However, it doesn't mean that the advice given is not applicable to smaller plants. Many of the results reported by this study apply to both small scale (skid size) and large-scale production units. Electrolysers will always be located inside buildings due to requiring electrical connections, avoiding weather influences, etc. Other equipment such the G/L-separators could be be located outdoors for large-scale production. For small-scale production, all equipment will be located indoors (or inside containers). The scope is also limited to operating pressures up to 60 bar.

2.2 Electrolysers

The scope (see shaded area in Figure 1) comprises green hydrogen electrolysers with multiple stacks and accompanying processing units, e.g. gas/liquid separators and knock out drums. Compressors, deoxidisers and other processing systems are not included in the project's scope, but are mostly part of the electrolyser site (see dotted frame in Figure 1). They are essentially no different from those in the traditional process industry and were therefore not further studied although they can affect process safety aspects. Note: any phenomena that directly affect the process safety aspect, such as external safety, fire safety and facility siting, of the installations within the project's scope have been taken into account.

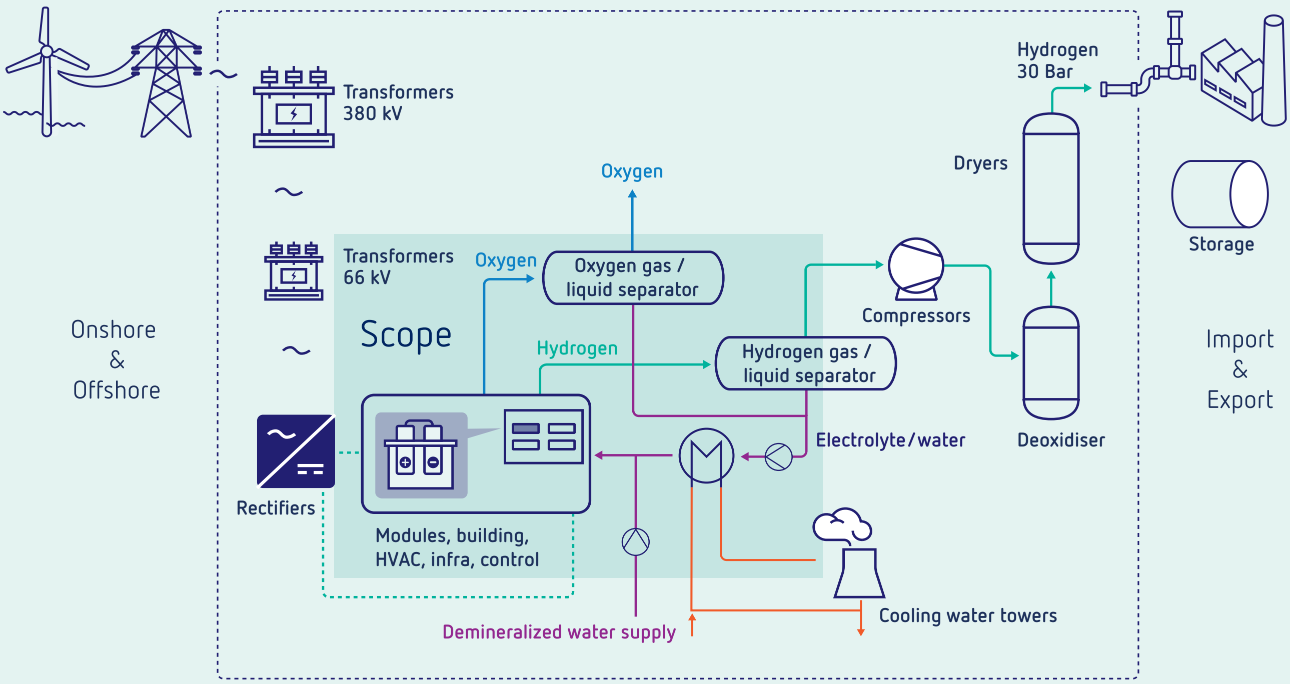

Figure 1: Visualisation of the scope for the safety studies

The operating conditions and modes for the study are:

- Low or high pressure AWE: atmospheric up to 60 bar, with small presure drop over diaphragm, typically 20 mbar.
- Differential pressure PEMWE: 0 - 40 bar (PEMWE pressure at oxygen side can range from slightly above atmosheric pressure to about 30 bar.
- Electrolysis temperature range: 20 - 90°C (PEMWE typically operates at 60°C and AWE at 80°C). Start-up, normal operation (stable or dynamic), standby, shutdown, emergency shut-down.

Higher pressure and temperatues are possible but not discussed here. Also. pressure at both sides of the membrane can be the same for PEM contrary to considered differential pressure.

2.3 Scenarios

The process safety hazards scenarios covered in the safety studies are:

- In-equipment hydrogen and oxygen mixing as well as ignition inside equipment
- Loss of containment of hydrogen and/or oxygen with ignition outside equipment.

Other process safety hazards are not covered by this study's scope (hot lye, oxygen burns, etc.)

The study focusses on consequences for people. Asset, environmental and commercial damage are mentioned for descriptive purposes only.

3. Methods and Data

3.1 Alkaline Water Electrolysis

Figure 2 shows a simplified schematic process diagram of an AWE plant. Typical for AWE operations is the (almost) equal pressure on either side of the membrane.

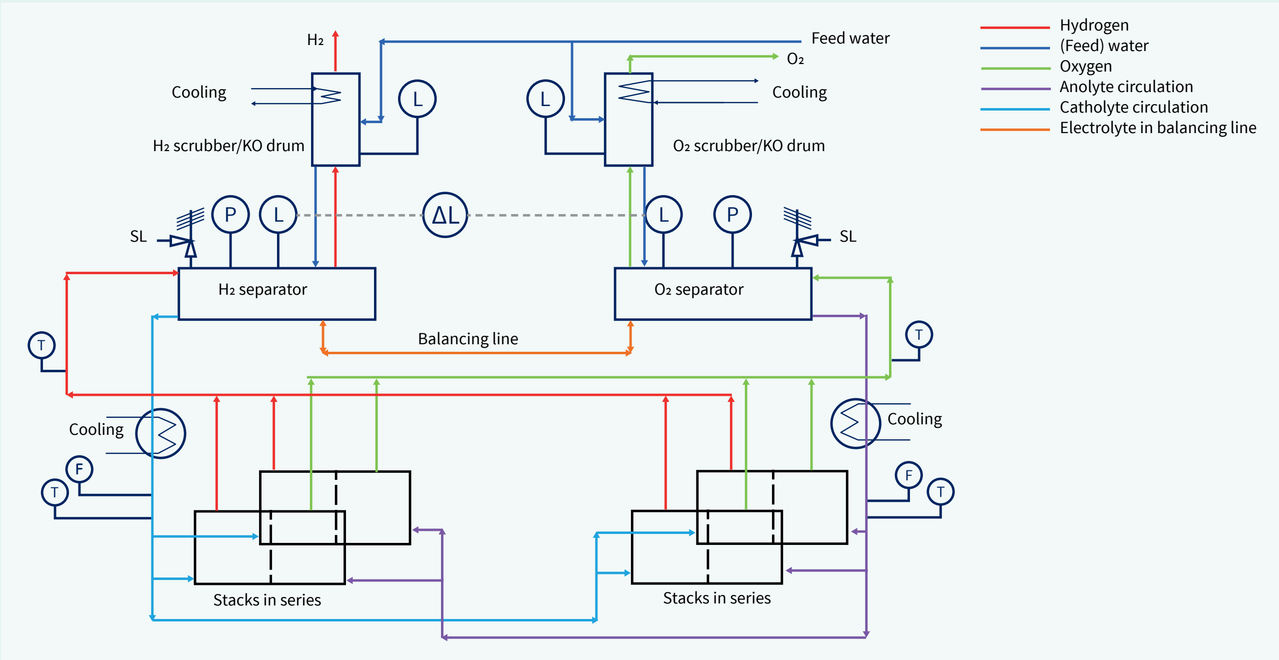

Figure 2: Simplified Process Schematic - Alkaline Water Electrolysis

There are a number of basic differences in design between the various suppliers of water electrolysis plants. Some examples:

- Instead of having separate electrolyte return flows to the anode and cathode sides of the stacks, a flow combining the anolyte and catholyte flows feeding both sides of the stacks may be applied.
- Plants may be operated at different temperature and pressure conditions, e.g. the temperature is between 55 - 90 °C and the pressure varies between atmospheric and 60 barg.
- Control philosophies vary, e.g.:
    - o The entire system's pressure is controlled by a pressure sensor and control valve in the outlet while the level difference between the G/L-separators is controlled by level sensors on both G/L-separators and a control valve in the hydrogen outlet of the G/L-separator
    - o Pressure and level are controlled on both the oxygen and the hydrogen side
- The balancing line can be open or contain valve(s) or may not even be present (fully separated electrolyte circulation flows).
- A demister or coalescer is often present to prevent water droplets in the hydrogen flow to downstream equipment.
- Location of feed water supply may vary.

3.2 Proton Exchange Membrane Water Electrolysis

A simplified schematic process diagram of a PEM plant is shown in Figure 3. Typical for PEM operations is that the pressure on the hydrogen side of the membrane is much higher than the pressure on the oxygen side. The latter could be close to atmopsheric pressure.

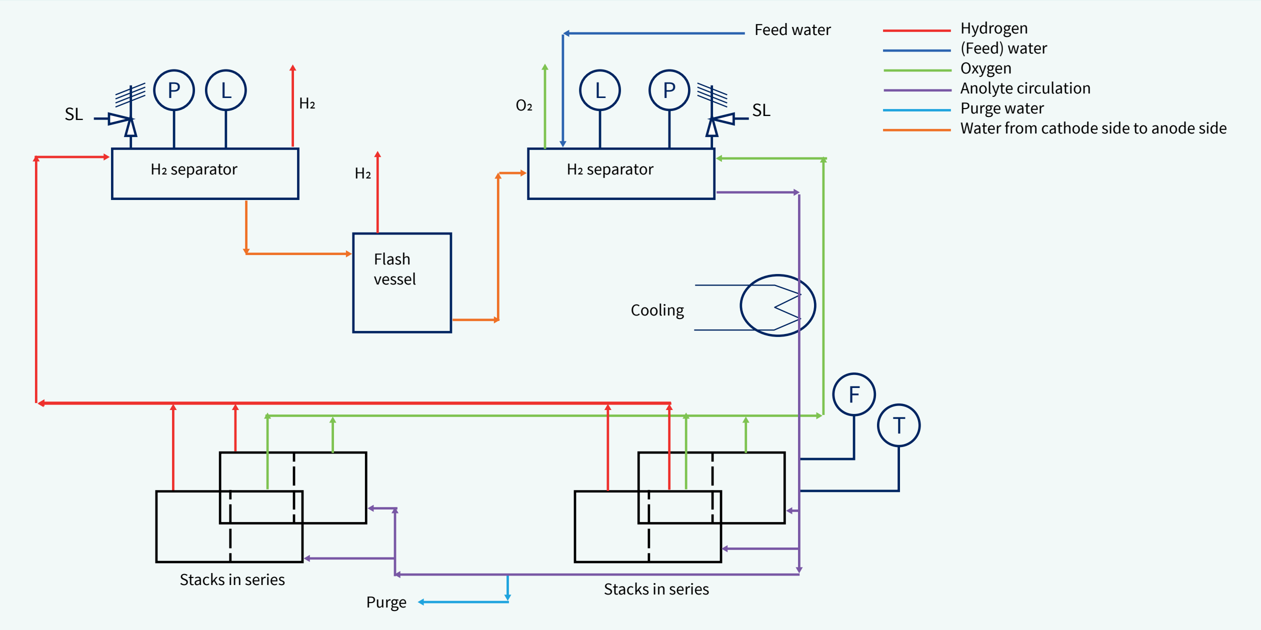

Figure 3: Simplified Process Schematic - PEM Water Electrolysis

Basic design differences also exist between the various PEM suppliers. Some examples:

- Instead of having a single electrolyte return flow to the anode side of the stacks, plants may have water supplies to both the anode and cathode sides. This influences in the purge philosophy.
- Location of feed water supply may vary.
- Location of purge water to water purification unit may vary.
- Pressure differences between the cathode and anode side may vary between 0 and 40 bar.
- Water from the flash vessel may be directed to another position in the anode electrolyte flow (with consequences for the purge philosophy).

4. Process safety management

4.1 Focus on Process Safety

Process safety focuses on preventing and mitigating catastrophic events and incidents that can result from industrial processes, including water electrolysis and downstream operations. Process safety is a combination of technical and organisational safety, and includes many aspects, such as external and environmental safety (control of major hazards), fire safety and control, explosion safety, functional safety, and process (installation) safety. Next to the operations also compliances, permitting and enforcement are therefore important. Technically, safety can be controlled by performing (technical) hazard and risk analysis, proper safety system design and emergency response planning. Organisational safety – including the overarching concept and policy – helps control process safety using working methods, procedures and training. Organisational safety can also extend to occupational safety, creating a safe, healthy working environment to protect people from injuries, illnesses or other harm that may occur at work. This is a different objective than that of process safety and is therefore not part of the scope of this report.illnesses or other harm that may occer at work. This is a different objective than that of process safety and is therefore not part of the scope of this report.

4.2 Safety in the Asset Life Cycle

The life cycle of an electrolyser plant, see Figure 4, refers to the stages an asset goes through from its conceptual phase to its final decommissioning. In each stage the safety aspects are addressed If properly defined, implemented and managed a high level of safety can be ensured. This requires extensive communication and coordination between the suppliers, engineering contractors and owner-operators, as well as authorities.

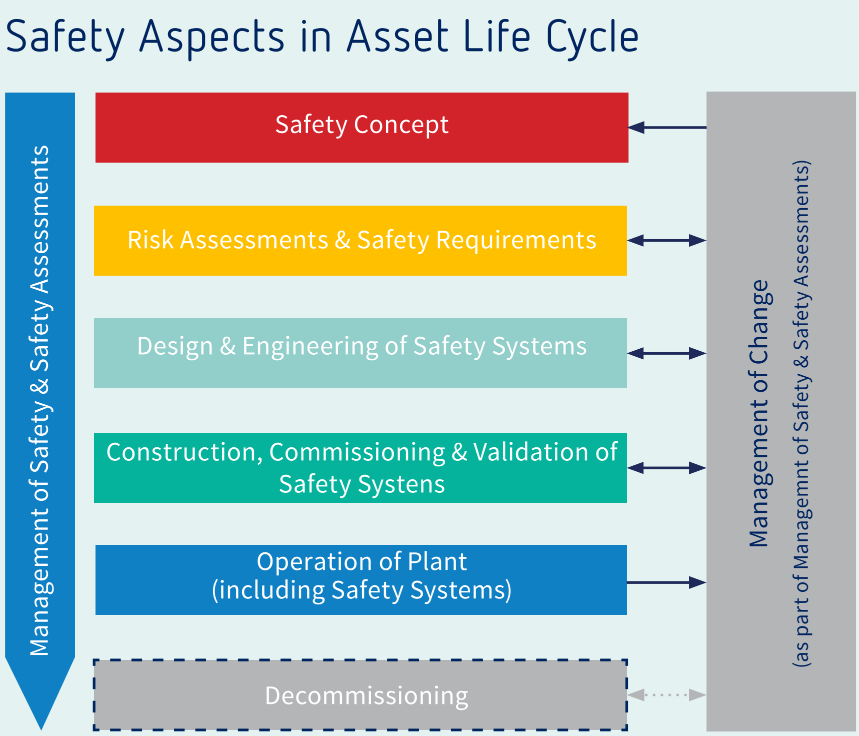

Figure 4: Safety in asset life cycle

Safety Concept: design of a comprehensive and company-appropriate safety strategy outlining safety goals, risk acceptance criteria and policies.

Risk Assessments and Safety Requirements: risk assessments identify potential hazards and the required protection layers and safety performance criteria are identified on the basis of the latter. These requirements constitute the starting point for a safe process installation design as well as for compliance with relevant standards and must be documented.

Design and Engineering of Safety Systems: the safety requirements identified are critical to ensuring the design of safe installations and processes. These requirements should be incorporated into the design and engineering phases. Additionally, the conceptual and final designs should be subjected to specific hazard analyses and overall compliance with safety standards and permit-related requirements must be obtained.

Construction, Commissioning and Validation: this phase integrates the design plans based on the safety requirements into the construction process. Before commissioning, compliance with relevant directives, and designs standards must be ensured. This includes checking safety features, conducting performance tests and ensuring that all safety systems function correctly. This validation is normally conducted during the Pre-Startup Safety Review (PSSR), which includes verification and certification steps.

Plant Operation: the entire system should be monitored during operation, both during active use and during shutdowns and maintenance. Regular minor and major maintenance, testing and inspections are necessary to ensure safety systems remain effective. [3]

Decommissioning: safe decommissioning procedures are essential at the end of the system's life cycle. This includes dismantling, responsibly disposing of materials and managing any remaining hazards.

Management of Change (MOC): is an essential procedure during every phase. During a MOC the risk of the change to a production process should be assessed to document that the safety is not adversely impacted. This can lead to the redesign and adjustment of safety systems and associated safety studies and requirements.

Management of process safety: Safety in the asset life cycle must be adequately managed by a safety management system (SMS). The SMS will evolve throughout the various phases, but must be fundamentally established during the conceptual phase. [4]

4.3 Risk Assessments and Protection Layers

There are different types of protection layers that occupy various positions in the control hierarchy. Higher level protection layers are preferable. CCPS [8] and IEC61511 [19] compare the different protection layers to the various shells of an onion as shown in Figure 5. The inner shell is the highest level of the hierarchy and that level drops as you progress outwards. Preventative safeguards are preferred over mitigating safeguards. Safeguards can also be classified as 'Technically Active', 'Technically Passive' and 'Organisational'. A brief description is given below.

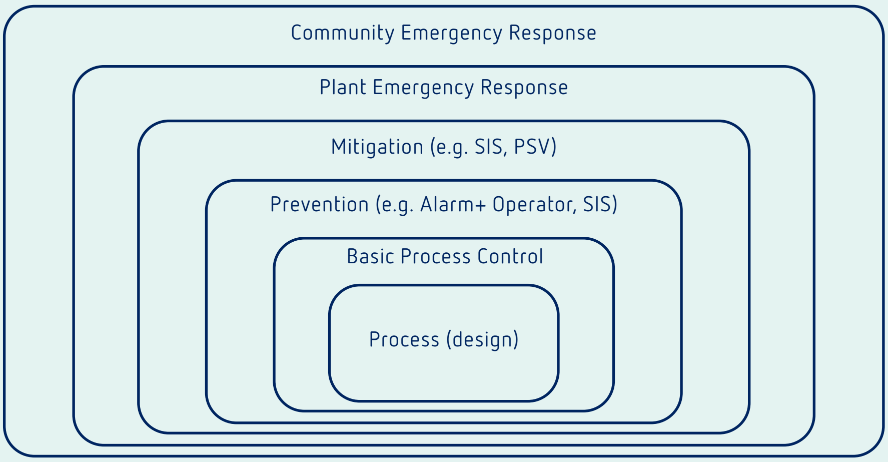

Figure 5: Protection layers

4.3.1 Active Technical Protection Layers

Active safeguards are those that are triggered after the process has run outside its normal operating limits. They prevent further escalation of the situation or mitigate the consequences. Active safeguards may consist of:

- Equipment that activate or deactivate other process equipment e.g. a temperature sensor closes a valve when its setpoint has been reached. IEC 61511 [19] covers functional safety with requirements for instrumental safeguards and final elements (such as valves, pumps, etc.) in the process industry and is also applicable to water electrolyser plants. Instrumental safeguards should put the process in a safe state thereby preventing a hazardous incident occurring. Examples of instrumental safeguards include hydrogen detectors, level/pressure/temperature switches or sensors with an action activated at the setpoint to bring the plant into a safe state

- Mechanical safeguards such as pressure relief valves. Such safeguards prevent further escalation of an incident, but cannot prevent a (contained) emission and do not put the process in another state.

- The safe state which an electrolyser plant must be put into when an instrumental safeguard has been activated depends on the reason for the process running outside normal operating limits and may vary from a defined standby situation to complete shutdown, for example:

    o In several instances stopping the power supply to the stacks is sufficient to prevent escalation

- o Some instances require depressurisation in addition to stopping the power supply
- o Other cases may even require purging with nitrogen after or even during depressurisation.

The required safe state is highly dependent on the technology, operating conditions and plant design. The safe state has to be determined for each active protection layer and is part of the plant control philosophy. After an emergency stop, there should always be a check and a manual reset before re-starting. A maintenance stop may require its own specific safe state. The nitrogen storage capacity should be based on scenarios requiring the maximum amount and flow of nitrogen when purging is needed to reach the safe state.

4.3.2 Passive Technical Protection Layers

Passive safeguards are always present and 'waiting' for an incident. Examples include blast walls (to protect against pressure effects and flying debris) and pits or bunds (to protect against soil/water pollution). Passive safeguards cannot prevent incidents, but can mitigate the consequences. The need for passive protection layers often depends on local circumstances (e.g. other buildings close by) and should be determined on a case-by-case basis for each electrolyser plant.
Increasing the design strength of equipment can also be regarded as a passive protection layer. For instance, the design strenght of a oxygen G/L separator would need to withstand the design pressure of the upstream system (the hydrogen separator/flash vessel) . Another example is that the increased design pressure of an oxygen G/L separator would retain its integrity at an internal explosion.

4.3.3 Organisational Safeguards

Organisational safeguards are often a combination of procedures which must be followed and other measures. An example is preventing people from approaching equipment by demarcating prohibited areas on site using coloured lines (or fencing), or an interlock on the doors of the electrolyser building/ container. Such areas require strict procedures for maintenance activities. Emergency response is also an example of an organisational safeguard (last resort).

4.3.4 Requirements for protection layers

In safety studies, protection layers are defined as indicated in Table 1. Only barriers fullfilling these requirements can reduce the risks.

Table 1: Requirements for protection layers and assigning significant risk reduction

	Description
Detect-Decide-Act (Specific)	Active barriers must contain all the detect-decide-act elements. A common error is listing the elements as separate barriers when they should be just one. Example: gas analyser detects too high a concentration of hydrogen in oxygen and trips plant(section).
Effectivity and reliability	A barrier must be effective in that it performs the intended function when demanded and to the standard intended, and is capable of preventing a threat from developing into a top event on its own. Suggestions such as 'training' and 'competency' are degradation controls and not barriers. Referring to the above example: the gas analyser and trip are only effective when the gas analyser detects and activates the trip before the hazardous situation really occurs. In IEC61511 [19] this is often referred to as the process safety time. IEC61511 sets requirements with respect to safeguards' required reliability. In the same example: the gas analyser is only reliable if its PFD is sufficiently low according to IEC61511.
Independence	Barriers should be independent of the causes of scenarios and of other barriers in the event sequence. Complete independence is rarely possible, however common failure points between multiple barriers should be kept to a minimum. Example: the electrolyte flow is controlled by a flow meter with an alarm function. In the event of an alarm (high or low) from this flow meter, the plant will trip. In the event the flow controller itself fails and causes the flow to be too low or too high, the alarm will also not work. The alarm is not independent from the cause and cannot be regarded as a barrier.
Auditability	Barriers should be capable of being audited to check if they work. Typically, performance standards should be assigned to the functionality of a barrier which will be used to demonstrate its performance during testing/inspection. Example: referring to the trip by the gas analyser above; the analyser and trip function should be tested periodically for correct functioning. Records of these tests should be available.

5. Approach to Safety Studies

ISPT studied the safety of both AWE and PEM and discussed this with project partners. The bowtie method, basic HAZOP principles (cause, consequences, safeguards) and LOPA (initiating event, scenario, (independent) protection layers) were applied to these studies. The studies were initially performed as deskstop studies of a design for a large-scale hydrogen plant (GW project) [2, 7, 20]. The generic hazardous scenarios for both AWE and PEM were developed from these studies. Since design details differ between plant suppliers, the generic scenarios can never replace those from plant-specific risk assessments. The studies' focus was on normal operation including low load. Other modes of operation were discussed briefly. Only potentially severe consequences for people were considered (hospitalisation or fatality). Other consequences e.g. asset or environmental damage were sometimes indicated for information purposes only.

5.1 Bow Tie Approach

Bow tie diagrams are a widely used tool in risk assessment, providing an intuitive, clear, causal illustration of events that result in a loss of control and the consequences for each credible hazardous scenario. The scenarios and bow ties developed during in first H_2 safety ISPT project [1] were used as starting points and updated based on discussions with project partners held during a workshop and as a result of the safety studies [38]. The new bow ties replace those from the first ISPT project.

The threats for in-equipment explosions are grouped into four categories:

- Design
- Cell/stack degradation
- Cell/stack maintenance/manufacturing
- Process control

The threats for Loss of Containment scenarios were similarly categorised.

5.2 Approach to Assessment of Cell Separator Degradation Mechanisms

The TNO study 'Understanding Safety Aspects of gas mixing in low temperature electrolysers' [3] covers mechanisms that contribute to gas crossover of hydrogen from the cathode to the oxygen side at the anode (vice versa) under normal operating conditions, conditions that deviate from normal and during failure scenarios. The TNO study's results were used to update the bow ties and to identify and understand hazardous scenarios.

5.3 Risk Evaluation

A scenario's risk is often represented as a combination of occurrence or failure frequency and the severity or impact related to HSE (and damage and reputation). It is usually plotted in a risk matrix or risk graph. No nationally or internationally agreed risk acceptance criteria are currently available. For this reason, the identified generic hazardous scenarios have not been risk rated. Companies should define their own risk assessment method and criteria whereas the actual risk will be plant specific. The standard for instrumental safeguards IEC61511 (Part 3) [19] provides a methodology for doing this.

5.3.1 Uncertainties in risk assessment

When conducting risk assessments, a conservative approach should be applied to any uncertainties:

- The presence of people: AWE and PEM are often designed to be remotely operated and are normally unmanned. Nevertheless, a few people in the vicinity e.g. for maintenance, gardening, etc. can be present and hence the presence of people is assumed for evaluating consequences. A less conservative assumption can only be made if it is supported by relevant information.

- During scenario development for in-equipment explosions, it is assumed that the gas volume inside equipment has a stoichiometric composition of hydrogen and oxygen, therefore resulting in the maximum probability of ignition and the greatest effect distances. A less hazardous composition can only be assumed if it is supported by relevant information.

- In the event of a flammable mixture, it is assumed that ignition will always occur. Ignition could occur due to equipment outside the scope of this study, the presence of catalyst, static electricity (insufficient grounding), etc. Also in this case, relevant lower ignition probability can only be assumed if it is supported by relevant information.

- Scenarios that develop so very slowly that it is unrealistic that they will not be discovered and stopped before the final consequences occur receive no risk rating with regard to severity and frequency. The reason(s) that the scenario is unrealistic should be mentioned including the monitoring/safeguarding.

5.3.2 Frequency Estimation

At this time there is no specific data on failure frequencies and Probability of Failure on Demand (PFD) available for water electrolysis equipment and protection layers. As a result, references generally used in the process industry may be used for approximation [8, 9, 10, 11, 12, 13, 14 ,15, 16, 17, 18]. In any case a conserative approach should be applied.

5.3.3 Severity Estimation

Quantification of a scenario's impact is very dependent on the system's specific design, geometry, congestion and location. Heat radiation from fires or vapour explosions can be calculated using authorised models, e.g. as described in the PGS 1 and 2 [33] and by using available software tools. Explosion overpressure modelling is more difficult as demonstrated in the previous ISPT project's report on the Safety of Water Electrolysis plants [1]. Nevertheless, the statement that low pressure operations (at equal volume) will typically have smaller effect distances and hence a lower risk, is generally true.

5.4 ATEX Considerations

The ATEX aspects have been examined as far as different for hydrogen and oxygen enriched areas is concerned [22]. The main aspects are presented that are important to hazardous area classification (as per the ATEX regulations) and the ventilation of water electrolyser rooms or containers. This study zooms in on technical issues relevant to fire and explosion prevention under normal operating conditions. An important issue discussed is the use of the Dutch NPR 7910-1 [4] standard for hydrogen applications. NPR 7910-1 is a simplification of IEC60079-10-1 [5], which describes methods for estimating the size and shape of hazardous areas in case of leakages. The essence of this shortcut is that a generic leak flow rate leads to a standard zone shape and radius, irrespective of the type of gas escaping. The major difference between hydrogen and propane is its low molecular weight. This influences the shape and size of hazardous areas.

6. Study Results

6.1 Bow ties

6.1.1 Top events

Bow ties have been created for two top events based on scenarios:

- In-equipment mixing of hydrogen and oxygen into the flammability are (above LFL and below UFL concentrations) (internal mixing) (hazard = hydrogen and oxygen present in different electrolyser process streams)
- Loss of containment of hydrogen (external leakage) (hazard = Hydrogen present in electrolyser process).

The safety studies and workshops with project partners resulted in the bow ties in Figure 6 for in-equipment explosions and Figure 7 for loss of containment. The barriers are not indicated to improve legibility. The complete bow ties with barriers are included in Annex 1.The bow ties mention 'fire, 'explosion' as consequences, but these are not the final consequences as these may harm people and cause damage to assets and the environment.

Note that the scope is restricted to the electrolyser units as discussed in Chapter 2. This means that causes from equipment outside the scope of this study e.g. compressors, utilities, etc. were not included.

6.1.2 In-equipment mixing

The main bow tie (sub)categories of identified threats are:

- Design
  - o Low load conditions not correctly defined
  - o Non-uniformities such as flow, current and temperature
- Degradation of cells or stack components
  - o Mechanical e.g. to solid particles in anolyte or catholyte flow or pressure variations
  - o Availability of green energy (load variations and frequent starts/stops)
  - o Chemical (PEM only)
- Membrane maintenance and manufacturing
  - o Overtightening
  - o Supplier error
  - o Assembly error
- Process control
  - o Level, temperature, flow and pressure control failures for both PEM and AWE
  - o Control failures specific to AWE: delta-level and delta pressure variations

- o Control failure specific to PEM: water quality
- o Low load due to current/voltage control failure.

6.1.3 Loss of Containment

The main bow tie (sub)(categories of identified threats are:

- Design
    - o Hydrogen embrittlement
    - o Alkaline corrosion
    - o Equipment fatigue
    - o Leakage
- Maintenance/Manufacturing
    - o External nearby activities e.g. lifting, excavation, etc.
    - o (In-equipment explosion)
- Process control e.g. temperature, pressure, etc. (including potential in-equipment explosions).

6.1.4 Barriers

All the threats listed can lead to an in-equipment mixing or loss of containment and a fire and/or explosion if not prevented or mitigated. The bow ties in Annex 1 include potential barriers. The emphasis is on the word 'potential' because whether a scenario materialises, depends on the barriers actually present at the plant under consideration.

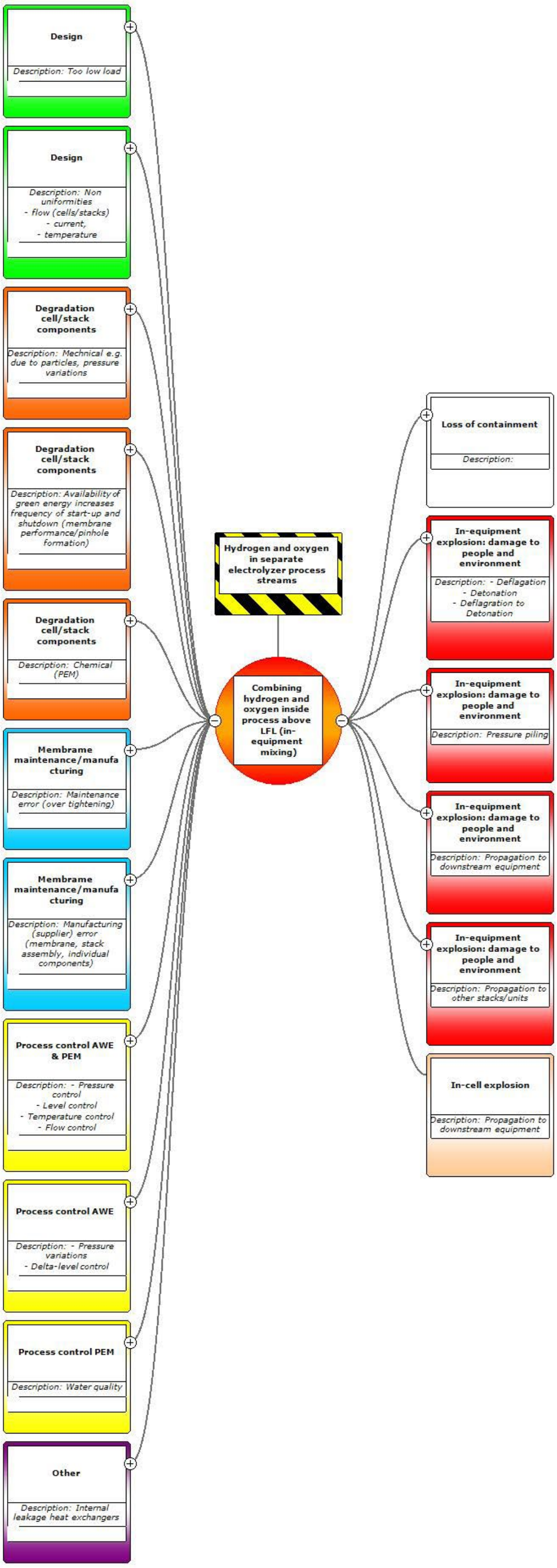

Figure 6: Bow Tie in-equipment Explosions

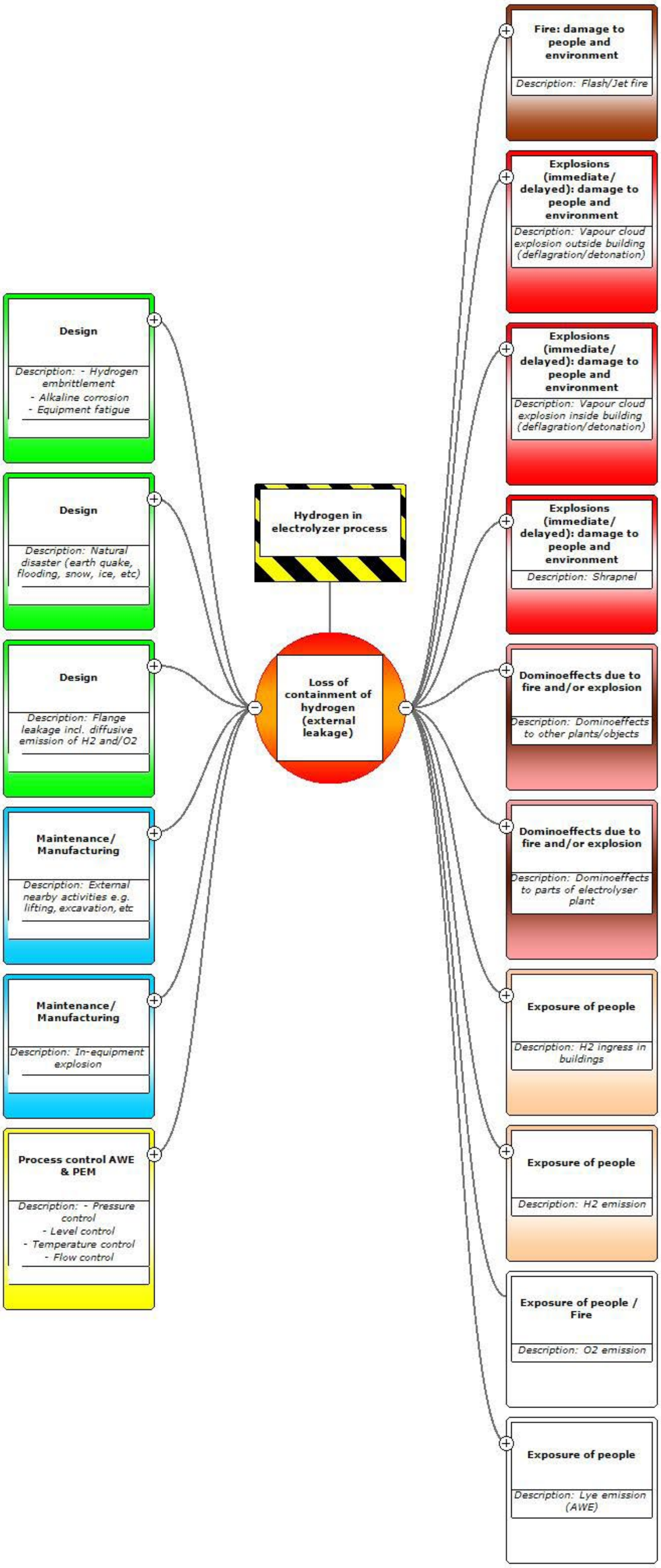

Figure 7: Bow Tie Loss of Containment

6.2 Critical Hazard Scenarios – In Equipment Mixing

Safety studies were conducted using a HAZOP/LOPA-like approach for plants' normal operation conditions. Load variation and frequency of start/stop aspects were discussed qualitatively. The failure mechanisms identified were limited to equipment and control failuress which are inside scope. For example, it does not list compressor surges. This is true for all deviations in equipment outside the scope of this study which may have consequences for the stacks and/or BoP.

The detailed generic hazard scenarios identified for AWE and PEM are provided in the tables Annex 2a and 2b, respectively. The AWE and PEM scenarios were divided into the main categories: Design, Degradation of Cell/Stack Components, Maintenance/Manufacturing of Membrane and Process Control.

6.2.1 Effectiveness of Gas Analysers

Gas analysers in G/L-separators are installed to detect hydrogen in oxygen and vice versa before a flammable combination develops. The effectiveness of the analysers depends on the speed that a scenario develops at. If it develops rapidly, the analysers will not be able to detect a flammable atmosphere in time to prevent serious consequences and will therefore be ineffective. Alternately, if the scenario develops slowly, they will likely detect a flammable atmosphere and be effective. The speed at which the scenario develops and the effectiveness of the gas analysers are indicated for each scenario in the fourth column of the tables in Annex 2. The characteristics of the gas analysers in situ should be checked for effectiveness.

The gas analysers on the G/L-separators act as effective safeguards in many scenarios. In general (depending on design details), they are not effective in the following cases:

AWE

- Failure of delta level or delta pressure control in combination with an open balancing line. Gas may quickly flow from one G/L-separator to the other
- Rupture of (many) membranes e.g. due to pressure difference

PEM

- Control failure of electrolyte flow from hydrogen flash vessel to the oxygen G/L-separator
- Membrane damage due to particles, control failures of temperature, flow, etc. easily causes a hazardous gas concentration.

6.2.2 Small Explosions and Flames

During the safety studies our partners mentioned they had experienced flames occuring inside cells, but no explosions downstream in the header or separator during pilots with smaller scale production units. According to our partners the absence of propagation observed is due to the dilution effect inside the header and the latter's 2-phase flow. Whether propagation will or will not occur depends to a great extent on the circumstances, particularly the gas composition at that specific time and location.

Figure 8 illustrates for PEMWE the dilution effect with leakage through a 0.56 mm pinhole and diffusion at high differential pressure through the membrane. The gas produced is collected in a header according to the design as shown in Figure 9. The effect is based on a stack consisting of 100 cells with the first cell having a damaged membrane or diaphragm. As Figure 8 shows, the concentration of hydrogen in oxygen is diluted to below LFL. The observations regarding leakage have been discussed with the OEMs participating in the project, indicating that the formation and characterisation of pinholes is complex and needs further investigation.

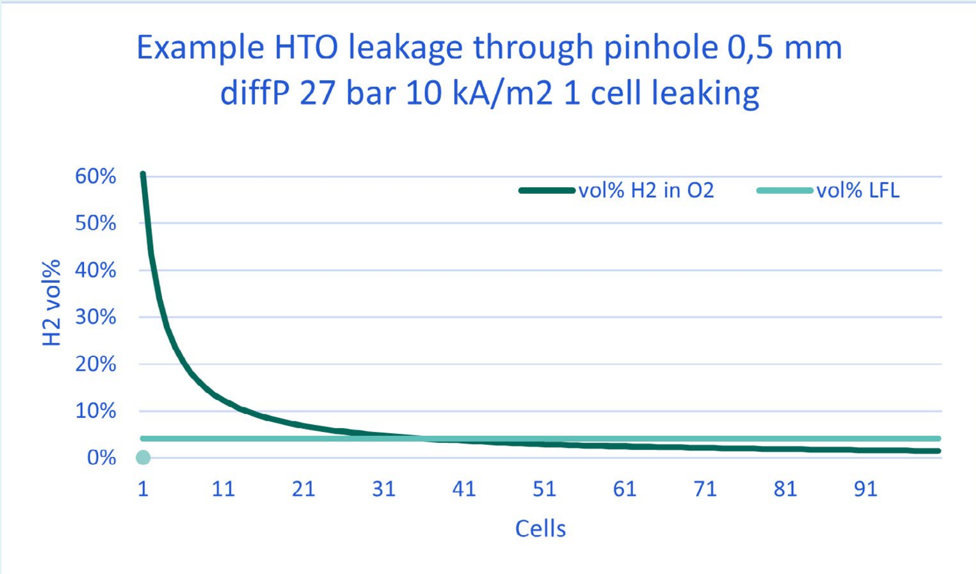

Figure 8: Dilution effect of leakage

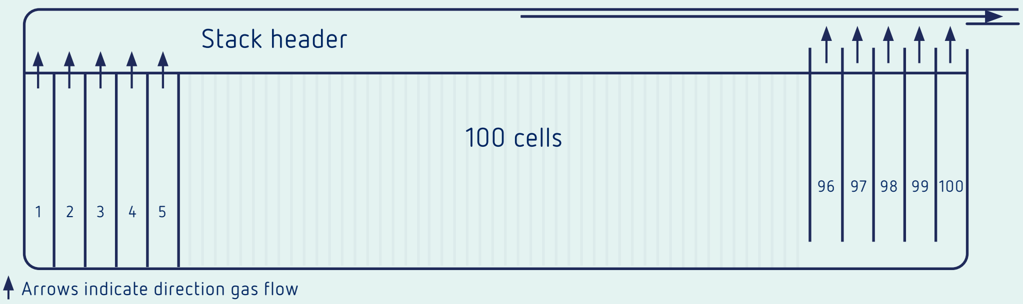

Figure 9: Schematic stack design used for calculations

6.2.3 Equipment outside the Scope of this Study

Due to the project's limited scope, the causes for scenarios are limited to equipment inside the study's scope. Nevertheless, there may also be consequences for equipment oputside the latter's scope. As a consequence, any scenarios caused by equipment outside the scope of this study are not included in the safety studies! Plant-specific safety studies should take the entire plant into account.

Another aspect is the potential hazard of hydrogen and oxygen accumulation in equipment they are normally not present in such as, for instance, cooling circuits, due to internal leakages.

6.2.4 Risk and Risk Reduction

Although there are no agreed risk criteria, water electrolysis plants are expected to need more risk reduction measures than present in the design example for the GW plant used in this study, including, for example:

- Advanced safety systems such as a SIS
- Mitigating barriers can be considered where preventative safeguards do not sufficiently reduce risk
- Reduction of the presence of people
- Explosion-proof designs can be considered where gas analysers are not effective.

Organisational measures including an effective (Process) Safety Management System are necessary to ensure that the plant's safety is well defined and is integrated into every design phase and remains highly safeguarded throughout the plant's lifespan.

6.3 Critical Hazard Scenarios –Loss of Containment

6.3.1 Loss of Hydrogen Containment

Only 2 scenarios were identified for loss of containment which are related to the plant's normal operation. These concern both small and large leakages e.g. due to gaskets, small or large holes in equipment, etc. The other threats mentioned in the bow ties relate to other reasons for loss of containment such as mistakes during design, maintenance, etc. Annex 2c only covers scenarios related to normal operation.

The bow tie only covers loss of hydrogen containment. Annex 2c (generic hazard scenarios) also covers a loss of oxygen containment.

In dicussions about the safety studies with project partners during the project, the occurrence of micro-flames on the outside of equipment in the event of very small holes was mentioned. These are difficult to detect due to hydrogen's (almost) colourless flame.

Both hydrogen and oxygen are well known gases that have been used in many processes for a long time now. A number of guidelines are available for handling and processing oxygen and hydrogen. These should be consulted to minimise incidents. They provide barriers for the other threats mentioned in the bow ties such as a corrosion and aging-minimising choice of materials [34, 35, 36].

6.3.2 Potential Development Pathways

The final consequences of hydrogen leak scenarios not only depend on the size of the leak and its pressure, but also on the specifics of the leak's location. Figure 10 provides the options. Basic ventilation systems are assumed to be present inside buildings and rooms.

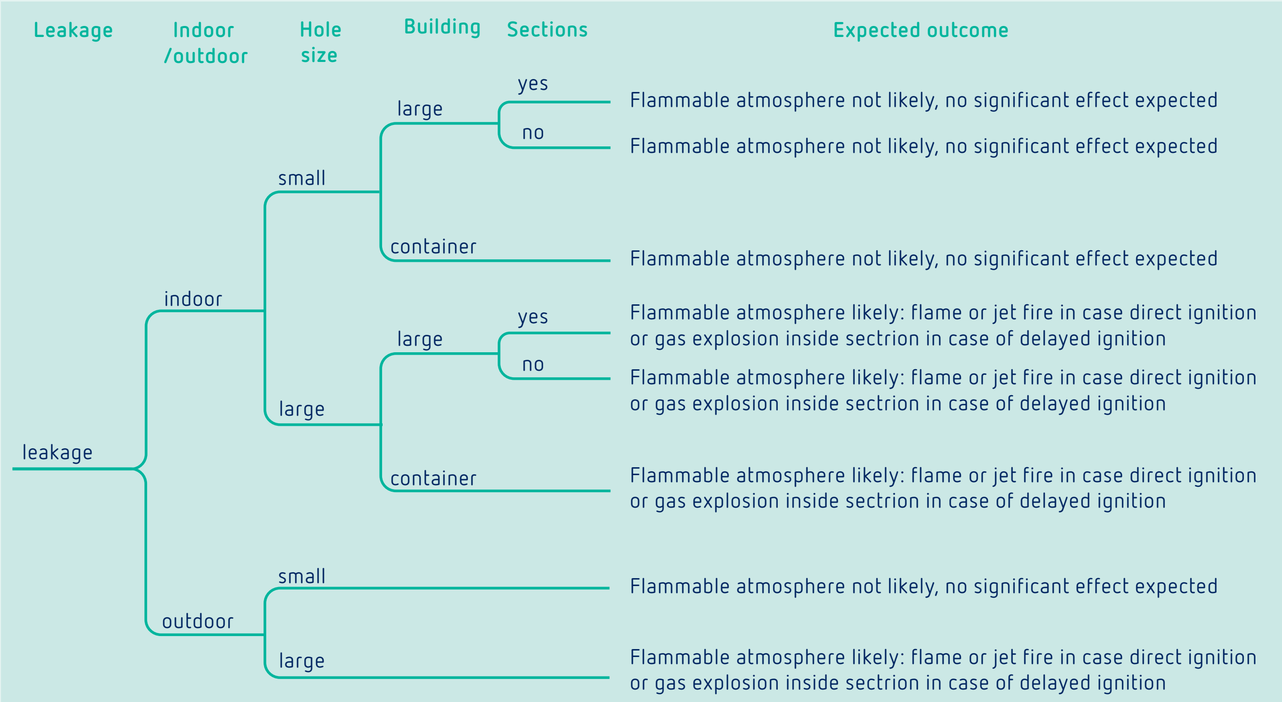

Figure 10: Potential scenarios for hydrogen leaks and expected effects / minimum ventilation present

6.3.3 Loss of Oxygen Containment

The oxygen concentration in air is approximately 21 vol%. Oxygen concentrations that are too low or high are hazardous to humans and increases the risk of fire, see Figure 11. Increased oxygen concentration in rooms or buildings is a potential hazard at electrolyser plants and the use of oxygen analysers in (small) rooms is recommended.

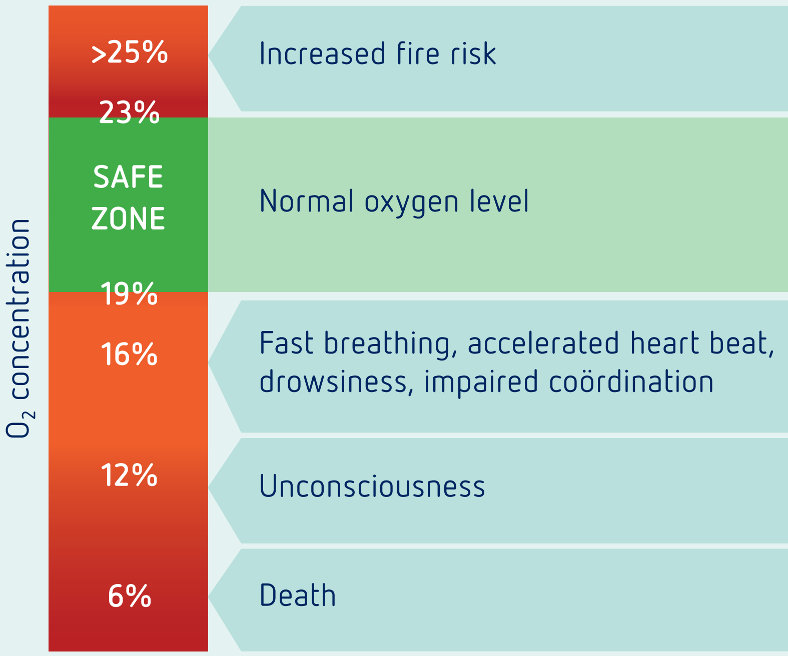

Figure 11: Hazard of low and high oxygen concentration

6.3.4 Release Calculations

As hydrogen is lighter than air it is expected to rise after a release. This is not always true. Some release calculations have been performed to study the dispersion behaviour of released hydrogen from a hole in a pipe or equipment. The Figures 12, 13 and 14 (side views) show the distance to a hole of a flammable cloud (at LFL) that is formed as a jet when hydrogen is released under the following conditions:

- Pressure: 5 barg and 0.01 barg
- Temperature: 10 °C
- Hole size: 3 mm and 10 mm
- Location of release: 1 m above the ground
- Release direction: horizontal
- Wind: 0.5 m/s in release direction

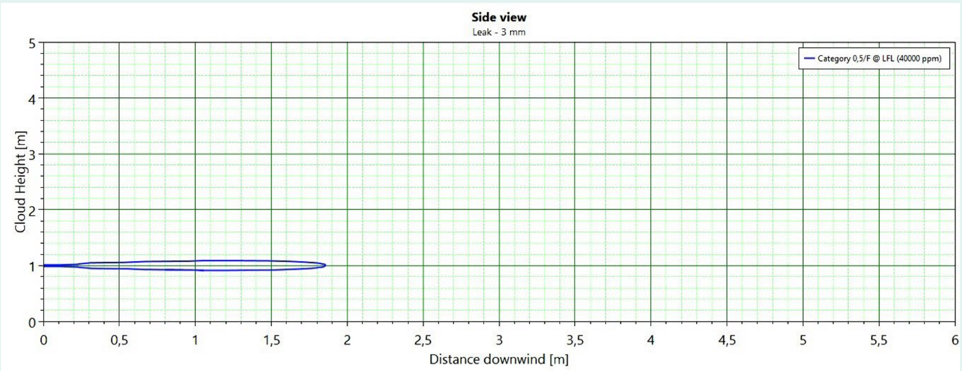

Figure 12: Horizontal release of hydrogen from a 3 mm hole at 5 barg

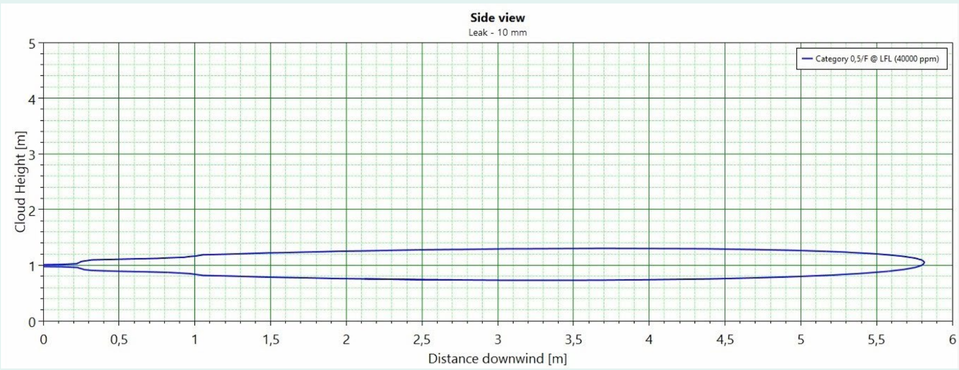

Figure 13: Horizontal release of hydrogen from a 10 mm hole at 5 barg

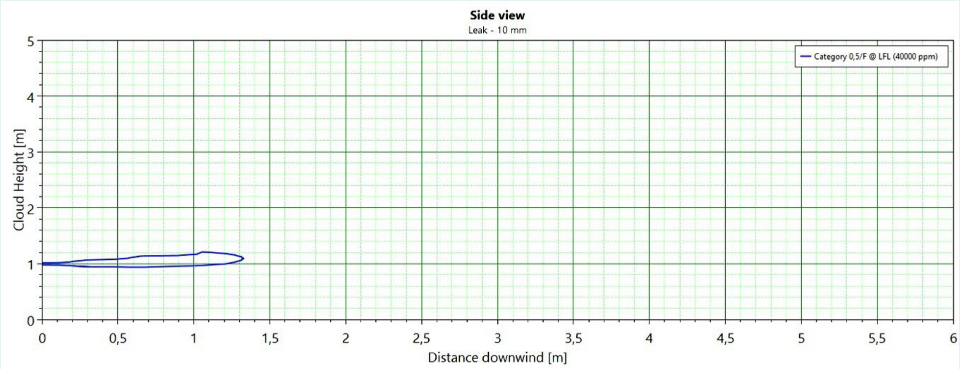

Figure 14: Horizontal release of hydrogen from a 10 mm hole at 0.01 barg

6.3.5 Buoyancy may not be expected

The Figures 12, 13, 14 clearly demonstrate that the cloud's tendency to rise is very limited especially under pressurised (5 barg or higher) conditions which are regarded as being representative of releases from pressurised water electrolysis plants. At almost atmospheric pressure (e.g. AWE) it is observed that the buoyancy effect causes the release to rise. Upward flow may only start at some distance from the release location. This causes significant different zoning for area classification.

6.4 Load variation and other Modes of Operation

The availability of green energy to power the electrolysers will in many cases be dependent on the availability wind and sun-generated electricity. This has consequences for the electrolysers' operation. There are several options for adapting to the fluctuating availability of green energy:

1. Adjusting the load to supplied power as far as possible within safe operating window
2. Switching off (a number of) electrolysers or modules (and turning them on again).

Both have consequences for the safe operation of electrolysers which are described below.

6.4.1 Switching between Full Load and Low Load

Decreasing the electrolysers' load will cause an increased concentration of H_2 in O_2 (and vice versa for AWE) [3]. No hazardous concentration will occur if the load stays above the minimum load. The minimum load itself depends to a great extent on the electrolyser technology's specific design details including BoP and can be close to 0%. The applicable minimum load must be determined for each individual plant. The limit should be set to the load at which a hazardous concentration (LFL on the anode side and UFL on the cathode side) can be reached. A safety margin of, for example, alarm at 25% of LFL and safety action at 50% of LFL, should be incorporated. It should be noted that concentration increase in the event of low load operations is a slow process and gas analysers combined with emergency shutdown can be an effective safeguard in case of aging. Over time, stack aging will result in increased crossover and will increase the minimum load. The minimum load requirement should therefore be incorporated into inspection and maintenance plans.

6.4.2 Frequency of Start-up and Shutdown

The intermittent nature of production based on renewable energy sources results in an increased start-up and shutdown frequency in comparison to constant and continuous production. Discussions with our partners revealed that this may accelerate membrane deterioration, leading to increased crossover and, as a result, shorter membrane lifespans. This 'accelerated' deterioration is a slow process and a hazardous concentration of hydrogen in oxygen and vice versa will most likely be detected by the gas analysers. According to the discussions, reduced plant output or efficiency in combination with trends in process parameter such as gas concentration will provide early warning signs of accelerated membrane deterioration. Care should be taken to properly define the safe state of an electrolyser plant or module.

6.4.3 Modular Set-up

In a modular set-up, the modules may (will) interact with each other and shutting down (and starting up) one or more modules may have (hazardous) consequences for other modules. These interactions can only be studied if detailed knowledge of design, set-up and operation are available. Examples of modules include:

- A number of stacks connected to one set of G/L-separators. One or a few stacks may be turned off, but not all the stacks connected to the same set of G/L-separators
- There may be multiple combinations of stacks with one of set of G/L-separators (unit). One unit may be shut down while the others are kept running.

Plant-specific risk assessments should pay attention to potentially (hazardous) interactions between modules, and safe states should be well defined.

6.5 Domino Effects

An incident which occurs in a specific part of the plant may propagate inside equipment and initiate secondary (or tertiary, etc.) effects at other locations in the plant. If an explosion causes equipment rupture, a pressure wave, debris/projectiles or heat radiation from jet fires or fire impingement may cause damage and the failure of other equipment within the effect distance. This includes water electrolysis plant equipment, but also equipment, systems and buildings outside the electrolysis plant. This may result in damage to the electrolyser plant and may even escalate the incident. Detailed analysis of these potential domino effects requires detailed knowledge of the specific situation and its location including other systems/plants inside the effect distances. In this project, domino effects can only be covered in general. Some examples of domino effects are mentioned below.

6.5.1 Internal Domino Effects (Limited to Electrolyser Plant)

- Ignition of a flammable mixture in the G/L-separator propagating to compressors and storage
- Pressure variations on the compressors' suction side causing level fluctuations in the G/L-separators and increased crossover (AWE)
- Propagation of an explosion from one set (module) of electrolyser stacks to other stacks
- Propogation of an explosion from one set of G/L-separators to another set (modular set-up)
- Rupture of G/L-separator and subsequent pressure wave causing damage to the electrolyser building which in turn may cause damage to electrolyser(s) and release of H_2.

6.5.2 External Domino Effects (from/to equipment or systems outside the electrolyser plant)

- Rupture of G/L-separator and subsequent pressure wave causing damage to a chemical warehouse close by and the release of chemicals
- Incident in chemical system close to the electrolyser plant causing damage to G/L-separator and subsequent release of H_2.

6.6 Key findings from the Safety Studies

Based on the safety studies the follwing conclusions have been drawn:

1. The scenarios developed as part of this project are generic scenarios and were based on studies with a limited scope. Plant-specific risk assessments are necessary to cover all the safety aspects and potential scenarios.
2. Some scenarios may develop very rapidly. Plant-specific risk analyses should pay specific attention to the speed of scenario development in relation to safeguard response speeds in general, but specifically with regard to the gas analysers' response speeds and their actions.
3. Although hydrogen is much lighter than other gases, its tendency to rise due to buoyancy depends greatly on release characteristics such as release direction and pressure. Sideways flow and even downward flow have to be taken into account.
4. Monitoring membrane degradation is important to identify and prevent hazardous gas compositions developing. Direct membrane monitoring is not possible, however (slow) changes in process parameter trends such as plant output, plant efficiency, increased cell and stack voltages, and gas concentrations may be indications of degraded membranes. Trend analysis is therefore important. Cell voltage monitoring may help in predicting the condition of the cells. In addition, maintenance programmes should pay attention to this aspect of electrolyser safety.
5. Pressure relief valves on G/L-separators in AWE plantsm ay result in hazardous scenarios instead of act as safeguard. Reliable instrumental level safeguarding is of utmost importance.

7. ATEX, Ventilation and Detection Aspects

7.1 ATEX

Because hydrogen is a highly flammable gas it is crucial to prevent explosive mixtures of hydrogen developing and to detect any leaks as soon as possible. The hazards posed by a flammable atmosphere and their risk assessment, including risk reduction, are determined in the EU by the ATEX regulations [30, 31]. The ATEX regulations apply to the formation of a flammable atmosphere due to foreseeable leakages. They do not include releases due to catastrophic events. Guidance on the interpretation of the regulations is given in IEC 60079-10-1 [5] for the EU and specifically for the Netherlands in NPR-7910-1 [4]. Both have been reviewed with respect to their application to hydrogen produced using water electrolysis in a study performed by RHDHV 'ATEX related criteria for ventilation of water electrolysis enclosures' [22]. The results and conclusions are summarised below. Special attention was paid to the validity of NPR7910-1 [4].

7.1.2 NPR7910-1 and IEC 60079-10

NPR7910-1 is a cut-down version of the methodology described in IEC 60079-10-1 for estimating the size and shape of hazardous areas in the event of leakages. This method's essence is that a generic leak flow rate leads to a standard zone shape and radius, irrespective of the type of gas that is leaking. Research into the origin of this cut-down method (experiments on propane gas leakages), revealed that NPR 7910-1 should not be applied to water electrolysis plants. The main reason being that hydrocarbon dispersion behaviour in air is not representative for hydrogen leaks. International standard IEC 60079-10-1, which presents formulas that take molecular mass into account, should be applied instead. The zone shape and size assumed in NPR 7910-1 was based on gases heavier than air, resulting in a zone which tends to increase in size in a downward direction. Conversely hydrogen, being a light gas, tends to rise when released. The exact size and shape of the hydrogen release depends on process conditions such as pressure, the release opening and release direction. The release calculations in Section 4 clearly show that hydrogen buoyancy can be limited close to the source of the release. A hazardous concentration may be present at locations lower and higher than the release opening.

7.1.2 Electrolysers

Hydrogen production using electrolysers demands a lot of energy supplied in the form of electricity at very high electrical current and voltage. With multiple stacks electrically in series voltage may also become high.

The presence of ignition sources cannot be prevented in the design of electrolyser stacks.

7.1.3 Other hydrogen and ATEX-related Specifics

The RHDHV study concluded that IEC 60079-10-1 can be used for hydrogen. Specific aspects that should be taken into account when using IEC 60079-10-1 for water electrolysis are:

- Natural ventilation may be an option, however obstructions in the air flow's flow path and potential shortcut pathways need to be carefully analysed. The maximum estimated dilution effect was rated as 'medium' and is only valid if no obstructions are present.
- Natural ventilation can be effective when the electrolysers are in operation and generating heat. Natural ventilation is much less effective if the electrolyser is in cold standby or shut down while still containing hydrogen.

- Classifying an entire building as a hazardous zone may be too conservative for large buildings. Computational Fluid Dynamics (CFD) simulations can be helpful for the realistic sizing of hazardous zones because these calculations provide more realistic dimensions of the area in which a hazardous concentration can be expected.
- Induced draft ventilation is preferred over forced draft, since this creates underpressure in the container.
- Induced draft ventilation will be more reliable than natural ventilation.
- The volume inside ventilation ducts, fans, etc. should be classified as Zone 2.
- Using cabinets for stacks may influence leak dilution, depending on the ventilation system's design. In Figure 15, stacks are shown located inside cabinets which will obstruct air flow in case of natural ventilation or room ventilation. These cabinets should have openings of sufficient size near the floor. Local suction may also be applied to enhance the dilution of hydrogen in the event of a leak. The cabinets act as confinements in the event opf major leaks,. However if the hydrogen is ignited, effects may be much more severe than in stacks that are not in cabinets.
- Hydrogen accumulation should be avoided. Hydrogen is much lighter than air and will readily rise. Once the gas, having mixed with air while migrating upwards, reaches any barrier such as a ceiling or roof, or even a horizontal and square HVAC duct, it tends to accumulate and spread horizontally under the obstruction. An ignitable hydrogen/air mixture may be formed and be sustained under closed horizontal surfaces. Important aspects for minimising such accumulation include:
  - Avoid flat roofs
  - Avoid corrugated roofs
  - Create permanent vent(s) at the highest point(s) in the roof
  - Avoid intermediate floors (e.g. for maintenance purposes) inside the room above the electrolyser stacks, G/L separators and hydrogen piping
  - If intermediate floors are required, use grated floors instead of solid floors
  - Wherever possible, install staircases on the outside of the building instead of inside
  - Install open staircases with grated steps (both inside and outside the building)
  - Avoid square HVAC ducting when situated above the electrolyser stacks, G/L separators and hydrogen piping
  - Ensure proper ventilation flow distribution that leaves no stagnant zones in the room
  - Minimise the number of obstructions in the potential flow path of leaked hydrogen, i.e. between potential leak sources and the venting locations
  - In case of any internal enclosures: ensure these are overpressured.

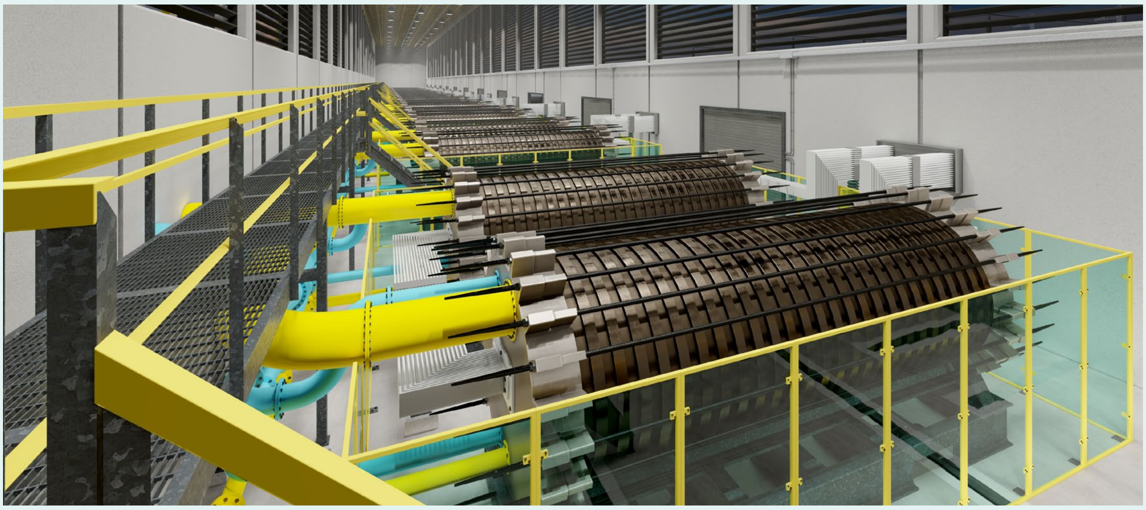

Figure 15: Artist impression of AWE electrolyser hall

7.2 Key findings from the ATEX Review

1. NPR7910-1 should not be used for hydrogen production and in hydrogen applications because both the shape and size of hazardous zones differ from those prescribed in NPR7910-1.
2. From an ATEX point of view, electrolysers and other equipment containing hydrogen should preferably be located outdoors to reduce the probability of the formation of a flammable cloud.
3. Natural ventilation cannot be regarded as an effective option to combat any possible release of hydrogen from pressurised electrolysers.
4. Natural or forced ventilation's goal is to dilute any gas released. Many factors influence ventilation effectivenes. The principal being:
    a. Flow rate
    b. Obstructions
    c. Accumulation
    d. Design philosophy including small rooms, large building, use of cabinets, etc.
5. Ventilation, whether forced or natural, may only be effective for leaks subject to the ATEX regulations, yet may be insufficient to prevent the formation of a flammable cloud in the event of major leaks (accidents).
6. Ventilation effectiveness depends to a great extent on the container, room or building's layout. Layout modifications, for example, adding additional (temporarary) equipment may adversely influence ventilation efficiency and should therefore be subject to a MOC procedure.

8. Hydrogen Sensor Considerations

The industry faces issues with regard to the effective detection of flammable atmospheres both inside and outside equipment in enclosures/buildings.

8.1 Hydrogen Sensors Inside Equipment

The effectiveness of gas-quality measurements in preventing in-equipment mixing was discussed and all the partners agreed that the only practical location for contemporary instruments for measuring gas quality was the gas/liquid separators. No technology currently exists that reliably measures gas composition in the cell stack. This is mostly due to the presence of liquid electrolyte which interferes with the detection mechanism. A significant time lag therefore exists between the moment in-equipment mixing (by whatever mechanism) occurs and the time at which it can be detected. Furthermore, since the gas composition analysed at the G/L-separators is the average of all the cells – of which there may be hundreds – it would be impossible to determine exactly where the point of in-equipment mixing had occurred, making corrective action unfeasible. The partners' consensus was therefore that gas quality measurement, instituted as a barrier, can be effective in preventing an explosive mixture from forming in the separators for some scenarios, but not within individual cells or even the header of a cell stack, especially if the degradation that results from in-equipment mixing occurs rapidly. Furthermore, gas quality measurements are only effective in cases of gradual/slow changes in concentration. In the event of rapidly changing concentrations, gas quality measurement is deemed not fast enough with respect to the desired response time.

8.2 Hydrogen Detectors in Enclosures/Buildings

An extensive discussion was dedicated to the placement of hydrogen sensors in enclosures/buildings to mitigate the consequences of a loss of hydrogen containment. All the partners indicated that it was a significant challenge to determine optimum locations for hydrogen detectors in buildings without first performing hydrogen dispersion simulations. Even so, there are factors that make the placement of hydrogen sensors a uniquely difficult task, namely:

- Location of leak – optimum hydrogen sensor placement is highly dependent on the location of the leak responsible for the loss of hydrogen containment. Unfortunately, it is not feasible to predict the location leaks and sensor placement must therefore be effected on the basis of the assumption that a leak may originate from any point in the process. At best, certain process segments may be highlighted as being particularly susceptible to leakages and sensor placements must account for that.
- Process and installation setup – the optimisation of hydrogen sensor placement is highly dependent on the internal configuration of the electrolyser process and should take the possible presence of low-lying confined areas where hydrogen may accumulate, the design of the roof, the height of the building, the presence of walls between units, the location of the ventilation point(s), the release rate and direction, the ambient temperature, etc. into account.

After the 2018 HySafe Research Priority Workshop on hydrogen safety, literature was published offering guidance on hydrogen sensor placement in mechanically ventilated enclosures [25]. This approach is still under development, especially with regard to large-scale setups. The following tentative recommendations for hydrogen sensor placements for reliable concentration measurement in ventilated enclosures have been proposed:

1. Detectors should not be placed in a direct airflow path from air inlets to exhaust fans
2. Detectors locations close to the floor are impractical
3. Detectors should be placed below the enclosure ceiling, but not be obstructed by piping, etc.

At this moment, there are many developments in the field of gas detectors e.g. leak detection based on sound, which may quickly render the conclusions of this report outdated.

8.3 Fire detection

Hydrogen jet fires are hard to detect with common used equipment. After ignition of hydrogen, detection of the flames can be done by:

- UV detectors
- UV detectors combined with IR detection for detecting secondary fires
- Triple IR detection

Also in the field of fire detection there are many developments at this moment This may quickly render the conclusions of this report outdated.

9. Options for Risk Reduction

The following design considerations are provided for electrolysers on the basis of the critical hazard scenarios. The list of options augments the generally accepted design practices in the (petro) chemical industry. Plant-specific safety studies and risk assessments should be used to determine whether options are applicable to a specific plant.

9.1 Technical

- Emphasisis on inherently safer design and conservativism in safety in design due to hydrogen's properties and limited experiences with the flexible/ intermittent operation of electrolyser technologies.
- Consider to apply "Accidental Load" aproach for safety critical systems [39]
- The required risk reduction factor for instrumental safeguards to reduce risks to an acceptable level, as determined by the HAZOP and LOPA, will often be higher than can be achieved with a basic control system (>10). A Safety Instrumented System (SIS) in accordance with IEC 61511 will be required to properly manage the risk.
- Avoiding (fugitive) leakages inside a building or container by minimising the number of flanges.
- Increasing the mechanical design pressure to contain in-equipment explosions and avoid loss of containment in cases in which instrumental safeguards are not sufficiently fast to prevent a flammable atmosphere.
- Specifying and, if need be, adjusting, low load conditions before initial start-up to avoid excessive gas crossover.
- Designing for the end-of-life conditions of electrolyser components, such as thinner membranes with increased gas crossover and risk of leakages.
- Designing ventilation and detection based on fugitive emissions, climatisation and process safety hazards, taking congested areas based on IEC60079-10-1 into account.
- The application of blast walls or building walls of increased strength where pressure effects from an explosion may potentially become too high for other buildings or structures.
- Windows provided with anti-splinter foil may be applied as passive safeguards where debris projection may be expected.
- H_2 and O_2 process vents should be carefully designed and always vent to a safe location, where any of possible scenarios (immediate/delayed ignition) can be demonstrated not to have hazardous consequences for nearby staff, the general public, equipment or buildings.
- Hydrogen leakages are difficult to detect since the available point sensors would need to be in close proximity of the leak. Detecting the sound of gas escaping is a promising technology, yet still needs to be proven.
- Hydrogen fires can be detected using IR and UV sensors.
- Installation of an effective ventilation system that takes the requirements due to hydrogen's specific properties into account.

9.2 Organisational

In addition to technical safety aspects, it is important to have a good, effective organisation for design, operation and maintenance. Water electrolysis plants are therefore recommended to have a Process Safety Management System in place which covers the following subjects (non-exhaustive):

1. Organisational and staffing aspects e.g. responsibilities, competences and training
2. Hazard, etc. identification and evaluation using HAZID, HAZOP, SIL, LOPA
3. Control of operations and asset integrity
4. Management of Change
5. Emergency management including incident scenario preparation and training incl. drills
6. Performance monitoring including management reviews and auditing.

An effective PSM system can be developed using NTA 8620 [23], AIChe - CCPS [24] or EPSC - Process Safety Management – European Practice [29], CLEAN HYDROGEN JOINT UNDERTAKING - Safety Planning and Management in Hydrogen and Fuel Cells Projects – Guidance Document [36].

- Occupation levels in the plant during operation can be minimised by:
    - o Utilising unmanned or remote operation
    - o Minimising local instruments, analysers and appendages, which need frequent inspections or calibration
    - o Minimising staffing levels during the simultaneous operation of adjacent stacks/ modules during maintenance/ inspection
    - o Specifying the maximum number of staff and the maximum hours per day if operations require regular operator assistance or inspections.
- All changes in plant/building/room layout should be carefully analysed with respect to their effect on ventilation effectiveness with regard to preventing a flammable atmosphere. Examples: positioning of louvres, obstacles in front of air inlets (outside building). All such changes could influence the ventilation.
- Seal tests should take temperature and pressure differences into account.

9.3 Electrolyser specific

For AWE, a number of scenarios result in a flow from one of the separators to the other separator along the balancing line. Initially, the flow will be liquid, but it will change to gas as soon as all the liquid from one separator has been pushed to the other. A flammable atmosphere will develop soon after the transition from liquid to gas. The liquid volume in the G/L-separators will delay the formation of a flammable atmosphere. More liquid volume means increased delay. Nevetheless, a reliable (delta-) level active safeguarding system which puts the plant in a safe state remains important.

Due to the pressure difference between the anode and cathode side which is often applied in PEM and the inability of gas analysers to detect a flammable atmosphere on time, an explosion-proof design for the anode side of the plant could be considered.

10. Key findings

Specific process safety risks related to the potential for gas explosions inside or outside equipment of water electrolysis plants have been identified and assessed.

Water electrolysis plants can be designed and operated safely if existing practices for project approach and risk assessment from the (petro)chemical industry are applied to water electrolysis plants. Hydrogen's properties are such that major incidents may occur and an advanced safeguarding philosophy is therefore essential. Hazard scenarios have been developed for water electrolysis that uses AWE or PEM technology. These scenarios are generic and will help companies undertake their plant-specific risk assessments. Plant-specific risk assessments remain necessary because the details of each plant, design and technology are different. Some scenarios may develop very rapidly. Plant-specific risk analyses should pay specific attention to the speed of scenario development in relation to safeguard response speeds in general, but specifically with regard to the gas analysers' response speeds and their actions. Monitoring membrane degradation is important to identify and prevent hazardous gas compositions developing. Direct membrane monitoring is not possible, however (slow) changes in process parameter trends such as plant output, plant efficiency, stack voltage and gas concentrations may be indications of degraded membranes. Cell voltage monitoring may help in predicting the condition of the cells. Trend analysis is therefore important. Sideways flow and even downward flow have to be taken into account depending on release characteristics such as release direction and pressure. Although hydrogen is much lighter than other gases, its tendency to rise due to buoyancy is not always as expected. The Europen standard IEC 60079-10-1 should be applied instead of NPR7910-1, because of the specific properties of hydrogen.

Detailed bow ties and hazards assessments for critical hazard scenarios have been made. Based on the above considerations, these results can assist authorities, developers, suppliers and the operators of water electrolysis plants to understand the risks and manage these. In this way, the finding of this project will contribute to avoiding or preventing accidents to happen.

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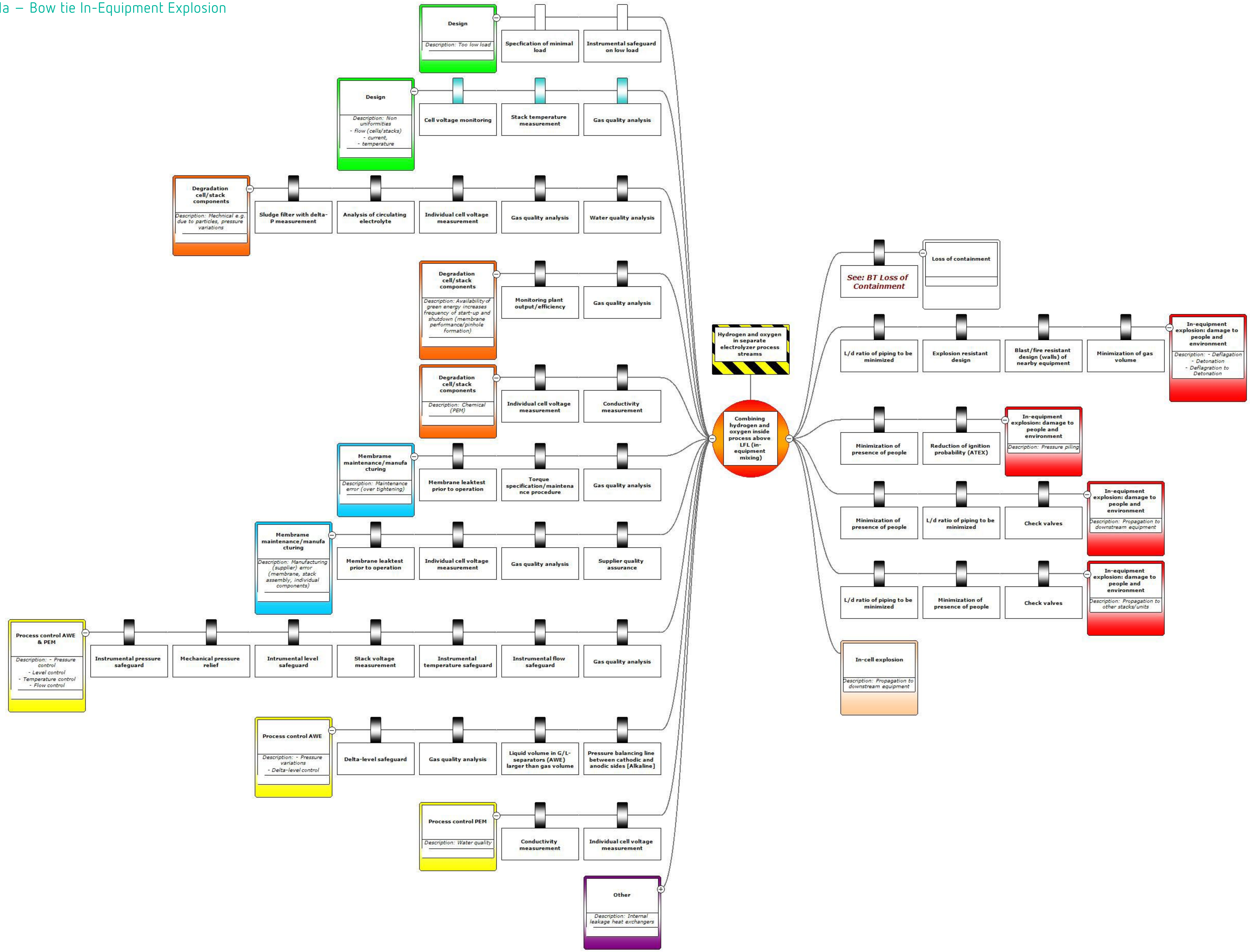
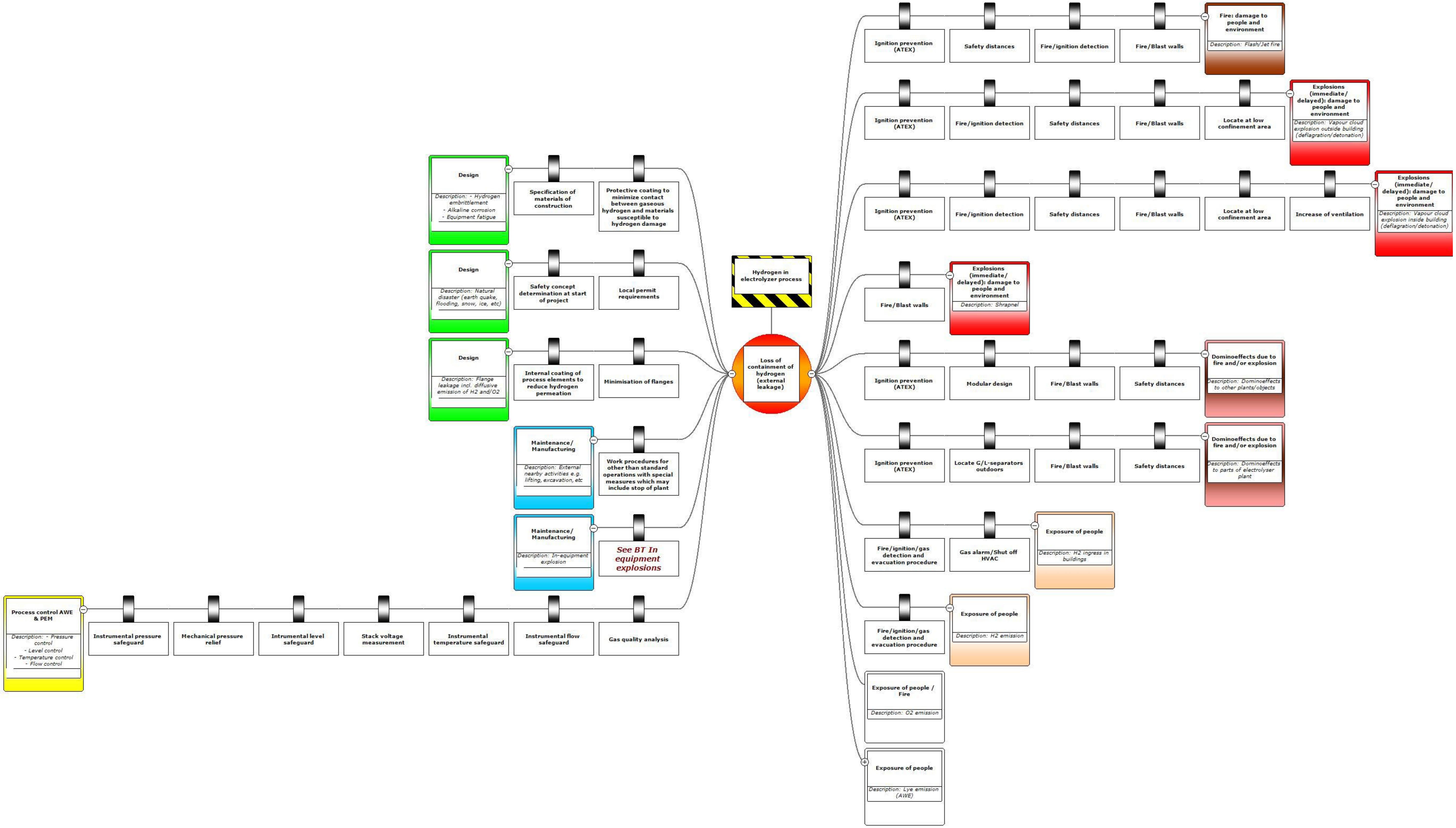


Design
Description: Too low load
Specfication of minimal load
Instrumental safeguard on low load
Design
Description: Non uniformities - flow (cells/stacks) - current, - temperature
Cell voltage monitoring
Stack temperature measurement
Gas quality analysis
Degradation cell/stack components
Description: Mechnical e.g. due to particles, pressure variations
Sludge filter with delta-P measurement
Analysis of circulating electrolyte
Individual cell voltage measurement
Gas quality analysis
Water quality analysis
Degradation cell/stack components
Description: Availability of green energy increases frequency of start-up and shutdown (membrane performance/pinhole formation)
Monitoring plant output/efficiency
Gas quality analysis
Degradation cell/stack components
Description: Chemical (PEM)
Individual cell voltage measurement
Conductivity measurement
Membrame maintenance/manufacturing
Description: Maintenance error (over tightening)
Membrane leaktest prior to operation
Torque specification/maintenance procedure
Gas quality analysis
Membrame maintenance/manufacturing
Description: Manufacturing (supplier) error (membrane, stack assembly, individual components)
Membrane leaktest prior to operation
Individual cell voltage measurement
Gas quality analysis
Supplier quality assurance
Process control AWE & PEM
Description: - Pressure control - Level control - Temperature control - Flow control
Instrumental pressure safeguard
Mechanical pressure relief
Intrumental level safeguard
Stack voltage measurement
Instrumental temperature safeguard
Instrumental flow safeguard
Gas quality analysis
Process control AWE
Description: - Pressure variations - Delta-level control
Delta-level safeguard
Gas quality analysis
Liquid volume in G/L-separators (AWE) larger than gas volume
Pressure balancing line between cathodic and anodic sides [Alkaline]
Process control PEM
Description: Water quality
Conductivity measurement
Individual cell voltage measurement
Other
Description: Internal leakage heat exchangers
Hydrogen and oxygen in separate electrolyzer process streams
Combining hydrogen and oxygen inside process above LFL (in-equipment mixing)
See: BT Loss of Containment
Loss of containment
L/d ratio of piping to be minimized
Explosion resistant design
Blast/fire resistant design (walls) of nearby equipment
Minimization of gas volume
In-equipment explosion: damage to people and environment
Description: - Deflagation - Detonation - Deflagration to Detonation
Minimization of presence of people
Reduction of ignition probability (ATEX)
In-equipment explosion: damage to people and environment
Description: Pressure piling
Minimization of presence of people
L/d ratio of piping to be minimized
Check valves
In-equipment explosion: damage to people and environment
Description: Propagation to downstream equipment
L/d ratio of piping to be minimized
Minimization of presence of people
Check valves
In-equipment explosion: damage to people and environment
Description: Propagation to other stacks/units
In-cell explosion
Description: Propagation to downstream equipment


Hydrogen in electrolyzer process
Loss of containment of hydrogen (external leakage)
Design
Description: - Hydrogen embrittlement - Alkaline corrosion - Equipment fatigue
Specification of materials of construction
Protective coating to minimize contact between gaseous hydrogen and materials susceptible to hydrogen damage
Design
Description: Natural disaster (earth quake, flooding, snow, ice, etc)
Safety concept determination at start of project
Local permit requirements
Design
Description: Flange leakage incl. diffusive emission of H2 and/O2
Internal coating of process elements to reduce hydrogen permeation
Minimisation of flanges
Maintenance/ Manufacturing
Description: External nearby activities e.g. lifting, excavation, etc
Work procedures for other than standard operations with special measures which may include stop of plant
Maintenance/ Manufacturing
Description: In-equipment explosion
See BT In equipment explosions
Process control AWE & PEM
Description: - Pressure control - Level control - Temperature control - Flow control
Instrumental pressure safeguard
Mechanical pressure relief
Intrumental level safeguard
Stack voltage measurement
Instrumental temperature safeguard
Instrumental flow safeguard
Gas quality analysis
Ignition prevention (ATEX)
Safety distances
Fire/ignition detection
Fire/Blast walls
Fire: damage to people and environment
Description: Flash/Jet fire
Ignition prevention (ATEX)
Fire/ignition detection
Safety distances
Fire/Blast walls
Locate at low confinement area
Explosions (immediate/ delayed): damage to people and environment
Description: Vapour cloud explosion outside building (deflagration/detonation)
Ignition prevention (ATEX)
Fire/ignition detection
Safety distances
Fire/Blast walls
Locate at low confinement area
Increase of ventilation
Explosions (immediate/ delayed): damage to people and environment
Description: Vapour cloud explosion inside building (deflagration/detonation)
Fire/Blast walls
Explosions (immediate/ delayed): damage to people and environment
Description: Shrapnel
Ignition prevention (ATEX)
Modular design
Fire/Blast walls
Safety distances
Dominoeffects due to fire and/or explosion
Description: Dominoeffects to other plants/objects
Ignition prevention (ATEX)
Locate G/L-separators outdoors
Fire/Blast walls
Safety distances
Dominoeffects due to fire and/or explosion
Description: Dominoeffects to parts of electrolyser plant
Fire/ignition/gas detection and evacuation procedure
Gas alarm/Shut off HVAC
Exposure of people
Description: H2 ingress in buildings
Fire/ignition/gas detection and evacuation procedure
Exposure of people
Description: H2 emission
Exposure of people / Fire
Description: O2 emission
Exposure of people
Description: Lye emission (AWE)

Annex 2a – Alkaline Water Electrolysis - Generic Hazard Scenarios

#	Cause	Type	Consequence	Speed of scenario development and Detectability by gas sensors in head space of G/L-separators	Remarks/Prevention/Mitigation
1	Unequal flow distribution to individual cells or stacks		Unequal flow distribution of electrolyte (catholyte and anolyte) in manifold to individual cells and/or header to multiple stacks can lead to damage to diaphragms due to deposition of particles, insufficient cooling/ wetting and therefore hotspots and therefore H2 to O2 and O2 to H2 crossover.	Slow/Yes	- Proper initial design. Equal distribution should be considered in hydraulic piping design of headers and manifold. - Uneven flow can be caused by an obstacle in the line. A filter with differential P measurement should be installed. - Valves in the circulation lines should be avoided made LO when they cannot be avoided.
2	Operating at too low load		Low load of the plant or individual stacks causes a higher concentration of H2 in the anolyte flow to the G/L-separator and higher concentration of O2 in the catholyte flow (crossover) due to ongoing diffusion and lower production. In case of too low load, the gas crossover increases gradually to reach or exceed LFL locally in the cell, the header and in the separator over time. The extent to which the concentration increases is technology and stack specific, changes over time due to aging and degradation, the actual conditions, and the minimum load set point for an individual stack.	Slow/Yes	- Operation at low load is design and supplier specific and should be determined in the design phase for each electrolyser stack or module and tested and fine tuned after start-up and prescribed by the supplier. Prevention is done by defining safe operating limits on load. Recommended safeguarding by automatic shutdown when current is out of range. - Prevention is done by load and efficiency monitoring (current/output) and by gas sampling. Gas analysis is slow but gives understanding of loads and crossover flows. Alarms can be set on trends.
3	Corrosion damage of cell components		The corrosion of cell components (hole in bipolar plate or failure of internal gasket) can lead to membrane damage and electrode damage and increased crossover. It initially concerns one or a few cells only. As a results flammable mixtures can occur in the cell, manifold. In the header the flammable mixture is diluted.	Slow/Yes	- Proper material selection of construction materials of stacks and piping during initial design. - Adequate QA/QC testing and inspections by stack vendor - Maintenance and inspections plans during operations. - Cell monitoring may help in predicting the condition of the cells.

4	Clogging or accumulation of small particles over time		Small particles can damage the diaphragm/membrane and potentially cause short circuit, reduced performance, hot spots, punctures and gas crossover. In case of prolonged and more severe corrosion of stack components, like bipolar plates, or piping, metal deposits in the manifold or cells may lead to unequal flow distribution, retention of gas bubbles, gas pockets and hots spots and ultimately clogging of stacks and increased gas crossover. As a result flammable mixtures can occur in the cell, manifold, header and separator. Also damage to the electrodes may occur. In practice small explosions inside cells are observed. Aforementioned is to be regarded as credible worst case.	Slow/Yes	- Filter in electrolyte flow and delta-P measurement on filter to detect saturation of filter. - Cell voltage monitoring may detect abnormalities in affected cells e.g. short circuit - Stack voltage monitoring may indicate deviations
5	Quality of fresh water/KOH supply		Depending on the quality, membrane damage may occur leading to increased crossover and the formation of a flammable atmosphere in the cell, stack and downstream equipment. In general quality aspect is less important for AWE compared to PEM.	Slow/Yes	End user must adhere to the specification given by the supplier of stacks and methods to control quality must be implemented.
6	Error during mounting of diaphragm/cells/stacks		In case stack product defects are not discovered during manufacture, possible leakages can occur. This can be external leakages but also internal when sealings are not according specs. After some time this can lead to possible membrane damage and crossover of gases. Depending on the product quality this can concern only one or a few cells but can also comprise more cells. In the header the flammable mixture is diluted.	Slow/Yes	- Depending on supplier specific design and QA/QC procedures when stack is assembled and tested. - Delta pressure test on cell or stack level can be considered. - Cell voltage measurement may detect some cell integrity failures
7	No fresh water supply		Levels in separator and other equipment will decrease due to ongoing water consumption. This will lead to increase of lye concentration and decrease of level in the G/L-separators. On the long term it may lead to the formation of solids/particles which in turn increase the gas crossover. Membrane damage may be prevented in case a filter is present in the electrolyte flows. But in that case flow may be reduced to a large extent due to blockage of that same filter. The scenario is comparable to " Clogging or accumulation of small particles over time".	Slow/Yes	- Fresh water supply control is supplier dependent and loss of fresh water supply should be detected and appropriate actions should be taken. Most appropriate will be level detection at the location where loss of fresh water supply is first noticeable.

#	Cause	Type	Consequence	Speed of scenario development and Detectability by gas sensors in head space of G/L-separators	Remarks/Prevention/Mitigation
			If not prevented the level in the G/L-separators may become that low that gas crossover via the balancing line will occur (on long term)		
8	Loss of (delta) pressure control on G/L separators		A pressure control failure could lead to higher differential pressure over the diaphragm and diaphragm damage (e.g. pinholes) and rupture of one or several diaphragms. Subsequently, the gas crossover increases and can reach or exceed LFL in the G/L-separators.	(could be)Fast/No, depends on extent of membrane damage	- Depending on supplier stack design and specific requirements to guarantee diaphragm integrity, design pressure variations over membrane should be below supplier specification. - Upon too much pressure difference the electrolyser needs to be tripped. The trip could be based on pressure difference and level difference in the G/L-separators
9	Flow control failure of anolyte and/or catholyte circulation		Unbalanced or low flow of catholyte and anolyte may lead to different differential pressures over the diaphragms and potential membrane rupture. It can also lead to a different level in the G/L-separators. Loss of electrolyte flow may also mean reduced cooling of diaphragm, hot spots, bubble release, gas pockets and damage/rupture and increased gas crossover. In practice small explosions inside cells are observed. Aforementioned is to be regarded as credible worst case.	(could be)Fast/No, depends on extent of membrane damage	- Depending on type of diaphragm and supplier specific admissible differential design pressures, variations over membrane, should be limited. The level control will compensate for differential hydraulic pressures. - Temperature indicators at outlet of stack trips the electrolysers
10	Failure of temperature control of electrolyte circulation flow		High temperature of the anolyte or catholyte may result in faster degradation of membrane and electrodes due to higher corrosion potential and release of particles. Excessive temperature can break-down the diaphragm leading to increased gas crossover and the formation of an ignitable atmosphere in the G/L separators. It initially concerns a few membranes only.	Slow/Yes	- High temperature safeguarding e.g. delta-T over stack and T at outlet of stack. First alarms followed by trip of the electrolysers. - Supporting information/ prediction of the quality of the membranes can be done by cell voltage monitoring for example
11	Failure of voltage or current control		Too high currents and voltages can lead to overheating in the stack, damage to the internals such as electrodes and membranes, increased crossover of H2 and O2 in the stack and possible formation of explosive mixtures. Depending on the current this can take some time or can be a quick process.	Slow/Yes	- Recommended safeguarding by alarms and automatic shutdown when current and voltage are out of range.

12	Failure of absolute level control G/L separator(s) or failure of delta-level control		Failures of absolute level control may lead to loss of level in (one of) the G/L-separator(s). This can result in gas transfer through the balancing line from one to the other G/L-separator and consequently mixing of hydrogen and oxygen. This depends on flow regime and potential formation of vortex.	Fast/No	- Level safeguarding on G/L-separators by means of Low/High Level trip. - Note: the normal operating liquid level in the G/L-separators determine how fast and how much flammable gas will be formed because initially only liquid will be transferred via the balancing line. If the liquid volume is larger than the gas volume a flammable mixture will not be formed in the G/L-separator but in downstream equipment.
13	Failure of pressure control of the G/L-separators		Failureof pressure control may lead to the same consequences as failure of level control	Slow/Yes	- Level safeguarding on G/L-separators by means of Low/High Level trip. - Pressure safeguarding on the G/L-separators by means of Low/High pressure trip. - Note: the normal operating liquid level in the G/L-separators determine how fast and how much flammable gas will be formed because initially only liquid will be transferred via the balancing line. If the liquid volume is larger than the gas volume a flammable mixture will not be formed in the G/L-separator but in downstream equipment.
14	Difference in relief pressure of relief valves on G/L-separators		Pressure relief valves in G/L-separators shall prevent overpressure and vessel bursting. The activation pressure of the PRV's on both the H2 and O2 G/L-separators will never be exactly the same and one will open before the other. When one opens, initially liquid and later gas, from the other separator will be pushed into the separator of which the relief valve has opened and hydrogen and oxygen will be mixed.	(could be)Fast/No	- Level safeguarding on G/L-separators by means of Low/High Level trip. - Pressure safeguarding on the G/L-separators by means of Low/High pressure trip. - Note: the normal operating liquid level in the G/L-separators determine how fast and how much flammable gas will be formed because initially only liquid will be transferred via the balancing line. If the liquid volume is larger than the gas volume a flammable mixture will not be formed in the G/L-separator but in quipment downstream of the separator.
15	Internal leakage of heat exchanger		Hydrogen or Oxygen will enter the cooling circuit and potentially cause a hazard situation (even at remote area)	Cannot be detected gas sensors on the G/L-separators	'Hydrogen and oxygen detection in storage tank of cooling liquid
16	Process disturbances in outside scope equipment.		Without additional knowledge of the details the scenario cannot be evaluated. Nevertheless, it is obvious they may have hazardous consequences and should be addressed in plant specific risk assessments.		

Annex 2b – Proton Exchange Membrane Water Electrolysis - Generic Hazard Scenarios

#	Cause	Consequence	Speed of scenario development and Detectability by gas sensors in head space of G/L-separators	Remarks/Prevention/Mitigation
DESIGN				
1	Operating at too low load	Low load of the plant or individual stacks leads to a higher concentration of H2 in the flow to the Oxygen G/L-separator and higher concentration of O2 in the flow to the Hydrogen G/L-separator.	Slow/Yes	- Operation at low load is design and supplier specific and should be determined in the design phase for each electrolyser stack or module and tested and fine tuned after start-up and prescribed by the supplier. Prevention is done by defining safe operating limits on load. Recommended safeguarding by automatic shutdown when current is out of range. - Prevention is done by load and efficiency monitoring (current/output) and by gas sampling. Gas analysis is slow but gives understanding of loads and crossover flows. Alarms can be set on trends.
CELL OR STACK DEGRADATION				
2	Corrosion damage leading to physical breakdown of cell components	Coatings pealing e.g. PTL and BPP off, being damaged, wear and tear, manufacturing defects, all of this may lead to corrosion and as a consequence Loss of containment and/or internal mixing of H2 in O2. Due to the pressure difference between cathode side and anode side H2 concentration quickly rises above LFL in stack header and piping to G/L-separator. (see also pinhole calculations)	Fast/No	Proper material selection during initial design, manufacturing QA/QC and maintenance and inspections plans.
3	Introduction of foreign material/ particles	The particles may cause damage to the membrane resulting in crossover of H2 into the O2 side of the membrane. It is expected that crossover starts with one (few) membrane(s), but the number of damaged membranes will increase over time and subsequently the crossover flow will also increase. Due to the pressure difference between cathode side and anode side H2 concentration quickly rises above LFL in stack header and piping to G/L-separator. (see also pinhole calculations).	Fast/No	Filter in electrolyte flow and delta-P measurement on filter to detect saturation of filter. It initially concerns one or a few cells only. In the header the flammable mixture is diluted. Side stream treatment removing the impurities
4	Quality fresh water supply	Metal ion (e.g. Fe^{3+}) contaminants in the water supply will promote and accelerate degradation of the electrolyser. Over time damage to the membrane will result in increasingly higher gas crossover until a threshold is reached where the membrane has developed a hole and rapid mixing occurs.	Typically Slow/Yes	Conductivity measurement

MEMBRANE MAINTENANCE OR MANUFACTURING				
5	Error during mounting of membrane overtightening) and/or stack	Excessive pressure on the active area leading to a damaged membrane (Puncture, creep…) and higher gas crossover with possible escalation due to a short-circuit. Same can happen at stack level.		Proper choice during initial design, manufacturing QA/QC and maintenance and inspections plans, see also ISO22734
PROCESS CONTROL				
6	Failure of temperature control in the recirculation or cooling waterflow	High temperature leads to accelerated degradation of the membrane and if excessively high then rapid breakdown of the membrane leading to a rapid crossflow of H2 in O2.	Slow/Yes	Temperature safeguarding e.g. T after HEX, T at stack inlet, T at stack outlet
7	Failure in voltage or current control	Voltage high: won't be able to develop higher voltage if corresponding current is not supplied.	Fast/No	Controlled by power supply. Recommended safeguarding by alarms and automatic shutdown when current and voltage are out of range.
8	No or low pure water supply control failure	No pure water supply results in gradually decreasing hold-up of water in system. At some point membrane can get dry and is damaged. As soon as the membrane dries out a temperature runaway will occur and damage to the membrane of a potential large number of cells in a stack resulting in a rapid H2 crossover driven by the differential pressure. This can result in a flammable atmosphere in the O2 G/L-separator. At max the entire G/L-separator is filled with a flammable mixture. The time needed to get dry depends on the normal amount of liquid present in the O2 G/L-separator.	Fast/No	Loss of fresh water supply should be detected, and appropriate actions should be taken. Most appropriate will be level detection at the location where loss of fresh water supply will occur first. Also recirculation flow is measured with low flow alarm and trip.
9	Water flow control failure to anode or cathode side	This results in no or reduced cooling and therefore will result in an increased temperature until the membrane overheats and is damaged. Then hydrogen flow driven by the differential pressure will flow through the hole to the O2 G/L separator. (See also temperature control failure)	Slow/Yes	Flow safeguarding in addition to temperature safeguarding can be applied
10	Flow control failure from H2-G/L separator to flash vessel	Full H2 pressure on the flash vessel potentially causing uncontrolled flow from flash vessel to O2-G/L separator and H2 flowing into the O2¬-G/L separator.	Fast/No	Flow control of water from the H2-G/L separator to flash vessel and to O2-G/L separator depends on the supplier. Reliable safeguarding is needed to protect against failure
11	Flow control failure from flash vessel to O2-G/L separator	Potential for flow of H2 directly into the O2 G/L separator	Fast/No	. Reliable safeguarding is needed to protect against flow control failure
12	Pressure control O2 G/L separator fails	The pressure will rise and a leakage will occur (and potential rupture) at the weakest spot resulting in a release of O2 inside the electrolyser building or outdoor and potential damage to equipment and people when in contact with O2 at high concentration.	n.a.	Pressure safeguarding by means of instrumental safeguards and/or pressure relief valve on O2-G/L separator.

13	Pressure control H2 G/L separator fails	In case of too high pressure: The pressure will rise, and a leakage will occur (and potential rupture) at the weakest spot resulting in a release of H2 inside the electrolyser building or outdoor and potential for fire and/or explosion. In case of too low pressure: Potential for O2 flowing from the O2 G/L separator into the flash vessel and/or H2 G/L separator	n.a. Fast/No	Pressure safeguarding by means of instrumental safeguards and/or pressure relief valve on H2-G/L separator. Pressure safeguarding by means of instrumental safeguards
OTHER				
14	Internal leakage of heat exchanger	Hydrogen or Oxygen will enter the cooling circuit and potentially cause a hazard situation (even at remote area)	Cannot be detected gas sensors on the G/L-separators	'Hydrogen and oxygen detection in storage tank of cooling liquid
15	Process disturbances in outside scope equipment.	Without additional knowledge of the details the scenario cannot be evaluated. Nevertheless, it is obvious they may have hazardous consequences and should be addressed in plant specific risk assessments.		

Annex 2c – Loss of Containment - Generic Hazard Scenarios

#	Leakage	Cause	Consequence	Remarks/Prevention/Mitigation
1	Leakages hydrogen	Aging, low gasket quality, maintenance error, not sufficient torque, flanges, vibrations, process control error, etc	A leakage e.g. from a gasket, hole in piping, etc. may be outdoor or inside the electrolyser building. Depending on the pressure, location and hole size of the leakage it could be a jet (large hole) or a small release (small hole). Ignition may occur due to ignition sources but auto-ignition may as well occur. In case of immediate ignition, depending on the size of the hole and pressure, a small local fire or a jet fire may occur which will harm people when they are in the vicinity of the leak source and cause damage to other nearby equipment. A vapour explosion may occur in case of delayed ignition causing damage to equipment, building and harm to people	- Welded valves, piping and fittings, minimisation of flanges - Forced ventilation - mounting of appendages such that flow is directed upwards -Installation of separators, equipment (excl. stacks) outdoors (restricted access) - ATEX certified equipment will reduce probability of ignition for small leakages but not for large ones - Gas detectors in building may not be effective
2	Leakages oxygen	Aging, low gasket quality, maintenance error, not sufficient torque, flanges, vibrations, process control error, etc	A leakage e.g. a gasket blowout, hole in piping, etc. may be outdoor or inside the electrolyser building. Oxygen may cause fires (auto-ignition) when coming into contact with materials which can be oxidised, which are many. These fires may cause damage to other parts of the plant and to people.	- Welded valves, piping and fittings, minimisation of flanges - Forced ventilation - Mounting of appendages such that flow is directed upwards

Annex 3 – Summary of Hydrogen properties

One of the most critical safety risks when handling hydrogen is its propensity to form explosive mixtures in an oxygenated environment. There is a broad range of hydrogen/air and hydrogen/oxygen mixtures in which flammability and explosivity pose very real threats to safety. Furthermore, this hazardous range of concentrations is subject – by differing degrees – to operating conditions which must be accounted for. Therefore, design considerations must include temperature and pressure effects on safe threshold limits of hydrogen mixtures. The results of experimental work conducted by the German Federal Institute for Materials Research and Testing (BAM) depicting the explosion characteristics of hydrogen mixtures as functions of temperature and pressure [26] are given in this appendix. Regarding explosion characteristics of hydrogen/oxygen/lye mixtures, there is no reliable data available, and it must be designated as an existing gap in knowledge. It is known that water vapour lowers the effect of hydrogen/oxygen explosions. Since the water vapour pressure of lye is lower compared to that of water, the favourable influence of water on the explosion effect is expected to less (at the same temperature and pressure).

Influence of Temperature on Explosive Limits

There is a clear linear relationship between the explosivity (both LFL and UFL) of hydrogen/air mixtures and temperature (seen in Table 5 and Figure 16). As the temperature increases, the explosive range of the mixture broadens significantly as well. Therefore, from a safety perspective, high temperature operation poses greater concerns and requires more planning. Graph and table of the explosivity data is shown below:

Table 5: Explosion limits of hydrogen/air mixtures at atmospheric pressure as a function of temperature according to DIN 51649-1

Temperature (°C)	Lower Explosion Limit (LFL) (mol% H2)	Upper Explosion Limit (UFL) (mol% H2)
20	3.9	75.2
100	3.4	77.6
200	2.9	81.3
300	2.1	83.9
400	1.5	87.6

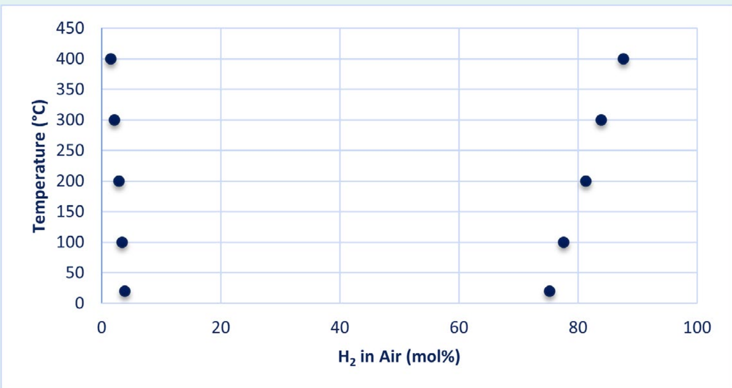


Figure 16: Explosion limits of hydrogen/air mixtures at atmospheric pressure as a function of temperature according to DIN 51649-1

Influence of Pressure on Explosive Limits - air

The explosive behaviour of hydrogen/air mixtures seen in Table 6 and Figure 17 below indicate a positive correlation between the LFL of hydrogen/air mixtures and initial pressure. Increasing initial pressure slightly narrows the range of explosivity, marking it as a positive relationship from a safety perspective. The trend in the UFL is more complex, displaying an exaggerated bow curve with increasing initial pressure. From 1 to 30 bar initial pressure, the UFL decreases and then increases again followed by another linear decrease. Regardless, the overall trend from 1 to 150 bar initial pressure is still a significant decrease, marking it as a positive relationship from a safety perspective. Graph and tables of the explosivity data are shown below.

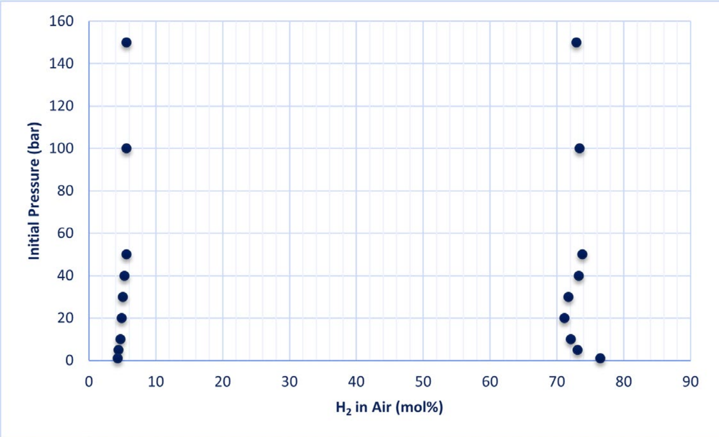


Figure 17: Explosion limits of hydrogen/air mixtures at room temperature as a function of initial pressure

Table 6: Explosin limits of Hydrogen/Air mixtures at room temperature as a function of initial pressure

Initial Pressure (bar)	Lower Explosion Limit (LEL) (mol% H2)	Upper Explosion Limit (UEL) (mol% H2)
1	4.3	76.5
5	4.4	73.1
10	4.7	72.1
20	4.9	71.1
30	5.1	71.7
40	5.3	73.3
50	5.6	73.8
100	5.6	73.4
150	5.6	72.9

Influence of Pressure on Explosive Limits - oxygen

The relationship between initial pressure and hydrogen/oxygen mixtures at room temperature is indicated in Figure 18 and Table 7. However, the major difference between the two is the position of the UEL. Hydrogen/oxygen mixtures are far more restrictive and hazardous than hydrogen/air mixtures with a UEL of 95.2% compared to a UEL of 76.5% respectively at atmospheric conditions. This may have extensive implications when considering in-equipment mixing of hydrogen and oxygen from a safety assessment perspective since the potential explosive window is much broader in hydrogen/oxygen mixtures.

Figure 18: Explosion limits of hydrogen/oxygen mixtures at room temperature as a function of initial pressure according to EN 1839(B) and EN 1939

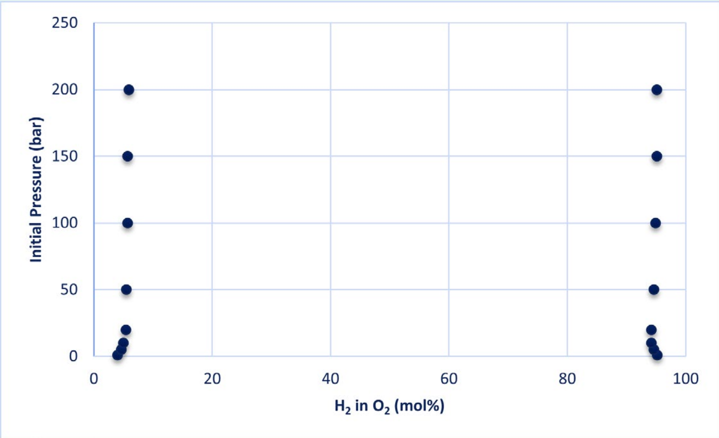


Table 7: Explosion limits of hydrogen/oxygen mixtures at room temperature as a function of initial pressure according to EN 1839(B) and EN 1939

Initial Pressure (bar)	Lower Explosion Limit (LEL) (mol% H2)	Upper Explosion Limit (UEL) (mol% H2)
1	4.0	95.2
5	4.6	94.6
10	5.0	94.2
20	5.4	94.2
50	5.5	94.6
100	5.7	94.9
150	5.7	95.1
200	5.9	95.1

Figure 19 and Table 8 display the explosion characteristics for hydrogen/oxygen mixtures at 80°C to gain insight into explosive limits that more closely match usual operating conditions of alkaline and PEM electrolysers. The trend in data is incredibly similar to the one observed in hydrogen/oxygen mixtures at room temperature – with the exception of the anomalous data point of the LEL at 150 bar initial pressure – but slightly broader and therefore more restrictive.

Figure 19: Explosion limits of hydrogen/oxygen mixtures at 80°C as a function of initial pressure according to EN 1839(B) and EN 1939

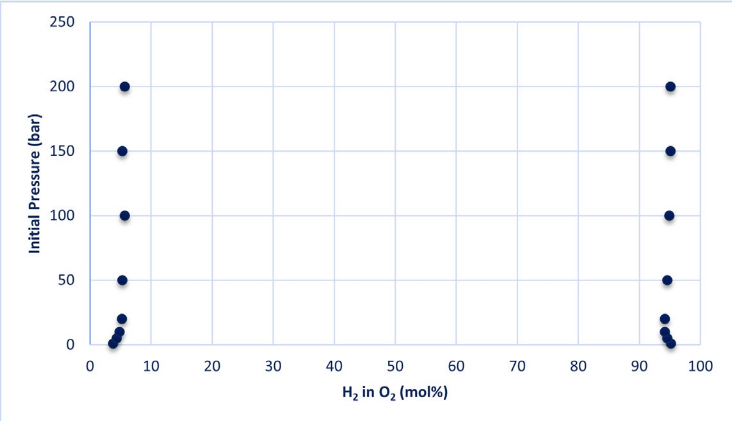


Table 8: Explosion limits of hydrogen/oxygen mixtures at 80°c as a function of initial pressure according to EN 1839(b) and EN 1939

Initial Pressure (bar)	Lower Explosion Limit (LEL) (mol% H2)	Upper Explosion Limit (UEL) (mol% H2)
1	3.8	95.2
5	4.4	94.6
10	4.8	94.2
20	5.2	94.2
50	5.3	94.6
100	5.7	94.9
150	5.3	95.1
200	5.7	95.1

Other safety properties of hydrogen/air or oxygen mixtures listed in [2] are:

Table 9: Safety Properties of Hydrogen/air, Methane/air and Hydrogen/Oxygen mixtures

Property	Hydrogen-air	Methane-air	Hydrogen-oxygen
Flammability limits (upward)	4-75%	5-16%	4-94%
Flammability limits (downwards)	9-75%	6-14%	
Detonation limits	18-59%	8-13%	15-90%
Stoichiometric concentration	29.6%	9.5%	66.7%
Minimum ignition energy	170 μJ	0.3 mJ	1.2 μJ
Autoignition temperature	585°C	580°C	570°C
Adiabatic flame temperature	2403 K	2328 K	3474 K
Detonation cell size (stoich.)	11 mm	≈ 20-30 cm	≈1 mm
Laminar burning velocity (stoich.)	2.1 m/s	37 cm/s	≈10 m/s

One specific remark on the explosive properties is the ability and wide area of compositions where detonations may occur. This means that, depending on geometry, transition from deflagration to detonation cannot be excluded.

Colophon

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