Public report

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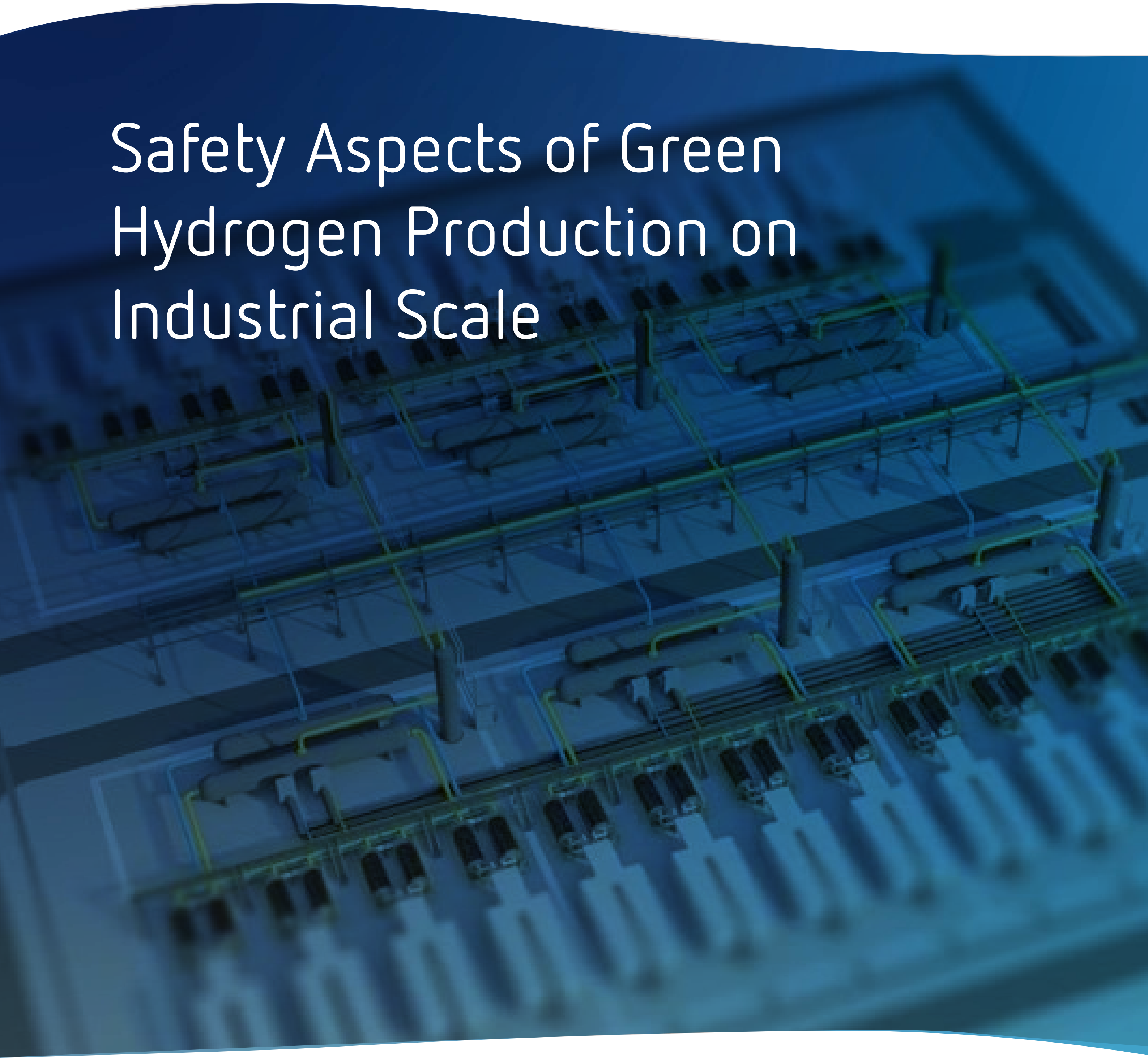

Safety Aspects of Green Hydrogen Production on Industrial Scale

TNO innovation for life

HyCC

Ørsted

Royal HaskoningDHV
Enhancing Society Together

YARA

DNV

Institute for
Sustainable
Process Technology

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- The Authors

Foreword by Jurgen Hoekstra

Hydrogen will undoubtedly play a role in shaping our future. With the transition to hydrogen, we can significantly reduce CO2 emissions in the Netherlands. The Dutch government, industry and science are working together to take this step as quickly as possible. As far as I am concerned, this cannot happen fast enough.

The Institute for Sustainable Process Technology (ISPT) plays an important role in this. We at ISPT bring all stakeholders together to share our knowledge and try to solve obstacles, to ensure that we are able to make this transition safely. Sharing knowledge in the field of safety in the chain must always be the priority. The urgency for safety in this new field of green hydrogen production is high as the first 100 MW green hydrogen plants are already being developed.

This report provides insight into the usefulness and especially the need for consistent risk assessment of explosion risks throughout the supply chain. It may seem obvious, but I cannot emphasise enough that safety risks are magnified as processes change. Careful management of change is essential, especially in an industrial scale-up such as this. It is crucial to ensure process safety of large-scale green hydrogen production and raise awareness throughout the industry. Standardisation and classification of different types of systems are useful for the development of harmonised risk analysis approaches and safety standards. Examples of inherently safer designs and unique barriers provide valuable insights.

Please use this report to gain such insights and, most importantly, continue to share them with each other. I truly believe that this will contribute to a rapid transition to green hydrogen and make the Netherlands even safer.

- Jurgen Hoekstra
Member of the Supervisory Board of ISPT,
Chairman of Veiligheid Voorop,
Vice President & Managing Director of Benelux BASF

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Executive summary

The need to ensure process safety of large-scale green hydrogen production

Green hydrogen production is expected to scale up at an unparalleled pace in the coming years. In the Netherlands, 500 MW of large-scale green hydrogen plants are scheduled for completion in 2025, producing nearly 0.5 million tonnes of hydrogen per year. The REPowerEU Plan reveals that the EU aims to produce 10 million tonnes of domestic renewable hydrogen, in addition to 10 million tonnes of imported renewable hydrogen, by 2030. An artist's impression of a Gigawatt Green Hydrogen plant is shown in Figure S.1.

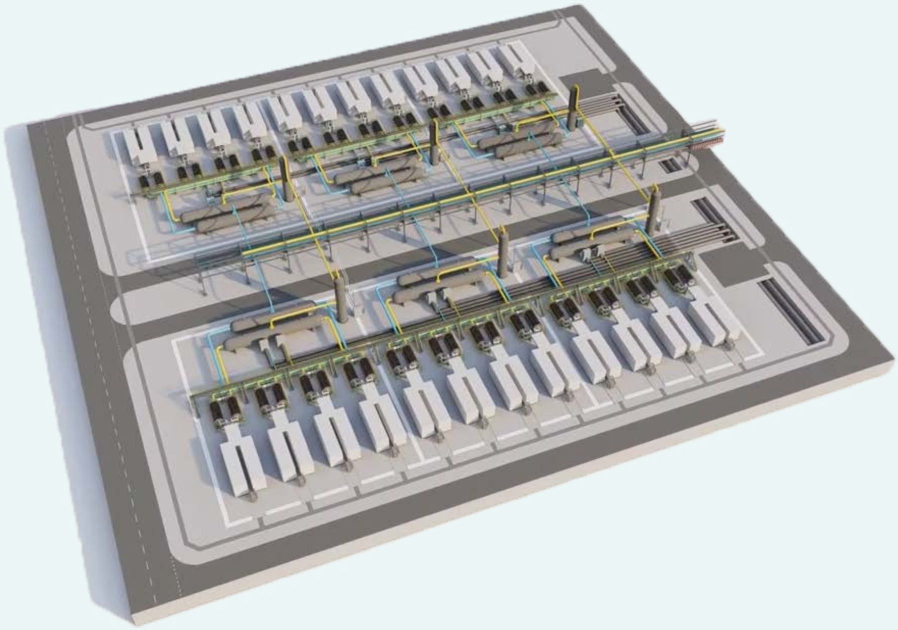

Figure S.1: Artist's impression of a Gigawatt Green Hydrogen plant[1]

This ambitious production ramp-up poses an important challenge to the industry. Large-scale industrial water electrolysis plants typically use hydrogen and oxygen inside the same equipment, separated by a membrane/diaphragm. Safeguarding process safety in the design, implementation and operation phases is a complex task. While experience with operations and maintenance is available for small plants, it is lacking for large-scale production.

The lack of historical data and validated models of failure frequencies and consequences means that electrolyser systems suppliers, asset owners and authorities have only limited data and knowledge on specific fire and explosion hazard scenarios. Due to the lack of a common understanding and standardised risk and design approach, different stakeholders may make different choices. This may then lead to delays in design and authorisation processes. It could potentially also lead to underestimation of the risks involved. The exchange of information on technical safety practices between all stakeholders will therefore be a cornerstone for enabling the hydrogen economy.

This public report aims to stimulate awareness about required safety levels regarding large-scale green hydrogen production. A special focus is placed on fire and explosion risks associated with the

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[1] Gigawatt Green Hydrogen plant: the advanced design

combination of oxygen and hydrogen in equipment and buildings. This project is a first step towards achieving a uniform and consistent risk assessment methodology for large-scale green hydrogen plants. In this way, we want to help the industry and stakeholders understand explosion risks and enable them to create safe designs for large-scale water electrolysis systems.

The report summarises the results of a year-long project involving extensive cooperation with safety experts from HyCC, Ørsted, Shell, Yara, DNV, RHDHV and TNO. This process was managed by the Institute for Sustainable Process Technology (ISPT). Interviews were held with electrolyser suppliers so that their input and feedback could be included in the project results.

> "A special focus is placed on fire and explosion risks associated with the combination of oxygen and hydrogen in equipment and buildings. We propose a uniform and consistent risk assessment methodology for large-scale green hydrogen plants."

Two top events that lead to explosions

Two typical scenarios were identified for events that might lead to an explosion or fire:

- in-equipment mixing of hydrogen and oxygen (in an electrolyser stack, pipe or separator);
- mixing of hydrogen and oxygen (from the air) as a result of loss of containment inside an electrolyser building.

Potential causes, consequences, safeguards and opportunities for inherently safe design were identified for both scenarios.

Main conclusion

The process/chemical industry has well-established tools to assess the safety of processes involving hydrogen, including GW-scale electrolyser plants. However, there is a lack of historical and validated data on failure frequencies, probability of failure on demand and probability of ignition at GW scale. In addition, data and corresponding models on deflagration and detonation are not as well developed for hydrogen as they are for hydrocarbon systems. This will require a conservative approach in assumptions and models for the design and operation of upcoming large-scale deployments.

Safety aspect of large-scale water electrolysis plants

Several points illustrate the importance of addressing safety aspects specific to large-scale green hydrogen production:

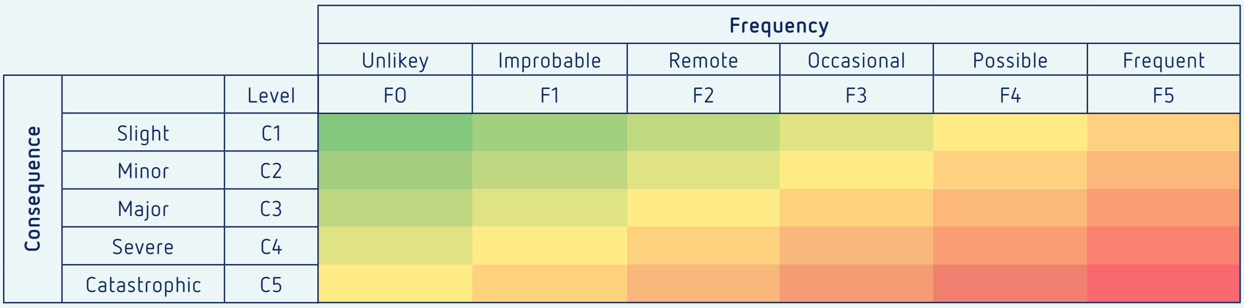
- Hydrogen's properties are different to those of hydrocarbons, resulting in different characteristics such as higher probability of ignition and potentially more severe consequences of explosions.
- The introduction of hydrogen as an energy carrier will lead to hydrogen being handled in a different production process and by a much wider range of stakeholders. Moreover, these stakeholders could be less familiar with process safety than the present actors in the chemical, oil and gas industries.
- In an electrolyser system, both oxygen and hydrogen are present inside the installation.

As a consequence, an explosive mixture could potentially occur inside the equipment or inside the building due to deviations in operating conditions, membrane/diaphragm failure, design flaws, human error or other causes.

- Large-scale hydrogen facilities differ considerably from small plants because of their combinations of modular constructions. This introduces a necessity to understand the impact of potential interaction between modules as well as failure rates for many successive components. These failures and domino effects play an important role in understanding and controlling plant safety.
- Green hydrogen production will largely follow the availability of renewable electricity. This will lead to frequent starts and stops, stand-by and load changes, which can potentially affect safety-related aspects.
- Technology is still under development, meaning that new technologies and materials, such as thinner membranes, push the performance limits. This has an impact on gas crossover and potential membrane/diaphragm assembly failures.
- Analysis of major historical accidents helps to identify hazards and their causes. The investigation revealed the need to devote sufficient attention to operation and maintenance.

Risk assessment approach

The risk management strategy is to avoid explosion scenarios and to apply risk control measures to achieve a tolerable level of risk. Risk matrices are often used for this purpose. Because there is no nationally or internationally agreed risk matrix, many companies have developed their own. This is illustrated in the risk matrix of Figure S.2. An unacceptable risk is indicated by the colour red while green indicates a risk that is generally accepted. Risks in the area between red and green are only accepted when sufficient risk reduction measures have been taken in accordance with company criteria.



			Frequency					
			Unlikey	Improbable	Remote	Occasional	Possible	Frequent
Consequence		Level	F0	F1	F2	F3	F4	F5
	Slight	C1	🟩	🟩	🟩	🟨	🟨	🟧
	Minor	C2	🟩	🟩	🟨	🟨	🟧	🟧
	Major	C3	🟩	🟨	🟨	🟧	🟧	🟥
	Severe	C4	🟨	🟨	🟧	🟧	🟥	🟥
	Catastrophic	C5	🟨	🟧	🟧	🟥	🟥	🟥

Figure S.2: Example of risk assessment matrix

We emphasise the need for scenario-based thinking in combination with the common process safety methods and tools used in the process industry (HAZID-HAZOP-SIL-LOPA). We call for an inherently safer design approach that eliminates possible causes of incidents, as well as the installation of effective safeguards where inherent safety is not possible.

The chain from cause to consequence with Independent Protection Layers (IPL) is shown in Figure S.3. The frequency of the final consequence is reduced by every IPL, which is indicated by a reduction in the thickness of the arrows after each IPL.

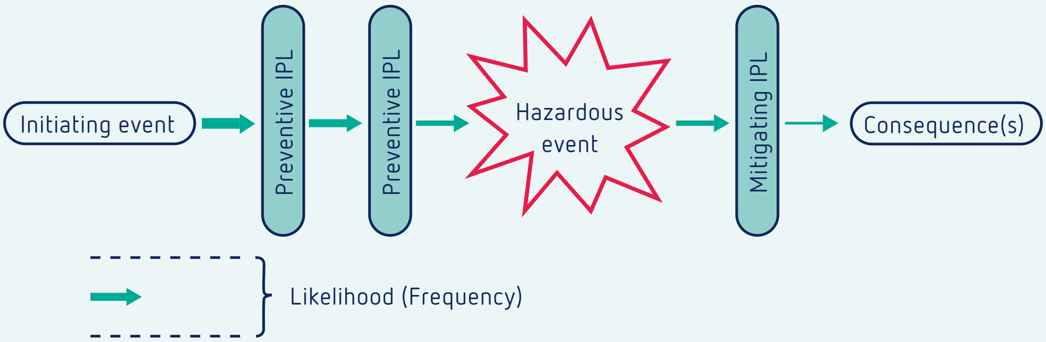


Figure S.3: Chain from initiating event to consequence(s) with 3 independent protection layers (IPL)

Frequency rates and probability of ignition

There is a clear lack of data on failure modes and probabilities for the safety assessment of electrolysis systems. For example, failure frequencies are not available for unit operations such as the current and new generations of electrolyser stacks. Understanding of failure mechanisms of hydrogen-specific equipment is lacking, especially with respect to electrolyser membrane/diaphragm failures. A loss of containment or a degradation of the internal separation between the gases could cause hydrogen to mix with oxygen or air. In that case, another set of probabilities comes into play, namely the probability of ignition. Compared to hydrocarbons, the minimum ignition energy required for hydrogen-air mixtures is low, and even lower for hydrogen-oxygen mixtures. The related probability assessment is complex and more experimental, and data and clear guidelines on this topic would be advantageous. Therefore, ignition probability, either immediate or delayed, is often simply equated to 1. No clear guidelines have been found on how to handle these probabilities. It must be noted that such risk assessment for hydrocarbons is equally difficult.

Effect models

Effect calculation models are often used in risk analysis to calculate the impact of events. This includes the shockwaves resulting from the dispersion and ignition of gradients of explosive hydrogen and oxygen mixtures. There is a clear difference in properties between hydrocarbons and hydrogen. More empirical models, which have been validated mainly for hydrocarbons, have been updated with hydrogen-specific data sets, but these models are only applicable to outdoor scenarios for far-field calculations. Only limited data is available for confined and congested areas, such as buildings or containers.

CFD modelling makes it possible to obtain results for some well-defined geometries of installations inside buildings as well as outside in near-field situations. For more confined geometries, this approach is labour-intensive as it requires computation involving a large number of parameters.

In the Netherlands, authorities impose the use of SAFETI-NL as the Quantitative Risk Assessment (QRA) software program of choice for external safety. It uses empirical models. This QRA program is applicable for hydrogen vapour cloud explosions including detonations.

All of these considerations show that there are uncertainties in the application range of the model, the results and the validity of the risk contours. An effect-based approach is often applied as an alternative, but has the obvious drawback of potential overestimation. Risk-based assessment of credible scenarios therefore needs to be considered with care.

Inherently safer design, barriers and good practices

The project has resulted in a list of examples of possible inherently safer designs of green hydrogen plants and protection layers, to eliminate or reduce risk. It illustrates the principles of preventive and mitigating barriers and good practices. Nevertheless, the validity of protection layers must be assessed for each individual design. In addition, the project identified good practices, most of which are already common practice in the process industry. Within this framework, it should be considered that electrolysers are a class of systems with a broad range of embodiments. Standardisation and classification of different types of systems will be useful for the development of large-scale green hydrogen systems.

Next steps

The approach for assessment and reduction of explosion risks in large-scale green hydrogen production plants is presented in this report. A follow-up project on standardisation with this consortium, selected electrolyser suppliers and the Netherlands Standardization Institute (NEN) has been started, building on the results in this report. The project will aim to create more accurate scenario descriptions (initial events, final consequences and barriers) in order to make recommendations for standards for the design and operation of water electrolysis plants. It will also enhance understanding between owner-operators, engineering companies, technology providers and authorities. This is important in order to reduce the risks of incidents that would have a negative impact on the whole sector.

List of abbreviations

ALARP	As Low As Reasonably Practicable
AWE	Alkaline Water Electrolysis
BST	Baker-Strehlow-Tang method
CAM	Congestion Assessment Method
CFD	Computational Fluid Dynamics
DDT	Deflagration-to-Detonation Transition
EFFECTS	Consequence modelling tool
EPC	Engineering Procurement Construction
ETA	Event Tree Analysis
EXIDA	Safety Equipment Reliability Handbook
EXIM	Explosion Simulation CFD software
FLACS	FLame ACceleration Simulator, CFD modelling tool
FMEA	Failure Mode and Effect Analysis
FRED	Fire, Release, Explosion and Dispersion consequence models
HAZID	Hazard Identification study
HAZOP	Hazard and Operability study
HSE	Health, Safety and Environment
IPL	Independent Protection Layer
KFX	Kameleon Fire and eXplosion software
KOH	Potassium Hydroxide
LOC	Loss of Containment
LOPA	Level of Protection Analysis
LFL	Lower Flammable Limit
ME	Multi-Energy method
OEM	Original Equipment Manufacturer
OREDA	Offshore and Onshore Reliability Data
PEM(WE)	Proton Exchange Membrane (water electrolysis)
PFD[2]	Process Flow Diagram
PFD[2]	Probability of Failure on Demand (=1/RRF)
PHAST	Process Hazard Analysis Software Tool
PHA	Process Hazard Analysis
PID	Process & Instrumentation Diagram
PPE	Personal Protective Equipment
QRA	Quantitative Risk Analysis
RRF	Risk Reduction Factor (=1/PFD)
SAFETI	Quantitative (Safety) risk management software
SCOPE	Shell Code for Overpressure Prediction in gas Explosions
SIL	Safety Integrity Level
SIS	Safety Integrity System
SMR	Steam Methane Reformers
UFL	Upper Flammability Limit
VCE	Vapour Cloud Explosion
WE	Water Electrolysis

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[2] In this report, the abbreviation PFD can refer to two terms. As both terms are widely known, the term referred to should be clear from the context.

1. Introduction

1.1 Why focus on hydrogen safety for large-scale electrolysis?

According to the EU Green Deal, large-scale production of green hydrogen through water electrolysis is essential in order to meet CO_2 emission reduction targets.[1] REPowerEU, a joint European action for more affordable, secure and sustainable energy, wishes to boost production and import of hydrogen to 20 Mt per year by 2030.[2] Construction of large-scale green hydrogen installations will start to become a reality before 2025, as financial investment decisions are expected any time now thanks to EU IPCEI funding approvals.[3] 500 MW of large-scale green hydrogen plants are already expected to be constructed in the Netherlands by 2025.

As a society we are accustomed to the chemical industry handling all different kinds of hazardous substances safely. A generic safety approach ensures that the risks of handling chemicals and energy carriers, including hydrogen, are reduced to acceptable levels. So why is this consortium initiating a programme specifically on hydrogen safety for large-scale electrolysis plants? One reason is that the technology will be rolled out on an unparalleled scale in the coming decade. From a relatively niche technology in the process industry, it is expected to reach a scale of tens or even hundreds of GW relatively quickly. Up to now, experience is limited to much smaller scale installations of 10-20 MW.

The ramp-up includes the design, construction and operation of a large number of GW-scale green hydrogen production plants based on water electrolysis. These large-scale units will have to run in a flexible manner with load variations for a period of 25 to 30 years. The large-scale electrolysis industry cannot rely on decades of experience, yet the same level of safety still needs to be achieved. This requires a good understanding of the risks associated with large-scale water electrolysis. Safe operation is made possible by using conservative assumptions, where needed, to address the particular uncertainties regarding hazards in existing electrolyser units.

A large number of specialised companies, such as component suppliers, technology providers, EPC contractors and authorities, routinely handle hydrogen safely. The introduction of hydrogen as an energy carrier, however, opens an entirely new industry sector, with a broader context, different applications and supply chains and new interfaces, with less experience in handling hydrogen.

Knowledge of fires and explosions involving hydrogen is limited compared to those involving well-known fuels such petrol, and natural gas. This is even more evident as both hydrogen and oxygen are present in the equipment, separated by a membrane. Due to the lack of a common understanding and approaches, there is a risk of different stakeholders making different choices. This may lead to overdesign, with some stakeholders investing substantially more to achieve very high safety levels than others. On the other hand, underestimating the risks should also clearly be avoided: incidents could have a negative impact on the whole sector.

1.2 What do we want to achieve?

The need to understand all safety aspects is recognised by the industry and is at the heart of the ISPT project 'Green Hydrogen Inherent Safety Practices on Large Industrial Scale'. The main objective of this project is to work towards a uniform and consistent risk assessment methodology for large-scale green hydrogen plants. The focus is on fire and explosion risks associated with oxygen and hydrogen mixtures in equipment and in buildings. Other risks, such as electrical risks, material compatibility risks, spills, and health, occupational health and product safety risks (CE), are not included in the project.

This project therefore aims to:

- Increase awareness of process safety for large-scale water electrolysis plants across the industry;
- Understand scenarios involving explosion risks with oxygen and hydrogen mixtures in equipment and buildings;
- Close knowledge gaps regarding scenario development, ignition probability (immediate/delayed) and effect modelling (deflagration, detonation, DDT);
- Provide guidance to the industry and stakeholders for the safer design of large-scale green hydrogen plants.

More specifically, this project addresses the following questions:

- Which new safety risks are relevant for water electrolysis and large-scale application of green hydrogen plants?
- How should we achieve the same level of safety across the industry?
- Are there commonalities in the process safety approaches of the project partners and suppliers of electrolyser systems (OEMs) that could serve as a basis for best practices?

The chosen level of detail in this report, outlining the risks, properties of hydrogen and mathematical models, supports experts of industry and authorities in increasing the safety level of green hydrogen production.

1.3 The project and the consortium

The Institute for Sustainable Process Technology (ISPT) and the consortium partners HyCC, Ørsted, Shell, Yara, DNV, RHDHV and TNO have cooperated on a green hydrogen safety project funded by Top consortium for Knowledge and Innovation (TKI) Energy & Industry.

This public report presents the main results of this project Green Hydrogen Inherent Safety Practices on Large Industrial Scale, including cases introduced by electrolyser suppliers in their meetings with partners during the project.

The project ran throughout 2022. A two-year follow-up project on safety standardisation with the existing consortium, selected electrolyser suppliers and the Netherlands Standardization Institute (NEN) has been launched in 2023. The project aims to create more accurate scenario descriptions (initial events, final consequences and barriers) in order to make recommendations for standards for the

2. Introduction to Green Hydrogen Production

design and operation of hydrogen plants.

2.1 History

Industrial hydrogen production with large-scale water electrolysers started in Norway almost a century ago, see Figure 1.[4] However, natural gas as a feedstock in steam methane reformers (SMR) was introduced in the USA as early as 1939 and became a cheaper route to manufacture hydrogen. This hydrogen was mainly used to produce ammonia in the Haber-Bosch process. The role of the large-scale industrial electrolysis process therefore remained limited. Since then, the industrial market for hydrogen has grown. Besides being used for ammonia production, hydrogen has been used in hydrogen crackers and desulphurisation units in refineries as well as in hydrogenation processes in the food and chemical industries for over fifty years. The petrochemical industry now has extensive knowledge on fire and explosion hazards as well as risk assessment and risk reduction measures in f

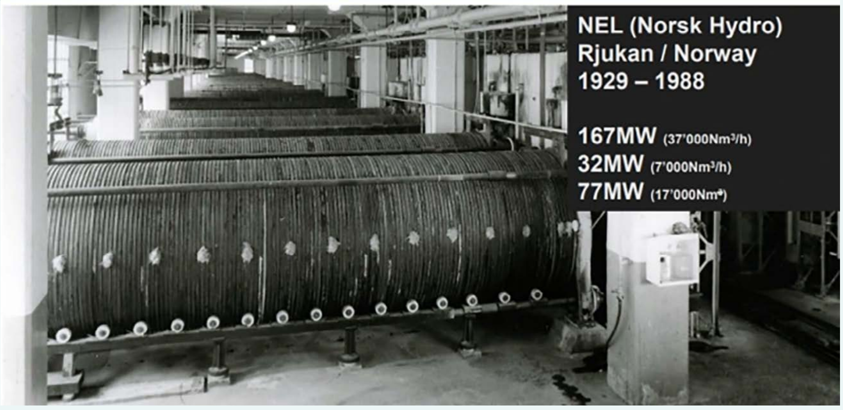

Figure 1: First known large-scale industrial water electrolysis from hydropower in Rjukan, Norway, Norsk Hydro, 1929-1988

Two mainstream technologies AWE and PEM are briefly described in the following sections.[5]

2.2 Alkaline electrolyser systems

In an alkaline electrolyser the oxygen (anode) and hydrogen (cathode) side of the cell are separated by a thin porous matrix called a diaphragm. This diaphragm is mounted in an assembly filled with electrolyte (30% vol KOH solution). It is conductive for the OH^- ions that need to pass through and is an effective separator for the gases on each side of the diaphragm.

The electrolyte is supplied to both sides of the electrolyser stack. After leaving the stack, the alkaline solution streams need to be separated from the gases produced. This is done in gas-water separators. These are usually placed at a given height above the stack. The water phase is removed at the bottom and the gas phase at the top. KOH/water flows back to the stack. The water column within the separator also serves as a buffer storage for changing load specifications. This process system is often referred to as Balance of Plant (BoP).

The water management system regulates the liquid level in each gas separator. Water permeation via the diaphragm must be taken into consideration in water management. Water can be transported to the anode side by osmotic drag. The water/KOH solutions of both separators are mixed, usually by means of a combined pipe that returns the stream to the electrolyser. As a result, the OH^- charges from the electrochemical half-reactions are balanced.

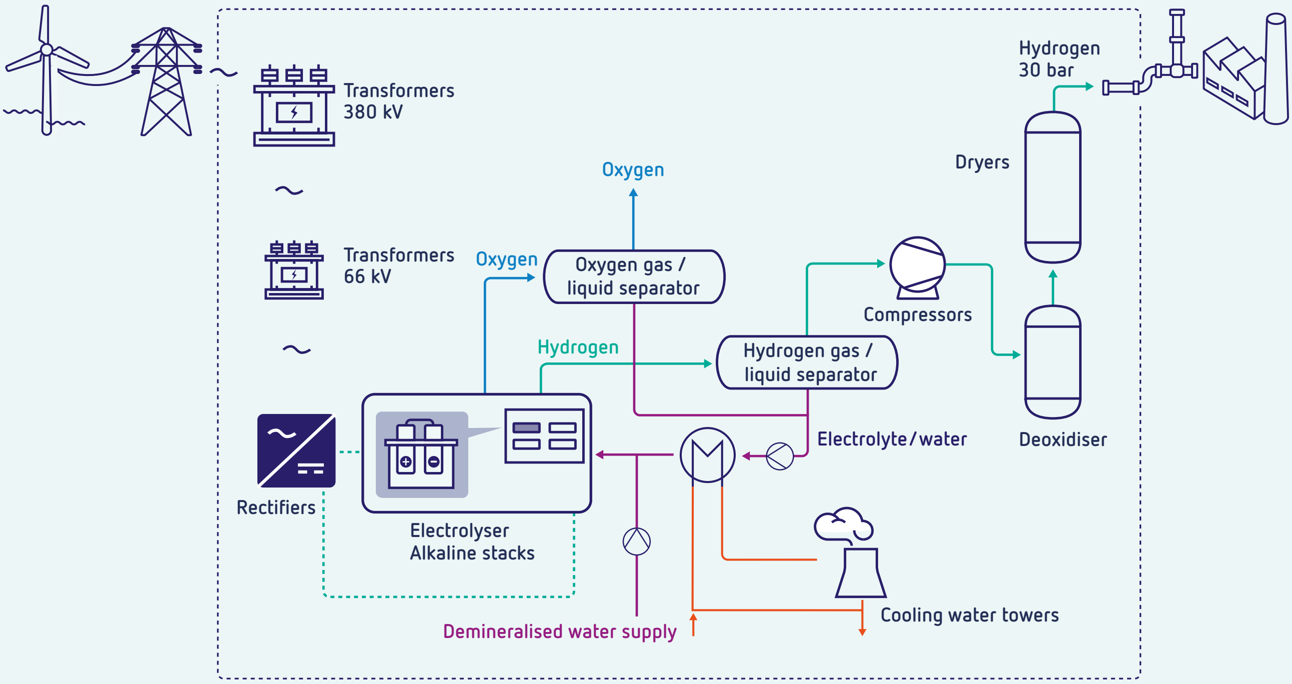

Figure 2: Typical layout of an alkaline electrolyser plant

The low differential pressure allowed over the diaphragm (about 50 mbar) and the requirement to balance the charges between anode and cathode, make the alkaline stack more challenging to operate than PEM stacks. Nevertheless, pressurised operation is possible and available in designs with pressures of up to typically 40 bar up to 200 bar. During such operations, both sides of the stack (hydrogen and oxygen) are kept at high pressure. The high-pressure configuration requires more resistant cell frames and Balance of Plant materials.

2.3 PEM systems

PEM systems are different from AWE as, for example, pure water is used instead of KOH and a solid membrane is applied, which conducts protons. They typically require the use of circulation pumps, heat exchangers, pressure control and monitoring only on the anode (oxygen) side. On the cathode side, a gas separator, a de-oxygenation component to remove remaining oxygen (typically not needed for differential pressure), a gas dryer, and a final compressor step are required.

For PEM systems, differential and balanced pressure can be chosen. Under a balanced pressure operation, the anode and cathode are designed to run at the same pressure level on both sides of the membrane. In the case of differential pressure, the differential pressure across the membrane is typically 30 to 70 bar. This requires a stronger membrane with improved mechanical stability. This, in turn, can decrease gas permeation, which reduces efficiency. It could also require an additional catalyst to re-convert any hydrogen back to water.

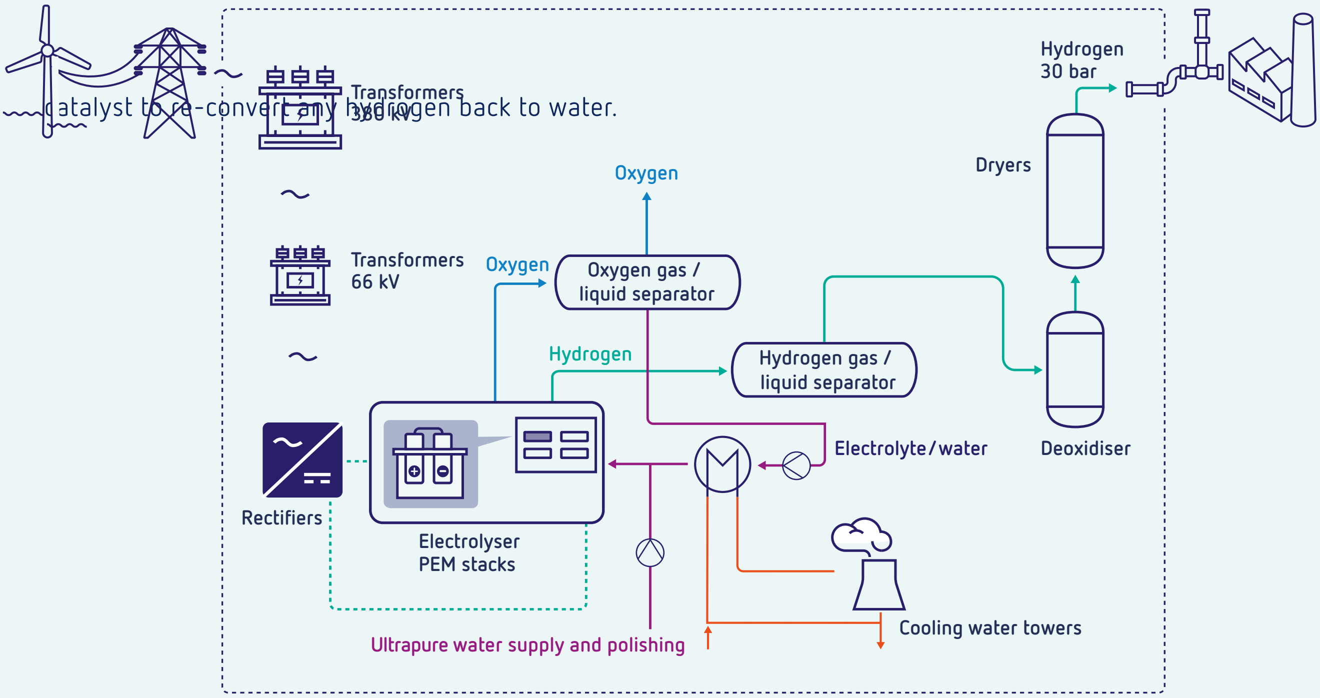

Figure 3: Typical layout of a PEM electrolyser system

2.4 Common aspects and differences

The Balance of Plant[6] of both systems has a number of aspects in common:

- In both cases, the circulating electrolyte stream is usually cooled to remove heat generated in the stack, although there are also electrolyser stack designs with separate cooling loops. Consequently, separation of large gas/liquid streams and a large recycle of liquid stream is necessary.
- For both alkaline and PEM, the separation of oxygen and hydrogen is not perfect. This leads to crossover of hydrogen to the oxygen side and vice versa. From a safety perspective, the concentrations should be kept below the value that is considered safe. The crossover does not scale with the load. Operation at partial load therefore leads to higher concentrations of oxygen in hydrogen and vice versa. Also, concentration may increase due to diaphragm/membrane degradation over time. Continuous monitoring of concentrations is therefore required.

The main differences arise due to the different types of membranes used.

- In the case of PEM, a solid polymer membrane can handle large pressure differences, allowing operation of the oxygen side at near atmospheric conditions, while the hydrogen side is operated at elevated pressure. This reduces the need to mechanically compress hydrogen, for example, to bring it to a required pressure for a pipeline or storage.
- Because of the transport of OH^- ions through the diaphragm in the case of an alkaline system, a concentration difference results when no mixing of the cathode and anode flow takes place. In addition, the diaphragm is sensitive to pressure differences and consequently to potential rupture leading to transport of oxygen to hydrogen and vice versa. The AWE system therefore usually requires some form of connection for liquid flow between the oxygen and hydrogen side

by means of a balancing line between the separators. In contrast, the PEM electrolyser works with pure or ultra-pure water and has no direct connection between the oxygen and hydrogen side.

- In PEM the electro-osmotic crossover increases with load.

2.5 Preliminary safety considerations of large-scale water electrolysis

Before going into more detail, some preliminary safety aspects of large-scale hydrogen production are discussed.

- There are many specialised companies that handle air, oxygen and hydrogen routinely and safely. With the introduction of hydrogen as an energy carrier, however, hydrogen will be handled by even more stakeholders, in a much broader range of types of locations. This may introduce additional hazards.
- The technology is still fully under development. This means that new technologies and materials, such as thinner membranes, push performance limits. This has an impact on gas crossover and membrane (assembly) failures. These new generations could potentially be operated alongside older generations, increasing complexity and risk during operation and maintenance.
- Where a chemical or petrochemical plant is expected to operate steadily at nominal capacity, green hydrogen production will largely follow the availability of renewable electricity. This leads to dynamic operation with more frequent ramping up and down and cold and hot stand-by operations.
- In an electrolyser system, both oxygen and hydrogen are present inside the installation separated only by a membrane. There is potential for explosive mixture forming inside the equipment. A release of hydrogen due to leakage or an explosion inside equipment potentially leads to the formation of an explosive mixture of fuel and air outside the equipment.
- In large plants, the stacks are often inside a container or building. This increases the risk of hydrogen accumulation. A vapour cloud explosion (VCE) may occur when a mixture of hydrogen and air is formed due to a leakage and comes within the flammable range.
- In large plants, multiple stacks may be connected to a single separator. In the event of a pipe rupture, the larger pipe diameter will cause a higher release flow rate and potential effects when ignited.

The setup of the electrolyser system in Figures 2 and 3 is highly simplified because it shows a single stack and module. In reality a large-scale system is modular and consists of multiple modules with a large number of grouped transformer-rectifiers, stacks and separators for a 1 GW green hydrogen plant, see Figure 4.[7] Many electrolyser manufacturers use a design in line with findings by ISPT.

Figure 4: General layout of a modular large-scale water electrolysis plant with multiple stacks and separators (Alkaline)

Large-scale, modular applications of water electrolysis introduce new risks as compared to single units, but may also have some favourable safety aspects. What is favourable depends on the local circumstances. For example, in a remote area with a limited number of people and other installations, a big unit may be preferred. However, smaller units may be preferred in areas with higher occupancy. Internal separation distances, walls and other containment structures might also be considered. The choice of technology and site-specific factors determine what combination of approaches is most effective.

Examples of risks introduced by large-scale production as opposed to small-scale production:

- Large-scale green hydrogen plants will consist of a number of electrolyser modules. This introduces the risk of a domino effect: in the event of fire and explosion in one stack or module this could have an impact on adjacent stacks and modules.
- Uncertainties in building design, ventilation and detection due to lack of engineering guidelines, minimum safety requirements and failure data.
- Increased complexity through interaction arises due to more stacks on a separator and more separators in a system. Risks can especially occur during start-up, stand-by and shut-down operations.
- Increasing number of repeating (parallel) elements could lead to increased risks due to systematic failures.
- Potentially, operators or maintenance staff could be present during a shutdown of some modules, with adjacent modules still running. This could be a hazard to people in the event of an incident and the risks should be carefully analysed.

- The size of equipment is reduced when the one big unit is replaced by a number of small units. This reduces the maximum effect in the event of an incident.
- In the case of a multi-cell/stack/separator arrangement, the effect of excessive oxygen or hydrogen crossover flow from a single, poorly performing cell or stack on the oxygen/hydrogen concentration in the common separator vessel is less pronounced than for a single cell/stack/separator arrangement. This is due to the fact that the excess oxygen/hydrogen from one or more cells in one stack is diluted by the other cells and stacks performing normally.

Example of the impact of multiple stacks

Concentration measurements are generally impossible in a gas/liquid mixture. Therefore, concentrations are generally measured in the gas stream at the outlet of the separator vessel. If the performance of one stack is completely disturbed, it may lead to mixing of hydrogen and oxygen in a stochiometric mixture (67% hydrogen, 33% oxygen). However, in the separator, the oxygen is diluted to 5.5% for six stacks per separator and 4.1% for a layout with eight stacks per separator. It would also take time to build up this concentration, depending on the size of the separator and stacks. The figure below shows an example. The blue line indicates the hydrogen concentration in the stream from the stack and the brown line shows the concentration build-up in the separator. The concentration build-up in the separator is six times lower. It also takes a while for the concentration to build up after a delay, due to the stream through piping from the stack to the separator. As this delay hinders failure detection, the diameter and length of the piping should be assessed.

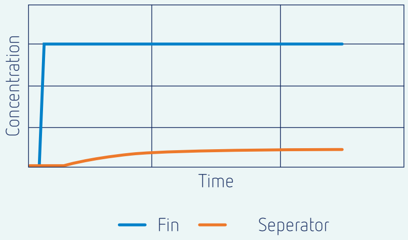

Figure 5: Dilution of hydrogen in a separator with a setup of 6 stacks per separator

Other safety aspects might also come into play, such as the probability of shrapnel hitting other units. This additional risk will be dependent on size, mutual position (such as direction, heights and shielding) and also on maintainability, exchange of components and other factors.

3. Basics of fire and explosion hazards of hydrogen

3.1 Types of explosions

Hydrogen properties are different to those of hydrocarbons. This suggests that risks related to the probability of ignition, or the severity of explosion, differ to those for hydrocarbons. This section discusses the relevant properties for safety.

Many hazards relevant to green hydrogen production can be managed through standard safety management approaches. However, explosion risk resulting from hydrogen leakage or other events has several specific characteristics. It therefore merits special attention in this framework.

Explosion damage is usually caused by the resulting pressure or shockwave (blast or blast wave). It destroys structures and can kill people directly and indirectly (for instance when a building collapses). Explosions can also produce deadly high-speed fragments, formed from pieces of an explosion structure (shrapnel). Additionally, a chemical explosion can cause a fireball or flame jet. The heat that radiates from it can lead to property damage and injuries or fatalities among people in the vicinity. Basic factors that determine the destructive effect of an explosion are the amount of energy released during the explosion and its speed (the energy release rate). There are different types of explosions, as depicted in Figure 6.

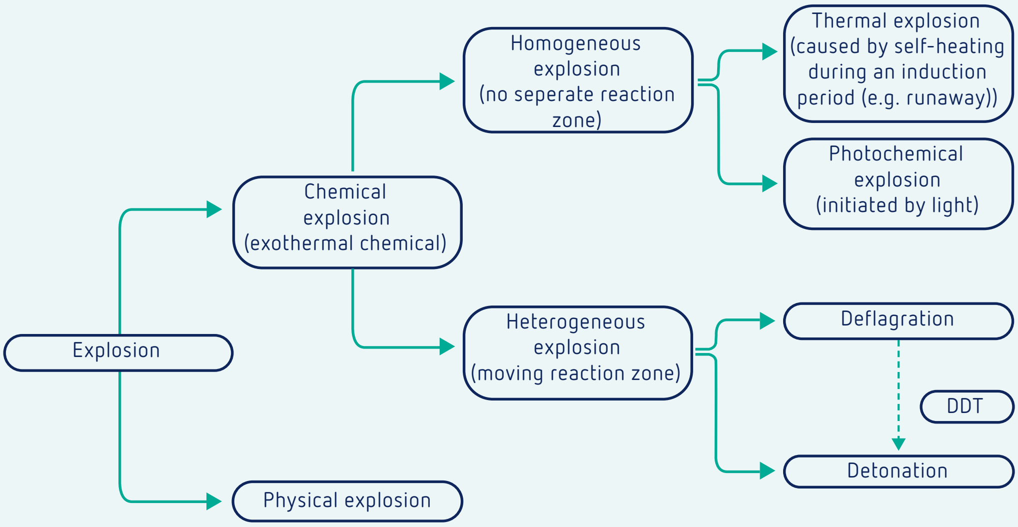

Figure 6: Classification of explosions

Two different types of heterogeneous chemical explosions can be defined. The type depends on the speed at which the flame front travels through the flammable volume with respect to the speed of sound of that medium in the prevailing conditions. If the flame speed is slower than the speed of sound (subsonic), the explosion is classified as a deflagration. If the flame speed is faster than the speed of sound (supersonic), the explosion is classified as a detonation. Detonations have the potential to cause more damage than deflagrations. Creating a direct detonation requires a very intense energy source. The resulting shockwave from an explosion, which causes injury to people and damage to property, travels at the speed of sound.

3.2 Deflagration-to-detonation transition (DDT)

The concept of a deflagration-to-detonation transition is one of the most difficult to predict combustion phenomena in the field. A DDT will depend on many different factors, such as temperature, ignition location, initial turbulence and roughness of the wall if inside equipment. It should be noted that the opposite is also possible: the flame front can decelerate from supersonic to subsonic speeds, for instance due to a change in concentration or increased heat loss (such as when going from a larger diameter tube to a smaller diameter tube).

DDT is promoted by turbulence and congestion, which helps create the crucial increase in velocity of the flame front. A hydrogen-air cloud in a highly congested area, and especially in-equipment mixing of hydrogen and oxygen, therefore provides far more favourable conditions for a DDT than a vapour cloud in an open space. Nonetheless, because of the specific properties of hydrogen, a DDT in a vapour cloud outside equipment cannot be ruled out.

A special situation with pressure piling during DDT occurs because of what is called an overdriven detonation. This is an unstable form of the detonation phase with speeds higher than the stable detonation speed. These pressure pulses usually only take milliseconds. In the event of an overdriven detonation, the pressures can be a factor of five to ten higher than in a deflagration, depending on mole ratio, and hence a factor of fifty to one hundred more in absolute terms compared to atmospheric pressure. As opposed to an unstable situation, the pressure increase in stable detonation conditions is typically a factor of two higher than the stable deflagration pressure. An example of overdriven detonation for a mixture of hydrogen and oxygen (stoichiometric) is given in Figure 7. Note that the reaction starts as deflagration and develops into detonation via DDT, with a pressure spike of a few milliseconds up to 45 times the initial pressure, which will quickly decay to the stable situation.[8]

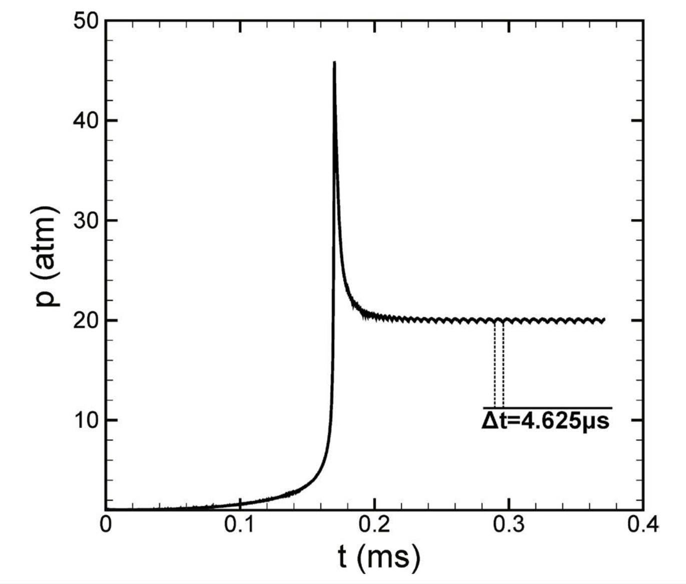

Figure 7: DDT with overdriven detonation

According to some OEMs, in-equipment explosions have occurred at the laboratory scale and in commercial/demonstration setups for both PEM and AWE type electrolysers. The observed explosions have been internally contained either in the stack, the piping or the separator. Whether these explosions were deflagrations or denotations remains unclear. No injuries to personnel have been reported. The only reported consequence was leakage in a damaged stack in a specific case. These observations should be followed up with R&D, mechanical design, experiments and possibly standardisation.

A key knowledge gap involves the prediction of the DDT, meaning that a flame front can accelerate from subsonic to supersonic. Predicting DDT for hydrogen in more complex situations with confined and congested areas and inside equipment is currently not possible. However, there are some models and correlations available to predict DDT under very specific geometries and conditions (concentrations). Note that the DDT mechanism of hydrocarbons is equally difficult to assess.

3.3 Ignition probability

In general, the probability of ignition is divided into 'direct ignition probability' and 'delayed ignition probability'. In the event of immediate ignition, the most likely outcome will be a fire or jet fire. Delayed ignition leads to a larger flammable cloud and enables flame acceleration. The resulting severity of the VCE will be significantly higher compared to direct ignition, causing more damage to property and possibly incidents in the immediate vicinity of the cloud. Other factors, such as the size of the leak, meteorological conditions and other parameters will also contribute to the actual severity of the explosion.

It is conservatively assumed that the total ignition probability for gaseous hydrogen is 1, meaning that in a Loss of Containment (LOC) scenario, hydrogen ignites in 100% of the cases. This is the case if the leak persists and the resulting mixture is flammable. Ignition probability is standardised for substances in stationary conditions by Dutch regulations for external safety purposes.[9] One experiment[10] shows expected behaviour for hydrogen-methane mixtures in the sense that increasing the hydrogen concentration lowers the ignition energy and thus increases the probability of ignition. At higher concentrations, the probability approaches unity for the tested ignition sources for confined releases. In unconfined releases, the probability would likely differ as mentioned in the same report due to hydrogen dispersing easily in air. Ignition probability will depend on the circumstances and needs to be considered further for electrolyser applications. Precursors, such as the presence of traces of catalysts and other nuclei, may also play a role. Ignition probability therefore depends on the mole ratio and the conditions. This topic is especially relevant for electrolysers.

In the EU, the use of electrical and other equipment in areas with a risk of vapour explosions is regulated by the ATEX Directive.[11] For electrolysers, ATEX compliance is a difficult subject due to limited validity for hydrogen in oxygen and enriched air, and the fact that the stack is an electrochemical device. Nevertheless, designing in accordance with the ATEX Directive reduces the probability of ignition.

3.4 Explosion properties of hydrogen with air or oxygen

For large-scale electrolyser systems, the most relevant locations of events involving hydrogen explosions are both inside equipment and outside equipment. Inside equipment this involves the mixture of hydrogen and oxygen mixtures, and outside equipment the mixture of hydrogen and air. The difference in risk profiles between hydrogen and hydrocarbons is caused by several different basic properties. Table 1 compares hydrogen-air, methane-air[3] and hydrogen-oxygen mixtures. It is much easier to ignite hydrogen compared to hydrocarbons. The force of an explosion with hydrogen can also be higher. Compared to hydrogen in air, the explosion range for hydrogen-oxygen mixtures is wider and the ignition energy is extremely low. A specific parameter that is highly relevant for explosions is the detonation cell size. This is an order of magnitude lower for hydrogen-air and even two orders of magnitude lower for hydrogen-oxygen mixtures compared to most hydrocarbon-air mixtures. This indicates a (much) higher tendency for detonation and deflagration to detonation.

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[3] Natural gas contains methane >90vol%.

Note that for deflagration the range is 4-94% for hydrogen-oxygen mixtures, compared to a range of 15-90% for detonation.[4] Compared to the hydrogen-air detonation range, the upper detonation limit for hydrogen-oxygen is higher. Only a small amount of oxygen is needed in combination with hydrogen to reach the upper detonation limit.

Table 1: Properties of hydrogen/air and hydrogen/oxygen mixtures compared to methane/air mixtures

Property	**Hydrogen-air**	**Methane-air**	**Hydrogen-oxygen**
Flammability limits (upward)	4-75%	5-16%	4-94%
Flammability limits (downward)	9-75%	6-14%	
Detonation limits	18-59%	8-13%	15-90%
Stoichiometric concentration	29.6%	9.5%	66.7%
Minimum ignition energy	17 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

Table 2 indicates the effect of pressure and temperature on the various ignition and explosion parameters for hydrogen-oxygen/air systems. When the temperature rises, the risk increases due to a reduction of ignition energy, a wider flammable range, an increased (laminar) burning velocity and a smaller detonation cell size. At higher pressure, the rate of pressure rise is faster. Pressure has only a weak effect on flammability limits.

Table 2: Effect of pressure and temperature on the ignition and explosion parameters for H_2/air and H_2/O_2 mixtures

Parameter	**T↑**	**P↑**
Minimum ignition energy	↓	↓
Lower flammability limit	↓	↑
Upper flammability limit	↑	↓
Explosion pressure	↓	↑
Rate of pressure rise	↓	↑
Detonation cell size	↓	↓
Laminar burning velocity	↑	↑

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[4] For water electrolysis the produced stochiometric volumetric hydrogen-oxygen mixtures is 2 to 1, so 33-67% vol.

3.5 Influence of initial pressure on explosion strength

The initial pressure has a big influence on the deflagration explosion of a hydrogen-air mixture, as shown in Figure 9.

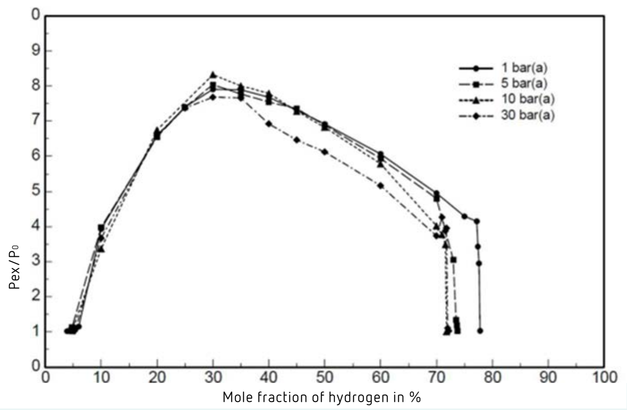


Figure 9: Ratio of deflagration explosion pressure and initial pressure as a function of hydrogen / air mixture composition [12]

Note that the final pressure is normalised with respect to the initial pressure. Hence, the absolute, final explosion pressure will increase proportionally with the increase in initial pressure. This has important consequences for electrolyser system design. The choice of operating pressure is essential. The pressure differential between the oxygen and hydrogen sides will have a significant impact on the event when separation integrity is lost. The greater the pressure difference, the more rapidly the gases will mix. A high absolute pressure on either side will lead to a potential for much higher maximum explosion pressures than in a system at atmospheric pressure. Consequently, systems operating at near-atmospheric pressure can be designed for lower maximum explosion pressures than systems operating at high pressure. The choice of the optimum operating pressure is a complex assessment with many implications for the cost of hydrogen produced. The cost of safety management is an important aspect in this analysis.

Also, for an atmospheric operating system, the starting pressure for a secondary explosion can be higher than the intended operating pressure when a combustible mixture elsewhere in the system has become pre-compressed by a primary explosion. This pressure piling effect could occur when a system is made up of interconnected compartments.

3.6 Influence of water

Inside the equipment, before the drying section, the gas mixtures will generally contain some water or even be fully saturated with water. No systematic review has been made of the impact of water content on the combustion properties of hydrogen-oxygen mixtures within the project. However, Figure 10 demonstrates that a key parameter such as laminar burning velocity strongly depends on water content.

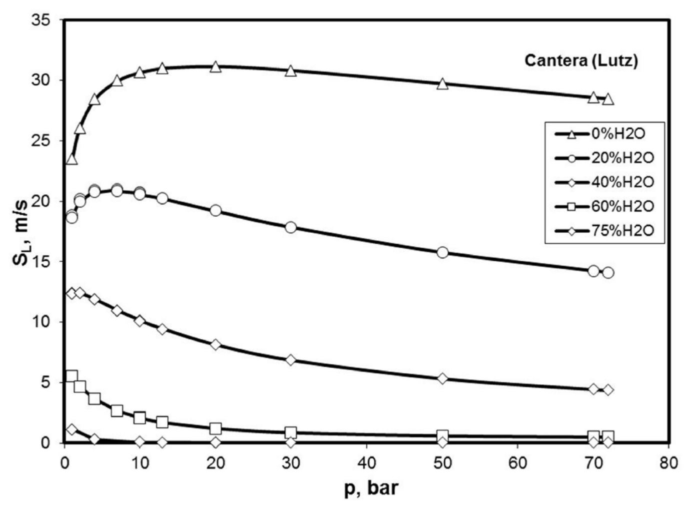


Figure 10: Modelled laminar burning velocity for stoichiometric hydrogen/oxygen mixtures as a function of initial pressure and in the presence of water vapour at 573 K [13]

3.7 Vapour cloud explosion

Hydrogen has some advantageous properties, such as buoyancy and high diffusivity, which often reduce the size of the gas cloud. Nevertheless, pressure and direction of the flow have a major influence on the formation of the vapour cloud. In current designs, electrolysers are often located inside a container or building, which increases the risk of hydrogen accumulation. A VCE may occur when a mixture of hydrogen and oxygen or air is formed due to leakage and comes within the flammable range. This can occur in equipment through membrane leakage in the electrolyser, for example, or in a building or enclosure in the event of leakage from equipment. It can also happen outdoors through leakage from outdoor equipment such as a pipe or separator.

4. Incidents involving water electrolysis

Accident and incident databases are important tools for identifying hazards in specific processes. An analysis of electrolysis-related incidents is therefore highly relevant. The following databases were assessed:

- Hydrogen tool [14]
- HIAD 2.0 database [15] [16]
- The ARIA database [17]
- US Department of Energy OSTI [18]

The first incident involved a hydrogen tank explosion at an alkaline water electrolysis pilot plant facility in Gangneung[19], South Korea on 23 May 2019, see photo in Figure 11. Two people were killed and six injured. The investigation showed that the hydrogen separator exploded due to oxygen crossover at low load conditions and human error. Ignition was caused by static electricity as proper earthing connections were lacking. This incident emphasises the need for communication of safety awareness and practices between OEMs, owners/operators and EPC contractors, as well as proper staff training on the requirement to follow procedures.

Figure 11: Hydrogen tank explosion at a pilot plant facility, South Korea, 2019

Analysis of the incident shows:
- The oxygen removing component was omitted during system design.
- No earthing was installed.
- The system was run below the lowest permitted operation power level.
- The operator ignored higher than 3% oxygen to hydrogen values.
- The hydrogen quality was not monitored daily, as it should have been.

Another incident took place at Laporte Industries Ltd, Ilford in the UK on 5 April 1975. One operator was killed as a result of severe skin burns with hot electrolyte (30% KOH) following an explosion of the oxygen-lye separator as a result of diaphragm rupture. The cause was corrosion of gauzes and damaged cell gaskets due to clogging with sludge. This led to hydrogen leakage to the oxygen gas-liquid separator. The chain from the initiating event through the top event to fatal consequences is shown in Figure 12 below. Regular maintenance/inspection of process equipment and use of hydrogen-in-oxygen analysers are obligatory.

Figure 12: Sequence of oxygen tank explosion at a Laporte Industries, 1975[20]

A third incident, at Kjørbo hydrogen fuelling station in Norway, occurred on 10 June 2019. Although this did not occur in an electrolyser plant, it is relevant. The incident was caused by delayed ignition, leading to a hefty explosion through deflagration. The root cause was an assembly failure of two plugs/bolts on one of the pressure vessels for the storage of hydrogen under 700 bar pressure. There were no fatalities or injuries on site, but some minor injuries were caused by airbags being activated in the vicinity. Current information reveals that no unit exploded, but that leaked hydrogen gas ignited in the open air.[21]

Some other incidents identified as relevant are listed in Table 3. The following lessons were learned through incident analysis:

- It is important to understand the relationship between gas permeability of the electrolyser membrane, its degradation, and the dynamic operation range due to fluctuating power levels of the photovoltaic system.
- It is necessary to secure automatic isolation of gas storage and an emergency stop of gas production when safety limits are exceeded.
- Hydrogen analysers must be used effectively.
- Process equipment must be maintained and inspected regularly; operation and maintenance procedures need to be prioritised and maintained at all times.
- Electrolysis failures also include:
    - Cell polarity reversal, causing hydrogen to enter a chlorine or oxygen flow.
    - Corrosion damage of electrolysis cell components, allowing hydrogen to mix with chlorine or oxygen.
    - Power surges or sudden shutdowns without appropriate interlocks to shut down downstream system components.

It can also be concluded that the number of incidents is too low to draw any statistically relevant conclusions. It must be noted that hardly any near misses have been reported.

Table 3: List of electrolyser incidents

CE = chlorine electrolysis WE = water electrolysis ? = cause unknown ! = cause identified

Year	Type	Source	Description	Cause	Lessons learned
2008	CE	HIAD #843	Fire in electrolyser cells	?	-
2010	CE	HIAD 2.0 #950	Hydrogen explosion (mercury-based electrolysis)	! (H_2/O_2)	Operational instructions
1998	WE	HIAD #243	Hydrogen-oxygen explosion	?	-
2005	WE	Literature	Explosion during operation of a HP WE	!	Risk assessment, design for pressure waves, always organise the safety management system
2012	WE	Literature	Membrane perforation in PEM FC cell	?	It will be difficult to promptly detect these cases.
?	WE	Literature	Destruction of a PEM FC short stack	?	Continuous monitoring of H_2/O_2
1998	WE	ARIA 20351/ HIAD 2.0 #243	H_2 entering an O_2 gasometer	?	-
2003	Na-ClO3	ARIA 25777	Deflagration of H_2/O_2 with short circuit	!	Prevent clogging
2004	WE	HIAD 2.0 #108	Fire, due to malfunction of electrolyser	?	-
1968	WE	HIAD 2.0 #664	Hydrogen gas holder exploded	!?	-

5. Risk assesment

5.1 Hazard identification

In the operation of complex processes, including large-scale water electrolysis, hazards need to be contained. This may vary from generic hazards, such as dropping loads, contact with hot surfaces, electricity and external events, to process-specific hazards. Hazard identification is the first step in risk management and is usually done systematically by means of checklists, HAZID, HAZOP and pre-HAZOP studies. In this project, the focus is on specific hazards related to the presence of hydrogen and oxygen and potential explosions during hydrogen production.

The industrial partners participating in the project (HyCC, Ørsted, Shell, Yara) are involved in risk assessment of green hydrogen systems as owner-operators. To identify common knowledge gaps, these partners were interviewed to assess whether there are common approaches in their risk handling policies. The partners indicated that the overall approaches and methods used follow the standard practices in the chemical industry. However, in several steps, there are knowledge gaps and a need for best practices. The potential technology operators are all experienced in risk assessments, although obviously not in the field of large-scale green hydrogen production. It is important to go through a risk analysis step by step. All project partners indicated that their process steps do not differ from risk analyses for other complex processes.
They utilise various methods such as HAZID, HAZOP and LOPA. The difference from conventional processes is the lack of data for large-scale electrolysis plants, forcing them to rely more on their expert judgement.

A good accident scenario should describe the most likely root causes of an event. Subsequently, it should relate how this could escalate to a top event with corresponding consequences. A definition of a credible scenario from the Dutch guideline PGS6 is:[22]
"A scenario that contains a description of the nature and scope, the course over time, and the fighting or management of a fire or accident at a location where environmentally harmful activities are carried out that, given the nature of the installation or the environmentally harmful activities, taking into account the preventive measures introduced therein, are considered to be real and typical:

- where damage can occur to buildings or persons in the vicinity of the location where the environ mentally harmful activities are carried out; and
- where preventive or repressive measures can be expected to have a clear effect, preventing an escalation of the fire or accident."

Water electrolysis is an electrochemical process of which the risks can be assessed by risk assessment methods which are common practice in the process industry. Process risk assessments consist of four steps:

- Scenario identification including causes, consequences and safeguards;
- Determination of the risk by frequency and severity estimation;
- Evaluating the risk using a company risk matrix, risk graph or limits set by authorities;
- Defining measures to reduce the risk to below the tolerable limit.

Risk assessments cover hazards from the process itself as well as hazards from other installations or natural phenomena (earthquakes, weather, etc.) to the process being studied. The latter hazards depend on the local circumstances and cannot be part of a generic study such as this one.

There are several hazard identification methods which are briefly explained below. For a more detailed description, the IChemE booklet "HAZOP, guide to best practice"[23] can be consulted. All risk assessment techniques are performed by a team of people with different areas of expertise to cover all potential aspects and to minimise unidentified hazards. It must be noted that different dialects exist for the same types of hazard studies.

5.1.1 Risk reduction and prioritisation

Risk assessments are often visulialised. The simplest form is shown in Figure 13.

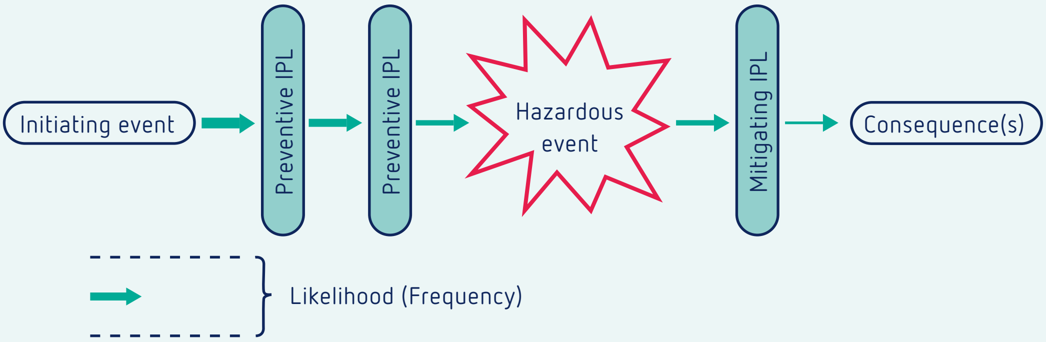


Figure 13: Model for incident scenario

The incident starts with an initiating event (e.g. equipment failure) which develops into a hazardous event, often a LOC, and will eventually result in a consequence, e.g. an explosion with fatalities. Two types of IPL can be present to reduce the risk. These are IPLs that prevent the hazardous event and IPLs that reduce the consequences of the hazardous event. Bow tie risk assessment usually identifies several threats (left side) and a number of consequences (right side).

The terminology used in the different types of risk assessment varies, which may cause confusion. Table 4 shows the synonyms used in the most common risk assessment methods.

Table 4: Synonyms used in Risk assessment methods

	HAZOP	LOPA	Bow tie
Start of scenario	Cause	Initiating event	Threat
End result	Consequence	Scenario	Consequence
Risk reduction by	Safeguards	(Independent) Protection Layers	Barriers/Control measures

Hazard identification often starts with a made-to-measure checklist for the specific process. The industrial project partners indicated that a publicly available checklist for large-scale green hydrogen production would be useful. Databases on previous incidents play an important role in hazard identification. For large-scale green hydrogen production, such databases do not exist or lack consistency.

Interviewed end users indicated that there are always site-specific factors to take into account. A fully standardised risk analysis is not feasible. The environment of the plant location defines the presence of other hazards and potential victims. The location thus forms the starting point for an analysis. Interviewees further indicated that national regulations can vary wildly, which leads to different risk analysis requirements.

> "What you don't have, can't leak!"
>
> - Trevor Kletz

If too high, risk should be reduced. Inherently safe design takes priority over applying risk-reducing safeguards. Designing in accordance with inherently safer design principles at an early stage of the design process will generally reduce the cost of active measures to control hazards and reduce risks. Hazards are thus avoided or eliminated instead of controlled. In particular, this can be attained by reducing the amount of hazardous material and the number of hazardous operations and equipment in a plant.[24]

The four principles of inherently safer design are (see also Annex B):

- Intensification/minimisation: reduce the quantity of chemicals;
- Substitution: substitute hazardous materials;
- Attenuation/moderation: use less hazardous conditions, less hazardous forms of material, or facilities that minimise the impact of a release of hazardous material;
- Simplification: design facilities that eliminate unnecessary complexity. This makes operating errors less likely to occur (and when they are made, the facilities are more forgiving).

Some examples of inherent safety are:

1. to reduce the possible flowrate from a large sudden leak: smaller pipe diameter, flow restriction orifices or devices inside pipes and tanks.
2. to reduce direct danger: shielding plates to direct possible leaks upwards and not onto other equipment, separation distances between equipment.

5.2 Methods and tools

HAZID

HAZID (Hazard Identification study) is a technique in which the main hazards of a process are identified qualitatively. The level of detail is often a Block Diagram or Process Flow Diagram (PFD). The main hazards may originate from the process itself or from outside the process. The method is used in an early stage of the design process.

HAZOP

HAZOP (Hazard & Operability analysis) is a structured method to identify all process hazards by analysing the deviations from normal process conditions at P&ID level.[25] It focuses on the loss of function of process equipment and human error. Key elements of HAZOP sessions are scenarios which consist of:

- Deviation
- Cause (for the deviation)
- Consequence (of the deviation)
- Installed safeguards to prevent or mitigate the scenarios

If the scenario is not accepted by the team, a recommendation is made, usually adding additional safeguarding or considering inherently safer design options to reduce the risk. Originally, the HAZOP method was a qualitative method. Nowadays, the team often also assigns risk to each scenario by estimating the severity and the frequency.

Bow tie

The bow tie method is a visual method to present the hazard scenarios identified. The general principle of a bow tie is shown in Figure 14 and is applied in this project for the identification of fire and explosion scenarios. Each scenario is a description of a chain of events from a threat or initiating cause or event (left side of bow tie), to a top event, such as H_2-O_2 mixing inside equipment (centre of bow tie), which subsequently leads to the release of a hazardous substance with potential consequences such as fire, explosion or other (physical) effects (right side of bow tie). Barriers to prevent or mitigate scenarios are also indicated in the bow tie. The top event is the critical event where loss of control occurs. Visualisation is a very useful tool for internal and external communication of scenarios.

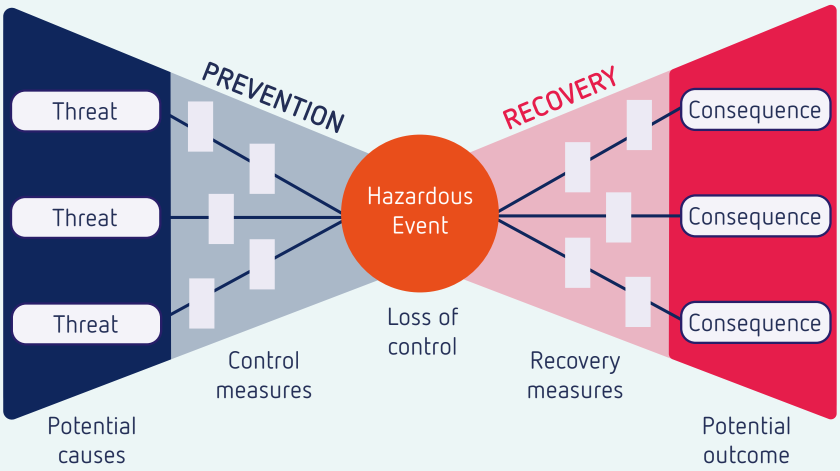


Figure 14: Bow tie diagram

Barrier types

There are different types of barriers:

- **(Inherent) design barrier:** These types of barriers often prevent (exclude) the scenario from happening or (drastically) reduce the effects.
- Barriers judged as **good practices related to engineering, operations and maintenance**: Good practices reduce the frequency of a scenario. Good practice is more a good habit (culture) than a protection layer. The risk-reducing effect relates to the frequency of the initial event. It is not common practice to assign a risk reduction factor or probability of failure on demand.
- **Passive protection layers:** Protection layers which are dormant and do not need to be activated, e.g. bunds, dikes, blast walls, etc. A risk reduction factor or probability of failure of demand can be assigned.
- **Active protections layers:** Protection layers which come into action when a process is no longer within accepted operating conditions. One could distinguish between instrumental protection layers, such as a temperature sensor and corresponding action, and others, such as pressure relief valves. A risk reduction factor or probability of failure of demand can be assigned. An operator action as a result of an instrument alarm is also regarded as an active protection layer.

Safety distances as a barrier

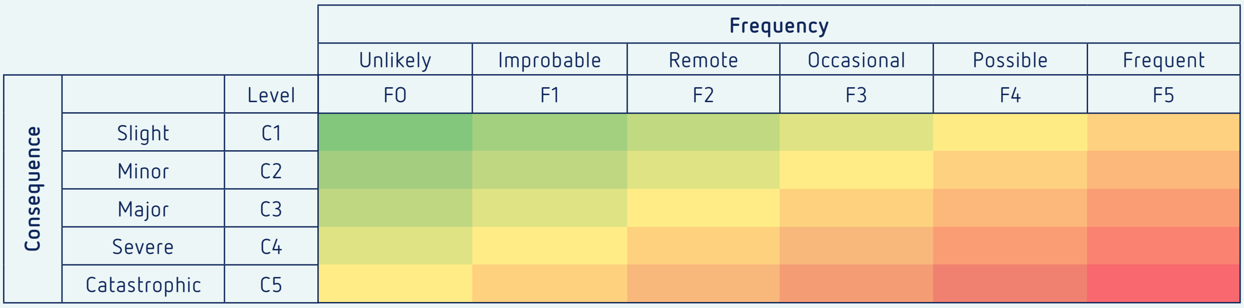
Safety distances can be regarded as a specific barrier. They are derived from the implementation of fixed-distance and indexing methods. In order to predict effect radius more accurately to determine safety distances, risk-based approaches have been explored for hydrogen-specific projects in recent years. These methods are yet to be standardised. This project provides an evaluative overview of risk assessment and safety distance determination.[26]

Fixed-distance methods and indexing methods for the determination of safety distances are easy to use and lead to reasonably good results. They require relatively little effort as opposed to risk-based methods for the determination of safety distances. Methods based on calculation of frequency and effects (risk-based) require significantly more effort but will result in more complete results. The lack of hydrogen-specific data is a problem here; this makes it difficult to carry out extensive risk assessments. Nevertheless, work is being done to increase knowledge in this area.[27]

5.3 Risk evaluation

5.3.1 Risk matrix

A risk matrix is often used as a tool to determine tolerability. An example is shown in Figure 15. The risk level of a scenario is represented as the combination of the frequency of occurrence of the undesired event and the severity of its consequences. The likelihood can be expressed in frequencies per year (10^{-6}, 10^{-5}, etc.) and the consequences are usually defined in terms of HSE impact and economic losses. All credible scenarios should be ranked and assessed. The risk matrix is a semiquantitative method for determining risk level. There is no nationally or internationally agreed or prescribed risk matrix. Risks in the green area are generally accepted, while in the yellow area it has to be demonstrated that the risk is as low as reasonbly practicable (ALARP). Risks in the green area are generally accepted, while in the area between green and red, tolerability has to be demonstrated (often referred to as the ALARP area). The likelihood and severity categories and risk acceptance level should be agreed upon at the start of a risk assessment. Many companies have defined their own risk matrices.



			Frequency					
			Unlikely	Improbable	Remote	Occasional	Possible	Frequent
Consequence		Level	F0	F1	F2	F3	F4	F5
	Slight	C1	🟩	🟩	🟩	🟨	🟨	🟧
	Minor	C2	🟩	🟩	🟨	🟨	🟧	🟧
	Major	C3	🟩	🟨	🟨	🟧	🟧	🟥
	Severe	C4	🟨	🟨	🟧	🟧	🟥	🟥
	Catastrophic	C5	🟨	🟧	🟧	🟥	🟥	🟥

Figure 15: Example of risk matrix

SIL and/or LOPA sessions are used to determine how much risk must be reduced through additional safeguards (protection layers) or when redesign is necessary.

5.3.2 Quantitative Risk Analysis

There are a number of risk analysis methods in which risks are calculated in much more detail. Some of these methods focus on calculation of the frequency of events (FTA, ETA), others on the consequences (CFD), and a third group (QRA) focuses on the combination of frequencies and consequences. For all methods, quantitative data should be available, accurate and validated. In some countries (UK, NL) a QRA is required and is used mainly for spatial planning,internal safety distances, and external safety purposes outside the industrial facility. The number of potential fatalities is calculated by means of prescribed models for heat radiation, toxic concentration and pressure for a selection of scenarios with the greatest effects. Prescribed frequencies are often used. QRA is a method in which a combination of consequences (fatalities) and frequency is calculated, leading to safety contours. The frequency of fatalities is determined by a number of parameters, such as occurrence of prescribed equipment failure rate, wind direction and other local circumstances. Fault Tree Analysis (FTA) and Event Tree analysis (ETA) focus on the determination of the frequency of a consequence based on the frequency of the initial event, PFDs and conditional modifiers. The consequence itself is determined using other tools (software and otherwise). All barriers which have an effect reduce the evaluated risk, and a risk reduction factor is assigned. A CFD model focuses on the calculation of consequences. The frequency of the initial event is determined by other means. In the event of uncertainties in data or assumptions in geometry, multiple runs are needed, which may lead to different dispersion clouds and hence safety contours.

5.3.3 Frequency determination

As is the case for identification methods, there are a number of quantification methods for risks. Usually, the risk is not really calculated but estimated. This means that most risk assessments are semi-quantitative. The risk is determined by the frequency and the severity of a scenario. The frequency of causes is estimated during HAZOP, LOPA and/or SIL assessments and based on publicly available databases or company data. Due to the lack of data on near-miss incidents, there is a lack of frequency data (source term, leaks) and as such, this can only be estimated. The influence of preventing and mitigating protection layers is taken into account to determine the frequency of the final consequence.

LOPA

A small team further analyses a subset of the most hazardous scenarios identified during a HAZOP and assesses the frequency of the scenario and severity of the consequence. Special attention is paid to independence of the different safeguards (protection layers) and assignment of risk reduction factors. The basic principle of LOPA is that every safeguard may fail and therefore the consequence of the non-protected scenario cannot be completely eliminated. Safeguards reduce the frequency of the final undesired consequence.[28] An order of magnitude calculation is carried out to determine whether the protection is adequate to keep risks to a tolerable level. It is essential to determine which barriers can be seen as independent protection layers (IPL). The requirements for an IPL are:

- They are independent of the initiating event and the other barriers;
- They are specific in the sense that they meet the requirement in every aspect with regard to preventing or mitigating a hazardous scenario (such as response time and capacity);
- They are dependable and provide risk reduction[29];
- They are auditable; the barrier must be regularly tested, leading to documented test results.

End users indicate that the assessment of whether a barrier is an IPL cannot be determined generically. It depends on the design of the electrolyser system. The electrolyser design, conditions and technologies clearly influence risks, safeguarding and mitigations as part of the inherent safety approach. Relevant factors of the electrolyser design include the volume potentially occupied by gas, sealing design, fluid dynamics design that determines the risk of hotspots, etc.

Conditional modifiers and enabling events

In a LOPA, factors other than protection layers may be taken into account. They are referred to as conditional modifiers or enabling events.[30] They include, but are not necessarily limited to (see also Figures 18 and 19):

- Probability of a hazardous atmosphere
- Probability of ignition or initiation
- Probability of explosion
- Probability of personnel presence
- Probability of consequences
- Probability of injury or fatality
- Probability of equipment damage or other financial impact.

SIL

SIL assessments are used specifically to assign risk reduction factors to instrumental safeguards.[31] The requirements for safety instrumented systems are described in IEC61508 and 61511. Four SIL levels are defined, with SIL 4 having a risk reduction factor of 10,000 to 100,000 and SIL 1 having a factor of 10 to 100.

FMEA

FMEA focuses on the failure of equipment parts (HAZOP on function loss) and their frequency and is generally used to determine maintenance strategies such as inspection intervals, repair times, spare parts, etc. The accuracy of the risk assessment strongly depends on the quality of the data used.

Data for assigning risk reduction factors

Currently, the data used are still partly based on generic equipment and component failure data from chemical processing, compressed gas, nuclear power and offshore petroleum industries.
In the process industry, for example, probabilities of generic events and failure rates of generic components are based on relevant historical data. Various databases are available to help estimate reliability data. In the absence of historic reliability data, the following approaches for assessing probabilities are possible:

a. Probability forecasts using predictive techniques. When historical data are unavailable or inadequate, it is necessary to derive probability from system analysis, activity, equipment details and associated failure or success states. Data from operational experience and/or published data sources may be combined in order to estimate the probability of an initiating or other event.
b. Expert opinion can be used in a systematic and structured process to estimate probability. Expert judgements should draw upon all relevant available information including system, project, experimental and design information.

Regarding electrolysers, failure data and failure frequencies for specific components are lacking. Sources for failure data of equipment and data can be found in:

- Hydrogen-specific methods: H2TOOLS[32], HIAD[33], NREL CPDs[34], CHS[35] and data collection tools
- Generic methods: IOGP database[36], PGS 3[37], CCPS[38] and HSE database [39]
- Reliability data: OREDA[40], SINTEF database [41], EXIDA[42] and IAEA[43].

End users interviewed indicated that the lack of data on probabilities results in a 'consequence-based approach'. Rather than estimate probability and determine risk, such an approach assesses whether consequences are acceptable. Other conservative approaches used in the absence of good reliability and probability data include the 'worst case approach'. Rather than estimate the likelihood of various scenarios, the scenario with the most serious consequences is taken as a starting point.

One of the key gaps with respect to probability involves the risk of membrane failure leading to hydrogen and oxygen mixing in the electrolyser. Data on incidents are very limited. Furthermore, the design of each electrolyser is different and manufacturers do not share internal design information. Properties of the design, such as flow distribution and risk of blockage leading to hotspots in membranes and separators, are largely unknown. The probabilities of ignition and detonation in equipment also remain largely unknown. Interviews with the OEM gave widely differing results on the occurrence and consequences of degradation or damage to membranes.

5.3.4 Severity estimation

In the event of a fire or explosion, the following three effects can be a source of damage to property or injury:

- Heat radiation (from a jet fire, fireball or flash fire)
- Overpressure
- Shrapnel

The severity of a scenario is estimated by the risk assessment team. In a number of cases, calculations are needed to determine potential effects in terms of injury to people and damage to other installations and the environment. Many different models are available to calculate the consequences of an explosion. These models have been developed for the chemical industry over a long period of time and are based on a wide range of hydrocarbons and other relevant chemicals. The available models and their applicability with respect to hydrogen explosions were analysed within the project. The most important models have been incorporated into commercial software models, including PHAST[44], SAFETI[45], FRED [46], SCOPE[47], EFFECTS[48], FLACS[49], KFX[50] and EXIM[51].

A summary of the most important software models available along with their pros and cons is provided in Table 5.[51]

Table 5: Models for explosion effects and contours

Method	Assumption	Limitations/Challenges
TNT equivalency	Blast propagation in idealised environment Obstacles not considered	The TNT equivalency model is not recommended as a method for modelling hydrogen explosions. The TNT equivalency method overestimates the overpressures in the near-field and converges to accurate values in the far-field. The method also does not consider plant geometry in its calculations. Furthermore, the pressure vs time profile obtained is different to what would be expected for a VCE, resulting in this method being more suitable for condensed phase explosions, which is not the case for hydrogen
Multi-energy (ME)	Contribution of congested zones to blast generation	Selection of initial blast strength according to degree of congestion
Baker-Strehlow-Tang (BST) method	Contribution of congested zones to blast generation	Specification of Mach number Sometimes underpredicts the explosion
Congestion Assessment Method (CAM)	Contribution of congested zones to blast generation	Applied only for unconfined congested regions (50-60% enclosed)

Fires

Heat radiation models applicable to hydrogen are available in the literature. They are integrated into some of the common effect modelling software used by the industry.

Explosions

Different models are used to calculate effects of explosions with shockwaves and to determine safety distances:

- Vapour cloud explosion (VCE) models such as the Multi-energy (ME) method, Congestion Assessment Method and Baker-Strehlow-Tang method. These blast curve models are suitable for overpressure calculations at large distances from the ignition source, except for the TNT equivalency model.
- Computational fluid dynamics (CFD) models can be used to calculate overpressure near the ignition source or highly congested areas.
- In-equipment explosion: CFD modelling is considered a viable option.
- In-building explosion models (for in-equipment explosions): phenomenological models are available in addition to CFD models.

These models have generally been validated for hydrocarbons. However, due to the different properties of hydrogen as compared to hydrocarbons, validity for hydrogen should be assessed carefully. Different methods of VCE modelling for calculation of safety distances are compared in Figure 16. Empirical models are not suitable for confined in-building explosions as these are based on one-dimensional considerations and are only valid for a limited number of variables. Further validation is required against a wider variety of experimental datasets in order to be able to draw reliable conclusions.

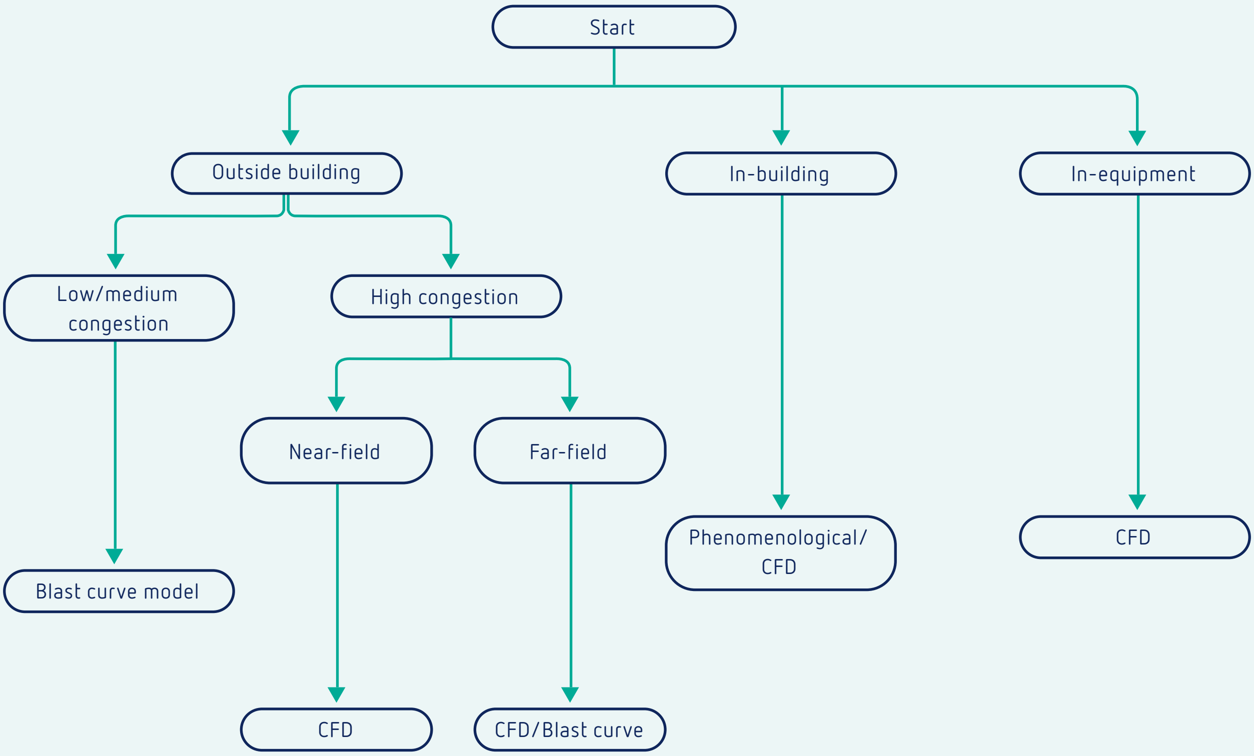


Figure 16: Guidance for explosion model type selection

For in-equipment explosions, CFD is the only option. CFD should also be considered for highly congested/confined spaces in a building and for near-field outdoors calculations. Blast curve models are a reasonable alternative for outdoor far-field calculations. Phenomenological models such as FRED/SCOPE can also be used. They are quick, but less accurate than CFD. However, CFD involves intensive modelling and requires a lot of data and runs. CFD modelling is not always the obvious choice for confined spaces and needs to be validated with experiments. A summary of the pros and cons of CFD models is provided in Figure 17.

Advantages

- Accurate geometry representation
- Detailed information of the flow field
- More accurate results compared to empirical and phenomenological models
- Suitable for overpressure close to explosion source
- Suitable for highly congested and confined areas

Limitations

- Limitations in accuracy:
  - The underlying empirical sub-models for
    - Reaction zone
    - Turbulence generation
    - Turbulence length scale
    - Turbulence combustion
- Limitations in computational time
- Degree of precision needs to be corroborated with benchmark tests

Figure 17: Advantages and limitations of Computational Fluid Dynamics (CFD) models

A vapour cloud explosion (VCE) outside buildings can be calculated using blast curve models ME or CAM. The empirical blast curve models have limited validity for congested areas, especially in confined spaces. To model effects within a confined building, phenomenological models and computational fluid dynamics (CFD) models can be used. CFD is the appropriate model for in-equipment explosions.

Shrapnel

The literature does not provide any integrated models to predict overall consequences from shrapnel that are suitable for industrial applications.[5]

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[5] There are only models available to predict individual parameters such as the initial velocity of missiles, but they are not suitable for real applications. Additionally, there are some correlations available from military experiments along with some models to calculate the impact of shrapnel to the plant from BLEVEs, but neither of them have been validated for VCEs.

6. Incident scenarios for large-scale green hydrogen production

6.1 Scenarios

Standard scenarios are available for many applications in which hazards must be contained. These scenarios are often based on long-term operating experience and, in particular, on past incidents. In the case of large-scale green hydrogen production such experience is limited. Several of the industrial partners interviewed indicated that scenario generation starts with a blank sheet of paper, using structured brainstorming techniques in multidisciplinary teams. In this project, the bow tie approach has been used to define the initiating events and consequences and also to identify barriers. Considering the specific risks associated with large-scale green hydrogen production, the project partners decided to consider two specific hazards as top events in the project:

1. Mixing of hydrogen and oxygen inside the equipment
2. Mixing of hydrogen and oxygen (in air) after loss of containment inside a building

The results are summarised in Sections 6.2 and 6.3, respectively. The bow tie diagrams for both top events, which were developed during the workshop, can be found in Annex A. The results are discussed in Section 6.4. Note that the scenarios were not extensively described during the bow tie sessions. For the in-equipment bow tie, the focus was on the occurrence of fires and explosions (potentially resulting in injuries and fatalities), while the focus during the session of the LOC bow tie was on the potential hazard to people due to fires and explosions. It should also be noted that environmental damage and hazards due to contact with chemicals (caustic and otherwise) did not receive sufficient attention.

6.2 In-equipment mixing of hydrogen and oxygen

In this section, the results are summarised based on the bow tie developed for in-equipment mixing of hydrogen and oxygen. Tables 6, 7 and 8 list the identified initiating events, consequences and barriers, respectively. The barrier type is also mentioned. For details, please refer to the bow tie diagrams themselves (Annex A).

Table 6: Initiating events for the bow tie with H_2/O_2 mixing top event

	List of initiating events generated during the bow tie workshop
1	Corrosion (e.g. bipolar plate) leading to leakage in cell
2	Mechanical degradation of membrane (clogging, thinning)
3	Mechanical stress causing membrane perforation
4	Manufacturing fault in membrane (hotspot)
5	Low/partial current density leading to (local) exceedance of crossover
6	Human error such as inadvertently opening a valve, causing an H_2/O_2 imbalance
7	Reverse current during process producing O_2 and H_2 on the wrong side of the membrane
8	Too high ΔP over membrane, causing damage
9	Dynamic operations: electrical load variations

Table 7: Potential consequences for the bow tie with H_2/O_2 mixing top event

	List of potential consequences generated during the bow tie workshop
1	Explosion in cell stack and equipment rupture, causing fatalities
2	Explosion in piping between cell stack and separator
3	Explosion in G/L separator
4	DDT (e.g. in piping to consumers and other vessels)
5	Blast, rupture, shrapnel
6	Escalation to nearby stacks/separators after explosion (domino effects)
7	Immediate detonation
8	Negative pressure after explosion in system (system remains closed)
9	Hot lye spray
10	Pressure piling
11	Loss of containment caused by backflow from other parts of the system
12	Heat radiation from combustion reaction inside affecting personnel/equipment outside
13	Jet fire after internal explosion

The scenarios generated by the project partners were presented to OEMs in a second round of interviews. In general, it was recognised that such a set of typical scenarios is useful. End users also indicated that starting with a blank sheet of paper, as some of them do today, is not ideal. Having standard scenarios and checklists will help create a more uniform approach for the sector and will help prevent specific scenarios from remaining overlooked. The use of consistent definitions also promotes uniformity.

Standard scenarios are available for various types of installations and processes. However, for large-scale green hydrogen production, such a list of standard scenarios does not exist and would also be useful. Therefore, several typical scenarios have been generated during the project. These could serve as a starting point for a standardised list of scenarios. Selection of credible scenarios requires quantification. Quantification of scenarios, however, requires assessment of consequences and probabilities. As shown in Sections 5.3.3. and 5.3.4, this is still a challenge in the case of hydrogen-specific scenarios.

Table 8: Barriers identified for the bow tie with H_2/O_2 mixing top event

I = inherent safety, G = good practice, A = active barrier, P = passive barrier

	Preventive (loss of control)	Type		Mitigating (consequence reduction)	Type
1	Material specification	G	27	Pressure relief	A
2	Protective coating	G	28	Conductivity control [6] (ignition prevention by grounding and earthing)	G
3	Monitoring of cell voltage and inspections	A	29	Explosion-proof design	I
4	Sludge filter indicating that corrosion is happening in the system, exceeding expected values	A	30	Minimise gas volume in stack and high surface-to-volume ratio to improve heat loss	I
5	Analysis of electrolyte for corrosion particles	A	31	Secondary containment	P
6	Preventive maintenance	G	32	Liquid in piping to prevent/reduce accumulation of charge (related to explosion in piping)	I
7	Process control system (flow, (Δ)pressure, level, temperature, power)	A	33	Filtering of catalyst to prevent particles	A
8	Gas quality analysers	A	34	ATEX design	G
9	Water quality analysers	A	35	Emergency shutdown by gas analysers	A
10	Cell voltage/stack voltage analysis	A	36	Flame arrestor	P
11	Factory Acceptance Test	G	37	Anti-vacuum breakers	A
12	Membrane leak test	A	38	Deflection of blast wave	I
13	Proper control of mechanical compression (membrane mounting)	G	39	Explosion curtain around equipment	P
14	Manufacturing quality assurance	G	40	Blast wall/bunkers	P
15	Independent level and pressure safeguarding	A	41	Modular design	I
16	Filling system more than 50% to prevent mixing of O_2 and H_2	A	42	Location of separators outside	P
17	Operator training, knowledge and expertise	G	43	Safety/separation distances	P
18	Pressure balancing line (related to too high Δ-P over membrane)	I	44	Minimisation of people present	G
19	Assessment of dynamic operation range vs membrane permeability	G	45	PPE	G
20	Polarisation unit	I	46	Splash screens	P
21	Current detection	A	47	Check valves	A
22	Proper trip sequence preventing reverse current	A			
23	Ramp-ramp-down procedure	G			
24	Human factor analysis	G			
25	Automation philosophy	G			
26	Operating procedures/manuals	G			

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[6] Earthing and bounding

6.3 Loss of Containment scenarios

In this section, the results are summarised based on the bow tie developed for LOC. Tables 9, 10 and 11 list the identified initiating events, consequences and barriers, respectively. For details, please refer to bow tie diagrams themselves (Annex A).

Table 9: Initiating events for the LOC bow tie

	List of initiating events generated during the bow tie workshop
1	Hydrogen-assisted corrosion not in bow tie: caustic initiated stress corrosion
2	High-temperature hydrogen attack
3	Hydrogen-induced stress cracking (HISC)
4	Overpressure in system
5	Equipment fatigue
6	External impact due to lifting operations
7	Natural disaster (earthquake, storm, etc.)
8	Flange seal failure, flanges, valves rotating/static equipment
9	Hydrogen emissive diffusion
10	Operator error e.g. valve misalignment

Table 10: Potential consequences for the LOC bow tie

	List of potential consequences generated during the bow tie workshop
1	Injuries/fatalities due to flash fire
2	Injuries/fatalities due to jet fire
3	Injuries/fatalities due to vapour cloud explosion (deflagration) outside building
4	Injuries/fatalities due to vapour cloud explosion (deflagration) inside building
5	Injuries/fatalities due to detonation
6	Injuries/fatalities due to missile projection due to explosion after loss of containment
7	Injuries/fatalities due to hydrogen dispersion and ingress in buildings

Table 11: Identified barriers for the LOC bow tie

I = inherent safety, G = good practice, A = active barrier, P = passive barrier

	Preventive (loss of control)	**Type**		**Mitigating (consequence reduction)**	**Type**
1	Material specification	G	11	Ignition control/prevention/ATEX design	G
2	Regular inspections and maintenance	G	12	Fire and gas detection	A
3	Pressure control/protection	A	13	Safety distance	P
4	Distance to lifting/hoisting areas	G	14	Passive fire protection/barriers/shielding	P
5	Lifting plans	G	15	Active cooling of other equipment	A
6	Design bases for natural disasters	G	16	Location in unconfined areas/prevent turbulent flow	G
7	Flange minimisation	G	17	Blast/fire walls	P
8	Human factors engineering	G	18	Mechanical ventilation	A
9	Operating procedures	G	19	Blast relief	A
10	Natural mechancal ventilation preventing accumulation of hydrogen (not in bow tie)		20	Close HVAC systems to prevent ingress	A

6.4 Discussion of scenarios

The consequences identified during the bow tie sessions do not indicate injury to people or damage to the environment but these can easily be distilled from Tables 7 and 10. The discussion focuses on fires and explosions. Other types of hazardous effects such as hot lye spray (injury to people and/or damage to environment) could also occur, but due to the domino effect, potential fires and explosions are considered to be the most important contributors.

Figures 18 and 19 present the sequence of events leading to an HSE incident and the associated probabilities. The barriers are not indicated. Whether an HSE incident will occur depends on the aggregated probabilities and the barriers in place. It is therefore important to consider the actual conditions required for a hazardous event and final consequences to occur. These conditions include geometric constraints, size and type of leakage, mechanical design, concentration, pressure and volumes.

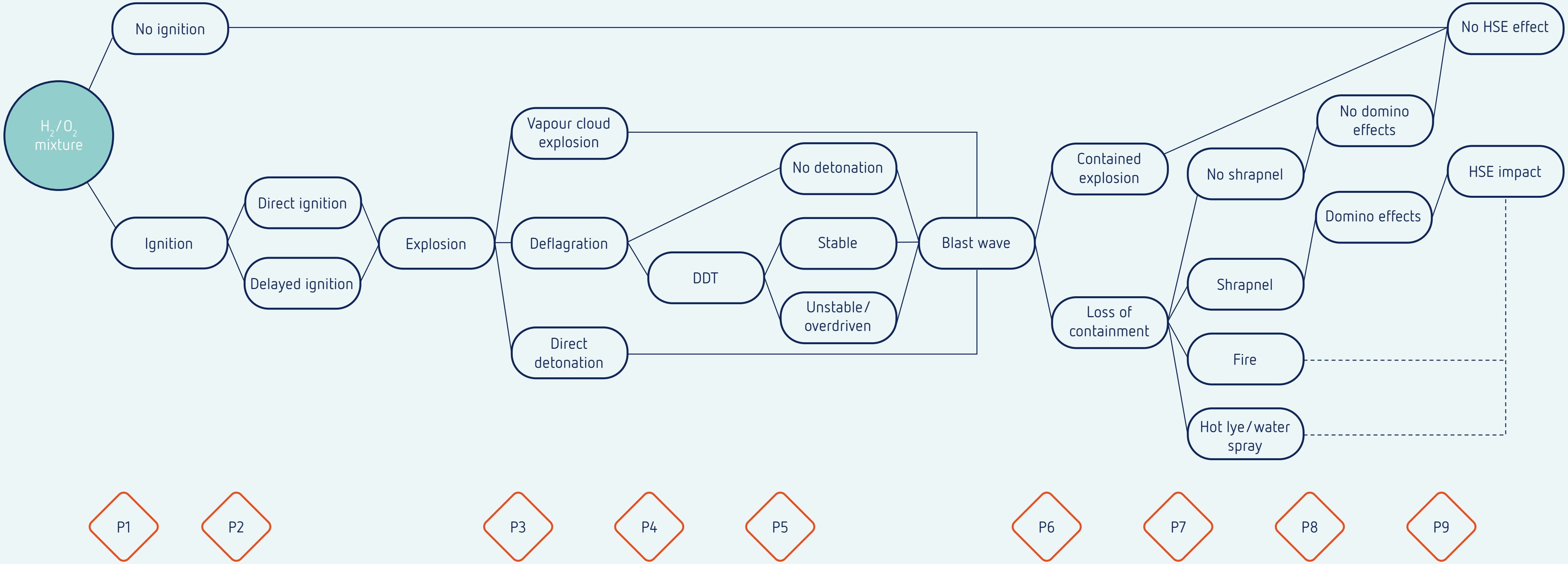

Figure 18: Overview of probable consequences for the case of in-equipment mixing of hydrogen and oxygen as top event

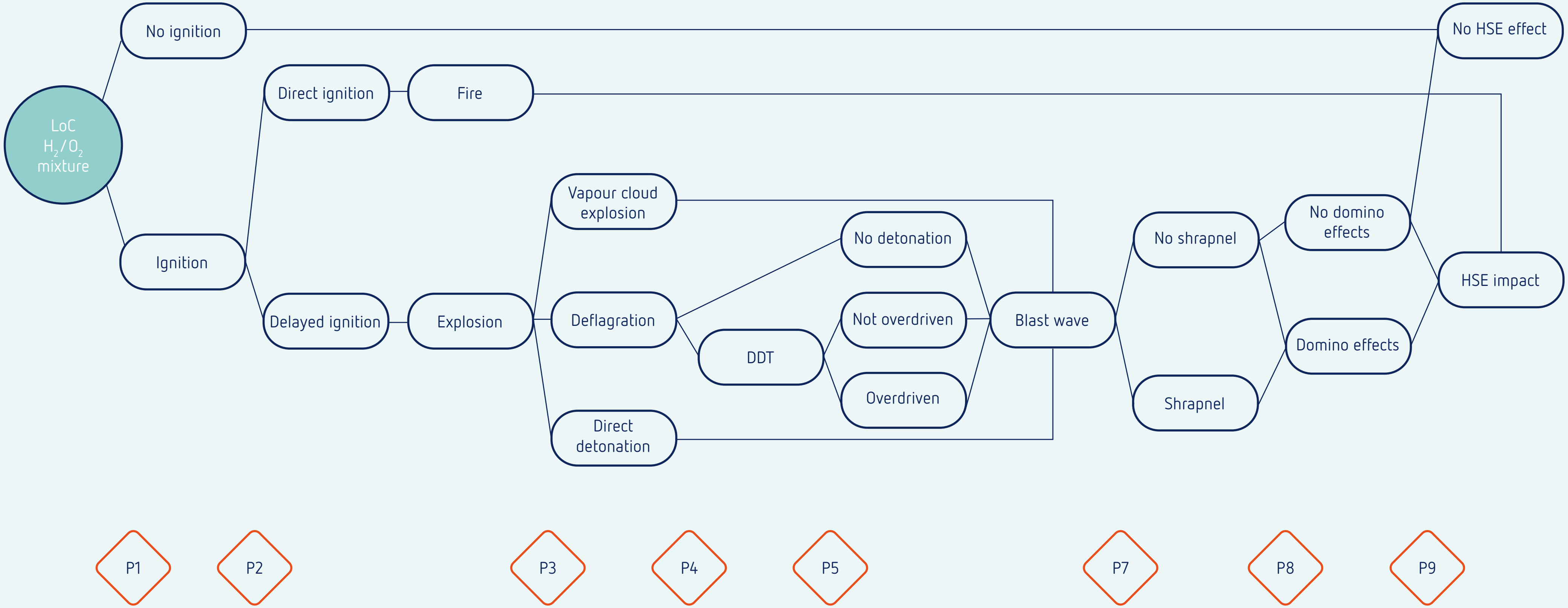

Figure 19: Overview of probable of consequences for the case of loss of containment for hydrogen as top event

The tables in Sections 6.2 and 6.3 show that all four types of barriers were identified during the bow tie workshop. Some of the barriers identified relate to inherently safe design and an RRF can be assigned to passive and active safeguards when detailed knowledge of the plant is available. These barriers are in line with those identified in the incident review. In Annex B, the barriers identified in both bow ties are grouped according to the four types: inherent safety, active barrier, passive barrier and good practice

Obviously, accidental mixing of H_2 and O_2 is an unwanted and potentially hazardous situation. Early detection of H_2 in O_2 and vice versa is very important. The red dots in Figure 20 represent potential locations for sensors for measurement of hydrogen in oxygen and oxygen in hydrogen. Due to gas crossover, design flaws or membrane failures, oxygen can be transferred to the hydrogen side or vice versa. The measurement location determines the response time. If the sensor could be connected in the two-phase flow of oxygen and hydrogen gas-liquid between the stacks and separators, the response time would be much faster than when measured behind the separators. A suitable sensor is not yet available on the market and a special setup will be required to separate gas from liquid.[52]

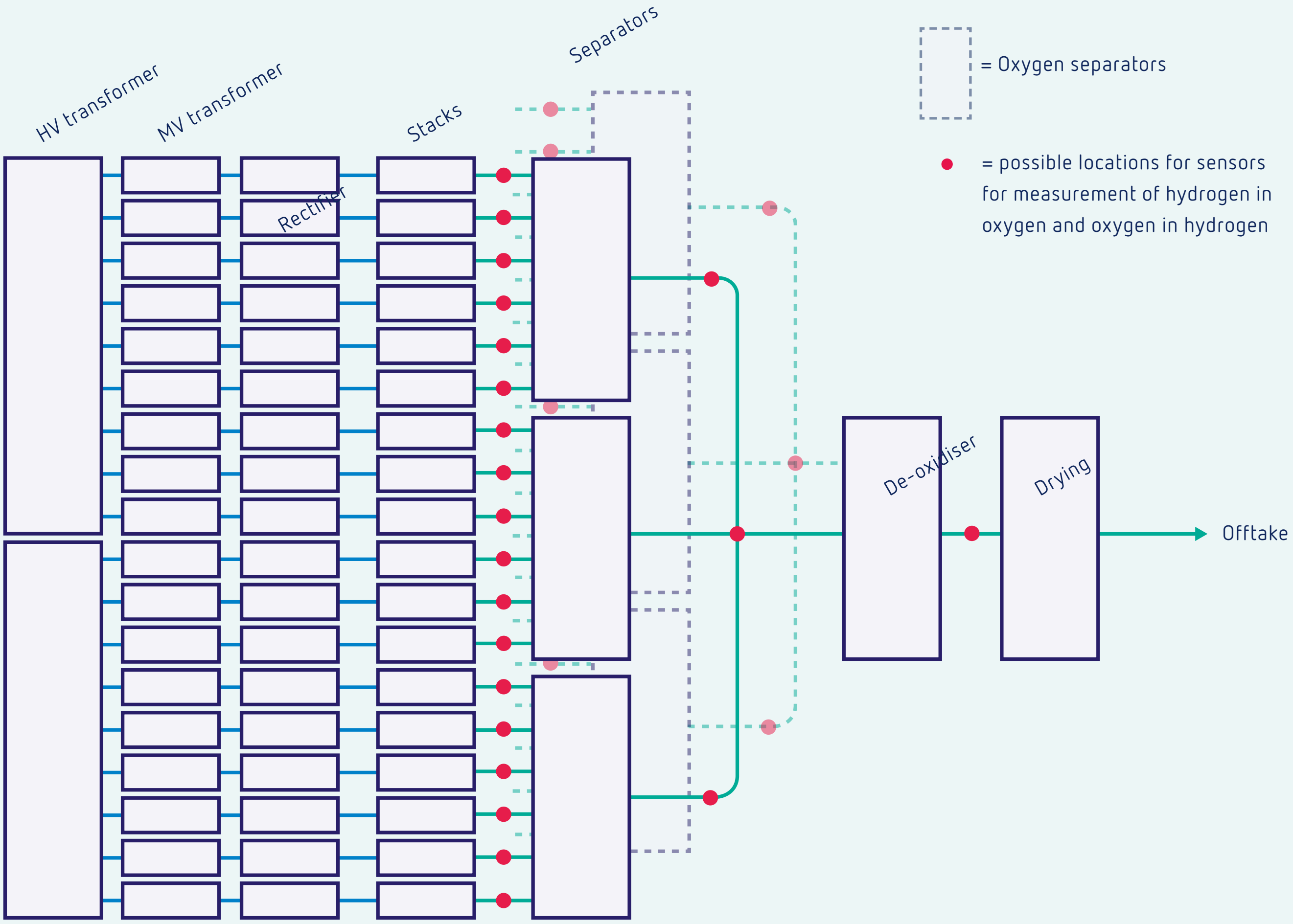

Figure 20: Possible locations of gas analysers

7. Conclusion

Methods and approaches used in the chemical industry can be applied to large-scale green hydrogen production to achieve the required safety levels. However, the property differences between hydrocarbons and hydrogen mean that input data for risk analysis cannot always be translated.

The process/chemical industry has well-established tools to assess the safety of processes involving hydrogen, including GW-scale electrolyser plants. However, historical and validated data on failure on demand and probability of ignition at GW-scale is limited. In addition, data and corresponding models for deflagration and detonation are not as well developed for hydrogen as they are for hydrocarbon systems. This will require a conservative approach in assumptions and models for the design and operation of upcoming large-scale deployments.

Detailed risk assessments require specific knowledge of the process and plant being built. The bow ties described in this report may serve as basis for a uniform approach of site-specific risk assessments. They were achieved by generating typical scenarios and potential barriers related to two specific hazards, namely mixing of hydrogen and oxygen in equipment and mixing of hydrogen and air inside buildings.

The Institute for Sustainable Process Technology (ISPT) and the consortium partners HyCC, Ørsted, Shell, Yara, DNV, RHDHV and TNO worked on this project throughout 2022. A two-year follow-up project on safety standardisation has since been started with the existing consortium, selected electrolyser suppliers and the Netherlands Standardization Institute (NEN). This new project builds on the results in this report.

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Annex A Bow ties

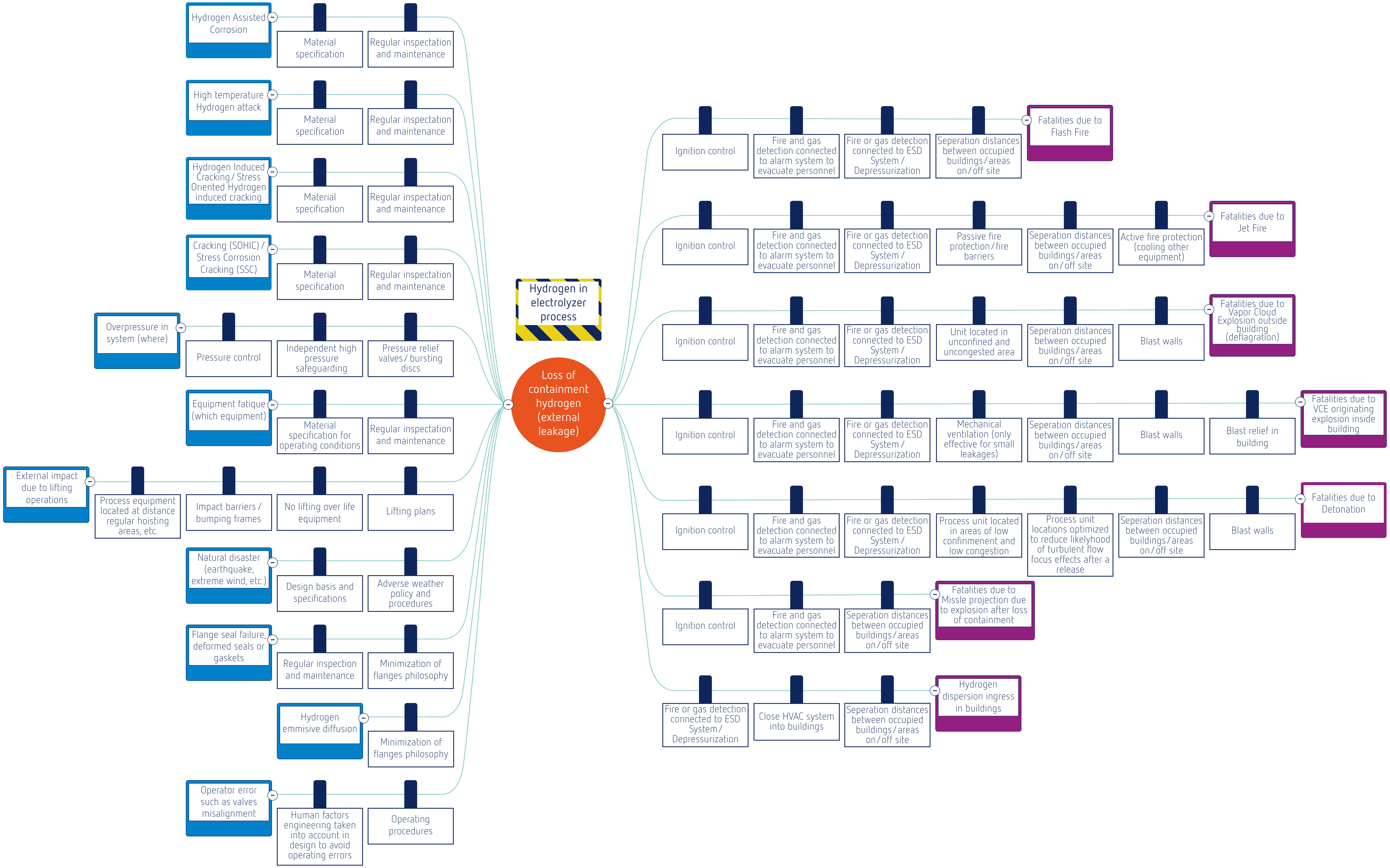

Figure A.1: Bow tie external leakage

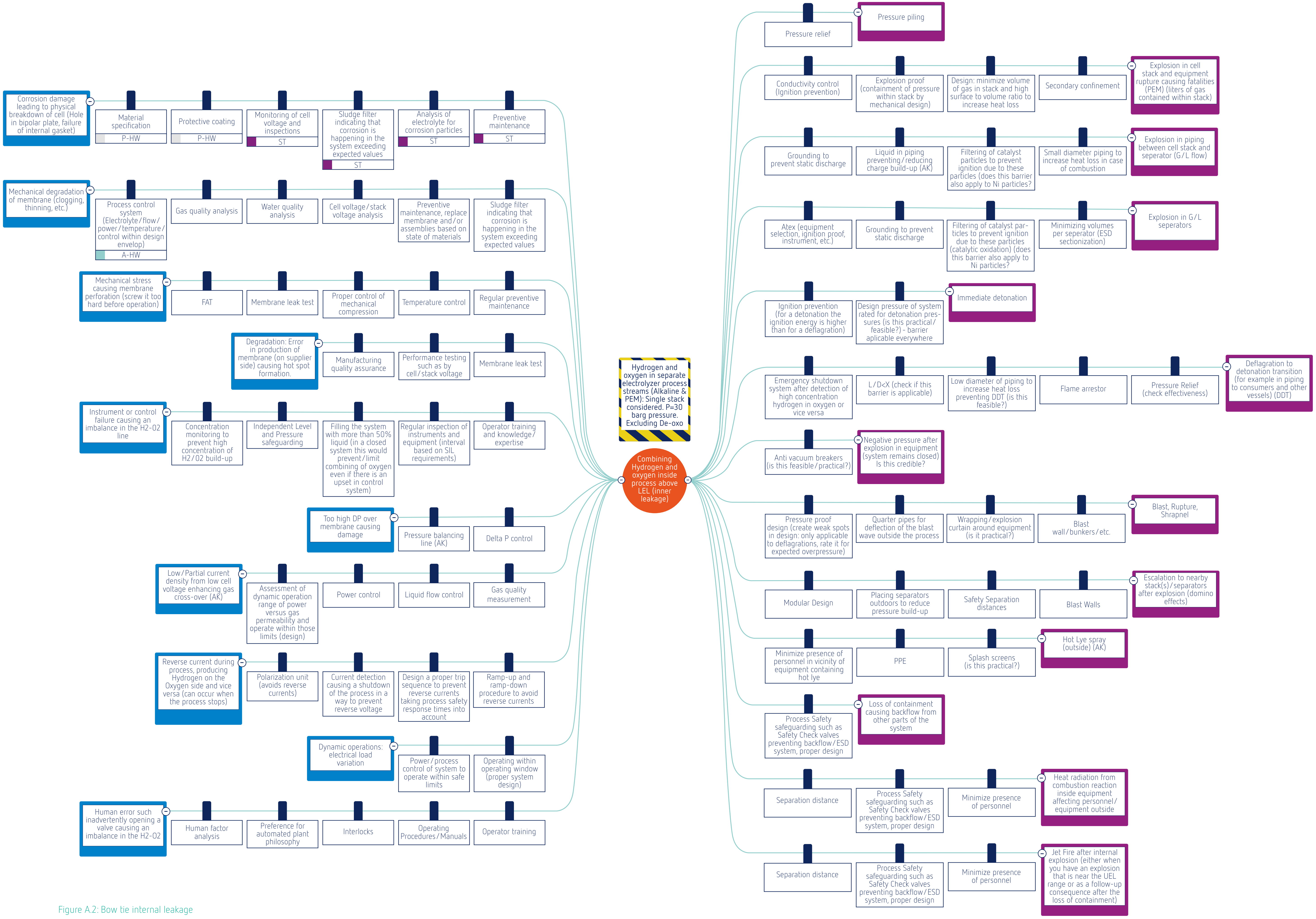

Figure A.2: Bow tie internal leakage

Annex B Identified inherent risk reduction measures

Identified inherent safe risk reduction measures

A. Intensification/minimize:

1. Reduce the size of the separation vessels and hence the volume of oxygen and hydrogen involved[1];
2. Improve separation performance and lower liquid residence time
3. Reduce the process water volume to be separated by adapting the stack design through cooling and process water flow distribution;
4. Design the electrolyser stack and piping so that the gas hold-up volume is reduced.

B. Substitution:

5. Compared with AWE, PEM technology substitutes lye (KOH 30%vol) for pure water;
6. Select alternative construction materials such as advanced reinforced membrane materials or protective coatings for cell or stack components to prevent material failure.

C. Attenuation/moderation:

7. Introduce more space in the design to create adequate safety distances;
8. Design stacks, piping and separators for sustained integrity in case of an internal explosion
9. Pressure balancing line [2]
10. Polarization unit
11. Anti-Vacuum breakers
12. Deflection of blast wave
13. Modulare design
14. Explosion proof design

D) Simplification:

15. Reduce operating pressure, quantities, gas-crossover;
16. Decrease the pressure at the oxygen side to reduce the impact of deflagrations or detonations;
17. If that is not feasible because of the required pressure difference over the membrane or diaphragm, reduce the oxygen pressure as close to the stack as possible;
18. Lower the process temperature to prevent corrosion, degradation and membrane failure;
19. Prevent backflow of hydrogen and oxygen by passive means such as the use of the process liquid (water, electrolyte) to form a barrier;
20. Reduce the risk of detonation by using small L/D pipe diameters and vessels;
21. Select passive means to control the pressure difference over the membrane or diaphragm

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[1] Simalar to reduction of the size of vessels, applying small pipe diameters and flow resctriction will reduce the release rate in case of failure of equipment (parts) and therefore reduce the potential effect

[2] A pressure balancing indeed is an inherent risk reduction measure for balancing the pressure between the G/L-separators for hydrogen en oxygen. Nevertheless, it introduces the possibility of hydrogen flowing into the oxygen G/L-separator and vice versa. To prevent this other measures should be taken such as keeping the G/L-separators for at least 50% filled. This latter measure may depend on procedures and is therefore not an intrinsic risk reduding measure

Annex C Identified barriers

Identified active barriers

1. Monitoring cell voltage
2. Monitoring stack voltage
3. Sludge filter indicating that corrosion is happening in the system
4. Filtering of catalyst
5. Analysis of electrolyte for corrosion particles
6. Process control (flow, pressure, temperature, level)
7. Independent safeguarding/trips
8. Gas quality analysers
9. Water quality analysis
10. Membrane leak test
11. Pressure relief
12. Check valves
13. Emergency response e.g. cooling of other equipment
14. Mechanical ventilation
15. Close HVAC systems to prevent ingress
16. Filling system with more than 50% to prevent mixing O_2 and H_2

Identified passive barriers

1. Secondary containment
2. Flame arrestor
3. Explosion curtain
4. Splash screens
5. Blast wall/bunker
6. Locate equipment outside
7. Separation distance

Identified good practices

1. Design basis taking into account external factors (weather, earthquakes, etc.)
2. Material specification
3. Flange minimisation
4. Protective coating
5. Preventive maintenance
6. Lifting/hoisting procedures
7. ATEX design
8. Factory acceptance test
9. Manufacturing quality assurance
10. Skilled maintenance people (membrane replacement)
11. Skilled operating people
12. Operating procedures/manuals
13. Assessment of all modes of operation
14. Human factor analysis
15. Automation philosophy
16. Minimization of people present
17. PPE

Colophon

Title

Safety aspects of Green Hydrogen Production on Industrial Scale

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About this report

This report was prepared by ISPT in close cooperation with partners. The study was performed by ISPT and partners.

The Green Hydrohub Safety project

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- HyCC
- Ørsted
- Yara
- Shell

and

- TNO
- DNV
- RoyalHaskoningDHV

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