Evaluating electrolyzer hazards in production of green hydrogen and ammonia

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Green hydrogen is increasingly touted as one of the cleanest sources of energy in the race to address climate change and, as such, has become the leading fuel of choice in energy discussions with respect to ESG (Environmental, Societal and Governance) strategies. Worldwide investments in green hydrogen and green ammonia are increasing rapidly and this is expected to continue as investment firms are making ESG strategies core to their investment portfolios. This rapid expansion brings the same teething issues experienced with previous energy transitions. One of the key issues is the rapid pace at which technology and production advances have been achieved vs. the comparatively slow pace of updated regulations. However, most producers, transporters, and end users of these technologies are aware of the safety implications of hydrogen and ammonia fuels. There is a desire to make use of existing safety learnings from adjacent industries to design adequate protections for the new energy economy.

This paper discusses some of the key hazards associated with electrolyzers from a "producer" perspective and the various applications where they are currently in use. Two key applications are considered: the production of green hydrogen and ammonia, and the manufacture of fuel cells. Both applications have very different issues involving electrolysis. This paper does not address building impacts or hazards to outdoor personnel from loss of containment (LOC) events. The focus is on the various causes that could result in hydrogen LOC events and the available mitigation systems.

For large-scale green hydrogen and green ammonia producers, the need for large-scale electrolysis capacity creates unique safety challenges associated with significant hydrogen generation in a limited space. For these facilities, the hazards are well known and mitigation can be addressed early in the design process.

Fuel cell test facilities in which engine manufacturers test hydrogen fuel cells for the transportation industry also present significant hazards due to space constraints and locations of test buildings in occupied areas. Identifying potential hydrogen release causes, effective detection, and subsequent mitigation are very important factors in keeping these facilities safe and operational.

Introduction

Globally, the energy industry is experiencing a wave of new green hydrogen and ammonia projects, some now at the early stages, some in construction, and many just starting production. This has caused organizations in adjacent industries also identifying value propositions and positioning themselves to avail of the vast opportunities both from consumers, but also from government funding and subsidies. Governments around the world are increasing their focus on supporting energy producers, users, and transporters to help reduce their carbon emissions and achieve their goals set by the Paris accord and subsequent agreements.

Electrolyzer technology sits at the center of green energy production, whether as a means to generate electricity, to fuel hydrogen-based vehicles, or to produce green ammonia as a fuel for large ships. It allows an almost "on demand" energy generation and can be well supported by non-deterministic power sources like that from solar or wind. However, as with any new technology there are problems to be overcome. Even though the push for green energy is somewhat recent, the electrolyzer technology available now is fairly mature and well understood. As long as the known hazards are considered early in the design, electrolyzer systems can be safely developed to meet the industry's tolerable risk criteria.

This paper discusses the high-level hazards and mitigations that can be considered in designing electrolyzer systems with a focus on the impacts to fuel cell manufacturers and green ammonia producers.

Electrolyzer Technologies

There are three key types of electrolyzer technology primarily used in the industry: Polymer Electrolyte Membrane (PEM), Alkaline Electrolyzer (AEL), and Solid Oxide. This paper addresses only PEM and AEL hazards since they are the most commonly used electrolyzers in the industry.

- Polymer Electrolyte Membrane (PEM)
    - The core of PEM electrolyzer technology is the proton conducting polymer membrane from which the name is derived.[1] This membrane separates the reaction compartments for hydrogen and oxygen, and also provides the ionic contact between the electrodes, which is essential for the electrochemical process. Production of the gas takes place on the surface of the respective precious metal electrode as shown in *Figure 1*.

[1] Ibrahim D, Abdullah A. "Electrolyzer Technology" Comprehensive Energy Systems, 2018

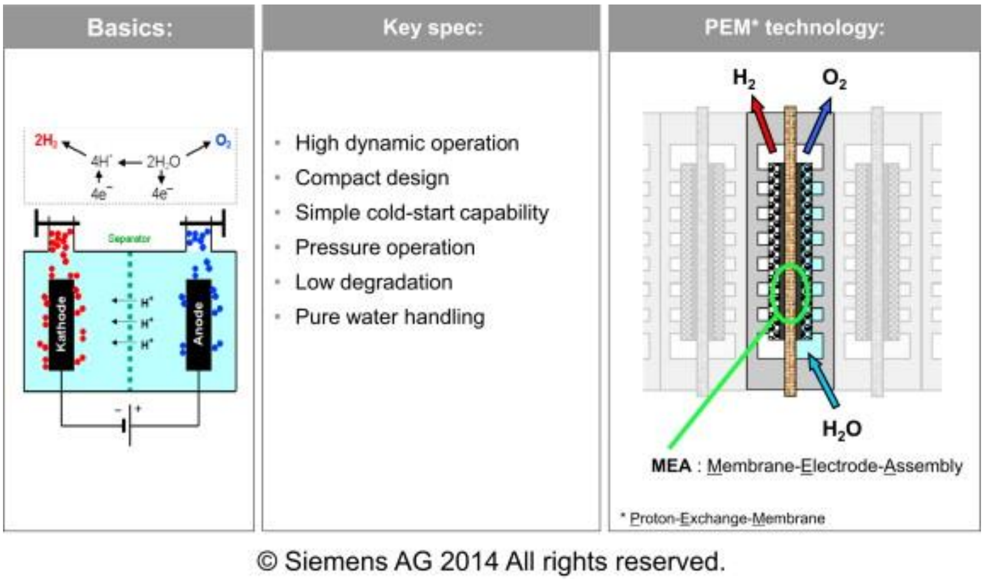

Figure 1. PEM Electrolysis (courtesy of Siemens AG 2014)

- Alkaline Electrolyzer (AEL)
    - AELs (shown in *Figure 2*) contain caustic water solution and 25%-30% of potassium hydroxide (KOH), sodium hydroxide (NaOH), and sodium chloride (NaCl)[2]. The liquid electrolyte allows ions to be transported between electrodes and not consumed in the chemical reaction, but need to be periodically replenished depending on the losses in AEL.

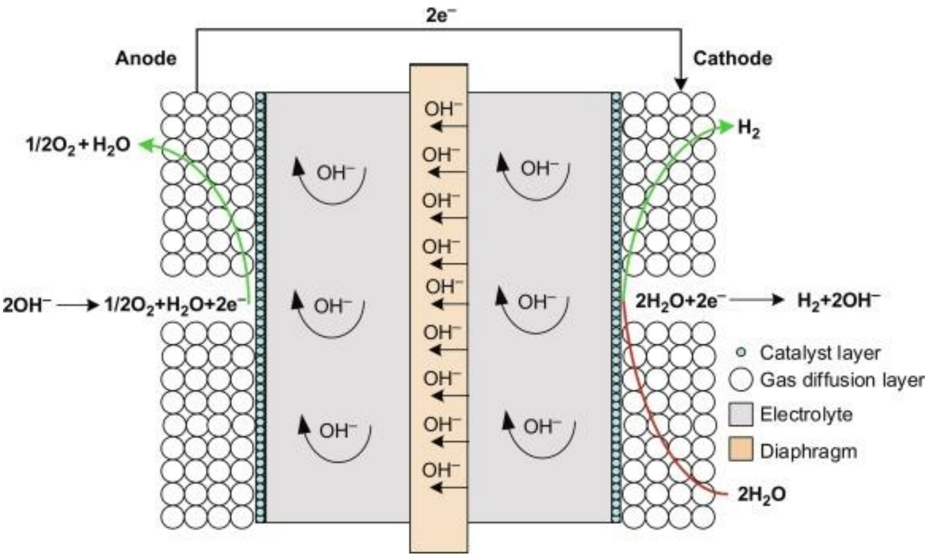

Figure 2. AEL (courtesy of Science Direct)

The advantages and disadvantages of PEM and AEL electrolyzer technologies are summarized in *Figure 3*.

[2] A Bhanu, T Nelabhotla, C Dinamarca."Alkaline Water Electrolysis". Hydrogen Electrochemical Production, 2018

PEM Advantages

- Ability to operate at high current densities
- Ability to operate with dynamic energy sources like wind and solar
- Ability to operate at high pressures with low ohmic losses
- High gas purity allows usage in fuel cell applications

PEM Disadvantages

- High manufacturing cost due to expensive materials and components
- Sensitive to imperfections and dust infiltration

AEL Advantages

- Mature technology
- Longer lifetime (tens of thousands of hours of operation)
- Ability to operate at current densities of 100-400 mA/cm^2

AEL Disadvantages

- Inability to effectively support dynamic energy sources like wind and solar
- High corrosive effects of the electrolytes at high temperatures

Figure 3. Advantages and Disadvantages of Electrolyzer Technologies

Hazard assessment

An important part in the review of a new design is to consider the hazards and implement design mitigations to reduce risk to a tolerable level. This exercise is increasingly important for the two applications discussed in the paper for the following reasons:

1. The global population is very aware of the hazards associated with hydrogen and ammonia due to previous incidents and are watching to see if these new technologies can develop over time to gain credibility as a viable, safe, and cost-effective option for reducing greenhouse gas emissions.
2. The new energy economy is growing rapidly with respect to available technology; at these fast paces, it is difficult to ensure safety maintains an equal pace to support production demands. With an appropriate emphasis on safe design and operation, plants can avoid downtime and other interruptions to operations.

Hazard assessments can be done qualitatively using established Process Hazard Analysis (PHA) methods like the Hazard and Operability Study (HAZOP), What-If, Structured What-If (SWIF) or other similar methods. A more quantitative approach can also be taken using screening-level dispersion modelling software or more detailed dispersion and explosion analysis using Computational Fluid Dynamics (CFD). A combination of both those approaches is recommended to take the pros of both the above-mentioned methods and develop results in timely and scientific manner. Flow chart for such an approach is shown in Figure 4.

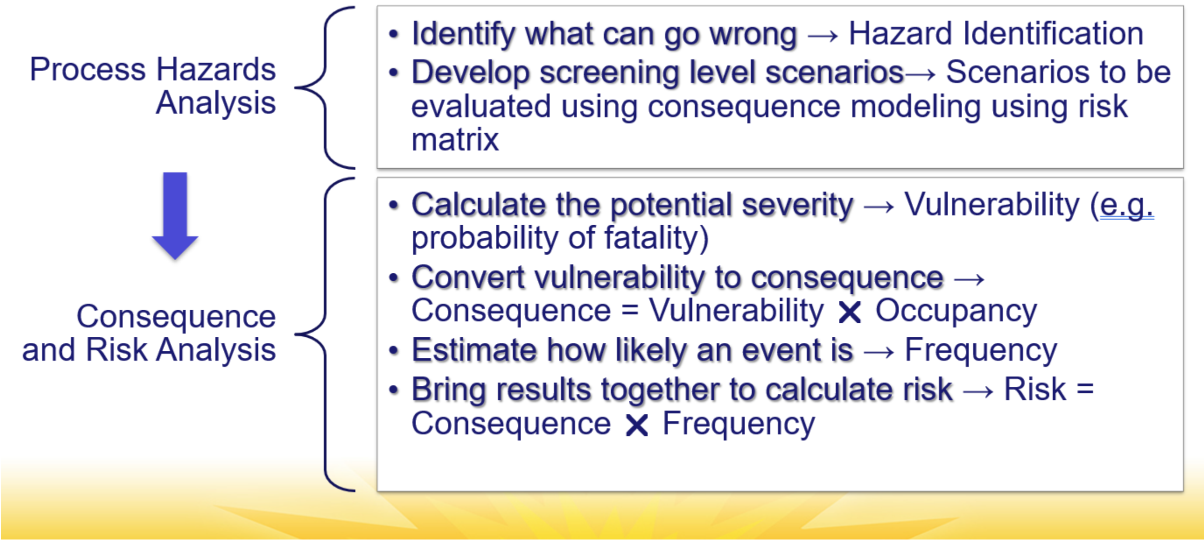

Figure 4. Combination of qualitative and quantitative risk analysis

1. A qualitative analysis can be used as a screening tool to identify scenarios that can potentially lead to dangerous conditions.
2. Based on scenarios identified from the PHA, further detailed quantitative analysis can be performed for certain scenarios to determine consequences considering factors such as the layout of the area, air flow rates, or existing mitigations in place.

Green hydrogen for fuel cell applications

Green hydrogen Fuel cell technology is increasingly being used in various modes of transportation, from forklifts that are replacing propane and batteries with hydrogen fuel cells to new designs for large vehicles including buses or trucks. A typical block diagram of a green hydrogen plant is shown in *Figure 5*. Large engine manufacturers are working on technology improvements both at lab-scale and at production-scale to bring these fuel cells from design to production to market in a very short period of time. As with typical engine manufacturing processes, extensive testing is performed to determine engine performance and reliability using hydrogen fuel cells. Similar tests are performed for the fuel cells as well.

To use the existing testing infrastructure, lab setups are being modified to allow the change from fluids such as diesel and gasoline to hydrogen. These types of test facilities are primarily located in large buildings with high occupant populations that are involved with performing tests on other types of engines or other office tasks. With gasoline or diesel, the primary hazard was fire; hence, the labs are set up to mitigate those hazards with adequate fire protection systems. Hence, legacy engine tests can be performed without significant safety risks to personnel not directly involved in testing of such engines, since fire hazards are generally limited to the lab area. With the transition to hydrogen, there is increased risk of flammability and explosion in small, confined spaces, with the potential to injure personnel regardless of location within the building.

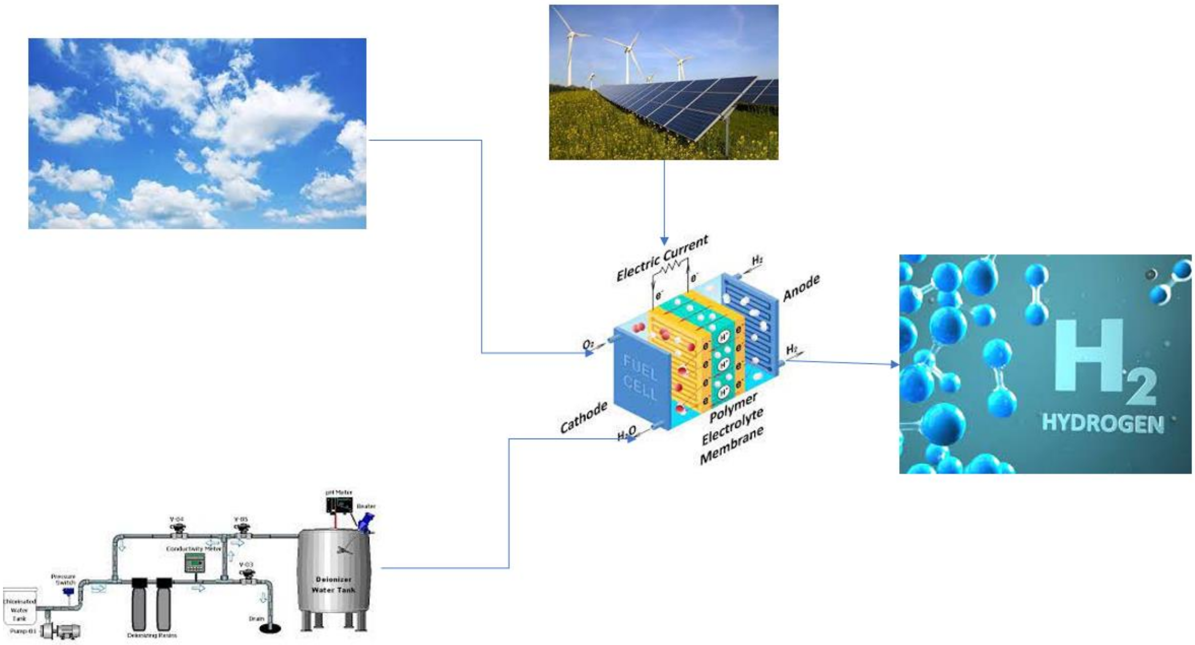

Figure 5. Typical green hydrogen plant block diagram

Green Ammonia Production

Ammonia is touted as an alternate fuel of choice for maritime applications to achieve the vision set by the International Maritime Organization (IMO), who have adopted mandatory measures for new ships to reduce emissions of greenhouse gases from international shipping under IMO's pollution prevention treaty (MARPOL) – the Energy Efficiency Design Index (EEDI) and the Ship Energy Efficiency Management Plan (SEEMP).[3]

The IMO strategy includes a specific reference to a "pathway of CO2 emissions reduction consistent with the Paris Agreement temperature goals." To assist with achieving these goals, the maritime industry and its fuel suppliers are increasingly looking at hydrogen and ammonia as the fuels of choice. Fertilizer producers are looking to support this industry by boosting the production of ammonia, and specifically green ammonia. Fertilizer producers are very familiar with the toxic hazards of ammonia. Many of them have used hydrogen as an input, but are not very familiar with the hazards of hydrogen production. A typical block diagram view of a green ammonia plant is shown in *Figure 6*.

[3] International Maritime Organization (IMO) website "Initial IMO GHG Strategy"

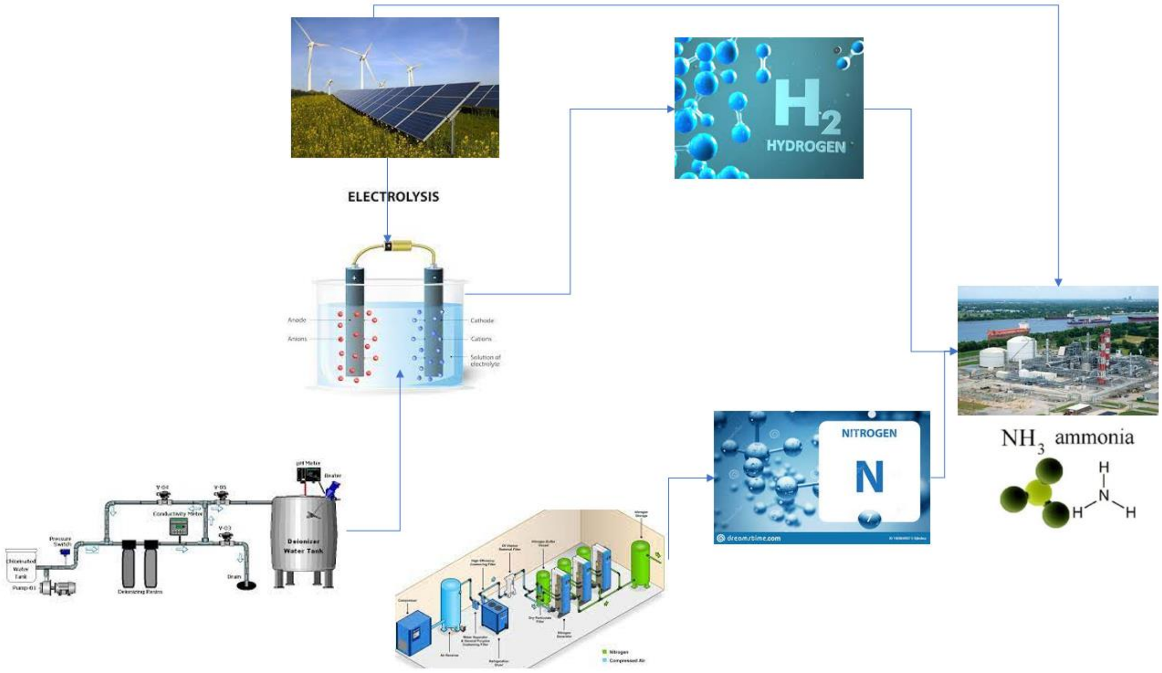

Figure 6. Typical green ammonia plant block diagram

Key Hazards

This section describes the key hazards that may be considered during a hazard analysis along with a high-level description of the mitigations to protect each identified key hazard.

1. High hydrogen pressure caused by blocked outlet or vent lines or current controller failure at the electrolyzer.

    a. Description: Typically, hydrogen generators work at fairly high pressure; while ranges differ, they can be 500 psig (35 barg) or higher. Piping design is generally performed using the maximum pressure possible. However, various conditions can result in a very high pressure, possibly overpressurizing some piping components or equipment. This can cause catastrophic failure of piping and/or equipment with release of hydrogen to the building.

    For fuel cell test labs, this can cause a stoichiometric mixture to form in the room very quickly. Due to the high voltage operations, ignition sources are present in the room. An ignition can result in a significant explosion with deflagration or detonation.

    For green ammonia applications, the installations are generally much larger with hydrogen compressors downstream. Depending on where the failure occurs, this could potentially represent a significant release of hydrogen. In most cases, multiple electrolyzers are required for large scale production applications and in this situation, failure from one of the electrolyzer piping systems may not form a stoichiometric mixture. The impact of this scenario depends on the location of the failure. A failure at the compressor outlet can be a significant scenario, which is why these compressors are generally located outside the building, in a shed.

    b. Protection and Mitigation: For scenarios that can result in a leak, depending on the size of the room, a steady state or dispersion model should be developed to determine if the HVAC flow will allow the gas to be diluted and prevent a stoichiometric mixture being formed. In some cases, the HVAC flow can be ramped up or scavenger system can be initiated during an incident to minimize build-up of hydrogen concentration in the room. Typical protections for high pressure scenarios include installation of a relief valve. In some cases, vented deflagration panels can be a valid mitigation mechanism, if designed correctly.

2. Overheating of the cell stack caused by loss of DI water or chilled water supply.

    a. Description: DI water is the key raw material for the electrolysis process. Similarly, chilled water is used for heat exchangers to maintain the cell stack at a stable temperature. This scenario is primarily applicable to the fuel cell scenario in which overheating of the cell stack can result in damage to the stack, with possible leaks of hydrogen inside the test lab area.

   b. Protection and Mitigation: Typical protections for such scenarios include temperature monitoring at the cell stack and any level monitoring to ensure DI and chilled water supply is maintained. Mitigations for such scenarios are the same as that described in #1 above.

3. High oxygen pressure caused by blocked valves or failure of pressure control.

   a. Description: In addition to hydrogen releases, oxygen releases are also a possible hazard in the electrolysis process. High pressure oxygen is produced and can be in the range of 200 psig (14 barg). If a condition like blocked flow occurs, it could result in a high-pressure release of oxygen. This can significantly increase flammability hazards from the ignition of hydrogen gas and subsequent explosion.

   b. Protection and Mitigation: Oxygen detection in the room with a quick response time can help reduce the hazards from a release of oxygen.

4. Mixing of hydrogen and oxygen due to membrane failure or diffusion.

   a. Description: With PEM electrolyzers, there is a concern regarding diffusion of some hydrogen molecules to the oxygen side, which can result in high pressure hydrogen and oxygen mixtures that can ignite and subsequently explode. Due to the pressure difference, the likelihood of such a mixture developing in a sufficient quantity to form a flammable mixture is low; however, a failure in the membrane could result in a similar ignition/explosion scenario.

   b. Protection and Mitigation: A sampling system and analyzers can help quickly detect such scenarios with a trip of the electrolyzer. Combustible gas analyzers in the room can also help mitigate this scenario by increasing the HVAC air flow.

5. Overpressure of the hydrogen vent lines due to water overflow into the vent.

   a. Description: If water gets carried over from the electrolyzer into the vent under low ambient temperature conditions, it could freeze and block the vent flow when needed in an overpressure situation. This scenario is similar to the overpressure scenario described in #1 above. In such a case, the safeguard of venting is not available to help protect against the overpressure.

      For fuel cell test lab applications, the proper design of vents is very important. There are applicable standards by NFPA and CGA that can help prevent overpressure. Due to the vent sizing for large electrolyzer applications similar to those in green ammonia production, it may take a long time for such a blockage to occur; however, if not monitored or maintained properly, such a condition can develop over a period of time.

   b. Protection and Mitigation: Typical mitigation includes appropriate design (per the standards) and installing heat tracing and insulation, as well regular draining of the lines to prevent water build-up.

6. Piping failure due to hydrogen embrittlement.

   a. Description: Similar to other hydrogen applications, embrittlement at low temperatures is a concern.

   b. Protection and Mitigation: Appropriate design plus regular monitoring and maintenance can help prevent embrittlement. In addition, minimizing sudden temperature drops through active monitoring can prevent such failures.

7. Higher diffusion due to loss of cooling water to the anolyte/catholyte coolers or high cell voltage.

   a. Description: For AEL type electrolyzers with anolytes and catholytes, loss of cooling water results in increased temperature and voltage at the cell, with damage to the cell. This could result in release of hydrogen to the building.

      For large electrolyzer installations, these scenarios can cause temperature increase to the cell stack, which if not monitored can cause damage to the cell with possibility of leaks.

   b. Protection and Mitigation: Adequate monitoring of the cooling water supply and temperature monitoring can help prevent loss of cooling water.

Conclusions

Electrolyzers are quickly becoming the work horse of the new energy economy and their use will continue to expand and become more important. It is important to review hazards of all new technology in light of the application in which it will be deployed. Hazard analysis in the early stages of such deployments can help reduce costly design changes and worst-case safety impacts to people both onsite and offsite.

In this paper, the discussion was focused on fuel cell producers and green ammonia producers. The size of the application and the hazards can differ significantly depending on where the equipment is located. In fuel cell testing facilities, electrolyzers will typically be installed in congested lab spaces, where detailed consequence analysis using CFD methods may be warranted to determine adequate mitigations. For larger applications like those for green ammonia manufacturing, the size of the electrolyzer package may be significantly large, requiring a detailed review of the layout, identification of possible leak locations, and supplying adequate HVAC air flow where needed.

The hazards analysis discussed in this paper can be used as a starting point, but a detailed review should be performed considering the individual site's operations and layout. It is important that companies using electrolyzer technology, including those who are new to the large scale production of hydrogen and ammonia, learn from years of industry experience in safely handling and operating with these gases. To ensure the safety of personnel and viability of these emerging new technologies, process safety incidents and their resulting disruption to markets, networks, supply chains, and public perception must be avoided to the extent practical.