Safety of Water Electrolysis Webinar Q&A

Key Words: electrolysis, electrolyte, water, oxygen, explosion, deflagration, electricity, procedure, ignition, ventilation, nitrogen, purge, OSHA, code, standard, incident

The information in this document provides answers to the questions that were raised during the Center for Hydrogen Safety April 29, 2021 webinar.

1. Would you briefly explain the process for preparation of the feed water and electrolyte solution?

Potassium hydroxide (KOH) and sodium hydroxide (NaOH) are the most common alkaline electrolyte chemicals in commercial use. These are very strong base chemicals that are very reactive and can be very hazardous if mishandled. They must be handled with full safety precautions and personal protective equipment according to the Safety Data Sheets available from suppliers and through online resources.

Electrolyte preparation and system charging are specific processes that differ per electrolyzer equipment manufacturer and should be defined in the supplied maintenance manual. Often the work is performed by a trained service technician. For most alkaline electrolysis systems, the cell stack anode and cathode and respective oxygen and hydrogen gas/liquid separator tanks are filled with alkaline aqueous electrolyte at a concentration specified by the equipment manufacturer. Alkaline electrolyzer manufacturers typically provide mixing equipment and instructions with their balance of plant. Dilution of a strong base in water to prepare the aqueous electrolyte is an exothermic reaction, so following supplier instructions and using proper equipment is essential.

Once the electrolyzer is charged with electrolyte at the manufacturer's specified concentration, only makeup deionized feed water to the process is necessary. Some electrolyzer suppliers prescribe a periodic electrolyte drain and replacement maintenance procedure to restore performance – see manufacturer's recommended maintenance procedure.

2. In the AEME incident, did they have a Deoxo? How did the O2 pass through the Deoxo unit?

From the public accounts provided, there may have been a deoxo catalytic unit in place, or one was inserted after the incident as a corrective action.

Catalytic recombination or deoxygenation is used to remove oxygen (O_2) impurities. The process is also known as a 'deoxo' process. The oxygen reacts with the hydrogen to form water vapor, which can then be removed by a dryer if necessary. The catalysts that are used are based on platinum group metals (PGM). Commercial deoxo units are designed to react trace (<1%) levels of O_2 with H_2, producing water vapor that is removed in a gas dryer. Anecdotal information suggests that a typical system could handle up to 3% O_2 in H_2. As the $H_2+O_2 \rightarrow H_2O$ reaction is exothermic, higher O_2 in H_2 concentrations will drive catalyst temperatures upward toward the 500C limit of catalyst supports (https://catalysts.basf.com/files/literature-library/BASF_0.1_-Pd_AS-R5279_Datasheet_A4.pdf). Ignition is also a significant risk at that temperature and at concentrations above the upper flammability limit of about 6% O2 in H2. High concentrations of O2 in H2 might occur due to a cell membrane mechanical failure, for example.

3. Is a hydrogen-oxygen explosion critical? What additional safeguards can be included in addition to hydrogen/oxygen detection?

While I believe H2/O2 detection is the most critical and effective in detecting an unacceptable cross-cell diffusion or leakage rate, other electrolysis process parameters such as pressure will also indicate unfavorable conditions that may result in an unacceptable cross-cell diffusion or leakage rate or indicate a catastrophic event in process. Cell stack voltages are difficult to trend in multi-cell stacks and it is often unwieldy to monitor individual cells.

4. What is your experience with ATEX zoning of containerized electrolysis units: apply Zone 2 (Atex) or can non-hazardous zones be expected possible or desired?

I have typically applied ATEX Zone 2 to containerized electrolysis process sections that contain H2 or O2, provided they are built according to norms and have active H2 and ventilation monitoring. I typically place process controls, feed water deionization, and power conditioning in a separate compartment or container declared non-hazardous by virtue of fresh air ventilation and separation. It is also possible in my experience to declare Zone 2 negligible extent certification for smaller units. For example, my former commercial electrolyzer company manufactures enclosed 30 barg H2 PEM electrolyzers that make 65kg/day H2. These units are classified for installation in Zone 2 negligible extent areas under manufacturer's instructions for proper area ventilation and active gas detection alarms with safety interlocks. These serial production electrolyzers have frequently been installed in ISO containers with the requisite ventilation and active H2 detection alarms. To be fair, these units have very small on-board hydrogen inventory <0.4% of the container volume. They have active H2 monitoring and fresh air ventilation, and pressure vessel P*V are such that they are PVD Category 1 or less.

5. Any ideas, thoughts about H2 explosion inside module containers; is explosion venting/suppression required to protect the container?

In my opinion it is always better to prevent the formation of an explosive mixture inside module containers (such as ISO shipping containers) through detection and dilution venting, rather than to react to an event with explosion venting or suppression methods. Early detection of a hydrogen in air or H2-O2 mixture approaching 20% of the LFL or UFL, in concert with a safety system that will stop the process, area dilution air ventilation, and depressurization of the electrolyzer hydrogen and oxygen gas volumes through vent stacks, has been my favored approach. If possible, eliminate any storage in the container, isolate the electrolyzer from external storage, and through technology selection, limit the electrolyzer contained volumes of gas to minimize the extent of any deflagration. Containers that must contain significant stored hydrogen may best be configured without a roof so that any deflagration will be directed up.

6. When selecting an explosion control protection schemes for electrolysis Hydrogen Equipment Enclosures (i.e. concentration reduction of O2, concentration reduction of H2, deflagration venting, deflagration containment per NFPA 2 Annex L), what are some of the main considerations you have? Do you typically layer these protection schemes? Could you give some examples and their pros/cons?

I am very appreciative of the advice given in NFPA 2 Annex L, although as you know, as of 2020 it is not a requirement. It may be possible in a PEM electrolyzer to design process vessels that contain < 0.4% of the container volume, or to design ventilation to manage the likely leak rate from a maintenance fitting that has not been adequately re-tightened. I prefer to analyze the container internal geometry regarding component congestion and areas of possible accumulation, then place my H2 in air detectors where they can best detect an accumulation near likely sources and outside of the main ventilation air stream. I think it is better to prevent the formation of an explosive mixture inside module containers through detection and dilution venting, rather than to react to an event with explosion venting or suppression methods. I have not entertained protective gas blanketing as a reactive control in that is yet another system to manage and, depending on the suppressant, can result in equipment damage. Early detection of a hydrogen in air or H2-O2 mixture approaching 20% of the LFL or UFL, in concert with a safety system that will stop the process, area dilution air ventilation, and depressurization of the electrolyzer hydrogen and oxygen gas volumes through vent stacks, has been my favored approach. If possible, eliminate any storage in the container, isolate the electrolyzer from external storage, and through technology selection, limit the electrolyzer contained volumes of gas to minimize the extent of any deflagration. Containers that must contain significant stored hydrogen may best be configured without a roof so that any deflagration will be directed up.

7. What role will hydrogen play in long term energy and decarboxylation strategy?

A very significant role, to be sure. Hydrogen can decarbonize mainstream industrial processes such as fertilizer and steel production. It has great potential as a seasonal renewable energy storage media in pipelines and underground. H2 is already making significant impact on decarbonizing mobility and transport in materials handling; look for significant impact in shipping and short-haul aviation. Synthetic fuels are yet another path toward reducing the need for fossil fuels.

8. With respect to safety, what are the key parameters of feed water quality?

Feed water quality must meet the electrolysis manufacturer's requirements for purity and filtration; a typical limit value for PEM systems is 1 micro-Siemen/cm or better. Sustained lack of process water quality monitoring and maintenance will lead to cell efficiency degradation; in the most severe cases it may be a contributor to cell failure, cell leakage, and H2 - O2 mixtures that can lead to downstream component deflagration and explosion if not detected. Ionic contaminants in PEM cells will preferentially occupy the proton ion exchange sites, causing cell voltages to increase; alkaline electrolyte will also be less able to transport -OH ions. Solid contaminants will clog cell flow passages and can lead to cell thermal damage or corrosion. Electrolysis systems certified to safety standard ISO 22734:2019 must have safety monitors to halt the process when unsafe conditions are detected. For example, most certified PEM electrolysis systems monitor circulating water and feed water quality for ionic contamination and low flow conditions, which can occur due to ineffective ionic and particulate filtration.

9. As well no mention on Process Safety operation by operator: any Standard operating procedure or Emergency operating procedure to implement?

Basic process safety information and operator instruction should be provided in the operations and maintenance manuals required with ISO 22734 certified electrolysis systems. Manufacturers should be held responsible to provide such information; many offer contract training and maintenance programs.

In my opinion, better water electrolysis systems are designed to shut down in a safe manner with no required operator intervention. Systems that I have delivered are designed to automatically depressurize and self-isolate upon loss of power or detection of a safety fault.

10. What can be expected about ignition of H2/O2 in separator vessels (alkaline system)? Direct ignition or should delayed ignition be expected?

It is not always simple to predict when an H2/O2 mixture will ignite, only that it will eventually ignite within the wide range of 4% to 94% H2 in O2, (allowing for some minor variation due to pressure). Predictive active gas analysis or similar safeguards are strongly recommended as primary protective methods. The presence of liquid electrolyte as a quenching medium is not to be relied upon, in my opinion. In my experience, there is always an ignition source, as the ignition energy is so small and almost any surface defect or small particle may work as the ignition site. I have witnessed repeated ignition of an H2 in O2 mixture within an atmospheric O2/water phase separator as a result of a single cell membrane mechanical failure – if left unmanaged, the repeated failures would have certainly propagated to other sections of the system with escalated hazardous results.

11. Are guides equally applicable to applications such as sodium hypochlorite generation where H2 is the by product or are they managed separately?

Brine electrolysis for the production of NaOH, Cl2, and H2 will carry additional hazards in addition to those presented by the production of H2. Consult with manufacturers of your equipment to start.

12. Can you speak on the differences between positive pressure ventilation and negative pressure ventilation in H2 generation spaces?

Both methodologies for providing dilution ventilation have been successfully deployed in packaged electrolysis products and systems. Negative ventilation is commonly provided in building installations. One consideration in packaged/containerized water electrolyzer systems is the proximity of non-classified associated equipment, such as controls and power conditioning. If this non-classified equipment is in an adjacent compartment, a positive pressure differential between the non-classified area and the classified area across a gas-tight demising wall is typically maintained – a negative pressure ventilation situation for the classified H2 generation space. The ISO 22734:2019 standard section 4.4 does not prescribe a pressurization scheme, only that the area is classified per IEC 60079-10-1 and appropriate protective means per the IEC 60079-0 series and section 4.4 are applied.

I encourage analysis of any ventilation scheme to consider likely leakage areas, equipment congestion and stagnant areas where leaked H2 may accumulate, proximal ignition sources, and placement of H2 detectors out of high-volume air streams which may over dilute leaked hydrogen to the point where it may delay early detection.

13. What is considered a safe oxygen partial pressure at high temperature operation (SOE) to prevent potential ignition/burning/oxidation of metal piping/equipment?

This publication by the US DOE / Idaho National Labs may be informative:

Sohal and Herring. Oxygen Handling and Cooling Options in High Temperature Electrolysis Plants. June 2008. Idaho National Laboratory Idaho Falls, Idaho 83415 USA

Another source with expertise in high temperature oxygen material compatibility may be WHA International. (wha-intl.com)

14. In your opinion, what are the main challenges with regard to safety in scaling up electrolysis to multi-MW scale?

It is likely that multi-MW electrolyzers will continue to be comprised of multiple sub-MW cell stacks and matched balance of plant. Regarding safety, I consider reliable early H2-O2 detection considering renewable energy load following operation to be important. A cell separator membrane failure is a single-point failure that can escalate in severity if undetected. Early detection is challenging considering the dilution effects of healthy cells and stacks connected to common gas receivers. Reliable gas detection at the stack level in multiple cell stack MW systems is of interest to me to address this. Second to this is pressure management during transients – balanced pressure alkaline systems rely on this much more than PEM systems to assure no cross-over either through cell separators or through the liquid balancing line between O2 and H2 electrolyte separators.

15. Are shutdowns in PEM electrolyzers a problem regarding H2/O2 limits? How is it done in practice?

In my experience with 100kW and MW scale PEM electrolyzers, where hydrogen was generated at pressure and oxygen was near ambient pressure, planned shutdowns were successfully managed by automatic depressurization of the pressurized hydrogen volume and extended water recirculation through the oxygen anode chambers of the cell stacks to remove nearly all of the oxygen gas. Forced shutdowns due to power loss or a (rare) pump failure would not accomplish the anode side flush; still we did not experience any cell, stack, or system damage or excessive H2/O2 limits. On startup, water circulation was always initiated first to flush the anodes of each cell, and H2 generation at pressure was delayed for a short while during current ramp up.

16. What is the value of the numerous industrial hydrogen plants, refineries, ammonia plants relative to hydrogen and oxygen monitoring? Perhaps this discussion instead focuses on the electrolyzer, and industrial experiences is a separate topic.

I have experienced a common North American industry practice to warn at about 1% H2 in air and alarm/shutdown at 2% H2 in air, which corresponds to 25% and 50% of the lower flammability limit, respectively. I have seen other regions use lower limits such as 0.8 and 1.6, or even lower, depending on the application.

I have seen industrial facilities monitor oxygen in air and alarm outside the OSHA limits for depleted and enriched O2, 19.5% and 23.5%, respectively. Other regions use similar values.

Regarding electrolyzers, electrolyzer safety certification standard ISO 22734:2019 prescribes that the manufacturer's risk assessment shall first determine if hydrogen in air, hydrogen in oxygen, or oxygen in hydrogen combustible gas mixture hazards can exist, require detection, and require emergency stop. If these hazards are credible (most often they are), then such emergency stop shall be initiated when the maximum volume fraction of 2 % hydrogen in air, 2 % hydrogen in oxygen, or 3 % oxygen in hydrogen, is exceeded.

Some manufacturers may set lower detection limits.

17. Is nitrogen purging required or recommended for certain situations? Or does this add unnecessary cost?

The use of nitrogen purging is common in many hydrogen systems prior to maintenance actions which will require opening hydrogen piping or vessels. Some manufacturers will prescribe nitrogen purging prior to initiating hydrogen generation to eliminate any recombination with oxygen/air that may be present because of maintenance or an extended shutdown.

However, my prior company has delivered hundreds of serial production PEM electrolysis systems from kW through MW scale that do not require nitrogen purging as part of routine startup, operation, and shutdown. These products all have current notified body certification to ISO22734. We demonstrated the ability to minimize any occurrence of hazardous H2/O2 mixtures through use of minimal contained volumes, proper containment design, and initial gas generation at near ambient pressure. In this way, we were able to offer lower installation and maintenance costs and spare a few fittings and valves too.

It may be prudent to develop a service procedure to safely depressurize and then nitrogen purge a system in advance of invasive hydrogen component maintenance, especially when significant volumes are involved. Importantly, such a procedure must support restoration of the system integrity after maintenance.

18. What's your recommendation to safely shut down an AEM electrolyzer?

My AEM experience only extends to the laboratory bench scale. However, as PEM and AEM system architecture are typically very similar in the use of an ion exchange membrane cell stack with anode side recirculation and cathode side H2 evolution, as well as similar downstream system components, I will offer for your own evaluation a similar approach to that commonly used in commercial PEM systems:

- Remove cell/stack current
- Isolate the system from any downstream H2 or O2 volumes or equipment
- Depressurize oxygen and hydrogen sides through a restrictor over several 10s of seconds
- During depressurization and for a short period thereafter, maintain anode side water/electrolyte circulation to sparge additional oxygen gas from the cell stacks
- Maintain hydration of the cell membranes by periodic recirculation and water/electrolyte maintenance
- Perform routine maintenance of filters and feed water deionizers

19. Would PSM 1910.119 apply to these type operations including say the maintenance, mechanical integrity and MOC areas?

PSM 1910.119 certainly applies to hydrogen as a category 1 flammable gas. I certainly would consider invoking PSM for operations where quantities will exceed the MAQ.

I would also look at NFPA 2 Chapter 13 for electrolyzers and Chapter 4-7 for downstream storage or use of hydrogen. Most states in the US have adopted NFPA 2 directly or through adoption of the IFC.

20. What do you think about the risks with the often applied 'liquid balancing line' connection between the two G/L separators of alkaline electrolyzers?

The liquid balancing line works to prevent an accumulation of electrolyte in one G/L separator over the other. Each G/L separator is back pressured to nearly identical pressures. If a pressure imbalance exceeding the balancing line static head pressure, gas mixing leading to a deflagration in a G/L separator is likely. However, many alkaline commercial systems have been deployed and have successfully managed the risk of a pressure imbalance through use of level and pressure process controls and gas mixture alarms. To my knowledge, shutdown of many alkaline systems requires a backup power source to help manage a controlled depressurization of the G/L separators to avoid reverse flow and gas mixing.

Many solid electrolyte cell systems such as PEM do not require the liquid balancing line and can shut down safely without a power backup, by virtue of the pressure differential capability of most solid electrolytes. Most PEM systems do use process controls to recover protonically pumped excess water from the H2 G/L separator back to the O2 anode circulation loop. In the event of multiple control failures, this too can devolve into a H2 in O2 hazard.

21. Any experience yet with large scale electrolyzers powered by fluctuating wind and solar power and the safety aspects related to that?

As an example, look at the QualyGridS project (FCH-02-1-2016) published in 2020, funded from the Fuel Cells and Hydrogen 2 Joint Undertaking. Several sub-MW systems were tested to grid renewable energy protocols. This work is now in process to be further developed as a testing protocol ISO TR 22734-2 in concert with electrolyzer safety standard ISO 22734.

22. What is normally done with the condensate from an H2 dryer to avoid accumulation and an accident, as in the example you mentioned?

It is common practice in larger systems to connect hydrogen dryer condensate drains to dedicated separator hydrogen vent and drain systems designed to safely vent hydrogen released from the condensate and to allow condensate to settle and degas fully. Interconnection with drain systems not designed to handle H2 venting must be avoided.

The example cited is for a 150kW enclosed electrolyzer certified to ISO22734. The internal classification of the fully enclosed electrolyzer process section is reduced to Zone 2 negligible extent by virtue of continuous forced fresh air dilution with active monitoring. Operating at 30 bar, the H2 pressure swing dryer condensate quantity is quite small. The condensate, saturated with H2 at near ambient pressure periodically drains from a float drain trap into an open sump at the base of the air-ventilated electrolyzer enclosure, where the water evaporates and the small amount of hydrogen from the water is diluted by the enclosure air ventilation to well below the lower flammability limit. Should the drain trap fail open, the worst consequence would be release and detection of H2 into an air ventilated enclosure with active ventilation and H2 monitoring alarms, which would halt the process. The installer failed to consult with the manufacturer to understand this design, and to modify the approved design by piping the condensate outside to a facility drain not designed for hydrogen.

23. What do you think about IoT, blockchain, AI, and such new technologies in control and safety systems? Do you have any experience with that?

I usually recommend the use of local safety integrated systems rated SIL-2, with any remote operator controls configured to be overridden by local controls. Additionally, for installations I have managed I insisted that service technicians possess the means to lock out any remote controls so as to prevent inadvertent activation of equipment while personnel are working.

24. Where is the H2/O2 mixture usually measured? Is it possible to detect the H2/O2 mixture dynamically?

When I have sampled at the gas/liquid separator inlet, I have witnessed effective H2 in O2 concentration detection at >0.1% H2 in O2. In at least one production product, I have seen H2 in O2 dynamic trend analysis to be quite effective as an indicator of ion exchange membrane pinhole leak progression and impending failure, but also as a built-in test for the sensor itself as it trends in concert with the expected process conditions.

25. Is there any legislation/regulation in US which is specific for safety in H2 production?

I would look to the adopted building code of most states that have adopted a version of the International Fire Code (IFC), which in turn cites NFPA 2 Hydrogen Technologies Code and NFPA 55 Compressed Gases Code. Look at NFPA 2 Chapter 13 for electrolyzers and Chapters 4-7 for downstream storage or use of hydrogen. Most states have adopted NFPA 2 directly or through adoption of the IFC.

26. Is there any way I can be automatically notified about an electrolyzer incident? A mailing list or similar?

As of now I must manually monitor industry reports and incident data bases such as the free access H2Tools/lessons learned, which reports without specific attribution. The HIAD 2.0 free access tool is not active as of this writing; HELLEN is accessed by European Hydrogen Safety Panel (EHSP) membership. Both data bases rely on industry to freely report incidents, so often this impedes timely reporting.

27. What is the safe and recommended way to dispose unneeded oxygen gas produced in MW size plant?

I recommend a dedicated oxygen vent stack installed with the aid of a safety design guide like EIGA IGC Document 154/09/E, Safe Location of Oxygen and Inert Gas Vents, and a separate independent gas dispersion analysis by expert third parties.

28. What's the difference between fail safe electrolyzers and the one needing active purging after shutdown?

First, ‘fail-safe’ is an unquantified term – what is ‘safe’? Every system has a finite number of sequential failures that it can withstand before the hazard risk becomes unacceptable to manufacturers and end users. The electrolyzer safety standard ISO 22734 section 4.2 requires a water electrolyzer to be designed, at a minimum, to address single faults that present a hazard or unacceptable risk. ISO22734 requires that manufacturers perform a risk assessment that demonstrates the risk of each expert-identified hazard is reduced to an acceptable level.

As an example, some electrolyzer designs, such as certain PEM electrolyzers certified to ISO22734, can withstand a forced outage of control power – one can ‘pull the plug’ and expect the system to depressurize and shut down with very low risk of an incident.

By contrast, certain alkaline liquid electrolyte systems that operating at balanced O2-H2 pressure require active depressurization control to prevent a pressure imbalance that could result in H2-O2 mixing through cell separators or through the pressure balancing leg commonly connecting the H2/electrolyte and O2/electrolyte separators. In this alkaline electrolyzer case, risk of forced power control power outage escalating into a H2-O2 mixture event may be reduced by including a battery backup power system. There are many alkaline electrolyzers that operate and shut down with minimal risk in this fashion. Purging the alkaline system volumes using a non-reactive gas source to dilute and remove H2 and O2 may be another means to reduce risk of recombination if done in a controlled manner to minimize risk.

29. How is the hydrogen peroxide mechanism controlled best?

Aggressive operating conditions such as elevated temperature, pressure, and current density can accelerate PEM degradation. This degradation is due in part to peroxide radical formation within the membrane when H2 and O2 can interact. The peroxide radicals attack and breakdown the fluorocarbon backbone in perfluorosulfonic acid membranes. Several PEM manufacturers for fuel cells and electrolyzers introduce additives into their membrane ionomer formulations or imbibing additives into the formed polymer membrane during processing to actively break down peroxide radicals. A review of relevant research literature will inform as to several methods that have been implemented with some success.

30. Is there any guidance available for emergency responders that have to deal with incidents at large scale electrolyzer plants?

Project managers and operators of large-scale hydrogen facilities have a responsibility to inform emergency responders of the hazardous aspects of their facilities, with particular emphasis on approach, personnel evacuation to safe areas, and access to emergency shutoffs. Three key hazards are combustible atmospheres due to an unexpected hydrogen release, medium voltage electrical equipment, and pressurized flammable gas storage containers. While water deluge is a common technique used to reduce risk of hydrogen storage fire escalation, emergency responders must also take note that electrolysis equipment is electrically energized and should likely be de-energized prior to subjected to water deluge.

I encourage first responders to push on new project developers early in the process to establish periodic training for emergency responders. In my own experience as a fueling station and hydrogen generation facility manager, I conducted yearly walk-through events for all shifts of my local emergency responders and provided simple one page safety orientation documents to incident commanders at the walk-through events and at the entry to my facility.

In many cases, industrial gas companies are participants in the project and can provide relevant emergency response training related to any on-site hydrogen and oxygen storage or transport.

In the USA, hydrogen safety organizations have been focusing on H2 fueling and transport applications. Even so, the following training is relevant to hydrogen emergency response:

https://www.aiche.org/academy/courses/ela253/introduction-hydrogen-safety-first-responders

31. It is said that flames from hydrogen fires are not visible, is there any development to make them visible?

Use of infrared detectors in combination with combustible gas detectors is the preferred method by emergency responders. Hydrogen production and dispensing facilities are now using triple IR (IR3) detectors with low incidence of false readings.

Hydrogen burning in air has a barely visible blue light, which is more visible after dark. Often, atmospheric dust and involved combustible materials will impart color to the flame. Hydrogen flame has low radiant heat, but atmospheric heat distortion may clearly be seen in daylight.