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## **Minutes of the FCH 2 JU Workshop on Safety of Electrolysis on 18 November 2020**

On 18 November 2020 from 14:00 to 17:30 (CET) an online workshop on “Safety of Electrolysis” was organized by the FCH 2 JU with the support of the European Safety Panel EHSP. The workshop is part of the support, the EHSP is providing to the FCH 2 JU at both, the project and the program level.

The workshop focused on the safety aspects of electrolysis technology and had three main objectives:

- 1- To summarize the state-of-the-art and standardization with regards to electrolyser safety;
- 2- To review the available experience with regard to safe design and operations, and the lessons learned from past accident; and
- 3- To exchange experiences and best practices related to hydrogen safety beyond project boundaries.

All FCH 2 JU projects involving electrolysers participated, 9 of them presented project specific approaches and experience with regard to safety planning, regulation codes and standards, risk assessment and incidences specifically related to electrolysis. In total more than 85 participants were connected online.

After a welcome by the chairperson Alberto Garcia FCH 2 JU PO, Bart Biebuyck made an introduction of the FCH 2 JU. He underlined the importance of this workshop having in view the scale-up of installed power per unit and in total, accompanied by the fact that there are new designs and new players in the field. The importance is also reflected by the fact that safety of electrolysis is considered a priority at IPHE level.

The introduction was concluded with Inaki Azkarate presenting the EHSP, its function, activities and services at project and program level of the FCH 2 JU. He briefly introduced the involved technology and the challenges associated with cost reduction and efficiency increase.

### **SESSION 1. Safety-related events and lessons learnt**

The first session consisted of two presentations. In the first presentation Pietro Moretto, JRC, highlighted the findings, lessons learnt, and recommendations from accident databases. In search of lessons learned from past accidents related to electrolysis processes, two hydrogen-specific databases were consulted: HIAD 2.0 and H2TOOLS. Table 1 in the appendix below lists all the cases found for chlorine electrolysis and Table 2 the electrolysis cases dedicated to hydrogen production (other accidents which occurred in electrolysis plants, not involving the electrolysis units, are excluded).

In the majority of the cases, accidents occurred in chlorine production by electrolysis, where hydrogen actually is a by-product. A typical cause of fires and explosion in this alkaline chlorine electrolysis is the

accidental creation and ignition of flammable gaseous mixtures (hydrogen-chlorine, hydrogen-air/oxygen) in the electrolyser cells, in the hydrogen handling system and at flare. The management of the various chemical flows (gases, liquids) to and from of the electrochemical cells, as well as the phase separation is a clear challenge in these plants, which are characterized by a limited level of automation. Due in particular to the needs of materials recirculation, it can happen that a failure on an auxiliary system, such as a recirculation pump, can produce flammable mixtures back in the electrolytic cells. Cell short circuit can be also an initiating event. Often these events occurred during maintenance or repair works or after tripping of components (e.g. compressors, pumps). This last observation points at a more difficult identification of hazards during non-operative circumstances, with the involvement of contractors<sup>1</sup>.

Fewer accidents in the databases affect electrolysis dedicated to hydrogen production. Their number is too small to deduce general trends and lesson learned. Two accidents occurred in a research laboratory. They could be studied in detail, shedding light on cell degradation phenomena of PEM electrolyser cells. This is typically a two-step process involving firstly the local perforation of the solid polymer electrolyte followed by the catalytic recombination of hydrogen and oxygen stored in the electrolysis compartments, which can bring to the destruction of the stack and the connections. A similar mechanism of internal breakdown of an alkaline electrolysis cell stack is considered the cause of the Laport, UK, accident in 1974. Excessive oxygen production and leaking into the hydrogen stream was the cause of an accident on a high-pressure electrolyser in Japan in 2005. In the recent accident (2019) with the alkaline electrolyser in Gangneung, Korea, the introduction of hydrogen into the oxygen stream was not caused by membrane perforation, but gases cross-over under low power operating conditions. Accidental creation of ignitable hydrogen-oxygen mixtures was also reported for an accident in 1998, however, without any further details.

Stuart Hawksworth, HSE/EHSP Task Force 2, presented some more details of the accidents with alkaline electrolysis in Laport and Gangneung in the second part of the first session. The huge cross-over at the low power operations of the Korean case was not detected and the usually installed catalytic oxygen removal ("deoxo") system was omitted. Thus, an explosive mixture of hydrogen and oxygen formed in the hydrogen storage containers and ignited by an unknown source (fast closing valve or strong acoustic shocks could ignite hydrogen-oxygen mixtures at elevated pressure). A possible conclusion from the Korean accident is the need for a more realistic testing at partial/low load cycles and stricter requirements for oxygen detection, possibly to be addressed in a revision of the related standard ISO 22734.

### **Key discussion outcomes**

Key take-aways from the Q&A session, chaired by Jennifer Wen, WARWICK / EHSP Task Force 3, are the following. Most of the few cases in HIAD are dealing with chlorine electrolysis and hydrogen as a by-product. However, it was suggested to use the broad experience in this field and to reach out to the respective community organized in Euro Chlor<sup>2</sup>.

Besides the gap with respect to testing electrolysers at partial or low load - what, by the way, was also emphasized at the ISO TC 197 plenary meeting in Grenoble, France, in 2019 - also particular normative elements for high temperature electrolysis are missing.

Pietro Moretto reminded about the reporting obligations of the projects and suggested to extend the reporting scope to near misses, incidents and no events. Off-normal conditions and near misses are important pre-cursors of accidents and deserve special attention. For discrimination of near misses, incidents and accidents and suitable definitions the EIGA document INCIDENT/ACCIDENT

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<sup>1</sup> For an overview of typical accidents related to chlorine production plants, see: A. Pennel, Hazards in the electrolysis of brine in mercury cells, 2nd Symposium in Chemical Process Hazard with Special Reference to Plant Design ; Manchester, 2-4 April, 1963, Available at <https://www.icheme.org/media/10627/ii-paper-06.pdf>

<sup>2</sup> Hydrogen in Chlorine Safety GEST 17/490, 1st Edition, June 2019 available via <https://www.eurochlor.org/>

INVESTIGATION AND ANALYSIS SAC Doc 90/13/E<sup>3</sup> was recommended by Thomas Jordan, KIT / EHSP Task Force 1.

The reporting and discussion about terminology induced a further discussion about using accident statistics or rather the “no severe accident” indication as a key performance indicator for the FCH 2 JU and follow-up program. It was commented that such probabilistic measures are difficult to quantify and to communicate. Considerations to include such a KPI, like  $< 10^{-5}$  severe accidents per project year were discarded for these reasons.

## **SESSION 2. Hazards Identification for electrolysis**

The second session was focusing on hazards and vulnerability identification processes, which usually are the initial steps of risk assessments. The set of prototypical hazards, prototypical risk assessment procedures and acceptance criteria were presented by Pratap Sathiah, SHELL / EHSP Task Force 1. The projects HYBALANCE, GRINHY, H2ME and PRETZEL, all characterized by smaller installations or more innovative concepts, presented their approaches. The presentations were not only addressing the hazard identification steps, rather described the whole risk assessment processes chosen.

### ***Key discussion outcomes***

All projects showed multi-tier approaches consisting of a HAZID, HAZOP, CHECKLIST and more quantitative risk assessment procedures. ATEX zoning is a generally required element in the safety concepts for the typically container-based solutions. One of the critical parts is the integration, the interfaces respectively, of the component or subsystem suppliers. In some cases there are inconsistent views and approaches with respect to safety among system integrators and the operators. More harmonized guidance could help.

The hazards generally addressed are small leaks via imperfect sealing, impurities and cross-over, in particular of oxygen into the hydrogen product and accumulations of flammable inventory in the phase separators, fire, thermal stresses in particular for the high temperature electrolysis.

Corrosivity of the electrolytes and failure of a membrane or separator, possibly induced by freezing water, were considered root causes for the strong oxygen ingress and potential oxygen accumulation on the hydrogen side.

Dealing with high pressure oxygen as a by-product seems to be a quite open issue. Volatility of the electric power was not mentioned explicitly as a hazard.

With respect to mitigation there are open issues regarding hydrogen and fire sensor qualification, active and passive ventilation strategies complying with the special properties of hydrogen and the need for more passive strategies, like bunkering of the electrolyser including purification stages. The latter was motivated by postulating a detonation in a phase separator as credible worst case scenario with subsequent fragmentation and missile formation.

Welded connections seem to offer a pathway to reduce requirements from ATEX zoning, whereas this seems to be an approach only generally accepted in Germany. Additionally the way for joining pipework may depend on the dimensions and loads on the connections. For higher temperatures encountered in high temperature electrolysis obviously welded connections are preferred.

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<sup>3</sup><https://www.eiga.eu/infromx.php?eID=dumpFile&t=f&f=2505&token=56fbc86f6968368d025ed9c0762147a19c9787a1#:~:text=Near%2Dmiss%3A%20An%20unintenfromd%20incident,machinery%2C%20damage%20to%20the%20environment>

From the presentation and the discussion the following list of hazards is derived:

- High voltage, electrical short circuits or discharges
- Corrosion caused by acidic/caustic electrolyte and electrochemistry
- Freezing of the cooling water in the stack
- Fracture of a pressurized pipe, compartment
- Excessive thermal stresses causing material degradation
- Hydrogen leakage from the stack
- Cross-over of oxygen into hydrogen and vice versa
- Break of membrane of bipolar plates
- Accumulation of explosive hydrogen/oxygen mixtures in the phase separator or in the gas storage

### **SESSION 3. Safety-related framework in electrolysis**

The third and last session was shifting the focus to risk assessment and regulations, codes and standards (RCS). The chairperson of the FCH 2 JU regulations codes and standards strategy coordination group RCS SCG Nick Hart, ITM, was providing a concise and complete overview on applicable, electrolysis specific RCS.

Besides the list provided in the text box below, there might be other national, application specific requirements, as for refuelling stations, which rather have the characteristics of an industry code or a code of practice. Authorities might refer to these and make them compulsory thus.

#### **List of RCS relevant to Electrolysis**

##### **Regulations (compulsory):**

*CE marking Directives (equivalent national Regulations), for example:*

- The Pressure Equipment Directive, European Directive 2014/68/EU (PED);
- The Machinery Directive, European Directive 2006/42/EC;
- The Low Voltage Directive, European Directive 2014/35/EU;
- The Electromagnetic Compatibility Directive, European Directive 2014/30/EU.
- Elements of the „ATEX Equipment Directive“, European Directive 2014/34/EU

*Others (national implementation of European Directives), for example:*

- Seveso (Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances)
- IED (Directive 2010/75/EU on industrial emissions (integrated pollution prevention and control))
- ATEX “Workplace” Directive (Directive 1999/92/EC on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres)

*National regulations (general) – examples:*

- Safety of pressure systems
- Safety of machinery
- Fire safety

##### **Standards (nominally voluntary):**

- **ISO 22734 – Hydrogen generators using water electrolysis** — Industrial, commercial, and residential applications
- Quality standards (ISO 14687, ISO 19880-8, EN 17124)
- Others (e.g. for grid injection)

The projects DJEWELS, REFHYNE, H2FUTURE, DEMO4GRID and MULTIPLHY, all characterized by large scale installations showed their safety approaches.

### ***Key discussion outcomes***

The Q&A session, chaired by Thomas Jordan, yielded following results.

All projects were using structured, multi-tier approaches for safety assessments. As regulation, like SEVESO directive, generally is not specific enough, some projects were relying on internal codes. So, guidance for proper application of generic regulation is missing. Similarly, even the more specific standards like the ISO 22734 are not addressing new technologies, like high temperature electrolysis HTEL. An update of this standard driven by the concerned industry is suggested. On the other hand, some work for reversible technology is ongoing at the IEC TC105, at least.

In some cases the different national implementations of European directives, like ATEX for instance, generated inconsistencies for the requirements on the side of the technology supplier and on the side of the operator.

Besides similar issues like in the discussion of Session 2 were addressed.

### **Closing Remarks**

Electrolysis has its specific hazards, but with its limited inventory, also the associated risks are small compared to high pressure storage or mechanical compression, for instance.

All projects have shown structured approaches for safety planning and management. Several open issues with respect to mitigation concepts, from passive measures to sensors, and with respect to sufficient guidance in RCS - in particular for innovative solutions - have been identified. Standardisation for testing partial load operations and high temperature electrolysis is recommended.

The confirmation of not having experienced any major incident nor accident might be considered as a success of the FCH JU program executed so far. However, a more pro-active attitude towards broader communication, including reporting near misses and off-normal conditions might help improving further and preventing major accidents reliably, also in the future.

*Table 1 - Overview of the recorded past accidents related to **chlorine electrolysis** (only events involving electrochemical systems are shown, others affecting only ancillary hydrogen systems, such as hydrogen compressor failures, are not shown)*

| Year | Source                 | Causes/Components affected                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | Fatalities<br><br>Injuries | Root causes / corrective actions / lesson learned                                                                                                                                                                                                                                                                                                                                                                                                                                         |
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| 1969 | H2-TOOL S <sup>4</sup> | <p>Explosion in a potassium hydroxide electrolyser</p> <p>Sludge deposits in the electrolyte passages started the following sequence of events, culminating in the explosion.</p> <p>Reduced electrolyte flow rates caused by sludge blockage resulted in increased cell temperatures and electrolyte concentrations. The increased electrolyte concentrations and linear velocities (due to obstructed passages) eventually led to severe corrosion/erosion damage of the cell electrodes and separators (hydrogen embrittlement may have also been a contributing factor). Physical breakdown of the cell separators allowed hydrogen and oxygen to mix and hydrogen to enter the oxygen separator drum. The gas mixture was ignited causing a violent explosion which ruptured the separator drum. A plant operator in the electrolysis room at the time of the explosion was fatally burned by the caustic solution sprayed from the ruptured drum.</p> | F = 1<br><br>I = 0         | The investigative report noted that the explosion could have been prevented by (among other things) a continuous gas analyzer test of oxygen and hydrogen product purity. The continuous analyzer should be interlocked to shut the electrolyzer down when product purity falls below some nominally critical values. This incident, illustrates the need for more widespread use of hydrogen analyzers, and the inverse relationship between hydrogen accidents and regular maintenance. |
| 1977 | HIAD #777              | <p>Explosion at the chlorine drying towers (mercury-based electrolysis)</p> <p>The mercury pumps stopped due to an electrical power system failure and the steel bottom plates in the cells became exposed, while the DC power and brine supply to the cells continued. This caused the generation of hydrogen at the steel plate cathode and oxygen at the anode. The flammable gas mixture passed to the chlorine drying towers and ignited. The three towers, made of PVC, were completely destroyed.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                | F = 1<br><br>I = 12        | <p>The Immediate cause was power failure with consequent stop of the mercury pumps. Moreover, a series of malfunction and non-optimal safety design (including the lack of alarm due to lack of power) contributed to the final event.</p> <p>To minimise ignition probability, the towers should be designed to prevent electrostatic sparks.</p>                                                                                                                                        |

<sup>4</sup> <https://h2tools.org/lessons/water-electrolysis-system-explosion>

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| 1977 | HIAD<br>#237 | <p>Explosion in a diaphragm-based electrolyser</p> <p>The exhaust pipe on the water circuit of the electrolyser was blocked due to the deterioration of the anticorrosion coating. Hydrogen permeated through the diaphragm and mixed with chlorine.</p>                                                                                                                                                                                                                                                                     | <p>F = 0</p> <p>I = 0</p> |                                                                                                                                                                                                                                                                                                                                                |
| 1985 | HIAD<br>#634 | <p>Explosion in a sodium hydroxide electrolysis unit</p> <p>The event occurred during maintenance operations The explosion occurred at the chlorine cooling tower and the chlorine transfer pipeline. The cause was a leak through the valve on the chlorine pipeline which was supposed to be closed after the air purging. Although fume removing equipment continued to operate, residual hydrogen gas in the cathode cell went into the chlorine pipeline, forming a hydrogen-air explosive gas mixture.</p>             | <p>F = 0</p> <p>I = 0</p> | <p>Not enough data to deduce a specific lesson learned. In general, the leaking of the chlorine system valve could indicate that the operative procedure was not followed correctly, or a valve malfunctioning.</p>                                                                                                                            |
| 1995 | HIAD<br>#99  | <p>Explosion in a mercury-based electrolyser</p> <p>Immediate cause was the breakdown of the hydrogen compressor, probably due to the blocking of the safe hydrogen release system by dirt. The stop of the compressor allowed the hydrogen to reach the cell-space through the mercury pump, reacting with chlorine. This intrusion of hydrogen caused at least locally the formation of an explosive mixture.</p>                                                                                                          | <p>F = 0</p> <p>I = 3</p> | <p>No electrical cause or human causes could be determined. Possible cause can be found in lack of safeguards control and maintenance.</p> <p>The aggregate affected was re-designed, avoiding the deposition of dirt (design change). Further, periodic checks were performed in the future (change in procedure, change in supervision).</p> |
| 1995 | HIAD<br>#253 | <p>Explosion in a mercury-based electrolyser</p> <p>Due to malfunctioning of a circuit breaker, one electrolysis unit continued functioning despite the general shutdown. The explosion occurred when restarting the chlorine recirculation pump.</p> <p>Possible cause for explosion: reaction of hydrogen and chlorine in the chlorine compressor. The formation of hydrogen and of sodium and potassium hypochlorite in the electrolyser cells was due to the absence of mercury to fix the sodium and the potassium.</p> | <p>F = 0</p> <p>I = 0</p> | <p>The corrective actions consisted in installing (a) a system avoiding magnetisation of the circuit breaker, and (b) and additional circuit breaker for the auxiliary systems.</p> <p>More in general, the event reveals a lack of diagnostic tools and automatic safeguards to avoid formation of explosive.</p>                             |

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| 2008 | HIAD<br>#843 | <p>Fire in electrolyser cells</p> <p>A leak of hydrogen in the electrolysis room followed by fire on three electrolysis cells (possibly started with an explosion). Injection of nitrogen the intervention of the firefighters of the site allowed the extinction of the fire</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | <p>F = 0</p> <p>I = 3</p> | The cause of the hydrogen leak is unknown                                                                                                                                                                                        |
| 2010 | HIAD<br>#950 | <p>Hydrogen explosion (mercury-based electrolysis)</p> <p>The explosion occurred when restarting the sodium chlorate production unit after maintenance, during which the mercury cells had remained under nitrogen purging. A hydrogen leak was detected on the nozzle of a cell collector. The nitrogen purging was stopped, to allow maintenance to intervene safely (avoiding anoxia hazards), but the power supply to electrolysis cells was not shut down again, as required by the procedures. The situation passed undetected because the wrong reading of the voltage of the cells (zero reading). Still under power, the cell produced hydrogen and oxygen. When the nitrogen purging was stopped for the repair, the two gases accumulated and mixed beyond the lower ignition limit, causing a large explosion occurred in the electrolysis room.</p> | <p>F = 0</p> <p>I = 2</p> | The causes are a combination of false diagnostics and inadequacy of the procedure, which relied strongly on manual actions.                                                                                                      |
| 2013 | HIAD<br>#935 | <p>Explosion on the hydrogen line of an electrolyser</p> <p>The explosion occurred during cutting a purge pipe on a hydrogen manifold in the chlorine electrolysis room. The explosion was caused by ignition of a hydrogen-air mixture. Probably hydrogen was still present despite the previous purging with nitrogen, due to uncompleted purging procedure and/or hydrogen desorption from the steel of the manifold.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                     | <p>F = 0</p> <p>I = 1</p> | The procedure for the purging of the hydrogen system was inadequate. Moreover, the working permit for the subcontractor executing the cutting was incomplete, because did not identified correctly risks and intervention areas. |

Table 2 - Overview of the recorded past accidents related to water electrolysis

| Year       | Source    | Causes/Components affected                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Fatalities<br>injuries | Root causes / corrective actions / lesson learned                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
|------------|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1975<br>UK | HIAD #778 | <p>The explosion was in an alkaline electrolysis plant.</p> <p>The electrolysis plant produced hydrogen for process use and oxygen as a waste product by electrolysis of potassium hydroxide solution. The explosion probably occurred on the oxygen separating drum into which hydrogen had leaked, apparently due to corrosion/erosion in the electrolysis cells. The internal breakdown of the cells had probably been initiated some time before the accident. The plant suffered extensive damage and one man who was injured subsequently died.</p> <p>There was a system of monitoring the purity of the hydrogen and oxygen streams by hourly gas analyses but apparently the analyses were not always carried out and that assumed values were entered in the process log.</p> <p>On the basis of the explosion damage, the 1690 l oxygen drum contained a 13.5% hydrogen and the explosion produced a shock wave equivalent to 22 kg of TNT.</p> | F = 1<br>I = 0         | <p>The main conclusion was that the principles of the legislation which regulates the thorough examination of steam boilers should be extended to pressure systems of this type.</p> <p>The following precautions should be taken in the operation of this type of plant:</p> <ol style="list-style-type: none"> <li>1. Both gas streams must be monitored by intrinsically safe continuous analysers inter-linked visual and audible alarms when oxygen purity falls to 98.8% or hydrogen purity to 99.7%. Plant should shut down oxygen purity falls to 98% or hydrogen purity to 99.5%.</li> <li>2. The continuous monitoring should be backed up by hourly manual gas analyses carried out by the expert operators, and these in turn should be checked by a similar analysis by laboratory. Clear instructions are needed.</li> <li>3. The internal condition of the plant should be systematically monitored: for example sludge formation, cell voltages and temperatures, gas /electrolyte temperature.</li> </ol> |

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| 1998          | HIAD #243                          | <p>Hydrogen-oxygen explosion</p> <p>An explosion occurred in the oxygen gas storage tank of the electrolysis plant, due to the entry of hydrogen into the oxygen system.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | <p>F = 0</p> <p>I = 0</p> | The cause for the hydrogen entrance into the oxygen system are unknown.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |
| 2005<br>Japan | Scientific Literature <sup>5</sup> | <p>An explosion occurred during the operation of a high-pressure hydrogen water electrolyser unit within a university campus (40 MPa, 30 Nm<sup>3</sup>/h). The electrolysis cell burned down, pipes burst and the peripheral equipment scattered all over the facilities.</p> <p>The titanium electrode in the electrolysis cell of the HHEG and/or hydrogen were burned, then water containing hydrogen flowed to the oxygen pipe.</p> <p>Two years before an explosion had already occurred on the site, in an older version of the electrolyser. Hydrogen had flowed into the oxygen separation tank because the water level had decreased between the tank and the electrolytic cells. As corrective measure, the holding water volume in new version of the electrolyser was increased. The new unit had started few days before the new accident.</p> | <p>F = 0</p> <p>I = 0</p> | <p>The initiating cause was the exposure of the Ti electrode to oxygen at high pressure and temperature. O<sub>2</sub> then leaked into the H<sub>2</sub> stream. A detailed analysis is given in the source. In brief, the domino effect was characterised by a self-sustained reaction in the electrolyser cells first, then in the gas and liquid pipes and storage tanks, even after the shutdown of the electrolyser. The reactions caused over-pressurisation of the components and their eventual burst.</p> <p>Among the Lesson learned given by the source are:</p> <p>Risk assessment should be done to identify required safety measures, even if the operation is under testing or operated temporarily.</p> <p>Pressure waves in a pipe may cause a pressure peak above the design strength of the pipe.</p> <p>All institutes, including university, should organize the safety management system, even if they do only test or temporary operations.</p> |

<sup>5</sup> Y. Wada et al., Relational information system for chemical accidents database with analysis of hydrogen accidents, International Conference on Hydrogen Safety ICHS, San Sebastian (Spain), September 11-13, 2007, [http://conference.ing.unipi.it/ichs2007/fileadmin/user\\_upload/PAP\\_ICHS07-Wada.pdf](http://conference.ing.unipi.it/ichs2007/fileadmin/user_upload/PAP_ICHS07-Wada.pdf)

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| 2009<br>Space | H2TOOLS <sup>6</sup>               | <p>Near miss on the oxygen generator on the International Space Station (ISS)</p> <p>The differential pressure across a pump supplying return water to a PEM electrolyser cell stack had increased and reached the shut-off limit. The reason was probably caused by water-borne catalyst particles accidentally released from the electrolytic cells and accumulated within the pump's inlet filter.</p> <p>The system had been designed for factory maintenance, and no contingency had been planned to handle field maintenance for such a circumstance. It has not been possible to execute an in-situ maintenance, because the risk of exposing to air the particles, consisting probably of platinum black and Teflon binder materials was deemed too high.</p>                                                            | <p>F = 0</p> <p>I = 0</p> | <p>The provision of oxygen was guaranteed by another oxygen generator. Nevertheless, the event showed that the risk assessment related to the operation of the PEM electrolyzers was incomplete.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                            |
| 2012          | Scientific Literature <sup>7</sup> | <p>Membrane perforation in PEM FC cell</p> <p>A PEM FC short stack was tested in a R&amp;I laboratory at elevated (1.8 A/cm<sup>2</sup>) current density.</p> <p>A failure was detected automatically by the continuous monitoring of individual cell voltage. Which suddenly fell below a threshold value of 1.5 V, suggesting the onset of an electrical short-circuit. A sharp increase of hydrogen in the oxygen production was also detected and the power supply was shut-down immediately to prevent the destruction of the stack.</p> <p>The cause was the perforation of a membrane. The hole was found in the upper area of the MEA, close to the exhaust pipe, and the membrane was significantly put out of shape. The chemical analysis of the white deposit observed in the vicinity of the hole revealed that</p> | <p>F = 0</p> <p>I = 0</p> | <p>Different membrane failure causes were considered, from local phenomena such as mechanical stresses, current hot spot and local drying of the membrane, to membrane thinning or formation of flammable H<sub>2</sub>-O<sub>2</sub> in one cell due to cross-permeation.</p> <p>The author did not find clear evidence pointing at one of these degradation phenomena.</p> <p>Independently from the initial cause of the membrane perforation, the investigators pointed at the possibility of a run-away reaction. The perforation of a membrane leads to an easily detected cell short-circuit. However, a hole does not cause immediate short-cutting</p> |

<sup>6</sup> <https://h2tools.org/lessons/potential-catalyst-fire-hazard-oxygen-generator-filter-change-out-maintenance>

<sup>7</sup> P. Millet et al., Cell failure mechanisms in PEM water electrolyzers, Int. Journal of Hydrogen Energy, 37 (2012) 1747-7487, <http://dx.doi.org/10.1016/j.ijhydene.2012.06.017>

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|  |  | <p>it mainly contained PTFE, suggesting the onset of a kind of local melting. . The bipolar plates were not perforated.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  | <p>of the current collectors. Even when the membrane is perforated, the unaltered surface can still play its role of cell separator. Therefore it will be difficult to timely detect these cases.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|  |  | <p>Destruction of a PEM FC short stack</p> <p>In the same R&amp;I laboratory, another test at high current density (1.8 A/cm<sup>2</sup>) induced a much bigger damage.</p> <p>The automaton used to monitor the system detected a failure situation in a sudden decrease of current and shut down the power supply. But it too late to avoid the destruction of the stack. The combustion of non-metallic cell components (MEAs and cell sealants) was total, leading to the formation of carbon deposits over the titanium bipolar plates. The electrolysis stack was destroyed by combustion within a few seconds.</p> <p>The combustion was not limited to the stack only, metallic elbow connectors were neatly perforate, indicating that a H<sub>2</sub>/O<sub>2</sub> combustion flame started in one cell and propagated to the whole stack and along the tubing section up to the first elbows, acting as a H<sub>2</sub>/O<sub>2</sub> torch flame. The lack of deformation indicated also that an explosion did not take place.</p> |  | <p>The author assessed the combustion energy available in the stack concluded that there is enough energy in an atmospheric pressure stack to destroy it.</p> <p>They pointed out the following preventive measures for high-current density operation of PEM electrolyzers (&gt;1.0 A cm<sup>2</sup>):</p> <p>(1) Circular cell geometry is preferred to rectangular geometry to avoid the risk of formation of gaseous atmospheres in the upper part, close to the cell outlet.</p> <p>(2) It is necessary to measure the charge density for each cell before operation checking risk of uneven distribution of current lines.</p> <p>(3) The electrolyser should operate at constant cell voltage and not constant current density. If for any reason the impedance of any cell increases, then the current dissipated in the stack will decrease.</p> <p>(5) It is desirable to monitor individual cell voltages : an increase in cell voltage can be related to inappropriate water distribution in the anodic compartment and a decrease in cell voltage can be due to a cell short-circuit and the formation of a hole in theme</p> |

|               |           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
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|               |           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                           | (6) Obviously continuous monitoring of the hydrogen content in oxygen and of the oxygen content in hydrogen is almost a must.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
| 2019<br>Korea | HIAD #970 | <p>Hydrogen explosion at renewable hydrogen production facility</p> <p>The hydrogen buffer tanks that exploded were part of an experimental facility experimenting generation of renewable hydrogen from a water electrolyser coupled to solar panels.</p> <p>The three hydrogen tanks (40 m3 capacity each at pressures of 1,2 MPa one of them and 0,7 MPa the two others) were receiving the hydrogen produced by the electrolyser. The 200 kW alkaline electrolyser had a capacity of 40 Nm3/hr and delivered hydrogen at 1.2 MPa.</p> <p>The most plausible initiating cause was the defective functioning of the electrolyser's membrane, at lower power, which caused oxygen diffusing into the hydrogen stream.</p> | <p>F = 3</p> <p>I = 6</p> | <p>The accident is still being investigated and no final report about the causes is yet available. According to a preliminary technical analysis, the plant showed design deficiency (lack of preventing and mitigating measures) and was operated at out-of-specification conditions.</p> <p>These shortcomings need to be corrected, for example by providing:</p> <p>(1) in-situ diagnostic system able to trigger emergency stops of the hydrogen production system and</p> <p>(2) automatic isolation of the storage tanks.</p> <p>If the initiating cause is confirmed, the following corrective actions are required to fill a global knowledge gap:</p> <p>(3) better understand the relationship between the gas permeability of the electrolyser membrane and dynamic operation range caused by the variability of renewable power sources (solar);</p> <p>(4) Improvement of standardised performance and safety tests, aiming at defining a more realistic testing requirements and conditions at partial/low load cycles (ISO 22734:2019 ""Hydrogen generators using water electrolysis").</p> |