# Metrology for sustainable hydrogen energy applications

## *EMPIR Grant Agreement number: 15NRM03 Hydrogen*

## Project short name: HYDROGEN

# WP1: Hydrogen purity measurements according to ISO 14687-2 and risk assessment for fuel cells

## Task 1.3: Risk Assessment

## Deliverable D1 (Report)

# Report on risk assessment of impurities in hydrogen for fuel cells and recommendations on maximum concentration of individual compounds based on the new fuel cell degradation studies and on the probability of presence

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# Summary

Monitoring hydrogen quality according to ISO 14687 is a challenge considering the increasing number of hydrogen refuelling stations and the strong requirement to reduce hydrogen cost. New methodology and guidelines were introduced recently in order to streamline hydrogen quality control as part of the revision of ISO 14687 and as part of the development of new standards (EN 17124, ISO 19880-8). The project 15NRM03 provided a support to them. The methodology of quality risk assessment is used to evaluate the probability of occurrence of each impurity to be above the threshold value given in the ISO 14687-2.

The report aimed at investigating the probability of presence of hydrogen contaminants from the main production processes: steam methane reforming with pressure swing adsorption, proton exchange membrane water electrolysis with temperature swing adsorption and chlor-alkali (membrane electrolysis).

- Chlor-alkali process critical impurities identified are: $O_2$ and $N_2$. Others are possible but with lower probability of occurrence: $CO_2$ and water.

- PEM WE + TSA process critical contaminants identified is $H_2O$. Others are possible but with lower probability of occurrence: $O_2$, $N_2$.

- SMR + PSA process critical impurities identified are: CO and $N_2$. Others are possible but with lower probability of occurrence: methane, argon and formaldehyde.

In order to provide evidence on contaminant presence from production processes, a campaign of sampling and analysis of various SMR with PSA and PEM water electrolyser with TSA was performed by national metrology institutes (NMIs). The reported analytical results confirmed that in eight different SMR with PSA and eight different PEM water electrolyser with TSA samples, no contaminants were above the threshold of ISO 14687-2. It confirmed the probability of contaminants presence made by the industrial expert for these two processes.

Impact of contaminants on fuel cell system was evaluated based on reversible and irreversible effects especially for three contaminants ($NH_3$, HCl, $C_4Cl_4F_6$). Based on these new studies, it can be concluded that the data for HCl was found to be in good agreement with the existing ISO 14687-2 standard, ammonia can be slightly relaxed from a threshold of 0.1 µmol/mol to 0.2 – 0.5 µmol/mol (high reversibility of the effect). The impact of $C_4Cl_4F_6$ was for the first time studied and appeared to be the most important among the three impurities with threshold proposal of 0.08 µmol/mol. These studies supported further work on contaminant impact at single cells and stack level and future revision of ISO 14687 for ammonia and halogenated compounds. The severity studies presented may be relevant for future revision of ISO 19880-8 especially for the risk assessment methodology

Finally, the report provides the first examples with technical evidences on risk assessment for contaminant presence in hydrogen, new evidences on impact of HCl, $NH_3$ and $C_4Cl_4F_6$ on single cell system. This report will support implementation of ISO 19880-8 and future revision of the standard.

# Table of contents

The expansion of fuel cell electrical vehicles (FCEV) is a crucial step to decarbonise the transport sector (Marbán & Valdés-Solís, 2007). The absence of contaminant in the hydrogen delivered at the hydrogen refuelling station (HRS) is critical to ensure the length life of FCEV (durability > 5000 hours (Caloprisco, 2018). The international standard ISO 14687 defined the maximum amount fraction of each contaminant in hydrogen for FCEV applications (ISO 14687-2, 2012). Therefore hydrogen suppliers and producers need to ensure hydrogen quality defined in ISO 14687 at each hydrogen refuelling station (HRS). Currently the analytical cost (sampling and analysis) to measure all these contaminants on a routine scheme is a barrier for decreasing hydrogen cost which is a prerequisite for the development of mass expansion of hydrogen into transport sector (Carré, 2018). European Directive 2014/94/EU on the deployment of an alternative fuels infrastructure (2014/94/EU, 2014) sets out that "The hydrogen purity dispensed by hydrogen refuelling points shall comply with the technical specifications included in the ISO 14687-2 standard (which will be replaced by the European standard EN 17124 (EN17124, 2018))."

The objective of this report is to demonstrate how hydrogen quality can be ensured according to the two international standards ISO 14687 and ISO 19880-8. The report provides technical evidences for the development of quality control plan according to the methodology of risk assessment defined in ISO 19880-8. Moreover new technical evidences on the impact of three contaminants (HCl, $NH_3$ and $C_4Cl_4F_6$) on fuel cell system are presented to support further evolution and revision of the ISO 14687 standards. These three contaminants are of high interest for quality control and on their threshold values in ISO 14687. It is mainly due to the lack of studies on their impacts and their relevance in new production method.

# 1 Probability of contaminants presence in H2 production processes for fuel cell electrical vehicle

The development and expansion of fuel cell electrical vehicles (FCEV) led to a strong increase in the number of hydrogen refuelling stations. Europe has over 100 HRSs in operation and over 100 under project or implementations (H2stations, 2018). The absence of contaminant in the hydrogen delivered at the hydrogen refuelling station (HRS) is critical to ensure the lifetime FCEV. Therefore the requirements of ISO 14687 need to be met for any production processes delivering hydrogen for HRS. The large number of contaminants to monitor may have a significant cost impact on the final price of hydrogen. Therefore the new ISO standard 19880-8 (ISO/DIS 19880-8, 2017) proposes two approaches in order to define a quality control plan based on the contaminants that can be present in the system and to decrease the frequency of analysis for contaminants that are practically impossible to be present. Two approaches are presented in ISO 19880-8; the prescriptive approach defines the list of contaminants to be monitored with the frequency of analysis based on the feedstock, transport, and infrastructure. This approach is defined in ISO 19880-8 annexes and has to be followed as defined. The other approach is based on risk assessment methodology. The aim is to define for each situation (each refuelling station) the probability of presence of each contaminant in the hydrogen produced. In order to perform the risk assessment, it is mandatory to have expert knowledge of the whole system including the technology and the different barriers and mitigation protocols and procedures in place. The risk assessment approach is then more representative of each refuelling station but it requires performing the evaluation for each of them.

In this report, the study has been limited to the production processes. Therefore only the feedstock was considered and the transport and the hydrogen refuelling station infrastructure were not considered.

The study will describe the methodology and then present the results for the three production processes: steam methane reforming with pressure swing adsorption, proton exchange membrane water electrolysis with temperature swing adsorption and chlor-alkali membrane electrolysis.

## 1.1 Methodology

The two primary principles of quality assurance plan are:

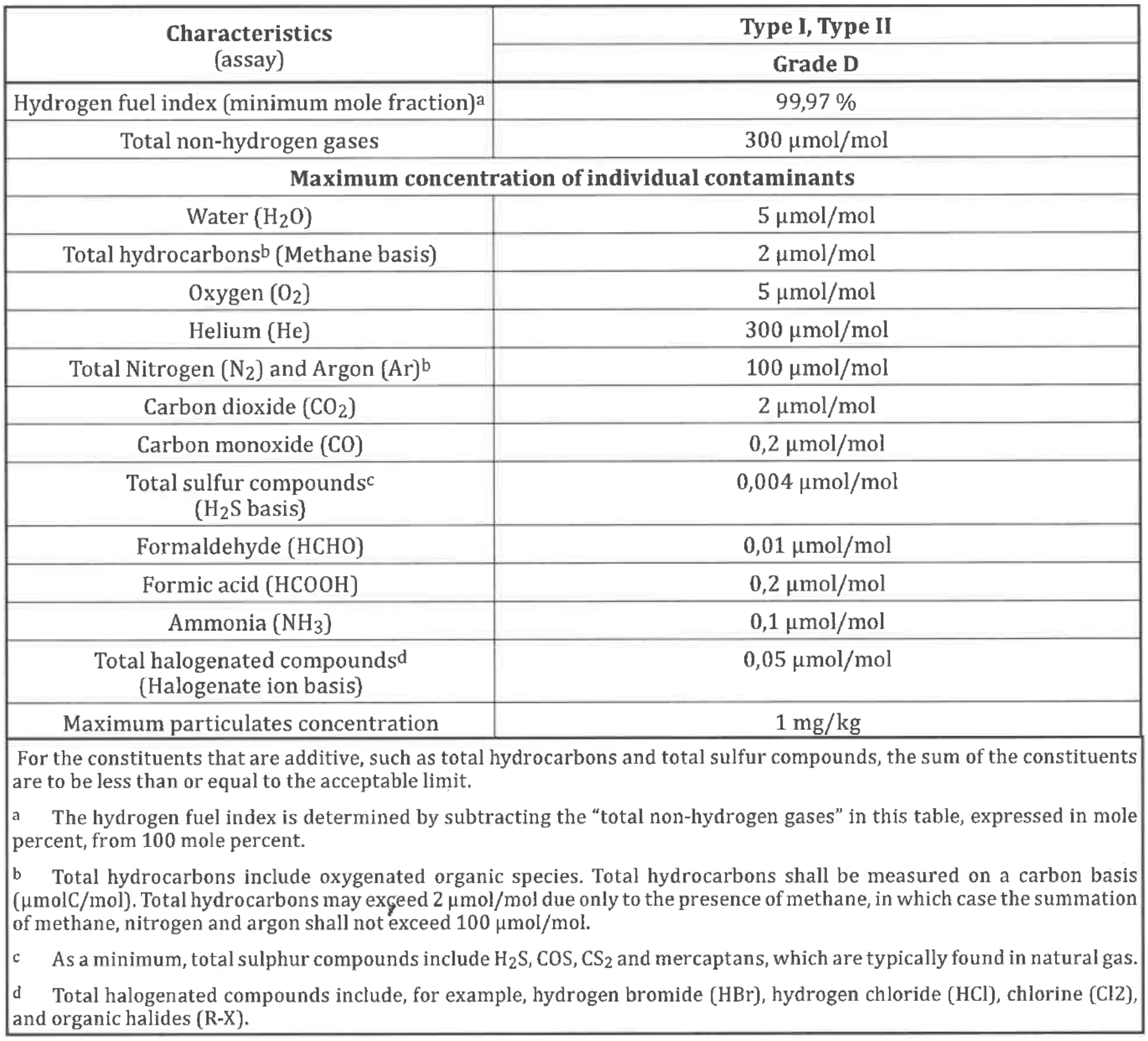
- The evaluation of the risk of non-compliance to quality requirements should be based on scientific knowledge and ultimately link to the protection of the fuel cell car
- The level of effort to implement the quality assurance process should be proportional with the level of risk.

As an aid to clearly defining the risk(s) for risk assessment purposes, three fundamental questions are often helpful:

- What might go wrong: which event can cause the impurities to be above the threshold value?
- What is the likelihood (probability of occurrence expressed relative to the number of refueling events) that impurities can be above the threshold value?
- What are the consequences (severity) for the fuel cell car?

In doing an effective risk assessment, the robustness of the data set is important because it determines the quality of the output. Revealing assumptions and reasonable sources of uncertainty will enhance confidence in this output and/or help identify its limitations. The output of the risk assessment is a qualitative description of a range of risk.

**Table 1. Fuel specification defined in ISO 14687-2:2012**



| **Characteristics** (assay) | **Type I, Type II** |
|---|---|
| | **Grade D** |
| Hydrogen fuel index (minimum mole fraction)[a] | 99,97 % |
| Total non-hydrogen gases | 300 µmol/mol |
| **Maximum concentration of individual contaminants** | |
| Water ($H_2O$) | 5 µmol/mol |
| Total hydrocarbons[b] (Methane basis) | 2 µmol/mol |
| Oxygen ($O_2$) | 5 µmol/mol |
| Helium (He) | 300 µmol/mol |
| Total Nitrogen ($N_2$) and Argon (Ar)[b] | 100 µmol/mol |
| Carbon dioxide ($CO_2$) | 2 µmol/mol |
| Carbon monoxide (CO) | 0,2 µmol/mol |
| Total sulfur compounds[c] ($H_2S$ basis) | 0,004 µmol/mol |
| Formaldehyde (HCHO) | 0,01 µmol/mol |
| Formic acid (HCOOH) | 0,2 µmol/mol |
| Ammonia ($NH_3$) | 0,1 µmol/mol |
| Total halogenated compounds[d] (Halogenate ion basis) | 0,05 µmol/mol |
| Maximum particulates concentration | 1 mg/kg |

For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents are to be less than or equal to the acceptable limit.

[a] The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent, from 100 mole percent.

[b] Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (µmolC/mol). Total hydrocarbons may exceed 2 µmol/mol due only to the presence of methane, in which case the summation of methane, nitrogen and argon shall not exceed 100 µmol/mol.

[c] As a minimum, total sulphur compounds include $H_2S$, COS, $CS_2$ and mercaptans, which are typically found in natural gas.

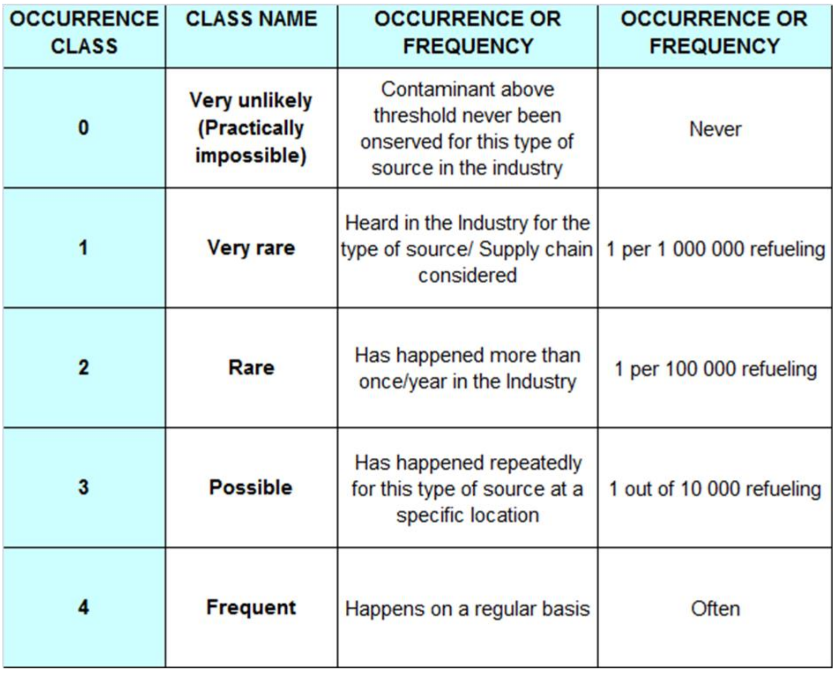
[d] Total halogenated compounds include, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl2), and organic halides (R-X).

For each impurity of the ISO 14687-2 specification and for a given $H_2$ source a risk assessment must be applied to define the global risk for the car user. Risk assessment consists of:

- Identification of the probability of occurrence to have in hydrogen each impurity above the threshold values of specifications given in ISO 14687-2 (see Table 2)
- Evaluation of severity level of each impurity for the fuel cell car (see Table 3)

For the probability of occurrence of the event: impurities in hydrogen exceed the threshold value, the following table of occurrence classes has been defined:

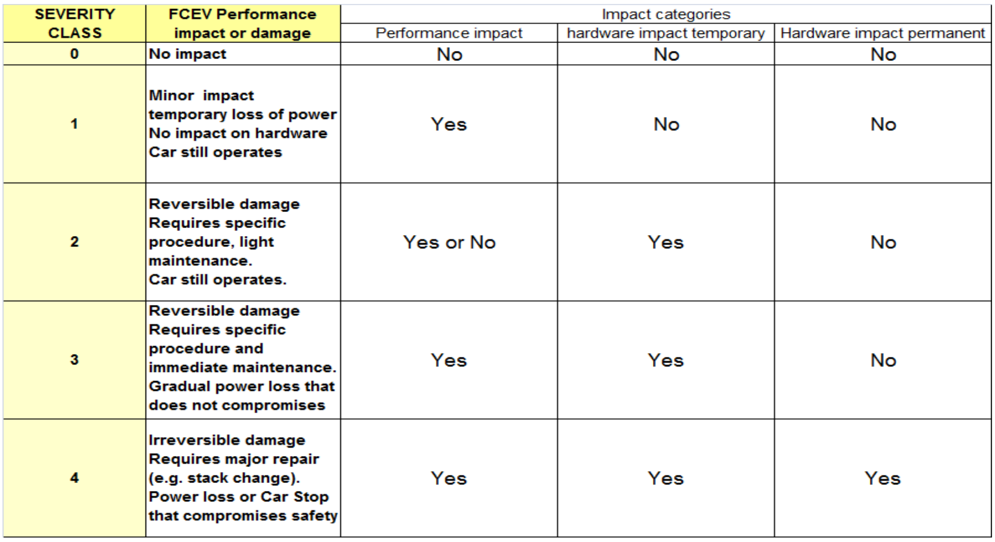
**Table 2. Definition of occurrence classes**



| OCCURRENCE CLASS | CLASS NAME | OCCURRENCE OR FREQUENCY | OCCURRENCE OR FREQUENCY |
|---|---|---|---|
| **0** | **Very unlikely (Practically impossible)** | Contaminant above threshold never been onserved for this type of source in the industry | Never |
| **1** | **Very rare** | Heard in the Industry for the type of source/ Supply chain considered | 1 per 1 000 000 refueling |
| **2** | **Rare** | Has happened more than once/year in the Industry | 1 per 100 000 refueling |
| **3** | **Possible** | Has happened repeatedly for this type of source at a specific location | 1 out of 10 000 refueling |
| **4** | **Frequent** | Happens on a regular basis | Often |

The range of severity level (level of damage for vehicle) is defined in Table 3.

**Table 3. Definition of severity classes**



| SEVERITY CLASS | FCEV Performance impact or damage | Impact categories | | |
|---|---|---|---|---|
| | | Performance impact | hardware impact temporary | Hardware impact permanent |
| 0 | No impact | No | No | No |
| 1 | Minor impact<br>temporary loss of power<br>No impact on hardware<br>Car still operates | Yes | No | No |
| 2 | Reversible damage<br>Requires specific procedure, light maintenance.<br>Car still operates. | Yes or No | Yes | No |
| 3 | Reversible damage<br>Requires specific procedure and immediate maintenance.<br>Gradual power loss that does not compromises | Yes | Yes | No |
| 4 | Irreversible damage<br>Requires major repair (e.g. stack change).<br>Power loss or Car Stop that compromises safety | Yes | Yes | Yes |

The final risk is defined by the acceptability table built by combination of both above tables (Table 4).

**Table 4. Definition of acceptability table**

| | | Severity | | | | |
|---|---|---|---|---|---|---|
| Occurrence As the combined probabilities of occurrence along the whole supply chain | | 0 | 1 | 2 | 3 | 4 |
| | 4 | 🟩 | 🟥 | 🟥 | 🟥 | 🟥 |
| | 3 | 🟩 | 🟨 | 🟥 | 🟥 | 🟥 |
| | 2 | 🟩 | 🟩 | 🟨 | 🟥 | 🟥 |
| | 1 | 🟩 | 🟩 | 🟩 | 🟨 | 🟥 |
| | 0 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 |
| Key | 🟥 Unacceptable risk : additionnal control or barriers are required | | 🟨 Further investigations are needed: existing barriers or control may not be enough | | 🟩 Acceptable risk area Existing controls acceptable | |

For each level of risk, decision has to be taken in order to:

- Either refuse the risk and find mitigation or barriers to reduce it;
- Or accept the risk level as it is.

Risk reduction might include actions taken to mitigate the severity and/or probability of occurrence. Using the risk assessment table elaborated for one hydrogen source, the risk acceptance table (table 4) is used to elaborate the appropriate quality assurance plan in order to reduce the risk of non-quality. This can be done either by barriers added to the process and / or by analytical control of impurities level. The quality assurance plan can only be defined on a case-by case basis.

## 1.2 Description of processes

The three different processes studied in this report are described in the Appendix 1. Description of the processes and the different barriers are presented in the appendix. Further details on the risk assessment and detailed conclusions are available in the peer reviewed article (Bacquart, et al., 2018).

## 1.3 Results of probability of presence of contaminants in $H_2$ from production methods

The results of the probability of contaminants presence are summarised in the section below for the three processes studied.

### 1.3.1 Chlor-alkali membrane electrolysis process

The contaminants potentially present in the hydrogen are depending on the process technology and on the purification step. It should be investigated on a case by case basis for each production source. Nevertheless, the general process can be used for the first approach. Table 5 gives a general classification of impurities on chlor-alkali process.

**Table 5. Probability of presence of impurities in Chlor-alkali process**

| Probability of presence of impurity | Impurity |
|---|---|
| Frequent | Possibly $O_2$ |
| Possible | None identified |
| Rare | $H_2O$ and $N_2$ |
| Very Rare | $CO_2$ |
| Unlikely | Argon, CO, $CO_2$, formaldehyde, sulfur compounds, ammonia, THC, formic acid, Halogenated compounds |

### 1.3.2 Quality risk assessment for H2 for fuel cell car: SMR process + PSA

The contaminants potentially present in the hydrogen are depending on the process technology and on the purification step. It should be investigated on a case by case basis for each production source. Nevertheless, general process can be used for the first approach. Table 6 gives a general classification of impurities on centralized Steam Methane Reforming (SMR) of natural gas with PSA purification.

**Table 6. Probability of presence of impurities in SMR process**

| Probability of presence of impurity | Impurity |
|---|---|
| Frequent | CO |
| Possible | $N_2$, He |
| Rare | Ar, $CH_4$, |
| Very Rare | Formaldehyde |
| Unlikely | $O_2$, $CO_2$, $H_2O$, sulfur compounds, ammonia, THC (except methane), formic acid, Halogenated compounds |

### 1.3.3 Quality risk assessment for H2 for fuel cell car: PEM Water Electrolysis + TSA

The contaminants potentially present in the hydrogen are depending on the process technology and on the purification step. It should be investigated on a case by case basis for each production source. Nevertheless, general process can be used for the first approach. Table 7 gives a general classification of impurities on decentralized PEM Water Electrolysis (WE) with TSA purification.

**Table 7. Probability of presence of impurities in PEM WE process**

| Probability of presence of impurity | Impurity |
|---|---|
| Frequent | - |
| Possible | - |
| Rare | $N_2$, $O_2$, $H_2O$ |
| Very Rare | $CO_2$ |
| Unlikely | Ar, CO, $CH_4$, He, halogenated products, formaldehyde, formic acid, THC, ammonia, sulfur compounds |

# 2 Analytical campaign for hydrogen production processes

In the EMPIR Hydrogen project, an analytical campaign has been organized to assess the level of contaminants listed in ISO 14687 in hydrogen from different production processes. In this report, analysis results of the Steam methane reforming process (SMR) analytical campaign, the Electrolysis process analytical campaign are presented for the contaminants analysed by four national metrology institutes (CEM, NPL, RISE and VSL). The scope of contaminants analysed corresponds to ISO standard 14687-2 (ISO 14687-2, 2012). The aim is to provide evidences to support the probability of presence of contaminants performed by process expert.

In between 2016 and 2018, 23 hydrogen sampling were performed on hydrogen production plants in Europe (PEM water electrolyser, steam methane reformer, chlor-alkali membrane process). Eight samplings were performed on different PEM water electrolysers with purification (temperature swing adsorption) in Europe covering different manufacturers and technologies. Nine samplings were performed on different steam methane reformer with purification (pressure swing adsorption) in Europe covering different manufacturers and technologies.

Five samplings were performed on different PEM water electrolyser without purification in Europe covering different manufacturers and technologies. One sampling was performed on a hydrogen refuelling stations with hydrogen from chlor-alkali membrane process.

## 2.1 Hydrogen sampling from production process

During the project, 23 independent sampling of hydrogen at various production process plants in Europe were performed using the sampling procedure is detailed in annex D. The project partners and the participants were extremely careful in order to avoid contamination during samplings by following the exact protocol and ensuring preparation of the sampling cylinder by evacuation. The cylinders used for sampling were different depending on availability, safety and laboratories requirements. The type of cylinders used are aluminium cylinder (5 and 10 Litres), aluminium cylinder (10 Litres) with SPECTRA-SEAL passivation (BOC, UK), stainless steel cylinder (1 litres) and stainless steel cylinders (1; 2 and 4 litres) sulfinert ® coated (Silcotek, US). The analyses were performed over a long period of time due to shipment delay between the sampling site and the partners. Even if the consortium minimised as much as possible the delay, it is important to consider that there could be several weeks to months between the sampling date and the analysis date. It is currently difficult to assess the impact of time between cylinder reception and analysis on the different contaminants especially for reactive species (i.e. total sulphur, formaldehyde…) due to the lack of stability studies.

## 2.2 Analytical methods

Four national metrology institutes (CEM, NPL, RISE and VSL) were involved in the sampling and the analysis of hydrogen quality for PEM water electrolyser and for SMR with PSA. Each NMIs performed part of the analysis according to the table below:

**Table 8. List of analytical methods used for ISO 14687-2 analysis by national metrology institute partners of EMPIR Hydrogen 15 NMR03. The list of acronyms used: CRDS: Cavity Ring Down spectrometer; FID: flame ionisation detector; GC: gas chromatography, MS: mass spectrometry; OFCEAS: optical feedback cavity enhanced absorption spectroscopy; PDHID: pulsed discharge helium ionization detector; TCD: thermal conductivity detector; TD: thermo-desorption.**

| Compounds | ISO 14687-2 threshold [µmol/mol] | NPL | VSL | RISE | CEM |
|---|---|---|---|---|---|
| **Water $H_2O$** | 5 | Quartz crystal microbalance | - | - | - |
| **Methane $CH_4$** | 2 | GC-methaniser-FID | - | GC-FID | - |
| **Non methane hydrocarbons** | 2 | GC-methaniser-FID | - | GC-FID | - |
| **Oxygen $O_2$** | 5 | GC-PDHID | - | GC-TCD | GC-TCD/ GC-PDHID |
| **Helium He** | 300 | - | - | - | GC-TCD |
| **Nitrogen $N_2$** | 100 | GC-PDHID | - | GC-TCD | GC-TCD/ GC-PDHID |
| **Argon Ar** | 100 | GC-PDHID | - | GC-TCD | GC-TCD/ GC-PDHID |
| **Carbon dioxide $CO_2$** | 2 | GC-methaniser-FID | - | OFCEAS | - |
| **Carbon monoxide CO** | 0.2 | GC-methaniser-FID | - | OFCEAS | - |
| **Total sulphur compounds** | 0.004 | GC-SCD | - | OFCEAS | - |
| **Formaldehyde HCHO** | 0.01 | - | CRDS | - | - |
| **Formic acid HCOOH** | 0.2 | - | CRDS | - | - |
| **Ammonia $NH_3$** | 0.1 | - | CRDS | - | - |
| **Total halogenated (HCl)** | 0.05 | - | CRDS | - | - |
| **C2 hydrocarbons** | 2 | - | - | TD-GC-FID/MS | - |
| **C3 hydrocarbons** | 2 | - | - | TD-GC-FID/MS | - |
| **C4 hydrocarbons** | 2 | - | - | TD-GC-FID/MS | - |
| **C5 hydrocarbons** | 2 | - | - | TD-GC-FID/MS | - |
| **C6 - C18 hydrocarbons** | 2 | - | - | TD-GC-FID/MS | - |

### 2.2.1 Description of the materials and methods used for hydrogen contaminants analysis

#### 2.2.1.1 NATIONAL PHYSICAL LABORATORY ANALYTICAL METHODS

Nitrogen, oxygen, argon

Nitrogen, oxygen, argon were analysed by gas chromatography (Agilent with pulsed discharge helium ionization detector (PDHID, VICI) using helium as a carrier gas. Gases are sampled directly from the gas cylinder to the analyser, a pressure regulator (set at 20 psig outlet) and a needle valve were used to restrict the flow to 30 ml/min. The GC/PDHID sampling loop was 1 ml and the sampled was then transferred onto capillary column molsieve 5A plot (30 m x 0.53 mm x 50 µm) and a second capillary column molsieve 5A plot (50 m x 0.53 mm x 50 µm). The GC oven was set at 30 degrees Celsius and the PDHID detector was set at 180 degree Celsius. NPL gravimetric gas standards in hydrogen containing nitrogen ($N_2$), carbon monoxide (CO), carbon dioxide ($CO_2$), methane ($CH_4$), ethane ($C_2H_6$) and oxygen ($O_2$) were used to calibrate the analyser. Gravimetric standard and/or dilution using mass flow controller system (Bronkhorst, NL) were used to generate calibration curve ranging from 1 to 75 µmol/mol of oxygen and 2 to 150 µmol/mol of nitrogen. The method can separate argon from oxygen.

Carbon monoxide, carbon dioxide, methane and non-methane hydrocarbons

Carbon monoxide, carbon dioxide, methane and non-methane hydrocarbons were analysed using a GC-methaniser-FID (Peak Laboratories, USA). The measurement of carbon monoxide, carbon dioxide and methane was done by separating them by retention time on a packed column Haysep D (60/80 mesh, length 186”). The non-methane hydrocarbon were back flushed after the elution of CO, $CO_2$ and $CH_4$. The non-methane hydrocarbons eluted as one peak. The carbon compounds were converted into methane using a methaniser set at 270 ± 1 °C. The detector is a flame ionisation detector (FID). Gases are sampled directly from the gas cylinder to the analyser. A needle valve was used to restrict the flow to 30 ml/min. The gas chromatography oven is set at 65 degrees Celsius and the injection loop equals to 5 ml. NPL gravimetric gas standards in hydrogen containing nitrogen (N2), carbon monoxide (CO), carbon dioxide ($CO_2$), methane ($CH_4$), ethane ($C_2H_6$) and oxygen ($O_2$) were used to calibrate the GC from 20 nmol/mol to 10 µmol/mol.

Total sulphur

Total sulphur was analysed by gas chromatography/Sulphur chemiluminescence detector (GC-SCD). The analysis of the sample is performed on an Agilent 7890A gas chromatograph (Agilent, USA) equipped with two detectors, a flame ionization detector and sulfur chemiluminescence detector (SCD 355, Agilent Technologies, USA). The GC/SCD sampling loop was 1 ml and the sampled was then transferred onto capillary column used is a HP-5, 30 m x 0.320 mm ID x 0.251 µm film thickness (Agilent, USA). The column program temperature is isothermal at 110 °C. Helium is used as a carrier gas at a flow rate of 20 ml/min. Gases are sampled directly from the gas cylinder to the analyser, a needle valve was used to restrict the flow to 20 ml/min. Total sulphur analysis was calibrated using dynamic dilution of a gravimetric gas standard of H2S in hydrogen. Sulphur compounds are unstable at low nmol/mol amount fraction. Dynamic standards were generated using a dilution system based on calibrated orifices and mass flow controller system (Bronkhorst, NL). The critical orifices dynamic system was validated using Molbloc system (Molbox, Fluke, NL). The traceable dynamic dilution was done using pure hydrogen (BIP®+ quality, Air Products, UK) and NPL gas standards (40, 400 and 1000 nmol/mol).

Water amount fraction

The measurement of water content in hydrogen sample was performed using quartz crystal microbalance, QMA401 and QMA (Michell, USA) and in few cases using cavity ring down spectroscopy (Tiger Optics, USA), for water amount fraction below 2 µmol/mol. Gases are sampled directly from the gas cylinder to the analyser, a valve was used to restrict the flow to 0.333 L/min for the QMA and to 1 L/min for the CRDS. The instruments were calibrated against primary reference standard by NPL humidity group. Standards of water amount fraction in hydrogen were used as quality control check. The gas line was extensively purged with high purity nitrogen (BIP® quality, Air Products, BE) prior to analysis in order to remove any moisture from the tubing.

Data evaluation and uncertainties

The data were scrutinised however no result was discarded without a technical reason. The calibration curve, results of analysis and uncertainties associated were determined using NPL software XLGENline (Smith & Onakunle, 2007). An expanded uncertainty using a *k* value of 2 was used. In some cases, a more conservative uncertainty was derived from scientist expertise.

### 2.2.1.2 VSL ANALYTICAL METHODS

During the sampling campaign, VSL performed analysis of four contaminants: formic acid, formaldehyde, hydrogen chloride and ammonia. Such data can help to support further revisions of ISO standard 14687-2 (ISO 14687-2, 2012) and other relevant hydrogen purity standards.

Measurement system

The 4 different analytes (formic acid, formaldehyde, hydrogen chloride and ammonia) are measured with the same Optical Parametric Oscillator (OPO)-based Cavity Ring Down (CRDS) spectrometer. Only the selected wavelength is different. A short description of the measurement system is given below, more details can be found for instance in peer reviewed articles (Persijn, Purity analysis of gases used in the preparation of reference gas standards using a versatile OPO-based CRDS spectrometer , 2018) (Persijn, Harren, & van der Veen, 2010).

CRDS spectrometer

Figure **1** shows a schematic overview of experimental set-up based on an OPO as light source and CRDS used for the gas detection. The pump laser of the OPO consists of a narrow line width fibre laser (NKT Photonics, output power set at 4.4 mW) which is amplified in a fibre amplifier (IPG Photonics). This combination provides a wide mode-hop free tuning range of 100 GHz and an output power up to 10.5 W at 1064 nm. The output of the amplifier is coupled into the OPO cavity via a collimator (COL), Faraday isolator (FI) and AR-coated focusing lens (L1). The periodically poled crystal (PPLN) from HC-Photonics is contained in an oven and has AR coatings for signal, pump and idler wavelengths. The mirrors are highly transparent for both idler and pump wavelengths and highly reflective for the signal wavelength. The backside of the mirrors is anti-reflective coated for both the pump and idler. Within the PPLN crystal the pump light is converted into the signal and idler with the signal resonating in the OPO cavity.

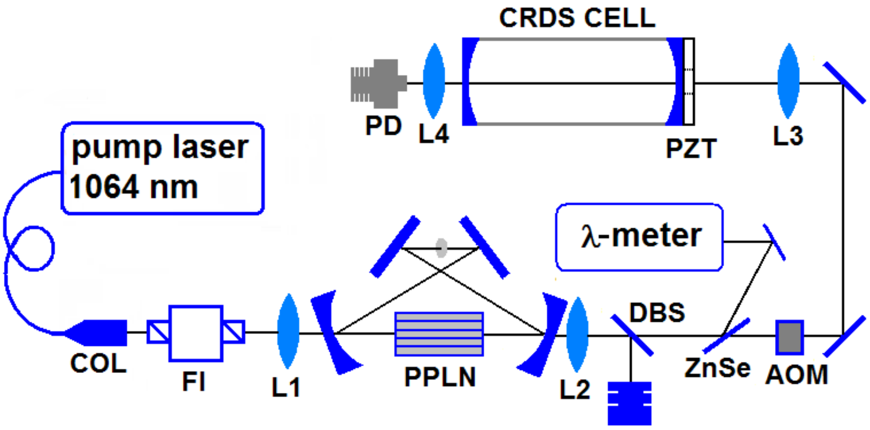


**Figure 1 Schematics of the singly resonant cw OPO and CRDS spectrometer. The output of the seed fiber laser is amplified up to maximum 10.5 W and coupled into the OPO cavity. Part of the idler is directed to a wavelength meter and the rest is directed via an Acoustical Optical Modulator (AOM) to the cavity ring down measurement cell.**

The output of the OPO is collimated using an uncoated CaF2 lens (L2). Signal and residual pump are separated from the idler using a dichroic beam splitter (DBS). Part of the idler beam is directed to a wavelength meter (Bristol instruments) using a ZnSe window placed near the Brewster angle.

Different PPLN crystals and mirror sets in the OPO cavity are used to cover the entire wavelength range of 2.3 - 5.1µm.

Formic acid, formaldehyde and hydrogen chloride are measured in a 10 cm-1 wavelength range where all 3 compounds strongly absorb (stronger absorption lines are available within the tuning range of the OPO but this would require significantly more time for the analysis). The background decay time is high (about 13.5 µs) which corresponds with a long effective absorption path length of about 4 km. Ammonia is measured at another crystal period and temperature. Here the background decay time is around 7 µs, corresponding to an absorption path length of around 2 km.

Flow system

Both the pressure regular and CRDS measurement cell are SilcoNert 2000 coated measurement cell to reduce adsorption and reaction effects (important for HCl, ammonia and formic acid but less relevant for formaldehyde). For the tubings either polymer tubings or SilcoNert 2000 coated stainless steel tubing are used (tubings are kept as short as possible by placing sample cylinders on the optical table near the CRDS cell). Measurements are typically performed using a flow rate of 30 L/h set by a mass flow controller (coated with SilcoNert® 2000). The cell pressure is controlled using a combination of a pressure regulator and a membrane pump and is normally set at atmospheric pressure.

The time response of the system is dependent on the compound: formaldehyde is very fast, followed by formic acid, ammonia and finally hydrogen chloride. As an example, the measurement reading for formaldehyde takes about 1 minute to stabilize while ammonia takes about 12 minutes to stabilize (before this, the flow system and reducer were exposed to clean $H_2$). Note that this time is amount fraction dependent for reactive compounds, the lowest amount fractions require the longest stabilization times. Depending on the compound and sample size the total measurement is typically 15-45 minutes per component (with formaldehyde and formic acid measured simultaneously).

Calibration

Static reference gas standards in nitrogen are available for ammonia (produced by VSL), hydrogen chloride (commercial supplier and certified by VSL) and formaldehyde (commercial supplier and certified by VSL). These are diluted with high purity hydrogen for calibration. For formic acid a commercial mixture in a hydrogen matrix is available. This mixture has been diluted with nitrogen to enable a comparison with the formic acid spectrum contained in the PNNL spectral database. Furthermore, a HCl in H2 gas standard developed by CEM has been used. Work using dynamic generation methods based on permeation devices and a magnetic suspension balance for all 4 compounds is still in progress at VSL.

### 2.2.1.3 CEM ANALYTICAL METHODS

*Helium*

For Helium, the samples were analysed using a micro gas chromatograph Agilent 3000A (micro-GC) with thermal conductivity detector (TCD). The micro-GC was equipped with a PLOT-U (3 m x 0.30 mm) pre-column and a Molsieve 5A column (10 m x 0.30 mm). A backflush injector type of 1 µL is installed. Argon BIP® is used as carrier gas and stainless steel tubing is used for sampling lines. Pressure regulators were used with samples and primary reference materials (PRMs) and 2 bar outlet pressure was used for sampling. After experience gained within first analysis, two 5-ways-valves are used for connecting the sampling cylinders and one of the standards with the analyser at the same time, this improves the purging and reduces the likelihood of air leak in the system. The lines are purged flushing 8 times before each analysis. With this method helium and hydrogen can be separated.

Analysis method for helium using Agilent 3000A Micro GC:

| | |
|---|---|
| Column: | 3m PLOT-U + 10m Molsieve 5A |
| Sample: | Hydrogen |
| Inj. Temp: | 55 °C |
| Oven Temp: | 50 °C |
| Carrier Gas: | Argon BIP® (20 psi) |
| Detector: | Thermal Conductivity Detector |

*Nitrogen, oxygen, argon*

For Oxygen, Argon and Nitrogen impurities, the two first batches of samples were analysed using the micro-GC analyser but with He BIP® as carrier gas instead of argon. Then, these impurities were analysed with an Agilent 6890 GC with a PDHID detector (Pulsed Discharge Helium Ionization Detector) from VICI-VALCO with a HP-MOLESIEVE 5A (30 m x 0.53 mm) capillary column. Using Helium BIP® as carrier gas and stainless steel tubing for samples and standards. Pressure regulators were used with samples and PSMs and 2 bar outlet pressure was used for injection. The lines and regulators are purged before each analysis (3 times). An automatic sampler (designed by VSL) is programmed using AGILENT-Chemstation software to inject all the samples and the PRMs in the same analytical sequence. Oxygen and argon are not completely separated but it is possible to asses if any of them is present in the sample at the required level.

Analysis method for oxygen, argon and nitrogen:

| | |
|---|---|
| Column: | 19095P-MS0 Molesieve 5A, 30m, 0.53mm, ID 50 µm |
| Sample: | Hydrogen |
| Sample Loop vol.: | 1 mL |
| Inj. Temp: | 50 °C (On) |
| Oven Temp.: | 26 °C (On) |
| Carrier Gas: | Helium BIP® |
| Flow rate: | 1.5 mL/min (constant flow) |
| Detector: | PDHID @ 100 ºC (On) |

*Calibration*

For oxygen calibration, the PRMs were prepared gravimetrically in accordance with ISO 6142-1:2015 (ISO6142, 2015) from some PRMs already present at CEM laboratory. Pure nitrogen ($N_2$) BIP® was used as balance. The calibration curve goes from 5 to 15 µmol/mol of oxygen. For helium calibration, the primary standard mixtures were prepared gravimetrically in accordance with ISO 6142-1:2015 in helium matrix starting from pure nitrogen ($N_2$) BIP® and pure helium (He) BIP ®. The calibration curve ranges from 9 to 80 µmol/mol of helium. For argon and nitrogen calibration, the primary standard mixtures (PRMs) were prepared gravimetrically in accordance with ISO 6142-1:2015 in helium matrix starting from pure nitrogen ($N_2$) BIP®, pure argon (Ar) BIP® and pure helium (He) BIP® with 25 (used lately) 50 (used lately), 80, 100 and 150 µmol/mol of argon and nitrogen in helium. In all cases it was necessary to carry out several dilution steps to reach the amount of fraction desired.

*Data evaluation and uncertainties*

During analysis of oxygen, argon, and nitrogen, some data were rejected because of certainty of existing air leak in the system. With helium, a poor performance of the purge was detected a few times. These issues could be tackled by increasing the number of injections per sample but in our case it did not work when the pressure in sample cylinders was lower than 2 bar. The calibration curve, results of analysis and uncertainties associated were determined using the methodology of ISO 6143:2001 (ISO6143, 2001) and in some cases a more conservative approach was used.

#### 2.2.1.4 RISE ANALYTICAL METHODS

From the cylinders, gas sampling bags (3 L Multi-layer foil, Restek) were filled. The bags were first washed out using RISE bag washout system, Pascal, using helium in order to reduce the quantity of nitrogen and oxygen in the bag to as low as possible. The system automatically performed the following sequence of events: emptying the bag during 20 seconds, filling the bags with Helium (with a piston of 200 ml which is filled 5 times with helium at 1.8 bar), emptying the bags in 20 seconds, the last two operations are repeated 3 times.

Sampling from each cylinder was also performed at controlled flow rates (50 ml/min) onto stainless steel sorbent tubes packed with Tenax TA (200 mg, 60-80 Mesh) during 1 min (50 ml totally) respective 2 min (100 ml totally). The gas was also analysed directly from the cylinders connected to two Proceas® (AP2E, FR) instruments to measure $O_2$, CO, $CO_2$, $H_2S$ and $H_2O$.

Nitrogen, oxygen, carbon dioxide, argon

Nitrogen, oxygen, argon and carbon dioxide are analysed by GC/TCD (gas chromatography with thermal conductivity detector) using helium as a carrier gas. Gases are sampled in special gas bags and a known volume of gas (typically 30 ml) is withdrawn from the bag by a pump to fill a loop of 100 µl with the gas to analyse which is subsequently introduced in the columns of the GC/TCD. A standard gas containing 100 µmol/mol of nitrogen (N2), 100 µmol/mol of argon (Ar), 10 µmol/mol of carbon dioxide (CO2) and 10 µmol/mol oxygen O2 was used to calibrate the GC. With this method, argon cannot be separated from oxygen. So the result is the sum argon + oxygen.

- Column for this analysis: Molecular Sieve 5A + Hayesep N
- Detector temperature > 110 °C with a filament temperature at 320°C
- Oven temperature: 80°C
- Loop of 100 µl

Carbon monoxide, carbon dioxide, hydrogen sulfide (oxygen and water)

These compounds are analyzed by optical feedback cavity enhanced absorption spectroscopy (OFCEAS). OFCEAS is a direct intensity measurement scanning spectroscopy technique. The use of a resonating cavity – a multipath gas cell using hyper-reflective mirrors – enables path length up to 10 km. The instrument used measures low ppm levels carbon monoxide (0.002 to 20 µmol/mol), carbon dioxide (0.2 to 2000 µmol/mol), hydrogen sulphide (0.001 to 0.2 µmol/mol), water (0.05 to 500 µmol/mol) and oxygen (1 to 2000 µmol/mol). The instrument is pre-calibrated and does not require daily calibration with certified gas mixtures.

The cylinder containing the sample is connected to a transfer line consisting of a stainless steel particle filter with 7 micron pore size and a stainless steel restrictor. The sample is withdrawn at 3-5 l/h using an internal pump. When using cylinders. a split is needed before the filter. When an analysis is started, the concentration of the targeted compound rises until it stabilizes.

Total hydrocarbons compounds as methane basis C

Methane and other light hydrocarbons (with 2 to 5 carbon atoms) are analysed by GC/FID (gas chromatography with flame ionization detector) using helium as a carrier gas and a Porous Layer Open Tubular (PLOT) columns which are well suited for the analysis of light hydrocarbons.

The gas is sampled in bags as contamination with air has been shown to be less than 100 ppm-vol with a proper handling of the bag. This level of contamination does not affect the concentration of methane and other hydrocarbons. A standard gas containing 104.6 ppm-vol of methane ($CH_4$), 99.8 ppm-vol ethane ($C_2H_4$), 76.4 µmol/mol propane ($C_3H_8$), 94.9 µmol/mol of isobutane and 101.6 µmol/mol of butane ($C_4H_{10}$), 101.4 µmol/mol of pentane, 93.8 µmol/mol of isopentane ($C_5H_{12}$) was used to calibrate the instrument. For calibration purpose, 50 and 20 times dilution of the standard were also used (calibration from 1-2 ppm to 100 µmol/mol for each compound).

Other impurities

Hydrocarbons (≥C6) and possibly other impurities are analysed by thermal desorption - gas chromatography/mass spectrometry - flame ionisation detection (TD-GC-FID/MS). The Tenax TA tubes are subjected to a two-stage thermal desorption process using a Thermal Desorption Unit (Markes TD100 desorber), where the adsorbed substances are released by heating the sorbent tubes at 275 °C for 7 min and then transferred to a cold trap packed with graphitised carbon for focusing at -10 °C. The trap is then rapidly heated up to 300 °C and components are released and reached the gas chromatography (GC) column for separation. The column effluent is split into two streams for the detection of individual components, one stream passing through a flame ionisation detector and the other stream through a mass spectrometer.

The analysis of the sample is performed on an Agilent 6890N gas chromatograph equipped with two detectors, a flame ionization detector and a mass spectrometer 5975C inert MSD operated in the electron impact mode under standard conditions (ionizing electron energy 70 eV, masses scanned from 29 to 300 amu). The column used is a BPX5, 50m x 32 mm ID x 1 µm film thickness (5% phenyl (equivalent) polysilphenylene-siloxane).

The column program temperature is monitored from 35°C (hold 4 min.) to 100 °C at 3 °C/min, to 220°C at 8 °C/min and then to 300 °C at 15 °C/min (hold 10 min.). Helium is used as a carrier gas at a flow rate of 2.6 ml/min. The FID detector temperature is set at 300 °C.

## 2.3 Final results of analysis of the hydrogen production sampling campaign

The objective was to provide a realistic overview of contaminants presence from PEM Water electrolyser with TSA and from SMR with PSA. The results presented below were the most reliable results from the four national metrology institutes measurements. All the results obtained from each NMI are provided in annexes 5 and 6 and some measurements were performed by more than one NMI.

### 2.3.1 Results of analysis from SMR with PSA

The results of analysis from SMR with PSA are presented as a range between the highest and the lowest values obtained from eight different and independent samplings at various SMR plants in Europe. The results covered a range of technology and system with the objective of providing a general overview of hydrogen quality from SMR with PSA. The results showed that no contaminants were above the threshold of ISO 14687-2. Even if the number of sampling is low, the complete absence of contaminant can be used to confirm the results of the probability of contaminant presence.

**Table 9. Range amount fraction of ISO 14687-2 contaminants in hydrogen from steam methane reforming with pressure swing adsorption. The results correspond to the range from the lowest to the highest values obtained in eight different samples from different SMR with PSA in Europe.**

| Compounds | ISO 14687-2 threshold [µmol/mol] | SMR with PSA (8 samples) Results [µmol/mol] |
|---|---|---|
| Water $H_2O$ | **5** | **< 2** |
| Methane $CH_4$ | **2** | **< 0.02 to 0.05** |
| Non methane hydrocarbons | **2** | **< 0.05** |
| Oxygen $O_2$ | **5** | **< 1.0** |
| Helium He | **300** | **< 54** |
| Nitrogen $N_2$ | **100** | **< 1.2 to 11** |
| Argon Ar | **100** | **< 0.5 to 1.3** |
| Carbon dioxide $CO_2$ | **2** | **< 0.02 to 0.45** |
| Carbon monoxide CO | **0.2** | **< 0.02** |
| Total sulphur compounds | **0.004** | **< 0.0036** |

| | | |
|---|---|---|
| Formaldehyde HCHO | 0.01 | < 0.005 |
| Formic acid HCOOH | 0.2 | < 0.1 |
| Ammonia $NH_3$ | 0.1 | < 0.1 |
| Total halogenated | 0.05 | < 0.005 |
| C2 hydrocarbons | 2 | < 0.5 |
| C3 hydrocarbons | 2 | <1 |
| C4 hydrocarbons | 2 | <1 |
| C5 hydrocarbons | 2 | <1 |
| C6 - C18 hydrocarbons | 2 | <0.05 |

### 2.3.2 Results of analysis from PEM water electrolysis with temperature swing adsorption

The results of analysis from PEM Water electrolyser with TSA are presented as a range between the highest and the lowest values obtained from eight different and independent samplings at various PEM Water electrolyser plants in Europe. The results covered a range of technology and system with the objective of providing a general overview of hydrogen quality from PEM water electrolyser with TSA. The results showed that no contaminants were above the threshold of ISO 14687-2. Even if the number of sampling is low, the complete absence of contaminant can be used to confirm the results of the probability of contaminant presence.

**Table 10. Range amount fraction of ISO 14687-2 contaminants in hydrogen from PEM water electrolysis with and without temperature swing adsorption. The results correspond to the range from the lowest to the highest values obtained in eight different samples from different PEM water electrolyser in Europe.**

| Compounds | ISO 14687-2 threshold [µmol/mol] | PEM water electrolysis with TSA<br>Results on 8 samples [µmol/mol] | PEM water electrolysis<br>Results on 5 samples [µmol/mol] |
|---|---|---|---|
| Water $H_2O$ | 5 | < 3 | > 100 |
| Methane $CH_4$ | 2 | < 0.02 | < 0.02 to 0.1 |
| Non $CH_4$ hydrocarbons | 2 | 0.08 to 0.2 | < 0.02 to 0 .09 |
| Oxygen $O_2$ | 5 | < 0.5 - 2 | 18- > 500 |
| Helium He | 300 | < 9 to 45 | < 9 |
| Nitrogen $N_2$ | 100 | < 1.0 to 4.6 | 1.2 to 4.5 |
| Argon Ar | 100 | < 0.5 | < 0.5 |
| Carbon dioxide $CO_2$ | 2 | < 0.02 to 0.25 | 0.2 to 5.4 |
| Carbon monoxide CO | 0.2 | < 0.02 | < 0.02 |
| Total sulphur compounds | 0.004 | < 0.0036 | < 0.0036 |
| Formaldehyde HCHO | 0.01 | < 0.005 | < 0.005 |
| Formic acid HCOOH | 0.2 | < 0.1 | < 0.1 |
| Ammonia $NH_3$ | 0.1 | < 0.1 | < 0.1 |
| Total halogenated | 0.05 | < 0.005 | < 0.005 |
| C2 hydrocarbons | 2 | < 0.5 | < 0.5 |

| | | | |
|---|---|---|---|
| C3 hydrocarbons | **2** | **<1** | **<1** |
| C4 hydrocarbons | **2** | **<1** | **<1** |
| C5 hydrocarbons | **2** | **<1** | **<1** |
| C6 - C18 hydrocarbons | **2** | **<0.05** | **<0.05** |

### 2.3.3 Additional results of analysis

Studying the presence of contaminants led into the importance of purification processes and sampling procedure. The probability of presence of contaminant should consider the impact of purification which was evaluated by comparing PEM water electrolysis with PEM water electrolysis plus purification (in this case: TSA). During the sampling campaign, contamination was observed in one sampling from SMR with PSA and from the sample form chlor-alkali process. It became evident that sampling procedure can led to presence of contaminant. The importance of understanding contamination of the sample against process contamination is critical to provide reliable evidences to the probability of contaminant presence study.

#### 2.3.3.1 PEM WATER ELECTROLYSIS WITHOUT TEMPERATURE SWING ADSORPTION

The importance of purification system is an important point regarding potential contaminant. One difference between PEM water electrolyser and SMR processes is about the production location. One advantage of PEM water electrolyser is on-site production; however the local production processes may not have staff on site that can perform maintenance in a short time frame. Therefore the impact of purification performance and the quickness of reaction of the maintenance team can lead to contaminant presence in the hydrogen produced on site. To evaluate the contaminant that may be present, five samplings and analysis were performed on PEM water electrolyser system without purification. The objective was to determine which contaminants are present if purification is not there or not working appropriately.

The sampling and analysis were performed by national metrology institutes on different European PEM water electrolysers. The results presented above showed that the only contaminants present are oxygen, carbon dioxide and water in PEM water electrolyser before purification. Therefore the quality control plan should focuses on these three contaminants that are the potential contaminants present in case of problem with the purification system (TSA).

#### 2.3.3.2 ISSUES WITH SAMPLING AND CONTAMINATION

During the sampling campaign, few sampling issues were observed leading to sample contamination by water and air. It is critical to ensure that the sampling system or the sampling procedure is not the source of contaminants. The validation of the sampling equipment and procedure is mandatory to ensure the reliability of the analytical results. In all cases, the contaminants introduced by the sampling issues led to fake positive. Considering it, the impact of wrong or not validated sampling procedure may led to improper corrective action plan or maintenance.

# 3 Impact of contaminants on fuel cell system

The risk assessment procedure requires defining the probability of presence of contaminant (risk) and the severity of the contaminant impact on the system (danger). To evaluate the impact of contaminant, it is important to use reliable source of contaminant (primary gas standard.

## 3.1 Definition of severity classes

In order to classify the impact of contaminants on fuel cell system, it is mandatory to define in qualitative terms their impact and their severity rank. Definitions are provided in the next tables with differentiation between reversible and irreversible effects. The objective of the severity classes is to provide a system to compare contaminant's impact and define the most significant or dangerous contaminant for fuel cell system. The severity class is always linked to the amount fraction defined with it. It is crucial to consider the impact and the amount fraction of the contaminant together.

**Table 11. Severity class for reversible damage of contaminant on fuel cell system**

| SEVERITY CLASS FOR REVERSIBLE DAMAGE | FCEV Performance impact or damage | Impact categories | Performance impact | FC/stack impact temporary | FC/stack impact permanent |
|---|---|---|---|---|---|
| No impact | | 0 | No | No | No |
| Minor impact | Temporary loss of power<br>- No impact on hardware<br>- FC/stack still operates | 1 | Yes | No | No |
| Low Reversible damage | Low reversible damage<br>No specific procedure required, recovery over time<br>FC/stack still operates | 2 | Yes | No | No |
| Medium reversible damage | Medium reversible damage<br>specific procedure required<br>Light maintenance required<br>FC/stack still operates including power loss (minor) | 3 | Yes or no | Yes | No |
| High reversible damage | High reversible damage<br>specific procedure required<br>immediate maintenance required<br>important FC/stack power loss including stop of the system | 4 | Yes | Yes | No |

**Table 12. Severity class for irreversible damage of contaminant on fuel cell system**

| SEVERITY CLASS FOR IREEVERSIBLE DAMAGE | FCEV Performance impact or damage | Impact categories | Performance impact | FC/stack impact temporary | FC/stack impact permanent |
|---|---|---|---|---|---|
| No impact | | 0 | No | No | No |
| Minor impact | Temporary loss of power<br>No impact on hardware<br>FC/stack still operates | 1 | Yes | No | No |
| Low irreversible damage | Low reversible damage<br>FC/stack still operates including power loss (minor) | 2 | Yes | No | Yes |
| Medium reversible damage | Medium reversible damage<br>Light maintenance required<br>important FC/stack power loss | 3 | Yes | No | Yes |
| High reversible damage | High reversible damage<br>immediate maintenance required<br>Requires major repair (e.g. stack change)<br>Major FC/stack power loss including stop of the system | 4 | Yes | No | Yes |

## 3.2 Review of existing information on contaminant’s impact

Based on literature review and expertise from project partner, a review of the contaminant impact on fuel cell system was performed. It is crucial to understand that only the fuel cell system was considered in this review and not the complete fuel cell electrical vehicles.

**Table 13. Definition of contaminant impact on fuel cell system for the contaminants mentioned in ISO14687. The contaminant impact was evaluated at the level 1, defined in the table, which may be different from the ISO 14687 threshold. The impact level is defined in Table 11 and Table 12 ranging from 0 (no impact) to 4 (high damage). The final impact is determined as the product of the reversible multiplied by the irreversible impact.**

| | | Risk for fuel cells | | |
|---|---|---|---|---|
| | | Reversible impact | irreversible impact | final impact |
| Impurities | level 1 [µmol/mol] (*: no level 1 value available so ISO 14687 value) | at level 1 value | at level 1 value | |
| water | 5* (can be relaxed at least to H2O condensation point in given conditions) | 0 | 0 | 0 |
| CH4 | 300 | 1 | 1 | 1 |
| Total hydrocarbon saturated | 2* | 1 | 1 | 1 |
| Total hydrocarbon (olefins aliphatic / aromatic) | 2* | 4 | 2 | 8 |
| oxygen | 5* | 1 | 1 | 1 |
| helium | 300 | 1 | 1 | 1 |
| N2 | 300 | 1 | 1 | 1 |
| Ar | 300 | 1 | 1 | 1 |
| CO | 1 | 4 | 2 | 8 |
| CO2 | 3 | 1 | 1 | 1 |
| Total S | 0.004* | 3 | 4 | 12 |
| Formaldehyde | 1 | 2 | 2 | 4 |
| Formic acid | 1 | 2 | 2 | 4 |
| Ammonia | 0.1 | | | |
| HCl | 0.05 | | | |

## 3.3 Studies on three contaminants impact on fuel cells system

The studies of three contaminants impact have been performed on a single cell.

### 3.3.1 Introduction and experimental part

A performance of single fuel cell (FC) with 25 $cm^2$ active area was investigated. The anode side of the cell was fed either with pure $H_2$ either with hydrogen containing impurities. The impact of 0.2 ppm of HCl, 0.2 ppm of $C_4Cl_4F_6$ and 2 ppm of $NH_3$ in hydrogen on the FC performance was examined using a mixed constant / dynamic current protocols. It is important to mention that the literature data on the impurities above are quite restricted (A. Talke, 2018) (H.J. Soto, 2003) (K. Hongsirikarn, 2010) (U. Misz, 2016) (N. Rajalakshimi, 2003) (X. Zhang, 2009) (R. Halseid, 2006) (H. Li, 2011) (O.A. Baturina, 2014) (Y.A. Gomez, 2018) and up to our best knowledge there are no works comparing the impact of contaminants on operating FC under different electrochemical test protocols. Most of the studies concentrate on high content of pollutants in $H_2$ or air and their impact on short term performance of FC under constant current. This allows rapid observation of FC characteristics degradation and saves time for research.

However, it is known that the effect of gas contaminants on FC performance is not linear in time and making extrapolations over thousands of hours on the basis of 10-50 h of operation is not completely correct. The impact of $C_4Cl_4F_6$ on FC performance has not been described before. This impurity was found in real $H_2$ fuel samples from hydrogen refuelling stations (HRSs) (Hsu, 2012) (T. Aarhaug, 2016). Probably, the source of the contaminant was pre-treatment of tubes.

The goal of this work was to quantify a performance loss caused by $NH_3$, HCl and $C_4Cl_4F_6$ impurities for the FC operating long term under New European Driving Cycling (NEDC) protocol (G. Tsotridis, 2015). Therefore, in total 5 long term tests (~900 h) were conducted: 2 baselines with pure $H_2$ supplied to the anode side and 3 tests with each separate impurity. The cathode side of the FC was fed with compressed air.

Harmonized European Automotive test conditions (G. Tsotridis, 2015) were chosen for FC tests. Anode / cathode temperature was maintained at 80°C, relative humidity 50% / 30%, pressure 2.5 / 2.3 bara, stoichiometry 1.3 / 1.5. Membrane electrode assembly (MEA) was prepared using commercial Pt/C catalyst TEC10V50E (46,8% Pt) supplied by Tanaka Co. Ltd. The ink containing catalyst was deposited onto a support and further decal transferred to both sides of Gore® 735.18 membrane. Anode and cathode catalyst loadings were 0.12 and 0.34 $mg_{Pt}/cm^2$ correspondingly. The electrochemical tests have been performed using Green Light (GL-60) test station equipped with Gamry ref. 3000 potentiostat. An example of V-t profile for one of the reference cells is shown in Figure 2.

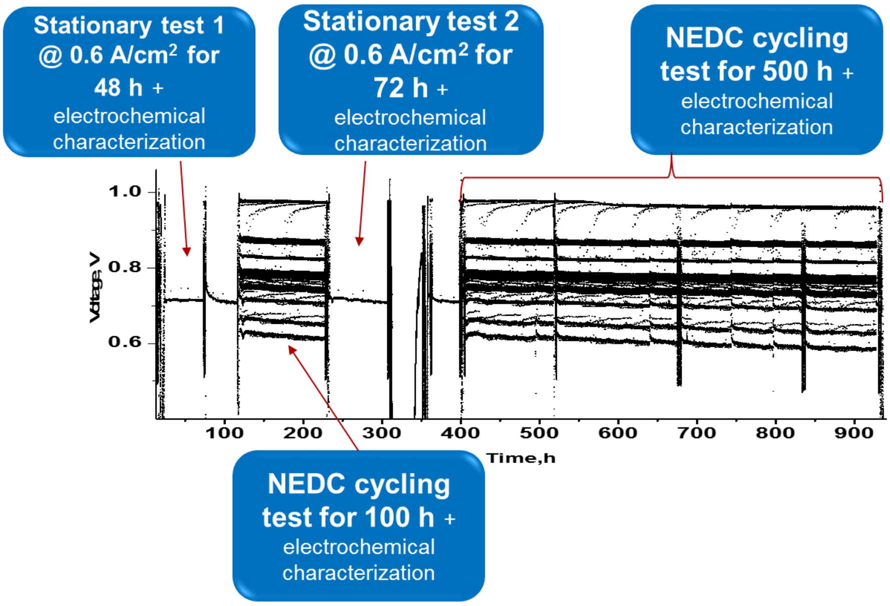


**Figure 2. Voltage vs time profile for the single 25 $cm^2$ FC tested with pure $H_2$/air at the anode/cathode sides at 80°C, 50/30% RH, 2.3 / 2.5 bara and 1.3 /1.5 stoichiometry.**

Blue boxes in

Figure **2** show different phases of the electrochemical test. After each phase of the test electrochemical characterization procedures were applied to estimate the state of health for the FC. In addition, purification protocols were applied to quantify recoverable losses provoked by hydrogen contaminants. These cleaning procedures usually included FC operation in pure $H_2$ and different levels of relative humidity. Below there is a detailed description of the electrochemical protocol steps.

1) FC break-in for 6 h
2) BoT electrochemical characterization: I-V curves, changing cell conditions to 80°C and 100% RH at 0.5 A/$cm^2$ for 2 h, cathode and anode cyclic voltammograms (CVs) to calculate catalyst electrochemical active surface area (ECSA), linear sweep voltammetry (LSV) to register

hydrogen permeation through the membrane, electrochemical impedance spectra (EIS) to estimate the cell resistance

3) Stationary test 1 for 48 h at 0.6 A/cm$^2$;
4) Cleaning in pure $H_2$ for 40 h at 100% RH
5) Electrochemical characterization protocol as for 2)
6) NEDC test for 100 h
7) Electrochemical characterization as for 2)
8) Stationary test 2 at 0.6 A/cm$^2$ for 48 h in $H_2$ + contaminant at the anode side followed by 24 h in pure $H_2$
9) Electrochemical characterization as for 2)
10) Cleaning in pure $H_2$ and 100% RH for 6 h
11) NEDC test for ~500 h
12) Electrochemical characterization as for 2)
13) Cleaning in pure $H_2$ and 100% RH for 36 h
14) EoT electrochemical characterization as for 2).

Reference tests with pure $H_2$ at the anode side were repeated 2 times to check reproducibility. To keep uniformity of test protocols, all the cells tested with and without impurities in fuel were subjected to same procedures 1-14 described above.

### 3.3.2 Preparation of gas mixtures

The ammonia in hydrogen gas mixtures were prepared gravimetrically in accordance with ISO 6142-1:2015 (ISO6142, 2015) starting from pure ammonia and pure hydrogen (BIP+ quality). NPL supplied CEA with a PRM of 500 µmol/mol of ammonia in hydrogen (Pressure of 100 bar) in a 10 L aluminium cylinder with spectraseal treatment (BOC, UK).

The $C_4Cl_4F_6$ in hydrogen gas mixtures were prepared gravimetrically in accordance with ISO 6142-1:2015 (ISO6142, 2015) starting from pure $C_4Cl_4F_6$ and pure hydrogen (BIP+ quality). NPL supplied CEA with a PRM of 5 µmol/mol of $C_4Cl_4F_6$ in hydrogen (Pressure of 100 bar) in a 10 L aluminium cylinder with spectraseal treatment (BOC, UK).

A 50 µmol/mol gas mixture of hydrogen chloride in hydrogen was provided by CEM to CEA. The gas mixture was prepared gravimetrically in accordance with ISO 6142-1:2015 (ISO6142, 2015), starting from pure hydrogen chloride (3.0 quality, Air Products) and pure hydrogen ($H_2$ BIP®). Three dilution steps where carried out before the preparation of the target mixture. The gas mixture was supplied in a 5L aluminium cylinder with no internal treatment and a pressure of approximately 140 bar. To accomplish the preparation of this kind of mixtures at CEM facilities was necessary a modification of the filling station, acquisition of a new control panel and new pipeline installation. The pure gases cylinders were located in a gas shed outside the filling laboratory because of safety requirements.

### 3.3.3 Results and discussion of electrochemical tests

#### 3.3.3.1 FC VOLTAGE DEGRADATION INDUCED BY IMPURITIES

Figure 3(a) compares voltage degradation for the 5 cells under constant current protocol tested with and without the contaminants in fuel. This step of a protocol corresponds to Stationary test 1 in Figure 2.

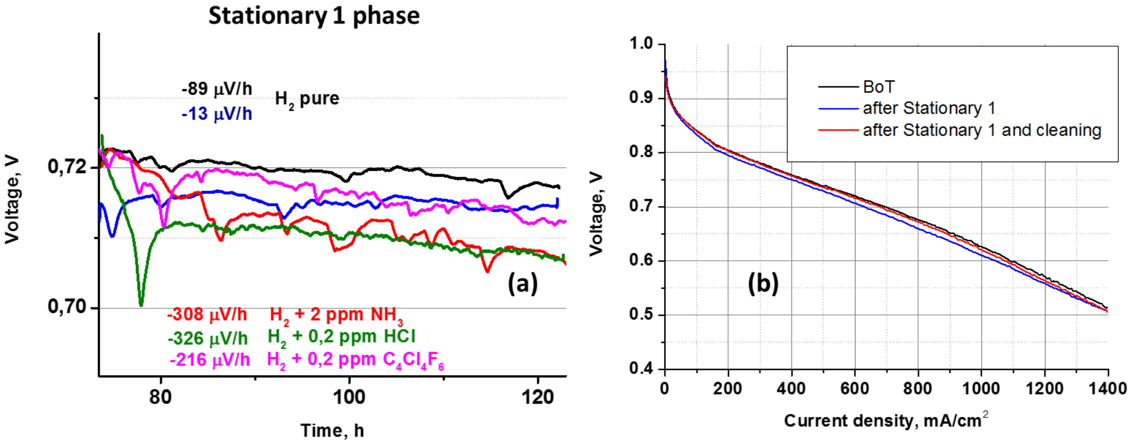


**Figure 3. Voltage degradation profiles for the 5 single fuel cells tested either with pure $H_2$ as a fuel at the anode side (black and blue curves) either with $H_2$+2 ppm $NH_3$ (red), $H_2$+0.2 ppm HCl (green) and $H_2$+0.2 ppm $C_4Cl_4F_6$ (pink) at 0.6 A/cm$^2$, 80°C, 50/30% RH, 2.3 / 2.5 bara and 1.3 /1.5 stoichiometry (a); polarisation curves measured at BoT and after the Stationary 1 phase for the cell tested with 0.2 ppm of HCl in fuel 9(b).**

The average voltage degradation rates are shown in Figure 3 for each cell. It is clear that in general FC performance loss was more important in presence of the 3 impurities compared to pure $H_2$ case even though there is a discrepancy in degradation rate values for the reference cells (-13 vs -89 µV/h). It is important to notice that the calculated values are approximate due to instability of voltage profiles and they reflect total FC performance loss trend, which usually consists of reversible and irreversible parts. Reversible degradation in fuel cells is mostly related to oxidation of cathode platinum-based catalyst at high voltages (>0.85 V vs RHE) and formation of platinum oxides, which has much lower catalytic activity compared to pure Pt (S. Kundu, 2008) (E. L. Redmond, 2014) (Y. Huanga, 2014). In addition, such factors as non-uniform water distribution and its evacuation from the MEA can also contribute to reversible performance loss.

To access the irreversible part of FC voltage decrease, polarisation curves data was taken at the BoT, after Stationary 1 step and after cleaning of the cell with pure $H_2$ and electrochemical characterization. It is believed that I-V curves reflect mostly irreversible degradation rate free from Pt oxide and water distribution effects. Figure 3(b) demonstrates a series of polarisation curves recorded for the cell tested with $H_2$ + 0.2 ppm HCl at the anode side. As one can see, there is quite important performance loss between BoT and Sationary 1 I-V curves. However, operation of the cell in pure $H_2$ for 40 h at high RH helps to recover a part of the performance, as shown by red curve in Figure 3(b). Finally, the calculated degradation rate was -60 µV/h for the cell tested with 0.2 ppm HCl while no irrecoverable decay was found for the other cells after Stationary 1 followed by purification. The effect of partial cell performance recovery after operation in pure $H_2$ in case of HCl contaminant can be explained by initial $Cl^-$ adsorption at the Pt surface and its further washing-off with high water flux during the cleaning step (S. M. M. Ehteshami, 2016). Irreversible impact of HCl on the performance of PEM FC is attributed to the electrochemical and chemical Pt catalyst dissolution in presence of chloride anions according to the following equations (O.A. Baturina, 2014):

$$\mathbf{Pt + 6Cl^- \rightarrow PtCl_6^{2-} + 4e^-} \qquad \mathbf{E^0 = 0.742\ V\ (vs.\ RHE)} \qquad \textbf{Equation 1}$$

$$\mathbf{Pt + 6HCl + O_2 \rightarrow PtCl_6^{2-} + 2H_2O + 2H^+} \qquad \textbf{Equation 2}$$

It should be mentioned that any impurity entering the FC with fuel flux is rapidly distributed in the entire MEA including cathode side active layer due to high permeability of the polymer membrane. That is why $H_2$ contaminants can lead to cathode catalyst poisoning and degradation at high voltages and/or in presence of oxygen as in Equation 1 and Equation 2.

Therefore, it can be concluded that during Stationary 1 step only temporary recoverable FC performance losses were observed in case of pure $H_2$ and in presence of $NH_3$ and $C_4Cl_4F_6$ contaminants, which can be recovered by 40 h operation in pure $H_2$. HCl provoked some irreversible voltage decay, which could not be recovered by applying cleaning protocol.

Figure 4(a) shows voltage degradation profiles with corresponding approximate total degradation rates for the cells tested with and without the impurities in $H_2$. NEDC harmonized protocol was applied (G. Tsotridis, 2015). Figure 4(b) demonstrates current and voltage profiles during one separate NEDC cycle and shows area of data extraction at 0.6 A/cm$^2$. This value has been chosen with the aim to compare stationary and dynamic protocols in identical conditions.

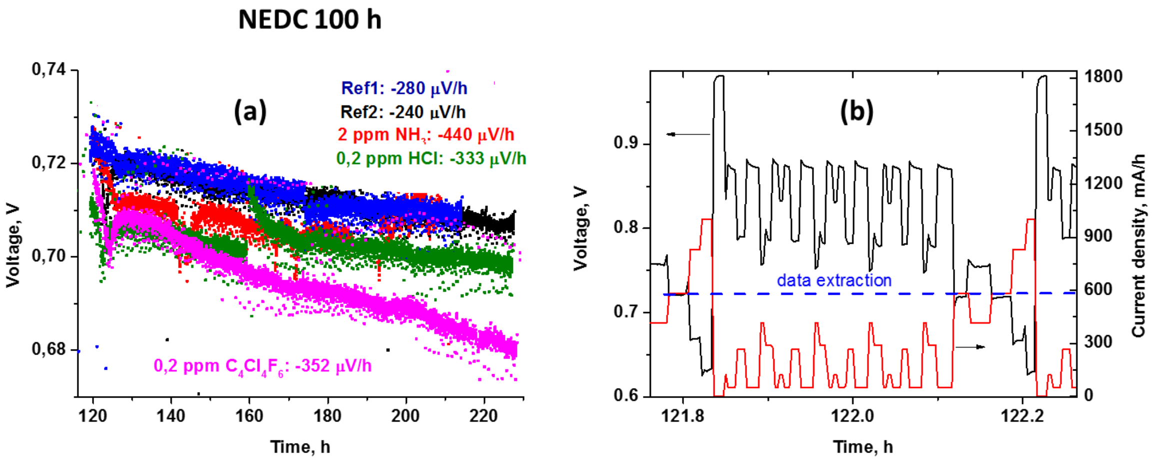


**Figure 4. Extracted FC voltage at 0.6 A/cm$^2$ for the cells tested with and without the impurities in hydrogen using NEDC protocol (a); detailed view of one NEDC cycle with current and cell voltage profiles (b).**

From the values of total voltage decay rates shown in Figure 4(a) it is evident that the presence of impurities in $H_2$ accelerate FC performance decrease. It is possible that the gas pollutants provoke massive Pt oxide formation at the cathode side via diffusion through the membrane (S. M. M. Ehteshami, 2016). Further, $PtO_x$ is reduced in the course of electrochemical characterization applied after NEDC 100 h step and this reversible effect is not visible on I-V curves. There is a high reproducibility for the two reference cells tested in pure hydrogen. Introducing NH3 impurity to the FC caused important cell voltage instability and fluctuations during the test, Figure 4(a). Irreversible FC performance losses were calculated based on polarisation curves and the obtained values are presented in Table 14.

**Table 14. Irreversible FC performance degradation rates calculated based on polarisation curves measured before and after NEDC 100 h protocol application.**

| | Reference pure $H_2$ | 2 ppm $NH_3$ | 0,2 ppm HCl | 0,2 ppm $C_4Cl_4F_6$ |
|---|---|---|---|---|
| **Irreversible degradation rates during NEDC 100 h phase @ 0.6 A/cm$^2$, µV/h** | -26 | -42 | -45 | -86 |

It should be mentioned that no cleaning protocol was used after NEDC 100 h step except of electrochemical characterization and it is possible that the degradation rates shown in Table 14 contain some reversible parts. In any case, injection of impure $H_2$ as a fuel is responsible for the elevated FC performance losses.

The second constant current step was applied to the cells after NEDC 100 h. Figure 5 shows voltage profiles for all the cells and polarisation curves for the 2 ppm ammonia case.

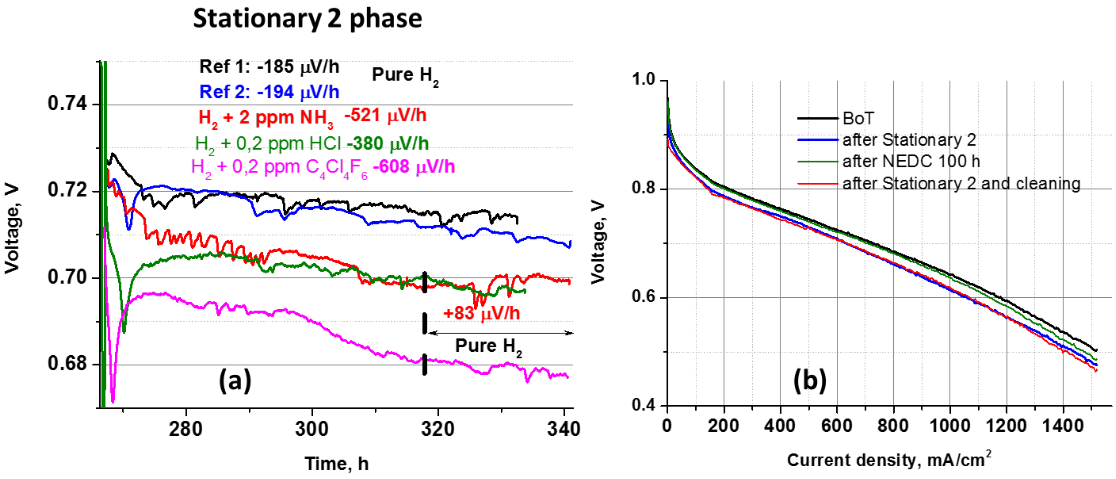


**Figure 5. Voltage degradation curves for the cells tested with and without the impurities in $H_2$ for 48 h and in pure $H_2$ for 24 h at constant current density of 0.6 A/cm$^2$ with corresponding performance loss rates (a); polarisation curves for the cell tested with $H_2$ + 2 ppm of $NH_3$ on the anode side recorded at different steps of electrochemical test protocol (b).**

Test protocol included cell operation with contaminants in harmonized automotive conditions (G. Tsotridis, 2015) at 50% / 30% RH for 48 h and further operation in the same conditions, but in pure $H_2$ for 24 h to see if the impact of pollutants can be mitigated without changing relative humidity. The common trend for increased total performance losses in presence of $H_2$ pollutants is clearly visible in Figure 5(a) similar to previous steps of the electrochemical test. In case of ammonia contamination there is a slight performance recovery (+83 µV/h) via operation in pure $H_2$ and no voltage recuperation for the cells tested under $H_2$ + HCl and $H_2$ + $C_4Cl_4F_6$. Electrochemical characterization was conducted after cleaning procedure, which consisted of 6 h FC operation at constant current in $H_2$ at 100 % RH. Irrecoverable voltage degradation rates are shown in Table 15.

**Table 15. Irreversible FC performance degradation rates calculated based on polarisation curves measured before and after Stationary 2 phase of the electrochemical test**

| | **Reference** | **2 ppm $NH_3$** | **0,2 ppm HCl** | **0,2 ppm $C_4Cl_4F_6$** |
|---|---|---|---|---|
| **Irreversible degradation rates after Stationary 2 phase @ 0.6 A/cm$^2$, µV/h** | 0 | -208 | +42 | +20 |

According to the data of Table 15, the highest irreversible loss was observed for the ammonia contaminant. Evolution of polarisation curves for this cell is depicted in Figure 5(b). Application of cleaning protocol for 6 h at 100% RH after 24 h at 50% / 30% RH did not give any considerable performance improvement (blue and red curves in Figure 5(b)). Possible mechanism for the FC poisoning by $NH_3$ impurity in fuel stream will be discussed in the next sub-chapter. The cells tested with HCl and $C_4Cl_4F_6$ demonstrated some performance recovery after Stationary 2 phase. Probably it is due to cleaning protocol application and recuperation of a part of performance loss induced earlier by NEDC 100 h step.

The last stage of the electrochemical test was 500 h operation using NEDC protocol. The resulting voltage profiles are shown in Figure 6(a). The same method of data extraction at 0.6 A/cm$^2$ was applied as in Figure 4(b).

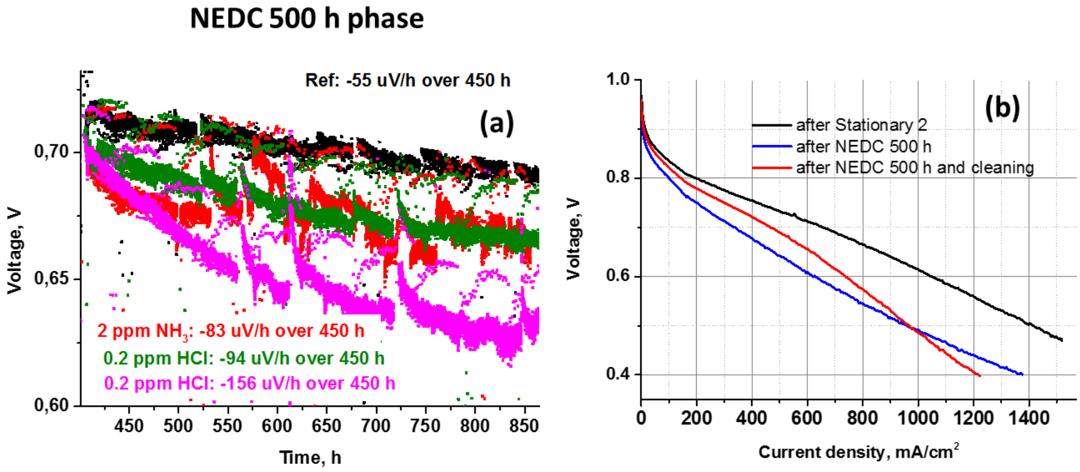


**Figure 6. Extracted FC voltage at 0.6 A/cm$^2$ for the cells tested with and without the impurities in hydrogen using NEDC protocol for 500 h (a); I-V curves recorded for the FC tested with $H_2$ + 0.2 ppm $C_4Cl_4F_6$ at the anode side before and after NEDC 500 h phase.**

One can see a pronounced effect of impurities on the total voltage degradation rates in Figure 6(a). Reference cell tested with pure $H_2$ has the lowest slope of voltage decay. Fluctuation of voltage is observed for ammonia impurity similar to NEDC 100 h phase in Figure 4(a). The highest total and irreversible performance loss was found for $C_4Cl_4F_6$ impurity in Figure 6 and Table 16. Figure 6(b) depicts dramatic performance loss during NEDC 500 h phase for this cell (black and blue curves). However, application of cleaning protocol for 36 h at 100% RH partially recovers the cell performance in activation and ohmic zones of the I-V curve up to 0.9 A/cm$^2$ while compromising mass-transfer region performance at higher current densities, Figure 6(b).

**Table 16. Irreversible FC performance degradation rates calculated based on polarisation curves measured before and after NEDC 500 h phase of the electrochemical test**

| | Reference | 2 ppm $NH_3$ | 0,2 ppm HCl | 0,2 ppm $C_4Cl_4F_6$ |
|---|---|---|---|---|
| **Irreversible degradation rates after NEDC 500 h phase @ 0.6 A/cm$^2$, µV/h** | -19 | -7 | -38 | -103 |

The cells tested with ammonia and HCl show moderate irreversible performance losses, Table 16.

Total and irreversible FC performance loss rates for all the steps of the test protocol are summarized in Figure 7.

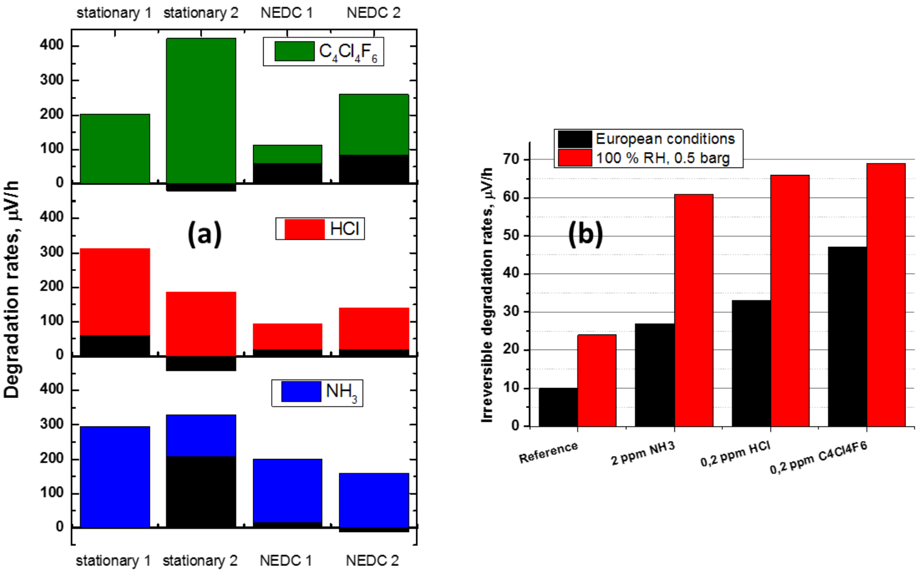


**Figure 7. Coloured column bars represent total FC performance degradation rates induced by each impurity at different steps of the test, the rates for the reference cell tested in pure $H_2$ are subtracted. Black column bars shows irrecoverable parts of performance decay. Stationary 1, 2 phases are compared at 48 h scale while NEDC 1 and NEDC 2 at 100 h and 500 h, correspondingly (a). Irrecoverable losses for the FCs calculated on the basis BoT and EoT (~900 h) polarisation curves recorded in European harmonized conditions and at 100% RH on both sides (b).**

Thus, looking at Figure 7(a), showing in colour total performance losses provoked by injection of each impurity, it is evident that using constant current test protocol leads to higher FC degradation compared to dynamic one (except of NEDC 500 h case for $C_4Cl_4F_6$). It can be accounted for by the fact that in case of stationary performance all the negative effects by impurities are cumulated via adsorption on the catalyst surface and blocking its active sites. When current density changes and especially increases, there is more water generation leading to partial washing-off of contaminants from the catalyst surface. In addition, using NEDC dynamic test protocol provokes short time overvoltages at the electrodes resulted in partial desorption and electrochemical reduction or oxidation of the impurities and their removal.

Irreversible performance losses are much lower compared to the total ones in Figure 7(a) (black column bars). It should be kept in mind that this difference between reversible and irreversible losses is also due to cell cleaning procedure applied before taking polarisation curves. Therefore, Figure 7(a) represents a situation when FC is periodically cleaned by operation in pure $H_2$ at low or high RH and subjected to CV scans, which helps to clean the catalyst surface. The picture can be changed to much higher FC performance losses in case of constant operation of a FC with impurities. “Positive” degradation rates in Figure 7(a) for some test steps, which in fact means cell recovery, are due to application of more efficient cleaning procedures at the end of a step compared to previous stage of the test.

Finally, considering irrecoverable FC performance degradation over full test (~900 h with FC break-in, main test, characterization and cleaning) shown in Figure 7(b), it is clear that reference cell tested in pure $H_2$ is the least impacted one. All the impurities are responsible for additional irreversible FC characteristics degradation. For all the cells degradation rates in European harmonized conditions are lower compared to 100% RH conditions, but demonstrate the same trend. This is due to the fact that at 100% RH flooding of the cell is favourable and even slight loss of hydrophobicity by microporous or gas diffusion layers of the MEA impedes mass transfer by excess of cumulated water. Therefore at 100% RH a FC is much more sensitive to MEA degradation phenomena. The most important performance loss was found for the cell tested with $C_4Cl_4F_6$, Figure 7(b) and possible reasons will be discussed in the next section.

### 3.3.3.2 RESULTS OF ELECTROCHEMICAL CHARACTERIZATION

*EIS spectra*

Electrochemical diagnostics of the cell was conducted at the BoT, EoT and after each step of the test protocol before and after cell cleaning procedure. It allows monitoring of the FC state of health. Figure 8 shows evolution of impedance spectra for each cell during ~900 h test.

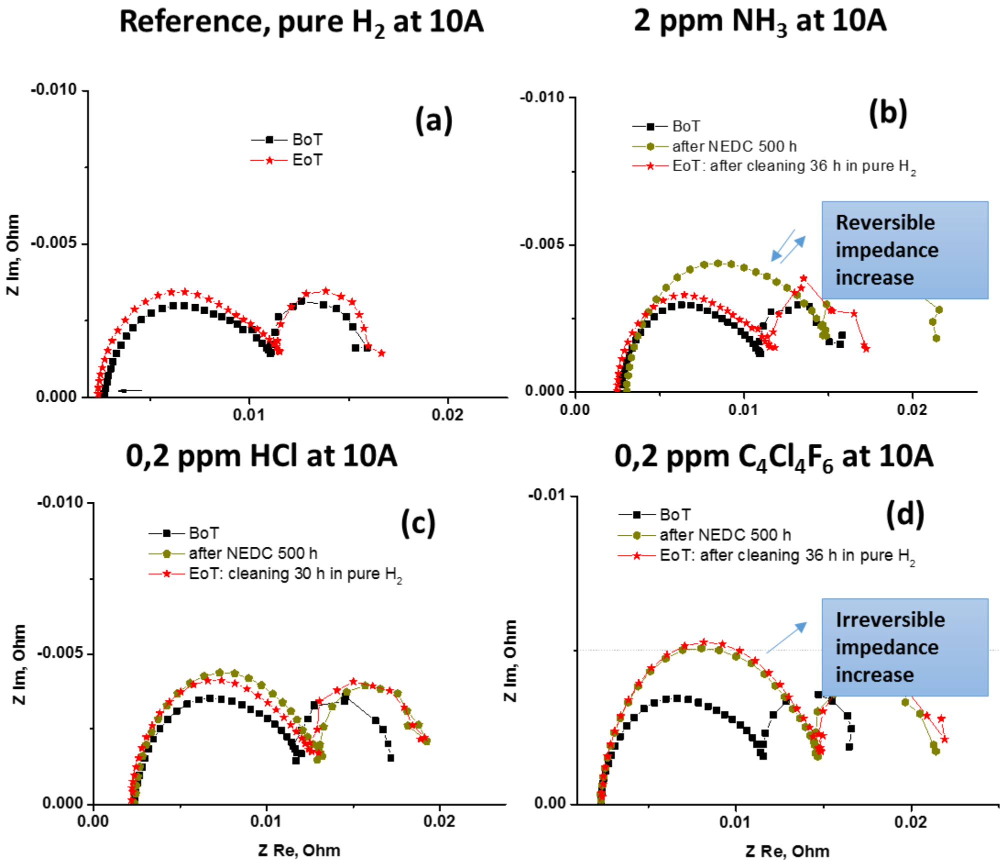


**Figure 8. Electrochemical impedance spectra taken at a constant current of 10 A and 0.8 A amplitude between 30 kHz and 0.1 Hz at different points of electrochemical test protocols for the FC tested with different fuel compositions: pure $H_2$ (a); $H_2$ + 2 ppm $NH_3$ (b); $H_2$ + 0.2 ppm HCl (c); $H_2$ + 0.2 ppm $C_4Cl_4F_6$ (c).**

In general, the obtained spectra consist of two semicircles. The first one is usually attributed to the charge transfer resistance phenomena related to main electrochemical reactions in a FC: oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) (Zhang, 2008). The largest contribution belongs to ORR since the kinetics of this reaction is much slower compared to HOR. The second smaller semicircle reflects transport phenomena (Zhang, 2008). Figure 8 demonstrates that BoT impedance for all 4 cells is quite reproducible. The size of the 1st semicircle is slightly increased by the EoT for the reference cell in Figure 8(a). Both semicircles were considerably enlarged after NEDC 500 h step for the FC tested with 2 ppm $NH_3$, Figure 8(b). It is interesting that this cell impedance growth was mostly reversible by operation in pure $H_2$ for 36 h as shown by red stars in Figure 8(b).

The mechanism for the FC contamination with ammonia was proposed previously. Uribe et al. proposed that ammonia in PEMFC can interact with protons of ionomer and membrane thus decreasing protonic conductivity (F.A. Uribe, 2009). This process can be described by the following equation:

**$NH_3$ + Nafion-$H^+$ ↔ Nafion-$NH_4^+$ Equation 3**

Also it was suggested that $NH_3$ is able to adsorb onto anode and cathode side catalyst surfaces inhibiting ORR and HOR (F.A. Uribe, 2009). The findings of the present work are in agreement with the proposed mechanisms. Considerable reversibility of the cell performance after contamination with $NH_3$ via operation in pure $H_2$ (see for example Figure 5(a) and Figure 8(b)) can be explained by desorption of ammonia from catalyst surfaces through pure $H_2$ flux. Cleaning of the FC at 100% RH was also efficient because it allowed reverse exchange of $NH_4^+$ to $H^+$ in the ionomer structure, Equation 3.

The cell tested in $H_2$ + 0.2 ppm HCl demonstrated an increase in both charge transfer ad transport resistance at the EoT, which was characterized by minor reversibility upon cleaning, Figure 8. It can be related to physical desorption of $Cl^-$ anions from the catalyst surface, as described in section 3.3.3.1. The origins of irreversible losses are probably due to the processes depicted by Equation 1 and Equation 2.

The impact of $C_4Cl_4F_6$ impurity on a FC performance was the most intriguing. As was shown in chapter 3.3.3.1, this cell demonstrated the highest reversible and irreversible degradation rates during the electrochemical test. It is in line with EIS results in Figure 8(c), where important and highly irreversible resistance growth is shown. We propose that $C_4Cl_4F_6$ molecule is decomposed on Pt catalyst surface in the conditions of fuel cell test and large amount of $Cl^-$ and $F^-$ ions is released. The possible mechanisms for FC poisoning by $Cl^-$ ions are described above while $F^-$ ion should not contribute much to the performance loss since this is a usual product of a FC membrane degradation (A. Kosoglu, 2017).

### *Cyclic voltammetry*

A method of cyclic voltammetry is a good measure of the electrochemical surface area for the catalysts. It is based on adsorption and desorption of a monolayer of hydrogen on Pt, which gives clear cathodic and anodic peaks on a CV curve. Integration of those peaks after a baseline correction allows calculation of ECSA. Figure 9 compares cathode and anode CVs obtained for the cells tested in pure $H_2$ and in $H_2$ + $C_4Cl_4F_6$.

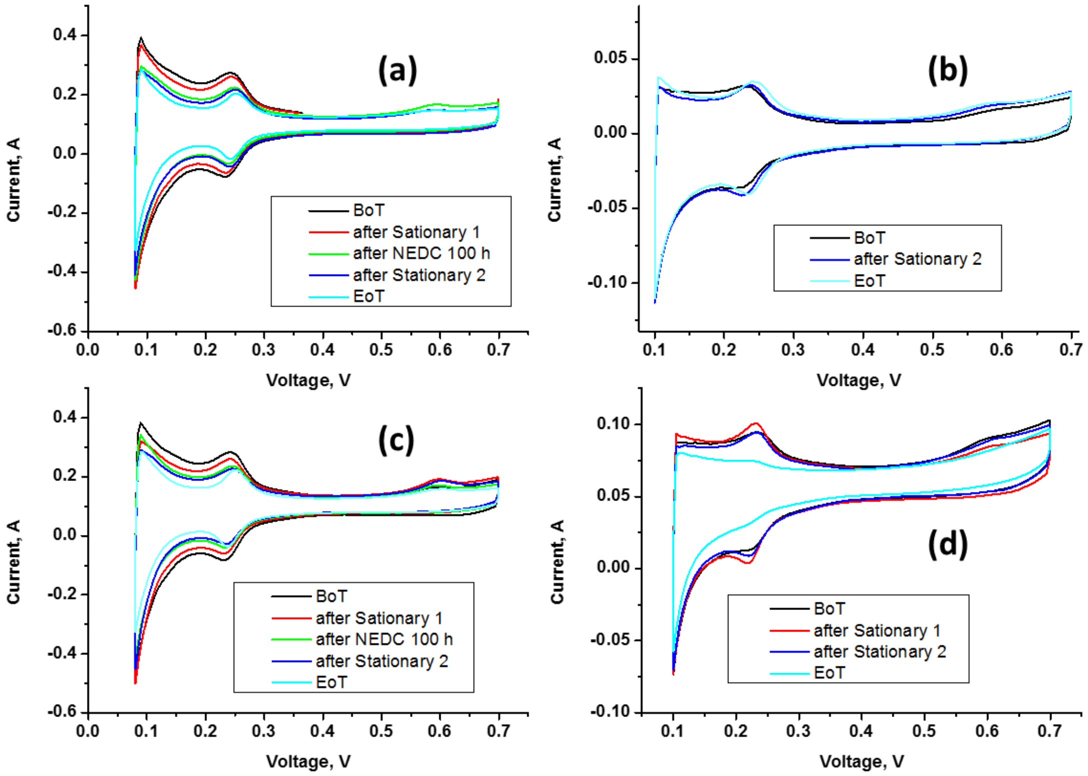


**Figure 9. Cyclic voltammograms taken at the cathode side of a FC with $N_2$ supplied at the cathode and $H_2$ supplied at the anode side, 80°C, 100% RH, 50 mV/s between 0.08 and 0.7 V vs RHE for the reference cell (a), for the cell tested with 0.2 ppm of $C_4Cl_4F_6$ (c); anode side voltammograms obtained by turning of a FC in same conditions for the reference cell (b) and for the cell tested with 0.2 ppm of $C_4Cl_4F_6$ (d).**

These two cells were chosen due to the fact that the reference cell showed the smallest degradation rate while that one tested with $C_4Cl_4F_6$ demonstrated maximum performance loss. Comparison of cathode side CVs in Figure 9 (a) and (c) leads to a conclusion that cathode catalyst active surface was severely reduced in both cases between the BoT and the EoT. It seems that there is no direct correlation between the electrochemical performance of the cell and its cathode ECSA in the conditions of the test. On the contrary to cathode side results, there is a clear difference in the evolution of the anode side catalyst ECSA for the two cells in Figure 9 (b) and (d). Anode ECSA for the reference cell seems to be stable over the test while there is a dramatic drop in ECSA between Stationary 2 and NEDC 500 h steps for the cell tested with $C_4Cl_4F_6$.

Comparison of relative ECSA evolution for all the cells in Figure 10 confirms the trends described above.

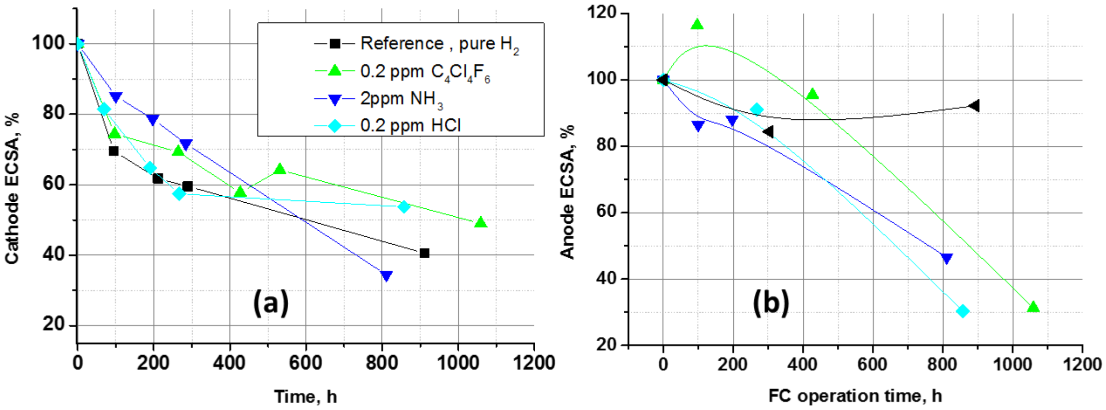


**Figure 10. Calculated relative changes of anode and cathode ECSAs for the cells tested with different fuel composition.**

There is very significant cathode ECSA decrease for all the cells (50-60% loss) in Figure 10(a). However, anode ECSA evolution was strongly related to presence or absence of the impurities in hydrogen, Figure 10(b). All three hydrogen contaminants provoked important reducing of the anode ECSA. It should be mentioned that the ECSAs obtained for the reference cell are reproducible since 2 parallel cells were tested. It is suggested that in presence of contaminants anode ECSA can be lost via Pt dissolution, nano-particle growth or irreversible blocking of the active catalytic sites (S. M. M. Ehteshami, 2016). In case of ammonia, protonic conductivity of the anode active layer can be considerably reduced in addition to above mentioned factors.

*Liner sweep voltammetry*

LSV was monitored after each step of the electrochemical test. This is a measure of membrane performance in terms of $H_2$ permeation from the anode to the cathode sides. Increase of $H_2$ permeation current means chemical and mechanical membrane decomposition. No any considerable change of $H_2$ permeation current was found for all the tested cells between BoT and EoT. Therefore, it is concluded that membrane degradation did not contribute to the observed differences in FC performance in presence and in absence of the impurities.

### 3.3.3.3 POST-MORTEM MICROSCOPY OBSERVATIONS

After completing electrochemical tests FC were dismantled and recovered MEAs were cut to prepare cross-section samples via embedding in epoxy-resin. Scanning Electron Microscopy (SEM LEO, 10 kV) has been performed to observe the thickness and morphology of MEA components. Figure 11 shows SEM images for a pristine MEA and once after electrochemical tests. Surface bubbles in Figure 11(e) are due to sample preparation.

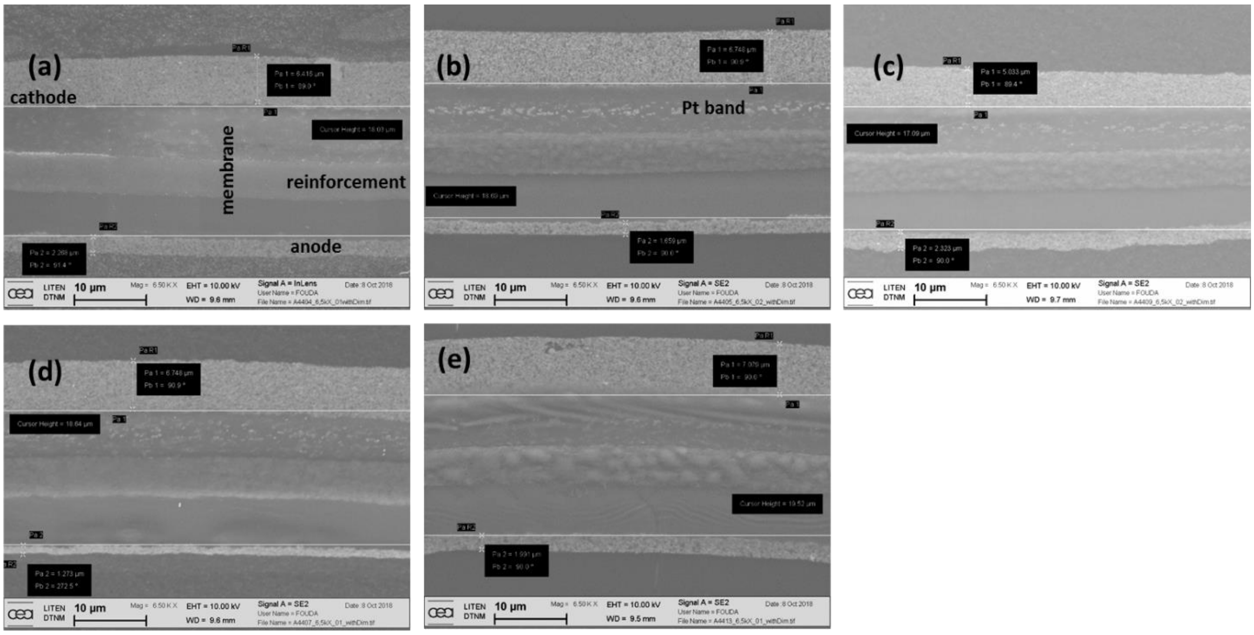


**Figure 11. Cross-section SEM images for the MEAs: pristine (a); after full electrochemical test and cell recovery protocol for the cell tested in pure $H_2$ (b), with 2 ppm $NH_3$ (c); with 0.2 ppm $C_4Cl_4F_6$ (d) and 0,2 ppm HCl (e).**

The thickness of cathode active layer (on the top of each image) was around 5-7 µm and seems not to change a lot after electrochemical tests. Reduction in cathode ECSA for the catalysts demonstrated in Figure 9 (a) and (c) and obtained using CV method is not directly related to the active layer thickness. Such mechanisms as Pt dissolution and Ostwald ripening are responsible for the cathode active surface loss (P. J. Ferreira, 2005). The evidence of Pt dissolution is shown in Figure 11. For the pristine MEA there are some bright deposits in the upper part of the membrane in Figure 11(a). These are Pt particles, which are incorporated into this type of a membrane by a manufacturer. These deposits became larger and more evident for all the cells after electrochemical tests in Figure 11(b)-(e).This phenomena is known as Pt electrochemical dissolution at the cathode side due to exposure to high potentials (>0.85 V vs RHE). $Pt^{2+}$ ions diffuse into a membrane where they are reduced chemically by hydrogen crossing over form the anode side of a FC according to the following equation:

$$\mathbf{H_2 + Pt^{2+} \rightarrow 2H^+ + Pt^0} \qquad \textbf{Equation 4}$$

This leads to a formation of Pt precipitation band in the membrane, Figure 11 (b)-(e). Nevertheless, despite of Pt loss by the active catalyst layer, the integrity of carbon/ionomer matrix is maintained after electrochemical tests, as clear from comparison of Figure 11(b)-(e) and Figure 11(a).

The thickness of a reinforced membrane also did not show much difference (17-19 µm) for the pristine and tested cells. Thus, membrane degradation did not take place during ~900 h test, which is also confirmed by the absence of $H_2$ permeation current increase (see 3.3.3.2). Interesting observation can be found via comparison of the anode active layers in Figure 11. Initially this active layer was thinner that the cathode one for all the cells and in addition the impurities were injected directly to the anode side for some of the cells. Anode catalyst layer thickness is varied between 1.6 and 2.3 µm after the tests. Again, similar to cathode side catalyst evolution, there is no straightforward relationship between the catalyst layer thickness and ECSA for the Pt-based catalyst (see 3.3.3.2). Thus, cells tested with $NH_3$ and HCl demonstrated high anode ECSA decay in Figure 10(b) while a morphological aspect of the active layers look similar to the pristine and reference MEAs, Figure 11. However, the anode catalyst layer for the cell tested with $C_4Cl_4F_6$ was depleted after the electrochemical testing. Figure 11(d) clearly shows morphological differences for this cell: its anode active layer is dense with no visible porosity, it is thin and it has a bright contrast on a SEM image. This can be a consequence of a massive carbon corrosion, compaction and loss of integrity for the carbon/ionomer matrix in addition to Pt dissolution.

We hypothesise that $C_4Cl_4F_6$ molecule can be adsorbed on a Pt surface, thus increasing HOR overpotential and favouring Pt dissolution. Further, organohalide compound can be partially catalytically decomposed with a formation of $Cl^-$ and $F^-$ ions thus activating additional mechanisms for Pt dissolution according to Equation 1 and Equation 2. More detailed investigation is necessary to clarify the mechanism of FC poisoning with $C_4Cl_4F_6$ contaminant. This is of high scientific and practical interest since this compound was found in real $H_2$ sample from HRS.

### 3.3.4 Estimation of acceptable concentrations of the contaminants in $H_2$

To compare the results obtained in the present study with existing $H_2$ quality standard ISO14687-2, calculations of the acceptable concentrations of the impurities were done. DOE technical target 2020 (DOE Fuel Cell Technologies Office. 2016 Multi-Year Research, Development, and Demonstration Plan, 2016) was taken. It suggests a criteria of <10% rated power loss for the fuel cell over 5000 h operation time. In the present work 0.6 $A/cm^2$ current density was chosen for calculation of performance losses. The latter was done based on polarisation curves after cell cleaning procedure, i.e. mostly only irreversible FC performance degradation was taken into account. First of all, lifetime for the reference cell was estimated before attaining of 90% of the initial performance (7500 h, Figure 12).

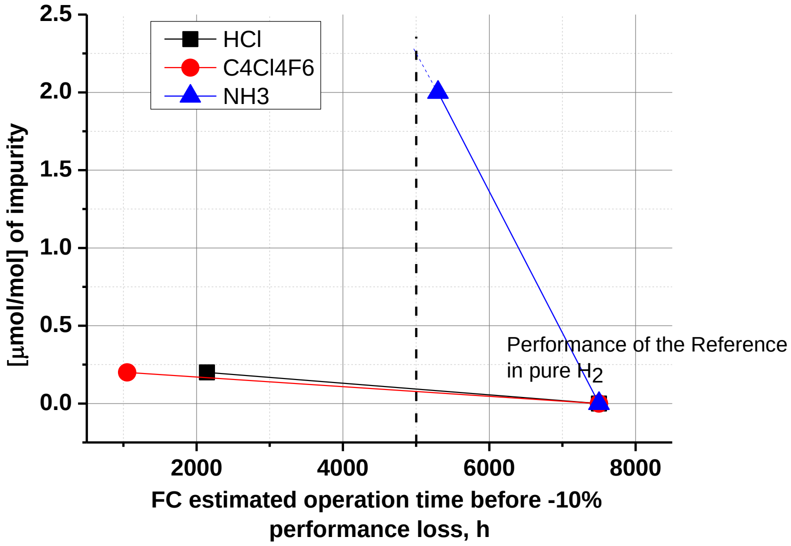


**Figure 12. Extrapolation of a FC operation time to 5000 h based on linear relationship between the concentration of impurity in $H_2$ and FC performance loss.**

After, lifetimes for the FC cells tested with the impurities were calculated using -10% performance criteria. Two main assumptions were made: 1) linear impact of the $H_2$ contaminant on a FC performance and 2) linear character of cell degradation with time. Finally, acceptable impurity concentration limits were extracted via extrapolations in Figure 12. It is clear that in reality the relationships between the main cell performance characteristics are not linear and need to be investigated in more details for each impurity concentration and experimental condition. However, an approach used in this work allows rough estimation of threshold impurity concentrations based on a FC degradation data obtained over 900 h and under dynamic load cycling. The calculated threshold concentrations for the impurities are summarized in Table 17.

**Table 17. Existing ISO14687-2 thresholds for the three fuel hydrogen contaminants and calculated values based on the results of the present work**

| Impurity in $H_2$ | [mmol/mol], taken for study in FC | Threshold calculated, [mmol/mol] | ISO14687-2 threshold value, [mmol/mol] |
|---|---|---|---|
| $NH_3$ | 2 | 0.90 | 0.1 |
| HCl | 0.2 | 0.09 | 0.05 |
| $C_4Cl_4F_6$ | 0.2 | 0.08 | 0.005 |

According to the results, ammonia threshold concentration might be relaxed since there is 9 fold difference between the existing and calculated values in Table 17. The limiting concentrations of HCl are in a good agreement. A threshold for $C_4Cl_4F_6$ is referred to halogen atom according to ISO14687-2, which is why it is 10 times lower compared to HCl acceptable concentration. However, based on polarisation curves and our method of calculation, there is no such a dramatic difference in acceptable threshold concentrations for the two halogen-based $H_2$ impurities. It can be related to the fact that $C_4Cl_4F_6$ molecules were only partially decomposed on a Pt catalyst surface. It is important to emphasize that the calculated threshold values in Table 17 are just estimation based on few simple assumptions and they are valid for given test conditions. Adoption of these thresholds for wide range of fuel cell stack designs, different impurity concentrations and various test conditions require further investigation.

# 4 Discussion and recommendations

## 4.1 Probability of contaminant presence and analytical campaign

### 4.1.1 Discussion on PEM Water electrolysis with TSA results

The results of analytical campaign for PEM water electrolyser with TSA agreed well with the expert study on probability of presence of contaminants. Within the 8 samples analysed, no contaminants were observed above the threshold of ISO 14687-2. It agrees with the fact that all contaminants were unlikely, rare or very rare.

Even if the number of sampling performed would not statically allow seeing event with the frequency proposed in Table 2, it provides the first technical evidences on contaminant amount fraction at the production process.

**Table 18. Summary of probability of contaminant presence and analytical campaign for PEM water electrolysis (*: LOD is too high for perfect assessment, a better analytical method required).**

| Probability of impurity presence | risk assessment by experts | Analytical campaign | Risk of occurrence confirmed |
|---|---|---|---|
| **Water** | 2 | Confirmed, all samples below ISO 14687-2 threshold | 2 |
| **$CH_4$** | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| **Total hydrocarbon** | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| **oxygen** | 2 | Confirmed, all samples below ISO 14687-2 threshold | 2 |
| **helium** | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| **$N_2$** | 2 | Confirmed, all samples below ISO 14687-2 threshold | 2 |
| **Ar** | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| **CO** | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| **$CO_2$** | 1 | Confirmed, all samples below ISO 14687-2 threshold | 1 |
| **Total S** | 0 | *Confirmed, all samples below ISO 14687 threshold | 0 |
| **Formaldehyde** | 0 | *Confirmed, all samples below ISO 14687-2 threshold | 0 |
| **Formic acid** | 0 | *Confirmed, all samples below ISO 14687-2 threshold | 0 |
| **Ammonia** | 0 | *Confirmed, all samples below ISO 14687-2 threshold | 0 |
| **HCl** | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |

According to the expert risk assessment water and oxygen were rated with a probability of rare (rating 2) which is coherent with the results obtained for PEM water electrolysis without TSA. The purification is eliminating the only contaminants present above the threshold in the production process. Therefore the risk for oxygen and water is coherent with the process contaminants observed in the analytical campaign.

Carbon dioxide is presented with a very rare probability of presence (rating 1). The rating is coherent with the results of analysis showing an amount of carbon dioxide in the hydrogen before purification and none after purification. Therefore the risk for carbon dioxide is coherent with the process contaminant observed in the analytical campaign.

The probability of presence for nitrogen is linked to the commissioning and maintenance of the installation. Therefore, it is difficult to observe nitrogen contamination in normal operation. The risk is linked to an issue in the maintenance and purging procedure of the installation.

An important point is the difficulty to obtain sample from maintenance or of electrolyser with technical issue. It should be bear in mind that all results of analysis were obtained from electrolyser performing as expected.

### 4.1.2 Discussion on steam methane reforming with PSA results

The results of analytical campaign for SMR with PSA agreed well with the expert study on probability of presence of contaminants. Within the 8 samples analysed, no contaminants were observed above the threshold of ISO 14687-2. Even if the number of sampling performed would not statically allow seeing event with the frequency proposed in the table 2, it provides the first technical evidences on contaminant amount fraction at the production process. In the case of carbon monoxide, it is difficult to observe variation of the process within a few sampling. However, it enhances the fact that the expert study is conservative. The probability of presence for nitrogen is linked to the commissioning and maintenance of the installation. Therefore, it is difficult to observe nitrogen contamination in normal operation. The risk is linked to an issue in the maintenance and purging procedure of the installation. An important point is the difficulty to obtain sample from maintenance or of electrolyser with technical issue. One should be bear in mind that all results of analysis were obtained from electrolyser performing as expected.

**Table 19. Summary of probability of contaminant presence and analytical campaign for steam methane reforming with PSA (*: LOD is too high for perfect assessment, a better analytical method required).**

| Probability of impurity presence | risk assessment by experts | Analytical campaign | Risk of occurrence confirmed |
|---|---|---|---|
| water | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| CH4 | 2 | Confirmed, all samples below ISO 14687-2 threshold | 2 |
| Total hydrocarbon | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| oxygen | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| helium | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| N2 | 3 | All samples below ISO 14687-2 threshold | 3 |
| Ar | 2 | All samples below ISO 14687-2 threshold | 2 |
| CO | 4 | All samples below ISO 14687-2 threshold | 4 |
| CO2 | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |
| Total S | 0 | *Confirmed, all samples below ISO 14687 threshold | 0 |
| Formaldehyde | 1 | *Confirmed, all samples below ISO 14687-2 threshold | 1 |
| Formic acid | 0 | *Confirmed, all samples below ISO 14687-2 threshold | 0 |
| Ammonia | 0 | *Confirmed, all samples below ISO 14687-2 threshold | 0 |
| HCl | 0 | Confirmed, all samples below ISO 14687-2 threshold | 0 |

## 4.2 Recommendations

### 4.2.1 Quality control for hydrogen – ISO 19880-8

The consortium study provided examples of probability of contaminant presence from SMR with PSA and PEM water electrolysis with TSA with measurements of all contaminants requested in ISO 14687-2.

Even if the analytical measurements and the expert studies agreed well, the project only investigated two of the main hydrogen productions processes. The alkaline electrolyser was presented in the annex of ISO 19880-8 however no analytical measurements of alkaline electrolyser hydrogen quality are currently available from this source. Chlor-alkali production process presents complexity for analytical purposes due to the low pressure of the process (~ 2bar). The analysis by all the NMIs requires more than 100 Litres of gas which made it extremely complex for this project to obtain production samples. Even if an important range of production sites have been investigated in the EMPIR Hydrogen project, the project scope did not enable a wide assessment of production sites around Europe. New production methods are emerging (i.e. autothermal reformer, biogas reforming) and would require to be assessed for contaminants following the procedure detailed in this report as steam methane reforming and PEM water electrolysis.

The requirement of ISO 19880-8 is to understand the probability of contaminant presence over the whole supply chain. The project tackled with the probability of contaminant presence in hydrogen at the production sites only. The next steps would be also to investigate probability of contaminant presence from the transport (pipeline, hydrogen carrier, storage) and from HRS infrastructure (compressor, high pressure buffer, and nozzle) in order to provide technical evidences for complete probability of presence of contaminant from feedstock to nozzle.

The imminent publication of ISO 19880-8 will benefit and support industrial hydrogen actors. Nevertheless, it should provide guidance and technical evidences to support the industrial expert. It could be evaluating the most likely contaminants present at each point of the supply chain through analytical measurements providing a first understanding of the contaminants and their amount fraction at each step of the supply chain.

The results of the studies demonstrated that only few contaminants need to be monitored on regular basis for the production method. These results would have a significant impact in the amount of analysis and analytical infrastructure required to monitor hydrogen quality. In the objective of hydrogen cost efficiency, it will significantly reduce the cost of the quality control without impacting the quality of hydrogen. The implementation of the probability of contaminant presence with technical evidences would support a restricted scope of analysis and orientate the development of online analyser and routine laboratories instrumentation.

The four recommendations are:

- Investigate new production processes and analyse hydrogen quality from these new production processes
- Investigate the supply chain including analysis of contaminants from each components of the supply chain
- Provide training and guidance on the implementation of probability of presence of contaminants according to ISO 19880-8
- Establish the hydrogen quality monitoring plan on real case scenario and its benefit in term of cost and reliability of the HRS

### 4.2.2 Hydrogen specification – ISO 14687-2

Results described in section 3.3 clearly demonstrate that each of the investigated impurity ($NH_3$, HCl or $C_4Cl_4F_6$) has its own specific impact on a FC performance. The common feature was high reversible FC performance losses provoked by the impurities, which was clear from the cell voltage profiles at constant and dynamic current loads. This means that constant presence of the contaminants in the concentrations used in this study will quickly destroy any FC system. Considering short-term FC exposure to contaminated $H_2$, no irreversible performance losses were found for the cells tested for 48 h with 2 ppm $NH_3$ and 0.2 ppm $C_4Cl_4F_6$. Therefore, short time injection of the two contaminants can be recoverable in the conditions of the experiment. It should be kept in mind that reversibility of the negative impact of contaminants was achieved via 40 h of operation in pure $H_2$ at 100% RH and applying CV scans. It seems that washing-off of the impurities with water flux through a FC at high RH is efficient cleaning strategy in case of pollutant adsorption or cationic exchange with a membrane. FC system recovery protocols should be available on-board of a FC vehicle in case of fuel contamination. Operation of a FC with contaminated $H_2$ over a long term always led to accumulation of irreversible degradation of MEA even if cleaning procedures were applied periodically.

Based on threshold calculations done in this work for the three contaminants, it can be concluded that the data for HCl was found to be in good agreement with the existing ISO 14687-2 standard. Relaxing of a threshold of 0.1 µmol/mol for ammonia to slightly higher value (0.2 – 0.5 µmol/mol) was possible based on the results obtained thanks to quite high reversibility of the effect of this $H_2$ contaminant. The impact of $C_4Cl_4F_6$ appeared to be the most important among the three impurities. Calculated threshold of 0.08 µmol/mol should be adjusted in a more detailed study taking into account necessary conditions for $C_4Cl_4F_6$ decomposition. It is reasonable to suggest that chloride anions forming upon breaking of the organohalide have the most detrimental impact on a FC performance.

The recommendations are:

- Investigate new contaminants as it was done for $C_4Cl_4F_6$ to allow the industry to evaluate its real impact
- Propose revision of the three contaminants threshold or further studies

### 4.2.3 Sampling of hydrogen

Based on the samplings performed within the project, it is obvious that sampling procedure can led to unreliable results. The sampling performed highlighted the importance of purging reaching an optimized sampling procedure and material leak checking. The development of sampling standard or guideline for hydrogen system is an important point to address especially looking at the increase in the number of studies, production plants and hydrogen refuelling stations.

The recommendations are:

- Standardise or provide guideline on sampling
- Evaluate stability of contaminant over time to define if there is an impact of late analysis.

### 4.2.4 Conclusion for further investigation

In the light of the recommendations above, it seems evident that a user-guide is needed for hydrogen industries and the end-user community supporting the monitoring of hydrogen quality. This technical guide would provide recommendations and actions to do according to the selected sampling method, the production process and the location of the sampling in the supply chain (at the exit of the production plant, after or before purification steps, before trailer, at the nozzle…) to provide reliable measurements following standardized specifications.

Hydrogen quality monitoring program has to be deepened extending to the whole supply chain, new production process with end users training and case studies. The assessment of contaminants in hydrogen along the supply chain requires reliable analysis of multiple samples to build up confidence and strong understanding of the probability of presence.

The investigation also has to reach out the level of impact following the end-use of hydrogen and its treatment use according to fuel-cells (old and new generations), injection in grids, feed electrical capacitances or combustion engines. It is obvious that contaminant impact studies are critical to evaluate each contaminants risk for the system. New contaminant found or suspected to be present in hydrogen requires experimental study on impact. Moreover standardization of contaminant impact testing is important especially regarding the testing mode (i.e. static versus dynamic) which presented differences in this report. All these considerations should drastically reduce the cost of hydrogen quality control without degrading the fuel reliability. Following the recommendations proposed in this report should support a quick implementation of ISO 19880-8, improve HRS reliability and reduce drastically the cost of hydrogen quality control. In a middle term, the report should support future revision of the ISO 14687 standard.

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# 6 Annexes

| | |
|---|---|
| **Annex 1** | **Report on probability of presence of impurities of the Steam Methane Reforming Process + Pressure Swing Adsorption (PSA)** |
| **Annex 2** | **Report on probability of presence of impurities of the PEM Water electrolysis process** |
| **Annex 3** | **Report on probability of presence of impurities of chlor-alkali process** |
| **Annex 4** | **Sampling procedure** |
| **Annex 5** | **Results of analysis of hydrogen samples from SMR + PSA** |
| **Annex 6** | **Results of analysis of hydrogen samples from PEM Water electrolysis** |

# Annex 1 Report on probability of presence of impurities of the Steam Methane Reforming process + Pressure Swing Adsorption (PSA)

# Metrology for sustainable hydrogen energy applications

# 15NRM03 HYDROGEN

# Task 1.1: Assessment of probability of impurities existing in real samples of hydrogen

## Report on activity A1.1.1 - Steam methane reforming

**Task 1.1**
**Report on activity 1.1.1**

**January 2017**
**Revision 1**

This work has been carried out by:
Martine Carré / Bruno Gozlan

# Summary

The evaluation of the impurities able to be found in hydrogen produced from steam methane reforming process is done for typical process design with purification by pressure swing adsorption.

The methodology of quality risk assessment is used to evaluate the probability of occurrence of each impurities to be above the threshold value given in the ISO 14687-2.

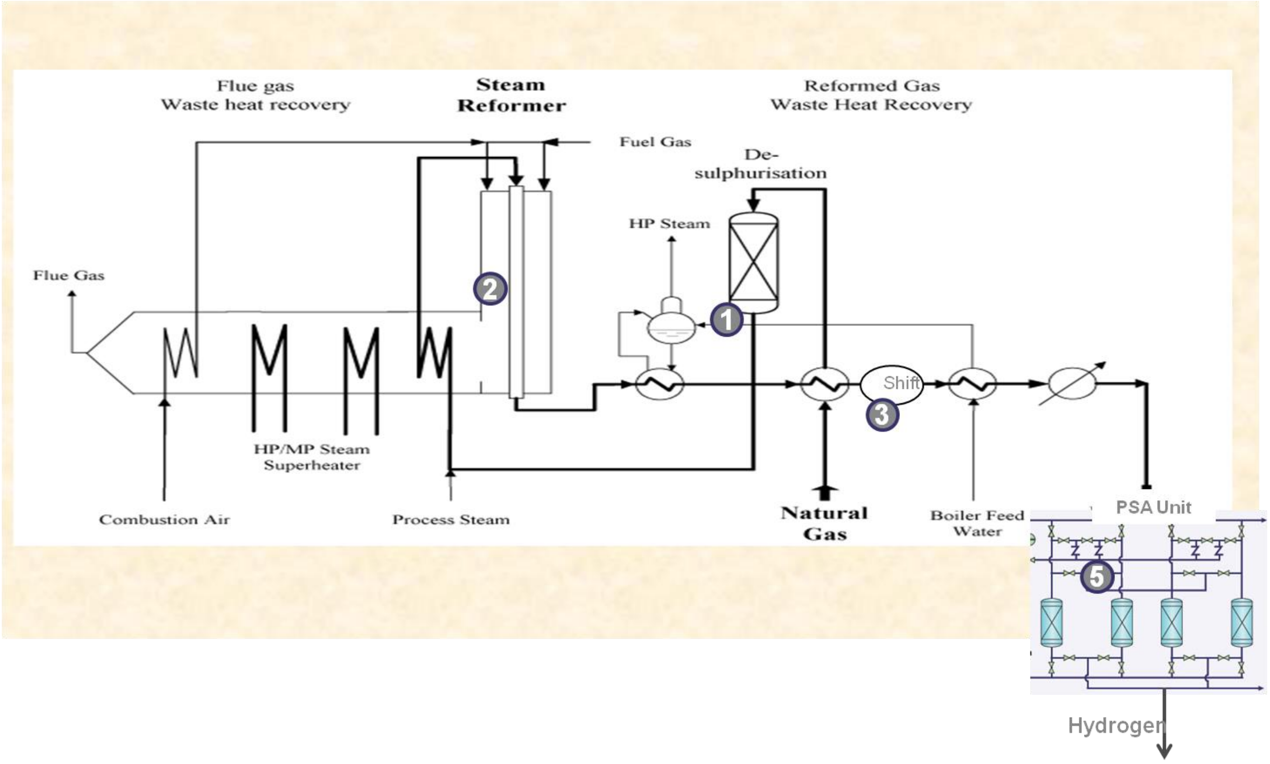
This method was applied to SMR + PSA process and the critical impurities identified are: CO and $N_2$.  Others are possible but with lower probability of occurrence: methane, argon and formaldehyde.

# Table of contents

# 1 Description of Steam Methane Reforming process with Pressure Swing Adsorption

Reforming is the most common $H_2$ production method today. It uses various types of feed-stocks, such as, natural gas, biogas, nafta, methanol, and ammonia. The feed materials natural gas, liquid gas or naphtha are endo-thermically converted with water steam into synthetic gas in catalytic tube reactors: CO + $H_2$ (Syngas). Then, the gas produced is purified by pressure swing adsorption (PSA) systems using specific adsorbents layers.

Our study is based on our internal SMR process which is described in the graph 1:



Graph 1: design of SMR process in Air Liquide

The natural gas used as raw material is first heated and introduced into a desulphurisation system (1). Indeed, there is potential sulphur components in the natural gas like $H_2S$, COS and mercaptans. These species must be removed from the natural gas because the catalysts used in the steam reformer and in the shift reformer are poisoned by sulphur components. Any trace of sulphur will have a detrimental effect on the efficiency of the syngas production. The purification of sulphur compounds should be done up to < 50 ppb and even it is generally below that. In the purification system all sulphur components are transformed in $H_2S$ which is absorbed on a specific adsorbent. Then only $H_2S$ could be observed after this step.

The desulfurized hydrocarbon feed is mixed with superheated process steam in accordance with the steam/carbon relationship necessary for the reforming process (2).

After that, this gas mixture is heated up and then distributed on the catalyst-filled reformer tubes. The gas mixture flows from top to bottom through tubes arranged in vertical rows. While flowing through the tubes heated from the outside, the hydrocarbon/steam mixture reacts, forming hydrogen and carbon monoxide in accordance with the following reactions:

$$CnHm + n\ H_2O \Rightarrow n\ CO + ((n+m)/2)\ H_2 \quad (1)$$
$$CH_4 + H_2O \Leftrightarrow CO + 3\ H_2 \quad (2)$$
$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (3)$$

To minimize the methane content in the synthesis gas while simultaneously maximizing the $H_2$ yield and preventing the formation of elemental carbon and keeping it from getting deposited on the catalyst, the reformer is operated with a higher steam/carbon relationship than theoretically necessary. Moreover a shift reactor (3) is also added to maximize the $H_2$ yield.

As the heat balance for the main reactions (1) - (3) is endothermic; the required heat must be produced by external firing. The burners for the firing are arranged on the ceiling of the firing area between the tube rows and fire vertically downward.

The hydrogen produced is then purified using pressure swing adsorption unit (5). This purifier removes most impurities coming from the reaction. Since, CO and $CO_2$ are the main impurities; the design of these purification units is done to have a specific level of CO at the outlet.

# 2 Quality risk assessment for $H_2$ for fuel cell car: main principles

The two primary principles of quality assurance plan are:

- The evaluation of the risk not to respect the quality requirement should be based on scientific knowledge and ultimately link to the protection of the fuel cell car
- The level of effort to implement the quality assurance process should be commensurate with the level of risk.

As an aid to clearly defining the risk(s) for risk assessment purposes, three fundamental questions are often helpful:

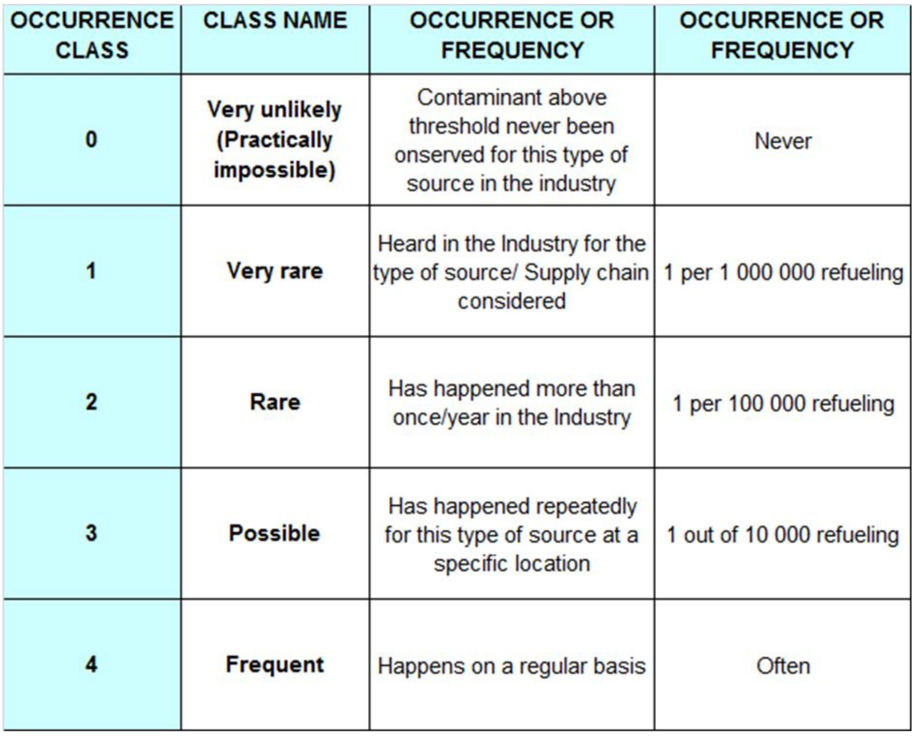
- What might go wrong: which event can cause the impurities to be above the threshold value?
- What is the likelihood (probability of occurrence expressed relative to the number of refueling events) that impurities can be above the threshold value?
- What are the consequences (severity) for the fuel cell car?

In doing an effective risk assessment, the robustness of the data set is important because it determines the quality of the output. Revealing assumptions and reasonable sources of uncertainty will enhance confidence in this output and/or help identify its limitations. The output of the risk assessment is a qualitative description of a range of risk.

For each impurity of the ISO 14687-2 specification and for a given $H_2$ source a risk assessment must be applied to define the global risk for the car user. Risk assessment consists of:

- Identification of the probability of occurrence to have in hydrogen each impurity above the threshold values of specifications given in ISO 14687-2 (see table 1)
- Evaluation of severity level of each impurity for the fuel cell car (see table 2)

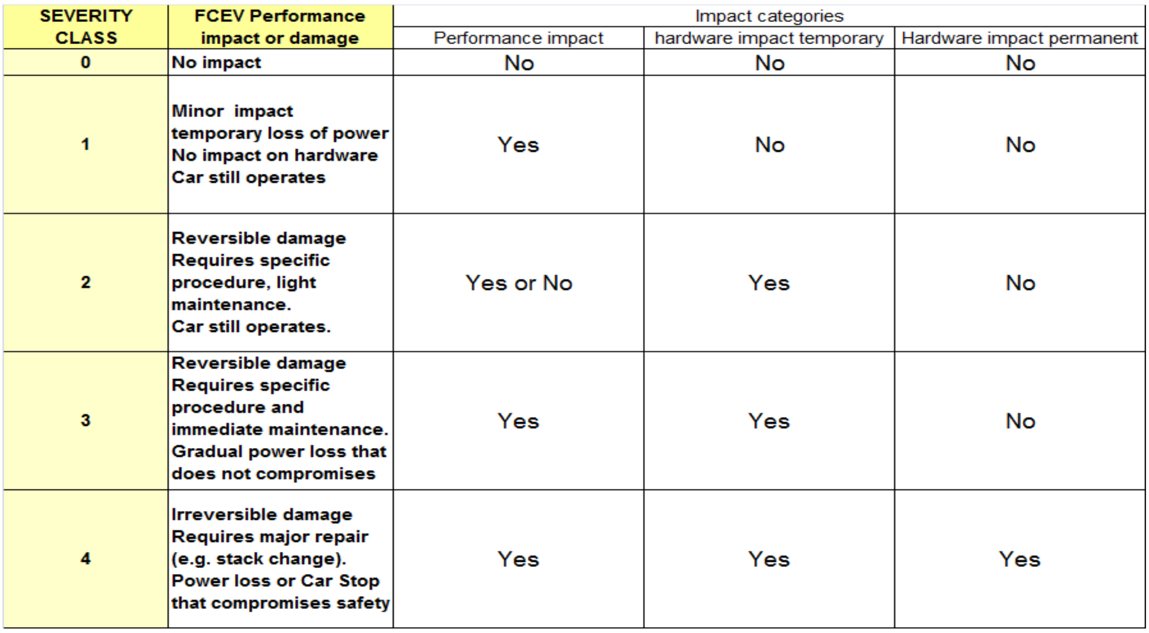
For the probability of occurrence of the event: impurities in hydrogen exceed the threshold value, the following table of occurrence classes has been defined:



| OCCURRENCE CLASS | CLASS NAME | OCCURRENCE OR FREQUENCY | OCCURRENCE OR FREQUENCY |
|---|---|---|---|
| 0 | **Very unlikely (Practically impossible)** | Contaminant above threshold never been onserved for this type of source in the industry | Never |
| 1 | **Very rare** | Heard in the Industry for the type of source/ Supply chain considered | 1 per 1 000 000 refueling |
| 2 | **Rare** | Has happened more than once/year in the Industry | 1 per 100 000 refueling |
| 3 | **Possible** | Has happened repeatedly for this type of source at a specific location | 1 out of 10 000 refueling |
| 4 | **Frequent** | Happens on a regular basis | Often |

Table 1: definition of occurrence classes

The range of severity level (level of damage for vehicle) is defined in the table 2.



| SEVERITY CLASS | FCEV Performance impact or damage | Impact categories | | |
|---|---|---|---|---|
| | | Performance impact | hardware impact temporary | Hardware impact permanent |
| 0 | No impact | No | No | No |
| 1 | Minor impact<br>temporary loss of power<br>No impact on hardware<br>Car still operates | Yes | No | No |
| 2 | Reversible damage<br>Requires specific procedure, light maintenance.<br>Car still operates. | Yes or No | Yes | No |
| 3 | Reversible damage<br>Requires specific procedure and immediate maintenance.<br>Gradual power loss that does not compromises | Yes | Yes | No |
| 4 | Irreversible damage<br>Requires major repair (e.g. stack change).<br>Power loss or Car Stop that compromises safety | Yes | Yes | Yes |

Table 2: definition of severity classes

The final risk is defined by the acceptability table build by combination of both above tables as described in the table 3.

| | | Severity | | | | |
|---|---|---|---|---|---|---|
| | | 0 | 1 | 2 | 3 | 4 |
| Occurrence As the combined probabilities of occurrence along the whole supply chain | 4 | 🟩 | 🟥 | 🟥 | 🟥 | 🟥 |
| | 3 | 🟩 | 🟨 | 🟥 | 🟥 | 🟥 |
| | 2 | 🟩 | 🟩 | 🟨 | 🟥 | 🟥 |
| | 1 | 🟩 | 🟩 | 🟩 | 🟨 | 🟥 |
| | 0 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 |
| Key | 🟥 Unacceptable risk ; additionnal control or barriers are required | | 🟨 Further investigations are needed: existing barriers or control may not be enough | | 🟩 Acceptable risk area Existing controls acceptable | |

Table 3: definition of acceptability table

For each level of risk, decision has to be taken in order to:

- Either refuse the risk and find mitigation or barriers to reduce it;
- Or accept the risk level as it is.

Risk reduction might include actions taken to mitigate the severity and/or probability of occurrence.

Using the risk assessment table elaborated for one hydrogen source, the risk acceptance table (table 3) is used to elaborate the appropriate quality assurance plan in order to reduce the risk of non-quality. This can be done either by barriers added to the process and / or by analytical control of impurities level. The quality assurance plan can only be defined on a case-by case basis.

# 3 Quality risk assessment for H2 for fuel cell car: SMR process + PSA

The contaminants potentially present in the hydrogen are depending on the process technology and on the purification step. It should be investigated on a case by case basis for each production source. Nevertheless, general process can be used for the first approach.

Table 4 gives a general classification of impurities on centralized Steam Methane Reforming (SMR) of natural gas with PSA purification:

| **Probability of presence of impurity** | **Impurity** |
|---|---|
| Frequent | CO |
| Possible | $N_2$, He |
| Rare | Ar, $CH_4$, |
| Very Rare | Formaldehyde |
| Unlikely | $O_2$, $CO_2$, $H_2O$, sulfur compounds, ammonia, THC (except methane), formic acid, Halogenated compounds |

Table 4: Probability of presence of impurities in SMR process

To have a better reliability of the potential impurities in the hydrogen source, quality risk assessment must be done for each source. It is important to know if the impurities that are given in the specification remain below the threshold values.

The possible cause of impurity is established impurity per impurity based on technical knowledge of the process (steam methane reforming) and purification system (PSA). It also takes into account the following:

- Existing barriers in the current process (as described in the table 5)
- On line analysis in the process

Then, the class of occurrence for being above the threshold value is defined for each impurity (see table 5 – column P).

| Contaminant | Threshold | Causes possible For the source studied | Existing barriers | | | | | | P | S | C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Inert gases : N2 | 100 | Present in Nat gas and Syngas<br>PSA malfunction | PSA | Double analysis + trip at xx ppm at PSA outlet<br>xx <100 ppm | | | | | 3 | 1 | 🟨 |
| Inert Gas Ar | | Only ATR and POx Present in O2 typical 0,6% in Syngas | PSA. Not sized to remove Argon.<br>Argon content may be higher if H2 comes from feeds with high Argon content | | | | | | 2 | 1 | 🟩 |
| Oxygen | 5 | Not present in Syngaz<br>Oxygen is unstable in the condition of reforming and shift reactions. Combines with H2, CO CH4 | PSA cannot be used with significant O2 content for safety reasons | | | | | | 0 | 0 | 🟩 |
| Carbon dioxide | 2 | Present in Syngas (%) | PSA<br>Adsorption strength of MS, Activated carbon, Silicagel higher for CO2 than CO.<br>A CO content lower than 10ppm insures a CO2 content lower than 2 ppm | | | | | | 0 | 1 | 🟩 |
| Carbon monoxide | 0,2 | Normal operation below threshold. Occasional peaks at ppm level | Double analysis + trip at xx ppm at PSA outlet (xx <10) | | | | | | 4 | 2 | 🟥 |
| Methane (CH4) | 100 | Present in Syngas at % level | In most cases CO is sizing the PSA, therefore CO<10ppm ==> CH4 < xx ppm depending on users spec (Europe pipeline 2 ppm.<br>In some cases CH4 is sizing the PSA and ther is a continuous analysis + trip related to CH4. | | | | | | 2 | 1 | 🟩 |
| Water | 5 | Syn gas saturated in H2O | PSA<br>Adsorbed in Alumina and MS Adsorption stmgth higher than CO2. A CO content lower than 10ppm insures a water content lower than 5 ppm. | | | | | | 0 | 4 | 🟩 |
| Total sulphured components | 0,004 | Sulfur from Nat Gas | Desulfuration upstream reformer (typical values)<br>Normal < 10 ppb<br>Max < 20 ppb<br>Guarantee < 50 ppb<br>Dilution factor 2,5 | Prereformer<br>Catalyst poisoning by sulfur irreversible<br>Sulfur trapped at this stage. In case of break through, process condition cannot be achieved | Reformer<br>Catalyst poisoning by sulfur irreversible<br>Sulfur trapped at this stage. In case of break through, process condition cannot be achieved | Shift<br>Catalyst poisoning by sulfur irreversible<br>Sulfur trapped at this stage. In case of break through, process condition cannot be achieved | PSA<br>Adsorption of H2S before CO, CO2, species | H2S Adsorption in pipe and vessels strong affinity with steel. | 0 | 4 | 🟩 |
| Ammonia | 0,1 | Traces present in Syngas. | PSA.<br>Adsorption strength of Alumina, MS Higher than CO<br>A CO content lower than 10ppm insures a Ammonia content lower than 0,1 ppm | | | | | | 0 | 4 | 🟩 |
| Total hydrocarbons | 2 | Traces of C2+ after reforming reaction | PSA<br>C2 C3, C4, C5+ adsorbed by Activated Carbon layer<br>A CO content lower than 10ppm insures a THC (CH4 excluded) content lower than 2 ppm | | | | | | 0 | 4 | 🟩 |
| Formaldehyde | 0,01 | Item Acide Formique…<br>Arreté par PSA | PSA.<br>Adsorption strength of Alumina, MS Higher than CO<br>A CO content lower than 10 ppm insures a Formaldehyde content lower than 0,1 ppm<br>To guarantee 0,01 ppm would require more experience of measuring at those levels | | | | | | 1 | 2 | 🟩 |
| Formic acid | 0,2 | May be present in Syngas essentially liquid | PSA.<br>Formic Adsorption strength of Alumina, MS Hgher than CO<br>A CO content lower than 10ppm insures a Formic acid content lower than 0,2ppm | | | | | | 0 | 2 | 🟩 |
| Halogenated compounds | 0,05 | Present in Nat Gas? | Any Cl present in Nat gas would be stopped by HDS | Prereformer<br>Catalyst poisoning by Cl irreversible<br>Cl trapped at this stage. I breakthrough, process | Reformer<br>Catalyst poisoning by Cl irreversible<br>Cl trapped at this stage. I breakthrough, process | Shift<br>Catalyst poisoning by Cl irreversible<br>Cl trapped at this stage. I breakthrough, | PSA<br>Adsorption of Cl before CO, CO2, species | | 0 | 4 | 🟩 |
| Helium | 300 | Not present in Nat Gas in N Europe (<10 ppm)<br>Passes through the whole process. Dilution factor 2,5 | | | | | | | 0 | 1 | 🟩 |

Table 5: Risk assessment table for SMR + PSA

Based on that study, the impurities coming from SMR sourcing are:

- Occurrence class 4 (highest probability) : CO
- Occurrence class 3 : $N_2$
- Occurrence class 2: $CH_4$ and Ar
- Occurrence class 1: Formaldehyde
- Occurrence class 0 (never observed): He, halogenated products, formic acid, THC, ammonia, sulfur compounds, $H_2O$, $CO_2$, $O_2$

Taking into account the severity class of each impurity, it is possible to calculate the acceptance for each impurity using the acceptable table (table 3).
Based on that acceptance table, CO and $N_2$ are the two impurities which are the most critical.

# Annex 2 Report on probability of presence of impurities of the PEM Water electrolysis process

# Metrology for sustainable hydrogen energy applications

# 15NRM03 HYDROGEN

## Task 1.1: Assessment of probability of impurities existing in real samples of hydrogen

### Report on activity A1.1.3 – PEM Water Electrolysis

**Task 1.1**
**Report on activity 1.1.3**

**April 2017**
**Revision : draft_rev.1**

This work has been carried out by:
AH2GEN: Guillaume Doucet, François Laridant, Eric Gernot, Fabien Auprêtre

# Summary

The evaluation of the impurities able to be found in hydrogen produced from PEM Water Electrolysis process is done for typical process design with purification by temperature swing adsorption.

The methodology of quality risk assessment is used to evaluate the probability of occurrence of each impurities to be above the threshold value given in the ISO 14687-2.

This method was applied to PEM WE + TSA process and the critical impurities identified is $H_2O$. Others are possible but with lower probability of occurrence: $O_2$, $N_2$.

# Table of contents

# 1 Description of PEM Water Electrolysis with Temperature Swing Adsorption

## 1.1 Introduction

Hydrogen production by water electrolysis represents only 4% of the world hydrogen production. The most used process is the Steam Methane Reforming (SMR). Among these 4 %, the principal part of the electrolytic hydrogen is produced by chlor alkali electrolysis (see Activity 1.1.5).
Water electrolysis has been used industrially to produce hydrogen for more than a century. But, as water electrolysis is an expensive way for obtaining hydrogen, especially for large scale production, use of electrolyser has been restricted to low hydrogen production capacity (< 500 Nm3/h) and only when no other hydrogen sources was locally available.

Interest in water electrolysis has increased again recently, influenced by its potential to provide hydrogen with a very low associated carbon footprint as well as for electrolysers to provide services, such as load response management, to changing electricity grids.

Three different types of electrolyser technology are currently available as commercial products, namely conventional alkaline electrolysers (liquid electrolyte), Proton Exchange Membrane (PEM) electrolysers and most recently also anion exchange membrane (AEM, also known as alkaline PEM) electrolysers. Historically, alkaline electrolysis has dominated the market and accounts for nearly all the installed water electrolysis capacity worldwide. PEM electrolysis has been commercial for close to 10 years, whereas AEM appeared on the market only very recently.

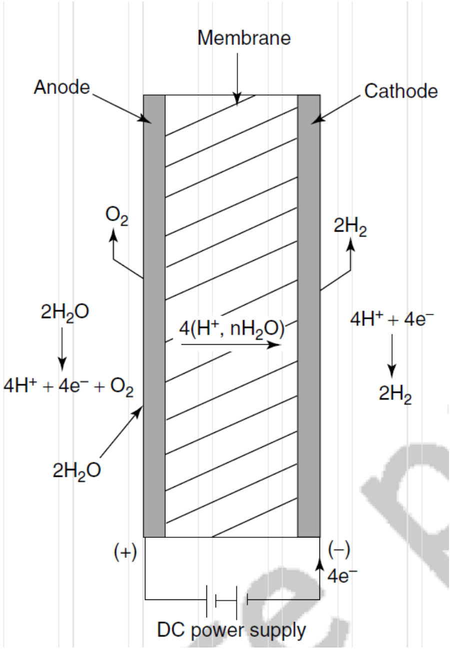
PEM electrolysis presents a lower technical maturity than the alkaline electrolysis because the first developments of PEM hydrogen generators were realised in the end of the 60s in the United States by General Electric Company for spatial and submarine military applications. However, PEM electrolysis permits to work at high current densities (> 2 A cm-2) with better electrical efficiencies than alkaline electrolysers. PEM electrolysers are also able to produce very pure gas (only O2 and water as pollutants) from low to high pressure. Finally, PEM electrolysis presents advantages with regard to the alkaline technology in terms of quick start and ability to react in front of rough current variations. That’s the reason why PEM electrolysis appears as an attractive solution for the new emerging applications:

- decentralized hydrogen production supplied with renewable energies for energetic applications (hydrogen gas stations or stations of bottles filling) or for chemical applications for the food or metallurgical industries, semiconductors;
- decentralized electricity production including hydrogen energy storage. This application could be interesting in geographical zones unconnected to the electrical grid.

## 1.2 Description of the PEM technology

The proton exchange membrane water electrolysis is based on the use of a polymeric proton exchange membrane as the solid electrolyte (Polymer Electrolyte Membrane) and was first proposed by General Electric for fuel cell, and later, electrolyser applications. The proton exchange membrane electrolyser technology was developed by ABB (formerly Brown, Boveri Ltd), Switzerland, over the years from 1976 to 1989. The following advantages of polymer electrolyte technology over the alkaline one have been proposed: (i) greater safety and reliability are expected since no caustic electrolyte is circulated in the cell stack; (ii) previous tests made on bare membranes demonstrated that some materials could sustain high differential pressure without damage and were efficient in preventing gas mixing; and (iii) the possibility of operating cells up to several amps per square centimeter with typical thickness of a few millimeters is theoretically afforded.

The principle of acid membrane water electrolysis is schematised on figure below. The centre of the cell is called the Membrane Electrode Assembly (MEA).



*Schematic diagram of a PEM water MEA (Membrane Electrode Assembly)*

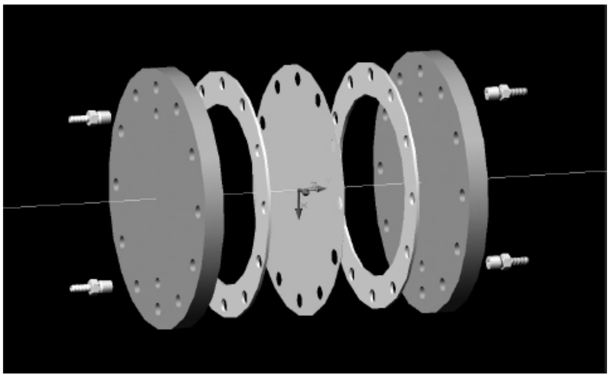
Two thin (<1 micron) microporous catalytic layers are deposited on the surface of both sides of a proton conductor polymer film (membrane). The assembly is immersed in ultrapure water. When a sufficient potential difference (1.23 V at 298 K under 1 bar) is applied between these two electrodes, electrolysis takes place. Water is oxidised at the anode, according to the following half-reaction:

$$H_2O \rightarrow 1/2\ O_2 + 2\ H^+ + 2\ e^-$$

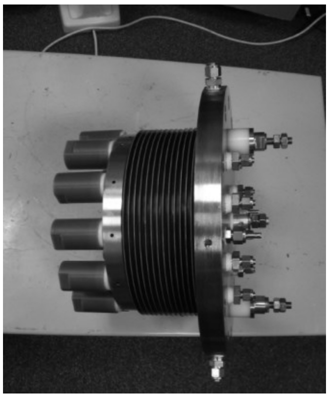
The protons migrate across the membrane under the effect of the electric field and are reduced at the cathode according to the following half-reaction:

$$2\,H^+ + 2\,e^- \rightarrow H_2$$

The MEA is clamped between two porous transport layer (PTL) and two bipolar plates to form a unit water electrolysis cell (see picture below, left side). Several unit cells are stacked in a filter-press system to form a cell stack (see picture below, right side).



Schematic representation (cross-sectional view) of a PEM water electrolysis cell



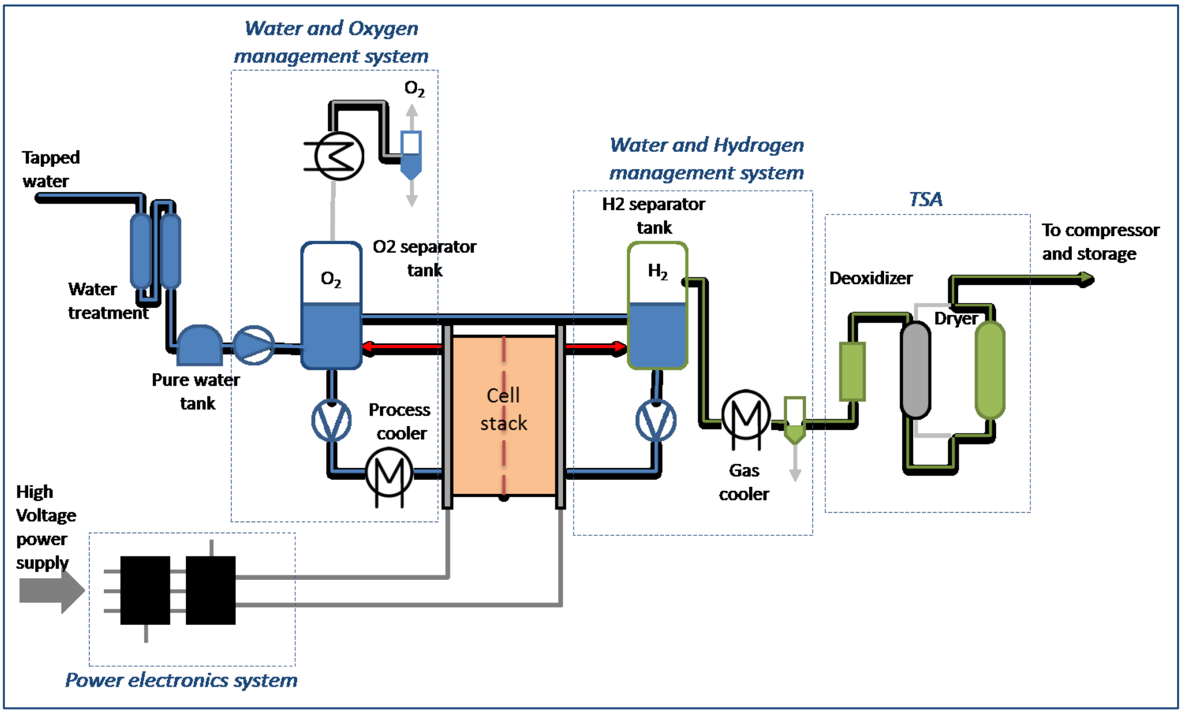
PEM water electrolysis cell stack

The membrane material therefore acts both as "solid" electrolyte and as separator to prevent chemical recombination of $H_2$ and $O_2$. In practice, the current is brought to the catalytic layers by titanium porous current distributors. Note that the protons which migrate across the polymer membrane are generally solvated, which results in water transfer from anode to cathode, known as electro-osmotic flow. The number of solvation water molecules depends partly on the structure of the polymer material. It is typically about 4 for commercial Nafion® membranes, which may lead to significant water transfer during operation.

Gas tightness of SPE (Solid Polymer Electrolyte) membranes is not perfect and show a low hydrogen (and oxygen) cross-over. Gas cross-permeation through the membrane during water electrolysis is due to hydrogen and oxygen solubility and diffusivity in perfluorosulfonic acid (PFSA) materials. This is a diffusion-controlled (Fickian) process. As a result, the hydrogen concentration in oxygen in the anodic side is not zero, and vice versa, the oxygen content in hydrogen in the cathodic side is not zero. Depending of membrane specification (material and thickness) and operating conditions of the process (current density, temperature, pressure in $O_2$ and $H_2$ side and pressure difference between both sides), $H_2$ content in $O_2$ may vary from few ppm to several %. As $O_2$ diffusion through the membrane is lower than $H_2$, $O_2$ content in $H_2$ is always lower than $H_2$ in $O_2$. This means that hydrogen produced by PEM water electrolysis is contaminated by $O_2$ traces and that depending on application requirement, hydrogen have to be purified before storing and/or consuming.

## 1.3 Description of the PEM Water Electrolysis process + Temperature Swing Adsorption (TSA) purification

Our study is based on our internal PEM Water Electrolyser process which is described in the figure below:



*Design of AH2GEN's PEM Water Electrolyser process with TSA*

Water electrolyser is composed of 5 mains subsystems:

- Cell stack
- Water purification unit for tap water purification
- Water and Oxygen management system
- Water and Hydrogen management system
- Power electronics system

The electrolyser's power electronics system filters, controls, transforms, and switches the main AC power input to various components throughout the unit. Depending on the size of the generator, the AC input can be single-phase or three-phase power, low voltage (200–240 V) or high voltage (480–500 V), and 50 or 60 Hz. Typically, the input power is divided to provide low voltage 24 DC power for control valves, pumps, sensors, etc., and high power for the electrolysis cell stack.

The electrolysis cell stack power supply converts incoming AC power to DC power at the proper voltage and current range to match the load characteristics of the electrolysis stack. The power supply subsystem provides monitoring of the stack voltage and amperage and variably controls stack hydrogen output via varying the amperage supply to the stack. The amount of amps applied to the stack directly corresponds to the volume of hydrogen (and oxygen) produced.

Tap water, used as raw material, is firstly purified by a reverse osmosis unit and stored in a dedicated tank at atmospheric pressure. This preliminary step is necessary to remove any contaminants and ions from the water before feeding the process with pure water (Conductivity < 0.1 µS/cm). Pure water is fed into the O2 separator tank using a lift pump. The pump take pure water at atmospheric pressure at the inlet and feed the water to the separator tank at operating pressure (up to 14 bar).

Water and Oxygen Management System (W&OMS) circulates water through the cell stack using a circulating pump. It also removes heat from the cell stack and maintains the stack temperature while regulating system pressure. Part of the pure water is oxidized into gaseous $O_2$ at the anodic side of the cell stack resulting in a gas/liquid mixture ($O_2$ + $H_2O$) at the outlet of stack. Liquid water phase is separated from the gaseous $O_2$ phase into the "$O_2$ separator tank". The oxygen gas that is generated is cooled before venting outside of the electrolyser enclosure. Resultant condensed water from this gas stream is drained or returned to the water reservoir for reuse. Other functions of the W&OMS are to monitor water purity, minimum stack water flow, water quantity/level, stack exit water/oxygen temperature, pressure, and level of $H_2$ content in oxygen gas production. Generally, a deionization water conditioner is present in the closed water loop to remove ionic contaminants coming from construction materials.

Water and Hydrogen Management System (W&HMS) circulates water through cathodic side of the cell stack using a circulating pump. Due to the effect of the electric field, protons generated at the anodic side of the cell stack migrate across the polymer membrane to the cathodic side where they are reduced to produce gaseous hydrogen ($H_2$). Due to the water electro-osmotic flow, water from the anodic side of the cell stack pass through the membrane to the cathodic side resulting in a gas/liquid mixture ($H_2$ + $H_2O$) at the outlet of the cathodic side of stack. Typically, nominal operating temperature of PEM electrolysers is between 50 to 60°C so gaseous hydrogen produced is water saturated. Liquid water phase is separated from the gaseous $H_2$ phase into the "$H_2$ separator tank". In order to minimize the amount of water consumption in the electrolyser, a pipe (with a normally closed valve) connects separator tanks in order to balance water levels in both separator tank. When water level reached the high limit threshold in the $H_2$ separator tank, valve opens and part of the water of $H_2$ separator tank is transferred to $O_2$ separator tank thanks to difference of pressure between $O_2$ side (up to 14 bar) and $H_2$ side (up to 35 bar). Then, valve closes when the water level reached the low limit threshold. As this water transfer is a critical step of the process, water reintroduction is typically done in two steps: i) Step 1 allows for the removal of dissolved hydrogen gas in the pressurized water, which effervesces out of solution at $O_2$ operating pressure (up to 14 bar) then first drained from the system and ii) Step 2, once the dissolved hydrogen has been allowed to release from solution, the remaining water can be introduced safely to the $O_2$ separator tank.

The hydrogen gas that is generated is preliminary cooled before going to the TSA purification unit. Resultant condensed water from this gas stream is generally drained out of the enclosure of the electrolyser. Typically, a deionization water conditioner is also present in the cathodic closed water loop to remove ionic contaminants coming from construction materials and the membrane (fluoride release). Hydrogen management system is responsible for creating and regulating system back pressure on the hydrogen side of the cell stack and monitoring system pressures, temperatures and water level.

After preliminary cooling, the hydrogen produced is then purified using temperature swing adsorption unit. This purifier removes i) oxygen traces coming from gas cross over through the membrane using catalytic deoxidizer and ii) water content using two dryer column. Since, $O_2$ and $H_2O$ are the main impurities; the design of this TSA purification unit is performed to have specific level at the outlet (typically <5 ppm of $O_2$ and < 5 ppm of $H_2O$).

# 2 Quality risk assessment for $H_2$ for fuel cell car: main principles

The two primary principles of quality assurance plan are:

- The evaluation of the risk not to respect the quality requirement should be based on scientific knowledge and ultimately link to the protection of the fuel cell car
- The level of effort to implement the quality assurance process should be commensurate with the level of risk.

As an aid to clearly defining the risk(s) for risk assessment purposes, three fundamental questions are often helpful:

- What might go wrong: which event can cause the impurities to be above the threshold value?
- What is the likelihood (probability of occurrence expressed relative to the number of refueling events) that impurities can be above the threshold value?
- What are the consequences (severity) for the fuel cell car?

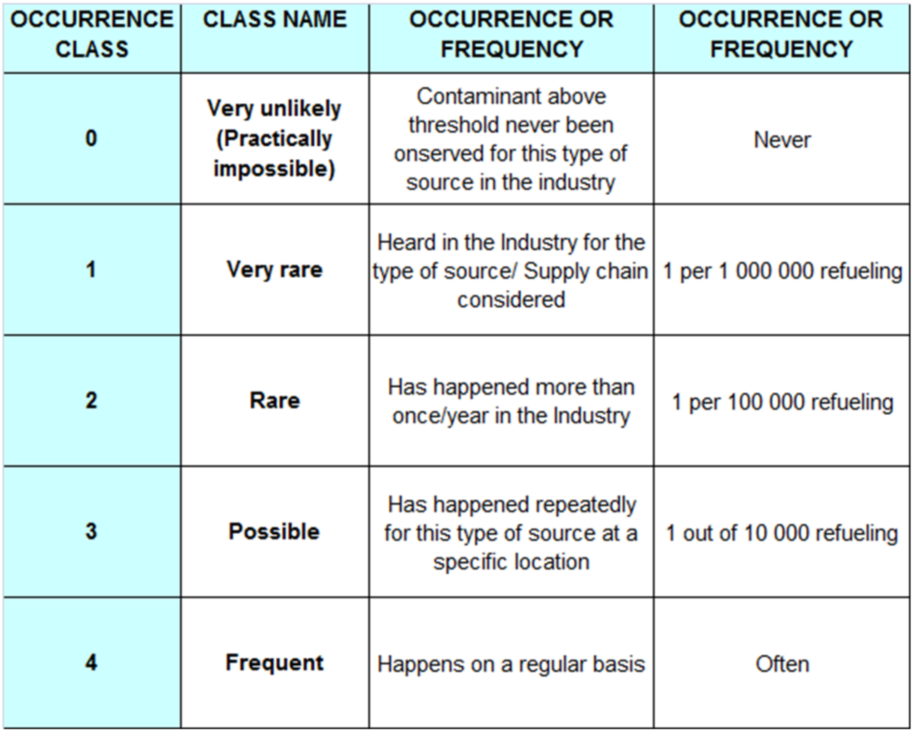
In doing an effective risk assessment, the robustness of the data set is important because it determines the quality of the output. Revealing assumptions and reasonable sources of uncertainty will enhance confidence in this output and/or help identify its limitations. The output of the risk assessment is a qualitative description of a range of risk.

For each impurity of the ISO 14687-2 specification and for a given $H_2$ source a risk assessment must be applied to define the global risk for the car user. Risk assessment consists of:

- Identification of the probability of occurrence to have in hydrogen each impurity above the threshold values of specifications given in ISO 14687-2 (see table 1)
- Evaluation of severity level of each impurity for the fuel cell car (see table 2)

For the probability of occurrence of the event: impurities in hydrogen exceed the threshold value, the following table of occurrence classes has been defined:

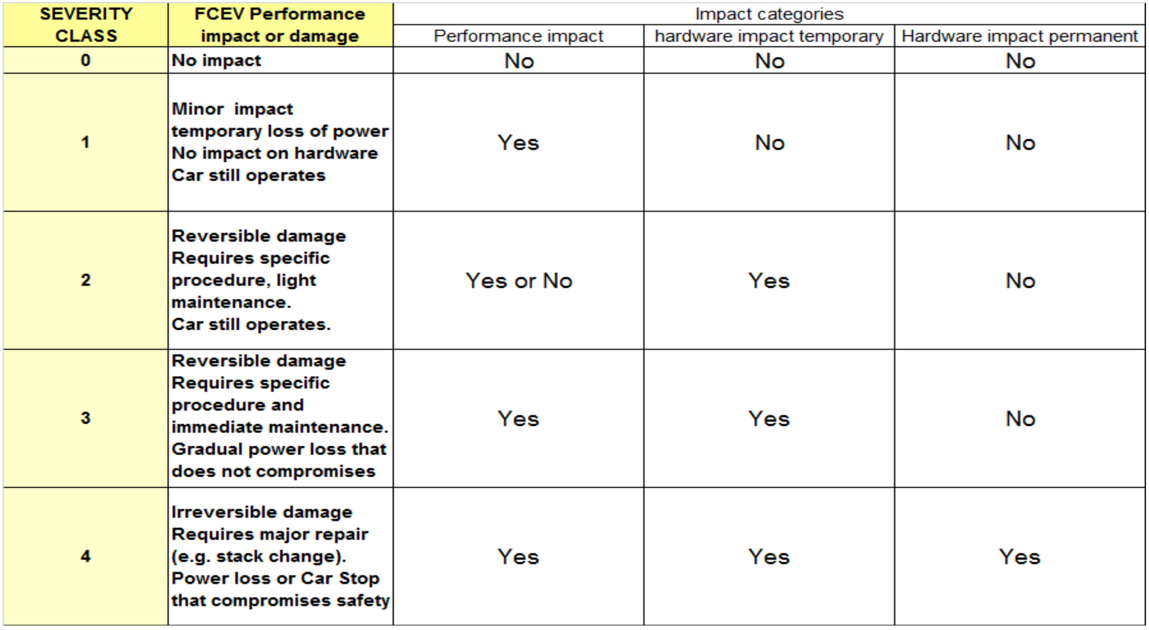
*Table 1: Definition of occurrence classes*



| OCCURRENCE CLASS | CLASS NAME | OCCURRENCE OR FREQUENCY | OCCURRENCE OR FREQUENCY |
|---|---|---|---|
| **0** | **Very unlikely (Practically impossible)** | Contaminant above threshold never been onserved for this type of source in the industry | Never |
| **1** | **Very rare** | Heard in the Industry for the type of source/ Supply chain considered | 1 per 1 000 000 refueling |
| **2** | **Rare** | Has happened more than once/year in the Industry | 1 per 100 000 refueling |
| **3** | **Possible** | Has happened repeatedly for this type of source at a specific location | 1 out of 10 000 refueling |
| **4** | **Frequent** | Happens on a regular basis | Often |

The range of severity level (level of damage for vehicle) is defined in the table 2.

Table 2: Definition of severity classes



| SEVERITY CLASS | FCEV Performance impact or damage | Impact categories | | |
|---|---|---|---|---|
| | | Performance impact | hardware impact temporary | Hardware impact permanent |
| **0** | **No impact** | No | No | No |
| **1** | **Minor impact**<br>**temporary loss of power**<br>**No impact on hardware**<br>**Car still operates** | Yes | No | No |
| **2** | **Reversible damage Requires specific procedure, light maintenance.**<br>**Car still operates.** | Yes or No | Yes | No |
| **3** | **Reversible damage Requires specific procedure and immediate maintenance.**<br>**Gradual power loss that does not compromises** | Yes | Yes | No |
| **4** | **Irreversible damage Requires major repair (e.g. stack change).**<br>**Power loss or Car Stop that compromises safety** | Yes | Yes | Yes |

The final risk is defined by the acceptability table build by combination of both above tables as described in the table 3.

*Table 3: Definition of acceptability table*

| | | **Severity** | | | | |
|---|---|---|---|---|---|---|
| **Occurrence As the combined probabilities of occurrence along the whole supply chain** | | **0** | **1** | **2** | **3** | **4** |
| | **4** | 🟩 | 🟥 | 🟥 | 🟥 | 🟥 |
| | **3** | 🟩 | 🟨 | 🟥 | 🟥 | 🟥 |
| | **2** | 🟩 | 🟩 | 🟨 | 🟥 | 🟥 |
| | **1** | 🟩 | 🟩 | 🟩 | 🟨 | 🟥 |
| | **0** | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 |
| **Key** | 🟥 Unacceptable risk : additionnal control or barriers are required | | 🟨 Further investigations are needed: existing barriers or control may not be enough | | 🟩 Acceptable risk area Existing controls acceptable | |

For each level of risk, decision has to be taken in order to:

- Either refuse the risk and find mitigation or barriers to reduce it;
- Or accept the risk level as it is.

Risk reduction might include actions taken to mitigate the severity and/or probability of occurrence.

Using the risk assessment table elaborated for one hydrogen source, the risk acceptance table (table 3) is used to elaborate the appropriate quality assurance plan in order to reduce the risk of non-quality. This can be done either by barriers added to the process and / or by analytical control of impurities level. The quality assurance plan can only be defined on a case-by case basis.

# 3 Quality risk assessment for H2 for fuel cell car: PEM Water Electrolysis + TSA

The contaminants potentially present in the hydrogen are depending on the process technology and on the purification step. It should be investigated on a case by case basis for each production source. Nevertheless, general process can be used for the first approach.

The table 4 gives a general classification of impurities on decentralized PEM Water Electrolysis (WE) with TSA purification:

*Table 4: Probability of presence of impurities in PEM WE process*

| Probability of presence of impurity | Impurity |
|---|---|
| Frequent | $O_2$, $H_2O$ |
| Possible | $N_2$ |
| Rare | |
| Very Rare | $CO_2$ |
| Unlikely | He, Ar, CO, $CH_4$, sulfur compounds, ammonia, THC (except methane), formaldehyde, formic acid, Halogenated compounds |

To have a better reliability of the potential impurities in the hydrogen source, quality risk assessment must be done for each source. It is important to know if the impurities that are given in the specification remain below the threshold values.

The possible cause of impurity is established impurity per impurity based on technical knowledge of the process (PEM water electrolysis) and purification system (TSA). It also takes into account the following:

- Existing barriers in the current process (as described in the table 5)
- On line analysis in the process

Then, the class of occurrence for being above the threshold value is defined for each impurity (see table 5 – column P).

*Table 5: Risk assessment table for PEM WE +TSA*

| Contaminant | Thresold [µmol/mol] | Possible cause for the source studied | Existing barrier | | | | P* | P | S | C |
|---|---|---|---|---|---|---|---|---|---|---|
| **Inert gas: N2** | 100 | Air intake into pure water tank at anodic side during normal operation | Operating conditions applied in anodic separator tank | PEM membrane (low cross over through the membrane) | | | 0 | 2 | 1 | 🟩 |
| | | N2 use for venting during emergency shut down and/or maintenance | Gas production temporary vented after restart for certain period of time (factory setting) | | | | 2 | | | |
| | | Leakage of H2 inerting valve (N2 used as inerting gas) | H2 operating pressure > N2 pressure supply | | | | 1 | | | |
| | | Leakage of pneumatic valves (N2 used as actionning gas) | | | | | 1 | | | |
| **Inert gas: Ar** | 100 | Not expected to be present. | | | | | 0 | 0 | 1 | 🟩 |
| **Oxygen** | 5 | O2 normally generated at the anodic side of cell stack and<br>O2 cross over through the PEM membrane<br>TSA malfunction | Deoxo of TSA<br>Temperature overshoot if O2 content too high. Temperature measurement + trip T°C > 50°C | Analysis + trip at xx ppm at TSA outlet xx < 5 ppm | Gas production temporary vented after restart for certain period of time (factory setting) | | 2 | 2 | 0 | 🟩 |
| **Carbon dioxide** | 2 | from tap water at anodic side | Reverse osmosis purification unit | anodic separator tank | Ion exchange resin in closed water loop | PEM membrane (low cross over through the membrane) | 1 | 1 | 1 | 🟩 |
| | | from air into PWT at anodic side | CO2 filter on pure water tank air intake | anodic separator tank | Ion exchange resin in closed water loop | PEM membrane (low cross over through the membrane) | 1 | | | |
| **Carbon monoxide** | 0.2 | Not expected to be present. | | | | | 0 | 0 | 2 | 🟩 |
| **Methane (CH4)** | 100 | Not expected to be present. | | | | | 0 | 0 | 1 | 🟩 |
| **Water** | 5 | reactant --> permeation through PEM membrane due to electro-osmosis + H2 water saturated at 60°C<br>TSA malfunction | TSA dryer | DP Analysis + trip at xx ppm at TSA outlet xx < 5 ppm | Gas production temporary vented after restart for certain period of time (factory setting) | | 2 | 2 | 4 | 🟥 |
| **Total sulphur compounds** | 0.004 | Materials gaskets, valve seats releasing ppb level of sulfur compound | Material specifications | | | | 0 | 0 | 4 | 🟩 |
| **Ammonia** | 0.1 | from tap water at anodic side | Reverse osmosis purification unit | PEM membrane (no transfer through the membrane) | | | 0 | 0 | 4 | 🟩 |
| **Total hydrocarbons** | 2 | Not expected to be present. | | | | | 0 | 0 | 4 | 🟩 |
| **Formaldehyde** | 0.01 | Not expected to be present. | | | | | 0 | 0 | 2 | 🟩 |
| **Formic acid** | 0.2 | Not expected to be present. | | | | | 0 | 0 | 2 | 🟩 |
| **Helium** | 300 | Not expected to be present. | | | | | 0 | 0 | 0 | 🟩 |
| **Halogenated compounds** | 0.05 | from tap water at anodic side | Reverse osmosis purification unit | | | | 0 | 0 | 4 | 🟩 |

Based on that study, the impurities coming from PEM WE sourcing are:

- Occurrence class 4 (highest probability) :
- Occurrence class 3 :
- Occurrence class 2: $N_2$, $O_2$, $H_2O$
- Occurrence class 1: $CO_2$
- Occurrence class 0 (never observed): Ar, CO, $CH_4$, He, halogenated products, formaldehyde, formic acid, THC, ammonia, sulfur compounds

Taking into account the severity class of each impurity, it is possible to calculate the acceptance for each impurity using the acceptable table (table 3).

Based on that acceptance table, $H_2O$ is the main impurity which is the most critical.

# Annex 3 Report on probability of presence of impurities of chlor-alkali process

# Metrology for sustainable hydrogen energy applications
# 15NRM03 HYDROGEN

# Task 1.1: Assessment of probability of impurities existing in real samples of hydrogen

## Report on activity A1.1.5 - Chlor-alkali process

**Task 1.1**
**Report on activity 1.1.5**

**May 2017**
**Revision 1**

This work has been carried out by:
Thomas Bacquart / Arul Murugan

# 15NRM03 WP1 – Assessment of probability of impurities existing in real samples of hydrogen - Chlor-alkali process

## Summary

The evaluation of the impurities able to be found in hydrogen produced from chlor-alkali process (membrane cell process) is done for typical process design.
The methodology of quality risk assessment is used to evaluate the probability of occurrence of each impurities to be above the threshold value given in the ISO 14687-2. This method was applied to chlor-alkali process and the critical impurities identified are: $O_2$ and $N_2$. Others are possible but with lower probability of occurrence: $CO_2$ and water.

# 15NRM03 WP1 – Assessment of probability of impurities existing in real samples of hydrogen - Chlor-alkali process

# Table of contents

# 1 Description of Chlor alkali process

The industrial production of chlorine and caustic soda (chlor-alkali process) is one such source of high purity waste hydrogen. The industry electrolyses brine (saltwater) on a massive scale, producing 12,544,000 tonnes of chlorine per year in Europe alone, according to eurochlor.org. The most common chlor-alkali process involves the electrolysis of aqueous sodium chloride (a brine) in a membrane cell. Saturated brine is passed into the first chamber of the cell where the chloride ions are oxidised at the anode, losing electrons to become chlorine gas (Figure 1.A.): $2Cl^- \rightarrow Cl_2 + 2e^-$
At the cathode, positive hydrogen ions pulled from water molecules are reduced by the electrons provided by the electrolytic current, to hydrogen gas, releasing hydroxide ions into the solution (Figure 1.C): $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
The ion-permeable ion exchange membrane at the center of the cell allows the sodium ions ($Na^+$) to pass to the second chamber where they react with the hydroxide ions to produce caustic soda (NaOH) (Figure 1.B). The overall reaction for the electrolysis of sodium chloride is thus: $2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$.

A membrane cell is used to prevent the reaction between the chlorine and hydroxide ions. Moreover it avoids contact between $Cl_2$ and $H_2$ gases which can react violently. For these reasons, chlorine is not expected to be found on the cathode side. The process takes place in the liquid phase, no organic compounds (ammonia, sulphur or carbon) are expected as gaseous by-products. The only organic by-product could be oxygen. Water can contaminate the hydrogen by-product, for this reason a drying step is included in the process. Nitrogen is often use in maintenance operation and for purging the process. It can contaminate the hydrogen stream.

Our study is based on membrane chlor-alkali process which is described in the Figure 1:

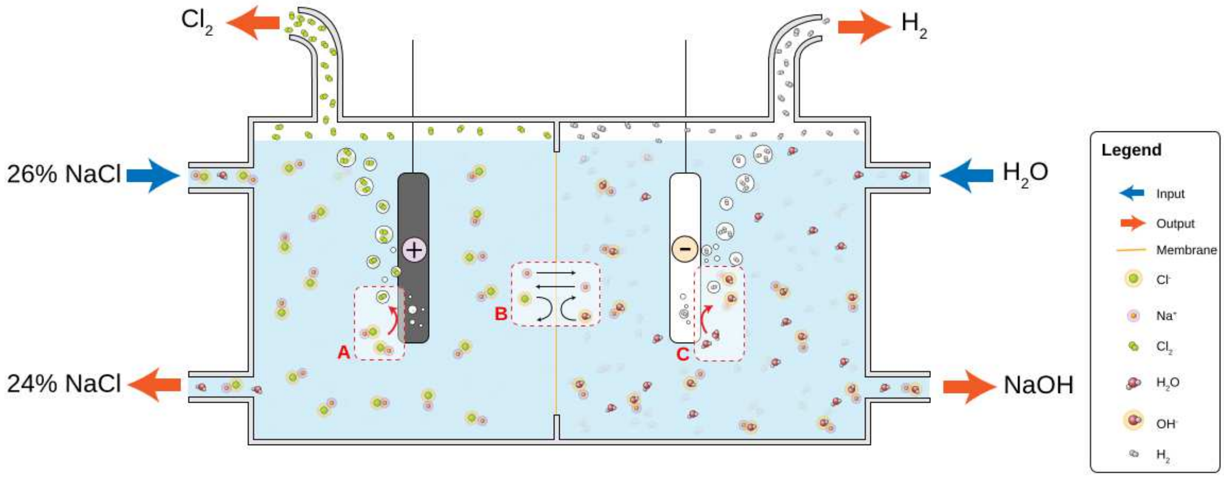


**Figure 1.** Basic membrane cell used in the electrolysis of brine. At the anode (A), chloride ($Cl^-$) is oxidized to chlorine. The ion-selective membrane (B) allows the counterion $Na^+$ to freely flow across, but prevents anions such as hydroxide ($OH^-$) and chloride from diffusing across. At the cathode (C), water is reduced to hydroxide and hydrogen gas. The net process is the electrolysis of an aqueous solution of NaCl into industrially useful products sodium hydroxide (NaOH) and chlorine gas.

# 2 Quality risk assessment for H2 for fuel cell car: main principles

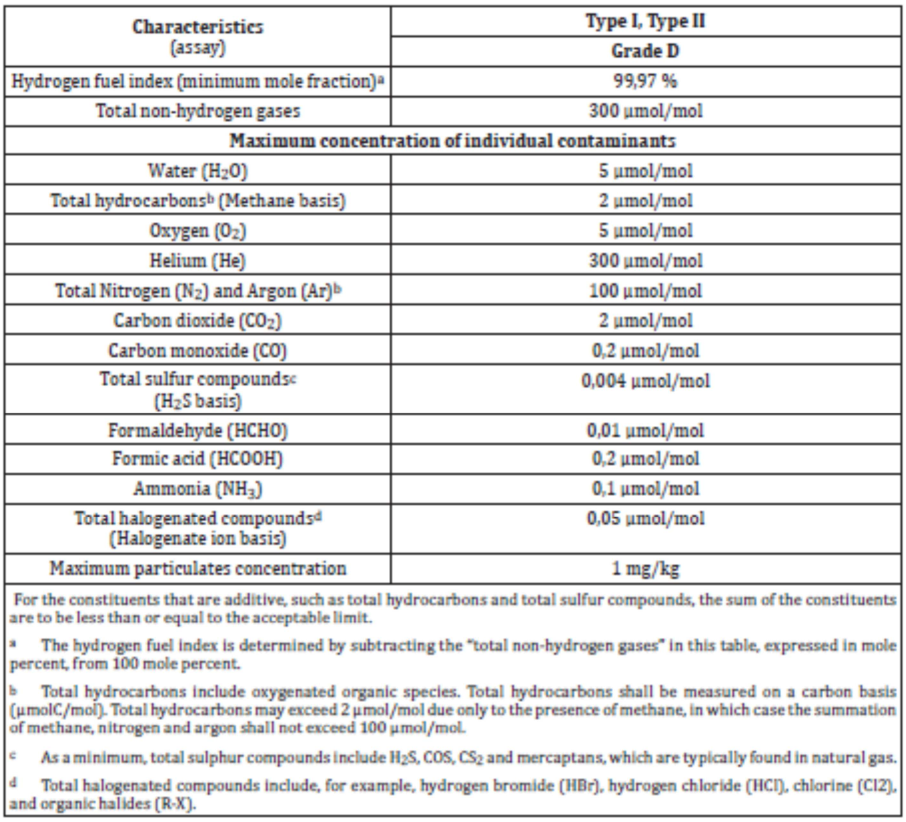
The two primary principles of quality assurance plan are:

- The evaluation of the risk of non-compliance to quality requirements should be based on scientific knowledge and ultimately link to the protection of the fuel cell car
- The level of effort to implement the quality assurance process should be proportional with the level of risk.

As an aid to clearly defining the risk(s) for risk assessment purposes, three fundamental questions are often helpful:

- What might go wrong: which event can cause the impurities to be above the threshold value?
- What is the likelihood (probability of occurrence expressed relative to the number of refueling events) that impurities can be above the threshold value?
- What are the consequences (severity) for the fuel cell car?

In doing an effective risk assessment, the robustness of the data set is important because it determines the quality of the output. Revealing assumptions and reasonable sources of uncertainty will enhance confidence in this output and/or help identify its limitations. The output of the risk assessment is a qualitative description of a range of risk.



| **Characteristics**<br>(assay) | **Type I, Type II** |
|---|---|
| | **Grade D** |
| Hydrogen fuel index (minimum mole fraction)[a] | 99,97 % |
| Total non-hydrogen gases | 300 µmol/mol |
| **Maximum concentration of individual contaminants** | |
| Water ($H_2O$) | 5 µmol/mol |
| Total hydrocarbons[b] (Methane basis) | 2 µmol/mol |
| Oxygen ($O_2$) | 5 µmol/mol |
| Helium (He) | 300 µmol/mol |
| Total Nitrogen ($N_2$) and Argon (Ar)[b] | 100 µmol/mol |
| Carbon dioxide ($CO_2$) | 2 µmol/mol |
| Carbon monoxide (CO) | 0,2 µmol/mol |
| Total sulfur compounds[c] ($H_2S$ basis) | 0,004 µmol/mol |
| Formaldehyde (HCHO) | 0,01 µmol/mol |
| Formic acid (HCOOH) | 0,2 µmol/mol |
| Ammonia ($NH_3$) | 0,1 µmol/mol |
| Total halogenated compounds[d] (Halogenate ion basis) | 0,05 µmol/mol |
| Maximum particulates concentration | 1 mg/kg |

For the constituents that are additive, such as total hydrocarbons and total sulfur compounds, the sum of the constituents are to be less than or equal to the acceptable limit.

[a] The hydrogen fuel index is determined by subtracting the "total non-hydrogen gases" in this table, expressed in mole percent, from 100 mole percent.

[b] Total hydrocarbons include oxygenated organic species. Total hydrocarbons shall be measured on a carbon basis (µmolC/mol). Total hydrocarbons may exceed 2 µmol/mol due only to the presence of methane, in which case the summation of methane, nitrogen and argon shall not exceed 100 µmol/mol.

[c] As a minimum, total sulphur compounds include $H_2S$, COS, $CS_2$ and mercaptans, which are typically found in natural gas.

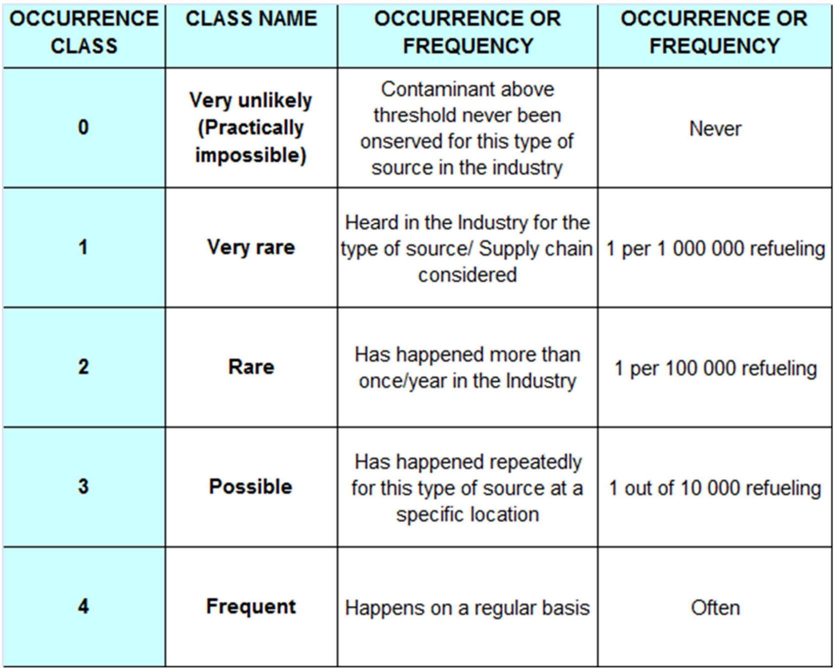
[d] Total halogenated compounds include, for example, hydrogen bromide (HBr), hydrogen chloride (HCl), chlorine (Cl2), and organic halides (R-X).

Table 1: Fuel specification defined in ISO 14687-2:2012

For each impurity of the ISO 14687-2 specification and for a given $H_2$ source a risk assessment must be applied to define the global risk for the car user. Risk assessment consists of:

- Identification of the probability of occurrence to have in hydrogen each impurity above the threshold values of specifications given in ISO 14687-2 (see table 2)
- Evaluation of severity level of each impurity for the fuel cell car (see table 3)

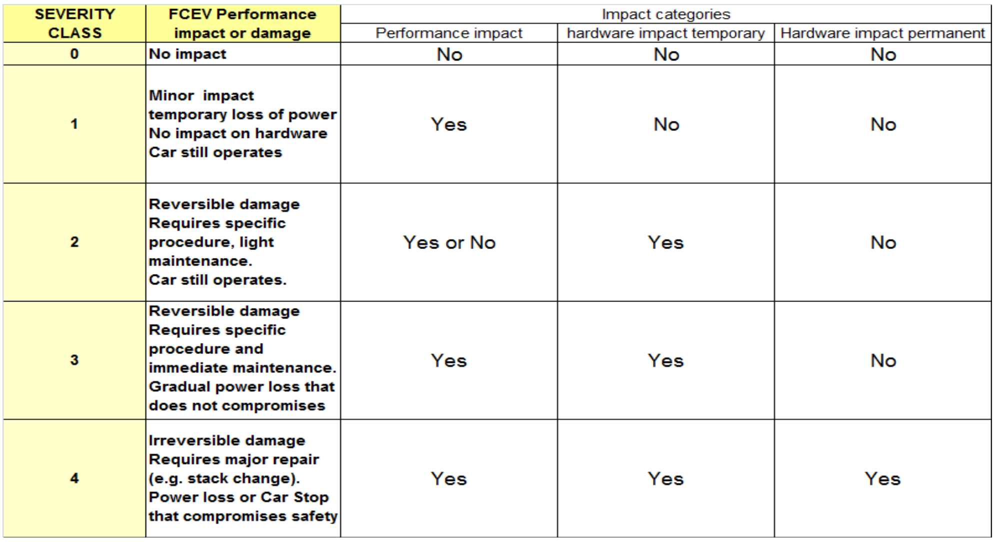
For the probability of occurrence of the event: impurities in hydrogen exceed the threshold value, the following table of occurrence classes has been defined:



| OCCURRENCE CLASS | CLASS NAME | OCCURRENCE OR FREQUENCY | OCCURRENCE OR FREQUENCY |
|---|---|---|---|
| 0 | **Very unlikely (Practically impossible)** | Contaminant above threshold never been onserved for this type of source in the industry | Never |
| 1 | **Very rare** | Heard in the Industry for the type of source/ Supply chain considered | 1 per 1 000 000 refueling |
| 2 | **Rare** | Has happened more than once/year in the Industry | 1 per 100 000 refueling |
| 3 | **Possible** | Has happened repeatedly for this type of source at a specific location | 1 out of 10 000 refueling |
| 4 | **Frequent** | Happens on a regular basis | Often |

Table 2: definition of occurrence classes

The range of severity level (level of damage for vehicle) is defined in the table 3.



| SEVERITY CLASS | FCEV Performance impact or damage | Impact categories | | |
|---|---|---|---|---|
| | | Performance impact | hardware impact temporary | Hardware impact permanent |
| 0 | No impact | No | No | No |
| 1 | Minor impact<br>temporary loss of power<br>No impact on hardware<br>Car still operates | Yes | No | No |
| 2 | Reversible damage<br>Requires specific procedure, light maintenance.<br>Car still operates. | Yes or No | Yes | No |
| 3 | Reversible damage<br>Requires specific procedure and immediate maintenance.<br>Gradual power loss that does not compromises | Yes | Yes | No |
| 4 | Irreversible damage<br>Requires major repair (e.g. stack change).<br>Power loss or Car Stop that compromises safety | Yes | Yes | Yes |

Table 3: definition of severity classes

The final risk is defined by the acceptability table build by combination of both above tables as described in the table 4.

| | | Severity | | | | |
|---|---|---|---|---|---|---|
| | | 0 | 1 | 2 | 3 | 4 |
| Occurrence As the combined probabilities of occurrence along the whole supply chain | 4 | 🟩 | 🟥 | 🟥 | 🟥 | 🟥 |
| | 3 | 🟩 | 🟨 | 🟥 | 🟥 | 🟥 |
| | 2 | 🟩 | 🟩 | 🟨 | 🟥 | 🟥 |
| | 1 | 🟩 | 🟩 | 🟩 | 🟨 | 🟥 |
| | 0 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 |
| Key | 🟥 Unacceptable risk ; additionnal control or barriers are required | | 🟨 Further investigations are needed: existing barriers or control may not be enough | | 🟩 Acceptable risk area Existing controls acceptable | |

Table 4: definition of acceptability table

For each level of risk, decision has to be taken in order to:

- Either refuse the risk and find mitigation or barriers to reduce it;
- Or accept the risk level as it is.

Risk reduction might include actions taken to mitigate the severity and/or probability of occurrence.

Using the risk assessment table elaborated for one hydrogen source, the risk acceptance table (table 4) is used to elaborate the appropriate quality assurance plan in order to reduce the risk of non-quality. This can be done either by barriers added to the process and / or by analytical control of impurities level. The quality assurance plan can only be defined on a case-by case basis.

# 3 Quality risk assessment for $H_2$ for fuel cell car: Chlor-alkali process

The contaminants potentially present in the hydrogen are depending on the process technology and on the purification step. It should be investigated on a case by case basis for each production source. Nevertheless, the general process can be used for the first approach.

The table 5 gives a general classification of impurities on chlor-alkali process:

| **Probability of presence of impurity** | **Impurity** |
|---|---|
| Frequent | Possibly $O_2$ |
| Possible | None identified |
| Rare | $H_2O$ and $N_2$ |
| Very Rare | $CO_2$ |
| Unlikely | Argon, CO, $CO_2$, formaldehyde, sulfur compounds, ammonia, THC, formic acid, Halogenated compounds |

Table 5: Probability of presence of impurities in Chlor-alkali process

To have a better reliability of the potential impurities in the hydrogen source, quality risk assessment must be done for each source. It is important to know if the impurities that are given in the specification remain below the threshold values.

The possible cause of impurity is established compounds per compounds based on technical knowledge of the process. It also takes into account the following:

- Existing barriers in the current process (as described in the table 6)
- On line analysis in the process

For chlor-alkali process, the presence of chlorine and hydrochloric acid in hydrogen gas required particular focus. Several barriers influencing their presence in the gas phase and in the final hydrogen gas product are present: NaOCl and HOCl equilibrate in liquid phase. Their expected concentration at the cathode is 10 mg per kg. Theoretically, there is an equilibrium between HOCl(l) with $Cl_2$(g) at the cathode, but this is probably too low to be significant. Both HCl(g) and $Cl_2$(g) has extremely high water solubility and would effectively leave with water in the drying clean up step of the process.

The transfer of $H_2$(g) and $Cl_2$(g) through the membrane could occur in the event of failure of liquid levels. A continuous gas phase through the membrane would be detected due to faster diffusivity of hydrogen gas. As hydrogen at the anode is monitored for safety reasons, the process would be shut down in time to avoid contamination of hydrogen with $Cl_2$(g).

Any possible presence of $Cl_2$(g) would be likely to convert to HCl(g) at the catalyst surfaces. Although the conversion has negative Gibbs free energy, an energy barrier is expected to slow down direct conversion.

# 15NRM03 WP1 – Assessment of probability of impurities existing in real samples of hydrogen - Chlor-alkali process

| Contaminant | Thresold [µmol/mol] | Cause possible for the source studied | Existing barrier | P |
|---|---|---|---|---|
| **Inert gas: $N_2$** | 100 | Only Nitrogen is used in process (only at start-up phase) so can be present. Problem seal / process use | | 2 |
| **Inert gas: Ar** | | Not expected to be present. | | 0 |
| **Oxygen** | 5 | can be present | 0 or 4 as concentration unknown | 0 or 4 |
| **Carbon dioxide** | 2 | This is not likely to be in the product as is remains in the caustic soda lye that is produced. $CO_2$(g) could also be formed from oxidation of organic matter in the brine.<br>The membrane is on the cathode side made conducting by carboxylic acid end groups. It has been speculated that the $CO_2$(g) formed could originate from degradation of the membrane. This is just speculation based on the finding of $CO_2$(g). | $CO_2$ is expected to remains in the caustic soda lye that is produced<br>No quantitative assessment of if the amount of $CO_2$(g) formed could amount to significant levels by degradation of membrane or oxidation of organic material and subsequent transport through membrane as $CO_2$(l) is known. | 1 |
| **Carbon monoxide** | 0.2 | It is not expected that CO is formed at the electrolysis process. | | 0 |
| **Methane ($CH_4$)** | 100 | Not expected to be present. | | 0 |
| **Water** | 5 | The source is from the process. | $H_2$ Often dried to a dew point of -20 degrees C. (dew point ~ 40 - 60) | 2 |
| **Total sulphur components** | 0.004 | It is not expected that S is formed or taken up at in the production process. | | 0 |
| **Ammonia** | 0.1 | From water introduced in the process / steam connection | We don't expect this compound in the $H_2$. It is not used in the production process and therefore not likely to be in $H_2$. The only form it could be introduced is in water, but then it is still unlikely that is will be in the $H_2$ gas phase. Often de-mineralized water is used in the production process and don't expect these components to be present. | 0 |
| **Total hydrocarbons** | 2 | Not expected to be present. | Hydrocarbons < 1 µmol/mol (detection limit) | 0 |
| **Formaldehyde** | 0.01 | | | 0 |
| **Formic acid** | 0.2 | | | 0 |
| **Helium** | 100 | Not expected to be present. | | 0 |
| **Halogenated compounds** | 0.05 | Not expected to be present. | | 0 |
| **Free chlorine** | | From process / higher pressure of hydrogen rather than $Cl_2$ | $Cl_2$ and $H_2$ are separated from each other and not expected to have $Cl_2$ in the hydrogen. This is important for various reasons, as one of it is that a mixture of $H_2$ and $Cl_2$ can give an explosive mixture. Therefore it is essential to ensure that no $Cl_2$ ends up in $H_2$.<br>The transfer of $H_2$(g) and $Cl_2$(g) through the membrane could occur in the event of failure of liquid levels. A continuous gas phase through the membrane would be detected due to faster diffusivity of hydrogen gas. As hydrogen at the anode is monitored for safety reasons, the process would be shut down in time to avoid contamination of hydrogen with $Cl_2$(g). | 0 |
| **HCl** | | Any possible presence of $Cl_2$(g) would be likely to convert to HCl(g) at the catalyst surfaces. | Although the conversion has negative Gibbs free energy, an energy barrier is expected to slow down direct conversion. | 0 |

Table 6: Probability of occurrence of impurities in Chlor-alkali process with the different barrier existing in the process

# Annex 4   Sampling Procedure

The sampling system design is presented in Figure A4-1 below. The operations to perform the sampling are defined below from 1 to 5.

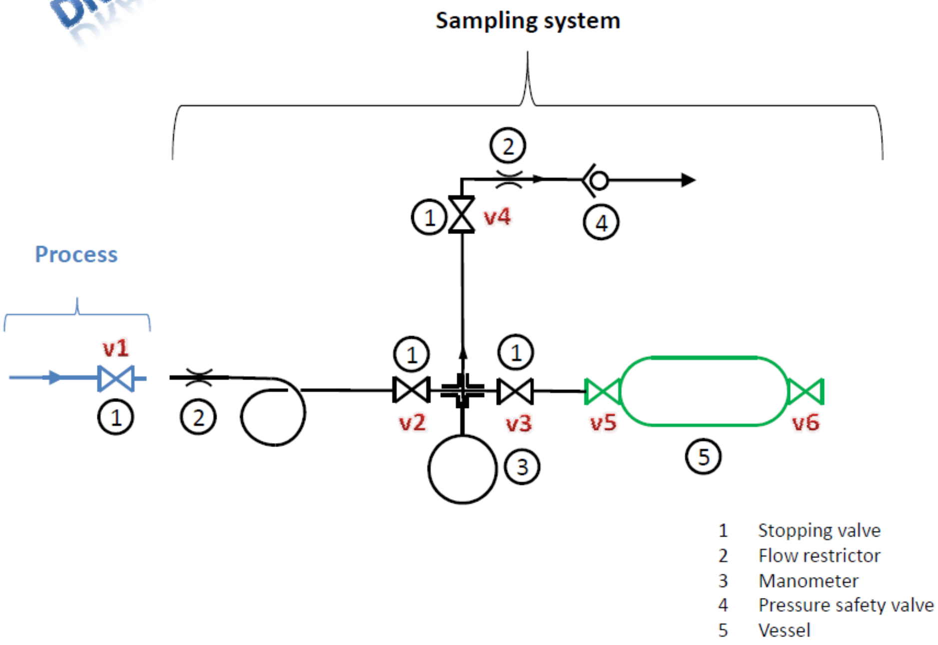


**Figure A4- 1 Schematic of the sampling system used in the project EMPIR Hydrogen 15NRM03**

**The sampling operation are covering the different steps from connecting the system, purging the sampling system, sampling and disconnecting. It is mandatory to perform and agree on the safety risk assessment prior to any actual sampling.**

### 1 Connection

- Check that all the valves are in the position « Closed »
- Connect the sampling system to the sampling point of the process

### 2 Leak check

- Open V1, V2 and V3 and wait 15 sec (to stabilize to pressure into the sampling system)
- Close V1
- Note the pressure on the manometer, wait 1 min to check any drift
- Close all the valves

### 3 Purge of the sampling system

- Open V1, V2 and V3 and wait 15 sec (to stabilize to pressure into the sampling system)
- Close V1
- Open V4 until the manometer indicate 2 bars then close V4
- Open V1, wait 15 sec and close V1

- Open V4 until the manometer indicate 2 bars then close V4
- Repeat the two last operations five times

### 4 Fill the vessel

- Open V1 and wait 15 sec (to stabilize to pressure into the sampling system)
- Open V5 and wait 15 sec then close V5
- Open V6 until the manometer indicate 2 bars then close V6 and wait 5 min
- Repeat the two last operations five times

### 5 Disconnection

- Close all the valves
- Open V2, then V3 and finally V4 (to depressurise the sampling system)
- Disconnect the vessel
- Disconnect the sampling system

# Annex 5 Results of analysis of hydrogen samples from SMR + PSA

|  | Results with expanded uncertainty (k=2) in µmol/mol |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 | Sample 8 | NMI |
| CO | < 0.053 | < 0.053 | < 0.01 | < 0.01 | < 0.01 | < 0.02 | < 0.02 | < 0.02 | NPL |
| CO | < 0.2 | < 0.2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | RISE |
| $CO_2$ | <0.1 | <0.1 | < 5 | < 5 | < 5 | < 0.5 | n.a. | n.a. | RISE |
| $CO_2$ | 0.042 ± 0.016 | < 0.02 | < 0.01 | < 0.01 | < 0.01 | < 0.02 | < 0.02 | < 0.02 | NPL |
| $CH_4$ | 0.044 ± 0.007 | < 0.02 | < 0.01 | < 0.01 | < 0.01 | < 0.02 | < 0.02 | < 0.02 | NPL |
| CH4 | n.a. | n.a. | ~ 0.01 | ~ 0.01 | ~ 0.01 | n.a. | n.a. | n.a. | VSL |
| Non CH4 hydrocarbons | < 0.05 | < 0.05 | < 0.01 | < 0.01 | < 0.01 | < 0.02 | < 0.02 | < 0.02 | NPL |
| $H_2O$ | < 0.6 | < 0.6 | < 0.5 | < 0.5 | < 0.5 | < 1.8 | < 1.5 | < 1.2 | NPL |
| $H_2O$ | n.a | n.a. | n.a. | n.a. | n.a. | < 2 | n.a. | n.a. | RISE |
| Total sulphur compounds | < 0.002 | < 0.002 | < 0.0036 | < 0.0036 | < 0.0036 | < 0.002 | < 0.002 | < 0.002 | NPL |
| H2S | <0.04 | <0.04 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | RISE |
| $O_2$ | n.a. | < 5 | n.a. | < 5 | < 5 | < 25 | < 25 | < 25 | CEM |
| $O_2$ + Ar | n.a. | n.a. | n.a. | n.a. | n.a. | < 50 | < 50 | < 50 | RISE |
| $O_2$ | 0.39 ± 0.13 | 0.39 ± 0.13 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 1.0 | < 0.5 | NPL |
| $N_2$ | n.a. | n.a. | < 100 | < 50 | < 60 | < 50 | < 50 | < 50 | RISE |
| $N_2$ | n.a. | < 25 | n.a. | n.a. | < 80 | < 25 | < 25 | < 25 | CEM |
| $N_2$ | 1.5 ± 0.6 | < 1.0 | < 1.2 | < 1.2 | < 1.2 | 5.2 ± 0.6 | 10.4 ± 1.1 | 5.5 ± 0.6 | NPL |
| Ar | n.a. | n.a. | < 30 | < 30 | < 30 | n.a. | n.a. | n.a. | RISE |
| Ar | n.a. | < 25 | n.a. | n.a. | < 80 | < 25 | < 25 | < 25 | CEM |
| Ar | 2.8 ± 0.1 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | 1.00 ± 0.10 | 1.30 ± 0.10 | 1.11 ± 0.10 | NPL |
| Total halogenated (HCl) | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | VSL |
| CH2O | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | VSL |
| CH2O2 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | VSL |
| NH3 | < 0.1 | < 0.1 | n.a. | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | VSL |
| He | 20 ± 4 | 12 ± 5 | n.a. | n.a. | < 50 | 44 ± 10 | 43 ± 10 | 43 ± 8 | CEM |
| Methane | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | RISE |
| C2 hydrocarbons | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | RISE |
| C3-hydrocarbons | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | RISE |
| C4-hydrocarbons | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | RISE |
| C5-hydrocarbons | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | RISE |
| C6 – C18 hydrocarbons | <0.050 | <0.050 | <0.050 | <0.050 | <0.050 | <0.050 | <0.050 | <0.050 | RISE |

# Annex 6 Results of analysis of hydrogen samples from PEM Water electrolysis

|  | Results with expanded uncertainty (k=2) in μmol/mol |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 | Sample 8 | NMI |
| CO | < 0.053 | < 0.02 | < 0.02 | < 0.02 | < 0.02 | < 0.02 | < 0.02 | < 0.02 | NPL |
| CO | < 0.2 | n.a. | < 0.02 | < 0.02 | < 0.02 | n.a. | n.a. | n.a. | RISE |
| CO2 | <0.1 | < 5 | < 5 | < 0.4 | < 0.4 | < 5 | n.a. | < 5 | RISE |
| CO2 | 0.443 ± 0.010 | 0.245 ± 0.010 | 0.229 ± 0.08 | < 0.02 | < 0.02 | < 0.01 | < 0.01 | < 0.01 | NPL |
| CH4 | 0.031 ± 0.006 | < 0.01 | < 0.01 | < 0.02 | < 0.02 | < 0.01 | < 0.01 | < 0.01 | NPL |
| Non $CH_4$ HC | < 0.05 | < 0.02 | < 0.02 | < 0.02 | < 0.02 | 0.156 ± 0.030 | 0.126 ± 0.026 | 0.111 ± 0.024 | NPL |
| H2O | < 0.6 | < 0.8 | < 1.4 | < 3 | < 3 | < 0.8 | < 1.2 | < 3 | NPL |
| H2O | n.a. | n.a. | n.a. | < 3 | < 5 | n.a. | n.a. | n.a. | RISE |
| Total sulphur compounds | < 0.002 | < 0.002 | < 0.002 | < 0.002 | < 0.002 | < 0.0030 | < 0.0030 | < 0.0030 | NPL |
| H2S | < 0.04 | - | - | < 0.004 | < 0.004 | n.a. | n.a. | n.a. | RISE |
| O2 | < 5 | < 5 | < 5 | < 5 | < 5 | < 5 | n.m. | < 5 | CEM |
| O2 + Ar | n.a. | < 5 | < 11 | < 5 | < 3 | < 25 | n.a. | < 25 | RISE |
| O2 | 0.45 ± 0.13 | < 0.5 | < 0.5 | < 0.6 | < 0.6 | 1.39 ± 0.36 | < 0.5 | 1.59 ± 0.45 | NPL |
| N2 | n.a. | < 40 | < 70 | - | - | < 100 | n.a. | < 100 | RISE |
| N2 | < 25 | < 50 | < 50 | < 50 | < 50 | < 80 | n.m. | n.m. | CEM |
| N2 | 2.0 ± 0.5 | 4.6 ± 0.3 | 4.2 ± 0.4 | < 1.5 | < 1.5 | 1.51 ± 0.2 | < 1.0 | 1.86 ± 0.2 | NPL |
| Ar | < 25 | < 50 | < 50 | < 50 | < 50 | < 80 | n.m. | n.m. | CEM |
| Ar | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | NPL |
| Total halogenated (HCl) | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | n.a. | < 0.005 | < 0.005 | VSL |
| CH2O | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | < 0.005 | VSL |
| CH2O2 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | VSL |
| NH3 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | n.a. | n.a. | n.a. | VSL |
| He | 34 ± 5 | < 5 | < 5 | 15 - 45 | < 5 | < 9 | < 9 | < 9 | CEM |
| Methane | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | n.a. | n.a. | n.a. | RISE |
| C2 hydrocarbons | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | n.a. | n.a. | n.a. | RISE |
| C3-hydrocarbons | <1 | <1 | <1 | <1 | <1 | n.a. | n.a. | n.a. | RISE |
| C4-hydrocarbons | <1 | <1 | <1 | <1 | <1 | n.a. | n.a. | n.a. | RISE |
| C5-hydrocarbons | <1 | <1 | <1 | <1 | <1 | n.a. | n.a. | n.a. | RISE |
| C6 – C18 hydrocarbons | <0.050 | <0.05 | <0.05 | <0.05 | <0.05 | n.a. | n.a. | n.a. | RISE |