CLEAN HEAT AND POWER FROM HYDROGEN

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DELIVERABLE REPORT

D4.1: SUMMARY OF INVESTIGATION INTO THE COMPOSITION OF LOW-GRADE HYDROGEN	
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SUMMARY	
Keywords	*Hydrogen; Hydrogen Quality; Contaminants; Hydrogen Production; Hydrogen Transmission; Hydrogen Storage*
Abstract	*This report aimed to identify the type and magnitude of impurities introduced into hydrogen during its production, storage and transmission. Key impurities were identified throughout the value chain and evaluated based on their likelihood of entering the hydrogen and impact on low-temperature Proton Exchange Membrane (PEM) fuel cell end-use. In this evaluation, carbon monoxide is the only impurity classified as high risk, and methane, carbon dioxide, nitrogen, hydrocarbons, and odorants are classified as medium risk with respect to end use in low temperature fuel cells.*

REVISIONS

Version	Date	Changed by	Comments
0.1	03.06.2024	TAA, KM, EC	Initial literature review
0.2	17.06.2024	EC, KM	Inputs after online workshop
1.1	31.10.2024	KM, EC	Final adjustments and implementation of risk evaluation after discussion at consortium meeting
2.0	02.12.2024	KM	Adjustments after feedback from consortium members

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A SUMMARY OF INVESTIGATIONS INTO THE COMPOSITION OF LOW-GRADE HYDROGEN

CONTENTS

1 INTRODUCTION

As the destructive impact of climate change is increasingly seen throughout the world, the push to find zero emission methods for the production, distribution, and use of energy is increasing. The extensive use of hydrogen as an energy carrier can allow the long-term storage and widespread distribution of zero-emission energy for geographical areas and industrial sectors that would otherwise be unable to decarbonise. However, with this widespread use of hydrogen comes challenges related to standardisation of hydrogen purity at all points within the value chain.

Though there are methods to produce green, high purity hydrogen, the vast majority of hydrogen used today is produced from techniques such as steam methane reforming (SMR), or as an industrial by-product, which are more likely to produce lower quality hydrogen that needs additional purification steps before use. In addition, other impurities may be introduced into hydrogen during its transmission and storage, and these can severely impact the performance and lifetime of end-use technologies such as fuel cells. It is therefore important to understand the types and quantities of impurities that may be introduced into hydrogen, both to inform quality standards and to facilitate purification where needed.

Currently there are standards, such as CEN TS17977, being developed for the transmission of hydrogen in new or repurposed natural gas pipelines, with discussions around suitable quality limits focussing on three options: 98, 99.5, and 99.97 %, of which 98 %, so called industrial quality hydrogen, is the cheapest.

As part of the Clean Heat and Power from Hydrogen (CLEANER) project,1] the use of industrial grade hydrogen in low temperature fuel cells is being explored. Thus, an investigation into the composition of this industrial grade hydrogen was performed to better understand the types of impurity present, and the potential impact of these impurities on fuel cell performance. This investigation includes a comprehensive literature review and two workshops to gather inputs on impurities found in hydrogen production methods, geological storage options, hydrogen carriers and transmission methods. This report summarises those findings along with a discussion on the probability of finding such impurities in product hydrogen, and how the impurities can then affect fuel cell performance.

2 METHODOLOGY

2.1 Information gathering

To gather information for this report, a literature survey was first performed on relevant methods for hydrogen production, storage, and transmission. Additionally, as end-user applications are of relevance, hydrogen purification strategies were summarised throughout the work.

The hydrogen production methods analysed in this work include:
- Naturally occurring hydrogen, or white hydrogen
- Grey hydrogen from stream methane reforming and partial oxidation of natural gas
- Biomass gasification
- Green hydrogen from proton exchange membrane, anion exchange membrane, solid oxide and traditional alkaline water electrolysis
- Hydrogen as a by-product from the chlor-alkali and sodium chlorate processes

With information from hydrogen production gathered, H_2 storage methods were analysed, with a focus on storage in geological features, such as:
- Salt caverns or porous geological traps
- Rock caverns
- Depleted oil reservoirs
- Aquifers

Finally, to cover hydrogen transport and transmission, hydrogen carriers and hydrogen transmission methods were researched, including the following hydrogen carriers:
- Liquid organic hydrogen carriers such as toluene
- Ammonia
- Methanol

As well as the following transmission methods:
- Pipelines, both repurposed natural gas pipelines and newly built hydrogen pipelines
- Tankers

To supplement the literature findings, two workshops were held to gather inputs from relevant stakeholders and actors, including industry, academic institutions, other EU projects participants (both previous and on-going), and others. The first workshop was held online on June 3rd, 2024, where Katie McCay from SINTEF presented the literature review findings so far, and three presenters gave inputs on relevant topics, namely:

- Laura Barrio, Euskal Herrika Unibertsitatea
  Presentation topic: *Impurities present in H_2 after LOHC + Dehydrogenation*2]

- Udo Lubenau, DBI Gas- und Umwelttechnik GmbH
  Presentation topic: *Impurities from repurposed natural gas pipelines*3]

- Jaione Ollo, Tecnalia
  Presentation topic: *Hydrogen purification from depleted reservoirs using membrane technology*4]

The format of the workshop was made to promote discussion with the participants to assist in the production of this report. Aspects from each of the presentations, as well as inputs and comments from the workshop chat were considered in this report.

The second workshop was held for CLEANER project participants on 22nd October 2024, where a summary of the findings of this report were presented by Katie McCay, and then project participants discussed the classification of impurities identified in this report as high, medium or low risk for fuel cell applications. Details of how this was carried out are explained in the next section.

2.2 Quantification of impurity risk

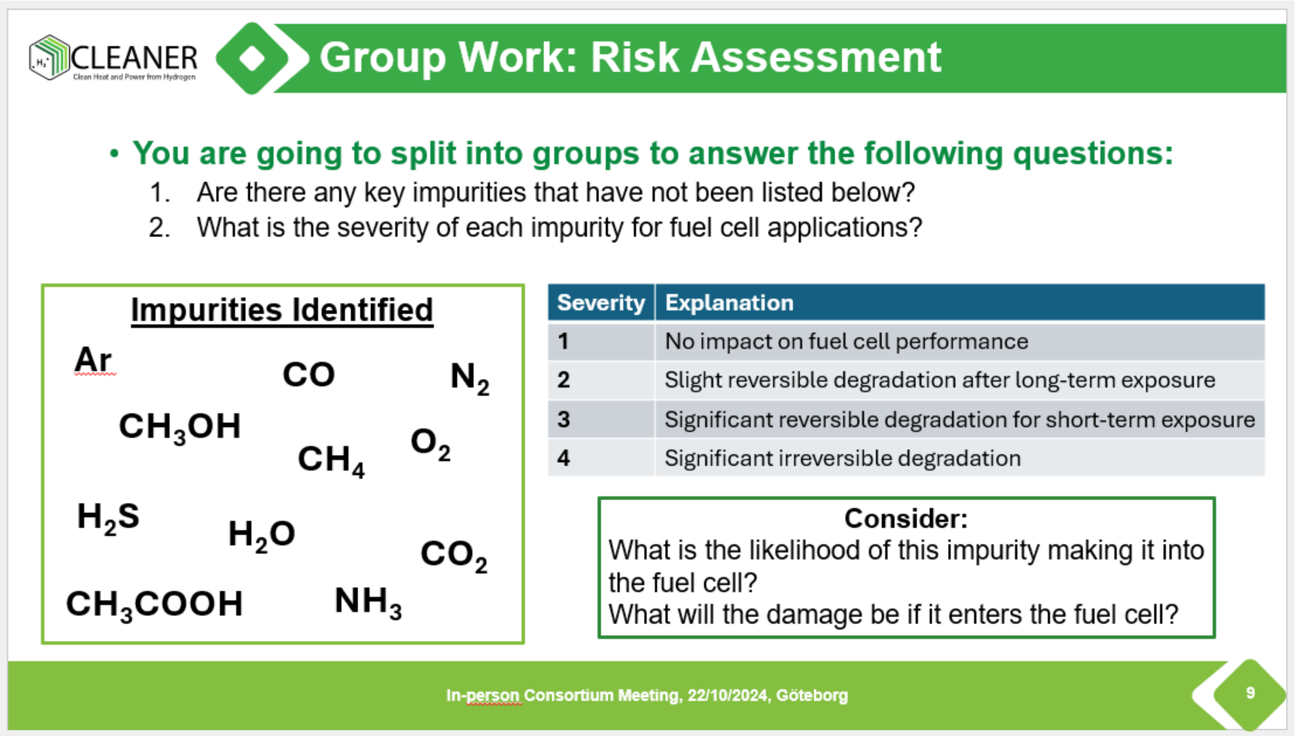
To come up with a quantification of the risk of finding impurities in H_2, an “impurity classification” workshop was conducted by Katie McCay in the M6 in-person consortium meeting of the CLEANER project. As mentioned, the goal of the workshop was to gather inputs from the consortium partners on the probability of occurrence, as well as risk severity of impurities found in H_2.

2.2.1 Probability of occurrence

First, the literature survey that was performed by SINTEF was summarised and presented to the consortium. Then a table was proposed based on the literature findings, where the probability of finding impurities in the various H_2 production, storage and transmission methods was provided. This was done by classifying impurities as being found “More frequently” or “Less frequently” in the H_2 source in question. A grade of 1 was given to those found “Less frequently” and a grade of 2 was given to those found “More frequently”. Consortium Partners then had a discussion on the proposed classification and changes were made to improve it.

2.2.2 Risk severity

To assess the severity of certain impurities on fuel cell performance, a group exercise was carried out. In this group exercise, the Consortium Partners were split into strategic groups, who were asked to answer the questions summarised on the slide shown in the figure below:



Group Work: Risk Assessment

- **You are going to split into groups to answer the following questions:**
  1. Are there any key impurities that have not been listed below?
  2. What is the severity of each impurity for fuel cell applications?

Impurities Identified

Ar CO N_2 CH_3OH CH_4 O_2 H_2S H_2O CO_2 CH_3COOH NH_3

Severity	Explanation
1	No impact on fuel cell performance
2	Slight reversible degradation after long-term exposure
3	Significant reversible degradation for short-term exposure
4	Significant irreversible degradation

Consider:
What is the likelihood of this impurity making it into the fuel cell?
What will the damage be if it enters the fuel cell?

In-person Consortium Meeting, 22/10/2024, Göteborg

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Figure 1. Group Work: Risk Assessment. Slide from M6 Consortium Meeting in Gothenburg.

The groups were given time for separate discussion before all Consortium Partners concluded on where each impurity should be placed on the Risk severity scale that was proposed in the slide. The outcome of the exercise was that each impurity was assigned a score from 1 to 4 for the following risk severity classes:

1. No impact on fuel cell performance.
2. Slight reversible degradation after long-term exposure.
3. Significant reversible degradation after short-term exposure.
4. Significant irreversible degradation.

2.2.3 Final risk quantification

To settle on a final risk quantification, the probability of occurrence was multiplied by the risk severity for each of the hydrogen production, storage and transmission methods. This allowed for the identification of high, medium of low-risk contaminants on fuel cell performance. An example was also provided for H_2 that is associated to a few of the summarised sources. For example, H_2 produced via PEM water electrolysis, then sent through a repurposed pipeline, prior to being delivered to an end user. With this assessment completed, it was possible to identify which impurities should also be studied during the stack testing of the CLEANER project, in addition to the planned CO and N_2.

3 KEY IMPURITIES AFFECTING PEMFC PERFORMANCE

The CLEANER project works on developing novel materials and processes to allow the use of industrial quality hydrogen in PEM fuel cells. However, in order to mitigate the degradation caused by impurities, it is crucial to understand the mechanisms. Therefore, this section of the report briefly addresses various types of impurities and the way in which they cause PEMFC degradation. The information here is limited only to the FC stack but other system components can also be impacted.

Table 1 summarises some key impurities that can have a negative impact on PEMFC stacks, and how each impurity can affect performance. It is based on a review of hydrogen purification technologies for fuel cell applications by Du *et al.*5], with some supplementary information taken from [6, 7]. For the PEMFC stack, the catalyst layers, which are usually platinum-based, and the polymer-based membrane within the stack, are most susceptible to damage from impurities in the fuel cell feed components.6] Chen *et al*.8] provide a detailed review on the effect of contamination on fuel cell performance, covering impacts, mechanisms and mitigation strategies.

Table 1: The effect of a selection of impurities on fuel cell stack performance[5, 7, 6]

Impurity	Possible damage from impurity in a fuel cell stack
H_2O	Impurities soluble in water (ex: Na^+, K^+) can reduce membrane conductivity for H^+. Water can also corrode metal parts of the cell.
Hydrocarbons (HC)	HCs can decrease catalytic performance by adsorbing to the catalyst surface. Some HCs (ex: CH_4) can also act as a dilutant for the H_2 feed, lowering performance.
O_2	O_2 is generally tolerated at low concentrations in the fuel cell. The H_2/O_2 explosive limits must be carefully monitored.
Inert gases (N_2, Ar, He)	Inert gases such as N_2 can dilute the H_2 feed and build-up in the anode recirculation loop, lowering performance. This can eventually lead to reverse current decay conditions and catalyst support corrosion.
CO_2	CO_2 acts as a dilutant for the H_2 feed. It can also react to form CO, which poisons the catalyst layer.
CO	CO reversibly binds onto the Pt catalyst layer and decreases the electrochemical active surface area available for reaction.
Sulphides	Sulphides can adsorb onto the catalyst layer, blocking active sites available to H_2 for the reaction. They can in turn react to form stable Pt sulphide species, contributing to irreversible fuel cell degradation.
Formaldehyde (HCHO) and formic acid (HCOOH)	HCHO and HCOOH can adsorb onto the catalyst layers and form CO, which leads to catalyst poisoning.

NH_3	Ammonia can adsorb onto the catalyst layer, blocking active sites. NH_4^+ ions can also reduce the proton conductivity of the membrane.
Halides	Halides can adsorb onto the catalyst and decrease the available area for the reaction. Cl^- can deposit in the polymer electrolyte membrane, leading to dissolution of the catalyst and irreversible performance loss.
Particulate matter	Particulate matter can block catalyst active sites and damage other fuel cell components. They could also degrade the membrane.

3.1 Existing H_2 fuel quality standards for PEMFCs and other applications

There are a number of existing quality standards, and directives for use of hydrogen in various applications. A non-exhaustive list can be found below.

3.1.1 Standards

- ISO 22734:2019. Hydrogen generators using water electrolysis — Industrial, commercial, and residential applications
- ISO/TR 15916:2015 Basic considerations for the safety of hydrogen systems
- ISO 17268, Gaseous hydrogen land vehicle refuelling connection devices
- SAE J2600 Compressed hydrogen surface vehicles fuelling connection devices
- SAE J2719:2020, Hydrogen Fuel Quality for Fuel Cell Vehicles
- IEC 31010:2019 Risk management — Risk assessment techniques
- ISO 14687 Hydrogen fuel quality — Product specification
- EN 17124 Hydrogen fuel – Product specification and quality assurance for hydrogen refuelling points dispensing gaseous hydrogen – Proton exchange membrane (PEM) fuel cell applications for vehicles
- EN 17127 Outdoor hydrogen refuelling points dispensing gaseous hydrogen and incorporating filling protocols
- ISO 19880-8 Gaseous hydrogen -- Fuelling stations -- Part 8: Fuel quality control
- CEN/TS 17977 Gas infrastructure - Quality of gas - Hydrogen used in rededicated gas systems

Of these standards, the most notable for fuel cell applications are ISO 14687 Grade D, EN 17124, and SAE J2719, which are mostly harmonised with respect the quality requirements for Fuel Cell Vehicles. In all cases, the minimum hydrogen quality requirement is 99.97 %, with the following impurity limits:

- <100 ppm of CH_4
- <2 ppm of other hydrocarbons
- <5 ppm of O_2
- <300 ppm for each of the inert components: He, Ar, N_2

- <2 ppm of CO_2
- <0.2 ppm CO
- <0.004 ppm sulphurs

For other applications, the purity requirement for internal combustion engines is outlined in ISO 14687 Grade A, which has a quality limit of 98 %. Standard CEN TS17977 for hydrogen that will be used in a repurposed gas grid also currently suggests an overall quality of 98 %, however there are some key differences between these two standards, including the limits for water, gaseous hydrocarbons, and the total sulfur content.

4 ANALYSIS OF POSSIBLE IMPURITY SOURCES

The main section of this report addresses possible sources of impurities throughout the hydrogen value chain. Various hydrogen production, storage, and transmission processes were investigated to determine which key impurities could be introduced to the hydrogen and in which quantity, as well as any purification strategies that may already be in place.

4.1 Hydrogen production methods

The first section of this work investigates impurities found in various sources of hydrogen, with naturally occurring hydrogen, and hydrogen produced through steam methane reforming, from biomass, by electrolysis, and as an industrial by-product being investigated. Each of the methods mentioned below require hydrogen separation and purification to fuel cell grade hydrogen. Some of the separation techniques mentioned below were also summarised in Jaione Ollo's presentation in the first CLEANER workshop,[4] where an overview of hydrogen purification strategies was provided, with a focus on H_2 purification from depleted reservoirs using membrane technology.

4.1.1 Naturally occurring hydrogen

Naturally occurring, or white hydrogen, is formed by natural processes such as the reaction of iron-rich rocks with water at elevated temperatures and pressures (serpentinization), and to a lesser extent natural radiolysis (dissociation of water by uranium or plutonium), or decomposition of organic matter.

After production of natural hydrogen, it can be directly released or vented at the surface, a process sometimes indicated by circular depressions colloquially referred to as "fairy circles". Surface measurements in these areas show release of low concentrations of hydrogen,[9, 10] less than 2 % and mostly in the 100s of ppm range, whilst deeper wells in the area of these features can show higher amounts of hydrogen, in one case up to 40 %.[11] The capture of this hydrogen that would otherwise be directly released is interesting as it can lead to a net reduction in emissions, however due to the disperse and low concentration nature of these hydrogen releases, it is largely impractical to capture and utilise. Instead, searching for naturally occurring hydrogen that has had its release hindered and has therefore built-up in underground storage sites can be of greater interest for worthwhile end-use volumes and concentrations.

Geologically, clay-rich rocks have been shown to delay hydrogen migration, and salt, halite, and igneous -type rocks can act as a sealant, leading to the buildup of hydrogen in underground stores. Release of hydrogen from these stores can be triggered by natural or man-made processes. Tectonic activity like volcanic eruptions and earthquakes can cause rock fracture and lead to the release of gaseous hydrogen, with quantities up to 8 % reported during earthquakes,[12] and even up to 93 % hydrogen measured in volcanic gasses released at various locations globally.[13] These sources of hydrogen are not practical to utilise but indicate a significant frequency of hydrogen stores in the earth's crust.

In 2019 it was estimated that the known sources of natural hydrogen produce 100 Tg/year (100 MT/year),[13] which was more than the global hydrogen consumption at the time. Of this, 23 Tg/year is geologically produced, although it is expected that this number will increase significantly as new sources are discovered. Nowadays, there is significant global interest in locating new natural hydrogen stores. Key exploration locations include Australia, the USA, and France, where a deposit of up to 250 million tons of hydrogen was recently discovered [14]. Historically, most natural hydrogen deposits have been found when exploring for oil, natural gas, or minerals. A selection of global hydrogen deposits found when drilling for other resources is shown in Table 2. Of these, the most notable discovery is a previously abandoned well in Mali that has been tapped to release hydrogen with 97.4 % purity. This hydrogen was utilised in a hydrogen combustion engine to produce green electricity for around 4000 people for at least ten years. The Mali reservoir is estimated to be at least 60 billion m^3 in size, containing 5 million tons of hydrogen.[15] This is the only case of utilisation of naturally occurring hydrogen to date.

Table 2. A selected list of global wells releasing hydrogen-containing gasses

Location	**Site Name**	**Hydrogen Composition / %**	**Key Impurities / %**				
			CH_4	**N_2**	**O_2**	**CO_2**	**Other**
Australia[16]	Robe 1	25.4	39.6	30.7	3.0	1.3	
Australia[16]	American Beach Oil	66.4 – 80	2.6 – 4.7	22.6 – 36	3.6 – 4.3	0.5 – 5.3	
Australia[16]	Ramsay Bore Oil	51.3 – 84	0 – 7.5	14.8 – 25.4	0 – 2.4		
Mali[17]	Bougou - 1	97.4		1.2		0.04	He 0.05
New Caledonia[18]	Baie du Carenage	32.4 – 36.1	13.7 – 15.7	50.3 – 51.9			
Oman[18]	Bahla	85.7	2.2	12.0			
Oman[18]	Haylayn	75 – 79.4	4.0 – 9.6	14.2 – 18.1			
Oman[18]	Abyiad	26.9 – 36.1	5.7 – 15.9	57.3 – 59.9			
Philippines[18]	Nagsasa	58.5	38.7	1.2			
USA[19]	Kansas Scott #1	17.2	45.1	34.6			He 1.5 Ar 0.6

In all cases, the purity of hydrogen found naturally is not high enough for direct use, and additional purification steps are needed. Impurities present in the Mali well, which is the highest purity found to date, include 1.2 % N_2, 0.05 % He, and 0.04 % CO_2, as well as traces of hydrocarbons (methane, ethane, propane, iso- and normal-butane, neo-, iso- and normal-pentane). Quantities of impurities can vary significantly in a small geographic area, and in the Mali case, some surrounding wells identified concentrations of H_2S and CO above 1000 ppm.

In most other cases, the key impurities found are nitrogen and methane. N_2-rich mixtures are associated with seepage of gas through water streams, whereas N_2-free mixtures are associated with dry seepage through fractures. Methane is regularly the dominating impurity, as H_2 has historically been found during natural gas exploration, but geological studies have determined that the occurrence of methane and hydrogen is caused by fundamentally different geological processes. Therefore, as new exploration of geological areas that are suitable for natural hydrogen production becomes more common, methane impurities may be less significant.

4.1.2 Grey hydrogen production

The most common pathways for grey hydrogen production are steam methane reforming, partial oxidation of natural gas and coal gasification, [6] where steam methane reforming (SMR) is the most common. In SMR, natural gas (methane) is reacted with steam to produce synthesis gas, mainly consisting of hydrogen and carbon monoxide. Carbon monoxide is then further reacted with water to produce hydrogen through the water gas shift reaction (WGSR). Both the reforming reaction and the WGSR are shown below:[20, 6]

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

In partial oxidation of natural gas with auto-thermal reforming (ATR), methane is partly reacted with oxygen to produce carbon monoxide and hydrogen. In the ATR step, steam is added to react with methane to form syngas[6]. The autothermal reforming of methane is shown below:[21]

$$3CH_4 + H_2O + O_2 \rightleftharpoons 3CO + 7H_2$$

The partial oxidation step provides the heat needed to drive the downstream reactions.[22, 21] Using air instead of oxygen could impact the fraction of nitrogen and other impurities e.g. argon in the produced hydrogen. Using purified oxygen could also introduce some argon, depending on the degree of purification.[6]

In coal gasification, the carbon source is reacted with oxygen and steam at high temperature and pressure to form a gas mixture of mostly hydrogen, carbon monoxide and carbon dioxide[6]. This is done through the main gasification reaction shown below, followed by the WGSR to produce more hydrogen.[23]

$$3C + O_2 + H_2O \rightarrow H_2 + 3CO$$

Coal gasification can be performed by fluidised bed, moving bed or entrained flow gasifiers using nitrogen or water to entrain the fluid. The quality of oxygen used in this process will impact the argon impurities in the produced gas, and using nitrogen as an entrainer can result in nitrogen impurities in the product gas.[6]

In the DYNAMIS project, impurities in hydrogen produced from decarbonised fossil fuels were studied for use in hydrogen fuel cells.[6] The estimated fuel composition used in the project is shown in Table 3. The tabulated data shows the gas product composition prior to entering PSA units for further hydrogen purification.

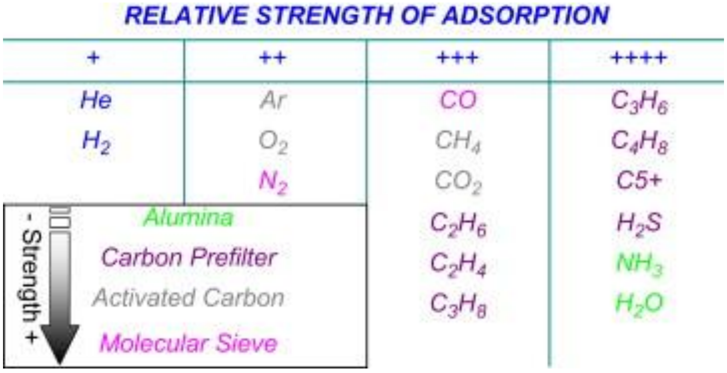
Table 3: Grey hydrogen production pathway compositions entering the feed streams of a PSA unit given by [6]. Coal introduction here is done with nitrogen fluid entrainment. The water content was less than 250 ppm in each stream.

Component	**Steam reforming**	**O_2-blown ATR**	**Coal gasification**
H_2	94.3%	93.2%	87.8%
CO	0.1%	1.4%	2.6%
CO_2	2.5%	1.7%	3.9%
N_2	0.2%	0.7%	5.0%
Ar	0%	0.6%	0.9%
CH_4	2.9%	2.4%	0.01%
H_2O	< 0.025%	< 0.025%	< 0.025%
T [°C]	33.3	35.0	30.0
P [bara]	26.3	25.0	28.0
Q [$Nm^3\ h^{-1}$]	17318	17631	19402

As can be seen from Table 3, the produced hydrogen quality is too low for any application of hydrogen fuel grades listed in ISO 14687. [24] Purification is therefore needed for downstream applications.

For high purity (> 99.97% fuel index) hydrogen production, pressure swing adsorption (PSA) is perhaps the most applied purification technique. Impurity-selective adsorbents are used to purify the hydrogen stream, and the adsorption/desorption process is enhanced by use of pressure cycling.[6] At least three columns are generally used to ensure a continuous hydrogen production process. PSA is mostly compatible with larger scale applications e.g. SMR facilities.

Adsorbents in PSA can be carefully selected to target specific impurities. Figure 2 illustrates relative adsorption strengths for typical adsorbent materials used.[6] PSA is least effective for impurities like He, Ar, O_2 and N_2 and most effective for components in the “++++” or “+++” columns.



RELATIVE STRENGTH OF ADSORPTION

+	++	+++	++++
He	Ar	CO	C_3H_6
H_2	O_2	CH_4	C_4H_8
	N_2	CO_2	C5+
		C_2H_6	H_2S
		C_2H_4	NH_3
		C_3H_8	H_2O

- Strength +
Alumina
Carbon Prefilter
Activated Carbon
Molecular Sieve

Figure 2. Examples of typical adsorbents and their affinity to known impurities in hydrogen. [6]

For a set PSA configuration, the impurity concentrations will show interdependencies. In a modelling example, [25] the impurities' dependence of hydrogen recovery is shown in Figure 3. For nitrogen, a hydrogen yield of 76.3% is sufficient to meet the ISO 14687 requirement of 100 ppm at the time of publication (today changed to 300 ppm). For CO however, a hydrogen recovery lower than 74% is needed to meet the ISO 14687 requirement of 200 ppb. At this recovery, nitrogen impurity is at 10 ppm.

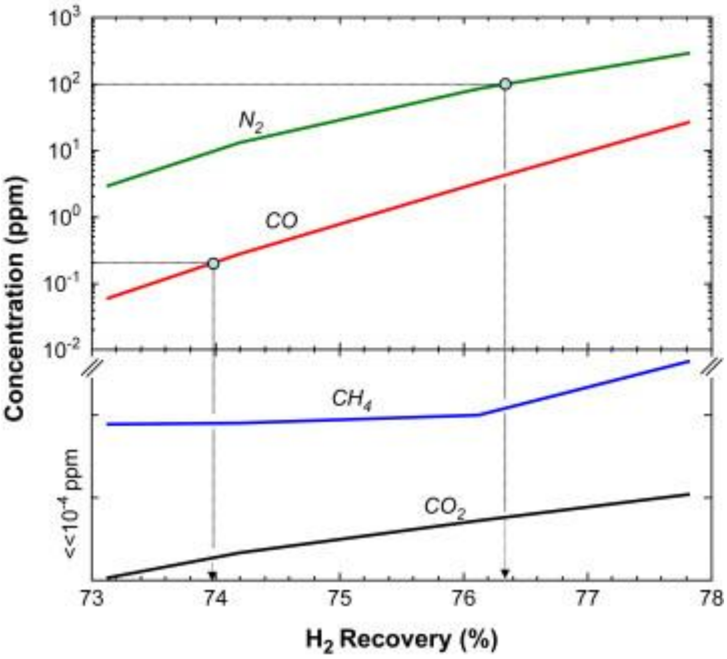


Figure 3. PSA modelling example illustrating the interdependence of impurities.

CO is in this example a limiting species for the hydrogen recovery setting of the process. Process quality control can therefore be conducted by monitoring the CO concentration online since the correlation with other impurities is known. For a target concentration of limiting species in a PSA process, the adsorbent volume, possible hydrogen yield and remaining impurity concentrations can be calculated.[6] Such information is reported for the purification via PSA of the three streams shown in Table 3.[6]

While PSA is a good process for achieving high purity hydrogen, it is possible that other separation units are needed to target specific components that may be present in higher amounts.

For example, in a simulation study of an integrated gasifier for hydrogen production (IGHP) plant, an acid gas remover was used to remove hydrogen sulphide prior to PSA.[23] Additionally, a carbon dioxide capture unit was used to remove CO_2 prior to the PSA. Ammonia can also be removed prior to PSA using a quench cooler.[6] In reformers, sulphur compounds are removed prior to the reactor to protect the catalyst.[6]

4.1.3 Hydrogen from biomass

An alternative to using fossil fuels as a source for hydrogen production is biomass. Biomass is a renewable organic material that can be available from a wide range of sources, such as animal, agricultural and municipal wastes, to name a few.[22] Multiple technologies can be used to convert biomass to hydrogen. Some are described in a literature review by Ahlström et. al., which focused on the conversion of sustainably harvested forest biomass to hydrogen.[26] The reviewed processes typically fall into three main categories: biological, electrochemical and thermochemical, the latter of which includes pyrolysis and gasification pathways, which have the highest technology readiness levels (TRL) and show some of the lowest production costs and highest production yields. Gasification has a higher efficiency and hydrogen yield than pyrolysis, making it more promising for industrial scale production.[27]

In the gasification reaction, biomass is thermochemically decomposed into H_2, CO, CO_2, CH_4, hydrocarbons, and tars in varying amounts, depending on the operating conditions of the process. The gasification process can also be upgraded to include ATR, SMR and/or WGSR to produce more hydrogen.[26]

To produce hydrogen via biomass gasification, some essential processing steps should be followed depending on the contaminants present.[28, 29] Following the gasification reactor, any particulate matter can be removed using units such as filters, cyclones, or scrubbing, while CO_2 or sulphur-containing gases can be removed using acid gas removal (AGR) units. Other hydrocarbons and tar can be removed from the stream by further reacting them via steam reforming.[28] After those mentioned gas cleaning steps, the WGSR can be used to adjust the gasification product stream for a higher hydrogen content. Then, the hydrogen gas can be purified via PSA.[28, 29] Depending on the process parameters, PSA can achieve H_2 purities of 98-99.9999 vol% H_2.[30, 31]

4.1.4 Green hydrogen production from electrolysis

Various processes can be used to produce hydrogen from electrochemical water splitting, which converts water to oxygen and hydrogen gasses. Generally, hydrogen production from water electrolysis results in a high purity product mainly contaminated by oxygen and water, but studies have shown that N_2, CO_2 or cations (K^+, Na^+) could also be present in some types electrolysis systems.[32, 33] In addition, polymeric balance of plant materials like O-rings and gaskets can introduce impurities such as polymer fragments or metal ions. Generally, O_2 and H_2O could be present in the produced hydrogen, but as mixtures of oxygen in hydrogen pose a safety risk, careful monitoring and removal of oxygen must be performed. N_2 could be present in the produced hydrogen mainly due to system venting/purging during startup/shutdown/maintenance operations. CO_2 could be present in the water fed to the system or from air intake to the system. Overall, adequate feed water processing and hydrogen downstream processing, as well as appropriate operation and maintenance of water electrolysis systems is needed to reduce the likelihood of impurities ending up in the produced H_2 product.

4.1.4.1 Alkaline electrolysis

One of the oldest and most proven technologies is the traditional alkaline electrolysis (AEL) process. In this process, a highly concentrated potassium hydroxide solution is used as an electrolyte and the cell generally consists of a nickel-based anode and cathode separated by a porous diaphragm. While this process is relatively low in cost, cell constraints limit the system to low current density operation and do not allow for operation at high pressures.[34] In the AEL, the hydrogen exiting the electrolyser is first separated from the electrolyte in a gas-liquid separator, then sent through a gas scrubber to remove any alkali impurities from the electrolyte.[35, 36] Residual oxygen in the hydrogen is then removed using a deoxidiser unit, and finally, water is removed from the hydrogen using dryers, which can also separate out any residual water-soluble impurities, such as Na^+ and K^+ from the electrolyte. The downstream separation sequence following the electrolyser can bring the hydrogen purity to 99.9998%.[35] Similar to PEM technology as described in the next section, organic impurities could be introduced into the AEL system in the process feed water/electrolyte. Such organics could oxidise at the anode producing carbon dioxide or carbon monoxide, which could contaminate the H_2 product gas.[37] Finally, despite the downstream processing to purify the H_2, cations could still be present in the hydrogen gas through the water that makes it into the product stream.[32]

Hydrogen sampled from an alkaline electrolyser at 9.8 bar after a deoxidiser and drying unit was analysed for ISO 14687 Grade D contaminants.[33] Results show that N_2, CO_2 and H_2O were present, however all below the ISO 14687 threshold, and the amount of all other ISO 14687 gaseous contaminants was below the threshold.[33]

4.1.4.2 PEM electrolysis

Proton exchange membrane water electrolysis (PEMWE) is a relatively more recent commercial electrolysis process, where a solid polymer electrolyte is employed instead of a liquid electrolyte, with platinum-based materials generally used as anode and cathode electrocatalysts. The two electrodes on either side of the membrane make up the membrane electrode assembly (MEA). The PEM cell design is compact, efficient and allows for higher current density operation as well as differential pressure operation.[38, 37]

In a typical PEMWE system, the produced hydrogen generally contains some oxygen and water impurities. Therefore, bulk water is first separated from the produced hydrogen in a gas-liquid separator, followed by a condenser and condensate trap. Then oxygen is removed in a deoxidiser unit by catalytically recombining O_2 with H_2 to form H_2O. Finally, residual water is removed to the desired H_2 purity using dryers, such as temperature/pressure swing adsorption columns.[38, 32]

High purity hydrogen (99.999 vol%) can be achieved from a PEMWE process.[39] For PEM electrolysers that operate with humidified air on the anode (instead of water as with traditional PEM technology), observable concentrations of nitrogen in the produced hydrogen are obtained due to crossover. Around 50 ppm N_2 has been measured in the H_2 stream in this case. [40] This nitrogen can be more difficult to remove than other impurities, for example O_2, but the concentration observed does not exceed ISO 14687 standards for use in PEMFCs, and thus is not of concern.

Feed water can also affect the purity of the hydrogen product in PEM electrolysis, despite the high purity water requirements. ASTM Type II water (1 MΩ cm) is compliant with PEM electrolysis technology and can contain up to 5 $\mu g\ L^{-1}$ of Na^+ and Cl^-, as well as 50 $\mu g\ L^{-1}$ of total organic carbon (TOC). [41] It is possible that Cl^- impurities present in the feed water could react via the chlorine evolution reaction (CER) at the anode of a PEMWE, competing with the oxygen evolution reaction (OER) under operating conditions.[37] Other halide ions that may be present in the water could also react to their gaseous form in similar reactions. While PEMWE systems typically include ion exchange resins to clean the process water during its recirculation, if these halide impurities are not removed as water is consumed during operation, they could increase in concentration to more significant quantities, potentially impacting the quality of the produced H_2 product. As for the TOC that could be present in the process water, organic impurities can oxidise to carbon monoxide or carbon dioxide at the anode in PEMWE.[37] If these impurities were to crossover to the cathode side of the cell, they could affect the purity of the hydrogen product.

Hydrogen gas sampled from a PEM water electrolyser system at 20 bar after temperature swing adsorption, was tested for ISO 14687 Grade D contaminants, showing that there is a presence of N_2, CO_2 and H_2O, where N_2 and CO_2 are present in quantities below the ISO 14687 threshold, while H_2O is present just above the threshold.[33] The authors did however note that while water is an expected contaminant in PEMWE, further work might be needed to validate whether some of it was introduced during sampling. The amount of all other analysed gaseous contaminants was below the ISO 14687 threshold.[33]

4.1.4.3 Solid Oxide Electrolysis

Another common electrolysis technology is solid oxide electrolysis (SOE), which unlike PEM and AEL technology, occurs at high operating temperatures in the range of 500 – 900°C. [42] At these operating temperatures, steam is electrolysed to hydrogen and oxygen with a decreased electrical energy requirement in comparison to other technologies, [43] which makes SOE favourable for processes that already have thermal energy available. SOE can occur with oxygen ions or protons as the conducting ion. In a typical system for solid oxide electrolysis with oxygen as the conducting ion, hydrogen gas produced at the cathode enters a hydrogen/steam separator to separate out the H_2O. This can be followed by a drier to further purify the hydrogen. [42] In SOE with proton conducting cells, hydrogen is directly produced at the cathode without any water vapour, [44] which can simplify downstream processing for high purity H_2 recovery.

4.1.4.4 AEM electrolysis

Anion exchange membrane water electrolysis (AEMWE) is an emerging electrolysis technology that makes use of the efficient and robust cell design used in PEMWE through the use of a polymer exchange membrane. However, in AEMWE, the alkaline environment allows for the use of low-cost non-noble metal cell materials like in AEL, resulting in a lower cost. [45] While there is limited data available for AEM system designs, a typical system was defined by IRENA in Reference [46], where the hydrogen produced mainly contains water as an impurity, requiring a drying unit downstream from the electrolyser stacks. Enapter [47], an AEM electrolyser company, reports the production of 99.95 %mol hydrogen ($H_2O < 500$ ppm, $O_2 < 5$ ppm), and 99.999 %mol after an optional dryer ($H_2O < 5$ ppm, $O_2 < 5$ ppm). [48] As with PEMWE and AEL, it is possible that oxidation of any organic impurities could produce CO_2 or CO, contaminating the H_2 product gas.[37]

4.1.5 By-product H_2

4.1.5.1 The chlor-alkali process

Several electrochemical processes have hydrogen reduction as their secondary product. For example, in the well-known chlor-alkali process, a salt solution (NaCl) is electrolysed to primary products chlorine and caustic soda, with hydrogen as a by-product. The electrochemical process is summarised with the reactions below: [49]

$$Anode:\ Cl^- \rightarrow Cl_2 + 2e^-$$
$$Cathode:\ 2H_2O + 2e^- \rightarrow 2OH^- + H_2$$
$$Overall\,reaction:\ 2H_2O + 2NaCl \rightarrow Cl_2 + 2NaOH + H_2$$

In this process, the Na^+ ions are transported from the anode to cathode side of the cell through an ion exchange membrane, for example. Having a membrane separating the anode and cathode side of the cell prevents the reaction between Cl_2 and OH^-, as well as Cl_2 and H_2.[32] Traditionally, the hydrogen surplus has been vented. Nowadays, there is more interest in utilising the hydrogen.

In the chlor-alkali process, the produced hydrogen can mostly be contaminated by water, CO_2 and nitrogen.[32] Water is already present in the electrolyte, while N_2 is commonly used for the safety purging in conjunction with system startup and shutdown. While unlikely, it is possible CO_2 could be present in the produced H_2 due to membrane degradation or oxidation of organic impurities in the electrolyte.[32] With H_2O being the primary impurity, hydrogen purification can be performed with drying towers, i.e. temperature swing adsorption. For any CO_2 present in the system, soda lime columns can be used, however there is a penalty on hydrogen yield from regeneration of the columns. N_2 removal requires getter-type membranes. Palladium membrane separation is also emerging as an economically feasible alternative for hydrogen purification for smaller capacity production. [7]

It is also possible that gas crossover through the membrane could occur in the event of a failure in the liquid levels of the cell. This could result in some Cl_2 being present on the hydrogen/cathode side of the cell. Furthermore, Cl_2 gas could convert to HCl gas in the presence of the catalyst. While these two components could contaminate the hydrogen product, it is expected that they would both be removed in the drying towers, due to their high water solubility.[32]

4.1.5.2 The sodium chlorate process

Another process that generates by-product hydrogen is sodium chlorate production. In this process, chlorine ions from brine are oxidised to Cl_2 gas at the anode, which further reacts in a series of equilibrium reactions to form sodium chlorate with ClO_3^- and Na^+ and ions.[7] At the cathode, water is reduced to H_2 in the alkaline hydrogen evolution reaction. The overall reaction of the process is shown below:[7]

$$NaCl_{(s)} + 3H_2O_{(l)} \rightarrow NaClO_{3(s)} + 3H_{2(g)}$$

In a typical sodium chlorate process, a series of scrubbers, followed by a carbon filter and a deoxygenation reactor are typically used to bring the H_2 product gas to around 99.7 % purity.[7] The main impurities to remove are chlorine gas from the anode side of the cell, and oxygen formed through side reactions. Cl_2 can be removed using scrubbers, and O_2 can be removed in a deoxidiser unit. Other impurities that can be present after this first stage of purification are H_2O, CH_4, N_2, and CO_2. To bring the H_2 gas to purity levels high enough for fuel cell applications (>99.97%), supplemental purification can be done using PSA or palladium-based membrane separation techniques.[7]

4.1.6 Summary: Impurities from hydrogen production

In summary, most hydrogen production processes have a well-established output, and when coupled with the correct post-processing equipment, can lead to high purity hydrogen. In particular, electrolysis can directly produce hydrogen with a purity compatible for end use in fuel cells. However, it is rare that a site of hydrogen production is directly coupled to an end-user, meaning the hydrogen must be stored and transported to where it is needed. This can introduce additional impurities, as will be covered in the next sections, that must be monitored and removed if necessary.

4.2 Hydrogen storage in geological features

Large-scale storage of hydrogen is required if the 2050 targets for hydrogen use in Europe and worldwide are to be met, and it has been shown that with sufficient underground hydrogen storage, the cost, sustainability, and utilisation of hydrogen can be significantly improved. [50] There are several types of subsurface site that have potential as hydrogen storage locations, including salt caverns, depleted reservoirs, saline aquifers, or rock caverns. [51, 52] Of these, only salt caverns have historically been in operation in the US and UK for long-term hydrogen storage (for example in the UK three caverns of 1 000 000 m^3 have been in operation for the last 50 years), although with few extraction/injection cycles.

There are many unanswered questions about the storage of hydrogen in underground features, including logistical aspects like will the storage sites be centralised or localised at end users, safety aspects particularly regarding the storage of hydrogen underground in heavily populated areas, and technical aspects such as whether there is interaction between the hydrogen and storage site, and what is the leak rate of hydrogen. As interest in the utilisation of hydrogen increases, there are numerous projects and studies that aim to investigate these questions for each type of storage site, and in this document, we will attempt to address the question of hydrogen quality after long-term storage in geological features.

The first aspect of this is that in all types of underground storage except for lined rock caverns, cushion gasses are used to maintain a minimum pressure in the storage site when some of the hydrogen has been extracted. A review by Taiwo et.al. reported that cushion gasses should constitute between 45 and 80 % of the site volume, depending on the type of underground storage site. [53] Several studies have investigated carbon dioxide, nitrogen and methane as potential cushion gasses when storing hydrogen in depleted reservoirs, and in general methane performs better than the others in terms of hydrogen extraction and reactivity with the storage site. [54] However, over time the cushion gas will to some extent mix and be extracted with the hydrogen, meaning that additional expensive purification steps are needed to meet standards. Therefore, gasses such as N_2 that have a higher tolerance limit in quality standards, or gasses that are easy to separate from hydrogen may be a better choice.

In addition, the interaction between hydrogen and any bacteria found in the storage location is important. There are many types of bacteria that can thrive in hydrogen rich environments, where they convert hydrogen into byproducts such as CO_2, H_2S, CH_4 and more. Both the consumption of H_2 by microbes, which will deplete the hydrogen over time to some extent, and the introduction of impurities into the hydrogen should be considered when designing geological hydrogen storage sites. However, the type and magnitude of impurities that may be introduced to the hydrogen are dependent on the specific microbial profile of each location, so are difficult to estimate in general. It has been shown that in underground hydrogen storage, four common microbial reactions are methanogenesis, acetogenesis, and sulphate and ferric reduction, which form methane (CH_4), acetic acid (CH_3COOH), hydrogen sulphide (H_2S), and iron oxide (Fe_3O_4), respectively. [55] Particularly concerning is the production of H_2S, which has an extremely low tolerance limit in ISO14687, of 0.004 ppm. It is therefore recommended that the quality of hydrogen coming out of the geological storage site is monitored so the appropriate purification processes can be undertaken.

4.2.1 Salt caverns/porous geological traps

There are numerous projects in Europe that are investigating the storage of hydrogen in salt caverns, including HyStock in the Netherlands, H2Salt in Spain, Hypster in France, HyCavMobil in Germany, and more.

Salts in this case mean rocks composed of evaporite minerals, especially halite. These salt rocks are crystalline and self-healing, therefore are in most cases impermeable to water, and gasses can be sealed within or below the rock bands to provide underground storage sites. [56] Salts are more mobile than other rock types, and their deformations can generate suitable trapping locations that can be utilised for gas storage. To produce a storage cavern, soluble minerals are mined from the cavern by pumping water into the rocks and removed the produced brine. Salt caverns have typical volumes from 100 000 to 500 000 m^3, depending on the shape of the salt deposit, and they are most suited for medium-size storage volumes with a medium discharge time of up to several months. [57]

In terms of hydrogen quality, the salts typically have limited interaction with hydrogen, but the impurities in the salt may react, an aspect that should be further investigated. In addition, if there are layers of minerals alongside the salt, these must be characterised to confirm they will not react with hydrogen or cause leakages. There are several types of rock that have been shown to react with hydrogen, including calcite, which decomposes to CH_4 and CO_2, [58] and pyrite or anhydrite which can react to form H_2S and other sulfides, [59] but only at elevated temperature and pressure. Quartz, K-feldspar and hematite have been shown to be mostly unreactive in the presence of H_2, [60] as have certain silicate and clay minerals. [53]

4.2.2 Rock caverns

For regions without suitable geology for salt caverns, mined rock caverns can be utilised. These caverns are often not gas-tight, meaning that a liner must be placed within the cavern to keep the hydrogen in place, adding significant costs. For this, hydrogen-compatible liner materials (e.g. steel, plastic) must be identified, and cushioning must be integrated between the liner and the rock to avoid damage or potential corrosion. This cushioning material is often a concrete layer, which adds further costs.

With respect to impacts on hydrogen purity, as the liner is specially designed for hydrogen storage, there should be little risk of impurities from interaction with the liner. For some liner materials, interaction with hydrogen can reduce material integrity over time through processes such as hydrogen embrittlement, but this should not impact the hydrogen purity. Additionally, there should not be any microbial interactions within the liner, leading to a reliable hydrogen quality (i.e. you get out what you put in). Another positive aspect of lined rock caverns is that the hydrogen can also be stored at relatively high pressures, leading to a greater hydrogen storage density. The Swedish project HyBrit, which produces the world’s first fossil-free steel, [61] has built a 100 m^3 lined rock cavern for H_2 storage and plans to demonstrate a full-scale > 100 000 m^3 storage facility later in the project.

4.2.3 Depleted gas reservoirs

Areas of porous, permeable sedimentary rocks located underneath an impermeable cap rock that have contained natural gas can be repurposed to store hydrogen. They can store large amounts of gas, but the injection and extraction rate are influenced by the rock's permeability, so these sites are most suitable for long-term gas storage. [62]

Initially, depleted gas reservoirs are likely to be used to store blends of hydrogen and methane, as they likely contain residual methane and other hydrocarbons. Therefore, deblending must be performed. Eventually, after thorough purging through many injection/withdrawal cycles, pure hydrogen may be used. With respect to purity in this case, it is unclear whether significant interaction between the hydrogen and bedrock takes place. Several studies have investigated the behaviour of calcite in a hydrogen environment, and the findings range from more than 30 % of hydrogen consumed due to reaction with calcite, to no reaction at all. [55] The key impurity formed from side-reaction was CH_4, with some CO_2, NH_3 or H_2S possible. In addition, side-reactions between hydrogen and the site have been shown to both increase and decrease the porosity of the rock, depending on the rock type, [55] thus affecting the security of the hydrogen store. Further studies and experiences from real-world sites are clearly needed to understand this further.

4.2.4 Aquifers

Similar in nature to depleted gas reservoirs, aquifers are porous sedimentary rock structures that contain water, but unlike depleted gas reservoirs, they have not been proven to be gas-tight, meaning thorough surveys must be performed before use. Many of the impurities introduced in hydrogen being stored in aquifers are similar to depleted reservoirs, and come from interaction of H_2 with sedimentary rocks, often catalysed by bacteria. In addition, water is a key impurity meaning that hydrogen must be dried upon extraction. There are no examples of aquifers in use for storing pure hydrogen today, but some projects are investigating the feasibility and plan to demonstrate within the next years.

4.3 Hydrogen carriers

As well as storage of gaseous hydrogen in geological sites, which can be both inefficient due to hydrogen's low volumetric energy density, and dangerous as it forms an explosive mixture with air, there are several alternative methods for the storage or transportation of hydrogen. One of these is the utilisation of hydrogen carriers, which are species that can be reversibly reacted to incorporate and release hydrogen.

4.3.1 Liquid organic hydrogen carriers

Liquid Organic Hydrogen Carriers (LOHCs) are gaining attention as a convenient way of storing and transporting hydrogen utilising existing fossil fuel transport infrastructure. LOHC technology can offer an efficient, safe, environmentally friendly method for high-capacity hydrogen storage under ambient conditions, making it favourable for large-scale, long-distance H_2 storage and transportation. [63, 64, 65] LOHC technology is a cyclic process, which works on the basis of storing hydrogen by hydrogenating an unsaturated organic liquid, such as toluene, then releasing hydrogen by dehydrogenating the H_2-saturated organic liquid, such as methylcyclohexane to release the hydrogen. [64] While an attractive process, utilising LOHCs does have its disadvantages, such as high costs for LOHC material and investment in equipment for hydrogenation/dehydrogenation, and the process itself can be energy consuming. [64]

Once H_2 has been released from the LOHC in a de-hydrogenation reactor, it can go through a gas liquid separator, where bulk H_2 is separated off from bulk LOHC liquid, and then a separate condenser can be used to reduce the levels of organic impurities. Then PSA can be used to further purify H_2 to the desired purity. [65] A study was conducted on a laboratory scale reactor system, demonstrating that high purity H_2 (>99.999%) could be achieved with less than 0.2 ppmv CO when released from pre-dried and pre-purified perhydro dibenzyltoluene (H18-DBT). [66] In their process, the dehydrogenation reactor was simply followed by a cooled gas liquid separator.

During the first workshop on hydrogen impurities organised by the CLEANER project, Laura Barrio presented on impurities present in H_2 after LOHC and dehydrogenation.[2] In this presentation, multiple sources of impurities in LOHCs were summarised for certain systems, including the following:

1. The production of the LOHC, for example dibenzyltoluene (DBT) and benzyltoluene (BT) can contain contaminants, such as oxygenates and water, which can lead to the formation of CO and CO_2.
   Water can be present if the H_2 used for hydrogenation of the LOHC is not dry, while oxygenates could be present in hydrogen-lean LOHCs, due to contact of the LOHC with oxygen during its production. [66]
2. The decomposition and vaporisation of the LOHC molecules during dehydrogenation can result in the formation of volatile hydrocarbons.
3. The methanation of CO and CO_2 could occur, forming methane.
4. Nitrogen impurities can be present as a result of system purging.
5. During the dehydrogenation process of methylcyclohexane, BT, and DBT, the formation of fluorene derivatives could occur.

It was also mentioned in the presentation[2] that the quality of the H_2 released in the dehydrogenation process increases with increasing cycling of the LOHCs due to a decrease in the presence of oxygenates and water. Presence of such impurities in the product H_2 can also be reduced prior to dehydrogenation by drying and pre-purifying the LOHC material.

4.3.2 Ammonia

Ammonia (NH_3) is considered a promising H_2 carrier as it can store hydrogen under mild conditions in a liquid phase at a higher volumetric density than liquid H_2. The energy density of liquid H_2 at -253°C and standard pressure is 2.4 kWh L^{-1}, while that for liquid NH_3 at -33°C and standard pressure is 3.5 kWh L^{-1}. [67] To obtain hydrogen from ammonia for use in H_2 fuel cells, a few steps need to be followed. First, stored NH_3 needs to be decomposed into H_2 and N_2, according to the following reversible reaction:

$$NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$$

Then H_2 needs to go through separation and purification steps before being compressed and stored in preparation for use in a fuel cell. According to the above reaction, ammonia cracking can produce a hydrogen: nitrogen product gas ratio of around 3:1 with some unreacted NH_3 present. The ammonia decomposition reaction is dependent on temperature, where conversion increases from around 90 to 100% when reaction temperatures increase from 250 – 700°C. The reaction is most dependent on temperature between around 250 and 450°C. [68, 69]

After NH_3 decomposition, hydrogen mainly needs to be separated from N_2 and any unreacted NH_3. While gas streams produced from NH_3 decomposition should not contain any sulphur of carbon-based compounds, if the ammonia used to produce hydrogen was made from natural gas or biomass, it is possible that supplementary separation processes would be needed to remove such compounds. One of the most developed and commercially available processes for purification of $NH_3/N_2/H_2$ streams is pressure swing adsorption (PSA). [67] As PSA is a well-developed technology, units able to provide the necessary H_2 purity are commercially available. According to the International Energy Agency G20 hydrogen report, PSA for N_2 removal from H_2 has an efficiency of around 80% hydrogen removal. [70] It should be noted that in this process, the cost associated to having enough columns for continuous processing could be high, and a portion of the product gas is usually used to purge the columns during the desorption step. [67, 71] Hydrogen permeable membranes can also be used to separate H_2 from the product gas, without the need for backflushing the system. For example, while costly, palladium alloy membranes can separate out hydrogen with high purity. [67] Finally, absorption can also be used for removing NH_3 from the gas produced during ammonia decomposition by putting the stream in contact with a liquid or by passing it through a solid packed bed. [68]

4.3.3 Methanol

Methanol (CH_3OH) is another candidate for a liquid hydrogen carrier able to produce high purity hydrogen. Methanol is advantageous due to its high hydrogen to carbon ratio (4:1) and its liquid phase at room temperatures and atmospheric pressure. It can also be converted to hydrogen at relatively low temperatures in comparison to other fuels. [72, 73] A few processes can be used to produce hydrogen from methanol, namely, the steam reforming of methanol, oxidative steam reforming of methanol, methanol decomposition and partial oxidation of methanol. Of those processes, methanol steam reforming, as shown in the reaction below, is favoured due to the higher concentration of hydrogen present in the product stream of the reaction. [74]

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$

The “raw” reformate gas from this reaction consists of around a 75:25 ratio of H_2:CO_2 on a dry basis, and depending on the operating conditions and design of the reactor, a certain amount of CO as well as unreacted methanol can also be present. [75] The reforming temperature, pressure and the steam to carbon (S/C) ratio are the main parameters that can affect the methanol steam reforming reaction. They can be adjusted for increased methanol conversion and hydrogen yield, while minimising the production of CO, an undesirable impurity for PEMFCs. In a recent study the optimal operating temperature, pressure and S/C ratio for the reaction were found to be 200 – 300°C, 1 atm and 1.6 – 2.0, respectively. [76]

Similar to hydrogen recovery from ammonia decomposition, PSA can be used to yield high purity hydrogen (99.99 vol%) at high pressures (>20 bar). High temperature diffusion through metal membranes, such as palladium, or low temperature diffusion through polymeric membranes, can also be used to yield high purity H_2. [75] Another common separation process for removing CO and CO_2 from hydrogen gas is solvent absorption using an absorber-stripper unit. For example, monoethanolamine can be used as a solvent to remove impurities from hydrogen in an absorber column. [75, 77]

4.4 Hydrogen transmission or transportation

There is often a physical decoupling of hydrogen production sites with storage sites, and end users. This means that transportation of hydrogen from one location to another is needed, and this transmission process can introduce impurities into the gas. As well as transportation of hydrogen in tankers, there is a possibility to repurpose existing natural gas pipelines for transport of hydrogen over long distances, as well as to construct new pipelines specifically for use with hydrogen.

4.4.1 Repurposed pipelines

It has been said that a pan-European hydrogen transmission network is needed to reach a fully decarbonised European energy system by 2050. [78] This European Hydrogen Backbone would contain over 30 000 km of repurposed natural gas pipelines, which need to be cleaned, dried, and purged before being used for hydrogen. Though cleaning (pigging) of old pipelines to remove organic residues may be possible in some cases, this is generally difficult for high pressure pipelines due to low standardisation of pipeline diameter. [3] In addition, it should be investigated whether the repurposed pipelines can withstand additional challenges arising from interaction of hydrogen with their material, which can cause for example hydrogen embrittlement. To avoid hydrogen embrittlement of materials, gaseous inhibitors such as CO, O_2 and SO_2 can be added, [79, 80] however these must be added in high quantities (oxygen has the lowest required concentration of inhibition at 100 ppmv), [81] and will therefore have a negative impact on H_2 quality. The benefits of adding inhibitors must therefore be weighed against the costs of additional purification.

In addition, before use of hydrogen in pipelines, there should be a standardisation of the quality of hydrogen injected into the pipelines. There is a general disagreement amongst pipeline operators about which quality to use, but a recommendation from the Hy4Heat project, which targeted use of hydrogen for domestic appliances, is that hydrogen quality should be above 98 % for pipeline transmission. [82] In this case, key impurities would be: CO < 20 ppm, total sulfur < 35 ppm, O_2 < 0.2 %, and total inert components < 2 %. These quality limits would be suitable for some applications, but 2 % of impurities could produce large enough deviations in the Wobbe index that would prevent the hydrogen from being used in gas turbines. There is therefore talk of a 99.5 % quality standard which would be high enough for the majority of applications, although not the 99.97 % required for PEMFCs. It is currently unclear which impurity limits would be targeted for the 99.5 % standard.

As well as questions about what gas quality will be introduced into the pipeline system, there is evidence that the hydrogen quality will be reduced whilst in the pipeline, due to desorption of compounds that have been adsorbed onto pipeline walls. Pipeline operators expect that hydrogen of quality 98% can be transported in pipelines without problems, but a quality of 99.97 % cannot be guaranteed in old pipes. [3] However, few experimental studies of impurities introduced into hydrogen from repurposed pipelines have been reported. One study from 2024 exposed steel pipelines built between 1960 and 2018 to hydrogen and classified the impurities based of ISO14687. [83] It was found that the pipeline age severely impacted the amount of contaminants present in the hydrogen, with older pipelines introducing a > 1000 times greater concentration of impurities compared to newer pipelines. The key contaminants found after exposure were odorants and hydrocarbons, with low concentrations of sulphur compounds, ammonia and halogenated hydrogen compounds. Contaminants found at a > 1 ppm level were propane and ammonia, with methane, butane, pentane, and several halogenated compounds (trichloromethane, dichlorobromomethane, trichloroethylene) as well as carbon disulphide observed at concentrations > 100 ppb. In contrast to this, the Hy4Transport report suggests that there is no evidence of a notable fraction of halogenated compounds in a repurposed gas network. [84] Even contaminants at the ppm level will have an impact on fuel-cell end use so levels should be monitored carefully. In the aforementioned 2024 study, other atmospheric compounds (CO_2, Ar, O_2, and N_2) were measured in the ppm range but values were not specified due to exposure of pipelines to air during transport to the testing site. [83]

Compounds such as odorants can have a long lifetime in the pipeline, as they adsorb onto pipe walls and are slowly released. [83] In fact, there are observations that it has taken over 25 years for a reduction of the concentration of naphthalene to below 1 ppm in old town gas pipelines.[3] However, there are few studies that show the development of contaminants over time in pipelines repurposed for hydrogen transport, so this is something that needs to be further explored.

Impurities can also be introduced when the pipelines are being maintained. EN 17124 standard, [85] which is harmonized with the ISO 14687 fuel specification mentions transport in pipeline. For normal, pressurized operation introduction of contaminants is very unlikely. During maintenance, it is required to purge with nitrogen until O_2 is below 2%. Normally, nitrogen will be purged by hydrogen to a level of 100 ppm, which implies O_2 concentrations lower than 2 ppm. With improper purging, e.g. 5 ppm O_2, the N_2 concentration will be 250 ppm, it therefore a risk for both impurities to be present in high concentrations after maintenance. Water is also mentioned as a potential contamination after maintenance, and it is generally challenging to remove water by purging with inert gas.

It is clear that hydrogen transported in repurposed natural gas pipelines will need to be cleaned to meet certain end-use applications that require high purity. In particular, desulphurisation to remove and long-lasting odorants is crucial before use in PEMFCs, and this would likely be combined with PSA or a molecular sieve to remove other impurities. In addition, removal of halogenated compounds is needed. However, it has yet to be clarified whether this responsibility lies with the suppliers of the hydrogen, the pipeline operators, or with the end-users. The implementation of centralised purification strategies may be cost- and energy-intense and is therefore not preferred, particularly as it may not be necessary for all end-users. [86] Once a pipeline quality standard has been agreed upon, purification strategies will be easier to implement.

4.4.2 A specifically built grid

The European Hydrogen Backbone estimates that by 2040, there will be 53 000 km of hydrogen pipelines in Europe, of which around 60 % would be repurposed natural gas pipelines. This leaves a significant demand for new infrastructure, which would be integrated into the repurposed grid. Like for the repurposed pipeline, during pressurised operation there is a low likelihood of introducing contaminants from the air, and for specifically built pipelines, this would be even lower. In addition, there should be no contaminants adsorbed onto the pipe walls that can desorb to impact hydrogen quality, as long as the pipelines have been pre-aged. In the USA, a hydrogen purity of 99.99 % has been achieved in new pipelines that have never been used for natural gas, although for brand new pipelines that have not been pre-aged, low levels of methanol and butanol have been reported.[3] However, in the gas network that contains both new and repurposed pipelines, hydrogen transported from repurposed into new pipelines will become contaminated and may lead to the adsorption of impurities onto the walls of new pipelines. The only way to avoid cross-contamination is to restrict flow in one direction only from new to repurposed pipelines, which is mostly impractical.

4.4.3 Tankers

Currently, there are several types of pressure vessels in use for storage of gaseous hydrogen: metallic pressure vessels, metallic vessels wrapped in resin composite fibre, fully composite vessels (plastic or carbon fibre) with a metal liner, or fully composite vessels with a polymer liner. [87] It is not expected that any of these vessel types should interact with the hydrogen to produce any impurities or side-reactions. [88] Therefore, the quality of gas extracted from the vessel is expected to be the same as that placed in the vessel.

However, there are ways in which impurities can be introduced to the vessel. If low quality gas has previously been present in the vessel, residual impurities can contaminate subsequent high purity hydrogen. In addition, during vessel maintenance, N_2 and O_2 impurities can be present and must be correctly purged to ensure sufficient quality. After introduction into the vessel, inert impurities such as N_2 can be present in small quantities for a long time.

4.5 Perspective

It is obvious that there are a large number of impurities that can be introduced into hydrogen from every part of the value chain. Monitoring and clean-up strategies are incredibly important to ensure good control of the type and concentration of impurities at each stage, particularly when linking together various production, storage, and transmission processes. However, purification is a cost-intensive process, and standardisation is therefore crucial to avoid wasting the money and energy needed to purify hydrogen to a higher standard than necessary. Clean-up is more difficult for some compounds (e.g. N_2, O_2, H_2O), particularly inert compounds with low adsorption energy, so it is most likely that these inert impurities will remain in the hydrogen after purification. The focus of the CLEANER project is therefore to identify materials and strategies for operating with lower grade hydrogen, including up to 2 % N_2.

5 RISK ASSESSMENT – THE SEVERITY AND OCCURRENCE OF IMPURITIES

In this section, the key impurities identified through the hydrogen value chain will be evaluated with respect to their frequency of occurrence, and the severity of the impact they have on PEMFC performance.

5.1 Previously performed risk assessment for hydrogen impurities

ISO 19880-8 [89] defines the quality control requirements for hydrogen fuel. Generally, there are two approaches to ensuring such quality, namely the prescriptive approach and the risk assessment approach. The prescriptive approach uses frequent sampling and analysis of the fuel to ensure its quality meets the requirements, whereas the risk assessment approach uses probability data for assessing the risk of fuel impurities. ISO 19880-8 [89] defines the occurrence classes for impurities found in hydrogen fuel, where the Occurrence class 2 "Rare" is equal to at least one occurrence per year.

Table 4. Occurrence classes defined by ISO 19880-8. Occurrence class is based on an HRS with refuelling 100 000 times per year.*

Occurrence class	**Class name**	**Occurrence or frequency at the production site**	**Equivalent occurrence or frequency for refuelling event**
0	Very unlikely (practically impossible)	Contaminant above threshold never observed for this type of source in the industry	Never
1	Very rare	Heard in the industry for this type of source/Supply chain considered	1 per 1000000 refuelling
2	Rare	Has happened more than once a year in the industry	1 per 100000 refuelling
3	Possible	Has happened repeatedly for this type of source at a specific location	1 per 10000 refuelling
4	Frequent	Happens on a regular basis	Often

*It should be noted that the table is currently being rescaled as no HRS undergoes refuelling 100 000 times in a year. This is a part of the HyQuality Europe project. [90]

As part of the MetroHyVe project, a study of the probability of occurrence for impurities was performed on three different hydrogen production processes, including *(i)* steam methane reforming (SMR) with hydrogen purification via pressure swing adsorption (PSA), *(ii)* PEM water electrolysis with hydrogen purification by temperature swing adsorption (TSA) and *(iii)* chlor-alkali membrane electrolysis also with hydrogen purification by TSA.[32]

For the SMR-PSA process, the two main impurities were identified as carbon monoxide, a product of the SMR reaction (in syngas), which falls into probability of occurrence Class 4, and nitrogen, likely present in the natural gas feedstock, which is in probability of occurrence Class 3. The main barrier for both CO and N_2 is the pressure swing adsorption step. Other impurities can be present; however, their occurrence class was found to be Class 2- *rare* or lower.

For the analysed PEM water electrolysis process, including TSA, N_2, O_2 and water were identified as the main impurities and all fall into probability of occurrence Class 2. The main possible cause of nitrogen was found to be from the N_2 used for venting the system during startup, maintenance, or emergency shutdown procedures. Proper implementation of such procedures would minimise the occurrence of nitrogen in the produced hydrogen. Water is of course the main reactant in PEM electrolysis and can permeate the membrane to the hydrogen side. The main barrier for water in hydrogen is the TSA dryer. Finally, the oxygen produced in the PEM process can cross the membrane over to the hydrogen side, however a catalytic deoxidizer is placed to remove the oxygen from the hydrogen stream. Other impurities in the PEM electrolysis process were found in probability of occurrence Class 1 – *very rare* or lower.

For the chlor-alkali process with TSA, O_2 was identified with the highest probability of occurrence in Class 4. Class 4 was chosen as a conservative estimate because there was a lack of available analysis on O_2 content in H_2 from the chlor-alkali process. As with PEM electrolysis, deoxidiser units can remove O_2 from hydrogen. Water, a process parameter, was identified in probability of occurrence Class 2, with a drying system in place as a barrier for water impurities in H_2. Finally, N_2 can be present as an impurity in this process as it is used for safety reasons during procedures such as system startup and maintenance. N_2 falls into occurrence Class 2. Barriers for avoiding N_2 impurities in the product H_2 include properly following procedures when purging the system.

The results of the impurity study for the three analysed processes are summarised in Table 5.

Table 5. Probability of occurrence for impurities in various production and purification schemes[32].

Probability of contaminant presence	**Steam methane reforming with PSA**	**Chlor-alkali process (membrane cell process)**	**PEM water electrolysis process with TSA**
Frequent	CO	O_2	None identified
Possible	N_2	None identified	None identified
Rare	CH_4, H_2O and Ar	N_2 and H_2O	N_2, O_2 and H_2O
Very rare	CH_2O	CO_2	CO_2
Unlikely	He, CO, O_2, CH_2O_2, NH_3, sulphur compounds,	He, Ar, CO, CH_4, CH_2O, CH_2O_2, NH_3, sulphur compounds,	He, Ar, CO, CH_4, CH_2O, CH_2O_2, NH_3, sulphur compounds,

Probability of contaminant presence	Steam methane reforming with PSA	Chlor-alkali process (membrane cell process)	PEM water electrolysis process with TSA
	hydrocarbons compounds, halogenated compounds	hydrocarbons compounds, halogenated compounds	hydrocarbons compounds, halogenated compounds

In this case, there was no further evaluation of the severity of the impact of each impurity on fuel cell performance.

5.2 Risk assessment in this work

5.2.1 Classification of occurrence

Based on the literature study performed in this work, and after discussion with CLEANER consortium partners, the classifications of impurity occurrence as shown in Table 6 were made. Here, there are only two categories for occurrence, these being more frequent and less frequent, with the more frequent compounds receiving a score of 2 for the further risk assessment, and less frequent compounds receiving a score of 1. This choice was made as there is little experimental information available to suggest the occurrence of impurities in line with the categorisations from ISO 19880-8, particularly for geological storage and transmission in repurposed pipelines.

Table 6. The occurrence classification for various impurities relevant to different hydrogen production, storage, and transmission methods, NB: HC = Hydrocarbons, F = Fluorine derivatives, OD = Odorants, HG = halogenated compounds, AA = CH3COOH

	Naturally occurring	**Production: electrolysis**	**Production: grey**	**Production: by-product**	**Storage: geological**	**Storage: hydrogen carriers**	**Transmission: repurposed**	**Transmission: new**
More Frequent	CH_4, N_2	H_2O, O_2, N_2	CO, CO_2, N_2	N_2, O_2, H_2O, CO, CO_2	CH_4, CO_2, N_2, H_2S, AA, HC	NH_3, N_2, CH_3OH, CO, CO_2	CH_4, N_2, O_2, HC, OD, HG	N_2, O_2
Less Frequent	H_2O	CO_2, CO	H_2O, CH_4			CH_4, HC, F		HC

In the interest of conciseness, the table is split into general categories for impurity introduction method. It should be noted that not all the impurities will be found at each frequency in each sub-category of production, storage and transmission.
In particular, comments from the CLEANER consortium addressed the presence of hydrocarbons in geological storage sites is more or less limited to depleted gas fields, with in particular lined rock caverns showing few of the impurities listed. In addition, the frequency of HCl or Cl_2 in by-product hydrogen production was commented upon. These impurities have previously been considered likely but have never been observed during sampling from these sources, and therefore are not included in this table, even under the “less frequent” classification.

5.2.2 Classification of severity

Each of the impurities identified in Table 6 was then classified with respect to the severity of its impact on fuel cell performance. In this case, only the impact on the fuel cell stack was considered, so there could be additional consequences for the complete powertrain. The meaning of each severity classification and the grouping of compounds is shown in Table 7.

Table 7. The severity classifications of each of the impurities identified in this report.

Severity	Explanation	Impurities with this classification
1	No impact on fuel cell performance	He, Ar, N_2, O_2, CH_4, H_2O
2	Slight reversible degradation after long-term exposure	CO_2, CH_3OH, CH_3COOH, other light hydrocarbons
3	Significant reversible degradation for short-term exposure	CO
4	Significant irreversible degradation	NH_3, H_2S, COS, other sulfur containing compounds

It is important to note that there was significant discussion between partners and the conclusions made were not unanimous, meaning that some of these classifications may be adjusted in the future. For example, there were discussions about the placement of CO in category 3 or 4, as its initial reversible degradation can become irreversible after a long enough exposure time. Also, for those impurities in category 1, loss of fuel cell performance due to dilution of hydrogen is not taken into account.

5.2.3 Overall evaluation

Finally, an overall evaluation of each impurity’s risk factor is performed. Here, both the occurrence type (more or less frequent) and the number of appearances each impurity has in Table 6 are considered. This total occurrence factor is then multiplied by the severity to give an overall risk evaluation as low, medium or high risk, as seen in Table 8.

Table 8. The overall risk classification for each impurity identified in this document.

Impurity	Occurrence Type	Number of occurrences	Severity	Final Evaluation
CH_3COOH	2	1	2	Low
	1	0		
CH_3OH	2	1	2	Low
	1	0		
CH_4	2	3	1	Medium
	1	2		
CO	2	3	3	High
	1	1		
CO_2	2	4	2	Medium
	1	1		
Fluorine derivatives	2	0	3	Low
	1	1		
H_2O	2	2	1	Low
	1	2		
H_2S	2	1	4	Low
	1	0		
Hydrocarbons	2	2	2	Medium
	1	2		
N_2	2	8	1	Medium
	1	0		
NH_3	2	1	4	Low
	1	0		
O_2	2	4	1	Low
	1	0		
Odorants	2	1	4	Medium
	1	0		

Only one impurity is classified as high risk, CO, due to both multiple occurrences throughout the value chain, and a high severity factor.

Impurities that have a low number of occurrences through the value chain, regardless of their severity rating are classified as low risk. Examples of this include ammonia, which is only likely to be introduced if using ammonia as a hydrogen carrier, and fluorine compounds which can be formed during dehydrogenation of LOHCs. In these two cases, the additional monitoring of these impurities should be included if these hydrogen carriers are used, otherwise the risk factor can increase. In addition, acetic acid and H_2S can be produced by the reaction of bacteria in underground hydrogen storage sites but given the lack of information about how many storage sites will contain bacteria that perform these reactions, it is difficult to conclude how prevalent these impurities may be. In this initial stage, these impurities have therefore also been assigned a low overall risk factor, as avoidance of these reactions is possible through use of lined rock caverns as storage sites. An exception to this is the case of odorants, which are introduced from repurposed gas pipelines. Despite this singular occurrence, repurposed pipelines are very likely to be utilised in any large-scale hydrogen distribution and therefore contamination is likely in most use-cases of hydrogen. In addition, they have a very long lifetime in said pipelines, up to 25 years, and therefore are classified as medium risk. The other medium risk impurities are methane, carbon dioxide, hydrocarbons, and nitrogen. All of these can be introduced at multiple points in the value chain, therefore even though they do not have a very high severity rating, they are likely to be present in hydrogen and therefore are of interest to investigate.

6 SUMMARY OF WORK AND CONCLUSIONS

In summary, this work has investigated the possible impurities associated with the production, transportation, and storage of hydrogen. Two workshops were conducted, and in conjunction with a literature study, this has allowed the classification of impurities as high, medium, or low risk for fuel cell end-users. The only impurity that has been identified as high risk during this work is carbon monoxide. This is due to its high likelihood to enter the hydrogen during the production stage, and its large impact on fuel cell performance.

Several impurities were identified as medium risk, and these are methane, carbon dioxide, nitrogen, hydrocarbons and odorants. Some of these, for example nitrogen, can be introduced into the hydrogen at every point in the value chain and thus it is crucial to understand the impact of nitrogen on fuel cell performance, and develop mitigation strategies if needed. For other medium risk impurities, there is less certainty about the exact frequency and quantity of impurity that can enter the hydrogen. Odorants, halogenated compounds, and hydrocarbons are likely to enter hydrogen during transmission in repurposed gas pipelines, but there have been few experimental studies to quantify expected concentrations, something that should be focussed on to further understand the risk classification.

Finally, a number of impurities were identified to be low risk, either due to their low impact on fuel cell performance (e.g. H_2O, O_2), or their unlikelihood to enter the hydrogen unless certain specific processes are undergone (e.g. ammonia is only relevant if used as a hydrogen carrier) and therefore in these cases additional measures can be put in place. This risk classification will now be used to inform testing procedures for the CLEANER project, and experimental activity on the impact of high- and medium- risk impurities on fuel cell performance will be performed.

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