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Abstract

This document provides the background for the H_2 quality recommendations given for the DYNAMIS project, having as main end user fuel cell vehicles (PEM). From the H_2 production perspective, the impurities of major concern are inert components and carbon monoxide (CO).

Inert components are produced in quantities far larger than the specifications under development at present (ISO/FDTS 14687-2, SAE J2719). CO is critical because of its poisoning effect on the fuel cell electrodes.

The report includes relevant documentation that gives reasons to suggest modifications to the specifications under development. These modifications will contribute to reduction of investments and operational costs of hydrogen production, without affecting PEM fuel cell performance.

The H_2 quality recommendations for the DYNAMIS project are given in Chapter 4.

The main conclusions are:

- Existing limits for inert components around 100-500 ppmv (micromole per mole) are the most challenging requirement for H_2 production in a HYPOGEN plant. Relaxation of inert compounds limit up to 2,000- 10,000 ppmv is strongly suggested since it will result in reduced CAPEX and OPEX for the H_2 production and considerable increase of H_2 yield.
- Experimental data for long term impact of inert compounds in PEM cells in the range of 5,000 to 10,000 ppmv are urgently needed.
- Although some references recommend a maximum concentration of CO of about 10 ppmv, the DYNAMIS recommendation is 0.5 ppmv, based on the extensive experimental work of Air Liquide.
- Expected developments by 2012 in high temperature PEM cells will most probably allow for considerable relaxation of CO concentration limit, possibly around 0.1%.
- Concentration limits for CO is the second limiting factor for the production of hydrogen in a HYPOGEN plant.

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1 INTRODUCTION

This document provides the background for the H_2 quality recommendations given for the DYNAMIS project.

The quality of the H_2 stream produced in a HYPOGEN plant depends on the end-use. As stated in Annex I and in the Project Policy document (PPD):
"The hydrogen yield shall correspond to 0-50 MW (HHV) due for delivery to an emerging European hydrogen infrastructure. The purity of the export hydrogen shall be in accordance with the specifications of European fuel cell vehicles (PEM) foreseen by 2012".

Therefore, the application of H_2 as fuel for fuel cell vehicles (PEM) has been selected as the general DYNAMIS quality recommendation. If other applications are envisaged, alternative quality recommendations should be developed, for instance:

- High quality network
- Refineries (case specific)

The Air Liquide Hydrogen Network in central Europe provides to date considerable amounts of high quality H_2, being an important reference to the DYNAMIS project in terms of existing experience.

Although it is practical to refer to a certain degree of purity, any quality recommendation should rather focus on establishing the maximum concentration allowed for each impurity.

The quality recommendation in DYNAMIS takes the existing hydrogen quality guidelines (SAE J2719, ISO/FDTS 14687-2) as a starting point and includes some modifications. The fuel specification, as recently expressed by Queille, P. [12], should take into account several issues, such as:

- Durability & performance requirement of the fuel cell and fuel cell system
- Need for consensus among PEM suppliers
- Experimental data, analysis & verification as a basis
- Feasibility of H_2 production and purification
- Practicality, sustainability and cost effectiveness at H_2 stations
- The use of applicable standardized methods for measurement monitoring

The effort in this project has been devoted to the concentration limits that are critical for the H_2 production processes proposed in DYNAMIS, namely inert components and CO. The report also includes some documentation that gives reasons to suggest further modifications to the existing hydrogen quality guidelines.

The modification proposed will contribute to reduction of investment and operational costs of hydrogen production without affecting PEM fuel cell performance.

As a final comment, it is worth mentioning that there might be advances in PEM materials and more experimental data available by 2015+ that can justify further relaxation of the quality recommendations presented here.

2 BACKGROUND INFORMATION

2.1 Effect of impurities in PEM Fuel cell applications

The table below summarizes the impact of some impurities at the Fuel Cell Stack:

Table 1 Impact of impurities on Fuel Cell Stack. Source: Collins, W. [3]

Species	Impact on Fuel Cell Stack
Carbon Monoxide (CO)	**Reacts, degrades performance (reversible?)**
Sulfur compounds	**Reacts, lost performance (irreversible!!!)**
Ammonia	**Degrades membrane ionomer conductivity**
Carbon Dioxide (CO_2)	**Tolerant at 100 ppmv – limited CO back shifting**
Hydrocarbons	**Aromatics, acids, aldehydes, etc. degrade performance**
Inert gasses (Helium, Argon, N_2)	H_2 dilution effect only
Particulates	May degrade membrane
Water	Tolerant to > 500 ppm
Oxygen	Tolerant to > 500 ppm

Carbon Monoxide (CO)
CO is one of the most critical impurities in PEM fuel cell applications. CO is a poison of fuel cell electrodes, in particular to the catalysts employed in the electrodes. The reason for this is that CO blocks the active sites in the Pt catalyst. Many catalysts do not tolerate CO at higher levels than 1 ppmv[1], or at most 10 ppmv. The tolerance to CO shows some dependence on the type of electrode catalyst. For instance, Pt-Ru electrode catalysts have the best tolerance, but it would appear that they will begin to suffer at levels above 10 ppm, and levels of 100 ppm would not be acceptable at all. Dayton et al. [4] refer to several authors recommending less than 10 ppm CO.

Experimental results from JARI Source show that 10 ppm CO can produce a voltage drop ratio of more than 2% for Pt/Pt Electrode catalyst while Pt-Ru catalyst has the tendency of preventing CO poisoning. Additional tests (2nd step evaluation tests) show that lower impurity concentrations have influence on the fuel cell performance (Pt/Pt electrode) and that the CO poisoning is reversible [12].

Air Liquide has done significant work in screening and testing PEM materials, measuring effect of gas impurities on fuel cell performances (cell voltage losses, polarization curve along the time of testing, % recovery or permanent loss, etc.) and compared with public data and ISO documents (PEM Fuel cell draft). In particular for CO, some of the tested materials showed some

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[1] In this report, concentration of gaseous impurities are expressed as ppmv (parts per million in volume), being equivalent to micromole/mole.

slight voltage losses at 0.5 ppmv and some materials are showing significant losses at 1ppm after some hours of operation. The conclusion from this work regarding CO is a recommendation on maintaining CO concentration below 0.5 ppmv [2].

Figure 1 shows that 1 ppmv CO results in voltage loss of 20% for a Pt catalyst.

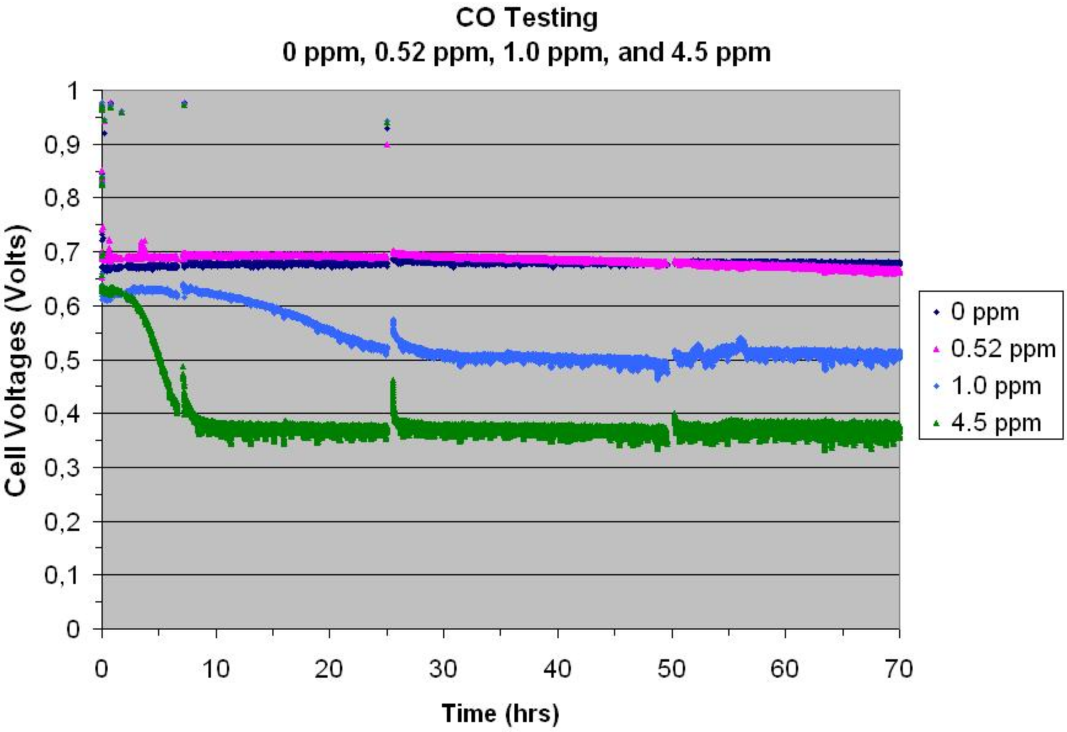


Figure 1 Experimental results from Air Liquide's laboratories assessing the impact of CO on electrode performance [12].

Nevertheless, it is reasonable to assume that, by 2012, there will be more high temperature PEMFCs, and that the limitations for these fuel cells on CO (and probably CO_2) will be considerably less stringent, possibly around 0.1% [1].

Sulfur compounds

Sulfur gases (mainly H_2S) can also poison the Pt catalyst in the electrodes. This sulfur can be present as the odorant in natural gas or be formed during coal gasification. Sulfur also deactivates the Ni-based fuel reforming catalysts [4].

As described by Queille [12], the mechanism for catalyst poisoning is adsorption of H_2S onto the Pt sites followed by oxidation to sulfur. The mechanism is cumulative in nature and not easily reversible. Experimental results are presented in the same reference showing that there is no observable voltage loss after 100 hours of operation at H_2S concentrations of 0.25 ppmv. For larger concentrations, the voltage drop over time increases linearly. The results also show that the recoverability after impurity removal is limited (Figure 2).

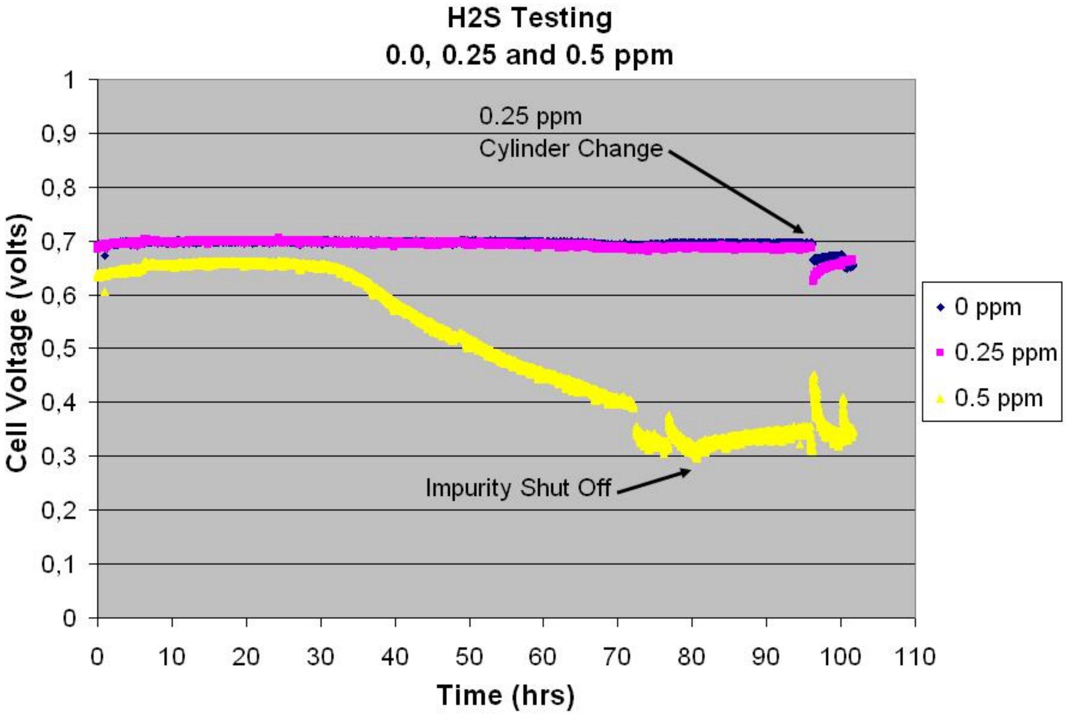


Figure 2 Experimental results from Air Liquide's laboratories assessing the impact of H_2S on electrode performance [12].

Ammonia

Ammonia can react with the sulphonate groups on PEM fuel cell membranes. These groups are normally united with hydrogen protons, and their presence allows hydrogen protons to hop from one side of the fuel cell to the other, where they eventually react with oxygen [15].
Long term exposure to NH_3 contaminant results in loss of proton conductivity with fairly high recovery even at several tens of ppmv contamination after some hours of operation without NH_3 contaminant [2].

The experimental work conducted at Air Liquide's laboratory shows considerable voltage drop (13%) at 44 ppmv NH_3 after 80 hours of operation while the impact of 9.0 ppmv NH_3 is far lower (Figure 3). Based on this experimental work, Cieutat [2] recommends to apply 5 ppmv as long term continuous contamination level limit.

As a comparison, Halseid [7] studied in his doctoral work the effect of ammonia on PEMFC by adding 10 ppmv NH_3 to the hydrogen fed to the PEMFCs based on Gore^{TM} PRIMEA$^{®}$ MEAs. The results show a significant loss in performance of the FCs. The author comments that the process is slow, taking 24 hours or more to reach a steady state. Additions of 1 ppmv NH_3 for one week also resulted in significant performance losses (Figure 4).

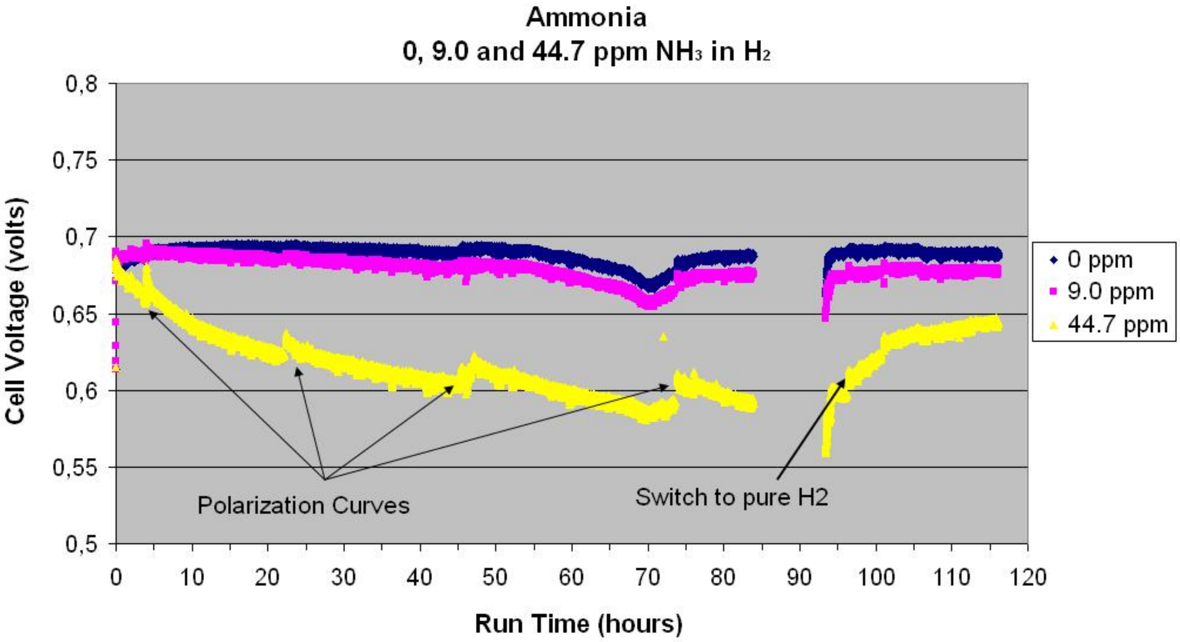


Figure 3 Experimental results from Air Liquide's laboratories assessing the impact of ammonia (NH_3) on electrode performance [12].

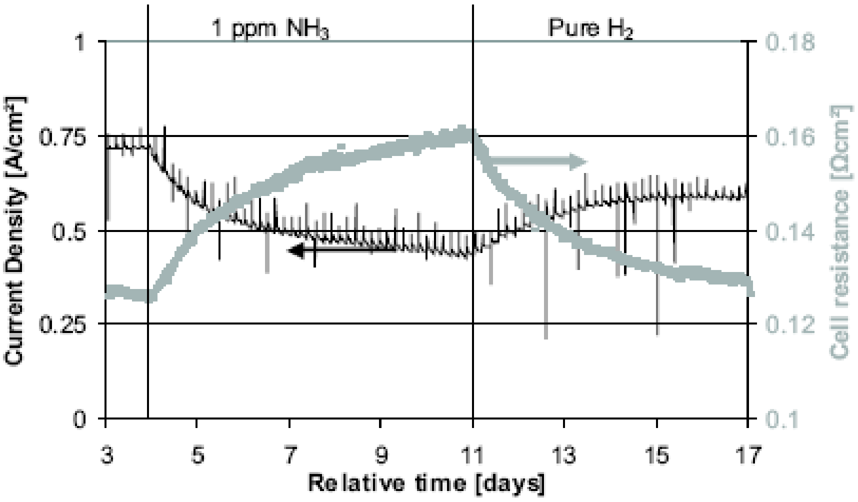


Figure 8.5: Performance of 10 cm^2 GORE™ MEA with addition of 1 ppm NH_3 for one week. The cell was running potentiostically at 0.50 V at 40 °C cell temperature, room temperature humidifiers, atmospheric pressure, 80% conversion of H_2, 40% conversion of O_2 in air, 10 and 20 mlN/min minimum flow on anode and cathode respectively. The data are not corrected for ohmic losses.

Figure 4 Experimental results showing the impact of 1 ppm NH_3. Source: Halseid [7]

One of the conclusions from the experimental work conducted by Halseid [7] is that the poisoning mechanism for ammonia in PEM fuel cells has only partly been identified, and that more work is needed in order to understand the mechanism of ammonia poisoning and its consequence for PEM fuel cell performance and durability. Halseid refers that tolerance levels towards ammonia need to be more firmly established.

CO_2

Dayton et al. [4] refer that Proton Exchange Fuel Cells (PEFC) are insensitive to $CO_{2.}$ According to Børrensen [1], there is an ongoing discussion on the effect of CO_2, which has shown to be somewhat larger than other inert compounds. There is a possibility for formation CO through reverse WGS, but more probable a CO_2-H_2 specie will be formed that is considerable weaker bound to the catalyst than CO. There seems to be some divergence in the literature regarding the species involved in CO_2 poisoning [7].

In particular, Halseid [7] studied in his doctoral work the mechanisms for Hydrogen Oxidation Reduction (HOR) on the PtRu anode catalyst. He measured polarization curves of hydrogen mixed with N_2, Ar, He and CO_2, both in fuel cells ($H_2|O_2$) and in symmetrical cells ($H_2|H_2$). His results show that the influence of CO_2 on the performance of the PtRu anode was significant (CO_2 concentration of 25%). The performance of cells exposed to H_2 containing CO_2 showed a steady decrease in performance which was much higher than what was observed for pure hydrogen or N_2 mixtures.

More over, he refers that the poisoning mechanisms for CO_2 can not be explained by formation of CO_{ads} through the reverse water-gas shift reaction alone. Other species may be involved.

Inert gasses (Helium, Argon, N_2)

Halseid [7] refers that available literature seems to indicate that nitrogen only has dilution effects, i.e., that nitrogen is not electrochemically active in Fuel Cells. He concludes from his experiments that nitrogen does not seem to have any effect on anode performance other than dilution, and that the dilution of hydrogen with nitrogen gave similar results to those from dilution with Ar and He.

Also according to Starr [15], Argon is unlikely to have a direct affect on fuel cell performance in terms of poisoning the catalyst or affect on hydrogen transport through the membranes in PEM fuel cells. However, if unused hydrogen has to be recycled back to the fuel cell then there may be a build up of argon, which could have an adverse affect on performance. The reason for this is that not all the hydrogen which enters the fuel cell is used, a portion passes through, as hydrogen molecules, which do not have time to be converted into hydrogen protons by the catalyst.
If there is a gradual build up in argon through recycling, the simplest solution would be to vent the hydrogen in the fuel cell periodically. The frequency of venting will probably depend on the design of the fuel cell.

Figure 5 shows polarization curves obtained by Halseid showing the effect of inert compounds and CO_2.

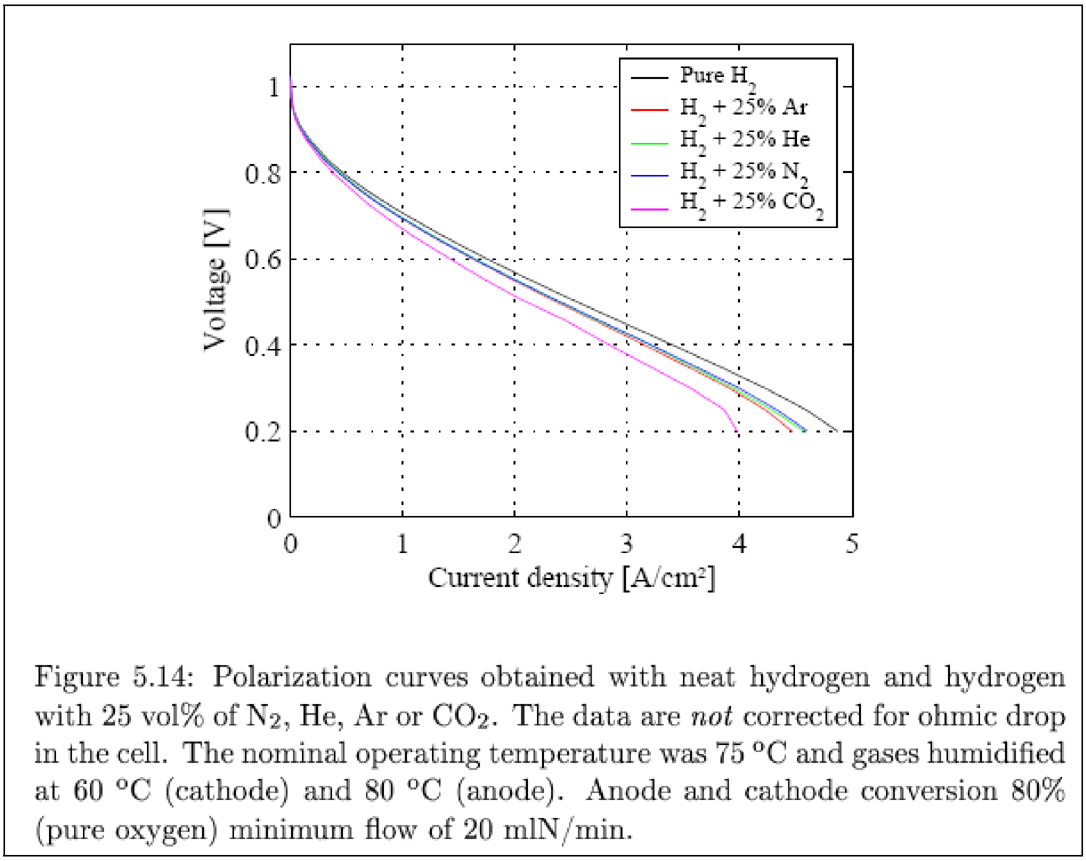


Figure 5.14: Polarization curves obtained with neat hydrogen and hydrogen with 25 vol% of N_2, He, Ar or CO_2. The data are *not* corrected for ohmic drop in the cell. The nominal operating temperature was 75 °C and gases humidified at 60 °C (cathode) and 80 °C (anode). Anode and cathode conversion 80% (pure oxygen) minimum flow of 20 mlN/min.

Figure 5 Experimental results showing effect of inert compounds and CO_2 on polarization curves. Source: Halseid [7]

The experiments conducted by Halseid suggest that the effect of inert gasses is limited to being an inert diluent with no further short term effects to the cell performance.

No information has been found referring to the long-term impact of inert compounds in PEM fuel cell performance.

2.2 H_2 purification by Pressure Swing Adsorption (PSA)

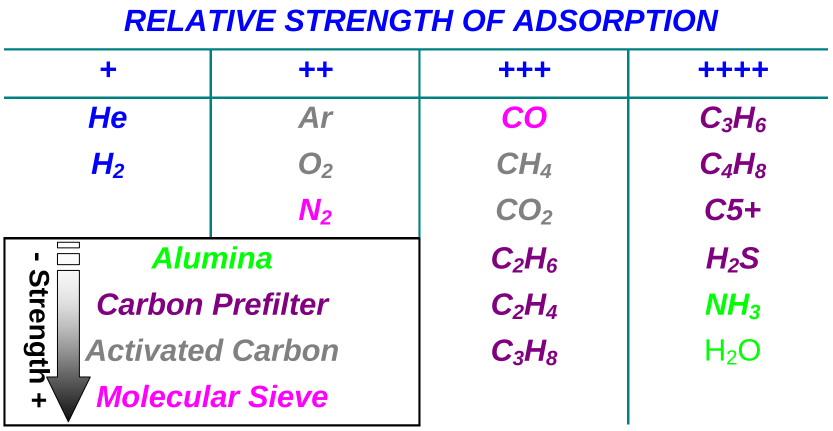
Pressure Swing Adsorption (PSA) is a non cryogenic gas separation process able to provide H_2 with a purity ranging from 99 to 99.9999%. PSA is based on adsorbents technology and can be used to purify H_2 from a mixture already containing H_2 and other components. Table 2 provides the range of performances for a PSA unit:

Table 2 Range of operation and performance for PSA unit. Hasanov et al. [11].

H_2 content in feed gas	50 to 99.8 %
H_2 Purity	99 to 99.9999 %
Recovery	50 to 95+ %
Feed gas pressure	6-50 bar
Feed gas temperature	0-45 °C
Tail gas pressure	1-9 bar
Capacity	100-100 000 Nm^3/h

A more detailed description of the operation of the PSA unit is given in D2.1.1 Options and evaluation of reforming processes [10].

The ability of the PSA unit to retain impurities depends on the type of impurity, in particular, the affinity between the adsorbent and the molecule to be trapped. The relative strength of adsorption is shown in Figure 6.



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

Figure 6 Gas/adsorbents affinity (Source: Air Liquide)

This means that a PSA unit will retain easily any of the compounds in the most right column of the table, among them sulfur compounds and ammonia**.**

It will also retain the compounds in column +++ relatively easy, if the adsorbents are correctly selected. This implies, for instance, that the PSA unit can be adjusted to provide very low levels of CO and CO_2.

However, the PSA unit will have difficulties retaining Argon, Oxygen and Nitrogen because of the similarities between these molecules and Hydrogen and Helium in terms of affinity between gas and adsorbents. Oxygen level in PSA feed gas must be very limited as adsorption concentrates O_2 in the adsorbent beds which can then reach the lower flammability limit [5].

The concentration and size of particulate that can be found in the product gas from the PSA will depend on attrition control on adsorbents in PSA.

As a final remark, because of the operation principle of the PSA, the concentration of each impurity in the product gas are not independent variables. They are interlinked by fairly linear but complex relationships that depend on the composition of the feed gas, the composition of the adsorbent, operation pressure, etc.

As an illustration, the following table presents an overview of H_2 product composition and hydrogen yield for a Shell gasifier, having hard coal as feed, where the only variation is the required CO concentration. The calculation is not optimized but shows how the specification of maximum concentration of CO in the product gas affects the presence of other impurities and how the limit on inert components concentrations affect the hydrogen yield:

Table 3 H_2 PSA estimated mass balance as a function of CO requirement.

	Case I	Case II	Case III	Case IV
CO (ppmv)	**<0.5**	**1**	**5**	**10**
N_2 (ppmv)	0	4960	8200	9060
Ar (ppmv)	500	2420	2580	2632
H_2 yield	83.0%	89.0%	89.3%	89.4%

Basis for calculation: Feed from hard coal gasifier (type of technology – Shell).
Feed gas composition: H_2-87.78%, CO-2.36%, CO_2-3.83%, N_2-5%, Ar-0.87%, H_2O-0.05%, CH_4-0.01%
Feed gas pressure: 28bar, Off gas pressure: 1,3 bar
Feed gas temperature: 30°C

2.3 Existing quality guidelines

The Information Report on the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles (SAE-J2719) presents hydrogen fuel quality guidelines. This information has been coordinated with ISO TC197/WG12 (H2 Fuel –Product Specification Working Group) and ASTM D 03 Committee and is consistent with ISO 14687 part 2 [13].

This document also refers that by November 2005 there was no US or international standard that specifies a grade of hydrogen fuel that is acceptable for PEM fuel cell vehicles and that the guideline should be considered as a reflection of current knowledge. Thresholds will be revised as additional information on long-term impacts and mechanisms of fuel cell impact are explored and understood.

The fuel quality guidelines presented by SAE are based on:

- Experimental results from Japan Automobile Research Institute (JARI), based on short-term exposures (10 hr) to evaluate the impact of assorted concentrations of each impurity on a single cell. Concentration that caused voltage drop of 2% or more were characterized as unacceptable.
- Information on CO, sulfur and halogenates brought by fuel cell developers from General Motors, Ballard and UTC
- Guideline used at the two stations of the California Fuel Cell Partnership

Table 5 shows the Hydrogen fuel quality specification guideline from SAE J2719 Issued in November 2005[2] [13]:

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[2] The table in SAE J2719 Issued NOV2005 includes a column with analytical methods and current detection limit, not included in this table.

Table 4 Hydrogen fuel quality specification guideline SAE J2719

- Units are µmol/mol unless otherwise specified
- All limits are subject to revision after additional testing under realistic operational conditions and improved standardized analytical procedures
- Limits are upper limits except for hydrogen fuel index where it is a lower limit.

Constituent	Chemical Formula	Limits
Hydrogen fuel index	H_2	> 99.99 %
Total allowable non-hydrogen, non-particulate constituents listed below		100
Acceptable limit of each individual constituent		
Water [a]	H_2O	5
Total hydrocarbons [b] (C1 basis)		2
Oxygen	O_2	5
Helium, Nitrogen, Argon	He, N_2, Ar	100
Carbon dioxide	CO_2	1
Carbon monoxide	CO	0.2
Total sulfur [c]		0.004
Formaldehyde	HCHO	0.01
Formic acid	HCOOH	0.2
Ammonia	NH_3	0.1
Total halogenates [d]		0.05
Max. particulate Size		< 10 µm
Max Particulates concentration		1 µg/l

a. Due to water threshold level, the following constituents should not be found, however should be tested if there is a question on water content:
Sodium (Na+) @.<0.05 µmole/mole H2 or < 0.05 µg/liter
Potassium (K+) @.<0.05 µmole/mole H2 or < 0.08 µg/liter
Or Potassium hydroxide (KOH) @.<0.05 µmole/mole H2 or < 0.12- µg/liter

b. Includes, for example, ethylene, propylene, acetylene, benzene, phenol (paraphines, olefins, aromatic compounds, alcohols, aldehyds)

c. Includes, for example, H_2S, COS, CS_2 and Mercaptans.

d. Includes, for example, HBr, HCl, Cl_2 and organic halides (R-X).

The US Department of Energy presents the same quality guideline and adds the following comments [6]:

> The primary purpose of this specification is to ensure acceptable fuel cell performance and durability in current demonstration vehicles. It does not take into account the economic impact of producing hydrogen of this quality. The limits in the table below are upper limits except for the hydrogen fuel index, which is a lower limit. Economic analysis of hydrogen production, delivery, and storage technologies; fuel quality R&D, fuel cell testing, and operational data from fuel cell vehicles; or improvements in the impurity tolerance of fuel cells, may lead to revisions of these limits. Hydrogen Program R&D planning will address hydrogen quality issues as they relate to cost and performance goals for each technology area – production, delivery, storage, fuel cells, safety, codes and standards. Those issues and R&D activities specific to each of these areas will be included in those sections of the RD&D Plan.

It is clearly stated that this specification is made to ensure appropriate lifetime of demonstration vehicles and that an economic analysis of the hydrogen production may lead to a revision of these limits.

The International Organization for Standardization has also prepared a draft for the Technical Specification for Hydrogen Fuel. Part 2 of this specification is dedicated to PEM fuel cell applications for road vehicles. It defines two new grades of hydrogen fuel: “Type I, Grade D” and “Type II, Grade D”, intended “*to apply to the pre-commercial demonstration of proton exchange membrane (PEM) fuel cell vehicles on a limited scale*”. Type I applies for gaseous hydrogen while Type II applies for liquid hydrogen.

Table 5 shows the limiting characteristics in the draft version of ISO/FDTS 14687-2[3] [9]:

Table 5 Directory of limiting characteristics according to ISO/FDTS 14687-2 (draft)

Characteristics (assay)	**Type I Grade D**	**Type II Grade D**
Hydrogen fuel index (minimum, %)[a,b]	99.99	99.99
Para-hydrogen (minimum, %)	NS	95.0
Non-hydrogen constituents (maximum content) Dimensions in micromoles per mole unless otherwise stated		
Total gases	100	100
Water (H_2O)	5	5
Total hydrocarbons [c] (C1 basis)	2	2
Oxygen (O_2)	5	5
Helium (He), Nitrogen (N_2), Argon (Ar)	100	100
Carbon dioxide (CO2)	2	2
Carbon monoxide (CO)	0.2	0.2
Total sulfur compounds [d]	0.004 [f]	0.004 [f]
Formaldehyde (HCHO)	0.01	0.01
Formic acid (HCOOH)	0.2 [f]	0.2 [f]
Ammonia (NH_3)	0.1 [f]	0.1 [f]
Total halogenated compounds	0.05	0.05
Max. particulates Size [e]	10 µm	10 µm
Max Particulates concentration [e]	1 µg/L @ NTP	1 µg/L @ NTP

a. The hydrogen fuel index is the value obtained when the value of Total gases (%) is subtracted from 100 %
b. The value of Total gases is summation of the values of impurities listed in this table except Particulates
c. THC may exceed 2 micromole per mole due only to the presence of methane, provided that total gases do not exceed 100 micromole per mol
d. As a minimum, testing shall include H2S, COS, CS2 and Mercaptans, which are typically found in natural gas
e. Recommended value for Particulates is subject to sampling under realistic operational conditions and improved standardized analytical procedures.
f. These values are based on detection limits of available instrumentation and test methods and serve as a basis for subsequent improvements in test methods and instrumentation. Recommended values for these constituents are subject to additional testing under realistic operational conditions and improved analytical procedures suitable for standardization.

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[3] The table in ISO/PDTS 14687-2 includes a column with laboratory test methods to consider, not included in this report.

3 DISCUSSION

Inert components

The major challenge being faced by a HYPOGEN plant in terms of hydrogen quality is the often suggested specification for inert components of 100-500 ppmv. The operating principle of the PSA unit has been explained in Section 2.2 as well as the reasons why N_2 and Argon are not easily trapped by the PSA.

If hydrogen is produced from coal instead of natural gas, the challenge is even larger since the feed gas into the PSA unit will contain higher amounts of Argon and N_2. The reason for this is that the coal is gasified with oxygen, usually containing around 3% Argon.

Air Liquide has conducted PSA simulation work in the DYNAMIS project both for the natural gas case and for several coal cases. The results for the hard coal gasifier show that even if the maximum CO content in the product stream does not exceed 1 ppmv, the amount of inert compounds in the product varies in the range from 500 ppmv to 10000 ppmv depending on the desired PSA efficiency and H_2 yield. Some of the results are shown in Figure 7.

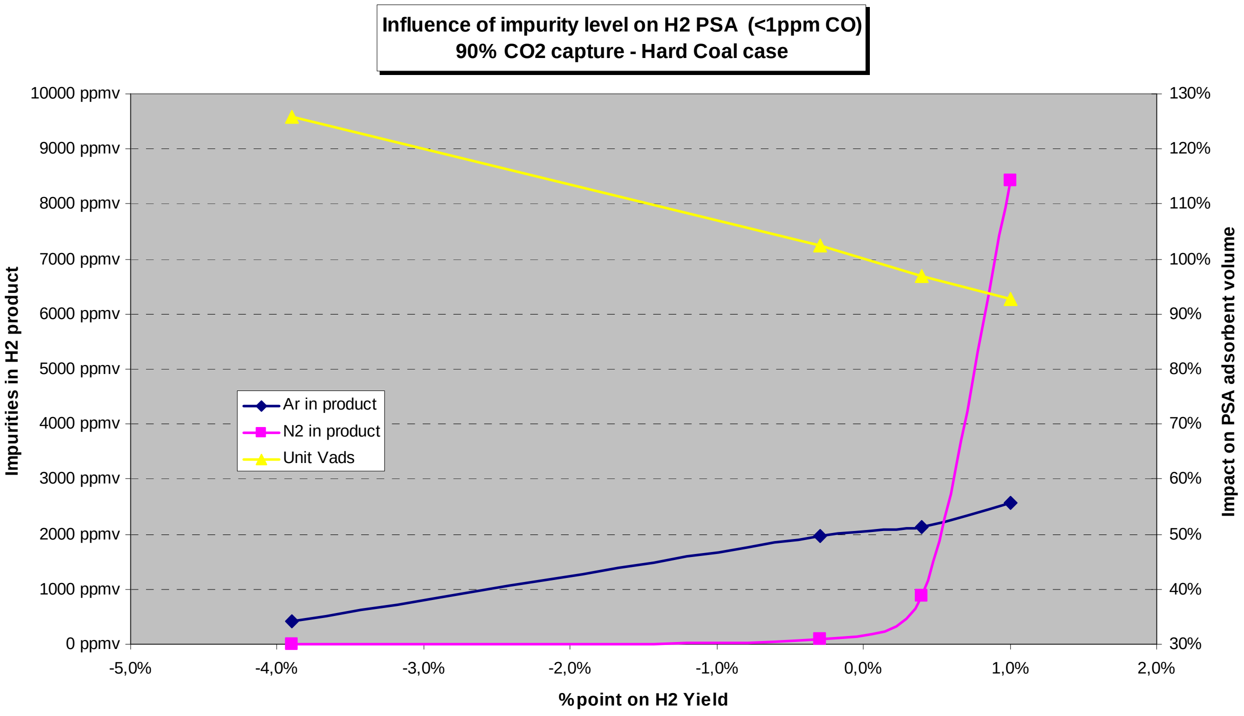

Figure 7 PSA simulation results showing impact of impurity level on Hydrogen yield and PSA size. (Source: Air Liquide)

The figure shows that N_2 can be effectively stopped by the PSA unit up to a certain level of hydrogen recovery (usually around 85-87% H_2 yield), while Argon content in the product gas is constantly increasing as hydrogen yield increases.

The figure also shows that if the total content of inert components is to be below 500 ppmv, this results in a decrease of hydrogen yield of about 4 % points, a considerable increase in PSA adsorbent volume and a consequent increase in unit size and costs.

Although achievable with current PSA technology for all cases considered in the DYNAMIS project, the requirement of 500 ppmv inert compounds is by far the most stringent limit to the operation of the PSA and the major barrier towards improved hydrogen production efficiency. CO content will be far below 0.5 ppmv if the inert compounds concentration is limited to 500 ppmv.

There are two possible solutions to the problem DYNAMIS is facing:

- Relax the tolerated concentration of inert compounds (more specifically Ar) to about 10000 ppmv. This will result in considerable improvements in the technology and economy of the H_2 production process
- Increase the purity of O_2, i.e. increase the size of the O_2 purification unit. The use of higher purity oxygen, with less than 0.5% argon should greatly help the hydrogen purification process (PSA), but it will result in increased oxygen production costs. Starr et al. [14] quotes IEA reporting that the energy cost will increase by about 12% and that presumably the capital costs of the ASU will also increase.

Although several references mention that the presence of inert components only has a dilution effect, there is a lack of experimental data regarding long-term impact of inert compounds in PEM fuel cell performance. This information is urgently needed in order to improve the economy of H_2 production from decarbonized fossil fuels.

As a summary, all the arguments regarding the H_2 production suggest considerable economic and technical benefits by relaxing the usual specification of 100-500 ppmv inert compounds to a level of 2000 – 10,000 ppmv (0.2-1%).
On the other hand, it was already mentioned in the introduction that the H_2 quality specifications should be acceptable to most PEM suppliers and, in addition, there is no information on the long-term impact of inert compounds.
These are the arguments for setting the DYNAMIS recommendation for maximum concentration of inert compounds to 500 ppmv but suggest strongly further relaxation of this limit.

CO

Some references recommend a maximum concentration of CO of about 10 ppmv. However, the extensive experimental work of Air Liquide gives reasons to believe that some PEM materials will not tolerate such a concentration and recommend a concentration limit of 0.5 ppmv.

The DYNAMIS recommendation for maximum concentration of CO is 0.5 ppmv. This recommendation should be revised if progress is made and documented in terms of PEM materials and tolerated temperatures.

If the concentration of inert compounds is relaxed to 10,000 ppmv, then the concentration of CO will be the limiting factor in terms of economics and overall efficiency for the DYNAMIS plant.

Sulfur compounds

Based on the experimental work of Air Liquide showing very limited impact of sulfur compounds in PEM cell performance for H_2S concentrations below 0.25 ppmv, the DYNAMIS recommendation for sulphur compounds is 0.01 ppmv (10 ppbv).
Nevertheless, a further relaxation of this limit is also suggested to the fuel cell community.

The recommendation of maximum concentration of sulphur compounds is not critical to the design of the DYNAMIS hydrogen production plant as the PSA unit can easily eliminate sulphur compounds.

Ammonia

The DYNAMIS recommendation for maximum concentration of ammonia is 0.1 ppmv. This is in agreement with the ISO 14687-2.

The experimental work of Air Liquide gives reasons to believe that this limit is rather conservative and suggest relaxing this limit.

On the other hand, the experimental work of Halseid presents considerable effect of ammonia in fuel cell performance and suggests that further work is required in this area.

As for sulphur compounds, the recommendation of maximum concentration of ammonia is not critical to the design of the DYNAMIS hydrogen production plant as the PSA unit can easily eliminate ammonia.

CO_2

The DYNAMIS recommendation for maximum concentration of CO_2 is 1 ppmv. This is in agreement with the ISO 14687-2.

However, the literature available regarding impact of CO_2 does not justify having this concentration limit even if the mechanisms for CO_2 poisoning are not well understood. These are the reasons for suggesting relaxation of this limit.

As for sulphur compounds and ammonia, the recommendation of maximum concentration of CO_2 is not critical to the design of the DYNAMIS hydrogen production plant as the PSA unit can easily eliminate it.

4 H_2 QUALITY RECOMMENDATIONS

As a result from the discussion conducted in the previous Chapter, the following quality recommendations are proposed for the DYNAMIS project, having as the main application PEM fuel cells. The “Comments” column in the table should **ALWAYS** follow the DYNAMIS H_2 quality recommendation.

Component	**DYNAMIS**	**Comment**
Hydrogen fuel index (minimum, %)	99.95	
Non-hydrogen constituents (maximum content) Dimensions in micromoles per mole unless otherwise stated		
Total gases	500	
Water (H_2O)	5	
Total hydrocarbons C2+ Methane	 2 100	
Oxygen (O_2)	5	
Helium (He), Nitrogen (N_2), Argon (Ar)	Sum: 500	Further relaxation of this limit to 0.2-1% should be considered by the Fuel Cell (FC) community. This could increase hydrogen recovery by up to 6% points for the coal based cases studied in DYNAMIS.
Carbon dioxide (CO_2)	1	Further relaxation of this limit to 100 ppmv should be considered by the FC community, based on experimental experience with long term operation.
Carbon monoxide (CO)	0.5	Limit because of long term voltage losses.
Total sulfur compounds	0.01	Further relaxation of this limit to 0.1 ppmv should be considered by the FC community
Ammonia (NH_3)	0.1	Further relaxation of this limit to 5 ppmv should be considered by the FC community, based on long-term experimental experience

5 CONCLUSIONS

- Existing limits for inert components around 100-500 ppmv is the most challenging requirement for H_2 production in a DYNAMIS plant using Pressure Swing Adsorption technology, specially for coal based H2 production. Relaxation of inert compounds limit up to 0.2-1% vol. will result in reduced CAPEX and OPEX for the H_2 production and considerable increase of H_2 yield.

- Experimental data for long term impact of inert compounds in PEM cells in the range of 5,000 – 10,000 ppmv are urgently needed.

- If the existing limits for inert compounds are relaxed, the limiting factor will be the concentration limit for CO. Improving material knowledge so that the CO content can increase should be given priority.

- Although some references recommend a maximum concentration of CO of about 10 ppmv, the extensive experimental work of Air Liquide gives reasons to believe that some PEM materials will not tolerate CO concentrations higher than 0.5 ppmv. This is the reason for the DYNAMIS recommendation.

- The recommendation for CO concentration limit should be revised before the HYPOGEN plant is built as it is reasonable to assume that, by 2012, there will be more high temperature PEMFCs, and that the limitations for these fuel cells on CO (and probably CO_2) will be considerably less stringent, possibly around 0.1%.

- PSA technology allows for extensive removal of sulfur compounds and ammonia. Nevertheless the existing quality specifications might be very conservative.

- Further research regarding the impact of ammonia in PEM fuel cells and poisoning mechanisms are encouraged.

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