Air Liquide creative oxygen AREVA H_2Gen

Hydrogen Workshop

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Risk assessment of impurities in hydrogen for fuel cell

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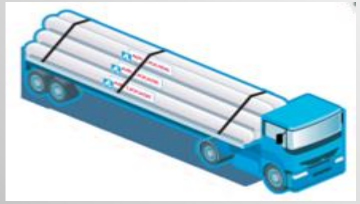
Outline

1. Objectives
2. H_2 source: PEM Electrolysis
3. H_2 source: Steam Methane Reforming
4. Conclusion

1 – Objectives



- **Production site**
- **SMR***
- **Electrolysis**

- **Transport**
- **GH2**
- **LH2**

- **Point of use**
- **Automotive and**
- **Stationnary applications**

Purity analysis

1 – Objectives

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

  Objectives:
  - assessment of the possible impurities that could be produced at the different stages of the hydrogen production process ;
  - provide the overall probability of these impurities being present in the end-product hydrogen (following purification steps);
  - 3 processes: steam methane reforming, electrolysis and chlor-alkali processes.

- **Task 1.2: Assessment of impact of impurities to fuel cell system**

  Objectives:
  - assess the impact of multiple impurities in hydrogen on fuel cells.

1- Assessment of the presence of impurities in H_2 produced with PEM electrolysis and SMR processes based on risk assessment approach

2- Analytical campaign of PEM electrolysis and SMR production sites

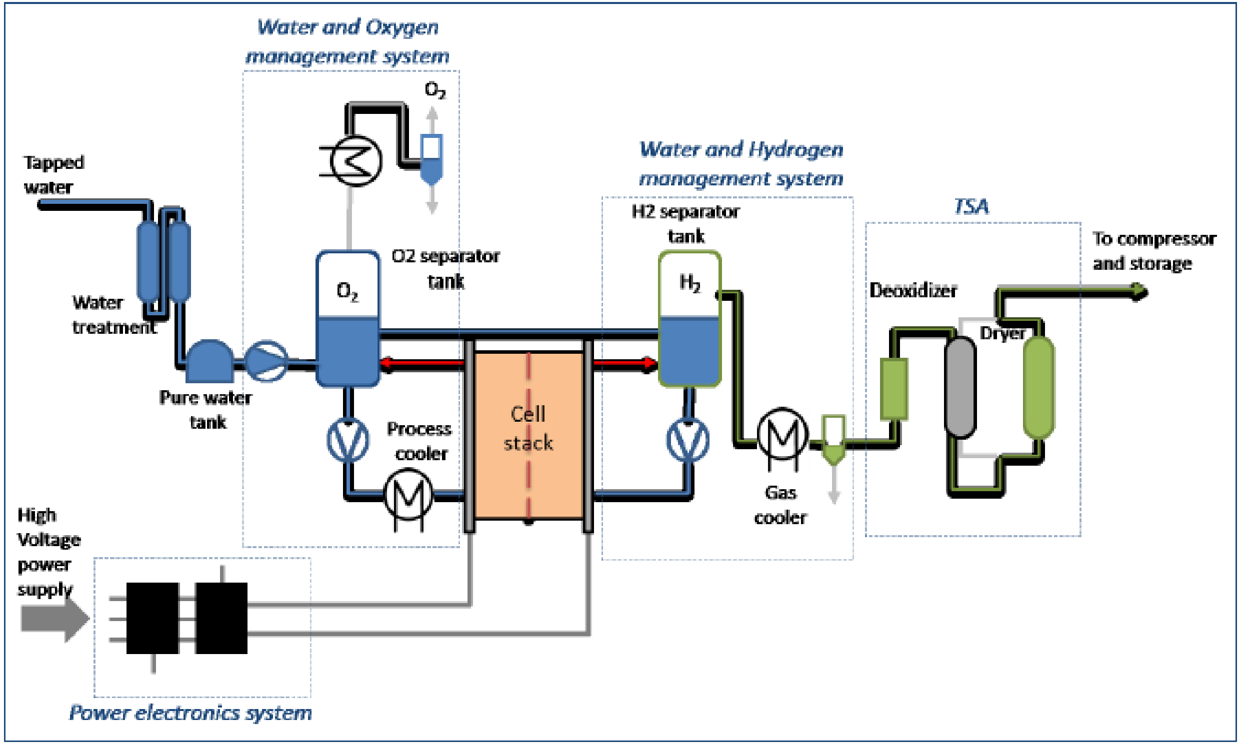
- **Task 1.3: Risk assessment**

  Objectives:

  perform a risk assessment of impurities in fuel cell hydrogen.

PEM Electrolysis

2 – PEM Electrolysis + TSA
Process



Design of AH2GEN's PEM Water Electrolyser process with TSA

2 – PEM Electrolysis + TSA

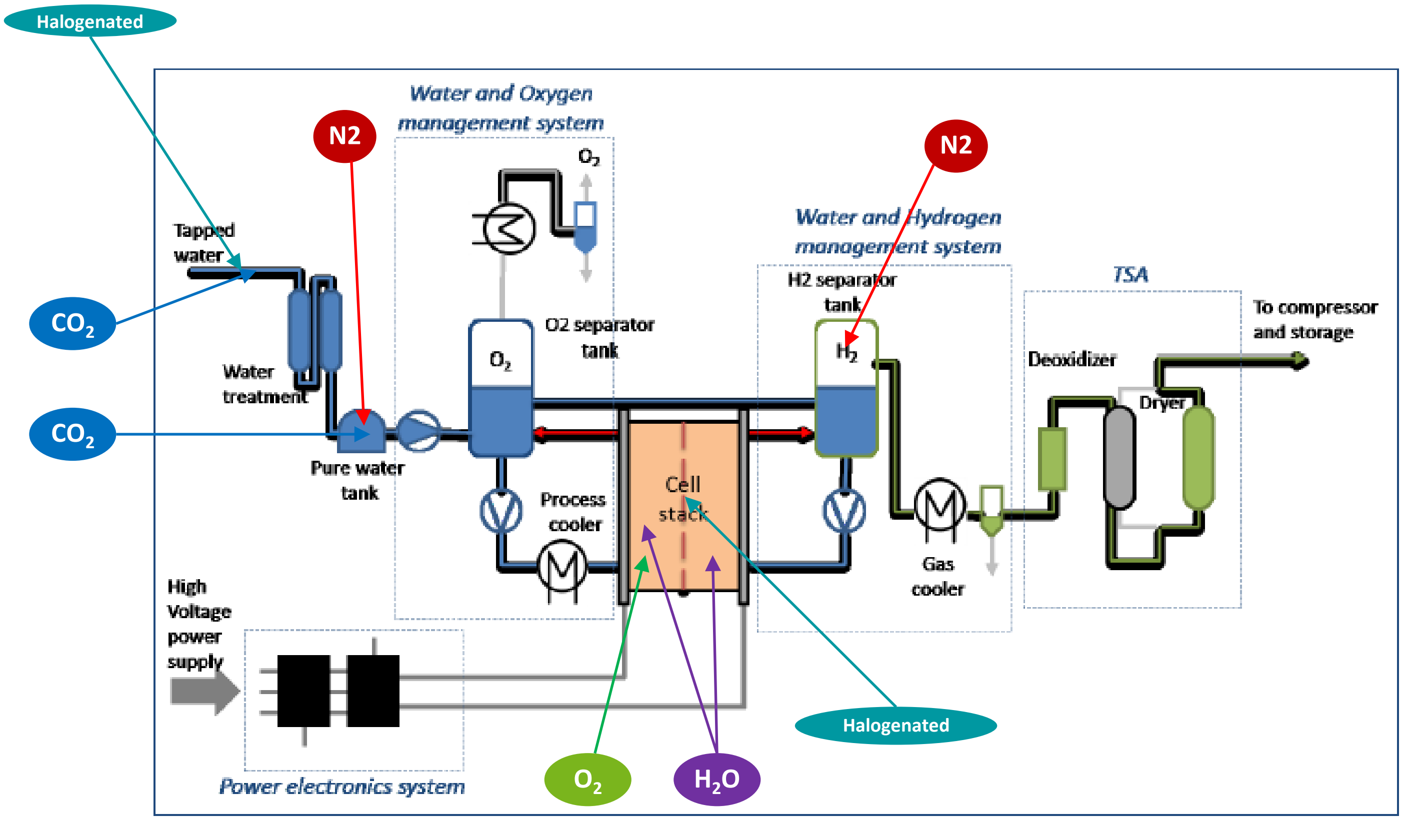
Impurities

General classification of impurities for PEM electrolysis + H2 purification

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

2 – PEM Electrolysis + TSA

Source of impurities

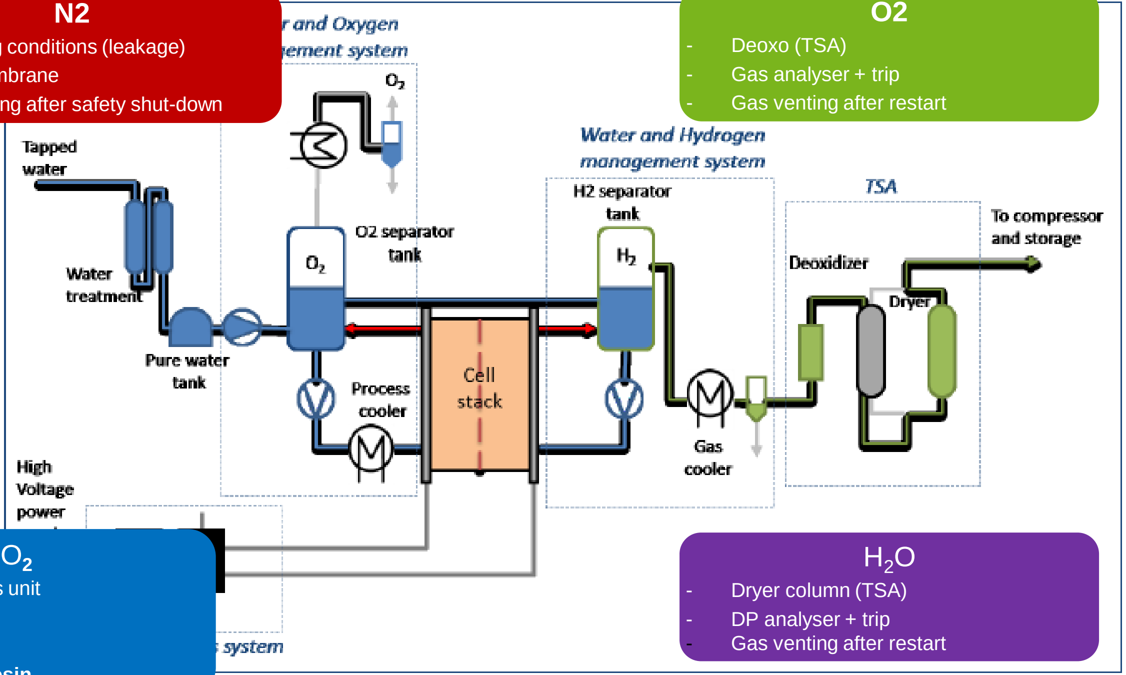


2 – PEM Electrolysis + TSA

Existing barriers

N2
- Operating conditions (leakage)
- PEM membrane
- Gas venting after safety shut-down

O2
- Deoxo (TSA)
- Gas analyser + trip
- Gas venting after restart



CO_2
- Reverse osmosis unit
- CO2 filter
- PEM membrane
- **Ion exchange resin**

H_2O
- Dryer column (TSA)
- DP analyser + trip
- Gas venting after restart

2 – PEM Electrolysis + TSA

Risk assessment

Air Liquide creative oxygen AREVA H_2Gen

Table 5: Risk assessment table for PEM WE +TSA

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

Occurrence class for each impurities

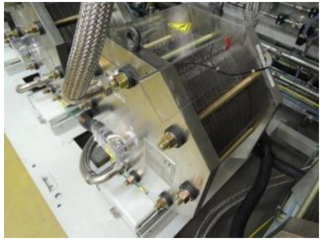
- Occurrence class 4 (highest probability) :
- Occurrence class 3 :
- Occurrence class 2: N_2, O_2, H_2O
- Occurrence class 1: CO_2
- Occurrence class 0 (never observed): Ar, CO, CH_4, He, halogenated products, formaldehyde, formic acid, THC, ammonia, sulfur compounds

2 – PEM Electrolysis + TSA

Analytical campaign

ELYTE E12-15 PEM electrolyzer

- H2 flow rate: 12 Nm³/h
- Operating pressure:
  - H_2: 15 bar
  - O_2: 14 bar
- Operating temperature: 60°C
- TSA purification unit
  - H_2: 99,998%
  - O_2 < 10 ppm
  - H_2O < 10 ppm



2 – PEM Electrolysis + TSA

H_2 analysis before purification

Samples 1 to 3 : before H2 purification unit

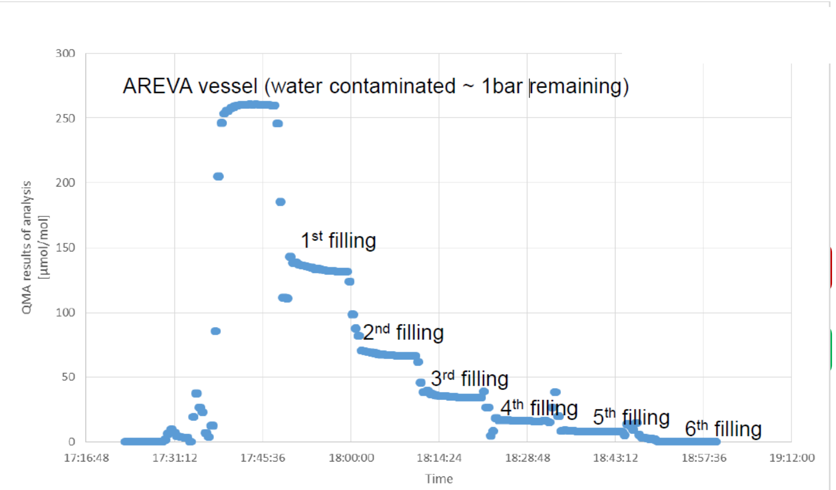
		Results with expanded uncertainty (k=2)		
Compounds	Unit	Sample 4-1	Sample 4-2	NMIs
CO	µmol/mol	< 0.01	< 0.01	NPL
CO_2	µmol/mol	< 5	< 5	SP
CO_2	µmol/mol	0.240 ± 0.012	0.221 ± 0.011	NPL
CH_4	µmol/mol	0.091 ± 0.007	0.086 ± 0.008	NPL
Non methane hydrocarbons	µmol/mol	< 0.01	< 0.01	NPL
H_2O	µmol/mol	> 100	> 100	NPL
Total sulphur compounds	µmol/mol	< 0.0036	< 0.0036	NPL
O	µmol/mol	Not analysed	Not analysed	CEM
O_2 + Ar	µmol/mol	< 25	< 30	SP
O_2	µmol/mol	20.9 ± 3.0	23.3 ± 3.8	NPL
N_2	µmol/mol	< 90	< 130	SP
N_2	µmol/mol	Not analysed	Not analysed	CEM
N_2	µmol/mol	< 1.2	< 1.2	NPL
Ar	µmol/mol	Not analysed	Not analysed	CEM
Ar	µmol/mol	< 0.5	< 0.5	NPL
Total halogenated (HCl)	µmol/mol			VSL
CH2O	µmol/mol			VSL
CH2O2	µmol/mol			VSL
NH3	µmol/mol			VSL
He	µmol/mol	< DL	< DL	CEM

- **Water saturated samples (DP= 7°C / 15 bar)**
- **Low O_2 content (stability?)**

2 – PEM Electrolysis + TSA

H_2 analysis after purification

Samples 4 to 6: O2 content in accordance with specification but high water content



Samples 7 to 9:

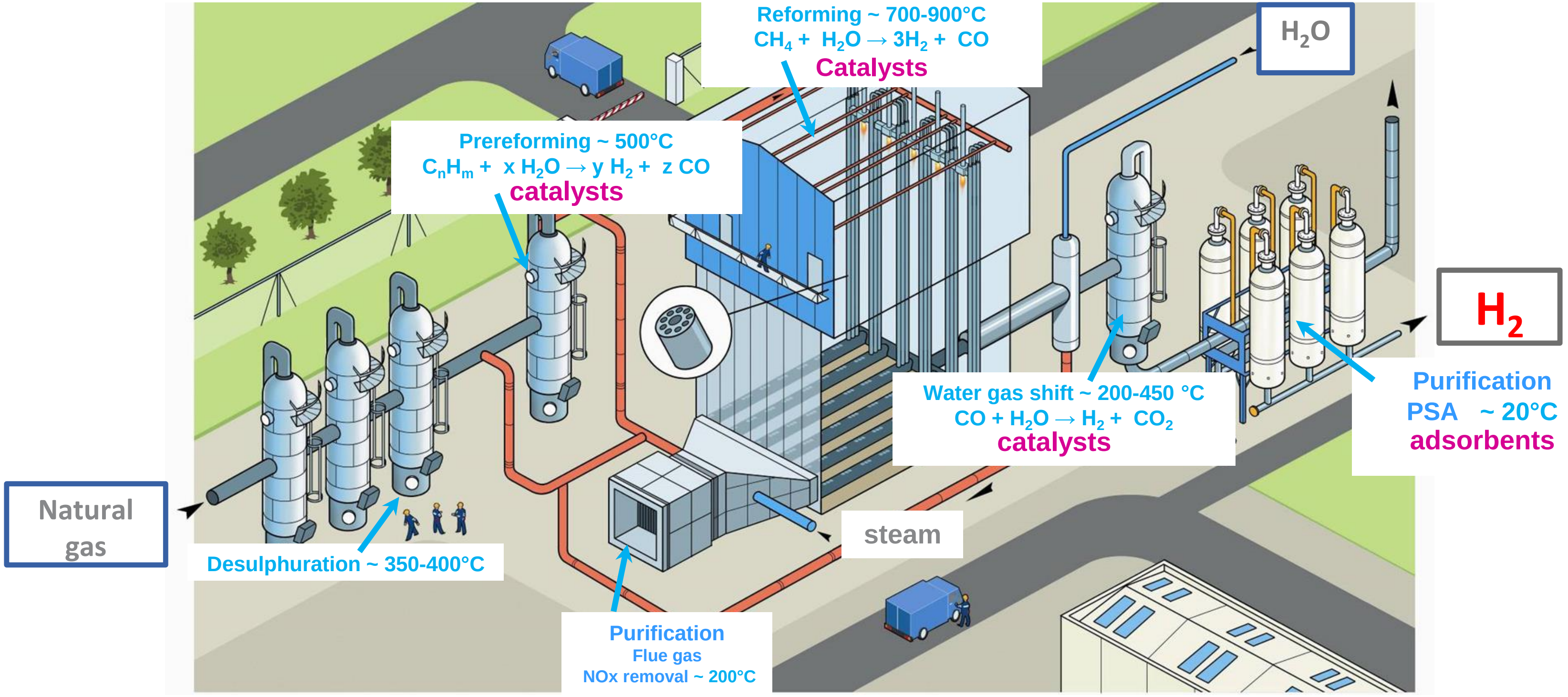
- H_2O content in accordance with specification < 2 ppm
- O_2 content in accordance with specification < 5 ppm

Samples 7 to 9 : after TSA purification unit

		Results with expanded uncertainty (k=2)			
Compounds	Unit	Sample 4-1	Sample 4-2	Sample 3	NMIs
CO	µmol/mol	< 0.02	< 0.02	< 0.02	NPL
CO_2	µmol/mol	< 5	n.a.	< 5	RISE
CO_2	µmol/mol	< 0.01	< 0.01	< 0.01	NPL
CH_4	µmol/mol	< 0.01	< 0.01	< 0.01	NPL
Non methane hydrocarbons	µmol/mol	0.156 ± 0.030	0.126 ± 0.026	0.111 ± 0.024	NPL
H_2O	µmol/mol	< 0.8	< 1.2	< 3	NPL
Total sulphur compounds	µmol/mol	< 0.0030	< 0.0030	< 0.0030	NPL
O_2	µmol/mol	< 5	n.m.	< 5	CEM
O_2 + Ar	µmol/mol	< 25	n.a.	< 25	RISE
O_2	µmol/mol	1.39 ± 0.36	< 0.5	1.59 ± 0.45	NPL
N_2	µmol/mol	< 100	n.a.	< 100	RISE
N_2	µmol/mol	< 80	n.m.	n.m.	CEM
N_2	µmol/mol	1.51 ± 0.2	< 1.0	1.86 ± 0.2	NPL
Ar	µmol/mol	< 80	n.m.	n.m.	CEM
Ar	µmol/mol	< 0.5	< 0.5	< 0.5	NPL
Total halogenated (HCl)	µmol/mol	n.a.	< 0.005	< 0.005	VSL
CH2O	µmol/mol	< 0.005	< 0.005	< 0.005	VSL
CH2O2	µmol/mol	< 0.1	< 0.1	< 0.1	VSL
NH3	µmol/mol	n.a.	n.a.	n.a.	VSL
He	µmol/mol	< 9	< 9	< 9	CEM

Steam Methane Reforming + PSA

3 – Steam Methane Reforming



PSA technology:

- Based on adsorbent technology:
  - Multiple adsorbents: silica, alumina, molecular sieves, activated carbons.
  - Adsorb different kind of gases
- Better quality of H2 is produced compared to other purifications process

  (between 99% to 99.9%)

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

3 – Steam Methane Reforming

Contaminant	Threshold	Causes possible For the source studied	Existing barriers						P
Inert gases : N_2	100	Present in Nat gas and Syngas PSA malfunction	PSA	Double analysis + trip at xx ppm at PSA outlet xx<100 ppm					3
Inert Gas Ar		Only ATR and POx Present in O_2 typical 0,6% in Syngas	PSA. Not sized to remove Argon. Argon content may be						2
Oxygen	5	Not present in Syngaz Oxygen is unstable in the condition of reforming and	PSA cannot be used with significant O_2 content for safety reasons						0
Carbon dioxide	2	Present in Syngas (%)	PSA Adsorption strength of MS, Activated carbon, Silicagel						0
Carbon monoxide	0,2	Normal operation below threshold. Occasional peaks at ppm level	Double analysis + trip at xx ppm at PSA outlet (xx<10)						4
Methane (CH_4)	100	Present in Syngas at % level	In most cases CO is sizing the PSA, therefore CO<10ppm ==> CH_4 < xx						2
Water	5	Syn gas saturated in H_2O	PSA Adsorbed in Alumina and MS Adsorption strngth						0
Total sulphured components	0,004	Sulfur from Nat Gas	Desulfuration upstream reformer (typical values) Normal < 10 ppb	Prereformer Catalyst poisoning by sulfur irreversible	Reformer Catalyst poisoning by sulfur irreversible	Shift Catalyst poisoning by sulfur irreversible	PSA Adsorption of H_2S before CO,	H_2S Adsorption in pipe and vessels	0
Ammonia	0,1	Traces present in Syngas.	PSA. Adsorption strength of Alumina, MS Higher than						0
Total hydrocarbons	2	Traces of C2+ after reforming reaction	PSA C2 C3, C4, C5+ adsorbed by Activated Carbon layer						0
Formaldehyde	0,01	Idem Acide Formique… Arreté par PSA	PSA. Adsorption strength of Alumina, MS Higher than						1
Formic acid	0,2	May be present in Syngas essentially liquid	PSA. Formic Adsorption strength of Alumina, MS Higher than						0
Halogenated compounds	0,05	Present in Nat Gas?	Any Cl present in Nat gas would be stopped by HDS	Prereformer Catalyst poisoning by Cl irreversible	Reformer Catalyst poisoning by Cl irreversible	Shift Catalyst poisoning by Cl irreversible	PSA Adsorption of Cl before CO, CO_2,		0
Helium	300	Not present in Nat Gas in N Europe (<10 ppm) Passes through the whole							0

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3 –Steam Methane Reforming

Occurrence class	impurities
4	CO
3	N_2
2	Ar, CH4
1	Formaldehyde
0	CO2, He, H2O, halogenated products, formic acid, THC, ammonia, sulfur compounds

3 – Steam Methane Reforming

Compounds	Unit	Results with expanded uncertainty (number of different samples: 3 and *k*=2)
CO	µmol/mol	< 0.01
CO_2	µmol/mol	< 0.01
CH_4	µmol/mol	< 0.01
Non methane hydrocarbons	µmol/mol	< 0.01
H_2O	µmol/mol	< 0.5
Total sulphur compounds	µmol/mol	< 0.0036
O_2	µmol/mol	< 0.5
N_2	µmol/mol	< 1.2
Ar	µmol/mol	< 0.5
Total halogenated (HCl)	µmol/mol	< 0.005
CH2O	µmol/mol	< 0.005
CH2O2	µmol/mol	< 0.1
NH3	µmol/mol	< 0.1
He	µmol/mol	< 50

Compounds	Unit	Results with expanded uncertainty (number of different samples: 3 and *k*=2)
C2 hydrocarbons	µmol/mol	< 0.5
C3-hydrocarbons	µmol/mol	<1
C4-hydrocarbons	µmol/mol	<1
C5-hydrocarbons	µmol/mol	<1
C6 – C18 hydrocarbons	µmol/mol	<0.05

For all the samples taken at SMR + PSA process:

→ all impurities are below the detection limit of analytical methods

Conclusion

4 – Conclusion

- The main impurities are identified for both PEM electrolysis and SMR processes
- The analysis of samples from PEM electrolyzer and SMR confirmed the risk assessment
- Appropriate actions and barriers can be added to reduce the risk if necessary

4 – Conclusion

For more details, see the publication:

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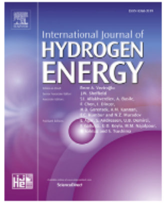

Probability of occurrence of ISO 14687-2 contaminants in hydrogen: Principles and examples from steam methane reforming and electrolysis (water and chlor-alkali) production processes model

Thomas Bacquart [a,*], *Arul Murugan* [a], *Martine Carré* [b], *Bruno Gozlan* [b], *Fabien Auprêtre* [c], *Frédérique Haloua* [d], *Thor A. Aarhaug* [e]

Thank you for your attention