HYDRAITE 1st OEM Workshop

Ulm, 07/03/2018

Hydrogen Quality from PEM electrolyzers

Fabien AUPRÊTRE – CTO

AREVA H_2Gen

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Outline

- AREVA H2Gen overview
- HYDROGEN JRP project
- Impurities risk assessment
- Electrolysis process analytical campaign

AREVA H_2Gen company overview

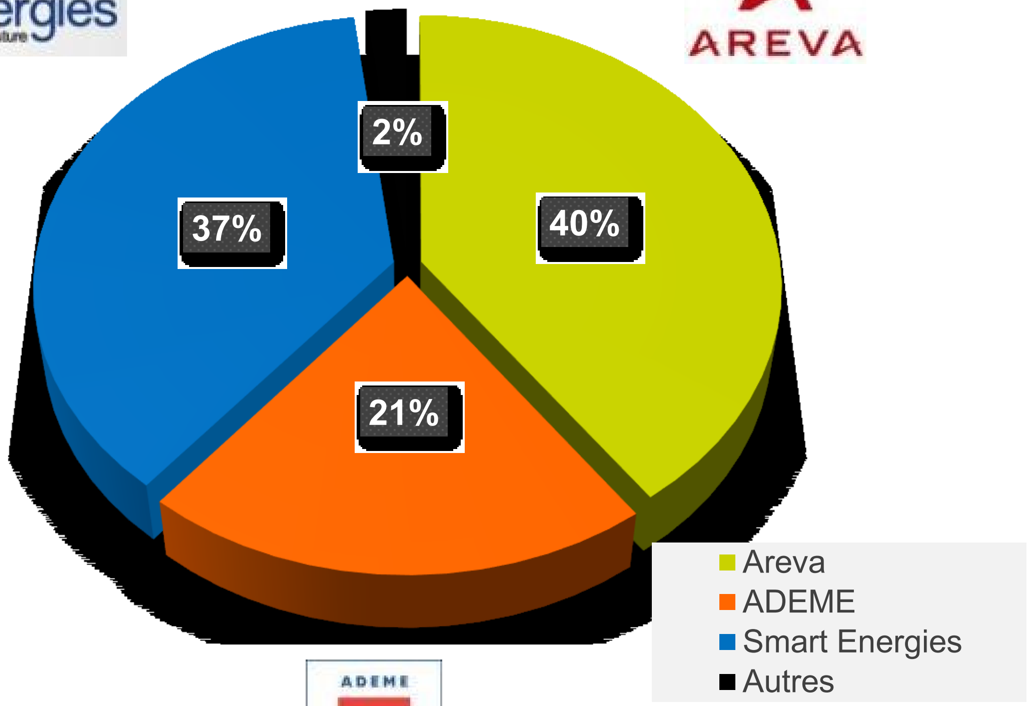
- **2014 : The merge of :**
  - **An industrial start-up** CETH2 **(owned by** smart energies **)**
  - **The electrolysis division of former** AREVA HELION HYDROGEN POWER
- **And venture capital funds from the French State**

ADEME Agence de l'Environnement et de la Maîtrise de l'Energie — Liberté • Égalité • Fraternité RÉPUBLIQUE FRANÇAISE — INVESTISSEMENTS D'AVENIR

» **A PEM electrolyser division within the AREVA Group**

Capital structure

- **3 main shareholders:**

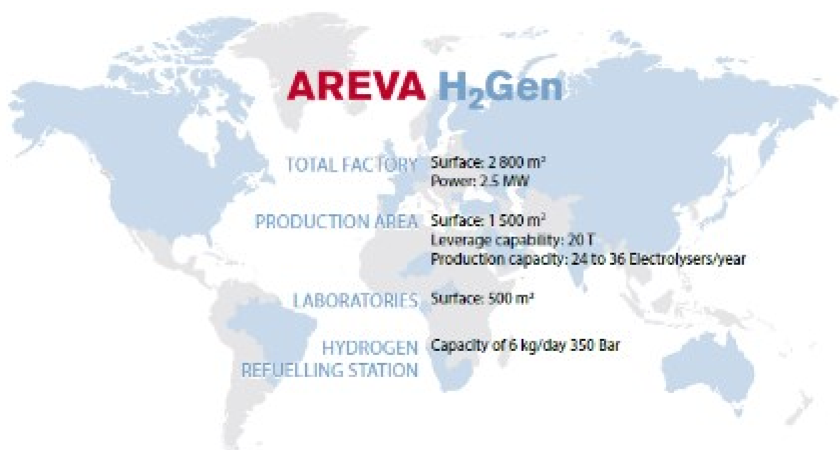


Localisation

- **Paris - France**
  - **Headquarter: 20 rue Quentin Bauchard 75008 PARIS**
  - **Production facility: 8 avenue du Parana 91940 LES ULIS**

- **One subsidiary: AREVA H2Gen GmbH (Carsten Krause)**

- **Worldwide network of partners**
  - UK
  - China
  - Egypt
  - India
  - Korea
  - Viet nam
  - Turkey
  - …



Factory

Overall area 2500 m²

Tertiary sector (offices):
- 600 m²

Production area :
- 1 500 m²
- Leverage capability 20 T

Production capacity :
- 24 to 36 electrolysers a year

Laboratories :
- 500 m²
- 10 test benches

3 Million € CAPEX

Product line

- A commercial product line from 5 to 120 Nm^3/h at 15 Bar and up to 240 Nm^3/h at 35 Bar

- Customs solutions multi MW projects :
  - Grid balancing services
  - Renewable hydrogen for petro-chemicals

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Hydrogen

- Duration: 36 months, start date: 1 June 2016
- Consortium: 5 National Metrology Institutes
  5 key industrial and research partners in fuel cells, storage devices and hydrogen-related technologies
- Coordinator: LNE

LNE Le progrès, une passion à partager · VSL Dutch Metrology Institute · NPL National Physical Laboratory · RISE Research Institutes of Sweden · CEM Centro Español de Metrología

MAHYTEC Innovative Energy Solutions · AIR LIQUIDE Creative Oxygen · Ha Foundation for the Development of New Hydrogen Technologies in Aragon · cea

- 2 collaborators

afnor NORMALISATION · ap2e

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The JRP *Hydrogen* aims at feeding the revision of two ISO standards: ISO 14687-2 and ISO 16111 standards under the direct responsibility of ISO TC 197 "Hydrogen technologies"

ISO 14687-2 : 2012 *Hydrogen fuel – Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles* at a Committee Draft (CD) stage

ISO 16111 : 2008 *Developing transportable gas storage devices - Hydrogen absorbed in reversible metal hydride* at a Draft International Standard (DIS) stage

Component	ISO standard target (µmol/mol)
Water (H_2O)	5
Total hydrocarbons (CH_4 basis)	2
Oxygen (O_2)	5
Helium (He)	300
Total Nitrogen (N_2) and Argon (Ar)	100
Carbon dioxide (CO_2)	2
Carbon monoxide (CO)	0.2
Total sulphur compounds (H_2S, COS , CS_2 and mercaptans as a basis)	0. 004
Formaldehyde (HCHO)	0.01
Formic acid (HCOOH)	0.2
Ammonia (NH_3)	0.1
Total halogenated compounds (HBr, HCl, Cl_2 or organic halides)	0.05

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Hydrogen

- **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.

1- Assessment of the presence of impurities in the PEM electrolysis process by production process risk assessment

2- Electrolysis process analytical campaign

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

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

- **Task 1.3: Risk assessment**

  Objectives:

  perform a risk assessment of impurities in fuel cell hydrogen.

Impurities risk assessment PEM WE + TSA

- **Objective:**
  - **Evaluation of the risk not to respect the quality requirement using PEM electrolyser in a HRS**
  - **Evaluation of measurement to implement quality assurance of HRS**
- **AIR LIQUIDE risk assessment methodology according to ISO:IEC Guide 73**
- **3 fundamental questions:**
  - What might go wrong: which event can cause the impurities to be above the threshold value?
  - What is the likelihood (probability of occurrence expressed relative to the number of refueling events) that impurities can be above the threshold value?
  - What are the consequences (severity) for the fuel cell car?

Impurities risk assessment PEM WE + TSA

Table 1: Definition of occurrence classes

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

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Table 2: Definition of severity classes

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

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Table 3: Definition of acceptability table

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

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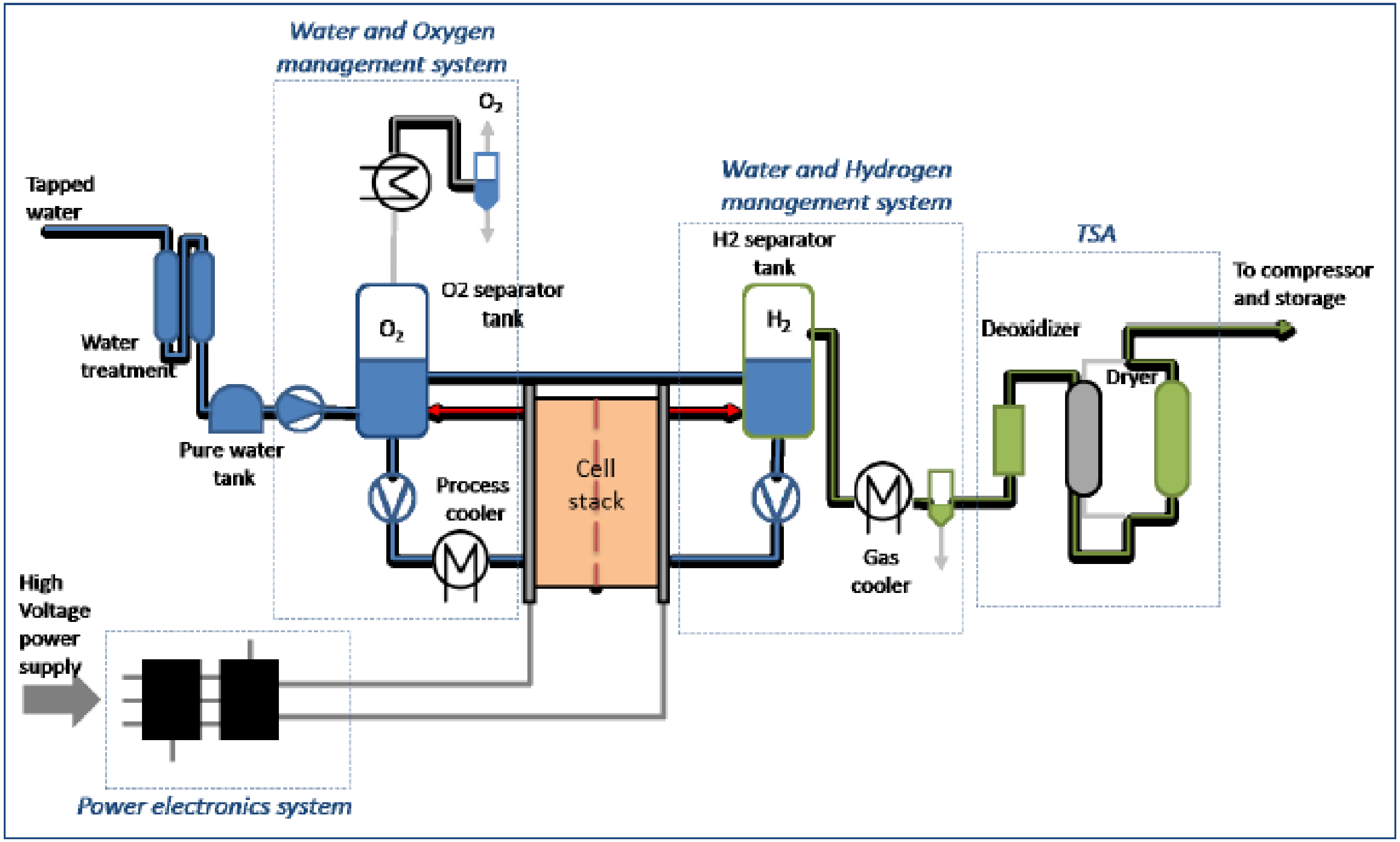
Impurities risk assessment PEM WE + TSA

PEM electrolysis + TSA H2 purification



Design of AH2GEN's PEM Water Electrolyser process with TSA

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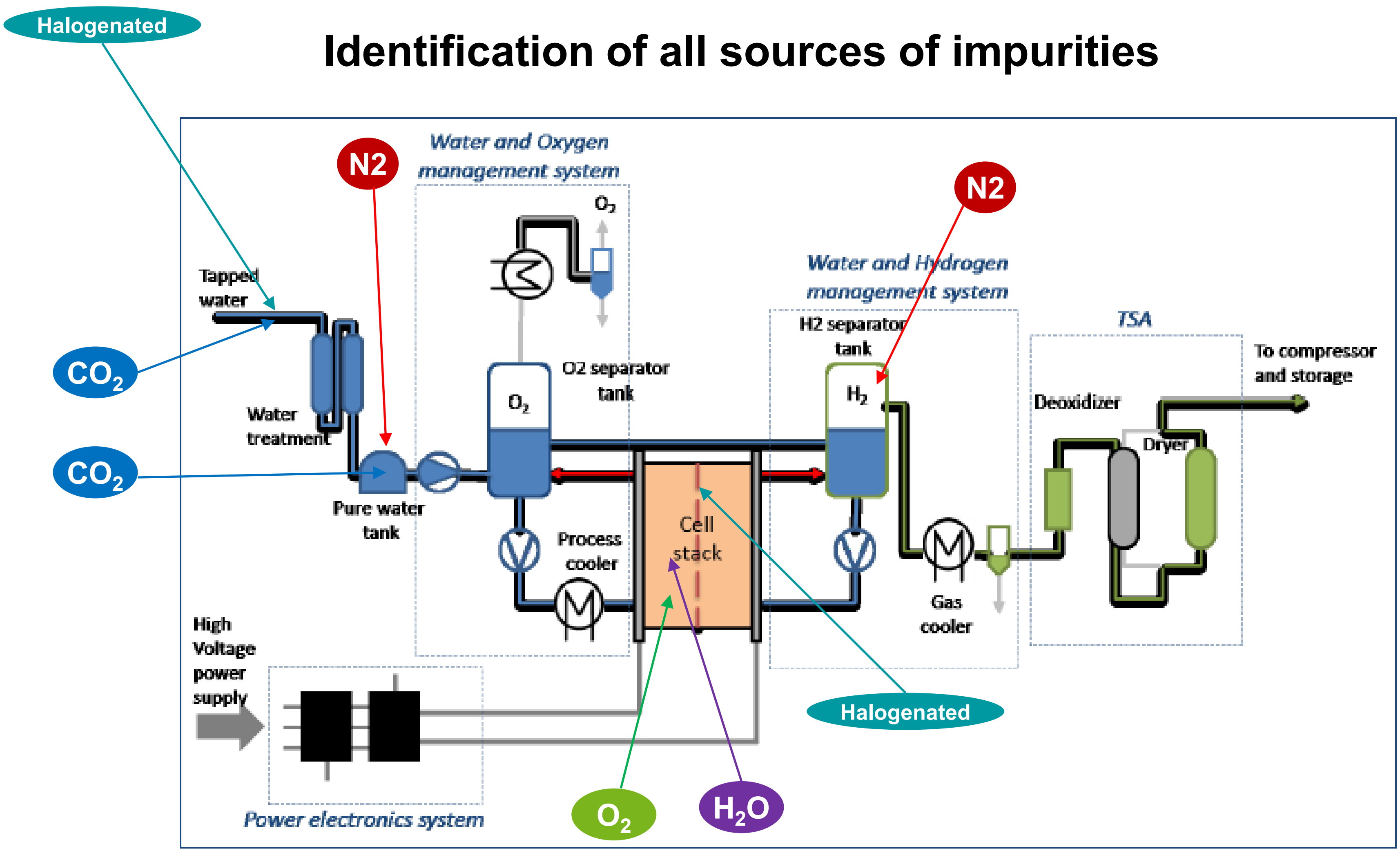
Impurities risk assessment PEM WE + TSA

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

Impurities risk assessment PEM WE + TSA

Identification of all sources of impurities



Design of AH2GEN's PEM Water Electrolyser process with TSA

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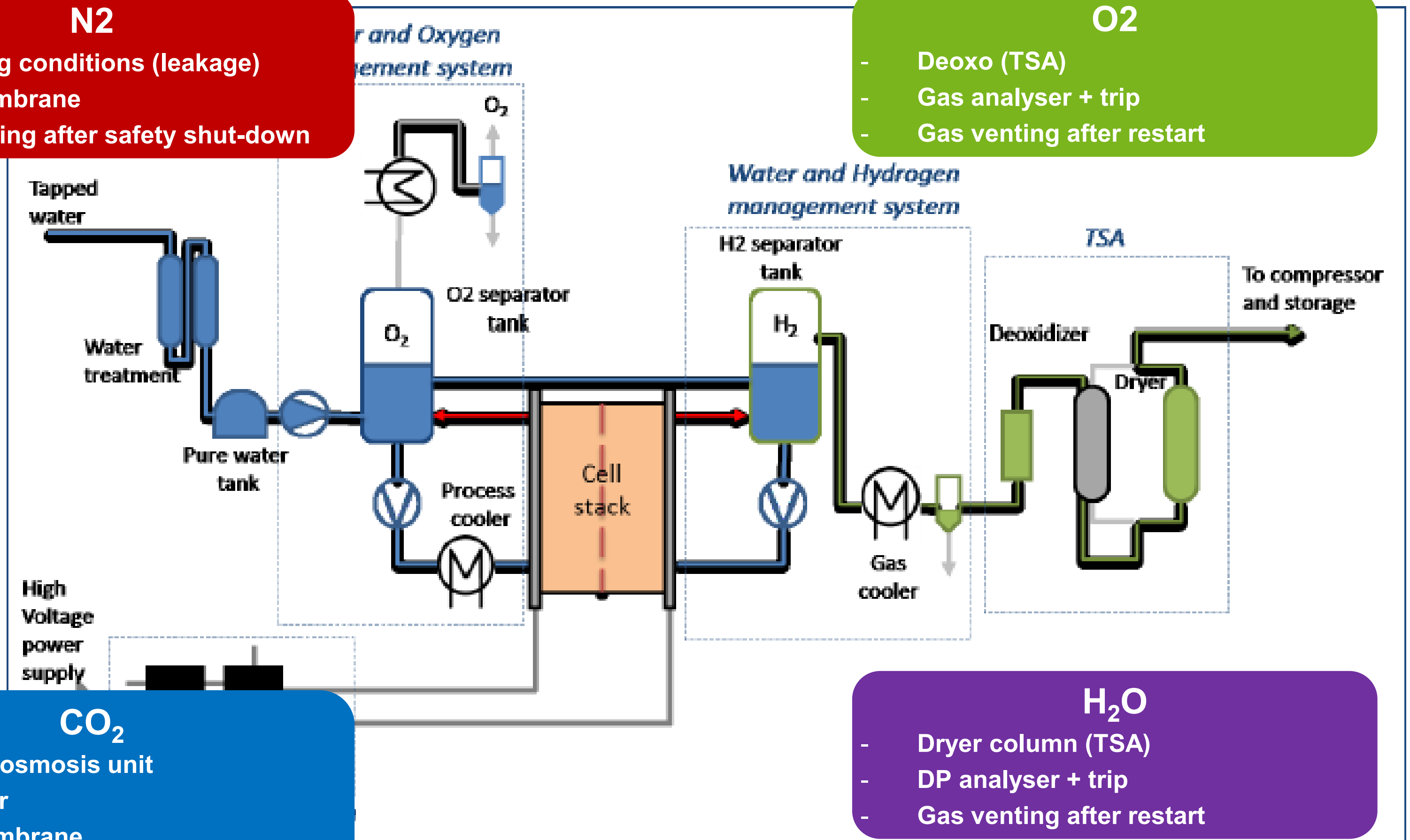
Impurities risk assessment PEM WE + TSA

Identification of all 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

…sign of AH2GEN's PEM Water Electrolyser process with TSA

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Impurities risk assessment PEM WE + TSA

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

Impurities risk assessment PEM WE + TSA

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	5	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	[illegible]	from tap water at anodic side	Reverse osmosis purification unit				0	0	4	

Electrolysis process analytical campaign

- **Step 1: Hydrogen production by PEM WE + TSA H2 purification**
  - **Production at steady state operation (before and after gas purification)**
  - **Gas sampling in pressure cylinders: 3 different samples**
  - **Send cylinders to partner**
- **Step 2: Gas samples analysis (13 parameters of ISO 14687-2:2012 except particulates)**
  - **NPL (UK): H_2O, CO_2, CO, total hydrocarbons, total sulphur compounds**
  - **VSL (Netherland): formaldehyde, formic acid, HCl for the total halogenated compounds, ammonia**
  - **CEM (Spain): O_2, Ar, N_2, He**
  - **RISE (Sweden): N_2, CO_2, He**

Electrolysis process analytical campaign

ELYTE E12-15 PEM electrolyzer

- H2 flow rate: 12 Nm^3/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

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Electrolysis process analytical campaign

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_2	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

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

Electrolysis process analytical campaign

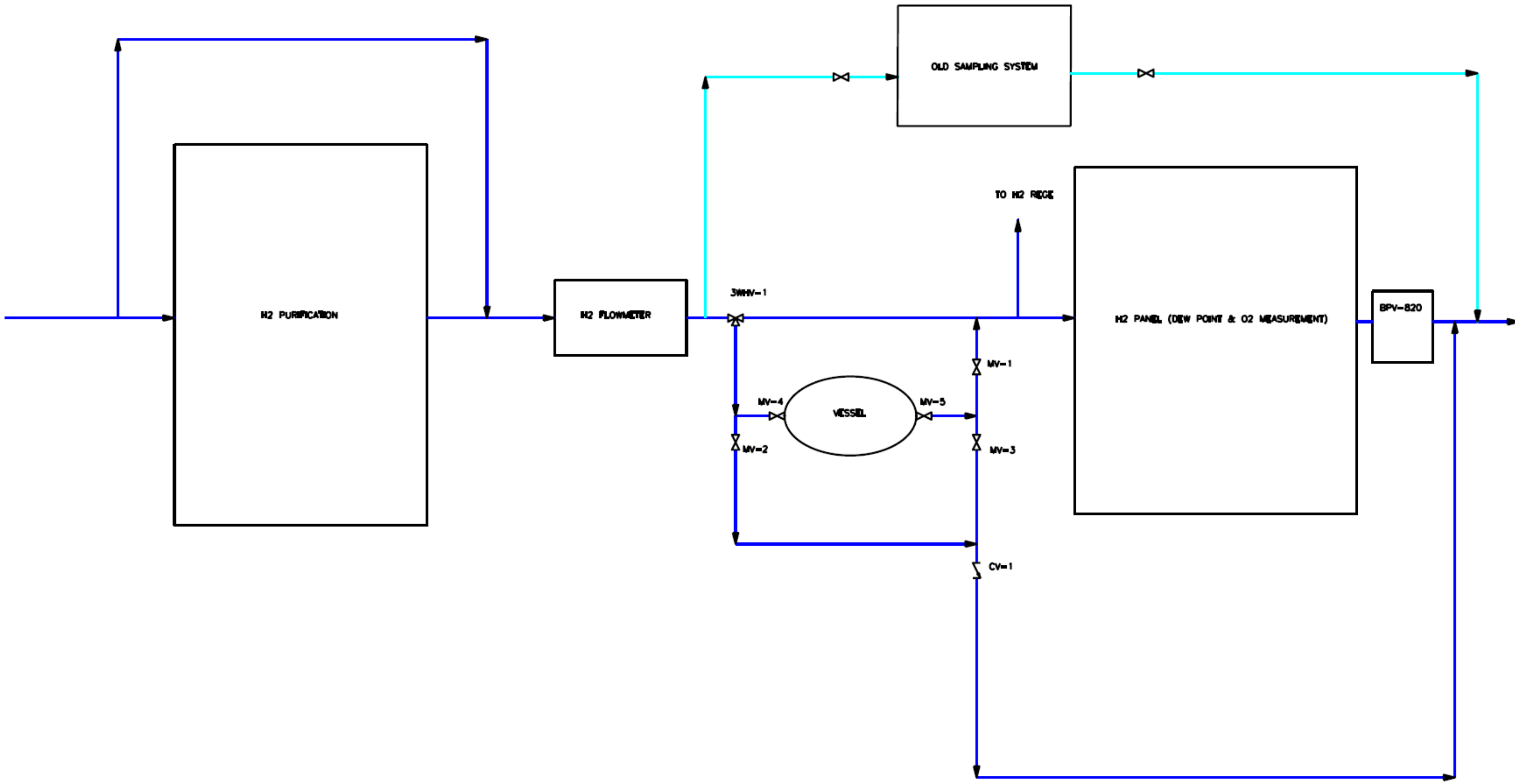
Samples 4 to 6 : after TSA purification unit

		Results with expanded uncertainty (*k*=2)		
Compounds	Unit	AREVA S3-1	AREVA S3-2	AREVA S4-1
CO	µmol/mol	< 0.02	< 0.02	< 0.02
CO_2	µmol/mol	< 0.01	< 0.01	< 0.01
CH_4	µmol/mol	< 0.01	< 0.01	< 0.01
Non methane hydrocarbons	µmol/mol	0.156 ± 0.030	0.126 ± 0.026	0.111 ± 0.024
H_2O	µmol/mol	> 250	> 250	> 250
Total sulphur compounds	µmol/mol	< 0.0030	< 0.0030	< 0.0030
O_2	µmol/mol	1.39 ± 0.36	< 0.5	1.59 ± 0.45
N_2	µmol/mol	1.51 ± 0.2	< 1.0	1.86 ± 0.2
Ar	µmol/mol	< 0.5	< 0.5	< 0.5

- **O_2 content in accordance with specification**
- **High water content not expected**

Probleme with sampling device

Electrolysis process analytical campaign



Electrolysis process analytical campaign

Samples 7 to 9 : after TSA purification unit

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

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

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Conclusion

- **Risk assessment :**
  - **WE process → 2 mains critical impurities**
  - **H_2O main critical impurity**

- **Test campaign :**
  - **PEM WE electrolyzer + TSA purification unit comply with purity requirement**
  - **Gas tightness of sampling device and cylinders**

Sampling at steady state operation BUT what about transient operation for grid services or wind/solar power supply?

Dr. Fabien AUPRÊTRE
CTO

AREVA H_2Gen
8 avenue du Parana
F-91940 Les Ulis– France
Mob: +33 6 30 75 42 68 – Tel: +33 1 81 87 12 60
fabien.aupretre@arevah2gen.com
www.arevah2gen.com