

Expected Purity Level of Hydrogen Economy to be fed into a European Hydrogen Infrastructure

Brussels – January 18, 2007
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Expert Workshop on Synergies between HYPOGEN and the Hydrogen Economy

Existing Hydrogen infrastructure

- Pipelines (~2000 km)
 - ✓ Specifications : Chemical Industry

- Large Plants (NG based SMR)
 - ✓ Specifications : Refineries

- LH2
 - ✓ Specifications : >99.9999%

- Cylinders
 - ✓ Various grade: Case-by-case basis

Future European Hydrogen Infrastructure

→ Driven by largest & most demanding consumer **Transport & PEM Fuel Cell**

- Large H₂ production plants (20 to >100,000 m³/h) able to produce H₂ at low cost with CO₂ mitigation, distributed by
 - ✓ Pipeline network
 - ✓ Cylinders
 - ✓ Liquid H₂
- Small delocalized production units

HYPOGEN

Hydrogen Fuel Quality Specification

(ISO TC197 WG12 – nov9, 2006, HNEI, Honolulu)

■ The fuel specification must

- ✓ Be compatible with automotive FC system performance & total life cycle costs
- ✓ Be developed via a consensus process using input from key stakeholders
- ✓ Be practical, sustainable & cost effective to implement & operate at H2 stations
- ✓ Be feasible for H2 production & purification
- ✓ Use applicable standardized methods for measurement & monitoring
- ✓ Be based on experimental data, analysis & verification
- ✓ Be compatible with durability & performance requirement of the FC

Actors

- ISO specifications issued (ISO TS14687-2)
- SAE : harmonized with ISO's
- ASTM
- Dynamis

ISO main specifications

H2 purity	> 99,99%	
		ASTM
Impurities	max level	Detection limits
	umole/mole	umole/mole
CO	0.2	0.2
CO2	1	0.1
Sulphur Compounds	0.004	0.004
THC	2	0.1
Oxygen	5	1
Ammonia	0.1	0.1
Inert Gases (N2, Ar, He)	100	60
Water	5	0.5
Halogens	0.05	0.01
Max Particulate Concentrations	20 ug/mole	
Max Particulate Size	10 um	1 um

Issues

- A moving target
 - ✓ FC requirements are changing with the development of new materials (lower precious metal loading)
- Lack of experimental data
 - ✓ Effect of various impurities
 - ✓ Long term effect
 - ✓ Numerous configurations

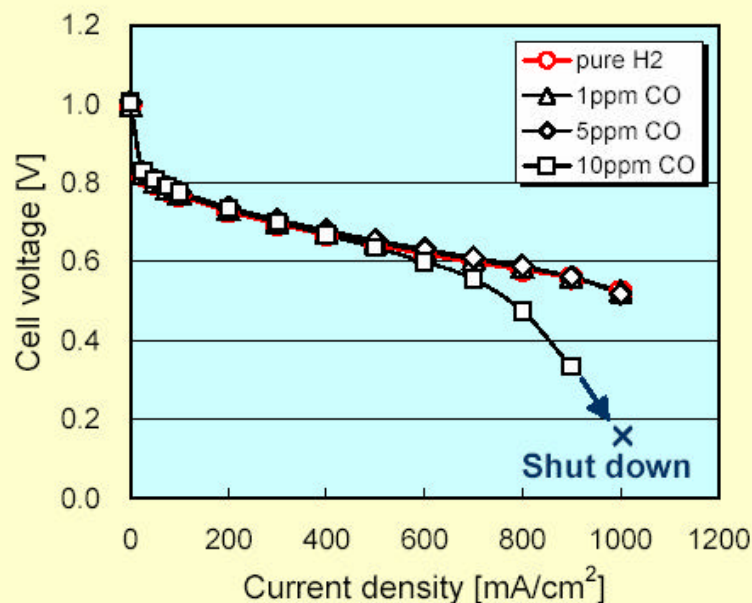
→ Non mature technology

■ Public & private Labs

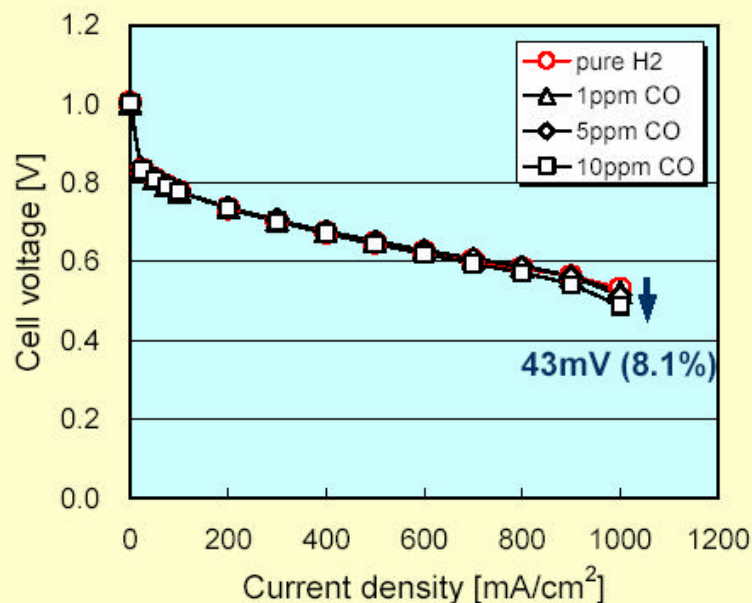
- ✓ JARI
- ✓ Los Alamos NL
- ✓ NERL
- ✓ GTI
- ✓ Technical University of Denmark
- ✓

- ✓ OMG dmc2
- ✓ Air Liquide & Axane
- ✓ ...

Examples of 1st step evaluation test (CO)



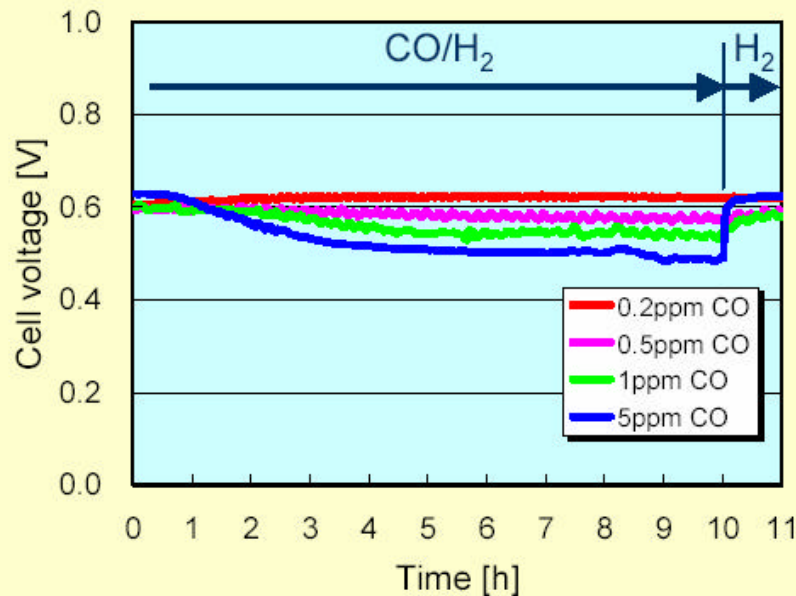
Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt/Pt



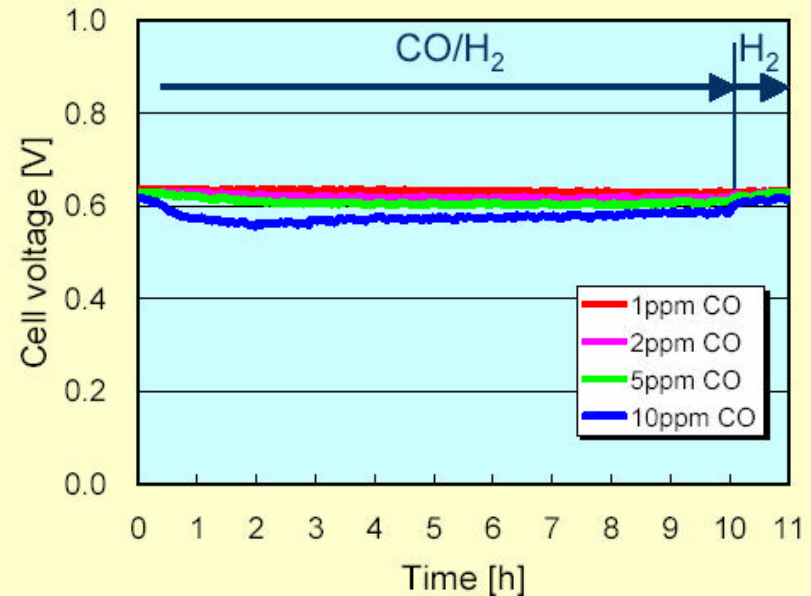
Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt-Ru/Pt

- If 10ppm CO is contained, the voltage drop ratio is more than 2%.
- Pt-Ru catalyst has the tendency of preventing CO poisoning.

Examples of 2nd step evaluation test (CO)



Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt/Pt



Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt-Ru/Pt

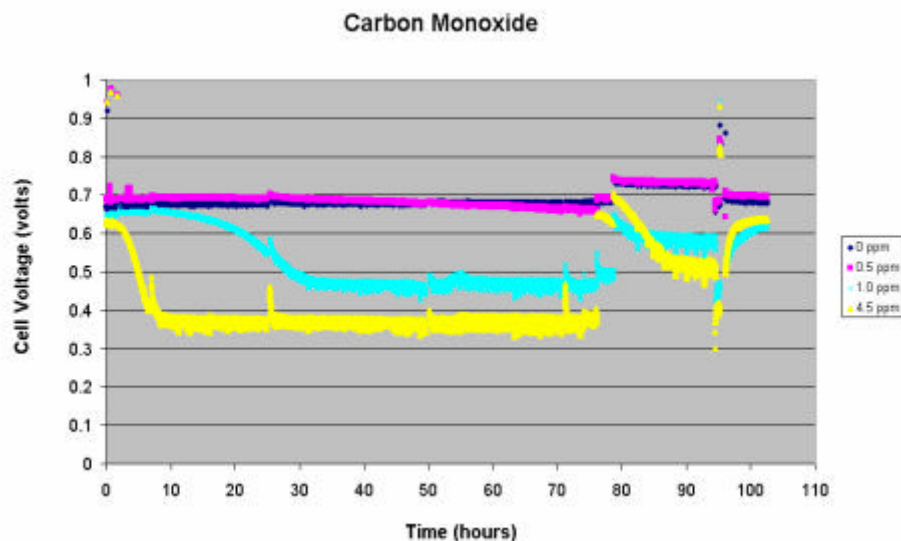
- Compared with 1st evaluation test, lower impurity concentration have influence on the fuel cell performance.
- After 10 hours test, the cell voltage is **recovered** by supplying pure hydrogen.

JARI Source

CO poisoning is reversible

■ Carbon Monoxide (CO)

- ✓ Mechanism – Adsorption of CO onto Pt sites, oxidation of CO to CO₂, desorption of CO₂
 - Equilibrium is established
 - Fully recoverable



✓ Results

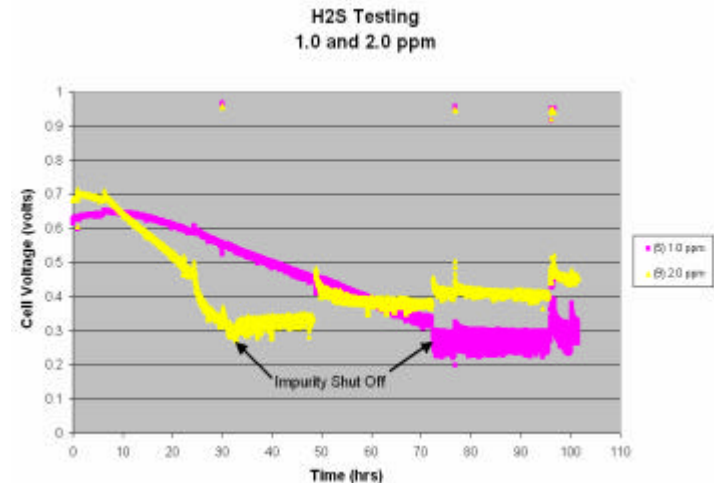
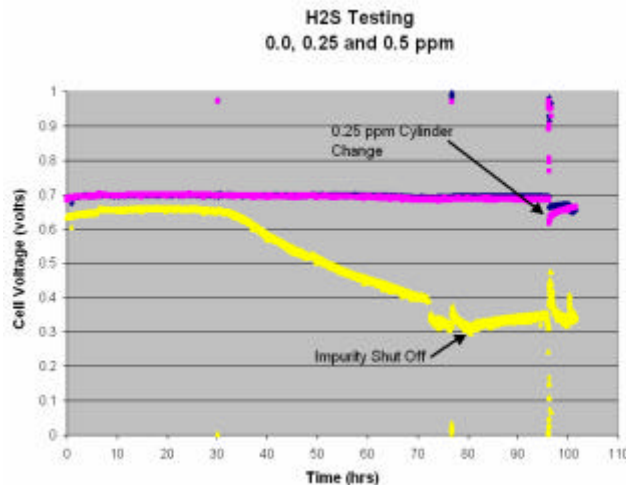
- 0.5 ppm – Small observable loss beginning at 70 hours
- 1.0 ppm – Time to reach equilibrium 32 hours, **20 % voltage loss**
- 4.5 ppm – Time to reach equilibrium 10.7 hours, **42 % voltage loss**

H₂ Impurities

(from Air Liquide's Labs)

■ Hydrogen sulfide (H₂S)

- ✓ Mechanism – Adsorption of H₂S onto Pt sites followed by oxidation to sulfur
 - Cumulative in nature
 - Not easily recoverable
- ✓ Concentrations tested → 0.25, 0.5, 1.0, 2.0

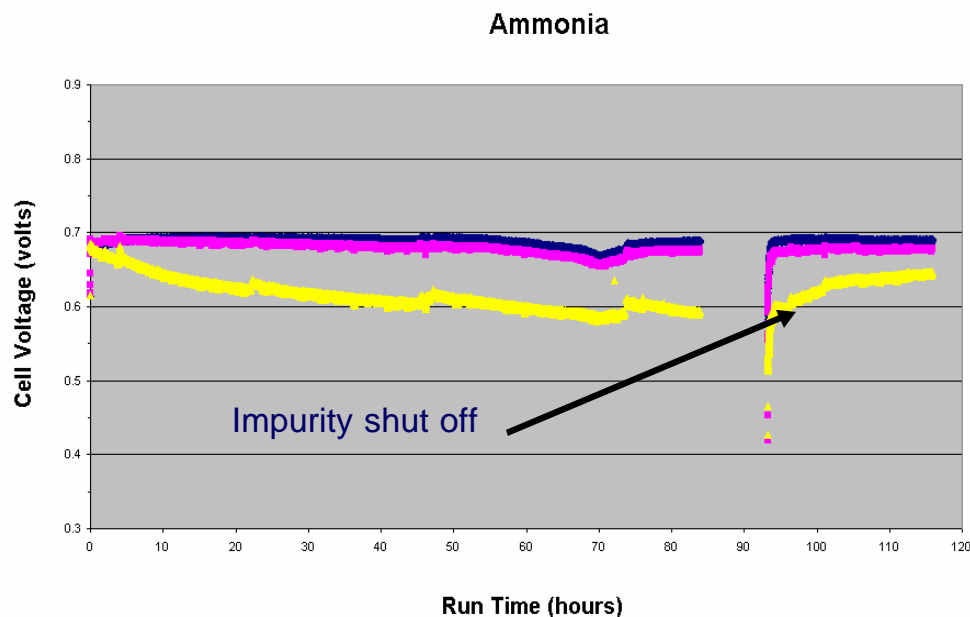


■ Results

- ✓ 0.25 ppm H₂S – No observable voltage loss (for 100 hours)
- ✓ Higher concentrations – “Linear” voltage drop over time
- ✓ Recoverability – Limited recoverability after impurity removal

■ Ammonia (NH₃)

- ✓ **Mechanism** – Long term exposure results in loss of proton conductivity
- ✓ **Concentrations tested** → 0, 0.5, 1.0, 9.0, 44 ppm NH₃



● Results

- 13 % drop of 44 ppm

● Recovery

- 93 % recovery after 20 hours for 44 ppm

	ISO	Dynamis
H2 purity	> 99,99%	> 99,99%
Impurities	max level umole/mole	max level umole/mole
CO	0.2	1
CO2	1	2
Sulphur Compounds	0.004	0.01
THC	2	1.5
Oxygen	5	6
Ammonia	0.1	10
Inert Gases (N2, Ar, He)	100	500
Water	5	10
Halogens	0.05	0.1
Max Particulate Concentrations	20 ug/mole	20 ug/mole
Max Particulate Size	10 um	10 um

2006 DOE Hydrogen, Fuel Cells & Infrastructure Technologies
Program Review

Controlled Hydrogen Fleet and Infrastructure Analysis

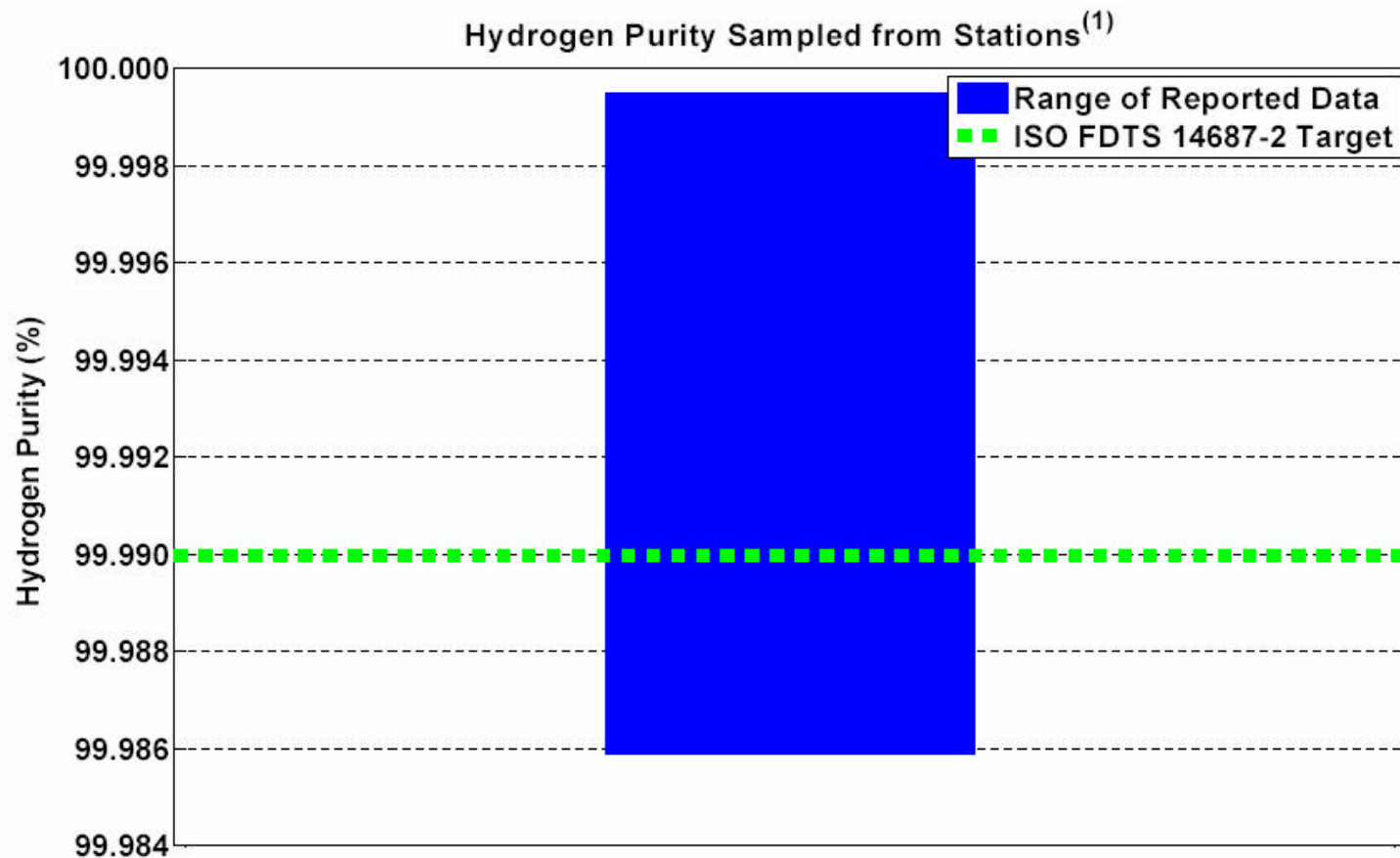
Keith Wipke, Senior Engineer II
NREL

May 19, 2006

Project ID# TV-12

This presentation does not contain any proprietary or confidential information

Hydrogen Purity Sampled from Stations Meets Target Majority of the Time

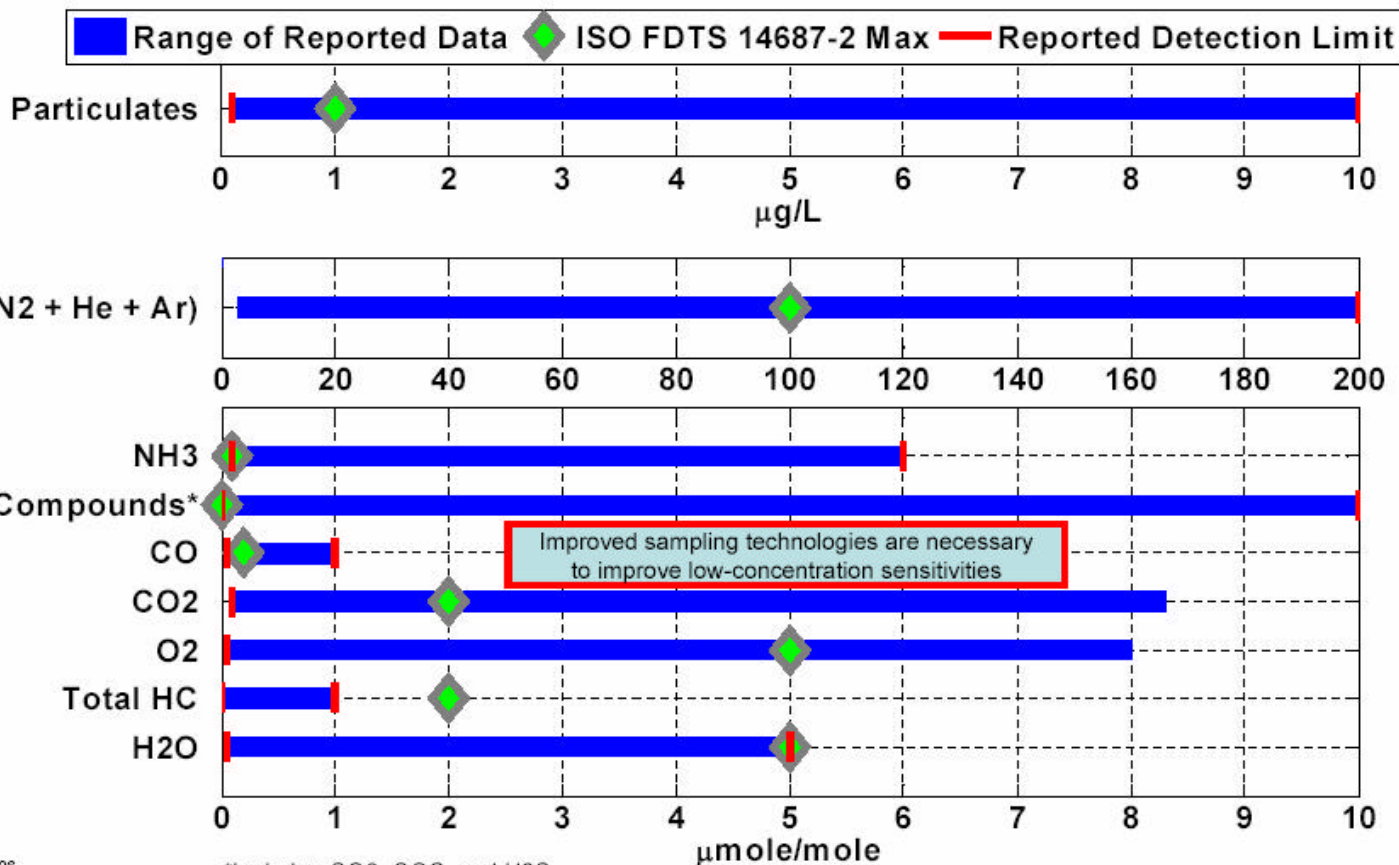


Created: 21-Feb-2006

(1) Includes sampling from both electrolysis and reforming

Hydrogen Impurities Sampled from All Stations – Includes On-Site Reformation, Electrolysis, and Delivered H₂

H₂ Impurities



Created: 23-Feb-2006

*Includes SO₂, COS, and H₂S.

Key Impurities

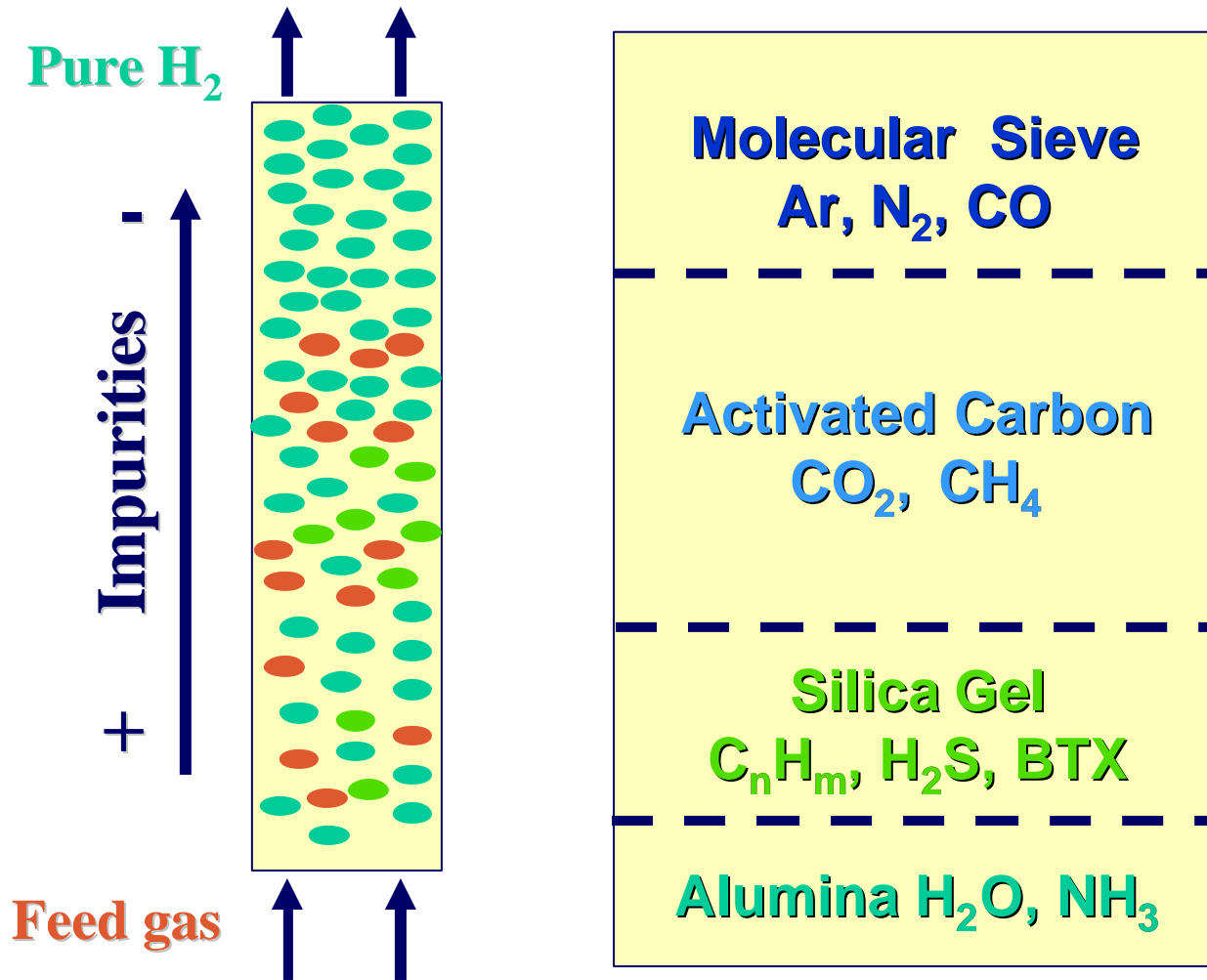
- CO
- S compounds
- NH₃
- Inerts (N₂, Ar, He)

H2 Purification

- NG SMR
- NG ATR/O₂ or Air
- Coal Gasification
- Lignite Gasification

➔ Pressure Swing Adsorption (PSA)

Example: 4 adsorbent layers



Gas / adsorbents affinity (2)

CHOICE OF ADSORBENTS			
Molecular Sieve	Activated Carbon	Silica Gel	Alumina
N_2 CO	Ar CO_2 O_2 CH_4	C_nH_m H_2S BTX^*	H_2O NH_3

* benzen, toluen, xylene

Gas / adsorbents affinity (1)

Relative strength of adsorption			
+	++	+++	++++
He H ₂	Ar O ₂ N ₂	CO CH ₄ C ₂ H ₆ CO ₂ C ₃ H ₈ C ₂ H ₄	C ₃ H ₆ C ₄ H ₈ C ₅ + H ₂ S NH ₃ BTX H ₂ O

The relative strength depends on the affinity between the adsorbent and the molecule you want to trap.

H_2 -PSA – a large range of plants

**Belgium,
100 000 Nm³/h**



**Spain,
49 000 Nm³/h**

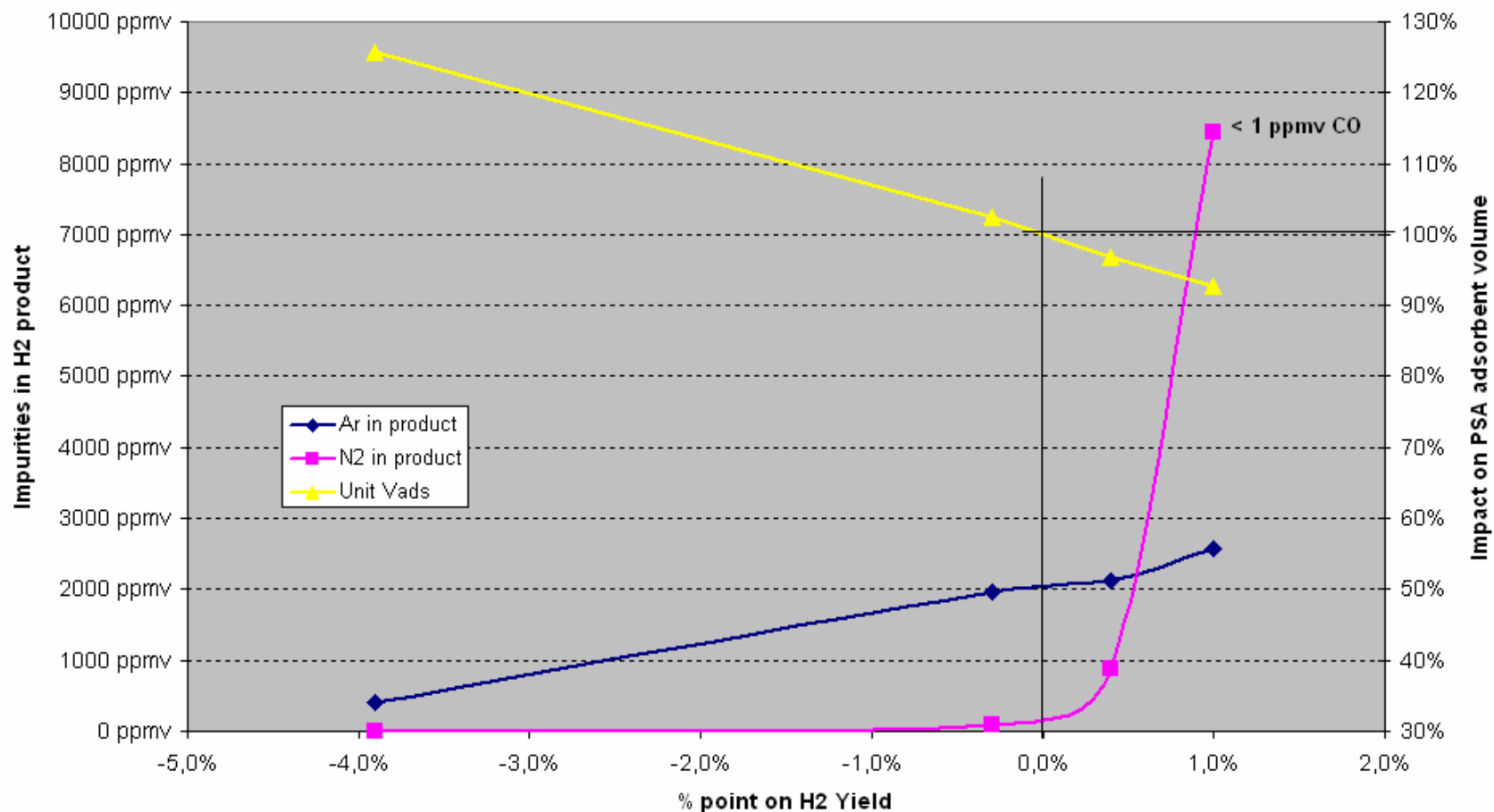


**Holland,
13 000 Nm³/h**



PSA Efficiency

Influence of impurity level on H2 PSA
90% CO2 capture - Hard Coal case



Effect of impurities on H₂ Storage & Distribution

■ Pipelines



■ Cylinders Metal to Polymers (Type IV)

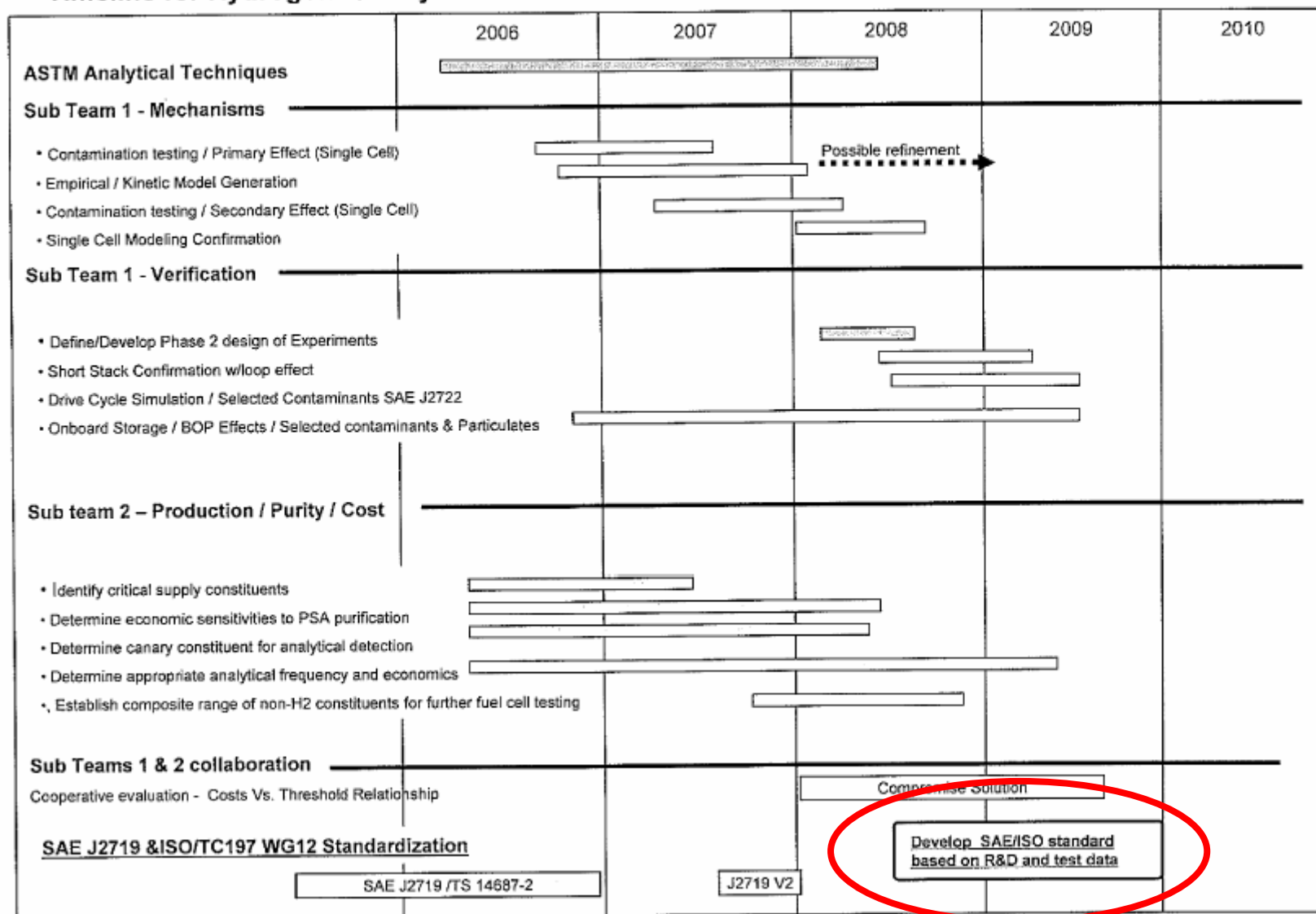
■ Cryogenic Tank

LH₂ 20°K <99.9999% (TSA Purification)

Technical Accomplishments/Progress: Fuel Quality – 5-year R&D/Testing Plan Defined

Topic of Investigation	2006	2007	2008	2009	2010
I. Consensus Testing Strategy					
A. Fuel cell-OEMs/fuel providers select n critical species from Table 1 based on key technical/economic drivers					
B. Develop R&D/test plan with WG12					
C. Coordinate activities, revise plan annually					
D. Derive optimal balance bet. fuel cell performance and fuel cost					
II. Fuel Cell Tests ('standard' MEA)					
A. Conduct failure mechanism tests w/re concn. at const. load, RH, T & P with critical constituents (CO, H ₂ S, etc.)	Determine mechanism	Identify regeneration alternatives	Alternate materials		
B. Conduct long-term tests (const. physical conditions) and const. & variable loads with critical constituents (CO, H ₂ S, etc.)	Aging/const load	Aging/variable load	Aging w/regen		
C. Conduct tests with selected combinations of critical constituents (CO, H ₂ S, etc.) and concentrations	Determine mechanisms	Identify regeneration alternatives	Alternative materials use (low cat. loading, etc.)	Commercial Materials	
D. Conduct "Simulated Drive Cycle" tests with H ₂ + critical constituents as fuel		Operations with limited contaminants and limits on conditions (load, SD/SU)	Operations with H ₂ Fuel & typical conditions		
E. Investigate performance/cost trade offs re: critical constituents					
III. H₂ Fuel Provider Integration					
A. Define H ₂ fuel quality variations based on current cleanup procedures (relative to critical constituent limits)					
B. Define contaminant species/ concentration variations as a function of planned H ₂ → sources					
C. Investigate H ₂ cleanup alternatives commensurate with fuel cell tests					
D. Conduct cost trade-offs re: critical constituents					
IV. Analytical Protocol/Instrumentation					
A. Evaluate adequacy of Table 1 info., set priorities based on IA					
B. Modify ASTM standards to measure critical constituents as needed	Determine variations to current practice	Investigate and incorporate required alternatives to SOP			
C. Validate test methodology and requirements for critical constituents	Identify key species required to be monitored		Finalize species and concns to be monitored		
D. Assess cost trade-offs, esp. in-line measurement					
V. OEM Engine/Vehicle Tests					
A. H ₂ Fuel with Priority Constituents		Correlate small scale fuel cell tests with large scale	Assemble and evaluate demo and fleet vehicle operations with H ₂ → fuel quality	Test and demonstrate vehicle/engine dyno tests with	
VI. Advance Storage Materials					
A. Track Development of Adv. Materials					

Timeline for Hydrogen Quality Standardization



Conclusions

■ Needs

- ✓ For additional research work on influence of impurities (including inerts), with more materials & longer test periods
- ✓ To better share information of consequences of unrealistic specifications (ex: 4 vpm S-compounds) on H2 production costs
- ✓ For stronger involvement of European actors into international organizations (ISO)