Session 5B

SENSORS

Co-Chairs: W. Buttner/NREL
L. Brett/JRC

Role of Hydrogen Sensors for safe H_2 deployment

- Provide critical safety factor
  - Alarm at unsafe conditions
  - Ventilation Activation
  - Automatic shutdown
  - Tool for modeling studies
- Bad things when sensors not used or misused (extracted from the H_2 Incidents database)
  - *Gaseous Hydrogen Leak and Explosion*
    - Lack of Hydrogen Detection Equipment
  - *Hydrogen Explosion and Iron Dust Flash Fires in Powdered Metals Plant*
    - No combustible gas monitoring or training
  - *Two False H_2 Alarms in Research Laboratory*
    - Nonspecific sensors alarmed twice ($10,000 fine)
    - H_2 specific sensors are not installed

Indoor Hydrogen Dispenser equipped with wall-mount and internal sensor

- Mandated by Code
  - **NFPA 2 10.3.19.1** Dispensing equipment shall be provided with gas detectors, leak detection, and flame detectors such that fire and gas can be detected at any point on the equipment [52,2010, 9.2.14]
  - **NFPA 2 3.3.219.2.2** Gas Detection System. One or more sensors capable of detecting hydrogen at specified concentrations and activating alarms and safety systems. [52,2010]
  - NREL C&S submitted a proposal to NFPA 2 providing guidance on sensor placement

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Innovation for Our Energy Future

An Assessment on the Quantification of Hydrogen Releases Through Oxygen Displacement Using Oxygen Sensors

The Energy Systems Integration Facility

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International Conference on Hydrogen Safety
Brussels, Belgium
September 9-11, 2013

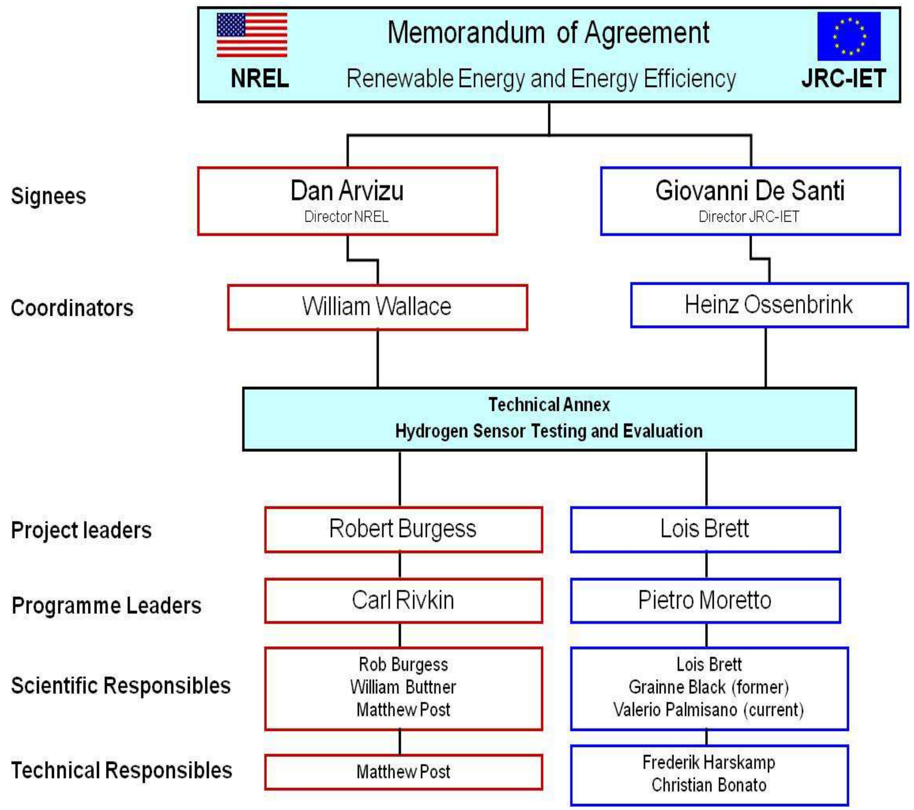
NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Performed under the auspices of the NREL-JRC MOA

DOE/NREL – JRC-IET MOA since 2010

(Synergize H_2 Sensor Assessment Activity)

- Minimizing duplicated R&D efforts
- International visibility and impact
- Expanded capabilities and expertise
- Facilitate implementation of the hydrogen infrastructure
- "Topical studies"
  - Educate H2 community on the proper use of sensors
- Outreach
  - Joint publications, presentations



NREL: http://www.nrel.gov/hydrogen/facilities_hsl.html

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H_2 determination via oxygen sensor measurements
Background

- Applications
  - **Actual**: Modeling of controlled releases
  - **Proposed:** Global Technical Regulation (GTR)
  - **Potential:** General Deployment?

Oxygen Sensors

Vol% O_2

Great for O_2 Determinations

From the GTR (Hydrogen Fueled Vehicles)

(Section B.6.1.2: Post-Crash Concentration Test for Enclosed Spaces)

"Sensors are selected to measure either the build-up of the hydrogen or helium gas or the reduction in oxygen (due to displacement of air by leaking hydrogen/helium)"

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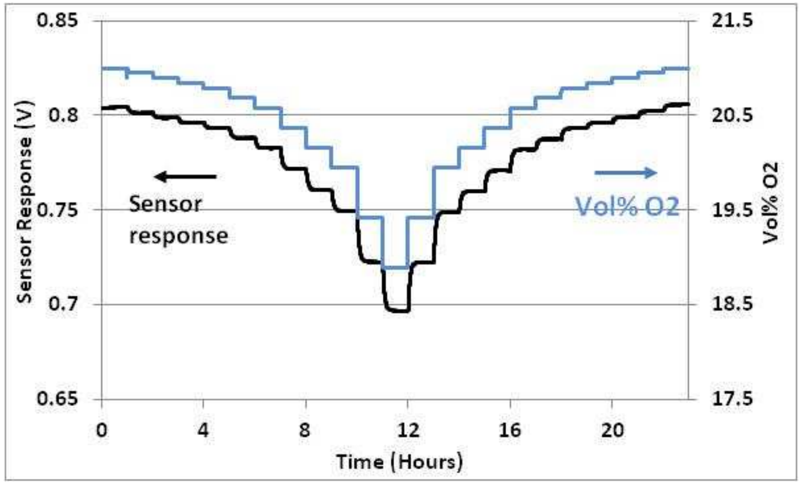
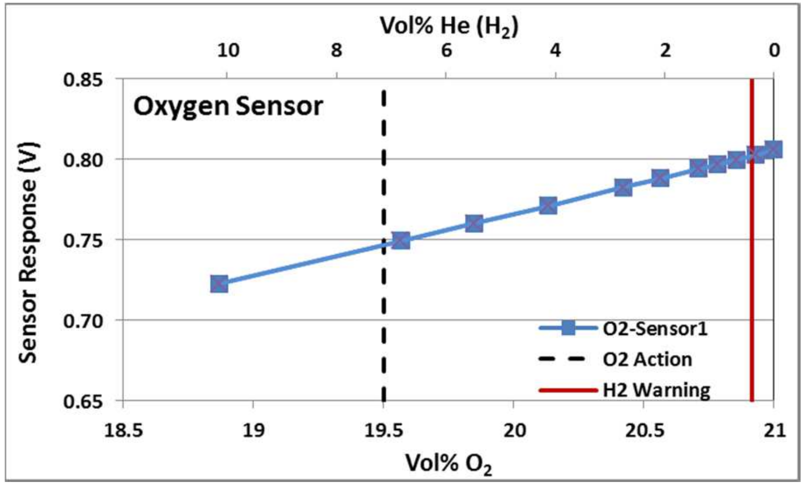
H_2 determination via oxygen sensor measurements
Basic Premise

- Basic Premise
  - Sensor Response ≈ K * Vol% O_2
  - Vol% O_2 = 21 – 0.21* Vol% Diluent
    - ➢ 1 vol% [Diluent] suppress ambient O_2 from 21 to 20.79 vol%
  - Applicable for H_2, He, (other)



- Advantages
  - O_2 Sensors--COTs, low-cost, simple
  - Broad-Range, Linear response to O_2



- Disadvantages
  - Small drift => significant [diluent]
  - Finite life (sometimes short)
  - Non-selective (for diluent)

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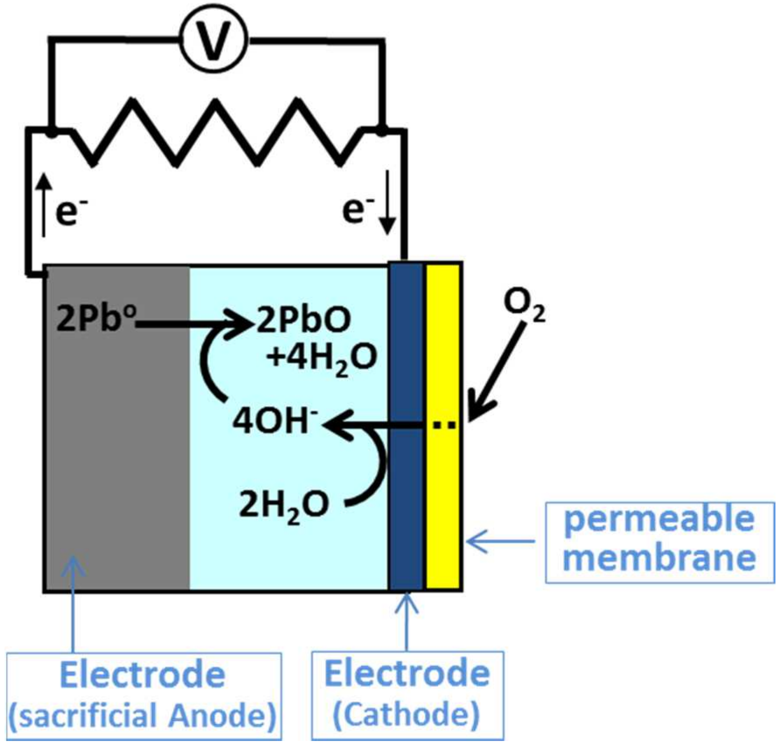
The Electrochemical (Galvanic) Oxygen Sensor

- Design Features
  - Most common platform
  - Used in published studies
  - Low cost, easy to use, “zero power”
  - Near-zero anaerobic response
  - SR ≈ K * Vol% O_2
  - Good for ambient oxygen levels

- Design Limitations
  - Finite operational lifetime
  - Restricted T range



Cathode: $O_2 + 2H_2O \rightarrow 4OH^-$

Anode: $2Pb + 4\ OH^- \rightarrow 2PbO + 2H_2O + 4e^-$

Cell: $2Pb + O_2 \rightarrow 2PbO$

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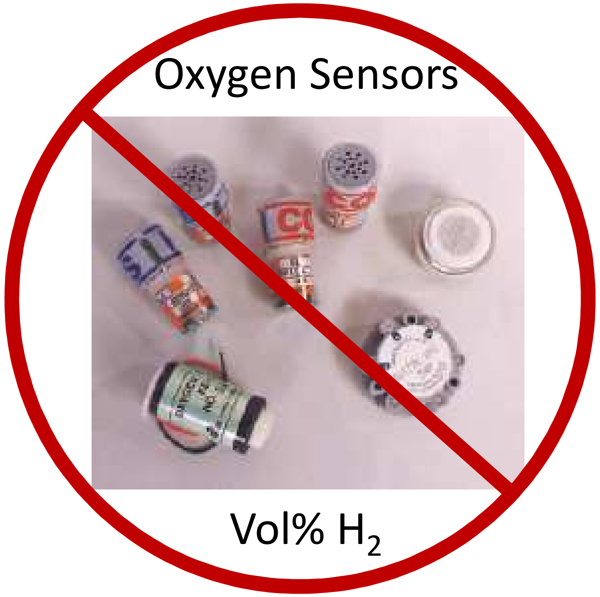
H_2 determination via oxygen sensor measurements
Assessment

- Reviewed O_2 Sensor Responses (for O_2 and H_2/He determinations)
  - Impact of environmental parameters
  - Short term stability and lifetime
  - Deployment Scenarios



Not Great for H_2 Determinations

CONCLUSION

The use of O_2 sensors to measure hydrogen/helium concentrations **should be discouraged** (and is not necessary)

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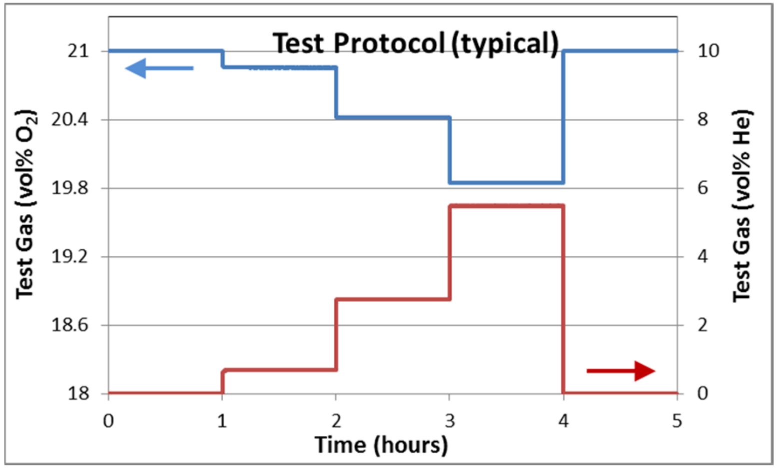
Experimental Approach and Assessments

- Test System
  (simultaneous deployment of sensors)
  - 2 O_2 sensors models
    - O2-Sensor1: Higher end, instrumented
    - O2-Sensor2: Low cost "sensing element"
    - 0 to 100 vol% O_2 (optimal 0 to 21 vol%)
  - TC hydrogen sensor (works for He)
    - H_2: 0 to 10 vol% (not a fundamental limitation)
    - He: 0 to 14 vol%
  - NREL/JRC Sensor Test Apparatus

- Protocols
  - Synthetic air (21 vol% O_2) and He diluent
  - Linear Range/Short-term stability
    - O_2: 21 to 0 vol% or 21 to 19.85 vol% (typical)
    - He: 0 to 100 vol% or 0 to 5.5 Vol% (typical)
  - Environmental Parameters (T, P, RH)
  - Open System vs. Closed System
  - Operational Lifetime Considerations



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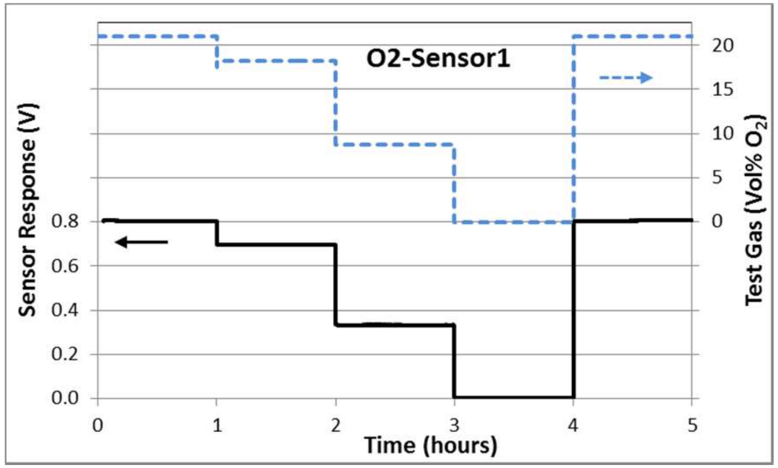
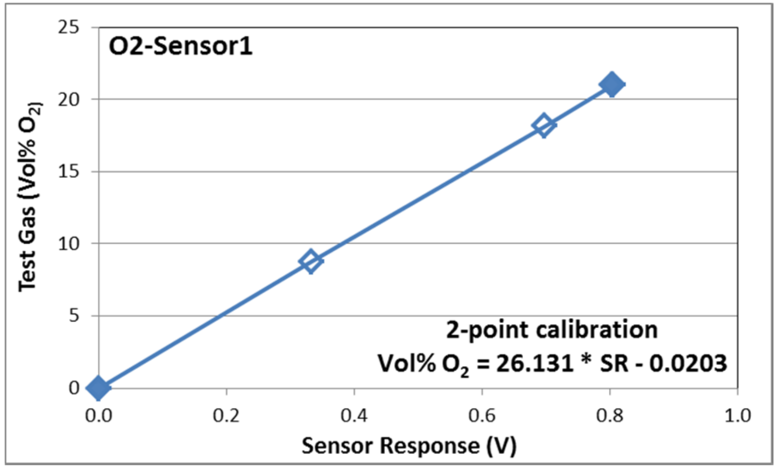
Oxygen Sensor calibration and use





- Typical O_2 sensor operation
  - 2 point calibration
    air (21 vol% O2) and inert (0 vol% O2)
    - Regulated T, P, RH
  - Generate calibration curve
    O2-Sensor 1: Vol% O_2 = 26.131 * SR – 0.0203
    O2-Sensor 2: Vol% O_2 = 1.8024 * SR – 1.2164
    Vol% O2 = 21 -0.21*Vol% Diluent
    1 point calibration is often used
- Diluent (Dil) Determination
  - Vol% Dil. = 100/21 * (21-Vol% O_2)
    - Dil = H_2, He, H_2O, N_2, CH_4, other
    - Vol% O_2 = 21 – 0.21* {**Σ**(Vol% Dil)$_i$}
  - 0.2 vol% O_2 ≈ 1 vol% H_2 or total Dil
    - Small drift can have a big impact

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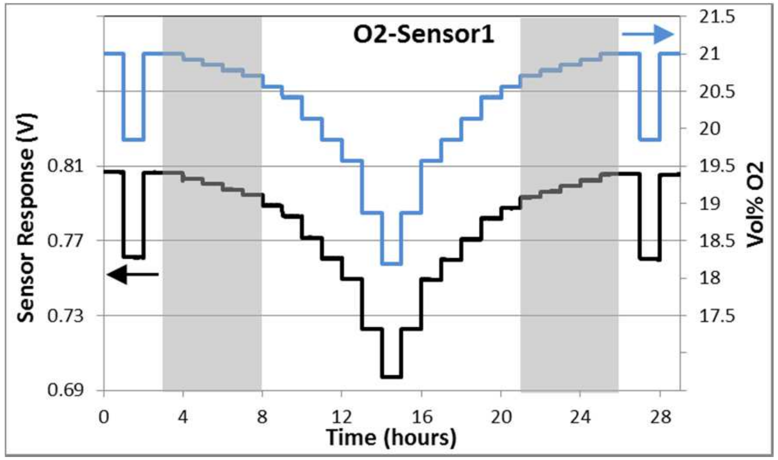
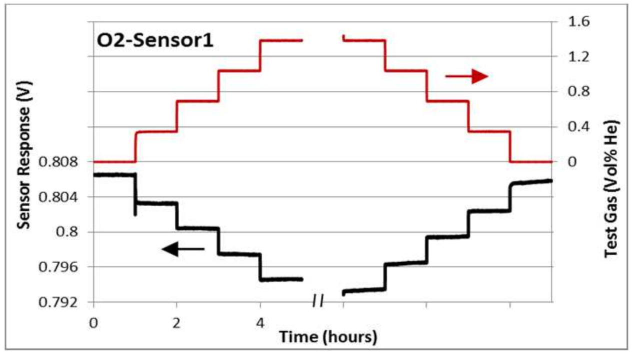
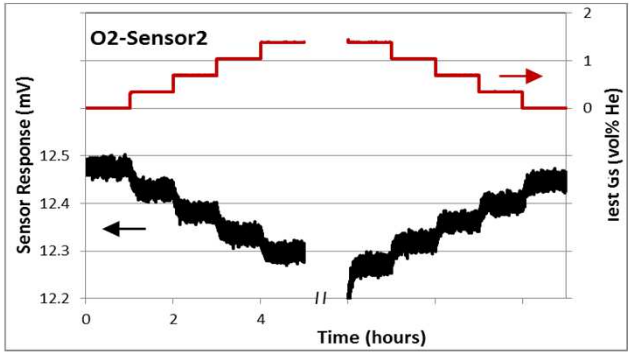
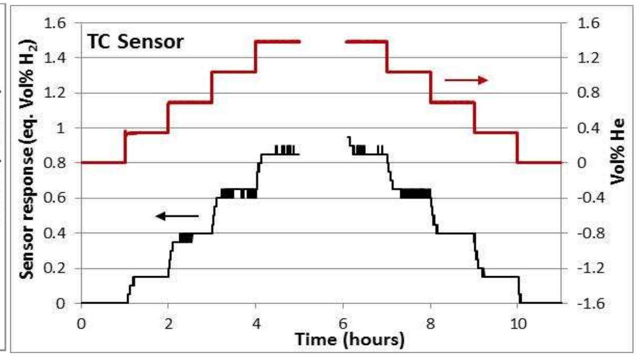
O2 Sensor Short Term Stability



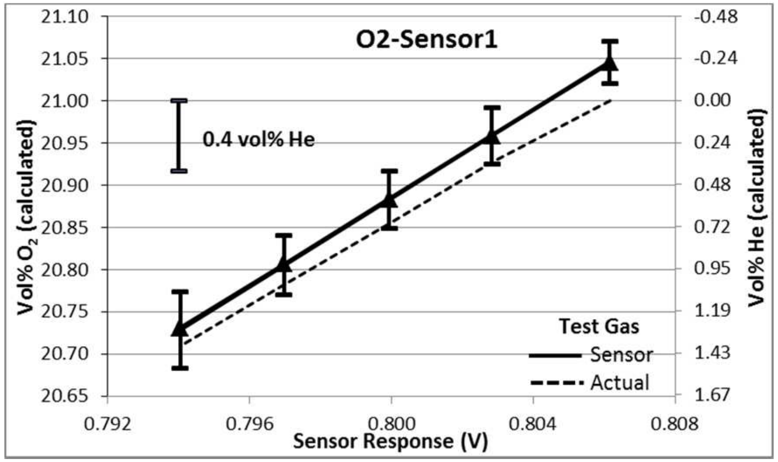
- 21 to 18.2 Vol% O_2 (0 to 13.4 Vol% He)
  - Regulated T (25°C), P (1 bar), RH (dry)
- O2 Sensor behavior
  - Small, near negligible drift in measured Vol% O_2
  - 5X greater impact on Vol% of diluent
  - Stability varies with sensor model/type
- TC Sensor behavior
  - Zero short term drift

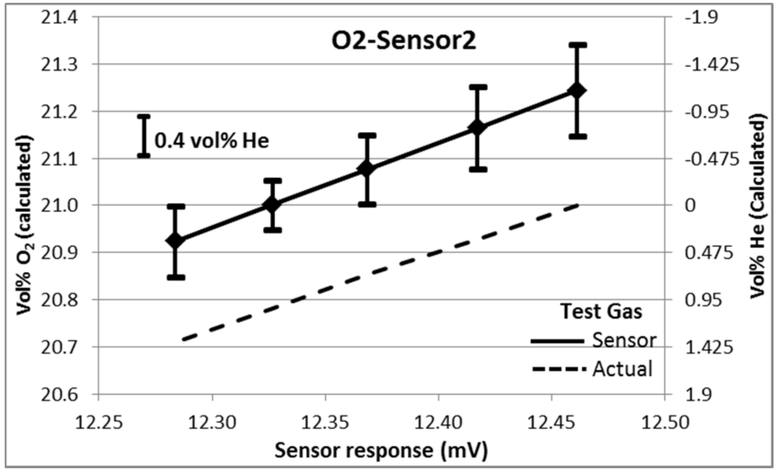






Short Term Drift Impact on diluent determinations





- Previous calibration factor
  - Long-term Drift observed in both sensors
- Oxygen Action Levels (OSHA)
  - Typical Ambient: 20.9 vol%
  - Confined Space Minimum: 19.5 vol%
- Hydrogen Action Levels
  - LFL: 4 vol%
  - Warning: 0.4 vol% (10% of LFL)
  - Alarm: 1 vol% (25% of LFL)
- Impact of drift
  - Systematic drift of +0.05 to +0.25 vol% O_2
  - Could lead to a false negative
  - Due to aging
  - Controlled T, P, RH
- Impact of noise
  - Limited ability to resolve O_2 levels (A.R.)
  - affects LDL for diluent (0.4 to 0.7 vol%)

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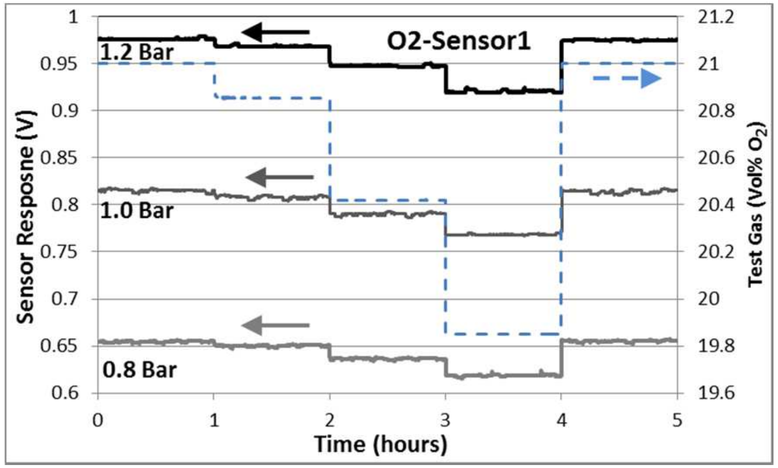
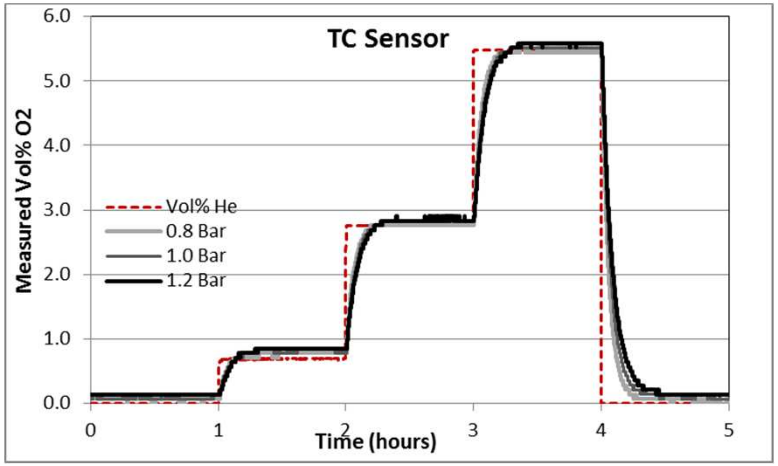
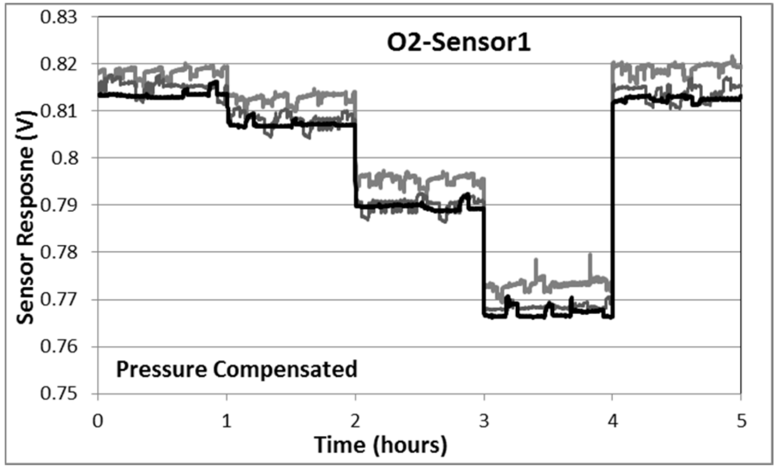
Impact of Environmental Parameters (Pressure)







- O_2 Sensor sensitive to P_{O2} NOT vol%
  - P_{O2} and vol% numerically equal at 1 bar
  - Common for many but not all sensor platforms
  - ΔP of 0.002 bar can be misread as 1 vol% H_2
- TC sensor response shown for comparison
  - Negligible impact of Pressure
- **O2 sensor dependence on P_{O2} significant for enclosed environments**

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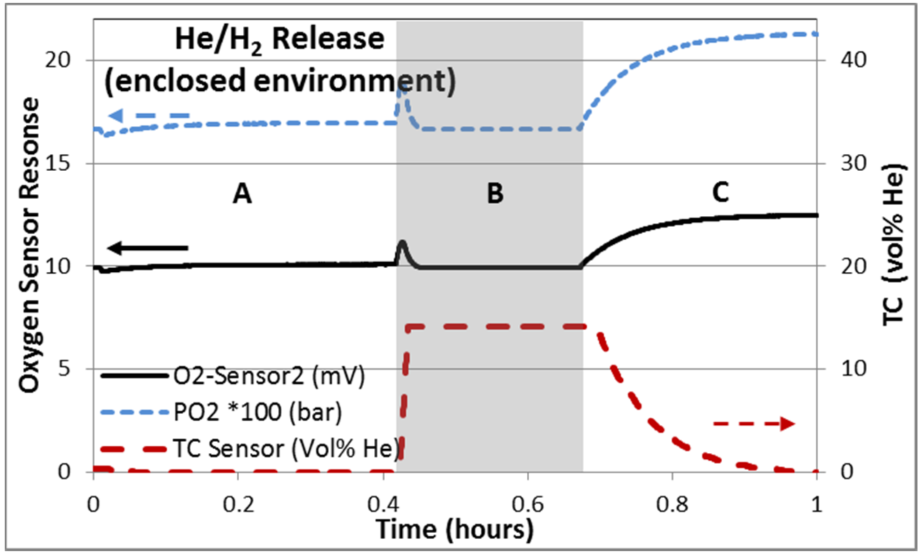
H_2 measurements via O_2 displacement in enclosed spaces

GTR Section B.6.1.2: Post-Crash Concentration Test for Enclosed Spaces)
"Sensors are selected to measure either the build-up of the hydrogen or helium gas **or the reduction in oxygen (due to displacement of air by leaking hydrogen/helium)**"



Closed System (Region A and B)

A: Air at 0.8 bar
21 vol% O2; P_{O2} = 0.17 Bar

B: Pressurize chamber to 1 Bar with Helium
17 vol% O2; P_{O2} = 0.17 Bar

Open System (Region C)

C: Purge chamber with air
21 vol% O2; P_{O2} = 0.21 Bar

- Gray Region: 20 vol% He
- No response for H_2/He release into closed system (P_{O2} vs. Vol% O_2)
  - Direct manifestation of the O_2 Sensor P_{O2} dependence
- TC range: 0 to 14 vol% He (not a fundamental limitation)
- **GTR Recommendation is inappropriate**

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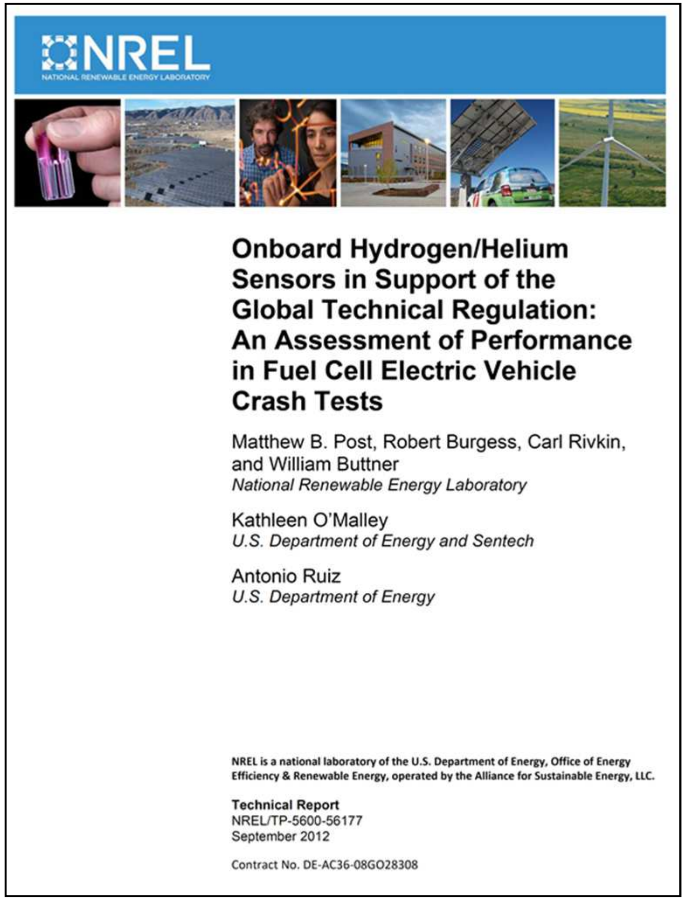
Support of DOT and the GTR

- GTR will be basis for FCV FMVSS
  - Vehicles to be subjected to standard crash test
  - H2 within vehicle must remain <4% following impact
  - Failure to meet this requirement may result in recall
  - Actual tests may be performed with helium surrogate
- Viability of TC sensor to meet GTR demonstrated
  - Viable for both H_2 and He (actual test was done with He) (survivability, sensitivity to He)
  - Use of Oxygen sensor is not necessary nor reliable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Onboard Hydrogen/Helium Sensors in Support of the Global Technical Regulation: An Assessment of Performance in Fuel Cell Electric Vehicle Crash Tests

Matthew B. Post, Robert Burgess, Carl Rivkin, and William Buttner
National Renewable Energy Laboratory

Kathleen O'Malley
U.S. Department of Energy and Sentech

Antonio Ruiz
U.S. Department of Energy

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Technical Report
NREL/TP-5600-56177
September 2012

Contract No. DE-AC36-08GO28308

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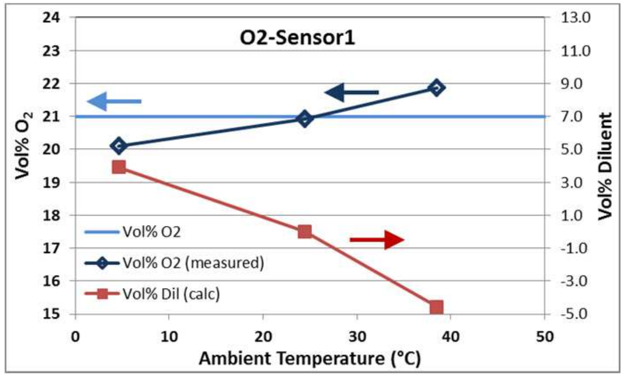
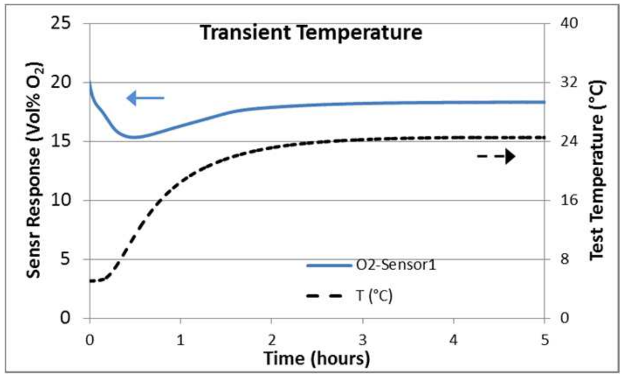
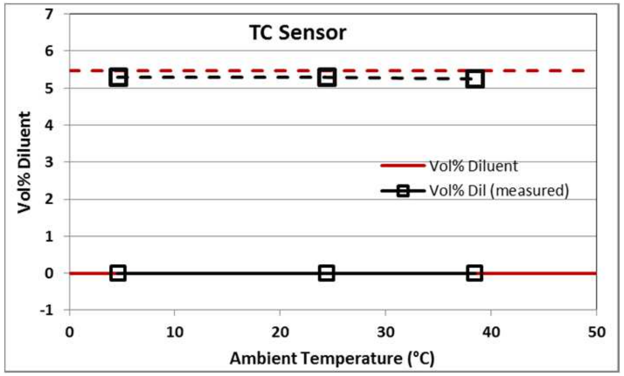
Temperature Dependence of the Oxygen Sensor

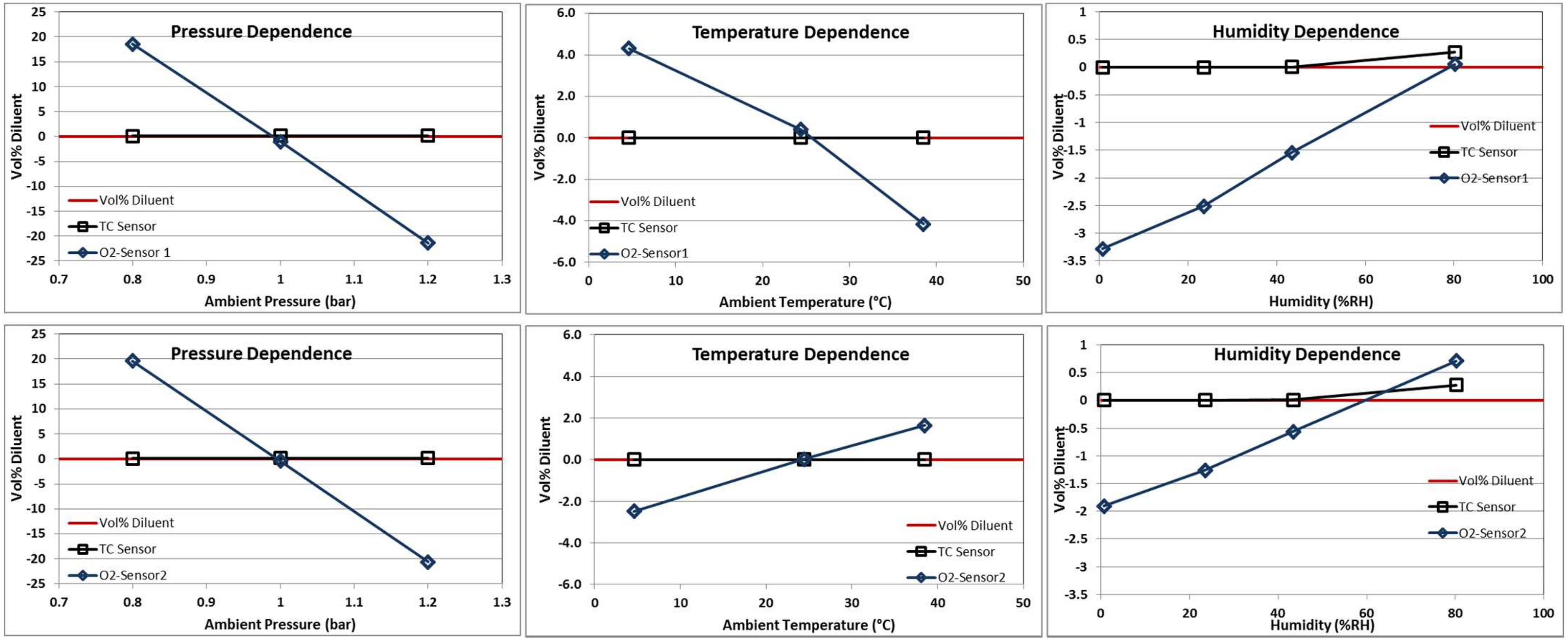
- Temperature Range: 0 to 40°C
  - Test Gas: Air (21 vol% O2 / 0 vol% He)
  - Comparable at different diluent levels
- Measured Vol% O_2 ranged 20.1 to 21.9
  - Transient impacts are greater
- Calculated Vol% Dil ranged 4.3 to -4.3
  - Negative drift: False alarm potential
  - Positive drift: False negative potential
- TC sensor minimal T dependence
  - Results shown for 0 to 40°C (can operate <-20°C to >80°C)
  - Results shown for 0 and 5.5 vol% He







He/H2 Determination (TC vs. O2 Sensor)
Impact of Environmental Parameters (T, P, RH)



Environmental Impacts (O_2 Sensors)

- Strong linear pressure dependences
- Strong (near-linear) temperature dependence
  - Varies with design
  - Limited Temperature range (>0°C < 40°C)
- RH dependence (contribution to total diluent level)

Environmental Impacts (TC Sensors)

TC Sensor

- Negligible P, T, RH dependences
- Board T range (from <-20 to >+80°)

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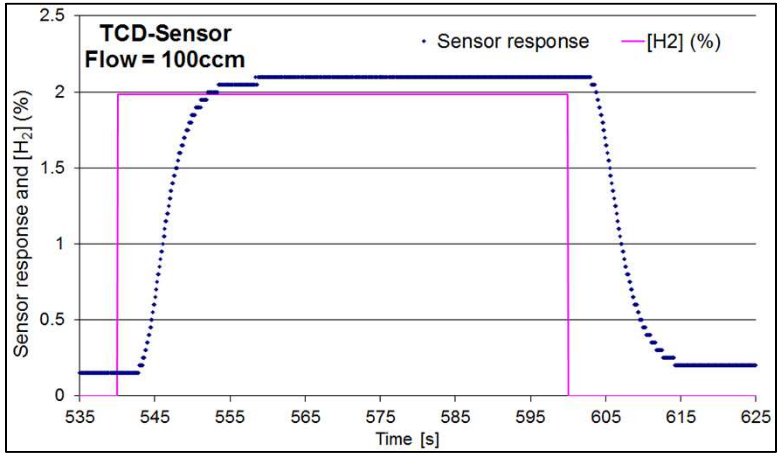
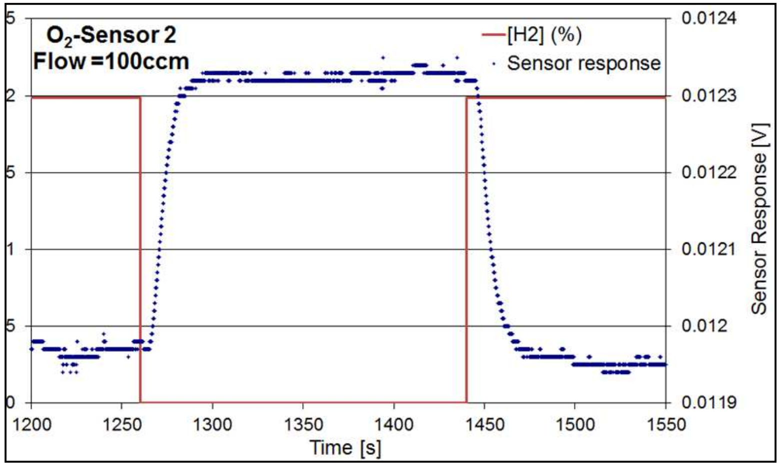
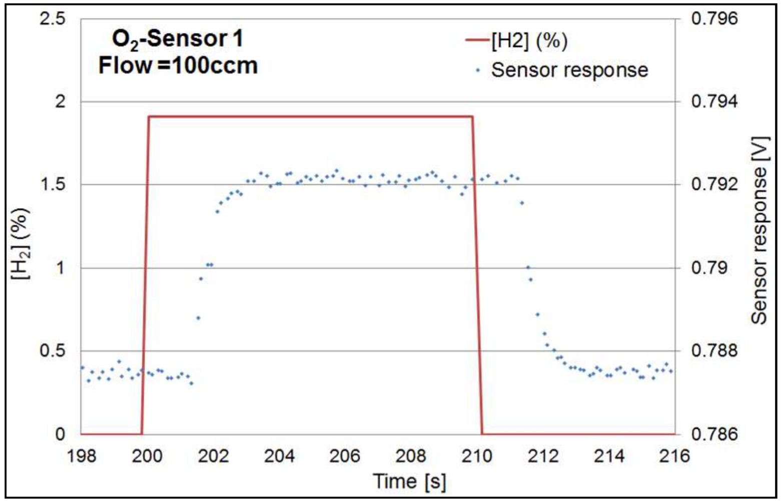
Response Time (O_2 vs. TC Sensor)







Response (T_{90}) and Recovery (T_{10}) Times

	T_{90} (s)	T_{10} (s)
O2-Sensor1:	2.3	2.5
O2-Sensor2:	23.6	19.7
TC	10.4	11.1
TC-2	4.0	4.0

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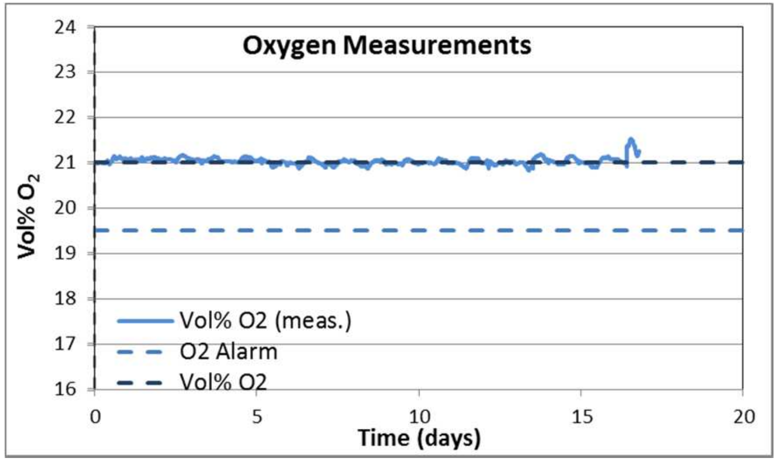
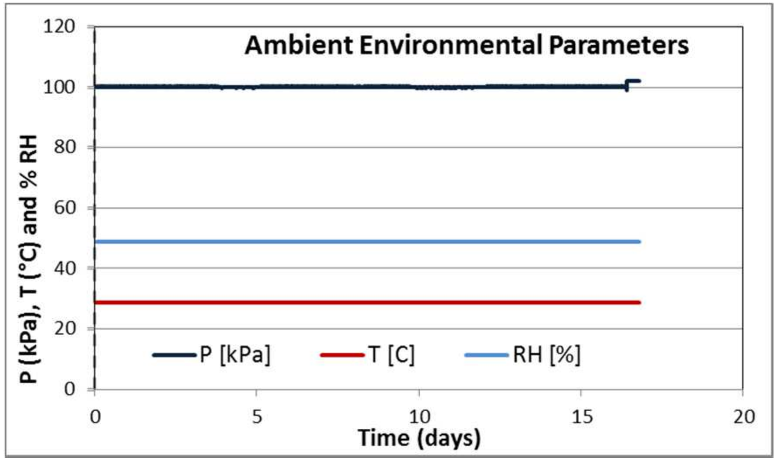
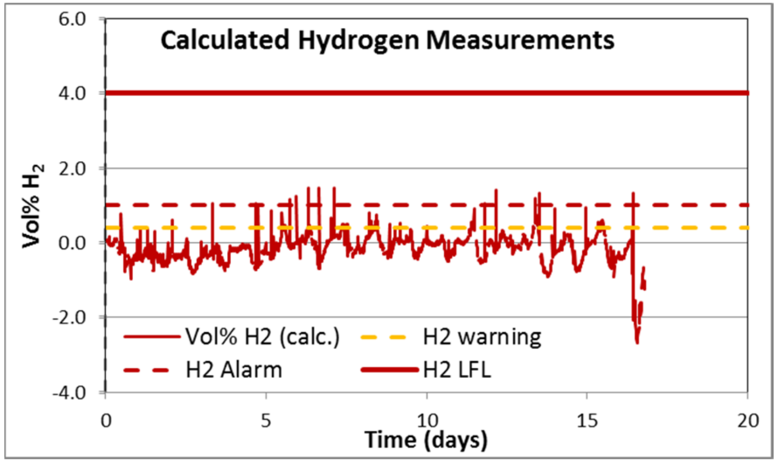
Indoor Monitoring—Long-term Stability







- Medium-long term monitoring
  - Oxygen measurements accurate and stable
  - Diluent level reach hydrogen warning and alarm levels

H_2 measurements via O_2 displacement
Hydrogen Sensor vs. O_2 Sensor

O_2 Sensor

Deployment

- Commercially Available
  - Sensing elements and instruments
- Low cost (for sensing elements)

Operational

- **Easy to use**
- **Low Power**
- Finite operational life (0.5 to 1 year)
  - Cathode typically heavy metal
- Works for H2 and He
  - No recalibration for different analytes
  - Responds equally to all diluents

H_2 Sensor (TC Platform)

Deployment

- Commercially Available
  - Sensing elements and instruments
- Low cost (for sensing elements)

Operational

- Easy to use
- Low Power
- Indefinite operational life
  - Inert or noble material
- Works for H2 and He
  - Different (but predictable) calibration factor
  - Much lower sensitivity to other vapors

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H_2 measurements via O_2 displacement (cont'd)

TC vs. O_2 Sensor

O_2 Sensor

Analytical

- Amenable for H_2 and He
  - Same calibration factor
  - Nonselective to any/all diluents
- Environmental Impacts
  - Strong T dependence
    - Restricted range (0 to 40°C)
  - Strong P dependence
  - Strong to Moderate RH dependence
- Moderate LDL (>0.4 vol% Dil)
- Moderate A.R. (>0.4 vol%Dil)
- Marginal Short Term Stability
  - Small drift can lead to False alarm
- Response Time
  - 2.3 sec (high-end only)
  - Slower for most models
- Broad Range, but
  - Indirect method (propagation of errors)
  - Positive drift ➔ negative [H_2]

H_2 Sensor (TC Platform)

Analytical

- Amenable for H_2 and He
  - Proportional calibration factor
  - Partial Selectivity
- **Environmental Impacts**
  - **Near-negligible T dependence**
    - **Broad range (<-20 to >+80 °C)**
  - **Near-negligible P dependence**
  - **Near-negligible RH dependence**
- **Excellent LDL (~0.05 vol% H_2)**
- **Excellent A.R. (<0.05 Vol% H_2)**
- **Good short term stability**
  - **Some models show slow drift**
- Response Time
  - T_{90} = 4 sec
  - Typical T_{90} ≈10s
- Broad Range
  - Direct method (0 to 10%, 0 to 100% H_2 /He)

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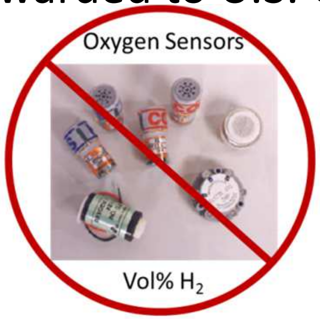
Summary
General critique of approach

- Oxygen Sensors are very good for oxygen determination
- Oxygen Sensors are NOT good for hydrogen monitoring
  - Indirect method for Hydrogen/Helium
  - Diluent ambiguity (H_2, He, and OTHER)
  - Propagation and amplification of measurement errors
  - Marginal detection limit, H2/He accuracy = 20% (at best) of O2 sensor resolution
  - Potentially misleading/inaccurate results
    - Inappropriate for general deployment
- Not necessary for hydrogen or hydrogen surrogates
  - TC sensor works for hydrogen/hydrogen surrogates
  - Other platforms (CGS, EC, MOX, PTF) appropriate for most applications
- GTR text on H2 determination via O2measurements inappropriate
  - Recommendation to delete forwarded to U.S. GTR representative



Not Great for H_2 Determinations

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- JRC-IET is supported through the European Commission's 7th Framework Programme (FP7) (Lois.BRETT@ec.europa.ec)

THANK YOU

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