Use of Hydrogen Safety Sensors Under Anaerobic Conditions – Impact of Oxygen Content on Sensor Performance

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ABSTRACT

In any application involving the production, storage or use of hydrogen, sensors are important devices for alerting to the presence of leaked hydrogen. Hydrogen sensors should be accurate, sensitive, and specific, as well as resistant to long term drift and varying environmental conditions. Furthermore, as an integral element in a safety system, sensor performance should not be compromised by operational parameters. For example, safety sensors may be required to operate at reduced oxygen levels relative to air. In this work we evaluate and compare a number of sensor technologies in terms of their ability to detect hydrogen under conditions of varying oxygen concentration.

1.0 INTRODUCTION

Safety is a major concern for the emerging hydrogen infrastructure. A reliable safety system is comprised of various elements that can include intrinsic design features (e.g., pressure control systems, venting systems), engineering controls (e.g., sample size minimization, removal of oxygen from in or around the system) and the use of hydrogen sensors to monitor for releases. Hydrogen sensors are typically independent of the main operational features of a system and are already required by code for various hydrogen operations [1]. These sensors should be accurate, sensitive, and specific, as well as resistant to long term drift and varying environmental conditions. Sensor performance metrics are typically determined through a variety of test procedures performed in a laboratory on a custom built test apparatus. To assure the availability of reliable safety sensors, the U.S. Department of Energy (DOE) has set up a sensor test facility at the National Renewable Energy Laboratory (NREL) in Golden, CO [2]. Similarly, the Joint Research Centre of the European Commission (JRC) has a sensor test facility at the Institute for Energy in Petten, the Netherlands [3, 4]. The sensor testing laboratories provide stakeholders (e.g., manufacturers, end users and code officials) an independent, unbiased evaluation of hydrogen sensor technologies. To facilitate sensor analysis and dissemination of the results, the NREL and JRC sensor testing laboratories have initiated round-robin testing of sensor technologies [5]; this collaboration has been formalized via an interlaboratory Memorandum of Agreement (MOA) between NREL and the Institute for Energy [6]. The MOA synergizes the laboratories' independently programmed activities to maximize the benefit of their respective institutional interests through cooperative activities. Several sensor platform types have been included in the round-robin test. To date, the round-robin tests have produced quantitatively consistent results between participating laboratories, thus providing a cross validation of each laboratory's apparatus and protocols. The results and performance evaluation from round-robin testing of the first round technologies is being prepared [7].

A critical mission of the JRC and NREL sensor testing laboratories is to educate end users on the proper use of hydrogen sensors and various topical studies are underway with this purpose. As an integral element in a safety system, sensor performance should not be compromised by operational parameters. Hydrogen operations are often performed under an anaerobic atmosphere in order to minimize fire and explosion risks that may be associated with the use of hydrogen. For example, a test system or the surrounding environment may be purged with nitrogen. Furthermore, many chemical and industrial processes utilize forming gas with up to 10% hydrogen in nitrogen (or 10% hydrogen in argon) because this blend cannot mix with ambient air to generate a hydrogen level that

exceeds the 4% lower flammable limit. Unfortunately many sensor platforms are deactivated when operated in an anaerobic atmosphere. Although the number of commercial sensors is quite large, most utilize sensor elements that can be classified into relatively few specific sensor platforms [3, 8]. Each sensor platform has unique operating principles that will ultimately control its performance. Thus, although a detector deployed in an anaerobic atmosphere may indicate that no hydrogen is present; this may not be the case. The nitrogen purge gas could in fact contain high levels of hydrogen and present a potentially dangerous situation when mixed with air upon venting. For example, because of its detection mechanism, a combustible gas sensor (CGS) will readily detect hydrogen in air, but is unable to respond to the presence of hydrogen in nitrogen. The impact of oxygen deprivation on other sensor platforms can be more subtle [8]. However, this potential deactivation of sensor performance under anaerobic conditions is generally not well known by many end users, nor to our knowledge has this topic been specifically investigated. The impetus for this study was in fact the proposed use by an end user of a CGS to monitor for hydrogen leaks under a nitrogen atmosphere.

Herein, we present the results of our investigation on the ability of three hydrogen sensors, based on different technologies, to accurately measure hydrogen at depressed oxygen levels. Thus far, we have investigated the impact of reduced oxygen concentration on hydrogen detectors that utilize the following types of sensing element:

1. combustible gas sensing element (CGS)
2. thermal conductivity sensing element (TC)
3. palladium thin film sensing element (PTF)

The results and observations made for these sensor types are reported here. However, this is an on-going investigation and will ultimately be expanded to other platform types including electrochemical detectors, metal oxide (e.g., tin oxide) detectors, and Field Effect Transistor (FET) systems; the results of the complete study will be reported separately. This work focuses on the ability of a hydrogen sensor to work at depressed oxygen concentrations, including anaerobic conditions. The impact of interferents and potential poisons, which may be exacerbated under anaerobic conditions, is not included in this study, but will be investigated separately.

2.0 EXPERIMENTAL

2.1 Sensor Test Facilities

Evaluation of hydrogen safety sensors is an on-going activity within the sensor test facilities at the JRC-Institute for Energy [4] and at NREL [2]. Both test facilities were designed with advanced capabilities, including parallel testing of multiple hydrogen sensors (limited by the size of the test chamber), sub-ambient to elevated temperature, sub-ambient to elevated pressure, active humidity control and accurate control of gas parameters with multiple precision digital mass flow meters operating in parallel. Test conditions (temperature, pressure, relative humidity and flow) are monitored using traceable probes. Gas composition can be continuously verified by supplemental gas analyzers (mass spectrometer or gas chromatograph) to provide independent and near real-time analysis of the test gas concentration. Evaluations are carried out in the sensor chamber, which isolates the test sensor from the external environment. Both systems are fully automated for control and monitoring of test parameters and for data acquisition. Although different design and control features are incorporated in the respective sensor test fixtures and slightly different test protocols are used, the round-robin testing of various sensor technologies [7] has cross validated the performance capability and accuracy of the NREL and JRC apparatus. Figure 1 shows the respective systems.
Although sensor performance data and general trends of various platform types obtained from the testing are openly distributed, it is the policy of both the NREL and JRC laboratories to treat data as proprietary and thus specific model types and manufacturers are not identified.

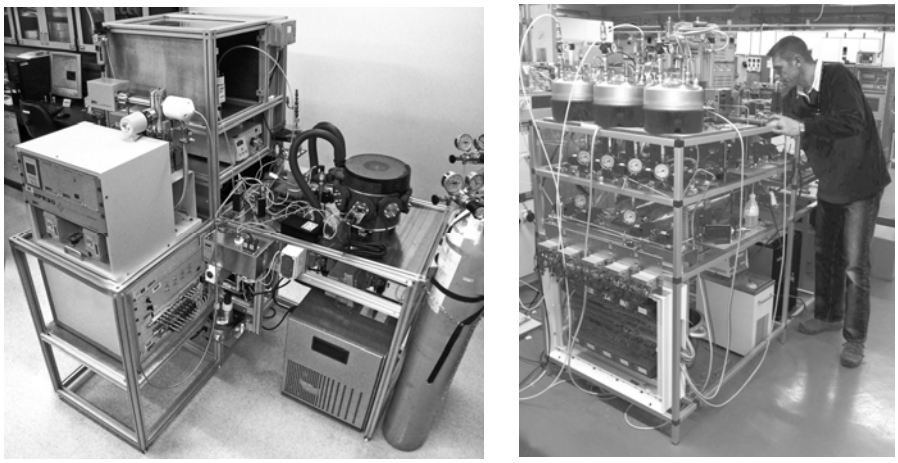

Figure 1: (LEFT) The NREL Safety Sensor Testing Laboratory (SSTL). (RIGHT) The JRC Sensor Testing Facility (SenTeF).

2.2 Oxygen Dependence Test Protocol

Hydrogen sensors are being jointly evaluated by NREL and JRC laboratories as part of a larger study involving the evaluation of commercial technology for safe implementation of the hydrogen infrastructure [7]. Typically, factory-calibrated detectors are obtained and tested by NREL and JRC as received from the manufacturer; no on-site calibrations were performed by either NREL or JRC personnel. The assessment of sensor oxygen dependence is part of this study. Different samples of identical sensor technologies were evaluated at NREL and JRC. A method was developed to evaluate the impact of depressed oxygen concentrations on the performance of commercial hydrogen sensors and to further assess their detection capabilities under completely anaerobic conditions. Hydrogen-air and hydrogen-nitrogen mixtures were produced from gas cylinders of air, nitrogen, 1% or 2% hydrogen in air and 1% or 2% hydrogen in nitrogen using the gas flow control system of the respective test apparatus. Air is considered here to be 20.9% oxygen in nitrogen. The air test gas was blended with nitrogen to form gas mixtures with decreased oxygen levels. Specifically, for 50% air (10.45% O_2) blends comprised of 50% air and 50% nitrogen were used; for 25% air (5.25% O_2) blends comprised of 25% air and 75% nitrogen were used; for 0% air (0% O_2) pure nitrogen was used. In all cases, the total gas flow rate was maintained at 1.0 L/min. An automated, continuous test protocol was developed that could be demarcated into four distinct sections:

(1). Aerobic Range Section (control)

The sensor was exposed to either a single or a series of hydrogen in air mixtures. Hydrogen concentrations of 1%, 0.5%, 0.1%, and 0.05% may be used (NREL testing used only the 1% hydrogen in air for the Aerobic Range Test; concentration effects in air were measured separately as per protocols developed for the round-robin testing [5]). Between hydrogen in air exposures the sensor was exposed to clean air (0% H_2). The exposure duration at each concentration was sufficiently long to ensure a stable sensor signal.

(2). Oxygen Variation Section

Immediately following the aerobic range test the sensor was exposed to 1% hydrogen in a series of gas mixtures comprising gradually decreasing oxygen concentrations. Nitrogen was used to displace the oxygen. Sensors were exposed to 1% H_2 in 50% air (10.45% O_2), 1% H_2 in 25% air (5.25% O_2), and 1% H_2 in 0% air (0% O_2 or 100% N_2). Prior to and following each of these exposures, the sensor was exposed to the relevant clean background gas corresponding to the given oxygen content. The aim of this section of the test was to show the influence of changes in oxygen concentration on the sensor response to 1 vol % hydrogen. Hydrogen exposures were performed twice at each oxygen concentration.

(3). Anaerobic Range Section

Immediately following the oxygen variation test, the sensor was exposed to decreasing hydrogen concentrations (0.5, 0.1, and 0.05 vol %) under anaerobic conditions in order to investigate its detection range in the absence of oxygen. The sensor was exposed to 100% nitrogen between each exposure and the exposure sequence was repeated.

(4). Aerobic Recovery Range Section

Following operation under anaerobic conditions, the procedure for the aerobic range test was repeated in order to assess the sensor's ability to recover from anaerobic operation. Sensors were exposed to hydrogen in air mixtures at the following concentrations; 1 %, 0.5 %, 0.1 %, and 0.05 % hydrogen in air (testing at NREL was performed only with 1% hydrogen in air). The sensor response was compared with the response recorded during the aerobic range section to determine whether oxygen deprivation had any long term effect on sensor response or whether the sensor recovered completely from operation under anaerobic conditions.

Figure 2 illustrates the test protocol. During the oxygen dependence test the following conditions were maintained:

Temperature:	25.0 ± 2° C
Pressure:	1.0 ± 0.05 bar
Relative Humidity:	Dry (<5% RH)
Gas flow rate:	1000 ± 20 nmls/min (sccm)

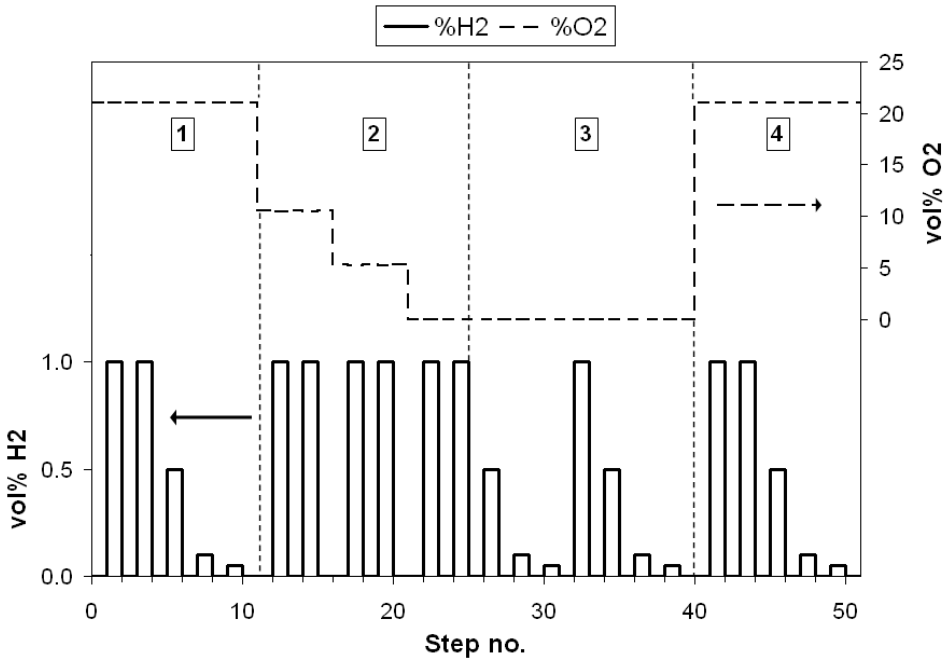

Figure 2: Hydrogen and oxygen concentration profiles during the (1) Aerobic Range, (2) Oxygen Variation, (3) Anaerobic Range and (4) Aerobic Recovery Range sections of the Oxygen Dependence Test. NREL testing in air included only 1% hydrogen in air for the Aerobic Range and Aerobic Recovery Range tests.

3.0 RESULTS

3.1 Combustible Gas Sensor (CGS)

The CGS consists of a heated ceramic bead embedded with a noble metal to provide a catalytic surface for hydrogen combustion. The device is heated electrically to 550° C. The coated surface catalyzes combustion when exposed to hydrogen or other combustible vapors. A thin platinum wire is encapsulated within the ceramic bead. Because the resistance of any material is affected by temperature, the surface combustion changes the resistance of the internal platinum wire, which essentially serves as an internal resistance temperature detector (RTD) device. Based on the mechanism of the CGS, it is to be expected that these devices will not function without oxygen since oxygen is essential for most combustion processes. Subjecting a CGS sensing element to the oxygen dependence tests should unequivocally demonstrate the need for oxygen for stable and accurate performance. Tests on this sensor were only performed by NREL. The results are shown in Figure 3.

In Figure 3, the output is presented in arbitrary units, since a sensing element was used with in-house built control circuitry whose output was in volts and was not converted to concentration units (i.e., % Hydrogen). The CGS sensing element has a finite baseline signal in the absence of hydrogen, which is typically accounted for when the sensing element is packaged in an instrumented detector. The sensor performance was not impacted by operation in 50% or 25% air, and the responses were indistinguishable from that observed for 100% air (Figure 3, right). However, in the absence of oxygen, the response of the CGS to 1% hydrogen was nearly completely quenched and it was unable to produce an analytically useful signal (Figure 3, right). Under anaerobic operation, the CGS sensor did not fully recover following exposure to hydrogen, resulting in a shift in the baseline (Figure 3, right). This shifted baseline remained when the sensor was return to an air matrix, as confirmed by a comparison of the aerobic (step 1) response to the post-aerobic (step 4) response (Figure 3, left). Clearly the operation of this sensor, based on the catalytically induced combustion of hydrogen, is impeded in the absence of oxygen. As expected, these results demonstrate that the CGS cannot operate under anaerobic conditions. It is, however, capable of operating at low oxygen levels, down to 5.25% in N_2.

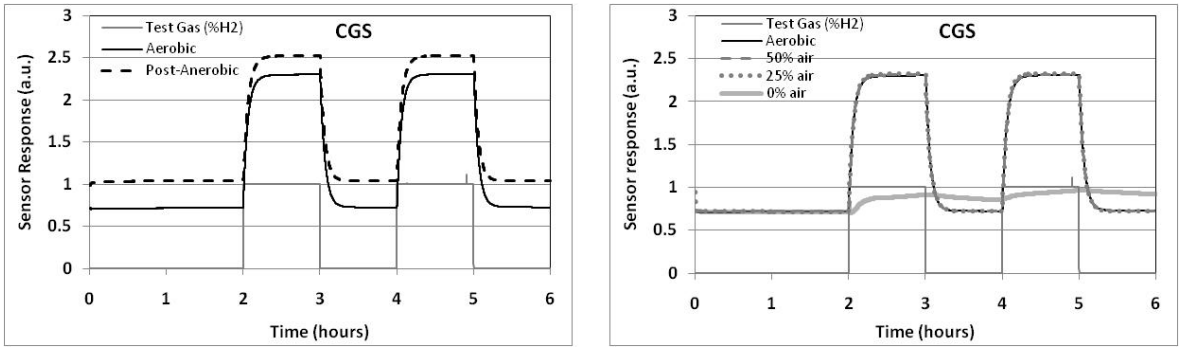

Figure 3: (LEFT) Response of a CGS sensing element to 1% hydrogen in air prior to (▬) and following (--) operation at depressed oxygen concentration. (RIGHT) Impact on the sensor response to 1% H_2 as air levels decrease from 100% to 0%. The response in air, 50% air and 25% air is indistinguishable, but the response in 0% air is almost totally quenched.

3.2 Thermal Conductivity Sensor (TC)

As with CGS, thermal conductivity (TC) sensors rely upon a temperature-induced change of an electrically heated sensing element following exposure to the analyte. A TC sensor is not heated to a temperature that induces combustion, but only to a temperature in which the resistance of the sensing element deviates from the linear range of Ohm's Law. This is a manifestation of the ability of the element to dissipate heat to the ambient environment as electrical energy is applied. This process is dependent upon the thermal conductivity of the surrounding gas matrix. Thermal conductivity is a property of a gas and thus as the gas composition surrounding the TC changes, the temperature of the TC will vary as the heat dissipation to the surrounding gas changes. The thermal conductivity

coefficient at 298 K and 1 atm for hydrogen of 174 {mW/(m·K)} is the greatest thermal conductivity of any known gas. Unlike almost every other hydrogen sensor platform, the TC sensor does not require oxygen for long-term, stable operation. This makes it amenable for use in process streams or for those applications which use a nitrogen purge. Subjecting a TC sensor to the oxygen dependence test was expected to confirm that this sensor can operate without oxygen.

In the NREL evaluations, a calibrated TC detector that exhibited an offset of approximately 1% was used; in other words, operation in air gave a 1% reading, and a 1% exposure to hydrogen in air would read 2%. The equivalent JRC unit exhibited a slightly lower offset of approximately 0.7% in air. Although the offset affected the output of the instrument (which was corrected via post-measurement analysis by subtraction of the baseline signal), this allowed us to measure the shift in the sensor baseline as the oxygen levels were depressed. If the baseline response had been zero, it would have fallen below zero during the course of this test. Because of the electronic design of this instrument, all signals that are less than zero are outputted as zero, and thus we would not have been able to observe the baseline shift. Figure 4 shows the logged output of the NREL TC detector with the 1% offset signal included (top) and with this offset signal subtracted (bottom). Although a shift in baseline is observed as the oxygen content is decreased (Figure 4, right), the sensor showed no change in sensitivity to hydrogen. This baseline shift can be attributed to the slightly lower thermal conductivity of N_2 compared with the O_2 that it displaces.

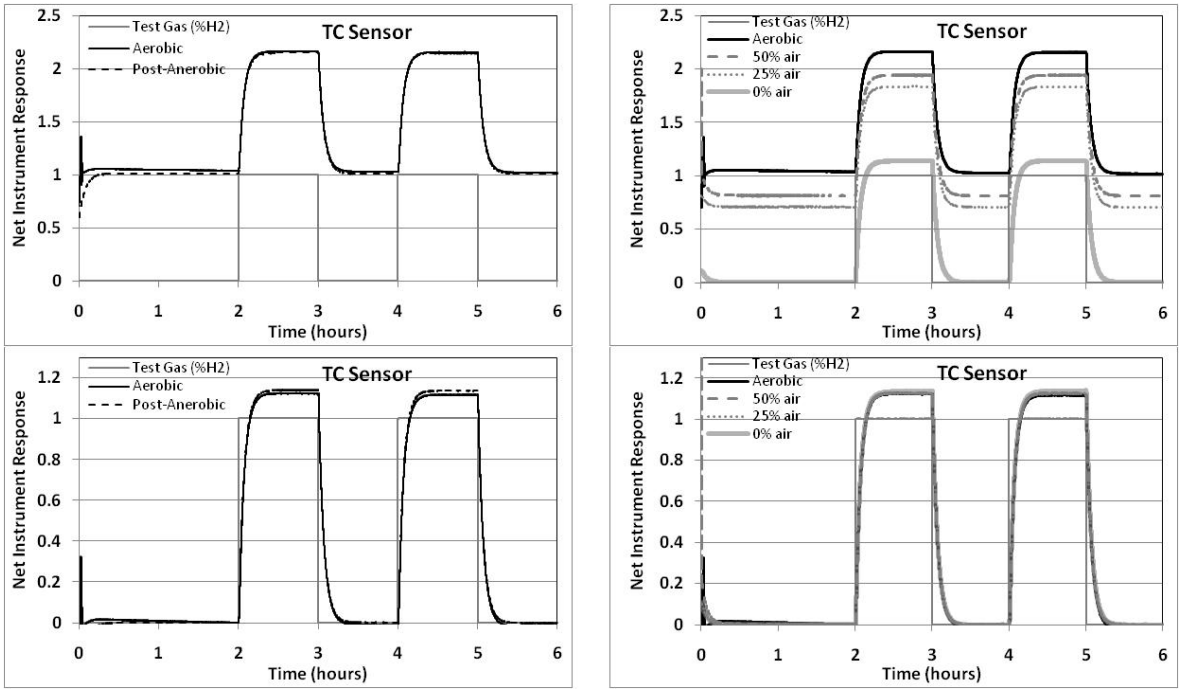

Figure 4: Impact of depressed oxygen on the performance of the NREL TC sensor. (TOP LEFT) Measured sensor response to 1% hydrogen in air prior to and following exposure to depressed oxygen levels. The sensor response curves are indistinguishable. (TOP RIGHT) Measured sensor response to 1% hydrogen in air/N_2 for 100% air, 50% air, 25% air and 0% air. Although the baseline of the sensor decreased as the oxygen level was decreased, the net response remained constant. (BOTTOM) Same data as the TOP traces, but with the baseline signal subtracted yielding the net sensor response, which was clearly not affected by the level of oxygen.

Figure 5 shows the measured response of the NREL TC sensor to 1%, 0.5%, 0.1%, and 0.05% hydrogen in nitrogen (top) and with the offset removed via post-measurement analysis (bottom). The sensor was capable of repeatable low levels hydrogen detection (down to 0.05% in nitrogen) under anaerobic conditions.

Although the TC showed a shift in response as the oxygen content changed, it remained sensitive to hydrogen and its net response was not affected. The baseline shift indicates that for maximum accuracy, the device needs to be calibrated in the matrix in which it will be deployed.

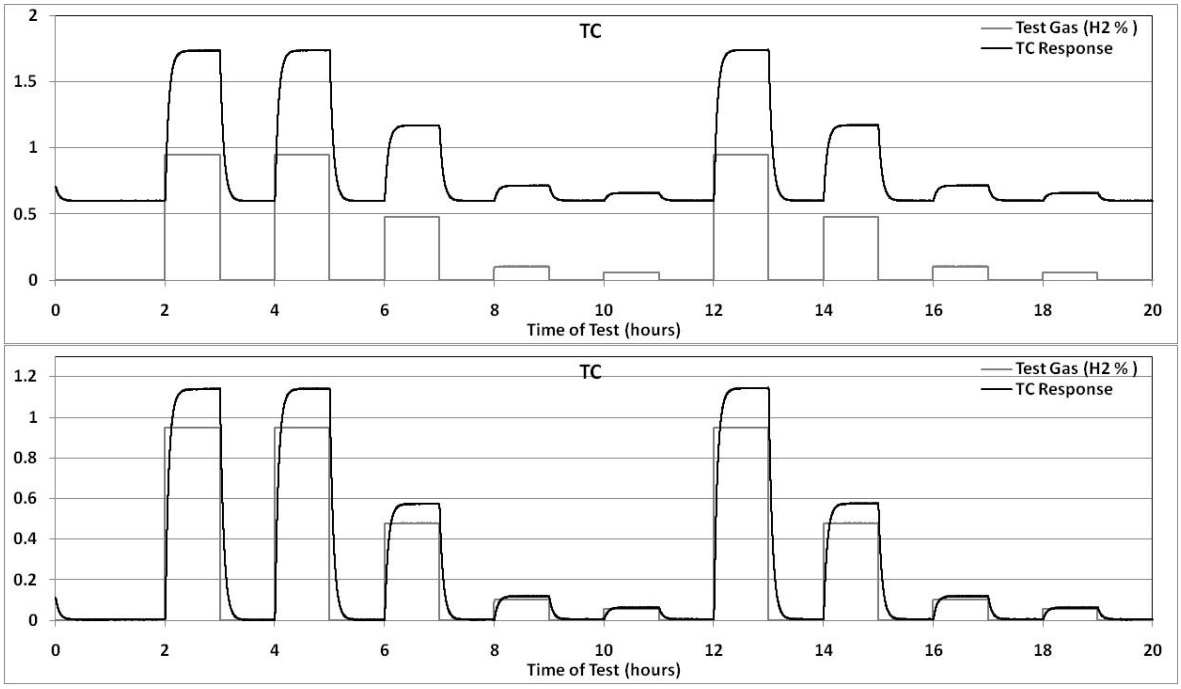

Figure 5: TC (NREL) response under anaerobic conditions. The sensor was exposed to 1%, 0.5%, 0.1% and 0.05% hydrogen in nitrogen. TOP: Measured sensor response including the offset baseline. BOTTOM: Net sensor response.

Figure 6 shows the TC sensor response profile obtained by the JRC as the hydrogen concentration was changed in different gas matrices over the duration of the test. The data was similar to that obtained at NREL. Both laboratories observed that the sensor baseline response decreased linearly with decreasing O_2 concentration due to the lower thermal conductivity of N_2 compared with O_2. The extent of this decrease was also similar (the zero signal decreased for both laboratories by about 0.02% per 1% decrease in O_2 concentration).

Furthermore, JRC tests affirmed that there was no significant effect of changing oxygen concentration on the net sensor response. Both the NREL and JRC laboratories noted the ability of the sensor to detect low concentrations (500 ppm) of hydrogen during operation under anaerobic conditions (Figure 6). A comparison of the net sensor response to various hydrogen concentrations during the aerobic range, anaerobic range and aerobic recovery range sections of the test, shown in Figure 7, highlights the quantitative agreement between the test laboratories and that the sensor's net response to different hydrogen concentrations was unaffected during and following operation in the absence of oxygen.

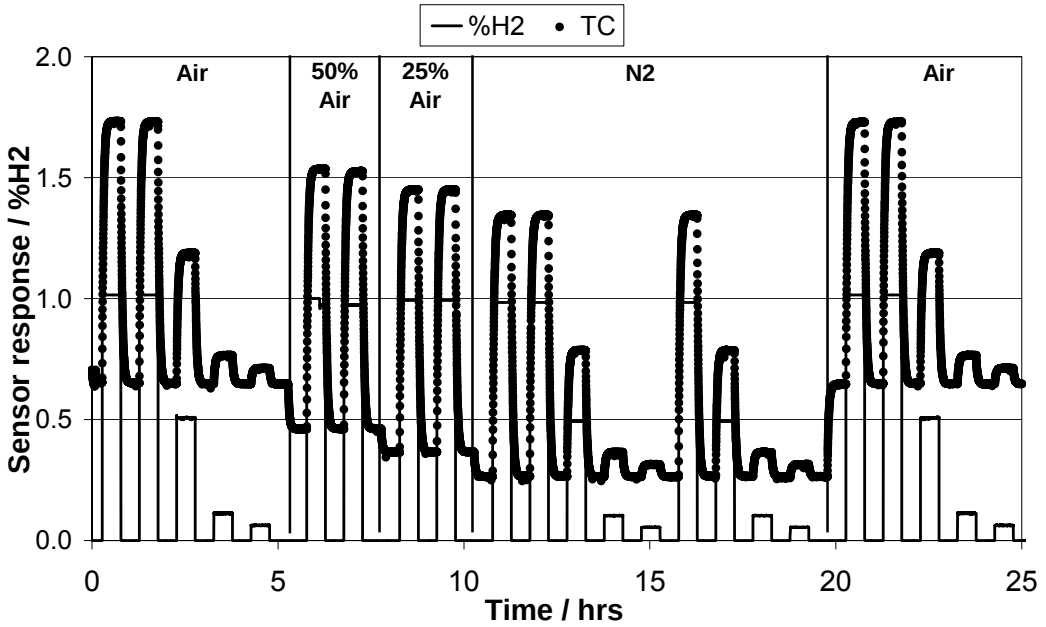

Figure 6: Response profile of the JRC TC sensor over the duration of the oxygen dependence test.

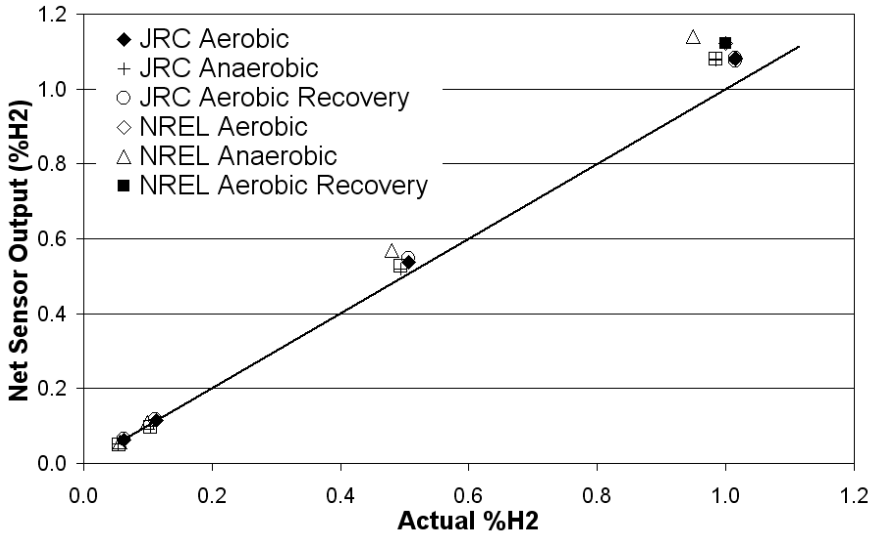

Figure 7: Net TC response as a function of hydrogen concentration under aerobic and anaerobic conditions. The solid line represents a sensor reading that corresponds to the actual hydrogen concentration.

3.3 Palladium Thin Film Sensors

The unique and highly selective permeability of hydrogen into palladium (Pd) is exploited on numerous sensor platforms. One basic technology that appears promising is a Pd thin film resistor sensing element. The film resistance changes with absorption of hydrogen. The absorption of hydrogen by palladium is not expected to be affected by the gas matrix and thus it can be predicted that these sensors will work in air or nitrogen. One secondary effect, which is beyond this study, but may be relevant for end users, is that palladium is susceptible to deleterious effects when exposed to poisons and interferents and that the recovery from such exposures may be impacted by the absence of oxygen. This secondary impact of anaerobic exposure to poisons and interferents will be investigated in future work. Figure 8 shows the response of a palladium thin film sensor to 1%

hydrogen at various oxygen levels as measured by NREL. No impact was seen, except at 0% oxygen where a slight increase in response was observed.

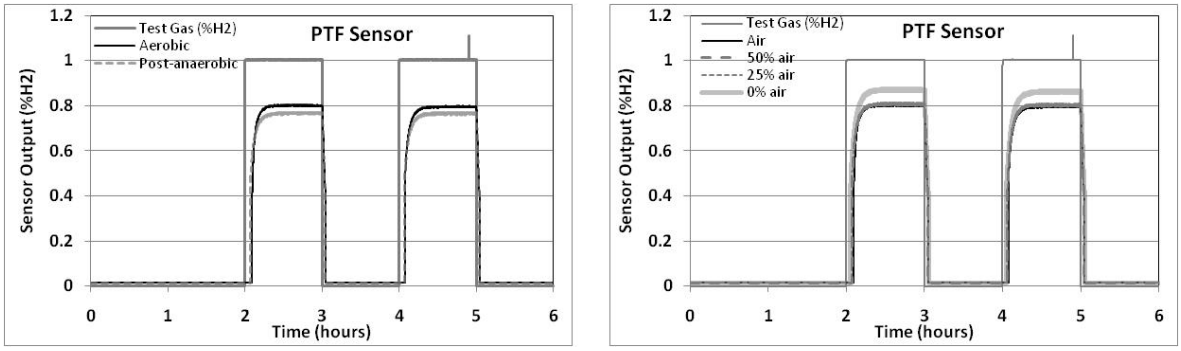

Figure 8: NREL data for PTF sensor. (Left) Response to 1% hydrogen in air prior to and following operation at depressed oxygen concentrations. (Right) Impact on the sensor response to 1% H_2 as air levels decrease from 100% to 0%. The responses in air, 50% air, and 25% air are nearly indistinguishable. A slight increase in sensitivity for anaerobic operation was observed at NREL.

Figure 9 illustrates the results obtained by the JRC for their PTF sensor. As can be seen there is strong agreement between both laboratories regarding the observations made during the oxygen dependence tests. The PTF sensor indicates a significantly lower hydrogen concentration compared with the actual concentration at all oxygen concentrations. It should be noted however, that the PTF sensors were used as delivered from the manufacturer and that the hydrogen responses were measured using the factory calibration. The obtained signals were quite repeatable, in air, and in the various depressed oxygen levels, including the anaerobic operation. On-site calibration, which could have improved instrument accuracy, was not performed. Thus, using the manufacturer-provided calibration, the sensor output in 1% hydrogen was 0.8% and 0.75% as observed by NREL and JRC respectively. The slightly lower sensor response from JRC's PTF sensor observed during the first post-exposure test compared to the second (Figure 9) is explained by the slightly lower hydrogen concentration in the test chamber at that time during the test. Changes in oxygen concentration had little effect on the sensor's final indication at 1% hydrogen (Figure 8, right and Figure 9) and the sensor worked well even in the absence of oxygen. The slight decrease in sensor response to 1% H_2 in air pre- and post-exposure to anaerobic conditions is in keeping with previous results of short term stability tests on this sensor, which indicate that its response decreases on repeated exposure to hydrogen [7].

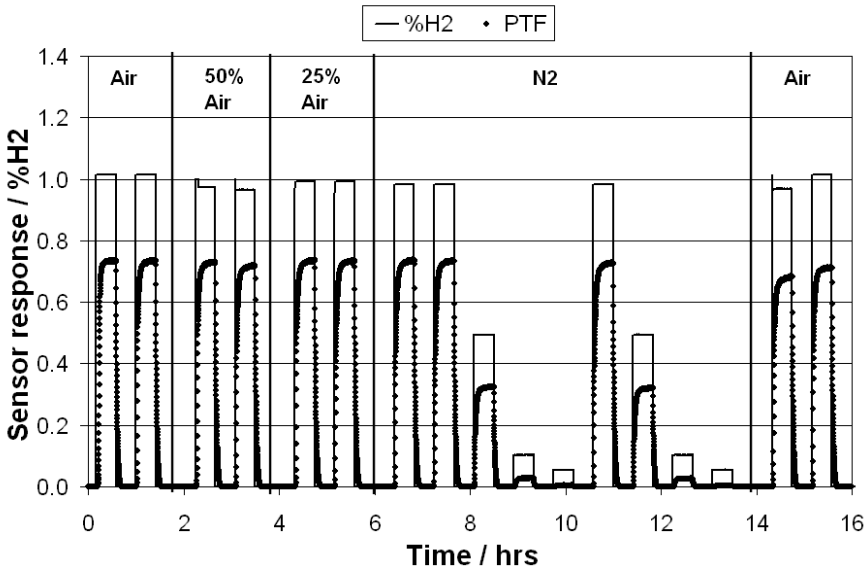

Figure 9: JRC data for PTF sensor. (Left) Response to 1% hydrogen in air prior to (aerobic) and following (aerobic recovery) operation at depressed oxygen levels. (Right): Impact on the sensor response to 1% H_2 as air levels decrease from 100% to 0%. The response in air, 50% air, 25% air and 0% air is nearly indistinguishable.

Figure 10 compares the normalised sensor output during the anaerobic range section and the aerobic recovery range section of the test. The sensor was exposed to mixtures containing approximately 1.0, 0.5, 0.1, and 0.05 vol% hydrogen in nitrogen during the anaerobic range section and then to the same exposure sequence in air during the aerobic recovery range section. It is evident that the sensor output is significantly lower than the actual hydrogen concentration.

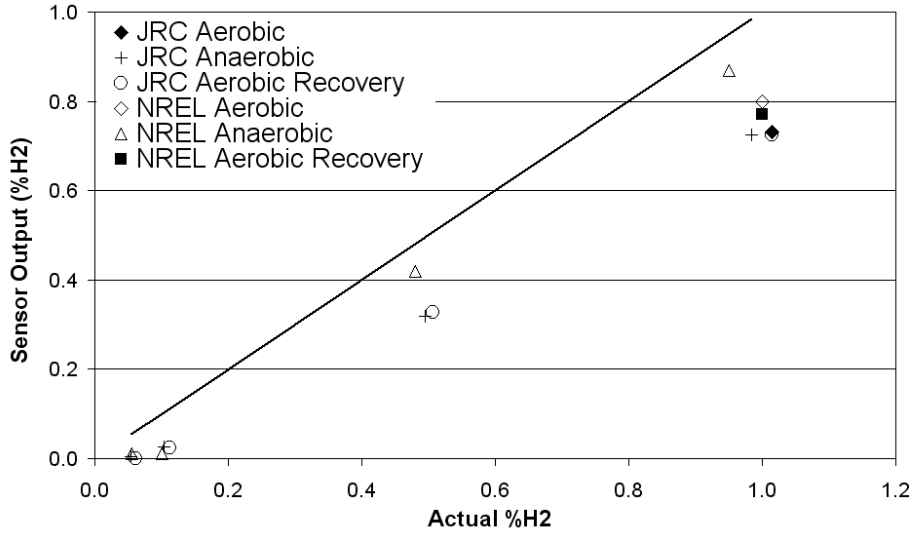

Figure 10: PTF sensor output as a function of the actual hydrogen concentration under aerobic and anaerobic conditions. The solid line represents a sensor reading that corresponds to the actual hydrogen concentration.

4.0 CONCLUSIONS

Presented herein are the initial results of an investigation to provide empirical data pertaining to the ability of various hydrogen sensor technologies to reliably function in depressed oxygen atmospheres. Although an understanding of the underlying sensing element detection mechanism can lead to a rational prediction on the ability of a sensor to perform in the absence of oxygen, end users do not necessarily have such an understanding. In addition, it may not be possible to fully predict the influence of oxygen on sensor operation based on theory alone. Although it is not within the end user responsibility to fully comprehend the underlying principles upon which an analyzer is built; it is within the end user's obligation to know its limitations. It is imperative that the capabilities and limitations of hydrogen safety sensor technologies are readily available to the hydrogen community and the experimental data reported herein are provided for that purpose.

Three sensor platforms (CGS, TC and PTF) were assessed for their ability to operate in oxygen-deficient environments and to detect low levels (≤1%) of hydrogen in nitrogen. One sensor, the CGS, was unequivocally shown to be inappropriate for anaerobic operation, although it could work in depressed oxygen levels. A second technology, the TC, showed a measurable gas matrix effect (e.g., baseline shift as the O_2/N_2 ratio was changed) but the net response and the sensitivity remained unaffected even under anaerobic conditions. The third platform, the PTF, showed a stable sensitivity and negligible baseline shift for all oxygen levels, including operation under anaerobic conditions. This is an on-going study and will be extended to additional sensing platforms, including metal oxide sensors, electrochemical sensors, FETs and other models types of the various platforms.

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