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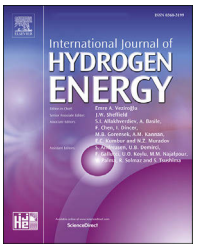

Empirical profiling of cold hydrogen plumes formed from venting of LH_2 storage vessels

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ABSTRACT

Liquid hydrogen (LH_2) storage is viewed as a viable approach to assure sufficient hydrogen capacity at commercial fuelling stations. Presently, LH_2 is produced at remote facilities and then transported to the end-use site by road vehicles (i.e., LH_2 tanker trucks). Venting of hydrogen to depressurize the transport storage tank is a routine part of the LH_2 delivery and site transfer process. The behavior of cold hydrogen plumes has not been well characterized because of the sparsity of empirical field data, which can lead to overly conservative safety requirements. Committee members of the National Fire Protection Association (NFPA) Standard 2 [1] formed the Hydrogen Storage Safety Task Group, which consists of hydrogen producers, safety experts, and computational fluid dynamics modellers, has identified the lack of understanding of hydrogen dispersion during LH_2 venting of storage vessels as a critical gap for establishing safety distances at LH_2 facilities, especially commercial hydrogen fuelling stations. To address this need, the National Renewable Energy Laboratory Sensor Laboratory, in collaboration with the NFPA Hydrogen Storage Task Group, developed a prototype Cold Hydrogen Plume Analyzer to empirically characterize the hydrogen plume formed during LH_2 storage tank venting. The prototype analyzer was field deployed during an actual LH_2 venting process. Critical findings included:

Hydrogen above the lower flammable limit (LFL) was detected as much as 2 m lower than the release point, which is not predicted by existing models.
Personal monitors detected hydrogen at ground level, although at levels below the LFL.
A small but inconsistent correlation was found between oxygen depletion and the hydrogen concentration.
A negligible to non-existent correlation was found between in-situ temperature measurements and the hydrogen concentration.

The prototype analyzer is being upgraded for enhanced metrological capabilities, including improved real-time spatial and temporal profiling of hydrogen plumes and tracking of prevailing weather conditions. Additional deployments are planned to monitor plume behavior under different wind, humidity, and temperature conditions. The data will

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be shared with the Hydrogen Storage Task Group and ultimately will be used support theoretical models and code requirements prescribed in NFPA 2.

Introduction

Liquid hydrogen storage

The use of hydrogen as an alternative fuel is increasing. Hydrogen-powered forklifts [2], stationary power systems for lighting [3], and backup power [4] are already commercially deployed. Further increased use of hydrogen as an energy carrier is expected as hydrogen-powered fuel cell electric vehicles (FCEVs) are commercially released into the consumer market. Infrastructure requirements for FCEVs include increased hydrogen production capacity, transport, storage, and a system of commercial fueling stations to accommodate the commercial sale of hydrogen for FCEVs. There are different strategies for maintaining a hydrogen supply at commercial fueling stations, which include on-site production, pipeline delivery, and road delivery of hydrogen for on-site storage. Presently, road delivery of pressurized gaseous hydrogen (GH_2) is by far the most common means to supply hydrogen to commercial fueling stations [5]. On-site high-pressure storage of GH_2 has sufficient capacity to meet the current market needs for FCEV fueling. However, as the FCEV fleet grows, the demand for hydrogen will increase. On-site storage in high-pressure tanks has limitations. In addition to the risks associated with the high pressure itself, GH_2 is characterized by a relatively low mass and energy density, even at elevated pressures. At 25 C, the density of GH_2 at 10 MPa is 7.67 kg/m^3, and at 5 MPa, the density is only 3.94 kg/m^3 [6]. Alternatively, liquid hydrogen (LH_2) at a storage temperature of 20.4 K has a density of 70.8 kg/m^3 [7], which is nearly 10 times that of 10 MPa GH_2. Because of its higher density, LH_2 storage is viewed as a viable means to provide sufficient hydrogen for the consumer FCEV fueling market. LH_2 can be an efficient and economical alternative to GH_2 storage for operations that require a reliable supply of hydrogen at quantities greater than that which can be conveniently and safely provided by high-pressure systems. Already fuel cell forklift operations typically use on-site LH_2 storage. LH_2 is routinely and safely used in numerous large-scale operations, which, in addition to forklifts, includes the aerospace industry [8] and various manufacturing applications. To date, LH_2 storage has been predominately within industrial facilities, which, from a safety perspective, are characterized by two main features–limited public access and a large geometric area for easy compliance to prescribed setback distances. Commercial fueling facilities present unique challenges for LH_2 storage because of increased public exposure within a facility that is often already space limited.

LH_2 is centrally produced at a remote facility and then transported, usually by road tanker vehicles, for on-site storage at or near the point of use. This requires the transfer of LH_2 from the transport storage tank to a permanent stationary storage vessel. The LH_2 transfer is accomplished by pressurization of the transport tank. Upon completion of the transfer process, it is necessary to vent up to 50 kg of hydrogen to depressurize the transport tank. Depressurization is necessary to assure that the vehicle complies to road regulations. Fig. 1 shows the depressurization process, which is often performed through the stationary tank vent stack but can also be performed through the delivery vehicle vent; the delivery vehicle vent is typically 3–4 m (10–13 ft) in height, which is considerably shorter than the stationary vent stack. This routine and often predictable release of hydrogen provides an opportunity to empirically profile the dispersion phenomena of cold hydrogen plumes under controlled temporal, but real-world conditions. This approach was used to deploy a hydrogen gas analyzer that was developed by NREL and used for one of the first empirical field measurements of LH_2 releases using hydrogen point detection technology to directly quantify concentration within the hydrogen plume during the delivery process.

Fig. 1 – LH_2 venting.

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Although limited, there have been previous LH_2 dispersion studies. In an early study focusing on the use of LH_2 as a propulsion fuel, D.H. Little investigated the flammability and hazards associated with released GH_2 and LH_2 [9]. Although the adverse impacts of ignition were less severe than hydrocarbon fuels, the ease of ignition was more likely, and a separation of nearly 180 ft was proposed. More recent investigations were performed by Health and Safety Laboratory (HSL) in the United Kingdom using indirect analytical methods to estimate hydrogen concentrations, such as with the adiabatic mixing assumption for a cold gas release [10,11]. As an indirect method, there is a potential for a larger uncertainty and measurement error. Further comparisons between hydrogen carbon fuels (LNG) and cold hydrogen were modeled [12]. NASA also looked at the vapor cloud dispersion [13]. This paper describes the development of the NREL analyzer for the direct measurement of cold hydrogen plumes during real-world venting operations and the findings and significance of the initial field measurements.

Requirements for safe LH_2 storage

Within the United States, National Fire Protection Association Standard 2 (NFPA 2) [1] and the International Fire Code (IFC) [14] provide the regulatory framework for the safe use of hydrogen. NFPA 2 provides fundamental safeguards for the generation, installation, storage, piping, use, and handling of hydrogen in compressed gas (GH_2) form or cryogenic liquid (LH_2) form. When adopted by a local jurisdiction, the requirements prescribed within these two documents are legally enforceable. Although not universally implemented, most jurisdictions within the U.S. adopt the IFC, and since NFPA 2 is referenced by the IFC, the requirements of NFPA 2 become legally binding upon adoption of the IFC. One controlling factor for the assurance of safety in LH_2 systems is the setback distance. Present setback requirements in NFPA 2 prescribed a radial line-of-site distance of 22.9 m (75 ft) to any structure or facility border from a LH_2 system. In urban environments, the lot size for fueling stations is often restricted and thus the NFPA 2 setback requirements may preclude LH_2 storage. However, NFPA 2 may allow lowering the setback distance requirement through the implementation of mitigation strategies that decrease the hazards associated with LH_2 storage and use. Active on-site monitoring, coupled with a better understanding of cold hydrogen release behavior, is one proposed mitigation strategy to ease the prescribed NFPA 2 setback distance requirement.

The NFPA 2 Hydrogen Storage Task Group, created in April 2014, was formed to explore approaches to mitigate the risks and hazards associated with LH_2 storage to facilitate its use in commercial applications, which in turn will facilitate FCEV market growth by providing a more reliable fuel supply. As part of its mission, the Task Group endeavored to understand the basis for the setback distances. The setback for LH_2 storage defined in NFPA 2 was based upon requirements established in earlier documents, the basis for which is presently unclear, but seems to have been more consensus than scientific, and thus is not based on any quantified risk reductions. The Task Group is striving to understand the dispersion of LH_2 releases under various release scenarios. One scenario is the release of a significant amount of hydrogen from the fixed storage tank following LH_2 transfer from the delivery tanker. The amount of vented hydrogen has been estimated to be on the order of 50 kg. It is noted that alternative depressurization methods are being investigated to minimize the amount of vented hydrogen. One strategy is to depressurize the transport tank by condensing the headspace GH_2 to LH_2. However, presently the hydrogen is typically vented through a vertical stack (approximately 10 m tall) on the stationary tank. This process is routinely performed and provides an opportunity for field studies to properly characterize LH_2 release behavior. The Task Group raised several questions regarding the hydrogen dispersion associated with this venting process (and other release scenarios), which include:

1. Will the hydrogen plume exist below the vent stack release point?
2. What will the cold hydrogen do to atmospheric gases (oxygen and nitrogen)?
3. Will the chilled air that is produced from contact with the cold hydrogen gas impact the hydrogen dispersion?
4. Will the hydrogen become entrained in any liquid oxygen or nitrogen produced from the cold hydrogen?
5. How significant is wind speed in impacting the hydrogen plume configuration?
6. Will there be significant ground-level hydrogen concentrations?
7. Can developing dispersion models account for the actual physical phenomenon occurring during a hydrogen venting event?
8. Does the visible vapor correlate to hydrogen levels in the air?

The questions identified by the Task Group exemplify the sparsity of the available data on cold hydrogen releases. There was not a clear consensus pertaining to the fate of the released hydrogen, particularly with regards to the vertical profile of the hydrogen (e.g., will hydrogen be observed below the point of release and if so, how close to ground level would detectable hydrogen be observed). It was unclear whether hydrogen buoyancy would be sufficient to preclude the presence of hydrogen below the release point. A sub-group of the NFPA 2 Hydrogen Storage Task Group was formed to address the questions identified above. The sub-group consists of experts in the areas of hydrogen measurements, hydrogen behavior and risks, LH_2 production and transport, on-site storage at a DOE facility and in industrial facilities, safety experts in the hydrogen community, and the chair of NFPA 2. One proposed strategy to address the questions identified by the sub-group was to perform actual field measurements to spatially and temporally profile the hydrogen plume resulting from a routine LH_2 venting process. Accordingly, a multipoint hydrogen analyzer was developed by the NREL Hydrogen Sensor Laboratory [15]. The following discussion presents the development of the tools to perform these measurements and preliminary findings obtained from the field deployment of the National Renewable Laboratory's (NREL's) prototype Cold Hydrogen Plume Analyzer for the multipoint profiling of hydrogen plumes.

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Design features of the analyzer

At the request of the NFPA 2 Sub-Group, the NREL Sensor Laboratory [15] was tasked with developing the analytical tools for the empirical profiling of the plume formed from a LH_2 release. It is noted that the design of the analyzer was guided by several constraints. As an exploratory research, development, and deployment effort with a limited budget, cost factors had to be considered. There were also metrological considerations. The physical behavior of the hydrogen plume from a cold hydrogen release is poorly understood and without extensive documentation. Thus, there was little guidance with regards to the number and positions of measurement locations. Nor was there information on the likely hydrogen concentration that could be encountered; obviously, pure H_2 is vented, but the manner by which it would mix with ambient air was unclear. Accordingly, there was a concern that individual sensing elements within the analyzer could be exposed to a high hydrogen concentration, if not pure hydrogen, even several horizontal feet from the release point. The potential for exposure to a high hydrogen concentration impacted both the selection of the sensors and the way they were deployed. Hydrogen sensor selection had to accommodate a broad dynamic range and a fast recovery from a potential exposure to a high hydrogen concentration. At the other extreme, a detection limit below 0.4 vol% H_2 was deemed necessary, because this concentration is 10% of the LFL (4 vol%) and is often the action level for a "warning" state in hydrogen operations. It was concluded that a flexible design for the analyzer needed to be developed that could be adapted and upgraded as more data and experience were obtained from field measurements. Remote detection methods, such as light detection and ranging (LIDAR) [16,17], and Schlieren [18], have been reported for hydrogen, but neither are noted for a good detection limit. These methods are also complicated to use and to independently validate. The use of high-power lasers for probing, especially for LIDAR, also presents a potential safety issue for the general use of these methods. Furthermore, these methods are also complicated and currently available except in research settings, and thus unsuitable for routine deployment. Instead, the strategy employed for the NREL analyzer was to use an array of robust, low-cost hydrogen sensors as the basis for the prototype, and to perform a screening measurement during an actual venting (depressurization) of a LH_2 storage tank. Supplemental chemical (e.g., oxygen) and physical (e.g., temperature and humidity) sensors were incorporated into the prototype analyzer design. The term "prototype" is used to describe the Cold Hydrogen Plume Analyzer to emphasize that the design described herein and used in the initial field studies was for demonstration purposes and preliminary data collection, and that modifications have been and will continue to be incorporated to improve the overall performance and metrological capabilities. This approach was necessary because there was little or no guidance as to what to expect in the field on hydrogen levels or transients at or away from the point of release. The intent of the initial measurements was to gain a basic understanding of the plume behavior and to attempt to answer some of the basic question posed by the NFPA Task Group; it was not intended to validate any fluid dispersion model. A second goal was to assess performance of the analyzer itself to guide upgrades and modifications of the design to improve the quality and quantity of the data. The design of the prototype analyzer is described below along with the results from the first deployment within a plume formed from the venting of a LH_2 storage tank. The significance of the field study is presented along with proposed upgrades that will significantly enhance the capability of the analyzer to profile hydrogen releases and to monitor for hydrogen over a wide area. It is now recognized that, with some modifications the NREL prototype analyzer can form the basis of a hydrogen wide area monitor (HyWAM) [19] for both GH_2 and LH_2 operations to support both research activity as well as a commercial safety system to facilitate deployment.

The prototype analyzer consisted of two main subsystems—the Support Structure and the Analyzer Box, which were configured into an integrated, field-deployable package. Operationally, the Analyzer Box was designed to remotely analyze test gas samples automatically collected from multiple measurement points situated at discrete locations along the Support Structure.

Support structure

The Support Structure was designed to be deployed directly within the hydrogen plume for vertical profiling. The prototype design can be deployed up to 10.67 m (35 feet) in height and accommodate up to ten measurement points distributed along a portion of the length of the Support Structure (typically from the top—35 feet and then down at 0.61 m (2-foot) intervals. These were numbered 1 through 10, with the lowest number referring to the highest position. The assembled Support Structure is shown in Fig. 2 and was based upon a commercially-available telescoping PVC pole for facile deployment in the field. Graduated markings on the pole allowed for precise location of measurement points. Two strategies exist for performing the analysis at the designated measurement points:

1 Mounting of sensors directly on the pole for in-situ analysis
2. Installation of a pneumatic line to draw the gas sample from the measurement point to a remote sensor for analysis.

In-situ sensors (Option 1) have the advantage of operating the detector directly within the actual gas cloud, which can allow for faster analyses and less corruption of the sample. However, remote gas detection through a pneumatic line has its own advantages, including minimization of fluctuation in environmental parameters (especially temperature), which can affect gas sensor accuracy, and operation of the electronic components (e.g., the sensors) outside the restricted zone. This alleviates the need for listed (and expensive) components, simplifies interfacing sensors and control elements to a data acquisition (DAQ) system for logging of sensor response, improves safety, and allows for easier assembly of the support structure. Moreover, fewer sensors would be required by remote detection by multiplexing the multiple sampling points into a single sensor array. Thus, Option 2, the use of a

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Fig. 2 – Support structure for the cold hydrogen plume analyzer.

pneumatic line to draw gas samples to a remote sensor array, was selected for the prototype analyzer. There was one pneumatic line made from 1/8-in. (3.2 mm) O.D., 1/16-in. (1.6 mm) I.D. polyethylene tubing for each gas measurement point. The support structure was, however, instrumented with eight K-type thermocouples for *in-situ* temperature measurements. During deployment, the Support Structure was stabilized by guy wires, a tripod support system, and a custom-designed base boot.

Analyzer Box

The Analyzer Box (Fig. 3) contains chemical sensors (e.g., hydrogen and oxygen sensors) and supplemental physical sensors (e.g., temperature and humidity sensing elements integrated into the hydrogen sensor) for the multi-point (vertical) characterization of gas samples extracted from multiple points within the hydrogen plume. Using an internal, fast-responding ten-position multiport valve, a single set of gas sensors was configured to analyze the gas samples collected from ten measurement points on the Support Structure. The multi-port valve sequentially and automatically directed gas samples drawn from each of the ten pneumatics lines to an electrochemical oxygen (O_2) sensor and a thermal-conductivity (TC) H_2 sensor mounted in series in the Analyzer Box. The multiplexing of numerous sample points to a single set of chemical sensors was implemented to minimize cost and instrument complexity, while at the same time

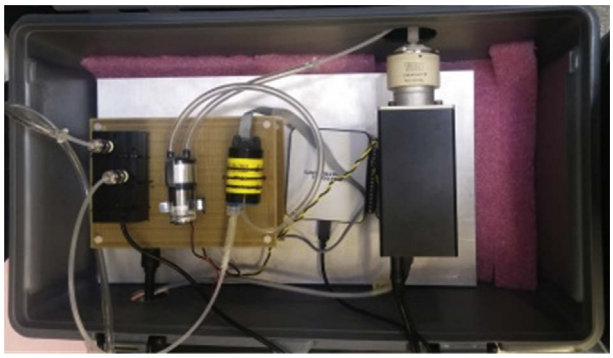

Fig. 3 – The Analyzer Box (45 by 24 cm and 15 cm deep) with (L to R) TC sensor (in a custom-built holder), pump, O_2 sensor, and valve.

maintain a significant number of measurement points for proper spatial characterization of the plume. Gas samples were collected using a gas pump mounted within the Analyzer Box. The gas sensor types and models, which are discussed below, were chosen because of their fast response time, measurement range, and stability. Moreover, the NREL and Joint Research Centre sensor laboratories had evaluated the performance of the selected gas sensors for other projects, and they were found to have, in general, very good metrological performance characteristics compatible for this application. The following specific sensors were selected for use in the analyzer.

TC hydrogen sensor with integrated temperature (T) and relative humidity (RH) sensing elements: There are numerous platforms for hydrogen sensors [20,21]. A thermal-conductivity hydrogen sensor (Xensor Integration, Model XEN-5320-USB) was selected for the prototype analyzer (see Fig. 4). Previous measurements verified that this sensor has a response time (t_{90}) of 250 ms [22]. The fast response time allows the sensor to quantify fast hydrogen transients. The TC sensor platform is also noted for a broad measuring range up to 100 vol% H_2. Because the TC sensor responds to changes in the physical environment through a heat transfer process as opposed to a chemical reaction with hydrogen, it is less prone than other

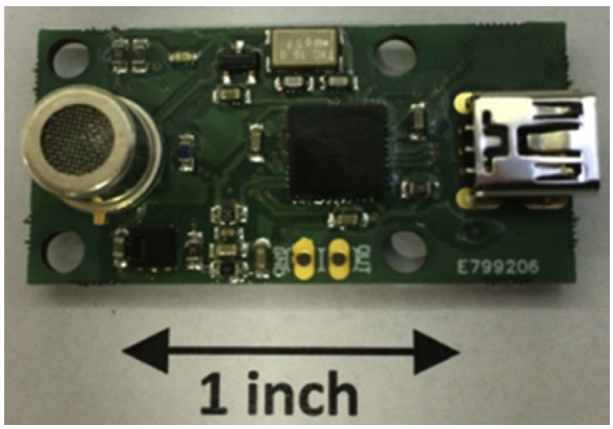

Fig. 4 – Thermal-conductivity sensor for H_2 sensor.

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sensor types to poisoning effects from chemical and environmental stresses. The physical transduction mechanism also allows for the sensor to quickly recover from a transient exposure to pure hydrogen. The Model XEN-5320-USB TC sensor also has integrated temperature (T) and relative humidity sensing (RH) elements, which can be used to measure the T and RH of the test gas.

Oxygen sensor: An electrochemical oxygen sensor was selected to monitor the concentration of oxygen in the test gas (Teledyne Analytical Instruments, Model UFO-130-2G, see Fig. 5). The selected model has a response time (t_{90}) of less than 1 s, which is a bit slower than the TC sensor. The oxygen sensor could quantify oxygen displacement, and thus be indirectly correlated to the hydrogen concentration. This method is not accurate at low hydrogen concentrations because of metrological limitations of the oxygen sensors [23], but was considered potentially useful in the analyzer for hydrogen levels beyond the linear range of the TC H_2 sensor. However, exposure of cryogenic hydrogen (LH_2: -253 C) to air has been reported to condense or even solidify nitrogen and oxygen components [11]. Thus, there are other causes of oxygen decreases in addition to displacement by hydrogen. Oxygen enrichment of the condensed air may also occur due higher boiling temperature of oxygen (182.6 C) relative to nitrogen (196 C), a phenomenon that may increase flammability hazards. With a range of 0–100 vol% O_2, the sensor could identify oxygen depletion due to the possible condensing of air by cryogenic hydrogen, as well as oxygen enrichment due to preferential evaporation of oxygen from condensed air. The possibility of oxygen condensing by the cold hydrogen release will affect the accuracy of the displacement approach to quantify high hydrogen levels.

Thermocouples with remote logger: K-type thermocouples with a nominal temperature range of 200 C to 1370 C were mounted directly on the Support Structure to measure *in-situ* the plume temperature at the gas measurement points. An eight-channel logger (Omega Engineering, Inc., model TC-08) was used to acquire the temperature readings from the thermocouples and store the resulting measurements in an electronic data file for subsequent workup. The temperature measurements were collected continuously at a frequency of 1 point/sec for each of the eight channels. The thermocouples were attached directly to the Support Structure at eight of the ten gas measurement points and interfaced to the remote logger. The temperature and gas sensors measurements were performed simultaneously. Since the thermocouple logger accommodated eight channels, two out of the ten measurement points for the gas sensors consisted only of a pneumatic line without temperature measurements. These two positions were identified as positions 9 and 10 and corresponded to the lowest positions on the Support Structure.

Fig. 5 – An electro-chemical O_2 sensor.

Integrated system

The prototype analyzer was designed for easy on-site assembly and placement for facile field deployment. The integrated system refers to the Analyzer Box pneumatically interfaced to the Support Structure and electronically connected to a computer DAQ and control system. Data collection of the sensor readings and control of the 10-position multiport valve was performed by a LabView®-based DAQ system operated by custom software developed specifically for the prototype analyzer (Bloomfield Automation, Denver, CO). The DAQ system controlled the position of the multiport valve as well as recorded the temporal output signals of the TC Sensor, the O_2 sensor, and the T and RH sensing elements integrated into the TC sensor. The integrated T and RH sensing elements analyzed the test gas after it had been drawn from the plume though the pneumatic system, while the thermocouples measured the gas temperature within the plume. The DAQ logging rate for the TC hydrogen and oxygen sensors was 4 pts/sec (e.g., the sensor response was updated every 250 ms) [22]. The DAQ displayed in real time the hydrogen concentration from the TC sensor for each of the ten measurement points. At the same time, the thermocouples mounted on the Support Structure measured the temperature of the plume through a remotely deployed eight-channel thermocouple reader and data logger. The logged data was designed to be analyzed following the deployment by spreadsheet software to provide temporal profiles for each of the ten gas sampling points, overlaid with temperature data from the eight thermocouples.

Operationally, the gas from one specific measurement point was sampled and analyzed by the sensors for a fixed time, typically 10 s, but longer times could be used. The pneumatic lines had an inner diameter of 0.16 cm (0.0625 in) and were up to 15.25 m (50 ft) in length for an approximate volume of 30 cm^3 and would be purged in 0.6 s at flow rates of 500 sccm. The actual measurement point was controlled by the position of the multi-port valve, which in turn was controlled by the DAQ. Since the sensors were logged at a rate of 4 pt/s, each 10-s window contained 40 data points. At the end of the 10-s sample time (or other user-selected measurement time), the valve position would be automatically advanced by the computer DAQ system to collect gas for analysis from the next measurement point. Once all ten measurement point positions were sampled (10 s at each), the cycle would repeat. Thus, in this field deployment each measurement point was analyzed once every 100 s.

Field deployment—performance and findings

The prototype Cold Hydrogen Plume Analyzer was field deployed at an industrial LH_2 storage facility during a

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scheduled delivery operation. This represented one of the first field measurements on an actual hydrogen plume formed during a routine LH_2 release. The delivery process included transfer of LH_2 from a road tanker truck to an on-site stationary storage vessel and the subsequent post-transfer depressurization venting. The depressurization process employed during the site visit differed from the protocol that was previously specified to the NFPA Task Group (e.g., approximately 50 kg of hydrogen is released through the stationary storage tank vent stack over a period of up to 1 h). The actual venting was performed for significantly less time than the 1-h estimate. The depressurization process during the field test included a venting through the tanker truck vent stack and through the vent stack associated with the stationary storage vessel. The height of the stack on the tanker truck was approximately 4 m tall (13 feet), compared to 9.5 m (31.5 feet) for the vent stack on the stationary tank. The higher height of the stationary tank vent stack provides for a safer venting process, especially at smaller facilities. A portion of the hydrogen released through the stationary tank vent stack is shown in Fig. 6. It is noted that Fig. 6 captures only a moment in time and that the wind was quite variable such that the vapor stream continuously changed position laterally as well as vertically.

During the deployment of the analyzer, gas measurements were collected at the ten measurement points along the Support Structure. Fig. 7A shows the results obtained for measurement point 5 and can be used to illustrate the operation of the prototype analyzer. Measurement point 5 corresponded to the 25 foot (7.62 m) marking on the support structure, which was approximately 2 vertical meters (6 feet) below the release point. Information about the test conditions is also provided (e.g., "Event a," which is the stationary tank venting, and "Event b," which is the tanker truck venting). Specifically, Fig. 7A is a temporal plot during the LH_2 release for the vol% H_2, vol% O_2, and temperature at the indicated measurement point. Fig. 7A illustrates the data format obtained from the prototype analyzer. Comparable data were obtained from each of the ten measurement points. The test duration was 50 min and included two controlled events. "Event a" corresponded to the depressurization venting through the stationary storage tank stack, while "Event b" corresponded to the depressurization venting through the tanker vent stack. The prototype analyzer was deployed at a radial distance of approximately 2.4–3.0 m (8–10 ft) from the stationary storage tank vent and approximately 6.1–9.1 m (20–30 ft) from the tanker vent stack.

During the 50-min test, the temperature (the green line in Fig. 7) was measured continuously at eight measurement points by the *in-situ* thermocouples and is plotted as degrees Celsius. The vol% H_2 and vol% O_2 are indicated by the red and blue traces, respectively, but only for the time at which the multi-port valve was in Position 5, which was for 10 s out of every 100 s for the duration of the test. Each 10-s measurement window appears as an isolated "dot" in Fig. 7A but is in actuality forty distinct data points for both the oxygen sensor and the TC hydrogen sensor. This is illustrated in Fig. 7B, which shows an expanded view of the selected area in Fig. 7A. Fig. 7B shows the eighth measurement cycle for position 5. Each symbol in Fig. 7B represents a logged data point from the indicated sensor.

Fig. 6 – Deployment of the prototype Cold Hydrogen Plume Analyzer. During LH_2 venting through a 9.5 m (31.5 ft) stack.

Field measurements

Fig. 7A presents T, vol% H_2, and vol% O_2 for position 5. Plots for the other nine measurement points are given in Fig. 8, and the main analytic findings (e.g., maximum hydrogen and oxygen concentrations, largest temperature spike) are summarized in Table 1. There are several significant observations. First, for "Event a," which was the hydrogen venting through the 9.5 m (31.5 feet) tall vent stack on the stationary tank, the presence of hydrogen at levels significantly above the LFL was observed for numerous measurements points, including several that were below the point of release. This unequivocally clarified a question posed by the NFPA Hydrogen Storage Task Group, namely whether hydrogen buoyancy would be sufficient to preclude the presence of hydrogen below the release point. It was demonstrated that buoyancy will not totally dominate the hydrogen dispersion process. Not only will hydrogen be observed below the release point, it can be observed at significant concentrations. A hydrogen concentration of 12 vol%, which is three times the LFL, was detected at 2 m (6 ft) below the point of release. Even at 2.6 m (8.5 ft) below the point of release, hydrogen was detected above the LFL (5.6 vol%). The hydrogen concentration at the various measurement points was fluctuating during the release event. This is likely due to the variable wind speed and direction around the analyzer during the release. Thus, it is likely that wind speed and direction, especially downward drafts, can have a significant

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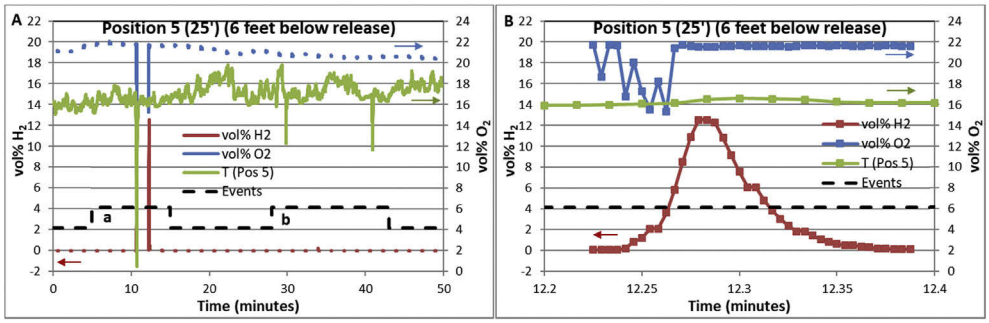

Fig. 7 – (A) T, vol% H_2, and vol% O_2 measurements from the prototype Cold Hydrogen Plume Analyzer for position 5 during the field deployment. (B) Expanded view of the indicated area in (A) that shows the transient high hydrogen concentration. Measurement details are given in the text.

impact, but this needs to be quantified. It was also found that the average temperature as measured by the thermocouples mounted on the support structure was essentially ambient (ca. 17 C–18 C), but there were sporadic and fast cold temperature transients. The temperature transients could be quite cold; for example, a temperature below 20 C was observed during "Event a" at measurement position 3, which was below the release point. There was not, however, a strong correlation of hydrogen level to the low-temperature transients, and thus, the transients were not likely due to droplets of hydrogen. It is postulated that these transients are due to condensed droplets of air or chilled air that came near the

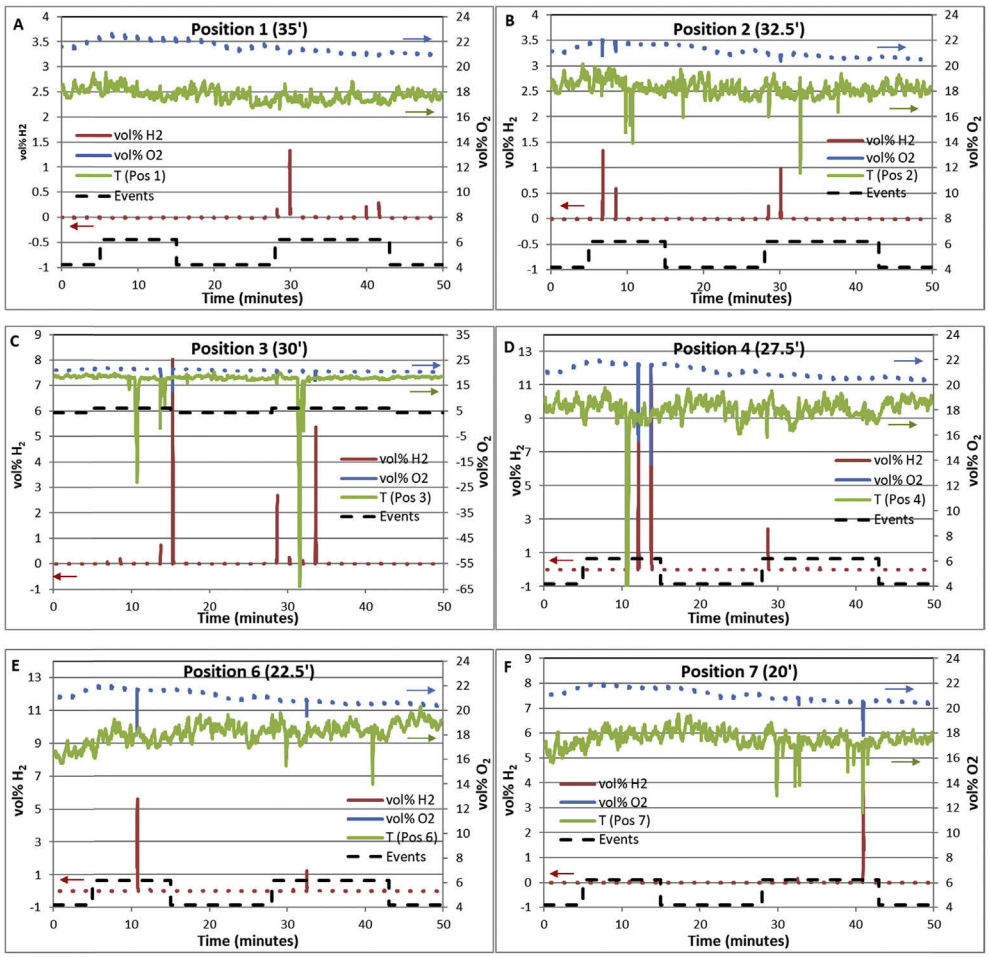

Fig. 8 – Vol% H_2, vol% O_2, and T measurements for nine measurement positions from the other nine measurement points (labeled A-I) on the prototype Cold Hydrogen Plume Analyzer during actual LH_2 releases. vol% % H_2, is plotted on the left abscissa, while vol% O_2, and T data is on the right abscissa.

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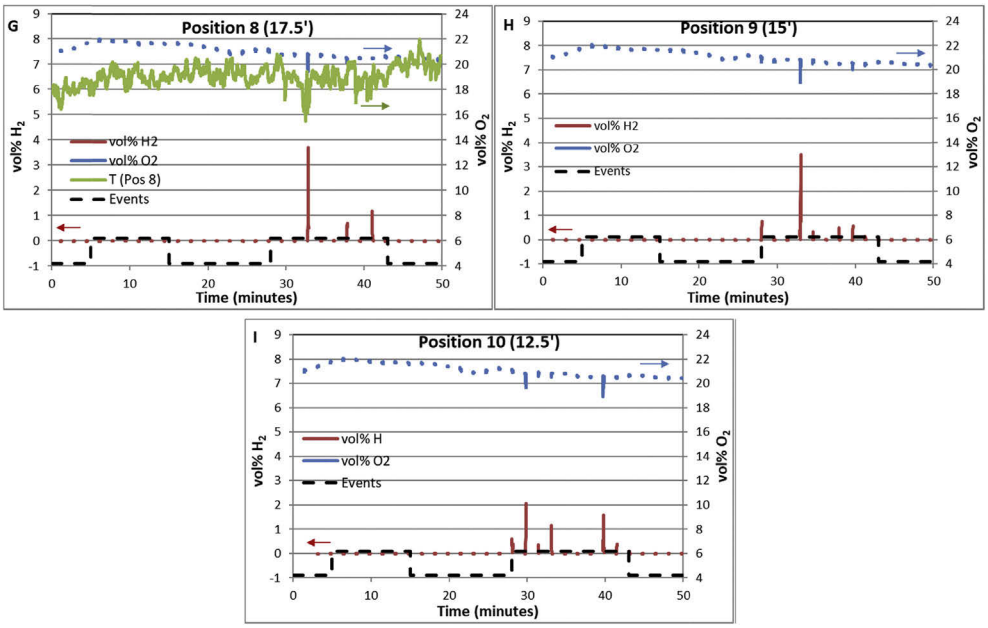

Fig. 8 – *(continued)*.

Table 1 – Summary of measurements by the prototype Cold Hydrogen Plume Analyzer for LH_2 venting.[a].

Position	Event A: Stationary Vent Stack (31 feet) (8–10 radial feet from release point)					Event B: Tanker Vent Stack (13 feet tall) (30–40 feet from release point)				
	Δheight (ft)	$(vol\%\ H_2)_{max}$	$(vol\%O_2)_{min}$	T_{min} (C)	T_{ave} (C)	Δheight (ft)	$(vol\%\ H_2)_{max}$	$(vol\%\ O_2)_{min}$	T_{min} (C)	T_{ave} (C)
1	4.0	0.02	21.47	16.8	18	18.0	1.3	20.9	16.7	17.4
2	1.5	1.34	20.4	13.9	18.5	15.5	1.0	20.4	11.6	17.9
3	1.0	8.05	12.64	23	17.8	13.0	5.4	17.2	64.0	16.8
4	3.5	11.73	12.69	14.6	17.9	10.5	2.4	20.4	15.9	17.9
5	6.0	12.55	1.22	0.5	16.8	8.0	0.2	20.4	11.7	17.2
6	8.5	5.58	18.15	15.7	17.9	5.5	1.2	19.6	14.0	18.3
7	11.0	0.7	20.81	15.6	17.7	3.0	4.4	17.9	11.7	17.2
8	13.5	0.1	20.77	16.4	18.9	0.5	3.7	19.4	15.5	19.0
9	16.0	0.1	20.8	–	–	2.0	3.5	19.0	–	–
10	18.5	0.01	20.8	–	–	4.5	2.1	18.9	–	–

[a] The temporal raw data (in an excel spreadsheet) is available upon email request to the corresponding author).

thermocouple, but this is at present not confirmed. It is noted that these observations are preliminary and were made on a prototype analyzer; the quantitative relationship between temperature fluctuations and hydrogen concentrations should to be investigated more carefully, since it is the basis for the adiabatic approximation method for estimating hydrogen.

It is also noted that oxygen depletion was observed sporadically during "Event a" and "Event b." The decreased oxygen level sometimes occurred simultaneously with the hydrogen spikes, but this was not true for every hydrogen spike. Furthermore, a displacement mechanism on the amount of oxygen decrease did not quantitatively correlate to the hydrogen level. Thus, we did not observe a strong correlation of the between changes in the oxygen level with hydrogen.

"Event b" had comparable behavior, but it is noted that the horizontal distance from the "Event b" release point was significantly greater than that for "Event a; " and thus there tended to be a lower hydrogen concentration. Although the hydrogen concentration was generally lower, it was observed at nearly every measurement point and more frequently, and on several occasions was above the LFL. Temperature transients were also still observed, one of which was down to below 60 C.

Summary

Highlights of the field deployment

The deployment of the prototype Cold Hydrogen Plume Analyzer was one of the first field deployments using hydrogen sensors or other hydrogen detection technologies to directly measure hydrogen plumes formed during real-world LH_2 releases. In this deployment, personnel from the NREL

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Sensor Laboratory worked directly with facility personnel. Although anecdotal, the consensus of the site personal was that hydrogen would be routinely observed below the vent stack, even at ground level, an impression that was based on personal in-the-field experience. Hydrogen was in fact detected by the analyzer at almost every measurement position on the analyzer. Moreover, as part of site protocol, personal gas monitors for hydrogen were worn by site personnel during the LH_2 transfer and depressurization process. These personal gas monitors detect hydrogen at ground level, usually below the LFL. However, the prototype analyzer detected hydrogen above the LFL several times during the release process, both for "Event a" and "Event b," and at vertical positions below the release point. This observation confirmed that hydrogen buoyancy will not be the sole factor controlling the dispersion of a cold hydrogen plume.

Although we did observe oxygen depletions during the operation of the analyzer during "Event a" and "Event b", it could not be quantitatively correlated to hydrogen by simple displacement of air/oxygen by hydrogen. Similarly, although a vapor cloud was observed, there was little relationship to high hydrogen concentrations at the measurement point, but this needs to be assessed under improved measurement protocols, such as those recommended below in the critique of the analyzer. Ambient weather conditions, most notably the wind speed and direction, did appear to have a strong influence on the measurements, and more data are necessary to quantify this effect, as well as the impact of ambient T and RH.

Critique and recommendation on the design and operation of the analyzer

The prototype Cold Hydrogen Plume Analyzer performed as designed and provided critical data on the behavior of LH_2 releases. Although the main goal of the field deployment was to provide the NFPA 2 Task Group with critical data on the behavior of the vented hydrogen, it was also important to assess the performance of the tools developed to obtain this information in order to improve data quality in future deployments. It is emphasized that the version of the NREL Cold Hydrogen Plume Analyzer used in this deployment was the first prototype that was built to perform preliminary characterizations of hydrogen releases.

In terms of analyzer performance, it was shown that the sample collection system to the remote sensors can provide quantitative information regarding the hydrogen plumes, including hydrogen transients, such as that depicted in Fig. 7B. Conversely, while economical, the multiplexing of a single set of sensors with multiple measurement points using the multiport valve significantly limited the metrological capability of the analyzer. The hydrogen levels were fluctuating, and there was a clear loss of temporal resolution. Incorporation of a dedicated sensor (or set of sensors for multiple target analytes) for each measurement point or sample line would eliminate the need for multiplexing. This simple step alone would improve the time response for hydrogen profiling from 100 s to 250 ms. The use of multiple sensors will lead to an increased cost, but the overall system would still be low cost (<$10,000), depending on the number of measurement points per analyzer. As an interesting embellishment, multiple analyzers could be used cost-effectively within a facility to provide low-cost wide area monitoring (WAM), which could serve as either a research tool or a facility safety monitor system [19]. The operation of the analyzer is simple and could be configured for operation by untrained personnel or even for autonomous, unattended operation. The impact of weather parameters was significant on the hydrogen plume. It is a simple and important enhancement to add a wind speed and direction sensor to the system. These recommended upgrades are being implemented. In summary, potential upgrades, modifications, and deployments include:

- Dedicated sensors for each sample point for better spatial and temporal profiling
- In-situ sensors (e.g., physical sensors, special gas sensors)
- Ruggedized, more easily implemented support structures and integrated system
- Multiple analyzers for hydrogen wide area monitoring (HyWAM)
- Deployments in coordination with industrial partner under various ambient conditions (T, wind, RH)
- Ambient weather sensors for wind speed, wind direction, and humidity
- Simplified "push button" instrument operation for ready use by untrained personnel (e.g., delivery truck drivers).

Hydrogen wide area monitoring (HyWAM)

The Cold Hydrogen Plume Analyzer could be adapted with minor embellishments for applications such as autonomous, unattended, or wide area monitoring for hydrogen (HyWAM) [19]. Hydrogen wide area monitoring (HyWAM) refers to the temporal and quantitative 3-dimenasional spatial tracking of hydrogen plumes following either intentional or unintentional hydrogen releases. HyWAM is a means to improve safety at medium sized facilities such as fueling stations to large scale hydrogen operations such as those envisioned by H2@Scale [24]. Although originally developed for LH_2 profiling, the analyzer is amenable for GH_2 facilities as well. The NREL HyWAM would include an array of ruggedized support structures, instrumented with multiple hydrogen measurement points. Additional gas sensors (e.g., oxygen, select air quality sensors) could be incorporated at appropriate measurement points. Physical sensors (T, pressure, RH) and environment sensors (wind speed, wind direction) will be also incorporated. The Analyzer Box for the gas sensors would be configured into a ruggedized, professional instrument case or panel with display. The support structures would be ruggedized and modified for easier deployment. Multiple structures or other mounting strategies could be used to situate units at various horizontal distances around the hydrogen storage and use facilities. Such a system would be a powerful research tool to properly characterize hydrogen plume dispersion following releases; it could also be a valuable facility safety monitor and could be one viable mitigation strategy to alleviate the NFPA 2 setback distances for LH_2 storage [1]. The integrated HyWAM system could include smart, remote, two-way communication to monitor hydrogen levels in and around the facility, providing notification of hydrogen releases and migration

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behavior, especially for out-of-normal events associated with a hydrogen release (e.g., a leak or improper dispersion following a release). The control system for the HyWAM could initiate warnings and operations shutdown if a hazardous situation is detected.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2018.10.231.

List of Abbreviations

C	degrees Celsius
cm	centimeter
DAQ	data acquisition
DOE	Department of Energy
FCEV	fuel cell electric vehicle
ft	feet
GH_2	gaseous hydrogen
H2	hydrogen
HSL	Health and Safety Laboratory (Buxton, United Kingdom)
HyWAM	Hydrogen Wide Area Monitoring
IFC	International Fire Code
in	inch
LFL	lower flammability limit
LH_2	liquid hydrogen
NFPA	National Fire Protection Association
NREL	National Renewable Energy Laboratory
O_2	oxygen
m	meter
RH	relative humidity
sccm	standard cubic centimeter per minute
T	temperature
TC	thermal-conductivity

REFERENCES

[1] NFPA 2. Hydrogen technologies code. 2016.
[2] Fuel Cell-Powered Forklifts in North America. Available from: https://docs.google.com/spreadsheets/d/128eaCVybwMhhGiaDF5zVYW5Qib8cthM1_5n8zoeLz2g/pub?output=html. [Accessed 30 March 2018].
[3] Sandia National Laboratories: News Releases: Fuel cell-powered mobile lights tested, proven, ready for commercial use n.d. Available from: https://share-ng.sandia.gov/news/resources/news_releases/mobile_lights/. [Accessed 30 March 2018].
[4] Fuel cells for backup power in telecommunications facilities–providing a constant, reliable electric power supply. DOE Brochure; 2009.
[5] Sprik S, Kurtz J, Saur G, Mike P. Hydrogen station data collection and analysis, 2017 DOE hydrogen and fuel cells annual merit review. 2017. Washington DC.
[6] Hydrogen Density at different temperatures and pressures | Hydrogen Tools n.d. Available from: https://www.h2tools.org/hyarc/hydrogen-data/hydrogen-density-different-temperatures-and-pressures. [Accessed 28 March 2018].
[7] McCarty RD, Hord J, Roder HM. Selected properties of hydrogen (engineering design data)–saturation properties for hydrogen — pressure increments. 1981. https://webbook.nist.gov/cgi/fluid.cgi?Action=Load&ID=C1333740&Type=SatT&Digits=5&PLow=.5&PHigh=1.5&PInc=.1&RefState=DEF&TUnit=K&PUnit=atm&DUnit=kg/m3&HUnit=kJ/mol&WUnit=m/s&VisUnit=uPa*s&STUnit=N/m.
[8] NASA report NSS 1740.16, safety standard for hydrogen and hydrogen systems: guidelines for hydrogen system design, materials selection, operations, storage and transportation. 1997.
[9] Cassutt LH, Maddocks FE, Sawyer WA. A study of the hazards in the storage and handling of liquid hydrogen. In: Timmerhaus KD, editor. Advances in Cryogenic Engineering. Springer US; 1960. p. 55–61.
[10] Hooker P, Willoughby D, Hall J, Royal M. Experimental releases of liquid hydrogen. Inst Chem Eng Symp Ser 2012;XXIII:496–504. Hazards.
[11] Royal M, Willoughby D. Releases of unignited liquid hydrogen, HSE Research Report. 2014. http://www.hse.gov.uk/research/rrhtm/rr986.htm. [Accessed 23 April 2018].
[12] Giannissi G, Venetsanos A. A comparative CFD assessment study of cryogenic hydrogen and LNG dispersion. Int J Hydrogen Energy 2018. https://ac.els-cdn.com/S0360319918319979/1-s2.0-S0360319918319979-main.pdf?_tid=54030404-d864-4520-97c3-05daf0c376b0&acdnat=1543520707_b0e0c4882d810a322d0003d8c6a36d1e. in press.
[13] Witcofski D, Chirivella J. Experimental and analytical analyses of the mechanisms governing the dispersion of flammable clouds formed by liquid hydrogen spills. Int J Hydrogen Energy Accept 1984;9:425–35.
[14] 2015 International Fire code (IFC). 2015.
[15] Buttner, William. The NREL hydrogen sensor laboratory–safety sensor testing laboratory. National Renewable Energy Laboratory (NREL), Golden, CO.; n.d.
[16] Hecht ES, Panda PP. Mixing and warming of cryogenic hydrogen releases. Int J Hydrogen Energy 2018. https://doi.org/10.1016/j.ijhydene.2018.07.058.
[17] Ninomiya H, Yaeshima S, Ichikawa K. Raman LIDAR systems for hydrogen gas detection. Opt Eng 2007;46. 094301-1 – 094301-4.
[18] Dennis K, Maley L, Liang Z, Radulescu MI. Implementation of large scale shadowgraphy in hydrogen explosion

Please cite this article as: Buttner WJ et al., Empirical profiling of cold hydrogen plumes formed from venting of LH_2 storage vessels, International Journal of Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2018.10.231

phenomena. Int J Hydrogen Energy 2014;39:11346–53. https://doi.org/10.1016/j.ijhydene.2014.05.002.
[19] Buttner W. NREL record of invention ROI-18-28 wide area monitor for hydrogen releases within hydrogen facilities (HyWAM). 2017.
[20] Buttner WJ, Post MB, Burgess R, Rivkin C. An overview of hydrogen safety sensors and requirements. Int J Hydrogen Energy 2011;36:2462–70. https://doi.org/10.1016/j.ijhydene.2010.04.176.
[21] Hübert T, Boon-Brett L, Buttner W. Sensors for safety and process control in hydrogen technologies. CRC Press; 2017. https://www.crcpress.com/Sensors-for-Safety-and-Process-Control-in-Hydrogen-Technologies/Hubert-Boon-Brett-Buttner/p/book/9781138894341. [Accessed 31 October 2017].
[22] Buttner W, Rivkin C, Burgess R, Hartmann K, Bloomfield I, Bubar M, et al. Hydrogen monitoring requirements in the global technical regulation on hydrogen and fuel cell vehicles. Int J Hydrogen Energy 2017;42:7664–71. https://doi.org/10.1016/j.ijhydene.2016.06.053.
[23] Buttner WJ, Burgess R, Rivkin C, Post MB, Boon-Brett L, Palmisano V, et al. An assessment on the quantification of hydrogen releases through oxygen displacement using oxygen sensors. Int J Hydrogen Energy 2014;39:20484–90. https://doi.org/10.1016/j.ijhydene.2014.03.252.
[24] DOE. H2@ scale. 2017. https://www.energy.gov/eere/fuelcells/h2-scale.

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