
700-bar Hydrogen Dispenser Hose Reliability Improvement

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Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Characterize and improve the reliability of 700-bar hydrogen refueling hose assemblies, and ultimately reduce the cost of dispensing hydrogen into fuel cell electric vehicles, by working closely with original equipment manufacturers (OEMs), such as SpirStar and others developing advanced high-pressure hydrogen hoses, to identify points of failure.
- Operate a fully automated test system that unifies the four stresses of pressure, temperature, time, and bending.
- Identify compounding impacts of high-volume 700-bar fuel cell electric vehicle refueling that has yet to be experienced in today's low-volume market.
- Determine any relative changes in bulk properties and degradation mechanisms of the inner hose liner due to the stress of repeated fueling events using pre- and post-cycling chemical and physical analysis.

Fiscal Year (FY) 2018 Objectives

- Continue hose cycling toward 25,000 cycles or until failure using the test apparatus that unifies the stresses to which the hose is subjected during high-volume fueling events.
- Gather and analyze data on hydrogen leakage rates, timing, and sources through the use of a vacuum sampling pump system with combustible gas detectors and the deployment of chemochromic leak-indication tape.
- Use data and observations to help inform preventative-maintenance schedules and standards development for hydrogen stations.
- Perform post-failure materials testing on failed field samples to further understand potential design flaws and stressors on the inner layer.

Technical Barriers

This project is conducting applied research, development, and demonstration to reduce the cost of hydrogen delivery systems. This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- (I) Other Fueling Site/Terminal Operations
- (J) Hydrogen Leakage and Sensors.

Technical Targets

This project aims to generate data that will help OEMs and hose developers improve reliability and replacement intervals for high-pressure gaseous hydrogen dispenser hoses. The data provided by this project ultimately will reduce the cost of hydrogen delivery from the point of production to the point of use in consumer vehicles by providing robust dispenser operation with reduced

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

maintenance costs and improved customer satisfaction.

- Target hose replacement interval: 25,000 cycles
- DOE ultimate target cost of hydrogen delivery: <\$2.00/gge.

FY 2018 Accomplishments

- Completed more than 5,000 cycles on Hose Assembly #2, running various cases of SAE J2601 H70-T40. Upgrades were implemented to the hose test stand to add hydrogen recycling and full-flow tankless capability analogous to SAE J2601 mass flow rates.
- Analyzed failed sample from field deployment of hydrogen refueling hose.
 - Pinhole leak observed at ~1,000–2,000 cycles, located 35 mm from nozzle end crimp fitting. Leak occurred despite using bend restrictors on hoses.
 - Steel overwrap braid layers observed as intact. Polyoxymethylene core around pinhole leak appeared to have significant impression damage from steel braids.

- Using optical microscopy and depth composition at 1,000-times magnification, groove impression depths were measured at 18 μm to 21 μm , a factor of 6 to 7 times deeper than a sample of pre-cycled hose with 2.5–3.2 μm impressions.
- Examined failure mode of pinhole leak and found evidence of plastic deformation and expanded polymer fibers near one end of pinhole. Other areas of pinhole exhibited sharp edges and loose fibers consistent with shear failure.
- Explored for evidence of high-density blistering on polyoxymethylene inner wall caused by hydrogen decompression. High-density blistering results were inconclusive, but large blister was observed 5 mm from failure with an area of 1,375 μm^2 , protruding 17 μm into hose core.
- Disseminated results and findings to OEMs, field station operators, and codes and standards groups to help inform inspection requirements and standards development.

INTRODUCTION

Operation and maintenance costs of dispensing are a large part of the cost of hydrogen stations. The National Renewable Energy Laboratory (NREL) has found that about 41% of maintenance hours for hydrogen fueling retail stations are associated with dispensers, with about 10% of those hours attributed to failed parts. This data can be found in NREL's infrastructure composite data products (CDPs) CDP-INFR-21 and CDP-INFR-24 [1]. These CDPs provide an early look at maintenance and reliability issues of the retail 700-bar vehicle refueling stations. Station operators have reported that they are replacing the high-pressure hoses earlier than expected, in intervals of a few months. Although high-pressure hoses are not a high-capital-cost item as compared to the nozzle and breakaway, the frequency of replacement could result in the high-pressure hoses becoming a significant lifetime cost over 10 years. This project focuses on accelerating the cycle rate, monitoring the leakage patterns, and continuing past the point of typical replacement to supply the OEMs with valuable data on post-cycled specimens to improve reliability.

APPROACH

This project aims to perform long-duration, accelerated life testing on commercial or prototype hose assemblies using high-pressure, low-temperature hydrogen to achieve realistic precooled fueling conditions closely following the SAE International J2601-2014 fueling protocol. This work is unique and goes beyond standard OEM and certification standards agency acceptance testing in that it simultaneously stresses the hose assembly by applying mechanical bending and twisting stress to the hose and nozzle assembly to simulate people refueling vehicles. The short time in between back-to-back fills simulates a busy station where the dispensing equipment is kept cold most of the time and subjected to frequent decompression and thermal cycles.

A hose reliability test stand, shown in Figure 1, was developed to support full 700-bar fueling simulation capabilities. The test stand uses a six-axis robot with pre-programmed motion paths to capture realistic stresses resulting from human interaction with the hose assembly while maintaining a compact footprint to safely operate in the high-pressure test bay, which offers a safe and controlled environment to test components to failure under high pressure while minimizing dangers to personnel or equipment. The test stand closely mirrors an actual dispenser in its design and pressure-ramping capabilities. A tankless control algorithm was successfully developed using the interaction of an air-loaded pressure regulator on the dispenser side of the test apparatus and flow control valves on the vehicle side. In FY 2018, upgrades were performed on the stand to add hydrogen recirculation capability and boost flow rates from 200 g/fill to 3–5 kg/fill.

The leakage rate of the hose is monitored over time using a hydrogen vacuum-pump sampling system attached to an outer protective sleeve near each flared crimp fitting to identify leaks as they occur. The flow rate is set to 400 mL/min and was calibrated to measure delayed response times. Chemoschromic leak-indication tape is wrapped over the hose end assemblies to further identify exact points of leakage, and potential inspection methods are verified at regular intervals. Data collected from the hose reliability test stand include pressure, temperature, and real-time leakage rates from crimp fitting areas. These data can be used to explore the dependency of leak intensity on current pressure and temperature.

Permeation of hydrogen through the polymer inner layers is a potential source of non-destructive leakage. Permeation activity typically follows the Arrhenius rate equation and is reduced with lower temperatures. However, temperatures that drop close to the glass transition temperature increase the brittleness of the polymer and the likelihood of internal damage to the polymer, allowing for easier permeation. Plotting the natural logarithm of the permeability rate and the inverse temperature allows correlation to the Arrhenius relationship and insights into the activation energy, or the ease of permeation of hydrogen through the polymer. Similar relationships have been tabulated for comparable polymers, but no study previously has been carried out for hydrogen and polyoxymethylene [2].



Figure 1. Hose reliability test stand

The project also includes analysis of the physical and mechanical property changes of the inner hose liner due to long-duration hydrogen cycling. Tests previously identified and performed on pre-cycled specimens include optical microscopy at 1,000- to 5,000-times magnification, and scanning electron microscopy to ultimately identify blistering and other surface damage. Superficial changes are expected due to several cycles of hydrogen permeation and rapid decompression during vent cycles.

Dynamical mechanical analysis is the primary characterization testing to identify material degradation and compositional changes by examining changes in thermal viscoelastic properties—including glass transition points—in response to applied stresses and temperature sweeps from -75°C to 150°C . These tests are repeated on post-cycled samples to compare any changes or degradations in the bulk polymer properties.

RESULTS

Hose Sample #2 had limited cycles this FY due to hydrogen station availability. Minor leaks continue to be observed. The amount of hydrogen lost per cycle was relatively small, with a mass loss rate of up to 500 microgram/s. Because the leak was smaller than many instrumentation tolerances, pressure checks did not fail and such a leak would go undetected in the field. There currently is only one code that has defined numerical criteria for leakage thresholds, set as 10 ccN/h, or 3,235 micrograms per second [3].

A failed field sample was sent to NREL from an operator of a hydrogen fueling station, who reported that hoses “were still experiencing through-wall failures. Blisters form on the ID which ultimately leads to a hole in the inner liner. The braids maintain hose integrity but not pressure integrity. Mean time before failure (MTBF) is on the order of 1,000–2,000 cycles.” The hose sample supplied had 250 mm long, 16 mm ID rigid bend restrictors installed on both ends. However, the leak was observed approximately 35 mm from the nozzle end, under the bend restrictor, in the same general location as the leaks observed in Hose Sample #2.

During disassembly of hose layers, each layer was inspected. The outer polyamide layer had a 25-mm large blister rupture due to buildup of leaking gas. All the steel overwrap braid layers were intact and undamaged. The polyoxymethylene inner core had significant damage, with an irregular through-wall hole and impressions on the external surface caused by the innermost steel overwrap braiding (Figure 2). There is no protective layer

between the innermost steel overwrap and the polyoxymethylene core. There was some extrusion of polymer material observed between the braids close to the failure location.

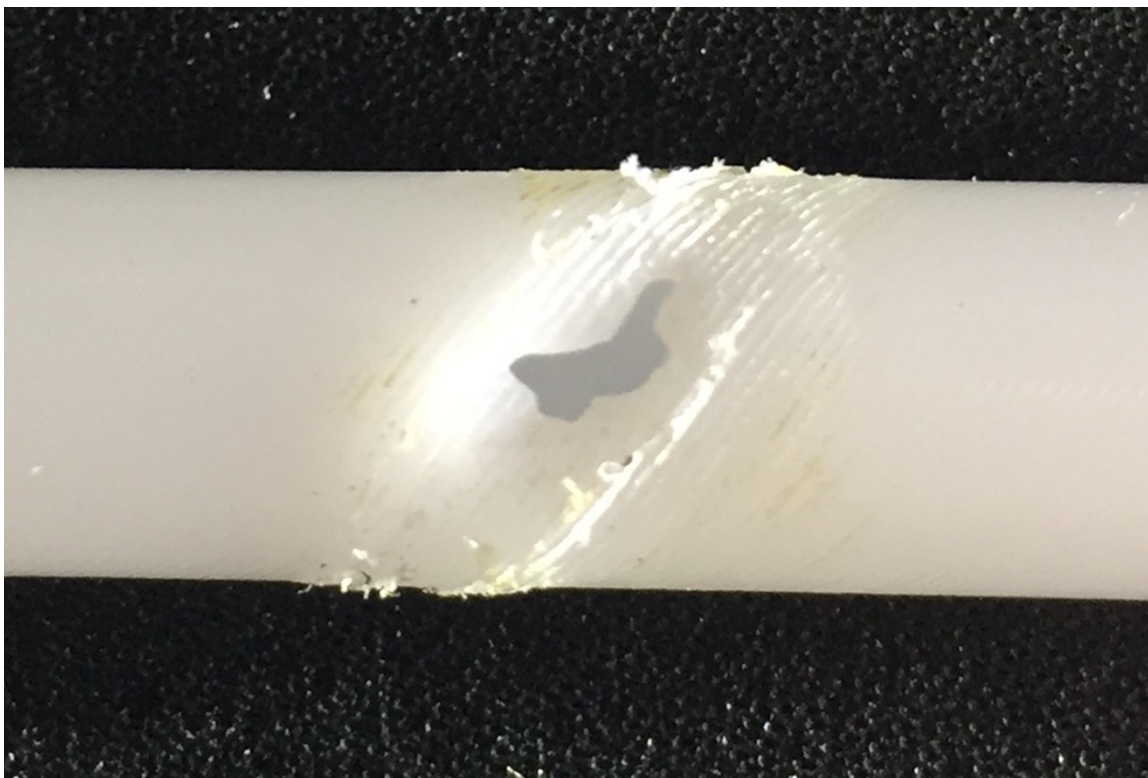


Figure 2. Hose inner-core pinhole leak and general damage

A Keyence VHX-5000 optical microscope with 1,000X lens and depth composition was used to measure the impression depths from the steel overwrap, compared to a pre-cycled specimen. The post-cycled failed sample was examined on the reverse side from the failure point. The measured impressions were 18–21 μm , and the pre-cycled specimen had impressions measured at 2.5 μm to 3.2 μm deep in the mid-hose (Figure 3). This is a factor of 6 to 7 times greater than pre-cycled, suggesting that continuous flexing of the inner braiding is impacting the core wall thickness and strength.

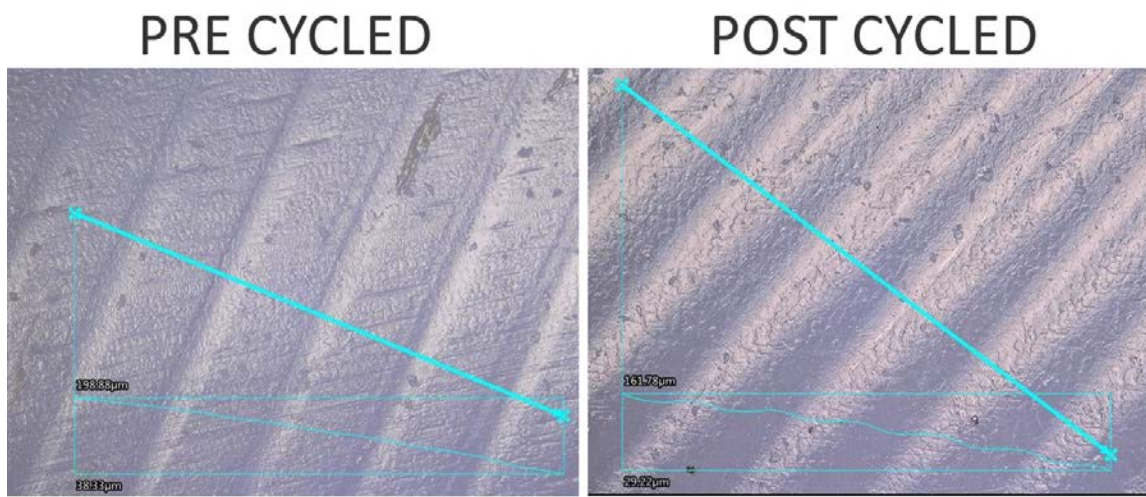


Figure 3. Comparison of wire-overwrap impressions on pre-cycled and post-cycled hose core

The pinhole leak was examined from the inside by cutting the core open, and evidence of plastic deformation and expanded polymer fibers was found near one end of the pinhole. Other areas of the pinhole inner wall exhibited sharp edges and loose fibers consistent with shear failure, suggesting that the pinhole leak started at soft spots in the wall and proceeded to expand through the core wall due to shear action of escaping hydrogen as shown in Figure 4. Small particulates from 90–300 μm were found on the outside wall, but no major particulates were found in the inner wall. The polyoxymethylene inner wall also was examined for evidence of high-density blistering caused by hydrogen decompression. Results were inconclusive at 1,000X compared to pre-cycled specimens, though some large isolated blisters were observed near the failure location. The largest blister observed was 5 mm from the failure location, with an area of 1,375 μm^2 , protruding 17 μm into the hose core.

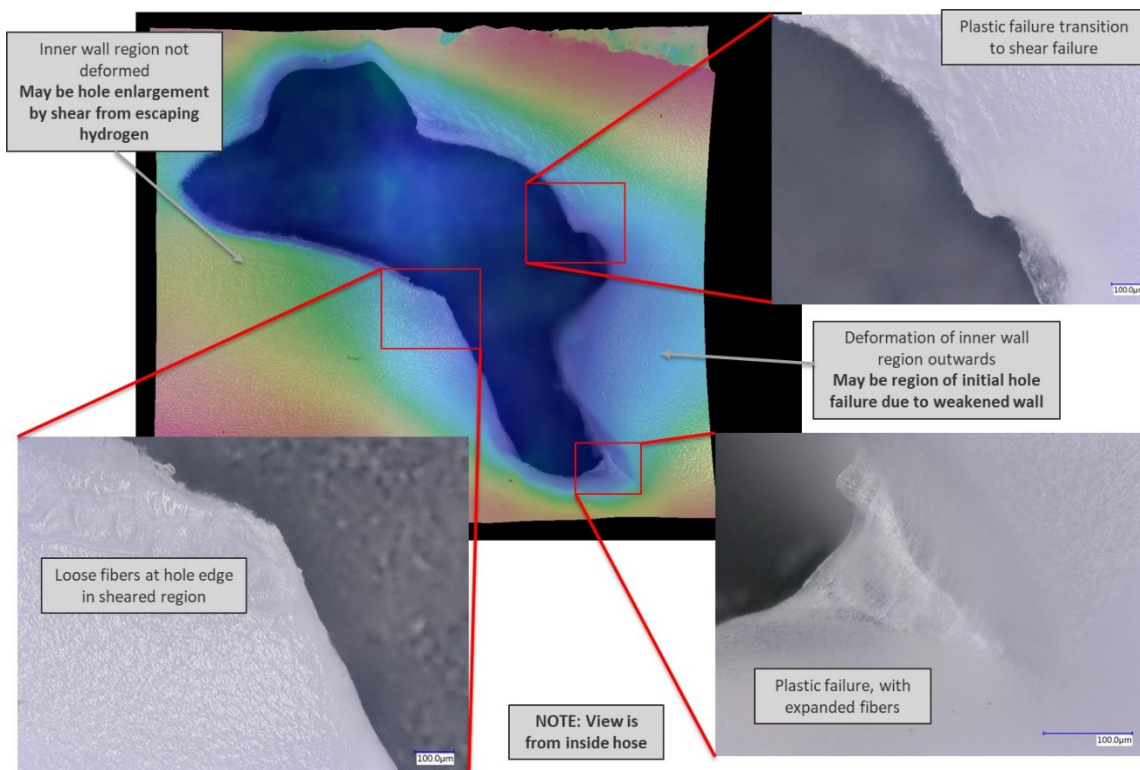


Figure 4. Analysis of pinhole leak failure modes

Data from these studies have been shared with the hose OEM, field station operators, and with standards groups such as the International Organization for Standardization to help inform standards development (e.g., ISO 19880-5 WG22).

CONCLUSIONS AND UPCOMING ACTIVITIES

- Conclusion:** Failures in the field occur in similar locations as those found in Sample #2, with damage observed from innermost steel-wire overwrap. These similarities indicate that test conditions at NREL simulate in-field conditions well. Large blisters were discovered on the inner layer, but the cause of high-density blistering is still inconclusive. There is evidence that plastic deformation led to initial failure.
- Upcoming:** Pull Sample #2, which has not failed but has a confirmed leak, to dissect and compare it to failed and pre-cycled samples. Using existing funding, set up dynamic mechanical analysis (Thermo-Fisher HAAKE MARS 60 with extended temperature chamber) to perform identified tests to measure viscoelastic response on failed hose, Sample #2, and pre-cycled samples.

- **Upcoming:** With future external funding, hoses from additional manufacturers can be tested and verified under similar test conditions and materials testing. The addition of high-flow controls and hydrogen recirculation will allow test profiles to be brought closer to real-world conditions and increase potential for thermal shocking.

REFERENCES

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