

700 Bar Hydrogen Dispenser Hose Reliability Improvement

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Project ID # PD100

Overview

Timeline

Project start date: June 2013

Project in continuous operation on sample hoses as directed by DOE, subject to hydrogen availability

Budget

To Date Total Spending: \$687.1k

- **\$96k carried over into FY18**
- **Remaining funds covers labor, maintenance, subcontracts**

Total DOE Project Value: \$775k

Internal NREL Funding

- **\$1.1M – 35/70MPa Fueling Station**
- **\$150k – Compression, storage, safety systems and chiller/HXR**

Barriers

• **3.2 – Hydrogen Delivery**

I. Other Fueling Site/Terminal Operations

“By 2020, reduce the cost of hydrogen delivery from the point of production to the point of use in consumer vehicles to <\$2/gge of hydrogen for the gaseous delivery pathway. (4Q, 2020)”

Partners

- **Spir Star AG**
 - Provided 3 hose assemblies for testing
- **NanoSonic, Inc.**
 - SBIR awardee and potential test articles
- **ISO Technical Committee 197 - WG 22**
 - Codes and standards development for hydrogen hoses
- **California Hydrogen Station Field Operators**
 - Shared operational experiences and failure rates
- **Sandia National Laboratory**
 - Burst testing on hose assembly
- **Colorado School of Mines**
 - Microscopy and rheology
- **Element One, Inc.**
 - Provided DetecTape leak indicator samples

Relevance - Project Objective

To characterize and improve upon 700 bar refueling hose reliability under mature market conditions

- By working closely with the original equipment manufacturers, the hose reliability project aims to **improve the reliability and thus reduce the cost** of 700 bar hydrogen refueling hose assemblies by identifying points of failure.
- NREL has designed a high-cycling test apparatus that **unifies the four stresses** to which the hose is subjected (Pressure, Temperature, Time and Mechanical) to reveal the compounding impacts of high volume FCEV refueling will be revealed.
- The work includes performing physical and chemical analysis on pre- and post-cycled hose material to understand any relative changes in its bulk properties and possible degradation mechanisms.



• This reporting period:

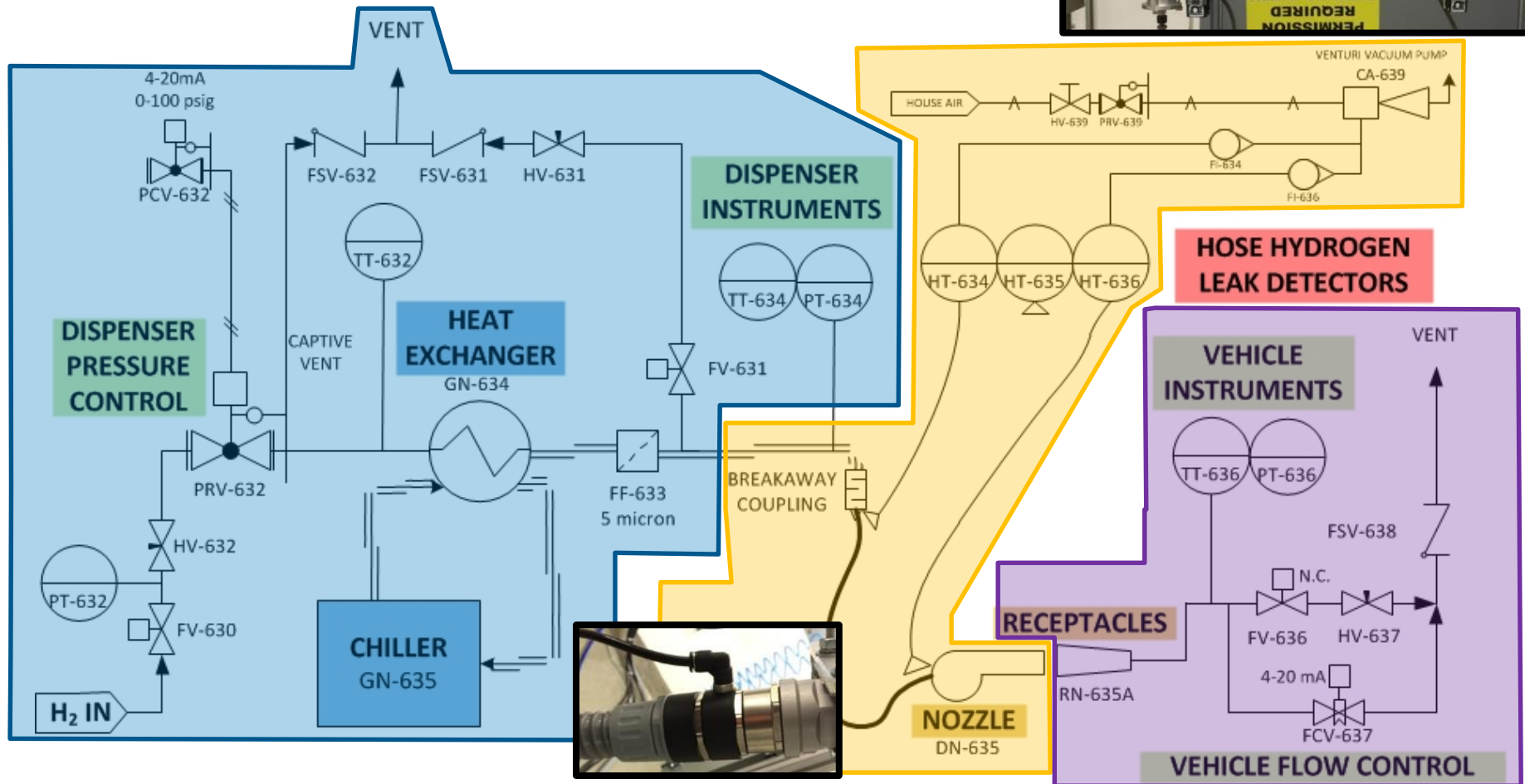
- SpirStar hose #2 leak continues, but remains functional
- Analysis of failed sample provided by partners:
 - Shows damage due to wear of innermost steel wire braiding
 - Failure on inside has both plastic and shear modes
 - Large blistering found on inner surface, no micro-blistering evident

Approach – Hose Test Stand System Design

- ‘Dispenser’ subsystem based on commercial dispensers

- Tankless flow control for low-mass, pre-cooled cycles

- Active leak sampling at hose interconnections



Progress – Hose Testing Status

Daily Operations

- 5000+ cycles completed* on Sample #2 running various cases of SAE J2601 H70-T40 with good accuracy on pressure controls. *As of 4/17/2018.
- Small, consistent leak previously reported still present, hose is still able to complete fills
- Hose operation rate dependent on station hydrogen availability, co-testing opportunities being explored to increase cycle rate

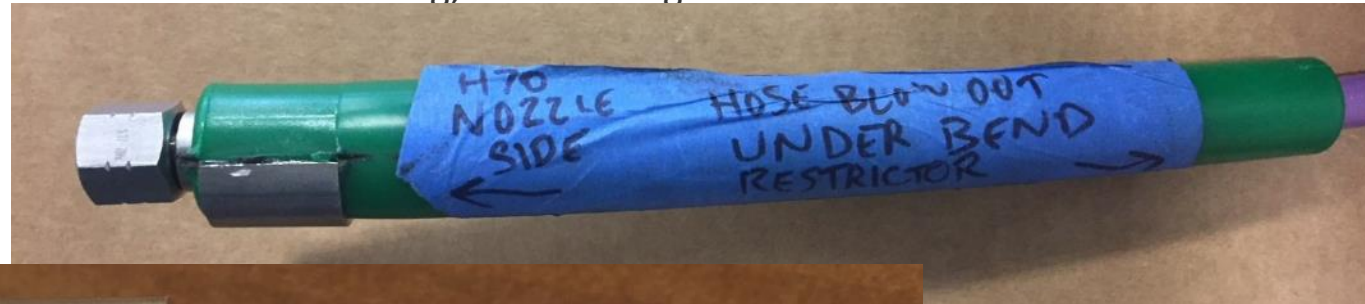
Failed Hose Analysis

- Data being gathered based on samples sent to NREL from field operator partners
- Current scope involves measurement of roughness and blistering via microscopy with depth composition
- Near-term scope involves repeating DMA testing using rheometer and a temperature sweep from -75C to 60C

Accomplishments – Failed Sample Analysis

– Report from Field Operator–

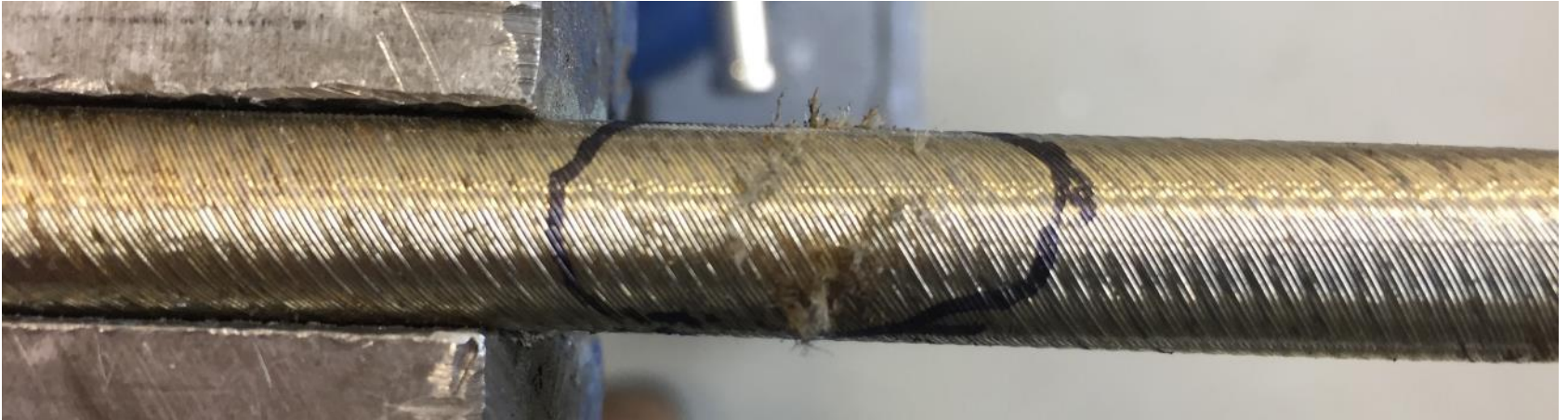
- “Still experiencing through wall failures. Blisters form on the ID which ultimately lead to a hole in the inner liner. The SS braids maintain hose integrity, but not pressure integrity. MTBF is on the order of 1000-2000 cycles.”
- Specific hose from station – had 250mm long, 16mm ID rigid bend restrictor



- 25 mm blister on outer jacket, centered 35 mm from nozzle crimp – similar location of consistent leaks on SpirStar hose #2. No other apparent blistering on outer layer or signs of damage on crimp.
- Wire braiding intact, yellow dirt observed between braiding and outer layer.
- Failed to hold any pressure – leaks from nozzle end. 275kPa leaks to atmosphere within 3 seconds.
- Observed some leaks still coming from permeation pinpricks during bubble check.

Accomplishments – Steel Overwrap

– Outer polyamide layer removed – fiber wrapping seen protruding through steel overwrap



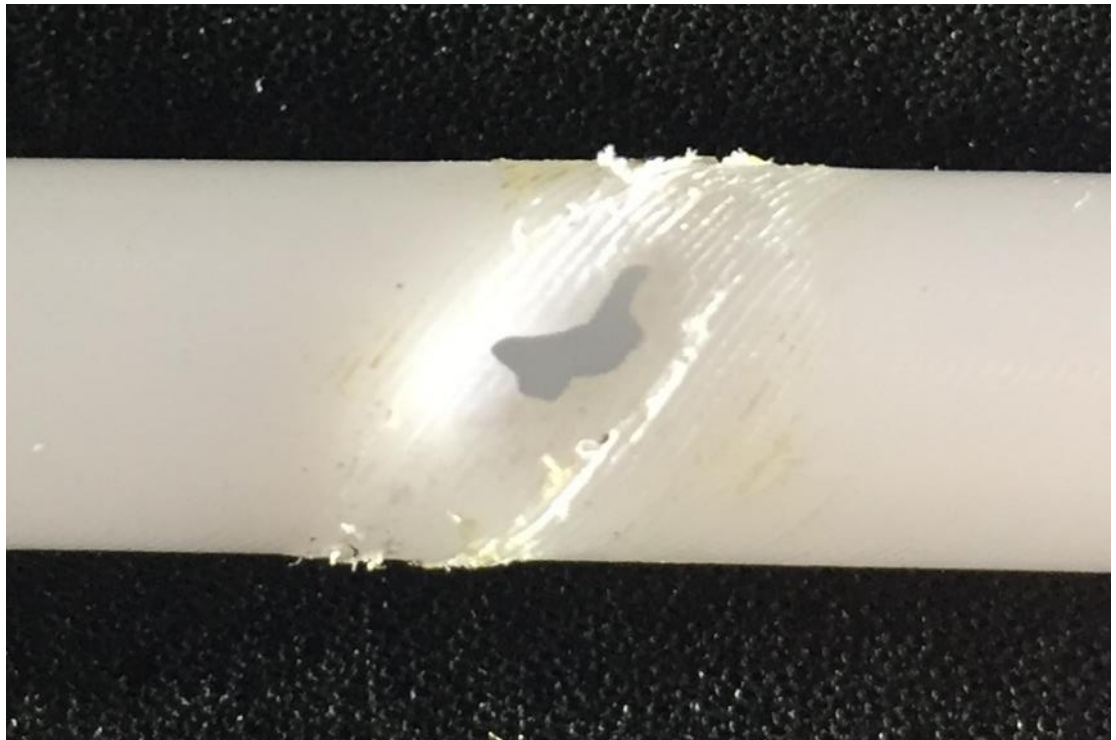
- Fiber wrap layers blown out by escaping gas for each layer. Steel wrap integrity intact. No damage or irregularity seen in any of the steel wraps, including first one directly on polyoxymethylene layer

Accomplishments – Inner Layer Damage

- All steel overwrapping removed. Polyoxymethylene inner layer shows light marking from steel overwrap and slight deformation from crimp fitting.

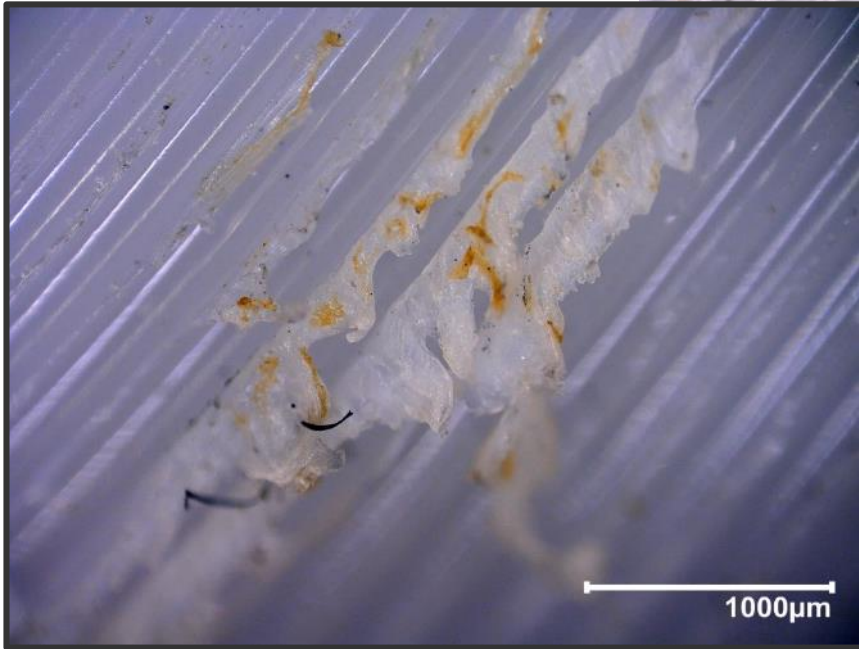
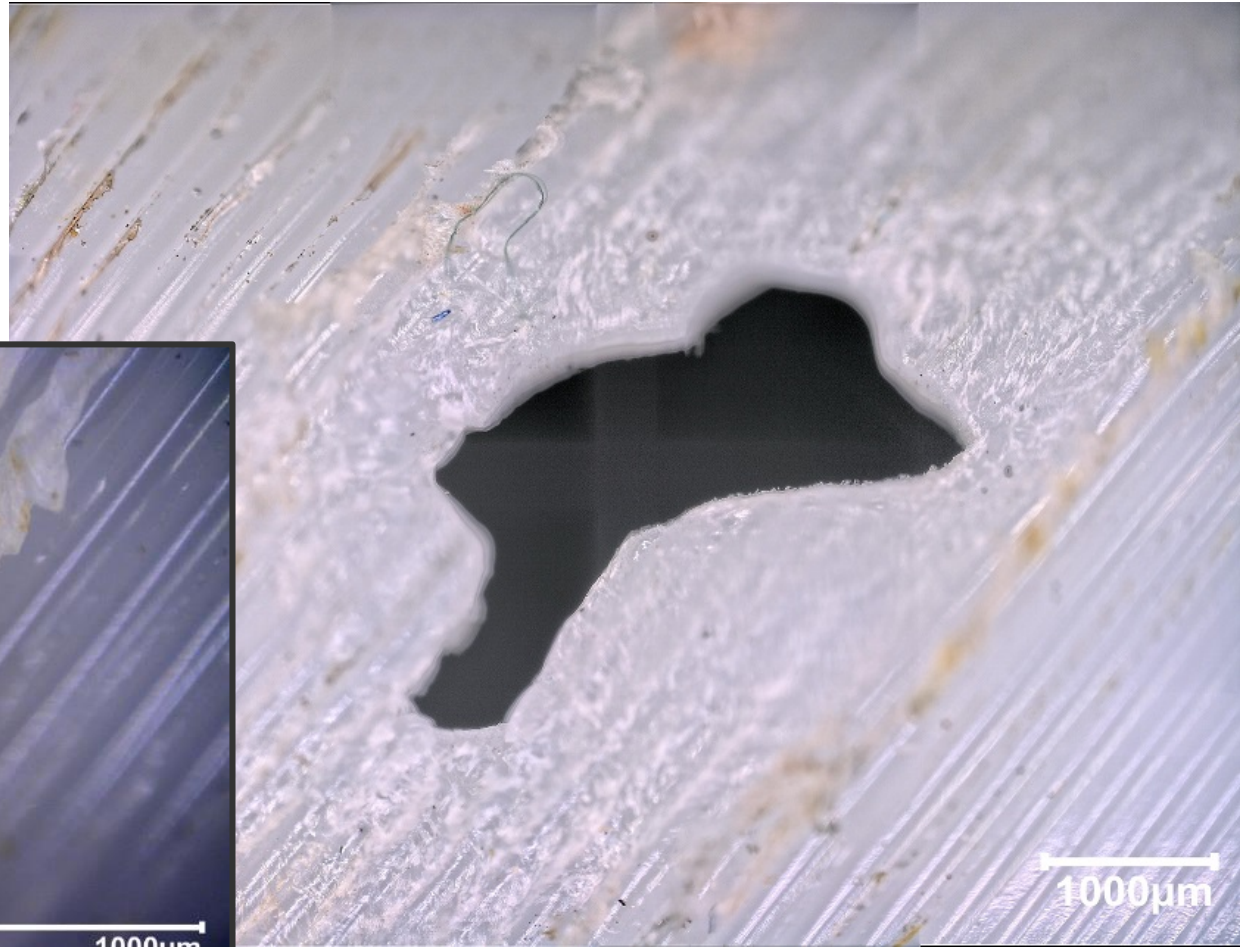


- Large hole in layer source of leak. Significant damage
- Hole irregularly shaped, 3.7mm x 1.3mm.
- Located along inner radius of longitudinal bending curve
- Gouge in inner layer following direction of first steel overwrap braiding, 9.2mm x 3.3 mm
- No protrusion into ID of hose
- Dirt observed in and around gouge



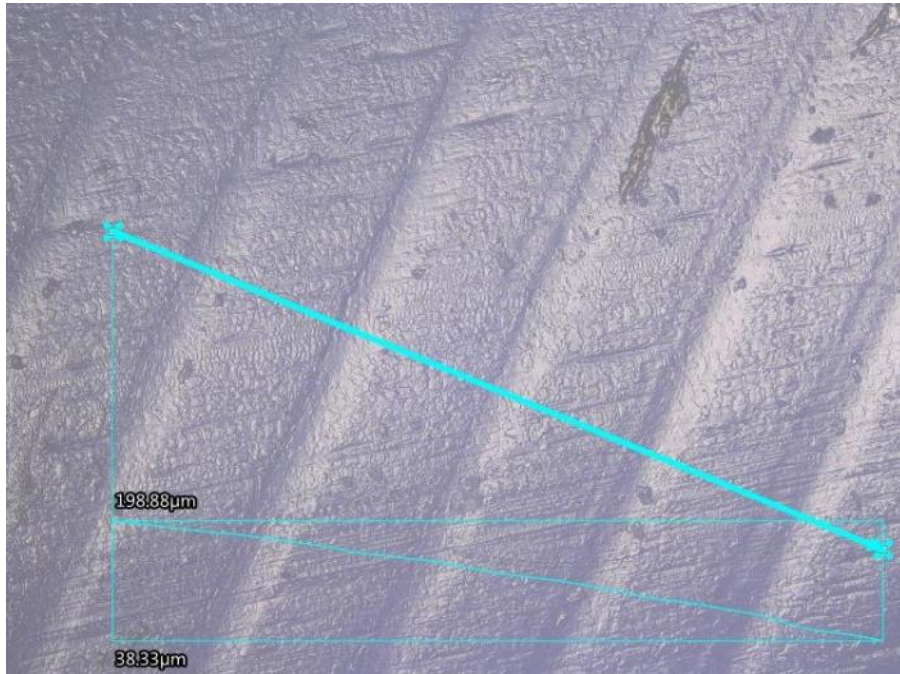
Accomplishments – Particulates

- Metal particles found distributed around hole
- Rust residue seen around polyamide outer layer hole
- 91-297 μm avg particulate size
- Extrusion of polyoxymethylene between wire braiding



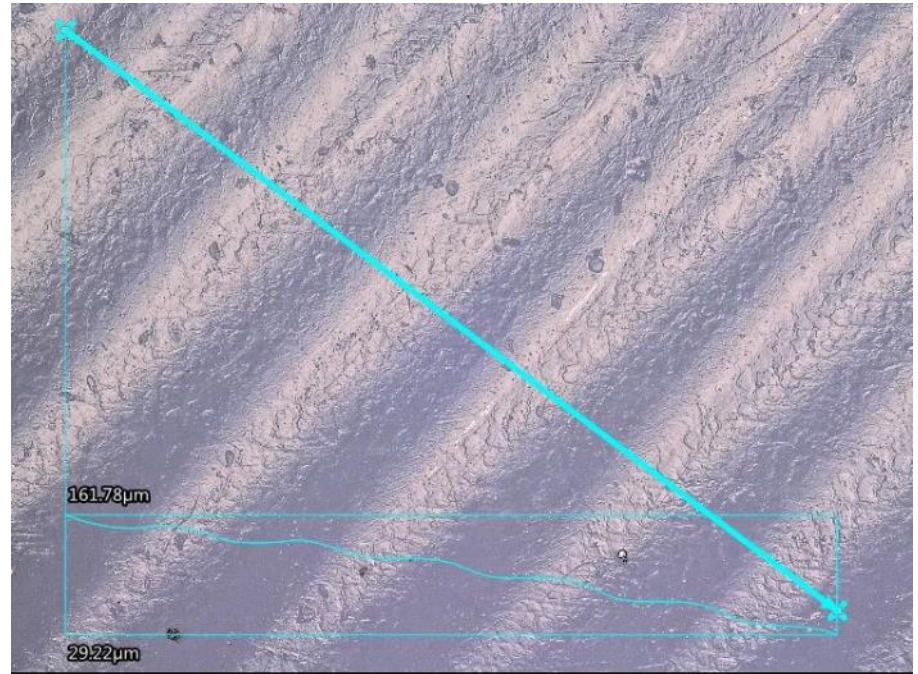
Accomplishments – Wire Braid Imprinting

PRE CYCLED



- Visible wire imprints along entire length of hose
- Sample taken from mid-range of hose
- Average depth of imprint: 2.5-3.2 μm

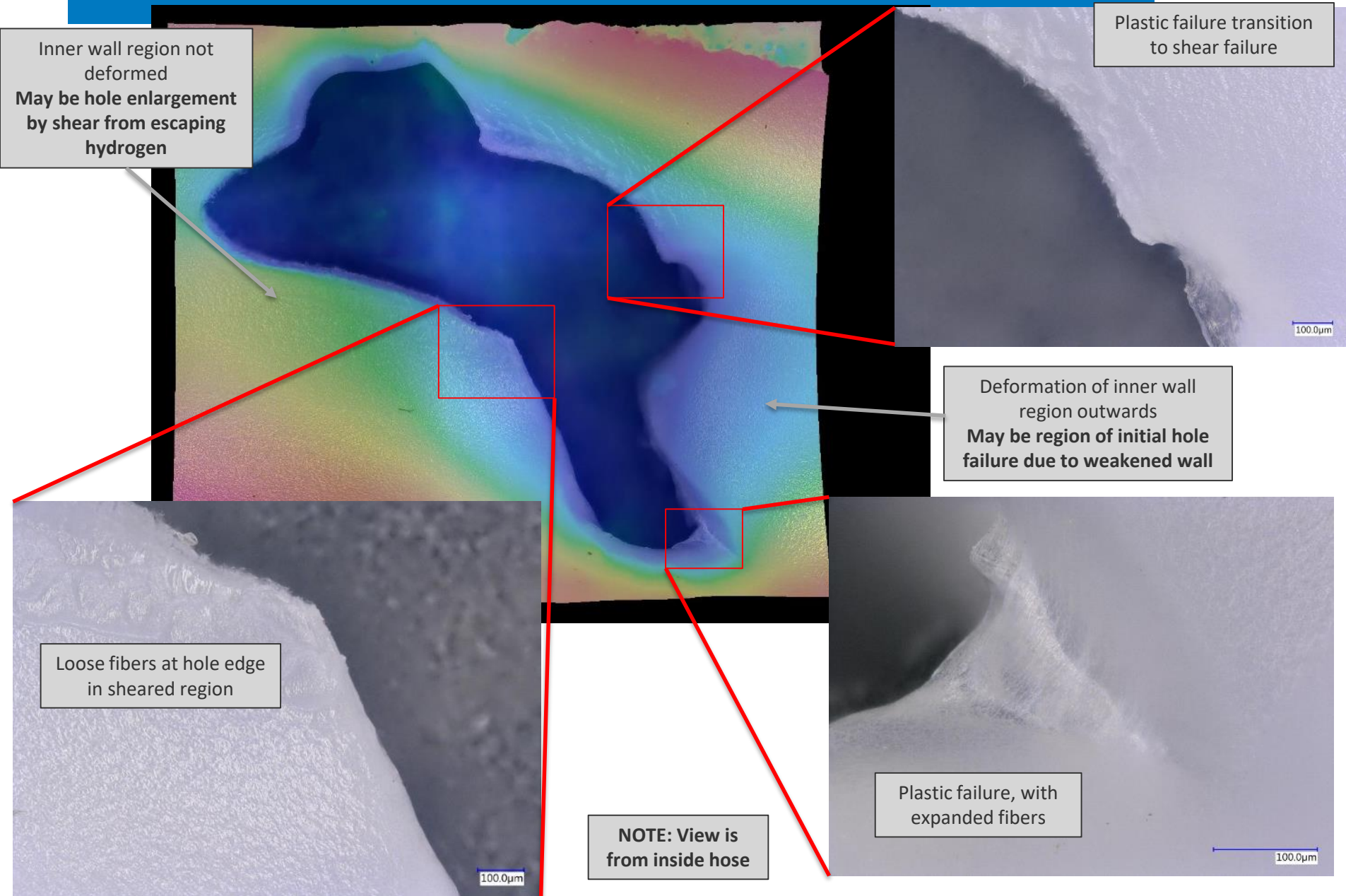
POST CYCLED



- Visible wire imprints along entire length of hose, more pronounced closer to nozzle end crimp fitting
- Sample taken from 7.5cm from end of hose, reverse side of failure area
- Average depth of imprint: 18-21 μm – **6-7x deeper**

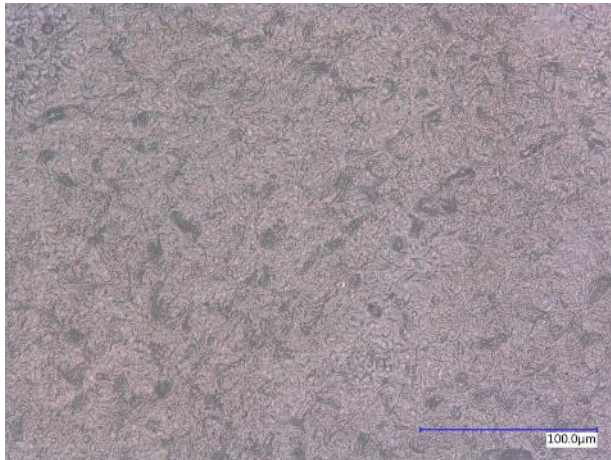
Images taken using Keyence VHX-5000 microscope with 100x-1000x lens and 3D depth composition measurement

Accomplishments – Failure Mode Analysis

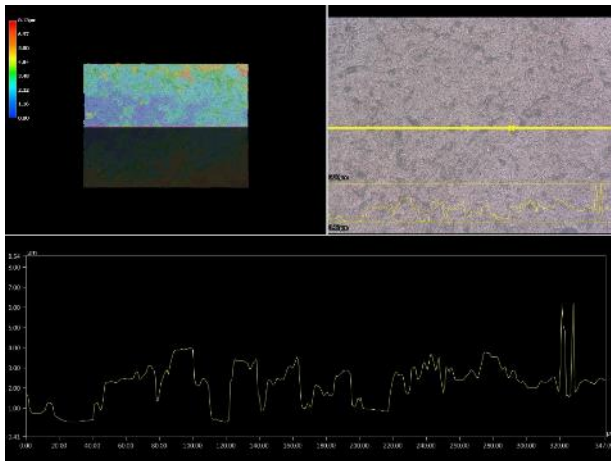


Accomplishments – Surface Blistering

PRE CYCLED

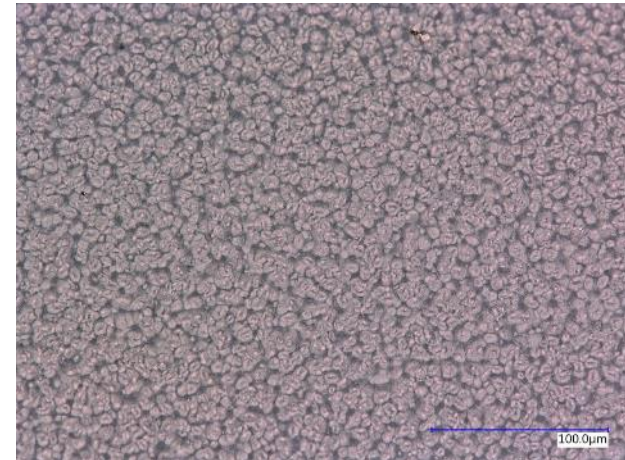


1000X magnification, surface appears glossier

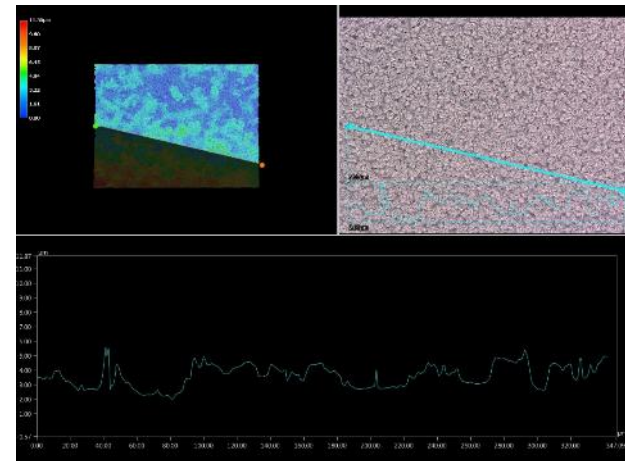


.75-3 μm depth, 15-30 μm width of surface irregularities

POST CYCLED



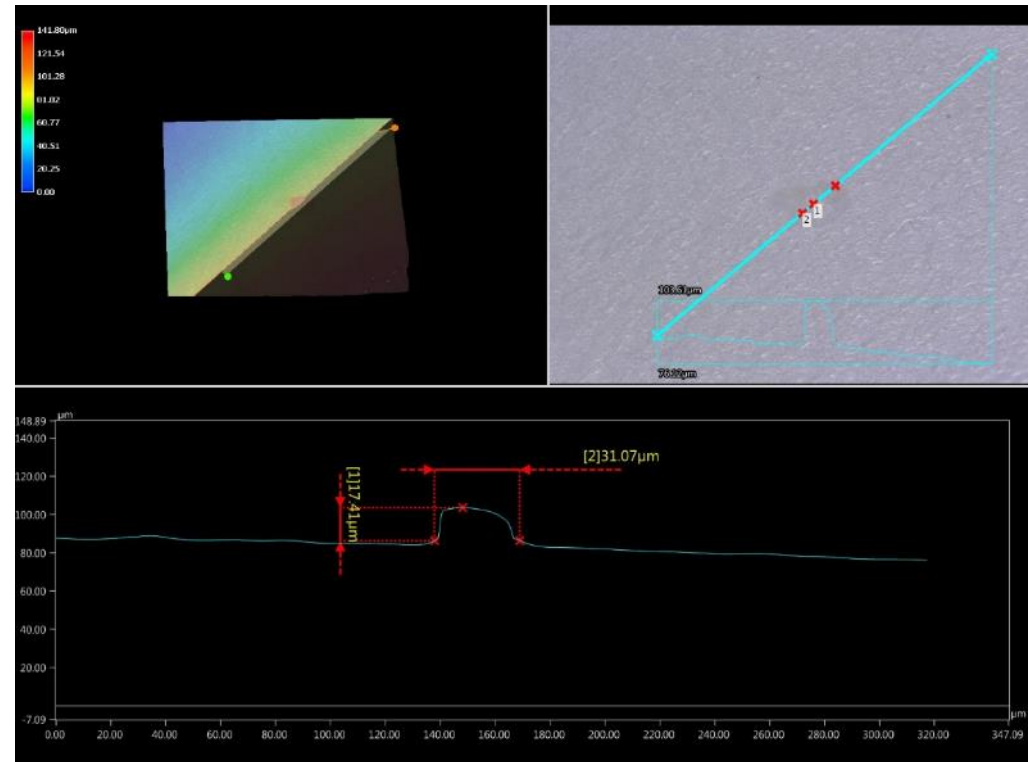
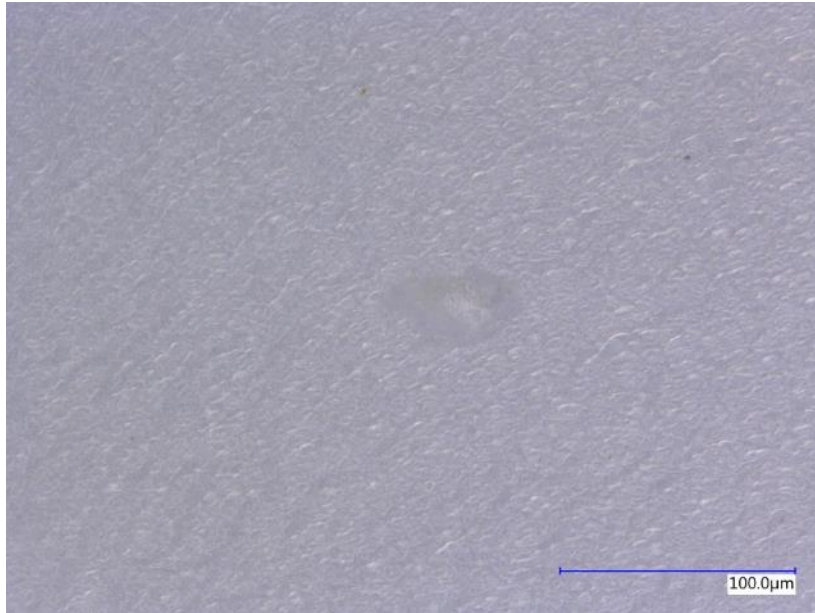
1000x magnification, surface appears more coarse



1-3.5 μm depth, 11-34 μm width of surface irregularities

Superficial change in surface, but no significant change in measured surface roughness at 1000X magnification that would indicate high-density blistering in mid-hose sample

Accomplishments – Large Blistering



- **Large blister discovered in sample at about 5mm away from failure region**
- Isolated blister, no other similar ones discovered nearby. Not suspected to be contaminant particle
- Blister protrudes into hose inner wall 17 μm, about 1375 μm² area

Progress - Leak Detection Comparison

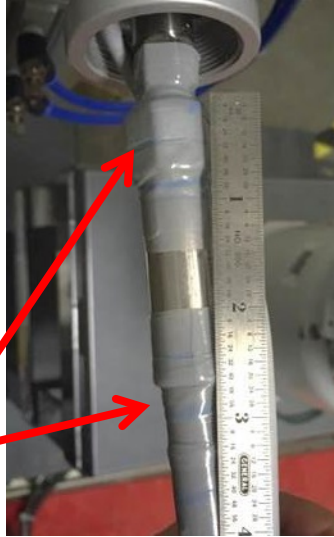


Chemochromic tape that darkens when exposed to hydrogen leaks.
- Provided by Element One, Inc.

Note: DetectTape has not yet been approved for use by the manufacturer under these conditions and this project is not intended to draw any conclusions on the performance of the tape.

Before

- Tape wrapped around hose near crimp fitting, and on metal fittings with leak detection ports
- No indications were seen after rechecking after 100 cycles without leaks



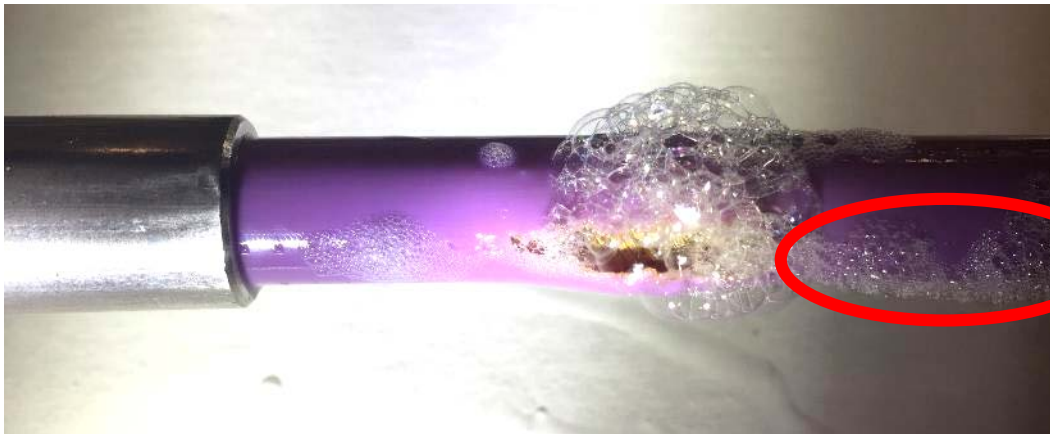
After – 1000 cycles

- Indication** seen on edge of hose crimp. May be due to gap between tape and fitting.
- Clear indications** seen on hose outer layer pinpricks at the nozzle-end crimp, around hose circumference
- No visible physical damage observed on hose surfaces, including at crimp fitting
- No indications on metal fitting leak detection ports



Comparison with Failed Sample:

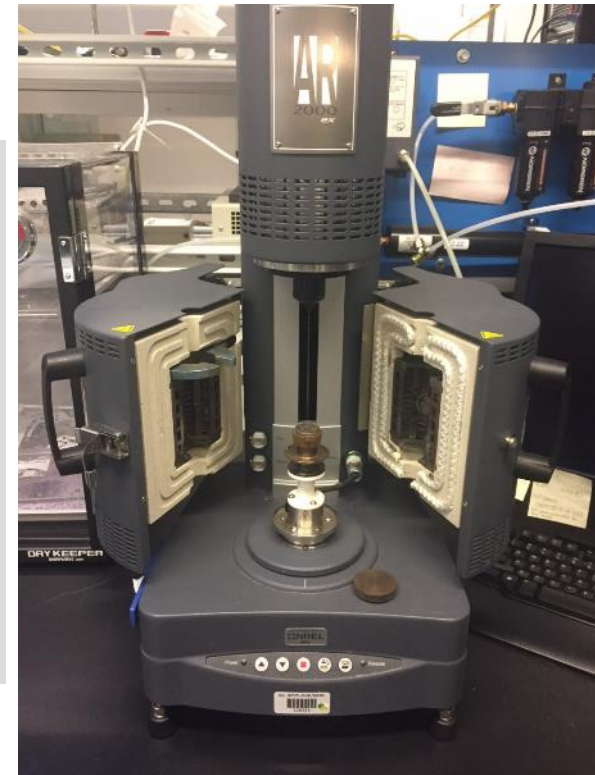
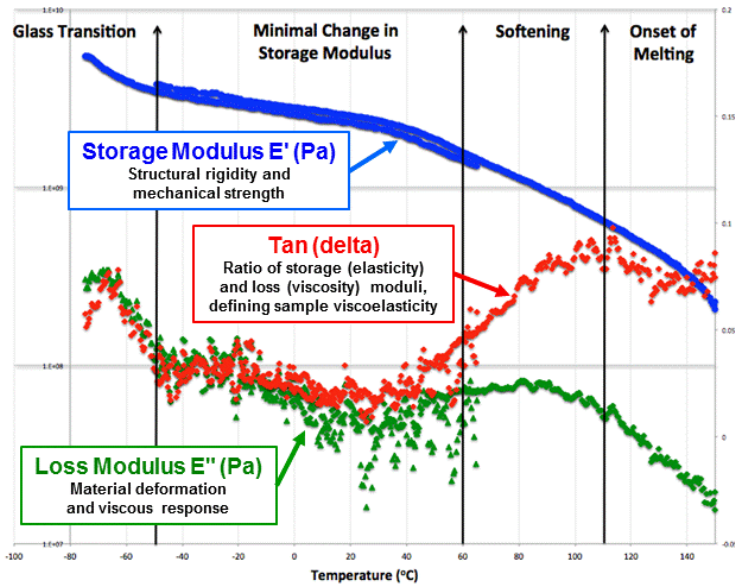
- Only one large leak source on failed sample
- Bubbles seen coming through nearby pinpricks during nitrogen test of failed sample. Likely transfer of gas through steel wire braiding



Chemochromic tape can be effective way to detect leaks on hoses, even when leak is not localized to tape

Future Work – DMA Rheology

PRE CYCLED



- TA Instruments AR-2000Ex rheometer being fitted with liquid nitrogen to enable temperature sweeps from -75C to 150C.
- Sample from section adjacent to failure point and sample from mid-point of hose will be compared to pre-cycled data to determine if glass transition points have shifted, and characterize changes in thermal viscoelastic properties in response to applied stress.

Any proposed future work is subject to change based on funding levels

Challenges – Resource Allocation

Prior Year Reviewer Comments

- The project needs to test faster and under more severe conditions to better replicate some of the failures seen in the field.
- The experiment needs to be able to isolate and mimic the conditions in the field to better understand the failure modes that the laboratory experiment is not addressing.
- The project should test under more rapid pressurization at both warm and cold temperatures and seek hoses that have failed in the field and apply analytical techniques to look at failure modes.

Station Resource Allocation

- Original cycle design was specified to minimize wasted gas, but still stretches the current hydrogen throughput to maximum
- HITRF (Hydrogen Infrastructure Testing and Research Facility) has multiple ongoing research projects and resource allocation is a challenge. Any concurrent project will mean that the hose testing project is put on standby.
- As part of station upgrades, a recycle system is being evaluated to recapture all hydrogen and pump back into station. This will enable both **increased cycle rates without excessively long recovery times** and **full-flow conditions, including rapid pressurization, thermal shock and warm gas mixing** to address reviewer concerns.

Future Work – Hose Cycle Testing

| Status | Milestones, Deliverables, or Go/No-Go Decision |
|---------------------------------------|---|
| Completed | Complete 1,000 cycles on Hose Assembly #2 or until failure (NREL Task 4) |
| Expected FY18 | Perform accelerated hydrogen cycling to 700 bar (nominal) on a hose sample to failure or 25,000 cycles, whichever occurs first. |
| Underway on failed hose sample | Perform post-cycling physical and chemical testing including DMA, SEM and other tests previously identified |

- Hose testing will continue in FY18 on Spir Star Hose #3 or other manufacturer samples as technical services agreements are developed.
- Hose Cycle Potential Upgrades:
 - Gas recycle system will be evaluated and installed to enable different cycle parameters to increase cycle rate, mass flow and potential for thermal shocks on hoses
 - Co-testing opportunities will be implemented when possible as part of hydrogen infrastructure research projects – i.e. using hose testing as a hydrogen sink from high pressure storage
- Any proposed future work is subject to change based on funding levels

Collaborations

- SpirStar AG
 - Provided dispenser hose test material and assemblies. Visited SpirStar headquarters to share feedback on project results.
- NanoSonic, Inc.
 - Candidate for future hose tests— SBIR Phase II “*Cryogenically Flexible Low Permeability Thoriaeus Rubber™ Hydrogen Dispenser Hose*” (Presented at 2017 AMR as **PD101**)
- ISO Technical Committee 197 – WG 22
 - Requested results for the standardization of ISO-19880-5 “*Gaseous hydrogen fueling station hoses*”
 - Ongoing conversation about leakage pass/fail criteria and methods of detection
- Colorado School of Mines
 - Performed SEM imaging and torsion rheology benchmark testing
- Sandia National Laboratories
 - Performed hose hydrostatic burst testing
- Element One, Inc.
 - Provided chemochromic hydrogen leak indicating DetecTape samples
- California Hydrogen Refueling Station Field Operator Info Sharing
 - Supply of failed hose samples for analysis and comparison
 - Operational/maintenance experiences and failure rates information has been shared with:
 - First Element
 - Air Products and Chemicals Inc.

Summary

Relevance & Impact

- Characterize reliability of 700 bar refueling hoses under mature market conditions. Reveal the compounding impacts (P, T, t and mechanical) of high volume 700 bar FCEV refueling that has yet to be experienced in today's low-volume market.

Progress & Accomplishments

- Over 5,000 cycles on Spir Star Hose Sample #2 with low-mass flow are meeting pressure, time and temperature limits set by SAE J2601 fueling protocols. Leak remains present but hose is functional.
- Failed hose sample dissected and analyzed with microscopy.
 - **Significant damage found on outer layer, suspected to be mainly result of wear from steel wire overwrap.**
 - **Plastic deformation and large blistering of inner layer may result in hole development, which may enlarge due to shear force of escaping high-pressure hydrogen**
 - **Generalized surface degradation (micro-blistering) is not evident in samples**

Future Work

- Upgrade cycle parameters and increase cycle rate on new samples and manufacturer supplied hoses
- Post-cycle DMA on sample to confirm material defects or property changes

Thank You

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Technical Back-Up Slides

(Include this “divider” slide if you are including back-up technical slides [maximum of five]. These back-up technical slides will be available for your presentation and will be included in Web PDF files released to the public.)

Relevance - Problem Statement

- Limited OEM competition, small FCEV market and extreme operating condition ranges result in high 70 MPa refueling equipment costs
- Low-volume FCEV refueling stations are replacing hoses at higher frequencies than expected. Operators are reporting intervals of a few months
- Other certification standards specify a range of acceptance testing. These test conditions do not reflect the combined stresses of real-world conditions. Accelerated real-world data may be valuable feedback to the OEMs.

| Component |  Hose Assembly |  Nozzle |  Breakaway |
|---------------------|--|--|--|
| Primary Supplier | SpirStar (Germany) | WEH (Germany) | |
| Cost | \$1,700 | \$6,800 (non-IR) | \$11,000 (IR) |
| Service Interval | ~ 6 months | 3 years | |
| Service Cost | \$1,700 | \$1,750 (standard) | \$5700 (with IR kit) |
| 10-Year Cost | \$34,000 | \$12,050 (non-IR) | \$28,100 (IR) |
| Alternate Suppliers | Yokohama Rubber (Japan) | Walther Präzision (Germany) | |

Approach – Pressure and Temperature

- Pressure profile closely follows SAE J2601 (2014)
 - H70-T40 Type fills, APRR ~ 20 MPa/min w/ Flow control
 - T_{fuel} -33°C to -40°C within 30s (measured prior to hose), $T_{\text{amb}} = 20^{\circ}\text{C}$
 - Cold Dispenser (Communications) tables primarily used, variety of cases
- 3 – 5 minute fills using ~ 100 g H_2 / cycle
 - Hydrogen not recycled
 - Target fill amounts 100g per fill to sufficiently cool gas
- Sets of rapid back to back cycles with warm-up periods
 - Delay times can be added between cycles to study leaks
- 6-axis robotic arm to provide repetitive mechanical stress of routine consumer refueling
 - Automated control of entire fueling process
- H_2 leak monitoring of crimp fittings on each end
 - Focus on ability to stay sealed while cold under high pressure and depressurization cycles

Approach – Mechanical Bending/Twisting

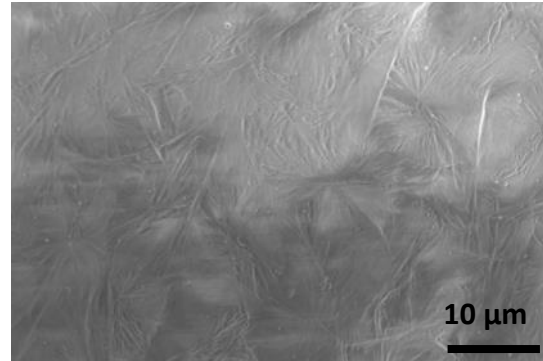
- Epson six-axis robot installed and programmed with realistic human motions from 'dispenser' to receptacles – total distance ~3 feet
- Double receptacle system to provide options for greater randomization of paths from dispenser
- **High repeatability, over torque tripping capability, anchored frame and calibration help reduce stresses on nozzle and receptacle**
 - Focus on crimped hose end connections and their ability to remain sealed under bending/twisting stress while cold.
 - Nozzle and other components are replaced as needed if they wear out.



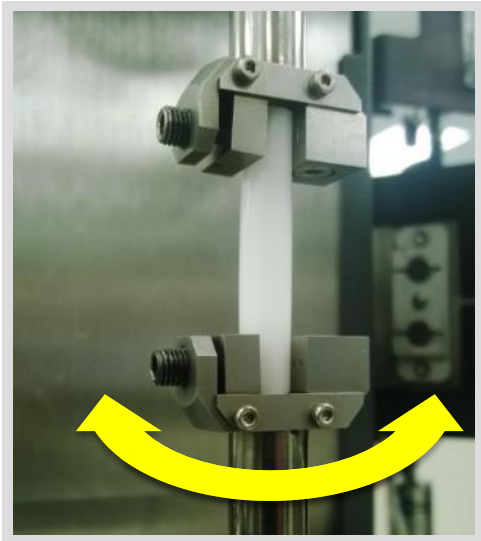
Approach – Materials Testing

Chemical and mechanical testing previously identified and performed on pre-cycled specimens

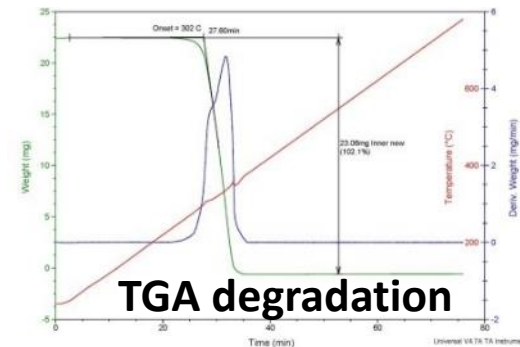
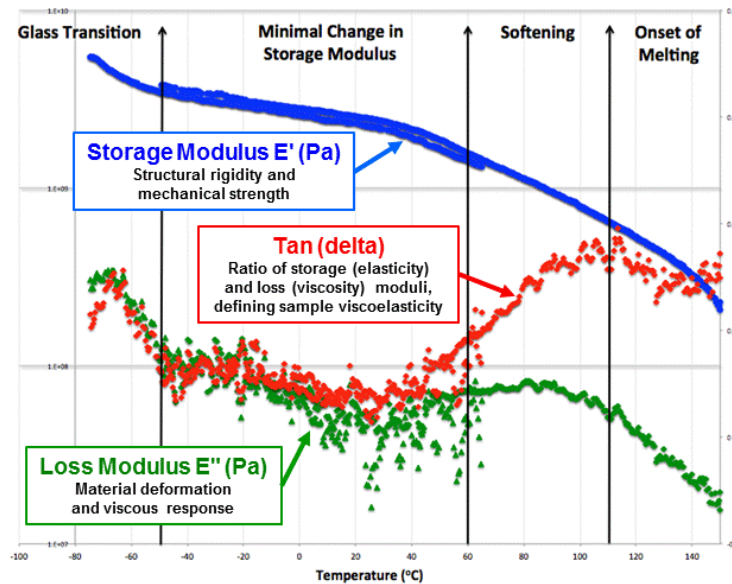
- Physical – hydraulic bursting (SNL), rheology, scanning electron microscopy
- Chemical – FTIR, DSC, XDS, XPS, TGA



SEM imaging



Torsion rheology



- All tests to be repeated on post-cycled materials