NATIONAL RENEWABLE ENERGY LABORATORY

# 700 Bar Hydrogen Dispenser Hose Reliability Improvement

Kevin Harrison (P.I)
Owen Smith (Presenter)

National Renewable Energy Laboratory
DOE 2017 Annual Merit Review
June 6, 2017

Project ID
**PD100**

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

# Overview

## Timeline

**Project start date: June 2013**

**Project in continuous operation on sample hoses as directed by DOE**

## Budget

**To Date Total Spending: $633.5k**

- **$141k carried over into FY17**
- **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)"

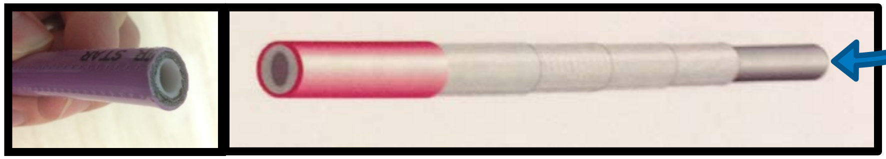
## Partners

- **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**

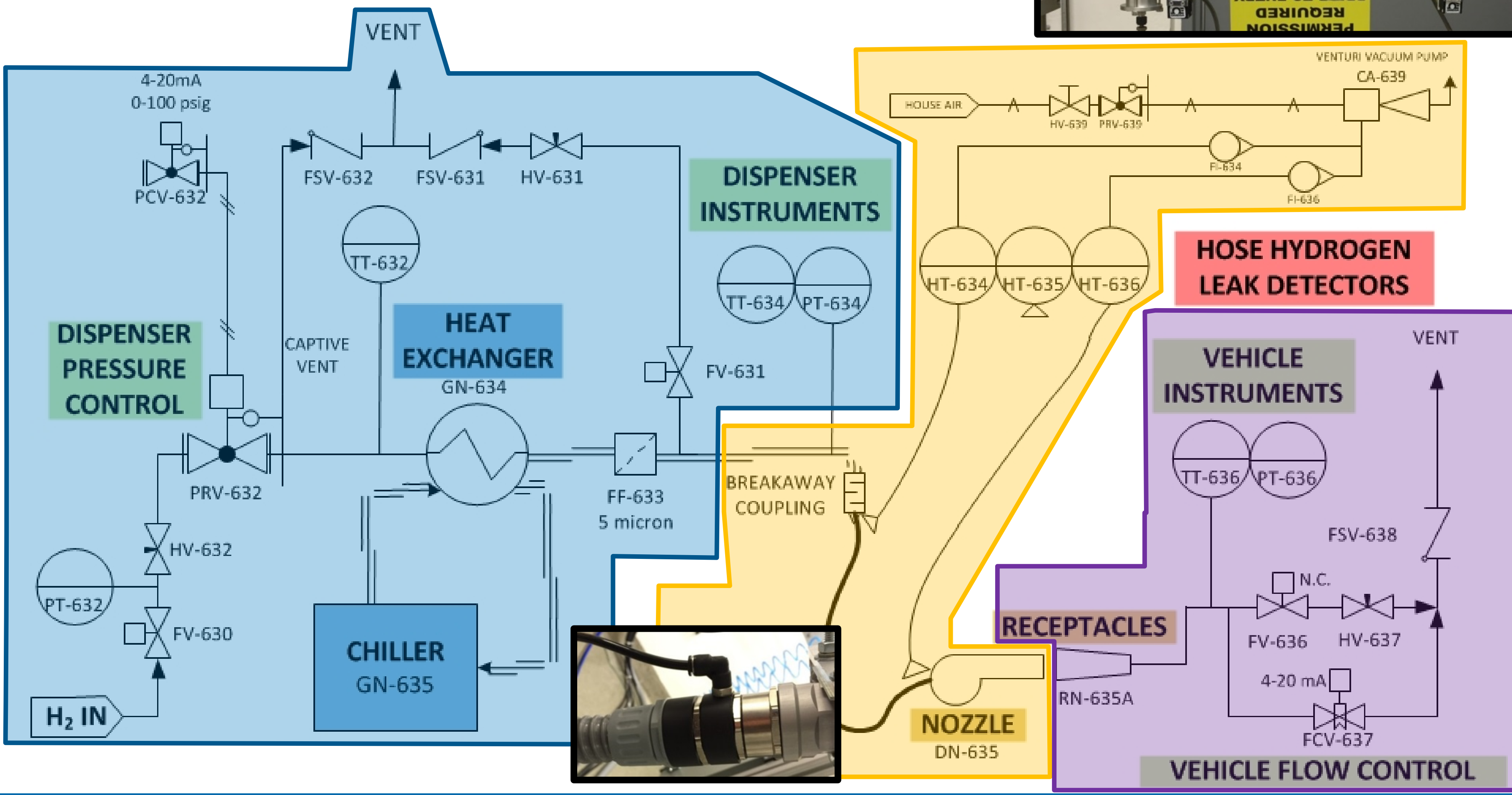
- **By working closely with the original equipment manufacturers, the hose reliability project aims to improve the reliability and thus reduce the cost of 700 bar hydrogen refueling hose assemblies by identifying points of failure.**
- **NREL has designed a high-cycling test apparatus that unifies the 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
  - Methods of leak detection/preventative maintenance
  - Leak rate analysis to explore permeation effects

# 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 – SpirStar Hose #2 Status

## Daily Operations

- 4700+ cycles completed* on Sample #2 running various cases of SAE J2601 H70-T40 with good accuracy on pressure controls. *As of 4/24/2017.
- Selected cases of H70-T20 and H70-T30 run for comparison of leak rates as a function of temperature.

## Leak Status

- Consistent small leakages observed at high pressure from the nozzle and dispenser sides, close to the crimp fitting. Leak is not isolated to the crimp fitting and permeates through the outer layer for up to 9-10 inches from the crimp fitting. No damage or external blistering observed yet.
- **Hose is passing standard leak checks and safety interlocks, and is still functional even after 1,500+ cycles with observed leakage.**
- **Lack of leak rate standards has been barrier to determining pass/fail rates**
- Multiple safety features implemented as part of experiment design allowing hose to be run unattended throughout leaks without risk.
- Permeation transport of hydrogen studied as potential leak driver

# Responses to Reviewers' Comments

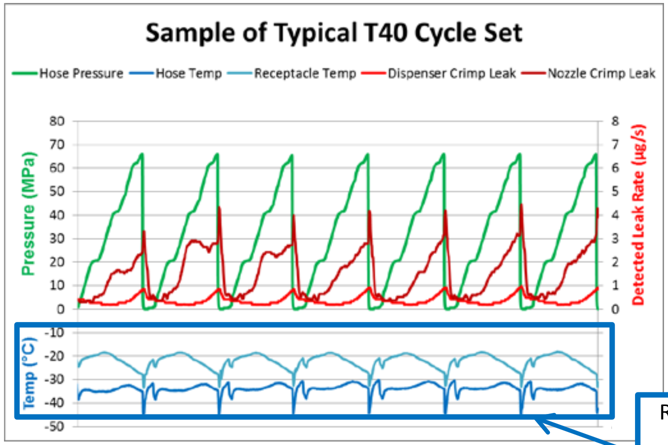
- Responses to comments from the 2016 AMR are given below:

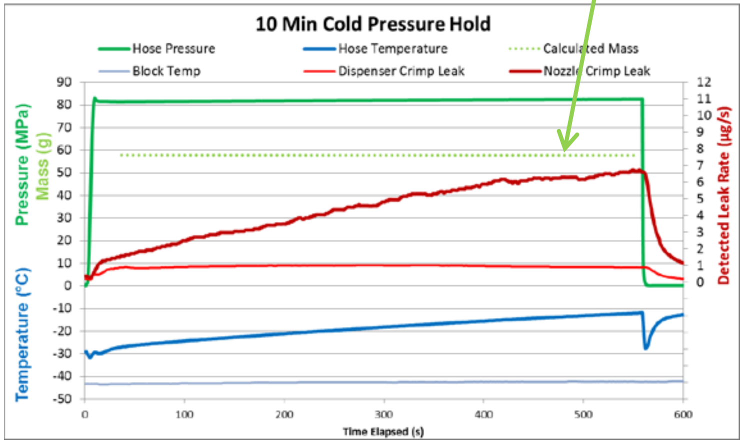
- *"This project is lacking a risk assessment plan, which is an important factor to consider. The risk assessment plan is necessary to allow the project to mitigate risks related to safety, reliability, cost and performance effectiveness, system limitations, and project schedule (i.e., project downtime)."*
  - NREL has performed a full Process Hazard Analysis on the hose test stand and it is located in a high-pressure blast cell designed for equipment testing to failure without danger to personnel.
  - The Hose Test Stand has a preventative maintenance schedule for all supplementary equipment and several spare parts on-hand.
  - System capabilities (hydrogen production rate and hydrogen compression rate) and resource allocations to other DOE projects have been an issue to date – station upgrades have helped with capabilities while scheduling conflicts have been mitigated with a lab-wide ESIF User Support System scheduling tool.
- *"The project needs to get additional hose collaborators and/or hoses for testing."*
- *"A NRTL, a breakaway manufacturer, and a nozzle manufacturer were not included in this effort. They would lend credibility and industry acceptance of the results."*
- *"The project should hold supplier workshops and involve the big station technology providers such as The Linde Group, Air Liquide, and Air Products."*
- *"The future work makes sense, although it does not seem systematically planned. It is not clear how the results will be shared with industry, not is it evident who is driving this process."*
  - Results have been discussed with SpirStar, and future collaboration is planned with Nanosonic under SBIR Phase 2B (PD101) to provide hose cycling and pre-and post- testing services.
  - Current focus is on hose reliability. Breakaway and nozzle equipment, along with valves, will be addressed with a new project (PD140)
  - Station operators (e.g. First Element, Air Products) have been engaged and we have shared updates between project status and field experiences.
- *"The progress to date is interesting. It is not clear whether the magnitude of the leaks has been determined and, if so, what the sizes of the Class 1 Zone 1 and Zone 2 volumes are."*
  - Leakage has been determined to be small without significant releases. The leak is detectable with instrumentation but does not fail leak checks.
  - There is not currently consistent standards in many hydrogen codes to properly address small leaks that may be part of normal operation.
  - Data from this project has been shared with codes and standards groups (ISO WG 22, DOE IRIG) to help inform code development.

# Progress – Hose Fitting Leak Detection

- **Dispenser-side hose crimp fitting had small leaks at Cycle 1856**
- **Nozzle-side hose crimp fitting consistently leaked at Cycle 3033**
  - Leaks occur during cycles, pressure holds, and venting

Starting mass: 57.880 grams
Ending mass: 57.776 grams
Mass loss: ~ 160 micrograms/sec




Receptacle temperature remains close to hose temperature – consistently cold hose with ~200 grams per cycle

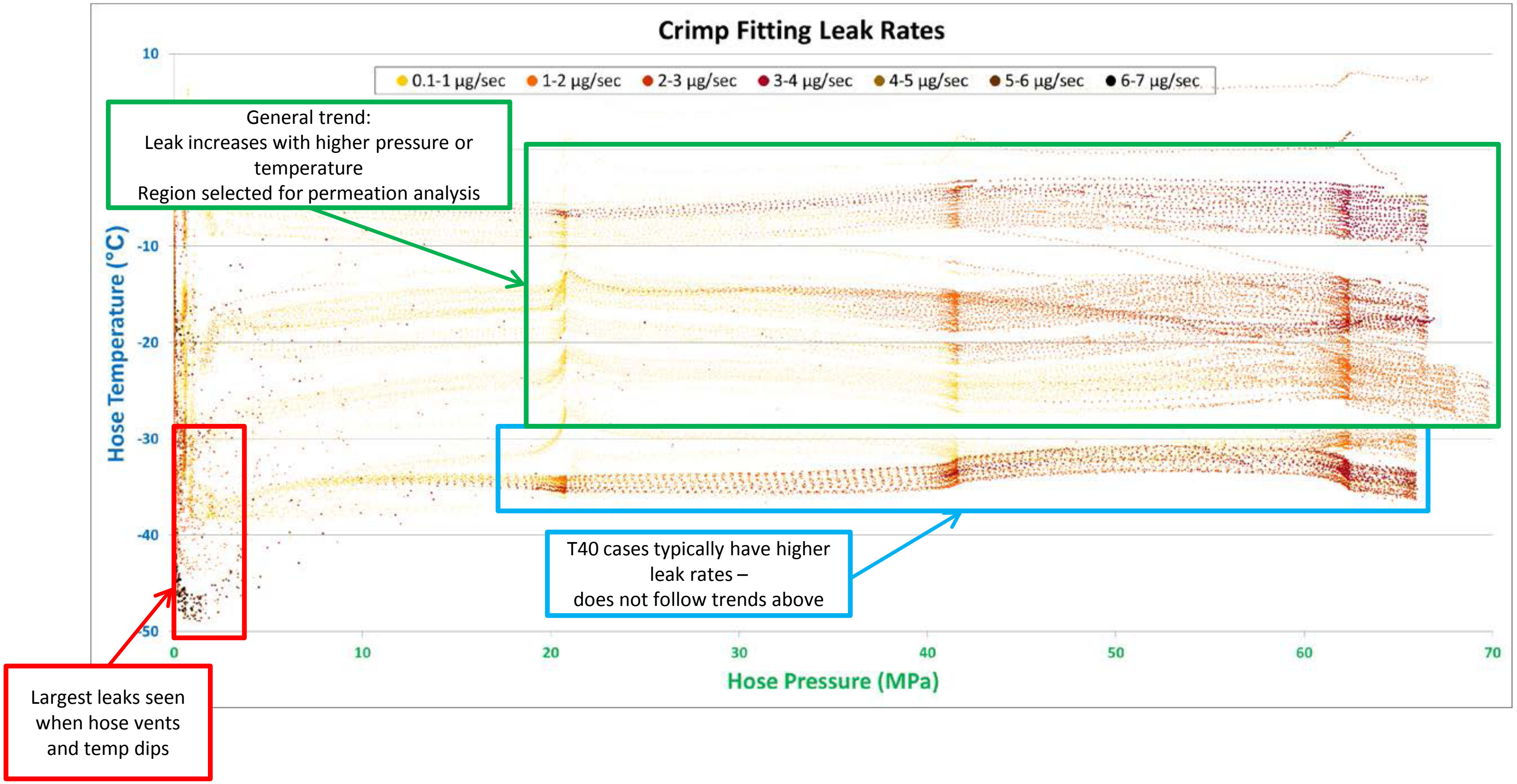
- >1500 cycles successfully achieved with consistent leaks present
- Pressure holds on the complete dispenser (including heat exchanger and valves) indicate a leak rate of approximately 100-500 micrograms per second – or a mass loss of **0.1% to 0.4%** over 10 minute holds
- Hose passes every 5-sec NFPA leak check common in commercial fueling
- **Hose passes the only pass/fail criteria in codes – 10 ccN/hr (3235 µg/s)**

# Collaboration - Acceptable Leak Thresholds

- **Does this leak rate necessitate early replacement of the hose assembly at increased lifetime cost?**
  - Does not affect ability of hose to complete fills within pressure tolerance ranges and does not fail pressure holds for 5-10 mins
  - Location of leak must also be considered – **direct human interaction**
  - SAE J2601 offers no guidance on leak thresholds.
  - NFPA 2 (2016):
    - **10.3.1.11.2 Hose Assemblies** *"Hose shall be tested for leaks… any **unsafe leakage** or surface cracks shall be reason for rejection and replacement"*
    - **A.7.1.13.1 – Removal from Service** *"Compressed gas systems in hydrogen service are subject to leakage; however, leakage has not been defined in quantitative terms."*
      - **3.9 micrograms/sec** – mass flow rate of hydrogen at quenching limit
      - **7.8 micrograms/sec** – minimum bubble leak warranting repair in unventilated spaces
      - **28 micrograms/sec** – flow rate to sustain a hydrogen flame on 6.3mm tube fitting
  - CSA HGV 4.2 (2013) & ISO 19880-5 WG22 (under development) :
    - *"A hose assembly shall not leak more than 10 ccN/hr (3235 micrograms/sec) using hydrogen"*
  - **150-500 micrograms/sec –** estimated SpirStar hose #2 leakage during pressure holds
- **Suggested action: PM schedules to check for small leaks and early replacement of hose assembly only if leakage is consistent**

# Progress – Leak Variation by Temperature

- **Profiles run at different temperatures to explore leak relationship**
  - T40 (typical), T30, T20 and -10C (not in J2601) cases at similar pressures
  - 157 total cycles in analysis, alternated to reduce cumulative effects

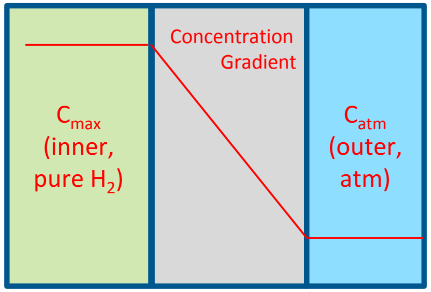


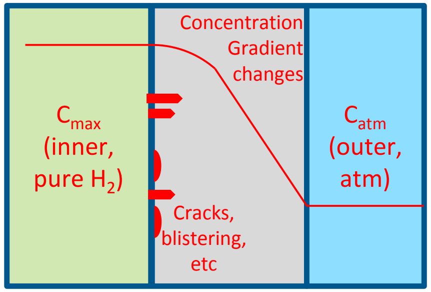
# Approach – Permeation Analysis

- **Permeation of hydrogen an important factor in polymer material selection**
  - Mass flux J dependent on permeability Φ and pressure gradient $P_H$ across material of thickness L
    - Permeability is product of diffusivity and solubility , Φ = D · S

$$J = \Phi \frac{\Delta p_H}{L} \qquad \Phi = \Phi_0 e^{\left(\frac{-E_A}{RT}\right)}$$

  - Temperature dependency a function of activation energy $E_A$ and permeability constant $\Phi_0$
  - Activation energy $E_A$ specific to $H_2$/Polyoxymethylene, found by plotting isobaric leak rates
- **Typical behavior – permeation decreases with lower temperature**
  - Change of rate constants and slower permeation after glass transition in static situations
    - Glass transition temperature for this polyoxymethylene sample previously determined to be **-50C**, at 0 MPa
- **Material defects can increase permeation by providing pathways for hydrogen**
  - Glass transition results in increased brittleness – easier to damage by mechanically stressing
  - Cracks, blistering increase surface area for solubility uptake and reduce thickness for diffusion

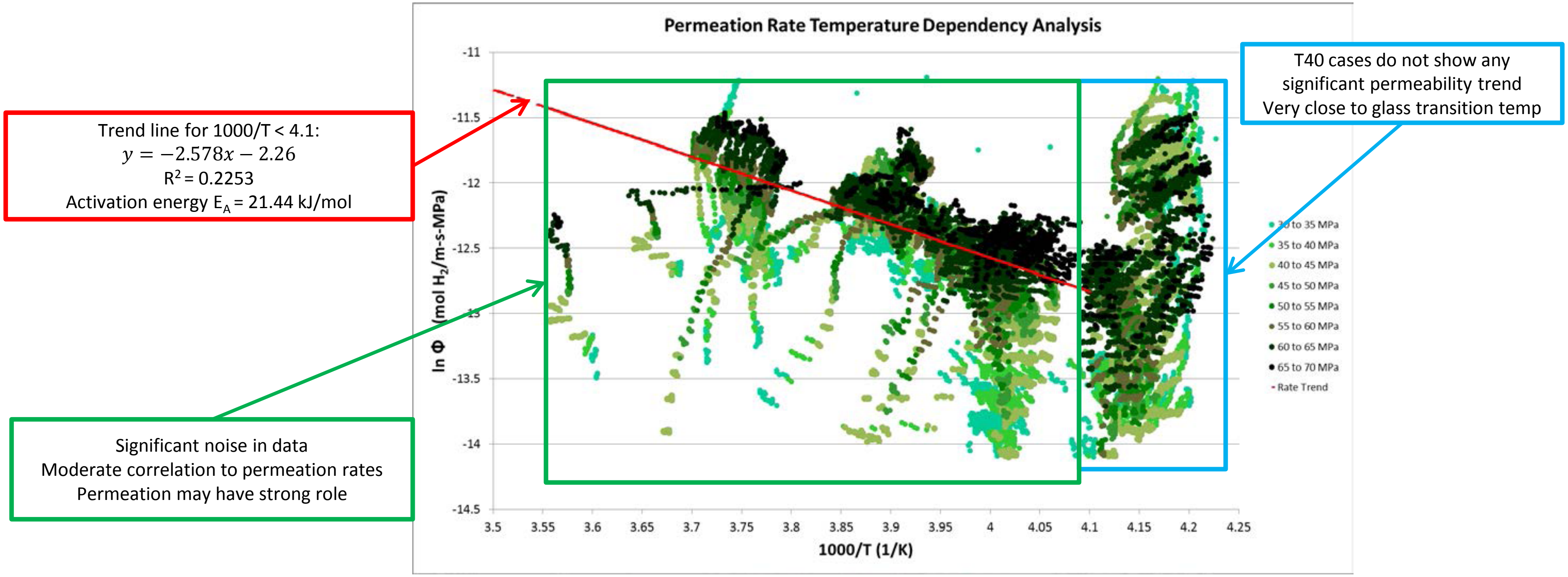



***<u>Given the consistent, relatively small leaks on hose sample – is this attributable to increased permeation activity?</u>***

# Progress – In-Cycle Permeation

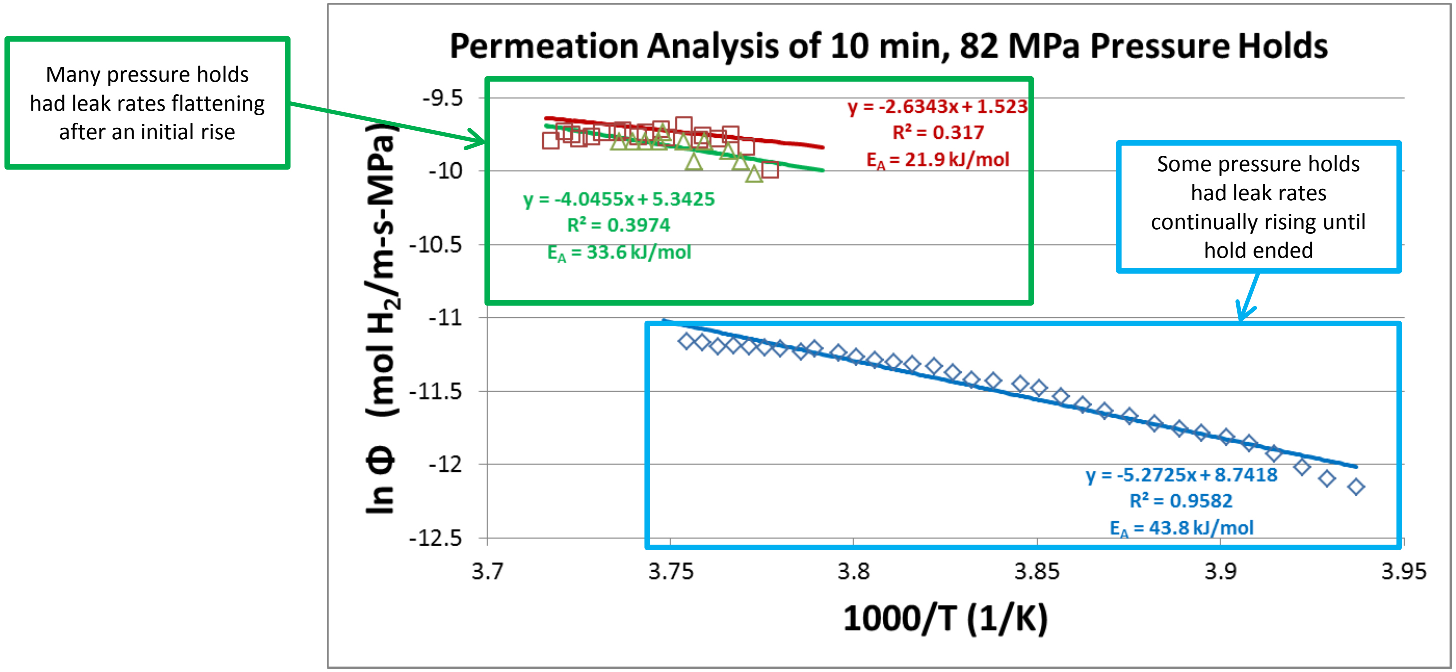
- **Permeation analysis performed on temperature variation cycle set**
  - Drawbacks: Pressure changes – not steady-state, time lag in effect
  - Permeability constant may be offset due to interference from leak sources (pinhole, crimp)
  - Can still look at the overall trends for temperature dependency indicating some effect from permeation or similar process
  - Only pressures > 30 MPa studied to reduce noise and leak carryover from previous cycle




  - **Data shows moderate possible permeation effects except for T40 cases**
  - **Glass transition (-50C @ 0 MPa) may be affecting results in T40 cases**

# Progress – Steady-State Permeation

- **Permeation compared to 10 minute pressure holds to determine a steady-state permeation result while hose warms up**




- Strong permeation correlation in some cases – typically pressure holds done immediately after cold cycles
- Weaker permeation correlation in many cases, often when hold does not immediately follow cold cycles
- Data is scarce for $H_2$/Polyoxymethylene combinations
- Some comparable polymers (unstressed) shown
  - Sandia National Laboratory report, 2013
- Recorded permeation 4 to 6 orders of magnitude higher than typical unstressed polymers

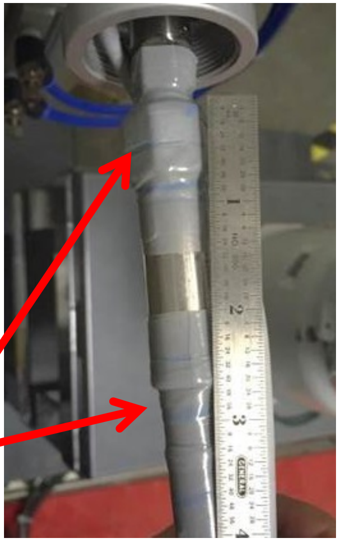
| Property | Units | HDPE | Polyamide | PTFE | POM |
|---|---|---|---|---|---|
| $\Phi \times 10^9$ | $\left(\frac{mol\ H_2}{m \cdot s \cdot MPa}\right)$ | 0.89 | 0.36 | 3.23 | 500-54000 |
| $\Phi_0 \times 10^3$ | $\left(\frac{mol\ H_2}{m \cdot s \cdot MPa}\right)$ | 0.053 | 0.006 | 0.019 | - |
| $E_A$ | $\frac{kJ}{mol}$ | 27 | 26 | 21.4 | 21-44 |
| $T_G$ | $^{\circ}C$ | -110 | 64 | 115 | -50 |

# Progress - Leak Detection Methods

DETECTAPE H2
Hydrogen Leak Detection

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

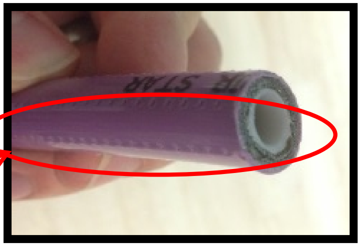
Note: DetecTape has not yet been approved for use by the manufacturer under these conditions and this project is not intended to draw any conclusions on the performance of the tape.

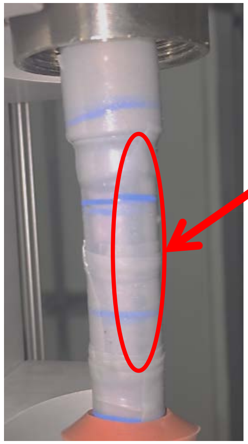


**Before**
-Tape wrapped around hose near crimp fitting, and on metal fittings with leak detection ports
-No indications were seen after rechecking after 100 cycles without leaks

**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

- Pinpricks designed to relieve pressure between outer and inner layer

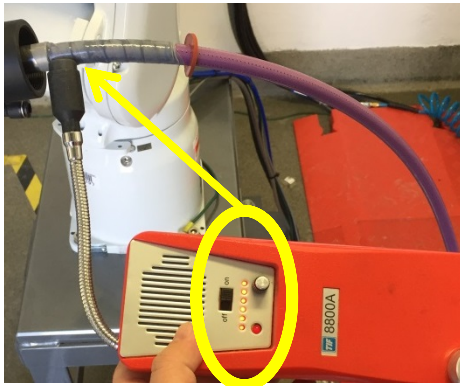


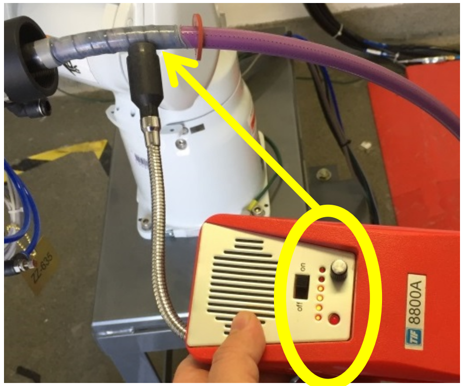


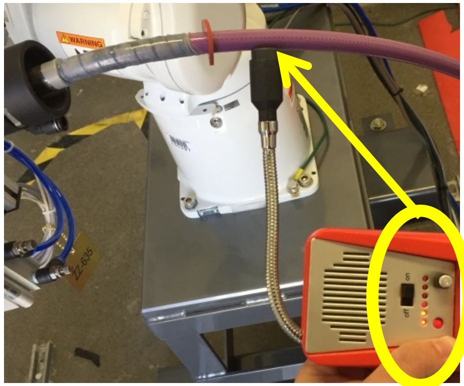
- On the dispenser-side crimp fitting on the same hose sample, which had only shown inconsistent, small leaks, tape was deployed with **faint indications**.
- Our fueling dispenser with a 3 year old hose (~1000 total cycles) had tape deployed as a control sample. There were **NO indications** after 1 month in which it had refueled 8 vehicles, and **NO indications** after one year of use

# Progress - Hose Fitting Leak Verification

- **How can we identify leaks without tape and sampling detectors if the hose passes NFPA leak checks and pressure holds?**
    - **Sound** – This leak is too small for operators to hear during refueling and pressure holds.
    - **Vision** – The hose shows no marks, blisters or deformation on the outer layer. **<u>Indication tape would be useful here as part of a PM schedule.</u>**
    - **Handheld gas detectors** – Commonly used handheld gas detectors are capable of detecting this type of leak.
        - The handheld detector also confirmed that hydrogen is coming from the pinpricks, with the greatest leak rate near the crimp and falling off in intensity up to 9-10 inches as shown below. No leaks were detected anywhere else on the hose length.







# Collaboration – California Field Operators

- **Discussions with CA station operators revealed that similar leaks are being seen on some failed hoses**
  - 1-year old hose below failed at 1700+ cycles at 12-18” from nozzle.
  - Wire braiding intact, indicating pinhole leaks instead of large rupture

  - Similar failure seen on another hose at 1000+ cycles, official cause blamed on silicon dioxide and metal dust
  - Bubbles/occlusions in outer layer reported on some hoses
  - Crimp fitting leaks that fail pressure holds are still much more common than through-wall leaks
  - Replacement time reported at about 700 cycles for one operator
- **California station operators have requested we share data and findings with them, particularly interested in any evidence of damage to inner layer from internal dust particle or external wear from wire braiding**

# Challenges – Leakage and Resource Allocation

## Leakage from other sources

- **Receptacle uncoupling leak**
  - Nozzle and receptacle have been observed to leak small amounts of hydrogen during decoupling. Similar leaks seen in field operation – dedicated fixed-area gas detector
- **Valve body seal failures**
  - Valves having difficulty with sustained cold temperatures – frequent maintenance required. Configured leak detector to minimize background leaks from valves.
  - Fixed-area hood gas detector located above receptacle and valve assemblies – shuts system down to prevent sampling detectors from picking up valve leaks

## Station Resource Allocation, Construction Downtime

- HITRF (Hydrogen Infrastructure Testing and Research Facility) has multiple ongoing research projects and resource allocation is a challenge
  - Meter Benchmark testing (TV037), OEM FCEV high-altitude testing, MC Method fill protocol testing, and Consolidation Scheme (PD133) preparation consumed large amounts of hydrogen
- Resource capacity limited to compression throughput to medium pressure tanks (2.2 kg/hr)
- Hose consumption larger than planned with new heat exchanger - ~200g/cycle and 2.4 kg/hr
- Major construction ongoing through past year due to station upgrades for Consolidation Scheme testing. Downtimes lasting several weeks, but upgrades also benefit hose testing
- **ESIF User Support System scheduling and allocation portal deployed in 2016 to aid in resource conflicts and project management**

# Future Work – Milestones and Testing

| Qtr | Due Date | Milestones, Deliverables, or Go/No-Go Decision | Status |
| --- | --- | --- | --- |
| Q1 | 12/31/2015 | Complete 1,000 cycles on Hose Assembly #1 or until failure | Completed |
| Q4 | FY17 | **Perform accelerated hydrogen cycling to 700 bar (nominal) on a hose sample to failure or 25,000 cycles, whichever occurs first.** | Delayed due to Resource Allocation Conflicts |
| Q4 | FY17 | Perform post-cycling physical and chemical testing including DMA, SEM, XPS, FTIR and other tests previously identified | On Target |

- Hose sample will be considered “failed” upon inability to hold pressures long enough to complete cycles or when safety features consistently stop cycling upon excessive leakage.
  - Likely will occur much later in life than when hose would “fail” a commercial dispenser NFPA leak check - provides clearer perspective into material changes
  - Reach out to station operators and work with codes & standards groups to help determine pass/fail criteria on NFPA leak checks, and other methods to monitor for early failure
- Test additional hoses from Nanosonic, other manufacturers – FY17- TBD
- 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 Thoraeus 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**
  - 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 4,700 cycles with low-mass flow are meeting pressure, time and temperature limits set by SAE J2601 fueling protocols
- Leak pattern is observed to be very small but largely consistent – remains functional and passes standard dispenser leak checks.
- Leakage may result from increased permeation due to weakened material and/or glass transition effects – potential indicator of future failure.
- Leakage can be detected by field operator preventative maintenance methods such as handheld CG detectors and leak indication tape
- Results shared with ISO WG 22 to inform codes development, SpirStar to provide feedback on failure modes, and field operators to improve maintenance efficiency

## Future Work

- Continue high rate of cycling on Sample 2 until failure
- Post-cycle DMA/SEM and other tests to confirm material defects or property changes

# Technical Back-up Slides

# 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) | | WEH (Germany) |
| Cost | $1,700 | $6,800 (non-IR) | $11,000 (IR) | $3,000 |
| Service Interval | ~ 6 months | 3 years | | 3 years |
| Service Cost | $1,700 | $1,750 (standard) | $5700 (with IR kit) | $850 |
| 10-Year Cost | $34,000 | $12,050 (non-IR) | $28,100 (IR) | $5,550 |
| Alternate Suppliers | Yokohama Rubber (Japan) | Walther Präsizion (Germany) | | Walther Präsizion (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), $T_{amb}$= 20°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

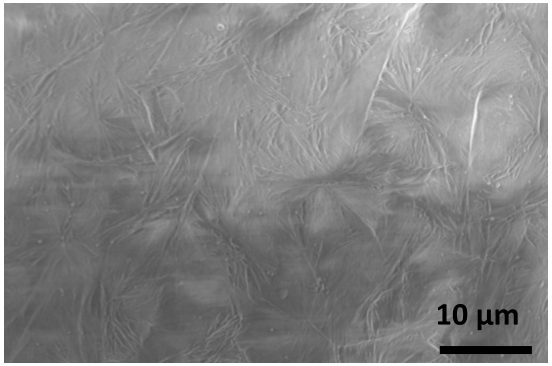
- **Epson six-axis robot installed and programmed with realistic human motions from 'dispenser' to receptacles – total distance ~3 feet**
- **Double receptacle system to provide options for greater randomization of paths from dispenser**

- **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.

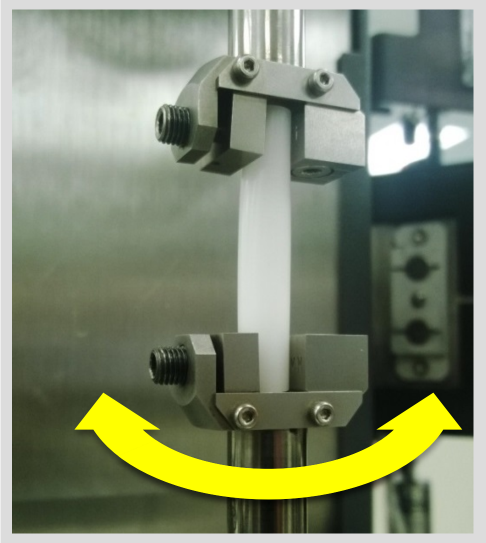
# Approach – Materials Testing

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

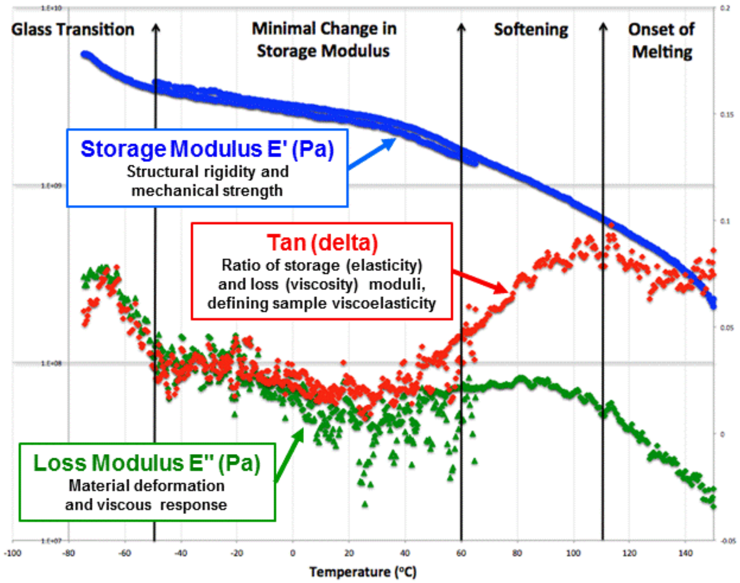
- Physical – hydraulic bursting (SNL), rheology, scanning electron microscopy
- Chemical – FTIR, DSC, XDS, XPS, TGA

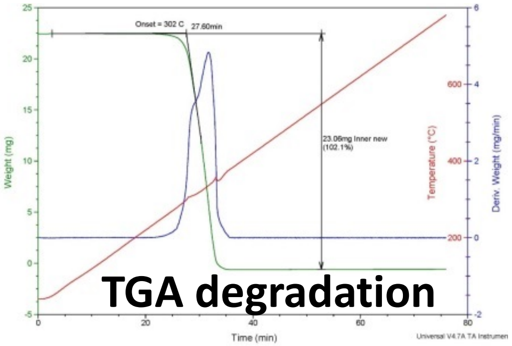



SEM imaging



Torsion rheology




TGA degradation

- **All tests to be repeated on post-cycled materials**

# Progress – J2601 Fueling Cases

## SAE J2601 cases are changed to improve variation in pressure cycles and to work within existing station pressures

| SAE J2601 Case | Target Pressure (MPa) | APRR (MPa/min) | Cycles Completed* |
|---|---|---|---|
| **H70-T20 2-4kg non-communication fill**<br>Standard, 0.5 MPa start pressure, 0 C ambient temp | 59.2 | 15.3 | 200 |
| **H70-T40 2-4kg non-communication fill**<br>Standard, 0.5 MPa start pressure, 10 C ambient temp | 66.1 | 27.0 | 1850+<br>(current case) |
| **H70-T40 4-7kg non-communication fill**<br>Cold Dispenser 0 C, 2 MPa start pressure, 25 C ambient temp | 72.7 | 22.9 | 375 |
| **H70-T40 4-7kg non-communication fill**<br>Cold Dispenser -10 C, 2 MPa start pressure, 20 C ambient temp | 71.6 | 27.7 | 900 |
| **H70-T40 2-4kg non-communication fill**<br>Cold Dispenser 0 C, 2 MPa start pressure, 10 C ambient temp | 73.8 | 28.5 | 877 |
| **H70-T40 7-10kg communication fill**<br>Cold Dispenser -10 C, 0.5 MPa start pressure, 0 C ambient temp | 81.4 | 19.9 | 150 |
| **H70-T40 4-7kg communication fill**<br>Cold Dispenser 0 C, 2 MPa start pressure, 0 C ambient temp | 84.6 | 28.5 | 105 |
| **H70-T20 2-4kg non-communication fill**<br>Standard, 2 MPa start pressure, -10 C ambient temp | 66.7 | 16.9 | 45 |
| **H70-T30 7-10kg non-communication fill**<br>Standard, 2 MPa start pressure, 10 C ambient temp | 70.0 | 17.0 | 23 |
| **H70-T30 4-7kg non-communication fill**<br>Cold Dispenser 0 C, 2 MPa start pressure, -10 C ambient temp | 68.2 | 25.4 | 63 |

***as of 4/24/2017**