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Compatibility of Polymeric Materials Used in the Hydrogen Infrastructure

Kevin Simmons, PNNL (PM, Presenter)
Dr. Kyle Alvine, PNNL (Principal Investigator)
Dr. Edward Duranty, PNNL
Dr. Chris San Marchi, SNL
Nalini Menon, SNL
Dr. Barton Smith, ORNL
Dr. Alan Kruizenga, SNL
Dr. Amit Naskar ORNL
Dr. Jong Keum, ORNL
Mike Veenstra, Ford

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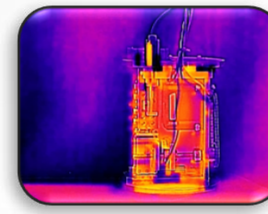

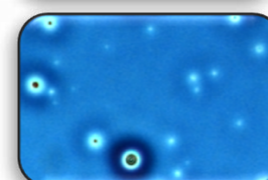

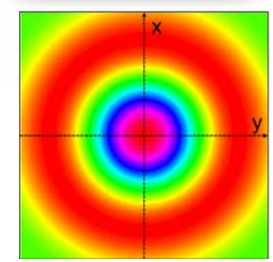

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PNNL-SA-125790
Project ID# SCS026

Overview

Timeline

- Project Start Date: October 2015
- Project End Date: September 2018
- % Completed: 50%

Budget

- Total Project Budget: $1800K
  - Total Federal Share: 100%
  - Total DOE Funds Spent**:

    $196K (PNNL) – includes Ford subcontract

    $75K(SNL)

    $27.4K (ORNL)

*No cost share required for National Laboratories

* *As of 3/24/17

Barriers

A. Safety Data and Information: Limited Access and Availability

G. Insufficient Technical Data to Revise Standards

J. Limited Participation of Business in the Code Development Process

K. No consistent codification plan and process for synchronization of R&D and Code Development

Partners

- PNNL (Project Lead)
- SNL
- ORNL
- Ford Motor Company

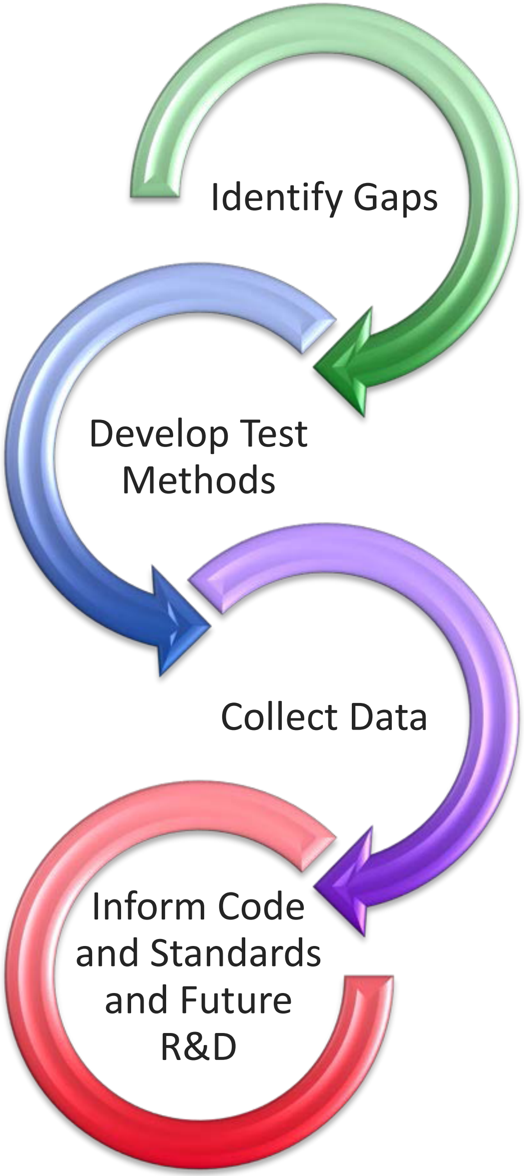
Relevance

Objectives: To develop a knowledge base of polymer and elastomer materials hydrogen compatibility through development of test methodologies that will enable a better understanding of material interaction in infrastructure that will guide future research and development activities

- Provide scientific and technical basis to enable full deployment of H2 and fuel cell technologies by filling the critical knowledge gap for polymer performance in H2 environments
- Develop standard test protocols for polymeric materials to evaluate their H2 compatibility for conditions, applications, and polymers of need by the hydrogen community
- Disseminate test protocols and compatibility information and support the deployment of H2 infrastructure

Barriers	Project Impact
A. Safety Data and Information: Limited Access and Availability	Develop H2 Tools webpage for data dissemination and hydrogen compatibility guidance
G. Insufficient Technical Data to Revise Standards	Develop test methodologies for evaluating polymer compatibility with high pressure H_2: (1) in situ tribology, (2) pressure cycle aging. Understand fundamental aspects of hydrogen damage in polymers through techniques like neutron scattering.
J. Limited Participation of Business in the Code Development Process	Performed FMEA analysis from technical experts and stakeholder input to prioritize required material attributes for test methods to evaluate conditions of interest for H2 compatibility. Disseminate project findings through conferences, publications, and website
K. No consistent codification plan and process for synchronization of R&D and Code Development	Engaging codes and standards community (CSA and others) early on and having discussions to synchronize our data collection and test method development with new codes and standards development like CHMC 2

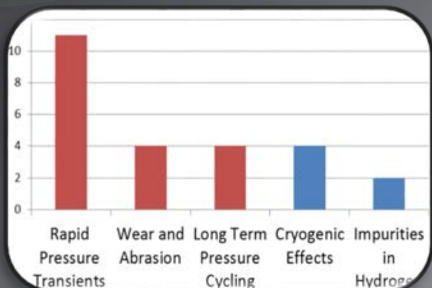
Approach: Objectives

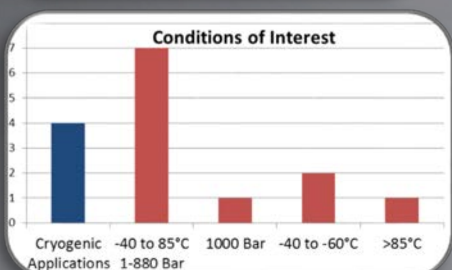


- Identify gaps in hydrogen compatibility of polymers understanding by literature, stakeholder engagement, and prioritization tools like FMEA (failure mode & effects analysis)
- Develop test methods to evaluate selected compatibility properties like friction and wear of polymers in high pressure hydrogen
- Collect experimental data on polymer compatibility like friction and wear as well as to collect data like neutron scattering to better understand the fundamentals of hydrogen effects
- Inform codes and standards by participating in committees and having high level discussions on our findings and committee needs. Provide guidance on future R&D activities

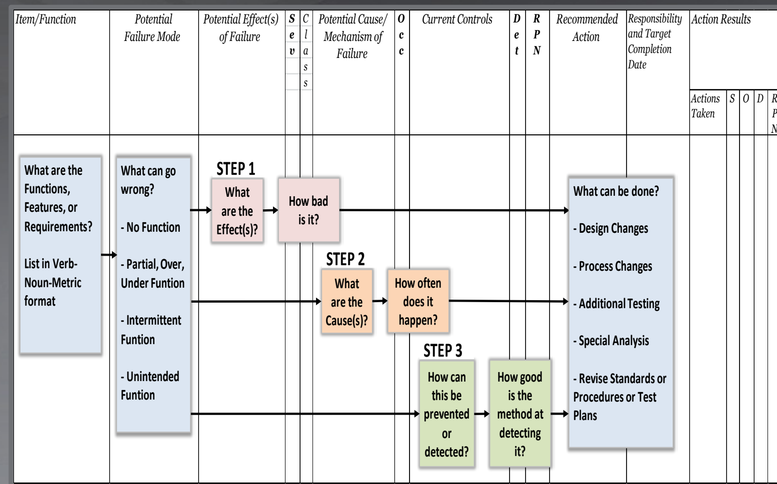
Approach

Identify the issues: Stakeholder Engagement (1st round complete)

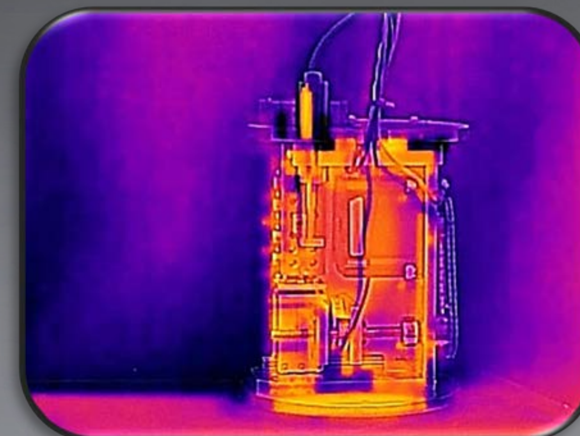




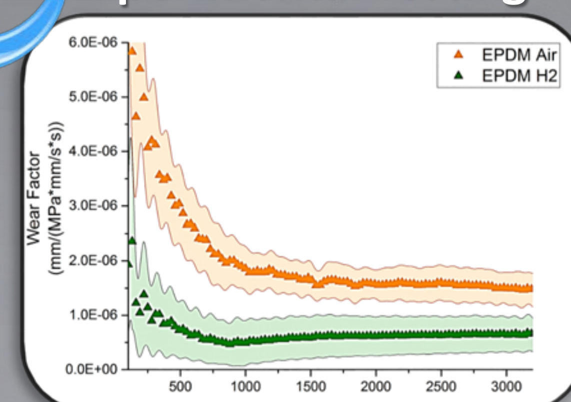
FMEA Prioritization of Critical Attributes



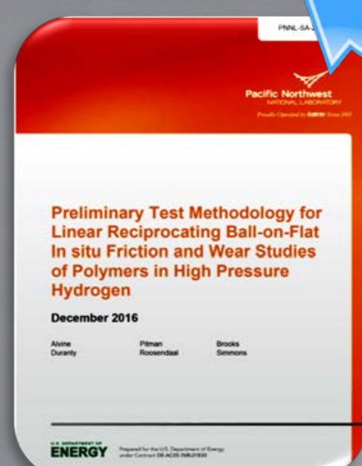
Test Method Development



Build the Database: Experimental Testing



Disseminate: Standards, Test Methods, Publications



Project Tasks

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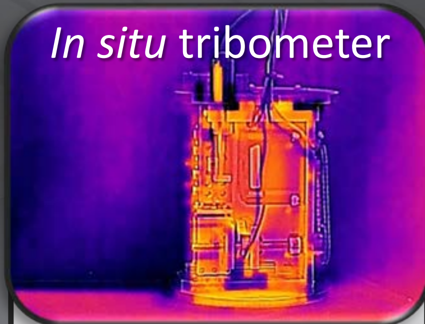
Task 1:

Stakeholder Engagement

- Materials of Interest
- Operating Conditions of Interest
- Challenges faced
- Test methods currently employed by them



Task 2:

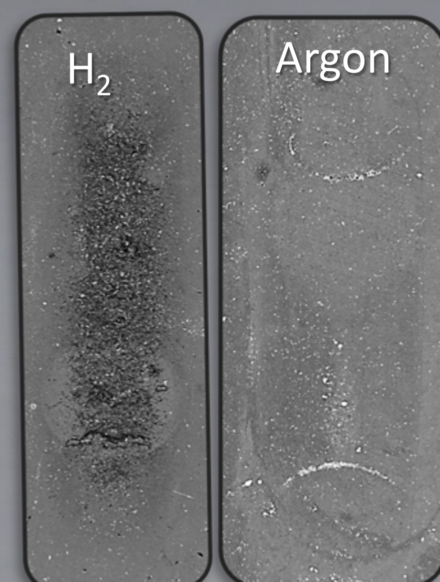
Test Methodology Development & Data Collection

- Selection of relevant polymers
- Determining preliminary test parameters
- Conducting preliminary tests and establishing optimum conditions of operation

Task 3:

Characterization of Polymers

- Baseline properties before and after exposure to H_2



Task 4:

Disseminate Information

- Lay the groundwork and deliver preliminary data for a database
- Share results with stakeholders
- Feedback from them to improve/modify test methodologies
- Identify dissemination approaches: Technical Reference

Approach: Work Flow

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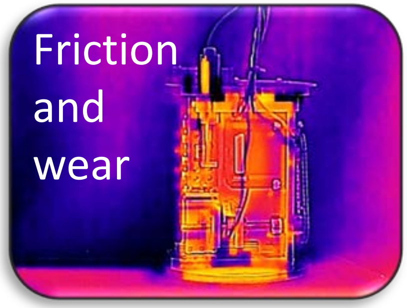


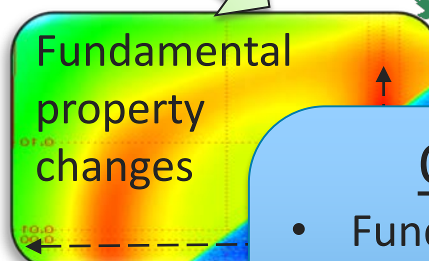
PNNL
- Project lead
- Friction and wear in hydrogen tests

Ford
- Subcontractor to PNNL
- Consulting on code and standards engagement

Critical handoffs:
SNL provides ORNL with samples for testing

Consultation

Consultation



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ORNL
- Fundamental property changes like porosity with neutron and X-ray scattering techniques

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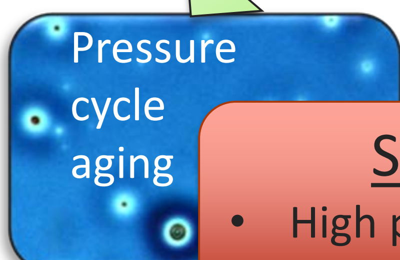
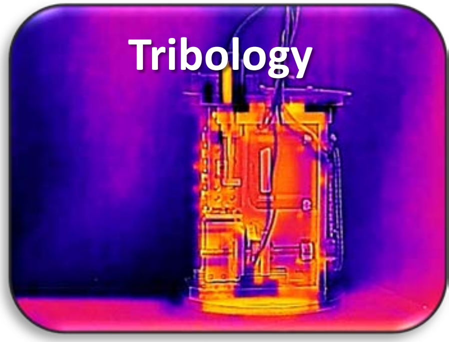


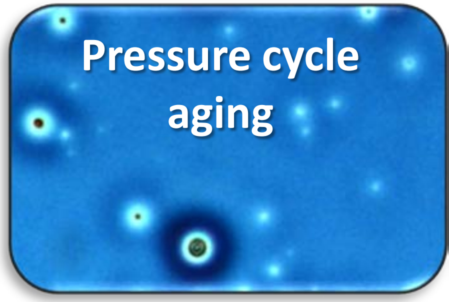
SNL
- High pressure cycle aging tests

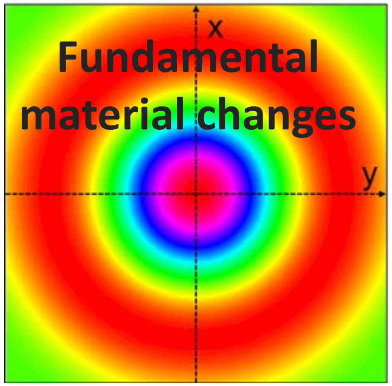
SNL provides samples to ORNL

Approach
Current Focus of Test Methodology Development

- Knowledge on hydrogen compatibility of polymers is lacking
- The team is developing test methods and collecting data to address this knowledge gap
- Tests currently being developed:
  - In situ friction and wear in high pressure hydrogen – tribology being developed at PNNL
    - Critically important for dynamic seals such as valves, compressors, and hoses
  - High pressure cycle aging being developed at SNL
    - Critically important for pressure cycling applications like valves, compressors, hoses, and other polymer components.
- Data collection
  - PNNL – friction and wear in HP hydrogen
  - SNL – pressure cycle aging in HP hydrogen
  - ORNL – fundamental material property changes with neutron scattering







Accomplishments and Progress
Engage Stakeholders and FMEA

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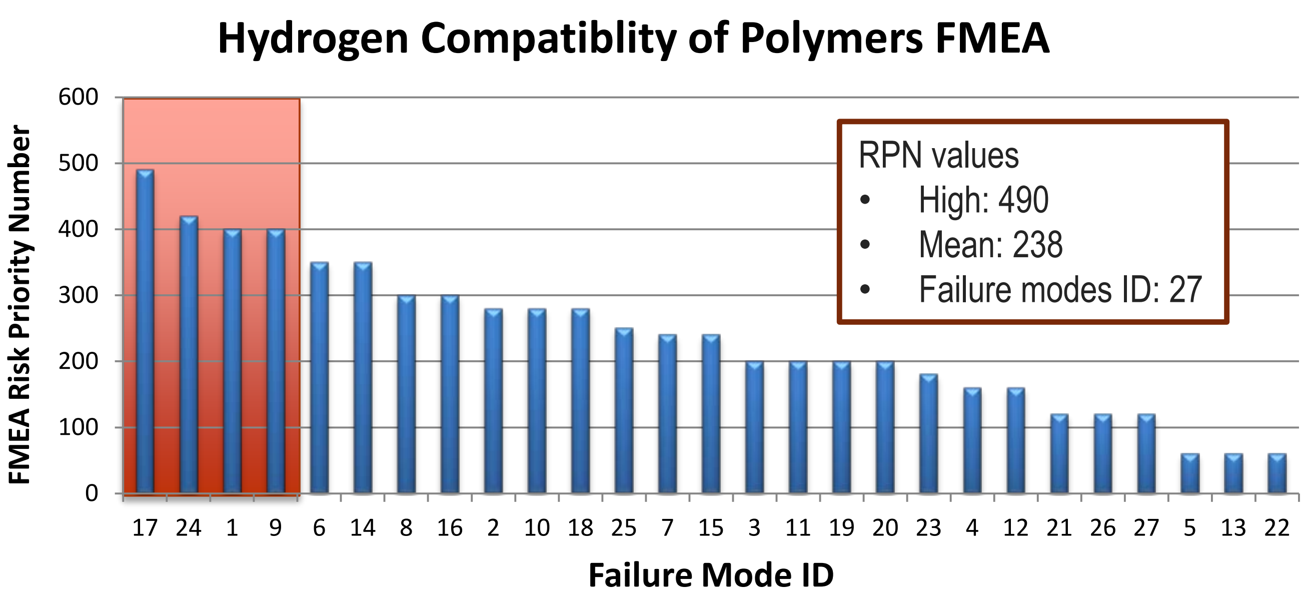
- Initial stakeholder engagement period complete
  - Reached out to approximately 40 stakeholders and held discussions with approximately 25
  - Industry, university, codes and standards committees
  - Applications include: Compressors, valves, seals, refueling stations, liners, others
- FMEA = Failure Mode and Effects Analysis (industry tool per SAE J1739)
  - Identifies and evaluates the potential failure of a product and its effects
  - Documents the risk and helps prioritize the key actions to reduce failures
- Team completed initial FMEA based on stakeholder feedback to prioritize test methodologies. Results will be discussed with industry as part of CSA CHMC 2 standard development.



FMEA focused on three key functions/applications based on containing hydrogen with:

- Static seal
- Dynamic seal
- Barrier

Accomplishments and Progress
Engage Stakeholders and FMEA

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- Top four RPN Items based on the initial FMEA assessment (>300):

Potential Cause	Failure Mode (RPN)	Function
#17 (1) Polymer seal material experiences a change in properties (strength, modulus, shear, hardness, etc.) due to hydrogen exposure	Seal exceeds allowable dynamic performance when exposed to hydrogen (initially, after pressure cycles, after temperature cycles, or over extended time). (490)	Contain hydrogen with dynamic seal at all operating pressures (5 to 875 bar) and temperatures (-40C to 85 C) until end of life - maintain seal dynamic performance
#24 (2) Polymer barrier material degrades from rapid high pressure differentials (explosive decompression) due to hydrogen exposure • material extrudes, cracks, or fragments	Liner exceeds allowable external leak rate limit when exposed to hydrogen (initially, after pressure cycles, after temperature cycles, or over extended time). (420)	Contain hydrogen with barrier liner at all operating pressures (5 to 875 bar) and temperatures (-40C to 85 C) until end of life - lower than acceptable external leakage rate of 10 Nml/h
#1 (3) Polymer seal material selected exceeds hydrogen permeation rate • unable to contain hydrogen through the material	Seal exceeds allowable external and/or external leak rate limit when exposed to hydrogen (initially, after pressure cycles, after temperature cycles, or over extended time). (400)	Contain hydrogen with static seal and dynamic seal at all operating pressures (5 to 875 bar) and temperatures (-40C to 85 C) until end of life - lower than acceptable external and internal leakage rate of 10 Nml/h
#9 (4) Polymer seal material geometry changes and volume swells or reduction due to hydrogen exposure • unable to maintain seal design and compression (compression set occurs) • material extrudes, cracks, or fragments	Seal exceeds allowable external and/or external leak rate limit when exposed to hydrogen (initially, after pressure cycles, after temperature cycles, or over extended time). (350)	Contain hydrogen with static seal and dynamic seal at all operating pressures (5 to 875 bar) and temperatures (-40C to 85 C) until end of life - lower than acceptable external and internal leakage rate of 10 Nml/h

Approach
Overview of the PNNL Unique In situ Tribometer

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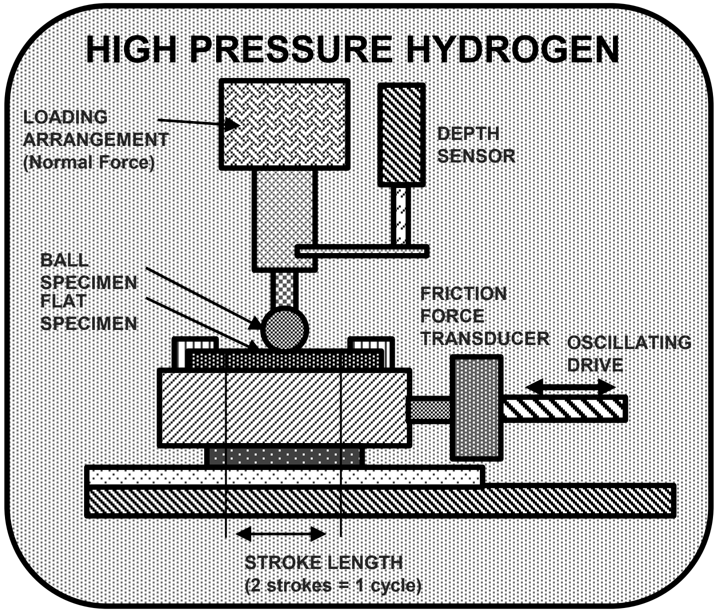

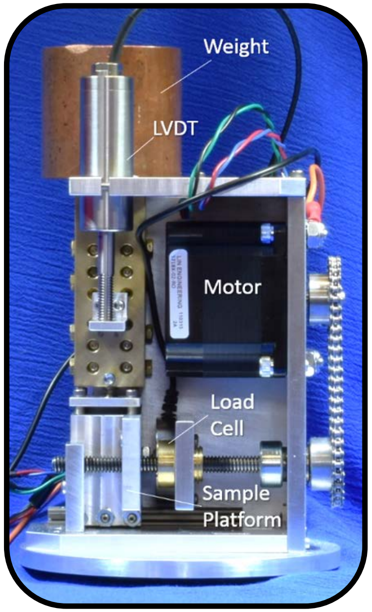

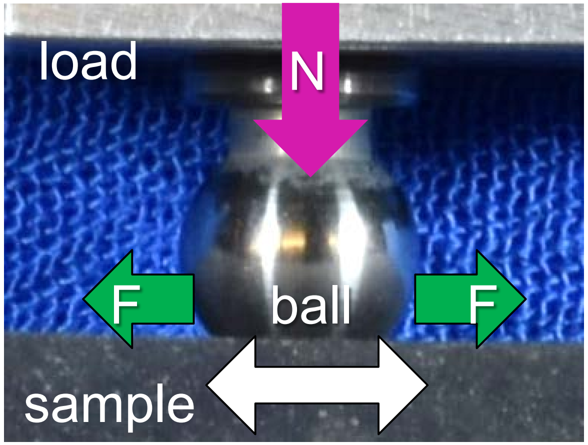

Overview of Tribometer

- Linear reciprocating adapted from ASTM G133
- Normal load (using weights) presses steel ball into moving sample
- Frictional force and vertical wear depth profiles measured in situ
- Pressures up to 5,000 psi hydrogen
- Ambient air and high pressure argon tests run for comparison

Accomplishments
Test Methodology Development, Tribology

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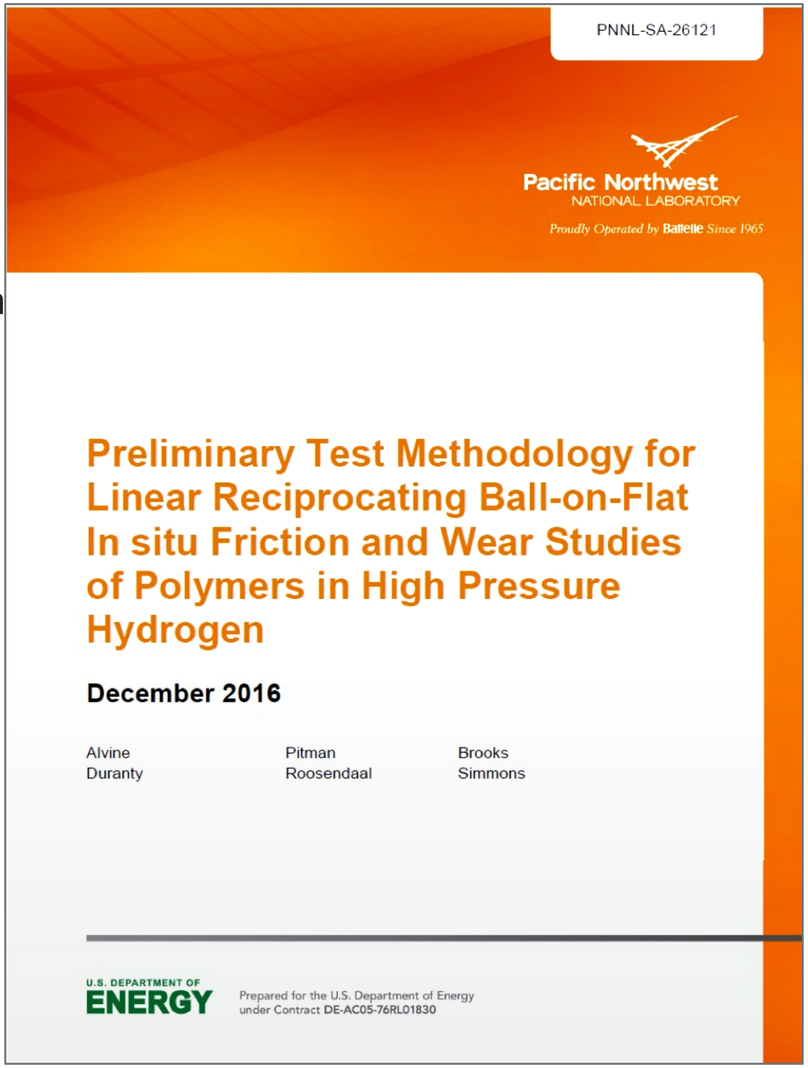
- We have developed a preliminary test methodology for in situ high pressure hydrogen testing of friction and wear
- Adaptation of ASTM G-133
- Test method has demonstrated differences in hydrogen argon, and ambient air
- Tested three materials following newly developed test method, NBR, EPDM, and PTFE
- Initial control parameters determined for Load, speed, track length, pin diameter, pin material
- Future Additions
  - Humidity testing
  - Additional Gas Species size comparison (Ar, He)
  - Full parameter testing (load, speed, etc)
  - Heating and cooling


PNNL-SA-26121

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Preliminary Test Methodology for Linear Reciprocating Ball-on-Flat In situ Friction and Wear Studies of Polymers in High Pressure Hydrogen

December 2016

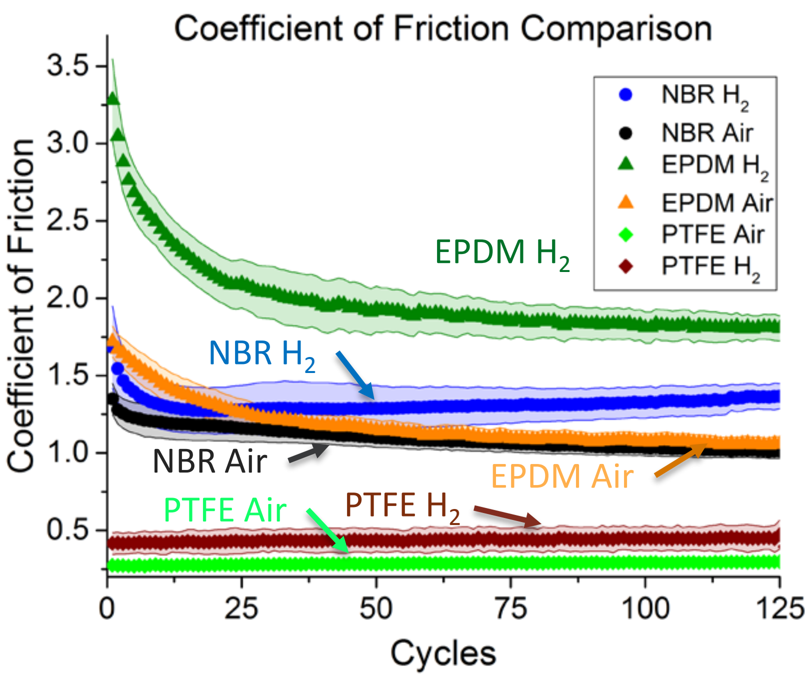
Alvine Duranty | Pitman Roosendaal | Brooks Simmons

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

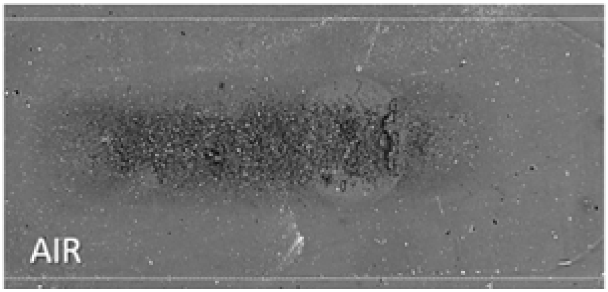
Data will be made available on h2tools.org

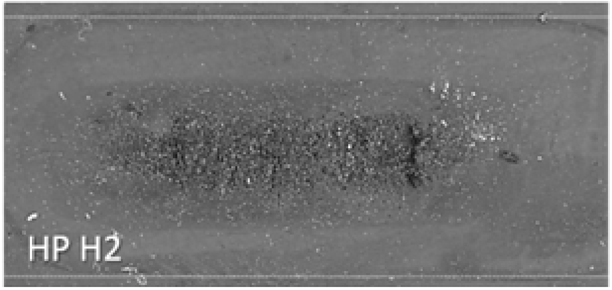
Accomplishments
HP Hydrogen Impact on Friction and Wear

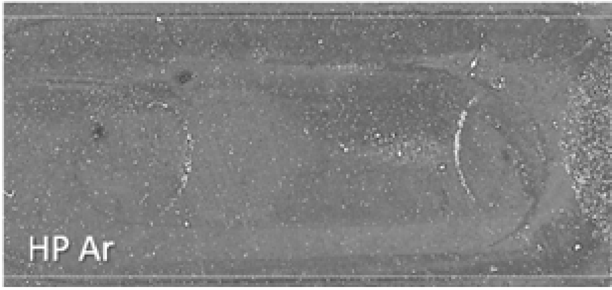


- Testing of NBR, EPDM, and PTFE show an increase in coefficient of friction in 4,000 psi hydrogen by factors of 1.4, 1.8, and 1.5 respectively as compared to ambient air
- Ex situ optical microscopy shows clear increase in wear in hydrogen and ambient air over high pressure argon for NBR
- Ex situ optical profilometry (interference) shows clear increased wear in high pressure hydrogen over ambient air, over high pressure argon for NBR
  - Ex situ wear track depths are 100 microns, 60 microns, and 7 microns respectively for high pressure hydrogen, ambient air, high pressure argon

Ex Situ Wear Tracks in NBR

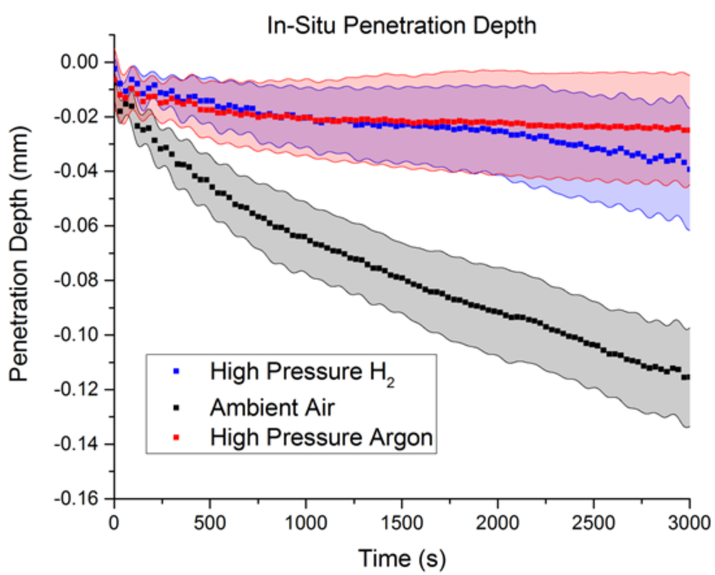


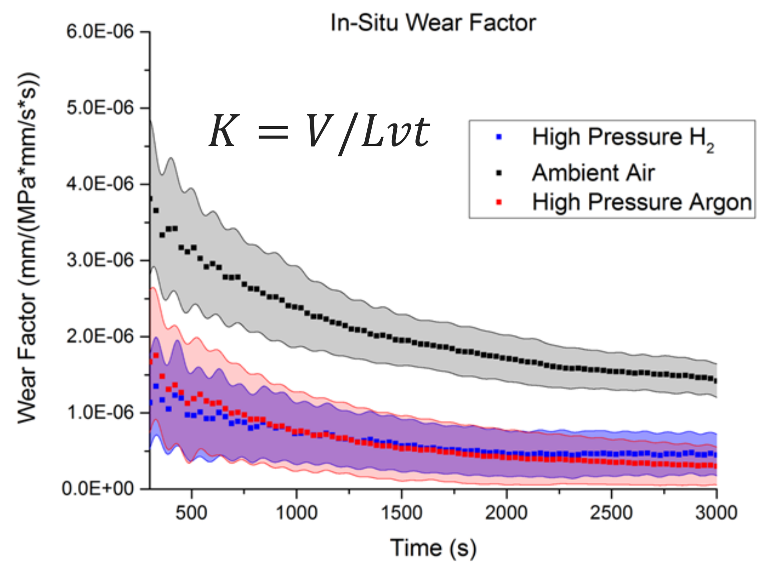




Accomplishments
In situ Pressure effects, Tribology

- In situ vs ex situ depth profiles enable separation of pressure vs gas species effects
  - Ex situ shows clear increase in hydrogen wear depth over argon and air
- In situ dimensional changes are pressure driven while friction and wear are gas species driven – reasons are likely due to lubricity and filler chemical changes

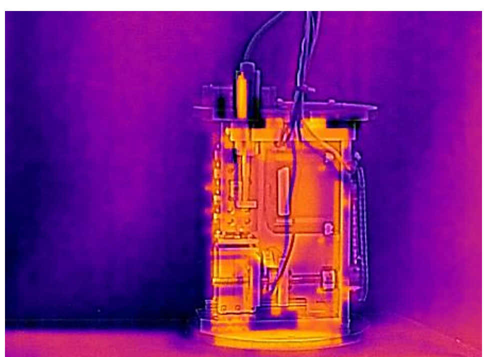


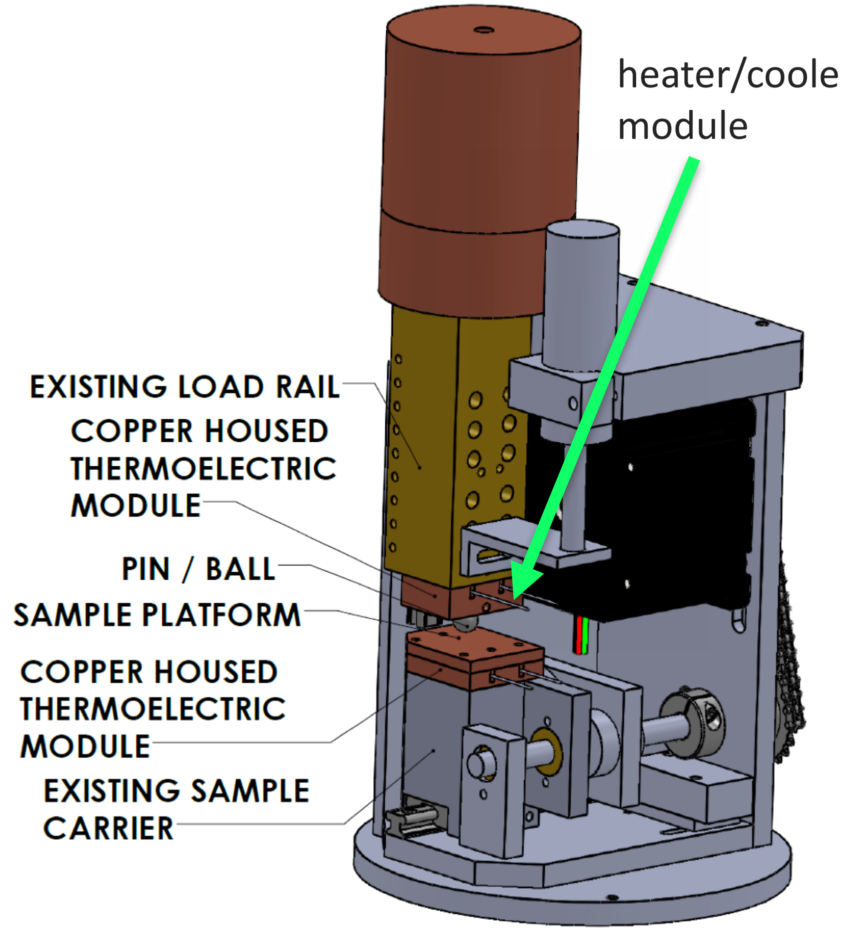


Progress
Tribometer Upgrade for In Situ Heating & Cooling

- Stakeholder feedback requires temperatures above or below ambient (-40 to +85 C) for infrastructure applications
- A current design using a thermoelectric heater/cooler stage for the system
  - Testing of heaters, Peltier's, thermocouples, etc. complete
  - Modification of pressure vessel top flange for thermocouple feedthroughs complete
  - IR analysis of heating of tribometer in progress
  - Design expected to be complete summer 2017
  - Build and debugging expected to take 1-2 months
  - Module will be tested after ambient tests are complete to ensure identical testing conditions

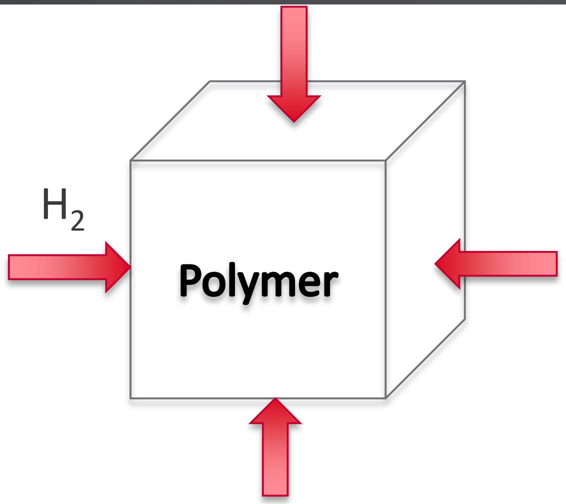
IR image of the tribometer in air after multiple cycles

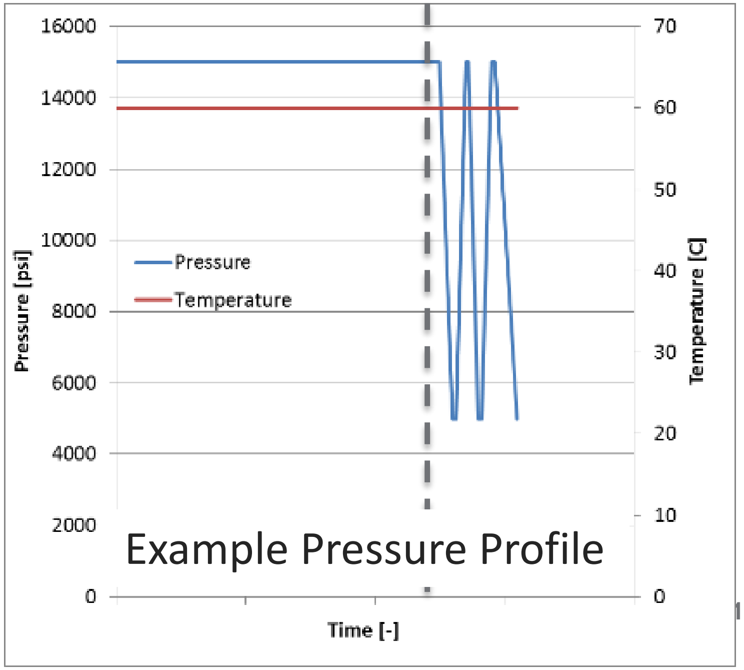




Approach
Pressure Cycling Effects

- Establish test method start up procedures
- Effects of purge gas on material properties at high pressure
- Determine the influence on compression set in samples from purge gas
- Build rapid decompression control system for pressure cycling
- Material characterization of thermal and pressure cycling effects from high pressure





Example Pressure Profile

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Approach

Behavior of Polymers in Helium, Helium/Hydrogen and Argon/Hydrogen environments: Motivation

Sandia National Laboratories

Motivation for current study

High pressure hydrogen cycling experiments with polymers for science-based approach to test methods in hydrogen may need leak detection	Test methodologies developed in the future may require purge step with inert gases prior to testing in hydrogen

Soft polymeric materials can be affected by purge/leak detection step prior to testing in hydrogen ***

High leak detection test pressures (100 MPa) can produce structural changes in polymers prior to hydrogen exposure	Minimum times of leak detection or purge (2 hours to 2 days) can affect the polymers so as to skew exposure data with hydrogen

Current studies: Exposure of polymers to helium, helium/hydrogen, and argon/hydrogen environments to understand possible effects

Helium effects vs helium/hydrogen effects for PTFE, Buna N and Viton A	Helium/hydrogen effects vs Argon/hydrogen effects for PTFE, POM, Nylon-11, NBR, Viton A and EPDM

*** = Menon, N.C., Kruizenga, A.M., Alvine, K.J., San Marchi, C., Nissen, A., Brooks, K., Behavior of polymers in high pressure environments as applicable to the hydrogen infrastructure, 2016 Proceedings of the ASME 2016 Pressure Vessels and Piping Conference (PVP 2016), 6B, paper no. PVP2016-63713, pp. V06BT06A037 16 pages ISBN: 978-0-7918-5043-5

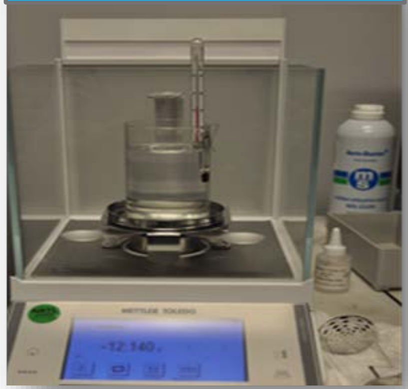
Progress
Behavior of Polymers in Helium, Helium/Hydrogen and Argon/Hydrogen environments: Experiments

- Polymers tested:
  - PTFE, Nylon-11, POM, EPDM, NBR, Viton A
- O rings of all polymers used (picture on right)
- Static conditions of exposure for all gases
- Experiment 1: Helium gas at 100 MPa for 40.5 hours >> polymers removed for characterization
- Experiment 2: Argon gas at 100 MPa for 108 hours followed by hydrogen at 100 MPa for 168 hours >> polymers removed for characterization
- Other sources of data: Helium gas at 100 MPa for 40.5 hours followed by hydrogen at 100 MPa for 168 hours (previous study) >> polymers removed for characterization
- Characterization tests: Modulus/T_g, compression set, density changes, mass loss, micro-(CT)

Sample holder with O ring specimens

Compression set test for elastomers

Density measurements set-up



Accomplishment and Progress
Summary of Results: Current Testing

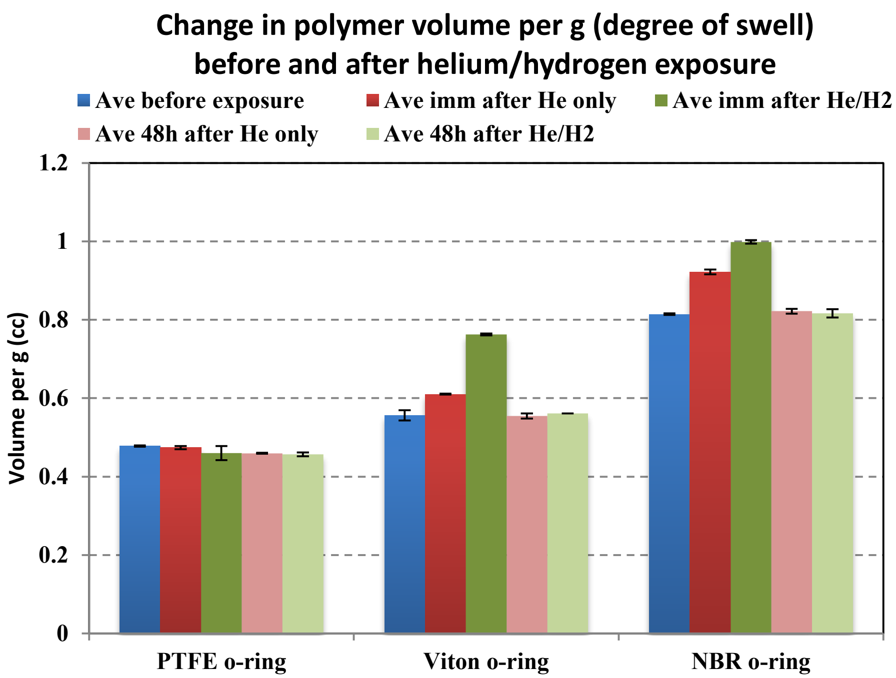
- Only most severe effects on polymers are shown in each category

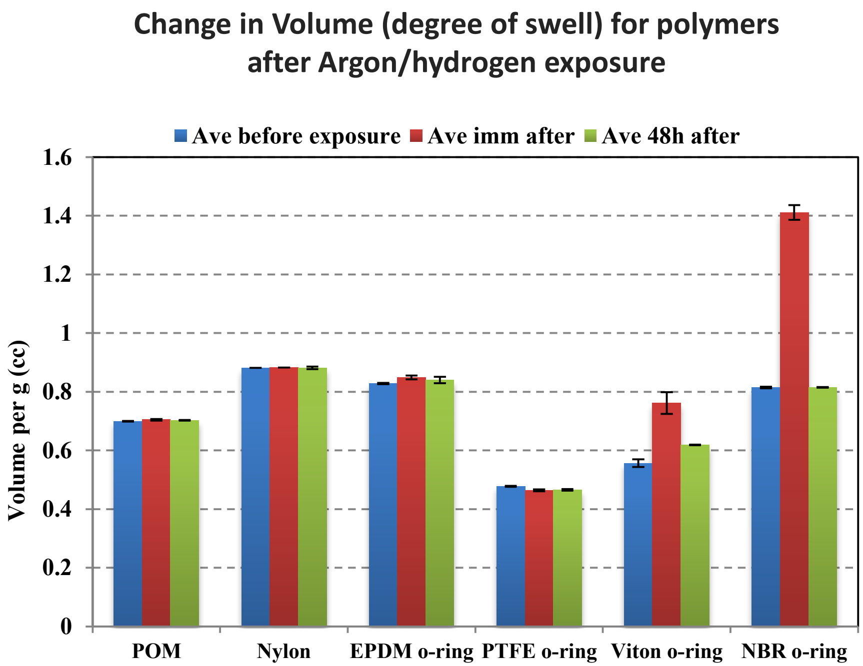
Polymer properties (Characterization methods)	Maximum Effects Seen in various gas environments		
	Argon/Hydrogen**	Helium/Hydrogen***	Helium
Swelling (Density measurements)	73% with 100% recovery seen with NBR	36% with 100% recovery seen with Viton A	14% with 100% recovery seen with NBR
Storage Modulus changes (DMTA)	41% decrease for Viton A	20% decrease with Buna N	No change observed
Compression set (Elastomers only)	5 times increase seen for Viton A	1.6 times increase with Viton A	2.0 times increase with Viton A
Mass loss (TGA) indicating gas diffusion out of polymer after 48 hours after removal from test	Highest mass loss	Mass loss is lower than unexposed	Lowest
Explosive Decompression (Micro CT)	Viton A shows severe damage; <u>much less effects on NBR and EPDM</u>	Viton A shows voids around specific fillers; <u>NBR and EPDM unaffected</u>	All polymers are unaffected

- **Argon/Hydrogen exposure produces severe effects in NBR and Viton A, minimal in EPDM rubber >>>> <u>Not suitable as purge or leak detection gas in polymer test methods</u>**
- **Helium/Hydrogen exposure has intermediate effects while Helium exposure exhibits minimal effects in polymers >>>> <u>Helium as leak detection gas choice is a possibility</u>**

** = Argon leak detection followed by Hydrogen exposure
*** = Helium detection followed by Hydrogen exposure

Progress
Behavior of Polymers in Helium, Helium/Hydrogen and Argon/Hydrogen environments: Data





- Thermoplastics (PTFE shown here) showed negligible effects with helium or helium/hydrogen exposure
- Viton A and NBR both show greater swell with helium and helium/hydrogen but recover almost completely in 48 hours
- Viton A and NBR both show greater swell with argon/hydrogen exposure but recover almost completely in 48 hours

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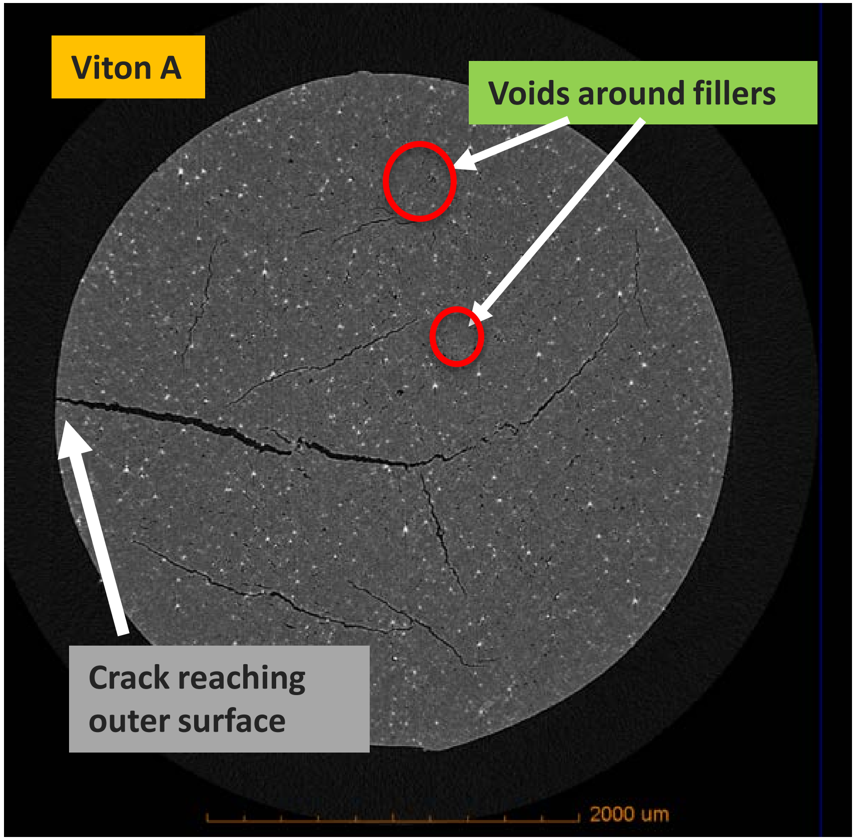
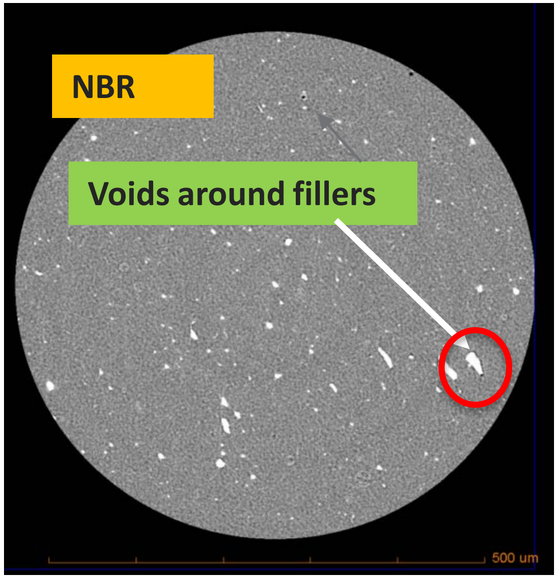
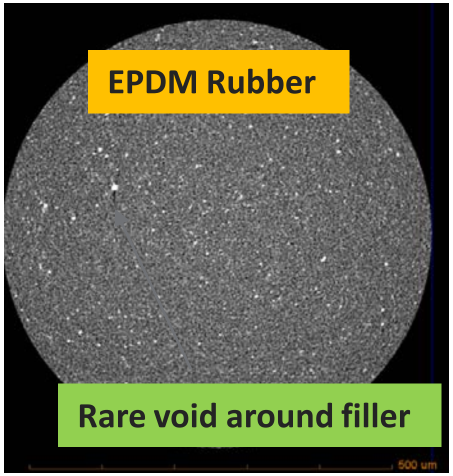
Accomplishments and Progress
Micro CT pictures of polymers: Argon/hydrogen



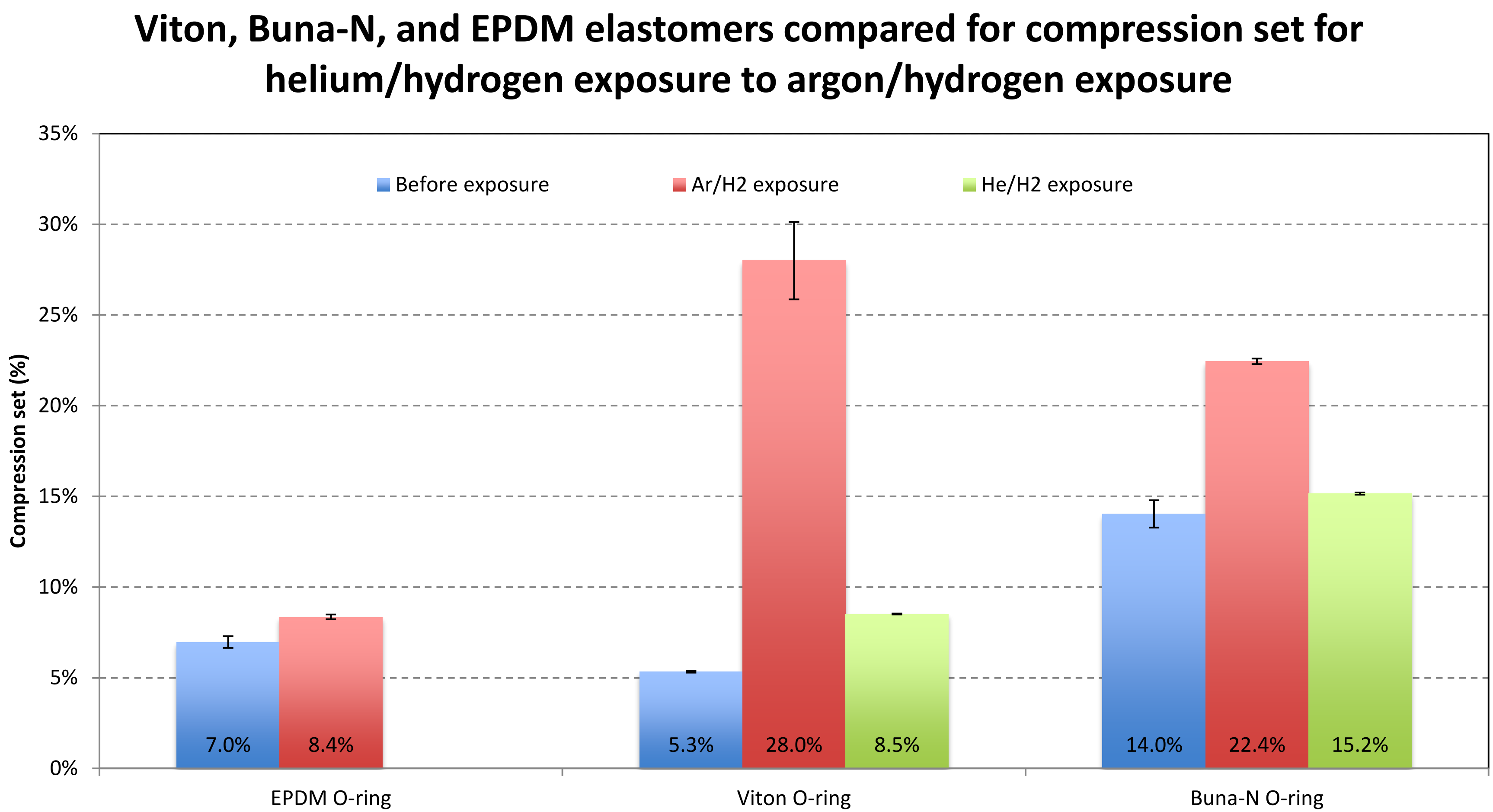




NBR and EPDM shown at 500 microns to magnify any voids or cracks

- Viton A shows cracks that reach the outside surface of the O ring, whereas NBR and EPDM are bereft of mini-cracks or voids after argon/hydrogen
- Micro CT of Viton A points to adjoining voids coalescing to form localized mini-cracks that further coalesce to form huge cracks that travel to the surface

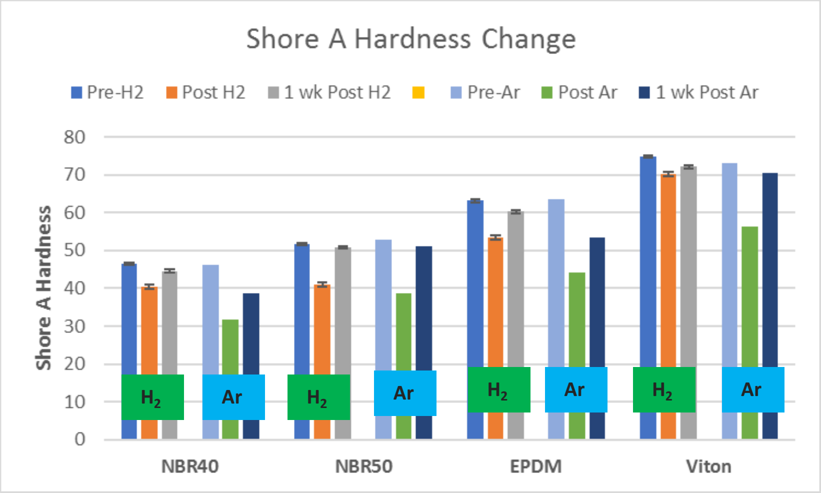
Progress
Behavior of Polymers in Helium, Helium/Hydrogen and Argon/Hydrogen environments: Data

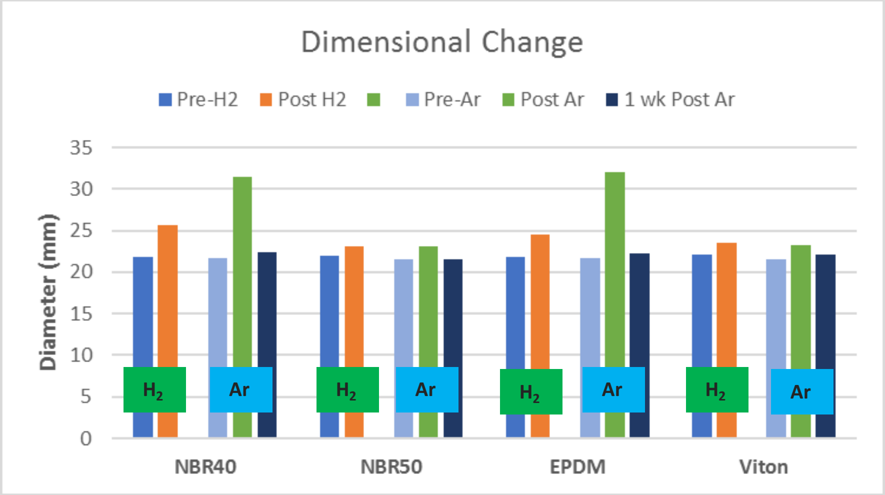


- Viton A and Buna N shows significant compression set with argon/hydrogen exposure compared to helium/hydrogen
- EPDM rubber exhibits increased compression set in argon/hydrogen also

Accomplishments
Characterization of Polymers

- PNNL measured some simple properties of materials before and after hydrogen exposure to look for correlations with other tests
  - Hardness changes – directly after exposure and 1 week after
  - Swelling – directly after exposure and 1 week after
  - Sensible with free volume and diffusion considerations
- Once PNNL and SNL test methods are established, the team will do a round robin testing on the material properties of the polymers to enable a direct comparison and provide a baseline for users of the data when using polymers from other vendors





- Ex situ hardness and swelling changes show a trend that is more related to gas molecular size with the swelling increasing for high pressure argon over high pressure hydrogen

Progress
Next Steps: Future Experiments planned

- High pressure cycling system is being built in two parts: a low pressure side and a high pressure side
- Exposure of polymers to high pressure hydrogen from 35 MPa to 103 MPa at RT, -60C and +110C isothermal conditions
- Goal : a science-based understanding of the behavior of select polymers under cycling conditions of pressure for individual temperatures of interest
- This is to enable selection of critical test parameters and material attributes for test methodology development

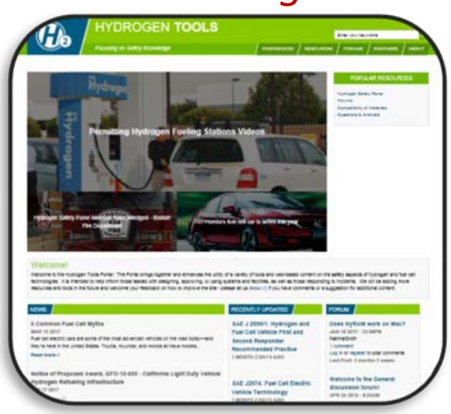
Approach Test Methodology Development Neutron Reflectometry Scattering

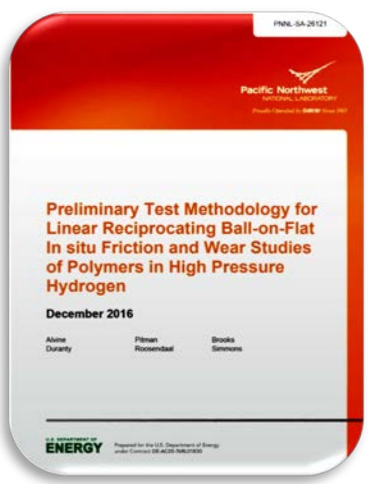
- Use in situ neutron reflectometry (NR) to investigate behavior of interfacial polymers and polymer nanocomposites while samples immersed in high-pressure hydrogen
  - Results of NR can provide understanding of interfacial phenomena occurring in polymeric material while stressed by extreme pressure
  - Discover morphology of the polymer crystal and amorphous regions
  - Determine local solvation of the polymer matrix
  - Examine effect of high-pressure hydrogen on interface between the loaded additive and the matrix
- In situ (U)SANS provides average pore size and pore-size distribution in a polymer structure, while in situ NR offers real-time distribution of pores along the vertical direction of a polymer film

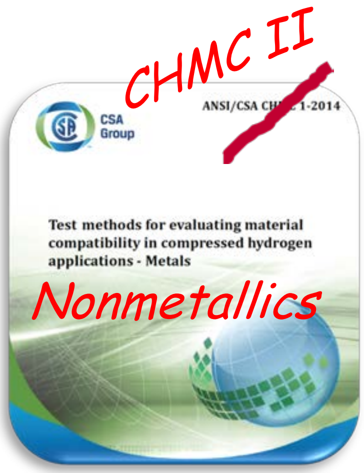
Accomplishments
Dissemination of Information

- The team is working to disseminate the information gathered on this project through presentations, publications, and involvement in code committee work
  - Team member Mike Veenstra is now chair of the CHMC II nonmetallic hydrogen compatibility code committee. For reference, CHMC I is a standard reference for metals compatibility.
  - The team now has given 8 presentations, including a keynote address to the International Hydrogen Energy Development Forum, and an invited talk at the Hydrogenius Research Symposium, both in Fukuoka, Japan
  - The team has 4 publications, and 3 under review, including a recent submission to Review of Scientific Instruments on the Tribology work
  - The team is working on a webpage to showcase this work and provide a database/guide on h2tools.org. This is expected to come online summer 2017

h2tools.org







Response to previous year's reviewers' comments

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Area of Comment	Comments	Response
Temperature and pressure reference	• SAE International J2601 -compliant fill and hence define the P, T domain of interest. • The temperature bands should be widened to provide a safety factor to address the impact of excursions • operative conditions in their lifetimes beyond their design values	We are working to address that with a modification to our testing setups. For tribology, room temperature testing needs to be completed first.
Previous work done	• Previous DOE activities related to hydrogen in polymers	We have reached out to other projects, including NREL hose work to learn what issues arose.
Stakeholders to be included in the future	• Neither a station provider nor a dispenser manufacture was included in the stakeholder list; the project team should include these additions. • An international interface is not mentioned.	We have had discussion with Linde and visited a station. We have also discussed dispensers and talked to Nanosonic.
Scope change	• The process for polymeric materials selection for testing could be improved.	We are currently testing the top 5 commonly used polymer materials.
Dissemination Efforts	• Thought is needed on how to supply this information to the stakeholders	Many discussions have been had with multiple code organizations about this. We are working on a guide/database and will provide information about this on h2tools.org later in FY17.

Collaborative Activities

Partner		Project Roles
U.S. DEPARTMENT OF ENERGY	DOE	Sponsorship, Steering
Pacific Northwest NATIONAL LABORATORY	PNNL	Project Lead, Polymer Characterization, Wear and Tribological Studies, Mechanical Properties and Moderate Pressure
Sandia National Laboratories	SNL	Exposure Pressure Cycling Studies, Mechanical Properties and High Pressure, Develop Technical Reference Documentation and Database
OAK RIDGE National Laboratory	ORNL	Neutron and X-ray Scattering Studies
Ford	Ford	Subcontracted Participant and Consultant, Represent OEM Perspective

Additionally, the team has reached out to over 40 industrial stakeholders for information and had discussions with over 25, including Linde and Parker, and Swagelok Application space includes compressors, valves, refueling stations, seals, liners, and academia.

Remaining Challenges and Barriers

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Challenges and Barriers	Mitigation
Large amount of polymers and elastomers to test	Test methodology developments are material focused from stakeholders
In situ temperature testing (-40 to 85°C)	Tribology investigating use of sample cooling and heating, pressure cycling system in environmental chamber
Testing time is long	When appropriate double up on sample soaking
Dissemination of data is a broad audience	Presentations to professional organizations, publications, h2tools.org with database and guide
Cannot see impact of hydrogen during long term cycling or frictional wear in a short test (Impact may not exist)	Target and test materials that are believed most likely to be impacted prior to evaluating other candidates
Working with high pressure H2	National lab experience working with high pressure hydrogen

Proposed Future Work

- FY 2017
  - Complete room temperature tribology testing of NBR, EPDM, PTFE, Viton, and POM
  - Complete modifications for tribometer heating/cooling stage and test
  - Complete SNL pressure cycle aging setup and being testing
  - SNL will provide ORNL with pressure cycle aged samples for neutron scattering studies to look at fundamental material changes like porosity
  - Complete webpage launch for disseminating project data
  - Continue involvement and leadership in CHMC II
- FY18
  - Continue involvement and leadership in CHMC II
  - Complete heating/cooling tribology testing for NBR, EPDM, and PTFE
  - Update website database/guide and continue publications and presentations
  - Complete pressure cycle aging studies on NBR, EPDM, PTFE, Viton, and POM
  - Complete neutron scattering experiments on pressure cycle aged polymers
  - Identify other critical areas of need for polymer/hydrogen testing

Technology Transfer

- Stakeholder Engagement
  - Continued outreach internationally with trip to Japan Hydrogenius conference added Japanese stakeholders
  - Present and publish results
  - Webpage on h2tools.org to be available later in FY17
- Code and Standards Committees
  - Leadership on CSA's new committee on CHMC II Polymers and Elastomers
- Industrial Collaborators
  - Maintain dialog with Collaborators to discuss pathways for qualification and technology transfer
  - Automotive and refueling station stakeholders

Papers and Notable presentations

Publications

- Nalini Menon, Alan Kruizenga, April Nissen, Christopher San Marchi, Kyle Alvine, Kriston Brooks, “Behavior of polymers in high pressure hydrogen environments as applicable to the Hydrogen Infrastructure,” accepted to the 2016 ASME Pressure Vessels & Piping Conference, Vancouver, BC, Canada, July 2016
- N.C. Menon, A.M. Kruizenga, A. Nissen, C. San Marchi, K. J. Alvine, K. Brooks, D. B. Smith and A. K. Naskar, “Polymer Behavior in High Pressure Hydrogen environments with relevance to the Hydrogen Infrastructure,” submitted to International Hydrogen Conference, Moran, WY, September 2016
- Alvine K., Brooks K., Duranty E., Menon N., Kruizenga A., San Marchi C., Smith B., Naskar A.,“Hydrogen Compatibility of Polymers for Infrastructure Applications: Friction and Wear.” Submitted to the 2016 International Hydrogen Conference, Moran, WY, September 2016
- Duranty E., Roosendaal T., Pitman S., Tucker J., Owsley Jr. S., Suter J., Alvine K., “An In Situ Tribometer for Measuring Friction and Wear of Polymers in a High Pressure Hydrogen Environment.” Submitted to Review of Scientific Instruments, April 2017

Presentations

- Alvine, Brooks, et al, “Hydrogen Compatibility of Polymers for Infrastructure Applications,” submitted to International Hydrogen Conference, Moran, WY, September 2016.
- Alvine, Brooks, et al, “Hydrogen Compatibility with Polymers: Tribology and Cycle Aging,” accepted to the 2016 ASME Pressure Vessels & Piping Conference, Vancouver, BC, Canada, July 2016
- Simmons et al, “Hydrogen Compatibility of Polymers Program Overview,” International Hydrogen Energy Development Forum,Fukuoka, Japan, February 2017 Invited Speaker
- Alvine et al, “In Situ Friction and Wear of Polymers in High Pressure Hydrogen.” HYDROGENIUS Research Symposium, Fukuoka, Japan, February 2017 Invited Speaker
- Menon et al, “High Pressure Cycling and Tribology effects on Polymers in Hydrogen Environments,” MSRF Workshop, Livermore, CA, March 2017

Accomplishment Summary

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- Stakeholder Engagement & Dissemination
  - Engaged 25 stakeholders for feedback
  - Stakeholder feedback identified four polymers/elastomers of interest (Viton™, EPDM, NBR, PTFE), Temp/Pressure of interest (-40 C to +85 C, 0 to 20,000 psi), and tests of interest (pressure transients, wear & abrasion, pressure cycling)
  - Completed FMEA to provide prioritization and future R&D activity focus
  - Team member M. Veenstra now chair of CSA CHMC 2 polymer-hydrogen code committee
  - 8 presentations, 4 publications, 1 invention disclosure: includes keynote speaker at International Hydrogen Energy Development Forum in Japan, and invited speaker at the Hydrogenius Research Symposium in Japan

Accomplishment Summary

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- Technical Accomplishments
  - PNNL completed development of a novel in situ tribometer and the test methodology for high pressure hydrogen and used it to collect data on NBR, PTFE, and EPDM
  - Completed tribology testing of NBR, EPDM, and PTFE in high pressure hydrogen and ambient air
    - The Coefficient of Friction in hydrogen of EPDM increased 80%, PTFE increased 50%, and NBR increased 40% compared to ambient air
    - Hydrogen demonstrates higher wear in NBR for the same number of cycles when compared to ambient air and high pressure argon with hydrogen wear at nearly 40% higher than ambient air and argon wear is nearly 90% lower than ambient air
- Sandia completed high pressure purge gas study to evaluate the gas effect on test startup
  - Argon/Hydrogen exposure produces severe effects in NBR and Viton A, minimal in EPDM rubber. Not suitable as purge or leak detection gas in polymer test methods
  - Helium/Hydrogen exposure has intermediate effects while Helium exposure exhibits minimal effects in polymers. Helium as leak detection gas choice is a possibility
- ORNL has completed preliminary investigations into HDPE pore formation after hydrogen exposure – samples provided by Sandia

Contacts

Pacific Northwest
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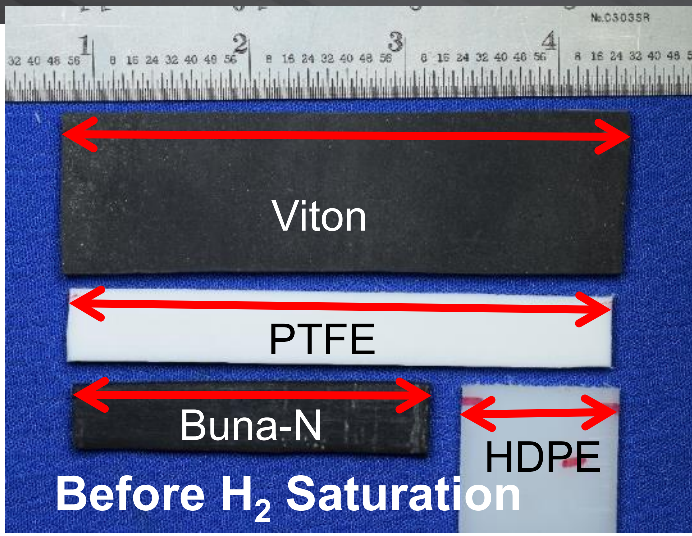
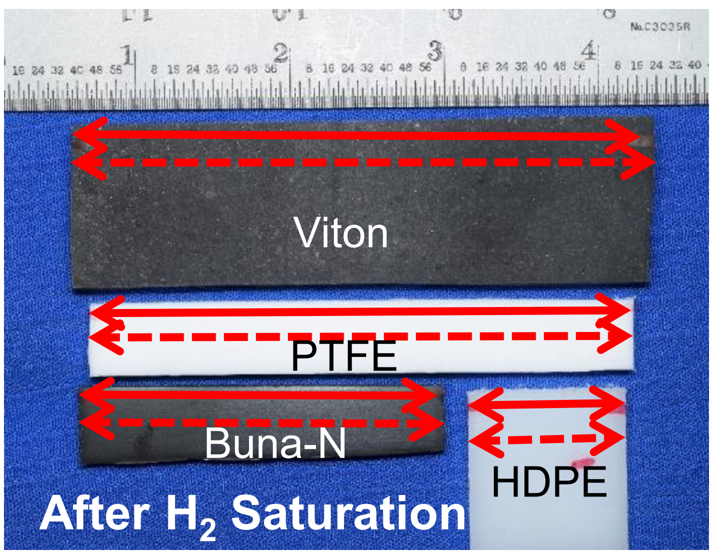
Kevin Simmons (PM)	☎: 509-372-4343	✉: kl.simmons@pnnl.gov
Kyle Alvine (PI)	☎: 509-372-4475	✉: Kyle.Alvine@pnnl.gov
Nalini Menon	☎: 925-294-4872	✉: ncmenon@sandia.gov
Barton Smith	☎: 865-574-2196	✉: smithdb@ornl.gov
Mike Veenstra	☎: 313-322-3148	✉: mveenstr@ford.com

Technical Backup Slides

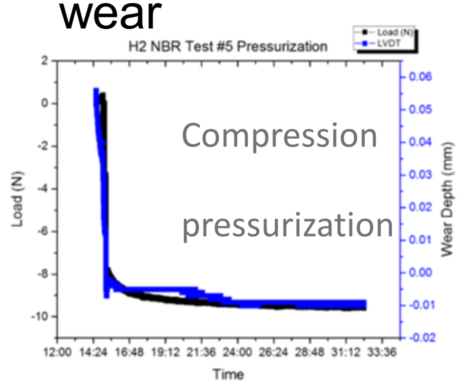
Test Methodology Development, Tribology

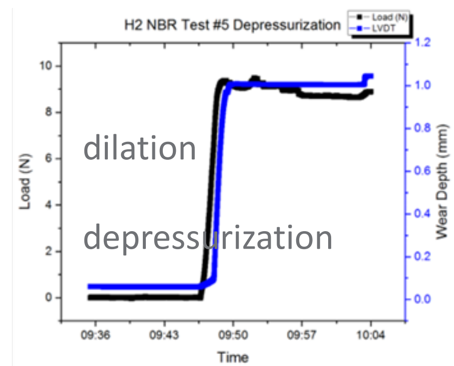




Obvious sample dilation due to high pressure hydrogen pressure is observed

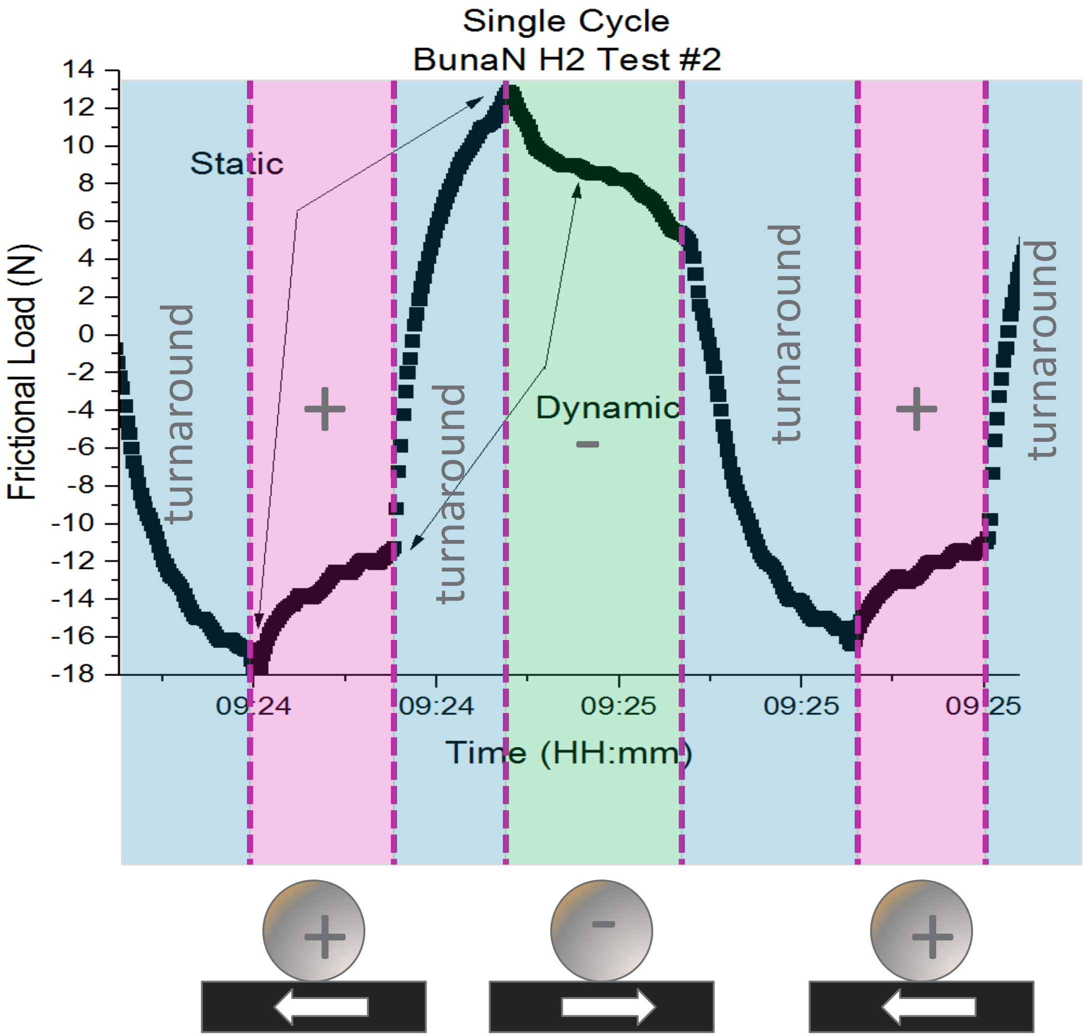
- Elastomers expand much more than thermoplastics
- Preliminary Data, exact quantification in progress
- Data will be used to better understand changes in wear





Material	Approximate expansion (4,000 psi)
Viton	6.9%
Buna-N	4.5%
PTFE	< 1%
HDPE	< 1%

Data Processing: Frictional Load



Load cell:

- Measures frictional load as function of
  - Cycles/time
  - Normal load
- Static and dynamic possible

Test Methodology Development

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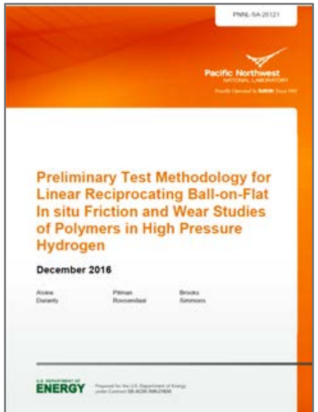
- PNNL has developed a new test methodology for *in situ* hydrogen measurement of friction and wear of polymers (tribology)
  - Infrastructure applications include:
    - Dynamic seals for compressors, valves (O-rings and seats), regulators
    - Delivery hose liners where frictional contact can occur
  - Failure mechanisms are:
    - Increased leak rates
    - Reduced mechanical efficiency
    - Reduced part lifetime due to part degradation
- Instrument Specifications*
  - Linear reciprocating instrument capable of up to 5,000 psi in situ hydrogen
  - Measures in situ frictional load and wear depth profile
- Tests to date:
  - Materials that have been tested or are in process include:
    - NBR (nitrile butadiene rubber or Buna-N) – completed 4,000 psi hydrogen, 4,000 psi argon, ambient air.
    - EPDM (ethylene propylene diene monomer) – completed 4,000 psi hydrogen, ambient air, 4,000 psi argon in progress
    - PTFE (polytetrafluoroethylene or Teflon) – completed 4,000 psi hydrogen, ambient air, 4,000 psi argon in progress
    - Viton – ambient air tests started
  - Above materials (NBR, EPDM, PTFE, Viton) & POM expected to be complete by end of summer 2017
- Upgrade planned late 2017 to include in situ heating and cooling
    - Targeted range -40 to +85 C
    - Heaters and Peltier initial testing for high pressure hydrogen compatibility complete
    - Preparing design
    - Build and integration planned after room temperature testing complete

Material	HP Hydrogen	Ambient	HP Argon
NBR	Complete	Complete	Complete
EPDM	Complete	Complete	Planned
PTFE	Complete	Complete	Planned
Viton	Planned	Planned	Planned
POM	Planned	Planned	Planned


Preliminary Test Methodology for Linear Reciprocating Ball-on-Flat In situ Friction and Wear Studies of Polymers in High Pressure Hydrogen

December 2016

*Duranty, Roosendaal, Pitman, Tucker, Owsley, Suter, and Alvine, “An In Situ Tribometer for Measuring Friction and Wear of Polymers in a High Pressure Hydrogen Environment”, submitted to Review of Scientific Instruments April 2017

Progress
Dissemination of Information

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Select application	Valve Seals	Weighting: Valve Seals	$C_s = w_1P + w_2F + w_3PCA + \ldots$

Scoring				Test Methodologies					
Polymer	Description	Composite score (1-10)	Temperature (°C)	Tensile Strength % change	Permeability $\Phi \times 10^9$ (mol H_2/m•s•MPa)	Friction and Wear $\mu_F/R_w(10^{-5}$ mm/s)	Pressure Cycle Aging	Swelling 10^{-3} %/psi	Test 5…
NBR	poly(butadiene-co-acrylonitrile)	3	25	85%	5.5	1.5/1.6	?	5	
Viton									
PTFE									
…									

Hyperlinked to datasheet details

- Give input selection box at top to change weighting based on application. I.e. compressor may increase friction and wear weighting, while a permeability barrier may increase the permeability weighting. Changing this repopulates the composite score and changes the list order.
- Include links in the data to either separate page or pop-up box describing the methodology for the test and analysis.
- Optional: include temperature and pressure range as an input.
- We should identify future tests including, but not limited to: blistering, in-situ tensile, compression set swelling, absorption (weight increase if any), impact of thermal excursions (high/low), cryogenic, off-gassing of impurities, transition temperature changes, plasticization, fracture/fatigue, other

In situ neutron reflectometry at ORNL using liquid reflectometer

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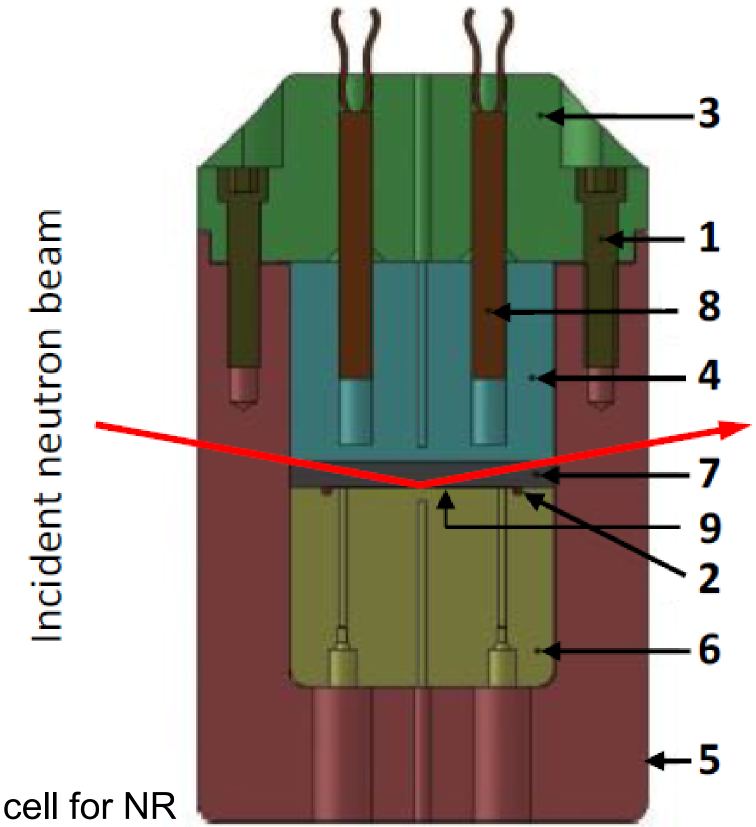
Pressure cell designed for neutron reflectometry at pressures up to 50 MPa and temperatures from room temperature to 200°C



Cross-sectional view of high-pressure cell for NR
(1) Pressure retaining fasteners, (2) O-ring seal, (3) pressure cell cap, (4) top support cylinder, (5) high-pressure cell body, (6) titanium support cylinder*, (7) wafer, (8) heater cartridges and (9) spin-coated film

**Alpha-phase titanium (α-Ti) is susceptible to hydride formation and embrittlement, so an insert made from hydrogen-compatible high-strength metal such as β-Ti will be used*