INCREASE YOUR H2IQ

The #H2IQ Hour

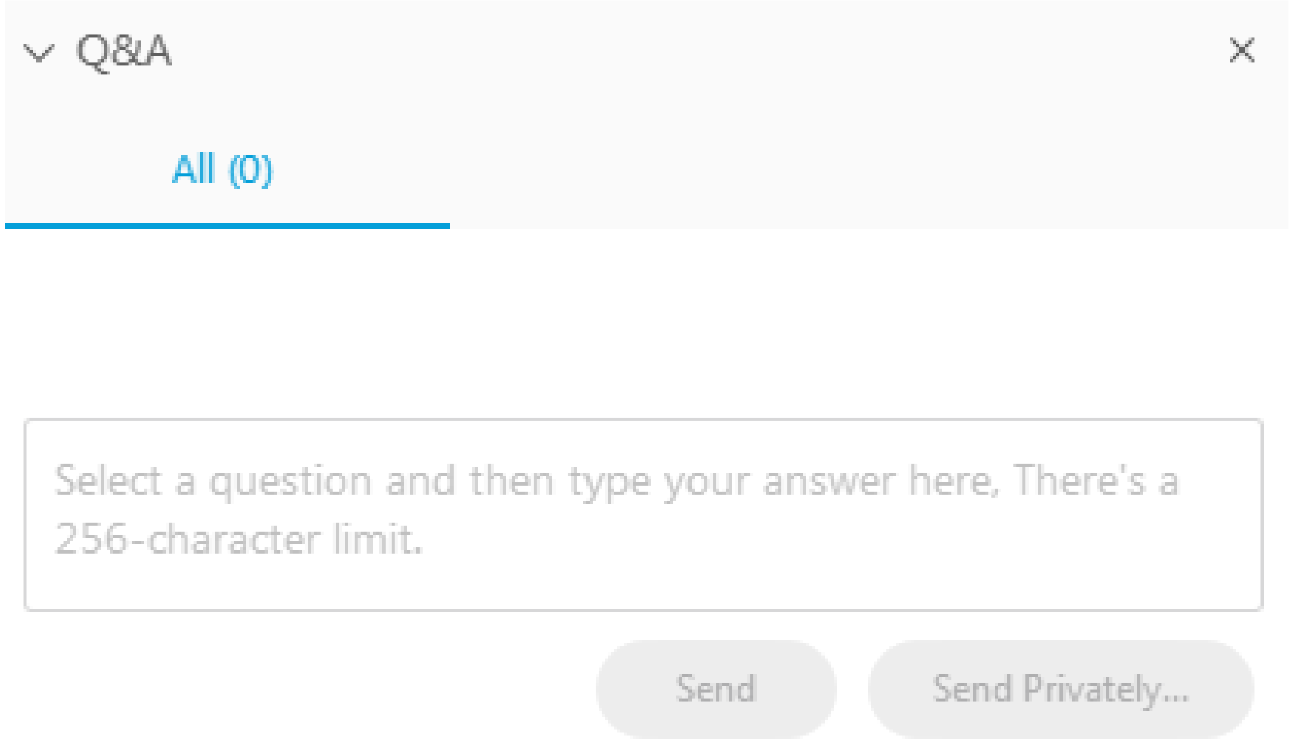
Today's Topic:

Cold and Cryo-Compressed Hydrogen Storage R&D and Applications

This presentation is part of the monthly H2IQ hour to highlight research and development activities funded by U.S. Department of Energy's Hydrogen and Fuel Cell Technologies Office (HFTO) within the Office of Energy Efficiency and Renewable Energy (EERE).

The #H2IQ Hour
Q&A

Please type your questions into the **Q&A Box**



U.S. DEPARTMENT OF
ENERGY
Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

Cold and Cryo-Compressed Hydrogen Storage R&D and Applications: Topic Introduction

Jesse Adams

Department of Energy

June 28, 2020


Pacific Northwest NATIONAL LABORATORY

Cold and Cryo-Compressed Hydrogen Storage R&D

Kevin L Simmons, PhD

Chief Engineer and Engineered Materials Team Lead

KL.Simmons@PNNL.Gov

U.S. DEPARTMENT OF ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy

Presentation Outline

- H2@Scale H-Mat Consortium
- Benefits of cold gas, cryocompressed, and liquid hydrogen storage
- Technical challenges
- H-Mat Cryo objectives
- Lab meeting results
- Materials testing
- Pressure vessel material models
- Pressure vessel failure models

Pacific Northwest NATIONAL LABORATORY

H-Mat Consortium Members

- Multi National Lab Consortium

H-Mat Hydrogen Materials Compatibility Consortium SM

Pacific Northwest NATIONAL LABORATORY

Oak Ridge National Laboratory

Sandia National Laboratories

SRNL

Argonne NATIONAL LABORATORY

Pacific Northwest NATIONAL LABORATORY

H-Mat Cryo Team

- Focused on addressing the material technical challenges, testing requirements, and modeling

Pacific Northwest NATIONAL LABORATORY

Kevin Simmons, Dan Merkel, B Nghiep Nguyen

Project Lead
Materials testing
Composite resin systems
Composites

Metals
Polymers
Pressure vessel material models

OAK RIDGE National Laboratory

Chris Bowland
Amit Naskar
Carbon fiber sizing
Composites

Sandia National Laboratories

Chris San Marchi
Hydrogen charging
Metals testing

Argonne NATIONAL LABORATORY

Hee Seok Roh
Pressure vessel model development

Cryocompressed offers a 90% increase in storage density

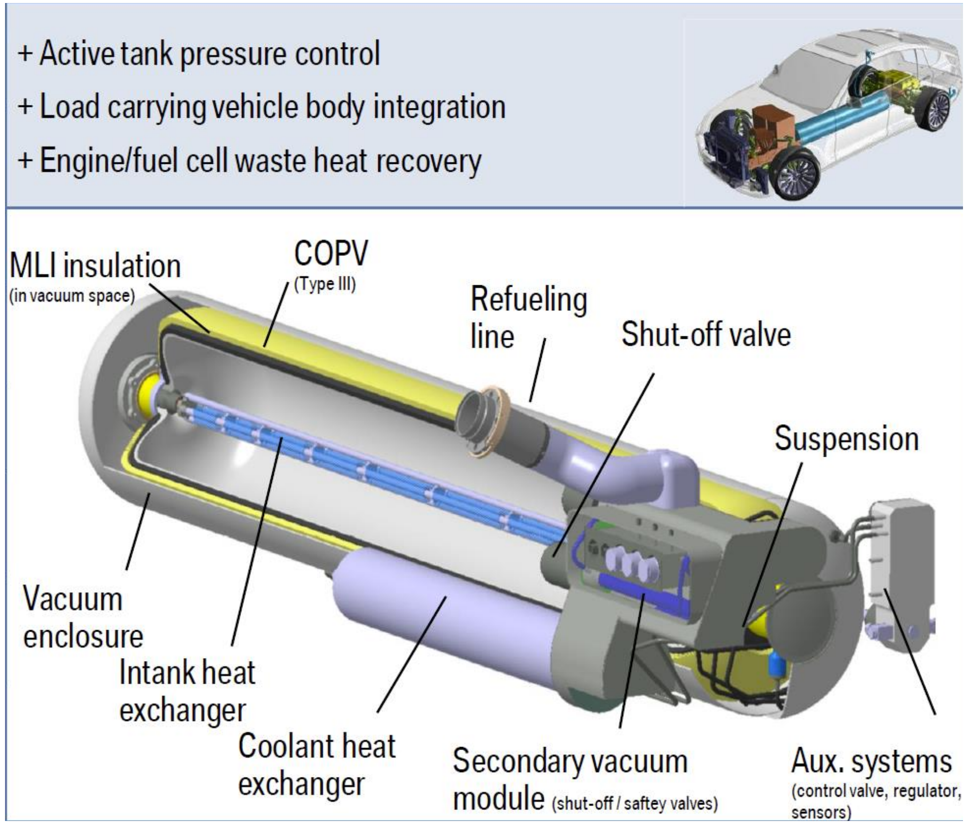
- Advantages of 500-bar CcH_2 system over Type 4, 700-bar, RT cH_2 storage system
  - 90% increase in storage density
  - 70% higher gravimetric capacity
  - 70% savings in carbon fiber composite
  - 20% saving in system cost at high volume manufacturing

Storage Method	cH_2	cH_2 [b]	cH2 Cold Gas [c]	CcH_2 [b]	CcH_2 [b]
Storage Pressure	350 bar	700 bar	500 bar	350 bar	500 bar
Liner	HDPE	HDPE	HDPE	2-mm SS	2-mm SS
Storage Temperature	288 K	288 K	200 K	62 K	67 K
Storage Density	24 g/L	40.2 g/L	42 g/L	71.2 g/L	76.7 g/L
Gravimetric Capacity	5.4%[a]	4.2%	3.9%	7.5%	7%
Volumetric Capacity	17.7 g/L[a]	24.6 g/L	23.4 g/L	35.5 g/L	44.2 g/L
CF Composite	61.9 kg[a]	96 kg	54.5 kg	20 kg	29 kg
Cost	$13/kWh[a]	$15/kWh	$13.3/kWh	$11/kWh	$12/kWh

[a] DOE Fuel Cell Technologies Office Record #13010 "Onboard Type IV Compressed Storage Systems-Current Performance and Cost," June 11, 2013
[b] 2018 Annual Merit Review, "System Level Analysis of Hydrogen Storage Options," R.K. Ahluwalia, Washington DC, June 13-15, 2018
[c] 2016 Annual Merit Review, "Enhanced Materials and Design Parameters for Reducing the Cost of Hydrogen Storage Tanks," Project No. ST101. David W. Gotthold, Washington DC, June 9, 2016.

Technical Challenges

- Small vacuum space necessary for system volumetric density efficiency
- The wide operating ranges from cryogenic to room temperature *challenges the* tank materials performance and alters the gas density, dormancy, H_2 burst energy
- Competing design objectives in storage system approach: *continuous use* vs. *long term dormancy periods* impact insulation design
- The *combination* of hydrogen exposure and thermal cycling, especially in metallic components
- Long term effect of hydrogen and thermal cycling on fatigue life and material aging.



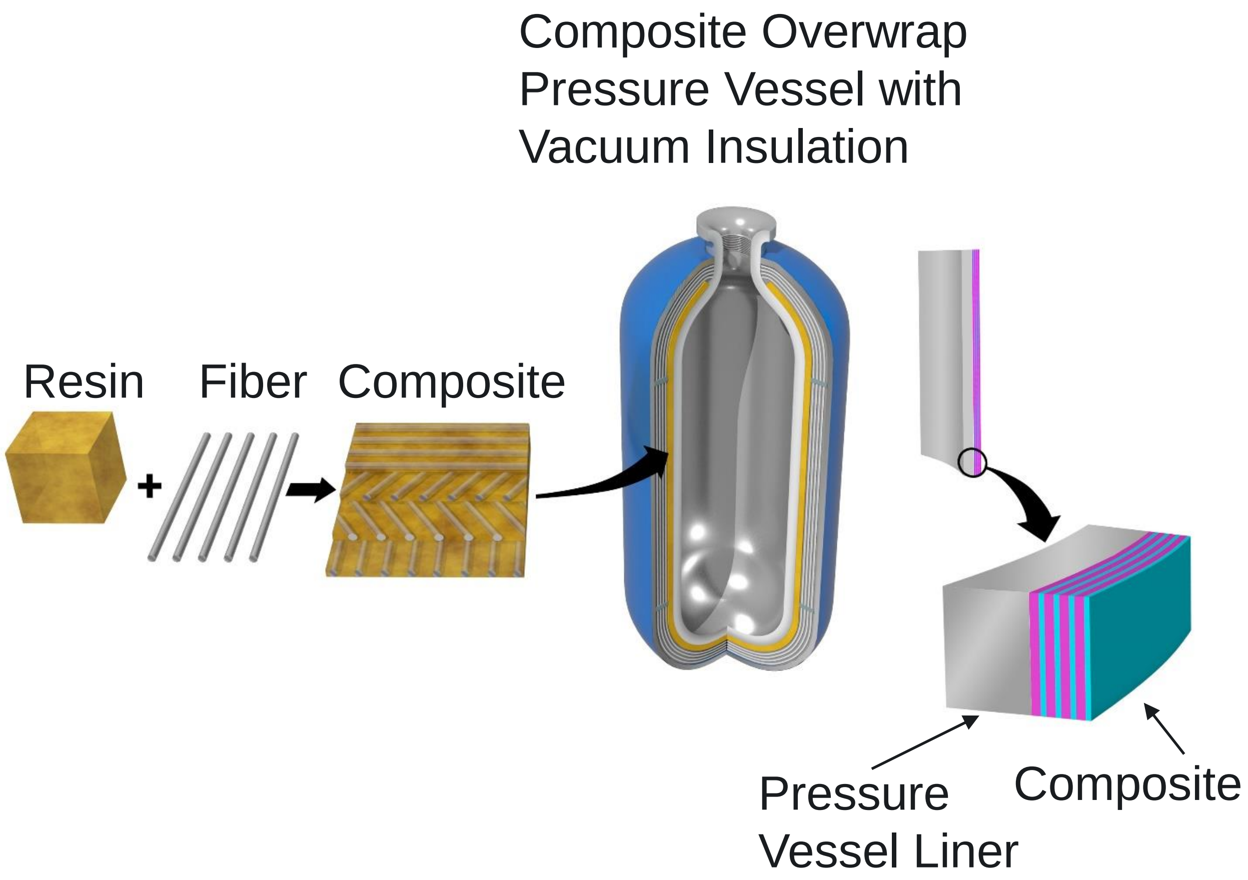
BMW Hydrogen Storage, September 28, 2012

Pacific Northwest
NATIONAL LABORATORY

H-Mat Cryo Objective

- Develop a material acceptance process that will provide detailed information to evaluate specialty resins and carbon fiber composite materials through thermomechanical testing by combining
  - cryogenic temperature and cycling temperatures from -253°C + 120°C
  - fatigue cycling at non-ambient conditions equivalent to the stress states in the composite at the maximum allowable working pressure and standard test cycles
- Develop screening methods for new pressure vessel materials from coupon level before transitioning to full scale tank testing that would provide more innovation through prescreening new concepts and materials
- Develop and establish test methods to evaluate resins, fibers, composites, and liner materials prior to full scale tank construction
  - Detailed characterization methods and materials properties testing in temperature range
- Use experimental data to feed tank level numerical modeling to predict temperature dependent burst pressures

Deconstruction of Pressure Vessel Constituents for Material Property Inputs



Pacific Northwest
NATIONAL LABORATORY

Cryogenic Materials Testing is Far Behind Ambient Temperatures

- Determined what test and materials need the most focus
- Ambient temperature material sets have low needs
- Cryogenic materials testing are information deficient

Ambient Temperature Materials Testing needs

	Liner	Fiber	Resin	Composite	Polymer	Joints
Ultimate Tensile Strength	Exists	Exists	Low	Low	Exists	Low
Modulus	Exists	Exists	Low	Low	Exists	Low
Shear	Exists			Low		Low
Compression	Exists			Low		Low
Fracture	Low	Low	Low	Low	Low	Low
Fatigue	High	Low	Low	Low	Low	High
Coefficient of Thermal Expansion	Exists	Low	Low	High	Low	Low
Thermal Conductivity	Low	Low	Low	Low	Low	Low
Design for Manufacturability	Low	Low	Low	Low	Low	Low
Stress-Strain	Low	Low	Low	Low	Low	Low

Cryogenic Temperature Materials Testing needs

	Liner	Fiber	Resin	Composite	Polymer	Joints
Ultimate Tensile Strength	Low	High	High	High	High	High
Modulus	Low	High	High	High	High	High
Shear	Depends		High	High		High
Compression						
Fracture	High	High	High	High	High	High
Fatigue	High	High	High	High	High	High
Coefficient of Thermal Expansion	High	High	High	High	High	High
Thermal Conductivity	Low	Low	Low	Low	Low	Low
Design for Manufacturability	Low	Low	Low	Low	Low	Low
Stress-Strain	High	High	High	High	High	High

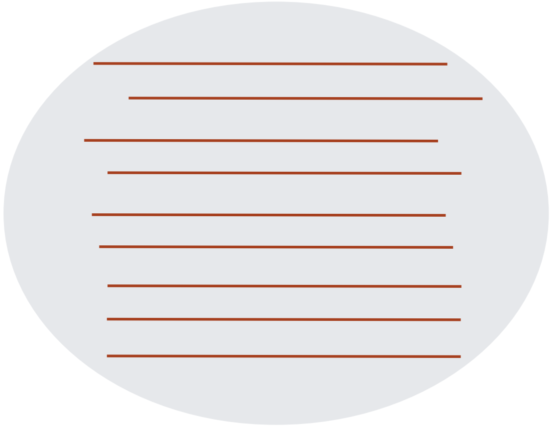
Pacific Northwest
NATIONAL LABORATORY

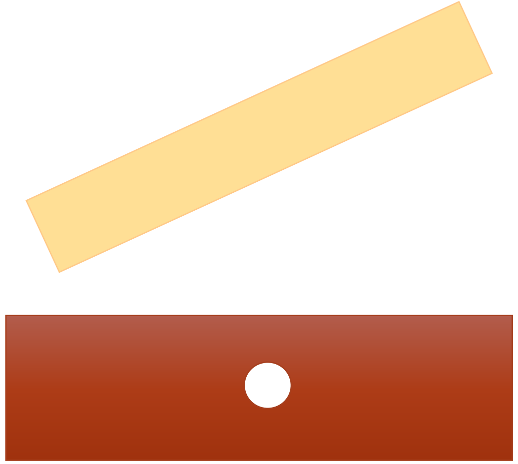
Lack of Cryogenic Materials Testing in Composites and Metals for Modeling

- Summary of meeting results
- Composites, resins, joints (welds), and metal liners were the priority outcomes from the meeting

Test Method / Properties	Material
Uniaxial Tension providing the stress-strain curve to failure at selected temperatures throughout the entire temperature range. **Resulting Properties: Elastic modulus, yield strength, ultimate strength, and ultimate elongation as a function of temperature.**	Metal Liner Polymer Liner **Composite Overwrap: Resin, Fibers, and Laminate**
Short Beam Shear: Interlaminar Shear Strength	Composite Laminate
Coefficient of Thermal Expansion (CTE) and thermal conductivity: The CTE and thermal conductivity of composite lamina and laminates changes when matrix cracking occurs	Metal Liner Polymer Liner **Composite Overwrap: Resin, Fibers, Lamina, Laminate**
Glass Transition Temperature	Polymer liner Composite resin
Fracture Toughness **Charpy Impact Test: Nil-ductility transition temperature as a function of combined hydrogen exposure and temperature**	Metal Liner Metal welds and joints
Fatigue Testing: Thermomechanical cyclic loading for laminates Thermal and pressure induced for composite overwrap.	**Metal Liner** Polymer Liner Composite Overwrap: Resin, Fibers, Lamina, Laminate **Joints (welds, etc)**
Thermal Properties: Conductivity, specific heat, and thermal expansion of many solid materials at cryogenic temperatures are available from the NIST Cryogenic Materials website https://trc.nist.gov/cryogenics/materials/materialproperties.htm The conductivity and specific heat of cryogenic liquids and gases are available at the NIST Chemistry WebBook website https://webbook.nist.gov/chemistry/fluid/	**Metal Liner** **Polymer Liner** Composite Overwrap: Resin, Fibers, Lamina, Laminate Hydrogen

Developing Models for Cryo-compressed H_2 Vessel Design from Constituents to Tank Structure





Micro and Meso scales

- CF & epoxy thermomechanical properties and stress/strain data as functions of temperature
- Homogenization & constitutive modeling (PNNL's EMTA & EMTA-NLA)

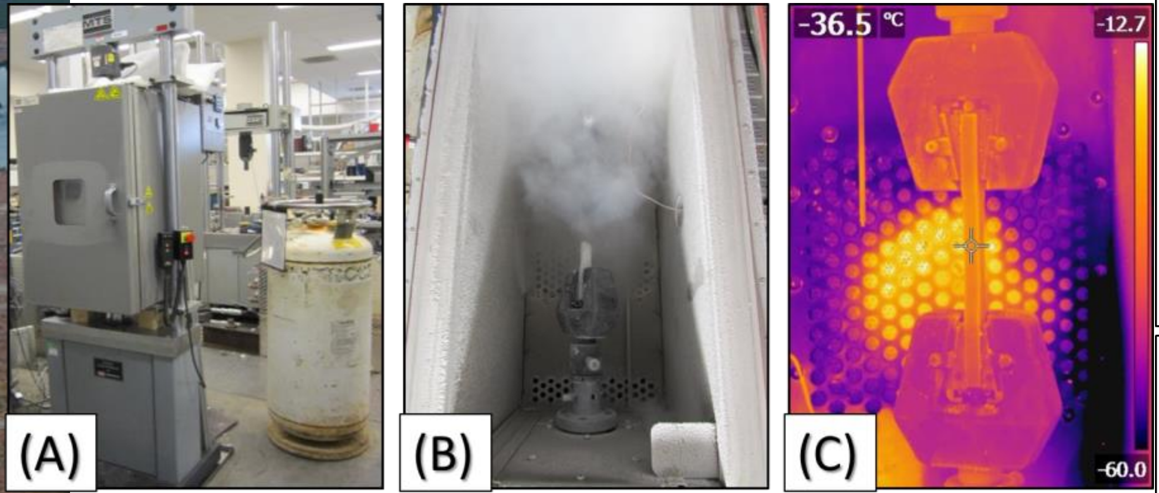
Macro scale 1

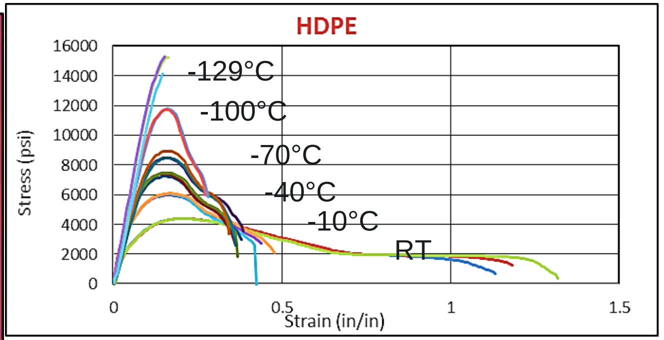
- Constitutive models validated on simple laminated specimens
- Predicted stress/strain responses and damage compared to experiments (EMTA-NLA/ABAQUS)

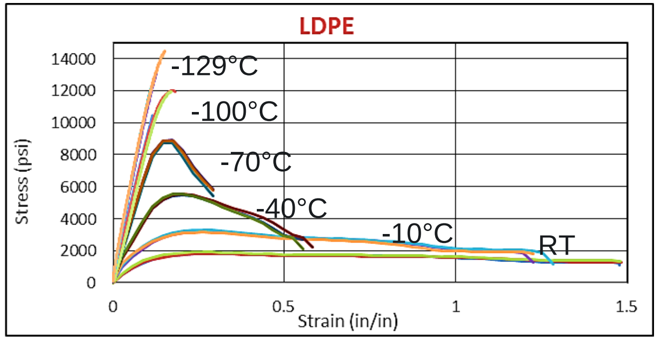
Macro scale 2

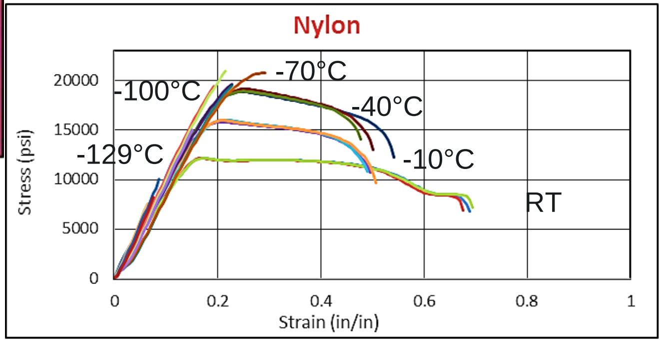
- Constitutive models validated on H_2 vessels
- Design vessel layup to sustain thermomechanical loadings (EMTA-NLA/ABAQUS)

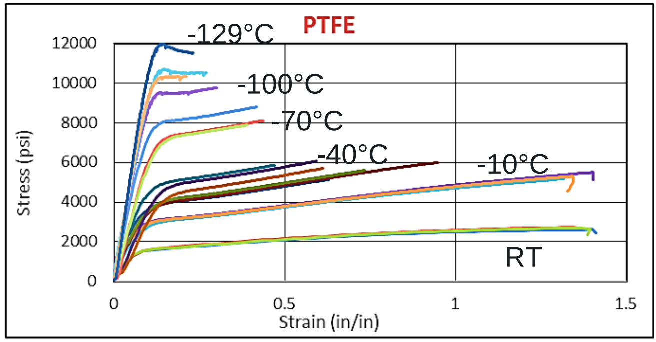
Sub Ambient Liner Materials Testing Illustrate Significant Temperature Sensitivity







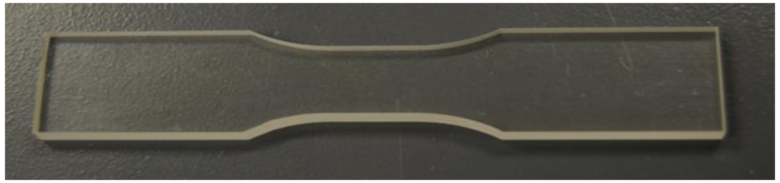


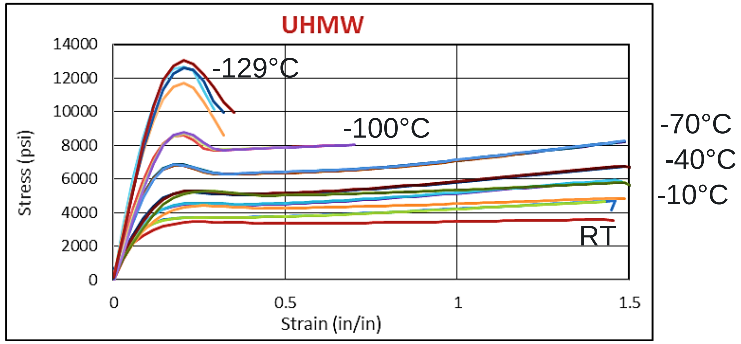


(A) MTS environmental chamber capable of -130°C to 315°C

(B) Environmental chamber at -40C for a tensile test.

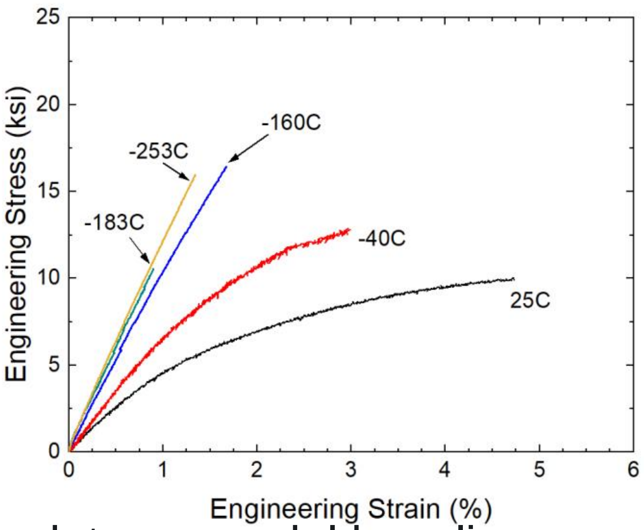
(C) Infrared thermograph of a tensile sample in the grips inside the chamber cooling down to -40°C for a tensile test.



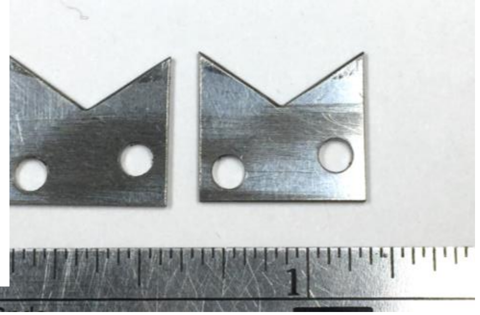


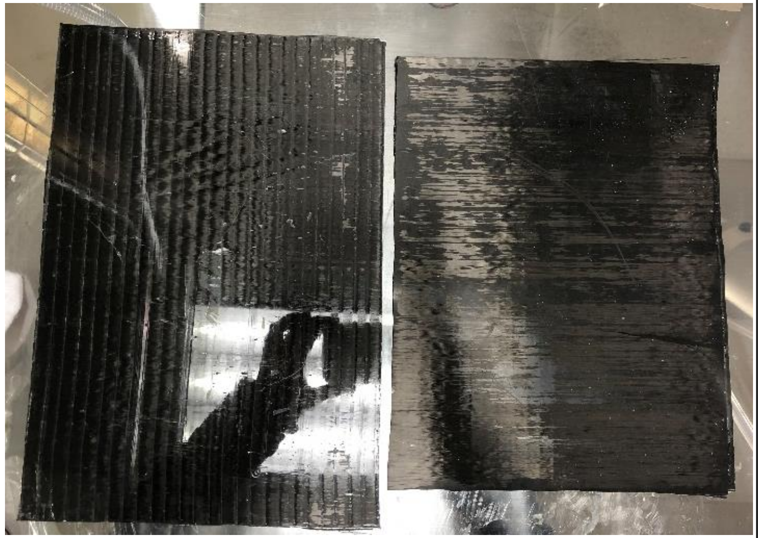
Resin Cryo Testing Shows Flaw Sensitivity

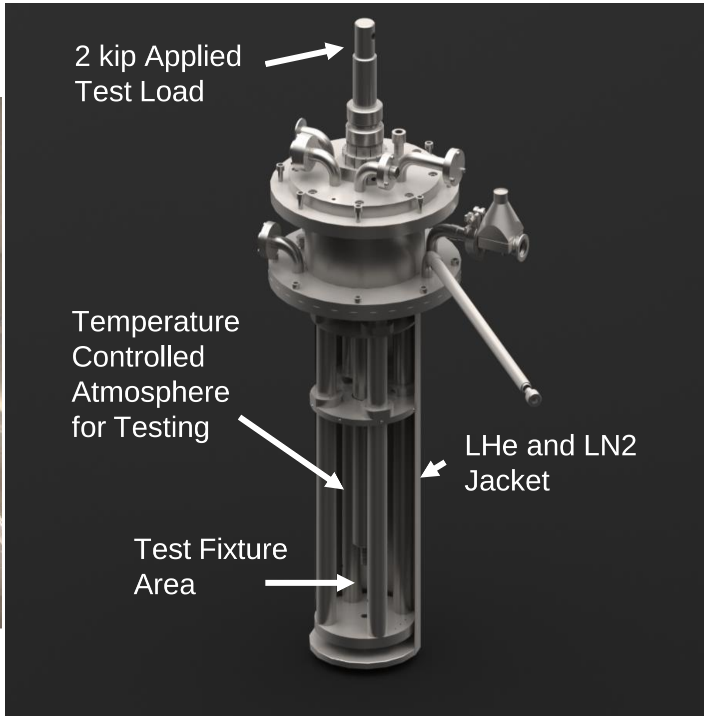
- Model resin and crosslinking systems used to investigate the cryogenic effects on material properties related chemical structure
- Developed extensometer attachment with rounded vee edges to mitigate stress
- Produced unidirectional and cross-ply composites with model resin system and Toray T700 fiber for SBS, tensile, and cracking investigations



Tensile data on model baseline resin throughout -253°C to 25°C



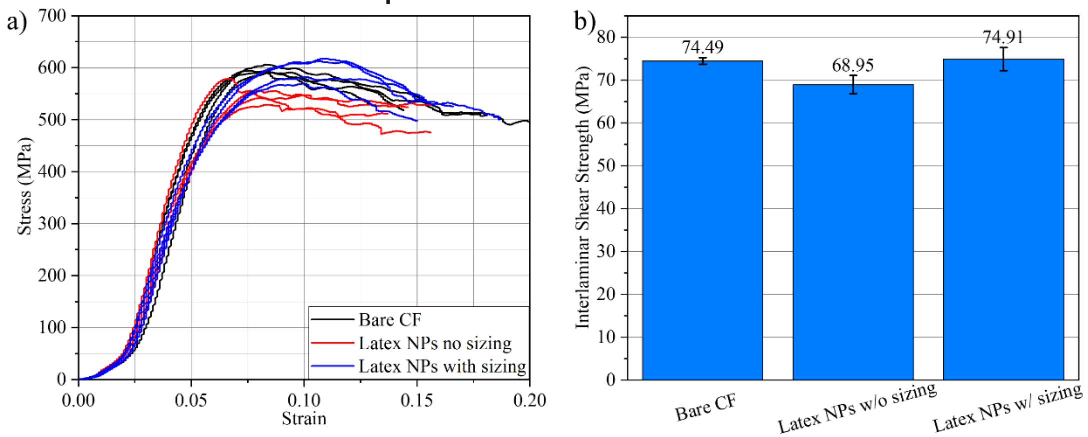




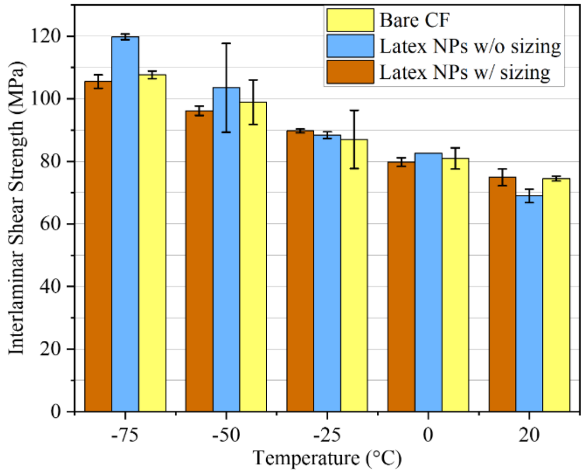
Fiber Sizing Surface Modifications can Increase Interlaminar Shear Strength

- Overall, the latex nanoparticles did not increase the ambient temperature ILSS of the composites
- The latex nanoparticles without sizing actually decreased the interlaminar shear strength in ambient conditions

Results from ambient temperature ILSS



- The composites with latex nanoparticles without sizing start to outperform the bare carbon fiber composite as the temperature decreases
- Overall, a maximum increase of 11% is seen at -75°C for the composite with latex nanoparticles but without sizing



Average results from the low temperature ILSS

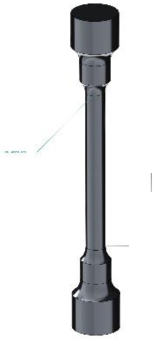
Difference Compared to Bare CF (%)		
Temperature	1:40 Latex NPs (no sizing)	1:40 Latex NPs with 1:40 sizing
20°C	-7.43	0.57
0°C	2.02	-1.43
-25°C	1.55	3.10
-50°C	4.66	-2.73
-75°C	11.26	-2.02

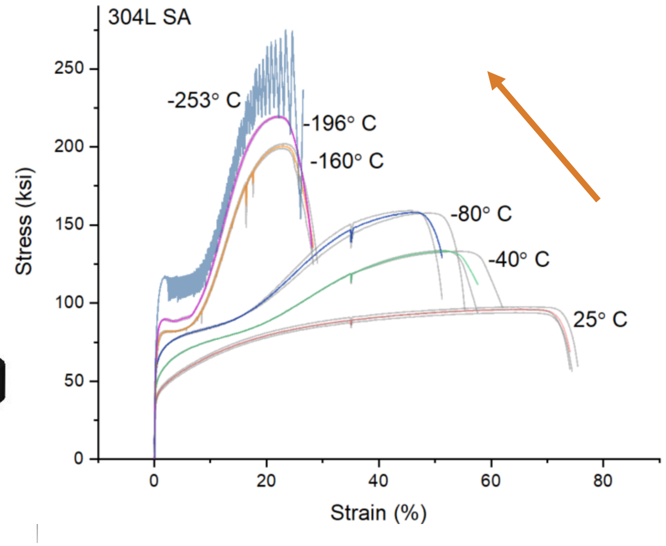
Composites at the different temperatures relative to the baseline carbon fiber composite

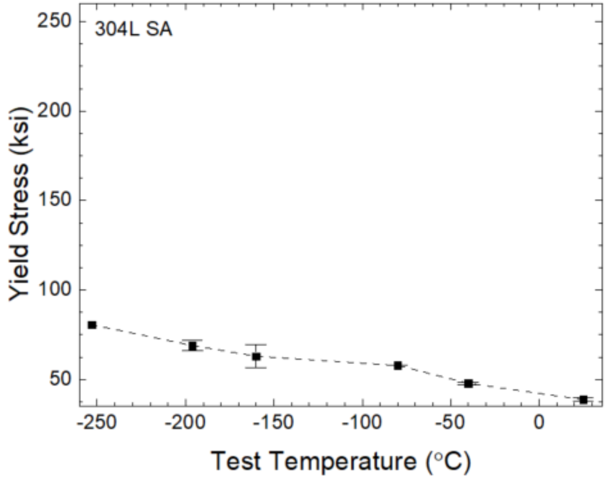
Metallic Mechanical Properties increase with Reduced Temperatures

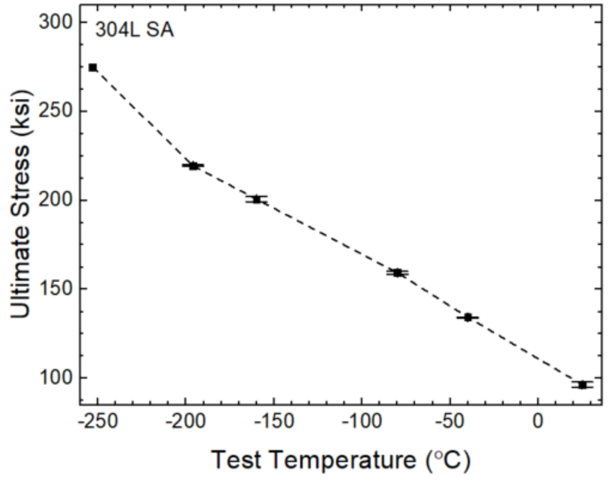
304L

- Increase in σ_y, σ_{UTS}
- Decrease in ε_f



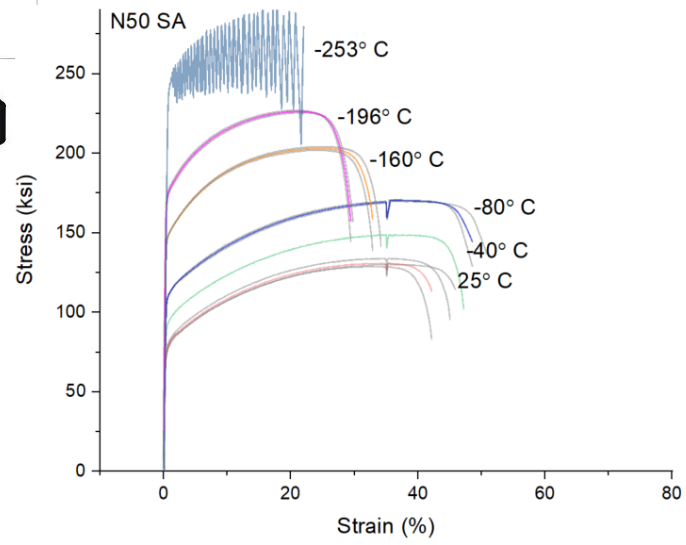


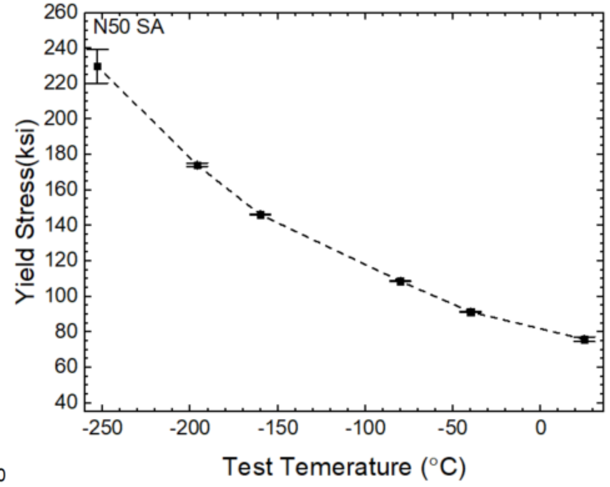


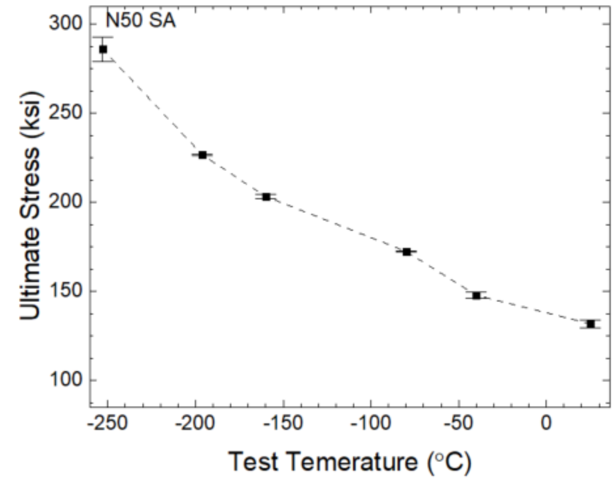


Nitronic 50

- Increase in σ_y, σ_{UTS}



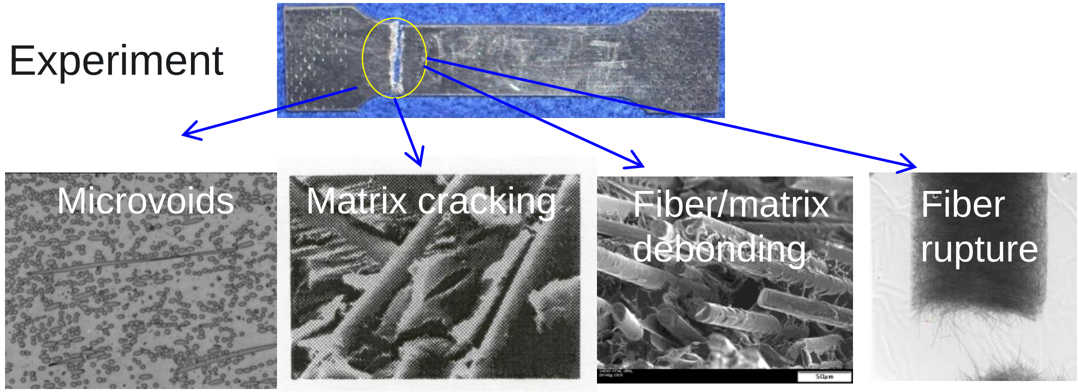




Multiscale Modeling Prediction of Composite Properties with EMTA and EMTA-NLA Software for Use with Finite Element Model

Pacific Northwest NATIONAL LABORATORY

Experiment

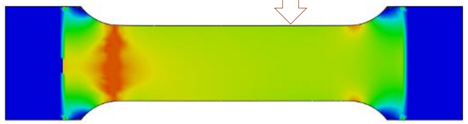


Nonlinear homogenization by EMTA-NLA

ABAQUS
Structural analysis

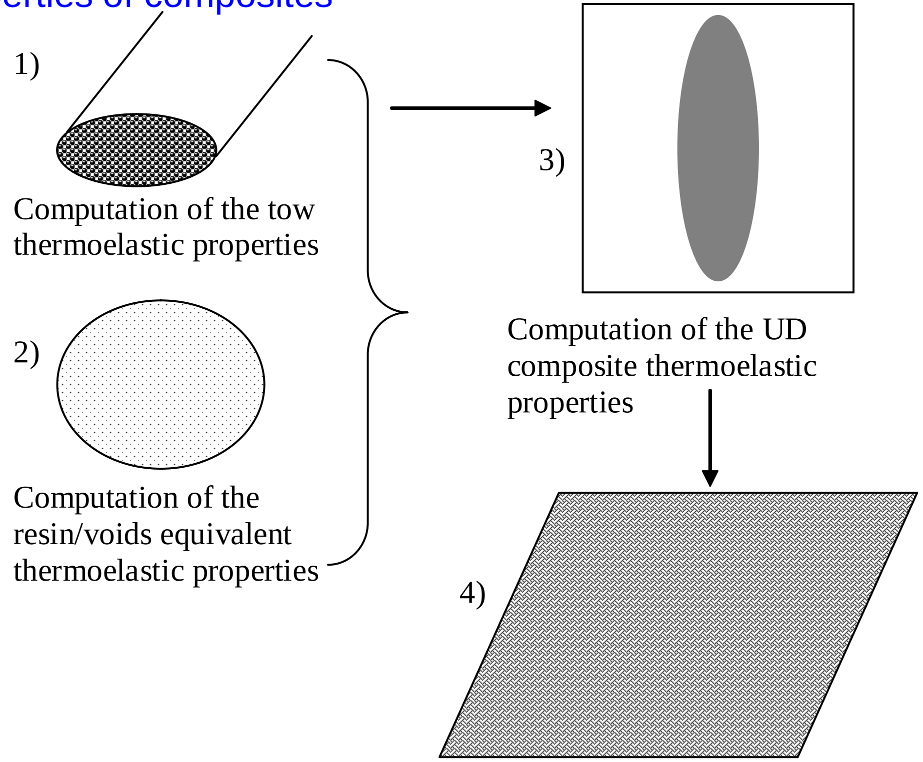
EMTA-NLA
- Nonlinear homogenization
- Integration of constitutive laws
- Damage & creep evolution laws

Prediction



EMTA-NLA: **E**shelby-**M**ori-**T**anaka **A**pproach to **N**on-**L**inear **A**nalyses implemented in **ABAQUS**

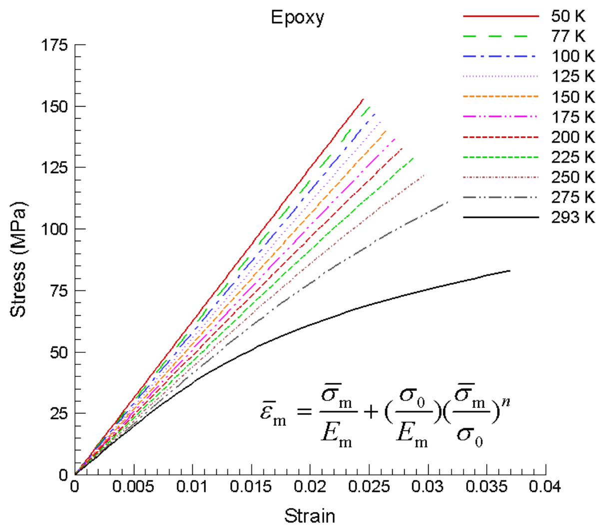
EMTA, a stand-alone software that implements the advanced **E**shelby-**M**ori-**T**anaka **A**pproaches for predicting the thermoelastic properties of composites

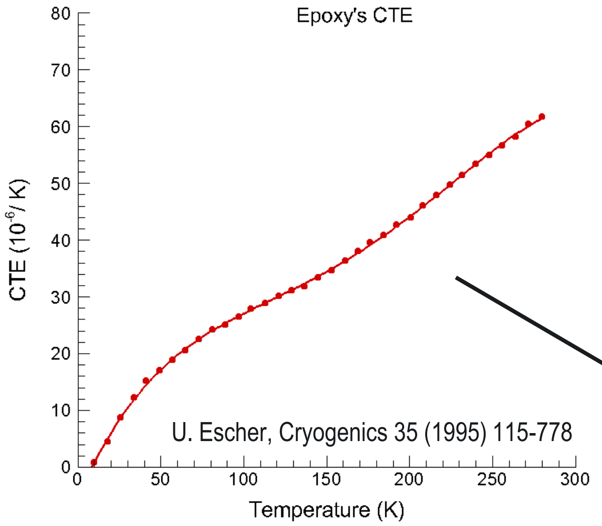


B.N. Nguyen et al., J. Comp. Mater. (2008) 42:1003.
B.N. Nguyen et al., J. Comp. Mater. (2009) 43:217.
B.N. Nguyen, V. Kunc, Int. J. Dam. Mech. (2010) 19:691

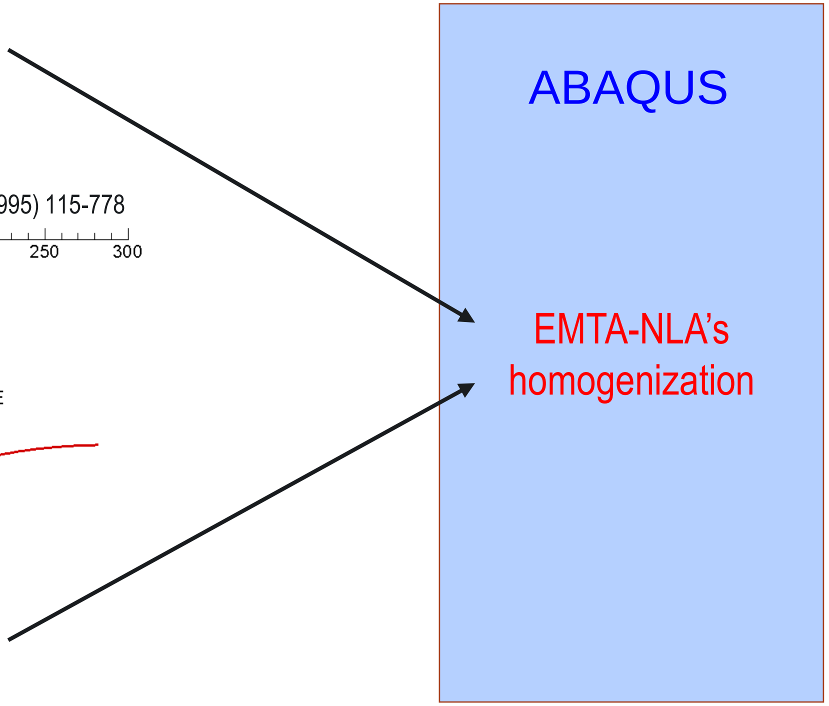
Constituent Thermomechanical Properties as Material Inputs provide Subroutine Material Output for FE Modeling

Epoxy's behavior is described by the Ramberg-Osgood relation



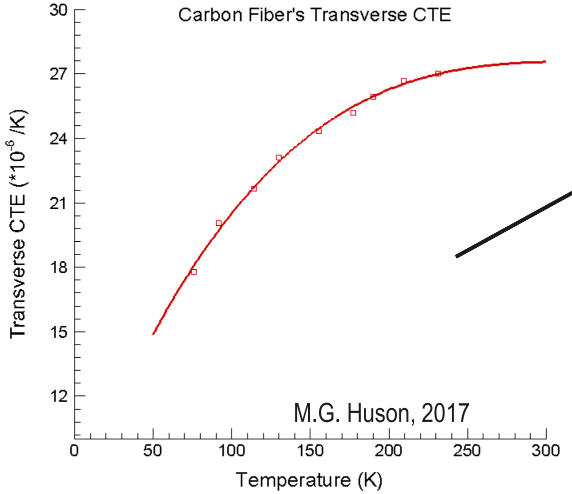


Constituent thermomechanical properties are used as material inputs for **homogenization** by PNNL's EMTA-NLA that acts as user subroutine UMAT of ABAQUS

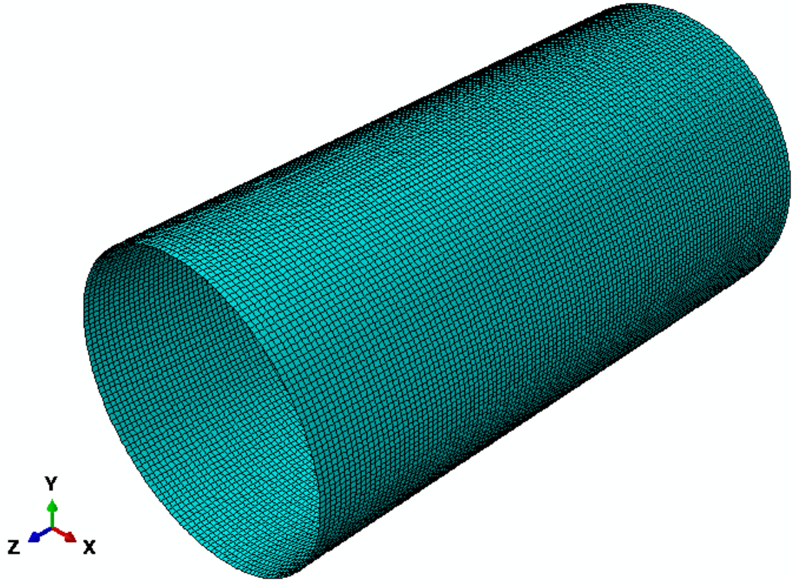


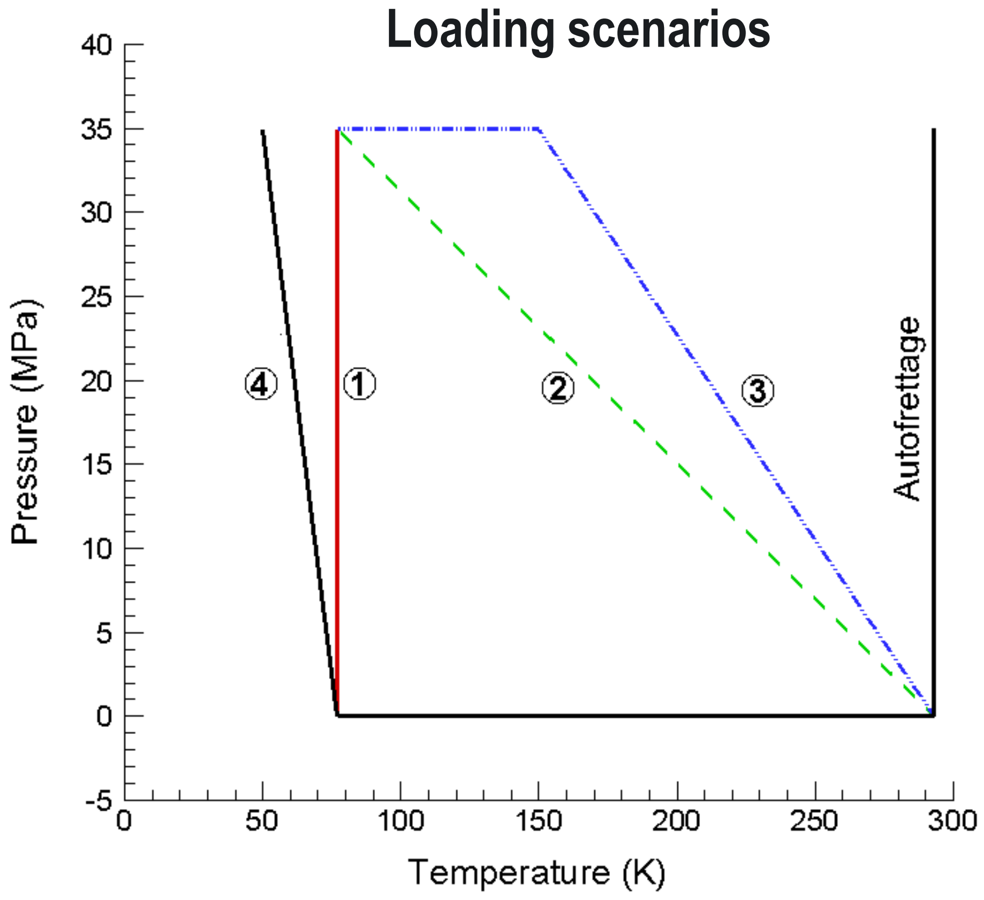
Elastic properties and longitudinal CTE of carbon fiber are assumed constant in the [50 K, RT} range

Elastic Moduli in MPa	Carbon fiber
E_{11}	230000
$E_{22} = E_{33}$	13800
$G_{12} = G_{13}$	12400
G_{23}	5520
$\nu_{12} = \nu_{13}$	0.2
ν_{23}	0.25



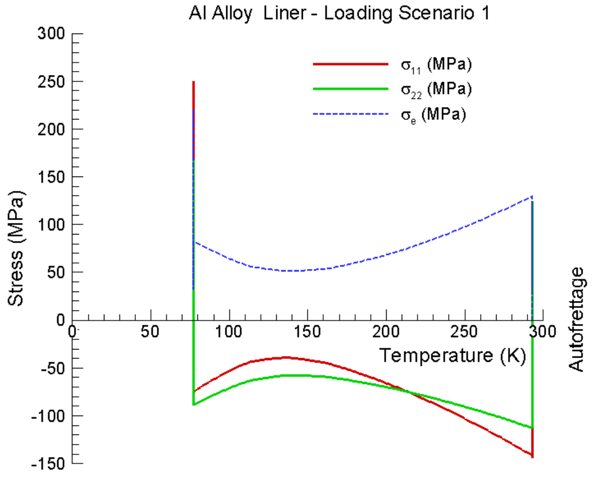
Developed Type 3 H_2 Pressure Vessel Cylinder for Loading Scenarios for Analysis by ABAQUS/EMTA-NLA

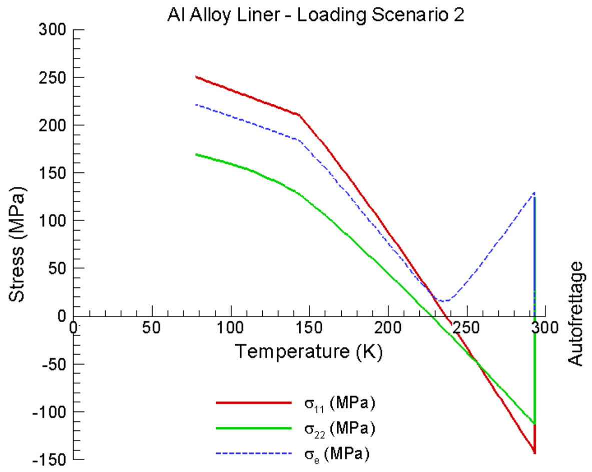


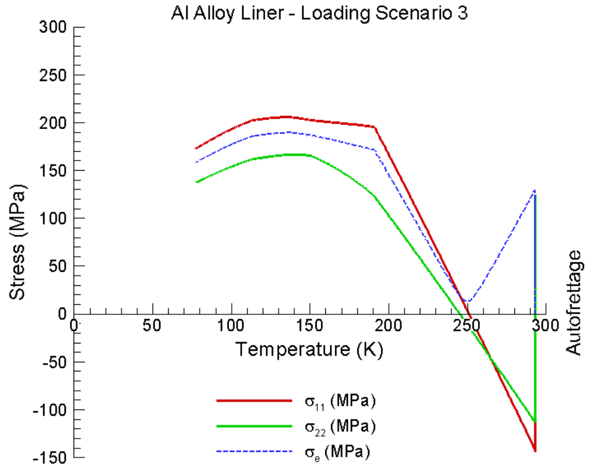


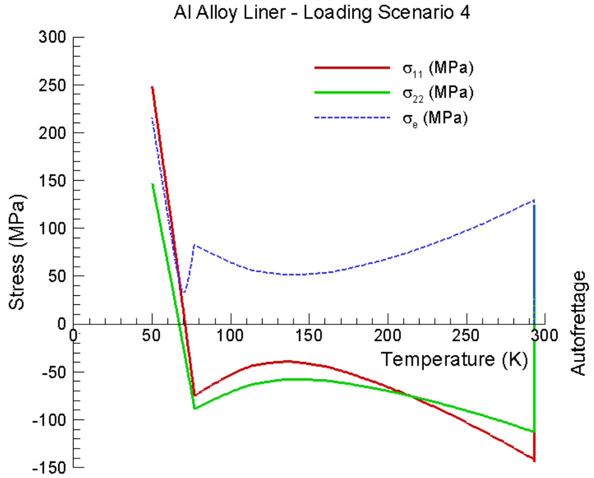
- Assumed layup: Al liner/90°/+10°/-10°/ (with respect to the axial direction)
- CF/epoxy with 0.6 fiber volume fraction. Thicknesses (mm): 9.5 / 7 / 1.5 / 1.5
- The cylindrical part of the vessel is discretized using the composite layered shell elements of ABAQUS
- The dome contribution is replaced by a distributed load at one end totalizing a force= $P \Pi R^2$ (R=internal radius, P, pressure)
- The thermo-elastoplastic model of EMTA-NLA is used via “User Material” option
- Accounting for variations of constituent thermomechanical properties with temperature

Abaqus/EMTA-NLA Model indicates the Al Alloy Liner Show Cylinder Section is below the Material Design Limit

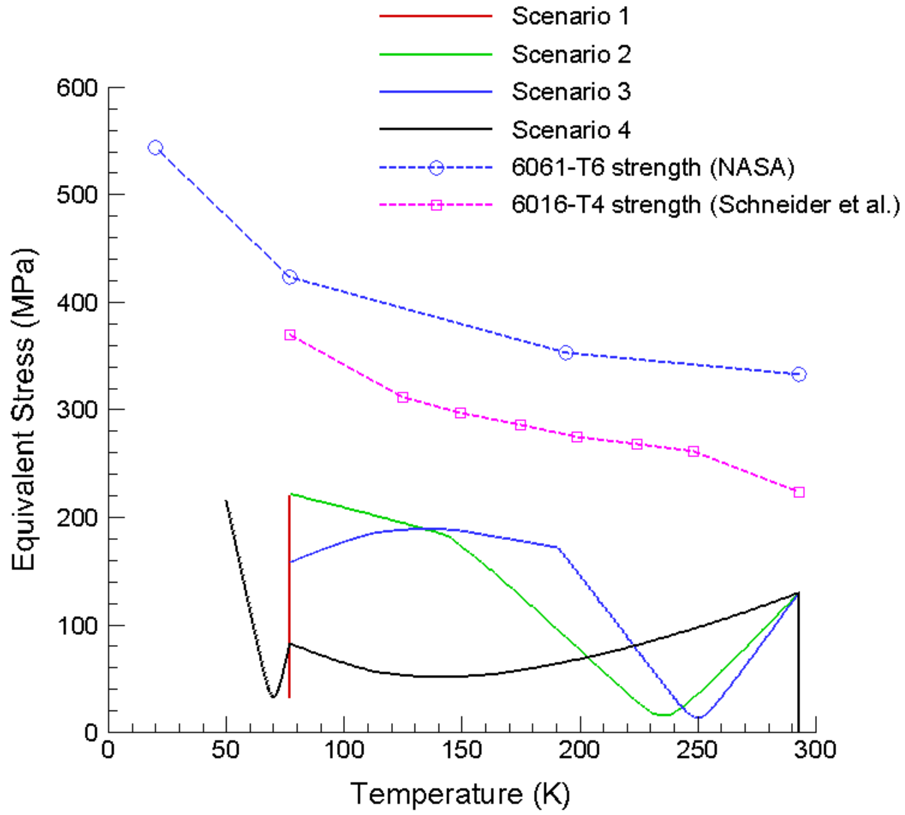




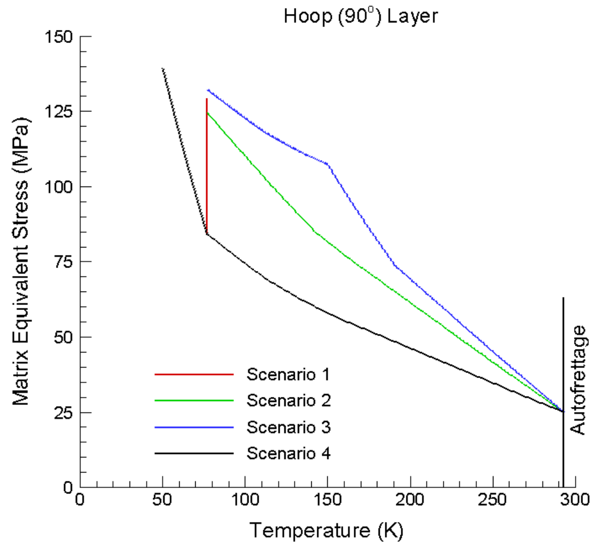


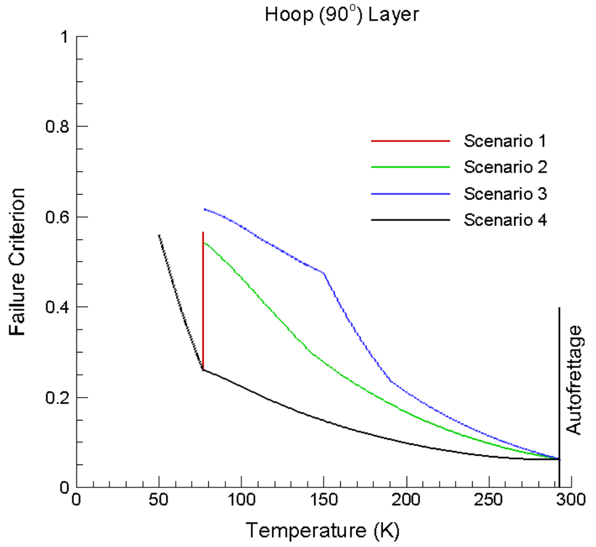


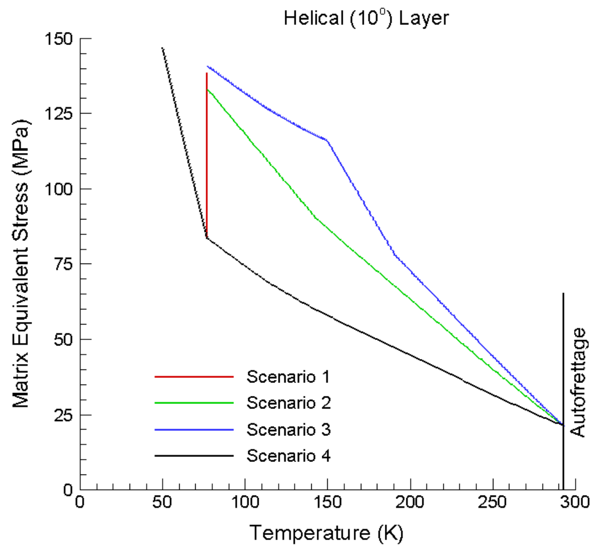
- Equivalent Von Mises stresses in the liner are significantly below typical strengths of Al alloys. Liner fracture is not predicted to occur.

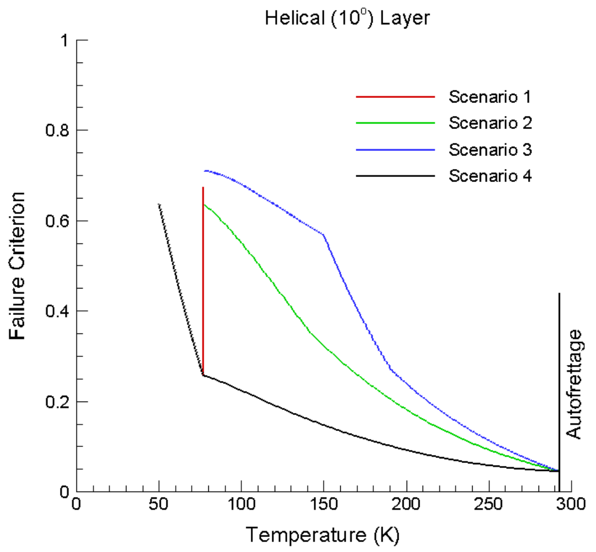


Composite Matrix Equivalent Stresses vs. Failure Criterion in Cylinder Section are below Design Limits





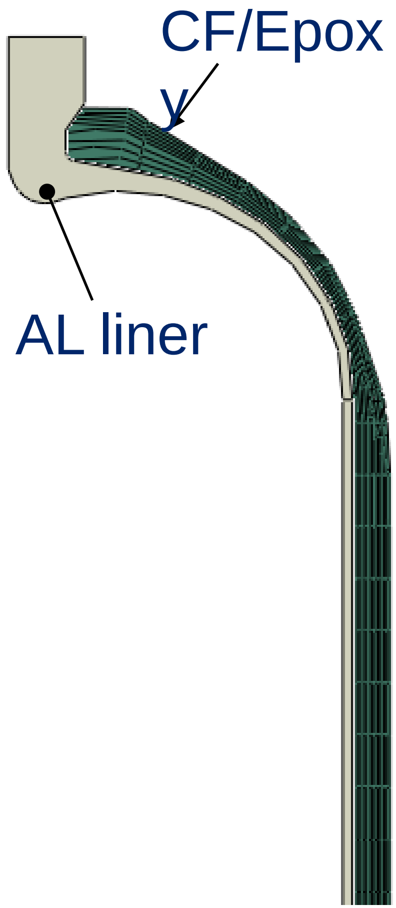




- Failure is predicted by a micromechanical criterion described in B.N. Nguyen et al. (2008), J. Comp. Mater., 43:217-246; B.N. Nguyen and K.L. Simmons (2013), J. Comp. Mater., 47:2113-2123.
- The failure criterion uses fiber strength, matrix strength and interfacial strength data. If the interfacial strength data is unavailable, the interfacial strength is assumed to be equal to the maximum shear strength of the resin matrix.
- The ply fails if the failure criterion is equal to 1.
- We assume epoxy’s strength increases when temperature decreases. This mitigates failure of the composite by matrix cracking when the vessel is cool down to cryogenic temperatures.
- It’s critical to achieve/produce high-strength epoxies.

Development of FE Analysis of Hydrogen Pressure Vessel

- Cryo-hydrogen tank
  - Operating pressure: 500 bar
  - Operating temperature: 34K ~ 80K
- FE model
  - 2D axisymmetric model
  - Assuming no bonding at the interface between metal liners and composite material
  - Cooled down to 80K from RT
  - Applying burst pressure (2.25x 500 bar)
  - Compared maximum strains along fiber direction

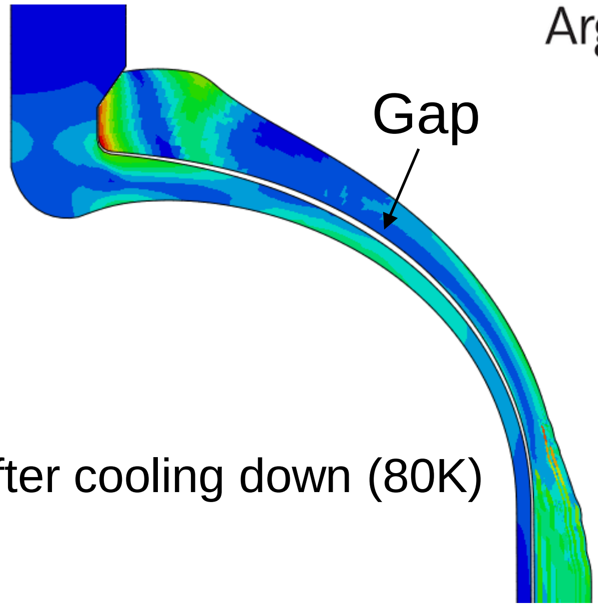


Liner Sensitivity Analysis Reveals High Stresses in the Boss Region from CTE Mismatch

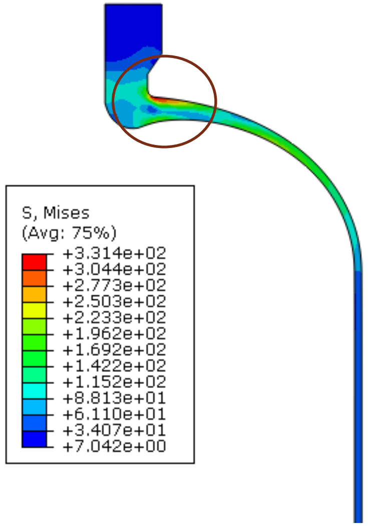
Pacific Northwest NATIONAL LABORATORY

Argonne NATIONAL LABORATORY

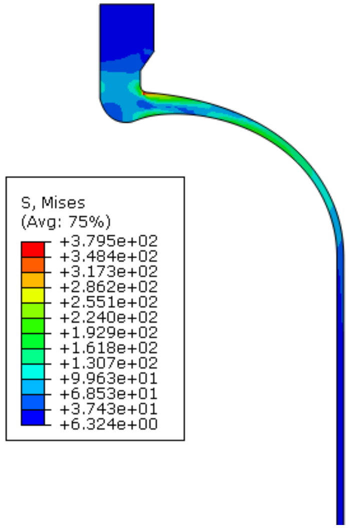
- Thermal stress due to CTE mismatch between aluminum and composite material was not significant since this study assumed that there is no bonding at the interface
- When the tank cools down, aluminum liner shrinks more than composite layers. Eventually, a gap forms between aluminum liner and composite layers upon the cooling down process.



After cooling down (80K)



Aluminum liner (80K) w/ empty pressure of 0.5 MPa

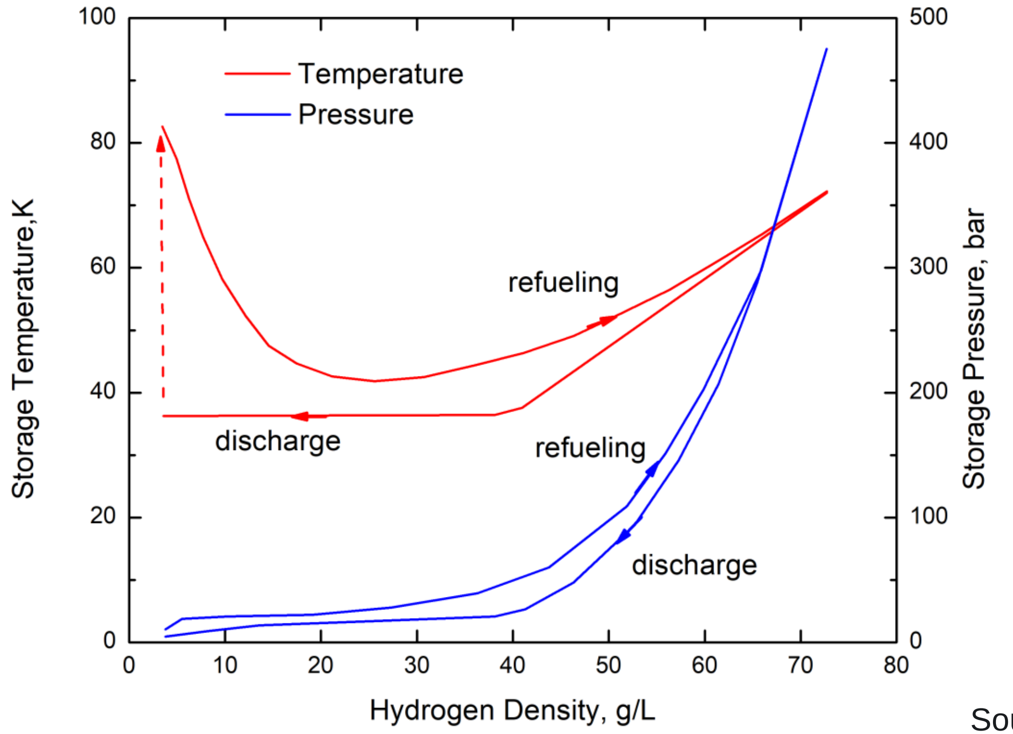


Steel liner (80K) w/ empty pressure of 0.5 MPa

- During cooling down step, cryo-tanks were empty. 0.5 MPa of empty pressure was applied. Both liner materials have the maximum stresses around the corner of the neck because composite layers resist to shrink.
- Plastic deformation occurred at the corner in aluminum liner, but did not occur in steel liner it.

Investigative Fatigue Loading Scenario

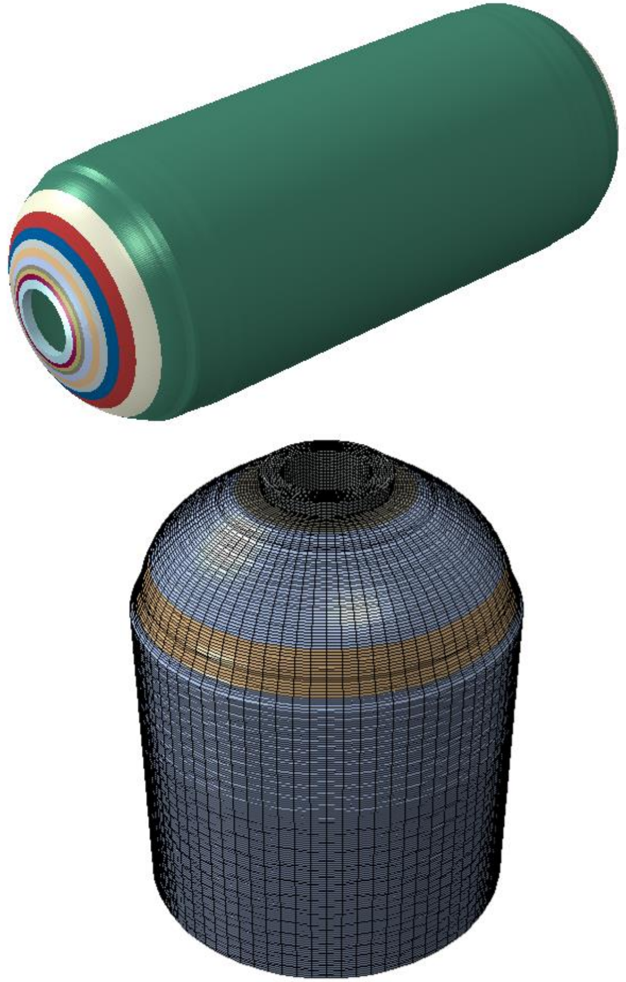
- Fatigue cyclic loads are imposed on the same condition as the refueling and discharging process. In this condition, temperature and internal pressure range from 35K to 80K and from 5 bar to 500 bar, respectively
- Also, temperature cycling from RT to 80K will be considered for fatigue analysis



Source: IJHE Vol 43 2018 pp10215-10231

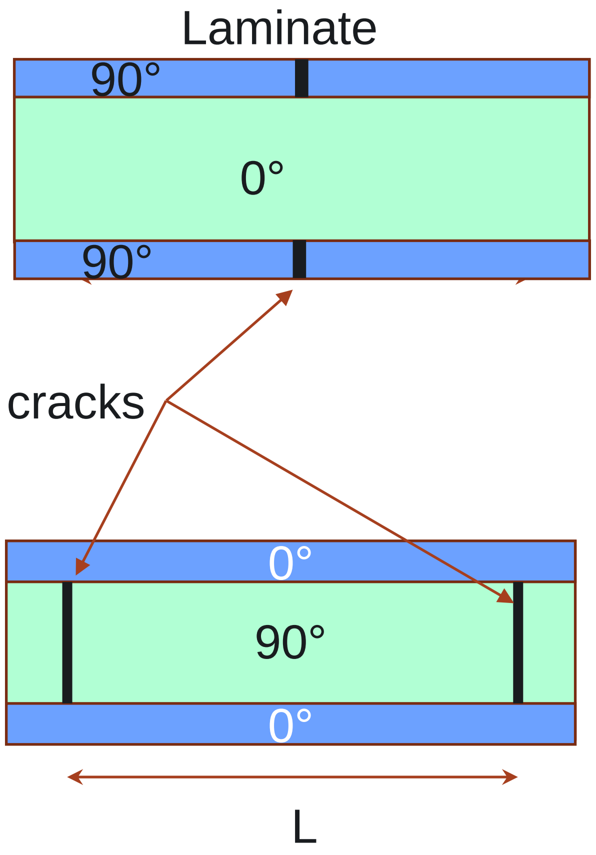
Failure Prediction of Hydrogen Tank (I)

- PNNL and ANL collaborate on analysis and design of H_2 cryo-compressed pressure vessels
- ANL develop 3D FE models of H2 pressure vessels and provide them to PNNL for analyses
- The mechanistic damage model of EMTA-NLA has been developed at PNNL and is used via “User Material” option
- Accounting for variations of constituent thermomechanical properties with temperature



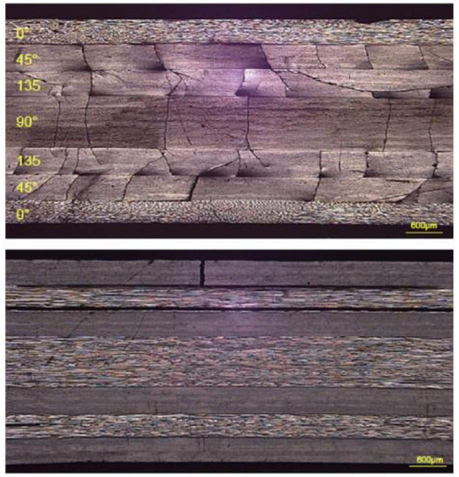
A 3D model for a H_2 cryo-compressed pressure vessel

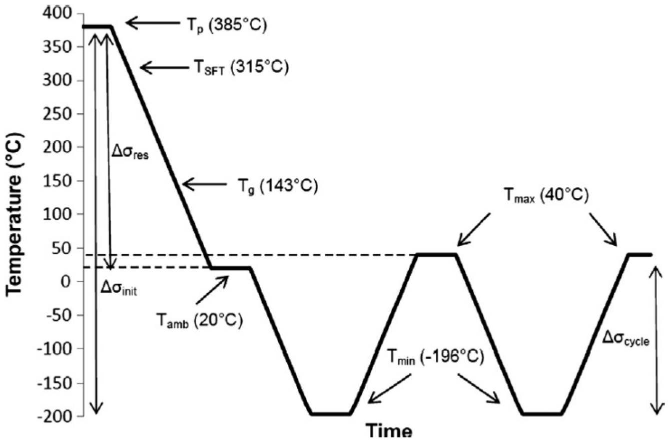
Cracking mechanics depends on not only layer fiber orientation but also layer position (external or internal)

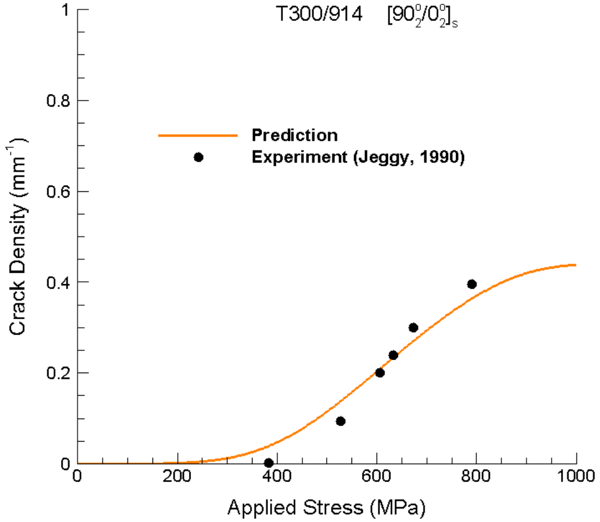


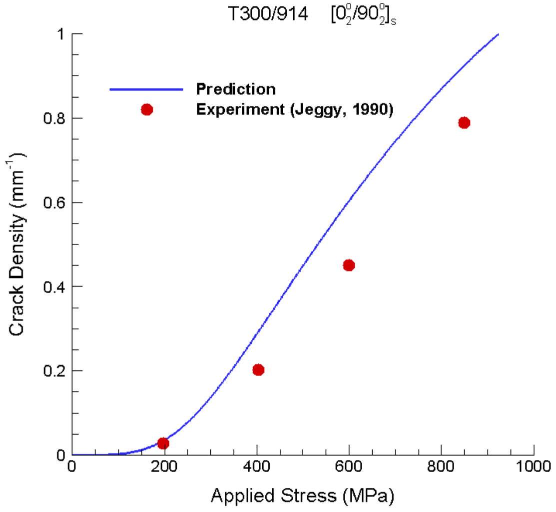
L=distance between cracks

D.M. Grogan et al. / Composites: Part A 66 (2014) 237–250



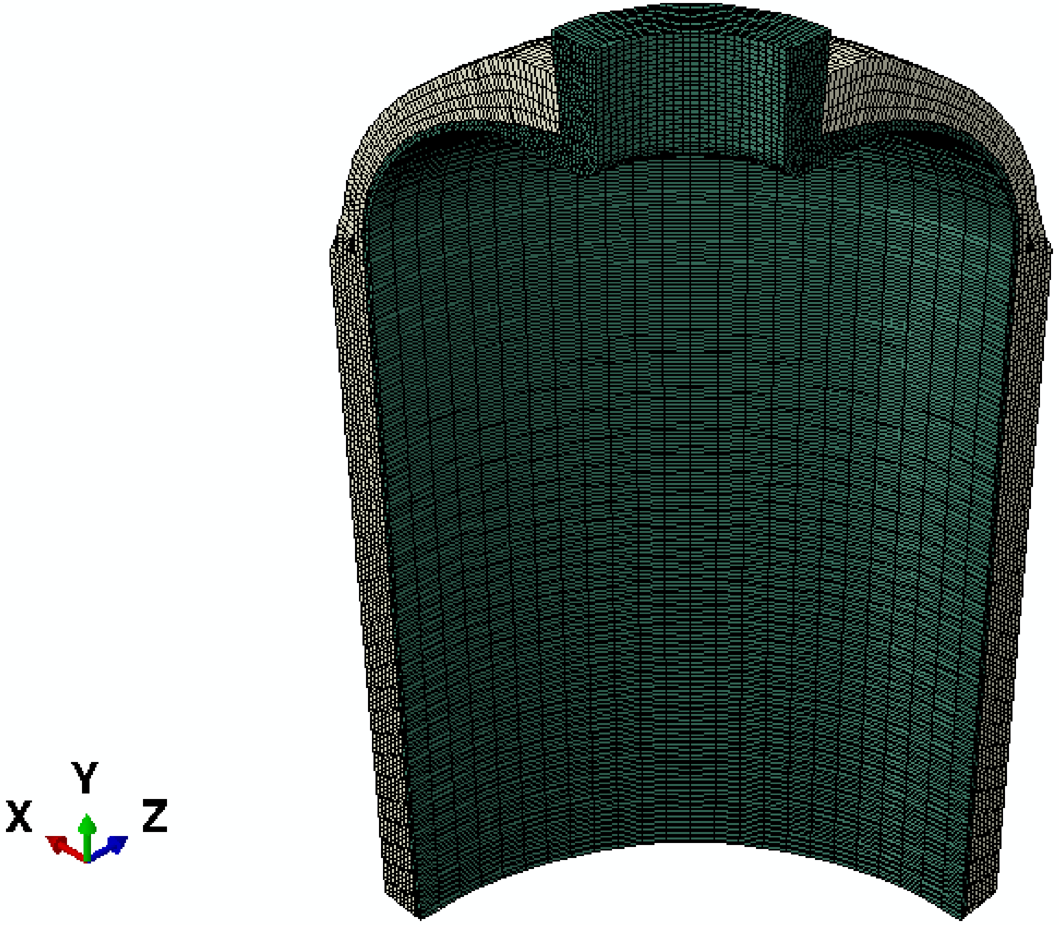


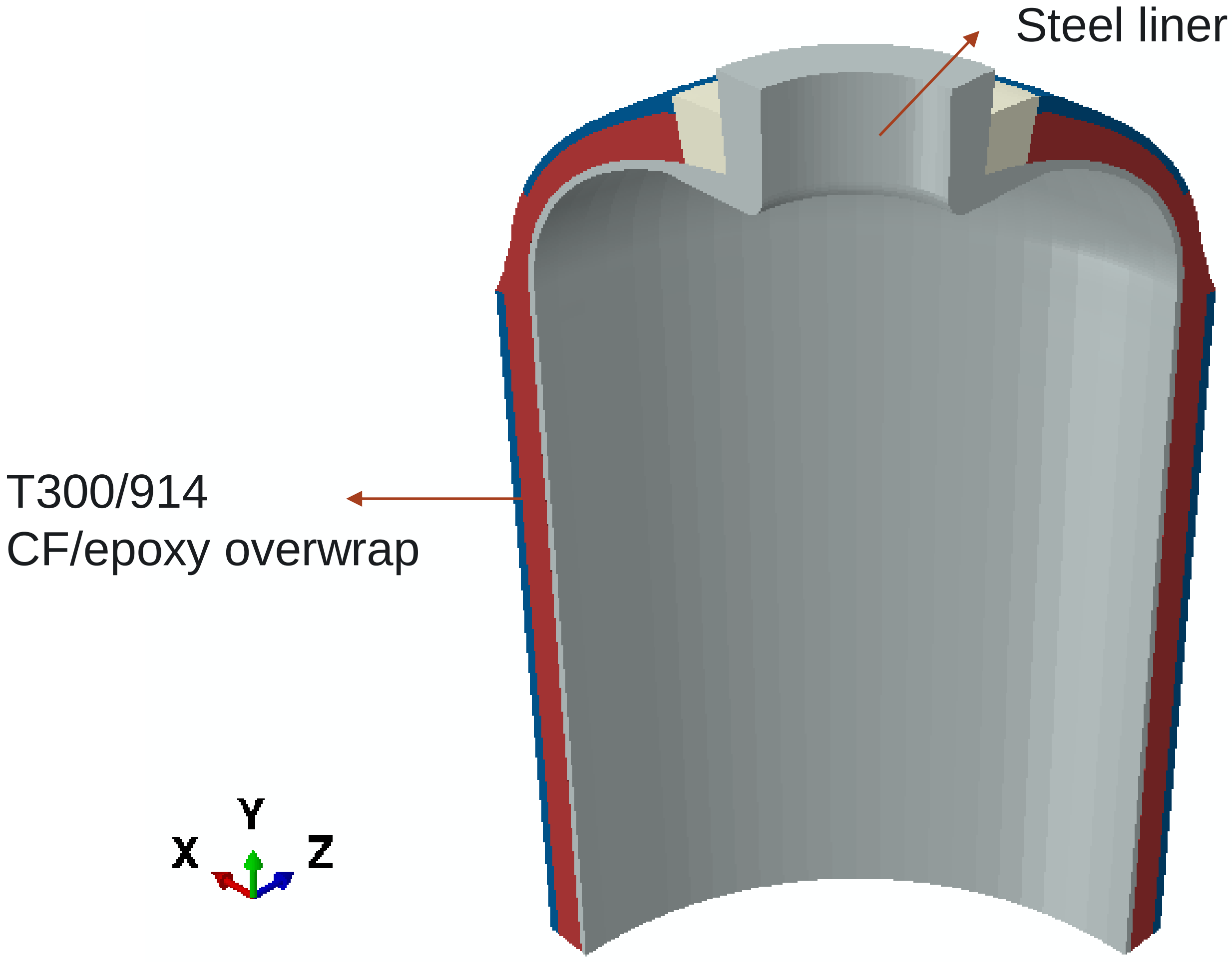




Damage Analysis Model Developed for Hydrogen Pressure Vessel

- Pre-analysis of a H_2 pressure vessel model subjected to autofrettage at 70 MPa and ramp up to bursting

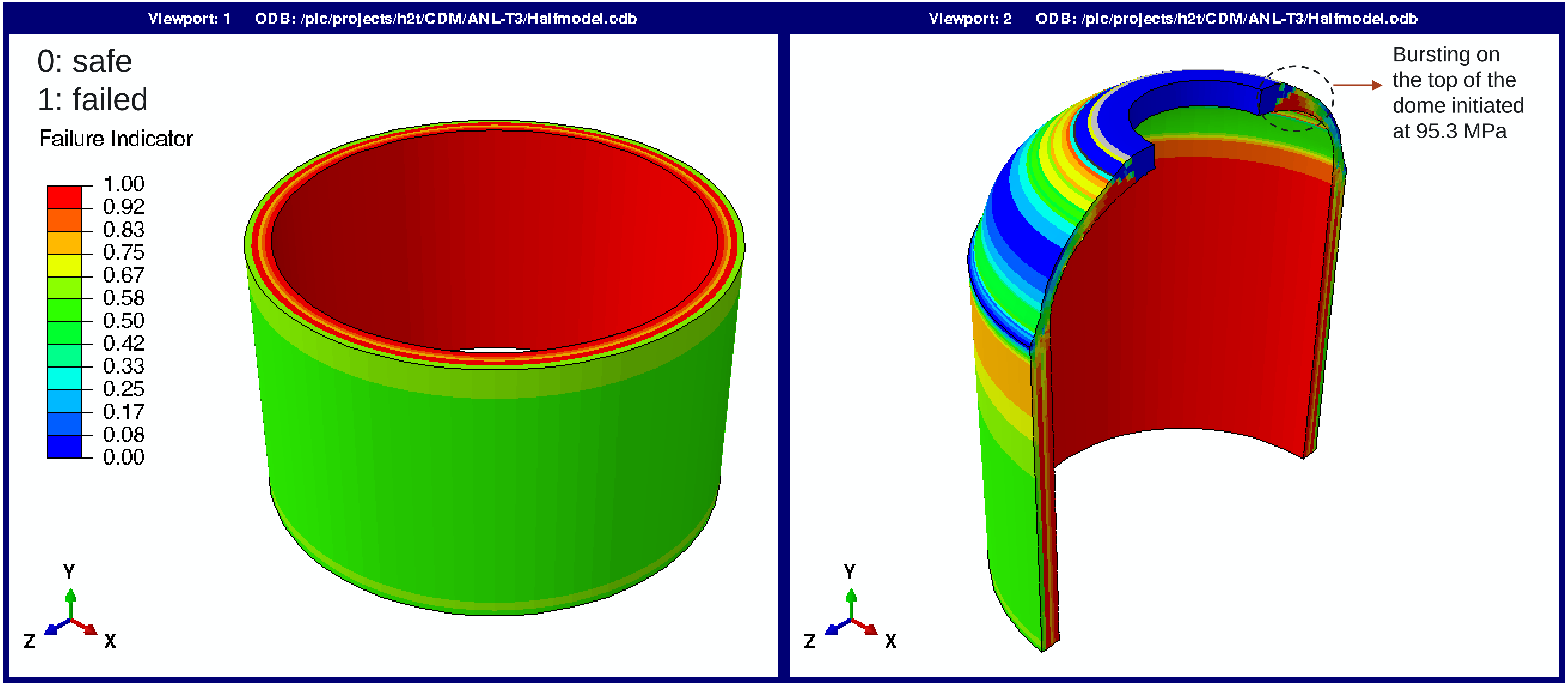




Steel liner(2mm)/15° (3mm)/90° (3mm)/-15° (3mm)/90° (3mm)

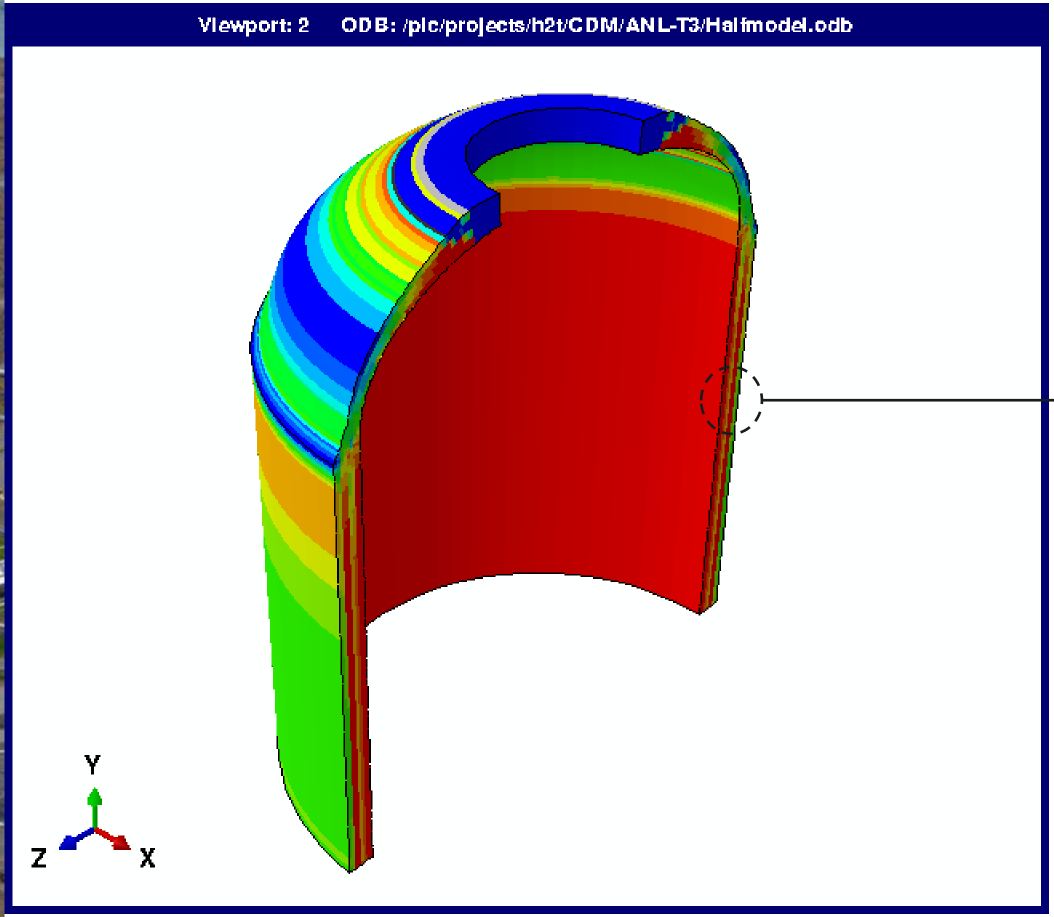
Matrix Cracking Damage Analysis indicates Lower Burst Pressure in H2 Pressure Vessel Model

Predicted matrix cracking damage and failure in the pressure vessel at 95.3 MPa pressure loading: (a) View through a horizontal section, and (b) View through a vertical section.

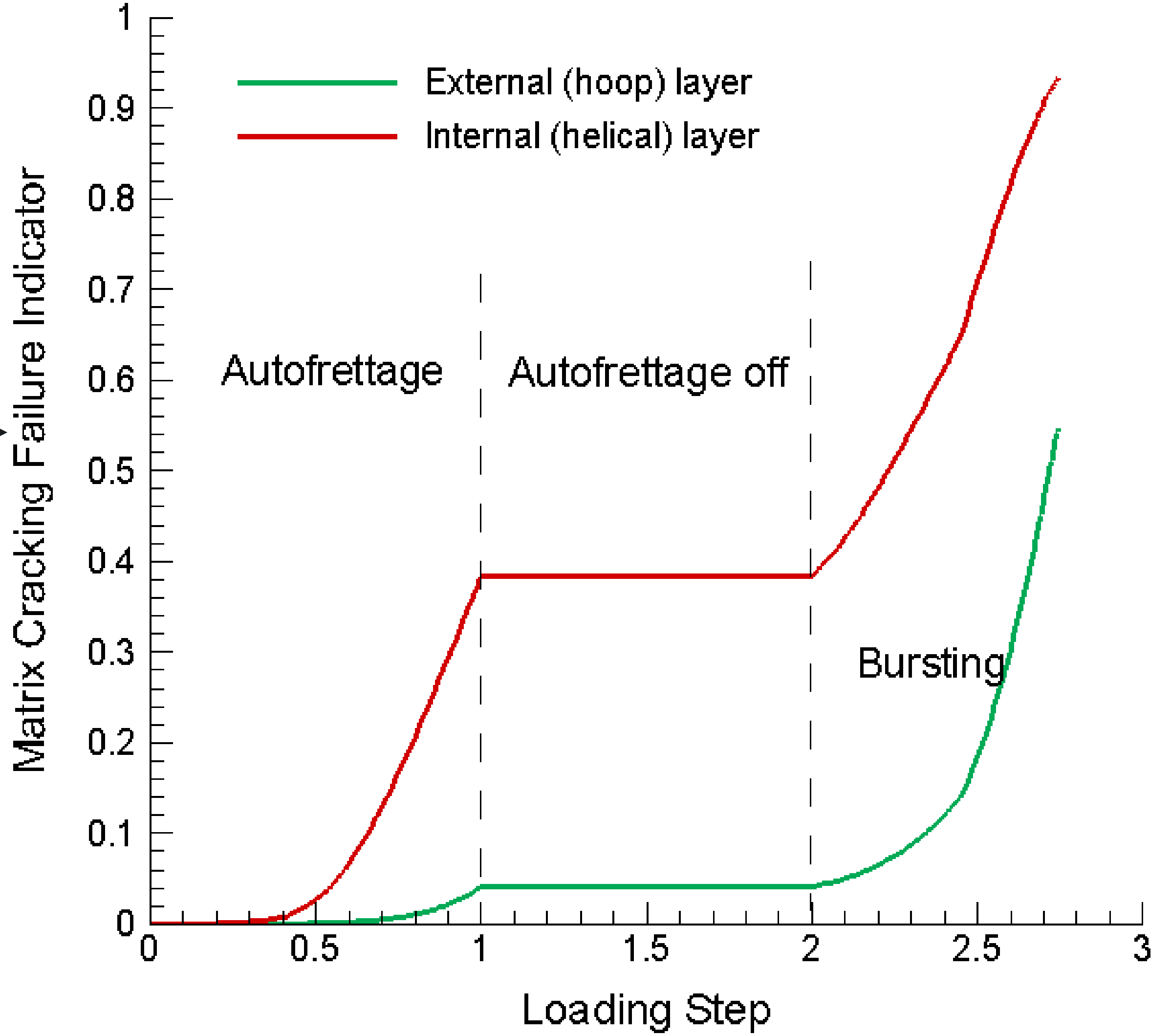


Autofrettage Pressure can increase the Matrix Cracking to Internal Layers and Decreasing Burst Pressure

Bursting on the top of the dome initiated at 95.3 MPa



Evolution of the matrix cracking failure indicator for a location on the cylindrical body



Summary

- H-Mat is developed materials testing protocol, data, and pressure vessel models to evaluate new material sets without expensive tank builds
- Developed cryogenic materials testing down to -253C (20K) to provide material inputs to models to predict pressure vessel performance
- Newly develop material failure criterion used in conjunction with FE tank models to predict burst pressures with the addition of crack density from thermal and pressure cycling fatigue
- Autofrettage conditions at cryogenic temperatures can impact burst pressure performance
- Higher strength resin systems can improved cryogenic composite tank performance
- Fiber surface modifications with latex nano beads can increase subambient interlaminar shear strength
- Stainless steel yield and ultimate strengths increase with lower temperatures

Acknowledgements

- Thank you to Ned Stetson, Jesse Adams, and Neha Rustagi for H-Mat program support
- This work was fully supported by the U.S. Department of Energy (US DOE), Office of Energy Efficiency and Renewable Energy (EERE), Hydrogen and Fuel Cell Technologies Office (HFTO) under Contract No. DE-AC05-76RL01830 and Contract No. DE-AC02-06CH11357. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the US DOE under contract DE-AC05-76RL01830.

- **Disclaimers**

Thank you

Kennedy Space Center

Overview of Liquid Hydrogen at NASA

Eric Dirschka, P.E.
Propellants Management
Kennedy Space Center

July 2020

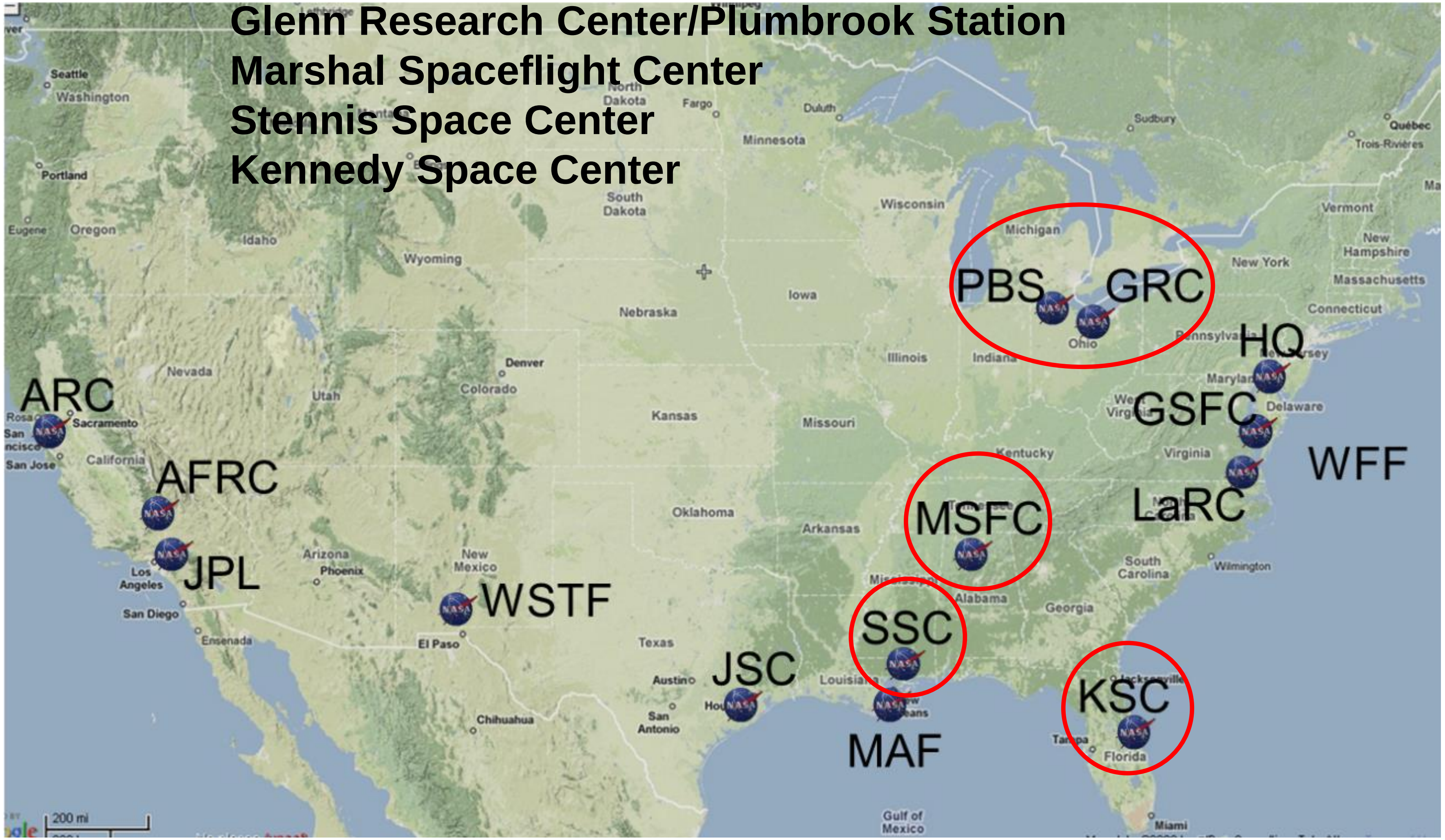
Kennedy Space Center

NASA Centers

SPACEPORT INTEGRATION & SERVICES

4 have routine LH2 requirements;

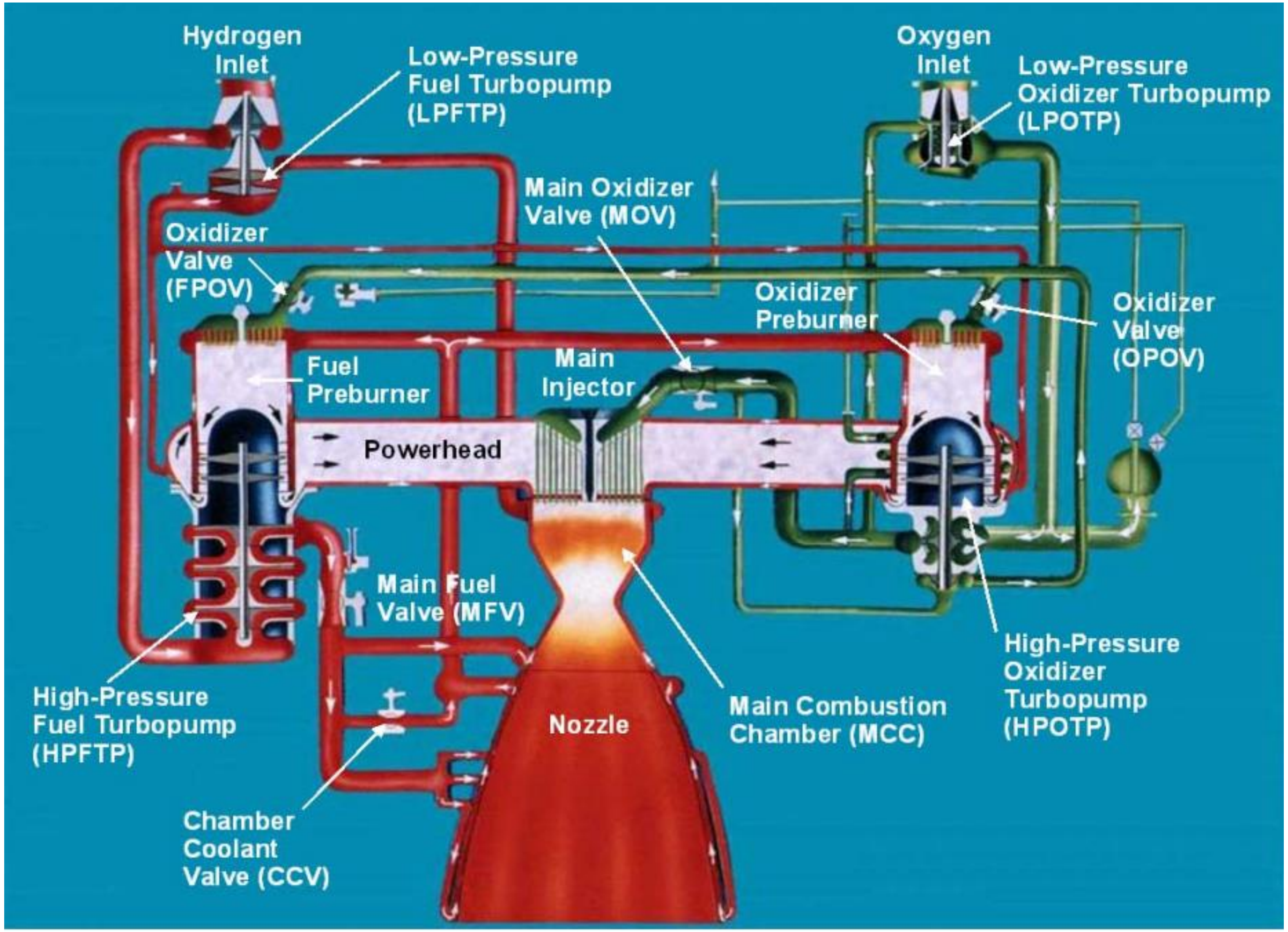
- **Glenn Research Center/Plumbrook Station**
- **Marshal Spaceflight Center**
- **Stennis Space Center**
- **Kennedy Space Center**



Why does NASA use LH2?

- Chemical rocket engines combust a mixture of fuel and oxidizer to produce thrust
- Rocket engine performance is maximized with hydrogen as the fuel and oxygen as the oxidizer
- in order to fit enough hydrogen and oxygen on board the rocket, they are refrigerated to become cryogenic liquids (liquefied); the gas to liquid volume ratio is about 800:1
- Operations (e.g., storage, transfer, loading) with cryogenics have a multitude of complications but the high performance makes it worth it

LH2/LO2 Engine



LH2 Operations

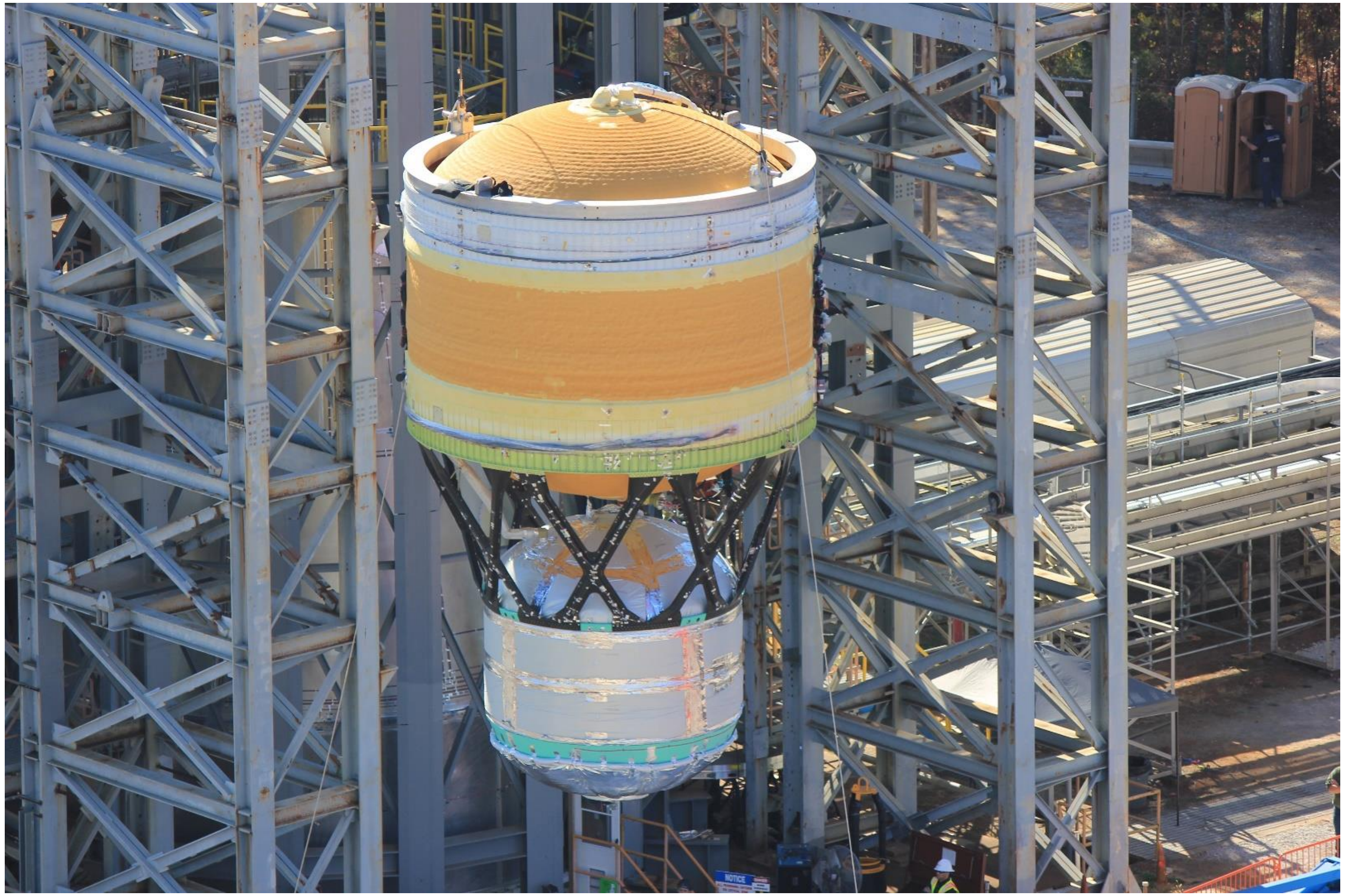
- GRC/PBS – cryogenic research, component development, and flight vehicle space environment simulation testing

SHIIVER is 13-foot diameter test tank built by NASA to evaluate technologies aimed at reducing the evaporation or “boiloff” losses in large cryogenic storage tanks for human exploration missions.

LH2 Operations

- MSFC – component and integrated system development testing

The ICPS is the liquid oxygen/liquid hydrogen-based propulsion stage that will give NASA's Orion spacecraft the in-space push needed to fly beyond the moon before it returns to Earth on the first flight of SLS and Orion



LH2 Operations

- SSC – operational rocket engine testing
  - NASA's largest user

Space Launch System (SLS) Core Stage;
The Green Run is the top-to-bottom integrated testing prior to its maiden flight. Including an eight-minute, full-duration hot fire of the stage's four RS-25 engines to generate 2 million pounds of thrust, as during an actual launch. LH2 flight tank volume = 539,000gals

LH2 Operations

Kennedy Space Center

- KSC – rocket and spacecraft ground support systems development and rocket launch

Launch Complex 39B

Kennedy Space Center

LH2 Operations

- ♦ LC39B upgraded for SLS

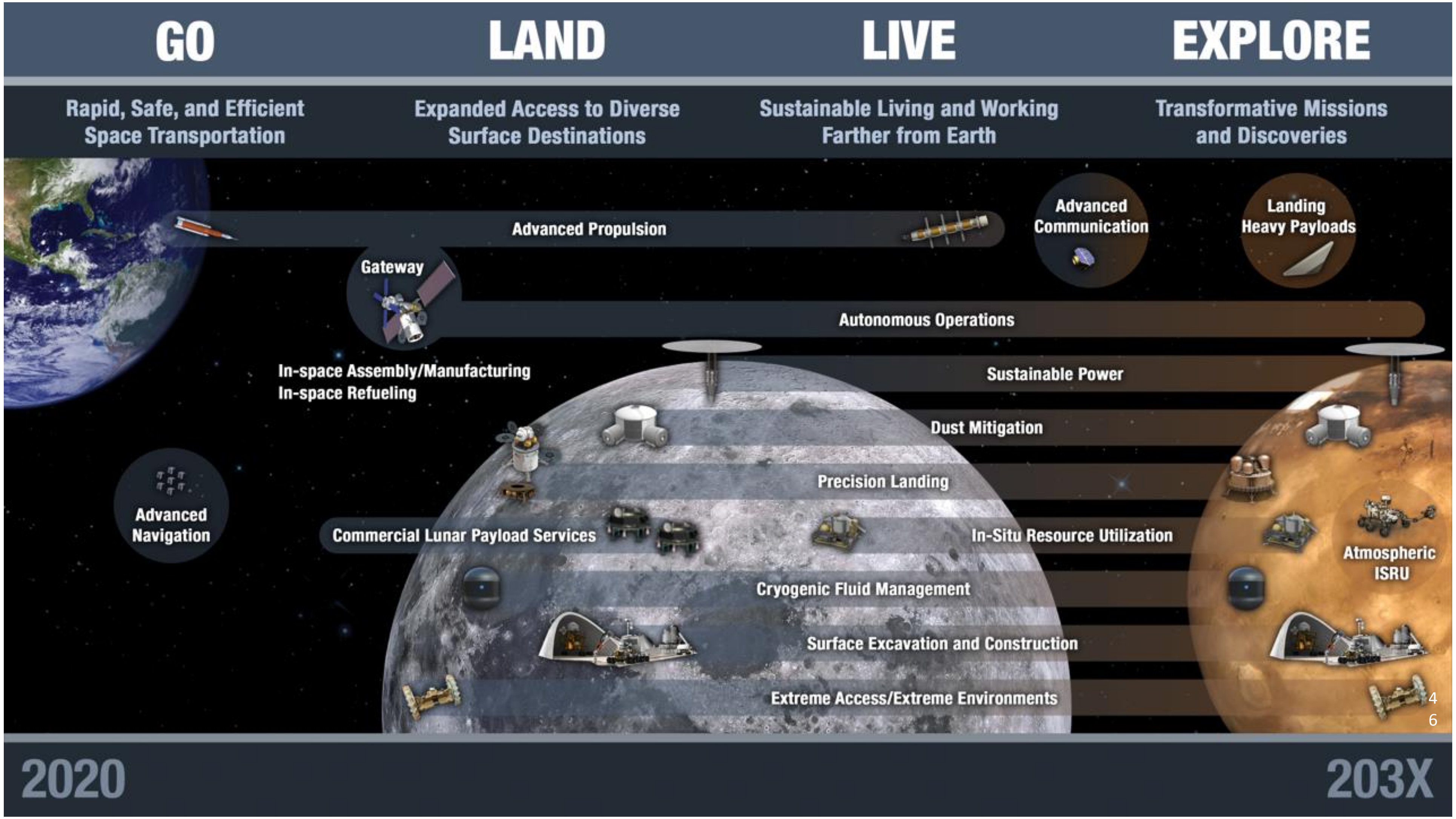
Logistics

- Purchase bulk liquid as a commercial item delivered via semi-truck tankers; up to 15,000gals net per tanker
- With few production plants in USA long-haul deliveries are typical
  - Round-trip from nearest plant to KSC is >1,000miles
- To minimize delivery transfer losses and scheduling impacts, SSC and KSC require 5 to 12 tankers in one day

Logistics

- Annual usage varies greatly
  - 3-10 million pounds per year
- Historically, only two suppliers have capability to meet NASA requirements;
  - Air Products and Chemicals
    - Production plant located in New Orleans, LA
  - Praxair
    - Production plant located in McIntosh, AL
- 4 new plants announced should help with competition and supply reliability
- Planning to solicit and award new supply contract(s) in 2021 as these plants come online

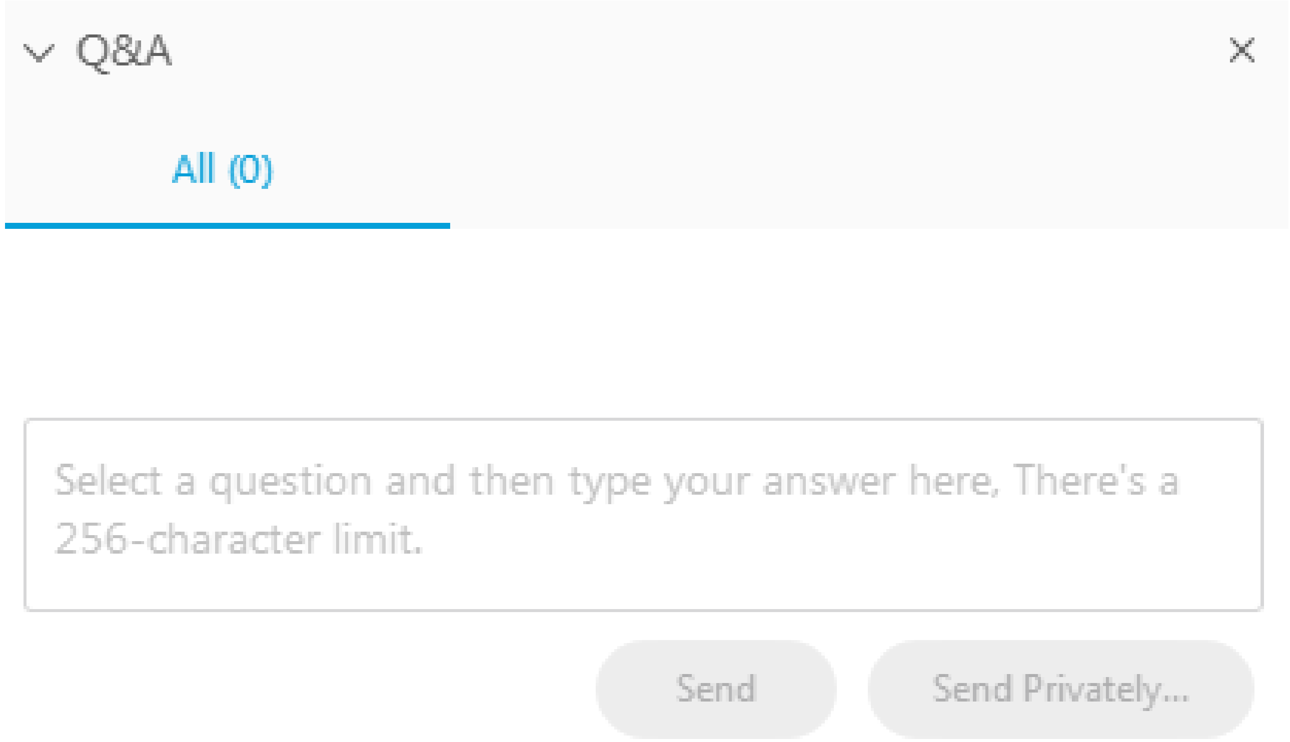
Future Plans



INCREASE YOUR H2IQ

The #H2IQ Hour Q&A

Please type your questions into the **Q&A Box**



The #H2IQ Hour

Thank you for your participation!

Learn more:

energy.gov/fuelcells
hydrogen.energy.gov