

R&D for Safety, Codes and Standards: Materials and Components Compatibility

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Overview

Timeline

- Project start date: Oct 2003
- Project end date: Sept 2022*
 - * Project continuation and direction determined by DOE annually

Budget

- Total Project Budget: \$10.8M
 - FY19 DOE Funding: \$550K
 - Planned FY20 Funding:
 - \$510K for Materials
 - \$600K for Tank Life Extension

Technical Barriers

- A. Safety Data and Information: Limited Access and Availability
- F. Enabling national and international markets requires consistent RCS
- G. Insufficient technical data to revise standards

Partners

- **SDO/CDO participation:** CSA, ASME, SAE, ISO
- **Industry:** FIBA Technologies, Tenaris-Dalmine, JSW, Swagelok
- **International engagement:** AIST-Tsukuba (Japan), I2CNER (Kyushu University, Japan), MPA Stuttgart (Germany), KRISS (Korea)

Relevance and Objectives

Objective: Enable technology deployment by **performing and applying foundational research toward the development of science-based codes and standards** that enable the deployment of hydrogen technologies

Barrier from 2013 SCS MYRDD

Project Goal

A. Safety Data and Information: Limited Access and Availability

Develop and maintain material property database and informational resources to aid materials innovation for hydrogen technologies

F. Enabling national and international markets requires consistent RCS

Develop science-based materials test methods and guidelines by working with SDOs and the international community to validate and incorporate methods in globally harmonized testing specifications

G. Insufficient technical data to revise standards

Execute materials testing to address *targeted* data gaps and critical technology deployment

- Coordinate activities with international stakeholders
- Evaluating feasibility of life extension of high-pressure components

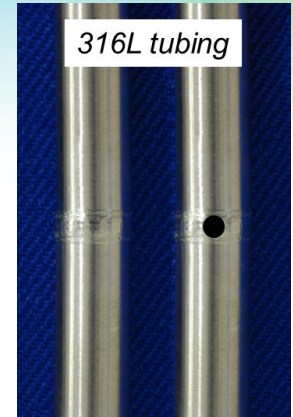
Project Approach and Milestones

MYRD&D 2013 Barrier	FY20 Milestone	Status
<p>A. Safety Data and Information: Limited Access and Availability</p>	<p>Advance state-of-the-art materials database for hydrogen compatibility</p>	<ul style="list-style-type: none"> • Sandia Hydrogen Effects Database (Granta MI) is publically accessible and populated with literature data. • Update to Technical reference is planned for FY20.
<p>F. Enabling national and international markets requires consistent RCS</p>	<p>Negotiate standard language and technical basis with international experts on materials compatibility testing for proposal to GTR IWG</p>	<ul style="list-style-type: none"> • Presented performance-based materials compatibility test methodology for vehicle applications to GTR IWG Nov. '19 • Revised performance-based materials test method in Appendix B of SAE J2579
<p>G. Insufficient technical data to revise standards</p>	<ul style="list-style-type: none"> • Develop test methodology for component-like configurations, such as hole-drilled orbital tube welds with internal H₂ • Evaluate method for fracture resistance of aluminum alloys in moist-hydrogen environments • Document results from low ΔK measurements in H₂ gas to provide guidance for assessing influence of small pressure fluctuations on life of tanks 	<p>Manuscripts relating to all 3 topics have been accepted to ASME Pressure Vessels & Piping conference (peer-reviewed conference proceedings)</p>

Approach: Development of test methodologies to target knowledge and data gaps

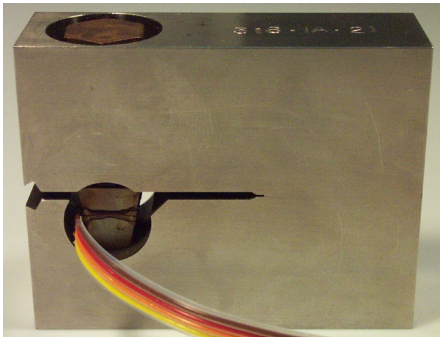
Advanced test methods for welds

Assessing hole drilled tubes / orbital welds as a means to develop fatigue test methodologies for common but challenging weld configurations



Critical assessment of aluminum

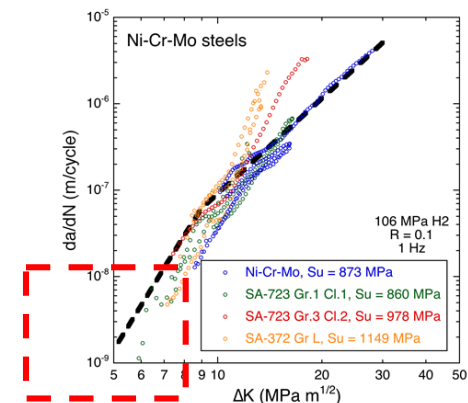
Establish a benchmark for stress corrosion cracking in presence of 'wet' hydrogen (>5 wppm H₂O) in aluminum alloys



Gaps in fatigue crack growth data

Evaluate fatigue behavior at low ΔK (i.e. small pressure cycles) where negligible data have been generated

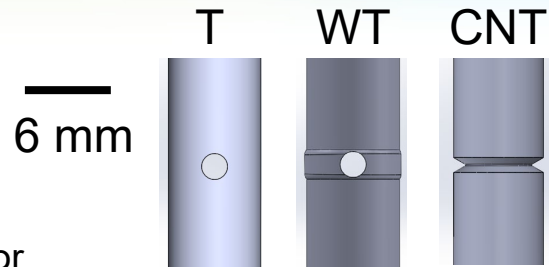
- Extrapolation of "master" design curves could be overly conservative, resulting in shortened design life



Accomplishments: Advanced test methods for welds

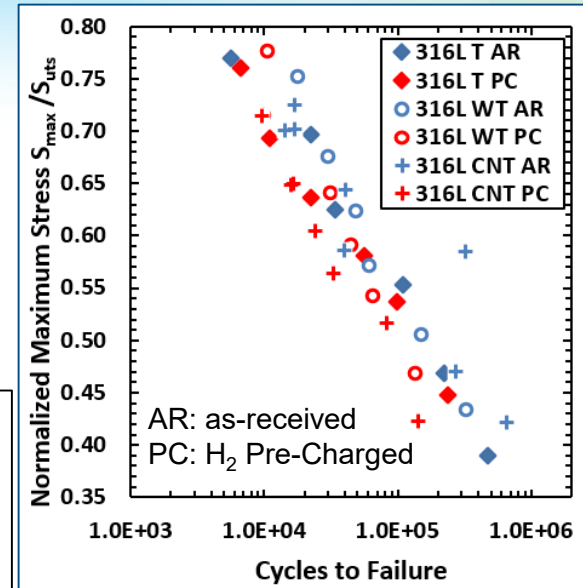
Hole-drilled tube specimens yield similar fatigue life to conventional circumferentially notched specimens

T: Tube
 WT: Welded Tube
 CNT: Circumferentially Notched Tension



$K_t = 3$, stress concentration factor

- Normalization of the stress to the tensile stress results in similar fatigue life between the different geometries
- Implies that other geometries could be considered to accommodate unique manufacturing or welding configurations



Accomplishments: Critical assessment of aluminum

Static fracture testing of 3 aluminum alloys in hydrogen containing 5 wppm H₂O



Alloy & temper	Yield strength (MPa)	Ultimate strength (MPa)	Result of 100 MPa H ₂ containing 5 wppm H ₂ O for 1000 hr
7050-T7451	450	517	No crack extension (2 tests)
7475-T7351	404	488	No crack extension (2 tests)
2219-T851	347	455	No crack extension (2 tests)

Result suggests that aluminum alloys in these tempers are not susceptible to stress corrosion cracking in fuel cell grade high-pressure hydrogen

Accomplishments: Gaps in fatigue crack growth data

Low ΔK fatigue crack growth rates in high pressure H₂ are bound by master design curves

- Data at low ΔK are challenging experiments to execute (several weeks, 10s of millions of cycles on seals)

Test conditions

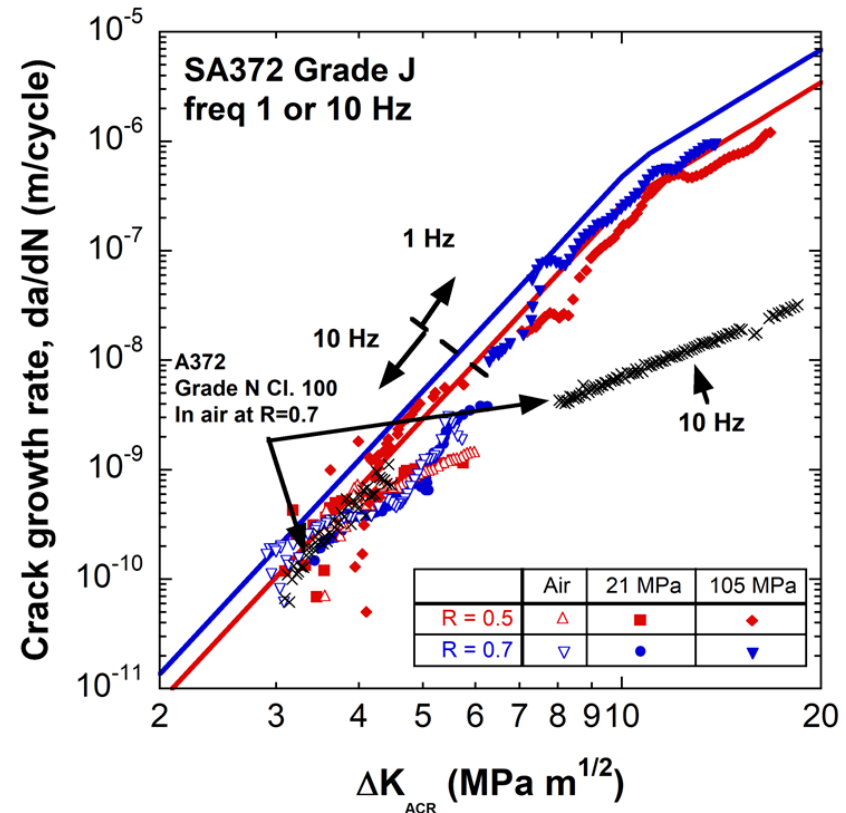
P = 21 or 105 MPa

R = 0.5 or 0.7

Frequency = 1 or 10 Hz

Master design curves from ASME Code Case 2938 established from measurement of $\Delta K > 6 \text{ MPa m}^{1/2}$

- Data in H₂ appear to overlap data in air at low ΔK
- Effects of crack closure were corrected via adjusted compliance ratio method (ΔK_{ACR}) resulting in better overlap of air and H₂ curves



- Operational ΔK_{th} (thresholds) were established to be between 3 and 4 MPa m^{1/2} meaning da/dN values ~ 10⁻¹⁰ m/cycle → Practical engineering limits for infinite design life
- More testing is needed before these trends can be generalized for behavior in low ΔK range

Accomplishments: Harmonization and simplification of standards

Summary of tests and requirements for hydrogen compatibility of materials for vehicle applications (*accepted* for Appendix B SAE J2579, *proposed* for GTR no 13 phase II)

		Notched method (option 1)	Smooth method (option 2)
Fatigue life	Test conditions	<ul style="list-style-type: none"> • H2 pressure = 1.25 NWP • Temperature = 293 ± 5K • Net section stress ≥ 1/3 S* • Frequency = 1 Hz 	<ul style="list-style-type: none"> • H2 pressure = 1.25 NWP • Temperature = 293 ± 5K • Net section stress ≥ 1/3 S* • Frequency = 1 Hz
	Number of tests	3	3
	Requirements for each test	N > 10 ⁵	N > 2x10 ⁵
SSRT	Test conditions	Not required	<ul style="list-style-type: none"> • H2 pressure = 1.25 NWP • Temperature = 233 ± 5K • Displacement rate ≤ 5x10⁻⁵ s⁻¹
	Number of tests		3
	Requirements for each test		Yield strength > 0.80 yield strength in air at same temperature

- Some debate still continues on smooth specimens (e.g. martensitic stainless steels might pass the smooth method, but fail the notched method)
- Significant revision and simplifications have been proposed to GTR no 13 phase II; however, some stakeholders have proposed *eliminating* the materials test.

Accomplishments: Harmonization and simplification of standards

Appendix B SAE J2579 Table Simplification

Table B2: Qualification of hydrogen compatibility based on usage conditions

Proposed Table

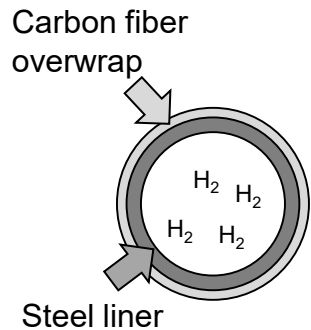
Material	Recommended Condition	Materials performance	Common hydrogen usage	Example alloys
Austenitic stainless steels (solid solution strengthened)	<ul style="list-style-type: none"> Ni > 8 wt% Minimize magnetic phases Strain-hardened condition can be acceptable 	<ul style="list-style-type: none"> Substantial reduction of tensile ductility Potential reduction of fatigue life in low-cycle regime 	Tubing, fittings, valve bodies, etc	304, 304L, 316, 316L, XM-11, XM-19
Austenitic stainless steels (precipitation hardened)	Avoid overaged condition	<ul style="list-style-type: none"> Substantial reduction of fracture toughness (~50 MPa m^{1/2}) 	Bosses, pressure volumes	A-286
Martensitic stainless steels	<ul style="list-style-type: none"> Tensile strength < 900 MPa use only with extreme caution, especially for high strength conditions 	<ul style="list-style-type: none"> Fracture toughness < 10 MPa m^{1/2} in high strength conditions Fatigue crack growth increased by factor of 10 to 100 	Valve stems, and sub-assemblies	17-4PH, PH13-8Mo, 15-5PH
Carbon steels	Tensile strength < 600 MPa	<ul style="list-style-type: none"> Fatigue crack growth increased by factor of 10 or more for $\Delta K > 8$ MPa m^{1/2} 	Line pipe	X42, X52, X60, X70, X80, A516
Low alloy steels	Tensile strength < 900 MPa	<ul style="list-style-type: none"> Fatigue crack growth increased by factor of 10 or more for $\Delta K > 8$ MPa m^{1/2} 	Transportable gas cylinders, stationary storage	A372, A723 (Q&T Cr-Mo & Ni-Cr-Mo steels)
Aluminum alloys	Avoid tempers susceptible to stress corrosion cracking	<ul style="list-style-type: none"> No known effects of gaseous hydrogen 	Pressure vessel liners	6061

Proposed Table categorizes material more clearly and describes broad characteristics that are favorable for use in H₂

- Previous table was crowded, standards specific, and included many caveats

Background / Approach: Tank Life Extension {New Task FY20}

Develop an understanding of opportunity space for life extension of high-pressure hydrogen vessels, initially focusing on Type 2 pressure vessels



Type 2 tanks are used at Hydrogen Refueling Stations (HRS)

Background:

- Type 2 tanks have finite design life over certain pressure range
 - e.g. Pressure range 13,500 psi to 8,900 psi, Design Life = 37,540 cycles or 20 yr
- Tanks are reaching cycle limit *much sooner* than expected (e.g. 7 yr)
- Conventional non-destructive evaluation (NDE) methods to inspect metal liner are incompatible with overwrap; therefore no means to inspect, recertify, and extend life of tank → **Result = tanks are retired**

Substantial savings can be achieved if:

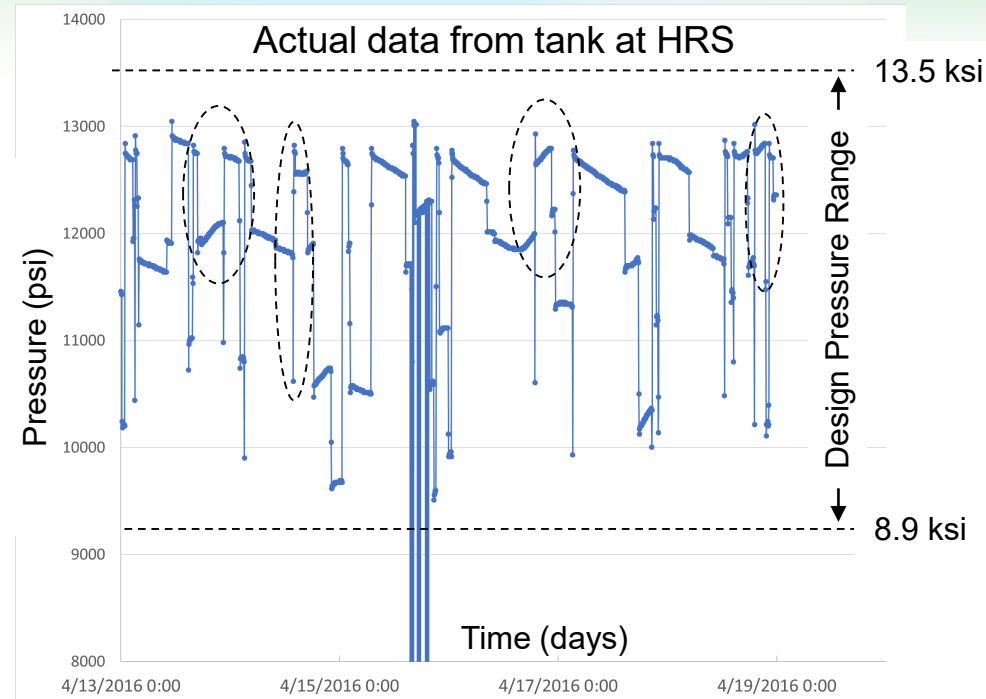
- 1) Design methods can show longer life of tanks
- 2) Tanks can be inspected to re-assess remaining life

Approach: Tank Life Extension (design methods)

Assessment of variable pressure cycles on projected design life of tanks

Industry is conservative and counts every refill of a tank = 1 cycle

- Should *partial* cycles be counted the same as *full* cycles?



Identify margins through rigorous analysis of pressure cycles

- Incorporate pressure variations in fatigue life assessment
 - Actively pursuing in-field pressure cycle data from HRS
- Identify gaps in experimental fatigue data needed to assess design life
 - Low ΔK in gaseous H₂
 - Variable amplitude testing (load-cycle history effects) in gaseous H₂

Accomplishments: Tank Life Extension (design methods)

Simulations show extended life for variable pressure cycles

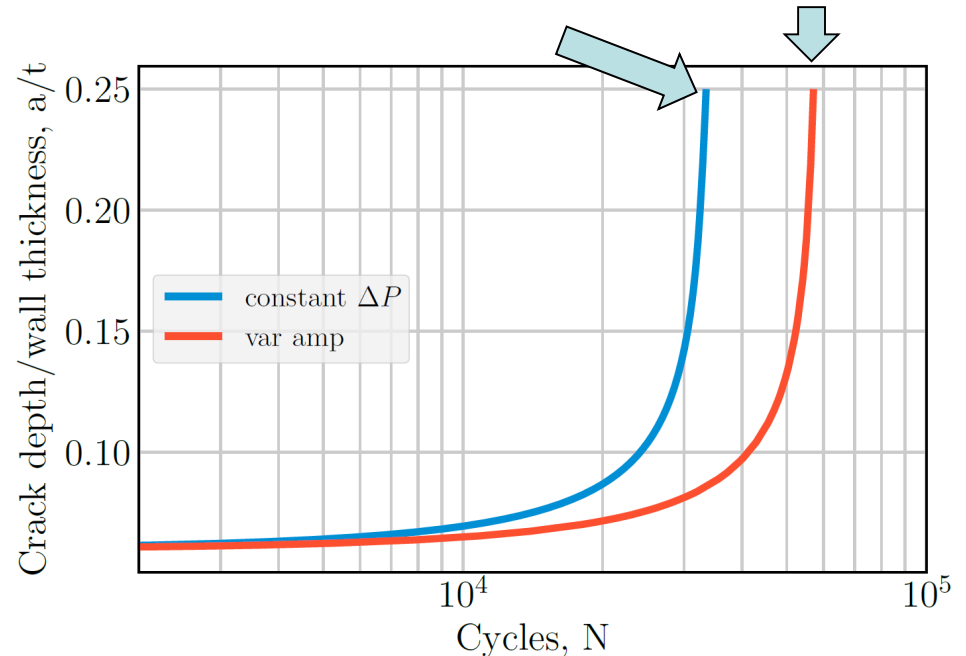
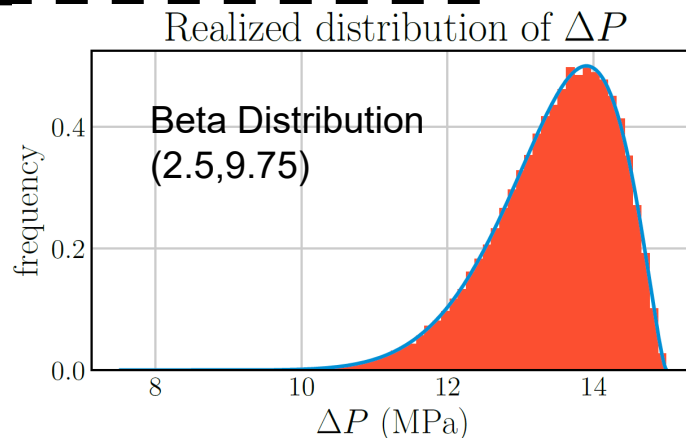
Assumptions:

- | Type 1 tank
- | $P_{max} = 45 \text{ MPa}$
- | $\Delta P = 15 \text{ MPa}$ or variable
- | End of life ($a/t = 0.25$)
- | $a_o = 0.86 \text{ mm}$
- | OD= 238 mm
- | $t = 14.4 \text{ mm}$



$\Delta P = 15 \text{ MPa}$
33k

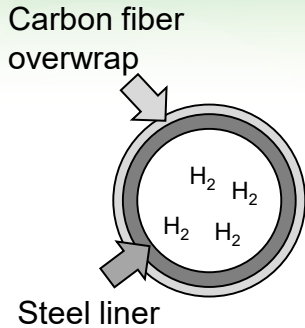
Variable ΔP
57k



- Assuming variable pressure swing (ΔP), design life of the tank is greater by a factor of more than 1.7X
- Other variables, such as flaw shape, also significantly influence design life calculations and are being explored

Approach: Tank Life Extension (inspection)

NDE techniques for life assessment of metal liner (Type 2 tanks)



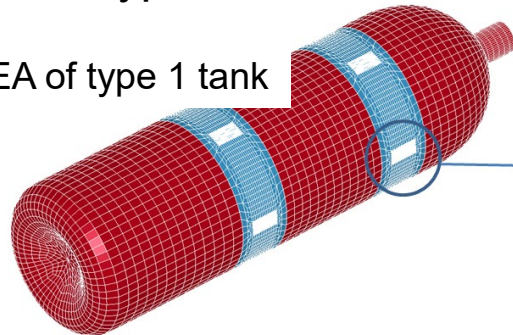
Access to metal liner is limited in Type 2 tanks
 → Perform internal inspection through bore using eddy current technique

Task 1: Demonstrate feasibility of Eddy Current (EC) technique for detecting flaws in type 2 vessels



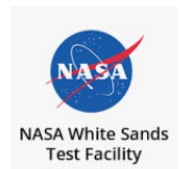
Type 1 tanks with internal flaws

FEA of type 1 tank



Calibration block of manufactured defects

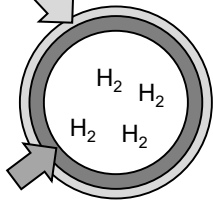
- Utilize type 1 tanks with manufactured defects on inner surface for proof of principle for EC technique
- Partnering with Hexagon Digital Wave and NASA-White Sands Test Facility for NDE development and measurements (contracts are pending)



Approach: Tank Life Extension (inspection) NDE techniques for life assessment of metal liner (Type 2 tanks)

Task 2: Demonstrate flaw detection capability on full-scale Type 2 tanks

Carbon fiber
overwrap



Steel liner



14'6" Length / O.D. = 17 in / Steel liner = 1.5" / Access port = 1.5" NPT

- Eddy current detection of flaws in metal liner through end ports
- Modal Acoustic Emission (MAE) on carbon fiber overwrap
- Partnering with Hexagon Digital Wave (contracts pending)



Benefits if Successful – Demonstration of a NDE technique capable of detecting flaws in metal liners of full-scale Type 2 tanks will facilitate life-extension via conventional life-extension practices (such as ASME PCC-3)

Response to Previous Year Reviewers' Comments

- *FY19 Reviewer Comment:* The overall project goal is not well defined. Material performance in various hydrogen environments could be researched through never-ending combinations of conditions and materials. However, good progress in some areas has been made to date, and integration with various databases and other efforts has been considered.
 - We agree, measurement of material performance is an endless endeavor. However, measurement of every combination of material, environment and stress has never been a goal of this work. We focus on providing the community with science-based tools to make engineering decisions. Our activities include (i) development and critical assessment of test methods for hydrogen (ii) compilation of informational resources and (iii) enabling technology deployment through benchmarking critical data (e.g., pressure vessel steels) and development of codes and standards.
- *FY19 Reviewer Comment:* The collaboration/coordination/partner list is extensive and international. Additional U.S. companies and researchers might be appropriate.
 - We invite US companies to partner with us. However, expertise and capability in materials compatibility seems to be more developed at international institutions than within US companies.
- *FY19 Reviewer Comment:* Other interested institutions and stakeholders have been identified, and collaborative efforts are under way. Maintaining that collaboration and obtaining consensus may be difficult barriers that were not identified.
 - Exactly correct: consensus (especially international) is a significant barrier and sometimes an under-appreciated barrier
- *FY19 Reviewer Comment:* Based on the information presented, one weakness of the project seems to be plans for future work beyond 2020.
 - We tend to focus on communicating next steps (near term). We have provided out-year content.

Collaborations

- **Standards Development Organizations (SDOs)**
 - SAE & UN GTR: Test method for SAE J2579 and proposed method for GTR no. 13 Phase II is based on extensive international discussion with organization stakeholders and automotive OEMs
 - ASME BPVC: Code case adds design guidance to Article KD-10; ASME community and stakeholders are engaged in tank life extension discussion as well as requesting assistance on fatigue life versus fatigue crack growth methodologies
- **Industry partners**
 - Partners communicate materials testing gaps/needs and provide technology-relevant materials (FIBA Technologies, Tenaris-Dalmine, JSW, Swagelok)
 - International MOU: evaluation of Ni-Cr-Mo PV steels, motivation of Code Case for ASME BPVC and future testing plans (threshold fatigue crack growth and $R < 0$)
 - NASA-WSTF and Digital Wave: non-destructive evaluation of metal liner in tanks
 - Becht Engineering and Air Products: comparison of actual service environments and design criteria, evaluation of margin in design and opportunity for life extension
- **International research institutions**
 - Performance-based fatigue evaluation in the context of SAE is focus of R&D collaboration with international community, including collaborative research activity in Japan (Kyushu Univ) and Germany (MPA Stuttgart)
 - Korea and China have expressed interest to participate as well

Remaining Challenges and Barriers

- Long-time scales (kinetics) associated with hydrogen-materials interactions challenges our ability to interrogate materials
 - Acceleration of fatigue testing is challenging and generally requires equal parts creativity and patience
 - Surface effects are difficult to characterize and even more difficult to quantify – thus establishing bounding behavior can be challenging
- Stationary pressure vessels remain a design challenge
 - Conventional steels are necessarily limited to relatively low strength
 - Design strategies are conservative with limited allowance for life extension
- International consensus on codes and standards
 - Consensus has always been a significant challenge and requires patience and sustained interaction
- Next generation materials/microstructures cannot be identified without fundamental understanding of the physical processes
 - Advanced scientific computing and innovative experimentation are needed to integrate new materials into design



Proposed Future Work

Remainder of FY20 (*Any proposed future work is subject to change based on funding levels*)

- ***Test method development for targeted data***
 - Explore requirements of fatigue life testing with ASME partners, including the potential applicability of the notched specimen methodology for fatigue design
 - Procure high moisture hydrogen gas for next set of Al-alloy tests
 - Assess fatigue crack growth in low ΔK (near threshold) regime & evaluate kinetic effects (e.g., frequency)
- ***Harmonization of standards***
 - Work with partners to evaluate smooth specimen methodology for fatigue metric in comparison to notched specimen geometry
 - Revise Technical Reference (pressure vessel steels & stainless steels)
- ***Tank life extension***
 - ***Assess pressure variations on design life of tanks***
 - Pursuing in-field operating data from tanks at HRS
 - Partnering with Becht Engineering for code-design calculations
 - ***Evaluation of NDE techniques for Type 2 tanks***
 - Establish proof of principle that eddy current technique is a viable means of detecting flaws on metal liner in Type 2 tanks (NASA-WSTF, Digital Wave)

Proposed Future Work

FY21 (*Any proposed future work is subject to change based on funding levels*)

- ***Test methods for negative load ratio***
 - Develop hardware designs for reverse loading and strain-based methods to extend test method development to negative load ratios
- ***Comprehensive revision of Technical Reference***
 - Recent advances in test methods, standards, and relevant data will be added to existing "handbook" informational resources to reflect state of knowledge
- ***Tank life extension***
 - Demonstrate that eddy current is feasible as NDE technique for Type 2 tanks for detecting flaws on metal liner

FY22 (project continuation and direction determined by DOE annually)

- ***Stress-based fatigue design methodology to complement fracture mechanics***
 - Develop methodology for fatigue life testing (i.e., development of SN curves) in gaseous hydrogen in collaboration with ASME stakeholders
- ***Quantification and guidance on role of environmental variables***
 - Leveraging outcomes from other projects, develop concrete guidance on role of environmental variables (i.e., gas blends) for applicable standards

Summary

- **Test methodology development**

- Test method for difficult-to-test welds was developed; other geometries could be considered to accommodate unique manufacturing or welding configurations
- Wet hydrogen (5 wppm H₂O) exhibited negligible effects on fracture toughness in select aluminum alloys, suggesting no concerns of SCC in fuel cell grade H₂
- FCGR at low ΔK in high pressure H₂ appears to converge with air data

- **Harmonization of standards**

- International coordination has resulted in a relatively simple fatigue metric for materials evaluation in vehicle applications: SAE J2579 and UN GTR no. 13

- **Tank life extension**

- Analysis shows that more accurate accounting of actual pressure cycles can extend useable life > 2X
- Eddy current is being pursued as possible NDE technique for Type 2 flaw inspection of metal liners

- **Extensive *international partnerships***

- *Research institutions*: AIST (Japan) , Kyushu University (Japan), KRISS (Korea), MPA Stuttgart (Germany)
- *Industry*: Japan Steel Works, Tenaris-Dalmine (Italy), FIBA Technologies (US), Hexagon Digital Wave (US), NASA-WSTF (US), Becht Engineering (US)