Sandia National Laboratories

H2FC Hydrogen and Fuel Cells Program

SAND2020-5400PE

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

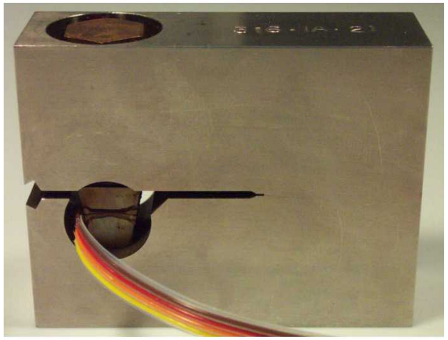
Project Approach and Milestones

MYRD&D 2013 Barrier	FY20 Milestone	Status
A. Safety Data and Information: Limited Access and Availability	Advance state-of-the-art materials database for hydrogen compatibility	• Sandia Hydrogen Effects Database (Granta MI) is publically accessible and populated with literature data. • Update to Technical reference is planned for FY20.
F. Enabling national and international markets requires consistent RCS	Negotiate standard language and technical basis with international experts on materials compatibility testing for proposal to GTR IWG	• 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
G. Insufficient technical data to revise standards	• Develop test methodology for component-like configurations, such as hole-drilled orbital tube welds with internal H_2 • Evaluate method for fracture resistance of aluminum alloys in moist-hydrogen environments • Document results from low ΔK measurements in H_2 gas to provide guidance for assessing influence of small pressure fluctuations on life of tanks	Manuscripts relating to all 3 topics have been accepted to ASME Pressure Vessels & Piping conference (peer-reviewed conference proceedings)

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



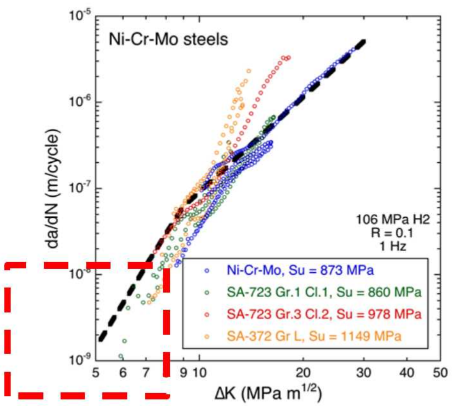
Critical assessment of aluminum

Establish a benchmark for stress corrosion cracking in presence of 'wet' hydrogen (>5 wppm H_2O) 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

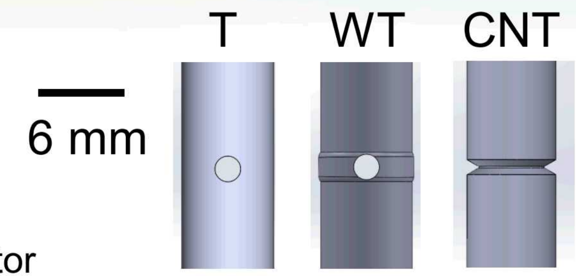


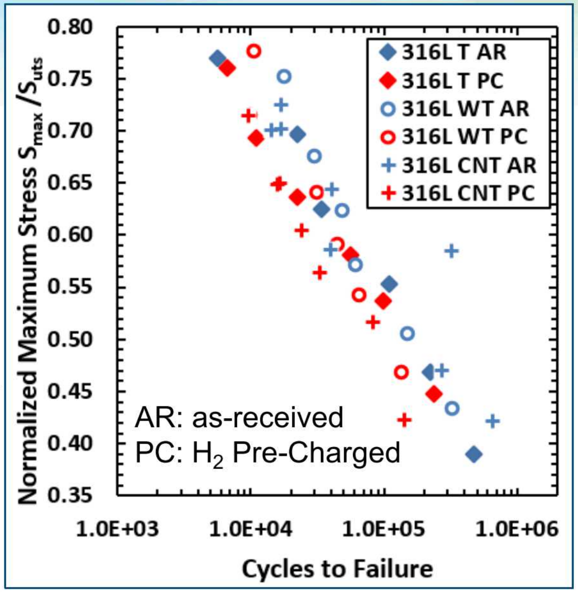
Accomplishments: Advanced test methods for welds

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 H_2O

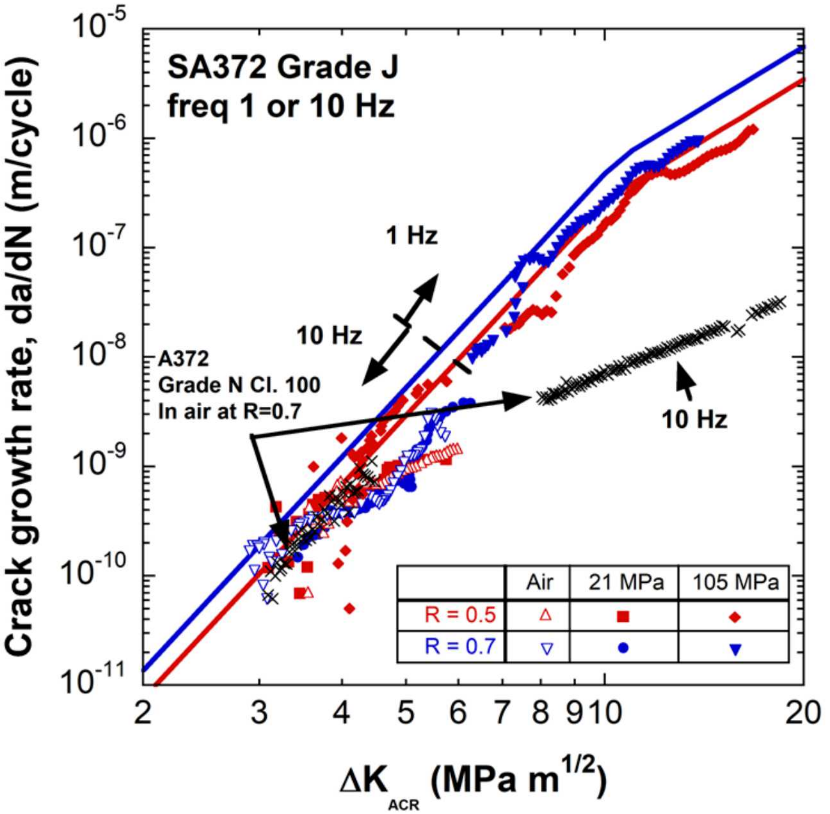
Alloy & temper	Yield strength (MPa)	Ultimate strength (MPa)	Result of 100 MPa H_2 containing 5 wppm H_2O for 1000 hr
7050-T7451	450	517	No crack extension (2 tests)
7475-T7351	404	488	No crack extension (2 tests)
2219-T851	347	455	No crack extension (2 tests)

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 H_2 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 ΔK > 6 MPa $m^{1/2}$

- Data in H_2 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 H_2 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	• H2 pressure = 1.25 NWP • Temperature = 293 ± 5K • Net section stress ≥ 1/3 S* • Frequency = 1 Hz	• 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	• 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)	• Ni > 8 wt% • Minimize magnetic phases • Strain-hardened condition can be acceptable	• 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	• Substantial reduction of fracture toughness (~50 MPa $m^{1/2}$)	Bosses, pressure volumes	A-286
Martensitic stainless steels	• Tensile strength < 900 MPa • use only with extreme caution, especially for high strength conditions	• 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	• 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	• 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	• No known effects of gaseous hydrogen	Pressure vessel liners	6061

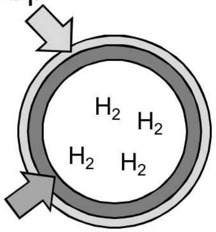
Proposed Table categorizes material more clearly and describes broad characteristics that are favorable for use in H_2

- 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

Carbon fiber overwrap



Steel liner

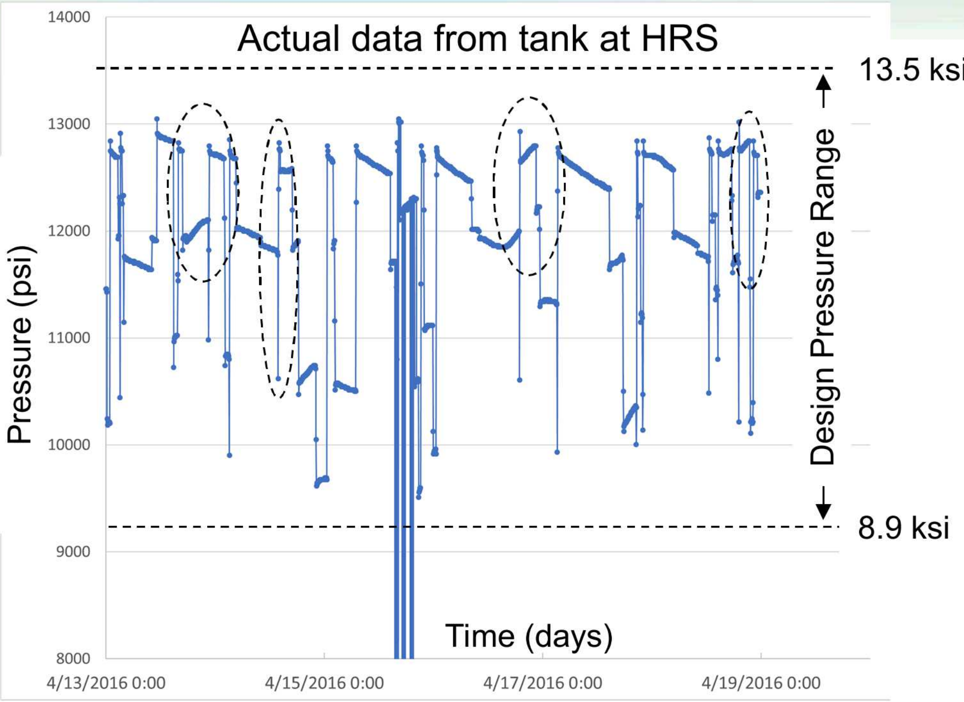
Type 2 tanks are used at Hydrogen Refueling Stations (HRS)

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 H_2
  - Variable amplitude testing (load-cycle history effects) in gaseous H_2

CS [2]1

Slide 11

CS [2]1 Just a few things to see in mind: (1) autofrettage is taken into consideration in the design of type 2 tanks, so you want to be careful about implying that this is new (sort of ambiguous here, but i still it's probably OK; (2) maybe not worth it here, but in actual communications, might be worth should actual cycles as variable (here they are all identical); (3) i tweaked title so as to be clear that this is part of the tank life extension activity - i may not have been immediately obvious to the reader

Chris San Marchi, 4/13/2020

Accomplishments: Tank Life Extension (design methods)
Simulations show extended life for variable pressure cycles

Assumptions:

Type 1 tank

P_{max}= 45 MPa

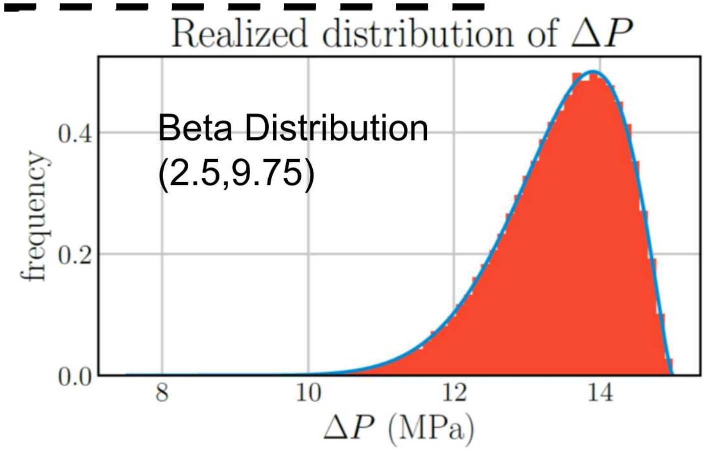
ΔP = 15 MPa or variable

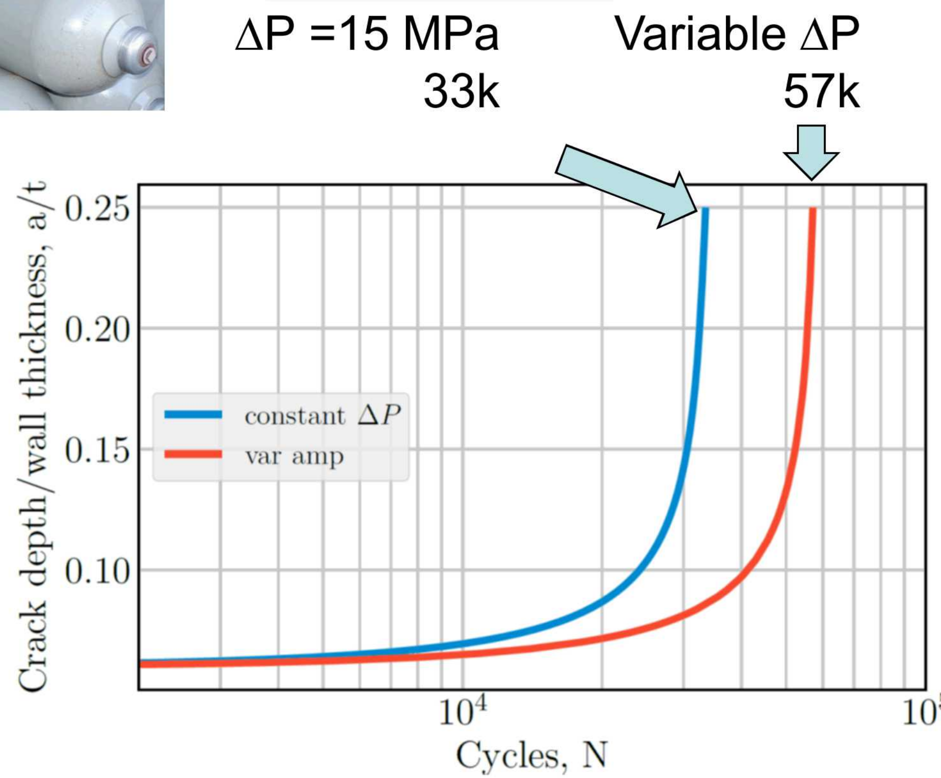
End of life (a/t =0.25)

a_o = 0.86 mm

OD= 238 mm

t = 14.4 mm

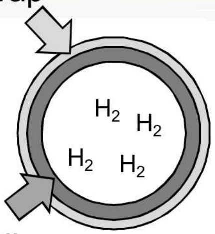




- Assuming variable pressure swing (ΔP), design life of the tank is greater by a factor of more than 1.7X
- Other variables, such as flaw shape, also significantly influence design life calculations and are being explored

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

Carbon fiber overwrap



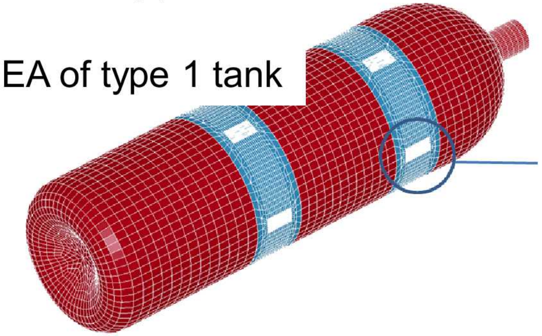
Steel liner

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

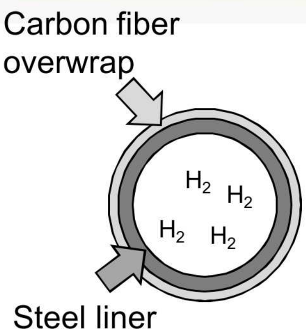
- Utilize type 1 tanks with manufactured defects on inner surface for proof of principle for EC technique
- Partnering with Hexagon Digital Wave and NASA-White Sands Test Facility for NDE development and measurements (contracts are pending)

NASA White Sands Test Facility

DIGITAL WAVE

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



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 → H-Mat℠ Hydrogen Materials Compatibility Consortium

Proposed Future Work

Remainder of FY20

- ***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 (project continuation and direction determined by DOE annually)

- ***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 H_2O) exhibited negligible effects on fracture toughness in select aluminum alloys, suggesting no concerns of SCC in fuel cell grade H_2
  - FCGR at low ΔK in high pressure H_2 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)

Technical Back-Up Slides

Reviewer-Only Slides

Critical Assumptions and Issues

1. The SCS program is strongly coupled to the core activities within the H-Mat project. The SCS program is focused on methodologies for standardized testing, engineering data and design. H-Mat is distinguished by a focus on illuminating the basic materials science and describing fundamental mechanisms of hydrogen behavior in materials. As such the activities are intended to be complementary and not duplicative – although they leverage and motivate one another where appropriate.
2. International collaborations are critical to successful harmonization of standards; we maintain relationships with many organizations such as HYDROGENIUS/AIST (Tsukuba, Japan) and I^2CNER (Kyushu University, Japan), MPA Stuttgart (Germany), and Korea Research Institute of Standards and Science. The value of building strong connections with collaborators cannot be overstated, but the invest to nurture those relationships is also significant.
3. We depend on stakeholders to provide guidance on materials of interest as well as supply technologically relevant materials for testing. It is imperative that we generate data for materials that represent those used in service. To date, we have been able to receive ample materials through our interactions with industry partners, e.g., FIBA Technologies, Swagelok, as well as both European and Japanese pressure vessel manufacturers. We must maintain and expand relationships with industry partners and SDOs not only so that we have a supply of materials but also access to their input into materials testing parameters. Additionally, the project is not intended to write standards or codes; therefore, the SDOs must initiate standards/code-writing activity and before the program can participate. For example, ASTM does not, to our knowledge, have an activity to address specifically materials testing in high-pressure gaseous hydrogen, while CSA, SAE and ASME are, or have been, active in developing documents specific to gaseous hydrogen.

Publications and Presentations (selected)

Publications

- J. Ronevich, C. San Marchi, K. Nibur, P. Bortot, G. Bassanini, M. Sileo, “Measuring fatigue crack growth behavior of ferritic steels near threshold in high pressure hydrogen gas,” (PVP2020-21263), Proceedings of the 2020 ASME Pressure Vessels & Piping Conference, 19-24th July 2020, Minneapolis, MN.
- B. Kagay, C. San Marchi, J. Foulk, V. Pericoli, “Hydrogen effects on fatigue life of welded austenitic stainless steels evaluated with hole-drilled tubular specimens,” (PVP2020-8576). Proceedings of the 2020 ASME Pressure Vessels & Piping Conference, 19-24th July 2020, Minneapolis, MN.
- C. San Marchi, M Schwarz, J. Ronevich, “Effect of high-pressure hydrogen and water impurity on aluminum alloys,” (PVP2020-6391). Proceedings of the 2020 ASME Pressure Vessels & Piping Conference, 19-24th July 2020, Minneapolis, MN.
- C. San Marchi, J. Ronevich, P. Bortot, Y. Wada, J. Felbaum, M. Rana: “Technical basis for proposed master curve for fatigue crack growth of ferritic steels in high-pressure gaseous hydrogen in ASME section VIII-3 code” (PVP2019-93907), Proceedings of the 2019 ASME Pressure Vessels & Piping Conference, 14-19 July 2019, San Antonio TX.

Presentations

- C. San Marchi, J. Ronevich, J. Sabisch, J. Sugar, D. Medlin, B. Somerday, “Effect of microstructural and environmental variables on ductility of austenitic stainless steels,” Proceedings of International Conference on Hydrogen Safety (ICHS), Sept. 24-26, 2019, Adelaide, Australia.
- C. San Marchi, J. Ronevich, “Hydrogen compatibility of materials and implications of hydrogen in the natural gas network” (SAND2019-12733PE), presented to the Hydrogen Safety Panel, Sacramento CA, 16 October 2019.
- C. San Marchi, “Proposed test method to establish hydrogen compatibility of materials for fuel cell vehicles” (SAND2019-13337PE), presented at the GTR IWG in Stuttgart Germany, November 2019.
- T.A. Venkatesh, D. Mahajan, “Hydrogen Economy: US DOE Initiatives” (SAND2019-12732PE), presented by SUNY Stonybrook at the TAP2G Workshop in Scotland, October 2019 (based principally on previous presentation content from San Marchi & Ronevich).