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Standards for Qualifying Materials for Hydrogen Service

November 7, 2012

Invited talk KRISS

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Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

SAND2012-9309P

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Objectives and Outline of Presentation

- Summarize *guidance* and *standards* relevant to materials selection for hydrogen service
- Demonstrate *limitations* of existing standards for qualifying materials and designs for hydrogen service
- Provide example of *science-based development* of rules for steel pressure vessels in hydrogen service (CSA HPIT1 document
- Summarize *developing standards* relevant to materials selection for hydrogen service
- Describe *new test standard* for qualification of materials for hydrogen service (CSA CHMC1 document)

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Standard practice for testing and materials selection

- ***Guidance on testing in high-pressure gaseous hydrogen***
  - Canadian Standards Association (CSA): ***CHMC1-2012***
  - American Society of Testing and Materials (ASTM): G142 (and G129)
- ***Guidance on materials selection for hydrogen service***
  - American Society of Mechanical Engineers (ASME)
    - B31.12 Hydrogen Piping and Pipelines
    - Hydrogen Standardization Interim Report for Tanks, Piping and Pipelines (STP/PT-003)
  - European Industrial Gases Association (EIGA)
    - IGC Doc 100/03/E Hydrogen Cylinders and Transport Vessels
    - IGC Doc 121/04/E Hydrogen Transportation Pipelines
  - NASA/AIAA (American Institute of Aeronautics and Astronautics)
    - AIAA G-095 Guide to Safety of Hydrogen and Hydrogen Systems

Standards for materials qualification in high-pressure gaseous hydrogen

- ***ISO 11114-4*** (International Organization for Standardization)
  - Three options for evaluating fracture resistance
  - Pass-fail criteria
- ***ASME KD-10*** (American Society of Mechanical Engineers)
  - Design method using measured fracture and fatigue resistance

These standards are specific to pressure vessels

- Some features of materials qualification also in draft standard ***CSA HPIT1*** (Canadian Standards Association)
  - Testing protocol for full-scale pressure vessel testing
  - Alternative: materials qualified by definition and application of traditional design analysis for fatigue

ISO 11114: Transportable gas cylinders – Compatibility of cylinder and valve materials with gas contents

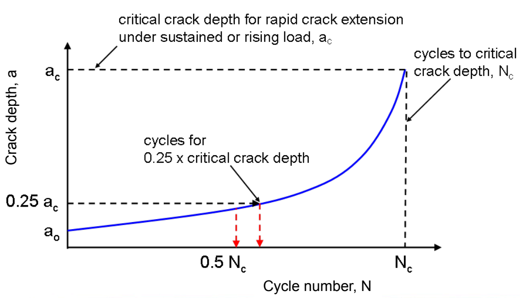
Part 4: Test methods for selecting metallic materials resistance to hydrogen embrittlement

- Testing options:
  - Disc rupture test
    - "burst" or rupture disks with Helium (He) and with Hydrogen (HH)
    - $P_{HH} > 0.50\ P_{He}$ (where P is rupture pressure)
  - Fracture mechanics test (linear elastic method)
    - Step loading of fracture mechanics specimens in gaseous hydrogen
    - $K_{IH} > (R_m / 950) \times 60$
  - Sustained load cracking test (linear elastic method)
    - Constant displacement (or load) of fracture mechanics specimens in gaseous hydrogen
    - No cracking with $K_{IAPP} = (R_m / 950) \times 60$

ASME Boiler and Pressure Vessel Code: Section VIII, Division 3, Article KD-10

Special requirements for vessels in high pressure gaseous hydrogen transport and storage service

- Fracture mechanics design approach (BPVC VIII.3 KD-4) using:
  - Sustained load cracking resistance (ASTM E1681): $K_{TH} \Rightarrow a_c$
  - Fatigue crack growth rates (ASTM E647): da/dN ⇒ crack depth = *f*(N)



Design fatigue life determined as lesser of:
- N at a = 25% of a_c
- N = 50% of N_c

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Known materials behavior suggests existing materials qualification methods are inadequate

In general, for steels in high-pressure gaseous hydrogen:

- Fracture resistance is degraded by gaseous hydrogen
- Fracture process is very ductile (i.e., not linear elastic)
  - Linear elastic methods are not appropriate for qualifying materials
- Fracture arrest threshold can be greater than fracture initiation threshold
  - *Sustained load cracking resistance is not sufficient for qualifying materials*
- Fatigue crack growth is accelerated by gaseous hydrogen
  - Qualification must consider fatigue behavior
- Fatigue process includes crack initiation and crack growth
  - *Methods that include fatigue crack growth only may be unnecessarily conservative*

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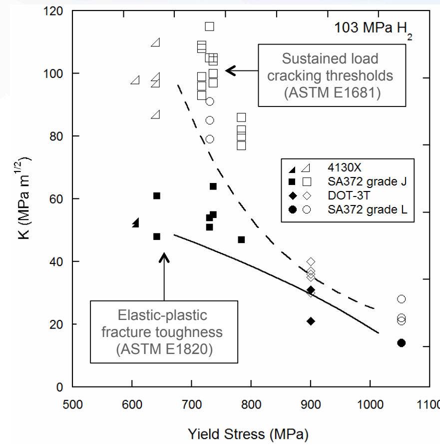
Sustained load cracking resistance is not sufficient for qualifying materials



Open symbols = *crack arrest threshold*
Closed symbols = *crack initiation threshold*
Ref. SAND2010-4633 (also Nibur et al. Metall. Mater. Trans. A, accepted)

- Sustained load cracking resistance in gaseous hydrogen is always greater than elastic-plastic fracture toughness in gaseous hydrogen
  - $K_{TH} > K_{JIC}$
- Origin:
  - strain-controlled fracture
  - differences in crack tip strain field for propagating crack compared to stationary crack
- Experiments confirm pressure vessels fail on pressurization (increasing load; not sustained load)

ISO 11114-4 and ASME BPVC VIII.3 KD-10 are non-conservative

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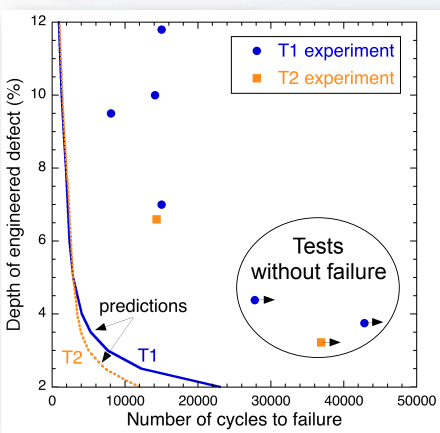
Methods that include fatigue crack growth only may be unnecessarily conservative



Ref: San Marchi et al., ASME PVP2012-78709
(also San Marchi et al., ICHS4, San Francisco CA 2011)

Comparison of life predictions based on *crack growth* only and full-scale pressure vessel tests

- Predictions are conservative by factor of 4 or more
- For small initial defects, effective safety factor approaches 10
- As-manufactured: >50,000 cycles with no failures

Fatigue analysis based on crack growth only was experimentally shown to be conservative

- Fatigue predictions from ASME BPVC VIII.3 KD-10 unnecessarily limit design space

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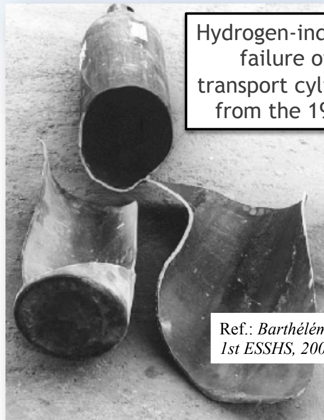
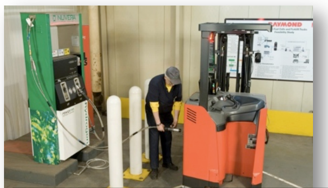
The challenge: How to design steel pressure vessels for extended fatigue life?

- Cr-Mo steel pressure vessels are extensively used for hydrogen containment
  - Pressure up to 42 MPa
  - Low number of pressurization cycles
- Emerging applications such as industrial trucks (e.g. forklifts) require >10,000 refueling cycles
- Existing standards limit design space



Hydrogen-induced failure of transport cylinder from the 1970s

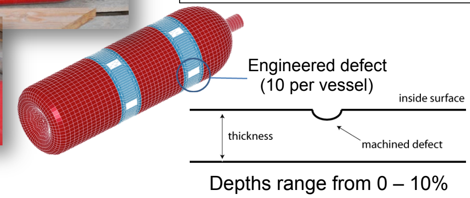
Ref.: *Barthélémy, 1st ESSHS, 2006*

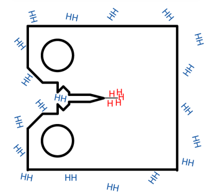


>3,000 hydrogen-powered forklifts operating in the US

Full-scale pressure vessel program developed to inform standards development

- Pressure cycling of vessels with gaseous hydrogen
  - As-manufactured condition
  - With engineered defects

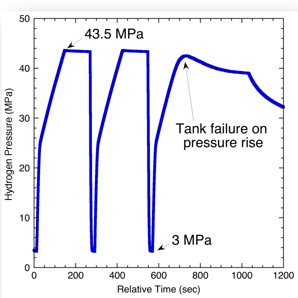




- Materials testing in gaseous hydrogen
  - Test specimens extracted from pressure vessels
  - Fatigue crack growth measurements (for predicting "life" using ASME BPVC)

Key learning from full-scale pressure vessel testing

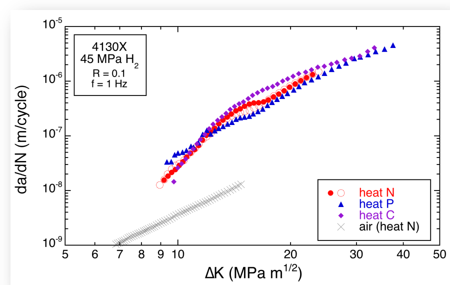
- All observed failures are leak-before-burst (LBB)
- All failures occur during pressure ramp
- Through-wall crack cannot be detected visually
- Developed test protocol for testing pressure vessel with engineered defects
  - Informs: SAE TIR J2579 and CSA HPIT1

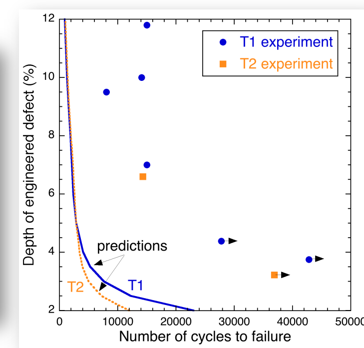


Through-wall crack in failed pressure vessel

Methods that include fatigue crack growth only are conservative

- Fatigue crack growth rates measured in gaseous hydrogen at pressure of 45 MPa and compared to measurements in air (3 heats of Cr-Mo steel: designated 4130X)
- Cycle-life predicted from this data
  - Fatigue crack growth only using ASME BPVC VIII.3 KD-10 specific to hydrogen tanks (based on KD-4)





Ref: San Marchi et al., ASME PVP2012-78709
(also San Marchi et al., ICHS4, San Francisco CA 2011)

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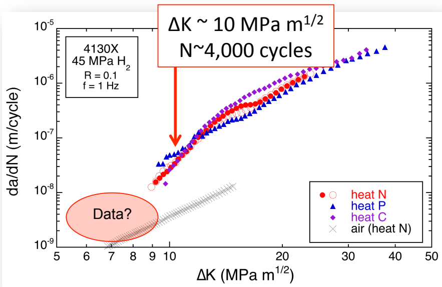
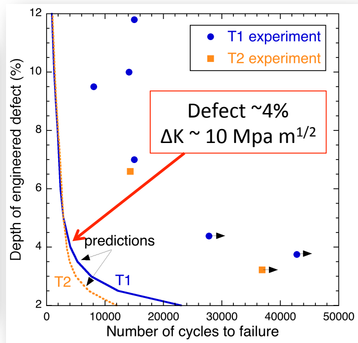
Fatigue crack growth testing in gaseous hydrogen at high ΔK has limited value

- Large growing defects (>4%) result in limited life (few thousands of cycles)
- Data is limited for low ΔK (< 8 MPa $m^{1/2}$), which is necessary for prediction of:
  - Small defects
  - High load ratios
  - Long cycle life (>10,000 cycle)





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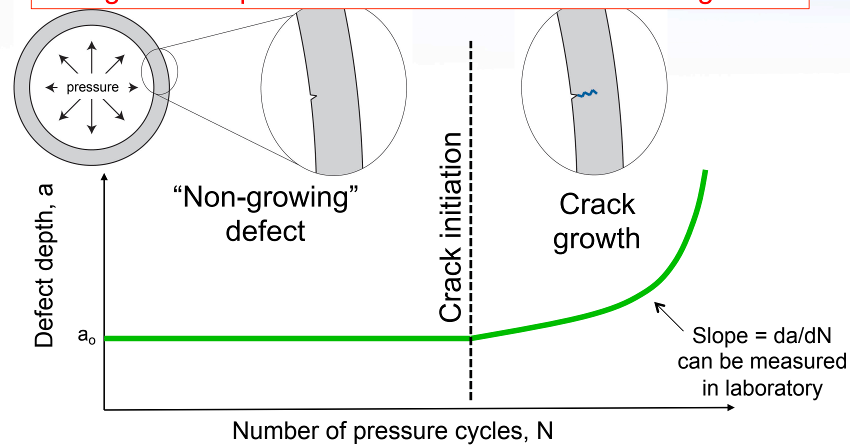
To account for longer experimentally observed fatigue life, consider fatigue initiation

Fatigue life depends on crack initiation and crack growth



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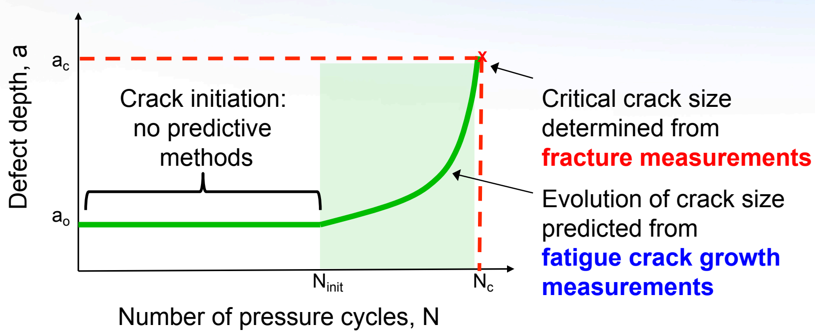
Fatigue life qualification by fracture mechanics does not account for initiation



- Implicit assumption of crack growth methods: cracks "initiate" at first cycle, i.e. N_{init} = 0

GAP ➡ how to account for fatigue crack initiation?

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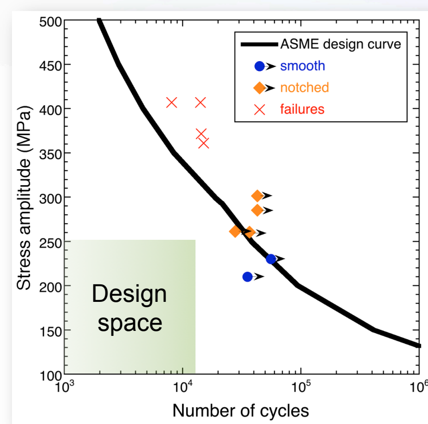
Fatigue stress-life methods offer framework for incorporating crack initiation



Comparison of design curve for fatigue in air from ASME BPVC VIII.3 KD-3 (traditional stress-life analysis) and stress analysis from tested pressure vessels

- By understanding the design space of hydrogen tanks, forklift tanks can be shown to be safe
- CSA HPIT1 defines allowable design space to ensure conservative design

Ref: San Marchi et al., ASME PVP2012-78709

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CSA HPIT1

Standard for Compressed Hydrogen Powered Industrial Truck On-Board Fuel Storage and Handling Components

Performance requirements for hydrogen containers

- Fatigue life verification by full-scale performance testing of pressure vessels with engineered defect
  - Based on test method development at SNL/CA for full-scale PV testing
  - Requirement: must reach 3X specified design life
- Option for all steel pressure vessels (type 1 tanks): Traditional design analysis for fatigue using ASME BPVC VIII.3 KD-3
  - Design curves for performance in air
  - Materials restrictions:
    - Quench and tempered Cr-Mo steels
    - Ultimate tensile strength (UTS) < 890 MPa
  - Design restriction:
    - Maximum wall stress <40% of UTS

CSA HPIT1 is currently a draft document with expected publication in 2012

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Standards being developed for materials qualification

- ***ISO 15399*** (International Organization for Standardization)
  - Options for determining hydrogen sensitivity factor in fatigue (cycle-based)
  - Specific to pressure vessels and their components (e.g. bosses and liners)
- ***SAE TIR J2579 appendices*** (Society of Automotive Engineers)
  - Three options for materials selection
  - One option includes materials qualification testing: establish performance relative to base materials properties
  - Specific to automotive fuel systems
- ***CSA CHMC1 revision*** (Canadian Standards Association)
  - Screening test to qualify alloys resistant to hydrogen-assisted fracture
    - Aluminum alloys and austenitic stainless steels
  - Methodology to design for hydrogen-induced degradation of fatigue properties (stress-based)
  - Rules for qualification of materials specifications

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ISO 15399 *(draft)*: Gaseous hydrogen – Cylinders and tubes for stationary storage

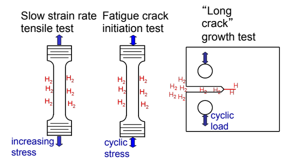
Document being developed, timeline unknown

- Testing options (subject to change):
  - Disc rupture fatigue test
    - Load cycle in nitrogen and in gaseous hydrogen
    - Use two load-ratios
    - Determine hydrogen sensitivity factor: ratio of cycles to failure for same load cycle
  - Fatigue test of tensile specimen with drilled hole
    - Load cycle in nitrogen and in gaseous hydrogen
    - Target failure between 10,000 and 30,000 cycles (in nitrogen)
    - Use two load-ratios
    - Determine hydrogen sensitivity factor: ratio of cycles to failure for same load cycle

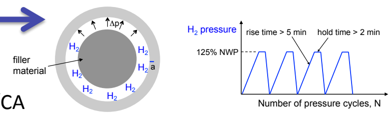
SAE TIR J2579 *(new draft)*
Fuel systems in fuel cell and other hydrogen vehicles

Appendices *still being developed*, which include options for performance-based materials selection:

- Materials compatibility exemption (Appendix B.2.3)
  - Acceptable materials include certain varieties of type 316 austenitic stainless and similar alloys; also 6061 aluminum
- Design Unrestricted (Appendix C.15)
  - Materials testing in hydrogen to establish performance similar to reference environment (i.e., establish no effect of hydrogen)
  - May eventually reference *CSA CHMC1* for materials testing



- Design Restricted (Appendix C.14)
  - Full-scale performance test of fuel system
  - Based on protocols developed at SNL/CA



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CSA CHMC1
Test method for evaluating material compatibility in compressed hydrogen applications: Phase 1 - metals

First edition – *published*: definition of procedures for mechanical property evaluation in gaseous hydrogen

Revised document – *draft*: methods for materials qualification (actively being developed, subject to changes)

- Level 1: screening tests to determine compatibility without special design requirements for hydrogen service
  - Acceptable for aluminum alloys and austenitic stainless steels
- Level 2: safety factor multiplier method
  - Fatigue testing determine additional safety factor for hydrogen for wide range of cycle life
- Level 3: design qualification method
  - Allows other documented fatigue design methods (ASME BPVC VIII.3)

Definitions for CSA documents

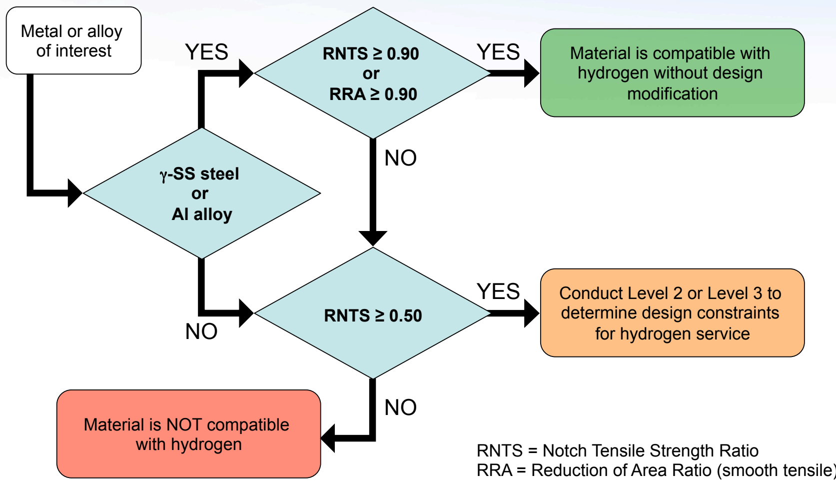
Hydrogen Suitability: *component evaluation*

- Generally used in the context of a component level test with gaseous hydrogen

Hydrogen Compatibility: *materials evaluation*
(commonly described as **Materials Compatibility**)

- Standardized materials testing to determine materials properties for design

CSA CHMC1: Logic Diagram



RNTS = Notch Tensile Strength Ratio
RRA = Reduction of Area Ratio (smooth tensile)

CSA CHMC1 Level 2: Safety Factor Multiplier Method

Notch Tensile Fatigue Tests

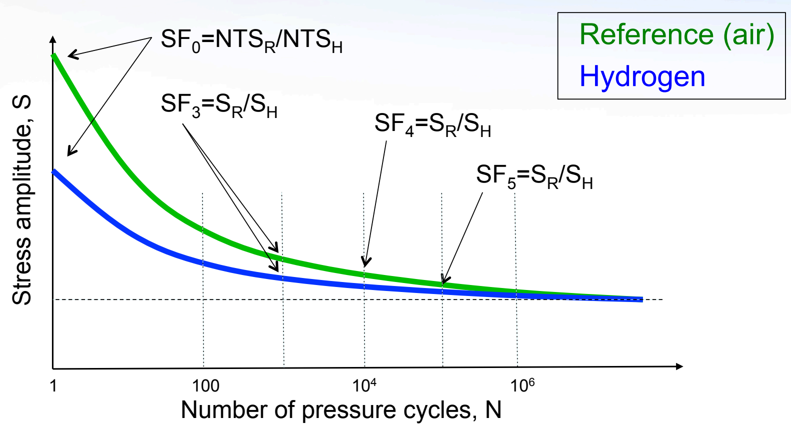
- Measure Wohler curves and determine stress amplitude (S) for number of cycles to failure (N) of 10^3, 10^4 and 10^5 in hydrogen and reference environments
  - $SF_3 = S3_R / S3_H$
  - $SF_4 = S4_R / S4_H$
  - $SF_5 = S5_R / S5_H$
  - $SF_0 = NTS_R / NTS_H$

S3 = stress amplitude for failure at N = 10^3
S4 = stress amplitude for failure at N = 10^4
S5 = stress amplitude for failure at N = 10^5
$_R$ = reference environment
$_H$ = hydrogen environment

- Hydrogen safety factor: $SF_H = \max(SF_0, SF_3, SF_4, SF_5)$

Safety factor for design ➔ $SF_{design} = SF_{component} \times SF_H$

Schematic representation of CHMC1 Level 2 approach



In this example: $SF_H = SF_0 > SF_3 > SF_4 > SF_5$

Summary of CSA CHMC1

- True material qualification test
  - Not specific to component or application
  - Specific to environment and material form
- Three levels of qualification
  - Method to determine if hydrogen effects are significant (Level 1)
  - Stress-based fatigue method to design for hydrogen (Level 2)
  - Other fatigue design methods allowed with appropriate data (Lvl 3)
- Qualification of materials from different sources requires a materials specification that defines the material
  - Compositional ranges
  - Mechanical properties, minimum and maximum values
  - Product form, processing route, etc
- Qualification of the materials specification requires testing of materials from 3 sources (or heats)
  - Additional testing is required when the materials specification changes

Summary of standards for qualifying materials for hydrogen service

- Several standards exist for hydrogen pressure vessels
  - *ISO 11114-4* and *ASME BPVC VIII.3 KD-10*
    - Significant limitations associated with the test methods in these documents
    - Limited scope
  - *CSA HPIT1* provides design definition approach
    - Based on development of experimental test method
    - Provides framework for considering stress-based fatigue analysis
- Several new standards are actively being developed
  - *ISO 15399* and new rules for materials in *SAE TIR J2579*
    - Limited scope
  - *CSA CHMC1* – new draft language
    - General rules for qualifying materials and specifications

Thank You for Your Attention

- The ongoing support from the US Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Program is gratefully acknowledged and supports the participation of Sandia National Laboratories in the development of codes and standards for hydrogen.
- Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000
- The expertise and wisdom of Kevin Nibur (chair of CSA CHMC1, Hy-Performance Materials Testing LLC) and Brian Somerday (Sandia National Laboratories) are also gratefully acknowledged.