



Joint Seminar for Hydrogen Safety and Study Group on Materials Testing and Qualification for Hydrogen Service

▪ Date : Thursday, July 21, 2022 ▪ Place : JW Marriott Las Vegas

▪ Sponsor : KRIS 한국표준과학연구원 Sandia National Laboratories

Study Group on Materials Testing and Qualification for Hydrogen Service

Marquis 1 - Thursday, July 21, 2022

JW Marriott Las Vegas Resort and Spa, Las Vegas

8:00am – 5pm (local time)

8:15	Opening Remarks and Introductions
Trends on carbon steels for hydrogen transmission	
	Chris San Marchi and Joe Ronevich , <i>Open Discussion: Current state of knowledge on hydrogen effects pipeline steels - property trends</i> • Mechanical variables: load ratio effects, rate effects • Environmental variables: pressure • Materials variables: grade and microstructure
10:30	Break
Standards for hydrogen transmission	
	Otto Jan Huising , <i>Open Discussion: Transferability of small-scale testing to full-scale pipelines</i>
	Brian Kagay , <i>Open Discussion: Gaps in standards for hydrogen transmission by pipeline</i>
	Joe Ronevich , <i>Open Discussion: Pressure cycle counting for hydrogen infrastructure</i>
12:00	Lunch (no host)
Environmental effects (impurities) and test methods	
	Rob Wheeler and Kevin Nibur , <i>Open Discussion: Effect of impurities on hydrogen-assisted fatigue and fracture</i>
	Kang Xu , <i>Open Discussion: Role of impurities on hydrogen embrittlement for stainless steels</i>
	Fabien Ebling , <i>Open Discussion: How can we increase the test capacity to meet the high demand for the upcoming H₂-economy? Is the hollow specimen technique a promising method?</i>
15:00	Break
Hydrogen effects in functional materials: high-strength materials and soft materials	
	Ramgo Thodla , <i>Open Discussion: Role of martensitic stainless steels, duplex, and high strength nickel based alloys in hydrogen storage technology</i>
	Rakish Shrestha , <i>Open Discussion: Hydrogen effects on MDPE/HDPE piping materials</i>
	Un Bong Baek , <i>Open Discussion: Performance certification of sealing materials of hydrogen refueling station storage tanks</i>
Free Discussion/Wrap-up	
17:00	Adjourn

Study Group on Materials Testing and Qualification for Hydrogen Service

July 21, 2022

Attendee list

Tim Reinhardt	U.S. DOE/FECM
Mark Richards	U.S. DOE/EE/HFTO
Yiyu Wang	Oak Ridge National Laboratory
Lisa Fring	Pacific Northwest National Laboratory
Milan Agnani	Sandia National Laboratories
Joe Ronevich	Sandia National Laboratories
Chris San Marchi	Sandia National Laboratories
Rakish Shrestha	Sandia National Laboratories
Rob Wheeler	Sandia National Laboratories
Tim Krentz	Savannah River National Laboratory
Anatasia Mullins	Savannah River National Laboratory
May Martin	NIST
Yingying Wei	Air Products
John Grimes	ASME
Bob Sims	Becht
Shane Finneran	DNV
TJ Prewitt	DNV
Brandon Rollins	DNV
David Baker	EMTEC
Greg Pioszak	EMTEC
Neeraj Thirumalai	EMTEC
Jeff Ellis	EWI
John Felbaum	FIBA
Claudio Lanzarini	FIBA
Cathy Shargay	Fluor
Kevin Nibur	HyPerformance Materials Testing
J. Ben Schaeffer	Lincoln Electric
Kang Xu	Linde
Simon Slater	Rosen
Fassett Hickey	Southwest Research Institute
Brian Somerday	Somerday Consulting
Sylvain Pillot	ArcelorMittal
Hubert Lejeune	CETIM
Fabien Ebling	Fraunhofer IWM
Otto Jan Huising	N.V. Nederlandse Gasunie
Irene Garcia	Repsol
Bostjan Bezensek	Shell
Brian Kagay	MPA Stuttgart
Paolo Bortot	Tenaris
Mihaela Cristea	Tenaris
Tommi Seppanen	VTT (Finland)
Jussi Solin	VTT (Finland)
Hyung-Seop Shin	Andong University
Brandon Hance	Hyundai Steel
Hyeong-Suh Kim	Hyundai Steel
Myeong-Gyu Seo	Hyundai Steel
Un-Bong Baek	Korea Research Institute of Science and Standards (KRISS)
Nak-Kwan Chung	Korea Research Institute of Science and Standards (KRISS)
Sang Koo Jeon	Korea Research Institute of Science and Standards (KRISS)
Seung Hoon Nahm	Korea Research Institute of Science and Standards (KRISS)
Jaeyeong Park	Korea Research Institute of Science and Standards (KRISS)
Hee Soo Yun	Korea Research Institute of Science and Standards (KRISS)
Hisao Matsunaga	Kyushu University

Carbon steels for hydrogen service

Chris San Marchi and Joe Ronevich
Sandia National Laboratories (Livermore CA)

Study Group on Materials
Testing and Qualification for
Hydrogen Service

21 July 2022



Based on SAND2022-8369 PE

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

Subsurface Hydrogen Storage: AGU Fall Meeting

AGU FALL MEETING

Chicago, IL & Online Everywhere
12–16 December 2022

SCIENCE LEADS THE FUTURE



- Home
- Sign In
- Search
- View Guidelines
- View Sessions/Submit an Abstract
- Index Terms
- Co-Organized Sessions
- Co-sponsored Sessions
- Convener Index
- Need Assistance?
- About
- Technical Support

H100 - Subsurface Hydrogen Storage: Opportunities and Challenges for Enabling a Low Carbon Future

[Submit an Abstract to this Session](#)

Hydrogen as an energy carrier has promise to enable the transition from our current dependence on fossil fuels towards a sustainable low-carbon future. Hydrogen is attractive because it can be generated using existing and emergent technologies. While industrial development is needed, leveraging existing infrastructure would accelerate the transition. However, the risks associated with hydrogen in our energy system are inadequately understood. Questions remain about underground hydrogen storage (UHS) feasibility, which is a necessary element of a hydrogen economy. Pressing challenges are assessing the technical practicability of storing vast amounts of hydrogen in existing or geo-engineered subsurface reservoirs, determining if natural accumulations exist, developing technologies for subsurface hydrogen monitoring, and informing policies and regulations to enable transition towards hydrogen as an energy carrier. This session seeks to include broad perspectives on UHS to enable discourse and advance our understanding for how hydrogen may be used to enable a low carbon future.

Primary Convener

[Nicolas J Huerta](#)

Pacific Northwest National Laboratory

Conveners

[Djuna M Gulliver](#)

NETL-DOE

[Megan M Smith](#)

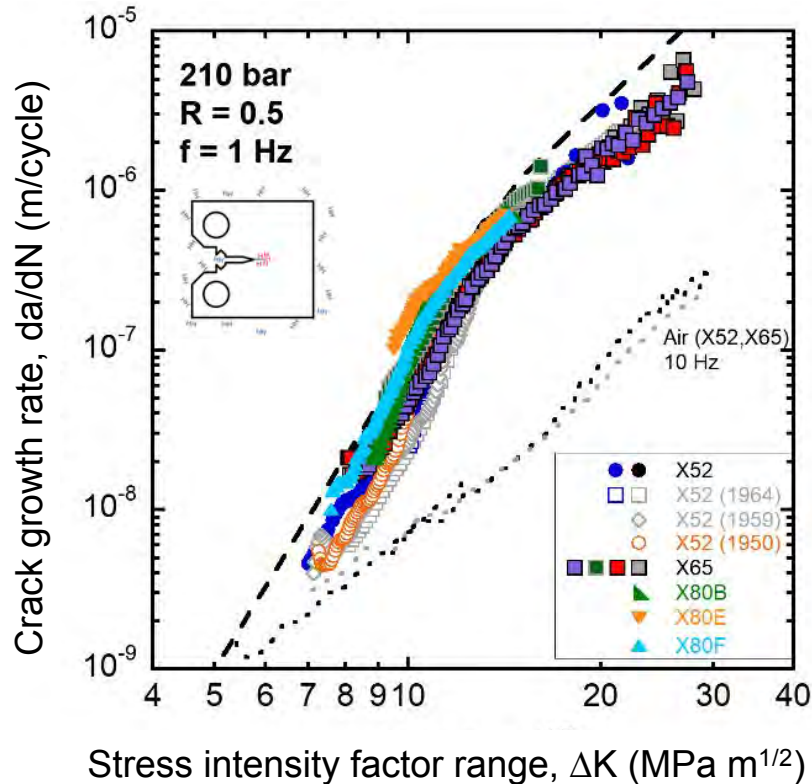
Lawrence Livermore Nat'l Lab

[Donald Conley](#)

Sandia National Laboratory

<https://agu.confex.com/agu/fm22/prelim.cgi/Session/161241>

Fatigue crack growth rates in gaseous hydrogen (GH2) do not vary much for API grade pipeline steels

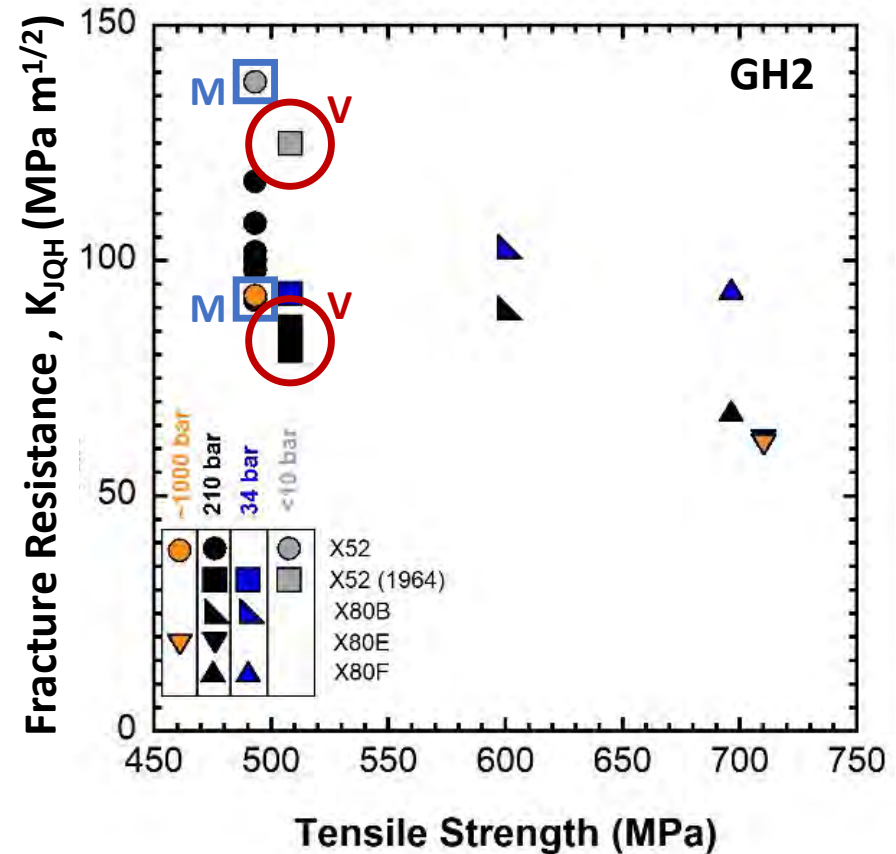
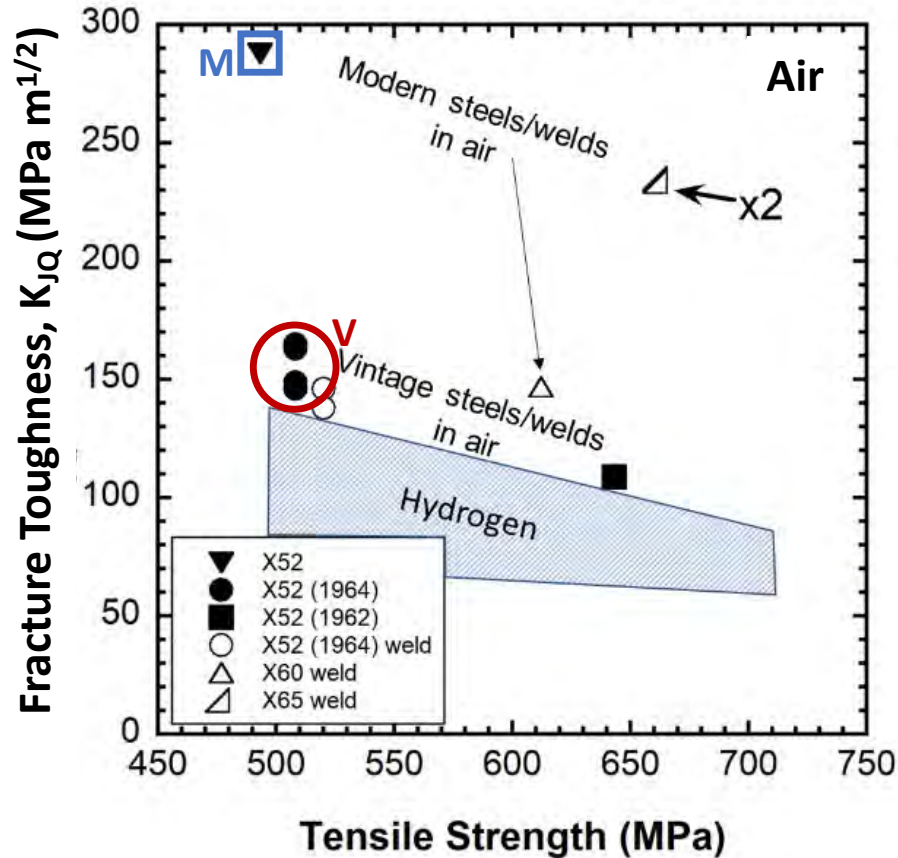


A wide variety of steel microstructures display nominally the same fatigue response in high-pressure GH2

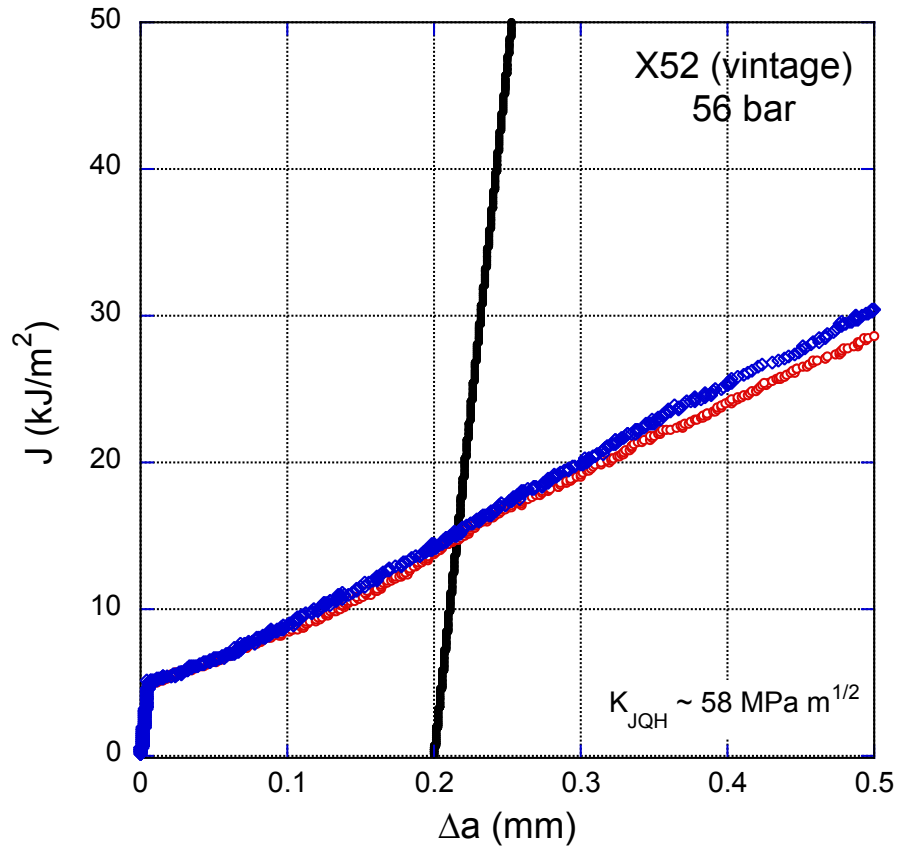
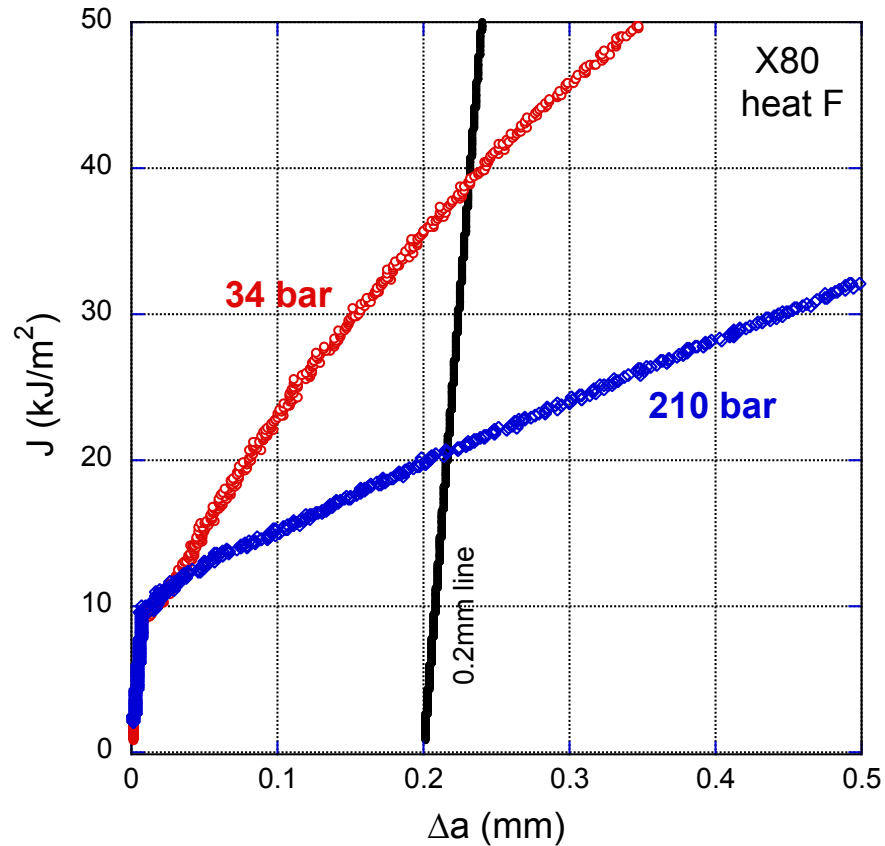
Material	Microstructure	S_y (MPa)
X52	PF + pearlite	334-490
X60	PF	434
X65	banded ferrite + pearlite	478
X80 (B)	90% PF + 10% AF (coarse)	565
X80 (E)	AF (fine)	593
X80 (F)	70% AF + 30% PF	552
X100	Bainite + PF	732

Data generated at both SNL and NIST-Boulder, contained in various publications

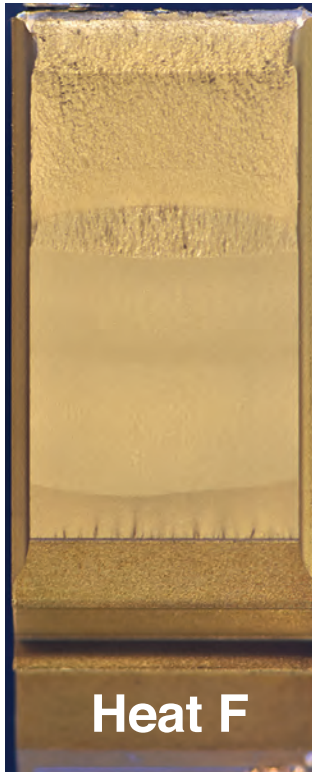
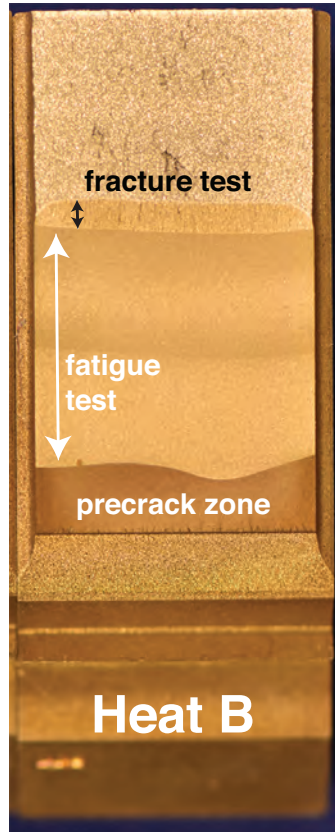
Hydrogen 'equalizes' the fracture behavior



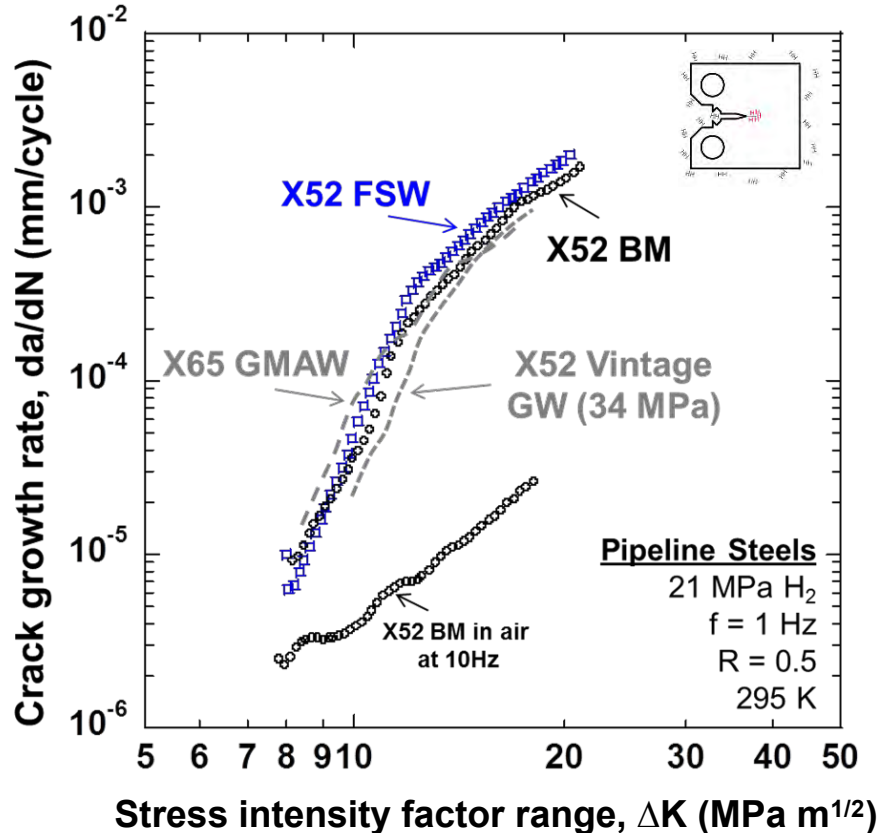
J-R curves of line pipe steels



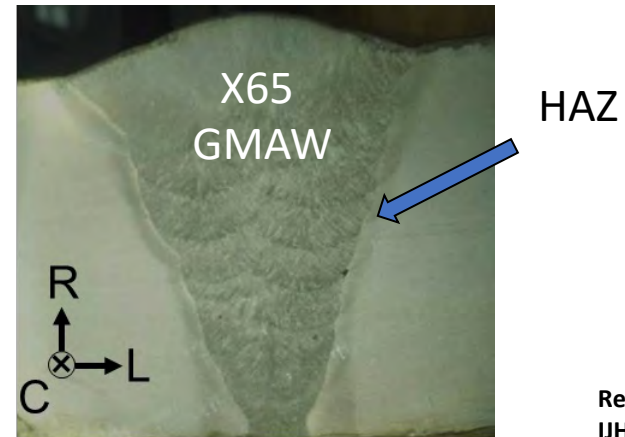
Fracture surfaces



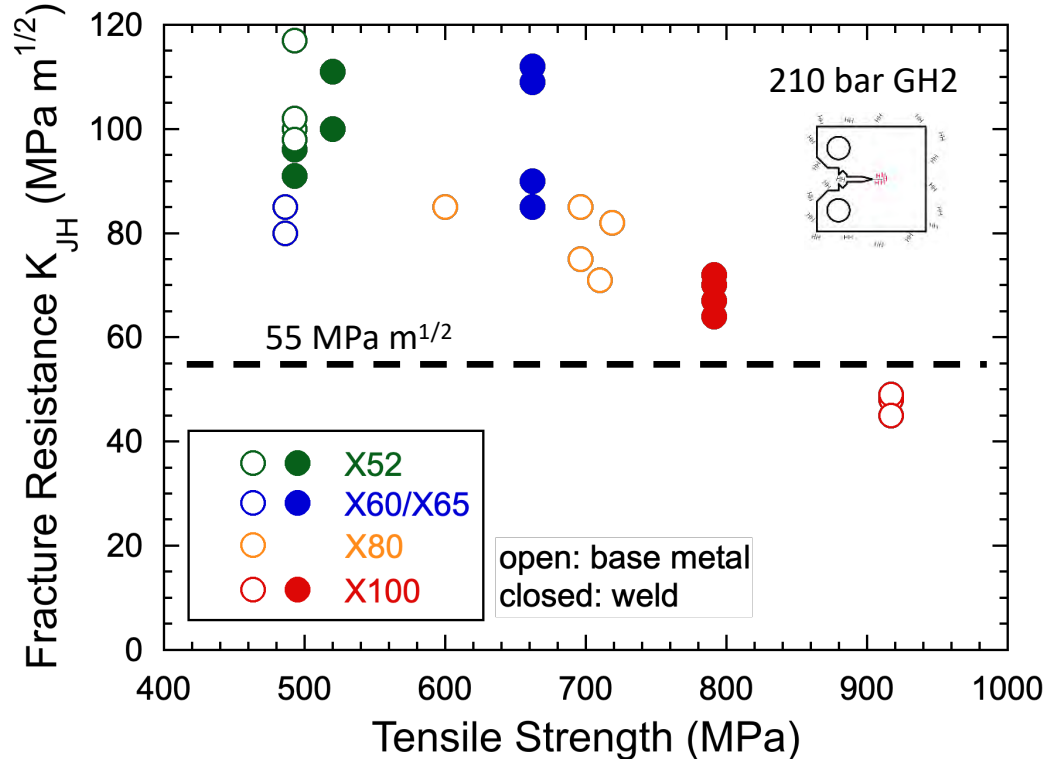
Welds and base materials behave similarly in GH2



- To first order and if residual stress is considered, welds show similar fatigue and fracture behavior in gaseous H_2 as the base metals
- Similar trends have been observed for a variety of weld processes

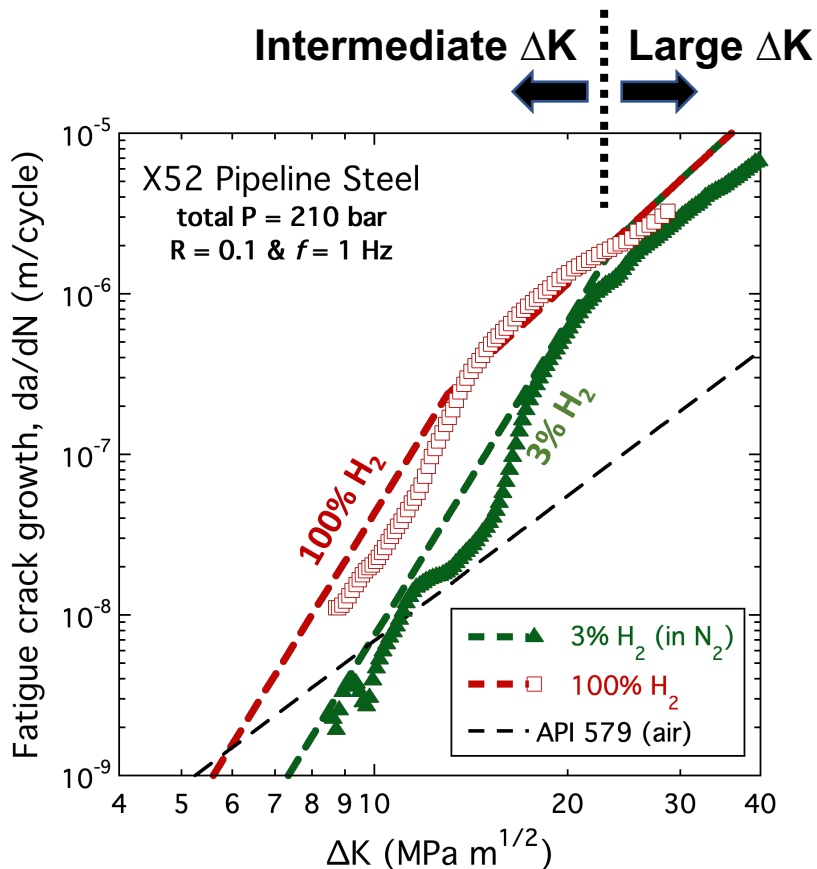


Fracture resistance trends for welds and base metals are similar in GH2



- Fracture resistance trends are similar for welds and base metals
- One should consider the influence of residual stresses on the lab tests
- The hardness is an important factor

Low hydrogen pressure = large effect on fatigue



- Large ΔK

FCG is independent of pressure

- Fatigue crack growth rate in 3% H₂ is the same as in 100% H₂

- Intermediate ΔK

FCG is dependent on hydrogen partial pressure

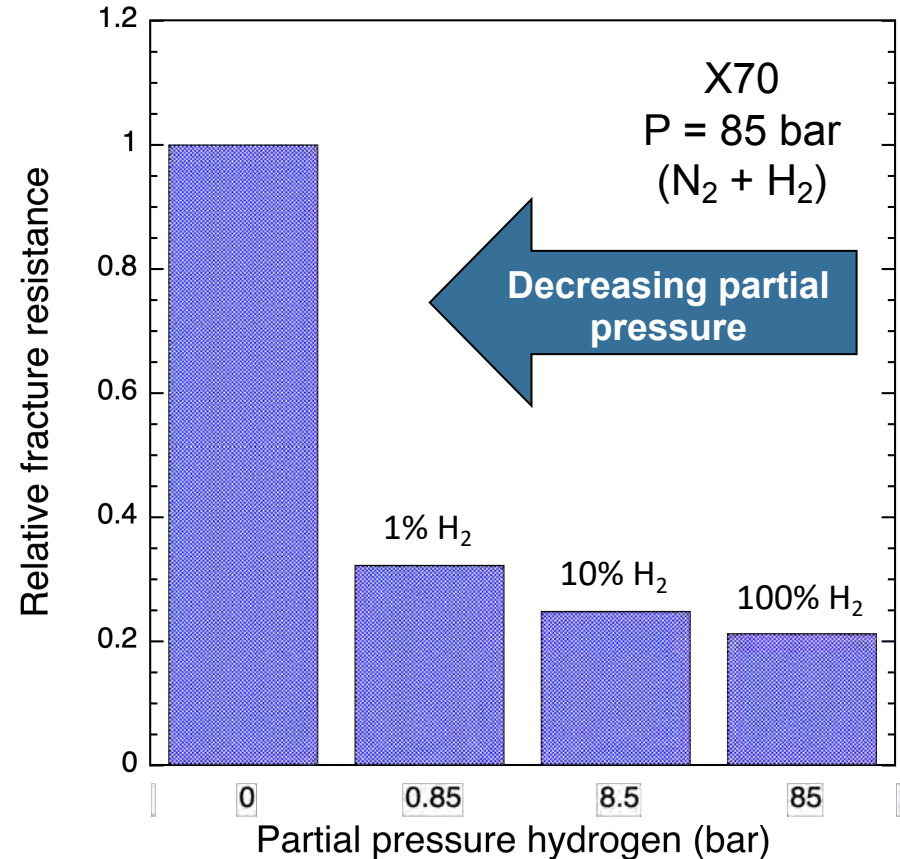
- Fatigue crack growth rate is slower in 3% H₂ than in 100% H₂

Dashed lines represent design curves that can be used to bound fatigue crack growth rates

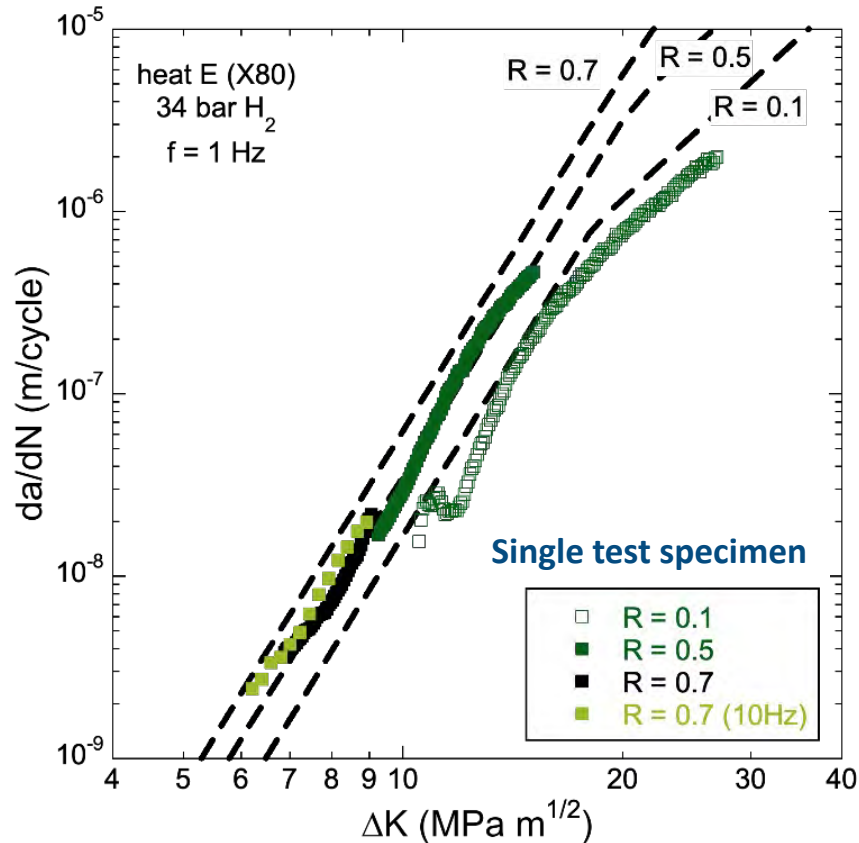
Low hydrogen pressure = large effect on fracture

- Measurements of fracture resistance in gaseous mixtures of H_2 and N_2 show substantial effects of H_2
- 1% H_2 is only modestly different than 100% H_2
- Fracture resistance does not scale linearly with pressure/fugacity

<1 bar of H_2 substantially reduces fracture resistance



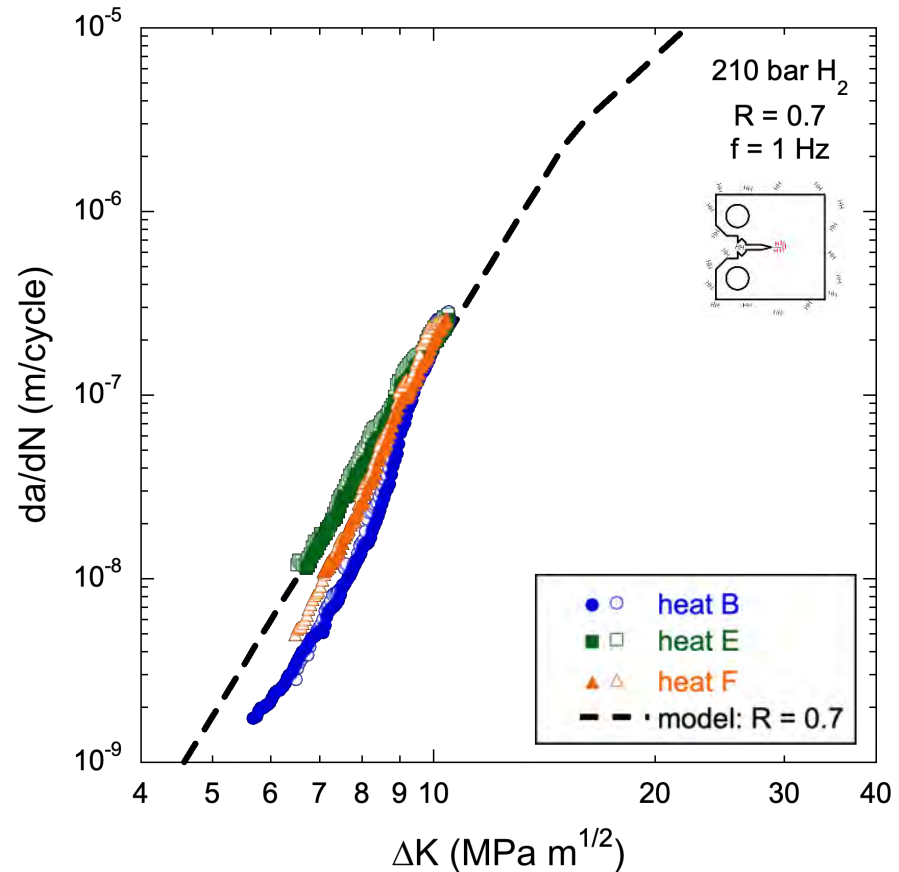
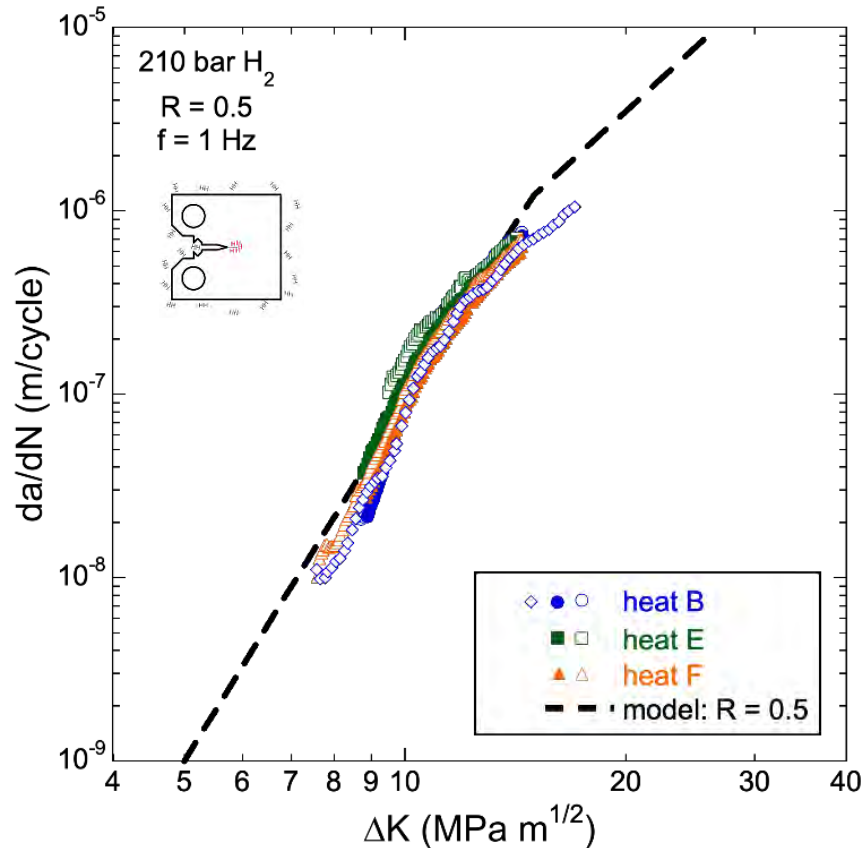
Fatigue crack growth in GH2 depends on the load ratio, R



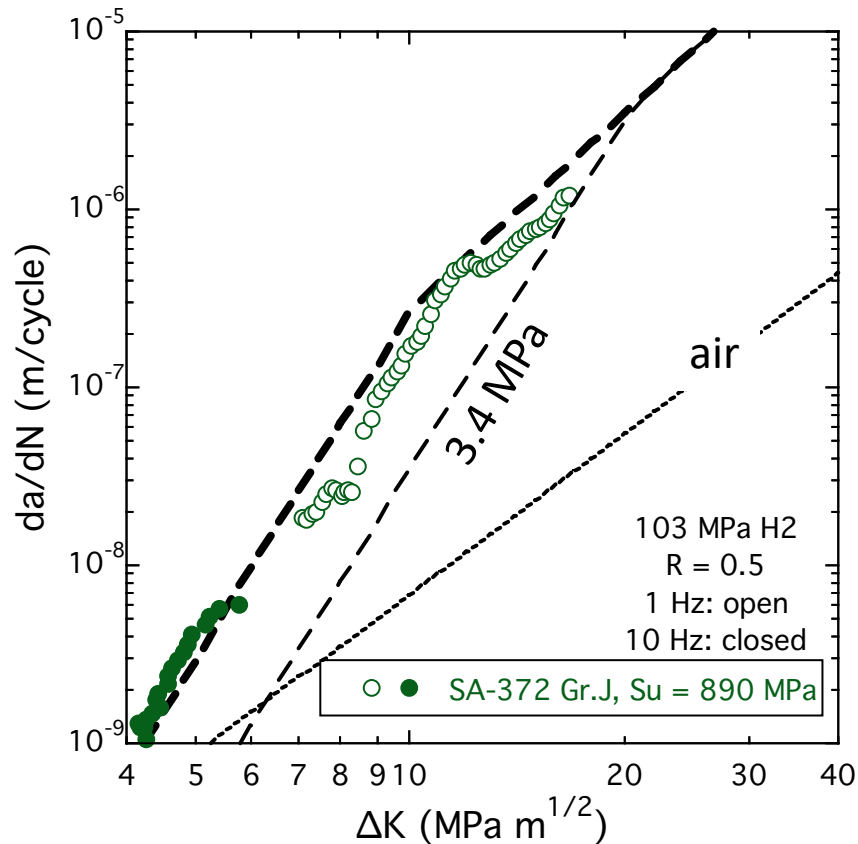
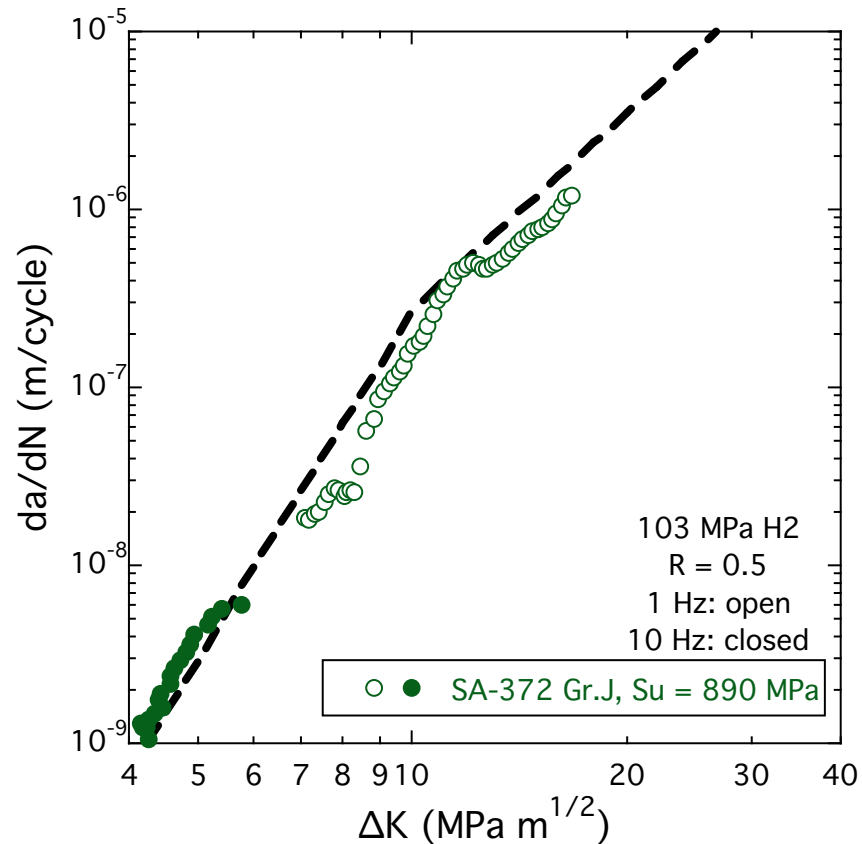
- In this test, three load ratios were evaluated
 - including the influence of frequency for $R = 0.7$
- Unlike tests in air and general recommendations in the codes, R has an effect on da/dN in hydrogen
- Higher frequency does not necessarily affect da/dN for low ΔK

Fatigue crack growth of X80: effect of R

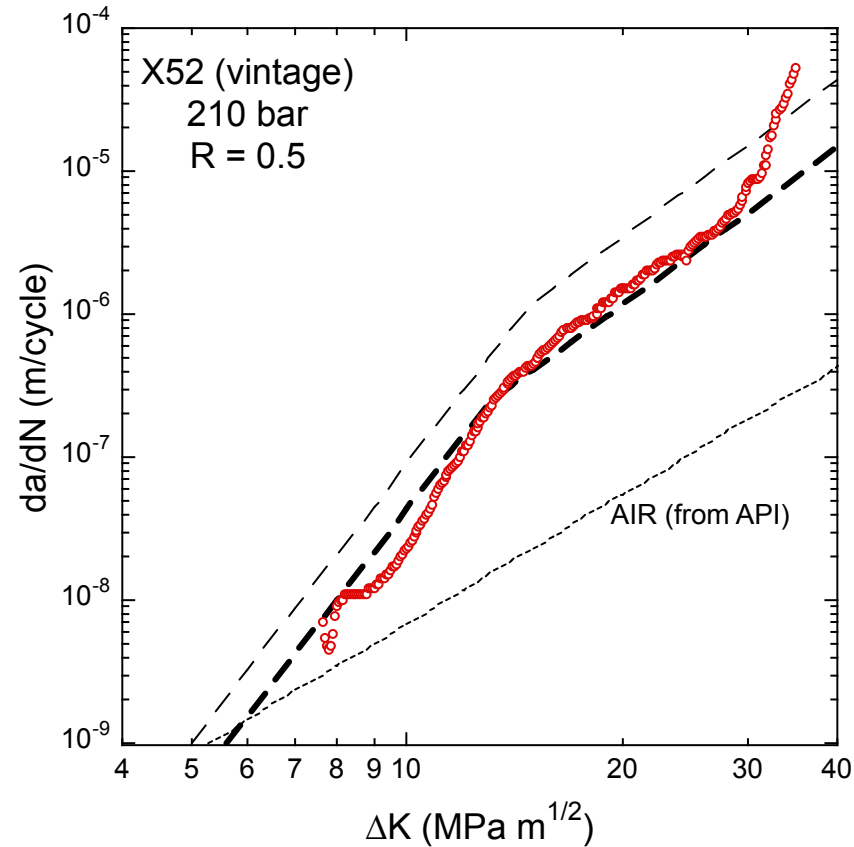
Ref.: San Marchi et al, PVP2022-84757



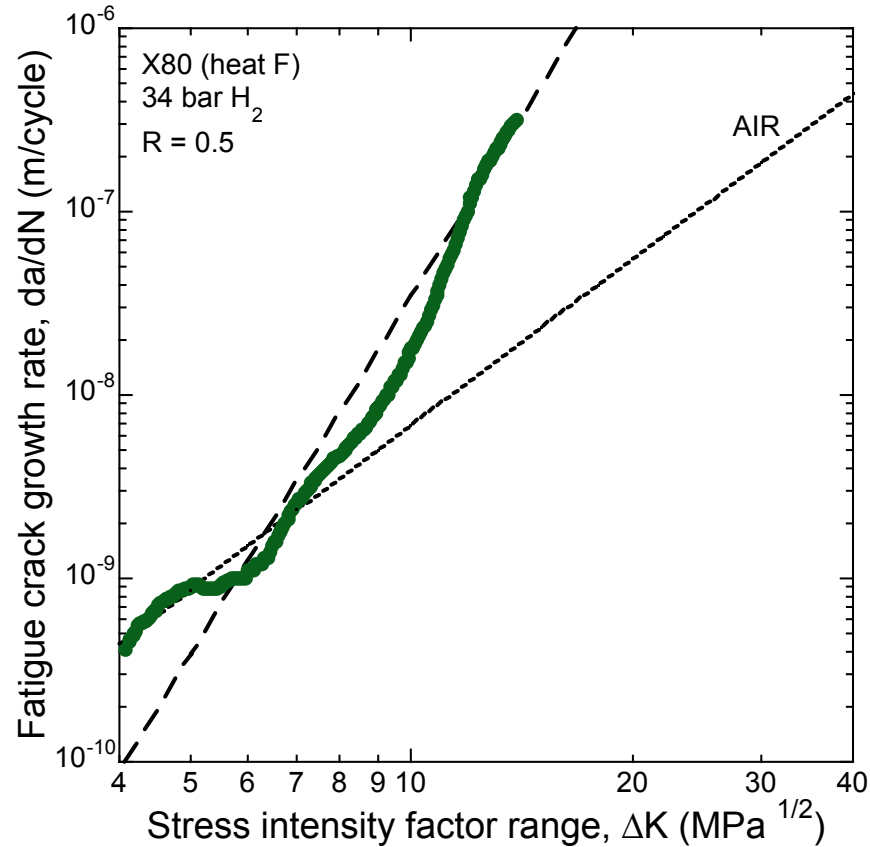
Fatigue at low rates



Fatigue crack growth

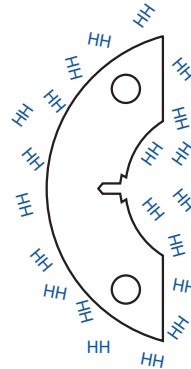


Fatigue at low rates

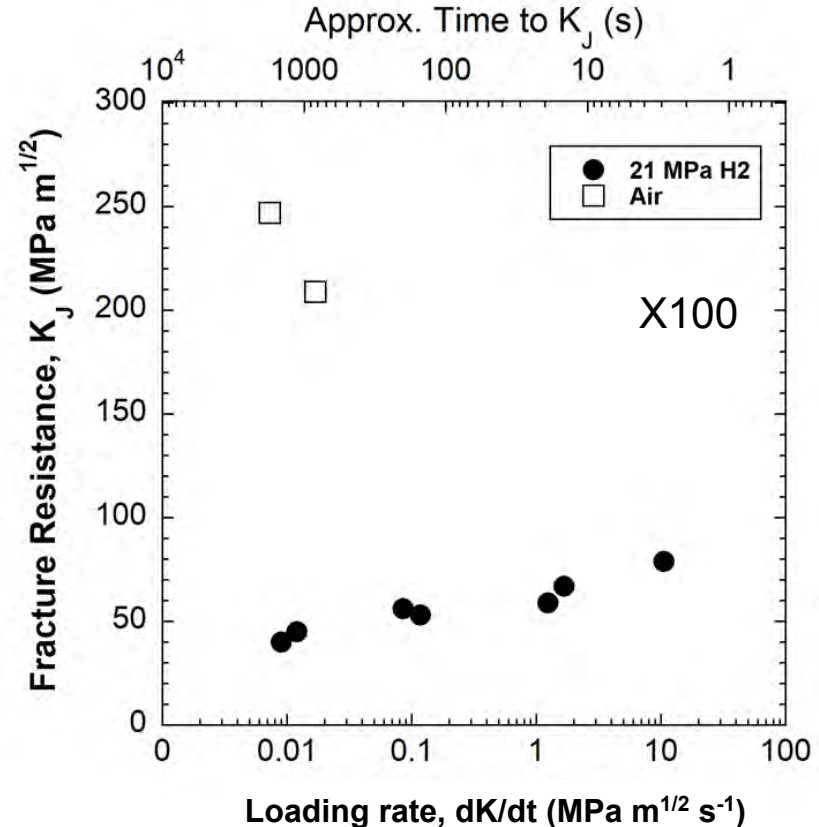


GH2 affects fracture at high deformation rate

- ASTM E1820 elastic-plastic fracture test (J-R curve) using arc geometry
- Estimate of strain rate:
 - $d\varepsilon/dt \sim 1$ EQPS/s for
 - $dK/dt \sim 10 \text{ MPa m}^{1/2} \text{ s}^{-1}$



Effect of H_2 on fracture at high rate is more significant than commonly assumed



Summary of *materials* behavior in GH2 (established)

- How does gaseous hydrogen affect fatigue and fracture of pipeline steels?
 - *Fatigue is accelerated by >10x*
 - *Fracture resistance is reduced by >50%*
- Does the magnitude of pressure affect fatigue and fracture and is there a threshold below which hydrogen effects can be ignored?
 - *Fatigue and fracture are affected by the magnitude of pressure*
 - *Even small amounts of hydrogen have large effects*
- What materials variables influence the fatigue and fracture in GH2?
 - *Materials pedigree has surprisingly little effect on FCG*
 - *Hydrogen-assisted fracture is influenced by strength*

Summary of *materials* behavior in GH2 (emerging)

- Are welds more susceptible to hydrogen than base metal?
 - *Welds (of comparable strength) have similar performance to base metals when residual stresses are accounted for*
- Do high deformation rates preclude influence of GH2 on fracture?
 - *Large reduction in fracture resistance is maintained at high fracture rates*
- Can oxygen (and other impurities) mitigate the effects of GH2?
 - *Under some circumstances in accelerated testing, O₂ can mitigate effects of GH2*
 - *In long-term testing (i.e., real-world conditions), O₂ appears less effective at mitigating effects of GH2*

Design curve formulation

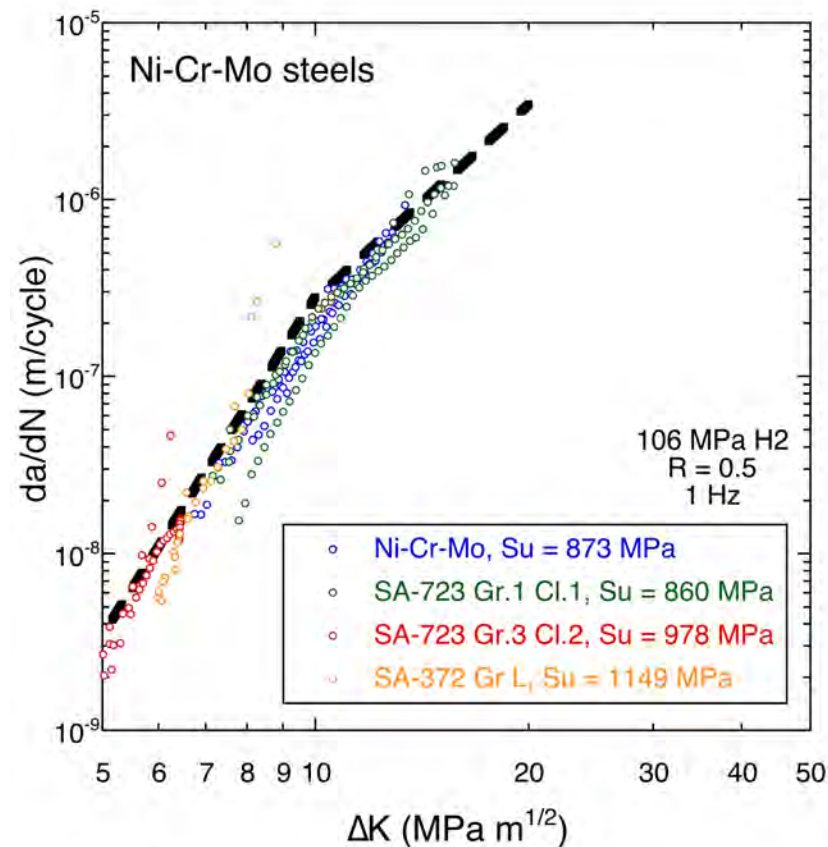
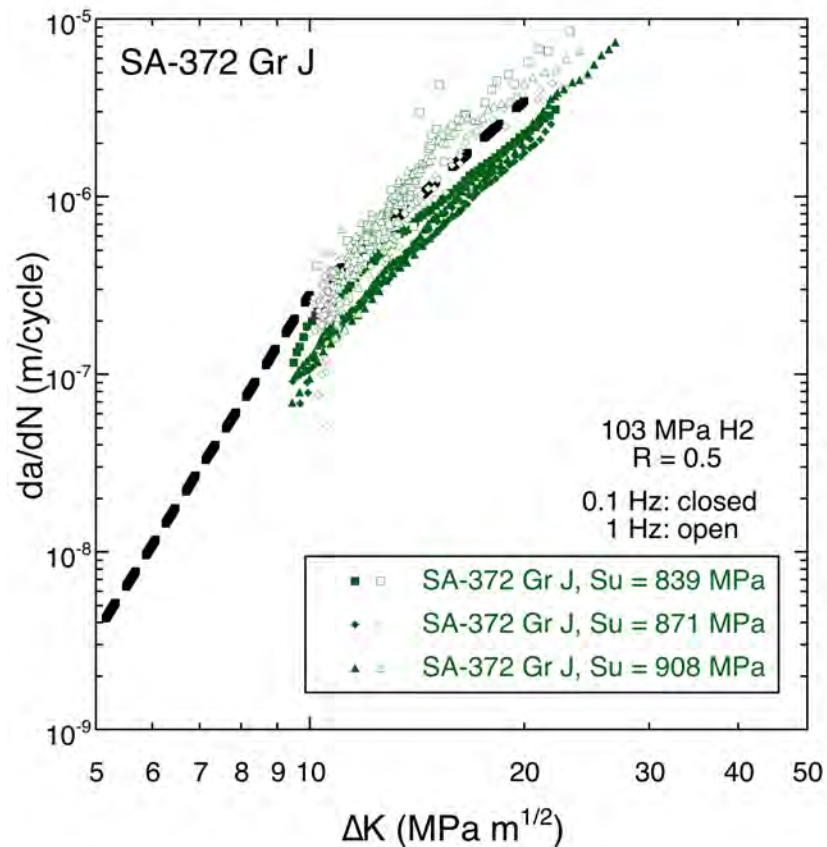
Are there simple relationships that capture fatigue crack growth rates in hydrogen and account for load ratio (R)?

- Assume two independent regimes, each with a relationship of the form: $\frac{da}{dN} = C_R \Delta K^m$ where C_R is function of R and m is a constant
- For each ΔK regime and R , determine C_R and m from power law curve fits
 - Determine best m value and adjust C_R to capture data
- Assume a functional form for $C_R = f(R)$ that can be applied in both regimes and for all R

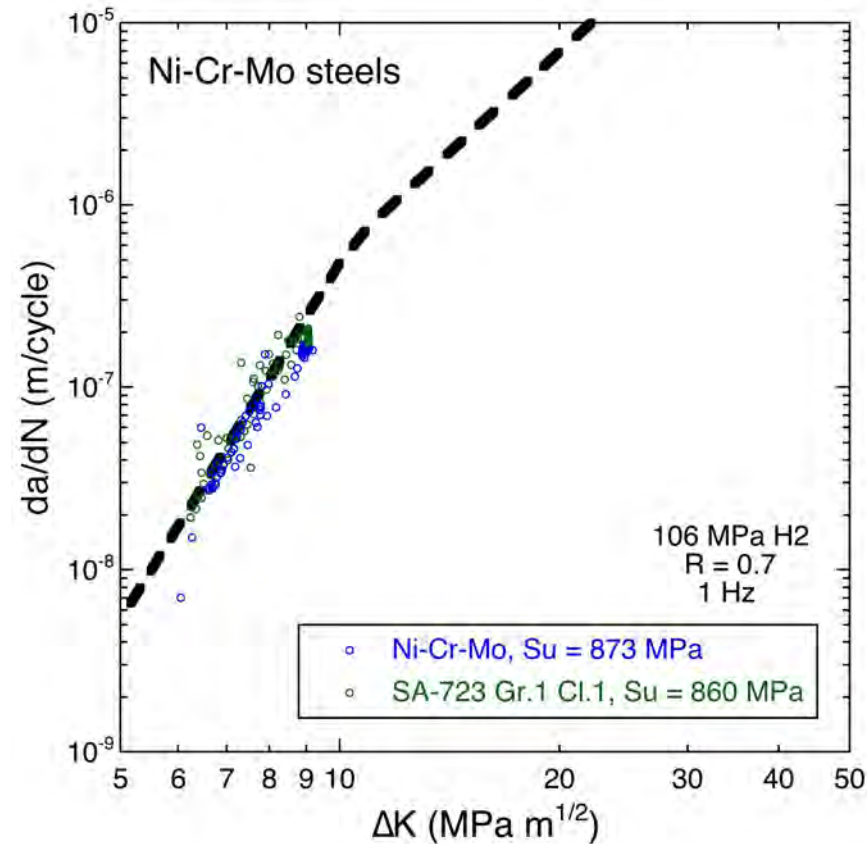
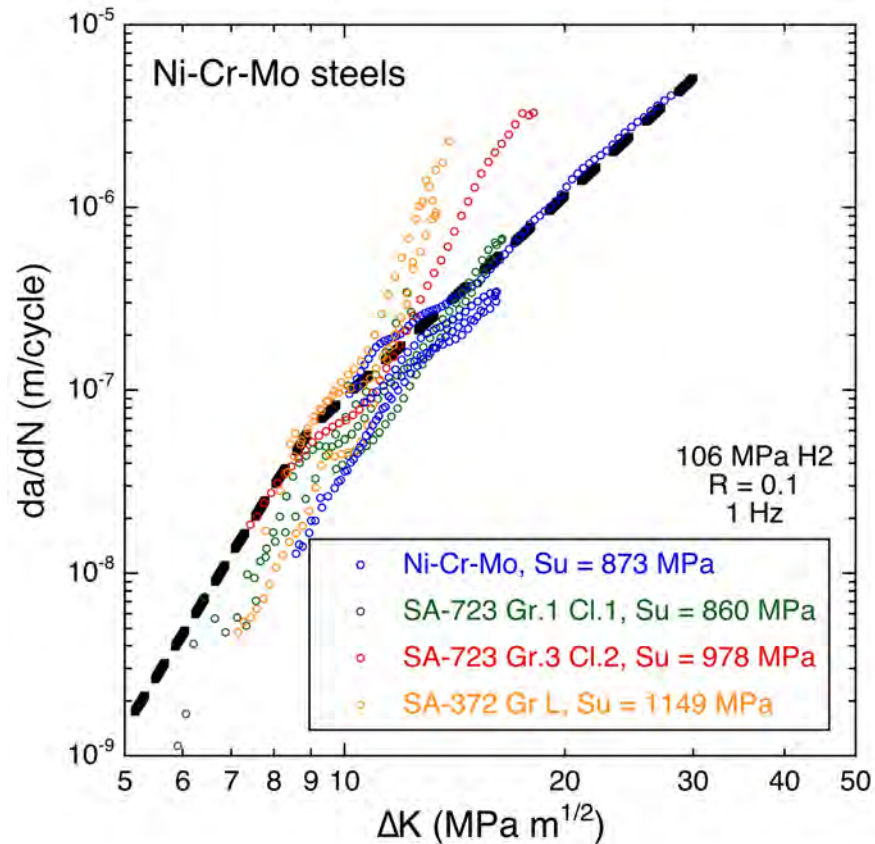
$$\frac{da}{dN} = C \left[\frac{1 + C_H R}{1 - R} \right] \Delta K^m$$

	da/dN_{low}	da/dN_{high}
C (m/cycle)	3.5×10^{-14}	1.5×10^{-11}
m	6.5	3.66
C_H	0.4286	2.00

Fatigue crack growth rates of pressure vessel steels



Fatigue crack growth rates of pressure vessel steels



Design curves

High ΔK : $\frac{da}{dN} = 1.5 \times 10^{-11} \left[\frac{1 + 2R}{1 - R} \right] \Delta K^{3.66}$

Pressure “independent”

Low ΔK : $\frac{da}{dN} = 3.5 \times 10^{-14} \left[\frac{1 + 0.4286R}{1 - R} \right] \Delta K^{6.5}$

$$\frac{da}{dN} = 3.5 \times 10^{-14} \left[\frac{1 + 0.4286R}{1 - R} \right] \Delta K^{6.5} \left(\frac{f}{f_{ref}} \right)^{1/2}$$

f is the thermodynamic pressure or fugacity

Pressure term

High ΔK : $\frac{da}{dN} = 1.5 \times 10^{-11} \left[\frac{1 + 2R}{1 - R} \right] \Delta K^{3.66}$

Low ΔK : $\frac{da}{dN} = 7.6 \times 10^{-16} \left[\frac{1 + 0.4286R}{1 - R} \right] \Delta K^{6.5} f^{1/2}$

- **Units are important!**

- *fugacity* is in units of < bar >
- da/dN : < m/cycle >
- ΔK : < MPa m^{1/2} >

Background: thermodynamics (origin of fugacity)

H in metals: $\mu^H = \mu_o^H + RT \ln c_H$

Gas phase: $\mu^{HH} = \mu_o^{HH} + RT \ln f_{HH}$

At equilibrium: $\frac{1}{2}H_2 \leftrightarrow [H]$

$$\frac{1}{2}\mu^{HH} = \mu^H$$

$$\frac{\frac{1}{2}\mu_o^{HH} - \mu_o^H}{RT} = \ln \frac{c_H}{(f_{HH})^{1/2}}$$

General form of
Sieverts' Law

$$K = \frac{c_H}{(f_{HH})^{1/2}}$$

Equation of state for H₂
Abel-Noble formulation

$$V_m = \frac{RT}{P_{HH}} + b$$

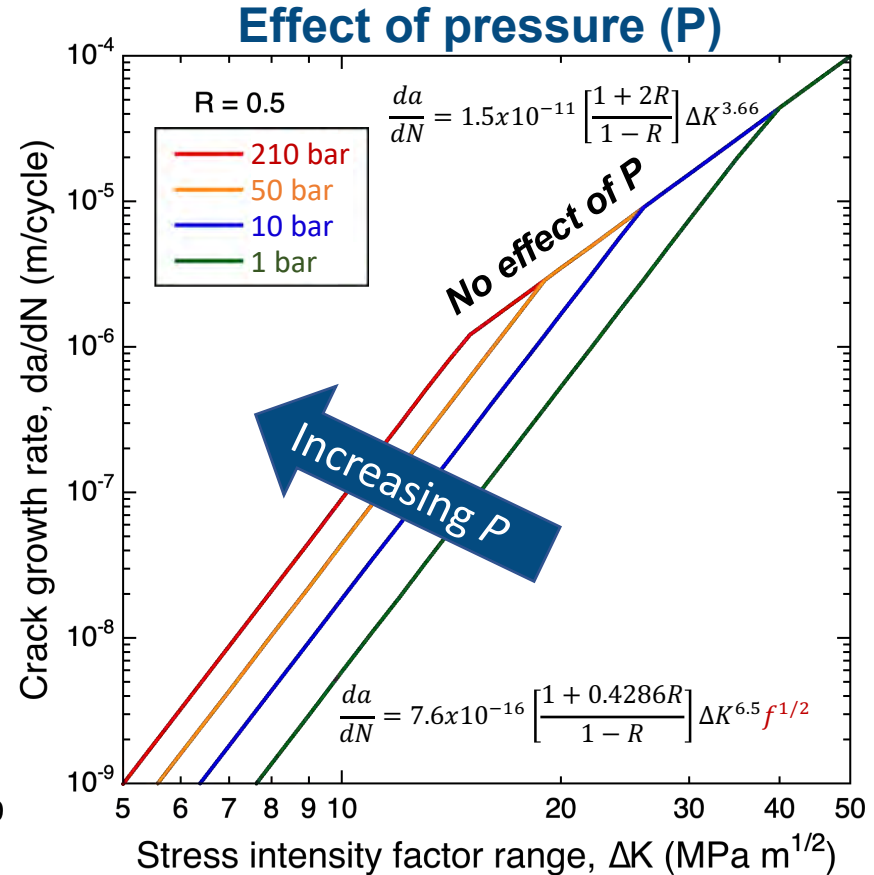
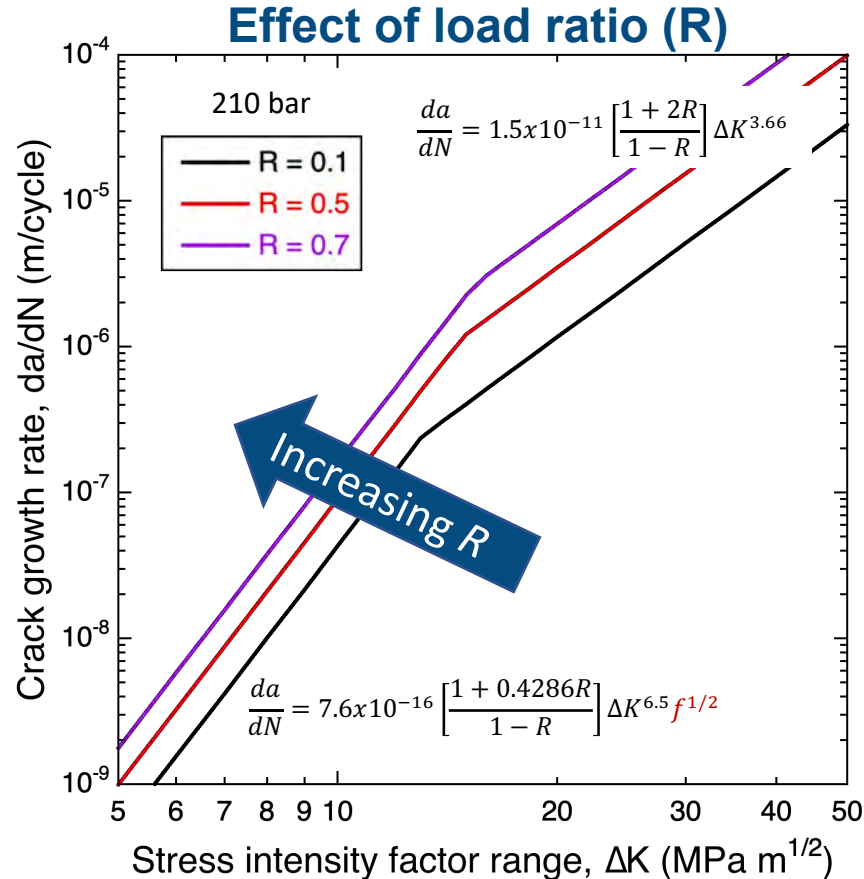
Pure gaseous H₂:

$$f_{HH} = P_{HH} \exp\left(\frac{bP_{HH}}{RT}\right)$$

Blended H₂:

$$f_{HH} = P_{HH} \exp\left(\frac{bP_{total}}{RT}\right)$$

Design curves enable upper bound prediction for fatigue crack growth as function of loading and pressure



Application of materials behavior to structural integrity analysis (simple example)

- **Material:**

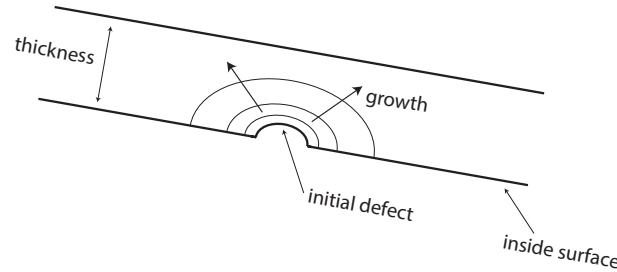
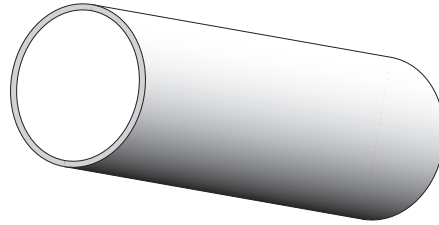
- API grade X52 pipe
- OD = 324 mm
- t = 12.7 mm

- **Environment:**

- Pressure = 200 bar
- GH2 = 20%, 100%

- **Stress:**

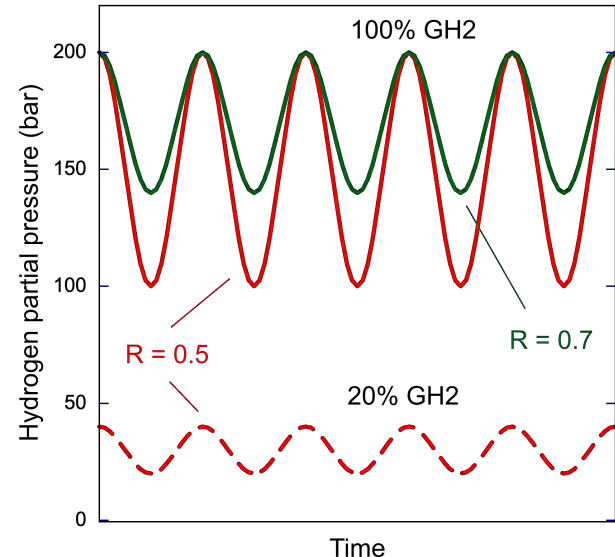
- Hoop stress: 68% SMYS
- Cyclic pressure: $R = P_{\min}/P_{\max} = 0.5, 0.7$
- Flaw
 - depth: 25% of wall thickness ($a/t = 0.25$)
 - length: 40 mm ($2c = 40\text{mm}$) – propagate with constant aspect ratio



Reminders

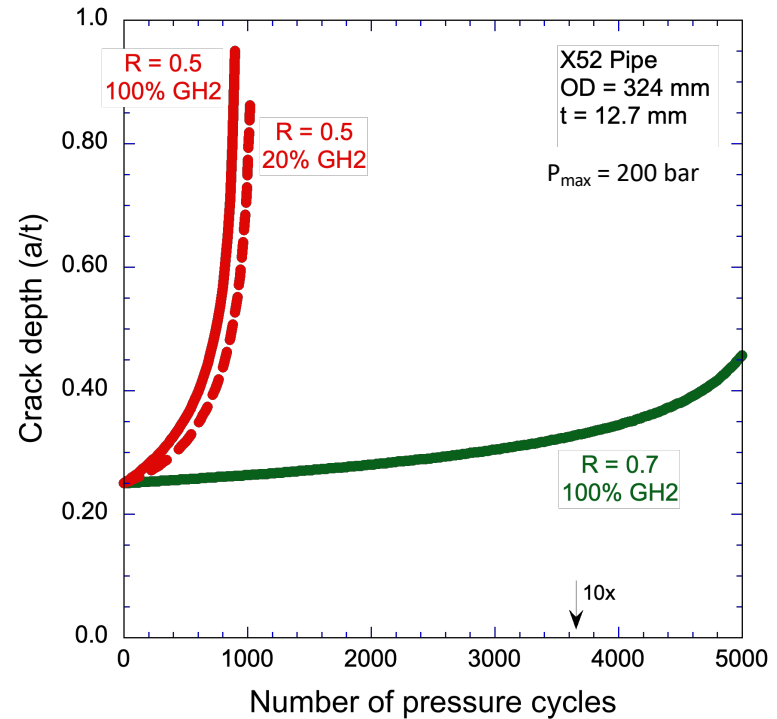
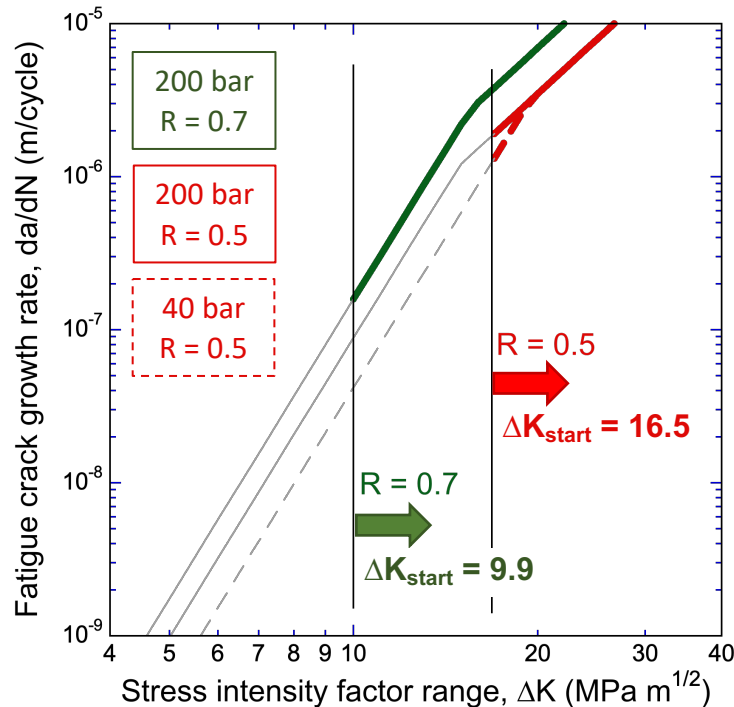
$$K \rightarrow \sigma \rightarrow P_{total}$$

$$\frac{f}{P_{HH}} \rightarrow P_{total}$$



Analysis of transmission pipe structure (simple example)

- Initial crack/ flaw: 40 x 3.2 mm
 - At start: $K_{\max} = 33 \text{ MPa m}^{1/2}$



The blending ratio has no effect on fatigue response (for $R = 0.5$)

Gaps in Standards for Hydrogen Transmission by Pipeline

Study Group on Materials Testing and Qualification for Hydrogen Service (PVP 2022)

Brian Kagay

MPA University of Stuttgart

Brian.Kagay@mpa.uni-stuttgart.de

+49 711 685 63784

SyWeST H2: Ongoing project to evaluate performance and suitability of pipeline steels and welds in H₂ based on ASME B31.12 standard

Collaboration between OGE, DVGW, and MPA University of Stuttgart

Example materials:

	Yield strength [MPa]	Tensile strength [MPa]	Elongation at break [%]	Impact energy [J]	Year produced
X70	510	650	19.5	50	1974
L485	530	680	26.0	258	2009

- Base material
- Weld metal (SG)
- Heat affected zone (HAZ)

Sampling from a pipe with a spiral seam



Additional materials being examined:

X56.7	WSTE420
St35	P355 NH
L485	GJS 400
X42	P355 NL1
X80	P460 QL1
St60.7	StE 360.7
L360 NE	St53.7
P460 NH	L360 NB
L415	

Assessing effects of:

- Gas pressure
- R-ratio
- Welds/microstructure
- Strength/hardness

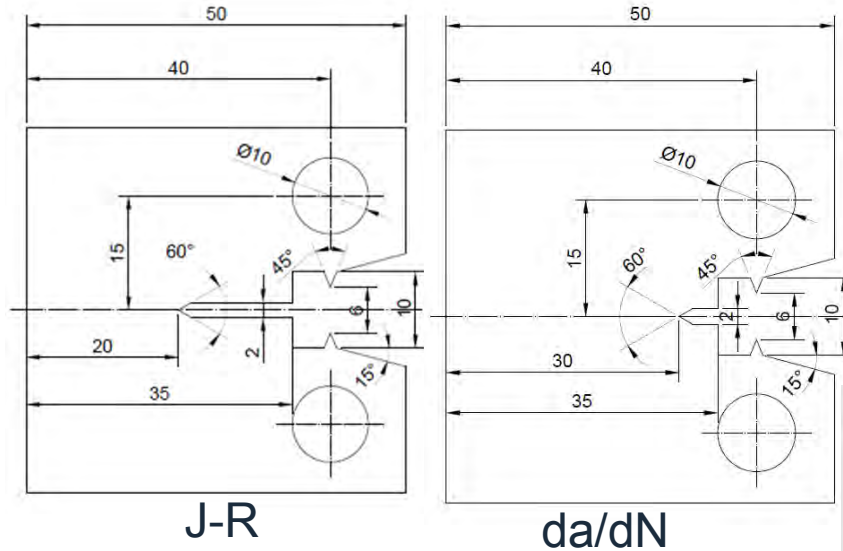
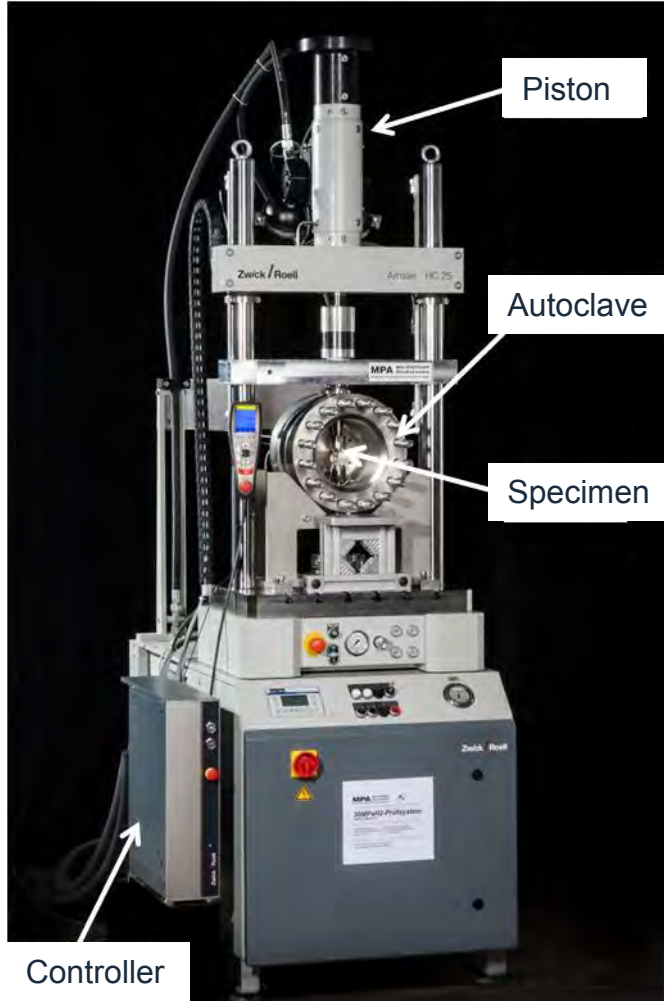
Results to this point previously published in:

Engel, Marewski, Schnotz, Silcher, Steiner, Zickler, “Bruchmechanische Prüfungen von Werkstoffen für Gasleitungen zur Bewertung der Wasserstofftauglichkeit: Erste Ergebnisse,” Pipelintech, 2020

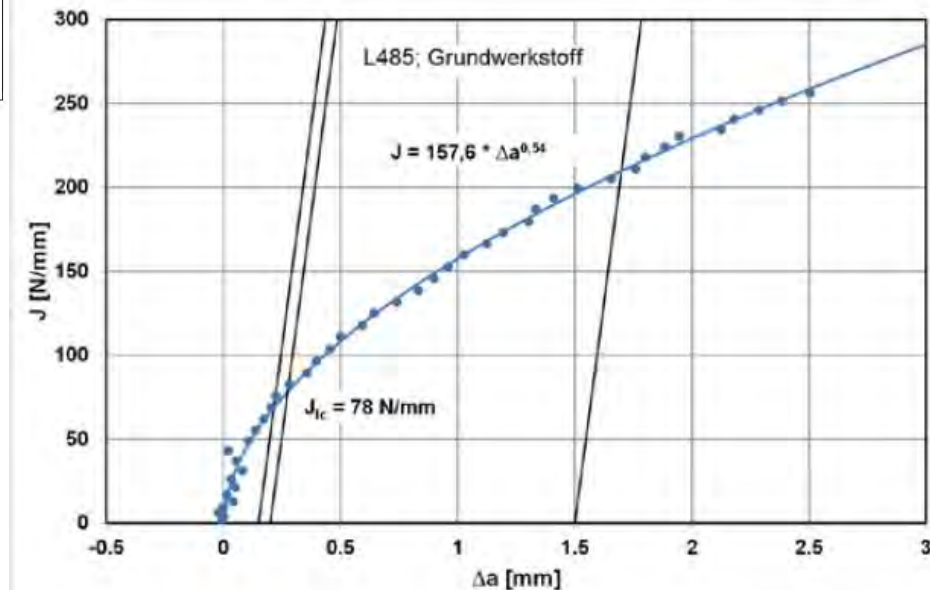
Schwarz, Silcher, Marewski, Steiner, “Bruchmechanische Bewertung von Gasleitungswerkstoffen unter Wasserstoffatmosphäre,” DBI Fachforum Energiespeicher, 2021

Günther, Marewski, Steiner, “Effect of hydrogen on the cracking behavior of pipeline steels,” 2022

Investigation of the elastic-plastic fracture resistance and the cyclic crack growth rate (da/dN) in hydrogen gas



Sample Geometry:
Compact tension, C(T)20 contour



Two options for material qualification from ASME B31.12

Option A: Prescriptive design method. Includes a performance derating factor (H_f) based on hydrogen pressure and tensile strength

Option B: Performance-based design method. Requires fracture mechanics-based testing to qualify a material

Option B can allow for higher design pressures because the H_f derating factor is not included

Option B Requirements:

Fracture toughness K_{IH} in hydrogen $\geq 55 \text{ MPa}\cdot\text{m}^{1/2}$

Additional conditions:

Phosphorus content $\leq 0.015 \text{ wt. \%}$

Tensile strength of the base material $\leq 758 \text{ MPa}$

Tensile strength of weld metal $\leq 758 \text{ MPa}$

SMYS $\leq 550 \text{ MPa}$

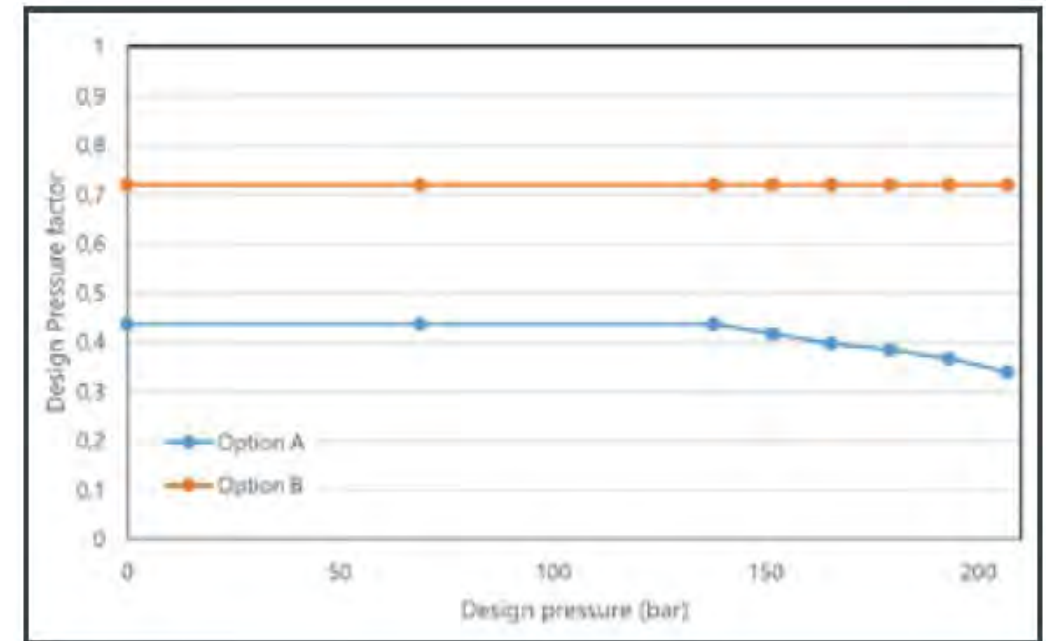


Figure 1: Design pressure factors for X60M for Option B vs Option A in areas characterized as Location Class 1, Division 2

Tazedakis, et al., "Qualification of high strength pipelines..."
Pipeline Technology Journal

Problem: Linear elastic fracture toughness testing is required, but pipeline materials are too ductile to meet LEFM requirements

B31.12 requires fracture toughness testing according to KD-10 of ASME Sec VIII Div 3 and ASTM E1681

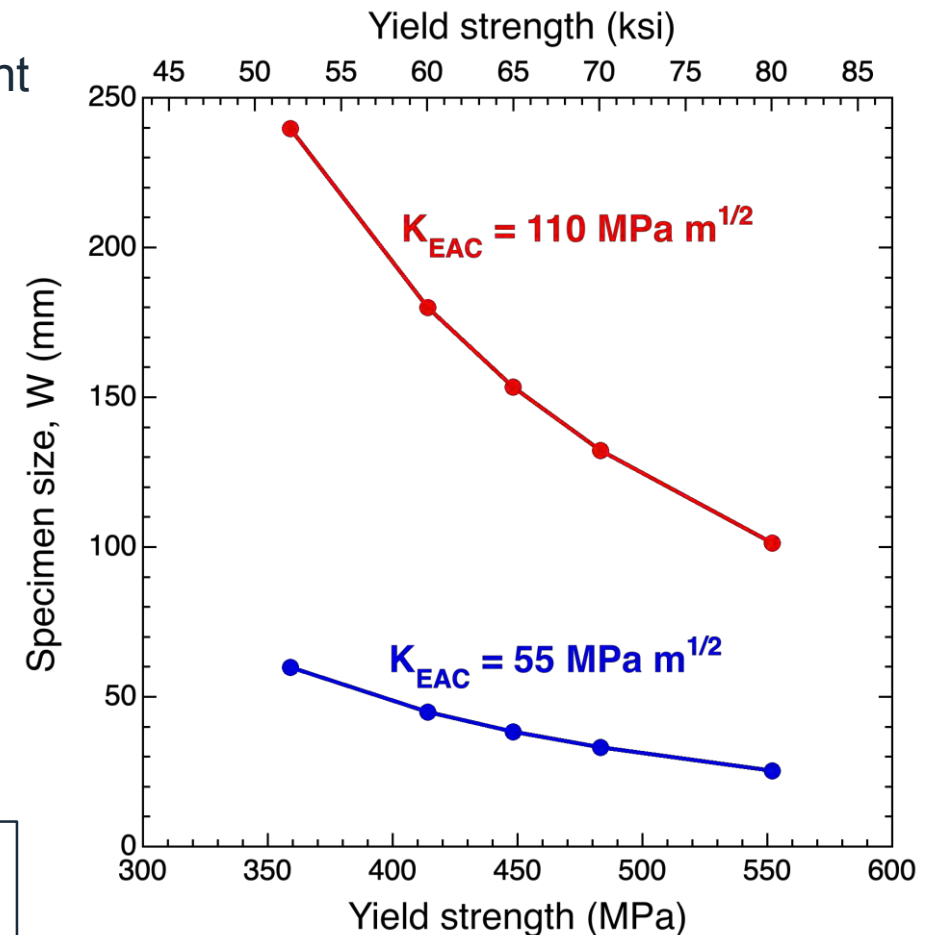
Pre-cracked specimen held at constant load or constant displacement in hydrogen gas for 1000 h and then checked for crack growth

What are the requirements for ASTM E1681 fracture testing?

- ASTM E1681 para. 9.3 – *validity check*
 - Para. 9.3.1: $(W - a) > 2.5 \left(\frac{K_{IEAC}}{\sigma_{YS}} \right)^2$
 - for plane strain
 - Para. 9.3.2 $(W - a) > \frac{4}{\pi} \left(\frac{K_{EAC}}{\sigma_{YS}} \right)^2$
 - for linear elasticity

Pipeline steels don't meet the requirements for linear elastic fracture mechanics according to ASTM E1681

Criteria for linear elasticity

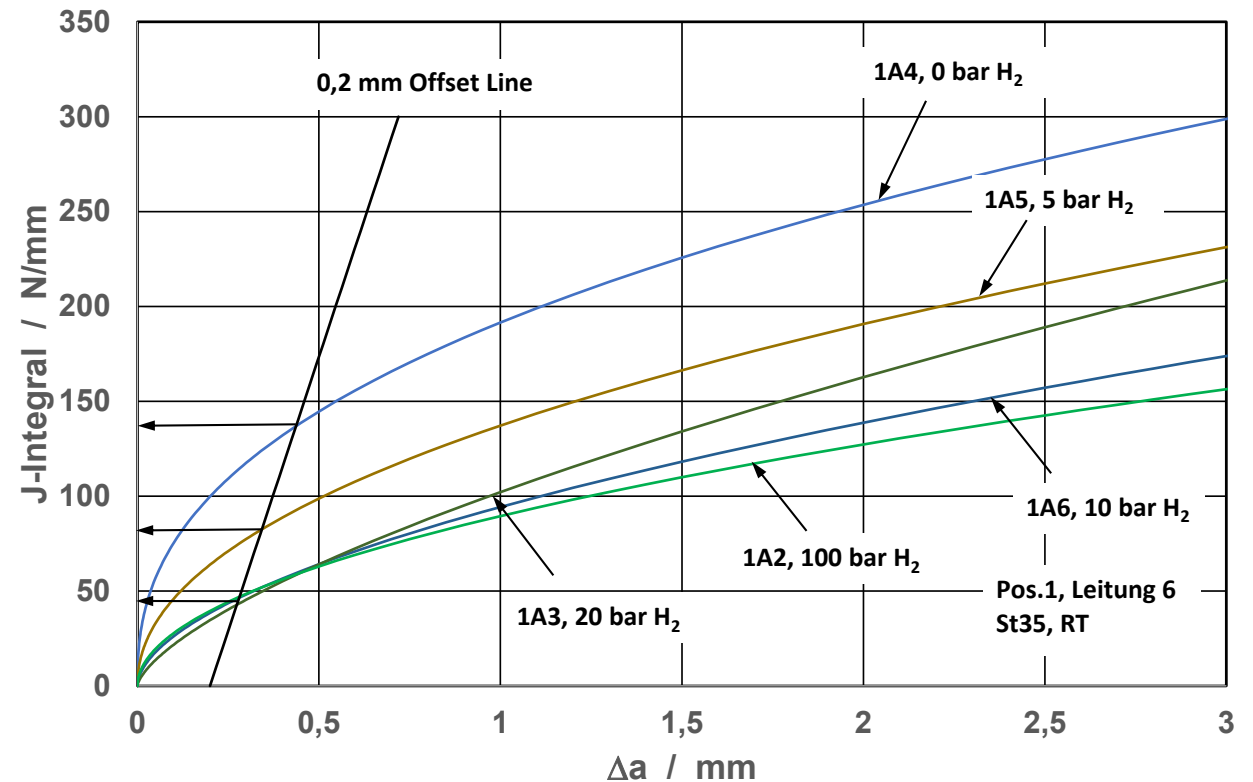
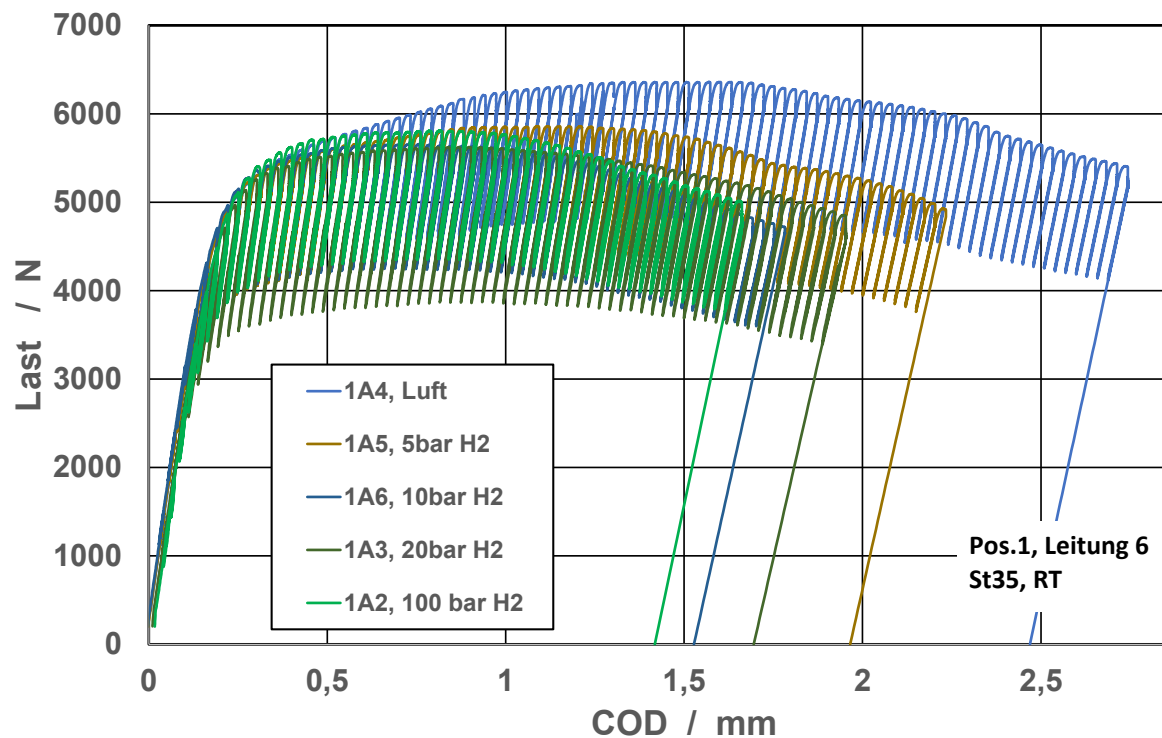


Assessing fracture toughness using elastic-plastic fracture mechanics according to ASTM E-1820 in ongoing project

Evaluating effects of hydrogen pressure on fracture toughness

Even low hydrogen pressures reduce the fracture toughness of the material

Minimum fracture toughness according to ASME 31.12 is always achieved

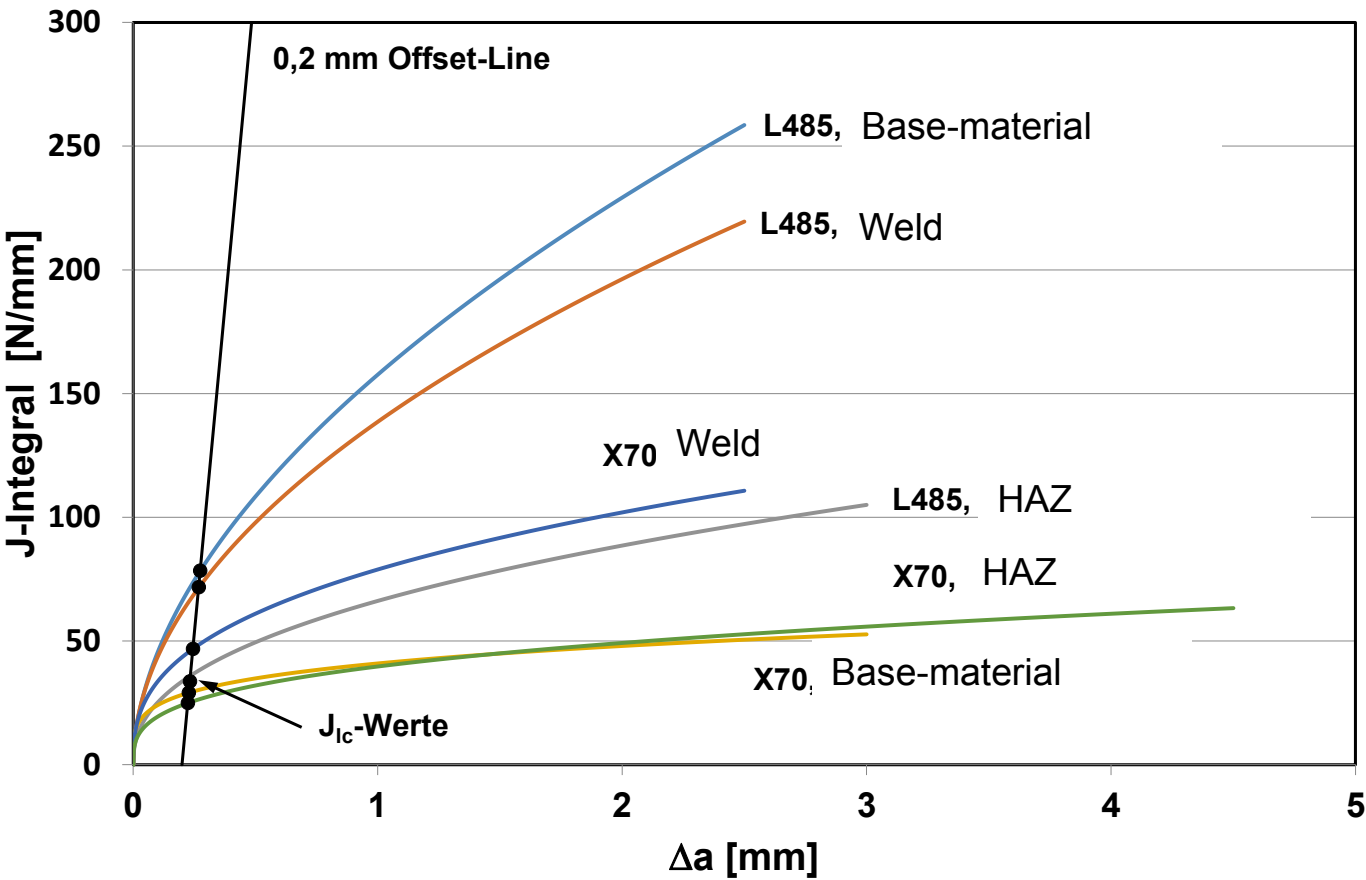


Higher fracture toughness of L485 in comparison to X70, but all base materials, welds, and heat affected zones meet B31.12 requirement ($K_{JIH} > 55 \text{ MPa}\cdot\text{m}^{1/2}$)

Table 3: Fracture toughness determined for materials X70 and L485 under hydrogen

material	base material KJlc [MPa√m]	middle of Weld KJlc [MPa√m]	heat affected zone KJlc [MPa√m]
X70	82	104	77
L485	135	129	92

H2, 100 bar, Room temperature



Design for fatigue according to B31.12

B31.12 provides a fatigue design curve that can be used in lieu of fatigue crack growth rate testing:

limit curve:
$$\frac{da}{dN} = a1\Delta K^{b1} + [(a2\Delta K^{b2})^{-1} + (a3\Delta K^{b3})^{-1}]^{-1}$$

Design curve created as a fit to upper bound of data from several steels

Limitations of fatigue curve:

- Doesn't account for different gas pressures
- Doesn't account for different R-ratios
- Only includes one fit despite presence of two regions and a „knee“

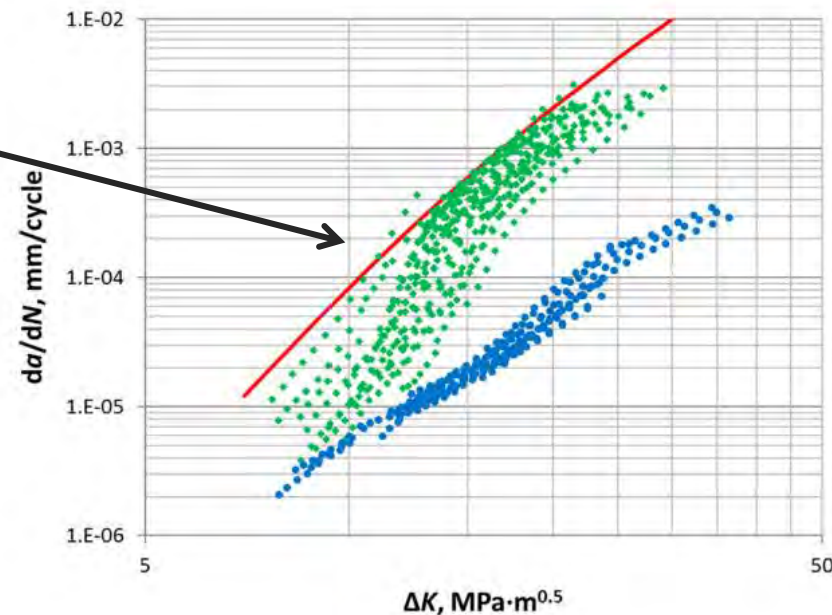


Fig. 19 Fatigue crack growth rate data in hydrogen gas for all four steels, shown as diamonds, with corresponding data in air shown as squares, and the fit of the upper bound shown as a line

coeff .	value
a1	4.0812E-09
b1	3.2106
a2	4.0862E-11
b2	6.4822
a3	4.8810E-08
b3	3.6147

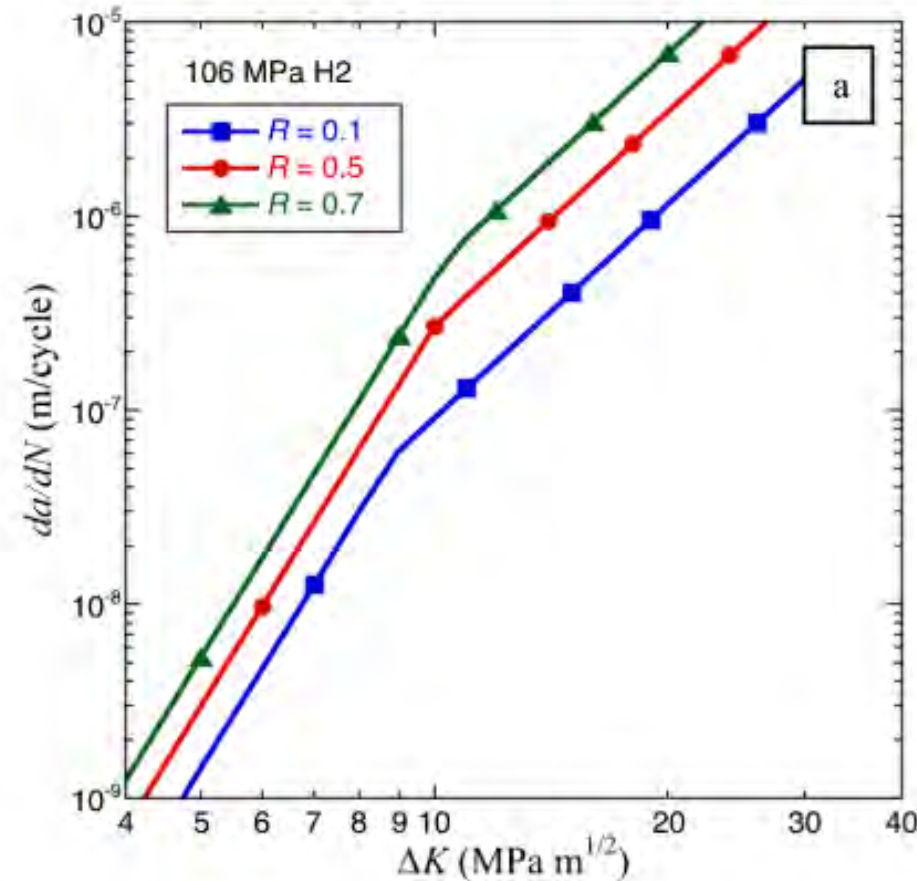
Slifka, et al., "Journal of Pressure Vessel Technology, 2018

Fatigue design curve in code case 2938 for pressure vessel steels in high pressure hydrogen gas

Master curve in code case 2938 includes two regions and accounts for effect of R-ratio

A term for accounting for pressure dependence has also been suggested:

$$da/dN = C \left[\frac{1+C_H R}{1-R} \right] \Delta K^m \left(\frac{f}{f_{ref}} \right)^{1/2}$$

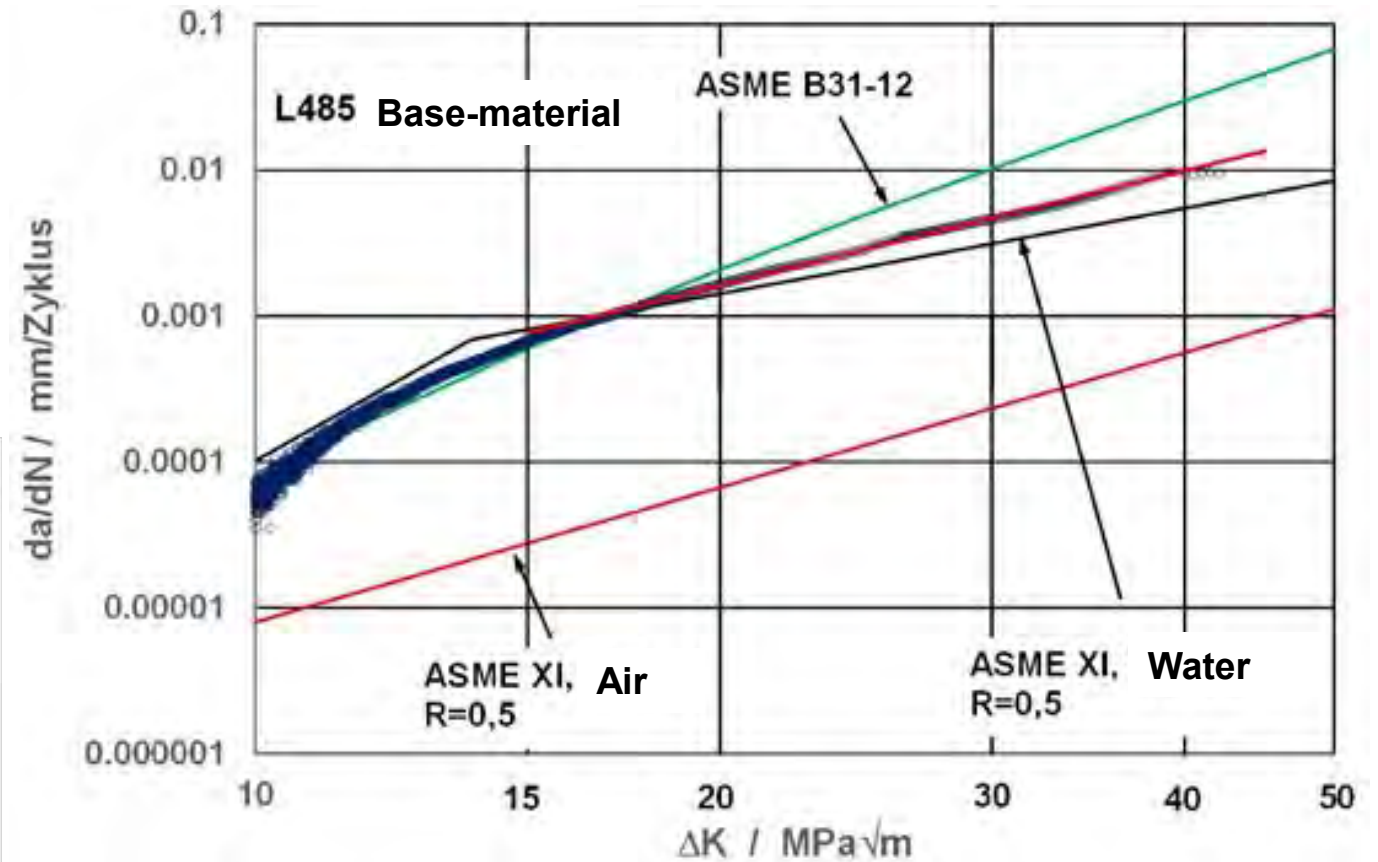
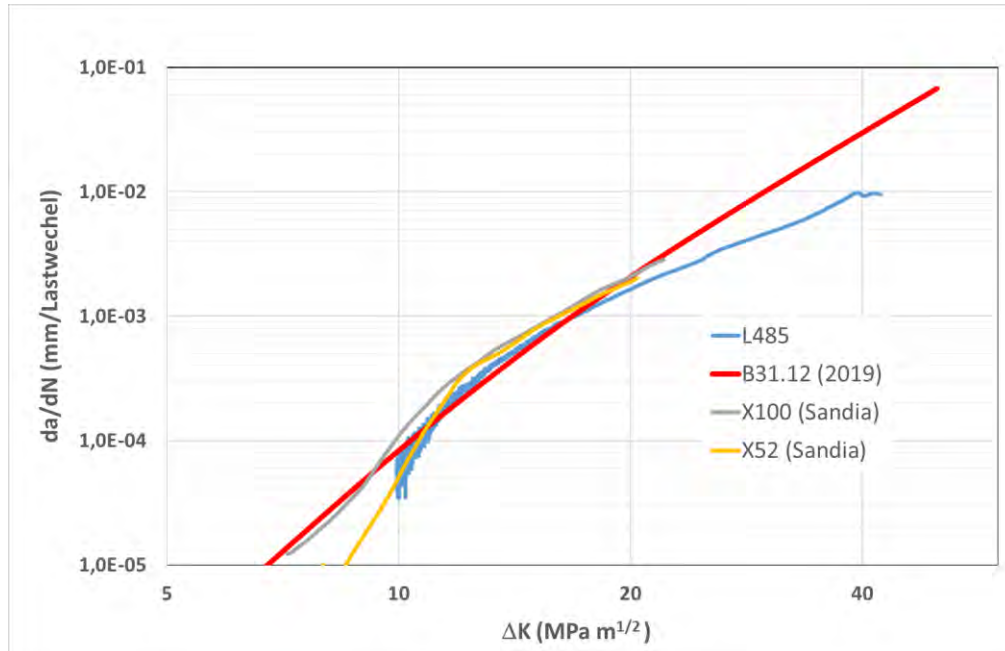


San Marchi, et al., PVP, 2019

Comparison of base material L485 with ASME regulations

Base material of the L485 in H₂

- at low stress intensities slightly above the ASME B31.12 curve for hydrogen
- at high stress intensities well below the ASME B31.12 curve for hydrogen

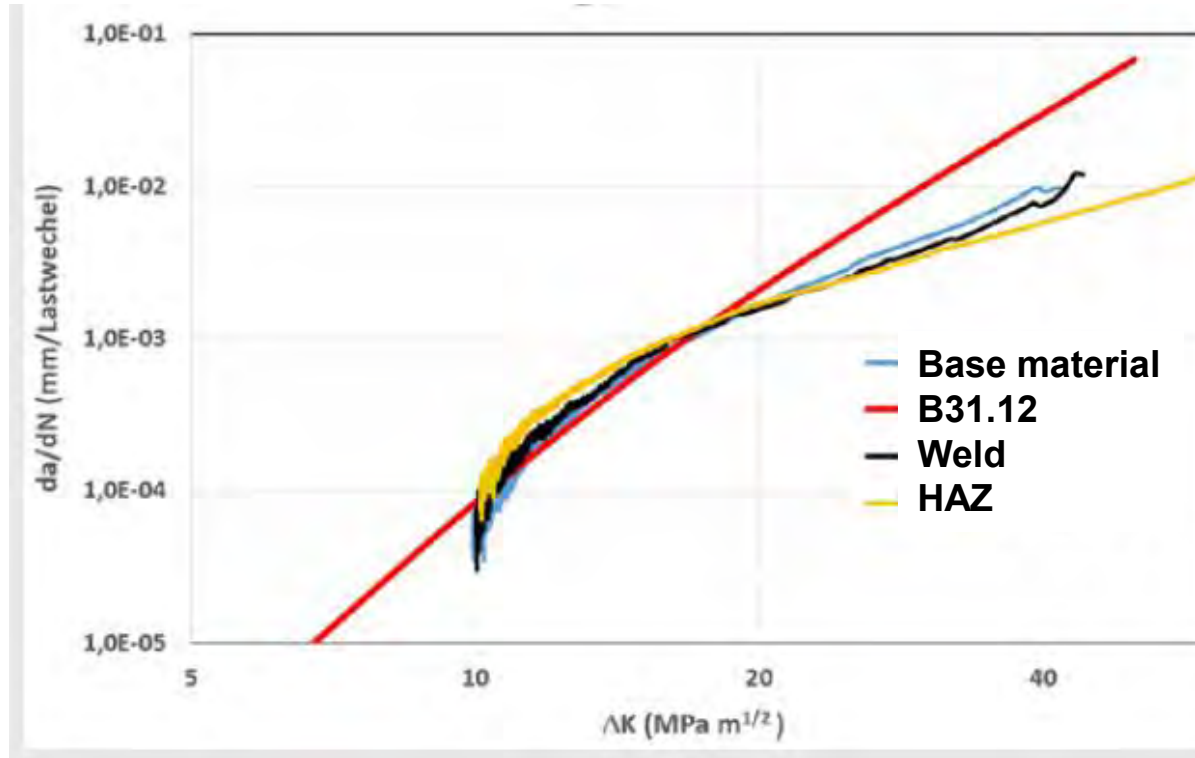


H₂, 100 bar, Room temperature, $R = 0.5$, $f = 1$ Hz

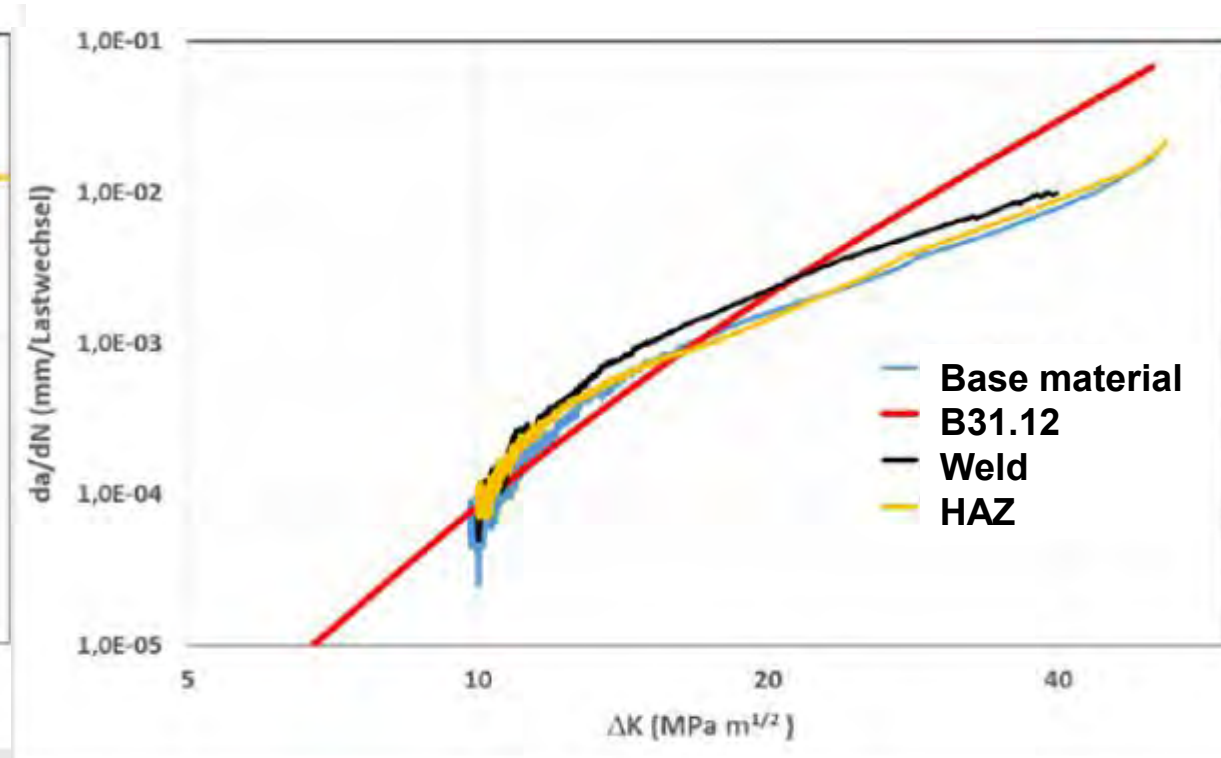
Good agreement with literature values for other pipeline steels [1]

[1] <https://energy.sandia.gov/programs/sustainable-transportation/hydrogen> (09/15/2021)

L485 : Base material, weld metal, and heat-affected zones show the same crack growth behavior under hydrogen



X70 : Weld metal with slightly higher crack growth rate than the heat-affected zone and the base metal



H₂, 100 bar, Room temperature, R = 0.5, f = 1 Hz

PL 3.21 of B31.12 provides guidance for conversion of existing pipelines to hydrogen service
However, detailed technical requirements are not included

How should existing damage be accounted for?

Not just internal cracking detected with NDE, but also external damage, dents, weld repairs, etc.

Additional topics:

Limit of 10% hydrogen content

Non-destructive evaluation methods

Welds

Alignment with international standards

Pressure cycle counting for hydrogen infrastructure

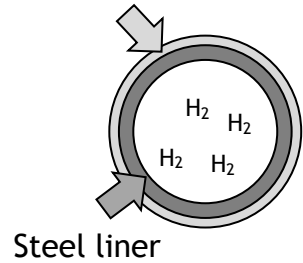
Joe Ronevich, John Emery, Peter Grimmer,
Robert Wheeler III, Chris San Marchi

*Study Group on Materials Testing and Qualification
for Hydrogen Service*

Issue → Avenues for life extension are needed for Type 2 vessels



Hoop wrapped carbon fiber



Type 2 vessels are commonly used at Hydrogen Refueling Stations (HRS)

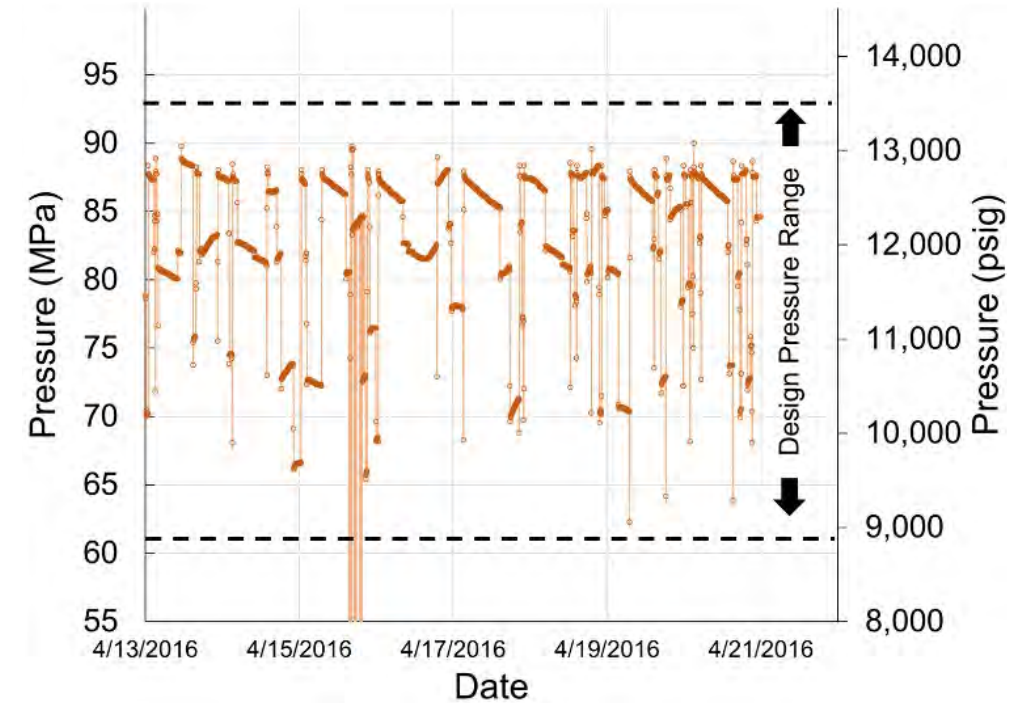
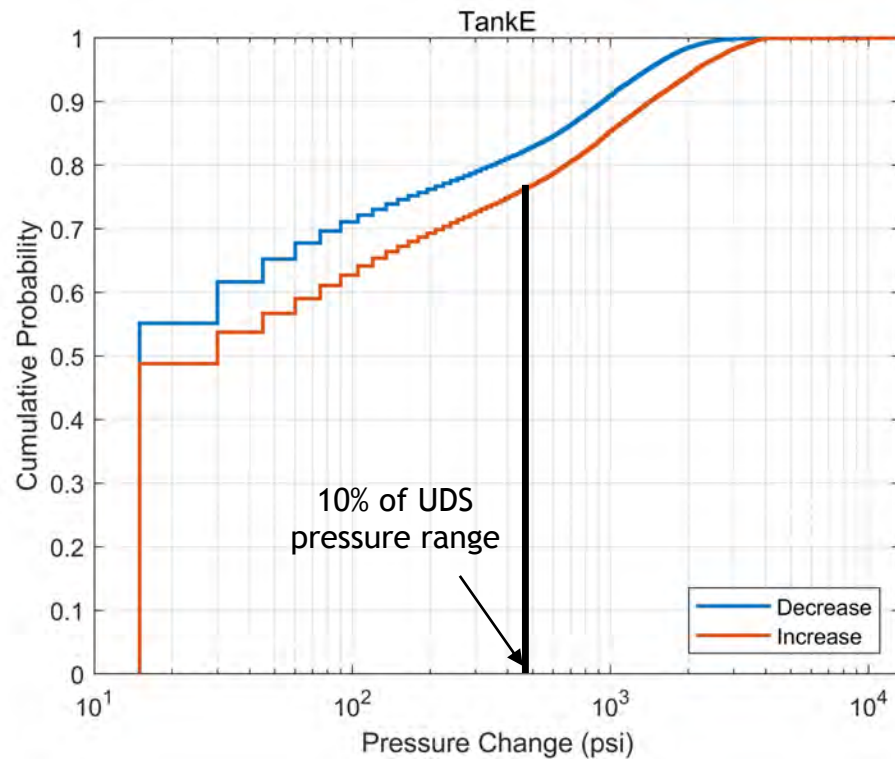
- **Fracture mechanics design** approach: ASME BPVC Section 8 Div 3
- Design cycle life is defined in User's Design Specification (UDS) **based on pressure range**
- Currently **no commercially available** means to perform non-destructive evaluate (**NDE**) on Type 2 vessels
= So vessels are retired!

Options for Life Extension		
(1)	(2)	(3)
Develop non-destructive evaluation (NDE) technique for Type 2	Reassess design life based on new & more complete data sets	Reassess design life based on in-service pressure cycles
Improve resolution and detectability	Code Case Curves	Provide guidance on cycle counting

Should every pressure fill count as a cycle?



- Actual operating pressures were **consistently less than UDS**
- Industry is conservative and *counts every* pressure fill as a cycle

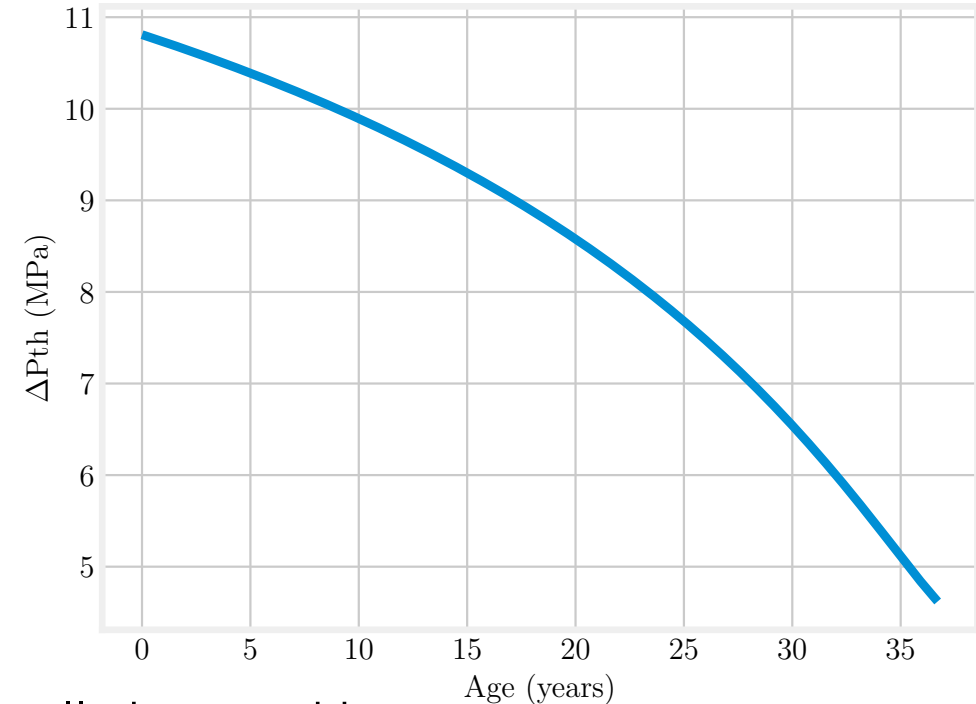
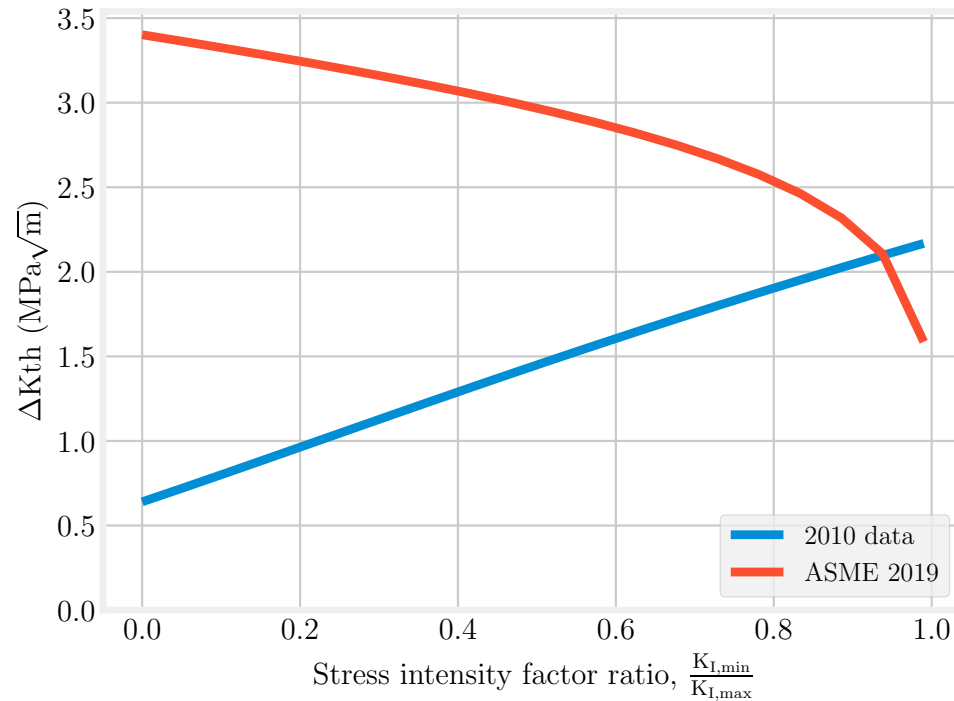


- *75% of operating cycles are less than 10% of design pressure range*
- *47% of operating cycles have a pressure swing < 1% of design pressure range*

4 Threshold pressure



ΔP_{th} is established using a threshold crack growth rate of 0.1 nm/cycle, and the curves relating crack length to driving force and fatigue cycle (age in years).



What guidance would actually be used by operators?

- Where should the guidance be located?
 - In Code?
 - In technical publication?

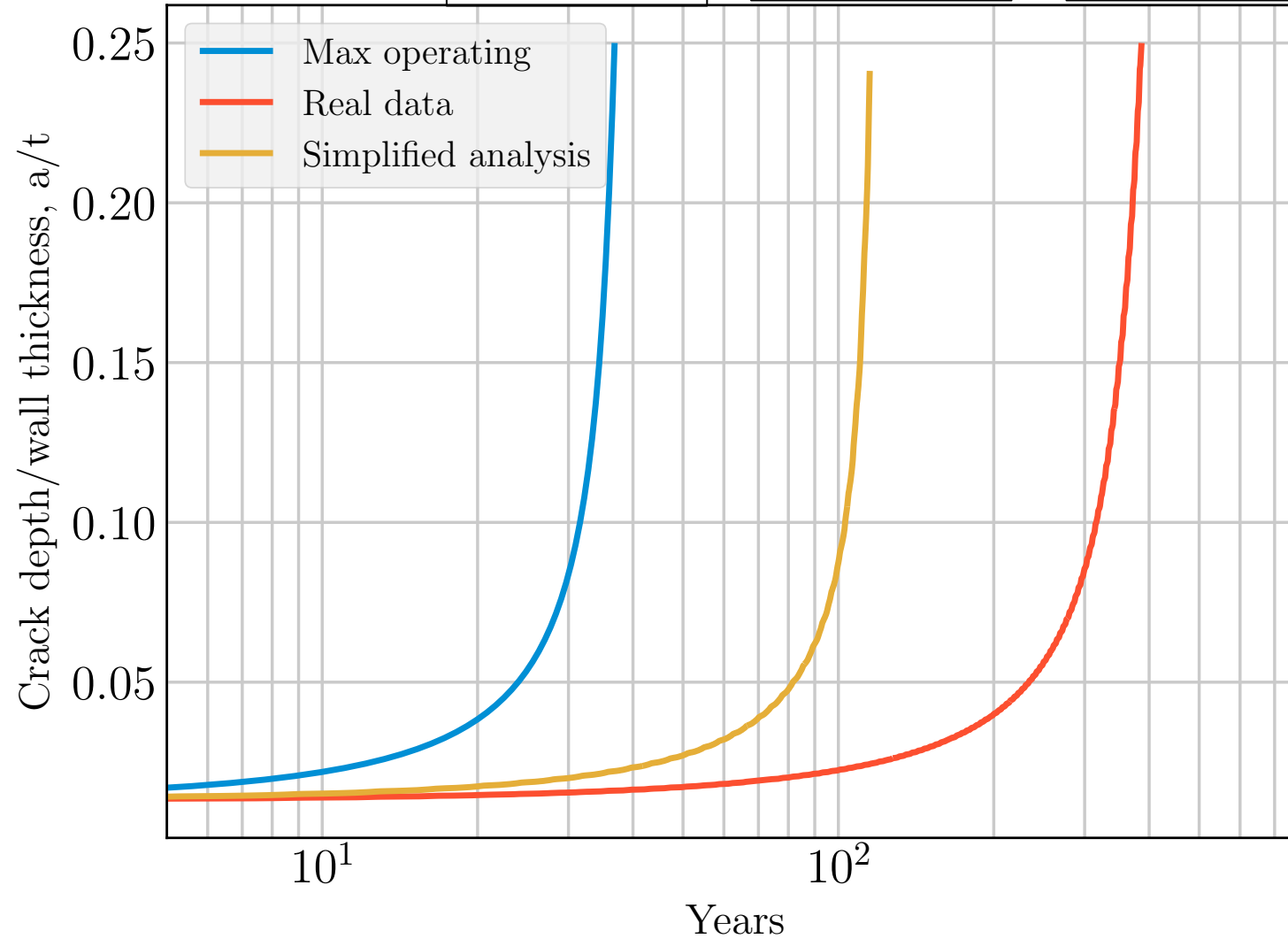
Simplified counting approach

Current approach

Count every ΔP as full pressure

Only count cycle when $\Delta P > \Delta P_{th}$

Count actual ΔP and integrate



Which approach is most likely to be chosen by industry?



Influence of ASME Code Case 2938 Design Curves



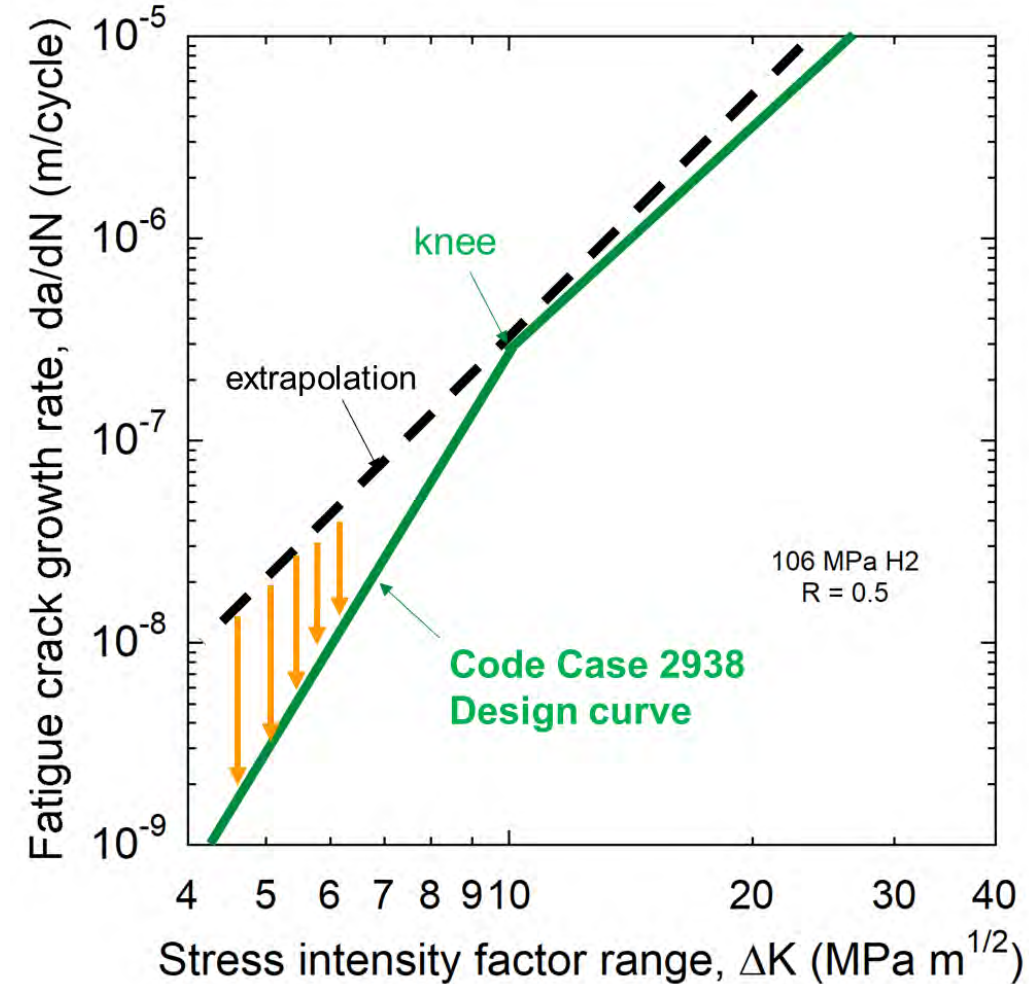
Case 1

- Original Design Data from 2010 (extrapolated line)
- UDS pressure range (61.3 MPa to 93 MPa)
- **Design life = 37,540 cycles**

Case 2

- **Code Case 2938 Design Curve (solid line)**
- UDS pressure range (61.3 MPa to 93 MPa)
- **Design life = 101,052 cycles**

~3X



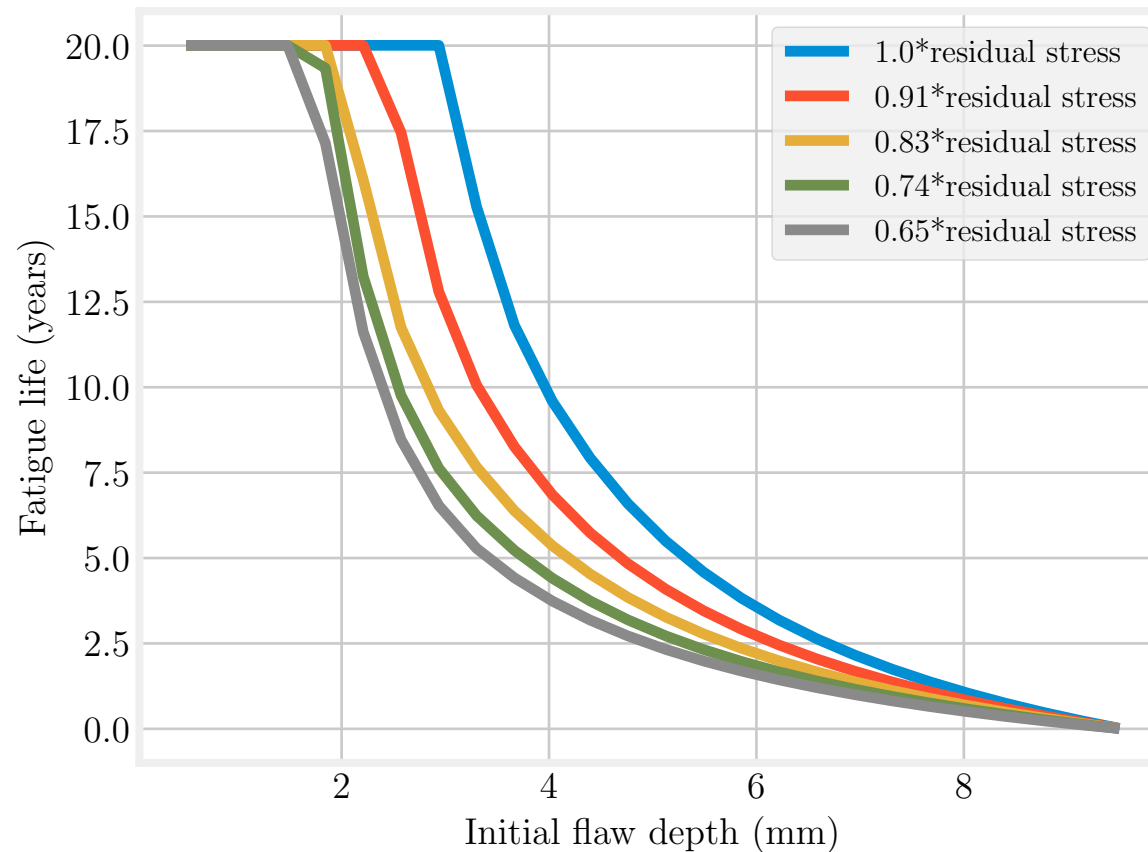
Utilizing Code Case 2938 design curves resulted in **2.7 times increase** in design life
→ Significance of impact will **depend on operating conditions & initial flaw size**

How much uncertainty is there in autofrettage process?



If only reach 90% of autofrettage pressure → results in 35% reduction in residual stress

What is the typical steel tensile properties used to specify autofrettage pressure?



Max UDS w/ 2019 crack growth rates

Discussion questions



There is clearly lack of guidance on cycle counting

- What should guidance look like? Located where?
- Does industry understand sensitivities to differences to small changes in liner hardening behavior?
- What about Design Curves for pressures less than 1000 bar?

→ **Composite reinforced pressure vessel (CRPV) service life is currently limited to 20 yr** (paragraph KG-512)

Benefits of Code Case 2938 design curves **are clear** for new construction

→ **Re-certification of existing tanks** is theoretically possible via approval of authorized inspector and NBIC based on **updated design calculations**

→ Currently no formalized pathway for reassessing design life



Exceptional service in the national interest

Effects of Oxygen Content on Hydrogen Environment-assisted Crack Growth

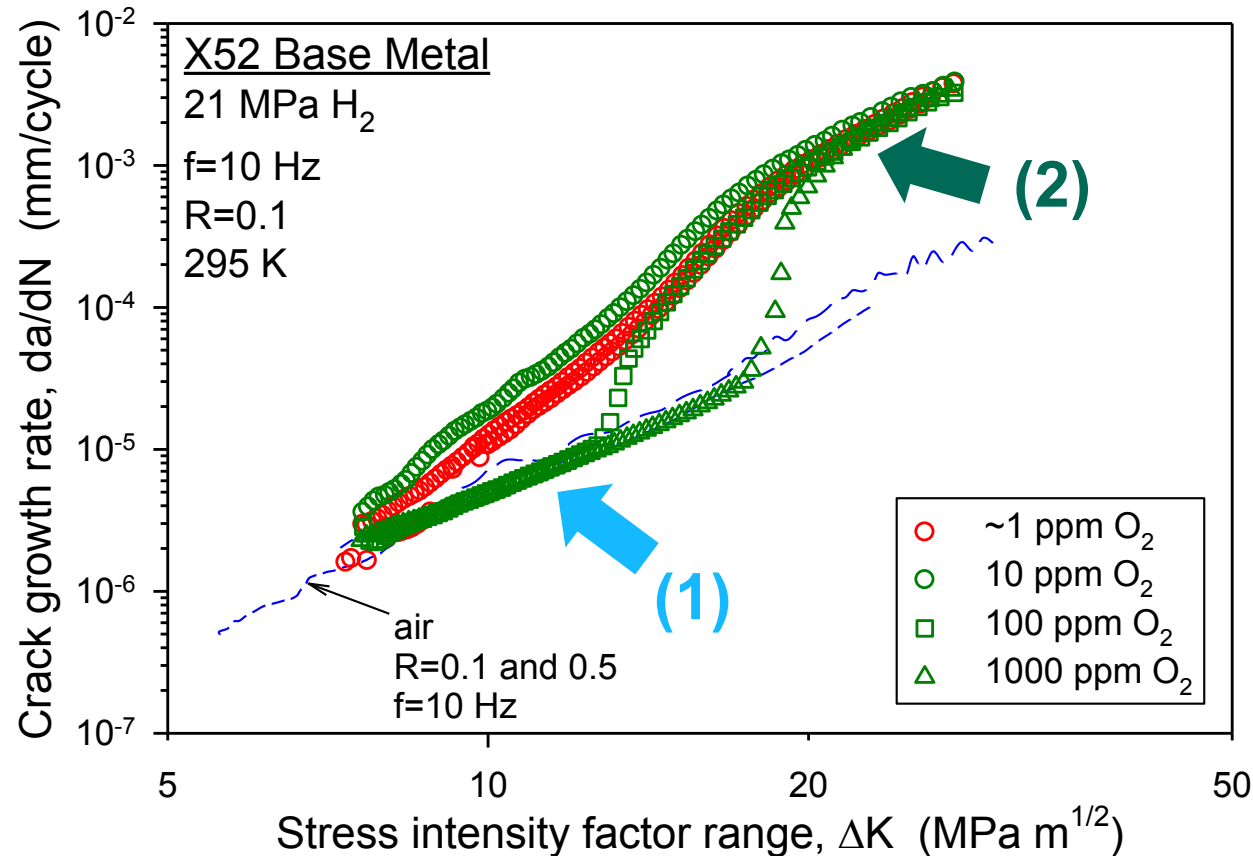
Preliminary Results

Rob Wheeler, Chris San Marchi, Joe Ronevich

PVP 2022 H₂ Study Group



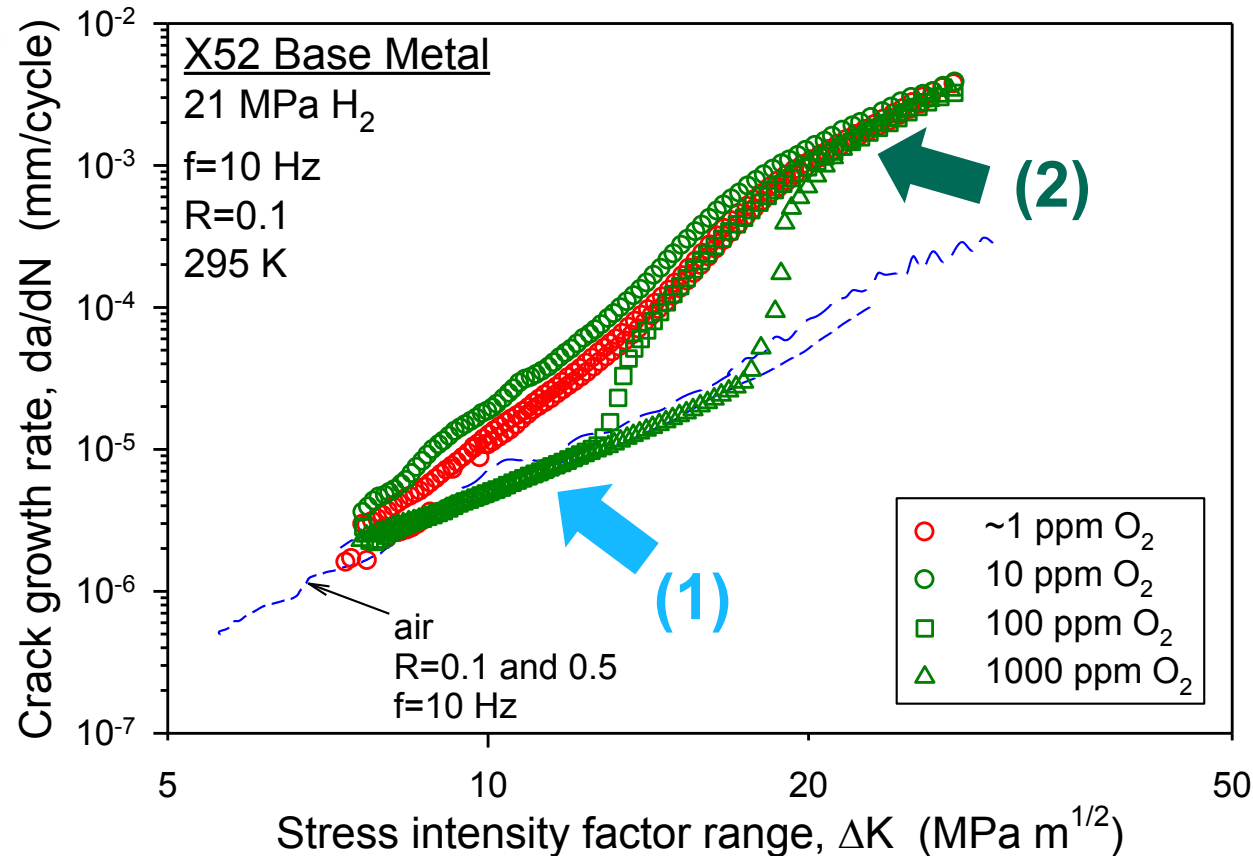
Oxygen is known to affect measurements of fatigue and fracture



- Numerous examples of trace gases mitigating crack growth in laboratory conditions
- Example:
 - (1) Oxygen reduces FCGR to air
 - (2) Oxygen has no effect on FCGR in H₂



Oxygen is known to affect measurements of fatigue and fracture



- Fatigue crack growth tests are typically performed at 1 Hz ($\pm$ decade)
 - $da/dN = 10^{-5}$ mm/cycle
 - Time for $\Delta a = 1$ mm: ~1 day
 - 1 day = 0.02% of 10 year life
- Are the time scales of a typical laboratory fatigue test sufficient to demonstrate kinetics over decades?
 - Better simulate the mechanical/environmental conditions that components see when in use

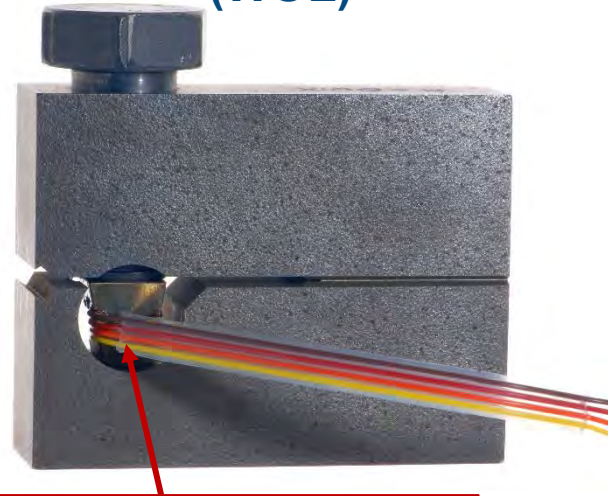


Sustained load/constant displacement testing can be executed over periods of days to years

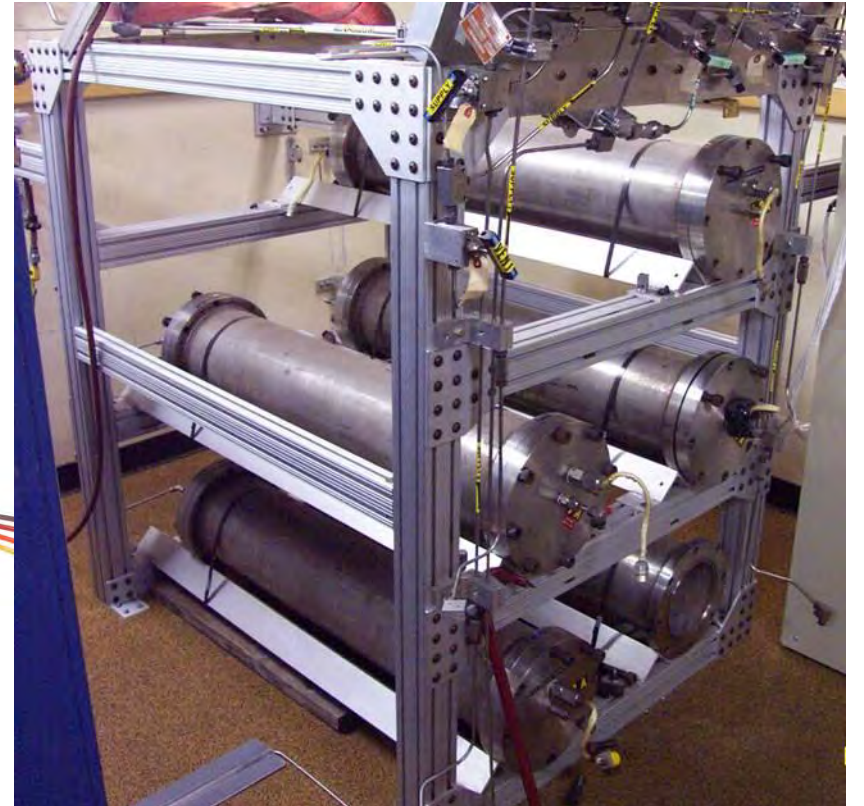
ASTM E1681 – Threshold Stress Intensity Factor for Environment-Assisted Cracking

- Fixed displacement tests
- Placed in pressure vessels & pressurized up to 140 MPa gaseous environment
- Test durations can range from weeks to years
- Instrumented reaction pins allows us to determine incubation time
- Precracked and loaded in air

Wedge-opened loaded (WOL)



Reaction pin (load tup) with strain gauge that is fed to external DAQ system and monitored throughout test





Preliminary results for effects of 100PPM and 1000PPM O₂ on hydrogen assisted fracture

Grade J F950 steel
YS = 700MPa

Grade L SA372 steel
YS = 730 MPa

X100 pipeline steel
YS = 760 MPa

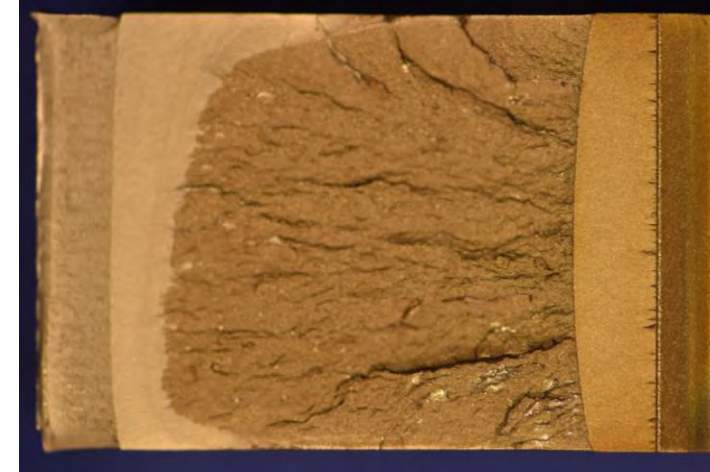
13-8 stainless steel
YS = 1480 MPa

103MPa/15ksi

Grade L



Grade J



X100

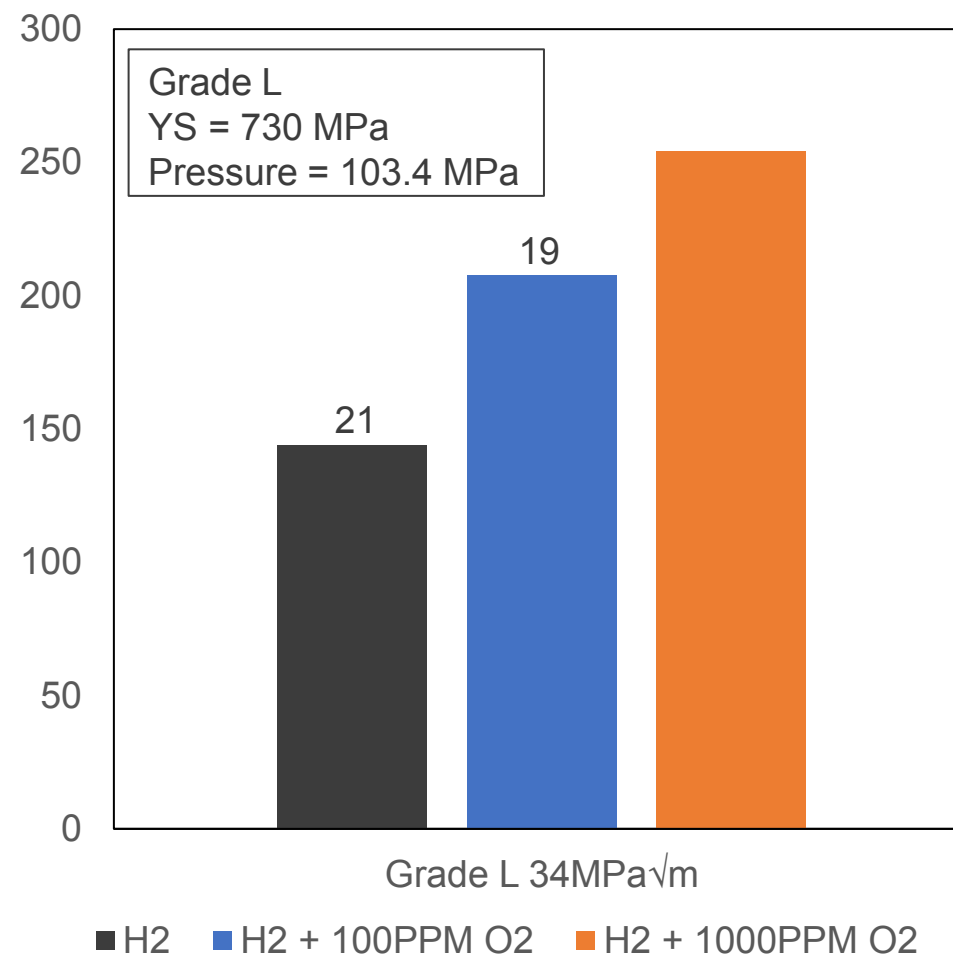
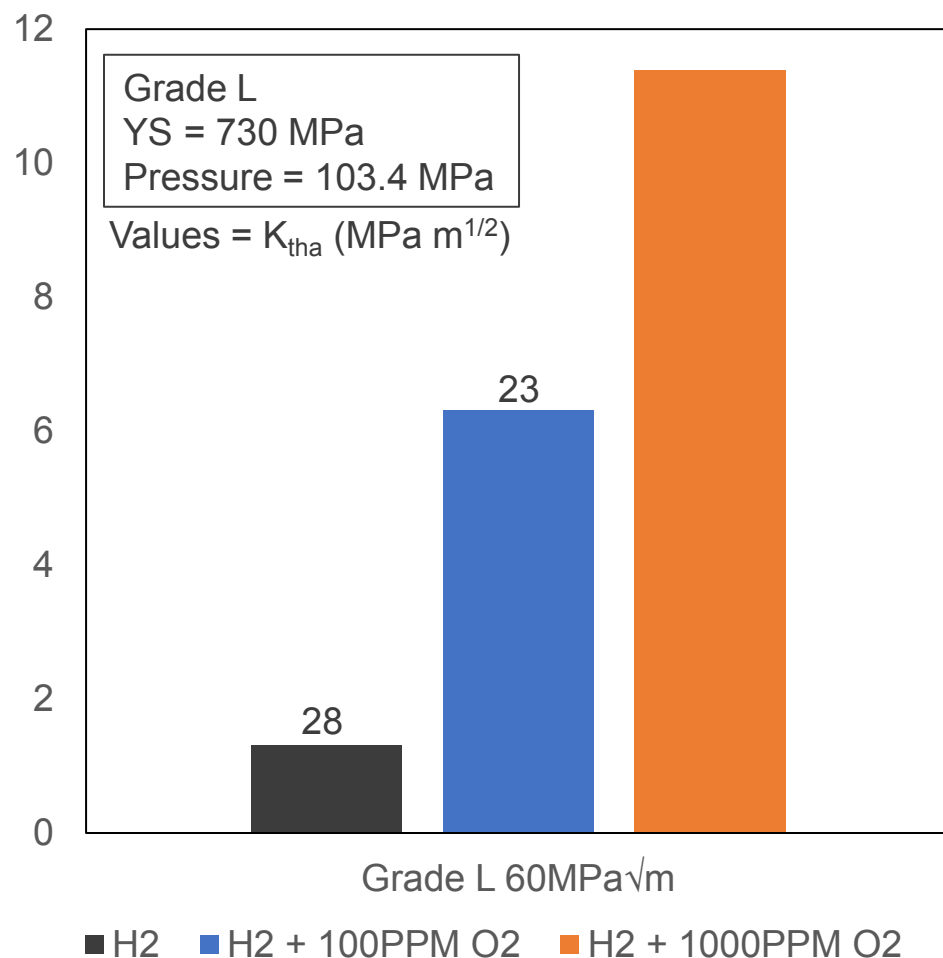


13-8





100PPM & 1000PPM O₂ delay incubation time

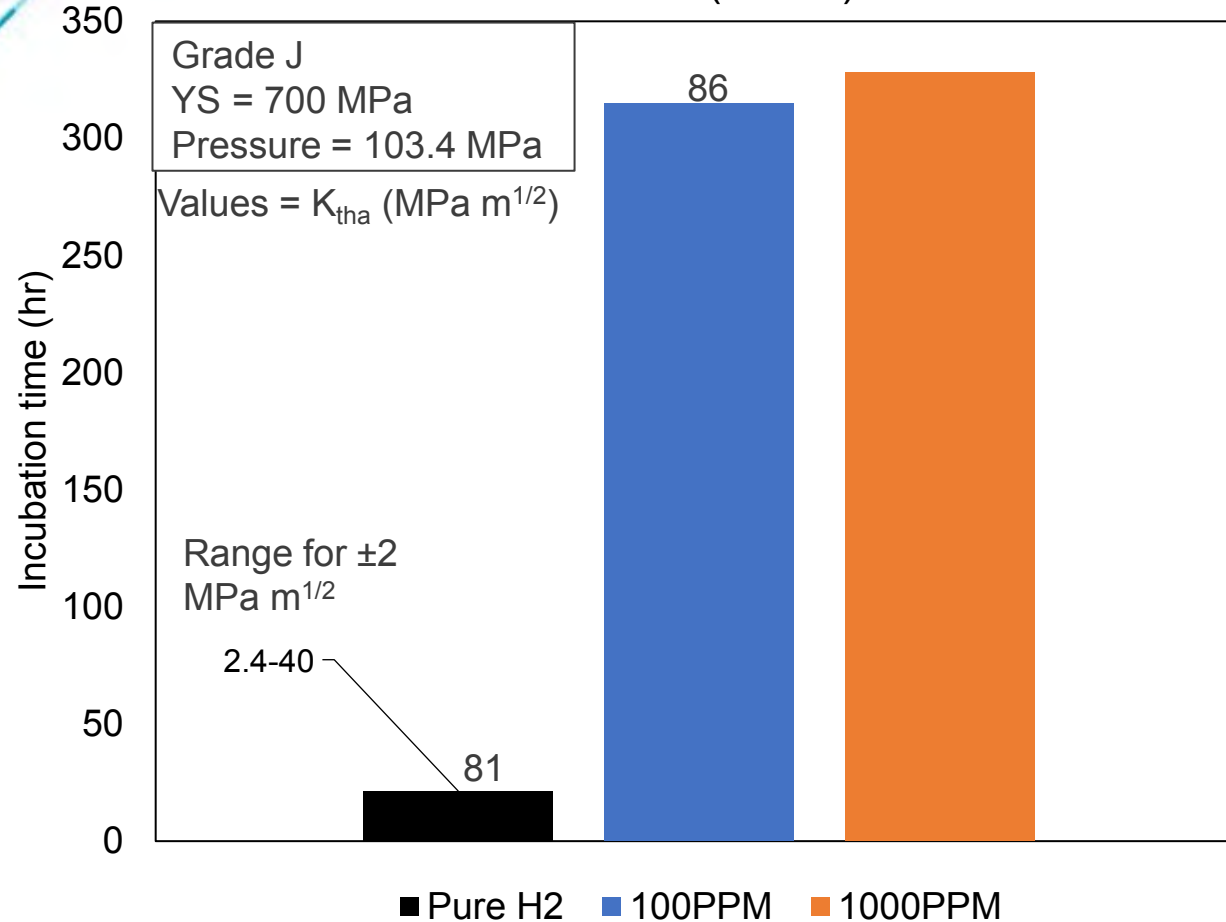


- Grade L shows a 5x delay at higher preload ($K_{app} = 60 \text{ MPa m}^{1/2}$) and a 1.5x delay at lower preload ($K_{app} = 34 \text{ MPa m}^{1/2}$)
- Similar crack arrest thresholds for both pure and 100PPM tests

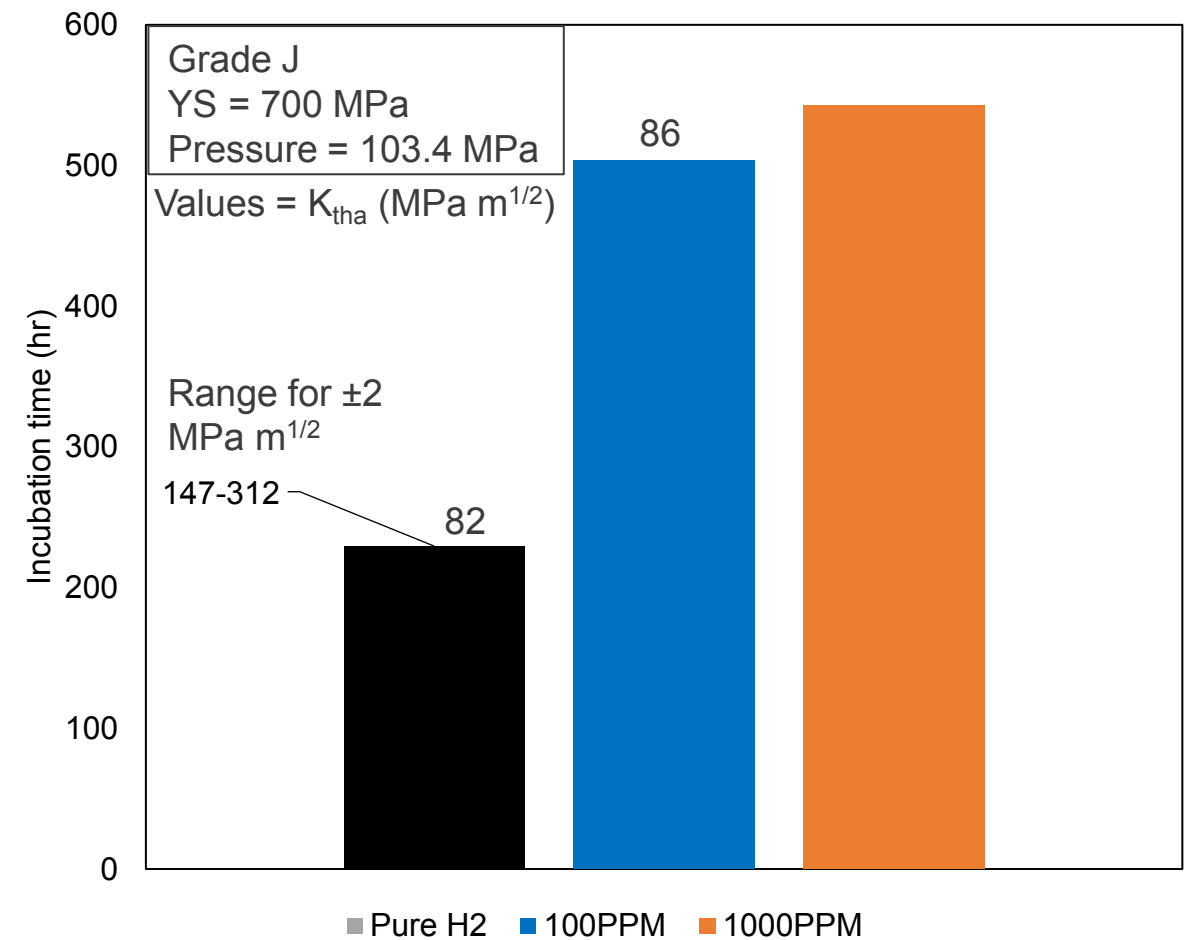


100PPM & 1000PPM O₂ delay incubation time

Grade J - 145MPa(m^{1/2}) Preload



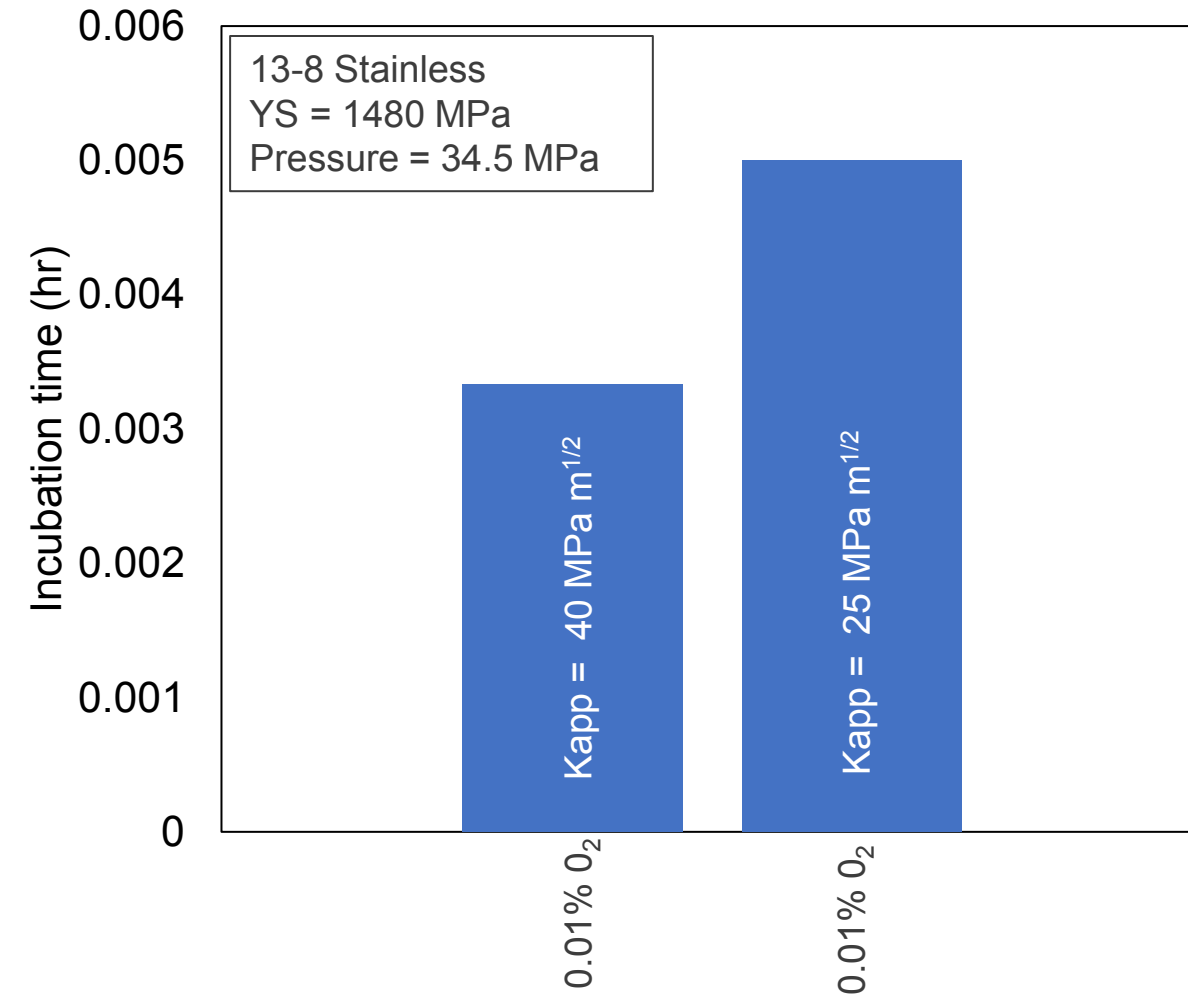
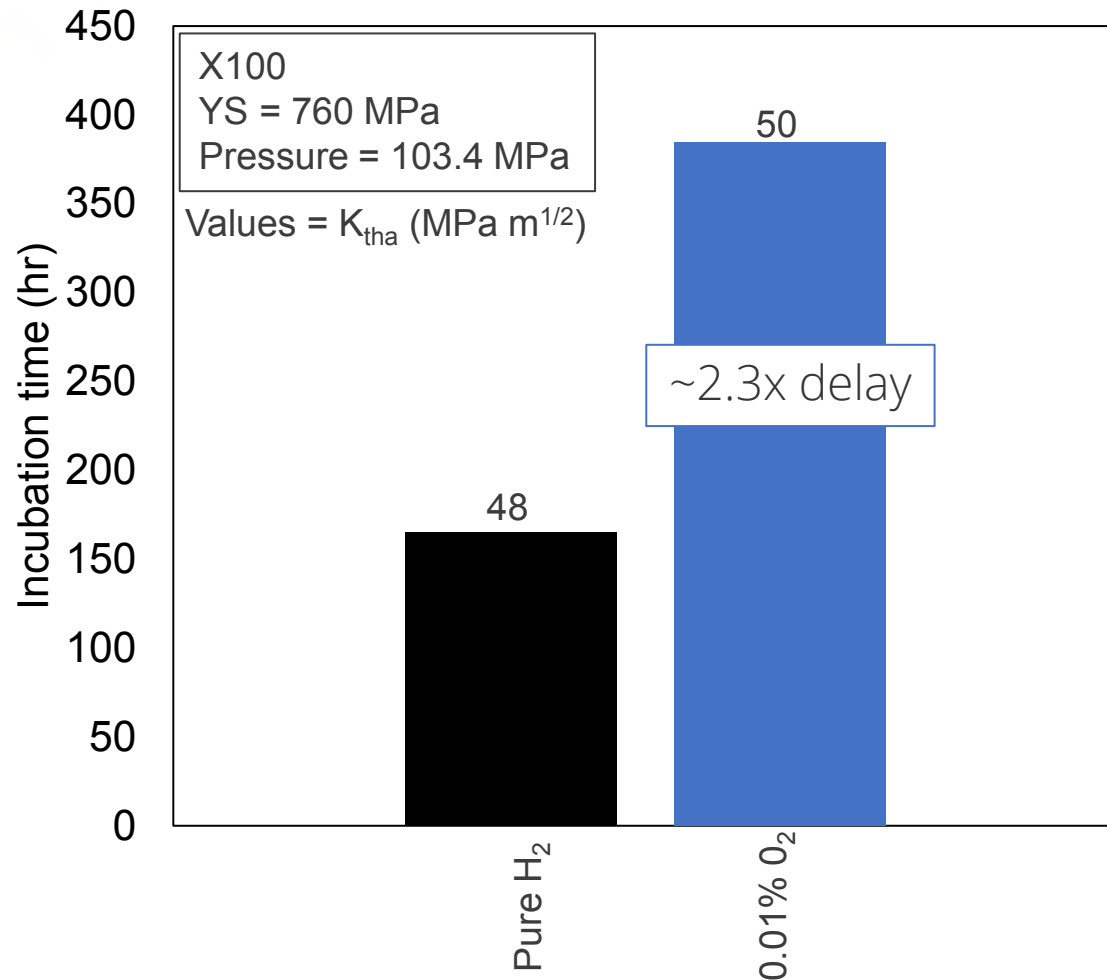
Grade J - 135MPa(m^{1/2}) Preload



- Similarly, the Grade J material showed delays of 15x at a higher preload ($K_{app} = 145$ MPa m^{1/2}) and a 2.2x delay increase at a lower preload ($K_{app} = 135$ MPa m^{1/2})
- K thresholds were between 77 and 86 MPa m^{1/2} for both the pure and mixed gas conditions



0.01% O₂ delays incubation time for X100, but 13-8 fractured immediately

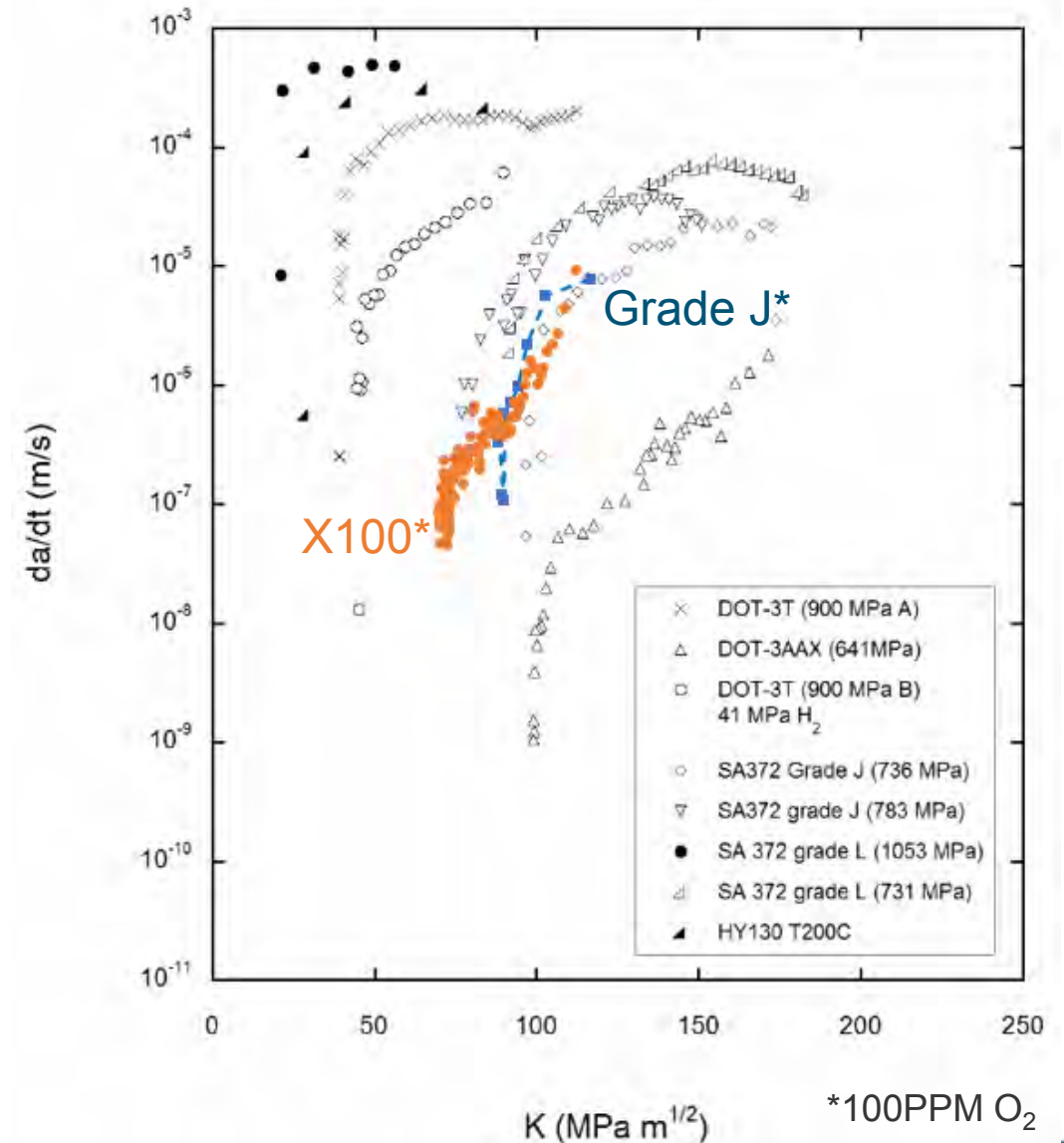


- X100 also saw a delay with 100PPM, but similar K_{tha} for a K_{app} of 120 MPa m^{1/2}
- Both 13-8 samples fractured ($a/W > 97\%$) almost immediately upon exposure to mixed gas



Similar crack growth rates and arrest thresholds for both H_2 and mixed gas environment

- Introducing 100PPM O_2 increased the incubation time by factors between 1.5x and 15x
- Increasing the O_2 from 100PPM to 1000PPM further delayed the incubation time, but had a smaller relative effect than going from pure H_2 to H_2 + 100PPM
- K_{THa} threshold appears to be independent from oxygen content
 - All 100PPM tests fall within the pure H_2 experimental spread (within $\pm 5 \text{ MPa m}^{1/2}$)
- Crack growth rates (da/dt) fall in the expected ranges from previous H_2 tests



*100PPM O_2

HOW CAN WE INCREASE THE TEST CAPACITY TO MEET THE HIGH DEMAND FOR THE UPCOMING H2-ECONOMY? IS THE TUBULAR SPECIMEN TECHNIQUE A PROMISING METHOD?

Fabien Ebling, Thorsten Michler, Ken Wackermann, Heiner Oesterlin, Carl Fischer



Freiburg, Germany

Mechanical testing in high pressure hydrogen - NASA cost estimation 1994

Table 1 Representative Cost of Air and Hydrogen Testing

Test Type	Multiplier ¹
Tensile Test	15
Low-Cycle Fatigue	55
High-Cycle Fatigue	55
Crack Growth (Region 2)	74
Crack Growth (Threshold)	147

E.J. Vesely, B.N. Bhat, W.B. McPherson, C.E. Grethlein, Reproducibility and repeatability of tensile and low cycle fatigue properties in propulsion grade hydrogen, in: N.R. Moody, A.W. Thompson, R.E. Ricker, G.W. Was, R.H. Jones (Eds.), Proc. 5th Intl. Conf. Eff. Hydrog. Behav. Mater., The Minerals, Metals & Materials Society, Moran, WY, USA, 1994: pp. 363–374.

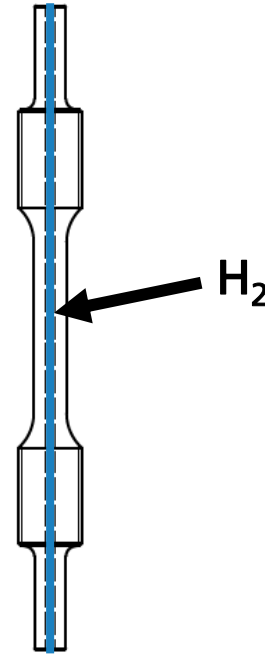
Comparison of two different methods for materials testing for gaseous hydrogen applications

High pressure H_2 autoclave



Conventional specimen

Tubular specimen with internal H_2 pressure

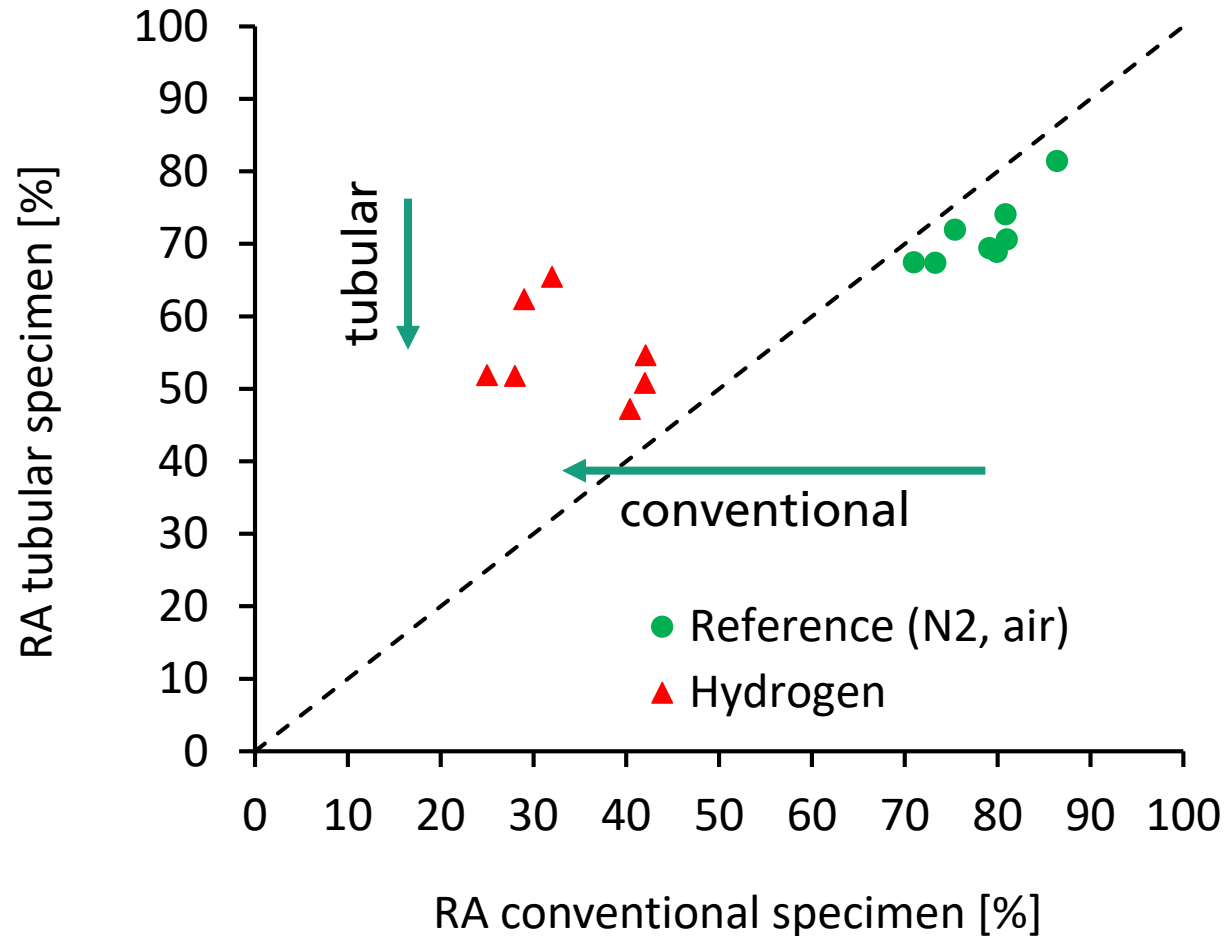


Comparison of two different methods for materials testing for gaseous hydrogen applications

High pressure H ₂ autoclave	Tubular specimen with internal H ₂ pressure
Pro + Well established method + Conventional, standardized specimens	Pro + Lower test costs + Easy heating / cooling (induction, liquid nitrogen bath,...)
Con – High test costs – Long test durations, especially at non ambient test conditions (p, T)	Con – Specimen geometry not yet standardized – Correlation of test results to those obtained by conventional specimens to be established

Comparison conventional / tubular specimen

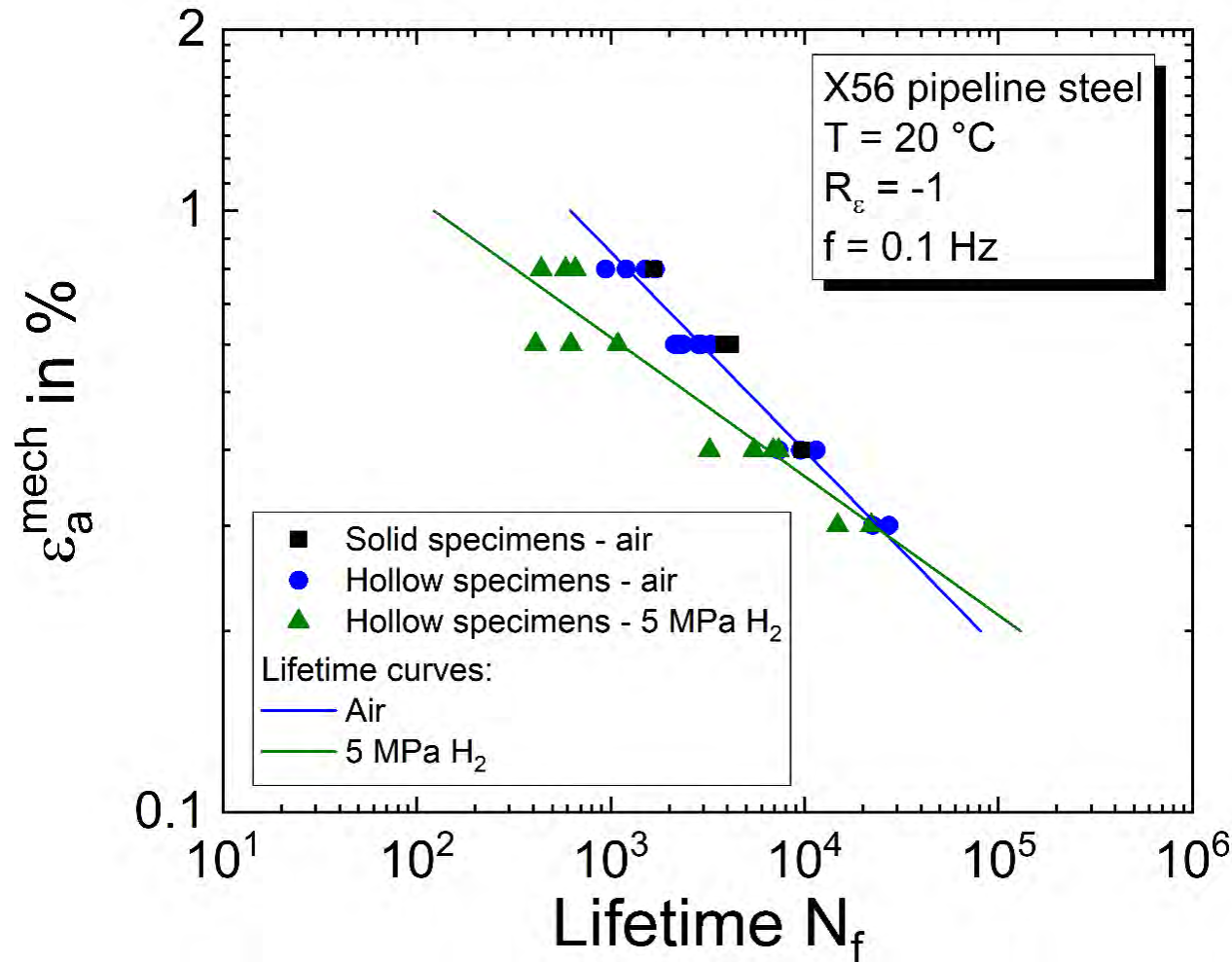
Tensile test - reduction of area



- Tests on 7 different steels
- Reference: $RA_{\text{Conventional}} > RA_{\text{Tubular}}$
- Hydrogen: $RA_{\text{Conventional}} < RA_{\text{Tubular}}$
- Sensitivity of tubular specimens to quantify HE effects in tensile tests using RA appears to be less compared to conventional specimens

Comparison conventional / tubular specimen

Low cycle fatigue lifetime



- Little influence of specimen geometry on lifetime
- Significant hydrogen effects visible when tested with inner hydrogen pressure

Open for discussion!

- How can we increase the test capacity to meet the high demand for material testing in the upcoming H2-economy?
- Is the tubular specimen technique a promising method? Even if it is less sensitive in tensile tests?
- Can the tubular specimen technique be an alternative to the autoclave in low cycle fatigue testing?



Exceptional service in the national interest

Testing of Medium Density Polyethylene (MDPE) in Hydrogen

Rakish Shrestha

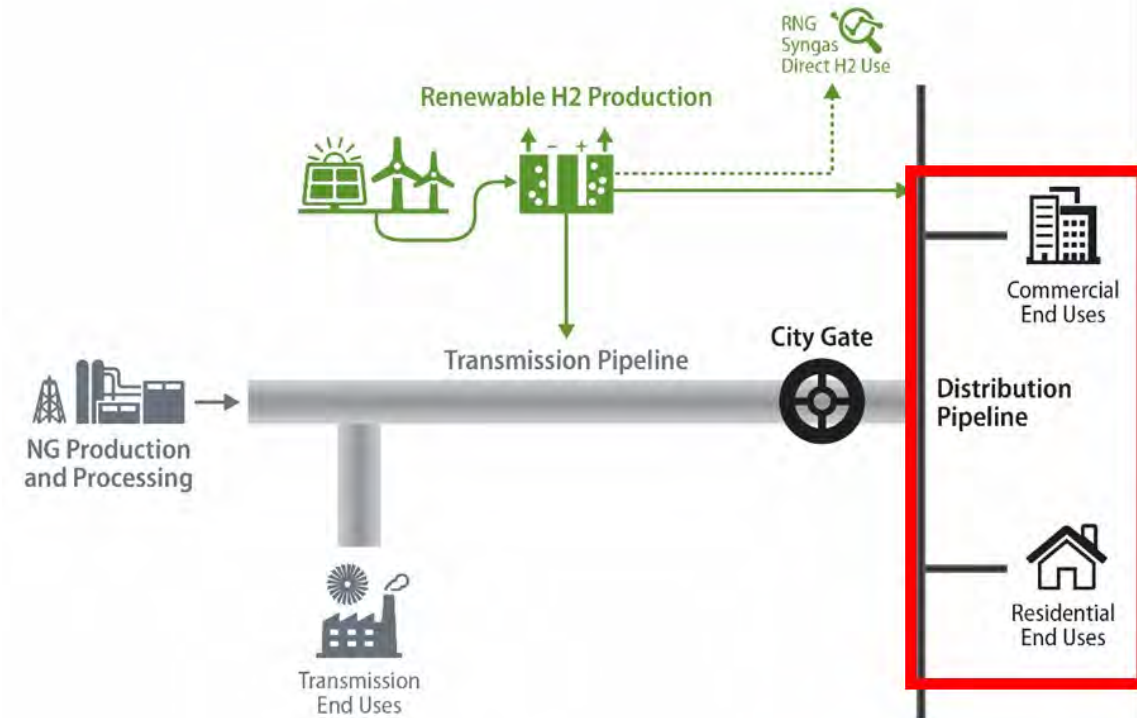
Sandia National Laboratories

07/21/2022

Motivations and Objectives

Motivations

- Hydrogen is a convenient medium for carrying/storing energy and can be an alternative to carbon based fuels
- Distribution of gaseous hydrogen in blended and in pure form
 - ❑ Developing new hydrogen distribution infrastructure is economically impractical
 - ❑ Distribution pipelines in natural gas infrastructure typically consists of medium and high-density polyethylene (MDPE and HDPE)

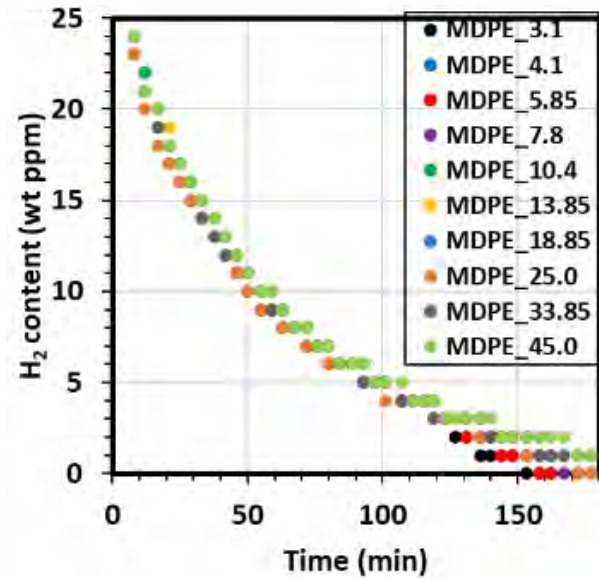


Objectives

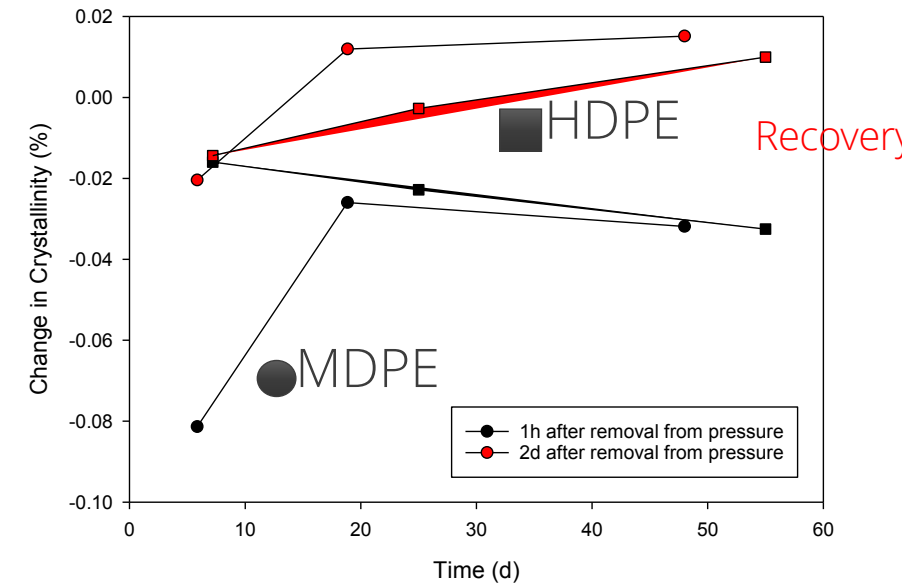
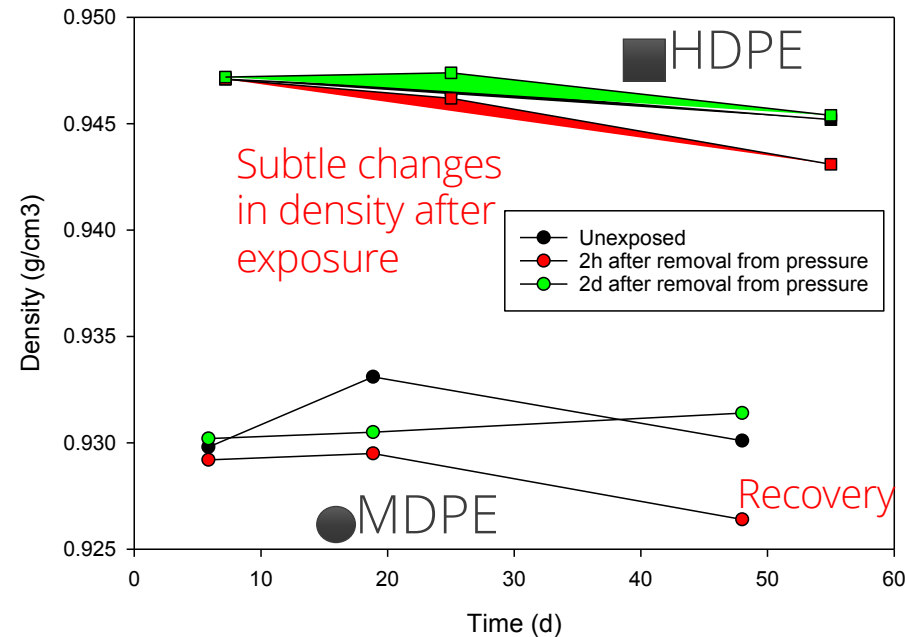
- Understand fatigue and fracture behavior of MDPE & HDPE polymer in the presence of gaseous hydrogen
- Conduct a failure assessment to determine the applicability of MDPE & HDPE for hydrogen application



Morphological effects: Initial reductions in crystallinity and density do not change with time in H₂ and recover after removal from H₂



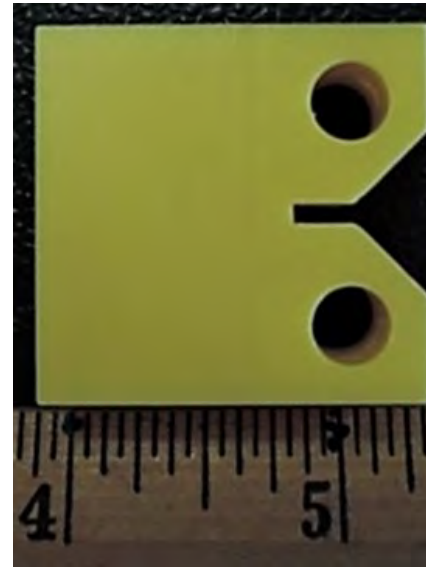
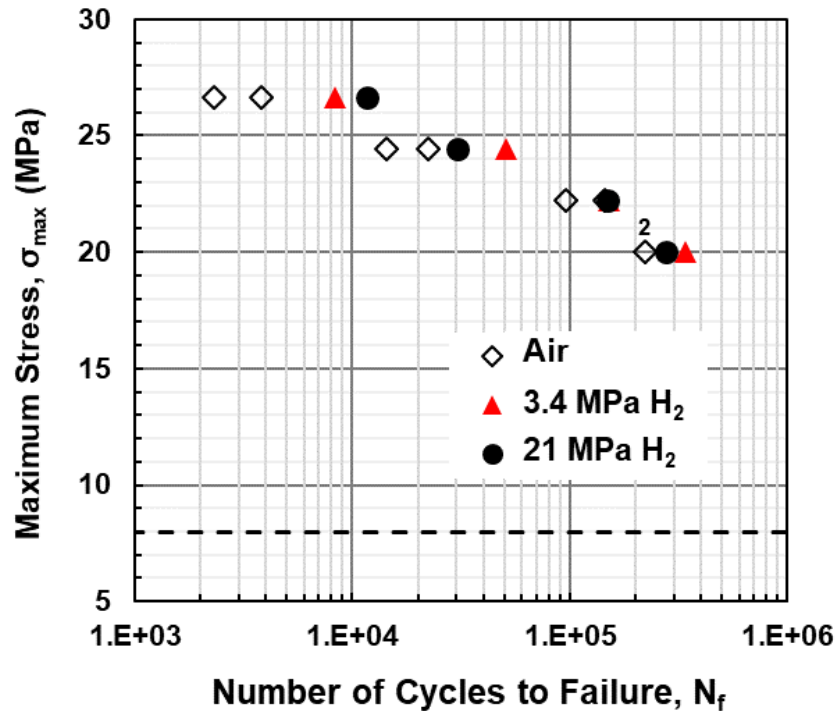
Hydrogen contents ~35 ppm for MDPE and ~32 for HDPE





Experimental Results: Fatigue life and fracture resistance of MDPE polymer did not degrade in the presence of gaseous hydrogen

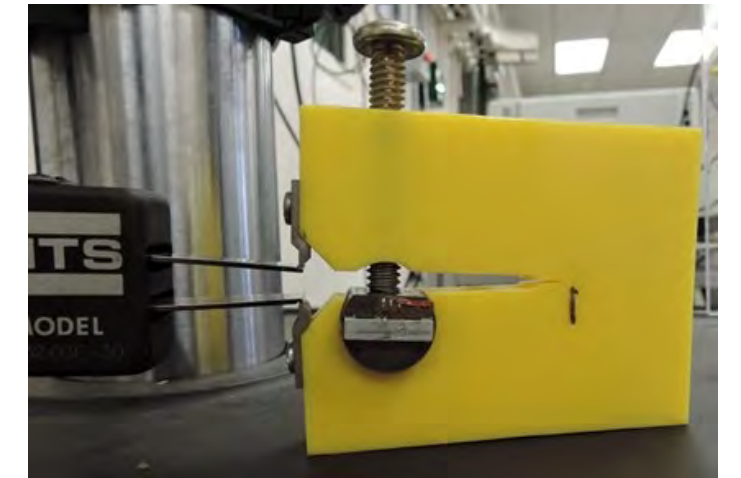
- $K_{Q_air} = 1.34 \text{ MPa}\sqrt{\text{m}}$
- $K_{Q_Hyd} = 1.11 \text{ MPa}\sqrt{\text{m}}$



H₂ Exposed



Air



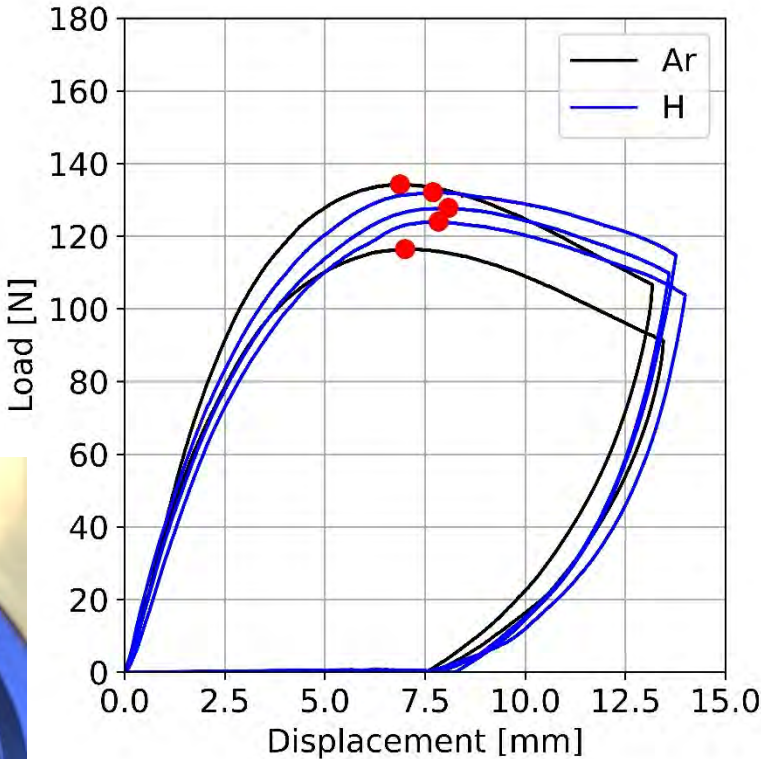
Loaded MDPE specimen to 3.4 MPa (500 psi) gaseous hydrogen for 500 hours showed no evidence of crack growth

- Are these test results sufficient to enable hydrogen deployment in MDPE?
- Are there any additional tests that can provide more valuable insight?
 - For instance, tests on vintage materials

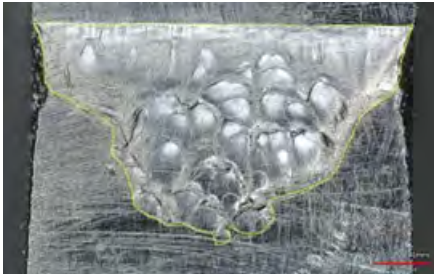
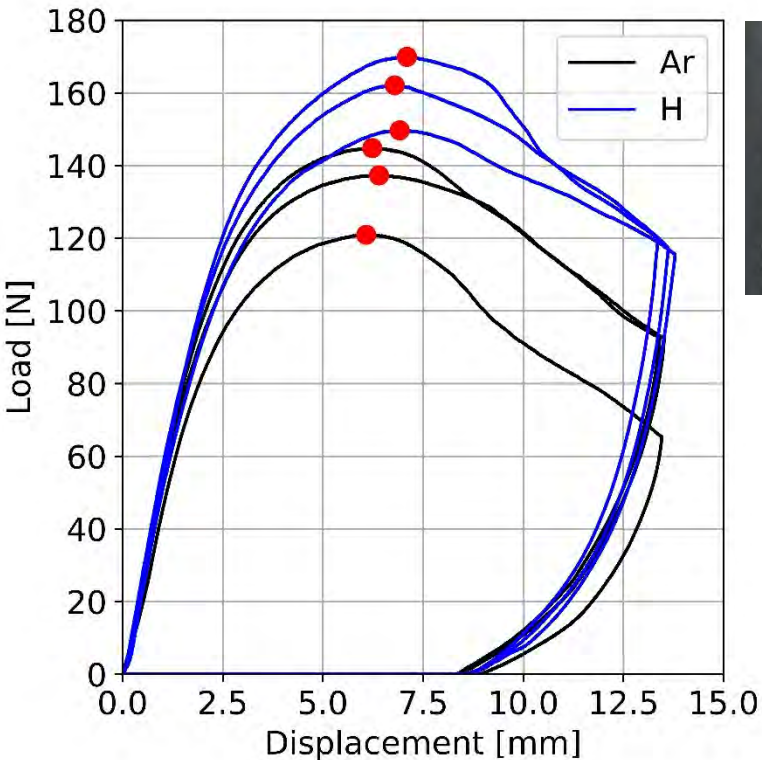


Fracture resistance of MDPE and HDPE did not degrade in pure hydrogen: Load-displacement curves

MDPE (2708)



HDPE (4701)

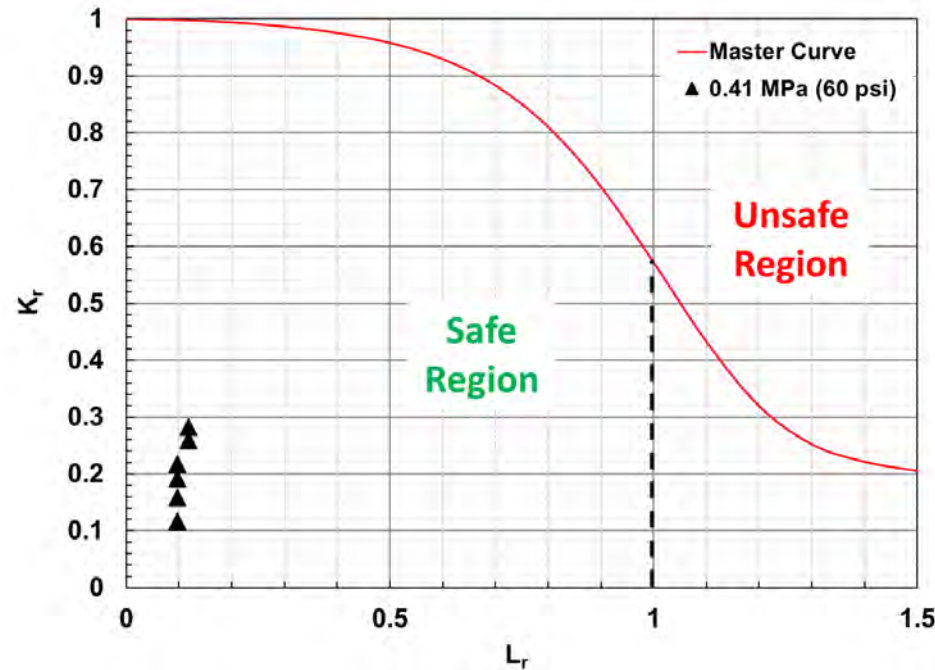


Similar trend observed in tensile testing – greater failure strain w/ H₂ exposure

Material	Gas	Ave. Max Load [N]	Ave. WofF [N*mm]
MDPE	Ar	125.4 ± 8.9 (7.1%)	1170.7 ± 65.3 (5.6%)
	H ₂	130.0 ± 2.2 (1.7%)	1252.7 ± 39.6 (3.2%)
HDPE	Ar	134.4 ± 10.0 (7.4%)	1300.2 ± 110.2 (8.5%)
	H ₂	161.0 ± 8.3 (5.2%)	1590.0 ± 53.4 (3.4%)



Failure Assessment Diagram: The assessment was conducted for new MDPE pipes



- Failure assessment Diagram (FAD) depends on the material properties such as fracture toughness and yield strength, which can degrade over long period of service life

- Is there a need to generate the data for vintage pipes for developing similar FAD?



PE Pipes: Study the effects of gas impurities

- Gas Impurities are discussed in metal systems, are they of interest for PE?
- If so, what gas impurities?

PE Pipes: Representative testing methodologies

- Due to relatively high toughness and viscoelastic properties, many tests such as fatigue crack growth test and valid fracture toughness tests are difficult to conduct in the case of PE materials
- **What tests are more representative to better understand the applicability of PE pipes for hydrogen applications?**



Open questions

- Are conventional fatigue and fracture test results **sufficient to enable** hydrogen deployment in MDPE & HDPE?
- Are there any additional tests that can provide more valuable insight?
- What about **vintage MDPE & HDPE** pipes?
- Are **gas impurities** a concern for MDPE & HDPE?
- Are their **other applications** within the hydrogen technology framework that the fatigue and fracture studies of polymeric materials will be of an interest?



Back up Slides



Sandia
National
Laboratories

Exceptional service in the national interest

ASME PVP 2022
Pressure Vessels & Piping
Conference
Las Vegas, NV
July 17-22, 2022

COMPATIBILITY OF MEDIUM DENSITY POLYETHYLENE (MDPE) FOR DISTRIBUTION OF GASEOUS HYDROGEN

Rakish Shrestha (Presenter)

Joseph A. Ronevich

Chris San Marchi

Sandia National Laboratories,
Livermore, CA

Lisa Fring

Kevin Simmons

Pacific Northwest National Laboratories,
Richland, WA

Noah D. Meeks

Southern Company Services,
Birmingham, AL

Zachary E. Lowe

Timothy J. Harris Jr.

Southern Company Gas,
Atlanta, GA

SAND2022-5613 V

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.





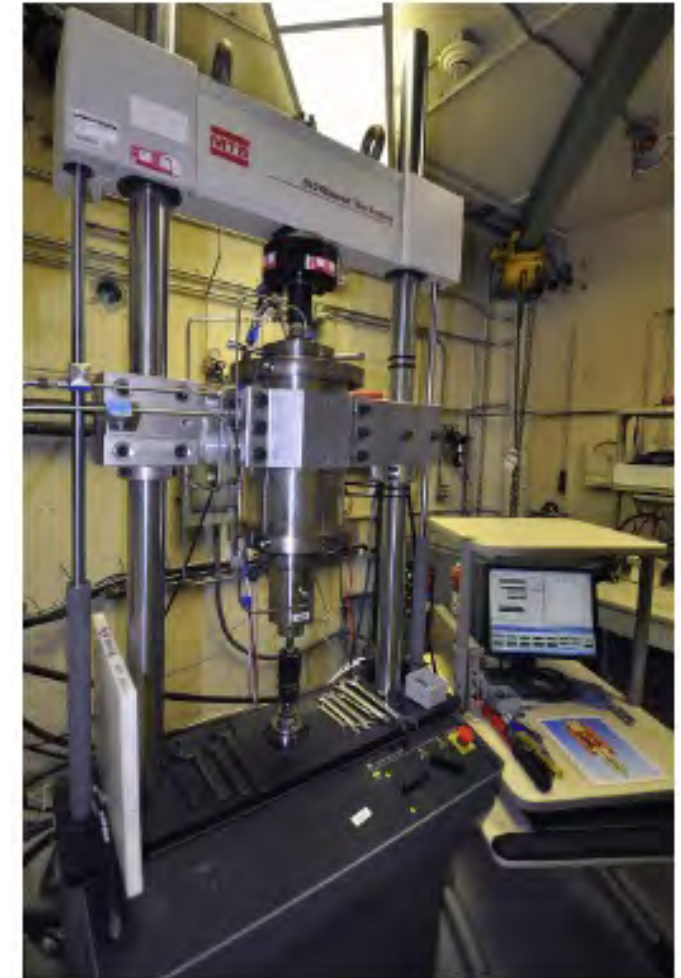
Experimental Setup: Fatigue life and fracture resistance investigated in air and in gaseous hydrogen

Fatigue Life Testing

- Fatigue life testing were conducted in load controlled mode in tension-tension configuration with R value of 0.1
- Test in air was conducted using MTS servo hydraulic test frame with 5kN load cell
- Test in gaseous hydrogen was conducted with custom designed load transducer integrated within MTS test frame

Fracture Resistance Testing

- Sharp razor blade notch was introduced on CT specimens up to a/W of 0.56
- Fracture resistance was determined based on ASTM D5045 Standard
- Fracture resistance tests were conducted at a displacement rate of 0.5 mm/min

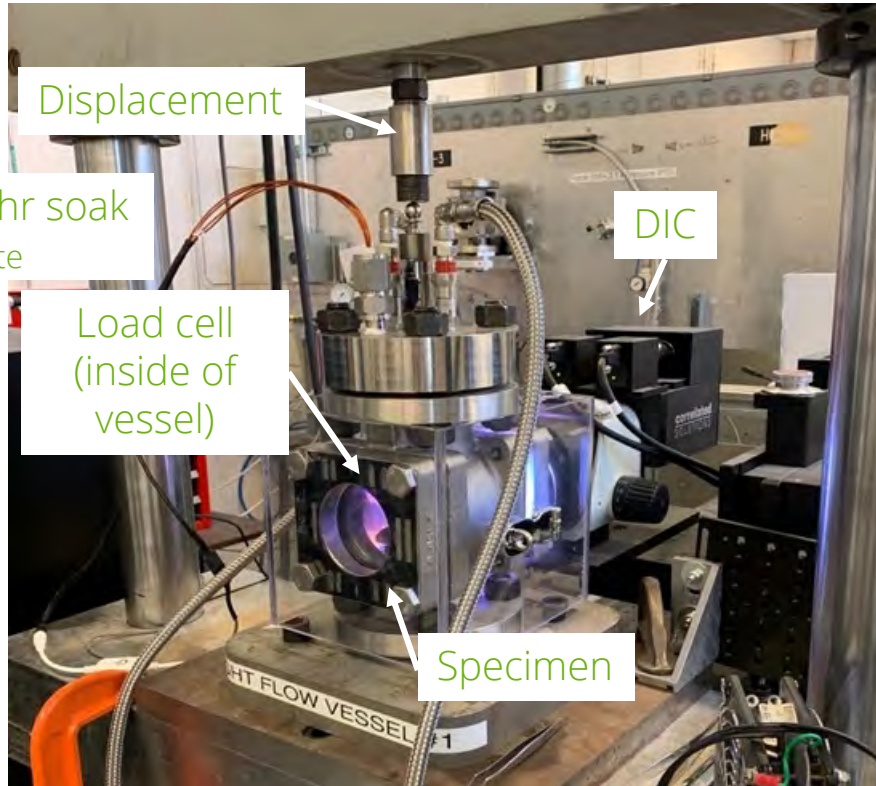


Somerday et al., International Journal of Hydrogen Energy, 42 (2017) 7314-7321.

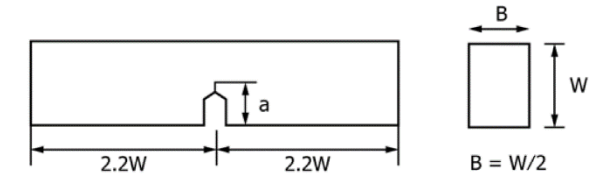
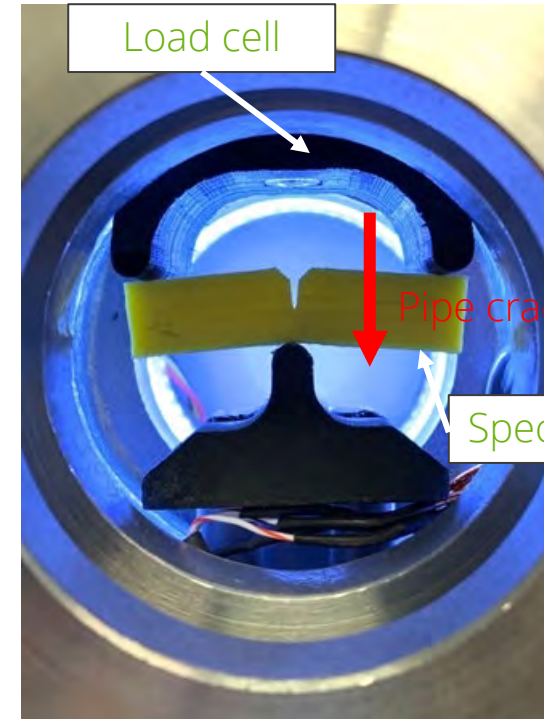


Fracture Resistance: SENB Test Setup

$$\text{Fracture Energy [N/mm]} = \frac{\text{Total work [N*mm]}}{\text{crack area [mm}^2\text{]}}$$



Ar or H₂ with 250 psi, 4hr soak
10 mm/min displacement rate



a Three Point Bend Specimen (SENB)

$B = 6.8 \text{ mm}$
 $W = 13.6 \text{ mm}$
 $a = W * 0.5$
Total length = 60 mm



- Load cell is located inside of the vessel. This separates the effect of the pressure and frictions from the measured loads.



Multi-scale Damage Morphology: HDPE

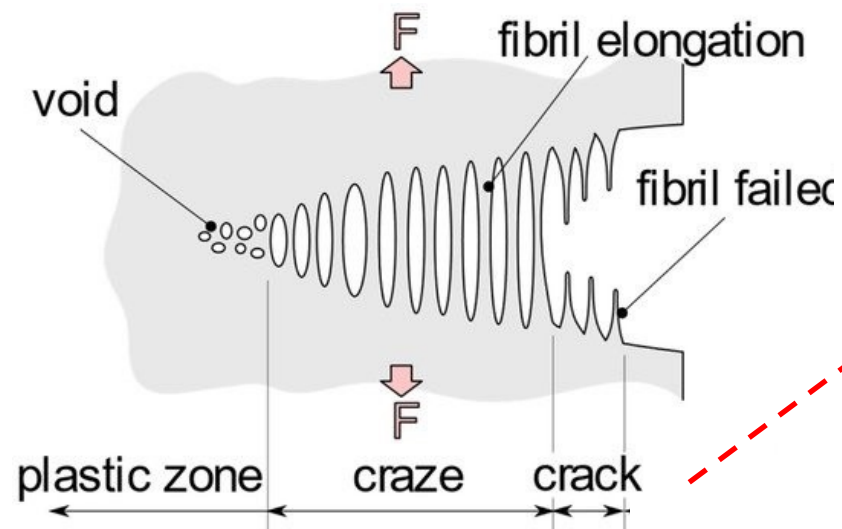
~ Nano scale



~ Micro scale



~ Macro scale



*SENB specimen was loaded up to the point corresponding to the load-displacement curve



~ Nano scale

Multi-scale Damage Morphology: MDPE

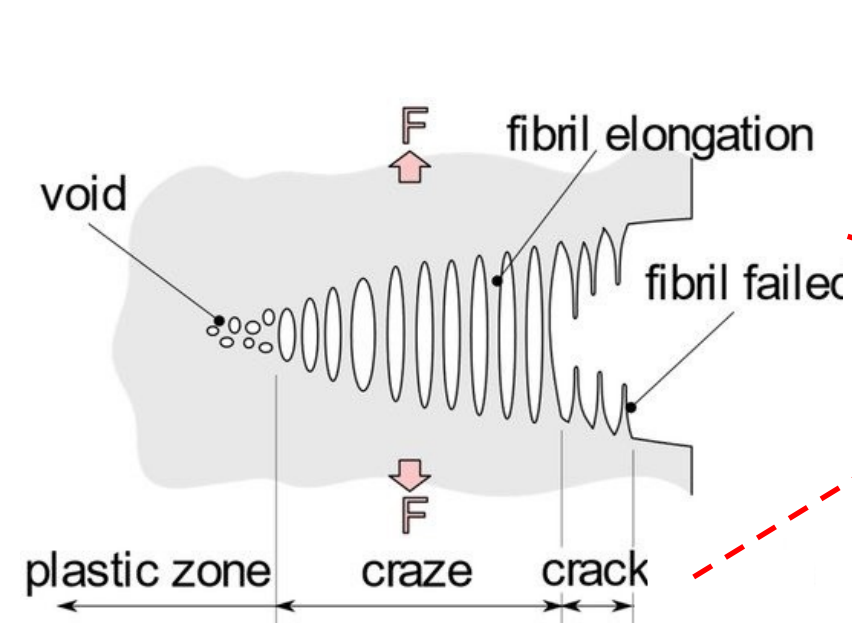
~ Nano scale



~ Micro scale



~ Macro scale



*SENB specimen was loaded up to the point corresponding to the load-displacement curve



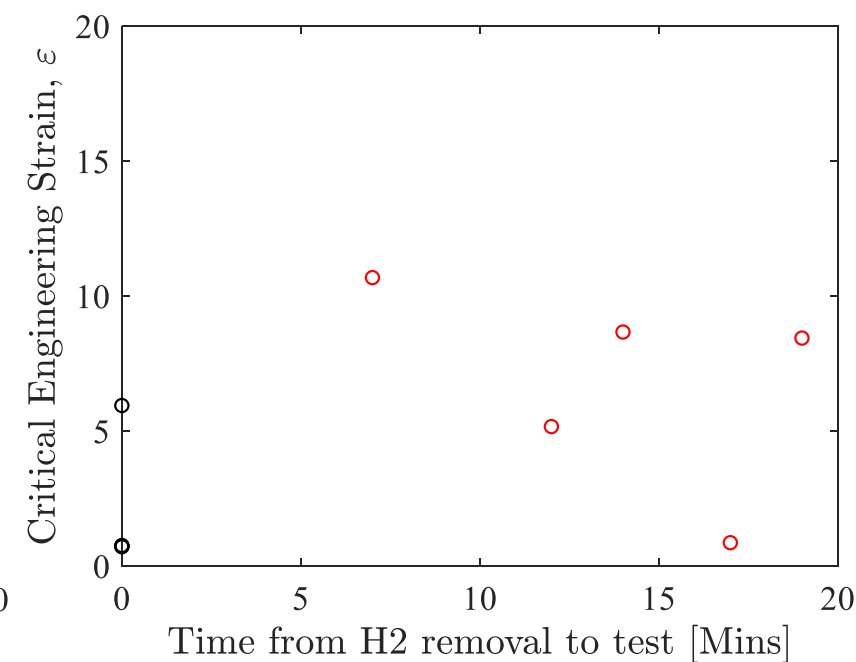
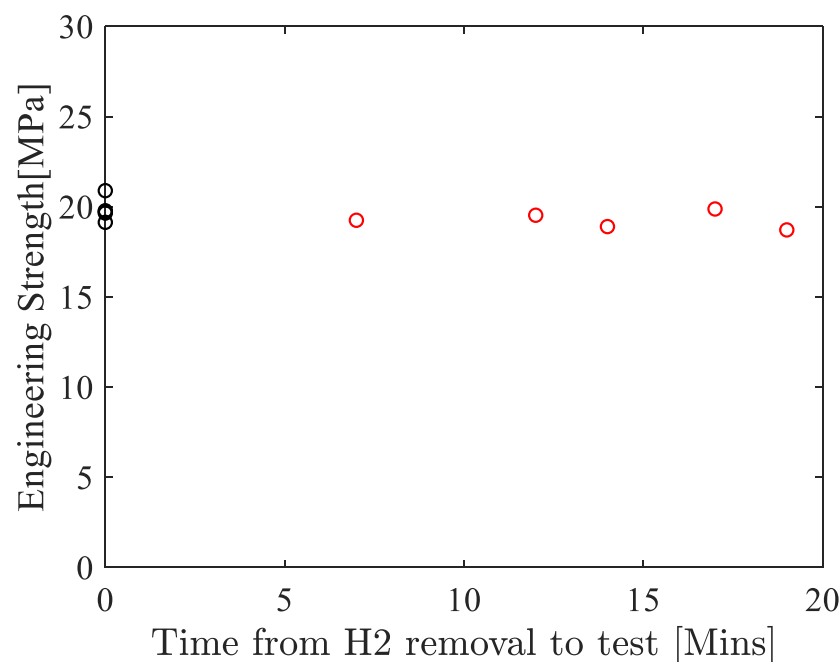
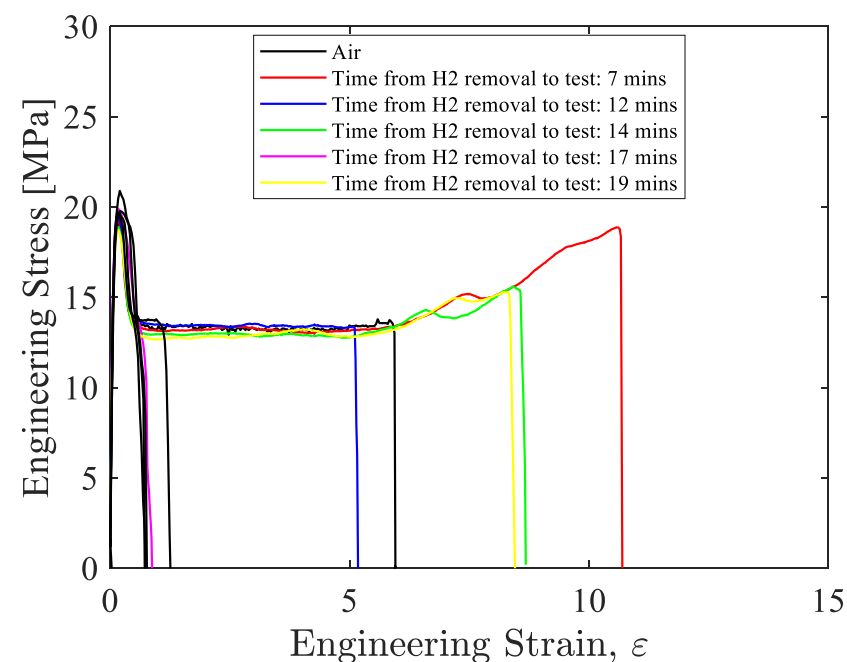
Uni-axial Tension: HDPE

Displacement rate = 100 mm/min

Type V Dogbone

1mm thickness

H₂: 250 psi, 600 hours



- Hydrogen improves the ductility of HDPE due to plasticization of hydrogen between polymer chains
- Yielding strength of HDPE was less affected by hydrogen



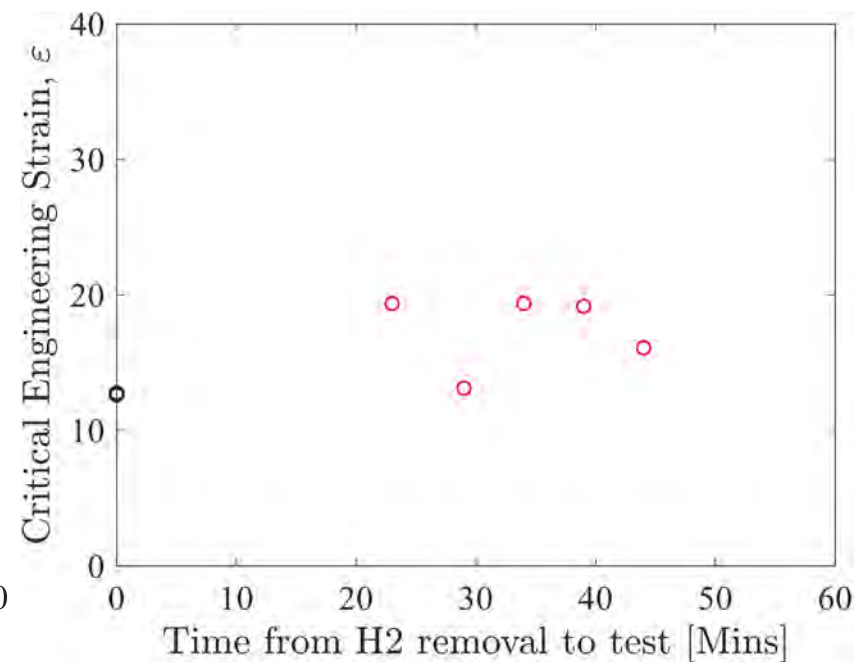
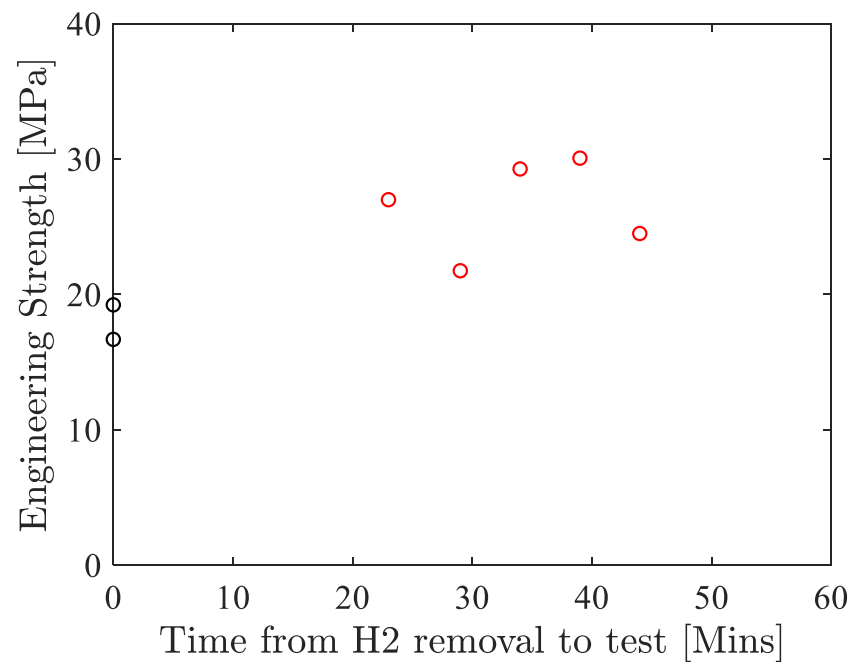
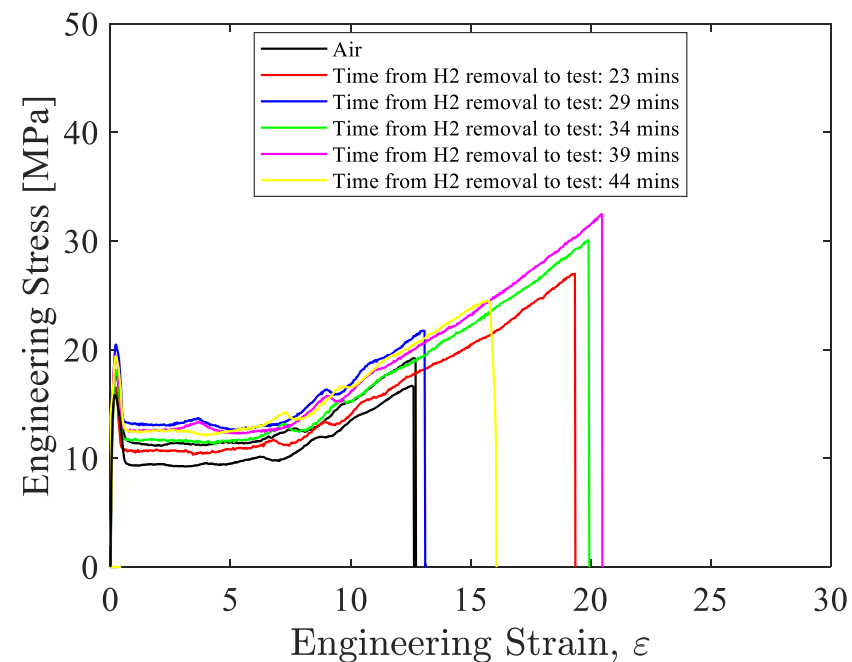
Uni-axial Tension: MDPE

Displacement rate = 100 mm/min

Type V Dogbone

1mm thickness

H₂: 250 psi, 792 hours

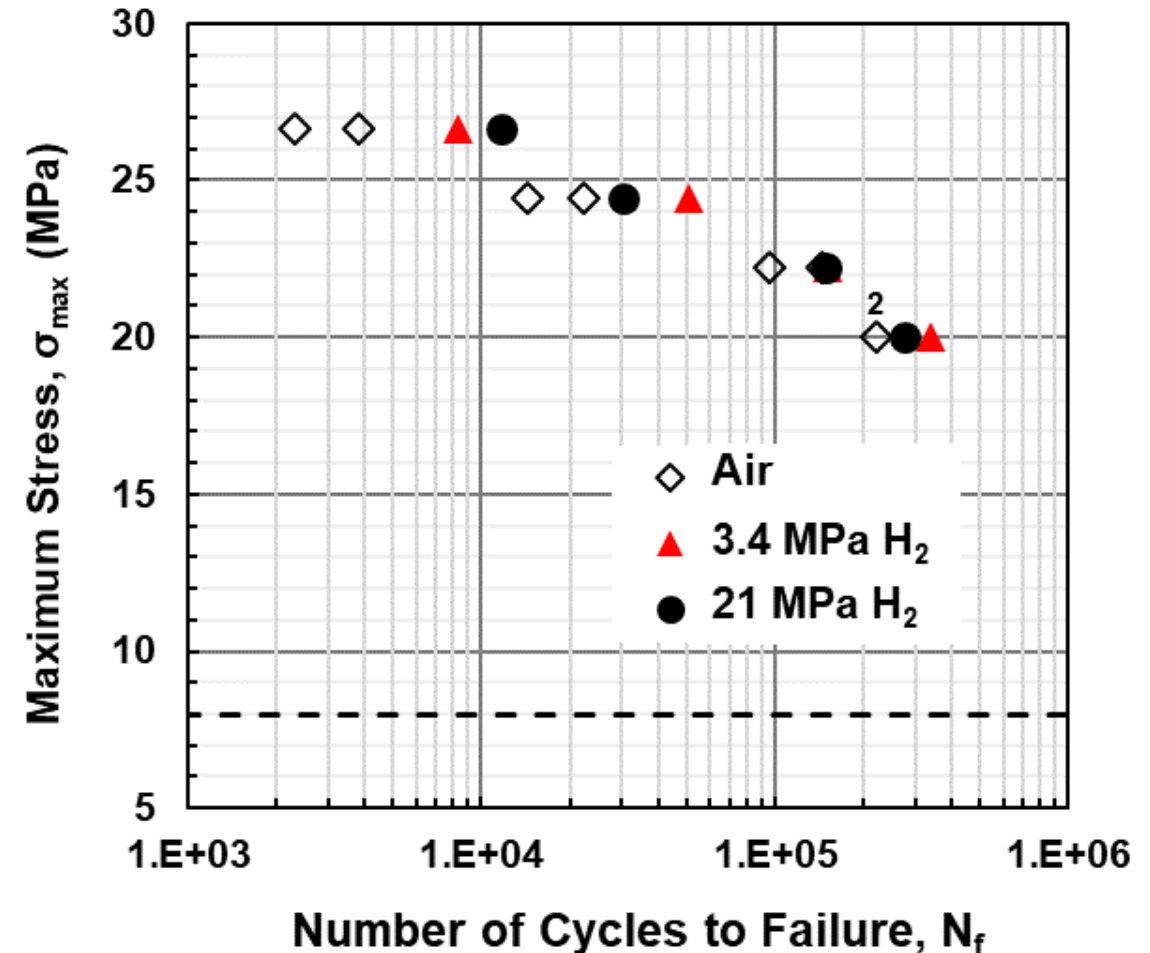
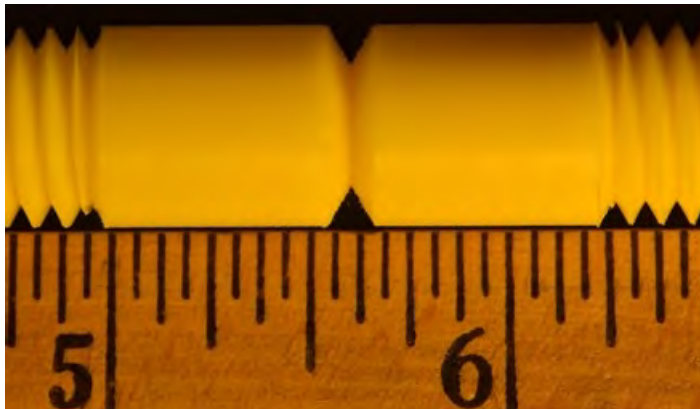


- Hydrogen improves the ductility of HDPE due to plasticization of hydrogen between polymer chains
- Yielding strength of MDPE was less affected by hydrogen



Experimental Results: Fatigue lives of MDPE polymer did not degrade in the presence of gaseous hydrogen

- At higher stress level, the fatigue lives of MDPE was observed to increase in the presence of gaseous hydrogen
- At lower stress levels, the fatigue lives in air and in presence of gaseous hydrogen were similar
- Both low and high pressure gaseous hydrogen exhibited similar effect on the resulting fatigue lives



Experimental Results: Presence of gaseous hydrogen had an insignificant effect on the fracture resistance on MDPE

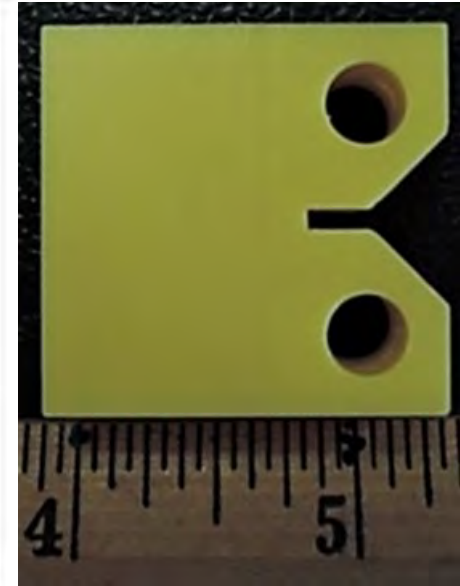
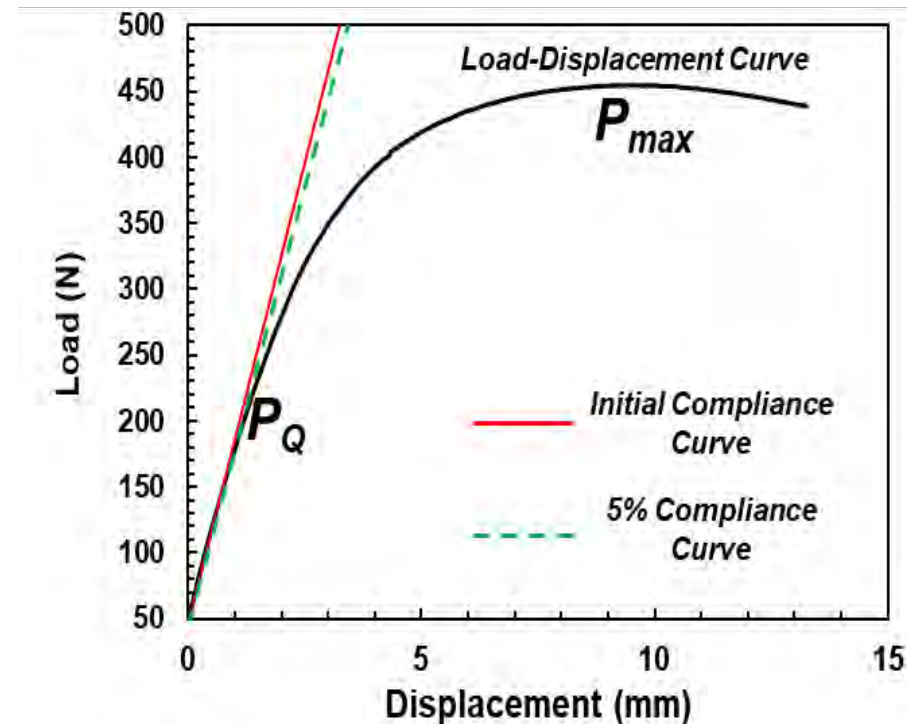
- Negligible decrease in the value of fracture resistance was observed in case of MDPE material in the presence of 3.4 MPa gaseous hydrogen
- Fracture resistance was determined based on ASTM D5045 Standard

$$\square K_Q = \left(\frac{P_Q}{B\sqrt{W}} \right) f(x)$$

$$\square f(x) = \frac{(2+x)(0.886+4.64x-13.32x^2+14.72x^3-5.6x^4)}{(1-x)^{\frac{3}{2}}}$$

- $K_{Q_air} = 1.34 \text{ MPa}\sqrt{\text{m}}$

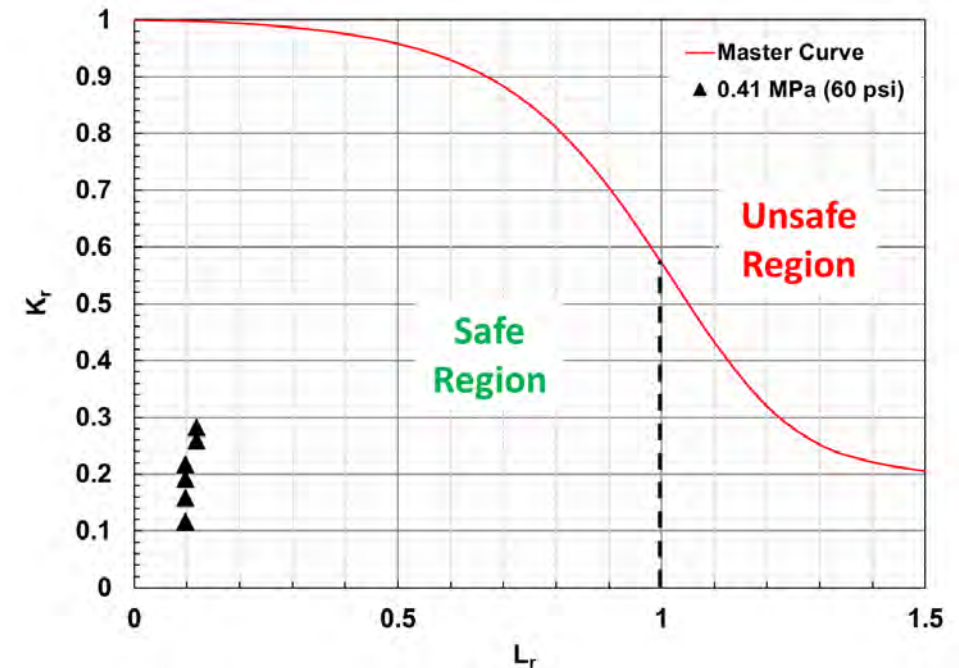
- $K_{Q_Hyd} = 1.11 \text{ MPa}\sqrt{\text{m}}$





Failure Assessment Diagram: Considering a deep crack and high internal pressure, MDPE pipe remained within the safe region

- Failure assessment Diagram (FAD) constructed based on API/ASME, “Fitness-for-service” document
- Equation of master curve is given by:
 - ❑ $K_r = (1 - 0.14(L_r^P)^2) * (0.3 + 0.7 \exp(-0.65 (L_r^P)^6))$
- K_r indicates nearness to unstable crack growth
 - ❑ $K_r = \frac{K_I^P + \phi K_I^{SR}}{K_{mat}}$
- L_r indicates nearness to plastic collapse
 - ❑ $L_r^P = \frac{\sigma_{ref}^P}{\sigma_{ys}}$
- Each data points represents different IPS pipe sizes with varying outside diameter and thickness
- For the assumed conditions, MDPE pipe remained within the safe region of FAD



Assumptions	
Flaw	Crack depth 20% of pipe thickness
σ_{ys}	20 MPa
K_{mat}	1.1 MPa√m

Performance certification for sealing materials of hydrogen refueling station storage tanks

2022. 07. 21.

Un Bong BAEK*

Korea Research Institute of Standards and Science
Division of Industrial Metrology
Yuseong, DaeJeon, Korea

KRISS 한국표준과학연구원





<https://www.h2news.kr/mobile/article.html?no=7651>

- Hydrogen refueling stations are increasing.
- Hydrogen gas leakage accidents occur at hydrogen refueling stations.
- The leakage occurs at the end-plug of the hydrogen storage tank.
- Although there are safety code for hydrogen storage vessel, but there is no standard to guarantee durability against hydrogen gas leakage from the end-plug.

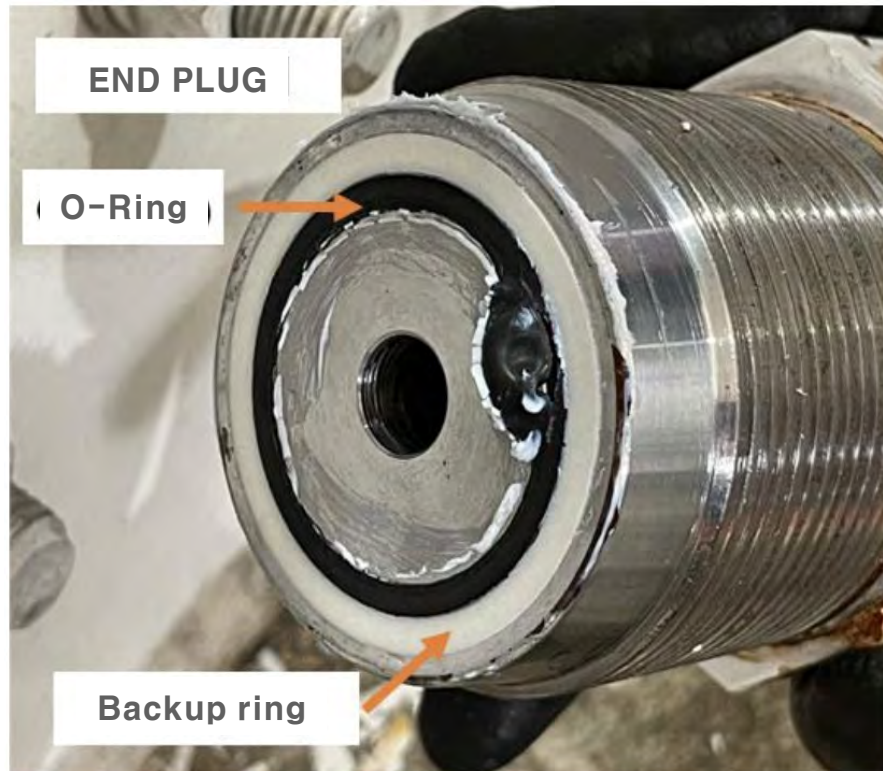
Hydrogen Leakage Case in Korea – 1 KRISs

- 1, Dae-Gu S-station
- 2, 2020, October
- 3, 3 months after operating at 85 MPa.
- 4, gas leak find out when Inspection (4000 ppm)



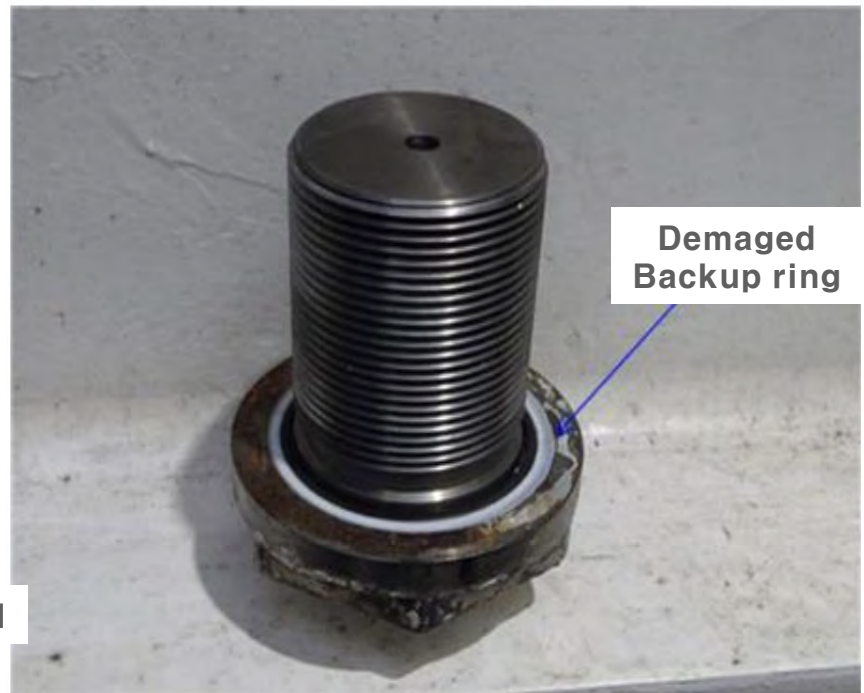
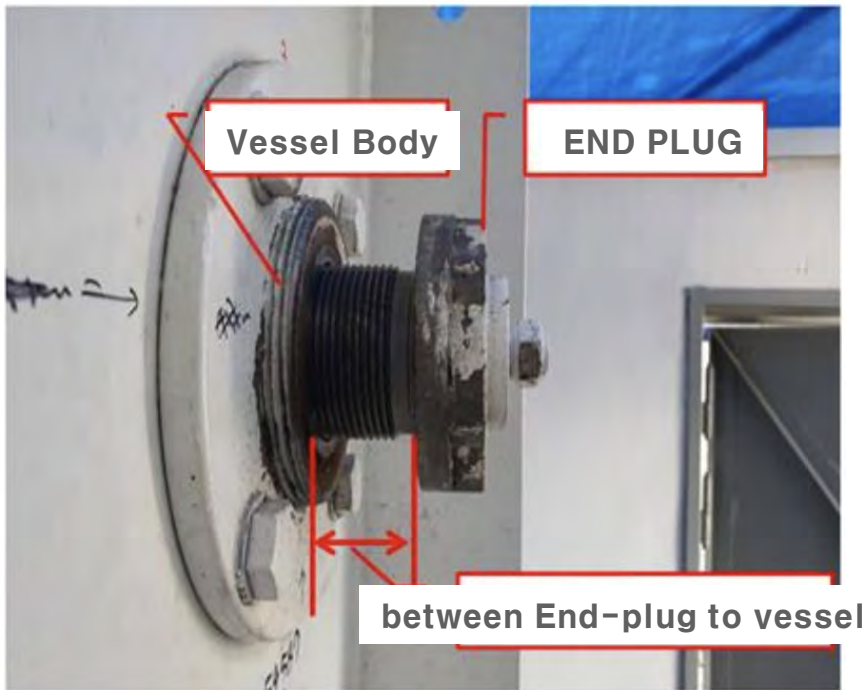
Hydrogen Leakage Case in Korea – 2 KRIS

- 1, Ul-san A-station
- 2, 2021, October
- 3, 4 year operating at 85 MPa.
- 4, gas leak find out when Inspection (> 5000 ppm)



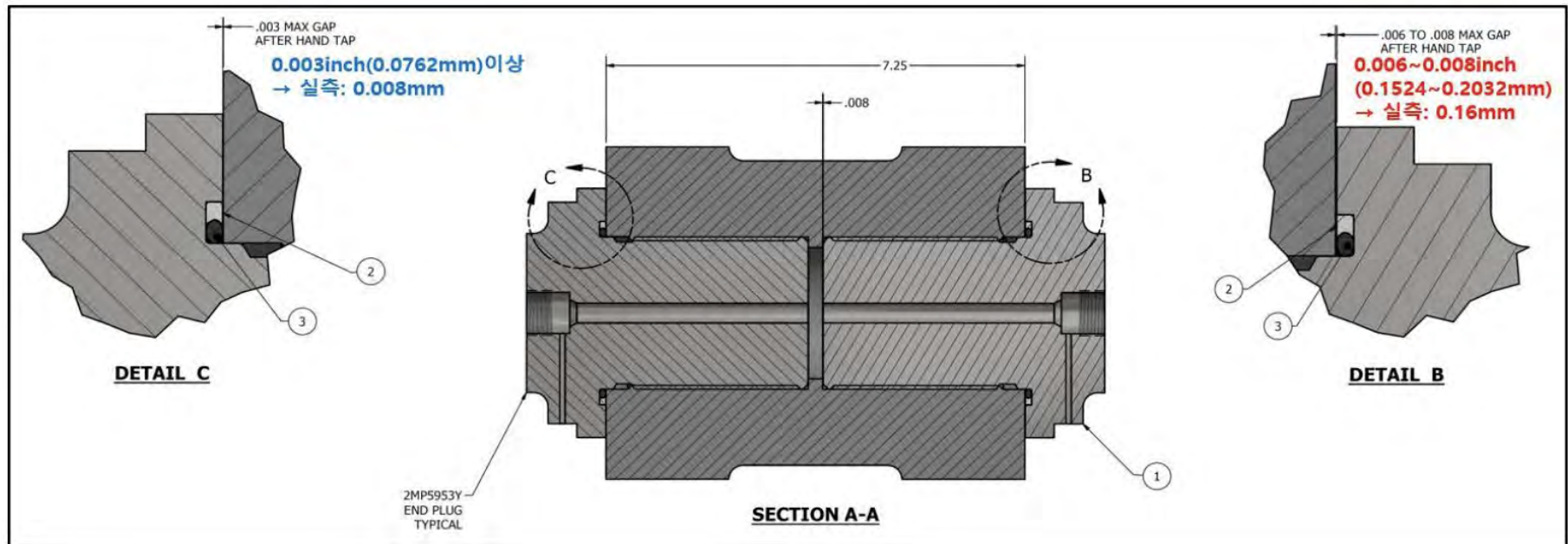
Hydrogen Leakage Case in Korea – 3 KRIS

- 1, Cheong Ju D station
- 2, 2020, August
- 3, 2 months after operating at 85 MPa.
- 4, gas leak find out from alarm.



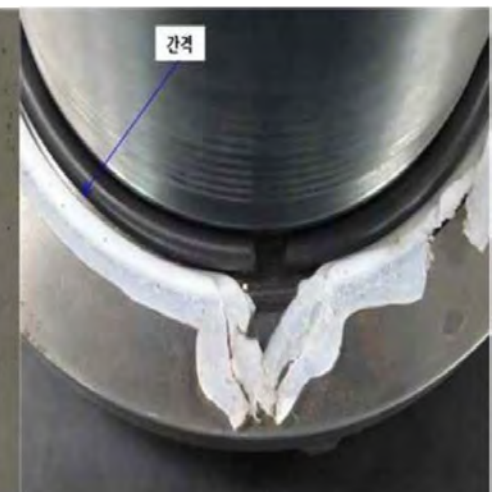
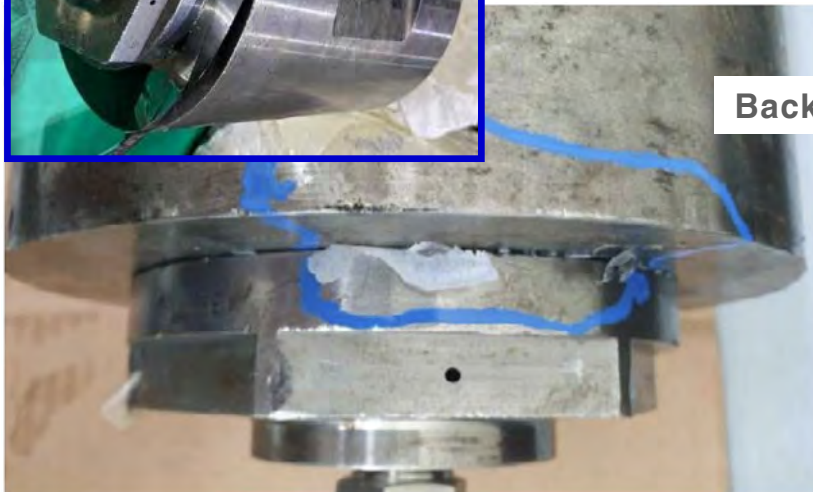
Analysis of leakage accidents in a Cheong Ju D station case

- Manufactured in the same way as the boss of the accidental vessel



Test Jig 1

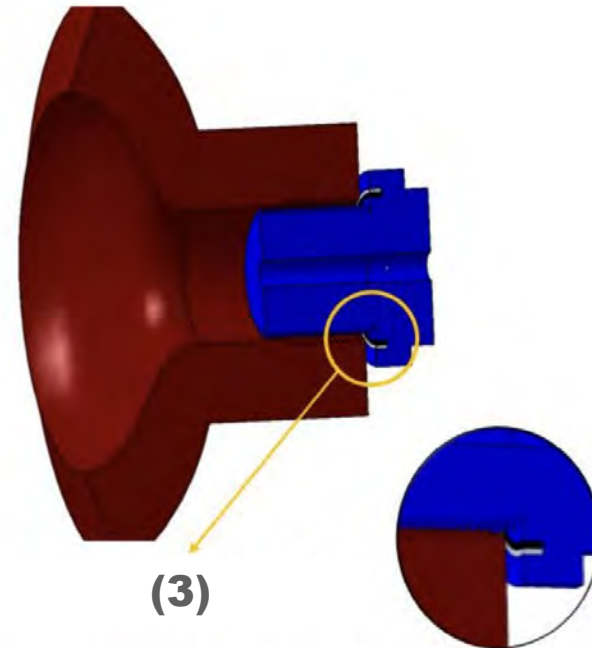
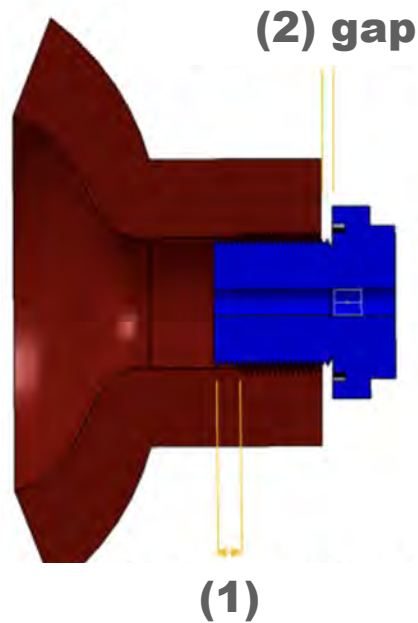
- 1, Leakage test at 96 MPa gaseous hydrogen (static)
- 2, Cyclic test between 50 MPa to 95 MPa gaseous hydrogen (cyclic)
- 3, After 4,433 cycle repeated -> Leak



Cause of Hydrogen Gas Leak

KRISS

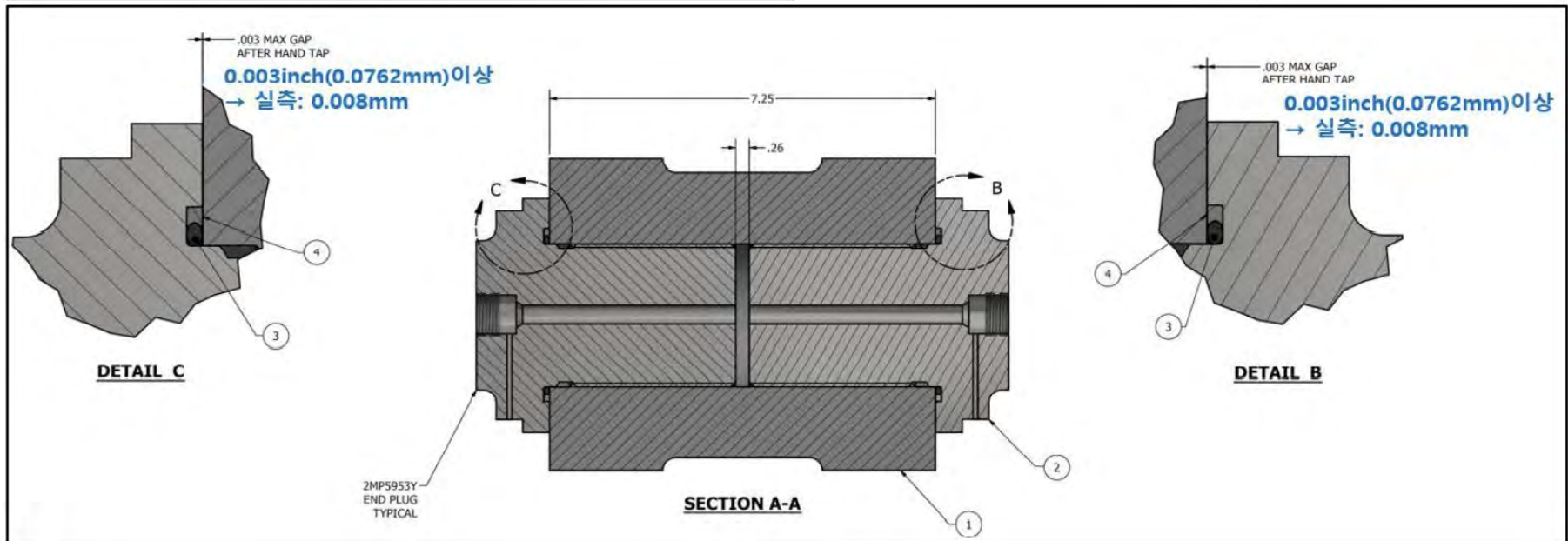
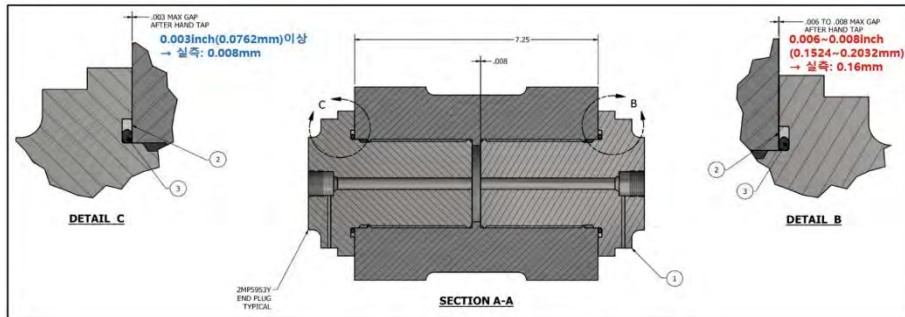
- 1, Pressure vessel internal threading.
- 2, Excessive interval between End-plug to vessel. (gap)
- 3, Insufficient backup ring strength.



Test Method for end-plug Part (Development)

KRISS

Manufactured differently from the boss of the accidental vessel(improvement)



Test Jig 2

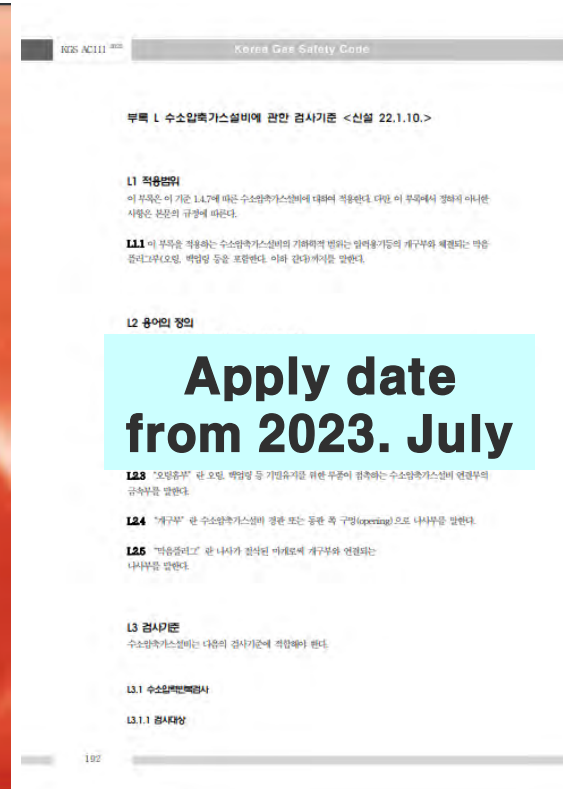
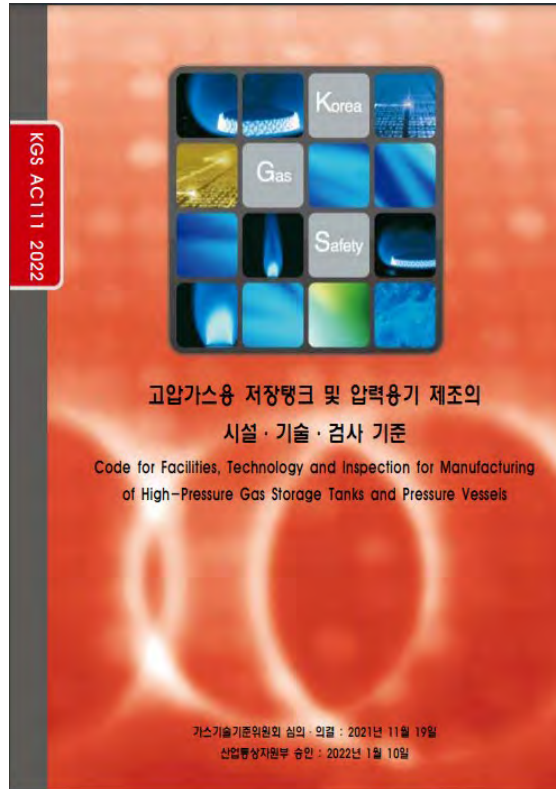
Cyclic Test Procedure

- 1, leakage test at 96 MPa gaseous hydrogen (static)
- 2, cyclic test between 50 MPa to 95 MPa gaseous hydrogen (cyclic)
- 3, 60,000 cycle repeated
- 4, leakage test at 96 MPa gaseous hydrogen (static)
- 5, pass when no leak.

Item	Test jig 1		Test jig 2	
Location	Left	Right	Left	Right
Gap	0.003 in	0.006 in (original)	0.003 in	0.003 in
Cycles	4,433	4,433	60,000	60,000
Backup ring	8 mm Extrusion (PTFE)	>10 mm Extrusion (PTFE)	2 mm Extrusion (PCTFE)	2 mm Extrusion (PCTFE)
O-ring (Viton 90)	Good	Failure	Good	Good

KGS AC111 (고압가스용 저장탱크 및 압력용기 제조의 시설·기술·검사 기준)
(Code for Facilities, Technology and Inspection for Manufacturing of High-Pressure Gas Storage Tanks and Pressure Vessels)

Appendix L : Inspection Code for High Pressure Hydrogen Tanks and Pressure Vessels



Inspection Code for High Pressure Hydrogen Tanks and Pressure Vessels

L3.1.2 시험방법

수소압력반복검사의 시험체는 최소 2개 이상의 연결부를 사용하여 다음 기준에 따라 실시한다.

(1) 시험체에 수소가스를 사용하여 설계압력까지 가압한 후 3분간 유지하여 누출여부를 확인한다.

(2) 누출여부 확인 후, 다음의 압력범위에서 수소를 사용하여 매 분당 10회 미만으로 60 000회 이상 가압한다.

(2-1) 설계압력이 87.5 MPa를 초과하는 수소압축가스설비의 경우에는 50 MPa부터 95 MPa까지의 압력구간. 다만, 설계압력이 95 MPa 미만인 경우에는 50 MPa부터 87.5 MPa까지로 한다.

(2-2) 설계압력이 87.5 MPa 이하인 수소압축가스설비의 경우에는 20 MPa부터 65 MPa까지의 압력구간. 다만, 설계압력이 65 MPa 미만인 경우에는 20 MPa부터 50 MPa까지로 한다.

(3) (2)에 따른 수소압력반복시험 후, (1)에 따라 시험체의 누출여부를 재확인한다.

L 3.1.2 Test method.

1, Leak test at design pressure using 95% N₂+ 5% H₂(or He)during 1,800 s.

2, Cyclic test(H₂ gas)

2-1, Design pressure > 87.5 MPa : 50 MPa to 95 MPa.

2-2, Design pressure : 87.5 MPa ~ 65 MPa : 20 MPa to 65 MPa.

2-3, Design pressure < 65 MPa : 20 MPa to 50 MPa.

3, 60,000 cycle repeated(10 cycle/1 minute)-125 day : 8 h/day

4, Leak test at design pressure using 95% N₂+ 5% H₂(or He)during 1,800 s.

5, Pass : no leak.

6, Minimum n = 2

The background of the slide is a vibrant blue sky with wispy white clouds and a single green paper airplane flying in the upper left. Below the sky is a lush green rolling hill with a single tree on the right. The entire scene is framed by a white window frame with two open shutters on the left and right sides. The text "Thank you for your attention !! " is written in a white, serif font across the center of the image.

Thank you for your attention !!