



HYDROGEN & FUEL CELL WEEK

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Fatigue and fracture of structural steels in gaseous hydrogen environments

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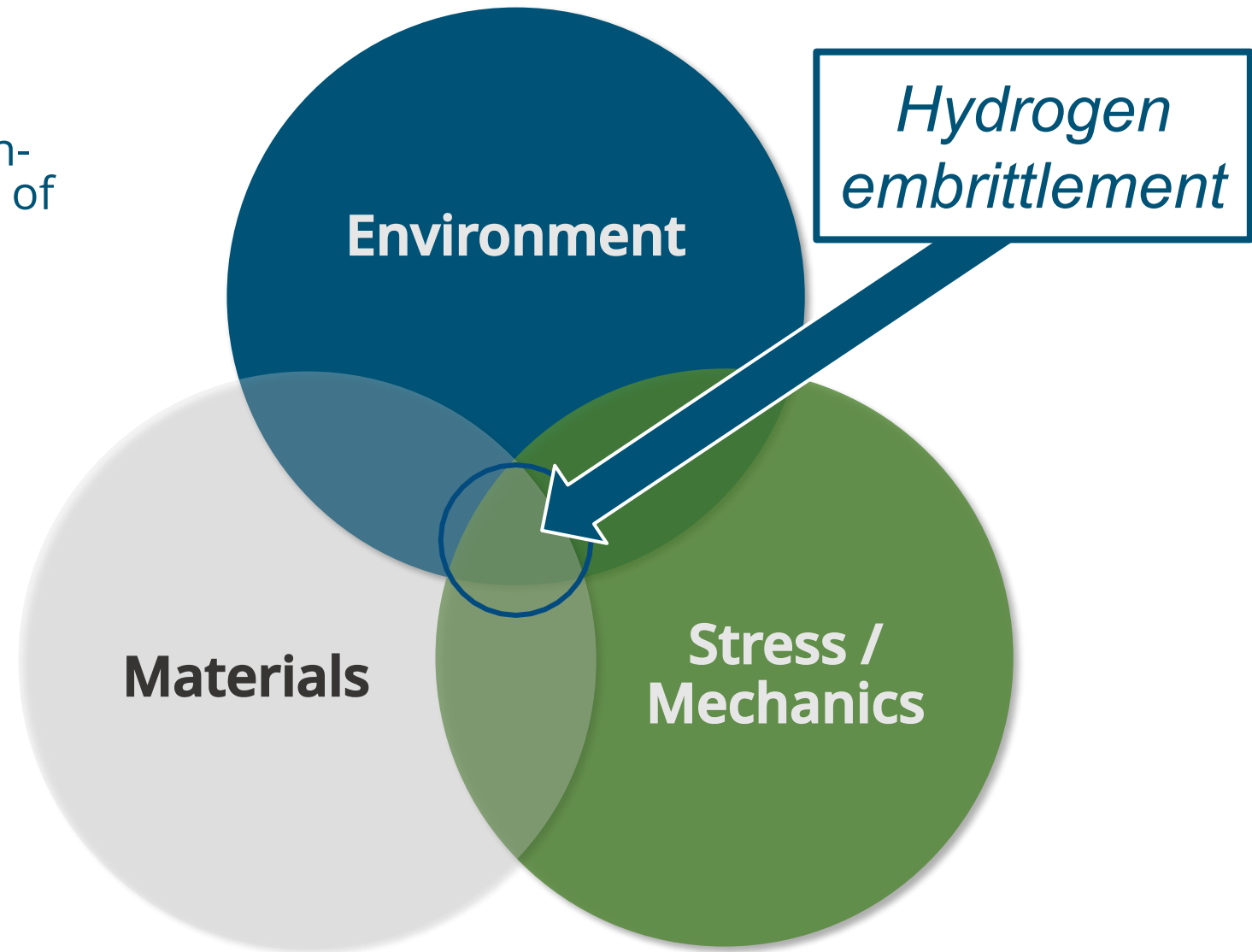


Hydrogen-assisted fatigue and fracture is sensitive to environmental, mechanical and materials variables

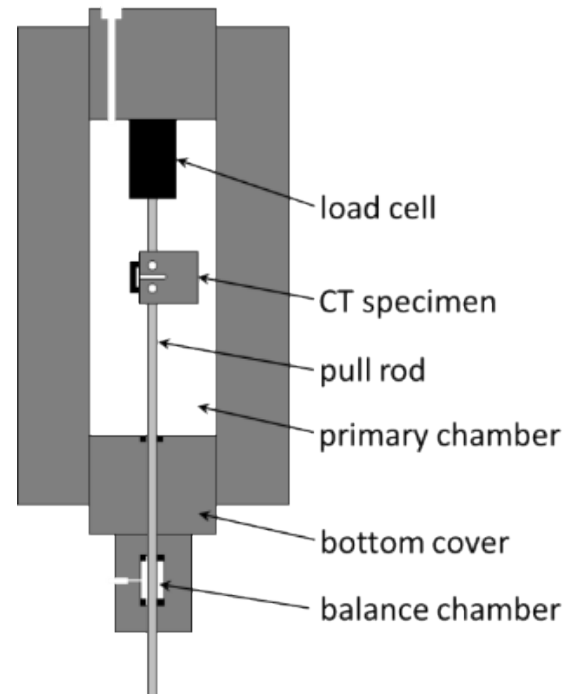
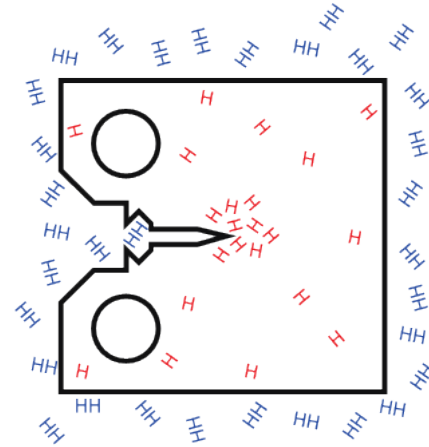
Presentation scope:

Overview of key aspects of hydrogen-assisted fatigue and fracture testing of pressure vessel and pipeline steels

- **Environment**
 - Hydrogen partial pressure
 - Impurities – oxygen/oxides
- **Mechanics**
 - Stress ratio (fatigue)
 - Fatigue frequency
 - Fracture rate
- **Materials**
 - Strength



Fatigue and fracture testing performed in gaseous H₂



Instrumentation

- Internal Load cell
- Clip gauge
- Direct Current Potential Difference (DCPD)

Fatigue crack growth: ASTM E647

- K-controlled testing
- Frequency can be varied
- Crack extension by compliance

Fracture: ASTM E1820 (J-integral)

- Loading rates can be varied
- Crack extension by DCPD

Environment

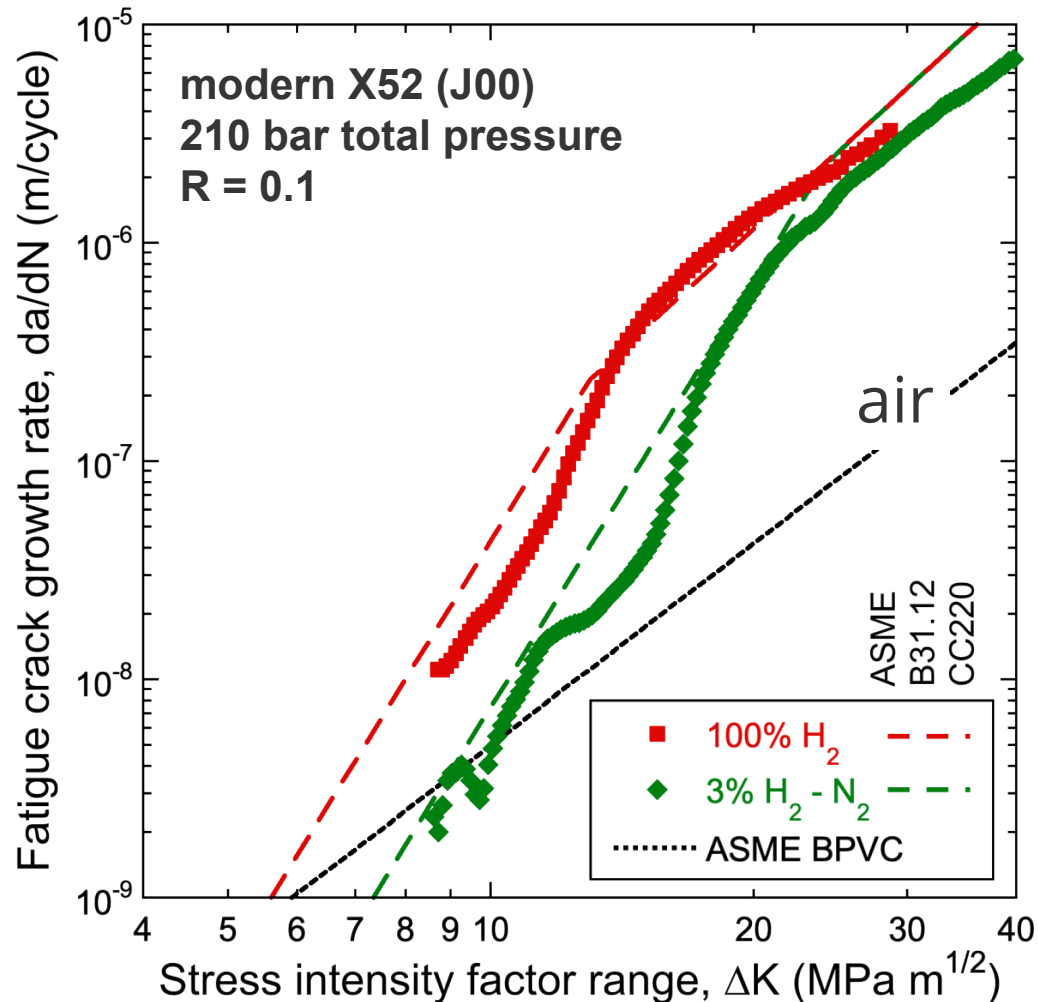
- gaseous H₂ (GH2) and gas mixtures
 - Pressure up to ~1,400 bar GH2
- Monitoring for oxygen and moisture



Environment



Environmental variables: H-assisted fatigue crack growth depends on hydrogen partial pressure for intermediate ΔK



- Thermodynamically, pressure effects should be characterized by the hydrogen fugacity (real gas behavior)
 - For intermediate ΔK , fatigue crack growth is proportional to $f^{1/2}$ (f is hydrogen fugacity – also called thermodynamic pressure)
 - At high ΔK , H-assisted fatigue crack growth is independent of fugacity

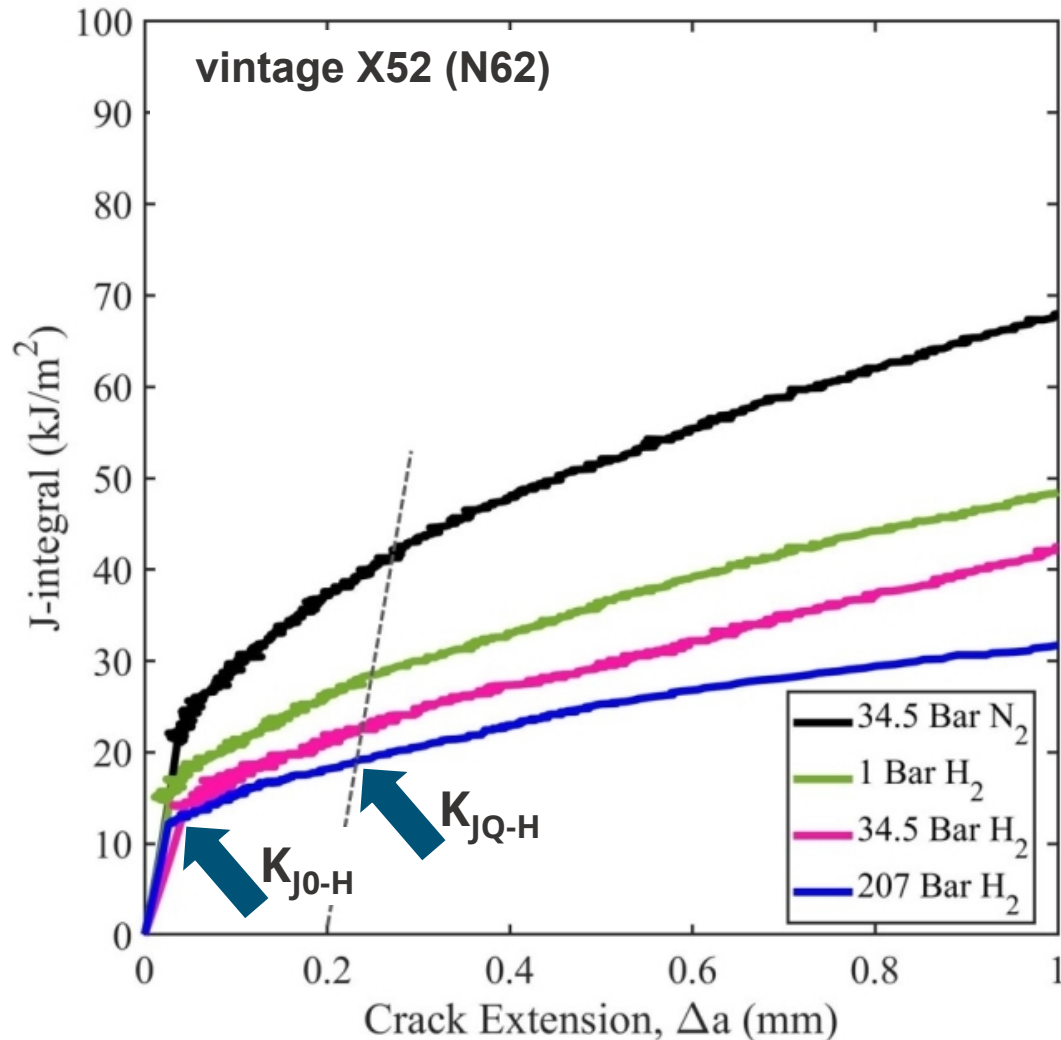
Abel-Noble EOS
Pure gas

$$\frac{f}{P_H} = \exp\left(\frac{P_H b}{RT}\right)$$

Regular solution model
Mixed gas

$$\frac{f}{P_H} = \exp\left(\frac{P_t b}{RT}\right)$$

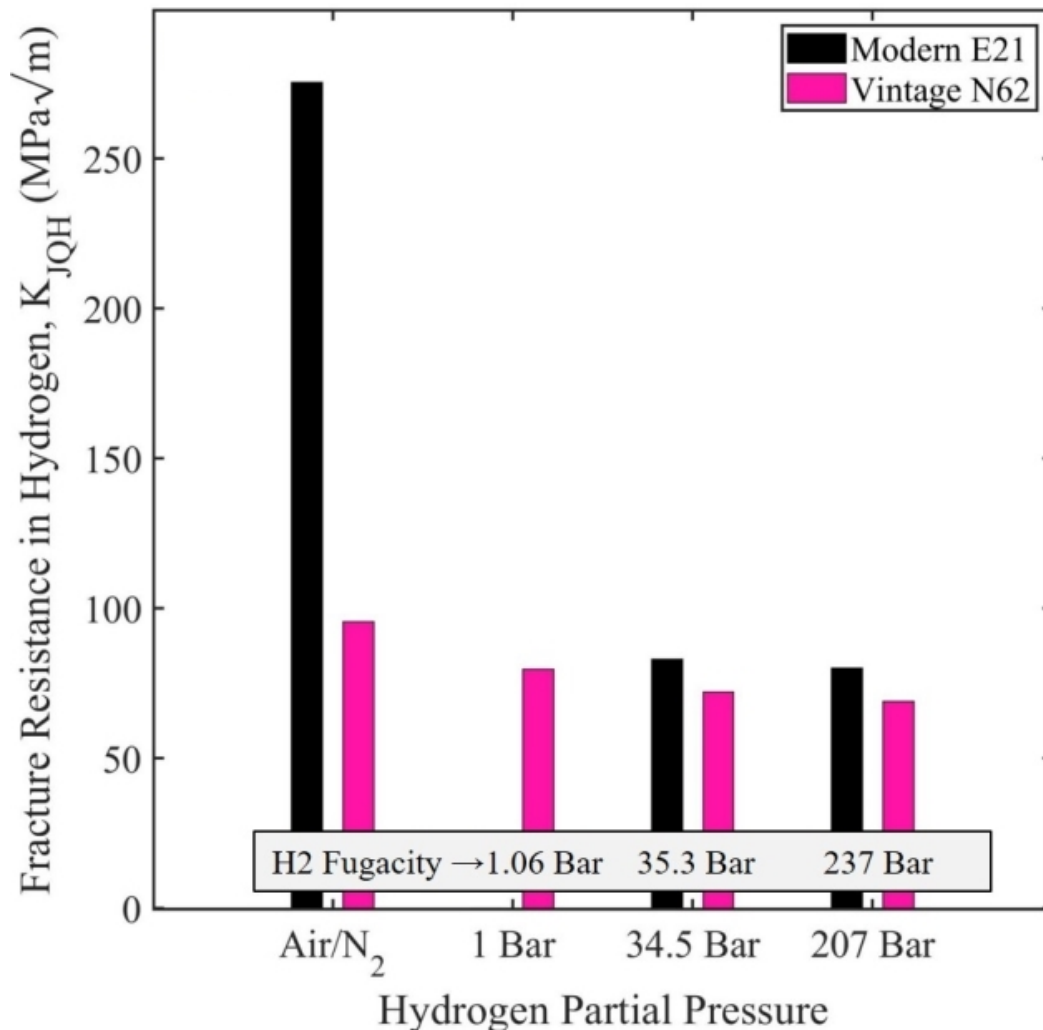
Environmental variables: H-assisted fracture degrades significantly in hydrogen partial pressure of 1 bar



- H-assisted fracture depends on the hydrogen partial pressure
 - Hydrogen partial pressure as low as 1 bar substantially reduces the fracture resistance
 - Fracture resistance continues to degrade for higher pressure, but relationship is non-linear
- Steels remain ductile in high-pressure GH2 (>200 bar), displaying elastic-plastic fracture behavior



Environmental variables: H-assisted fracture of modern steels shows greater relative reduction than vintage steels

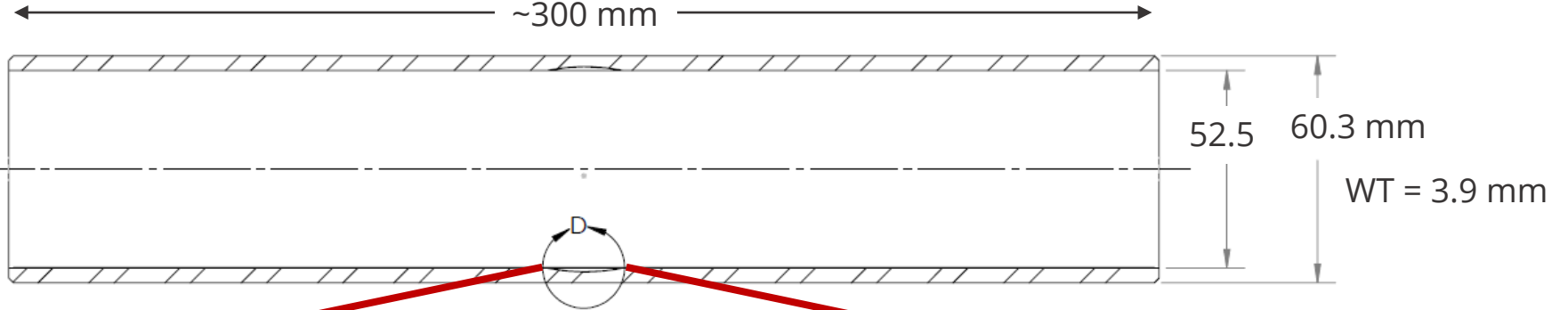
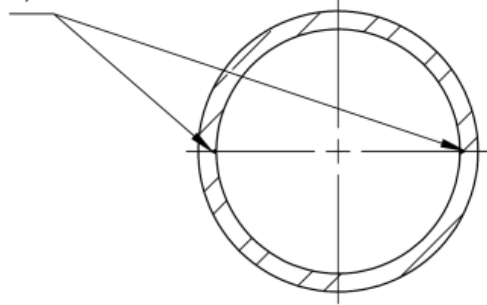


- In air, fracture toughness of modern steels is 2-4x greater than vintage steels
- In GH2, relative reduction of fracture resistance for modern steels is much greater than for vintage steels
- In high pressure GH2, the fracture resistance of modern and vintage steels is comparable
 - Similar trend with pressure for modern and vintage steels



Environmental variables: What is the role of the surface condition, oxides and oxygen on influence of hydrogen?

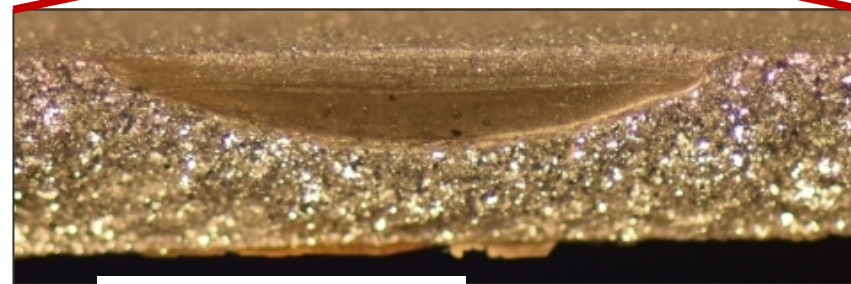
Symmetrical notches.



External defect (EDM notch)



WT



Internal defect (EDM notch)

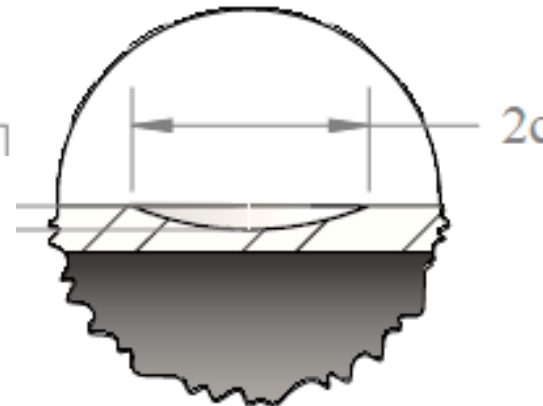
a

Nominal defect

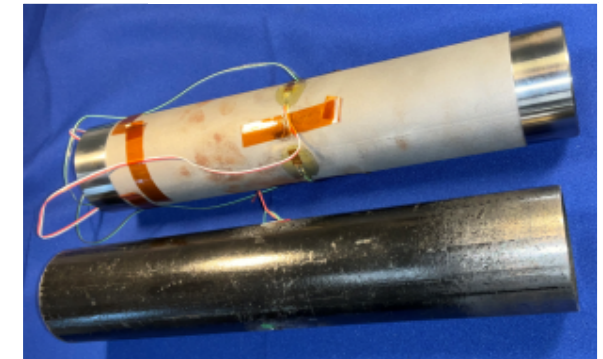
$a = 2 \text{ mm}$

$2c = 40 \text{ mm}$

(both internal and external)



NPS 2, Schedule 40



Black pipe
ASTM A53

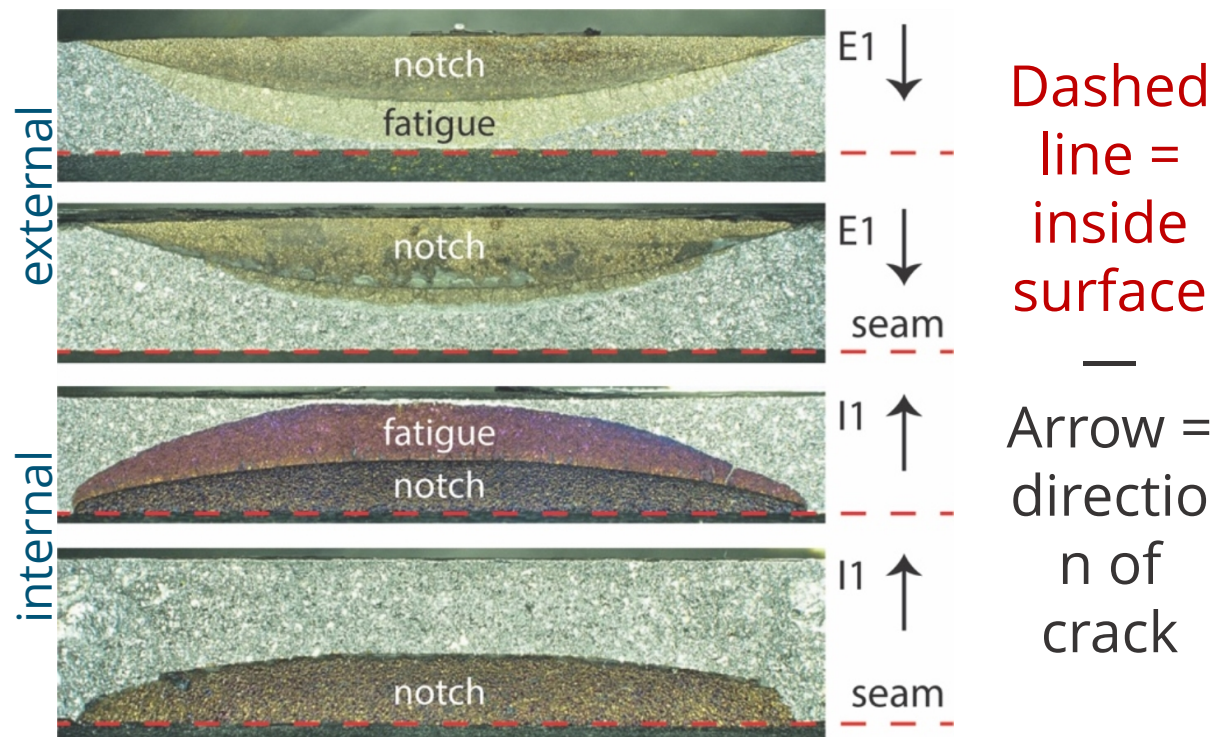
SMYS = 205 MPa
Meas. YS ~ 260 MPa



Environmental variables: Can surface oxides prevent hydrogen-assisted fatigue and fracture?

Experimental plan: compare influence of internal and external (engineered) defects on fatigue failure during pressure cycling of pipe

Specimen	Measured cycles to Failure	
	Hydrogen	Nitrogen
Internal	636	18,880
External	1,097 - 1,191	13,356



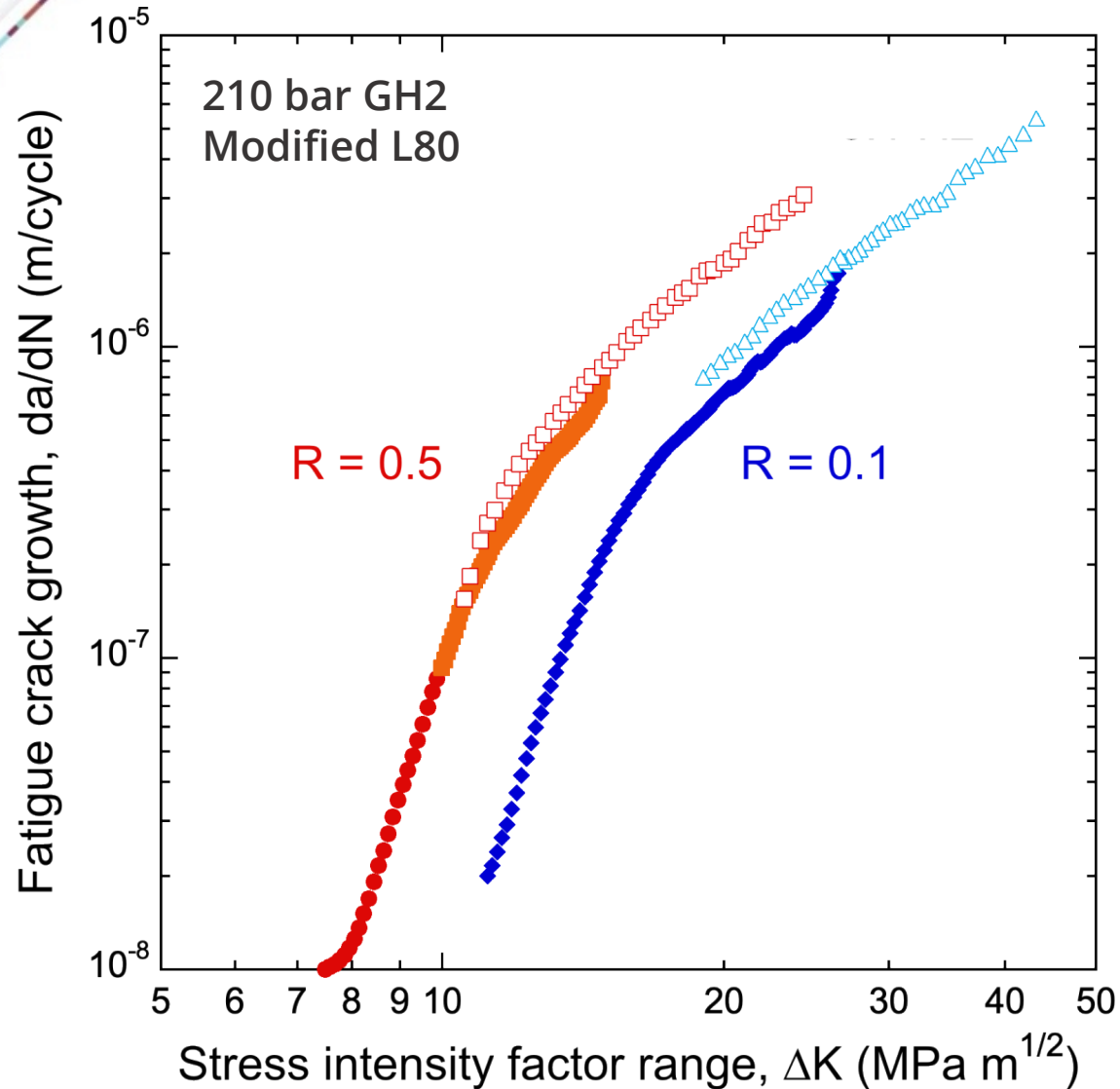
- Surface oxides on inner pipe surface do NOT prevent H-assisted fracture
- Oxygen? Stick around for talk in ~30 minutes



Mechanics



Mechanics variables: Stress ratio (R) has a significant influence on H-assisted fatigue crack growth



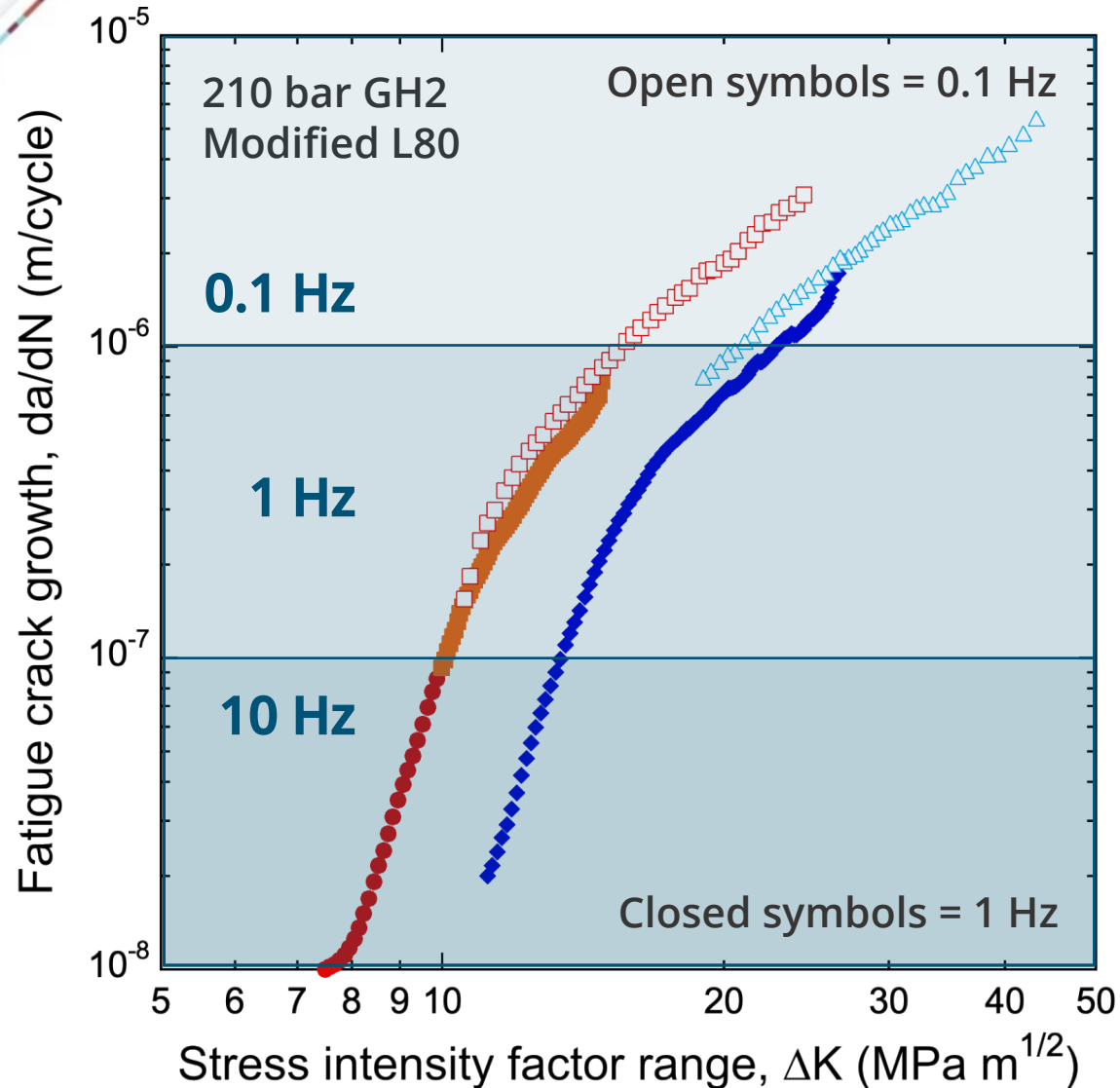
- H-assisted fatigue crack growth is more sensitive to stress ratio than fatigue in air
 - Likely related to the influence of strength on hydrogen effects
- H-assisted fatigue crack growth is characterized by a two-part power law relationship

$$\frac{da}{dN} = C \underbrace{f(R_k)}_{\text{stress ratio dependence}} \underbrace{\Delta K^m}_{\text{power law}}$$

\nearrow constant



Mechanics variables: Appropriate frequency for hydrogen testing depends on the crack growth rate



- If fatigue crack growth rates are related to hydrogen transport ahead of the crack tip, then frequency dependence will depend on the growth rate regime
 - In other words, if the crack is growing slowly, then the frequency can be higher to achieve the same da/dt

$$f^* < \frac{\dot{a}_c}{da/dN}$$

Maximum frequency

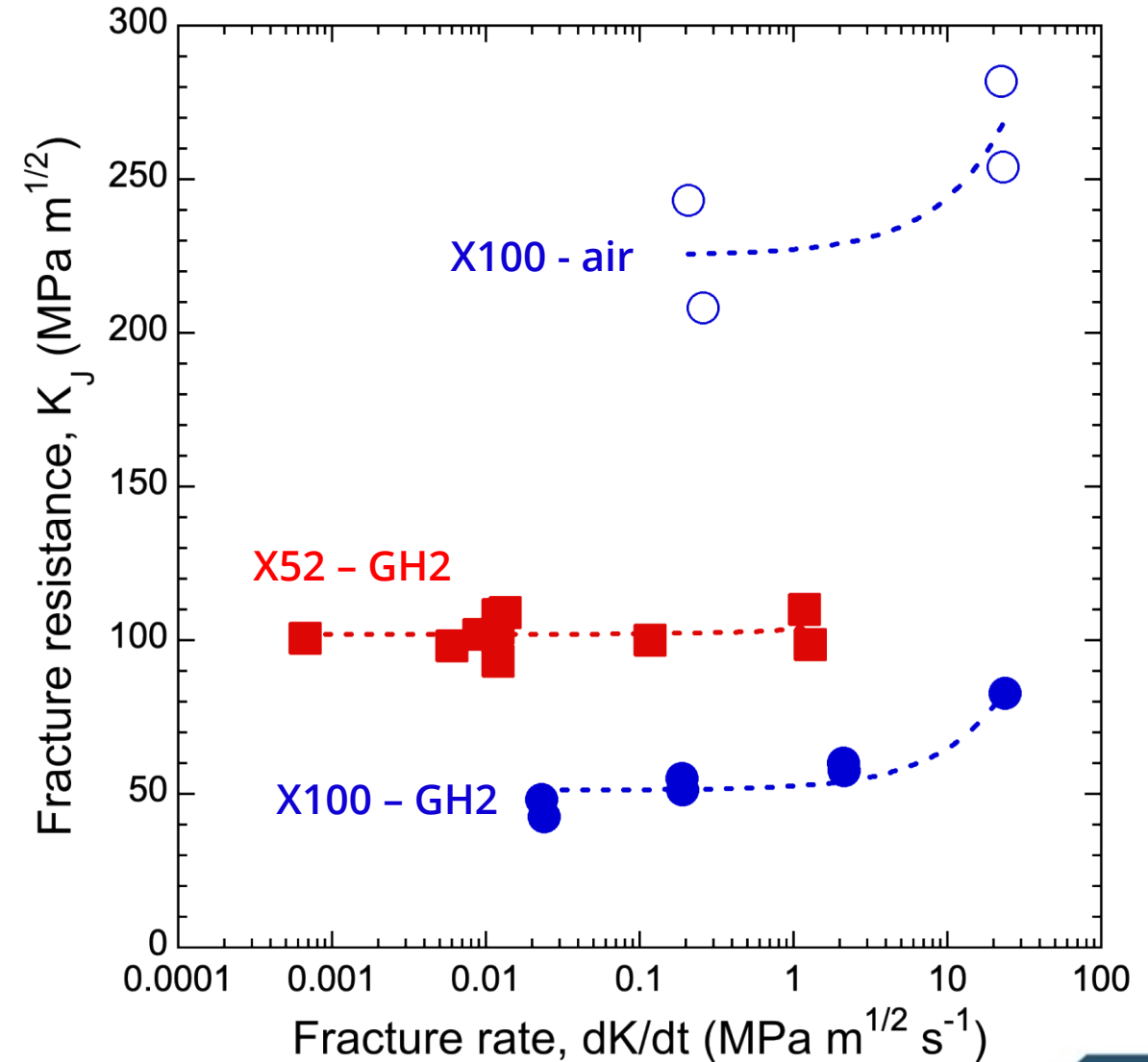
Critical crack extension rate (constant da/dt)



Mechanics variables: Testing rate is an important parameter in measurement of H-assisted fracture

- Fracture measurements can be sensitive to rate both in air and GH2
 - Substantial influence of hydrogen is evident, even when fracture test is performed rapidly (seconds)
 - Rate effects in air and GH2 show similar trend

Exceptionally slow fracture testing is generally not necessary

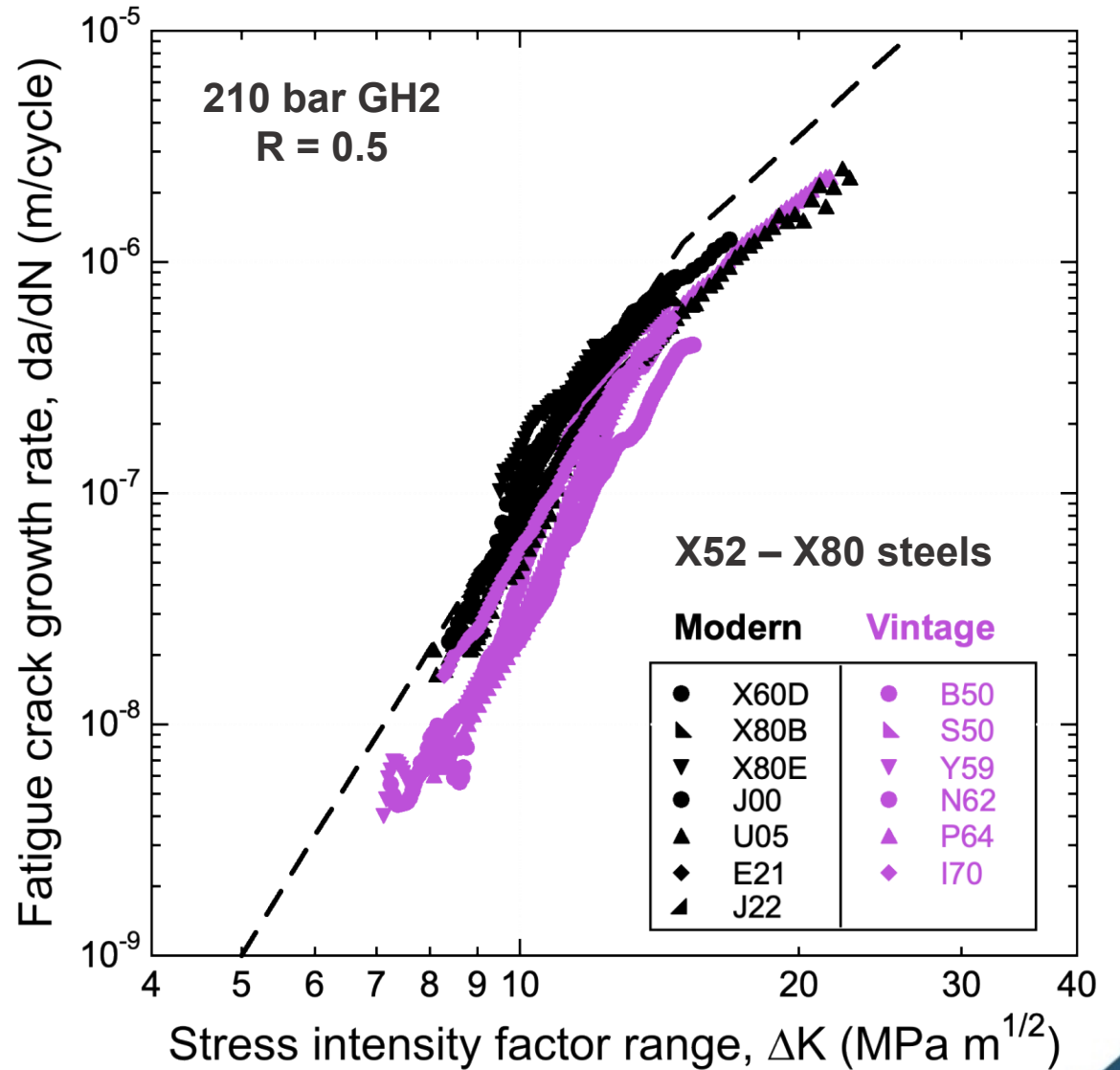
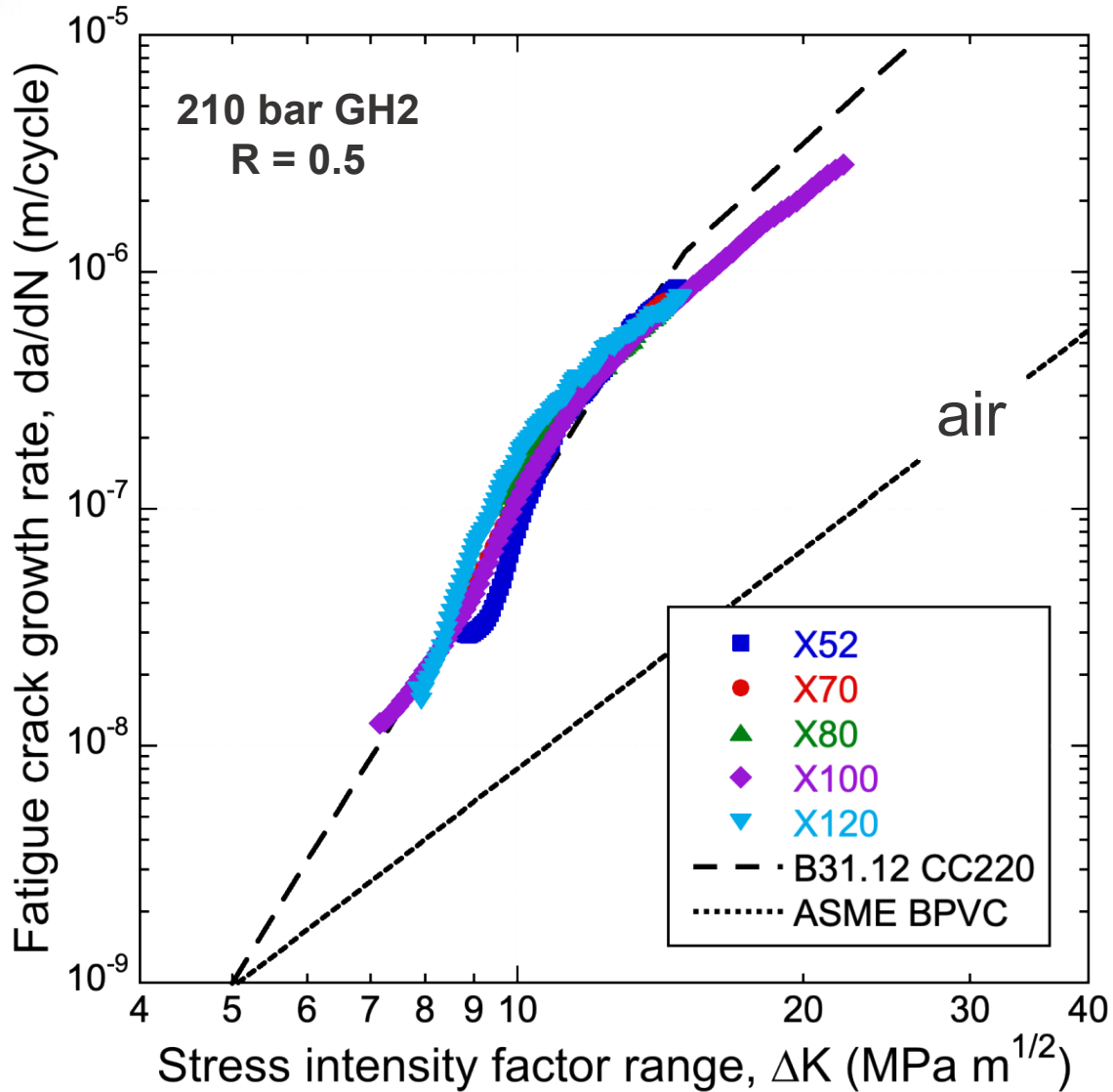


The image features a central dark blue diamond shape with the word "Materials" written in white. This diamond is surrounded by a white border and is flanked by two diagonal lines that cross each other. Each of these lines is composed of several colored segments: cyan, light blue, purple, orange, green, and dark blue. The background is white with some faint, light blue abstract shapes on the right side.

Materials



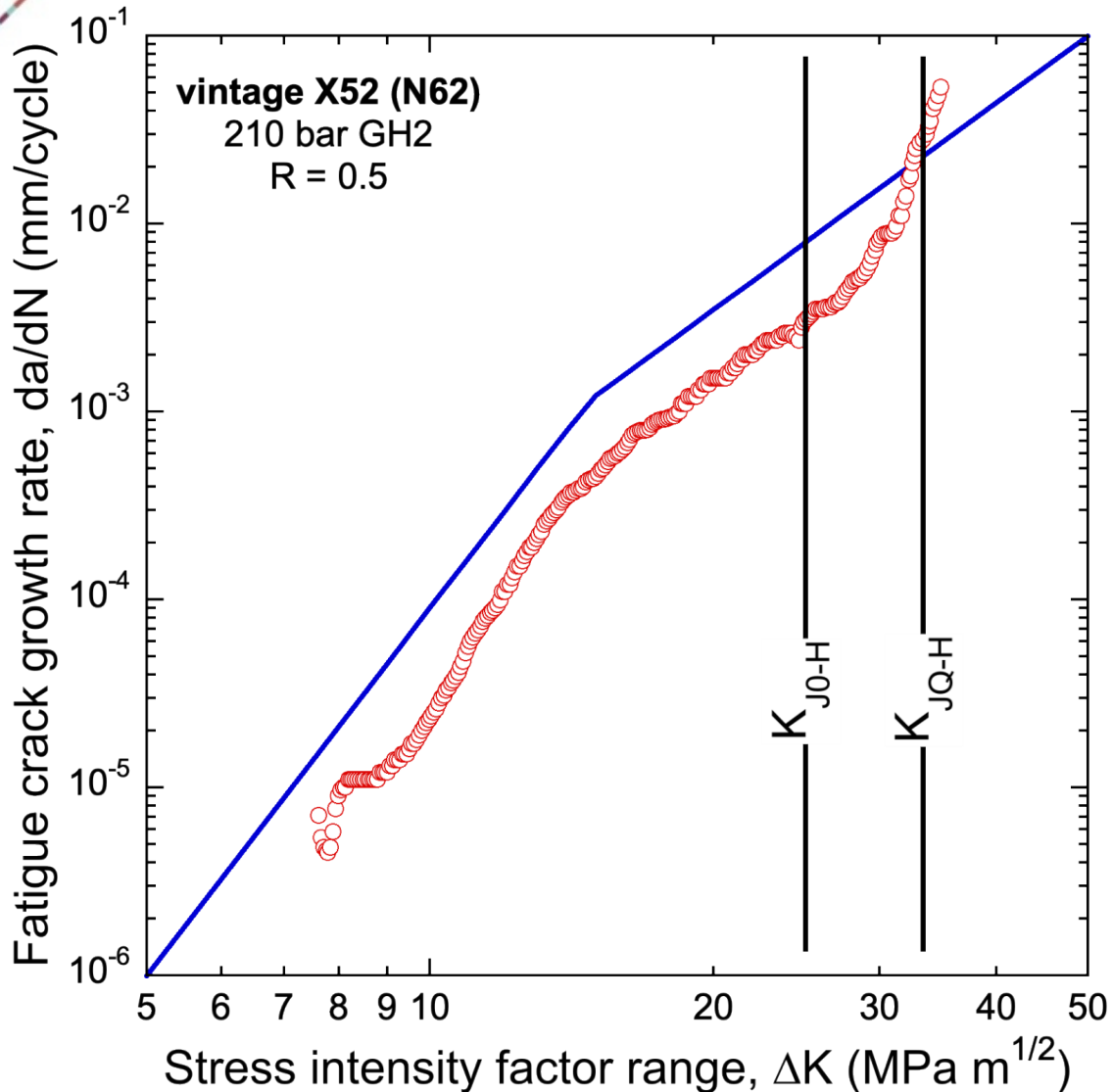
Materials variables: H-assisted fatigue crack growth does not degrade as strength increases





Caution:

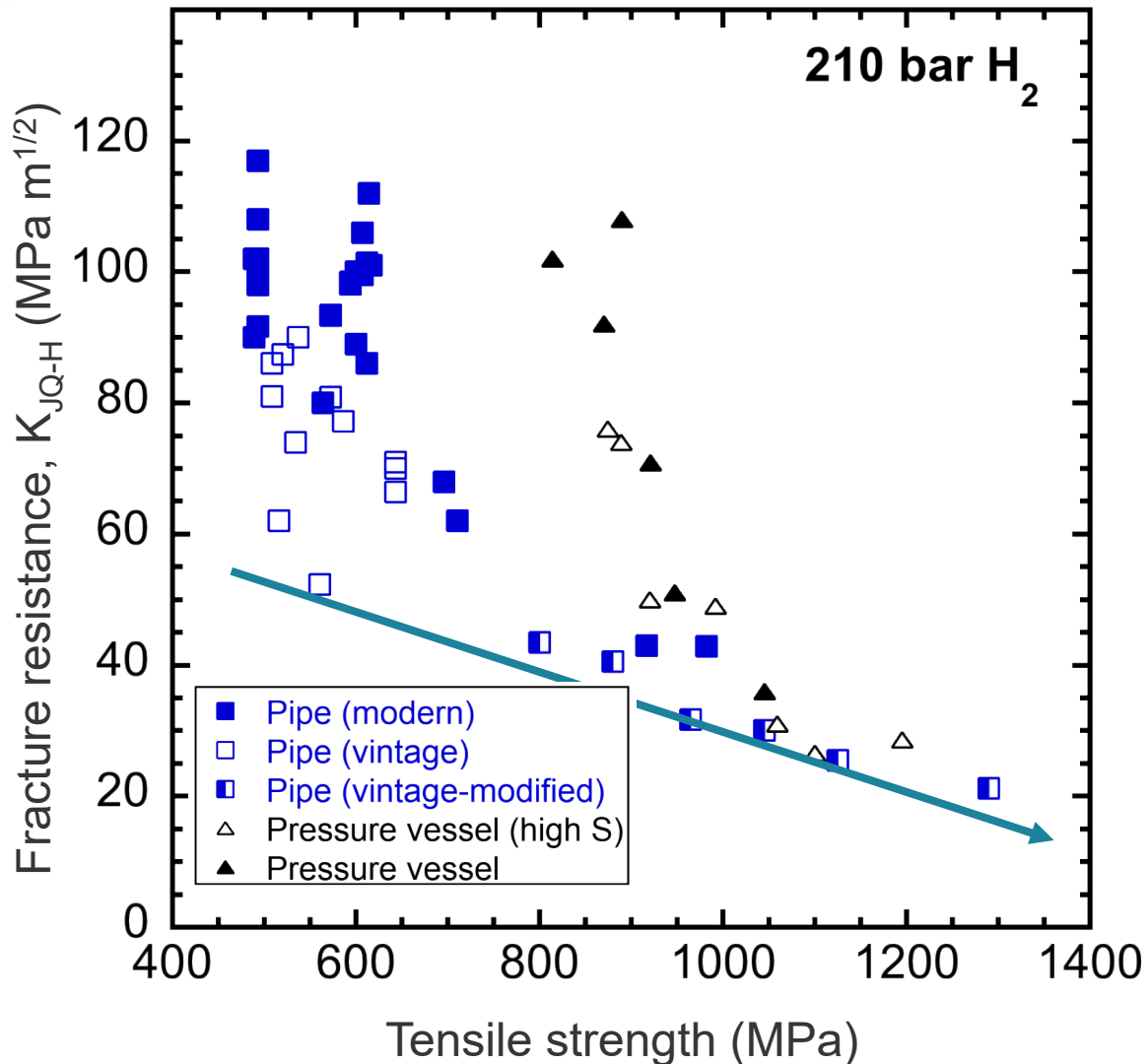
H-assisted fatigue can be influenced by the onset of fracture



- Hydrogen-assisted fracture must be considered when testing at large ΔK
 - Stable crack extension can be observed for:
$$K_{\max} (\text{fatigue}) > K_{J0-H} (\text{fracture})$$
 - However, crack extension in this region is rate sensitive
- High-strength steels will be rate sensitive (i.e., frequency dependent) at low ΔK



Materials variables: H-assisted fracture resistance degrades with strength



- Fracture resistance shows a decreasing lower bound as strength increases
 - Similar to basic trends in air
 - As a rule-of-thumb, materials with tensile strength >900-950 MPa should be avoided in hydrogen service
- High hardness in welds, and potentially hard spots in base metals, will limit fracture resistance
 - Critical size of hard zones remains an open question
- Modern steels tend to have modestly higher fracture resistance than vintage
 - Compared to very large differences in air (not shown)



Conclusions – H-assisted fatigue and fracture of structural steels

- **Hydrogen-assisted fatigue**
 - Crack growth scales non-linearly with hydrogen fugacity: $da/dN \propto f^{1/2}$
 - Stress ratio (R) has greater effect on FCGR in hydrogen than in air
 - Frequency should be considered in context of crack growth rate
 - Strength has little effect on H-assisted fatigue crack growth
- **Hydrogen-assisted fracture**
 - “first molecule is the worst molecule” – fracture is weak function of pressure
 - Slow testing rates ($\frac{dK}{dt} < 0.1 \text{ MPa m}^{1/2}$) may not be necessary
 - Steels with tensile strength > 900-950 MPa should be avoided in hydrogen service (or used with caution)



Thank you for your attention!

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Additional resources

<https://h-mat.org/>

<https://www.sandia.gov/matsTechRef/>

<https://granta-mi.sandia.gov/>

<https://helpr.sandia.gov/>



Hydrogen Effects on Materials Laboratory

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Rob Wheeler
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Brendan Davis
James McNair
Keri McArthur
Tanner McDonnell



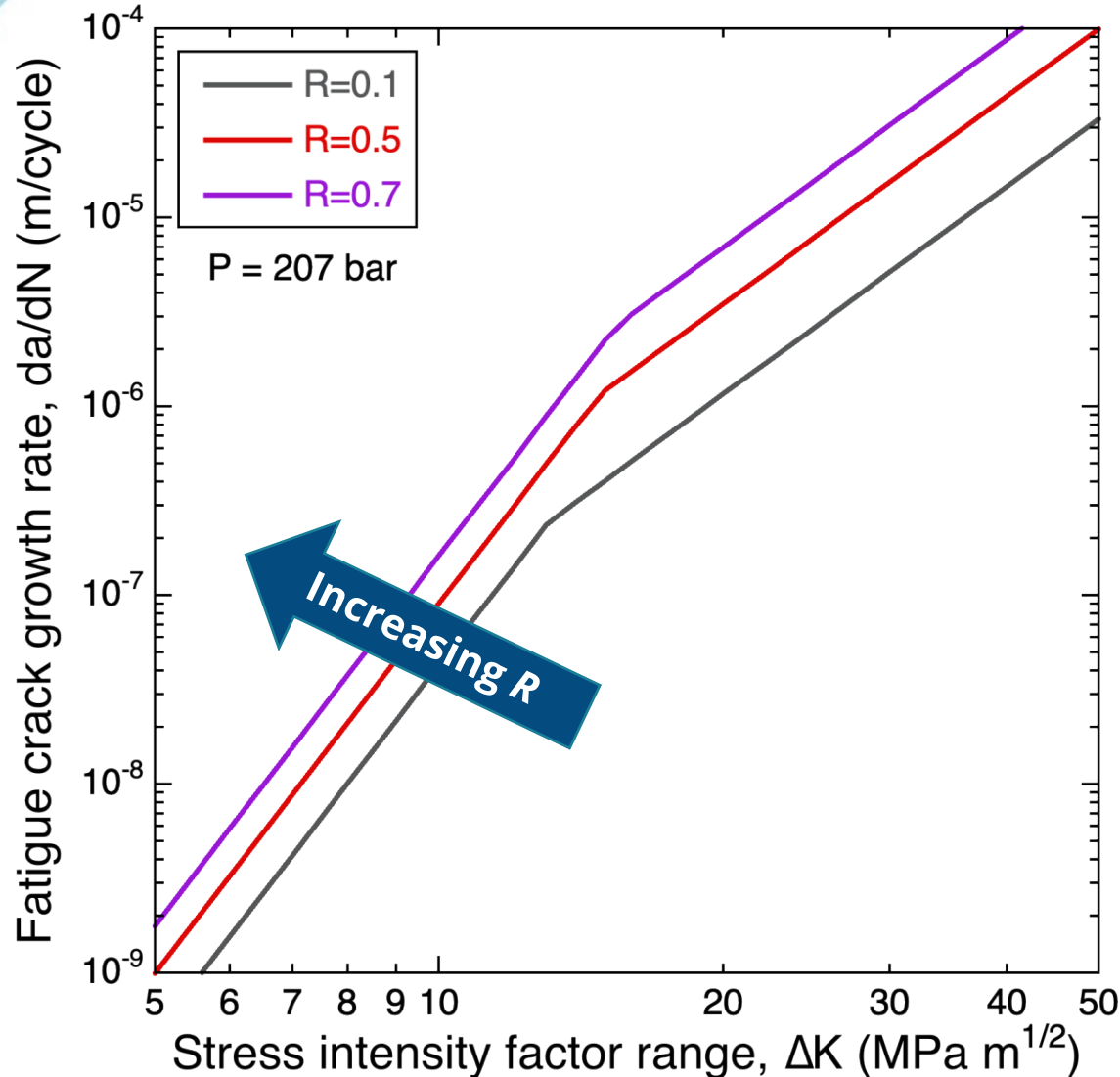
For details on HyBlend, email:
<HyBlend_CRADA@nrel.gov>

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Mechanics variables: H-assisted fatigue is sensitive to stress ratio (R) and stress intensity factor range (ΔK)



- Based on extensive data, ASME adopted generic fatigue design curves for hydrogen, featuring:
 - Two-part power law formulation analogous to form in ASME codes
 - Single formulation for pressure vessel and linepipe steels (similar to existing design curves)
 - “pressure” term proportional to the square root of the hydrogen fugacity

$$\frac{da}{dN} = C \underbrace{f(R_k) \Delta K^m}_{\text{basic ASME form}} \underbrace{f(P)}_{\text{Pressure term}}$$