

# Hydrogen-assisted fatigue and fracture of pipeline materials in natural gas infrastructure: trends and implications on structural integrity

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

*Derived from:*

SAND2022-8360-DE

2022 Center for Hydrogen  
Safety Americas Conference

20-22 September 2022



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.

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.

## Motivation

With growing interest in decarbonization, hydrogen is being considered as a means to reduce carbon in energy infrastructure

## Challenge

Hydrogen degrades fatigue and fracture resistance of steels, and the effects on pressure vessel and line pipe steels are significant

### Environment

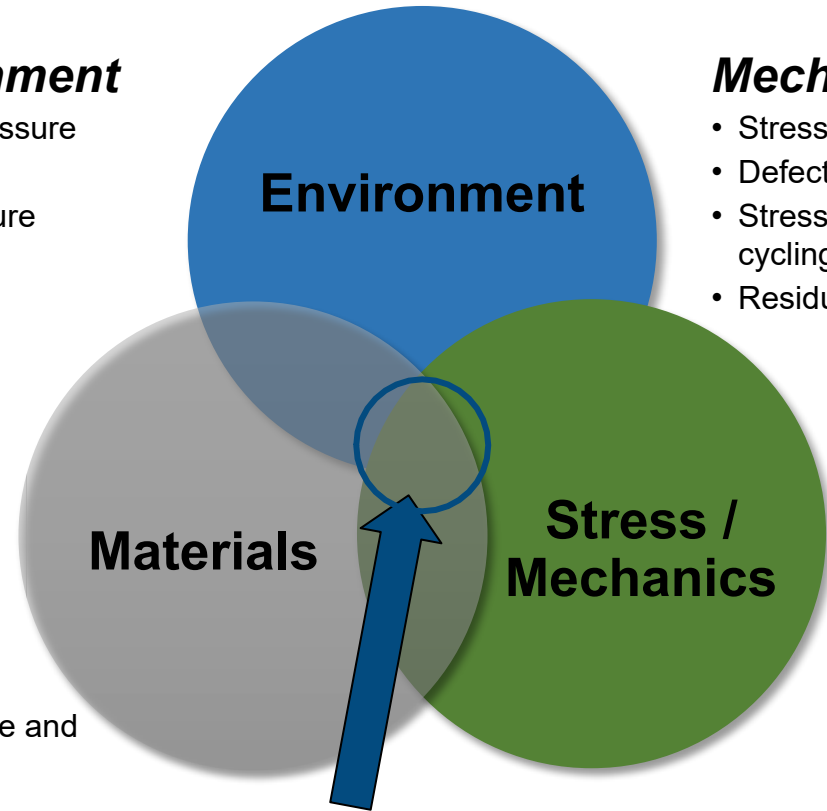
- Partial pressure
- Impurities
- Temperature

### Mechanics

- Stress
- Defects
- Stress (pressure) cycling
- Residual stresses

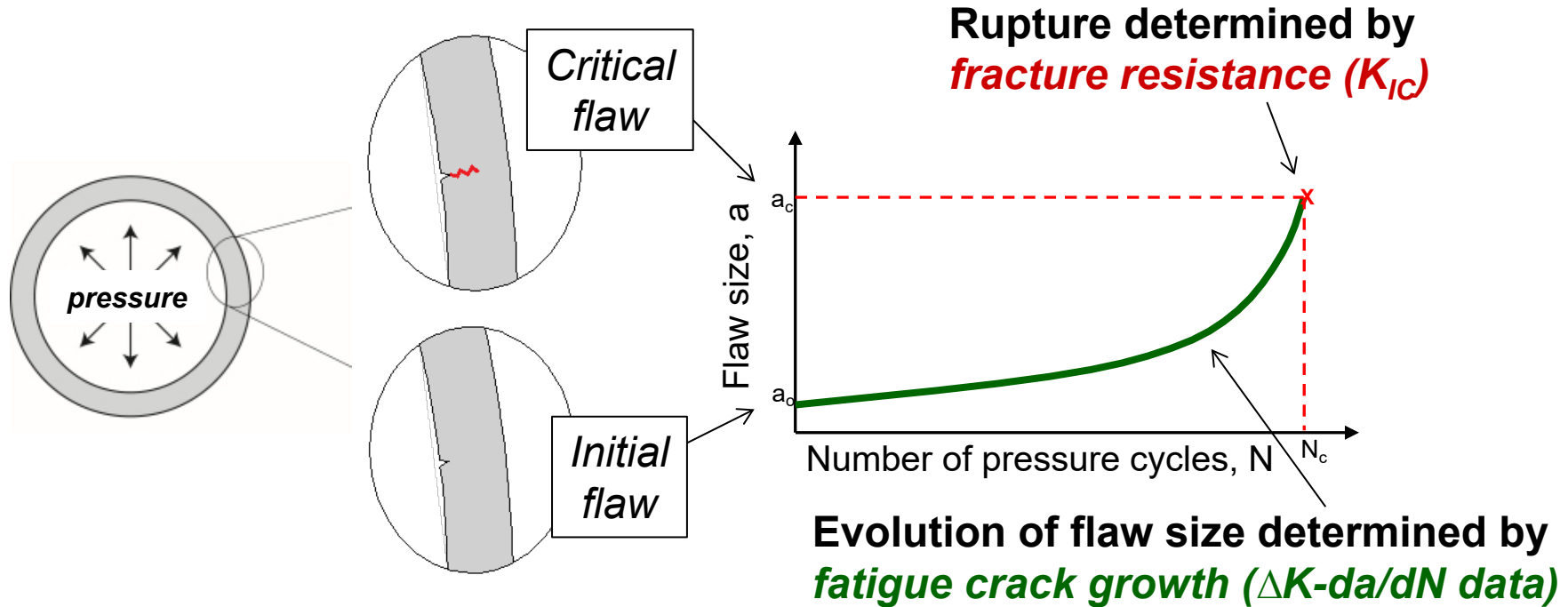
### Materials

- Strength
- Microstructure and homogeneity



*Hydrogen embrittlement occurs in **materials** under the influence of **stress** in hydrogen **environments***

# Structural integrity assessment: Basic requirements



ASME B31.12 describes rules for hydrogen pipelines with reference to ASME BPVC Section VIII, Division 3, Article KD-10




# Outline

- **Materials variables**
  - Microstructure and Welds
- **Environmental variables**
  - Pressure
- ~~**Mechanics variables**~~
- **Application of knowledge to structural integrity assessments for hydrogen service**

# Outline

- **Materials variables**
  - Microstructure and Welds
- **Environmental variables**
  - Pressure
- ~~**Mechanics variables**~~
- **Application of knowledge to structural integrity assessments for hydrogen service**



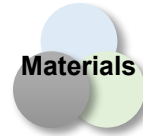
**Materials  
performance**



**Structural  
performance**

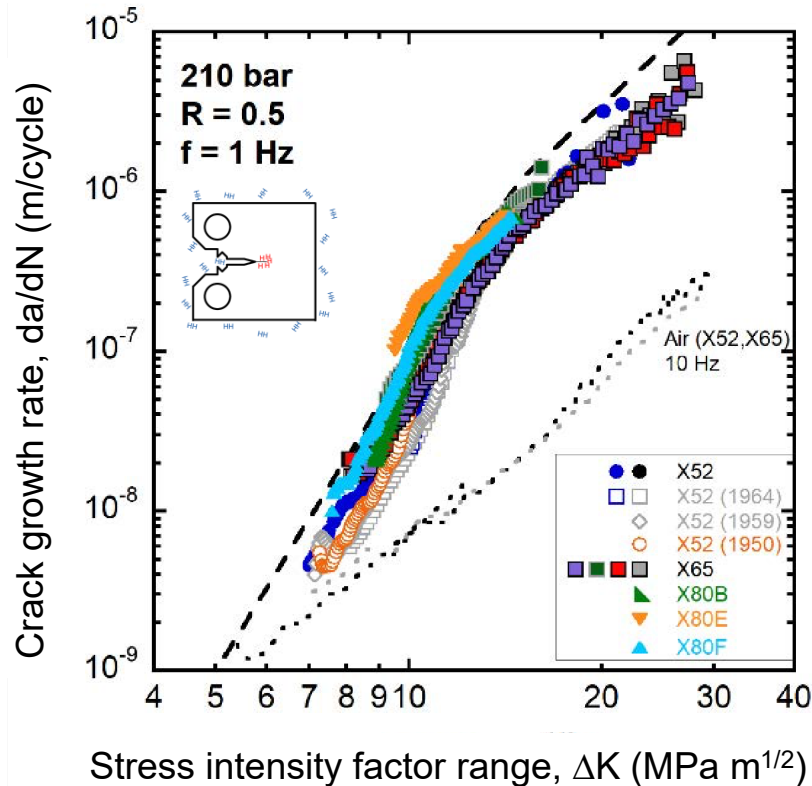
# Outline

- **Materials variables**
  - **Microstructure and Welds**
- Environmental variables
  - Pressure
- ~~Mechanics variables~~
- Application of knowledge to structural integrity assessments for hydrogen service



**Materials  
performance**

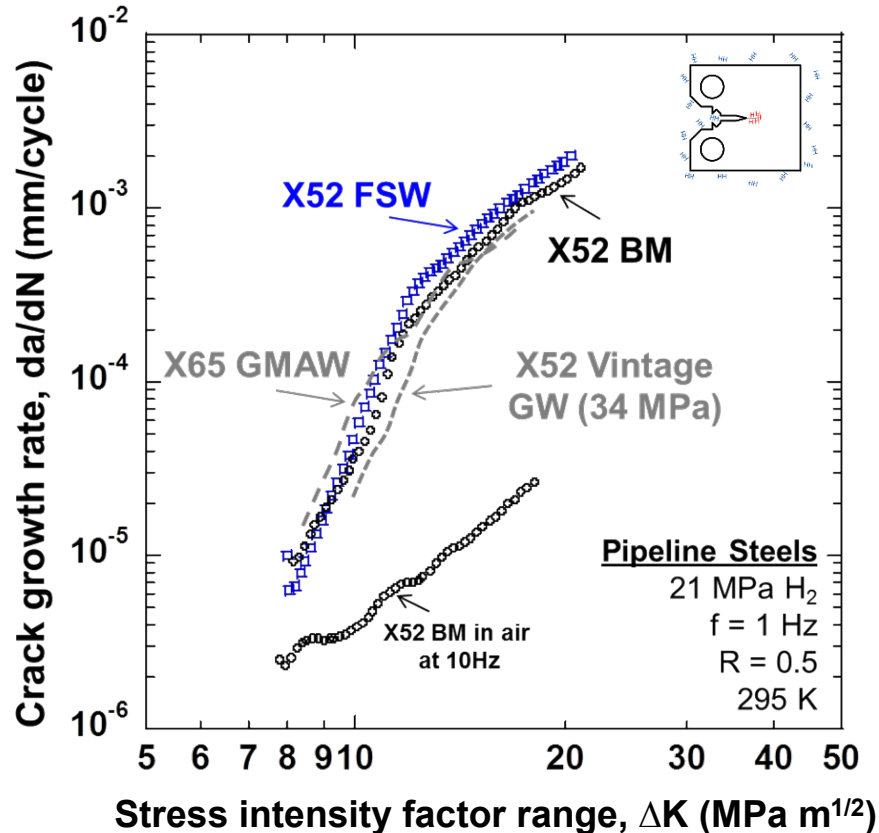
# Fatigue crack growth rates in gaseous hydrogen (GH2) similar for all grades of API pipeline steels



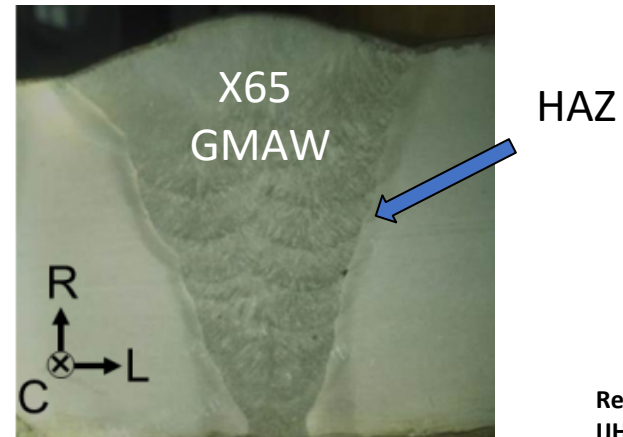
**A wide variety of steel microstructures display nominally the same fatigue response in high-pressure GH2**

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

# Welds and base materials behave similarly in GH2

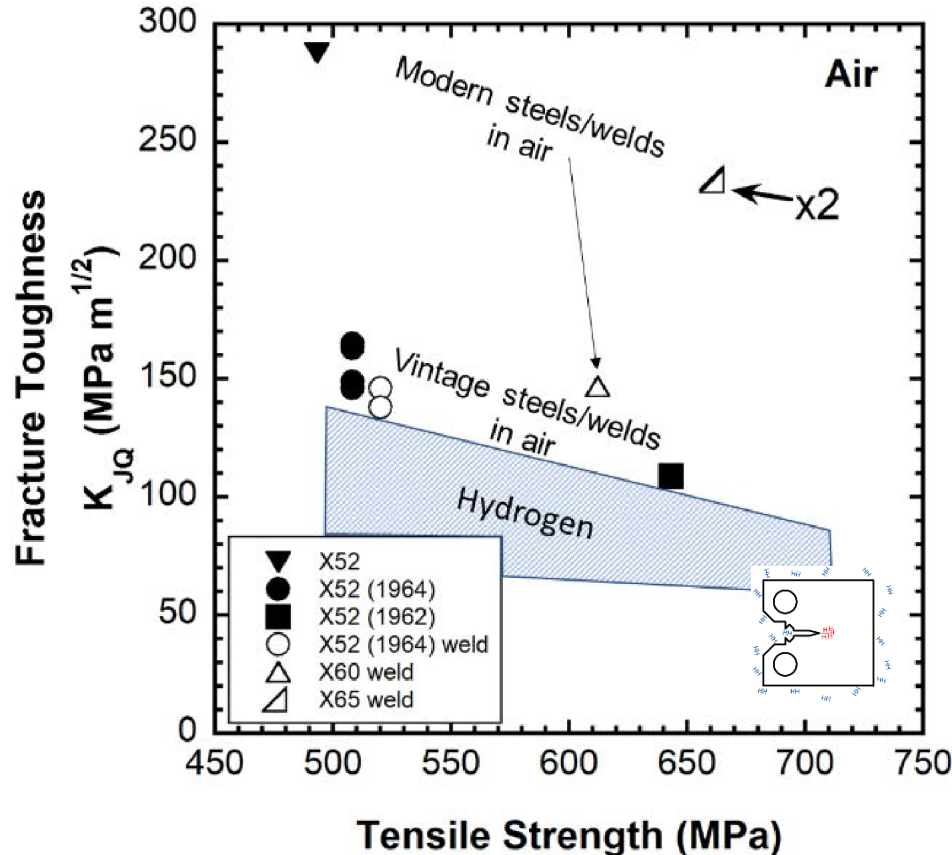


- To first order and if residual stress is considered, welds and HAZ show similar fatigue behavior in gaseous  $\text{H}_2$  as the base metals
- Similar trends have been observed for a variety of weld processes



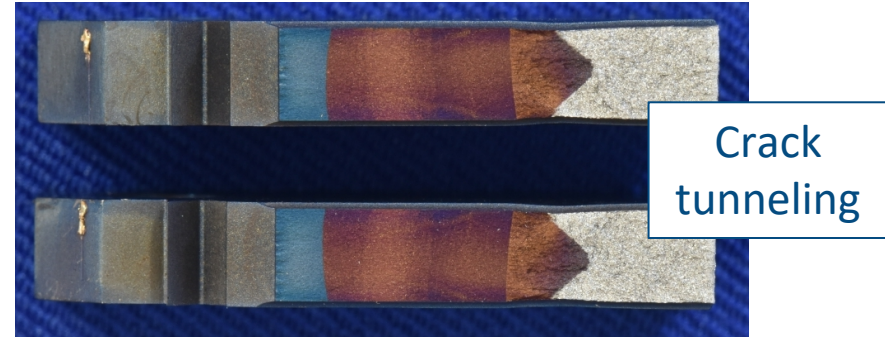
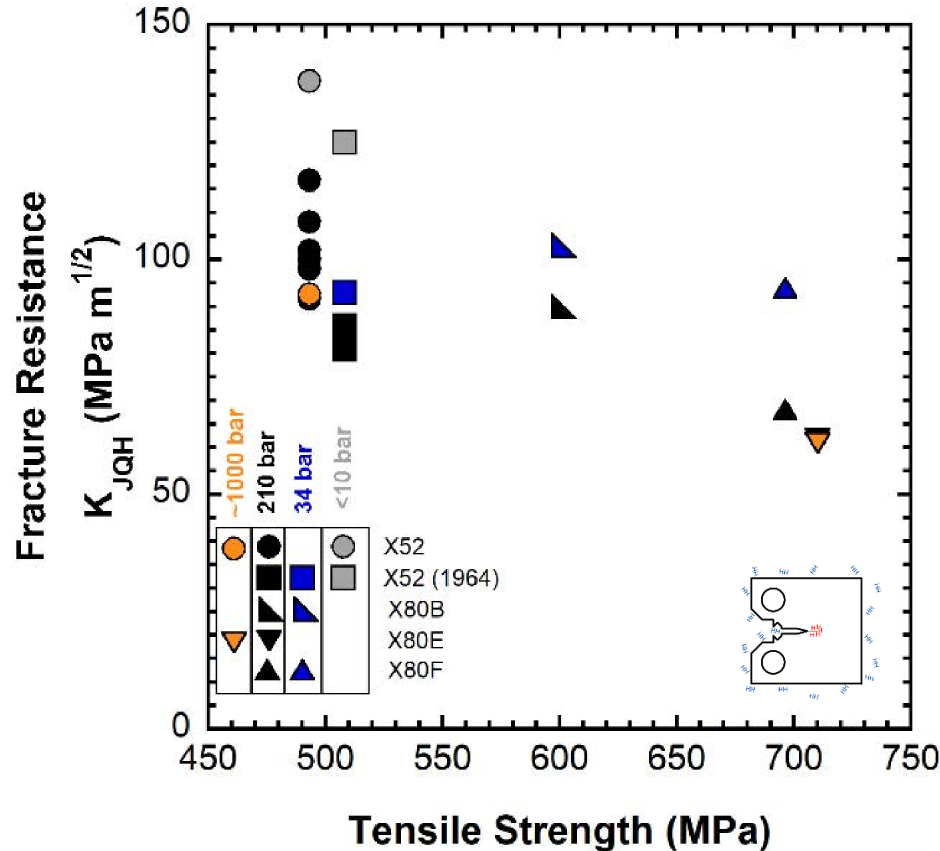


# Fracture toughness of API grade pipeline steels depends on steel vintage and strength



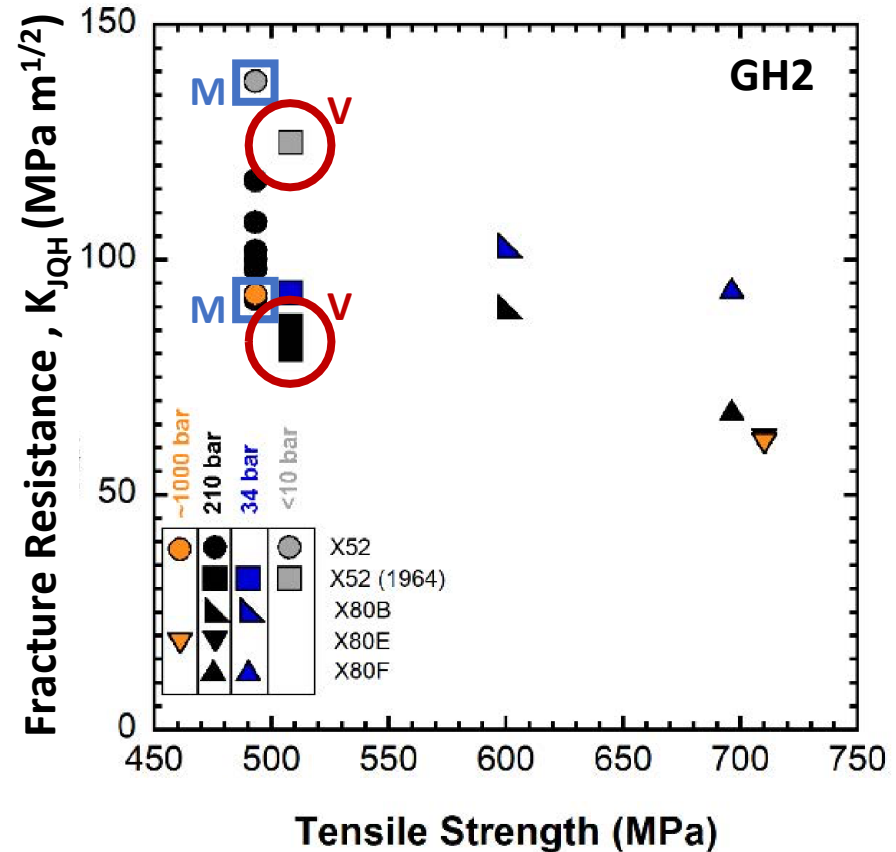
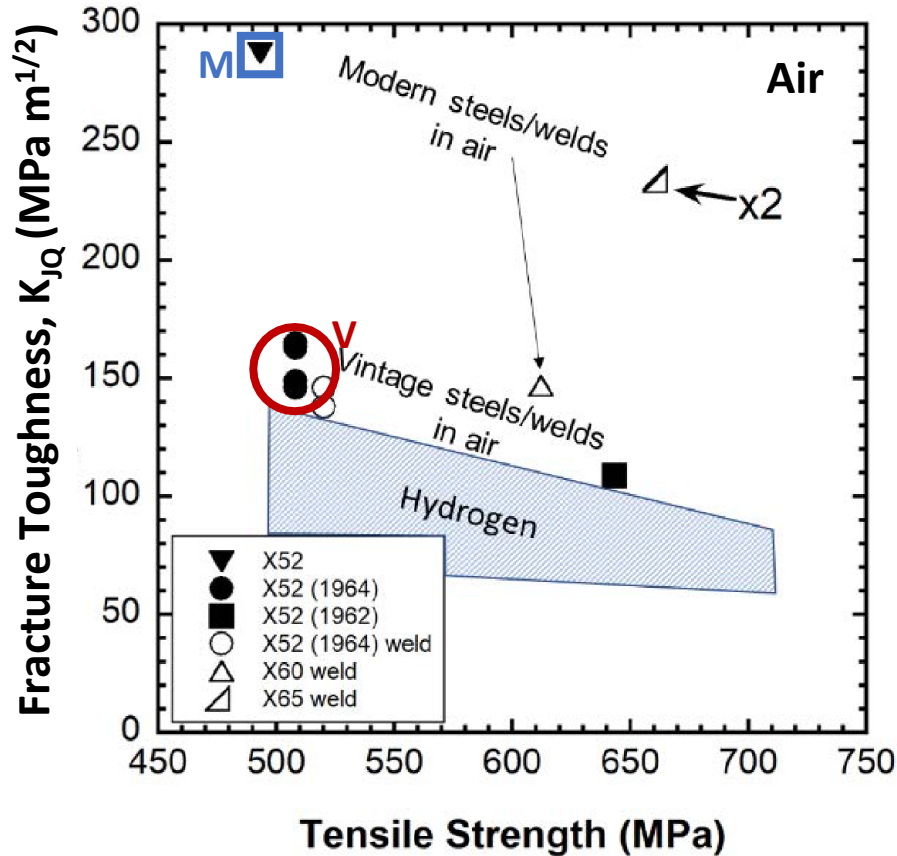
- In general, modern steels have very high fracture toughness in air
- Modest trend with tensile strength in air:  
*higher strength* → *lower fracture toughness*
- Hydrogen 'equalizes' the fracture behavior

# Fracture resistance in GH2 does not necessarily reflect the fracture toughness in air

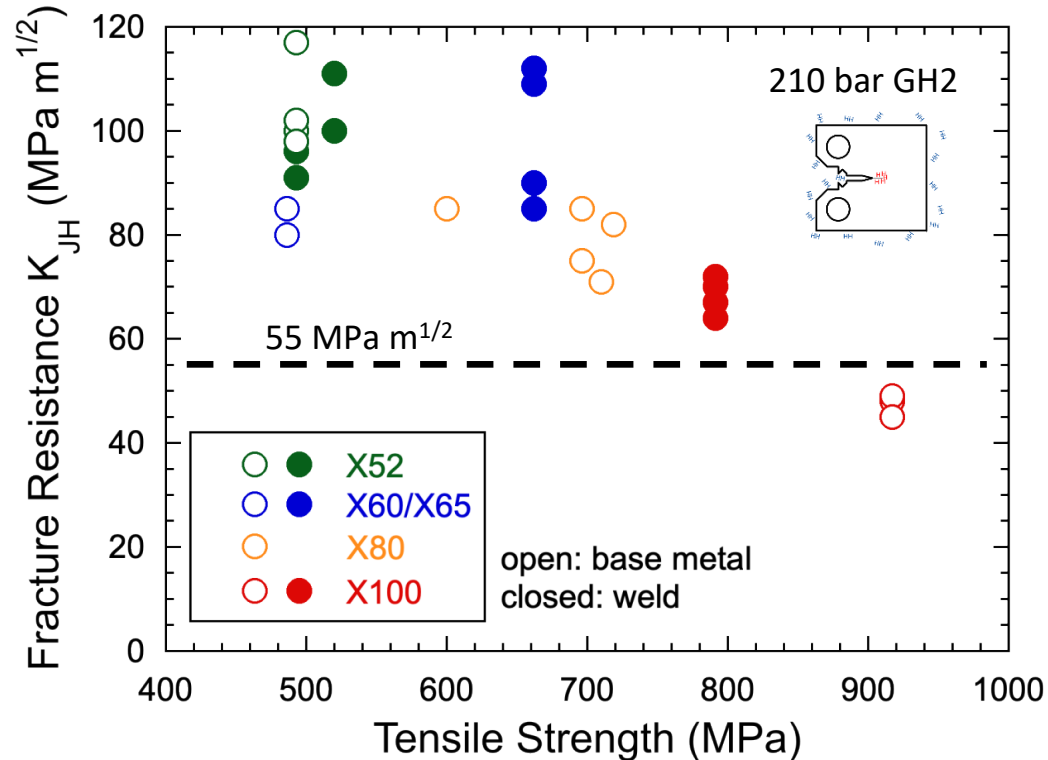


- In GH2 (as in air)  
*higher strength* → *lower fracture resistance*
- $K_{JQH}$  is generally greater than 55 MPa m<sup>1/2</sup>

# Hydrogen 'equalizes' the fracture behavior



# 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
- Hardness is an important factor
  - Local hard spots can be detrimental in GH2



# Outline

- Materials variables
  - Microstructure and Welds
- **Environmental variables**
  - Pressure

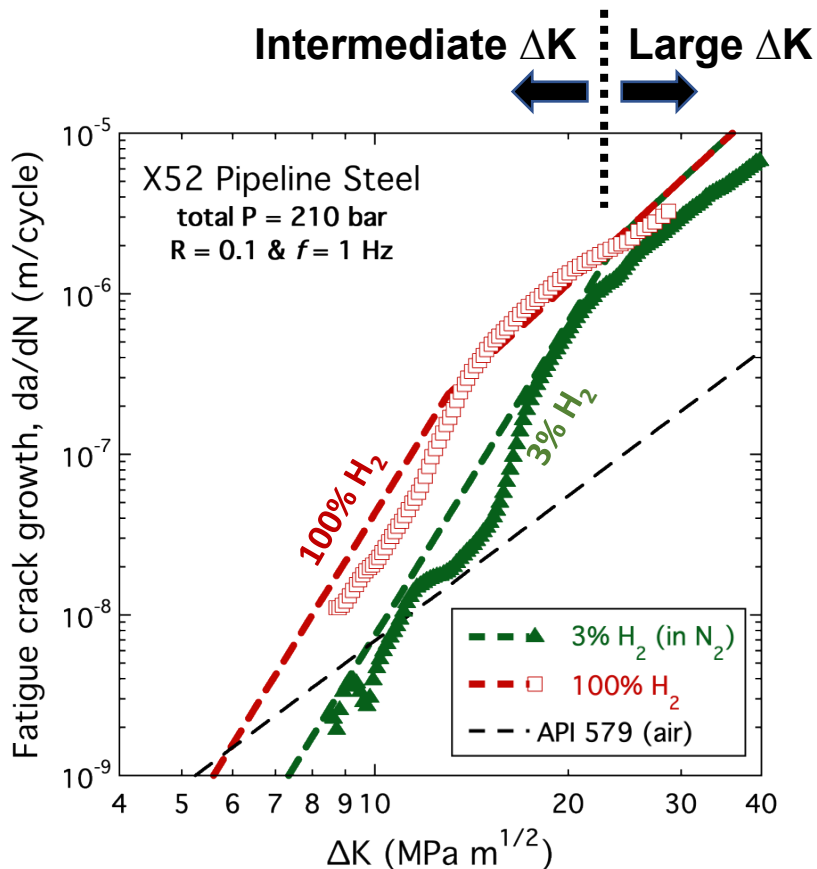


~~• Mechanics variables~~

- Application of knowledge to structural integrity assessments for hydrogen service

**Materials  
performance**

# Low hydrogen pressure = large effect on fatigue



- Large  $\Delta K$

FCG is independent of pressure

- Fatigue crack growth rate in 3% H<sub>2</sub> is the same as in 100% H<sub>2</sub>

- Intermediate  $\Delta K$

FCG is dependent on hydrogen partial pressure

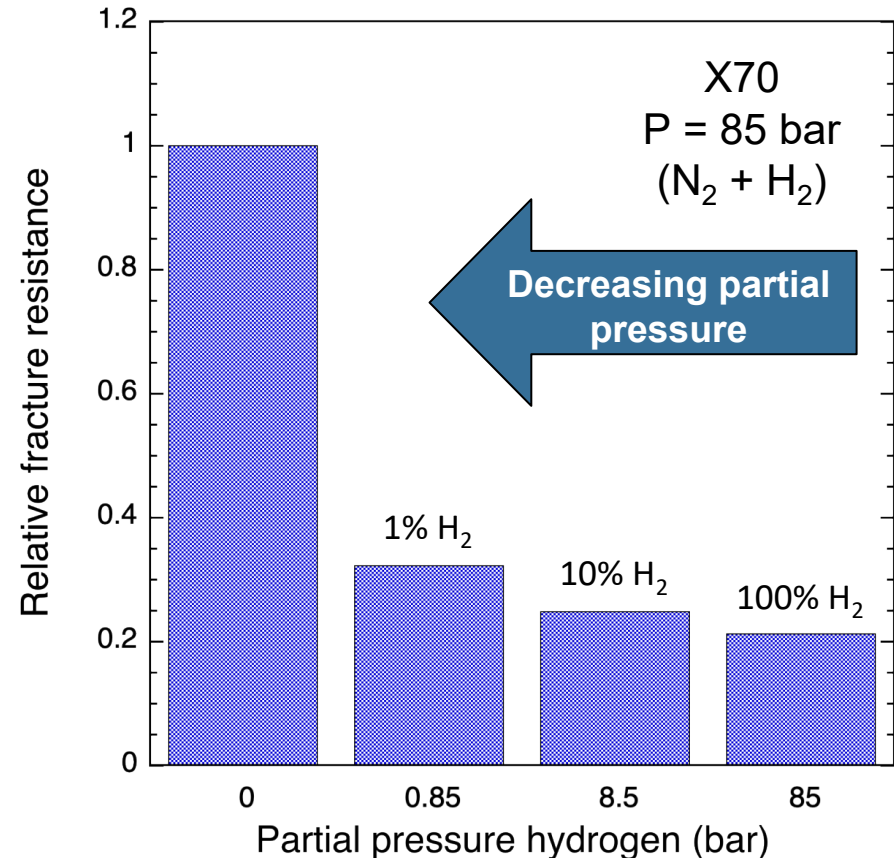
- Fatigue crack growth rate is slower in 3% H<sub>2</sub> than in 100% H<sub>2</sub>

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**



# Summary of materials performance in GH2

- How does GH2 affect fatigue and fracture of pipeline steels?
  - *Fatigue is accelerated by >10x*
  - *Fracture resistance is reduced by >50%*
- Does pressure affect fatigue and fracture?
  - *Fatigue and fracture are affected by pressure and there's no obvious threshold (low pressure can 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*
  - *Welds (of comparable strength) have similar performance to base metals*



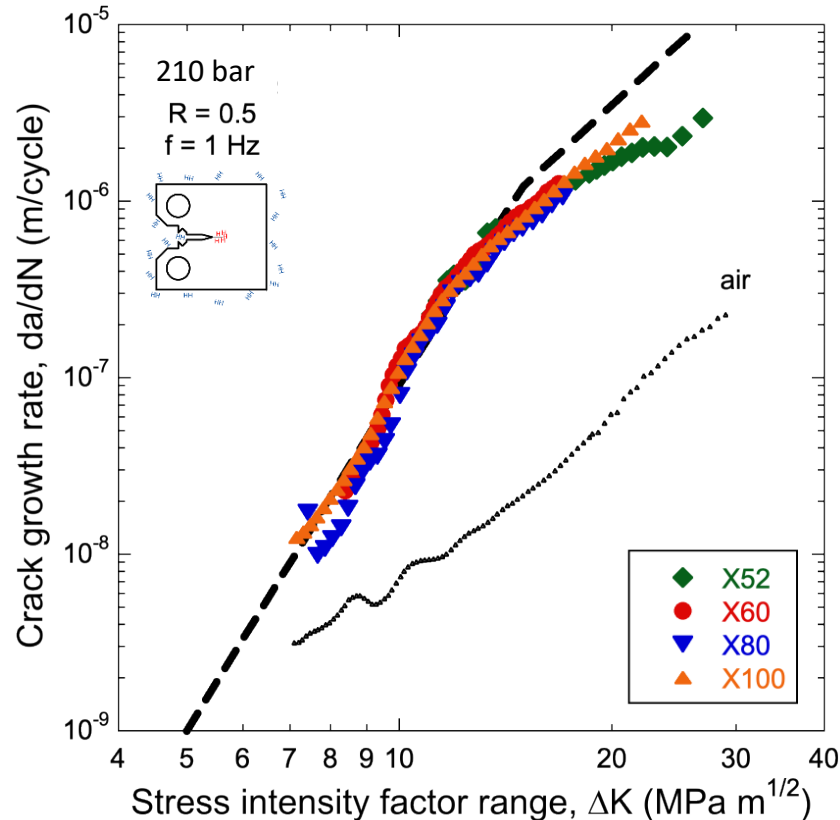
# Outline

- Materials variables
  - Microstructure and Welds
- Environmental variables
  - Pressure
- ~~Mechanics variables~~
- **Application of knowledge to structural integrity assessments for hydrogen service**



**Structural  
performance**

# General bounding (design) curve captures the behavior of pipeline steels in GH2



## Master design curve formulation

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

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

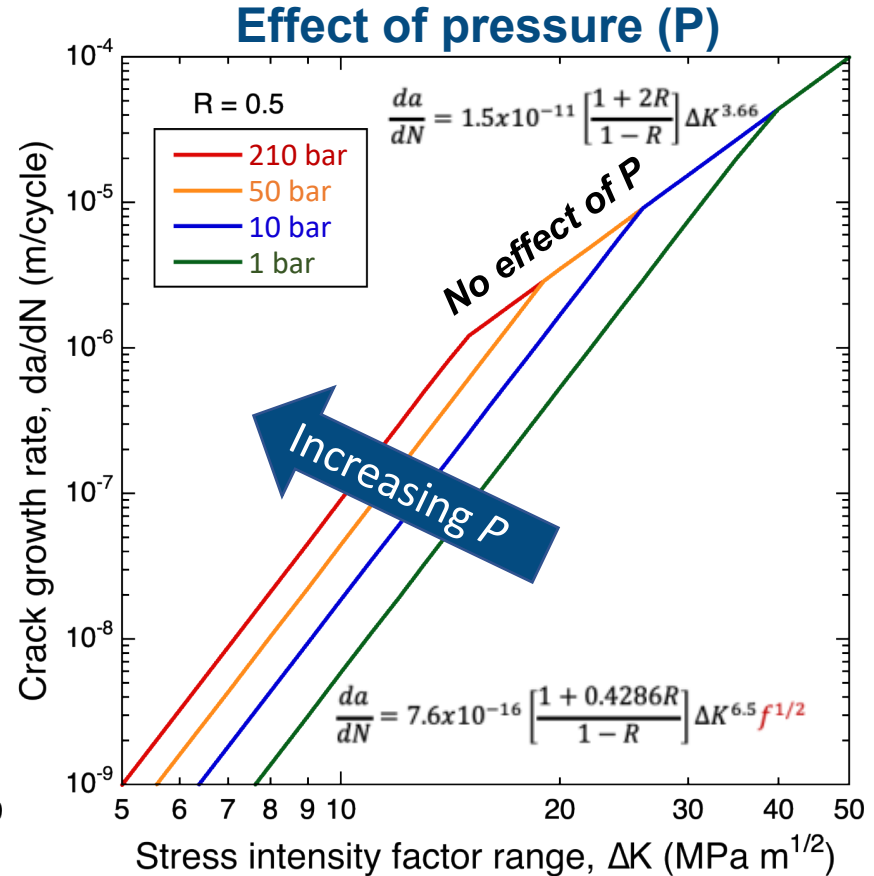
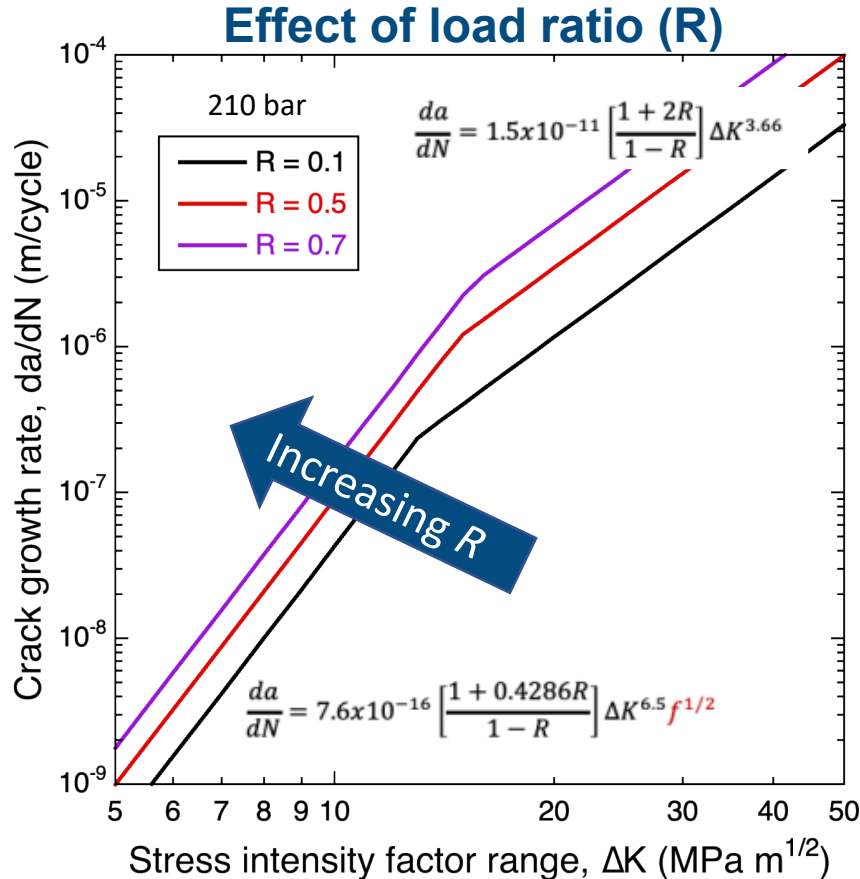
Pressure term

$f$  is the thermodynamic pressure or fugacity

Refs: San Marchi et al, PVP2019-93803  
San Marchi et al, PVP2021-62045  
San Marchi et al, PVP2022-84757

- Units are important!
- In the above formulation:
  - *fugacity* is in units of < bar >
  - $da/dN$ : < m/cycle >
  - $\Delta K$ : <  $\text{MPa m}^{1/2}$  >

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



# Application of materials behavior to structural integrity analysis: Blends

- **Material:**

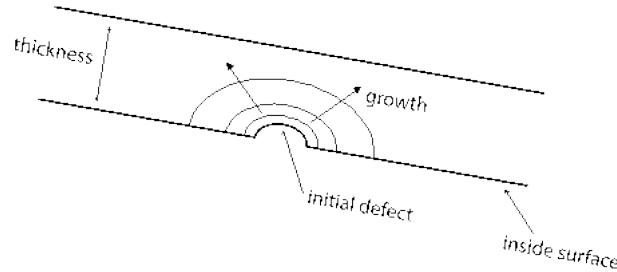
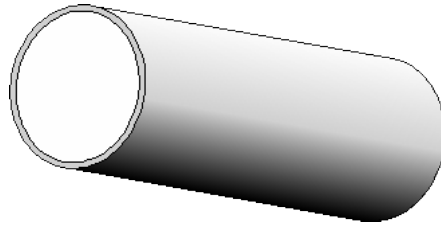
- API grade X52 pipe
- OD = 324 mm
- t = 12.7 mm

- **Environment:**

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

- **Stress:**

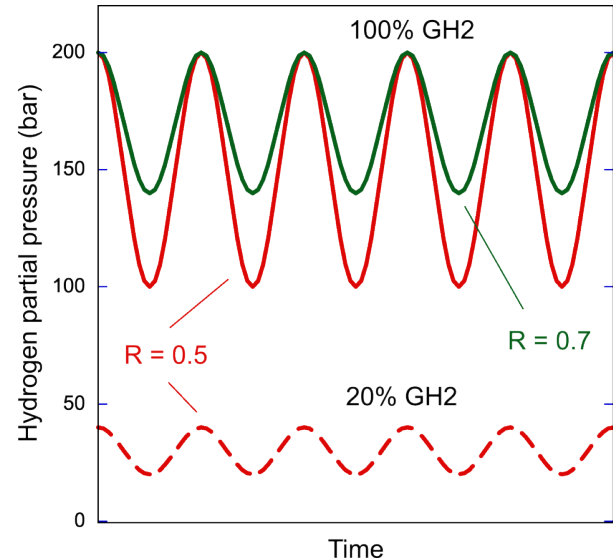
- Hoop stress: 68% SMYS
- Cyclic pressure:  $R = P_{\min}/P_{\max} = 0.5, 0.7$
- Flaw
  - depth: 25% of wall thickness ( $a/t = 0.25$ )
  - length: 40 mm ( $2c = 40\text{mm}$ ) – propagate with constant aspect ratio



Reminders

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

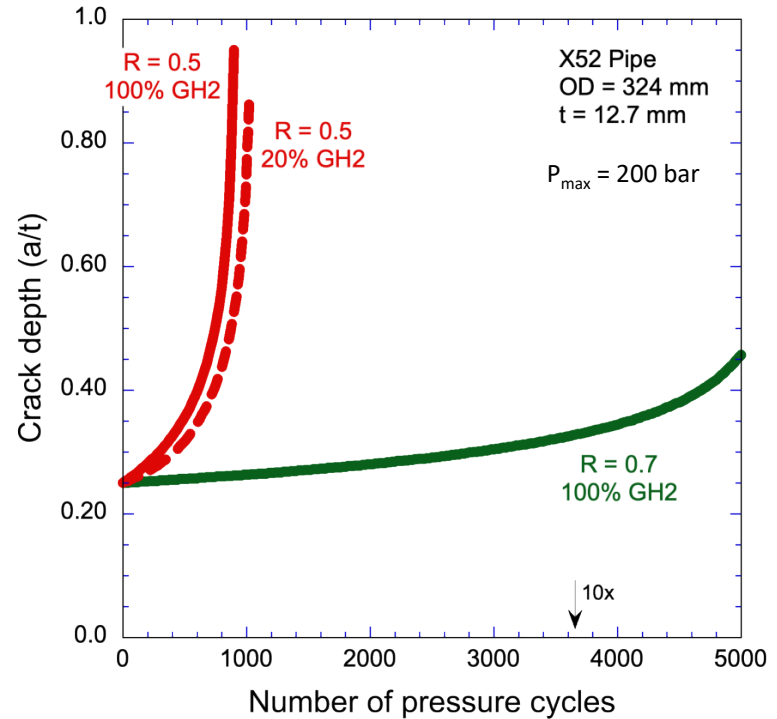
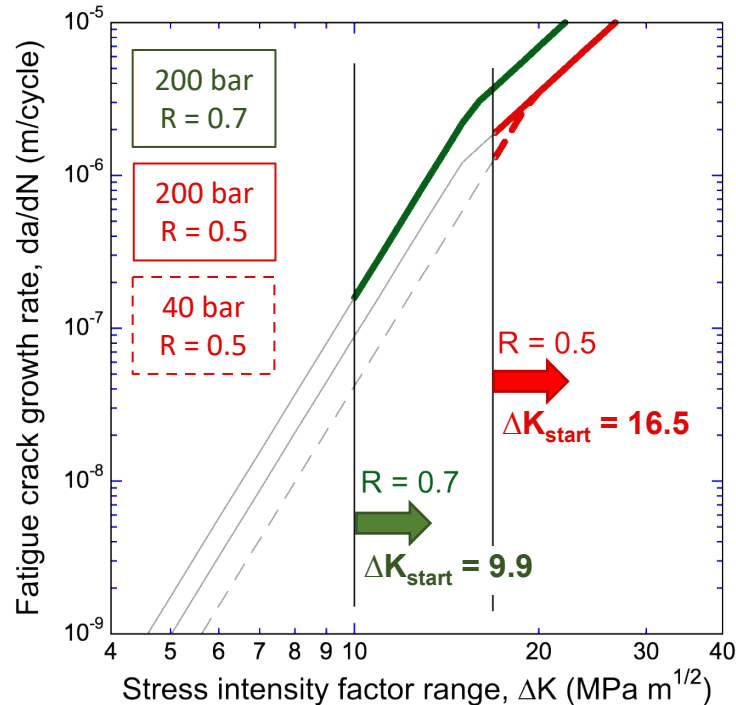
$$\frac{f}{P_{HH}} \rightarrow P_{total}$$





# Analysis of transmission pipe structure: Blends

- 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  $R = 0.5$ )**

# Analysis: 'Real-world' example (100% GH2)

- Material:

- X52
- OD = 36 inch
- $t = 0.406$  inch

- Flaw

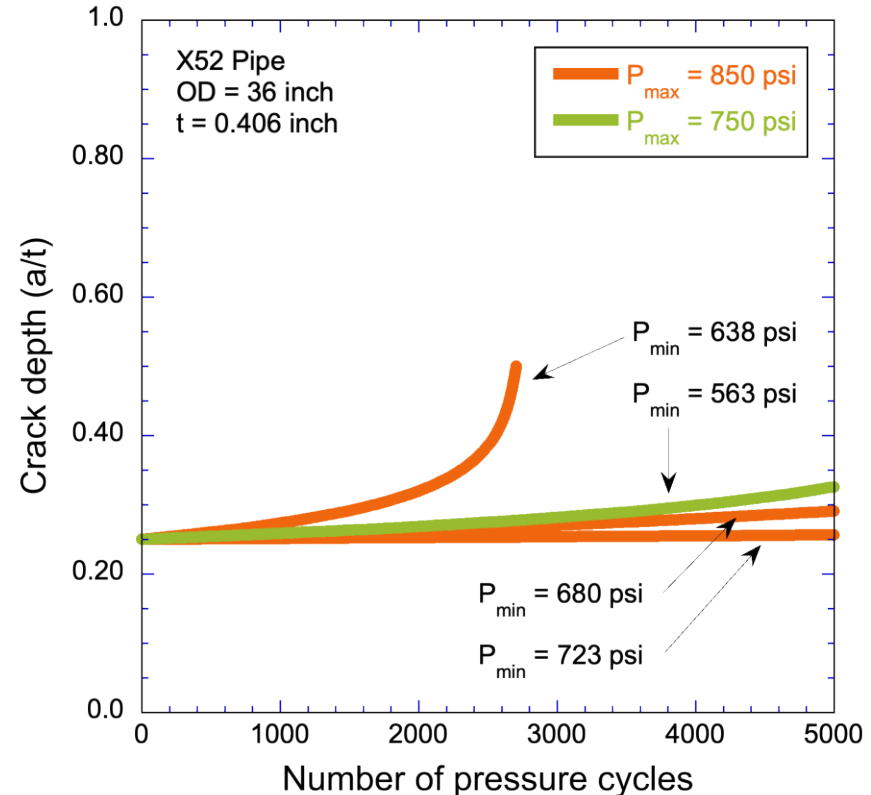
- depth:  $a/t = 0.25$
- length: 40mm

- Environment:

- GH2 = 100%

Analysis of pipeline operating data:  
nominally 24-hour cycles over one year

- $P_{\max} < 700$  psi
- Maximum hoop stress  $< 60\%$  SMYS
- $R > 0.9$

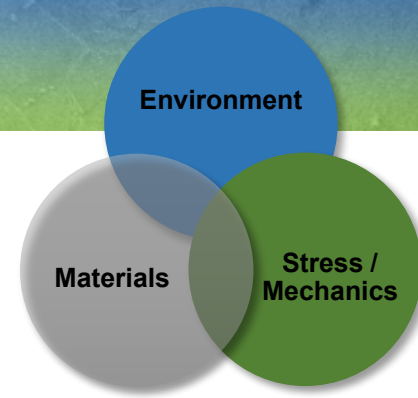


# Summary of structural performance with GH2

- Can GH2 be safely injected into natural gas transmission pipe?

*It depends...*

- *Structural integrity depends sensitively on the pipe dimensions, the pipe condition and operating conditions*
- *For given pipe dimensions and operating conditions, the base material is a secondary consideration*
- *External loading and the condition of the asset (e.g., defects) will likely dominate overall risk exposure*
- *Blending ratio will not be the principal concern in most cases*
- *Pressure cycling will likely need to be managed*
- *Hard spots could be problematic (e.g., vintage welds)*



# Thank You!

**Chris San Marchi**  
**cwsanma@sandia.gov**

**Joe Ronevich**  
**jaronev@sandia.gov**



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

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

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

Special thanks to Sandia's  
HyBlend team:

James McNair  
Brendan Davis  
Keri McArthur  
Brandon Owens  
Remi Dingreville  
Ben Schroeder  
Khalid Hattar  
Kathryn Small  
Matthew Brownell

And the many former contributors  
to the work on pipeline steels



# Informational resources

- **Technical Reference for Hydrogen Compatibility of Materials**
  - <https://www.sandia.gov/matlsTechRef/>
  - Report no. SAND2012-7321 (Technical Reference v.2)
  - Report no. SAND2013-8904 (polymers)
- **Technical Database for Hydrogen Compatibility of Materials**
  - <https://granta-mi.sandia.gov/>
- **Study Group on Materials Testing and Qualification for Hydrogen Service**
  - Annual topical discussion group: international and industrial participation
- **ASME Pressure Vessels and Piping Division Annual Conference (2005 - current)**
  - *Materials for Hydrogen Service*: session organization (2014-current)
- **Expanded resources under development at**
  - Including H-Mat DataHUB (<https://h-mat.org> )

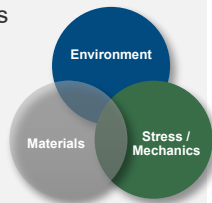
# Materials activities in HyBlend Pipeline Blending CRADA: Structural integrity for hydrogen gas infrastructure



## How do we assess structural integrity of infrastructure with hydrogen?

### Database of design properties for NG assets with hydrogen

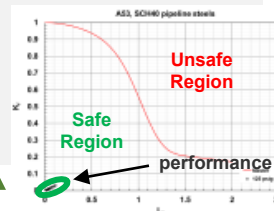
- Assessment of critical parameters determining materials response in hydrogen environments
- Survey of critical materials in ancillary equipment (e.g., pumping stations)
- Long-duration aging of polymers in piping systems
- Evaluation of vintage materials in existing infrastructure



## What is the structural risk to NG assets with blended hydrogen?

### Pipeline Structural Integrity Tool

- Tools to evaluate probability of rupture of NG assets based on Nuclear Regulatory Commission (NRC) framework
- Uncertainty analysis to inform experimental evaluation
- Sensitivity analysis to determine opportunities for system and operational improvements
- Regulations, Codes, and Standards (RCS)-based structural integrity assessment



## How do we formulate mechanistic models into predictions?

### Physics-based mechanisms of hydrogen embrittlement relevant to NG assets

- Develop deeper understanding of mechanisms of hydrogen embrittlement
- Establish models and framework for implementing physical phenomena into structural integrity tool
- Inform materials selection guidance and establish basis for potential future materials development activity

### Guidance on operating conditions



+ partners

### Industry-focused probabilistic framework for risk assessment



State-of-the-art characterization



International coordination *facilitates* definition of requirements, *reduces* redundancy, *enhances* rigor, and *improves* breadth of structural integrity tools

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

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

General form of  
Sieverts' Law

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

Equation of state for  $H_2$   
Abel-Noble formulation

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

Pure gaseous  $H_2$ :

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

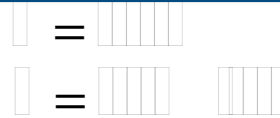
Blended  $H_2$ :

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

# Background: stress intensity factor, $K$

What is this in the stress intensity factor,  $K$ ?

$$K = \sigma \sqrt{\pi a} \times f(\text{geometry})$$



$$\Delta = \text{[bar]} - \text{[bar]}$$

$$R = \frac{K_{min}}{K_{max}}$$

- $K$  characterizes the stress state at a crack tip
  - analogous to the stress, but for the case of cracks in structures
- $K$  is a transferable parameter that is used to generalize the state of a crack and transfer information between one geometry and another
  - for example between a laboratory test and a real-world application

