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Materials Evaluation for Hydrogen Service

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Hydrogen Materials Compatibility Consortium

U.S. DEPARTMENT OF ENERGY

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Outline

- Very brief background
- Basic trends in steels
  - Hydrogen-assisted fatigue crack growth
  - Hydrogen-assisted fracture
  - Structural integrity assessments
  - Materials behavior versus structural integrity
- A few comments on polymers
- General materials guidance

Motivation

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

Challenge

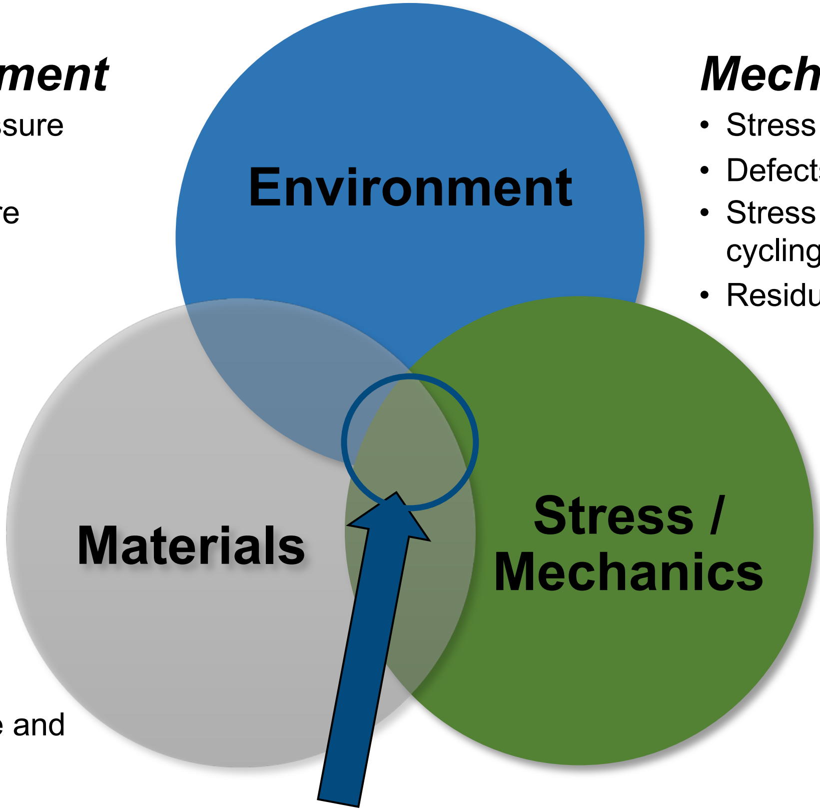
Hydrogen degrades fatigue and fracture resistance of steels, and the effects on pressure vessel and line pipe steels are significant

Environment

- Partial pressure
- Impurities
- Temperature

Mechanics

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

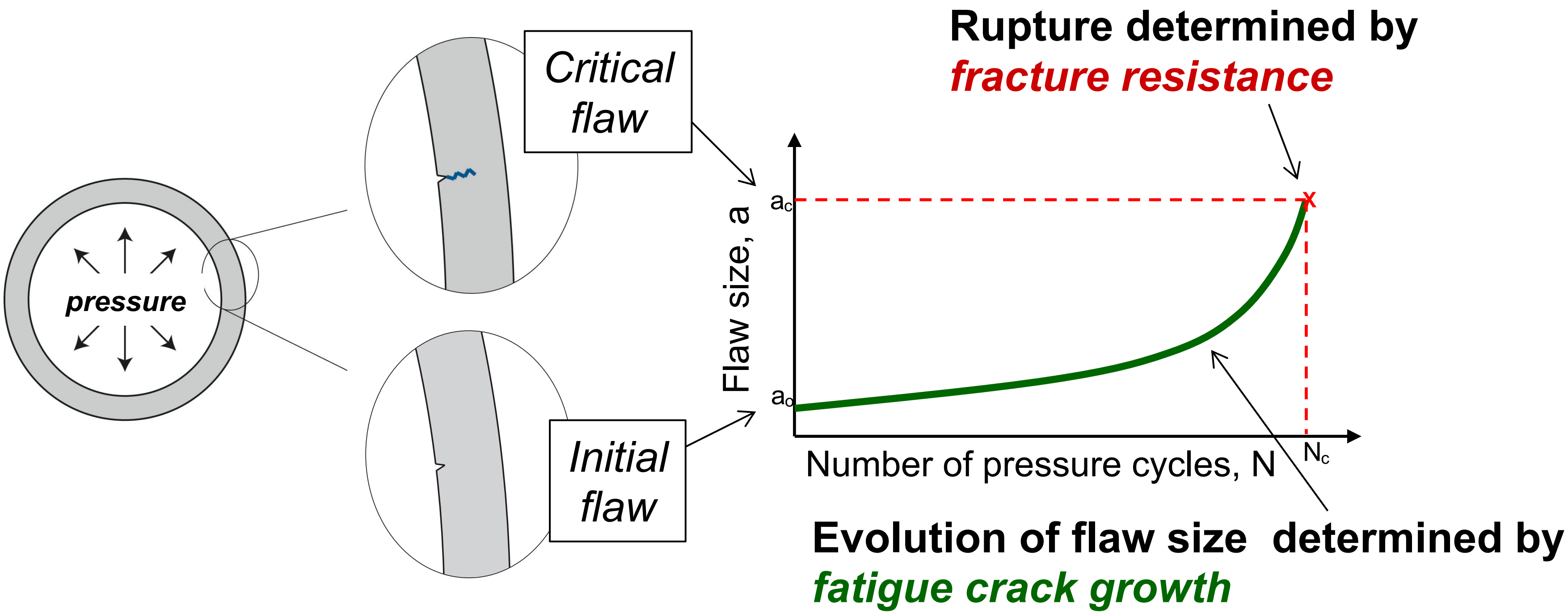


Materials

- Strength
- Microstructure and homogeneity

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

Structural integrity assessment includes fracture mechanics-based analysis



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

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The effects of high-pressure hydrogen on fatigue crack growth in pressure vessels steels are characterized by the ASME CC2938 design curve

The pressure compensation term is not described in CC2938

f is the thermodynamic pressure or fugacity
f_o is a reference fugacity

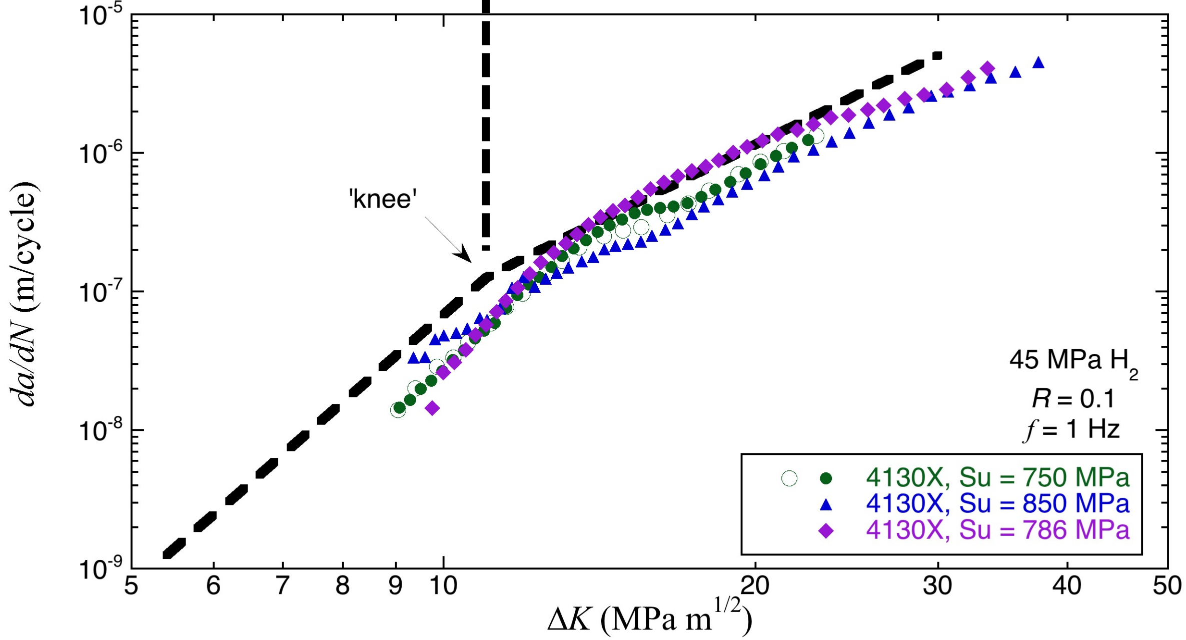
Ref: San Marchi et al, PVP2019-93803

$$\frac{da}{dN} = C_1 \left[\frac{1 + C_2 R}{1 - R}\right] \Delta K^{m_1} \left(\frac{f}{f_0}\right)^{1/2}$$

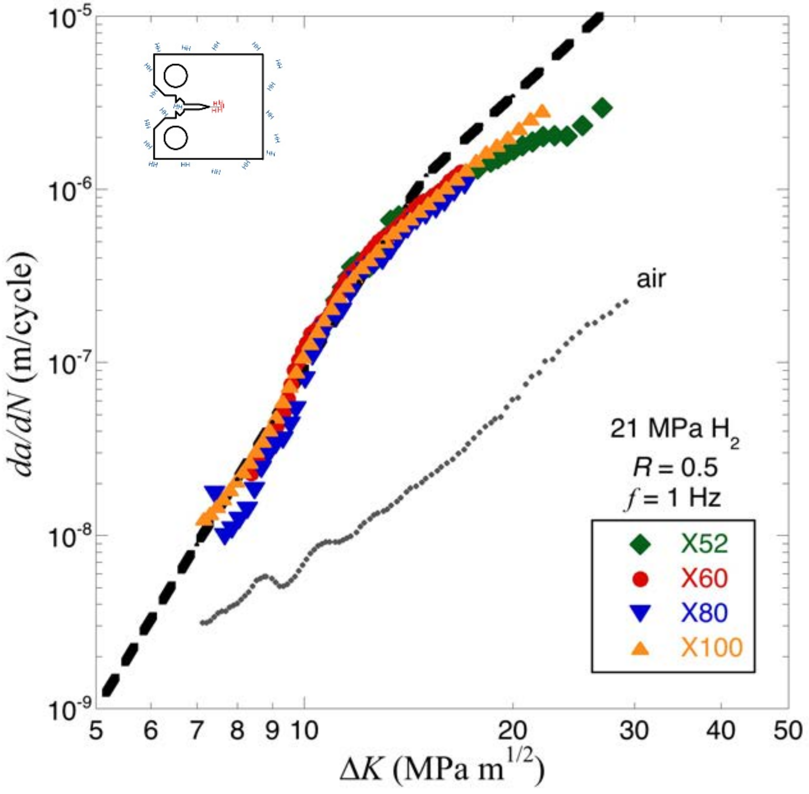
$$\frac{da}{dN} = C_3 \left[\frac{1 + C_4 R}{1 - R}\right] \Delta K^{m_2}$$

Pressure dependent | *NOT pressure dependent*

Intermediate ΔK | **Large ΔK**



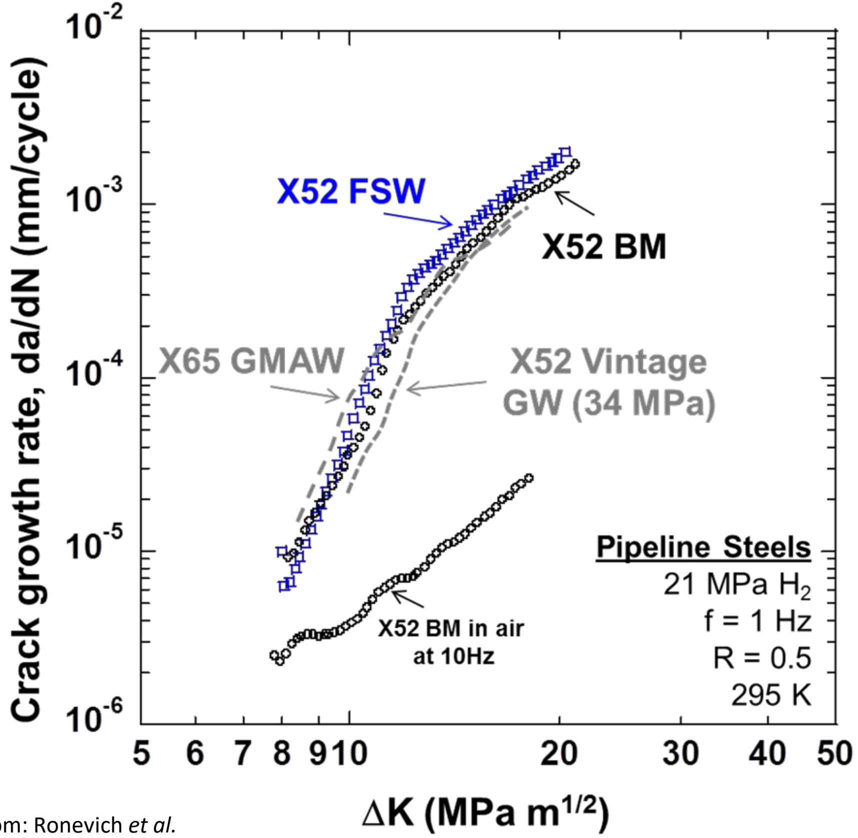
The effects of hydrogen on pipeline steels are captured by CC2938 design curve for pressure vessels



Similar fatigue crack growth behavior is observed in API grade pipeline steels for:
- **Wide range of strength**
- **Wide range of microstructure**

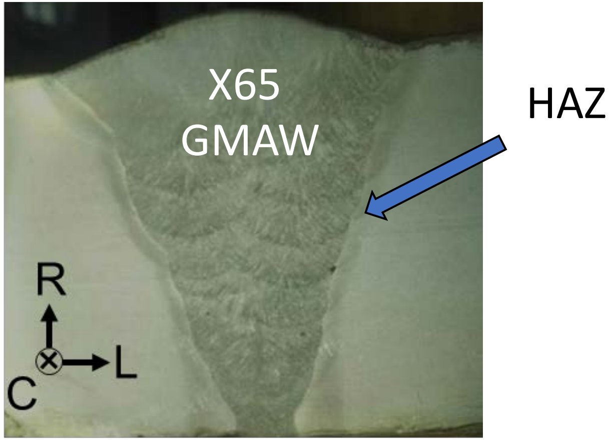
- **What about welds?**
- **Does this design curve capture fatigue behavior of relevant piping and pipeline steels at low pressure?**
- **What is the effect of pressure on fracture?**

Welds and base materials behave similarly



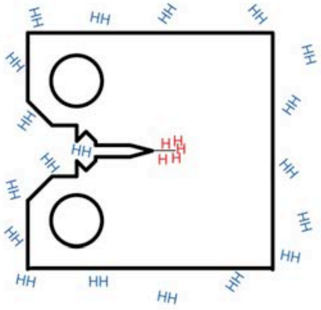
From: Ronevich *et al.*
IJHE 42 (2017)

- 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



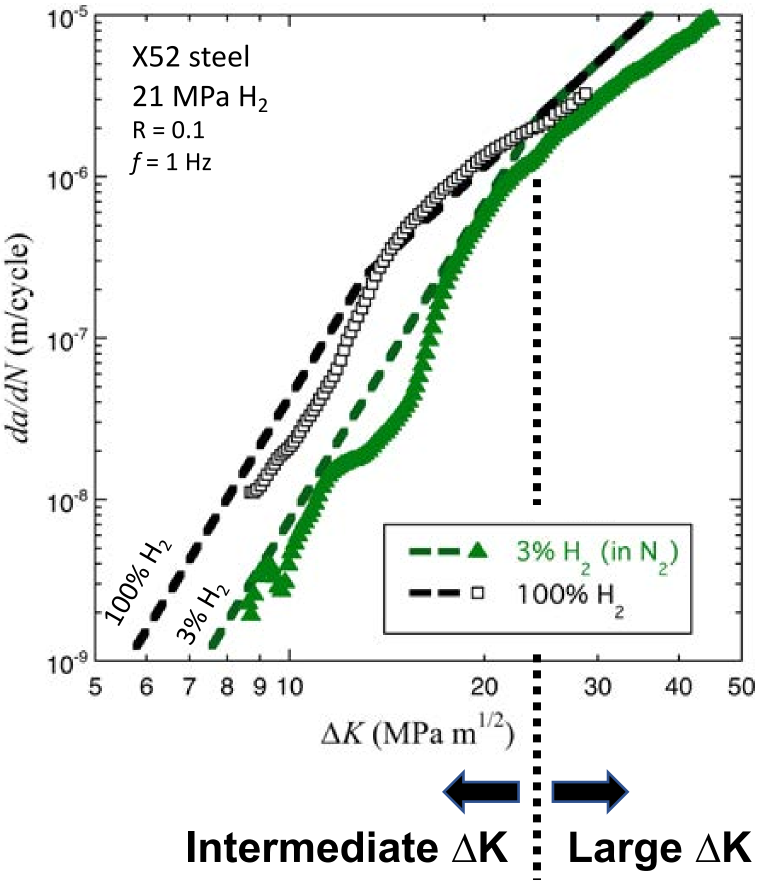
Fatigue crack growth and fracture resistance have been measured in low partial pressure hydrogen

Material Evaluation: transmission pipe



- ***Material***: **API grade X52**
  - **Fe-0.87Mn-0.06C, polygonal ferrite with ~10% pearlite**
  - **YS = 429 MPa, TS = 493 MPa**
- ***Environment***:
  - **21 MPa total pressure: pure H_2**
  - **21 MPa total pressure: 3% H_2 (in inert) ~ 0.6 MPa hydrogen partial pressure**
- ***Stress***:
  - **Fatigue crack growth rate measured consistent with ASTM E647**
    - **fatigue typically terminated at a/W ~ 0.65**
  - **Elastic-plastic fracture resistance evaluated consistent with ASTM E1820 (rising load J_{IC} value)**
    - **Determined at the conclusion of the fatigue crack growth test**

Fatigue crack growth of X52 is strongly affected by low partial-pressure hydrogen



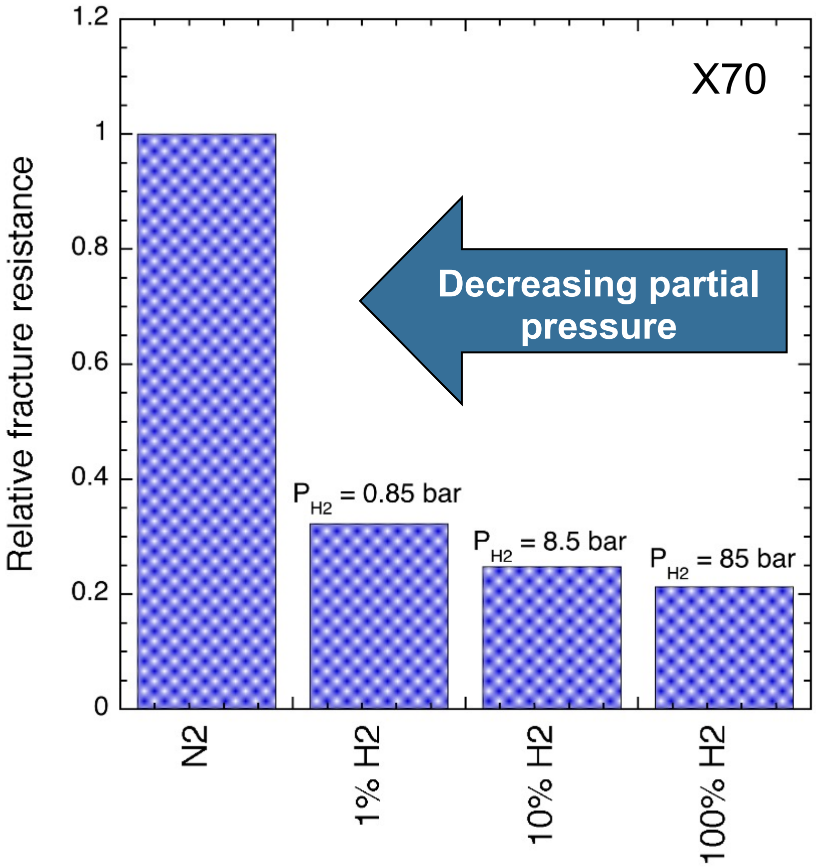
- <u>Large ΔK</u>
  FCG remains independent of pressure
  - FCG in hydrogen at partial pressure of 0.6 and 21 MPa converge
- <u>Intermediate ΔK</u>
  FCG is dependent on hydrogen partial pressure
  - Dashed lines represent pressure-corrected predictions from ASME CC2938 for 100% and 3% H_2 at total pressure of 21 MPa

Ref: San Marchi et al, PVP2021-62045

Hydrogen-assisted fracture is apparent in low partial-pressure hydrogen

- **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 reduces fracture resistance



Ref.: Briottet et al, PVP2018-84658

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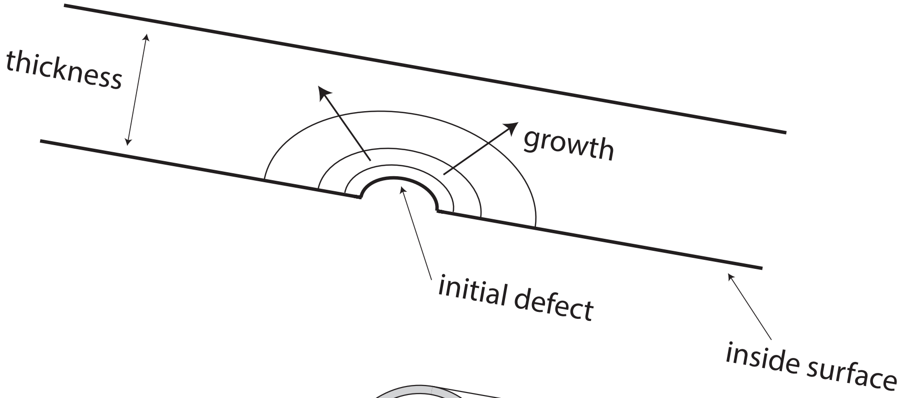
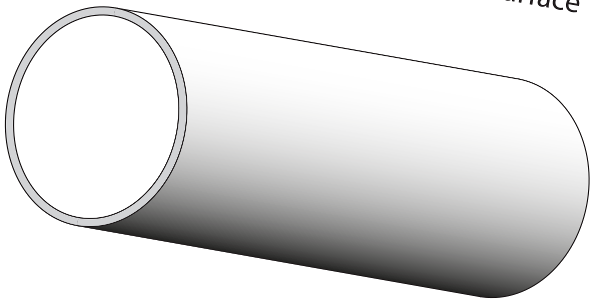
Analysis of transmission pipe structure

Structural Evaluation: transmission pipeline

- ***Material***:
  - API grade X52 pipe
  - OD = 324 mm
  - t = 12.7 mm
- ***Environment***:
  - Pure hydrogen at pressure of 10 MPa
  - Consider aggressive service environment (100% H_2)
- ***Stress***:
  - Hoop stress ~ 120 MPa (~35% SMYS)
  - Cyclic pressure: ΔP = 5 MPa
  - Flaw depth: 25% and 50% of wall thickness
    propagate with constant aspect ratio of 3:1 (length:depth)

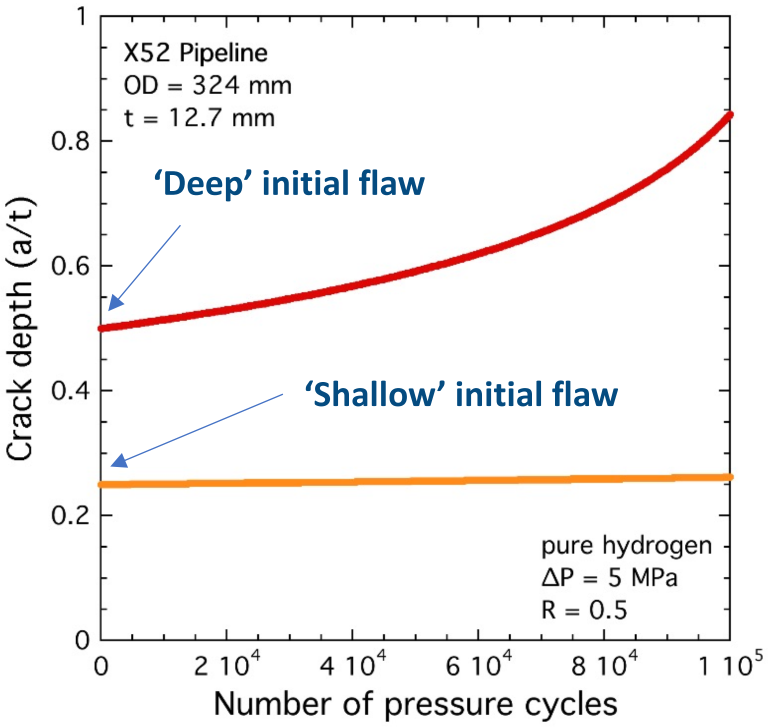




Analysis of transmission pipe structure

- **Stress is rather modest in this example, where P = 10 MPa, ΔP = 5 MPa**
- **Initial flaw depth (a/t) = 0.25**
  - **$K_{applied}$ = 11.2 MPa $m^{1/2}$**
  - **Crack does not extend significantly after 100,000 cycles with ΔP = 5 MPa**
- **Initial flaw depth = 0.50**
  - **$K_{applied}$ = 16.5 MPa $m^{1/2}$**
  - **Nearly 100,000 cycles required to extend crack to a/t = 0.80**
- **Crack depth = 0.80**
  - **$K_{applied}$ = 22 MPa $m^{1/2}$**
  - **$K_{material}$ > 100 MPa $m^{1/2}$**

Structural Evaluation: transmission pipeline

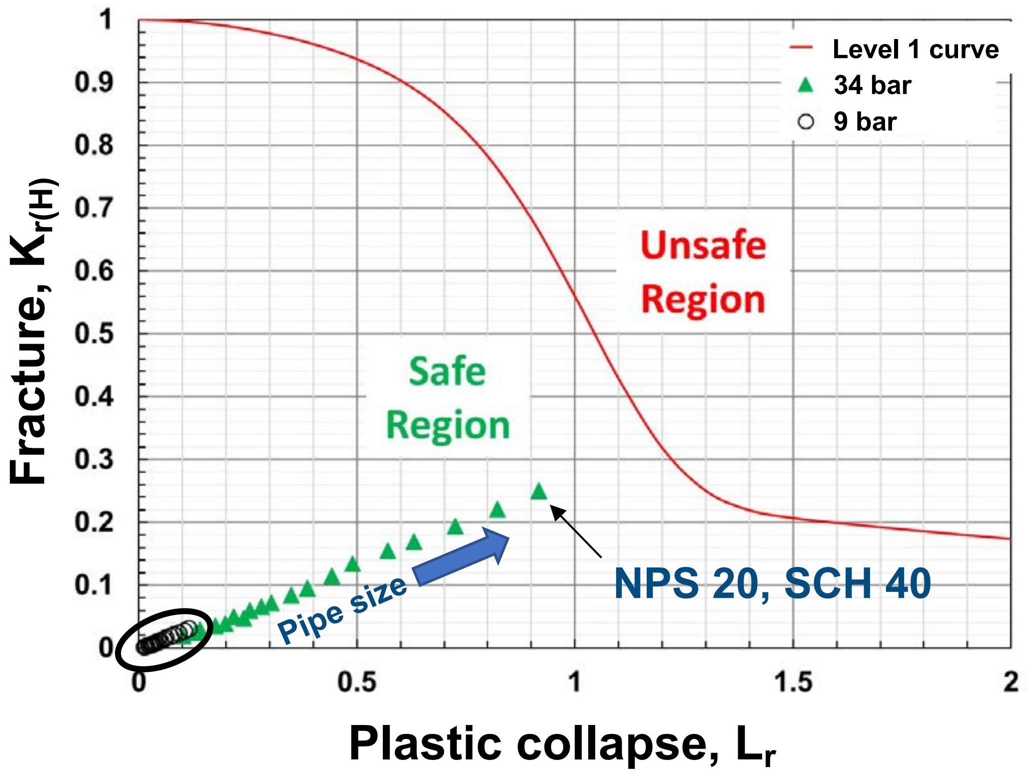


Failure Assessment Diagram (FAD) for black pipe shows large margins for failure

- $K_{r(H)}$ characterizes unstable crack growth in hydrogen
- L_r characterizes plastic collapse (%SMYS)
- Idealized example calculations assuming crack depth 80% of wall thickness

After: API 579-1/ASME FFS-1

Structural Evaluation: distribution piping



Hydrogen seems very unlikely to induce unstable fracture in low-pressure piping from quality steels

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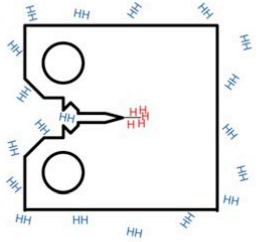
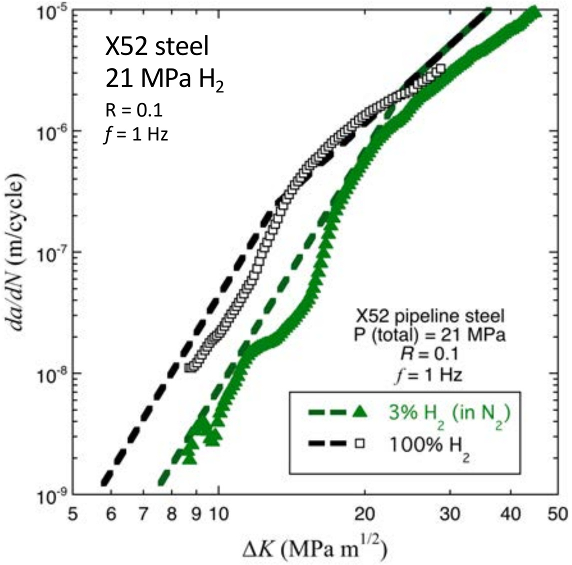
Summary: Materials Perspective

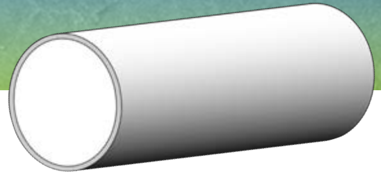
Gaseous hydrogen strongly affects fatigue and fracture properties of steels, even at low pressure

- Fatigue crack growth
  - for small ΔK < 5 MPa m$^{1/2}$, FCG is exceptionally slow (<10^{-9} m/cycle) , even for pure hydrogen
  - for intermediate ΔK, FCG depends on square root of hydrogen fugacity
  - for large ΔK, FCG >10x faster in hydrogen than air and FCG is independent of pressure
- Fracture resistance decreases with pressure, but but remains >100 MPa m$^{1/2}$ in 21 MPa hydrogen



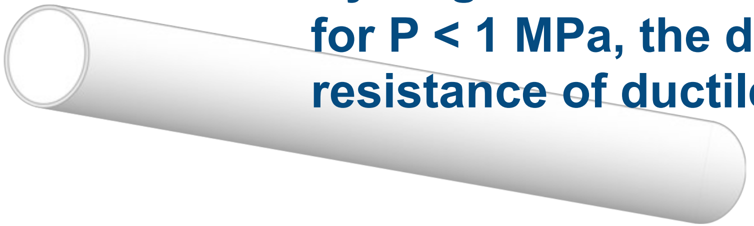


Summary: Structural Integrity Perspective



Gaseous hydrogen will not substantially accelerate fatigue crack growth in fatigue and fracture will not become unstable if the stresses (driving forces) are sufficiently low

- ***Transmission pipeline example***
  - For realistic conditions, very large flaws are needed to ‘activate’ cracking, and fracture resistance of ductile steels remains relatively high in hydrogen environments
  - Actual results will depend on stresses and defect population
- ***Distribution piping***
  - Hydrogen is unlikely to be an issue for ductile steels: for $P < 1$ MPa, the driving force will be >10x less than fracture resistance of ductile steels ($K_{max} < 5$ MPa m$^{1/2}$)



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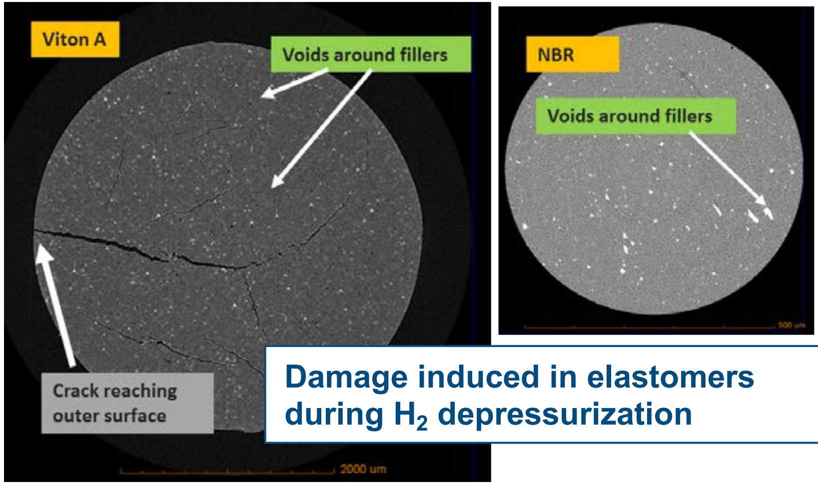
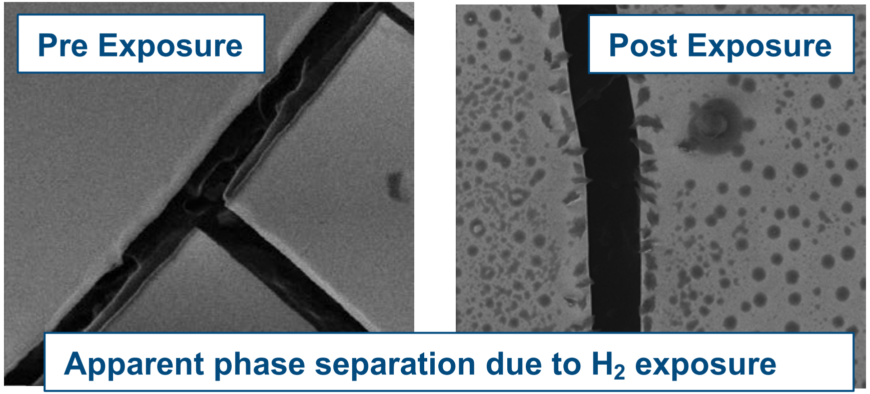
Materials considerations for polymers are quite different than for metals

- Gaseous hydrogen exposure can induce physical and chemical changes in polymers
  - Elastomers are more sensitive to rapid decompression with hydrogen than other gases
    - Blister formation
    - Microcracking
  - Emerging evidence suggests that hydrogen can induce chemical changes
    - Such as phase separation of plasticizer



Damage induced in elastomers during H_2 depressurization

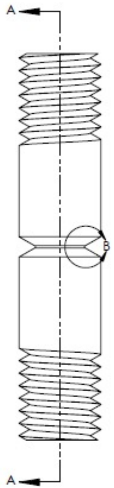


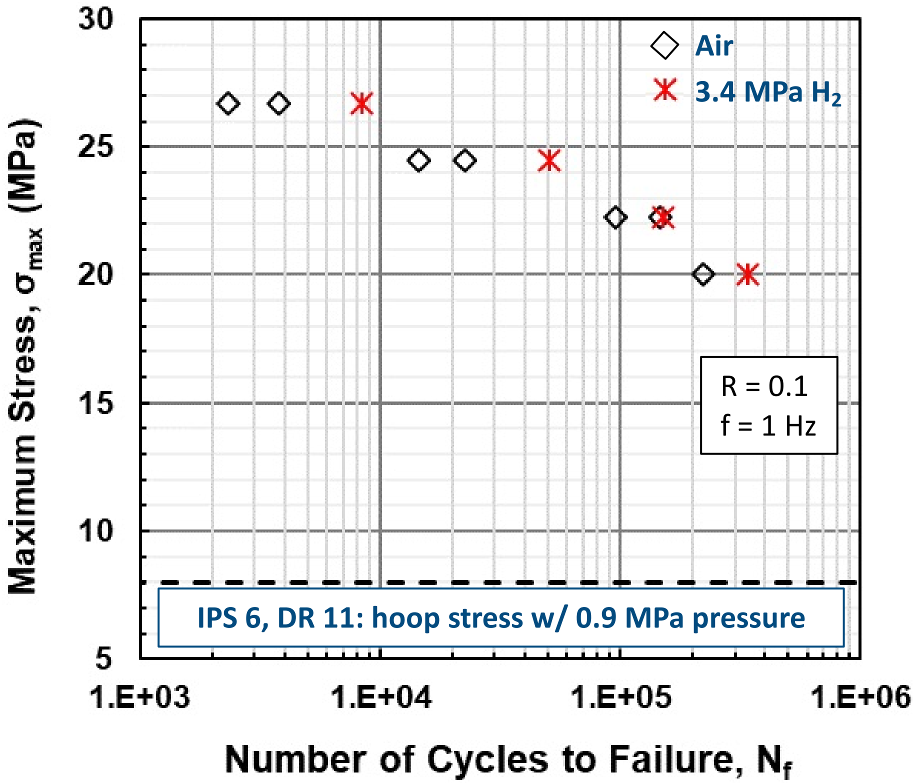
Apparent phase separation due to H_2 exposure

Fatigue life testing of yellow pipe in gaseous hydrogen shows no short-term degradation

Material Evaluation: distribution piping

- ***Material***: **ASTM D2513, PE2708 (yellow pipe)**
  - **Medium density polyethylene (MDPE)**
  - **IPS 6, DR 11 (standard size designation)**
- ***Environment***: **pure H_2**
  - **3.4 MPa pressure (500 psi)**
- ***Stress***:
  - **Fatigue life testing consistent with ASTM E466**
    - **Tension-tension configuration (R = 0.1)**
    - **Notched axial geometry**





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General materials guidance: steel

- Austenitic stainless steels
  - 316/316L is standard for hydrogen service (but still affected)
  - Other stainless steels can display similar fatigue and fracture behavior (or better – eg, ‘strain-hardened’ materials)
- Nickel alloys
  - Diverse response in H_2 – often related to strength
- Carbon and low alloy steels
  - Common low-strength steels (TS ≤ 900 MPa) behave similarly for wide range of microstructure and composition
- High-strength alloys (TS > 950MPa) are suspect for H_2

General materials guidance: polymers

- Polymers should be evaluated on a case-by-case basis
  - Generic classifications do not provide sufficient detail to describe material response (eg, not all fillers are equivalent)
- Elastomers
  - Viton and NBRs tend to show more damage
  - EPDM and HNBRs tend to show less damage
  - Chemical and physical changes vary based on compound (eg, phase separation of plasticizers)
- Thermoplastics
  - Polyethylene (PE) is used extensively in hydrogen
  - PTFE (‘Teflon’) can behave well in hydrogen

HyBlend: assessment of technical barriers and value proposition to blending hydrogen in natural gas pipelines

- NREL (lead), SNL, PNNL, ANL, NETL
- More than 20 partners from industry and academia
- 2-year project
  - >$12 million from DOE-EERE
  - + $3-4 million anticipated from partners
  - Anticipated start Fall 2021

HyBlend
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Three research tasks in HyBlend:

1) Hydrogen compatibility of piping and pipelines
   - Both metals and polymer piping (SNL, PNNL)
2) Life-cycle analysis (ANL & NETL)
3) Techno-economic analysis (NREL)

Important pipeline tasks:

- Structural Integrity and Risk Assessment of Hydrogen Pipelines
  - key deliverable: Probabilistic fracture mechanics framework for structural integrity of assessment of natural gas pipelines in hydrogen service
- Degradation of Structural Properties (metals and polymers)
  - key deliverable: fundamental understanding of behavior of materials in natural gas network (emphasis on pipelines and piping)

Thank You!

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