SAND2019-12733PE

Hydrogen Compatibility of Materials and Implications of Hydrogen in the Natural Gas Network

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Sandia National Laboratories

Hydrogen Safety Panel
October 16, 2019

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Motivation and Outline

- Why hydrogen in pipelines?
- What is hydrogen embrittlement and when is it important?
- How does gaseous hydrogen affect fatigue and fracture of pipeline steels?
- Is there a threshold below which hydrogen effects can be ignored?
- Can the effects of hydrogen be masked by other physics?
- What is the implication of hydrogen on life of pipelines?

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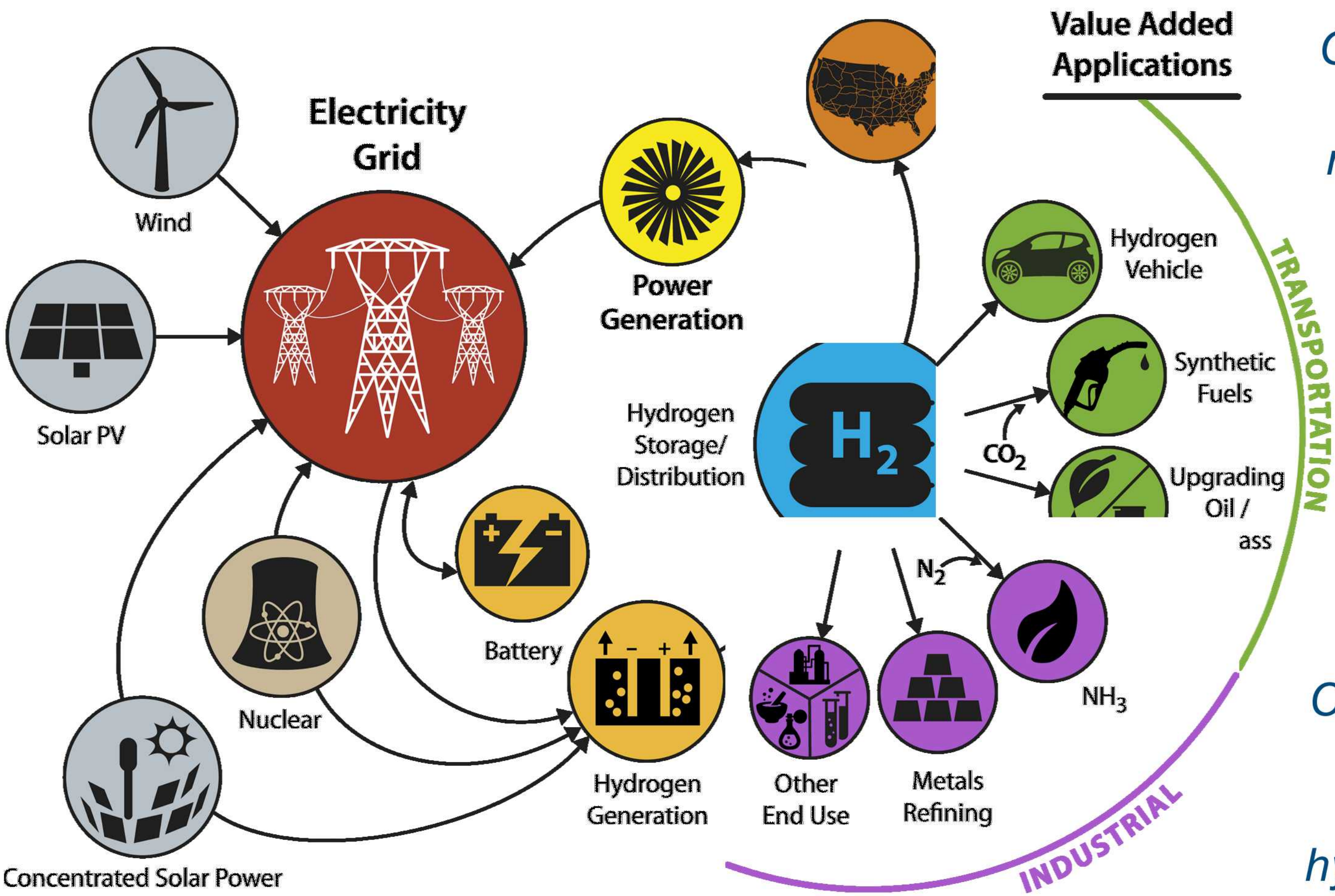
Hydrogen can be used as an energy carrier to store and convey energy as well as to serve a wide range of industrial and transportation applications



Current H2 usage in the US is about 10 million MT annually, mostly for refining and fertilizer production

Close to 1,000 km of pipeline in the US are dedicated to hydrogen coveyance

Illustrative example, not comprehensive; from H2@Scale Concept, developed by FCTO/DOE

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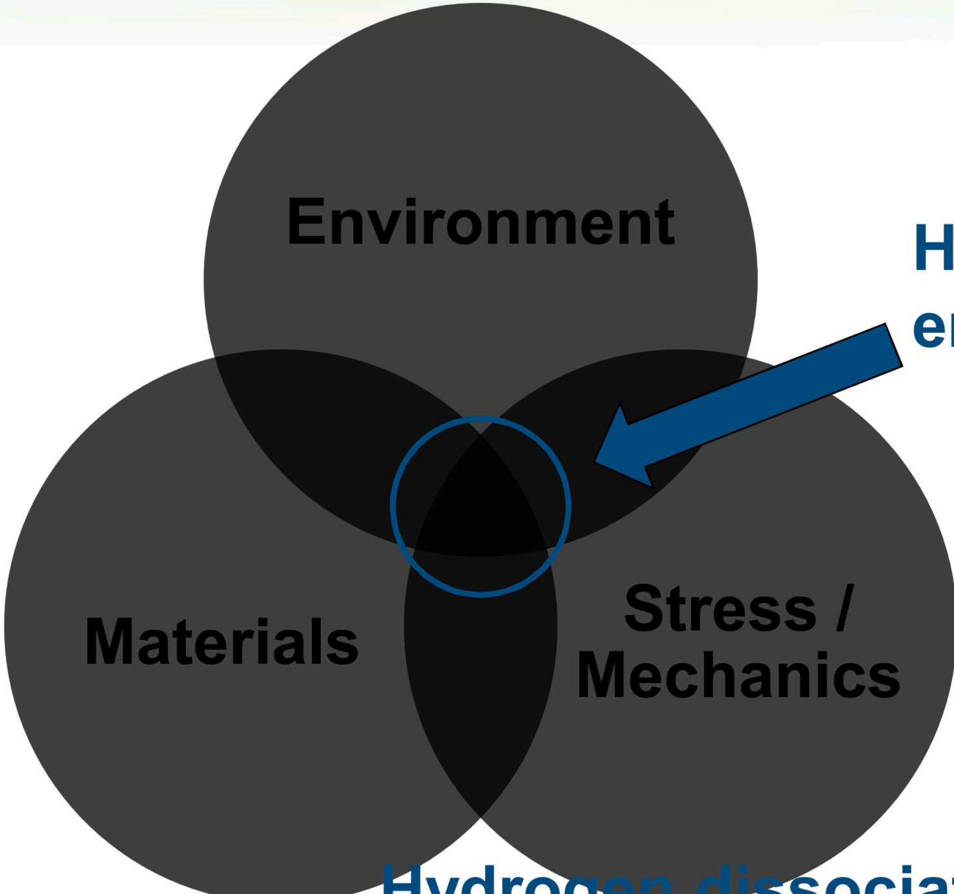
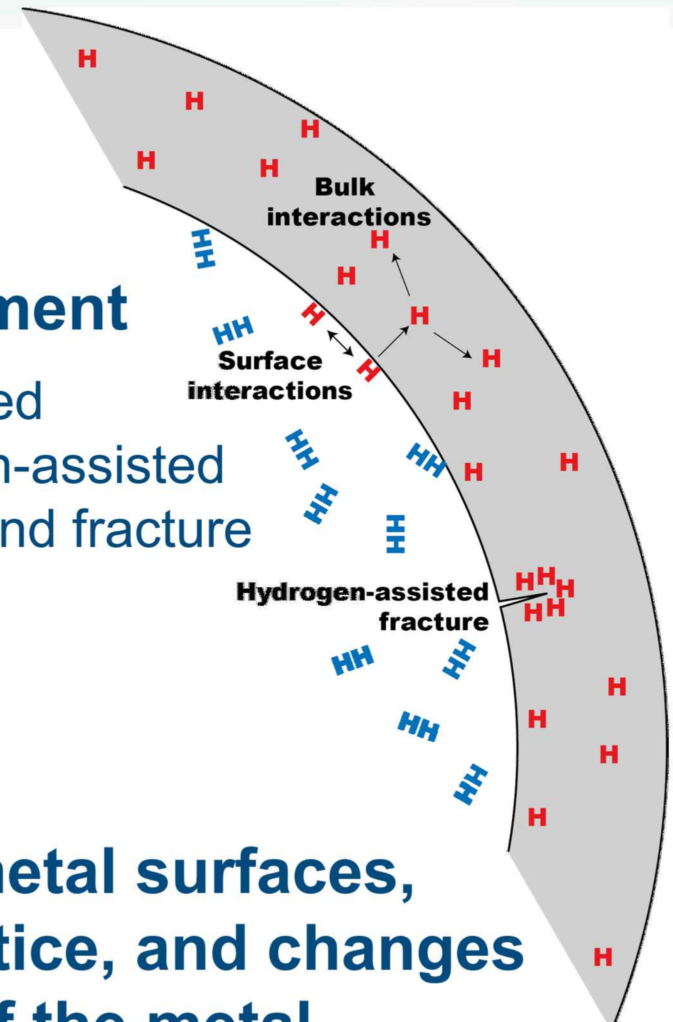
Hydrogen embrittlement occurs in materials under the influence of stress in hydrogen environments



Hydrogen embrittlement

also called hydrogen-assisted fatigue and fracture



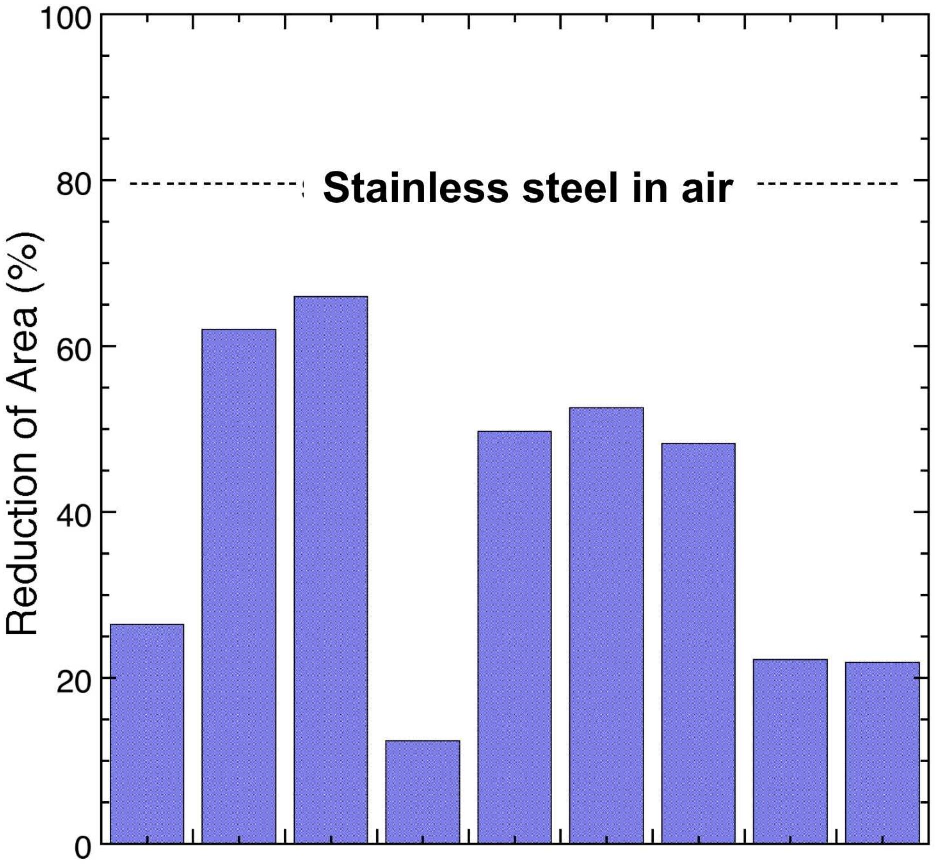
Hydrogen dissociates on metal surfaces, dissolves into the metal lattice, and changes the mechanical response of the metal

Pop Quiz

Pop

Poll

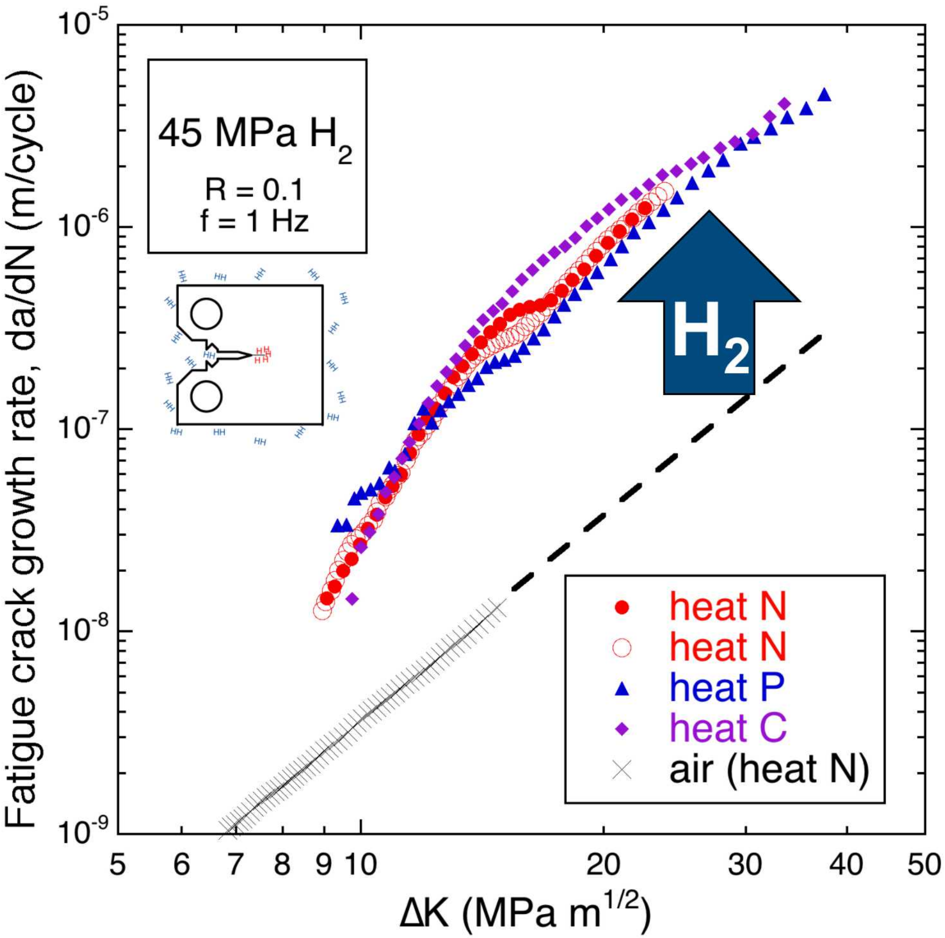
Which of these materials should be on an approved list for use in gaseous hydrogen?



Tension

- **Tensile testing in gaseous hydrogen reveals a loss of ductility**
- **Which of these materials should be on an approved list for hydrogen service?**
  - **(a) all**
  - **(b) none**
  - **(c) RA > X%**

Is this material safe for use in gaseous hydrogen?

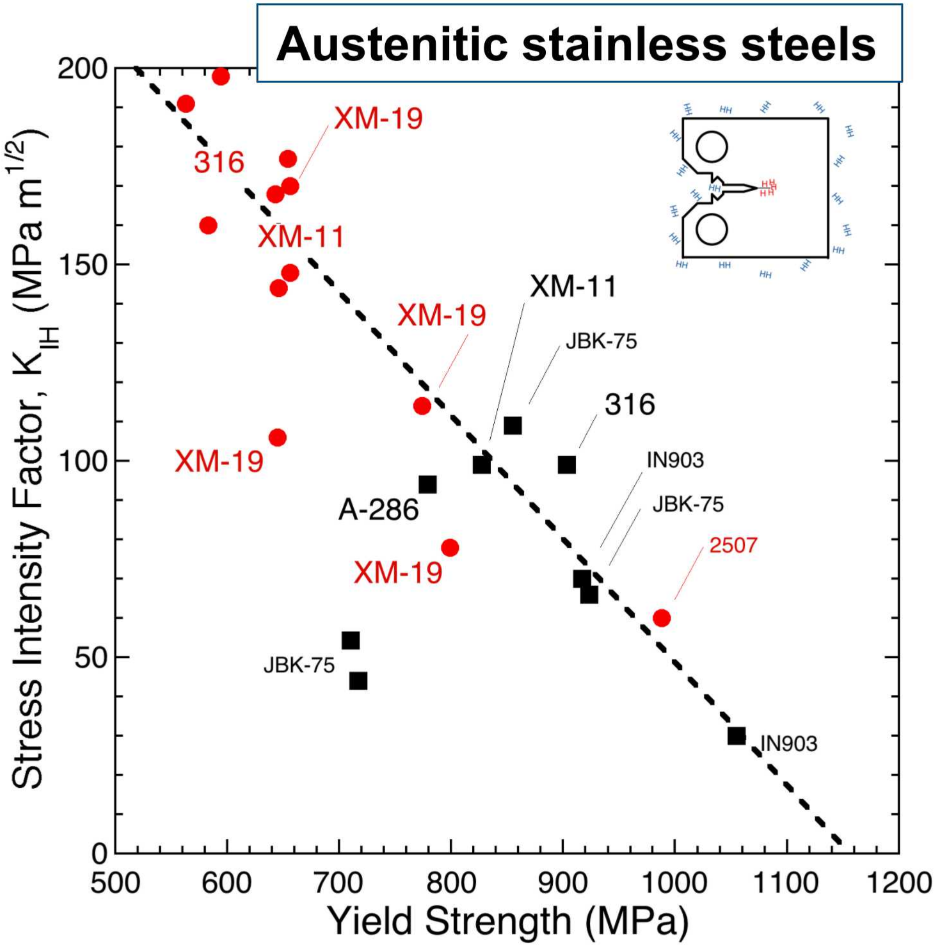


Fatigue

- Fatigue crack growth rate is accelerated by >10X in H2 compared to air
- This material is safe for use in gaseous hydrogen?
  - (a) True
  - (b) False

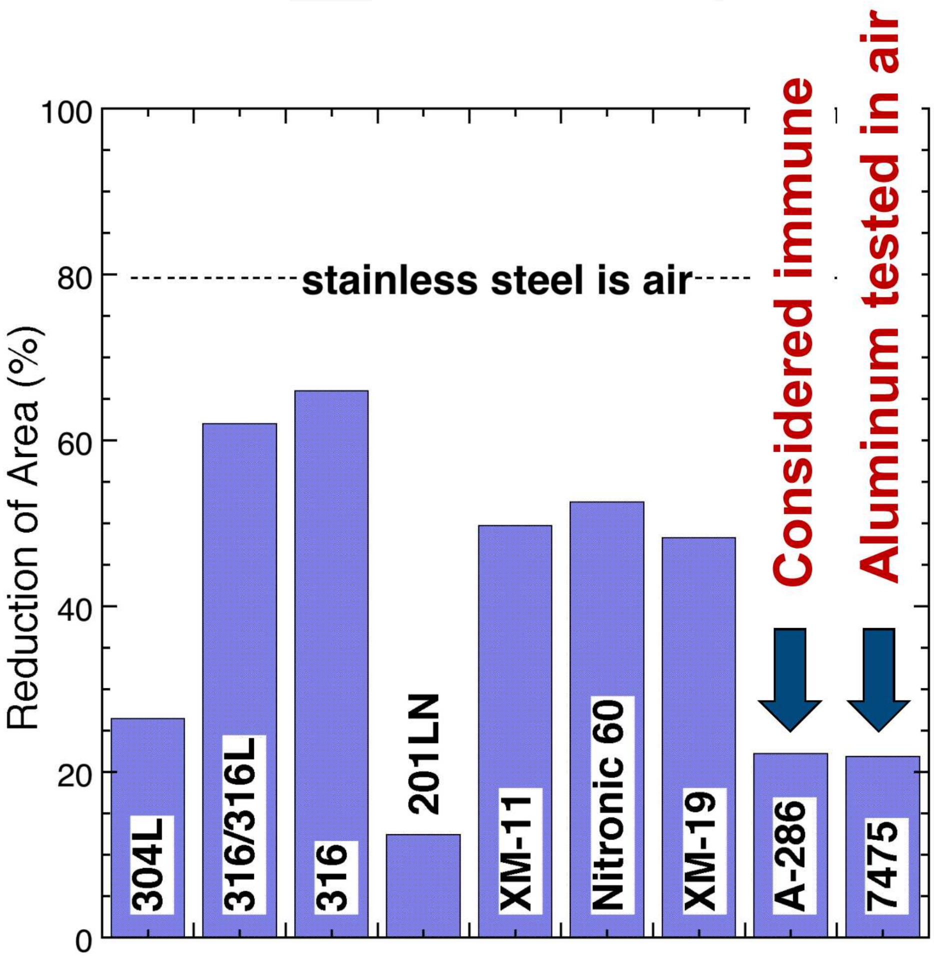
Are any of these materials appropriate for hydrogen service?

Fracture



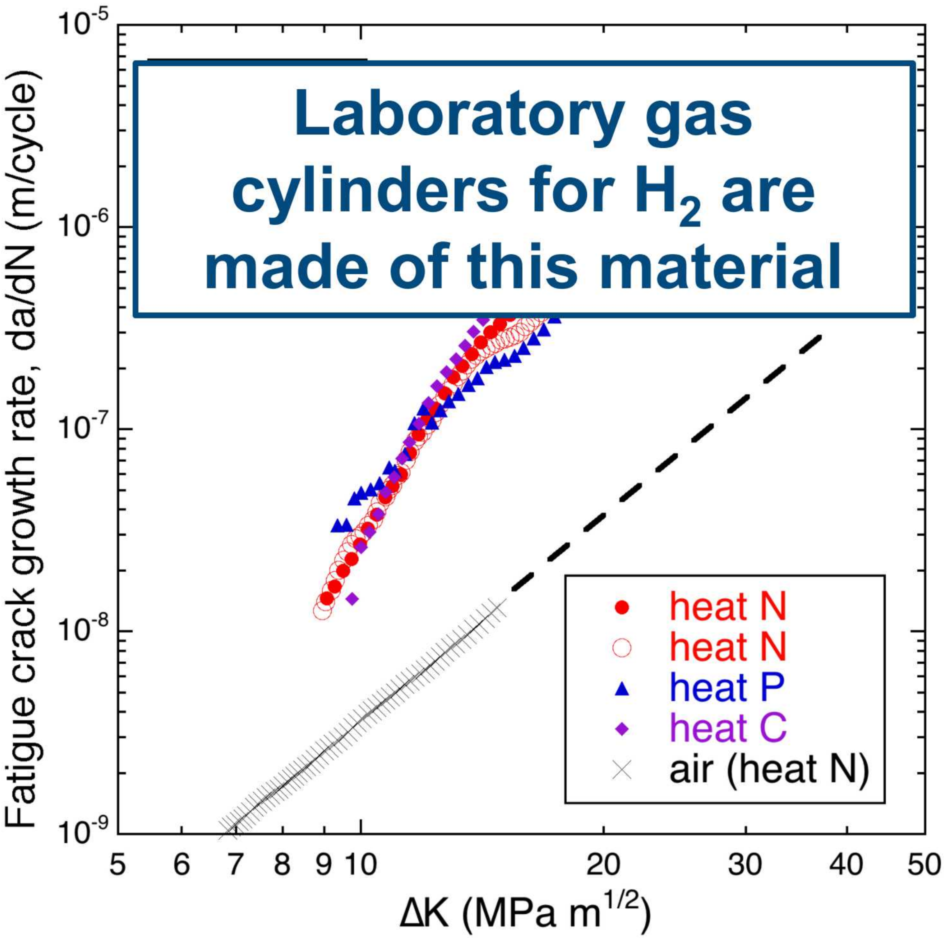
- Fracture resistance in gaseous hydrogen (K_{IH}) is reduced by >50% for all steels on this plot
- Which if any can be used in hydrogen?
  - (a) all
  - (b) none
  - (c) the ones in red

Which of these materials should be on an approved list for use in gaseous hydrogen?



- Tensile response depends on many factors
- Some materials have low ductility in air: aluminum
- Kinetics may bias data of other materials: A-286
- Difficult to interpret tensile ductility in the context of materials selection without additional information

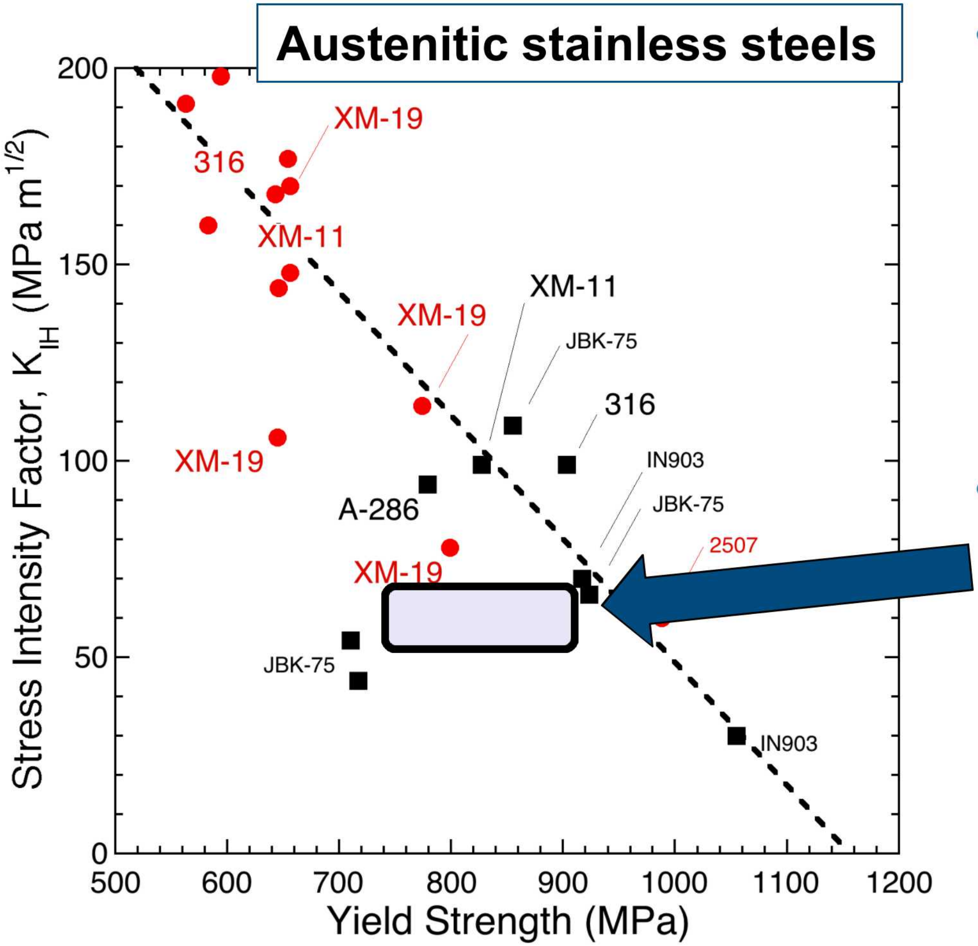
Is this material safe for use in gaseous hydrogen?



Materials requirements depend on the application and the design

- Gas cylinders are made from relatively low strength steels
- Wall stresses are relatively low
- Number of pressure cycles are modest
- Manufacturing defects are well characterized

Are any of these materials appropriate for hydrogen service?



- **Fracture resistance in gaseous hydrogen (K_{IH}) remains quite high for the majority of steels on this plot**
- **Compare, for example, typical range of properties for pressure vessel steels used in gaseous hydrogen**

Pop Poll Results

Materials selection is neither straightforward nor simple.

Materials selection depends on the application (*i.e.*, environment) and design features (*i.e.*, stresses)

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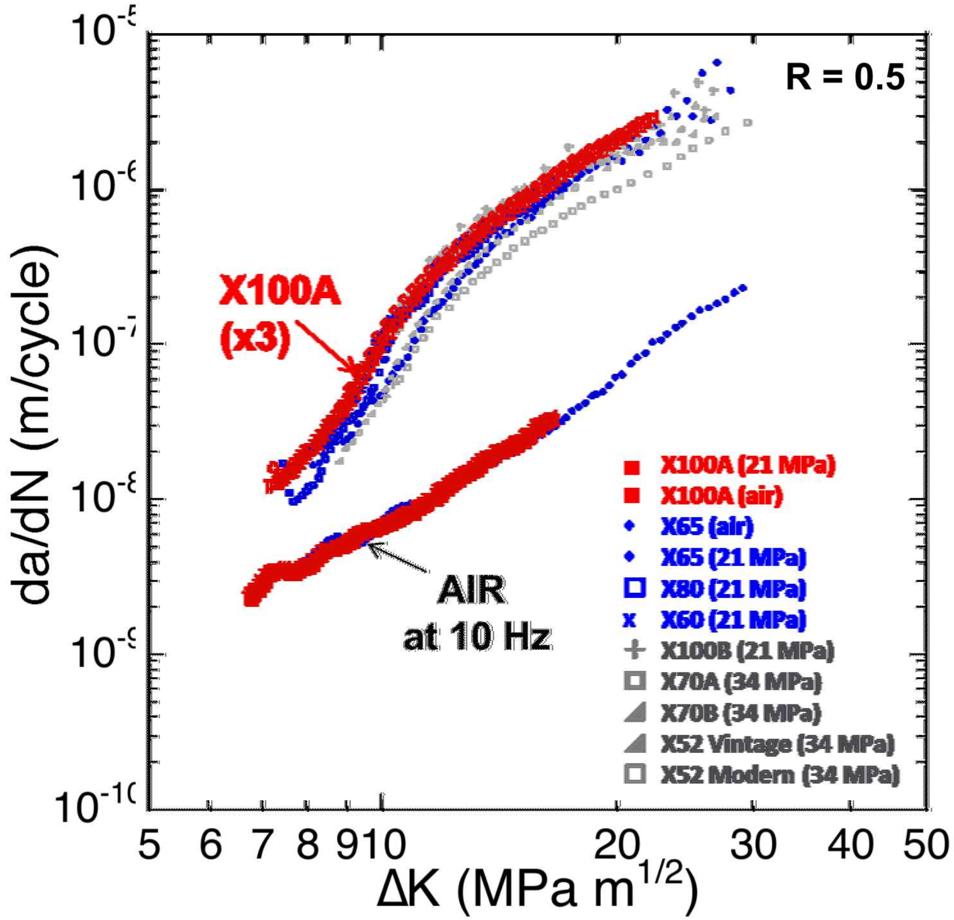
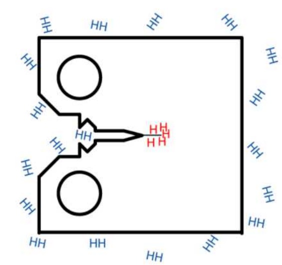
- **How does gaseous hydrogen affect fatigue and fracture of pipeline steels?**
- Is there a threshold below which hydrogen effects can be ignored?
- Can the effects of hydrogen be masked by other physics?
- What is the implication of hydrogen on life of pipelines?

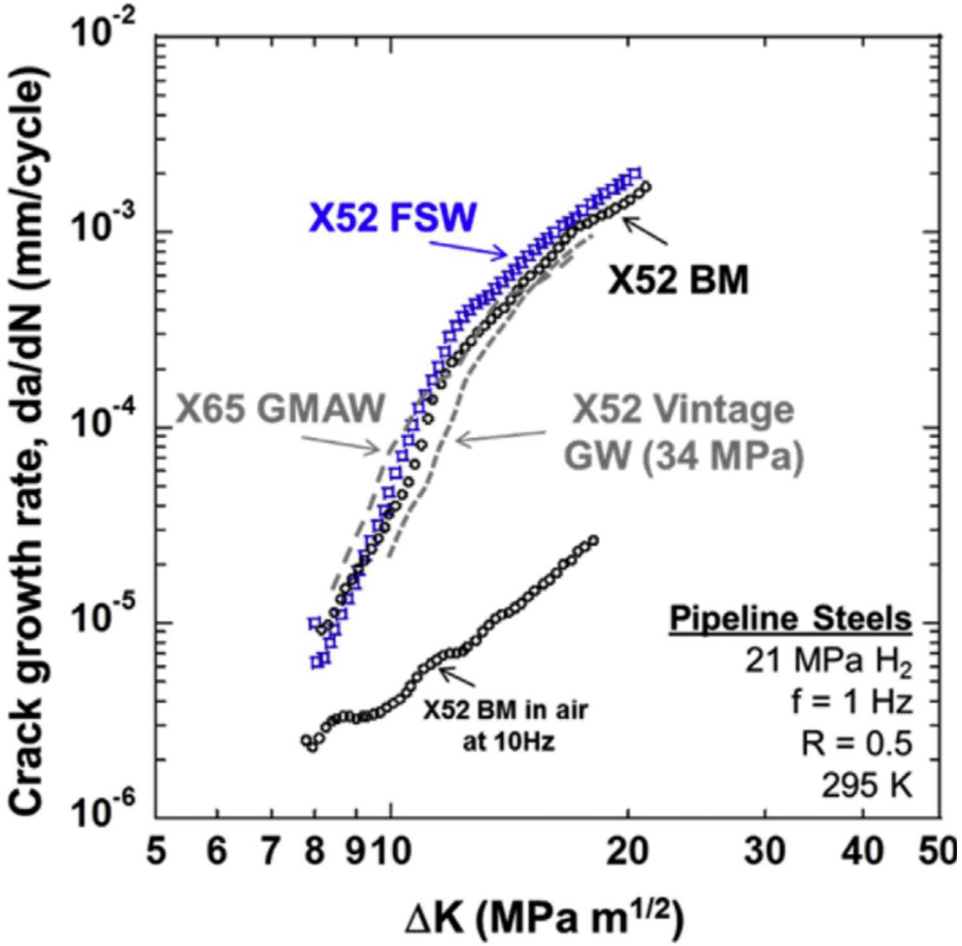
Pipeline steels tend to show very similar fatigue crack growth rates in gaseous hydrogen



- A wide variety of pipeline steels display nominally the same fatigue response in high-pressure gaseous hydrogen
- The effect of pressure on fatigue crack growth rates is modest for high-pressure hydrogen

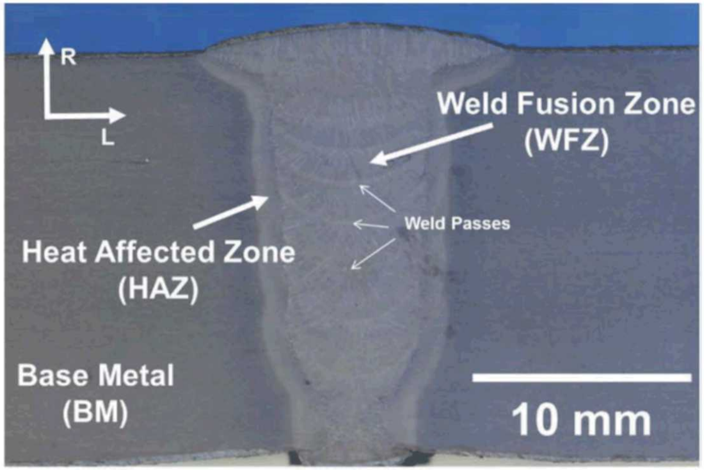


Welds in pipelines tend to show similar fatigue crack growth rates as the base metals in hydrogen

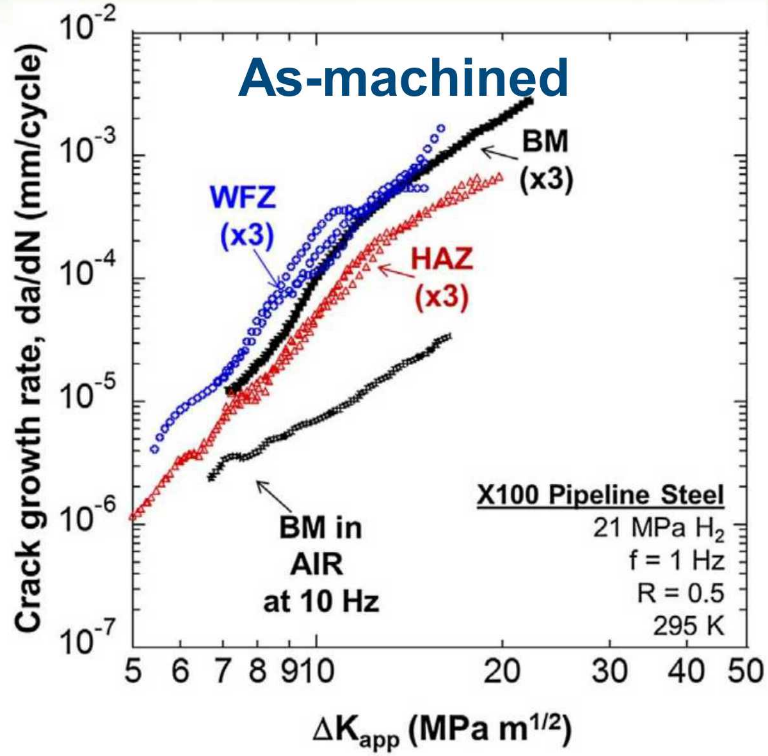


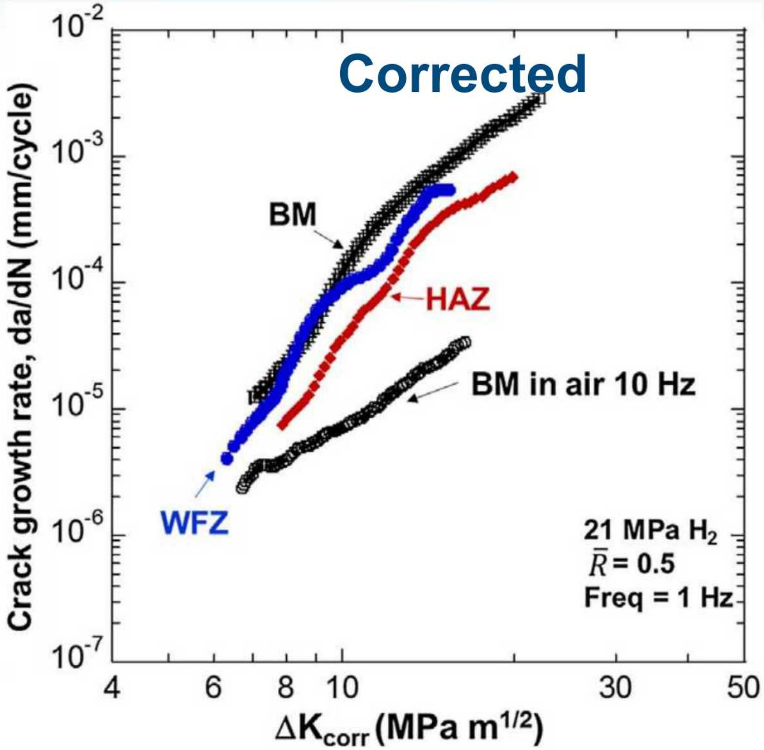
From: Ronevich et al, Eng Fract Mech 194 (2018) 42-51.

- To first order, welds behave similarly in gaseous hydrogen as the base metals
- Similar trends have been observed for a variety of weld processes



Residual stresses impact fatigue crack growth rates in hydrogen as in ambient environments

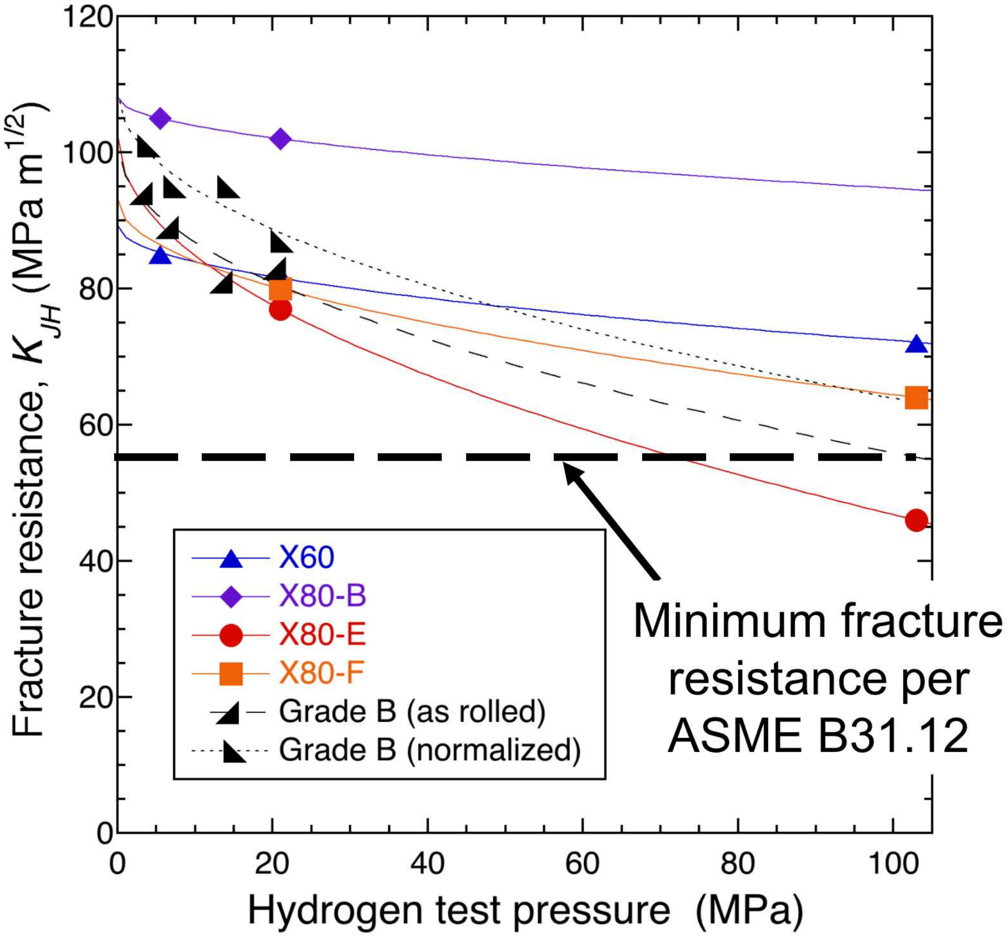




- Residual stresses should be considered, both for influence on measurements and in design
- Base metal properties generally represent weld metal

From: Ronevich et al, Eng Fract Mech 194 (2018) 42-51.

Pipeline steels have relatively high fracture resistance in gaseous hydrogen



- Data sets that evaluate effect of pressure on fracture are relatively limited
- Available data suggest fracture depends on pressure
- Fracture resistance (even at low pressure) is significantly lower than in air

From: San Marchi et al, ASME PVP-2011 conf.

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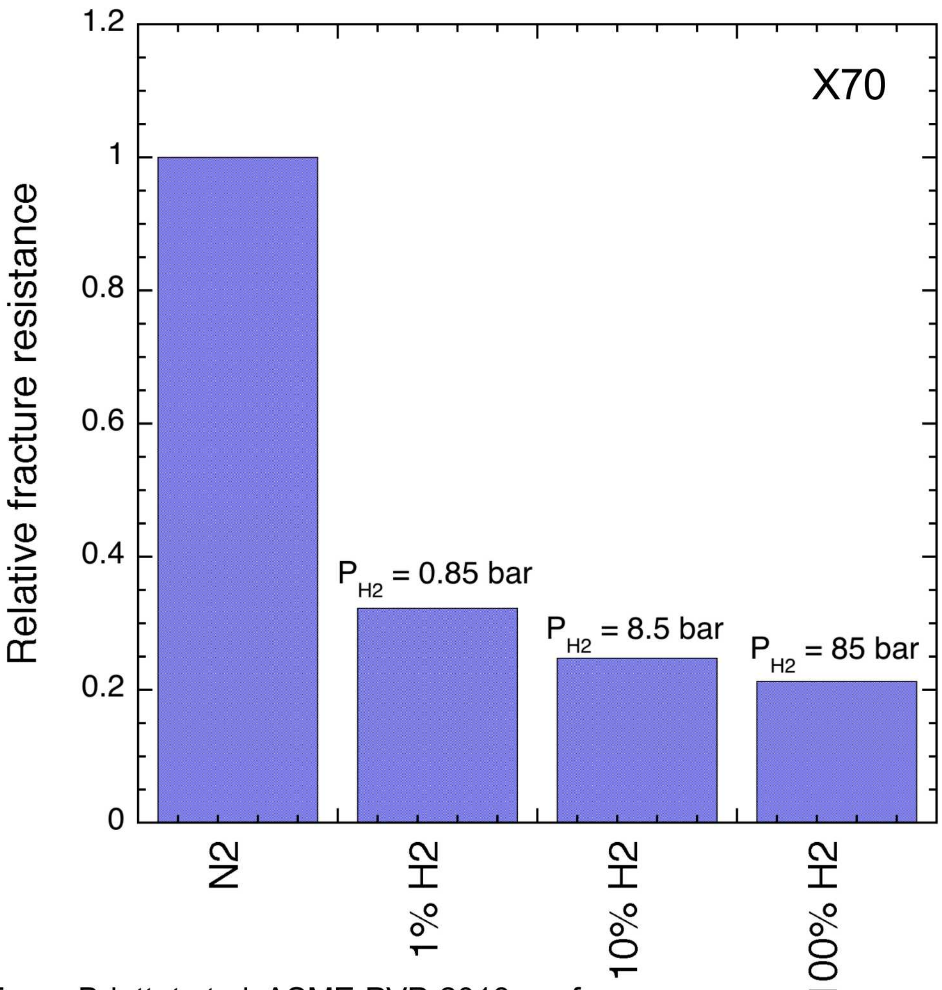
- What is the implication of hydrogen on life of pipelines?

Low pressure H2 has substantial effect on fracture resistance of pipeline steels

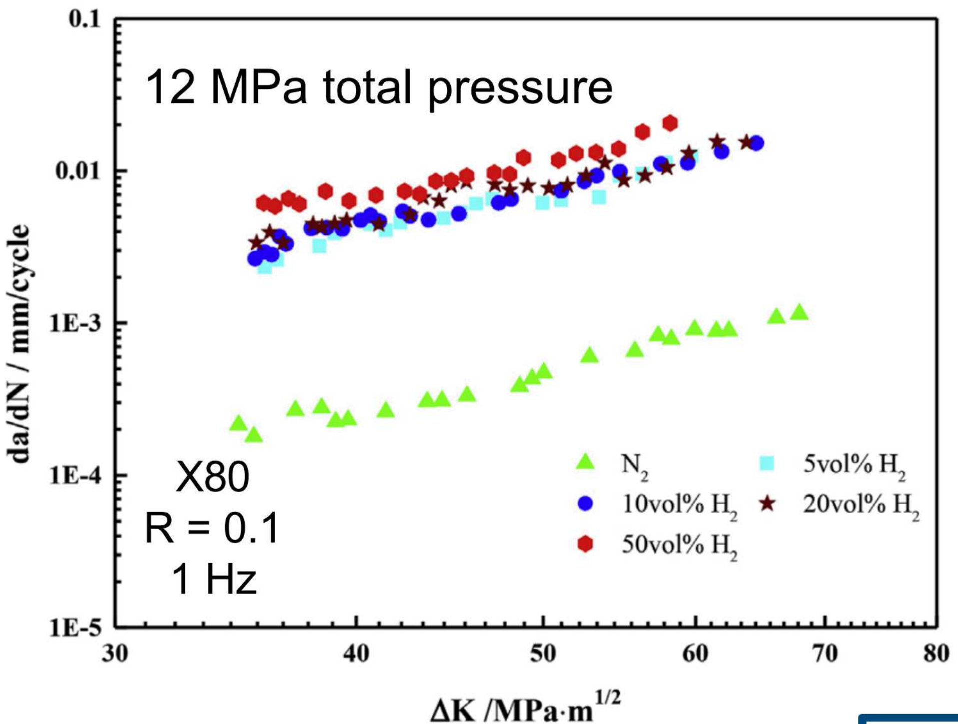


From: Briottet et al, ASME PVP-2018 conf.

- **Measurements of fracture resistance in gaseous mixtures of H2 and N2 show substantial effects of H2**
- **1% H2 is only modestly different than 100% H2**

<1 bar of H2 reduces fracture resistance

Low pressure H2 has substantial effect on fatigue crack growth of pipeline steels



From: Meng et al, *IJ Hydrogen Energy* **42** (2017) 7404.

- **Measurements in gaseous mixtures of H2 and N2 show acceleration of fatigue crack growth rate with 5% H2**
  - **But little additional acceleration with higher H2 content**

Small amounts of hydrogen can have substantial effect on fatigue and fracture

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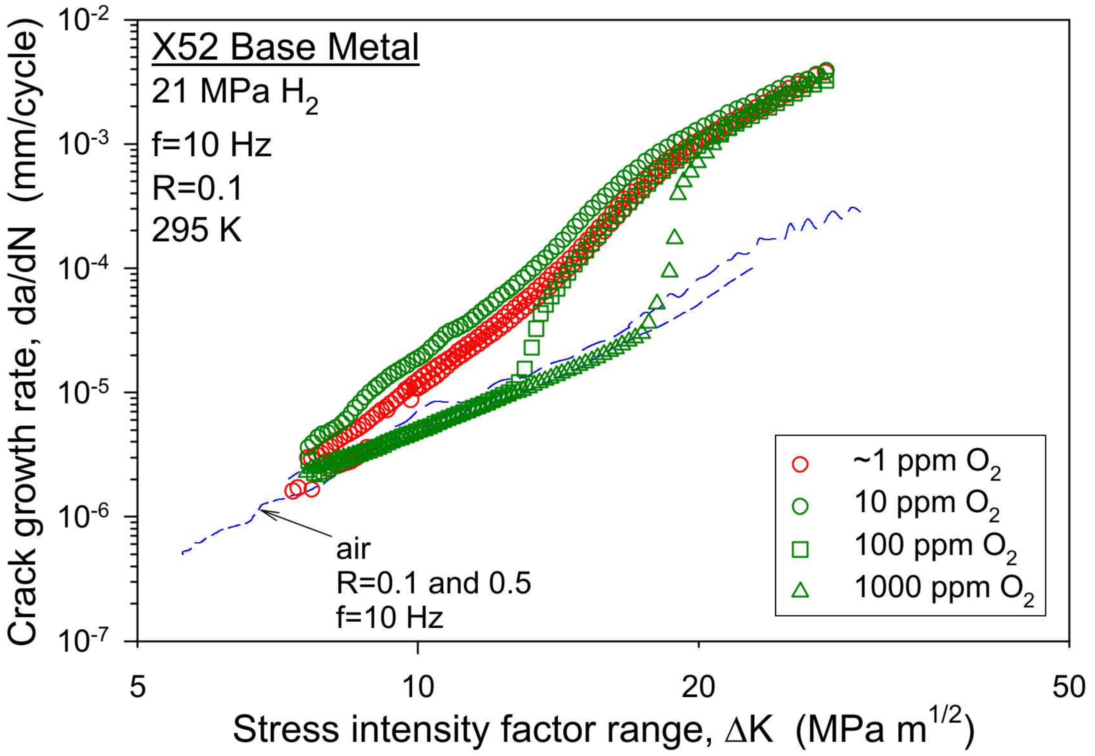
- What is the implication of hydrogen on life of pipelines?

Impurities can influence measurements, but can also provide pathways to mitigate the effects of H2



- **Oxygen mitigates H2-accelerated fatigue crack growth rates at low ΔK**
- **Attributed to oxygen diffusion to new crack surfaces**

From: Somerday et al, *Acta Mater* **61** (2013) 6153.

Impurity content in H2 can have substantial effects on both measurements and in-service performance

The role of mixed hydrogen gas environments and impurities should be considered carefully

- Small partial pressure of gaseous H2 can have substantial effects on fracture and fatigue of steels
- Oxygen can mitigate effects of H2 in ferritic steels
  - Sensitive to mechanical and environmental variables
  - Other passivating species can have similar effects
- Structural integrity of pipelines carrying mixed gases will depend sensitively on the details
  - NG has many impurities, which can mitigate H2 effects
  - Pure methane is inert and even small additions of H2 can be significant

Materials compatibility for hydrogen containment structures depends on the application and the design

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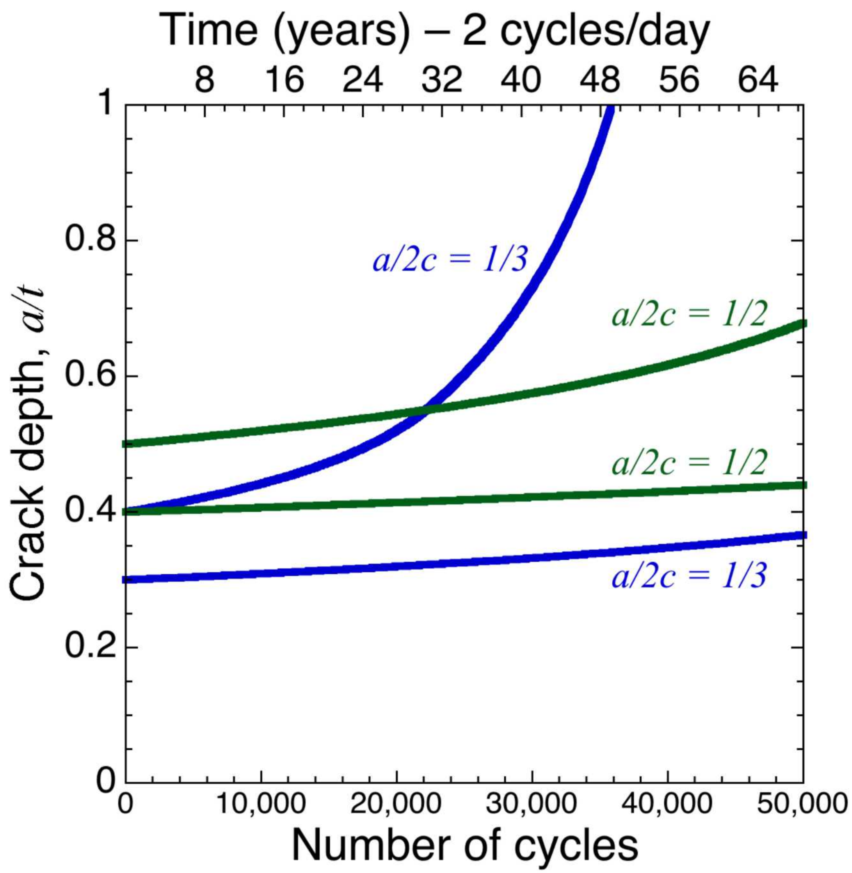
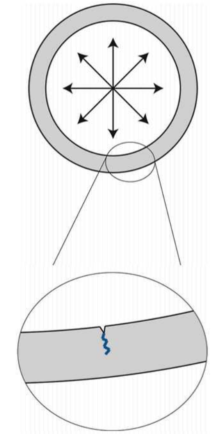
- **What is the implication of hydrogen on life of pipelines?**

Predicted lifetime of pipeline with growing fatigue cracks in hydrogen



<u>Assuming</u>

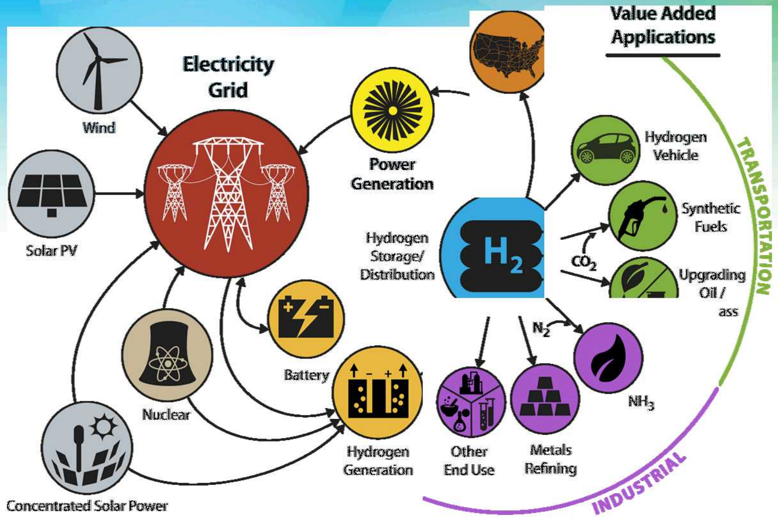


- OD = 762 mm, t = 15.9 mm
- Pressure cycles between 4 and 7 MPa
- Constant crack shape ($a/2c$)
- Large initial defects
- Fatigue crack growth rates in pure H2 (at higher pressure)

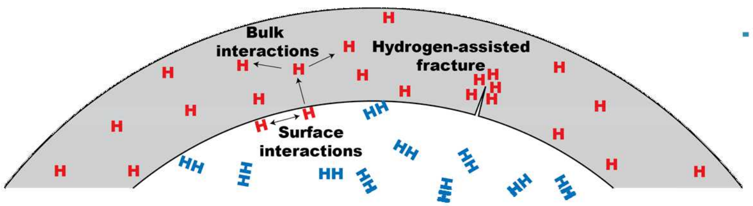
> - **10,000s of cycles are needed to extend the crack**
> - **At 2 cycles per day, decades are needed to advance the crack**

Summary

- **Why hydrogen in pipelines?**
  - *Hydrogen is a carbon-free energy carrier and enables renewables*

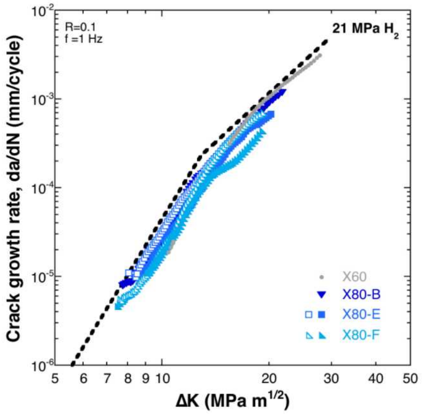


- **What is hydrogen embrittlement and when is it important?**

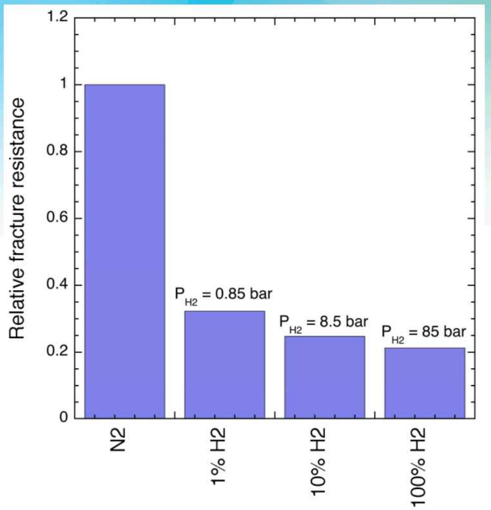


  - *Hydrogen degrades mechanical properties of most metals*

- **How does gaseous hydrogen affect fatigue and fracture of pipeline steels?**
  - *Fatigue is accelerated by >10x and fracture resistance is reduced by >50%*

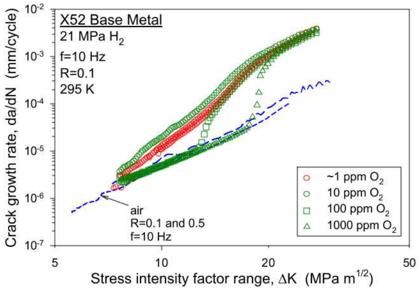


Summary



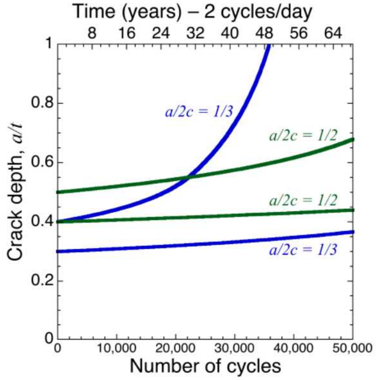
- **Is there a threshold below which hydrogen effects can be ignored?**
  - ***NO, even small amounts of hydrogen have large effects***

- **Can the effects of hydrogen be masked by other physics?**



  - ***Oxygen can mitigate the effects of hydrogen in some cases, which perhaps can be exploited***

- **What is the implication of hydrogen on life of pipelines?**
  - ***If fatigue cycles are modest, lifetime calculations suggest long life in hydrogen***



Thank you for your attention

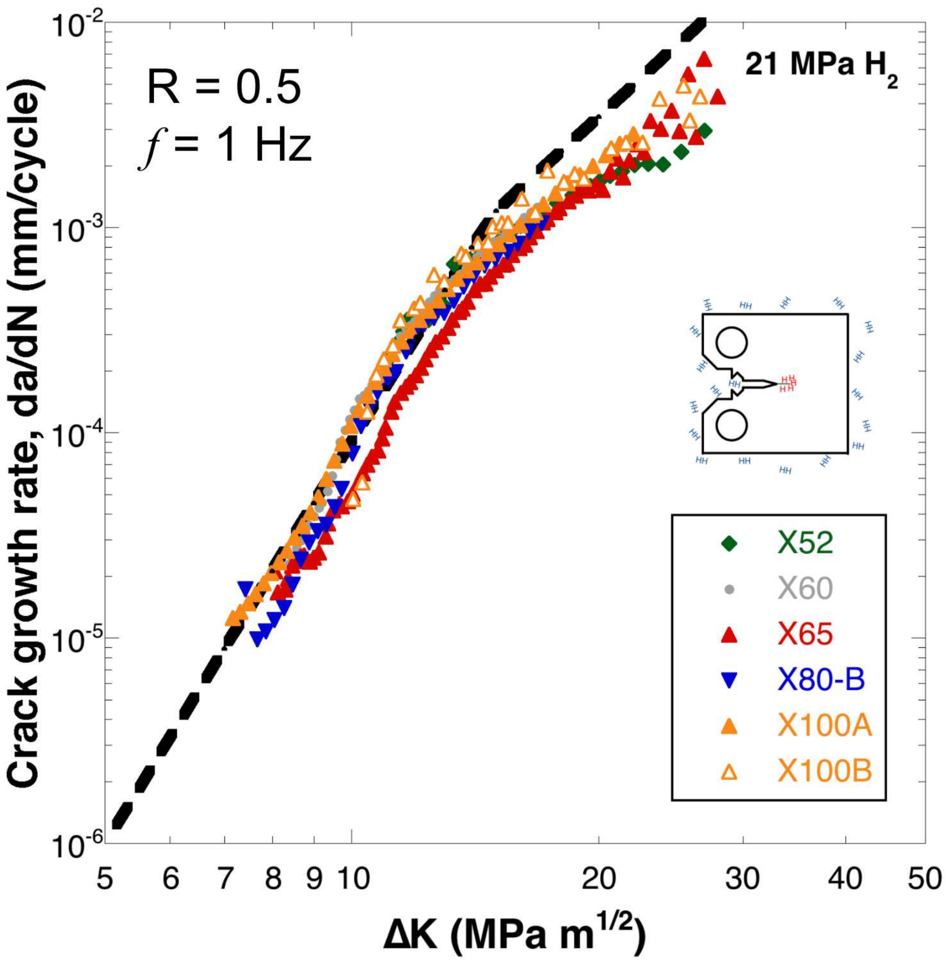
Contacts:

– Chris San Marchi cwsanma@sandia.gov
– Joe Ronevich jaronev@sandia.gov

Additional resources:

– https://energy.sandia.gov/transportation-energy/hydrogen/materials-components-compatibility/
– Technical Reference: https://www.sandia.gov/matlsTechRef/
– Hydrogen-materials database: https://granta-mi.sandia.gov

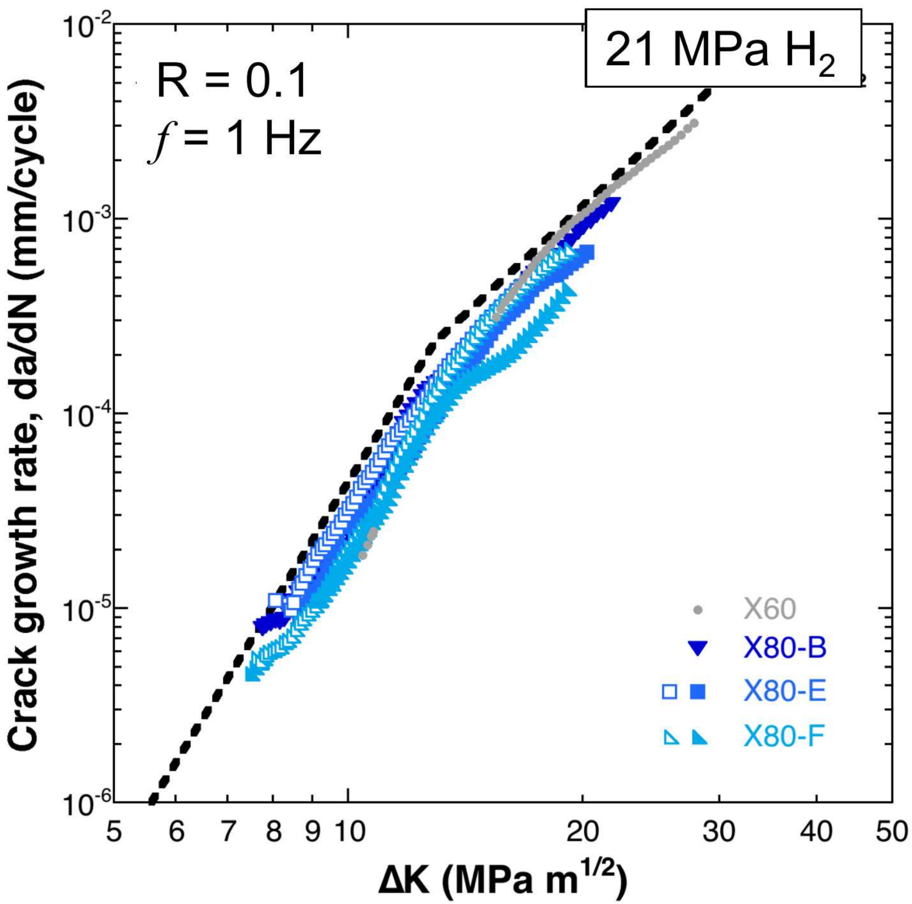
The effects of H2 on fatigue crack growth in steels can be captured with "master" design curve

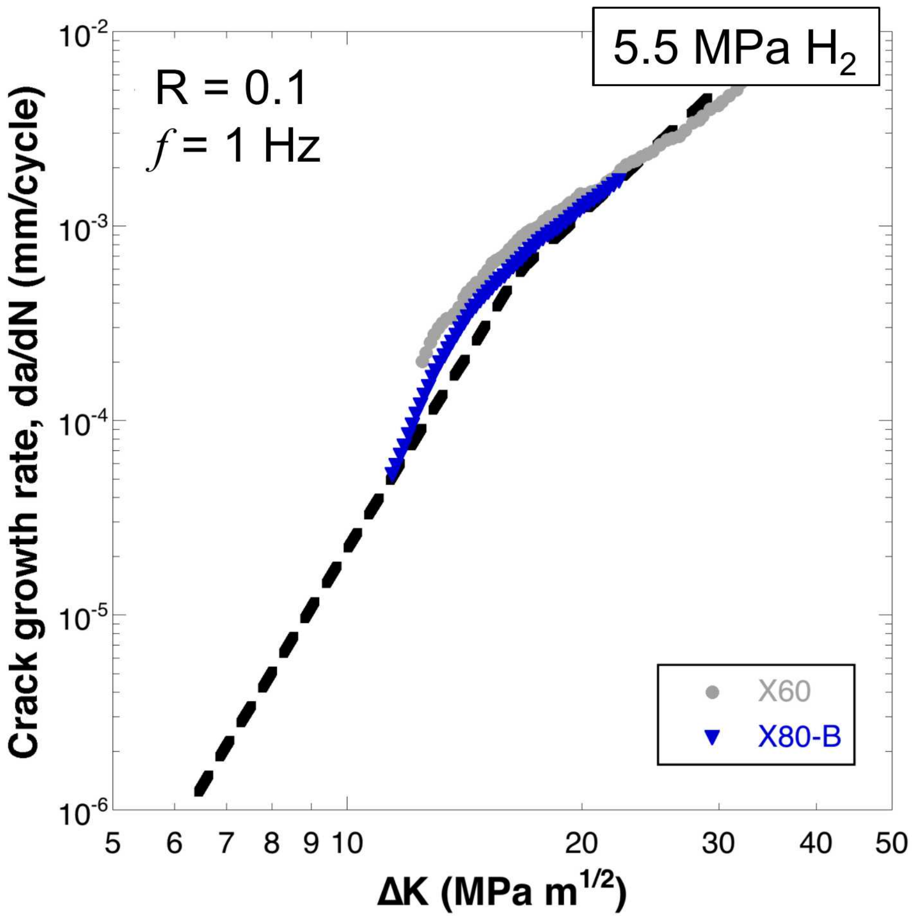


- Tested steels represent:
  - Wide range of strength
  - Wide range of microstructure
- A relatively simple master curve has been developed (dashed line) that bounds fatigue crack growth performance in gaseous hydrogen

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

Simple formulation of “master” design curves captures the trends in experimental data



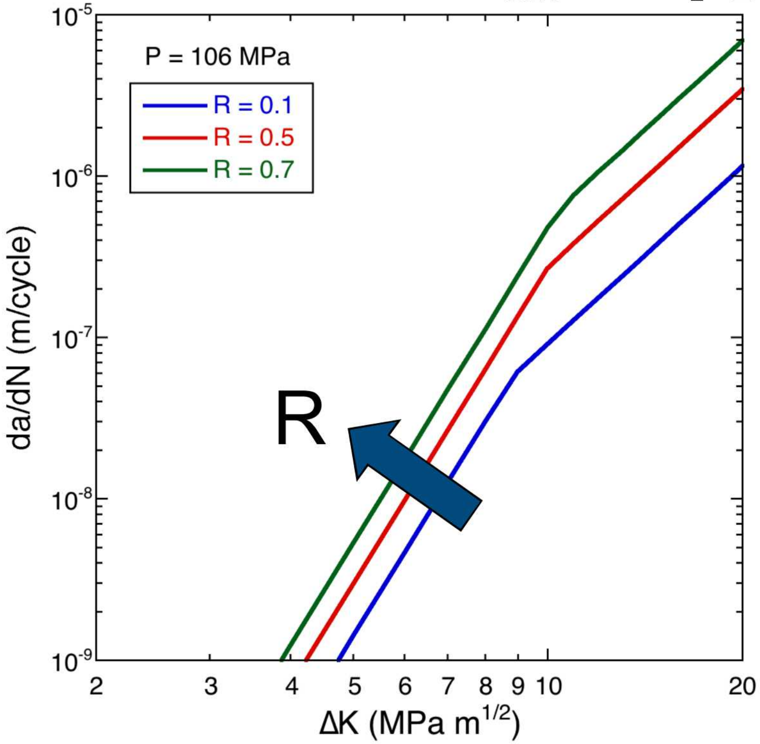


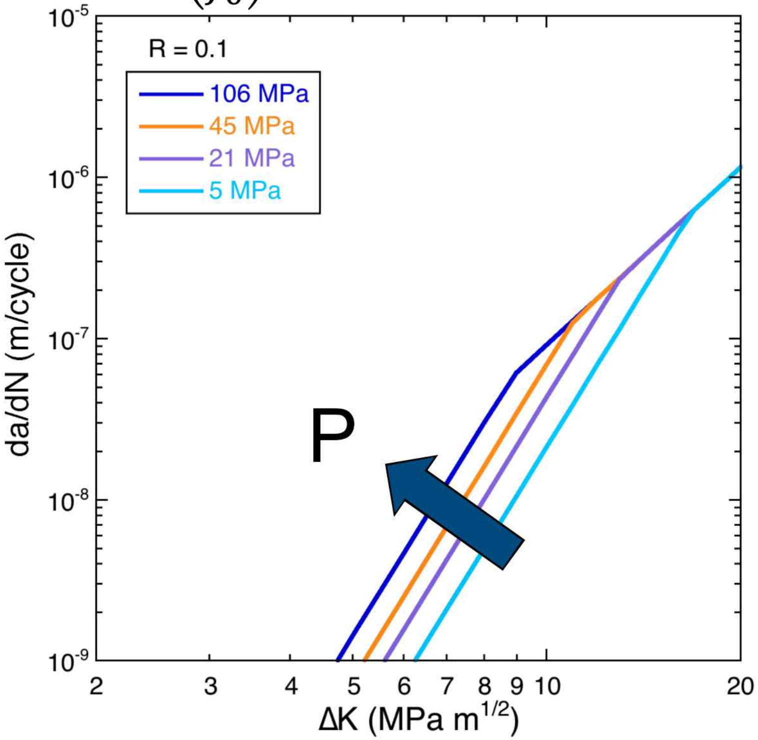
Sandia National Laboratories

H2FC Hydrogen and Fuel Cells Program

The "master" design curve enables prediction of bounding behavior for load ratio and pressure

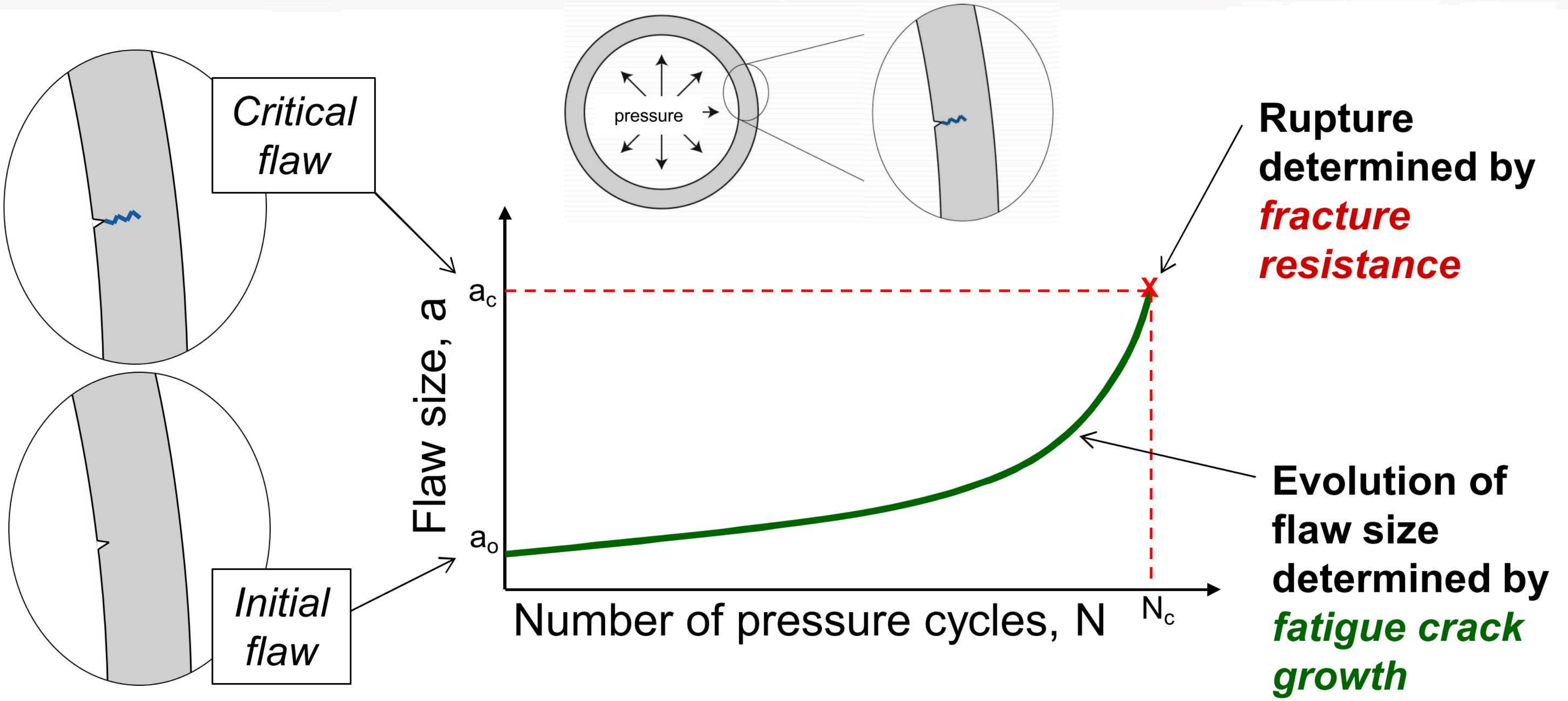
$$\frac{da}{dN} = C_1 \left[\frac{1 + C_2 R}{1 - R}\right] \Delta K^m \left(\frac{f}{f_0}\right)^{1/2}$$





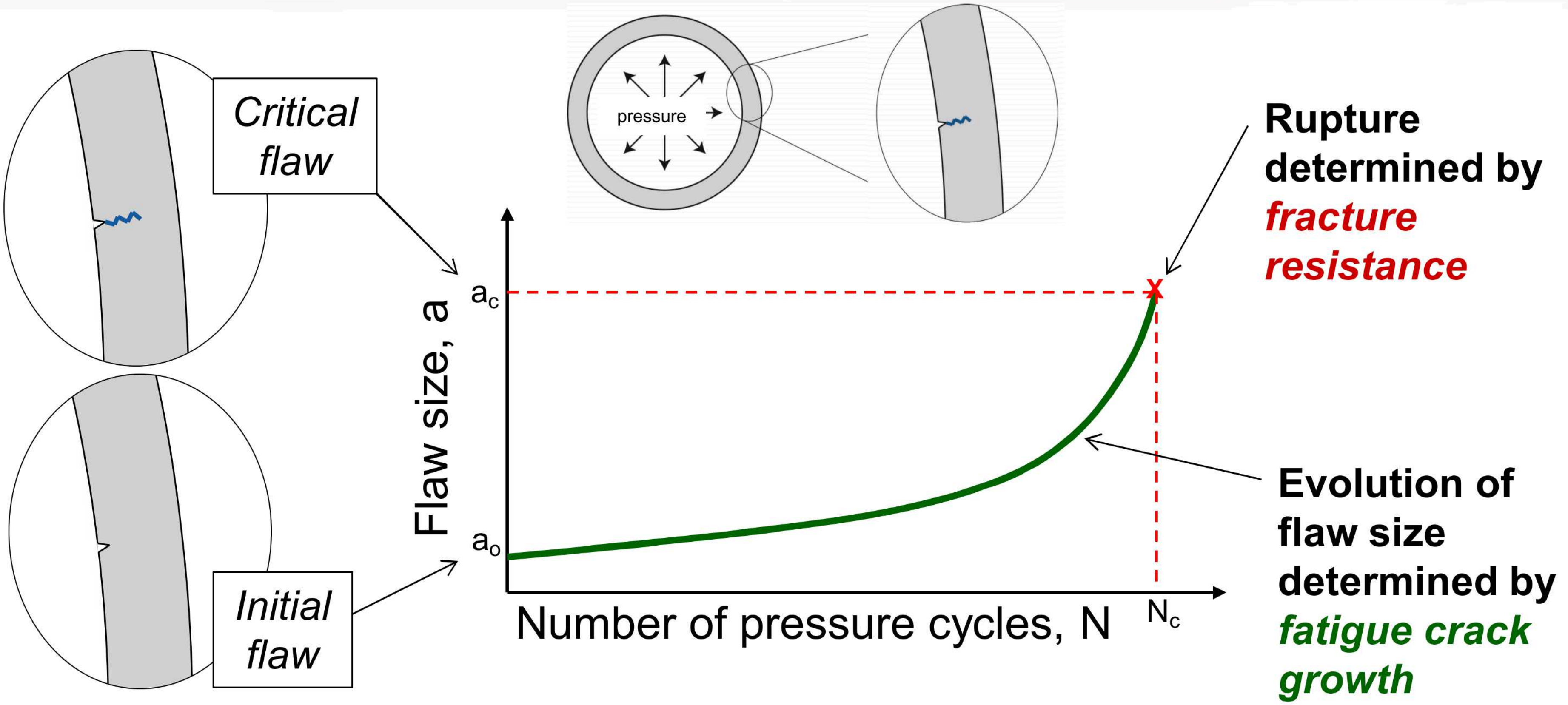
The bound at high ΔK is dependent on R (i.e., K_{max}), but not sensitive to pressure

Fracture mechanics-based assessment of fatigue and fracture of pipelines



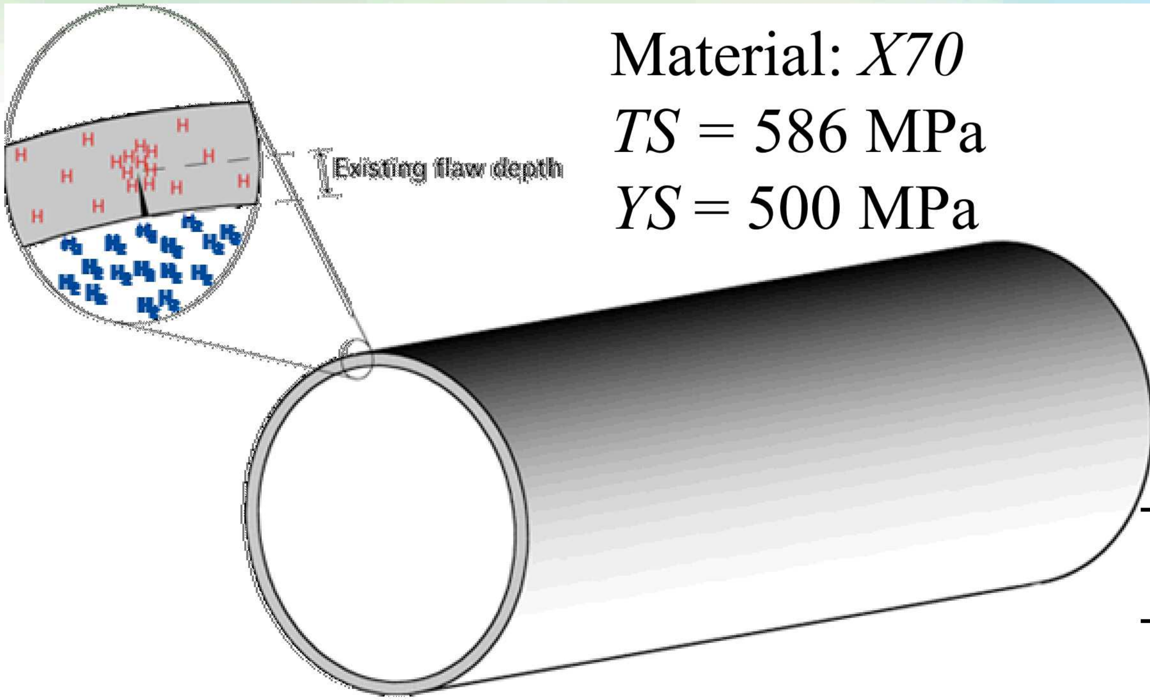
ASME B31.12 describes rules for hydrogen pipelines with reference to ASME BPVC Section VIII, Division 3, Article KD-10

Fracture mechanics-based assessment of fatigue and fracture of pipelines



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

Consider a typical "high-pressure" pipeline



Material: *X70*

TS = 586 MPa

YS = 500 MPa

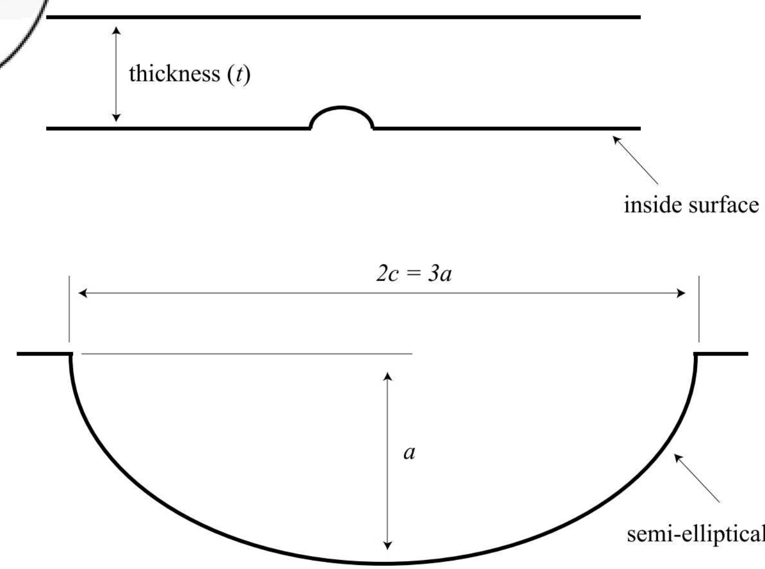
OD = 762 mm

t = 15.9 mm

P_{max} = 7 MPa

P_{min} = 4 MPa

Semi-elliptical crack



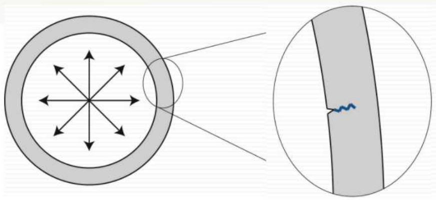
a/t = crack depth

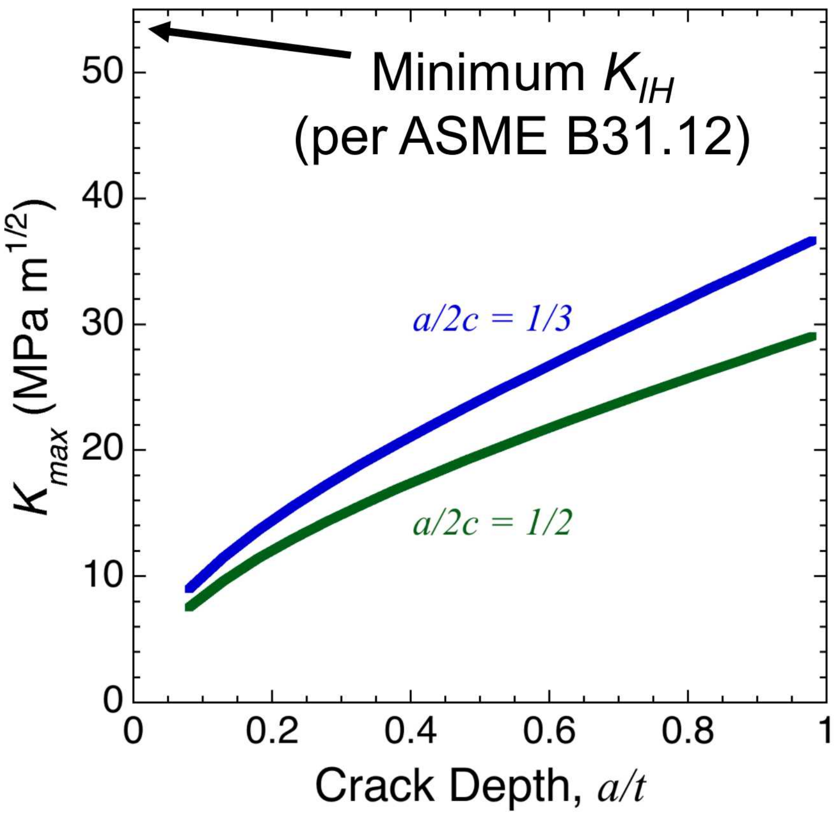
$a/2c$ = depth to length ratio

natural crack shape: $a/2c = 1/2$

ASME crack shape: $a/2c = 1/3$

Stress intensity associated with semi-elliptical crack in "high-pressure" pipeline

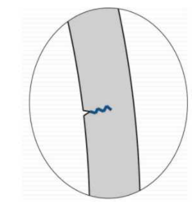




Hoop stress at $P_{max} = 162$ MPa
stress ratio: hoop/TS = 28%

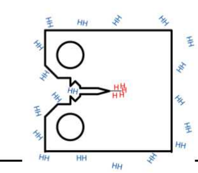
Driving force on semi-elliptical crack:

$$K_{max} < 40 \text{ MPa m}^{1/2}$$



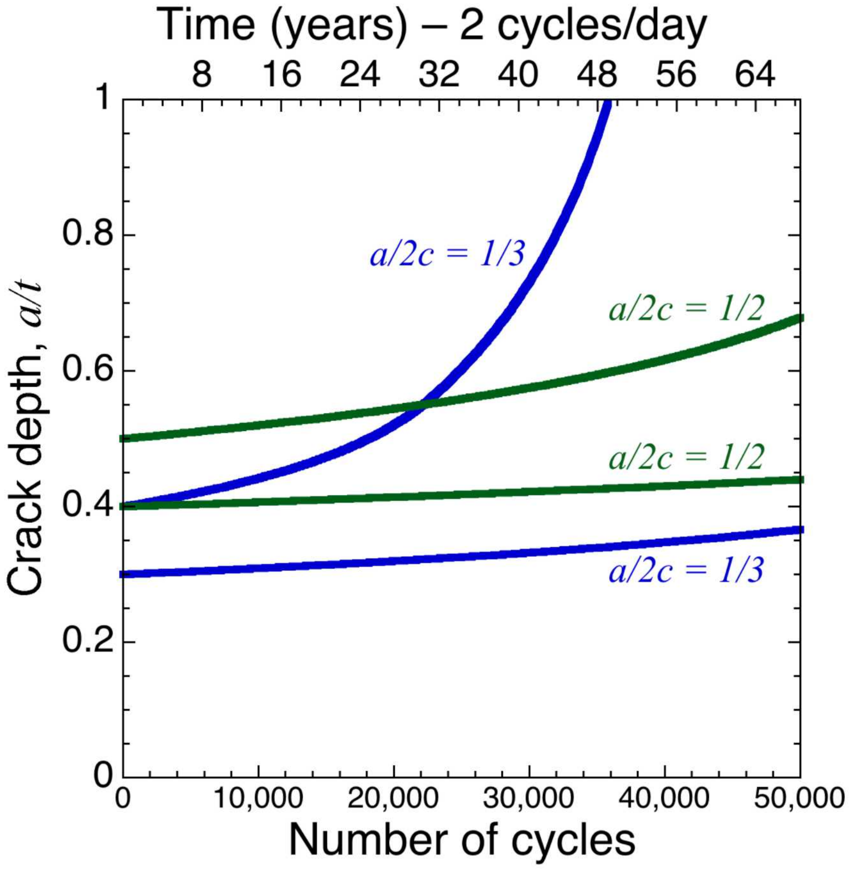
Typical pipeline material fracture resistance:

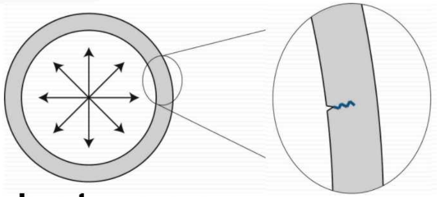
$$K_{JH} > 75 \text{ MPa m}^{1/2}$$



Fracture resistance of pipeline steels in H2 is greater than driving force on semi-elliptical cracks

Predicted lifetime of pipeline with growing fatigue cracks in hydrogen





<u>Assuming</u>

- Pressure cycles between 4 and 7 MPa
- Constant crack shape ($a/2c$)
- Large initial defects
- Fatigue crack growth rates in pure H2 (at higher pressure)

- **10,000s of cycles are needed to extend the crack**
- **At 2 cycles per day, decades are needed to advance the crack**