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Hydrogen Effects on Pipeline Steels and Blending into Natural Gas

Joe Ronevich and Chris San Marchi
Sandia National Laboratories, Livermore, CA

American Gas Association
Sustainable Growth Committee
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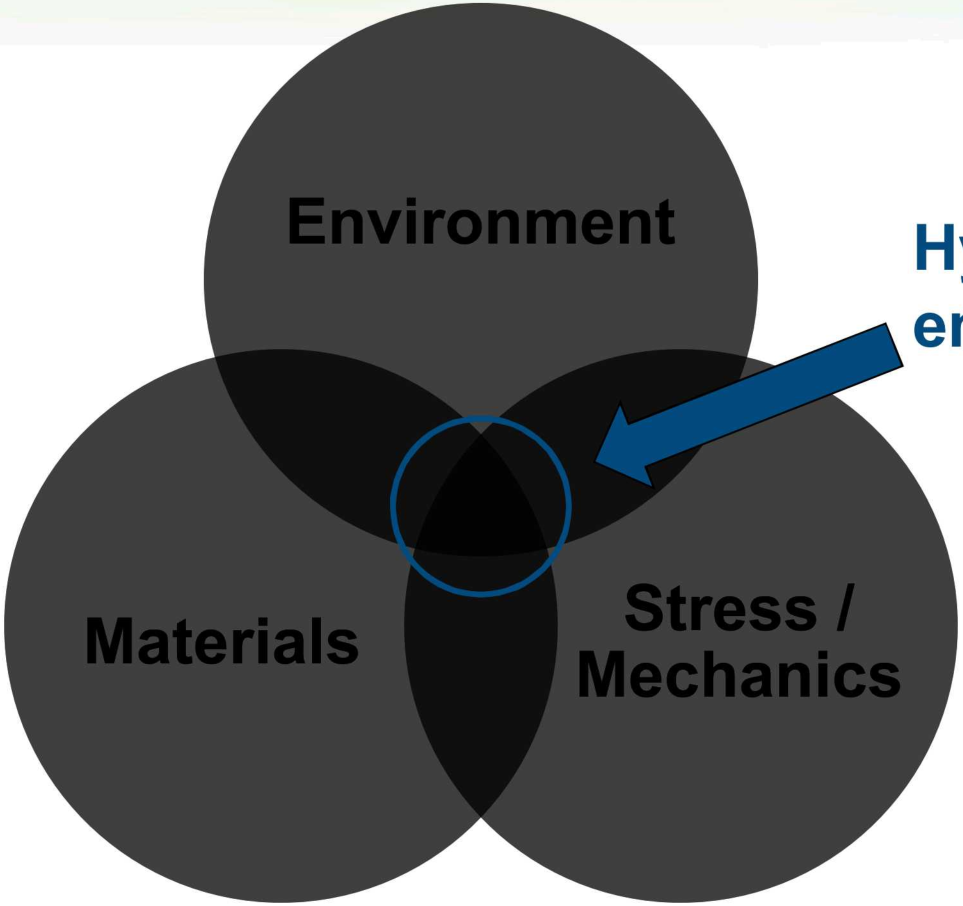
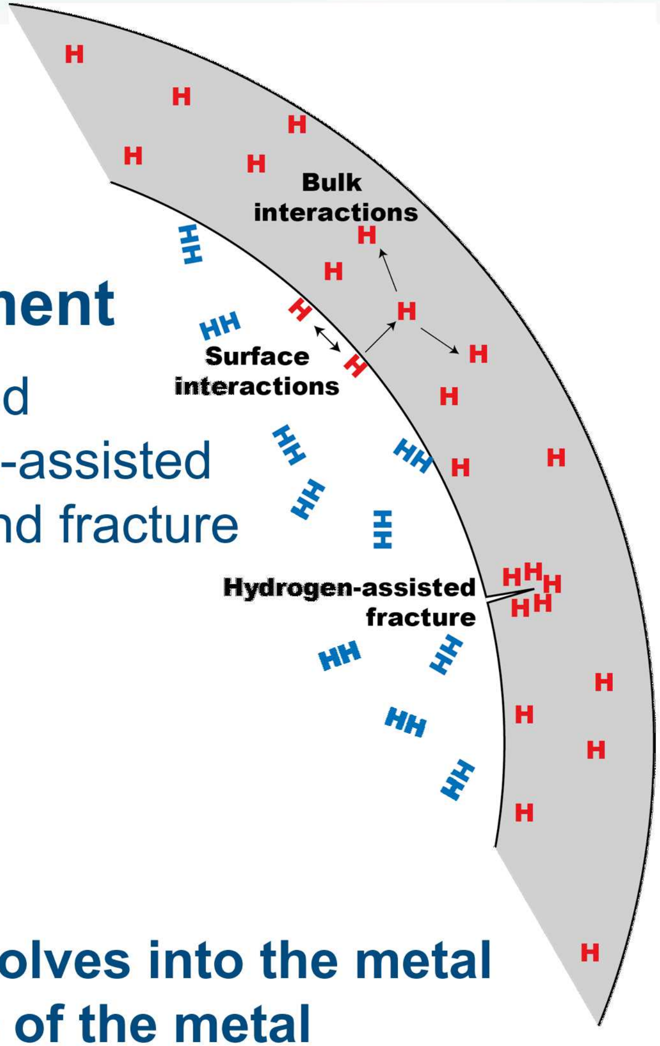
Hydrogen embrittlement occurs in materials under the influence of stress in hydrogen environments



Hydrogen embrittlement

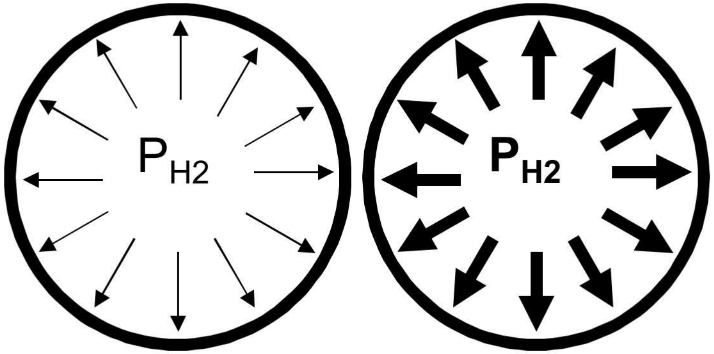
also called hydrogen-assisted fatigue and fracture

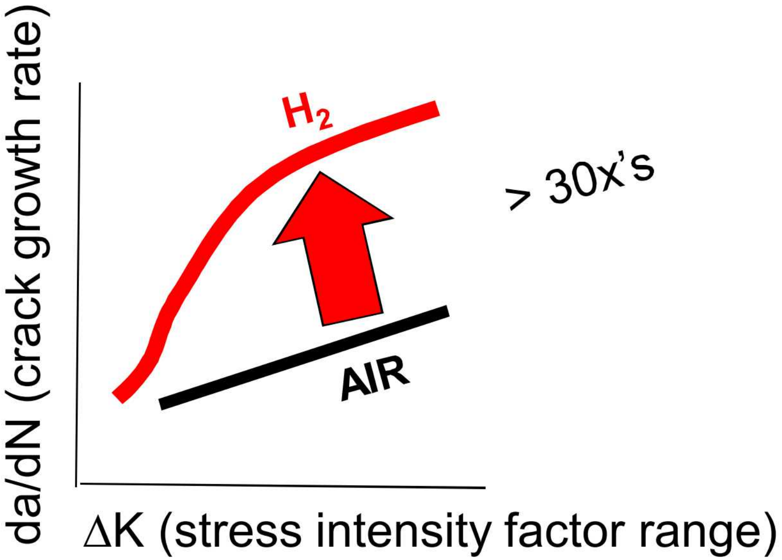


Hydrogen dissociates on metal surfaces, dissolves into the metal lattice, and changes the mechanical response of the metal

Hydrogen Embrittlement =
Hydrogen Accelerated Fatigue Crack Growth (HA-FCG)

- Pressure **fluctuations** can result in ***fatigue*** loading of the pipe

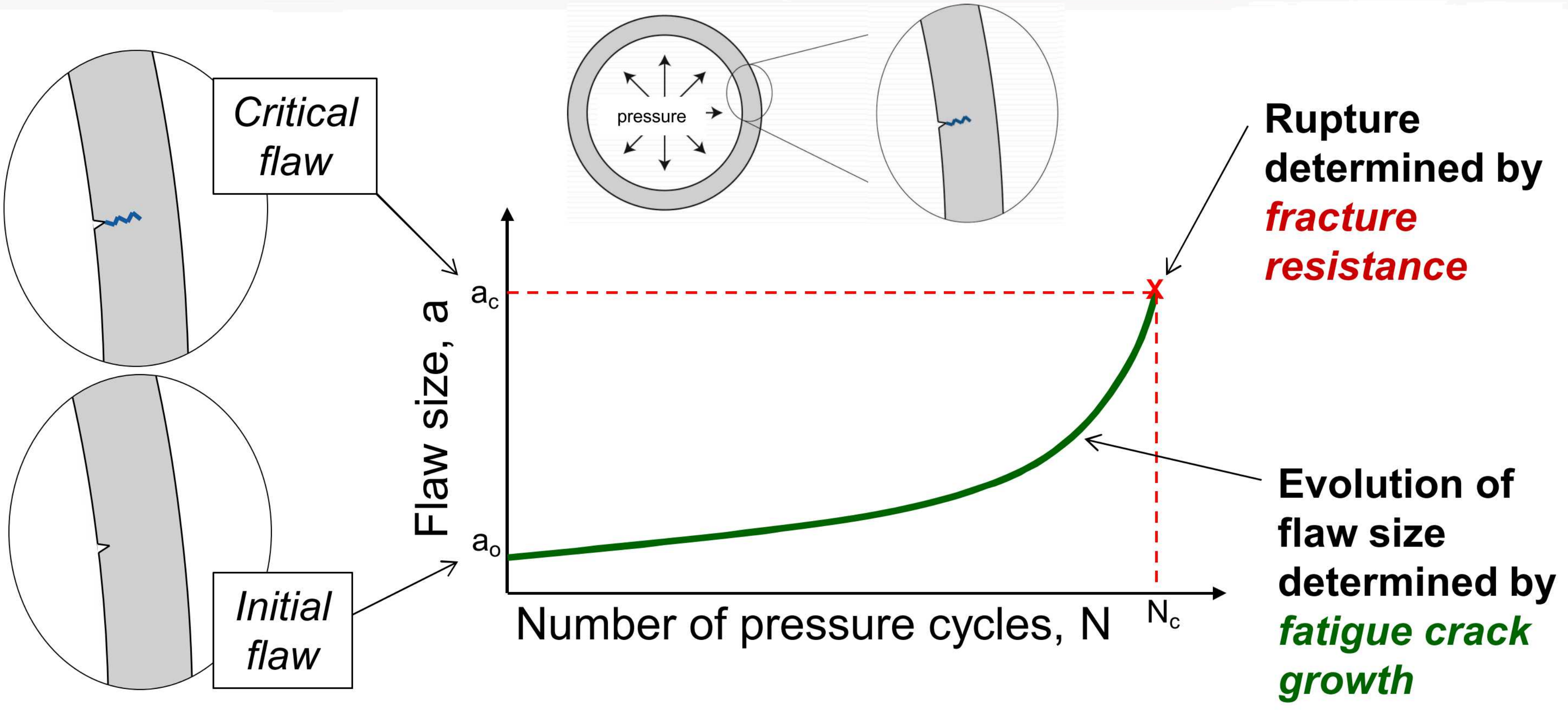




- Fatigue crack growth rates can increase by over an order of magnitude in pipeline steels

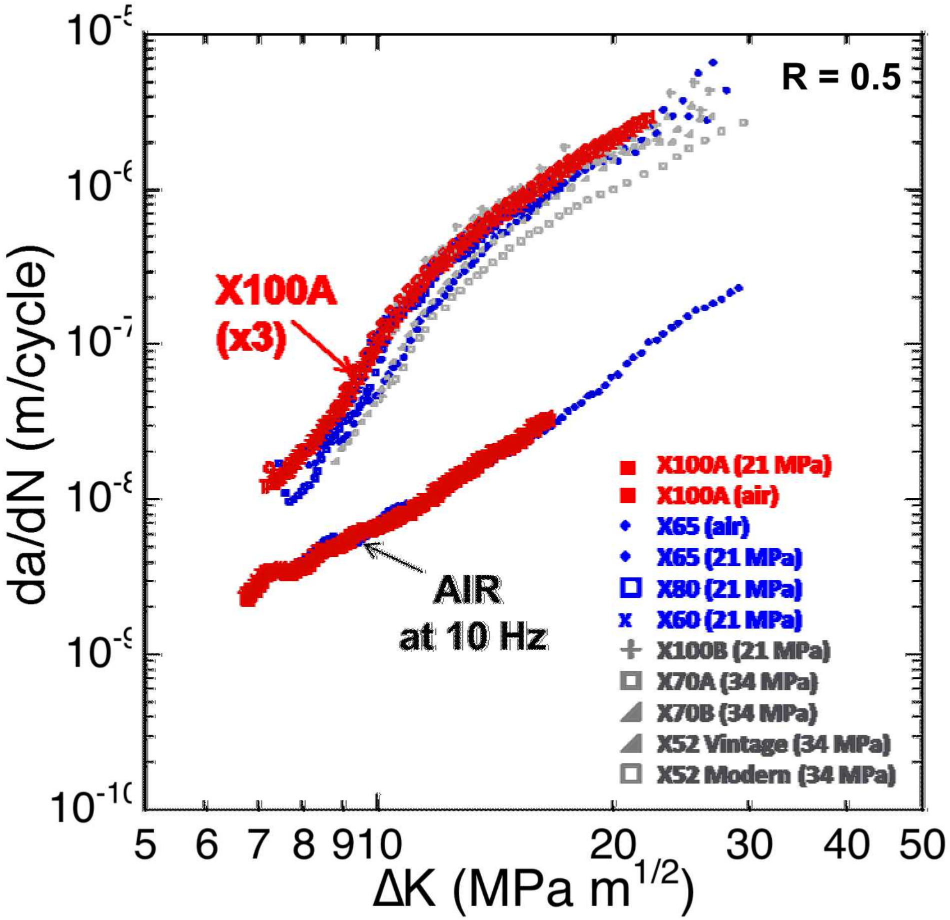
HA-FCG does not preclude material from usage but necessitates proper design

Fracture mechanics-based assessment of fatigue and fracture of pipelines

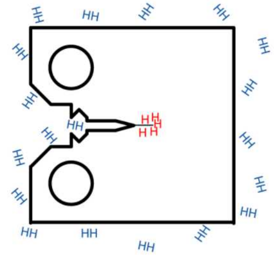


ASME B31.12 describes rules for hydrogen pipelines with reference to ASME BPVC Section VIII, Division 3, Article KD-10

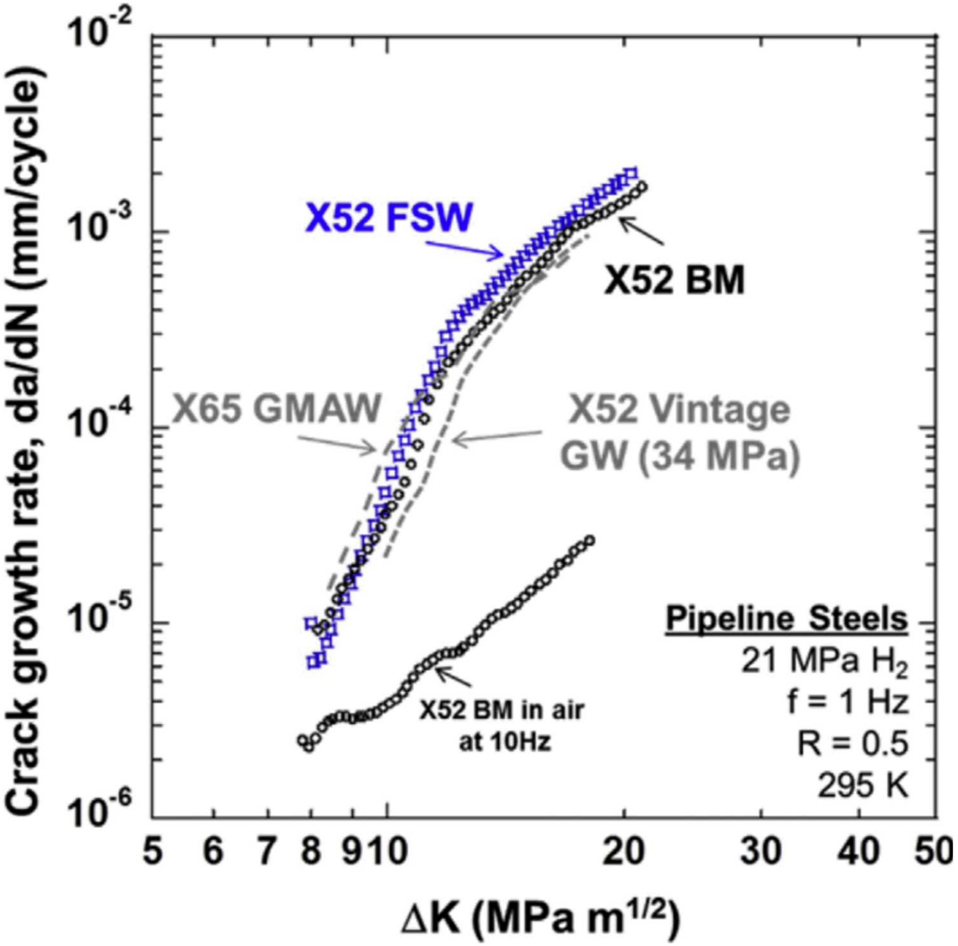
Various pipeline steels tend to show very similar fatigue crack growth rates in gaseous hydrogen



- 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

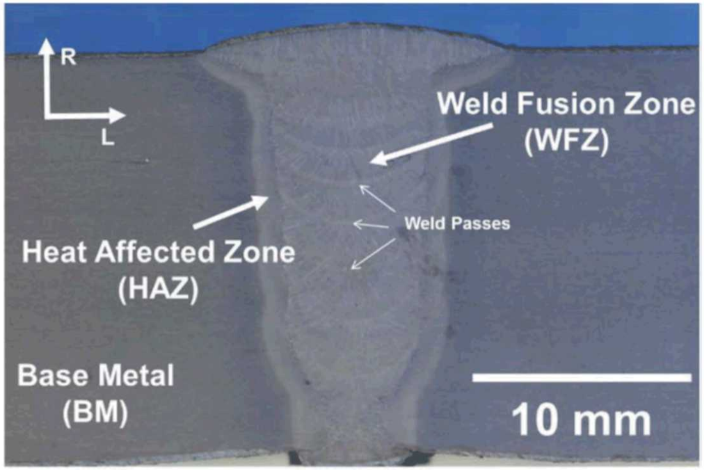


Welds in pipelines tend to show similar fatigue crack growth rates as the base metals in hydrogen

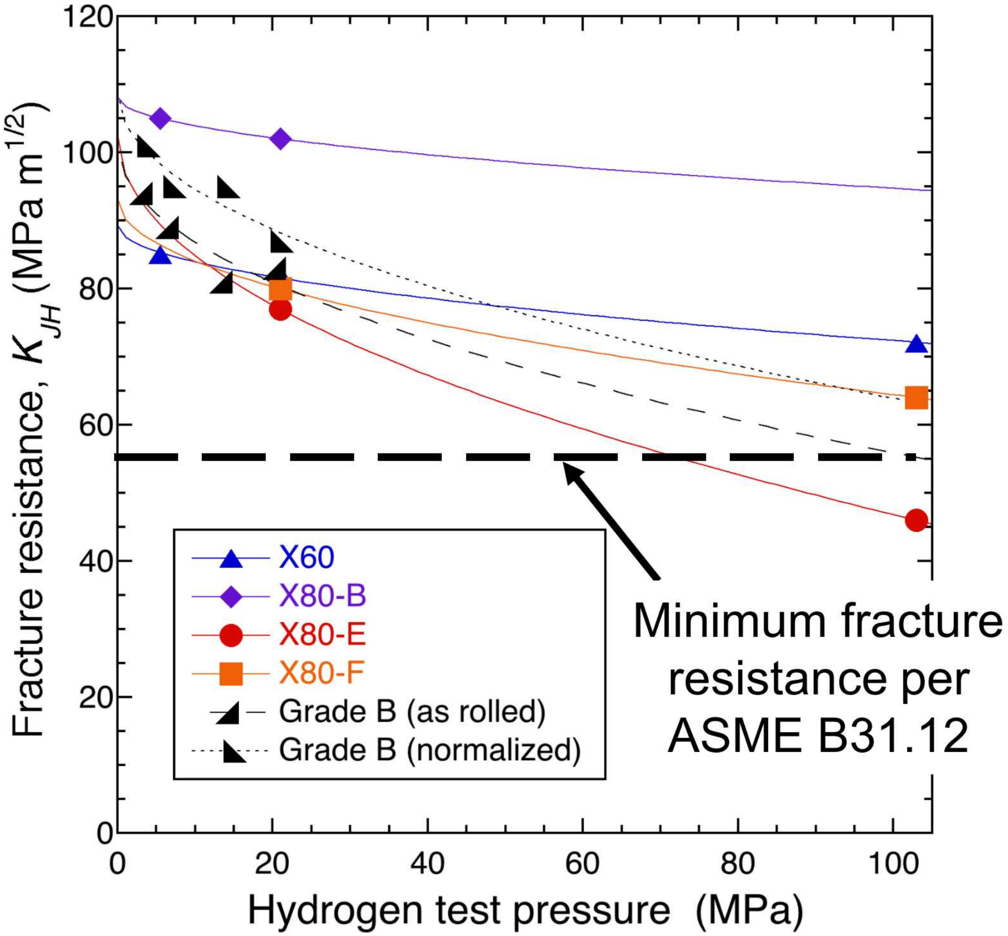


From: Ronevich et al, *Int J. of Hydrogen Energy*, 2017

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



Pipeline steels have relatively high fracture resistance in gaseous hydrogen

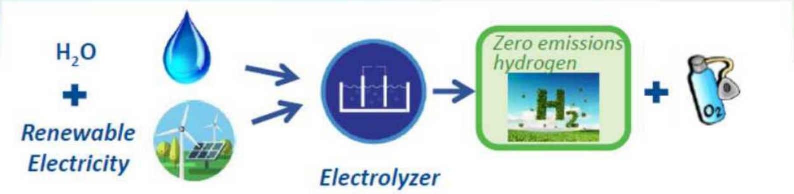


- **Data sets that evaluate effect of pressure on fracture are relatively limited**
- **Available data suggest fracture depends on pressure**
- **Fracture resistance (even at low pressure) is significantly lower than in air**

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

Growing interest in using hydrogen blends in natural gas to reduce carbon emissions

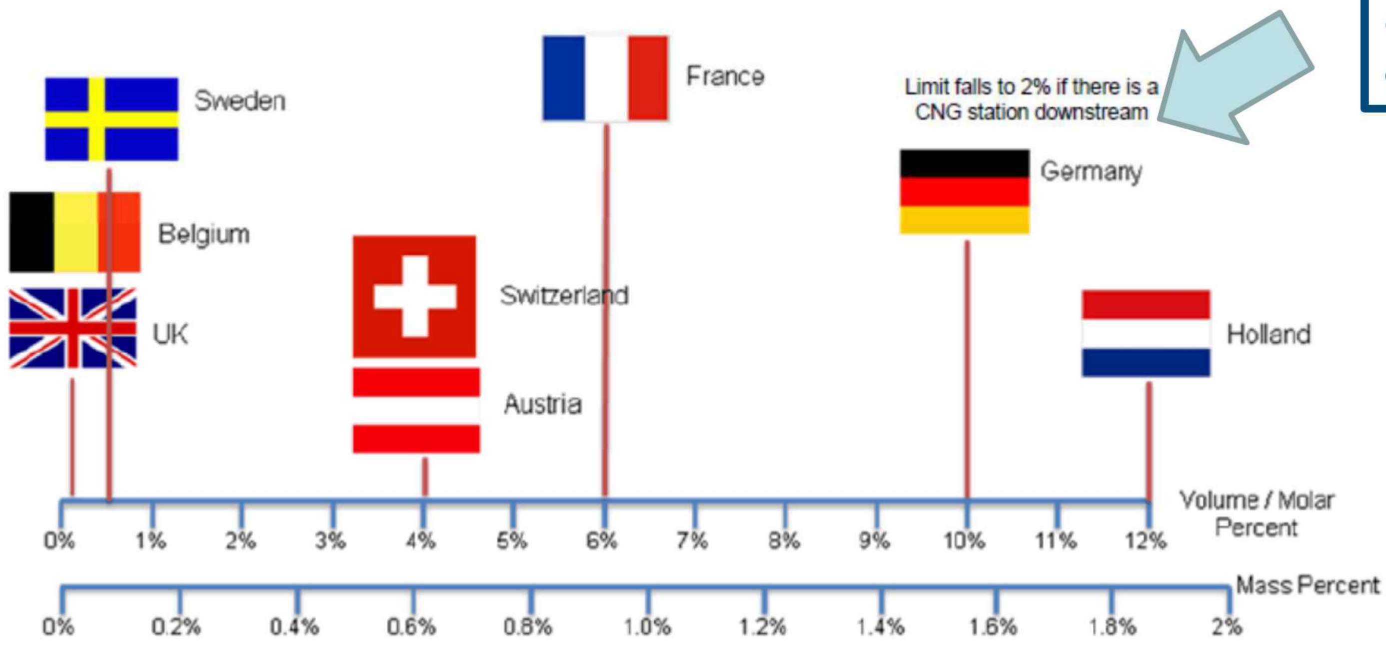
→ Power-to-gas (P2G) using excess renewable electricity to produce hydrogen and inject into pipeline



EU Hydrogen Limits for Injection into the HP Gas Grid

Covered by a range of local laws and EU Directives

No harmonization of allowable hydrogen concentration in natural gas



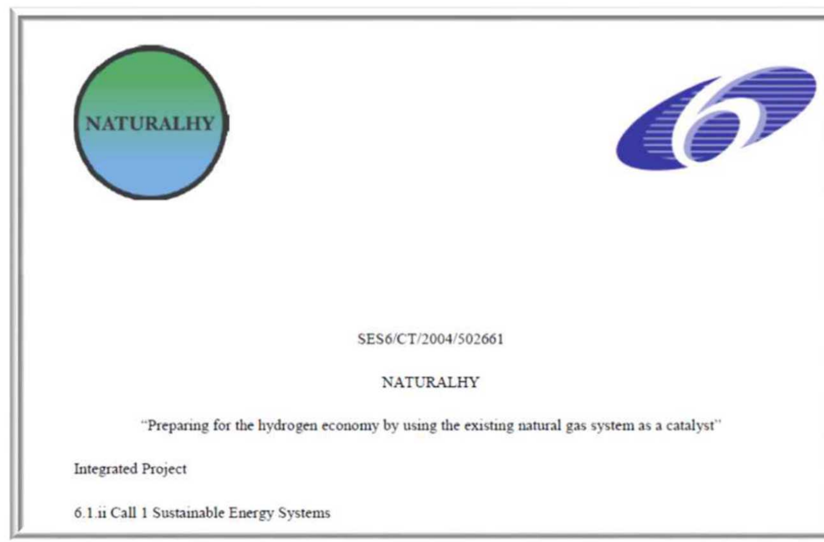
Ref: George Minter, SoCal Gas "New Natural Gas Pathways for California: Decarbonizing the Pipeline" Presentation 2014.

Ref: SoCal Gas, "Hydrogen: Market Fundamentals, Trends and Opportunities", California Hydrogen Business Council, December 11, 2018.

Many demonstration projects are being performed around the world

France – Dunkirk **6% up to 20% H_2** into buses and 200 residential homes
Italy – Snam **5% H_2** into gas transmission network
UK – H21 Leeds CityGate Project – converting existing NG network to **100% H_2**
UK – HyDeploy at Keele University (up to **20% H_2** blend)
US – SoCalGas / UC Irvine – blending H_2 from excess renewable electricity to campus pipeline
Germany – Trial of 170 customers supplied with up to **10% H_2** blend by E.ON Technologies
Netherlands – up to **20% H_2** blend injected in Amerland

Many references point to results from NaturalHy report, 2010



SES6/CT/2004/502661

NATURALHY

"Preparing for the hydrogen economy by using the existing natural gas system as a catalyst"

Integrated Project

6.1.ii Call 1 Sustainable Energy Systems

https://www.engie.com/en/businesses/gas/hydrogen/power-to-gas/the-grhyd-demonstration-project/

https://www.azernews.az/region/148145.html

https://www.northerngasnetworks.co.uk/wp-content/uploads/2017/04/H21-Report-Interactive-PDF-July-2016.compressed.pdf

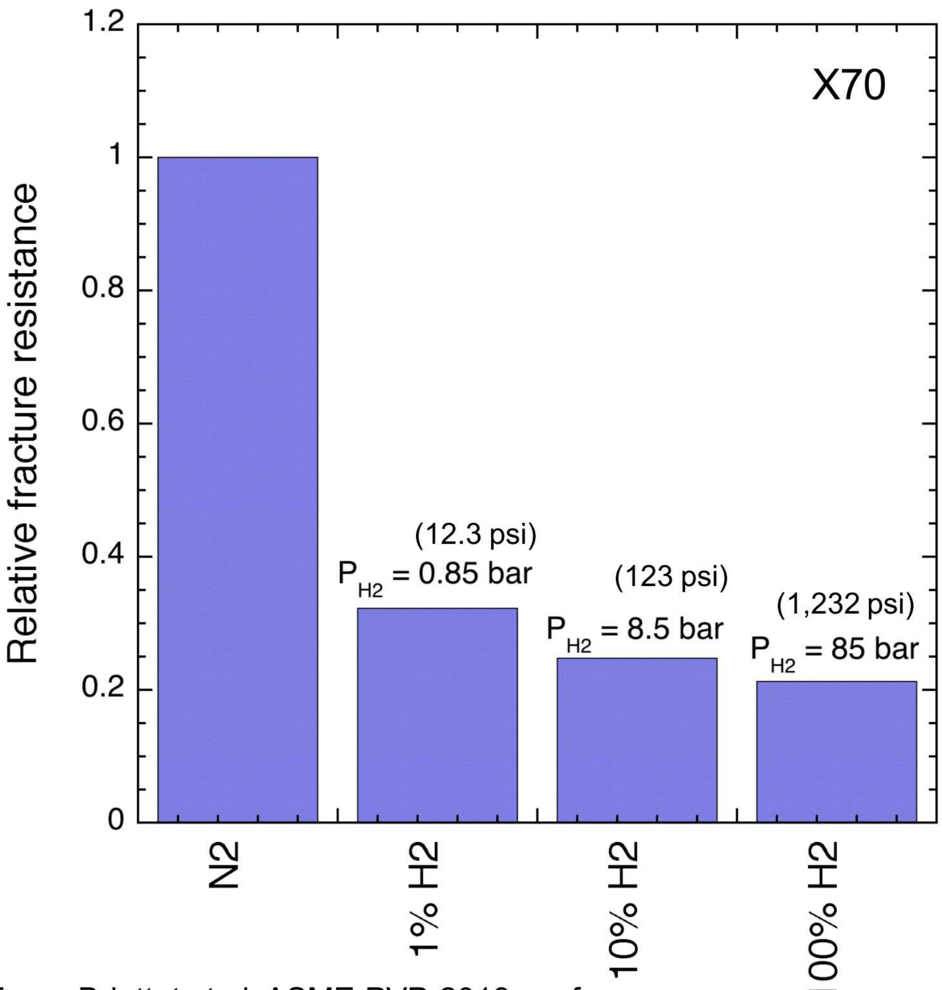
https://www.elp.com/articles/2016/12/socalgas-uc-irvine-test-hydrogen-energy-technology-to-store-renewable-energy.html

So how much hydrogen is allowed in natural gas?

A) 2%?
B) 5%?
C) 10%?
D) It depends on your operating conditions and your definition of the word "allowed".

Often times these values (2,5,10% H_2) are based on performance of burners, not measurements of material compatibility with hydrogen

Low pressure H_2 has substantial effect on fracture resistance of pipeline steels

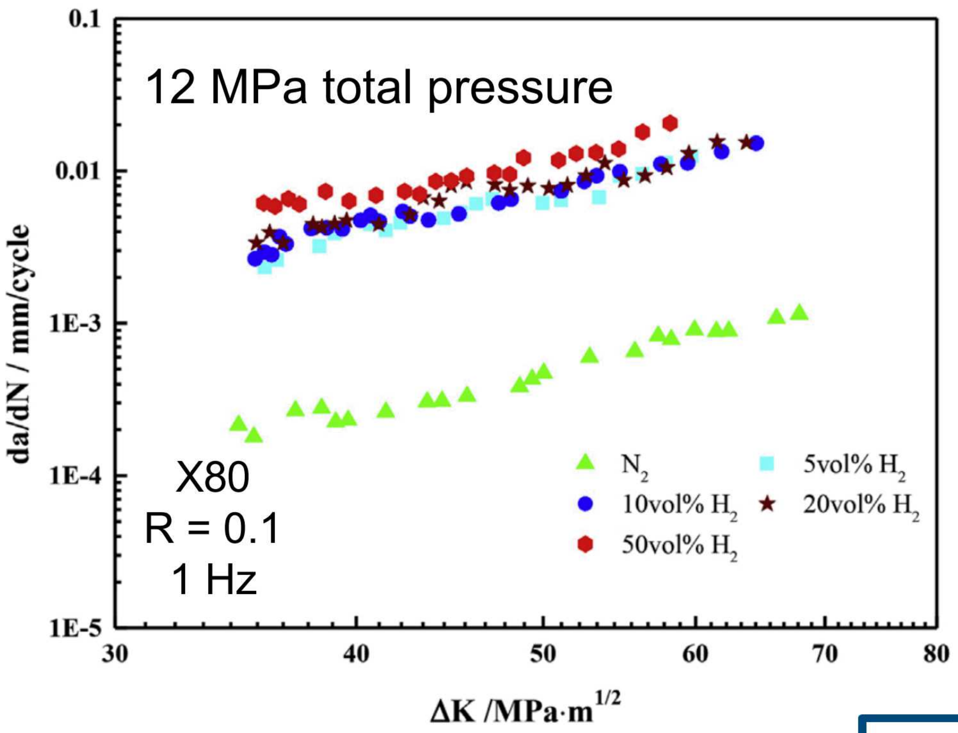


From: Briottet et al, ASME PVP-2018 conf.

- 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 H_2 has substantial effect on fatigue crack growth of pipeline steels

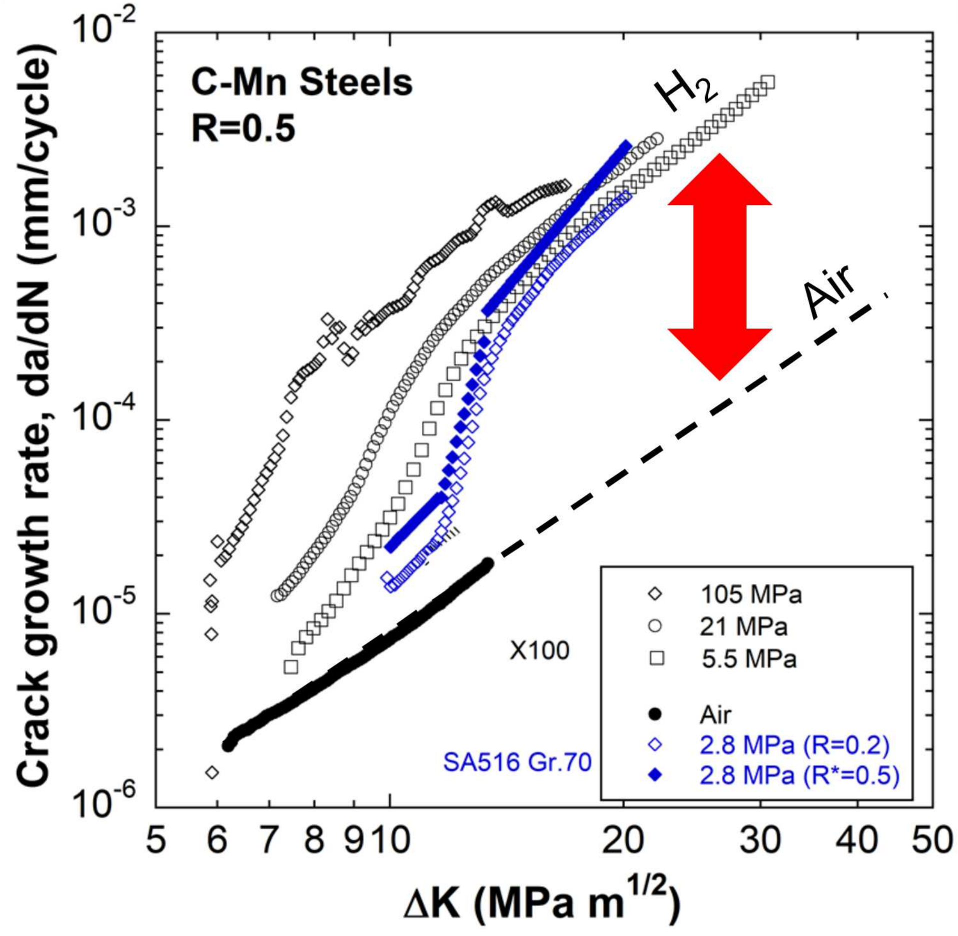


From: Meng et al, *IJ Hydrogen Energy* **42** (2017) 7404.

- **Measurements in gaseous mixtures of H_2 and N_2 show acceleration of fatigue crack growth rate with 5% H_2**
  - **But little additional acceleration with higher H_2 content**

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

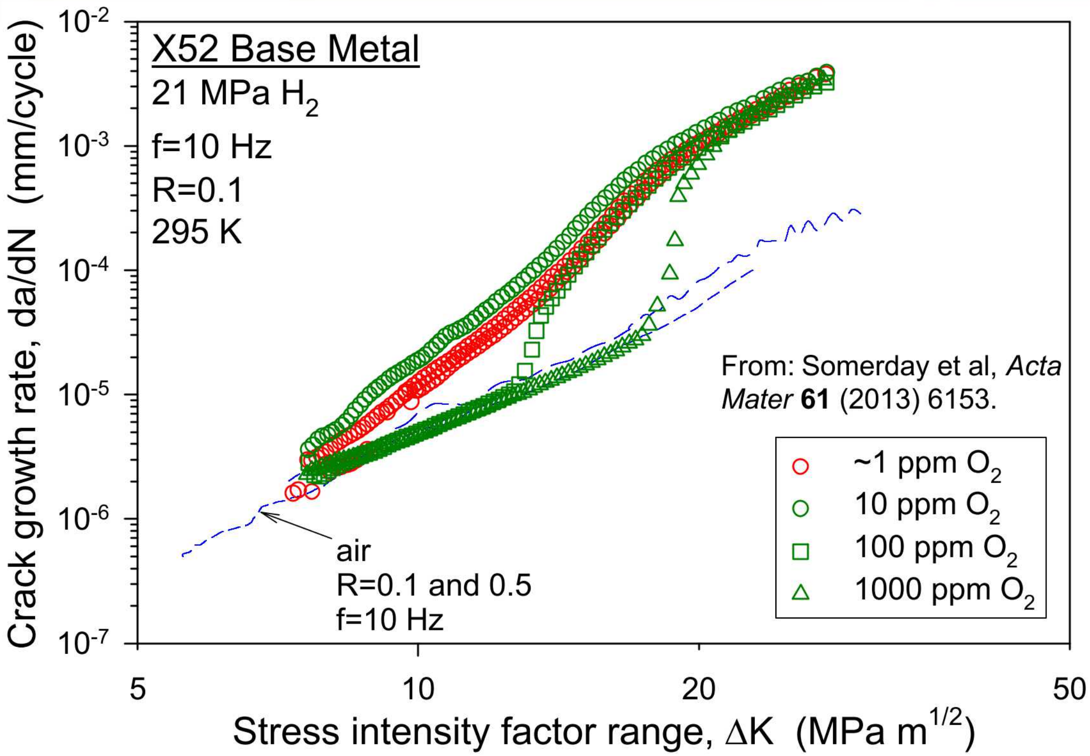
In lower ΔK range, lower pressures still exhibit sizeable increases in FCGR



SNL data (taken from various published and unpublished sources)

Pressures ranging from 15,000 psi to 400 psi H_2 still exhibit accelerated fatigue crack growth rates

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



- **Oxygen mitigates H_2-accelerated fatigue crack growth rates at low ΔK**
- **Attributed to oxygen diffusion to new crack surfaces**
- **Natural gas may have sufficient O_2 to mitigate hydrogen (0.1% = 1000 ppm O_2)**

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 H_2 can have substantial effects on fracture and fatigue of steels
- Oxygen can mitigate effects of H_2 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 H_2 effects
  - Pure methane is inert and even small additions of H_2 can be significant

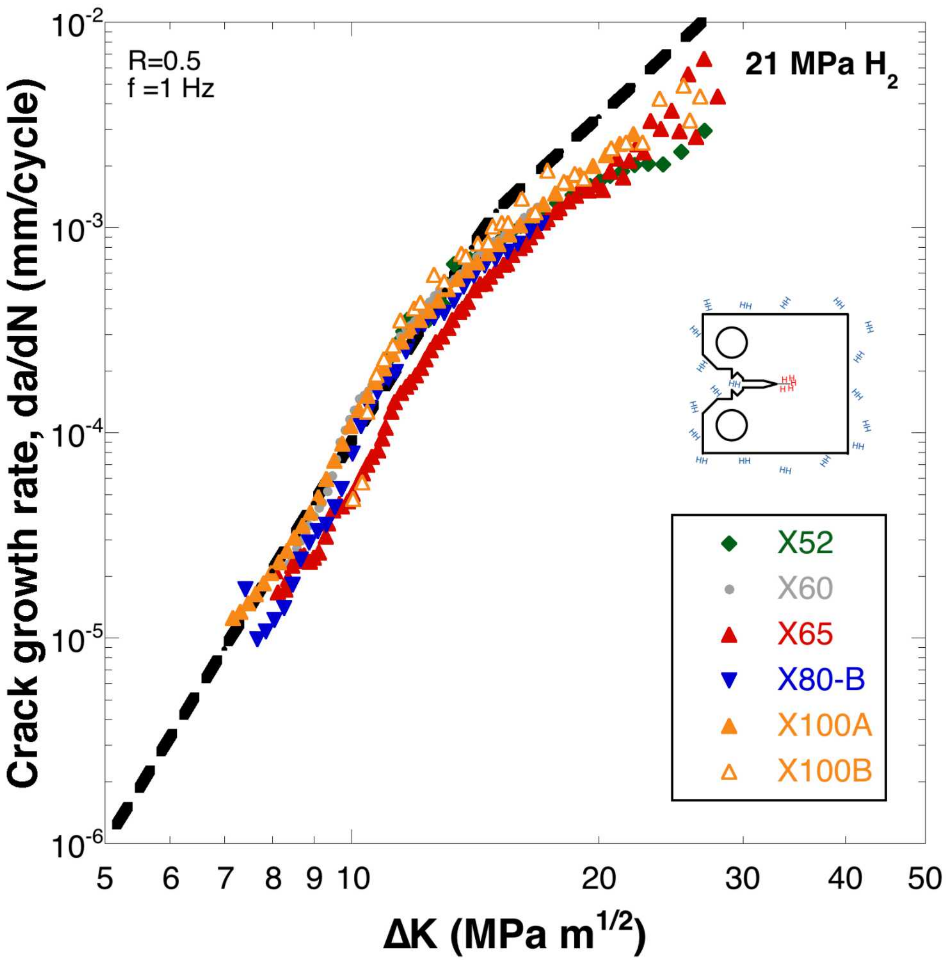
Materials compatibility for hydrogen containment structures depends on the application and the design

Summary

- 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 >30x and fracture resistance is reduced by >50%*
- 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*

Back up Slides

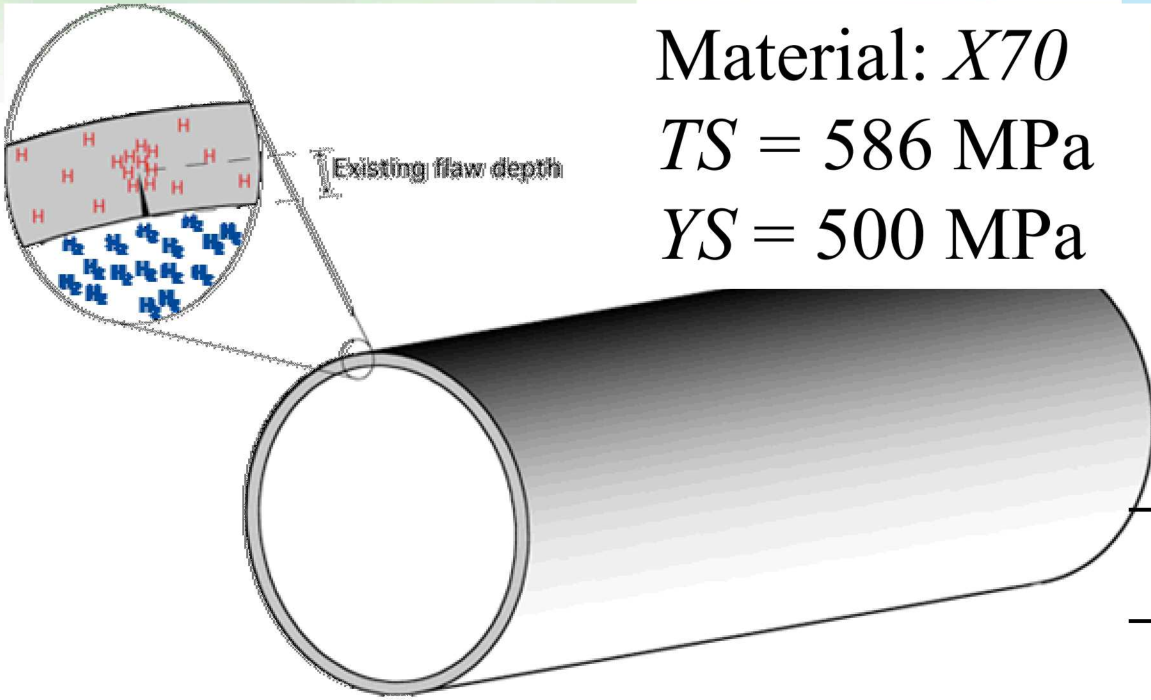
The effects of H2 on fatigue crack growth in steels can be captured with "master" design curve



- 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

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

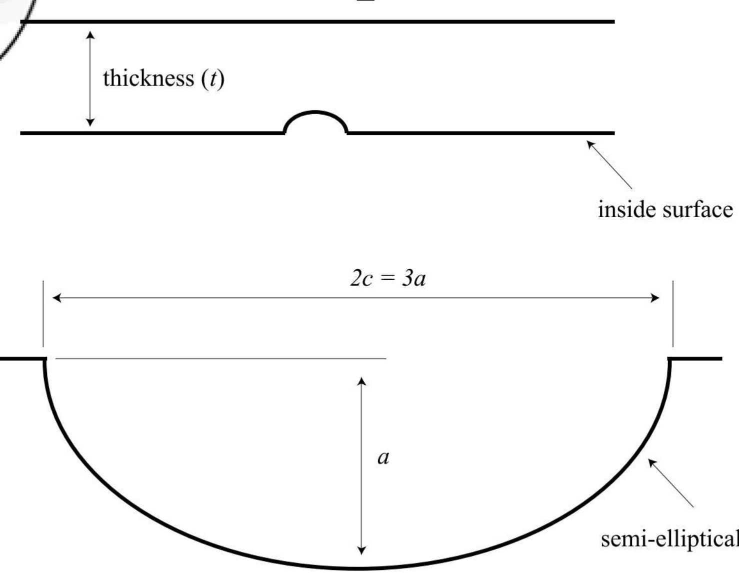
Consider a typical "high-pressure" pipeline



Material: *X70*
TS = 586 MPa
YS = 500 MPa

OD = 762 mm
t = 15.9 mm
P_{max} = 7 MPa
P_{min} = 4 MPa

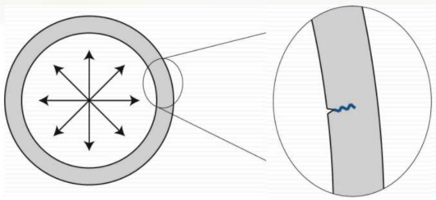
Semi-elliptical crack

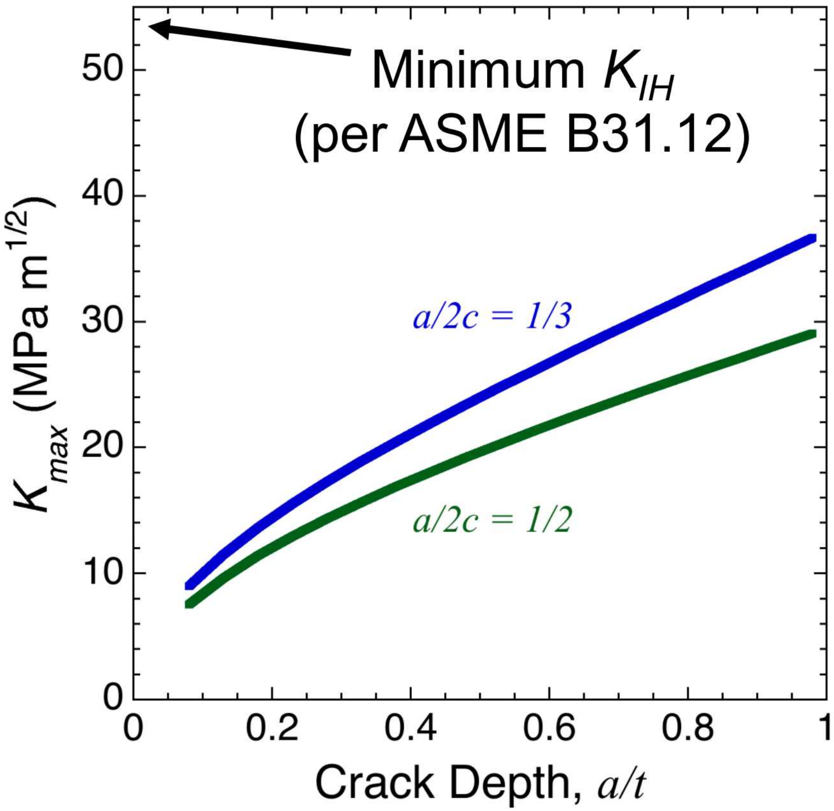


a/t = crack depth
$a/2c$ = depth to length ratio

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

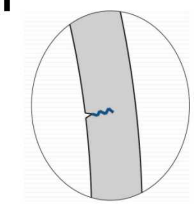




Hoop stress at $P_{max} = 162$ MPa
stress ratio: hoop/$TS = 28\%$

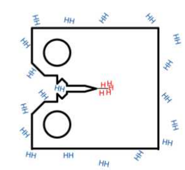
Driving force on semi-elliptical crack:

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



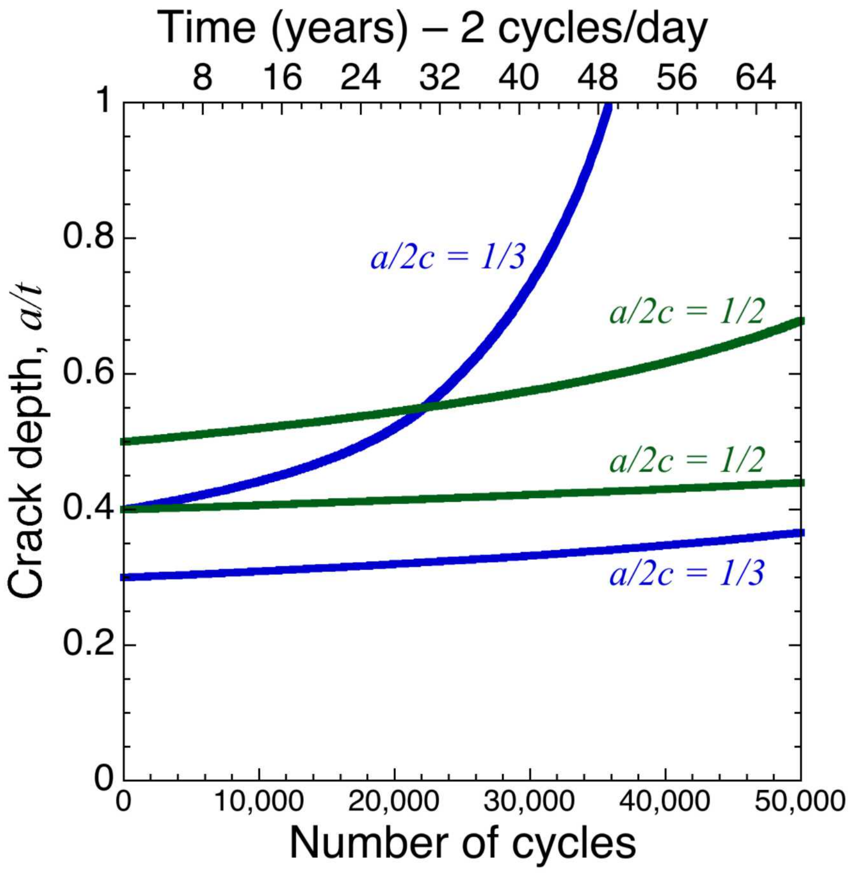
Typical pipeline material fracture resistance:

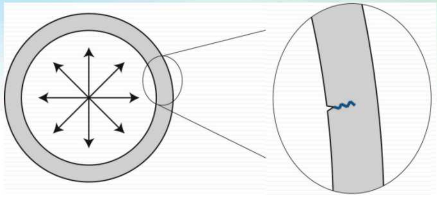
$$K_{JH} > 75 \text{ MPa m}^{1/2}$$



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





Assuming

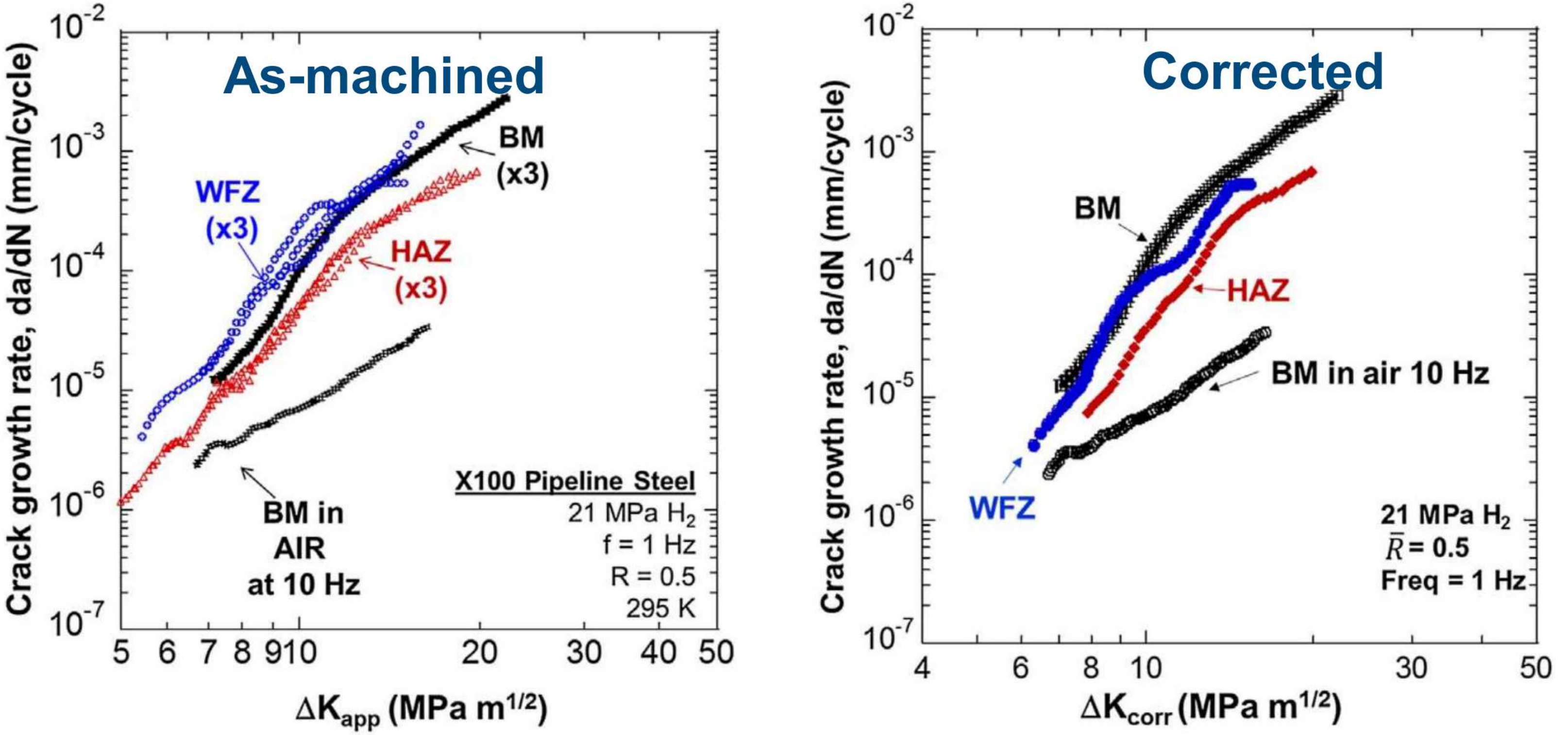
- Pressure cycles between 4 & 7 MPa
- Constant crack shape (*a/2c*)
- Large initial defects
- Fatigue crack growth rates in pure H2 (at higher pressure)

Using:

$$a = a_i + \left({da}/{dN} \right)^{a=a_i} \Delta N$$

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

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



- **Residual stresses should be considered for design**
- **Base metal properties generally represent weld metal**

From: Ronevich et al, Eng Fract Mech 194