

Hydrogen Effects on Materials for CNG / H₂ Blends

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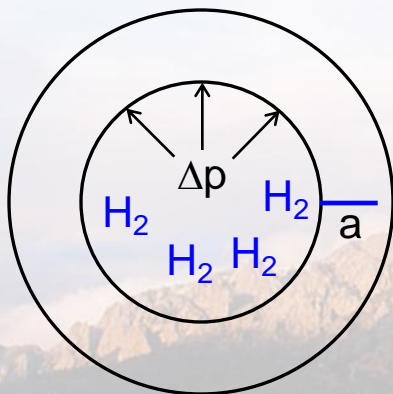
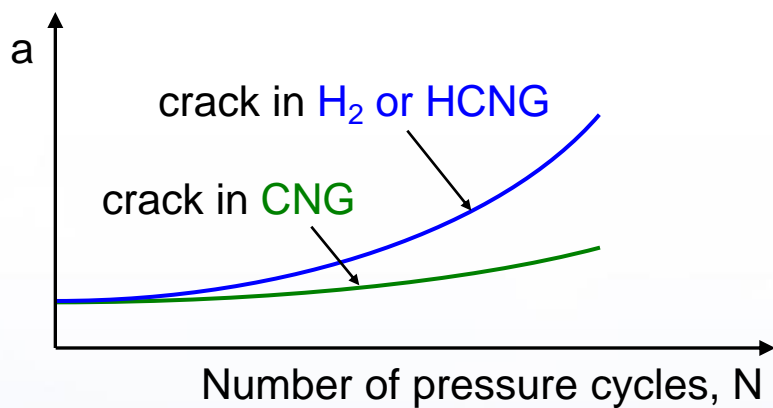
Issue: Can existing CNG on-board storage tanks be used for HCNG?

- **What are considerations for**
 - Type 1, 2, 3, 4 tanks?
 - 20% H₂ and less?
 - higher than 20% H₂?
- **Type 3 and Type 4 are likely fine**
 - Comments from manufacturers
- **Concern is primarily for steel Type 1 and Type 2 tanks**
 - Commonly designed and manufactured according to NGV-2 and ISO 9809-1



What is the concern for steel HCNG storage tanks?

H₂-assisted fatigue cracking



H₂ cylinder



Barthélémy, 1st ESSHS, 2006

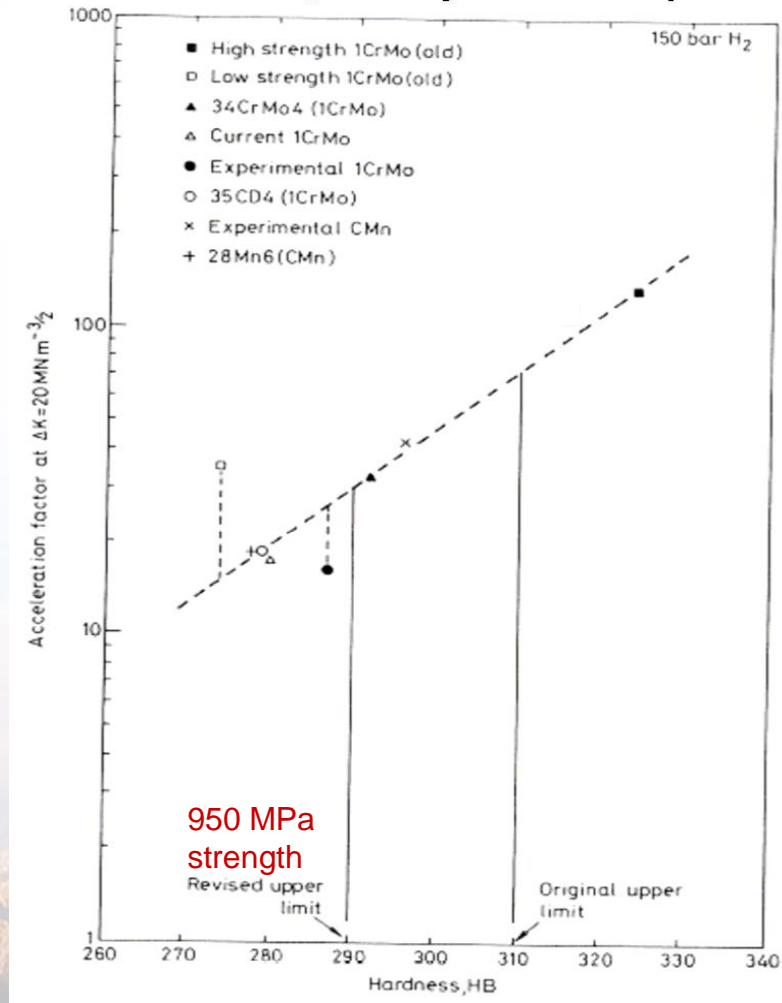
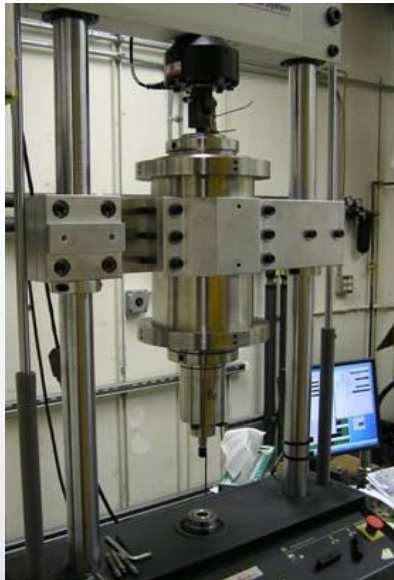
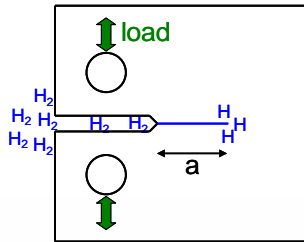


No concerns for HCNG in steel storage tanks if material strength is limited

- **H₂ compatibility of Cr-Mo steel cylinders designed to ISO 9809-1 demonstrated through service experience**
 - Example: typical duty cycle for steel H₂ trailer tubes in USA
 - ◆ H₂ pressure ~20 MPa
 - ◆ pressure cycles ~2/week (50 year life)
 - Such service conditions bound the H₂ partial pressure and number of pressure cycles for steel HCNG storage tanks
 - H₂ transport cylinders must have tensile strength < 950 MPa
- **All HCNG blends expected to be compatible with steel CNG tanks provided tensile strength < 950 MPa**
- **But CNG tanks designed to ISO 9809-1 allow tensile strength up to 1100 MPa**



Issue: H_2 -assisted fatigue cracking enhanced in higher strength steel



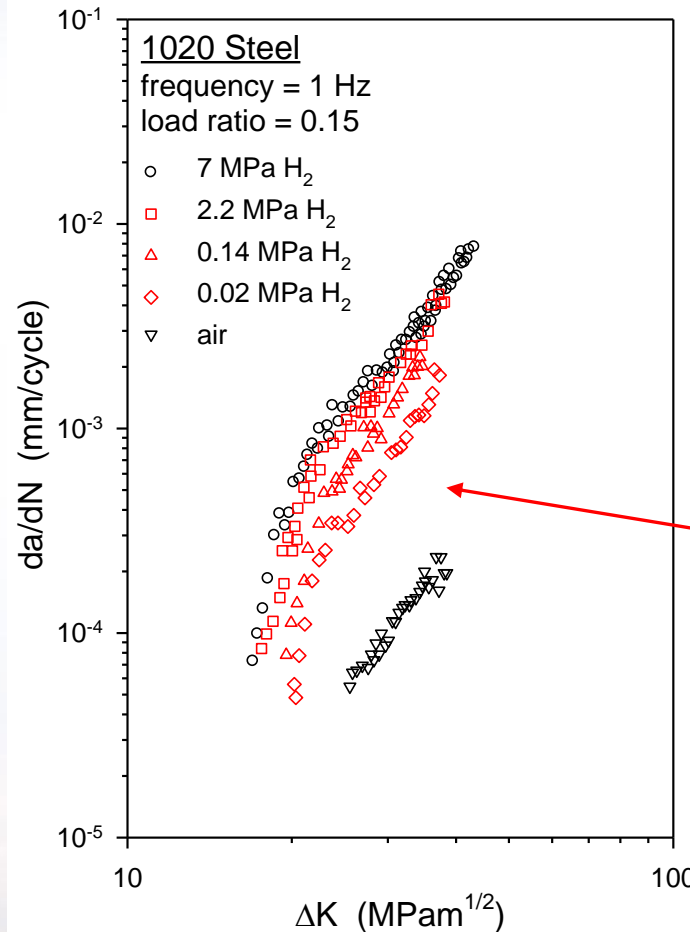
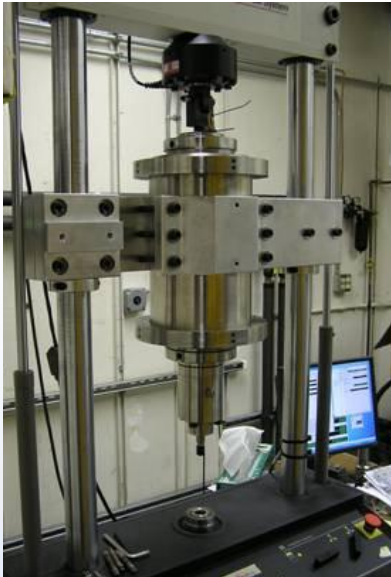
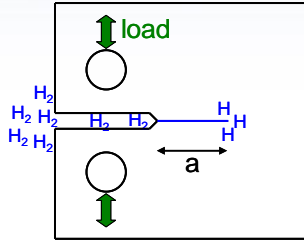
ISO 11114-4 addresses H₂ compatibility of steel cylinders with strength > 950 MPa in two ways

1) Lower H₂ partial pressures

- **According to ISO 11114-4, cylinders may be designed to ISO 9809-1 (i.e., with strength up to 1100 MPa) “if at least one of the following conditions for intended gas service is fulfilled:**
 - the working pressure of the filled embrittling gas is less than 20% of the test pressure of the cylinder
 - the partial pressure of the filled embrittling gas of a gas mixture is less than 5 MPa (50 bar) in the case of hydrogen...”
- **Based on ISO 11114-4, CNG tanks are suitable for HCNG blends with <20% H₂**
- **However, guidance apparently not developed from fatigue cracking data nor service experience**



Issue: steels are susceptible to H_2 -assisted fatigue cracking at low H_2 pressures



Technical Reference on Hydrogen Compatibility of Materials, Sandia, 2008

Fatigue cracking rates in H_2 pressure < 5 MPa can be notably higher than rates in air

- Recommend evaluating H_2 -assisted fatigue cracking in higher strength steels at low H_2 pressure

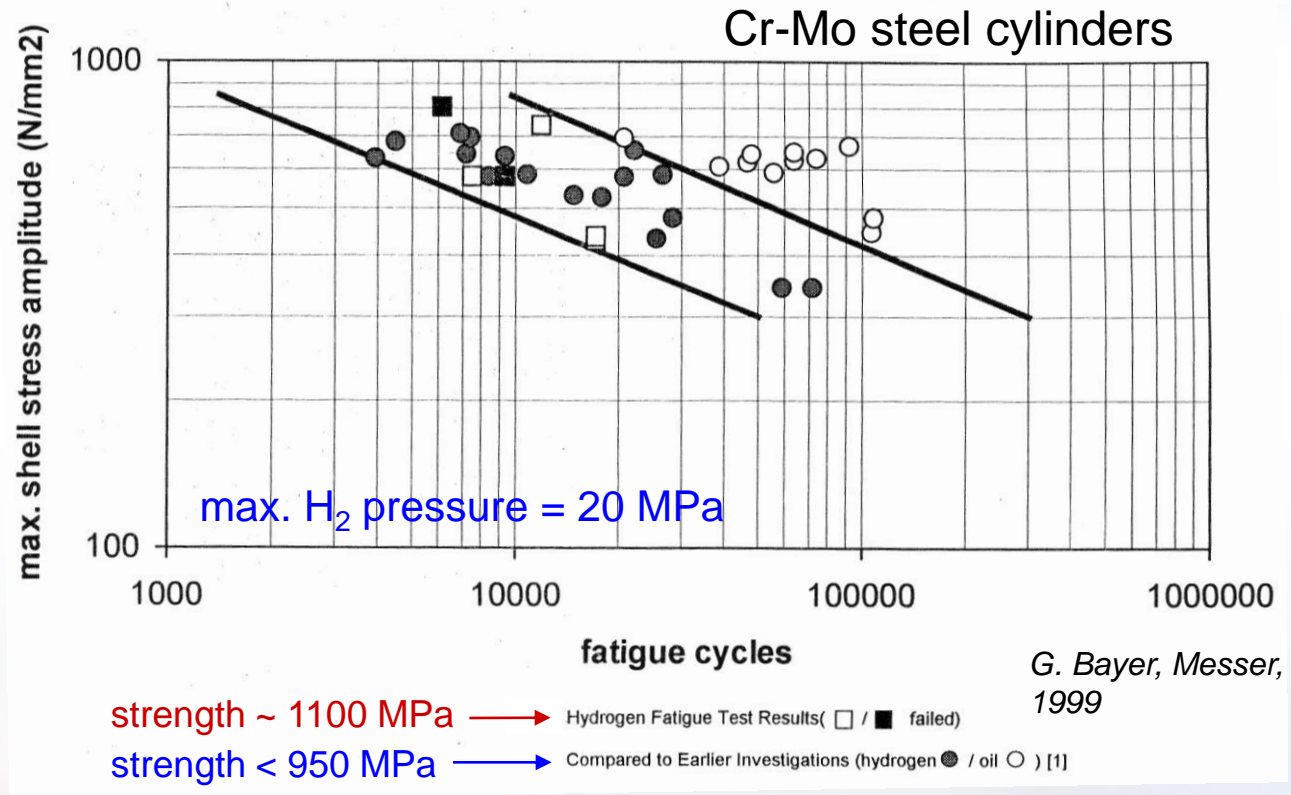
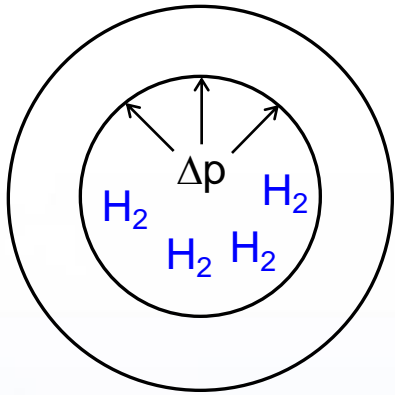
ISO 11114-4 addresses H₂ compatibility of steel cylinders with strength > 950 MPa in two ways

2) Higher H₂ partial pressures

- **ISO 11114-4 specifies that steels with strength >950 MPa can be qualified based on materials testing in H₂ gas**
- **Evolving ISO 11114-4 currently specifies 3 tests:**
 - Method A (disc rupture test)
 - Method B (crack propagation threshold test under step loading)
 - Method C (crack propagation threshold test under static load)
- **Based on ISO 11114-4, CNG tanks suitable for HCNG blends with >20% H₂ if steel passes qualification test**
- **However, qualification tests do not directly evaluate H₂-assisted fatigue cracking**
- **Recommend evaluating H₂-assisted fatigue cracking in higher strength steels at H₂ partial pressure in blend**



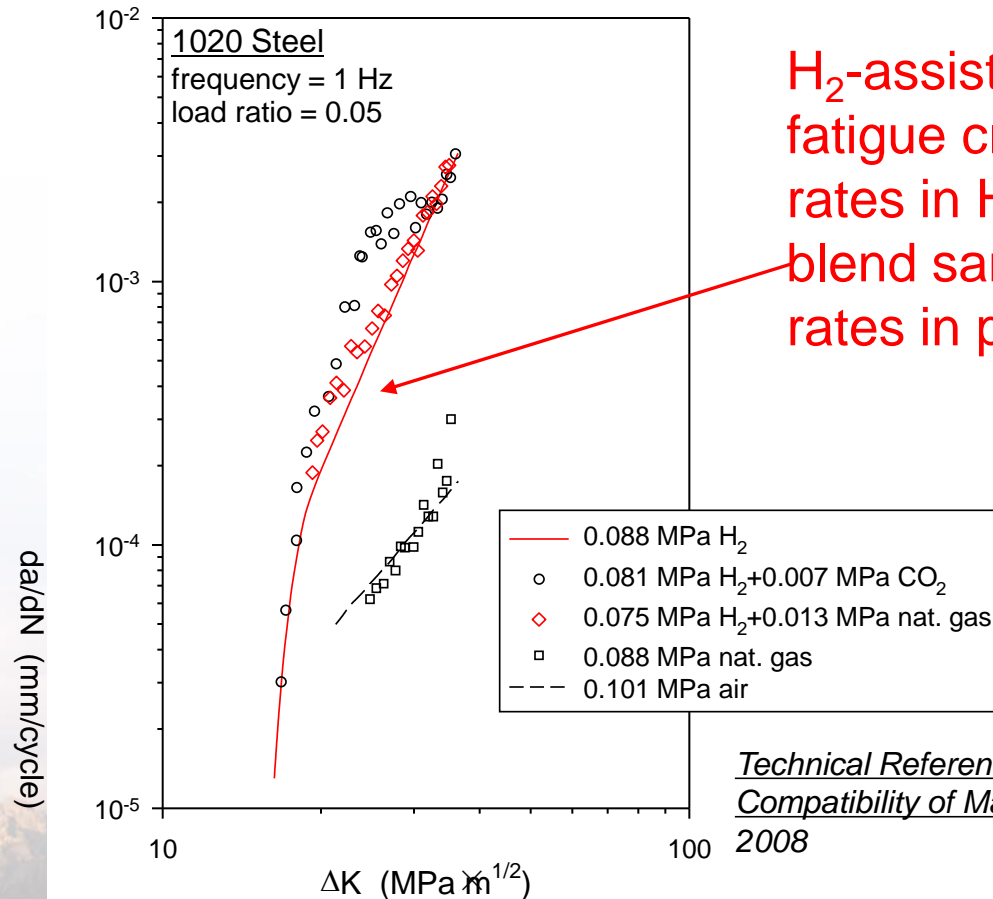
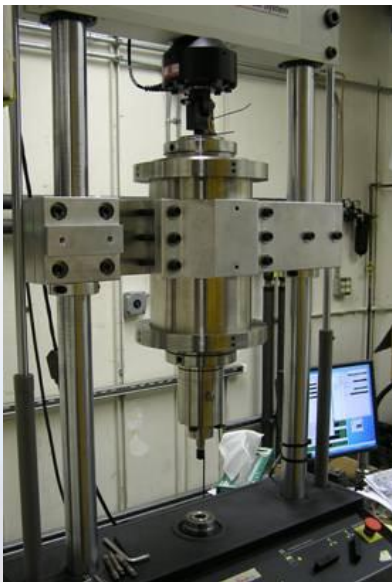
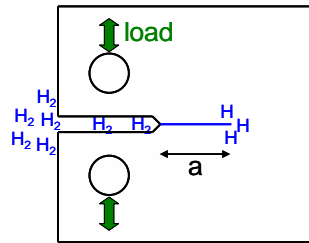
Limited H_2 -assisted fatigue cracking data for higher strength steel cylinders are promising



- Higher strength cylinders with 400 MPa wall stress did not exhibit cracking in H_2 after 17,000 cycles

Issue: Does CNG modify H₂-assisted fatigue cracking of steels in gas blends?

Some data show H₂-assisted fatigue cracking same in HCNG and H₂ ...



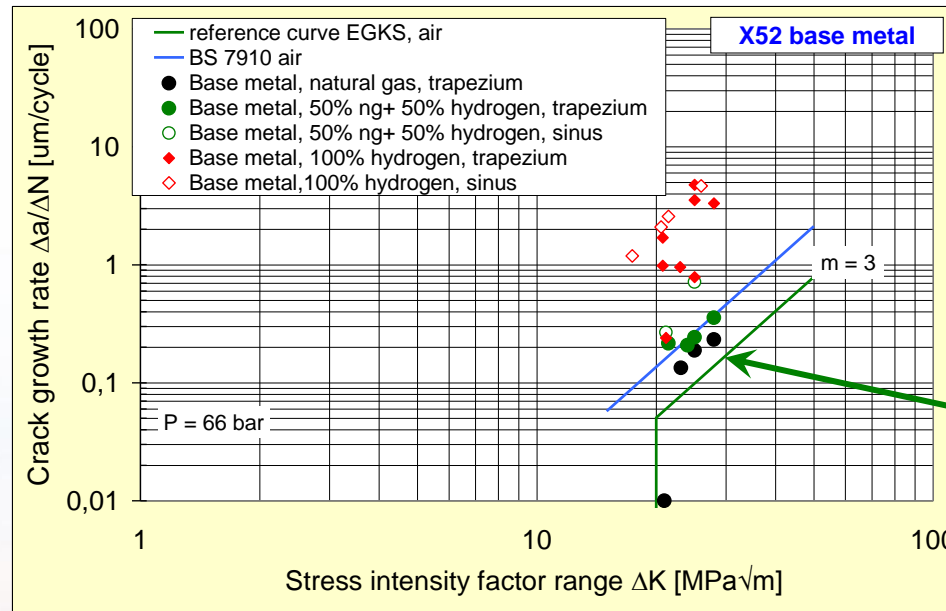
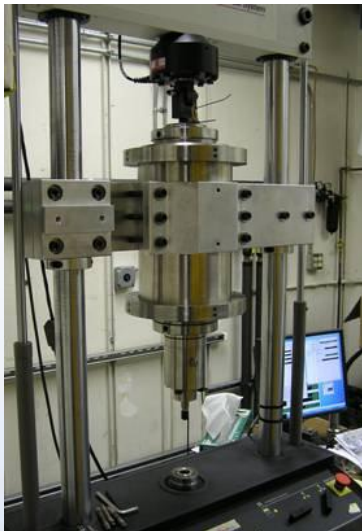
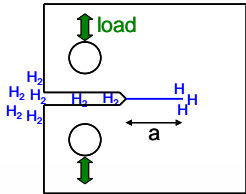
H₂-assisted fatigue cracking rates in HCNG blend same as rates in pure H₂

Technical Reference on Hydrogen Compatibility of Materials, Sandia, 2008



Issue: Does CNG modify H₂-assisted fatigue cracking of steels in gas blends?

... but other data show lower cracking rates in HCNG compared to H₂



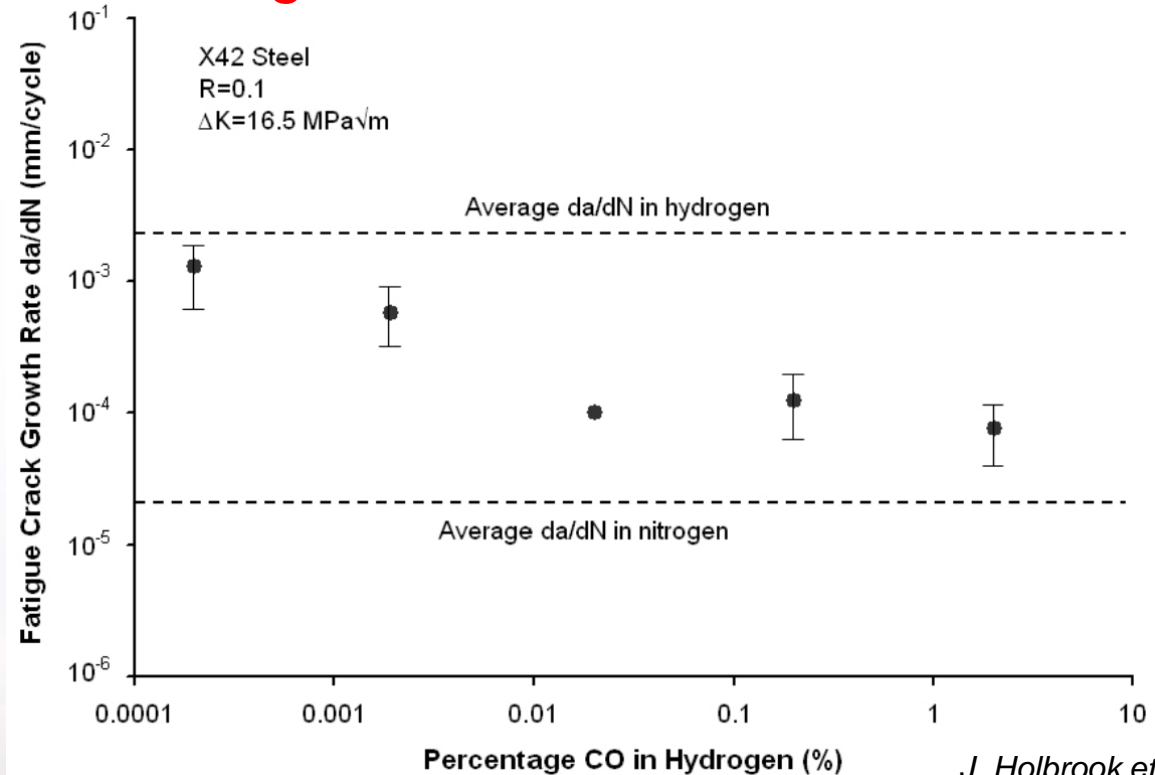
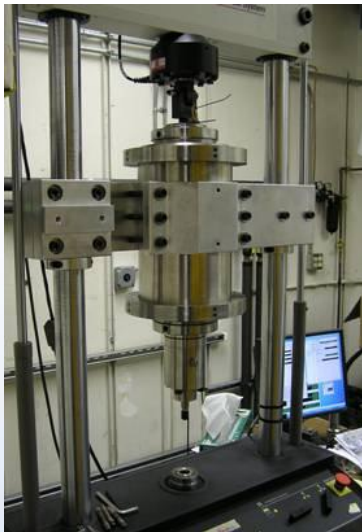
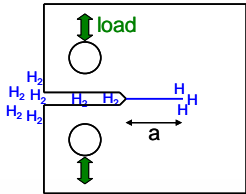
Fatigue cracking rates in HCNG notably less than rates in pure H₂

I. Alliat, NATURALHY EC project, 2007

- Why are fatigue cracking data for HCNG blends not consistent?

Constituents in CNG can inhibit H_2 -assisted fatigue cracking

Gases such as O_2 and CO are known to inhibit H_2 -assisted cracking



J. Holbrook et al.,
BNL report, 1986

- Can CNG constituent such as CO ensure resistance to H_2 -assisted fatigue cracking?





Summary

- **No concerns for HCNG in steel storage tanks if material strength is < 950 MPa**
- **Recommend evaluating H₂-assisted fatigue cracking in higher strength steels at H₂ partial pressure in blend**
 - Limited fatigue testing on higher strength steel cylinders in H₂ shows promising results
- **Impurities in CNG (e.g., CO) may provide extrinsic mechanism for mitigating H₂-assisted fatigue cracking in steel tanks**

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ICHS 2011

International Conference on Hydrogen Safety

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