



Considerations of Hydrogen Compatibility of Materials for Blending Hydrogen into the Natural Gas Network

Chris San Marchi, Sandia National Laboratories

Kevin Simmons, Pacific Northwest National Laboratory

Hydrogen Blending Webinar

April 9, 2020

Supported by DOE's Fuel Cell Technologies Office in the Office of Energy Efficiency and Renewable Energy



Motivation and Outline

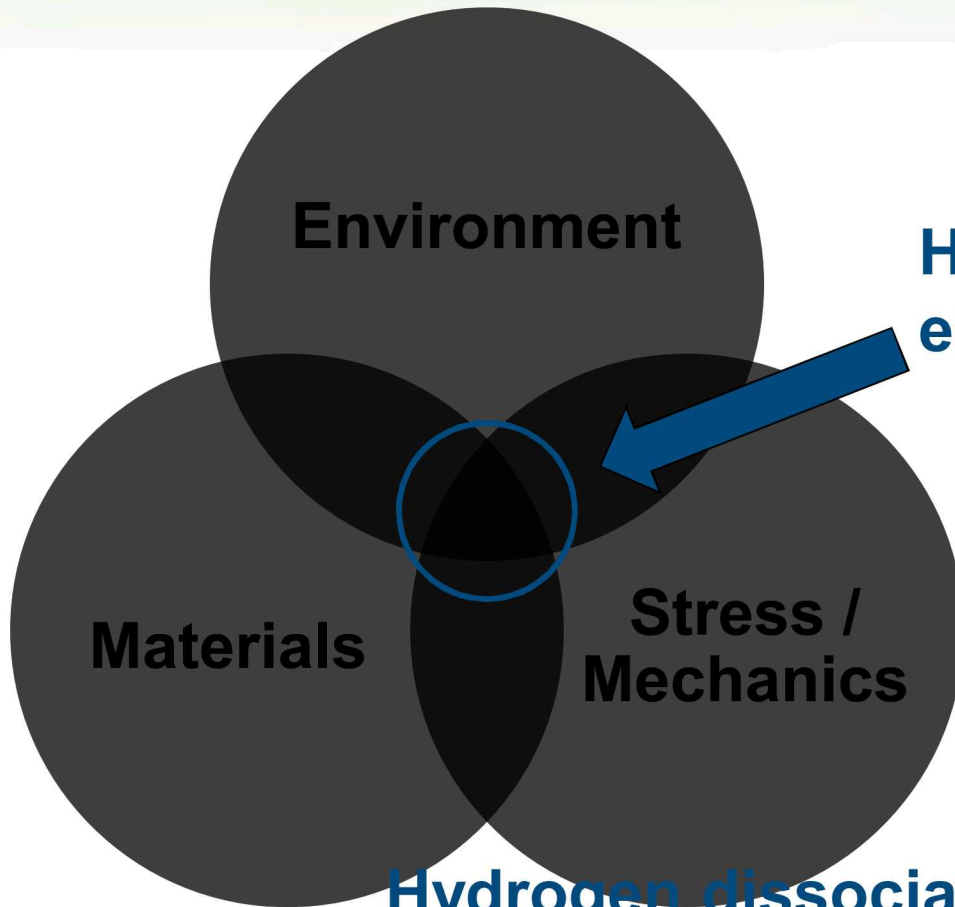
- **What is hydrogen embrittlement and when is it important?**
- **How does gaseous hydrogen affect fatigue and fracture of pipeline steels?**
- **Is there a threshold below which hydrogen effects can be ignored?**
- **Can the effects of hydrogen be masked by other physics?**
- **Where are the gaps in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



Motivation and Outline

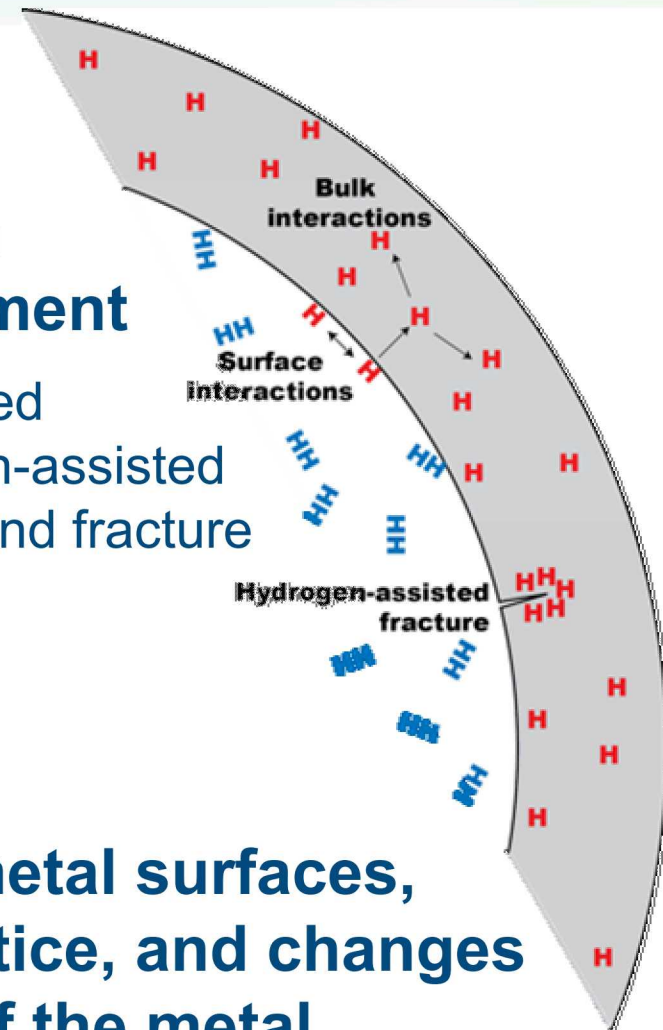
- **What is hydrogen embrittlement and when is it important?**
- How does gaseous hydrogen affect fatigue and fracture of pipeline steels?
- Is there a threshold below which hydrogen effects can be ignored?
- Can the effects of hydrogen be masked by other physics?
- Where are the gaps in understanding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

Hydrogen embrittlement occurs in metals 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-induced damage in polymer materials also includes different phenomena than observed in metals

- **Polymers are used in extensively in hydrogen infrastructure**

- Low-pressure piping and pipelines
- Liners of composite structures
 - Flexible hoses
- **Seals**
 - O-rings
 - Gaskets (e.g., pistons)
 - Soft seats
- Potting and other pressure boundaries (e.g., feed-thrus)



Thermoplastics
 HDPE, Nylon, PEEK,
 PEKK, PET, PEI, PVDF,
 Teflon, PCTFE, POM

Elastomers
 EPDM, NBR/HNBR
 Silicone, Viton,
 Neoprene, polyurethanes

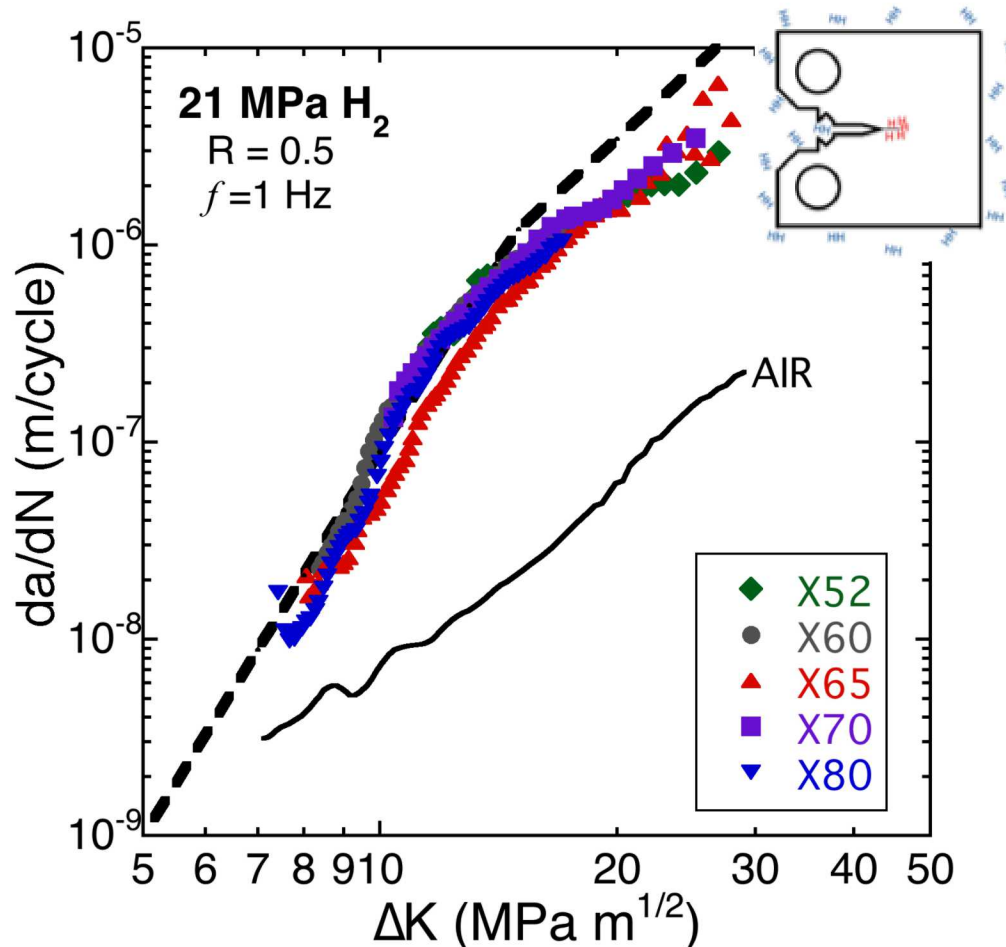
Thermosetting polymers
 Epoxy, PI, Polyurethane



Motivation and Outline

- 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?
- Where are the gaps in understanding structural integrity of hydrogen pipelines and piping?
- What is the implication of hydrogen on life of pipelines and piping?

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



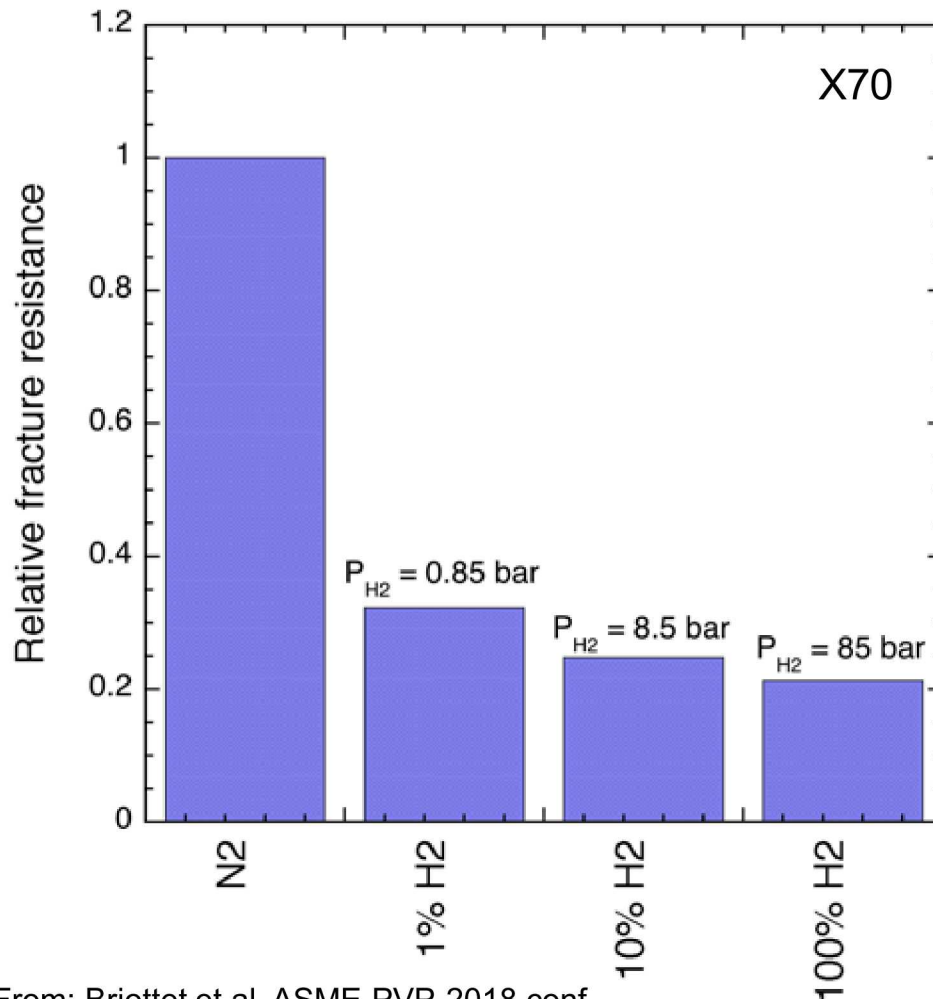
- A wide variety of pipeline steels display similar fatigue response in high-pressure gaseous hydrogen
- Fatigue crack growth rates in hydrogen scale approximately with square root of pressure (not shown)
 - Upper ‘plateau’ is independent of pressure



Motivation and Outline

- 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?
- Where are the gaps in understanding structural integrity of hydrogen pipelines and piping?
- What is the implication of hydrogen on life of pipelines and piping?

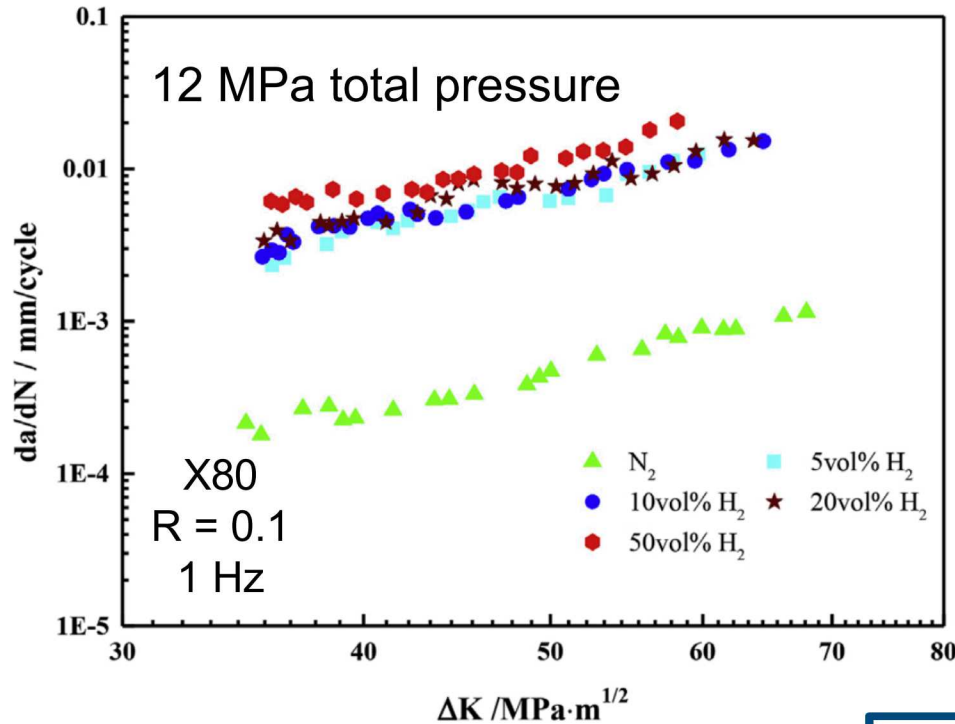
Low pressure hydrogen has substantial effect on fracture resistance of pipeline steels



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



- 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

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

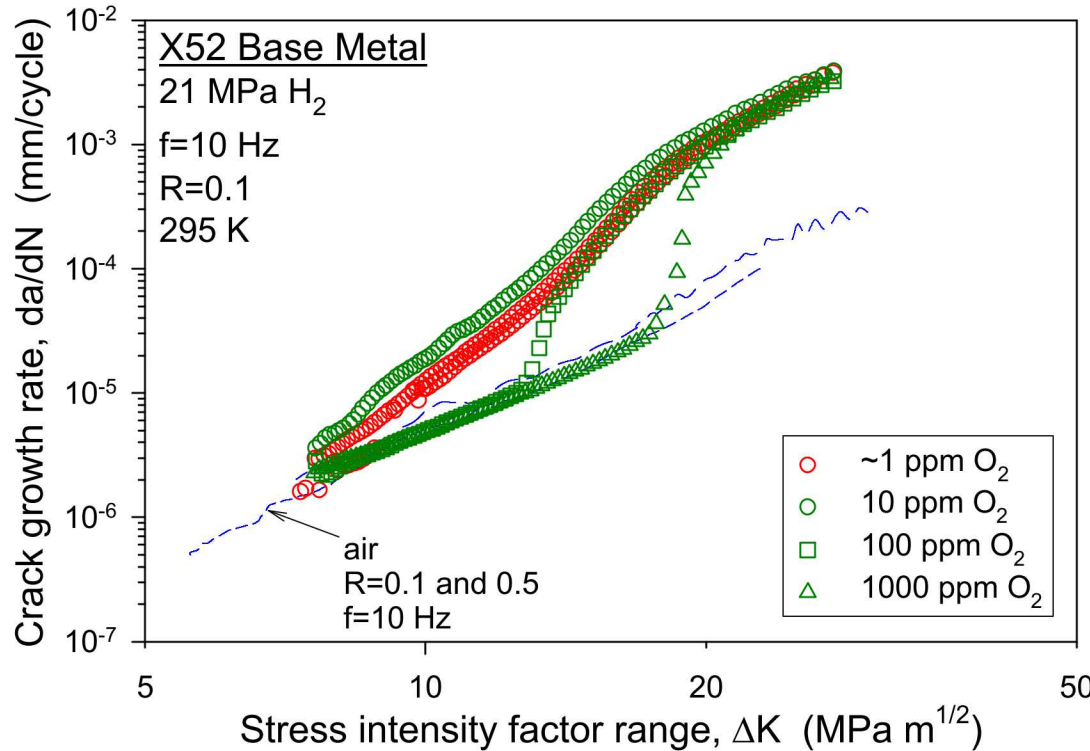
Small amounts of hydrogen can have substantial effect on fatigue and fracture



Motivation and Outline

- 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?**
- Where are the gaps in understanding structural integrity of hydrogen pipelines and piping?
- What is the implication of hydrogen on life of pipelines and piping?

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



- **Passivating chemical species can mitigate H₂-accelerated fatigue crack growth rates at low ΔK**
- **Attributed to diffusion to new crack surfaces**

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

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

Note: These oxygen contents are well below the flammability limit.

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

- **Small partial pressure of gaseous H₂ can have substantial effect 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



Motivation and Outline

- 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?
- **Where are the gaps in understanding structural integrity of hydrogen pipelines and piping?**
- What is the implication of hydrogen on life of pipelines and piping?

Materials data suggest no ‘showstoppers’ to integration of hydrogen in existing infrastructure

- **Transmission pipelines**

- API steel grades (including welds): wealth of data exists for fatigue & fracture properties measured in gaseous H₂

- **Distribution piping and components**

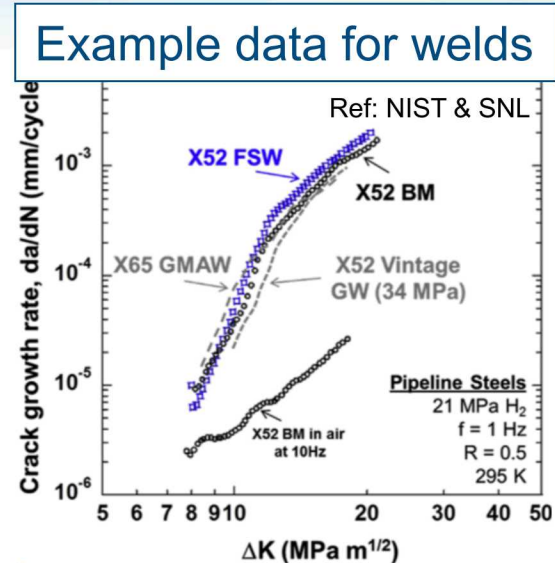
- Includes a diverse range of materials, many of which have not been evaluated

- PE pipe: Hydrogen effects on fatigue and fracture of polyethylene (PE) pipe have not been systematically studied

- Pressure and resulting stresses are generally low, suggesting cautious optimism (PE also used in FCEV fuel tanks)

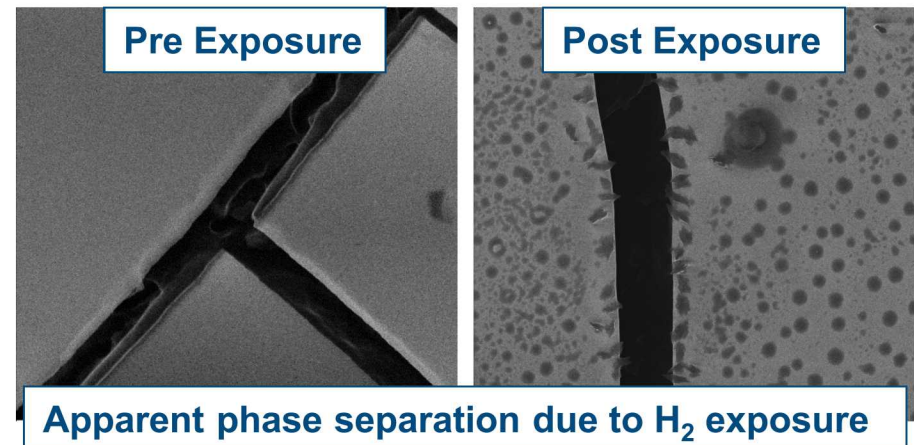
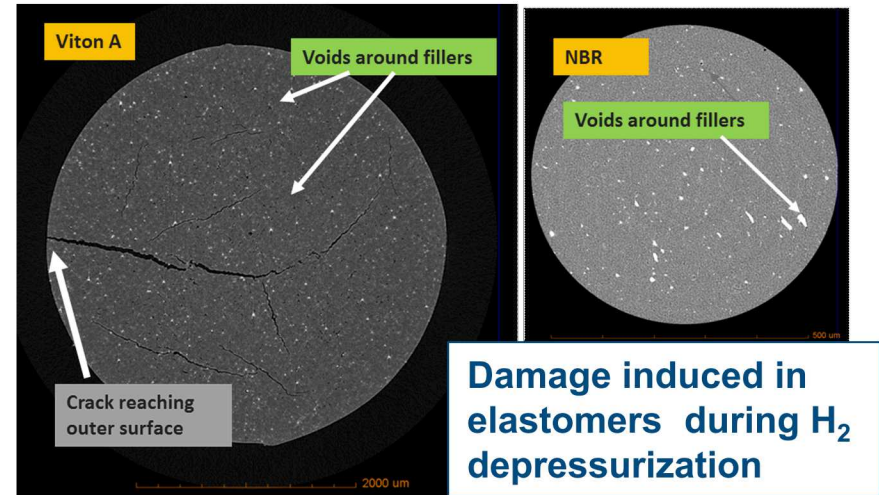
- **Blended gas environments**

- Role of gas impurities is not well understood, especially in dynamic environment (may not need to consider blended gas environments if systems are designed for pure hydrogen)



Materials considerations for polymers can be quite different than for metals

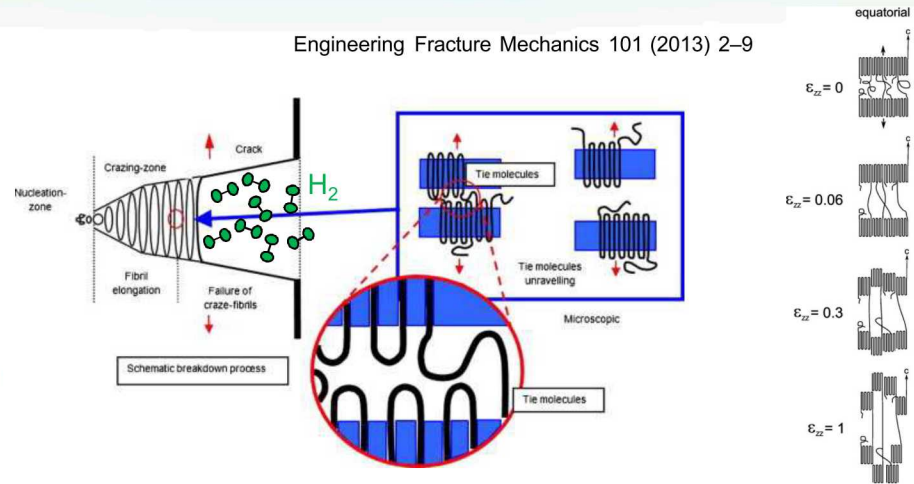
- Gaseous hydrogen exposure can induce physical and chemical changes in polymers
 - Elastomers are more sensitive to rapid decompression with hydrogen than other gases
 - Blister formation
 - Microcracking
 - Emerging evidence suggests that hydrogen can induce chemical changes
 - Such as phase separation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



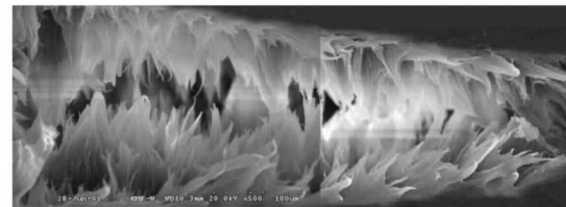
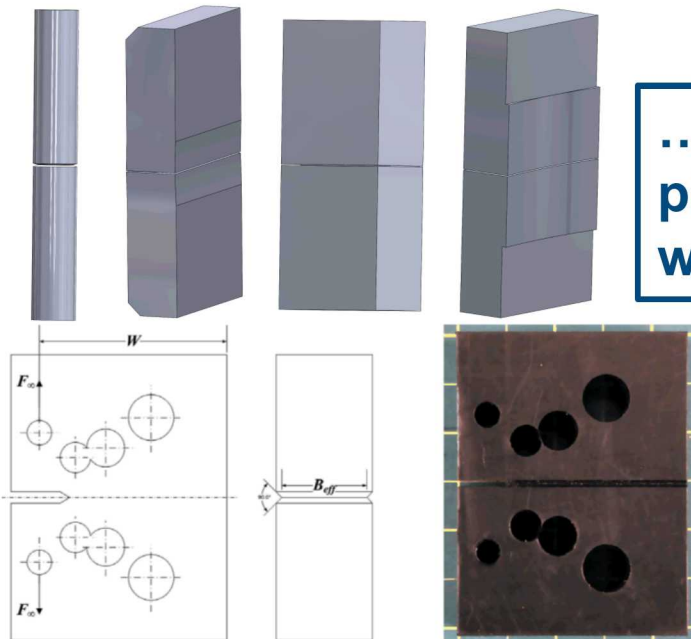
Evaluation of hydrogen-assisted fracture of PE pipe may require innovative test configurations...

Testing methods for environmental-assisted fracture:

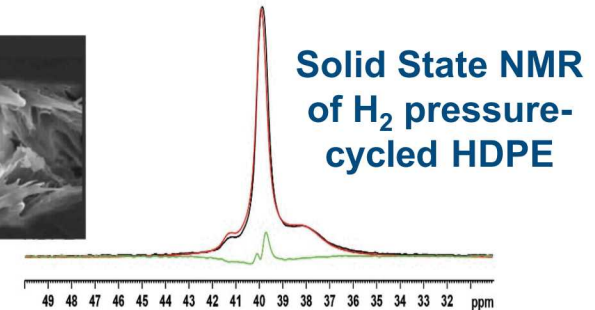
- Slow crack growth (SCG)
- Creep crack growth
- Fatigue resistance
- Effects of weld microstructure



... which address characteristic fracture phenomena and unique damage associated with H_2 and H_2 -pressure cycling



A. Chudnovsky et al. / International Journal of Engineering Science 59 (2012) 108–139

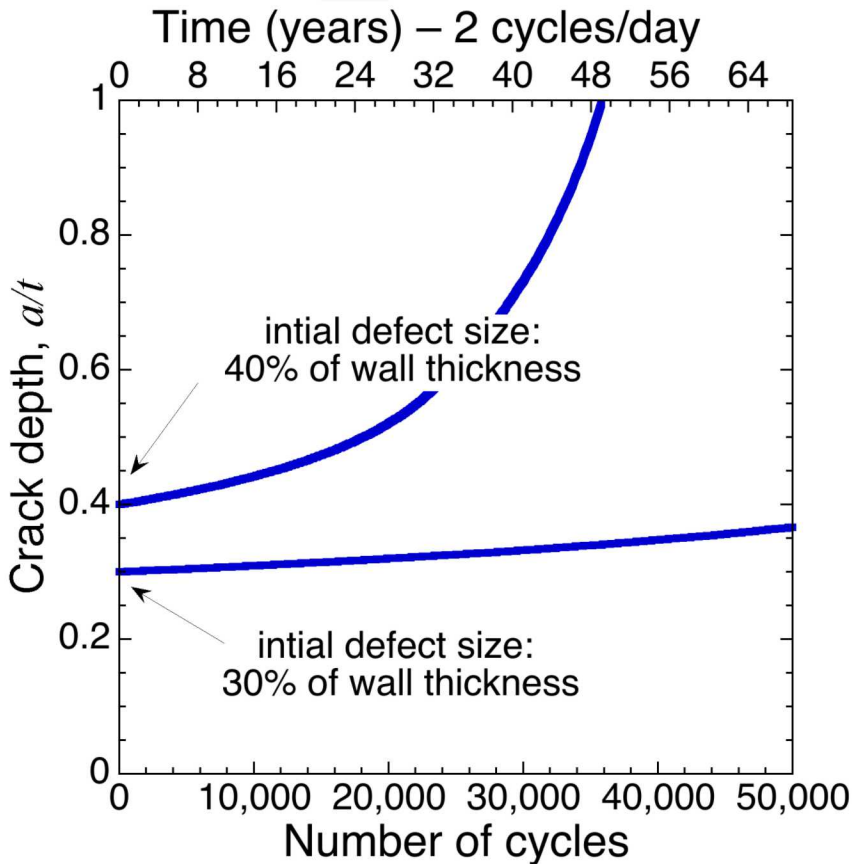




Motivation and Outline

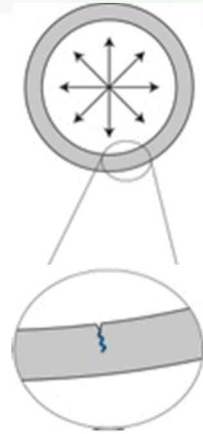
- What is hydrogen embrittlement and when is it important?
- How does gaseous hydrogen affect fatigue and fracture of pipeline steels?
- Is there a threshold below which hydrogen effects can be ignored?
- Can the effects of hydrogen be masked by other physics?
- Where are the gaps in understanding structural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

Example of predicted lifetime of steel pipeline with growing fatigue crack in H₂



Assuming

- 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)



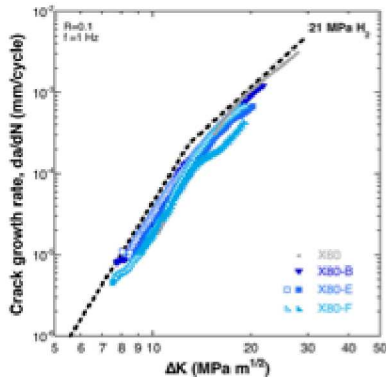
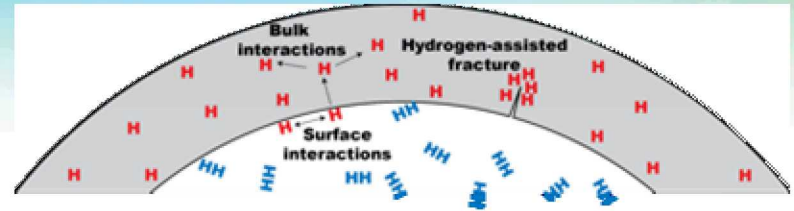
- **10,000s of cycles are needed to extend the crack**
- **At 2 cycles per day, decades are needed to advance the crack**

Available data is insufficient for similar assessment of PE pipe

Summary

- What is hydrogen embrittlement and when is it important?

- Hydrogen degrades mechanical properties of most materials
- Hydrogen gas interactions in polymers are not well understood chemically or physically

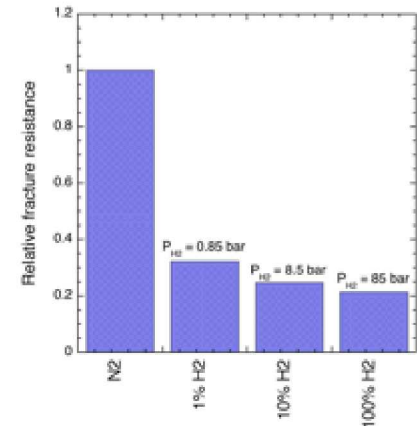


- How does gaseous hydrogen affect fatigue and fracture of pipeline steels?

- Fatigue is accelerated by >10x and fracture resistance is reduced by >50%

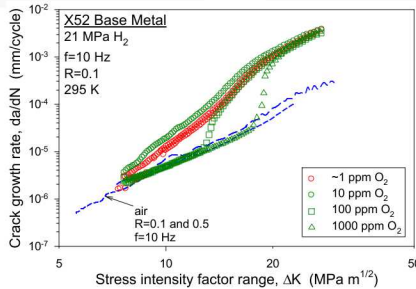
- Is there a threshold below which hydrogen effects can be ignored?

- **NO**, even small amounts of hydrogen have large effects



Summary

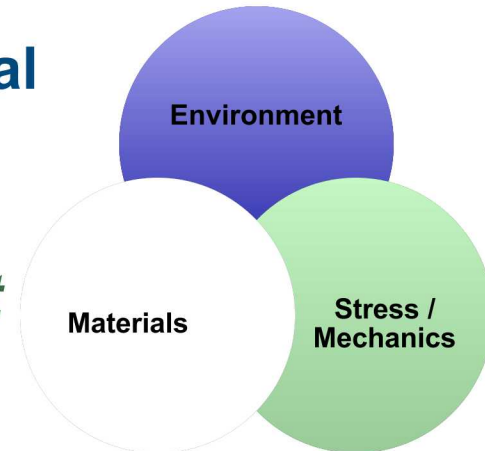
- Can the effects of hydrogen be masked by other physics?



– *Oxygen and other passivating chemical species can mitigate the effects of hydrogen in some cases, which perhaps can be exploited*

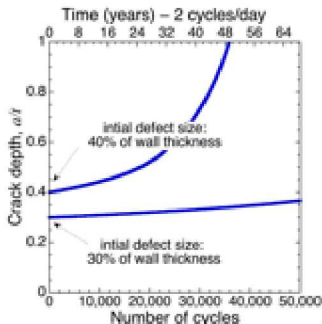
- Where are the gaps in understanding structural integrity of hydrogen pipelines and piping?

– *Materials on the distribution side have not been thoroughly evaluated – but operate at low pressure and low stress*



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

– *In most cases, hydrogen does not threaten the structural integrity of pipelines and piping*



Thank you for your attention

Contacts:

- Chris San Marchi cwsanma@sandia.gov
- Joe Ronevich jaronev@sandia.gov
- Kevin Simmons kl.simmons@pnnl.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>
- Additional detail on hydrogen effects in pipeline steels and life calculations can be found in SAND2018-14013 PE