

# H<sub>2</sub> Permeability and Integrity of Steel Welds

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*PD\_43\_Feng*

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# Overview

## Timeline

- Start – March 2004
- Finish – September 2011
- 40% Complete

## Budget

- Total Project Funding
  - DOE share: \$815,000
  - Contractor share: N/A
- Funding received in FY08:
  - \$300,000
- Funding for FY09: \$0

## Barriers Addressed

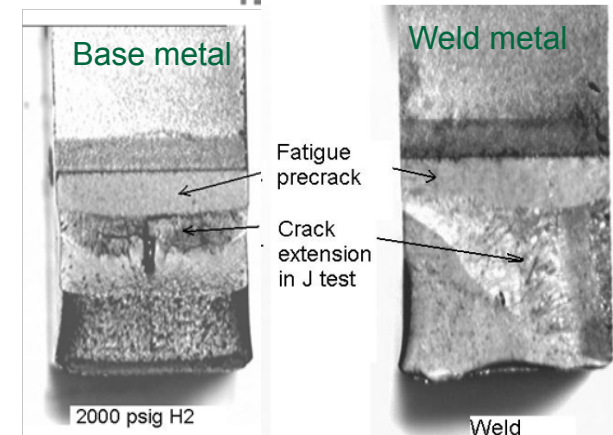
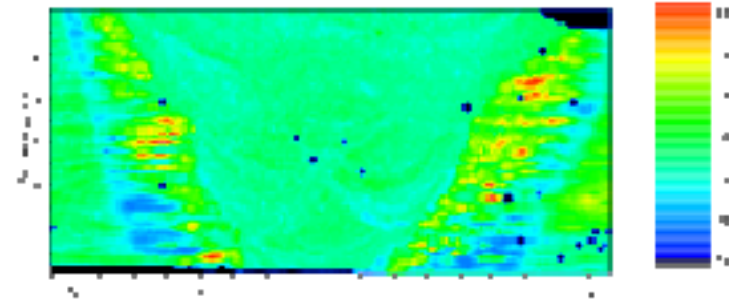
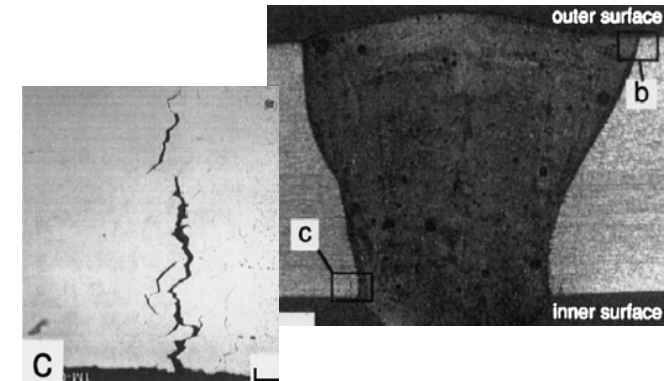
- High capital cost and hydrogen embrittlement (HE) of steel pipelines
  - Preventive measures for HE and permeation
  - Improved joining methods to reduce cost and mitigate HE
- Safety, codes and standards

## Partners

- Oak Ridge National Laboratory
- Savannah River National Laboratory
- University of Illinois
- Praxair
- MegaStir Technologies
- Edison Welding Institute

# Project Focus: Weld Property Assessment & Welding Technology Development

- Challenges:
  - Weld region is generally more vulnerable to hydrogen induced property degradation (sensitized microstructure, high weld residual stress, exposure to hydrogen)
  - Existing testing methods are not suitable to quantify the tolerance level to HE of weld
  - Lack of technical basis and guidelines for managing hydrogen, stresses, and microstructure in the weld region to ensure the structural integrity and safety of H<sub>2</sub> delivery infrastructure
- Goal: Improve resistance to hydrogen embrittlement (HE) in steel weldment and reduce welding related construction cost



# Objectives

- Quantify the effects of high-pressure hydrogen on property degradation of weld in pipeline steels
- Develop the technical basis and guidelines for managing hydrogen, stresses, and microstructure in the weld region to ensure the structural integrity and safety of H<sub>2</sub> pipelines; &
- Develop welding/joining technology to safely and cost-effectively construct new pipelines and/or retrofit existing pipelines for hydrogen delivery.

# Approach

- Understand hydrogen transport behavior in steels and weld region
  - High pressure (up to 5,000 psi) hydrogen permeation and diffusion measurement and modeling
  - Effect of steel composition and microstructure
  - Effect of surface conditions
- Determine mechanical property degradation in weld region
  - Effective testing methods for welds
    - Quick screening/comparative test
    - Weld property generation for fracture mechanics based pipeline design
  - Evaluation of weld microstructure effect in old and new pipeline steels
- Welding technology development for new construction, repair and retrofitting existing pipeline infrastructure for hydrogen delivery
  - Weld residual stress and microstructure management
  - Hydrogen management
- Develop technical basis and guidelines for welding construction and maintenance of hydrogen pipelines

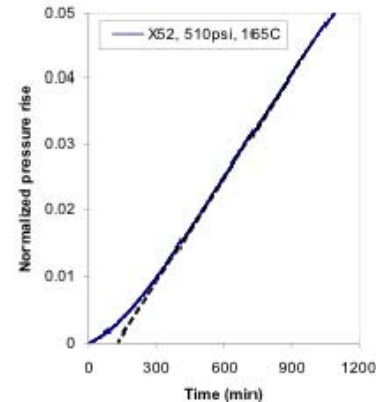
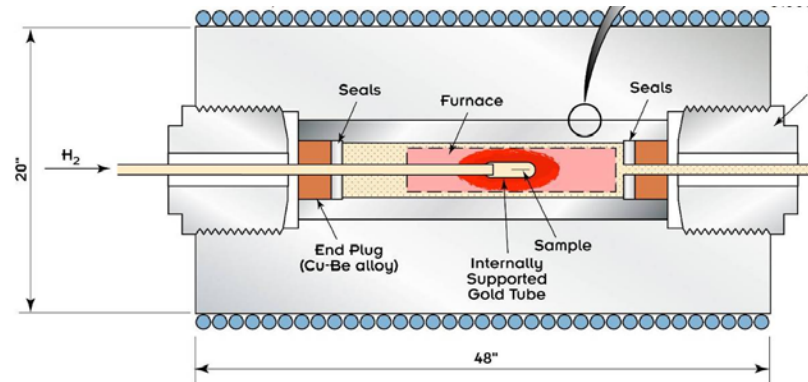
# Technical Accomplishments: Previous Years

- High-pressure hydrogen permeation measurement system development and verification
- Baseline high-pressure hydrogen diffusion and permeation measurement with pure Iron
- Effect of weld microstructure on hydrogen trapping, diffusion and permeation
- Initial study on friction stir welding of pipeline steels
- Concept design and initial development of testing methods on weld mechanical property degradation

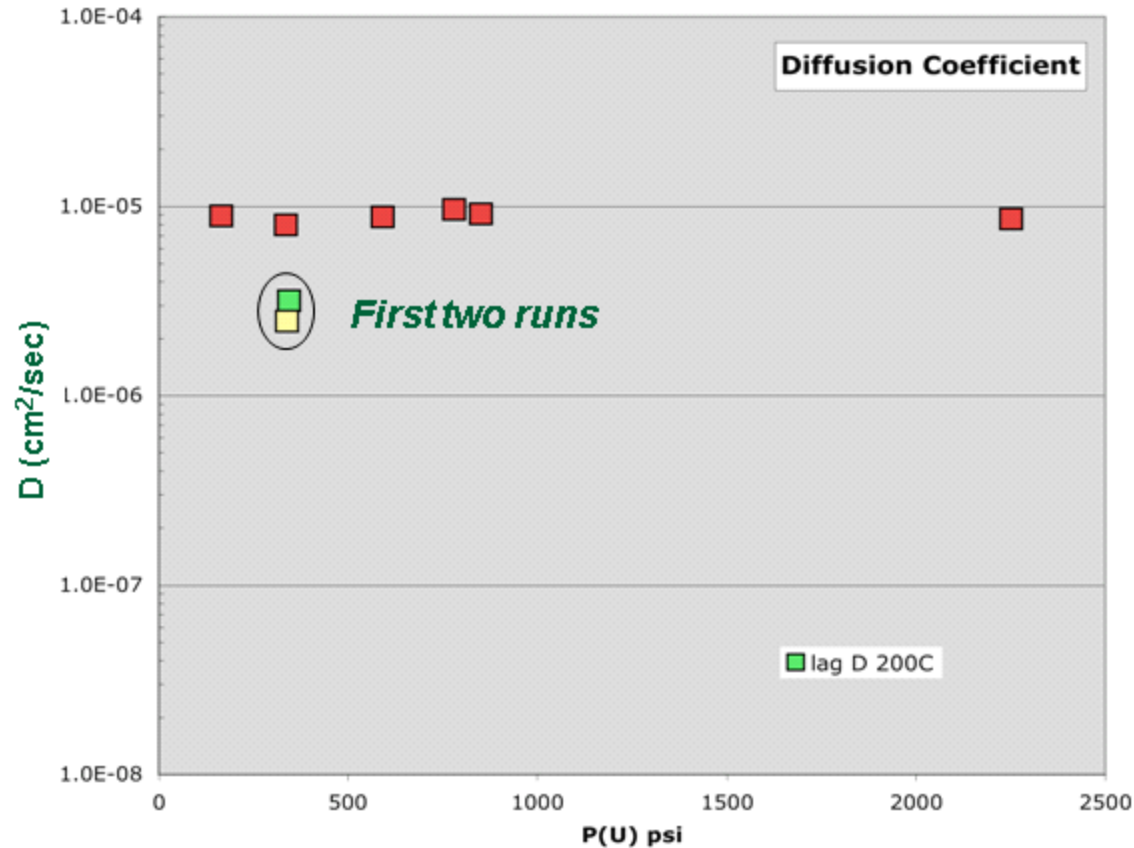
# Technical Accomplishments: H Permeation & Diffusion Measurements

- Investigate the hydrogen transport behavior
  - Hydrogen absorption/surface effect
    - Influences amount and rate of hydrogen entering steel
  - Hydrogen diffusion
    - Influences crack propagation rate
  - Hydrogen solubility/concentration
    - Influences the degree of mechanical property degradation
- Under conditions relevant to hydrogen delivery infrastructure
  - Gaseous hydrogen: composition and purity level
  - Pressure range: up to 5,000 psi H<sub>2</sub>
  - Temperature range: -40 to 150°C
  - Material: Pipeline steels and their welds; Polymer/composite materials
  - Surface condition: Naturally formed surface oxide layer; Surface coating/modification; Others

- Utilizing ORNL's unique high-pressure permeation measurement system
  - Charging pressure up to 150,000psi
  - Temperature range: 0 to 1000°C
  - Small disk specimen



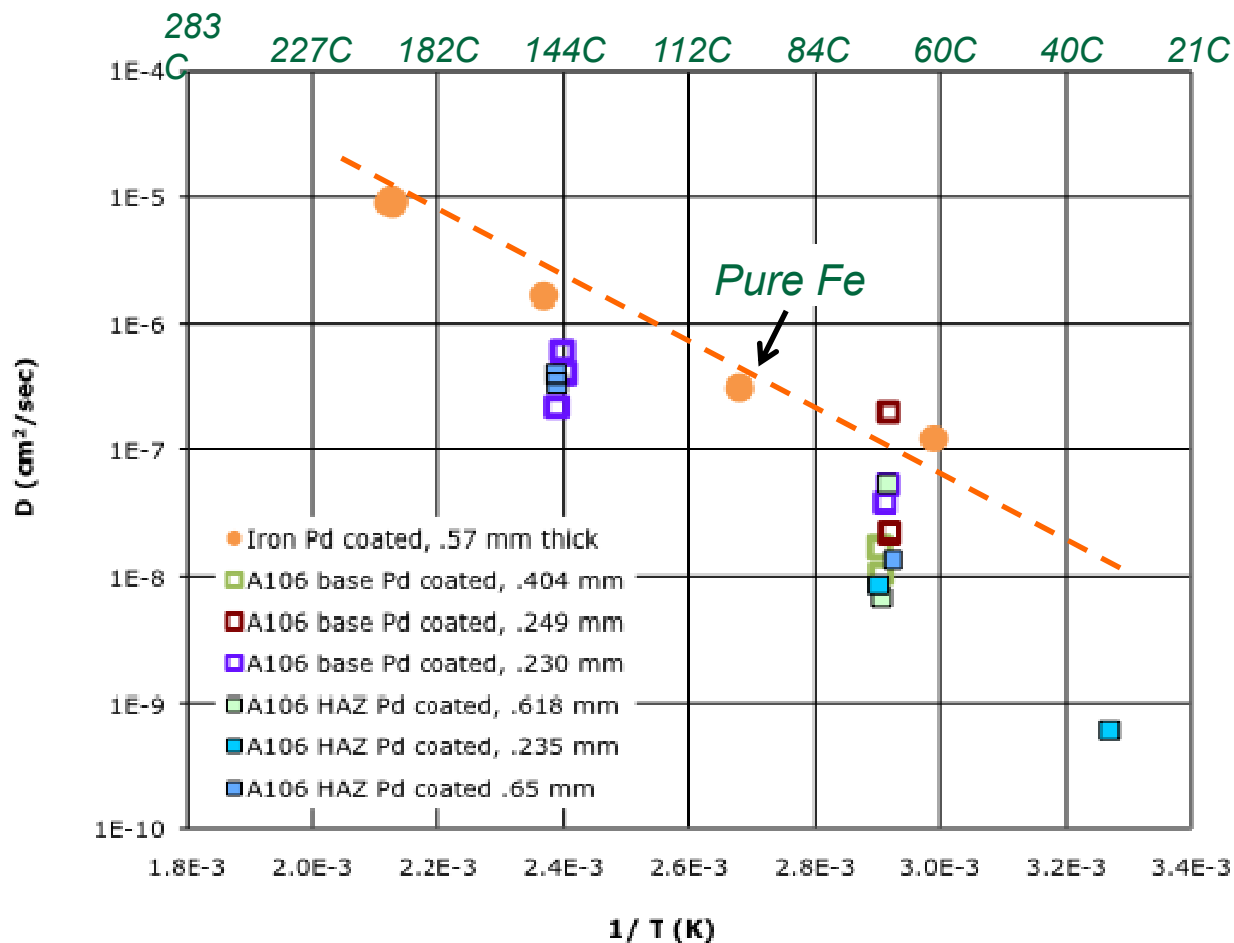
# Technical Accomplishments: Pressure Effects on Hydrogen Diffusivity



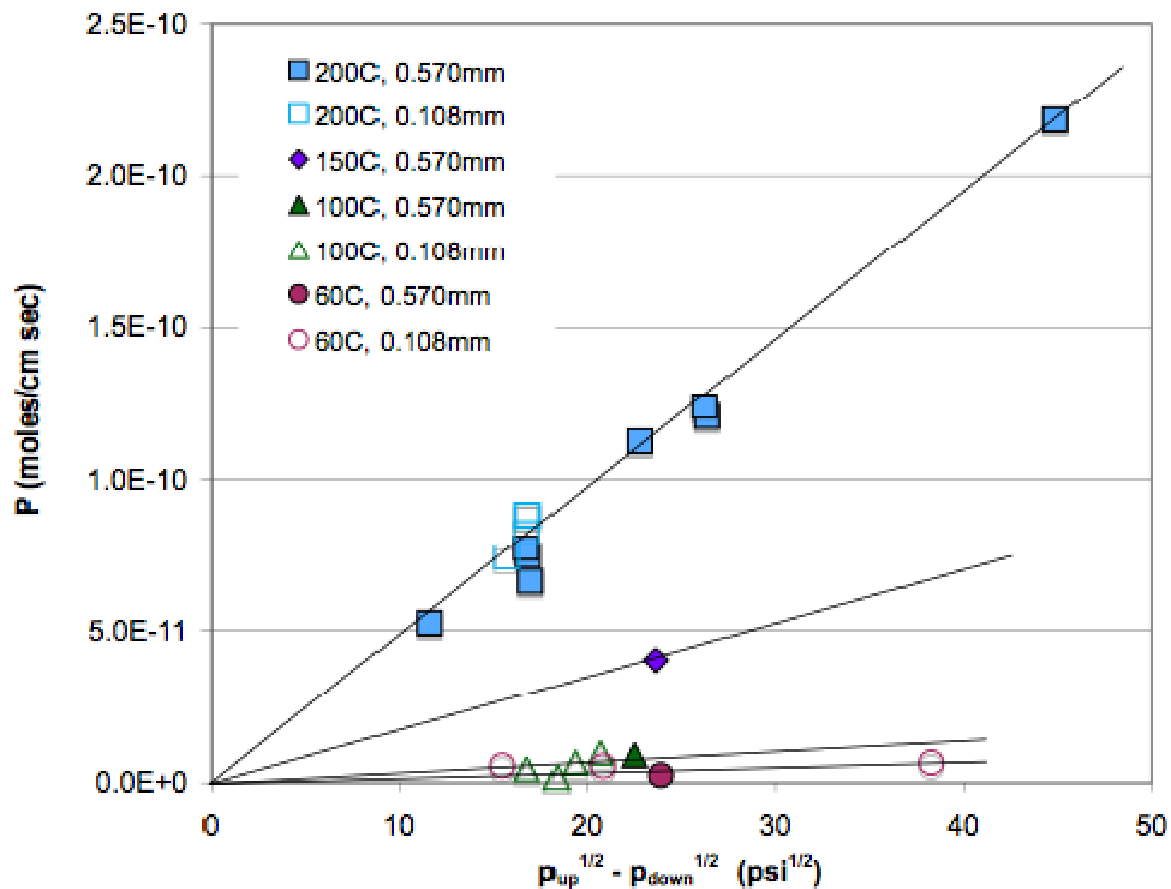
- Pd Coated Pure Iron at  $200^\circ\text{C}$
- Lower “effective” diffusivity of first two runs were due to hydrogen traps and/or surface conditions



# Technical Accomplishments: Diffusivity of Pure Iron and Steel A106 Gr B of Different Microstructures



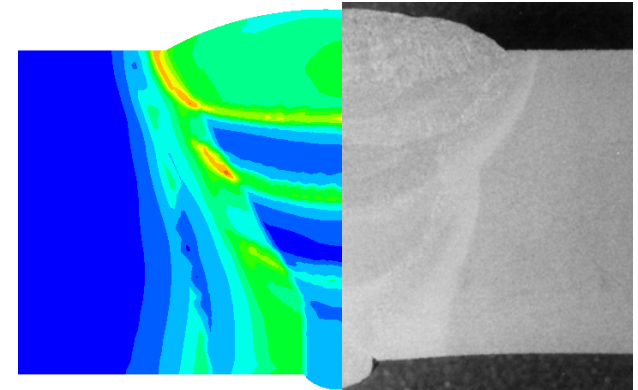
# Technical Accomplishments: Pressure Effects on Permeability (Pd Coated Pure Iron)



- Permeation rate has square root dependency on pressure at given temperature

# Mechanical Testing of Weld Hydrogen Embrittlement

- Existing mechanical testing methods are generally designed for homogenous materials (base metal) and difficult to reliably test the weld region due to the complex microstructural and property gradients
- Two types of test methods are developed
  - Multi-notch tensile specimen as a simple way for screening and comparative test of different regions of weld and HAZ relative to the base metal
  - Spiral notch torsion test (SNTT) for sustained-load threshold value ( $K_{th}$ ) of weld and HAZ
  - Determine the tolerance level to hydrogen of different weld microstructures
  - Both methods are under patent application
- Features of test methods
  - Miniature specimen geometry
  - Miniature self-loading rig (sustained load) inside the autoclave
  - Continuous load monitoring
  - Sampling various regions of a weld in a single test to determine the most susceptible region to HE in a weld
  - Low cost and time effective

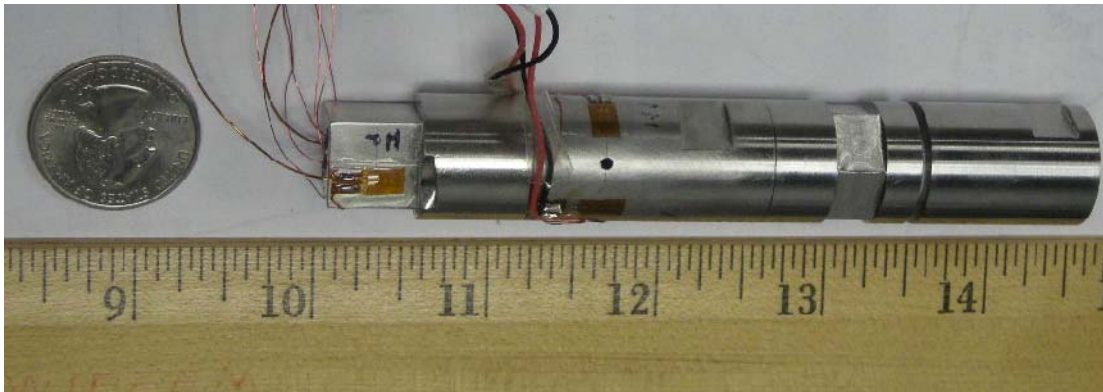


# Technical Accomplishments: Multi-Notch Tensile Comparative Test

*Designed for cost-effective evaluation of weld microstructure in long-time exposure to high-pressure H<sub>2</sub>. Hydrogen induced crack will initiate and grow in the most sensitive (weakest) microstructure region*



Miniature notch tensile specimen (3mm dia.) with notches to sample different microstructures in weld, HAZ and base metal for comparative evaluation



Miniature self-loading fixture with strain gage load sensor



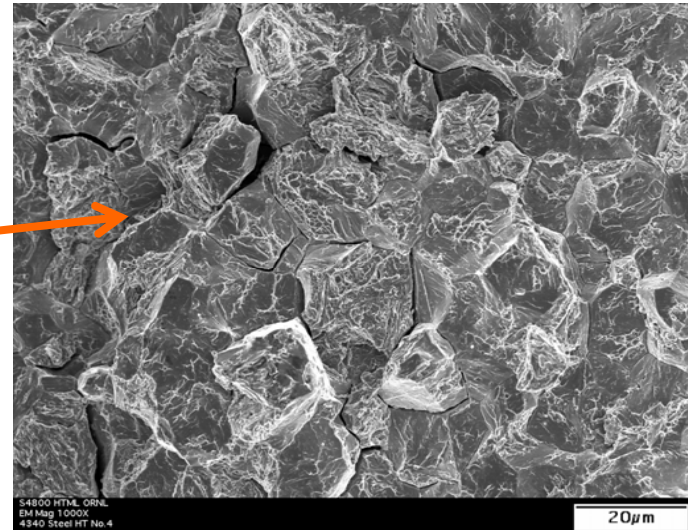
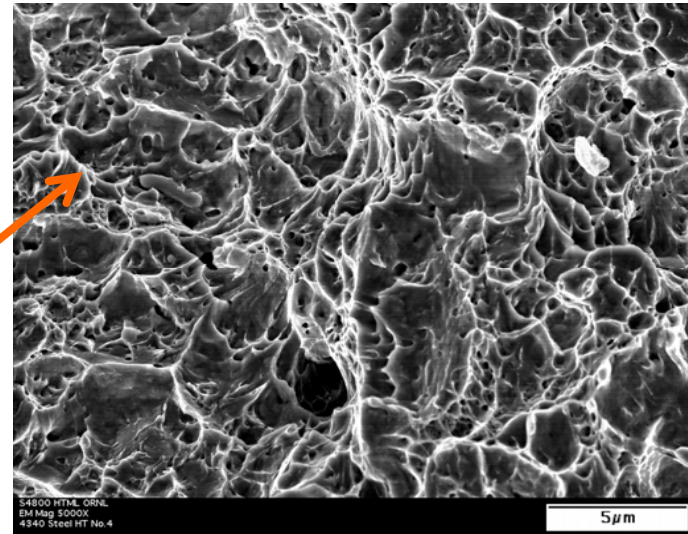
Pressure vessel and instrumentation capable of multiple tests at a time

# Technical Accomplishments: Baseline Test with AISI 4340 Steel

- AISI 4340 steel
  - Fully hardened to  $\sim 50$  Rc,  $S_{ult}=285$ ksi
  - Expected to be sensitive to HE
- Testing procedure development
  - Overall design of testing device
  - Effectiveness of self-loading and strain gage load cell
  - Sensitivity to quantify degree of HE
  - Hydrogen uptake rate
  - Testing protocol

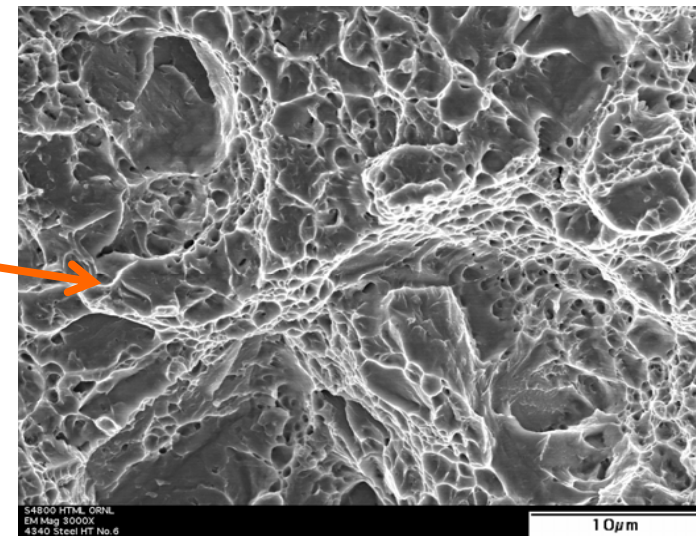
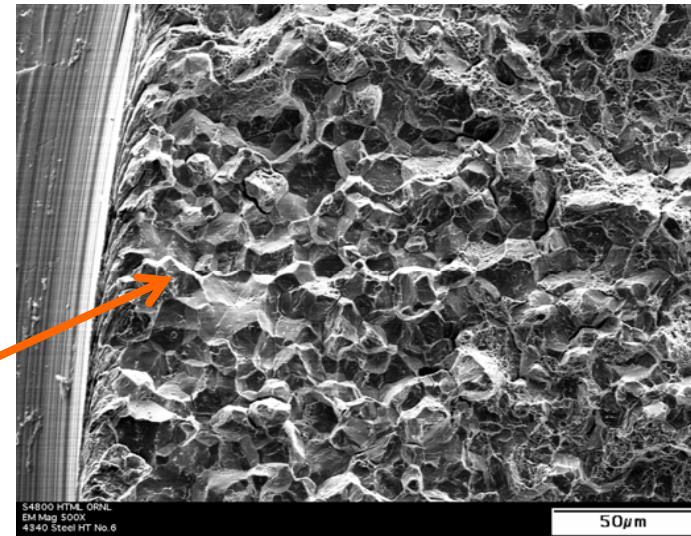
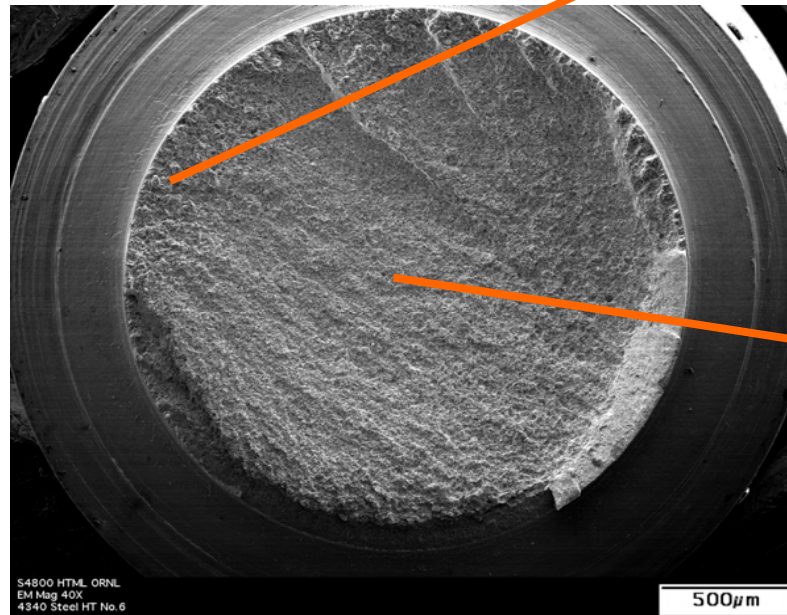
# Technical Accomplishments: Multi-Notch 4340 Sample in 2000psi H<sub>2</sub>

- Pd surface coating
- Critical fracture load: ~ 45% of failure load in air
- Incubation time to failure: ~ 30 min



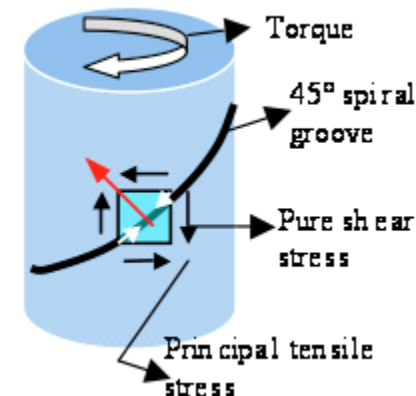
# Technical Accomplishments: Multi-Notch 4340 Sample in 2000psi H<sub>2</sub>

- Pd surface coating
- Pre-load to 1700N (26% of failure load in air)
- No noticeable HE initiation/growth in hydrogen for 6 days at 23°C
- Sample was pulled broken within 5 min after removing from 2000psi H<sub>2</sub> to check hydrogen level in sample
- **Hydrogen was not saturated to specimen center (~1.5 mm from surface) after 6 days H<sub>2</sub> for charging**



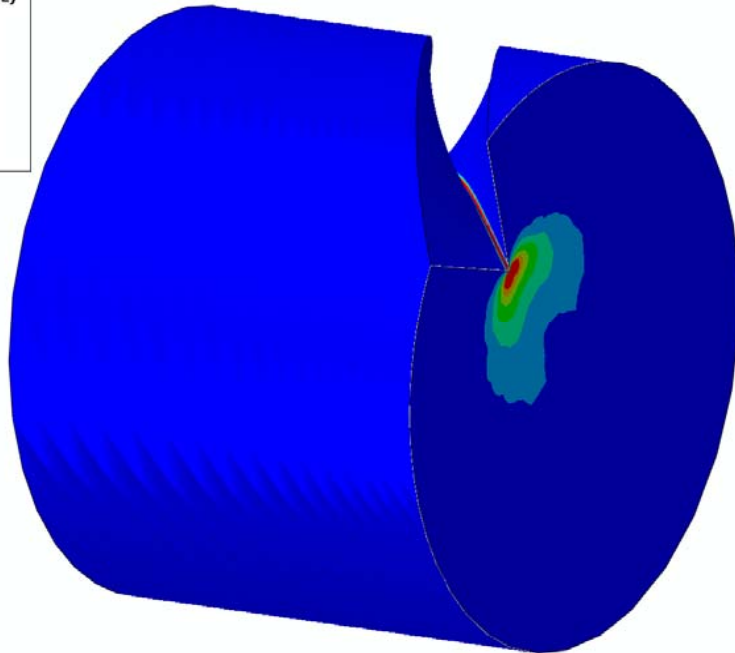
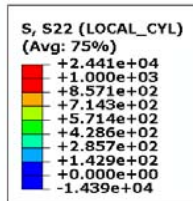
# Technical Accomplishments: SNTT for $K_{th}$ Measurement in high- pressure $H_2$

- Based on a R&D100 award-winning method invented by ORNL
- 45 deg spiral notch and twist loading result in Mode I (opening mode) of the spiral notch
- Development for  $H_2$  testing
  - Miniature load cell
  - Finite element analysis was used to determine the stress intensity factor
  - AISI 4340 steel was used for baseline testing procedure development

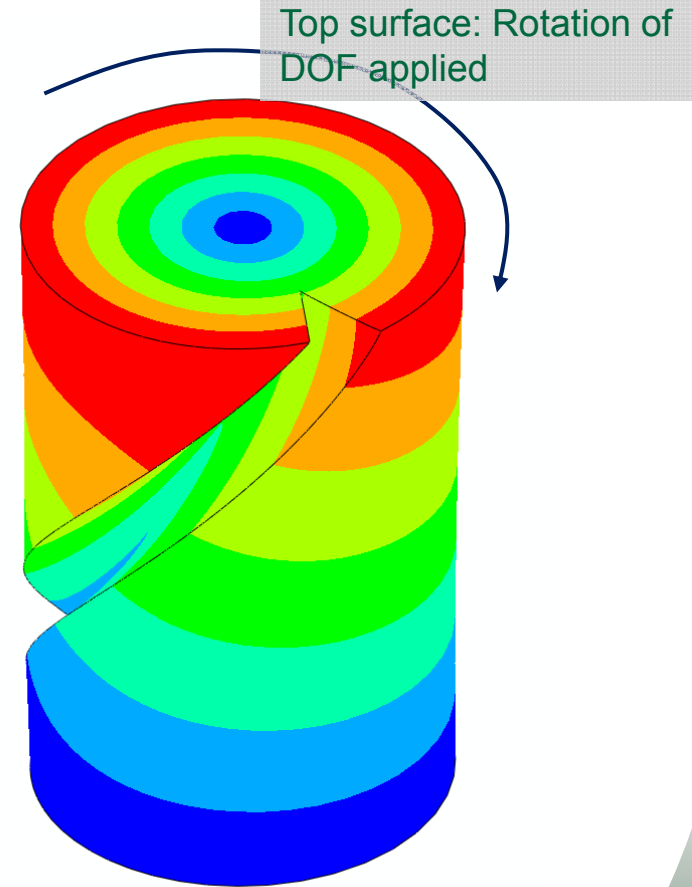
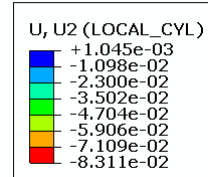




# Technical Accomplishments: FEM analysis of SNTT



Circumferential stress  
(crack opening stress)



Circumferential displacements

# Technical Accomplishments: SNTT Testing of AISI 4340 Steel

- In air :  $K_{IC} = 67.4 \text{ ksi-in}^{1/2}$ 
  - Consistent with reported 65 - 75  $\text{ksi-in}^{1/2}$  by standard CT specimen of the same steel (Bandyopadhyay et al, Metallurgical Transactions A, 1983)
- Under 2000psi  $\text{H}_2$ 
  - $K_{th} = 36 - 39 \text{ ksi-in}^{1/2}$  (multiple samples)  $\sim 55\%$  of  $K_{IC}$  in air.



# Proposed Future Work

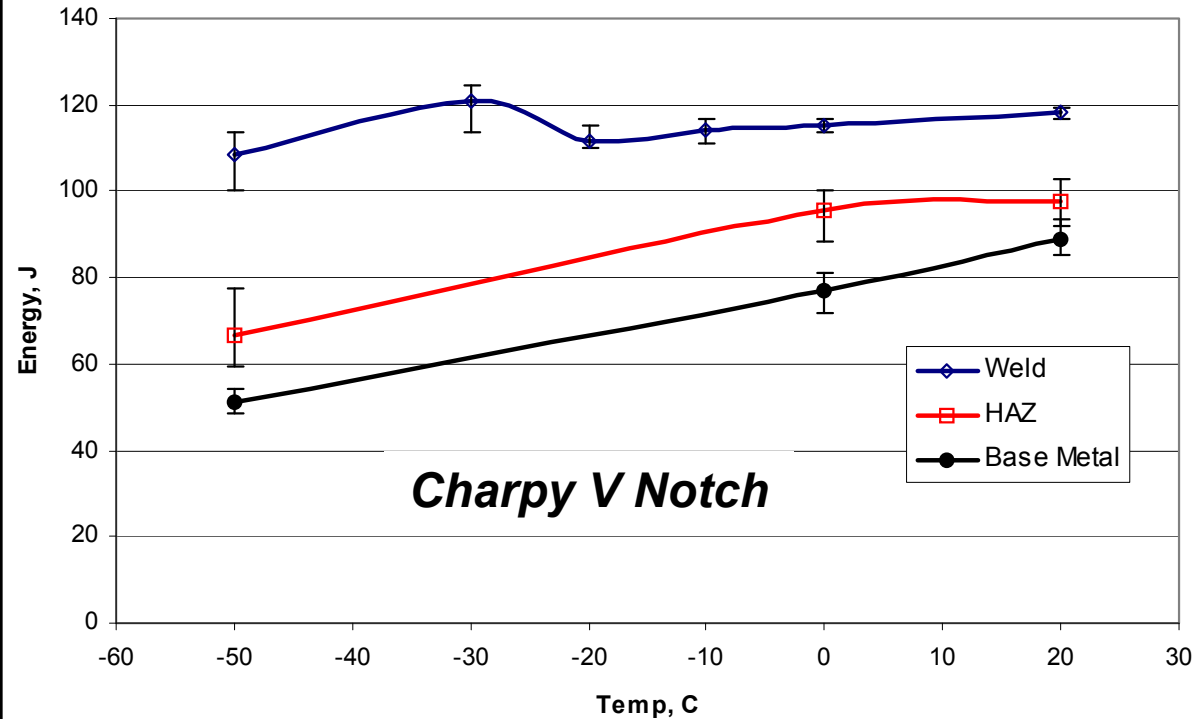
- Permeation/Diffusion in High Pressure Hydrogen
  - Complete comparative measurement on different grades of pipeline steels both weld and base metal (A106, X52, and X100)
  - Study of effect of surface conditions and hydrogen purity (experiment and modeling)
- Mechanical Property Test of Weld
  - Comparative test of X52 welds and X100 welds with multi-notch tensile delay cracking test
  - Kth test with SNTT
  - Cost effective fatigue life test
- Welding technology development
  - Friction stir welding
  - Weld residual stress and microstructure management
  - Cost-effective hydrogen management
- All depending on DOE funding priority and level

# Welding Technology Development: Friction stir welding

- A solid-state joining process, no melting
- Extensive thermomechanical deformation during FSW results in wrought weld microstructure with improved properties
  - Conventional fusion welds have cast microstructure
- Eliminate/reduce the coarse grain HAZ (the hard spot) that is generally associated with HE in steel welds
- ORNL is working with major energy and welding equipment companies for natural gas and oil pipeline applications
  - Expect 15-30% cost saving compared to today's pipeline welding construction technology
  - Superior weld property (better than base steel) has been demonstrated
  - [http://www1.eere.energy.gov/industry/intensiveprocesses/pdfs/flexible\\_hybrid\\_friction.pdf](http://www1.eere.energy.gov/industry/intensiveprocesses/pdfs/flexible_hybrid_friction.pdf)

# Superior Weld Properties – Better Than Base Metal

API 5L grade X-65 steel tested *in air*.



**ERW Line Pipe**  
**OD: 12.75", 0.25" t**  
**Base metal properties :**  
**Yield: 67 ksi, Tensile: 77 ksi,**  
**Elongation: 33%**



# Friction Stir Welding of Steel Pipe (Prototype Pipe Welding System by MegaStir/ESAB)



# Summary

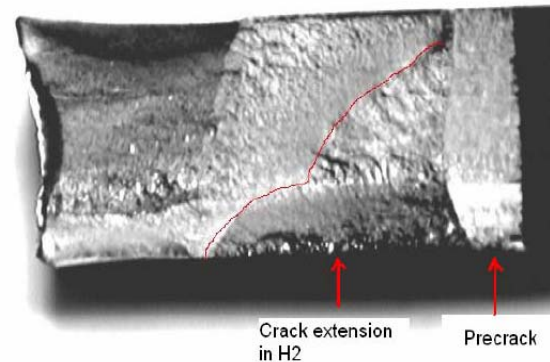
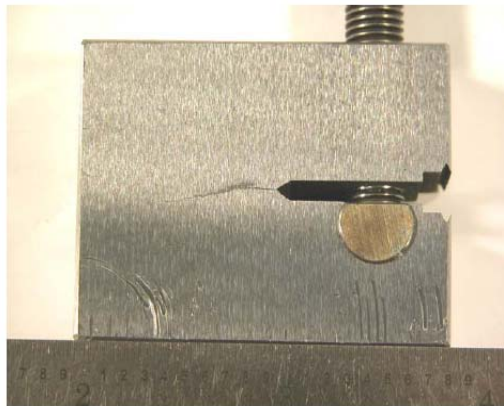
- Project Focus: Integrity of weldment in steel hydrogen delivery pipeline infrastructure
  - Goal: improve tolerance to HE in steel weldment and reduce construction and retrofitting cost associated with welding
- Technology Development
  - Testing methods suitable for weld property measurement with the complex microstructure and property gradients
    - Two testing methods are under patent application
  - Welding technologies for weld microstructure improvement, residual stress control and hydrogen mitigation
    - Friction stir welding can be a cost-effective construction technology
- Close interactions with other related projects on pipeline steel development and material property testing

# Backup Slides



# Recent Evidence

- The weld region exhibit less resistance to HE than the baseline pipe steels
  - Xu: X80 with high  $C_{eq}$  (0.5)
  - SRNL: A106 Grade B Carbon Steel
    - BM specimens did not crack after 2000 hrs exposure.
    - All weld specimens cracked on one side of the specimen (root pass side)

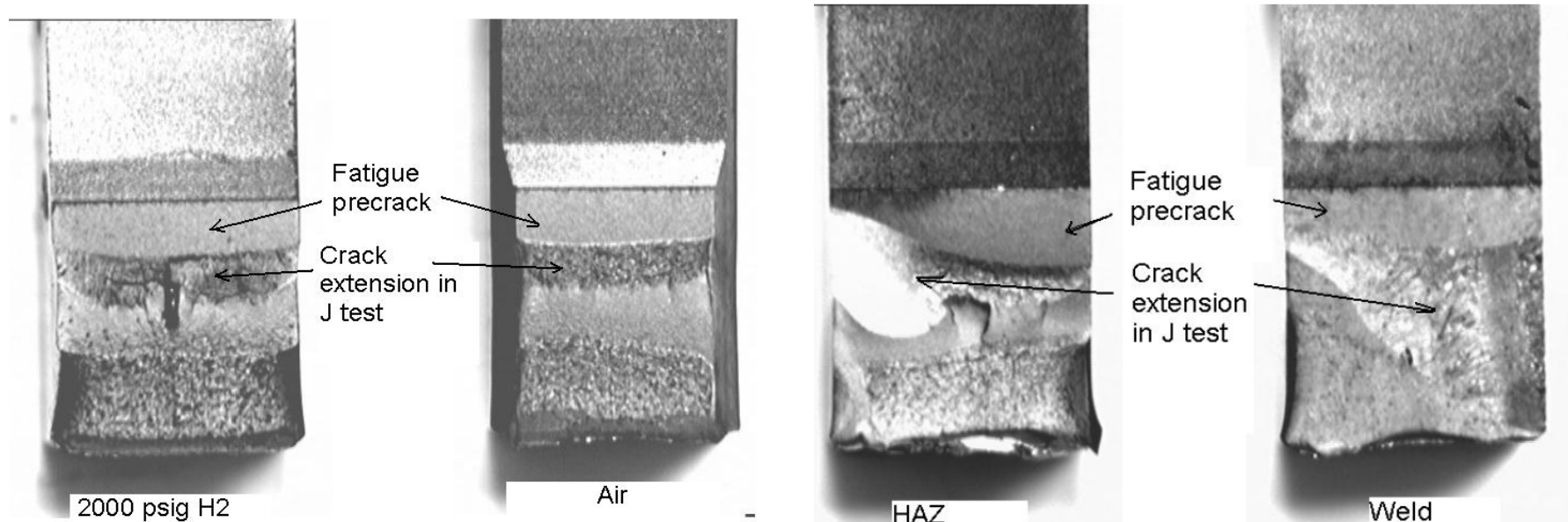


*(Xu, 2005, ASTM HE Workshop, X80 steel)*

# Complications of Inhomogeneous Weld Property – Inadequacy of Current Testing Methods

*Valid  $J_{1c}$  test of base metal*

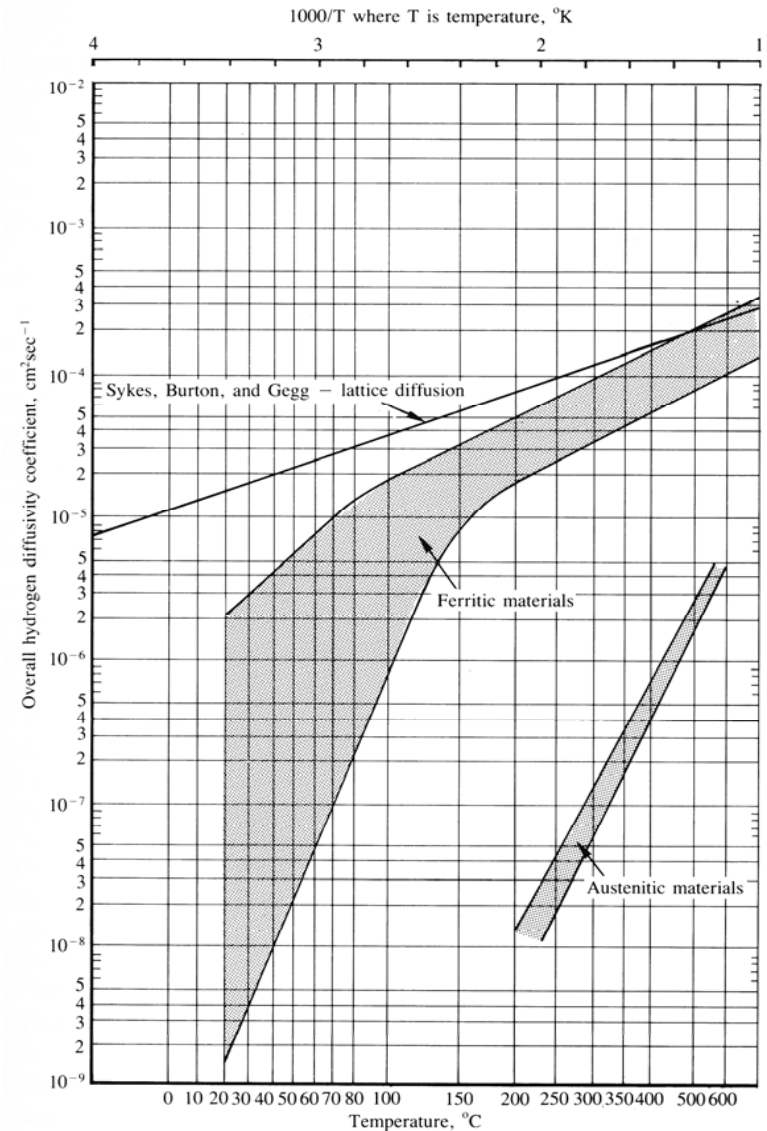
*Invalid  $J_{1c}$  test of weld and HAZ due to uneven crack front*



*(Xu, 2005, ASTM HE Workshop)*

# Hydrogen Diffusivity Data in Literature

- Extensive data available from electrochemical charging at low gaseous pressure ( $< 1\text{atm}$ ), mostly under “controlled” laboratory surface conditions
  - Clean, polished surface
  - Surface coating (Pd) to eliminate surface effects
- Very limited data for high-pressure gaseous hydrogen in “real-world” pipeline environment
  - Surface effects
  - Microstructure effects
  - Hydrogen purity
- Literature data indicates that hydrogen will permeate through pipeline steel during long-term ( $>20$  years) service



Bailey et al, in *Welding without Hydrogen Cracking*

# What Really Happens In Permeation Test

- Several major processes operate simultaneously

- On entrance surface:

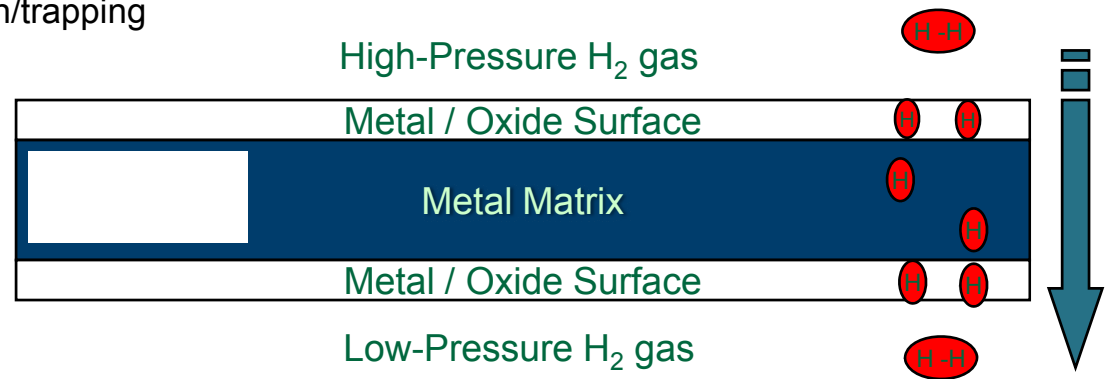
- Hydrogen molecule adsorption/trapping
- Hydrogen dissociation
- Hydrogen dissolution

- Within metal

- Hydrogen diffusion
- Hydrogen trapping

- On exit surface

- Hydrogen recombination
- Hydrogen desorption



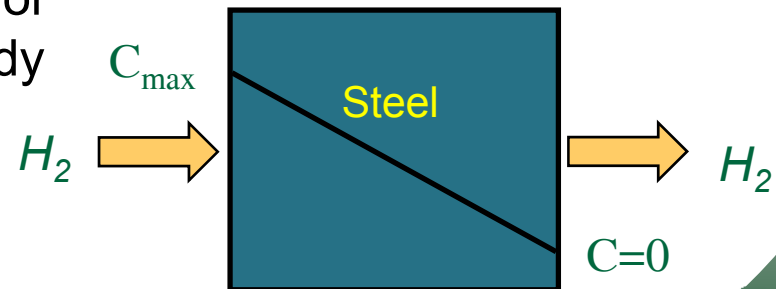
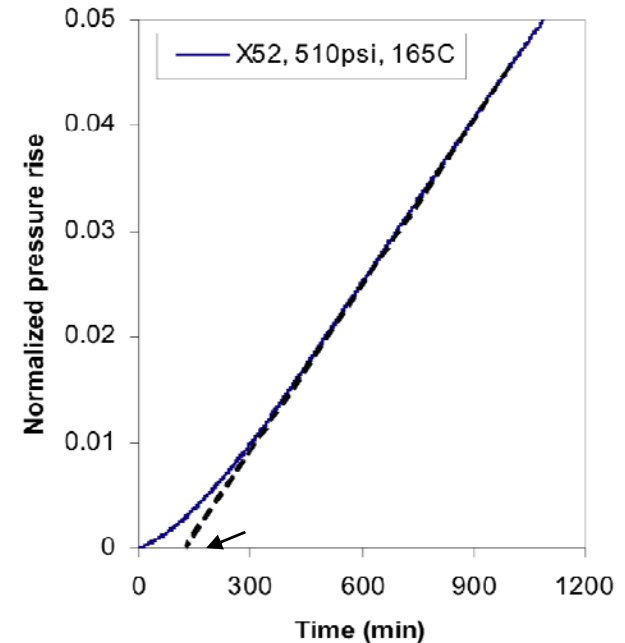
- In order to determine hydrogen diffusion in bulk metal, the surface processes must be controlled and their influence on the kinetics (rate of permeation) must be minimized or separated

- If  $J_{\text{surface}} \ll J_{\text{bulk}}$  (i.e. rate at surface dominate), then  $J_{\text{measure}} = J_{\text{surface}}$  and diffusivity of metal cannot be determined reliably

- Once the bulk diffusivity is understood, separate tests can be performed to specifically study the surface effects on hydrogen transport in metal.

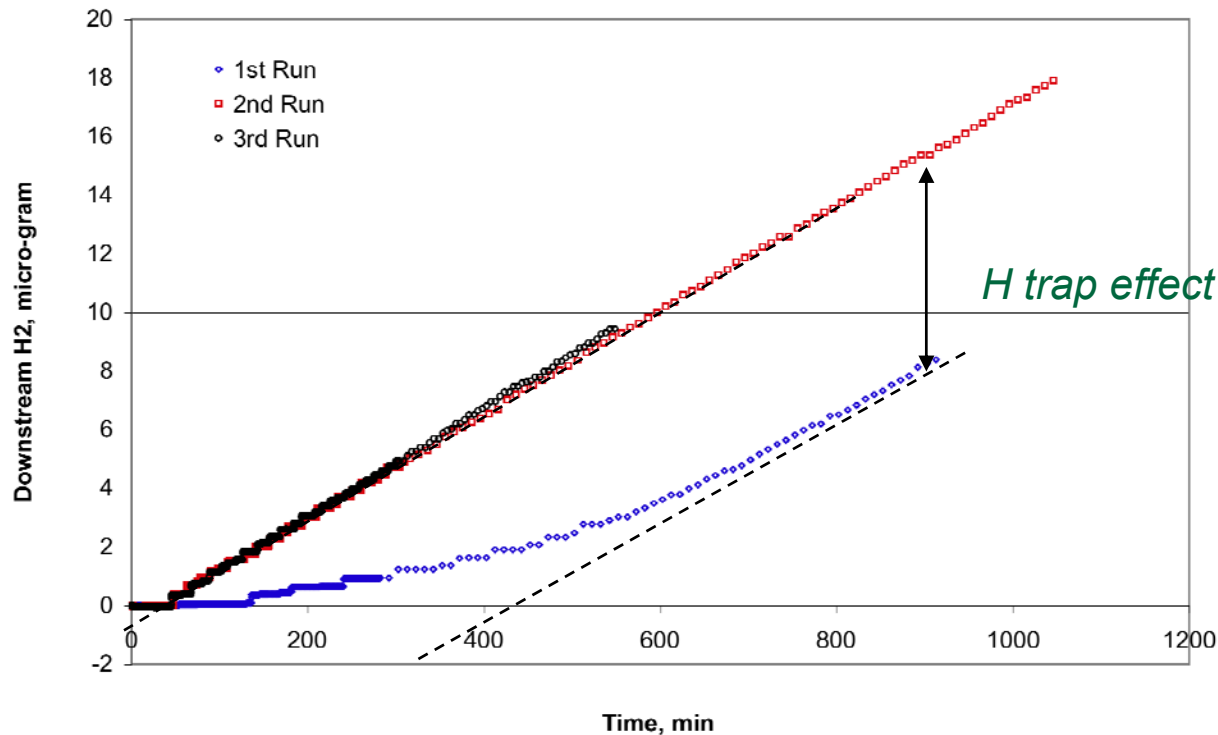
# Determination of “Effective” Diffusivity and Solubility from Permeation Test

- Basic assumptions:
  - Diffusivity is independent of H concentration
  - Surface processes are so fast that the permeation rate is control by the bulk diffusion process in metal
- “Effective” diffusivity is determined from the accumulated pressure vs time curve using the asymptotic slope method
- Atomic hydrogen concentration on the upstream surface (max concentration or solubility) is determined from the steady state permeation rate and diffusivity:



# Permeation Curves of Pipeline Steel A106 Grade B (Coarse Grain Heat Affected Zone)

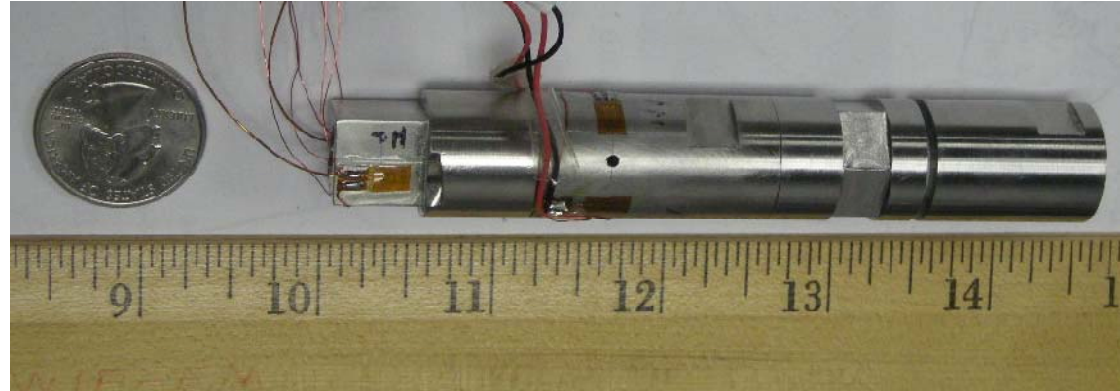
- Multiple runs on one sample at 300psi H<sub>2</sub> and 150°C reveals the effect of hydrogen trapping on diffusion
- Hydrogen traps contributes to the differences between 1st and 2nd runs
  - Can be used to estimate the trapped hydrogen concentration
- Nearly identical 2nd and 3rd runs indicate high repeatability of measurement
- Same permeability at steady-state



# Weld Hydrogen Embrittlement Test Device



**Pressure vessel and instrumentation for HE test**



**Miniature self-loading device**



**Miniature notch tensile specimen**