DOE Hydrogen Program

H_2 Permeability and Integrity of Steel Welds

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PDP 35

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Oak Ridge National Laboratory

Overview

Timeline

- Start – March 2004
- Finish – September 2010
- 30% Complete

Budget

- Total Project Funding
  - DOE share: $815,000
  - Contractor share: N/A
- Funding received in FY07:
  - $350,000
- Funding for FY08: $300,000

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 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_2 pipelines; &
- Develop welding/joining technology to safely and cost-effectively construct new pipelines and/or retrofit existing pipelines for hydrogen delivery.

Milestones

- High-pressure hydrogen permeation measurement system development and verification, June 2007 (complete)
- Baseline high-pressure hydrogen diffusion and permeation measurement with pure Iron, September 2007 (complete)
- Baseline study on friction stir welding of pipeline steels, December, 2007 (complete)
- Effect of weld microstructure on hydrogen trapping, diffusion and permeation, June 2008
- Initial study on weld mechanical property degradation, September 2008

Approach

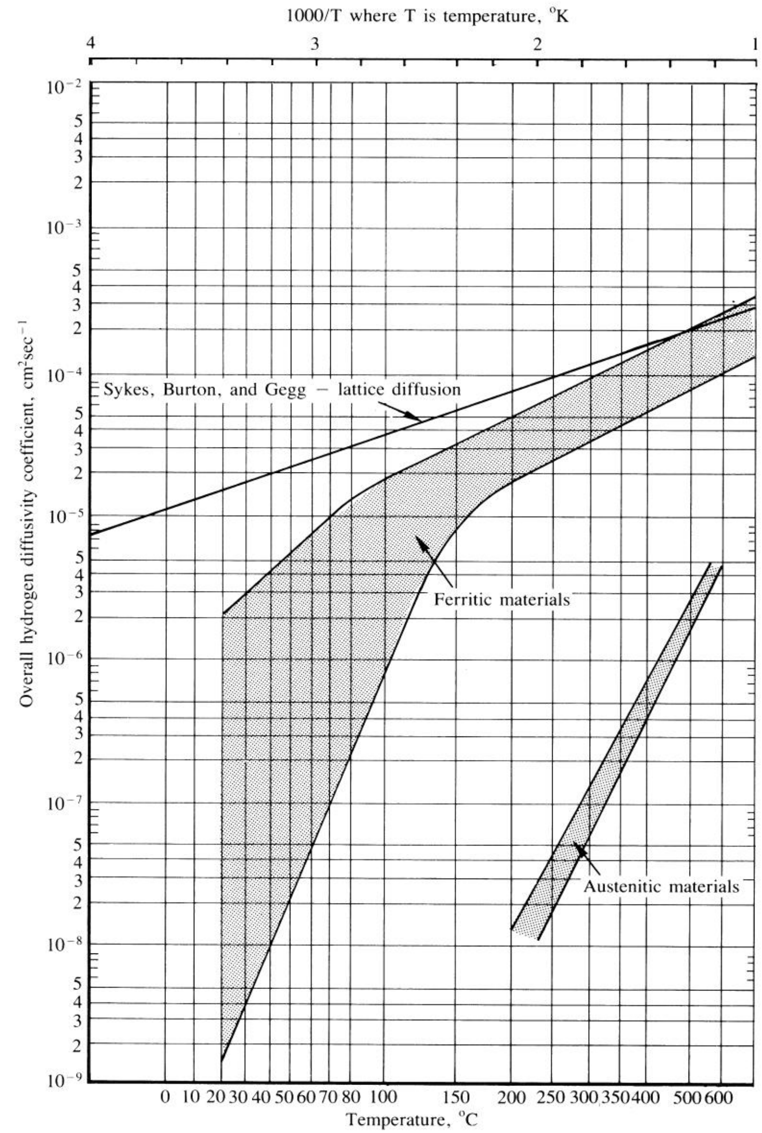
- Understand hydrogen transport behavior in steels and weld region
  - High pressure (up to 5,000 psi) hydrogen permeation and diffusion measurement and modeling
  - Effect of steel composition and microstructure
  - Effect of surface conditions
- Determine mechanical property degradation in weld region
  - 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

Hydrogen Permeation & Diffusion Study

- To understand the hydrogen transport behavior
  - Hydrogen absorption/surface effect
    - Influences amount and rate of hydrogen entering steel
  - Hydrogen diffusion
    - Influences crack propagation rate - the kinetics
  - 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_2
  - 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

Hydrogen Diffusivity Data in Literature

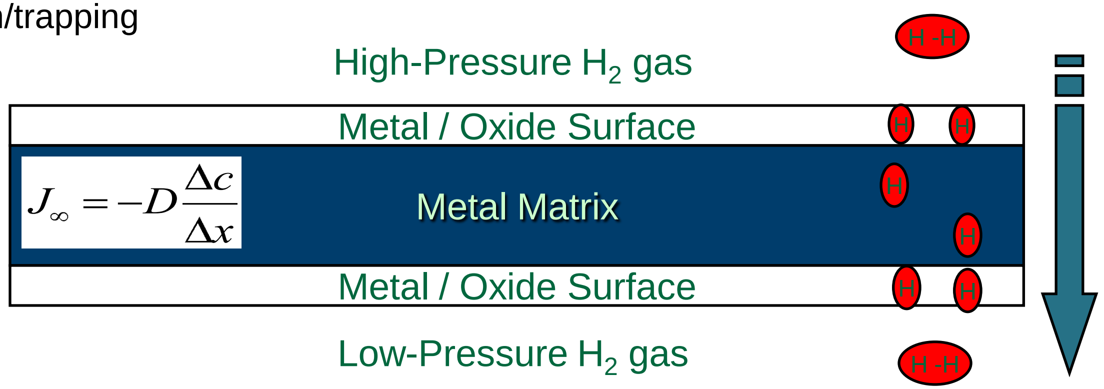
- Extensive data available from electrochemical charging at low gaseous pressure (< 1atm), mostly under “controlled” laboratory surface conditions
  - Clean, polished surface
  - Surface coating (Pd) to eliminate surface effects
- Very limited data for high-pressure gaseous hydrogen in “real-world” pipeline 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

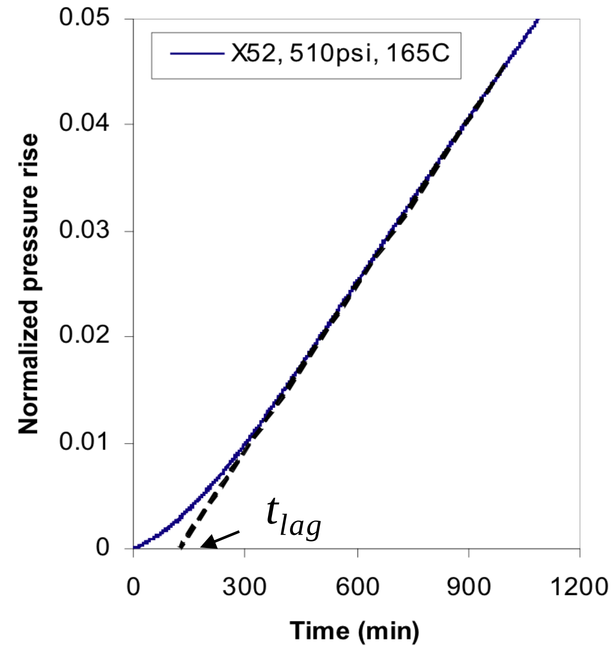


- In order to determine hydrogen diffusion in bulk metal, the surface processes must be controlled and their influence on the kinetics (rate of permeation) must be minimized or separated
  - If $J_{surface} << J_{bulk}$ (i.e. rate at surface dominate), then $J_{measure} = J_{surface}$ and diffusivity of metal cannot be determined reliably
- *<u>Once the bulk diffusivity is understood</u>*, 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

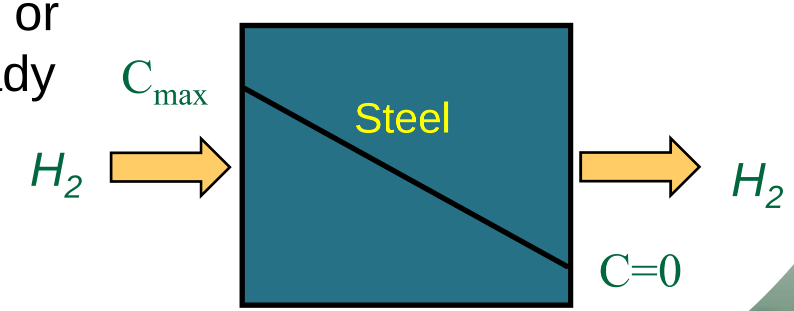
- Basic assumptions:
  - Diffusivity is independent of H concentration
  - Surface processes are so fast that the permeation rate is control by the bulk diffusion process in metal
- "Effective" diffusivity is determined from the accumulated pressure vs time curve using the asymptotic slope method

$$D_{eff} = l^2 / 6t_{lag}$$



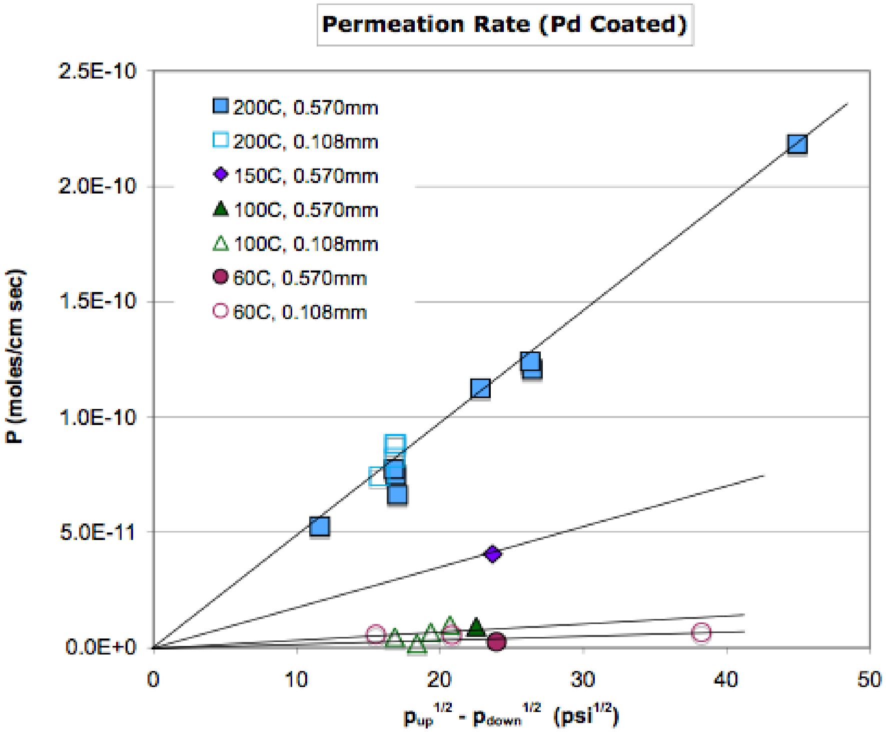
- Atomic hydrogen concentration on the upstream surface (max concentration or solubility) is determined from the steady state permeation rate and diffusivity:

$$C_{\max} = J_{ss} \frac{l}{D_{eff}}$$



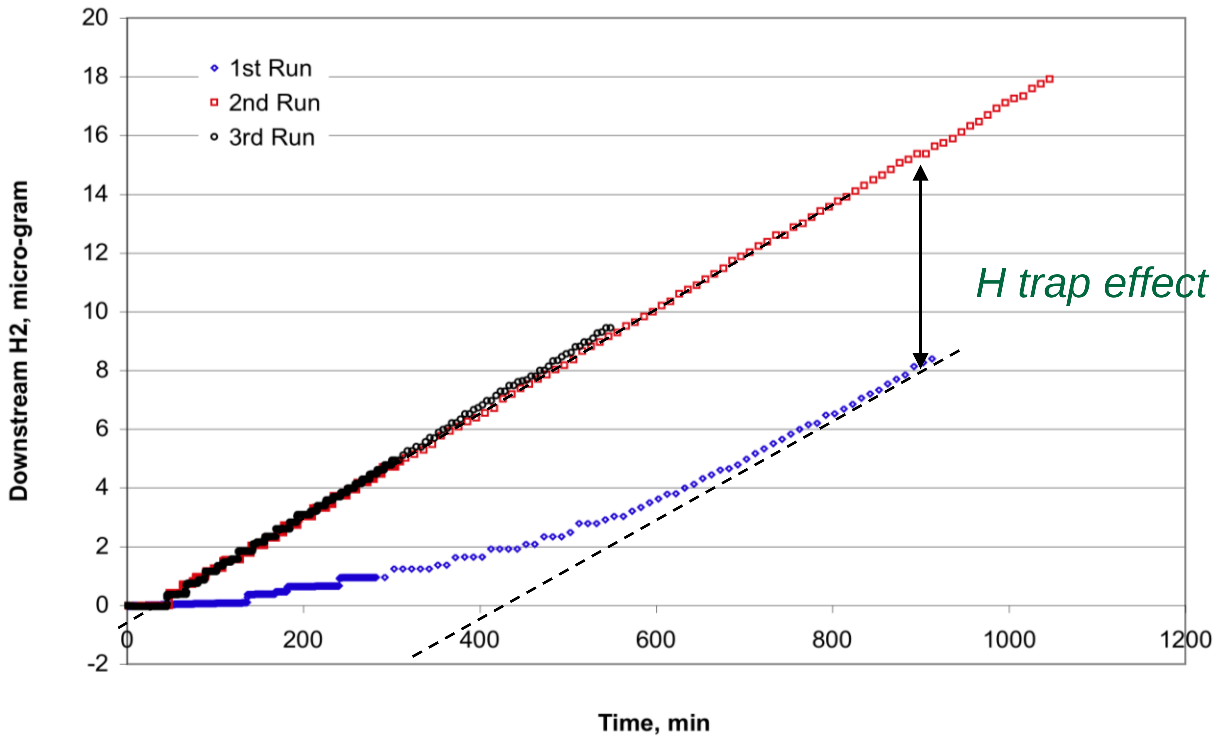
Fe is a “clean” material to develop baseline information for pipeline steel

- Well annealed pure iron minimizes hydrogen trap effect
- Verification of testing and data analysis procedure
- Key findings
  - Surface coating with Pd (20nm thick) is necessary
    - Eliminate or reduce the surface effect for meaningful diffusivity measurement
    - Resulted in repeatable consistent measurement
  - Temperature and pressure effects were determined
    - Solubility increases as charging pressure increases
    - Permeation rate shows square-root dependency on pressure
- High-pressure H2 permeation measurement system was verified



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

- Multiple runs on one sample at 300psi H_2 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



Effective Diffusivity and Concentration of H in A106 HAZ – Effects of Temperature and Hydrogen Traps

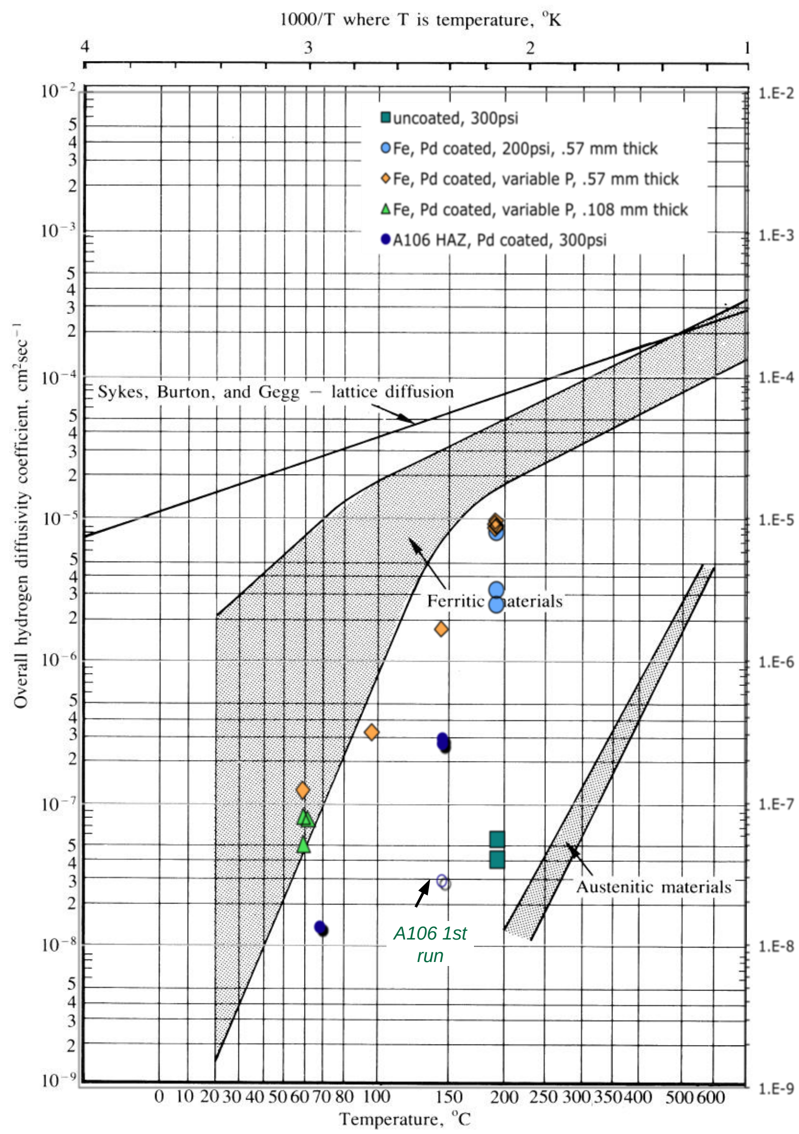
Sample condition	**Temp** (C)	**Pres** (psi)	D_{eff} (cm^2/sec)	**Cmax*** (ppm, mg/kg)	**Cmax** (mol-H/m^3)	**Solubility** (mol/m^3/$Pa^{1/2}$)
1st run	150	300	2.85×10^{-8}	N/A**		
2nd run	150	300	2.60×10^{-7}	19.8	155.5	0.108
3rd run	150	300	2.81×10^{-7}	19.0	149.2	0.103
4th run	70	300	1.34×10^{-8}	10.5	82.5	0.057

* Cmax is the H concentration at the upstream surface
** Solubility can't calculated due to effect of trap on D

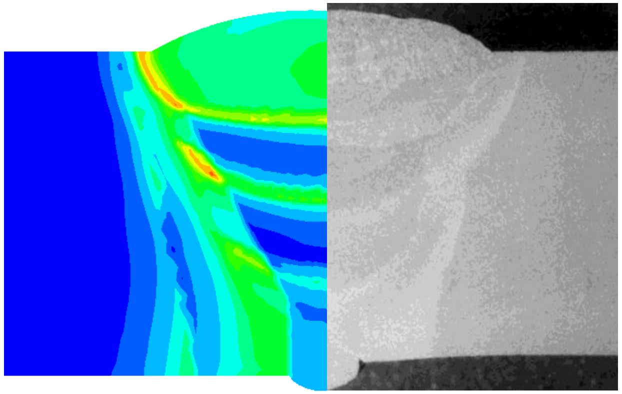
Estimate of trapped hydrogen concentration @150°C: 26.6ppm

Comparison with Literature Data

- Generally at the low end of literature data
- Surface condition has great influence
- Unfilled hydrogen traps reduce effective diffusivity



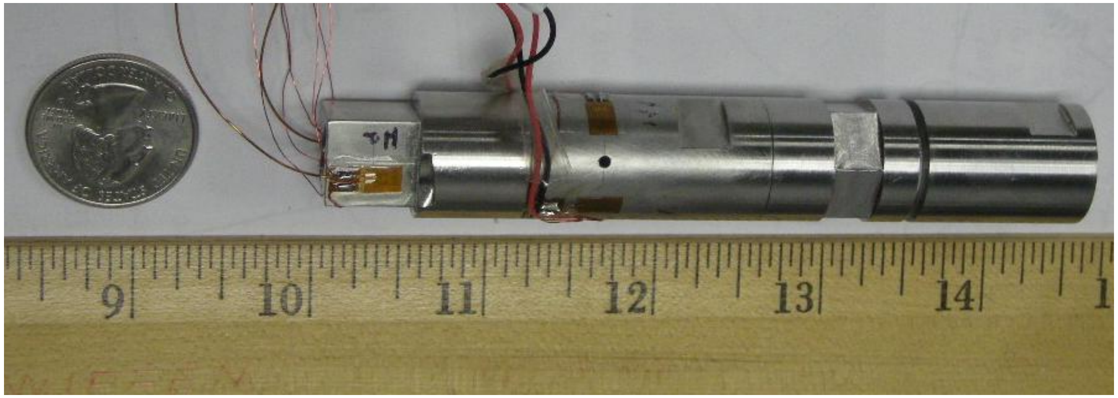
Mechanical Testing of Weld Hydrogen Embrittlement



- 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 being 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
- Features of test methods
  - Miniature specimen geometry
  - Miniature self-loading rig (sustained load) inside the autoclave
  - Continuous load monitoring (strain gage based with temperature and H2 pressure self compensation)
  - 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

Weld Hydrogen Embrittlement Test Device

Pressure vessel and instrumentation for HE test

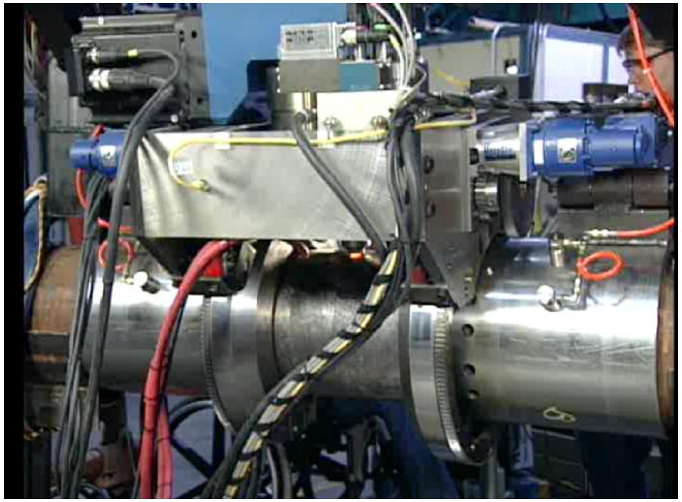


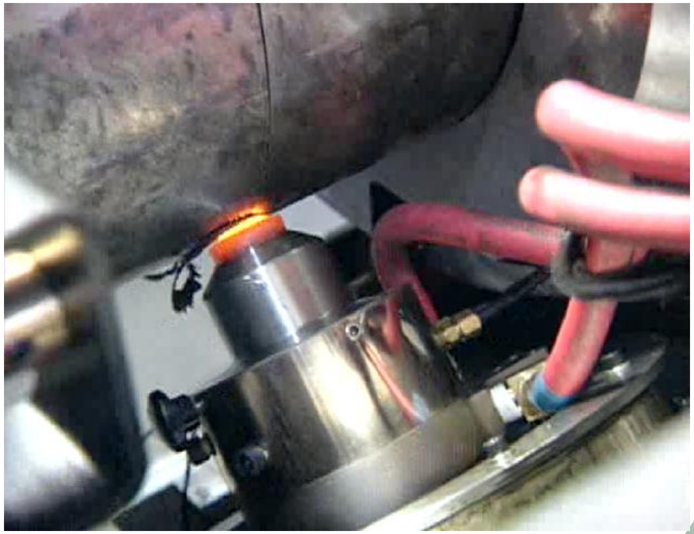
Miniature self-loading device

Miniature notch tensile specimen

Welding Technology Development: Friction stir welding

- A solid-state joining process, no melting
- No solidification casting-like microstructure
- Extensive thermomechanical deformation during FSW results in wrought weld microstructure with improve properties
  - Conventional fusion welds have cast microstructure
- No need for filler metal
  - Eliminate the weld mismatch issues for high strength steels
- Eliminate/reduce the coarse grain HAZ (the hard spot) that is generally associated with HE in steel welds

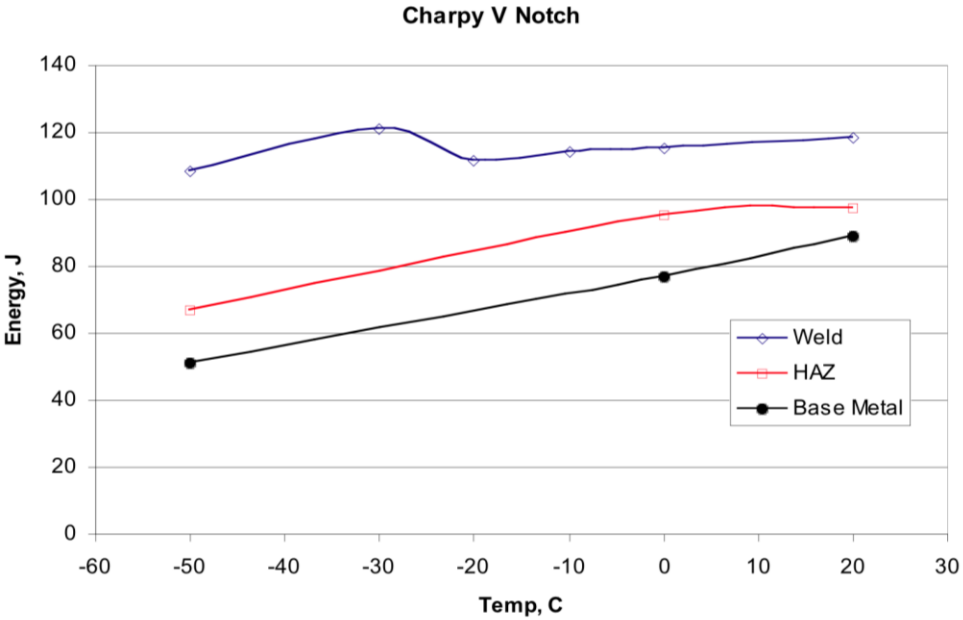




Prototype FSW system for pipeline welding by MegaStir

Superior Weld Impact Toughness by FSW

API 5L grade X-65 steel tested *in air.*
(Properties in hydrogen service to be tested)



ERW Line Pipe

OD: 12.75”, 0.25” t

Base metal properties per mill specification:

Sys: 67 ksi, Sult: 77 ksi, Elongation: 33%

Future Work

- Permeation/Diffusion (FY2008)
  - 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 (FY2009)
  - 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 (FY2010)
  - Friction stir welding
  - Other means for weld residual stress and microstructure management
  - Cost-effective hydrogen management

Summary

- Project Focus: Integrity of weldment in steel hydrogen delivery pipeline infrastructure
  - Weld region is generally more vulnerable to hydrogen induced property degradation
  - Development of testing methods suitable for weld property measurement with the complex microstructure and property gradients
  - Development of welding technologies for weld microstructure improvement, residual stress control and hydrogen mitigation
- Goal: improve tolerance to HE in steel weldment and reduce construction and retrofitting cost associated with welding
- Close interactions with other related projects on pipeline steel development and material property testing