Permeation, Diffusion, Solubility Measurements: Results and Issues

**ORNL:** Zhili Feng and Lawrence M. Anovitz

**SRNL:** Paul Kironko, Andy Duncan and Thad Adams

**UIUC:** Petros Sofronis

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Presentation Outline

- Project Objectives
- ORNL Activities
- SRNL Activities
- UIUC Activities
- Plan for FY08 and future
- Conclusion
Research Objectives

- To understand the hydrogen transport behavior
  - How does gaseous hydrogen enter material (absorption)?
  - How fast does hydrogen move inside material (diffusion)?
  - How much hydrogen is there in material (solubility)?

- Under conditions relevant to hydrogen delivery infrastructure
  - Gaseous hydrogen: composition and purity level
  - Pressure range: up to 10,000psi H₂
  - Temperature range: -40 to 150°C
  - Service life: 50 years and beyond
  - Material
    - Pipeline steels and their weld
    - Polymer/composite pipeline
  - Surface condition
    - Naturally formed surface oxide layer
    - Surface coating/modification
    - Others
  - Others
Needs for Hydrogen Transport R&D

- Steel pipeline infrastructure
  - Mechanical property degradation due to hydrogen embrittlement

- Polymer/composite pipeline infrastructure
  - Permeation rate/leak resistance
Degradation of Fracture Toughness as Function of H₂ Pressure

Pressure Vessel Steels

- AISI 4145 ($\sigma_{YS}=670$ MPa)
- AISI 4147 ($\sigma_{YS}=725$ MPa)

Loginow and Phelps, *Corrosion*, 1975

- SA 372 Grade J
  - $\sigma_{YS}=715$ MPa

- A-286
  - $\sigma_{YS}=780$ MPa
  - *Perra, 1981*

Somerday et al., *Proc. Enerav Development E*

$K_{TH}$ (MPa$\sqrt{m}$)

$H_2$ gas pressure (MPa)

3000psi
Hydrogen Embrittlement

- The degree of HE depends on hydrogen pressure (hydrogen concentration) for many metallic materials (including high-strength steels).

- Successful application of steels for hydrogen storage relies on systematic engineering design so that the system operates under the threshold with a safety margin
  - Need to quantify the degree of mechanical property degradation as function of hydrogen pressure (concentration), microstructure and temperature
So We Need to Learn the Following from Hydrogen Transport Study

- Hydrogen solubility/concentration in steel
  - Influences the degree of mechanical property degradation

- Hydrogen diffusivity
  - Influences crack propagation rate - the kinetics

- Hydrogen absorption/surface effect
  - Influences amount and rate of hydrogen entering steel

- Hydrogen transport knowledge will be needed for
  - Safe operation of hydrogen pipeline infrastructure
  - Laboratory mechanical property testing
Prior R&D on Hydrogen Transport

- Abundant data under electrochemical charging and at low pressure (< 1 atm)
- Very limited data exists for high-pressure gaseous hydrogen in “real-world” pipeline environment
  - Surface absorption kinetics
  - Diffusivity
  - Solubility
  - Others
How do We Study Hydrogen Transport Behavior?

- Primary method
  - Hydrogen gas permeation experiment

- Other techniques
  - Hydrogen traps: thermal desorption spectroscopy
  - Diffusible hydrogen concentration
    - Gas chromatography
    - Fluid displacement methods (glycerin, silicon oil, mercury)
  - Total hydrogen concentration:
    - Thermal extraction
    - Gas chromatography

- Microstructure characterization

- Surface analysis

- Isotopic exchange with depth profiling
Permeation Test Principle

- Gaseous hydrogen on the upstream side (charging side) is maintained at predetermined pressure
- Hydrogen atoms/protons diffuse through the test sample, and are collected in the downstream side to determine the permeation rate
- Determination of hydrogen permeated through the sample
  - Record $\text{H}_2$ pressure increase in a constant volume chamber recorded as function of time (ORNL)
  - Ion pump and gas chromatography (SRNL, UIUC)
What really happens in a permeation test

- Involves several major steps
  - 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.
Permeability

- Permeability: the rate of hydrogen flux passing through the material

\[ J = P \frac{\sqrt{\Delta p_{H_2}}}{l} \]

- In this study, permeability is determined after the flux reaches steady-state

\[ P = J_{ss} \frac{l}{\sqrt{\Delta p_{H_2}}} \left( \frac{\text{mole}}{cm \text{ sec} \ psi^{1/2}} \right) \]
Determination of “Effective” Diffusivity and Solubility from Permeation Test

- ASTM G148-97 (for electrochemical charging)
- Basic assumptions:
  - Diffusivity is independent of H concentration
  - Surface processes are so fast that the permeation rate is controlled by the bulk diffusion process in metal
- “Effective” diffusivity is determined from the accumulated pressure vs time curve using the asymptotic slope method
  \[ D_{eff} = \frac{l^2}{6t_{lag}} \]
- Atomic hydrogen concentration on the upstream surface (max concentration or solubility) is determined from the steady state permeation rate and diffusivity:
  \[ C_{max} = J_{ss} \frac{l}{D_{eff}} \]
  \[ J_{ss} = D_{eff} \frac{C_{max} - C_0}{l} \]
Effect of Hydrogen Traps on Permeation Measurement (ATMS G148-97)

**NOTE** 1—Rising permeation transients for BS 970 410S21 stainless steel in acidified NaCl at 77°C. Results show irreversible trapping (1st transient) and dependency on charging conditions (C₀ value). Note the time of delay and steepening of the curves relative to lattice diffusion (Fick's law), the similarity of second and third transients and the independence of thickness.

**FIG. 3** Permeation Transients
Diffusivity Data in the Open Literature

- High temperature (>100°C):
  - Low pressure (<1 atm) gas permeation measurement
- Low temperature (<100°C):
  - Low pressure gas permeation
  - Electrochemical charging permeation
  - Permeation from acid
- Mostly under “controlled” laboratory surface conditions
  - Clean, polished surface
  - Surface coating (Pd) to eliminate surface effects (per ASTM G148)
- Hydrogen will permeate through pipeline steel during long-term (>20 years) service
Hydrogen Diffusivity of Micro-Alloyed Steels and Low-Carbon Steels

Fig. 13. Scatterband for hydrogen diffusion coefficients in micro-alloyed and low carbon structural steels
ORNL Progress and Status

- High-pressure hydrogen permeation test
  - System upgrade
  - System verification test with Pd
    - Confirm high-pressure hydrogen permeation measurement system and testing procedure
  - Baseline permeation tests with pure Iron
    - Test procedure development
    - Temperature effect
    - Pressure effect
    - Surface effect
    - Data reduction procedure
  - Permeation measurement for polymers
  - Interactions with other permeation test groups
System Upgrade

- Improved temperature control below 300°C
  - Low temperature control was essential for HE in steel and polymer composites
  - Verified long-term stability/accuracy: 0.2-0.3°C

- Improvement on low pressure measurement sensitivity and accuracy to 0.1 torr (0.002psi)
  - Essential for detection of break-through time and determination of diffusivity
System Verification: Palladium

- Diffusion data for palladium are fast and relatively consistent (Alefeld & Volkl, 1978 p324)
- A good system test - do our data agree?
Caveats

- Lower temperature palladium experiments measured permeability and calculated diffusivity from published PCT (solubility) data.

- Data are corrected from measured (Fickian) diffusion coefficients to (Einstein) diffusion coefficients that correct for variable concentration as a function of pressure and temperature, and a ‘site-blocking’ factor

- Many of the data sets were measured at low-pressure conditions - P dependence not evaluated
Permeation Data

- Our data at 10 and 35°C agree well with published results
- Samples annealed at 850°C for 90min
- Multiple runs very consistent
**Diffusion Data**

- Our measured $D$ values ($P \sim 23$ bars) are similar to, but a bit faster than the uncorrected Hamilton and Swansinger (1994) data ($P \sim 1200$ torr).
- $D$ values calculated from $P$ and measured (T extrapolated) solubility data also agree with corrected literature values and are very consistent.
- Suggests PCT dependence to $D$. 
Conclusions from Palladium Test

- High-pressure permeation system works - replicates literature data
Baseline Measurement with Pure Iron

- A “clean” material to develop baseline information for pipeline steel
  - Well annealed pure iron minimizes hydrogen trap effect
  - Further develop testing and data analysis procedure
  - Study surface effect (alloy system dependent)

- Sample preparation
  - 99.995% pure, 0.25 to 2 mm thick
  - Annealed at 1000°C for 2 hrs before testing
  - Hydrogen purity: 99.9995% (research grade)
Pure Iron with Bare, Clean Surface

- Sample surfaces were mechanically ground and acetone cleaned
- Tested at 200°C to reduce trapping effects
- Pressure: 330psi
- Diffusivity is three orders of magnitude too low
- Permeability is also low
- Suggest surface effect dominating
Pure Iron with Pd Coating

- 20 nm Pd coating on both sides
Temperature Dependency (Pd Coated Pure Iron)
Pressure Dependency (Pd Coated Pure Iron)

- Solubility increases as charging pressure increases
- Permeation rate has square root dependency on pressure, at given temperature
Pressure Dependency of Diffusivity (Pd Coated Pure Iron) (@200C)
Effect of Sample Thickness

- Pd coating may not completely eliminate surface effects
- Refined data reduction procedure is being worked to separate bulk diffusion from surface effect
Summary of ORNL Task

- High-pressure measurement system has been verified
- Measurements on pure iron provide baseline data to study steels and welds
- More rigorous data reduction procedure is being developed
- Complete measurements on pure iron and then move to steels
SRNL Progress and Status
SRNL Weld/HAZ Permeation & Embrittlement

Introduction

- Main Project Focus to Determine the Relationship Between Hydrogen Transport -- Permeation Diffusivity, Solubility in Weld/HAZ Microstructures in Steel Pipeline Materials and the Link to Susceptibility to Hydrogen Embrittlement

- Collaborations with ORNL, EWI, and Praxair in FY07
  - Samples from Welded Pipe Sections
    - Permeation Measurements at Pressures up to 700Torr and Temperature to 200°C
  - GLEEBLE Simulations of HAZ
    - Permeation Testing of Simulated Microstructures
SRNL Weld/HAZ Permeation & Embrittlement Progress

- Received Welded Pipe Materials—Praxair—API 5L Grade B/A106 Grade B—SMAW Girth Weld w/ TIG Root Pass
- Sectioned Weld and Identified Base, HAZ, and Weld Regions
  - Harvested Permeation Disk Samples from Three Regions
  - Approx. 0.030” thickness
- Low Pressure Permeation Testing in SRNL
  - E-beam Weld into 2 1/8” Flange
  - Pressure up to 700Torr
  - Temperature up to 200°C
- Measure Hydrogen Permeability and Diffusivity
- Solubility Determined from Permeation Test Data
SRNL Weld/HAZ Permeation & Embrittlement Progress

- Simulations of Weld HAZ Microstructures
  - Collaborated with EWI on Weld Simulations Modeling to Develop Input for GLEEBLE Thermal Simulation
    - V-Groove Joint Design
    - TIG Root Pass
    - Multi-Pass SMAW Fill

- Designed GLEEBLE Samples from A106 Grade B Pipe Stock for Thermal Treatment
  - 0.375” Diameter Cylinders Harvested from Pipe Wall
  - GLEEBLE Control Software Program Developed
  - GLEEBLE Treatments Initiated
SRNL Weld/HAZ Permeation & Embrittlement Progress

- Questions Concerning Low-Pressure H2 Permeability Measurements
  - SRNL Conducted Previous Studies of 304L SS Alloy
- SRNL Data in Comparison to Previously Published Literature Shows Good Agreement
- Agreement Between Published Data and Collected Data Demonstrates feasibility of using Low Pressure Permeation Measurements
- Testing Conducted at 700T H2 Pressure @ 150°C, 175°C, and 200°C

**Diffusivity and Permeation**

**Proofing SRNL System & Test Methodology**
SRNL Weld/HAZ Permeation & Embrittlement Progress

- Permeability Measurements of HAZ—700T @150, 175, and 200°C
- SNL Technical Reference on Carbon Steels Provides an Expression for Permeability (Φ) for Several CS Alloys (normalized, spherodized, and Q&T)—SRNL HAZ Data Compared to 1020 Alloy
  - Φ = 3.77E-05 exp (-35.07/RT)
- SRNL Measured Permeability Data for A106 Grade B.—C-content =0.185
  - 150°C =3.92 E-10 mol/m s MPa^{1/2}
  - 175°C= 3.23 E-10 mol/m s MPa^{1/2}
  - 200°C= 2.87 E-10 mol/m s MPa^{1/2}
SRNL Weld/HAZ Permeation & Embrittlement Progress

- Diffusivity Determined from Permeation Tests of HAZ—700T @150, 175, and 200°C

- SNL Technical Reference on Carbon Steels Provides an Expression for Permeability ($\Phi$) and Solubility ($S$) for Several CS Alloys (normalized, spheroidized, and Q&T)—SRNL HAZ Data Compared to 1020 Alloy
  - $D = \Phi S$—Plot Data Calculated Using SNL Tech Reference

- SRNL Measured Diffusivity Data for A106 Grade B.—C-content =0.185
  - 150°C =1.34 E-11 m²/s
  - 175°C= 2.36 E-10 m²/s
  - 200°C= 7.87E-11 m²/s
- Solubility Determined from Permeation Tests of HAZ—700T @150, 175, and 200°C
- SNL Technical Reference on Carbon Steels Provides an Expression for Solubility (S) for Several CS Alloys (normalized, spheroidized, and Q&T)—SRNL HAZ Data Compared to 1020 Alloy
  - \( S = 159 \exp \left( -23.54/RT \right) \)
- SRNL Calculated Solubility Data for A106 Grade B.—C-content =0.185
  - 150°C =29.25 mols/m³ MPa\(^{1/2}\)
  - 175°C= 1.36 mols/m³ MPa\(^{1/2}\)
  - 200°C= 3.64 mols/m³ MPa\(^{1/2}\)
SRNL Weld/HAZ Permeation & Embrittlement
Path Forward FY08

- **FY08 AOP Plan**
  - Closer Collaboration with ORNL, Univ. of Illinois Test Programs
  - Focus on Understanding Link Between HAZ Microstructure and Hydrogen Diffusivity/Solubility and Connection to Susceptibility to Hydrogen Embrittlement
  - Focus on HAZ Materials via GLEEBLE Simulation
    - HAZ Thermal Simulations
    - Microstructure Characterization
  - Permeation/Diffusivity/Solubility Measurements
  - Focus Testing on A106 Gr. B/X42 and X52 Alloys
  - SRNL to Prepare GLEEBLE Samples for Testing and to Provide Companion Samples to ORNL/Illinois for Low-Pressure vs High Pressure Comparisons
  - Initiate Basic Tensile Property Data of GLEEBLE HAZ Materials
    - ASTM G142—Notched/Unnotched Tensile
    - Demonstrate Increased Susceptibility in HAZ
Permeation Measurements at Illinois

- Currently conducting permeation tests with high purity iron to set the baseline. Permeation tests for C-Type steel microstructure (X60/70) from Oregon Steel Mills have been done.

- Materials analyzed
  - Oregon Steel Mills (A,B, C, D microstructures)
  - SECAT (sample with Schott North America coating on)
  - Pipelines in service
    - AirLequide pipeline
    - Air-Products pipeline
    - Kinder Morgan pipeline

- Coupling permeation measurements with finite element simulations to extract the trap density and binding energy
  - In conjunction with Thermal Desorption Spectroscopy
UIUC Permeation

- Hydrogen is introduced on one side of the sample
- Permeates through sample
- Detected by ion pump

- 4.75 cm disks
- 100 micron thickness
- Palladium coating on exit side
- Testing coatings on hydrogen side

Real-world pipeline specimens are in our possession for testing
Air Liquide and Air Products provided the coupons
UIUC Hydrogen Permeation Measurements: C-steel

Ultrahigh vacuum (10^{-9} \text{ torr})
Hydrogen pressure (10 \text{ torr})

\begin{align*}
J_{\infty} &= 6.26 \times 10^{12} \frac{H \text{ atoms}}{\sqrt{MPa \cdot m \cdot s}} \\
\int J \, dt &= 2.0 \times 10^{18} \text{ atoms/m}^2 \\
t_T &= 6.8 \text{s} \\
P &= 4.7 \text{torr} = 627 \text{Pa}
\end{align*}

\text{Sample}
Hydrogen Detector
Turbo pump

• Oregon Steel Mills sample: thickness 120 microns
• room temperature
Comparison of Data (ORNL, SRNL, UIUC)
FY08 Plan

- Close coordination among ORNL, SRNL and UIUC (ORNL lead)
  - Sample preparation procedure
  - Testing procedure
  - Data analysis and reduction procedure
  - Round-robin test on selected steels
  - Testing matrix (steels, welds, surface conditions)
- Focus on generating reliable data for pipeline steels and welds
  - Effect of microstructure
  - Effect of temperature
  - Effect of pressure
- ORNL:
  - High pressure permeation
- SRNL:
  - Low pressure permeation
- UIUC:
  - Modeling and hydrogen trap study
  - Low pressure permeation
Questions?