Permeation, Diffusion, Solubility Measurements: Results and Issues

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Presentation Outline

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

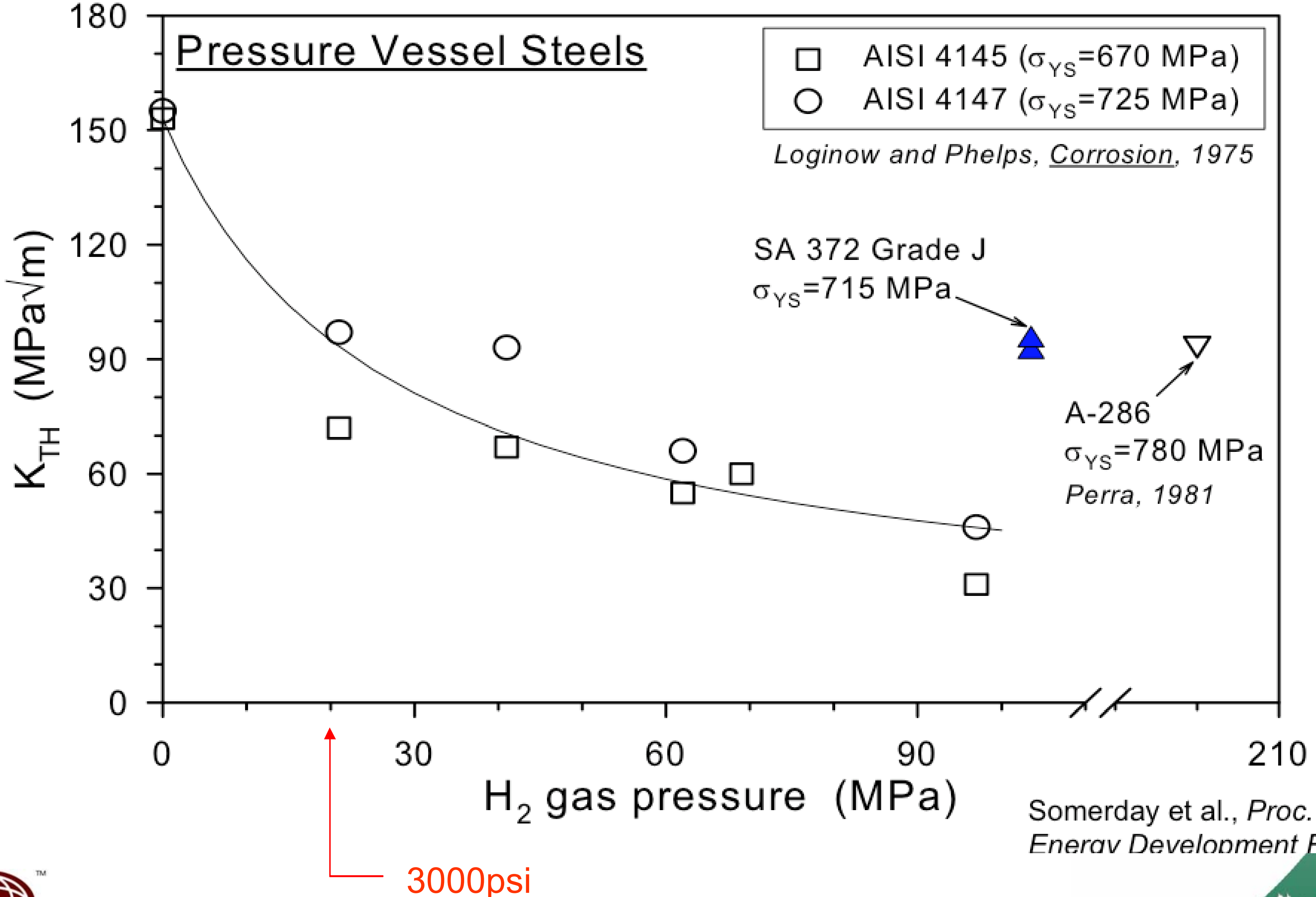
Research Objectives

- 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 H_2
  - Temperature range: -40 to 150C
  - 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 H_2 Pressure



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

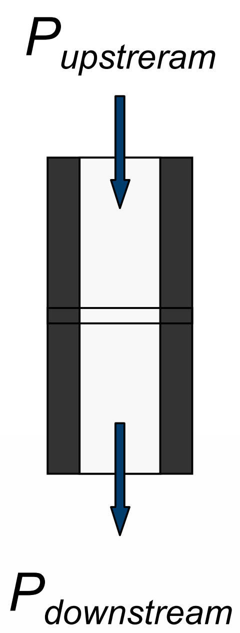
- Abundant data under electrochemical charging and at low pressure (< 1atm)
- Very limited data exists for high-pressure gaseous hydrogen in "real-world" pipeline environment
  - Surface absorption kinetics
  - Diffusivity
  - Solubility
  - Others

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**

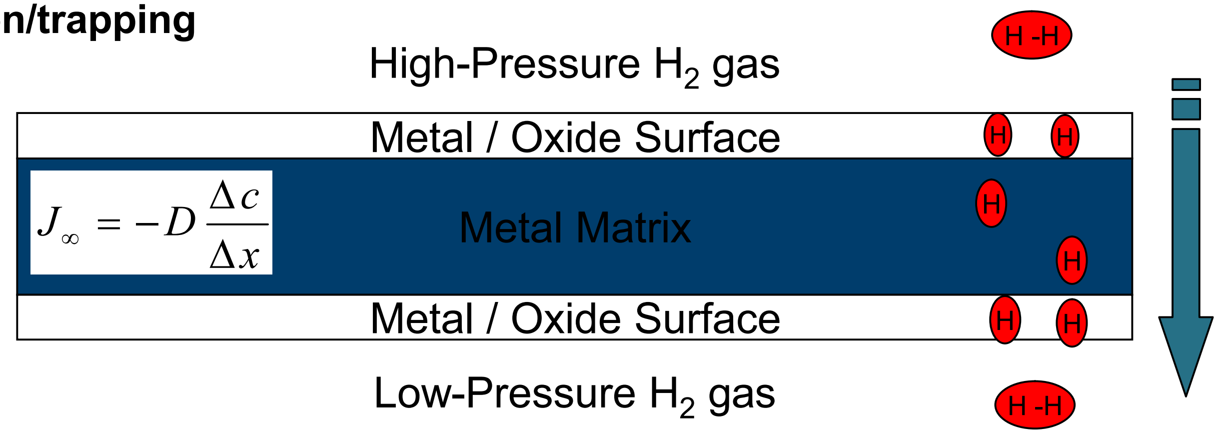
Permeation Test Principle

- Gaseous hydrogen on the upstream side (charging side) is maintained at pre-determined 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 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 $J_{surface} << J_{bulk}$ (i.e. rate at surface dominate), then $J_{measure} = J_{surface}$ 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**

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

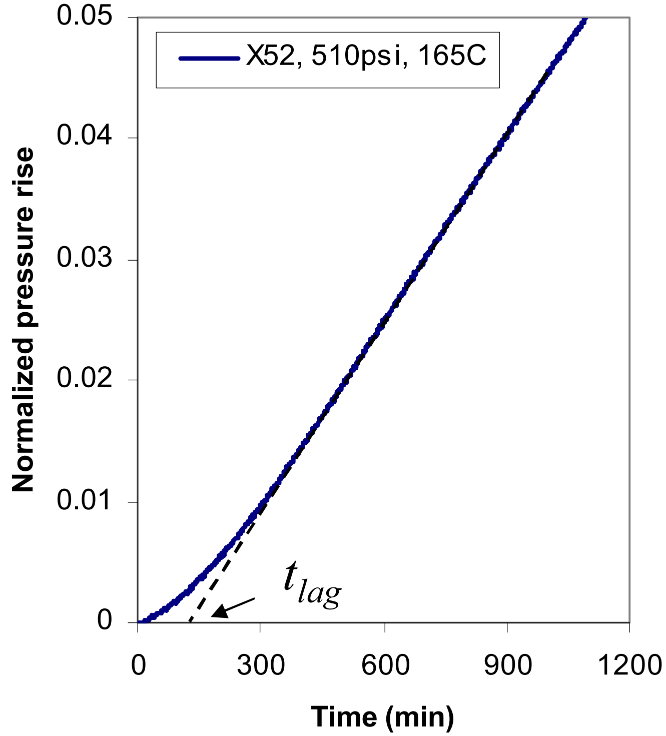
- **In this study, permeability is determined after the flux reaches steady-state**

$$P = J_{ss}\frac{l}{\sqrt{\Delta p_{H_2}}} \quad \left(\frac{mole}{cm\ \sec\ psi^{1/2}}\right)$$

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 control by the bulk diffusion process in metal**
- **"Effective" diffusivity is determined from the accumulated pressure vs time curve using the asymptotic slope method**

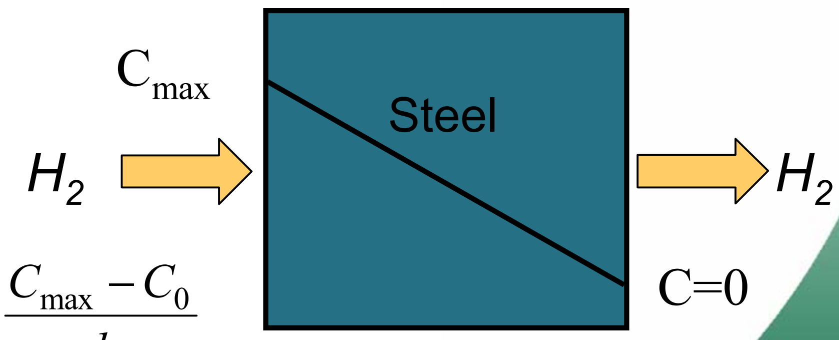
$$D_{eff} = l^2 / 6t_{lag}$$



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

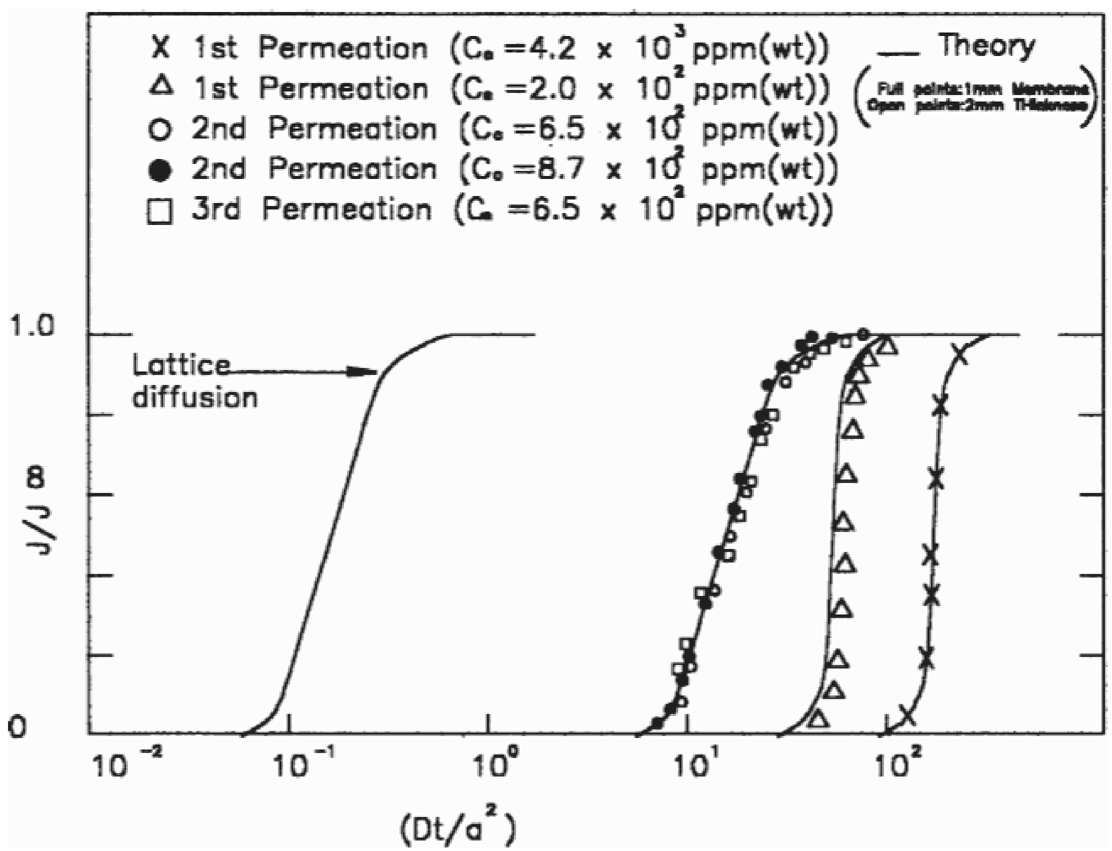
$$C_{max} = J_{ss} \frac{l}{D_{eff}}$$

$$J_{ss} = D_{eff} \frac{C_{max} - C_0}{l}$$



Effect of Hydrogen Traps on Permeation Measurement (ATMS G148-97)

G 148 – 97 (2003)



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 (C_0 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

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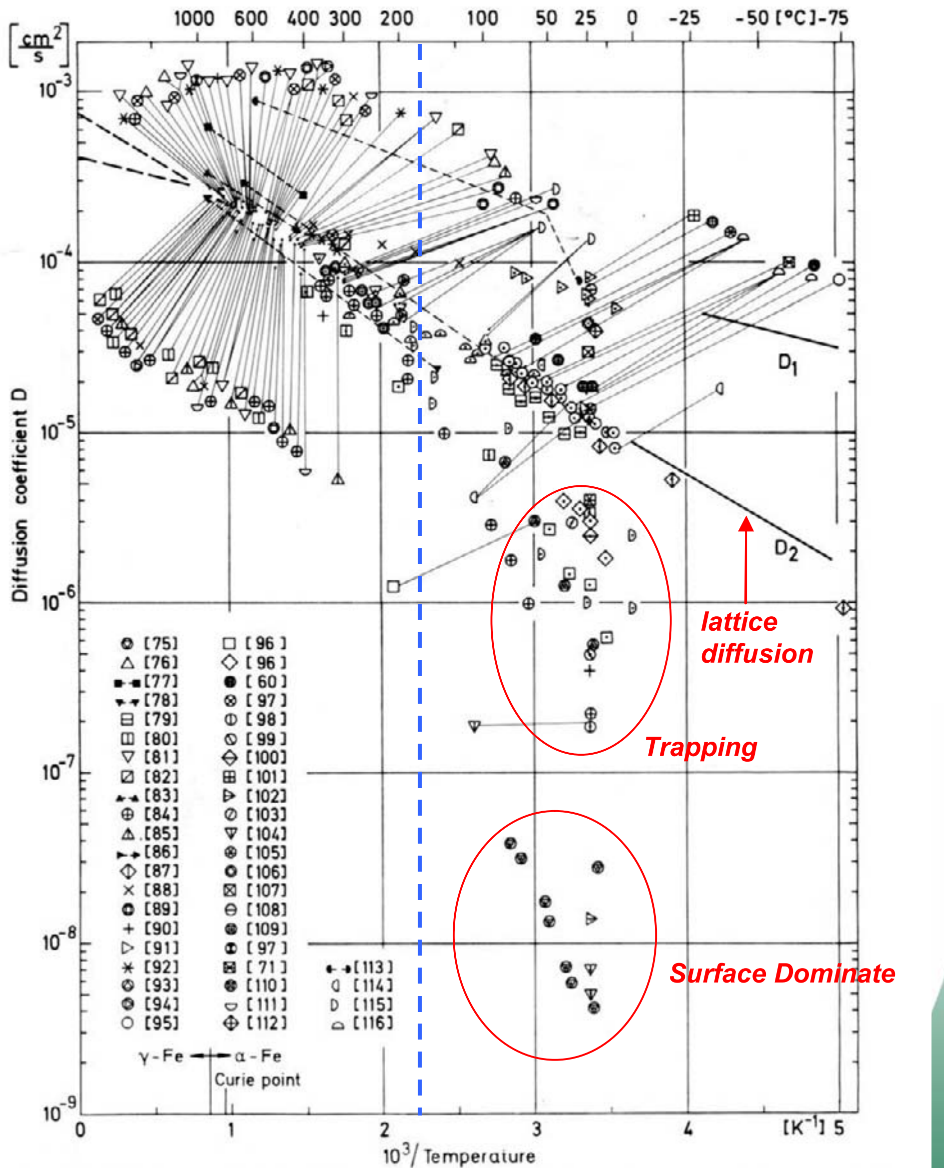
Diffusivity Data in the Open Literature

- **High temperature (>100C):**
  - low pressure (< 1atm) gas permeation measurement
- **Low temperature (<100C):**
  - 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**



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Hydrogen Diffusivity of Micro-Alloyed Steels and Low-Carbon Steels

(Boellinghaus et al., "A scatterband for hydrogen diffusion coefficients in micro-alloyed and low-carbon structure steels," Welding in the World, v35n2 83-96)

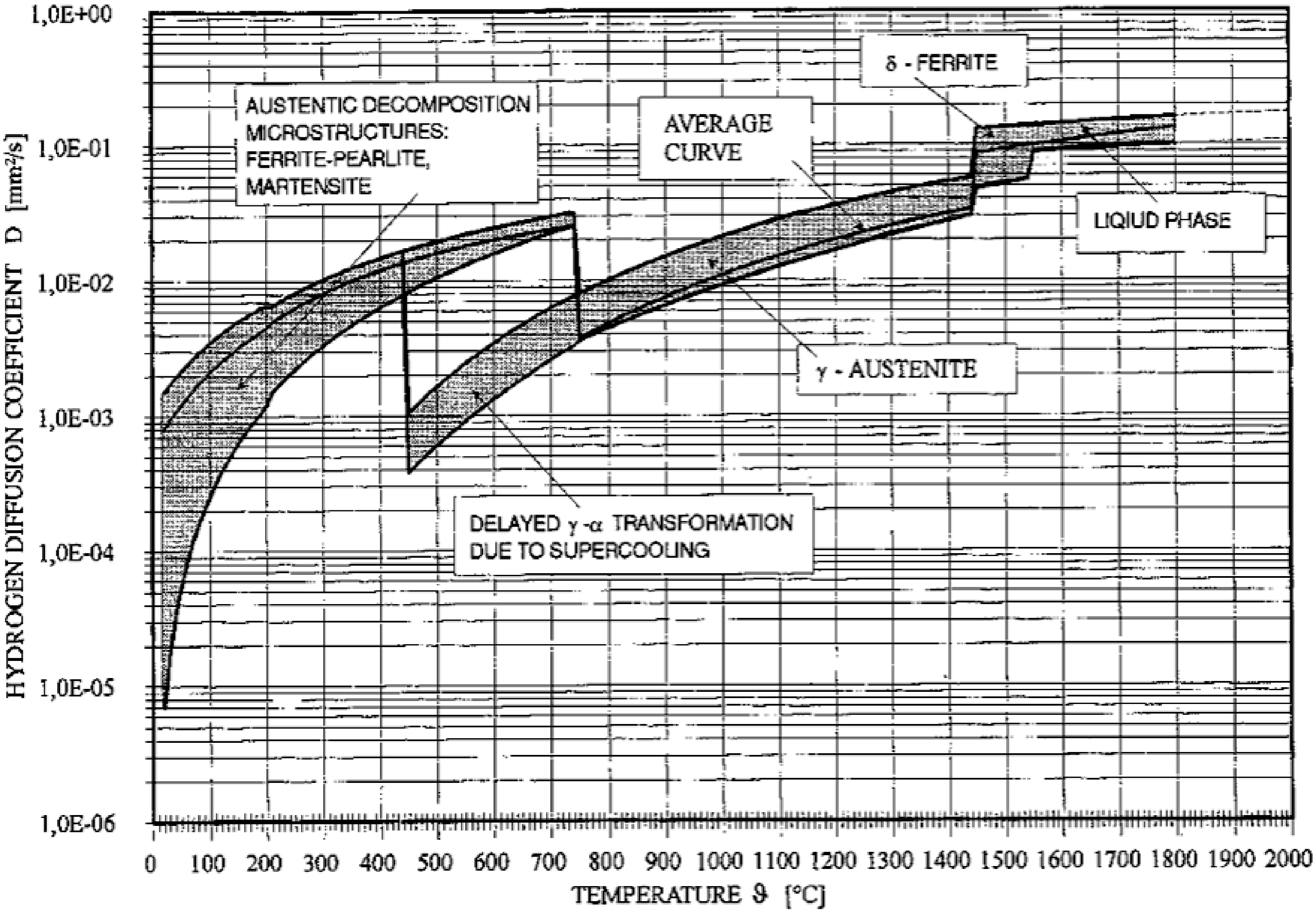

Fig. 13. Scatterband for hydrogen diffusion coefficients in micro-alloyed and low carbon structural steels

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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

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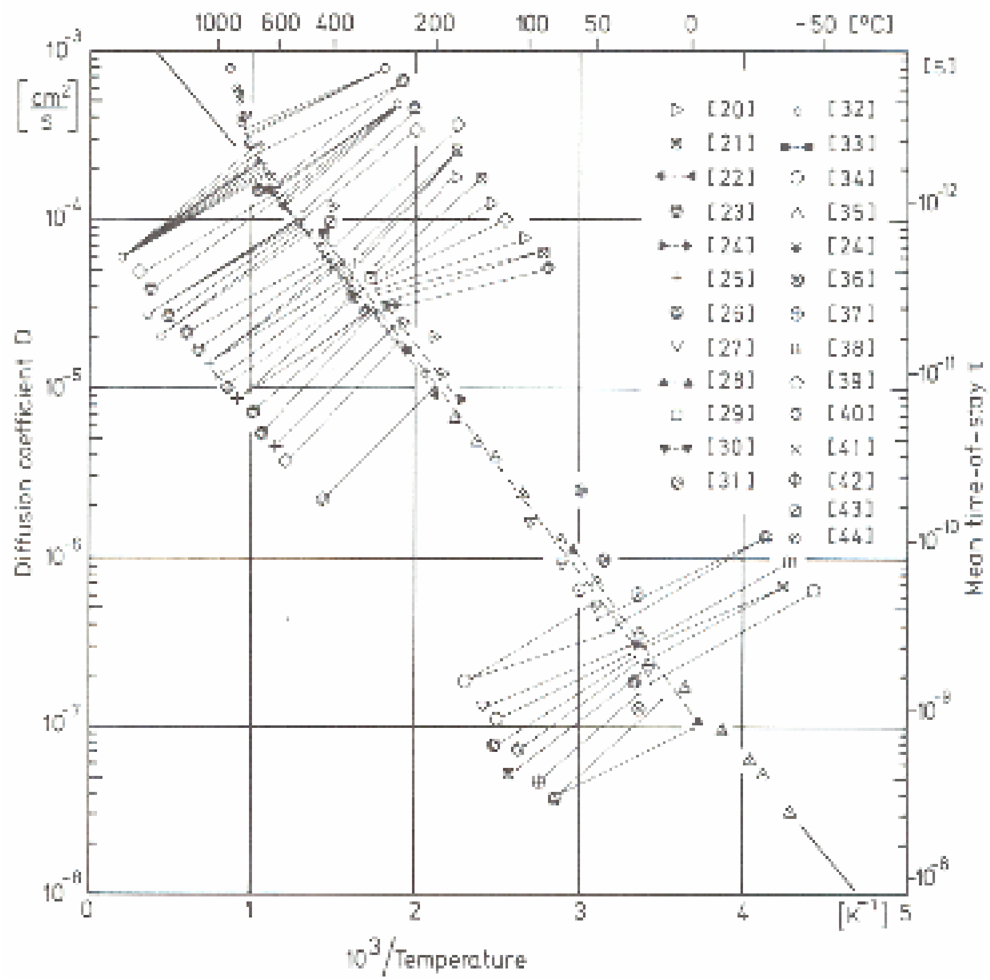
System Upgrade

- 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 ?**

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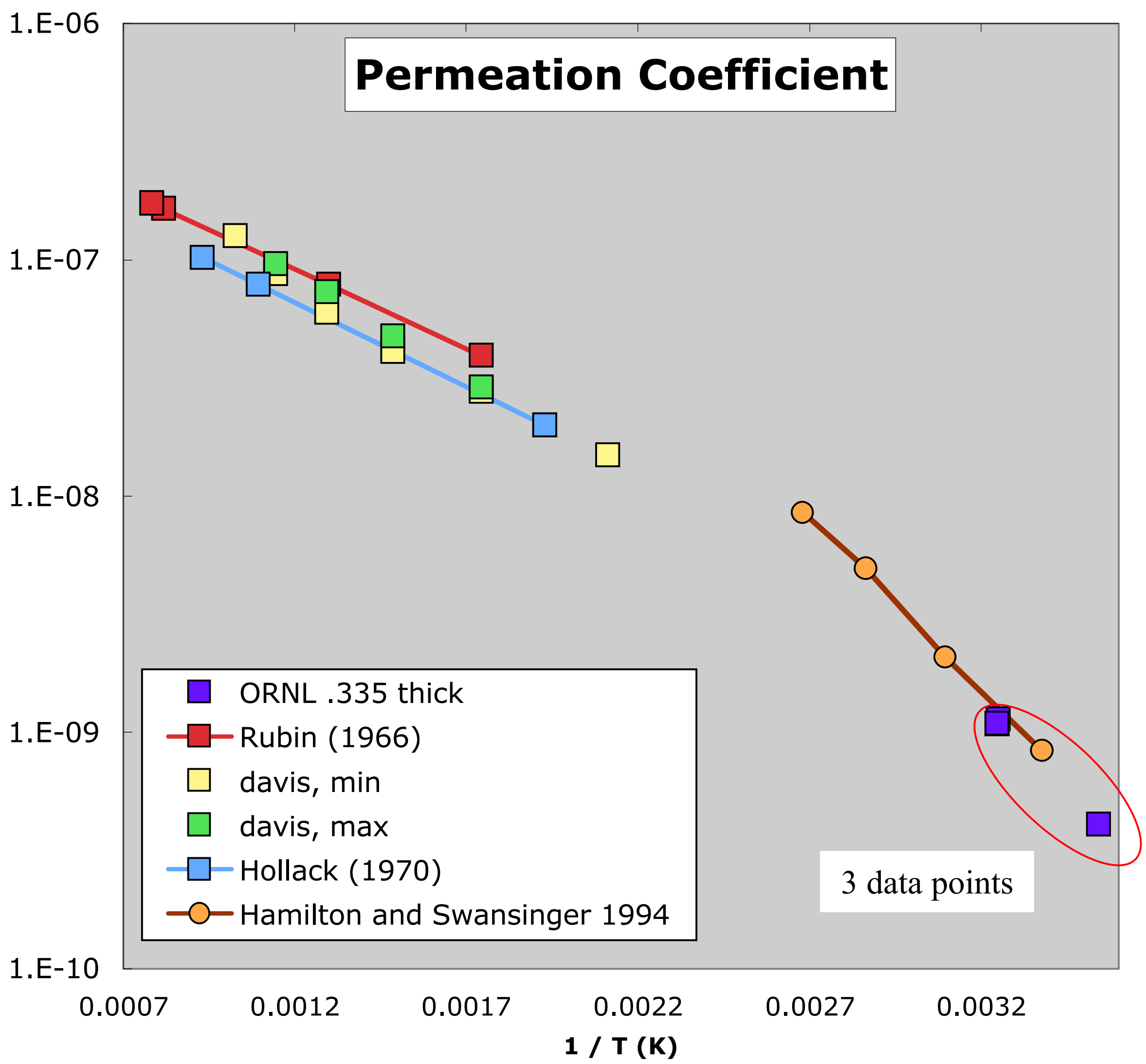
Caveats

- 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

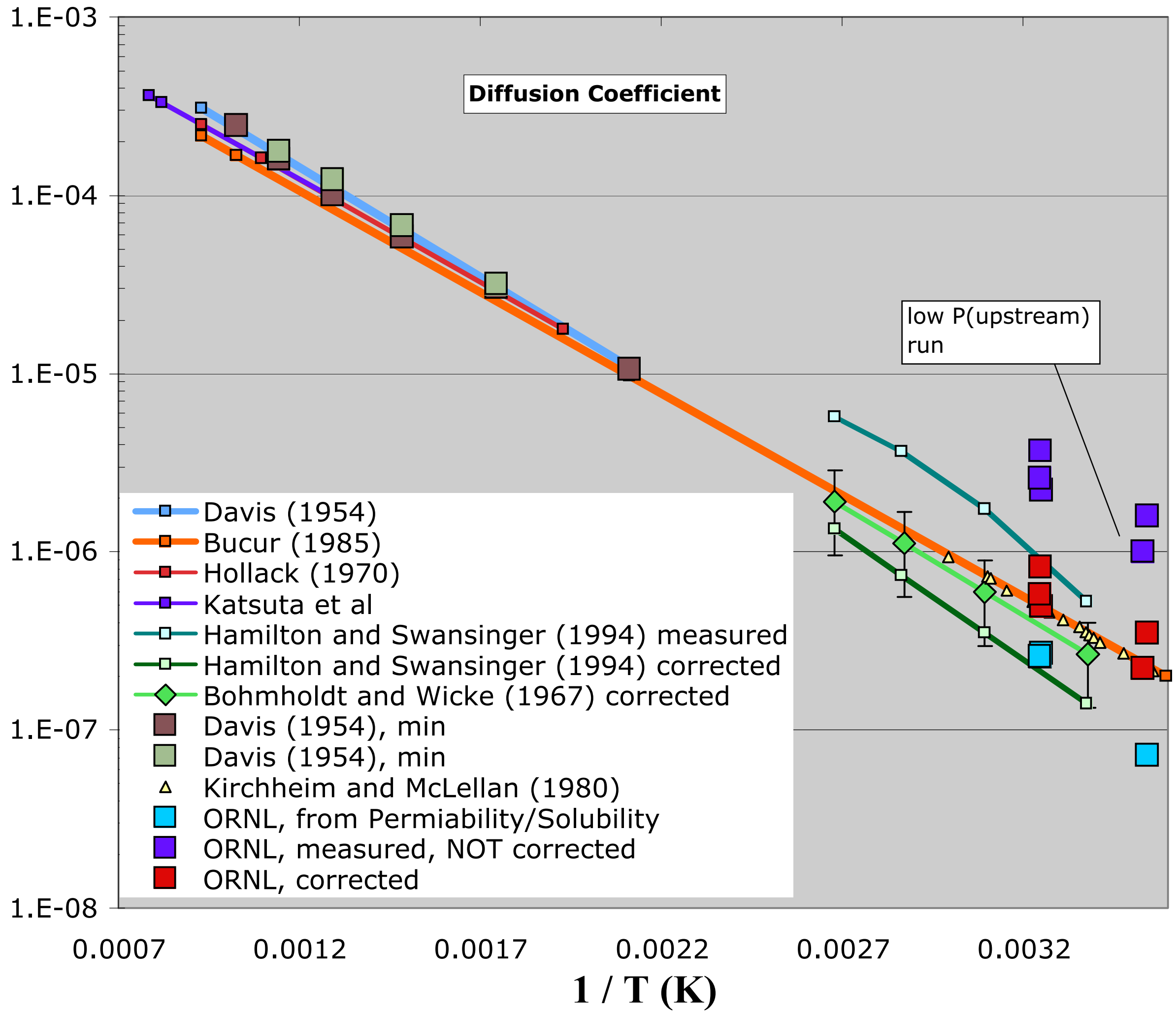
- Many of the data sets were measured at low-pressure conditions - P dependence not evaluated

Permeation Data



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

Diffusion Data



- **Our measured D values (P ~ 23 bars) are similar to, but a bit faster than the uncorrected Hamilton and Swansinger (1994) data (P ~ 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

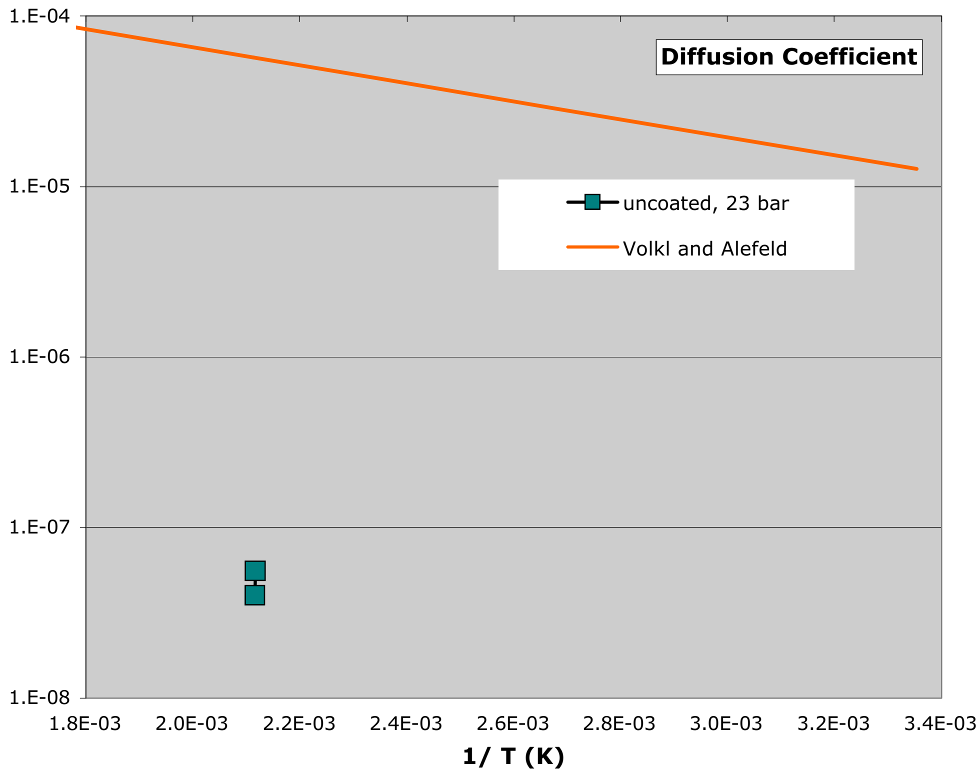
- High-pressure permeation system works - replicates literature data

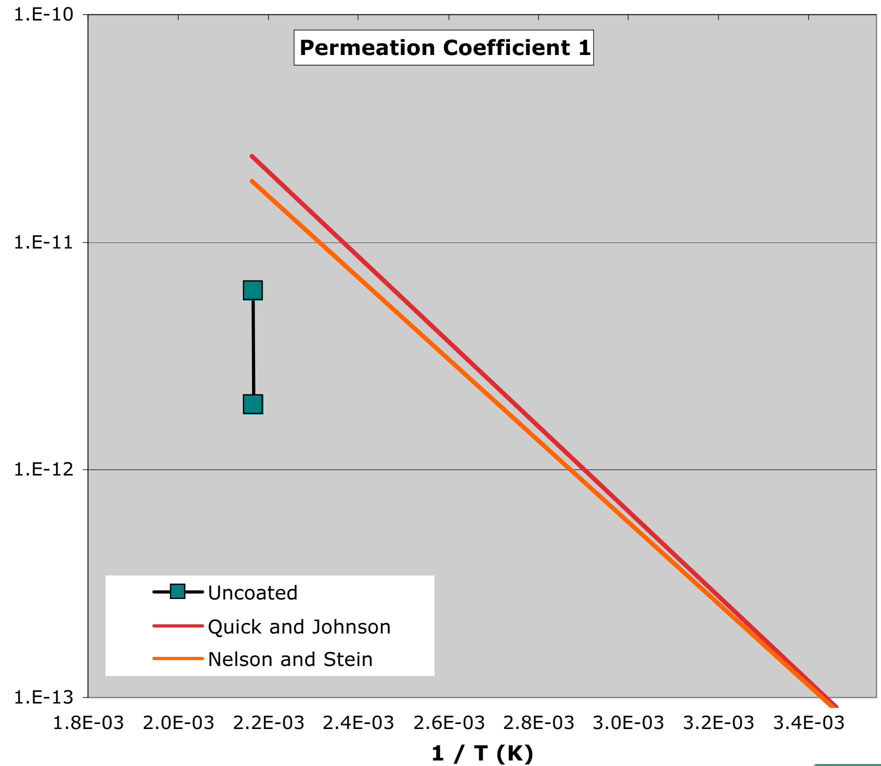
Baseline Measurement with Pure Iron

- 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





280C 20C

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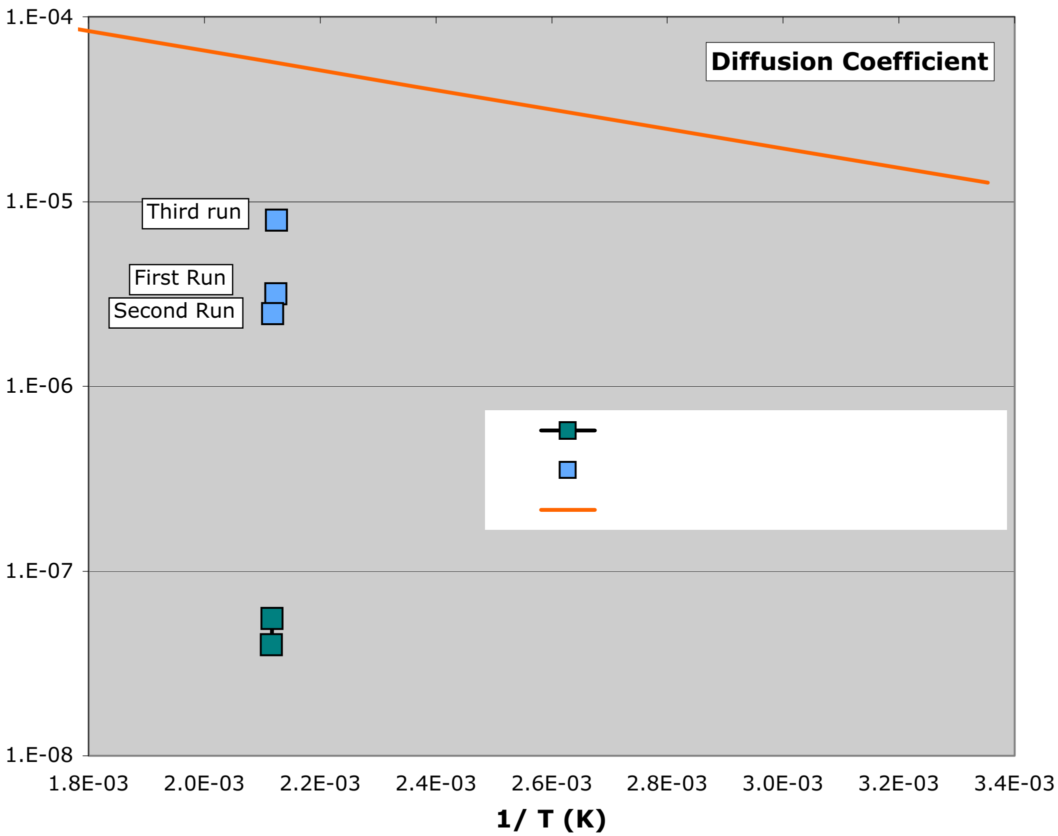
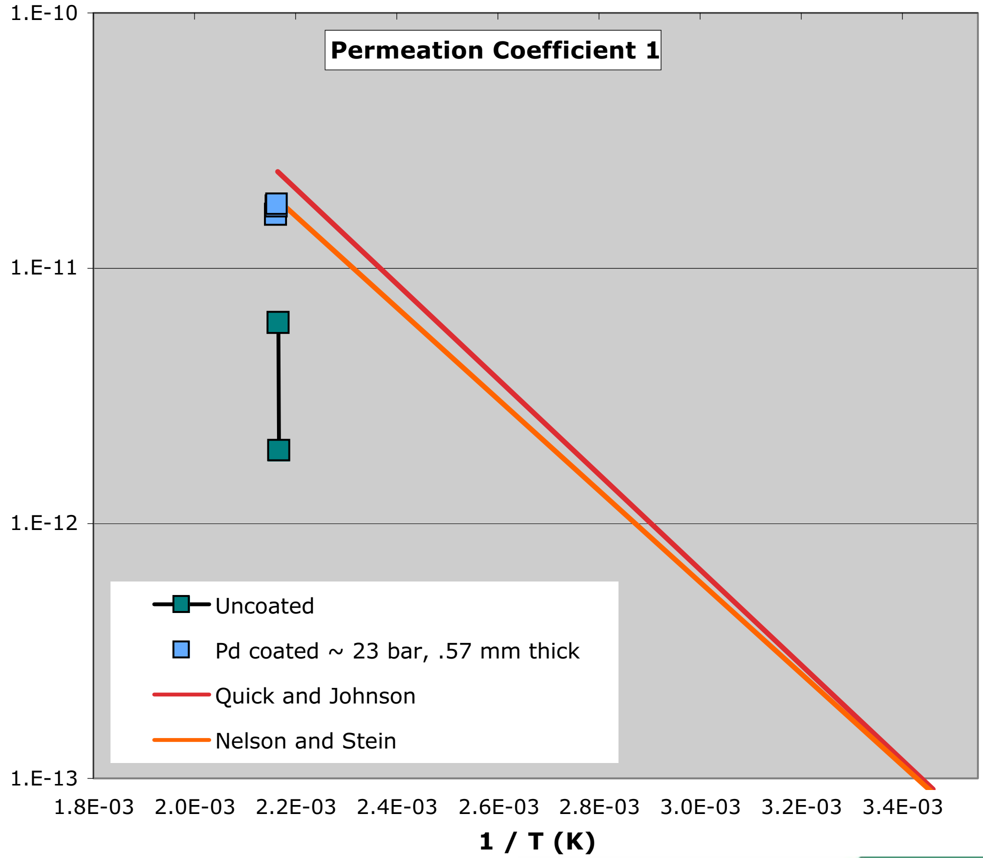
Pure Iron with Pd Coating

- 20 nm Pd coating on both sides





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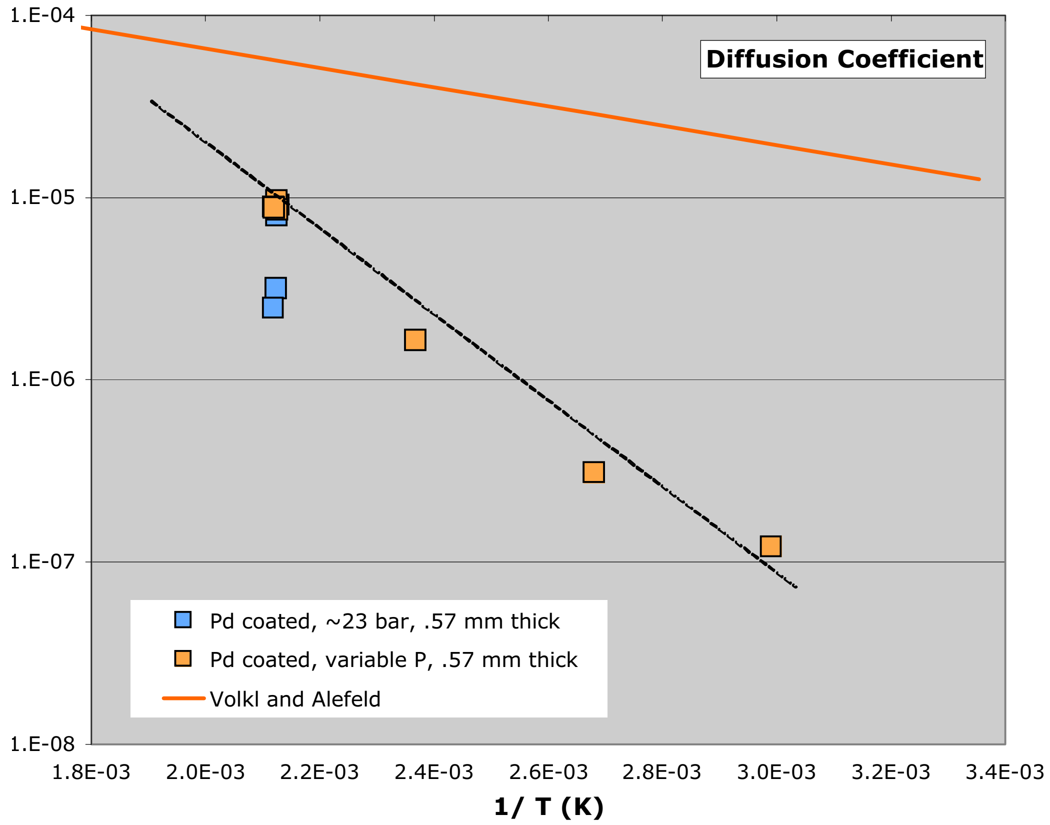
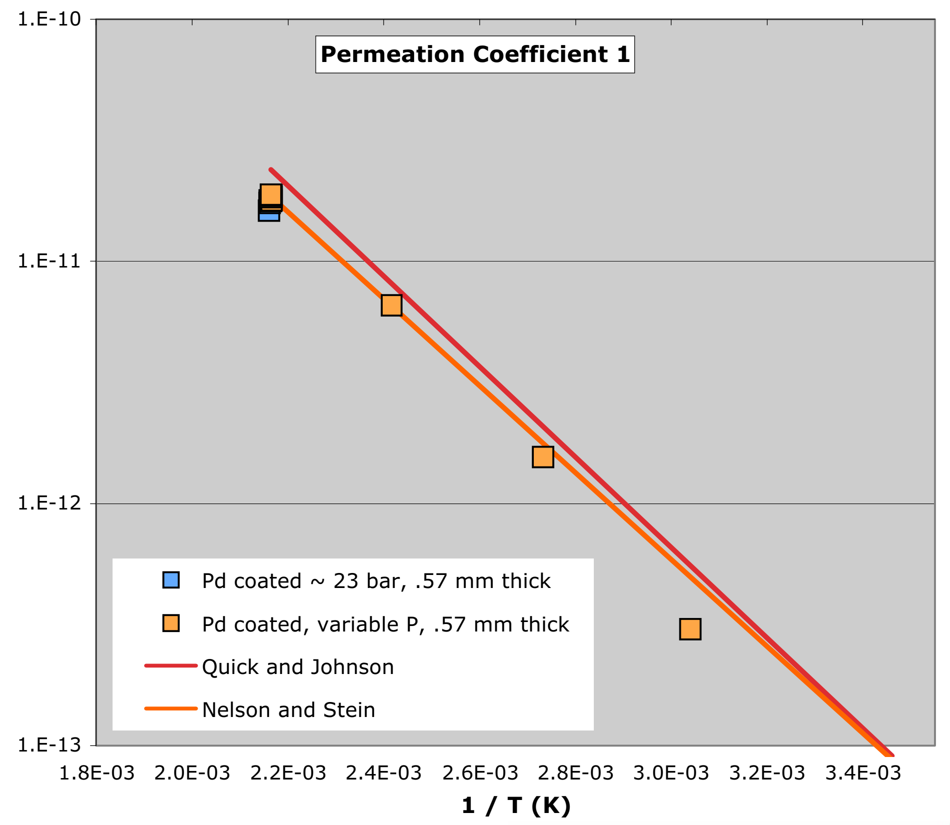
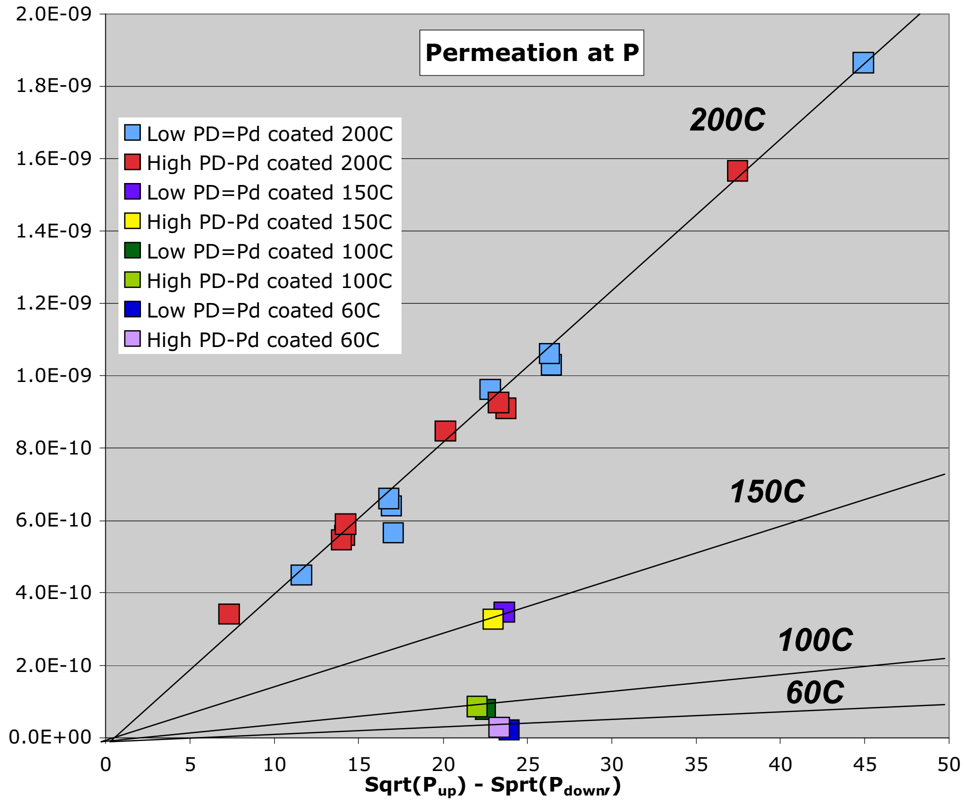
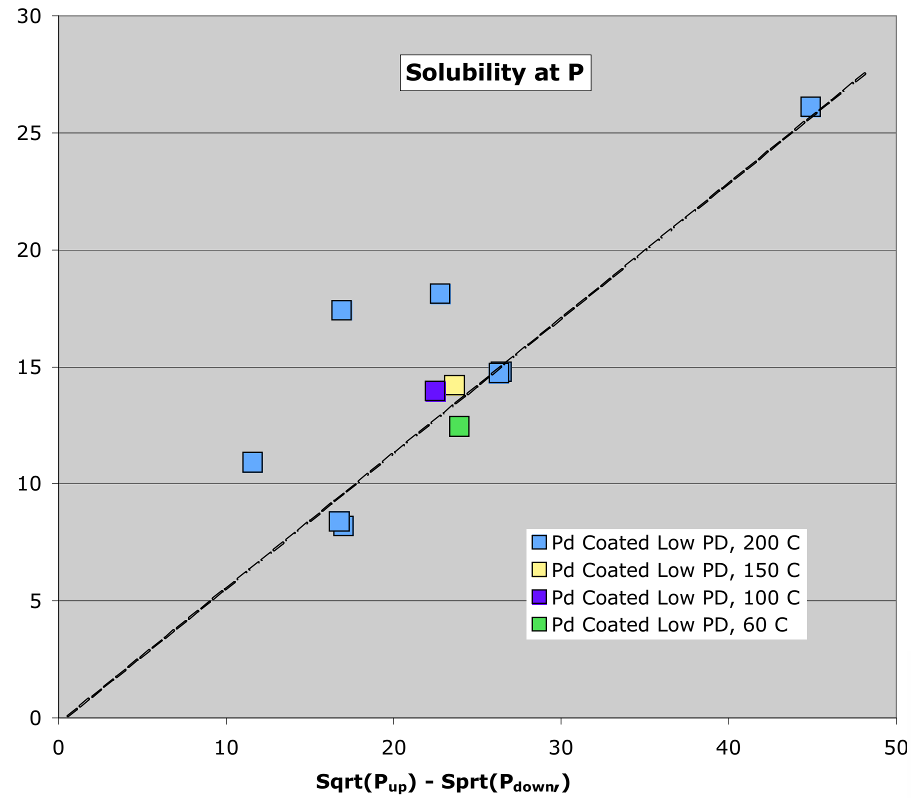
Temperature Dependency (Pd Coated Pure Iron)





Pressure Dependency (Pd Coated Pure Iron)





- **Solubility increases as charging pressure increases**
- **Permeation rate has square root dependency on pressure, at given temperature**

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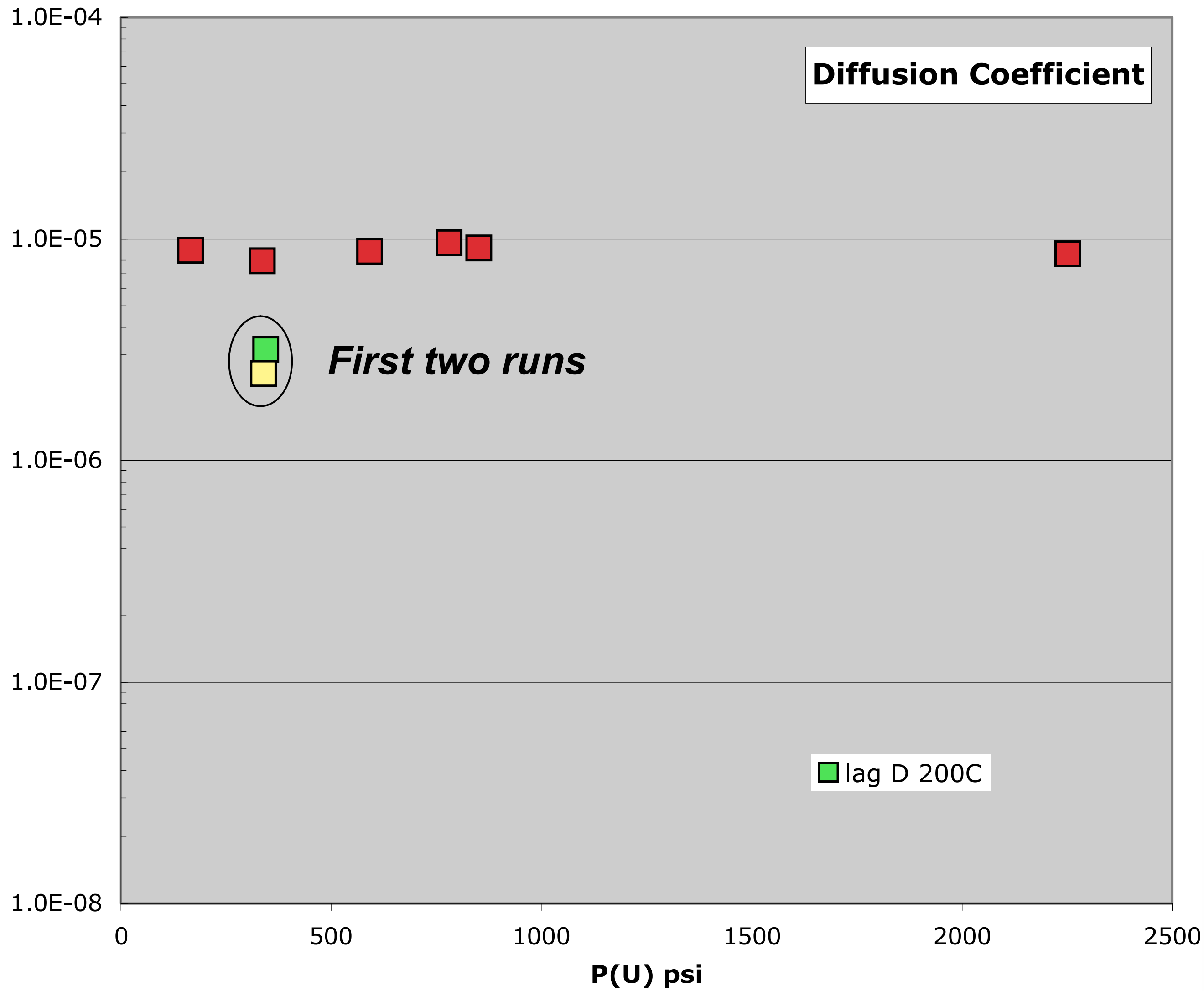
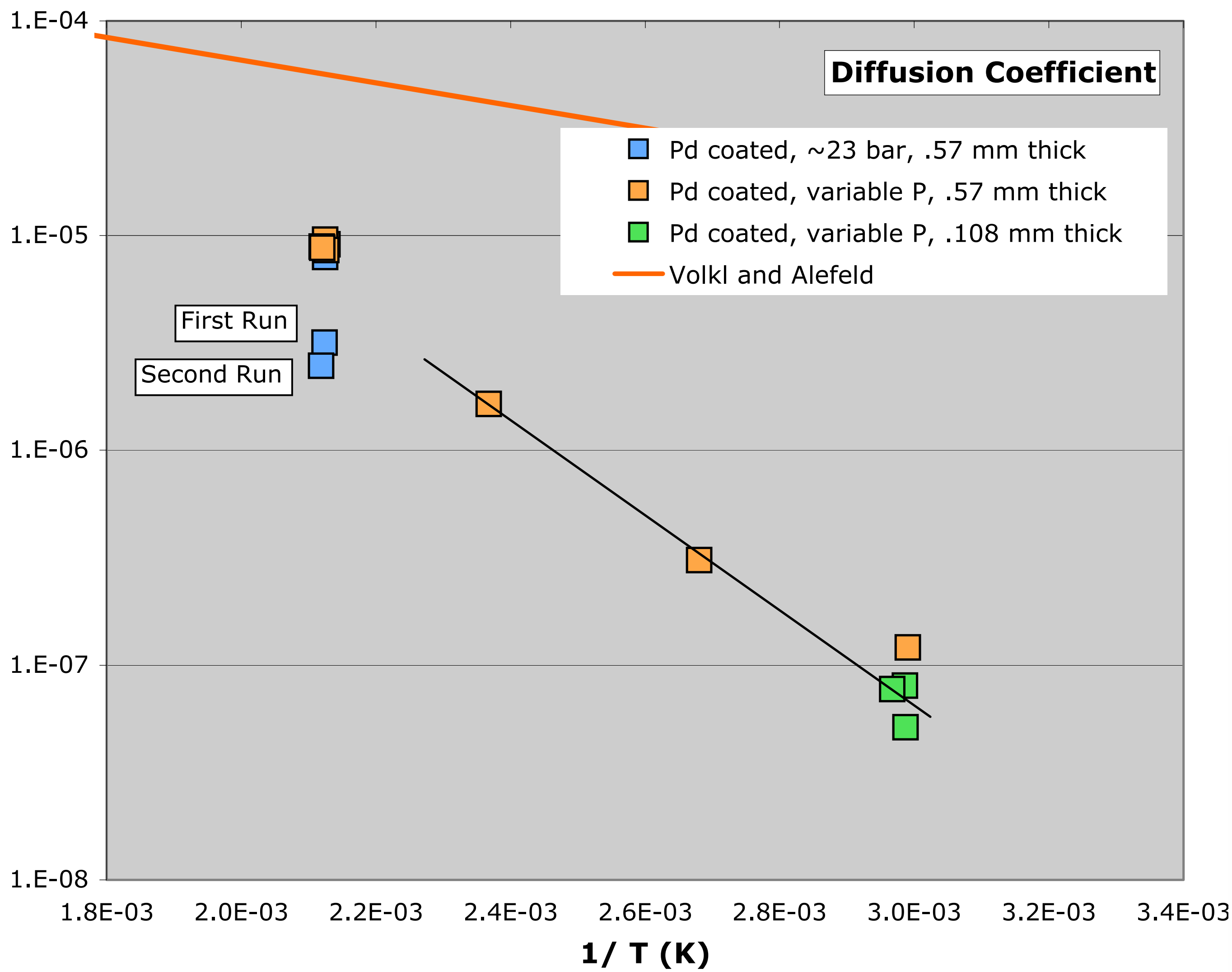
Pressure Dependency of Diffusivity (Pd Coated Pure Iron) (@200C)



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



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Summary of ORNL Task

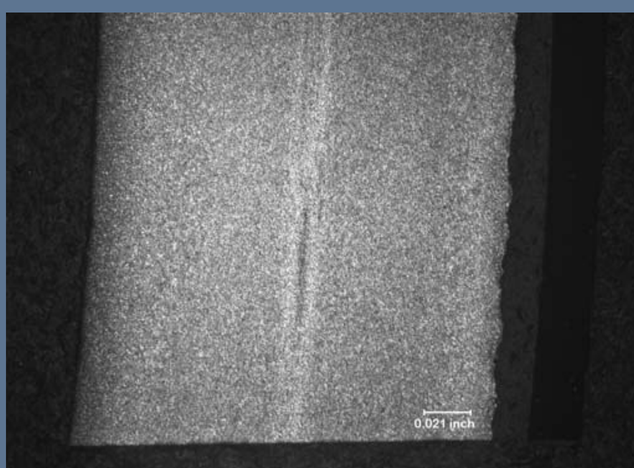
- High-pressure measurement system has been verified
- Measurements on pure iron provide baseline data to study steels and welds
- More rigorous data reduction procedure is being developed
- Complete measurements on pure iron and then move to steels

SRNL Progress and Status

SRNL Weld/HAZ Permeation & Embrittlement

Introduction

Girth Weld A106 Grade B Pipe



Seam Weld API X42 Pipe

- **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**

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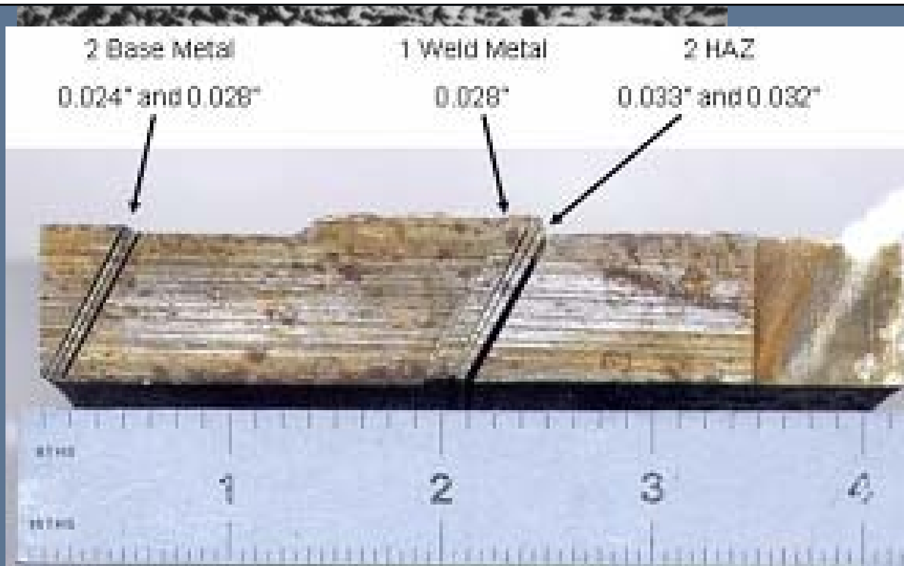
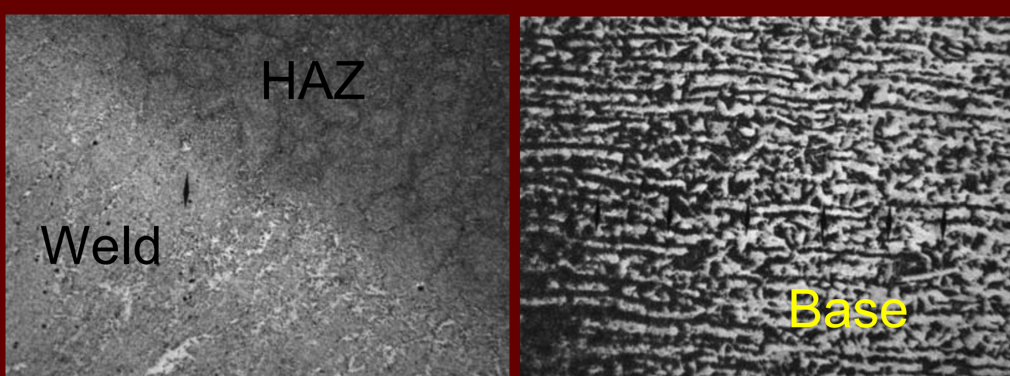
SRNL Weld/HAZ Permeation & Embrittlement

Progr□ss



Permeation Samples A106 Pipe Weld



- **Received Welded Pipe Materials—Praxair—API 5L GradeB/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

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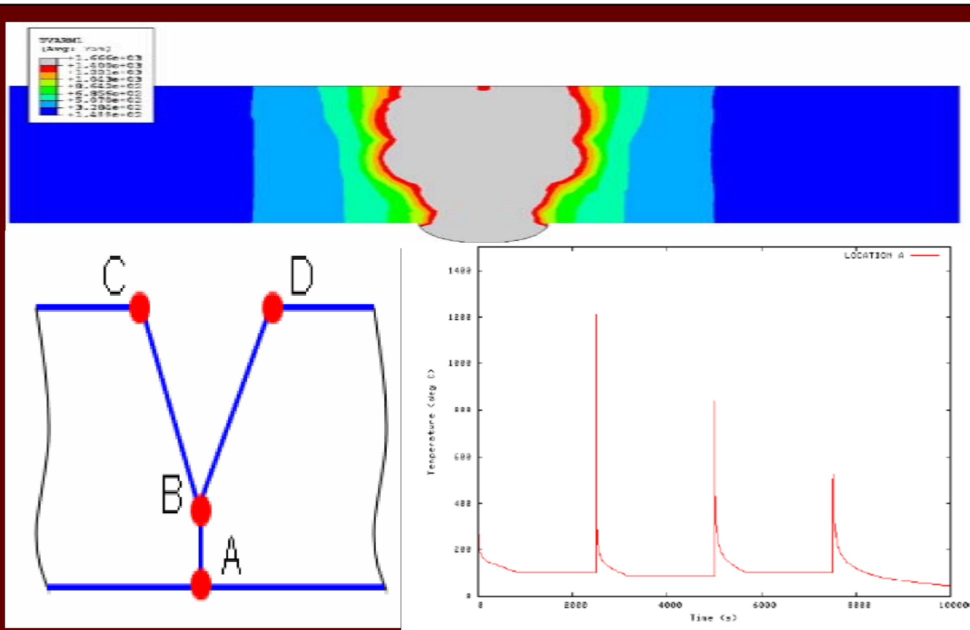
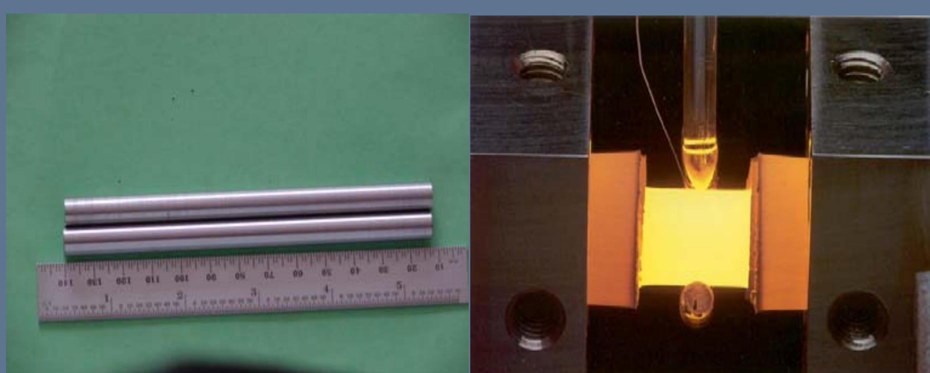


Weld Modeling with EWI

- 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



SRNL GLEEBLE Operations

- 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

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SRNL Weld/HAZ Permeation & Embrittlement
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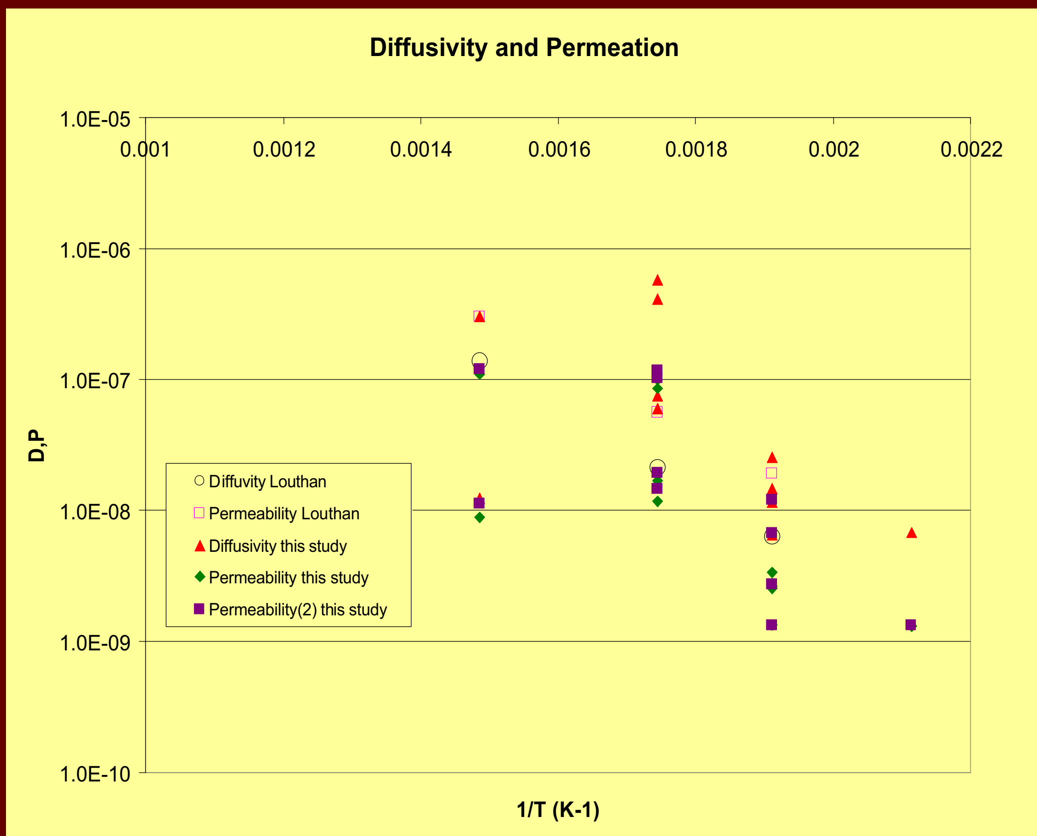

Proofing SRNL System & Test Methodology

- **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**
- **Current SRNL Testing Methodology and System is Proofed—Testing of HAZ Materials from A106 Gr. B Pipe Weld Initiated.**
- **Testing Conducted at 700T H2 Pressure @ 150°C, 175°C, and 200°C**

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SRNL Weld/HAZ Permeation & Embrittlement
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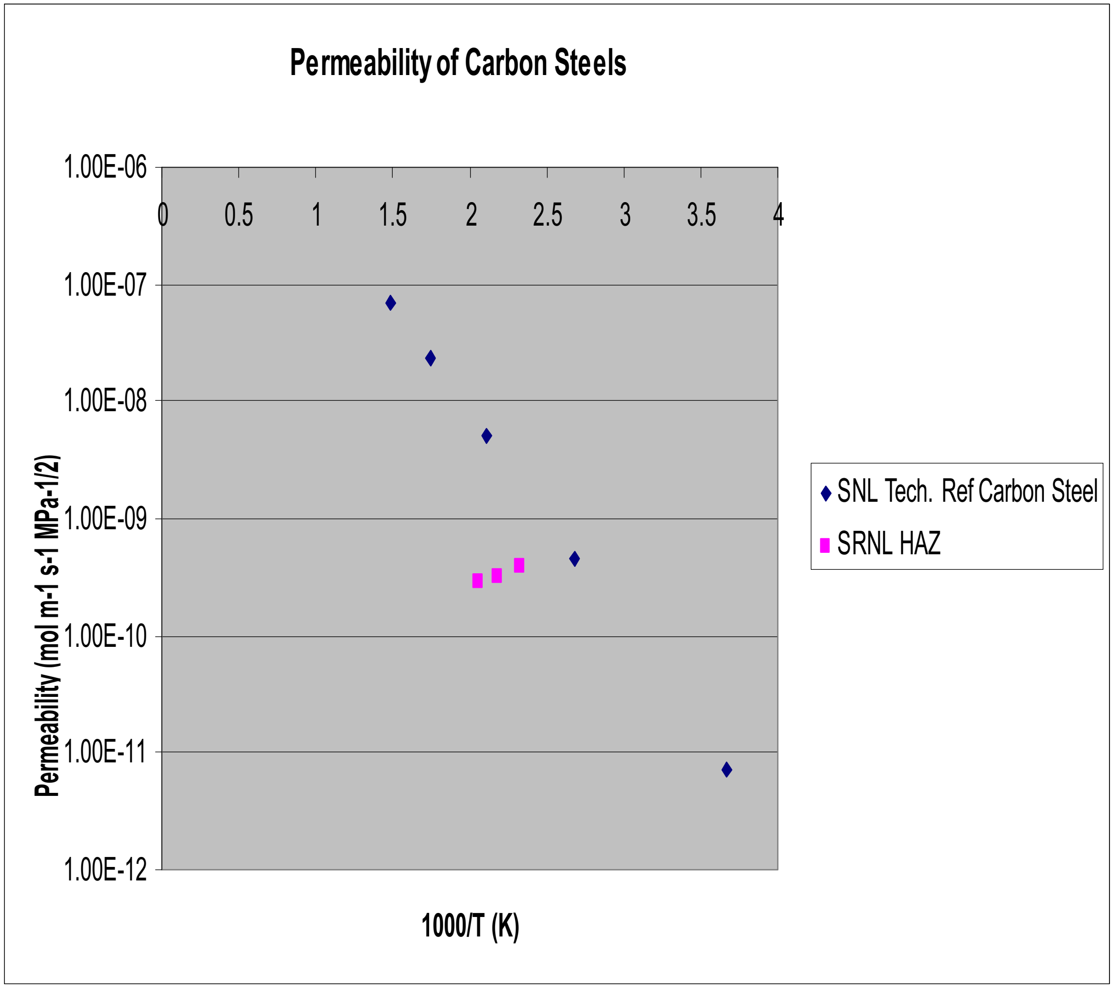
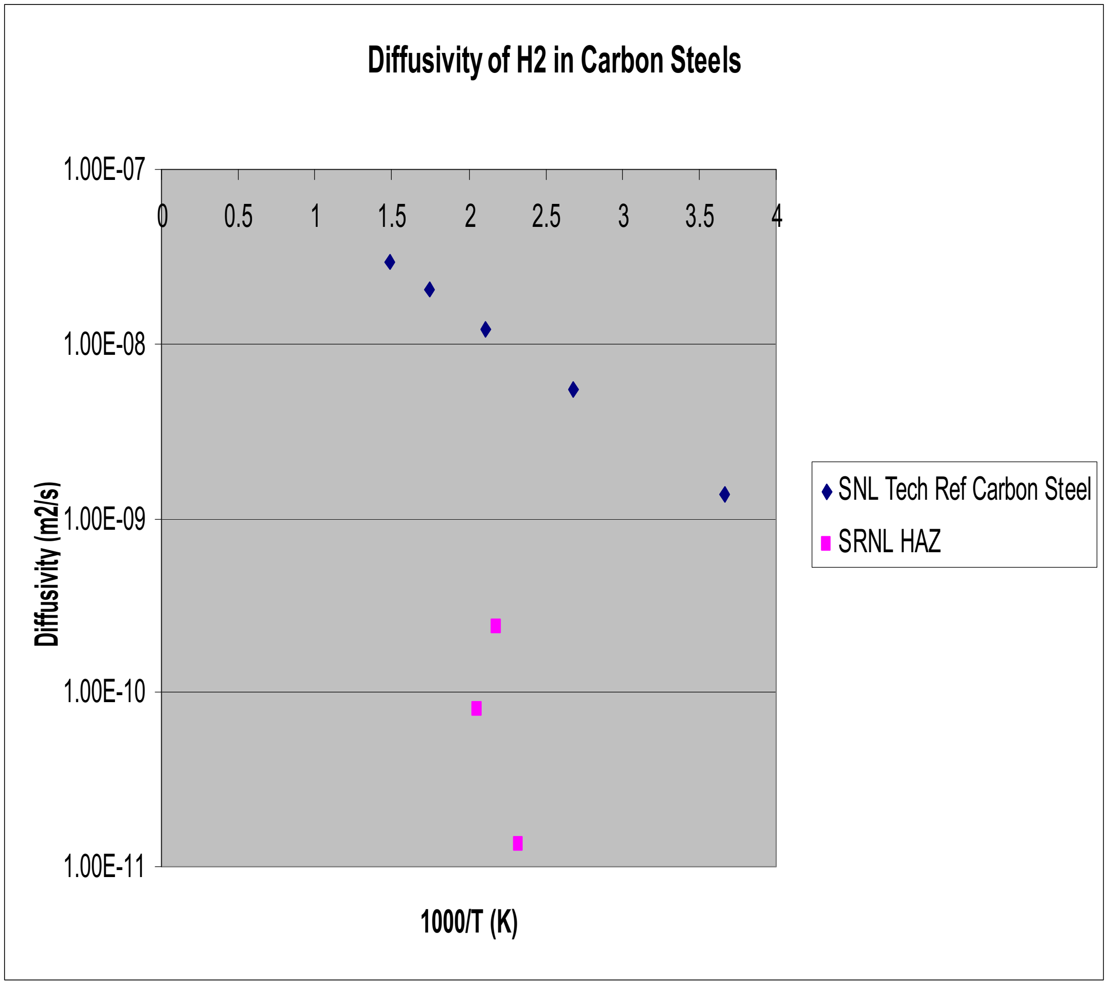


- **Permeability Measurements of HAZ—700T @150, 175, and 200°C**
- **SNL Technical Reference on Carbon Steels Provides an Expression for Permeability (Φ) for Several CS Alloys (normalized, spherodized, and Q&T)—SRNL HAZ Data Compared to 1020 Alloy**
  - **Φ 3.77E-05 exp (-35.07/RT)**
- **SRNL Measured 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 (Φ and Solubility (S) for Several CS Alloys (normalized, spherodized, and Q&T)—SRNL HAZ Data Compared to 1020 Alloy**
  - **D= Φ S—Plot Data Calculated Using SNL Tech Reference**
- **SRNL Measured Difusivity Data for A106 Grade B.—C-content =0.185**
  - **150°C =1.34 E-11 m^2/s**
  - **175°C= 2.36 E-10 m^2/s**
  - **200°C= 7.87E-11 m^2/s**

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SRNL Weld/HAZ Permeation & Embrittlement

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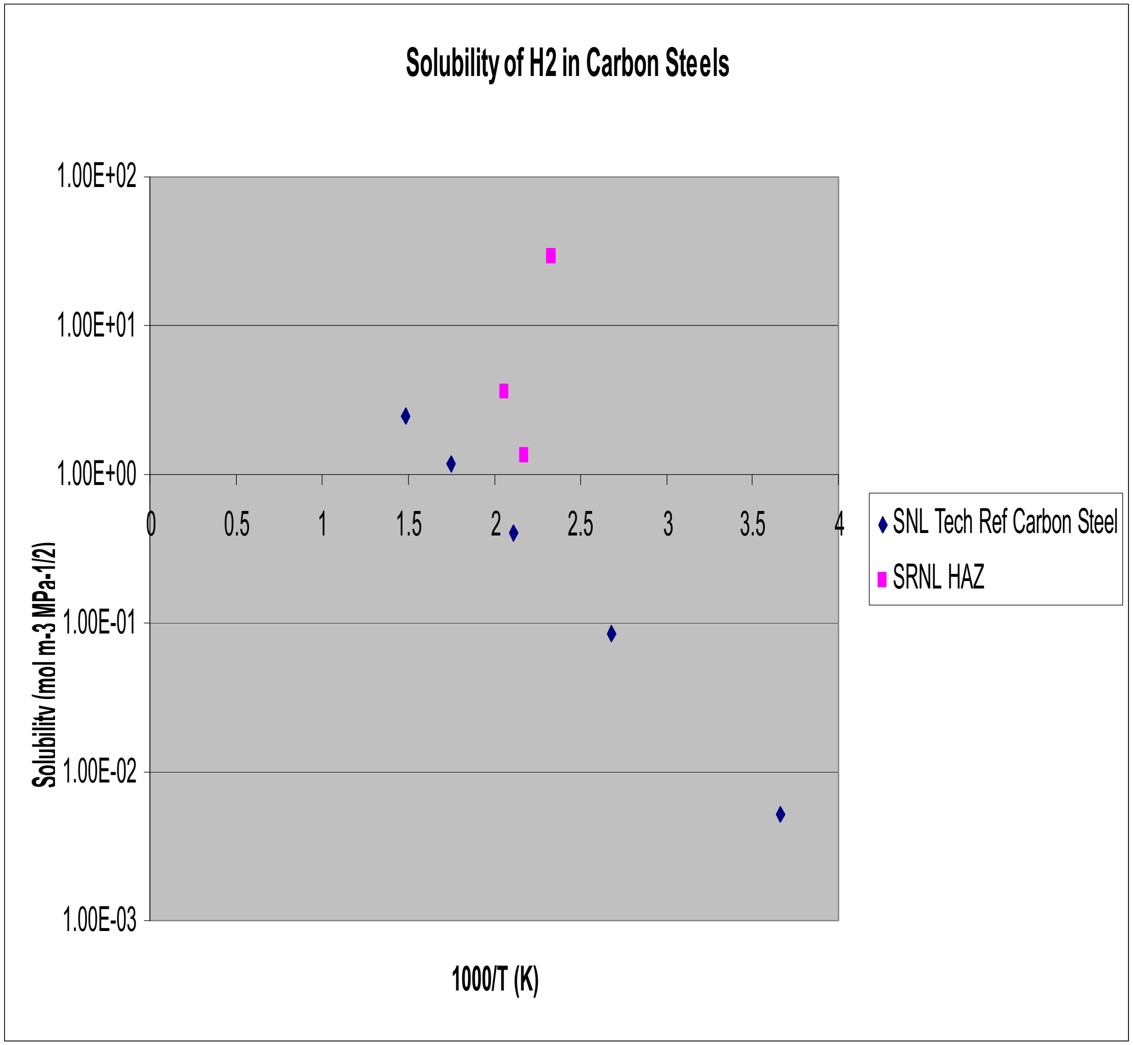
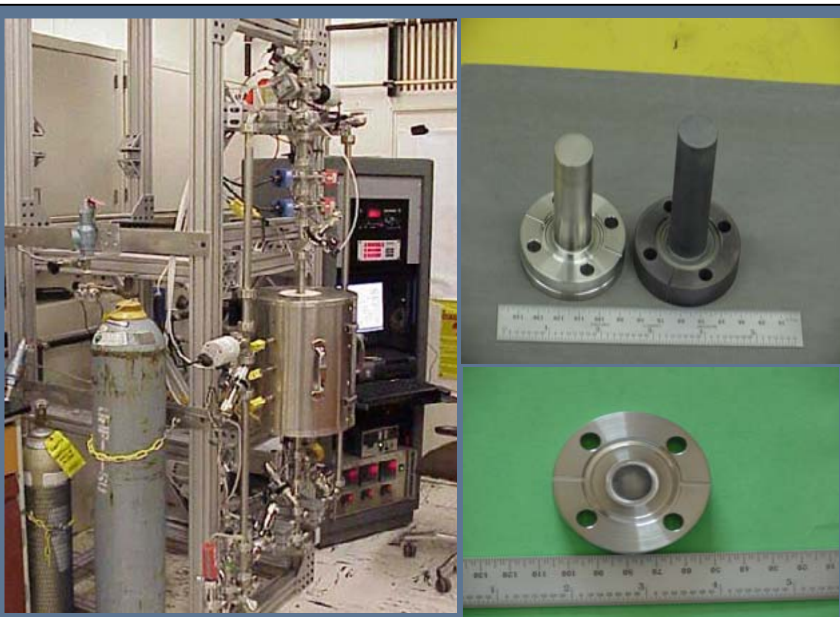


- **Solubility Determined from Permeation Tests of HAZ—700T @150, 175, and 200°C**
- **SNL Technical Reference on Carbon Steels Provides an Expression for Solubility (S) for Several CS Alloys (normalized, spherodized, and Q&T)—SRNL HAZ Data Compared to 1020 Alloy**
  - **S= 159 exp (-23.54/RT)**
- **SRNL Calculated Solubility Data for A106 Grade B.—C-content =0.185**
  - **150°C =29.25 mols/m^3 $MPa^{1/2}$**
  - **175°C= 1.36 mols/m^3 $MPa^{1/2}$**
  - **200°C= 3.64 mols/m^3 $MPa^{1/2}$**

SRNL Weld/HAZ Permeation & Embrittlement
Path Forward FY08



SRNL Weld/HAZ Permeation Samples

SRNL GLEEBLE 1500

- **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 Embrittlment**
  - **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**

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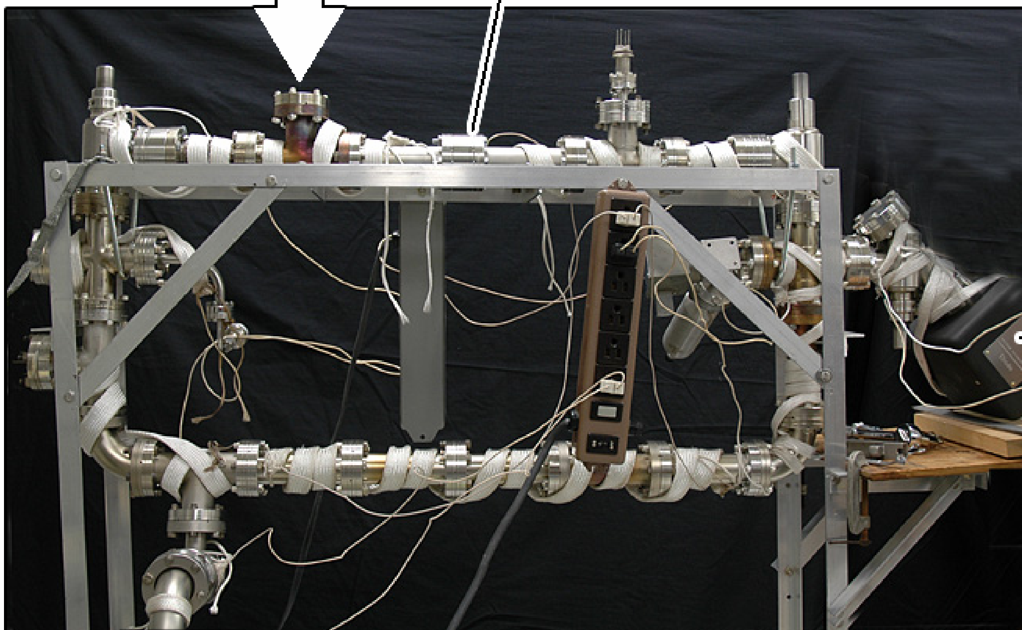
University of Illinois Progress and Status

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

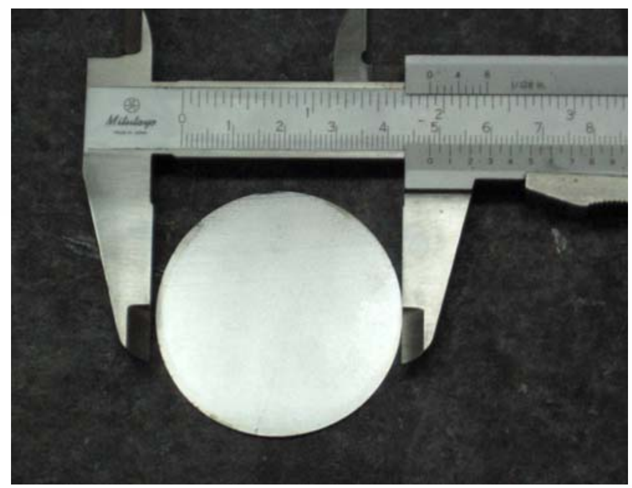
UIUC Permeation



- 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

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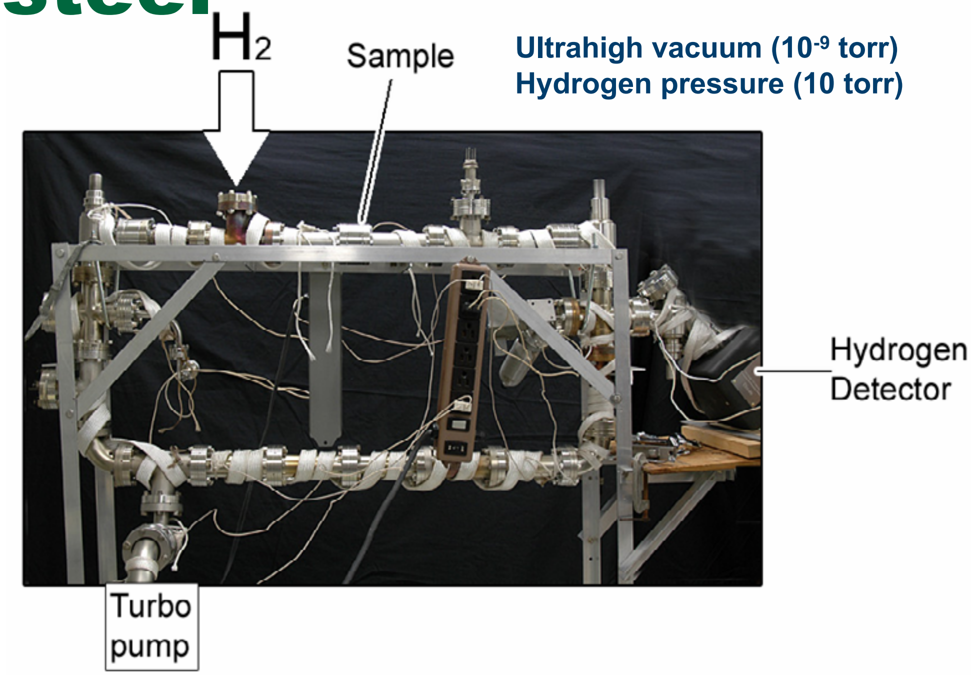
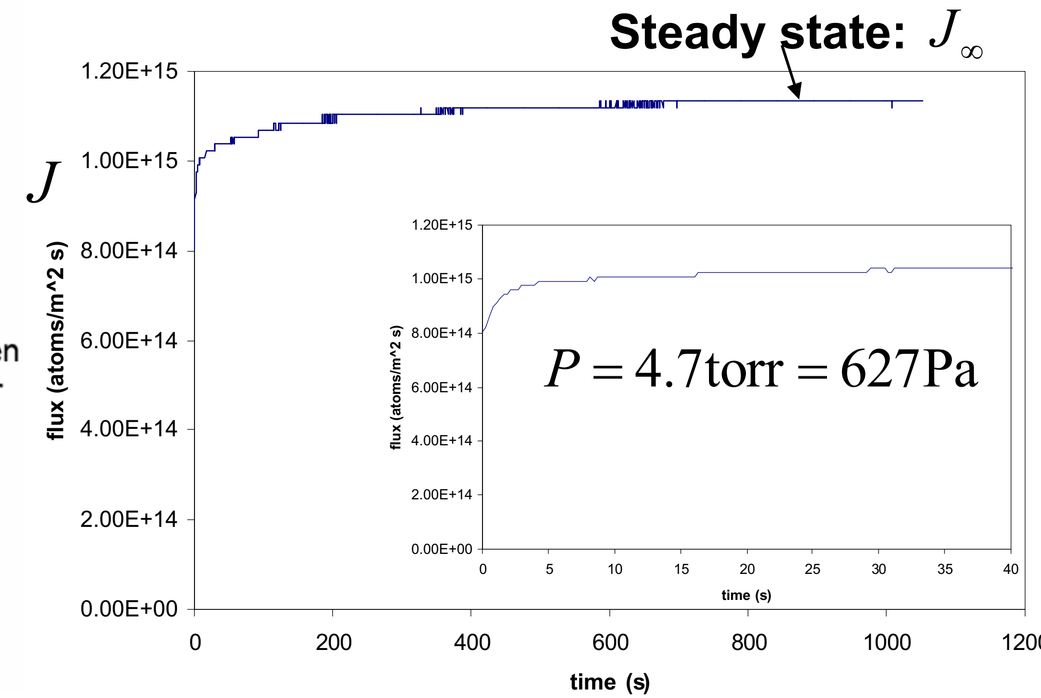
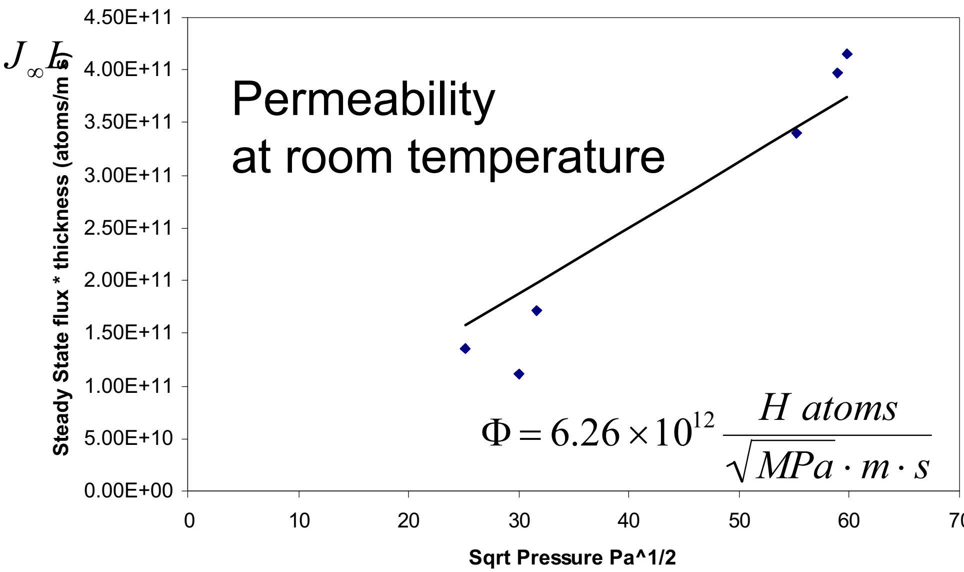
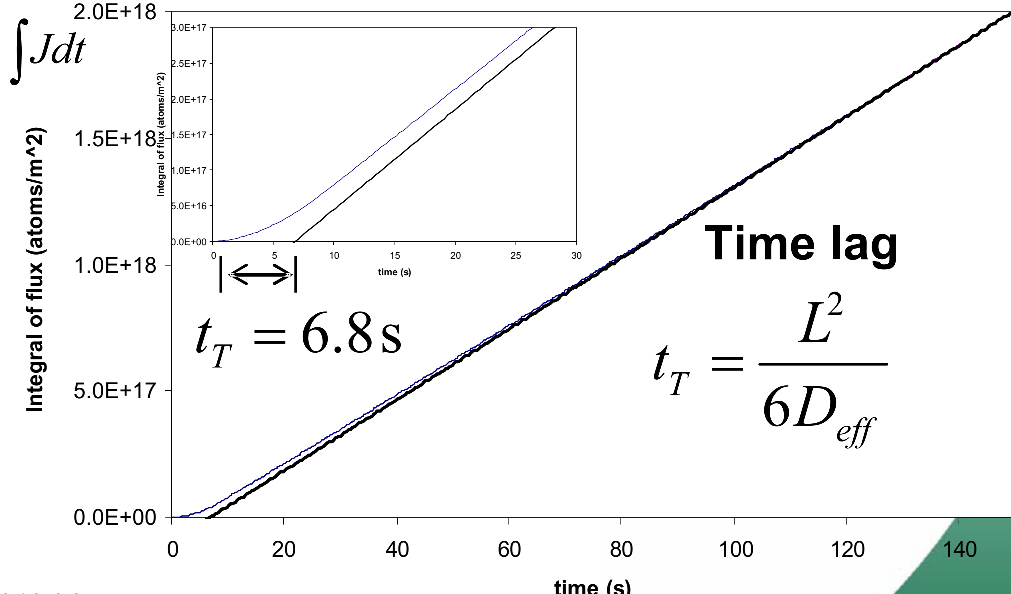
UIUC Hydrogen Permeation Measurements: C-steel



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







- Oregon Steel Mills sample: thickness 120 microns
- room temperature

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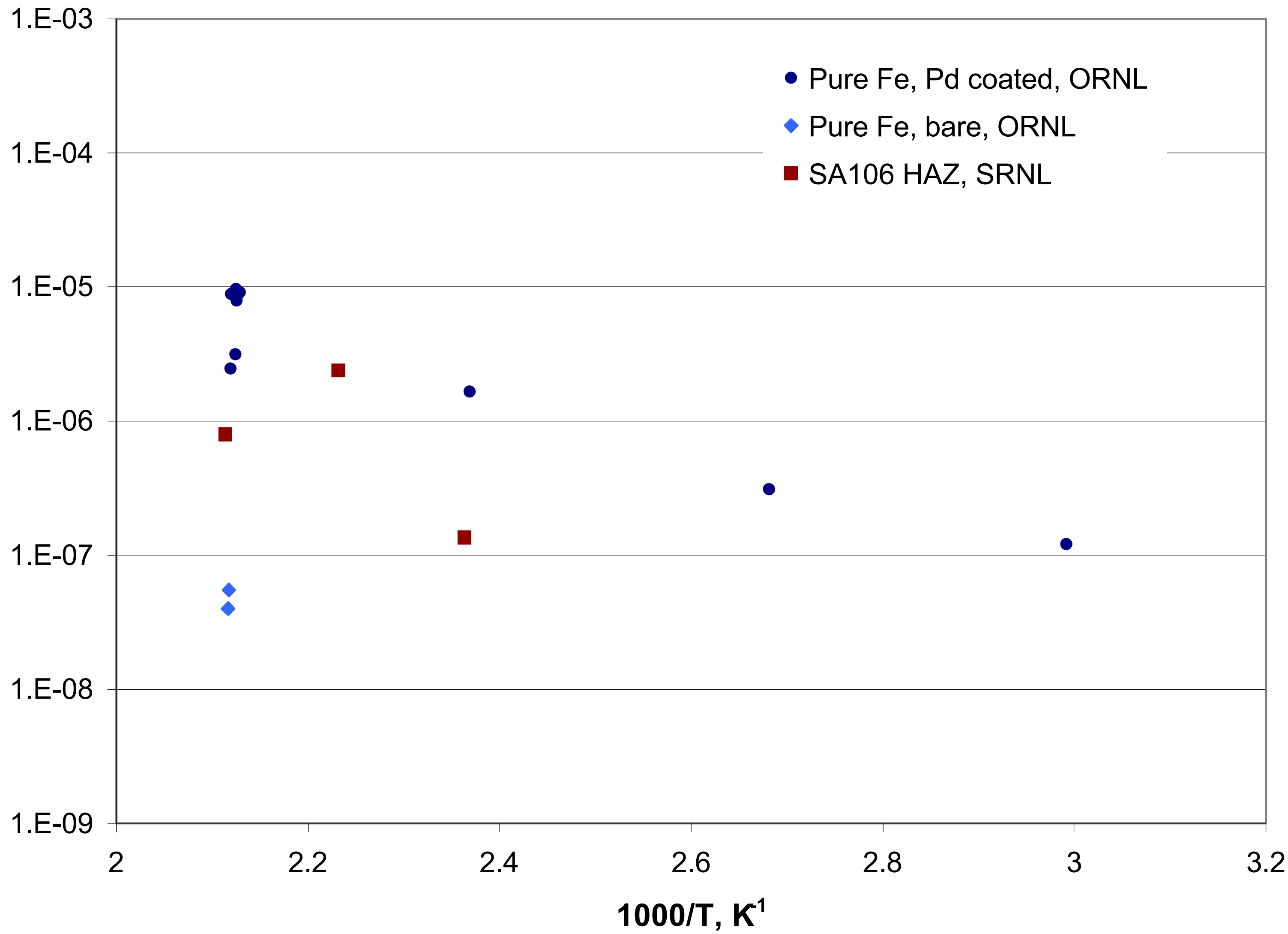
Comparison of Data (ORNL, SRNL, UIUC)



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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?