Hydrogen Permeability and Integrity of Hydrogen Delivery Pipelines

Z. Feng*, L.M. Anovitz*, J.G. Blencoe*,

S. Babu*, and P. S. Korinko**

* Oak Ridge National Laboratory
* Savannah River National Laboratory

August 30, 2005

Partners and Collaborators

- Oak Ridge National Laboratory
  - Project lead
- Savannah River National Laboratory
  - Low H_2 pressure permeation test
- Edison Welding Institute
  - Pipeline materials
- Lincoln Electric Company
  - Welding electrode and weld materials for pipelines
- Trans Canada
  - Commercial welding of pipelines and industry expectations
- DOE Pipeline Working Group and Tech Team activities
  - FRP Hydrogen Pipelines
  - Materials Solutions for Hydrogen Delivery in Pipelines
  - Natural Gas Pipelines for Hydrogen Use

Funding and Duration

- Project start date: March 2004
- Project end date (projected): Sept 2007
- DOE Funding
  - FY2004: $150,000
  - FY2005: $200,000

Project Objectives

- To gain basic understanding of hydrogen permeation behavior (absorption, diffusion, trapping, etc.) and its impact on hydrogen embrittlement of pipeline steels under high gaseous pressures relevant to hydrogen gas transmission pipeline
- To develop suitable welding technology for H_2 pipeline construction and repair
- To develop technical basis and guidelines to ensure the integrity and safety of H_2 pipelines

Approach

- High-pressure H_2 permeation and mechanical tests using ORNL's internally heated pressure vessel (IHPV)
  - Hydrogen permeation (solubility and diffusivity) and embrittlement behavior as function of pressure and temperature
  - Effects of steel composition, microstructure, and surface condition (including coating)
  - Effects of welding: weld microstructure, residual stress, and geometrical discontinuities
  - A database for common pipeline steels
- Low Pressure H_2 permeation testing using SRNL's permeation test facility
  - Hydrogen permeation (solubility and diffusivity) to verify Sievert's law behavior
  - Effects of coating, surface activators, and temperature
- A risk assessment based approach to ensure the integrity and safety of H_2 pipelines
- Investigation of modern, hydrogen-cracking resistant, high-strength pipeline steels for hydrogen delivery and storage
- Development of welding/joining technology for H_2 pipelines
  - Weld microstructure management
  - Weld residual stress management
  - Hydrogen management

Our research so far has focused on permeation behavior of pipeline steels

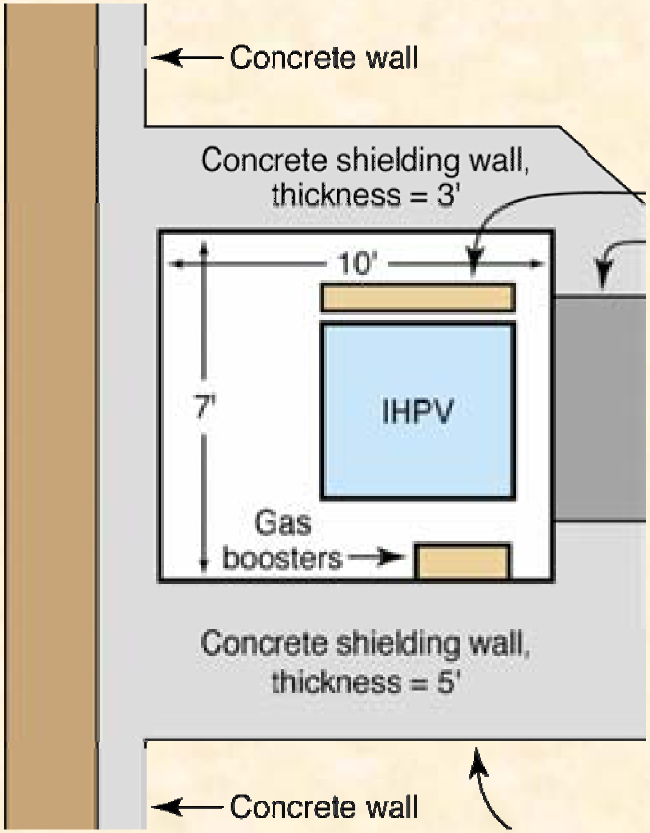
- Lack of hydrogen permeation data for pipeline steels under high-pressure gaseous hydrogen conditions in the open literature
- Progress to date
  - Developed high-pressure H_2 permeation testing apparatus and testing procedure
  - Selection of pipeline steels and weld material
  - Initial H_2 permeation data at both low and high pressure levels

Pipeline steels X52 and X65 and a weld metal with high-aluminum content were selected for current research

- API Grade X52 steel - 1950 production
  - 20 inch dia - 0.312 inch thick
  - Fe, 0.3%C, 1.16%Mn (wt.%)
- API Grade X65 steel - 1990 production
  - 16 inch dia - 0.500 inch thick
  - Fe, 0.18%C, 1.36%Mn (wt.%)
- Weld metal
  - Self-Shielded Flux Cored Arc Weld
  - Fe, 0.22%C, 0.53%Mn, 1.77%Al (wt.%)

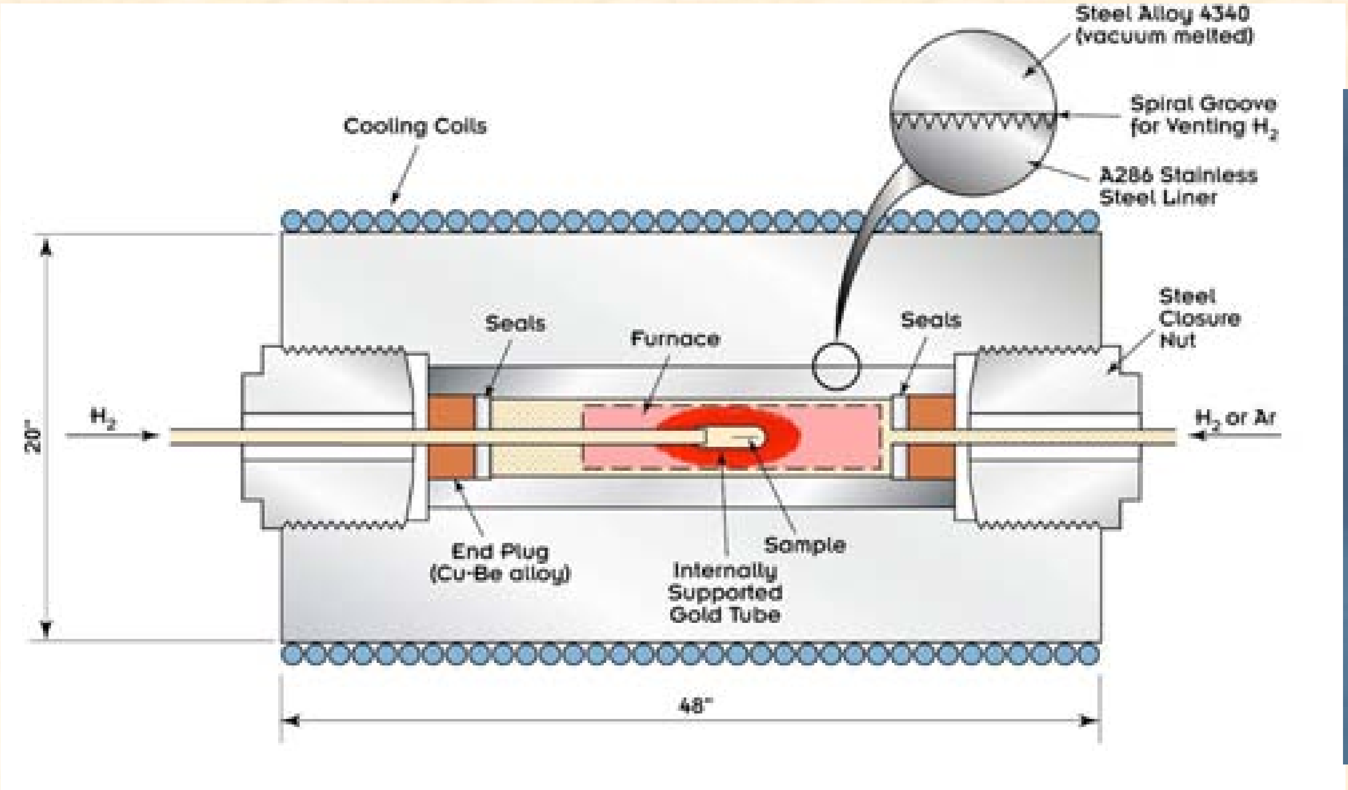
High-pressure H_2 testing apparatus

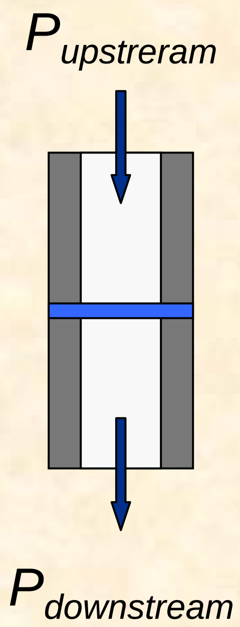
- ORNL has a internally-heated pressure vessel (IHPV) commissioned for high-pressure gaseous hydrogen experiments
- This vessel has been upgraded for high-pressure hydrogen permeation and mechanical testing
- The entire facility is designed and engineered for safety



IHPV high-pressure H_2 testing apparatus

- High hydrogen pressures can be achieved from room temperature to 1000°C
  - Vessel rated for operation at pressures up to 150,000 psi
- Pressure measurements accurate to 0.1 psi
- Temperature measurements accurate to 0.1°C.
- A large internal "working cavity"

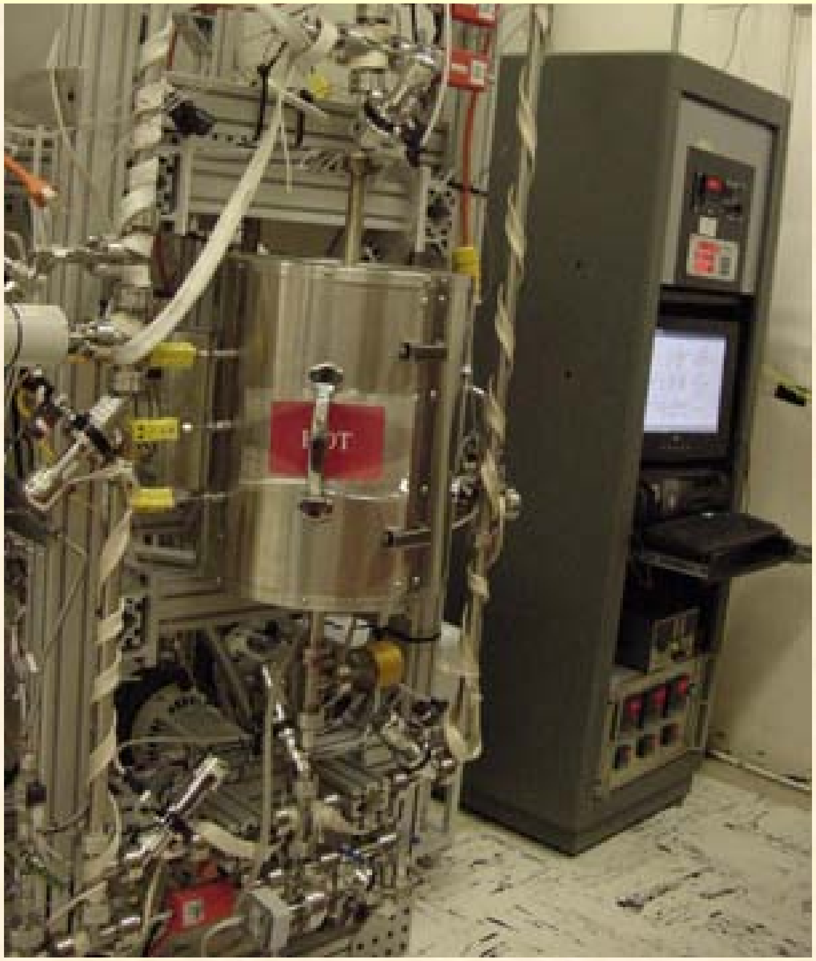




In parallel with the high pressure tests, we also conducted low-pressure permeation experiments

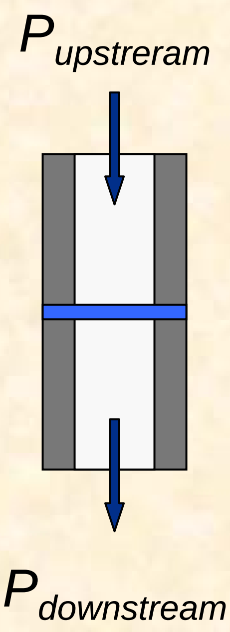
Simple conflat flange design made of the testing steel

SRNL's low pressure apparatus: up to 1000 torr (19 psia) & 500°C

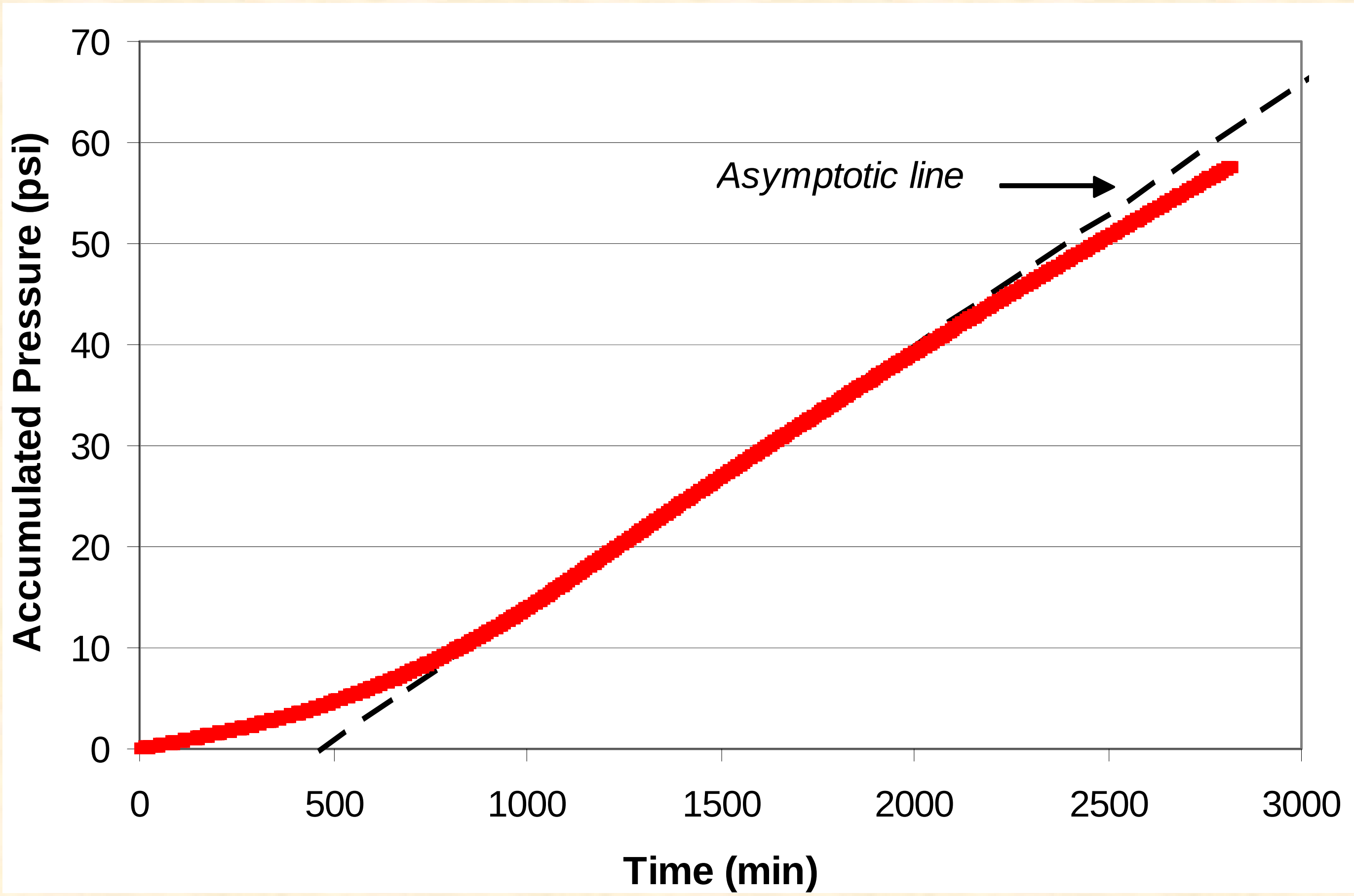


Permeation Test Basics

- H_2 at the upstream side (charging side) is maintained at pre-determined pressure level
- Atomic hydrogen diffuses through the testing sample and collects at the downstream side into a constant volume chamber
- H_2 pressure increase in the CV chamber is recorded as function of time



Typical permeation curve under high H_2 pressure



X52 steel (P1-7-18-05), H_2 charging condition: 545 psi, 170°C
No measurable background leak, temperature is very stable

Determination of "effective" diffusivity and concentration from permeation test

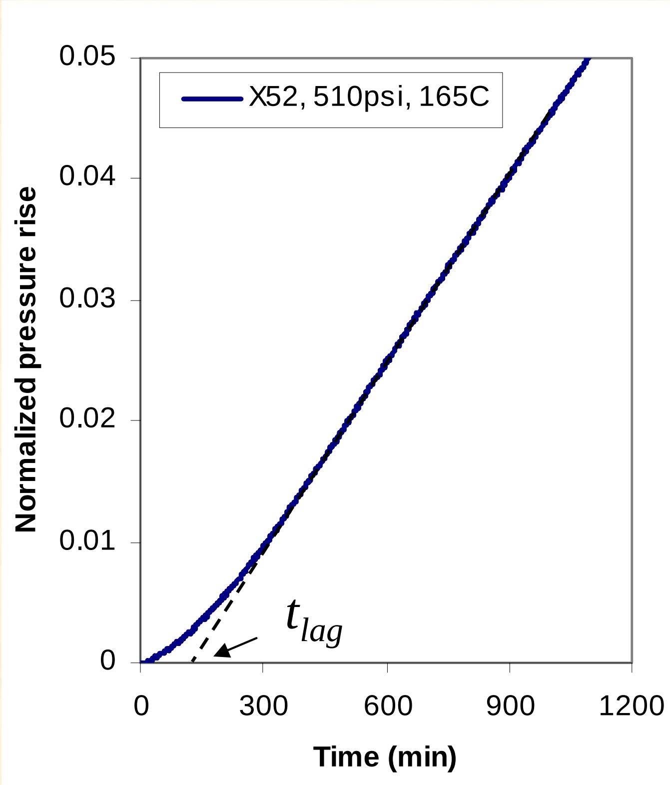
- Basic assumption:
  - Diffusivity is independent of H concentration
- "Effective" diffusivity determined from the accumulated pressure vs time curve using the asymptotic slope method

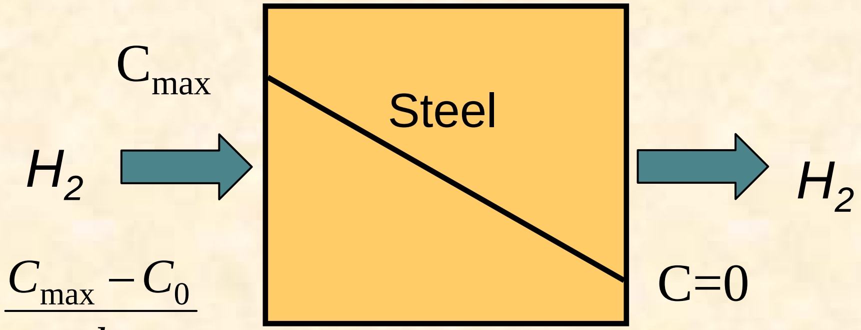
$$D_{eff} = l^2 / 6t_{lag}$$

- Atomic hydrogen concentration at the upstream side (max concentration) determined from the steady state permeation rate and diffusivity:

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

- Data analysis procedure will be further refined in FY06 to deal with the surface effects and concentration dependent diffusivity issues





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

Permeability

- Permeability: the rate of hydrogen flux passing through the material
  – A good direct index of the H_2 leak rate though the pipe

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

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

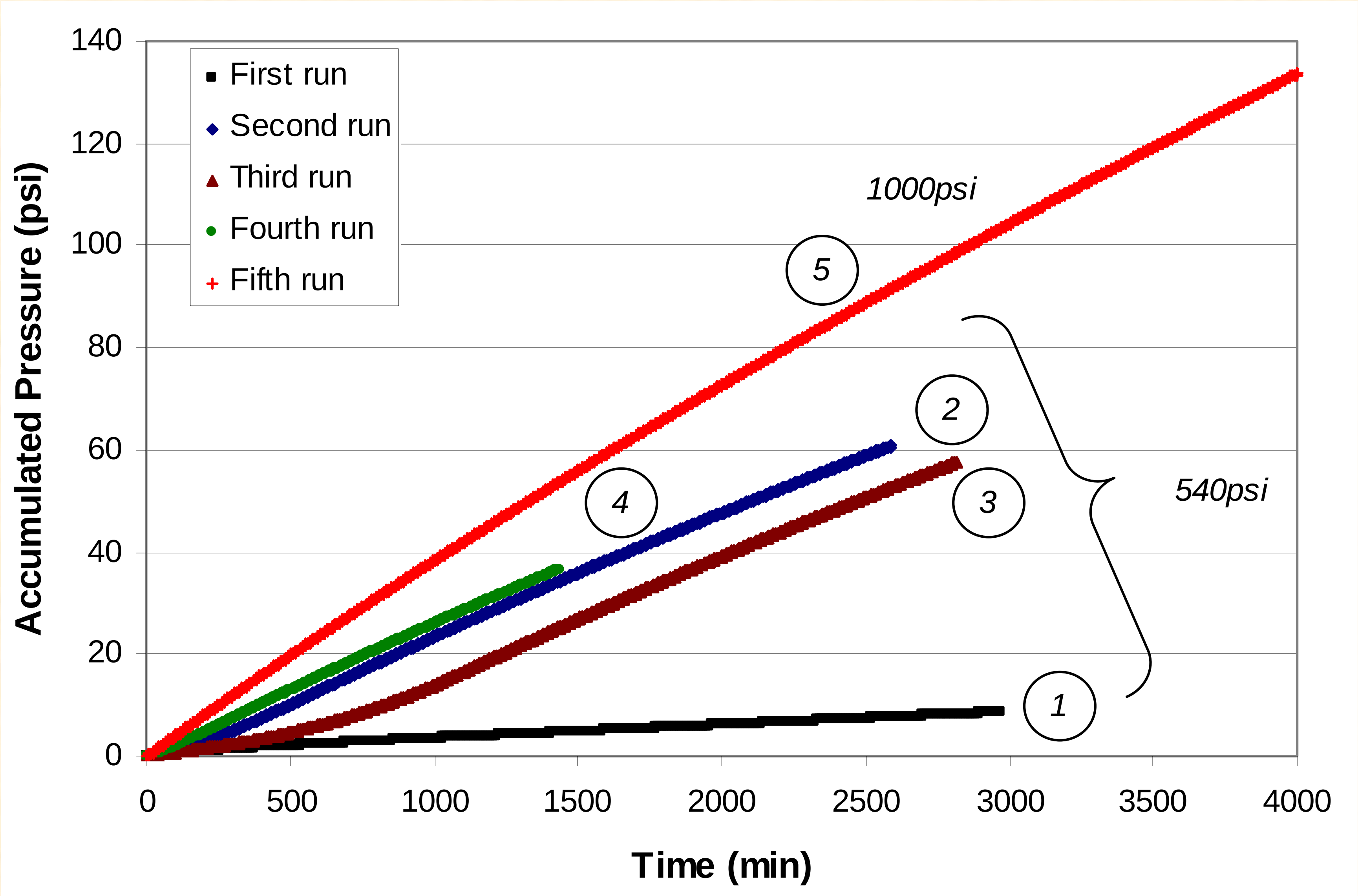
$$P = J_{ss} \frac{l}{\sqrt{\Delta p_{H_2}}} \quad \left(\frac{psi^{1/2}}{cm \sec}\right)$$

- The amount of hydrogen is converted to pressure in a 1 cm^3 volume at 25°C

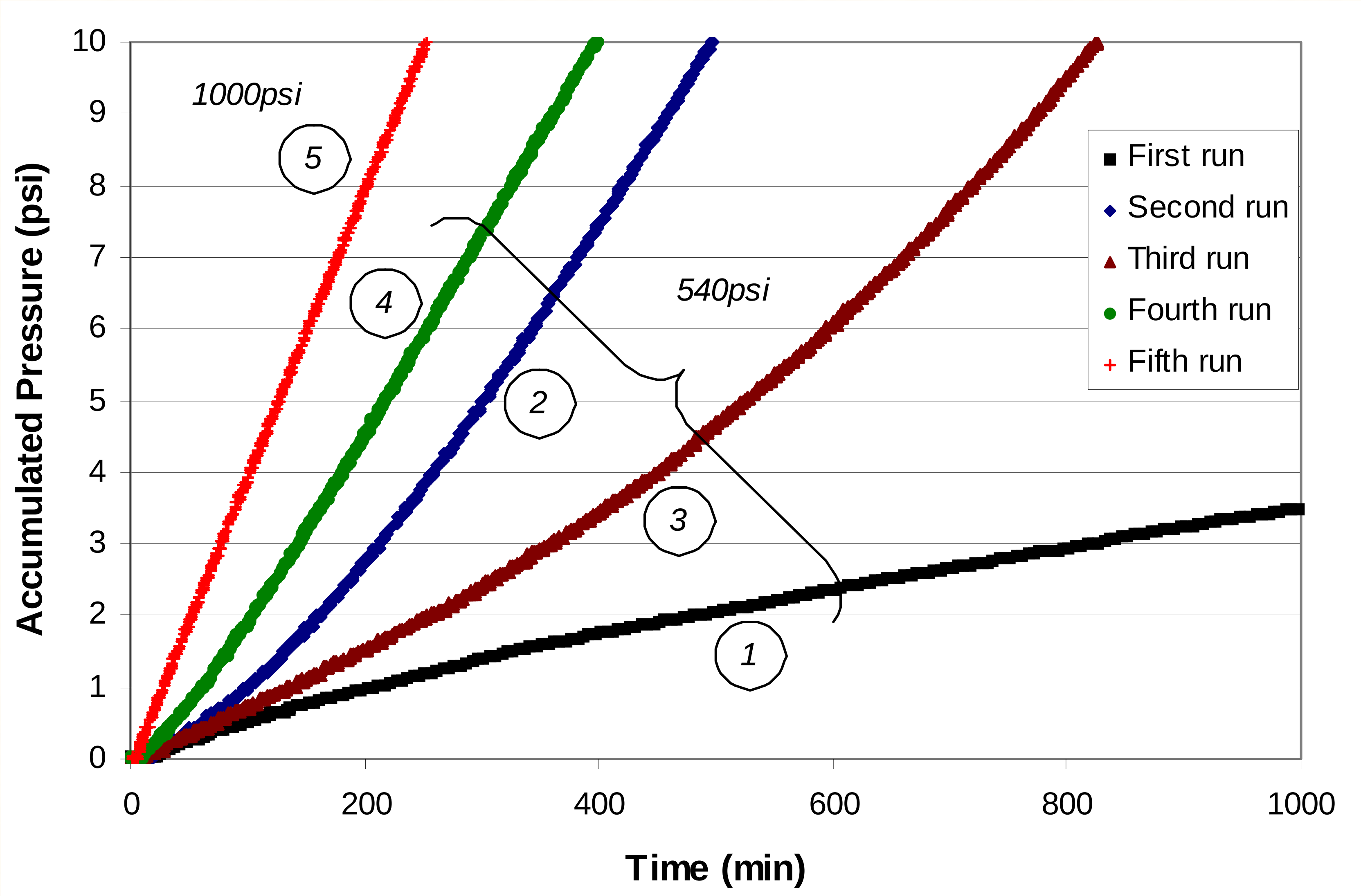
High-Pressure Permeation Measurement

- X52 steel
- Surface condition:
  - Upstream side: EDM cut surface
  - Downstream side: hand-polished with grit 600 sandpaper
- One temperature (~170°C) and two pressure levels (~540, and 1020 psi)
- One sample charged several times
  - Degassing at testing temperature for >4x saturation time
  - Diffusible hydrogen is sufficiently removed, but trapped hydrogen (if any) will remain in the sample

Permeation Curves for X52 under High H2 Pressure



Initial transients varied considerably



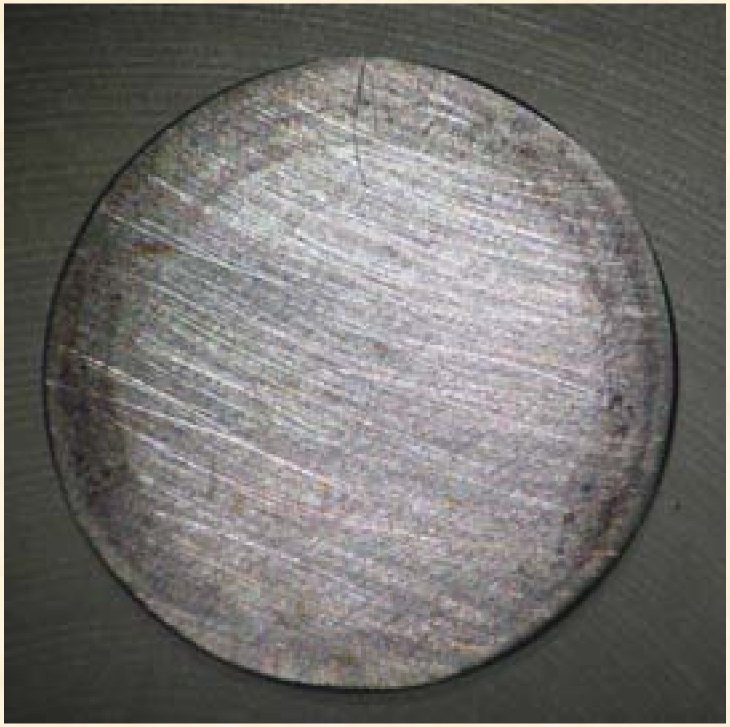
Effective Diffusivity & Permeability

Test Condition	First run	Second run	Third run	Fourth run	Fifth run
Temperature, (C)	165	169	169	169	170
Thickness, (cm)	0.05	0.05	0.05	0.05	0.05
Upstream pressure, psi	499	533	544	550	1022
Permeability ($psi^{1/2}$/sec/cm)	4.364E-06	4.273E-05	4.112E-05	4.233E-05	4.685E-05
Tlag, (min)	-333.9	121.0	464.7	26.1	3.6
Diffusivity, (cm^2/sec)	**N/A**	**5.74E-08**	**1.49E-08**	**2.66E-07**	**1.95E-06**

- First run (virgin sample) had negative t_{lag}
- Considerable variation in effective diffusivity
  - For same condition testing (between 2nd to 4th run): one order of magnitude
  - Effect of initial transient
  - High pressure level, higher diffusivity
- Permeability: very consistent
  - Pressure is standardized for $1cm^3$ volume at 25°C
- Causes of initial transient variation are unclear

High-pressure testing sample: no noticeable surface color change

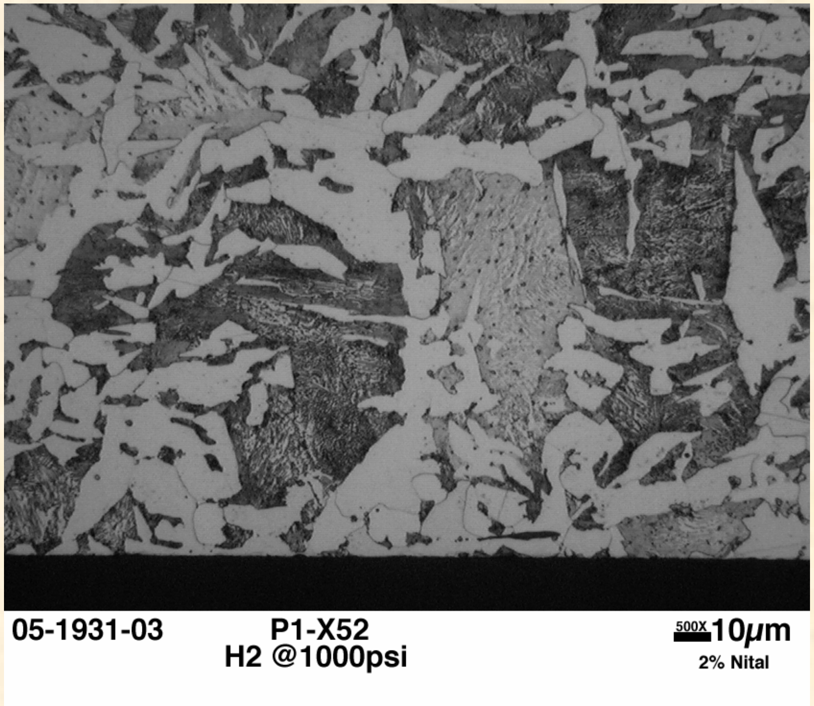
Upstream side: EDM cut surface



Downstream side: hand-polished with 600 grit sandpaper

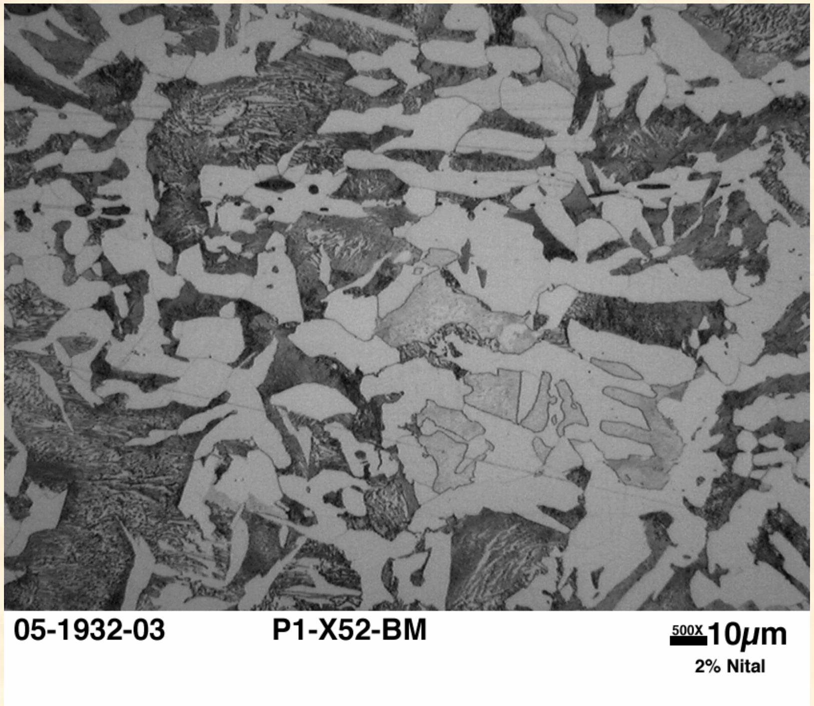
Microstructural changes are not significant after exposure to many days of high-pressure H2 at 170°C

After repeated H2 charge



Microhardness: 181Hv

Before H2 charge

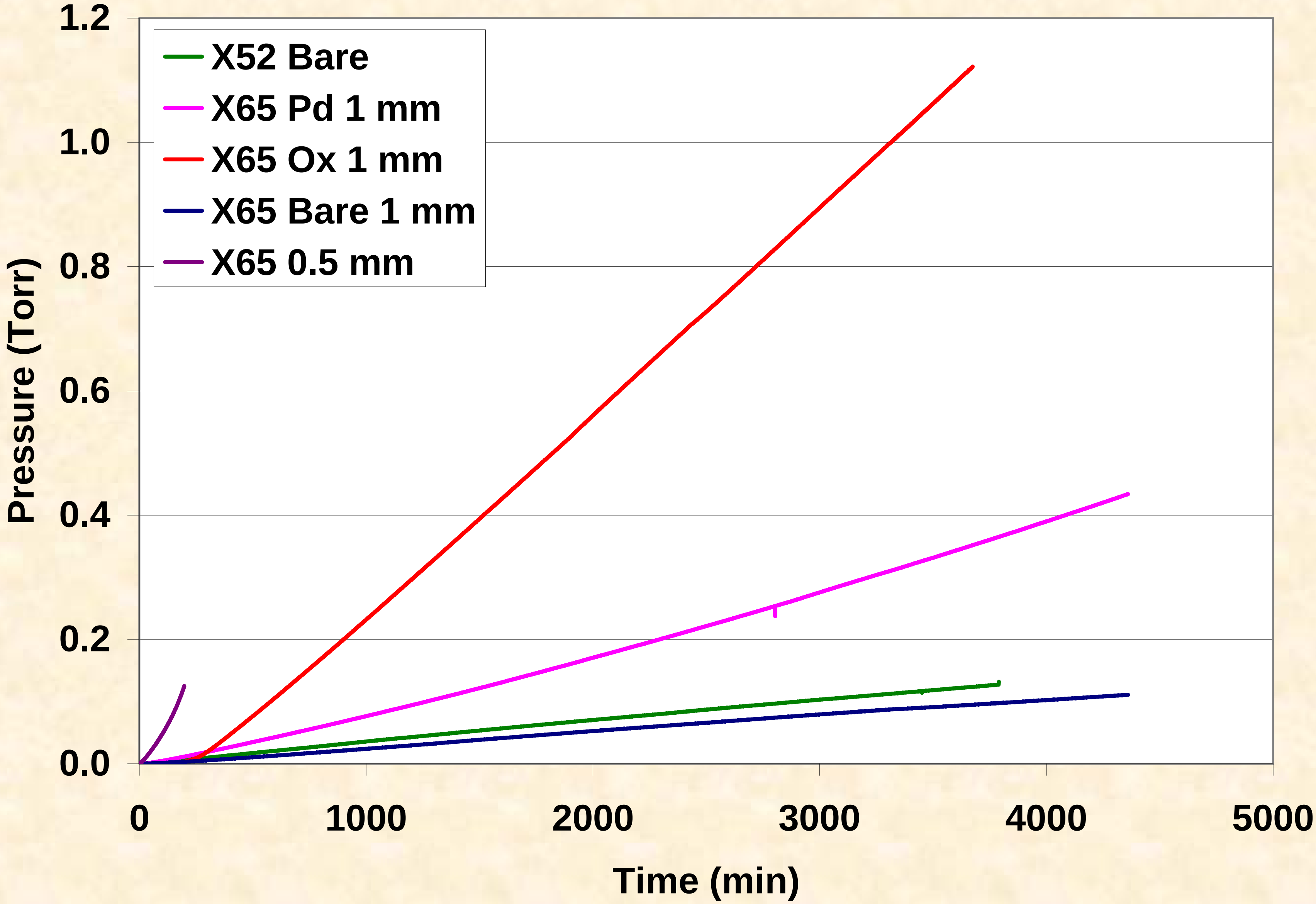


Microhardness: 189Hv

Low pressure permeation testing

- To investigate the effects of surface condition
  - Different surface coatings
- To separate surface and hydrogen trap effects by using two different sample thickness

Low Pressure Permeation Test Results 150C 700 Torr



Data Compilation: Both Labs

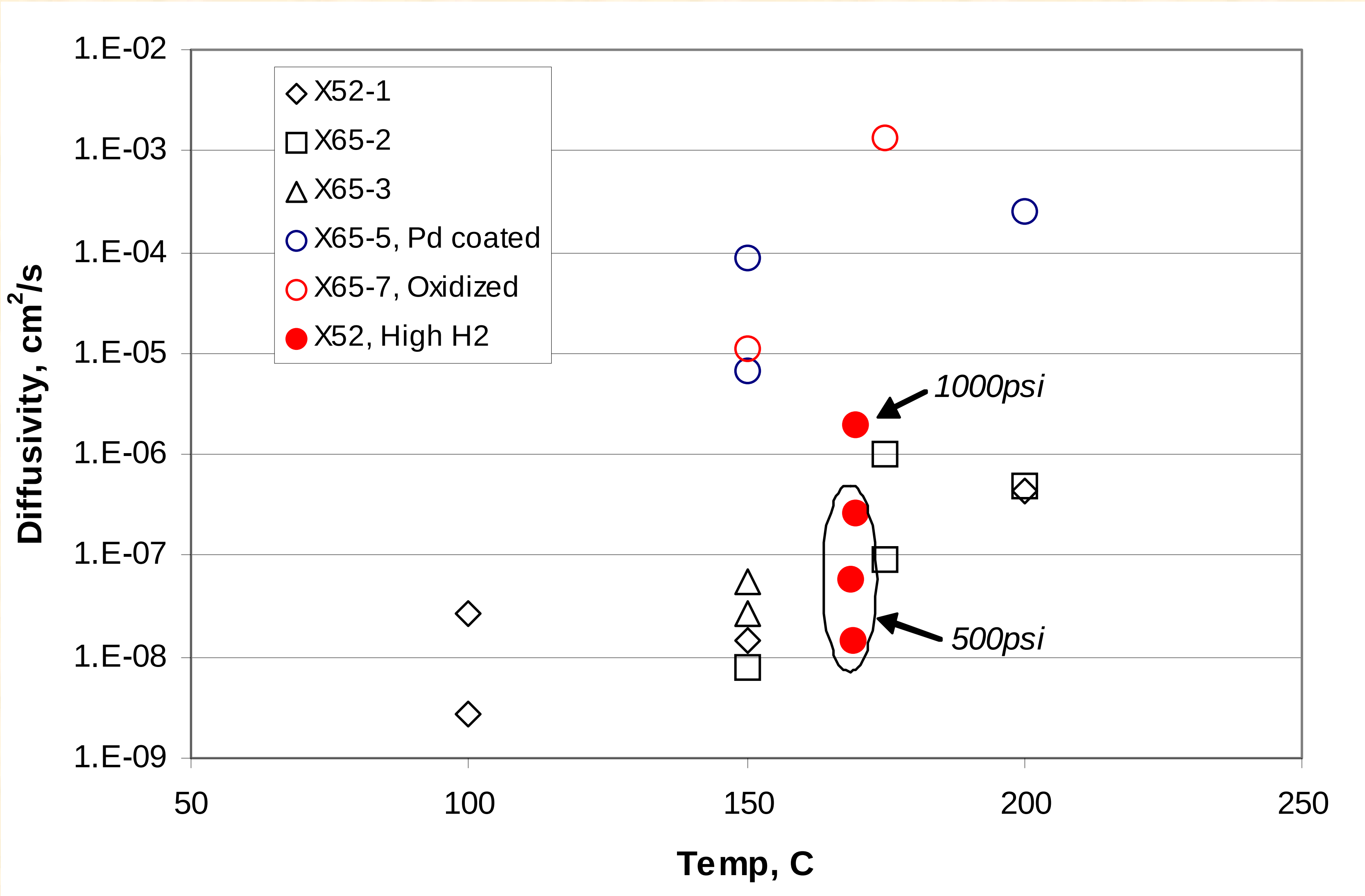
Sample ID	Temp (^oC)	Pressure (psi)	Surface	Thickness (cm)	Diffusivity (cm^2/s)	Permeability ($psi^{1/2}/cm/s$)
P1-2	100	13.5	Lt grind	0.0508	2.78E-09	4.03E-07
P1-2	100	13.5	Tested	0.0508	2.73E-08	4.02E-07
P1-2	150	13.5	Tested	0.0508	1.46E-08	1.08E-06
P1-2	200	13.5	Tested	0.0508	4.42E-07	7.93E-07
P2-2	150	13.5	Tested	0.0508	7.95E-09	5.24E-07
P2-2	175	13.5	Tested	0.0508	9.39E-08	1.18E-06
P2-2	175	13.5	Tested	0.0508	9.92E-07	1.67E-06
P2-2	200	13.5	Tested	0.0508	4.82E-07	2.36E-06
P2-3	150	13.5	Lt grind	0.0508	2.75E-08	1.25E-06
P2-3	150	13.5	Tested	0.0508	5.43E-08	1.47E-07
P2-5	150	13.5	Pd Coated	0.1016	6.68E-06	2.96E-06
P2-5	150	6.75	Tested	0.1016	8.67E-05	2.41E-06
P2-5	200	13.5	Tested	0.1016	2.47E-04	2.43E-05
P2-7	150	13.5	200C/4 hours	0.1016	1.08E-05	9.00E-06
P2-7	175	13.5	Tested	0.1016	1.32E-03	1.53E-05
P1-ORNL	165	499.1	Lt grind	0.0508		4.36E-06
P1-ORNL	169	533.2	Tested	0.0508	5.74E-08	4.27E-05
P1-ORNL	169	544.3	Tested	0.0508	1.49E-08	4.11E-05
P1-ORNL	169	549.8	Tested	0.0508	2.66E-07	4.23E-05
P1-ORNL	170	1022.2	Tested	0.0508	1.95E-06	4.68E-05

Surface condition variations due to excessive temperature excursion at the beginning of testing

Low pressure side (cleanliness of two bare samples and gold tint of oxidized)

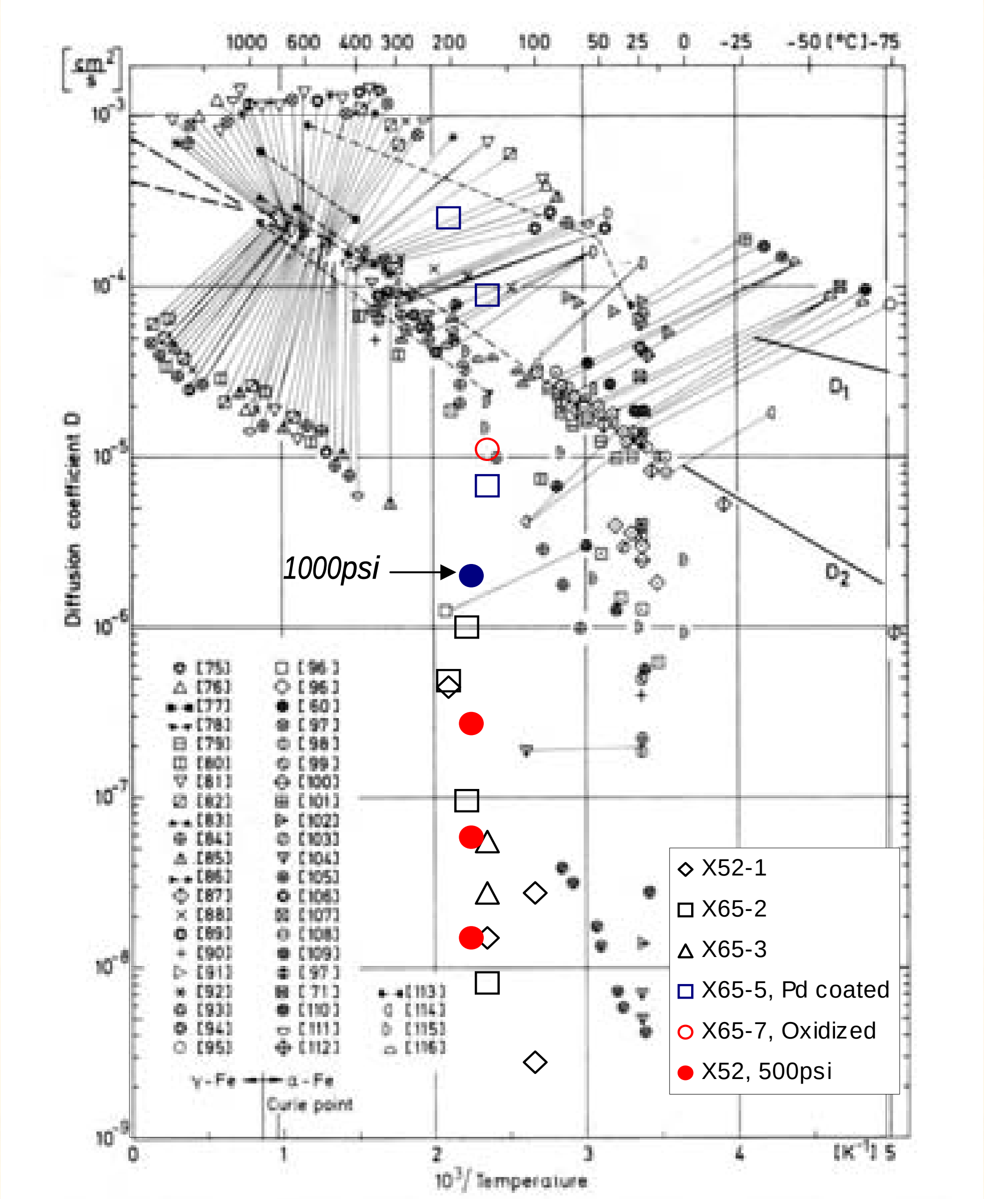
Hydrogen source side (gold in oxidized, metallic gray in P1-x, and violet for P2-6)

Diffusivity data obtained in this program

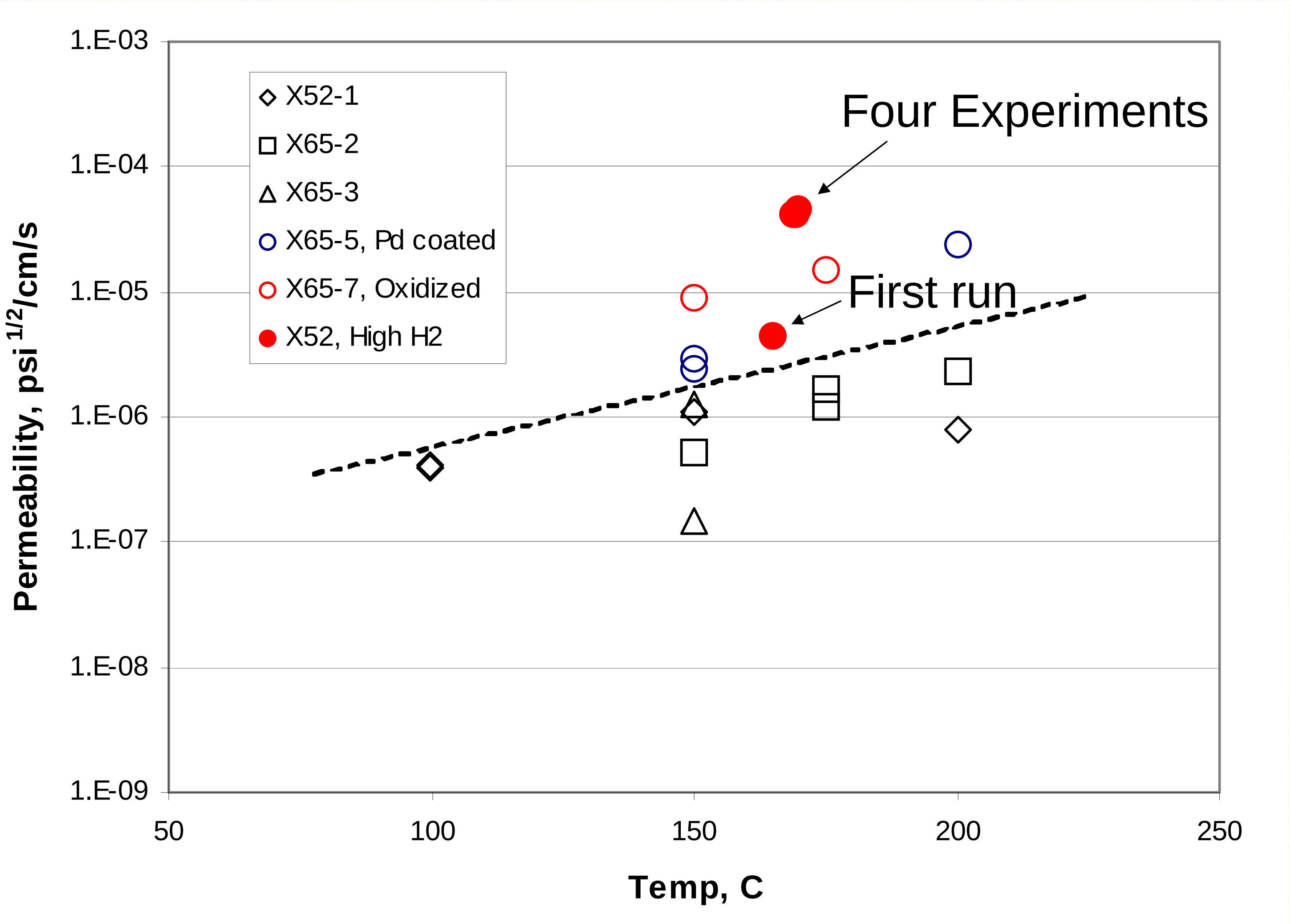


Comparison with diffusivity data in the open literature

- Measured diffusivity under gaseous H_2 charge is generally lower than these in literature - obtained electrochemically
- Perhaps due to differences in surface conditions



Permeability Results



Estimated leak rate in steel pipelines

- Assuming: 1 mile long, 36” dia, ½” thick steel pipe at 5000 psi (gas volume = 1.3x10^7 SCF @ 25°C, 1 atm) for one day

$$Leak\ Rate\ (\frac{SCF}{day \cdot mile}) = JAt = \frac{P\sqrt{\Delta p}}{l}\pi DLt\frac{0.0328^3}{14.8}$$

	Upper bound	Lower bound
Permeability (psi$^{1/2}$/cm/s)	4.50E-05	1.00E-07
Leak rate, SCF/day/mile	2.40E+04	53
Leak rate, psi/day	9.470	0.021

- Upper bound: 170°C, highest permeability
- Lower bound: extrapolation to 25°C

Summary

- High-pressure hydrogen permeation system and experimental procedures have been developed
- Initial H_2 permeation measurement completed
  - Surface conditions appeared to strongly influence diffusivity
  - Reasons for variations in diffusivity need to be investigated
- Permeability
  - Leak through steel pipe wall has been estimated based on measured permeation data

Future Plans

- FY06

Milestone	Completion Date
Complete hydrogen permeation study on the effects of hydrogen pressure for two pipeline steels	4/06
Complete hydrogen permeation study on the effects of base metal microstructure for two pipeline steels	6/06
Complete characterization of microstructure of steels with and without hydrogen charging	6/06
Complete characterization of microstructure changes in simulated weld and HAZ of pipeline steels	9/06
Finalize testing apparatus design for mechanical property degradation	3/06
Obtain initial experimental results on hydrogen induced property degradation of different pipeline steels	9/06

Weld!

- FY07 and beyond
  - Complete evaluation of hydrogen embrittlement and permeation behavior of selected high-strength steels and their welds
  - Develop a H2 permeation and mechanical properties database for both existing pipeline steels and next-generation high-strength steels under gaseous high-pressure hydrogen environment.
  - Report on the suitability of welding practices for construction and repair of hydrogen pipelines.

Questions?

Hydrogen cracking has been a safety concern for welding construction of steel pipelines

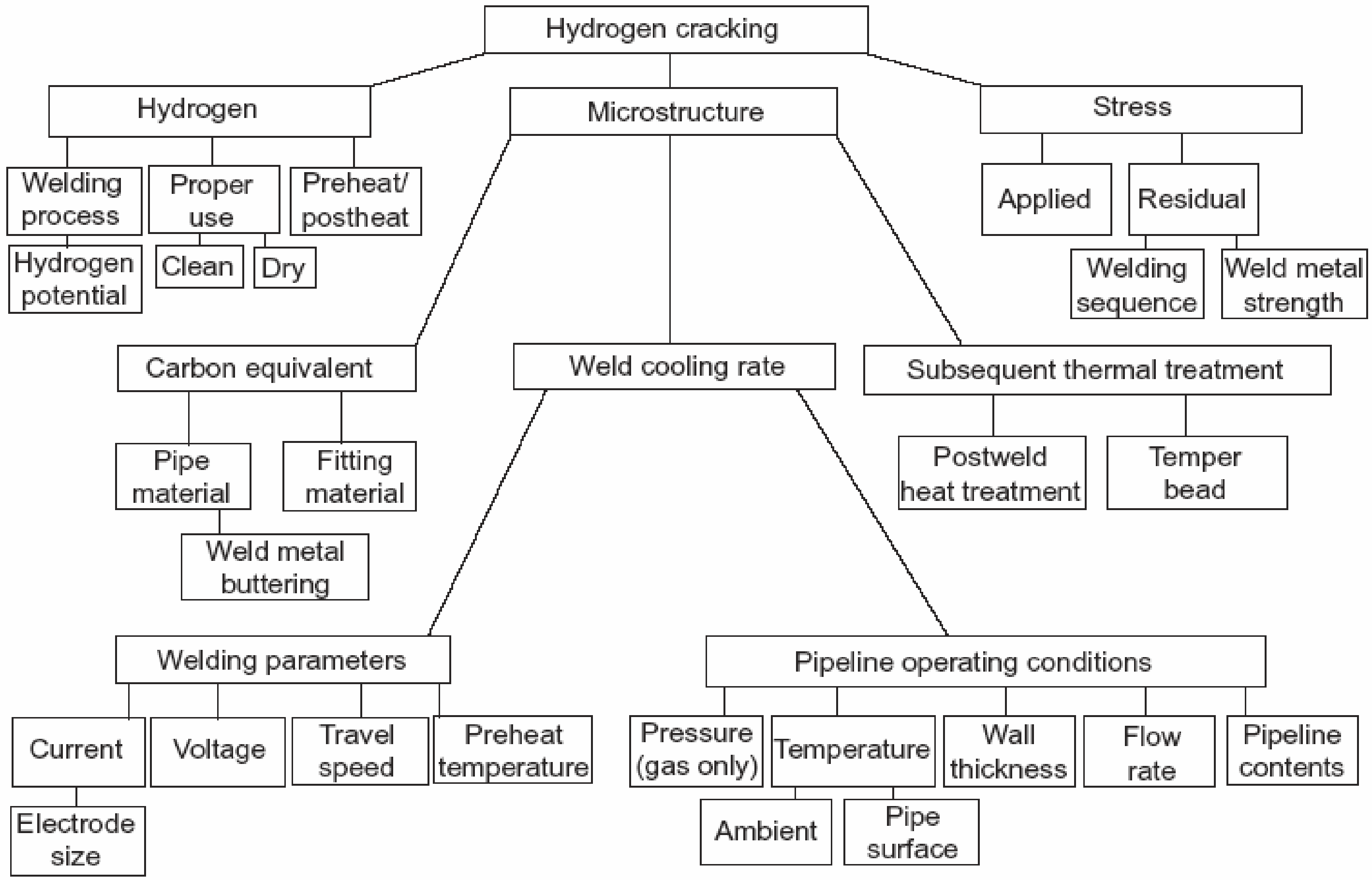


Figure 12. Factors influencing HIC in weldments (Timmins 1997).

- Three factors: Susceptible microstructure,Tri-axial state of stress & Presence of diffusible hydrogen

New challenges for hydrogen pipelines

- Inside of the pipe will be always exposed to high pressure of hydrogen

Special Sample Holder Design to Eliminate Background Lead during High-Pressure Permeation Test