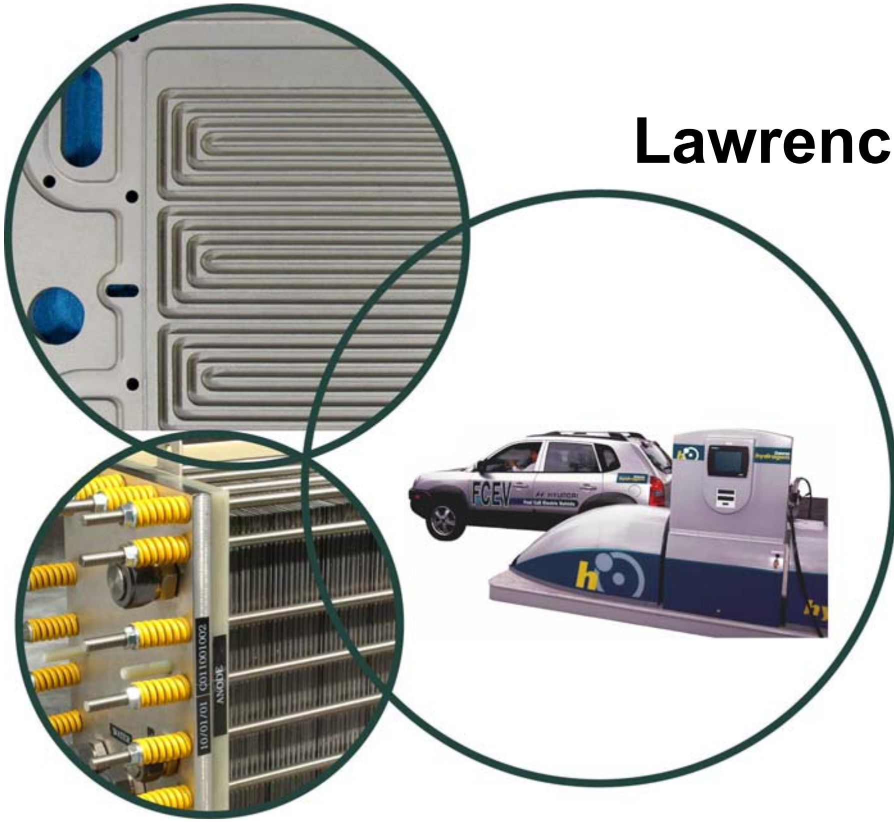
Composite Technology for Hydrogen Pipelines



Barton Smith, Barbara Frame, Lawrence Anovitz, Timothy Armstrong

Oak Ridge National Laboratory

Annual Merit Review
Arlington, Virginia
June 11, 2008

Project ID #: PD19

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

- Start: Jan 2005
- Finish: Project continuation & direction determined annually by DOE

Budget

- Total project funding
  - DOE: $1.05M
- Funding received in FY 07
  - $450k
- Funding for FY 08
  - $450k

Barriers

- D. High Capital Cost and Hydrogen Embrittlement of pipelines
- Technical Targets on next slide

Partners & Collaborators

- Fiberspar, PolyFlow
- Arkema, Ticona, Fluoro-Seal
- SRNL
- Pipeline Working Group

Overview

- **Technical Targets**

Category	2005 Status	2012	2017
Pipelines: Transmission			
Total Capital Investment (16-in pipeline, $/mile)	$720k	$600k	$490k
Pipelines: Distribution			
Total Capital Investment (2-inch pipeline, $/mile)	$320k	$270k	$190k
Pipelines: Transmission and Distribution			
Reliability/Integrity (including 3rd-party damage issues)	Acceptable for current service		Acceptable for H_2 as a major energy carrier
H_2 Leakage *	Undefined	TBD	< 0.5%

* Leakage targets are being reviewed by the Delivery Tech Team

Project Milestones

Month-Year	Milestone or Go/No-Go Decision
May 2008	Milestone: Initial round of polymer diffusivity and permeability measurements completed.
Sep 2008	Go/no-go decision: Hydrogen compatibility evaluation of composite pipeline materials and construction completed and reported (on track) Milestone: Survey of existing modifications and treatments available for reducing permeability in liner materials completed and reported (40% complete) Milestone: Recommendations for sensor integration, manufacturing and joining technologies completed and reported (20% complete)

Plan & Approach

50% complete

- **Task 1: Pipeline Materials Compatibility**
  - Accelerated aging in H_2
  - Testing and evaluation

60% complete

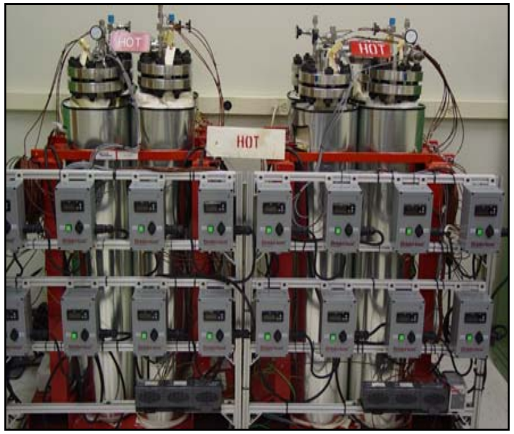
- **Task 2: Liner permeability**
  - Survey and measure polymer *D* and *P*
  - Assess modification and treatment options

20% complete

- **Task 3: Joining and sensor technologies**
  - Assess coupling, termination, repair
  - Assess needs for structural health monitoring, leakage and gas property sensing

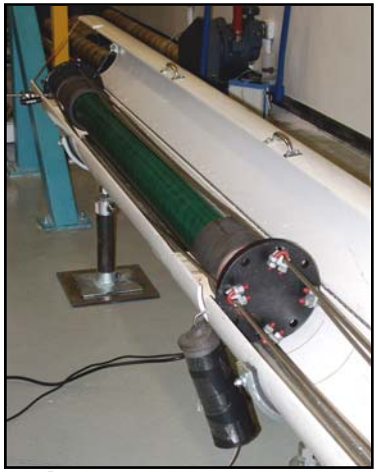
Technical Accomplishments

- **Task 1: Pipeline materials compatibility testing**
  - One-month hydrogen exposure completed with no materials degradation; longer-term exposure underway
  - Initial pipeline leakage measurements completed: smaller than expected leak rate (0.03% per day); additional measurements underway
  - Blowdown testing of FRP pipeline specimen in progress



H_2 exposure station at SRNL

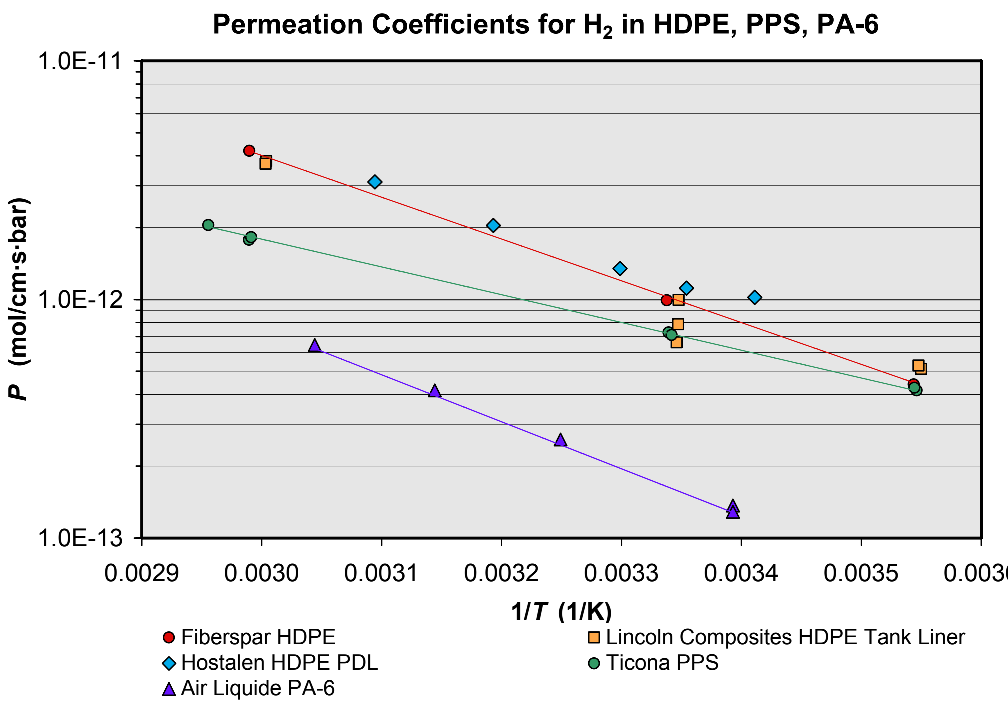
Pipeline test specimens



Leakage measurement at ORNL

Technical Accomplishments

- **Task 2: New contributions to polymer permeation literature**
  - Permeation coefficients for H_2 in HDPE exhibit pressure dependence
  - Coefficients for H_2 in PA and PPS are smaller than those for HDPE
  - Evaluation of surface fluorination treatment in progress



Technical Accomplishments

- **Task 3: Joining and sensor technologies**
  - Indirect evaluation of hydrogen leakage through Fiberspar LinePipe™ connectors showed very low leakage rate (<$3x10^{-6}$ mol/s)
  - Collaborative effort with SRNL to assess joint loading, pipeline flexure, and pressure/temperature cycling on hydrogen leakage for both Fiberspar and PolyFlow connectors

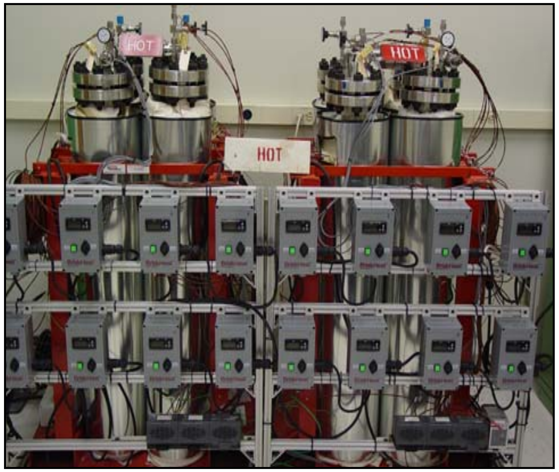
FiberSpar connector with compressive o-ring seals

PolyFlow swaged connector

One-month accelerated aging of Fiberspar materials completed

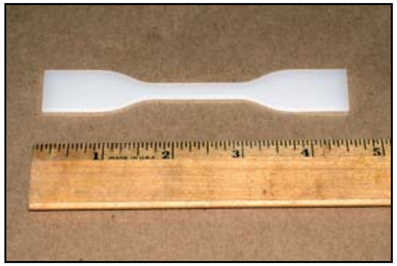
- **Accelerated aging procedure used to screen for long-term effects of hydrogen exposure on composite pipeline under normal-usage conditions**
- **Specimens of Fiberspar pipelines and constituent materials**
  - **Immersion in 1000 psi H_2**
  - **Accelerated aging at 140°F (60°C)**
  - **1 month & 8 month exposures**

4-pt bending test specimen



SRNL H_2 exposure station

Compression test specimen



Tensile-test specimen of liner material

No measurable degradation in materials performance after accelerated aging

- **Post-exposure testing of pipeline specimens and materials**
  - 4-point bending test to assess laminate cracking
  - Short-term pressure burst test (ASTM D1599)
  - Parallel plate compression test (ASTM D2412)
  - Tensile tests and DMA of liner, matrix resin, glass filaments
- **No statistically significant differences between as-received, air-exposed and hydrogen-exposed pipeline specimens and materials**

4-pt bending test at Fiberspar

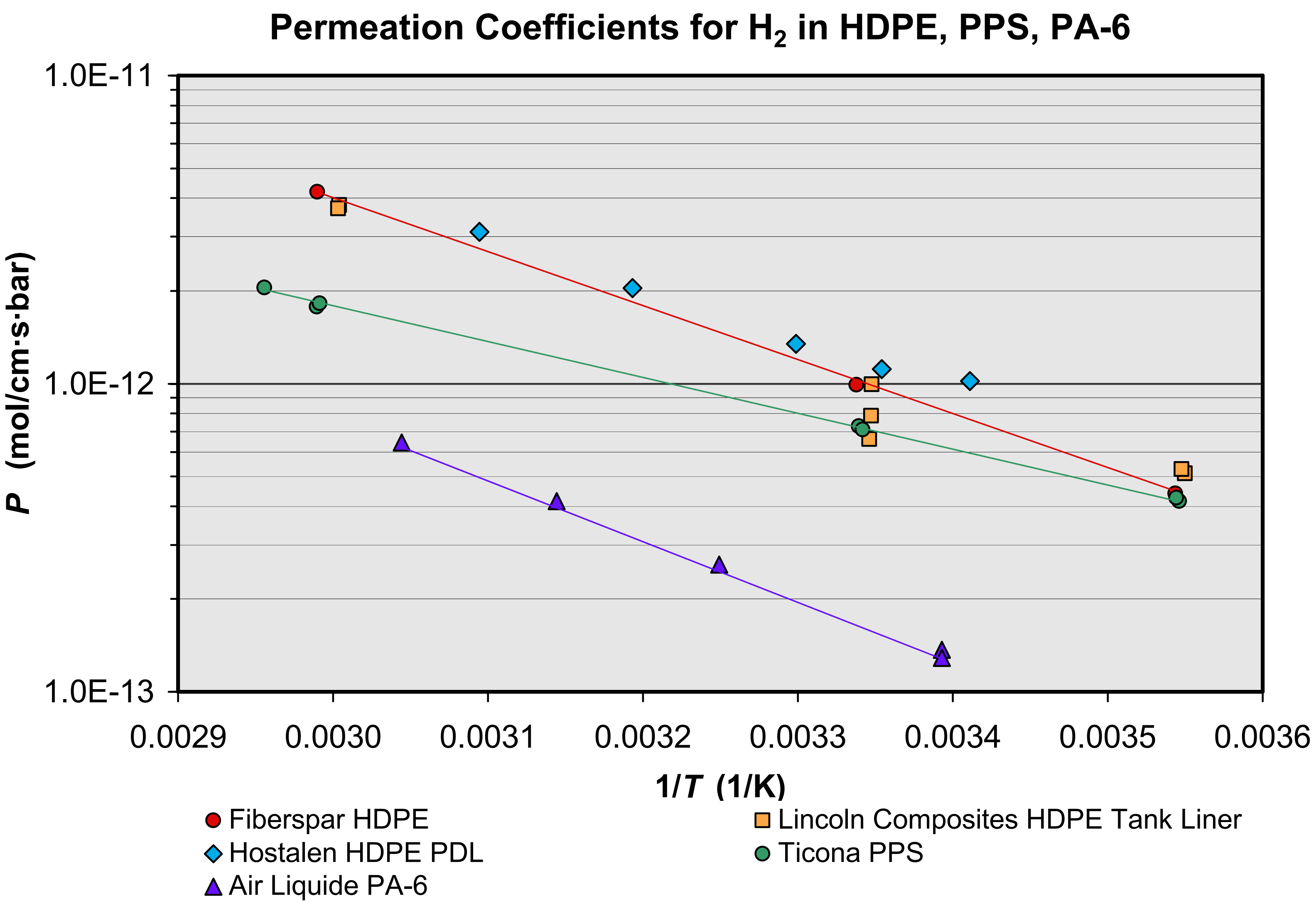
Single glass filament used for strength, elongation and modulus measurements

No reduction in tensile properties of epoxy matrix resin

	Epoxy Matrix Resin Conditioning	
Test (dog bone)	**Air** @ 140°F 1 month	**1000 psi H_2 *** @ 140°F 1 month
Tensile Strength	7,891 psi (27.9)	8,791 psi (20.2)
Elongation	2.9 % (43.1)	3.5 % (40.0)
Tensile Modulus	371 ksi (1.1)	371 ksi (0.6)

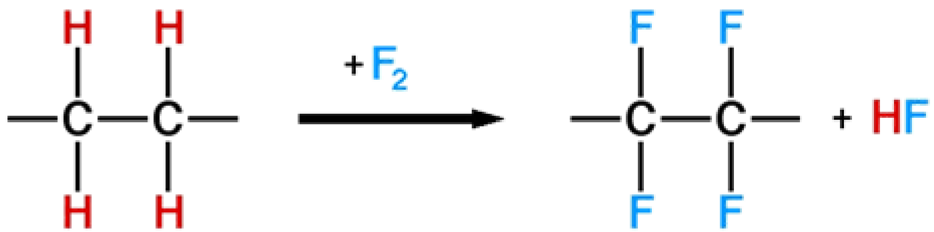
* H_2 conditioning at SRNL.
Numbers in parentheses are % coefficients of variation for data set.

New permeation coefficient measurements for H_2 in HDPE, PPS



Polymer surface modification in progress

- **Polymer surface modification via fluorination**
  - **Surface fluorination used in packaging industry to reduce emission of VOCs**
  - **Reduces *D* and *P* of VOCs by factors of 1.5 to 4.5 in HDPE containers**
- **Surface fluorination proceeds via free radical mechanism in molecular exchange along polymer chains at surface**



- **Fluoro-Seal is providing fluorination treatment of pipeline-grade HDPE, PPS, PA**
- **Expect results in 4th reporting period**

Prediction of H_2 leak rate for Fiberspar pipeline with HDPE barrier tube

- **Fiberspar LinePipe 4-1/2 1,500 (E)**
  - **Barrier tube: extruded PE-3408**
  - **Tube inner radius = 5.05 cm**
  - **Tube outer radius 5.576 cm**
- **Hydrogen leak rate per unit length of barrier tube given by**

$$\frac{dn}{dt} = \frac{2\pi P}{\ln(b/a)}(p_0 - p_1) \qquad \mathrm{mol \cdot s^{-1} \cdot m^{-1}}$$

where

P **= permeation coefficient for hydrogen in HDPE**

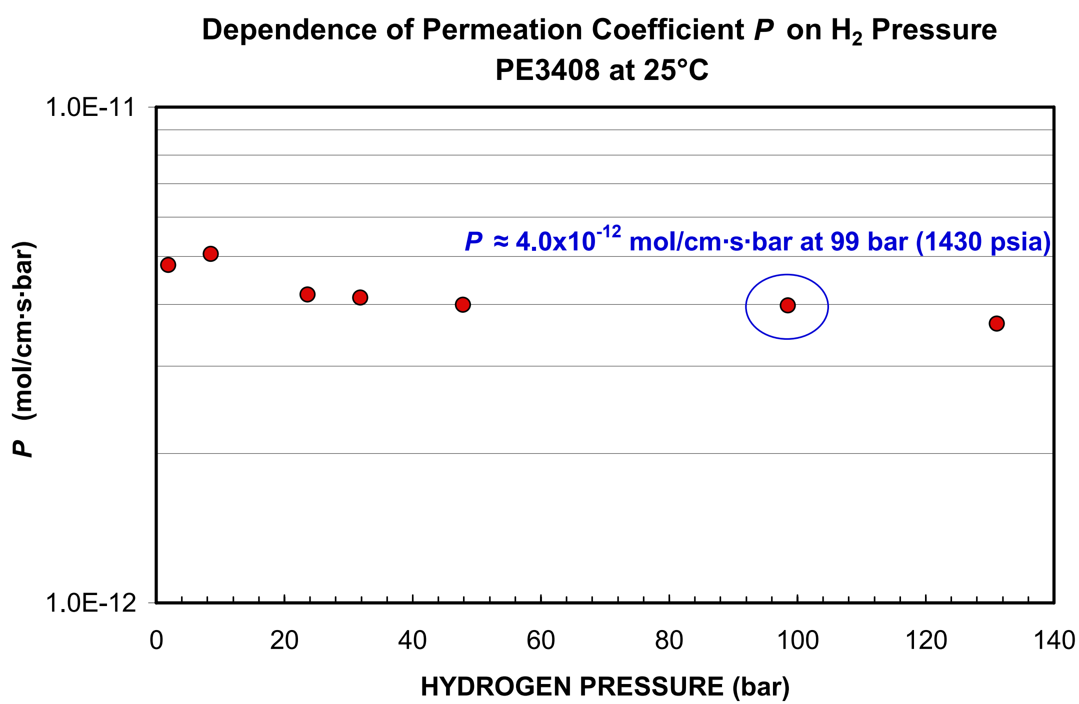
a,b **= inner, outer radii of tube wall**

p_0, p_1 **= hydrogen pressures inside, outside tube**

Prediction of H_2 leak rate in Fiberspar pipeline with HDPE barrier tube

- **Parameter values**
  - $P \approx 4\text{x}10^{-12}$ mol/cm·s·bar
  - a= 5.05 cm, b= 5.576 cm
  - p_0= 99 bar, p_1= 1 bar

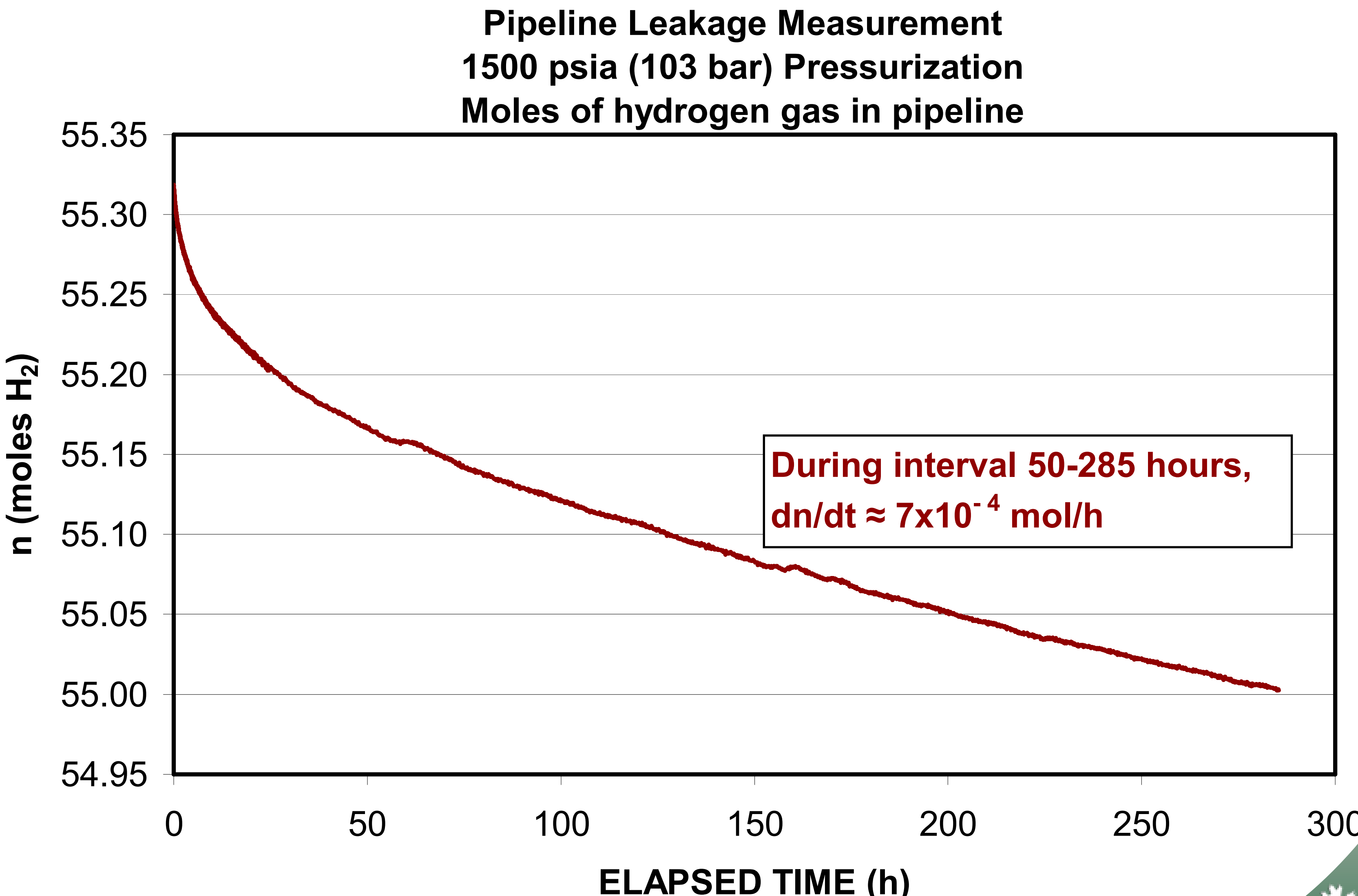
- **Predicted hydrogen leak rate in 1.83-m pipeline**
  - dn/dt = $1.7\text{x}10^{-2}$ mol/h
  - This leak rate would be equivalent to a loss of $3.4\text{x}10^{-5}$ kg/h



Measurement of H_2 leak rate in Fiberspar pipeline with HDPE barrier tube

- **Pressure decay measurement**
  - Using quartz pressure transducer with digital output
    - Range: 0-3000 psia (0-200 bar)
    - Accuracy: 0.01% (0.3 psi / 20 mbar) in 0-70 °C range
- **Temperature compensation for pipeline pressure**
  - RTD sensors inside pipeline measure gas temperature
  - Pressure corrected using Able-Noble EOS for hydrogen
- **Volumetric expansion compensation**
  - Pressure-induced expansion and contraction involves bi-axial stress-strain relationships, differing axial and hoop moduli, Poisson ratios for major and minor axes
    - Change in volume expected to be < 0.01% per psi at 1500 psia and RT → no correction applied

Measurement of H_2 leak rate in Fiberspar pipeline with HDPE barrier tube



H_2 leak rate in pipeline with HDPE barrier tube is better than expected

- Leakage from end cap seals is not a significant contribution to total leak rate
- Product loss due to permeation
  - $dn/dt = 7x10^{-4}$ mol/h → $2x10^{-2}$ mol/d
  - Pipeline under test contained approx. 55 mol H_2
  - Loss due to barrier tube permeation and end cap seal leakage was 0.03% per day, about 20 times less than that predicted using permeation coefficient for PE-3408 liner

Hydrogen blowdown testing of composite pipelines in progress

- **Guidance: API 15S - Qualification of Spoolable Reinforced Plastic Line Pipe***
  - **Fill specimen with hydrogen to pressure rating, heat specimen to temperature rating, and hold these conditions until pipeline structure is saturated with gas**
  - **Following hold period, de-pressurize specimen at a rate not less than 1000 psi/min**
  - **Examine specimen liner for evidence of blistering or collapse**

1-meter pipeline specimen instrumented for blowdown testing

***API 15S Appendix D specifies that supercritical CO_2 be used for blowdown testing**

Future Work

- **FY 2008**
  - Report test results from 8-month accelerated aging and hydrogen exposure of pipeline and material specimens
  - Continue measurements of liner materials, including measurements of surface fluorination samples
  - Construct diffusion and permeation apparatus for polymers, with additional capabilities
- **FY 2009**
  - Begin assessment of possible hydrogen-induced cracking in the reinforcement layers during cyclical strain, perform long-term stress rupture tests, perform high-pressure cyclical fatigue tests, assess joint sealing under cyclic loading
  - Complete assessment of joining and integrated sensor technologies and report results
  - Collaborate on development of codes & standards for hydrogen-service FRP pipelines

Project Summary

Relevance: Need viable alternative to metallic pipelines to achieve cost and performance targets for hydrogen transmission and distribution

Approach: Investigate applicability of composite pipelines in use in oil & gas gathering operations and develop path forward for hydrogen delivery

Progress: Cost scenario shows composite pipelines are meet DOE 2012 goals and are close to 2017 goals; hydrogen compatibility of pipeline materials is acceptable; pipeline leakage rates are better than predicted

Collaborations: Pipeline and polymer industries, National Lab

Future: Codes & standards; prototype FRP pipeline system for H_2 delivery; demonstration project