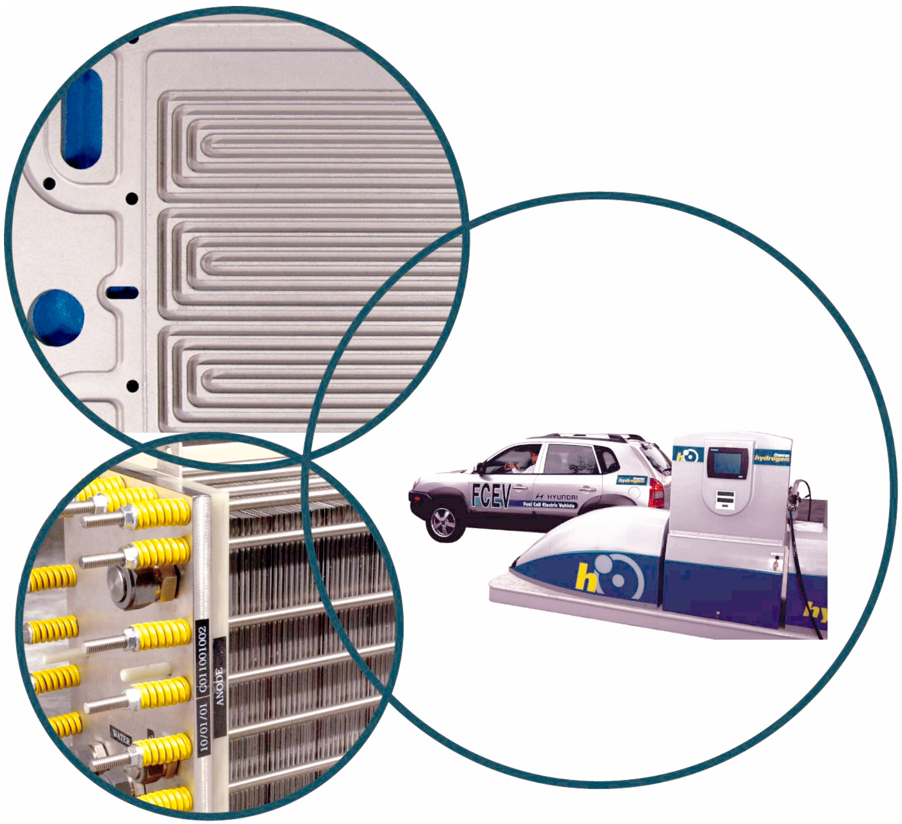
Lifecycle Verification of Polymer Liners in Storage Tanks



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Annual Merit Review
Washington, DC
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Project ID #: ST053

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Overview

Timeline

- Start: June 2008
- Finish: Project continuation & direction determined annually by DOE

Barriers

- Barriers and Technical Targets on following slide

Budget

- Total project funding
  - DOE: $750k
- Funding for FY 2012
  - $200k

Partners & Collaborators

- Manufacturers of Type 4 storage tanks
- NIST NCNR
- Storage Tech Team

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Relevance – Barriers and Technical Targets

Technical Barriers Addressed:

D. Durability of on-board storage systems – lifetime of at least 1500 cycles

G. Materials of construction – vessel containment that is resistant to hydrogen permeation

M. Lack of Tank Performance Data and Understanding of Failure Mechanisms

Technical Targets:

Operational cycle life (1/4 tank to full) –
FY 2017: 1500 cycles; Ultimate: 1500 cycles

Environmental health & safety –
Permeation and leakage: Meets or exceeds applicable standards
Loss of useable H_2 (g/h/kg H_2): FY 2017: 0.05; Ultimate: 0.05

Barriers and technical targets are from the Fuel Cell Technologies Program MYRDD Plan, Section 3.4 - Hydrogen Storage, September 2011 interim update.

Collaborations

- **High-pressure compressed gas tank manufacturers**
  - Manufacturers of Type 4 composite compressed hydrogen and compressed natural gas storage tanks high-pressure fiber-reinforced polymer pipelines
  - Provide tank liner specimens and advisement on testing methods
- **NIST National Center for Neutron Research**
  - SANS and USANS scattering measurements on tank liner polymers
- **Storage Tech Team**
  - Provide project review and guidance

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Approach – FY 2012 Tasks and Milestone

- **Complete temperature cycling-permeation measurements tests on tank liners**
  - Tests on new liner materials
  - Perform post-cycling analysis

- **Develop Test Method for Cyclic Testing of Sectioned Storage Tanks**
  - Collaborate with tank manufacturers to obtain their advisement on the testing procedure and their provision of tank sections

Date	Milestone or Go/No-Go Decision
May 2012	Complete first 1,500 thermal cycles and permeation measurements on a future liner polymer
Sept 2012	**SMART Milestone:** Complete thermal cycling and permeation measurements on new set of polymer specimens at both 430 and 860 bar, and use data to assess ability of tank liners to retain a steady state hydrogen discharge rate that does not exceed 110% of the 75 Ncc/min permeation requirement of SAE J2579 § 5.2.2.1.3, and report results

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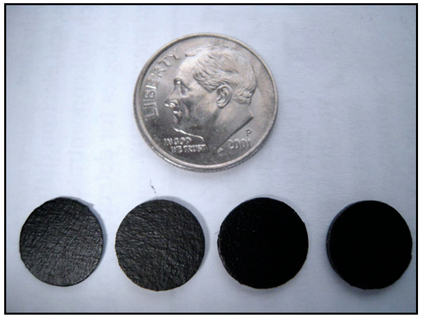
Approach – Technical Highlights

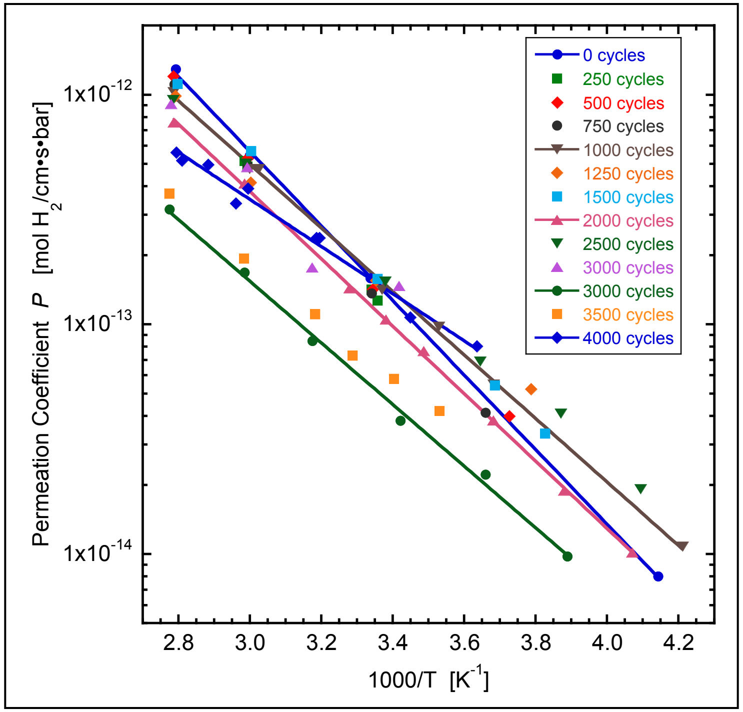
- **Temperature cycling alters H_2 permeability in HDPE**

  Permeation measurements on HDPE (with carbon) tank liner show progressive changes in the slope and pre-exponential scaling factor of the permeation curves that occur as the specimen undergoes simulated lifecycle temperature variations.



1-cm dia. x 1-mm thick specimens machined from 7.1-mm-thick HDPE liner

Hydrogen permeation coefficients *P* in HDPE specimen, measured at a differential pressure of 430 bar

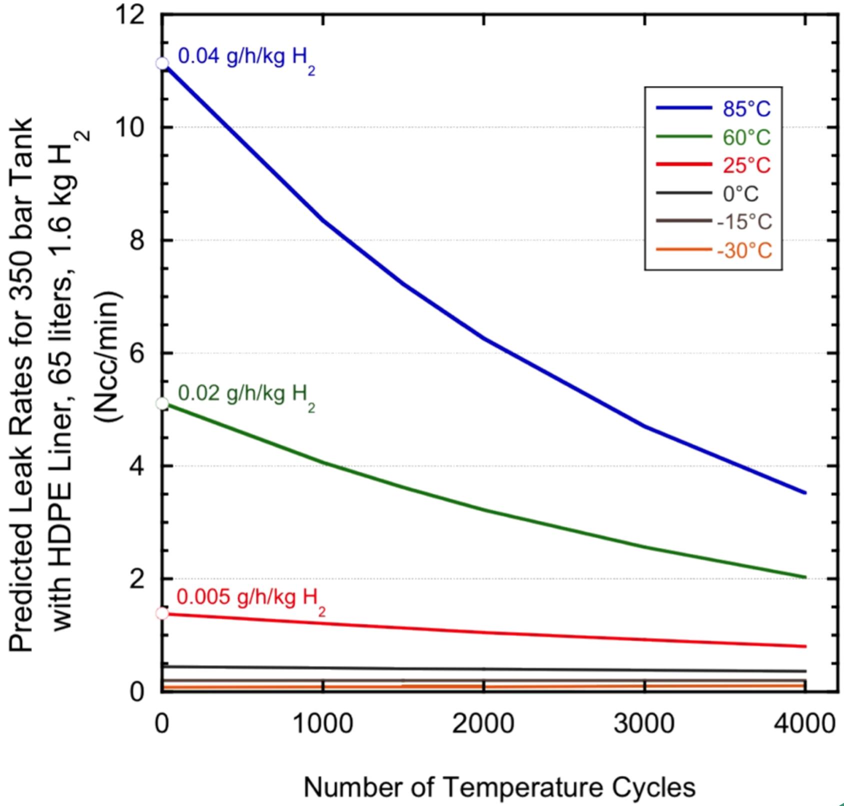


Approach – Technical Highlights

- **We predict H_2 leakage in HDPE-lined tank should remain below technical target**

  Using permeation coefficient data, we predict the HDPE liner in a 350-bar tank can be expected to maintain a H_2 leak rate that meets applicable leakage standards throughout the tank lifecycle

Predicted leak rate values for HDPE liner plotted as a function of liner temperature and number of temperature cycles for 350 bar tank



Approach – Technical Highlights

- **New temperature cycling and permeation measurement system is now online**
  - Temperature cycling between –40°C and 85°C
  - Shorter-duration temperature cycles: ~20 minutes (40% shorter than cycling time in original apparatus)
  - Maximum differential pressure across specimen is ~900 bar (13,000 psia)
  - Uses less hydrogen and substantially less power

- Difficulties leading to a delay in getting system online have impacted project schedule
  - Necessary to move system to a new lab in a different building
  - May milestone (completion of first 1500 cycles and permeation measurements on PA-6 liner) will probably slip to June completion

Improved temperature-cycling system – hydrogen manifold, high-pressure accumulator, temperature cycling controls, low-temperature chiller

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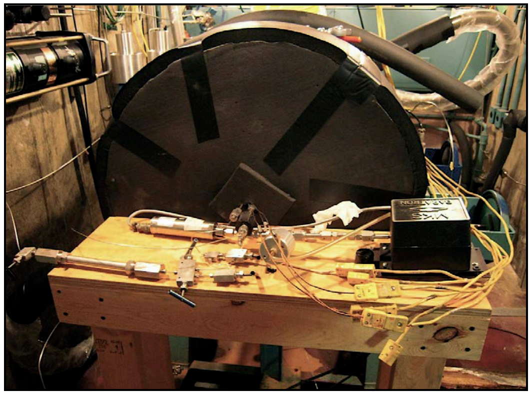
Technical Approach – Test protocol

- **Durability measurements of polymer liners in high-pressure storage tanks**
  – Subject polymer specimens to extreme-temperature cycling (–40 ⇆ 85°C) while specimens are differentially pressurized with hydrogen
  – Measure hydrogen permeation at prescribed intervals to assess the ability of the liner materials to maintain the required hydrogen barrier capability
    - Measurements at -40, 25, 60 and 85°C at completion of every 250 cycles (through 1500 cycles) and every 500 cycles (cycles 2000-5500)
  – Test protocol based on performance requirements specified in SAE J2579, *Technical Information Report for Fuel Cell and Other Hydrogen Vehicles* (Jan 2009)



High-pressure temperature-cycling system, modified from its original use for constant temperature D & P measurements in steels

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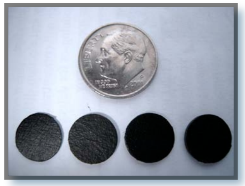
Technical Approach – Sample preparation

- **Original temperature cycling system uses 10-mm diameter disc specimens**
  - 1 mm wide annular ring sealing surface is insufficient to maintain high-pressure seal at low temperature extreme
- **New system was designed to use larger 60-mm-diameter thin disc specimens**
  - Faster, more reproducible permeation measurements
  - Enough material for post-cycling tensile tests
- **Specimens are machined from cylindrical tank liner sections**
  - Liner is lathe-turned at room temperature to thickness of 1 mm
  - Disc cut to specimen size using knife-edge punch
  - Disc surfaces wet-sanded to remove surface imperfections and improve sealing

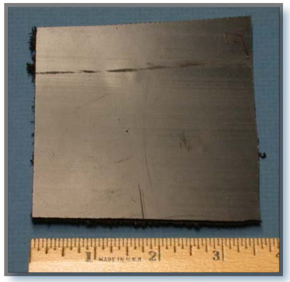


10-mm HDPE disc

60-mm PA-6 disc

PA-6 disc in pressure cell

PA-6 liner section provided by tank manufacturer



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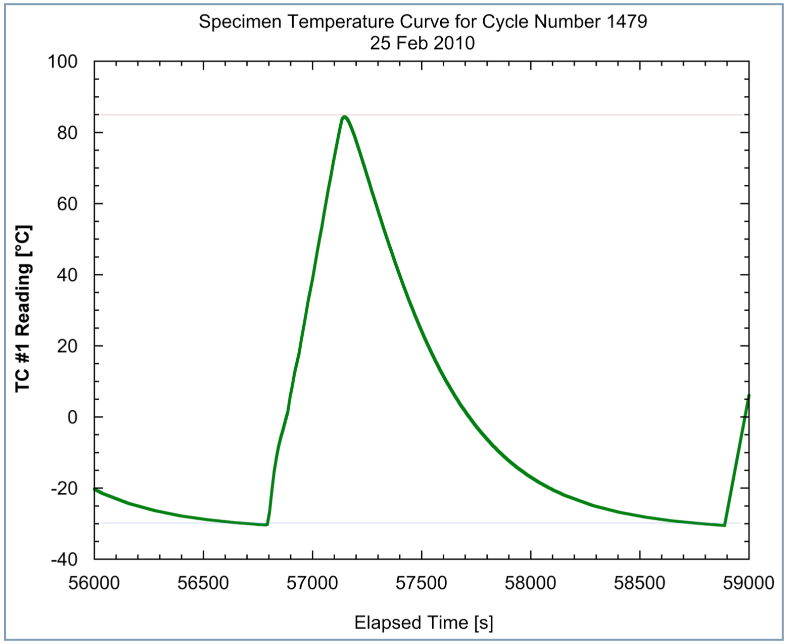
Technical Approach – Test protocol

- **Durability measurements of polymer liners in high-pressure storage tanks**

From SAE J2579 § 5.2.2

– 5500 temperature cycles: –40 ⇆ 85°C

- Upper and lower temperatures are the expected maximum and minimum tank service temperatures
- Cycle consists of a 5.75 minute heating interval (+20°C/minute), followed by a 28 minute cooling interval (~2 cycles/hour)



In original system, cycle minimum temperature is due to high H_2 leak rates through seals at temperatures below about –30°C

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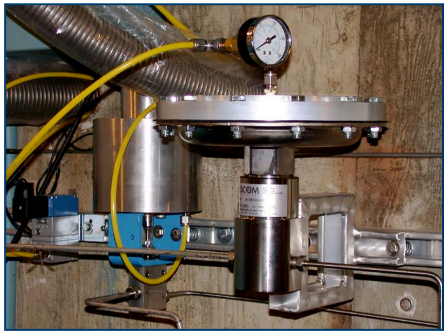
Technical Approach – Test protocol

- **Durability measurements of polymer liners in high-pressure storage tanks**
  - Upstream hydrogen pressures:
    430 and 860 bar (6,250 and 12,500 psia)
  - Constant pressure differential across maintained using computer-controlled accumulator/regulator system
    - We maintain the high upstream pressure during temperature cycling using a computer-controlled high-pressure regulator fed from high-pressure large-volume accumulators
    - We keep the downstream pressure at or below atmospheric pressure by continuously evacuating the downstream volume with a dry pump



High pressure hydrogen regulator

High pressure hydrogen accumulators

Technical Approach – Expanded set of tank liner materials in FY 2012

Tank Liner Polymer Specimens	Measurement Status
HDPE (extruded)	Extensively studied in early project years (completed)
HDPE (injection molded)	In progress
PA-6 (extruded pipe, w carbon black)	In progress
PA-6 (extruded pipe, w/o carbon black)	To be done
HDPE with nano clay (injection molded)	To be done
HDPE with nano TiO2 (injection molded)	Low priority
EVOH ("low permeation")	Low priority
MDPE (extruded pipe)	Low priority

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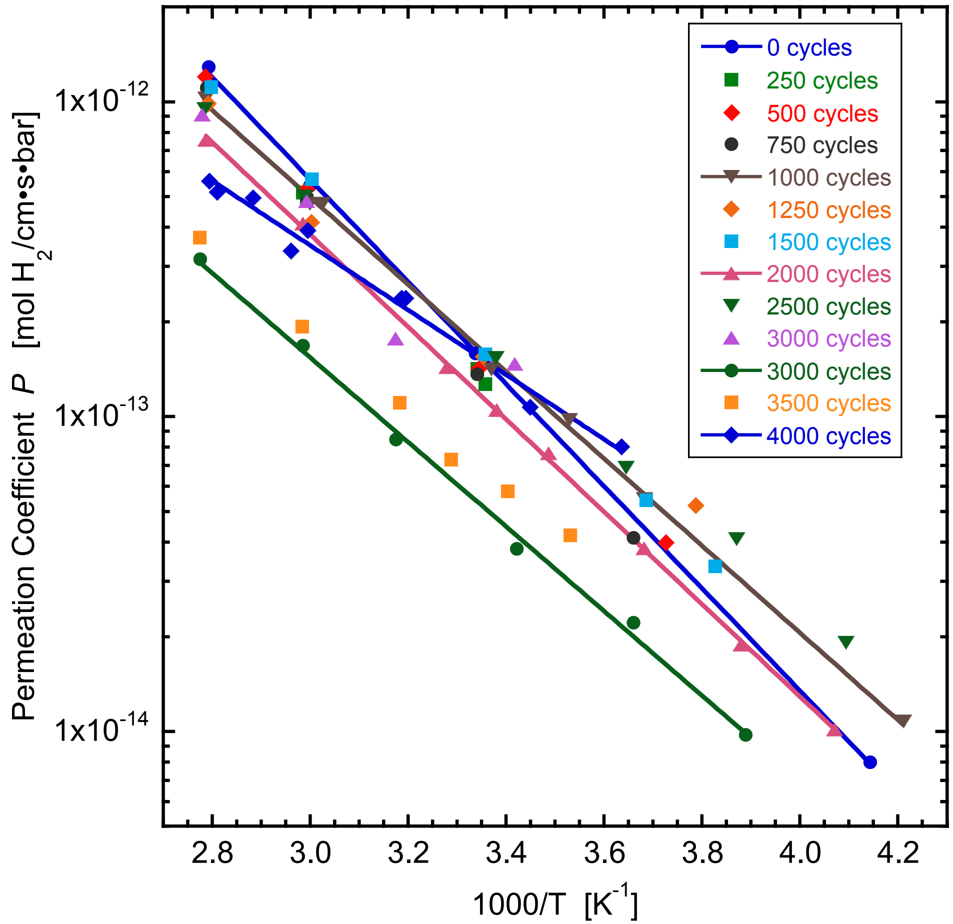
Technical Progress – Measured *P* through 4000 temperature cycles (FY 2011)

- **Completed permeation coefficient measurements* through 4000 cycles**
  - Permeation coefficients have temperature dependence of activated process (Arrhenius relationship)

    $P = P_0 \exp(-E_A/RT)$

    where P_0 and E_A are independent of T
  - Decreasing slope and shift in scaling with increasing cycles indicates changes are occurring in P_0 and E_A
  - **No statistically significant departures from Arrhenius relationship indicative of microcracking or a change in T_g**



Permeation coefficients *P* for hydrogen in polymer specimen, measured at 430 bar

*Measurements conform to ASTM D1434, *Determining Gas Permeability Characteristics of Plastic Film and Sheeting* (2003).

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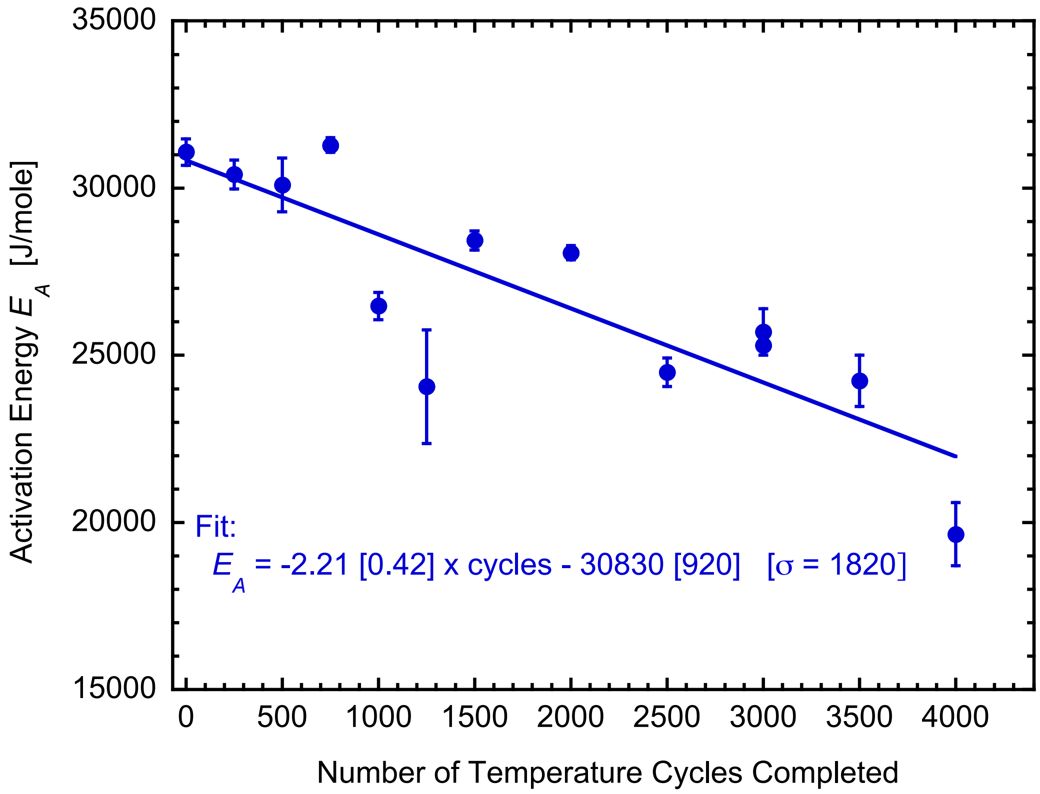
Technical Progress – Observed change in activation energy of permeation process

- **Analysis of changes in activation energy E_A**
  - Changes in E_A as specimen is subjected to repeated cycling could indicate polymer is undergoing microscopic changes in polymer matrix
  - Measurements show E_A is decreasing with increasing number of temperature cycles (slope in E_A *vs.* cycles is 5 standard deviations from zero)



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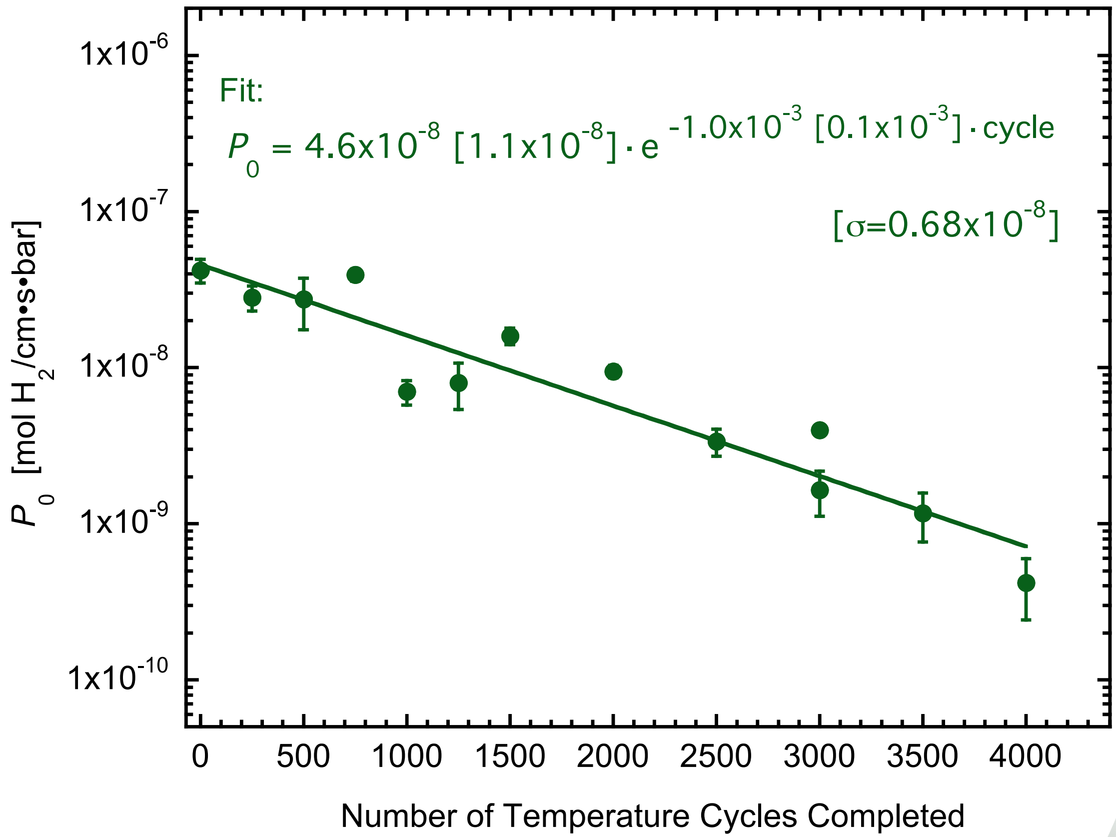
Technical Progress – Observed changes in pre-exponential scaling factor

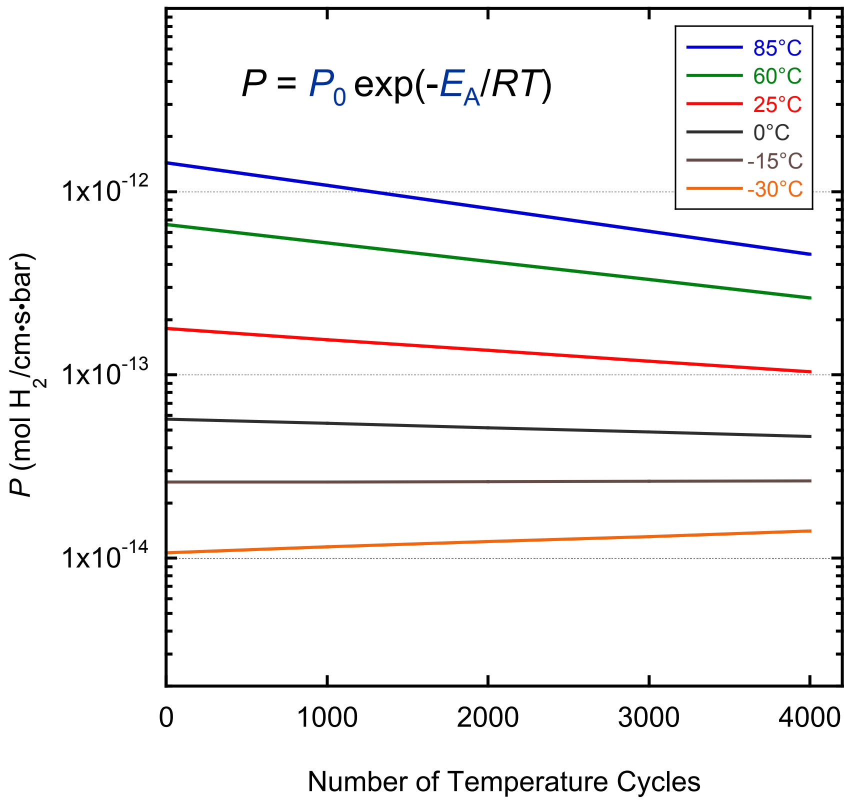
- **Analysis of changes in pre-exponential scaling factor P_0**
  - Changes in P_0 as specimen is subjected to repeated cycling could also indicate polymer is undergoing microscopic changes in polymer matrix
  - Measurements show that P_0 is also decreasing with increasing number of temperature cycles, (slope in log P_0 *vs.* cycles is 4 standard deviations from zero)



Technical Progress – Prediction of tank liner durability

Effects of Temperature Cycling on Tank Liner Leak Rates

- Used fitted P_0 and E_A values to model behavior of permeation coefficients P as a function of T and number of cycles
- Values of P generally decrease slightly with cycle count, probably due to microscopic changes induced in polymer by cycling or H_2 exposure or both
- Temperature dependence of P narrows with cycle count



Coefficients model for hydrogen permeation in polymer specimen with 430 bar differential pressurization, where P_0 and E_A vary with number of temperature cycles

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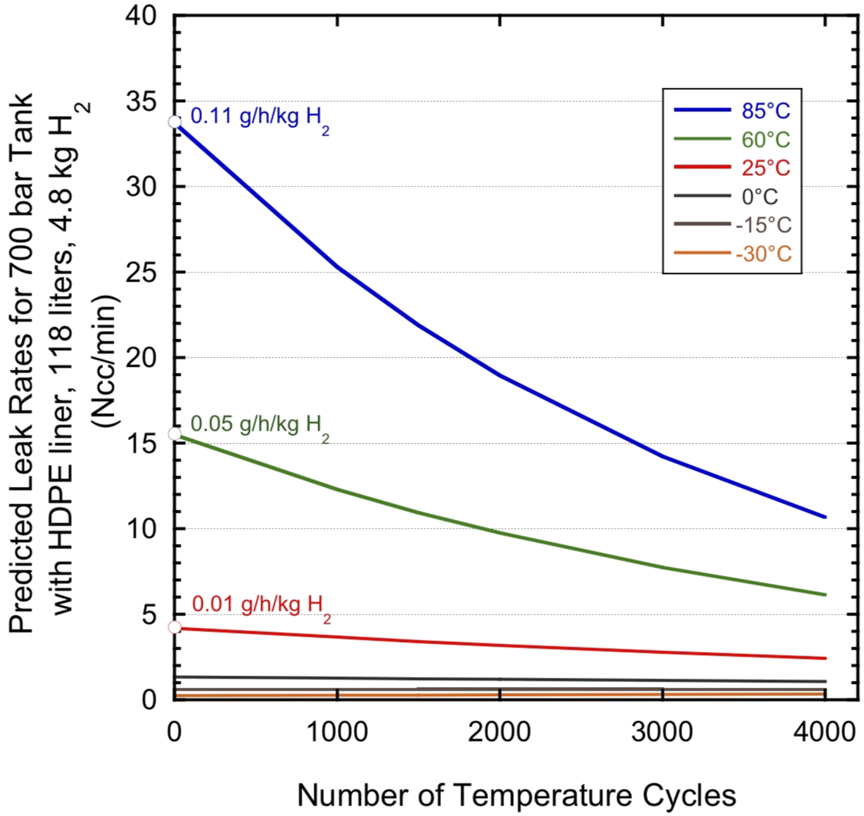
Technical Progress – Prediction of tank liner durability

Effects of Temperature Cycling on Tank Liner Leak Rates

- Used modeled *P* coefficients to predict leak rates in hypothetical HDPE-lined cylindrical tank with hemispherical end caps as tank experiences temperature cycling due to fill operations and variations in ambient temperature
- **Predicted leak rate remains below 75 Ncc/min at *all* temperatures and at or below 0.05 g/h/kg H_2 for temperatures ≤ 60°C (technical targets)**



Predicted leak rate values as a function of liner temperature and number of temperature cycles for tank pressurized to 700 bar

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Future Work (remainder of FY 2012)

- **Quick screening/accelerated evaluation of liner materials**
  - During initial HDPE cycling, P_0 and E_A decreased steadily with number of temperature cycles and decreases were statistically significant by completion of 1500 cycles
    - To accelerate the evaluation of the liner materials, perform a quick screening through the first 1500 cycles and assess the significance of the permeation trends
  - The new system promises faster cycle time of ~20 minutes
    - About 21 days to complete 1500 cycles
  - Abbreviate number of permeation measurements
    - Measure P at -40, -10, 30, 85°C at 0, 750, 1500 cycle intervals
    - Measure P at -40 and 85°C at 250, 500, 1000, 1250 cycles
    - About 20 days to conduct these measurements
  - Total time to complete 1500 cycles would be 41 days
    - With this accelerated approach, four high priority liner specimens could be evaluated by the end of FY 2012

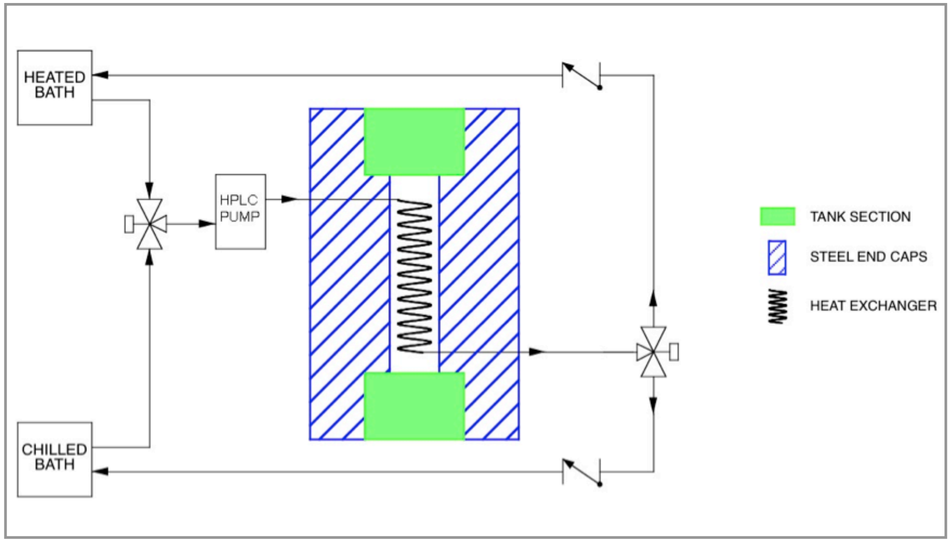
Future Work

- **Proposed work beyond FY 2012 is based on comments made by reviewers to us following the 2011 Annual Merit Review and the July 2011 STT meeting**
  - We need to expand the investigation beyond tests of the existing tank liner materials to future materials, as several tank manufacturers have recently introduced liners made from new, less-expensive and potentially higher performance (lower permeation) materials
  - There is a need to expand the scope of our investigation of the durability of the tank liners (isolated from the carbon fiber reinforcement structure) to an investigation of the durability of the tank liners in combination with the reinforcement structure
    - Will require a significant amount of cooperation with tank manufacturers to provide tank sections and advisement on the testing procedure
    - Will require construction of pressure cell for tank section (differential pressurization, with high pressure hydrogen on the liner side and atmospheric or below-atmospheric pressure outside the reinforcement)
    - Perform temperature cycling experiments on tank section in our new cycling/permeation measurement system

Future Work – Test Method for Cyclic Testing of Sectioned Storage Tanks

Preliminary design for rapidly cycling the gas temperature in a cylindrical section of a Type 4 tank while it is internally pressurized to 860 bar (10 ksi)

- In the first project year we developed high-pressure "soft" seals for metal-to-polymer interfaces (a slight modification on a reversed Bridgman seal)
- We can use this sealing method to form a robust seal between the polymeric tank liner and the steel cap that encloses the open ends of the cylinder.
- Actual gas volume present in the section will be small to minimize the quantity of hydrogen required
- Gas (and liner) will be heated and cooled using a heat exchanger located within the gas volume.



Cycling between temperature extremes will be facilitated by automated switching between separate reservoirs of low temperature (–40°C) and high temperature (85°C) coolant.

Diameter of the heat exchanger tubing will be quite small, so an HPLC pump (~5000 psi) will be required to provide sufficient coolant flow to effect cooling and heating of the gas.

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Project Summary

Relevance:	Verification of the durability of polymer liners in Type 4 pressurized storage tanks over the anticipated performance life of these storage systems
Approach:	Extreme temperature cycling of polymer specimens, combined with high-pressure hydrogen permeation measurements, predictions of tank liner leak rates as a function of the number of fill or temperature cycles
Progress:	Results of cycling on extruded HDPE with carbon black liner indicate temperature cycling produces microscopic changes in polymer (changes in permeation activation energy and pore size or structure) but cycling is not expected to increase the hydrogen leak rate in an HDPE liner
Collaborations:	Manufacturers of high-pressure composite tanks, polymer manufacturers and experts, FCT program advisement organizations
Future:	Use temperature cycling systems to test proposed future tank liner materials; perform lifecycle testing of liner material bonded to the composite matrix layer for an *in toto* evaluation of the tank liner durability

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