Lifecycle Verification of Polymeric Storage Liners

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Project ID #: ST053

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Overview

Timeline

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

Budget

- Total project funding
  - DOE: $600k
- Funding received in FY10
  - $200k

Barriers

- D. Durability/Operability
- Technical targets
  |             | 430 bar | 860 bar |
  | Liner Durability | 5500 cycles | 5500 cycles |

Partners & Collaborators

- Lincoln Composites
- Quantum Technologies
- Ticona
Relevance - Objective

**Project goal:** Perform durability qualification measurements on polymeric tank liner specimens and assess ability of liner materials to maintain required hydrogen barrier performance.

<table>
<thead>
<tr>
<th>Month-Year</th>
<th>Milestone or Go/No-Go Decision</th>
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<tbody>
<tr>
<td>April 2010</td>
<td><strong>Milestone:</strong> Complete thermal cycling and permeation measurements in Lincoln Composites liner materials (75% complete)</td>
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<tr>
<td>July 2010</td>
<td><strong>Milestone:</strong> Complete thermal cycling and permeation measurements in Quantum Technologies liner materials (15% complete)</td>
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<td>July 2010</td>
<td><strong>Milestone:</strong> Complete measurements of hydrogen solubility, uptake and effects of hydrogen-induced swelling in tank liner materials (10% complete)</td>
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<tr>
<td>September 2010</td>
<td><strong>Milestone:</strong> Go/No-Go decision on acceptability of existing liner materials (20% complete)</td>
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Relevance - Objective

- The Technical Plan for Storage* has durability targets for on-board storage for LDVs
  - Durability target for compressed storage tanks:
    - Lifecycle: 1500 fill cycles (cycle = 1/4 tank ↔ full tank)
    - Permeation and leakage of tank must meet applicable standards, e.g. 75 Ncc H₂/min
    - Cycle life variation for permeation and leakage must not exceed 99% of mean with a 90% confidence interval
  - SAE J2579 does not specifically address lifecycle testing of the tank liner
  - Project objective is to verify tank liner meets permeation and leakage standards throughout tank lifecycle

*Fuel Cell Technologies Program MYRDD Plan, Table 3.3.2, April 2009.
Relevance - Milestones

• Progress toward milestone completion was hampered by equipment failures in previous project year

• To overcome these failures we
  – Devised an improvement for the standard conical metal-on-metal seals in high-pressure make/break connections; the application of Kynar film to conical surface minimized leakage to a workable value at temperatures below -40 °C
  – Devised a multilayer seal and pre-compression technique to prevent leaking at the sealing surface of the polymer specimen during temperature cycling
Technical Highlights

• FY 2010
  – Permeation measurements on specimen of Lincoln Composites Type IV tank liner (HDPE) indicates that permeability coefficients are relatively unchanged through 2000 temperature cycles
  – Designed and assembled improved temperature-cycling apparatus; first results with new apparatus expected in 3rd quarter of project year
Technical Approach

- Verify durability of polymer liners in high-pressure storage tanks
  - Subject polymer specimens to extreme-temperature cycling 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.
Technical Approach-Test Protocol

- From SAE J2579 § 5.2.2 (January 2008)
  - 5500 temperature cycles: -30 to 85°C
    - Upper temperature for specimen (85°C) is limited by glass transition temperature for polymer; lower temperature is determined by limitations of high-pressure seals in apparatus
    - Cycle consists of 5.75 minute heating interval (+20°C/minute), followed by 28 minute cooling interval (~2 cycles per hour)
  - Upstream hydrogen pressures: 430 and 860 bar (6,250 and 12,500 psia)

- Measure permeation rates at -30, 25, 60 and 85°C at completion of every 250 cycles (250-1500 cycles) and 500 cycles (2000-5500 cycles)
Technical Approach

- Temperature cycling profile
  - 5.75 min heating interval corresponds to a 20°C per min heating rate
  - 27.6 min cooling interval determined by thermal mass of specimen holder
Technical Approach

- Constant pressure differential maintained using computer-controlled accumulator/regulator system
  - High upstream pressure maintained during temperature cycling using computer-controlled high-pressure regulator fed from high-pressure large-volume accumulators
  - Downstream pressure is maintained at a value below atmospheric pressure
Technical Progress

- Completed permeation measurements* through 2000 temperature cycles
  - Temperature dependence of permeation coefficient is described by Arrhenius relationship
    \[ P = P_0 \exp\left(-\frac{E_P}{RT}\right) \]
  - Measurement intervals: 0, 250, 500, 750, 1000, 1250, 1500 and 2000 cycles
  - Linear relationship in log $P$ vs $1/T$ plot indicates that activation energy $E_P$ remains constant

- Through 2000 cycles, no statistically significant departures from Arrhenius relationship that would indicate microcracking or changes in glass transition temperature in polymer

Technical Progress

- Analysis of activation energy $E_P$
  - Changes in $E_P$ as specimen is subjected to repeated cycling could indicate polymer is undergoing microscopic changes in polymer matrix
  - Measurements give slight indication that $E_P$ could be decreasing, but at present decrease is almost statistically insignificant
Collaborations

- Lincoln Composites – tank liner specimens
- Quantum Technologies – tank liner specimens
- Ticona – plastic pipeline grade PPS specimens
Future Work

- **FY 2010**
  - Complete initial lifecycle verification measurements and report durability assessments of Lincoln Composites specimen through 5500 cycles
  - Begin temperature cycling of Lincoln Composites specimen at 860 bar (12,500 psia) pressurization
  - Begin temperature cycling of Quantum Technologies specimen at 430 bar (6,250 psia) pressurization

- **FY 2011**
  - Complete all lifecycle verification measurements and report assessments for Lincoln Composites and Quantum Technologies
  - Complete temperature cycle testing of an alternative liner material (PA-6, PA-11, PPS) and compare to HDPE liner materials
  - Measure hydrogen solubility in tank liner materials
Project Summary

Relevance: Durability of polymeric tank liners over the performance lifetime of high-pressure storage systems must be verified and validated.

Approach: Use relevant portion of SAE J2579 to develop and carry out durability test cycling measurements.

Progress: Measurement of permeation coefficients through 2000 cycles suggests slight changes in polymer microstructure, but no indication that liner permeability has been adversely affected.

Collaborations: Lincoln Composites, Quantum Technologies, Ticona.

Future: Long-term measurements of multiple liners at 430 and 860 bar, possible measurements of alternative liner materials, measurements of hydrogen solubilities in tank liner polymers.