IV.G.2 Lifecycle Verification of Polymeric Storage Liners

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Perform durability qualification measurements on specimens of high-pressure storage tank liners.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Storage section (3.2.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) Durability/Operability

Technical Targets

This task addresses the following technical targets for on-board hydrogen storage systems research and development:

- Cycle life variation, expressed as % of mean (min) at % confidence:
  - Fiscal Year 2010: 90/90
  - FY 2015: 99/90
- Environmental Health and Safety:
  - Permeation and leakage: Meets or exceeds applicable standards
  - Loss of usable H_2 (g/h/kg H_2 stored): FY 2010: 0.1; FY 2015: 0.05

Accomplishments

- Modified the ORNL internally heated high-pressure vessel (IHPV) diffusion/permeation measurements test stand to provide rapid thermal cycling between -40 and 125°C by adding a low-temperature chiller with continuously circulated low-temperature refrigerant and by replacing the heater controller to provide thermal cycling control.
- Developed a novel technique for sealing polymer samples against high-pressure hydrogen at subzero temperatures.

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Introduction

The objective of this task is to perform durability qualification measurements on specimens of high-pressure storage tank liners. Modern high-pressure hydrogen storage tanks use a polymeric liner as a permeation barrier, typically high-density polyethylene (HDPE). Storage tank liners can, however, be stressed by cyclical excursions between temperature extremes, and the cumulative effects of repeated stress could harm the tank's durability. Ultra-high environmental temperatures can promote large hydrogen permeation rates and hydrogen saturation in the liner material. Ultra-low environmental temperatures can severely stress liner materials and possibly induce microcracking. In addition, increasing the pressure of gas in such a tank during filling necessarily raises the temperature of the gas and therefore the enclosing tank. Over the course of many fill cycles during the lifetime of the tank this might affect the permeability characteristics of the liner. Failure modes for the liner's performance–based on the interaction of high pressure and extreme temperature cycling–might be possible. Hydrogen leakage through a liner microcracked by extreme temperature cycling could accelerate under sustained high temperature and pressure, or hydrogen saturation of the reinforcement layers external to the liner could put backpressure on the liner as the tank pressure decreases during vehicle operation, thereby causing the liner to separate from the reinforcement layers. Minimum temperatures during winter months in northern states may reach -40°C, and maximum temperatures after filling during summer months may reach 125°C. Thus, the purpose of this project is to cycle typical tank liner materials between these temperature extremes to determine whether such a degradation in properties occurs, and, if so, its extent.

Approach

Hydrogen permeation verification measurements for storage tank liner materials are being carried out using ORNL's IHPV, shown in Figure 1. The IHPV can be used for semi-automatic hydrogen diffusion

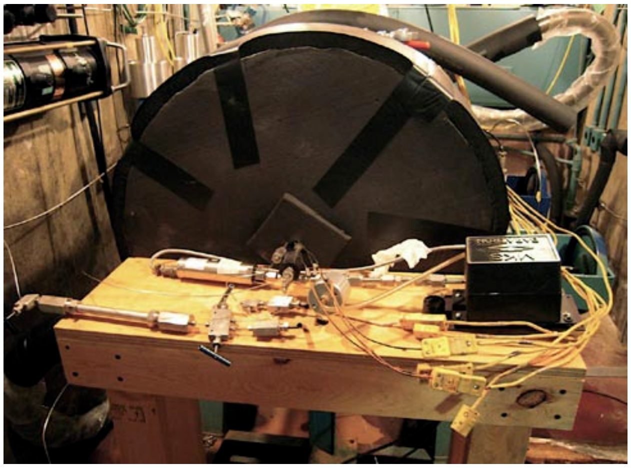

FIGURE 1. IHPV modified to provide rapid cycling between temperature extremes of -40°C to 125°C at differential pressures across the specimen of up to 86 kPa. The photograph shows the specimen loading and permeation measuring end of the IHPV.

and permeation measurements at temperatures over the range 10 to 1,000°C and at pressures as large as 276 MPa (40,000 psi). This apparatus has also supported the hydrogen delivery program in determining real-time hydrogen permeation in low-carbon steels and polymer materials. Materials characteristics such as the temperature- and pressure-dependent hydrogen solubilities, diffusion coefficients and permeation coefficients are extracted from measurements of real-time hydrogen flux through steels and polymers.

We are using the relevant portion of the test protocol specified in Society of Automotive Engineers J2579 to guide our performance of durability test cycling measurements of high-pressure polymeric tank liners. The J2579 test protocol for compressed hydrogen storage systems prescribes long-term thermal cycling at high pressures of hydrogen. The requirement is to subject tank liner specimens to 5,500 thermal cycles over the temperature range -40 to 125°C at hydrogen pressurizations of 43 MPa (6,250 psia) and then 86 MPa (12,500 psia). Testing at 43 and 86 MPa, with rapid cycling between -40 and 125°C, requires an automated temperature control strategy. To replicate the rapid temperature rise in the tank liner during fill cycles (approximately 100°C temperature rise in 3 minutes), required us to decouple the cooling and heating control systems in the IHPV. A low-temperature chiller with low-temperature refrigerant circulated to and from a sealed reservoir cools the IHPV's exterior containment vessel to approximately -50°C. A resistive heater situated in the permeation cell is used to ramp the specimen temperature from -40°C to 125°C. A heater controller controls the thermal cycling of the polymer specimen in the cell by applying and removing power to the heater. Process control software that was developed for the temperature-controlled permeation measurements in steels and polymers was modified to provide automated, unattended operation and Internet access so the tests can be remotely monitored and controlled.

The verification measurements occur at regular intervals during the 5,500 temperature cycles. The hydrogen flux is to be measured at three temperatures (-40, 25 and 125°C) at each interval, if practicable. The first measurements occur after the completion of 250, 500, 750, 1,000, 1,250 and 1,500 cycles. The remaining measurements occur at 500-cycle intervals until 5,500 temperature cycles have been reached. A second verification test on a fresh tank liner specimen will be carried out at 86 kPa following the same protocol.

Results

We developed a new technique for sealing a thin (0.5 mm) polymer sample against high-pressure hydrogen at subzero temperatures. The sealing method is illustrated in Figure 2. The high-pressure hydrogen is incident against the upper surface of the polymer sample. At subzero temperatures the polymer shrinks (thins) and loses firm mechanical contact with the conical copper sealing ring. We found that it is possible to alleviate this contact loss by pre-forming the polymer to have a conical shape similar to the sealing ring. This was done by placing the polymer specimen against a previously tested (and formed) steel specimen, and then tightening the sandwiched polymer and steel specimens in the specimen holder to force the polymer specimen to acquire a conical contour at its edges without deforming the specimen thickness. The sandwiched specimens were then removed and replaced by the polymer specimen alone.

Initial verification measurements involving 1,500-plus temperature cycles at 43 MPa hydrogen pressure will be completed during last quarter of FY 2009. These initial measurements are being carried out on an HDPE specimen provided by Lincoln Composites. The specimen is being cycled between -40 and 125°C approximately once per hour.

Conclusions and Future Directions

- Perform verification measurements on Quantum Technologies high-pressure tank liner materials.
- Perform verification measurements on pipeline-grade polyphenylene sulfide (ORNL has demonstrated that it has lower hydrogen permeation than HDPE at all temperatures), polyamide 6 (Air Liquide has demonstrated that the permeation of this material is 10x lower than HDPE), and/or polyamide 11 (Arkema is in the process of obtaining approval for use of PA-11 in unreinforced natural gas pipelines).

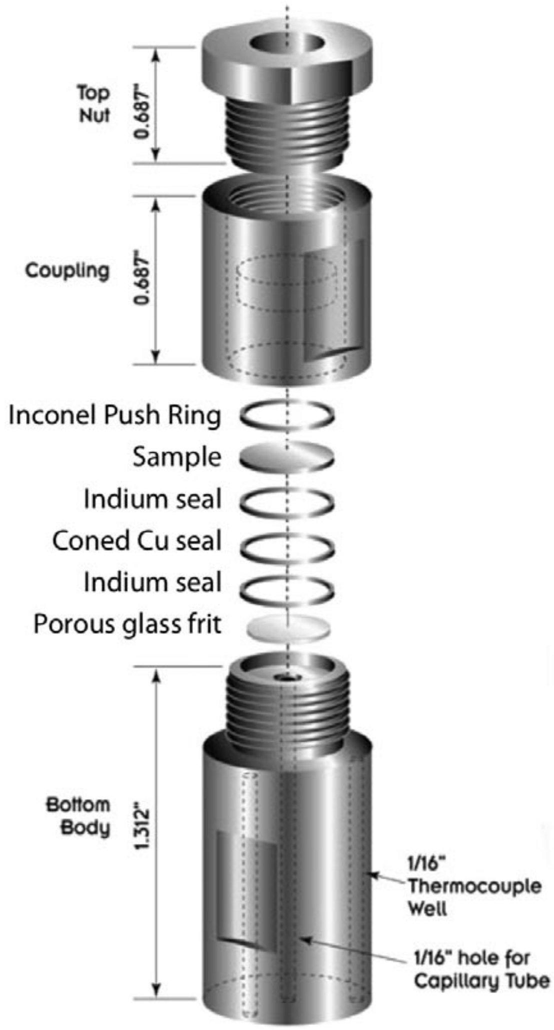

FIGURE 2. Illustration of method developed for sealing polymer specimen against high-pressure hydrogen at subzero temperatures.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Annual Merit Review – Arlington, Virginia – May 19, 2009. Presentation STP01.

References

1. HFCIT MYRDD Plan, Table 3.3.2, "Technical Targets: On-Board Hydrogen Storage Systems," October 2007.

2. SAE J2579, "Technical Information Report for Fuel Cell and Other Hydrogen Vehicles (January 2009)," Fuel Cell Standards Committee, SAE International.