III.11 Composite Technology for Hydrogen Pipelines

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Objectives

- Investigate the use of composite pipeline technology (i.e., fiber-reinforced polymer [FRP] pipelines) for transmission and distribution of hydrogen, to achieve reduced installation costs, improved reliability and safer operation of hydrogen pipelines.
- Evaluate current composite pipeline liner materials with respect to their performance as a hydrogen barrier; consider the hydrogen permeabilities of the materials to determine the degree of improvement (if any) that is necessary, and propose a path forward based on the available liner materials and modifications or treatments.
- Assess joining methods for composite pipelines.
- Determine integrated sensing and data transmission needs pipelines to provide health monitoring and operational parameters; report on state-of-the-art in structurally integrated sensing and data transmission.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Delivery section (3.2.4.2) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines

Technical Targets

The long-term project objective is to achieve commercialization and regulatory acceptance of FRP pipeline technology for hydrogen transmission and distribution. Accordingly, the project tasks address the challenges associated with meeting the DOE Hydrogen Delivery performance and cost targets for 2017 [1]:

- Transmission pipeline total capital cost: \$490K per mile
- Distribution pipeline total capital cost: \$190K per mile
- Hydrogen delivery cost: <\$1.00/gasoline gallon equivalent (gge)
- Transmission and delivery reliability: Acceptable for H_2 as a major energy carrier
- Hydrogen pipeline leakage: <0.5% (leakage target is currently under review by Delivery Tech Team)

Accomplishments

- Completed evaluation of Polyflow braided aramid fiber reinforced pipeline:
  - Hydrogen leakage is below nominal target for pipeline delivery.
  - Co-extruded polyphenylene sulfide-polyamid (PPS-PA) liner has lower permeation than a comparable high-density polyethylene (HDPE) liner.
  - Hydrogen blowdown test produced delamination of layer in co-extruded liner.
- Hydrogen compatibility measurements for glass fiber used as FRP underway with preliminary results showing no deleterious effects of hydrogen on fiber tensile strength.
- New and improved polymer diffusion and permeation measurement apparatus now in operation.

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Introduction

Pipelines could be a feasible long-term solution for delivering large quantities of gaseous hydrogen over long distances and distributing it in urban and rural settings. However, there are hydrogen compatibility issues in steel pipelines, and the capital costs for pipeline installation must be dramatically reduced. Composite pipeline technology is a promising alternative to low-alloy high-strength steel pipelines from both performance and cost considerations. For instance, FRP pipelines are engineered composite pipelines that are widely used in upstream oil and gas operations and in well interventions. FRP pipelines typically consist of an inner non-permeable liner that transports the fluid (pressurized gas or liquid), a protective layer applied to the liner, an interface layer between the protective layer and the reinforcement layers, multiple glass or carbon fiber reinforcement layers, an outer pressure barrier layer, and an outer protective layer. The pipeline has large burst and collapse pressure ratings, high tensile and compression strengths, and tolerates large longitudinal and hoop strains. Thousands of feet of continuous pipe can be unspooled and trenched as a seamless entity, and adjoining segments of pipeline can be joined in the trench without welding using simple connection techniques. The emplacement requirements for FRP pipelines are dramatically less than those for metal pipe; installation can be done in a narrower trenches using light-duty, earth-moving equipment. This enables the pipe to be installed in areas where right-of-way restrictions are severe. In addition, FRP pipe can be manufactured with fiber optics, electrical signal wires, power cables or capillary tubes integrated within its layered construction. Sensors embedded in the pipeline can be powered from remote locations and real-time data from the sensors can be returned through fiber optics or wires. This allows the pipeline to be operated as a smart structure, providing the unique advantage of lifetime performance and health monitoring.

Approach

The challenges for adapting FRP pipeline technology to hydrogen service consist of evaluating the constituent materials and composite construction for hydrogen compatibility, identifying the advantages and challenges of the various manufacturing methods, identifying polymeric liners with acceptably low hydrogen permeability, critiquing options for pipeline joining technologies, ascertaining the necessary modifications to existing codes and standards to validate the safe and reliable implementation of the pipeline, and determining requirements for structural health monitoring and embedded real-time measurements of gas temperature, pressure, flow rate, and pipeline permeation.

These challenges are being addressed by performing bench-scale tests of FRP pipelines and constituent materials to determine their long-time compatibility with hydrogen, identifying pipeline liner materials that exhibit good performance in hydrogen environments, evaluating current methods for pipeline joining with consideration of the unique requirements for hydrogen service, and assessing the state-of-the-art in integrated sensing technologies for composite structures.

Results

We completed hydrogen leak rate measurements in Polyflow Thermoflex® FRP pipeline. These measurements were designed to assess how well this particular pipeline contains high-pressure hydrogen gas. The specimen was a 4.8-cm inside diameter, 6.1-cm outside diameter, 77-cm-long specimen of Thermoflex®, which had a liner of coextruded PPS (inner layer) and nylon PA-6 (outer layer), with each layer ~1.7 mm thick. The fiber reinforcement architecture was aramid fiber rovings helically braided on top of the liner and laid over four longitudinal rovings. The pipeline had an exterior jacket of 2-mm-thick polypropylene with damage indicating colorant. The pipeline ends were terminated with swaged steel couplings and sealed with threaded steel caps. The specimen was pressurized to ~100 bar (1,500 psia), which is the maximum allowable operating pressure, and leak rate measurements were made at 30 and 60°C. The leak rate determinations were based on our typical temperature-corrected pressure-decay measurement technique. The hydrogen decay curves are shown in Figure 1. The leak rates associated with the two temperatures are shown with the curves. These rates are approximately 50% less than those measured in similar lengths of glass fiber reinforced pipeline with a 5-mm-thick HDPE liner. For both pipelines – PPS-PA6 lined, aramid-reinforced and HDPE lined, glass-fiber-reinforced – the leak rates are significantly below the nominal 0.5% leakage target.

Following the completion of the leak rate measurements we performed a hydrogen blowdown test on the Thermoflex® specimen. We used the procedure in Appendix D of American Petroleum Institute (API) standard 15S to perform the test [2]. We pressurized the specimen with hydrogen to its 1,500-psi maximum pressure rating, heated the specimen to its 60°C temperature rating, and held it at these conditions until the pipeline liner was saturated with hydrogen gas. Following this hold period, we depressurized the specimen at -3,800 psi/min, which was almost four times greater than the prescribed rate of 1,000 psi/min. (We used a simple ball valve to

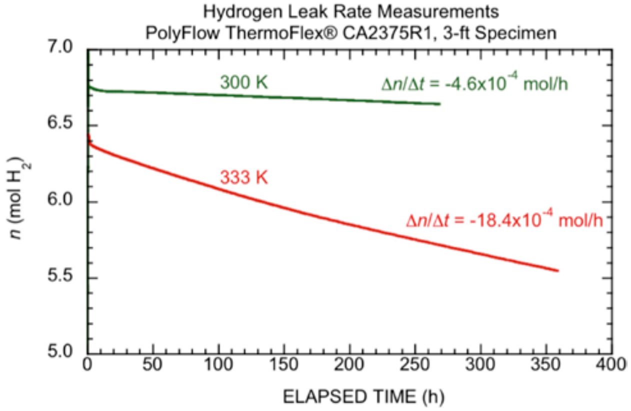

FIGURE 1. Hydrogen leakage curves dn/dt, where n is the number of moles of hydrogen in the pipeline, for a 77-cm-long Polyflow Thermoflex® pipeline specimen.

vent the hydrogen, which made it difficult to control the depressurization rate in this "one-shot" scenario.) Following the depressurization, we disassembled the end caps from the specimen and examined the liner for evidence of blistering, collapse or delamination. We observed extensive damage to the liner. (See Figure 2.) The inner layer of PPS separated from outer layer of nylon on approximately half of the tube circumference, along entire length of specimen. The outer layer of nylon remained adhered to fiber reinforcement matrix. A precise analysis of the failure mode was beyond the present scope of the project, but close examination of the liner suggests two possible failure modes: buildup of high-pressure hydrogen in microscopic void between co-extruded layers forced the liner collapse, or unbalanced shear stresses in the layers induced delamination leading to collapse. We recently performed a second blowdown test on a similar pipeline specimen, at the prescribed depressurization rate, to determine if the result is reproducible. In this second test there was no visible sign of liner collapse or delamination following blowdown, although a thorough analysis was incomplete at the time of this writing. This second result suggests that an extremely rapid depressurization–one much more aggressive than 1,000 psi/min–could be problematic for coextruded liners.

In previous project years we used a straightforward accelerated aging process to screen for hydrogen-induced damage in glass-reinforced composite pipelines (Fiberspar LinePipe™) and the pipeline constituent materials. In the evaluation of the glass fiber filaments we observed a small decrease in the tensile strengths of fibers that were aged for eight months in hydrogen compared to those that were aged in air. Although statistically significant, we could not rule out the possibility that the reduction in tensile strength was due to improper post-conditioning handling. Thus we are in the process of repeating the hydrogen conditioning and accelerated aging on a larger number of glass fibers with better controls, performing more tensile tests at shorter intervals, and using statistical analysis that reduces the large error bars due to extreme values in the data sets. Table 1 displays selected measurement results obtained on fibers tested weekly through 11 weeks (2.5 months) of exposure. These fibers have not exhibited any significant degradation in tensile strength. The tests will continue through a minimum of 35 weeks (eight months) of exposure.

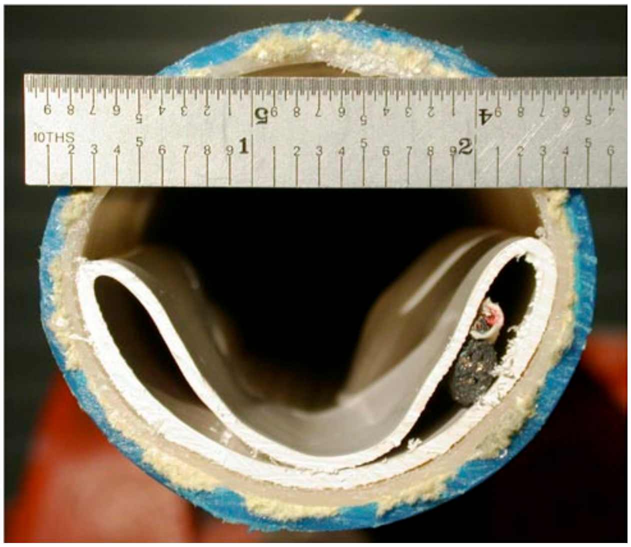

FIGURE 2. Polyflow Thermoflex® pipeline following an extremely aggressive hydrogen blowdown procedure, cut transversely to examine the collapsed liner. The inner layer of co-extruded PPS (white) separated from outer nylon layer (beige) during blowdown. The cable for the resistance temperature detector sensor is visible inside the collapsed liner.

TABLE 1. Results of tensile tests performed on glass filaments subjected to accelerated aging in air and high-pressure hydrogen environments.

Selected Glass Filament Test Results

Test Property	Hydrogen 1000 psi 60°C 5 weeks	Control ambient air ~25°C 5 weeks	Hydrogen 1000 psi 60°C 11 weeks	Control ambient air ~25°C 11 weeks
Strength (ksi)	268.6 (26.6)	320.9 (26.1)	305.1 (23.4)	275.6 (23.8)
Modulus (Msi)	9.8 (14.3)	11.2 (17.7)	9.3 (18.3)	8.6 (16.3)
Elongation (%)	2.8 (28.8)	2.9 (23.8)	3.0 (19.6)	3.3 (19.6)

Numbers in parentheses are coefficient of variation (in %) for the data set.

Conclusions and Future Directions

Conclusions from this year's work:

- Hydrogen leakage rates in off-the-shelf FRP pipelines with different liner materials, liner constructions and reinforcement architectures are comparable in magnitude, are lower than predicted using a simple analytical model, and a strong argument can be made that they are significantly lower than the leakage target.
- Liners constructed from co-extruded polymers could have reliability and longevity problems in instances where rapid pipeline depressurization occurs.

During the remainder of this project year and the entirety of the next we plan to:

- Begin the next phase of hydrogen compatibility testing by evaluating composite pipelines for environment- and strain-induced hydrogen deterioration.
  - Objective: Verify that the combinations of hydrogen environment and stress do not

adversely affect composite pipeline integrity and service life.

- Update our economic feasibility analysis to determine if additional pipeline cost reductions can be realized from recent advancements in composite pipeline technology.
- Perform long-term stress rupture tests and high-pressure cyclic fatigue tests:
  - Stress rupture testing is the API prescription for qualifying the pressure rating of the pipeline.
  - High-pressure cyclic fatigue tests provide information on pipeline integrity after repeated hydrogen gas pressurization-depressurization cycles.
  - Fatigue tests provide information that can't be derived from constant pressure testing, including liner collapse resistance (similar to blowdown testing), resistance to micro-cracking, crazing, crack propagation, fiber-resin interface failure of composite reinforcement layer, resistance to environmental stress-corrosion phenomena.
- Subject pipeline specimens to 4-pt flexural bending to produce microcracks before leak rate measurements to reveal the extent that microcracking increases permeation and leakage.
- Measure hydrogen pressure inside pipeline wall as a function of depth in wall and within composite layers to determine hydrogen concentration gradient in the wall.
- Assess the integrity of joint attachment/joint sealing under cyclic loading.

Our out-year plans are to:

- Evaluate feasibility of large-scale manufacturing operations, plan prototype manufacturing for a demonstration project, manufacture prototype FRP pipeline for hydrogen service, coordinate commercial demonstration of pipeline technology.

FY 2010 Publications/Presentations

1. 2010 DOE Hydrogen Program Annual Merit Review – Washington, D.C. – June 7, 2010, Presentation PD024.

References

1. HFCIT MYRDD Plan, Table 3.2.2, page 3.2-13, and footnote *b*, page 3.2-16.

2. *Qualification of Spoolable Reinforced Plastic Line Pipe*, API Recommended Practice 15S, First Edition, March 2006.