III.16 Composite Technology for Hydrogen Pipelines

Barton Smith (Primary Contact),
Barbara J. Frame and Lawrence M. Anovitz
Oak Ridge National Laboratory (ORNL)
P.O. Box 2008
Oak Ridge, TN 37831
Phone: (865) 574-2196; Fax: (865) 574-9407
E-mail: smithdb@ornl.gov

DOE Technology Development Manager:
Monterey Gardiner
Phone: (202) 586-1758; Fax: (202) 586-9811
E-mail: Monterey.Gardiner@ee.doe.gov

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

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 Hydrogen, Fuel Cells and Infrastructure 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/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 the Delivery Tech Team)

Accomplishments

- Pipeline materials compatibility testing:
  - Completed long-term hydrogen immersion exposure of FRP pipelines and performed post-immersion qualification testing. Evaluations showed no evidence of hydrogen-induced degradation of the materials or pipeline performance.
  - Completed pipeline leakage measurements in Fiberspar FRP pipelines. The measured hydrogen leak rate of 0.02% per day is significantly smaller than that predicted using permeation coefficient measurements in liner material.
- Installed a new apparatus for measuring hydrogen diffusion and permeation coefficients in pipeline polymers.

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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 have been using a straightforward accelerated aging process to screen for hydrogen-induced damage in FRP pipelines (Fiberspar LinePipe™) and pipeline constituent materials. The process involves immersion of FRP pipeline specimens in high-pressure (69 bar) hydrogen at an elevated temperature (60°C) to promote an accelerated interaction of hydrogen with the pipeline structure. To assess specific effects on the constituent materials in the pipeline, specimens of fiberglass rovings, resin matrix and liner materials were immersed simultaneously with the pipeline specimens, and all specimens were subjected to either a 1-month exposure (reported in the previous year) or an eight-month exposure (current year) to this hydrogen environment. At the conclusion of the exposure interval, the pipeline specimens were evaluated by Fiberspar for degradation using hydrostatic burst pressure tests to assess the overall integrity of the structure, compression tests to assess the integrity of the polymer matrix, and bend testing to assess the integrity of the laminate. The results of these tests were compared to the results obtained from identical tests performed on un-conditioned specimens from the same manufacturing run. Tensile tests and dynamic mechanical analysis were performed at ORNL on multiple specimens of constituent materials. The results of the specimens conditioned in hydrogen were compared to specimens that were conditioned in ambient-air for identical intervals.

Our results from the eight-month exposure were largely consistent with those from the one-month exposure; *there were no statistically significant differences between the test results of off-the-shelf and hydrogen-aged pipeline specimens and materials*. We found a small difference, however, between the tensile strengths of 1-month conditioned and 8-month conditioned glass fibers. Although statistically significant, these results are not conclusive. Thus we are in the process of repeating the hydrogen conditioning and accelerated aging on a larger number of glass fibers, 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.

We completed our measurements of the hydrogen leak rate in short sections of FRP pipeline. These measurements were designed to assess how well the pipeline contains high-pressure hydrogen gas. The measurements were done on off-the-shelf 10-cm inside diameter specimens of Fiberspar LinePipe™. The pipeline liner was 0.526-cm-thick pipeline grade high density polyethylene (PE-3408). The hydrogen pressurization in the pipelines was 103 bar (1,500 psia), which is the pipeline pressure rating, and all measurements were done at ambient lab temperatures. The pipeline was closed on each end using capped Fiberspar LinePipe™ connectors with elastomer (O-ring) seals. The leak rate was calculated from the temperature-corrected pressure decay curve. Changes in pipeline volume that occurred due to pressure-induced dimensional changes in the pipeline length and circumference were measured using strain gauge sensors. These volumetric changes occurred at the earliest measurement times and diminished to near zero at the long measurement times during which the steady-state leak rate was determined.

To predict the hydrogen leak rate per meter of liner we used the expression

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

where n is moles of hydrogen, P is the permeation coefficient for hydrogen in PE-3408, a=5.05 cm and b=5.576 cm are the inner and outer radii of the liner tube, and p_0=100 bar and p_1=1 bar are the hydrogen pressures inside and outside the liner. Our measurement of the permeation coefficient for PE-3408 found that $P \approx 4\times10^{-10}$ mol/m·s·bar. Thus the predicted leak rate for a 2.7-meter long pipeline specimen is -2.4×10^{-2} mol H_2/h, assuming the leakage through the seals on the steel end caps seals is negligible compared to the leakage through the polymer liner.

Figure 1 shows the results of a long-term measurement of the hydrogen gas leak rate dn/dt in a 2.7-meter-long pipeline. During the first 500 hours the apparent leak rate steadily decreased. We attribute this apparent leak rate, which is larger than the constant leak rate observed after 500 hours, to two phenomena. First, the pipeline volume initially increased slightly as the composite structure slowly expanded under the stress of pressurization. This volumetric expansion produced a slight reduction in pressure and yielded an apparent reduction the number of moles of gas. Second, the pipeline wall (liner and reinforcement layers) absorbed and retained hydrogen after it was presssurized. This also yielded an apparent decrease in the number of moles of gas. In the interval from 500 to 6,400 hours (20 to 270 days) the leak rate dn/dt was constant, and a linear least-squares fit to the leak rate in this interval gave a value of -5.4×10^{-4} mol H_2/h. This leak rate is equivalent to a stored hydrogen loss of about 0.02% H_2 per day at a pressurization of 100 bar.

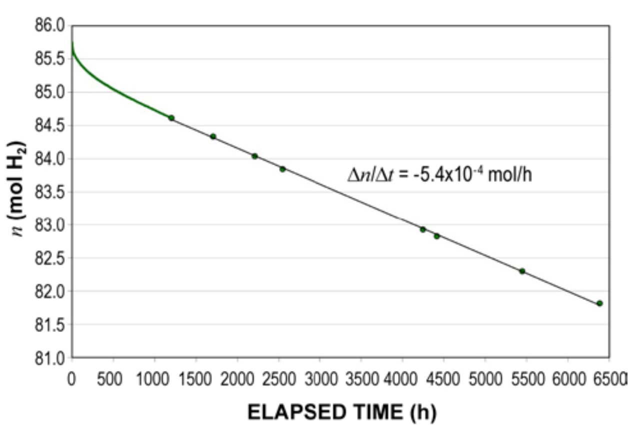

FIGURE 1. The leakage measured in a 2.7-m (9-ft) long specimen of 10-cm inside diameter Fiberspar LinePipe™ FRP pipeline with 0.5-cm thick high-density polyethylene liner, pressurized to approximately 100 bar (1,500 psia), was found to have a long-term (~6,400 hours observation) steady-state leak rate of 5.4×10^{-4} moles H_2 per hour leakage rate. This leakage rate is equivalent to a loss of 0.02% per day of hydrogen, a value substantially below the provisional 0.5% leakage goal.

Table 1 shows the results of leak rate measurements of three lengths of pipeline. The three pipelines were identical with the exception of their lengths. The same pair of connector end caps was used on all specimens. In all three lengths the measured leak rate was significantly lower than the predicted rate. The leak rate should have increased in direct correspondence to the pipeline length, but for the two shorter lengths we probably terminated the measurement before the leak rate decreased to its steady-state (actual) value. (The pipeline wall might not yet have been saturated with hydrogen.)

TABLE 1. Results of hydrogen leak rate measurements in three Fiberspar LinePipe™ FRP pipeline specimens. All pipelines were identical with the exception of their lengths. The same pair of capped connectors was used on all specimens. The measurement intervals on the two shorter lengths were probably too brief to obtain a constant leakage rate, i.e., the pipeline wall was still being saturated with hydrogen, producing a virtual leak.

Pipeline Length m (ft)	Nominal Pressure bar (psia)	Measurement Duration h	Measured Leakage Rate mol/h	Predicted Leakage Rate mol/h
0.9 (3)	100 (1,500)	145	-4.4×10^{-4}	-8.1×10^{-3}
1.8 (6)	100 (1,500)	285	-5.5×10^{-4}	-1.6×10^{-2}
2.7 (9)	100 (1,500)	6,400	-5.4×10^{-4}	-2.4×10^{-2}

We built a new, improved apparatus for measuring diffusion and permeation coefficients in pipeline polymers. This apparatus is being used to assess the efficacy of surface treatments on polymer specimens. We expect to be able to provide results of these measurements by the end of the project year.

We began the next step in hydrogen compatibility testing: evaluating composite pipelines for environment- and strain-induced hydrogen deterioration. The stress-related embrittlement behavior of pipeline steels in hydrogen environments is well known; it is therefore important to verify that the combinations of hydrogen environment-and-stress do not adversely affect composite pipeline integrity and service life. The evaluations we will perform are long-term stress rupture tests and high-pressure cyclic fatigue tests. The stress rupture tests measure time-to-rupture under constant hydrogen pressure. Stress rupture testing is the American Petroleum Institute (API) basis for qualifying the pressure rating of the pipe body [2]. High-pressure cyclic fatigue tests provide information on pipeline integrity after repeated hydrogen gas pressurization-depressurization cycles. The fatigue tests will 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, etc. of composite reinforcement layer, resistance to environmental stress-corrosion phenomena, and an assessment of the integrity of joint attachment/joint sealing under cyclic loading. We expect to publish results of these tests in the next project year.

Conclusions and Future Directions

- No observed hydrogen incompatibility in composite pipeline materials after accelerated aging testing.
- Hydrogen leakage rates in off-the-shelf FRP pipelines are much better than expected, and a strong argument can be made that they are significantly lower than the leakage target.
- We expect 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.
- 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.
- Out-year plans: 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 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Annual Merit Review – Arlington, Virginia – May 19, 2009, Presentation PDP24.

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.