III.13 Composite Technology for Hydrogen Pipelines

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

DOE Manager
Scott Weil
Phone: (202) 586-1758
E-mail: Kenneth.Weil@ee.doe.gov

Start Date: January 2005
Project End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2011 Objectives

- Investigate the use of composite pipeline technology (i.e., fiber-reinforced polymer [FRP] matrix composite 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

This project addresses the following technical barriers from the Hydrogen Delivery section (3.2.4.2) of the Fuel Cell Technologies Program (FCT) 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 the Delivery Tech Team)

FY 2011 Accomplishments

- Completed tests on aging of glass reinforcement fibers in high-pressure hydrogen, and tensile tests indicate that long-term exposures to high-pressure hydrogen has a negligible effect on the strength of the fibers.
- Began cyclic fatigue testing on FRP pipeline specimen using cyclical hydrogen pressurization to pipeline maximum allowable working pressure. Measurements of the pressure-stress relationship and hydrogen leakage rate will provide information on liner collapse resistance and crack propagation, reinforcement layer resistance to micro-cracking, crazing, crack propagation, fiber-resin interface failure, and integrity of joint sealing.

✧ ✧ ✧ ✧ ✧

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 used a straightforward accelerated aging process to evaluate the possibility that hydrogen could weaken the load-bearing capability of the glass fibers that are used as reinforcement in glass fiber-reinforced pipelines being considered for hydrogen delivery. Designing a test to screen for hydrogen-induced failures in glass fibers is difficult because potential chemical incompatibilities are largely unknown and because the permeation of hydrogen into glass is typically 3 to 7 orders of magnitude smaller than it is in most polymers and metals. Previous studies of the effects of hydrogen on glasses have focused on the ability of the glasses to store hydrogen or on the tendency of hydrogen to produce attenuation centers in the glasses (e.g., as in optical fibers).

To assess possible hydrogen-induced changes in mechanical strength of the glass fibers, we measured fiber tensile strengths in boron-free e-glass fibers (Advantex® SE 1200 Type 30) before, during and after accelerated aging in a pressurized hydrogen reactor. Our accelerated aging protocol was based on the Arrhenius model for an activated process where the aging rate is proportional to $e^{-\lambda/kT}$, where λ is the activation energy, T is the aging temperature, and k is the Boltzmann constant. We aged the fibers in a 70 bar pressure of hydrogen at a temperature of 60°C, which were the maximum allowable working pressure and temperature of the FRP pipeline. There were no stressors other than high-pressure hydrogen (i.e., no oxygen, water, chemicals, untraviolet light). From previous measurements done by others and us, we know that simply heating the fibers to 60°C for long periods of time does not degrade their tensile strength when it is subsequently measured at room temperature. We included tensile tests of untreated control specimens to compare with the specimens treated in hydrogen.

We removed fibers from the reactor at intervals of 1, 5, 11, 20, 39 and 62 weeks of exposure to perform tensile tests on fiber specimens with gauge lengths of 25 mm. We tested 30-100 fibers of both the hydrogen exposed and control groups at each interval. The distribution of tensile strength can be approximated by the two-parameter Weibull distribution

$$P(\sigma) = 1 - \exp(-L/L_0[\sigma/\beta]\alpha)$$

where α is the shape parameter, β is the scale parameter, and L and L_0 are the fiber gauge and reference lengths. Figure 1 shows representative test results in Weibull coordinates for the shortest and longest hydrogen exposures.

Using the Weibull parameters determined from the tensile strength measurements performed at each exposure interval, we calculated survival probabilities for the hydrogen-treated and control fibers. These survival probabilities are plotted versus exposure duration in Figure 2. The large error bars in the survival probabilities are likely due to the presence of both surface and bulk flaws in the fibers. Funding and time constraints did not allow us to censor the strength data by doing fractographic analysis to identify the type of flaw in each fiber tested, which would have allowed us to separate the data by flaw type and thereby obtain Weibull distributions with straight-line slopes. Nevertheless, the survival probabilities for the treated and untreated fibers do not change qualitatively with aging, implying that there was no hydrogen-induced degradation in the fibers during the 62-week exposure duration.

Fatigue testing using high-pressure hydrogen pressure cycling is the basis for verifying that combination of hydrogen environment and pressure-induced stress does not adversely affect composite pipeline integrity and service life. The results of high-pressure cyclic fatigue tests provide information on pipeline integrity after repeated hydrogen gas pressurization-depressurization cycles [2].

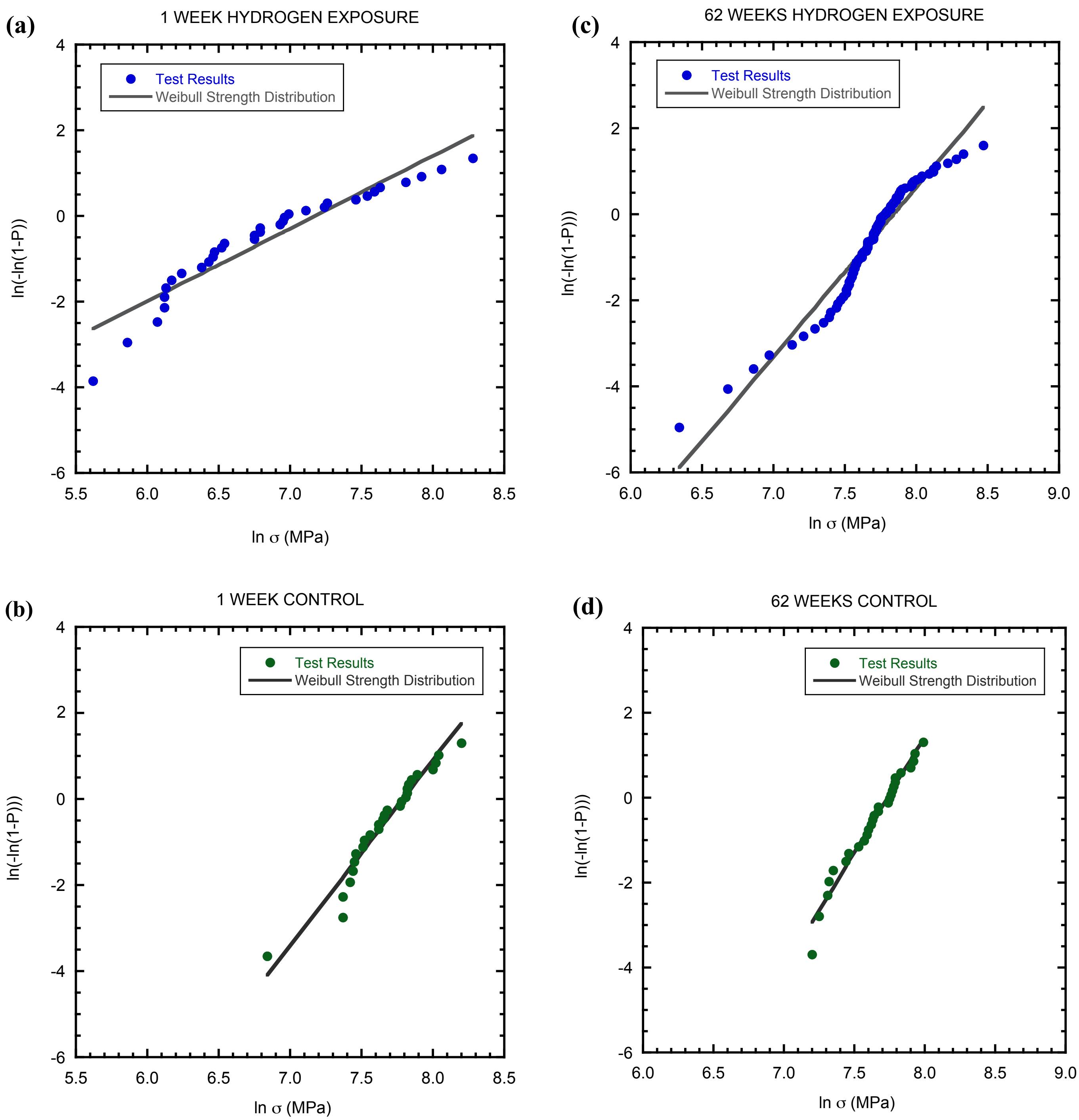

FIGURE 1. Representative test results in Weibull coordinates for fiber strengths measured following (a) 1-week and (c) 62-week hydrogen exposures. Circles are measured tensile strengths and the solid lines are the calculated Weibull distributions for the measured strengths. The corresponding tensile strength measurements for the control fibers are shown in (b) and (d).

Fatigue testing provides 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 integrity of joint attachment/joint sealing under cyclic loading. We began cyclic fatigue testing of a Fiberspar glass-reinforced polymer pipeline in this project year and are on schedule to meet the milestone for this task, but the measurement results and analysis will not be completed until near the end of the

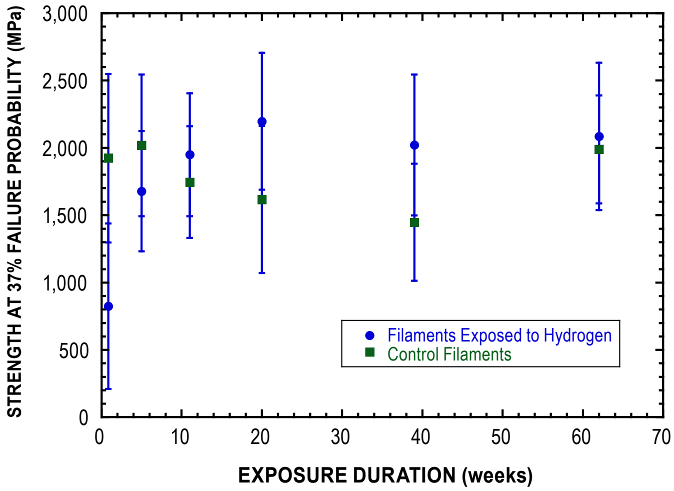

FIGURE 2. Survival probabilities of hydrogen-treated and untreated (control) fibers plotted versus accelerated aging duration. There was no statistically significant decrease in tensile strength during the 62-week exposure period.

fiscal year and will be reported in the last quarterly report of the year.

Conclusions and Future Directions

Conclusions from this year's work:

- E-glass fibers similar to those used as reinforcement in composite pipelines did not lose their tensile strength during a long-term exposure to high-pressure hydrogen gas. The intensity of the glass-fiber exposure was significantly higher than the actual exposure of fibers in the pipeline epoxy matrix and exceeded even a worst-case scenario. The conclusion reached is that e-glass should be durable in hydrogen service and the glass fibers should retain their mechanical function in a glass-fiber-reinforced pipeline during the anticipated hydrogen service lifetime.

During the remainder of this project year we expect to complete the first series of long-term stress rupture tests and report on the durability of the pipeline to further verify the expectation that composite pipelines can achieve the 2012 DOE H_2 transmission target of <\$0.90/gge H_2:

- Our plans for the next project year are (1) to participate in the codification of fiber-reinforced (composite) pipelines in the American Society of Mechanical Engineers (ASME) B31.12 Hydrogen Piping Code by helping to identify and provide data needed to guide lifecycle management of composite pipelines, and (2) to monitor the performance of composite pipeline used to store hydrogen in a hydrogen and fuel cell market transformation project demonstration project at the Hawaii Natural Energy Institute. The opportunity to monitor the field demonstration of the pipeline is uncertain and is extremely contingent on funding and scheduling constraints. Nevertheless, the FCT program will have the chance to get initial real-world field data on the use of FRP pipe for hydrogen (e.g. pressure cycling, environmental exposure, and post-use microstructural analysis), which is particularly important as we begin to work with ASME on establishing a set of codes and standards for the commercialization of FRP (composite) pipelines.

FY 2011 Publications/Presentations

1. 2011 DOE Hydrogen Program Annual Merit Review – Arlington, Virginia – May 10, 2011, poster 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.