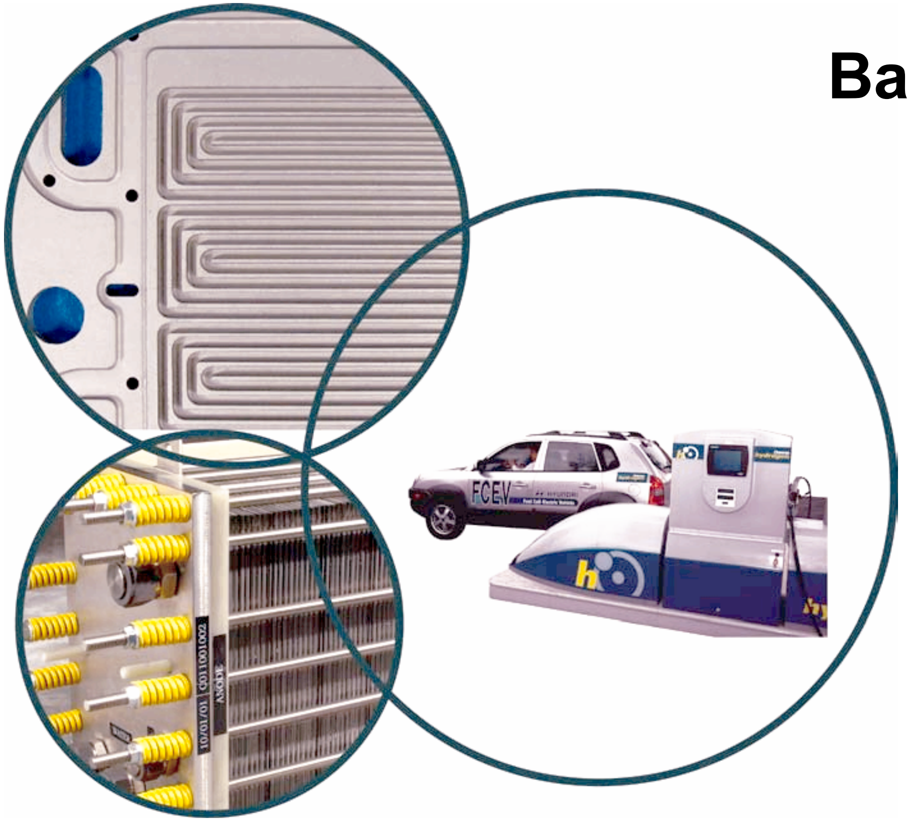
Composite Technology for Hydrogen Pipelines



Barton Smith, Barbara J. Frame, Lawrence M. Anovitz

Oak Ridge National Laboratory

Annual Merit Review
Washington, DC
June 9, 2009

Project ID #: PD024

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Managed by UT-Battelle
for the Department of Energy

Overview

Timeline

- Start: Jan 2005
- Finish: Project continuation & direction determined annually by DOE

Budget

- Total project funding
  - DOE: $1.85M
- Funding for FY 10
  - $50k

Barriers

- D. High Capital Cost and Hydrogen Embrittlement of pipelines
- Technical Targets on next slide

Partners & Collaborators

- Fiberspar, PolyFlow
- Arkema, Ticona, Fluoro-Seal
- Pipeline Working Group

Overview

- **Technical Targets**

Category	2005 Status	2012	2017
Pipelines: Transmission			
Total Capital Investment (16-in pipeline, $/mile)	$720k	$600k	$490k
Pipelines: Distribution			
Total Capital Investment (2-inch pipeline, $/mile)	$320k	$270k	$190k
Pipelines: Transmission and Distribution			
Reliability/Integrity (including 3rd-party damage issues)	Acceptable for current service		Acceptable for H_2 as a major energy carrier
H_2 Leakage *	Undefined	TBD	< 0.5%

* Leakage targets are being reviewed by the Delivery Tech Team

Relevance – Objectives and Milestones

Project objectives: Assess, primarily from a materials performance perspective, the compatibility of fiber-reinforced polymers and engineered plastics in high-pressure hydrogen environments; to define research and development issues for adapting the technology for hydrogen use; and to develop a path to commercialization for the technology.

Month-Year	Milestone or Go/No-Go Decision
May 2010	Milestone: Hydrogen compatibility evaluations of next group of composite pipeline materials and construction completed and reported (90% complete)
Sep 2010	Cyclic testing completed (25% complete)
Sep 2010	Milestone: Next round of polymer diffusivity and permeability measurements completed (50% complete)

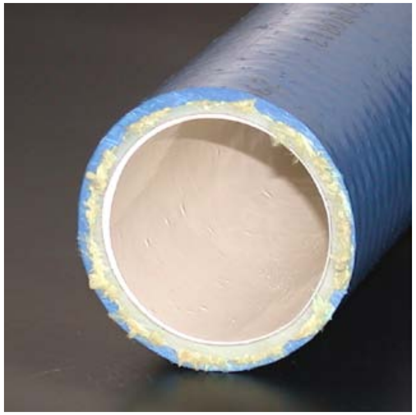
Technical Highlights

- FY 2010
  - Completed evaluation of Polyflow braided aramid fiber reinforced pipeline
    - Hydrogen leakage is below nominal target for pipeline delivery
    - Co-extruded PPS-PA liner has lower permeation than comparable 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

Technical Accomplishments

- **Hydrogen leak rate measurements in specimens of Polyflow Thermoflex® FRP pipelines**
  - **Liner materials: Coextruded polyphenyl sulfide PPS (inner layer) and nylon PA-6 (outer layer)**
  - **Reinforcement architecture: aramid fiber rovings braided on liner, laid over four longitudinal rovings**
    - **Burst strength determined by braid angle, not by number of plies**
  - **Exterior jacket: Polypropylene with damage indicating colorant**
  - **Couplings with swaged metal seals**

Polyflow ThermoFlex® CA2325R1
6.1 cm OD, 4.8 cm ID

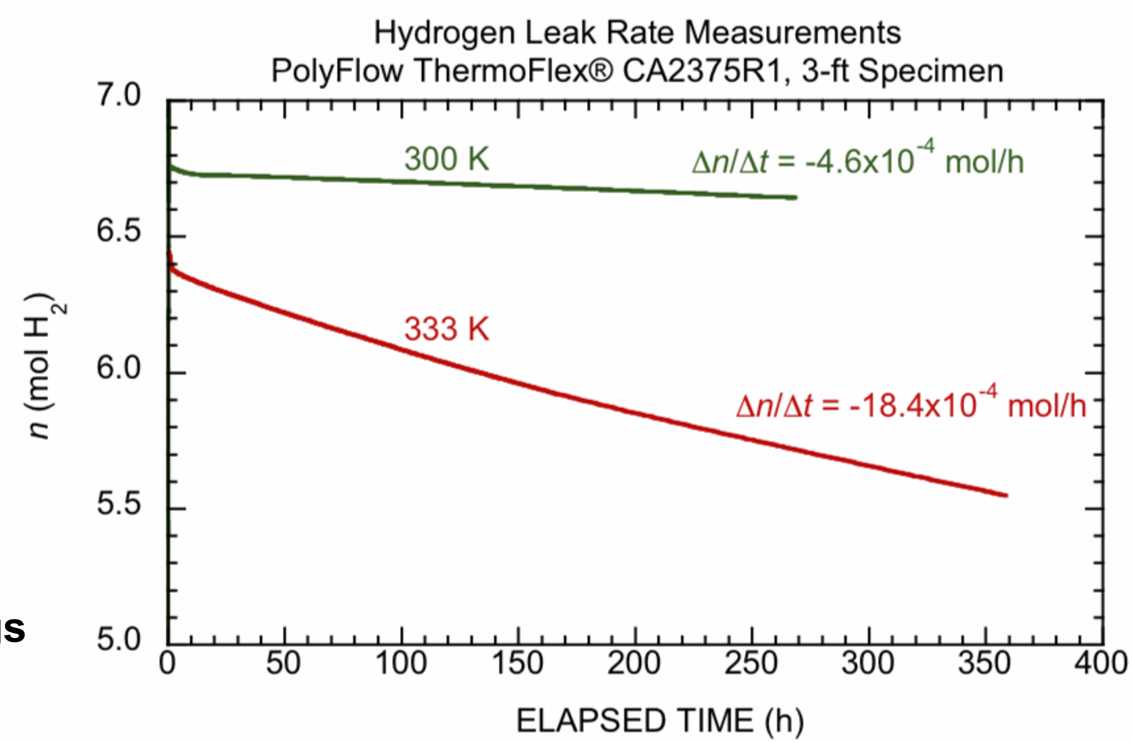


Technical Accomplishments

- Hydrogen leak rate measurements in specimens of Polyflow Thermoflex® FRP pipelines
  - Leak rate determination based on temperature-corrected pressure decay measurement
    - Pipeline pressurized to maximum operating pressure
    - Used quartz pressure transducer with digital output
      - Range: 0-3000 psia (0-200 bar)
      - Accuracy: 0.01% (0.3 psi / 20 mbar) in 0-70 °C range
    - RTD sensors inside pipeline measured gas temperature
    - Pressure corrected using Abel-Noble EOS for hydrogen
  - No compensation for pressure-induced volumetric expansion
    - Pressure-induced expansion and contraction involves bi-axial stress-strain relationships, differing axial and hoop moduli, Poisson ratios for major and minor axes
    - Change in volume expected to be < 0.01% per psi at 1500 psia and room temperature

Technical Accomplishments

- **Leak rate measurements in Polyflow Thermoflex®**
- **Pipeline specimen**
  - **OD = 6.1 cm, ID = 4.8 cm, L = 77 cm**
  - **Liner of co-extruded PPS and nylon (each polymer ~1.7 mm thick), braided aramid fiber reinforcement, 2-mm thick PP jacket**
  - **Pipeline ends terminated with swaged steel couplings and sealed with threaded steel caps**
  - **Pressurized to 1500 psi (max allowable operating pressure)**
  - **Hydrogen leak rate measurements made at 30 and 60°C**

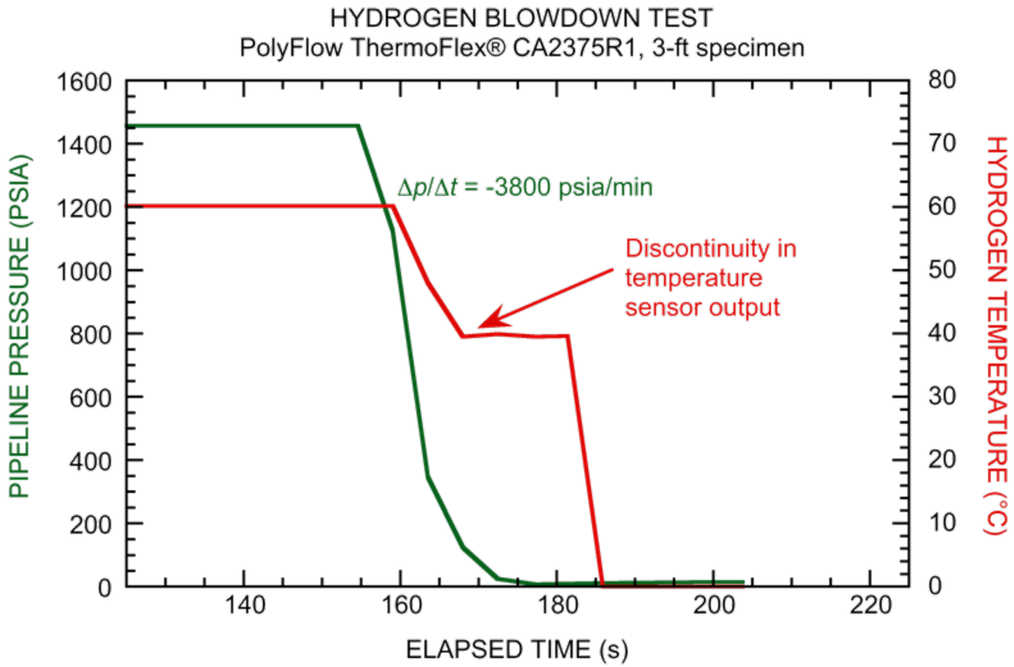


Leak rates in PPS/nylon pipeline are comparable in magnitude to rates obtained in similar length of glass fiber reinforced pipeline with 5-mm thick HDPE liner. PPS/nylon liner provides about 50% decrease in hydrogen leak rate compared to HDPE.

Technical Accomplishments

- **Hydrogen blowdown test for Polyflow Thermoflex®**
- **Guidance: API 15S, "Qualification of Spoolable Reinforced Plastic Line Pipe," Appendix D**
  - **Fill specimen with hydrogen* to pressure rating (1500 psig), heat specimen to temperature rating (60°C), and hold these conditions until pipeline structure is saturated with gas**
  - **Following hold period to allow for hydrogen saturation, de-pressurize specimen at a rate not less than 1000 psi/min**
  - **Examine specimen liner for evidence of blistering or collapse**

***API 15S specifies the use of supercritical CO_2 for blowdown testing**

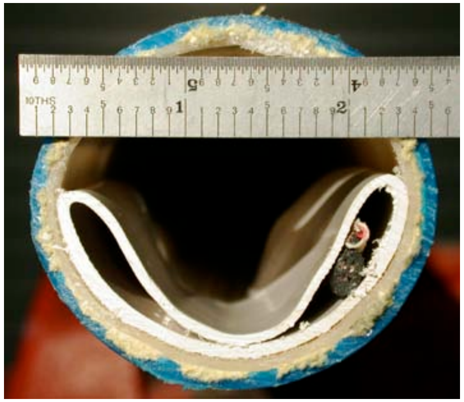


Depressurization was almost 4 times faster than specified minimum rate. RTD temperature sensor output failed near end of depressurization interval.

Technical Accomplishments

- **Post blowdown analysis**
  - **Examined liner for blistering or collapse**
    - **Inner layer of PPS separated from outer layer of nylon on approximately half of tube circumference, along entire length of specimen**
    - **Outer layer of nylon remained adhered to fiber reinforcement matrix**
    - **Possible failure modes: Buildup of high-pressure hydrogen in microscopic void between co-extruded layers or unbalanced shear stresses in layers**
  - **Blowdown testing can cause coextruded liners to fail**

Pipeline following hydrogen blowdown procedure, cut transversely to examine collapsed liner. Strain gauges for hoop and longitudinal strain are visible on top of pipeline. Cable for RTD temperature sensor is visible inside collapsed liner.



Inner layer of co-extruded liner (white PPS) separated from outer layer (beige nylon) during blowdown

Technical Accomplishments

- **Comparison of pipeline leakage measurements**

Specimen	Construction	Nominal Pressure (bar)	Measured Leakage Rate (mol/h per m)	Predicted Leakage Rate (mol/h per m)
Fiberspar LinePipe™ 10-cm ID	0.5-cm thick PE-3408 liner, glass fiber epoxy matrix reinforcement	100	3×10^{-4}	9×10^{-3}
Polyflow ThermoFlex® 4.8-cm ID	0. 34-cm thick PPS+PA liner, aramid braid reinforced, PP jacket	100	6×10^{-4}	$\sim 1 \times 10^{-3}$

The leakage rate for each of two FRP pipelines with different liners and reinforcement schemes is well below the rate that corresponds to the 0.5% leakage target.

Technical Accomplishments

- **Accelerated aging of glass fibers in high-pressure hydrogen environment is being used to screen for long-term effects of hydrogen on composite reinforcement materials**
- **Simplified protocol for accelerated aging based on Arrhenius model**

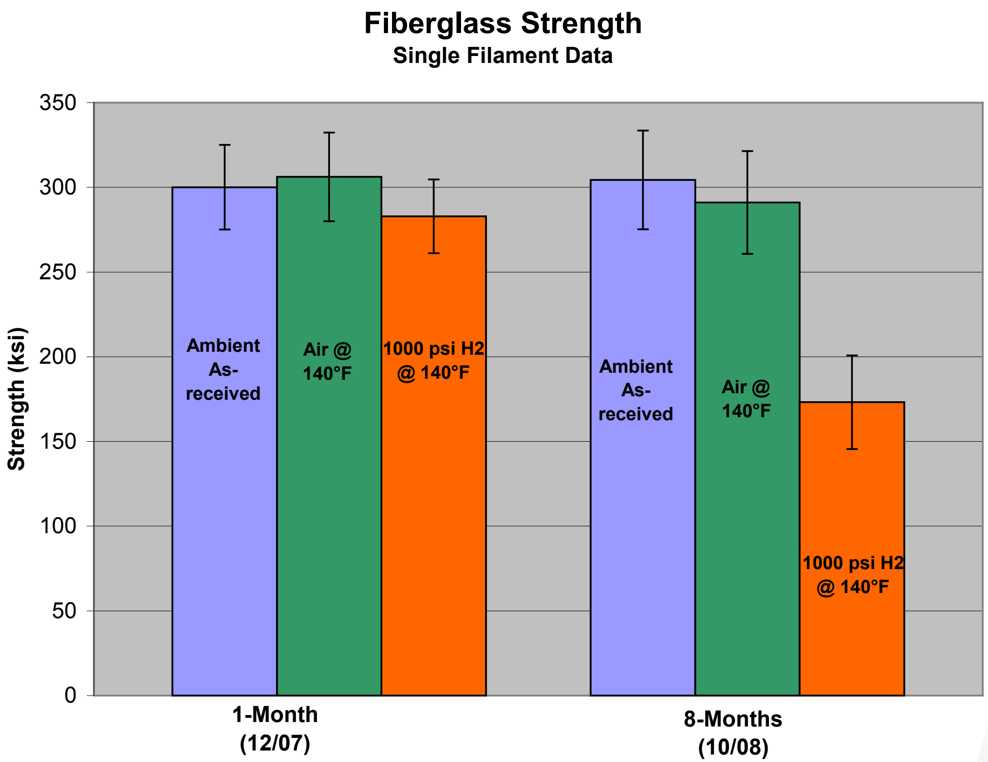
$$\text{reaction rate} = Ae^{-\lambda/kT}$$

where A is a rate constant, λ is the activation energy, k is the Boltzmann constant and T is the temperature

- **Following hydrogen exposure, tensile tests of glass filaments are performed to measure changes in fiber reinforcement properties**
- **Single elevated temperature of 60°C (rated maximum temperature of pipeline)**
- **No stressors other than hydrogen (i.e., no oxygen, water, chemicals, UV)**
- **Assume elevated temperature itself does not degrade fibers (inclusion of thermal control specimens treated in air, concurrently with specimens treated in hydrogen)**

Technical Accomplishments

- Earlier post-hydrogen exposure testing of glass filaments showed statistically significant loss in tensile strength
- Results were equivocal, however, because glass fibers were possibly damaged during shipping following hydrogen exposure



Single glass filaments are used for strength, elongation and modulus measurements

Technical Accomplishments

- Glass filament degradation is being re-evaluated using better controls and testing at shorter intervals
- Results obtained so far (11 weeks of exposure) do not show a degradation in tensile strength
- Tests will continue through 35 weeks (8 months), possibly longer

	Filament Conditioning			
Test Result	1,000 psi Hydrogen @ 60°C; 5-weeks	Ambient air @ ~25°C; 5-weeks (control)	1,000 psi Hydrogen @ 60°C; 11 weeks	Ambient air @ ~25°C; 11-weeks (control)
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)

Future Work

- **FY 2010**
  - Continue assessment of possible hydrogen-induced cracking in the reinforcement layers during cyclical strain, perform long-term stress rupture tests, perform high-pressure cyclical fatigue tests, assess joint sealing under cyclic loading
  - Revisit economic feasibility analysis for additional pipeline cost reductions
  - Codes & standards development for hydrogen-service FRP pipelines
- **FY 2011**
  - Initiate joint industry pipeline demonstration project
  - Perform tests to evaluate effects of third-party damage to hydrogen delivery performance
  - Collaborate on development of codes & standards for hydrogen-service FRP pipelines

Collaborations

- Fiberspar, LLC, Houston, TX – Provided pipeline specimens and connectors, cost-modeling information, post-hydrogen exposure testing, co-author on paper (in preparation)
- Polyflow, Inc, Philadelphia, PA - Provided pipeline specimens and connectors, cost-modeling information
- Flexpipe Systems (pending collaboration) – TBD, but probably pipeline specimens and connectors, cost-modeling information
- Ticona – Provided pipeline grade PPS specimens
- Dow Chemical (pending collaboration) – Specimens of pipeline grade bimodal PE for hydrogen permeation testing
- Fluoro-Seal – Permeation-reducing surface treatments of polymer specimens used in permeation coefficient measurements

Project Summary

Relevance: Need viable alternative to metallic pipelines to achieve cost and performance targets for hydrogen transmission and distribution

Approach: Investigate applicability of composite pipelines in use in oil & gas gathering operations and develop path forward for hydrogen delivery

Progress: Cost scenario shows composite pipelines meet DOE 2012 goals and 2017 goals are achievable;; pipeline leakage rates are lower than predicted; composite pipeline materials are chemically and mechanically compatible with hydrogen with no deleterious hydrogen-induced effects

Collaborations: Pipeline and polymer industries, National Lab

Future: Codes & standards; prototype FRP pipeline system for H_2 delivery; demonstration project