### Overview

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

**Budget**
- Total project funding
  - DOE: $1.05M
- Funding received in FY 07
  - $450k
- Funding for FY 08
  - $450k

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

**Partners & Collaborators**
- Fiberspar, PolyFlow
- Arkema, Ticona, Fluoro-Seal
- SRNL
- Pipeline Working Group
# Overview

## Technical Targets

<table>
<thead>
<tr>
<th>Category</th>
<th>2005 Status</th>
<th>2012</th>
<th>2017</th>
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<tbody>
<tr>
<td><strong>Pipelines: Transmission</strong></td>
<td></td>
<td></td>
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<tr>
<td>Total Capital Investment (16-in pipeline, $/mile)</td>
<td>$720k</td>
<td>$600k</td>
<td>$490k</td>
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<tr>
<td><strong>Pipelines: Distribution</strong></td>
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<tr>
<td>Total Capital Investment (2-inch pipeline, $/mile)</td>
<td>$320k</td>
<td>$270k</td>
<td>$190k</td>
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<tr>
<td><strong>Pipelines: Transmission and Distribution</strong></td>
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<tr>
<td>Reliability/Integrity (including 3rd-party damage issues)</td>
<td>Acceptable for current service</td>
<td>Acceptable for H₂ as a major energy carrier</td>
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<tr>
<td>H₂ Leakage *</td>
<td>Undefined</td>
<td>TBD</td>
<td>&lt; 0.5%</td>
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</table>

* Leakage targets are being reviewed by the Delivery Tech Team
# Project Milestones

<table>
<thead>
<tr>
<th>Month-Year</th>
<th>Milestone or Go/No-Go Decision</th>
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<tr>
<td>May 2008</td>
<td>Milestone: Initial round of polymer diffusivity and permeability measurements completed.</td>
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</table>
| Sep 2008   | Go/no-go decision: Hydrogen compatibility evaluation of composite pipeline materials and construction completed and reported (on track)  
Milestone: Survey of existing modifications and treatments available for reducing permeability in liner materials completed and reported (40% complete)  
Milestone: Recommendations for sensor integration, manufacturing and joining technologies completed and reported (20% complete) |
Plan & Approach

- **Task 1: Pipeline Materials Compatibility**
  - Accelerated aging in $H_2$
  - Testing and evaluation

- **Task 2: Liner permeability**
  - Survey and measure polymer $D$ and $P$
  - Assess modification and treatment options

- **Task 3: Joining and sensor technologies**
  - Assess coupling, termination, repair
  - Assess needs for structural health monitoring, leakage and gas property sensing
Technical Accomplishments

- **Task 1: Pipeline materials compatibility testing**
  - One-month hydrogen exposure completed with no materials degradation; longer-term exposure underway
  - Initial pipeline leakage measurements completed: smaller than expected leak rate (0.03% per day); additional measurements underway
  - Blowdown testing of FRP pipeline specimen in progress
Technical Accomplishments

- **Task 2: New contributions to polymer permeation literature**
  - Permeation coefficients for H₂ in HDPE exhibit pressure dependence
  - Coefficients for H₂ in PA and PPS are smaller than those for HDPE
  - Evaluation of surface fluorination treatment in progress
Technical Accomplishments

• Task 3: Joining and sensor technologies
  – Indirect evaluation of hydrogen leakage through Fiberspar LinePipe™ connectors showed very low leakage rate (<3x10^{-6} mol/s)
  – Collaborative effort with SRNL to assess joint loading, pipeline flexure, and pressure/temperature cycling on hydrogen leakage for both Fiberspar and PolyFlow connectors
One-month accelerated aging of Fiberspar materials completed

- Accelerated aging procedure used to screen for long-term effects of hydrogen exposure on composite pipeline under normal-usage conditions

- Specimens of Fiberspar pipelines and constituent materials
  - Immersion in 1000 psi $H_2$
  - Accelerated aging at 140°F (60°C)
  - 1 month & 8 month exposures

- 4-pt bending test specimen
- Compression test specimen
- SRNL $H_2$ exposure station
- Tensile-test specimen of liner material
No measurable degradation in materials performance after accelerated aging

- Post-exposure testing of pipeline specimens and materials
  - 4-point bending test to assess laminate cracking
  - Short-term pressure burst test (ASTM D1599)
  - Parallel plate compression test (ASTM D2412)
  - Tensile tests and DMA of liner, matrix resin, glass filaments

- No statistically significant differences between as-received, air-exposed and hydrogen-exposed pipeline specimens and materials
No reduction in tensile properties of epoxy matrix resin

<table>
<thead>
<tr>
<th>Test (dog bone)</th>
<th>Air @ 140°F 1 month</th>
<th>1000 psi H₂* @ 140°F 1 month</th>
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<tbody>
<tr>
<td>Tensile Strength</td>
<td>7,891 psi (27.9)</td>
<td>8,791 psi (20.2)</td>
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<tr>
<td>Elongation</td>
<td>2.9 % (43.1)</td>
<td>3.5 % (40.0)</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>371 ksi (1.1)</td>
<td>371 ksi (0.6)</td>
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*H₂ conditioning at SRNL. Numbers in parentheses are % coefficients of variation for data set.
New permeation coefficient measurements for H₂ in HDPE, PPS

Permeation Coefficients for H₂ in HDPE, PPS, PA-6

- Fiberspar HDPE
- Hostalen HDPE PDL
- Lincoln Composites HDPE Tank Liner
- Ticona PPS
- Air Liquide PA-6
Polymer surface modification in progress

- Polymer surface modification via fluorination
  - Surface fluorination used in packaging industry to reduce emission of VOCs
  - Reduces $D$ and $P$ of VOCs by factors of 1.5 to 4.5 in HDPE containers

- Surface fluorination proceeds via free radical mechanism in molecular exchange along polymer chains at surface

- Fluoro-Seal is providing fluorination treatment of pipeline-grade HDPE, PPS, PA

- Expect results in 4th reporting period
Prediction of H$_2$ leak rate for Fiberspar pipeline with HDPE barrier tube

- Fiberspar LinePipe 4-1/2 1,500 (E)
  - Barrier tube: extruded PE-3408
  - Tube inner radius = 5.05 cm
  - Tube outer radius 5.576 cm

- Hydrogen leak rate per unit length of barrier tube given by

$$\frac{dn}{dt} = \frac{2\pi P}{\ln(b/a)} (p_0 - p_1) \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-1}$$

where

- $P =$ permeation coefficient for hydrogen in HDPE
- $a,b =$ inner, outer radii of tube wall
- $p_0, p_1 =$ hydrogen pressures inside, outside tube
Prediction of $\text{H}_2$ leak rate in Fiberspar pipeline with HDPE barrier tube

- **Parameter values**
  - $P \approx 4 \times 10^{-12}$ mol/cm$\cdot$s$\cdot$bar
  - $a = 5.05$ cm, $b = 5.576$ cm
  - $p_0 = 99$ bar, $p_1 = 1$ bar

- **Predicted hydrogen leak rate in 1.83-m pipeline**
  - $dn/dt = 1.7 \times 10^{-2}$ mol/h
  - This leak rate would be equivalent to a loss of $3.4 \times 10^{-5}$ kg/h

![Dependence of Permeation Coefficient $P$ on $\text{H}_2$ Pressure PE3408 at 25°C](chart.png)

$P \approx 4.0 \times 10^{-12}$ mol/cm$\cdot$s$\cdot$bar at 99 bar (1430 psia)
Measurement of $H_2$ leak rate in Fiberspar pipeline with HDPE barrier tube

- **Pressure decay measurement**
  - Using 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

- **Temperature compensation for pipeline pressure**
  - RTD sensors inside pipeline measure gas temperature
  - Pressure corrected using Able-Noble EOS for hydrogen

- **Volumetric expansion compensation**
  - 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 RT $\rightarrow$ no correction applied
Measurement of H$_2$ leak rate in Fiberspar pipeline with HDPE barrier tube

Pipeline Leakage Measurement
1500 psia (103 bar) Pressurization
Moles of hydrogen gas in pipeline

During interval 50-285 hours, $dn/dt \approx 7 \times 10^{-4}$ mol/h
H₂ leak rate in pipeline with HDPE barrier tube is better than expected

- Leakage from end cap seals is not a significant contribution to total leak rate

- Product loss due to permeation
  - \( \frac{dn}{dt} = 7 \times 10^{-4} \text{ mol/h} \rightarrow 2 \times 10^{-2} \text{ mol/d} \)
  - Pipeline under test contained approx. 55 mol H₂
  - Loss due to barrier tube permeation and end cap seal leakage was 0.03% per day, about 20 times less than that predicted using permeation coefficient for PE-3408 liner
Hydrogen blowdown testing of composite pipelines in progress

- Guidance: API 15S - Qualification of Spoolable Reinforced Plastic Line Pipe*
  - Fill specimen with hydrogen to pressure rating, heat specimen to temperature rating, and hold these conditions until pipeline structure is saturated with gas
  - Following hold period, de-pressurize specimen at a rate not less than 1000 psi/min
  - Examine specimen liner for evidence of blistering or collapse

*API 15S Appendix D specifies that supercritical CO₂ be used for blowdown testing

1-meter pipeline specimen instrumented for blowdown testing
Future Work

- **FY 2008**
  - Report test results from 8-month accelerated aging and hydrogen exposure of pipeline and material specimens
  - Continue measurements of liner materials, including measurements of surface fluorination samples
  - Construct diffusion and permeation apparatus for polymers, with additional capabilities

- **FY 2009**
  - Begin 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
  - Complete assessment of joining and integrated sensor technologies and report results
  - Collaborate on development of codes & standards for hydrogen-service FRP pipelines
# Project Summary

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<thead>
<tr>
<th>Relevance:</th>
<th>Need viable alternative to metallic pipelines to achieve cost and performance targets for hydrogen transmission and distribution</th>
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<tbody>
<tr>
<td>Approach:</td>
<td>Investigate applicability of composite pipelines in use in oil &amp; gas gathering operations and develop path forward for hydrogen delivery</td>
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<tr>
<td>Progress:</td>
<td>Cost scenario shows composite pipelines are meet DOE 2012 goals and are close to 2017 goals; hydrogen compatibility of pipeline materials is acceptable; pipeline leakage rates are better than predicted</td>
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<td>Collaborations:</td>
<td>Pipeline and polymer industries, National Lab</td>
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<tr>
<td>Future:</td>
<td>Codes &amp; standards; prototype FRP pipeline system for H₂ delivery; demonstration project</td>
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