Evaluation of Natural Gas Pipeline Materials for Hydrogen Service

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Savannah River National Laboratory
DOE Hydrogen Pipeline R&D Project Review Meeting
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Hydrogen Technology at the Savannah River Site

- Tritium Production/Storage/Handling and Hydrogen Storage/Handling since 1955
  - Designed, built and currently operate world’s largest metal hydride based processing facility (RTF)
  - DOE lead site for tritium extraction/handling/separation/storage operations
- Applied R&D provided by Savannah River National Laboratory
  - Largest hydrogen R&D staff in country
- Recent Focus on Related National Energy Needs
  - Current major effort on hydrogen energy technology (storage, production and infrastructure development)
  - Developing strategic university, industrial and other partnerships in hydrogen energy R&D and demonstrations.

Advanced Hydride Laboratory

Fuel Cell Vehicle w/MH Storage
SRS Tritium Defense Program has a $200 M budget with $25 M allocated to SRNL
Hydrogen Technologies

- Metal & Complex Hydride
  - storage
  - compressors/pumps
  - purifiers/separators
  - heat pumps/refrigeration
- Battery / Fuel Cells
  - Ni metal hydride
  - Fuel Cells
- Sensors
  - fiber optic
  - composite (ceramic)

- Hydrogen Production
  - membranes
  - electrolysis
  - thermochemical water splitting
  - biohydrogen
- Materials Compatibility
  - H2 embrittlement
  - failure analyses
- Safety
  - H2 safety analyses
  - codes and standards
Hydrogen Isotope Compatibility
Understanding & Mitigation of Effects on Metals & Polymers

1E-10
1E-09
1E-08
1E-07
1E-06
1E-05
0 1 02 03 04 05 06 07 08 09 0
Stress Intensity MPa-m\(^{1/2}\)

Crack Growth Rate, m/s

300 appm Helium
600 appm helium
Decay Helium
Reduces
Threshold For
Cracking

Tritium Causes Slow Crack Growth
Decay Helium Reduces Threshold For Cracking

Cracking Thresholds for Structural Alloys

Dynamic Mechanical Analysis for Polymers

- Tritium (Beta Radiation) Degradation of UHMW-PE Valve Stem Tip

Tritium and Decay Helium Embrittlement of Stainless Steel Weld Heat Affected Zone

Universal V2.6D TA Instruments

A 1 Hz

Storage Modulus (MPa)

-100 -50 0 50 100 150
Temperature (°C)

UHMW PE 140°C Exposure

• Tritium and Decay Helium Embrittlement of Stainless Steel Weld Heat Affected Zone

• Tritium (Beta Radiation) Degradation of UHMW-PE Valve Stem Tip

Cracking Thresholds for Structural Alloys
Hydrogen Isotope Compatibility
Hydrogen Isotope Charging and Mechanical Testing

Tritium Charging Facility Schematic and Mock-up

Testing Tritium Exposed Samples
Hydrogen Isotope Compatibility
Hydrogen Isotope Effects on Polymers

Effects Characterized Using DMA, FT-IR, Color Measurements, Density, Offgas

DMA - Present Study of Ultrahigh Molecular Weight Polyethylene (UHMW-PE), Vespel™, Teflon™

FT-IR of Non-Exposed and T₂-Exposed UHMW-PE

Colorimetry Used to Indicate Degree of Radiation Damage and Remaining Service Life
Hydrogen Isotope Compatibility
Hydrogen Isotope Effects on Containment Alloys

Fracture Toughness Samples Taken from Welds and Base Metal

- Samples Exposed to Tritium in Charging Facility
- Aging and Testing to Characterize Effects of Tritium and Decay to Helium

Investigate Material Processing Effects (Forging, Welding, HAZ) on Embrittlement from Tritium and Decay to Helium
Hydrogen Isotope Compatibility
Permeation Barrier Development and Testing

Al-rich Permeation Barriers

Schematic and Photograph of Permeation Test Rig
SRNL is Addressing the Major Challenges to a Hydrogen Economy

Major Needs per DOE Hydrogen Roadmap:

• **Hydrogen Storage** (*R&D w/major industrial partners*)
  – Develop lightweight, compact, low-cost systems

• **Supply & Infrastructure** (*w/automotive, energy and utility partners, including regional demonstrations*)
  – Create a national supply and delivery infrastructure
  – Develop low cost, efficient H2 production from non-fossil energy sources (*nuclear hydrogen production studies*)

• **Fuel Cells** (*w/university and industrial partners*)
  – Reduce costs and develop mass production
  – Increase lifetime and durability
• 60,000 ft² Center for Hydrogen Research in Progress
  – Located at Savannah River Research Park
  – 30,000 ft² reserved for academic & industrial partners
• Construction Started, Operation Scheduled for October 2005
• Focus on Hydrogen Technology R&D
  – Advanced storage
  – Separation, production, sensors, safety and hydrogen effects on materials
  – User Center/Demonstration Facility (e.g. Pipeline Project)
Purpose:
The project will provide a facility for the testing of safety codes and standards with emphasis on the development of components, materials, and repair techniques for piping in high pressure hydrogen service.

Partners:
ASME and SRNL will partner with industry and government to provide a demonstration project relevant to the needs for a new hydrogen economy.

Key Issue for the Demonstration Project

- Design
  - Leakage of mechanical joints
  - Fracture prevention and mitigation
  - Fatigue at high pressure
  - Repair technology
  - Compression technology

- Fabrication
  - Joint quality
  - Liner technology

- Materials
  - Hydrogen embrittlement
  - New materials technology and testing
  - Heat to heat variation of ASTM specifications
  - Coating development

- Inspection
  - Internal inspection
  - Sensor development
Hydrogen Pipeline Demonstration Project

ACTL – Aiken County Technology Lab
HRTL – Hydrogen Research Technology Lab
SRNL is Addressing the Major Challenges to a Hydrogen Economy

SRNL

• is a recognized expert in hydrogen production, separation and hydrogen storage R&D.

• has ongoing R&D programs in several key areas of hydrogen technology.

• has a good track record in working with industrial, academic, and other government agencies.

• can provide complete solutions to customer problems (from research to process development to system demonstration).
DOE Goal for Hydrogen Delivery

DOE Hydrogen Delivery Focus

“Develop hydrogen fuel delivery technologies that enable the introduction and long long-term viability of hydrogen as an energy carrier for transportation and stationary power”

-DOE Hydrogen Delivery Goal
H₂/NG Distribution Systems

Use Existing NG Pipeline System for H₂ or H₂+NG Transport

- NG Transmission Pressure Range 500-1200 psig
- Few 100’s Miles of Transmission Pipeline
- NG Distribution Pressure Range <100 psig
- Few Million Miles of Distribution Piping
# Current Hydrogen Pipeline Infrastructure

<table>
<thead>
<tr>
<th>Location</th>
<th>Pipeline Material</th>
<th>Years of Operation</th>
<th>Diameter (mm)</th>
<th>Length (km)</th>
<th>Pressure (kPa) and Gas Purity (%)</th>
<th>Experience Reported</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEGEC, Alberta, Canada</td>
<td>Gr. 290 (SSX 42)</td>
<td>Since 1983</td>
<td>272 x 9.8 WT</td>
<td>2,7</td>
<td>0.76 kPa – 59.9</td>
<td>No</td>
<td>Operational</td>
</tr>
<tr>
<td>American Air Liquide Texas/Louisiana, USA</td>
<td>API 5LXG, X32, X60 and others</td>
<td>5</td>
<td>3&quot; to 14&quot;</td>
<td>200</td>
<td>0.150 kPa (700 PSI)</td>
<td>Yes</td>
<td>Operational</td>
</tr>
<tr>
<td>Air Products, Houston area, USA</td>
<td>Since 1969</td>
<td>114.3 – 321</td>
<td>100</td>
<td>245 – 253 (Part HI)</td>
<td>No</td>
<td>Operational</td>
<td></td>
</tr>
<tr>
<td>Air Products, Louisiana</td>
<td>ASTM 106</td>
<td>1997</td>
<td>101.6 – 304.8</td>
<td>48.3</td>
<td>3,471</td>
<td>Yes</td>
<td>Operational</td>
</tr>
<tr>
<td>Air Products, Sarnia (Desc to Dime plant)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air Products, Texas</td>
<td>Cas, natural gas line (steel)</td>
<td>&gt;10</td>
<td>144.3</td>
<td>8</td>
<td>5,000 – Part HI</td>
<td>Yes</td>
<td>Operational</td>
</tr>
<tr>
<td>Air Products, Texas</td>
<td>Steel, mild steel 40</td>
<td>&gt;8</td>
<td>285.0</td>
<td>19</td>
<td>6,000 – Part HI</td>
<td>Yes</td>
<td>Operational</td>
</tr>
<tr>
<td>Air products, Nederland</td>
<td></td>
<td></td>
<td>45.8m</td>
<td></td>
<td>(throughput~50 ton/day)</td>
<td></td>
<td>Operational</td>
</tr>
<tr>
<td>Chemische Werke Hutting AG, Med, Germany</td>
<td>Seamless equipment to SAE 1020 steel</td>
<td>Since 1958</td>
<td>106.3 – 273</td>
<td>215</td>
<td>6,560 psig gas (throughput ~ 200 x 100 m³)</td>
<td>Yes</td>
<td>Operational</td>
</tr>
<tr>
<td>Corus B.C., Canada</td>
<td>Carbon Steel (ASTM A106 Grade B)</td>
<td>Since 1964</td>
<td>5.0 x 0.125 WT</td>
<td>46</td>
<td>&gt;294,000 psig to 100% pure H2</td>
<td>No</td>
<td>Expiry</td>
</tr>
<tr>
<td>Gulf Pressure Co., (Feusswalt- Varenna)</td>
<td>Carbon Steel, seamless, Sch. 40</td>
<td></td>
<td>106.3</td>
<td>16</td>
<td>55% H2, 75% methane</td>
<td>No</td>
<td>Operational</td>
</tr>
<tr>
<td>Hoechst Chemical, Inc.</td>
<td>ASTM A253 Gr. B</td>
<td>3</td>
<td>152.4</td>
<td>2.2</td>
<td>8,991.6</td>
<td>Yes</td>
<td>Operational</td>
</tr>
<tr>
<td>ICI Billingham, UK</td>
<td>Carbon Steel</td>
<td></td>
<td></td>
<td>15</td>
<td>30,000 kPa, pure</td>
<td>No</td>
<td>-</td>
</tr>
<tr>
<td>L'Air Liquide, France, Netherlands, Belgium</td>
<td>Carbon Steel, seamless,</td>
<td>Since 1966</td>
<td>3.0 in up to 12&quot;</td>
<td>879</td>
<td>6,400 – 10,000 kPa, pure and raw</td>
<td>No</td>
<td>Operational</td>
</tr>
<tr>
<td>LASL, N.M.</td>
<td>ASME A357Gr.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Las Alcan, N.M.</td>
<td>5 Cu – 31 Al (ASME A357 Gr. 5)</td>
<td></td>
<td>4</td>
<td>30</td>
<td>13,750 pure</td>
<td>Yes</td>
<td>Abandoned</td>
</tr>
<tr>
<td>Linde, Germany</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NASA-SSC, Fla</td>
<td>300-55 (acetavite)</td>
<td>&gt;16</td>
<td>60</td>
<td>1.6-2</td>
<td>42,000 kPa</td>
<td>No</td>
<td>Operational</td>
</tr>
<tr>
<td>NASA-MCC, Ala</td>
<td>ASTM A106 Grade B</td>
<td>8</td>
<td>76.2</td>
<td>0.091</td>
<td>38470</td>
<td>Yes</td>
<td>Abandoned</td>
</tr>
<tr>
<td>Phillips Petroleum</td>
<td>ASTM A335</td>
<td>4</td>
<td>104-3.5</td>
<td>70.9</td>
<td>10,000-12,000</td>
<td>Yes</td>
<td>Operational</td>
</tr>
<tr>
<td>Praxair, Gulf Coast, Ta, Indiana, California</td>
<td>Carbon Steel</td>
<td></td>
<td>458 km</td>
<td></td>
<td></td>
<td></td>
<td>Operational</td>
</tr>
<tr>
<td>Alabama, Louisiana, Michigan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rockwell International S.</td>
<td>30-106</td>
<td>&gt;10</td>
<td>220</td>
<td></td>
<td>&gt;100,000 kPa, ultra pure</td>
<td>No</td>
<td>-</td>
</tr>
<tr>
<td>South Africa</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Current National Hydrogen Pipeline Infrastructure

- Predominately Carbon Steel Materials
  - X42, X52, X60, A106 Grade B, A357 Grade 5
  - Transmission Pressure Limited to $\approx 800$psi
  - Pipe Sizes up to 12”
Key Challenges for H$_2$ Delivery

Key Challenges

- **Pipelines**
  - Retro-fitting existing NG pipeline for hydrogen
  - Utilizing existing NG pipeline for Hythane
  - New hydrogen pipeline: lower capital cost
  - Leakage/Seals
  - Hydrogen Effects on Materials

- Lower cost and more energy efficient compression Technology

- Lower cost and more energy efficient liquefaction Technology

- Novel solid or liquid carriers

- Operational Challenges: Retrofitting Compression/Leakage
- Materials Challenges: Hydrogen Embrittlement
**Example - Compare H2 and Natural Gas Compression & Pipeline Transmission:**

- Compress from $P_{\text{initial}} = 1$ to $P_{\text{final}} = 1000$ PSIG
- 4-stage, inter-cooled compression equipment
- Initial temp = 70 °F, Inter-stage temp = 90 °F
- Compress the same volumetric quantity of each gas, i.e. XX million SCF/day:

**Hydraulic characteristics of H2 and Natural Gas are quite different:**

- 100 miles of 20” I.D. Pipeline
- Gas temp = 70 °F = constant
- Initial Pressure = 1000 PSIG
- Find volume rates of Natural Gas and H2 delivered with 200 PSI $\Delta P$:

<table>
<thead>
<tr>
<th></th>
<th>Natural Gas</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delivered Energy consumed in the Compression Process</td>
<td>0.31 %</td>
<td>1.33 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Natural Gas</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of Gas Delivered (SCFH)</td>
<td>7.0 MM</td>
<td>18.4 MM</td>
</tr>
</tbody>
</table>

*Transports Hydrogen across the existing Natural Gas Infrastructure may result in a capacity “de-rating” (on a delivered energy basis) of approximately 20-25%.*
Combining Compression Energy and Hydraulic loss calculations:

<table>
<thead>
<tr>
<th></th>
<th>Natural Gas</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of Gas Delivered (SCFH)</td>
<td>7.0 MM</td>
<td>18.4 MM</td>
</tr>
<tr>
<td>LHV Energy Delivered (BTU/Hr)</td>
<td>6,391 MM</td>
<td>5,060 MM</td>
</tr>
<tr>
<td>Less Compression Energy (BTU/Hr)</td>
<td>(20) MM</td>
<td>(69) MM</td>
</tr>
<tr>
<td>Net Energy Delivered (BTU/Hr)</td>
<td>6,371 MM</td>
<td>4,991 MM</td>
</tr>
</tbody>
</table>

Transporting Hydrogen across the existing Natural Gas Infrastructure may result in a capacity “de-rating” (on a delivered energy basis) of approximately 20-25%.
Leakage

- Gaskets and Seals are more critical (compared to Natural Gas)

- H2 (commercial purity) has no odor.
  - Adding odorants as for Natural Gas, LPG etc. adds a contaminant that is poisonous to many fuel cell technologies
  - This will add cost to the H2 energy picture, either in pretreatment to remove the contaminants, or in reduced service life of the affected systems.

- Owing to the lower ignition energy and wider flammability limits, H2 leaks are more likely to ignite than a Natural Gas leak.

- Lower flame temperatures produce fires that are less damaging than Natural Gas fires.
Figure 8. BASELINE NATURAL GAS LEAKAGE FOR INDUSTRIAL TEST LOOP

Adapted from Jasionowski et al., Hydrogen for Energy Distribution, 1978
Figure 9. LEAKAGE CHARACTERISTICS OF THE INDUSTRIAL TEST LOOP IN HYDROGEN OPERATION

Adapted from Jasionowski et al., Hydrogen for Energy Distribution, 1978
Figure 10. BASELINE NATURAL GAS LEAKAGE OF THE RESIDENTIAL/COMMERCIAL MODEL

Adapted from Jasienowski et al., Hydrogen for Energy Distribution, 1978
H2/NG Distribution Systems Operational Challenges

Figure 11. HYDROGEN LEAKAGE OF THE RESIDENTIAL/COMMERCIAL MODEL

Adapted from Jasionowski et al., Hydrogen for Energy Distribution, 1978
Materials of Construction

- Hydrogen Embrittlement
  - Presence of atomic hydrogen in carbon steel (permeability)
  - Toughness or ductility of the metal is decreased
    - Results in Cracking or Fissuring of the Metal

Potentially Catastrophic Failure of Pipelines!

Higher Strength Materials are more susceptible to Hydrogen Embrittlement.
Control of Hydrogen Embrittlement

The effect and level of hydrogen embrittlement on materials is dependent on a large number of variables such as:

- Environment temperature and pressure
- Hydrogen purity and concentration
- Hydrogen exposure time
- Stress state, secondary stresses, temperature range etc.
- Metal microstructure, physical, mechanical properties
- Metal surface finish and conditions
- Type of material crack front
H2/NG Distribution Systems Materials Challenges

Figure 1. Yield strength dependence of delayed failure in cathodically charged carbon-manganese steels.

Adapted from S. L. Robinson, Hydrogen for Energy Distribution, 1978
Figure 3. Hydrogen caused ductility loss in a Cr-Mo steel tempered to different strength levels. [7] Figure after Ref. 34.

Adapted from S. L. Robinson, Hydrogen for Energy Distribution, 1978
Figure 4. Schematic illustration of the strain rate, temperature, and hydrogen concentration effects upon ductility losses in hydrogen.

Adapted from S. L. Robinson, Hydrogen for Energy Distribution, 1978
Photographs and Fractographs of A516 Alloy Specimens Tested in Air and in Hydrogen (Surface cracking is noticeable on the specimen tested in hydrogen, and the corresponding fractograph shows an area of the fracture surface exhibiting quasi-cleavage.)

Figure 6. Tensile bar appearance and fracture surface morphology for a carbon-manganese steel tested in high pressure hydrogen.

Adapted from S. L. Robinson, Hydrogen for Energy Distribution, 1978
### TABLE II. TENSILE DATA FOR CARBON STEELS TESTED IN HYDROGEN

<table>
<thead>
<tr>
<th>Material</th>
<th>Specimen Configuration</th>
<th>Test Environment</th>
<th>0.2% Yield Strength (psi)</th>
<th>Ultimate Strength (psi)</th>
<th>True Stress at Failure, psi</th>
<th>Uniform Elongation %</th>
<th>Reduction of Area</th>
<th>Notched Strength Ratio †</th>
<th>Unnotched Strength Ratio †</th>
</tr>
</thead>
<tbody>
<tr>
<td>A515-70(1)</td>
<td>Smooth</td>
<td>Air</td>
<td>52,100</td>
<td>80,700</td>
<td>19.9</td>
<td>63.0</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Smooth</td>
<td>600 psi H₂</td>
<td>48,400</td>
<td>79,800</td>
<td>15.6</td>
<td>37.2</td>
<td>0.88</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Notched(1)</td>
<td>Air</td>
<td>61,500</td>
<td>99,100</td>
<td>4.6</td>
<td>22.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Notched(1)</td>
<td>H₂ Charged +600 psi H₂</td>
<td>70,800</td>
<td>87,500</td>
<td>2.9</td>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>A515(2)</td>
<td>Smooth</td>
<td>104 psi He</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>42</td>
<td>67</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Smooth</td>
<td>104 psi H₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>29</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Notched</td>
<td>104 psi He</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Notched</td>
<td>104 psi H₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>A516-70(1)</td>
<td>Smooth</td>
<td>Air</td>
<td>43,700</td>
<td>74,000</td>
<td>21.0</td>
<td>75.7</td>
<td>-0.99</td>
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<tr>
<td></td>
<td>Smooth</td>
<td>Charge + 600 H₂</td>
<td>46,700</td>
<td>73,300</td>
<td>-</td>
<td>17.6</td>
<td>35.4</td>
<td></td>
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<tr>
<td></td>
<td>Notched</td>
<td>Air</td>
<td>60,100</td>
<td>102,700</td>
<td>-</td>
<td>8.6</td>
<td>46.3</td>
<td>0.85</td>
<td></td>
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<tr>
<td></td>
<td>Notched</td>
<td>Charge + 600 H₂</td>
<td>70,600</td>
<td>86,800</td>
<td>-</td>
<td>2.7</td>
<td>17.6</td>
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<tr>
<td>A106-8</td>
<td>Smooth</td>
<td>103 psi N₂</td>
<td>52,300</td>
<td>75,350</td>
<td>154,700</td>
<td>16.1</td>
<td>61.4</td>
<td>p1</td>
<td>~0.97</td>
</tr>
<tr>
<td></td>
<td>Smooth</td>
<td>103 psi H₂</td>
<td>63,100</td>
<td>79,230</td>
<td>126,750</td>
<td>10.8</td>
<td>54.0</td>
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<tr>
<td></td>
<td>Notched</td>
<td>Air</td>
<td>88,400</td>
<td>108,700</td>
<td>-</td>
<td>3.4</td>
<td>21.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Notched</td>
<td>103 psi H₂</td>
<td>84,600</td>
<td>105,300</td>
<td>-</td>
<td>3.7</td>
<td>13.8</td>
<td></td>
<td>~0.97</td>
</tr>
</tbody>
</table>

(1) Unpublished results, present author; notch acuity, $p \sim 0.005$ inch.

(2) W. T. Chandler, R. J. Walter; notch acuity: $p \sim 0.001$ inch, † Based on ultimate strength.

Adapted from S. L. Robinson, Hydrogen for Energy Distribution, 1978
Fig. 4—Influence of temperature on the threshold stress intensity of the 3\(^{1/2}\) NiCrMoV steel in 307 kPa (30 psig) hydrogen.

Fig. 5—Influence of hydrogen pressure on the threshold stress intensity of the 3\(^{1/2}\) NiCrMoV steel at 25 °C.

Adapted from Akhurst and Baker, Met Trans 12A, 1981
FIGURE 9. J-RESISTANCE CURVES FOR X42 STEEL BASE METAL TESTED IN 1000 psig HYDROGEN AND IN 1000 psig NITROGEN

Adapted from J. H. Holbrook et al, Battelle Labs, 1988
H2/NG Distribution Systems Materials Challenges

FIGURE 6. FATIGUE-Crack-Growth Rate in X42 Pipeline Steel as a Function of Stress Ratio

Adapted from J. H. Holbrook et al, Battelle Labs, 1988
Figure 9. Burst test data for internally flawed pipe showing a 15% loss of hoop stress at failure when exposed to 1000 psi hydrogen.

Adapted from S. L. Robinson, Hydrogen for Energy Distribution, 1978
H2/NG Distribution Systems Materials Challenges

Pressure versus time for a typical petroleum products pipeline.
Figure 5. Acceleration of fatigue crack growth rates in carbon manganese steels fatigued in high pressure hydrogen.

Adapted from S. L. Robinson, Hydrogen for Energy Distribution, 1978
FIGURE 19.  FATIGUE-CRACK-GROWTH RATE FOR X42 STEEL IN VARIOUS GASES

$\Delta K = 15 \text{ ksi} \sqrt{\text{in}}, \; R = 0.1$

Adapted from J. H. Holbrook et al, Battelle Labs, 1988
“Rule of Thumb” Control of Hydrogen Embrittlement

• Avoid High Strength Steels
• Avoid Pressure Cycles of the Pipeline
• Limit Hardness of Pipe and Weld Materials

There is no consensus within the Technical community on specific limits discussed above. Additional research to establish design, construction and operating limits will be beneficial.
Performance Criteria for Materials in Hydrogen Service

The following should be considered when choosing piping material for hydrogen systems:

• Hydrogen state (slush, liquid, or gas)
• Temperature, and/or temperature range
• Pressure
• Other secondary loading conditions
• Compatibility with operating environment (also include effects due to corrosion)
• Ease of fabrication and assembly
• Potential to minimize damage due to hydrogen fires.
• Cost
To Mitigate the Effect of Hydrogen Embrittlement

• Select materials for which sufficient performance data and industry consensus for suitability in hydrogen service is available.

• Evaluate welding procedures used in manufacturing and field joints for fitness for service in hydrogen environment

• Avoid sources of stress concentration

• Proper surface finish

• Incorporate a thorough integrity management plan.
  • Incorporate appropriate in service inspection method to discern hydrogen assisted cracking, and embrittlement

• Explore the Use hydrogen attack inhibitors/permeation barriers
Materials Data Needs for Hydrogen Service

- Minimum Specified Yield Strength
- Minimum Specified Tensile Strength
- Yield Strength to tensile Strength Ratio
- Steel Chemistry
- Weld-ability
- Minimum Design Temperature
- Fracture Initiation Toughness
- Corrosion resistance, and corrosion prevention
- Failure prevention program including periodic inspection
- Resistance to environmentally caused degradation

“Coordinated research efforts is necessary to understand how line pipe steels are affected when exposed to hydrogen (particularly at high pressures), how to prevent or minimize the failure probability of a system, and finally to gather critical data that is essential for the development of codes and standards and government regulations”

• Mohitpour, Tempsys Pipeline Solution Inc, CANADA, 2004
SRNL H2 Pipeline Program

Evaluation of Natural Gas Piping Materials for Hydrogen Service

• SRNL Program Focused on Hydrogen Embrittlement Effects of Archival NG Piping Materials
  • Initial Two-Year Program Beginning in FY05
  • FY05 Funding Level: $150K Fully Burdened
  • Archival NG Piping Provided by South Carolina Electric and Gas

• SRNL Program Scope for FY05
  • Baseline and H₂ Exposed Mechanical Property Measurements
  • Hydrogen Threshold Stress Intensity Measurements
  • Burst Prediction Modeling Development and Verification

• SRNL Year-Two Program Scope
  • Fracture Toughness – Constraint Modified J-R Curve Testing
  • Fatigue Testing
  • Weld Effects Testing
• API 5L-X-42; 4.5” ODx 0.188 wall thickness
• Yield Strength: 42ksi (min)-72ksi(max)
• Tensile strength: 60ksi(min)-110ksi(max)
• Elongation in 2”= 1.944(A^2/U^9)
### Table 2A—PSL 1 Chemical Requirements for Heat and Product Analyses by Percentage of Weight

<table>
<thead>
<tr>
<th>Grade &amp; Class</th>
<th>Carbon, Maximum</th>
<th>Manganese, Maximum</th>
<th>Phosphorus</th>
<th>Sulfur, Maximum</th>
<th>Titanium, Maximum</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seamless</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A25, C1 I</td>
<td>0.21</td>
<td>0.60</td>
<td>0.030</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A25, C1 II</td>
<td>0.21</td>
<td>0.60</td>
<td>0.045</td>
<td>0.030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.22</td>
<td>0.90</td>
<td>0.030</td>
<td>0.030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.28</td>
<td>1.20</td>
<td>0.030</td>
<td>0.030</td>
<td>0.04</td>
<td>b, c, d</td>
</tr>
<tr>
<td>X42</td>
<td>0.28</td>
<td>1.30</td>
<td>0.030</td>
<td>0.030</td>
<td>0.04</td>
<td>c, d</td>
</tr>
<tr>
<td>X46, X52, X56</td>
<td>0.28</td>
<td>1.40</td>
<td>0.030</td>
<td>0.030</td>
<td>0.04</td>
<td>c, d</td>
</tr>
<tr>
<td>X60f</td>
<td>0.28</td>
<td>1.40</td>
<td>0.030</td>
<td>0.030</td>
<td>0.04</td>
<td>c, d</td>
</tr>
<tr>
<td>X65f, X70f</td>
<td>0.28</td>
<td>1.40</td>
<td>0.030</td>
<td>0.030</td>
<td>0.06</td>
<td>c, d</td>
</tr>
</tbody>
</table>

| Welded       |                 |                    |            |                 |                   |       |
| A25, C1 I    | 0.21            | 0.60               | 0.030      | 0.030           |                   |       |
| A25, C1 II   | 0.21            | 0.60               | 0.045      | 0.030           |                   |       |
| A            | 0.22            | 0.90               | 0.030      | 0.030           |                   |       |
| B            | 0.26            | 1.20               | 0.030      | 0.030           | 0.04              | b, c, d|
| X42          | 0.26            | 1.30               | 0.030      | 0.030           | 0.04              | c, d  |
| X46, X52, X56| 0.26            | 1.40               | 0.030      | 0.030           | 0.04              | c, d  |
| X60f         | 0.26            | 1.40               | 0.030      | 0.030           | 0.06              | c, d  |
| X65f         | 0.26            | 1.45               | 0.030      | 0.030           | 0.06              | c, d  |
| X70f         | 0.26            | 1.65               | 0.030      | 0.030           | 0.06              | c, d  |

### Table 2B—PSL 2 Chemical Requirements for Heat and Product Analyses by Percentage of Weight

<table>
<thead>
<tr>
<th>Grade</th>
<th>Carbon, Maximum</th>
<th>Manganese, Maximum</th>
<th>Phosphorus</th>
<th>Sulfur, Maximum</th>
<th>Titanium, Maximum</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Welded</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.24</td>
<td>1.20</td>
<td>0.025</td>
<td>0.015</td>
<td>0.04</td>
<td>d, e</td>
</tr>
<tr>
<td>X42</td>
<td>0.24</td>
<td>1.30</td>
<td>0.025</td>
<td>0.015</td>
<td>0.04</td>
<td>c, d</td>
</tr>
<tr>
<td>X46, X52, X56, X60f</td>
<td>0.24</td>
<td>1.40</td>
<td>0.025</td>
<td>0.015</td>
<td>0.04</td>
<td>c, d</td>
</tr>
<tr>
<td>X65f, X70f, X80f</td>
<td>0.24</td>
<td>1.40</td>
<td>0.025</td>
<td>0.015</td>
<td>0.06</td>
<td>c, d</td>
</tr>
</tbody>
</table>

- **API 5L-Spec 2004**
- **X-42**
  - C: 0.22 max
  - Mn: 1.30 max
  - P: 0.025 max
  - S: 0.015 max
  - Ti: 0.04 max
  - Other: <0.15%
SRNL H2 Pipeline Program

- X42 Archival NG Pipe
  Microstructure—Polished and Etched
- Ferrite/Pearlite Microstructure
- Single Weld Seam Pipe
- Evidence of banding
• Mechanical Property Testing will be Conducted in Both Ar and Hydrogen

• Both Longitudinal and Transverse Samples will be Harvested from Archival NG Pipe

• Testing will be conducted at pressures in the range of 100-1000 psi

• Testing will be conducted at Room Temperature $\approx 25^\circ C$
SRNL High Pressure Hydrogen Facility

• Mechanical Property Testing in Hydrogen
  • Temperature: Up to 350°C
  • Pressure: Up to 30,000psi
  • Sub-miniture Specimens: 1” gage length

• Fracture Toughness Testing
  • C-Shaped Specimens
## TABLE 2. SMOOTH-BAR TENSILE PROPERTIES OF PIPE STEELS*

<table>
<thead>
<tr>
<th>API-5LX Pipe Grade</th>
<th>Test Environment</th>
<th>0.2-Percent-Offset Yield Strength, MPa (ksi)</th>
<th>Ultimate Tensile Strength, MPa (ksi)</th>
<th>Percent Elongation in 1 inch</th>
<th>Percent Reduction of Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Axial (Longitudinal) Orientation</td>
<td>Transverse Orientation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X42</td>
<td>Air</td>
<td>366 (53)</td>
<td>511 (74)</td>
<td>21</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>6.9 MPa H₂</td>
<td>331 (48)</td>
<td>483 (70)</td>
<td>20</td>
<td>44</td>
</tr>
<tr>
<td>X70</td>
<td>Air</td>
<td>584 (85)</td>
<td>669 (97)</td>
<td>20</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>6.9 MPa H₂</td>
<td>548 (79)</td>
<td>659 (95)</td>
<td>20</td>
<td>47</td>
</tr>
</tbody>
</table>

Adapted from J. H. Holbrook et al, Battelle Labs, 1988

* Tests conducted at an engineering-strain rate of $10^{-4}$ sec$^{-1}$. 
SRNL H2 Pipeline Program

Figure 1.
HEE observed in double-notched tensile specimens.

CHANGE IN REDUCTION OF AREA (%) vs. HYDROGEN PRESSURE P (MPa)

Adapted from Gutierrez-Solana and Elices, ASM, 1982.
H$_2$/NG Threshold Stress Intensity Testing

• Hydrogen Threshold Stress Intensity Testing—Bolt Loaded Sample
  • Multiple Samples with Load Range from 0-500 lbs.
  • Crack Dimensions: a/W$\leq$0.5, Root Radius$\leq$0.003in

• C-shaped Samples will be Harvested from 4.5” and 2” Archival NG Pipe

• Testing will be conducted at pressures of 500, 1000, and 1500psi

• Testing will be conducted at Room Temperature $\cong$ 25°C

• Hydrogen Concentration will be Estimated Analytically Using DIFF

• $K_{TH}$ will be Reported for Initial Conditions (i.e., crack growth initiation)
Determination of Burst Pressure

Finite Element Analysis of Burst Pressure

- For defected, repaired, or welded pipelines with geometry and material discontinuities
- For degraded pipelines with local material property variation due to previous NG service or hydrogen exposure
- For actual material tensile property input (full stress-strain curves up to failure)
Year-Two Program Focus

Component Fatigue and Hydrogen Environments

**Figure 6.** Fatigue-crack-growth rate in X42 pipeline steel as a function of stress ratio

Adapted from J. H. Holbrook et al, Battelle Labs, 1988
Year-Two Program Focus

Welds and Weld Metal Embrittlement Effects

<table>
<thead>
<tr>
<th>Process</th>
<th>Test Environment</th>
<th>0.2% Yield Strength, 1000 psi</th>
<th>Ultimate Strength, 1000 psi</th>
<th>Uniform Elongation</th>
<th>Total Elongation</th>
<th>% R.A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Metal</td>
<td>Air</td>
<td>57.9</td>
<td>82.5</td>
<td>19.3</td>
<td>30.5</td>
<td>71.6</td>
</tr>
<tr>
<td></td>
<td>103 psi H₂</td>
<td>56.8</td>
<td>81.0</td>
<td>14.0</td>
<td>16.6</td>
<td>24.7</td>
</tr>
<tr>
<td>GTA</td>
<td>Air</td>
<td>64.8</td>
<td>84.4</td>
<td>7.3</td>
<td>12.5</td>
<td>71.3</td>
</tr>
<tr>
<td>GTA</td>
<td>103 psi H₂</td>
<td>62.4</td>
<td>86</td>
<td>8.2</td>
<td>11.0</td>
<td>38.0</td>
</tr>
<tr>
<td>SMA†</td>
<td>Air</td>
<td>56.3</td>
<td>79.1</td>
<td>8.0</td>
<td>13.0</td>
<td>68.7</td>
</tr>
<tr>
<td>SMA†</td>
<td>103 psi H₂</td>
<td>53.6</td>
<td>79.1</td>
<td>9.6</td>
<td>14.1</td>
<td>47.6</td>
</tr>
</tbody>
</table>

† GTA: GAS - Tungsten Arc, AWS, E70S-2 Filler
††: Shielded Metal Arc, AWS - E7018 Low H₂ Filler

Adapted from S. L. Robinson, Hydrogen for Energy Distribution, 1978

(Smooth Bar Tests)
Advanced Fracture Modeling

• Traditional fracture mechanics uses K (linear elastic materials) or J (elastic-plastic materials) to characterize fracture processes and failure events.

• $J_{IC}$ and J-R Curves show certain amount of specimen geometry dependence (data from 3PB, CT, CCP, SCP, SENB, SENT, DECP, etc.)

• Develop a three-term asymptotic solution ($J - A_2$) for a stationary crack.

• Identify $A_2$ as an additional fracture parameter.

• $J-A_2$ controlled crack growth.
Advanced Fracture Modeling

Constraint Modified J-R Curves

Traditional ASTM J-R Curve:

\[ J(\Delta a) = C_1(\Delta a)^C_2 \]

Constraint Modified J-R Curve:

\[ J(\Delta a, A_2) = C_0(A_2) + C_1(A_2)(\Delta a)^{C_2(A_2)} \]

The results can have full transferability from test specimen to large structure.
SRNL Fracture Testing for A285
Crack Resistance (J-R) Curves

Typical fracture surface

Fatigue Crack Front
Final Crack Front

0.1 in.

Stable Crack Extension

Specimen size-dependent J-R curves

REF:
SRNL Program is Focused on Developing the Necessary Materials Data for Demonstrating the Use of Existing NG Pipeline Network for Hydrogen Service

- Mechanical Property Studies on Archival and New NG Pipe
- Fracture Mechanics Testing and Approaches for NG Pipeline Materials
- Component Fatigue Testing
- Burst Prediction and Modeling

The Initial Focus of this Program is Centered on Metallic Transmission NG Pipeline Materials; However, the approach and methodology developed under this program could be adapted to evaluating distribution piping materials which include both metallic and polymeric materials

SRNL is working to leverage its experience at developing and operating hydrogen production, storage, and delivery Technologies to develop the necessary technical data for qualification of the existing NG pipeline network for hydrogen service
Acknowledgements

Researchers
Dr. Robert Sindelar
Dr. Poh Sang lam
Dr. Elliot Clark
Mr. George Rawls

Lab Specialist/Technicians
Tina Stefek
Thaddeus Reown