

SRNLTM
SAVANNAH RIVER NATIONAL LABORATORY

We Put Science To Work

Evaluation of Natural Gas Pipeline Materials for Hydrogen Service

Dr. Thad M. Adams

Materials Technology Section

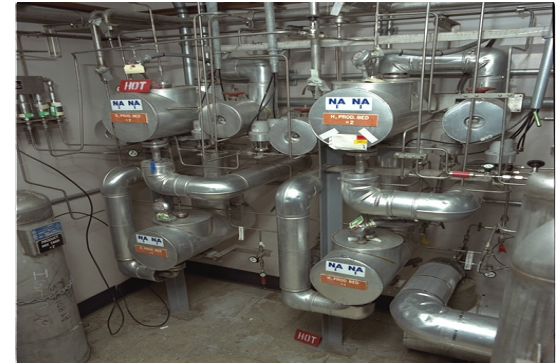
Savannah River National Laboratory

DOE Hydrogen Pipeline R&D Project Review Meeting

January 5-6, 2005

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.

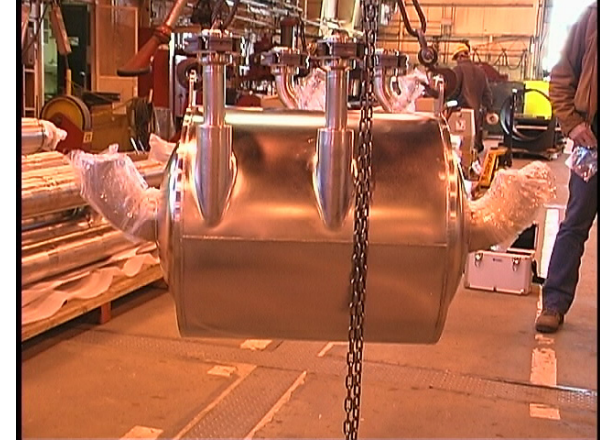
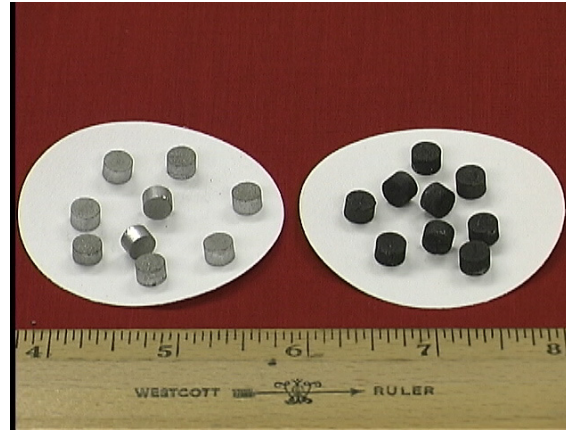


Advanced Hydride Laboratory

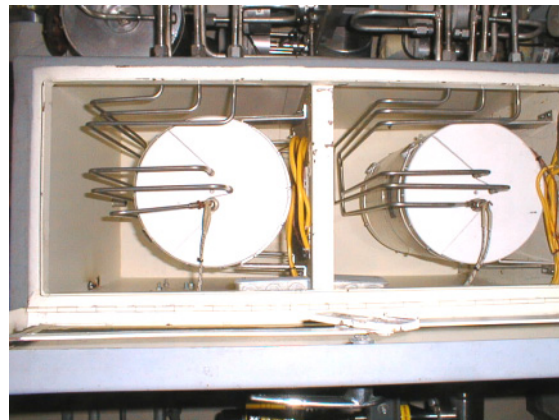


Fuel Cell Vehicle w/MH Storage

Tritium Storage and Separation Technology



*SRS Tritium Defense Program
has a > \$200 M budget with
> \$25 M allocated to SRNL*

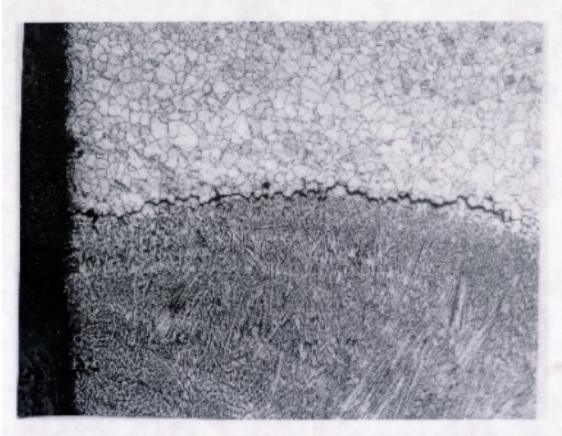


Hydrogen Technologies

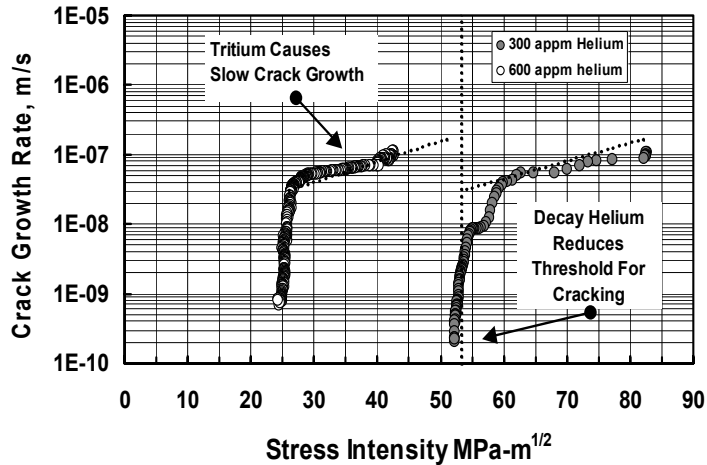
- Metal & Complex Hydride
 - storage
 - compressors/pumps
 - purifiers/separators
 - heat pumps/refrigeration
- Battery / Fuel Cells
 - Ni metal hydride
 - Fuel Cells
- Sensors
 - fiber optic
 - composite (ceramic)
- Hydrogen Production
 - membranes
 - electrolysis
 - thermochemical water splitting
 - biohydrogen
- Materials Compatibility
 - H₂ embrittlement
 - failure analyses
- Safety
 - H₂ safety analyses
 - codes and standards

Hydrogen Isotope Compatibility

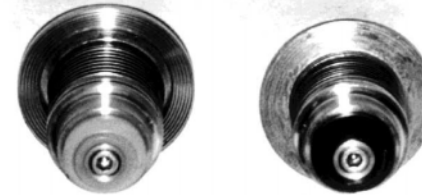
Understanding & Mitigation of Effects on Metals & Polymers



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

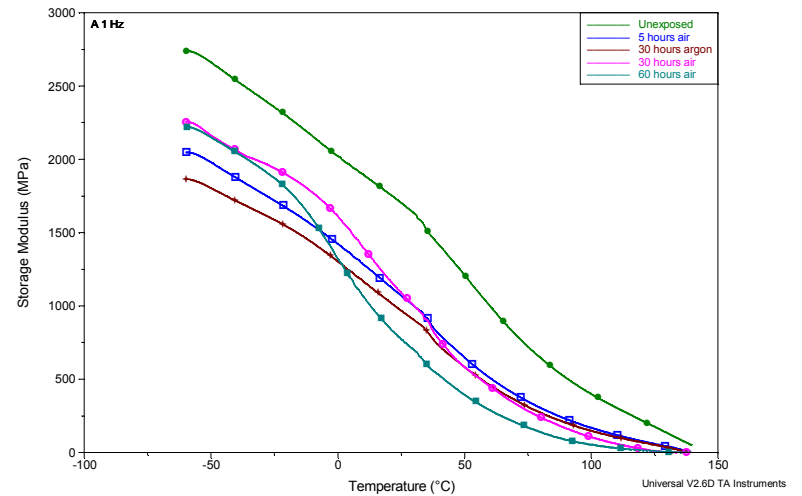


Cracking Thresholds for Structural Alloys



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

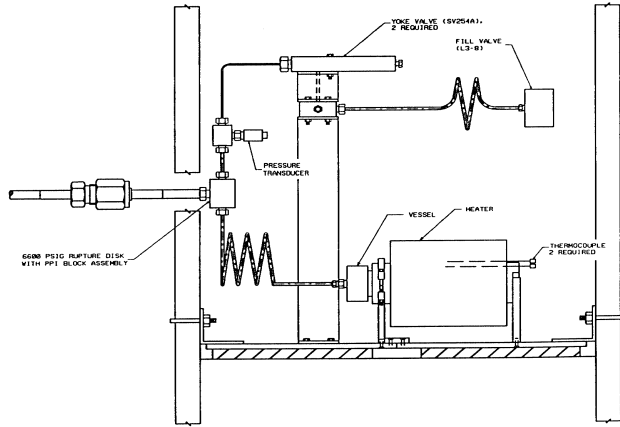
UHMW PE 140C Exposure



Dynamic Mechanical Analysis for Polymers

Hydrogen Isotope Compatibility

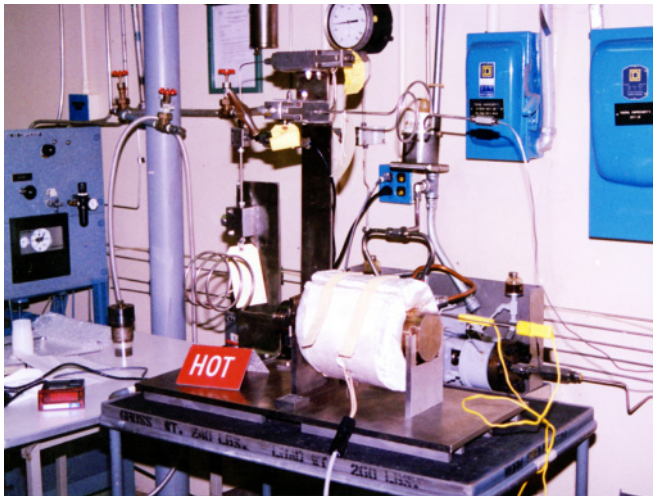
Hydrogen Isotope Charging and Mechanical Testing



Tritium Charging Facility Schematic and Mock-up



Testing Tritium Exposed Samples



Hydrogen Isotope Compatibility

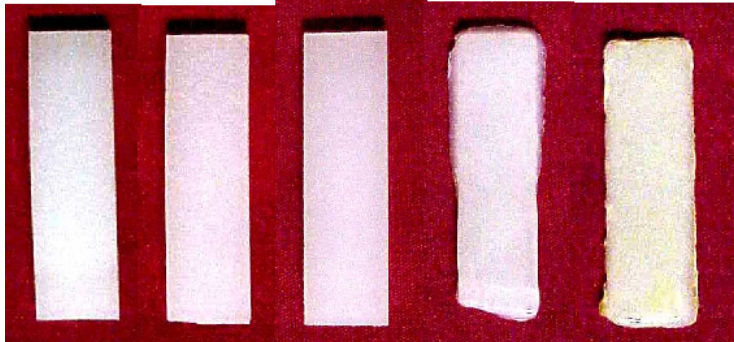
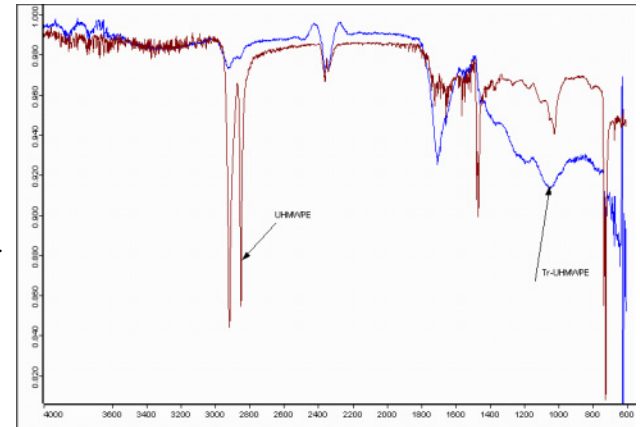
Hydrogen Isotope Effects on Polymers

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



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

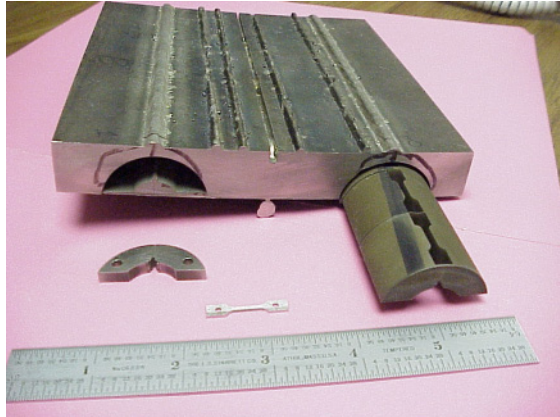
FT-IR of Non-Exposed and T₂-Exposed UHMW-PE



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

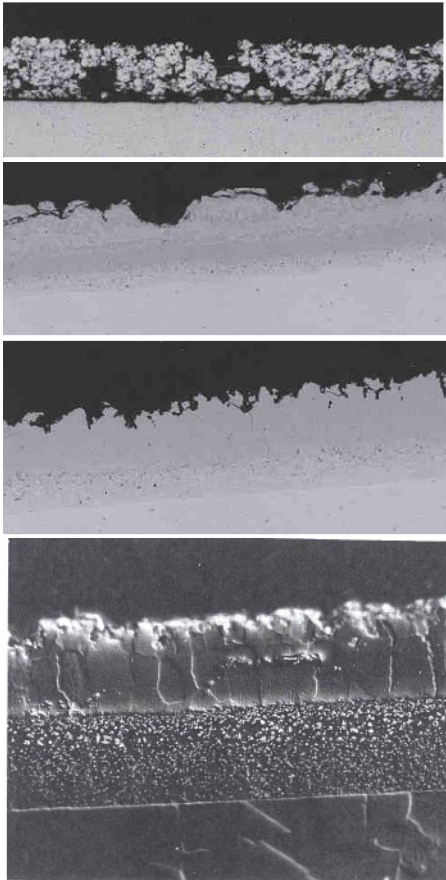
- Samples Exposed to Tritium in Charging Facility
- Aging and Testing to Characterize Effects of Tritium and Decay to Helium



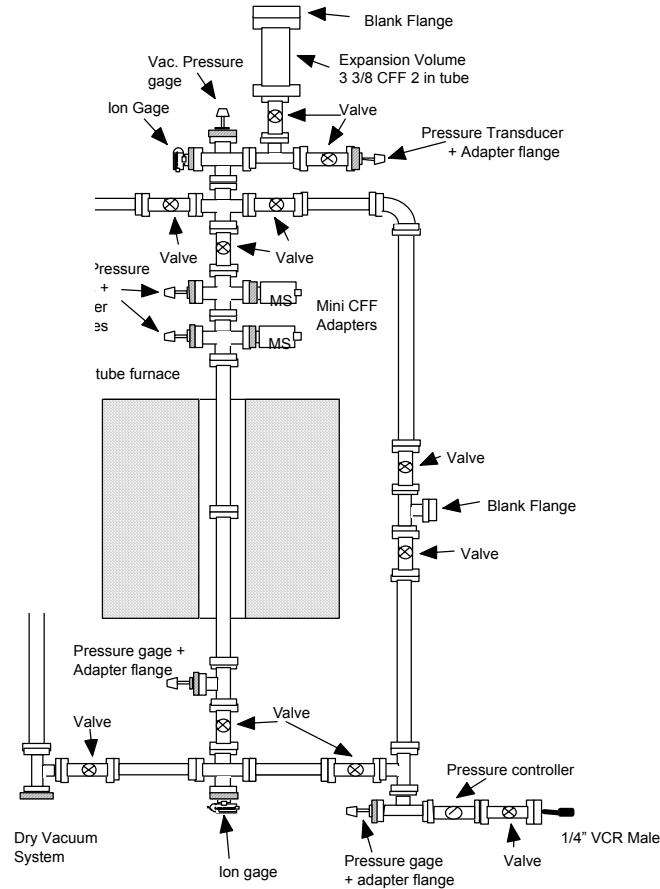
← Investigate Material Processing Effects (Forging, Welding, HAZ) on Embrittlement from Tritium and Decay to Helium

Hydrogen Isotope Compatibility

Permeation Barrier Development and Testing



Al-rich Permeation Barriers



Schematic and Photograph of Permeation Test Rig

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

New Hydrogen Research Laboratory



- 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.

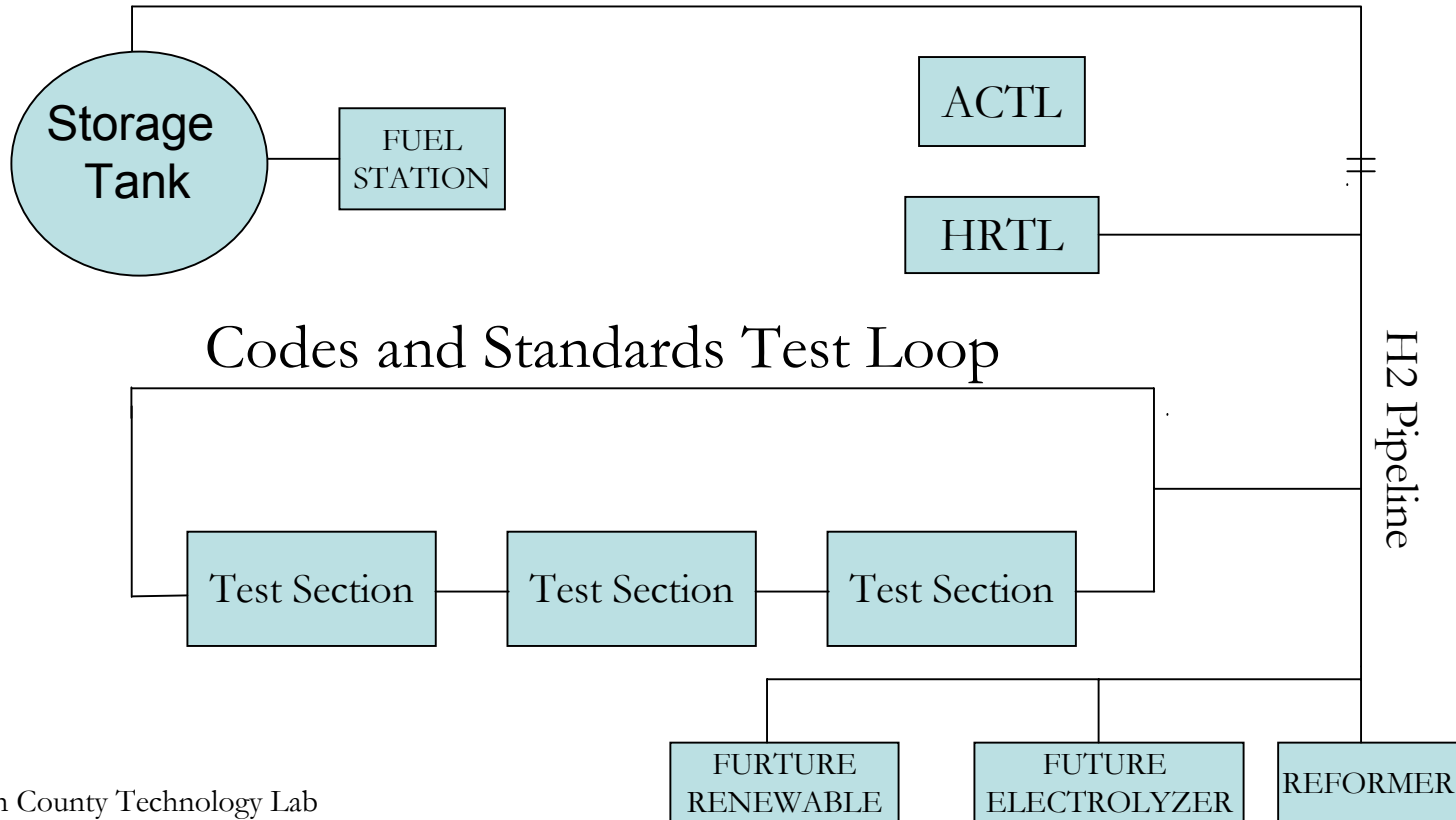
• Partners:

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
- Materials
 - Hydrogen embrittlement
 - New materials technology and testing
 - Heat to heat variation of ASTM specifications
 - Coating development
- Fabrication
 - Joint quality
 - Liner technology
- Inspection
 - Internal inspection
 - Sensor development

Hydrogen Pipeline Demonstration Project



ACTL – Aiken County Technology Lab
HRTL – Hydrogen Research Technology Lab

H2 GENERATION



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 Hydrogen Delivery Focus

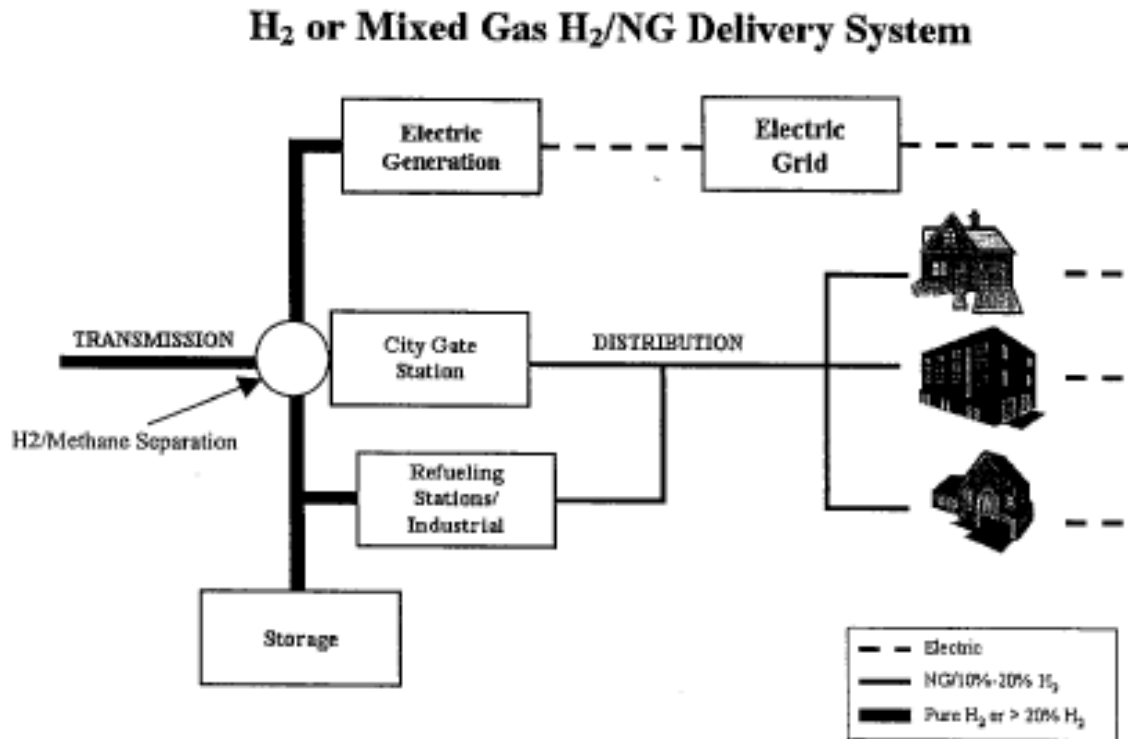
| | | |
|---|--|---|
|  | Gaseous | Pipeline |
| | | Truck |
| | | Onsite reforming |
|  | Liquid H ₂ & Chem. Carriers | Liquid H ₂ <ul style="list-style-type: none">- Pipeline- Truck- Rail |
| | | Hydrides |
| | | Other Carriers |
| | | |

“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

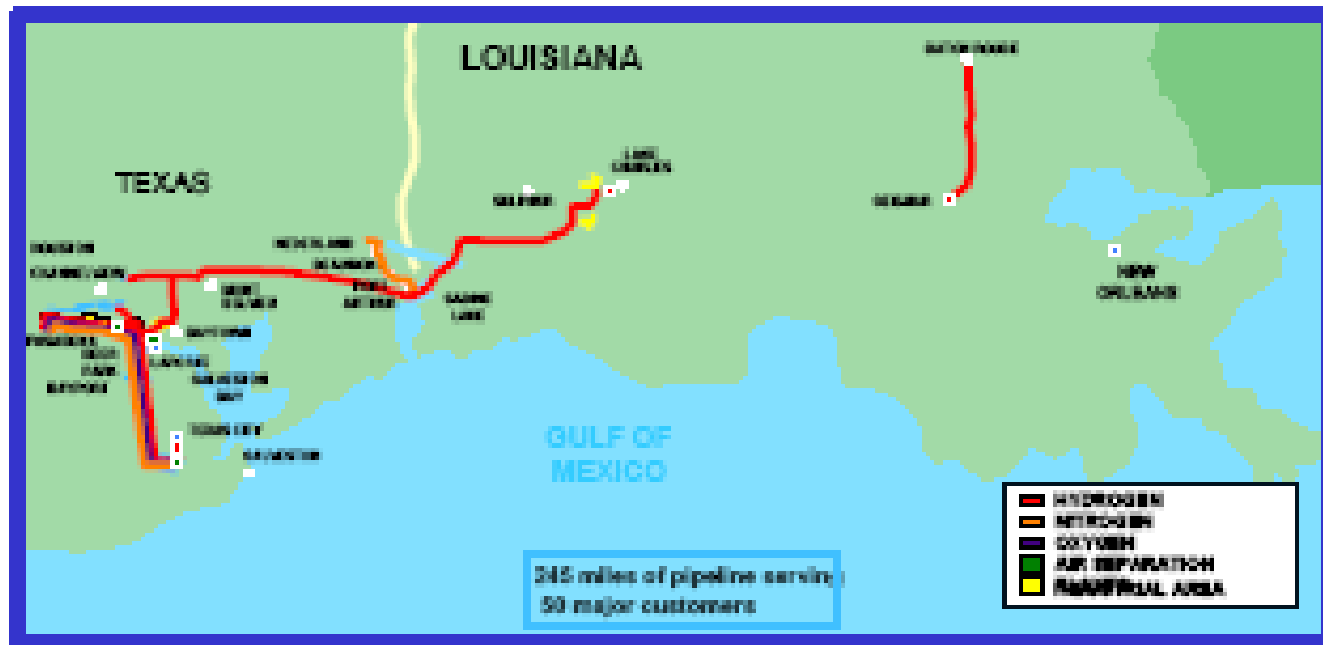
H₂/NG Distribution Systems

Current Hydrogen Pipeline Infrastructure

| Location | Pipeline Material | Years of Operation | Diameter (mm) | Length (km) | Pressure (kPa) and Gas Purity (%) | Experience Reported | Status |
|--|--------------------------------------|--------------------|-----------------|-------------|--|---------------------|-------------|
| AGEC, Alberta, Canada | Gr. 290 (5LX X42) | Since 1987 | 273 x 4.8 WT | 3.7 | 3,790 kPa – 99.9 | No | Operational |
| American Air Liquide Texas/Louisiana, USA | API 5LX42, X52, X60 and others | ? | 3" to 14" | 390 | 5100 kPa (740 PSI) | Yes | Operational |
| Air Products, Houston area, USA | | Since 1969 | 114.3 – 324 | 100 | 345 – 5,516 (Pure H ₂) | No | Operational |
| Air Products, Louisiana | ASTM 106 | 1999 ? | 101.6 – 304.8 | 48.3 | 3,447 | Yes | Operational |
| Air Products, Sarnia (Dow to Dome plant) | | | | 3 app. | | No | Operational |
| Air Products, Texas | Conv. natural gas line (steel) | >10 | 114.3 | 8 | 5,500 – Pure H ₂ | Yes | Operational |
| Air Products, Texas | Steel, schedule 40 | >8 | 219.0 | 19 | 1,400 – Pure H ₂ | Yes | Operational |
| Air products, Nether land | | | | 45 Km | (throughput= 50 tons/day) | | Operational |
| Chemische Werke Huis AG- Marl., Germany | Seamless equipment to SAE 1016 Steel | Since 1938 | 168.3 – 273 | 215 | to 2,500; raw gas (throughput = 300 x 106 m ³) | Yes | Operational |
| Cominco B.C., Canada | Carbon Steel (ASTM 210 seamless) | Since 1964 | 5 x 0.8125 WT | 06 | >30,000.62 to 100% pure H ₂ | No | Standby |
| Gulf Petroleum Cnd, (Petromont- Varunes) | Carbon Steel, seamless, Sch. 40 | -- | 168.3 | 16 | 93.5% H ₂ ; 7.5% methane | No | Operational |
| Hawkeye Chemical, Iowa | ASTM A53 Gr. B | 3 | 152.4 | 3.2 | 2,757.6 | Yes | Operational |
| ICI Billingham, UK | Carbon Steel | - | - | 15 | 30,000 kPa, pure | No | - |
| L'Air Liquide, France, Netherland, Belgium | Carbon Steel, seamless, | Since 1966 | sizes up to 12" | 879 | 6,484 – 10,000 kPa; pure and raw | No | Operational |
| LASL, N.M. | ASME A357-Gr.5 | - | 25.4 | 6.4 | 13,788 | Yes | Abandoned |
| Los Alamos, N.M. | 5 Cr. – Mo (ASME A357 Gr. 5) | >8 | 30 | 6 | 13,790 pure | Yes | Abandoned |
| Linde, Germany | - | - | - | 1.6 – 3.2 | - | - | - |
| NASA-KSC, Fla | 316 SS (austenitic) | >16 | 50 | 1.6-2 | 42,000 kPa | No | Operational |
| NSA-MSFC, Ala | ASTM A106-B | - | 76.2 | 0.091 | 34470 | Yes | Abandoned |
| Phillips Petroleum | ASTM A524 | 4 | 203.2 | 20.9 | 12,133-12,822 | Yes | Operational |
| Praxair, Golf Coast, Tx, Indiana, California, Alabama, Louisiana, Michigan | Carbon Steel | | | 450 Km | Commercial Purity H ₂ (500 MSCFD) | | Operational |
| Rockwell International S. | SS-116 | >10 | 250 | - | >100,000 kPa; ultra pure | No | - |
| South Africa | | | | 80 | | | ? |

TABLE 2: WORLD HYDROGEN PIPELINE EXDPERIENCE (MOHITPOUR ET AL., 1990 & 2003)

Current National Hydrogen Pipeline Infrastructure



- Predominately Carbon Steel Materials
 - X42, X52, X60, A106 Grade B, A357 Grade 5
 - Transmission Pressure Limited to $\cong 800$ psi
 - Pipe Sizes up to 12”

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

H₂/NG Distribution Systems Operational Challenges

Example - Compare H₂ and Natural Gas Compression & Pipeline Transmission:

- Compress from P_{initial} = 1 to P_{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 ΔP:

| | Natural Gas | H ₂ |
|--|-------------|----------------|
| Delivered Energy consumed in the Compression Process | 0.31 % | 1.33 % |

| | Natural Gas | H ₂ |
|--------------------------------|-------------|----------------|
| Volume of Gas Delivered (SCFH) | 7.0 MM | 18.4 MM |

Transporting 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:*

| | Natural Gas | H ₂ |
|----------------------------------|-------------|----------------|
| Volume of Gas Delivered (SCFH) | 7.0 MM | 18.4 MM |
| LHV Energy Delivered (BTU/Hr) | 6,391 MM | 5,060 MM |
| Less Compression Energy (BTU/Hr) | (20) MM | (69) MM |
| Net Energy Delivered (BTU/Hr) | 6,371 MM | 4,991 MM |

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.

H2/NG Distribution Systems Operational Challenges

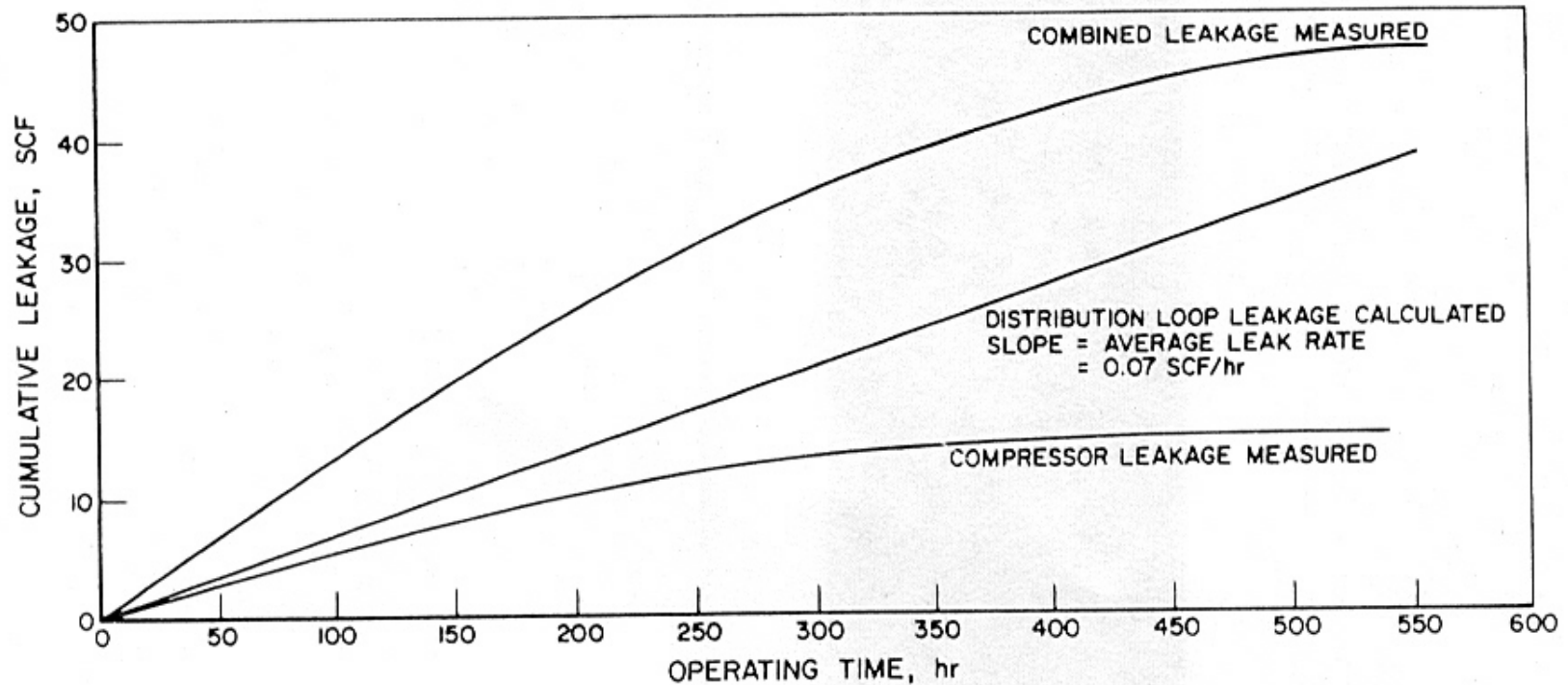


Figure 8. BASELINE NATURAL GAS LEAKAGE FOR INDUSTRIAL TEST LOOP

H2/NG Distribution Systems Operational Challenges

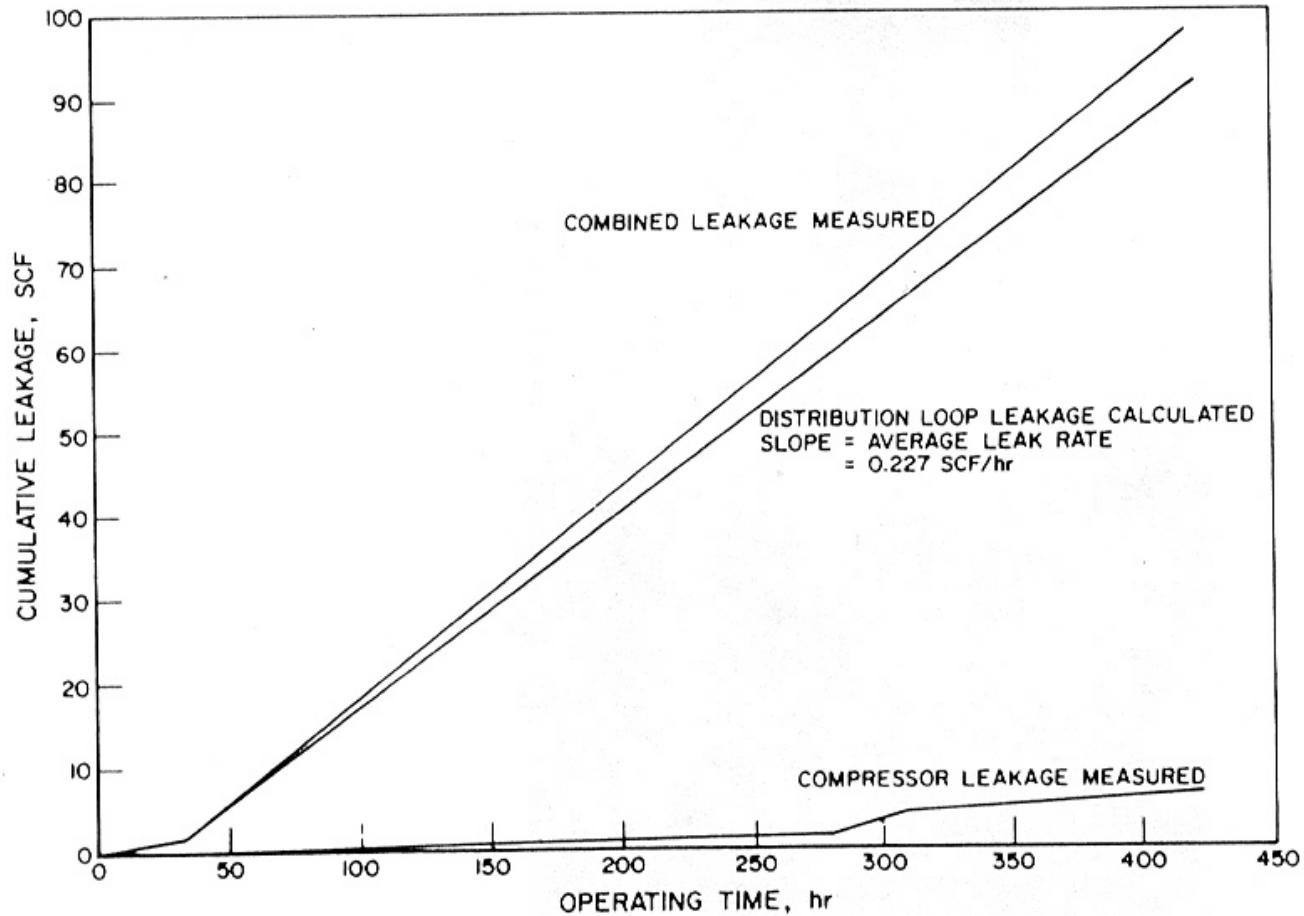


Figure 9. LEAKAGE CHARACTERISTICS OF THE INDUSTRIAL TEST LOOP IN HYDROGEN OPERATION

H2/NG Distribution Systems Operational Challenges

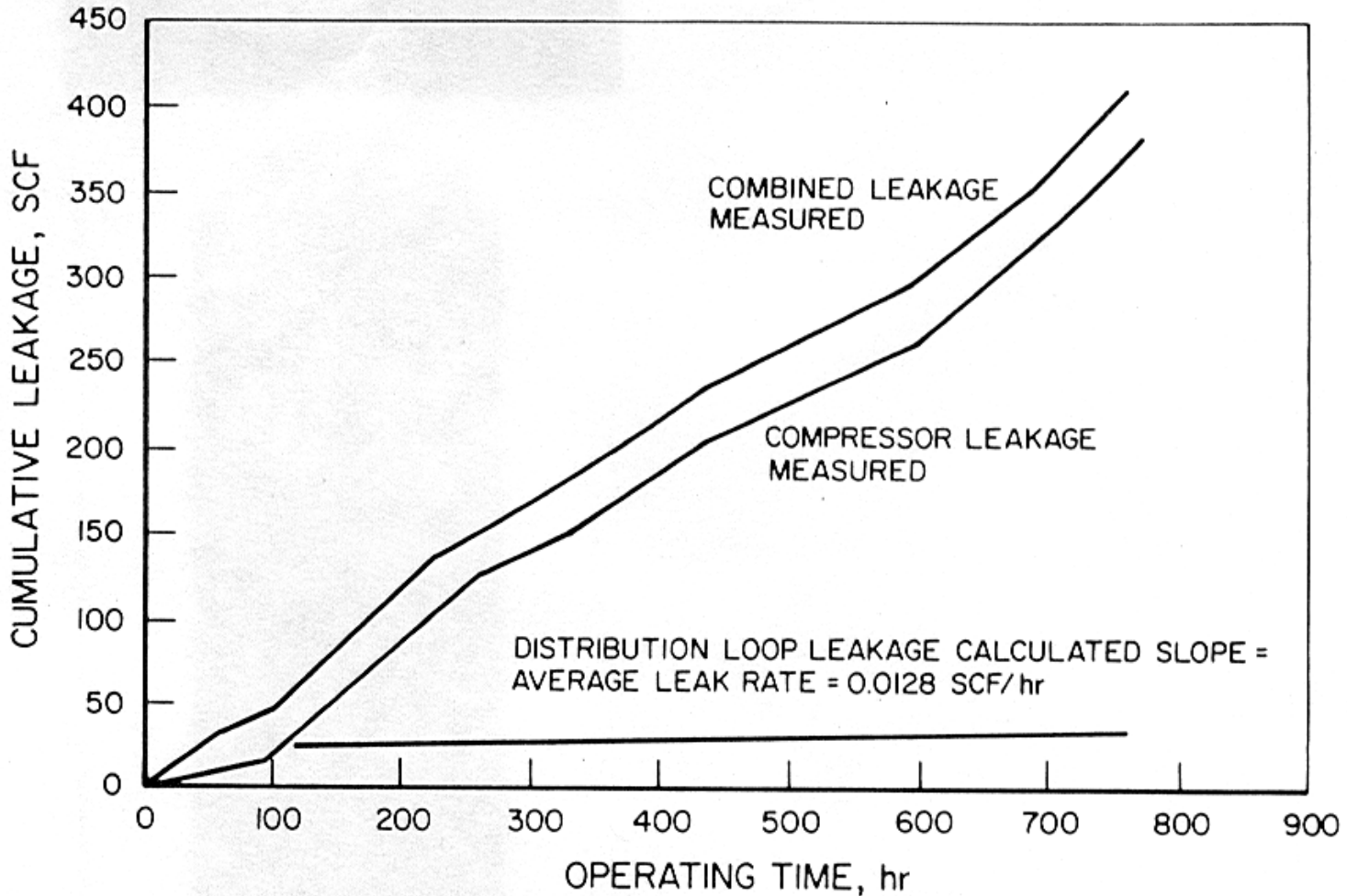


Figure 10. BASELINE NATURAL GAS LEAKAGE OF THE RESIDENTIAL/COMMERCIAL MODEL

H2/NG Distribution Systems Operational Challenges

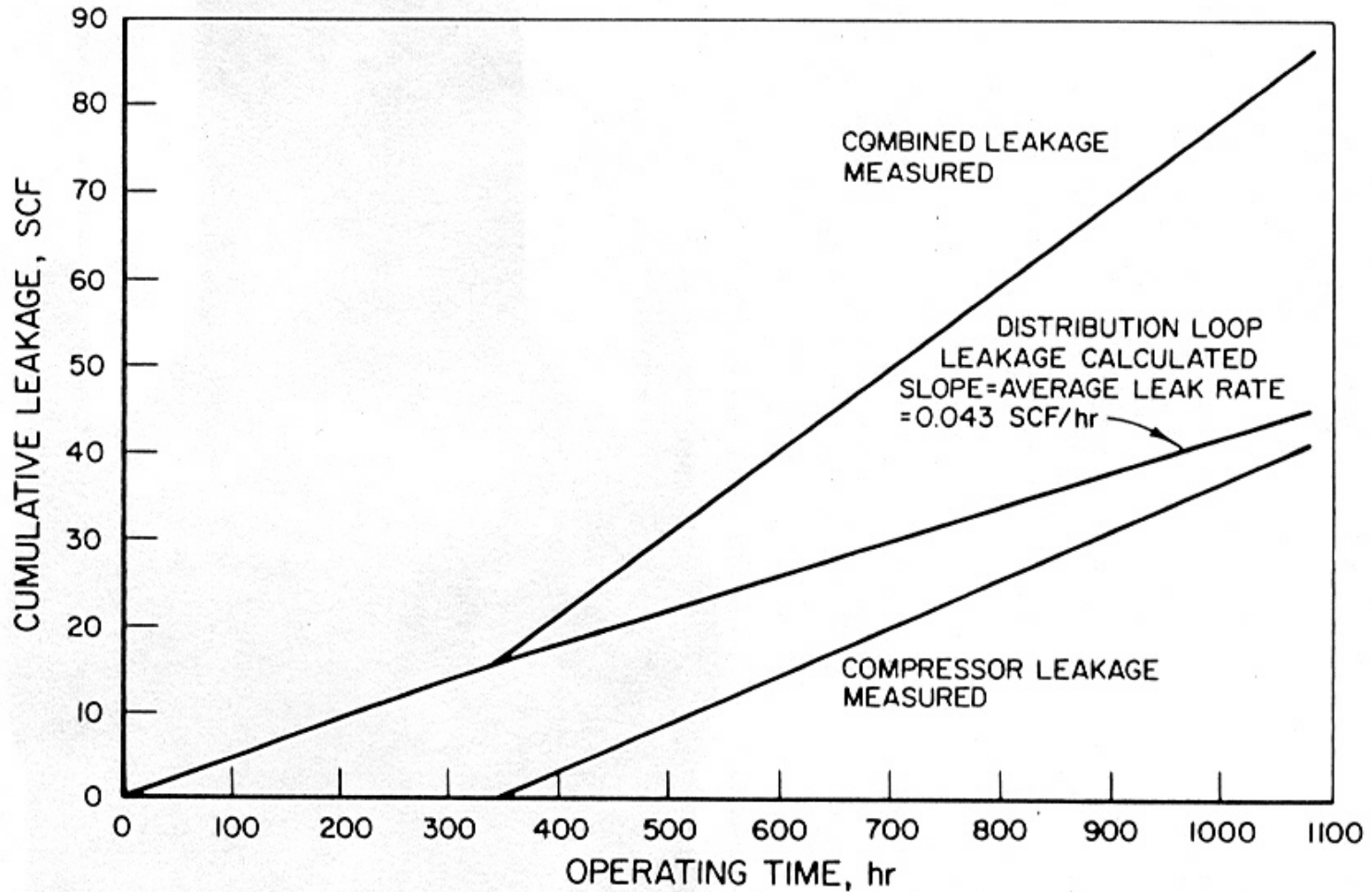


Figure 11. HYDROGEN LEAKAGE OF THE RESIDENTIAL/COMMERCIAL MODEL

H₂/NG Distribution Systems Materials Challenges

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.

Examination in the scanning electron microscope reveals Intergranular cleavage, characteristic of hydrogen embrittlement.

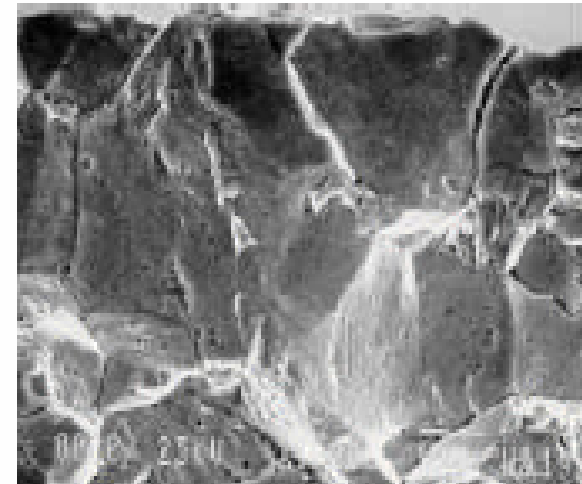


Photo Courtesy of NASA/Kennedy Space Center Materials Lab

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

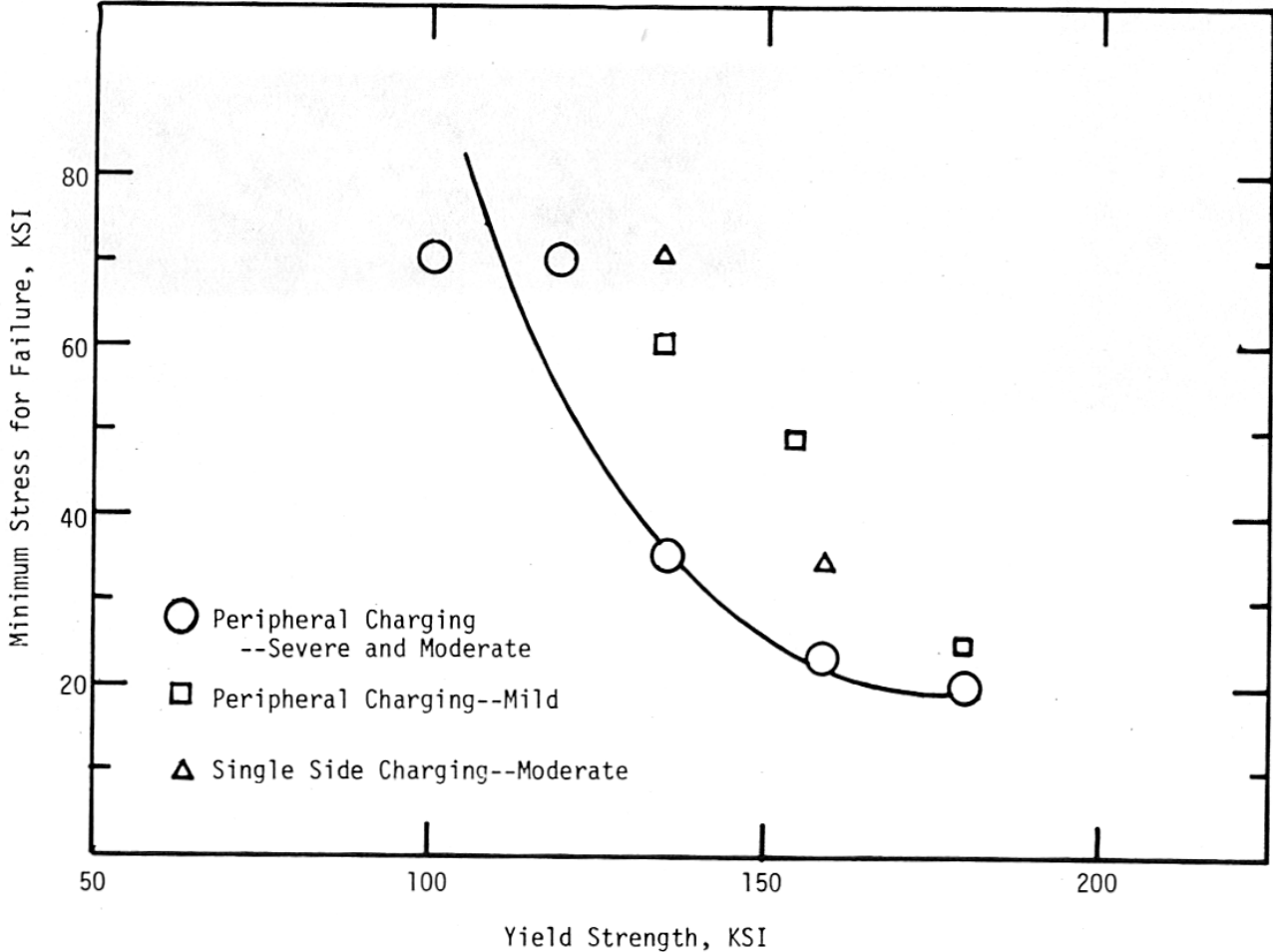


Figure 1. Yield strength dependence of delayed failure in cathodically charged carbon-manganese steels.

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

H2/NG Distribution Systems Materials Challenges

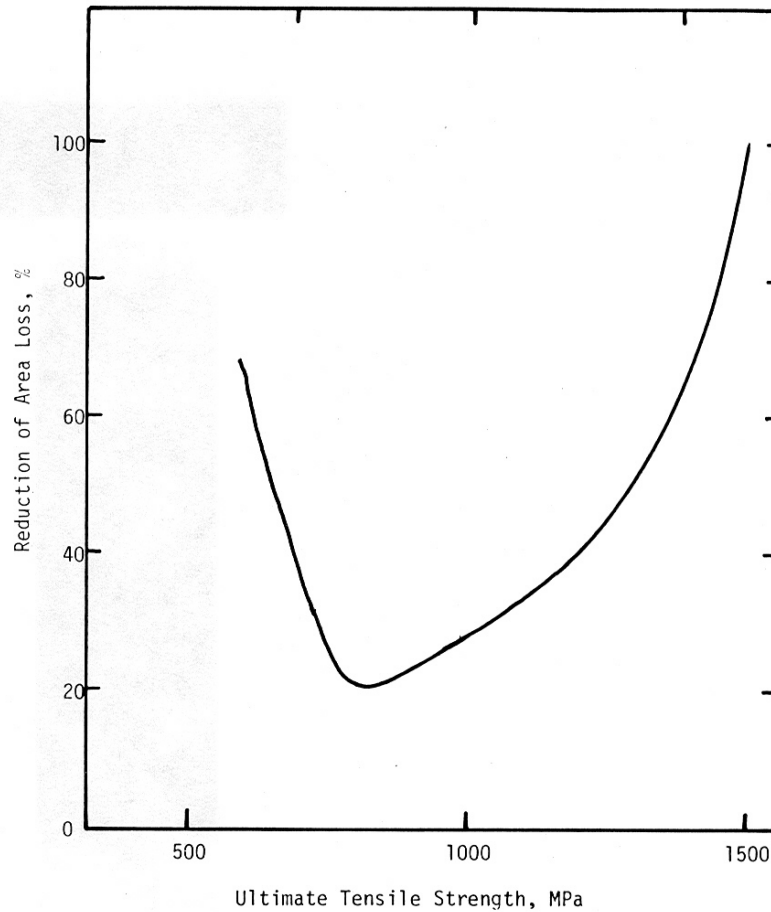


Figure 3. Hydrogen caused ductility loss in a Cr-Mo steel tempered to different strength levels. (7) Figure after Ref. 34.

H2/NG Distribution Systems Materials Challenges

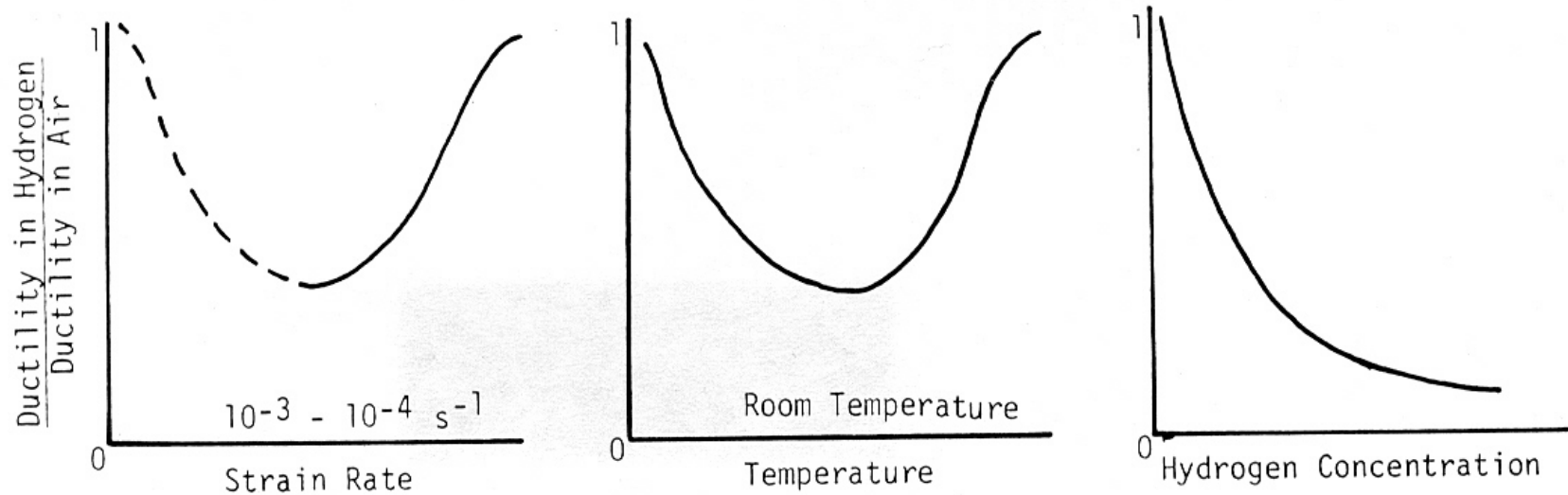
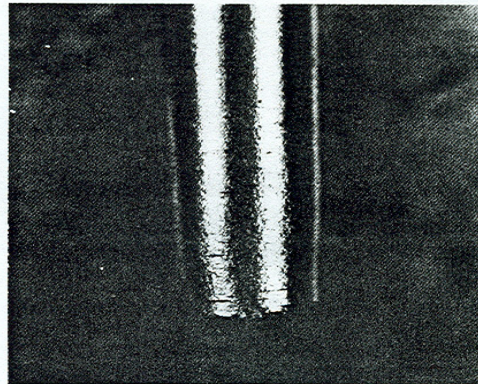
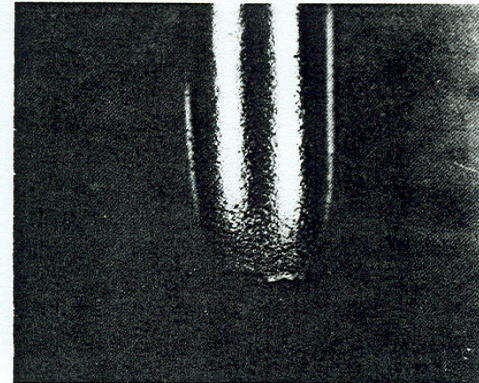


Figure 4. Schematic illustration of the strain rate, temperature, and hydrogen concentration effects upon ductility losses in hydrogen.

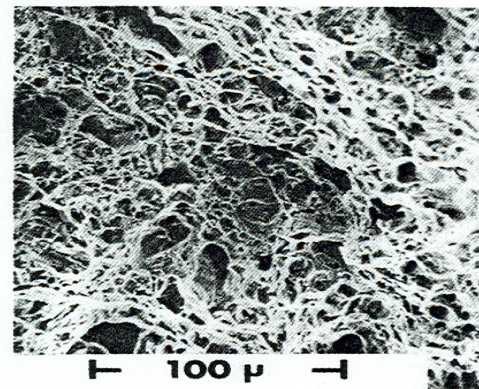
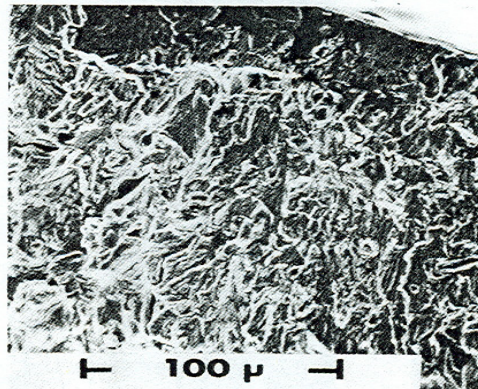
H2/NG Distribution Systems Materials Challenges



A516 Steel
 Thermal Charge
 Test in 4.1 MPa (600 psig) H₂



A516 Steel
 No Charge
 Air Test



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.

H2/NG Distribution Systems Materials Challenges

TABLE II. TENSILE DATA FOR CARBON STEELS TESTED IN HYDROGEN

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

(1) Unpublished results, present author; notch acuity, $\rho \sim .005$ inch.

(2) W. T. Chandler, R. J. Walter; notch acuity: $\rho \sim .001$ inch, † Based on ultimate strength.

H2/NG Distribution Systems Materials Challenges

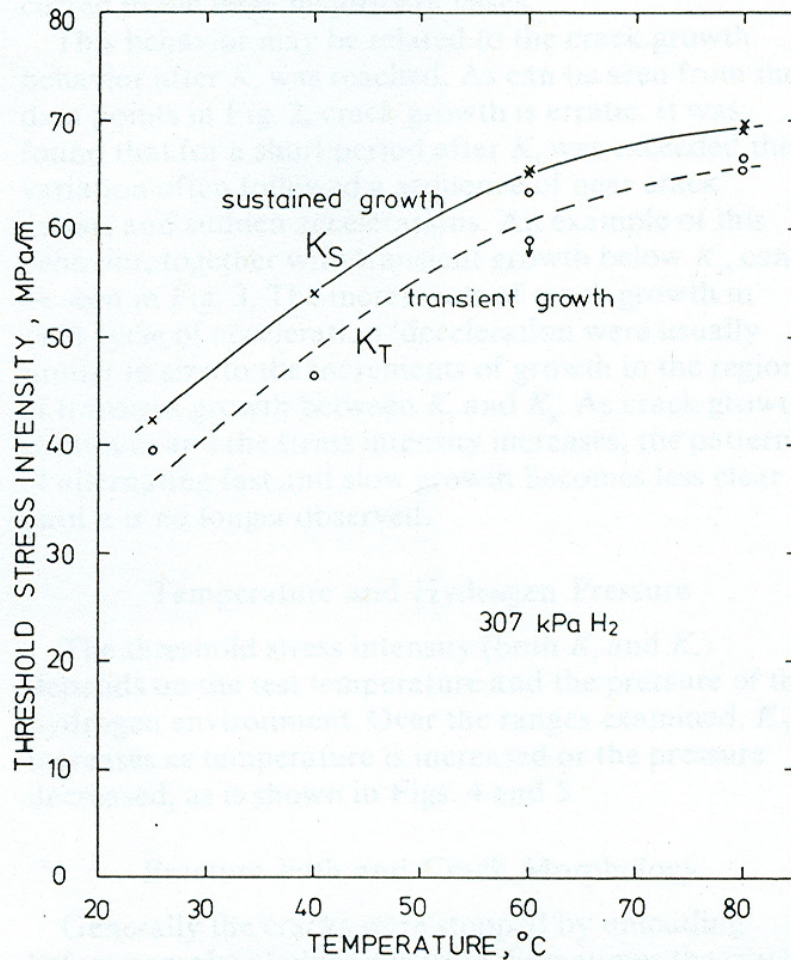


Fig. 4—Influence of temperature on the threshold stress intensity of the 3¹/₂ NiCrMoV steel in 307 kPa (30 psig) hydrogen.

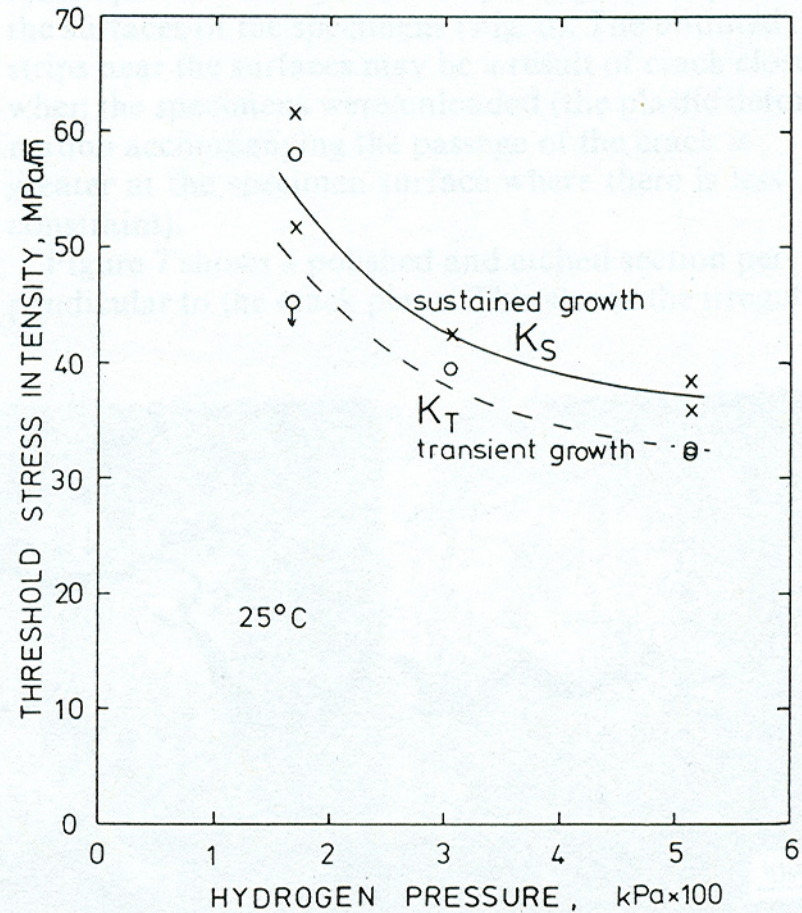


Fig. 5—Influence of hydrogen pressure on the threshold stress intensity of the 3¹/₂ NiCrMoV steel at 25 °C.

H2/NG Distribution Systems Materials Challenges

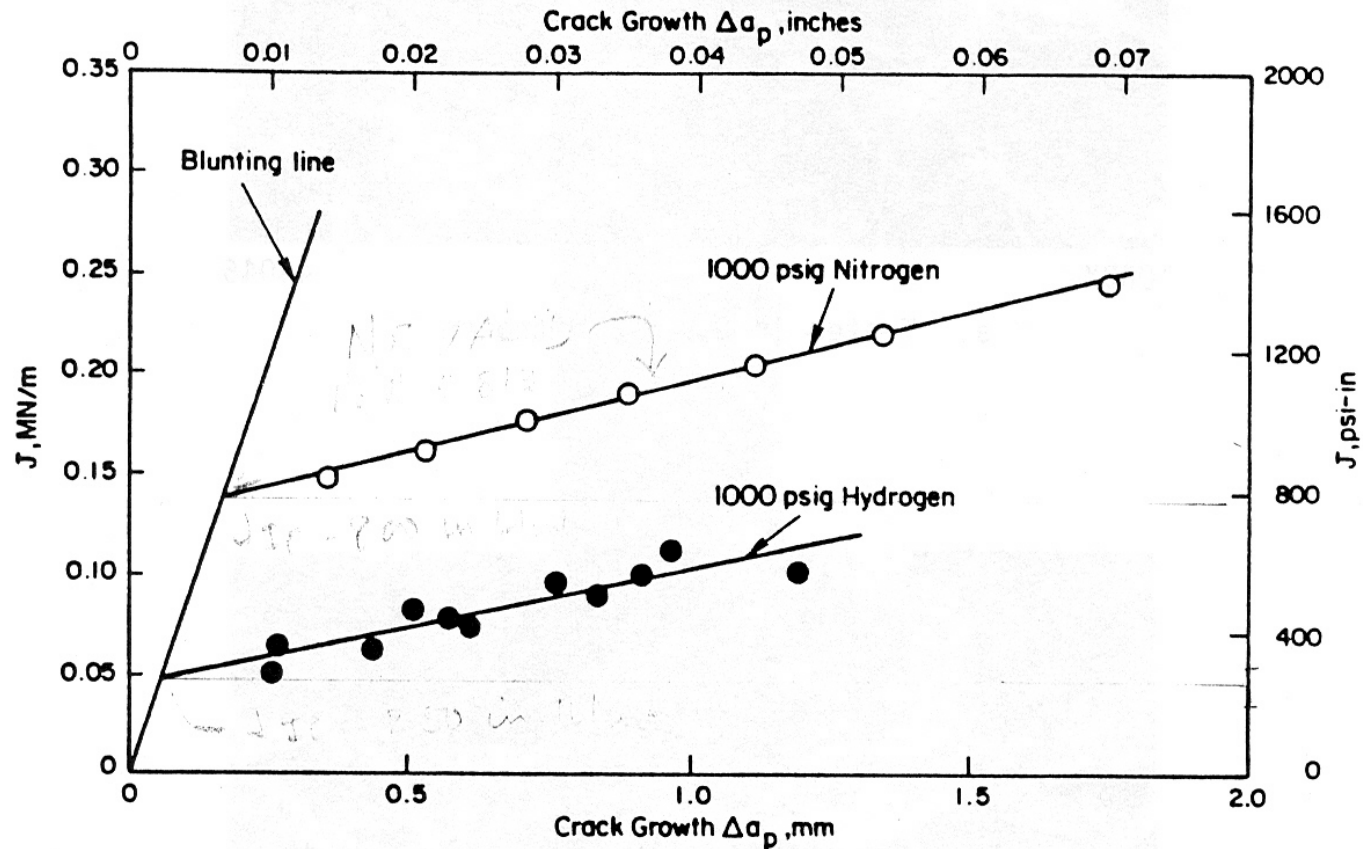


FIGURE 9. J-RESISTANCE CURVES FOR X42 STEEL BASE METAL TESTED IN 1000 psig HYDROGEN AND IN 1000 psig NITROGEN

H2/NG Distribution Systems Materials Challenges

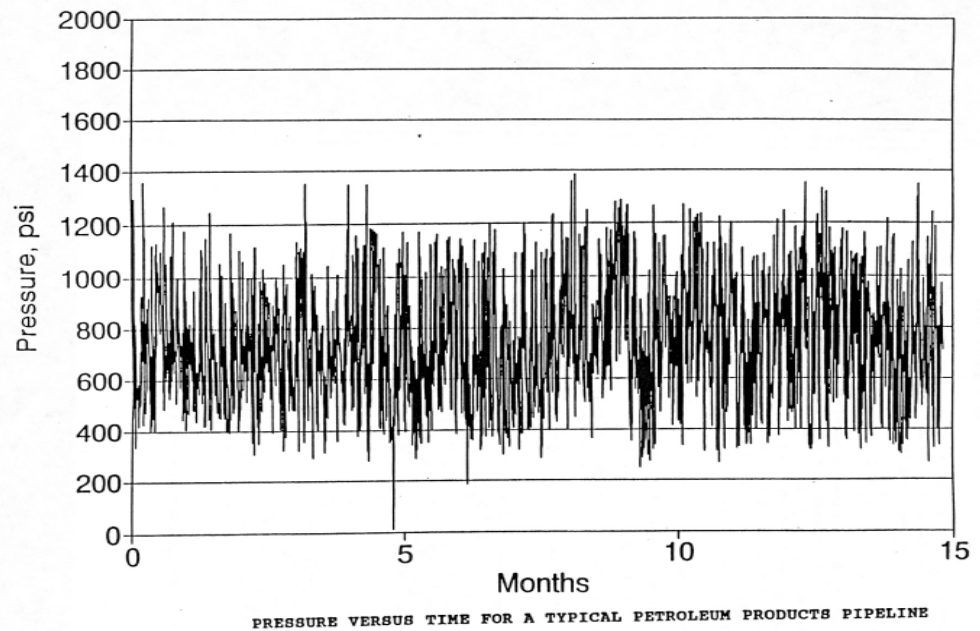
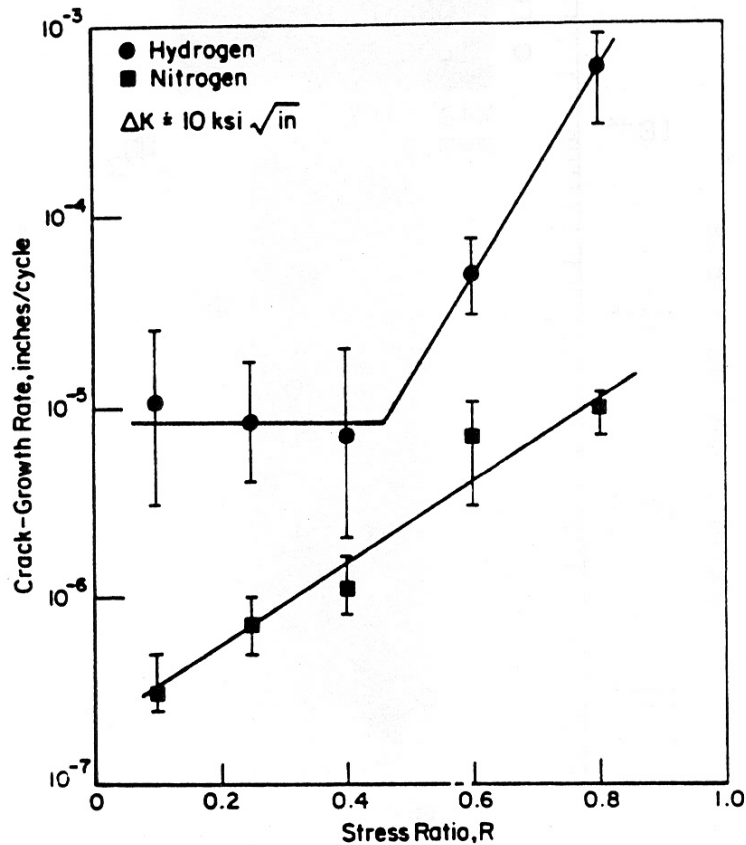


FIGURE 6. FATIGUE-CRACK-GROWTH RATE IN X42 PIPELINE STEEL AS A FUNCTION OF STRESS RATIO

H2/NG Distribution Systems Materials Challenges

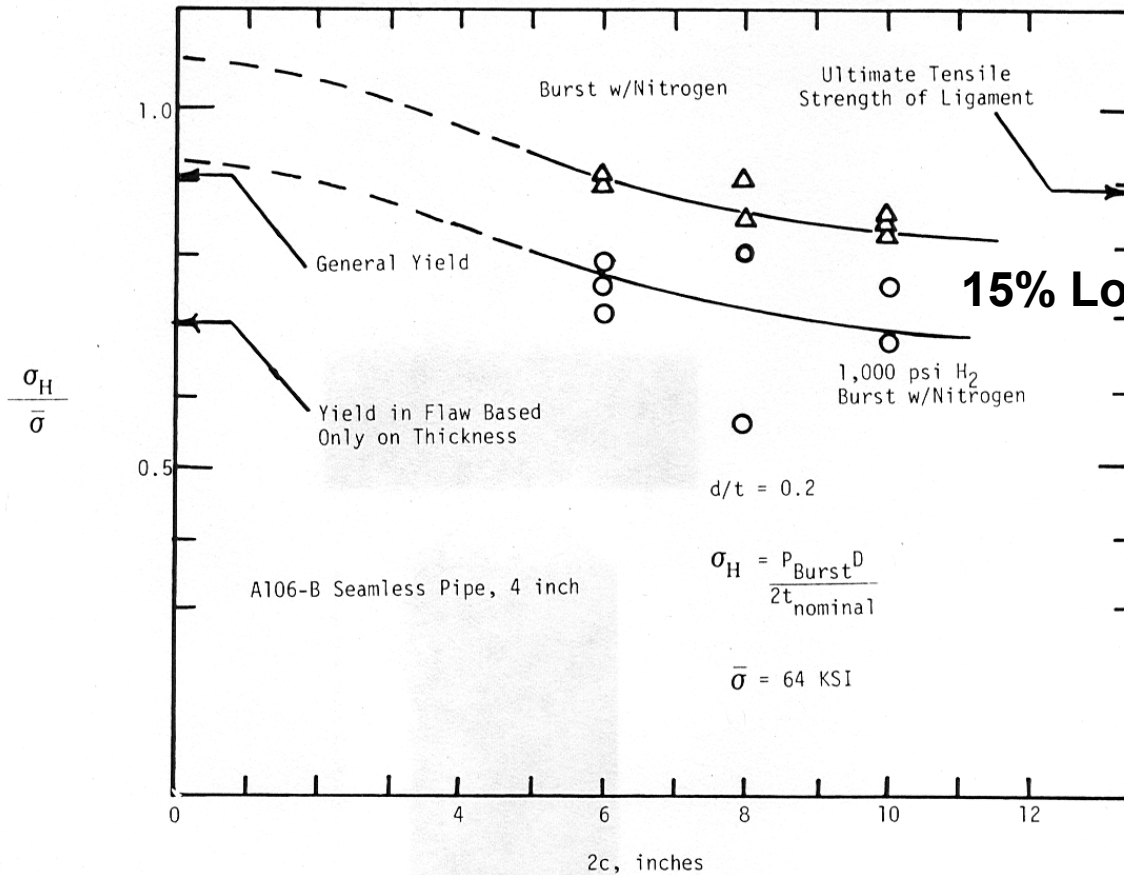
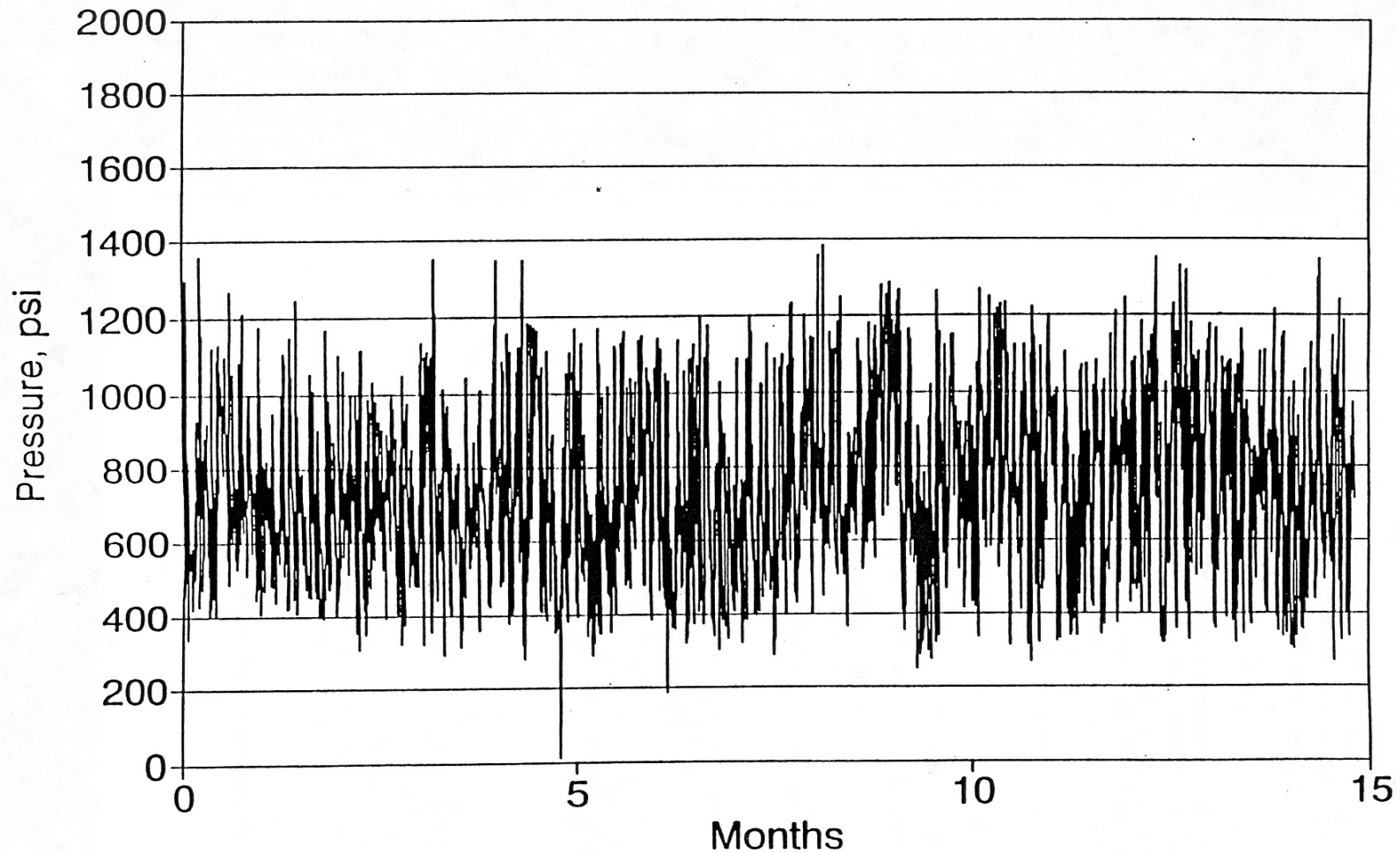


Figure 9. Burst test data for internally flawed pipe showing a 15% loss of hoop stress at failure when exposed to 1000 psi hydrogen.

H2/NG Distribution Systems Materials Challenges



PRESSURE VERSUS TIME FOR A TYPICAL PETROLEUM PRODUCTS PIPELINE

H2/NG Distribution Systems Materials Challenges

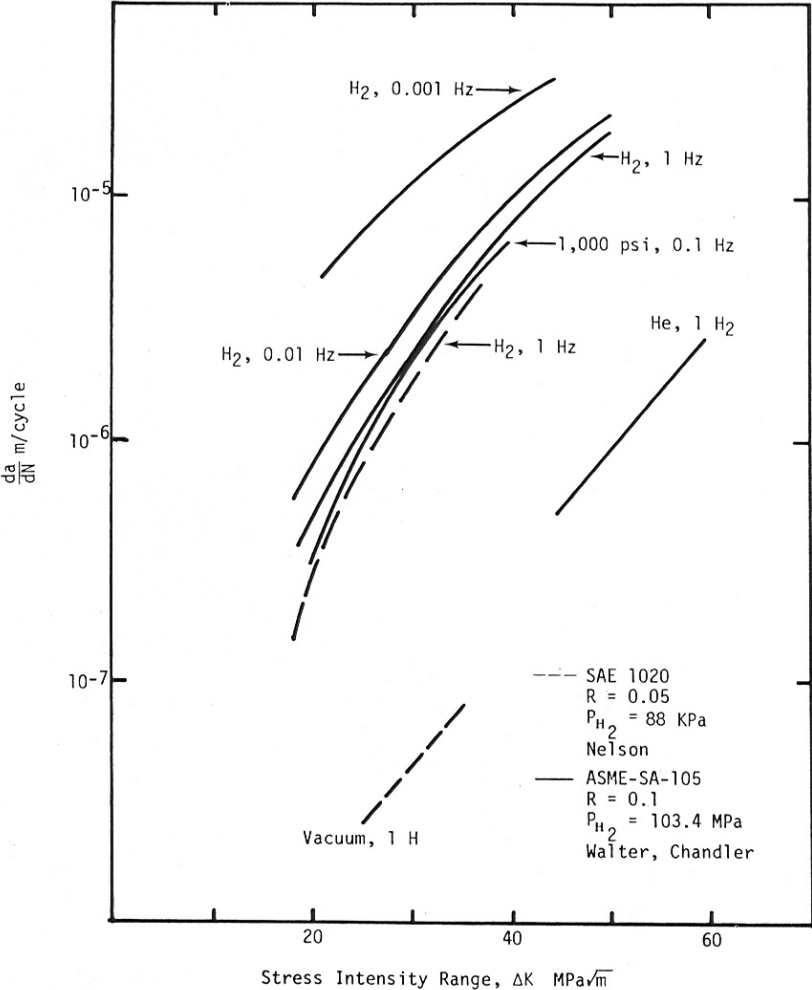


Figure 5. Acceleration of fatigue crack growth rates in carbon manganese steels fatigued in high pressure hydrogen.

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

H2/NG Distribution Systems Materials Challenges

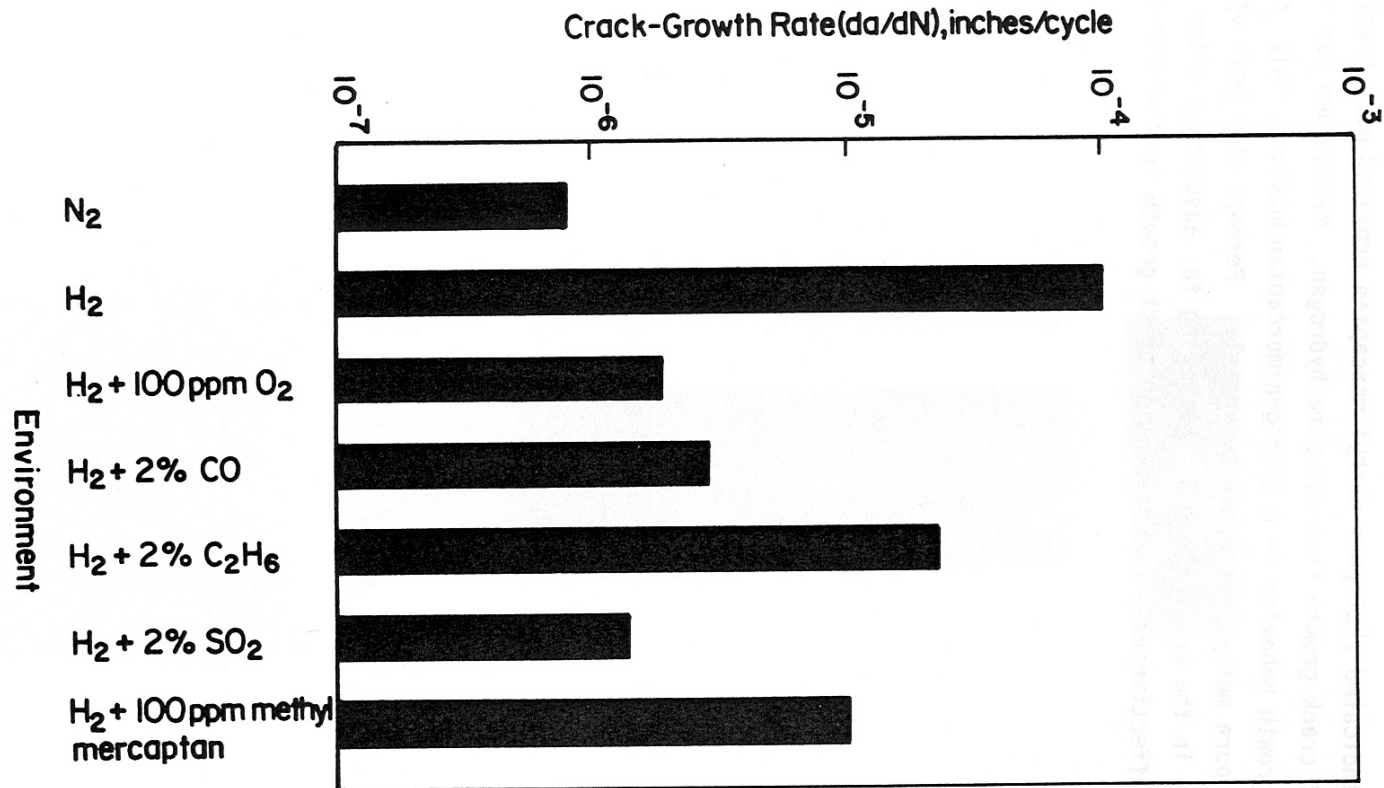


FIGURE 19. FATIGUE-CRACK-GROWTH RATE FOR X42 STEEL IN VARIOUS GASES

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

“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

H2/NG Distribution Systems Materials Challenges

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

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(A²/U⁹)**

SRNL H2 Pipeline Program

Table 2A—PSL 1 Chemical Requirements for Heat and Product Analyses by Percentage of Weight

| (1) Grade & Class | (2) Carbon, Maximum ^a | (3) Manganese, Maximum ^a | (4) Phosphorus | | (5) Sulfur, Maximum | (6) Titanium, Maximum | (7) Other |
|-------------------------------------|--|---|-------------------|---------|---------------------------|-----------------------------|--------------|
| | | | Minimum | Maximum | | | |
| Seamless | | | | | | | |
| A25, CII | 0.21 | 0.60 | | 0.030 | 0.030 | | |
| A25, CI II | 0.21 | 0.60 | 0.045 | 0.080 | 0.030 | | |
| A | 0.22 | 0.90 | | 0.030 | 0.030 | | |
| B | 0.28 | 1.20 | | 0.030 | 0.030 | 0.04 | b, c, d |
| X42 | 0.28 | 1.30 | | 0.030 | 0.030 | 0.04 | c, d |
| X46, X52, X56 | 0.28 | 1.40 | | 0.030 | 0.030 | 0.04 | c, d |
| X60 ^f | 0.28 | 1.40 | | 0.030 | 0.030 | 0.04 | c, d |
| X65 ^f , X70 ^f | 0.28 | 1.40 | | 0.030 | 0.030 | 0.06 | c, d |
| Welded | | | | | | | |
| A25, CII | 0.21 | 0.60 | | 0.030 | 0.030 | | |
| A25, CI II | 0.21 | 0.60 | 0.045 | 0.080 | 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 |
| X60 ^f | 0.26 | 1.40 | | 0.030 | 0.030 | 0.04 | c, d |
| X65 ^f | 0.26 | 1.45 | | 0.030 | 0.030 | 0.06 | c, d |
| X70 ^f | 0.26 | 1.65 | | 0.030 | 0.030 | 0.06 | c, d |

- API 5L-Spec 2004
- X-42

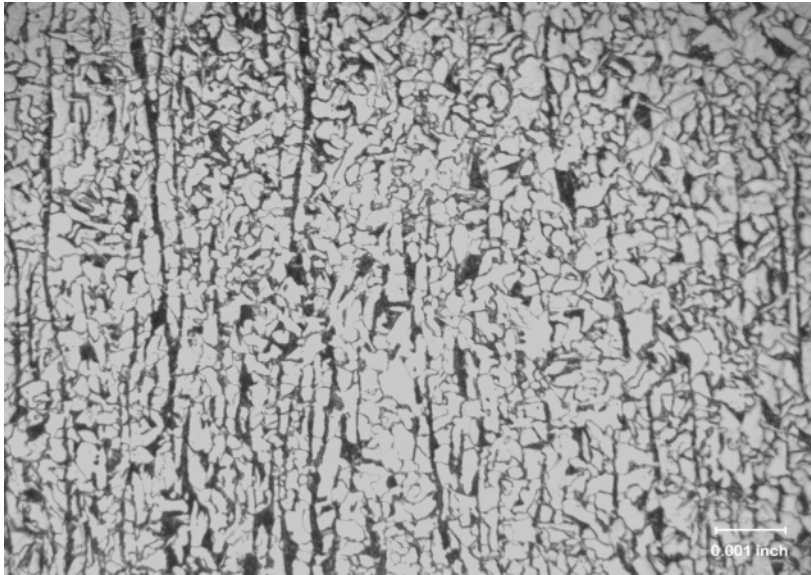
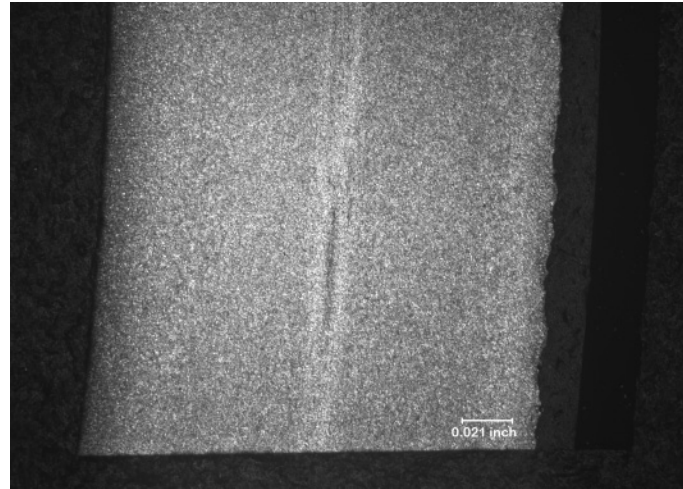
- C:0.22 max
- Mn: 1.30max
- P:0.025max
- S:0.015max
- Ti:0.04max
- Other: <0.15%

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

| (1) Grade | (2) Carbon, Maximum ^a | (3) Manganese, Maximum ^a | (4) Phosphorus, Maximum | (5) Sulfur, Maximum | (6) Titanium, Maximum | (7) Other |
|--|--|---|-------------------------------|------------------------|-----------------------------|--------------|
| Seamless | | | | | | |
| B | 0.24 | 1.20 | 0.025 | 0.015 | 0.04 | d, e |
| X42 | 0.24 | 1.30 | 0.025 | 0.015 | 0.04 | c, d |
| X46, X52, X56, X60 ^f | 0.24 | 1.40 | 0.025 | 0.015 | 0.04 | c, d |
| X65 ^f , X70 ^f , X80 ^f | 0.24 | 1.40 | 0.025 | 0.015 | 0.06 | c, d |
| Welded | | | | | | |
| B | 0.22 | 1.20 | 0.025 | 0.015 | 0.04 | d, e |
| X42 | 0.22 | 1.30 | 0.025 | 0.015 | 0.04 | c, d |
| X46, X52, X56 | 0.22 | 1.40 | 0.025 | 0.015 | 0.04 | c, d |
| X60 ^f | 0.22 | 1.40 | 0.025 | 0.015 | 0.04 | c, d |
| X65 ^f | 0.22 | 1.45 | 0.025 | 0.015 | 0.06 | c, d |
| X70 ^f | 0.22 | 1.65 | 0.025 | 0.015 | 0.06 | c, d |
| X80 ^f | 0.22 | 1.85 | 0.025 | 0.015 | 0.06 | c, d |

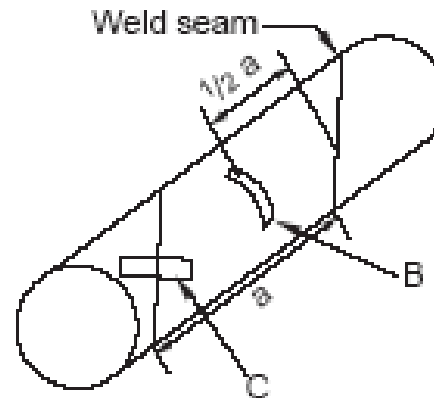
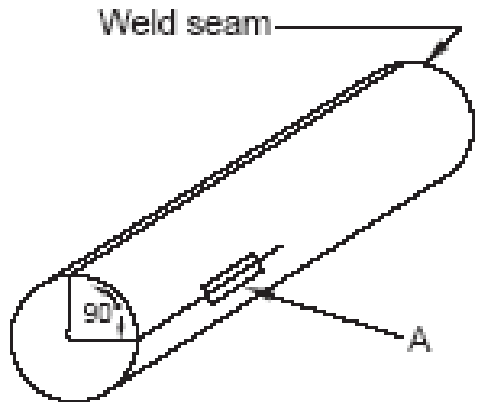
SRNL H2 Pipeline Program

- X42 Archival NG Pipe
- Microstructure—Polished and Etched
- Ferrite/Pearlite Microstructure
- Single Weld Seam Pipe
- Evidence of banding

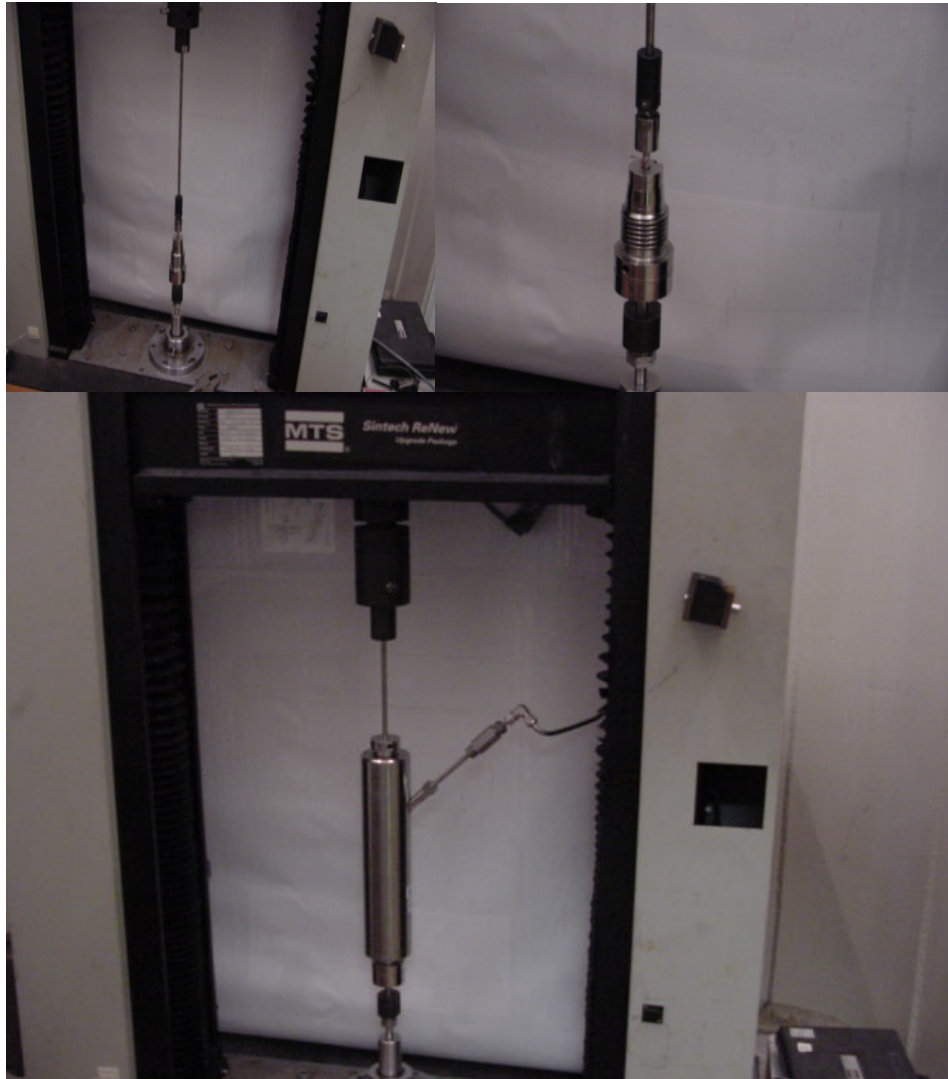


H₂/NG Mechanical Property Testing

- 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 $\cong 25^{\circ}\text{C}$



H₂/NG Mechanical Property Testing



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

SRNL H2 Pipeline Program

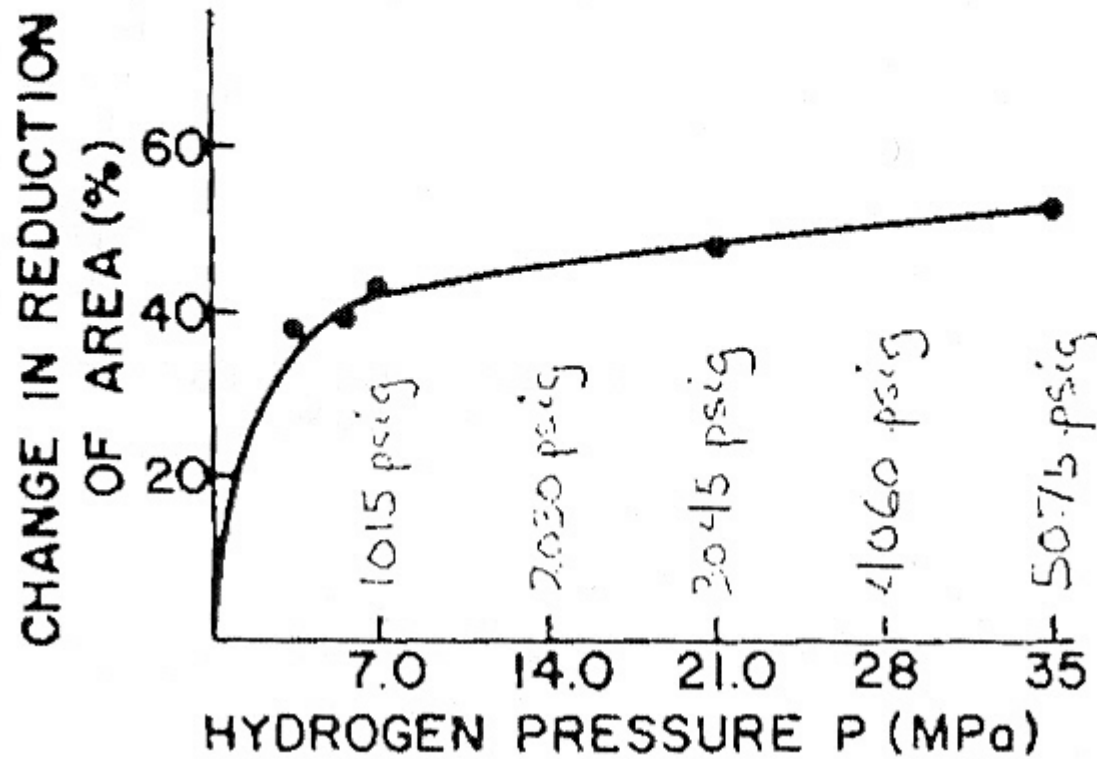
TABLE 2. SMOOTH-BAR TENSILE PROPERTIES OF PIPE STEELS*

| API-5LX Pipe Grade | Test Environment | 0.2-Percent-Offset Yield Strength, MPa (ksi) | Ultimate Tensile Strength, MPa (ksi) | Percent Elongation in 1 inch | Percent Reduction of Area |
|---|------------------------|--|--|------------------------------------|---------------------------------|
| <u>Axial (Longitudinal) Orientation</u> | | | | | |
| X42 | Air | 366 (53) | 511 (74) | 21 | 56 |
| | 6.9 MPa H ₂ | 331 (48) | 483 (70) | 20 | 44 |
| X70 | Air | 584 (85) | 669 (97) | 20 | 57 |
| | 6.9 MPa H ₂ | 548 (79) | 659 (95) | 20 | 47 |
| <u>Transverse Orientation</u> | | | | | |
| X42 | Air | 311 (45) | 490 (71) | 21 | 52 |
| | 6.9 MPa H ₂ | 338 (49) | 476 (69) | 19 | 41 |
| X70 | Air | 613 (89) | 702 (102) | 19 | 53 |
| | 6.9 MPa H ₂ | 593 (86) | 686 (99) | 15 | 38 |

* Tests conducted at an engineering-strain rate of 10^{-4} sec⁻¹.

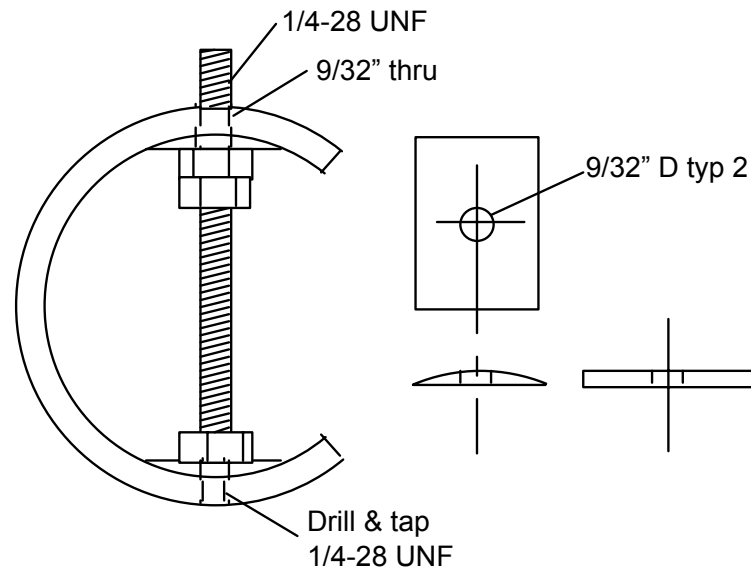
Figure 1.

HEE observed in double-notched tensile specimens.



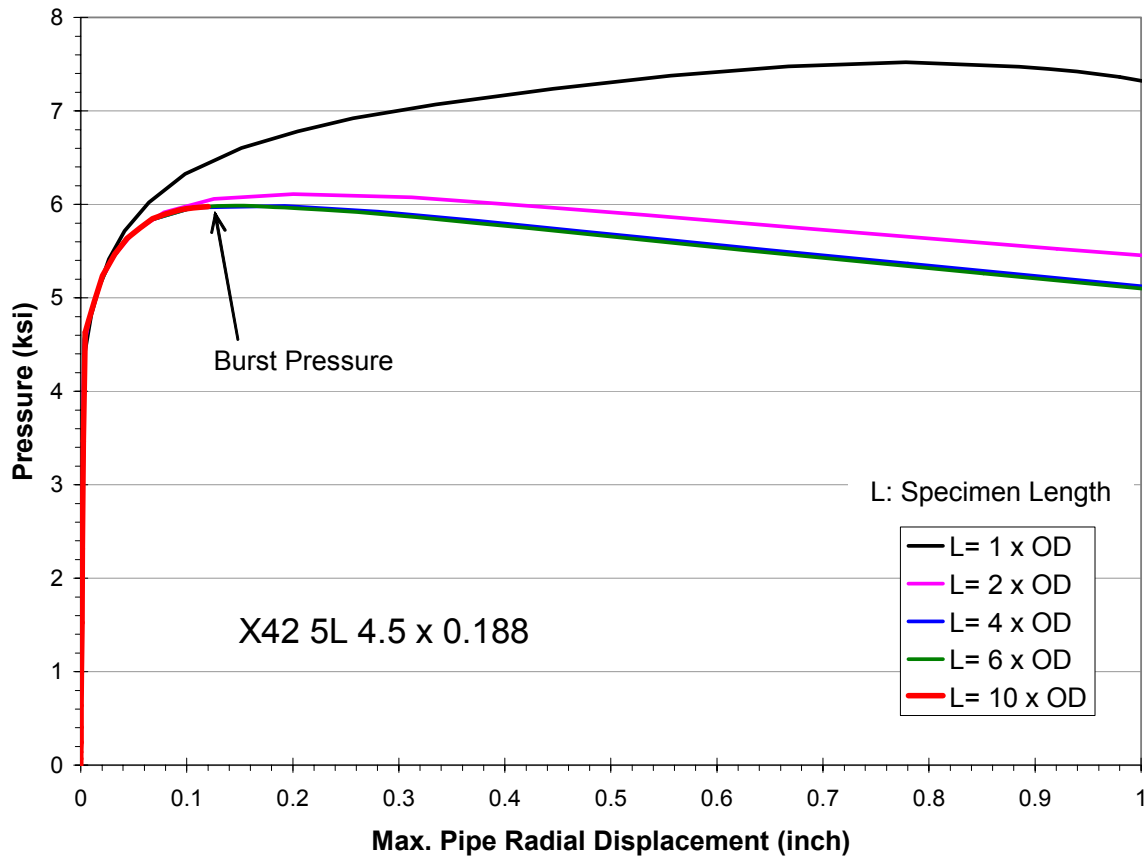
H₂/NG Threshold Stress Intensity Testing

- Hydrogen Threshold Stress Intensity Testing—Bolt Loaded Sample
 - Multiple Samples with Load Range from 0-500 lbs.
 - Crack Dimensions: $a/W \cong 0.5$, Root Radius $\cong 0.003$ in
- 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 $\cong 25^\circ\text{C}$
- Hydrogen Concentration will be Estimated Analytically Using DIFF
- K_{TH} will be Reported for Initial Conditions (i.e., crack growth initiation)



H2/NG Threshold Stress Intensity Testing





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)

Component Fatigue and Hydrogen Environments

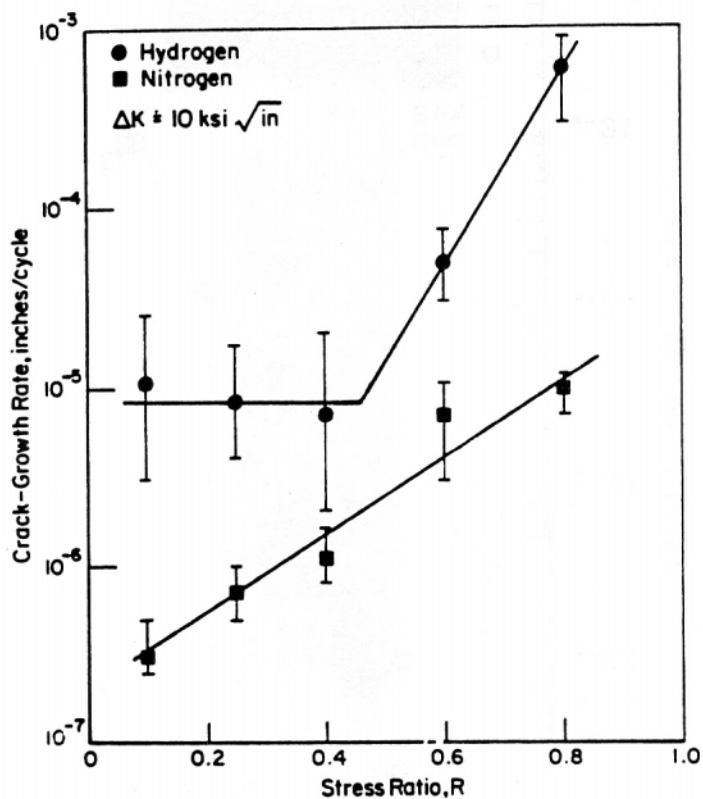
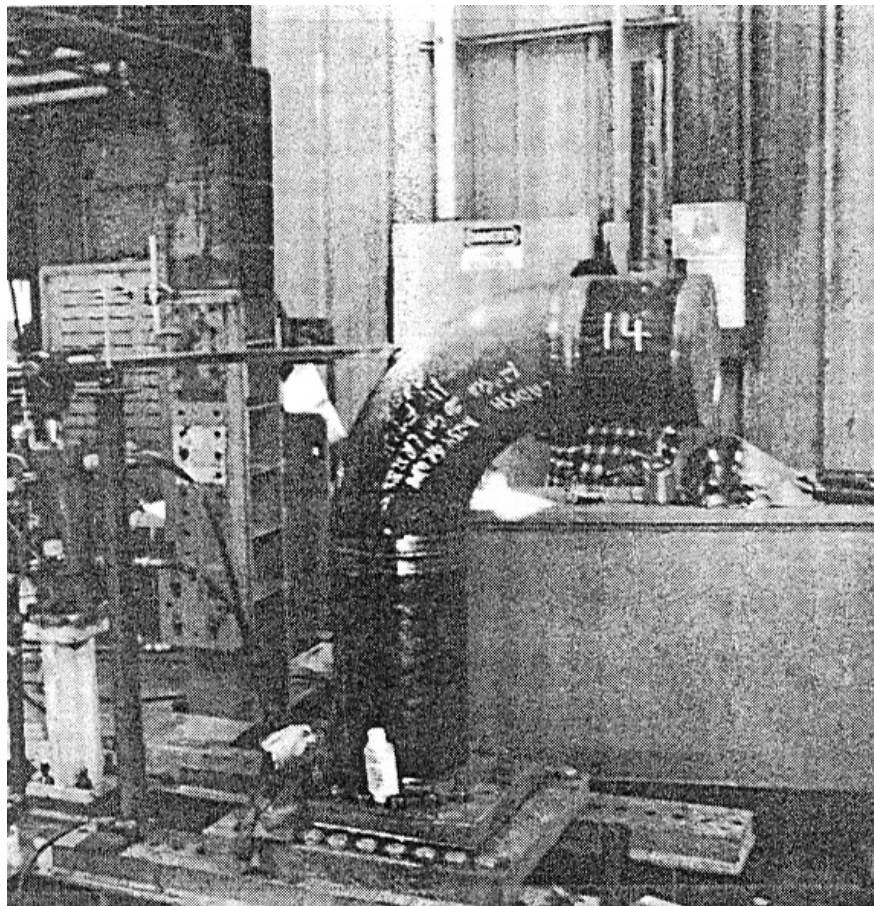


FIGURE 6. FATIGUE-CRACK-GROWTH RATE IN X42 PIPELINE STEEL AS A FUNCTION OF STRESS RATIO



Year-Two Program Focus

Welds and Weld Metal Embrittlement Effects

TABLE VI. TENSILE DATA FOR FILLER METALS AND PROCESSES,
TESTED IN HIGH PRESSURE HYDROGEN

| Process | Test Environment | 0.2% Yield Strength, 1000 psi | Ultimate Strength, 1000 psi | Uniform Elongation | Total Elongation | % R.A. |
|--------------------|------------------------|-------------------------------|-----------------------------|--------------------|------------------|--------|
| (Smooth Bar Tests) | | | | | | |
| Base Metal | Air | 57.9 | 82.5 | 19.3 | 30.5 | 71.6 |
| | 103 psi H ₂ | 56.8 | 81.0 | 14.0 | 16.6 | 24.7 |
| GTA [†] | Air | 64.8 | 84.4 | 7.3 | 12.5 | 71.3 |
| GTA | 103 psi H ₂ | 62.4 | 86 | 8.2 | 11.0 | 38.0 |
| SMA ^{††} | Air | 56.3 | 79.1 | 8.0 | 13.0 | 68.7 |
| SMA | 103 psi H ₂ | 53.6 | 79.1 | 9.6 | 14.1 | 47.6 |

† GTA : GAS - Tungsten Arc, AWS, E70S-2 Filler

†† : Shielded Metal Arc, AWS - E7018 Low H₂ Filler

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

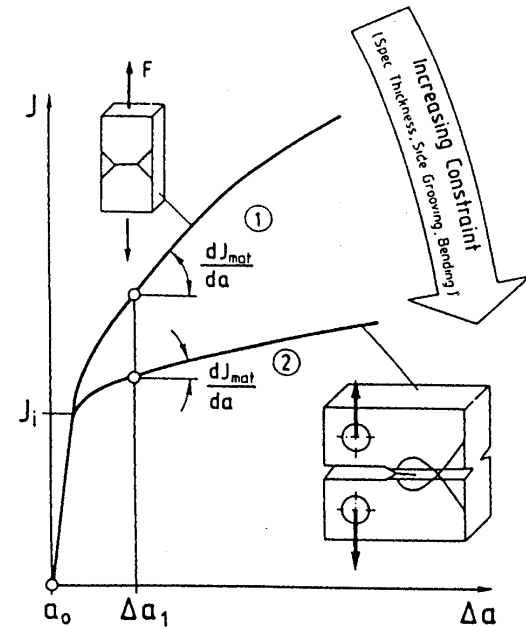
Constraint Modified J-R Curves

Traditional ASTM J-R Curve:

$$J(\Delta a) = C_1(\Delta a)^{C_2}$$

Constraint Modified J-R Curve:

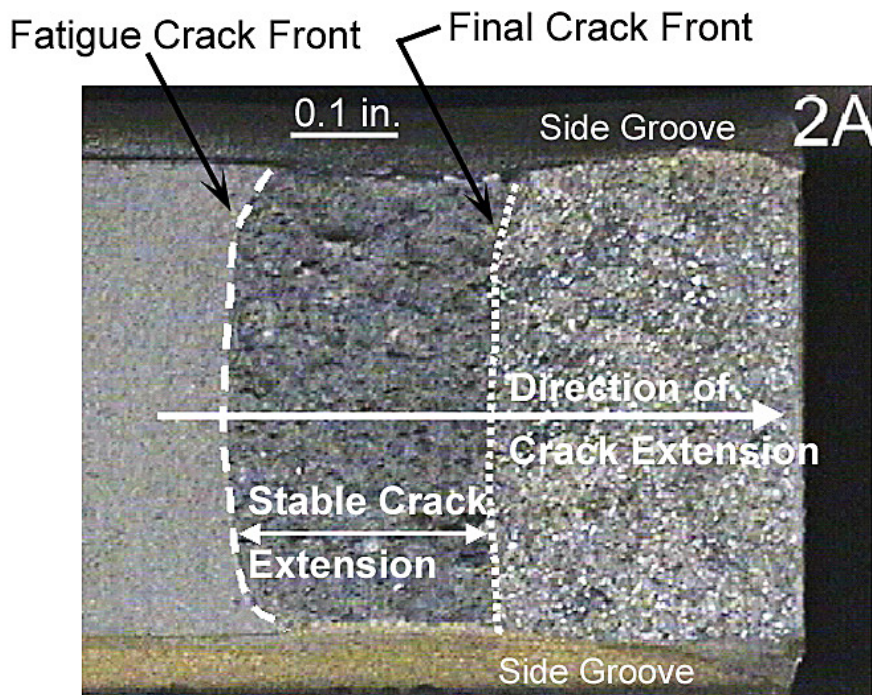
$$J(\Delta a, A_2) = C_0(A_2) + C_1(A_2)(\Delta a)^{C_2(A_2)}$$



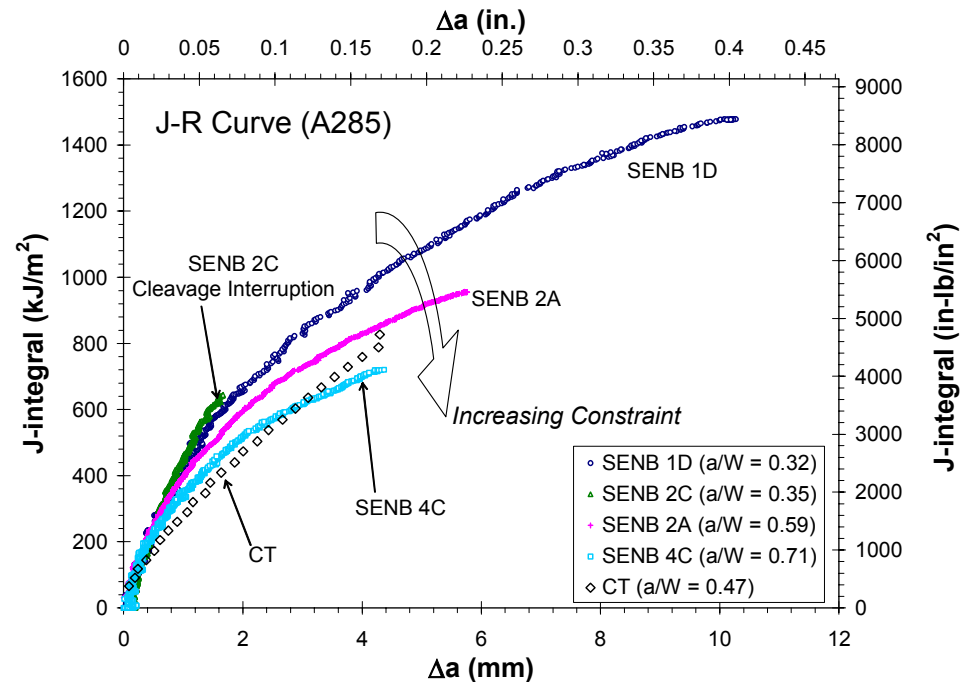
The results can have full transferability from test specimen to large structure

SRNL Fracture Testing for A285 Crack Resistance (J-R) Curves

Typical fracture surface



Specimen size-dependent J-R curves



REF:

Lam, P.S., Chao, Y.J., Zhu, X.K., Kim, Y., Sindelar, R.L., "Determination of Constraint-Modified J-R Curves for Carbon Steel Tanks," J Press Vessel Tech, 12, pp.136-143, 2003

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

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