Overview

Timeline
• Project start date Jan. 2007
• Project end date Oct. 2013*
• Percent complete 70%

Budget
• Total project funding (to date)
  – DOE share: $1100K
• FY13 Funding: $105K

Barriers & Targets
• B. Reliability and Costs of Gaseous H₂ Compression
• K. Safety, Codes and Standards, Permitting
• D. High As-Installed Cost of Pipelines

Partners
• DOE Pipeline Working Group
  – Federal Labs: Sandia, Oak Ridge, Savannah River, NIST
  – Universities: Univ. of Illinois
  – Industry: Secat, industrial gas companies, ExxonMobil
  – Standards Development Organizations: ASME

*Project continuation and direction determined annually by DOE
Objectives/Relevance

- Why should steel hydrogen pipelines be used?
  - Safety of steel pipelines is well understood (e.g., third-party damage tolerance, vulnerability of welds)
  - Hydrogen pipelines are safely operated under static pressure

Project purpose is to:
- Demonstrate reliability/integrity of steel hydrogen pipelines for cyclic pressure applications
  - Address potential fatigue crack growth aided by hydrogen embrittlement, particularly in welds
- Enable a pipeline reliability/integrity framework that accommodates hydrogen embrittlement
  - Ensure relevance to H₂ pipeline code ASME B31.12

FY12-13 tasks
- Test model for effects of O₂ impurities on fatigue crack growth for X52 steel in H₂ gas
- Measure fatigue crack growth laws in H₂ gas for girth welds from X65 steel
Approach

• Apply unique capability for measuring fracture properties of steels in high-pressure H₂ gas
  – Fracture properties serve as inputs into reliability/integrity assessment as specified in ASME B31.12 pipeline code
  – Milestone: Measure the fatigue crack growth ($da/dN$ vs $\Delta K$) relationship at constant H₂ gas pressure in X65 pipeline girth weld supplied by industry partner (~50% complete)

• Pipeline steels and their welds were identified by stakeholders as a high priority
  – Provide feedback to stakeholders through DOE Pipeline Working Group
Approach:

Reliability/integrity assessment framework in ASME B31.12 requires fracture data in H₂

- Two fracture properties in H₂ needed
  - Fatigue crack growth law
  - Fracture threshold

- Reliability/assessment framework accommodates H₂ embrittlement

\[ \Delta K = \Delta p[f(a, t, R_o, R_i)] \]

\[ \frac{da}{dN} = C[\Delta K]^m \]
Approach:
Fracture data in H₂ measured using unique lab capabilities: fatigue crack growth

- **Material**
  - X52 and X65 pipeline steels

- **Instrumentation**
  - Internal load cell in feedback loop
  - Crack-opening displacement measured internally using LVDT
  - Crack length calculated from compliance

- **Mechanical loading**
  - Triangular load-cycle waveform
  - Constant load amplitude (increasing ΔK)

- **Environment**
  - Primary supply gas: 99.9999% H₂
  - Other supply gases: H₂ with 10-1000 ppm O₂
  - Pressure = 3,000 psi (21 MPa)
  - Room temperature
Previous Accomplishment:

Measured onset of H₂-accelerated fatigue cracking as function of $\Delta K$, $f$, and O₂ content

• Increasing O₂ concentrations systematically inhibit H₂-accelerated fatigue crack growth
  – Onset of H₂-accelerated fatigue crack growth displaced to higher $\Delta K$ or $f$
• O₂-affected fatigue crack growth laws lead to enhanced reliability/integrity for steel H₂ pipelines
Accomplishment:

**SNL-I^2CNER finalized model for predicting effect of O_2 on H_2-accelerated cracking**

- Oxygen adsorption on crack-tip surface inhibits hydrogen uptake
- Extent of oxygen adsorption depends on crack-tip area, proportional to “mechanical” crack growth rate, $da/dN$
- Assume hydrogen uptake depends on quantity of adsorbed oxygen
  
  $\frac{d[H]}{dN} \propto \frac{1}{z}$

  $z$ = layers of adsorbed oxygen

- Based on these physics, develop model that relates adsorbed oxygen (H uptake) to mechanical and environmental variables

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Accomplishment:
Model developed based on idealized crack tip and crack channel geometry

Model assumptions:
- $O_2$ adsorption rate-limited by diffusion in crack channel
- Steady state $p_{O_2}$ profile
- $p_{O_2} = 0$ at crack tip

Mass balance between $O_2$ diffusion flux and $O_2$ adsorbed on fresh crack-tip surface during one cycle yields:

$$z = \frac{0.3 \chi D p_{tot} (1 - \nu^2)}{(da/dN)f \pi \theta_o R_g T E \sigma_0} \left( \frac{\Delta K}{\sqrt{a^*} (1 - R)} \right)^2$$

- Model predicts effects of mechanical and environmental variables on $O_2$ adsorption ($z$)
- By extension, model can predict effects of mechanical and environmental variables on $H_2$-accelerated cracking
Accomplishment:

Model employed to predict critical $da/dN$ and $f$ levels for H$_2$-accelerated crack growth

- Assumption: sufficient H uptake for accelerated cracking when $z = z_{\text{crit}}$

symbols → measurements
dash-dot lines → model results

\[
\frac{da}{dN}_{\text{crit}} = \frac{0.3 \chi D p_{\text{tot}} (1 - v^2)}{f \pi z_{\text{crit}} \theta O R_g T E \sigma_0 \left( \frac{\Delta K}{\sqrt{a^* (1 - R)}} \right)^2}
\]

\[
f_{\text{crit}} = \frac{0.3 \chi D p_{\text{tot}} (1 - v^2)}{(da / dN) \pi z_{\text{crit}} \theta O R_g T E \sigma_0 \left( \frac{\Delta K}{\sqrt{a^* (1 - R)}} \right)^2}
\]

Agreement between model and experiment validates physics and demonstrates predictive capability
Accomplishment:

More advanced model accounts for varying O$_2$ profile in “breathing” crack

Model based on “breathing” crack retains dependence on O$_2$ concentration ($\chi$) and frequency ($f$)
Accomplishment:

DFT calculations provide mechanistic insight into role of O₂ in inhibiting H₂ embrittlement

- Trajectory of H₂ dissociation on Fe(100)
  - Energy vs. Distance from surface
  - Weak attractive force

- Trajectory of O₂ dissociation on Fe(100)
  - Energy vs. Distance from surface
  - Strong attractive force

- Trajectory of H₂ dissociation on oxygen-rich Fe(100)
  - Energy vs. Distance from surface
  - Repulsive force

- Attractive force: $F = -\frac{dE}{dR}$

- Density functional theory (DFT) results from collaborator (I²CNER) reveal that surface-adsorbed oxygen impedes H₂ dissociation on iron (steel)
- DFT is theoretical tool for identifying other inhibitors
Model impact: interpret laboratory results or component behavior, e.g., mixed NG + H₂

- Possible impurities in natural gas such as O₂ and CO may explain varying results for crack growth rates in mixed NG + H₂
- Model could identify and quantify influence of impurities on experimental data or steel pipeline performance
Fatigue crack growth measurements must emphasize welds: potential vulnerability

- Measured fatigue crack growth rates for technologically relevant girth weld in H₂ gas

- API 5L X65 steel
  - Minimum yield strength: 65 ksi (428 MPa)
Accomplishment:
Completed initial measurements on base metal, fusion zone, and heat affected zone

- Duplicate measurements for HAZ yield nearly identical results
- Initial results: crack growth rates lower for HAZ compared to base metal in lower $\Delta K$ range
- Need modified procedures to establish reliable data for fusion zone

Results from fusion zone specimen not valid due to non-uniform pre-crack front

[Graph showing crack growth rate vs. stress intensity factor range]
Collaborations

• **DOE Pipeline Working Group (PWG)**
  – Participants funded by DOE FCT Office
    • Federal Labs: Sandia, Oak Ridge, Savannah River
    • Universities: Univ. of Illinois
    • Industry: Secat
  – Participants not funded by DOE FCT Office
    • Federal Labs: NIST
    • Industry: industrial gas companies, ExxonMobil
    • Standards Development Organizations: ASME
  – Extent of collaborations include:
    • PWG meetings (~ 1/year)
    • Supplying materials (e.g., ExxonMobil-Sandia)
    • Coordinating testing (e.g., NIST-Sandia)
• **International Institute for Carbon-Neutral Energy Research (I²CNER), Fukuoka, Japan** (e.g., modeling)
Proposed Future Work

Remainder of FY13
• Complete multiple fatigue crack growth measurements for girth weld in H₂ gas to demonstrate reliable data

FY14
• Measure fatigue crack growth laws in H₂ for seam weld from technologically relevant pipeline steel
• Conduct reliability/integrity analysis of H₂ pipeline using operating parameters supplied by industry partner
• Expand pipeline steel testing beyond X52 and X65, e.g., transition to higher-strength steels such as X70 and X80
Summary

• Measured fracture thresholds and fatigue crack growth laws allow evaluation of reliability/integrity of steel H₂ pipelines
  – Hydrogen embrittlement accommodated by measuring fracture properties in H₂ following ASME B31.12 design standard

• Analytical model quantifies inhibiting effect of O₂ on H₂-accelerated fatigue crack growth, including variables such as load-cycle frequency and O₂ concentration
  – Model may provide insight into effects of gas impurities on H₂-accelerated fatigue crack growth for mixed natural gas + H₂

• Conducted initial measurements of fatigue crack growth laws for pipeline steel girth weld in H₂ gas
  – Testing challenges (e.g., non-uniform crack fronts) require multiple measurements to confirm data reliability
Technical Back-Up Slides
Accomplishment (in coordination with Safety, Codes and Standards):
Hosted meeting on Advancing Materials Testing in Hydrogen Gas at SNL/CA

• Goal: exchange test system design details and initiate international collaboration on next-generation testing capabilities

• Attendees: ~25 people from universities, national labs, and industry world-wide

• Output:
  – Catalogue design concepts, best practices, and safety features
  – Determine test system limits
  – Identify gaps in existing testing capabilities
  – Make meeting presentations publically available
  – Identify pathways and resources for development of capabilities
  – Identify collaboration opportunities