Hydrogen Embrittlement of Structural Steels

Brian Somerday
Sandia National Laboratories
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Overview

Timeline
- Project start date Jan. 2007
- Project end date Oct. 2012*
- Percent complete 60%

Budget
- Total project funding (to date)
  - DOE share: $1000K
- FY11 Funding: $200K
- FY12 Funding: $100K

Barriers & Targets
- Pipeline Reliability/Integrity
- Safety, Codes and Standards, Permitting
- High Capital Cost and Hydrogen Embrittlement 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 steel hydrogen pipelines?
  – Safety of steel pipelines well understood (e.g., third-party damage tolerance, vulnerability of welds)
  – Hydrogen pipelines safely operated under static pressure

• Demonstrate reliability/integrity of steel hydrogen pipelines for cyclic pressure
  – Address potential fatigue crack growth aided by hydrogen embrittlement, particularly in welds

• Enable pipeline reliability/integrity framework that accommodates hydrogen embrittlement
  – Ensure relevance to H₂ pipeline code ASME B31.12

• FY11-FY12: quantify effects of O₂ impurities on fatigue crack growth laws for X52 steel in H₂ gas
Approach

• Apply unique capability for measuring fracture properties of steels in high-pressure $H_2$
  – Fracture properties serve as inputs into reliability/integrity assessment as specified in ASME B31.12 pipeline code
  – Milestone: Determine the threshold level of $O_2$ concentration required to mitigate accelerated fatigue cracking for X52 steel in 21 MPa $H_2$ gas (~100% complete)
  – Milestone: Measure the fatigue crack growth law for X65 pipeline girth weld in $H_2$ gas (10% complete)

• Emphasize pipeline steels and their welds identified by stakeholders as high priority
  – Provide feedback to stakeholders through DOE Pipeline Working Group
Reliability/integrity assessment framework in ASME B31.12 requires fracture data in H\textsubscript{2}.

- Two fracture properties in H\textsubscript{2} needed
  - Fatigue crack growth law
  - Fracture threshold

- Reliability/assessment framework accommodates H\textsubscript{2} embrittlement
Fracture data in $H_2$ measured using specialized lab capabilities: fatigue crack growth

- **Material**
  - X52 ERW pipeline steel

- **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 $\Delta K$)

- **Environment**
  - Primary supply gas: 99.9999% $H_2$
  - Other supply gases: $H_2$ with 10-1000 ppm $O_2$
  - Pressure = 3,000 psi (21 MPa)
  - Room temperature
Measured fracture properties of technologically relevant steel: API 5L X52

• Tested same X52 steel from DOE Pipeline Working Group tensile property round robin
  – Stakeholders expressed interest in X52 steel

• Tensile properties
  – Yield strength: 62 ksi (428 MPa)
  – Ultimate tensile strength: 70 ksi (483 MPa)
Accomplishment:

Measured onset of H₂-accelerated fatigue cracking as function of ΔK and O₂ concentration

- Increasing O₂ concentrations systematically mitigate H₂-accelerated fatigue crack growth
  - Onset of H₂-accelerated fatigue crack growth displaced to higher ΔK
- At O₂ concentrations <100 ppm, H₂-accelerated cracks propagate along grain boundaries
- O₂-affected fatigue crack growth laws lead to enhanced reliability/integrity for steel H₂ pipelines
Accomplishment:
Quantified effects of load-cycle frequency on O$_2$-modified, H$_2$-accelerated fatigue cracking

- Inhibiting effect of O$_2$ more pronounced at lower load-cycle frequencies
- Threshold level of O$_2$ concentration required to mitigate accelerated fatigue cracking depends on load-cycle frequency
  - H$_2$-accelerated fatigue cracking effectively suppressed for all O$_2$ concentrations >10 ppm when frequency <0.1 Hz
Accomplishment:
Quantified effect of load ratio ($R=K_{\text{min}}/K_{\text{max}}$) on O$_2$-modified, H$_2$-accelerated fatigue cracking

- At higher O$_2$ concentrations, increasing R ratio magnifies retarding effect of O$_2$ on H$_2$-accelerated fatigue cracking
  - No accelerated cracking observed in H$_2$ + 1000 ppm H at higher R ratio
- Effect of O$_2$ on enhancing reliability/integrity more pronounced if H$_2$ pipeline operated at higher pressure ratios (i.e., $p_{\text{min}}/p_{\text{max}}$)
Developed model for role of mechanical crack growth rate in stimulating H₂-accelerated cracking

- $K_{\text{max}}$ governs crack-tip stresses that activate intergranular cracking
- $\frac{da}{dN}$ governs rate of bare-metal exposure and atomic hydrogen uptake

$$\frac{d[H]}{dN} \propto \theta_H = (1 - \theta_O)$$

$$\theta_O \propto \frac{1}{\frac{da}{dN}}$$

$\theta = \text{fractional surface coverage of hydrogen (}\theta_H\text{) or oxygen (}\theta_O\text{)}$

Assume $\theta_H + \theta_O = 1$

Physics-based model presumes that cracking accelerates when threshold levels of $K_{\text{max}}$ and "mechanical" $\frac{da}{dN}$ exceeded

(Wei and Simmons, Fatigue: Environment and Temperature Effects, 1983)
Accomplishment:
Model based on rate-limiting O₂ diffusion predicts effects of O₂ concentration, R ratio, and frequency

Assumptions: H uptake when \( \theta_0 < 1 \)
O₂ diffusion rate limiting

• O₂ diffusion model assumptions:
  - steady state
  - \( p_{O_2} = 0 \) at crack tip

• Mass balance between O₂ flow in gas during one cycle and O₂ adsorbed on fresh crack-tip surface yields:

\[
\frac{da}{dN} = \frac{Dp_{O_2}}{\theta_o \tau \nu RT} \cdot \frac{0.6(1 - \nu^2)}{E\sigma_0} \left( \frac{\Delta K}{\sqrt{a(1-R)}} \right)^2
\]

• Predictions of “mechanical” da/dN required for \( \theta_0 < 1 \)
  - Point 1: 1 ppm O₂
  - Point 2: 10 ppm O₂
  - Point 3: 100 ppm O₂
  - Point 4: 1000 ppm O₂, R=0.5

• Model enables extrapolation of laboratory data to predict effects of O₂ in pipeline
Collaborations

• **DOE Pipeline Working Group (PWG)**
  – Participants funded by DOE FCT Program
    • Federal Labs: Sandia, Oak Ridge, Savannah River
    • Universities: Univ. of Illinois
    • Industry: Secat
  – Participants not funded by DOE FCT Program
    • Federal Labs: NIST
    • Industry: industrial gas companies, ExxonMobil
    • Standards Development Organizations: ASME
  – Extent of collaborations include:
    • PWG meetings (up to 2 times/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., $O_2$ diffusion model)
Proposed Future Work

Remainder of FY12

• Measure fatigue crack growth law of girth weld fusion zone from X65 steel in H$_2$ gas (Milestone: June 2012)

FY13

• Measure fatigue crack growth law of girth weld heat-affected zone (HAZ) in H$_2$ gas
• Conduct reliability/integrity analysis of X52 H$_2$ pipeline using operating parameters supplied by industry partner
• Expand pipeline steel testing beyond X52, 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

• Measurements on X52 steel in H₂ gas with O₂ impurities reveal the following trends:
  – O₂ systematically retards H₂-accelerated fatigue crack growth as concentration increases from 10 ppm
  – Inhibiting effect of O₂ more pronounced at high load ratio
  – Threshold level of O₂ concentration required to mitigate accelerated fatigue cracking depends on load-cycle frequency

• Effects of O₂ concentration, R ratio, and frequency on O₂-modified, H₂-accelerated fatigue can be predicted from model