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Hydrogen Embrittlement of Structural Steels

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Project ID # PD025

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000

Overview

Timeline

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

Barriers & Targets

- B. Reliability and Costs of Gaseous H_2 Compression
- K. Safety, Codes and Standards, Permitting
- D. High As-Installed Cost of Pipelines

Budget

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

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:

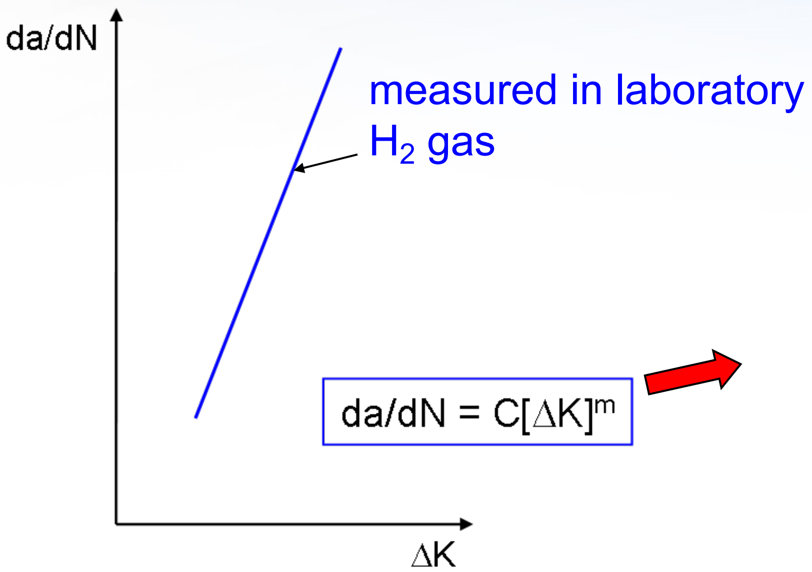
- Demonstrate reliability/integrity of steel hydrogen pipelines for *cyclic pressure* applications
  - Address potential fatigue crack growth aided by hydrogen embrittlement, particularly in welds
- Enable a pipeline reliability/integrity framework that accommodates hydrogen embrittlement
  - Ensure relevance to H_2 pipeline code ASME B31.12
- FY12-13 tasks
  - Test model for effects of O_2 impurities on fatigue crack growth for X52 steel in H_2 gas
  - Measure fatigue crack growth laws in H_2 gas for girth welds from X65 steel

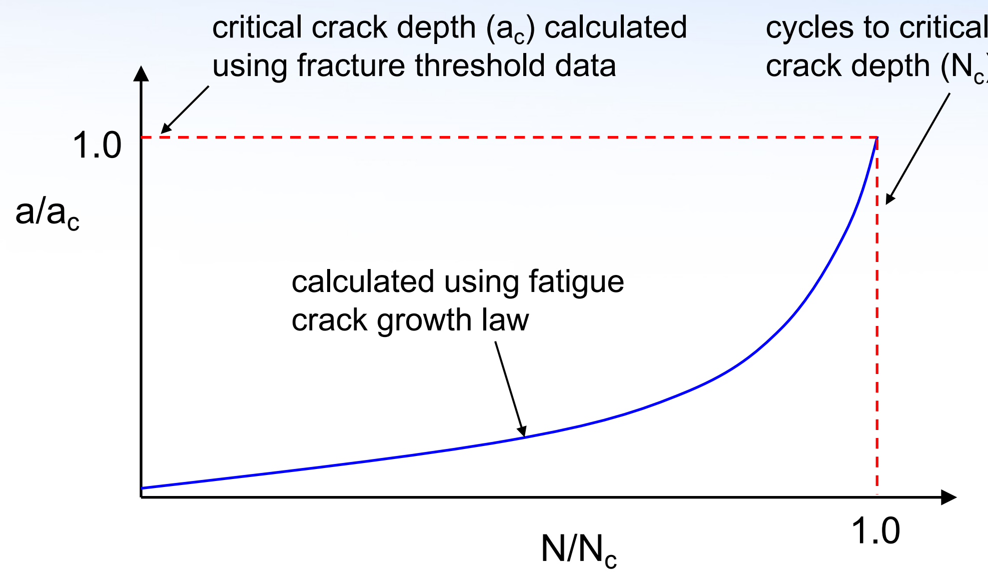
Approach

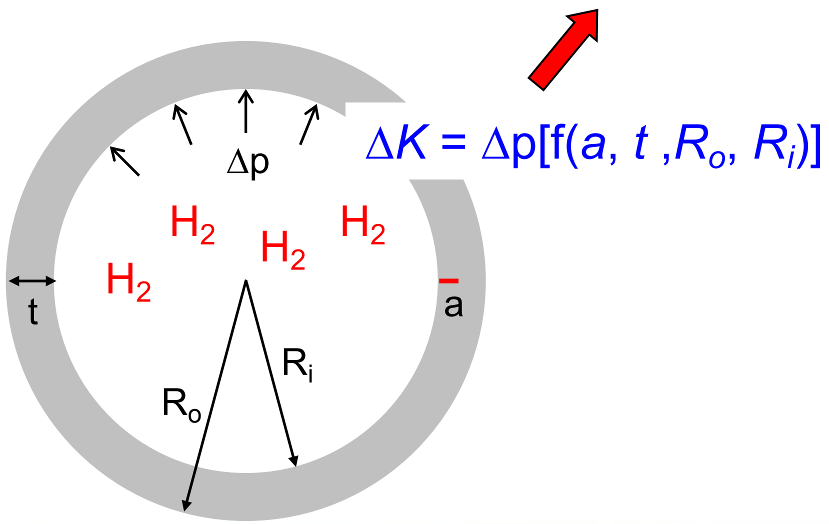
- Apply unique capability for measuring fracture properties of steels in high-pressure H_2 gas
  - Fracture properties serve as inputs into reliability/integrity assessment as specified in ASME B31.12 pipeline code
  - Milestone: Measure the fatigue crack growth (*da/dN vs ΔK*) relationship at constant H_2 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 H_2



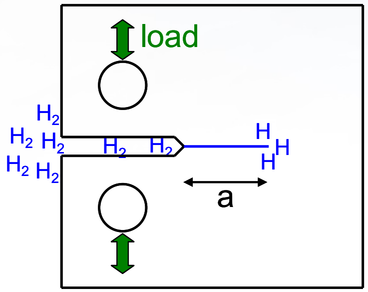


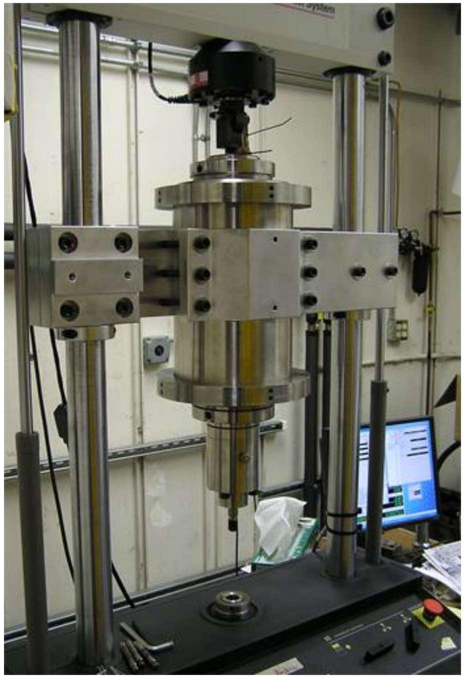


- Two fracture properties in H_2 needed
  - Fatigue crack growth law
  - Fracture threshold
- Reliability/assessment framework accommodates H_2 embrittlement

Approach:

Fracture data in H_2 measured using unique lab capabilities: fatigue crack growth

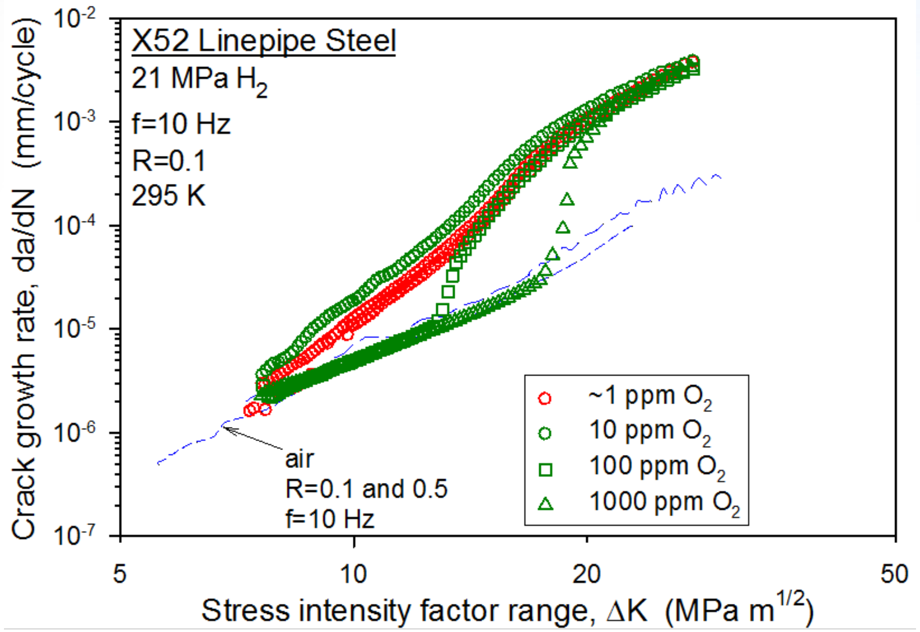


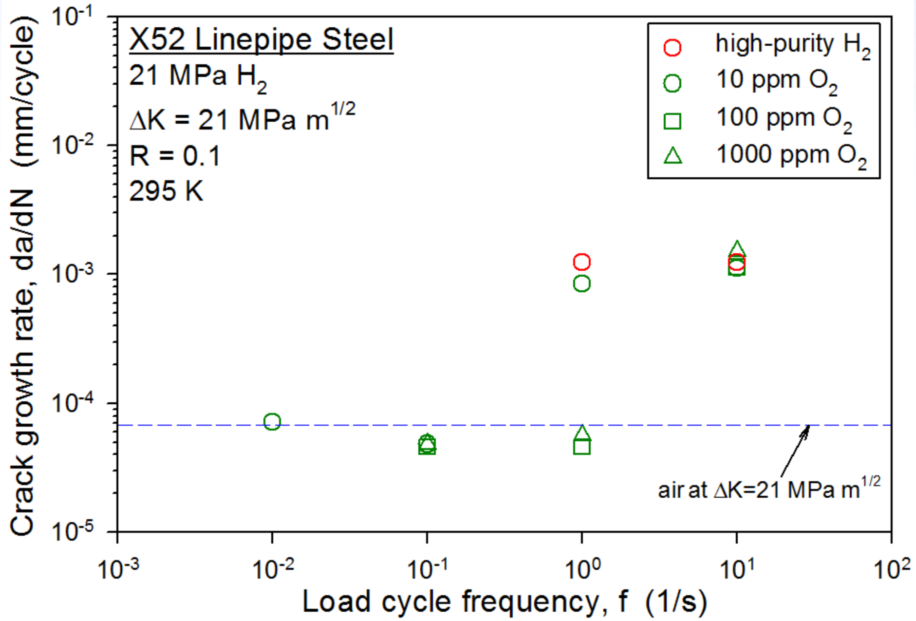


- Material
  - X52 and X65 pipeline steels
- Instrumentation
  - Internal load cell in feedback loop
  - Crack-opening displacement measured internally using LVDT
  - Crack length calculated from compliance
- Mechanical loading
  - Triangular load-cycle waveform
  - Constant load amplitude (increasing ΔK)
- Environment
  - Primary supply gas: 99.9999% H_2
  - Other supply gases: H_2 with 10-1000 ppm O_2
  - Pressure = 3,000 psi (21 MPa)
  - Room temperature

Previous Accomplishment:

Measured onset of H_2-accelerated fatigue cracking as function of *ΔK*, *f*, and O_2 content





- Increasing O_2 concentrations systematically inhibit H_2-accelerated fatigue crack growth
  - Onset of H_2-accelerated fatigue crack growth displaced to higher *ΔK* or *f*
- O_2-affected fatigue crack growth laws lead to enhanced reliability/integrity for steel H_2 pipelines

Accomplishment:

SNL-I²CNER finalized model for predicting effect of O_2 on H_2-accelerated cracking

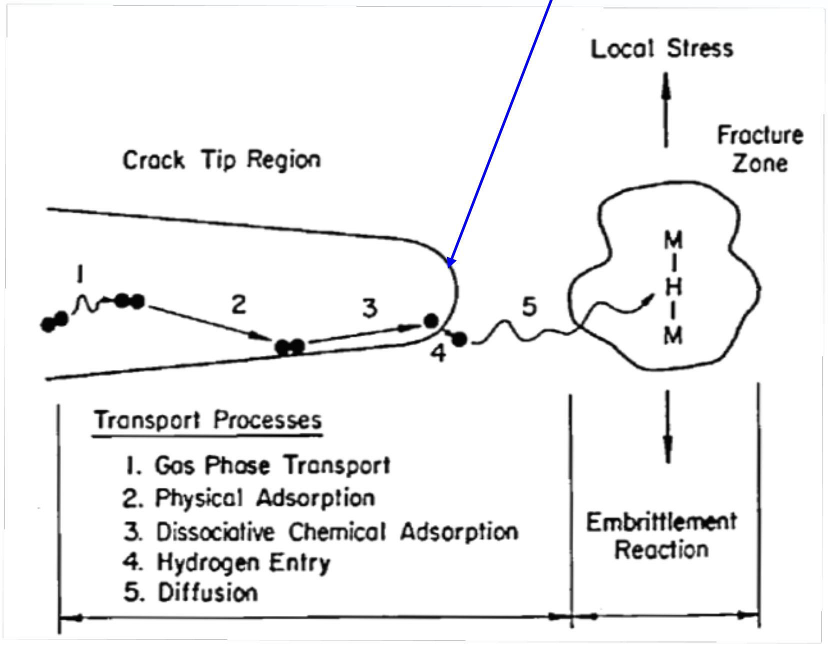
- Oxygen adsorption on crack-tip surface inhibits hydrogen uptake
- Extent of oxygen adsorption depends on crack-tip area, proportional to "mechanical" crack growth rate, *da/dN*
- Assume hydrogen uptake depends on quantity of adsorbed oxygen

$$\frac{d[H]}{dN} \propto \frac{1}{z}$$

z = layers of adsorbed oxygen

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

crack-tip area ~ *da/dN*



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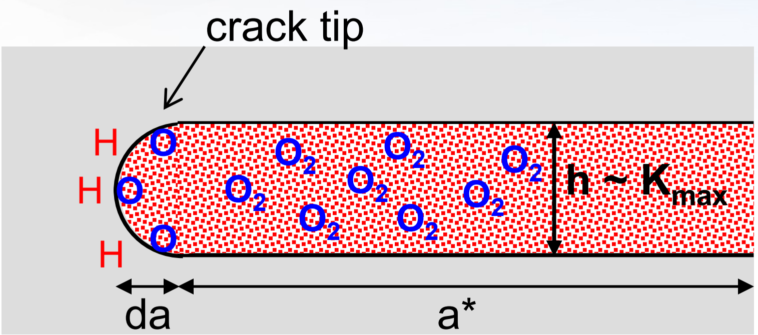
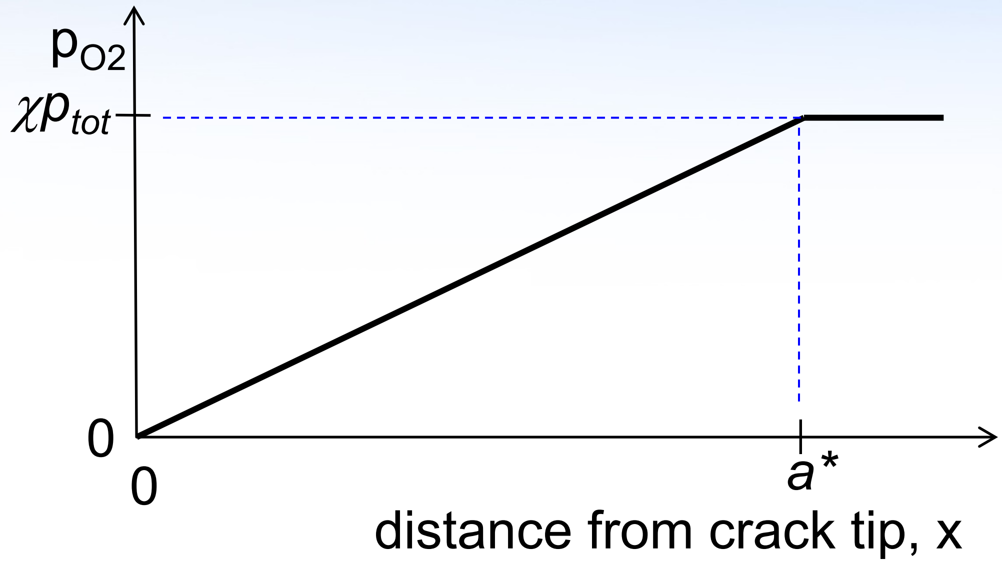
Accomplishment:

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_{O2} profile
  - p_{O2} = 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

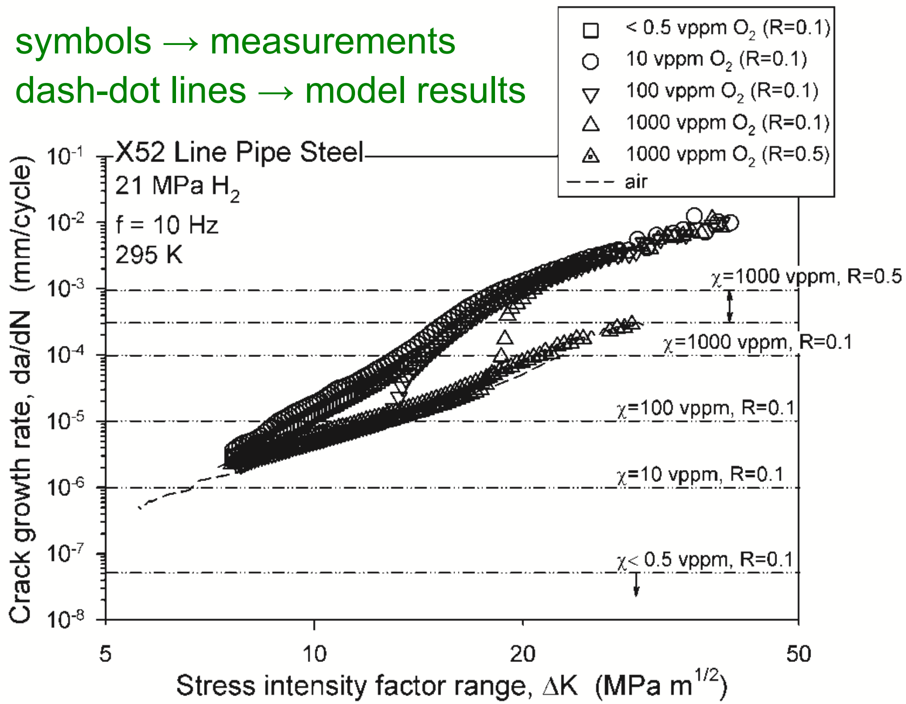
Accomplishment:

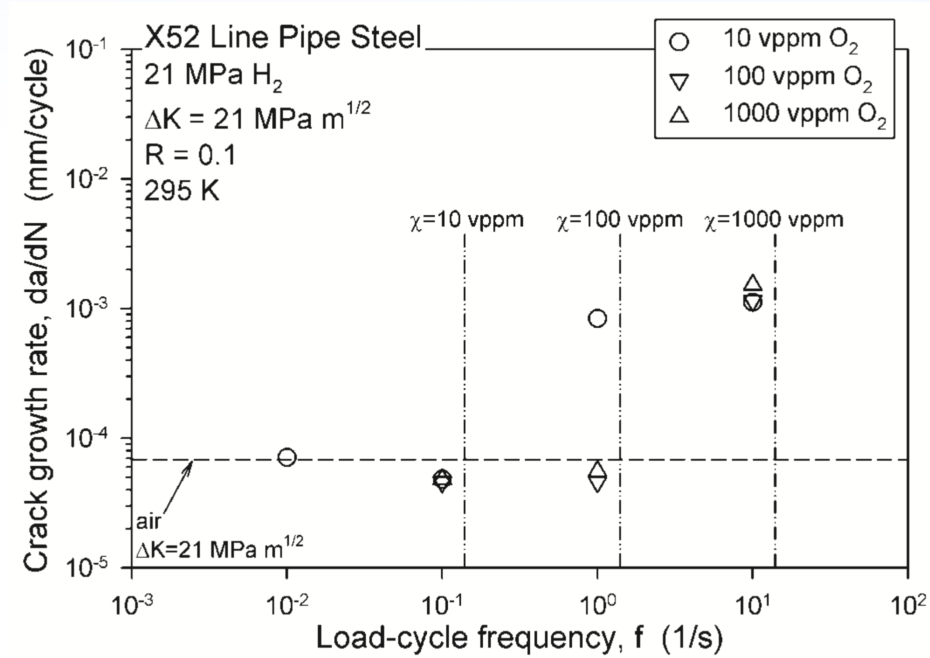
Model employed to predict critical *da/dN* and *f* levels for H_2-accelerated crack growth

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

symbols → measurements

dash-dot lines → model results





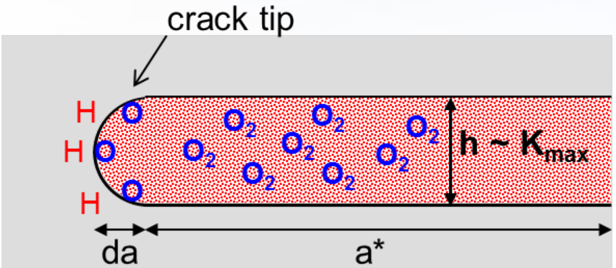
$$\left.\frac{da}{dN}\right|_{crit} = \frac{0.3\chi D p_{tot}(1-\nu^2)}{f\pi z_{crit}\theta_O R_g T E \sigma_0}\left(\frac{\Delta K}{\sqrt{a^*}(1-R)}\right)^2$$

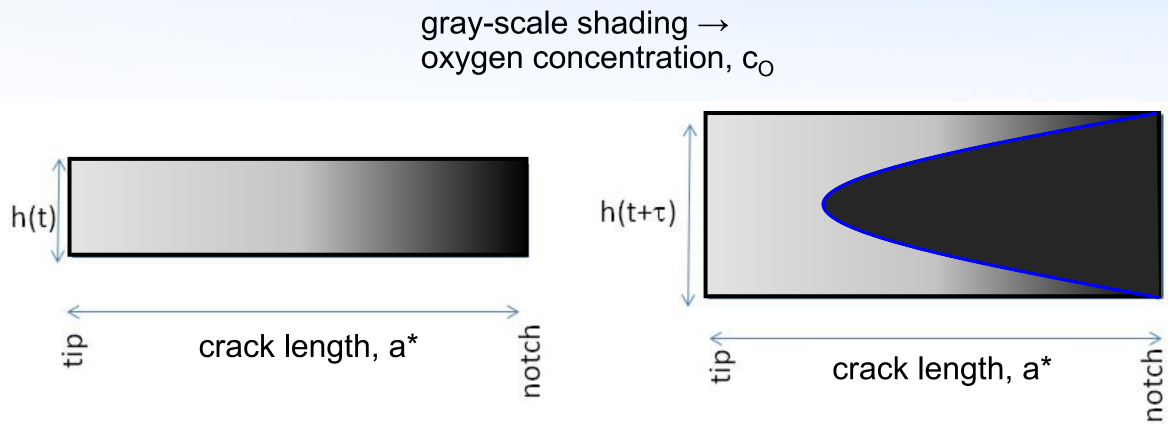
$$f_{crit} = \frac{0.3\chi D p_{tot}(1-\nu^2)}{(da/dN)\pi z_{crit}\theta_O R_g T E \sigma_0}\left(\frac{\Delta K}{\sqrt{a^*}(1-R)}\right)^2$$

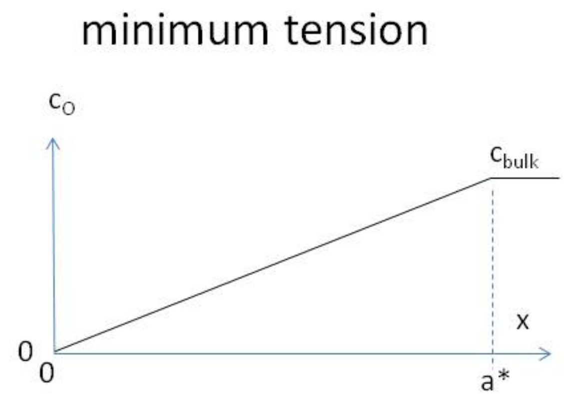
- Agreement between model and experiment validates physics and demonstrates predictive capability

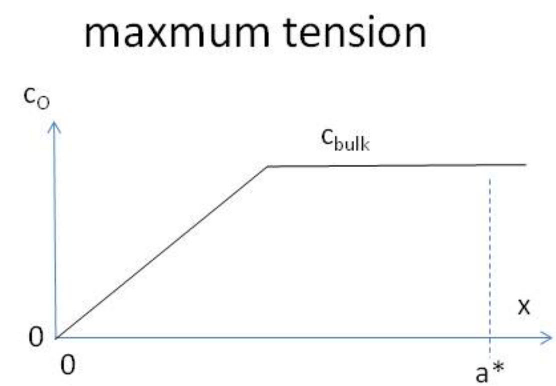
Accomplishment:

More advanced model accounts for varying O_2 profile in “breathing” crack









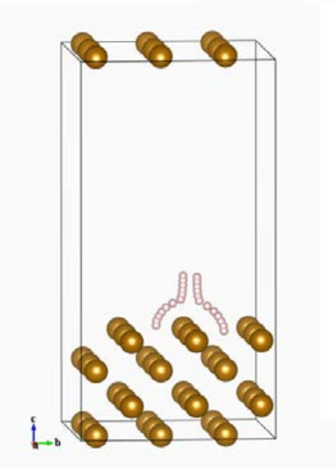
$$z = \frac{0.3\chi D p_{tot}(1-\nu^2)}{(da/dN) f \pi \theta_O R_g T E \sigma_0 a^*}\bar{h}$$

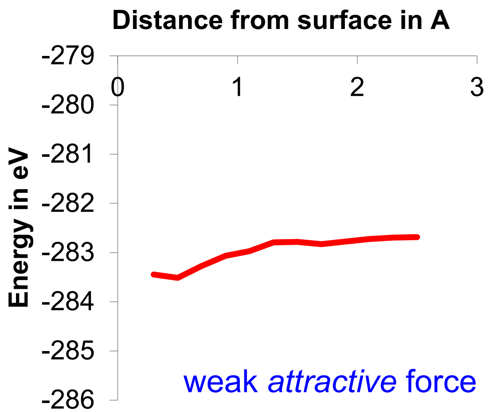
- Model based on “breathing” crack retains dependence on O_2 concentration (χ) and frequency (*f*)

Accomplishment:

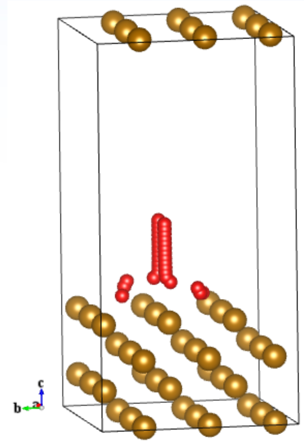
DFT calculations provide mechanistic insight into role of O_2 in inhibiting H_2 embrittlement

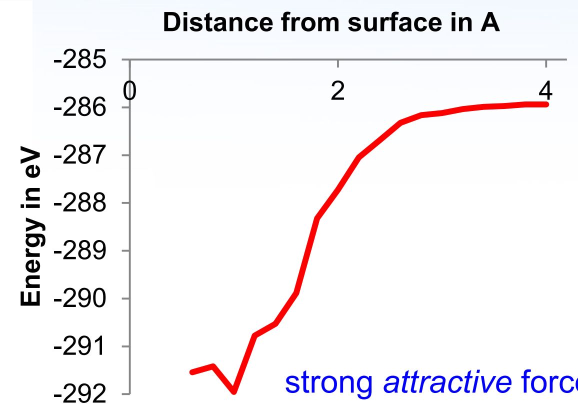
Trajectory of H_2 dissociation on Fe(100)





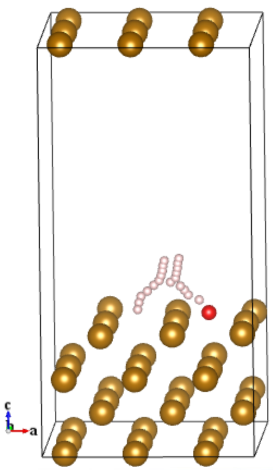
Trajectory of O_2 dissociation on Fe(100)

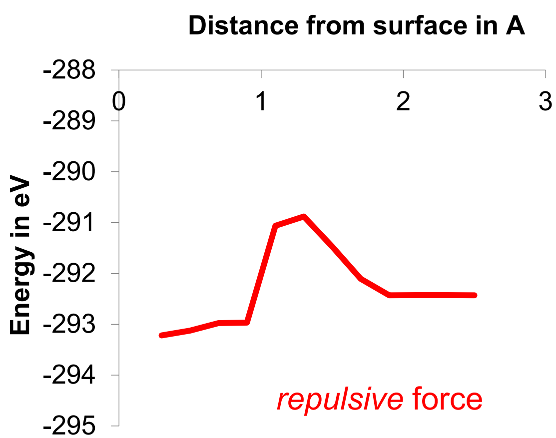




Attractive force: $$F = -\frac{dE}{dR}$$

Trajectory of H_2 dissociation on oxygen-rich Fe(100)

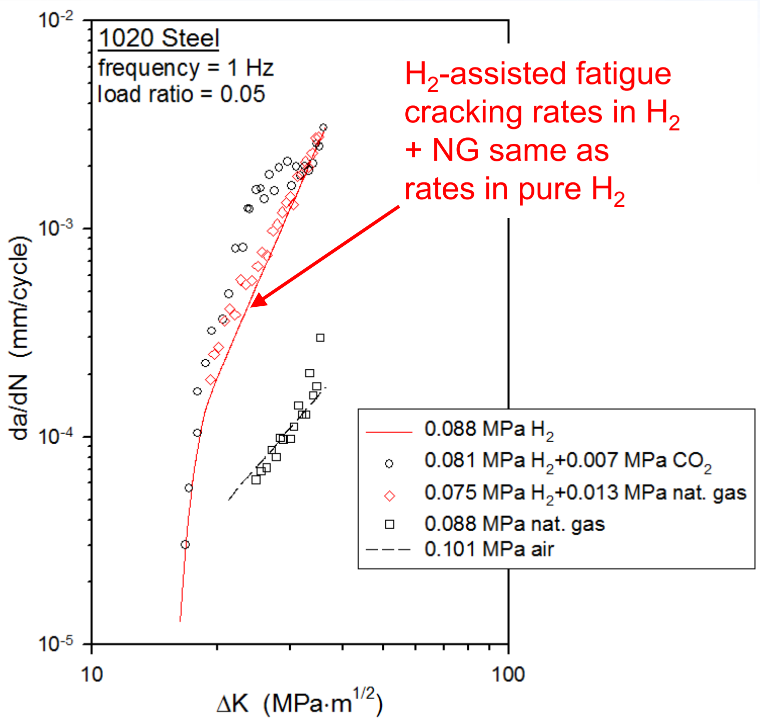


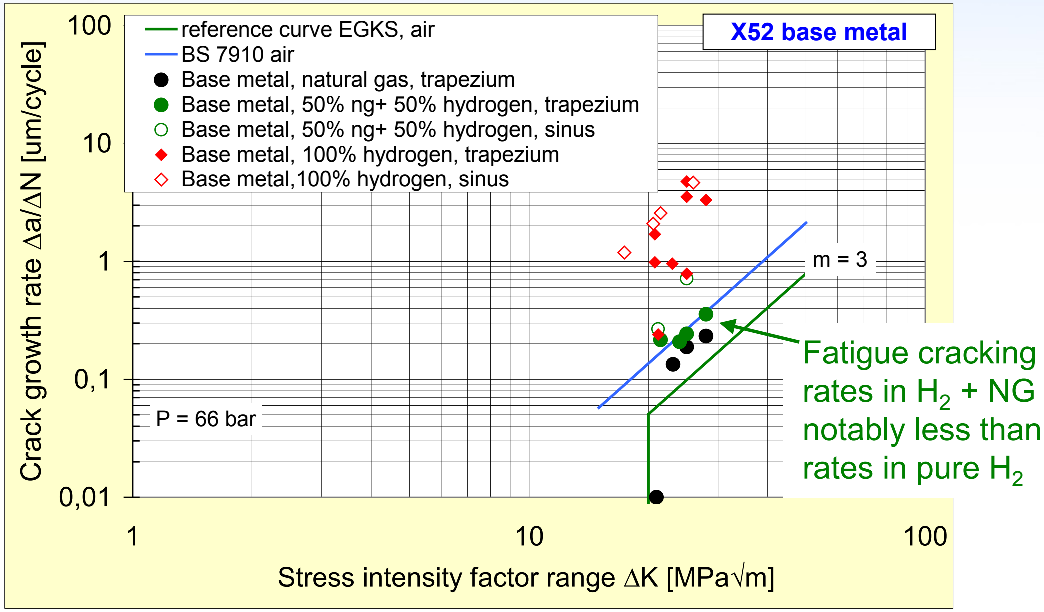


- Density functional theory (DFT) results from collaborator (I²CNER) reveal that surface-adsorbed oxygen impedes H_2 dissociation on iron (steel)
- DFT is theoretical tool for identifying other inhibitors

Model impact: interpret laboratory results or component behavior, e.g., mixed NG + H_2

Tech. Ref. Hydrogen Compatibility Materials, Sandia, 2008





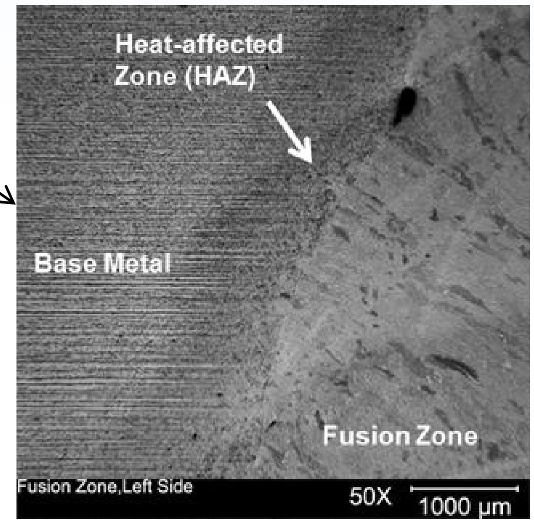
I. Alliat, NATURALHY EC project, 2007

- Possible impurities in natural gas such as O_2 and CO may explain varying results for crack growth rates in mixed NG + H_2
- Model could identify and quantify influence of impurities on experimental data or steel pipeline performance

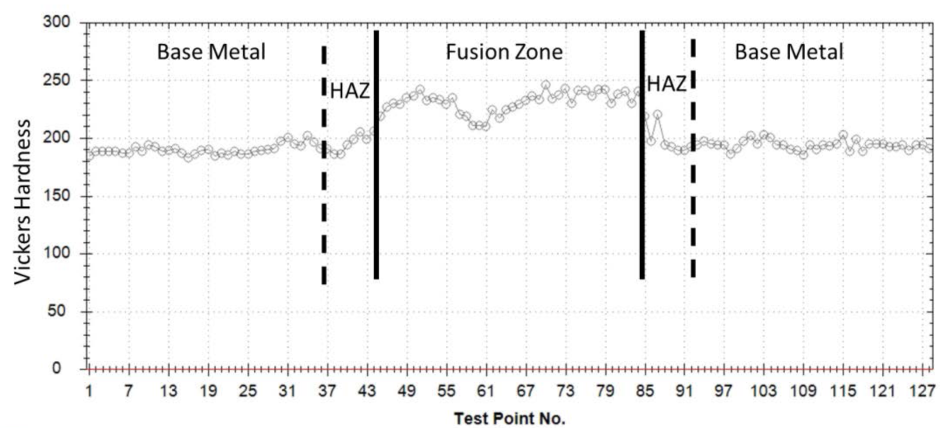
Fatigue crack growth measurements must emphasize welds: potential vulnerability

- Measured fatigue crack growth rates for technologically relevant girth weld in H_2 gas

girth weld



- API 5L X65 steel
  - Minimum yield strength: 65 ksi (428 MPa)



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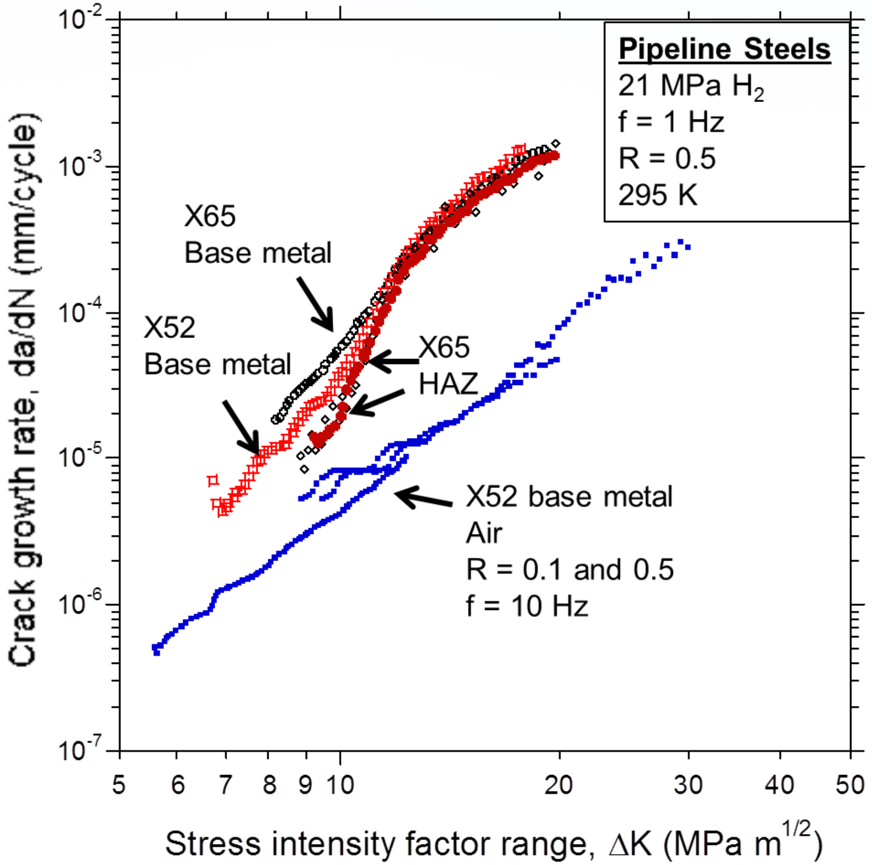
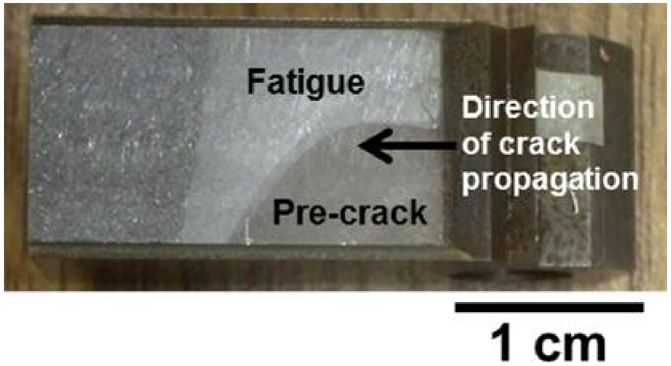
Accomplishment:

Completed initial measurements on base metal, fusion zone, and heat affected zone



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



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

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 (I^2CNER), Fukuoka, Japan (e.g., modeling)

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Proposed Future Work

Remainder of FY13

- Complete multiple fatigue crack growth measurements for girth weld in H_2 gas to demonstrate reliable data

FY14

- Measure fatigue crack growth laws in H_2 for seam weld from technologically relevant pipeline steel
- Conduct reliability/integrity analysis of H_2 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 H_2 pipelines
  - Hydrogen embrittlement accommodated by measuring fracture properties in H_2 following ASME B31.12 design standard
- Analytical model quantifies inhibiting effect of O_2 on H_2-accelerated fatigue crack growth, including variables such as load-cycle frequency and O_2 concentration
  - Model may provide insight into effects of gas impurities on H_2-accelerated fatigue crack growth for mixed natural gas + H_2
- Conducted initial measurements of fatigue crack growth laws for pipeline steel girth weld in H_2 gas
  - Testing challenges (e.g., non-uniform crack fronts) require multiple measurements to confirm data reliability

Technical Back-Up Slides

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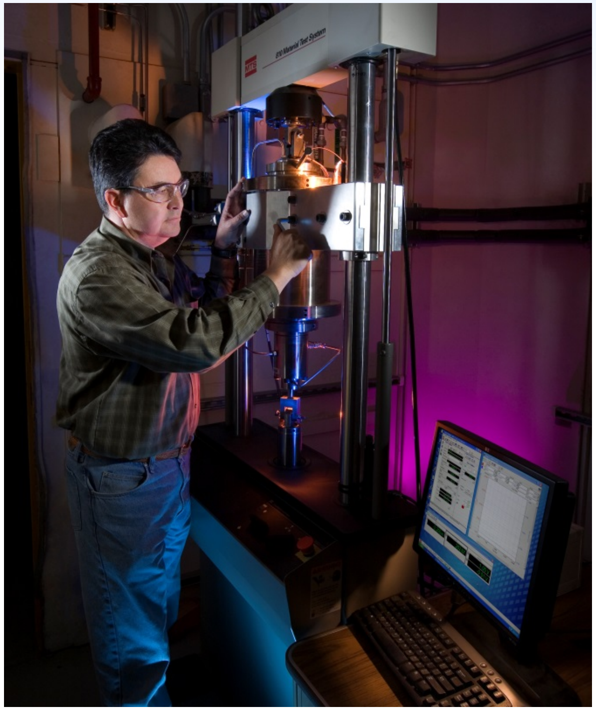
Accomplishment (in coordination with Safety, Codes and Standards):

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