A combined Materials Science/Mechanics Approach to the Study of Hydrogen Embrittlement of Pipeline Steels

P. Sofronis, I. M. Robertson, D. D. Johnson

University of Illinois at Urbana-Champaign

2008 DOE Hydrogen Program Review

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Project ID #PD17_sofronis

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- **Project start date:5/1/05**
- **Project end date: 4/30/10**
- **Percent complete: 50%**

Budget

- **Total project funding: 300k/yr**
  - **DOE share: 75%**
  - **Contractor share: 25%**
- **Funding received**
  - **FY2005: $180 K**
  - **FY2006: 80 K**
  - **FY2007: $473 K**

Barriers

- **High Capital Cost and Hydrogen Embrittlement of Pipelines**
  - Determine suitable steels or other materials of construction to provide safe and reliable transport in pipelines while reducing the capital costs
  - Explore whether existing natural gas pipelines can be used to transport mixtures of natural gas and hydrogen without hydrogen embrittlement

Partners

- **Industrial (SECAT)**
  - **DGS Metallurgical Solutions, Inc.**
  - **Air Liquide**
  - **Air Products**
- **National Laboratories**
  - **Oak Ridge National Laboratory**
  - **Sandia National Laboratories**
- **Codes and Standards**
  - **ASME**

Objectives

- **To come up with a <u>mechanistic understanding</u> of hydrogen embrittlement in pipeline steels in order to devise <u>fracture criteria</u> for safe and reliable pipeline operation under hydrogen pressures of at least 15MPa and loading conditions both static and cyclic (due to in-line compressors)**
  - Study existing natural gas network of pipeline steels (Kinder Morgan)or hydrogen pipelines (Air-Liquide, Air Products)
  - Propose new steel microstructures (SECAT)

- **It is emphasized that such fracture criteria are lacking and there are no codes and standards for reliable and safe operation in the presence of hydrogen**
  - There is no engineering of pipelines based on the fundamental science underlying the hydrogen effect on materials
  - Current design guidelines for pipelines only tacitly address subcritical cracking by applying arbitrary, conservative safety factors on the applied stress

- **Illinois mechanism-based fundamental science approach**
  - Will provide guidelines for the testing and design of pipelines for safe and reliable operation
  - Avoid unnecessary repairs and shut-downs by minimizing unnecessary levels of conservatism in the operation of pipelines
  - Reduce capital cost by avoiding conservatism

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Project Milestones

- **Validated permeation measurement system**
  - Completed. Collaboration with Oak Ridge National Laboratory
- **Microstructural characterization**
  - Completed. Materials from pipelines in service from Air-Liquide, Air-Products, and new steel microstructures from Oregon Steel Mills (SECAT)
- **Development of finite element code for transient stress-driven hydrogen transport analysis coupled with large-strain elastoplastic deformation**
  - Completed. Code has been tested and validated against analytical solutions and numerical results at Los Alamos National Laboratory
  - Time to steady in fracture process zone ahead of a crack tip is ~minutes
- **Simulation and identification of deformation and constraint characteristics at an axial crack on the ID surface**
  - Completed. Laboratory specimen type (hydrostatic constraint guidelines) has been identified to investigate fracture conditions in a real-life pipeline
- **Ab-initio calculations for decohesion energy calculations**
  - Validation competed. Results for grain boundaries in BCC iron have been obtained

Go/No-Go Decisions and Milestones for 2008

- **Go/No-Go Decision: Thermodynamic theory of Mishin et al. (*Acta Materialia*, 50, 3609-3622, 2002) for hydrogen- induced interfacial decohesion has been adopted.**
  - Applies to any scenarios of interfacial separation including fast and slow
  - Parameter calibration through ab-initio calculations

- **Milestones for 2008**
  - Complete measurements of diffusivity, permeability, and solubility
  - Integrate modeling
    - microstructural information (e.g. trapping characteristics)
    - ab-initio results/thermodynamics of hydrogen-induced decohesion
    - finite element calculations at the micro/macro scale
  - Integrate modeling with experiment to determine the resistance of material against crack initiation
    - Predict fracture toughness based on the mechanism of embrittlement

Approach

- **Permeation experiments to identify diffusion characteristics (ORNL)**

- **Experiments (subcritical crack growth) to determine (Sandia National Laboratories)**
  - Hydrogen effect on crack initiation
  - What constitutes "safe hydrogen concentrations" at Threshold Stress Intensities
  - Stability of crack propagation to assess catastrophic failure scenarios

- **Identification of deformation mechanisms and potential fracture initiation sites under both *static* and *cyclic* loading conditions in the presence of hydrogen solutes**
  - SEM studies of fracture surfaces in the presence of hydrogen and TEM analysis of the material microstructure
  - Combined effort between Illinois and Sandia

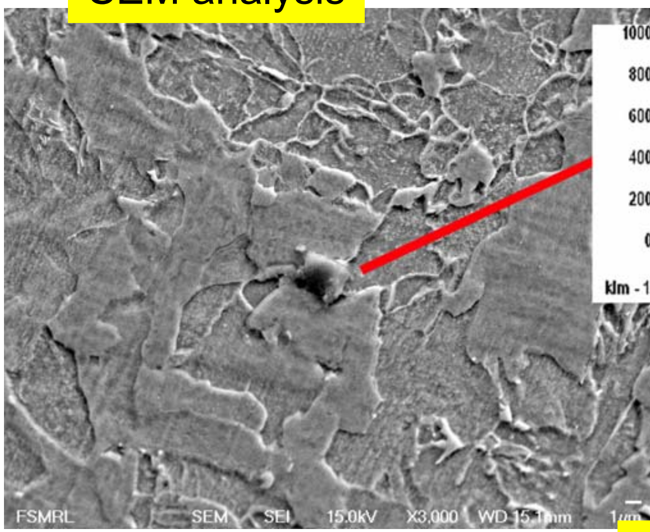
- **Thermodynamics and first principles calculations for the determination of the cohesive properties of particle/matrix and grain boundary interfaces as affected by the presence of hydrogen solutes**
  - Judicious passing of information from ab-initio calculations to thermodynamic model of decohesion and then to continuum finite element simulations for the investigation of the hydrogen effect on fracture resistance of materials

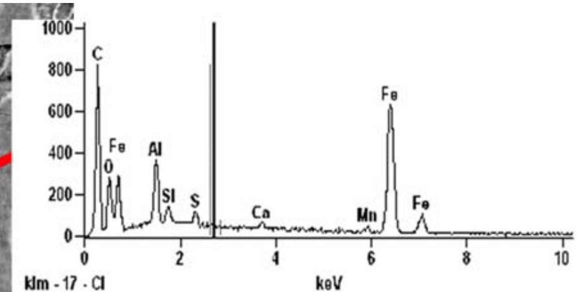
- **Finite element simulations of the coupled problem of material elastoplasticity and transient hydrogen diffusion in the neighborhood of a crack tip accounting for stress-driven diffusion and trapping of hydrogen at microstructural defects.**

Microstructural Characterization

- Completed microstructural analysis of four “promising” pipeline steels provided by Oregon Steel Mills, and microstructures provided by Air-liquide and Air Products
- Needed for hydrogen transport analysis

SEM analysis

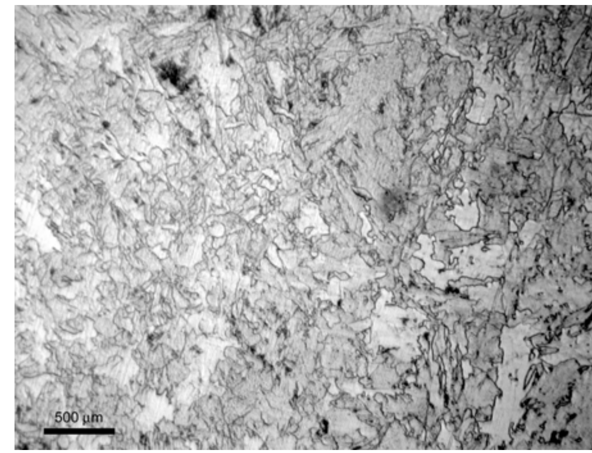




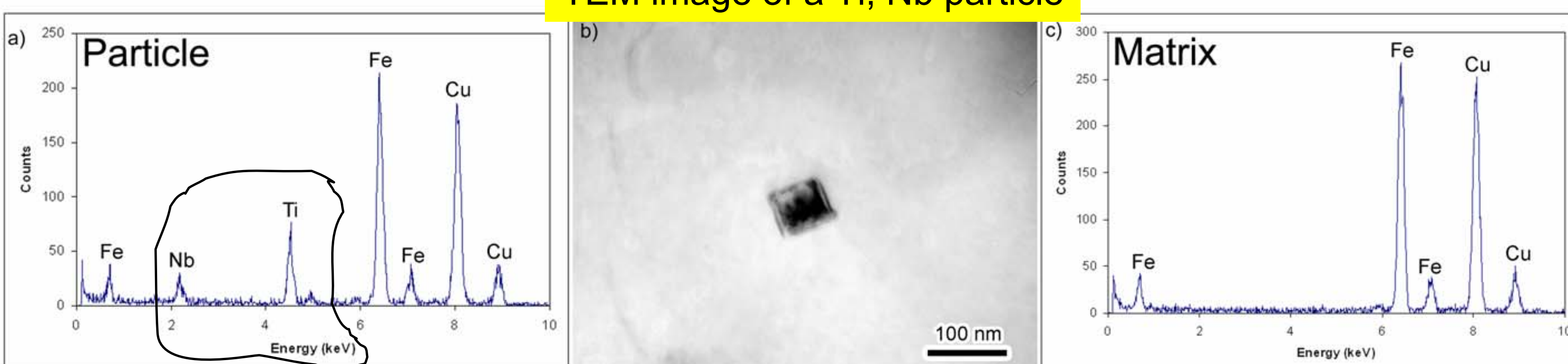
Al rich particle
Most likely sulphide

Optical analysis

Average grain size 35 microns, 3% pearlite



TEM image of a Ti, Nb particle

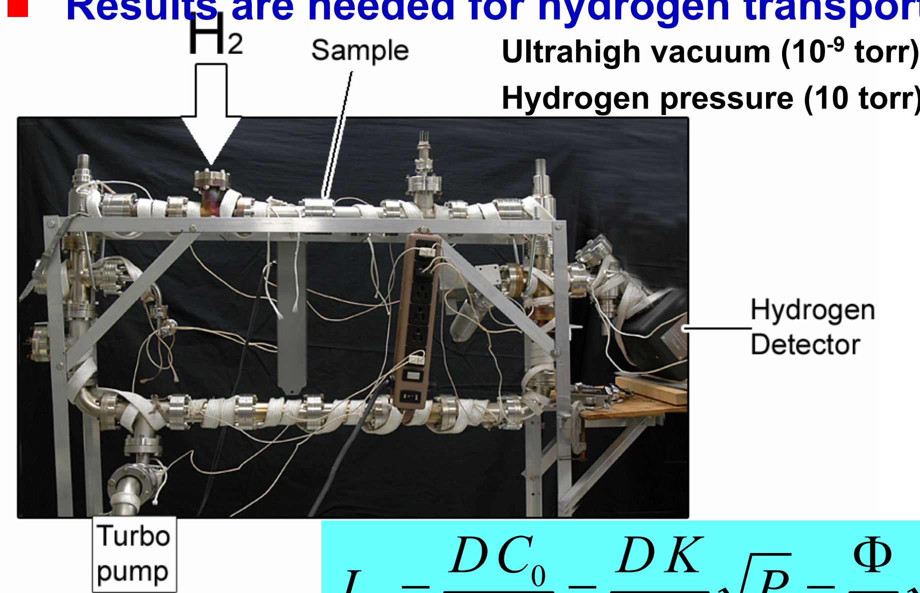


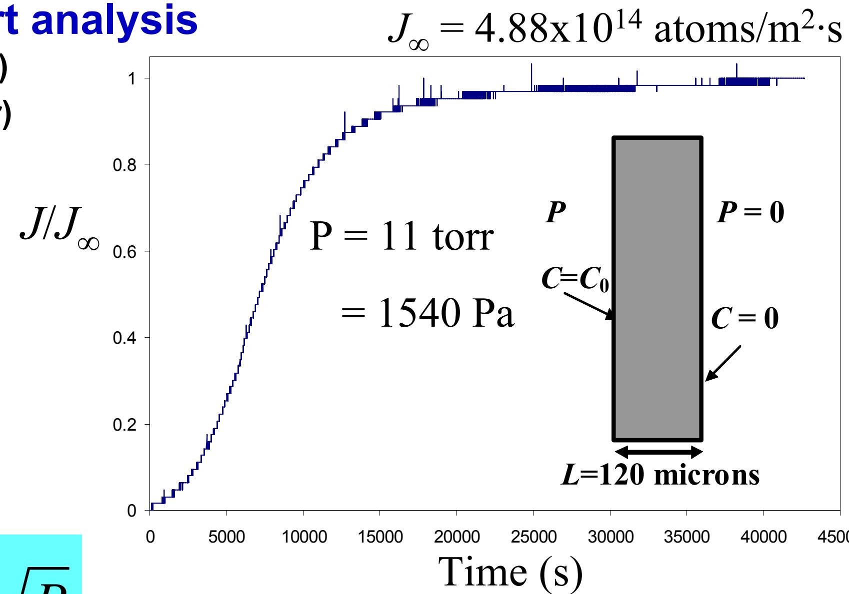
Energy Dispersive Spectroscopy Spectra

window detector: C, N, O not detected

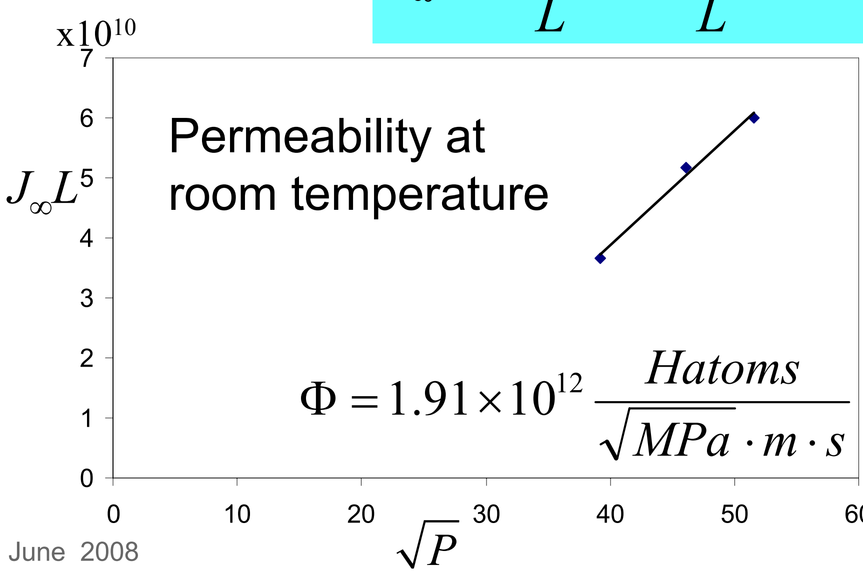
Hydrogen Permeation Measurements

- **Significant progress toward hydrogen permeation measurements. Performance of devise has been validated through measurements at Oak Ridge National Laboratory**
- **Results are needed for hydrogen transport analysis**

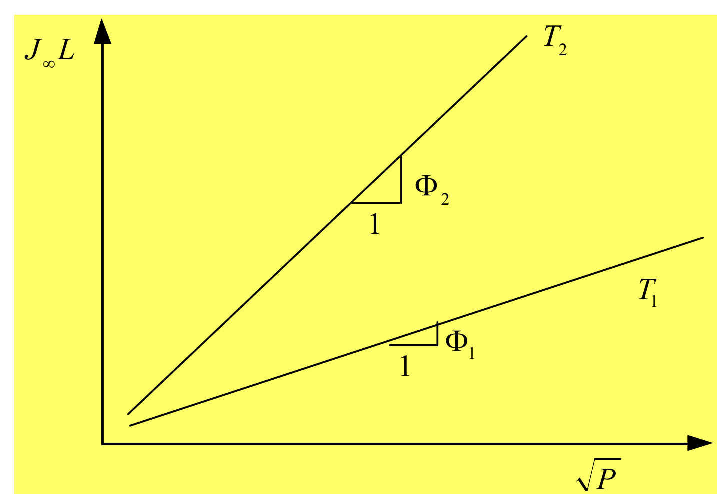




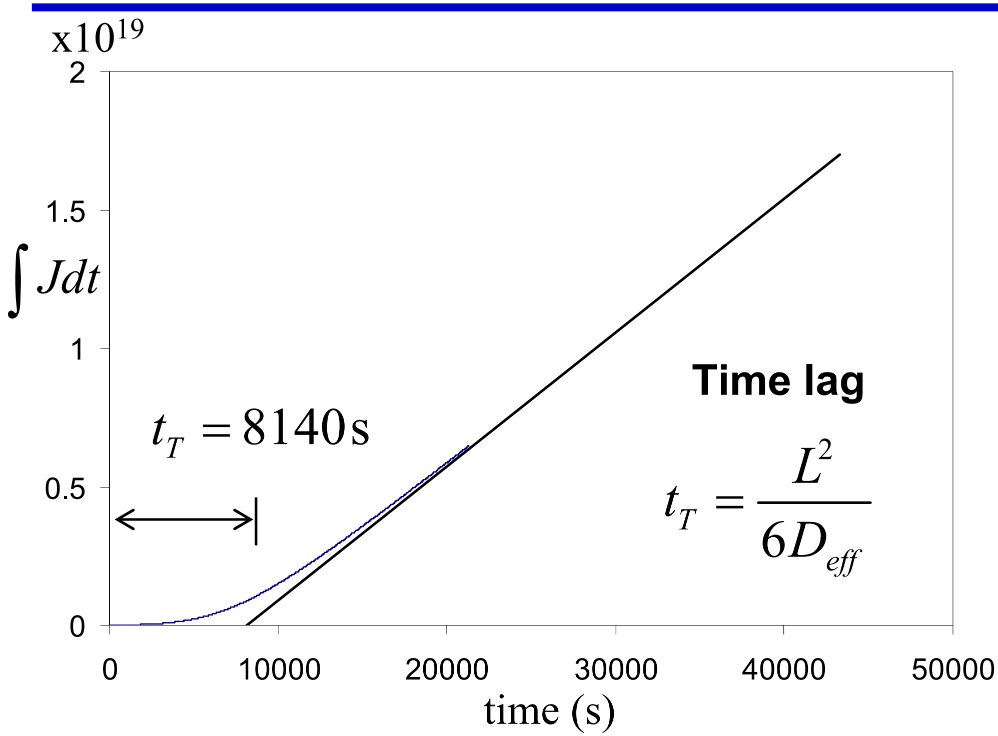
$$J_\infty = \frac{D C_0}{L} = \frac{D K}{L}\sqrt{P} = \frac{\Phi}{L}\sqrt{P}$$



Determine permeability as a function of temperature



Hydrogen Permeation Measurements

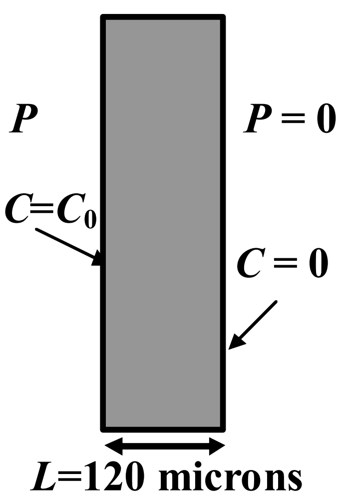


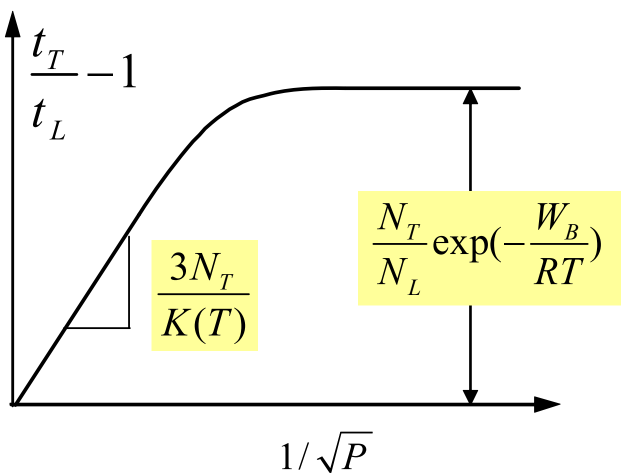
Time lag measurements at high temperature will give the diffusion coefficient *D*

$$t_L = \frac{L^2}{6D}$$

Obtain solubility *K* as a function of temperature

$$\Phi = D\,K$$





Obtain trap characteristics needed for hydrogen transport analysis

Trap density: N_T

Trap binding energy: W_B

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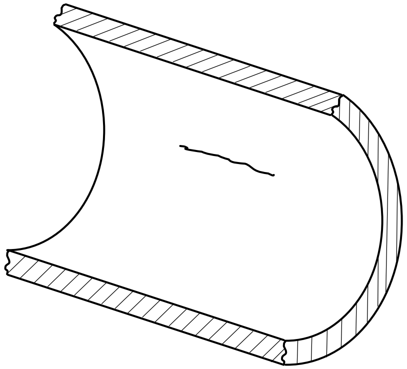
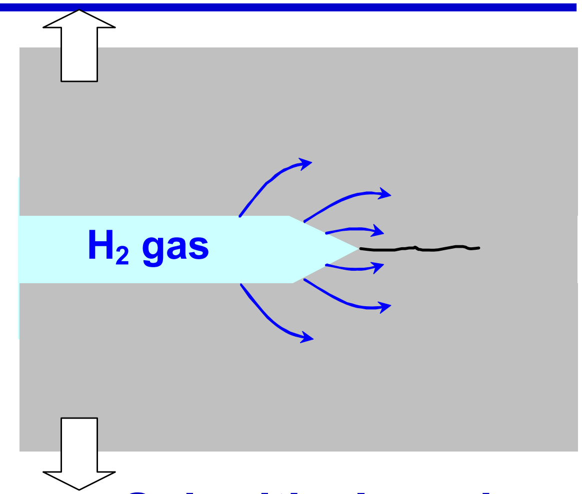
Fracture Mechanics Approach to Design of Pipelines
Actual-Pipeline Solution vs Laboratory-Specimen Solution



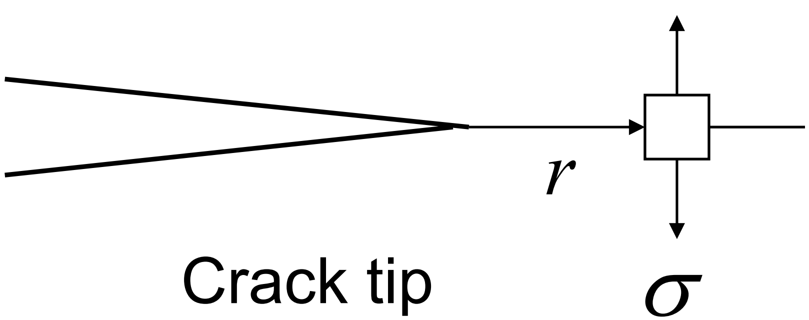
H_2-Pressure of 15MPa

Is there a similarity between the full-field (pipeline) solution and that at laboratory specimens?



Subcritical crack growth experiments carried out at Sandia

If yes, we conjecture that parameters which characterize fracture in the laboratory specimen can be used to characterize fracture in the pipeline



$$\sigma = \frac{K_I}{\sqrt{2\pi r}}$$

If K_I characterizes fracture in the specimen, can it be used to characterize fracture in the pipeline in the presence of hydrogen?

Transferability

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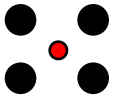
Hydrogen Transport Analysis

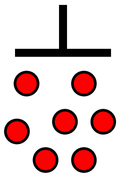
- **Diffusing hydrogen resides at**
  - **Normal Interstitial Lattice Sites (NILS)**

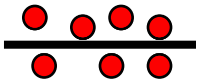


C_L

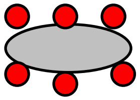
  - **Trapping Sites** C_T
    - **Microstructural heterogeneities such as dislocations, grain boundaries, inclusions, voids, interfaces, impurity atom clusters**

dislocations



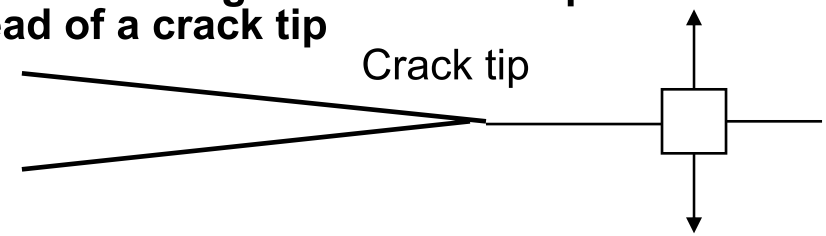


Grain boundaries



inclusions

- **Diffusing hydrogen interacts with stresses and strains**
  - **Hydrogen dilates the lattice and thus interacts with hydrostatic stress**
    - **Moves from regions under compression toward regions under tension, e.g ahead of a crack tip**



$$\sigma > 0$$

  - **Hydrogen enhances dislocation mobility, thus it facilitates plastic flow**

- **As hydrogen diffuses stresses and strains change. At the same time local stresses and strains affect the diffusion paths. So the problem is coupled**

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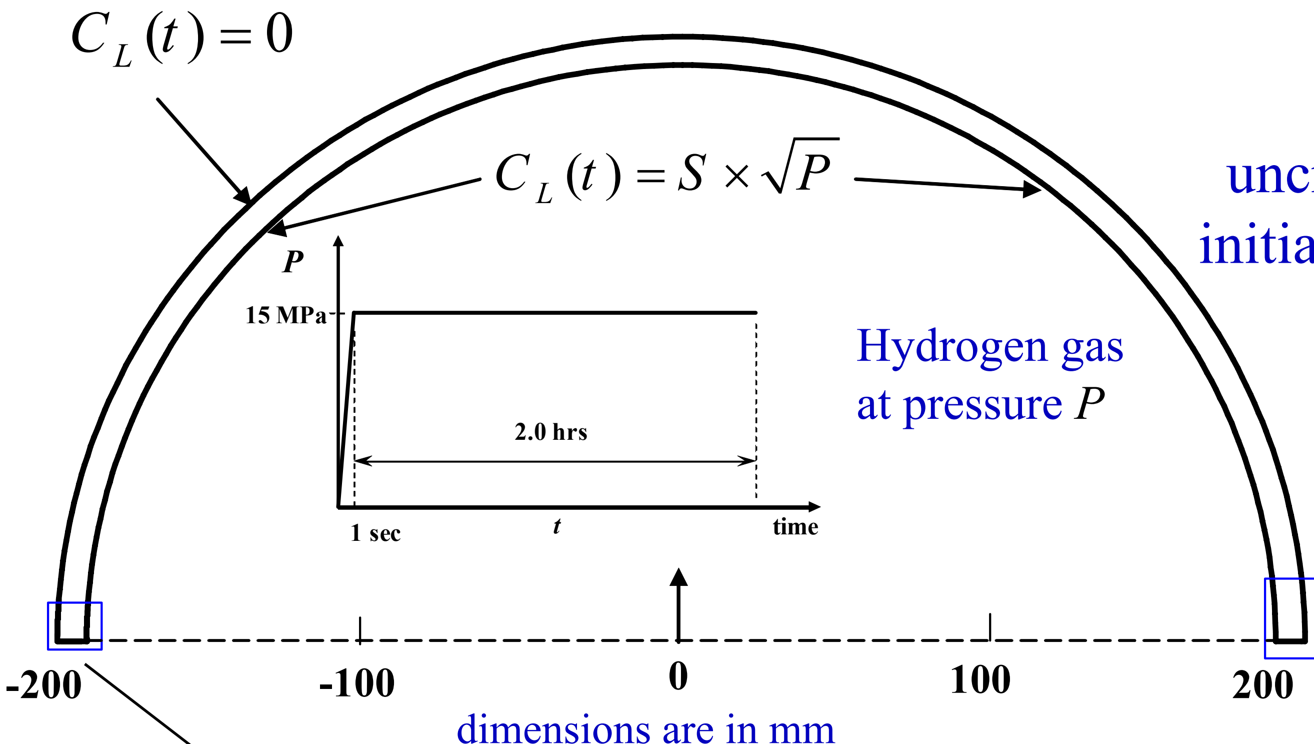
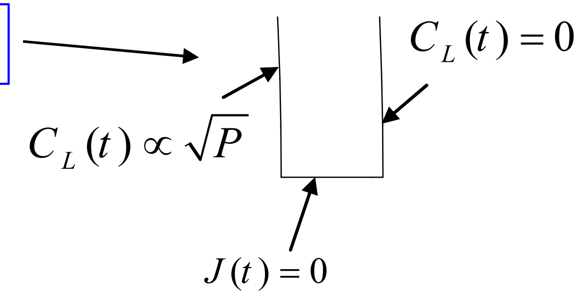
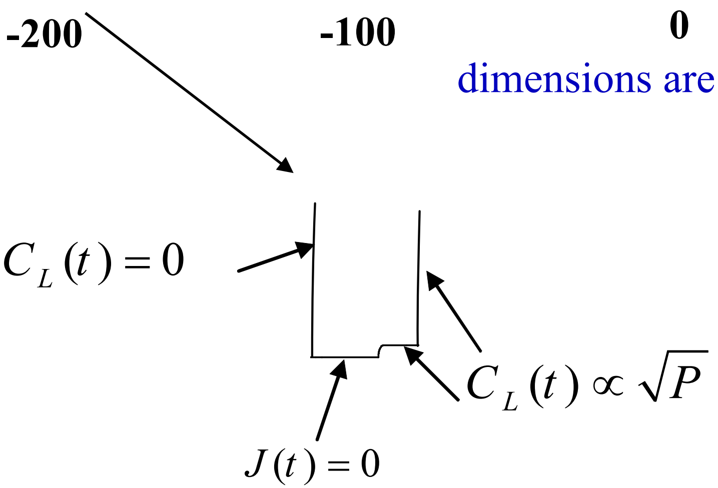
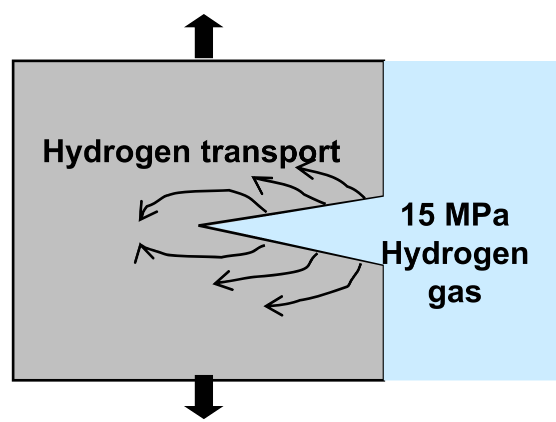
Cracked Pipeline: Problem Statement

Outer Radius: 8”
Thickness: 0.375”
uncracked ligament: 0.3”
initial crack opening: 1.5 μm

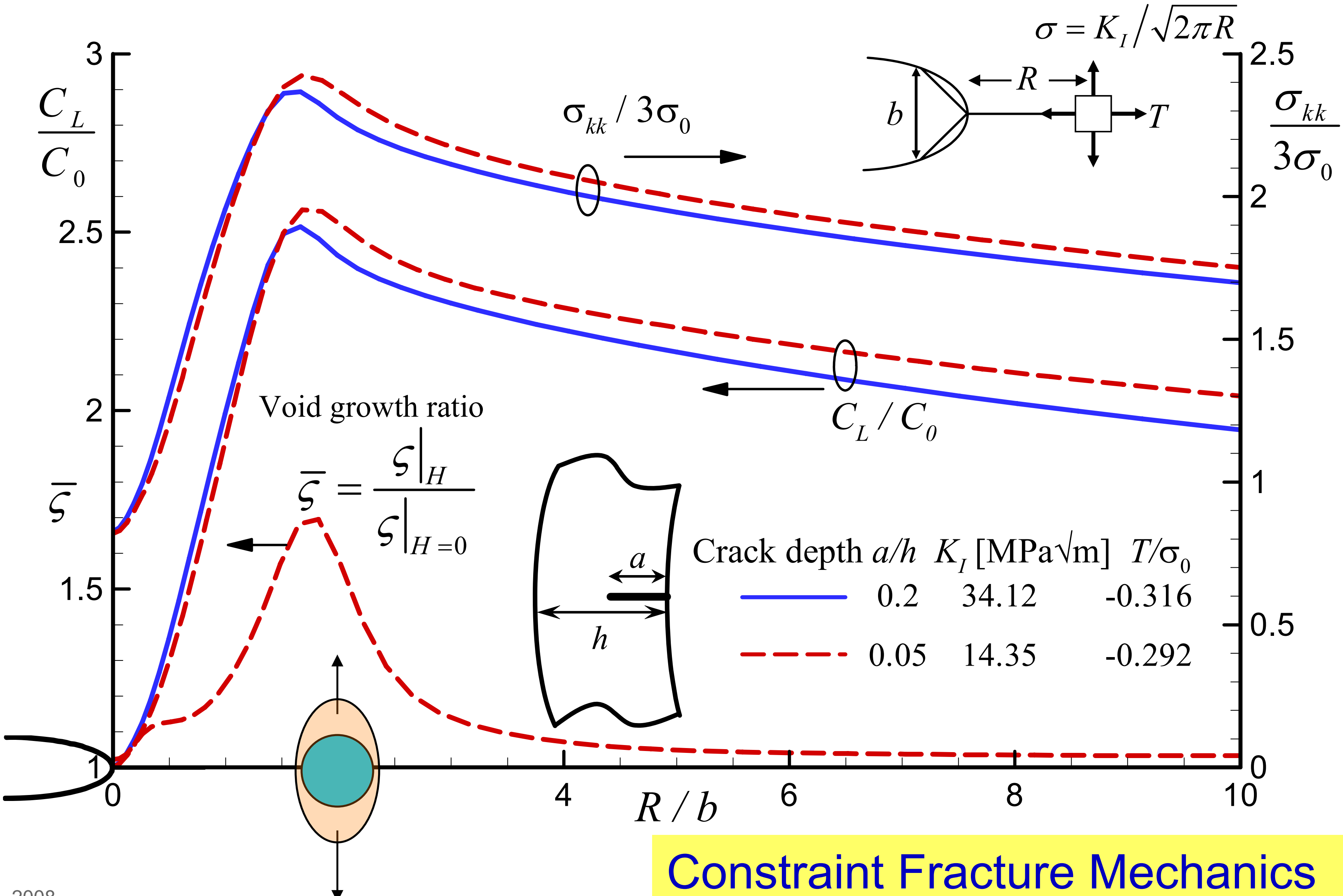








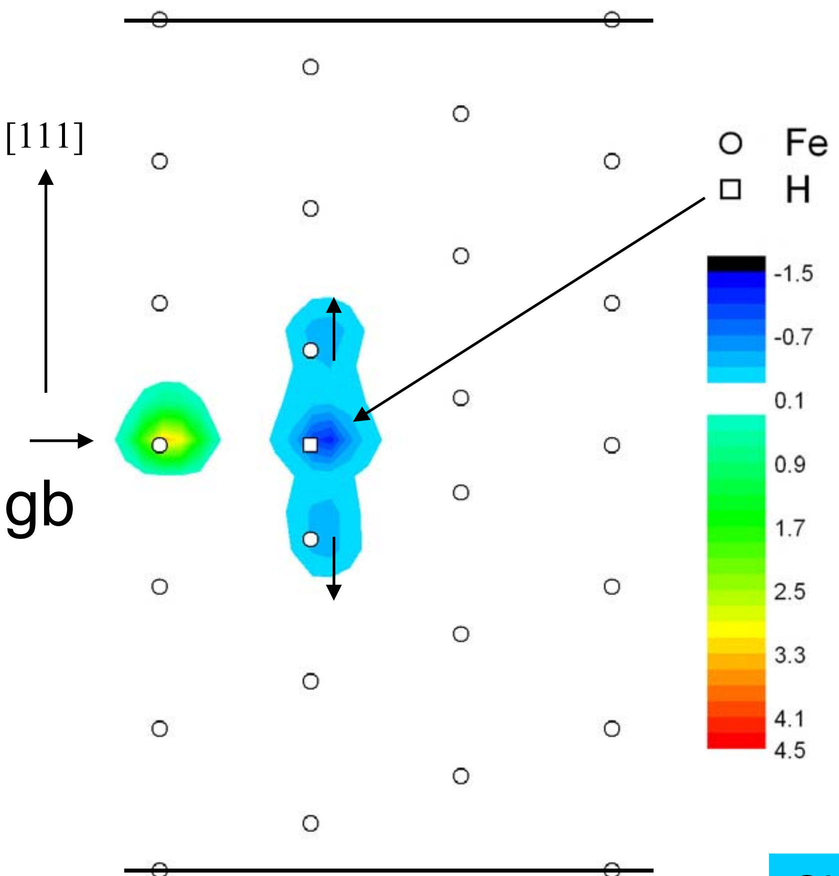
Crack-Tip Fields Scale with K_I and T-stress Hydrogen Accelerates Void Growth



Constraint Fracture Mechanics

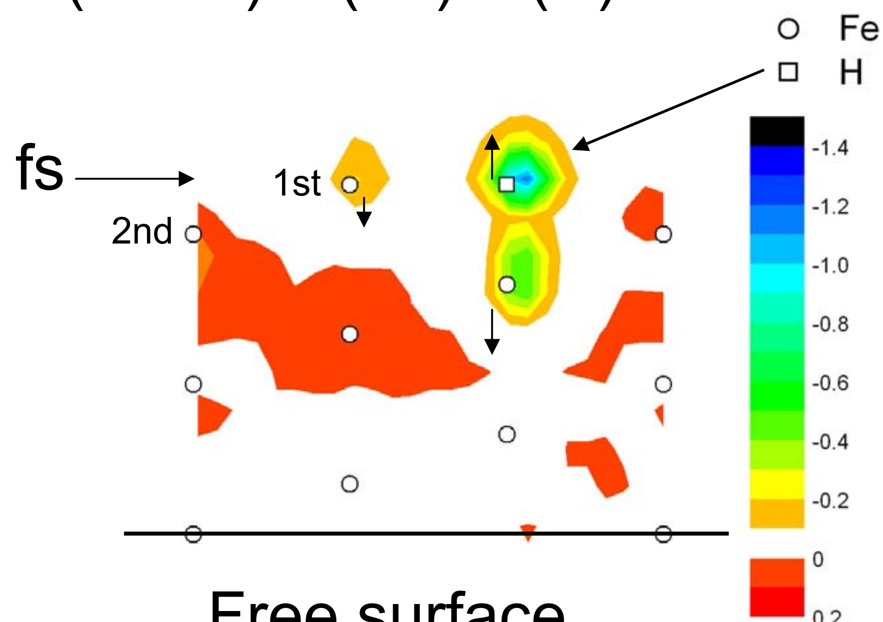
Density Functional Theory Calculations
Hydrogen Changes the Electron Density

Charge density difference= (Fe+H) − (Fe) − (H)



$\Sigma 3[1\bar{1}0](111)$

Grain Boundary

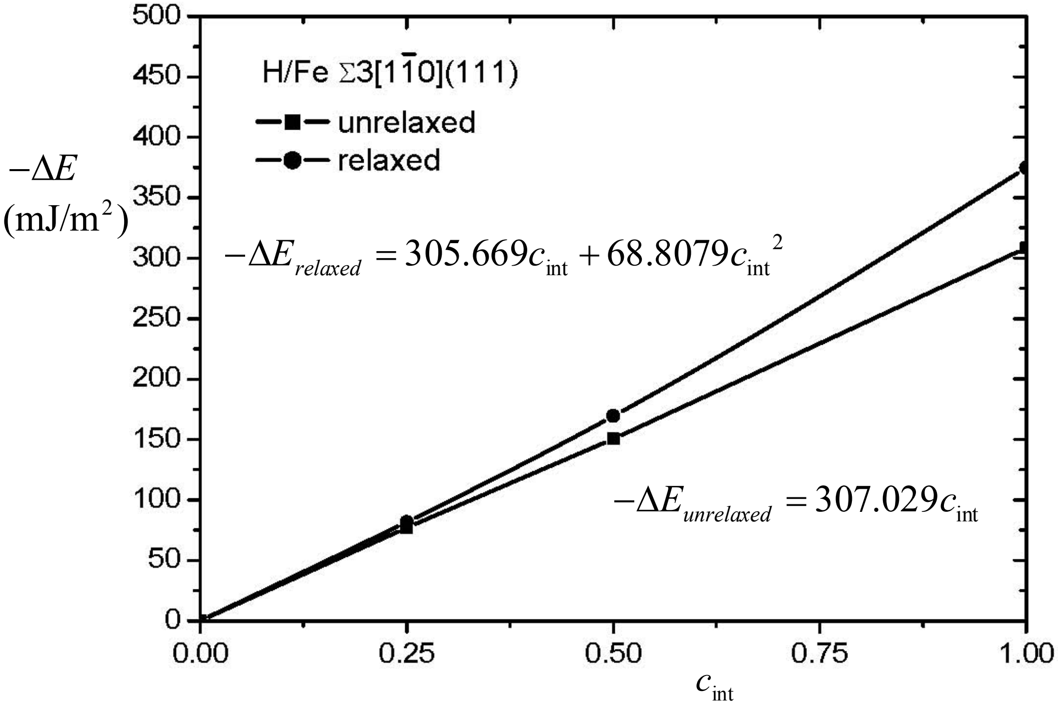


Free surface

$$\Delta E = \left(E_s - 2\gamma_s\right) - \left(E_{gb} - \gamma_{gb}\right)$$
$$= \left(2\gamma_{\mathrm{int}}\right)_{c_{\mathrm{int}}} - \left(2\gamma_{\mathrm{int}}\right)_{c_{\mathrm{int}}=0}$$

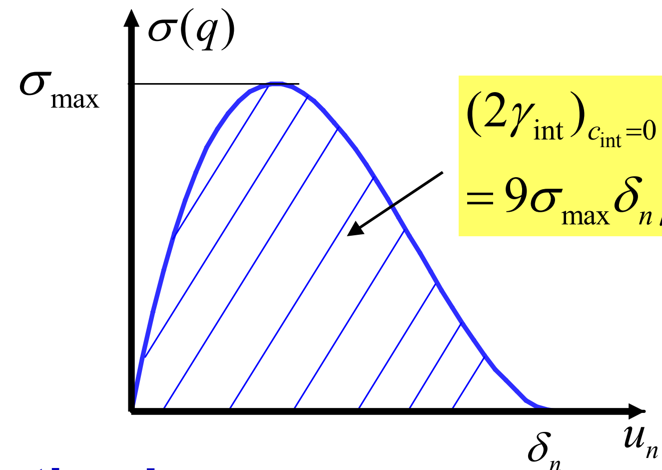
Charge density around hydrogen decreases
As a result, atomic bond becomes weaker

From Ab-Initio to Continuum: Thermodynamics of Decohesion



$$\Delta E = (E_s - 2\gamma_s) - (E_{gb} - \gamma_{gb})$$
$$= (2\gamma_{\text{int}})_{c_{\text{int}}} - (2\gamma_{\text{int}})_{c_{\text{int}}=0}$$

2598 mJ/m^2



$$(2\gamma_{\text{int}})_{c_{\text{int}}=0} = 9\sigma_{\max}\delta_n/16$$

Interfacial Traction-Separation Law

Mishin et al. (2002)

$$\sigma(c_{\text{int}}, q) = \frac{27}{4}\sigma_{\max}\left[1 + (\kappa - 1)c_{\text{int}}\right] q(1-q)^2$$

H-concentration at the interface

Interfacial separation= $q = u_n/\delta_n$

$\sigma_{\max}$ = maximum cohesive stress in the absence of hydrogen

$$k = 1 + \frac{\Delta E}{2\gamma_s - \gamma_{gb}} \frac{1}{\theta_{\text{int}}} \approx 0.85$$

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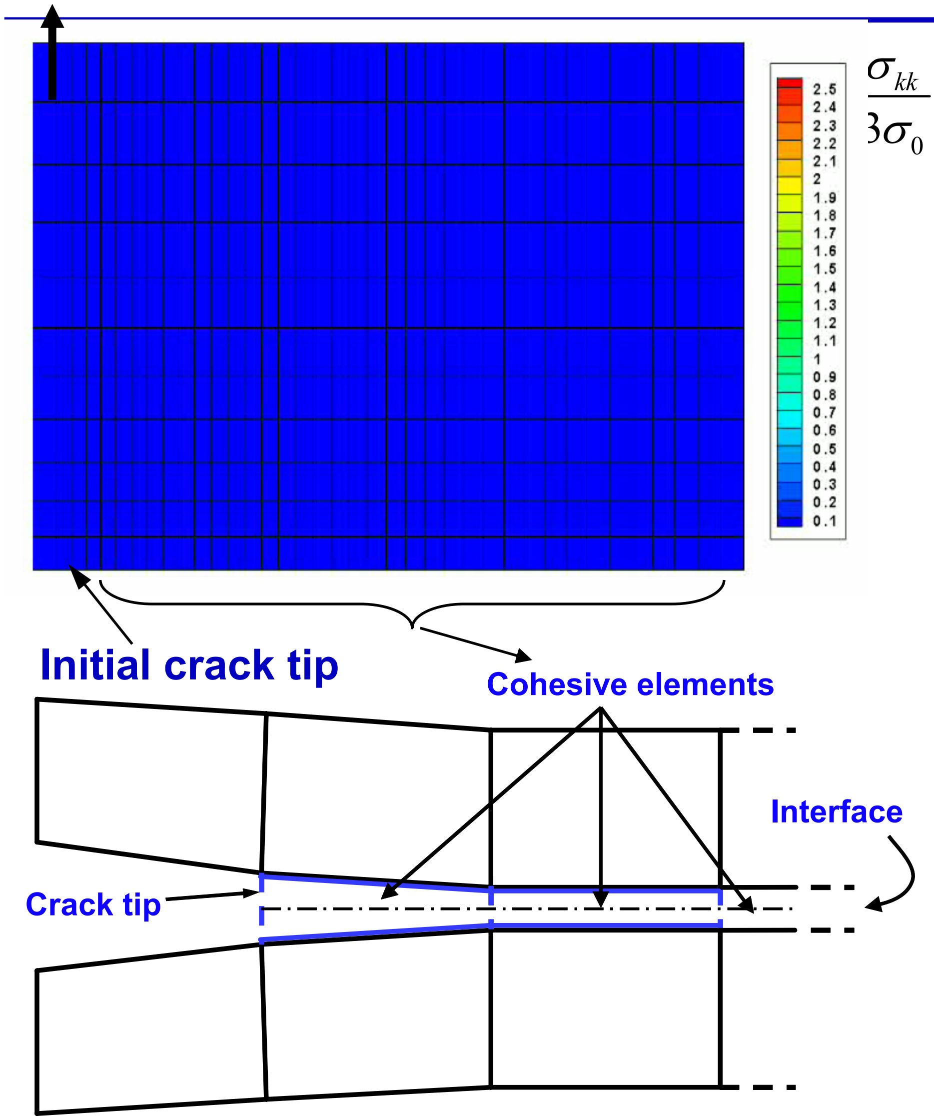
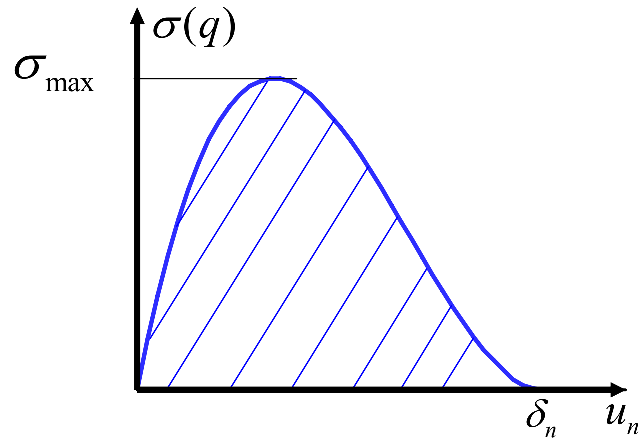
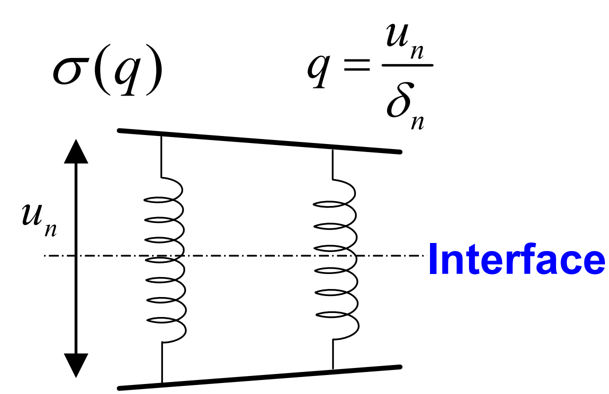
Crack Growth Simulation in Compact Tension Specimen

Developed the finite element technology to carry out crack propagation simulations

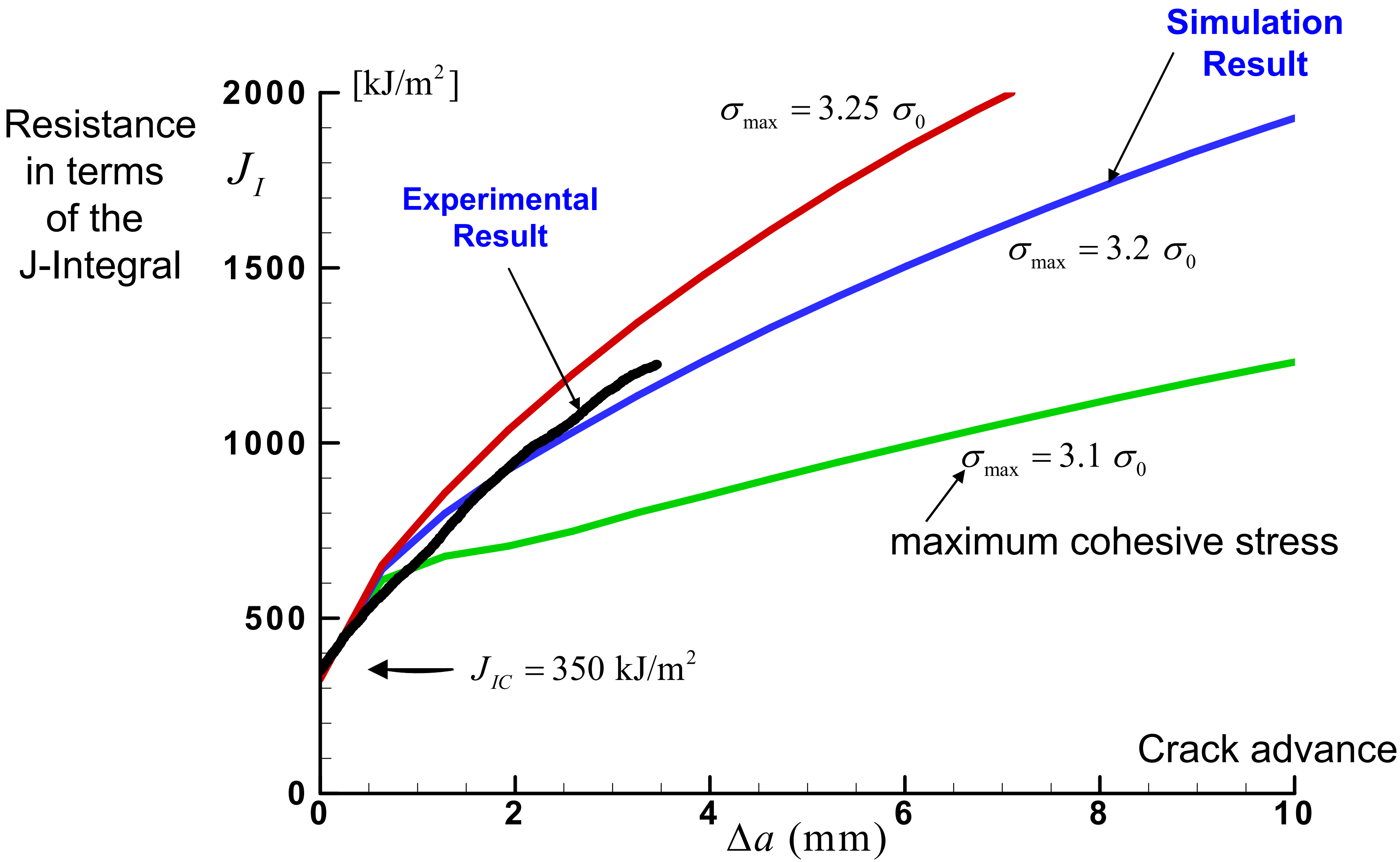






Traction-separation Law

Determination of Crack-Growth Resistance Curve for X100



Experimental work by Sandia National Labolatories

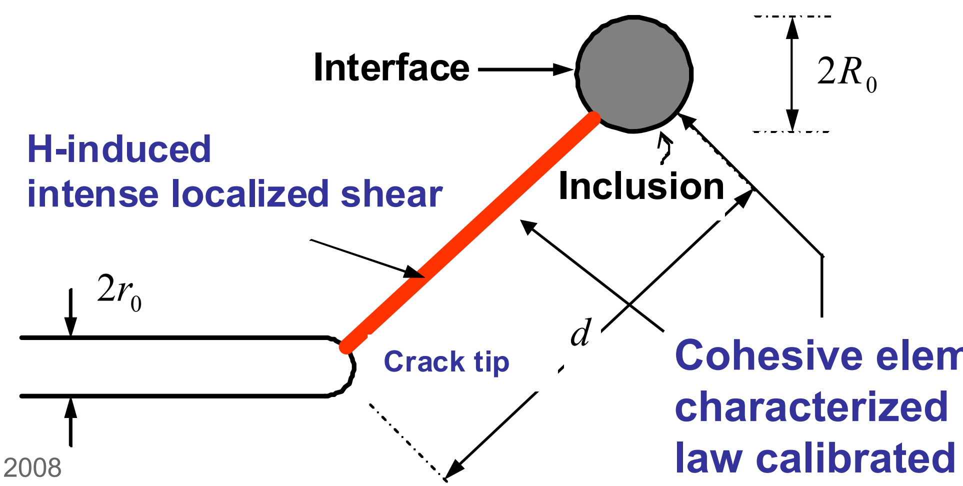
Future Work

Experiment (FY08)

- Finish determination of diffusion characteristics in collaboration with ORNL and carry out Thermal Desorption Spectroscopy measurements at Sandia (student summer visit)
- Carry out fracture toughness testing
- Characterization of fracture surfaces to establish the fracture mechanisms

Modeling and Simulation (FY08)

- Ab-inito calculations of cohesive properties of Fe/MnS interface, carbide/matrix interface.
- Integrate ab-initio calculation results through the thermodynamic theory of decohesion with finite element simulations at the continuum level.
- Establish critical toughness for fracture initiation by identifying the load at which the hole forming around an inclusion links with the main crack

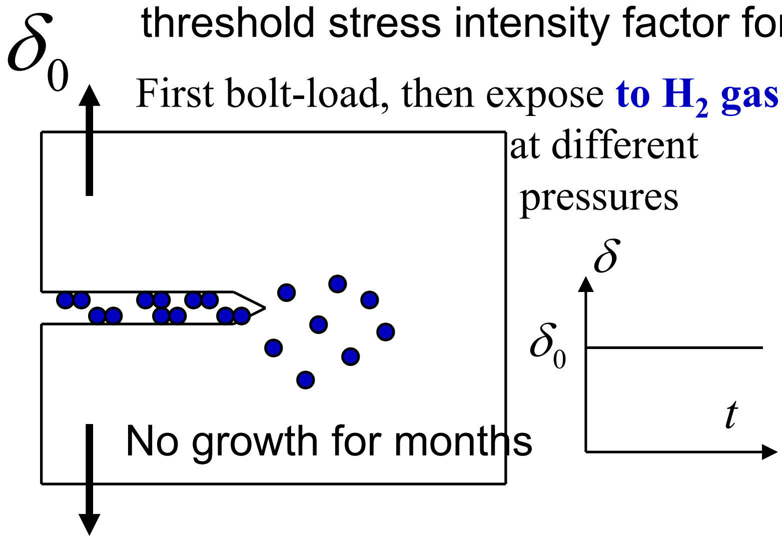


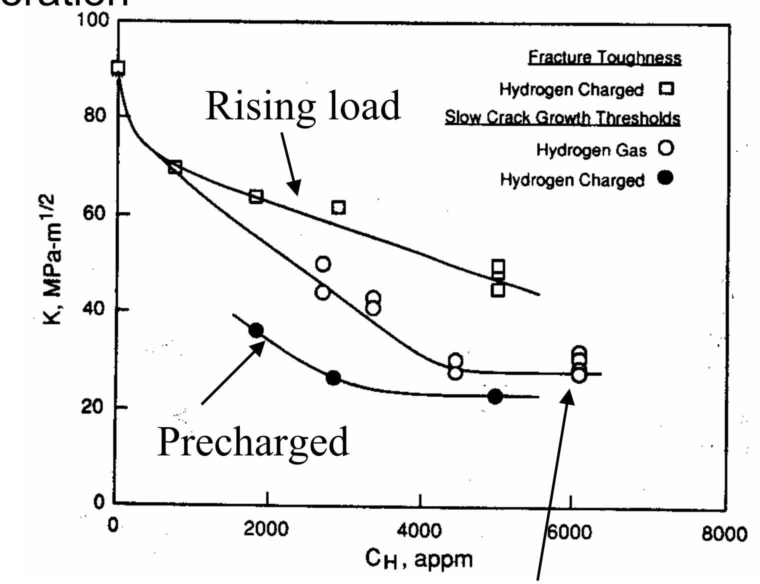
Determine Hydrogen Effect on

K_{IC}

Future Work

- **Experiment (FY08-09)**
  - investigate sustained-load cracking (Collaboration with Sandia)
- **Modeling and Simulation (FY08-09)**
  - Simulate sustained-load cracking in the presence of hydrogen to establish the threshold stress intensity factor for safe operation





Boundary and initial condition on crack faces

$$\frac{\partial c_L}{\partial t} = \frac{1}{\tau R \Theta}(\mu_g - \mu)$$

$K_{threshold}$

τ : characteristic time of adsorption

It can reflect species competition for adsorption sites on the crack surfaces

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Summary

Relevance

- Study of the mechanisms of hydrogen embrittlement in pipeline steels and propose fracture criteria with predictive capabilities.
- Current codes and standards for safe and reliable pipeline operation in the presence of hydrogen are rather arbitrary, not mechanism-based, and rely on safety factors not based on rigorous fracture mechanics
  - Our approach vs the limited SMYS approach

Approach

- Mechanical property testing at the micro/macro scale
- Microstructural analysis and TEM and SEM observations at the nano/micro scale
- Ab-initio calculations of hydrogen effects on cohesion at the atomic scale
- Finite element simulation at the micro/macro scale

Accomplishments and Progress

- Permeation measurements
- Microstructural characterization of Kinder Morgan, Air Liquide, Air Products, and OSM steels
- Finite element analysis of hydrogen transport
- Thermodynamic theory for hydrogen-induced decohesion and Ab-initio calculations

Collaborations

- Active partnership with SECAT, Oak Ridge National Laboratory, Sandia National Laboratories, ASME codes and Standards, JAPAN (Hydrogenius Institute)

Proposed future research

- Finish permeation measurements for diffusion, solubility, and trap characteristics
- Fracture testing
- Calculation of hydrogen effect on interfacial cohesion through first principles calculations
- Integration of microstructural analysis/ab-initio, decohesion thermodynamics, and finite element
- Understanding R-curve response and threshold stress intensities in the presence of hydrogen