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

2009 DOE Hydrogen Program Review

May 21, 2009

Project ID
#pd_41_sofronis

Overview

Timeline

- **Project start date:5/1/05**
- **Project end date: 12/31/10**
- **Percent complete: 70%**

Budget

- **Total project funding: $1.2m**
- **Share**
  - **DOE : 75%**
  - **Contractor : 25%**
- **Funding received**
  - **FY2005: $180 K**
  - **FY2006: $80 K**
  - **FY2007: $473 K**
  - **FY2008: $166 K**

SECAT

Sandia National Laboratories

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**
  - **Kinder Morgan**
- **National Laboratories**
  - **Sandia National Laboratories**
  - **Oak Ridge National Laboratory**
- **Codes and Standards**
  - **ASME**
  - **Japan Automotive Industry**

Objectives - Relevance

- **To come up with a mechanistic understanding of hydrogen embrittlement in pipeline steels in order to devise fracture criteria 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)
  - Working with Oregon Steel Mills (SECAT, DGS Metallurgical Solutions, Inc.), propose new steel microstructures

- **It is emphasized that such fracture criteria are lacking and there are no codes and standards for reliable and safe operation of pipelines in the presence of hydrogen**
  - 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 and 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
  - Help avoid unnecessary repairs and shut-downs by minimizing unnecessary levels of conservatism in the operation of pipelines
  - Reduce capital cost by avoiding conservatism

Approach – Milestones

- **Permeation experiments to identify diffusion characteristics**
  - Collaboration with Oak Ridge National Laboratory
- **Microstructural characterization**
  - Materials from pipelines in service from Air-Liquide, Air-Products, and new steel microstructures from Oregon Steel Mills (SECAT, DGS Metallurgical Solutions, Inc.)
- **Development of finite element code to simulate transient, stress-driven hydrogen diffusion coupled with material elastoplastic deformation**
  - Time to steady in fracture process zone ahead of a crack tip is ~minutes
  - Simulated subcritical crack growth and crack initiation at MnS for natural gas pipelines
- **Thermodynamic theory for the determination of the cohesive properties of particle/matrix interfaces and grain boundaries as affected by the presence of hydrogen solutes**
- **Ab-initio calculations of cohesive properties**
  - Needed to calibrate the thermodynamic model
  - Results for effect of hydrogen on grain boundary cohesion in BCC iron
- **Simulation and identification of deformation and constraint characteristics at an axial crack on the inner diameter (ID) surface**
  - Laboratory specimen type (hydrostatic constraint guidelines) has been identified to investigate fracture conditions in a real-life pipeline

Milestones for 2009-2010

- **Rising-load fracture toughness and subcritical crack growth experiments to determine**
  - Hydrogen effect on crack initiation
  - Magnitudes of “safe hydrogen concentrations” at Threshold Stress Intensities
  - 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

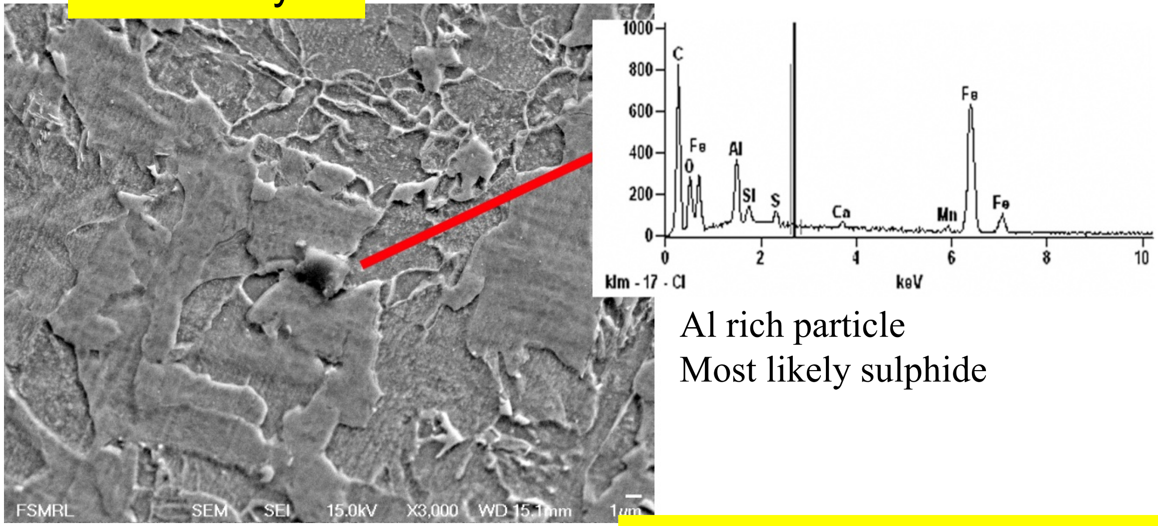
- **Fracture experiments combined with the simulation tools already in place will lead to the development of models with predictive capabilities**
  - Integrate modeling with experiment
  - We have the tools to decide whether a crack in a steel pipe does not run unstably under given hydrogen pressure and pipe dimensions.

- **Collaborative effort between Illinois and Sandia National Laboratories, Livermore**

Technical Accomplishment: 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**

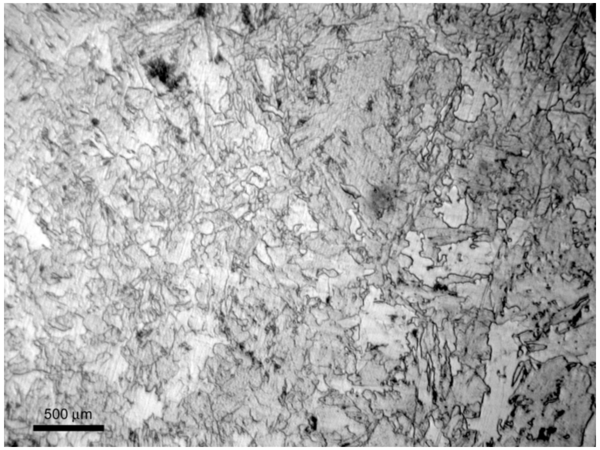
SEM analysis



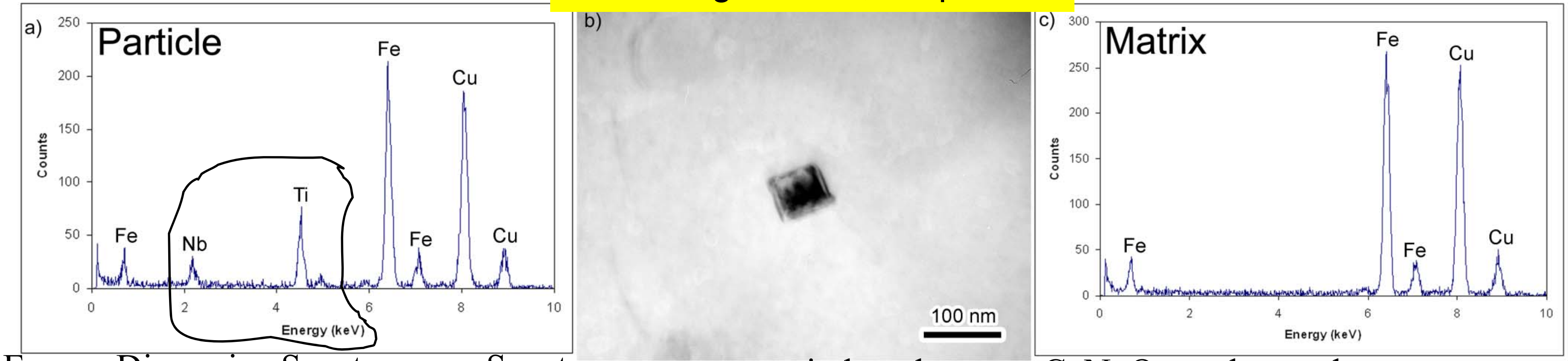
Al rich particle
Most likely sulphide

Optical analysis

Average grain size 35 microns, 3% pearlite



TEM image of a Ti, Nb particle

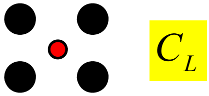


Energy Dispersive Spectroscopy Spectra

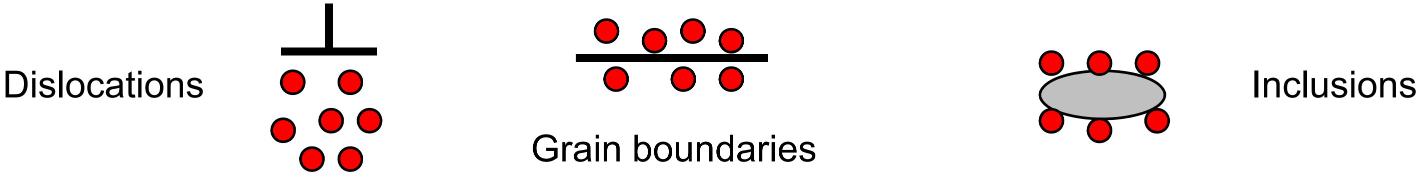
window detector: C, N, O not detected

Technical Accomplishment: Hydrogen Transport Model

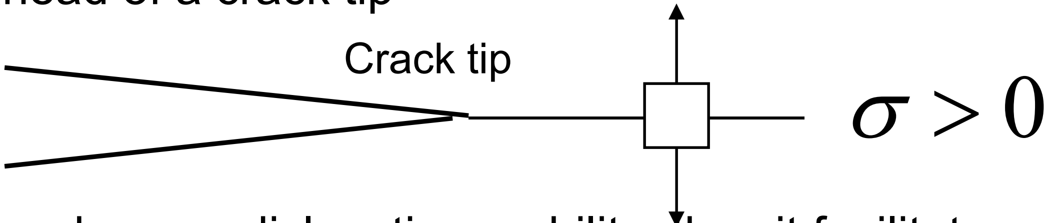
- **Diffusing hydrogen resides at**
  - **Normal Interstitial Lattice Sites (NILS)**



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



- **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



  - 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. The problem is coupled, and solution involves iterations**

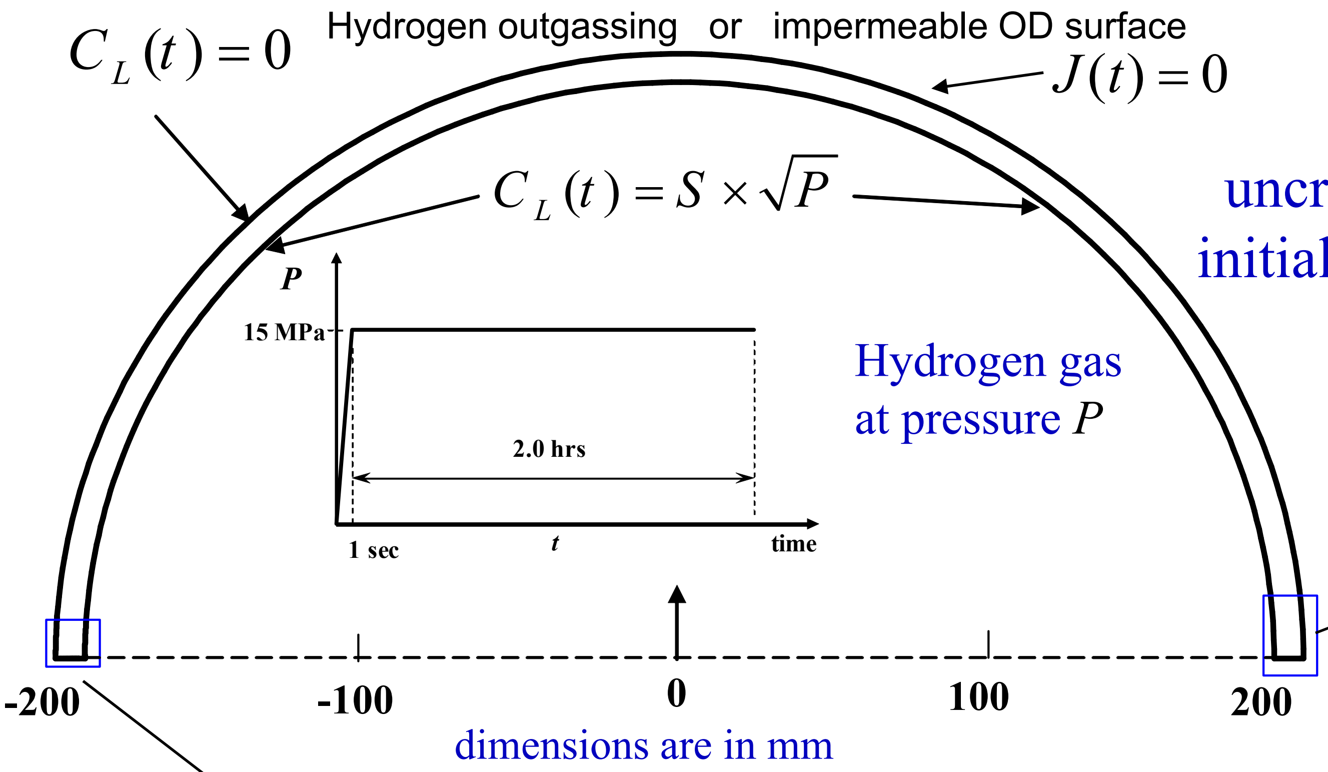
Technical Accomplishment: Analysis of Cracked Pipeline

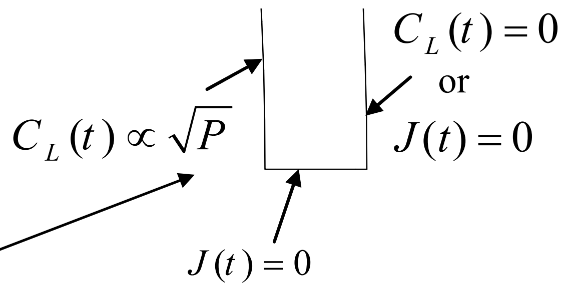
outer radius: 8”

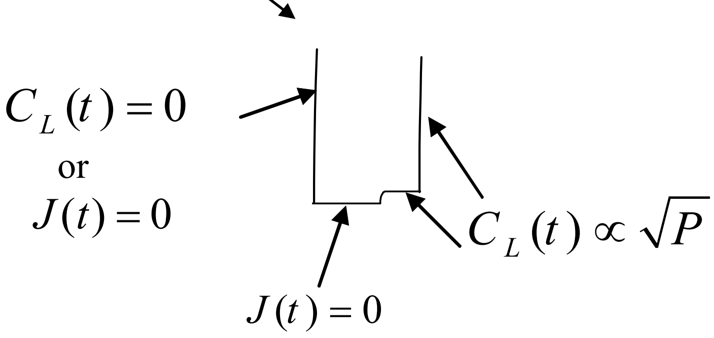
thickness: 0.375”

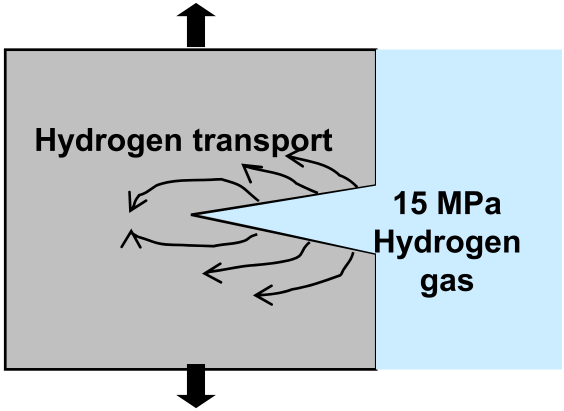
uncracked ligament: 0.356”

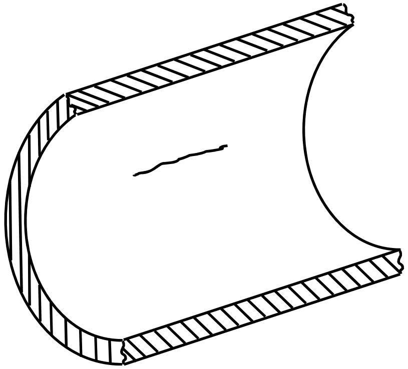
initial crack opening: 0.3 µm







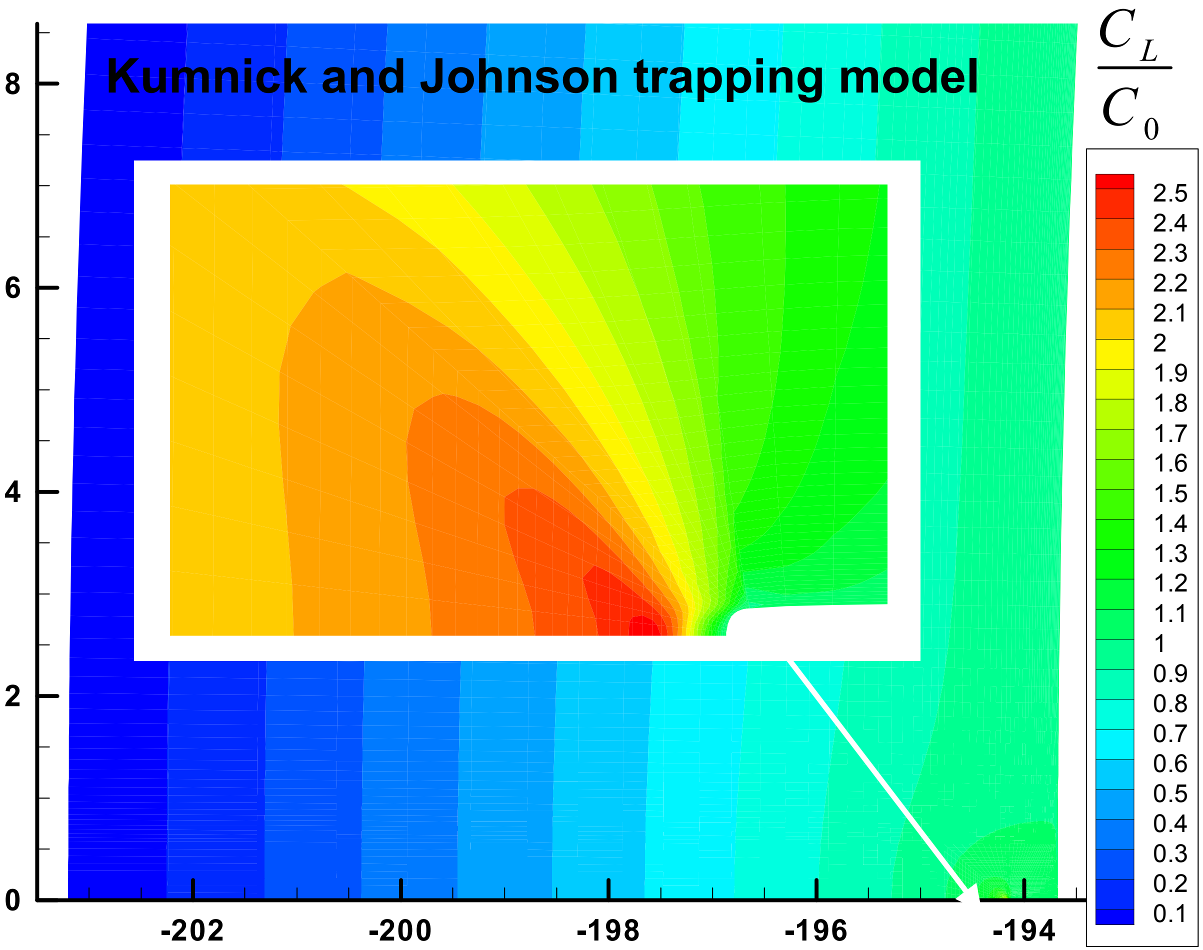


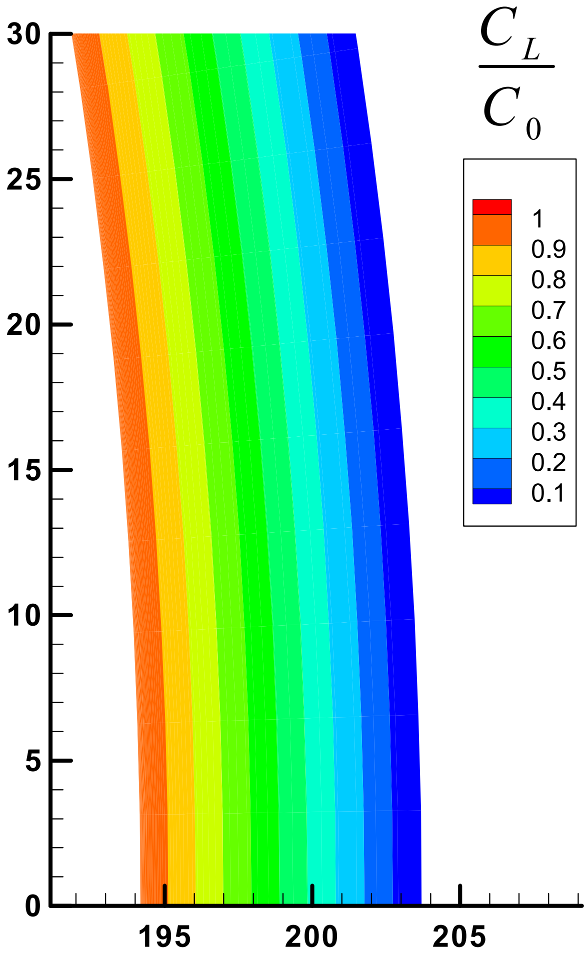


Hydrogen Concentration at Steady-State

Technical Accomplishment

Time to steady-state: 2.0 hr



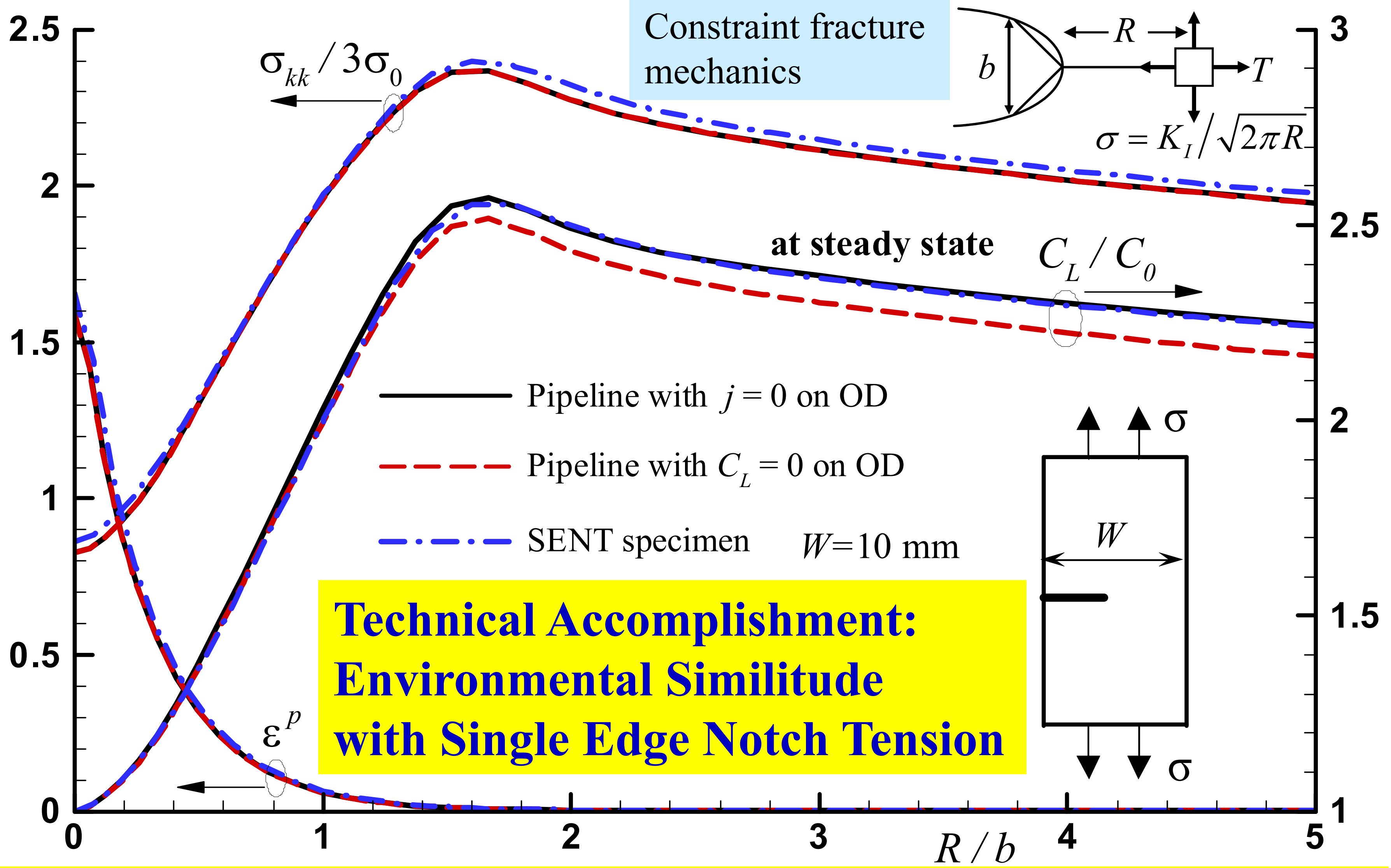


$$C_0 = 2.65932\times10^{22}\ \mathrm{H\,atom/m^3}$$

corresponds to lattice concentration at

$$P = 15\ \mathrm{MPa}$$

Cracked-Pipeline Fields vs. SENT-Specimen Fields



Technical Accomplishment:
Environmental Similitude
with Single Edge Notch Tension

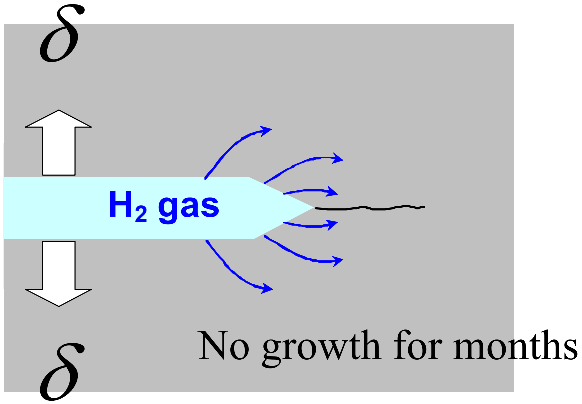
- Pipeline fields scale with the stress intensity factor and *T*-stress at the axial crack.
- Single Edge Notch Tension (SENT) specimens can be used to study fracture resistance of a pipeline with an axial crack

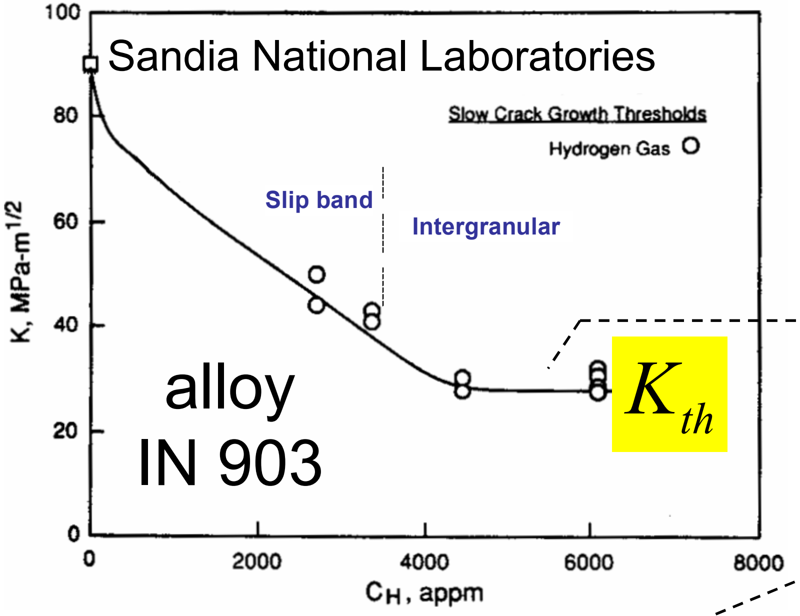
Simulation of Sustained-load Intergranular Cracking

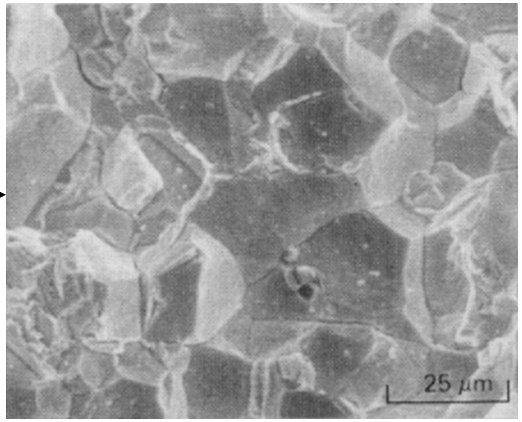
Technical Accomplishment

Wedge Open Load (WOL) specimen

First bolt-load the specimen and then expose to hydrogen gas at different pressures





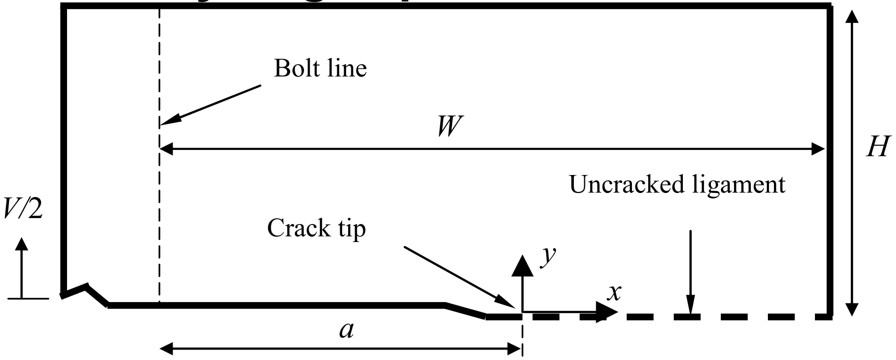


- **Simulate controlled intergranular cracking through cohesive element methodology**
- **Grain boundary cohesive stress is furnished by thermodynamic theory of grain-boundary decohesion**
- **Objective is to predict K_{th}**

Simulation of Sustained-load Intergranular Cracking

Technical Accomplishment

Hydrogen pressure 207 MPa



Initial crack length: $a_0 / W = 0.471$

Initial month opening: $V_0 = 0.5588\,\mathrm{mm}$

$$K_{IC} = 90\,\mathrm{MPa}\sqrt{\mathrm{m}}$$

Load at $K_I^0 = 57.8\,\mathrm{MPa}\sqrt{\mathrm{m}}$

Threshold $K_{th} = 33.5\,\mathrm{MPa}\sqrt{\mathrm{m}}$

Grain-Boundary Traction-Separation Law

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

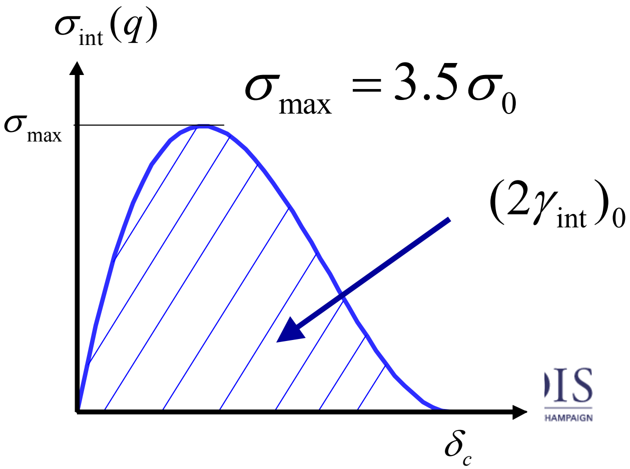
H-concentration at grain boundary

Grain-boundary separation= $q = u_n / \delta_n$

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

$$\kappa = \frac{(2\gamma_{\text{int}})_{\theta_{\text{int}}=1}}{(2\gamma_{\text{int}})_0} = \frac{\text{cohesive energy of saturated GB}}{\text{cohesive energy of hydrogen-free GB}}$$

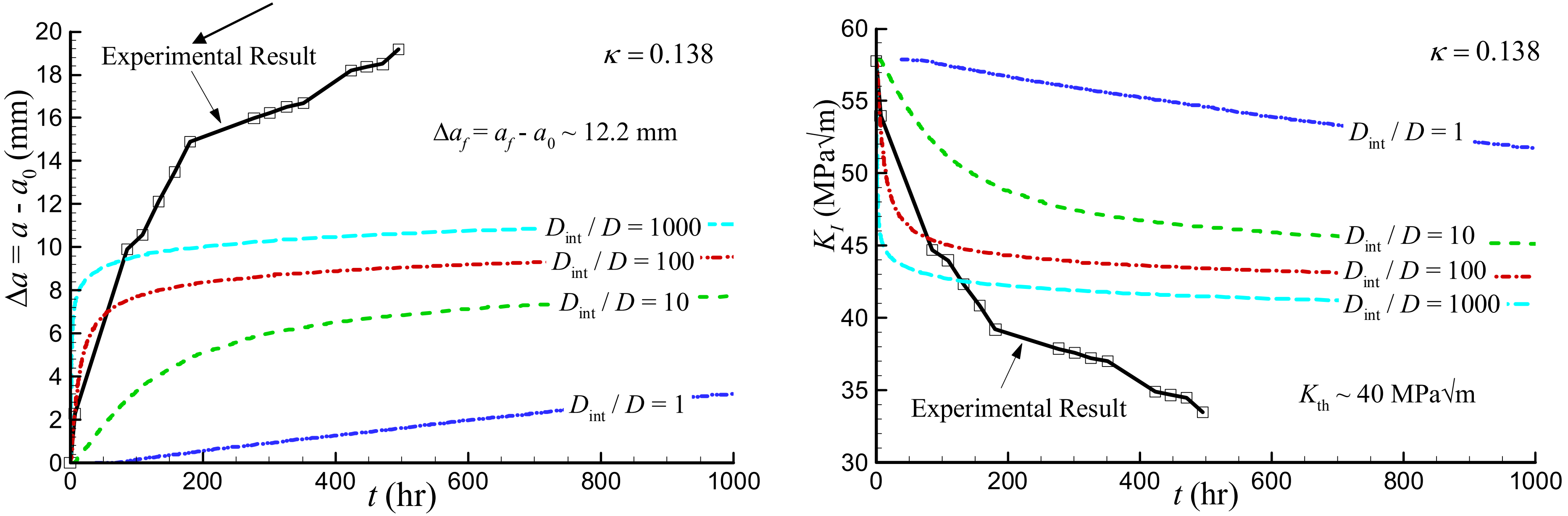
$$(2\gamma_{\text{int}})_0 = \frac{K_{Ic}^2(1-\nu^2)}{E} \square\ 52\ \mathrm{kJ/m^2} \qquad \kappa = \left(\frac{33.5}{90}\right)^2 = 0.138$$



Simulation of Sustained-load Intergranular Cracking

Technical Accomplishment

Sandia National Laboratories

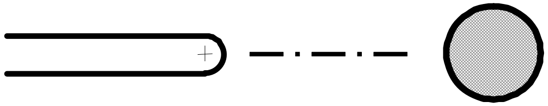


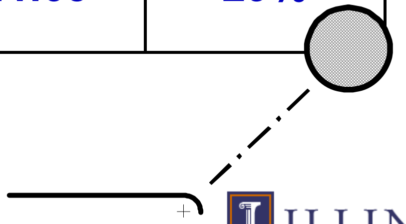
- **Analysis fully coupled**
  - Bulk stress-driven diffusion accounting for trapping at dislocations and precipitates
  - Grain boundary diffusion
  - Bulk elastoplastic deformation
  - Grain boundary cohesive stress with magnitude depending on hydrogen coverage
- **Predictions depend strongly on the magnitude of grain boundary diffusion** D_{int}
- **Prediction of threshold stress intensity** K_{th}

Critical Stress Intensity for Void Nucleation at MnS/Matrix Interface

Technical accomplishment: used thermodynamic theory of hydrogen-induced decohesion and the developed finite element methodology to predict the hydrogen effect on fracture-process initiation

σ_{max} / σ_0	$K_I \quad [\mathrm{MPa}\sqrt{\mathrm{m}}]$					
	Inclusion at 0° angle			**Inclusions at 45° angle**		
	No hydrogen	**hydrogen**	**Percent Reduction**	**No hydrogen**	**hydrogen**	**Percent Reduction**
3	**53.65**	**36.15**	**55%**	**36.75**	**29.70**	**34%**
2	**25.60**	**20.90**	**34%**	**21.05**	**17.20**	**35%**
1	**17.20**	**15.45**	**18%**	**13.35**	**11.65**	**29%**



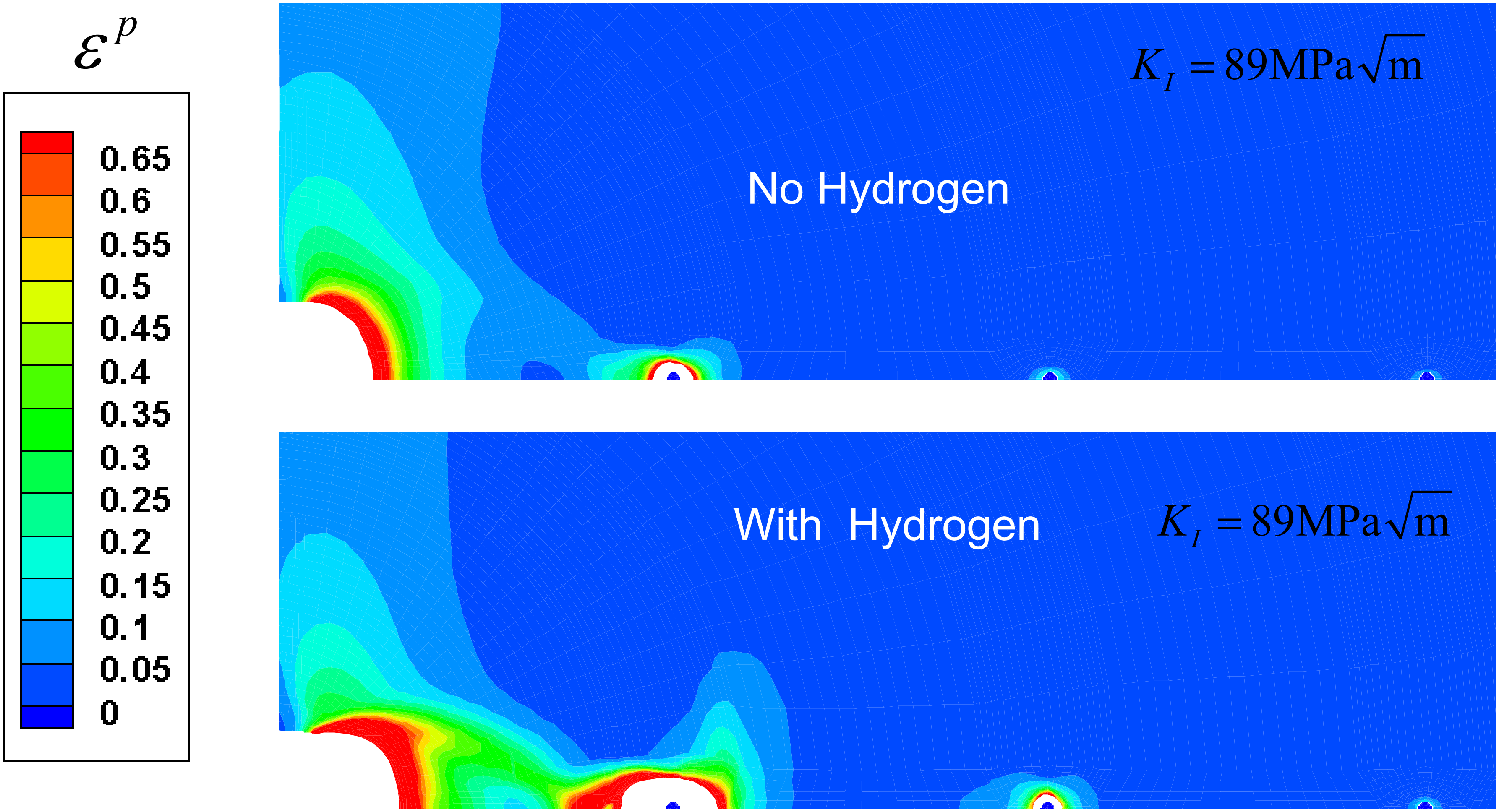


$$\kappa = \frac{(2\gamma_{\mathrm{int}})_{\theta_{\mathrm{int}}=1}}{(2\gamma_{\mathrm{int}})_0} = 0.85 = \frac{\text{cohesive energy of saturated interface}}{\text{cohesive energy of hydrogen-free interface}}$$

Technical Accomplishment: Crack/Inclusion Interactions

Mechanism of fracture for mild/medium strength steels

$t = 89 \ \text{sec}$



Hydrogen-induced softening intensifies plastic flow localization

Collaborations

Industrial Partners

- **SECAT, DGS Metallurgical Solutions, Inc., Oregon Steel MIlls**
  - Collaboration on new steel microstructures. Microstructural analysis includes Transmission/Scanning Electron Microscopy, Optical Microscopy, Energy Dispersive Spectroscopy, etc.
- **Air Liquide, Air Products**
  - Collaboration on microstructural analysis and testing of coupons from hydrogen pipelines in service
- **Kinder Morgan**
  - Natural gas pipeline in the presence of hydrogen (microstructural analysis and hydrogen uptake)
- **ExxonMobil Corporation**
  - Collaboration on the effect of microstructure on hydrogen embrittlement

National Laboratories

- **Sandia National Laboratories, Livermore**
  - Collaboration on all aspects of hydrogen embrittlement: fundamentals, experiments, and simulation. Collaboration includes summer visits by students and the PIs to the Laboratory at Livermore.
- **Los Alamos National Laboratory**
  - Collaboration on issues of fracture similitude between laboratory specimens and real-file components for gas transfer systems.
- **Oak Ridge National Laboratory**
  - Collaboration on hydrogen permeation measurements

Collaborations

- **ASME Codes and Standards**
  - Collaboration on safety factor calculations for hydrogen pipelines

- **International Collaborations (Japan)**
  - **Institute for Hydrogen Industrial Use and Storage (HYDROGENIUS) at Kyushu University, Fukuoka, Japan**
    - Collaborative research agreement between Kyushu and Illinois was signed on February 4, 2008 for faculty and student exchanges
    - Annual visits to the Institute by the project PIs.
    - Collaboration on all aspects of embrittllement (e.g., fundamentals, microstructural analysis, experiments, simulations)
  - **Annual meetings with HYDROGENIUS and the Automobile Industry of Japan (Toyota, Honda, Nissan) on Hydrogen Technology Standards**

Future Work

Experiment (FY09)

- Carry out rising-load fracture toughness testing to assess the hydrogen effect on fracture initiation
- Subcritical crack growth experiments to measure Threshold Stress Intensities
- Characterization of fracture surfaces to establish the fracture mechanisms

Modeling and Simulation (FY09-FY10)

- Finite element simulation of the fracture experiments (integration)
- Ab-inito calculations of cohesive properties of interfaces (e.g. slip planes, particle/matrix, grain boundaries) to calibrate thermodynamic model for decohesion
  - ratio of cohesive energy at hydrogen saturation to cohesive energy in the absence of hydrogen
- Simulation of adsorption kinetics (competition for adsorption sites on the crack flanks) $\partial c / \partial t = (\mu_g - \mu) / \tau R \Theta \quad \tau = \text{adsorption characteristic time}$

Devise fracture criteria in the presence of hydrogen (FY10)

- Initiation $K_{IC}^{hydrogen}$ (can it be predicted as a given fraction of K_{IC} ?)
- Threshold stress intensity K_{th}
- Damage tolerance assessment: for a given hydrogen pressure and pipeline dimensions determine tolerable crack size for safe operation

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

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

Accomplishments and Progress

- Mechanical property testing at the macroscale (macroscopic flow characteristics)
- Permeation measurements
- Microstructural analysis: TEM and SEM observations at the nano/micro scale
- Microstructural characterization of Kinder Morgan, Air Liquide, Air Products, and OSM steels
- Ab-initio calculations of hydrogen effects on cohesion at the atomic scale
- Thermodynamic theory for hydrogen-induced decohesion
- Finite element simulation capabilities of hydrogen transport interaction with material microstructure
    - Unique simulation capabilities of the hydrogen effect on mechanical properties
    - Simulation of fracture initiation and subcritical crack growth tests

Collaborations

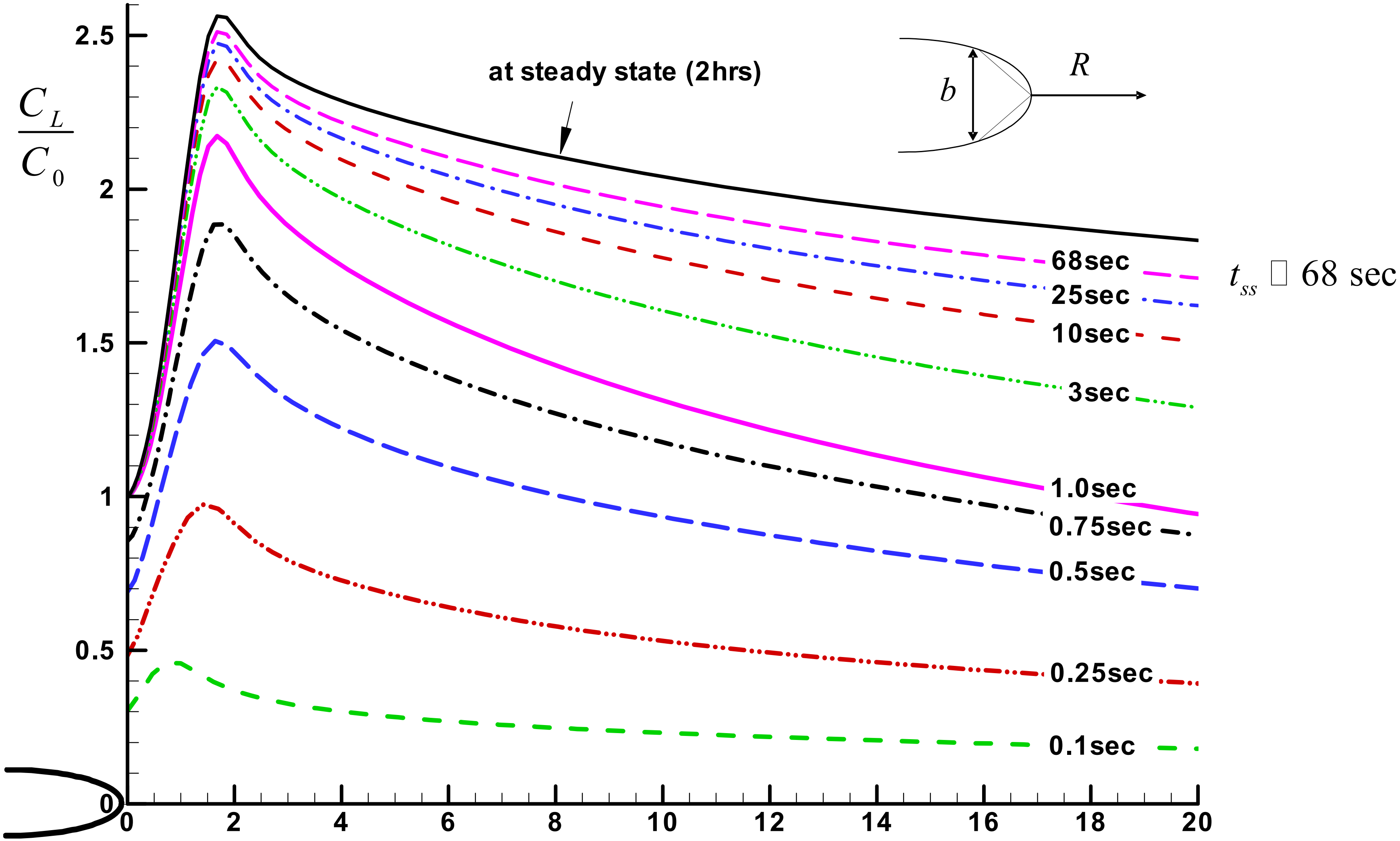
- Active partnership with Sandia National Laboratories, Los Alamos National Laboratory, ASME codes and Standards, JAPAN (Hydrogenius Institute), Industrial Partners (e.g. ExxonMobil, SECAT)

Proposed future research

- Fracture testing (rising-load toughness and sustained-load cracking) and simulation
- Assess fracture resistance in the presence of hydrogen as a fraction of that in the absence of hydrogen
- Damage tolerance assessment (safe operation of a cracked pipeline under given pressure)
- We understand the embrittlement problem and we have the means to tame it.
    - Similar experience with fatigue cracking in the aerospace industry

Supplemental Slides

Evolution of Hydrogen Concentration at NILS

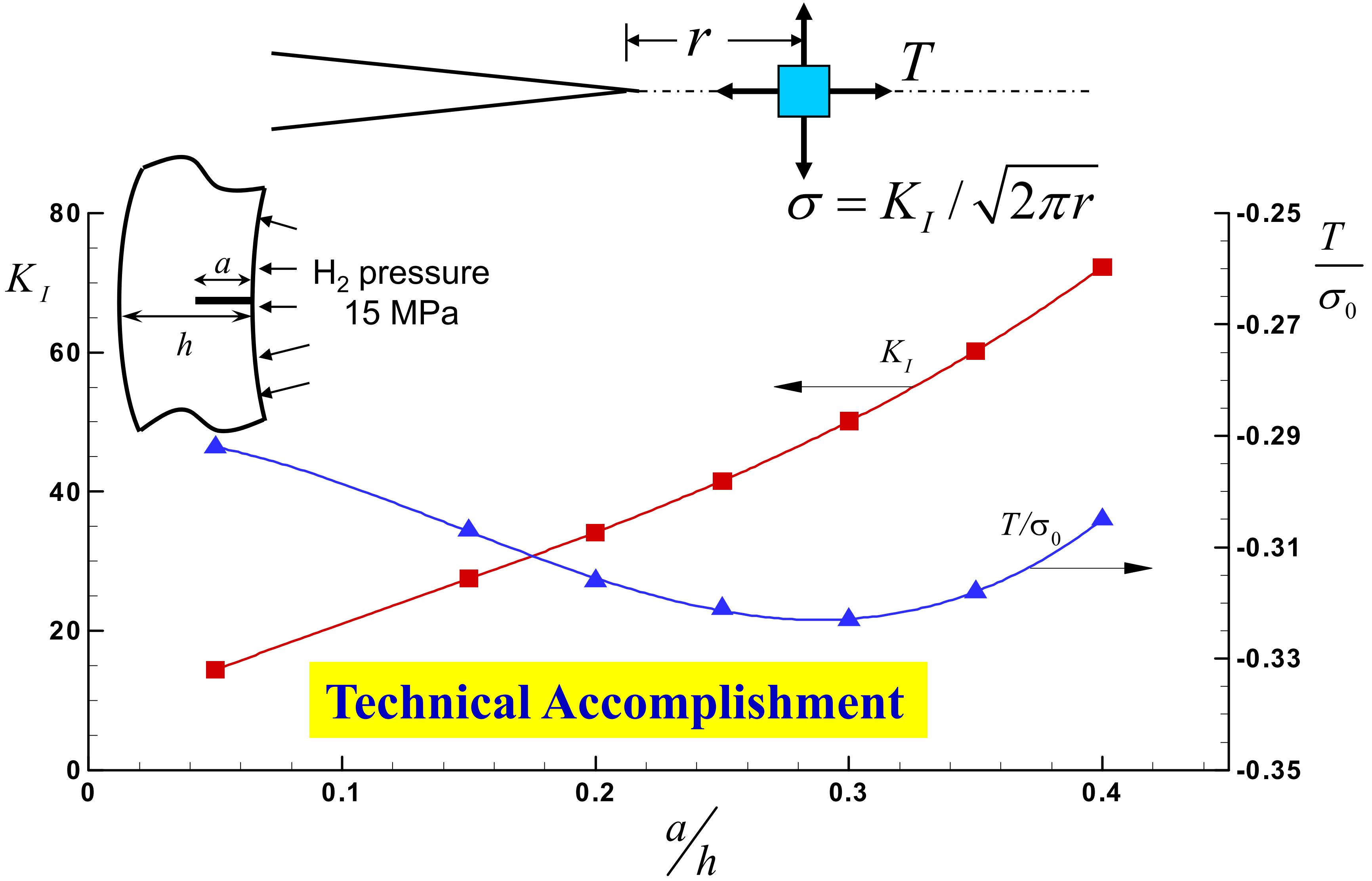


R/b

$b = 1.17$ μm

Technical Accomplishment

Fracture Mechanics Parameters: From the Full Pipeline to the Laboratory Specimen

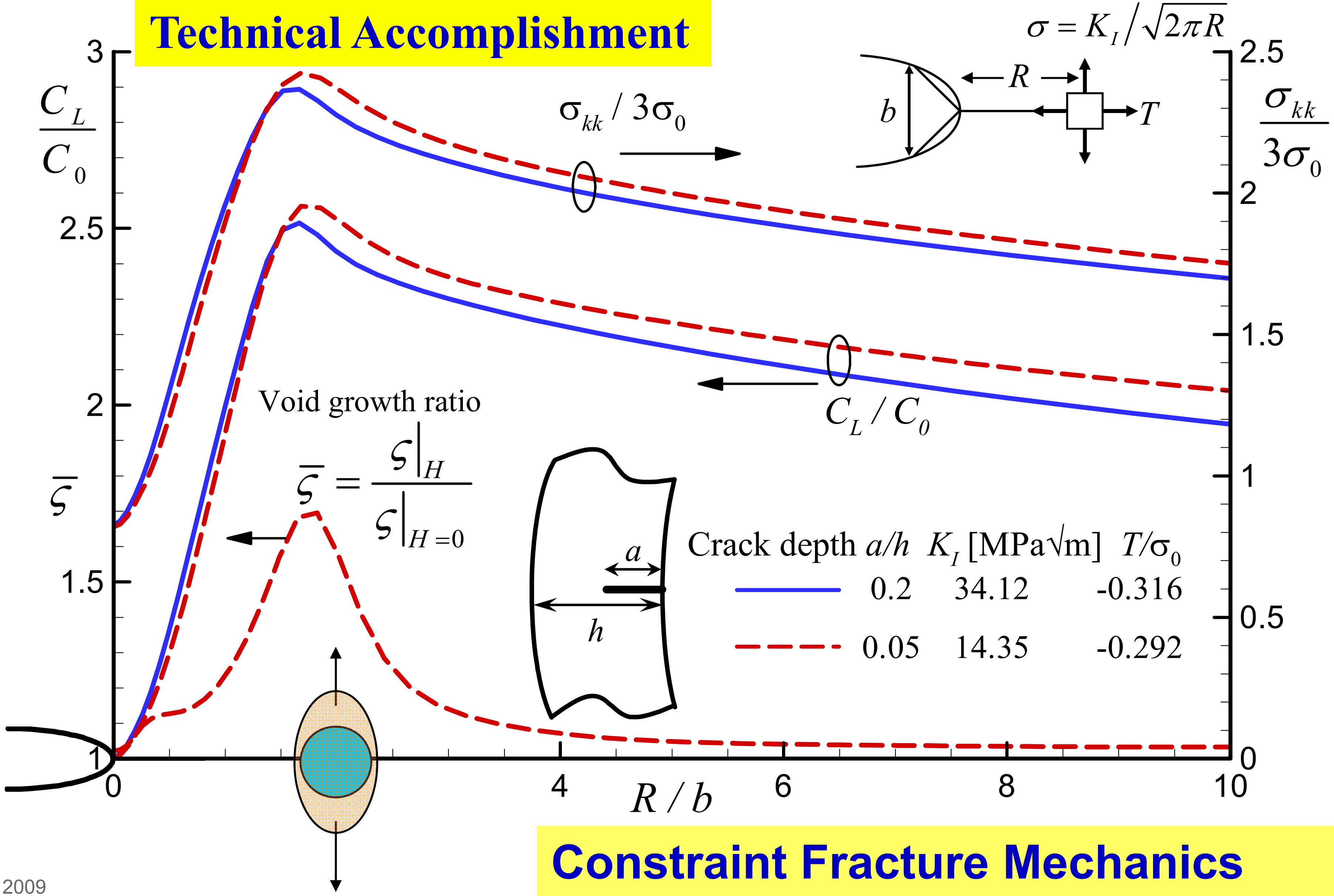


Technical Accomplishment

Crack depth/pipe thickness

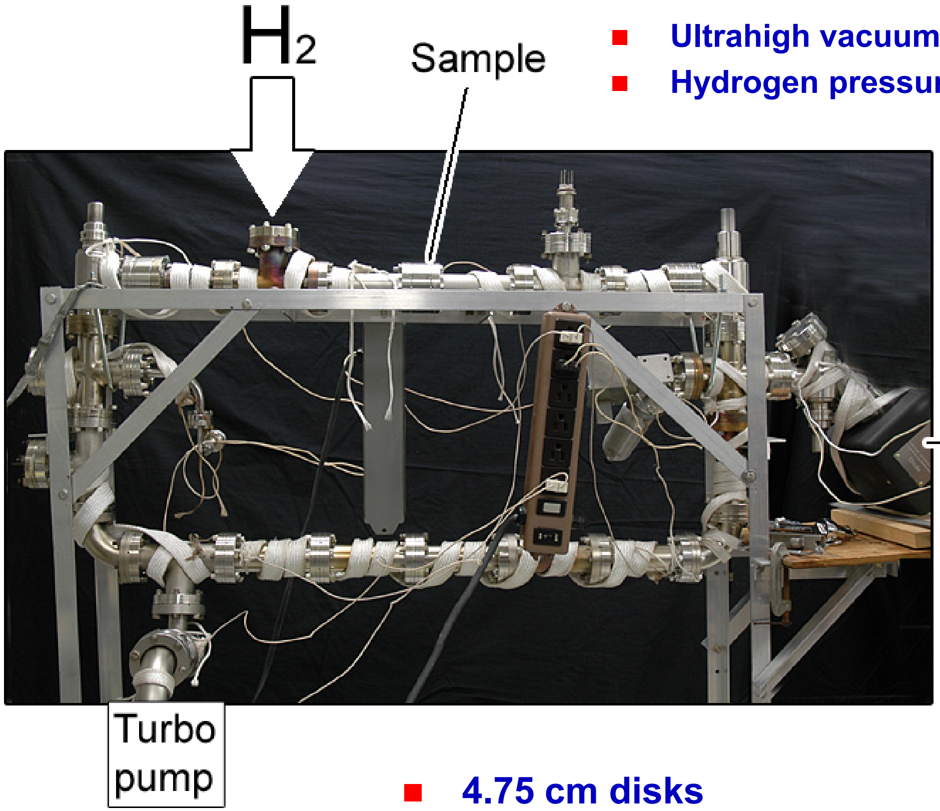
Crack-Tip Fields Scale with K_I and T-stress Hydrogen Accelerates Void Growth

Technical Accomplishment



Constraint Fracture Mechanics

Permeation



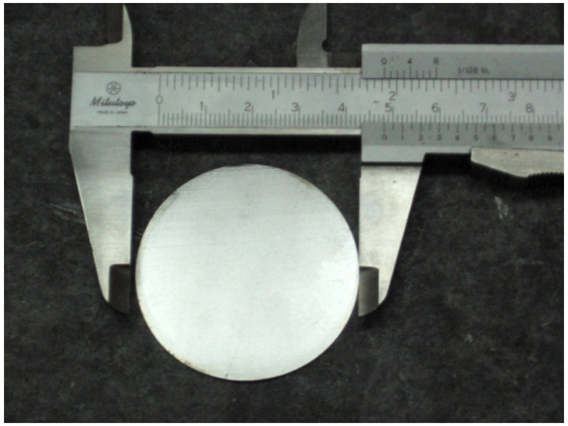
- Ultrahigh vacuum (10^{-9} torr)
- Hydrogen pressure (10 torr)

- Hydrogen is introduced on one side of the sample
- Permeates through sample
- Detected by ion pump

Technical Accomplishment

- 4.75 cm disks
- 100 micron thickness

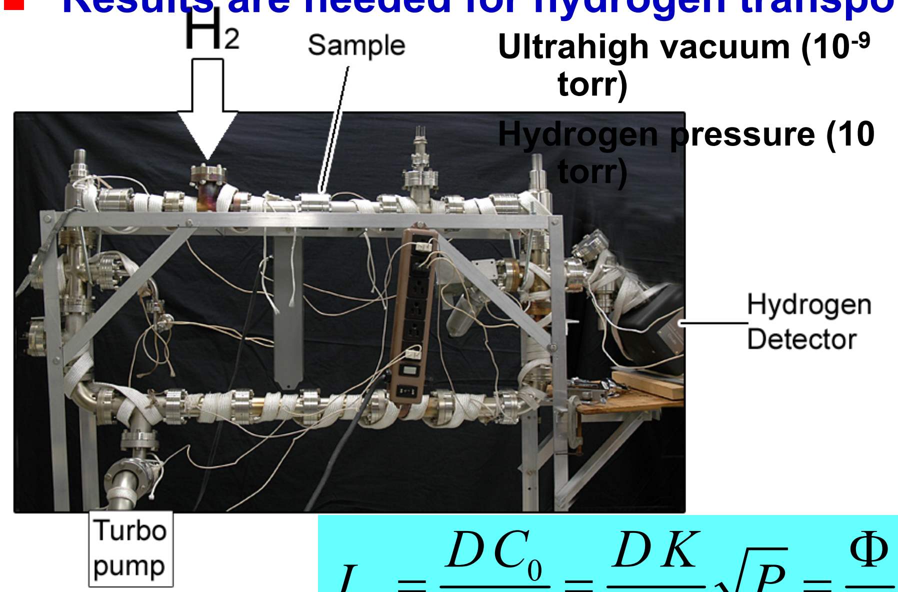
- Palladium coating on exit side
- Testing coatings on hydrogen side



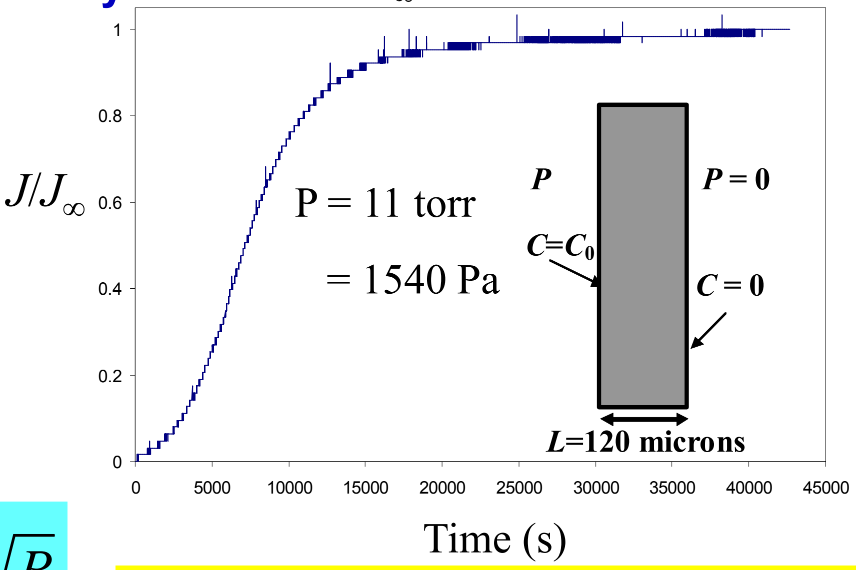
Real-world pipeline specimens are in our possession for testing
Air Liquide and Air Products provided the coupons

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**

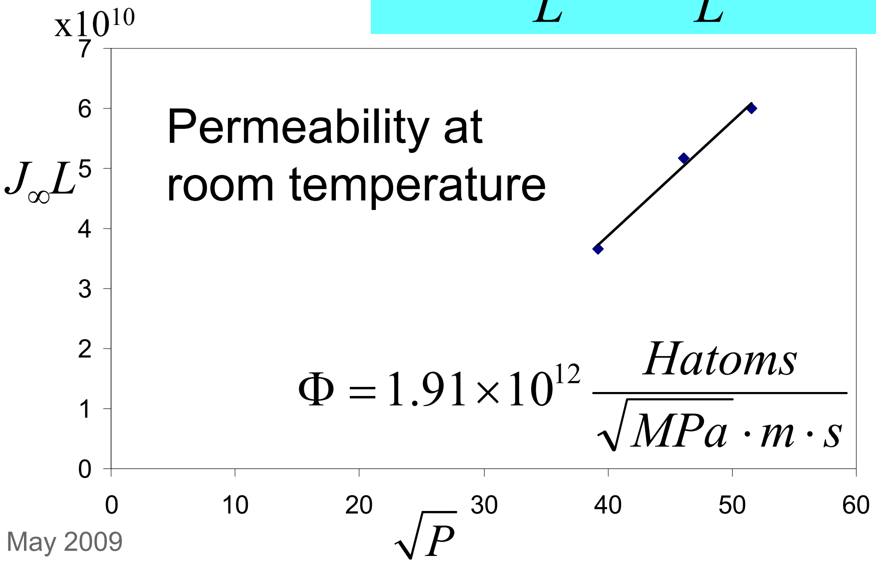


$J_\infty = 4.88\text{x}10^{14}$ atoms/m²·s



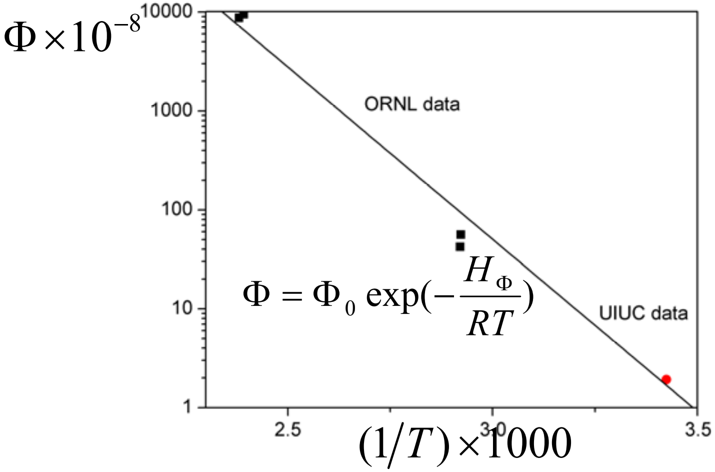
$$J_\infty = \frac{D\,C_0}{L} = \frac{D\,K}{L}\sqrt{P} = \frac{\Phi}{L}\sqrt{P}$$

Technical Accomplishment



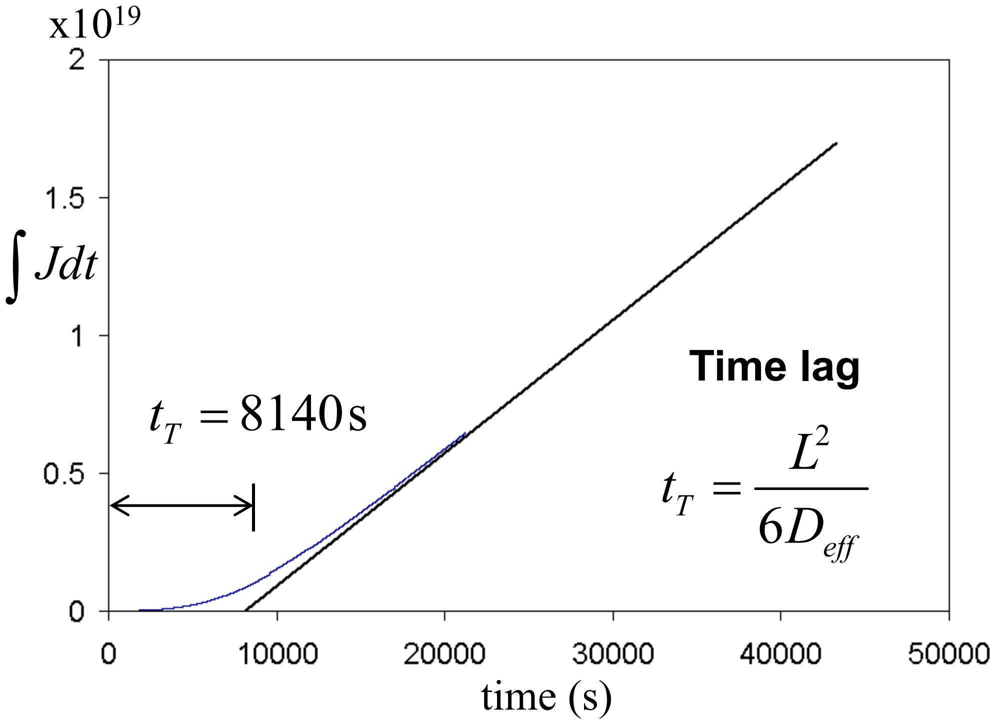
Permeability at room temperature

$$\Phi = 1.91\times10^{12}\,\frac{Hatoms}{\sqrt{MPa}\cdot m\cdot s}$$



$$\Phi = \Phi_0 \exp\left(-\frac{H_\Phi}{RT}\right)$$

Hydrogen Permeation Measurements

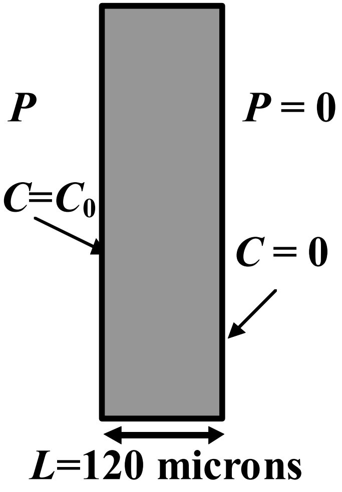


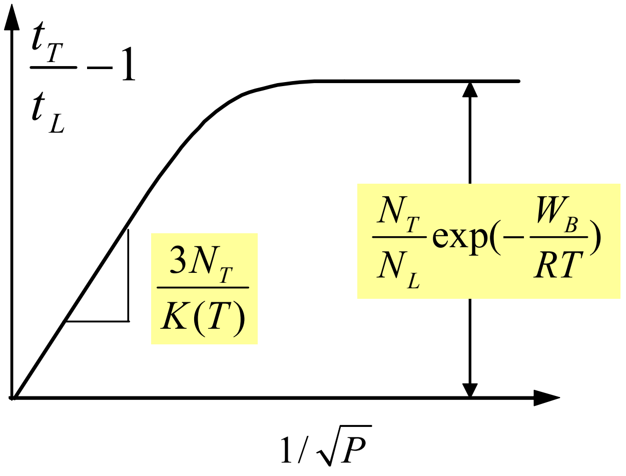
Time lag measurements at high temperature will give the diffusion coefficient *D*

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

Obtain solubility *K* as a function of temperature

$$\Phi = D\,K$$



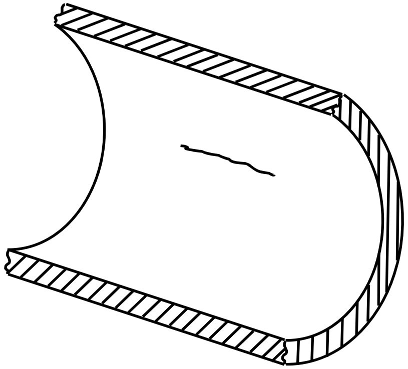


Obtain trap characteristics needed for hydrogen transport analysis

Trap density: N_T

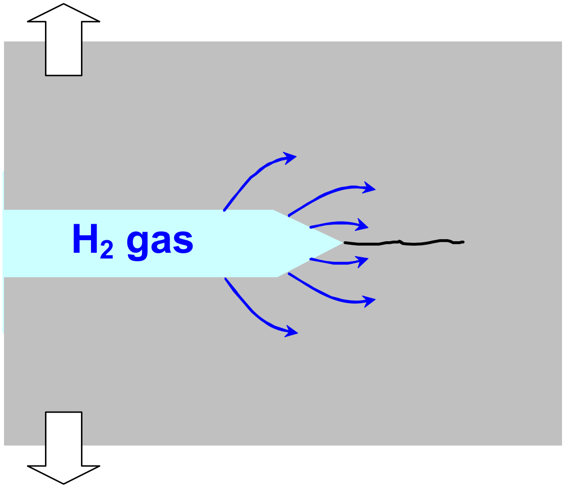
Trap binding energy: W_B

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



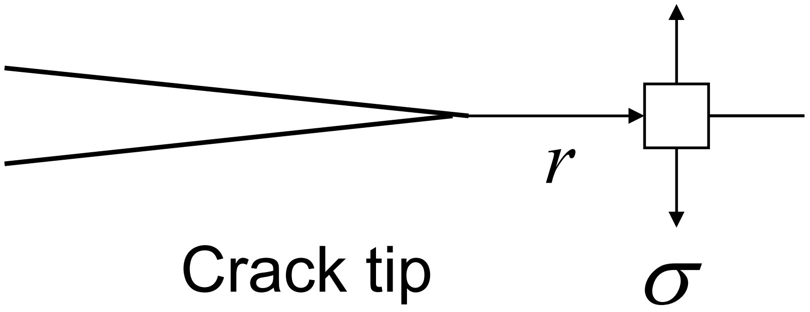
H_2-Pressure of 15MPa

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



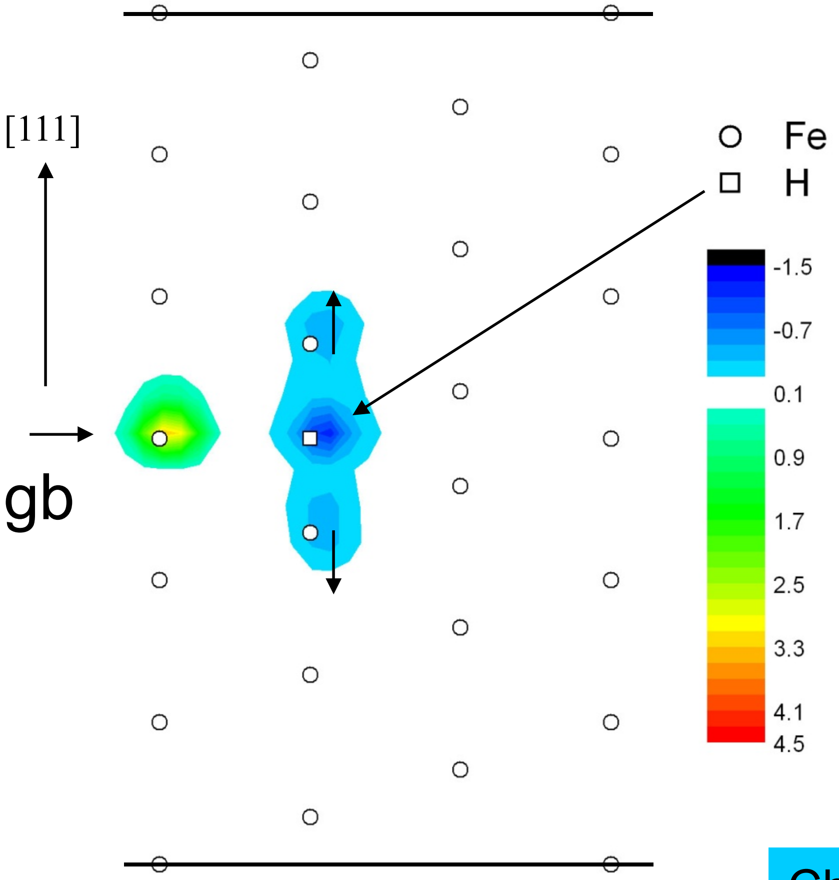
$$\sigma = \frac{K_I}{\sqrt{2\pi r}}$$

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

Transferability

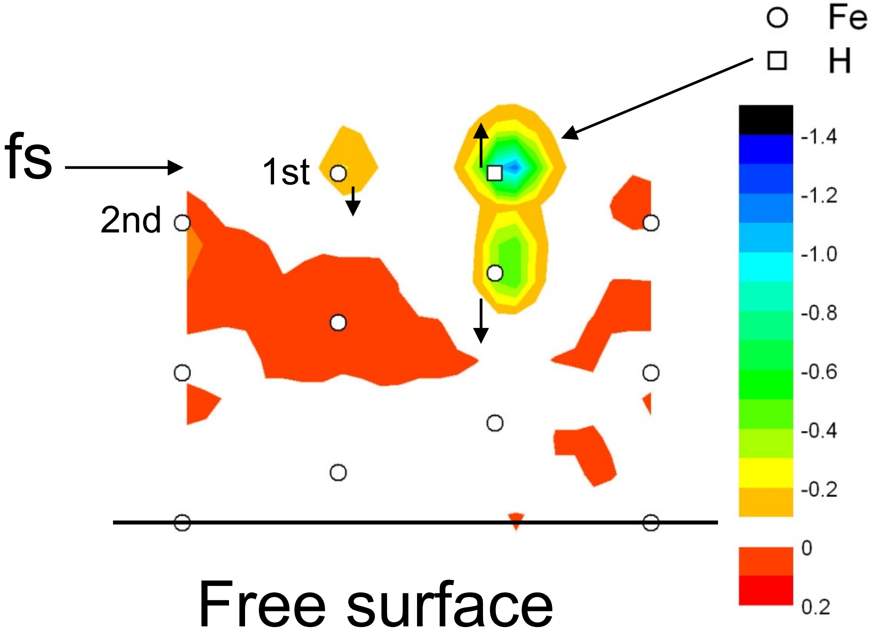
Density Functional Theory Calculations
Hydrogen Changes the Electron Density

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



$\Sigma3[1\bar{1}0](111)$

Grain Boundary



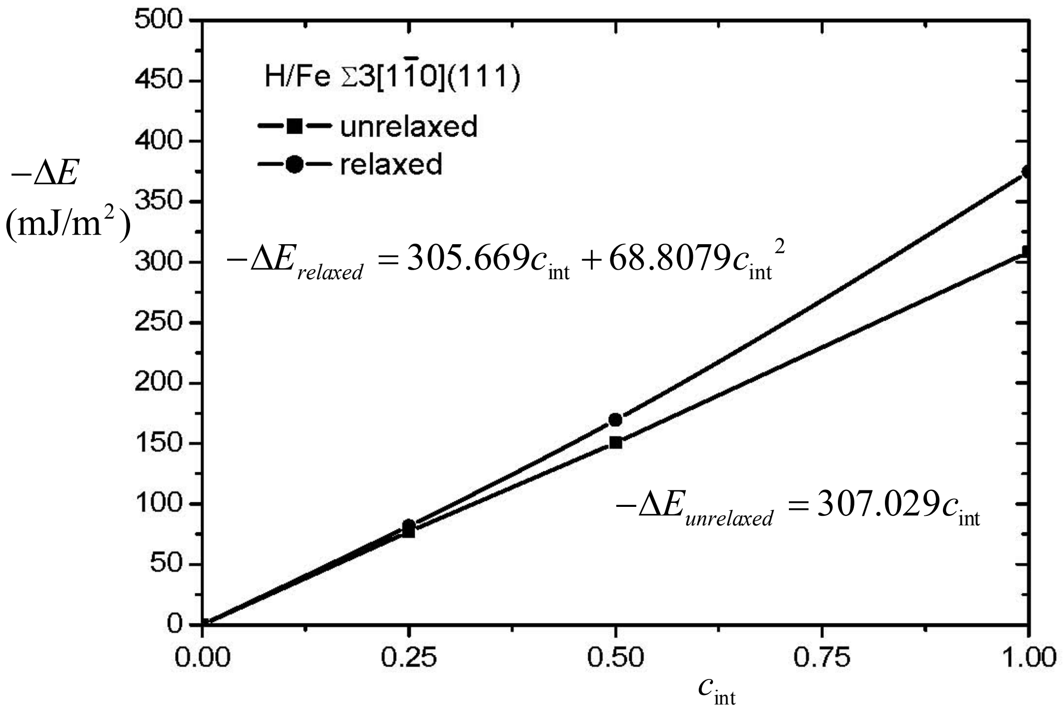
Free surface

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

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

Technical Accomplishment

From Ab-Initio to Continuum: Thermodynamics of Decohesion

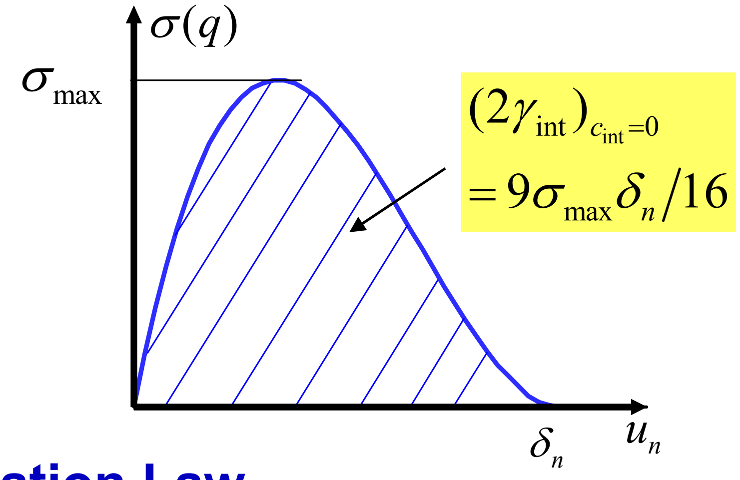


$$\Delta E = \left(E_s - 2\gamma_s\right) - \left(E_{gb} - \gamma_{gb}\right)$$

$$= \left(2\gamma_{\text{int}}\right)_{c_{\text{int}}} - \left(2\gamma_{\text{int}}\right)_{c_{\text{int}}=0}$$

$\uparrow$

$2598\ \text{mJ/m}^2$



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

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

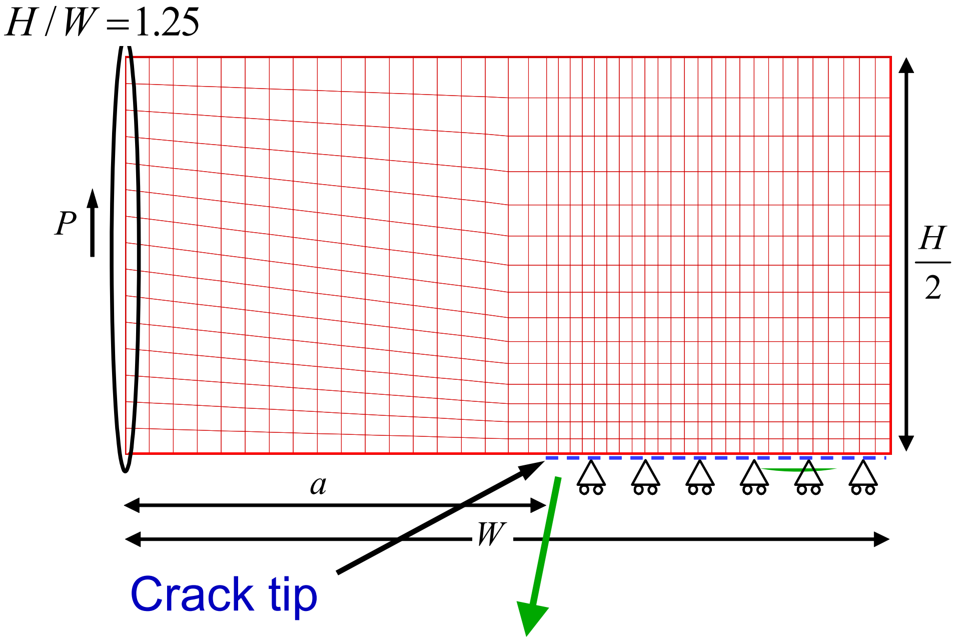
Technical Accomplishment

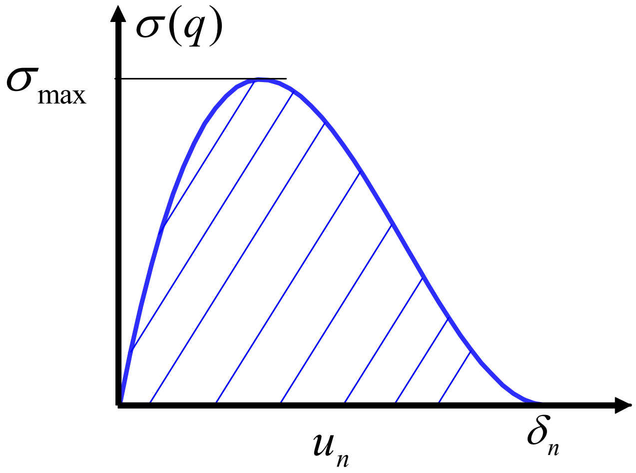
$$k = 1 + \frac{\Delta E}{2\gamma_s - \gamma_{gb}}\frac{1}{\theta_{\text{int}}} \approx 0.85$$

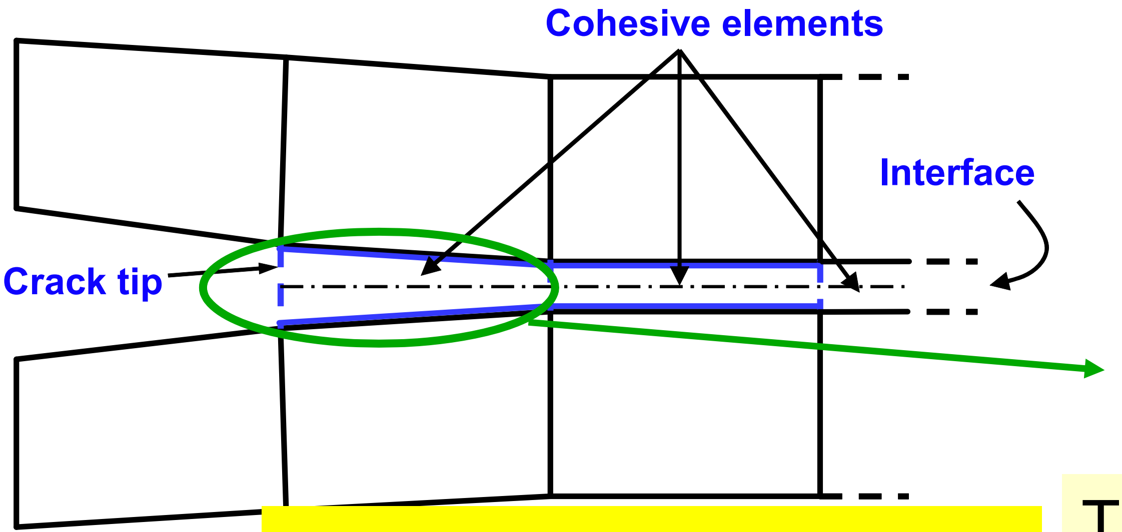
ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

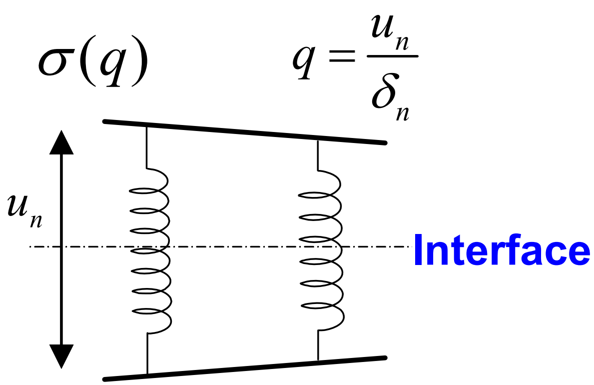
Crack Growth Simulation in Compact Tension Specimen

Developed the finite element technology to carry out crack propagation simulations





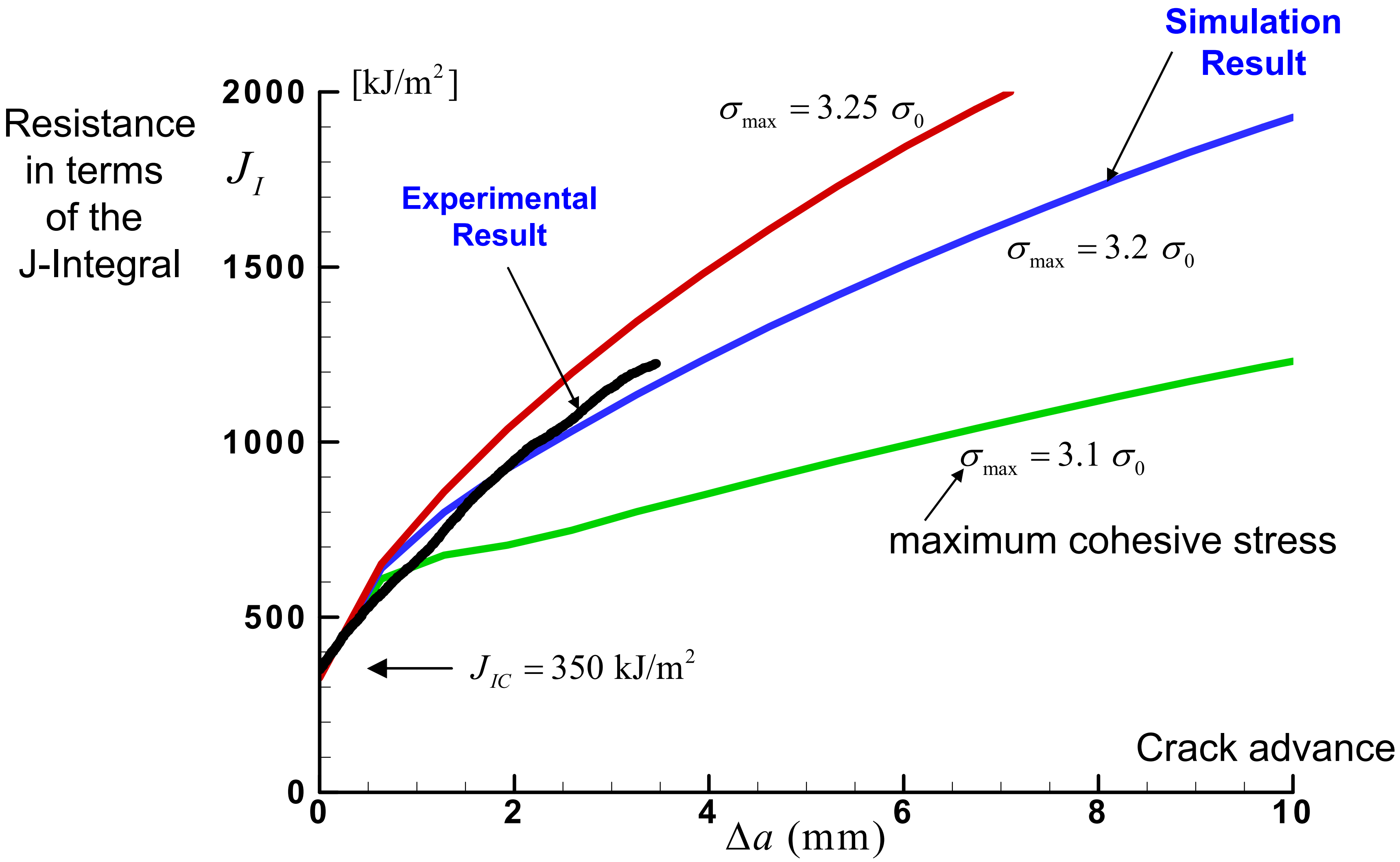




Technical Accomplishment

Traction-separation Law

Determination of Crack-Growth Resistance Curve for X100

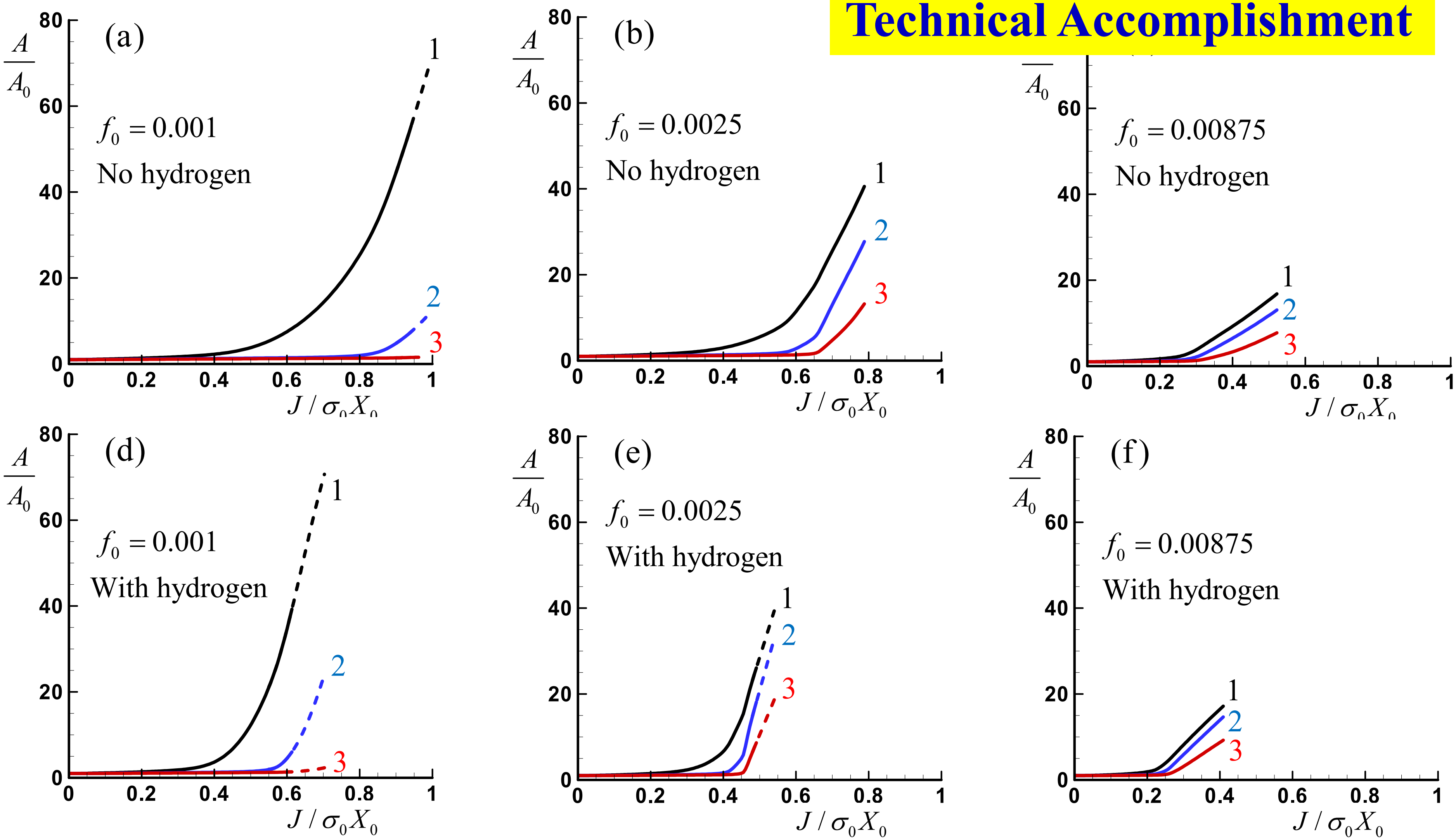


Experimental work by Sandia National Labolatories

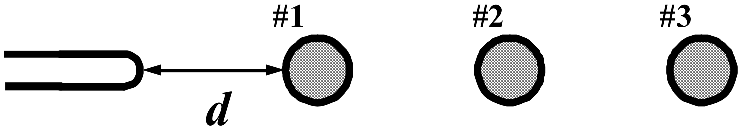
Technical Accomplishment

Void Growth at Various Initial Inclusion Volume Fractions

Technical Accomplishment



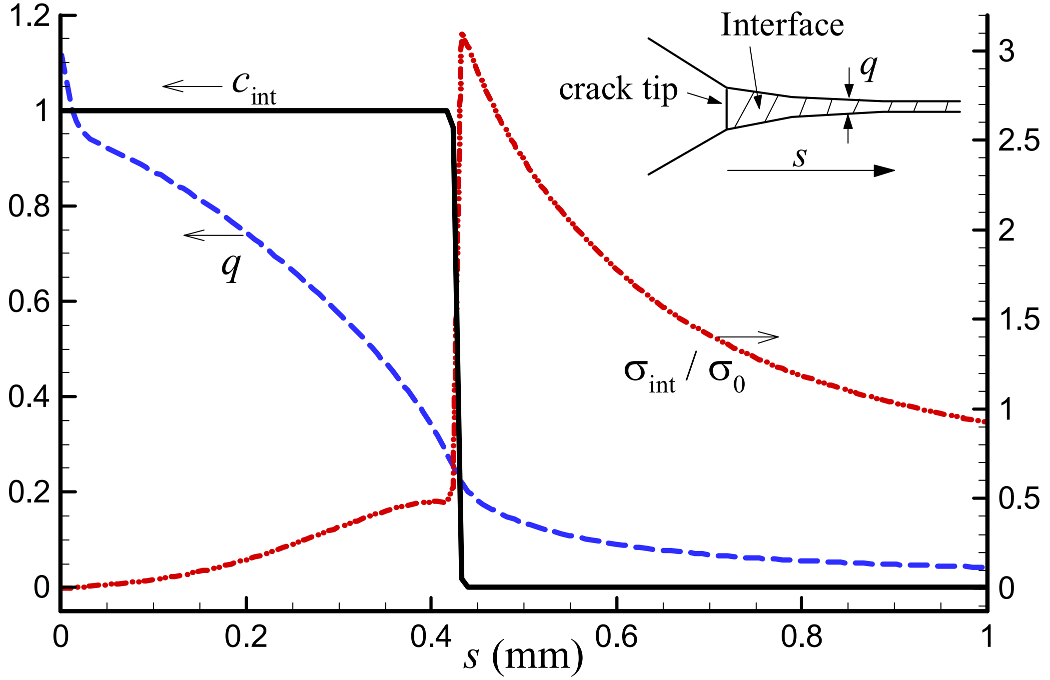
H Increases void growth rate and reduces fracture toughness

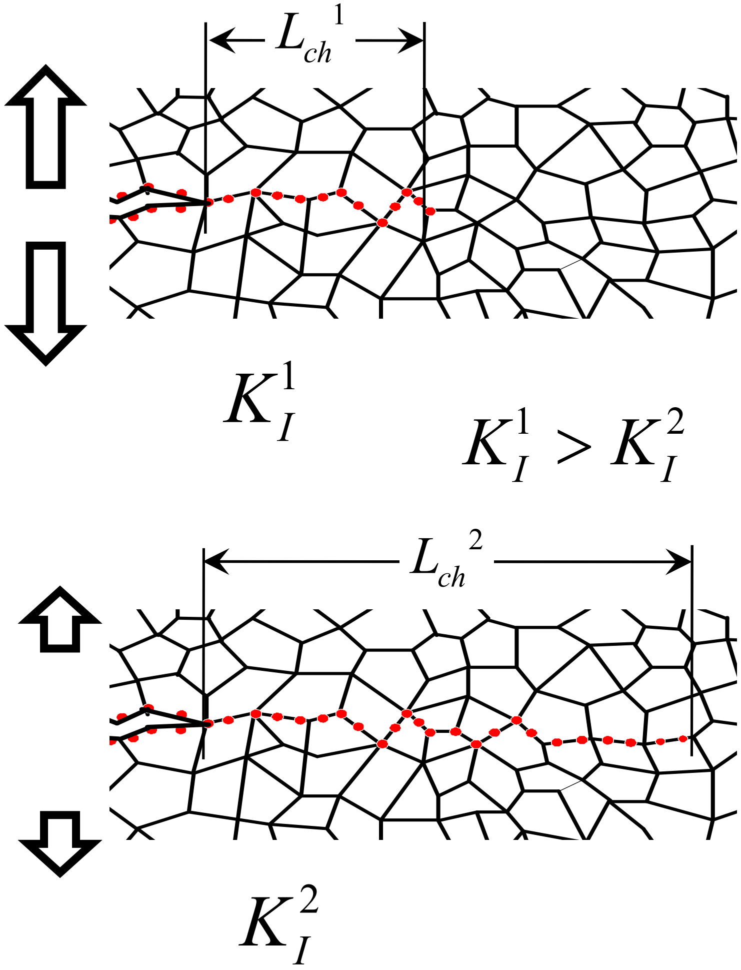


ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Crack Growth Simulations

Technical Accomplishment





- **We need a certain concentration plateau to maintain crack propagation (*characteristic length*)**
  - **Dependence on parameter κ and load K_I**