Hydrogen Embrittlement of Pipelines: Fundamentals, Experiments, Modeling

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2007 DOE Hydrogen Program Review

May 16, 2007

Project ID
#PD13_sofronis

This presentation does not contain any proprietary or confidential information

Overview

Timeline
- Project start date:5/1/05
- Project end date: 30/4/09
- Percent complete: 15%

Budget
- Total project funding: 300k/yr
  - DOE share: 75%
  - Contractor share: 25%
- Funding received in FY2005
  - $100 K
- Funding received in FY2006
  - $80 K
  - Due to reduced funding Experiments and Ab-initio calculations were on hold
- Funding for FY2007
  - $80 K

Barriers
- Hydrogen embrittlement of pipelines and remediation (mixing with water vapor?)
- Suitable steels, and/or coatings, or other materials to provide safe and reliable hydrogen transport and reduced capital cost
- Assessment of hydrogen compatibility of the existing natural gas pipeline system for transporting hydrogen

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

OAK RIDGE NATIONAL LABORATORY
U.S. DEPARTMENT OF ENERGY

SECAT SRNL SCHOTT glass made of ideas ILLINOIS UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Objectives

- 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 7MPa and loading conditions both static and cyclic (due to in-line compressors)
  - Existing natural gas network of pipeline steels
  - 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 in the presence of hydrogen
  - Hydrogen pipelines in service operate in the absolute absence of any design criteria against hydrogen-induced failure
  - There are no criteria (codes and standards) with predictive capabilities
  - Pipeline steels are extremely and dangerously susceptible to fatigue failure in the presence of hydrogen

- Illinois mechanism-based approach
  - Develop design criteria to be used for codes and standards 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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Approach

- **Tension experiments to identify macroscopic plastic flow characteristics**
- **Permeation experiments to identify diffusion characteristics**
- **Experiments (subcritical crack growth) to determine**
  - The hydrogen effect on crack initiation
  - What constitutes "safe hydrogen concentrations" at Threshold Stress Intensities
  - The 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
  - Our contention, which needs to be verified through experiment, is that embrittlement is a result of the synergistic action between decohesion at an inclusion/matrix interface (void nucleation) accompanied by shear localization in the ligament between the opening void and the tip of the crack
- **Thermodynamics and first principles calculations for the determination of the cohesive properties of particle/matrix interfaces as affected by the presence of hydrogen solutes**
- **Finite element simulations of the coupled problem of material elastoplasticity and hydrogen diffusion in the neighborhood of a crack tip accounting for stress-driven diffusion and trapping of hydrogen at microstructural defects.**
- **Development of a mechanistic model that incorporates the fracture mechanisms to establish fracture criteria with predictive capabilities**

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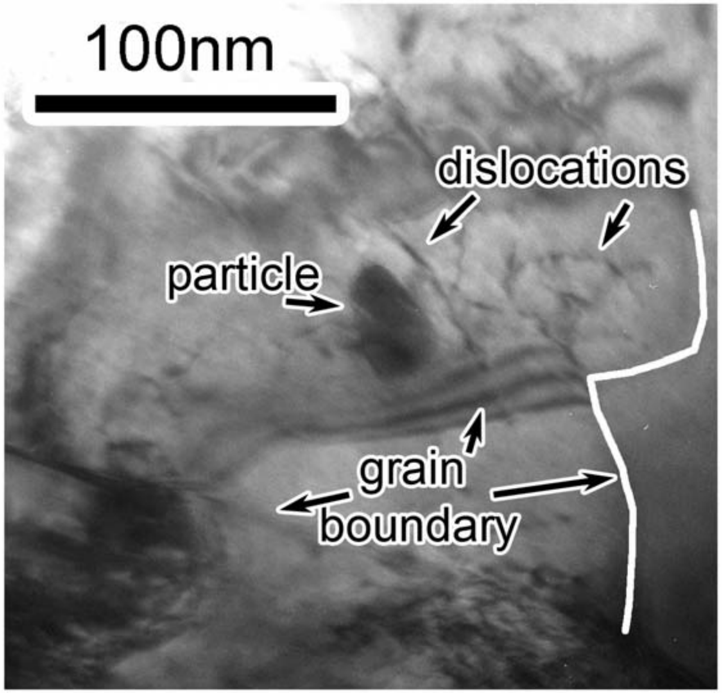
New Steel Microstructure-Oregon Steel Mills (OSM)

API Grade	C	Mn	Si	Cu	Ni	V	Nb	Cr	Ti
X70/80	0.04	1.61	0.14	0.22	0.12	0.000	0.096	0.42	0.015

Defects in microstructure, particularly precipitates, act as trap sites for hydrogen



- High dislocation density in some regions
- Irregular grain boundaries and small grains, indicative of microstructure that has not been fully recrystallized and recovered.

Relatively low precipitate density (inside the matrix)

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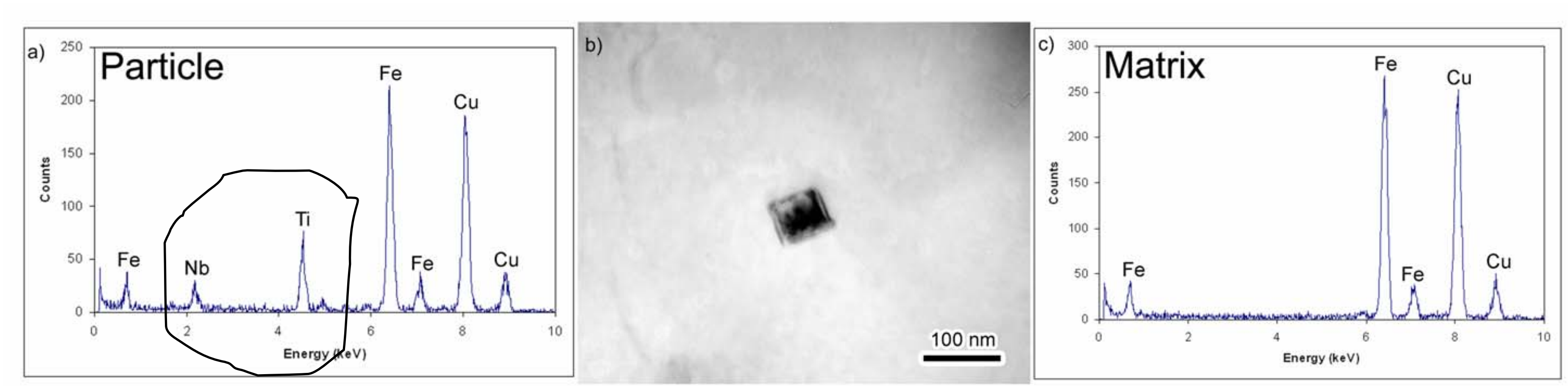
Particle Composition
Energy Dispersive Spectroscopy

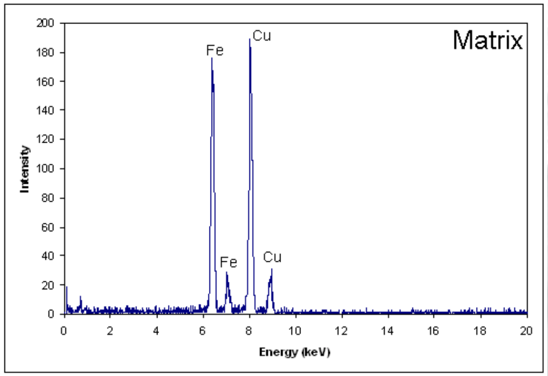


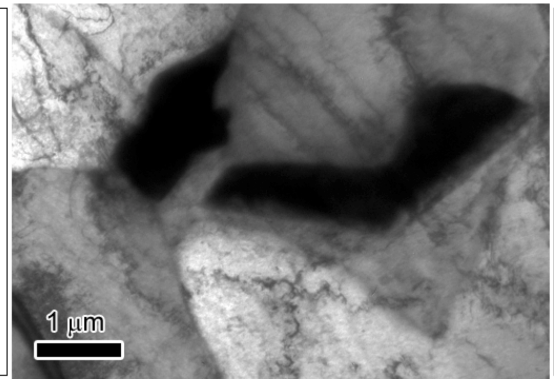
- **a) EDS spectrum from particle**
- **b) Bright field TEM image of typical rectangular particle**
- **c) EDS spectrum from matrix**

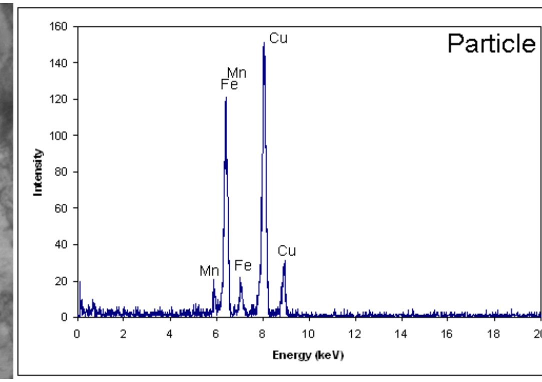
- **EDS analysis of fine precipitate inside ferrite grain suggests that precipitate is composed of Ti and Nb**

(window detector: C, N, O not detected)

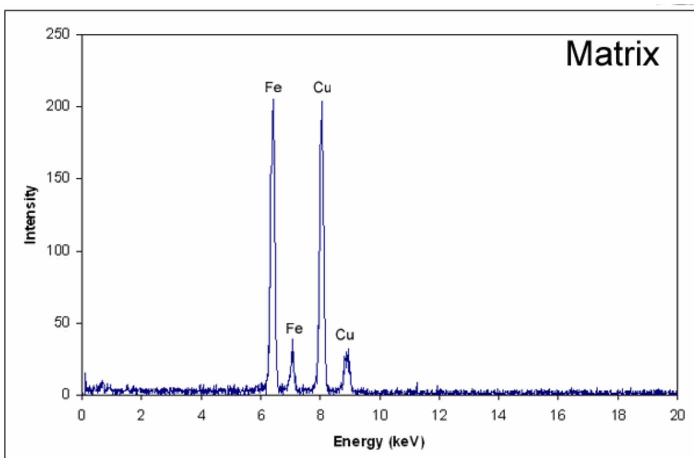
Steel Microstructure-Air Liquide Pipeline

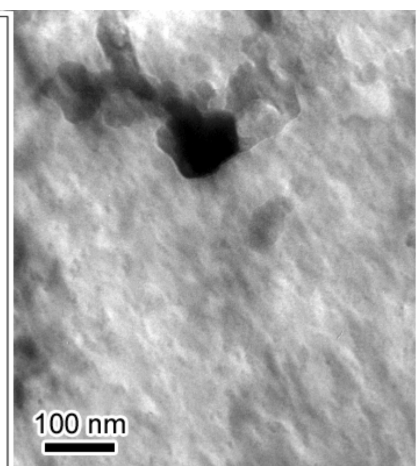


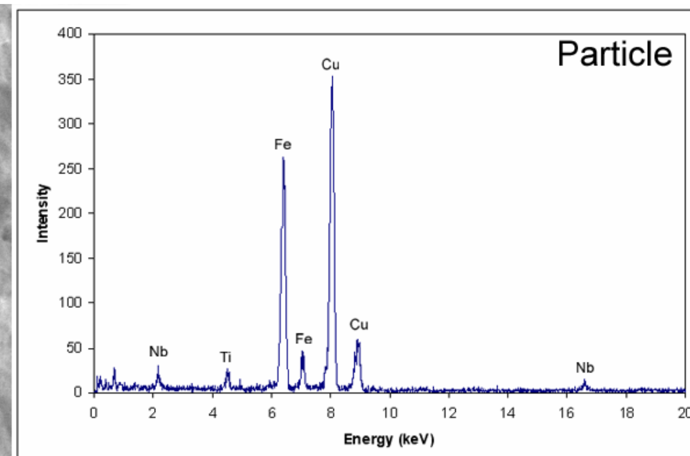




Large intergranular particles (cementite)







Small intragranular particles (carbides with Nb and Ti)

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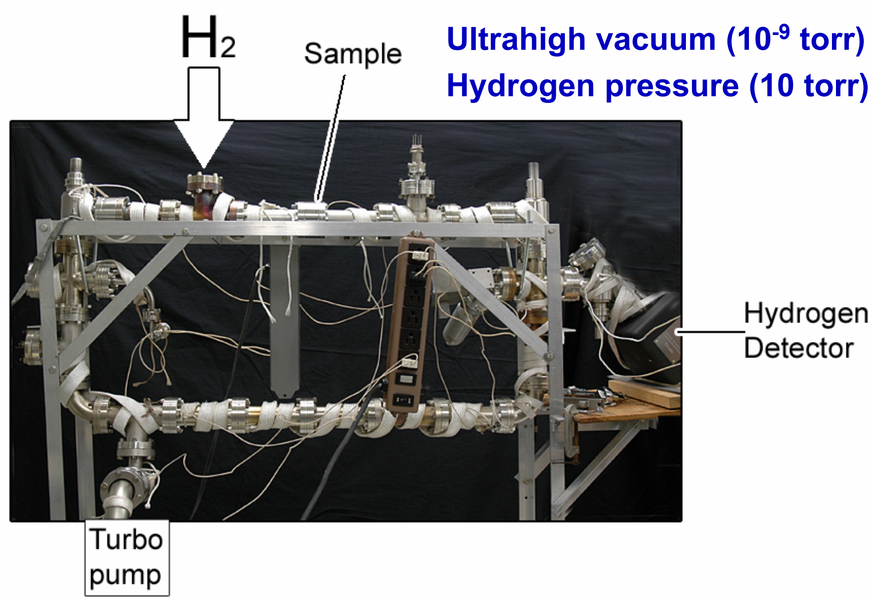
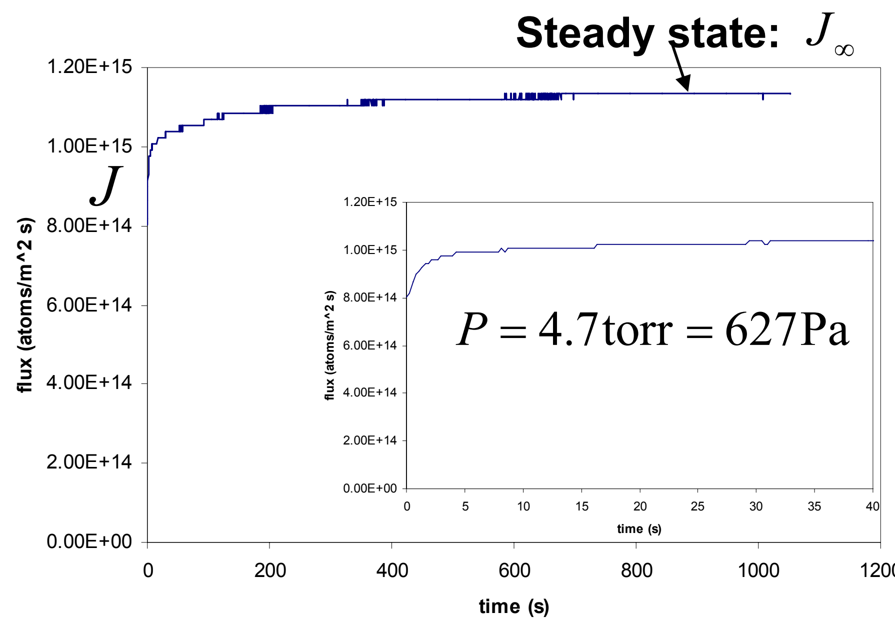
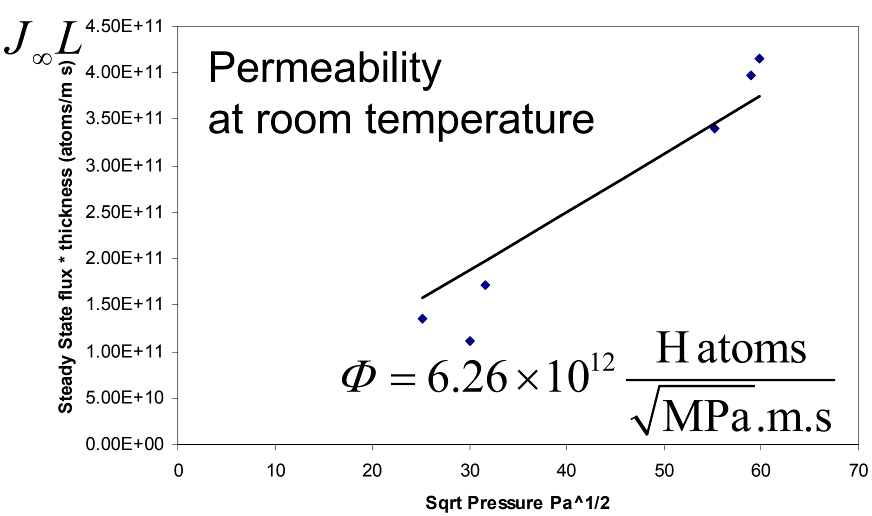
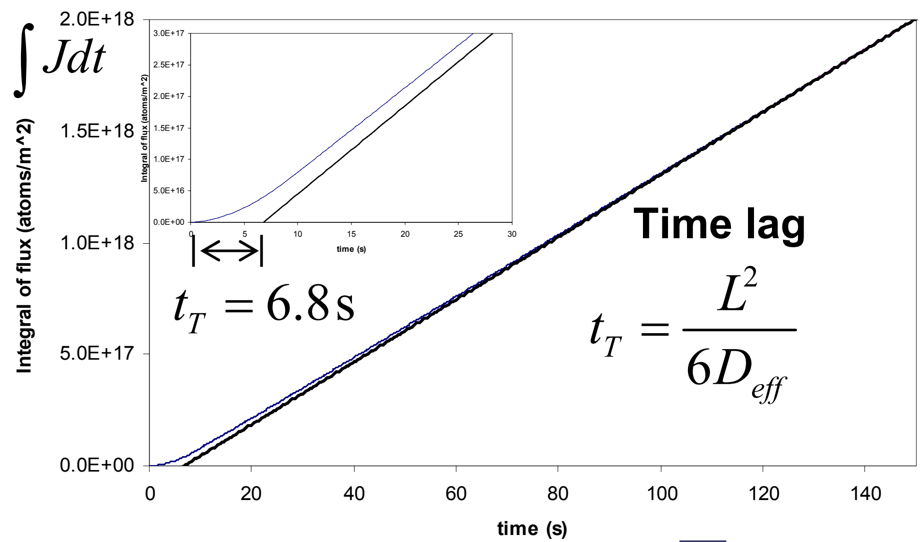
Hydrogen Permeation Measurements







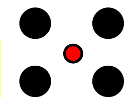


- Oregon Steel Mills sample: thickness $L = 120\,\mathrm{microns}$
- room temperature

Hydrogen Transport Analysis

Diffusing hydrogen resides at

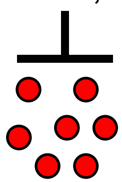
- **Normal Interstitial Lattice Sites (NILS)** $C_L = \beta\theta_L N_L$

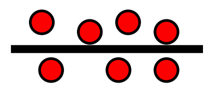


θ_L = NILS occupancy
β = number of NILS per solvent atom.
N_L = number of solvent atoms/m^3.

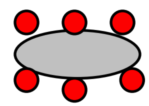
- **Trapping Sites** $C_T = \alpha\theta_T N_T$
  - Microstructural heterogeneities such as dislocations, grain boundaries, inclusions, voids, interfaces, impurity atom clusters

dislocations





Grain boundaries



inclusions

θ_T = trap occupancy
α = number of sites per trap.
N_T = number of traps/m^3.

Hydrogen populations in NILS and trapping sites are assumed to be in equilibrium according to Oriani's theory

$$\frac{\theta_T}{1-\theta_T} = \frac{\theta_L}{1-\theta_L}\exp\left(\frac{W_B}{RT}\right)$$

W_B = Trap binding energy
T=Temperature
R=gas constant

- Trap density may evolve dynamically with plastic straining

Hydrogen Transport Equation

$$\frac{D}{D_{eff}}\frac{dC_L}{dt} = DC_{L,ii} - \left(\frac{DV_H}{3RT}C_L\sigma_{kk,i}\right)_{,i} - \alpha\theta_T\frac{\partial N_T}{\partial\varepsilon^p}\frac{d\varepsilon^p}{dt}$$

d/dt = time differentiation
C = Hydrogen concentration
D = diffusion coefficient
D_{eff} = Effective diffusion
$= D/(1+\partial C_T/\partial C_L)$ accounting for trapping
σ_{kk} = hydrostatic stress
ε^p = plastic strain
V_H = partial molar volume of H
N_T = trap density
$(\ )_{,i} = \partial(\ )/\partial x_i$

- Note the effect of stress and plastic strain

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Material Data (OSM)

$$S = 6.54696 \times 10^{18} \frac{\text{H atoms}}{\text{m}^3 \sqrt{\text{Pa}}}$$

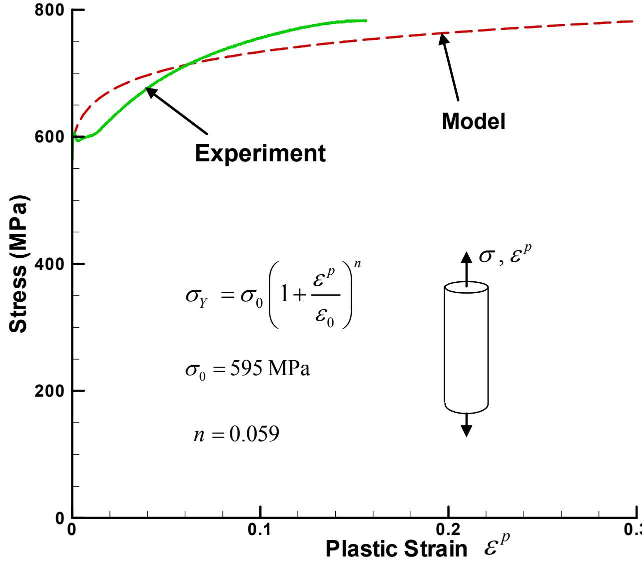
$$C_0 = 2.084 \times 10^{21} \ \text{H atom / m}^3 \qquad P = 1 \ \text{atm}$$

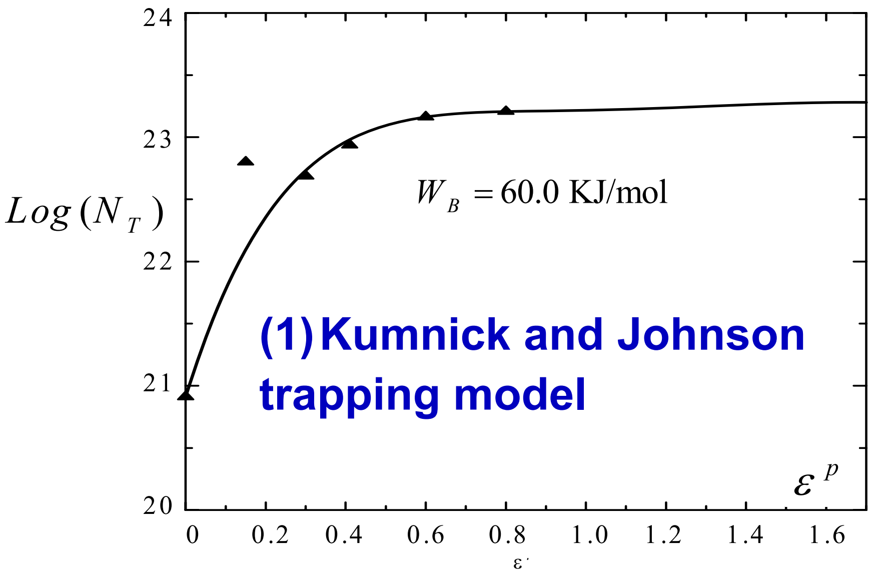
$$C_0 = 2.65932 \times 10^{22} \ \text{H atom / m}^3 \qquad P = 15 \ \text{MPa}$$

Lattice diffusion coefficient

$$D = 1.271 \times 10^{-8} \ \text{m}^2/\text{s}$$

Stress-strain





(1) Kumnick and Johnson trapping model

(2) Dislocation trapping modeling

$$N_T = \frac{\sqrt{2}\rho}{a} \qquad W_B = 20.2 \ \text{KJ/mol}$$

$$\rho = \begin{cases} \rho_0 + \dfrac{\gamma}{0.15}\varepsilon^p & \varepsilon^p \le 0.15 \\ \text{const.} & \varepsilon^p > 0.15 \end{cases}$$

$$\rho_0 = 10^{10} m^{-2}, \ \gamma = 10^{16} m^{-2}$$

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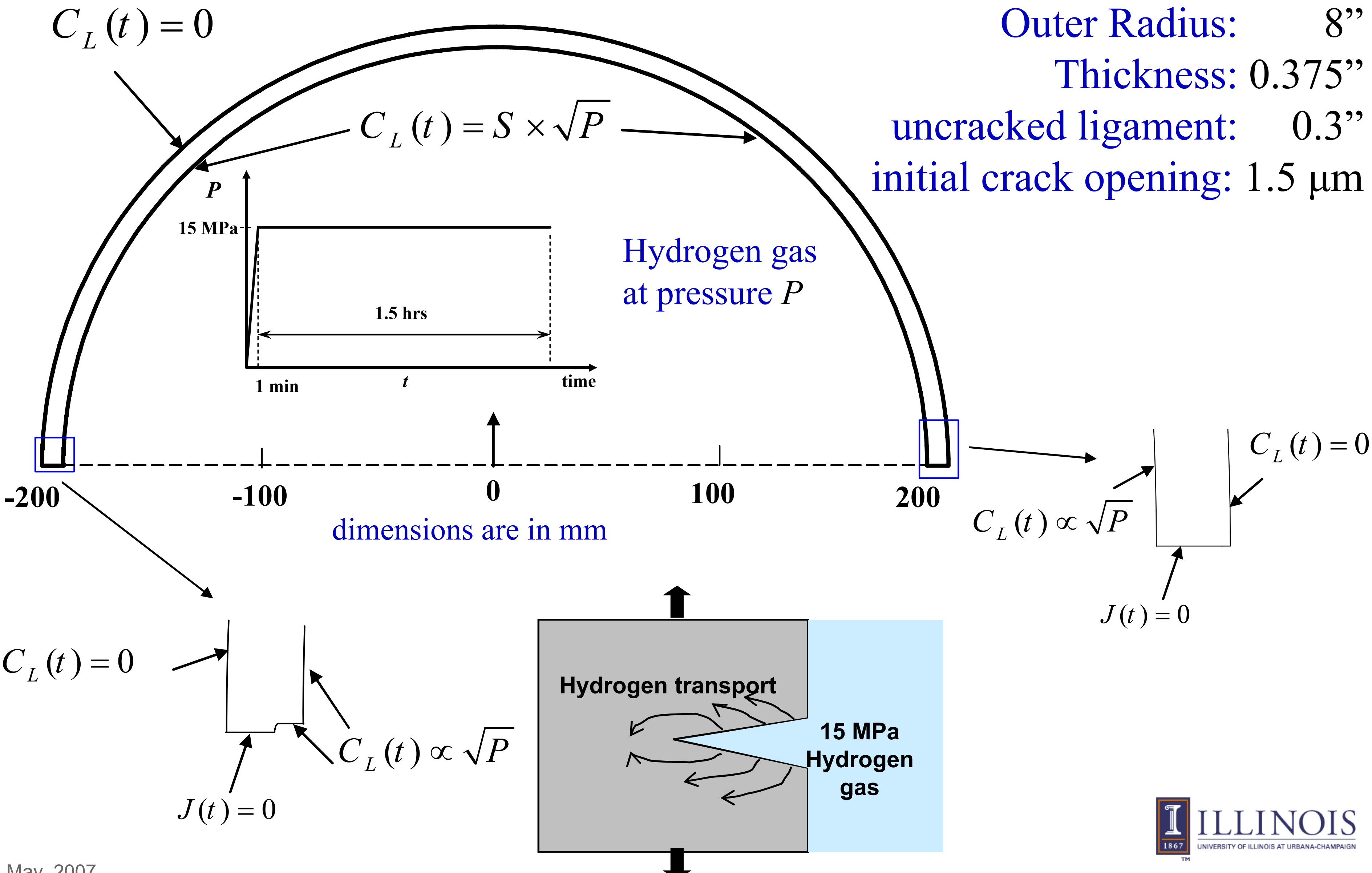
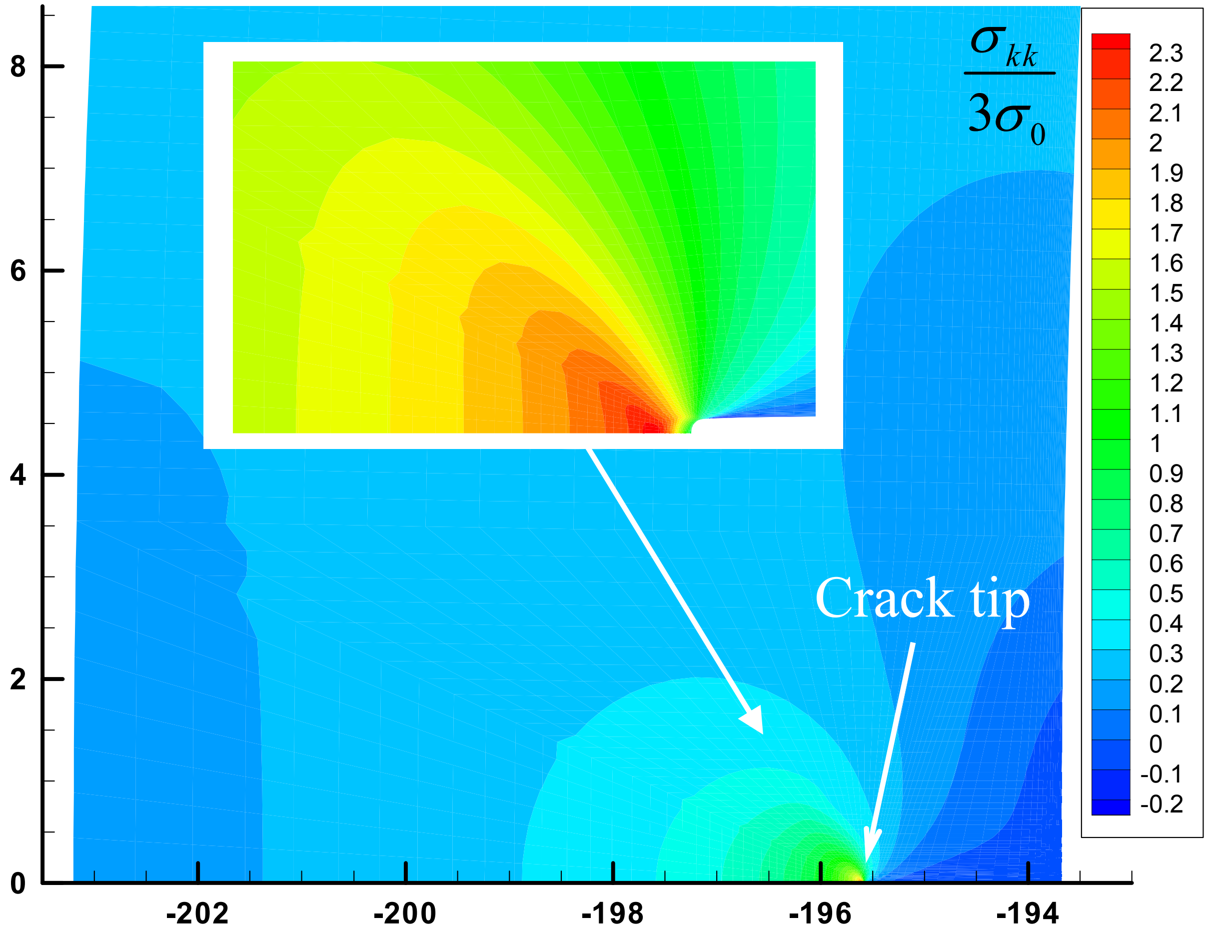
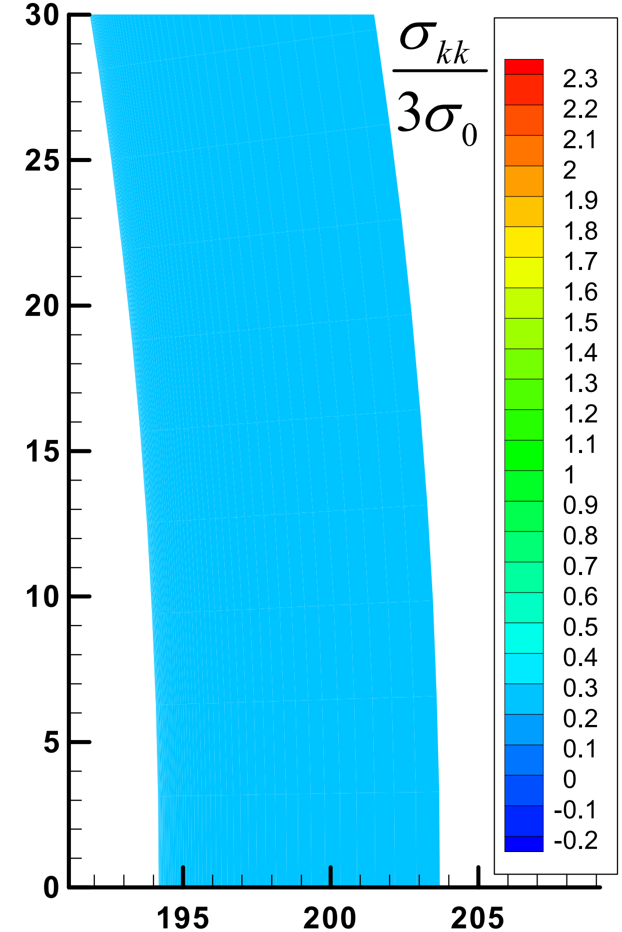
Cracked Pipeline: Problem Statement

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



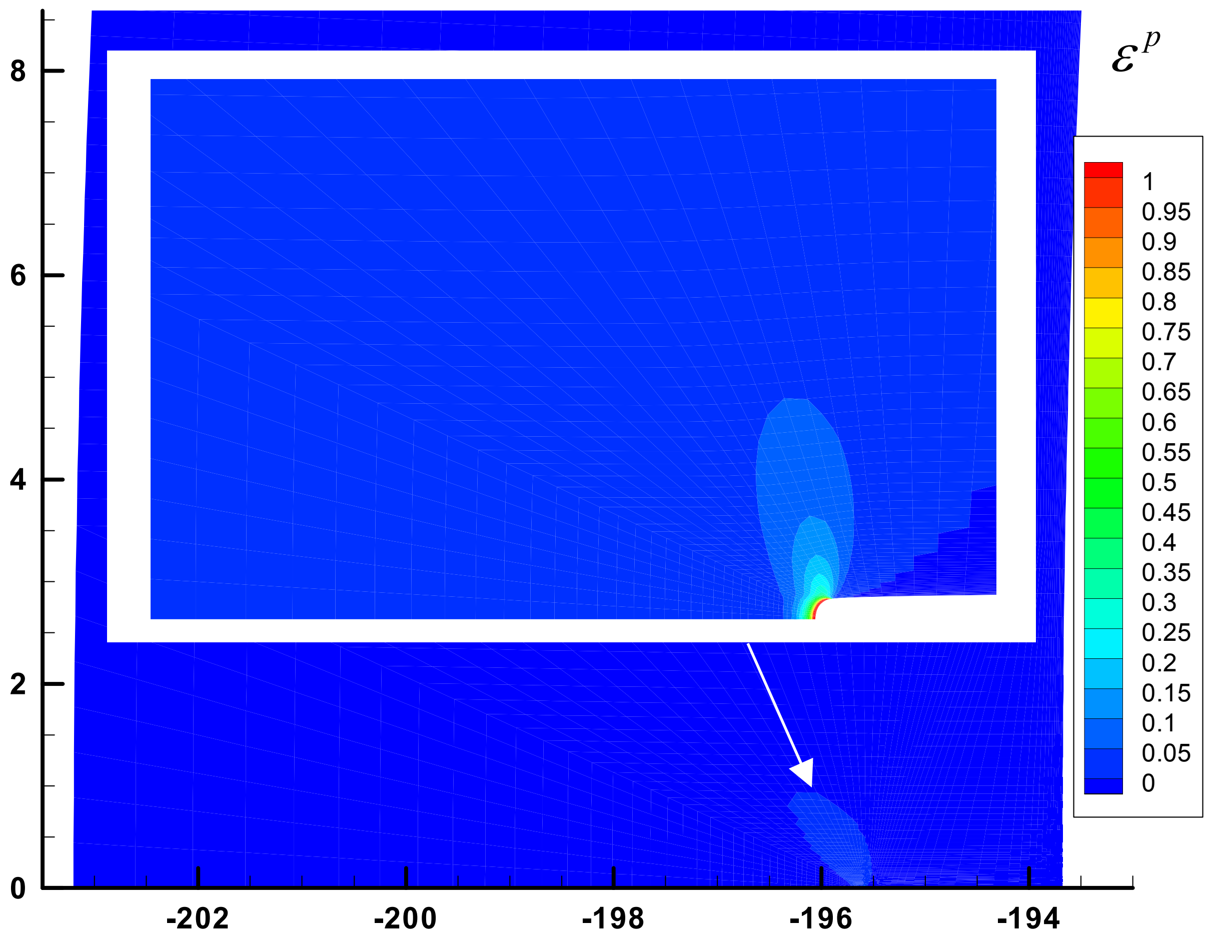
Hydrostatic Stress at Pressure 15 MPa

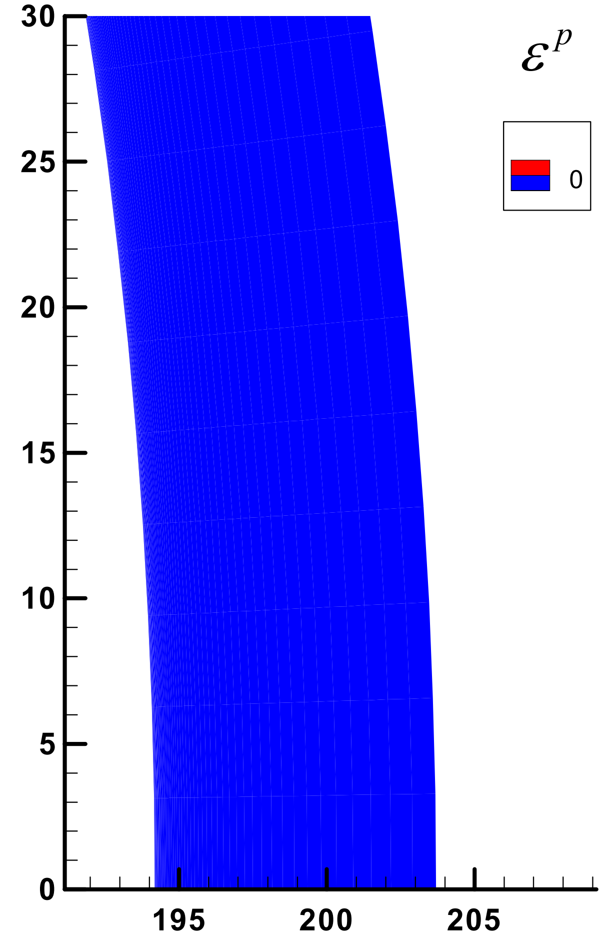




Geometric dimensions are in mm

Plastic Strain at Pressure 15 MPa





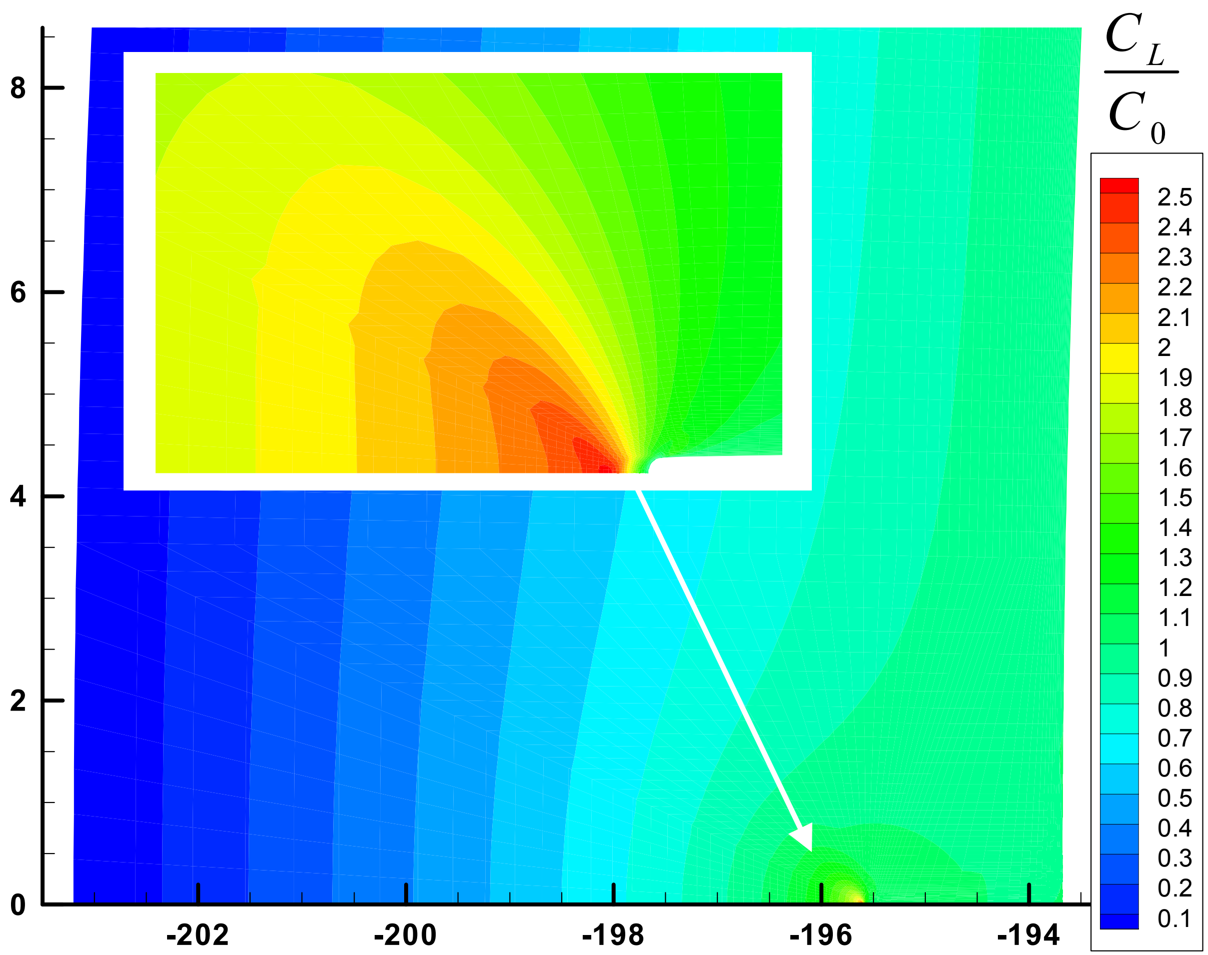
Geometric dimensions are in mm

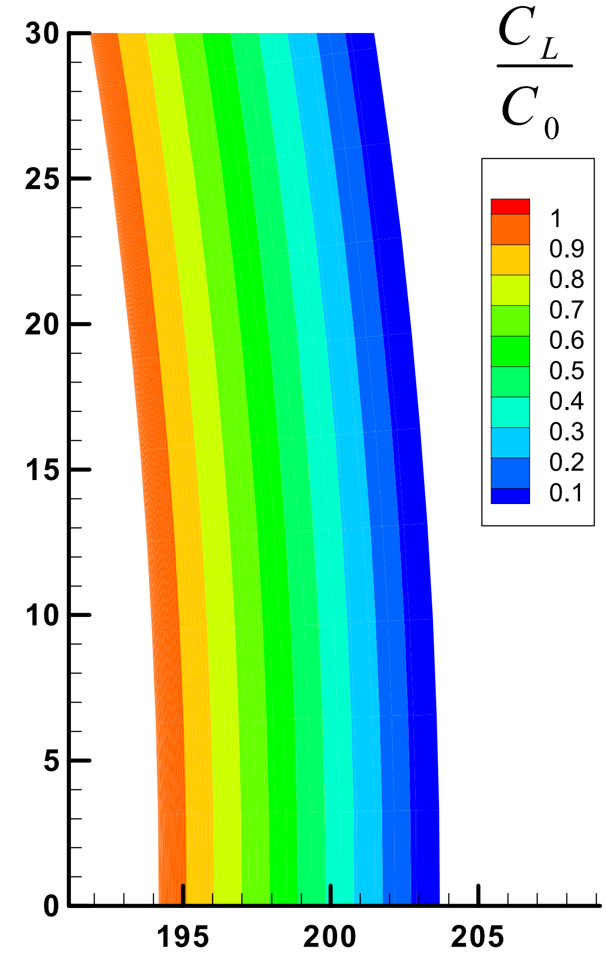
Lattice Hydrogen Concentration at Steady State

Kumnick and Johnson trapping model

Time to steady-state: 1.5 hrs

$t_{ss} = 8 \text{ min}$





$C_0 = 2.65932 \times 10^{22} \text{ H atom / m}^3$ $\quad P = 15 \text{ MPa}$

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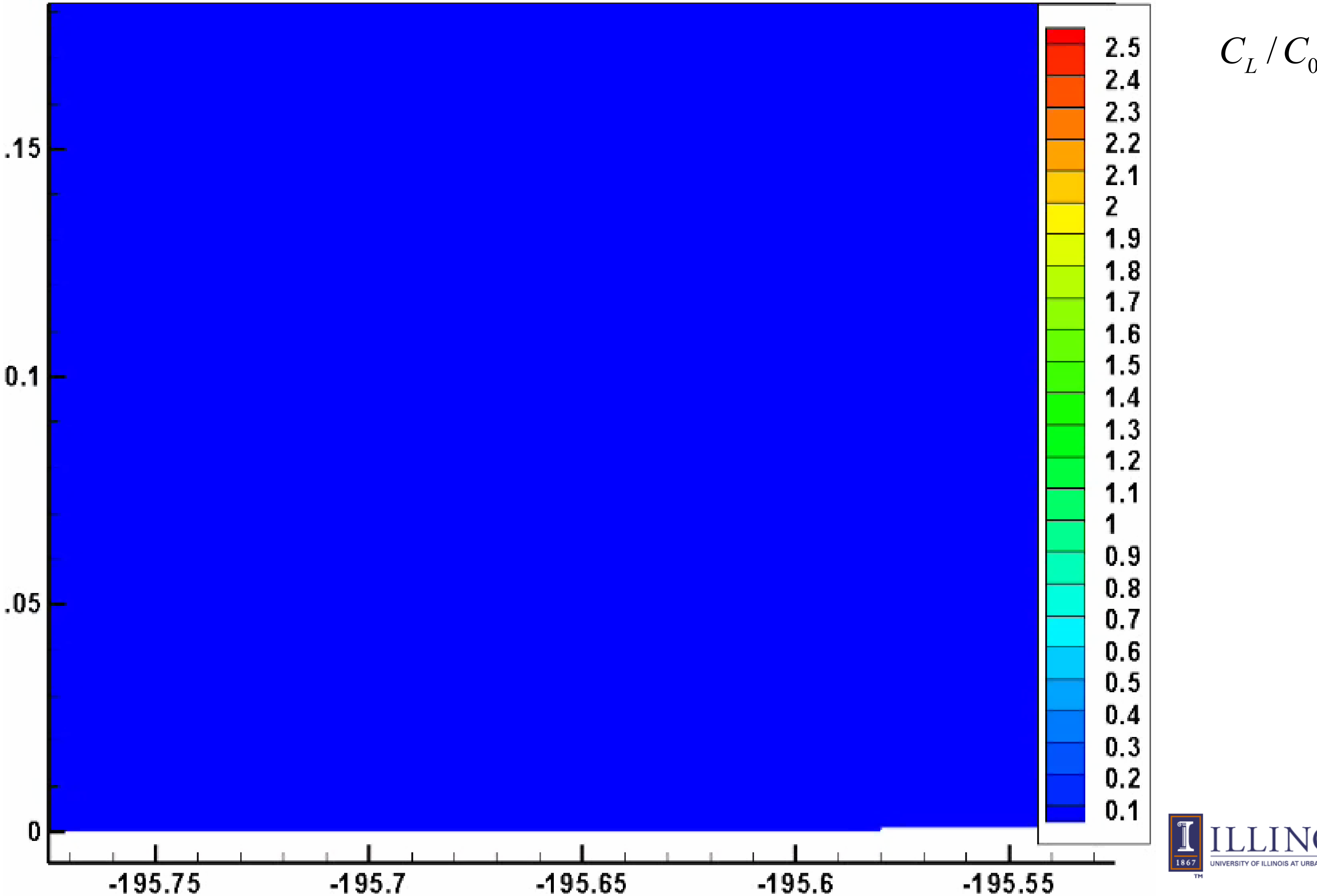
Transient to Steady State - Lattice Concentration



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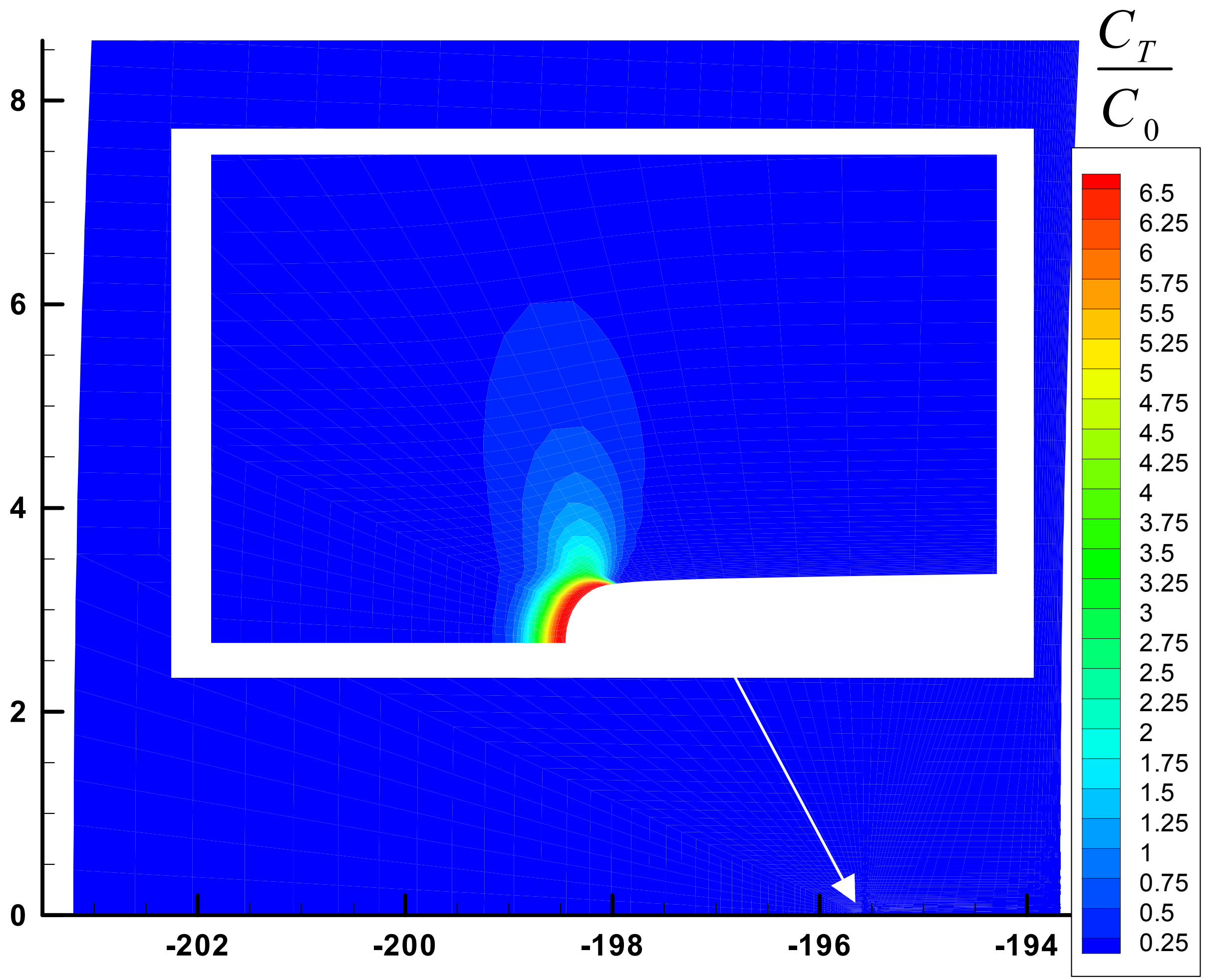
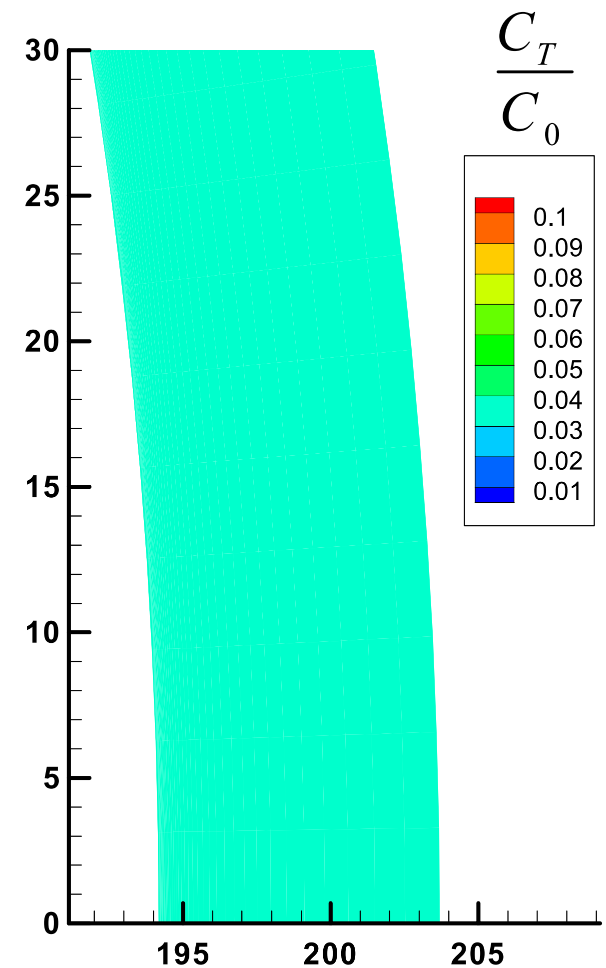
Trapped Hydrogen Concentration at Steady State

Kumnick and Johnson trapping model





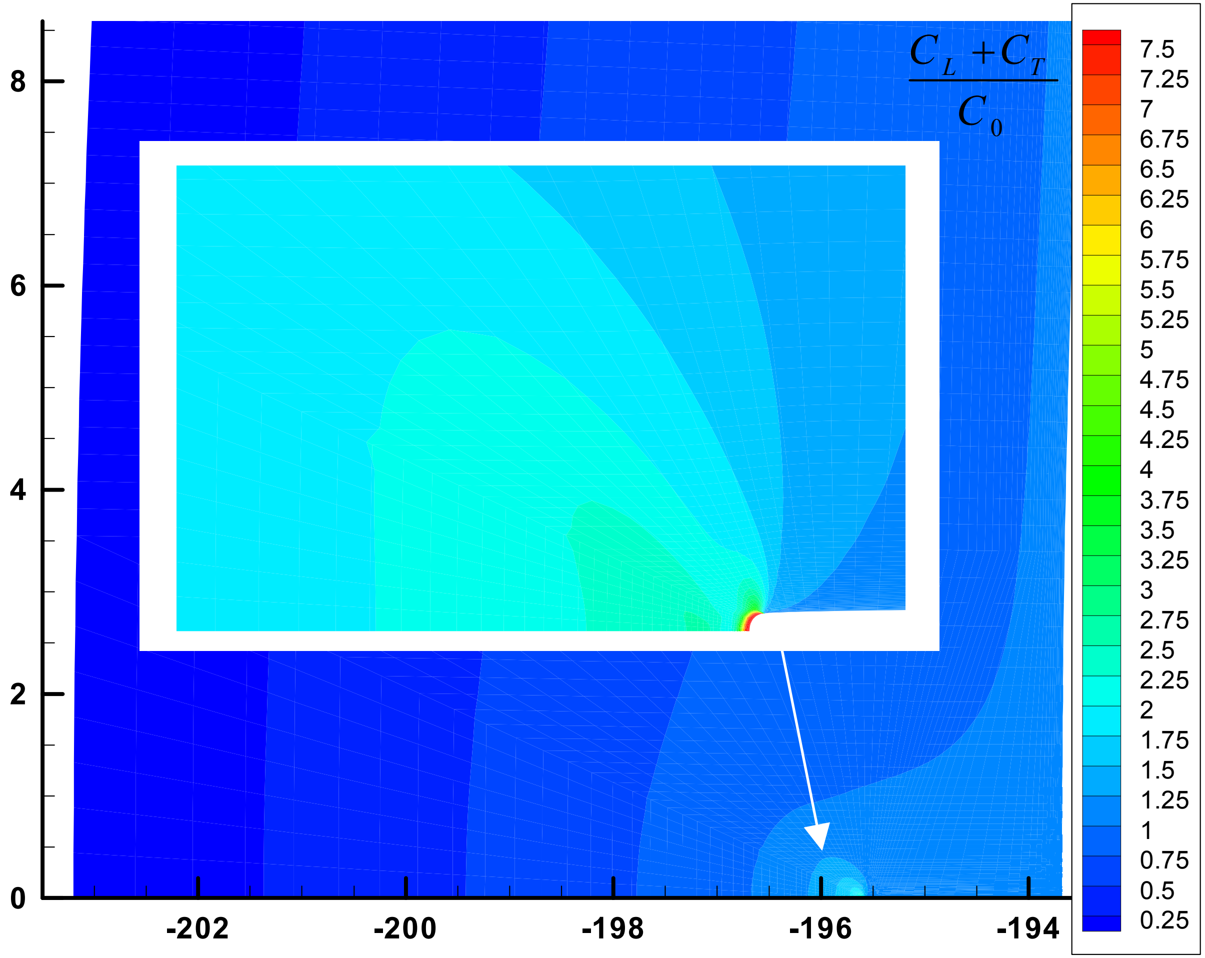
$C_0 = 2.65932 \times 10^{22}\ \mathrm{H\,atom/m^3}$ $\qquad P = 15\ \mathrm{MPa}$

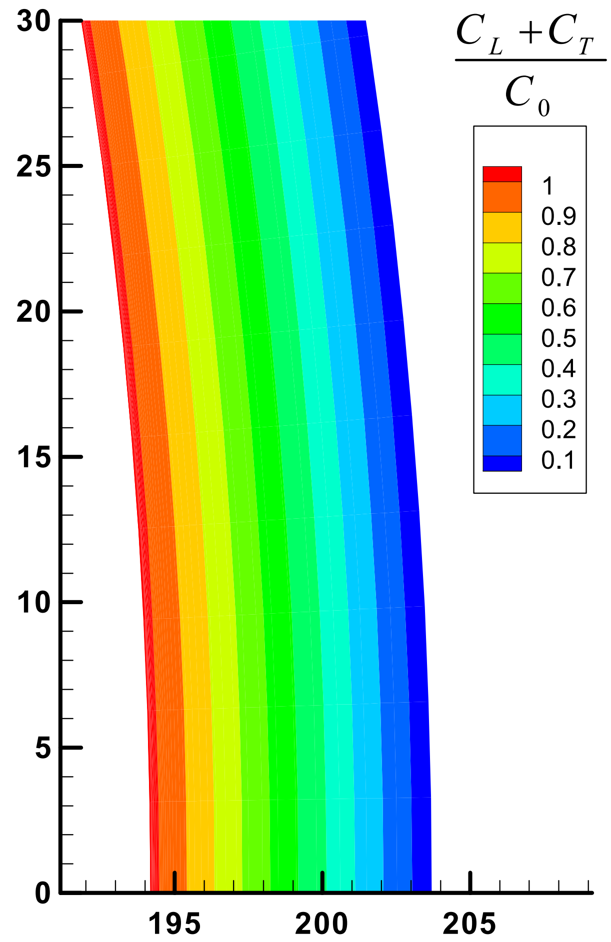
Total Hydrogen Concentration at Steady State

Kumnick and Johnson trapping model

Time to steady-state is 1.5 hrs

$t_{ss} = 8 \text{ min}$

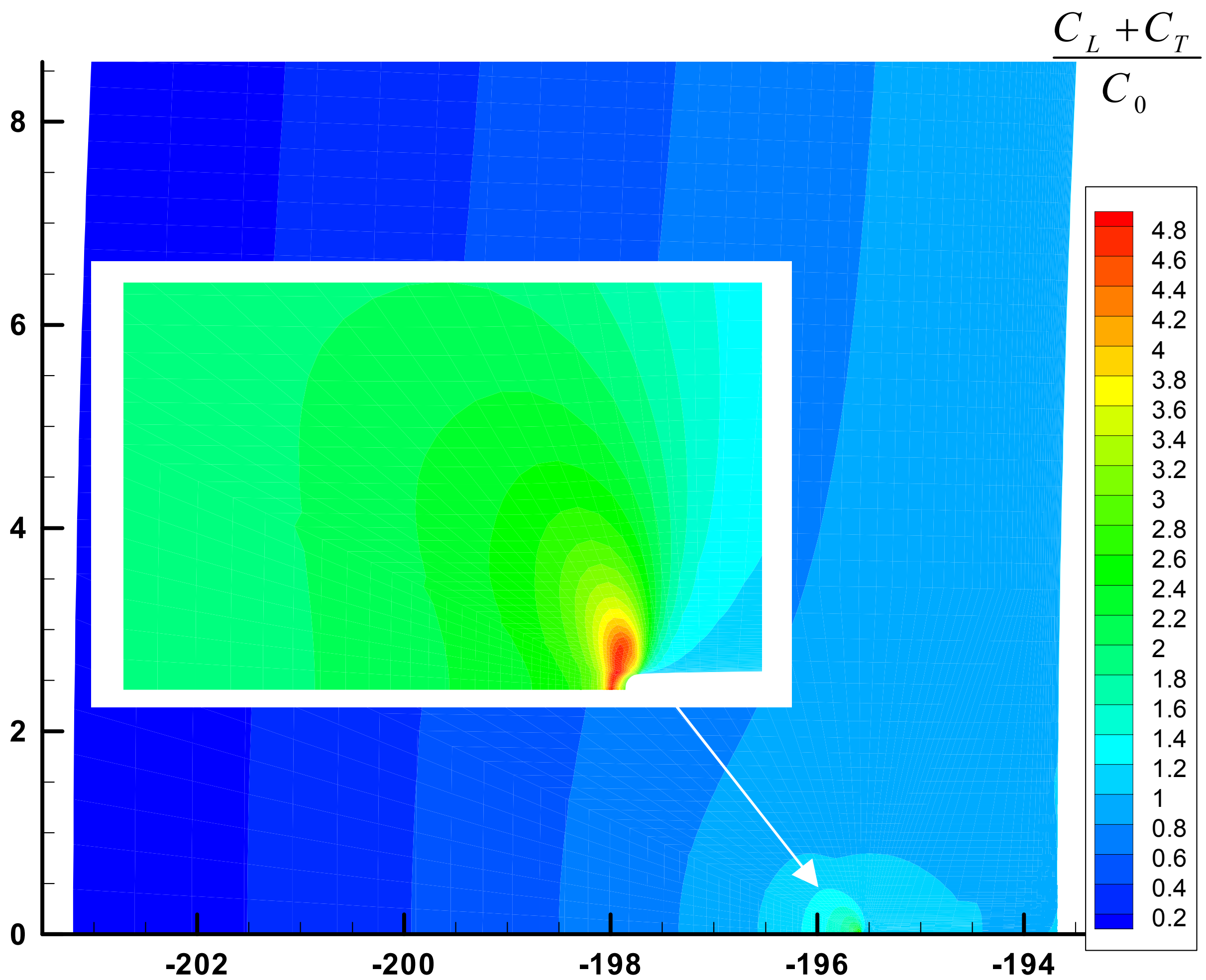


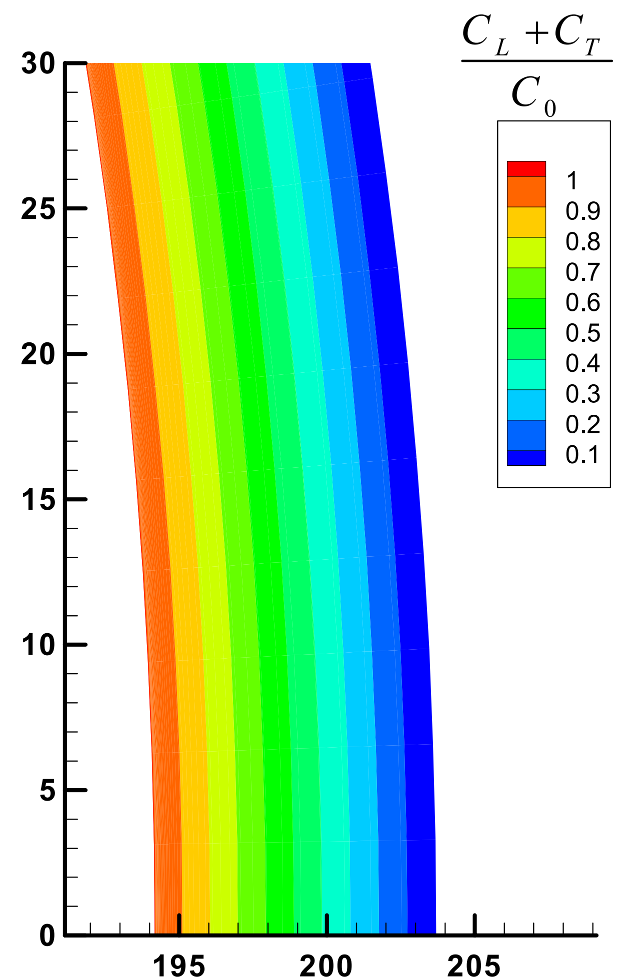


$C_0 = 2.65932 \times 10^{22} \text{ H atom / m}^3$ $\quad P = 15 \text{ MPa}$

Total Hydrogen Concentration at Steady State

Dislocation trapping model





$C_0 = 2.65932 \times 10^{22}$ H atom / m^3 $\quad$ $P = 15$ MPa

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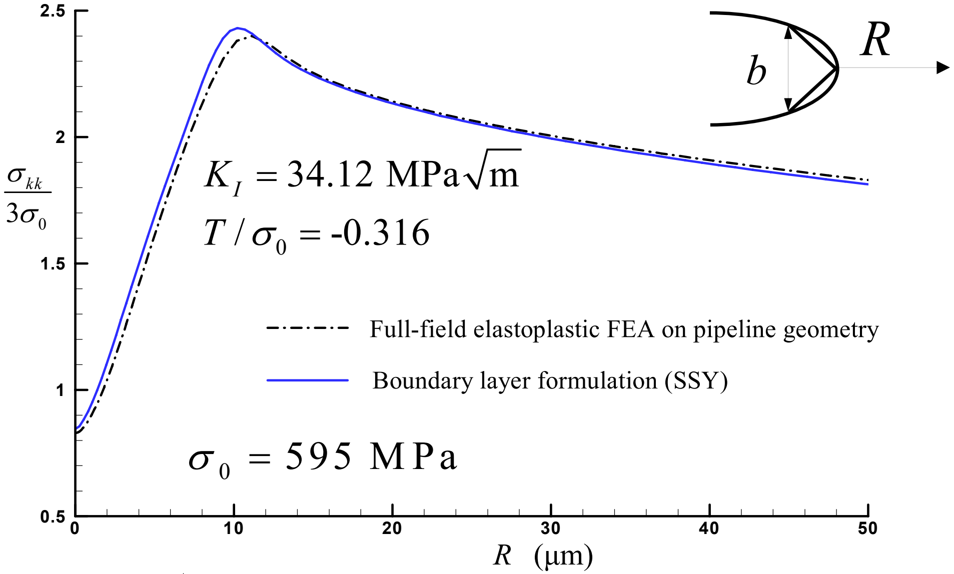
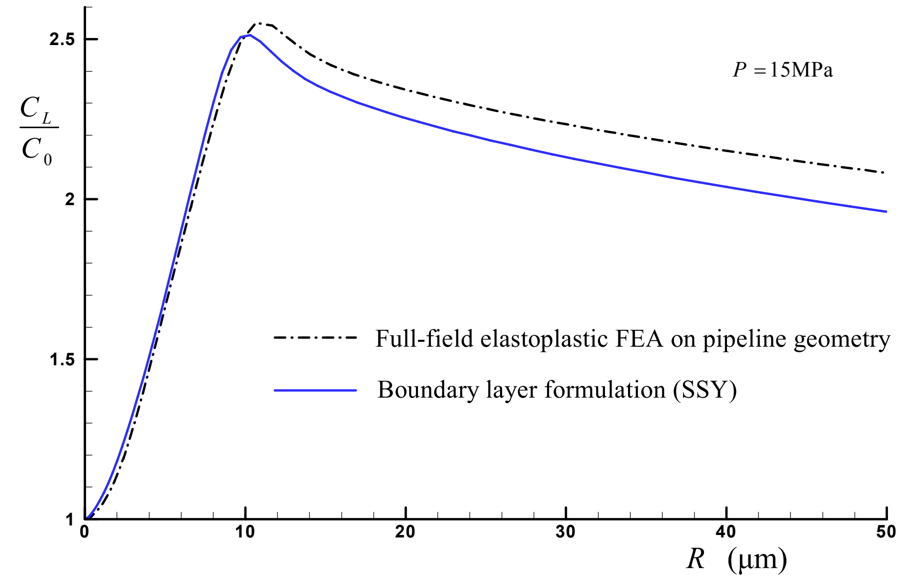
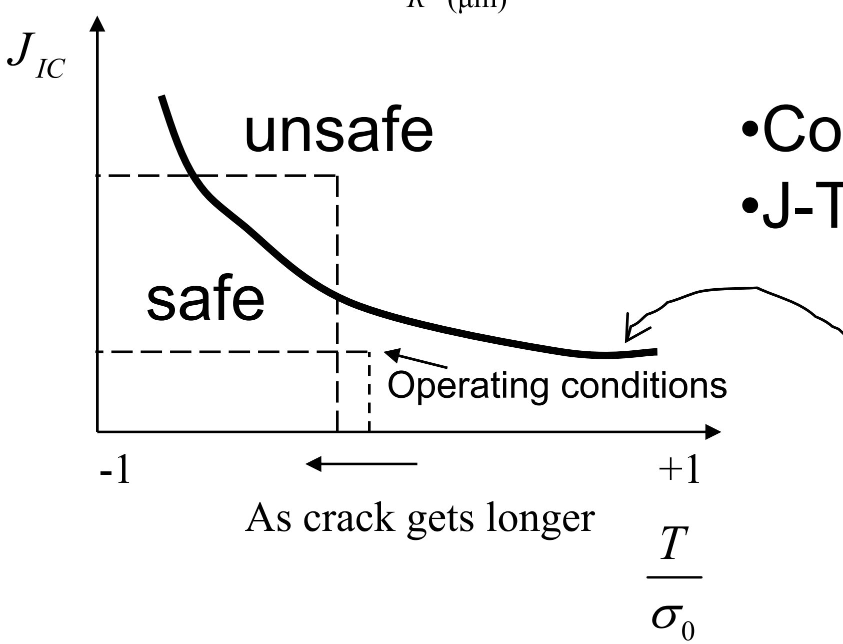
Fracture Mechanics Assessment







- Constraint based fracture mechanics
- J-T controlled fracture

The deep-notch toughness data in the presence of hydrogen need not necessarily lead to a conservative fracture toughness assessment for shallow cracked geometries as is commonly assumed in the absence of hydrogen

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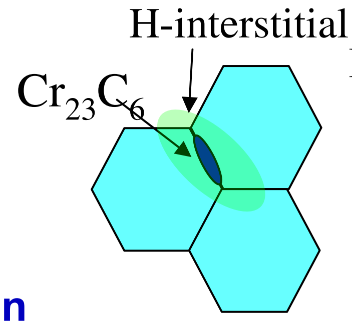
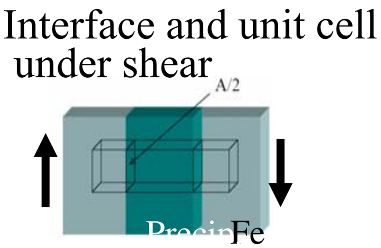
Accomplishments vs. Project Milestones and Objectives





- **Design of permeation measurement system**
  - Complete. Measurements are underway
- **Microstructure characterization**
  - Ongoing for both new and existing pipeline steels
- **Macroscopic flow characteristics in uniaxial tension of new material microstructures (micro-alloyed steels)**
  - Complete in the absence of hydrogen. Experiments in the presence of hydrogen are planned this summer (it depends on the funding situation)
- **Development of finite element code for transient stress-driven hydrogen transport analysis coupled with large-strain elastoplastic deformation**
  - Complete. Code has been tested and validated against analytical solutions and code at Los Alamos National Laboratory
- **Simulation to the problem of hydrogen transport at a cracked pipeline**
  - Ongoing
- **Collaboration with ASME on validating the proposed safety factors to be used for the design of pipeline steels under a range of hydrogen pressures**
  - Done (Hayden Liu)
- **Validation of ab-initio calculations for decohesion energy calculations**
  - Complete. Unrelaxed binding energies (eV) and their differences for H in Fe grain boundary (GB) and free surface (FS) calculated by VASP PAW-GGA and FLAPW (Zhong *et al*., 2000)
  - Continuing research in this area depends on project funding

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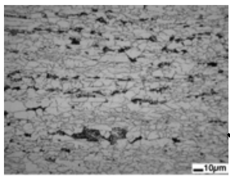
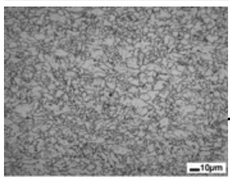
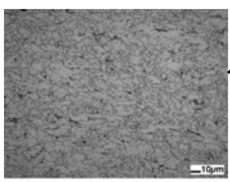
Future Work

Experiment

- **Establish the diffusion characteristics of existing and new pipeline steel microstructures**
  - Existing pipeline steel samples provided by Air Liquide and Air Products. Specimens are in our laboratory
  - New micro-alloyed steels (new microstructures) provided by Oregon Steel Mills through DGS Metallurgical Solutions, Inc.







	API/ Grade	C	Mn	Si	Cu	Ni	V	Nb	Cr	Ti	
A	X70	0.08	1.53	0.28	0.01	0.00	0.050	0.061	0.01	0.014	Typical natural gas pipeline steel
B	X70/80	0.05	1.52	0.12	0.23	0.14	0.001	0.092	0.25	0.012	Ferrite/acicular ferrite
C	X70/80	0.04	1.61	0.14	0.22	0.12	0.000	0.096	0.42	0.015	Ferrite/acicular ferrite
D	X52/60	0.03	1.14	0.18	0.24	0.14	0.001	0.084	0.16	0.014	Ferrite/low level of pearlite

  - **Collaboration with ORNL and Schott North America for coating of our samples**

- **Determine uniaxial tension macroscopic flow characteristics in the presence of hydrogen**

- **Carry out fracture testing: Collaboration with Sandia, Livermore**

- **SEM and TEM studies on existing and new pipeline material microstructures**
  - Fracture surfaces, particle, dislocation, and grain boundary characterization

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Future Work

Modeling and Simulation

- **Determine the time it takes for the hydrogen population profiles to reach steady state as a function of the crack depth.**

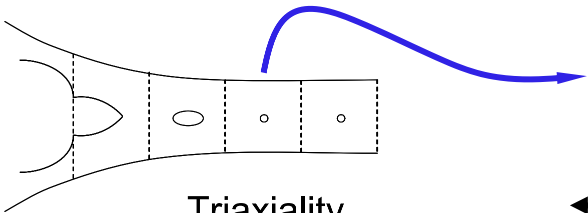
- **Complete the stress analysis to establish the dependence of the stress profiles ahead of an axial crack tip in term of the Stress Intensity Factor and the T-stress**
  - We expect strong dependence on hydrogen-induced material softening
  - Set hydrostatic constraint guidelines for testing standard fracture specimens in the presence of hydrogen

- **Simulate crack growth propagation in the presence of hydrogen**
  - Requires cohesive laws in the presence of hydrogen
  - Establish critical toughness for fracture initiation
  - Establish the tearing resistance of the material upon crack propagation
  - Explore subcritical crack growth propagation in the presence of hydrogen

- **Ab-inito calculations of cohesive properties of Fe/MnS interface**
  - Establish criteria for interfacial decohesion needed to assess void nucleation at Mns/Fe particles
  - Explore whether thermodynamic criteria (e.g. Hirth and Rice) are suitable to analyze hydrogen-induced decohesion at interfaces

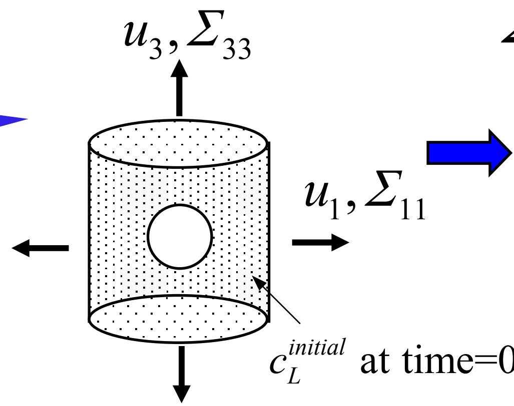
Long Term Objective: Multiscale Fracture Approach

(a) Crack tip fracture process zone

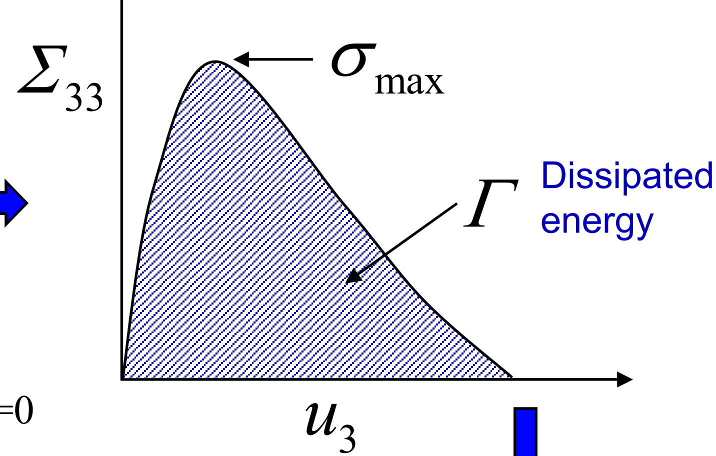


Triaxiality
Hydrogen concentration

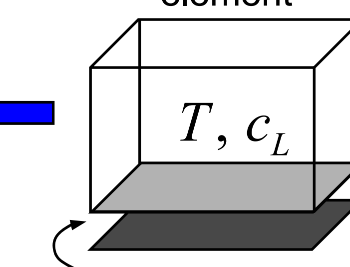
(b) Axisymmetric unit cell model



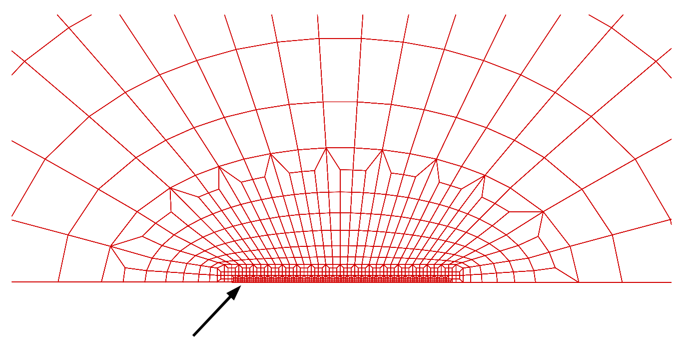
(c) Traction - separation law

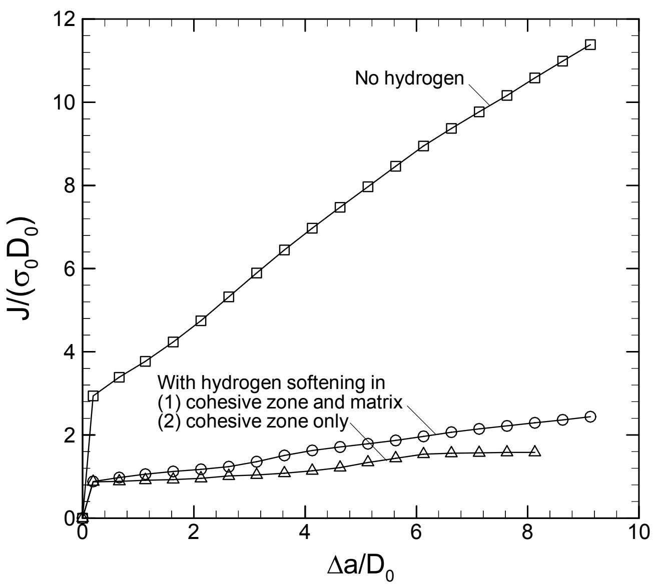


Adjacent finite element



(d) Cohesive element





(e) Cohesive elements characterized by a traction-separation law based on the unit cell model

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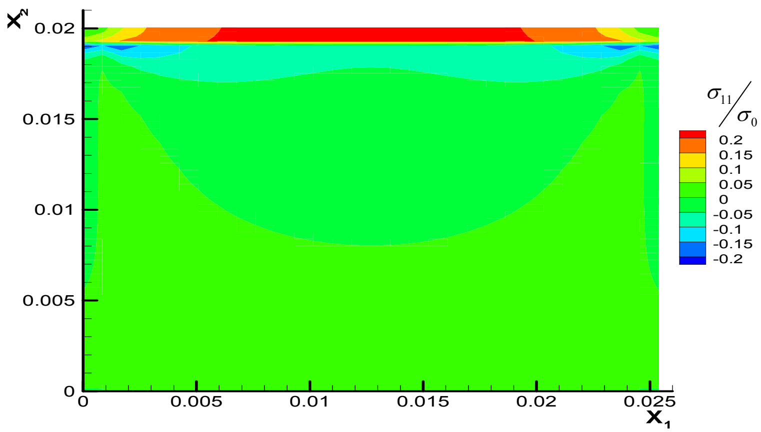
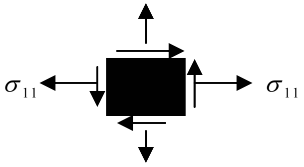
Future Work

- **Other Activities**
  - **Finite element analysis of residual stresses of a Schott Coating sitting on the substrate**



Average tensile stress σ_{11} in the coating is 125 MPa

Note that substrate is under large compression (-100Mpa) at the edges (possible delamination cause)



  - **Continue collaboration with ASME on establishing guidelines for codes and standards**
- **Continue our ongoing collaboration with the Japan program for materials solutions for the Hydrogen Economy**
  - **Hydrogen National Institute for Use and Storage (Hydrogenius)**
    - **Kyushu University (Prof. Y. Murakami)**
- **Continue our ongoing collaboration with the NATURALHY Project sponsored by the European Union**
  - **Interaction of hydrogen in a pipeline with a corrosion induced-crack on the external wall**

Summary

- **Relevance**
  - Identify the mechanisms of hydrogen embrittlement in pipeline steels and propose fracture criteria with predictive capabilities.
  - There are no codes and standards for safe and reliable pipeline operation in the presence of hydrogen
- **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
  - Study of tensile properties of new micro-alloyed steels
    - Good in H_2S sour natural gas service
  - Microstructural characterization of Air Liquide, Air Products, and OMS steels
  - Finite element analysis of hydrogen transport
  - Validation of ab-initio calculations
- **Collaborations**
  - Active partnership with SECAT, Oak Ridge National Laboratory, Sandia National Laboratories, ASME codes and Standards, JAPAN (Hydrgenius Institute)
- **Proposed future research**
  - Permeation measurements for diffusion and solubility characteristics
  - Fracture toughness testing
  - Calculation of hydrogen effect on interfacial cohesion through first principles calculations
  - Simulation of hydrogen transport in conjunction with fracture-mechanism modeling
  - Understanding R-curve response and threshold stress intensities in the presence of hydrogen