Hydrogen Embrittlement of Pipeline Steels: Causes and Remediation

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

University of Illinois at Urbana-Champaign

Hydrogen Pipeline Working Group Workshop

Augusta, GA, August 30, 2005

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Funding and Duration

- **Timeline**
  - **Project start date: 7/20/05**
  - **Project end date: 7/19/09**
  - **Percent complete: 0.1%**

- **Budget: Total project funding: 300k/yr**
  - **DOE share: 75%**
  - **Contractor share: 25%**

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

Team and Collaborators

- **Industrial Partners: SECAT**
  - **Novel coating materials, adhesion issues**
    - **Applied Thin Films**
    - **Chemical Composite Coatings**
    - **Schott North America**
  - **Current and future pipeline materials**
    - **Oregon Steel Mills**
  - **End users/field solutions**
    - **Columbia Gas Kentucky**
    - **Napa Pipe Corporation**
    - **Advanced Technology Corporation**
  - **Codes and Standards**
    - **ASME**

- **Collaboration with National Laboratories**
  - **Oak Ridge National Laboratory**
    - **Alloy design and development**
    - **High pressure mechanical property testing**
  - **Savannah River National Laboratory**
    - **Weldments**
    - **High pressure testing**
  - **Sandia National Laboratories, Livermore**
    - **Constitutive modeling and testing**

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Objectives

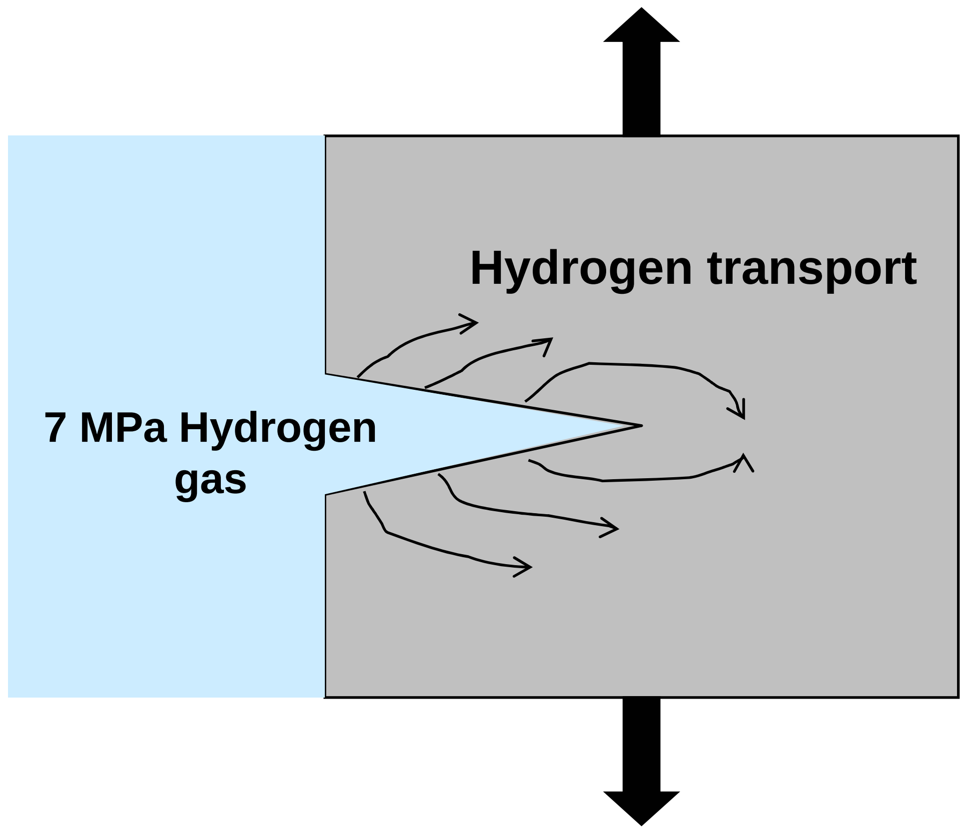
- **To come up with a mechanistic understanding of hydrogen embrittlement in pipeline steels in order to devise a fracture criterion for safe and reliable pipeline operation under hydrogen pressures of at least 7MPa and loading conditions both static and cyclic (due to in-line compressors)**

- **To mitigate hydrogen-induced failures by studying the effect on the fracture processes of internal coatings and water vapor/oxygen**

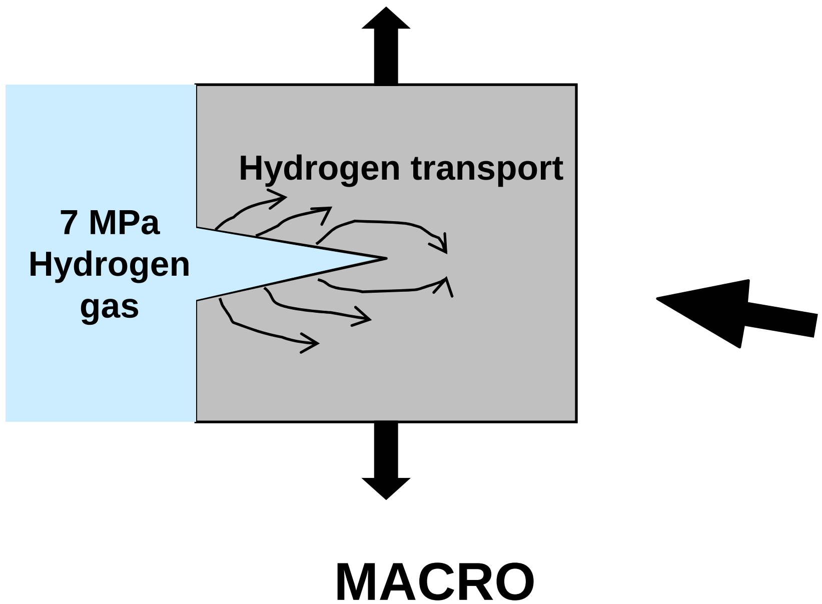
- **Development of such a fracture criterion and mitigation requires**
  - **Identification of deformation mechanisms and potential fracture initiation sites in the presence of hydrogen solutes**
  - **Measurement of hydrogen adsorption, bulk diffusion, and trapping characteristics of the material microstructure in both coatings and pipeline steels**
  - **Finite element simulation of hydrogen diffusion and interaction with material elastoplasticity under high-pressure hydrogen gas environment**

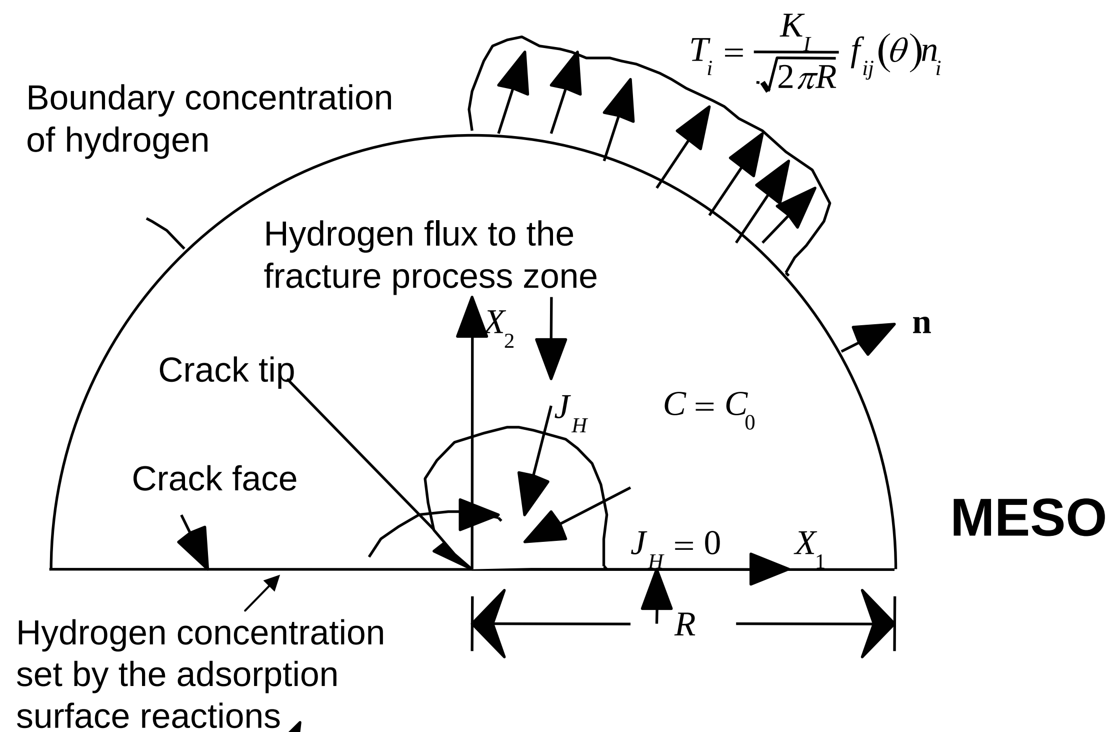
Approach: Identify the Fracture Environemnt

- **Circumferential or axial cracks at the inner surface of the pipe or welds**
  - Crack faces are exposed to a hydrogen gas pressure and hydrogen diffuses into the material while the crack surfaces are maintained at a hydrogen concentration in equilibrium with the gas pressure

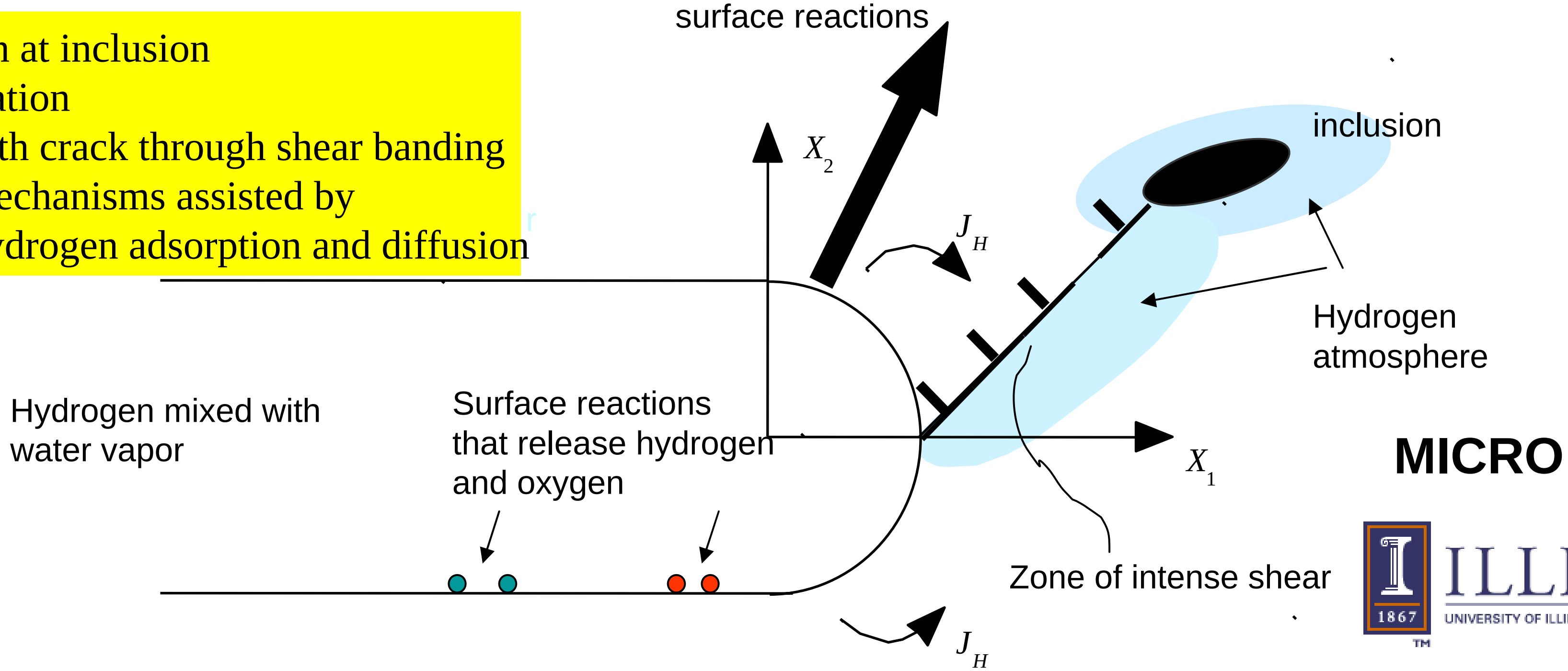


Approach: Ductile Transgranular Fracture





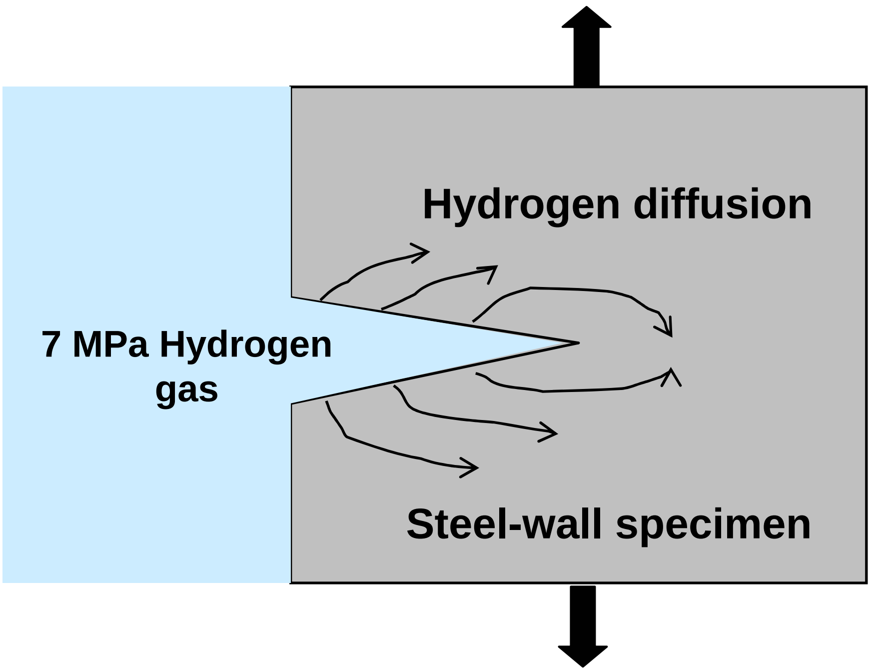
- Decohesion at inclusion
- Void formation
- Linking with crack through shear banding
- Fracture mechanisms assisted by transient hydrogen adsorption and diffusion



Approach: Analyze Hydrogen Transport

Hydrogen transport equation accounts for hydrostatic stress drift and trapping at material defects

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



d/dt = time differentiation

C = Hydrogen concentration

D = diffusion coefficient

D_{eff} = Effective diffusion accounting for trapping

σ_{kk} = hydrostatic stress

ε^p = plastic strain

T = temperature

V_H = partial molar volume of H

N_T = trap density

θ_T = trap occcupancy

α =trapping sites per trap

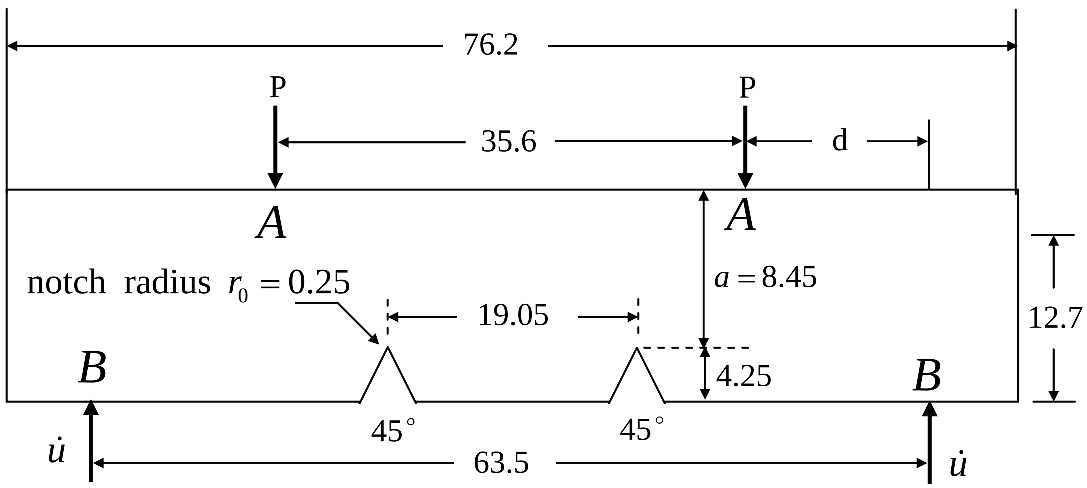
$(\ )_{,i} = \partial(\ )/\partial x_i$

Modify our in-house finite element codes to treat hydrogen diffusion with boundary and initial conditions appropriate to pipeline environment: at time zero crack face concentrations are at equilibrium with hydrogen gas while the bulk/internal hydrogen concentrations are zero

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Results

Finite element simulation of hydrogen transport at a double-notch 4-point bend specimen



All dimensions are in mm.

Material data for 4340 steel

$$C_0 = 2.46 \times 10^{-8} \text{H/Fe}$$

$$D = \text{diffusion coefficient} = 1.25 \times 10^{-8} \text{m}^2/\text{s}$$

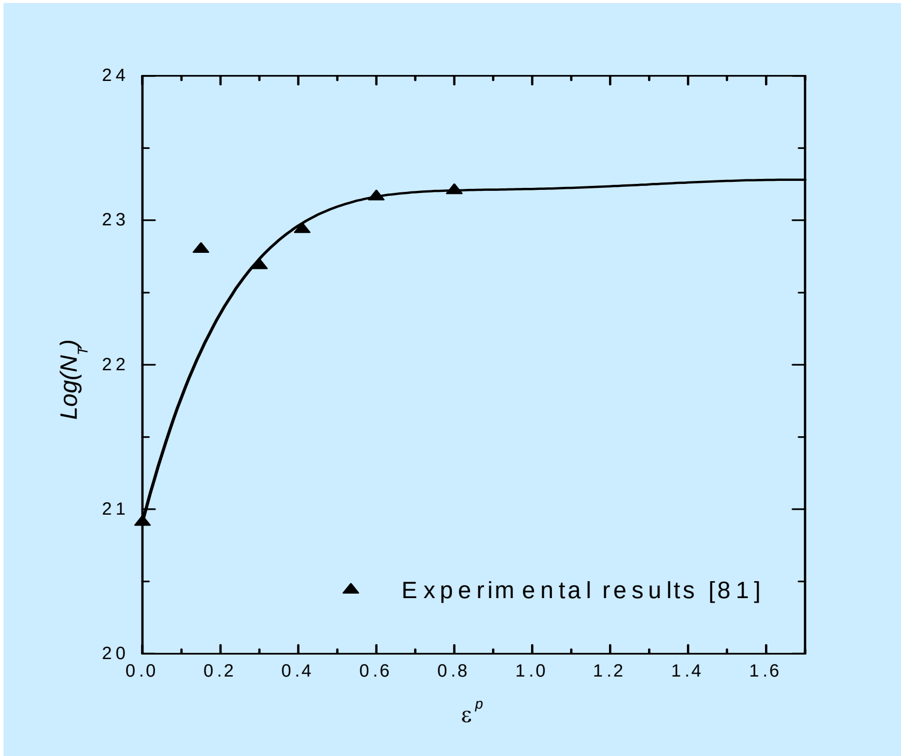
$$\sigma = \sigma_0 (1 + \varepsilon^p / \varepsilon_0)^N$$

$$\sigma_0 = 1380 \text{MPa}$$

$$N = 0.025$$

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Trap Density Iron as Function of Plastic Strain

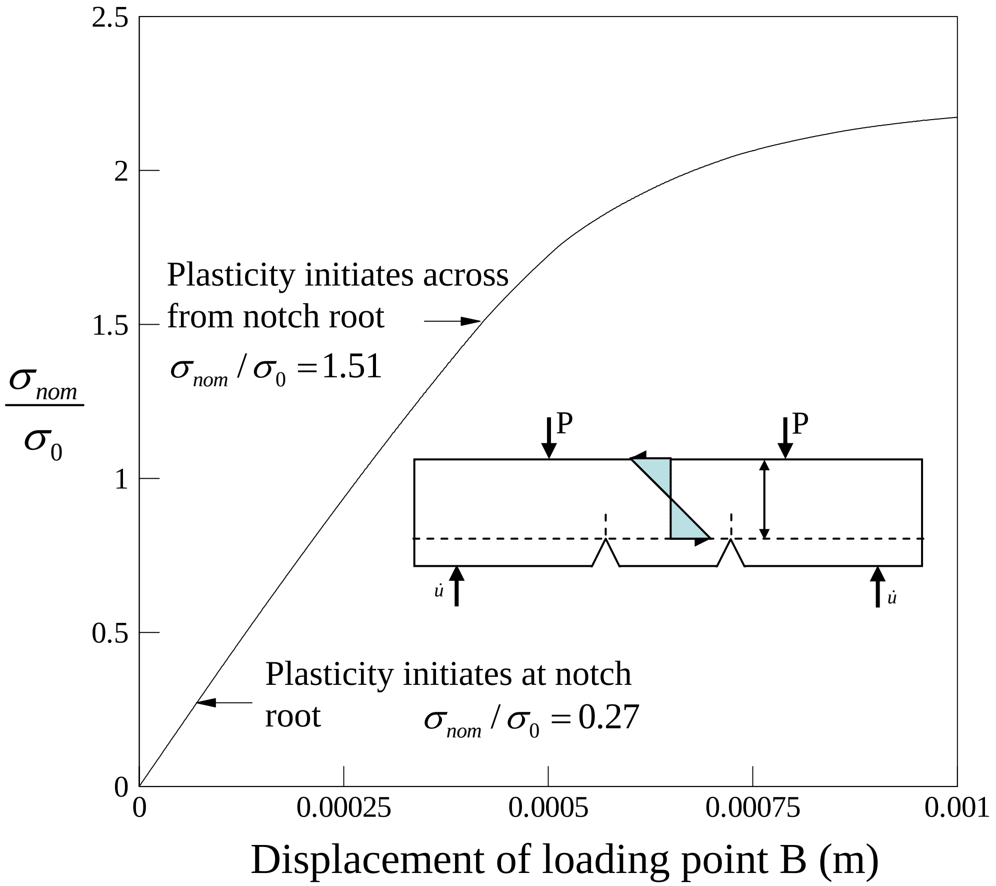


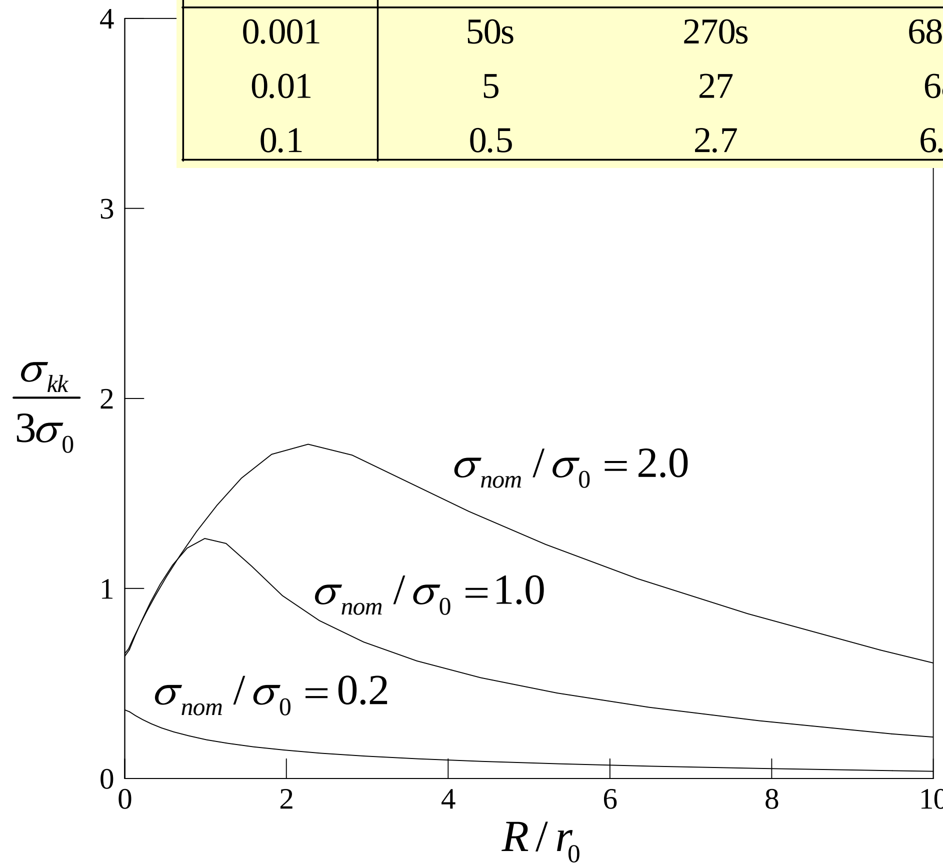
Experimental results of Kumnick and Johnson (1980)

Nominal and Hydrostatic Stresses vs Displacement of Loading Point

Time it takes for nominal stress levels to be attained depends on the loading rate

loading rate (mm/s)	$\sigma_{nom}/\sigma_0 = 0.2$	$\sigma_{nom}/\sigma_0 = 1.0$	$\sigma_{nom}/\sigma_0 = 2.0$
0.001	50s	270s	680s
0.01	5	27	68
0.1	0.5	2.7	6.8



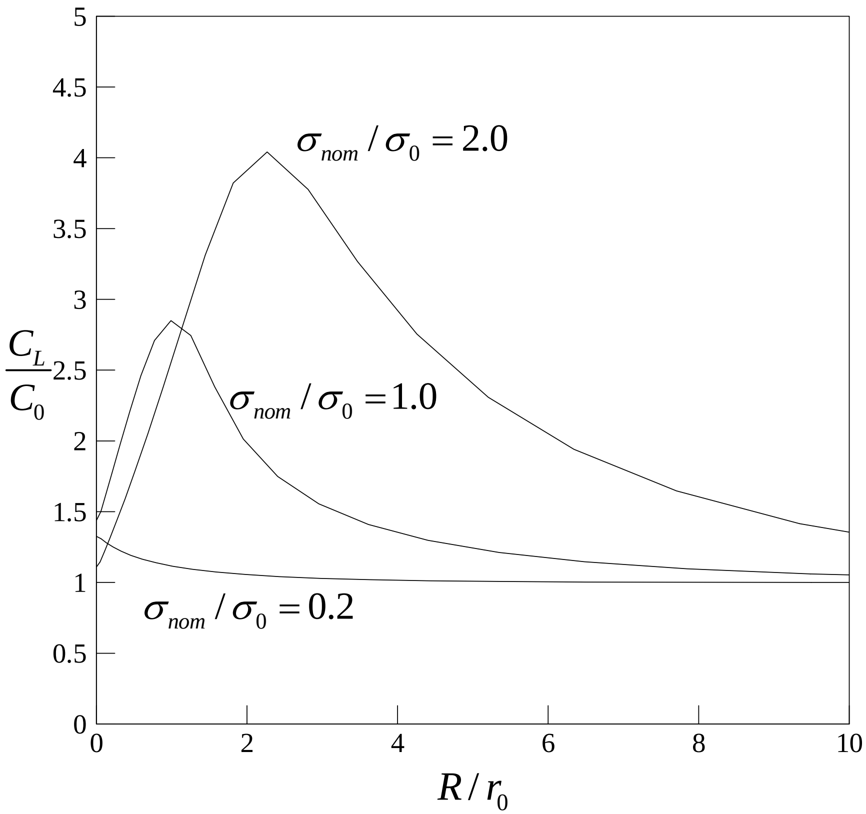


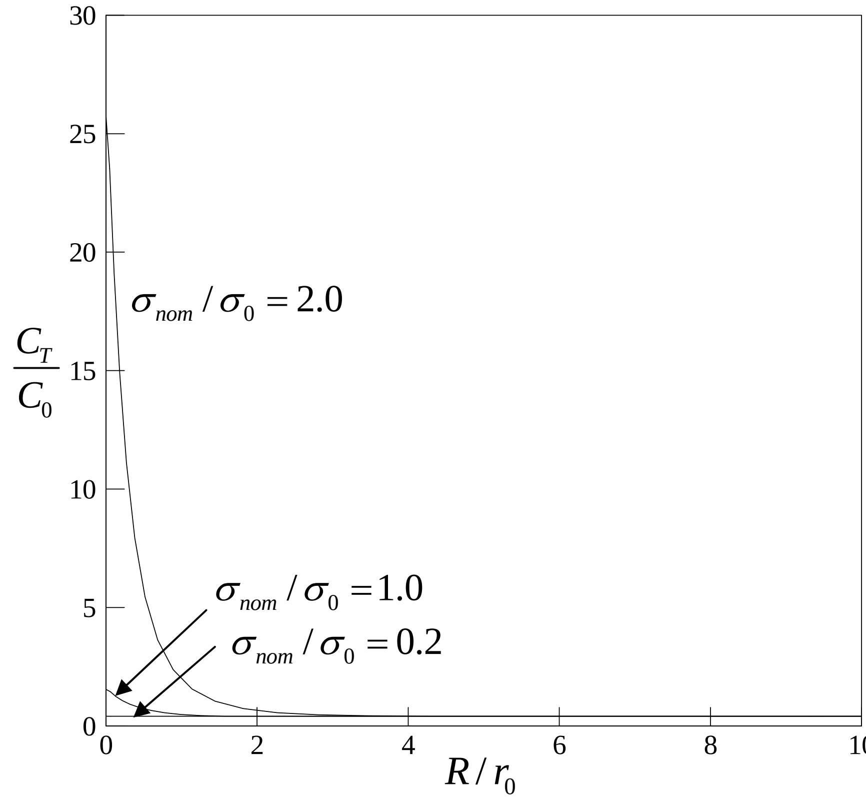
$$\sigma_{nom} = \frac{6Pd}{wa^2}$$

P is the reaction force at point A
d is the bending moment arm between points A and B
a is the unnotched ligament
w is the specimen thickness

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Lattice and Trapping Site Concentrations ahead of the Notch

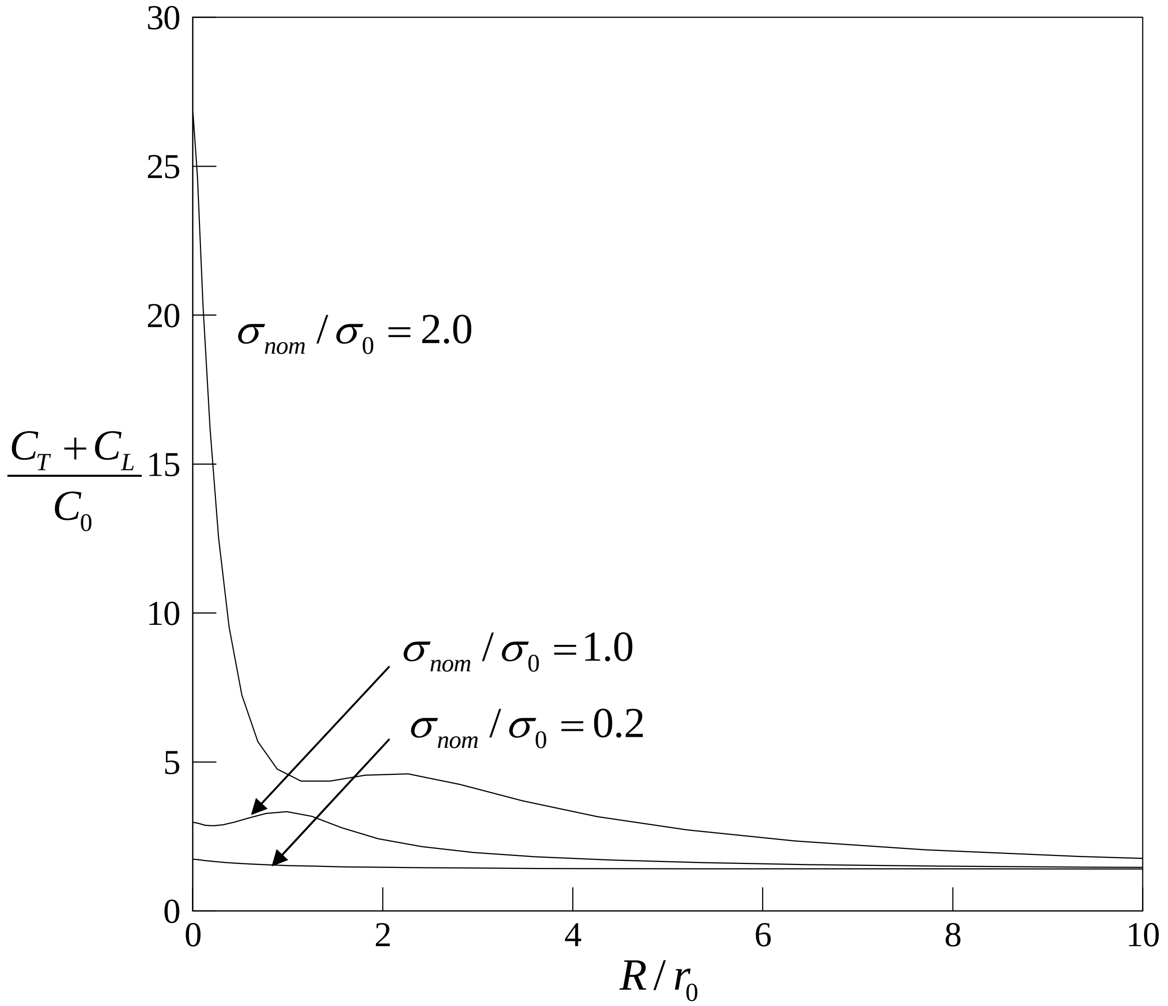




$\dot{u} = 0.001\,\text{mm/s}$

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Total Concentration

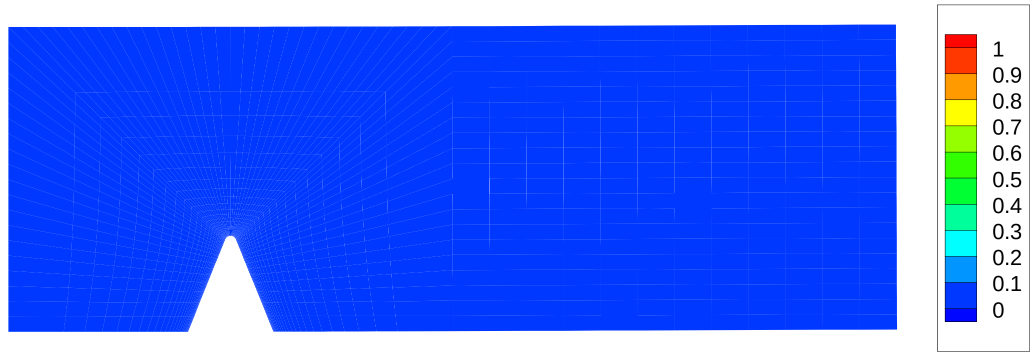


$\dot{u} = 0.001\,\text{mm/s}$

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Plastic Strain as Loading (nominal stress) Increases

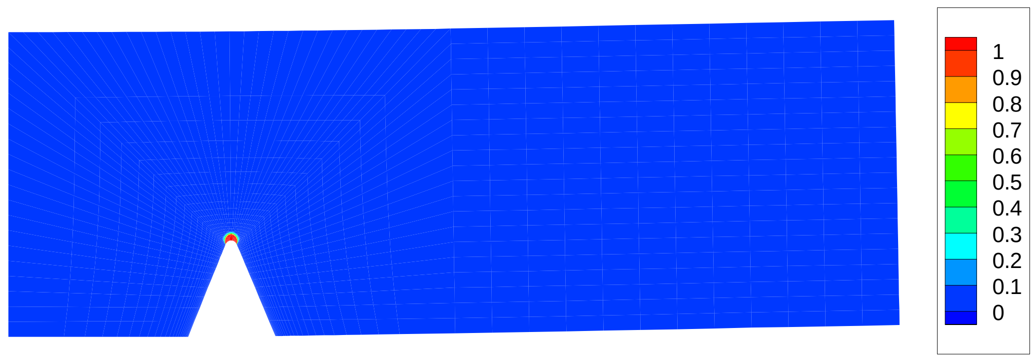
Only elastic



$\sigma_{nom} / \sigma_0 = 0.2$

$t = 50\ \text{s}$

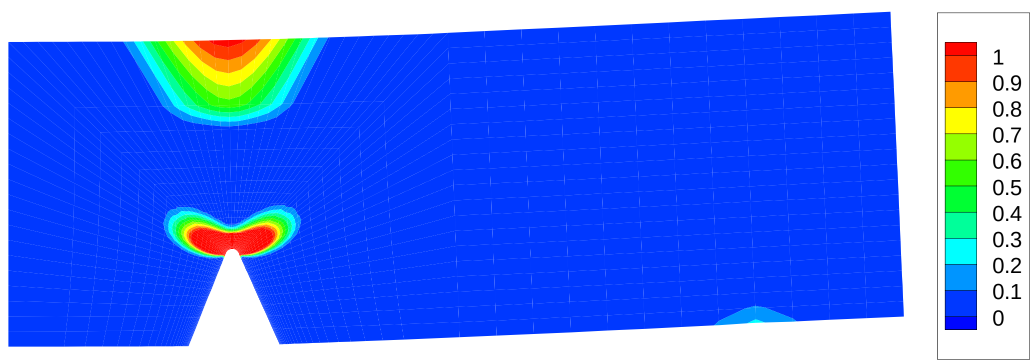
Contained plasticity



$\sigma_{nom} / \sigma_0 = 1.0$

$t = 270\ \text{s}$

Plasticity spread on the opposite side



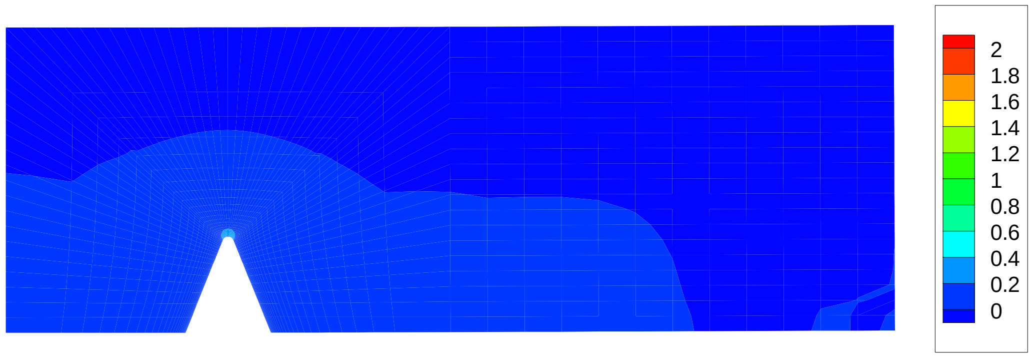
$\sigma_{nom} / \sigma_0 = 2.0$

$t = 680\ \text{s}$

$\dot{u} = 0.001\ \text{mm/s}$

Hydrostatic Stress as Loading Increases

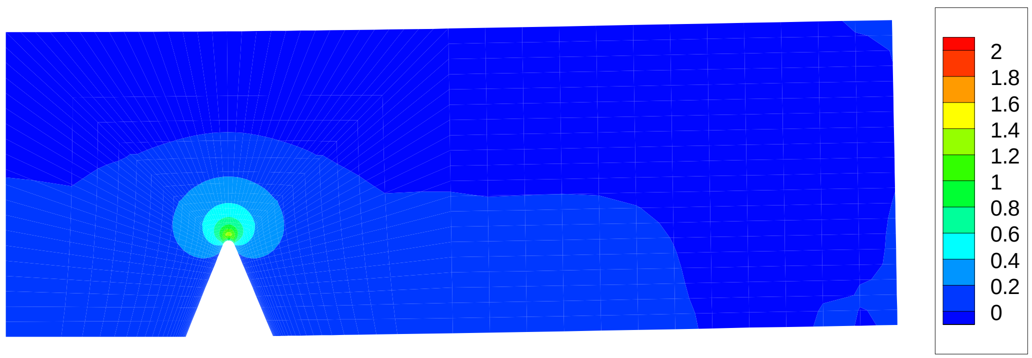
Only elastic



$$\sigma_{nom} / \sigma_0 = 0.2$$

$$t = 50 \text{ s}$$

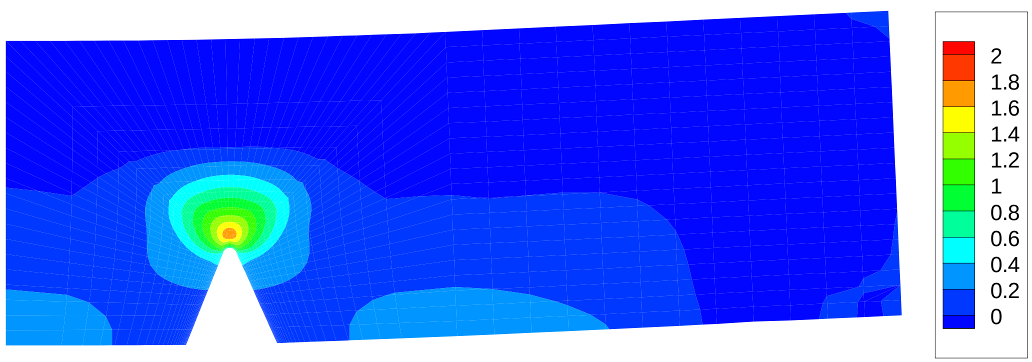
Contained plasticity



$$\sigma_{nom} / \sigma_0 = 1.0$$

$$t = 270 \text{ s}$$

Plasticity spread on the opposite side



$$\sigma_{nom} / \sigma_0 = 2.0$$

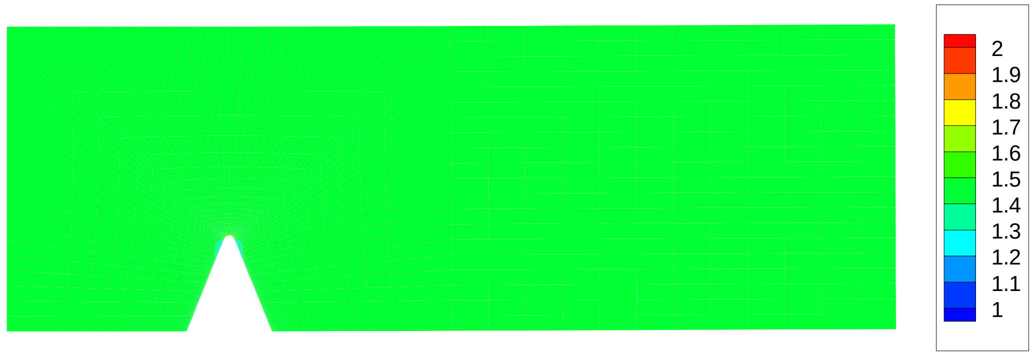
$$t = 680 \text{ s}$$

$$\dot{u} = 0.001 \text{ mm/s}$$

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

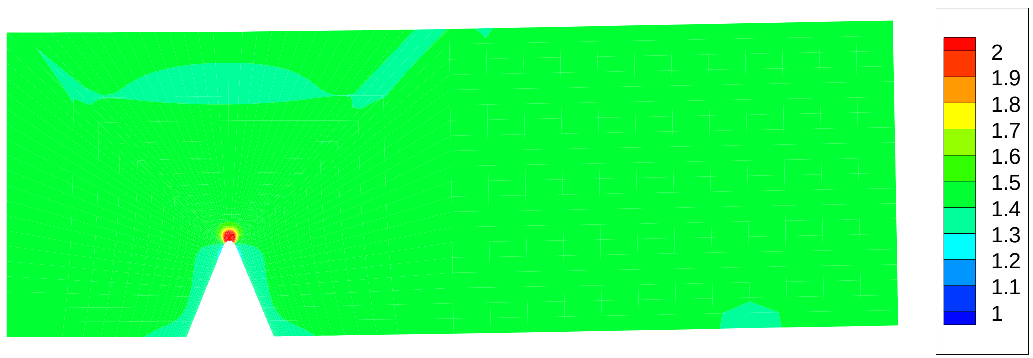
Total Concentration as Loading Increases

Only elastic



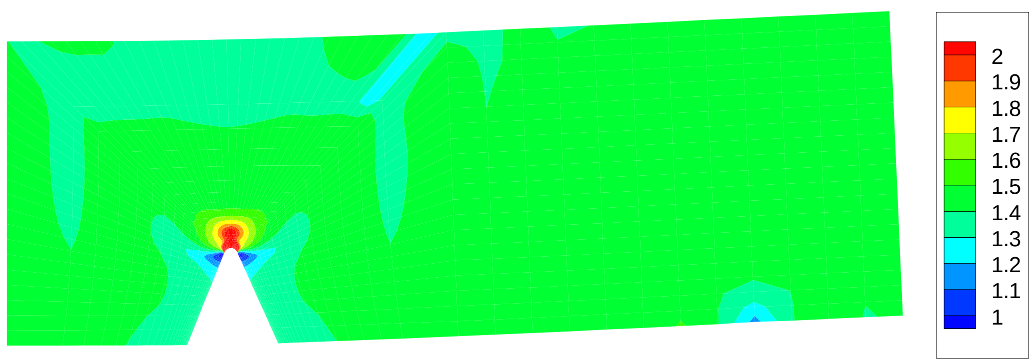
$$\sigma_{nom} / \sigma_0 = 0.2$$
$$t = 50 \ \text{s}$$

Contained



$$\sigma_{nom} / \sigma_0 = 1.0$$
$$t = 270 \ \text{s}$$

Plasticity spread
On the opposite
side



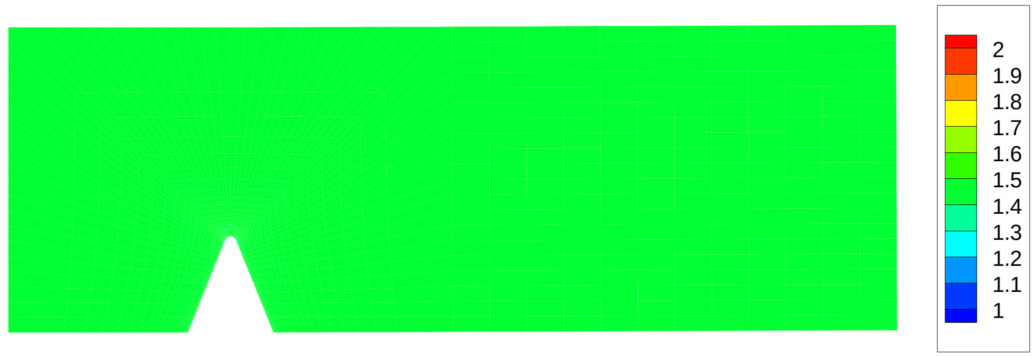
$$\sigma_{nom} / \sigma_0 = 2.0$$
$$t = 680 \ \text{s}$$

$$\dot{u} = 0.001 \, \text{mm/s}$$

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Total concentration as loading increases

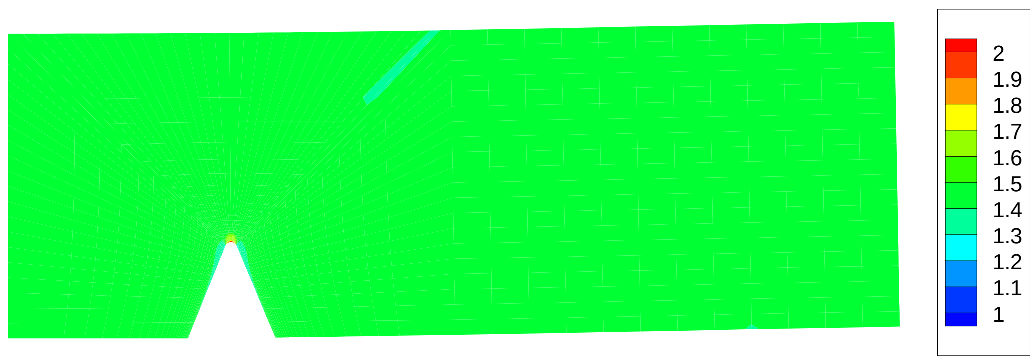
Only elastic



$$\sigma_{nom} / \sigma_0 = 0.2$$

$$t = 0.5 \text{ s}$$

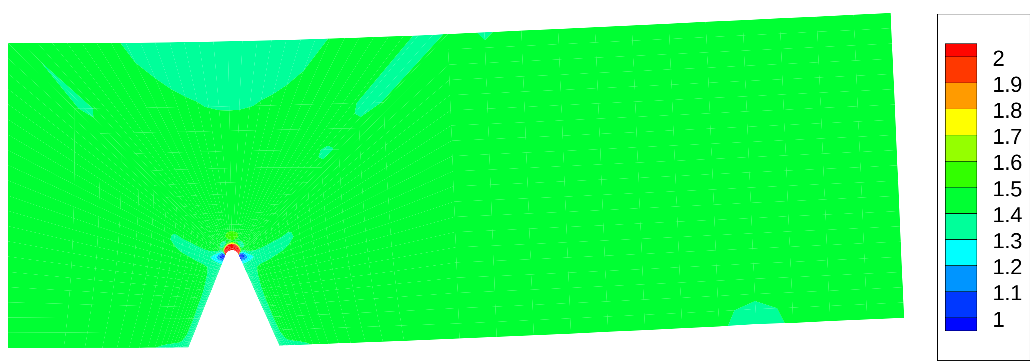
Contained



$$\sigma_{nom} / \sigma_0 = 1.0$$

$$t = 2.7 \text{ s}$$

Plasticity spread
On the opposite
side



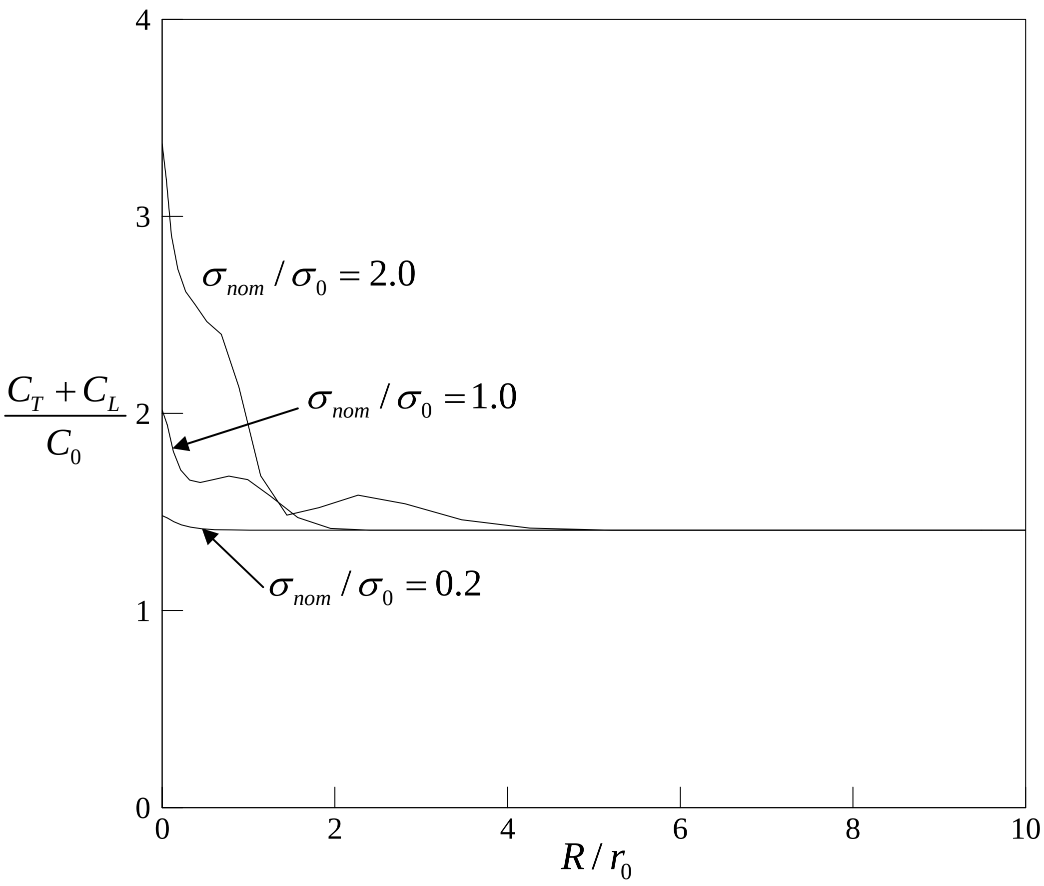
$$\sigma_{nom} / \sigma_0 = 2.0$$

$$t = 6.8 \text{ s}$$

$$\dot{u} = 0.1 \text{ mm/s}$$

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Total Concentration



$\dot{u} = 0.1\,\mathrm{mm/s}$

Ongoing Research-Future Plans

- **Collaboration with *SECAT, ORNL,* and *Oregon Steel Mills* (D. Stalheim) to identify steel compositions (e.g. MO1677, D2 Low C API X80) with promising hydrogen compatibility**
  - **Carry out mechanical property testing to determine elastic and flow characteristics**
    - Sandia National Laboratories
  - **Identify the fracture mechanisms in the presence of hydrogen (accelerated void nucleation and coalescence)**
  - **Nature of important traps (Thermal Desorption Spectroscopy)**
    - Inclusions/precipitates, grain boundaries, dislocations
  - **Measure the trap binding energy**
    - 60kj/mole?
  - **Measure the trap density**
    - If density evolves with dislocation structure, what is the corresponding relationship?

- **Experimental measurement of hydrogen diffusion constant**
  - **One atmosphere measurements at the *University of Illinois***
    - Apparatus under construction
  - **High pressure measurements at *Oak Ridge National Laboratory and Savannah River National Laboratory***

- **Begin work in collaboration with SECAT (Applied Thin Films, Chemical Composite Coatings, Schott North America) on how a thin coating film over the steel surface affects hydrogen adsoprtion and subsequent diffusion through the film toward the interior of the steel wall**
  - **Experiments and fist principle calculations on adsorption**

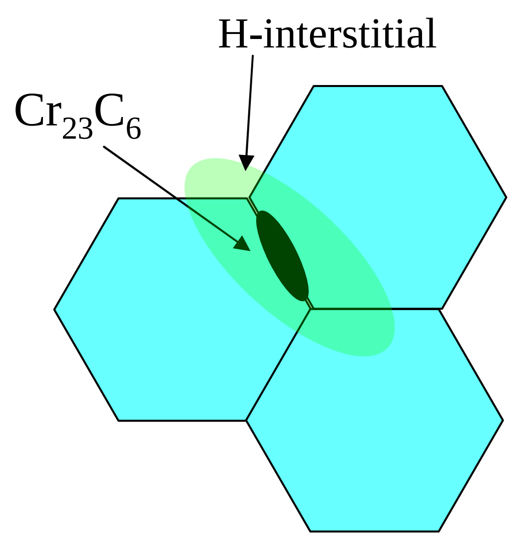
ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Ongoing Research-Future Plans

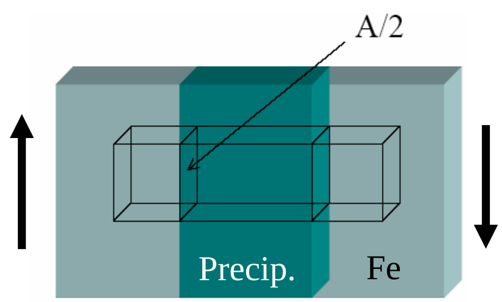
- **Assessment of interfacial strength of second-phase particles in pipeline steels in hydrogen and water environments**

  - **Ferrite-based alloys have $Cr_{23}C_6$ and MnS precipitates at grain boudnary interfaces. Substitutional solutes (e.g. Cr, Mn, Si) or interstitials (e.g. H, N, C) modify structure and stability**
    - **H (N of C) interstitials alter bonding and cohesion**
    - **Cr is depleted near $Cr_{23}C_6$ interface while Fe preferentially occupies Cr sites not bonded to C**

  - **Obtain cohesive energies via first-principles, Density Functional Theory (DFT) calculations with distribution of atoms near interfaces based on periodic cell approximations**



Interface and unit cell under shear



- **Determine feasibility of using equilibrium criteria to address decohesion at internal interfaces. If not feasible, transient models will be explored via continuum mechanics models (fast-separation limit for interfacial thermodynamics)**