# Hydrogen Embrittlement of Pipeline Steels: Causes and Remediation

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**2005 DOE Hydrogen Program Review**

**May 16, 2006**

This presentation does not contain any proprietary or confidential information

Project ID #PDP16

# Overview

## Timeline

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

## 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 are on hold

## 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 Lequide
  - 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

# 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)**
  - **Existing natural gas network of pipeline steels**
  - **Propose new steel microstructures**

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



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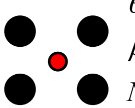
# Approach

- **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.**
- **Tension experiments to identify macroscopic plastic flow characteristics**
- **Permeation experiments to identify diffusion characteristics**
- **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**
- **Development of a mechanistic model that incorporates the fracture mechanisms to establish the fracture toughness of the material in the presence of hydrogen**
  - **Experiments and simulations of crack propagation (subcritical crack growth) to determine**
    - The hydrogen effect on crack initiation as described the value of the J-integral, $J_{IC}$
    - What constitures “safe hydrogen concentrations” at Threshold Stress Intensities
    - The stability of crack propagation to assess catastrophic failure scenarios

# Results on Hydrogen Transport Analysis

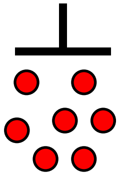
- **Diffusing hydrogen resides at**
  - **Normal Interstitial Lattice Sites (NILS)** $C_L = \beta\theta_L N_L$

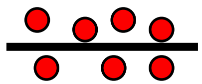


$\theta_L$ = NILS occcupancy
$\beta$ = number of NILS per solvent atom.
$N_L$ =number of solvent atoms/m$^3$.

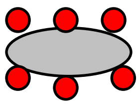
  - **Trapping Sites** $C_T = \alpha\theta_T N_T$
    - Microstructural heterogeneities such as dislocations, grain boundaries, inclusions, voids, interfaces, impurity atom clusters

dislocations





Grain boundaries



inclusions

$\theta_T$ = trap occcupancy
$\alpha$ = 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**

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

  - Note the effect of stress and plastic strain

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

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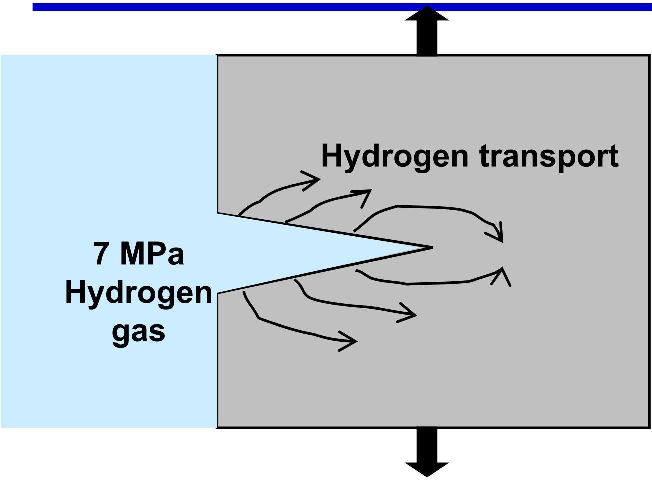
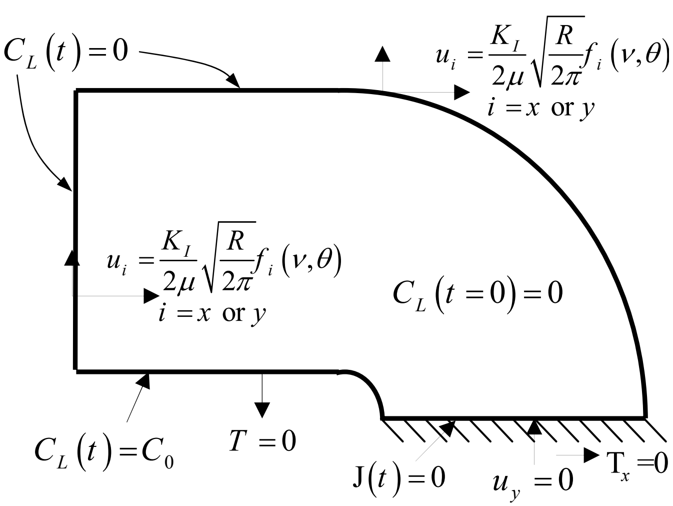
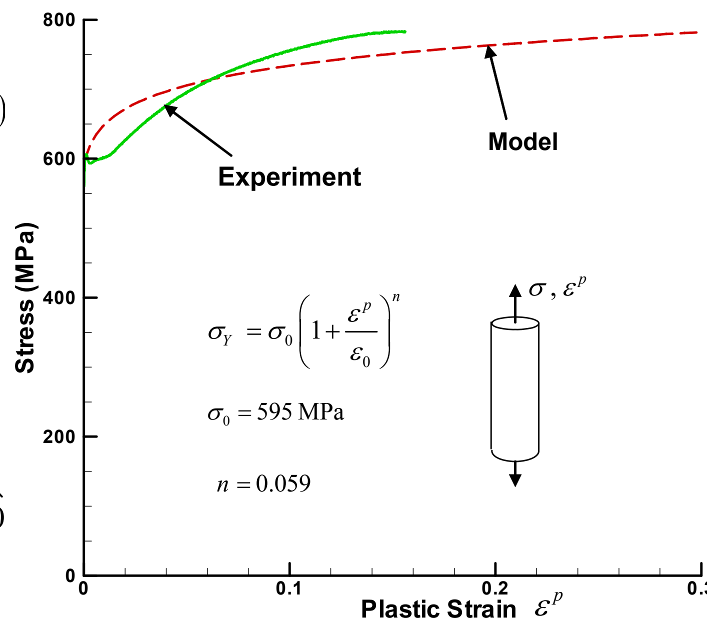
# Hydrogen Diffusion at Constant Applied Stress Intensity K



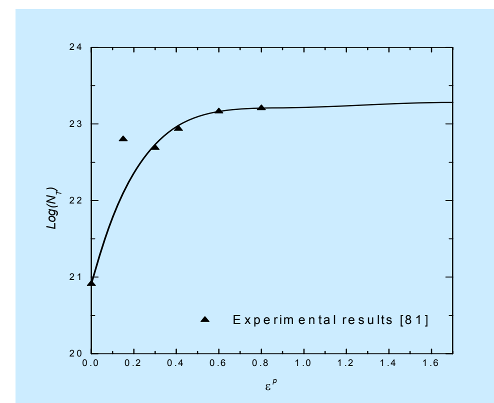

- Circumferential or axial cracks at the inner surface of the pipe or weld
- Outer surface loaded with the linear elastic K-field
- Hydrogen diffuses while crack surface is maintained at fixed concentration
- Prediction of hydrogen populations for extremely long times




## Stress-strain




## Trap density




$$C_0 = 2.46\times10^{-8}\ \text{H atom / Metal atom}$$

Lattice diffusion coefficient: $D = 2.0\times10^{-11}\ \text{m}^2/\text{s}$



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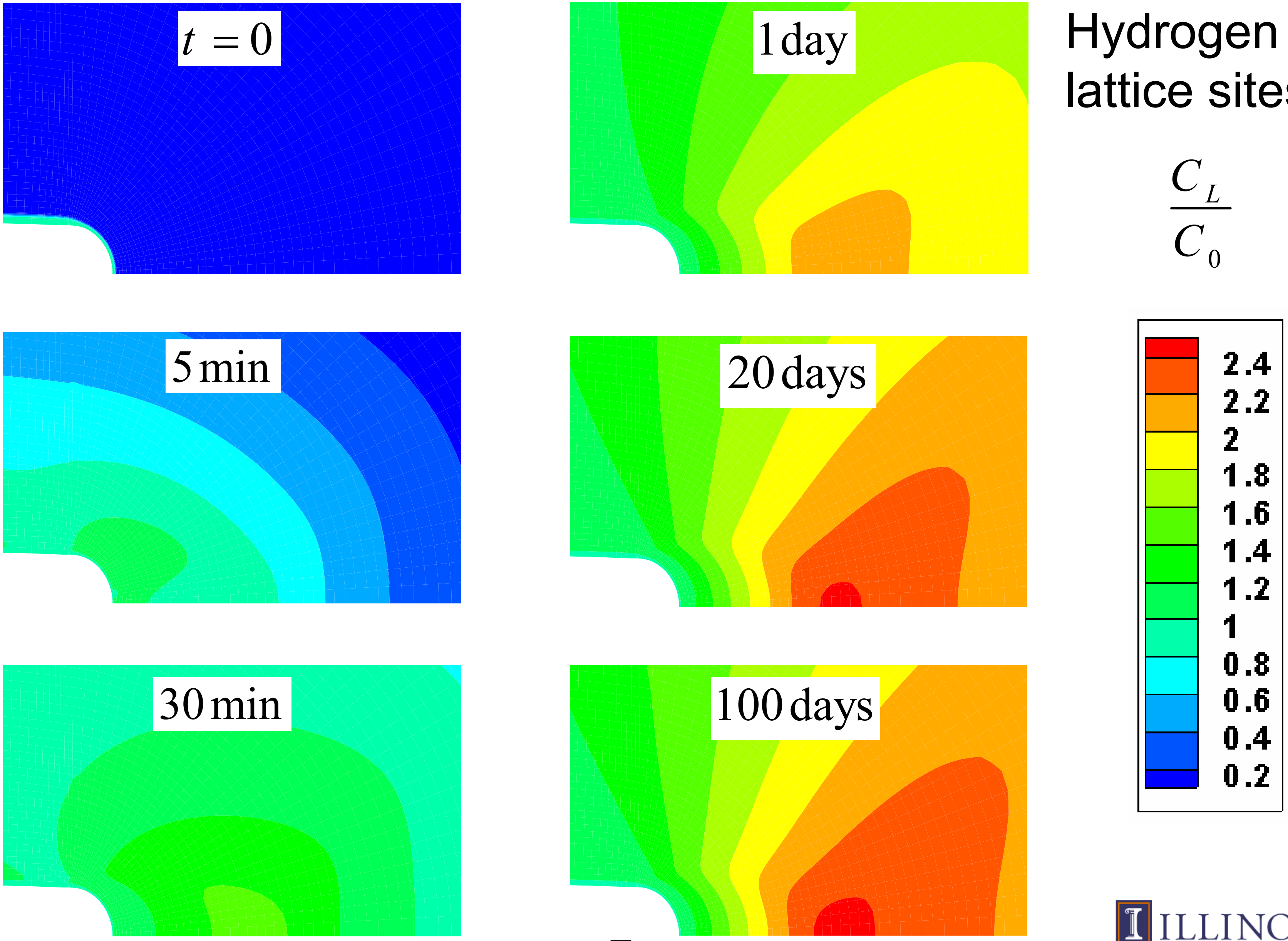
# Hydrogen Diffusion at Constant Applied Stress Intensity K

Hydrogen in lattice sites

$$\frac{C_L}{C_0}$$




$\mathrm{K} = 55\,\mathrm{MPa}\sqrt{m}$



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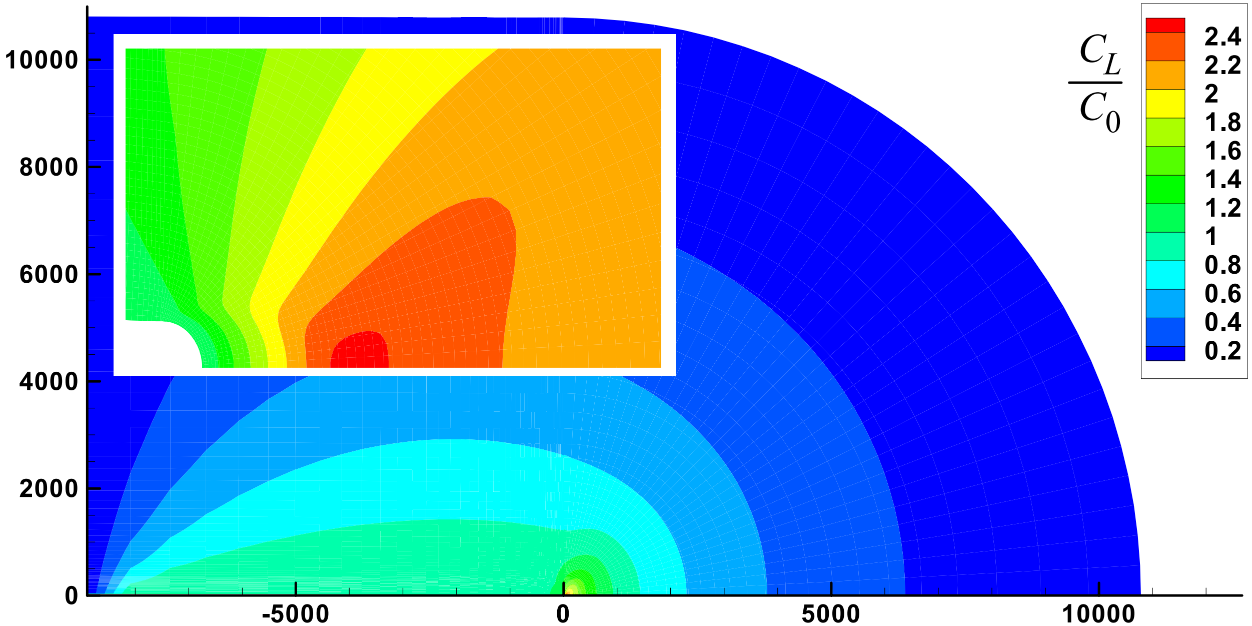
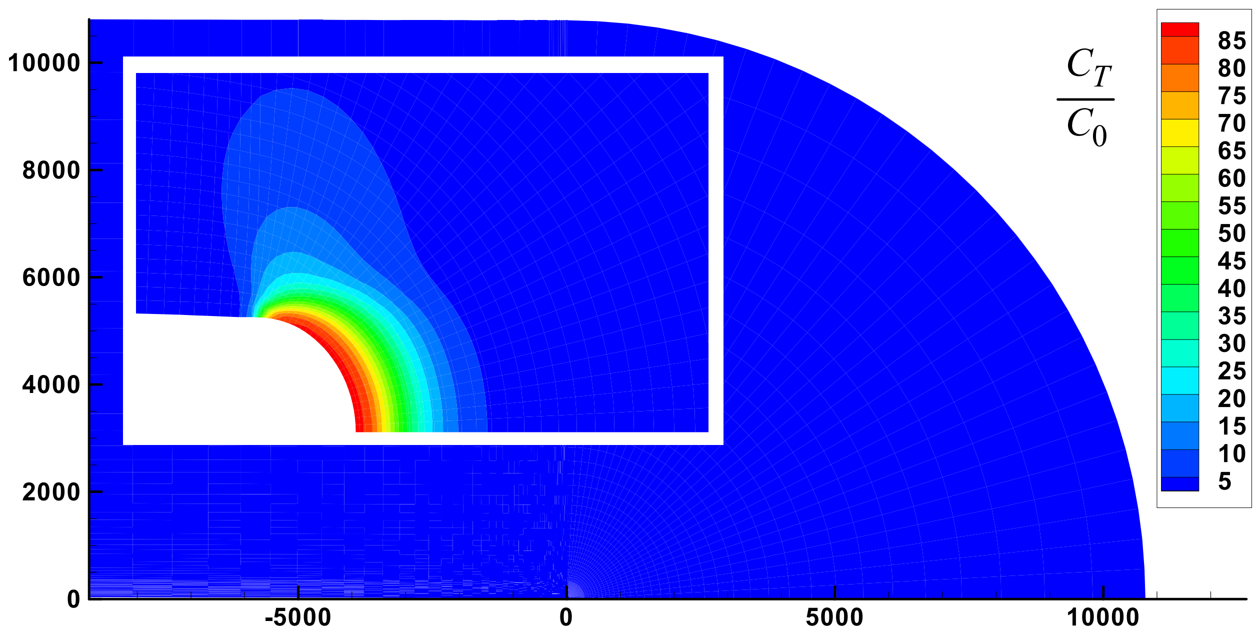
# Hydrogen Diffusion at Constant Applied Stress Intensity K




Hydrogen in lattice sites

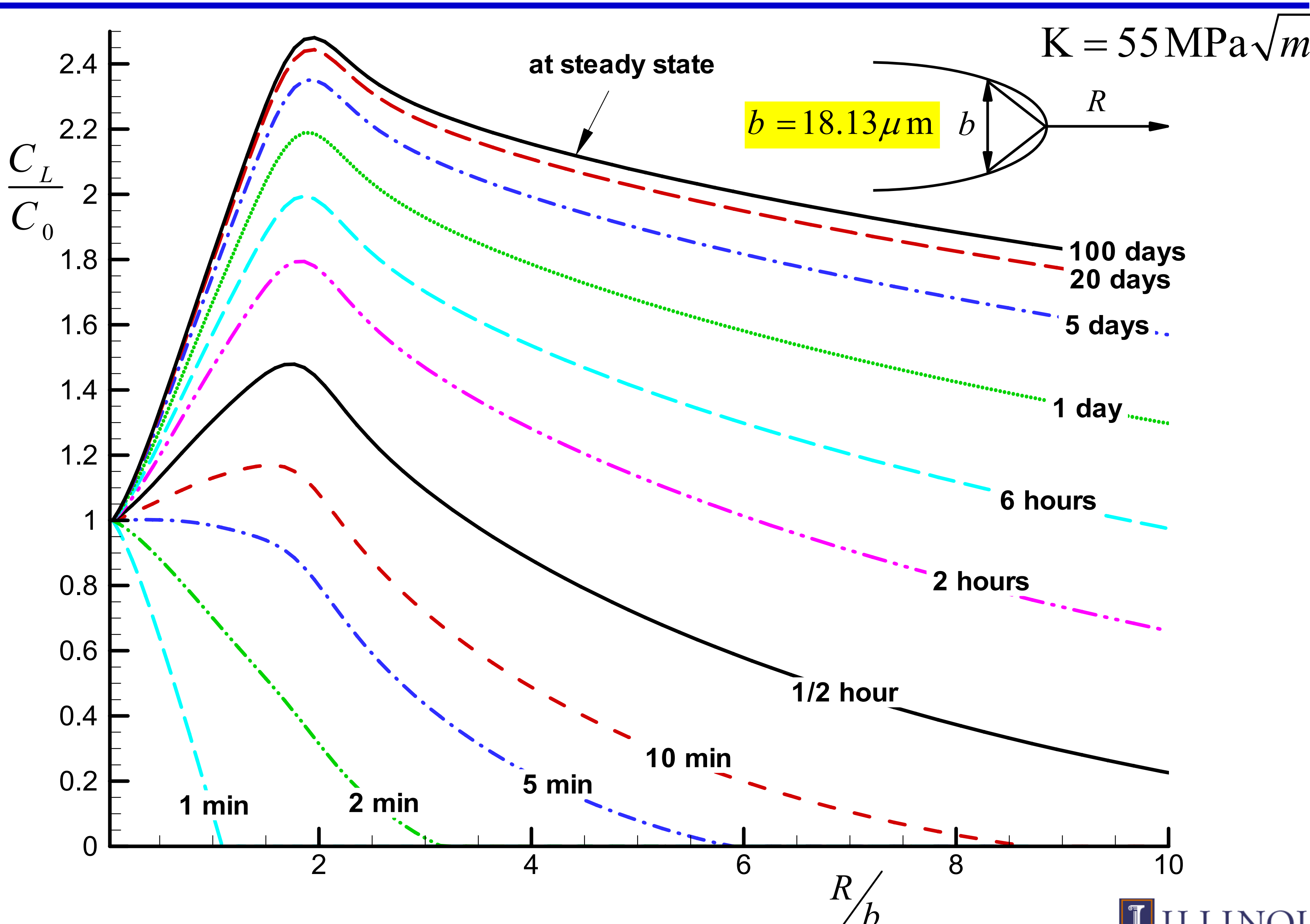
**At steady state**

$t \approx 100$ days




Hydrogen in trapping sites

# Hydrogen Diffusion at Constant Applied Stress Intensity K

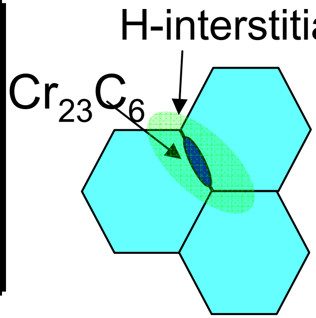



Crack tip opening displacement at time zero: $b = 6\mu m$

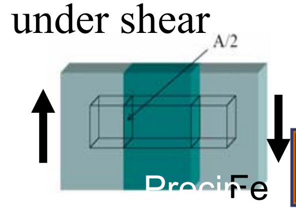
# Accomplishments vs Project Milestones and Objectives

- **Literature Review**
  - **Complete**
- **Development of finite element code for transient stress-driven hydrogen transport analysis coupled with large-strain elastoplastic deformation**
  - **Code has been tested and validated against analytical solutions. Additional validation on stress-driven diffusion is planned in collaboration with Los Alamos National Laboratory**
- **Design of permeation measurement system**
  - **Complete. Construction and measurement when funding resumes**
- **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 when funding resumes**
- **Validation of ab-initio calculations for decohesion energy calculations**
  - 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).

| | | GB | FS | GB-FS |
|---|---|---|---|---|
| Unrelaxed binding energies | VASP PAW-GGA | -3.23 | -3.57 | +0.34 |
| | FLAPW GGA (Zhong *et al.*, 2000) | -3.09 | -3.42 | +0.33 |




Interface and unit cell under shear



# Future Work

## Modeling and Simulation

- Determine possible correlation between time for steady state hydrogen transport, applied stress intensity, and material diffusivity in order to come up with an estimate of an expected upper limit on the incubation time for embrittlement at a crack tip

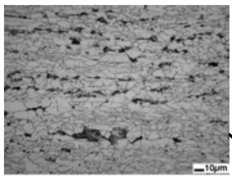
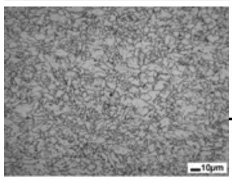
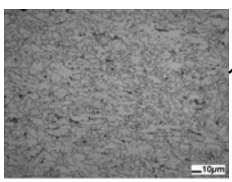
- Simulate the fracture response of alloy IN-900 in collaboration with Sandia Livermore to establish a computational methodology for the coupling/integration of fracture mechanisms-ductile and intergranular-with the analysis of transient hydrogen transport
  - Choice of IN-900 because no data on fracture of our pipeline microstructures in the presence of hydrogen are available due to funding cuts
  - Study threshold stress intensities from subcritical crack growth experiments to calculate what constitutes a “safe hydrogen concentration” ahead of a crack tip

- 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

# Future Work

## Experiment

- **Construct permeation measurement system and establish the diffusion characteristics of existing and new pipeline steel microstructures**
  - Existing natural gas pipeline steels provided by AirLequide 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 Schott North America for coating of our samples

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

- **Carry out fracture toughness testing**

- **TEM studies on existing and new pipeline material microstructures**
  - Obtained the first TEM images
  - Graduate assistant is learning sample preparation and how to perfect the images



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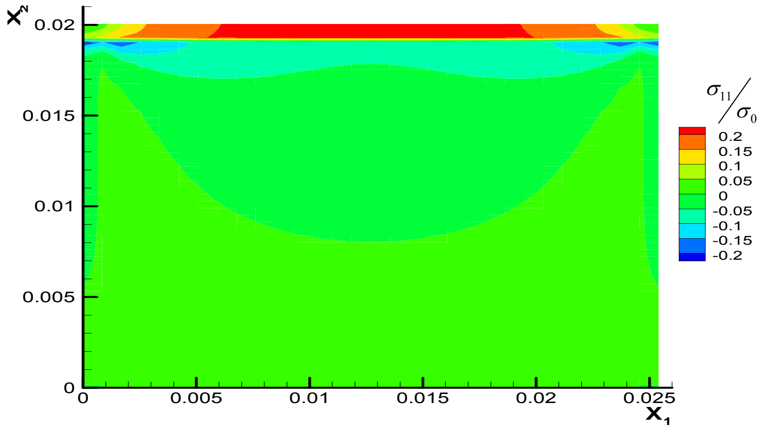
# Future Work

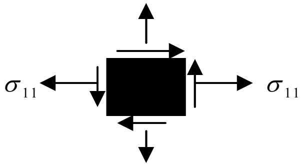
## Other Activities

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




Average tensile stress $\sigma_{11}$ in the coating is 125 MPa

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



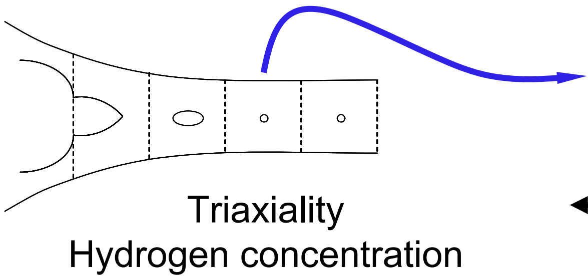

- Collaboration with ASME on numerically validating the proposed safety factors to be used for the design of pipeline steels under a range of hydrogen pressures

## Visit Japan under a fellowship from the Japan Society for Promotion of Science

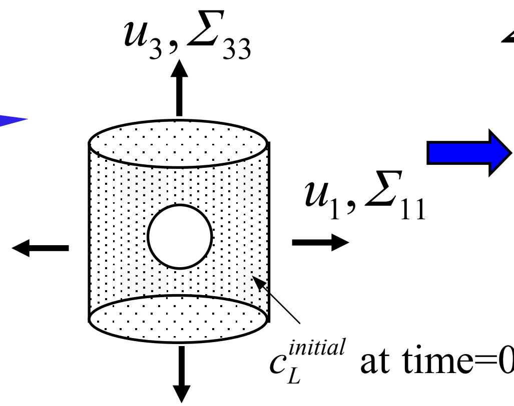
- Hydrogen National Institute for Use and Storage (Hydrogenious)
- Japan Gas Agency,
- Universities of Kyushu, Osaka, Kyoto, and Nagoya

# Long Term Objective: Multiscale Fracture Approach

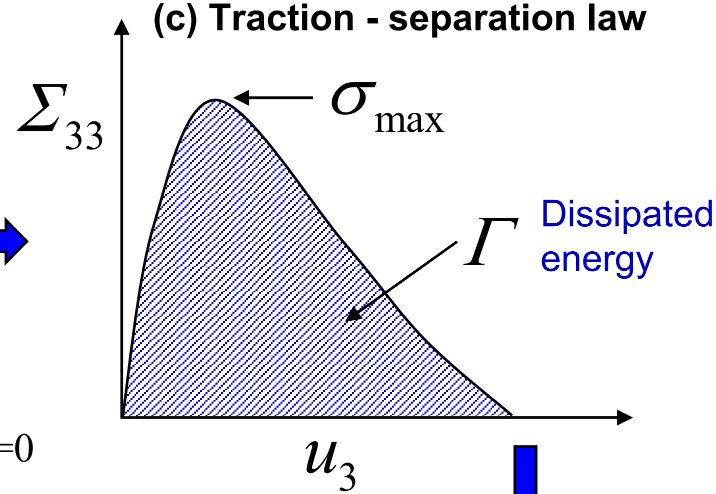
**(a) Crack tip fracture process zone**

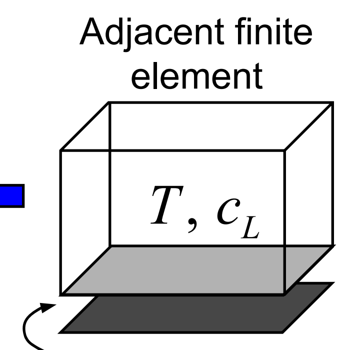



**(b) Axisymmetric unit cell model**

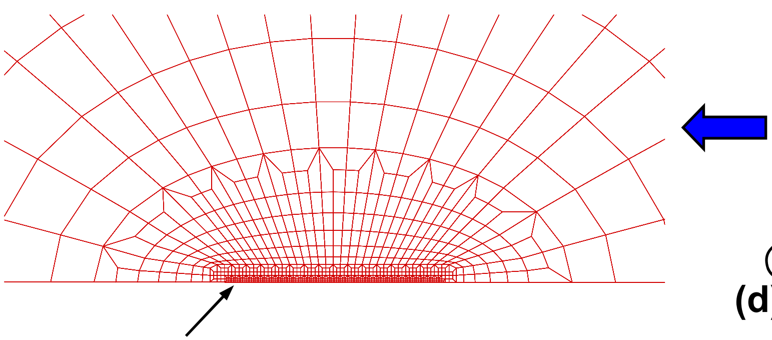



**(c) Traction - separation law**

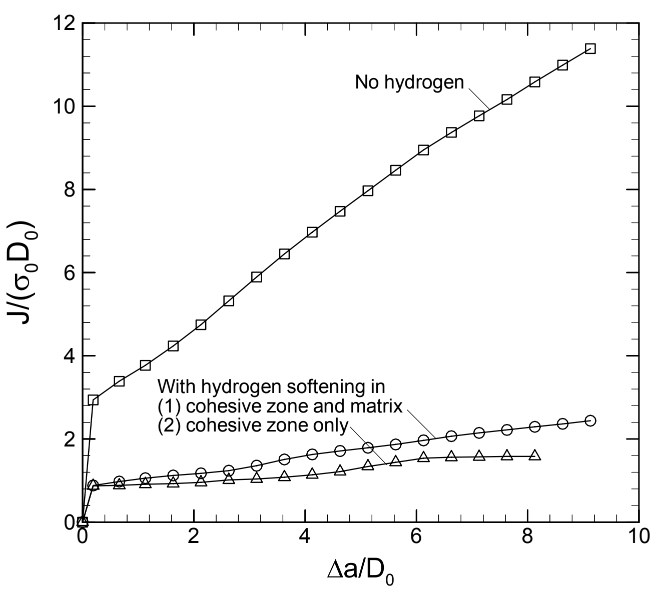



**(d) Cohesive element**



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



# Summary

- **Relevance**
  - Understanding the fundamental mechanisms of hydrogen embrittlement mechanims in pipeline steels and propose remedies and criteria for safe operation
- **Approach**
  - Mechanical property testing at the micro/macro scale
  - Microstructural analysis and TEM 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**
  - Finite element analysis of hydrogen transport
  - Validation of ab-initio calculations
  - Study of tensile properties of new micro-alloyed steels
    - Good in $H_2S$ sour natural gas service
- **Collaborations**
  - Active partnership with SECAT, Oak Ridge National Laboratory, Sandia National Laboratories, ASME codes and Standards, JAPAN
- **Proposed future research**
  - Permeation measurements for diffusion and solubility characteristics
  - Fracture toughness testing
  - Simulation of hydrogen transport in conjunction with fracture mechanism modeling
  - Calculation of hydrogen effect on interfacial cohesion through First principles calculations
  - Long term goal is the understanding of R-curve response and the determination of the threshold stress intensities in the presence of hydrogen

# Response to Reviewer’ Comments

- **Weaknesses**
  - **None was identified as the project was new**

- **Recommendations**
  - **Coordination with Oak Ridge National Laboratory**
    - **Collaboration is in place.**
    - **ORNL project on hydrogen permeation measurements has been stopped due to lack of funding**

  - **Much of knowledge must exist already in the steel and pipeline industries since hydrogen pipelines already exist without apparent problems. Use should be made of that knowledge**
    - **Knoweldge on fracture mechanisms by void nucleation and shear localization will be used**
    - **Apparent problems do not exist because of extremely conservative design. Pipelines operate in the absolute absence of a any design criteria against hydrogen-induced failure**
    - **There is no criteria with predictive capabilities for safe pipeline operation against hydrogen-induced fracture**
    - **Pipeline steels are extremely susceptible to fatigue failure in the presence of hydrogen**

# Response to Reviewer' Comments

- **Recommendations**
  - **Assessment should be made of the coating integrity during installation**
    - **Permeation measurement to investigate whether coatings are blocking hydrogen are to be conducted**
    - **The problem is being studied in collaboration with Schott Company**
    - **Conditions for coating delamination upon application are studied**
  - **Project needs to stay close to applied researchers and make sure learning is applied**
    - **Development of fracture criteria against hydrogen induced failure is an extremely important engineering tool for safe pipeline operation**
    - **Research is carried out in collaboration with the Engineering Departments of ORNL and Sandia National Laboratories**
    - **Collaboration with hydrogen pipeline installation companies: Air-Lequide and Air Products**
    - **Collaboration with ASME on setting pipeline design criteria against hydrogen embrittlement**
    - **Collaboration with the Japan Gas Company**

# Presentations

- Sofronis, P. (invited) “Materials for the new hydrogen economy: embrittlement problems and remediation.” University of Pennsylvania, Department of Mechanical Engineering and Applied Mechanics, February 2, 2005.
- Robertson, I. M. and Birnbaum, H. K. “Dislocation mobility and hydrogen-A brief review,” *11$^{th}$ International Conference of Fracture, Symposium on Hydrogen Embrittlement*, Torino, Italy, March 20-25, 2005.
- Robertson, I. M. (invited) “The effect of hydrogen in solid solution on the deformation and fracture of metals.” Studvik Nuclear Power Company, Studvik, Sweden, 2005.
- Sofronis, P., Aravas, N., Liang, Y., and Dodds, R. J. (invited) “Mechanics models for hydrogen-induced shear localization and void growth in materials,” *11$^{th}$ International Conference of Fracture, Symposium on Hydrogen Embrittlement*, Turin, Italy, March 20-25, 2005.
- Somerday, B., Novak, P. and Sofronis, P. “Mechanisms of hydrogen-assisted fracture in austenitic stainless steel welds,” *11$^{th}$ International Conference of Fracture, Symposium on Hydrogen Embrittlement*, Turin, Italy, March 20-25, 2005.
- Bammann, D. J. and Sofronis, P. “ A coupled dislocation-hydrogen based model of inelastic deformation,” *11$^{th}$ International Conference of Fracture, Symposium on Hydrogen Embrittlement*, Turin, Italy, March 20-25, 2005.
- Mechanisms and Models for Hydrogen Embrittlement,” McMAT2005, Joint ASCE/ASME/SES Conference on Mechanics of Materials, Baton Rouge, LA, June 1-3, 2005
- Sofronis, P. invited *plenary speaker* on “hydrogen embrittlement” at the International Symposium of Hydrogen in Matter (ISOHIM 2005), Angstrom Laboratory at Uppsala University, Sweden, June 13-17, 2005.
- Sofronis, P and Robertson, I. M. (invited) “Materials for hydrogen delivery: embrittlement problems and remediation,” at the Materials for the Hydrogen Economy Symposium to be held at the Materials Science and Technology 2005 Meeting, Pittsburgh, PA, September 26-28, 2005.
- Sofronis, P. invited as a JSPS fellow to visit Japan from June 10 to June 25, 2006 to collaborate with Prof. Murakami at Kyushu University on a joint project of “Fatigue Mechanisms for Steels in Hydrogen Environment ”
- Sofronis, P., “Materials for the Hydrogen Economy,” Clean Power Systems: Applications, Corrosion, and Protection Symposium, 135th Annual Meeting of the TMS, San Antonio, TX, March 12-16, 2006.
- Sofronis, P. (invited) “On the Development of Fracture Criteria for Hydrogen Embrittlement of Pipeline Steels,” Hydrogen Gas Embrittlement Workshop, ASTM Meeting, Dallas, TX, November 8, 2005

# Publications

- Liang, Y., D. C. Ahn, P. Sofronis, R. Dodds, and D. Bammann, “Hydrogen Effects on Void Growth and Coalescence in Metals and Alloys,” submitted to *Mechanics of Materials*, under review.
- Sofronis, P. and Robertson, I. M., “Viable Mechanisms of Hydrogen Embrittlement-A Review” To be published in the proceedings of the International Symposium of Hydrogen in Matter (ISOHIM 2005) held at the Angstrom Laboratory, Uppsala University, Sweden, June 13-17, 2005.
- M. Dadfarnia, P. Sofronis, I. Robertson, B. P. Somerday, G. Muralidharan, D. Stalheim, “Numerical Simulation of Hydrogen Transport at a Crack Tip in a Pipeline Steel,” submitted for the proceedings of IPC2006, 6$^{th}$ International Pipeline Conference, September 25-26, 2006, Cargary, Alberta, Canada.
- M. Dadfarnia, P. Sofronis, I. Robertson, B. P. Somerday, G. Muralidharan, D. Stalheim, invited paper “Micromechanics of Hydrogen Transport and Embrittlement in Pipeline Steels,” Proceedings of the 2006 ASME International Mechanical Engineering Congress and Exposition, November 5-10, 2006.

# Critical Assumptions and Issues

- **Hydrogen-induced cracking in existing pipeline steels initiates at second phase particles by hydrogen-induced decohesion followed by shear localization of ligaments**
  - Fracture toughness testing and SEM/TEM studies will verify this assumption
- **Embrittlement of acicular ferrite initiates at the needle-pearlite/ferrite interface**
  - Fracture toughness testing and SEM/TEM studies will verify this assumption
- **Hydrogen dramatically degrades the resistance of steel to fatigue crack growth. Possible remediation by water vapor and oxidation**
  - Experiments to study the oxidation effects
- **Lack of funding does not allow**
  - Hire personnel
  - Construct experimental devices
  - Carry out testing