V.A.5 Hydrogen Embrittlement of Pipeline Steels: Causes and Remediation

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Objectives

- Develop 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 7 MPa in both static and cyclic loading conditions (due to in-line compressors).
- Explore methods of mitigation of hydrogen-induced failures through inhibiting species (e.g., water vapor) or regenerative coatings (e.g., surface oxidation).
- Explore suitable steel microstrutures, and/or coatings, or other materials to provide safe and reliable hydrogen transport and reduced capital cost.
- Assess hydrogen compatibility of the existing natural gas pipeline system for transporting hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

- D. High Capital Cost and Hydrogen Embrittlement of Pipelines
- H. Storage Tank materials and Cost (as affected by hydrogen embrittlement)

Technical Targets

The targets of this project are: (i) to identify the deformation mechanisms and potential fracture initiation sites in the presence of hydrogen solutes in both pipeline steels and welds; (ii) to measure hydrogen adsorption, bulk diffusion, and trapping characteristics of the material microstructure in both coatings and pipeline steels; (iii) to carry out finite element simulations in order to study the interaction of transient hydrogen diffusion with material elastoplasticity under high-pressure hydrogen gas environment; and (iv) to establish the fracture resistance of the pipeline materials and welds under both static and fatigue loadings. These studies will help toward assessing pipeline compatibility and reliability with hydorgen and protection from potential hydrogen embrittlement, thus meeting the Hydrogen Delivery targets as outlined in Table 3.2.2 of the March 2005 version of the HFCIT Multi-Year RD&D Plan.

Approach

First, mechanical property testing will be carried out to determine the elastic and flow characteristics of pipeline materials in the presence of hydrogen. Testing of specific steel specimens provided by Oregon Steel Mills has been arranged to be carried out in a high pressure gaseous environment at the Sandia National Laboratories at Livermore, CA. Thermal desorption spectroscopy will also be carried out to identify the hydrogen trap characteristics and the associated binding energies. In particular, equipment for permeation experiments is currently being designed at the University of Illinois to determine the dynamic behavior of traps and their evolution with plastic straining. Permeation measurements are also planned on pipeline coatings, e.g. an Al-rich phosphate "glass" provided by Applied Thin Films and Cerablak provided by Chemical Composite Coatings.

Subcritical crack growth and fatigue crack growth experiments at a 7 MPa hydrogen atmosphere are to be conducted to determine respectively the threshold stress intensity factor and the effect of cyclic loading at frequencies of 1 cycle/day, which is a real-world scenario given the in-line compressor operation schedule. An important outcome expected from these tests is the identification of the fracture mechanisms in the presence of hydrogen. Preliminary fracture experiments (Figure 1) indicate that the fracture mode in pipeline steels is ductile transgranular with the fracture initiating by hydrogen-assisted decohesion at second phase particles/inclusions and promoted by hydrogen-accelerated void coalescence. Similar fracture experiments will also be conducted on weld materials to identify the corresponding mode of fracture.

Finite element simulation of transient hydrogen transport will be carried out to model both the subcritical crack growth and fatigue crack growth tests mentioned above. The simulations will account for trapping at microstructural defects, stress driven diffusion, and hydrogen-induced lattice dilatation and flow stress reduction (Figure 2). The trapping characteristics as determined by our experiments will be input in the simulations so as to model hydrogen transport at a crack tip under dynamic microstructural evolution conditions. The simulations will be carried out using our in-house finite element codes which have been developed and tested on hydrogen-related research at the Materials Research Laboratory of the University of Illinois.

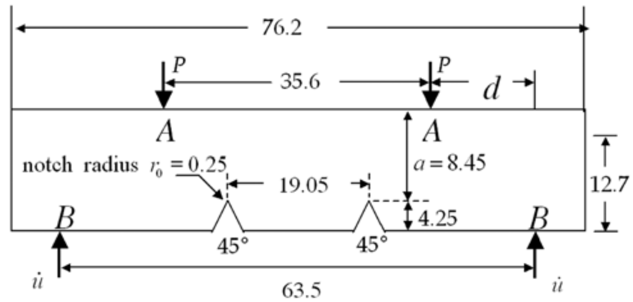

Figure 1. Loading and specimen geometry for a double-notch bend steel specimen; all dimensions are in mm.

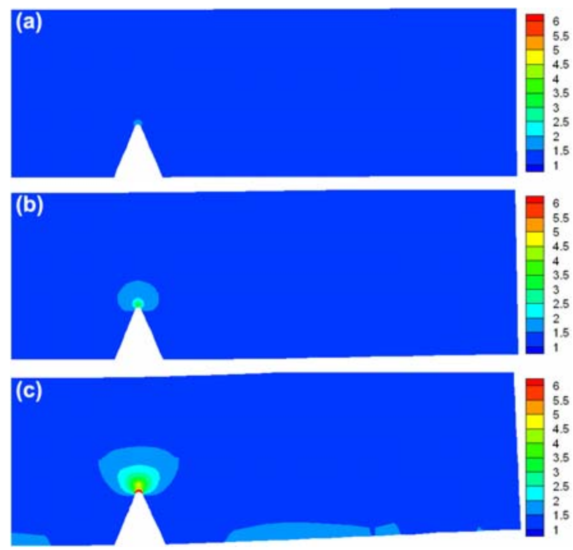

Figure 2. Contour plots of normalized hydrogen concentration (in both trapping and interstitial sites) over the right-half of the specimen shown in Figure 1 strained at a loading rate $\dot{u}$ = 0.001 mm/s when: (a) the deformation is purely elastic and $\sigma_{nom}/\sigma_0 = 0.2$; (b) plasticity is constrained at the notch root and $\sigma_{nom}/\sigma_0 = 1.0$; (c) plasticity has spread on the opposite side of the notch and $\sigma_{nom}/\sigma_0 = 2.0$. The normalizing concentration is the stress-free lattice concentration in equilibrium with hydrogen pressure of 1Atm, σ_{nom} is the maximum bending stress in the specimen in the absence of the notch, and σ_0 is the yield stress of the material. Large strain deformation causes observable macroscopic changes in the specimen shape.

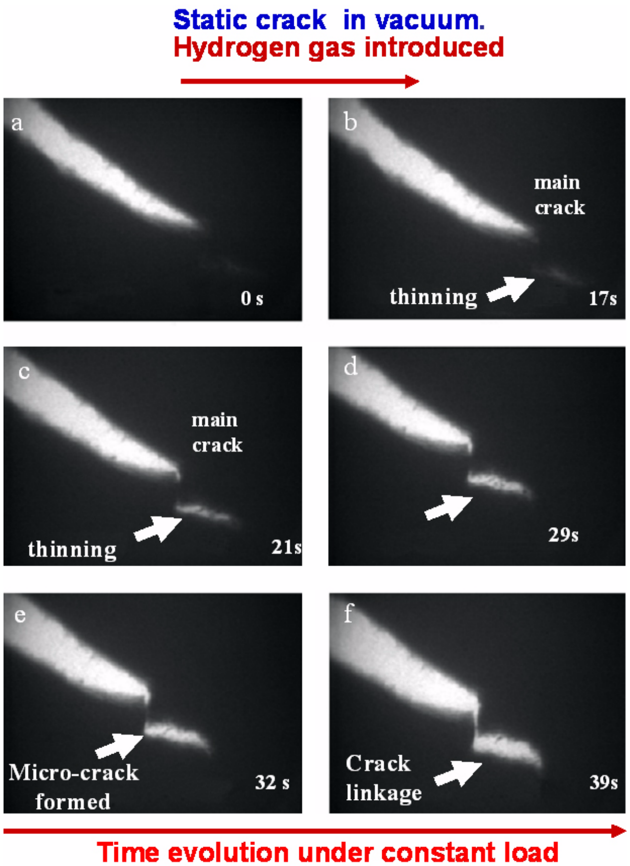

Figure 3. *In situ* TEM study of hydrogen-induced crack propagation in alloy IN 903 under dead-loading conditions: a) main crack is static under load at time t = 0s; b), c) specimen thinning is observed ahead of the main crack after the introduction of hydrogen while the load is maintained constant; d) specimen thinning continues while the main crack is blunting under constant load; e) A microcrack forms ahead of the main crack; f) microcrack links with the main crack.

In order to understand the hydrogen effect on fracture initiation at second phase particles/ inclusions, density functional theory (DFT) is currently used to calculate directly the hydrogen concentration effects on the interfacial separation forces and the associated work expenditure in body-centered cubic (bcc) Fe that contains MnS inclusions. At an initial stage, computational validation "experiments" for bcc Fe with hydrogen at grain-boundaries and surfaces are carried out, especially to obtain the most proper DFT exchange-correlation energies. These calculations will then be extended to obtain the MnS/matrix interface traction-separation curves for several hydrogen concentrations. The results will be used in conjunction with *in-situ* transmission electron microscopy (TEM) experiments (Figure 3) and finite element simulations of hydrogen distributions (as shown in Figure 2) around an inclusion in the neighborhood of a crack tip to assess the conditions for hydrogen–induced microcracking ahead of a main crack.