V.A Pipelines

V.A.1 Hydrogen Permeability and Integrity of Hydrogen Transfer Pipelines

Zhili Feng (Primary Contact), Larry Anovitz, Paul Korinko, Suresh Babu, and Jim Blencoe
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6095
Phone: (865) 576-3797; Fax: (865 0 574-4928; E-mail: fengz@ornl.gov

DOE Technology Development Manager: Mark Paster
Phone: (202) 586-2821; Fax: (202) 586-9811; E-mail: Mark.Paster@ee.doe.gov

National Laboratory Collaborator:
Savannah River National Laboratory, Aiken, SC

Start Date: 2004
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Quantify and develop the knowledge base for hydrogen permeability and embrittlement of pipeline steels and their welds under high-pressure gaseous hydrogen exposure relevant to hydrogen gas transmission pipeline.
- Optimize the base metal and weld metal composition and microstructure to avoid excessive hydrogen permeation and increase service performance of hydrogen pipelines.
- Evaluate welding technologies suitable for joining high-pressure hydrogen pipelines.
- Develop a risk assessment based approach to manage the integrity and safety of hydrogen pipelines including weld joints.

Technical Barriers

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

- D. High Capital Cost and Hydrogen Embrittlement of Pipelines
- J. Safety, Codes and Standards, Permitting and Sensors.

Technical Targets

This project is to gain the basic understanding of hydrogen permeation behavior and its impacts on hydrogen embrittlement under high-pressure gaseous hydrogen environment, and to develop the technical basis and guidelines for management of the hydrogen, stress and microstructure of pipeline steels and their welds for structural integrity and safety of hydrogen delivery pipelines. Insights gained from these studies will be applied toward the hydrogen delivery infrastructure that meets the following DOE 2015 hydrogen pipeline delivery targets:

- Cost: $0.8 Million/Mile
- Cost of delivery of hydrogen <$1.00/gge
- High Reliability of operation with metrics to be determined.

Approach

- Conduct high-pressure H_2 permeation and mechanical tests using ORNL's unique internally heated pressure vessel to quantify the following:
  - Hydrogen permeation (solubility and diffusivity) and embrittlement behavior as a function of pressure and temperature
  - Effect of steel composition and microstructure, and surface condition (including coating)
  - Effects of welding: weld microstructure, residual stress, and geometrical discontinuities
- Characterize the microstructure before and after hydrogen charging for both base metal and weld region
- Investigate the suitability of existing natural gas pipeline welding practice and standard to hydrogen pipeline, develop new welding technology and/or improve existing welding technology for H_2 pipeline construction and repair
- Evaluate the economic and technological benefits of modern, hydrogen-cracking resistance, high-strength pipeline steels for hydrogen delivery and storage
- Develop a risk assessment based approach and a database for common pipeline steels to ensure the integrity and safety of H_2 pipelines

Accomplishments

- Developed high-pressure hydrogen permeation testing procedure.
- Completed system apparatus upgrade necessary for the high-pressure hydrogen permeation and mechanical testing.
- Obtained baseline hydrogen permeation results for existing pipeline steels under both high and low gaseous hydrogen pressures. Preliminary analyses of the data suggest that the hydrogen diffusivity under the gaseous environment is considerably lower than that under electrolytic charging or electrochemical reaction conditions reported in the literature.

Future Directions

- Complete hydrogen permeation study on the effects of hydrogen pressure, steel microstructure (both base metal and weld), and surface conditions.
- Characterize the effects on microstructure of steels due to hydrogen charging.
- Complete mechanical property degradation measurement and assessment of selected high-strength steels and their welds.
- Evaluate welding technologies suitable for joining high-pressure hydrogen pipelines.
- Develop risk assessment-based approach to manage the integrity and safety of hydrogen pipelines including weld joints.

Introduction

Hydrogen, once produced, must be transported from the point of production to the point of use. A cost-effective and energy-efficient hydrogen delivery infrastructure must be developed for introduction and long-term viability of hydrogen as an energy carrier for transportation and stationary power. Among a number of hydrogen delivery options, an extensive pipeline infrastructure would be the most cost-effective and energy-efficient manner currently known to transport very large amounts of hydrogen to much of the market, as is done with natural gas [1]. Hydrogen delivery by pipeline would require the gaseous hydrogen (H_2) to be transmitted under high pressure levels (up to about 2000 psi) and would have to use economically viable pipeline materials such as pipeline steels. Concerns about potential hydrogen embrittlement of the pipelines, particularly in the weld region, need to be thoroughly addressed to ensure the safe, cost-effective operation and long-term reliability of the hydrogen delivery pipeline infrastructure.

Approach

While there have been extensive studies in the past on hydrogen embrittlement and hydrogen induced degradation of pipeline steels, the high-pressure hydrogen delivery pipeline presents some unique issues that have not been adequately addressed At the center of the issues is the permeation behavior of hydrogen – at the present time, very limited knowledge is available about the rate of permeation and amount of hydrogen in the steel in a high-pressure gaseous environment. Therefore, the first major effort in this project is directed toward high-pressure H_2 permeation and mechanical performance tests using ONRL's unique internally heated pressure vessel to systematically study hydrogen permeation behavior and to evaluate the tolerance level of different steels to hydrogen before significant mechanical property degradation would occur.

As in the case of natural gas and other energy carrier transmission pipelines, the weld joint in the steel pipeline is expected to be a critical region more susceptible to hydrogen embrittlement due to the formation of unfavorable microstructures and high residual stresses. The second major activity of this project will focus on developing new welding technology and/or improvement of existing welding technology to optimize weld microstructure and proactively control the weld residual stress for H_2 pipeline construction and repair. Finally, a risk assessment-based approach will be developed to manage the integrity and safety of hydrogen pipelines including the weld joints.

The proposed approach will effectively utilize the extensive knowledge base, expertise, and advanced testing equipments of the project team in the areas of hydrogen permeation and mechanical behavior testing, welding, microstructure characterization, and pipeline integrity assessment.

Results

In FY 2005, we conducted preliminary hydrogen permeation tests under both high-pressure and low-pressure hydrogen charging conditions, after the completion of the high-pressure hydrogen testing apparatus upgrade in the second quarter of FY 2005. Sections of two pipeline steels (API Grade X52 and API Grade X65) were salvaged from natural gas transmission pipelines by our industry collaborator. The 20-in diameter, 0.312 –in. wall-thick X52 steel pipe was a typical 1950s production that is still in service in many parts of the country. The 16-in diameter, 0.5 in. wall- thick X65 steel pipe was a 1990s production, representing the other end of the spectrum of steels widely used in natural gas transmission pipelines. Chemical analysis and microstructure characterization revealed that the higher strength X65 steel has much lower carbon content (0.18% wt) than the lower grade X52 steel (0.30% wt). This is a reflection of the trend in pipeline steel making in the last few decades – the widespread use of microalloying and/or thermomechanically controlled processing techniques has resulted in newer generations of steels that not only are of higher strength and toughness but also have much improved weldability and resistance to hydrogen cracking at the welds and under sour service conditions (e.g., high sulfur content).

The high-pressure H_2 permeation tests were conducted using ORNL's internally heated pressure vessel, which has been specifically designed for high-pressure gaseous hydrogen experiments. Major upgrade of the testing vessel was completed in the second quarter of FY 2005 specifically for the high-pressure H_2 permeation and mechanical testing task of the hydrogen delivery infrastructure project. The upgraded testing apparatus makes it possible to conduct H_2 permeation testing under controlled temperatures (up to 1000°C) and very high H_2 pressures (up to 12,000 psi, 3.44×10^7 Pa). Figure 1 shows the basic set-up of the high-pressure H_2 test apparatus.

To complement the high-pressure test, low pressure hydrogen permeation testing was conduced at Savannah River National Laboratory. The measurements were carried out at one pressure level of 700 torr (13.5 psi, 9.33×10^4 Pa, or approximately 1 atmosphere) and different temperatures between 100 and 200°C.

In both high-pressure and low-pressure tests, the hydrogen pressure at the upper-stream side (the

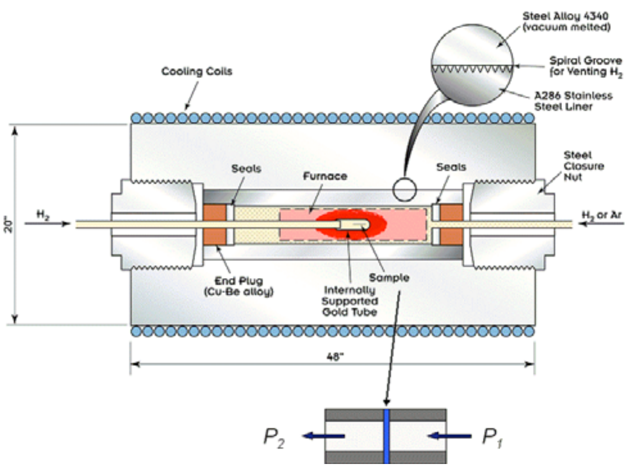

Figure 1. High-Pressure H_2 Permeation Test Apparatus

charging side) maintained the pre-determined pressure level. Hydrogen that permeated through the steel sample was collected on the downstream side into a constant volume chamber. The transient pressure rise in the downstream constant volume chamber was used to determine the effective diffusivity by the time lag technique [2]. The solubility was then calculated from the steady state flux and the effective diffusivity.

For all measurements, steel samples were cut by electrical discharge machining (EDM) from the steel pipes. The sample surface was polished with grit No. 600 sandpaper to remove the heavy machining marks. The sample was then cleaned with alcohol/ acetone. It is important to note that we did not electroplate the sample surface with Pd, as was done in many previous studies to eliminate the flux-limiting surface impedances, as understanding the roles of surface coating (including the naturally grown surface oxide layer) in hydrogen permeation is a major focus of the project.

Figure 2 presents an example of the measured pressure rise curve for X52 steel. The H_2 charging pressure was set at 510 psi, and testing temperature was at 165°C. In the figure, the pressure transient was normalized to the H_2 charging pressure. As shown in the figure, it only took about 30 minutes before hydrogen broke through the 0.5-mm thick sample. In addition, the permeation flux reached the steady-state in about 600 minutes (10 hours) where the hydrogen concentration in the sample is saturated.

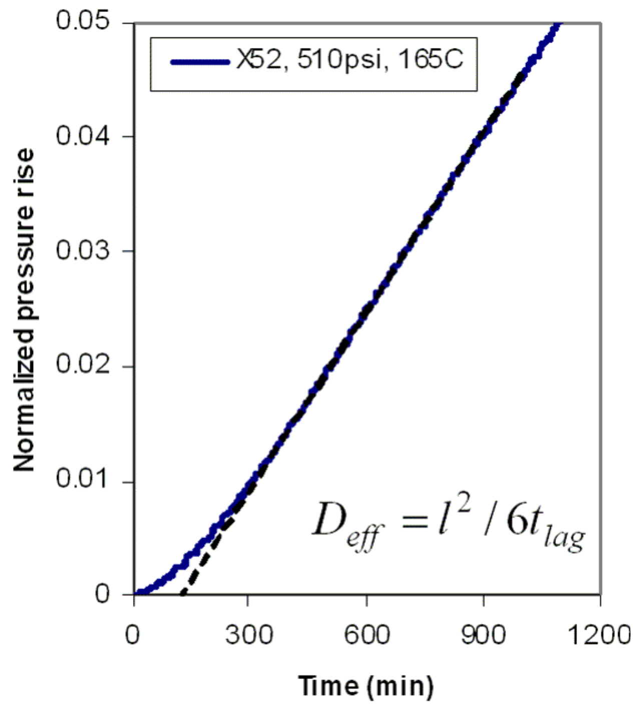

Figure 2. Pressure Rise Curve for X52 Steel During High-Pressure H_2 Permeation Measurement (The measured downstream pressure is normalized to the charging pressure on the upstream side. Hydrogen charging pressure: 510 psi; testing temperature: 165°C.)

Figure 3 shows the diffusivity results for both high-pressure (510 psi) and low pressure (13.5 psi) cases measured in this study. For comparison, the diffusivity data compiled by Alefeld and Volkl [3] from open literature are also provided in the same figure. Overall, the diffusivity measured in this project under both high-pressure and low-pressure conditions are considerably lower than these collected by Alefeld and Volkl. The causes of this difference are under investigation. Probable causes include H_2 absorption and dissociation mechanisms at the surface under a gaseous environment, and the presence of a passive surface oxide layer in our test samples which generally retards the hydrogen permeation. Additional measurements with different surface conditions are underway to elucidate the effects of surface oxide layer.

Comparing the permeation data obtained from high-pressure and low-pressure tests suggests that the effects of hydrogen charging pressure on the

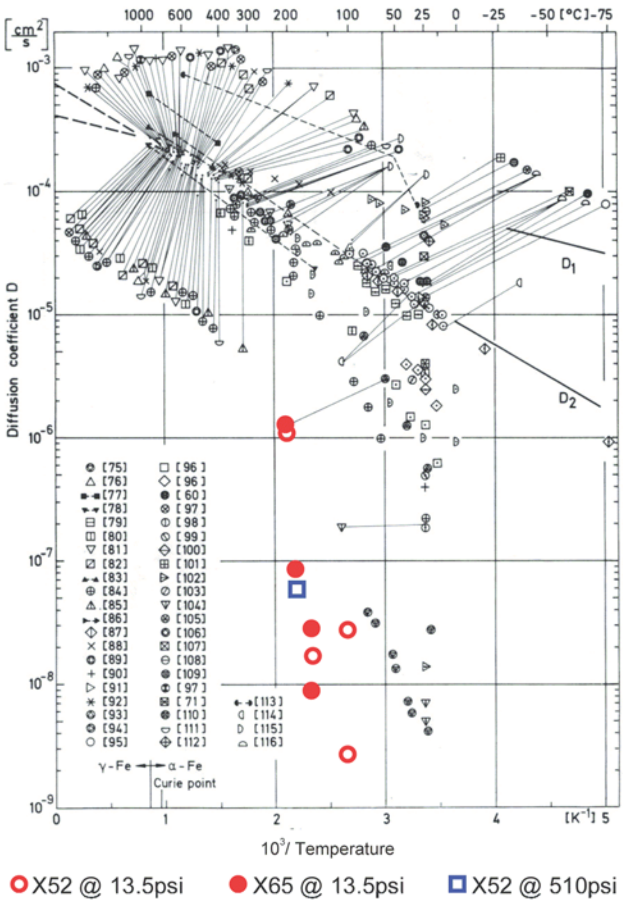

Figure 3. Hydrogen Diffusivity as Function of Temperature (The effective diffusivity data of X52 and X65 pipeline steels obtained under gaseous hydrogen charging condition in this study are compared with the results compiled by Alefeld and Vollkl.)

diffusivity are relatively insignificant, at least for the preliminary tests conducted so far. On the other hand, the hydrogen concentration is highly dependent on the hydrogen charging pressure, as expected by the *Sievert's* law. For example, at 165°C, the saturated hydrogen concentration at 510 psi is about 200 parts per million mass (ppm), whereas it is about 70 ppm at 13.5 psi. Higher hydrogen content in the steel would be more detrimental to the structural integrity of pipeline steels. Further measurements are planned in next year to verify this observation under a wide range of pressure, temperature and surface conditions.

Summary

The following major milestones have been achieved in FY 2005:

- Major upgrade of the high-pressure H_2 permeation testing apparatus has been completed and the apparatus is operational.
- A testing procedure for high-pressure H_2 permeation measurement has been developed.
- Preliminary hydrogen permeation measurements have been conducted under both high-pressure and low-pressure conditions. The effective diffusivity under the gaseous hydrogen charging condition is considerably lower than these in open literature under electrolytic charging conditions.

FY 2005 Publications/Presentations

1. Z. Feng, et al, "Hydrogen Permeability and Integrity of Hydrogen Delivery Pipelines," DOE 2005 Hydrogen Program Annual Review Meeting, May 23-26, 2005, Arlington, VA.
2. S. Babu, Z. Feng, L. Anovitz, and P. Korinko, "High Pressure Hydrogen Transfer through Steel Pipeline: Issues, Challenges, and Path Forward," Materials Science & Technology 2005, TMS, Sept., 25- 28, 2005, Pittsburgh, PA

References

1. US Department of Energy, "Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan," January 21, 20053-40.
2. Frank, J, 1975. "The Mathematics of Diffusion", Second Edition, Oxford University Press, p52.
3. Alefeld and Volkl, 1978. "Hydrogen in Metals I – Basic Properties", Springer-Verlag, New York, p328.