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

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Projected End Date: 2008

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 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 Delivery section (3.2.4.2) 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

The objective of this project is to gain basic understanding of hydrogen permeation behavior and its impacts on hydrogen embrittlement under a high-pressure gaseous hydrogen environment, and to develop the technical basis and guidelines for management of the stress and microstructure of pipeline steels and their welds for structural integrity and safety in 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.

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.

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 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) be transmitted under very high pressure levels (up to 3,000 psi) and the use of 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 material property degradation of pipeline steels, the high-pressure hydrogen delivery pipeline presents some unique issues that have been seldom addressed in the past. At the center of these 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 under the 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 to hydrogen of different steels before considerable 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 mostly susceptible to hydrogen embrittlement due to the formation of unfavorable microstructure and high residual stresses. The second major activity of this project will focus on developing new welding technology and/or improve 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.

Results

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. 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-inch diameter, 0.312 inch thick X52 steel pipe was a typical of 1950s production that are still in service in many parts of the country. The 16-inch diameter, 0.5 inch thick X65 steel pipe is typical of 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 resulted in newer generations of steels that are not only of higher strength and toughness but also with much improved weldability and resistance to hydrogen cracking for both welding construction and sour service conditions.

The high-pressure H_2 permeation tests were conducted using ORNL's internally heated pressure vessel specifically designed for high-pressure gaseous hydrogen experiments. The testing apparatus makes it possible to conduct H_2 permeation tests under controlled temperature (up to 1,000°C) and very high H_2 pressure (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, a low pressure hydrogen permeation test was conduced at Savannah River National Laboratory. The measurements were carried out at 700 torr (13.5 psi, 9.33×10^4 Pa, or approximately 1 atmosphere) and different temperatures between 100 to 200°C.

In both the high-pressure and low-pressure tests, the hydrogen pressure at the upper-stream side (the charging side) was maintained at the predetermined 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 from the steel pipes. The sample surface was polished with No. grit 600 sand paper to remove the heavy machining marks. The

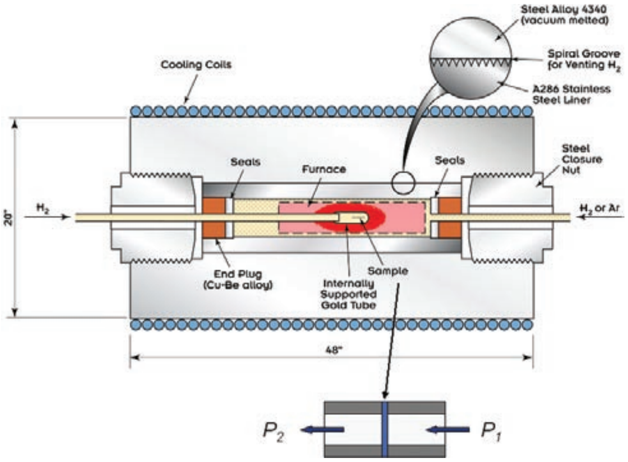

FIGURE 1. High-Pressure H_2 Permeation Test Apparatus

sample was then cleaned with alcohol/acetone. It is important to note that we did not electroplate the sample surface with Pd as 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 the testing temperature was set 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 steady-state in about 600 minutes (10 hours) where the hydrogen concentration in the sample is saturated.

Figure 3 shows the diffusivity results for both high-pressure (510 psi) and low pressure (13.5 psi) cases measured in this study. For compassion, the diffusivity data compiled by Alefeld and Volkl [3] from open literature are also provided in the same figure. Overall, the diffusivities 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 hydrogen permeation. Additional measurements with different surface conditions are underway to elucidate the effects of the 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 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 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.

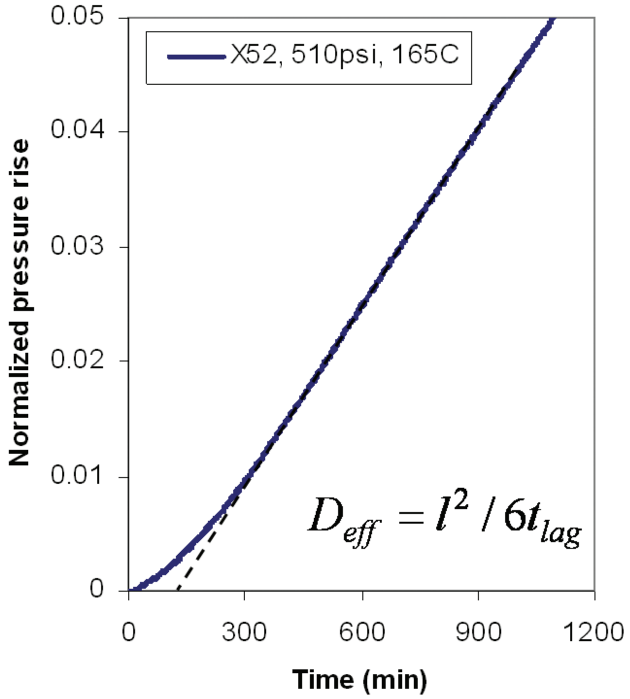

FIGURE 2. Pressure rise curve for X52 steel during high-pressure H_2 permeation measurement. The measured downstream pressure is normalized to the charging pressure on the upstream side. Hydrogen charging pressure: 510 psi; testing temperature: 165C.

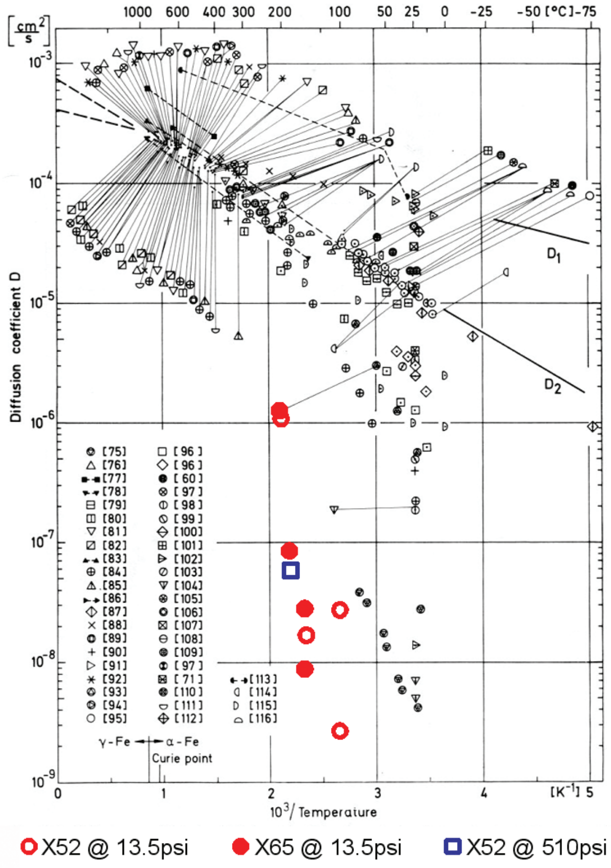

FIGURE 3. Hydrogen diffusivity as function of temperature. The effective diffusivity data of X52 and X65 pipeline steels obtained under gaseous hydrogen charging conditions in this study are compared with the results compiled by Alefeld and Vollkl.

Conclusions and Future Directions

- Preliminary hydrogen permeation measurements have been conducted under both high-pressure and low-pressure conditions. The effective diffusivity under gaseous hydrogen charging conditions is considerably lower than those in the open literature under electrolytic charging conditions.
- Complete hydrogen permeation study on the effects of hydrogen pressure, steel microstructure (both base metal and weld), and surface conditions.
- 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.

References

1. U.S. Department of Energy, “Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan,” January 21, 2005, page 3-40.

2. Frank, J, 1975. “The Mathematics of Diffusion”, Second Edition, Oxford University Press, p. 52.

3. Alefeld and Volkl, 1978. “Hydrogen in Metals I – Basic Properties”, Springer-Verlag, New York, p. 328.