SANDIA NATIONAL LABORATORIES
HYDROGEN PRODUCTION AND DELIVERY PROGRAM

QUARTERLY PROGRESS REPORT FOR JANUARY 1, 2011–MARCH 31, 2011

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RECIPIENT: SANDIA NATIONAL LABORATORIES

CONTENTS

Sandia National Laboratories

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ENABLING HYDROGEN EMBRITTLEMENT MODELING OF STRUCTURAL STEELS

COVERING PERIOD: JANUARY 1, 2011 THROUGH MARCH 31, 2011

DATE OF REPORT: APRIL 30, 2011

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FY 2011 MILESTONES/DELIVERABLES

Task	Planned	Percent complete	Status
Task 2—Enabling Hydrogen Embrittlement Modeling of Structural Steels			
Subtask 2.1—*Measure fracture properties of X52 seam weld at constant H_2 gas pressure*	12/31/10	60%	Completed initial fatigue testing
Subtask 2.1—*Measure the da/dN vs ΔK relationship for steel girth weld at constant H_2 gas pressure*	03/31/11	10%	Obtained X65 girth weld for testing
Subtask 2.2—*SMART milestone: Determine the threshold level of oxygen impurity concentration required to mitigate accelerated fatigue crack growth of X52 steel in hydrogen at gas pressures up to 3000 psi*	09/30/11	0%	

PROJECT OBJECTIVE

The principal objective of this project is to provide an experimental component to the development of prognosis models for steel hydrogen gas pipelines. These models include both mechanism-based simulations of hydrogen embrittlement as well as structural integrity analyses to predict safety margins for pipelines. The aim of the experimental effort is to establish physical models of hydrogen embrittlement in steels and to generate material properties that serve as model inputs. The focus of the latter is on fracture mechanics properties such as crack propagation thresholds and fatigue crack growth relationships.

BACKGROUND

Carbon-manganese steels are candidates for the structural materials in hydrogen gas pipelines, however it is well known that these steels are susceptible to hydrogen embrittlement. While hydrogen embrittlement compromises the structural integrity of steel components, decades of research and industrial experience have allowed many salient variables that affect hydrogen embrittlement of steels to be identified. As a result, there are established paths for managing hydrogen embrittlement in steels and quantifying safety margins for steel hydrogen containment structures. For example, fatigue crack growth aided by hydrogen embrittlement is a potential failure mode for steel hydrogen containment structures subjected to pressure cycling. Applying appropriate structural integrity models coupled with measurement of relevant material properties allows quantification of safety margins against fatigue crack growth in hydrogen containment structures.

STATUS

The principal activity during FY11 Q2 was measuring the fatigue crack growth relationship for electric resistance welds (ERW) from X52 line pipe steel in hydrogen gas. The fatigue crack growth rate (da/dN) vs stress-intensity factor range (ΔK) relationship is a necessary material-property input into damage-tolerant life prediction models applied to steel hydrogen pipelines. One such design life methodology for steel hydrogen pipelines was recently published in the ASME B31.12 code. The measurements of crack propagation thresholds and fatigue crack growth relationships in this task support the objective of establishing the reliability/integrity of steel hydrogen pipelines.

The X52 line pipe steel was selected for this task because of its recognized technological relevance for hydrogen pipelines. The X52 steel from the round robin tensile property study (FY08) was tested for the following reasons: 1) some characterization of the material was already provided from the round robin study, 2) ample quantities of material were still available, and 3) the X52 steel was in the form of finished pipe, which is the most relevant product form and also allows samples to be extracted from the ERW seam weld.

The hydrogen-affected fatigue crack growth relationship (da/dN vs ΔK) for the structural steel is the basic element in pipeline life-prediction models. The ASME B31.12 code requires measurement of the fatigue crack growth relationship for pipeline steels at the hydrogen gas operating pressure. Initial measurements of the fatigue crack growth relationship for X52 steel base metal were conducted in 21 MPa hydrogen gas (the upper limit specified for hydrogen pipelines in the ASME B31.12 code) at a load-cycle frequency equal to 1 Hz and load ratio (R = minimum load/maximum load) equal to 0.1 (Figure 1). This load-cycle frequency was selected to balance test effectiveness and test efficiency, since fatigue crack growth rates can be enhanced at lower test frequency but the test duration can become prohibitively protracted. Two replicate measurements were conducted at R=0.1 and 1 Hz to evaluate data variability (Figure 1).

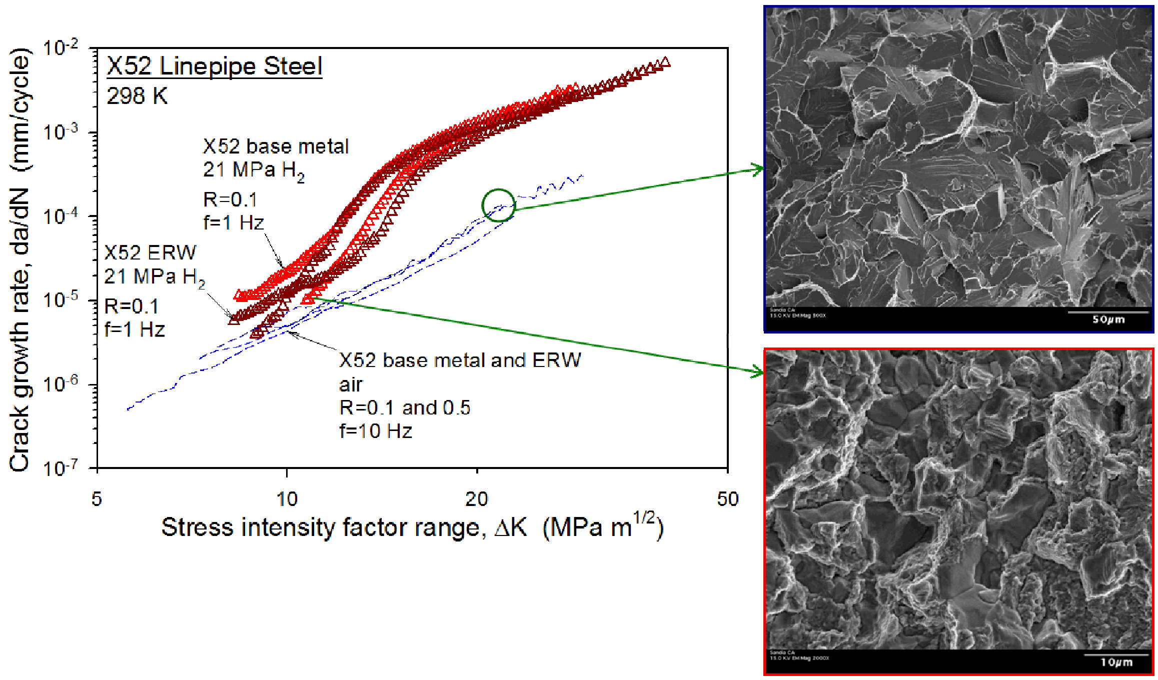

Figure 1. Fatigue crack growth rate (da/dN) vs stress-intensity factor range (□K) plots for X52 steel in hydrogen gas and air. The fractographs show cleavage fracture for the ERW tested in air (Kmax > 40 MPa m1/2) and intergranular fracture for the base metal tested in hydrogen gas.

The fatigue crack growth relationship for the X52 ERW was successfully measured in 21 MPa hydrogen gas. Since steel microstructures in welds are not easily controlled, these weld microstructures can be inhomogeneous. Consequently, it is important to conduct replicate fatigue crack growth tests on welds to characterize potential variability in the data. Figure 1 shows the fatigue crack growth relationships measured for the X52 ERW from replicate tests. These tests were conducted at R=0.1 and 1 Hz so that the results could be directly compared to those for the X52 base metal. The following details are notable in Figure 1: 1) the da/dN vs ΔK relationships for the X52 ERW exhibit significant variability, 2) the da/dN vs ΔK relationships for the X52 base metal also exhibit variability, and 3) despite the variability in the da/dN vs ΔK relationships, it is apparent that the fatigue crack growth rates are similar for the base metal and the weld in hydrogen gas.

While microstructure is one salient variable that can contribute to variability in the da/dN vs ΔK relationships for X52, other variables must be considered as well. For example, the hydrogen test gas was sampled at the conclusion of both tests conducted on the X52 ERW. The leak rates from the pressure vessel were unusually high, and such an abnormal operating condition prompted sampling of the test gas. The hydrogen test gas contained unusually high concentrations of oxygen (>10 vppm) for both tests. Since oxygen is known to inhibit hydrogen uptake into steels, it is possible that the high levels of oxygen in the test gas affected the results. Additional tests will be conducted on the ERW material to clarify whether variability in the da/dN vs ΔK relationships can be attributed to oxygen in the test gas.

A fatigue crack growth test was also conducted on the X52 ERW in air. Such data serves as a baseline for comparison to the data for the ERW measured in hydrogen gas as well as for comparison to the data for the base metal measured in air. Test conditions for the ERW in air included R=0.5 and a load-cycle frequency of 10 Hz. Figure 1 shows that the da/dN vs ΔK relationship for the ERW measured in air is similar to the relationship measured for the base metal in air. However, the test on the ERW was unexpectedly terminated at Kmax~40 MPa m1/2 by unstable crack extension. As illustrated in Figure 1, this rapid crack extension is associated with cleavage fracture. This result suggests that some region of the ERW microstructure has extremely low fracture toughness. The consequence of this inherently low fracture resistance on hydrogen-assisted subcritical cracking needs to be explored.

One of the objectives for FY11 is to conduct fatigue crack growth testing on girth welds of pipeline steels in hydrogen gas. It has been a challenge to identify a source for pipeline steel girth welds, but an evolving relationship with ExxonMobil has enabled the procurement of technologically relevant girth welds. ExxonMobil has supplied a generous quantity of girth weld in an X65 steel pipe (Figure 2). This X65 girth weld will be included in test plans for the remainder of FY11.

Figure 2. X65 steel girth weld supplied by ExxonMobil.

PLANS FOR NEXT QUARTER AND KEY ISSUES

The focus for FY11 Q3 is conducting replicate tests on X52 ERW and initiating testing on the X65 girth weld in hydrogen gas.

PUBLICATIONS / PRESENTATIONS

- "Fracture Toughness and Fatigue Crack Growth of X80 Pipeline Steel in Gaseous Hydrogen", C. San Marchi, B. Somerday, K. Nibur, D. Stalheim, T. Boggess, and S. Jansto, *Proceedings of the ASME 2011 Pressure Vessels & Piping Division / K-PVP Conference (PVP11)*, Baltimore, MD, 2011, Paper No. PVP2011-57684
- "Improving the Fatigue Resistance of Ferritic Steels in Hydrogen Gas", B. Somerday, I2CNER Kick-off Symposium, Fukuoka, Japan, Feb. 2011 (invited).

GEOLOGIC STORAGE OF HYDROGEN

COVERING PERIOD: JANUARY 1, 2011 THROUGH MARCH 31, 2011

DATE OF REPORT: APRIL 30, 2011

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FY 2011 MILESTONES/DELIVERABLES

Task	Planned	Percent complete	Status
Task 3—Geologic Storage of Hydrogen			
Subtask 3.1—*Letter report: Status report*	10/2010	100%	Funding received 4/2010
Subtask 3.1—*SAND report: Summary report of task to date*	12/2010	60%	Included in White Paper
Subtask 3.2—*GIS Map Interface: Letter report*	9/2011	90%	Included in White Paper

PROJECT OBJECTIVE

This year's project consists of two objectives, (1) to develop geologic storage parameters for the Hydrogen Delivery Scenario Analysis model (HDSAM), and (2) to incorporate a GIS interactive map interface as part of the Hydrogen Energy and Demand Model.

Sandia will work with Argonne National Laboratory and National Renewable Energy Laboratory to help update the HDSAM with the latest hydrogen underground geologic storage parameters and cost estimates. The initial step will concentrate on providing NREL with realistic geologic storage costs estimates for a specific storage scenario they provided to Sandia.

The GIS interface will allow for map data to be extracted that will allow for the user to conceptualize geographically the geologic underground storage options available in the region of interest.

BACKGROUND

Geologic storage is used extensively in the oil, natural gas, and compressed air energy industries. To understand the scale of this utilization, 800 million barrels of oil and 100's of billion cubic feet of natural gas are stored geologically in the U.S. The basic drive for geological storage is that the cost per volume-stored is 3 to 5 times less than surface storage. With this relatively inexpensive way to store large volumes, storage can be situated to buffer seasonal demands, provide continuity in case of disruption in the supply chain, and control congestion in the pipeline system. For example, industry analysis estimates that the current natural gas storage in the U.S. reduces the need for pipelines by 50%.

Geologic cavern storage of hydrogen for industrial use already exists at several locations in Texas. In addition, an evolving hydrogen economy and infrastructure raises similar needs as the natural gas and oil infrastructures. Analyses of the hydrogen infrastructure (Ogden, Williams, Simbeck and Chang, Lord) indicate that there may be an important role for geologic storage. This need, similar to fossil energy stocks, is to buffer seasonal demands, provide continuity in case of disruption in the supply chain, and control congestion in the pipeline system.

To date a white paper has been written describing the various types of underground geologic storage options available for the storage of natural gas. The report includes four location maps showing the available underground storage sites in the U.S. The three most likely geologic candidates for the underground storage of hydrogen are 1) salt caverns, 2) depleted oil/gas reservoirs, and 3) aquifers. The report was published as a documentable internal report (i.e. SAND report).

In addition a model has been developed that characterizes the costs entailed in developing and operating three types of hydrogen underground storage facilities; 1) salt caverns, 2) depleted oil/gas reservoirs, and 3) aquifers. The work was presented at the 28th USAEE/IAEE North American Conference in New Orleans, December 2008. A summary report was completed as a documentable internal SAND report, which will allow for public distribution.

STATUS

The funding for the current task was received July, 2010.

SUB-TASK 3.1

This quarter Sandia is working with Argonne National Laboratories by providing cost parameters for geologic storage of hydrogen in salt caverns for four metropolitan cities for HDSAM.

SUB-TASK 3.2

A draft version of the GIS interface has been refined.

PLANS FOR NEXT QUARTER AND KEY ISSUES

Next quarter Sandia will continue to work with Argonne National Laboratories to incorporate underground geologic storage parameters into HDSAM. In addition, a user manual will be written for the GIS module.

PATENTS

None

PUBLICATIONS / PRESENTATIONS

- Lord, A.S., P.H. Kobos, and D.J. Borns, *A Life Cycle Cost Analysis Model Framework for Geologic Storage of Hydrogen*, SAND2010-3677C, Sandia National Laboratories, Albuquerque, NM, 2010.
- Lord, A.S., P.H. Kobos, and D.J. Borns, *A Life Cycle Cost Analysis Framework for Geologic Storage for Hydrogen: A Scenario Analysis*, SAND2010-6939, Sandia National Laboratories, Albuquerque, NM, 2010
- Lord, A.S., *Investigating the Potential for Hydrogen Geostorage with Igneous and Metamorphic Rocks: A Status Report*, SAND2010-6938, Sandia National Laboratories, Albuquerque, NM, 2010.