IX.5 Materials and Components Compatibility

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Objectives

(1) Technical Reference on Hydrogen Compatibility of Materials:
  - Compile historical data from published technical documents in an Internet-based resource.
  - Update published Technical Reference chapters to reflect new data from current applied research activities.

(2) Materials Testing:
  - Fill gaps in database by generating benchmark data on compatibility of structural materials in hydrogen gas, emphasizing commercial materials tested in high-pressure gas.
  - Optimize efficiency and reliability of test procedures for generating design data for structural materials in high-pressure hydrogen gas.

(4) Codes and Standards Advocacy:
  - Perform testing and analysis to provide the technical basis for codes and standards.
  - Participate in the hydrogen codes and standards development/change process.

Technical Barriers

This project addresses the following technical barriers from the Codes and Standards section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(F) Limited DOE Role in the Development of International Standards
(I) Conflicts between Domestic and International Standards
(N) Insufficient Technical Data to Revise Standards

Contribution to Achievement of DOE Codes and Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Codes and Standards section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 21:** Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies (4Q, 2012). This project enables the development and implementation of codes and standards by providing expertise and data on hydrogen compatibility of structural materials.
- **Milestone 25:** Draft regulation for comprehensive hydrogen fuel cell vehicle requirements as a GTR approved (United Nations Global Technical Regulation). (4Q, 2010)

Accomplishments

- Completed cutting-edge measurements and report on fracture threshold measurements of tank steels in H_2.
- Testing completed on stationary tank materials to meet immediate needs for market transformation.
- Testing performed on forklift tank materials to meet immediate needs for market transformation.
- Measurements performed to illuminate pathway to optimization of procedures in American Society of Mechanical Engineers (ASME) Article KD-10 standard.
- Updated "Technical Reference for Hydrogen Compatibility of Materials" to include single-phase nickel alloys.
- Initiated testing and analysis effort to evaluate the cycle-life of steel tanks and inform the design qualification standards for hydrogen-powered industrial trucks (e.g. forklifts).

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Introduction

A major barrier to the deployment of hydrogen technologies is the lack of validated safety codes and standards. The purpose of this project is to provide the technical basis for assessing the safety of hydrogen-based systems with the accumulation of knowledge feeding into the development or modification of relevant codes and standards. The materials compatibility effort focuses on developing optimized materials qualification methodologies and assembling a resource entitled the Technical Reference on Hydrogen Compatibility of Materials. This effort is driven by the needed for a materials guide, as identified in the Multi-Year Research, Development and Demonstration Plan (Table 3.7.5). The content of the Technical Reference is developed by identifying and documenting materials data from journal articles and institutional reports. Voids in the database uncovered during the process of composing the Technical Reference are addressed through a materials testing activity. Results from this materials testing illuminate the pathways to optimize materials qualification methods, enabling efficient, high quality testing to support rapid technology deployment.

Approach

The focus of the Materials and Components Compatibility project is to optimize materials characterization methodologies, generate benchmark data for materials to enable technology deployment, and compose the Technical Reference on Hydrogen Compatibility of Materials. Two activities proceed in parallel: generating new data and understanding through materials testing, and identifying and compiling existing data from technical documents. The high-priority structural materials featured in these activities are low-alloy and carbon steels, austenitic stainless steels, and aluminum alloys. The materials testing activity emphasizes high hydrogen gas pressures (>100 MPa), fracture mechanics methods, and material fabrication and service variables (e.g., welds, temperature). The data from materials testing are critically reviewed to identify pathways to improve the test methods and to ensure the data are suitable for implementation in structural design. The qualification methods developed in this program are then validated on real components to enable effective incorporation into codes and standards.

As part of codes and standards advocacy, Sandia personnel are actively engaged in the codes and standards development process through direct participation in standards development organizations such as ASME, Canadian Standards Association (CSA), Society of Automotive Engineers, and the International Organization for Standardization. This participation ensures that the standards development organizations have the most current technical information on structural material compatibility. Sandia personnel provide guidance in the development of both component design standards as well as materials testing standards.

Results

Technical Reference

The Technical Reference is an evolving document, where individual chapters are published via Web site (http://www.ca.sandia.gov/matlsTechRef/) and updated as information is collected. In addition, a formal report (SAND2008-1163) has been distributed to stakeholders and will be revised periodically. When available, the data featured in the Technical Reference are those that enable application of design standards such as ASME Article KD-10 and ASME B31.12. In addition, permeability data are needed to calculate the rate of hydrogen release from containment structures. There are currently 22 material-specific chapters whose content has been informed by input from stakeholders including industry and standards development organizations. In FY 2010, a new chapter on single-phase nickel alloys was incorporated. The data contained in this reference is often used for materials selection in technology design and for standards development and will continue to be an enabling product of the Codes and Standards program element.

Material Measurements

Efforts in FY 2010 focused on improving methods for measuring fatigue crack growth rates of structural metals in high-pressure hydrogen gas and generating high-demand fatigue crack growth data to enable the implementation of ASME Article KD-10 for short-term technology deployment. We developed and evaluated a new load cell capable of operation in high-pressure hydrogen gas. The performance of the load cell was then assessed by conducting a fatigue crack growth test on the line pipe steel X52 in high-pressure hydrogen gas. In this case, the fatigue crack growth test was conducted using control software that required a feedback signal from the load cell. The test was successfully conducted, and the resulting fatigue crack growth (da/dN) *vs* stress-intensity factor range (ΔK) data from the test are displayed in Figure 1. Test systems capable of measuring fatigue crack growth rates under high-pressure hydrogen are rare, and the implementation of this platform at Sandia establishes a valuable capability that will be leveraged to generate critical data for hydrogen service materials.

The need to determine the cycle-life of steel hydrogen storage tanks on lift trucks emerged as a high priority during FY 2010. In response, a new activity was initiated to establish cycle-life prediction methodologies

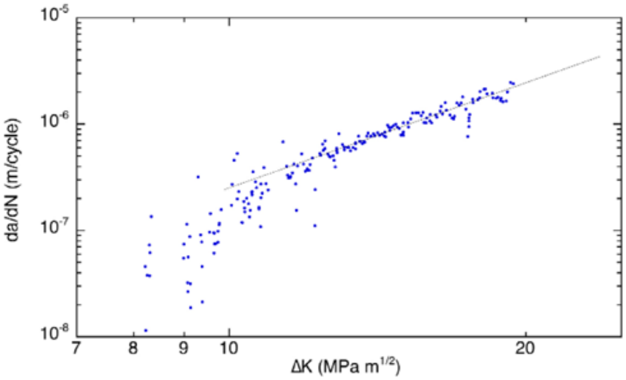

FIGURE 1. Fatigue crack growth rate data measured for X52 line pipe steel in 3,000 psi (21 MPa) hydrogen gas at a load cycle frequency of 1 Hz and load ratio of 0.5. This fatigue crack growth test represents the successful performance of the new strain gauge-based load cell in the test system.

and support standards development for lift-truck tanks. One of the cycle-life prediction methodologies explored in this lift-truck tank activity is based on structural analysis, i.e., ASME Article KD-10. This analytical framework for calculating the cycle life of steel hydrogen pressure vessels requires measurements of fatigue crack growth data for the steel in hydrogen gas. Since one objective of the Materials and Components Compatibility activity has been to measure fatigue crack growth rates for pressure vessel steels in hydrogen gas, this activity is well positioned to contribute critical data for the lift-truck tank effort. The lift-truck tanks are fabricated from the DOT 3AAX (4130X) steel, which we evaluated previously while measuring the sustained-load cracking thresholds of pressure vessel steels. The parameters for the fatigue crack growth tests were developed in consultation with several industry partners. Based on these interactions, the hydrogen gas test pressure and initial stress-intensity factor range were selected as 6,500 psi (45 MPa) and about 9 MPa $m^{1/2}$, respectively, for the fatigue crack growth tests. Two variables that are known to affect measured fatigue crack growth rates in hydrogen gas are the load cycle frequency and the load ratio, i.e., ratio of minimum applied load to maximum applied load (R). Since the rationale for specifying values of load cycle frequency and load ratio are still being developed for fatigue crack growth testing in hydrogen gas, it was decided to test the 4130X over a range of load cycle frequencies and load ratios.

A summary of the fatigue crack growth test matrix, the measured fatigue crack growth rate (da/dN) vs. stress-intensity factor range (ΔK) curves, as well as the status for each test on the 4130X steel are provided in Table 1 and Figure 2. The table indicates that three heats of 4130X are included in the test matrix, in which each steel heat was supplied by a different industry partner. Results in Figure 2 show that the fatigue crack growth rates in hydrogen gas exhibit a complex dependence on the applied stress-intensity factor range. The fatigue crack growth rate relationships (da/dN vs. ΔK) are being used, along with data generated in the full-scale tank tests, to better understand crack initiation in hydrogen gas and to validate the engineering analysis method for design and qualification of steel tanks for use in hydrogen, especially the lift-truck application. Heats 2 and 3 in Table 1 represent specimens taken from the tanks that are being tested in the full-scale tests.

Fatigue crack growth testing of ASME SA-372 Grade J in hydrogen gas at 100 MPa pressure has also been a recent focus of testing activities. Results from this testing directly impact market transformation, since our industry partner will use the data to qualify a stationary hydrogen tank design for a refueling station. Sandia was approached by the industry partner since no commercial test facilities exist in North America with capabilities to execute the testing required by the ASME Article KD-10 code at the service pressure of 100 MPa. Our testing is designed to meet the requirements of the ASME code for hydrogen tanks: three heats of steel tested at a frequency of 0.1 Hz. The low specified test frequency is intended to accommodate the kinetics of hydrogen transport in the steel, but the resulting extended test durations can present a challenge. Table 1 summarizes the matrix for the SA-372 Grade J fatigue testing, and includes the durations for tests completed on both the SA-372 Grade J as well as the 4130X. The da/dN vs. ΔK relationships from the completed test matrix on the SA-372 Grade J steel are plotted in Figure 2. Fatigue crack growth tests in air can be characterized by a power law relationship over a wide range of ΔK, which is represented by a line in a log-log plot such as Figure 2.

Component Testing and Codes and Standards Advocacy

Members of the Sandia Materials and Components Compatibility team were actively involved in the development of standards for lift truck tanks, CSA Hydrogen Powered Industrial Trucks (HPIT) 1. An experimental and analysis project was initiated in FY 2010 to perform hydrogen pressure-cycle testing and engineering analysis of commercial Type 1 hydrogen pressure vessels to build consensus for design methodologies and code development processes for high-frequency refueling applications. The effort provides the technical basis for CSA HPIT 1. The project addresses fatigue crack initiation and growth in steel tanks used in high-cycle applications. The tanks under test are sourced from two fuel cell forklift partner companies and tank manufacturers. We are developing design methodologies for steel tanks in this environment and validating the methodologies with experiments that emulate the real environment of the storage tank.

TABLE 1. Summary of Fatigue Crack Growth Tests for Tank Steels

Material	Yield strength (MPa)	Test conditions		Test duration (hours)†	completion	Objective
		Frequency (Hz)	Load ratio, R			
4130X Heat 1	600	1	0.5	8	FY 2010 Q1	Investigate frequency and R-ratio
		1	0.1	21	FY 2010 Q1	
		0.1	0.5	52	FY 2010 Q1	
		0.1	0.1	340	FY 2010 Q2	
4130X Heat 2	765	1	0.5	14	FY 2010 Q2	Compare with heat 1; same steel as tank testing
		1	0.1	23	FY 2010 Q2	
		0.1	0.5	62	FY 2010 Q2	
		0.1	0.1	(56)*	FY 2010 Q2	
4130X Heat 3	544	Specimens prepared, not yet tested			n/a	Extend range of tested YS; same steel as tank testing
SA372 Grade J Heat 1	642	1	0.5	3	FY 2009 Q2	Benchmark steel; effect of YS
		0.1	0.2	40	FY 2010 Q3	Qualify steel according to ASME KD-10
		0.1	0.5	56	FY 2010 Q2	
		0.1	0.5	>100	FY 2010 Q3	
SA372 Grade J Heat 2	731	1	0.5	3	FY 2009 Q2	Benchmark steel; effect of YS
		0.1	0.2	135	FY 2010 Q3	Qualify steel according to ASME KD-10
		0.1	0.5	84	FY 2010 Q2	
		0.1	0.5	59	FY 2010 Q3	
SA372 Grade J Heat 3	784	1	0.5	3	FY 2009 Q2	Benchmark steel; effect of YS
		0.1	0.2	59	FY 2010 Q2	Qualify steel according to ASME KD-10
		0.1	0.5	71	FY 2010 Q2	
		0.1	0.5	60	FY 2010 Q3	

† excludes preparation and analysis
* unintended interruption of test
YS – yield strength; Q1 – first quarter; Q2 – second quarter; Q3 – third quarter

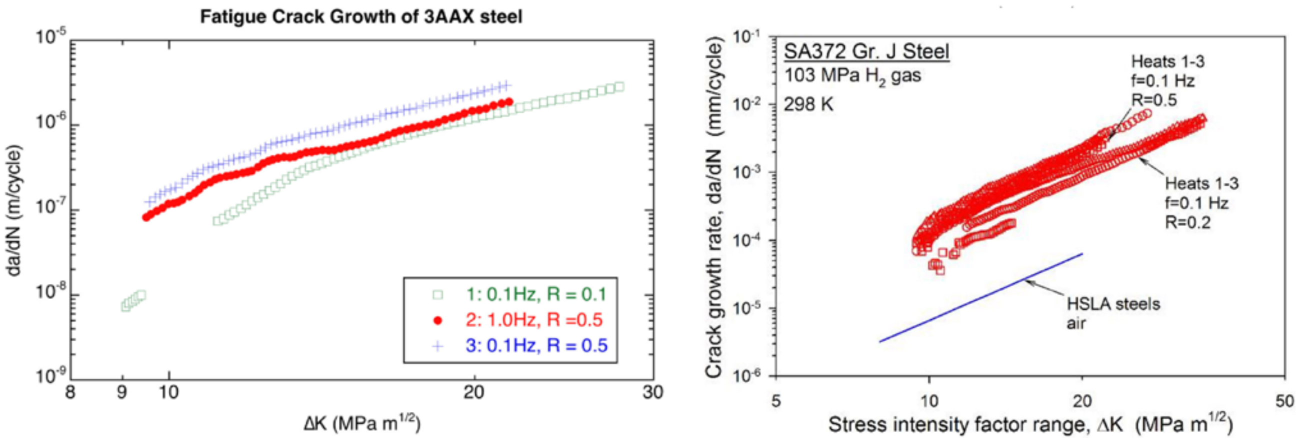

FIGURE 2. Fatigue crack growth rate (da/dN) vs. stress-intensity factor range (ΔK) relationships measured for 4130X tank steel (Heat 1) in 6,500 psi (45 MPa) hydrogen gas and for SA-372 Grade J tank steels (Heats 1-3) in 15,000 psi (103 MPa) hydrogen gas.

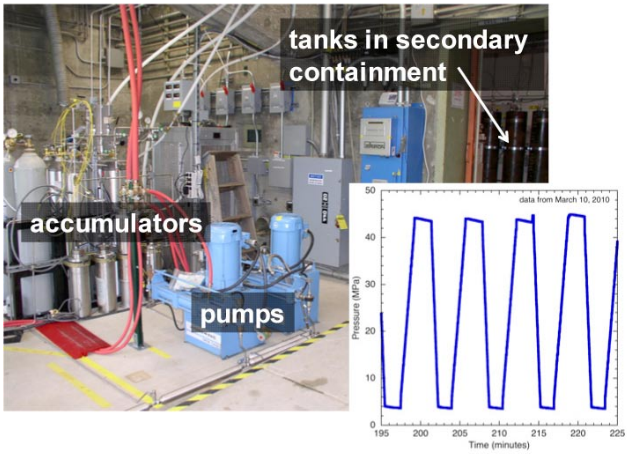

FIGURE 3. Tank Life-Cycle Experimental Setup Including Real Pressure Profile Data

A tank cycling apparatus was developed in a high-pressure facility at Sandia (Figure 3). This is a closed-loop cycling manifold that allows efficient hydrogen utilization. The system has the engineering and administrative controls in place to accommodate tank failure, which is desired in order to understand life-cycles of steel pressure vessels. A periodic pressure profile involves a 2 minute fill to 6,350 psi, a 2 minute hold, and a 2 minute vent which was deemed appropriate by the CSA HPIT 1 Materials working group. This accelerated fatigue cycling allows for up to 250 cycles per day. The test manifold is designed to operate up to 10 tanks in parallel. A test plan was developed in conjunction with the CSA HPIT 1 Materials working group. Two different tanks are under test from two separate manufacturers. Both as-manufactured tanks as well as tanks with engineered defects are tested to understand how cracks imitate and grow through the tank walls. Output from this project provides data in the area of crack initiation in components and validation of performance-based design qualification methods as will be codified in CSA HPIT 1 and the GTR.

Conclusions and Future Directions

In FY 2010:

- A report was completed on fracture threshold measurements of tank steels in hydrogen gas. The data has enabled revision of the ASME Article KD-10 tank standard.
- Fatigue crack growth testing was conducted on tank steels in hydrogen gas following ASME Article KD-10 to meet immediate needs for technology deployment in refueling stations and forklifts.
- We determined that the application of the ASME Article KD-10 standard indicates a path for optimization by establishing fatigue crack growth test frequencies that shorten test duration without compromising data quality.

Future Work:

- Update “Technical Reference” chapters on ferritic steels with new data.
- Establish ability to test properties of materials at variable temperature and pressure.
- Complete and distribute report on results from fatigue crack growth and fracture threshold testing of SA372 Grade J tank steel in hydrogen.
- We will complete fatigue crack growth testing of forklift tank steels in hydrogen to provide data for tank testing activity and enable standards development.
- Establish optimum load cycle frequencies for fatigue crack growth testing of steels in high-pressure hydrogen to enable standards revision.
- Complete first phase of materials qualification standard development for vehicle components (i.e., fittings, regulators, etc.) in collaboration with international partners.
- Conduct testing on additional materials (e.g., aluminum) that impact market transformation (FY 2011–2012).
- Complete materials qualification standard development for vehicle components (i.e., fittings, regulators, etc.).

FY 2010 Publications/Presentations

1. (invited) “Hydrogen-Assisted Fracture: Mechanisms and Technological Implications”, B. Somerday, Gordon Research Conference on Hydrogen-Metal Systems, Barga, Italy, July 2009.

2. “Fracture Control of Hydrogen Containment Components”, B. Somerday, C. San Marchi, and K. Nibur, 3rd International Conference on Hydrogen Safety, Ajaccio, France, Sept. 2009.

“Methods for Measuring Cracking Thresholds of Ferritic Steels in Hydrogen Gas”, K. Nibur, B. Somerday, and C. San Marchi, ISO/TC 58/WG 7 Meeting on H2Testing Methods, Ajaccio, France, Sept. 2009.

3. (invited) “Design Qualification for Hydrogen Containment Components”, B. Somerday, International Hydrogen Energy Development Forum 2010, Fukuoka, Japan, Feb. 2010.

4. “Measurement of Fatigue Crack Growth Rates for Steels in Hydrogen Containment Components”, B. Somerday, K. Nibur, and C. San Marchi, 3rd International Conference on Hydrogen Safety, Ajaccio, France, September 16–18, 2009.

5. “On the Physical Differences Between Tensile Testing of Type 304 and 316 Austenitic Stainless Steels with Internal Hydrogen and in External Hydrogen”, C. San Marchi, T. Michler, K. Nibur and B. Somerday, International Journal of Hydrogen Energy, 2010, in press.

6. “Fracture and Fatigue Tolerant Steel Pressure Vessels for Gaseous Hydrogen”, K. Nibur, C. San Marchi and B. Somerday, Proceedings of the ASME 2010 Pressure Vessels & Piping Division / K-PVP Conference (PVP2010), July 18–22, 2010, Bellevue, Washington, USA.

7. “Measurement and Interpretation of Threshold Stress Intensity Factors for Steels in High-Pressure Hydrogen Gas”, K. Nibur, B. Someday, C. San Marchi, J. Foulk, M. Dadfarnia, P. Sofronis and G. Hayden, SAND2010-4633, Sandia National Laboratories, Livermore, CA, 2010.