III.7 Vessel Design and Fabrication Technology for Stationary High-Pressure Hydrogen Storage

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Subcontractors:

- Global Engineering and Technology LLC, Camas, WA
- Ben C. Gerwick Inc., Oakland, CA
- MegaStir Technologies LLC, Provo, UT
- University of Michigan, Ann Arbor, MI

Project Start Date: October 1, 2010 Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- To address the significant safety and cost challenges in high-pressure stationary hydrogen storage technology
- To develop and demonstrate a novel steel/concrete composite vessel (SCCV) design and fabrication technology for stationary hydrogen storage systems

Fiscal Year (FY) 2013 Objectives

- Demonstrate the SCCV technology through design, engineering, analysis, and construction of a representative mock-up SCCV
- Determine the effectiveness of preventing hydrogen intake to mitigate hydrogen embrittlement of the layer steel vessel design
- Scale up the friction stir welding (FSW) process for thick-sectioned multiple layer vessel manufacturing

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Delivery section (3.2.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan: (E) Gaseous Hydrogen Storage and Tube Trailer Delivery cost

Technical Targets

This project aims at developing and demonstrating the novel design and fabrication technology for low-cost and high-safety SCCV for stationary gaseous hydrogen storage. The flexible and scalable composite vessel design can meet different stationary storage needs (e.g., capacity and pressure) at hydrogen fueling stations, renewable energy hydrogen production sites, and other non-transport storage sites. As shown in Table 1, the current generation composite vessel made using the existing design and manufacturing technology can readily exceed DOE's 2015 cost target. Moreover, with the successful development of advanced manufacturing technology such as the highly-automated FSW process, the next generation vessel has a high potential to meet DOE's 2020 capital cost target. Details of the cost analysis are given in [1].

TABLE 1. Progress towards Meeting Technical Targets for Stationary Gaseous H_2 Storage Tanks (for fueling sites, terminals, or other non-transport storage needs)

Pressure	DOE 2015 Target	Current SCCV	DOE 2020 Target	Next Generation SCCV
Low Pressure (160 bar) Purchased Capital Cost (\$/kg of H2 stored)	\$850	\$681	\$700	\$652
Moderate Pressure (430 bar) Purchased Capital Cost (\$/kg of H2 stored)	\$900	\$713	\$750	\$684
High Pressure (860 bar) Purchased Capital Cost (\$/kg of H2 stored)	\$1,200	\$957	\$1,000	\$919

FY 2013 Accomplishments

- Completed detailed design and engineering of a ¼-sized mock-up composite SCCV capable of storing 90 kg gaseous hydrogen at 430 bar, and obtained vendors quotes from both steel vessel manufactures and concrete construction company.
- Demonstrated the effectiveness of the novel hydrogen mitigation technology to prevent hydrogen entering the structural steel layer. Achieved more than 95% reduction of hydrogen intake in the outer carbon steel layers when compared to the benchmark case without using the mitigation technology.

 Demonstrated superior mechanical properties with 0.6 inch thick multi-pass, multi-layer friction stir weld (MM-FSW) of A572 G50 steel. Multi-layered pipe structure was also fabricated by the MM-FSW technique. Scaling up MM-FSW to ASTM International (ASTM) SA724B steel intended for use in the ¼-sized mock-up is underway and expected to complete by the end of FY 2013.

INTRODUCTION

Low-cost hydrogen delivery infrastructure is critical to successful market penetration of hydrogen-based transportation technologies, such as off-board bulk stationary hydrogen storage. Stationary storage is needed in many locations ranging from hydrogen production plants to refueling stations. The design capacity and pressure of the stationary storage vessel are expected to vary considerably depending on the intended usage, the location, and other economic and logistic considerations. For example, storage vessels at a hydrogen refueling station may have higher pressures but smaller storage capacity when compared to that at a renewable energy hydrogen production site. Therefore, it is important to make storage vessel design flexible and scalable in order to meet different storage needs. Moreover, as it provides the surge capacity to handle hourly, daily, and seasonal demand variations, the stationary storage vessel endures repeated charging/discharging cycles. Therefore, the hydrogen embrittlement in structural materials, especially the accelerated crack growth due to fatigue cycling, needs to be mitigated to ensure vessel safety. Therefore, safety and economics are two prevailing drivers behind the composite hydrogen storage technology.

In this project, ORNL leads a diverse multidisciplinary team consisting of industry and academia to develop and demonstrate an integrated design and fabrication technology for cost-effective high-pressure steel/concrete composite storage vessel that can meet different stationary hydrogen storage needs.

APPROACH

To address the cost and safety issues of current steel storage vessels, a SCCV concept is proposed, which features a multi-layer steel vessel surrounded by reinforced concrete. As illustrated in Figure 1, the shell section of the steel vessel is a layered structure. The innermost layer directly exposed to the high-pressure hydrogen is made of an austenitic stainless steel (e.g., AISI 316L or 304L), which excels as a hydrogen permeation barrier. The other layers are made of high-strength low alloy steel (e.g., ASTM SA724), which costs about four times less than stainless steel. The layered steel vessel technology is proven and accepted in industry standards and codes (e.g., American Society of Mechanical Engineers Boiler and Pressure Vessel Code). It has significant cost and safety advantages over the conventional singlesection steel vessel. Moreover, the layered steel vessel is amiable to the advanced fabrication technology based on FSW for further reducing fabrication cost.

The steel vessel is encased in the pre-stressed concrete sleeve, which shares the structural loads with the steel inner vessel at an even lower cost when compared to structural steel. The optimal use of commodity materials (i.e., stainless steel, structural steel and concrete) is essential to the costeffectiveness and safety of composite pressure vessel. Sensors will be embedded into both inner steel tanks and outer concrete sleeve to ensure the safe and reliable operation



FIGURE 1. Schematic showing the design of a steel/concrete composite vessel comprising inner layered steel tanks and outer pre-stressed concrete confinement.

in field. The composite vessel shown in Figure 1 has the modular design with scalability and flexibility for meeting different storage pressure and capacity needs.

RESULTS

The major tasks in FY 2013 include: (1) engineering design of a 1/4 mock-up composite vessel and estimation of construction cost, (2) development of testing facility and evaluation of hydrogen permeation through multi-layered steel structures, and (3) demonstration of ORNL-patented MM-FSW for joining of thick steel sections. The key results from this year's substantial development are as follows.

Mock-up composite vessel design and construction:

The mock-up vessel has all the essential features and functionality of the full-size SCCV. It contains the inner steel vessel and the outer pre-stressed concrete reinforcement containment. The steel has a stainless steel inner layer as the hydrogen permeation barrier, hydrogen charging and discharging ports, and trunions for tank handling during the concrete construction and in-service installation. In addition, a manway on the top is added to the mock-up vessel, as it is an essential feature in the construction, inspection, and repair of the full-size steel vessel. The reinforcement skirt has a 6 inch-thick concrete layer and five layers of prestressing wires. This mock-up vessel is designed to store 89 kg of hydrogen compressed to 430 bar (6,250 psi, or 43 MPa), which is roughly $\frac{1}{4}$ of the full-scale vessel in terms of storage capacity (375 kg H₂ per tank at 430 bar). Figure 2 shows the completed engineering drawings of the mock-up vessel.

This mock-up SCCV will be constructed in two steps. The inner tank will be fabricated by a steel vessel manufacturer, and then transported to a construction company for concrete casting and reinforcing. The SCCV will then be transported and installed for testing. Initial manufacturing quotes have been received from vendors. Construction contracts will be released to the vendors in the fourth quarter of FY 2013.

Hydrogen permeation mitigation by multi-layered structure:

In order to evaluate the effectiveness of the hydrogen permeation mitigation concept, a special lab-scale highpressure hydrogen permeation testing apparatus was designed and fabricated for this project. This apparatus made it possible to simulate the hydrogen permeation behavior through multi-layered steel structures under conditions similar to those expected in an SCCV. The testing system consisted of four layers of carbon steel. Each layer of the specimen was 3 mm in thickness. The specimen was placed inside a pressure vessel and maintained at a pressure about 2,000 psi. The diffusible hydrogen through these layers was measured using the technique described in [2] with 99.5%



FIGURE 2. Engineering drawing of the 1/4-sized mock-up SCCV.

pure glycerin. Initial testing at the ambient temperature $(20^{\circ}C)$ revealed that the hydrogen diffusion/permeation rate was extremely slow that meaningful experimental results would take months to obtain. In order to increase the hydrogen diffusion rate, a hot oil bath was used to heat up the entire experimental apparatus including the pressure vessel to $150^{\circ}C$.

The principle of the four-layer experimental design is shown in the insert of Figure 3. The high-pressure hydrogen (2,000 psi) permeating through the first layers (labeled as 1 and 4 in the insert) is recombined as H_2 molecules at the interface between the first layer and the second layer (which remains intimate contact under the high-pressure hydrogen) and escaped through the interface into the collecting points A and C. As in the case of the multi-layered vessel design, the collecting points effectively maintains at the pressure level of 1 atm (14.7 psi). As such, the second layers (labeled as 2 and 3 in the inset) are expected to experience a much reduced hydrogen pressure (thereby the amount of hydrogen permeated through) to avoid hydrogen embrittlement. The amount of hydrogen diffused through the second layer is measured at the collecting point B.

The quantitative measurement results along with the schematics of the specimen structure are shown in Figure 3. The hydrogen collection rate through the first layer was about 0.16-0.17 ml/in²/hr at steady state. On the other hand, the collection rate significantly dropped to 0.0032-0.0058 ml/in²/hr after the second layer, which is only about 3 percent of the permeation rate of the first layer. Therefore, we successfully demonstrated that the multilayer steel vessel design is very effective in preventing the hydrogen permeation and mitigating hydrogen embrittlement.



FIGURE 3. Measurements of the diffusible hydrogen through the layered structure (the insert schematic shows the layered experiment design)

Scale up demonstration of FSW technology:

A 15-mm-thick MM-FSW sample was fabricated using A572 G50 steel plates. Transverse tensile, Charpy V-impact toughness, and microhardness tests were performed. The details of the mechanical testing results and microstructure characterization are in Publication 2.

The average yield and ultimate tensile strengths of the weld material were 60 ksi and 76.3 ksi, respectively, which were comparable to the base metal. For all samples tested, the failure locations were in the base metal region of the transverse tensile specimen as shown in Figure 4, illustrated the superior strength of the weld region. Charpy V-impact test results show the toughness of the stir zone (SZ) and heataffected zone (HAZ) were generally higher than the base metal, which can be related to the grain size of the SZ and HAZ. From scanning electron microscopy, the size of refined grains in SZ (ferrite and very small carbides inside ferrite) is less than 10 μ m, while the grain size is more than 30 μ m for the parent metal (mainly ferrite and small portion of pearlite). This grain refinement is typically observed in the SZ due to dynamic recrystallization during FSW. This observation can be related to the measured hardness of the SZ, HAZ, and base metal. Variations in hardness with grain size follow a Hall-Petch relationship [3]. With proven improvement in mechanical properties, MM-FSW technology is scaled up to fabricate 1.5 inch-thick multi-steel samples. Six layers of ¹/₄-inch plates will be FSW and mechanical properties will be measured on this thick sample.



FIGURE 4. (a) Top view of the broken tensile specimen showing final failure location at top layer (b) Cross section view of tensile specimen showing initial and final failure locations after tensile test. (c) Digital image correlation image presenting strain level for the initial failure at middle and bottom layers.
(d) Digital image correlation image displaying the strain map for the final failure at the top layer. Failure locations had high strain levels and both failure locations were found in the base metal.

CONCLUSIONS AND FUTURE DIRECTIONS

- A ¹/₄-size mock-up composite vessel has been designed. Finite element analysis and design optimization are underway. Fabrication of the mock-up vessel is planned to start in FY 2014 and the completion date will be determined when the order is placed.
- The effectiveness of the hydrogen permeation mitigation using the multi-layered structure was experimentally shown to be more than 95%. The effectiveness of stainless steel inner layer as hydrogen permeation bearer will be performed in the future.
- Weld quality on the MM-FSW samples was proven to be superior to the base material. Multilayered pipe structure was manufactured by the MM-FSW technique. Thick MM-FSW samples are under fabrication and will be tested in the near future.

PATENTS ISSUED

1. US Patent No 8,453,515 "Apparatus and method for fatigue testing of a material specimen in a high-pressure fluid environment". Inventors: Jy-An Wang, Zhili Feng, Lawrence Anovitz, Ken Liu.

FY 2013 PUBLICATIONS/PRESENTATIONS

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2. Y.C. Lim, S. Sanderson, M. Mahoney, D. Qiao, Y. Wang,
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3. W. Zhang, F. Ren, Z. Feng, and J. Wang, "Manufacturing Cost Analysis of Novel Steel/Concrete Composite Vessel for Stationary Storage of High-Pressure Hydrogen", Oak Ridge National Laboratory Report, ORNL/TM-2013/113, Oak Ridge National Laboratory, Oak Ridge, TN, Mar. 2013.

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1. W. Zhang, F. Ren, Z. Feng, and J. Wang, "Manufacturing Cost Analysis of Novel Steel/Concrete Composite Vessel for Stationary Storage of High-Pressure Hydrogen", Oak Ridge National Laboratory Report, ORNL/TM-2013/113, Oak Ridge National Laboratory, Oak Ridge, TN, Mar. 2013.

2. D.J. Ball, W. J. Gestal, Jr. and E.F. Nippes, "Determination of diffusible hydrogen in weldments by the RPR silicone-oil extraction method", *Welding Journal*, 1981, 50-s-56-s.

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