III.6 Low Cost Hydrogen Storage at 875 bar Using Steel Liner and Steel Wire Wrap

Amit Prakash (Primary Contact) and Ashok Saxena Wiretough Cylinders, LLC 14570 Industrial Park Rd., Suite C Bristol, VA 24202 Phone: (276) 644-9120 Email: aprakash@wiretough.com; asaxena@uark.edu

DOE Manager: Neha Rustagi Phone: (202) 586-8424 Email: Neha.Rustagi@ee.doe.gov

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Subcontractors:

- Oak Ridge National Laboratory, Oak Ridge, TN
- N & R Engineering, Parma Heights, OH
- CP Industries, McKeesport, PA
- Ashok Saxena, Consultant, Fayetteville, AR
- Structural Integrity Associates, Inc., San Jose, CA
- Hy-Performance Materials Testing, LLC, Bend, OR

Project Start Date: September 15, 2014 Project End Date: June 14, 2017

Overall Objectives

The goal of this project is to develop a pressure vessel to safely store hydrogen at 875 bar with a safety factor of 3 or higher that also meets the DOE storage tank cost target of <\$1,000/kg hydrogen. The objectives are:

- To wire wrap a standard American Society of Mechanical Engineers (ASME) approved, 406 mm diameter and 9.14 m long cylinder with a capacity of 765 L rated at a pressure of 460 bar to boost its pressure capacity to 875 bar and meets the ASME Pressure Vessels and Piping (PVP) Section VIII-Division 3, KD-10 requirements for storing hydrogen.
- To keep the cost of producing the storage tanks to less than \$1,000/kg of stored hydrogen, maintain a design life of 30 yr, and deliver hydrogen that meets the SAE J2719 hydrogen purity requirements.

Fiscal Year (FY) 2016 Objectives

- Perform a detailed elastic-plastic stress analysis to assist in the fine tuning the design of the pressure vessel.
- Explore the possibility of reliably detecting initial flaw sizes that are larger than 2% of the liner wall thickness.

- Commence testing of steel wrapping wires in hydrogen environment.
- Conduct testing to explore the effects of negative load ratios on fatigue crack growth rate behavior of the liner material.
- Develop full length cylinder wire wrap machine capable of wrapping 9.1 m to 12.2 m long cylinders.
- Obtain ASME certifications for use of wire wrapped cylinders for high pressure hydrogen storage.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(E) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs

Technical Targets

This project's goals are to meet the 2020 targets for highpressure hydrogen storage in the 2012 version of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, as shown in Table 1.

TABLE 1. Wiretough's Progress toward Meeting Technical Targets for High Pressure Hydrogen Ground Storage Systems (Fuel Cell Technologies Office 2012 Multi-Year Research, Development, and Demonstration Plan)

Characteristics	2020 Target	Wiretough
High Pressure (860 bar) Purchased Capital Cost (\$/kg of H ₂ stored)	\$1,000	On target to meet in 2017

FY 2016 Accomplishments

- Elastic-plastic finite element analysis was conducted to simulate the autofrettage process and subsequent service pressure cycle conditions to estimate maximum, minimum and cyclic stresses in the critical regions of the cylinder.
- Finite element model was used to identify approaches to reduce stresses in transition region between the wire wrap and the dome of the liner.
- Fatigue crack growth tests in hydrogen at negative load ratios were performed and the study was completed.

- Fatigue testing in hydrogen was performed on high strength wire at Oak Ridge National Laboratory.
- Alternate methods of nondestructive evaluation were explored to reliably detect flaw sizes greater than 2% of the wall thickness, which is a significant improvement over the current industry standard of greater than 3% of the wall thickness.
- Specifications were developed for wire wrapping machine for 9.1 m to 12 m long cylinders, and an order was placed. Installation of the machine is scheduled to begin in July of 2016 with a completion date of end of August of 2016.
- After a review of the stress analysis, manufacturing process, and inspection standards conducted by an ASME team, an ASME U3 Stamp was granted on March 9, 2016. The approval is for the following design:
 - Approval was granted under ASME's Boiler and Pressure Vessel Code Section VIII- Division 3.
 - Liner outer diameter of 406 mm (16 in), length ranging from 7.7 m (25 ft) to 9.2 m (30 ft) with a capacity of 700+ L.
 - Round and flat wires using SA905, Class 1 minimum ultimate tensile strength = 2.04 GPa (296 ksi), minimum yield = 1.8 GPa (260 ksi), wires with the specified pre tension.
 - Allowable maximum pressures in the range of 69 MPa (10,000 psi) to 103.4 MPa (15,000 psi).
 - Certification applies to pressure vessels for ground storage of gases such as compressed natural gas, hydrogen, air etc. For storage of hydrogen, an additional step of self-certification of compliance with ASME KD-10 requirements is necessary.

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INTRODUCTION

The Fuel Cell Technologies Office within the Office of Energy Efficiency and Renewable Energy is supporting research and development activities leading to the development of low cost, high pressure hydrogen storage systems for use in hydrogen refueling stations (forecourt). The goal of this project is to develop a pressure vessel to safely store 750 L of gaseous hydrogen at 875 bar that meets the ASME PVP Section VIII- Division 3 design requirements and also meets the DOE storage tank cost target of <\$1,000/kg H, stored.

APPROACH

Type I metal cylinders (406 mm outer diameter) have been used for compressed natural gas and hydrogen storage for several decades but are limited to pressures of 55 MPa for various technical reasons. Wiretough has a patented process to wrap these commercially available cylinders with ultrahigh strength steel wires (2 GPa in strength) to approximately double the pressure capability of the cylinders with a proven record of safely storing hydrogen. These wire-wrapped cylinders are further subjected to an autofrettage process in which they are subjected to pressures high enough to plastically deform the inner liner, but the wire jacket remains elastic. Upon release of the autofrettage pressure, the inner liner is left with high residual compressive hoop stresses. This process decreases the maximum tensile hoop stress in the liner under the operating pressure and can thus enhance the fatigue life of the vessel very significantly. In this project, this concept was first demonstrated using short, 1.9 m long cylinders and is now being extended to 9.14 m long cylinders.

RESULTS

<u>Design Analysis and Optimization</u>: Finite element analysis was performed to conduct sensitivity analyses in support of fine tuning of the design as described below:

- Effect of varying orthotropic properties of the wrap on liner stresses was systematically explored using the finite element model. Analyses were conducted assuming elastic properties of the wrap in the radial and axial directions to be 5%, 10%, and 20% of the properties in the circumferential directions. The maximum difference in maximum stress values observed was less than 2%. Thus, determining the orthotropic elastic properties of the wrap was only of marginal value.
- The effects of varying wire pre tension load from 17.8–35.6 N (4–8 lb) on the maximum stress in the liner wall was investigated using the finite element model. It was shown that increasing the wire pretension load did not significantly affect the maximum wall stress on the inside surface of the liner.
- The effect of extending the wrap further toward the dome region of the liner was explored. In the baseline analysis, the wire wrap is assumed to begin at approximately 25.4 mm (1 in) from the start of the dome region. Extending the wrap to the transition point leads to a stress reduction of approximately 11%. Moving the wrap from the baseline case to a point on the head provides a stress reduction of approximately 20%. It is therefore beneficial to extend the steel wrap as far as possible in the direction of the dome. Further reductions in maximum stress are possible by reinforcing a portion of the dome with carbon fiber composite.
- The effect of varying yield strength of the liner material on the peak stresses in critical locations of the cylinder was explored. It was shown that reducing yield strength of the liner material was the most effective means of reducing the stress in the critical region. Liner material with a

lower yield strength allows for a lowering the autofrettage pressure. The peak stress was shown to be reduced by 45%. The stresses in the dome region are not affected because the dome does not have a wrap around it.

Effect of Hydrogen on the Fatigue Crack Growth Rate Behavior in the Liner Material: Sandia National Laboratory data on the effect of hydrogen on the fatigue crack growth rate (FCGR) behavior of ASME SA372 Grade J Class 70 steels used in the liner shows a significant acceleration of the crack growth rates relative to the rates in benign environment [1-3]. However, this data is only for load ratios, R, between 0.1 and 0.5. Wiretough's wire-wrapped and autofrettaged cylinder design places the liner wall into compression when there is no pressure. Thus, service loading conditions consist of negative load ratios and fatigue crack growth rate data are needed for negative load ratios. Wiretough designed and verified a single-edge-notch-tension geometry specimen to obtain this data. The hydrogen pressure during these tests was approximately 10 MPa and the tests were performed at room temperature in accordance with the latest version of American Society for Testing and Materials (ASTM) Standard E647: Standard Method for Fatigue Crack Growth Testing. The FCGR behavior for $-1.0 \le R \le 0.2$ is shown in Figure 1. The constants in the regression fits, Equation 1, for the various trends are also given in Figure 1.

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$$\frac{da}{dN} = C(\Delta K)^m \qquad \qquad \text{Equation 1.}$$

Where, *C* and *m* are constants that are derived from regression of the da/dN versus ΔK data in the hydrogen environment. The ΔK for the negative load ratios of -1 and -0.5 are based only on the positive K portion of the loading cycle since K is defined only for crack opening conditions. Values of *C* in Equation 1 are listed for the mean trend and the upper bound of the 95% confidence interval. For comparison, the values of *C* and *m* are also listed for air environment from ASME Section VIII Division 3 Article KD-4 [4].

Tests were performed under constant ΔK conditions to explore the effects of cyclic frequencies between 0.001 Hz and 6 Hz on the FCGR behavior in hydrogen. There appear to be no systematic effects of frequency, and the tests at 1 Hz appear to provide representative conditions for assessing crack growth behavior of the liner materials at all frequencies. Similarly, the differences between the FCGR behavior in hydrogen pressures of 10 MPa and 100 MPa were addressed using literature data at R values of 0.1 and 0.2 and the behavior was found to be comparable. This is consistent with the observations in the literature in that no significant trends related to loading frequency and hydrogen pressure are found for several high strength low alloy steels [2] especially



FIGURE 1. Fatigue crack growth rate data in hydrogen at a pressure of 10 MPa for load ratios between -1.0 and 0.2. The trend line labeled Sandia data was taken from Somerday et al. [2]. The air trend line from ASME KD-4 [4].

at low R values and in the ΔK range of 8–25 MPa(m)^{1/2}. In fact, the behavior in hydrogen and in air seems to converge near ΔK values of 10 MPa(m)^{1/2} and lower.

Design Life Estimation: The above data were used in a crack growth calculation to estimate design lives of wire wrapped hydrogen storage cylinders containing SA 372 Grade J steel liners that were 406 mm (16 in) outside diameter with a wall thickness of 31.75 mm (1.25 in). The method of calculation followed the procedure outlined in ASME Section VIII, Division 3 article KD-10 [5]. The initial flaw sizes assumed for the calculations were (i) based on the currently used nondestructive testing capability that is said to reliably detect flaws that have a depth of 3% of the wall thickness or greater and (ii) based on recent work performed by Wiretough Cylinders in collaboration with its suppliers of liners that showed that cracks that are 2% of the wall thickness or greater can also be reliably detected. The initial flaw length on the surface (2c) is taken as three times the depth. a. The final crack size is assumed to be 0.25 of the wall thickness because of the high toughness of the steel used in the liners. The K-expressions for these calculations were from Newman and Raju [6,7]. For a stress level of 310 MPa (45 ksi), design lives of 30,000 and 21,000 cycles were estimated for initial flaw sizes of 0.03 and 0.02 of the wall thickness, respectively. These cycles are sufficient for the design life of 30 yr at 2 cycles/d.

Reinforcement of the Cylinder to Dome Transition Region Using Carbon Fiber Composite: The process development for wrapping the cylinder to dome transition region of the cylinder with carbon fiber composite was completed. The liners were first wrapped with 48 layers of wire starting 25.4 mm from the transition zone between the cylinder and hemisphere. Six layers of wire were each stepped back from the transition zone by 3 mm per step. Each step of wire consisted of six layers for total a total of 48 layers of wire. Next, approximately 6.25 mm wide carbon fiber ribbons were wrapped on two of the ends to approximately 16 mm thickness. Each layer of the carbon wrap was started at the beginning of the transition region and extended to 38 mm beyond the hemisphere boundary for the first six passes. This was done at 13.35 N (3 lb) tension for the first six layers. To prevent the carbon tape from slipping, a very light spray of "77" adhesive was used on the bare cylinder and on consecutive six pass layers. Each six layer assembly was stepped toward the transition zone 1 mm and wrapped at only 4.45 N (1 lb) tension in order to reduce slippage of the layers underneath. Figure 2 shows a successful carbon fiber wrapped cylinder.

ASME Certification of the Wiretough Pressure Vessel Design: Structural Integrity Associates conducted an analysis of a 406 mm (16 in) outside diameter cylinder with a wall thickness of 8.8 mm (0.346 in) and a length of approximately 1,981 mm (78 in). The wire wrap consisted of a flat wire currently approved by ASTM with a tension of about 20 N



FIGURE 2. Carbon fiber wrap over transition areas of the cylinder

(4.5 lb). These results were incorporated by Structural Integrity Associates in the code case application. After a review of the stress analysis of the structure, manufacturing process, and inspection standards conducted by an ASME Team, ASME U3 Stamp was granted on March 9, 2016. Approval was gained under ASME's Boiler and Pressure Vessel Code Section VIII- Division 3 for a liner outer diameter of 406 mm (16 in) and liner length ranging from 7.7 m to 9.2 m (25 ft to 30 ft) with a capacity of 700+ L. Both round and flat wires using SA905, Class 1 minimum ultimate tensile strength = 2.04 GPa (296 ksi), minimum yield = 1.8GPa (260 ksi) wires with specified pretension are admissible, and the allowable maximum pressures are in the range of 69.9 MPa to 103.4 MPa (10,000 psi to 15,000 psi). The certification applies to pressure vessels for ground storage of gases such as compressed natural gas, hydrogen, air etc. This authorization opens the door for self-certifications of future designs based on rules specified by ASME Section VIII-Division 3 Article KD-10.

CONCLUSIONS AND FUTURE DIRECTIONS

- The results produced during FY 2016 on this project appear promising for meeting the targets set by DOE as scheduled. All major milestones for Budget Period 2 are on target.
- Finite element model analysis to optimize transition region design will be further fine-tuned.
- Complete FCGR testing in hydrogen environment and document the results in the form of a report.

- ASME KD-3 and KD-10 analysis of the 9.5 m long cylinder will be completed in support of the self-certification of Wiretough's design.
- Explore yield strength and ultimate tensile strength reduction of liner material for reducing autofrettage pressures and peak stresses.
- Complete the development of nondestructive evaluation criteria for liners based on initial crack sizes to be 2% of the wall thickness.
- Testing of wires in hydrogen environment to be completed by Oak Ridge National Laboratory.
- 9.5 m long (750 L) cylinders will be produced and wire wound to demonstrate the manufacturing processes and cost estimates.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. A. Prakash, G.R. Sharp, B.T. Deeken, W.J. Head, W.H. Thomson, "Steel Wrapped Pressure Vessel," U.S. Patent 9,266,642B2, Issue date February 23, 2016.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. A. Prakash and A. Saxena, "Low Cost Hydrogen Storage at 875 Bar Using Steel Liner and Steel Wire Wrap," DOE Hydrogen and Fuel Cells Program Annual Merit Review, Washington, D.C., June 6–10, 2016.

2. A. Saxena, A. Prakash, K.A. Nibur, I. Miller, "Considerations of the Effects of H_2 in Design of Type II Storage Vessels Built for Fatigue Resistance," Paper accepted for presentation at the 2016 International Hydrogen Conference, Jackson Hole, WY, September 11–14, 2016.

REFERENCES

1. B.P. Somerday, K.A. Nibur, C. San Marchi, "Measurement of Fatigue Crack Growth Rates for Steels in Hydrogen Containment Components," Unpublished data reproduced with permission.

2. B.P. Somerday, C. San Marchi, Kevin Nibur, "Measurement of Fatigue Crack Growth Rates for SA372-Gr J Steel in 100 MPa Hydrogen Gas Following Article KD-10," Proceedings of the ASME 2013 Pressure Vessels and Piping Conference, PVP 2013, July 14–18, 2013, Paris, France. Reproduced with permission.

3. K.A. Nibur, B.P. Somerday, C. San Marchi, J.W. Foulk, M. Dadafarnia, P. Sofronis, Met Trans., Vol. 44A, 2013, pp. 248–269; reproduced with permission.

4. ASME Section VIII Division 3, Article KD-4, PVP Code, Fracture Mechanics Evaluation, ASME, 2013.

5. Rana, M.D., Rawls, G.B., Sims, J.R., Upitis, E., "Technical Basis and Application of New Rules on Fracture Control of High Pressure Hydrogen Vessel in ASME Section VIII Division 3, PVP 2007–2603, 2007, ASME PVP Conference, July 22–26, San Antonio, TX.

6. Newman, J.C. and Raju, I.S., "Stress-Intensity Factors for Internal Surface Cracks in Cylindrical Pressure Vessels," Transactions of the ASME, Vol. 102, 1980, pp 342–346.

7. Raju, I.S. and. Newman, J.C., "Stress-Intensity Factors for Internal and External Surface Cracks in Cylindrical Vessels," Journal of Pressure Vessel Technology, Vol. 104, 1982, pp 293–298.