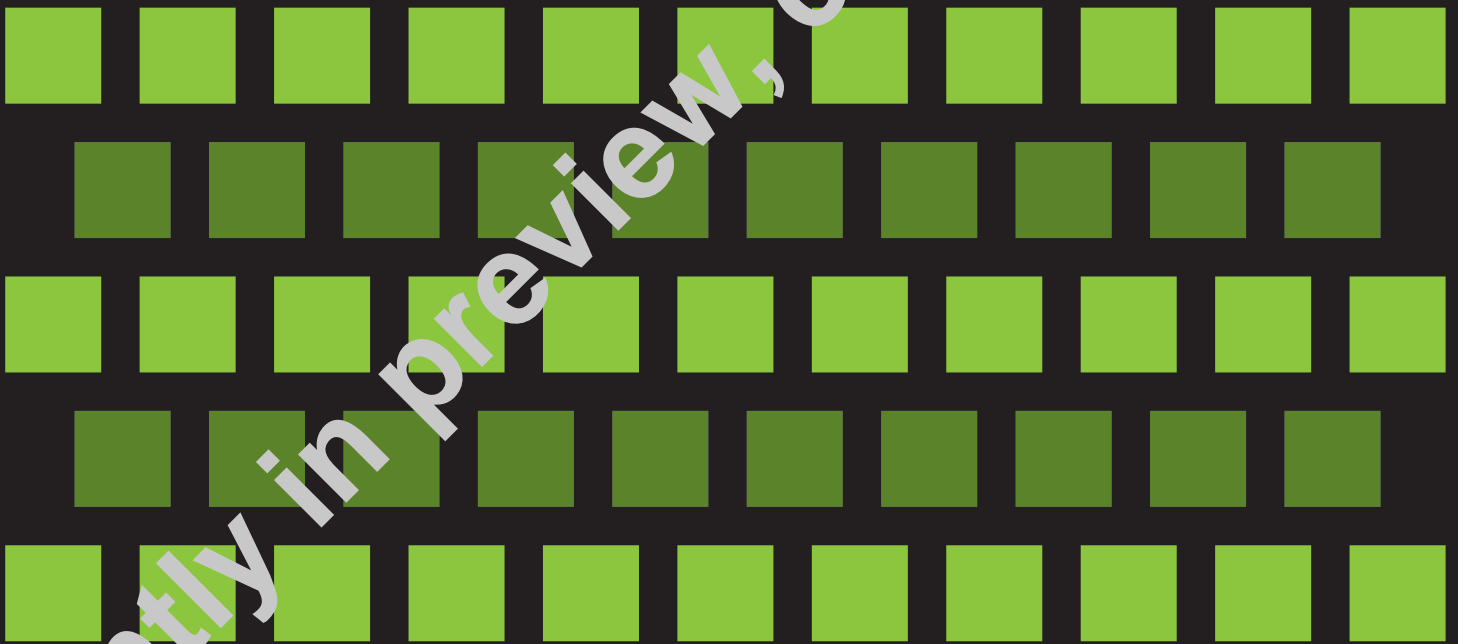


STP-PT-017

# PROPERTIES FOR COMPOSITE MATERIALS IN HYDROGEN SERVICE



ASME STANDARDS  
TECHNOLOGY, LLC

STP-PT-017

# PROPERTIES FOR COMPOSITE MATERIALS IN HYDROGEN SERVICE

*Prepared by:*

Ernie Webster, P.Eng.

Powertech Labs Inc.

ASME STANDARDS  
TECHNOLOGY, LLC

Date of Issuance: March 19, 2008

This report documents the work sponsored by National Renewable Energy Laboratory (NREL) and the ASME Standards Technology, LLC (ASME ST-LLC).

Neither ASME, ASME ST-LLC, Powertech Labs Inc, nor others involved in the preparation or review of this report, nor any of their respective employees, members, or persons acting on their behalf, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe upon privately owned rights.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by ASME ST-LLC or others involved in the preparation or review of this report, or any agency thereof. The views and opinions of the authors, contributors, reviewers of the report expressed herein do not necessarily reflect those of ASME ST-LLC or others involved in the preparation or review of this report or any agency thereof.

ASME ST-LLC does not take any position with respect to the validity of any patent rights asserted in connection with any items mentioned in this document, and does not undertake to insure anyone utilizing a publication against liability for infringement of any applicable Letters Patent, nor assumes any such liability. Users of a publication are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, is entirely their own responsibility.

Participation by federal agency representative(s) or person(s) affiliated with industry is not to be interpreted as government or industry endorsement of this publication.

ASME is the registered trademark of the American Society of Mechanical Engineers.

No part of this document may be reproduced in any form, electronic retrieval system or otherwise, without the prior written permission of the publisher.

ASME Standards Technology, LLC  
Three Park Avenue, New York, NY 10016-5990

ISBN No. 0-7918-3179-5

Copyright © 2008 by  
ASME Standards Technology, LLC  
All Rights Reserved

**TABLE OF CONTENTS**

Foreword ..... vii

Abstract ..... ix

1 PURPOSE AND USE..... 1

2 HYDROGEN EMBRITTLEMENT RESISTANCE OF AA6061-T6 AT 103 MPa (15,000 PSI) .2

    2.1 Summary ..... 2

    2.2 Applicable Standards..... 2

    2.3 Material ..... 2

        2.3.1 Chemistry ..... 2

        2.3.2 Mechanical Properties ..... 3

    2.4 Test Procedure ..... 3

        2.4.1 Specimen Preparation ..... 3

        2.4.2 Specimen Loading ..... 4

        2.4.3 Exposure to Hydrogen Gas ..... 4

        2.4.4 Post-Test Procedure ..... 4

    2.5 Macroscopic Results..... 5

    2.6 Scanning Electron Microscopy (SEM) Results ..... 5

    2.7 Conclusion..... 5

3 INVESTIGATION OF FILAMENT WINDING LARGE DIAMETER THIN-WALLED LONG LENGTH VESSELS..... 11

    3.1 Background ..... 11

    3.2 Measurements on Tanks..... 11

    3.3 Test Data on Tanks..... 11

    3.4 Manufacturing Considerations ..... 14

        3.4.1 Dynetek Industries..... 14

        3.4.2 Lincoln Composites..... 14

    3.5 Conclusion..... 14

4 EFFECT OF COMPOSITE WALL THICKNESS ON FIBER STRESS..... 15

    4.1 Background ..... 15

    4.2 Tank Manufacturing ..... 15

    4.3 Description of Tests..... 18

    4.4 Discussion ..... 21

    4.5 Conclusion..... 21

5 TEST METHODS FOR NON-METALLIC MATERIALS IN HIGH PRESSURE HYDROGEN ..... 22

    5.1 Summary ..... 22

    5.2 Applicable Standards..... 22

    5.3 Background ..... 22

    5.4 Materials..... 23

    5.5 Test Procedure ..... 23

        5.5.1 Tensile Test Specimens ..... 23

|                                  |    |
|----------------------------------|----|
| 5.5.2 Environment Exposure ..... | 25 |
| 5.5.3 Tension Tests .....        | 25 |
| 5.6 Results and Discussion ..... | 25 |
| 5.7 Conclusions.....             | 42 |
| 5.8 Recommendations.....         | 42 |
| References.....                  | 44 |
| Acknowledgements.....            | 45 |
| Abbreviations and Acronyms ..... | 46 |

## LIST OF TABLES

|                                                                 |    |
|-----------------------------------------------------------------|----|
| Table 1 - Chemistry of Aluminum Alloy 6061 (ASTM B210) .....    | 2  |
| Table 2 - Measured Mechanical Properties of 6061-T6 Alloys..... | 3  |
| Table 3 - Summary of Test Conditions.....                       | 4  |
| Table 4 - Results of FTIR Testing .....                         | 23 |
| Table 5 - Initial Geometry Measurements .....                   | 24 |
| Table 6 - Tensile Test Results for Material G.....              | 28 |
| Table 7 - Tensile Test Results for Material K.....              | 31 |
| Table 8 - Tensile Test Results for Material Q.....              | 35 |
| Table 9 - Tensile Test Results for Material T .....             | 38 |

## LIST OF FIGURES

|                                                                                                   |    |
|---------------------------------------------------------------------------------------------------|----|
| Figure 1 - Compact Tension Specimen and Taper Pin Geometry .....                                  | 6  |
| Figure 2 - Fatigue Pre-Cracking of Compact Tension Specimen .....                                 | 7  |
| Figure 3 - Pin-Loading of Compact Tension Specimen.....                                           | 7  |
| Figure 4 - Pin Loaded Sample.....                                                                 | 8  |
| Figure 5 - Fracture Surface of Specimen 1A .....                                                  | 8  |
| Figure 6 - Sample 1B Fracture Surface.....                                                        | 8  |
| Figure 7 - Sample 1C Fracture Surface.....                                                        | 9  |
| Figure 8 - Sample 1D Fracture Surface .....                                                       | 9  |
| Figure 9 - Sample 1A Fracture Surface (22x).....                                                  | 10 |
| Figure 10 - Sample 1A Boundary between Cracks (110x) .....                                        | 10 |
| Figure 11 - Sample 1B Boundary between Cracks (110x) .....                                        | 10 |
| Figure 12 - Straight Edge Illustrating Profile on a Type 3 Design of 2800 mm (110 in) Length..... | 12 |
| Figure 13 - Detail of Profile on a Type 3 Design of 2800 mm (110 in) Length.....                  | 12 |
| Figure 14 - Straight-Edge Profile on Type 4 Tank of 3058 mm (120 in) Length.....                  | 12 |
| Figure 15 - Detail of Profile Variation on Type 4 Tank of 3058 mm (120 in) Length.....            | 13 |
| Figure 16 - Straight-Edge Profile on Type 3 Tank of 1811 mm (71.3 in) Length.....                 | 13 |

|                                                                                                                                           |    |
|-------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 17 - Straight-Edge Profile on Type 2 Tank of 6000 mm (236 in) Length .....                                                         | 13 |
| Figure 18 - Detail of Strain Gage Used on Internal Fiber Layers .....                                                                     | 16 |
| Figure 19 - Installation of Strain Gage on Sidewall during Winding (Note White Plastic Liner Showing under Carbon Fiber Wrap Layers)..... | 17 |
| Figure 20 - Detail of Strain Gage Installed on Innermost Fiber Layers .....                                                               | 17 |
| Figure 21 - Pressure Vessel Label .....                                                                                                   | 18 |
| Figure 22 - Strain Measurements on Innermost Sidewall Fiber Layers – 241.3 MPa.....                                                       | 19 |
| Figure 23 - Strain Measurements on Innermost Dome Fiber Layers - 241.3 MPa.....                                                           | 19 |
| Figure 24 - Appearance of Tank after Pressurization to 241.3 MPa - Note Also Strain Gages Attached to External Dome and Sidewall.....     | 20 |
| Figure 25 - Comparison of Internal and External Strain on Dome and Sidewall - 103 MPa .....                                               | 20 |
| Figure 26 - Rectangular Tensile Test Specimen Dimensions.....                                                                             | 23 |
| Figure 27 - As-Machined Plastic Tensile Specimens .....                                                                                   | 24 |
| Figure 28 - Bubbles Formed in Material T During Hydrogen Exposure .....                                                                   | 25 |
| Figure 29 - Optical Micrograph of Bubble in Hydrogen-Exposed Sample T-5 (7x).....                                                         | 26 |
| Figure 30 - Optical Micrograph of Pore in as-Received Sample T-5 (7x) .....                                                               | 26 |
| Figure 31 - High Temperature Ageing of Liner Materials.....                                                                               | 27 |
| Figure 32 - Material Q Discoloration from High Temperature Ageing .....                                                                   | 27 |
| Figure 33 - Stress-Strain Curves for as-Received Samples G1-3.....                                                                        | 28 |
| Figure 34 - Fractured Samples G1-3 .....                                                                                                  | 29 |
| Figure 35 - Stress-Strain Curves for High-Temperature Aged Specimens G4-6 .....                                                           | 29 |
| Figure 36 - Fractured Samples G4-6 .....                                                                                                  | 30 |
| Figure 37 - Stress-Strain Curves for Hydrogen-Exposed Specimens G7-9 .....                                                                | 30 |
| Figure 38 - Fractured Samples G7-9 .....                                                                                                  | 31 |
| Figure 39 - Stress-Strain Curves for as-Received Samples K1-3.....                                                                        | 32 |
| Figure 40 - Fractured Samples K1-3 .....                                                                                                  | 32 |
| Figure 41 - Stress-Strain Curves for High-Temperature Aged Specimens K4-6 .....                                                           | 33 |
| Figure 42 - Fractured Samples K4-6 .....                                                                                                  | 33 |
| Figure 43 - Stress-Strain Curves for Hydrogen-Exposed Specimens K7-9 .....                                                                | 34 |
| Figure 44 - Fractured Samples K7-9 .....                                                                                                  | 34 |
| Figure 45 - Stress-Strain Curves for as-Received Samples Q1-3.....                                                                        | 35 |
| Figure 46 - Fractured Samples Q1-3 .....                                                                                                  | 36 |
| Figure 47 - Stress-Strain Curves for High-Temperature Aged Specimens Q4-6 .....                                                           | 36 |
| Figure 48 - Fractured Samples Q4-6 .....                                                                                                  | 37 |
| Figure 49 - Stress-Strain Curves for Hydrogen-Exposed Specimens Q7-9 .....                                                                | 37 |

|                                                                                 |    |
|---------------------------------------------------------------------------------|----|
| Figure 50 - Fractured Samples Q4-6.....                                         | 38 |
| Figure 51 - Stress-Strain Curves for as-Received Samples T1-3.....              | 39 |
| Figure 52 - Fractured Samples T1-3 .....                                        | 39 |
| Figure 53 - Stress-Strain Curves for High-Temperature Aged Specimens T4-6 ..... | 40 |
| Figure 54 - Fractured Samples T4-6 .....                                        | 40 |
| Figure 55 - Stress-Strain Curves for Hydrogen-Exposed Specimens T7-9 .....      | 41 |
| Figure 56 - Fractured Samples T4-6 .....                                        | 41 |

## FOREWORD

Commercialization of hydrogen fuel cells, in particular fuel cell vehicles, will require development of an extensive hydrogen infrastructure comparable to that which exists today for petroleum. This infrastructure must include the means to safely and efficiently generate, transport, distribute, store and use hydrogen as a fuel. Standardization of pressure retaining components, such as tanks, piping and pipelines, will enable hydrogen infrastructure development by establishing confidence in the technical integrity of products.

Since 1884, the American Society of Mechanical Engineers (ASME) has been developing codes and standards (C&S) that protect public health and safety. The traditional approach to standards development involved writing prescriptive standards only after technology has been established and commercialized. With the push toward a hydrogen economy, government and industry have realized that they cannot afford a hydrogen-related safety incident that may undermine consumer confidence. As a result, ASME has adopted a more anticipatory approach to standardization for hydrogen infrastructure which involves writing standards with more performance based requirements in parallel with technology development and before commercialization has begun.

Today, ASME codes and standards are used for hydrogen storage, transmission and distribution. The anticipated requirements of the hydrogen economy will require local refueling stations with the capability to fill gaseous hydrogen vehicle tanks rapidly to pressures as high as 15,000 psig (100 MPa). Although current standards could be used to build pressure tanks, piping and pipelines meeting these operating requirements, it is likely that the resulting components would not, as a practical matter, enable commercialization of the technology.

ASME has worked closely with the Department of Energy (DOE), national laboratories and other standards developing organizations (SDOs) to identify and organizations to address the need for standards for hydrogen applications. ASME was selected to lead the efforts for pressure tanks, piping and pipelines for storage, transportation and distribution of hydrogen. Initial work of the ASME Hydrogen Steering Committee led to the formation of volunteer task forces under the ASME Board on Pressure Technology Codes and Standards (BPTCS) to explore the standardization requirements for storage tanks, transportation tanks, portable tanks, piping and pipelines for hydrogen-specific applications. The task forces submitted their recommendations at the end of 2003 and these recommendations led to initiation of standards actions, formation of project teams and commencement of supporting research.

The ASME Boiler and Pressure Vessel (BPV) Standards Committee appointed a project team to develop new Code rules in the Boiler and Pressure Vessel Code Section VIII (pressure vessels) and Section XII (transport tanks) for hydrogen storage and transport tanks to be used in the storage and transport of liquid and gaseous hydrogen and metal hydrides. Rules for gaseous storage tanks with maximum allowable working pressures (MAWPs) up to 15,000 psig (100 MPa) will be needed. Research activities are being coordinated to develop data and technical reports concurrent with standards development and have been prioritized per Project Team needs. The Project Team may identify additional needs and gaps as drafts are developed.

The Technical Reports to be developed will establish data and other information to be used to support and facilitate separate initiatives to develop ASME standards for the hydrogen infrastructure. These reports will target specific disciplines and fill the gaps identified by ASME's hydrogen task forces. An initial report, developed under the sponsorship of the National Renewable Energy Laboratory (NREL), Hydrogen Standardization Interim Report for Tanks, Piping and Pipelines was issued on May 3, 2005. This interim report addressed priority topical areas within each of the four pressure technology applications for hydrogen infrastructure development: storage (stationary) tanks, transport tanks, piping and pipelines and vehicle fuel tanks.

The present report builds on the work of the interim report and investigates properties of composite materials in hydrogen service.

Established in 1880, the American Society of Mechanical Engineers (ASME) is a professional not-for-profit organization with more than 127,000 members promoting the art, science and practice of mechanical and multidisciplinary engineering and allied sciences. ASME develops codes and standards that enhance public safety, and provides lifelong learning and technical exchange opportunities benefiting the engineering and technology community. Visit [www.asme.org](http://www.asme.org) for more information.

The ASME Standards Technology, LLC (ASME ST-LLC) is a not-for-profit Limited Liability Company, with ASME as the sole member, formed in 2004 to carry out work related to new commercialized technology. The ASME ST-LLC mission includes meeting the needs of industry and government by providing new standards-related products and services, which advance the application of emerging and newly commercialized science and technology and providing the research and technology development needed to establish and maintain the technical relevance of codes and standards. Visit [www.stllc.asme.org](http://www.stllc.asme.org) for more information.

## ABSTRACT

Studies were conducted to address three specific questions related to the use of composite-reinforced pressure vessel designs for the transportation of compressed hydrogen at pressures up to 103 MPa (15,000 psi). These studies involved determining the hydrogen embrittlement resistance of AA6061-T6 aluminum alloy material typically used as a liner in composite-reinforced cylinder designs; determining whether composite-reinforced pressure vessels using plastic or thin-wall metallic liners were subject to distortion during the filament winding process; and identifying test methods that can be used to establish the long-term performance of non-metallic materials exposed to high-pressure hydrogen environments.

Long-term hydrogen embrittlement tests were conducted on AA6061-T6 samples using compact tension specimens according to ISO 11114-4, Method C. Specimens were fatigue pre-cracked, following which the fatigue cracks were pre-loaded to various stress intensity factors. The specimens were then inserted into a pressure vessel containing hydrogen at 103 MPa (15,000 psi). After 1,000 hours exposure, there was no evidence observed of any hydrogen-induced crack growth in the aluminum.

A variety of composite-reinforced pressure vessels that use plastic liners and thin-walled aluminum liners, and having lengths up to 3058 mm, were inspected. There was no evidence of any axial distortion. In addition, pressure cycle and burst test data between composite-reinforced pressure vessels of relatively short length and relatively long length were compared, confirming that the designs of different length had the same performance.

Plastic liner materials cut from four high-pressure hydrogen storage tanks of different design were tested for effects of high-temperature ageing and of long-term exposure to high-pressure hydrogen. Specimens were tensile tested in the as-received condition, after one-month exposure to 70 MPa (10,000 psi) hydrogen and after one-month exposure to 85°C atmosphere. The 70 MPa hydrogen exposure for 30 days had no noticeable effect on the strength of the materials but did create some bubbles in the surface. On average, ageing three of the materials for 30 days at 85°C caused an increase in tensile strength. It was concluded that more samples needed to be tested to develop a more acceptable statistic average of the mechanical properties, and that full-scale testing should be performed on complete pressure vessels at both high and low service temperatures with hydrogen pressure.

INTENTIONALLY LEFT BLANK

## 1 PURPOSE AND USE

This report is intended to answer three specific questions related to the use of specific materials and composite-reinforced pressure vessel designs for the transportation of compressed hydrogen at pressures up to 103 MPa (15,000 psi). The individual studies involve:

- Determining the propensity for hydrogen embrittlement to occur in AA6061-T6 aluminum alloy material typically used as a liner in composite-reinforced cylinder designs.
- Determining whether the manufacture of composite-reinforced pressure vessels of relatively long length over thin-wall metallic liners or plastic liners can result in sagging of the vessels, thus affecting the tension in the filament winding process.
- Identifying test methods that can be used to establish the long-term performance of non-metallic materials exposed to high-pressure hydrogen environments.

## 2 HYDROGEN EMBRITTLEMENT RESISTANCE OF AA6061-T6 AT 103 MPA (15,000 PSI)

### 2.1 Summary

Long-term hydrogen embrittlement tests were conducted according to ISO 11114-4, Method C [1]. Compact tension (CT) specimens were withdrawn from the sidewall of a 6061-T6 aluminum alloy cylinder liner. Four samples were machined from the material with the direction of crack propagation longitudinal to the cylinder liner axis. Each specimen was fatigue pre-cracked and then a pin was inserted into a tapered hole to impart a stress intensity of 21.4 MPa-√m for 6061-T6. After loading, the specimens were placed in a cylinder and pressurized to 103 MPa (15,000 psi) with 100% hydrogen.

After 1000 hours of exposure, the samples were visually examined for obvious signs of crack propagation. To ensure that the crack mouth opening displacement (CMOD) had not changed drastically during the test, their values were measured and corresponding stress intensities were calculated. Since crack extension was not visible, the specimens were cyclically loaded to create fatigue striations, marking the end of any hydrogen induced crack propagation. After breaking apart the specimens, it was determined that the cracks did not propagate any further. This was confirmed by taking high magnification micrographs with a scanning electron microscope (SEM).

### 2.2 Applicable Standards

The test was performed according to Method C of ISO 11114-4, “Transportable Gas Cylinders–Compatibility of Cylinder and Valve Materials with Gas Contents–Part 4: Test Methods for Selecting Metallic Material Resistant to Hydrogen Embrittlement.” Specimen dimensions and the fatigue pre-cracking procedure were taken from ISO 7539-6, “Corrosion of Metals and Alloys–Stress Corrosion Testing” [2] and ASTM E1820-01, “Standard Test Method for Measurement of Fracture Toughness” [3].

### 2.3 Material

#### 2.3.1 Chemistry

The 6061-T6 aluminum alloy was removed from the liner of a hoop-wrapped cylinder manufactured by the CNG Cylinder Co. The design chemistry is described in Table 1.

**Table 1 - Chemistry of Aluminum Alloy 6061 (ASTM B210)**

| Element | Min (%) | Max (%) |
|---------|---------|---------|
| Mg      | 0.8     | 1.2     |
| Si      | 0.4     | 0.8     |
| Cu      | 0.15    | 0.4     |
| Cr      | 0.04    | 0.35    |
| Ti      | -       | 0.15    |
| Fe      | -       | 0.7     |
| Mn      | -       | 0.15    |
| Zn      | -       | 0.25    |