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Identification of Hydrogen Material Risk Research Areas

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ABSTRACT

This report presents a research framework for the application of quantitative risk assessment to hydrogen materials, based on the identification of potential areas of research, a literature review, and a plan for future work in the area of hydrogen materials risk. After outlining basics on hydrogen infrastructure, with a focus on pressure vessels, a number of materials risk topics are identified and discussed. Of these, four important areas of risk application to hydrogen materials are highlighted and discussed in further detail. The four topics are initial crack distribution in metals, damage and stress rupture in composites, and polymer behavior in high pressure hydrogen. These topics vary in scope, specificity, level of anticipated resources required, and potential impact to the field. Finally, recommendations are made for future research on the highest priority topics.

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CONTENTS

1. Objectives, background, and approach 10
   1.1. Objectives 10
   1.2. Background 10
   1.3. General Approach 10
2. Hydrogen Pressure Vessels 12
   2.1. Introduction 12
   2.2. Hydrogen Pressure Vessel Types 12
   2.3. Hydrogen Pressure Vessel Requirements 14
      2.3.1. Pressure Vessels in Vehicles 14
      2.3.2. Stationary Stoage Pressure Vessels 15
   2.4. Hydrogen Cylinder Failure Modes and Mechanisms 15
3. Material Risk Challenges 18
   3.1. Introduction 18
   3.2. Crack Formation in Metals 18
      3.2.1. Description 18
      3.2.2. Evaluation for Future Research 19
   3.3. Cylinder Recertification 19
      3.3.1. Description 19
      3.3.2. Evaluation for Future Research 20
   3.4. TPRD Removal 20
      3.4.1. Description 20
      3.4.2. Evaluation for Future Research 22
   3.5. Composite Hydrogen Storage Materials 22
      3.5.1. Description 22
      3.5.2. Evaluation of Damage in Composite Materials for Future Research 24
      3.5.3. Evaluation of Stress Rupture for Future Research 25
   3.6. Polymer Compatibility 25
      3.6.1. Description 25
      3.6.2. Evaluation for Future Research 26
4. Summary and Recommendations 28
   4.1. Recommended Stress Rupture of Composite Pressure Vessels Research 29
   4.2. Recommended Initial Crack Distribution in Metal Pressure Vessels Research 30

References 31

Appendix A. Materials Risk Capabilities of Sandia National Laboratories 34
   A.1 Introduction 34
   A.2 Risk Capabilities 34
   A.3 Hydrogen Behavior Capabilities 34
   A.4 Metal Vessel Testing Capabilities 35
   A.5 Composite Characterization Capabilities 35
   A.6 Polymer Testing Capabilities 35
   A.7 Other Materials Characterization Capabilities 36

LIST OF FIGURES

Figure 1 - Fiber properties, taken from [6]. Black dots denote carbon fiber, red dots signify aramid, and blue dots denote glass. 13
Figure 2. Conceptual schematic of resource investment requirements and potential effect on hydrogen vehicles 29

LIST OF TABLES

Table 1 - Failure modes and mechanisms of hydrogen pressure vessels 15

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ACRONYMS AND DEFINITIONS

Abbreviation	Definition
AISI	American Iron and Steel Institute
ANSI	American National Standards Institute
ASME	American Society of Mechanical Engineers
BPVC	Boiler and Pressure Vessel Code
CNG	compressed natural gas
CRADA	Cooperative research and development agreement
CVEF	Clean Vehicle Education Foundation
DOE	Department of Energy
DOT	Department of Transportation
EPMA	electron-probe microanalysis
FCTO	Fuel Technology Office
FMVSS	Federal Motor Vehicle Safety Standards
GTR	Global Technical Regulation
HDPE	high-density polyethylene
LNG	liquefied natural gas
MVFRI	Motor Vehicle Fire Research Institute
NFPA	National Fire Protection Association
NWP	nominal working pressure
PHMSA	Pipeline and Hazardous Materials Safety Administration
PRA	probabilistic risk assessment
PRD	pressure relief device
QRA	quantitative risk assessment
SCS	Safety, Codes & Standards
Sandia Labs	Sandia National Laboratories
SEM	scanning electron microscopy
SUV	sport utility vehicle
SwRI	Southwest Research Institute
TCL	Turbulent Combustion Laboratory
TEM	transmission electron microscopy
TPRD	thermally-activated pressure relief device

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1. OBJECTIVES, BACKGROUND, AND APPROACH

1.1. Objectives

The objective of this report is to identify significant barriers to the progress of the hydrogen fuel cell industry by capitalizing on the capabilities of Sandia National Laboratories (Sandia Labs) in hydrogen materials and quantitative risk assessment (QRA). This project is intended to improve the basis or application of safety codes and standards by quantifying the risk of hydrogen pressure vessel failure due to materials interaction. Additionally, this project will identify a path forward to characterize the risk of hydrogen pressure vessel failure. This area of research should provide a better understanding of pressure vessel failure to cylinder manufacturers, the hydrogen fuel cell safety community, and has the potential to improve safety across all areas and scales of hydrogen applications and storage.

Tanks, cylinders, pressure vessels, and pressure-containing equipment encompass different form factors and applications for the containment of hydrogen at positive pressure. For the purposes of this report, the authors used the term "pressure vessel" in a broad way, with the understanding that many of the phenomena can be applicable for other applications.

This research plan has been developed by the Sandia Labs Risk and Reliability Department and sponsored by the office of Energy Efficiency and Renewable Energy's (EERE) Fuel Technologies Office (FCTO) Safety, Codes & Standards (SCS) program for the U.S. Department of Energy (DOE).

1.2. Background

Sandia Labs has provided technical leadership in hydrogen QRA for the EERE/FCTO SCS program for well over a decade. This work has included both research and development activities focused on developing, validating, and creating QRA methods, models, and tools to address critical barriers and gaps related to hydrogen infrastructure deployment. Sandia possesses core capabilities in fundamental scientific hydrogen research, including hydrogen QRA, hydrogen behavior, and hydrogen materials. This project intends to capitalize on these strengths to address additional challenges facing the hydrogen fuel cell industry.

1.3. General Approach

This report presents a research framework based on the identification of potential areas of research, a literature review, and recommendations for future work. First, the scope of the research project is defined, and background information is offered that relates to hydrogen infrastructure and pressure vessels. Second, a number of issues are identified that could potentially benefit from applying risk quantification methods to further the understanding of the issue. These include removal of pressure relief devices, pressure vessel re-certification, and failure mechanisms for various materials used in hydrogen pressure vessels. This discussion is informed through a literature review as well as discussions with experts in materials science, safety codes and standards, and risk. In discussing each of these potential issues, some will be eliminated from future consideration under this project, and some will be identified as potentially important for future efforts. Finally, suggestions for the best fit of materials risk problems with Sandia Labs capabilities will be presented.

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2. HYDROGEN PRESSURE VESSELS

2.1. Introduction

Hydrogen storage technologies are an enabler for hydrogen applications, ranging from infrastructure for transportation to implications for large grid-scale systems. Determining how to account for material properties within a QRA framework is a key scientific question. Sandia Labs has developed a framework for analyzing overall risk of the system from knowledge of reliability of various components, such as storage tanks. However, there is little data to predict reliability of some components, especially more novel components such as composite storage vessels. Without extensive published reliability data, it is necessary to use knowledge of material properties, defects, and design elements to predict reliability and risk.

Applying QRA concepts to pressure vessel or cylinder reliability analysis can create a framework that can be broadened beyond cylinders. Similarly, using these approaches will generate new pressure vessel data that can be used within a QRA framework as part of system-level safety assessment. Addressing the root causes of hydrogen release will impact every application of hydrogen as an energy solution. Any system that uses hydrogen, from large grid scale application (such as those proposed in H2@Scale) to an individual hydrogen vehicle refueling station, requires hydrogen storage of some size and could benefit from this intersection of risk analysis and materials properties research capabilities.

Hydrogen can be stored in several ways, including pressure vessels, chemical storage, or in a dewar in a liquefied state. Chemical hydrogen storage (e.g., hydrides, sorbents) has the potential to increase hydrogen storage density but suffers from additional system complexity and materials challenges. Liquid hydrogen storage shows great promise for bulk storage and transport [1], and has been demonstrated for vehicle use [2]. Despite the increased storage density of liquid vs. gaseous hydrogen, liquefied hydrogen must be kept very cold, increasing energy and insulation costs as well as adding to the volume and weight necessary for storage. Furthermore, as liquid hydrogen warms, it must vent to the atmosphere, losing hydrogen over time and making medium- or long-term storage problematic [1]. Most commonly, hydrogen is stored in pressure vessels as an ambient temperature gas at high pressure. This report thus focuses on hydrogen storage pressure vessels due to the need for further development of liquid and solid hydrogen storage, and the wider usage of pressure vessels for gaseous hydrogen storage leading to more of an impact on the field.

2.2. Hydrogen Pressure Vessel Types

Hydrogen pressure vessels are manufactured in five configurations, commonly called "types", which are used in different applications dependent on weight, fuel storage requirements, and cost. The first cylinder configuration is an all metal cylinder made of either steel or aluminum, called a Type I cylinder, which results in a thick and heavy, yet inexpensive, design [3]. Type I cylinders usually hold an approximate maximum pressure of 25 MPa, depending on cylinder design [4].

Type II cylinders have a metal liner, made of either aluminum or steel, with a composite fiber resin hood wrap [3]. Type II cylinders generally hold pressures from 45 to 80 MPa. Type I and II cylinders are not typically used for hydrogen fuel cell vehicles due to their immense weights, even though they have a lower production cost [4].

Type III hydrogen cylinders are composed of an aluminum or steel metal liner reinforced with a full fiber resin composite wrap and usually have a nominal working pressure (NWP) of 35 MPa [3, 4]. Type II and III cylinders differ in that Type II cylinders have only hoop wraps as opposed to the full wraps on Type III cylinders. The full composite wrap on Type III cylinders also allow for a more lightweight vessel but increases costs. Hydrogen cylinders have utilized austenitic stainless steel (specifically AISI 316 and 304 as well as AISI 316L and 304L) and alloys of copper and aluminum due to their low susceptibility to dry hydrogen atmospheres at ambient temperatures [5]. The composite fibers used to wrap hydrogen cylinders can be composed of varieties of carbon fiber, aramid fibers, or fiberglass (see Figure 1) [5].

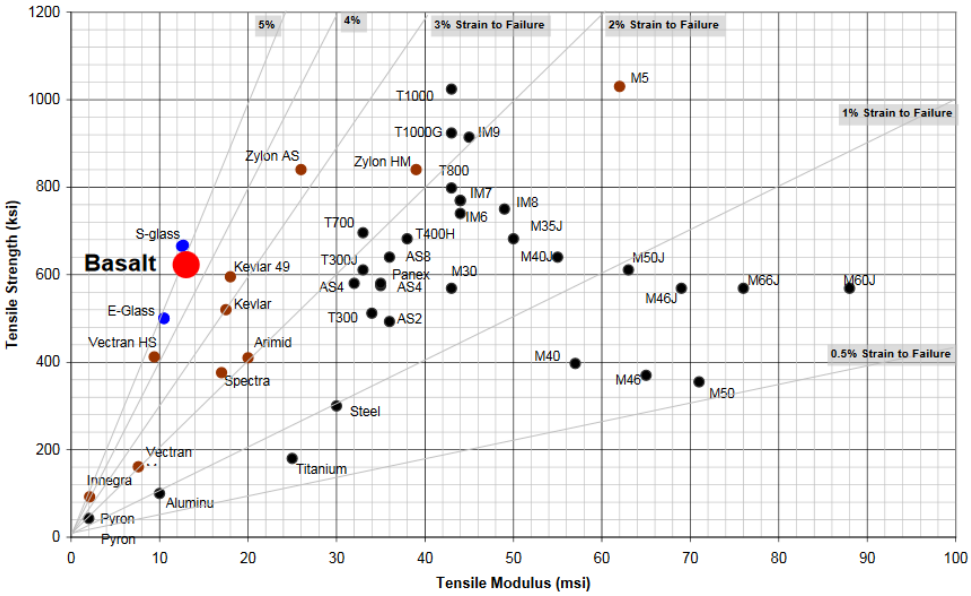


Figure 1 - Fiber properties, taken from [6]. Black dots denote carbon fiber, red dots signify aramid, and blue dots denote glass.

Type IV hydrogen cylinders are fully-overwrapped composite tanks with a plastic liner inner layer (e.g. high-density polyethylene) instead of a metal liner. It is common for this type of cylinder to have an additional outer protective layer as well (such as fiberglass), but outer protective layers may be applied to any cylinder type. Type IV cylinders are used within hydrogen fuel cell vehicles such as the Toyota Mirai and generally have a normal operating pressure of 70 MPa. Type IV hydrogen cylinders are capable of holding a maximum pressure of 87.5 MPa [4, 7]. These vessels are more lightweight than both of the Type I and II hydrogen cylinders while still maintaining the same safety standards, making them ideal for use within automotive vehicles; however, Type IV cylinders cost more than their Type I and II counterparts [3, 4].

Type V cylinders are all-composite tanks with no liner. The lack of a metallic or polymer liner reduces both weight and material interaction complexity and instead relies on the composite itself to be the gas retention barrier. These types of vessels are relatively new, having been first demonstrated for space applications [8]. Little information is available on these tanks, including pressure limitations and cost performance, due to the novelty of the designs and small market size.

Composite materials offer a beneficial strength/weight ratio and are consequently desired for non-stationary storage of hydrogen, such as vehicle fuel cylinders. In this case, the composite is used to add hoop-strength to a Type II cylinder or to provide a majority of (if not all) strength using a full overwrap of a liner in a Type III or Type IV cylinder. In Type V cylinders, the composites make up the entirety of the tank. The conjunction of composite, metal and polymer materials means that there are many different ways in which a composite pressure vessel can fail; if either the metal liner or the composite overwrap fails, the entire vessel will almost certainly fail. For Type III cylinders, this means that failure mechanisms from both metal tanks as well as composite-specific failures must be considered. Furthermore, composites are combinations of multiple materials, which requires complex materials-interactions to be considered when examining behavior. Composites used in these applications can be composed of very different materials, meaning a property or behavior of one material may simply not apply to a functionally similar but compositionally different pressure vessel, thus presenting an additional complication.

Regardless of these differences in characteristics, every cylinder configuration must meet safety requirements for a given application.

2.3. Hydrogen Pressure Vessel Requirements

Hydrogen pressure vessels must meet a variety of safety requirements depending on the application of the pressure vessel. For example, hydrogen vehicles have robust requirements based on other alternative fuel vehicle requirements, such as compressed natural gas (CNG). This section describes those specific requirements pertinent to the protection of the pressure vessel in vehicles and stationary applications.

2.3.1. Pressure Vessels in Vehicles

Hydrogen fuel in vehicles is stored in the gaseous state. Current storage systems have pressures of 35 MPa and 70 MPa (5,000 and 10,000 psi respectively). According to Global Technical Regulation No. 13 (GTR #13), most high-pressure hydrogen storage containers used in fuel cell vehicles consist of two layers: an inner layer preventing gas leakage/permeation and an outer layer that provides structural integrity, therefore Type III or Type IV pressure vessels. GTR #13 provides requirements for the integrity of compressed and liquid hydrogen motor vehicle fuel containers. The GTR #13 test procedures and methods include pressure cycling tests (pneumatic and hydraulic with temperature variations), burst test, permeation test, and a bonfire test (localized and engulfing). The pressure cycling test evaluates a container's durability to withstand, without burst, 22,000 cycles of pressurization and depressurization, representing a 4.3 million-mile life time with a vehicle range of 200 to 350 miles. Also, the tank must not leak for 5,500 to 11,000 cycles depending on the local requirements of the participating country. A burst test evaluates a container's initial strength and resistance to degradation over time. The bonfire test evaluates the container's thermal pressure relief device's (TRPD's) ability to open in a fire scenario. This test starts with a localized fire at 600°C impinging on a portion of the tank distant from the TPRD for 10 min, followed by an engulfing fire at 800°C for an additional 10 minutes. The TPRD must release before the end of the test and this release must be uninterrupted until the tank reaches of a pressure of 1 MPa. The tank cannot burst or leak during the test. If the TPRD does not release during test, the tank is considered to have failed. These test requirements are more stringent than the FMVSS No. 304 requirements for CNG tanks.

2.3.2. *Stationary Stoage Pressure Vessels*

There are many specifications for bulk hydrogen storage containers. One example is the ASME Boiler and Pressure Vessel Code (BPVC), Section VIII, Division 1 [9]. National Fire Protection Association (NFPA) 55, titled "Compressed Gases and Cryogenic Fluids Code," section 7.1.5.1 states that cylinders, containers, and tanks shall be designed, fabricated, tested and marked in accordance with DOT regulations, Transport Canada regulations, or ASME BPVC Section VIII [10]; however bulk hydrogen storage will likely be designed to ASME BPVC specifications. The ASME BPV code provides extensive information on design requirements, such as material selection. While these codes and standards are voluntary, many jurisdictions have adopted them.

2.4. Hydrogen Cylinder Failure Modes and Mechanisms

Hydrogen cylinders can fail in three ways: catastrophic rupture, massive leak, and slow leak [11]. These failure modes apply to all cylinder types. For each failure mode, there are a number of specific mechanisms that can lead to that type of failure. Some failure mechanisms are applicable to multiple cylinder types, while others are more unique. Metal cylinders have been in operation for many years, particularly in CNG applications where Type I pressure vessels are most prevalent. Because of this history, the failure of metal pressure vessels is better understood than composite pressure vessels. Composite pressure vessels have been used in other industries for decades, but failure modes and mechanisms are not as well documented as metal pressure vessels. McLaughlan et al. listed the following known failure mechanisms for composite pressure vessels: (1) Burst from Over-Pressurization, (2) Fatigue Failure of the Metallic Liner, (3) Burst Resulting from Metallic Liner or Composite Damage, and (4) Stress Rupture of the Composite Overwrap [12]. These failure mechanisms are included in Table 1 along with the failure mechanisms from other cylinder types.

About half of the failure mechanisms can affect all five types of cylinders, including abusive handling, faulty operation of TPRD, TPRD failure, manufacturing defects, and tank puncture. However, these mechanisms have always existed for pressurized cylinders, so mitigations and procedures are in place to address these failure mechanisms. Abuse testing and damage induced failures are especially problematic for pressure vessels on vehicles and regulations to address this include GTR #13 and the CSA Group/American National Standards Institute (ANSI) Natural Gas Vehicle (NGV) 2. The focus of this analysis will be on the less understood failure mechanisms to include fatigue failure for metals, composites, and polymers, and composite stress rupture.

Table 1 - Failure modes and mechanisms of hydrogen pressure vessels

	Failure Modes			Pressure Vessel Type				
Failure Mechanisms	**Catastrophic Rupture**	**Massive Leak**	**Slow Leak**	**Type I**	**Type II**	**Type III**	**Type IV**	**Type V**
Abusive Handling	X	X	X	X	X	X	X	X
Composite Fatigue Failure		X	X		X	X	X	X
Composite Stress Rupture	X				X	X	X	X

Failure Mechanisms	Failure Modes			Pressure Vessel Type				
	Catastrophic Rupture	Massive Leak	Slow Leak	Type I	Type II	Type III	Type IV	Type V
Faulty Operation of Pressure Relief Device		X	X	X	X	X	X	X
Manufacturing Defect	X	X	X	X	X	X	X	X
Metal Fatigue Failure		X	X	X	X	X		
Polymer Liner Fatigue Failure		X	X				X	
Pressure Relief Device Failure (Over-Pressurization)	X			X	X	X	X	X
Tank Puncture	X	X		X	X	X	X	X

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3. MATERIAL RISK CHALLENGES

3.1. Introduction

There are a variety of intersections between the application of quantitative risk assessment and the study of materials. An energy-dense and reactive gas such as hydrogen leads to materials challenges and safety concerns. Just as with any fuel, hydrogen must be handled appropriately to meet consumer expectations and safety requirements in any application. The reactivity of hydrogen is one of its benefits, but it does mean that materials-related challenges are inherently present. Thus, the application of risk is beneficial to better quantify safety.

An example of risk applied to materials-related challenges is the Sandia Labs' framework of a probabilistic fracture mechanics assessment code called xLPR (Extremely Low Probability of Rupture). The purpose of xLPR is to evaluate degradation mechanisms in piping systems at nuclear power plants and to predict the probability of a rupture, specifically analyzing the primary water stress corrosion cracking in dissimilar metal welds in pressurizer surge nozzles. The work performed on the xLPR project demonstrates how the intersection of materials behavior with risk analysis can be used to assess challenging problems [13].

This chapter outlines various materials-related challenges for risk that have been identified. This list and discussion was obtained through a literature search and discussion with various experts and is meant to represent the current state-of-the-art and challenges in multiple areas. Some of these areas are inherent to the materials being used and others are more focused on design requirements. This chapter includes a description of the issue followed by the authors' evaluation of the impact of the issue on the hydrogen industry and the codes and standards that permit and regulate its use through the application of risk. This initial elimination from consideration is not meant to imply that the issues are solved, trivial, or un-important, but rather may simply indicate that the inclusion of a risk-informed methodology at this point may not be the best fit for the present challenge.

3.2. Crack Formation in Metals

3.2.1. Description

Metal fatigue failure is the growth of cracks in a metallic pressure vessel (or liner) due to pressure cycling. The pressure cycling of a vessel causes oscillating stress fields which enlarge the crack; when the crack length approaches the wall thickness of the vessel, a leak or catastrophic failure will occur (depending on the material properties and shape of the crack). Modern pressure vessels are designed with this in mind, and thus are often designed to leak before they catastrophically fail. This leak-before-burst design is included in pressure vessel safety codes and standards and is required for certain types of vessels. Fatigue crack growth above a certain size can be predicted using well-known fracture mechanics modeling after identifying a known distribution of initial cracks.

Currently, fatigue crack growth propagation studies begin by assuming a crack is present. Characterizing the probability of crack initiation and identifying functional parameters that influence this phenomenon can lead to a better understanding of the risk of a hydrogen vessel failure.

Two components of metallic pressure vessel crack behavior are the probability of detection and the growth of a crack. The ability to detect a crack in metals has been the subject of extensive scrutiny by

industry and governmental groups and will not be considered here. The growth of a fatigue crack from an existing defect can be modeled using traditional fracture mechanics [14]. However, the start of a crack at a defect is not well understood. Efforts are currently underway to observe this behavior more directly in order to understand it more fully [15].

A study by Lyle et al. found that defects from the manufacturing process were responsible for failure-inducing cracks [16], and Chamberlain notes that modeling efforts assume that these manufacturing defects are the starting point for crack-induced failure modeling [14]. Other methods of defect introduction, such as damage or operational errors, were not considered in those studies, and are not considered for this topic. Chamberlain was unable to ascertain an initial crack size distribution for as-manufactured natural gas cylinders in the U.S. due to the unwillingness of tank manufacturers to release proprietary data [14]. Chamberlin subsequently researched a new probabilistic fracture mechanics model of the corrosion fatigue failure of steel CNG cylinders using two different probability functions to predict the existence of a crack and the size of that crack, if it exits. Crack sizes were predicted using limited information from welds and tanks in the nuclear industry, and the existence of a crack was estimated from a single source. Some effort was made to modify the probability of a crack existing to account for the different sections of the cylinder (side walls, end caps, shoulder regions, etc.) but these estimations are not validated by experimental data. There is substantial room for improvement in the determination of initial crack/defect distributions in various materials and designs.

3.2.2. Evaluation for Future Research

Crack growth modeling in metallic pressure vessels would be greatly improved by additional characterization of the initial population of defects that can lead to cracks. Generic defect distributions are helpful in the absence of data but can be misleading since they lack an empirical basis. Obtaining, analyzing, anonymizing, and publishing data from various tank manufacturers and a variety of tank materials and designs would be important to advancing crack initiation research. However, this effort is almost totally dependent on the willingness of tank manufacturers to provide data; otherwise, a large experimental campaign would be required to produce enough useful reliability data. There are areas where risk-informed methods can be useful, and analysis of past pressure vessel failures would allow for a more focused search. Data from prior failures can highlight particular parts of the pressure vessel that fail more often or have a larger consequence, allowing the search for or generation of experimental data to be focused on those parts of the cylinder.

3.3. Cylinder Recertification

3.3.1. Description

CNG cylinders have been used in vehicles for decades. The Code of Federal Regulations (CFR) 571.304, "Compressed Natural Gas Fuel Container Integrity", requires that a cylinder must have a label with the statement "Do Not Use After_____" with the month and year inserted based on the manufacturer's recommended service life of the container [17]. The 2016 edition of NFPA 52, titled "Vehicular Natural Gas Fuel Systems Code", states that fuel containers whose service life has expired shall be removed from service [18]. If a cylinder reaches its expiration date, the vehicle owners have two options: retire the vehicle or replace the cylinder.

In 1992, the natural gas vehicle industry created CSA/ANSI NGV 2-1992, a CNG cylinder certification standard which limited the service life of a CNG cylinder to 15 years [19]. The 1998 revision of the standard extended the allowable cylinder life certification to 20 years and in 2007 it was raised to 25 years [19]. Although CSA/ANSI NGV2 is a voluntary standard, it has been adopted by most countries for CNG cylinders.

ANSI NGV2 and CFR 571.304 has a guideline of inspecting cylinders at least every 36 months or 36,000 miles by a certified CNG fuel system inspector or after a motor vehicle accident or fire [17, 20, 21]. The goal of the inspections is to identify whether the cylinder has been damaged or deteriorated while in service. The inspector looks for impact damage from a collision, cuts and abrasions, corrosion from de-icing salts, exposure to fire, and/or over-pressurization by a defective station [20]. Depending on the level of visible damage, the cylinder could be repaired by the customer, returned to the manufacturer for repair, or condemned and removed from service. Even if the manufacturer repairs the cylinder, the initial service life date remains.

3.3.2. Evaluation for Future Research

There is currently no method for recertifying a cylinder used on vehicles once its service life reaches the expiration date. In the past, there has been a difference in the pressure vessel service life for CNG cylinders and the service life of the CNG vehicle itself. This discrepancy in vehicle life verses cylinder service life caused the manufacturer to either replace the cylinder or the vehicle entirely. A process was considered for recertifying older tanks, however liability and technical challenges rejected the idea [19]. The service life of a new CNG cylinder was subsequently extended to 25 years, therefore the recertification issue is not as problematic as it was when the service life was 15 years. Hydrogen cylinders have not been in service as long as CNG and service life dates will probably be less of an issue for the industry because there are fewer old hydrogen vehicle tanks currently in use, compared to CNG vehicle tanks. In addition, new hydrogen tanks will likely be designed to a longer lifetime certification, similar to CSA/ANSI NGV2.

There are other issues with inspecting and recertifying composite cylinders. Inspections are more difficult for composite cylinders, since most techniques, including visual inspection, do not necessarily discover damage before failure. Even failure testing is not necessarily predictive of future life for composite cylinders, since composites undergo different failure mechanisms than all-metal cylinders [22]. Thus, an alternate inspection method may need to be developed for composite cylinders. Additionally, most codes and standards do not take test data scatter into account; for example, different levels of deviation around the mean can lead to different values of safety risk for the same designed safety factor [23]. Additional research is needed to determine the best way to account for test data scatter in safety codes and standards.

3.4. TPRD Removal

3.4.1. Description

The main safety feature of a hydrogen pressure vessel is the pressure relief device (PRD) and all hydrogen cylinders are equipped with a thermally-activated PRD (TPRD). Pressure-activated PRDs are used on most pressure systems; however, pressure-activated PRDs are not sufficient to protect against fire since a partially-filled cylinder may not reach the activation pressure in a fire. For composite

pressure vessels, the low thermal conductivity of the composite further confounds pressure-activated devices as the composite thermally insulates the gas, preventing pressure activation. Therefore, TPRDs are used for all composite and non-composite hydrogen cylinders. In the event of a fire, the TPRD provides a controlled release of gaseous hydrogen so the cylinder itself does not overpressure and potentially rupture. TPRDs are intended to vent the gaseous hydrogen rapidly and do not reseal or allow for the container to be re-pressurized. TPRDs open when temperatures reach approximately 108-110°C [4].

TPRDs allow for a controlled release of hydrogen that may result in an intense flame for a short time (until the cylinder pressure is relieved) instead of a catastrophic failure. However, TPRDs might fail when properly installed, either by premature activation or by failing to vent properly. A TPRD could fail and prematurely activate if it becomes corroded or otherwise damaged or has improper maintenance. A TPRD may fail to vent properly if blocked by dirt, stones, or other objects, is improperly installed or defective, or a fire heats a portion of the tank without heating the TPRD. In addition, first responders could inadvertently cool down the TPRD in an emergency event and cause the TPRD to not vent as designed.

CNG vehicles with pressure vessel cylinders have been used for decades. Newhouse et al. concluded that there were eight cylinder ruptures between 1993-2001 [24]. Of those incidents, Zalosh stated that at least two CNG cylinders ruptured when the TPRD did not actuate in a fire [25]. A 2010 NHTSA report found that since 2000 there have been over 20 failures of CNG tanks on-board vehicles with a majority of these failures attributed to the TPRD failing to operate properly in a fire [26]. On January 27, 2015, two CNG cylinders ruptured on a trash truck in Indianapolis, Indiana [27]. The fire began in the compactor refuse area and quickly grew with such intensity that it impinged upon the CNG fuel tanks atop the truck's cab. The fire burned for more than 30 minutes from the initial detection prior to cylinder rupture. According to the CVEF investigation, there was no evidence that the TPRD experienced sufficient heat input to trigger and relieve the gas pressure [28]. The cylinders in the trash truck fire ruptured and ejected shrapnel in a 360-degree pattern, injuring one firefighter [29]. One of the tanks traveled a quarter mile. This investigation from this incident concluded that a TPRD may not always activate in time to prevent rupture in fires and first responders should not spray water on the cylinder enclosure [28].

If the TPRD does not activate on a hydrogen tank, the tank will likely rupture and produce a blast wave and a fireball similarly to the rupture of a CNG tank. Extensive testing has been performed to investigate hydrogen cylinder ruptures simulating TPRD failure, sponsored by the Motor Vehicle Fire Research Institute (MVFRI) and conducted by the Southwest Research Institute (SwRI) [30-33]. All tests were conducted using 35 MPa Type III or Type IV compressed hydrogen cylinders with the TPRD removed. The Type III bonfire tests were conducted with a tank mounted on an SUV and the Type IV bonfire tests were standalone tests. Conclusions were summarized and included here from [26]. Results from the testing demonstrated that fireballs produced have maximum diameters in the range of 8 to 24 m and have a flame emissive power (the radiant energy emitted per unit time per unit flame surface area) of approximately 340 kW/m^2 [26]. Tank fragments from the Type IV cylinder were projected at distances up to about 82 m while some vehicle fragment projectiles traveled over 100 m [26]. Blast wave peak overpressures from the vehicle test were around 13.8 kPa at a distance of 15.24 m from the event (which could cause eardrum rupture) and around 6.89 kPa at a distance of 19.81 m from the event (which could break windows) [26]. And finally, in the Type IV stand-alone bonfire

test, the pressure and temperature inside the cylinder did not rise sufficiently to activate a pressure- or thermally-activated PRD [30-33].

John Dimmick, former Director of the Clean Vehicle Education Foundation (CVEF), presented on his experience with CNG vehicles during the 21st Hydrogen Safety Panel meeting held on March 3-5, 2015 in Sacramento, California [34]. One of Dimmick's main concerns was that TPRDs are effective in fire tests but not in fires that do not mimic the fire test conditions. As discussed earlier in this section, if a fire affects a portion of the cylinder where the TPRD is not located, it could cause the cylinder to overpressure without the TPRD actuating. Dimmick argued that the fire tests for CNG were built around invalid implicit assumptions, including: fires will be in liquid pools, fires will attack from underneath, cylinders will be in or under the vehicle, cylinders and PRDs will have little or no shielding, the fire will have low intensity and nonluminous flames, there will be no wind or firefighting, and the cylinders will be empty after a fire. CGA is aware of this issue and in its S-1.1 code for Pressure Relief Device Standards Part 1- Cylinders for Compressed Gases states that: "relief devices may not prevent burst of a cylinder under all conditions of fire exposure. When the heat transferred to the cylinder is localized, intensive, and remote to the relief device, or when the fire builds rapidly, such as in an explosion, the cylinder can weaken sufficiently to rupture before the relief device operates, or while it is operating" [28]. The risk of the TPRD not working as designed has not been analyzed against the risk of including a TPRD.

Dimmick explained that there have been seven known incidents of container rupture in a fire and the U.S. Department of Transportation (DOT) Pipeline and Hazardous Materials Safety Administration (PHMSA) is seriously considering eliminating TPRDs for most compressed gases, but only for metallic vessels [34]. Dimmick also stated that the distinction between the designation of metallic and not composite vessels was not clear. During questioning from the Hydrogen Safety Panel, Dimmick stated that based on the data there are more successful TPRD operations than failures, maybe twice as many; however, he recommended that more research should be done into alternatives and the better design of the TPRD and cylinder itself [34]. For example, if the tank is designed to withstand a one-hour burn test (either using thermal protective wraps or another design), it would decrease the need for a TPRD.

3.4.2. Evaluation for Future Research

The risk of having or not having a TPRD has not been fully analyzed. Although this knowledge gap has primarily been seen in CNG cylinders and vehicles, the hazard would likely be the same for hydrogen cylinders. Regardless of analyzing the risk of TPRDs, the bonfire test method in GTR #13 used to analyze the proper operation the TPRD should be reevaluated for local flame impingement and other external fire scenarios.

3.5. Composite Hydrogen Storage Materials

3.5.1. Description

Local damage is a much more important consideration for composites compared to all-metal vessels. This is due to the fact that external damage in metals is typically obvious under simple visual inspection, while external abuse can cause damage below the surfaces of composites, rendering it undetectable by visual inspection. External abuse can cause delamination of composite laminate layers,

though isolated single delaminations have been shown to not contribute to significant decreases in burst strength [35]. There are also differences in composite materials used; Kevlar and glass fibers have been shown to be more damage tolerant than carbon fibers [12]. Composite cylinder designs have recently improved to become more damage resistant by adding more material to damage-sensitive areas, and adding sacrificial layers to the outside of the entire tank [12]. These changes have made more recent designs much more damage-tolerant than older designs that were known to be highly sensitive to small amounts of damage.

Local flame impingement on a pressure vessel is a concern due to local weakening as well as heating (leading to increased pressure) of the contained gas. Furthermore, composite pressure vessels have additional concerns with local flame impingement because the composite matrix is itself flammable. Therefore, the composite material can rapidly degrade, leading to catastrophic failure. Numerical results have shown an example of local flame impingement in which half of the composite was completely consumed in 400 seconds [36]. This was compounded by both the calculated increasing pressure of the contained hydrogen gas as well as decreased strength of the heated composite even before the composite burns [36]. Protective layers covering the composite can mitigate this issue, but at a financial and weight cost.

Stress rupture is an important and not fully understood problem with composite tanks. It occurs when multiple fibers randomly fail next to each other. Normally when a single fiber fails, surrounding fibers can take on the load that was previously carried by the failed fiber. However, when multiple fibers fail very close to each other, surrounding fibers are suddenly put under much higher load, leading them to fail, and so on until the entire vessel ruptures. One way these fibers may fail is due to corrosion, such as oxidation of carbon fibers [37]. This mechanism has been studied under various atmospheres (including air) and at various temperatures, and found that high temperature samples in air had the highest rates of failure [37]. One problem with the study of stress rupture is the inherently stochastic mechanism it follows. Fibers can fail more or less randomly, and so it is inherently random if a sufficient number of fibers happen to fail in a cluster close to each other. This means that experimental studies of this phenomenon need high numbers of samples, typically with high lifetimes in order to produce failures. This can be addressed using Weibull statistics, taking into account limited numbers of samples and tests that were ended before failure [38]. To further complicate matters, stress rupture is typically studied for constant loads over long periods of time; however, predicting the likelihood of failure in a pressure vessel that undergoes pressure cycles will be more complex.

Another factor of composite tanks that must be considered is the interaction of the composite overwrap with the metal liner. Each component can fail, leading to failure of the entire vessel, but the way each component behaves will depend on the other. Deformation of the liner will induce different stresses in the composite, and heating (local or global) of the tank will cause the liner and composite to expand differently due to thermal expansion mismatches. This is a complex issue and will depend on the material and design of each component. This complexity adds scatter to test data, which current codes and standards do not account for [23]. One example of this behavior was studied for fast filling of a composite tank; the increased mechanical and thermal stresses (due to pressure and temperature increases) were studied using numerical models [39]. In this case, an aluminum metal liner was used in the design, and the plastic deformation of this liner was shown to isolate the thermal stress, meaning the mechanical stress dominated the behavior of the vessel [39]. Other materials may not behave in

the same way, and combinations of different materials need to be considered together instead of isolated studies.

Stress rupture is a failure mechanism unique to composite cylinders. Stress rupture is a situation in which the composite experiences degradation, as a function of time, which results in a sudden structural failure of the pressurized vessel's composite overwrap [12]. This overwrap failure results in the rapid release of the vessel's contents and the stored energy of the pressurized gas. This failure can occur at normal operating pressures and temperatures at maintained stresses well below the ultimate strength for an extended time [38]. This failure has little or no advanced warning and can lead to catastrophic results. This failure mechanism is the least understood, although research is currently being conducted by academia and NASA to better understand this type of failure [12, 38]. Stress rupture occurs at high pressures, meaning that keeping the load on the composite pressure vessel low will help to avoid this failure mechanism [40].

However, there are two benefits to higher pressures. First, a higher operating pressure means that more hydrogen can be stored per tank. The corresponding effective reduction in composite material per unit hydrogen stored could lead to significant cost savings. However, this must be done in a way that maintains the safety of the cylinder and a better understanding of stress rupture could allow for better cylinder designs that account for this or better detection of problems well before failure; both of these benefits could lead to lower required safety factors which would directly translate into less material used per cylinder.

Second, metal pressure vessels (including metallic liners in Type II and III composite pressure vessels) benefit from an initial hold at a pressure higher than the service pressure. This hold plastically deforms the metal cylinder in a process called autofrettage. When the pressure is lowered, a compressive stress is introduced in the metal cylinder, which is partially offset by tensile stress induced at the operating pressure. High autofrettage pressures (~2.5 times the operating pressure) have been shown in composite tanks to increase cycling life and induce a preferred leak-before-burst at the neck of the cylinder [41]. Thus, hydraulic proof testing and autofrettage can introduce benefits to the metal liner, and the pressure vessel overall [41, 42], as long as the pressure used in these processes is kept below a damage threshold (typically estimated at 50% of the ultimate strength of the composite) [12, 40].

3.5.2. Evaluation of Damage in Composite Materials for Future Research

Early composite pressure vessel designs were sensitive to small amounts of damage; in vehicles, this could be problematic if the entire fuel tank had to be replaced at the first sign of potential damage, making even minor fender-benders very expensive. Improvements in both materials and vessel designs have made subsequent vessels more damage tolerant, but a critical obstacle for composite pressure vessels still exists: damage inspection and detection. Various non-destructive test methods for all-metal pressure vessels have proven to be very effective at the detection of damage that could lead to vessel failure. Not the least of which is simple visual inspection, as critical cracks (especially from external damage) will be visible on the surface of the pressure vessel, required after a motor vehicle accident, fire or at least every 36 months or 36,000 miles by CFR 571.304. Unfortunately, predictive test methods are not as developed for composite materials, both for testing manufacturing defects as well as damage detection. This is an active area of research, and the use of risk methods to inform which test methods are reliably able to detect damage significant enough to cause vessel failure within

rated lifetimes would benefit the industry. Safety codes and standards may benefit from implementation of damage-detection into approved test and inspection methods.

3.5.3. Evaluation of Stress Rupture for Future Research

Additional materials science research can help explain the underlying phenomena of stress rupture and statistical methods can help to describe the inherent stochasticity. However, many test methods utilized by current safety codes and standards (e.g., GTR #13) do not directly account for stress rupture. This is not due to an oversight of the code committees, but rather a lack of a test method with sufficient predictive power for this failure mechanism. The incorporation of complex statistics into a code-approved test methodology is not trivial but can provide a framework for inclusion of this important failure mechanism into hydrogen pressure vessel codes and standards.

Various mechanisms may behave differently under differently operating conditions (temperature, pressure, atmosphere) and so it is important to understand these mechanisms to determine what parameter-space is applicable for a test methodology. Furthermore, certain operating parameters (especially internal pressure) are extremely important as they directly affect the consequence of a stress rupture event. However, dealing with high pressure by over-designing cylinders leads to much higher costs which could be avoided if the underlying mechanism was better understood. The application of risk can be useful for implementing current understanding into safety codes and standards, but particularly for identifying which sets of conditions are especially important to avoid.

3.6. Polymer Compatibility

3.6.1. Description

Polymer materials are used throughout the hydrogen industry for seals in connections, compression equipment, tubing, dispensing, and valves as well as the lining of the Type IV cylinders. Barth et al. states that in hydrogen applications, there are four classes of polymer materials based on their microstructure: semicrystalline thermoplastics, amorphous thermoplastics, elastomers, and epoxies [43]. Polymers are used to construct pressure vessels: Type III cylinders have an epoxy resin that is wound with the glass or carbon fibers to protect the metal liner from external impacts. Typically, Type IV vessels are comprised of a seamless, high-density polyethylene (HDPE) liner that is overwrapped with carbon fibers set in an epoxy resin matrix [44]. Polymer liners have several advantages, including high strength, low thermal conductivity, and corrosion resistance [45]. Type V tanks are made up entirely of composites (resin and fibers). Most importantly, Type IV and Type V tanks are the lightest types of pressure vessels, which is critical in mobile applications.

Polymers, whether used in seals, compressors, tubing, or pressure vessels, can fail in a variety of ways. Unlike in metals, hydrogen does not dissociate and remains a diatomic molecule in most of the polymers used [43]. While the hydrogen embrittlement mechanisms in metals appear to be absent in polymers, exposure to high-pressure hydrogen does affect the mechanical performance of polymers. Hydrogen, being one of the smallest molecules, can diffuse into and through polymers much more easily than other gases. While some polymers can maintain properties while operating in hydrogen, this is not a well understood or studied area [43]. Furthermore, as hydrogen absorbs into and diffuses through polymer components during operation at high pressure, if rapid depressurization occurs, hydrogen is not able to diffuse back through the polymer, and instead forms small bubbles within the

material, causing damage. If the depressurization is substantial and rapid enough, these bubbles can exit the polymer violently, causing substantial damage and failure of the component. This rapid gas decompression can occur even on the timescale of hours, meaning this effect is not limited to sudden and drastic changes in pressure [43]. While this effect has been examined somewhat in certain polymers, thermoplastics in particular have not been thoroughly investigated for this failure mechanism [43].

Polymers have a variety of melt and glass transition temperatures, and so must be matched to the operating conditions of interest, but this can be difficult in situations where the operating conditions vary widely. Compressors and vehicle pressure vessels can have wide ranges of pressures, and consequently large temperature variation as well. Many polymers have not been extensively tested at high pressures, in a hydrogen atmosphere, or both [43]. There is no standardized or even widely accepted test method for evaluating polymers [43]. Finally, the high pressure used to store hydrogen can have some effects on plasticization of the polymers, and this is not well understood [43]. Current research into these issues is underway through a joint effort of Pacific Northwest National Laboratory, Oak Ridge National Laboratory, and Sandia Labs [46].

3.6.2. Evaluation for Future Research

The DOE FCTO has sponsored work in the compatibility of polymeric materials with high-pressure hydrogen systems. A gap analysis was conducted in 2013 by Barth et al. which identified areas in which fuller characterization is needed to assess material suitability for hydrogen service, particularly high-pressure gaseous hydrogen [43]. The gaps included: fracture and fatigue, failure modes, rapid gas decomposition, friction and wear, test methods, plasticization, transport properties, and contaminants. A risk assessment could help categorize and characterize failure modes by considering both likelihood as well as consequences of various types of failures on various components in the system. Furthermore, a risk-based analysis could aid in the creation of standardized methodologies to evaluate and qualify materials for resistance to known failure modes. Specifically, this would help to identify critical materials properties that have the largest effect on the most impactful failure modes. The Barth et al. gap analysis stated that standard test methods are needed in many areas for polymers and the identification of failure modes would support the development of appropriate test methods to evaluate and qualify materials. Polymer materials science is a varied and highly active area of research; even limiting the scope to those materials with proven usefulness in hydrogen systems, there are likely many specific areas in which a risk-informed analysis can contribute significantly to the usefulness of future materials science work by helping to provide framing and direction. There are likely many different opportunities in this area. Considering the risk of different system component failures or degradation can focus further research efforts on high priority items, for example the failure of a small polymer fitting on a low-pressure fuel line would have a less hazardous consequence than a polymer fitting on a high-pressure hydrogen compressor. This prioritization can focus future efforts on better understanding of high risk components.

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4. SUMMARY AND RECOMMENDATIONS

The six topics evaluated in this report are: crack formation in metals, cylinder recertification, TPRD removal, damage in composite materials, stress rupture, and polymer compatibility. Four areas of risk application to hydrogen materials were selected based on their feasibility and potential for impact to improving safety, codes and standards: crack formation in metals (specifically initial crack distribution), damage in composite materials, stress rupture, and polymer compatibility. These vary in scope, specificity, level of anticipated resources required, and potential impact to the field. These will be briefly summarized in this section, followed by specific recommendations based on the authors' current understanding of these topics.

Determining the initial crack distribution for metal pressure vessels would have a large impact on the field due to the direct application to traditional fracture mechanics models and the wide usage of metal (Type I-III) cylinders. If data on manufacturing defects can be obtained from multiple tank manufacturers, the Risk and Reliability team at Sandia Labs could incorporate the data into a functional distribution in a relatively straightforward way. While the anticipated level of resources required to complete this effort would be relatively small, it is almost wholly dependent on the willingness and ability of tank manufacturers to supply this data. However, given the benefits of being able to characterize this probability, it is worth the efforts required to solicit this data utilizing non-disclosure agreements and cooperative research and development agreements.

Determination of damage in composite materials will have increasing importance due to the wide (and growing) usage of composite cylinders for hydrogen storage and transport. The ability to test for accumulated damage would allow damaged cylinders to be removed from use and would reduce the number of usable tanks unnecessarily removed from service. The application of risk can be useful in identifying critical types of damage, but this task is primarily viewed as a materials science problem as new or improved characterization techniques are required to do this type of damage assessment. The amount of characterization required would likely necessitate a large resource investment.

Stress rupture in composite pressure vessels is a poorly understood but potentially very consequential phenomena. The stochastic nature of this process makes direct experimental study of this mechanism difficult and expensive in both time and resources. The application of statistics has and continues to improve the understanding and application of observed stress rupture tests, but the improved application of risk (including Bayesian networks) could lead to a better understanding and improved safety in real-world applications.

There are many potential applications of risk in the field of polymers as they interact with hydrogen, especially at high pressure. The broad and varied nature of this field, as well as the many different applications in hydrogen infrastructure, leads to many possible opportunities for a quantitative risk framework to make substantial impacts. Furthermore, while a number of polymers are currently in use with hydrogen-wetted components, more are being developed. Polymer applications in hydrogen need to be examined further for specific use-cases in which risk can make the most impact.

Two of the most important considerations for research is the level of resource investment required and the level of impact the work could have on the field. Unfortunately, both considerations are difficult to quantify due to the nature of research. Figure 2 shows the best estimate based on the

current understanding of these issues. This schematic helps to frame the recommendations that follow.

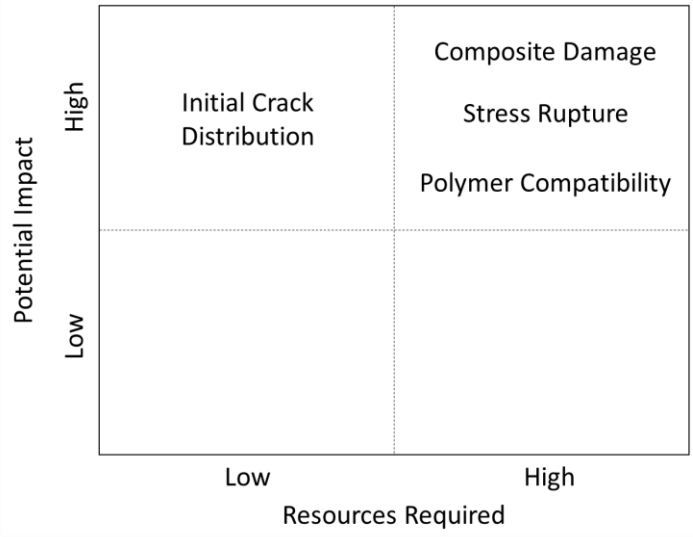


Figure 2. Conceptual schematic of resource investment requirements and potential effect on hydrogen vehicles

Resource allocation decisions are difficult and ultimately the purpose of this report is to provide information rather than a final decision. However, there is still value in providing succinct recommendations based on the information provided in this report. As such, a rank-ordered list of the four topics discussed above is provided, based on the literature survey, survey of industry experts, and the authors' current understanding and best estimates of resources required, impact on the field, and match to capabilities highlighted in Appendix A.

Rank-Ordered Recommended Research Topics for Materials Risk:

1. Stress Rupture of Composite Pressure Vessels
2. Initial Crack Distribution in Metal Pressure Vessels
3. Polymer Compatibility in High Pressure Hydrogen
4. Damage in Composite Pressure Vessels

Recommended research projects on the first two topics are provided and discussed below.

4.1. Recommended Stress Rupture of Composite Pressure Vessels Research

The objective of the recommended study will be to quantify the behavior of stress rupture for composite cylinders in order to reduce unnecessary safety factors. Composite stress rupture is not well understood. Pressure vessel designs address this failure mechanism by over-designing using a variety of safety factors for the thickness of the materials depending on the specific materials used in the cylinder walls. This additional material can add significant cost to the composite cylinder, which hinders the transportation and adoption of hydrogen for some mobile applications. Improving the

fundamental understanding of stress rupture could allow for safety factors to be reduced if they are not contributing to safety. Phase I of this study will include conducting an in-depth and targeted literature search on stress rupture for different composite materials, establishing cooperative research and development agreements (CRADAs) with tank manufacturers in order to learn from and leverage anonymized proprietary data, and determining critical experimental data that may be missing. Phase II of this study will include performing necessary experimental tests, analyzing available failure data, quantifying updated risk metrics based on modified safety factors, and documenting results to suggest improvements to codes and standards committees.

4.2. Recommended Initial Crack Distribution in Metal Pressure Vessels Research

The purpose of this recommended study will be to calculate a distribution for defect sizes and locations on metal pressure vessels. In order to calculate these distributions, anonymized data provided from manufacturers will be used to analyze the location of the defect on the cylinder and the size of the crack and determine if there is a correlation between the two. The distributions will inform crack initiation research by highlighting parts of the pressure vessel that fail more often or have a larger consequence and focusing the experimental analysis on those cylinder areas. Phase I will include collecting cylinder failure data and establishing CRADAs with tank manufacturers, developing the analytical method for organizing the data, and conducting a targeted literature review on this topic. Phase II will include analyzing the data, calculating the distributions for crack number, size, and location on the cylinder, and documentation of results, including suggesting improvements to codes and standards.

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APPENDIX A. MATERIALS RISK CAPABILITIES OF SANDIA NATIONAL LABORATORIES

A.1 Introduction

Sandia National Laboratories has a number of core capabilities both in the calculation and evaluation of risk as well as materials characterization. Experience in both evaluating safety risk both qualitatively and quantitatively allows for useful comparisons to be made based on the level of information available about a problem, which is useful for emerging technologies such as hydrogen vehicles. Characterization of materials properties and behavior will be used to obtain critical data where none exists, in order to better inform the risk evaluation being performed. This section highlights a number of capabilities at Sandia Labs, both in terms of risk assessments themselves as well as characterization capabilities for a number of different materials used with hydrogen infrastructure.

A.2 Risk Capabilities

In simple terms, risk represents the likelihood of an adverse event and the consequences of that event occurring to produce realistic risk estimates for complex systems. The resulting analyses explore the often subtle and non-intuitive interactions among initiating events, hardware failures, human errors, and operational and organizational factors that influence the risk profile for a system. Sandia has over 30 years of experience developing and applying probabilistic risk assessment (PRA)—a systematic, logical analysis process—to civilian nuclear power applications. This risk experience has been utilized for other high-consequence industries, including analyzing the risk of hydrogen fueling stations to update codes and standards.

Sandia Labs' QRA team develops methodologies to identify hazards, understand risk drivers, and develop strategies to reduce risk in hydrogen infrastructure. The models, data, methods, and tools developed by Sandia facilitate the use of science and engineering to support the development of codes and standards that ensure the safe use of hydrogen. The Sandia QRA team focuses on two key activities: development of the technical basis for QRA and accumulation of the technical basis and other knowledge to support modification of relevant codes and standards. Development of the technical basis involves development of data and models for understanding hazards, developing accident scenarios, predicting physical effects, and characterizing the impact of hazards on people and structures. This entails ongoing collaboration with other groups at Sandia whose primary research is focused on the behavior of hydrogen to develop and experimentally validate first-order predictive models for hydrogen physical phenomena. Accumulation of this technical basis and other knowledge puts the state-of-the-art science and engineering models in the hands of decision makers such as SCS developers and station designers. Through the development of high fidelity models, data, and tools for QRA, Sandia has introduced, and continues to advance, the application of risk-informed decision making within the hydrogen community.

A.3 Hydrogen Behavior Capabilities

The Turbulent Combustion Laboratory (TCL) provides a well-controlled, lab-scale environment for testing hydrogen release characteristics. Outfitted with laser diagnostic systems, the TCL is uniquely suited to make high-fidelity, non-intrusive measurements of hydrogen release and combustion phenomena. The optical diagnostics employed in this laboratory include line-imaged Raman

scattering, Raleigh Scattering, laser-induced fluorescence, particle imaging velocimetry, and Schlieren flow visualization.

A.4 Metal Vessel Testing Capabilities

The materials and components compatibility program element applies Sandia's core capability in hydrogen embrittlement to address fundamental questions about the mechanical behavior of materials when exposed to high-pressure gaseous hydrogen. The cornerstone of Sandia's core capability in hydrogen embrittlement is the Hydrogen Effects on Materials Laboratory where specialized assets reside for conducting mechanical testing of materials with concurrent exposure to gaseous hydrogen at pressures from 1 MPa to greater than 100 MPa. The laboratory includes a range of specialized assets for evaluating materials performance in high-pressure gaseous hydrogen:

- Thermal Precharging – Materials and test specimens are exposed to high-pressure gaseous hydrogen (up to 140 MPa) at elevated temperature (up to 300 ˚C) before subsequent evaluation.
- Static-load Crack Growth Testing – Instrumented specimens subjected to constant-displacement loading (e.g., wedge-opening load specimens) are exposed to gaseous hydrogen at pressure up to 200 MPa and temperatures over the range of -70 ˚C to 170 ˚C. The material properties measured are the crack velocity and subcritical cracking threshold.
- Dynamic-load Testing – Specimens are exposed to gaseous hydrogen at pressure up to 140 MPa while concurrently subjected to different loading formats, e.g., monotonically increasing or cyclic. Material properties measured include tensile strength and ductility, fatigue strength, fatigue crack growth rates, and subcritical cracking thresholds under rising loading.

Sandia Labs is responsible for maintaining the Technical Database for Hydrogen Compatibility of Materials and the Technical Reference for Hydrogen Compatibility of Materials which provide a repository of technical data measured in hydrogen.

A.5 Composite Characterization Capabilities

The Mechanics of Materials Department performs experimental and analytical studies to characterize and predict the thermal-mechanical behavior of materials, from atoms to continuum, specializing in fracture and failure. Motivated by observations, mathematical models are developed to simulate material responses under various loading and environmental conditions. We develop numerical methodologies so that our material models can be implemented in high-performance computing simulations, ranging from atomic to continuum scales. The experimental mechanics labs are used to characterize the mechanical behavior of materials and structures and to validate mathematical models of failure and fracture in foams, metals, ceramics, and composites. These capabilities include a number of test frames (both servo-hydraulic and electro-mechanically driven), axial and torsional bi-axial test frames, and high-rate test frames, among others.

A.6 Polymer Testing Capabilities

Sandia Labs is developing test methodologies for analyzing polymers in high pressure hydrogen systems. Specifically, Sandia Labs is planning on performing high pressure cycling aging tests for a variety of polymer materials. Many of the capabilities for testing metals in high pressure hydrogen can

be used to also test polymer materials as well (see Section A.4). High pressure cycle aging is critically important for pressure cycling applications, such as valves, compressors, hoses, and other polymer components. The goal of the testing is to better characterize the effects of thermal and pressure cycling to enable the selection of critical test parameters and material attributes for test methodology development.

A.7 Other Materials Characterization Capabilities

Sandia Labs has a variety of materials reliability and analytical chemistry capabilities. Organization 1800 in NM and 8300 in CA have expertise to analyze the failure of a product, component, or process by using advanced materials characterization and chemical analysis equipment and techniques. With techniques such as metallography, image analysis, scanning electron microscopy (SEM), fractography, electron-probe microanalysis (EPMA), chemical analysis, surface analysis, and x-ray diffraction, Sandia failure analysts not only determine the cause of failure but also provide recommendations for preventing future issues. In addition, researchers are actively engaged in advancing the understanding of hydrogen-materials interactions through both fundamental and applied research projects in the Hydrogen Trapping (8367) and Transport Laboratory and the Hydrogen-Surface Interactions Laboratory (8366). Within the materials reliability department, material science investigators perform incoming material inspection, troubleshooting, impurity detection and compositional analysis, in addition to metallurgy, transmission electron microscopy (TEM), Infrared/Raman and surface analysis. Failure analysis is performed on all types of materials including metals, ceramics, polymers, electronics, and biological matter to resolve issues related to defective materials, unexpected loading environments, manufacturing process failures, in-service failures, inappropriate-use and age-related degradation and defects.

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