IV.E.4 Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of Hydrogen Storage Materials and Systems

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Objectives

Provide improved definition of the DOE Environmental Health and Safety (EH&S) target and its link to material reactivity to guide research of storage materials. Detailed objectives include:

- Develop qualitative and quantitative analysis tools to evaluate risks for materials-based hydrogen storage systems before and after mitigation methods.
- Perform dust characterization tests for metal hydride, chemical hydride and adsorbent materials.
- Characterize chemical reactions for material exposures associated with both risk events and mitigation approaches using time resolved X-ray diffraction (XRD).
- Assess the trade-offs between residual risk after mitigation and the system weight and volume as well as reaction rates.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

(F) Codes and Standards
(A) System Weight and Volume
(E) Charging/Discharging Rates

Technical Targets

The key technical target of this project is EH&S, having a focus on the safety sub-target with some consideration for toxicity. The technical target for safety is specified generally as "Meets or exceeds applicable standards." For metal hydride, chemical hydride and adsorbent materials and systems, however, no such standards exist today. Furthermore, standards currently under development will be high-level in scope, primarily focused on systems and will not provide adequate guidance for evaluating and selecting viable candidate materials. As part of this effort, trade-offs will be evaluated between residual risks after mitigation of the two technical barriers: System Weight and Volume, and Charging/Discharging Rates.

Accomplishments

- Developed customized failure mode and effects analysis (FMEA) for conceptual baseline designs of on-board reversible (using $NaAlH_4$) and off-board regenerable (using AlH_3) storage systems. Potential safety hazards, failure modes and accident imitators were identified and ranked based on their risk significance.
- Developed and quantified event tree (ET) models for risk-significant accident initiating events identified from FMEA of the on-board reversible storage system.
- Developed fault tree (FT) models for a range of injury categories for blast waves from aluminum dust dispersion. Also, developed FT model for hydride dust dispersion.
- Constructed a framework for economic consequence analysis.
- Identified existing safety Codes & Standards (C&S) (for compressed natural gas [CNG] and compressed hydrogen gas [CHG] applications) that could be modified and credited as hazards control measures in qualitative risk analysis of on-board reversible hydrogen storage systems.
- Performed dust combustion characterization testing of discharged alane powder and Maxsorb activated carbon powder in air and in air-hydrogen

atmospheres. Also, completed testing of partially discharged $2LiBH_4 + MgH_2$.

- Designed a rapid depressurization rig to experimentally mimic accidental hydride storage vessel breach and its influence on powder particle size and durability of powder compactions.

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Introduction

Safety is one of the most significant issues affecting consumer acceptance and adoption of hydrogen fueled vehicles. Through DOE efforts to understand general public opinions, people have indicated that when selecting a fuel supply, safety is the most important factor. The current project, in close coordination with efforts at Savannah River National Laboratory (SRNL) and Sandia National Laboratories (SNL), will provide quantitative insights to this target and support the development of future risk-informed C&S. The results from these collaborative efforts will also have nearer term impact in guiding storage materials research and the development of materials/systems risk mitigation methods.

Approach

The current project has five distinct elements as follows:

- **Risk Analysis:** Formal analysis methods are developed and employed to produce tools which provide increasingly quantitative assessment of the risks associated primarily with on-board vehicle hydrogen storage before and after the use of mitigation methods.
- **Standardized Materials Testing:** A set of standard materials tests, focusing on dust explosion, are performed on storage materials to quantify their combustion characteristics under potential risk scenarios and conditions.
- **Chemical Reaction Kinetics Testing and Modeling:** Fundamental studies are performed to evaluate the chemical kinetics of material reactions with oxygen, water and various fluids (primarily gases) using time-resolved XRD and other techniques to support the development of risk mitigation methods.
- **Risk Mitigation:** Concepts to reduce the consequences of risk-significant failure modes and critical hazards will be devised and investigated both at the material and system levels. The impact on DOE system performance targets will also be determined.
- **Prototype System Testing:** This activity was originally planned but unlikely to be pursued given the revised project scope.

Results

During this year (Q4 Fiscal Year 2008 to Q3 FY 2009), the current project accomplished several milestones that are grouped into four categories as follows:

I. Qualitative Risk Analysis (QLRA)

I.1 Developed FMEA for conceptual system configurations of on-board reversible (using $NaAlH_4$) and off-board regenerable (using AlH_3) storage systems.

I.2 Defined an expert panel for opinion pooling for FMEA of the on-board reversible (using $NaAlH_4$) system and employed the Delphi process to elicit subject matter experts (SMEs) risk scorings [2]. The panel included SME from DOE, UTRC, SNL, SRNL, automaker original equipment manufacturers, Type-III/Type-IV storage vessel manufacturers, the National Fire Protection Association, University of Maryland Center for Technology Risk Studies, as well as SMEs from Germany, Japan, and Canada. Figure 1 shows the aggregated risk scorings for the top 10 critical hazards/failure modes. The results are based on the first round of SME elicitation using the Delphi iterative process. In this figure, the X-axis represents the identification numbers of the top 10 failure modes [2] of which the top three failure modes are:

- Catastrophic failure of the hydride storage vessel caused by vehicular collision.
- Hydrogen leak caused by pipe rupture in the on-board storage system.
- Hydride storage vessel burst by overpressurization caused by external fire with direct flame impinging upon the storage vessel in conjunction with vessel thermally-activated pressure relief device (TPRD) failure to activate as designed.

In Figure 1, each risk priority number (RPN) is represented by a mean and one standard deviation

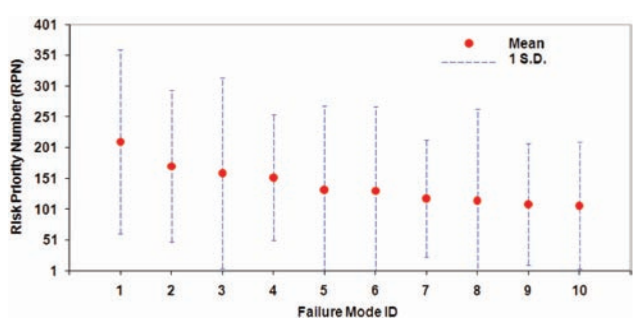


FIGURE 1. FMEA/Expert Panel Risk Scorings of the Top 10 Failure Modes

around the mean. The standard deviations reflect the uncertainties of the risk scores assigned by the panel SMEs. It is expected that these uncertainties will decrease in the second round of the Delphi iterative process.

I.3 The major insights of QLRA of the on-board reversible storage system are:

I.3.1 The hydride storage vessel is the most risk significant component in the system, and represents vulnerability of the system to single-point failure should the vessel fail catastrophically. High-severity consequences are associated with scenarios involving catastrophic vessel failure.

I.3.2 The most risk significant accident initiating events (IEs) are: a) vehicular collision leading to hydride vessel rupture, b) external fire leading to vessel burst by overpressurization given failure of vessel TPRD to activate and vent as designed, c) leakage of hydrogen gas from the on-board storage system into a confined (or partially confined) space leading to early or delayed H_2 ignition with possible explosion (deflagration/detonation), and d) water intrusion into the hydride storage vessel leading to in-vessel chemical reaction of the hydride material.

I.4 Crediting Safety Codes and Standards in Qualitative Risk Analysis

Existing as well as newly developed C&S for hydrogen/fuel cell vehicles, such as ANSI/CSA HGV2 [3] and SAE J2579 [4], respectively, are focused on CHG and there is no equivalent C&S for on-board reversible hydrogen storage systems [5]. Part of the current project QLRA included a discussion on the reciprocity between QLRA safety insights and C&S [3]. The discussion demonstrated that structure, system, and component compliance with applicable C&S can be used to support QLRA. Conversely, QLRA insights can support future risk-informed C&S activities related to the on-board storage system. For example, the bonfire test requirements and acceptance criteria in SAE J2579, FMVSS 304 [6] and CSA HGV2, and also the crashworthiness test requirements and acceptance criteria in SAE J2578, SAE J2579, ISO 23273-1 (FCV) and FMVSS 303 can be modified and credited as hazard control measures in FMEA of the on-board reversible hydrogen storage system [5].

II. Quantitative Risk Analysis (QRA)

Three ET models were developed and quantified using the EPRI ETA-II software package. The ET models represented the three risk-dominant accident initiators: vehicle collision, external fire and hydrogen leakage from the on-board reversible storage system. Figure 2 shows the external fire ET model [5]. The ET top events include hardware failures (e.g., vessel rupture/burst and TPRD failure to vent) and phenomenological events such as hydrogen explosion, hydride chemical reaction with air or water and hydride dust cloud explosion. The ET includes 15 probable accident sequences and associated outcomes (DS-1 through DS-15). The ET also models FMVSS 304 bonfire test acceptance criteria, namely, either the vessel TPRD vents as designed or the vessel survives the fire for 20 minutes [6].

III. Dust Cloud Testing

Dust cloud testing was performed for AX-21 activated carbon, charged and partially-discharged $2LiBH_4 + MgH_2$ and discharged alane. Figure 3 shows the measured pressure rise as a function of time for the materials tested. The largest peak pressure was associated with the discharged alane which is indicative that the metallic form of this material is more reactive than the hydride form. Also for the sample concentration of 250 g/m^3, $\left(\frac{dP}{dt}\right)$ was the largest of all materials tested to date. The results of dust cloud combustion characterization tests provided useful insights to the probabilistic modeling of dust explosion using fault tree analysis.

IV. Storage Vessel Rapid Depressurization Test

Figure 4 shows the design configuration of a rapid depressurization rig to experimentally mimic accidental hydride storage vessel breach and its influence on powder particle size as well as durability of powder compactions as a risk mitigation method. The key components of the test rig shown in Figure 4 include the hydride powder storage vessel, rupture disk, hydrogen gas supply line, nitrogen purge line, vacuum line and the hydride powder collection vessel.

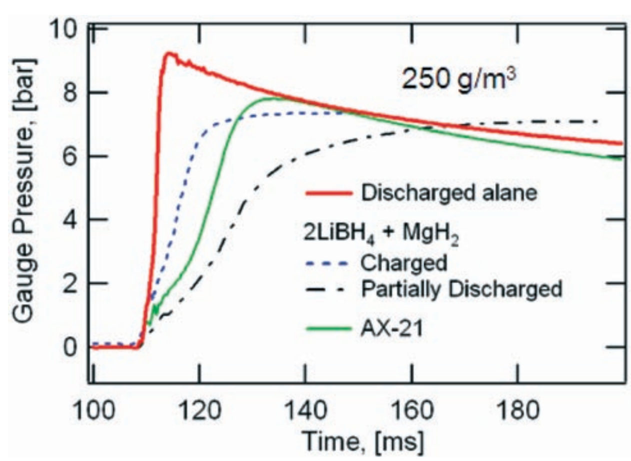
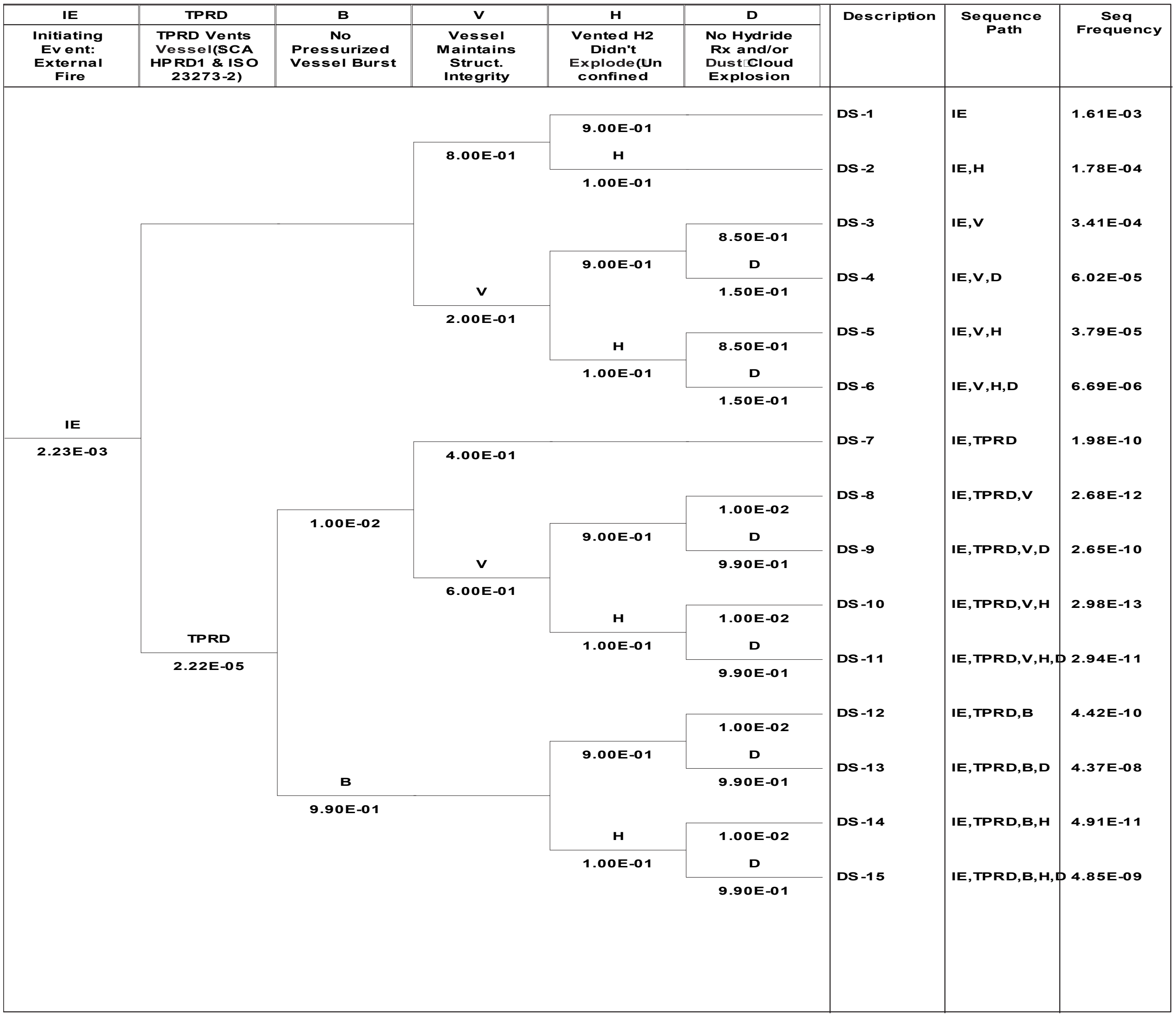


FIGURE 2. Pressure Profiles of Materials Tested (per ASTM E1226)



Description of Top Events:

IE = Initiating event: external fire, TPRD = Thermally-activated PRD vents vessel (per CSA HPRD1 & ISO 23272-2), B = No pressurized vessel burst, V = Vessel maintains structural integrity for 20 min (per FMVSS 304), H = Vented H_2 gas didn't explode (*assumption: H_2 vented in an unconfined space*), D = No hydride reaction and/or dust cloud explosion (ASTM and NU tests).

FIGURE 3. External Fire Event Tree Model

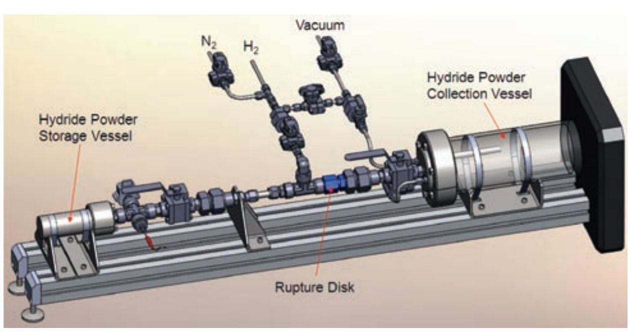


FIGURE 4. Storage Vessel Rapid Depressurization Test Rig

Conclusions and Future Directions

The information generated to date included QLRA, QRA and experimental studies. The QLRA included FMEA of two conceptual baseline designs of on-board reversible and off-board regenerable hydrogen storage systems. The QRA covered FT modeling of key phenomena such as hydride dust dispersion, ET modeling of key accident initiating events and framework for economic consequence analysis. The experimental work focused on dust cloud testing of selected hydrogen storage materials.

Future work will focus on:

I. Continue QLRA efforts by completing design FMEA of the off-board regenerable (using alane) system and analyzing the expert panel's pooled risk scorings for this system.
II. Continue QRA efforts in three areas: a) ET development and quantification for the remaining dominant accident initiating events, b) economic consequence analysis and assigning monetary safety benefits of selected risk mitigation methods, and c) incorporate results from the experimental and modeling activities at SNL and SRNL into QRA.
III. Continue experimental efforts in three areas: a) additional dust cloud testing on alane and other materials, b) validation of effectiveness of selected risk mitigation methods, and c) fabrication of the designed rapid depressurization apparatus which mimics hydride storage vessel breach and experimentally investigate the influence of rapid depressurization on powder particle size as well as durability of powder compactions as a risk mitigation method.

FY 2009 Publications/Presentations

1. D.A. Mosher, Y.F. Khalil, X. Tang, B. Laube, and R. Brown, "Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of hydrogen Storage Materials & Systems," Technical Team Meeting, USCAR Office, Southfield, MI (April 16, 2009).

2. Y.F. Khalil, D.A. Mosher, X. Tang, B. Laube, and R. Brown, "Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of hydrogen Storage Materials & Systems," DOE Hydrogen Program, Annual Merit Review Meeting Arlington, VA (May 18–22, 2009).

3. Y.F. Khalil and D.A. Mosher, "Risk Quantification of Hydride Based Hydrogen Storage Systems for Automotive Applications," 3rd International Conference on hydrogen Safety, Congress Palace, Ajaccio, Corsica, France (September 16–18, 2009).

4. Y.F. Khalil and D.A. Mosher, "Reciprocity of Safety Insights between Risk Analysis and Codes 7 Standards of vehicular hydrogen Storage," Invited Paper at the 2009 Risk Management Conference, Washington, D.C. (November 15–19, 2009).

References

1. Multi-Year Research, Development and Demonstration Plan, Technical Plan - Storage: http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/storage.pdf

2. Y.F. Khalil and D.A. Mosher, "Risk assessment for on-board reversible hydrogen storage: Conceptual baseline design and FMEA worksheet," Internal Document, United Technologies Research Center (January 2009).

3. ANSI/CSA HGV2 Fuel Containers (Draft), Basic Requirements for Compressed-Hydrogen Gas Vehicle Fuel Containers, (July 2007).

4. SAE J2579, Technical Information Report for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles, (January 2009).

5. Y.F. Khalil and D.A. Mosher, "Reciprocity of Safety Insights between Risk Analysis and Codes 7 Standards of vehicular hydrogen Storage," Invited Paper at the 2009 Risk Management Conference, Washington, D.C. (November 15–19, 2009).

6. FMVSS 304 (FMVSS 49 CFR 571.304), Compressed Natural Gas Fuel Container Integrity.