

## 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), liquid reactivity and other specialized testing.
- 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 Fuel Cell 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 and the two technical barriers: System Weight and Volume, and Charging/Discharging Rates.

### Accomplishments

- Qualitative risk analysis (QLRA): identified potential safety-significant failure modes that challenge the integrity of the storage vessel in an on-board reversible system.
- Quantitative risk analysis (QRA):
  - Used the fault tree methodology to perform system-level failure analysis of a baseline design of an on-board reversible storage system.
  - Defined a probabilistic importance measure to estimate contributions of system components to the total failure probability of the on-board system.
  - Developed and quantified a fault tree model to assess the consequences of accidental air intrusion into a hydride-based storage vessel.
  - Developed and applied a stochastic approach using interactive simulation in conjunction with Monte Carlo sampling to manage uncertain inputs in quantitative risk analysis.
  - Defined a probabilistic risk reduction importance measure to quantify the magnitude of safety improvement that can be achieved by reducing the probability of occurrence of undesired events and failure of components credited in the risk model.
- Risk mitigation: experimentally evaluated hydride powder compaction as a potential risk mitigation method.



## 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 codes and standards. 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 (QLRA and QRA).
- Materials reactivity testing.
- Chemical reaction kinetics testing and modeling.

- Risk mitigation.
- Limited scope prototype testing.

Figure 1 outlines the risk analysis framework of this project.

## Results

### 1. QLRA

Identified safety-significant failure modes associated with the on-board reversible storage vessel (Figure 2). These failure modes include catastrophic vessel rupture due to a vehicular collision and vessel burst due to an external fire in conjunction with failure to vent the vessel. Other failure modes include accidental intrusion of air or water into the storage vessel and the potential for stored hydrogen diffusion/permeation through the vessel walls.

### 2. QRA

2.1 Developed a system-level fault tree (FT) model for a baseline design of an on-board vehicle reversible hydrogen storage system (Figures 3 and 4). The hydride storage vessels and associated pressure relief devices are among the key components credited in

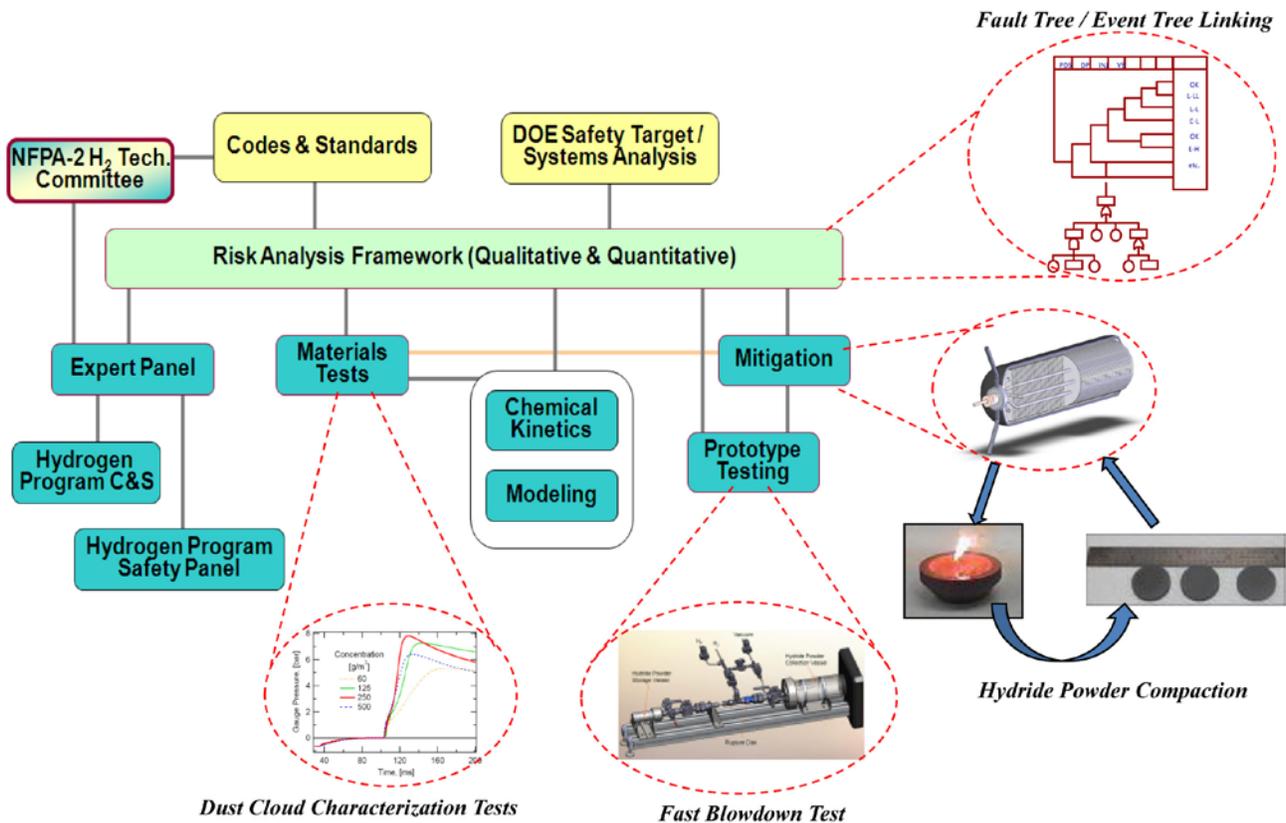


FIGURE 1. Risk Analysis Framework

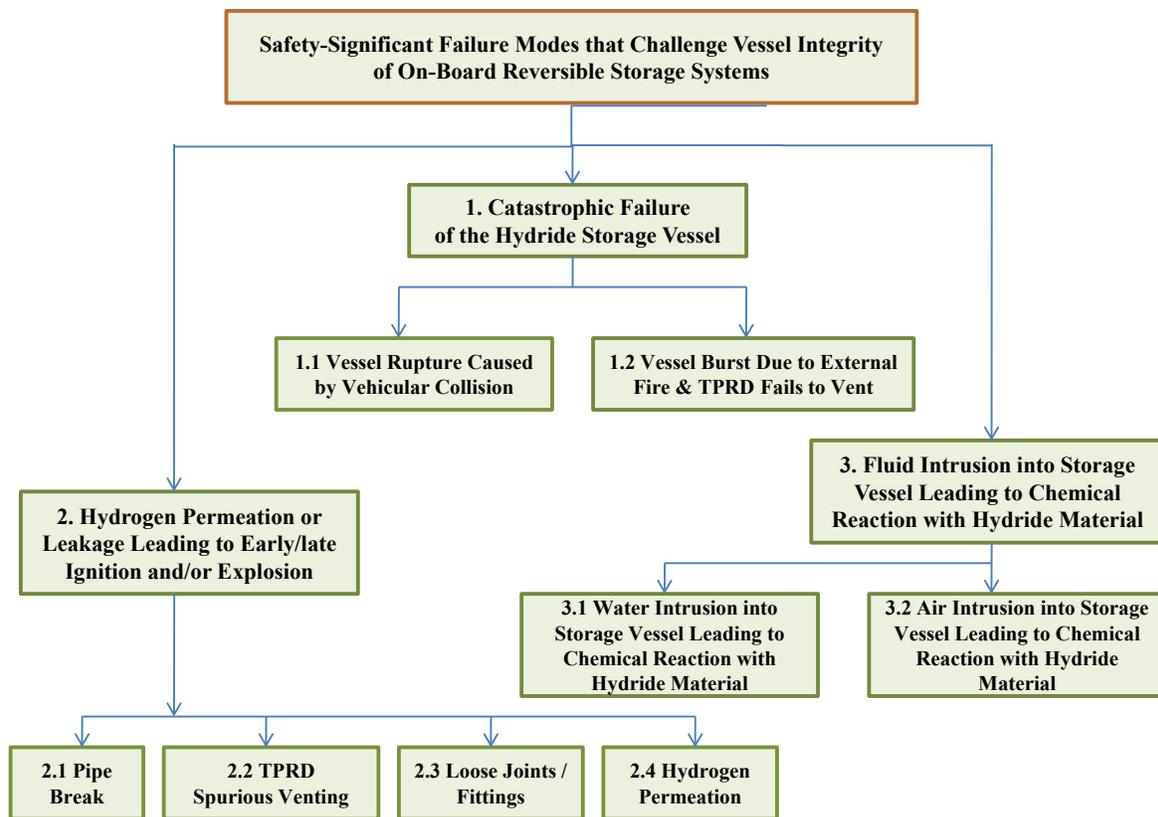


FIGURE 2. Safety-Significant Failure Modes of On-Board Reversible Storage Vessels

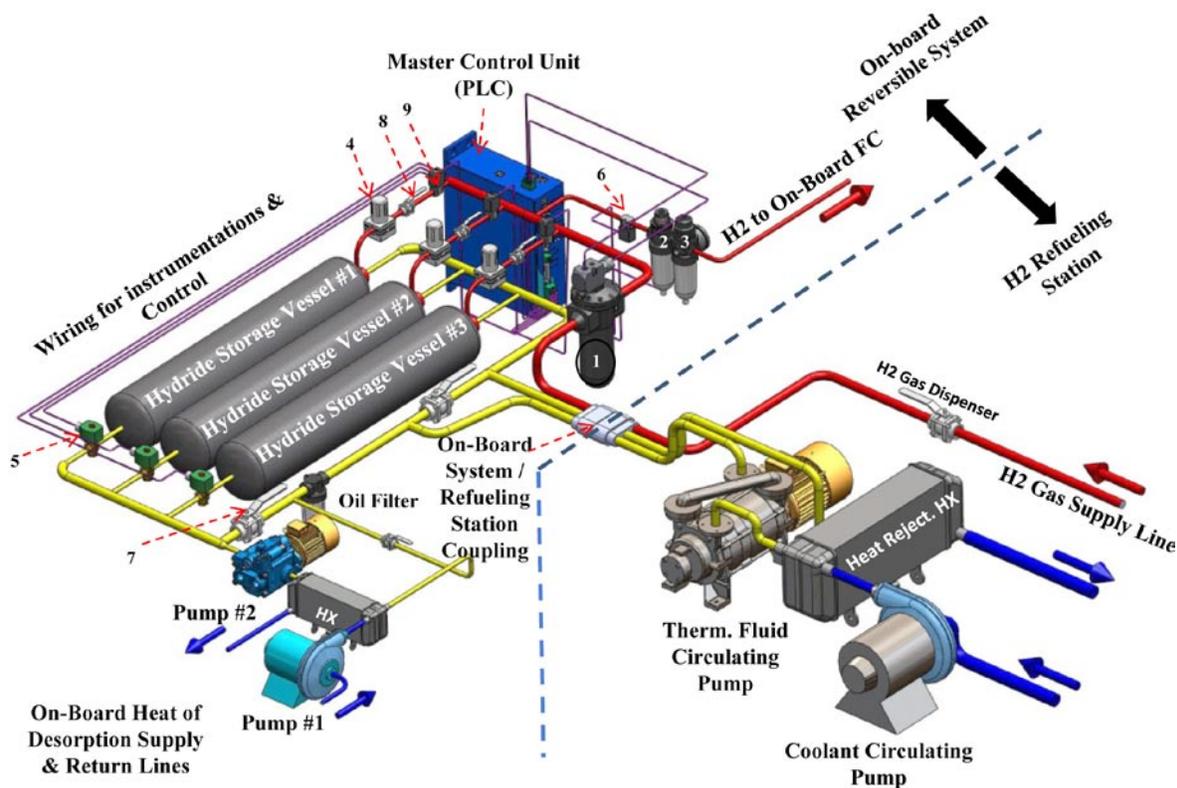
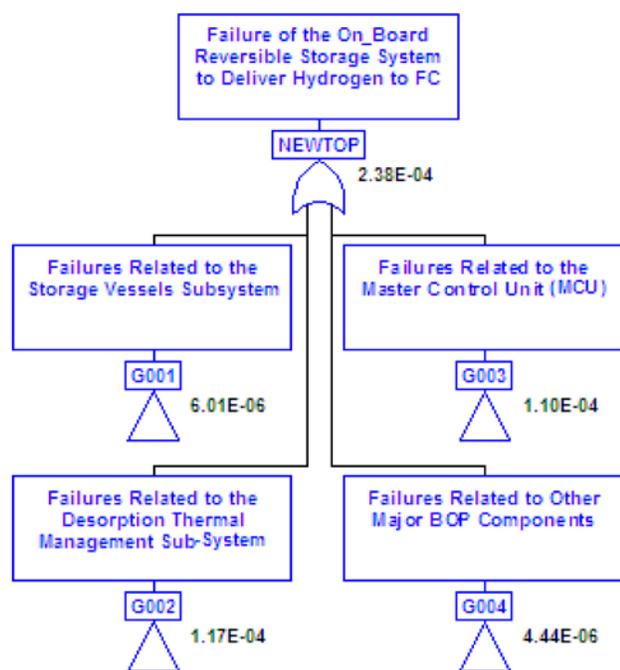


FIGURE 3. Baseline Design of an On-Board Reversible Hydrogen Storage System



**FIGURE 4.** System-Level Fault Tree Model (only Top Level is Shown) of a Baseline Design of an On-Board Reversible Storage System

the FT model. Published components failure data are used in the FT model quantification process which calculates the overall failure probability of the on-board system.

- 2.2 Developed a fault tree model which quantifies the consequences of accidental air intrusion into a hydride storage vessel. In this model, air leakage into the vessel was the initiating event and vessel burst was conditional on failure of the safety relief device to open and vent the vessel.

### 3. Risk Mitigation – Experimental Studies

- 3.1 A series of scoping tests were conducted to evaluate the hydride material reactivity under selected environmental conditions that could be encountered during a vehicular accident. Catalyzed sodium alanate ( $\text{NaAlH}_4 + 4\text{mole}\% \text{TiCl}_3$ ) was used in these experiments.

3.1.1 In immersion tests, loose powder as well as powder compacts (wafers) were immersed in different liquids at room temperature. The liquids selected were water, windshield washing fluid, engine coolant (antifreeze), engine oil and NaCl solution (brine), respectively. These tests were repeated using powder compacts.

3.1.2. In the droplet tests, water, windshield washing fluid, engine coolant (antifreeze), engine oil and brine, respectively, were dropped on loose powder and powder compacts (wafers).

Test results demonstrated that powder compaction has the potential to reduce risk by suppressing material reactivity (in the liquids tested) and preventing consequential ignition of the evolved reaction gases. Additional validation tests are in progress.

- 3.2 The scope of our risk mitigation scoping tests was extended to include the following high-temperature tests:

3.2.1. Sodium alanate wafers (1-gram each) were immersed in 50-ml hot water at 80°C and in 50-ml thermo-oil at 100°C, respectively. In both cases, only a benign reaction at the wafer's surface was observed and the evolved reaction gases did not ignite.

3.2.2. The consequences of contacting powder compacts with hot surfaces in the presence of air were investigated; a condition that could be encountered during postulated accident scenarios. In this test, the hydride wafer was placed on an electrically-heated surface. Thermocouples were used to measure the wafer's temperature. When the temperature of the wafer reached  $\approx 85^\circ\text{C}$ , it ignited and the evolved gases burned but the wafer did not disintegrate. The insights gained from this test will drive the development of additional risk mitigation to prevent the observed hydride fires.

- 3.3 Experimentally investigated the impact of extended immersion time of catalyzed sodium alanate wafers in different liquids. In these tests, hydride wafers (1-gram each) were immersed for 8 hours (soaking time) in water and in windshield washing fluid, respectively. The experimental observations showed very mild hydride/liquid reactions and the emitted reaction gases did not ignite.
- 3.4 Performed fast blowdown tests using our project's specially designed and fabricated test rig that mimics hydride storage vessel rupture. The pressure profile during each blowdown test was recorded and the results showed that depressurization from 100 bars to 20 bars was completed in  $\approx 40$  msec. Results of tests with  $\text{NaAlH}_4$  powder showed that  $\approx 16\%$  of the initial powder mass (30 grams) was entrained to the collection vessel of the rig as a result of the blowdown. Future tests will be conducted using powder compacts instead of the loose powder which was used for establishing a baseline for comparison purposes.

## Conclusions and Future Directions

The work conducted in this year included QLRA, QRA and risk mitigation tests. The QLRA identified key safety significant failure modes of the hydride storage vessel (which represents a single point failure in the on-board system). The QRA covered: a) fault tree modeling and quantification of consequences of accidental air intrusion into the storage vessel, b) system-level failure analysis of a baseline design of a hydrogen storage system and c) developing a stochastic approach for managing uncertainties in risk quantification. The experimental work focused on risk mitigation tests to evaluate the hydride material reactivity (both loose powder and powder compacts) under wide ranges of environmental conditions and postulated accident scenarios.

Future work will focus on:

- Risk Analysis
  - Continue accident sequences development and quantification for the remaining risk-dominant initiating events.
  - Complete risk analysis framework (both QLRA and QRA) incorporating results from dust cloud tests, experimental and modeling activities at SNL and SRNL.
  - Evaluate candidate risk mitigation methods (material reactivity based and system-based).
- Economic Consequence Analysis
  - Perform economic consequence analysis for the identified most probable and worst-case scenarios and assign monetary safety benefits of selected risk mitigation methods.
- Experimental Studies (including those planned and coordinated with SNL material reactivity project)
  - Complete dust explosion tests for at least one mitigated material structure.
  - Complete X-ray diffraction characterization test for at least one mitigated material structure.
  - Perform material reactivity tests for selected mitigated and unmitigated material structures. Conduct fast depressurization tests on selected unmitigated and mitigated material structures.

## FY 2010 Publications/Presentations

1. Khalil, Y.F., D. Mosher, F. Sun, B. Laube, X. Tang, and R. Brown, “Quantifying and Addressing the DOE Safety Target with Analysis and Testing of Hydrogen Storage Materials and Systems,” Technical Team Meeting, USCAR Office, Southfield, MI, April 15, 2010.

2. Dedrick, D.E. et al. (SNL) and Khalil, Y.F. (UTRC), “Mitigating hazards During Accident Scenarios Involving Metal Hydride Materials,” Proceedings of the National Hydrogen Association (NHA) Conference, Long Beach, CA, May 3–6, 2010.

3. Khalil, Y.F., D. Mosher, F. Sun, B. Laube, X. Tang, and R. Brown, “Quantifying and Addressing the DOE Safety Target with Analysis and Testing of Hydrogen Storage Materials and Systems,” 2010 U.S. Department of Energy (DOE) Hydrogen Program Annual Peer Review Meeting, Washington, D.C., June 8, 2010.

4. Khalil, Y.F., “On-Board Reversible Hydrogen Storage Systems: Risk Assessment and Mitigation,” invited presentation at the 14<sup>th</sup> Hydrogen Safety Panel Meeting, Center for Hydrogen Research, Savannah River National laboratory, Aiken, SC, June 23, 2010.

5. Khalil, Y.F. and M. Modarres, “Safety Importance Measures for a Conceptual Baseline Design of an On-Board Reversible Hydrogen Storage System,” Proceedings of the First International Conference on Materials for Energy, UTRC/University of Maryland Joint Paper # 1368, DECHEMA e.V., Karlsruhe, Germany, July 4–8, 2010.

6. Khalil, Y.F., D. Mosher, J. Cortes-Concepcion, C. James, J. Gray and D. Anton, “Adverse Reactivity Effects and Risk Mitigation Methods for Candidate Hydrogen Storage Materials,” Proceedings of the First International Conference on Materials for Energy, UTRC/SRNL Joint Paper # 1369, DECHEMA e.V., Karlsruhe, Germany, July 4–8, 2010.

7. Khalil, Y.F. (UTRC), Newhouse, N.L. (Lincoln Composites, Inc.) and Simmons, K.L. (PNNL), “Potential Diffusion-Based Failure Modes of Hydrogen Storage Vessels for On-Board Vehicular Use,” invited paper accepted for presentation at the Hydrogen Storage System Engineering and Applications – Risk Reduction Session, AIChE Topical Conference, Salt lake City, UT, November 7–12, 2010.

8. Dedrick, D.E., et al. (SNL) and Khalil, Y.F. (UTRC), “Mitigation Technologies for Hydrogen Storage Systems Based on Reactive Solids,” invited paper accepted for presentation at the Hydrogen Storage System Engineering and Applications – Risk Reduction Session, AIChE Topical Conference, Salt lake City, UT, November 7–12, 2010.

## References

1. Multi-Year Research, Development and Demonstration Plan: Planned Program Activities for 2005-2015, Technical Plan-Storage: <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/storage.pdf>, updated April 2009.