IV.E.1 Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of Hydrogen Storage Materials and Systems

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Fiscal Year (FY) 2011 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 methods and tools to evaluate risks for materials-based hydrogen storage systems before and after risk 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]:

(A) System Weight and Volume
(F) Codes and Standards

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:

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

FY 2011 Accomplishments

- Quantitative risk analysis (QRA): developed and quantified fault tree (FT) models for:
  - On-board reversible hydrogen storage system.
  - Solid ammonia borane (AB) off-board regenerable storage system.
  - On-board solid AB thermolysis reactor.
  - Hydrogen permeation/leakage from Type-III and Type-IV storage vessels.
  - Finally, developed a risk reduction worth (RRW) methodology for quantifying the importance of each basic event (BE) in a fault tree system model.
- Qualitative risk analysis (QLRA):
  - Identified critical risks and failure mechanisms of a baseline design of an off-board regenerable alane-based (AlH_3) storage system.
- Risk mitigation:
  - Theoretical studies - performed atomic and thermodynamic modeling of sodium alanate ($NaAlH_4$) oxidation and hydration reactions.
  - Experimental studies - performed the following tests for $NaAlH_4$, $3Mg(NH_2)_2.8LiH$, and NH_3BH_3:
    - Material reactivity in different fluids (water, windshield washing fluid, brine, antifreeze, and engine oil).
    - Fast blowdown (depressurization) which mimics accidental storage vessel breach.

- Dust cloud combustion characterization. Tests also included Maxsorb (AX-21).
- Mechanical impact sensitivity.
- Hot surface contact tests.
- XRD tests for material characterization.

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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 the DOE safety target and support the development of future risk-informed hydrogen safety codes and standards (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: 1) risk analysis framework (QLRA and QRA), 2) materials reactivity testing, 3) chemical reaction kinetics testing and modeling, 4) risk mitigation methods, and 5) limited scope prototype testing.

Results

QRA

Developed and quantified FT models for: a) on-board reversible hydrogen storage system, b) solid AB off-board regenerable alane-based storage system, c) on-board solid AB thermolysis reactor, and d) hydrogen permeation/

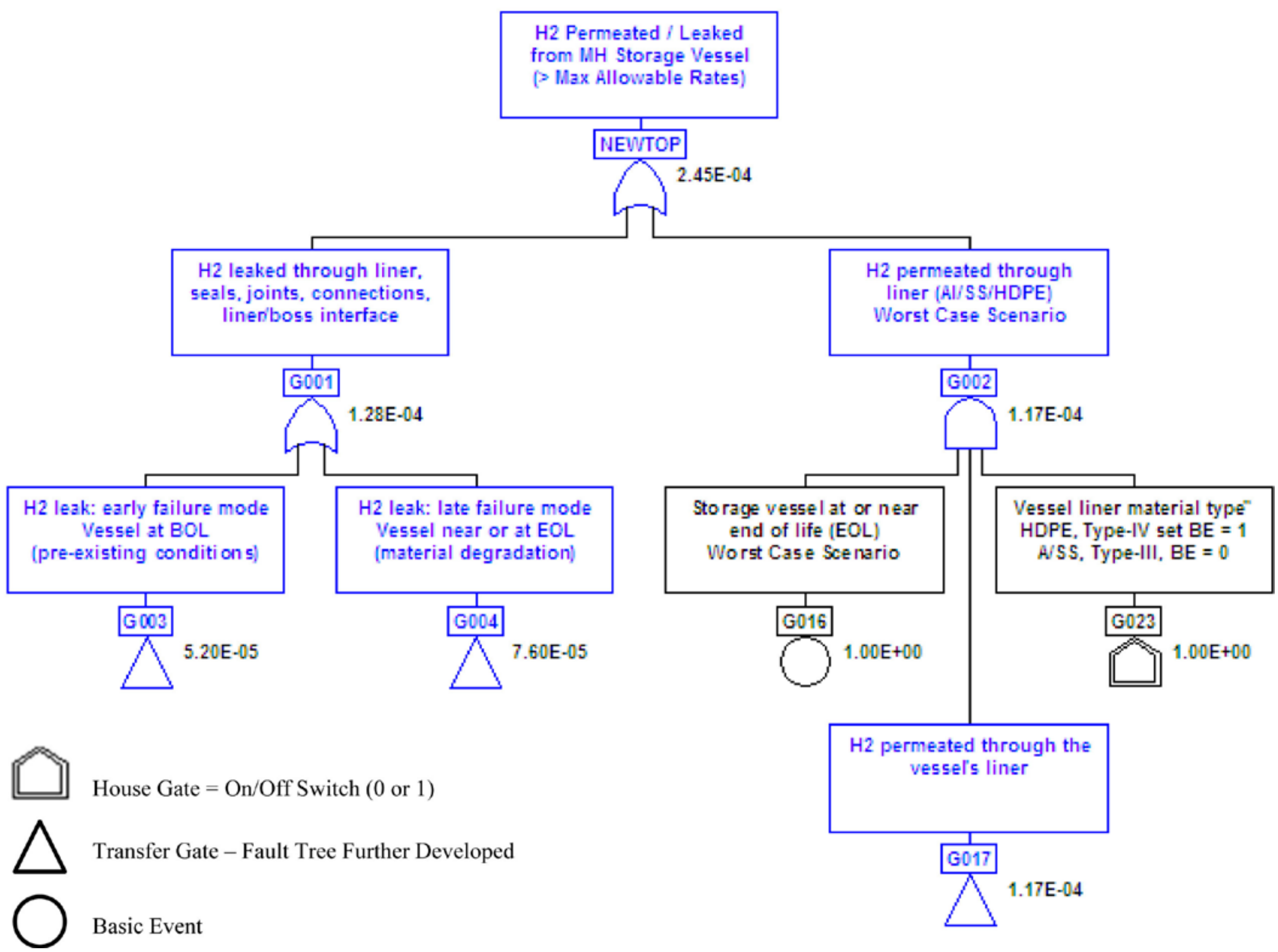

FIGURE 1. Fault Tree Model for Gaseous Hydrogen Permeation/Leakage through Type-III and Type-IV Liners

leakage from Type-III and Type-IV storage vessels. Figure 1 shows the top portion of the FT model for the hydrogen permeation/leakage from the storage vessel. The complete FT model, quantification results, minimal cutsets (i.e., sequences leading to hydrogen permeation or leakage from the storage vessel), and potential failure mechanisms are discussed in detail in reference [2]. The two failure modes for hydrogen leakage through the vessel's seals, joints, connections, liner/boss interfaces include: i) an early failure mode due to pre-existing conditions (Gate G003) in Figure 1 and ii) a late failure mode caused by time-dependent failure mechanisms with the vessel at or near end of life (EOL), Gate G004 in Figure 1. The time-dependent failure mechanisms include cyclic fatigue stresses leading to crack growth and propagation and material aging. Hydrogen permeation through the vessel liner is more likely to be a dominant failure mechanism when the vessel is at or near EOL. As part of the FT modeling and quantification, a RRW methodology has been developed for quantifying the safety importance of each BE in the fault tree model [2].

QLRA

- Developed a baseline design of an off-board regenerable hydrogen storage system using alane (AlH_3) as the solid-state storage medium (Figure 2).
- Performed failure mode and effects analysis (FMEA) for the proposed baseline design.
- Identified the following safety-significant failure mechanisms for this alane-based system:
  - Failure to transport the fresh alane powder through the on-board system.
  - Failure to transport the spent fuel (discharged alane) to the on-board collection tank.
  - Failure of thermal management subsystem of the on-board alane thermolysis reactor.
  - One of the critical hazards of the alane-based off-board regenerable system is related to the accidental exposure of discharged alane powder (spent fuel) to air. Under such postulated condition, the resulting

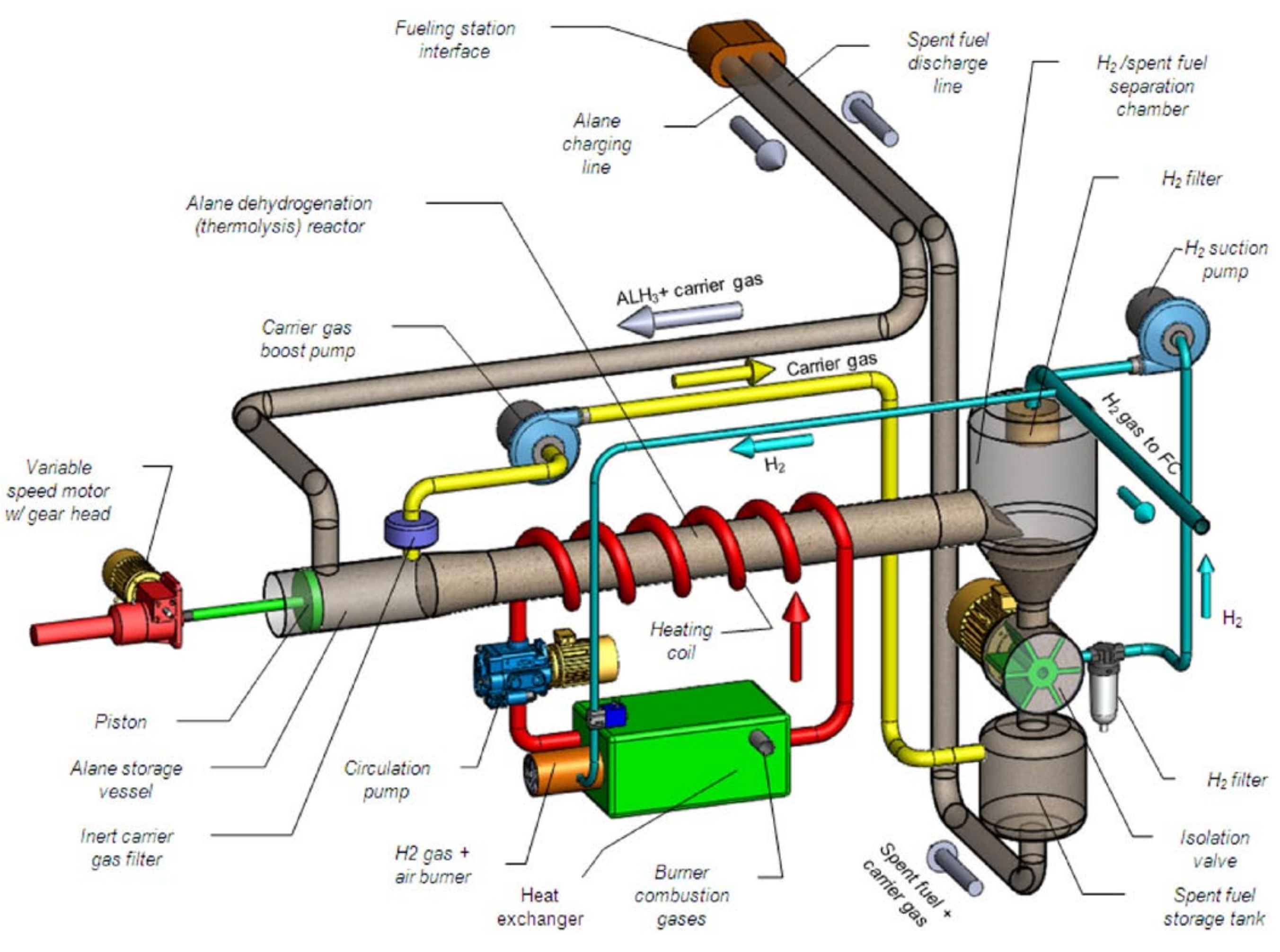

FIGURE 2. UTRC Baseline Design of an Off-Board Regenerable Alane-Based System

dust cloud explosion would be more severe compared to an accidental exposure of charged alane dust to air (Table 1).

Risk Mitigation – Experimental Studies

- Performed a series of scoping tests to evaluate the reactivity of selected complex metal hydrides, $NaAlH_4$ and $3Mg(NH_2)_2.8LiH$, and chemical hydride, NH_3BH_3, under environmental conditions that may exist during a postulated vehicular accident.
  - 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, thermo-oil, engine coolant (antifreeze), engine oil and NaCl solution (brine), respectively. These tests were repeated using powder compacts.
  - In the droplet tests, each of these liquids was dropped on the hydride loose powder and powder compacts (wafers).

The results of these tests demonstrated that powder compaction has a potential for reducing reactivity risks by suppressing the hydride/liquid reaction and, thus, preventing consequential ignition of the evolved reaction gases.

- Performed mechanical impact sensitivity tests (Figure 3) for complex metal hydrides (partially-charged $NaAlH_4$ and charged $3Mg(NH_2)_2.8LiH$) and an as-received chemical hydride (NH_3BH_3). The results of the tests

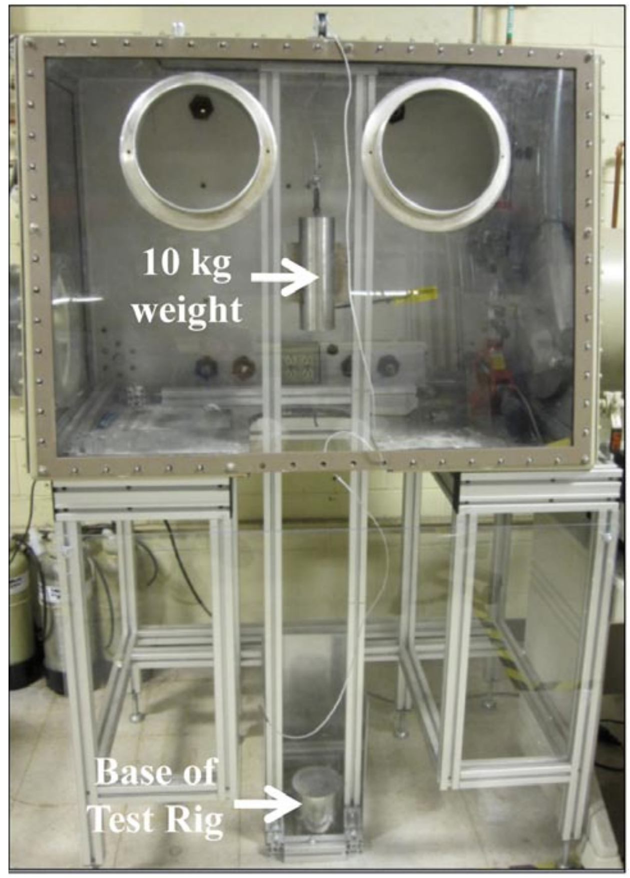

FIGURE 3. UTRC Mechanical Impact Sensitivity Test Rig

TABLE 1. Dust Cloud Combustion Characterizations of Solid-State Hydrogen Storage Materials.

Parameter	Solid-State Hydrogen Storage Materials (Metal Hydrides, Chemical Hydrides, and Adsorbents)							
	Maxsorb (AX-21)	Charged AlH_3	Discharged AlH_3	$2LiBH_4$ + MgH_2	Charged $NaAlH_4$	NH_3BH_3 (as received)	ASTM Reference Material Pittsburgh Seam Coal	H_2 Gas
$(\Delta P)_{MAX}$ Bar-g	8.0	3.7	10.3	9.9	11.9	18.4	7.3	7.9 @ 29 vol% H_2 in air
$(dP/dt)_{max} = R_{MAX}$, bar/s	449	370	4,082	1,225	3,202	2,840	426	5435 @ 29 vol% H_2 in air
K_{ST} bar-m/s	122	101	1,100	333	869	771	116	1,477
MIE, mJ	Range 500-1,000	<10	<10	<9.2	<7	<8.9	110	0.02
MEC, g/m^3	80	30	125-250	30	140	<20	65	4 vol% H_2 in air
T_C, ^0C	760	200	710	230	137.5	n/a	585	n/a
Hazard Class	St-1	St-1	St-3	St-3	St-3	St-3	St-1	
Explosion Severity (ES)	1.16	0.44	13.5	3.9	12.3	16.54	1.0	13.8
Dust Classification	Class-II	Footnote (1)	Class-II	Class-II	Class-II	Class-II	Class-II	n/a

(1) Dust is combustible but not Class-II based in ES criterion alone.
n/a - not applicable; MIE - minimum ignition energy; MEC - minimum explosive concentration

showed that $NaAlH_4$ and $3Mg(NH_2)_2.8LiH$ powder compacts were sensitive to mechanical impact where the test samples ignited on the first impact. The NH_3BH_3 power compact, however, did not ignite during the impact tests.

- Conducted risk mitigation tests to prevent the observed mechanical impact sensitivity of $NaAlH_4$. In these tests, the hydride powder was ball milled for 15 minutes, before compaction, with different flame retardant additives (10 wt% and 20 wt%, respectively) including aluminum oxide (AL_2O_3), aluminum hydroxide ($Al(OH_3)$), magnesium hydroxide ($Mg(OH)_2$), and melamine, respectively. None of these chemical additives was successful in preventing the sensitivity of sodium alanate to mechanical impact. More testing with other chemical additives is in progress.

Risk Mitigation – Atomic and Thermodynamics modeling

The thermodynamic modeling showed that $NaAl(OH)_4$ is the most favorable product to form when 1 mole $NaAlH_4$ reacts with ≥2 moles O_2 or ≥4 moles H_2O in an inert atmosphere. The atomic modeling showed the $NaAl(OH)_4$ product can favorably form a coherent, non-passivating layer on the $NaAlH_4$ surface (Figure 4).

Dust Cloud Combustion Characterization Tests

Table 1 summarizes the results of dust cloud combustion characterization tests for complex metal hydride (charged $NaAlH_4$), chemical hydrides (as received NH_3BH_3, charged/discharged AlH_3), and Maxsorb (AX-21).

Conclusions and Future Work

Conclusions - the work performed this period covered QRA, QLRA, risk mitigation tests, dust cloud characterization tests, and atomic and thermodynamics modeling. The QLRA identified safety significant failure mechanisms of the alane-based off-board regenerable system. The QRA covered FT modeling and quantification of on-board reversible, off-board regenerable systems, and hydrogen permeation/leakage from the storage vessels. The risk mitigation tests evaluated the reactivity of selected complex metal hydrides [$NaAlH_4$ and $3Mg(NH_2)_2.8LiH$] and chemical hydride [NH_3BH_3] (loose powder and powder compacts) under different environmental conditions and postulated scenarios. Finally, performed atomic and thermodynamic modeling of sodium alanate ($NaAlH_4$) oxidation and hydration reactions.

Future work will focus on:

- **Risk Analysis:** 1) complete risk analysis framework (both QLRA and QRA) incorporating results from dust cloud characterization tests, experimental and modeling activities at SNL and SRNL and 2) develop an economic consequence analysis framework for the identified most probable and worst-case scenarios to assess the safety benefits of selected risk mitigation methods.

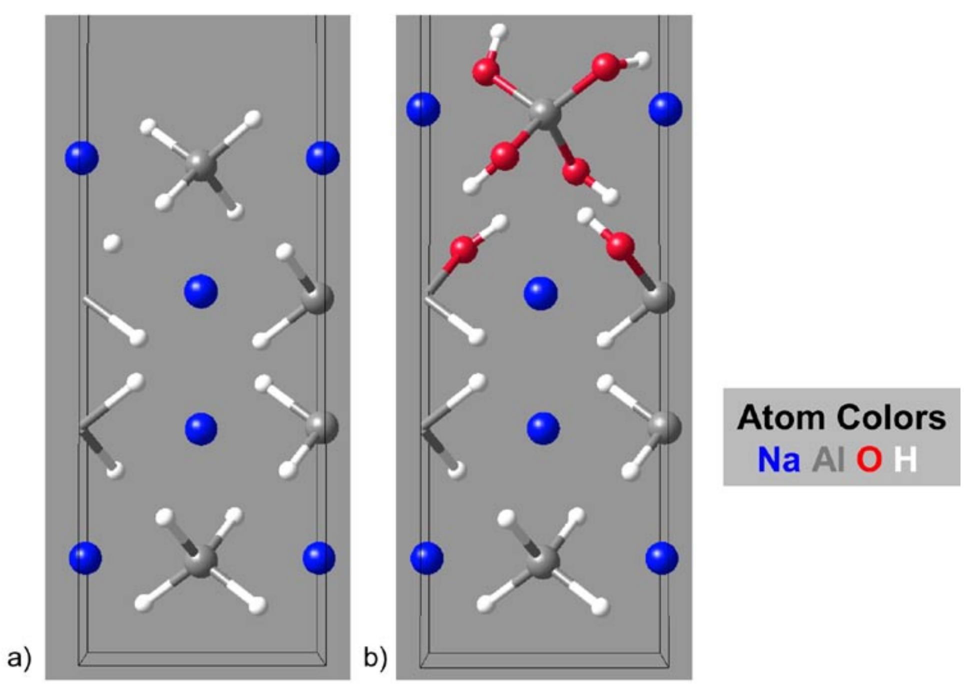

FIGURE 4. Atomic and Thermodynamics Modeling of $NaAlH_4$ Reactions with Air and Water

- **Atomic and Thermodynamic Modeling:** Additional atomic modeling and thermodynamic modeling are underway to identify the mechanisms for $NaAl(OH)_4$ decomposition to the elemental oxide and hydroxide phases under inert and ambient conditions.
- **Risk Mitigation Experimental Studies (including those planned and coordinated with SNL material reactivity project:** 1) evaluate the effectiveness of fire-retardant chemical additives to eliminate the mechanical impact sensitivity of $NaAlH_4$ powder compact and 2) perform the localized flame impingement (external fire) test using UTRC Prototype-2 Type-III storage vessel. Currently, this task is being coordinated with SNL [3].

Special Recognitions & Awards

1. The International Energy Agency, Hydrogen Implementation Agreement (IEA/HIA), Task-31 (Hydrogen Safety) selected Dr. Y. (John) Khalil to lead its Subtask-B on Hydrogen Storage Materials Reactivity, Safety, and Materials Compatibility.

FY 2011 Publications/Presentations

1. 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.

2. 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.

3. 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.

4. Dedrick, D.E., at 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.

5. Khalil, Y.F. and D.E. Dedrick, "Flame Impingement Test Plan for UTRC Prototype-2 Storage Vessel," Joint Presentation, DOE Technical Team Review Meeting, Web-based Conference, November 18, 2010.

6. Khalil, Y.F., "Quantifying & Addressing the DOE Material Reactivity Requirements with Analysis & Testing of Hydrogen Storage Materials & Systems," DOE Quarterly Report 4Q2010, January 30, 2011.

7. Khalil, Y.F., "Quantifying & Addressing the DOE Material Reactivity Requirements with Analysis & Testing of Hydrogen Storage Materials & Systems," DOE Quarterly Report 1Q2011, April 30, 2011.

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2. Khalil, Y.F., N.L. Newhouse, K.L. Simmons, and D.E. Dedrick, "Potential Diffusion-based Failure Mechanisms of Hydrogen Storage vessels for On-Board Vehicular r Use," AIChE Topical Conference, Salt lake City, UT, November 7–12, 2010.

3. Khalil, Y.F. and D.E. Dedrick, "Flame Impingement Test Plan for UTRC Prototype-2 Storage Vessel," Joint Presentation, DOE Technical Team Review Meeting, Web-based Conference, November 18, 2011.