

## Final Technical Report

**Project Title:** Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of Hydrogen Storage Materials & Systems

**Project Period:** June 1 2007 to January 31, 2012

**Date of Report:** April 30, 2012

**Recipient:** United Technologies Research Center (UTRC)

**Award Number:** DE-FC36-07GO17032

**Working Partners:** Kidde-Fenwal, Combustion Research Center

**Cost-Sharing Partners:** N/A

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### Project Objective:

The objective of this project is to examine safety aspects of candidate hydrogen storage materials and systems being developed in the DOE Hydrogen Program. As a result of this effort, the general DOE safety target will be given useful meaning by establishing a link between the characteristics of new storage materials and the satisfaction of safety criteria. This will be accomplished through the development and application of formal risk analysis methods, standardized materials testing, chemical reactivity characterization, novel risk mitigation approaches and subscale system demonstration. The project also will collaborate with other DOE and international activities in materials based hydrogen storage safety to provide a larger, highly coordinated effort.

### Background:

The DOE Hydrogen Storage technical target for safety has been specified generally as "Meets or exceeds applicable standards," but for metal hydrides, chemical storage materials and adsorbent materials and systems, no such standards currently exist. Furthermore, such future standards would be high level with limited detail, being primarily focused on systems certification and would not provide guidance to assist developers of new storage media in understanding the safety significance of their materials. This project, in collaboration with the Savannah River National Laboratory, Sandia National Laboratories and other organizations, will fill a gap in the current DOE Hydrogen Storage Program.

**The effort of this project is divided into five tasks as follows:**

**Task 1: Risk Analysis:**

Formal risk analysis methods will be employed and customized to develop a tool which provides an increasingly quantitative description of risks for materials and systems throughout the project before and after the use of mitigation methods.

**Task 2: Standardized Materials Testing:**

A set of materials tests based on ASTM, United Nations and other procedures will be performed on storage materials to quantify their reactivity under conditions of potential risk scenarios. Emphasis for UTRC will be on dust explosion tests of at least three materials in a number of chemical and physical conditions.

**Task 3: Chemical Kinetics Testing and Diagnostic Modeling:**

Fundamental studies will be performed to evaluate the chemical kinetics of material reactions with O<sub>2</sub>, water and other fluids (primarily gaseous state) using time resolved X-ray diffraction & other techniques to support reaction kinetics understanding and risk mitigation development.

**Task 4: Risk Mitigation:**

Concepts to reduce the dominant risks will be devised and investigated both at the material and system levels. The impact on system gravimetric and volumetric performance will also be determined.

**Task 5: Prototype / Representative System Element Testing:**

In coordination with SRNL and SNL safety projects, representative system element evaluation tests will be defined and evaluated through testing. Examples of the system element tests include: a) conducting experiments on NaAlH<sub>4</sub> based prototype system(s) fabricated in Contract DE-FC36-02AL67610 to assess hazards and mitigation / neutralization methods. b) designing and constructing fast depressurization test rig to mimic accidental vehicular collision leading to hydride storage vessel rupture and ex-vessel dispersal of the enclosed powder. These experiments and application of resulting data will be coordinated with companion SRNL and SNL hydrogen storage material reactivity efforts.

The project is divided into two phases with the first covering two years. A Go/No-Go decision was made at the end of Phase-I to guide activities in Phase-II.

**Status:****Task 1: Risk Analysis*****Accomplishments***

- Developed a formal risk analysis framework which includes qualitative risk assessment (QLRA) and quantitative risk assessment (QRA) as well as the more detailed material reactivity measurements and modeling with the higher level DOE safety target and codes and standards. Additional data from the SRNL and SNL DOE projects as well as from international partners in an associated International Partnership for the Hydrogen Economy (IPHE) project were incorporated into the risk analysis.
- Developed customized design failure modes and effects analysis (d-FMEA) framework and set of failure mechanisms for a conceptual baseline design of on-board reversible systems using prior  $\text{NaAlH}_4$  material and system experience as guidance. The d-FMEA framework was constructed based on accepted standards<sup>1,2</sup>, but customized regarding the scoring details for probability of occurrence, severity of consequences, and detestability as well as data fields to track the impact on performance targets, technology readiness levels for mitigation approaches and the connection to DOE multi-project plans. The d-FMEA was reviewed by a diverse expert panel for hazard descriptions and risk scoring. As detailed data were developed through testing and analysis, the expert panel assessment was updated and analyzed for confidence levels.
- Developed customized design failure mode and effects analysis (d-FMEA) for a conceptual baseline design of off-board regenerable, using alane ( $\text{AlH}_3$ ), storage systems. Potential safety hazards, failure modes and accident imitators were identified and ranked based on their risk significance.
- Identified the following safety-significant failure mechanisms for the alane-based system (conceptual baseline design): a) Failure to transport the fresh alane powder through the on-board system, b) Failure to transport the spent fuel (discharged alane)

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<sup>1</sup> "Potential Failure Mode and Effects Analysis in Design (Design FMEA) and Potential Failure Mode and Effects Analysis in Manufacturing and Assembly Processes (Process FMEA) and Effects Analysis for Machinery (Machinery FMEA)," SAE document J1739, August 2002.

<sup>2</sup> "Recommended Failure Mode and Effects Analysis (FMEA) Practices for Non-Automobile Applications," SAE document ARP5580, July 2001. (replaces military standard MIL-STD-1629).

to the on-board collection tank, and c) 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 dust cloud explosion would be more severe compared to an accidental exposure of charged alane dust to air.

- Formed an expert panel for opinion pooling for d-FMEA of the on-board reversible (using  $\text{NaAlH}_4$ ) system and employed the Delphi process to elicit subject matter experts (SMEs) risk scorings<sup>3</sup>. 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. The results of the aggregated risk scorings showed that the top three failure modes are: a) Catastrophic failure of the hydride storage vessel caused by vehicular collision, b) Hydrogen leak caused by pipe rupture in the on-board storage system, and c) 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.
- Developed event tree (ET) models and fault tree (FT) models for key risks identified through the design failure mode and effects analysis (d-FMEA). In the event tree analysis (ETA), a sequence of events was defined with dependencies and probabilities of occurrence. A set of end state results from the event tree and severity or consequence levels were determined for each end state. For example, a vehicle subjected to the initiating event of an accident / collision. Subsequent accident progression events then involve whether or not 1) the hydride storage vessel ruptures, 2) a critical amount of hydride is released, 3) the environment is wet (ex. rain), and other potential events. Those analyses were continually refined as information was gained from the material reactivity testing and modeling from UTRC, SRNL, SNL and the IPHE collaborators.
- Developed fault tree (FT) models for a range of injury categories for blast waves from aluminum dust dispersion. Also, developed a fault tree (FT) model for hydride dust dispersion given a postulated vehicular accident scenario.

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<sup>3</sup> Khalil, Y. F. and D.A. Mosher, "Risk assessment for onboard reversible hydrogen storage: Conceptual baseline design and FMEA worksheet," Internal Document, United Technologies Research Center (January 2009).

- 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.
- The major insights of the qualitative risk analysis (QLRA) of the on-board reversible storage system are: i) 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 and ii) 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 onboard storage system into a confined (or partially confined) space leading to early or delayed H<sub>2</sub> 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.
- Evaluated the impact of 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<sup>4</sup> and SAE J2579<sup>5</sup>, respectively, are focused on CHG and there is no equivalent C&S for on-board reversible hydrogen storage systems<sup>6</sup>. Also, discussed the reciprocity between QLRA safety insights and C&S<sup>4</sup>. The discussion demonstrated that structures systems and components 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 onboard storage system. For example, the bonfire test requirements and acceptance criteria in SAE J2579, FMVSS 304<sup>7</sup> 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

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<sup>4</sup> ANSI/CSA HGV2 Fuel Containers (Draft), Basic Requirements for Compressed-Hydrogen Gas Vehicle Fuel Containers, (July 2007).

<sup>5</sup> SAE J2579, Technical Information Report for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles, (January 2009).

<sup>6</sup> Khalil Y. F., "Reciprocity of Safety Insights between Risk Analysis and Codes and Standards of vehicular hydrogen Storage," Invited Paper at the 2009 Risk Management Conference, Washington, D.C. (November 15–19, 2009).

<sup>7</sup> FMVSS 304 (FMVSS 49 CFR 571.304), Compressed Natural Gas Fuel Container Integrity.

credited as hazard control measures in FMEA of the on-board reversible hydrogen storage system<sup>6</sup>.

- Developed and quantified three event tree (ET) models using the EPRI ETA-II software package.<sup>8</sup> The ET models represented the three risk-dominant accident initiators: vehicle collision, external fire, and hydrogen leakage from the on-board reversible storage system. The ET top events included 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 included 15 probable accident sequences and associated outcomes (DS-1 through DS-15). The ET also modeled FMVSS-304 bonfire test acceptance criteria, namely, either the vessel TPRD vents as designed or the vessel survives the fire for 20 minutes<sup>9</sup>.
- 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.
- Developed a system-level fault tree (FT) model for a baseline design of an on-board vehicle reversible hydrogen storage system. The hydride storage vessels and associated pressure relief devices (PRDs) are among the key components credited in 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.
- 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.
- Developed and quantified fault tree (FT) models for: a) Solid ammonia borane (AB) off-board regenerable storage system, b) On-board solid AB thermolysis reactor, and c) Hydrogen permeation / leakage from Type-III and Type-IV storage vessels.

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<sup>8</sup> ETA-II software, EPRI Risk & Reliability (R&R) workstation, EPRI, Palo Alto, CA 94304.

<sup>9</sup> FMVSS 304 (FMVSS 49 CFR 571.304), Compressed Natural Gas Fuel Container Integrity.



- Developed a risk reduction worth (RRW) methodology for quantifying the safety importance of each basic event (BE) in a fault tree system model.

## **Task 2: Standardized Material Reactivity Testing**

### ***Accomplishments***

- Performed dust explosion testing for the complex hydride material  $2\text{LiBH}_4 + \text{MgH}_2$  in the hydrided (*fully charged*) and partially dehydrided (*partially discharged*) states. Also, evaluated the effect of particle size on the dust explosion characteristics. The key dust explosion characteristics that were measured includes the maximum pressure rise ( $\Delta P_{\text{MAX}}$ ) the maximum rate of pressure rise  $[(dP/dt)_{\text{MAX}}]$ , minimum ignition energy (MIE), minimum explosible concentration (MEC), minimum ignition temperature ( $T_C$ ). From these measured parameters, the following explosion sensitivity parameters were calculated: explosion severity index ( $K_{\text{ST}}$ ), explosion severity (ES), and ignition sensitivity (IS), respectively. The dust explosion tests followed ASTM standards as follows: ASTM E-1226 for  $(\Delta P_{\text{MAX}})$  and  $(dP/dt)_{\text{MAX}}$ , ASTM E-1515 for MEC, ASTM E-2019 for MIE, and ASTM E-1491 for  $T_C$ . In all the dust explosion tests, bituminous coal and Lycopodium spores, which are well-defined dust, were used to calibrate dust explosion test devices and to form a baseline for comparison with the hydrides dust explosion characteristics. When compared with dust explosion tests for  $\text{NaAlH}_4$ , the characteristics of the  $2\text{LiBH}_4 + \text{MgH}_2$  and  $\text{NaAlH}_4$  powder samples were found to be similar except for the minimum explosible concentration (MEC).

The  $2\text{LiBH}_4 + \text{MgH}_2$  powder was partially desorbed at  $330^\circ\text{C}$  for 2 hours under vacuum. The resulting material had a coarse, sintered consistency, and dust explosion testing in this state would not be meaningful. If one considers the breach of a storage system vessel under moderately high pressures (100 bar, shortly after charging), the sudden drop of pressure and/or rapid velocity of the released hydrogen jet could break up the material into finer particles. To mimic this, the material was ball milled for 2.5 minutes and sieved to separate the powder into three particle size ranges: 40 to 100 mesh ( $420\ \mu\text{m}$  to  $150\ \mu\text{m}$ ), 100 to 200 mesh ( $150\ \mu\text{m}$  to  $75\ \mu\text{m}$ ), and <200 mesh ( $<75\ \mu\text{m}$ ) and tested separately to examine the influence of particle size. In general, as expected, the reactivity was decreased for the larger particle sizes. The most significant influence was on the important  $(dP/dt)_{\text{MAX}}$  and associated  $K_{\text{ST}}$  parameter. The results showed that increasing the particle size reduced the material to the lowest dust classification for which  $K_{\text{ST}} < 200\ \text{bar} \cdot \text{m/s}$ . Those results motivated additional work within the IPHE team to measure particle size distributions resulting from dispersion events after absorption/desorption cycling.

- Performed dust explosion testing of charged alane ( $\text{AlH}_3$ ) powder, discharged alane powder, and Maxsorb activated carbon (AX-21) powder in air and in air-hydrogen atmospheres. The hydrogen concentration in air was 2 mole %, 4 mole %, 6 mole%, and 29 mole%, respectively. These series of dust explosion tests were intended to mimic postulated accident scenarios in which the activated carbon powder was

dispersed in air as a result of a vehicular collision leading to storage vessel rupture. For the alane dust explosion tests, 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.

The results of dust cloud combustion characterization tests provided useful insights to the probabilistic modeling of dust explosion using fault tree analysis.

### **Task 3: Chemical Kinetics Testing and Diagnostic Modeling**

#### ***Accomplishment***

- Conducted time-resolved XRD on  $2\text{LiBH}_4 + \text{MgH}_2$  during exposure to humid air (48% relative humidity) and analyzed the XRD patterns to determine crystalline product evolution which supported material reactivity modeling.

The reaction kinetics during humid air exposure were evaluated using time-resolved XRD on the  $2\text{LiBH}_4 + \text{MgH}_2$  mixture in the hydrided and partially dehydrided states and also on the individual hydrides. This material undergoes a complex sequence of steps during hydrolysis/oxidation starting with adsorption of water, formation of a deliquescent paste, release of hydrogen that produces bubbles (and spatters material), followed by longer term drying and recrystallization of the products. The XRD patterns were analyzed using whole pattern fitting with the *JADE* software package to determine the crystalline compounds. In general, the  $\text{LiBH}_4$  material reacted much more rapidly than  $\text{MgH}_2$  both when tested separately and in the 2:1 mixture. Some  $\text{Li}_3\text{BH}_6$  and other crystalline products were formed before disappearing (becoming amorphous) with the exception of  $\text{MgH}_2$ . From XRD plots, it was observed that the amount of  $\text{MgH}_2$  was nearly constant and decreased slightly. Those data were combined with information from SRNL and SNL to develop reaction kinetics models that can be used in evaluating larger scale hazard scenarios of the risk analyses.

- Performed thermodynamic modeling of chemical reactions and phase equilibria. Thermodynamic calculations were made with HSC Chemistry software<sup>10</sup> to evaluate the bulk reactivity of  $\text{NaAlH}_4$  with  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$  gases over the 25–325 °C temperature ranges at 1 bar. The most favorable reactions were identified through the combination of Gibbs minimization equilibrium and thermochemical reaction calculations. The phases included in the Gibbs minimization calculations, included: Al

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<sup>10</sup> Outokumpu, HSC Chemistry for Windows, version 5.1, 2002.



(all phases),  $\text{AlH}_3$ ,  $\text{Al}_2\text{O}_3$  (all phases),  $\text{Al}(\text{OH})_3$  (Gibbsite and Bayerite),  $\text{AlO}^*\text{OH}$  (Boehmite),  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{NaAl}(\text{OH})_4$ ,  $\text{NaO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{Na}_2\text{O}^*\text{Al}_2\text{O}_3$ ,  $\text{NaOH}$ ,  $\text{NaOH}^*\text{H}_2\text{O}$ ,  $\text{NaAlH}_4$ ,  $\text{NaH}$ . These calculations are for bulk phases and do not take surface effects into account. While most of the relevant phases parameterized in the HSC thermodynamic database are crystalline (*i.e.*,  $\text{NaAlH}_4$ ,  $\text{Na}_2\text{O}^*\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{NaH}$ ) or gaseous species, several of the sodium aluminate product phases were parameterized based upon the conditions for their precipitation in aqueous solution. In particular, the properties of hydrated sodium meta-aluminate phase,  $\text{NaAl}(\text{OH})_4$ , was determined from boehmite ( $\text{AlO}^*\text{OH}$ ) solubility and potentiostatic measurements in Na-bearing alkali solutions<sup>11</sup>.

- Conducted atomic modeling in concert with thermodynamic modeling to mechanistically probe the reaction pathways of gaseous species with the  $\text{NaAlH}_4$  nanocrystallite surfaces that led to the products observed by experimentation. The goal here was to elucidate the origin of  $\text{NaAlH}_4$  pyrophoricity, and determine the rate limiting mechanisms for  $\text{NaAlH}_4$  conversion into reaction products. The atomic calculations minimized the atomic positions of periodic  $\text{NaAlH}_4$  surface slab models with various reaction intermediates and also interface models of reaction products. The atomic calculations were conducted with the plane wave basis *Vienna ab initio simulation package* (VASP) density functional theory code with projector augmented wave (PAW) potentials and the Perdew, Burke, and Ernzerof (PBE) generalized gradient approximation for the exchange correlation functional<sup>12,13,14,15,16</sup>. Regular PBE potentials were used for all atoms, except the Na\_pv potential with the semi core p states treated as valence used to represent Na. Standard parameters utilized for all of the nonpolarized models included a plane wave expansion cutoff of 410 eV, a 0.3 /Å or finer space k-point mesh, Gaussian smearing with an energy broadening of 0.2 eV, and an electronic self-consistent field convergence of  $10^{-6}$  eV. The ground

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<sup>11</sup> I. Diakonov, G. Pokrovski, J. Schott, S. Castet, and R. Gout, "An experimental and computational study of sodium-aluminum complexing in crystal fluids," *Geochim. Cosmochim. Ac.* 60(2) (1996) 197–211.

<sup>12</sup> Kresse G and Hafner J 1993 Ab initio molecular dynamics for liquid metals *Phys. Rev. B* 47 558–61.

<sup>13</sup> Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total energy calculations using a plane wave basis set *Phys. Rev. B* 54 11169–86.

<sup>14</sup> Kresse G and Joubert D 1999 from ultrasoft pseudo potentials to the projector augmented wave method *Phys. Rev. B* 59 1758–75.

<sup>15</sup> J. P. Perdew, K. Burke, and M. Rev. Lett. 77 (1996) 3865–3868.

state structures were minimized with the conjugate gradient algorithm until the Hellmann-Feynman forces were all below 0.005 eV/Å. The input structures for the solid-state crystalline phases were obtained from ICSD<sup>17</sup>.

## **Task 4: Risk Mitigation**

### ***Accomplishments***

- Experimentally evaluated hydride powder compaction as a potential risk mitigation method.
- Conducted a series of scoping tests to evaluate the hydride material reactivity under selected environmental conditions that could be encountered during a vehicular accident. Catalyzed sodium alanate (NaAlH<sub>4</sub>+4mole% TiCl<sub>3</sub>) was used in these experiments. 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. 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. The scope of risk mitigation scoping tests was also extended to include the following high-temperature tests: a) 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 and b) 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 were used to drive the development of additional risk mitigation to prevent the observed hydride fires.

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<sup>17</sup> ICSD (Inorganic Crystal Structure Database) © FIZ Karlsruhe and National Institute of Standards and Technology, accessed using Materials Design MedeA Interface and Infomatica Databases © 1998-2011 Materials Design, Inc.

- 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.
- Performed the following tests for  $\text{NaAlH}_4$ ,  $3\text{Mg}(\text{NH}_2)_2 \cdot 8\text{LiH}$ , and  $\text{NH}_3\text{BH}_3$ : i) Material reactivity in different fluids (water, windshield washing fluid, brine, antifreeze, and engine oil), ii) Mechanical impact sensitivity, and iii) Hot surface contact tests. 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 for complex metal hydrides (partially-charged  $\text{NaAlH}_4$  and charged  $3\text{Mg}(\text{NH}_2)_2 \cdot 8\text{LiH}$ ) and an as-received chemical hydride ( $\text{NH}_3\text{BH}_3$ ). The results of the tests showed that  $\text{NaAlH}_4$  and  $3\text{Mg}(\text{NH}_2)_2 \cdot 8\text{LiH}$  powder compacts were sensitive to mechanical impact where the test samples ignited on the first impact. The  $\text{NH}_3\text{BH}_3$  power compact, however, did not ignite during the impact tests.
- Conducted risk mitigation tests to prevent the observed mechanical impact sensitivity of  $\text{NaAlH}_4$ . 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 ( $\text{Al}_2\text{O}_3$ ), aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ), magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ), 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.

### **Task 5: Prototype / Representative System Element Testing**

- Designed a rapid depressurization test rig to experimentally mimic accidental hydride storage vessel breach and its influence on the hydride powder particle size and durability of powder compactions as a risk mitigation method. The key components of the test rig include the hydride powder storage vessel, rupture disk, hydrogen gas supply line, nitrogen purge line, vacuum line and the hydride powder collection vessel. The pressure profile during each depressurization (blowdown) test was recorded and the results showed that depressurization from 100 bars to 20 bars was completed in about 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 test rig as a result

of the blowdown. The remaining tests were conducted using powder compacts instead of the loose powder which was used for establishing a baseline for comparison purposes.

**Filed Invention Disclosures (ID):**

UTRC ID-0020085-US was filed to document our recent finding that monoammonium phosphate (40 wt%) was a successful chemical additive that eliminated both the pyrophoricity and mechanical impact sensitivity of sodium alanate. This finding provides a successful risk mitigation pathway for safer use of this complex hydride as a solid-state hydrogen storage medium for mobile and stationary applications.

**Special Recognitions & Awards**

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, Systems, Safety, and Materials Compatibility.

## Communications / Publications / Presentations:

1. Khalil, Y. F., "Ammonia Borane Dust Cloud Combustion Characterization," presentation at the DOE Hydrogen Storage Engineering Center of Excellence, Santa Fe, NM, October 10-14, 2011.
2. Khalil, Y. F., et al., "Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of Hydrogen Storage Materials and Systems," DOE Hydrogen Program, Annual Merit Review (AMR) and Peer Evaluation Arlington, VA, May 9-13, 2011.
3. Khalil, Y. F., "Risk Mitigation Tests for Selected Hydrogen Storage Solid-State Media," The International Energy Agency (IEA), Task 31 (Hydrogen Safety) meeting, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, 2011.
4. Khalil, Y. F., et al., "Potential Diffusion-Based Failure Modes of Hydrogen Storage Vessels for On-Board vehicular Use," Manuscript in preparation for the Proceedings of the AIChE Conference, Hydrogen Storage System Engineering and Applications – Risk Reduction Session, Salt Lake City, UT, November 7-12, 2010.
5. Khalil, Y. F., "Selected Risk Mitigation Tests and Failure Mechanisms of On-Board Vehicle Hydrogen Storage Systems," Invited Presentation, Hydrogen Safety Task 19, International Energy Agency, Rome, Italy, October 4-6, 2010.
6. 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.
7. 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.
8. Khalil, Y. F. 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).
9. Khalil, Y. F., et al., "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).
10. 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).

11. Khalil, Y. F. and D. Mosher, “Probabilistic Treatment of Expert Judgment on Aleatory and Epistemic Uncertainties Associated with On-board Vehicle Hydrogen Storage Systems,” International Topical Meeting on Probabilistic Safety Assessment & Analysis, PSA08, Knoxville, TN, September 7-11, 2008.
12. Mosher, D., Y. Khalil, and X. Tang, “Fundamental Safety Testing & Analysis of Solid State Hydrogen Storage Materials & Systems,” IEA Task 22 Meeting, Quebec, Canada, March 2-5, 2008.
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