

IV.E.3 Fundamental Environmental Reactivity Analysis of Hydrogen Storage Materials

Donald L. Anton (Primary Contact),
Joshua Gray, Bruce Hardy, Will James,
David Tamburello, Jose Cortes and
Kyle Brinkman

Savannah River National Laboratory
Bldg 999-2W
Aiken, SC 29803
Phone: (803) 507-8551; Fax: (803) 652-8137
E-mail: DONALD.ANTON@SRNL.DOE.GOV

DOE Technology Development Manager:
Ned Stetson
Phone: (202) 586-9995; Fax: (202) 586-9811
E-mail: Ned.Stetson@ee.doe.gov

Project Start Date: October 1, 2007
Project End Date: September 30, 2011

Objectives

- Develop internationally recognized standard testing techniques to quantitatively evaluate both materials and systems risks.
- Determine the fundamental thermodynamics and chemical kinetics of the environmental reactivity of hydrogen storage materials.
- Build a predictive capability to determine probable outcomes of hypothetical accident events.
- Develop amelioration methods and systems to mitigate the risks of using these systems to acceptable levels.

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 in descending order of impact:

- (F) Codes and Standards
- (P) Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

This project is conducting fundamental studies of the air and water exposure of numerous solid state hydride materials in order to assess their risks. Insights

gained from these studies will be applied toward the design of risk mitigation methodologies that meet the following DOE 2010 and 2015 hydrogen storage target:

- Environmental Health and Safety: Meets or exceeds applicable standards.

Accomplishments

- Standardized United Nations (UN) test hazard analyses completed on $2\text{LiBH}_4 \cdot \text{MgH}_2$ and NH_3BH_3 in the fully charged state.
- Water contact completed in charged and discharged states.
- Calorimetric characterization of NH_3BH_3 completed.
- Environmental exposure risk mitigation strategy invention disclosure filed.
- Initial thermal and chemical kinetic model completed having predictive capabilities for environmental exposure and reactivity scenarios.



Introduction

This report gives a summary of standardized UN tests for material packing and shipping, along with calorimetric experiments performed in order to quantify both the rate and the amount of the energy released for hydrogen storage materials. A mathematical modeling effort has been started to predict hydride behavior for hypothesized accidental exposure of the storage materials to an ambient environment, which facilitates an assessment of the risk associated with the utilization of a particular hydrogen storage material. An idealized finite volume model was developed to represent the behavior of dispersed hydride from a breached storage tank or container. Thermodynamic calculations and substantiating calorimetric experiments were performed in order to quantify the energy released, the energy release rates and the reaction products resulting from water and air exposure of ammonia borane. This thermodynamic data will be used in the computational fluid dynamics (CFD) model to predict both the hydrogen generation rates and concentration profiles along with localized temperature distributions. The results of these numerical simulations will be used in future work to predict safety windows and to assist in the design of environmental exposure mitigation strategies.

Approach

In order for the information generated by this project to be widely accepted and globally distributed, an international program was established linking laboratories in North America, Europe and Asia to perform specialized tasks specific to their organizations capabilities. A set of materials testing procedures, based on internationally accepted standards drawn from UN testing procedures has been defined. These tests include exposure to air, humidity, water, and could be modified to include proposed cooling fluids. Numerous potential hydrogen storage materials such as activated carbon, NaAlH₄, NH₃BH₃, LiNH₂+MgH₂, AlH₃ and 2LiBH₄+MgH₂ have been tested identically under these conditions to quantitatively determine their reactivity under normally occurring environmental conditions. Independent studies have been performed to understand the chemical kinetics of these reactions with air, oxygen and water as both liquid and vapor as a function of temperature. Calorimetric studies are continuing to investigate the time-dependent reaction rates of the materials. Mathematical simulations are being developed to predict the behavior of these hydrogen storage materials upon accidental environmental exposure.

Results

UN Tests

The standard materials testing procedures employed are based on existing UN testing protocols that are used to determine the material classification and ensure safe transport and handling [1]. Six standardized tests were performed including (1) water immersion, (2) water

surface contact, (3) water drop testing, (4) pyrophoricity, (5) burn rate, and (6) dangerous self heating. Large amounts of materials were required for some of the tests, in particular the burn-rate and self-heating tests, which presented a challenge in terms of procuring and preparing the material in a standardized state using ball-milling techniques. The UN tests were modified to include visual recording of the testing event, and the addition of thermocouples in those experiments where this was possible.

The first two materials to be evaluated were 2LiBH₄·MgH₂ and NH₃BH₃. The results of the air and water contact tests have previously been reported for the fully charged state of 2LiBH₄·MgH₂. These tests have been now been completed for NH₃BH₃, as reported in Table 1.

Calorimeter Experiments

The heat of reaction during dry gas (argon/air) and humid gas (argon/air) exposure was measured for an ammonia borane complex using a gas circulation cell at 40°C and 30% relative humidity for the fully charged and discharged state. The measured heat flow was small and endothermic relative to previous materials tested. The heat flow for ammonia borane in the presence of 30% water vapor for the charged and discharged material under argon and air caused an exothermic reaction to occur. The discharged state has a significantly higher release of heat compared to the charged materials because of the reactivity of the products being formed as the hydrogen is being released and oxidized. The extent of reaction is very slow based on the broadness of the heat flow curves as compared to the previously reported destabilized lithium borohydride and magnesium hydride system.

TABLE 1. Results of the UN Standardized Tests for 2LiBH₄·MgH₂ and NH₃BH₃

Material/ ^{UN} Test	State	Pyrophoricity	Self-Heat	Burn Rate	Water Drop	Surface Contact	Water Immersion
2LiBH ₄ ·MgH ₂	C	No ignition event. Hygroscopic material absorbed H ₂ O from air.	Self-heated ~300°C within 5 min at T _{oven} = 150°C is approached.	Flame propagated in 5 sec with burn rate of 52 mm/sec	2 H ₂ O drops required for near-instant combustion.	Material combusted	No Ignition event recorded. Gas evolved at longer times. (5 min)
	D	Not tested	Not tested	Not tested	1 H ₂ O drop required for near-instant ignition	Reaction observed with no flame	Reaction observed with no flame
NH ₃ BH ₃	C	No ignition event. Hygroscopic material absorbed H ₂ O from air.	Self-heated ~300°C within 10 min, 5 min at T _{oven} = 150°C	Flame propagate in 6 sec with burn rate of 33 mm/sec	No reactivity detected	No ignition event recorded. Gas evolved at longer times. (5 min)	No reactivity detected
	D	Not tested	Not tested	Not tested	No reaction	No reaction	No reaction

An X-ray diffraction (XRD) examination of the crystalline products was performed of each ammonia borane sample that was exposed to humidified argon and liquid water. In both cases, the XRD of the crystalline products indicated only the presence of ammonia borane. In the case of the liquid water mixing, the expected reaction was $\text{NH}_3\text{BH}_3 + \text{H}_2\text{O} \rightarrow \text{BO}_2^- (\text{a}) + \text{NH}_4^+ (\text{a}) + 3\text{H}_2(\text{g})$. From the difference in expected and measured enthalpies (-222 vs 17 kJ/mol), it is more reasonable for the following to be actual reactants, $\text{NH}_3\text{BH}_3 + \text{NH}_3\text{BH}_3 = \text{H}_2\text{O}$.

Numerical Simulations

The numerical simulation examined an environmental exposure of storage material in four different exposure scenarios. In each scenario, the hydride has been released from its containment vessel and formed an axisymmetric pile, making a two-dimensional axisymmetric model appropriate. The governing equations solved for each analysis include mass, momentum, and energy balances. FLUENT, a general purpose CFD package, was used to solve the equations using the finite volume approximation method [2]. In each scenario, a pile of hydrogen storage material in an arbitrary form is exposed to the ambient air, resulting in a chemical reaction that releases hydrogen and heat. However, the location and magnitude of the generation source is different for each scenario. These source locations correspond to hydride falling on a dry surface on a dry day, a wet surface on a dry day, a wet surface on a rainy day and a dry surface on a rainy day. Preliminary heat generation is based on the overall heat of reaction for the production of NaAlH_4 forming from NaH , while the hydrogen mass generation is based on material meeting the DOE 2010 Technical Targets for hydrogen storage [3]. Further details of the mathematical model are available in previous quarterly reports for this project.

For hydrogen ignition, the most important parameters are the upper and lower flammability (UFL, LFL) and explosive limits (UEL, LEL). Another important limit is the autoignition temperature for hydrogen. These limits have been spatially and temporally modeled for the four accident scenarios described above. Hydrogen and heat generation rates hypothetical to simulated results and determine efficacy of the modeling effort and do not represent actual chemical kinetics or thermal discharge rates. Note that each simulation was initialized at 27°C with 0.00% mol fraction of H_2 . Figure 1 presents contour plots of the hydrogen concentration for each scenario after one second. Note that the flammability and explosive limits are marked with solid black lines and that each scenario is marked with a small schematic. Initial results showed that the lower flammability (4%) and lower explosive (17%) limits are reached in less than one second for each

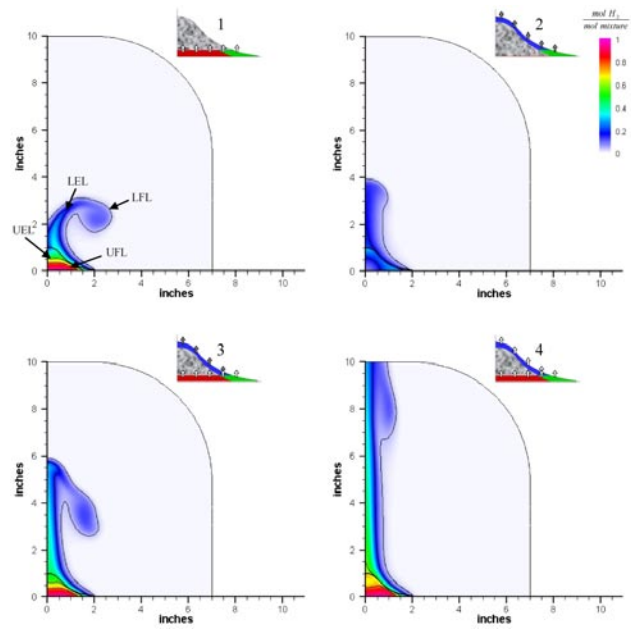


FIGURE 1. Modeling results showing spatial and temporal definition of UFL, LFL, UEL and LEL for hypothetical material ejected from a tank onto the ground after one second under (1) wet surface on a dry day, (2) a dry surface on a wet day, (3) a wet surface on a humid day and (4) a wet surface on a rainy day.

scenario given the constant heat and mass generation sources. In addition, within the pile of material, the upper flammability (75%) and upper explosive (56%) limits are reached in less than one second for Scenarios 1, 3, and 4. The concentration for Scenario 2, which has a top only source at 30% of the maximum generation rate, stays below 35% mol fraction after one second.

Conclusions and Future Directions

Conclusions

1. $2\text{LiBH}_4 \cdot \text{MgH}_2$ in the fully charged state is comparable to NaAlH_4 in risk of ignition during environmental exposure.
2. NH_3BH_3 in the fully charged state poses significantly less risk of ignition than NaAlH_4 during environmental exposure.
3. The mathematical modeling is an effective method of determining heat and hydrogen concentrations developed during simulated accident scenarios.

Future Directions

1. Conduct standardized testing of activated carbon and AlH_3 as decided in consultation with the Centers of Excellence.

2. Continue the thermodynamic and kinetic testing with AlH_3 and $8\text{LiH} \cdot 3\text{Mg}(\text{NH}_2)_2$ to feed information into the numerical simulations.
3. Continue modeling effort to include actual chemical kinetics to render predictive capabilities.
4. Evaluate proposed mitigation strategies utilizing calorimetry and modified UN tests.

Special Recognitions, Awards/Patents Issued

This project has been recognized by the International Partnership for the Hydrogen Economy. Partners include the National Institute for Advanced Industrial Science and Technology in Japan, Forschungszentrum Karlsruhe in Germany, Université du Québec à Trois-Rivières in Canada, United Technologies and Sandia National Laboratories in the U.S.

FY 2009 Presentations

1. Fundamental Safety Testing and Analysis of Solid State Hydrogen Storage Materials and Systems, D. Anton, D. Mosher, M. Fichtner, N. Kuriyama, R. Chahine & D. Dedrick, 2nd International Conference on Hydrogen Safety, San Sebastian, Spain, 2008.
2. Solid-State Hydrogen Storage System Development and Engineering Analysis, T. Motyka, D.L. Anton, 2008 ACS/ASM National Meeting on Hydrogen Energy, Cocoa Beach, FL, 2008.
3. The Hydrolysis and Oxidation Behavior of Lithium Borohydride and Magnesium Hydride Determined by Calorimetry, K. Brinkman, J. Gray, B. Hardy, and D. Anton, Materials Research Society (MRS), March 24–28, 2008, San Francisco, California.

4. Environmental Reactivity of Solid State Hydride Materials: Standardized Testing of $2\text{LiBH}_4 \cdot \text{MgH}_2$ for Air and Water Exposure, J. Gray, K. Brinkman, B. Hardy, and D. Anton, Materials Research Society (MRS), March 24–28, 2008, San Francisco, California.
5. Environmental Reactivity of the $2\text{LiBH}_4 + \text{MgH}_2$ System, D.L. Anton, K. Brinkman & J. Gray, MH2008, Reykjavik, Iceland, June 23–28, 2008.

FY 2009 Publications

1. Fundamental Safety Testing and Analysis of Solid State Hydrogen Storage Materials and Systems, D. Anton, D. Mosher, M. Fichtner, N. Kuriyama, R. Chahine and D. Dedrick, International Journal of Hydrogen Energy, J. Hydrogen Energy, (in press).
2. Design, Fabrication and Testing of NaAlH_4 Based Hydrogen Storage Systems, J. Alloys and Compounds (in press).
3. Hydrogen Storage Properties of Na-Li-Mg-Al-H Complex Hydrides, J. Alloys and Compounds (in press).

References

1. United Nations: Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 4th Revised Ed., ISBN 92113906800, (2000).
2. FLUENT6, Fluent, Inc., 2005.
3. Hardy, B.J., Integrated Hydrogen Storage System Model. Report, WSRC-TR-2007-00440, rev. 0. Savannah River National Laboratory. Available from: <http://sti.srs.gov/fulltext/WSRC-TR-s002-00440.pdf>. November 16, 2007.