Fundamental Reactivity Testing and Analysis of Hydrogen Storage Materials

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Overview

Timeline

- Start: 10/1/05
- End: 9/30/10
- Percent complete: 66%

Budget

- Funding received in FY08
  - $500K
- Planned Funding for FY09
  - $400K

Barriers Addressed

F. Codes and Standards

P. Understanding of Hydrogen Physisorption & Chemisorption

Q. Reproducibility of Performance

Partners

- M. Fichtner, Forschungszentrum Karlsruhe, Germany
- N. Kuriyama, National Institute for Advanced Industrial Science and Technology, Japan
- R. Chahine, Université du Québec à Trois-Rivières, Canada
- D. Mosher, United Tech. Res. Ctr., USA
- D. Dedrick, Sandia NL, USA
The objectives of this study are to understand the safety issues regarding solid state hydrogen storage systems through:

• Development & implementation of internationally recognized standard testing techniques to quantitatively evaluate both materials and systems.

• Determine the fundamental thermodynamics & chemical kinetics of environmental reactivity of hydrides.

• 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.
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<td>Risk Assessment and Standardized Test Development</td>
<td>Chemical Kinetics &amp; Thermodynamics Measurements</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td></td>
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<tr>
<td>Numerical Simulation</td>
<td></td>
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<td>3</td>
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<tr>
<td>Risk Mitigation</td>
<td>Mitigation strategies are being developed based on experimental and numerical results</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Numerical Simulation is being built on top of the existing experimental work</td>
<td></td>
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<tr>
<td></td>
<td>Program began with standardized testing and calorimetric analysis</td>
<td></td>
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</table>
Materials Test Plan

- All three major classes of condensed hydrogen storage materials are being studied:
  1. metal hydrides
  2. chemical hydrides
  3. adsorbents
- The priority of materials to be analyzed is being conducted in consultation with the three Materials CoE’s and DoE.
- Tested:
  - 2LiBH₄·MgH₂
  - NH₃BH₃
- Investigating:
  - activated carbon, AX-21
  - AlH₃
Material Standardized Testing (DE-FC36-02AL67610)


- **Flammability**
  - Flammability Test
  - Spontaneous Ignition
  - Burn Rate

- **Water Contact**
  - Immersion
  - Surface Exposure
  - Water Drop
  - Water Injection
NH₃BH₃ Self-Heating Results

- Fill 25x25x25 mm sample holder with material
- Sample holder pre-fitted with micro thermocouples
- Heat sample to 150°C
- Observe temperature within sample spatially resolved to determine if self-heating occurs

- Sample begins to self-heat after about 11 minutes
  - Time at set-point = 5 min
- Temperature spiked as material combusted
  - Green flames observed from oven door
- Maximum Temperature observed = 439°C
NH₃BH₃ Self-Heating & Burn Rate

• NH₃BH₃ expanded through mesh. Inspection of interior sample container reveals no damage after debris is removed.

• Burn rate = 33.3 mm/sec
  • 37% slower than the burn rate measured for
    • NaAlH₄ (51 mm/sec)
    • 2LiBH₄·MgH₂ (52 mm/sec)
<table>
<thead>
<tr>
<th>Material / UN Test</th>
<th>State</th>
<th>Pyrophoricity</th>
<th>Self-Heat</th>
<th>Burn Rate</th>
<th>Water Drop</th>
<th>Surface Contact</th>
<th>Water Immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>2LiBH$_4$·MgH$_2$</td>
<td>C</td>
<td>No ignition event. Hygroscopic material absorbed H$_2$O from air.</td>
<td>Self-heated $\sim$300 °C within 5 min at as $T_{oven} = 150$ °C is approached.</td>
<td>Flame propagated in 5 sec with burn rate of 52 mm/sec.</td>
<td>2 H$_2$O drops required for near-instant ignition.</td>
<td>Material ignited</td>
<td>No ignition event recorded. Gas evolved at longer times. (5 min)</td>
</tr>
<tr>
<td>SRNL</td>
<td>D</td>
<td>Not tested</td>
<td>Not tested</td>
<td>Not tested</td>
<td>1 H$_2$O drop required for near-instant ignition</td>
<td>Reaction observed with no flame</td>
<td>Reaction observed with no flame</td>
</tr>
<tr>
<td>NH$_3$BH$_3$</td>
<td>C</td>
<td>No ignition event. Hygroscopic material absorbed H$_2$O from air.</td>
<td>Self-heated $\sim$300 °C within 10 min, 5 min at $T_{oven} = 150$ °C</td>
<td>Flame propagated in 6 sec with burn rate of 33 mm/sec</td>
<td>No reactivity detected</td>
<td>No ignition event recorded. Gas evolved at longer times. (5 min)</td>
<td>No reactivity detected</td>
</tr>
<tr>
<td>SRNL</td>
<td>D</td>
<td>Not tested</td>
<td>Not tested</td>
<td>Not tested</td>
<td>No reaction</td>
<td>No reaction</td>
<td>No reaction</td>
</tr>
<tr>
<td>3Mg(NH$_2$)$_2$·8LiH</td>
<td>C</td>
<td>Ignition event recorded in room temp experiment</td>
<td>Material failed pyrophoricity test</td>
<td>Flame Propagates at 463 mm/sec</td>
<td>Not tested</td>
<td>Material ignited</td>
<td>Not tested</td>
</tr>
<tr>
<td>AIST</td>
<td>D</td>
<td>Ignition event recorded in room temp experiment</td>
<td>Material failed pyrophoricity test</td>
<td>Not tested</td>
<td>Not tested</td>
<td>Not tested</td>
<td>Material ignited</td>
</tr>
</tbody>
</table>
Thermo-Chemical Analysis of Water Contact

**Liquid Mixing Cell**

- Water Drop (~ 1 mL)
- Teflon® Membrane
- Sample (5-20 mg)

**Gas Flow Cell**

- Gas Inlet
- Gas Outlet

Gas Inlet is a function of:
- Dry Air/Argon
- Air/Argon with water vapor
- Temperature

Sample (5-20 mg)
NH$_3$BH$_3$ Water Vapor Calorimetry

Experiment
- Argon gas flow with 30% RH at 40°C

Result
- Small exothermic reaction probably due to water absorption

XRD of crystalline products revealed water vapor does not alter the NH$_3$BH$_3$
**NH₃BH₃ Water Calorimetry**

- **Liquid Phase Calorimetry**

  *Expect:*
  \[ \text{NH₃BH₃} + 2\text{H₂O} \rightarrow \text{BO}_2^- (\text{a}) + \text{NH}_4^+ (\text{a}) + 3\text{H}_2(\text{g}) \]
  \[ \Delta H = -222 \text{ kJ/mol exotherm at 40°C} \]

  *Result:*
  \[ \text{NH₃BH₃} + \text{H₂O} = \text{NH₃BH₃} (\text{a}) \]
  (dissolved, but solvated or ionic?)
  \[ \Delta H = 17 \text{kJ/mol endothermic at 40°C} \]

  *XRD analysis of crystalline products revealed only starting NH₃BH₃ material present after drying dissolved NH₃BH₃ + H₂O solution*
8LiH+3Mg(NH$_2$)$_2$ Calorimetry

8LiH+3Mg(NH$_2$)$_2$ $\rightarrow$ Mg$_3$N$_2$+4Li$_2$NH+8H$_2$
7wt% H$_2$ 140<T<200°C
Nakagawa et. al., 2007

8LiH+3Mg(NH$_2$)$_2$
Material received from N. Kuriyama, AIST
Liquid water hydrolysis calorimetry at 40°C

- Bulk of heat released within 15 min.
- XRD analysis of crystalline products revealed Mg(OH)$_2$ and Li$_2$CO$_3$ from atmospheric CO$_2$
8LiH:3Mg(NH₂)₂

- Gas Phase Calorimetry

Air \( \Delta H = 171 \text{ kJ/mol} \)

Argon \( \Delta H = 165 \text{ kJ/mol} \)

Enthalpy of reaction similar and final products the same with humid Ar or Air; Hydrolysis in the presence of air proceeded quicker.

XRD analysis of crystalline products same in Ar and Air humid atmosphere at 40°C: Mg(OH)₂ and LiOH·H₂O

*Mg(OH)₂

#LiOH·H₂O
Modeling Overview

• A very large number of experiments would be required to investigate all hypothetical accident scenarios and subtle variations
  • Accident scenarios are complex & have many potential variations

• Use simplified models (numerical or correlation based) that bracket potentially hazardous scenarios
  • Can also be used to suggest / verify concepts for mitigation

• Parameters & mechanisms governing metal hydride combustion are not well known
  • Need to determine physical mechanisms controlling media-environment interactions
  • Need experiments to identify important physical mechanisms that must be incorporated into models

• Objectives
  • Identify those scenarios most likely to result in hydride ignition
  • Obtain an initial idea of mechanisms that precede onset of hydride ignition
  • Identify the magnitude of mitigation required to minimize ignition probability
Accident Scenario: Storage system ruptured and media expelled to environment in either dry, humid or rain conditions.

Risk: Under what conditions will the expelled media ignite?

Temperature
Humidity
Water presence
Media geometry

Media Temperature Depends on $T_a$, $T_i$, $dH/dt$, $k_{eff}$, $c_{peff}$, ...

Heat Generated by Chemical Reaction Volume

Possible Water Film

Ambient Atmosphere at Temperature Contains $O_2$, $N_2$, $CO_2$ & $H_2O_l$, $H_2O_g$

Liquid Water

Surface

x

y

H$_2$

Spilled Media

Penetration

Storage Vessel

Punctured / Ruptured Tank
Governing Equations

Mass Balance (Gasses)
\[
\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \vec{v}) = S_i
\]

Fluid Motion
\[
\frac{\partial}{\partial t} (\rho \vec{v}) + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla p + \nabla \cdot (\tau) + p \vec{g} + \vec{F}
\]
\[
\tau = \mu \left[ (\nabla \vec{v} + \nabla \vec{v}^T) - \frac{2}{3} \nabla \cdot \vec{v} I \right]
\]

Relation Between Pressure Gradient and Mass Averaged Gas Velocity (Blake-Kozeny Equation)
\[
\vec{v} = -\frac{D_p}{150 \mu (1 - \varepsilon)^2} \nabla P
\]

Energy Balance
\[
(1 - \varepsilon)\rho \frac{\partial T}{\partial t} - \nabla \cdot \kappa \nabla T = -\varepsilon \rho C_p,\text{ Solid} \left( \frac{\partial T}{\partial t} + \vec{v} \cdot \nabla T \right) + \frac{1}{T_{\text{ref}}} \left( \frac{\partial P}{\partial t} + \varepsilon \vec{v} \cdot \nabla P \right) + \text{Source}
\]

Diffusion Equations (Stefan-Maxwell)
- Could Use Fick’s as Well
\[
\frac{\nabla c_i}{c} = -\sum_{j=1}^{n} \frac{x_i \nu_i (\nu_i - \nu_j)}{D_{ij} / \tau}
\]

Rate Equations
\[
\frac{1}{V} \frac{\partial n_i}{\partial t} |_{\text{Reaction}} = f_i(c_{\text{gas}}, c_{\text{Hyd}}, T, P) \quad \text{Gasses}
\]
\[
\frac{1}{V} \frac{\partial n_{\text{Hyd}, j}}{\partial t} |_{\text{Reaction}} = f_j(c_{\text{gas}}, c_{\text{Hyd}}, T, P) \quad \text{Solids}
\]

Total Gas Concentration
\[
c = \sum_{i=1}^{n} c_i
\]

Gas Pressure
\[
P = cRT \quad \text{Ideal Gas Eqn of State}
\]

Relation Between Gas Concentration and Mass Density
\[
\rho = \sum_{i=1}^{n} M_i c_i
\]

Relation Between Mass Averaged Velocity and Species Velocities
\[
\vec{v} = \sum_{i=1}^{n} \frac{M_i c_i \vec{v}_i}{\rho}
\]

Total Number of Unknowns and Equations are Equal

Closed System
Modeling Approach

• Phase I – Proof of Concept
  • Generic material (estimate properties)
  • Multiple species
  • Assumed heat and mass generation *(no chemical reactions)*
  • Multiple software platforms

• Phase II – Partial Chemical Reactions
  • Approximate chemical reactions within the media
  • Specific materials
    • Calorimetry data
    • Experimental properties

• Phase III – Full Models
  • Accident scenarios
  • More complete chemical reactions
    • Multiple-stage reactions
    • Dynamic boundary conditions

<table>
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<tr>
<th>Phase Introduced</th>
<th>Parameter Name</th>
<th>Symbol</th>
</tr>
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<tbody>
<tr>
<td>I</td>
<td>Bed porosity</td>
<td>(\varepsilon)</td>
</tr>
<tr>
<td>I</td>
<td>Mean particle diameter</td>
<td>(D_p)</td>
</tr>
<tr>
<td>I</td>
<td>Solid phase specific heat</td>
<td>(C_p \text{ Solid})</td>
</tr>
<tr>
<td>I</td>
<td>Bed thermal conductivity</td>
<td>(k)</td>
</tr>
<tr>
<td>I</td>
<td>Particle mass density of bed</td>
<td>(\rho_{\text{Solid}})</td>
</tr>
<tr>
<td>I</td>
<td>Heats of reaction</td>
<td>(\Delta H_{Rxn})</td>
</tr>
<tr>
<td>II</td>
<td>Gas component kinetics</td>
<td>(\frac{\partial n_i}{\partial t}_{\text{Reaction}})</td>
</tr>
<tr>
<td>II</td>
<td>Solid component kinetics</td>
<td>(\frac{\partial n_{\text{Hyd}}}{\partial t}_{\text{Reaction}})</td>
</tr>
<tr>
<td>III</td>
<td>Bed tortuosity factor</td>
<td>(\tau)</td>
</tr>
<tr>
<td>III</td>
<td>Wetted interface velocity</td>
<td>(v_{\text{wet}})</td>
</tr>
</tbody>
</table>
Phase I Model (Assumed Heat & Mass Generation Rates)

**FLUENT model:**
- 2-D axisymmetric
- Double-precision
- Pressure-based, 2\textsuperscript{nd}-order implicit, unsteady formulation
- Laminar Viscosity
- Heat transfer and Species models enabled

**Material Properties – porous NaAlH\textsubscript{4}:**
- Porosity ($\varepsilon$) = 0.5
- Particle Diameter ($D_p$) = 3.7x10\textsuperscript{-6} m
- Density ($\rho$) = 720 kg/m\textsuperscript{3}
- Thermal conductivity ($k$) = 0.325 W/m-K
- Specific heat ($C_p$) = 820 J/kg-K
- Heat Generation ≤ 40,000 J/mol
  (overall heat of reaction for NaAlH\textsubscript{4} from NaH)
- Mass Generation ≤ 0.5 kg H\textsubscript{2}/m\textsuperscript{3}-s
  (loading based on DOE 2010 Technical Target)

**Initial conditions:**
- Dry air @ 1 atm & 298 K
- Dry air mass fraction is 80% N\textsubscript{2}, 20% O\textsubscript{2}

**Grid Information:**
- 26,700 elements; 26,400 nodes
- Fixed sizing function: 0.25mm to 2.5mm with a growth rate of 1.02

![Diagram showing grid information and boundary conditions](image)
# Phase I Model Accident Scenarios

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Description</th>
<th>Generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Bottom only</td>
<td>Material on wet surface in dry air</td>
<td>Sources B and C:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Heat Generation = 40,000 J/mol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass Generation = 0.5 kg H₂/m³-s</td>
</tr>
<tr>
<td>2. Top only</td>
<td>Material on a dry surface with the pile exposed to 30% RH air</td>
<td>Sources A and C:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Heat Generation = 12,000 J/mol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass Generation = 0.15 kg H₂/m³-s</td>
</tr>
<tr>
<td>3. Dual with reduced source</td>
<td>Material on a wet surface with the pile exposed to 30% RH air</td>
<td>Source A:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Heat Generation = 12,000 J/mol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass Generation = 0.15 kg H₂/m³-s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sources B and C:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Heat Generation = 40,000 J/mol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass Generation = 0.5 kg H₂/m³-s</td>
</tr>
<tr>
<td>4. Dual with full source</td>
<td>Material on a wet surface in the rain</td>
<td>Sources A, B, and C:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Heat Generation = 40,000 J/mol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass Generation = 0.5 kg H₂/m³-s</td>
</tr>
</tbody>
</table>

Note: Heat and mass generation sources remain constant throughout the simulations.
Phase I Model Results: H₂ Generation

Flow time = 1.0 seconds

With assumed heat and mass generation…

- The flammability (4% & 75%) and explosive (17% & 56%) limits are marked with solid lines.
- Within the media, the UEL (56%) and UFL (75%) are reached in less than 1 second for scenarios 1, 3, & 4.
- The LFL (4%) is reached in less than 1 second for each scenario.
- The LEL (17%) is reached in less than 1 second for each scenario.
Phase I Model Results: H$_2$ Generation

Flow time = 120 seconds

Scenario 1: Bottom generation

Scenario 2: Top generation

Scenario 3: Dual gen. reduced source

Scenario 4: Dual gen. full source

With assumed heat and mass generation...

- H$_2$ concentrations within the media are lower after 2 minutes than after 1 second.
- The top generation source (scenario 2) allows the H$_2$ to dissipate into the ambient fluid rather than pool within the media.
Phase I Model Results: Temperature

Flow time = 1.0 seconds

- **Scenario 1:** Bottom generation
- **Scenario 2:** Top generation
- **Scenario 3:** Dual gen. reduced source
- **Scenario 4:** Dual gen. full source

With assumed heat and mass generation...

- **Bottom generation** (scenarios 1, 3, & 4) sustains heat accumulation within the media.
- **Top generation** (scenario 2) promotes heat dissipation from the media.
Phase I Model Results: Temperature

Flow time = 120 seconds

Scenario 1: Bottom generation
Scenario 2: Top generation
Scenario 3: Dual gen. reduced source
Scenario 4: Dual gen. full source

With assumed heat and mass generation...

- The auto ignition temperature for H₂ (ranges from 500 to 571°C) is marked by solid black lines.

- **Bottom generation (scenarios 1, 3, &4) reaches the auto ignition temperature within the media after:**
  - 42 seconds – Scenario 1
  - 41 seconds – Scenario 3
  - 37 seconds – Scenario 4

- Dual generation with full sources (scenario 4) reaches the auto ignition temperature in the fluid space above the media.
Modeling Development

- **Phase I – Proof of Concept**
  - Alter material property estimates
  - Alter heat and mass generation rates
  - Multiple software platforms

- **Phase II – Partial Chemical Reactions**
  - Approximate chemical reactions within the media
  - Specific materials
    - Calorimetry data
    - Experimental properties
  - Add chemical reaction approximations to the media (based on calorimetry data)

- **Phase III – Full Models**
  - Accident scenarios
  - More complete chemical reactions
    - Multiple-stage reactions
    - Dynamic boundary conditions
  - Add water vapor and other species to the model calculation
  - Account for permeation and changes in generation location within the media
  - Test additional model scenarios
  - Explore additional software platforms
  - Alter the model to account for the rate of reaction, changes in generation rate, etc.
  - Update material properties (based on experimental data)
Risk Mitigation Strategies

- Passive neutralization methods are of primary interest
  - Activate when hydride release occurs
- Preliminary system mitigation strategies have been identified
- Tests are being outlined to determine efficacy of strategies
- Invention disclosure on passive neutralization of hydrides has been filed with SRNL
Summary

- Standardized UN tests hazards analysis tests completed on 2LiBH$_4$·MgH$_2$ and NH$_3$BH$_3$ in the fully charged state
- Water contact completed in charged and discharged states
- Calorimetric characterization of NH$_3$BH$_3$ completed
- Mitigation strategy invention disclosure filed
- Modeling effort initiated to develop predictive capabilities for environmental exposure and reactivity scenarios
Proposed Future Work

• Conduct standardized testing of activated carbon and AlH₃ as decided in consultation with the Centers of Excellence

• Continue the thermodynamic and kinetic testing with AlH₃ and LiH:Mg(NH₂)₂ to feed information into the numerical simulations

• Continue modeling effort to Phases II and III to render predictive capabilities

• Evaluate mitigation strategies utilizing calorimetry and modified U.N. Tests