Environmental exposure of 2LiBH$_4$+MgH$_2$ using empirical and theoretical thermodynamics

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**Article Info**

Keywords:
- Hydrogen storage
- Environmental reactivity
- Lithium borohydride
- Magnesium hydride
- Calorimetry

**Abstract**

It has been shown that the consequence of environmental exposure can be qualitatively predicted by modeling the heat generated as a result of environmental exposure of reactive hydrides along with heat loss associated with conduction and convection with the ambient surroundings. To this end, an idealized finite volume model was developed to represent the behavior of dispersed hydride from a breached system. Semi-empirical thermodynamic calculations and substantiating calorimetric experiments were performed in order to quantify the energy released, energy release rates and to quantify the reaction products resulting from water and air exposure of a lithium borohydride and magnesium hydride combination. The hydrides, LiBH$_4$ and MgH$_2$, were studied in a 2:1 “destabilized” mixture which has been demonstrated to be reversible. Liquid water hydrolysis reactions were performed in a Calvet calorimeter equipped with a mixing cell using pH-neutral water. Water vapor and gaseous oxygen reactivity measurements were performed at varying relative humidities and temperatures by modifying the calorimeter and utilizing a gas circulating flow cell apparatus. The results of these calorimetric measurements were used to develop quantitative kinetic expressions for hydrolysis and air oxidation in these systems. Thermodynamic parameters obtained from these tests were then incorporated into a computational fluid dynamics model to predict both the hydrogen generation rates and concentrations along with localized temperature distributions. The results of these numerical simulations can be used to predict ignition events and the resultant conclusions will be discussed.

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1. Introduction

An extensive study on the safe handling and properties of hydrogen gas released in air has been previously published by Fischer [1]. It was concluded that the most probable risks were associated with possible hydrogen gas release, ignition, and/or combustion. For hydrogen to be used in vehicular applications, high volumetric densities must be maintained to insure the utility of the vehicle is not compromised. To achieve these high volumetric densities, hydrogen storage in condensed chemical forms are being investigated. While the risks of using hydrogen gas are reasonably well understood, the risk of storing and using hydrogen in chemically condensed forms has not been thoroughly evaluated. A number of recent publications have begun to explore the risks of environmental exposure of these materials [2–5]. Either liquid or gaseous water contact has been identified as leading to the most vigorous reactions with complex hydrides generally speaking. This study will investigate, in depth, one specific candidate hydride, “destabilized” 2LiBH$_4$MgH$_2$, both empirically and
through three dimensional heat flow analyses. The “destabili-
zied” mixture has been reported to have a >10 wt% H₂
capacity and rechargeable under reasonable pressure and
temperature (1–10 atm and 20–100 °C) [6,7].

Environmental exposure studies of candidate storage
materials are needed to quantify the reaction pathway, prod-
ucts and the quantity of heat released after a possible storage
tank rupture or release scenarios. For example, the hydrolysis
of lithium borohydride reacts with water as follows:

\[
\text{LiBH}_4 + 2\text{H}_2\text{O}(l) \rightarrow \text{LiBO}_2 + 4\text{H}_2(g)
\]  

(1)

The hydrogen producing reaction, Equation (1), is an
exothermic reaction with an enthalpy of 65.25 kJ/mol H₂. The
heat released from this reaction may be combined with the
released hydrogen and, along with oxygen present in the
surrounding air, could provide the necessary conditions for
ignition. The risks of this occurring depends on the kinetics
of the reaction, the heat liberated through reaction, the
concentration of the reactants and their spatial distribution,
ambient conditions, balanced against heat loss through radi-
ation, conduction and convection. Therefore, it is important
to understand and quantify the potential risk of ignition result-
ing from accidental environmental exposure of condensed
phase hydrogen storage materials under differing environ-
mental exposure scenarios. This paper describes a modeling
and experimental study with the aim of predicting conse-
quences of the accidental release of 2LiBH₄ + MgH₂ from
hydrogen storage systems. The methodology and results
developed in this work are directly applicable to any solid
hydride material and/or accident scenario using appropriate
boundary conditions and empirical data.

2. Experimental details

2.1. Calorimetry

To quantify the heat released through contact with dry and
humidified air and liquid water, oxidation and hydrolysis
studies were performed in a Calvet calorimeter. The heat flow
(mW) was normalized with respect to hydride and plotted
versus time. Liquid water tests were performed using a mixing
cell with pH-neutral water to react 5–10 mg of solid with 1 ml
of water. Controlled humidity air reaction measurements
were conducted at varying relative humidity levels (30 and
60% RH) and temperatures (40 and 70 °C). For these
measurements, the calorimeter equipped with a flow cell
utilizing either argon or air as the carrier gas with a flow rate of
10 ml/min reacting with 5–10 mg of solid. Specimens were
prepared by mixing commercially pure MgH₂ and LiBH₄
purchased from Aldrich Inc. Milling was conducted in a Spex
mill for 1 h, under an argon atmosphere with a ball-to-sample
ratio of 20:3.

2.2. Numerical modeling

The modeling effort has focused on incorporating chemical
reaction rate data into the Navier–Stokes and energy
conservation equations to create realistic simulations of heat
and mass flow from hydrogen. The environmental scenario is
described as a suspended sphere of materials with variable
radius having a specified porosity. The radially symmetrical
geometry was utilized to determine the critical pellet radius
above which would lead to a potential reaction event. This
geometry also minimized computational intensity by ignoring
ground contact effects. Fig. 1 provides the basic model sche-
natic. The governing equations solved for each analysis
include mass, momentum, and energy balances, plus addi-
tional kinetics equations based on the calorimetry data at
70 °C for loosely-packed 2LiBH₄–MgH₂ in contact with liquid
water. This is a worst case scenario at the given environ-
mental conditions. The thermal data was divided into four
time segments, with each segment fit to a 4th-order poly-
nomial. Table 1 lists the model parameters and constants for
these models [8,9]. The following assumptions were made to
simplify the analysis.

- The ambient fluid is dry air.
- The calorimetry data at 70 °C for the liquid water and
  2LiBH₄–MgH₂ is assumed to be the worst case scenario with
  the fast reaction rate and highest heat of reaction for this
  system.
- The heat and mass generation source is based upon the
  worst case scenario as stated in the assumption above and
  is modeled as temperature, pressure, and material compo-
  sition independent. Thus, the heat and mass generation
  source, which varies with time and position, will continue
  regardless of the fluid or material temperature, fluid pres-
  sure, or species concentrations.
- All reactions begin in the outer shell of the hydride sphere.
- The material is a uniform 50% porous sphere.
- Mass transport considerations and limitations within the
  porous sphere that would be present due to binders or other
  pelletization considerations are not addressed in this work.

![Fig. 1 – Axisymmetric sphere model schematic.](image-url)
pathways occurred. Amorphous lithium products were observed at the lower 40 °C temperature along with Mg(OH)₂, while crystalline lithium compounds such as Li(H₂O)ₓB(OH)₄H₂O were observed in the higher temperature hydrolysis reaction at 70 °C. The integrated area under the heat flow signal at time t in Fig. 2a divided by the total reaction enthalpy (total area under the heat flow signal) was used to estimate the reaction progress in (percent) as displayed in Fig. 2b. The result allows us to quantify the increase in reaction rate: a temperature increase of 30 °C (from 40 to 70 °C) resulted in an increase of the reaction progress from 40 to 70% after 1 h.

3.2. Water vapor calorimetry

3.2.1. Air versus argon carrier gas

The effects of water vapor in air versus water vapor in an argon carrier gas were studied to separate the effects of hydrogen oxidation with air from gas phase water hydrolysis. Fig. 3 displays the heat flow signal from LiBH₄ reacted with water vapor (30% relative humidity) at 40 °C using air and argon as a carrier gas flowing at 10 ml/min. The energy release during the reactions were approximately the same for both cases: 30% RH air carrier gas 352 kJ/mol, 30% RH Argon carrier gas 340 kJ/mol, however the reaction in the presence of air reaches completion more quickly than in the presence of argon. XRD identified products were: air carrier gas (LiB(OH)₄, LiB(OH)₂O₂, H₂B₂O₆ and residual LiBH₄); argon carrier gas (LiB(OH)₄) illustrating different reactions occurred in the presence of oxygen. These results do not indicate oxidation of hydrogen after its release from the sample through hydration. This oxidation event would have resulted in a significantly increased heat of reaction.

3.2.2. Relative humidity effects

The heat flow signal was measured during humid air exposure for the mixture 2LiBH₄:MgH₂ at 40 °C with both 30% RH and 60% RH. Fig. 4 displays the multiple heat releasing events that were observed in these experiments. The total amount of heat released was approximately the same at different relative humidity levels, with a value of 268 kJ/mol at 40 °C 30% RH and 251 kJ/mol at 40 °C 60% RH. The XRD results indicate LiB(OH)₄ and residual MgH₂ crystalline products for both levels of

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### Table 1 — Model parameters for porous 2Li(BH₄)₄MgH₂.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material porosity ($\rho$)</td>
<td>0.5</td>
</tr>
<tr>
<td>Particle diameter ($D_p$)</td>
<td>$3.7 \times 10^{-5}$ m</td>
</tr>
<tr>
<td>Material density ($\sigma$)</td>
<td>927 kg/m³</td>
</tr>
<tr>
<td>Material thermal conductivity ($k$)</td>
<td>0.5 W/m K</td>
</tr>
<tr>
<td>Material specific heat ($C_p$)</td>
<td>1583 J/kg K</td>
</tr>
<tr>
<td>Heat/mass generation</td>
<td>Based on calorimetry data</td>
</tr>
<tr>
<td>Reaction propagation</td>
<td>0.03 mm/s²</td>
</tr>
<tr>
<td>Model dimensions:</td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>$r_1$ (in)</td>
</tr>
<tr>
<td>$r_2$ (in)</td>
<td>0.05</td>
</tr>
<tr>
<td>$r_3$ (in)</td>
<td>0.05</td>
</tr>
<tr>
<td>$r_4$ (in)</td>
<td>0.05</td>
</tr>
</tbody>
</table>

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- The material properties are constant during the simulation.
- The ambient air properties are allowed to change with temperature and pressure via the ideal gas law.
- The built-in hydrogen–air reaction within FLUENT [10] is used to mark the hydrogen ignition even when/if it occurs. However, the model is only designed to capture the events leading up to the ignition event and is not designed to model the ignition event itself or the events following the ignition event.

3. Results and discussion

3.1. Liquid water calorimetry

Fig. 2a gives a typical calorimetric result of heat flow versus time for liquid water hydrolysis of 2LiBH₄:MgH₂ at 40 and 70 °C. As displayed in Fig. 2a, a temperature increase of 30 °C (from 40 to 70 °C) resulted in a modified calorimetric signal. Both the total heat released for the hydrolysis reaction was different at the two temperatures as well as the final crystalline phase composition suggesting different reaction

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![Fig. 2](image-url)  
Fig. 2 — a) Heat flow from neutral water hydrolysis of 2LiBH₄:MgH₂ at 40 °C and 70 °C and b) the reaction progress as a function of time determined from the integrated calorimetric signal.
relative humidity. In gas phase hydrolysis, the amount of water vapor seems only to impact the reaction time and not the pathway or final products. An increase in water vapor available for hydrolysis decreases the time required to complete the reaction. The reaction of $2\text{LiBH}_4:\text{MgH}_2$ with air at 70 °C and 30% relative humidity were performed, resulting in approximately the same crystalline products ($\text{LiB(OH)}_4$, and $\text{MgH}_2$) and total heat release (242 kJ/mol) as the reaction at 40 °C at varying relative humidity levels. The only impact of increased temperature seems to be an increase in the amount of water vapor in the air, thus speeding up the hydrolysis reaction.

### 3.3. Water vapor versus liquid calorimetry

Due to experimental constraints such as the geometry and pressure rating of the sample cells, and the type of experiment being conducted (gas or liquid contact), there is a range in the amount of water supplied to the starting material as a function of time. In a liquid water mixing experiment, an excess of 32 times the stoichiometric amount of water is added which remains constant during the duration of the experiment. In contrast, the amount of water added during gas flow experiments is determined by the flow rate, the gas and reaction temperature and thermodynamics of the water liquid/vapor equilibrium expressed through the relative humidity indicator. Since water vapor is added in a flow through configuration, the quantity provided for the hydrolysis reaction increases linearly with time. The saturation vapor pressure of water increases with temperature so that higher temperatures and higher relative humidity levels increase the amount of water available for the hydrolysis reaction.

Figure 5 displays the normalized heat flow (mW/mg) for the $2\text{LiBH}_4:\text{MgH}_2$ reaction with liquid water at 40 °C and 30% relative humidity air at 40 °C (10 ml/min flow rate). The amount of total water addition in excess of stoichiometry is 32 times for liquid water and 4 times (after a reaction time of 12 h) for the conditions of 40 °C and 30% relative humidity. The qualitative difference observed by heat flow is believed to be due to the difference in gas/solid versus liquid/solid interfacial reactions and is currently under further investigation. The total energy release of the water vapor reaction was greater ($\sim$268 kJ/mol) than the energy release upon liquid water hydrolysis ($\sim$223 kJ/mol). In addition the final crystalline reaction products were different in the two cases: the reaction with 30% relative humidity air resulted in $\text{LiB(OH)}_4$ and residual $\text{MgH}_2$, while the

![Fig. 3](image_url) — Normalized heat flow from $\text{LiBH}_4$ reacted with 30% relative humidity using air and argon as a carrier gas at 40 °C.

![Fig. 4](image_url) — Normalized heat flow (mW/mg) for $2\text{LiBH}_4:\text{MgH}_2$ reacted with a) air at 40 °C and 30% relative humidity and b) air at 40 °C and 60% relative humidity.

![Fig. 5](image_url) — Normalized heat flow (mW/mg) during hydrolysis/oxidation of $2\text{LiBH}_4:\text{MgH}_2$ with liquid water at 40 °C and with 30% relative humidity air at 40 °C (10 ml/min flow rate).
liquid water hydrolysis resulted in LiB(OH)$_4$, H$_6$B$_2$O$_6$ and LiB(OH)$_2$(O$_2$) phases along with amorphous components. Overall, in both the liquid mixing and gas flow reactions the trend is for a lower measured energy compared to the thermodynamically predicted reactions. A corollary to this is that the actual observed products do not match those predicted from thermodynamics and often have a significant degree of amorphous character. However, despite discrepancies in theoretical versus experimental thermodynamic properties, the kinetics of energy release empirically determined for these materials via calorimetry are of prime importance for modeling the environmental reactivity under accident scenarios as described in the subsequent section.

3.4. Numerical modeling results

Two sets of initial conditions were used to evaluate different scenarios. For the first, the hydride is initialized with ambient air filling the porous media. These scenarios assume that the hydride has been released from its container for a short amount of time prior to any chemical reaction occurring, which allows all of the hydrogen gas to evacuate from the hydride prior to the reaction and be replaced with ambient air. Results from these simulations are shown in Figs. 6 and 7 and summarized in Table 2. The smallest diameter hydride spheres (0.05 inch and ¼ inch models) never reach the lower flammability limit (LFL = 0.04) for hydrogen concentration,

![Flow time = 255 seconds](image1)
![Flow time = 260 seconds](image2)

**Fig. 6** – Mole fraction of H$_2$ before (a) and after (b) the hydrogen ignition for the axisymmetric sphere with a ½ inch radius.

![Flow time = 255 seconds](image3)
![Flow time = 260 seconds](image4)

**Fig. 7** – Mole fractions of H$_2$, O$_2$, and H$_2$O before and after hydrogen ignition (255 s and 260 s, respectively) for the axisymmetric sphere with a ¼ inch radius.
which means no reaction event occurs. For the larger spheres (½ inch and higher models), the LFL and/or the auto-ignition temperature (500 °C or 571 °C depending on the H₂ concentration) of hydrogen is reached and a reaction event occurs. Thus, there is a critical radius between ¼ and ½ inch that indicates the minimum amount of material necessary for a hydrogen ignition event to occur given the assumptions listed above.

Fig. 6 highlights the H₂ concentrations before (Fig. 6a, time = 255 s) and after (Fig. 6b, time = 260 s) the hydrogen ignition event occurs for the ½ inch hydride sphere model. The H₂ concentration (26.6% mf) is well above the LFL prior to the reaction event and then drops off rapidly after the event (~1.5% mf). Fig. 7 shows the species concentration for the other components of the hydrogen—air reaction for the ½ inch sphere model. Note that as the H₂ and O₂ burn away, water vapor (H₂O) increases in their place. Similar results are seen for the larger spheres (1 inch and greater models), but are not shown.

For the second scenario, the hydride is initialized with hydrogen gas filling the porous media. This scenario assume that the chemical reaction occurs immediately after the hydride is released from its container, which means the porous space within the hydride is still full of 100% hydrogen gas at the start of the numerical simulation. It was observed that due to the high dissipation rate of H₂ into the ambient atmosphere, most of the hydrogen has been expelled from the hydride prior to the start of the chemical reaction (mass/heat generation) within the simulation. Thus, the hydrogen-initialized hydride models yielded similar results to the air-initialized hydride models and are not shown.

Table 2 – Axisymmetric sphere results for air-initialized hydride.

<table>
<thead>
<tr>
<th>Model</th>
<th>H₂ ignition event</th>
<th>H₂ mole fraction (mf)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 in</td>
<td>None</td>
<td>Maximum value of 0.0123 at t = 160 s and 60 s</td>
<td>Maximum temperature of 164.2 °C at t = 300 s</td>
</tr>
<tr>
<td>0.25 in</td>
<td>None</td>
<td>LFL reached between t = 55 s and 30 s</td>
<td>Maximum temperature of 752.4 °C at t = 370 s</td>
</tr>
<tr>
<td>0.50 in</td>
<td>Between t = 255 s and 260 s, H₂ mf = 0.266, Temp = 569 °C and 571 °C</td>
<td>LFL reached between t = 30 s and 35 s</td>
<td>Maximum temperature of 1422 °C at t = 540 s</td>
</tr>
<tr>
<td>1.0 in</td>
<td>Between t = 255 s and 260 s, H₂ mf = 0.332, Temp = 327 °C and 361 °C</td>
<td>LFL reached between t = 25 s and 30 s</td>
<td>Maximum temperature of 2184 °C at t = 963 s</td>
</tr>
<tr>
<td>1.5 in</td>
<td>Between t = 180 s and 185 s, H₂ mf = 0.343, Temp = 263 °C and 316 °C</td>
<td>LFL reached between t = 20 s and 25 s</td>
<td>Temperature reaches 2250 °C at t = 1000 s (and still rising)</td>
</tr>
<tr>
<td>2.0 in</td>
<td>Between t = 170 s and 175 s, H₂ mf = 0.361, Temp = 234 °C and 293 °C</td>
<td>LFL reached between t = 20 s and 25 s</td>
<td>Temperature reaches 2563 °C at t = 1000 s (and still rising)</td>
</tr>
<tr>
<td>2.5 in</td>
<td>Between t = 180 s and 183 s, H₂ mf = 0.410, Temp = 255 °C and 668 °C</td>
<td>LFL reached between t = 20 s and 25 s</td>
<td>Temperature reaches 2312 °C at t = 1000 s (and still rising)</td>
</tr>
</tbody>
</table>

4. Conclusions

The heat flow of destabilized 2LiBH₄·MgH₂ system was measured under different conditions that represented various environmental exposure conditions (dry, humid, and wet). The total heat released and the final crystalline products were different for the hydrolysis reaction at 40 °C and 70 °C. Amorphous lithium products were observed at the lower 40 °C temperature, while crystalline lithium compounds were observed at 70 °C. In the gas phase reaction, the presence of water vapor increased the reaction time, but does not change the final product. However, the larger heat flow in the presence of liquid water versus water vapor could be attributed to the gas/solid versus liquid/solid interfacial reactions. Given the numerical simulation assumptions, there is a definitive amount of material (i.e. critical radius of 0.25” < r < 0.50”) needed for a hydrogen reaction event to occur. When the spherical radius is smaller than this critical radius, hydrogen is released to the ambient without a reaction event. When larger amounts of hydride are present (i.e. the spherical radius is larger than the critical radius), enough heat and hydrogen are evolved simultaneously so that an ignition event is possible.

Acknowledgements

The authors would like to thank David Missimer and Joseph Wheeler for their XRD and laboratory support, respectively. This work was funded under the U.S. Department of Energy (DOE) hydrogen storage testing, safety, and analysis program managed by Dr. Ned Stetson.

References


