Quantifying & Addressing the DOE Material Reactivity Requirements with Analysis & Testing of Hydrogen Storage Materials & Systems

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DOE Hydrogen Program
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Project ID: STP_50_Khalil

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Overview

- **Timeline**
  - Start: June 2007
  - End: May 2010
  - Percent complete: 35% (spending)

- **Budget**
  - $1.34M Total Program
    - $1.07M DOE
    - $0.27M UTRC
  - FY08: $300k
  - FY09: $400k

- **Barriers**
  - F. Codes & Standards
  - A. System Weight & Volume

- **Target**
  - EH&S: “Meets or exceeds applicable standards”

- **Partners**
  - Kidde-Fenwal: dust cloud testing
  - Multiple collaborators
Collaborations

Other DOE Reactivity Projects
- Savannah River National Lab
- Sandia National Labs

IEA HIA Task 22 / IPHE Project (with SRNL & SNL)
- FZK (Germany, Government lab)
- AIST (Japan, Government lab)
- UQTR (Canada, University)

Canadian Government Project
- HSM Systems, Inc. (Industry)

Additional Collaborations
- DOE Hydrogen Program Codes & Standards
- DOE Hydrogen Program Safety Panel
- NFPA Hydrogen Technology Committee
- IEA HIA Task 19
Project Objectives & Associated Tasks

**High Level Objectives**
- Contribute to quantifying the DOE On-Board Storage Safety Target: “Meets or exceeds applicable standards.”
- Evaluate reactivity of key materials under development in the material Centers of Excellence.
- Develop methods to reduce risks.

**Primary Tasks**
- Risk analysis
  - Qualitative risk analysis for a broad range of scenarios
  - Quantitative risk analysis for key scenarios
- Material testing
  - Dust cloud: standard and modified ASTM procedures
  - Reaction kinetics: air exposure / time resolved XRD
- Risk mitigation
  - Material oriented risk reduction
  - System configuration level
- Subscale prototype demonstration
Detailed Testing and Modeling will supplement the Risk Analysis Framework to serve as the basis for risk informed reactivity and C&S decisions.

Key input being provided by SRNL and SNL for material testing & modeling.
Collaborations

Coordinated DOE & IEA / IPHE Task Matrix

<table>
<thead>
<tr>
<th>Risk Analysis</th>
<th>UTRC</th>
<th>SRNL</th>
<th>SNL</th>
<th>AIST</th>
<th>FZK</th>
<th>UQTR</th>
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<tbody>
<tr>
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<td>X</td>
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<table>
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<td>Dust Cloud</td>
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<th>Prototype Demonstration</th>
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<td>TBD</td>
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</table>
Materials & Systems

Examine hydrogen storage material candidates and related system configurations which are being developed within the DOE Hydrogen Program.

Current Focus Materials:
- $2\text{LiBH}_4 + \text{MgH}_2$
- Activated carbon
- $\text{AlH}_3$
- $\text{NH}_3\text{BH}_3$
- Others can be added based on material development progress

General System Classes:
- On-board reversible hydride bed systems (guided by NaAlH$_4$ prototypes)
- On-board reversible adsorbant systems (based on activated carbon)
- Off-board regenerable based systems (variants for alane & ammonia borane)
Overview of Technical Accomplishments

- Qualitative Risk Analysis / design FMEA
  - Conceptual system configuration designs developed for baseline FMEAs of on-board reversible and off-board regenerable storage systems.
  - Definition of Expert Panel and preliminary opinion pooling for on-board reversible system FMEA.

- Quantitative Risk Analysis
  - Event tree model was developed, having vehicle collision as an accident initiator, which included hazard scenarios of hydrogen leakage and dust dispersion both as a cloud and deposited layer.
  - Fault tree models were developed for a range of damage categories from pressure waves produced by hydride and aluminum dust cloud events.
  - Framework for economic consequence analysis.

- Dust Clouds Testing
  - Completed testing for partially discharged 2LiBH₄ + MgH₂.
  - Full matrix for AX-21 carbon in air.
  - Partial matrix for discharged alane.

- Air Reactivity / TR-XRD
  - Ammonia borane.
Risk Analysis Overview

**Qualitative – Broad Scope**
- Expert panel
- Material test data
- Modeling
- Mitigation strategies

**Failure Modes and Effects Analysis (FMEA)**
Standard approach for Automotive Industry and Consumer Products

**Hazard and Operability Analysis (HAZOP)**
Standard approach for the Chemical Industry

- Potential deviations from normal operating conditions (ex. vehicle operation)
- Consequences
- Recommendations for Engineered Safety Features

**Quantitative – Key Risks**

**Fault Tree Analysis (FTA)**
Standard approach used by Nuclear Power Industry & NASA

**Event Tree Analysis (ETA)**

- FTA/ETA Linking
- Quantified Accident Sequences
- Consequence Analysis
- Uncertainty Analysis
- Parameter Sensitivity Studies

*SAE J1739 Standard

SAPHIRE
U.S. NRC / INEL

CAFTA

*SAE International
1. Diagram system’s components and describe their intended functions

2. Identify potential failure modes of each component

3. Identify potential system-level effect(s) of each failure mode

4. Identify potential cause(s) of each failure mode

5. Evaluate current detection and control methods

6. Calculate RPN of each failure mode

3.1 Determine consequence (C) of each effect

4.1 Determine probability (P) of occurrence of each failure mode

5.1 Determine detectability (D) level

7. RPN ≤ threshold?

8. Identify risk mitigation methods and reassess scorings

RPN = C * P * D
C, P, D: 1-10

DONE

Hydrogen Storage Expert Panel

Delphi process
FMEA Spreadsheet

- Initial assessment based on NaAlH₄ material and system due to existing knowledge – applicable to other on-board reversible materials.
- Risk Priority Number = Consequence * Probability * (lack of) Detectability
- Acceptable / threshold risk: $\text{RPN}_{\text{th}} = 80$
### FMEA Spreadsheet

<table>
<thead>
<tr>
<th>Additional Mitigations</th>
<th>Consequence</th>
<th>Probability</th>
<th>New Risk Priority Number (RPN)</th>
<th>TRL of Mitigation Approach</th>
<th>Impact on DOE Non-Safety Technical Targets (Low, Medium, High)</th>
<th>Specific Recommended Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passive hydride material to reduce reactivity</td>
<td>4</td>
<td>2</td>
<td>80</td>
<td>0.0</td>
<td>Kidde Fenwal dust cloud explosion tests could provide useful insights for: a) Minimum explosive concentration (MEC) b) Minimum ignition temperature (MIT) c) Minimum oxygen index (MOI) d) dP/dt and other Applicable modes</td>
<td>Obtain site vessel experience data on failure modes (applicable to all 1.1 X FM)</td>
</tr>
</tbody>
</table>

- If $RPN > RPN_{th}$, develop recommended actions which include Mitigation Development and Uncertainty Reduction (additional testing/modeling).
- Interpret mitigation Feasibility not as cost, but Technology Readiness Level (TRL).
- Examine impact on non-safety Technical Targets (weight, volume, …).

Customized FMEA framework developed for on-board reversible hydrides. Population of entries by the multi-project team will be on-going.
Initial FMEA / Expert Panel Risk Scoring

- Partial set of pooled FMEA risk scorings from the expert panel (round one elicitation).
- Three of the top failure modes are:
  - Vehicle collision leading to large break in hydride storage vessel (wet environment)
  - \( \text{H}_2 \) leak caused by pipe rupture resulting from impact during a vehicular collision.
  - External fire in close proximity to the vehicle, causing heating of the hydride material.
- High variability will be reduced in subsequent rounds of the Delphi iterative process.

The Linear Opinion Pool Model was used with a weighing Factor = 1/n where \( n \) is the number of experts.
Quantitative Analysis: ETA / FTA

- Event Tree (ET) describes accident progression from initiating event to end states.
- The CAFTA computer program is being employed; can be exported to SAPHIRE.
- The probability assigned to each node will be estimated from a Fault Tree Analysis (FTA), experiments / modeling, or expert judgment.

### Event Tree (ET) Description

- **Vehicle Collision (VC):** initiating event
- **Water contact with hydride**
- **Sequence of outcomes or end states (consequence severity)**
- **Probability of water contact given prior events**
Event Tree Analysis for Hydrogen Leakage

An Event Tree for Hydrogen Leakage (without mitigation) has been constructed and quantified.

Preliminary probabilities to be progressively refined.
Event Tree Analysis for Hydrogen Leakage

The Event Tree represents a set of mutually exclusive sequences with different outcomes and probabilities of occurrence (ex. Sequence #5).

Preliminary probabilities to be progressively refined.
Elements of the Fault Tree structure are represented for Sequence #5.
Event Tree Analysis for Hydrogen Leakage

In CAFTA, a branch probability can be derived from a detailed Fault Tree or a Basic Event with a probability distribution to address uncertainties.

Preliminary probabilities to be progressively refined.
Fault Tree Model for Dust Cloud Dispersion

Dust cloud test characterization results are incorporated into the fault tree model.

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Preliminary probabilities
Fault Tree Model for Dust Cloud Dispersion

Dust cloud test characterization results are incorporated in the fault tree model.

Preliminary probabilities
Fault Tree Model - Basic Event Uncertainties

Preliminary probabilities
Supporting Information Sources

A wide range of information has been searched and insights implemented in the risk analyses

<table>
<thead>
<tr>
<th>Information Source Category</th>
<th>Description / Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>▪ Covers FMEA and provides general guidance in the application of this methodology.</td>
</tr>
<tr>
<td>▪ ASTM E-1226</td>
<td>▪ Maximum pressure, rate of pressure rise and $K_{st}$</td>
</tr>
<tr>
<td>▪ ASTM E-1515</td>
<td>▪ Minimum concentration of combustible dusts (MC)</td>
</tr>
<tr>
<td>▪ ASTM E-2019</td>
<td>▪ Minimum ignition energy of a dust cloud in air (MIE)</td>
</tr>
<tr>
<td>▪ ASTM E-1491</td>
<td>▪ Minimum ignition temperature of dust clouds ($T_c$)</td>
</tr>
<tr>
<td>NFPA-2: Hydrogen Technologies</td>
<td>Hydrogen transportation, storage, refueling stations, leakage in road tunnels and fire.</td>
</tr>
<tr>
<td>ISO TC-197</td>
<td>Several working groups on hydrogen generation, storage, transportation, refueling stations, and detection.</td>
</tr>
<tr>
<td>ISO / FDIS 16111</td>
<td>Reversible metal hydrides – portable applications.</td>
</tr>
</tbody>
</table>
## Supporting Information Sources

<table>
<thead>
<tr>
<th>Information Source Category</th>
<th>Description / Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANSI / CSA NGV2</td>
<td>Requirements for compressed natural gas vehicles.</td>
</tr>
<tr>
<td>International Codes Council (ICC)</td>
<td>Numerous topics related to hydrogen safety and infrastructures.</td>
</tr>
<tr>
<td>Road Safety Improvement Programs and Benefit-Cost Analyses</td>
<td>Insights for economic sequence analysis such as costs associated with risk avoidance of injuries due to motor vehicle crashes.</td>
</tr>
<tr>
<td>Literature on Thermodynamics and Reaction Kinetics of Hydride Materials</td>
<td>Relevant thermodynamic and kinetics information on hydride materials are utilized in discussion of FMEA.</td>
</tr>
<tr>
<td>Publications on Dust Dispersion</td>
<td>Insights on dust cloud characteristics and consequences such as aluminum dust dispersion studies.</td>
</tr>
<tr>
<td>EPRI Software Packages: CAFTA and ETA-II</td>
<td>- Part of EPRI’s risk and reliability (R&amp;R) workstation.</td>
</tr>
<tr>
<td></td>
<td>- Used by the nuclear industry, NASA, Boeing and others.</td>
</tr>
<tr>
<td>ASME</td>
<td>Risk standards; Boiler and pressure vessel code.</td>
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</table>
Materials Testing: Dust Cloud

Measurements (ASTM tests)
- $P_{\text{max}}$, $(dP/dt)_{\text{max}}$, $K_{\text{st}}$ (E1226)
- Minimum Concentration (E1515)
- Minimum Ignition Energy (E2019)
- Minimum Ignition Temperature (E1491)

$K_{ST} = \left( \frac{dP}{dt} \right)_{\text{max}} \times V^{1/3}$

<table>
<thead>
<tr>
<th>Dust Class</th>
<th>$K_{st}$ bar-m/s</th>
</tr>
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<tbody>
<tr>
<td>St-1</td>
<td>Up to 200</td>
</tr>
<tr>
<td>St-2</td>
<td>201-300</td>
</tr>
<tr>
<td>St-3</td>
<td>301+</td>
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</tbody>
</table>

Standard 20 L Kühner apparatus (E1226 & E1515)

United Technologies Research Center
AX-21 Carbon

AX-21 has similar characteristics to standard reference materials except for the MIE.

Future testing to be conducted with hydrogen additions.
Partially Discharged $2\text{LiBH}_4 + \text{MgH}_2$

Completion of dust cloud testing: 40 to 100 mesh material.

<table>
<thead>
<tr>
<th></th>
<th>Hydrided</th>
<th>Partially Dehydrided</th>
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<tbody>
<tr>
<td></td>
<td>As-milled</td>
<td>&lt; 200 mesh</td>
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<tr>
<td>$P_{\text{max}}$, bar-\text{g}</td>
<td>10.7</td>
<td>9.9</td>
</tr>
<tr>
<td>$(dP/dt)_{\text{max}}$, bar/\text{s}</td>
<td>2036</td>
<td>1225</td>
</tr>
<tr>
<td>$K_{\text{ST}}$, bar-\text{m/\text{s}}</td>
<td>553</td>
<td>333</td>
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<tr>
<td>Dust Class</td>
<td>St-3</td>
<td>St-3</td>
</tr>
<tr>
<td>$MC$, g/\text{m}^3</td>
<td>30</td>
<td>30</td>
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<tr>
<td>$T_C$, °C</td>
<td>150</td>
<td>230</td>
</tr>
<tr>
<td>MIE, mJ</td>
<td>&lt; 9</td>
<td>&lt; 9</td>
</tr>
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</table>

Material was SPEX ball milled for 2.5 min. & sieved.

Quantification of particle size influence on dust cloud characteristics.
Discharged Alane

Semi-quantitative XRD
- Al: 97.8 wt%
  (100 nm crystallite size)
- LiCl: 1.4 wt%
- AlOCl: 0.7 wt%
- NaCl: 0.1 wt%

Due to current limited material quantities, full $K_{st}$ & MC determinations could not be made. This will be addressed in future efforts.

<table>
<thead>
<tr>
<th></th>
<th>Discharged Alane</th>
<th>Pittsburgh Seam Coal</th>
<th>Lycopodium Spores</th>
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</thead>
<tbody>
<tr>
<td>MC, g/m$^3$</td>
<td>125 to 250</td>
<td>65</td>
<td>30</td>
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<tr>
<td>$T_c$, °C</td>
<td>710</td>
<td>585</td>
<td>430</td>
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<tr>
<td>MIE, mJ</td>
<td>&lt; 10</td>
<td>110</td>
<td>17</td>
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</table>

Sieve Analysis
- > 200 mesh (75 μm): 6% 16% 0%
- < 200 mesh (75 μm): 94% 85% 100%

For 250 g/m$^3$, $dP/dt$ is the largest of materials tested to date.
Air Exposure: Ammonia Borane

Real time measurement of composition evolution to complement SRNL calorimetry and SNL flow-through reactor efforts.

Starting Material
Source: Sigma-Aldrich
Preliminary XRD indicates nearly all tetragonal \( \text{NH}_3\text{BH}_3 \) with trace levels of \( (\text{BH}_2\text{NH}_2)_4 \).

TR-XRD of ammonia borane at \( \approx 50\% \) relative humidity and 23°C.

Reactivity with ambient air is very slow relative to some of the other hydrogen storage material candidates (\( \text{NaAlH}_4 \), \( 2\text{LiBH}_4 + \text{MgH}_2 \), ...).
Future Work

**FY09**

Risk Analysis
- Complete compilation of input from Expert Panel for multiple rounds of scoring regarding the on-board reversible risk assessment.
- Refine quantitative ETA / FTA risk analyses for key hazards of the on-board reversible system.

Material Testing & Mitigation
- Complete AX-21 and AlH₃ testing.
- Develop and test risk mitigation methods.
- Design and construct powder cycling and dispersion apparatus to subject material to cyclic / vibratory conditions and simulate vessel breach.

Go / No Go decision

**FY10**

Risk Analysis
- Develop quantitative ETA / FTA risk analysis for an off-board regenerated system.
- Pending Go / No-Go decision, determine subscale prototype configuration and conduct related risk analysis.

Material / System Testing & Mitigation
- Refine risk mitigation methods.
- Pending Go / No-Go, develop and test representative subscale prototype.
Objective: Develop a greater understanding of the relationships between material reactivities and the acceptance of automotive systems.

Approach: Due to the objective complexity and scope, establish a multi-organization, multi-national collaborative team.

Scope: 

Materials: metal hydrides, chemical hydrides, adsorbants
- $2\text{LiBH}_4 + \text{MgH}_2$
- $\text{AlH}_3$
- $\text{NH}_3\text{BH}_3$
- Activated carbon

Methods:
- Qualitative & quantitative risk analyses
- Materials testing ranging from mechanistic to combined effects. Integration into reactivity & spatial / scaling modeling.
- Development of mitigation methods & demonstrations.