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: 90%

Budget

- Funding received in FY09
  - $400K
- Funding for FY10
  - $350K

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
  J. Khalil, United Tech. Res. Ctr., USA
- **D. Dedrick,** Sandia NL, USA
- **T. Autrey**, PNNL, USA
- **R. Zidan**, SRNL, USA

Relevance – Objectives

The objective 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.**

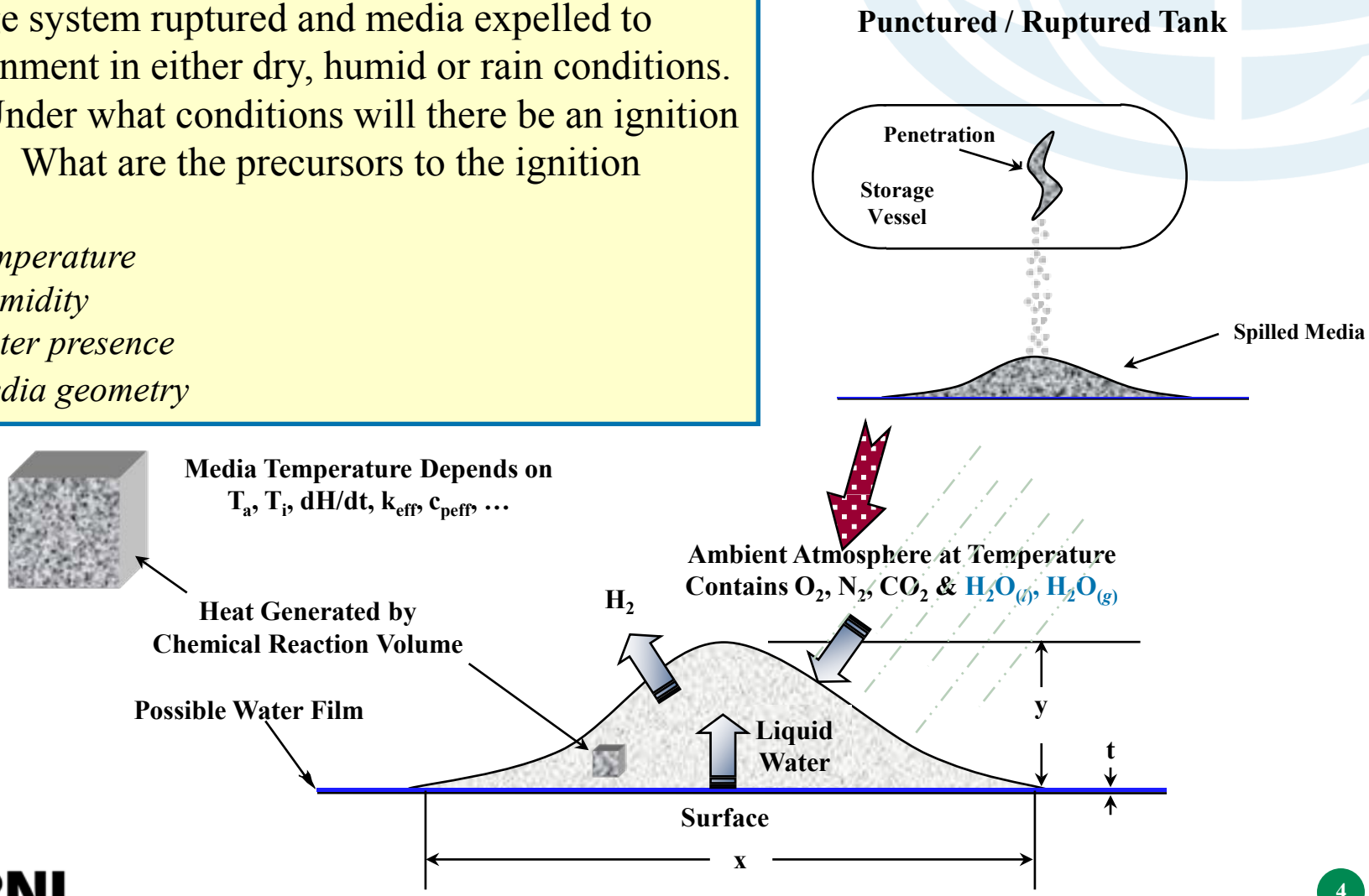
Relevance – Modeling and Risk Mitigation

Special thanks to United Technologies Research Center for their collaboration

Accident Scenario (from UTRC risk assessment): Storage system ruptured and media expelled to environment in either dry, humid or rain conditions.

Risk: Under what conditions will there be an ignition event? What are the precursors to the ignition event?

- *Temperature*
- *Humidity*
- *Water presence*
- *Media geometry*



Approach – Materials Test Plan

- The priority of materials to be analyzed is being conducted in consultation with the three Materials CoE's, HSECoE and DoE. This includes metal hydrides, chemical hydrides, and adsorbents.
- Tested (UN Testing and Calorimetry):
  - $2LiBH_4 \cdot MgH_2$
  - NH_3BH_3
  - $8LiH:3Mg(NH_2)_2$
  - Activated Carbon
  - AlH_3 (in progress)
- Modeling:
  - $2LiBH_4:MgH_2$
  - NH_3BH_3
  - AlH_3

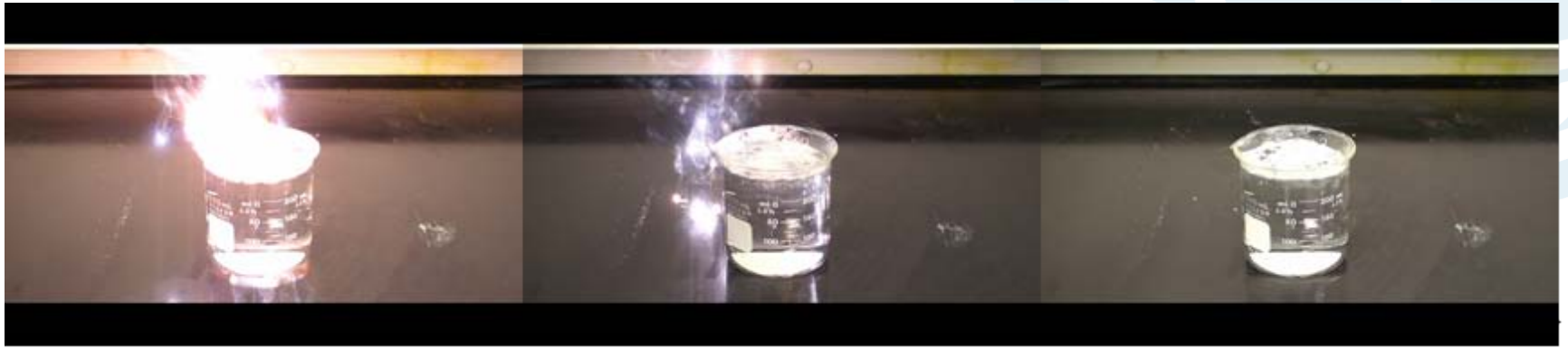
Approach – UN Test Summary

Special thanks to AIST for their collaboration

Material / UN Test	State	Pyrophoricity	Self-Heat	Burn Rate	Water Drop	Surface Contact	Water Immersion
$2LiBH_4 \cdot MgH_2$ SRNL	C	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated ~300 °C within 5 min at as T_{oven} = 150 ° is approached.	Flame propagated in 5 sec with burn rate of 52 mm/sec.	2 H_2O drops required for near-instant ignition.	Material ignited	No ignition event recorded. Gas evolved at longer times. (5 min)
NH_3BH_3 SRNL	C	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated ~300 °C within 10 min, 5 min at T_{over}=150 °C	Flame propagated 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
$3Mg(NH_2)_2 \cdot 8LiH$ AIST	C	Ignition event recorded in room temp experiment	Material failed pyrophoricity test	Flame Propagates at 463 mm/sec	Material ignited	Material ignited	Not tested

- **Flammability**
  - *Flammability Test*
  - *Spontaneous Ignition*
  - *Burn Rate*
- **Water Contact**
  - *Immersion*
  - *Surface Exposure*
  - *Water Drop*
  - *Water Injection*

Technical Accomplishments and Progress – Alane Water Immersion Test



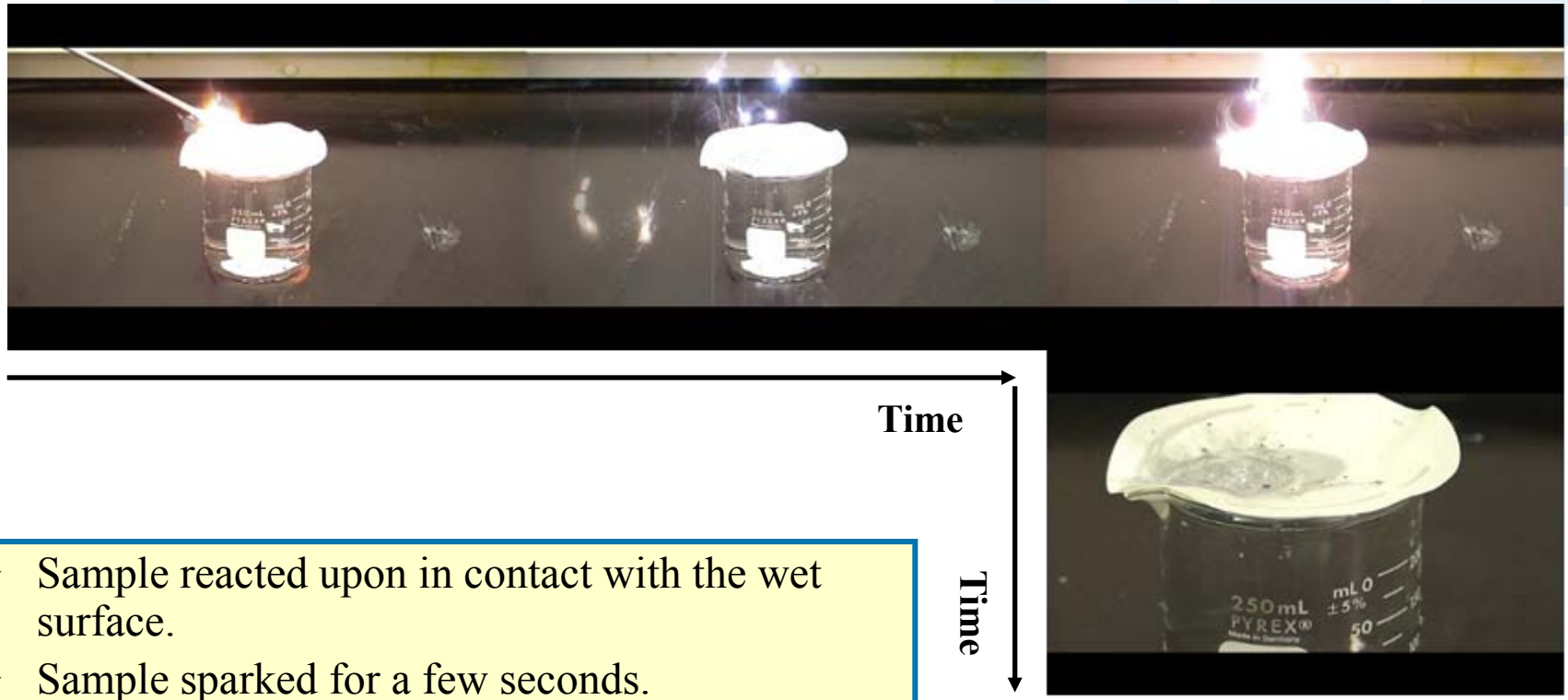
- Material was synthesized chemically (Finholt et al. J. Chem. Soc., 69 (1947))
- Identity of material was confirmed by XRD as α-AlH3 with aluminum impurity. A crystallite size of 40 nm was calculated by Sherrer method. (R. Zidan, SRNL)
- Material sparked upon contact with water. Precipitate formed upon completion of reaction.

Technical Accomplishments and Progress – Alane UN Water Drop Test

Time

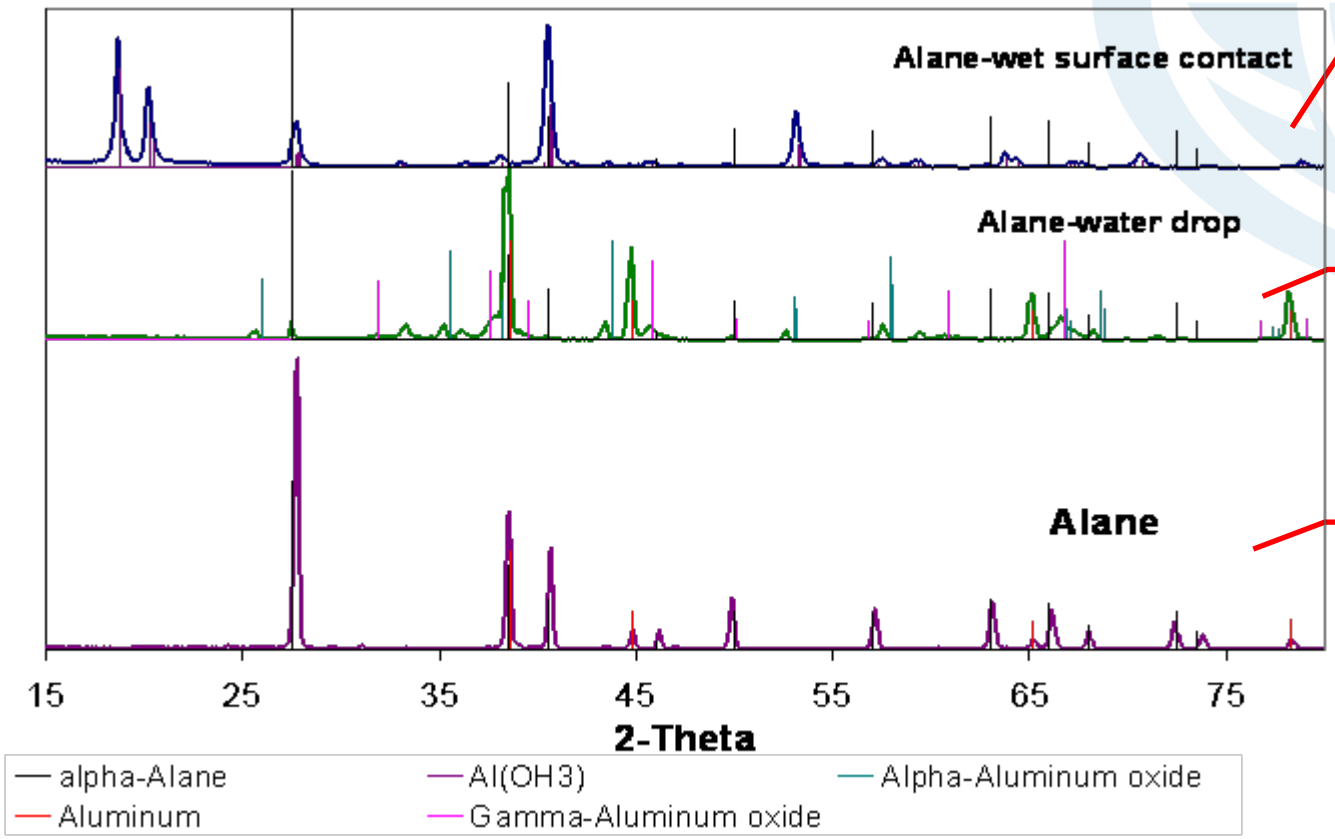
- A conical-shaped pile of Alane was set. A water drop is added on the top of the pile.
- Sample reacted upon contact with water, initiating an ignition event. The pile showed an orange-white flame.

Technical Accomplishments and Progress – Alane Wet Surface Contact



- Sample reacted upon in contact with the wet surface.
- Sample sparked for a few seconds.
- Residual material bubbled for about 15 minutes.

Technical Accomplishments and Progress – XRD Results for Alane Water Reactivity



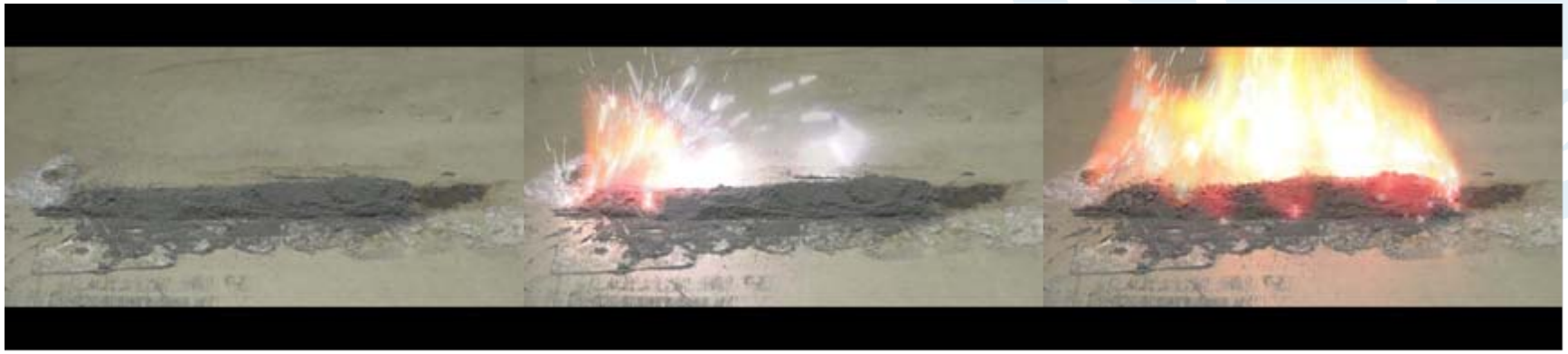
$Al(OH)_3$, α-AlH_3

Al, α-AlH_3, α-Al_2O_3, γ-Al_2O_3

α-AlH_3, Al

- In the Water Drop Test, the heat generated by droplet initiates the combustion of Alane that forms primarily aluminum oxide.
- The larger amount of water present in the Wet Surface Contact Test, dissipates heat to avoiding ignition beyond sparks. Material releases hydrogen as it produces aluminum hydroxide.

Technical Accomplishments and Progress – Alane Burn Rate Test

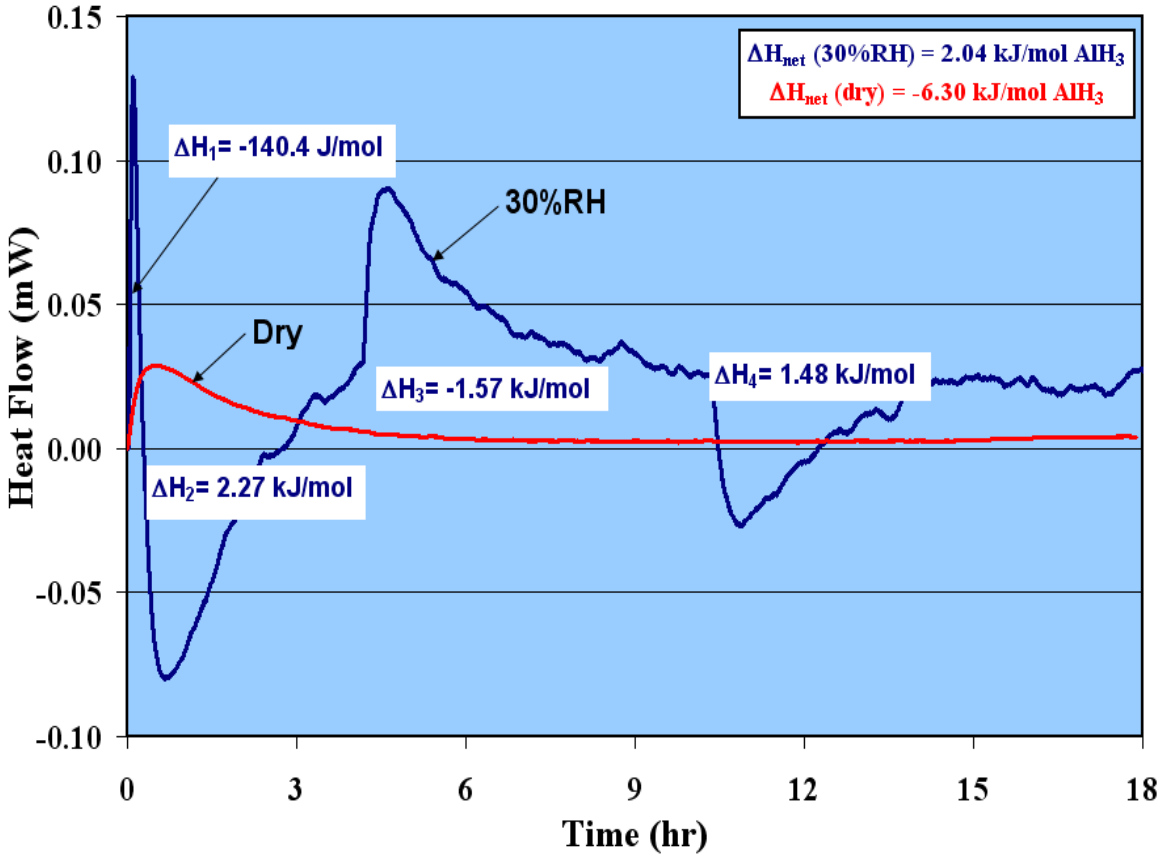


- Modified scale burn rate test was conducted (100 mm L x 10 mm H x 20 mm W).
- Test result validity has been assessed with other materials (~3% difference).
- Flame propagation rate ~ 250 mm/sec.

Reactivity Rank:

$8LiH:3Mg(NH_2)_2$ > AlH_3 > $NaAlH_4$ > $2LiBH_4:1MgH_2$ > NH_3BH_3

Technical Accomplishments and Progress – Isothermal Calorimetry of Alane: Air exposure at 40 °C



$$2AlH_3 \rightarrow 2Al + 3H_2$$

- The initial exothermic event (ΔH_1) is due to the water vapor interaction with AlH_3.
- A competing effect is believed to take place between the dehydrogenation of AlH_3 (endothermic) and the oxidation of Al (exothermic).
- Subtle changes in crystal structure are difficult to identify from reacted samples by XRD. In-situ XRD and NMR studies are currently underway to understand this behavior.

Approach – Model Development

Model 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**

- **Phase 1 – Proof of Concept** ← **Finished**
  - Test the capabilities of off-the-shelf modeling software to capture the physics
    - Incorporate heat transfer, fluid dynamics, species generation, and chemical reactions
    - Use generic material properties and constant heat and mass generation source.
- **Phase 2 – Simple, "1-D" geometries**
  - Use realistic materials
    - Non-constant H_2 and Heat generation sources (time dependent) from calorimetry data
    - Implement simple kinetics models tuned to match experimental results
  - Identify measurements needed in future experiments
- **Phase 3 – Model "3-D" experiments**
  - Expand one-dimensional model to represent two- and three-dimensional experiments
  - Add temperature, pressure, and composition dependence to the kinetics

Technical Accomplishments and Progress – Phase 2: "1-D" Sphere of $2LiBH_4 \cdot MgH_2$

Special thanks to Sandia National Laboratories for their collaboration

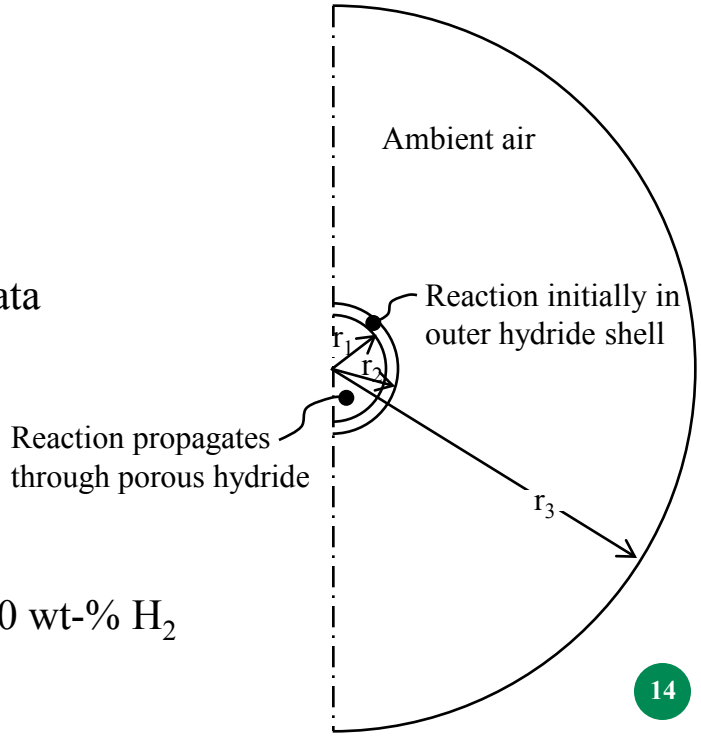
FLUENT model:

- 2-D, double-precision, axisymmetric
- Pressure-based, 2nd-order implicit, unsteady formulation
- Laminar Viscosity
- Heat transfer and Species models enabled
- Built-in hydrogen-air reaction enabled

Model	r_1 (in)	r_2 (in)	r_3 (in)
0 in	0.00	0.05	10.05
¼ in	0.20	0.25	10.25
½ in	0.45	0.50	10.50
1 in	0.95	1.00	11.00
1.5 in	1.45	1.50	11.50
2 in	1.95	2.00	12.00
2.5 in	2.45	2.50	12.50

Material Properties – porous $2LiBH_4 \cdot MgH_2$:

- Porosity (ε) = 0.5
- Particle Diameter (D_p) = 3.7×10^{-6} m
- Density (ρ) = 0.927 g/m^3
- Thermal conductivity (k) = 0.5 W/m-K
- Specific heat (C_p) = 1.583 J/g-K
- Heat & Mass Generation – based on SRNL's Calorimetry data
  ($2LiBH_4 \cdot MgH_2$ reacted with liquid water at 70 °C)
- Reaction propagation = 0.03 mm/s
  (from Sandia's contamination model by Dedrick et al.)



Initial conditions:

- Dry air @ 1 atm & 298 K
- Dry air is 76 wt-% N_2, 23.4 wt-% O_2, 0.6 wt-% H_2O, and 0.0 wt-% H_2

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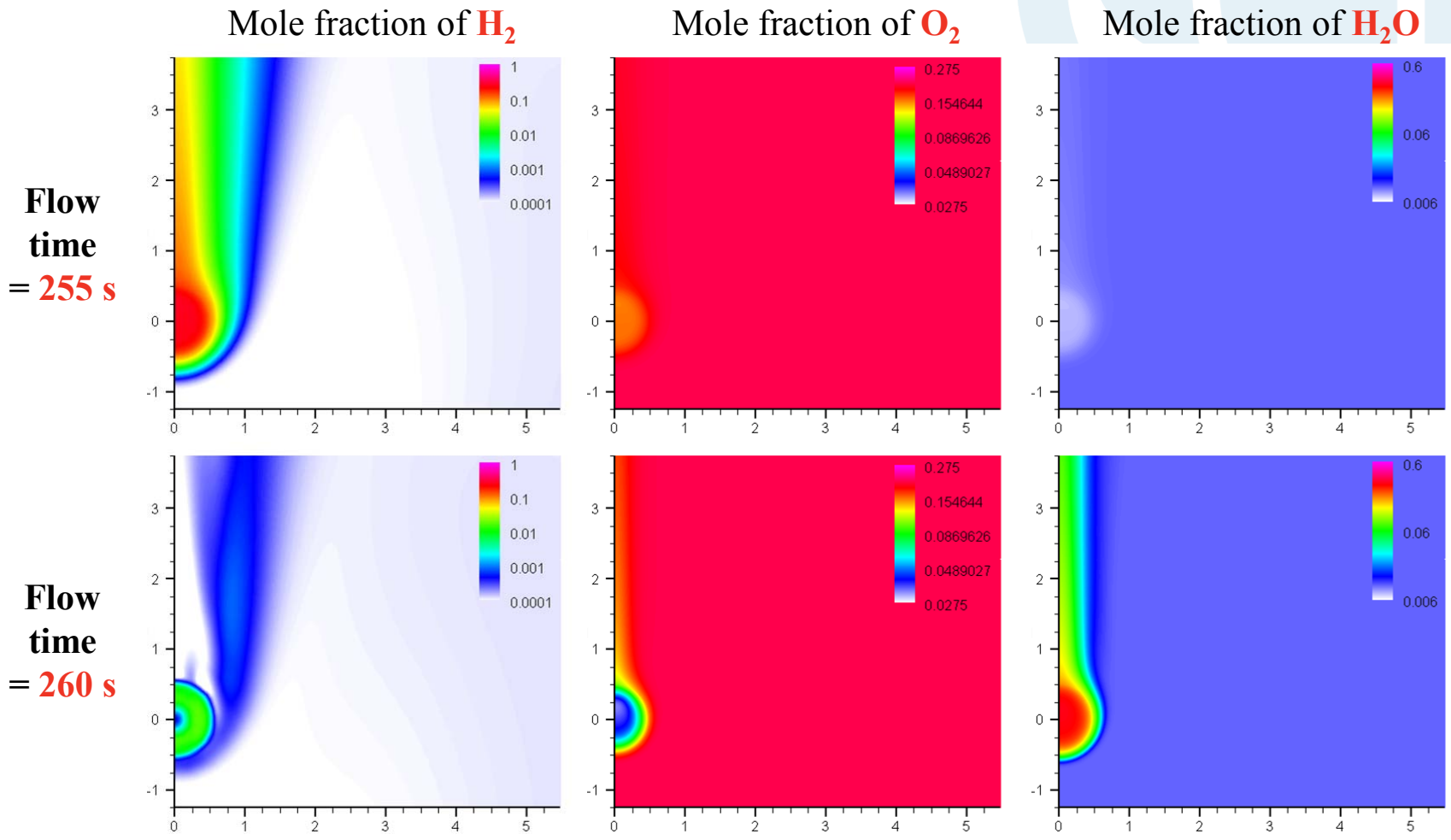
Technical Accomplishments and Progress – Phase 2: $2LiBH_4 \cdot MgH_2$ Sphere with 0.50" Radius



$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

- Maximum mole fraction of H_2 is 26.6% (> LEL).
- Maximum temperature is 571°C (within the hydride, near the surface).
- Ignition event occurs between 255 and 260 seconds.

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Technical Accomplishments and Progress – Phase 2: $2LiBH_4 \cdot MgH_2$ Sphere Results

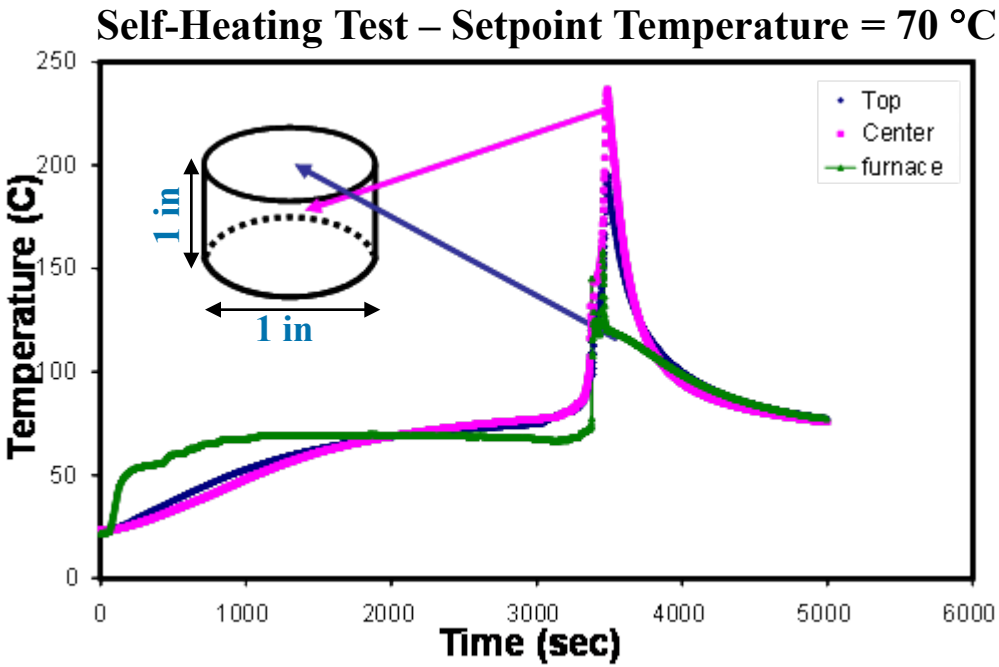
Model	Ignition Event	H_2 mole fraction	Temperature
0.05 in	None	Maximum value of 0.0123 at t = 160s	Maximum temperature of 164.2°C at t = 300s
0.25 in	None	LFL reached between t = 55s and 60s Max of 0.135 at t = 230s	Maximum temperature of 752.4°C at t = 370s
0.50 in	Between t = 255s and 260s: H_2 mf = 0.266 and 0.015 Temp = 569°C and 571°C	LFL reached between t = 30s and 35s Max of 0.266 at t = 255s	Maximum temperature of 1422°C at t = 540s

- Models can be used to examine several parameters quickly, such as pellet size.
- **Pellet size can be used as a mitigation strategy:**
  - **No ignition event occurred for pellets with radii of 0.25 inches or smaller.**
  - **The smallest pellet never reached the LFL.**
  - **As pellet size increased, the time required to have an ignition event decreased.**
- Similar results were shown when the pellet was initialized with ambient air or hydrogen gas filling the porous space.

Approach – Phase 3: NH_3BH_3 Cylinder Self-Heating

- **Model additions:**
  - Temperature dependent material properties.
  - Temperature and concentration dependent reaction kinetics.
  - Change modeling package from FLUENT to COMSOL.
- **Cylindrical self-heating test data:**
  - Experimental differences between the cylinder and cube self-heating tests
    - Identical experimental chamber and setup
    - Similar volumes: Cube volume = 1 in^3; Cylinder volume = 0.8 in^3
  - A 2-D cylinder is simpler to model than a 3-D cube
    - Reduces model size (number of equations) and calculation time (time to convergence)
- **Ammonia Borane (NH_3BH_3):**
  - Ammonia Borane is one of the hydrides of interest to the Hydrogen Storage Engineering Center of Excellence (HSECoE).
    - Well-studied, high capacity hydride with advantageous reaction rate.

Technical Accomplishments and Progress – NH_3BH_3 Cylinder Self-Heating Results



- Sample begins to self-heat after about 58 minutes
  - Time at set-point = 1 min
- Maximum Temperature observed = 236°C
- No ignition event was observed

Approach – Phase 3: NH_3BH_3 Cylindrical Model

Special thanks to Pacific Northwest NATIONAL LABORATORY for their collaboration

COMSOL model:

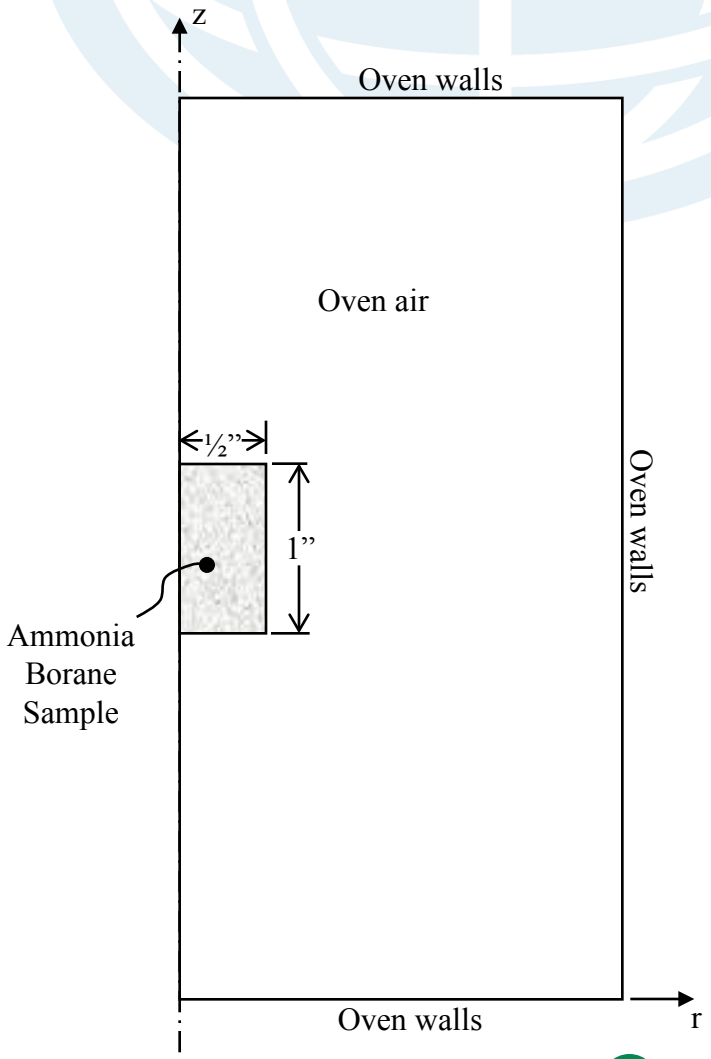
- 2-D, double-precision, axisymmetric
- Conduction and Convection Heat Transfer
- Species Convection and Diffusion
- Continuity
- Chemical reaction kinetics – f(T, P, C, t)

Material Properties – porous NH_3BH_3:

- Bulk Density (ρ) = 0.765 g/cm^3
- Thermal conductivity (k) → temperature dependent correlation **based on PNNL data**
- Specific heat (C_p) → temperature dependent correlation **based on Florida Solar Energy Center data**
- Heat Generation → temperature dependent correlation **based on SRNL calorimetry data**
- Mass Generation → temperature dependent correlation **based on mix of PNNL data and SRNL calorimetry data**

Initial conditions:

- Dry air in an oven (self-heating test) @ 1 atm & 250 °C



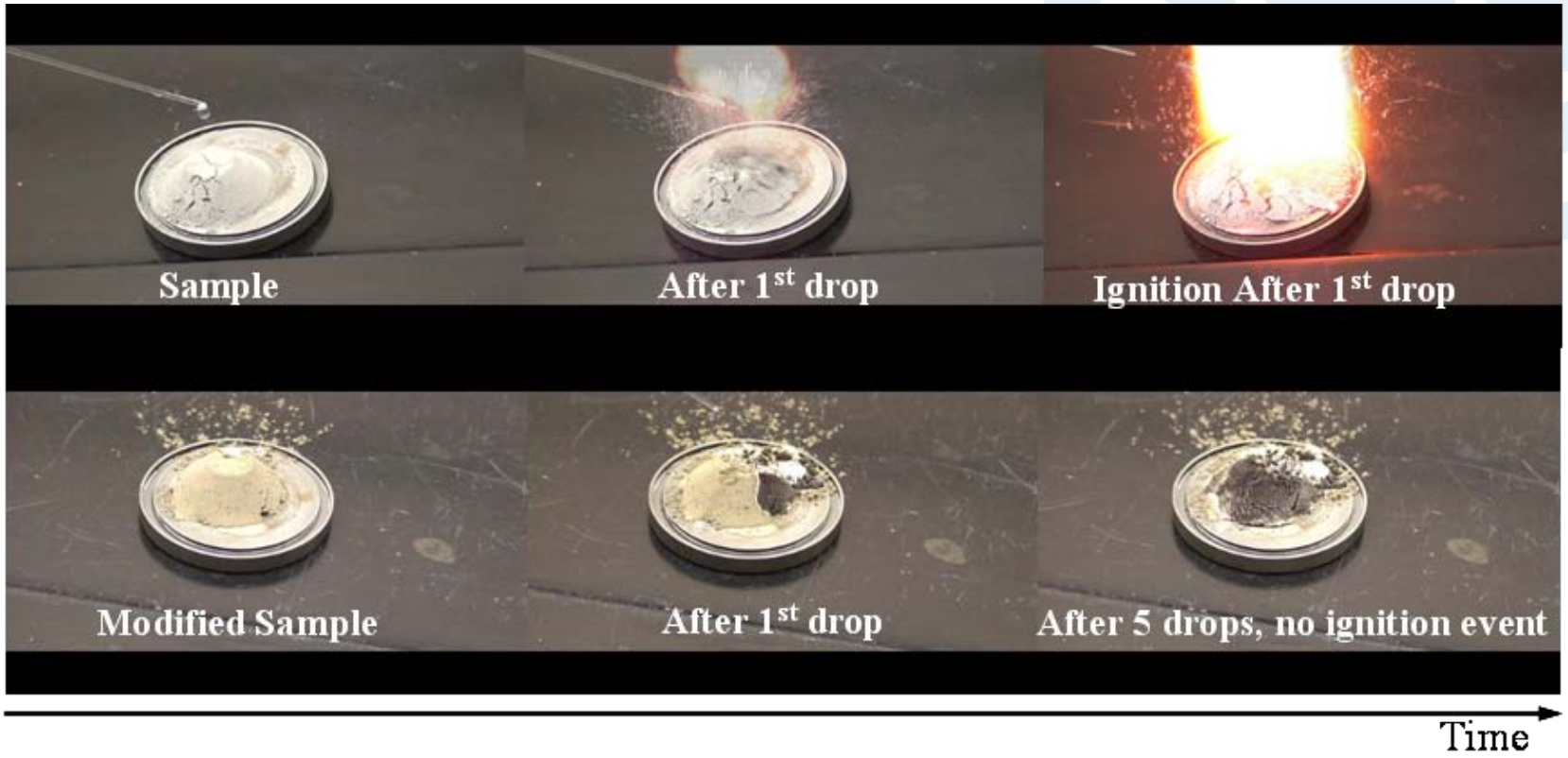
Approach – Risk Mitigation

Special thanks to HSECoE for their collaboration

- Four risk mitigation strategies (A, B, C, D) have been identified.
- Currently submitted for invention disclosure.
- Tests are being conducted on materials based on information provided by the HSECoE. These materials include:
  - $8LiH:3Mg(NH_2)_2$
  - $2LiBH_4:1MgH_2$
  - $NaAlH_4$+4% (mol) $TiCl_3$
- Testing strategies include:
  - UN Water Drop Testing
  - Water Vapor Calorimetry
  - Cycling Experiments w/ Seivert's Apparatus

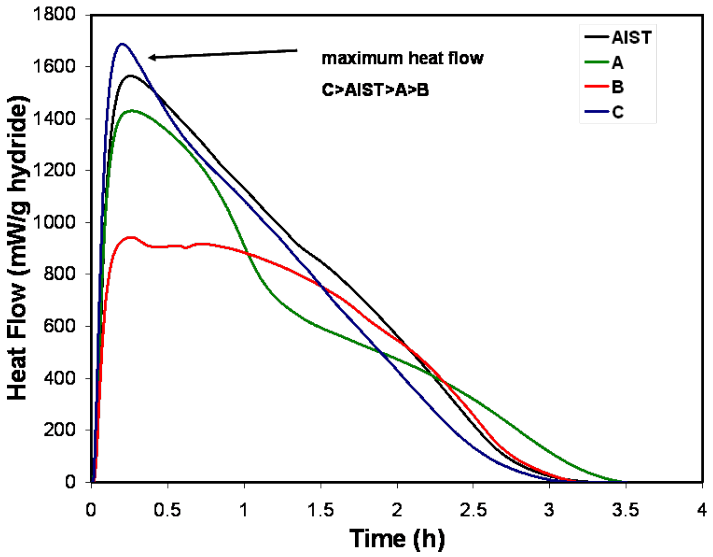
Approach – 8LiH:3Mg(NH$_2$)$_2$ Water Drop Test

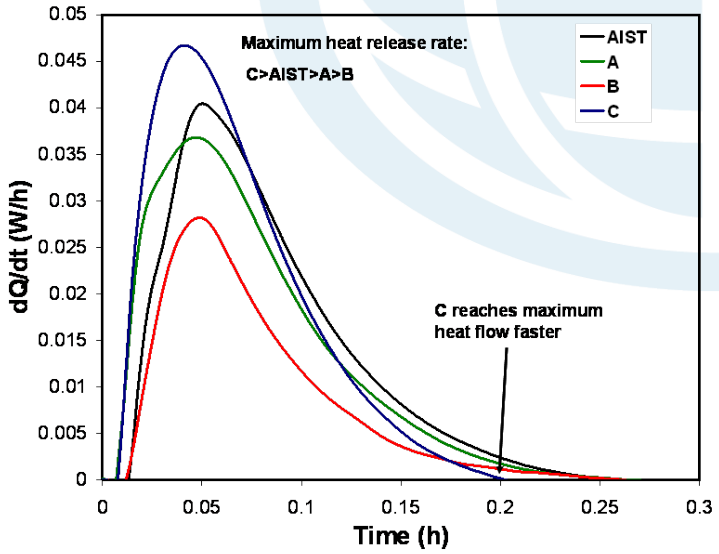
Special thanks to AIST for their collaboration



- Reactivity towards water is reduced.
- Risk mitigation strategy A avoid ignition event characteristic of unmodified sample

Technical Accomplishments and Progress – Risk Mitigation-Calorimetry, T=40°C, RH=30%





- **Comparable heat release for unmodified samples to A and C.**
  - **Mitigant might not be affecting the release of hydrogen**
- **The rate of heat release:**
  - **C > AIST > A > B**
- The maximum is achieved faster by sample C
- B has lowest total heat release

Summary

- A modified burn rate test has been developed and verified using less than ½ the material required for the standard burn rate test.
- Alane has unique environmental reactivity properties; non-pyrophoric, but highly water-reactive resulting in "sparking" as opposed to ignition.
- Modeling has been used to determine a critical radius for pelletization of $2Li(BH_4)$-MgH_2.
- The self-heating test has been modified to a cylindrical geometry to more thoroughly support the modeling effort.
- Four mitigation strategies have been evaluated preliminarily and several have been promising enough to be evaluated under cyclic sorption conditions.

Proposed Future Work

- Conclude the modeling effort through Phase 3
  - NH_3BH_3 (in progress)
  - AlH_3
- Conclude the UN testing and calorimetry of Alane.
- Conclude the UN testing of various metal hydrides mixed with automotive fluids.
- Experimentally verify the pellet size results from Phase 2 of the modeling effort.
- Utilize newly purchased high pressure DSC to improve the reaction rate calculations of the metal hydrides for the modeling effort.