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

SRNL SAVANNAH RIVER NATIONAL LABORATORY

Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft

AIST

Institut de recherche sur l'hydrogène Université du Québec à Trois-Rivières

Kidde Fenwal

Sandia National Laboratories

United Technologies Research Center

Relevance - Objectives

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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Task Plan

Risk Assessment and Standardized Test Development **1**	Chemical Kinetics & Thermodynamics Measurements **2**
Numerical Simulation **3**	
Risk Mitigation **4**	

Mitigation strategies are being developed based on experimental and numerical results

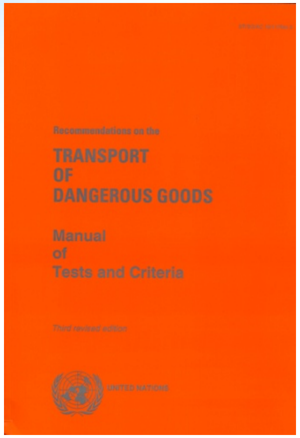
Numerical Simulation is being built on top of the existing experimental work

Program began with standardized testing and calorimetric analysis

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:
  - $2LiBH_4{\cdot}MgH_2$
  - NH_3BH_3
- Investigating:
  - activated carbon, AX-21
  - AlH_3

Material Standardized Testing (DE-FC36-02AL67610)

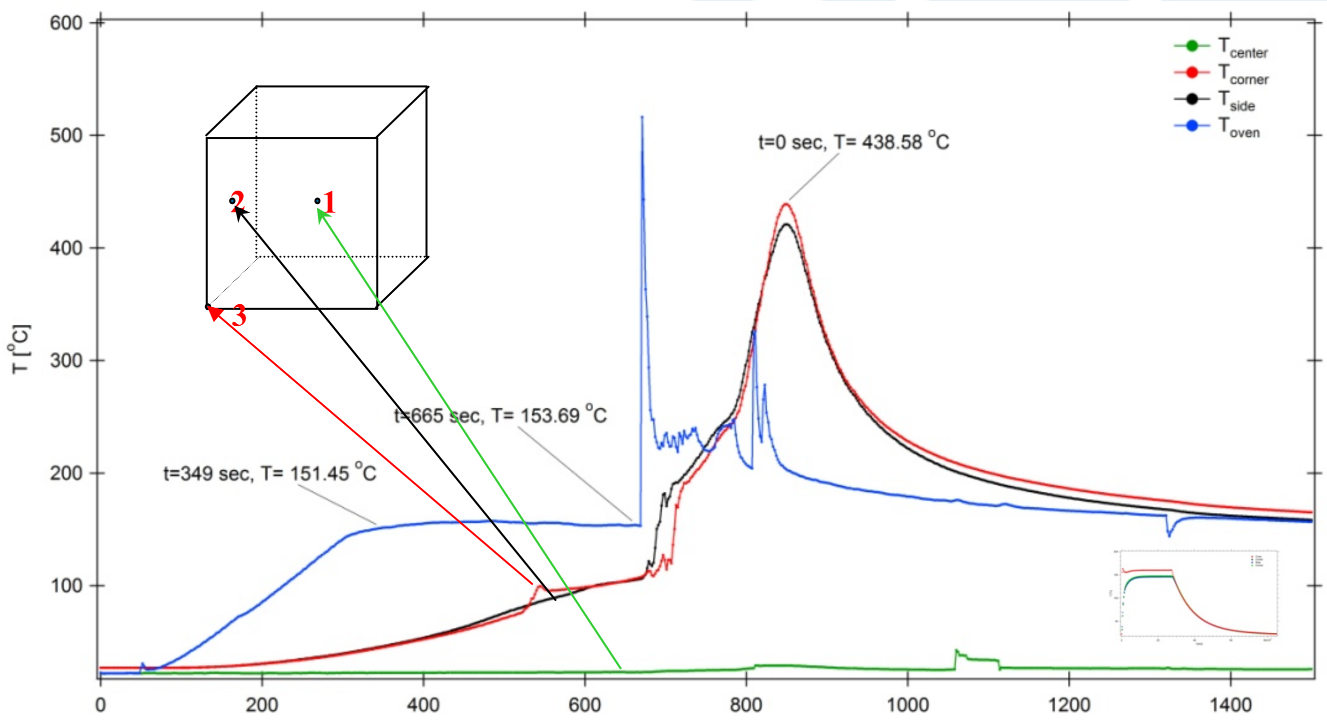


DOT/UN Doc., *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 3rd Revised Ed., ISBN 92-1-139068-0, (1999).

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

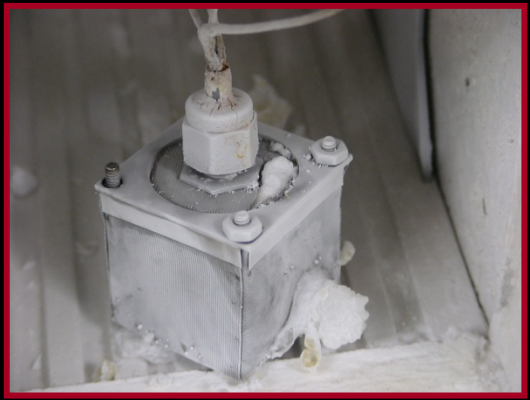
NH_3BH_3 Self-Heating Results

- 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**

NH_3BH_3 Self-Heating & Burn Rate



- **NH_3BH_3 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
  - $NaAlH_4$ (51 mm/sec)
  - $2LiBH_4 \cdot MgH_2$ (52 mm/sec)

UN Test Summary

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)
	D	Not tested	Not tested	Not tested	1 H_2O drop required for near-instant ignition	Reaction observed with no flame	Reaction observed with no flame
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
	D	Not tested	Not tested	Not tested	No reaction	No reaction	No reaction
$3Mg(NH_2)_2 \cdot 8LiH$ AIST	C	Ignition event recorded in room temp experiment	Material failed pyrophoricity test	Flame Propagates at 463 mm/sec	Not tested	Material ignited	Not tested
	D	Ignition event recorded in room temp experiment	Material failed pyrophoricity test	Not tested	Not tested	Not tested	Material ignited

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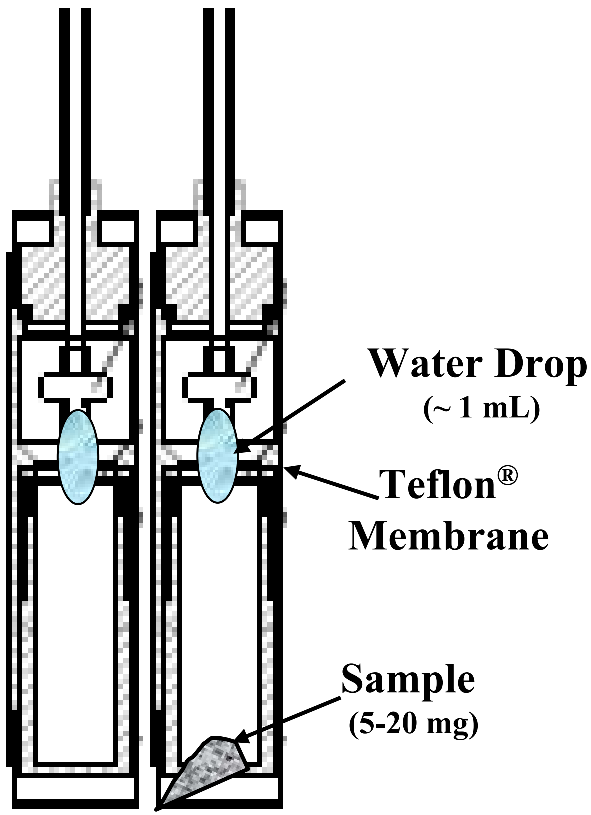
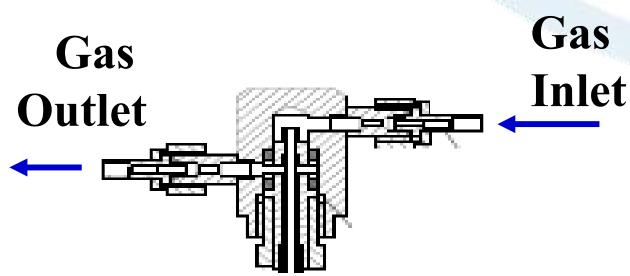
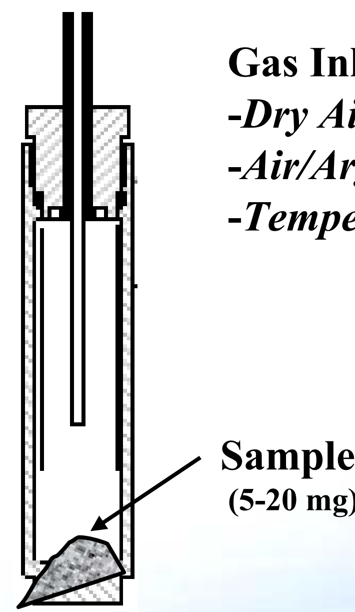
Thermo-Chemical Analysis of Water Contact

Liquid Mixing Cell



Gas Flow Cell





Gas Inlet is a function of:

-Dry Air/Argon

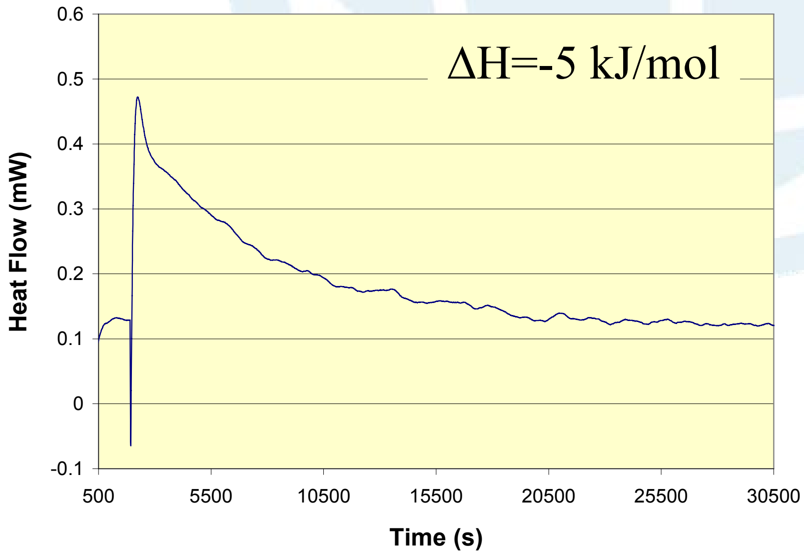
-Air/Argon with water vapor

-Temperature

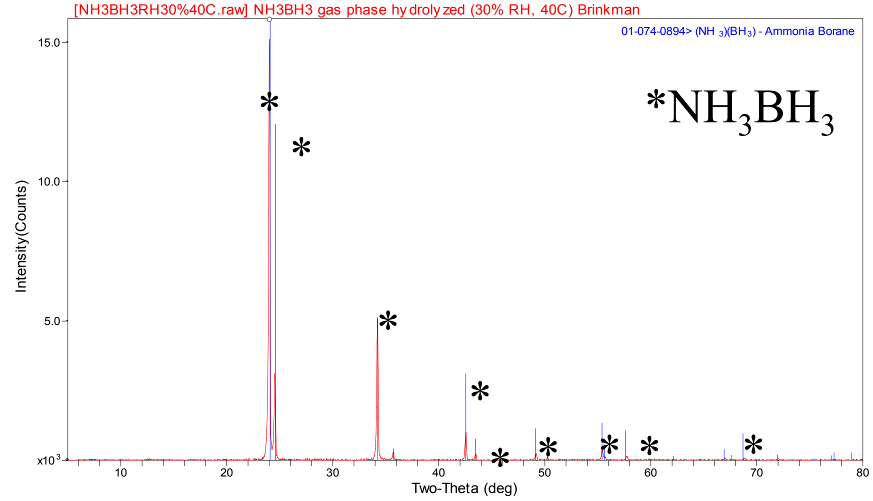
NH_3BH_3 Water Vapor Calorimetry

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_3BH_3



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NH_3BH_3 Water Calorimetry

- **Liquid Phase Calorimetry**

Expect:

$NH_3BH_3 + 2H_2O \rightarrow BO_2^-{}_{(a)} + NH_4^+{}_{(a)} + 3H_2(g)$

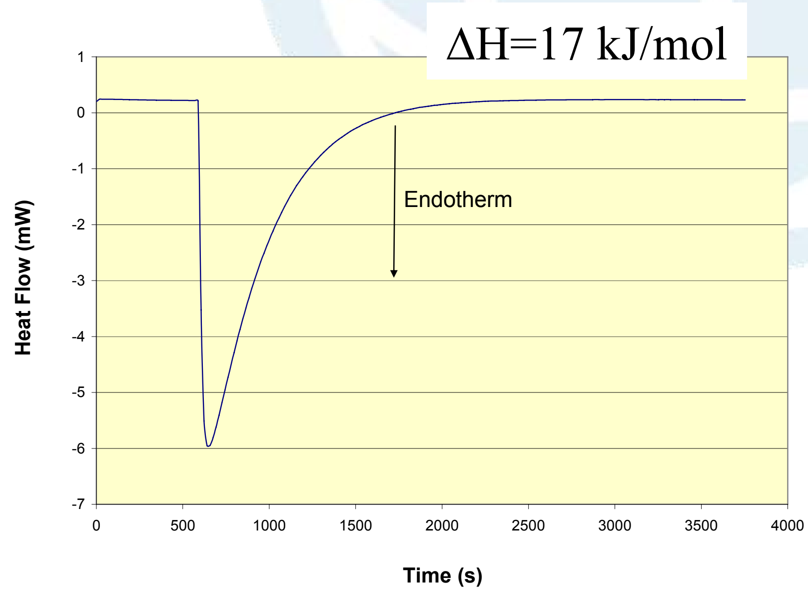
ΔH=- 222 kJ/mol exotherm at 40°C

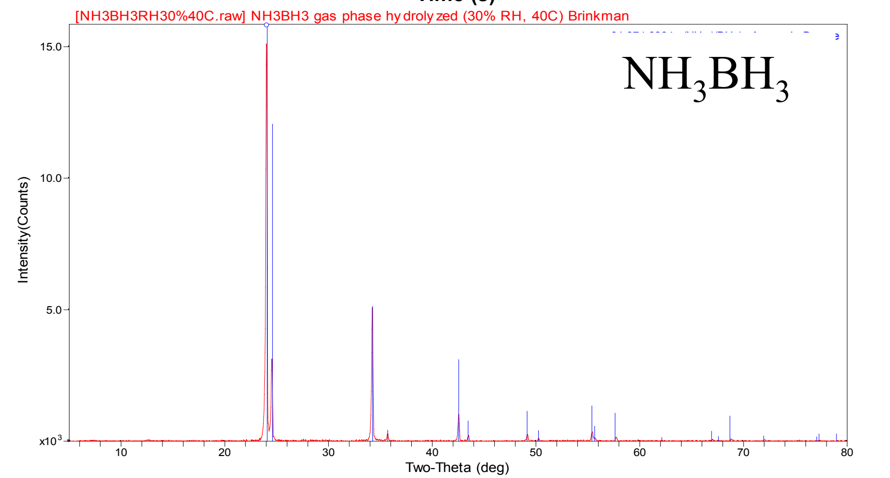
Result:

$NH_3BH_3 + H_2O = NH_3BH_3$ (a)

(dissolved, but solvated or ionic?)

ΔH=17kJ/mol endothermic at 40°C





XRD analysis of crystalline products revealed only starting NH_3BH_3 material present after drying dissolved NH_3BH_3 + H_2O solution

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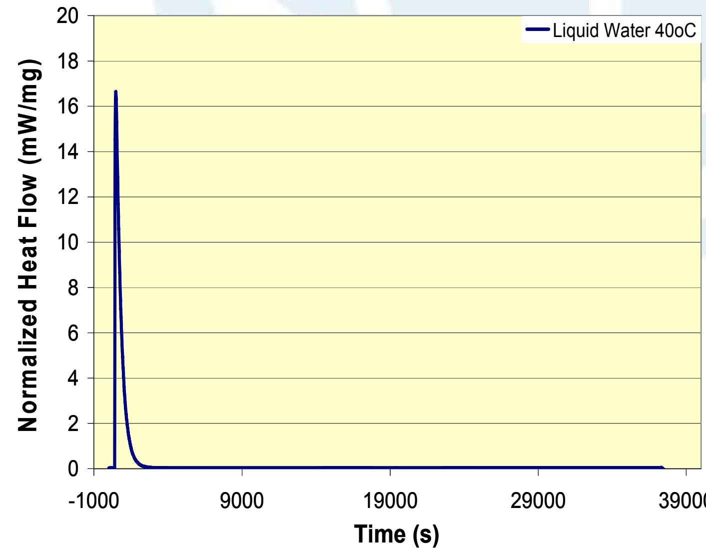
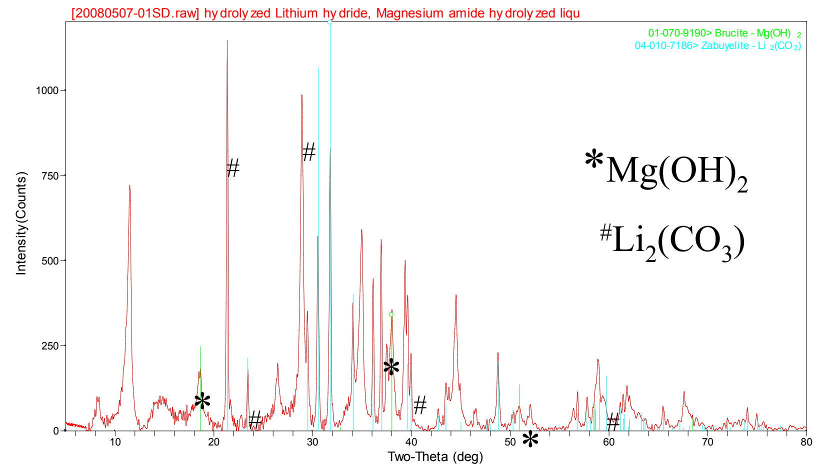
$8LiH+3Mg(NH_2)_2$ Calorimetry

$8LiH+3Mg(NH_2)_2 \rightarrow Mg_3N_2+4Li_2NH+8H_2$
7wt% H_2 $140<T<200^oC$
Nakagawa et. al., 2007



$8LiH+3Mg(NH_2)_2$
Material received from N. Kuriyama, AIST
Liquid water hydrolysis calorimetry at 40^oC



- Bulk of heat released within 15 min.
- XRD analysis of crystalline products revealed $Mg(OH)_2$ and Li_2CO_3 from atmospheric CO_2

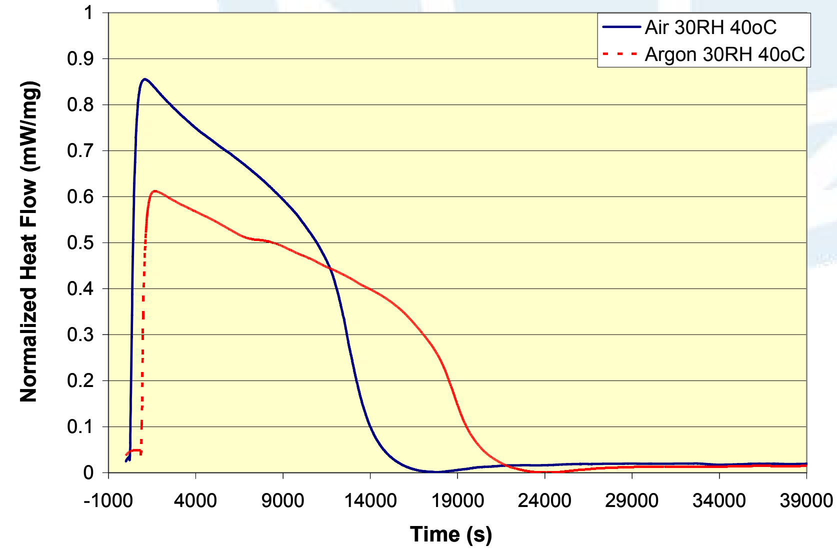
$8LiH:3Mg(NH_2)_2$

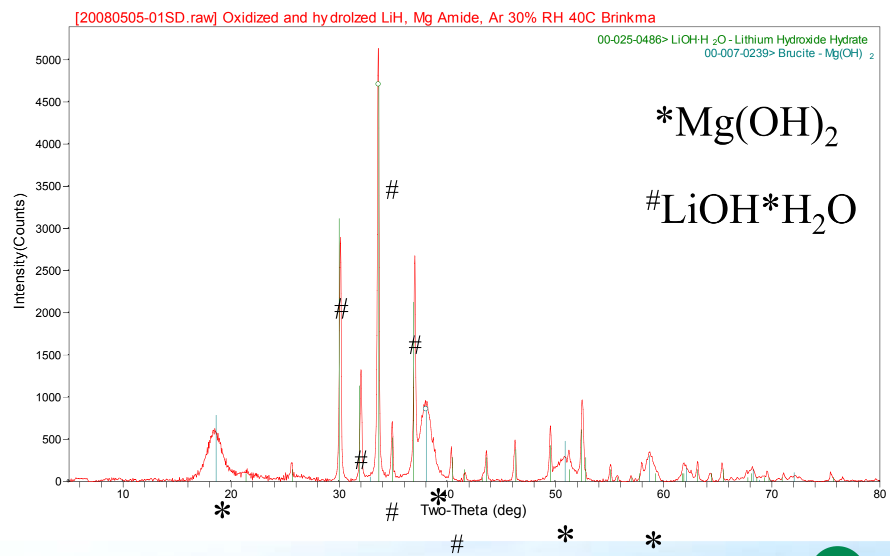
- **Gas Phase Calorimetry**

Air ΔH=171 kJ/mol

Argon ΔH=165 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 $LiOH*H_2O$

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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

Accident Scenario: Storage system ruptured and media expelled to environment in either dry, humid or rain conditions.

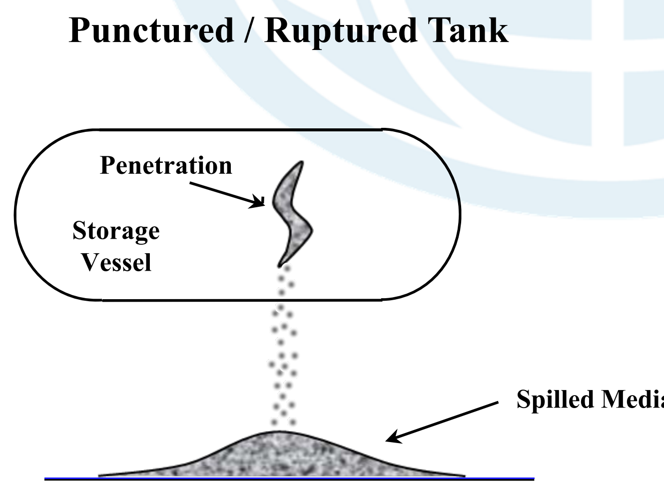
Risk: Under what conditions will the expelled media ignite?

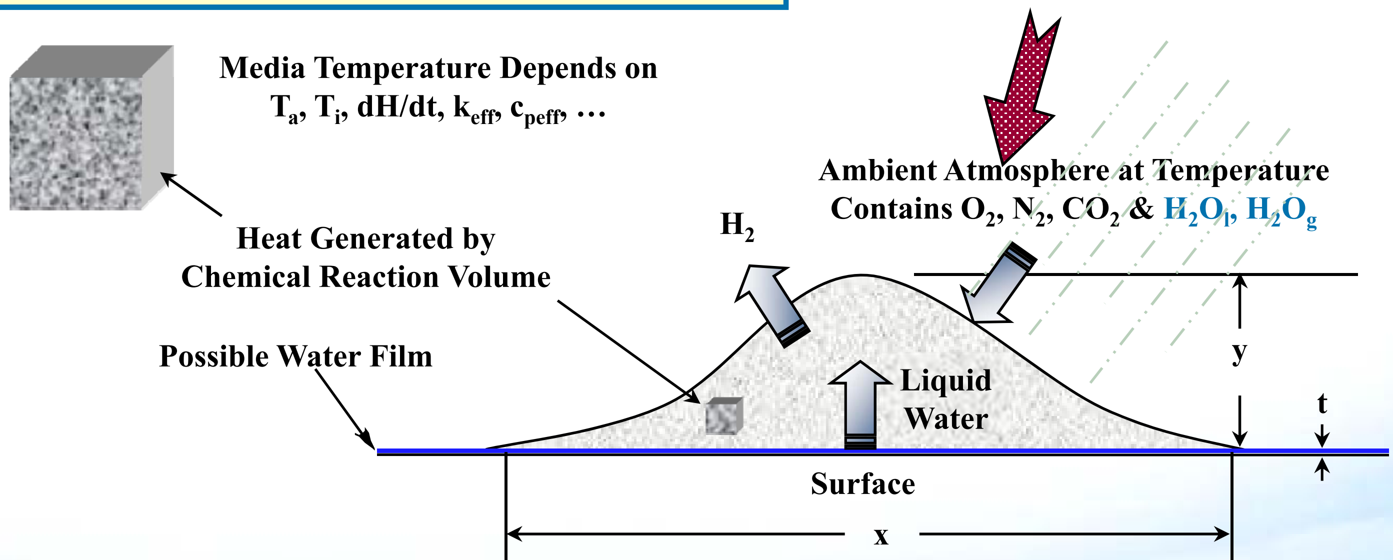
Temperature

Humidity

Water presence

Media geometry





Governing Equations

Mass Balance (Gasses)

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \left(c_i \vec{v}_i\right) = S_i$$

Fluid Motion

$$\frac{\partial}{\partial t}(\rho\vec{v}) + \nabla\cdot(\rho\vec{v}\vec{v}) = -\nabla p + \nabla\cdot\left(\bar{\bar{\tau}}\right) + \rho\vec{g} + \vec{F}$$

$$\bar{\bar{\tau}} = \mu\left[\left(\nabla\vec{v} + \nabla\vec{v}^{T}\right) - \frac{2}{3}\nabla\cdot\vec{v}I\right]$$

Relation Between Pressure Gradient and Mass Averaged Gas Velocity (Blake-Kozeny Equation)

$$\vec{v} = -\frac{D_p{}^2}{150\mu}\left(\frac{\varepsilon}{1-\varepsilon}\right)^2 \nabla P$$

Energy Balance

$$(1-\varepsilon)\left[\rho C_p\right]_{Solid}\frac{\partial T}{\partial t} - \nabla\cdot k\nabla T = -\varepsilon\left[\rho C_p\right]_{gas}\left(\frac{\partial T}{\partial t} + \vec{v}\cdot\nabla T\right) + \frac{1}{T_{ref}}\left(\frac{\partial P}{\partial t} + \varepsilon\vec{v}\cdot\nabla P\right) + Source$$

Diffusion Equations (Stefan-Maxwell) - Could Use Fick's as Well

$$\frac{\nabla c_i}{c} = -\sum_{j=1}^{n}\frac{x_i x_j\left(\vec{v}_i - \vec{v}_j\right)}{Đ_{ij}/\tau}$$

Rate Equations

$$\frac{1}{V}\frac{\partial n_i}{\partial t}\bigg|_{Reaction} = f_i\left(\underline{c}_{gas}, \underline{c}_{Hyd}, T, P\right) \quad \textbf{Gasses}$$

$$\frac{1}{V}\frac{\partial n_{Hyd\ j}}{\partial t}\bigg|_{Reaction} = f_j\left(\underline{c}_{gas}, \underline{c}_{Hyd}, T, P\right) \quad \textbf{Solids}$$

Total Gas Concentration

$$c = \sum_{1=1}^{n} c_i$$

Gas Pressure

$P = cRT$ **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

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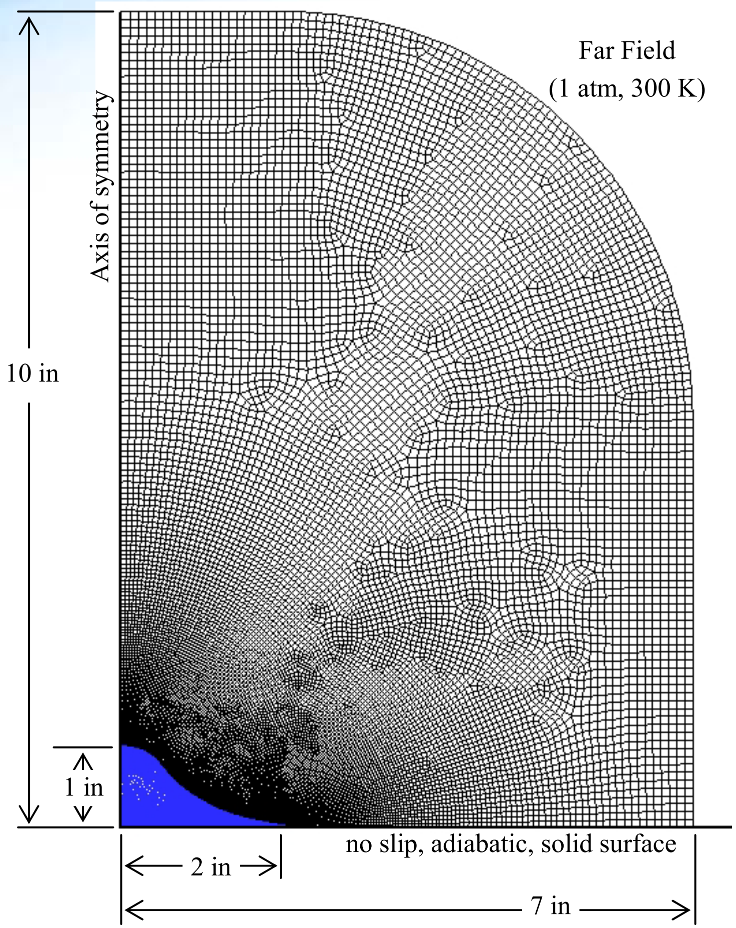
Modeling Approach

- **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

Phase Introduced	Parameter Name	Symbol
I	Bed porosity	ε
I	Mean particle diameter	D_p
I	Solid phase specific heat	$C_{p\ Solid}$
I	Bed thermal conductivity	k
I	Particle mass density of bed	ρ_{Solid}
I	Heats of reaction	ΔH_{Rxn}
II	Gas component kinetics	$\left.\frac{\partial n_i}{\partial t}\right\|_{Reaction}$
II	Solid component kinetics	$\left.\frac{\partial n_{Hyd\ j}}{\partial t}\right\|_{Reaction}$
III	Bed tortuosity factor	τ
III	Wetted interface velocity	v_{wet}

Phase I Model (Assumed Heat & Mass Generation Rates)



Grid Information:

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

FLUENT model:

- 2-D axisymmetric
- Double-precision
- Pressure-based, 2nd-order implicit, unsteady formulation
- Laminar Viscosity
- Heat transfer and Species models enabled

Material Properties – porous $NaAlH_4$:

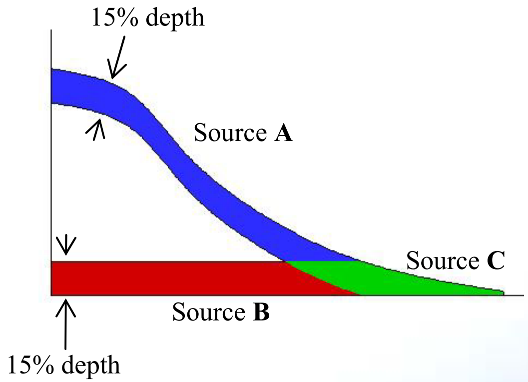
- Porosity (ε) = 0.5
- Particle Diameter (D_p) = 3.7×10^{-6} m
- Density (ρ) = 720 kg/m^3
- Thermal conductivity (k) = 0.325 W/m-K
- Specific heat (C_p) = 820 J/kg-K
- Heat Generation ≤ 40,000 J/mol (**overall heat of reaction for $NaAlH_4$ from NaH**)
- Mass Generation ≤ 0.5 kg H_2/m^3-s (**loading based on DOE 2010 Technical Target**)

Initial conditions:

- Dry air @ 1 atm & 298 K
- Dry air mass fraction is 80% N_2, 20% O_2

Phase I Model Accident Scenarios

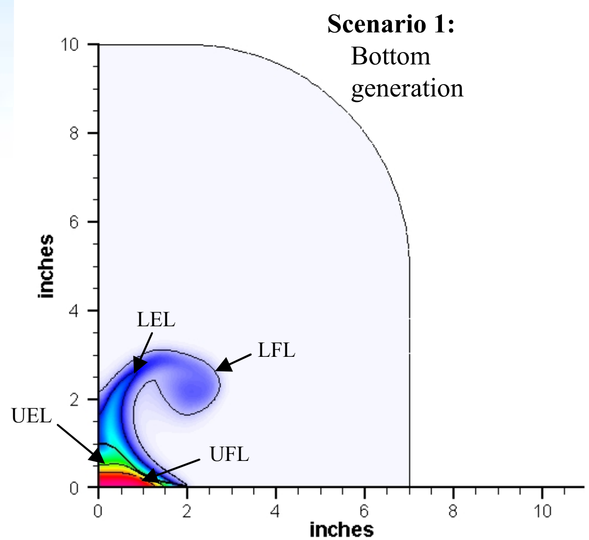
Scenario	Description	Generation
1. Bottom only	Material on wet surface in dry air	Sources **B** and **C**: Heat Generation = 40,000 J/mol Mass Generation = 0.5 kg H_2/m^3-s
2. Top only	Material on a dry surface with the pile exposed to 30% RH air	Sources **A** and **C**: Heat Generation = 12,000 J/mol Mass Generation = 0.15 kg H_2/m^3-s
3. Dual with reduced source	Material on a wet surface with the pile exposed to 30% RH air	Source **A**: Heat Generation = 12,000 J/mol Mass Generation = 0.15 kg H_2/m^3-s Sources **B** and **C**: Heat Generation = 40,000 J/mol Mass Generation = 0.5 kg H2/m^3-s
4. Dual with full source	Material on a wet surface in the rain	Sources **A**, **B**, and **C**: Heat Generation = 40,000 J/mol Mass Generation = 0.5 kg H_2/m^3-s

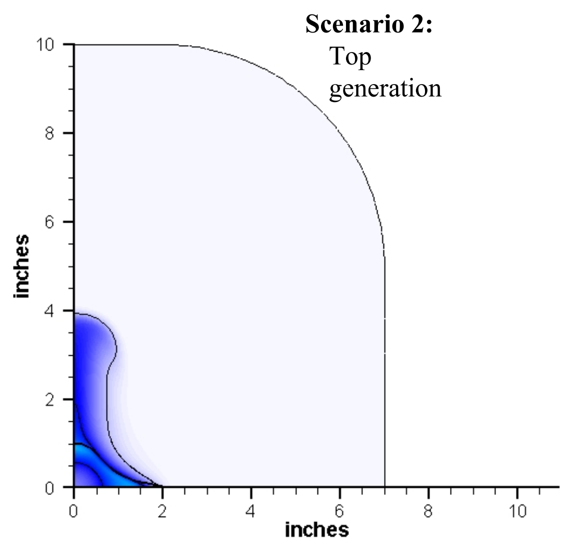


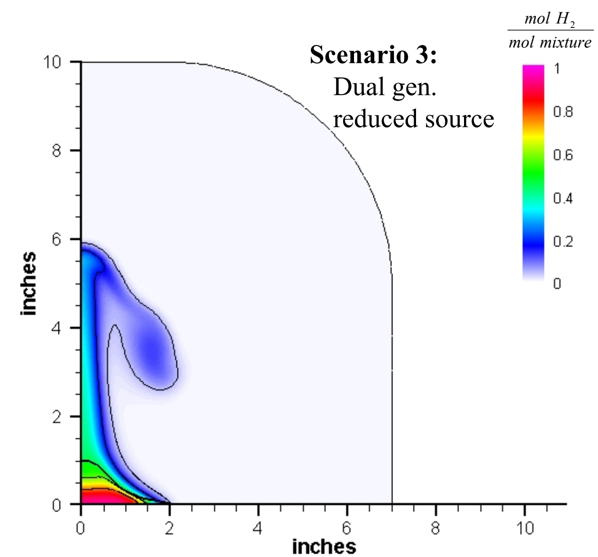
Note: Heat and mass generation sources remain **constant** throughout the simulations.

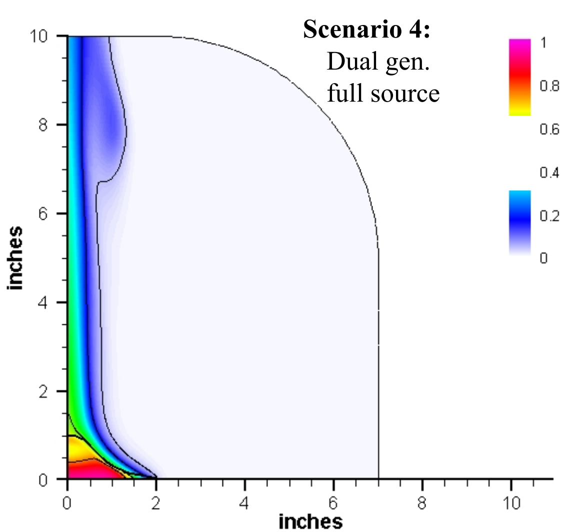
Phase I Model Results: H_2 Generation

Flow time = 1.0 seconds







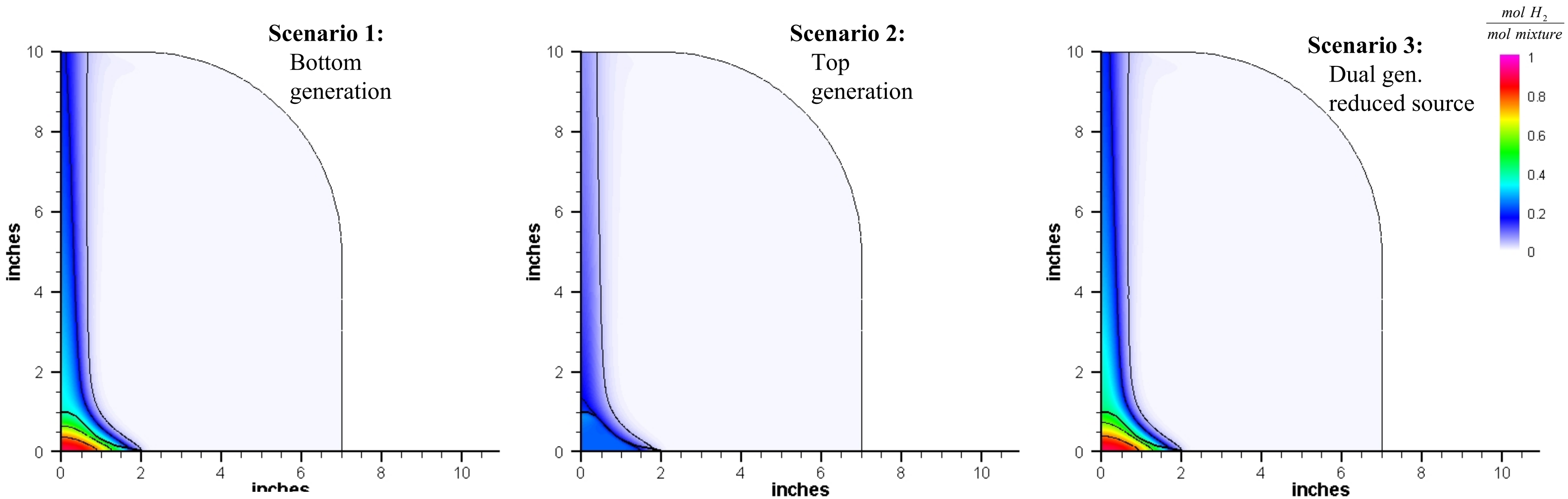


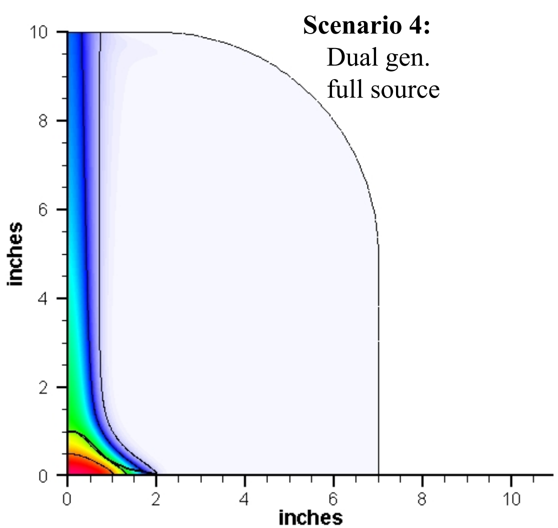
With assumed heat and mass generation…

- 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



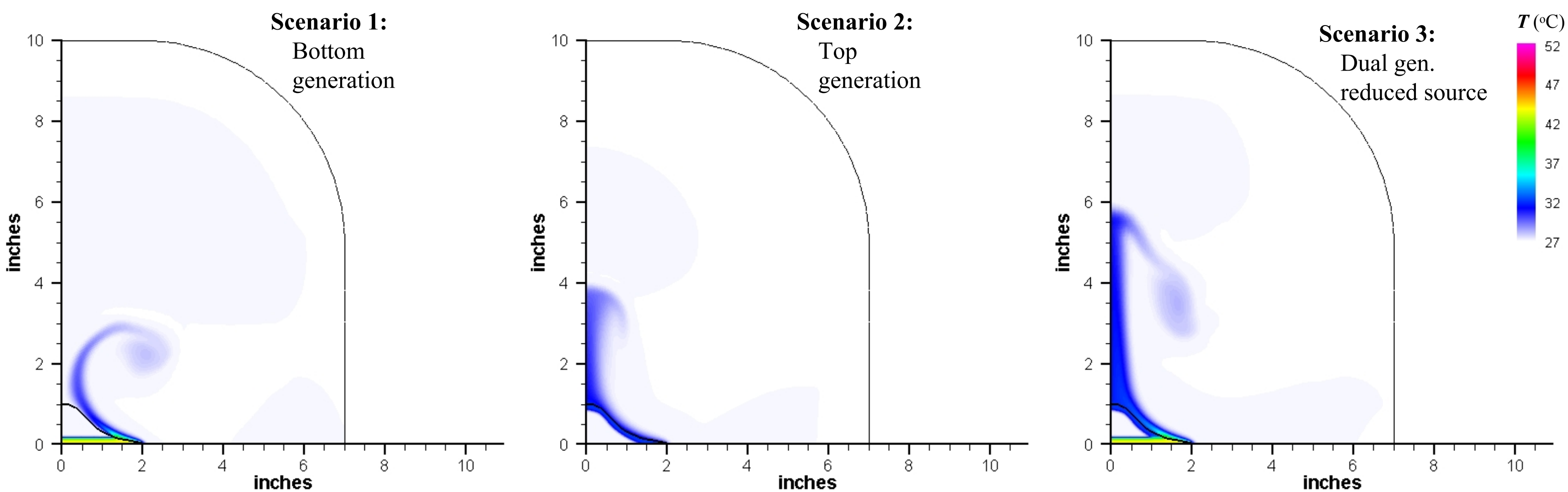


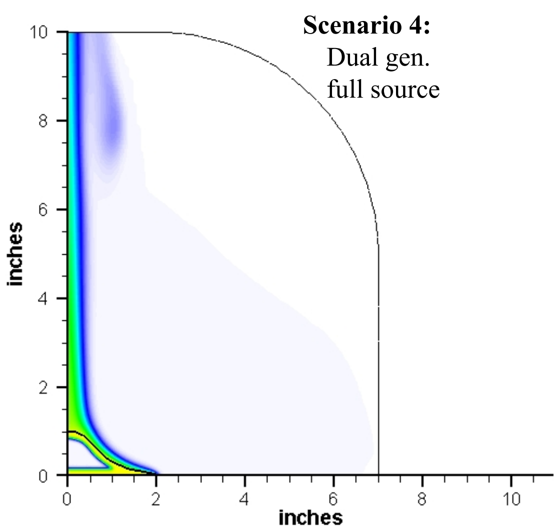
<u>With assumed heat and mass generation</u>…

- **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



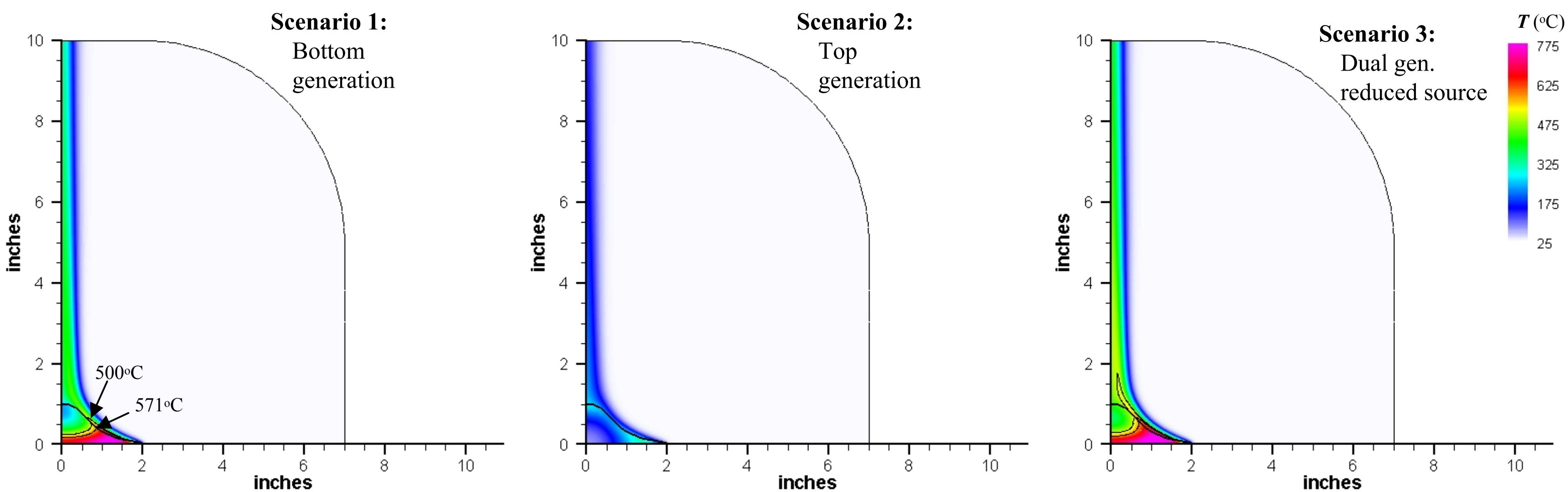


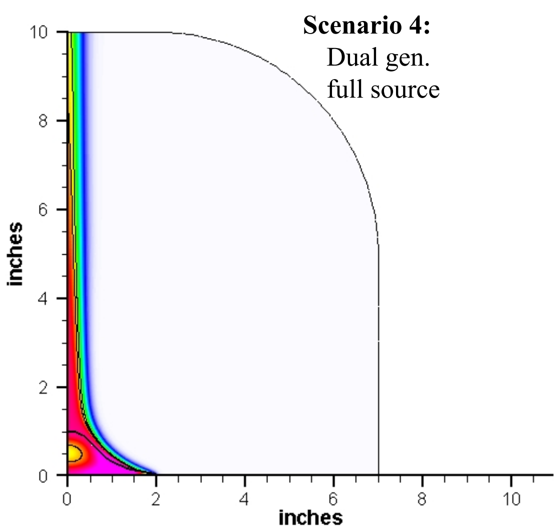
With assumed heat and mass generation…

- **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





With assumed heat and mass generation…

- The auto ignition temperature for H_2 (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**

  →
  - Test additional model scenarios
  - Explore additional 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)
  - Alter the model to account for the rate of reaction, changes in generation rate, etc.
  - Update material properties (based on experimental 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

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 $2LiBH_4 \cdot MgH_2$ and NH_3BH_3 in the fully charged state
- Water contact completed in charged and discharged states
- Calorimetric characterization of NH_3BH_3 completed
- 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 AlH_3 as decided in consultation with the Centers of Excellence**
- **Continue the thermodynamic and kinetic testing with AlH_3 and $LiH:Mg(NH_2)_2$ 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**