Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

The reactivity properties of hydrogen storage materials in the context of systems

2010 DOE FCT Program Annual Merit Review

Daniel E. Dedrick
Sandia National Laboratories
June 9th, 2010

Mike Kanouff, Joe Cordaro, Craig Reeder
Bob Bradshaw, George Sartor, Jay Keller

Project ID
ST013

Overview

Timeline

- Start: July 2007
- End: September 2010
- Percent complete: 75%

Budget

- $2.1M

  (100% DOE H_2 program)
- 750K in FY09
- 310K for FY10

Barriers

On-Board Hydrogen Storage

- –Durability/Operability (D)
- –Codes and Standards (F)
- –Reproducibility of Performance (Q)

Partners

SRNL - Anton
UTRC – Khalil
IPHE

AIST

SRNL™
SAVANNAH RIVER NATIONAL LABORATORY

Kidde Fenwal

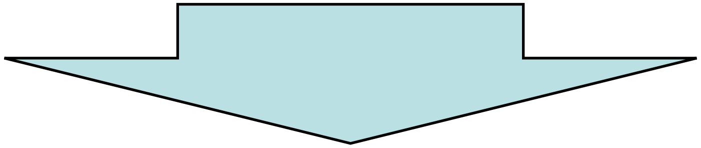
Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

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

United Technologies
Research Center

Relevance: Overall Objective

Understand behavior of hydrogen storage materials and systems in preparation for deployment

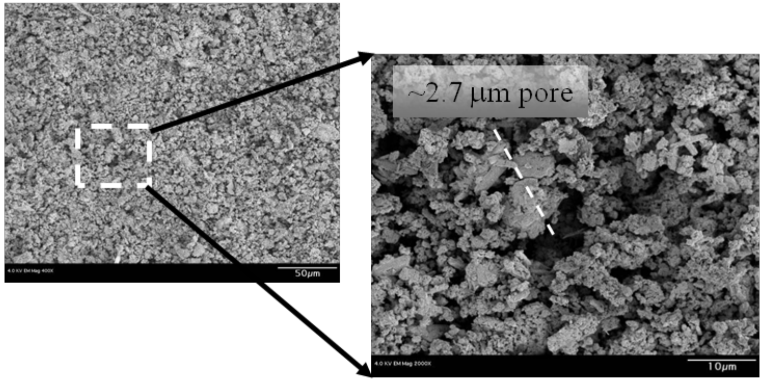


Eventual Impact:

- Enable the design, handling and operation of effective hydrogen storage systems for FCT applications.
- Provide technical foundation for eventual C&S efforts

Relevance: Metal hydrides are reactive

- “Metal hydrides” include a wide range of reactive materials
  - Interstitial hydrides, Laves phase, etc (AB , AB_2 , AB_5 , A_2B)
  - Complexes (alanates, borohydrides, amides, etc)



- Generally, the materials are also reactive with air
  - Pyrophoric
  - Water reactive
  - High surface area

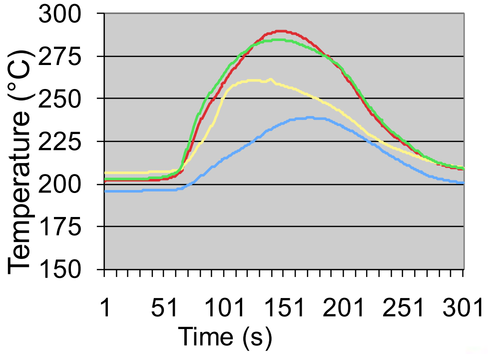
For example: sodium alanates react with dry air:

$$4\ O_2 + 2\ NaAlH_4 \Leftrightarrow 2\ NaOH + Al_2O_3 + 3\ H_2O$$

ΔG	**ΔH**
kcal/mol	kcal/mol
-350.71	-362.23

As with any new technology, unwanted behavior is managed to enable commercialization

Resulting exotherm



Relevance: Metal hydride storage technologies will continue to be developed for FCT applications

A couple of recent R&D examples:

GM/SNL hydride system:

D. Dedrick, "Heat and mass transport in metal hydride based hydrogen storage systems", HT2009-88231 Proceedings of HT2009 ASME Summer Heat Transfer Conference July 19-23, 2009, San Francisco, California

DOE/UTRC hydride system:

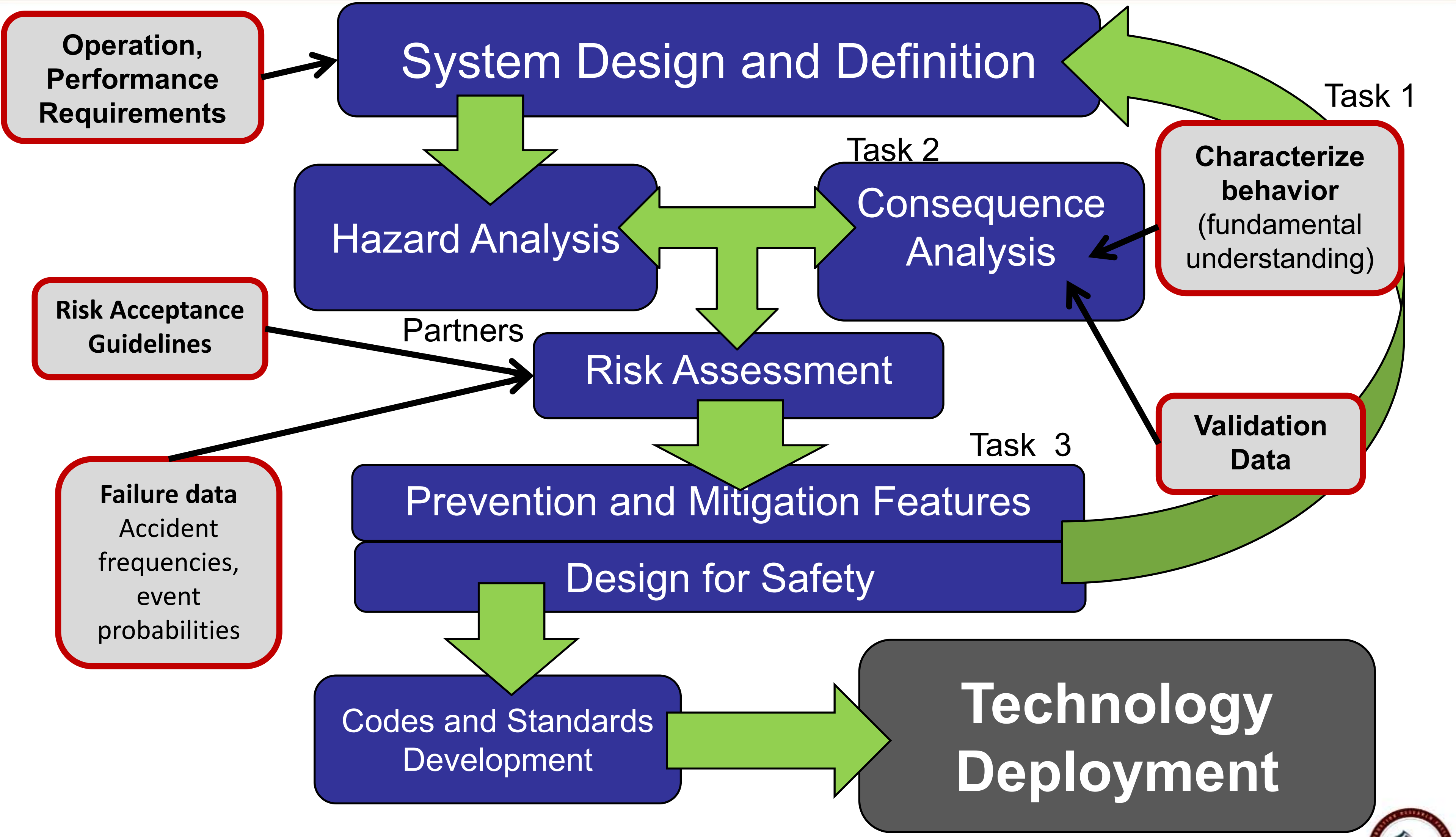
D. Mosher, "High Density Hydrogen Storage System Demonstration Using $NaAlH_4$ Complex Compound Hydrides, 2007 DOE H_2 Annual Peer Review, Arlington, VA May 16, 2007

The future of metal hydrides:

Courtesy of Nuvera fuel cells

We need to understand the behavior of these systems to enable market penetration

Approach: This program develops the key elements to enabling deployment of advanced hydrogen storage technologies



Approach: Project organized into three inter-dependent and collaborative tasks

Task 1 – Characterize Behavior (quantify fundamental processes)

- Illuminates the fundamental contamination mechanisms
- Results in chemical-kinetic reaction models

Task 2 – Consequence analysis (predict processes during accident scenarios)

- Extends process predictive capability to the application scale

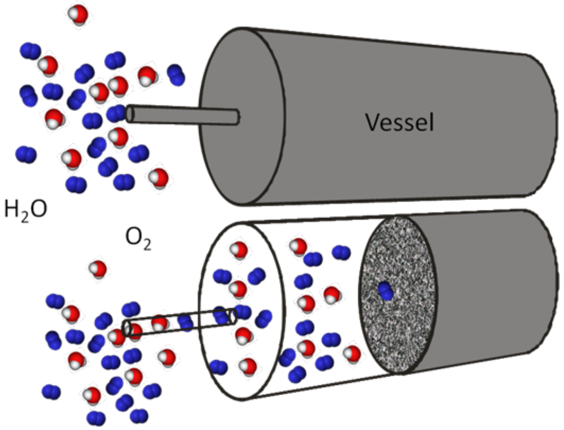
Task 3 – Mitigation (identify and demonstrate hazard mitigation strategies)

- Identify contaminated bed treatment methods
- Assess methods for controlling contamination reactions

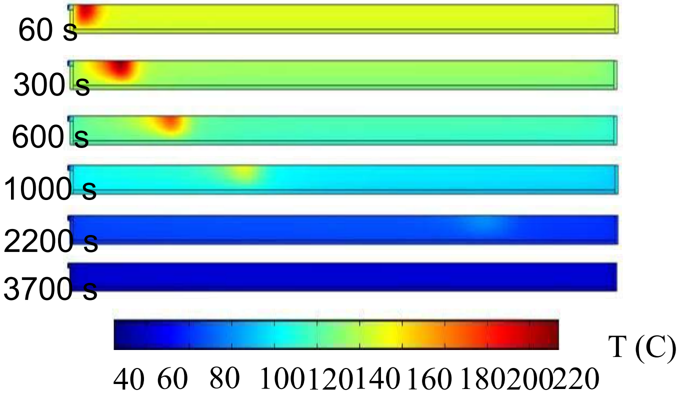
All hydrogen materials are sourced from collaborators (DOE programs, IPHE) to ensure relevance and continuity!

FMEA activities identify two failure modes of interest for consequence analysis

- Breach in tank
  - Plumbing leak
  - Humid air exposure
  - Deterministic modeling indicated an advancing reaction front (FY09)



Reaction front proceeding through a metal hydride bed (FY09)



- Pool or impinging fire
  - Collision with hydrocarbon vehicle
  - Collision with hydrogen fueled vehicle

Fire impingement modeling indicates rapid decomposition is a possible outcome

Fire assumptions:

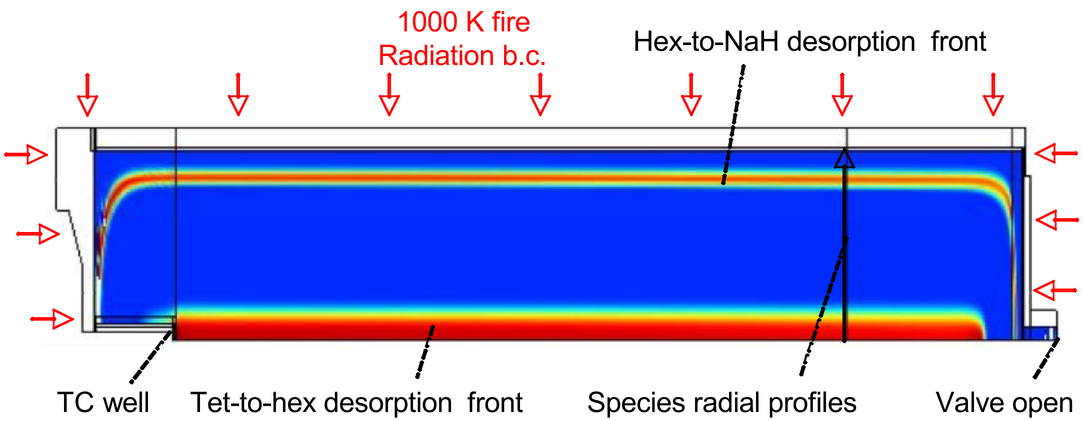
- Fire is represented by a source at a 1000K
- Bed emissivity is 1 (black body)

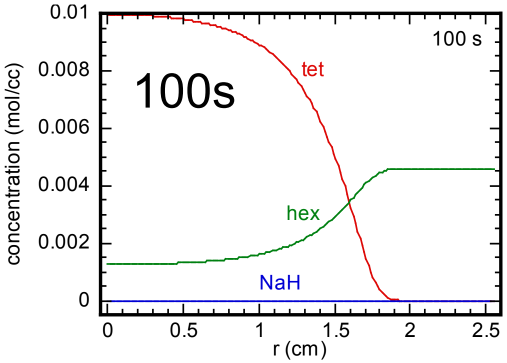
Hydride assumptions:

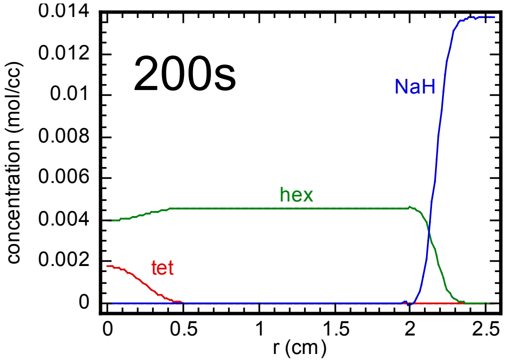
- Modified and catalyzed sodium alanate (tetrahydride)
- No oxidation –assumed to proceed after full release of H_2
- Kinetics of NaH decomposition to Na and H_2 not included

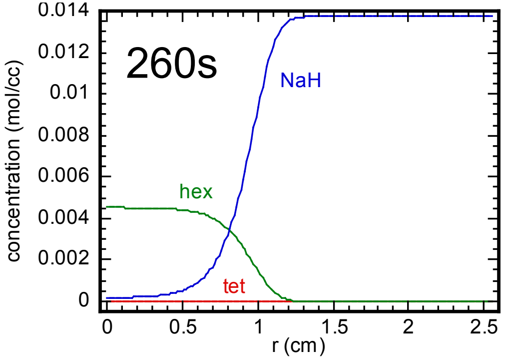
Vessel assumptions:

- PRD fails at full open (open tube)
- Initial temperature of 140 °C
- Bed is 0.3m long and 2.54cm in diameter





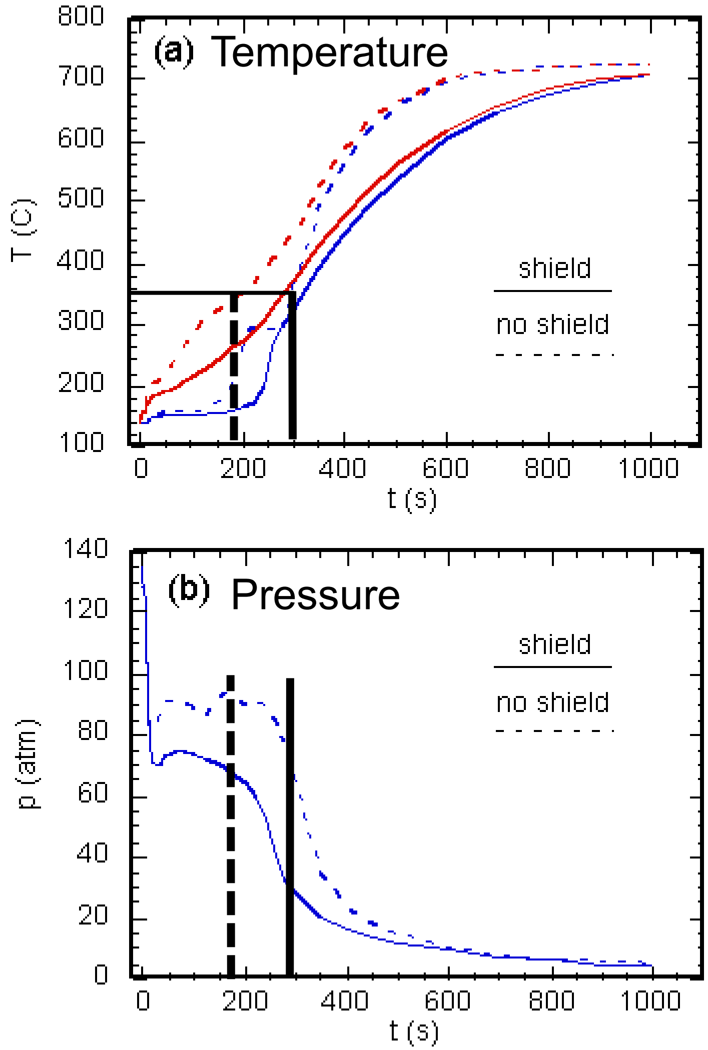




Accomplishment: Heat shielding may provide a good mitigation strategy during fire

- Un-shielded bed
  - Temperatures exceed 350 °C within 180s
  - Decomposition of NaH will begin to occur in the presence of a catalyst
  - The presence of sodium metal is assumed to be undesirable
- Heat shielding mitigation
  - thin metal cylinder forming a ~3mm air gap
  - Over temperature delayed to 300s

Enables science-based design recommendations and code development

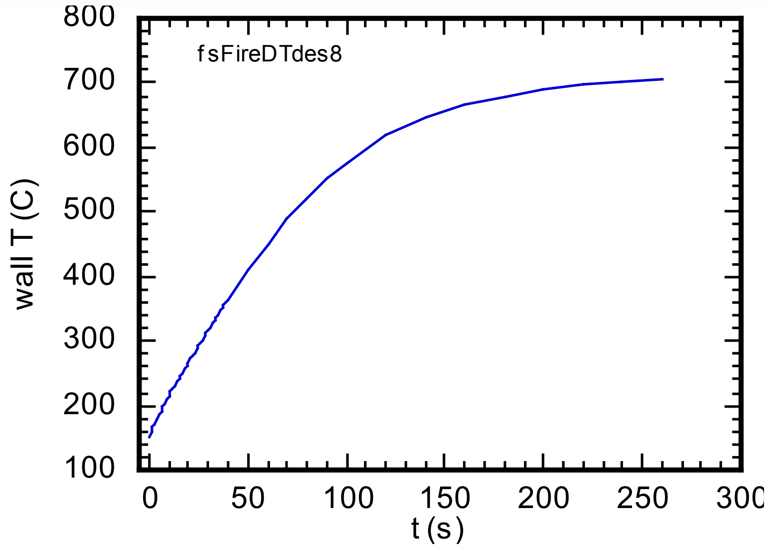


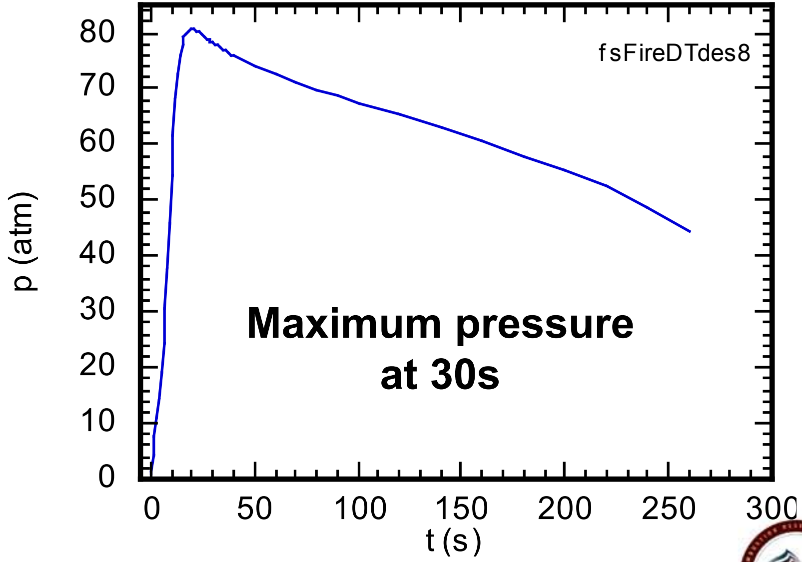
Note: Validation data is needed for these simulations

Alane Simulation results indicate that an over pressure scenario could be an outcome

- Alane (α-AlH_3) system will respond similarly
  - Kinetics from Graetz
  - Uses developed transport models
  - Low pressure system
- Allows for the vessel design recommendations
  - MAWP of 80 atm (unshielded)

Enables science based design recommendations and code development



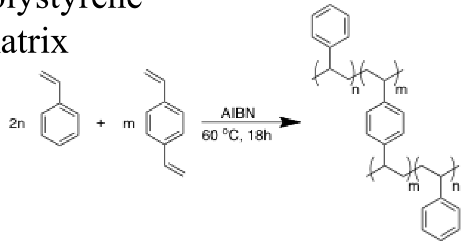


Maximum pressure at 30s

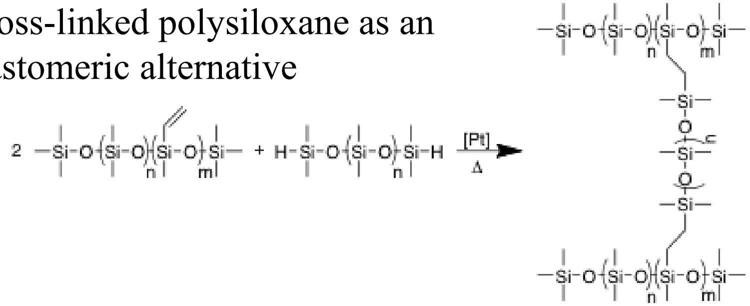
Mitigation of predicted outcomes may be addressed through the use of a matrix

- Goals of mitigation technology during accident scenarios
  - Reduce reaction extent and rate
  - Reduce dispersion of reactive solids
  - Contribute less than 10% to the overall weight and volume of the hydrogen storage system
  - Do not inhibit hydrogen uptake/release rates or capacity during normal operation
  - Low cost
- Mitigation technologies under development:

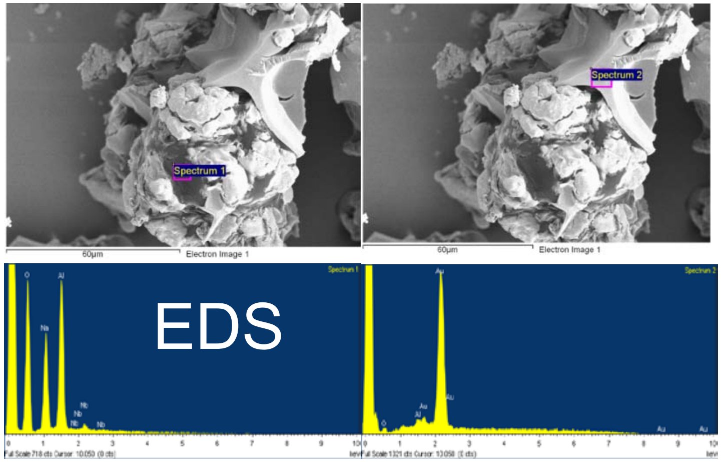
Cross-linked polystyrene as composite matrix



Cross-linked polysiloxane as an elastomeric alternative



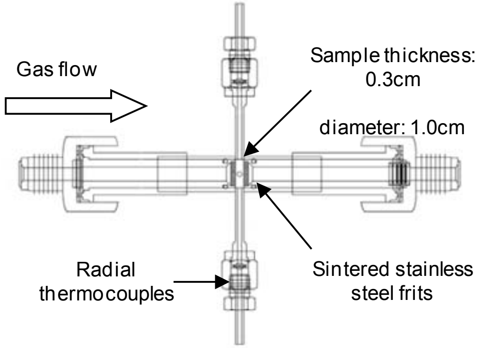
Ti – catalyzed $NaAlH_4$ with polystyrene

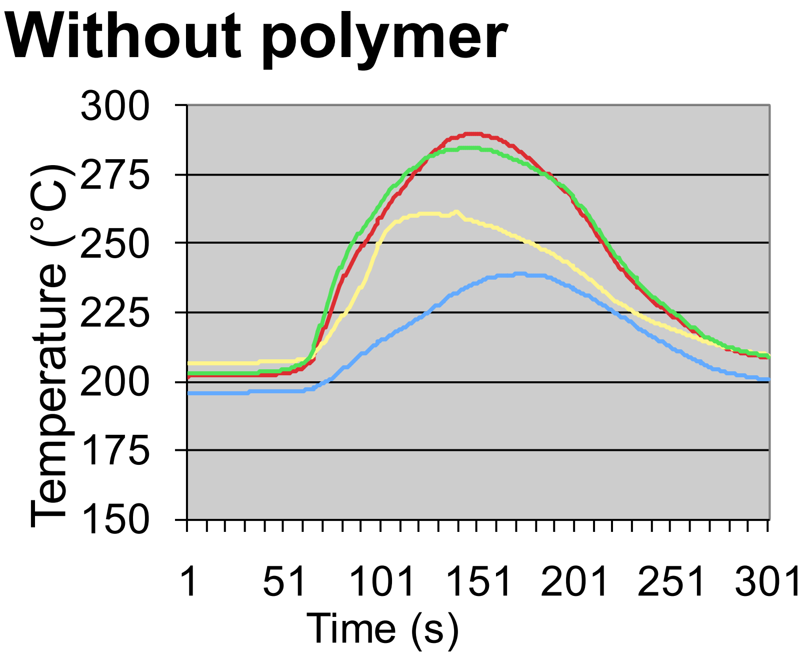


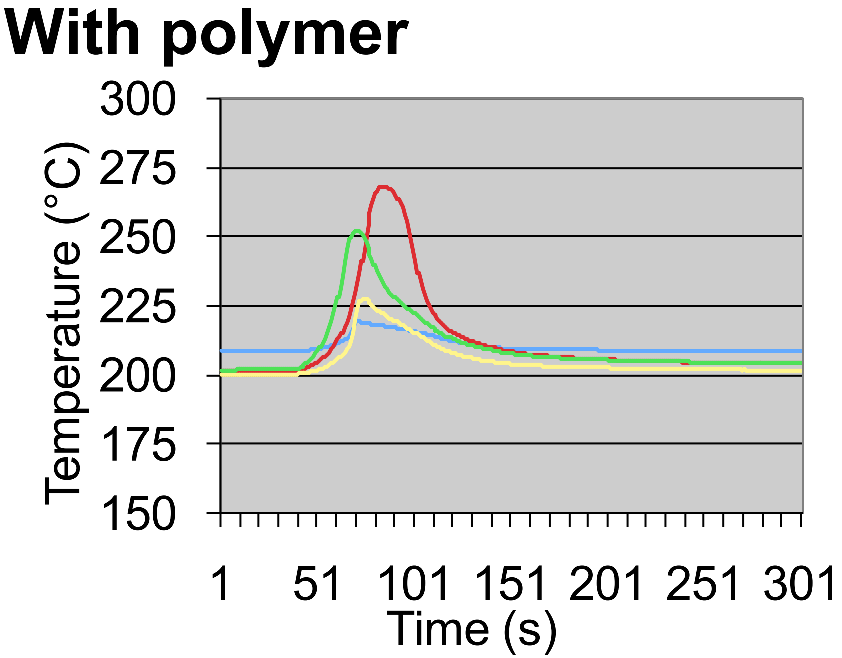
Accomplishment: Initial flow-through oxidation studies indicate success in mitigation

Oxidation flow-through reactor experiments:

- Nearly a 70% reduction in heat release
- Very little NaOH formed in mitigated sample



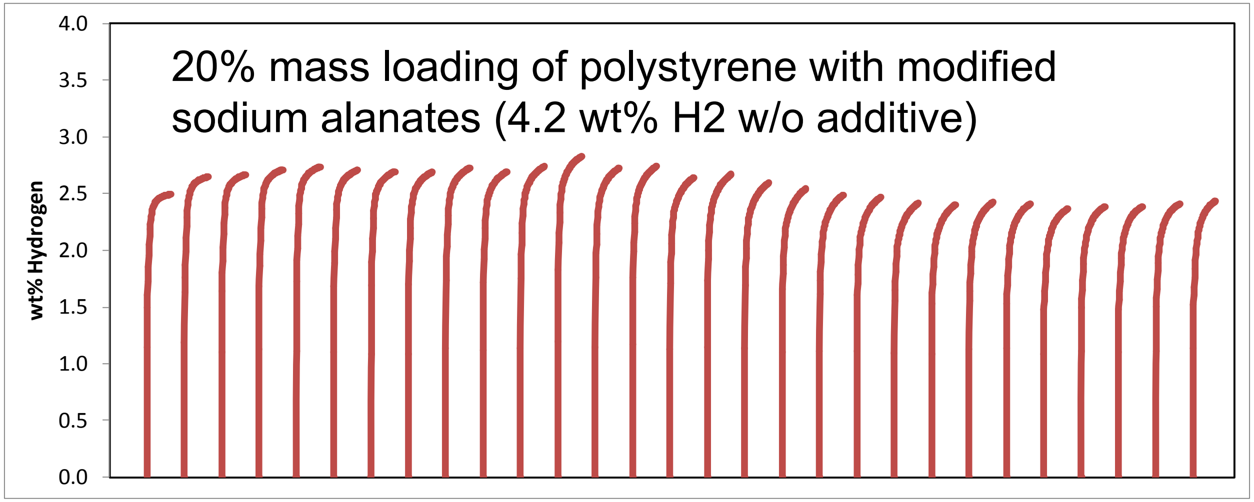




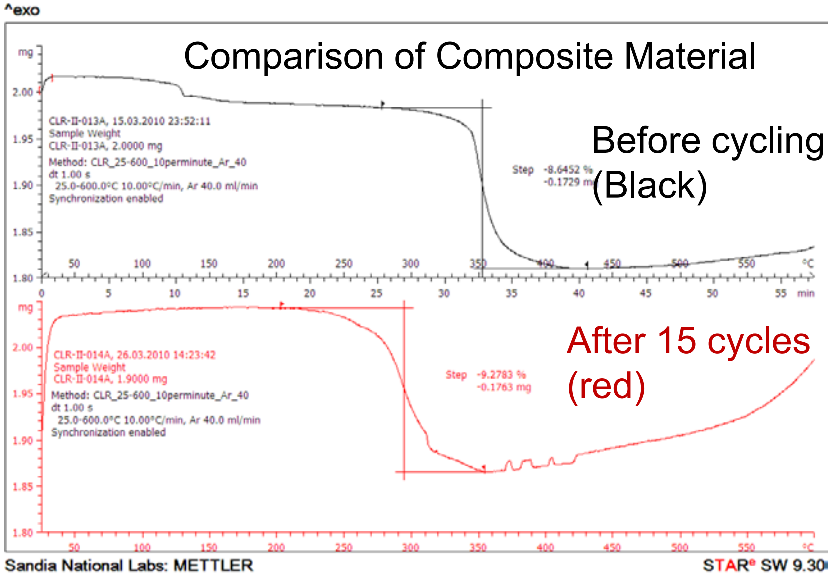
Accomplishment: Samples hydrogen cycle successfully without loss in activity

- Quickly activated
- Matrix does not interact with catalyzed material
- Cycles near max capacity (2.8 wt%)
- Demonstrates nearly identical mass loss (TGA)
  - 8.65 wt% before
  - 9.3 wt% after
- A small shift in decomposition temperature is observed (down)

This approach looks promising to provide mitigating support of hydrides



20% mass loading of polystyrene with modified sodium alanates (4.2 wt% H2 w/o additive)



Comparison of Composite Material

Before cycling (Black)

After 15 cycles (red)

active material +
1:1 Styrene : Divinyl
benzene
cross-linked polymer

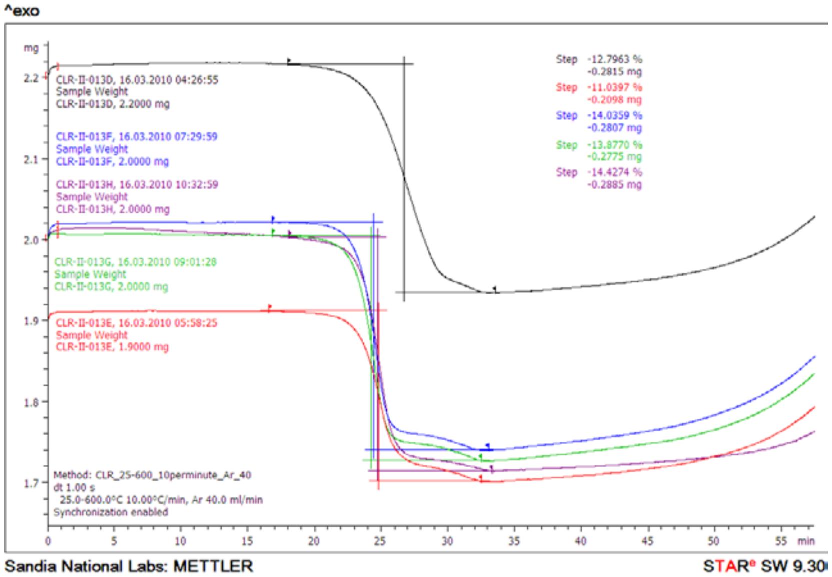
Accomplishment: Mitigation matrix can be tailored based on desired structural properties of matrix

- Cross-link density
  - has a large effect on the structural properties of the composites (i.e. tough or brittle)
  - but doesn't have a large effect on thermal properties/ weight loss

- Structural properties can be selected based on mitigating properties
  - brittle, ease of handling
  - ductile, compaction/powder control
  - etc.

<u>Monomer Molar Ratios</u>
(Styrene : Divinyl benzene)

1:1, black	**3:1, red**	**5:1, blue**	**7:1, green**	**10:1, purple**



Accomplishment: Qualitative testing indicated that mitigated samples are effective during exposure to fluids

- Tests performed at UTRC (J. Khalil and R. Brown)
- mitigating polymer acted to keep the material intact
- “neat” samples quickly dissolved in the contacting liquid
- Reaction of mitigated samples were “*mild”* compared to the neat samples

Hydride Samples from SNL	Experimental Observations				
	Water	**Windshield Washing Fluid**	**Engine Coolant (Antifreeze)**	**Engine Oil**	**1M NaCl Solution**
“Neat” Material A mixture of NaH, Al, Ti, and NaCl plus 10 wt% expanded natural graphite (ENG)	Vigorous reaction, gases evolved, no ignition, wafer material quickly dissolved in water, Temp. rose to ~ 108^{o}C in 30 sec.	Observations similar to the water test. Temp. rose to about 88^{o}C in 30 sec.	Observations similar to the water test but more bubbles were formed around the wafer material. Temp. rose to about 75^{o}C in 30 sec.	No chemical reaction, no ignition, and no temperature rise.	Observations similar to the water test. Temp. rose to about 124^{o}C in 30 sec.
“Mitigated” Material Same composition as “Neat” material plus 20% polystyrene supported loading	Very mild reaction, gases evolved, no ignition, wafer geometry remained unchanged, Temp. rose from 25.9^{o}C to about 80^{o}C in 30 sec.	More vigorous reaction compared to water, no ignition, geometry unchanged, Temp. rose to about 75^{o}C in 30 sec.	Observations similar to the windshield washing fluid test. Temp. rose to about 79^{o}C in 30 sec.	No chemical reaction, no ignition, and no temperature rise.	No sample was available to perform this test.

Collaborations have enabled relevance to the greater FTC program

Program made relevant with the help and support of:

Reactivity Project Partners:	Savannah River NL – D. Anton
	UTRC – D. Mosher
Alanes:	Brookhaven NL – J. Graetz
Ammonia boranes:	Pacific Northwest NL – T. Autrey
Activated carbons:	Caltech – C. Anh
	UTRQ – R. Chanine
$2LiH+Mg(NH_2)_2$:	IPHE Partners
Borohydrides:	Sandia NL – J. Cordaro
	HRL – J. Vajo
Properties Measurement:	Purdue – T. Pourpoint
Systems:	GMR – S. Jorgensen

Future work focuses on mitigation technology development and validation

Final year of program focuses on ***mitigation***

- Scale up production of mitigated materials to 100 g
- Develop and characterize new matrix materials
- Demonstrate mitigating technology performance during
  - Normal life-cycle
  - Accident events involving infiltration of air
  - Accident events involving fire
  - Accident events involving loss of containment

Continued vision enables technology commercialization

- Validate contamination scenarios and hazard mitigation methods at application appropriate scales.
- Collaborate with storage system engineers to enable design-for-safety
- Provide SDOs with validated science-based analysis to enable the development of functional code and standards

Summary Slide for 2010 AMR

- Fire scenarios are an important design consideration in deployed solid-state systems
- A mitigation technology is being developed that is able to:
  - Contribute a small weight penalty
  - Withstand hydrogen cycling
  - Mitigate unfavorable reactions
  - Structurally support fine reactive solids

This program has developed the tools and understanding for eventual codes and standards development and market penetration of metal hydride systems