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Engineering Systems Analysis & Properties Measurement for Metal Hydride Storage

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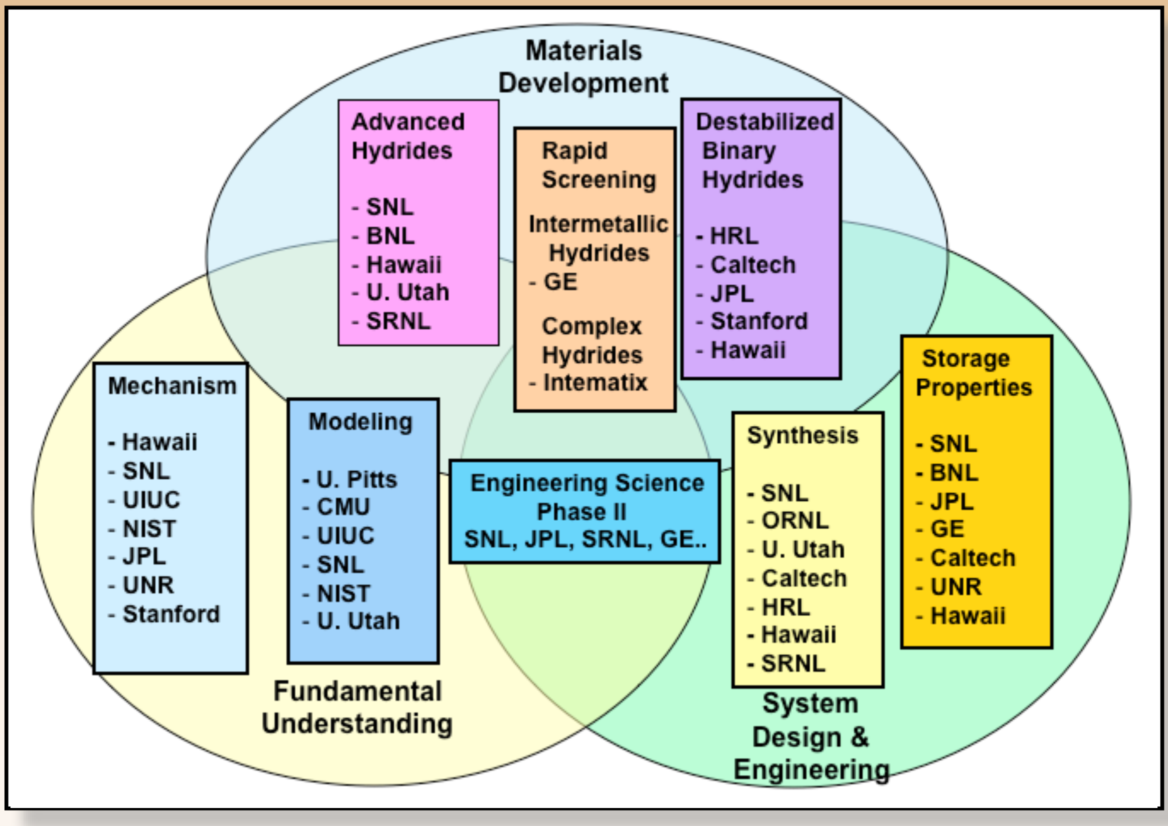
The Metal Hydride Center of Excellence (MHCoE) partners cover a full range of expertise.



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Objective and approach

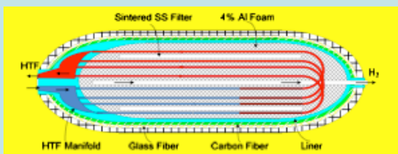
- Objective: Develop new metal hydride materials that provide high performance on-board storage for H_2 vehicles consistent with DOE goals.

- Approach for Phase I: Close collaboration between engineering system performance analysis and material development effort to define material parameter space for efficient systems.
  - System performance models
  - Ab initio calculations
  - Hydride property measurements
    - Thermal properties
    - Mechanical properties
    - Thermodynamic and kinetic parameters
  - Feed-forward approach - Use system level models to determine performance for a given set of measured metal hydride properties
  - Inverse approach - Use system level models to determine metal hydride properties required to obtain a given level of performance (subject to constraints).

The Metal Hydride Center of Excellence (MHCoE) is working towards DOE's hydrogen storage vessel goals.

Other Non-MHCoE DOE funded Activities (i.e. ANL)

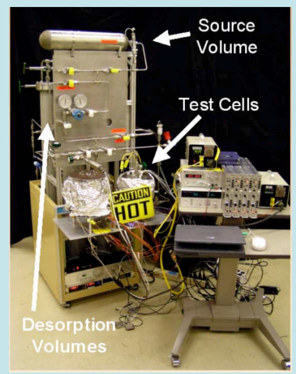
- MHTool: Metal Hydride Hydrogen Storage System Analysis Tool



1. Material Characterization Module
2. Storage Capacity Module
3. Heat Transfer Module
4. System Module
5. Dynamic Module

Sandia National Lab (SNL)

- Develop new metal hydride materials
  - System performance models
  - Ab initio calculations
  - Hydride property measurements



Savannah River National Lab (SRNL)

- Storage Vessel System Integration Design
  - Storage vessel prototype design
  - System performance models
  - Media scale-up
  - Media engineering data
  - Storage vessel design calculations
  - Testing of prototype storage vessel

Vessel System Integration Design

Materials Development

△ Tank Delivery

2005 2006 2007 2008 2009 2010

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Metal Hydride Center of Excellence (MHCoE) FY06 system analysis activities.

- Model bed transport with variable properties
  - 1-D heat transfer
  - General geometry (not design specific)
  - Absorption and desorption kinetics

- Low-level system integration model
  - Dynamic (Simulink) model for load/unloading
  - Couple with bed transport model

- Combined model with provide first-cut projection of bed material properties to system performance

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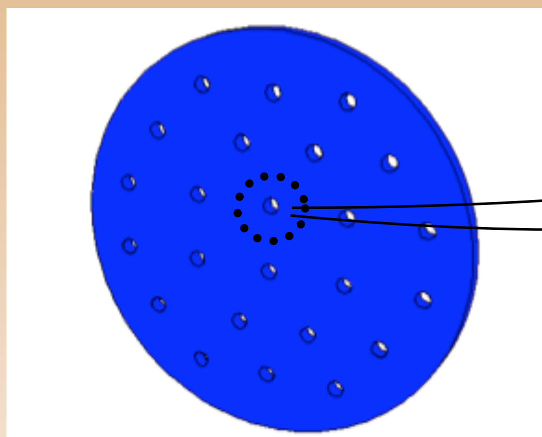
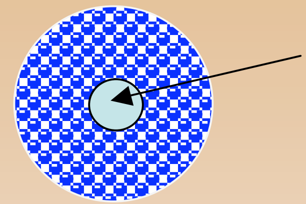
We will deliver an engineering system level storage transport model.

- Based on behavior of unit-cell of large scale storage tank



Cross-section of large-scale metal hydride storage tank

Unit Cell Model



T_{fluid}

$q_{conv} = h(t_{wall} - t_{fluid})$

- Energy balance

$$\rho c_v \frac{\partial T}{\partial t} = \nabla \cdot \vec{q} + \dot{q}$$

$$\vec{q} = -k_{cond} \nabla T$$

- Species kinetics

$$\frac{\partial C_i}{\partial t} = K(T) \cdot F(C) \cdot F(P)$$

$$K(T) = K_o \exp(-E/RT)$$

For example:

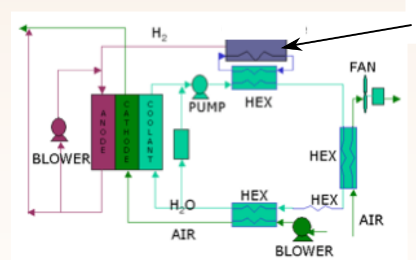
$NaH + 1/3\ Al + ½\ H_2 \Leftrightarrow 1/3\ Na_3AlH_6$

$1/3\ Na_3AlH_6 + 2/3\ Al + H_2 \Leftrightarrow NaAlH_4$

- Model input parameters
  - Size and spacing of cooling passages
  - Packing density of metal hydride bed
  - Contact resistance between cooling passages and hydride bed
  - Variable thermal properties
  - Kinetics for different hydride materials
  - H_2 pressure on bed
  - Fluid temperature
- Model output system performance parameters
  - H_2 absorption or desorption rate versus time
  - Total charging or discharging time
  - Amount of heat to be supplied to release H_2 from bed or amount of heat to be removed to charge bed

- Model can be integrated with other system models

System Level Storage Model Module



* From: D. Moser et al., UTRC

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The engineering systems model requires measured property data for the metal hydride bed material.

Engineering Properties *as a function of phase, cycle, and pressure*

1. Thermal conductivity
2. Heat capacity
3. Wall resistance
4. Packing density

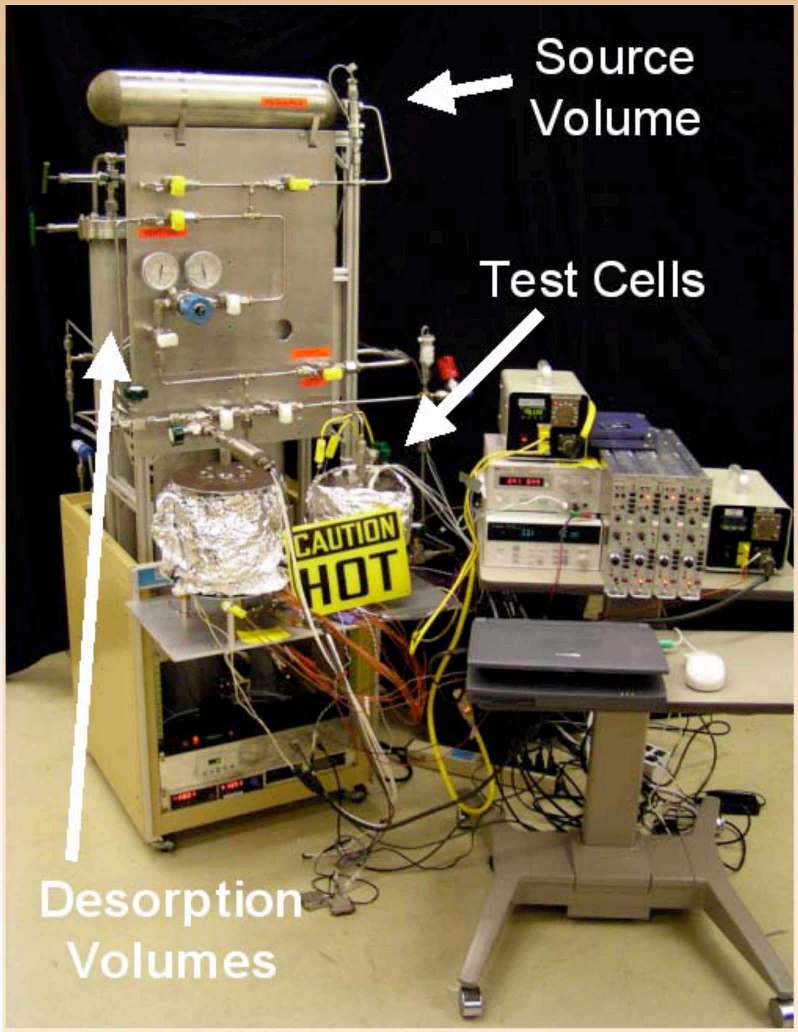
Thermodynamics & Kinetics Properties

1. Reaction rate model uses Arrhenius equations
2. Desorption & absorption enthalpy
3. Rates of absorption and desorption

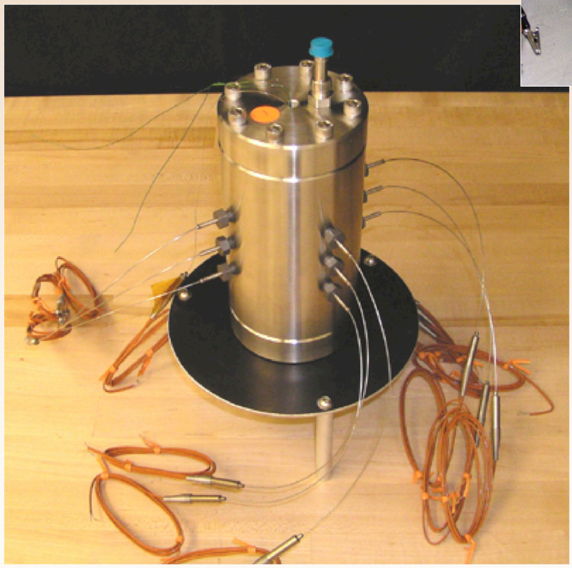
Mechanical Properties *as a function of cycle and phase*

1. Pressure exerted on a vessel wall
2. Densification effects

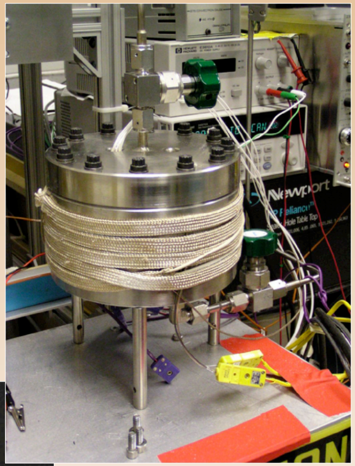
The MHCoE has built a custom manifold and test cells to measure engineering properties of hydrogen storage materials.



Thermal



Mechanical



The MHCoE thermal properties measurement method has been optimized for complex hydrides.

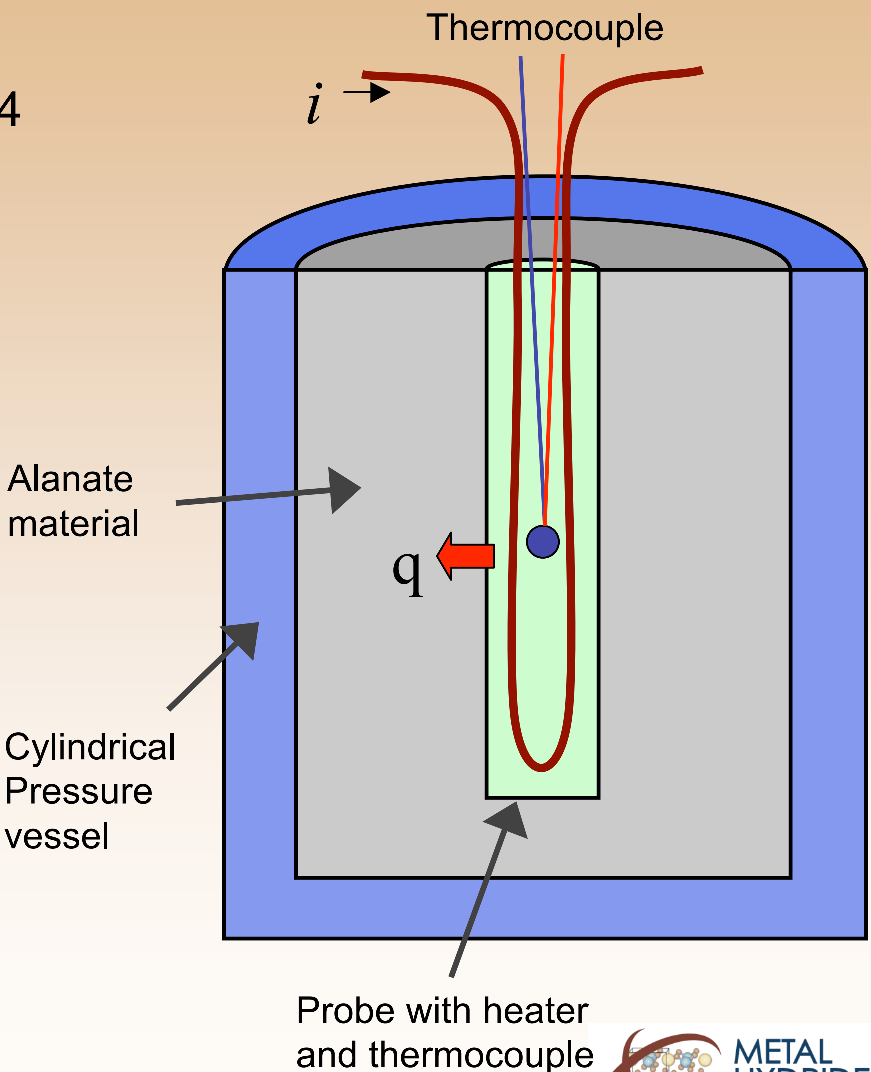
- Identified method based on ASTM D5334 and Blackwell

- Transient temperature measurements of the probe can be fit to determine K_{th}, C_{p}, h_{wall}

- Probe temperature is fit by:
  $$T(t) = A\ln(t) + B + \tfrac{1}{t}\left[C\ln(t) + D\right]$$

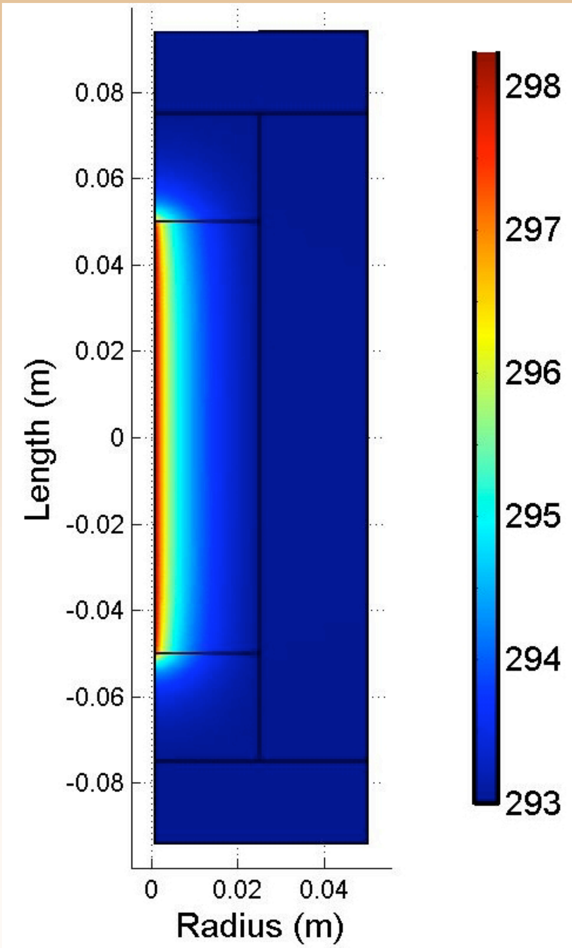
where $A = \dfrac{r_p Q}{2k}$

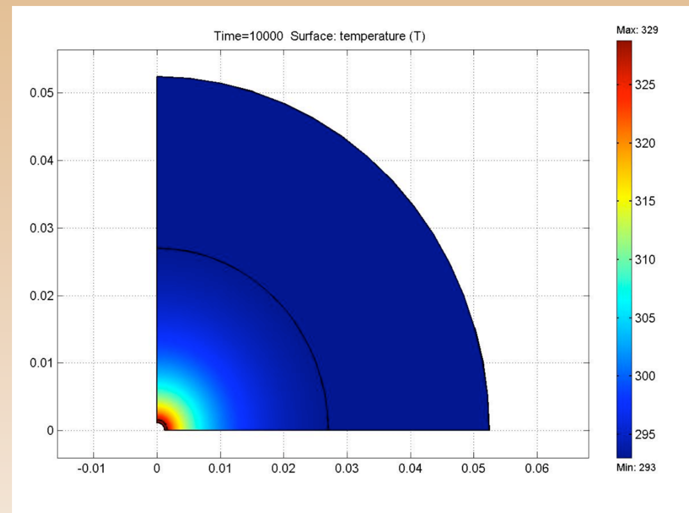
and numerical methods



The measurement chamber geometry was optimized using a 2-D thermal model

Example FEMLAB output





Axisymmetric 2D model exercised to:

✓ predict effective measurement limits of design (<10% error up to 3.0 W/m-K)

✓ find the minimum probe length appropriate for 1D analysis (minimize end-effects)

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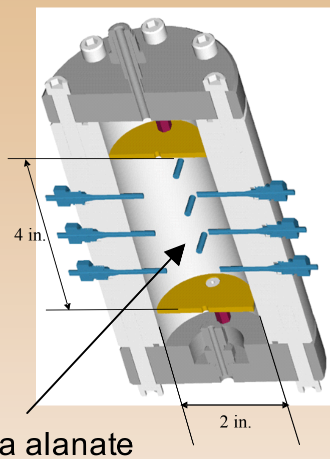
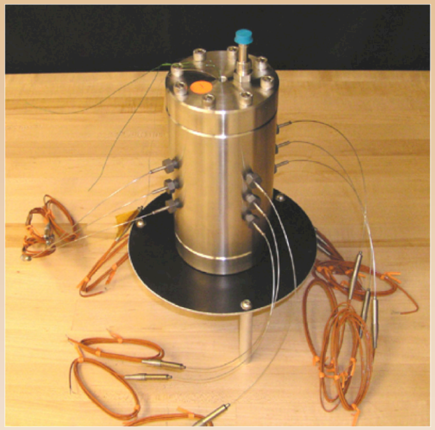
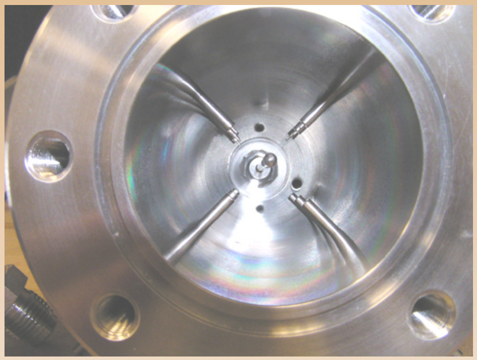
The MHCoE apparatus was built and calibrated with materials of known properties prior to using it to determine the properties of sodium alanate.



136g Na alanate





End View

Calibration Data		
Material	**Measured Kth (W/m-K)**	**Literature Kth (W/m-K)**
Teflon	0.25	0.26 - 0.30
Polyurethane Foam	0.03	0.033
Ottawa sand	0.30	0.25 - 0.33

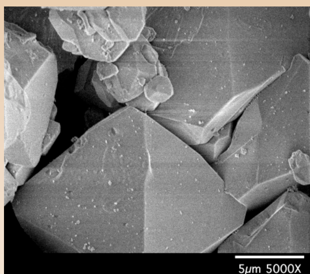
Chamber calibrated using solid PTFE, polyurethane foam, and Ottawa sand

Sodium alanate experiences significant physical changes during hydrogen sorption.

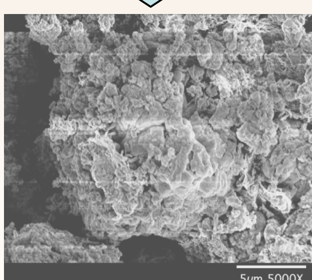
Total Theoretical Capacity = 5.6 wt% hydrogen

$NaAlH_4 \Rightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \Rightarrow NaH + Al + 3/2H_2$

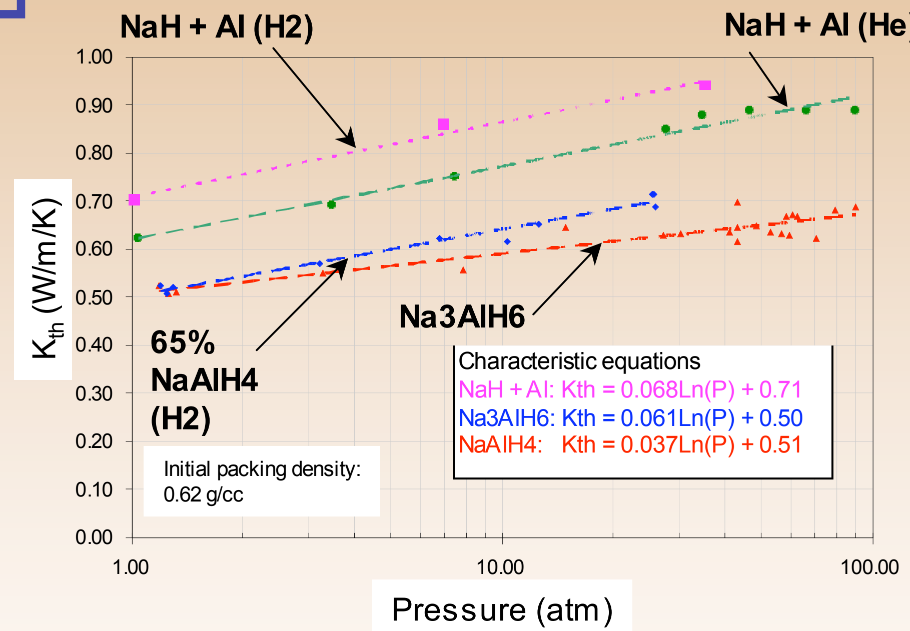
3.7 wt.%   1.9 wt.%



Engineering properties change significantly with hydrogen sorption



Fully cycled material thermal conductivity varies >70% with phase and gas pressure



- Morphology changes with cycle and influences thermal properties
- Gas pressure enhances thermal conductivity

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Reaction rate expressions have been determined for the sodium alanate system.

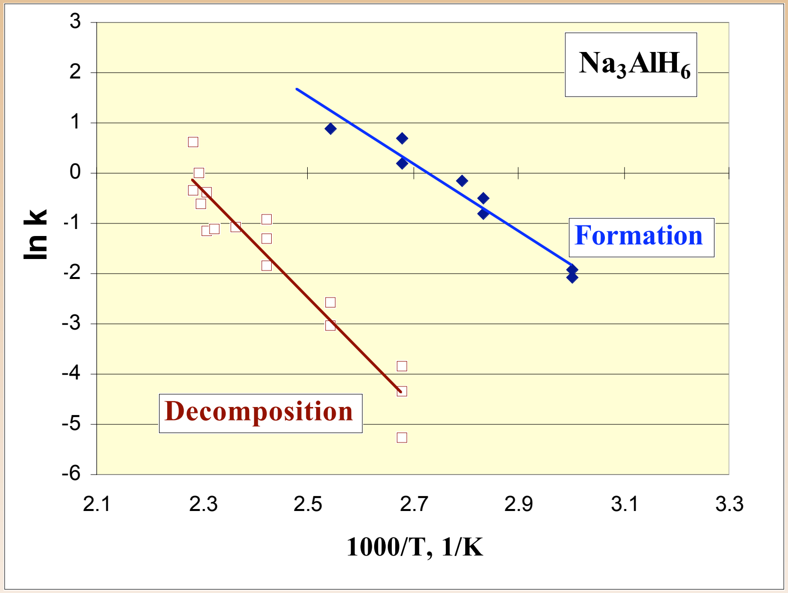
$$\text{Rate} = k * C^n * b * \ln(P/P_{eq})$$

$NaH + 1/3\ Al + ½\ H_2 \Leftrightarrow 1/3\ Na_3AlH_6$
$1/3\ Na_3AlH_6 + 2/3\ Al + H_2 \Leftrightarrow NaAlH_4$

Rate = k * F(C) * F(P)
n = 1 or 2;
b = 1 or –1.
$k = k_o \exp(-Q_a/RT)$
k: rate constant;
k_o: pre-exponential factor;
Q_a: activation energy
C: H-wt %

P_{eq}: From K. Gross, Appl. Physics, 2001. (Van't Hoff plot).
No hysteresis was considered.

Arrhenius Plots: Na_3AlH_6



$$\text{Rate} = K_o \exp(Q_a/RT) * C^n * b * \ln(P/P_{eq})$$

		K_o	-Qa, kJ/mol	K_o*	-Qa, kJ/mol*
$NaAlH_4$	Formation	6.25×10^8	61.6	---	---
	Decomposition	1.9×10^{11}	85.6	1.81×10^{11}	80
Na_3AlH_6	Formation	1.02×10^8	56.2	---	---
	Decomposition	2.9×10^{10}	88.3	1.85×10^{12}	97.5

* G. Sandrock, K. Gross and G. Thomas, J. Alloys and Compounds, 339 (2002) 299-308

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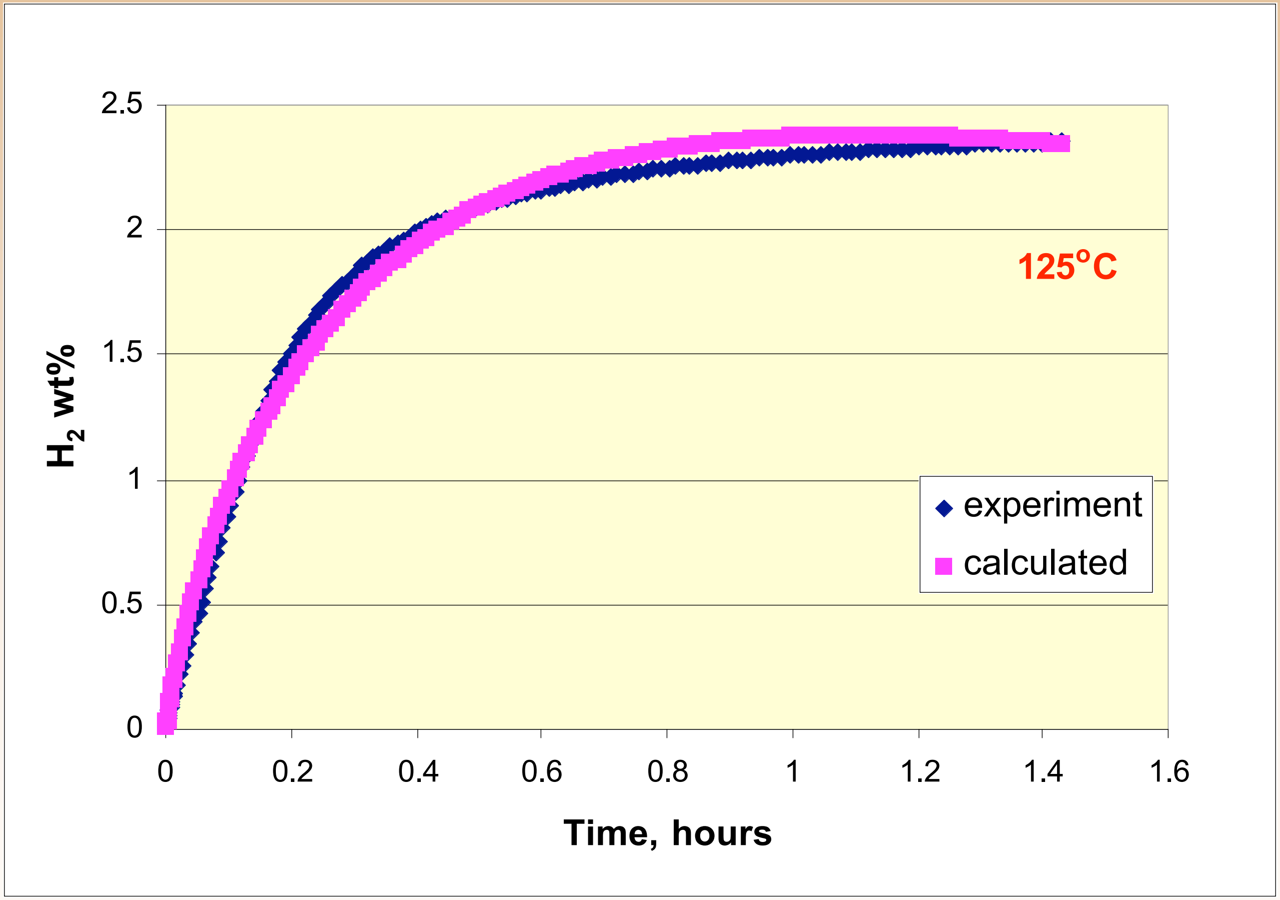
Calculated desorption rates from the kinetics expressions are in agreement with experimental measurements.

Desorption at 125˚C



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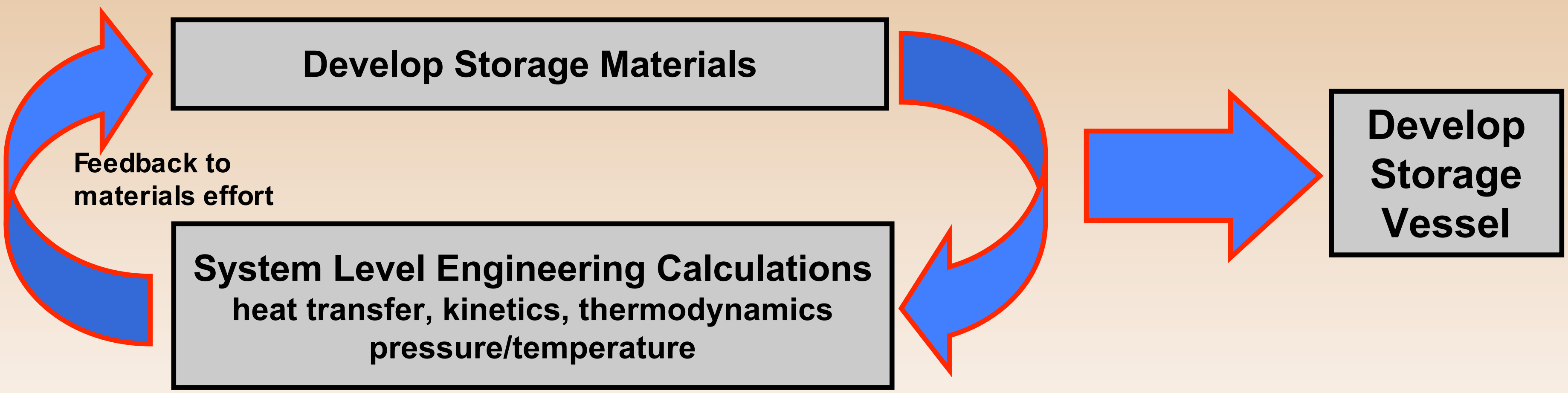
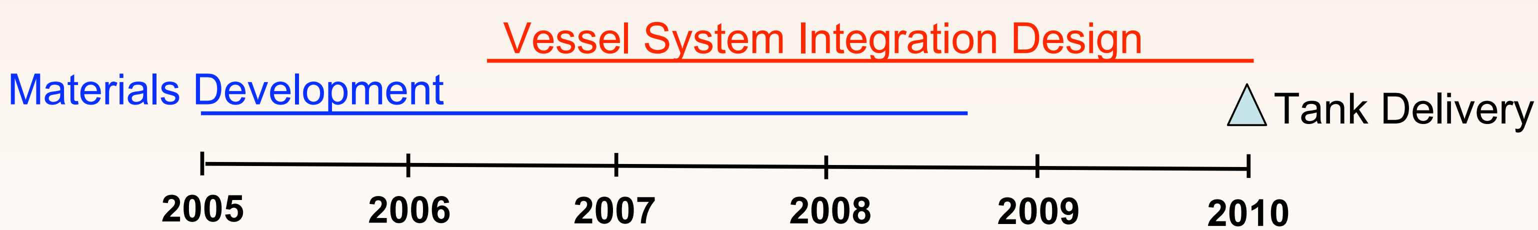
Summary

- **The Metal Hydride Center of Excellence (MHCoE) is a collaborative effort working towards DOE's hydrogen storage vessel goals.**





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