Hydrogen Storage Engineering
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Systems Engineering of Chemical Hydride, Pressure Vessel, and Balance of Plant for On-Board Hydrogen Storage

Pacific Northwest National Lab (principal) Engineering Team

D. Herling (P.I.) , D. King, S. Rassat, K. Simmons, E. Ronnebro, T. Samuel,

DOE Hydrogen Program Annual Merit Review,
EERE: Hydrogen, Fuel Cells and Infrastructure Technologies Program
Washington, DC
May 18-22, 2009
Program Manager: Monterey Gardiner

DOE Hydrogen Program

U.S. Department of Energy
Energy Efficiency and Renewable Energy
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Project ID: STP_07_Herling

Overview

- Timeline
  - Start: Feb. 2009
  - Project End: Jan. 2014
    - End Phase 1: 2011
    - End Phase 2: 2013
    - End Phase 3: 2014
  - Percent complete: 3%

- Budget
  - $6.2M Total (PNNL) Program
    - DOE direct funded
    - No cost-share required for National Lab
  - FY08: $0k
  - FY09: $600k

- Barriers
  - System cost
  - Gravimetric & volumetric capacity
  - Durability/Operability
  - Hydrogen discharging rates & transient response
  - Hydrogen purity
  - System regeneration

- Partners

PNNL Roles in HSECoE

- PNNL Technology Development and System Engineering
- Technology Area Lead (TAL) for *Materials Operating Requirements*
- Coordinate activities as the Technology Team Lead (TTL)
  - Bulk Materials Handling *(Transport Phenomena)*
  - Pressure Vessels *(Enabling Technologies)*
  - Manufacturing and Cost Analysis *(Performance Analysis)*
- Liaison to OVT's Hydrogen Reactivity (safety) and Hybrid Vehicle research and development activities
- Liaison to the HFCIT's Manufacturing projects

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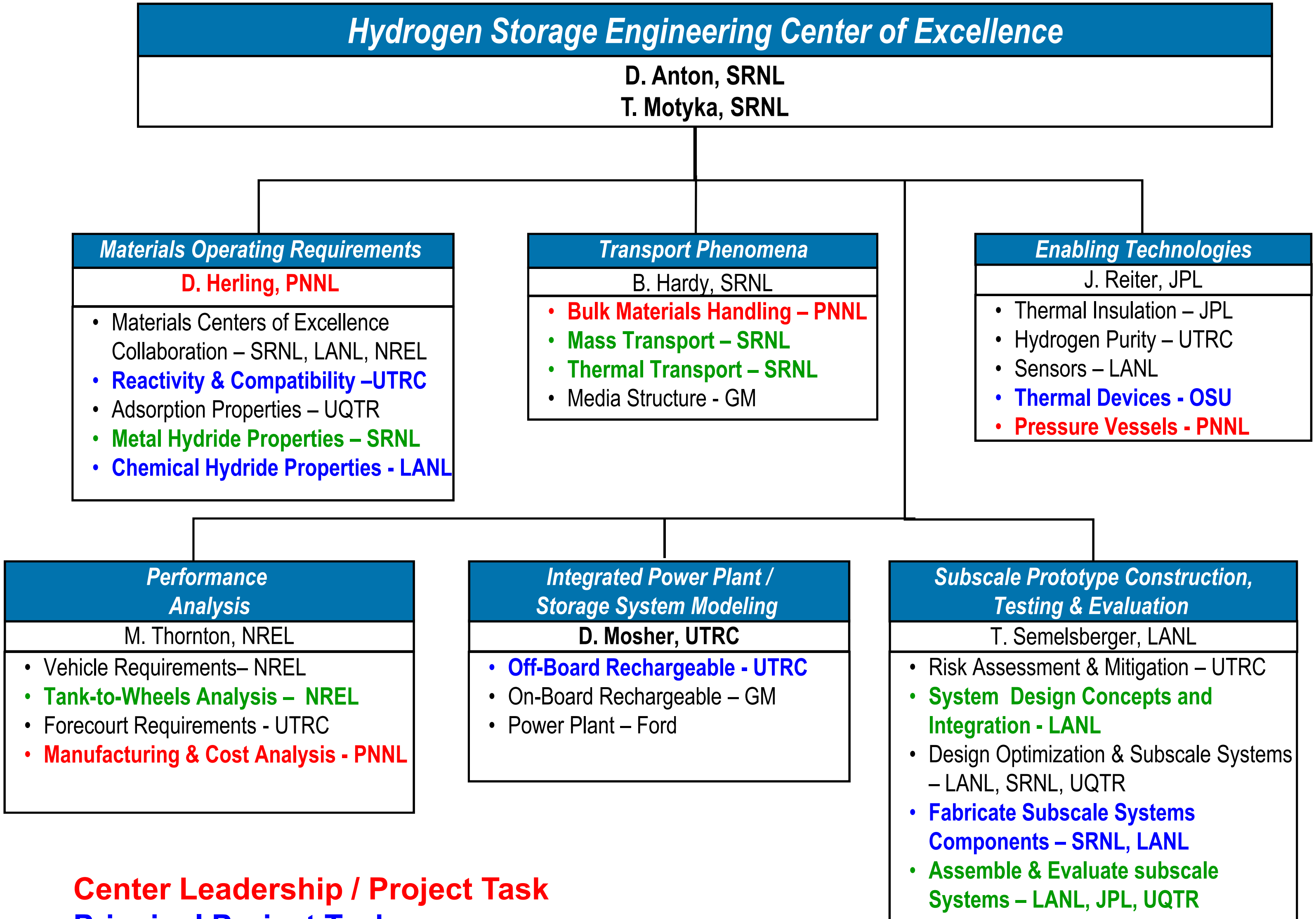
Center Structure – Roles & Collaborations



Center Leadership / Project Task
Principal Project Task
Contributing Center Support

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Technology Area: Materials Requirements
Technology Team: HSMCoE Collaborations
March 2009 v1

Technology Team Lead:
T. Semelsberger, A. Dillion, D. Anton
Team members: LANL, NREL, SRNL

Objectives:

Liaison for HSECoE with the respective Materials Centers

- Help to establish open communications and vehicle for requests with HSMCoEs
- POC for coordinating and disseminating storage materials data for HSECoE partners

Accomplishments:

- Established liaisons and connections with HSMCoEs

Key Milestones:

1. Establish connections with HSMCoEs *(4/09)*
2. Request and receive data from HSECoEs *(6/09)*

Issues:

- Collaboration and access to program information after HSMCoEs end
- Material availability (IP?)
- Synthesis details and/or material supply to HSECoE

HSECoE

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Technology Area: Materials Operating Requirements

Technology Team: Reactivity & Compatibility

March 2009 v1

Technology Team Lead: D. Mosher

Team members: JPL, LANL, PNNL, SRNL, UTRC, UQTR

Objectives:

Determine the effects from adverse reactivity/incompatibility of storage materials with system/component materials & potential contaminants.

- Collaborate with the DOE Reactivity Projects to evaluate the effects from exposure to contaminants (H2O, O2).
- Conduct cyclic or moderate endurance tests for storage material / system material combinations.
- Characterize H2 and storage materials compatibility with system components/materials (if data not available).
- Recommend and/or review materials for use in construction of prototypes for H2 compatibility.

Accomplishments:

Key Milestones:

1. Compile list of storage material candidates, potential system materials and operation conditions. *(9/09)*
2. Screen for compatibility of the top (potential & risk) material combinations under representative operation conditions. *(3/10)*

Issues:

- Determine the level of material CoE involvement in kinetics and composition tests.
- Establish initial guidelines for importance level of accident scenario safety in the Phased development.
- Agree on approach for hydrogen embrittlement.

HSECoE

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Technology Area: Materials Requirements

Technology Team: Materials Properties: Adsorbents

March 2009 v1

Technology Team Lead: R. Chahine

Team members: BASF, Ford, GM, NREL, UQTR

Objectives:

- Develop selection criteria and down select base adsorbent
- Develop initial base line model
- Establish materials properties database for use in modeling and system engineering by HSECoE partners
  - Perform initial screening tests (calorimetry, kinetics, composition) for storage system materials
  - Produce material characterization and generate engineering property data base
- Model H2 uptake (serves also for metering)
- Derive Heat of adsorption

Accomplishments:

Key Milestones:

1. Develop adsorbent selection criteria *(4/09)*
2. Indentify materials properties needed for center modeling and engineering activities *(4/09)*
3. Establish who, what, when for property characterization measurements *(4/09)*
4. Model base line adsorption *(5/09)*
5. Survey available adsorbents *(5/09)*
6. Down select candidate *(6/09)*

Issues:

- Need to establish proper distribution of measurement tasks
- Availability of analytical resource (equipment, etc)
- Material availability for evaluation, or information to synthesize materials

Technology Area: Materials Requirements

Technology Team: Materials Prop's: Metal Hydride

March 2009 v1

Technology Team Lead: T. Motyka

Team members: GM, SRNL, UTRC

Objectives:

- Develop selection criteria and down select base adsorbent
- Develop initial base line model
- Establish materials properties database for use in modeling and system engineering by HSECoE partners
  - Perform initial screening tests (calorimetry, kinetics, composition) for storage system materials
  - Produce material characterization and generate engineering property data base

Accomplishments:

Key Milestones:

1. Develop metal hydride selection criteria *(4/09)*
2. Indentify materials properties needed for center modeling and engineering activities *(4/09)*
3. Establish who, what, when for property characterization measurements *(4/09)*
4. *Identify baseline model for screening and down selection of material options (5/09)*

Issues:

- Need to establish proper distribution of measurement tasks
- Availability of analytical resource (equipment, etc)
- Material availability for evaluation, or information to synthesize materials

HSECoE

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Technology Area: Materials Requirements **Technology Team Lead:** T. Semelsberger

Technology Team: Materials Prop's: Chem. Hydride **Team members:** LANL, PNNL

March 2009 v1

Objectives:

Establish materials properties database for use in modeling and system engineering by HSECoE partners

- Perform initial screening tests (calorimetry, kinetics, composition) for storage system materials
- Produce material characterization and generate engineering property data base

Accomplishments:

Key Milestones:

1. Indentify materials properties needed for center modeling and engineering activities *(3/09)*
2. Establish who, what, when for property characterization measurements *(4/09)*

Issues:

- Need to establish proper distribution of measurement tasks
- Availability of analytical resource (equipment, etc)
- Material availability for evaluation, or information to synthesize materials

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PNNL Technical Scope Objectives

- Demonstrate high level of performance that meets DOE 2015 targets using solid chemical hydrogen storage
- Optimize design of structured storage bed and system performance
- Reduce system volume and weight and optimize system storage capability, fueling, and dehydriding performance
- Mitigate materials incompatibility issues associated with hydrogen embrittlement, corrosion, and permeability
- Demonstrate the performance of economical, compact, lightweight vessels for a hybridized storage
- Guide design and technology down selection through cost modeling and manufacturing analysis

PNNL Technology Development and System Engineering Tasks

1) Low Volume Storage Systems for Solid Chemical Hydrides
2) Process Engineering, Kinetics and Testing
3) Miniaturization Using Efficient Microarchitectures
4) Materials Compatibility and Selection
5) Containment and Pressure Vessel Development
6) Manufacturing and Cost Analysis

Focus is on Process Engineering,
System Design and Functional Integration

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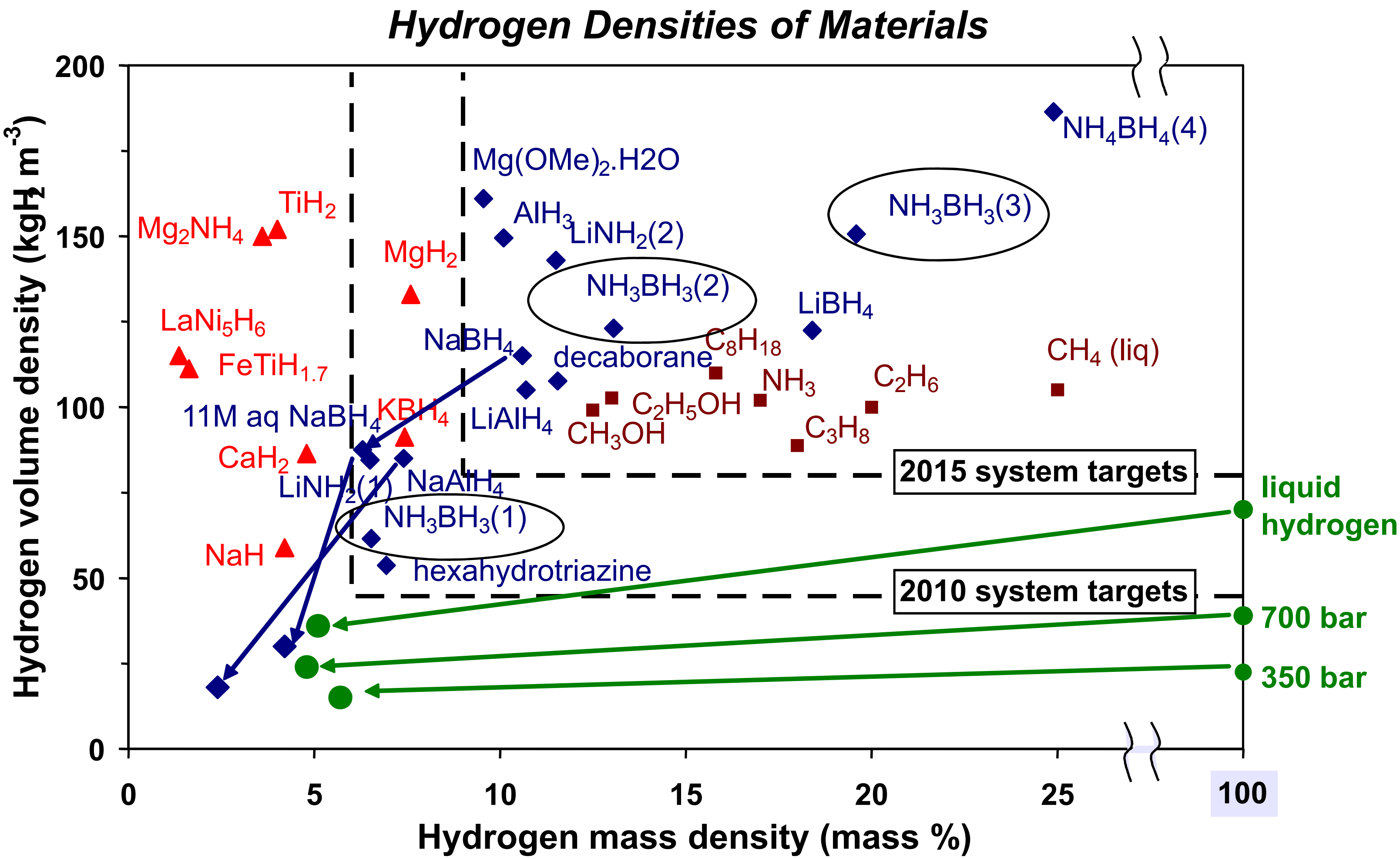
Ammonia Borane Shows Promise



Courtesy of G. Thomas

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Primary Engineering Barriers for Chemical Hydride Systems

- Chemical Hydrides are Not ‘Reacted’ in the Fuel Tank
  - AB thermolysis at <100°C, but how will AB respond to storage in hot climates?
  - Solids handling engineering part of any system concept
- DOE Technical Targets:
  - Maximum Operating Ambient Temperature: 50°C (2010) & 60°C (2015)
  - “No allowable performance degradation … to 40°C”
  - Loss of Useable Hydrogen (g/hr)/kg H_2 stored: 0.1 (2010) & 0.05 (2015); loss includes venting, if required
- Ammonia Borane foams on reaction – potential limitation to practical engineering application
- Performance impact of contaminants and volatile byproducts?

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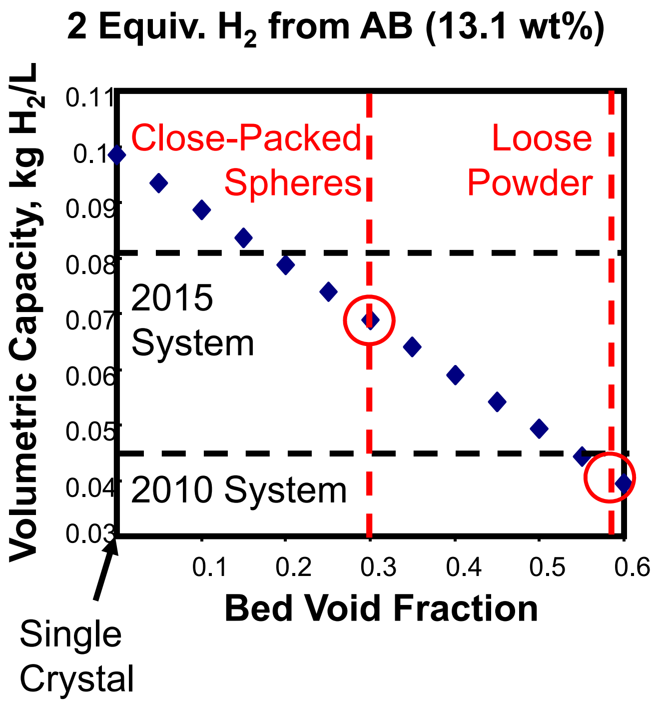
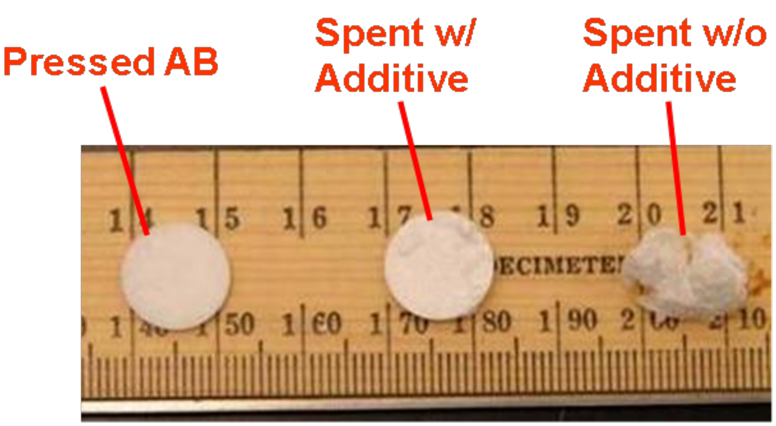
Engineered Form-Factor for Solid AB





Additive suppresses foaming and enables monolithic fuels

- System targets are difficult for granulated materials
- AB foams when it releases hydrogen – not conducive to engineering
- Antifoaming approaches key
  - More than 50 additive formulations tested with 2-3 successful (CHCoE study)
  - Scaffold materials also demonstrate foam suppression at lower AB:scaffold loadings
  - Paves way for system with monolithic fuel & high volumetric density

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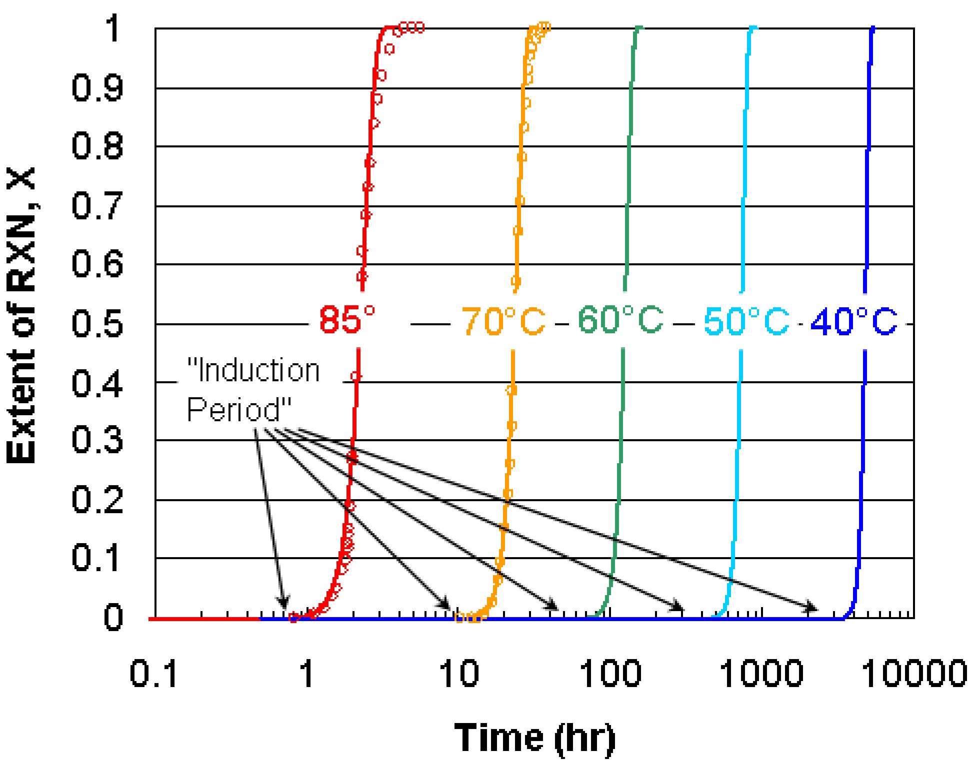
Source: PNNL CHCoE

AB Thermal Stability Calculations – Assumptions and Insight

- 1st equivalent only – Avrami kinetics
- 70-90 °C isothermal DSC data* used for initial fit of parameters
- Adiabatic assumed as a worst case
- Model AB bed properties
  - 1000 mol AB = 4 kg H_2 (2 H_2 equiv.)
  - 6.0 wt% H_2 in a storage unit including >50 wt% structure
  - No temperature gradients

Extrapolation of DSC Data to Lower Isothermal Temperatures



*Wolf et al., Thermochimica Acta 343, (2000) 19

Source: PNNL CHCoE

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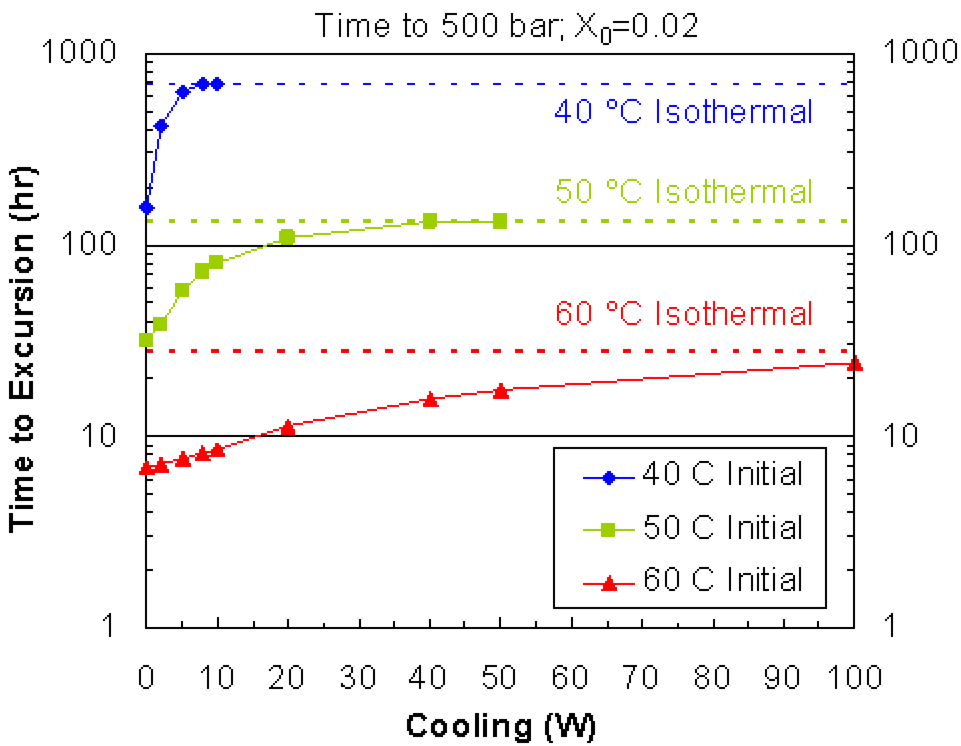
Heat Management to Stabilize Stored AB



- Under adiabatic conditions, the AB bed temperature and reaction rate increases due to the heat evolved as H_2 is released (e.g., -22 kJ/mol)
- Small amounts of cooling and lower temperatures greatly increase the thermal stability of the packed AB bed (e.g., storage tank)
- Computationally, cooling was not allowed to decrease T below the initial value

Source: PNNL CHCoE

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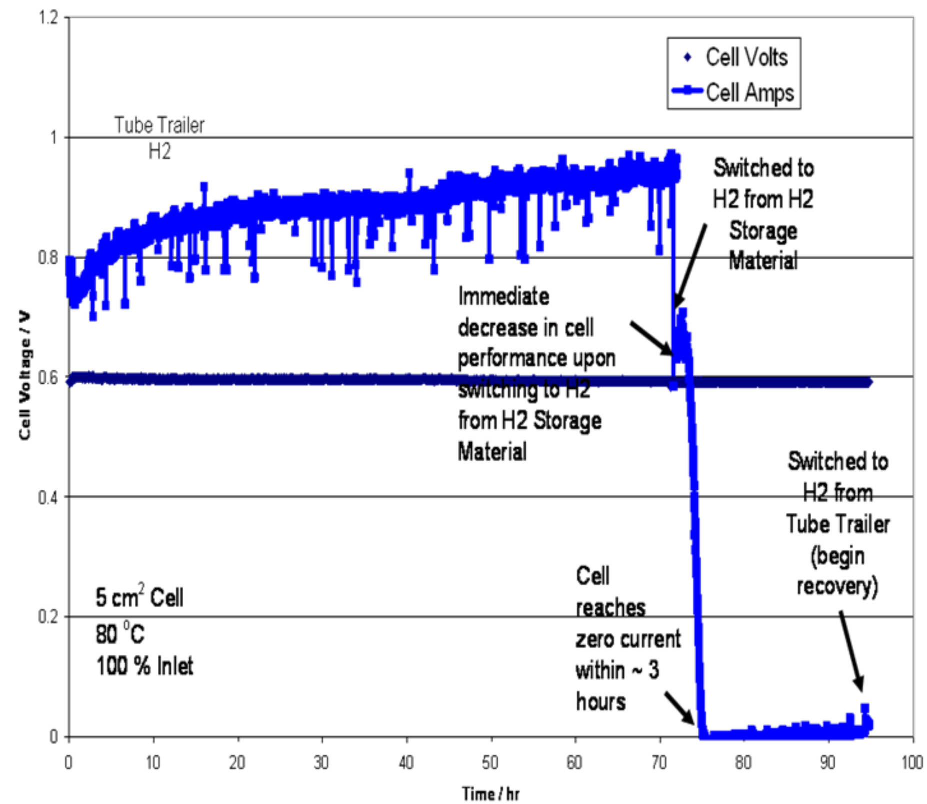
Importance of Hydrogen Purity

- Fuel cell activity degrades quickly when switching from bottled hydrogen to hydrogen from AB fuel storage source
- After deactivation activity recovered when run on bottled H_2
- Membrane does not appear to suffer damage
- Filtration/separation can be used to run fuel cell on AB fuel



Courtesy of LANL: Semelsberger, Borup

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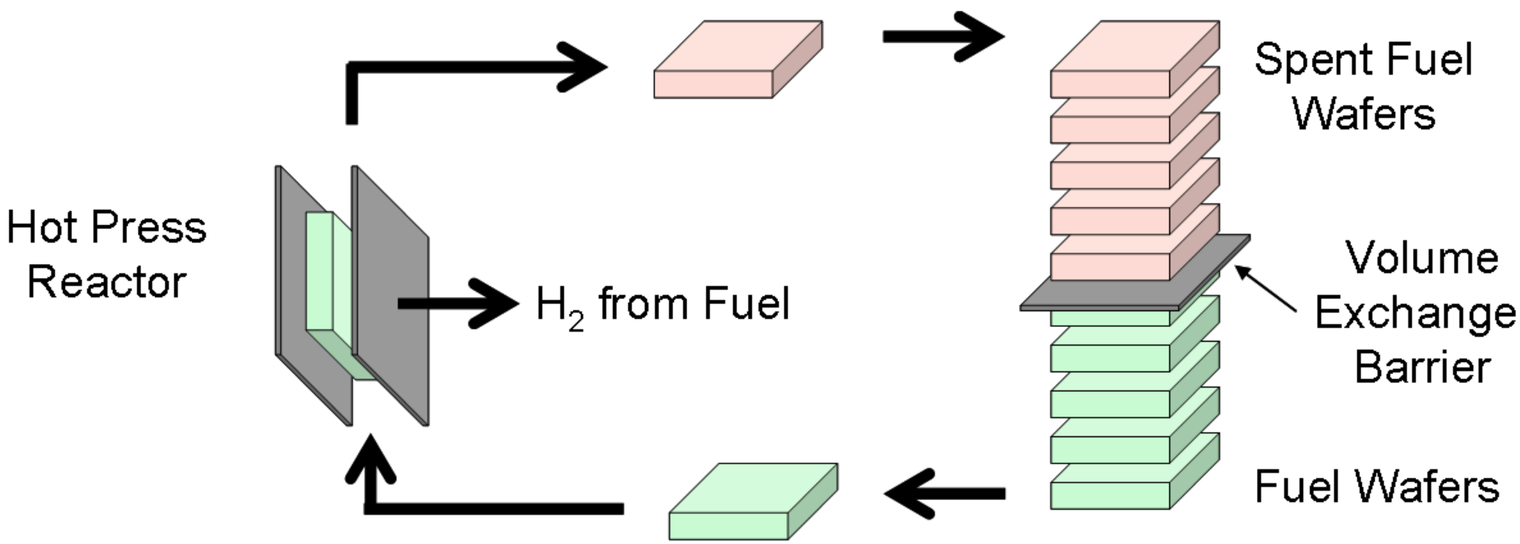
Low Volume Storage for Solid Chemical Hydrides *(Task 1)*

- Chemical hydride system design and performance modeling
- Solids handling design for monolithic fuel
- Chemical reactor engineering and prototyping



Flow chart indicating how monolithic fuel might be cycled within a chemical hydrogen fueling system to reduce impact on total volume.

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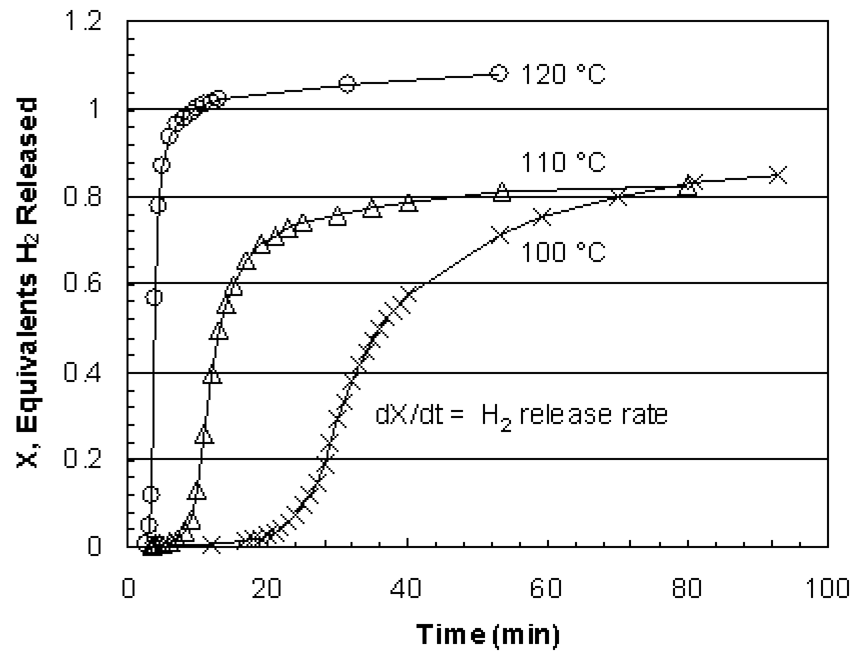
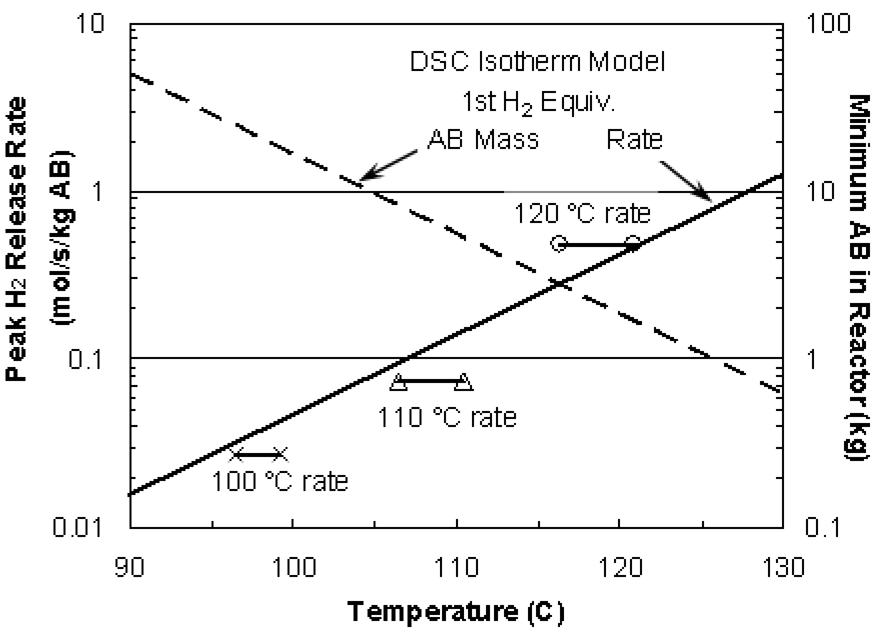
Process Engineering, Kinetics and Testing *(Task 2)*

- Process modeling and engineering
- Systems component integration and testing
- System and bulk materials kinetics





Release curves for AB (above) and predicted fueling rate requirement to meet US DOE target of 0.01 mol H2/s/kW for an 80 kW fuel cell (left)

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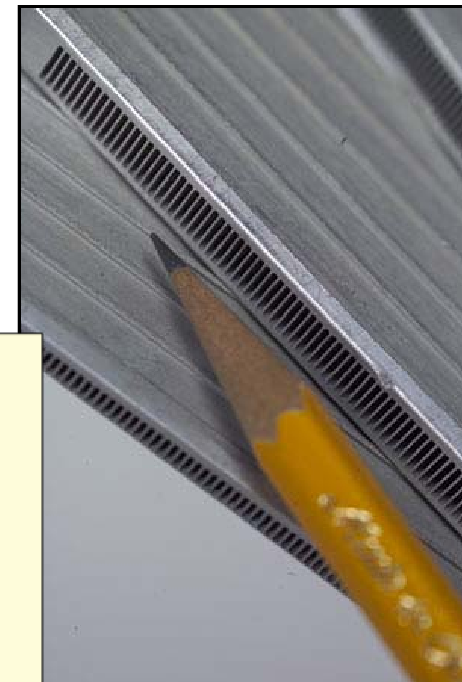
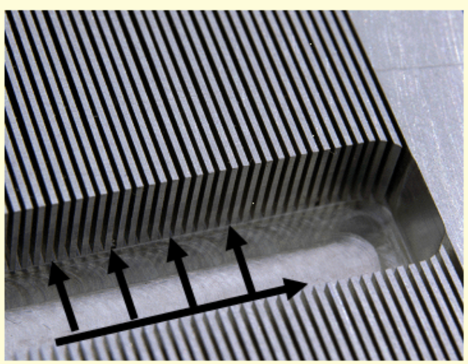
System Miniaturization Using Efficient Microarchitectures *(Task 3)*

- Balance of plant component model and design
- Microchannel device model and design
  - Heat exchangers (tank internal/external)
  - Other chemical/thermal devices
- Microchannel device fabrication
- Microchannel device testing



Microchannel Technology



~ 0.01 inch

Vs.

StandardTechnology

~ 1 inch

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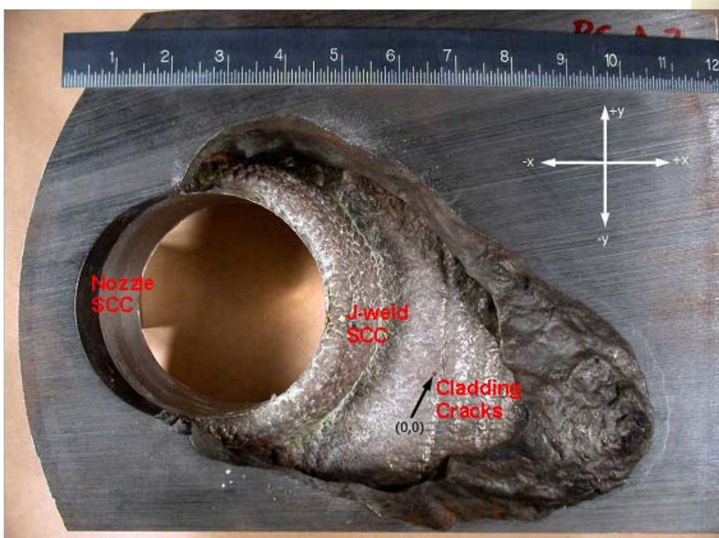
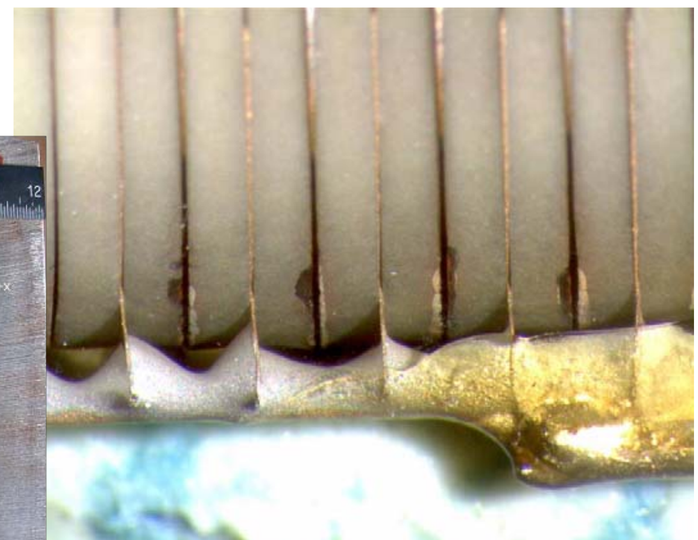
Materials Compatibility and Selection *(Task 4)*

- Materials compatibility issues
  - Hydrogen compatibility with seals, piping, etc is a concern
  - Proper materials selection important
- Component performance impact





Example of materials degradation in hydrogen environment

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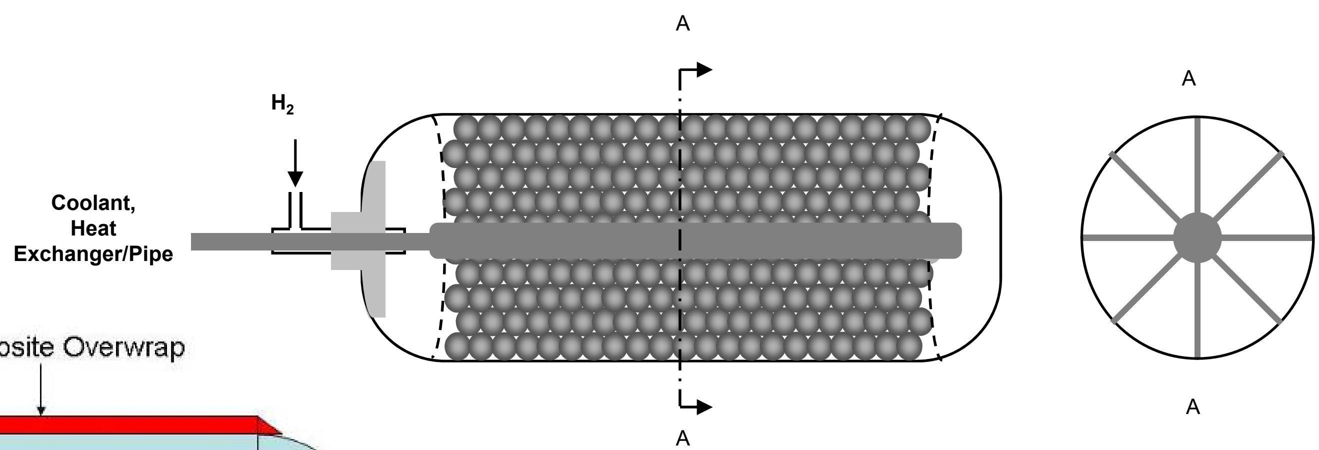
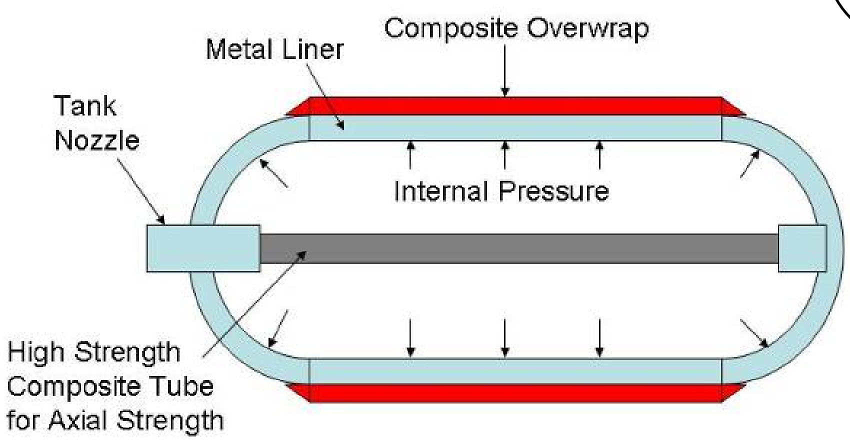
Containment and Pressure Vessel Development *(Task 5)*

- Hybrid pressure vessel integration
- Hybrid pressure vessel fabrication
- Heat exchanger and pressure vessel integration





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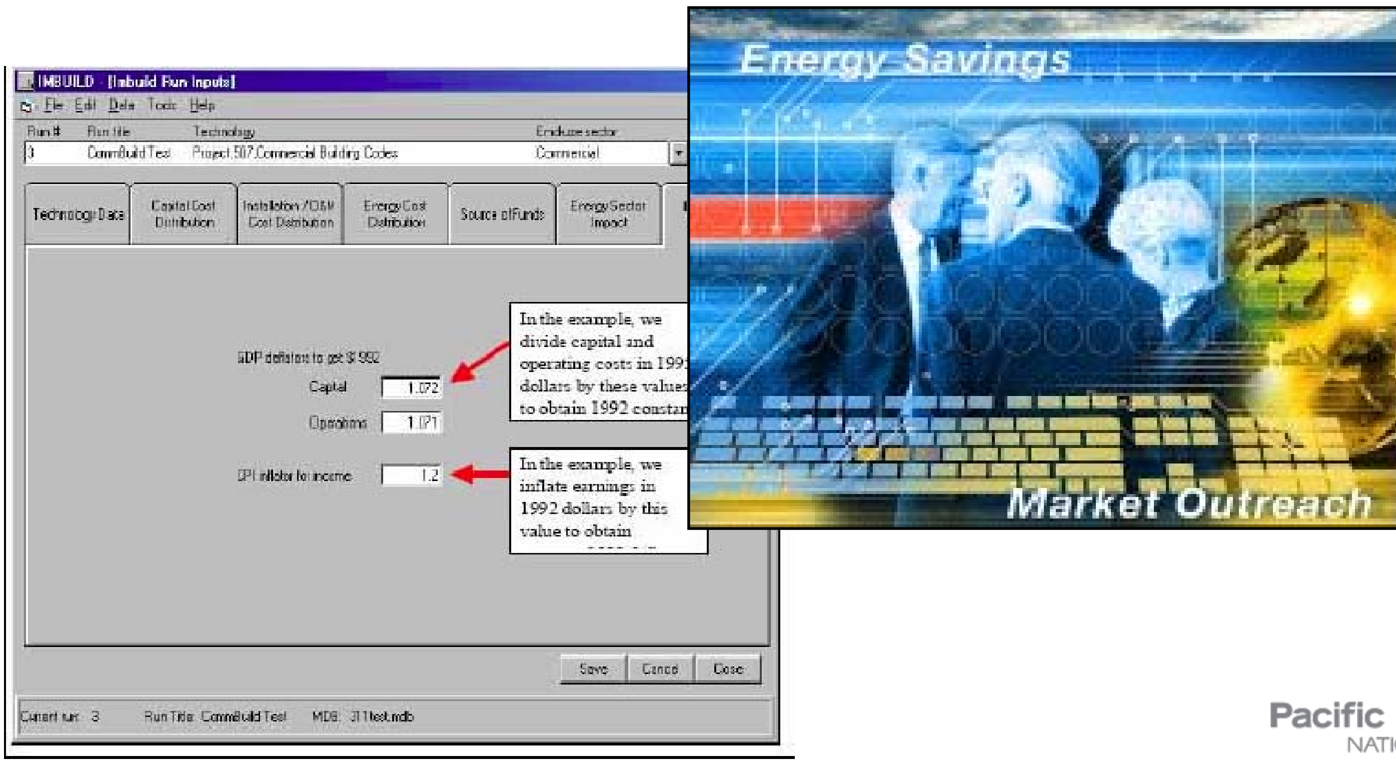
Manufacturing and Cost Analysis *(Task 6)*

- Cost Modeling
- Technology analysis and tradeoff study
- Energy efficiency and performance impact



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Summary

- Goal

  To develop and demonstrate low-cost, high-performing, on-board solid-state hydrogen storage through a fully integrated systems design and engineering approach.

- Approach

  Advance the state of chemisorbed and physisorbed hydrogen storage systems through process engineering and application of novel component design and systems integration, facilitated through better understanding of material/system requirements and properties, plus modeling and simulation assessments.

- Accomplished through

  Series of technical tasks, coupled by close collaboration with HSECoE partners, that address the main project objectives. Primary emphasis is on chemical hydride systems, with secondary efforts supporting adsorbant and metal hydride systems design.

PNNL Work Breakdown Structure

PNNL Task No.	Subtask Title	Phase 1								Phase 2								Phase 3			
		2009 (Q)				2010 (Q)				2011 (Q)				2012 (Q)				2013 (Q)			
		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
1.1	Chemical hydride system design and performance modeling				M1				M3								G5		M17		
1.2	Solids handling design for monolithic fuel							M2	G1								G6				
2.1	Chemical reactor engineering								M4								G7				
2.2	Chemical reactor fabrication														M14						D3
2.3	Chemical hydride component testing																M16				
2.4	System and bulk materials kinetics								M5				M11								
3.1	Microchannel heat exchanger model and design								M6				M12				G8				
3.2	Microchannel device fabrication																				D4
3.3	Microchannel device testing																G9				D5
3.4	Balance of plant component model and design								M7				M13				G10				
4.1	Materials compatibility issues and component performance impact								M8							M15					
5.1	Hybrid pressure vessel architecture model and design								M9						G3						
5.2	Hybrid pressure vessel fabrication																				D6
5.3	Heat exchanger and pressure vessel integration								M10							G4					
6.1	Cost modeling				D1												G11				
6.2	Technology analysis and tradeoff study								G2							D2	G12				
6.3	Energy efficiency and performance																G13				
Report	Quarterly reports																				
	Annual reporting																				
	Annual merit reviews																				

M = Milestone; D = Deliverable; G = Go/No-Go

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FY 2009 Activities and Deliverables

- Activities
  - Construct a heat/mass transfer model that will be use to simulate hydrogen release in monolithic fuels in order to guide system design. (Task 1)
  - Complete a conceptual design for a solid chemical hydride reactor that will provide input to the HSECoE's Phase 1 Go/No-go decision making process. (Task 2)
  - Develop model for heat exchange using microarchitecture devices for chemisorption and physisorption systems. (Task 3)
  - Development of modeling approach, assumptions, and basic model structure to simulate various pressure vessel geometries and layered structures. (Task 5)
  - Create first revision of cost model, structure details and spreadsheet for the evaluation cost of technologies and systems components for assistance in down selection. (Task 6)
- Deliverables & Milestones
  - Formal quarterly/annual reports
  - Determination potential for achieving H_2 release rate target of 1.6 g H2/s for an 80 kW fuel cell. (Q4, FY2009)
  - Provide insight, through conceptual design and modeling efforts, into the ability of such a system to meet the 2010 volumetric capacity target of 1.5 kWh/L. (Q3, FY2009)
  - Establish basic heat exchanger requirements for each of the 3 hydride systems and initiate model development. (Q3, FY2009)
  - Establish the modeling approach, assumptions, and basic model structure to simulate various pressure vessel geometries and layered structures, including model parameters that account for basic cost and performance. (Q3, FY2009)
  - Provide Rev.0 cost model, structure details and spreadsheet to Center partners for their evaluation. (Q4, FY2009)

Key Project Staff: PNNL

PNNL Principal Investigator

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Solid Chem. Hydride System

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Kinetics & Storage Mat'ls

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Daiwon Choi

Process Engring & Microtech

Dale King
James Davis
Greg Whyatt
Paul Humble

Pressure Vessel & Materials

Kevin Simmons
Ken Johnson
Sachin Laddha

Manufacturing & Cost Analysis

Todd Samuel
Mark Weimar

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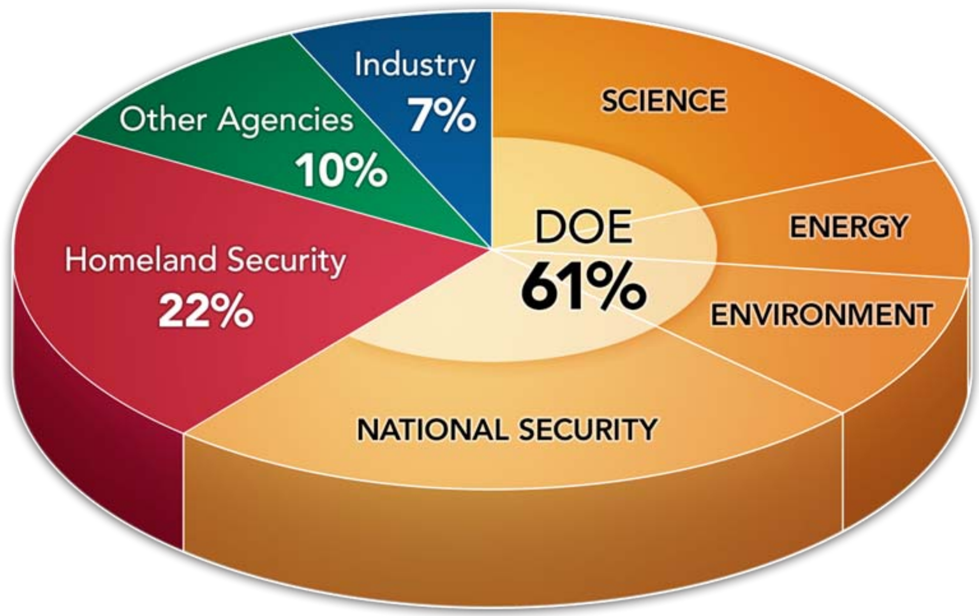

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