SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence

Design and Testing of Metal Hydride and Adsorbent Systems

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Savannah River National Laboratory

June 9, 2010

Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Project ID#ST092

This presentation does not contain any proprietary, confidential or otherwise restricted information

Overview

Timeline

- Start: February 1, 2009
- End: July 31, 2014
- 20% Complete (as of 3/31/10)

Barriers

- System Weight and Volume
- H_2 Flow Rate
- Energy Efficiency

Budget

- FY 09 Funding: $888,945*
- FY10 Funding: $1,640,000*

* Includes $241,200/$360,000 for the University of Quebec Trois Rivieres (UQTR) as a subrecipient for FY09/FY10

Partners

SRNL SAVANNAH RIVER NATIONAL LABORATORY
Pacific Northwest NATIONAL LABORATORY
Los Alamos NATIONAL LABORATORY
United Technologies Research Center
JPL
NREL National Renewable Energy Laboratory
BASF The Chemical Company
OSU Oregon State UNIVERSITY
HRI UQTR
CALIFORNIA INSTITUTE OF TECHNOLOGY
MICHIGAN
H HSM SYSTEMS
Ford
LINCOLN COMPOSITES A Member of Hexagon Composites Group
GM

Relevance: Overall Project Objectives

Phase 1: 2009-2011

- Compile all relevant **metal hydride materials data** for candidate storage media and define future data requirements.
- Develop engineering and design models to further the understanding of on-board storage **transport phenomena requirements**.
- Apply **systems architecture** to “up select” specific metal hydride systems capable of meeting DOE storage targets.

Phase 2: 2011-2013

- Develop **innovative on-board system concepts** for metal hydride and adsorption hydride materials-based storage technologies.
- Design components and experimental test fixtures to **evaluate the innovative storage devices** and subsystem design concepts, validate model predictions, and improve both component design and predictive capability.

Phase 3: 2012-2014

- Design, fabricate, test, and decommission the **subscale prototype systems** of each materials-based technology (adsorbents and metal hydrides storage materials).

Relevance: Phase 1 Objectives

Collect Media Property Data for Metal Hydrides and Adsorbents

- Kinetics data and models
- Thermal and mass transport data
- Evaluate completeness of available data
- Propose experiments to obtain missing data
- Interface with MHCoE and independent projects

Collect Operational Data for Storage Systems

- Heat transfer
- Mass transfer
- Identify additional data required

Develop General Format for Models

- Extension of "Hierarchical Modeling System"
- Apply preliminary system model boundary conditions

Assemble and Test Models

- Conduct preliminary validation

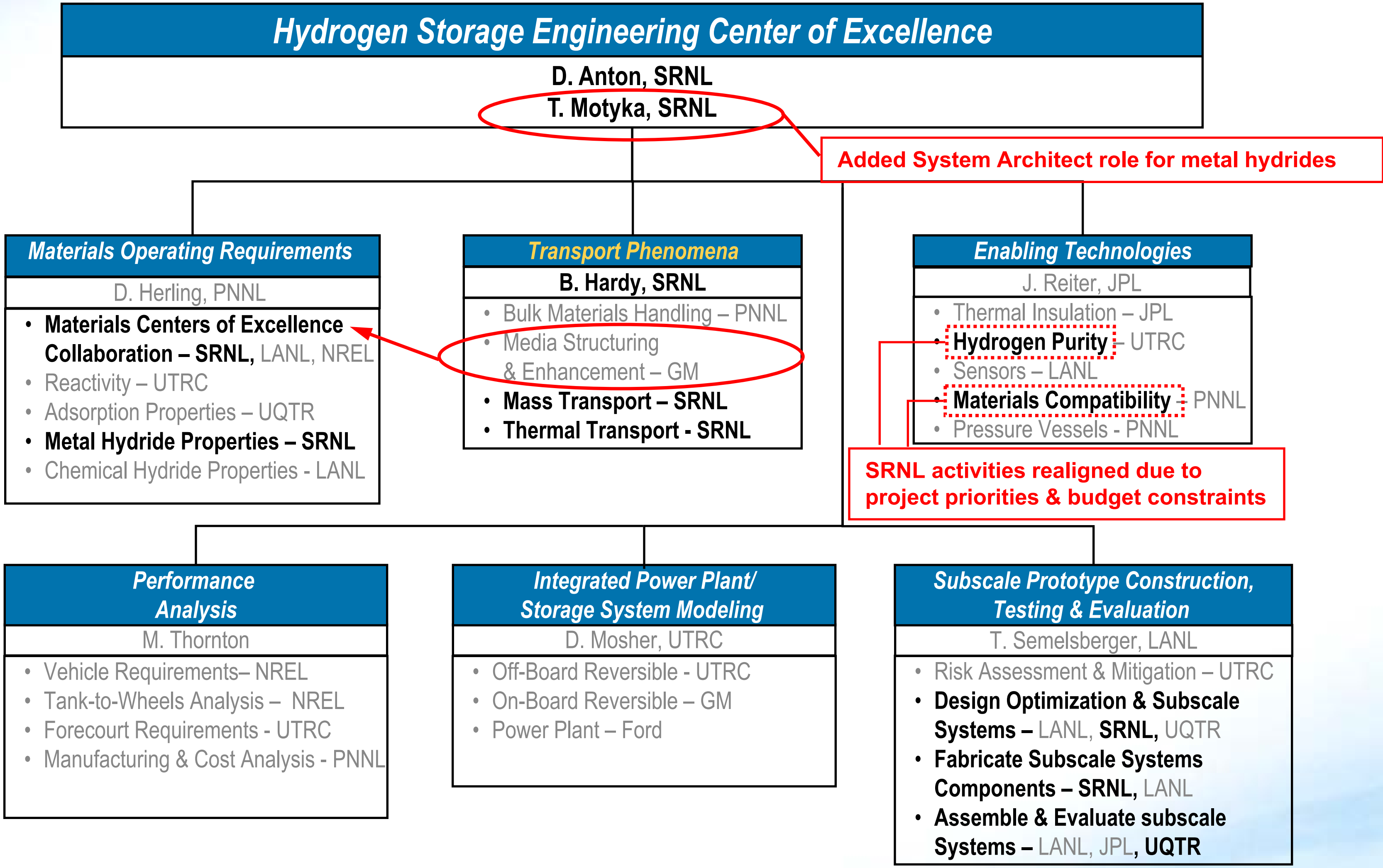
Develop "Acceptability Envelope" of Media Characteristics Based on 2010 & 2015 DOE Technical Targets

- Determine which existing metal hydrides have characteristics lying within the "acceptability envelope"

Apply System and Engineering Models to Evaluate Metal Hydride Systems Against 2010 DOE Technical Targets

- As the Metal Hydride System Architect determine which existing metal hydride systems have the potential to meet the Phase I Go/No-Go decision

Approach: SRNL's Major HSECoE Technical Activities



Hydrogen Storage Engineering Center of Excellence

D. Anton, SRNL
T. Motyka, SRNL

Added System Architect role for metal hydrides

Materials Operating Requirements

D. Herling, PNNL

- **Materials Centers of Excellence Collaboration – SRNL,** LANL, NREL
- Reactivity – UTRC
- Adsorption Properties – UQTR
- **Metal Hydride Properties – SRNL**
- Chemical Hydride Properties - LANL

Transport Phenomena

B. Hardy, SRNL

- Bulk Materials Handling – PNNL
- Media Structuring & Enhancement – GM
- **Mass Transport – SRNL**
- **Thermal Transport - SRNL**

Enabling Technologies

J. Reiter, JPL

- Thermal Insulation – JPL
- **Hydrogen Purity** – UTRC
- Sensors – LANL
- **Materials Compatibility** – PNNL
- Pressure Vessels - PNNL

SRNL activities realigned due to project priorities & budget constraints

Performance Analysis

M. Thornton

- Vehicle Requirements– NREL
- Tank-to-Wheels Analysis – NREL
- Forecourt Requirements - UTRC
- Manufacturing & Cost Analysis - PNNL

Integrated Power Plant/ Storage System Modeling

D. Mosher, UTRC

- Off-Board Reversible - UTRC
- On-Board Reversible – GM
- Power Plant – Ford

Subscale Prototype Construction, Testing & Evaluation

T. Semelsberger, LANL

- Risk Assessment & Mitigation – UTRC
- **Design Optimization & Subscale Systems –** LANL, **SRNL,** UQTR
- **Fabricate Subscale Systems Components – SRNL,** LANL
- **Assemble & Evaluate subscale Systems –** LANL, JPL, **UQTR**

Bold = SRNL Projects

Approach: Phase 1 Milestones, Deliverables and Go/No-Go Criteria

Milestones

- **Compile Metal and Adsorption Hydride Data**
  - Chemical kinetics
    - Equilibrium hydrogen capacity
    - Model development
  - Heat transfer parameters
  - Mass transfer parameters
- **Develop Preliminary Hierarchical Model**
  - Use model to define "acceptability envelope" of metal and adsorption hydride properties to meet DOE2010 and 2015 goals
- **Develop Material Test Plan and Matrix**

Deliverables (Programmatic Go/No-Go Criteria)

- **Preliminary Envelope of Properties for Acceptable Media**
- **Report Describing Phase 1 Activities and Results in Detail**

Technical Go/No-Go Criteria

- **"Up Select" Media Falling Within Acceptability Envelope**

Accomplishments: Material Operating Requirements

- **Selected sodium aluminum hydride ($NaAlH_4$) material as initial baseline hydride candidate material for transport phenomena and system modeling development**
- **Databases completed for:**
  - $NaAlH_4$ (with and without catalysts)
  - 2:1 $LiNH_2$:MgH_2
  - MgH_2 (without catalysts)
  - TiCrMn
  - Mg_2Ni
- **Determination of properties not listed in literature is underway**
  - i.e. Equilibrium pressure and packing density of 1:1 $LiNH_2$:MgH_2

Accomplishments: Metal Hydride Models

- **Model Development and Validation**
    - 0-D kinetics model – MathCAD®
    - Baseline numerical model – Comsol®
    - Model validation against data
- **Optimization Studies**
    - Unit cell models – Comsol®
    - Results
    - Materials Requirements
- **Novel Concepts**
    - Assessment

Accomplishments: Metal Hydride Models: 0-D MathCAD® Kinetics Model

Example: $NaAlH_4$ + 4%$TiCl_3$

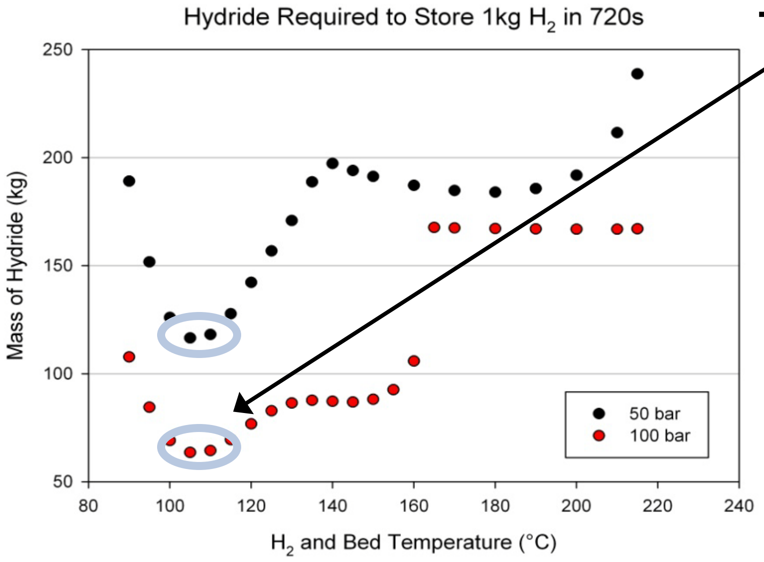
UTRC kinetics and saturation parameters

Assumptions:

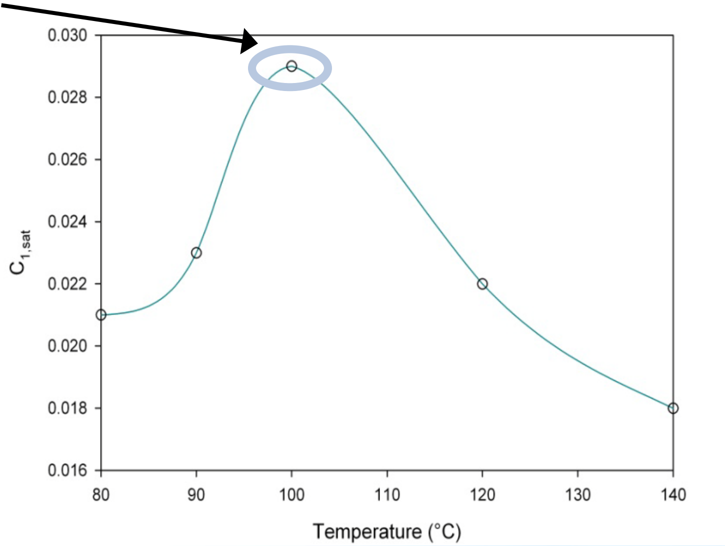
- **Isothermal**
- **Isobaric**
- **Kinetic limitations only**

Results

- Feed at 100 bar H_2 yields a significantly larger optimum temperature range
- Na_3AlH_6 saturation term reduces rate of formation of $NaAlH_4$
- Saturation weight fraction ($C_{1,sat}$) controls optimal temperature



Optimum Temperature Range



Accomplishments: Metal Hydride Models: Fill Time - Metal Hydride ($NaAlH_4$)

Mass H_2 Stored

- **5.5 kg in 4.2 min (2010 Target)**
- **Includes compressed gas in voids (~50% porosity)**

Total Tank Volume: 0.32 m^3

- **4 Tanks**
  - Length: 4 ft (1.2 m)
  - Diameter: 1 ft (0.3 m)

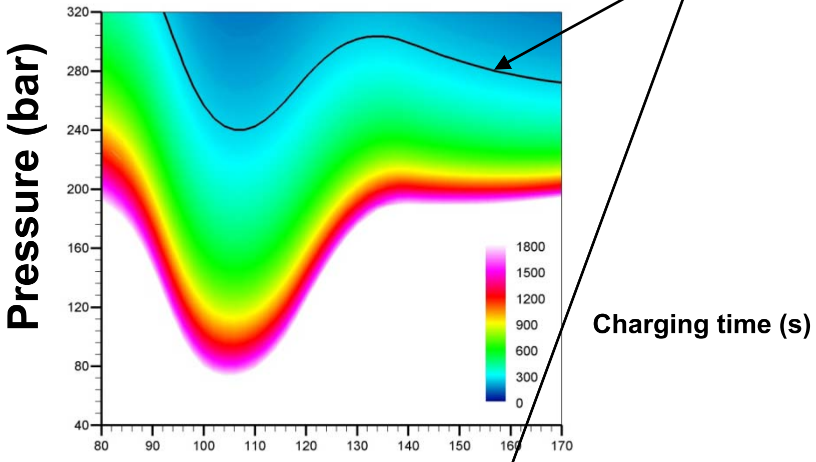
Discharge Conditions:

- **Pressure: 4 bar**
- **Temperature: 170   C**

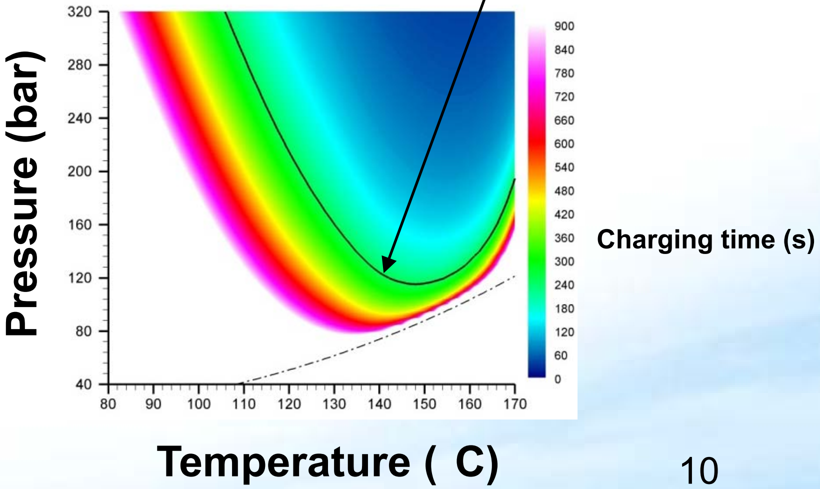
Model shows conditions required to achieve specific fill times for two ($NaAlH_4$) materials with different kinetic properties

2010 target charging times

UTRC Prototype 1 Kinetics



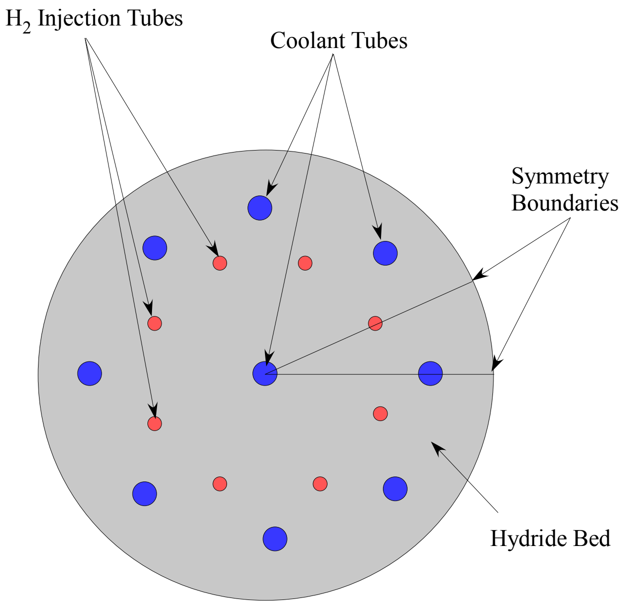
UTRC Prototype 2 Kinetics



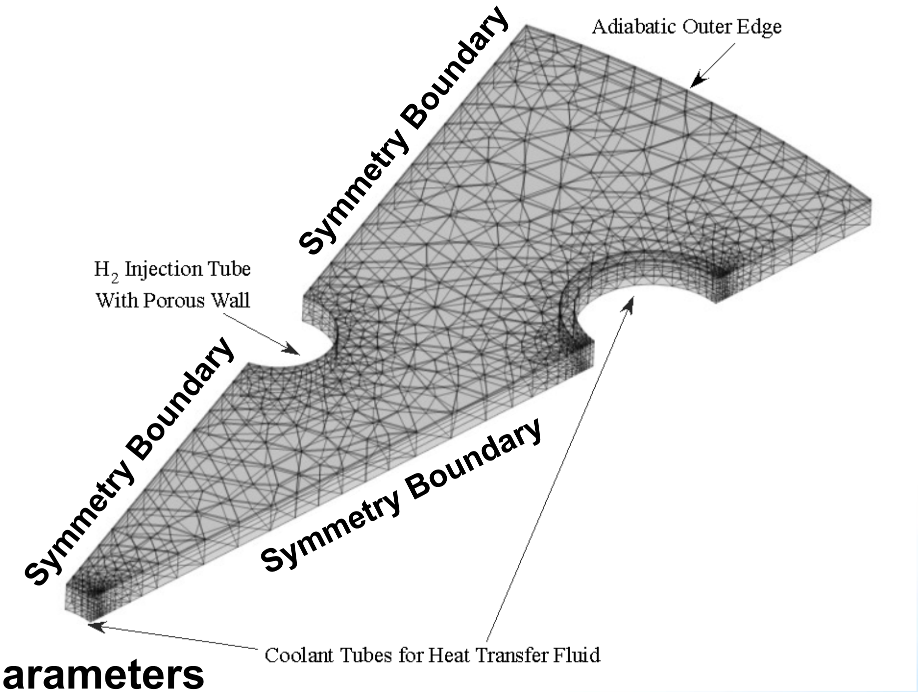
Accomplishments: Metal Hydride Models: Geometric Representation

This is a specific example of a generalized FEM model that can be applied to any geometry and set of thermal properties.

Sample Cross-Section Schematic



Sample Geometry Used in 3-D Model



Sample Geometric Parameters

- **Diameter 23.0 cm**
- **Length 68.90 cm**
- **Fin Thickness 0.0313 cm**
- **Axial Spacing of Fins 0.64 cm**

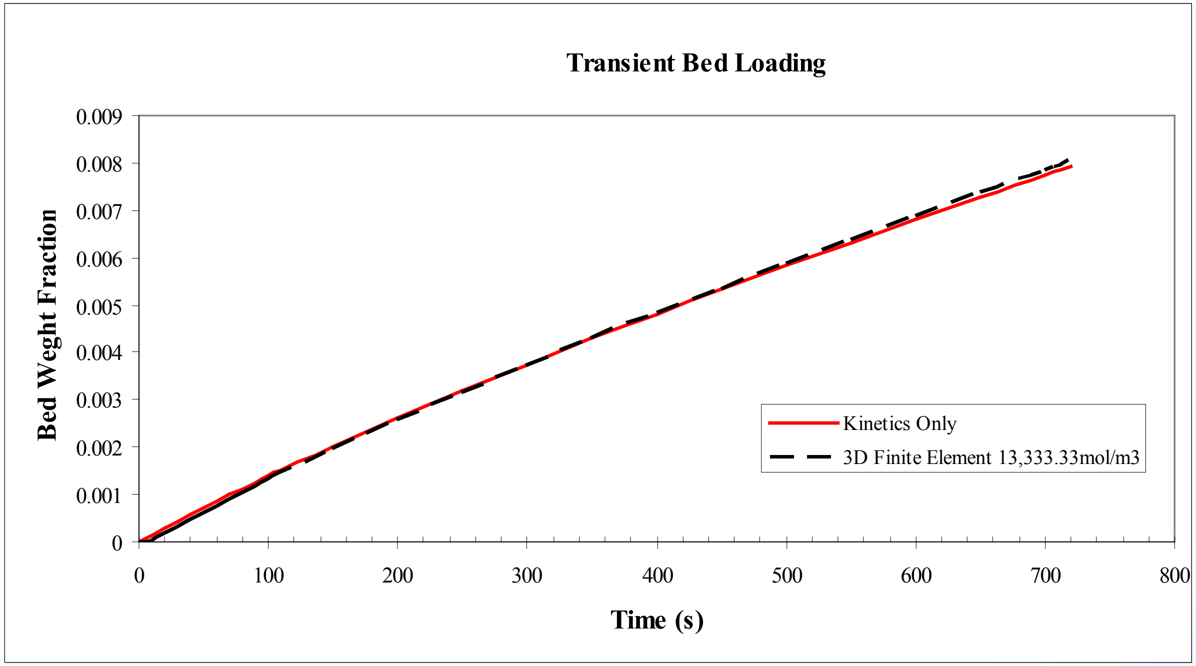
Accomplishments: Metal Hydride Models: $NaAlH_4$ Kinetics Vs Storage Vessel Charge Rate

Coolant and Feed Hydrogen Temperatures Fixed at 100°C

Charging Pressure of 50 bar

Initially 13,333.33 mol/m^3 of NaH
0 mol/m^3 of $NaAlH_4$ and Na_3AlH_6

Results show that for good heat transfer conditions with $NaAlH_4$, the charge rate is limited by kinetics.



Accomplishments: Metal Hydride Models: Novel Concepts

Longitudinal Fins

Symmetry assumed

- Each tube independent
- End effects neglected (Assumed 2-D)
- 60   wedge

Spatially uniform H_2 pressure assumed

Explicit fin and tubes

Media-metal thermal contact resistances included

Conditions (Adjustable)

- 50 bar H_2 feed pressure
- 100 C cooling fluid

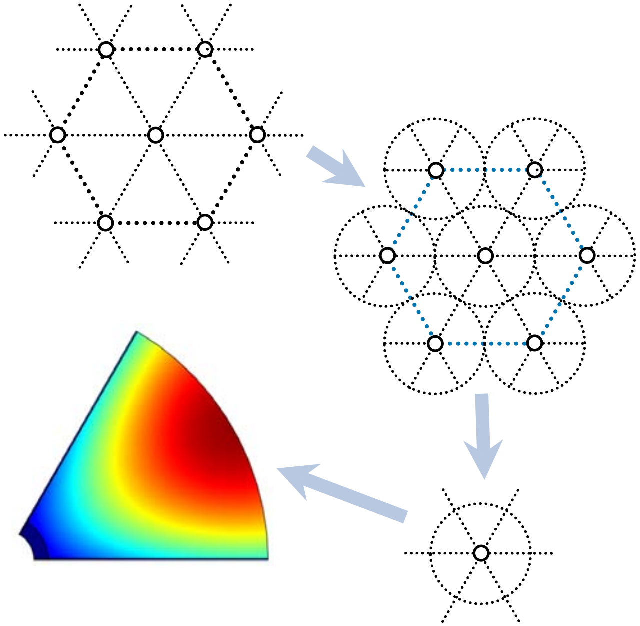
Advantages

- **Media Packing**

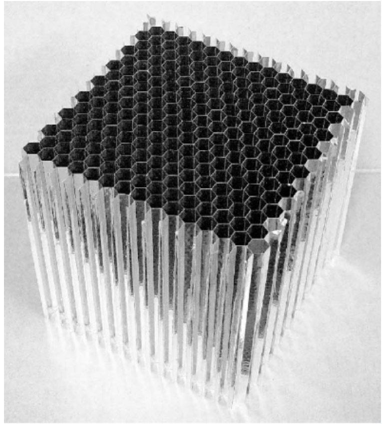
Disadvantages

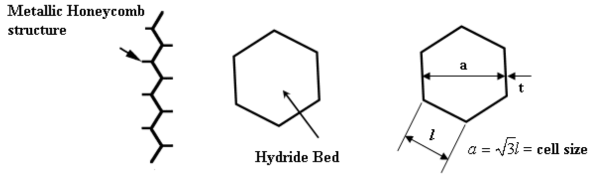
- **Construction Cost**

also applies to MHS (below)



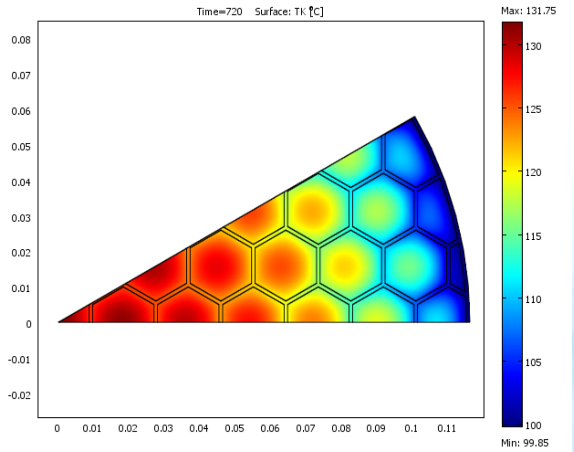
Metallic Honeycomb Structure (MHS)





Thickness t (in)	0.04		
Cell size l (in)	1	1/2	3/8

- Symmetry assumed (30°)
- Axial hydrogen injection at 50 bar
- Contact resistance not considered

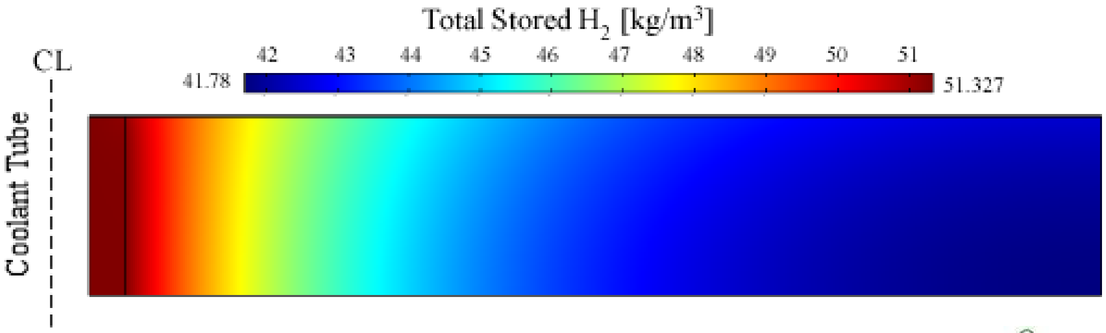


Accomplishments: Adsorbent Models: Scoping Model

- Unit cell
  - Half-thickness of fin & media
  - Central coolant channel
- Energy balance only
  - Prescribed pressure transient
- Optimizes Parameters (uses Mathlab® - Comsol® Interface)
  - Cooling tube (inner) diameter
  - Cooling tube thickness
  - Tube (horizontal) spacing
  - Fin thickness
  - Fin-Fin (vertical) spacing

Advantages:

- Executes quickly
- Analogous to SRNL heterogeneous cell metal hydride scoping models
- Suitable for large number of runs



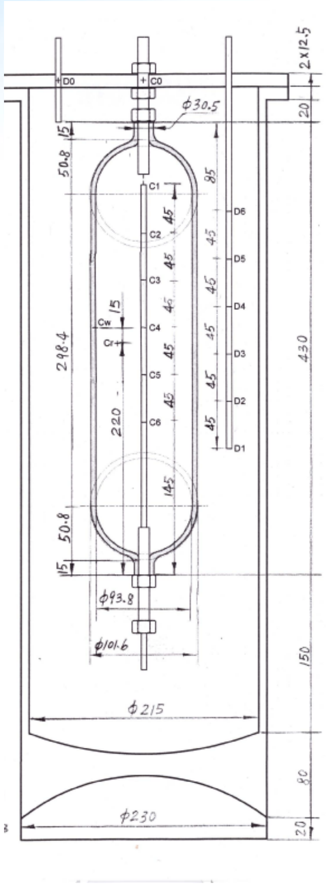
Accomplishments: Adsorbent Models - Detailed MaxSorb® (AX-21®)

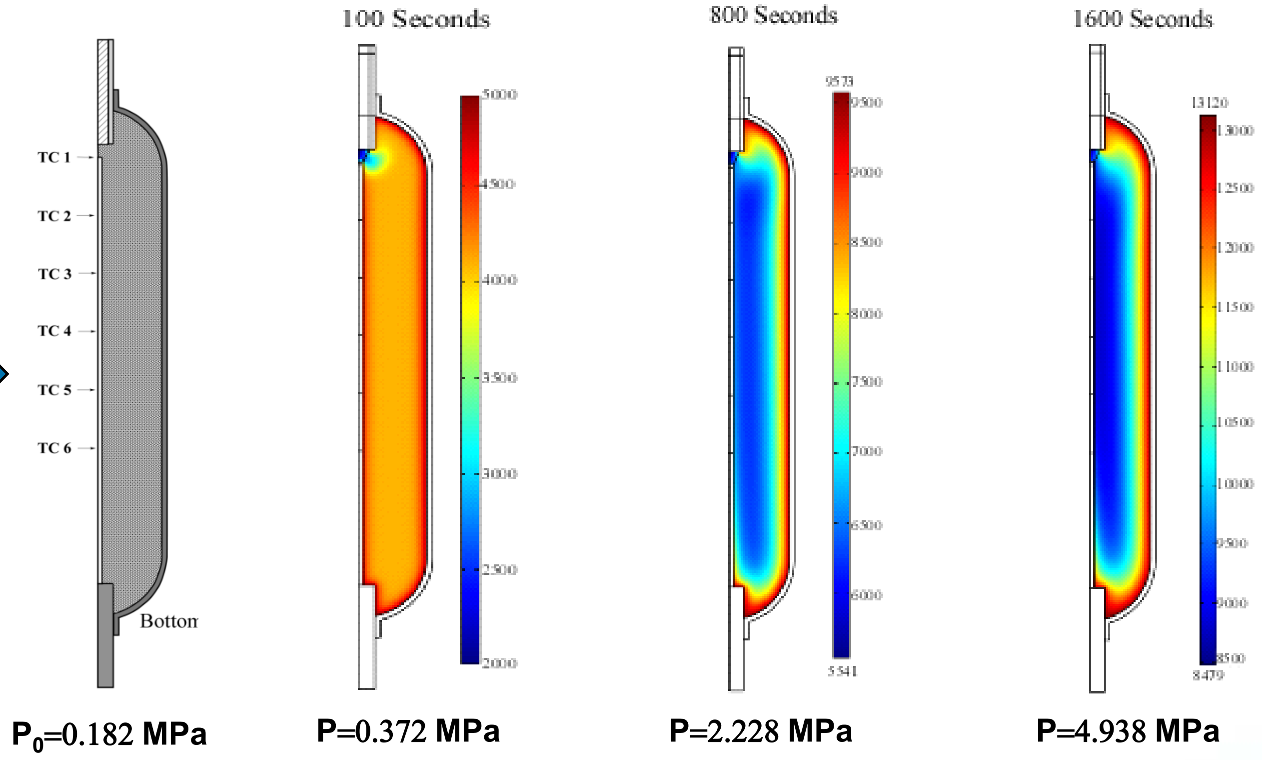
- **Solves conservation equations for mass, momentum and energy in 2 or 3 dimensions**
  - Uses weakly compressible Brinkman equations in all of flow domains
  - Includes thermal radiation
  - Temperature dependent fit for carbon specific heat
  - Correlations for non-ideal hydrogen properties from NIST REFPROP 23 V8.0 database
    - Valid for $0.05 \leq P \leq 35.0$MPa and $70 \leq T \leq 450$K
    - Compressibility factor
    - Enthalpy
    - Viscosity
    - Thermal conductivity

- **AX-21® thermodynamic models for absolute adsorption and internal energy of adsorbed hydrogen obtained from:**
  - *Richard, Bénard and Chahine. "Gas Adsorption Process in Activated Carbon Over a Wide Temperature Range Above the Critical Point. Part 1: Modified Dubinin-Astakhov Model."*
  - *Richard, Bénard and Chahine. "Gas Adsorption Process in Activated Carbon Over a Wide Temperature Range Above the Critical Point. Part 2: Conservation of Mass and Energy."*

Accomplishments: Adsorbent Models: Distribution of Stored H_2

Calculates hydrogen loading for actual UQTR Adsorbent System





P_0=0.182 MPa

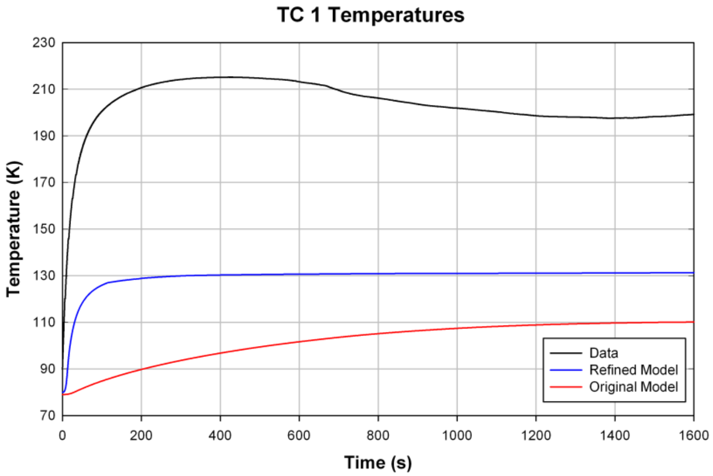
P=0.372 MPa

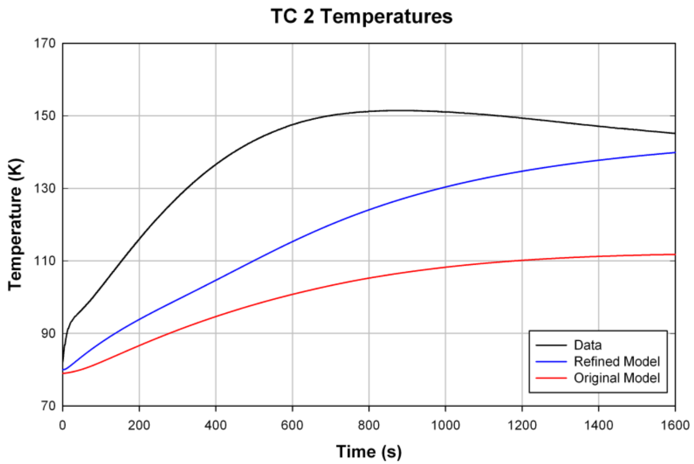
P=2.228 MPa

P=4.938 MPa

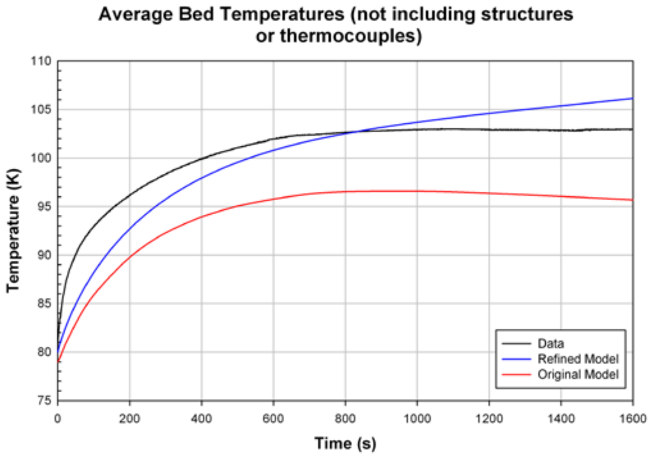
total hydrogen concentration (mol/m^3) during loading

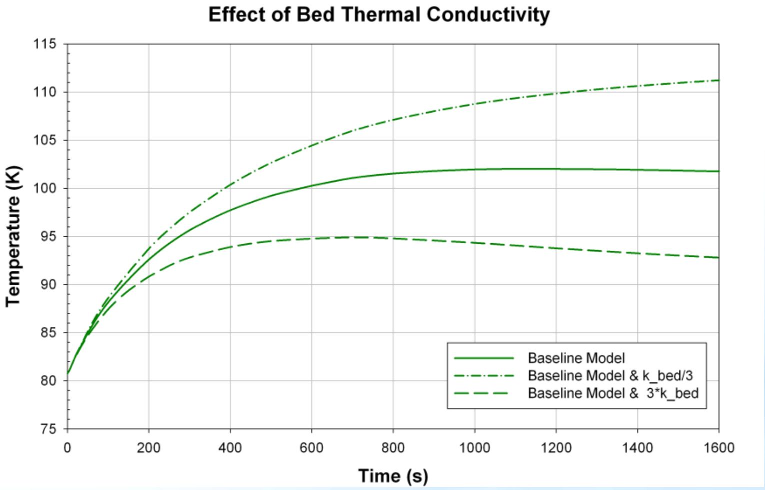
Accomplishments: Adsorbent Models: Temperature Profiles


TC 1 Temperatures


TC 2 Temperatures

Compares temperature results from the model with those measured in the actual adsorbent system evaluated at UQTR


Average Bed Temperatures (not including structures or thermocouples)


Effect of Bed Thermal Conductivity

HSECoE

UQTR

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

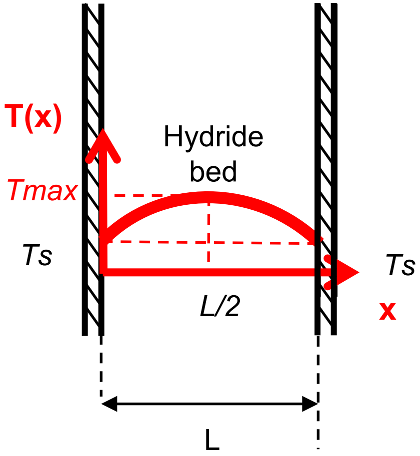
Accomplishments: Acceptability Envelope

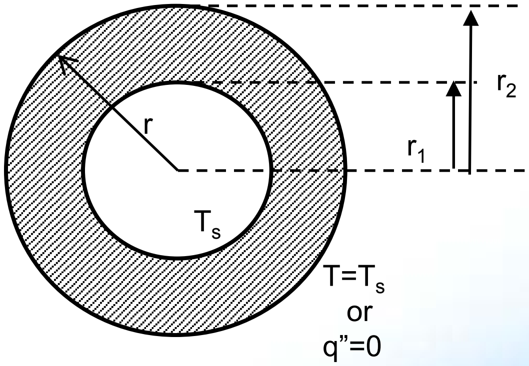
The "Acceptability Envelope" or "BlackBox Analysis" determines range of characteristics necessary for coupled media and system to meet storage system performance targets

- **Based on energy balance**
- **Serves as media screening tool**
    - Guide for material development
- **Uses technical targets to establish values for parameter "grouping"**
    - Defines ranges of parameters for media & storage vessel

Current analysis applies to metal hydrides

- Rectangular coordinates (RC)
- Cylindrical coordinates (CC)





Accomplishments: Acceptability Envelope: Equation

For both rectangular and cylindrical geometries

$$\Delta T = -\frac{1}{m}\left[\frac{L^2}{k}\Delta H_{overall}\frac{\rho_{Hydride}}{M_{Hyd\_eff}M_{H2}}\frac{\Delta m_{H2}}{\Delta t}\right]$$

$$\Delta T = T_{max} - T_{min}$$

$$m = \begin{cases} 8 & \textbf{rectangular} \\ 4 & \textbf{cylindrical} \end{cases}$$

$$L^2 = r_1^2 - r_2^2 \quad \textbf{cylindrical}$$

$$L = (\text{plate spacing}) \quad \textbf{rectangular}$$

Rearrange to get

$$\underbrace{\left(\frac{1}{L^2}\right)}_{\textbf{Vessel parameter}}\underbrace{\left(\frac{k\ M_{Hyd\_eff}\ \Delta T}{-\Delta H_{overall}\ \rho_{Hydride}}\right)}_{\textbf{Media parameters}} = \frac{1}{mM_{H2}}\underbrace{\frac{\Delta m_{H2}}{\Delta t}}_{\textbf{Charging/discharging rate}}$$

Linear relation between charging/discharging rate and media and system parameters

Physical interpretation of parameters

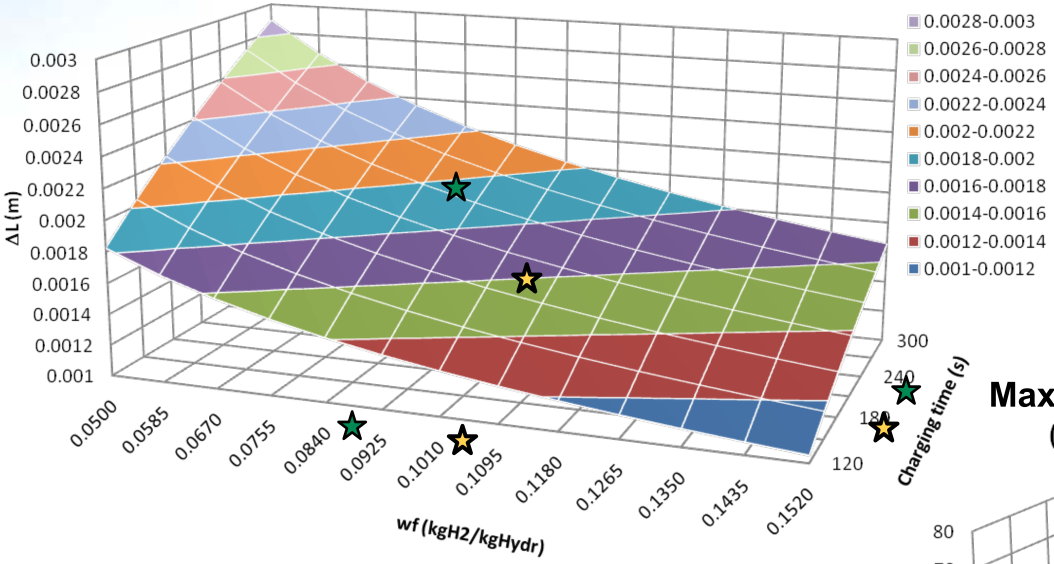
L	**Distance between heat transfer surfaces**
ΔT	**Temperature range for acceptable chemical kinetics (to give charge/discharge rate of $\Delta m_{H2}/\Delta t$)**
M_{Hyd_eff}	**Mass of hydride (in reference form) required to load target amount of hydrogen in specified time (relates to kinetics)**
$\Delta H_{overall}$	**Overall heat of reaction**
$\rho_{Hydride}$	**Hydride density (in reference form)**
k	**Bed thermal conductivity**
$\Delta m_{H2}/\Delta t$	**Required rate of charging/discharging (from DOE Technical Targets)**

Accomplishments: Acceptability Envelope:

Varying Thermal Conductivity & Heat Transfer Surface Spacing

$NaAlH_4$ System:
Maximum HX Surface Spacing (in m)

(RC, wall fixed T, ρ=720 kg/m³,k=0.5W/mK,ΔH=40.3kJ/molH2)



DOE 2010 ★ **5 kg in 4.2 min**

DOE 2015 ★ **5 kg in 3.3 min**

ΔT_{max}= 5°C

k = thermal conductivity

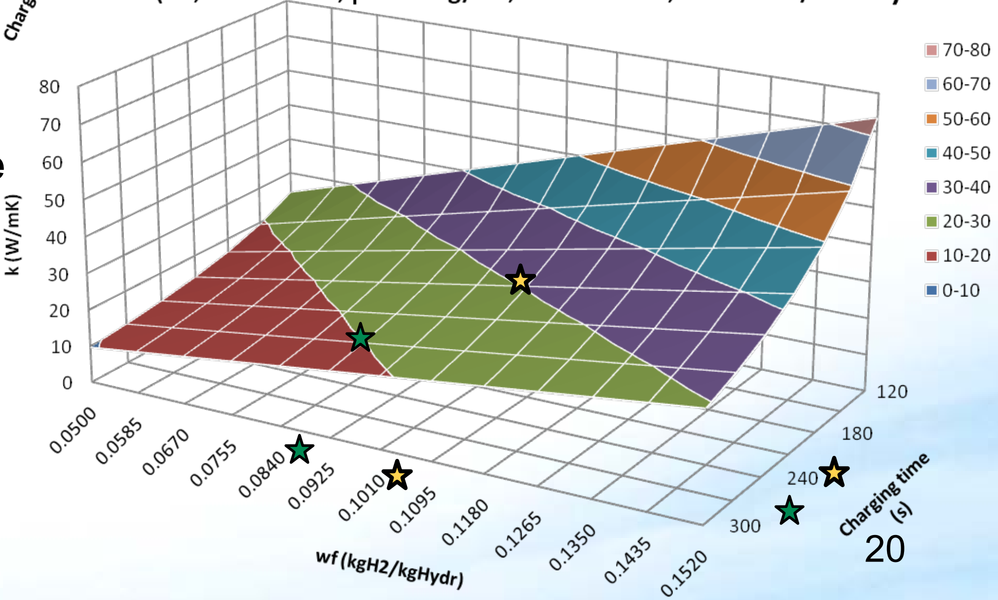
ΔL is distance between surfaces

- **at low thermal conductivities a high rate of heat removal is required which leads to very close HX surface spacing**
- **at more reasonable HX spacing higher thermal conductivities are needed**

<u>Alternatives</u>: reduce $\Delta H_{overall}$ or increase ΔT_{max}

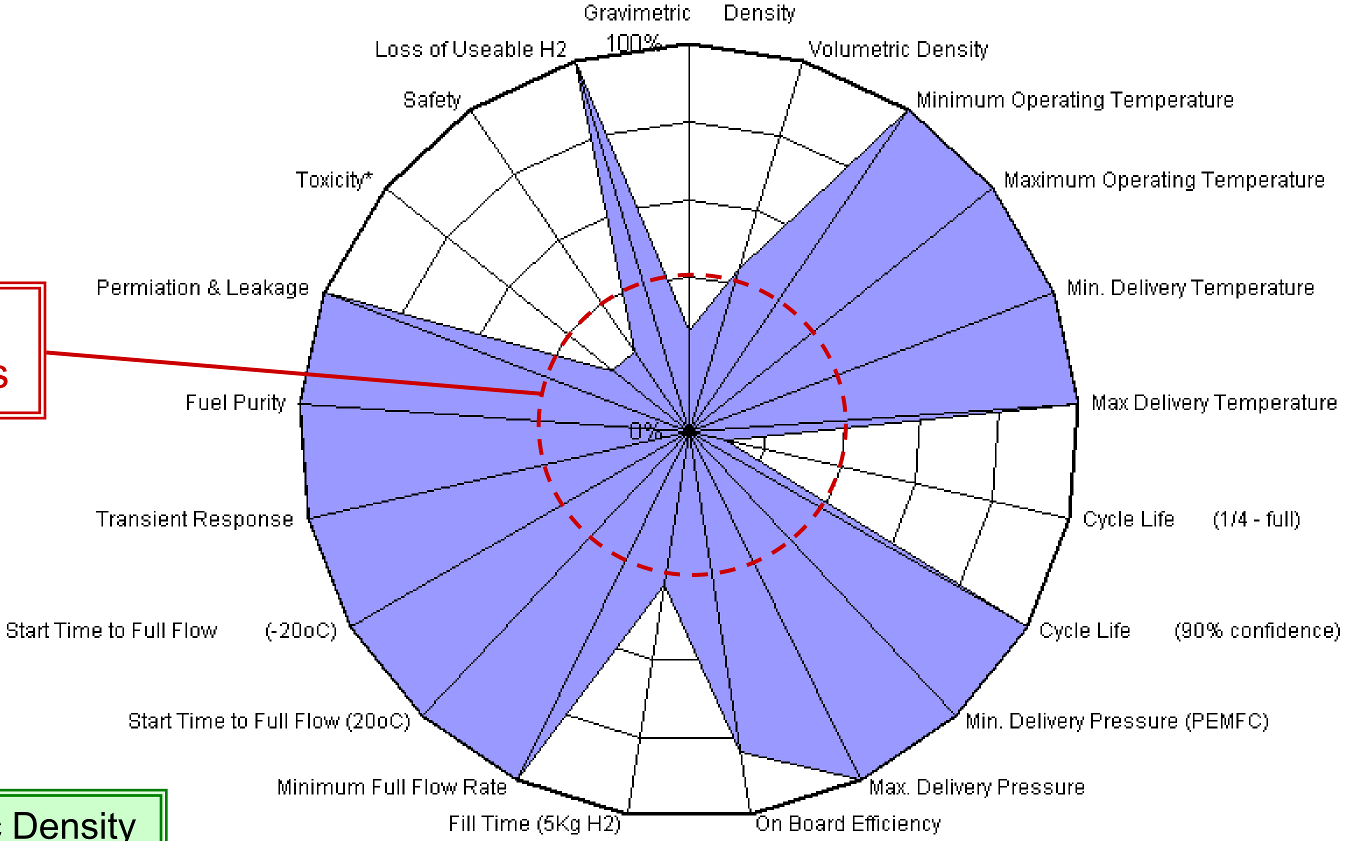
$NaAlH_4$ System:
Maximum Req'd Bed Thermal Conductivity (in W/m K)

(RC, wall fixed T, ρ=720 kg/m³,ΔL=0.0127 m,ΔH=40.3kJ/molH2)



HSECoE

Accomplishments: System Architect Analysis: Sodium Aluminum Hydride¥



40% of DOE 2010 Targets

1. Gravimetric Density
2. Cycle Life
3. Safety*
4. Toxicity*

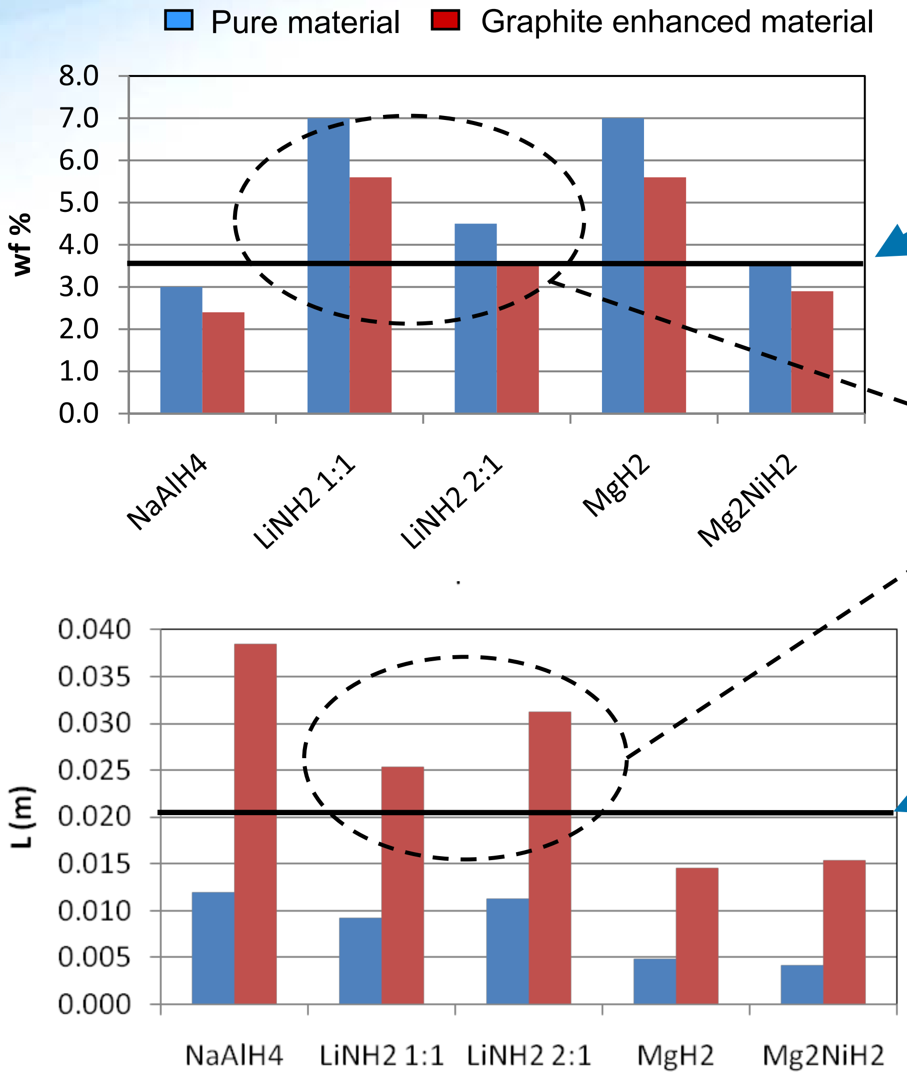
- 17 Targets fully met
- 4 Targets below 40% minimum

¥ based on system analysis performed by GM and UTRC

* Safety and Toxicity values are currently rough estimates more quantitative values are being developed

Accomplishments: System Architect Analysis:

Applying Acceptability Envelope Model to Various Materials



Minimum required H_2 wt% stored on the material to meet 40% of the DOE 2010 gravimetric density target (assuming a 50:50 material to system gravimetric ratio)

Suggests that Li-Mg-N materials may be the most promising metal hydrides for further consideration

Minimum recommended value for heat transfer surface spacing based on $NaAlH_4$ system analyses

Pure material:
ΔT=15°K,
k=0.7 W/m K
Fill time = 10.5 min

Graphite enhanced material:
ΔT=15°K
k=8.5 W/m K
Fill time =10.5 min

Collaborations

Material Operating Requirements

- Ewa Ronnebro, PNNL
- Jason Graetz, BNL (Alane data)
- Weifang Luo, Sandia (2 $LiNH_2$: 1 MgH_2 data)

Metal Hydride System Modeling

- Mikhail Gorbounov, Daniel Mosher, Bart van Hassel, UTRC
- Jacques Goyette, Maha Bhouri, UQTR
- Sudarshan Kumar, GM
- Kevin Drost, Goran Jovanivich, Anna Garrison, OSU

Adsorbent System Modeling

- Richard Chahine, M. A. Richard, UQTR
- Andrea Sudik, Ford

Acceptability Envelope Development and Applications

- Ewa Ronnebro, PNNL (Material Screening)

System Architect Analyses

- Sudarshan Kumar, GM
- Bart van Hassel, UTRC
- Michael Veenstra, Ford (Assistant MH System Architect)

Proposed Future Work

Metal Hydride Material Operation Requirements

- Complete databases for 1:1 LiNH2:MgH2 material with and without catalysts
- Determine needed engineering properties for all up selected materials

Metal Hydride System Modeling

- Perform more detailed modeling and scoping studies (includes H_2 mass transfer, H_2 in gas phase, coolant tube HX coefficients etc.)
- Examine longitudinal fins and additional, non-connecting fins
- Explore metal honeycomb structure including cell size and additional cooling
- Perform parameter sensitivity studies

Adsorbent System Modeling

- Conduct validation experiments that reduce parasitic heat transfer
- Compare performance of MOF-5® and MaxSorb®
- Use baseline models in 2 and 3 dimensions for design and sensitivity studies
- Conduct process-specific experiments (validate models and test conceptual vessel designs)
- Reduce models to form suitable for use in system analysis
- Apply models to prototype design

Acceptability Envelope Applications and Development

- Include effects of system parameters
- Complete application to metal hydrides (include coupled parameter ranges and candidate material evaluations)
- Develop and apply model for adsorbents

System Architect Analyses

- Extend System Architect analysis from Sodium Alanate to other metal hydride systems
- Complete System Architect analysis on metal hydride candidate systems for Phase I Go/No-Go Decision

Project Summary

Relevance

As both the overall lead and a major technical contributor to the HSECoE project, SRNL is using its extensive expertise in metal hydride technology, hydrogen materials compatibility, transport phenomena modeling & analysis, and hydrogen storage system & component design & fabrication to evaluate a solid-state hydrogen storage system for vehicle application that meets or exceeds DOE's 2010 and 2015 goals.

SRNL, through a subcontract grant, is also utilizing the expertise of the UQTR, which has been internationally recognized for its work in hydrogen adsorbent material and system development and testing.

Approach

In Phase I and II SRNL will:

- lead in the collection and screening of material property and engineering data for metal hydride and adsorbent materials.
- lead the overall project in Transport Phenomena modeling and analysis concentrating on metal hydride and adsorbent systems and components designs.
- lead System Architect activities for metal hydride systems.

Technical Accomplishments and Progress (as of 3/10)

- Collected material operating data for 5 metal hydride candidates and AX-21® adsorbent material (UQTR)
- Issued a technical report that evaluated the feasibility of membrane separation for metal hydride systems purification
- Developed acceptability envelope for metal hydrides
- Performed comparisons between metal hydride models & available data
- Developed baseline models for metal hydrides
- Performed optimization studies and modeling of various vessel configurations
- Completed System Architect analysis of Sodium Alanate vs. DOE 2010 technical hydrogen storage targets

Collaborations

HSECoE partners, Materials Centers, SSAWG, IPHE, IEA etc.

Proposed Future Work (Phase I/II)

- Complete metal hydride and adsorption data collection
- Use detailed models to compare storage system behavior for different media (metal hydrides, MOF-5® and AX-21®)
- Develop and apply Acceptability Envelope to adsorbent systems
- Continue sensitivity analyses
- Pursue novel concepts (micro & mini-channel heat exchangers and structured media)
- Conduct preliminary system designs
- Complete System Architect analysis on final candidate metal hydride system for Phase I GO-NO-GO Decision