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 8, 2010

Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Project ID#ST044

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

Relevance: Transport Phenomena Within the HSECoE

Hydrogen Storage Engineering Center of Excellence

D. Anton, SRNL
T. Motyka, SRNL

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

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

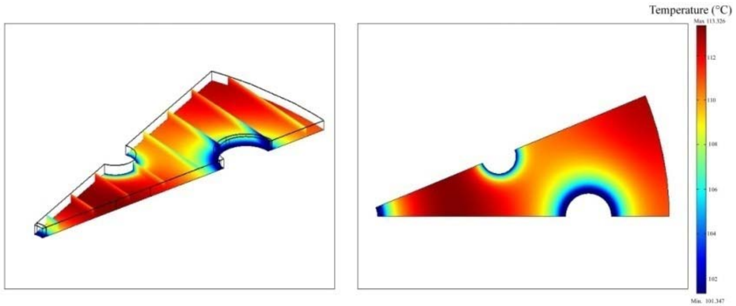
- Risk Assessment & Mitigation – UTRC
- **Design Optimization & Subscale Systems –** LANL, **SRNL,** UQTR
- **Fabricate Subscale Systems Components – SRNL,** LANL
- **Assemble & Evaluate subscale Systems –** LANL, JPL**, UQTR**

Bold→SRNL Projects

Transport Phenomena provides the modeling and analysis required for prototype design, along with interpretation and scaling of prototype data

Relevance: Phase 1 Objectives – Transport Phenomena

- **Collect and Assimilate Property Data for Metal Hydrides and Adsorbents**
  a. Kinetics data and kinetics models
  b. Thermal and mass transport data
  c. Evaluate completeness of available data
  d. Propose experiments to obtain missing data
  e. Interface with MHCoE and independent projects



- **Collect Operational Data for Storage Vessel Configurations**
  a. Heat transfer
  b. Mass transfer
  c. Identify additional data required
- **Develop General Format for Models**
  a. Suitable for sensitivity/scoping studies and detailed analyses
  b. Metal hydrides and adsorbent models to be developed by SRNL/UQTR
  c. Chemical hydride models to be developed by PNNL and LANL
- **Assemble and Test Models**
  a. Conduct preliminary validation
- **Develop "Acceptability Envelope" of Media Characteristics Based on 2010 & 2015 DOE Technical Targets**
  a. Determine whether candidate metal hydrides have characteristics lying within the "acceptability envelope"

Principal Objectives:
- **Development of an "Acceptability Envelope" for metal hydride properties**
- **Develop numerical models for system optimization and sensitivity studies**

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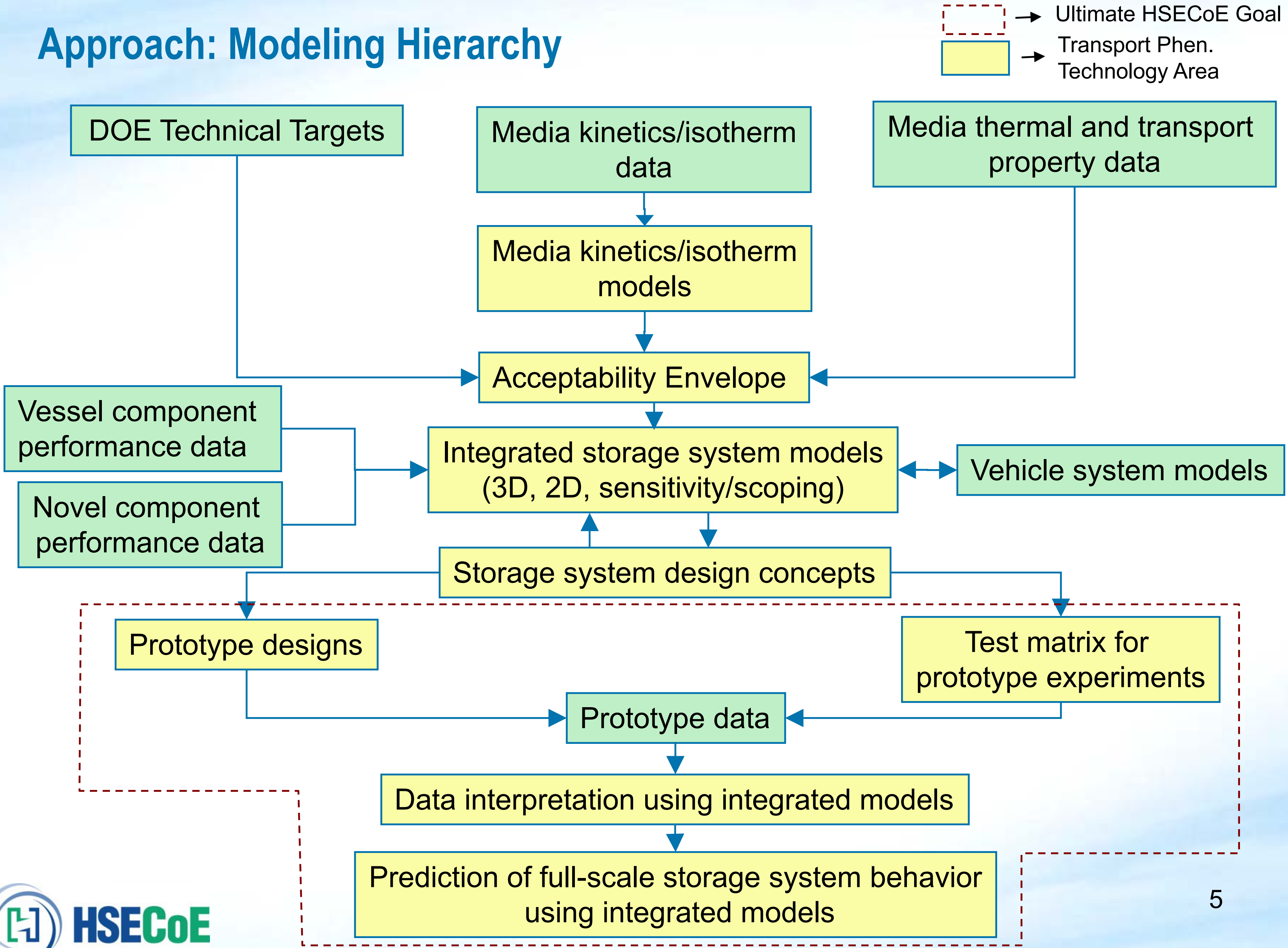
Approach: Modeling Hierarchy



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Technical Accomplishments: 0-D MathCAD® Kinetics Model for Metal Hydrides

UTRC Prototype 2 Kinetics

Hydride: $NaAlH_4$ + 2% $TiCl_3$x1/3$AlCl_3$+0.5% $FeCl_3$

Mass H_2 Stored

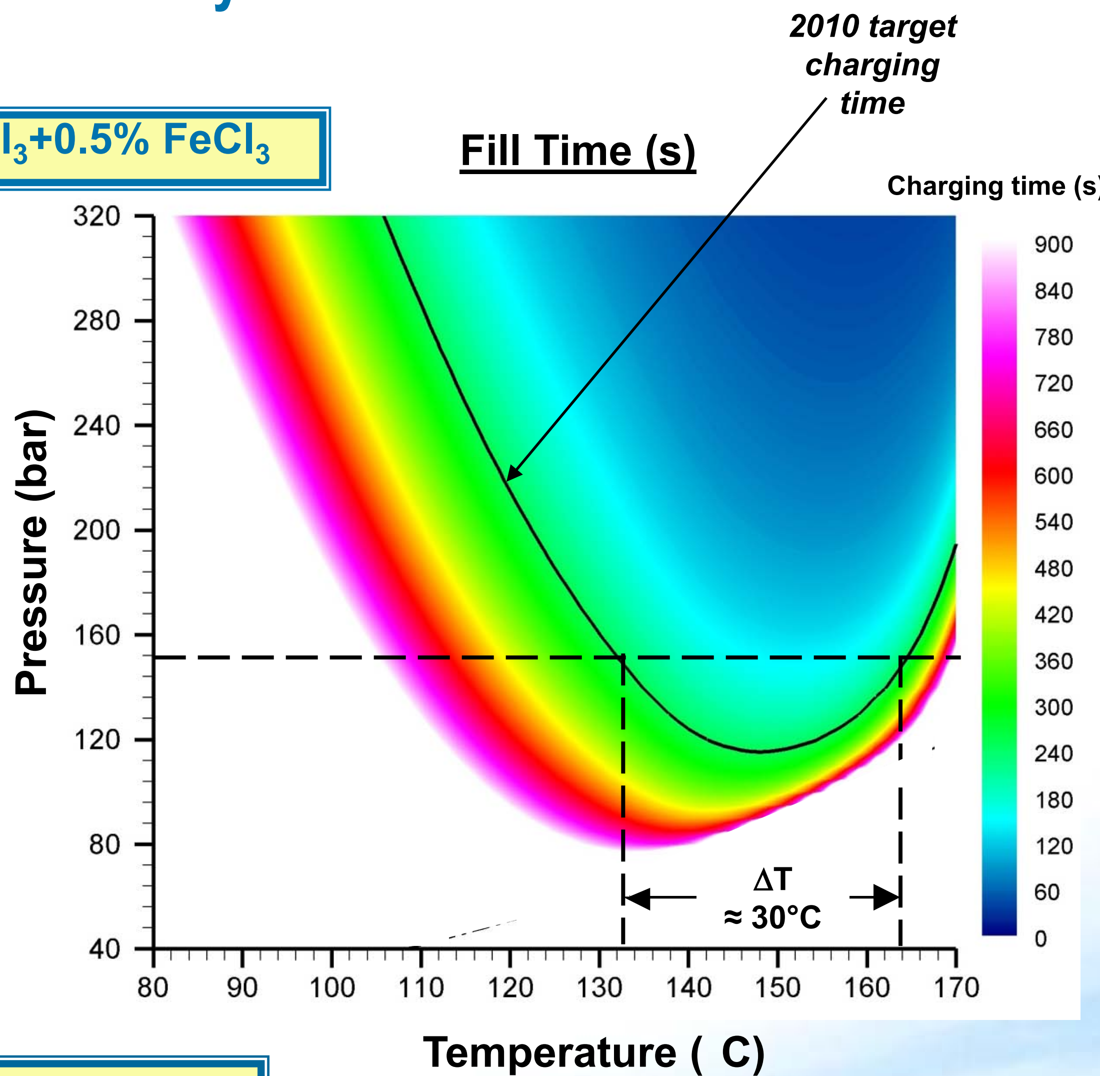
- **5.5 kg in 4.2 min (2010 Target)**
- **Includes compressed gas in voids (~50% porosity)**

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**



ΔT is used in the "Acceptability Envelope"

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Approach: Physics for Integrated Metal Hydride Models

Conservation of Mass (Hydrogen)

$$\frac{\partial C}{\partial t} + \nabla \cdot \left(C\vec{v} \right) = \left(\frac{S_{H_2}}{\varepsilon} \right)$$

Conservation of Momentum (Blake-Kozeny Equations)

$$u = -\frac{D_p^{\,2}}{150\mu}\left(\frac{\varepsilon}{1-\varepsilon}\right)^2 \frac{\partial P}{\partial x}$$

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

$$w = -\frac{D_p^{\,2}}{150\mu}\left(\frac{\varepsilon}{1-\varepsilon}\right)^2 \frac{\partial P}{\partial z}$$

Conservation of Energy in Bed

$$\rho_{bed} Cp_{bed} \frac{\partial T}{\partial t} - \nabla \cdot k \nabla T = -\varepsilon \rho_{H_2} Cp_{H_2} \left(\frac{\partial T}{\partial t} + \vec{v} \cdot \nabla T \right) + \left(\frac{\partial P}{\partial t} + \varepsilon \vec{v} \cdot \nabla P \right) - \left(\sum_i \left[\frac{1}{M_i} \frac{\partial \rho_i}{\partial t} \Delta H_i \right] \right)$$

Plus Non-Ideal Hydrogen Equations of State and Transport Properties, Material Property Correlations, Correlations for Physical Processes, Ancillary Equations, etc. !!!

$$\underbrace{NaAlH_4}_{\text{Species 1}} \underset{\text{Reaction 1}}{\leftrightarrow} \underbrace{\frac{1}{3} Na_3AlH_6 + \frac{2}{3} Al + H_2}_{\text{Species 2}} \underset{\text{Reaction 2}}{\leftrightarrow} \underbrace{NaH}_{\text{Species 3}} + Al + \frac{3}{2} H_2$$

$$r_{1F} \equiv C_{eqv} A_{1F} \exp\left[-\frac{E_{1F}}{RT}\right]\left[\frac{P(C,T) - P_{eq1}(T)}{P_{eq1}(T)}\right]$$

$$r_{1B} \equiv -C_{eqv} A_{1B} \exp\left[-\frac{E_{1B}}{RT}\right]\left[\frac{P_{eq1}(T) - P(C,T)}{P_{eq1}(T)}\right]$$

$$r_{2F} \equiv -C_{eqv} A_{2F} \exp\left[-\frac{E_{2F}}{RT}\right]\left[\frac{P(C,T) - P_{eq2}(T)}{P_{eq2}(T)}\right]$$

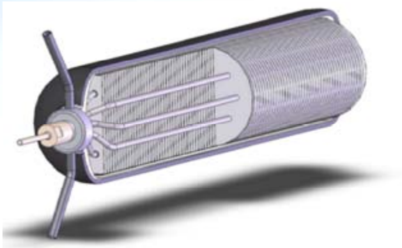
$$r_{2B} \equiv C_{eqv} A_{2B} \exp\left[-\frac{E_{2B}}{RT}\right]\left[\frac{P_{eq2}(T) - P(C,T)}{P_{eq2}(T)}\right]$$

$$\frac{dC_1}{dt} = \begin{cases} r_{1F}\left[\dfrac{3C_2(t)}{C_{eqv}} - C_{2sat}(T)\right]^{\chi_{1F}} & \text{if} \quad P \ge P_{eq1}(T) \\ r_{1B}\left[\dfrac{C_1(t)}{C_{eqv}}\right]^{\chi_{1B}} & \text{if} \quad P < P_{eq1}(T) \text{ and } C_1(t) \ge 0 \end{cases}$$

$$\frac{dC_2}{dt} = -\frac{1}{3}\left(\frac{dC_1}{dt} + \frac{dC_3}{dt}\right)$$

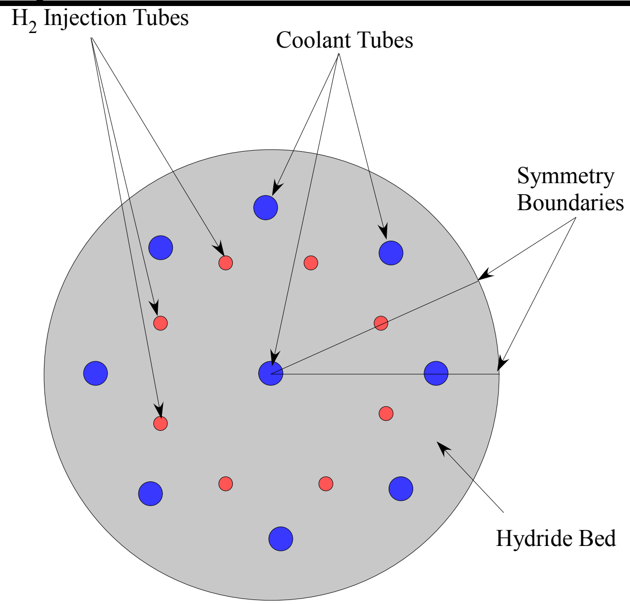
$$\frac{dC_3}{dt} = \begin{cases} r_{2F}\left[\dfrac{C_3(t)}{C_{eqv}} - C_{3sat}(T)\right]^{\chi_{2F}} & \text{if} \quad P \ge P_{eq2}(T) \\ r_{2B}\left[\dfrac{3C_2(t)}{C_{eqv}}\right]^{\chi_{2B}} & \text{if} \quad P < P_{eq2}(T) \text{ and } C_2(t) \ge 0 \end{cases}$$

Approach: Sample Geometric Representation - Metal Hydride Model

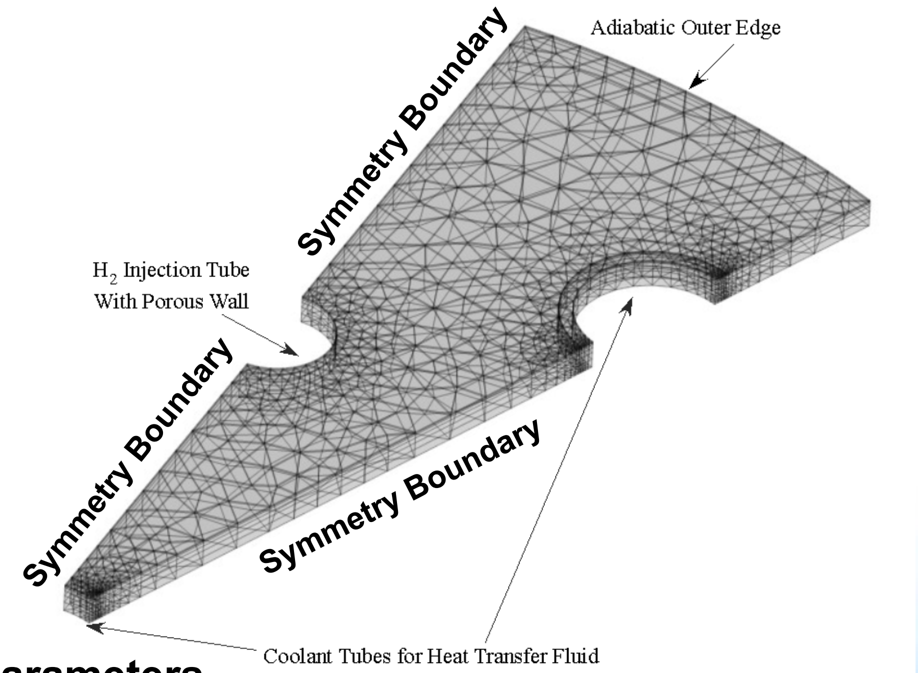


This is a specific example.
The generalized FEM model can be applied to any geometry and set of thermal properties.

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

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Approach: Unit Cell Model for Heat Removal Scoping Studies

Symmetry assumed

- Each tube independent
- End effects neglected (Assumed 2-D)
- Axially symmetric

Spatially uniform H_2 pressure assumed

Explicit representation of fin and tubes

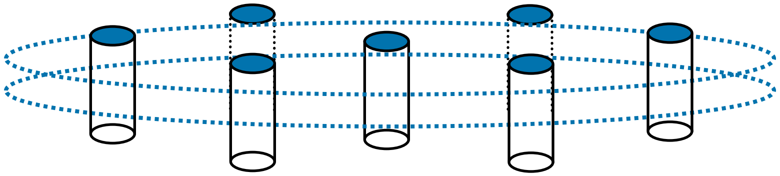
Media-metal thermal contact resistances explicitly included

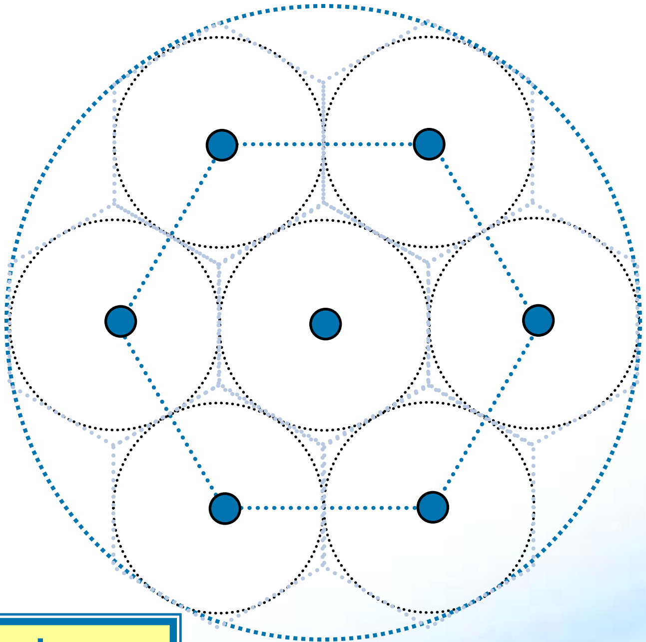
Conditions (Adjustable)

- $NaAlH_4$ + 4% $TiCl_3$ kinetics parameters
- 50 bar H_2 feed pressure
- 100 C cooling fluid

Optimized Parameters (Use Matlab®-Comsol® Interface)

- Cooling tube (inner) diameter
- Cooling tube thickness
- Tube (horizontal) spacing
- Fin thickness
- Fin-Fin (vertical) spacing





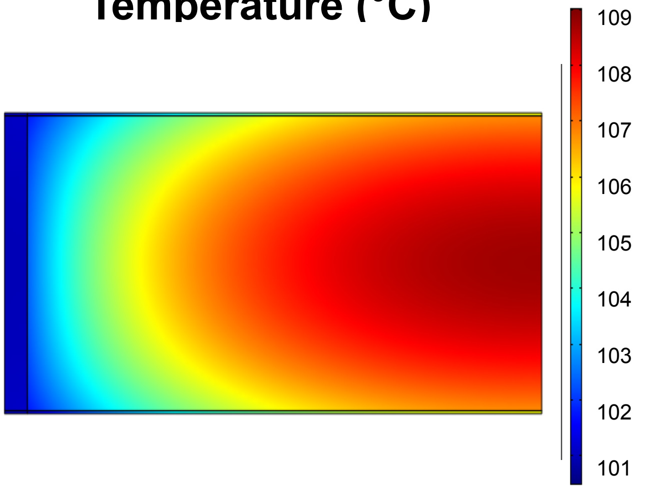
Grid or Nelder-Mead (Downhill Simplex) Optimization

Technical Accomplishments: Systematic Optimization Method

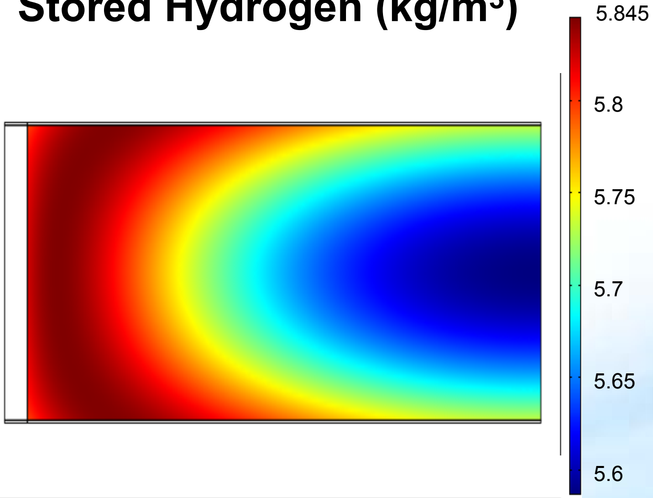
Store 1 kg of hydrogen in 12 min. (720s)
50 bar feed pressure; $NaAlH_4$+4%$TiCl_3$

	Nelder-Mead
Cooling tube ID:	0.085 in
Cooling tube thickness:	0.020 in
Fin length:	0.296 in
Fin thickness:	0.004 in
Fin-Fin spacing:	0.220 in
Number of units:	126050
Media mass:	126 kg
Heat exchanger mass:	17 kg
Heat exchanger vol. %:	3.4%

Temperature (°C)



Stored Hydrogen (kg/m³)



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Technical Accomplishments: Novel Concepts

Longitudinal Fins

Symmetry assumed

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

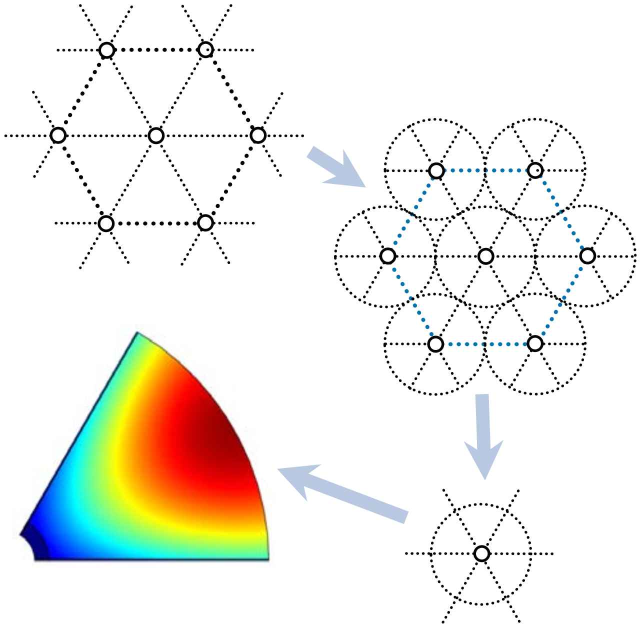
Spatially uniform H_2 pressure assumed

Explicit fin and tubes

Media-metal thermal contact resistances included

Conditions (Adjustable)

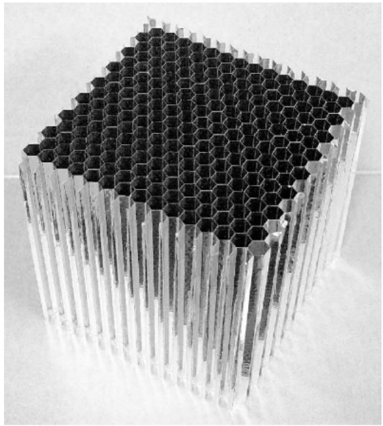
- 50 bar H_2 feed pressure
- 100 C cooling fluid

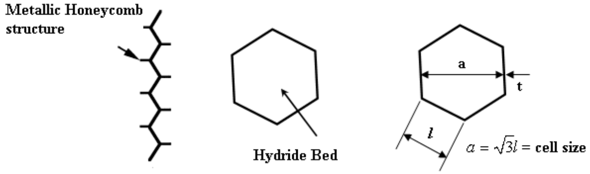


Advantages
- Media Packing

Disadvantages
- Construction Cost

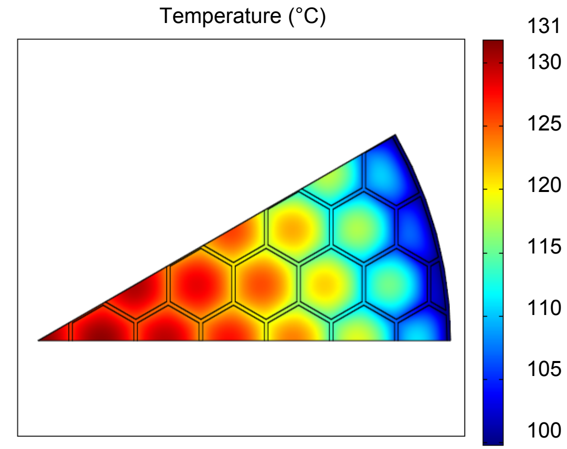
Metallic Honeycomb Structure





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



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Progress: Summary and Current Results for Metal Hydrides

Developed and validated baseline Comsol® models for metal hydride storage systems

Incorporated improved models into optimization routines

- **With given constraints optimal designs require very small spacing of HX surfaces**
- **Methods easily extendable to new systems**
  - New hydrides
  - New catalysts for $NaAlH_4$
  - Adsorbent systems
  - New tank designs

Principal issues for design of metal hydride based storage systems

- **Variations in powder composition and catalyst material**
  - Large impact on the charging and discharging kinetics
  - Large impact on capacity
- **Substantial increase (x50) in $NaAlH_4$ kinetics required to meet 2010 DOE target for refueling time**
  - Heat removal becomes an issue for ΔH associated with most metal hydrides
- **Short refueling times for $NaAlH_4$ (e.g., 4.2 min. versus 15 min) impact**
  - System gravimetric capacities
  - System volumetric capacities

Proposed Future Work : Metal Hydrides

Depends on Results from "Acceptability Envelope"

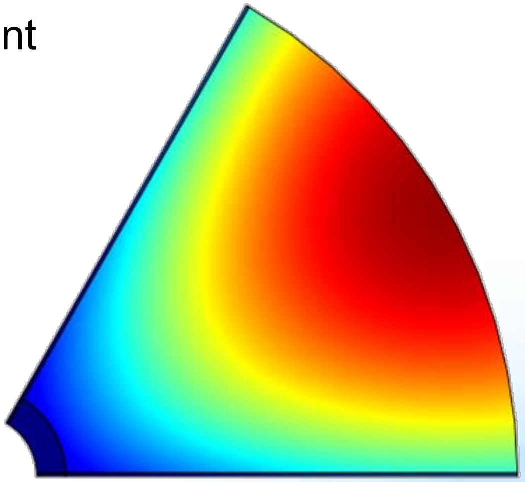
More Detailed Modeling in Scoping Studies

- **Consider mass transfer limitations**
- **Include hydrogen stored in gas phase**
- **Include cooling at tank wall/surface**
- **Identify minimum coolant tube thickness**
  - Dependent on operating pressure and tube internal diameter
- **Use appropriate convection heat transfer coefficient in coolant tube**
  - Dependent on coolant tube internal diameter & coolant flow rate
- **Consider pressure vessel mass**
  - Important for hybrid (high pressure) storage

$$u = -\frac{D_p^{\,2}}{150\mu}\left(\frac{\varepsilon}{1-\varepsilon}\right)^2 \frac{\partial P}{\partial x}$$

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

$$w = -\frac{D_p^{\,2}}{150\mu}\left(\frac{\varepsilon}{1-\varepsilon}\right)^2 \frac{\partial P}{\partial z}$$



Evaluate Novel Concepts

- **Longitudinal and other fin configurations**
- **Metal honeycomb structures**
  - Cell size
  - Addition of cooling channels

Approach: Adsorbent Models – MaxSorb® (AX-21®)

- **Solves conservation equations for mass, momentum, and energy in 2 or 3 dimensions**
  - Uses weakly compressible Brinkman equations in all 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."*

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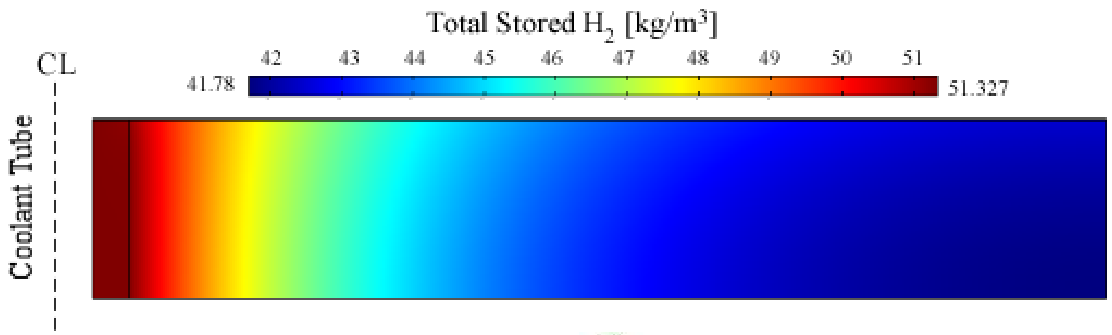
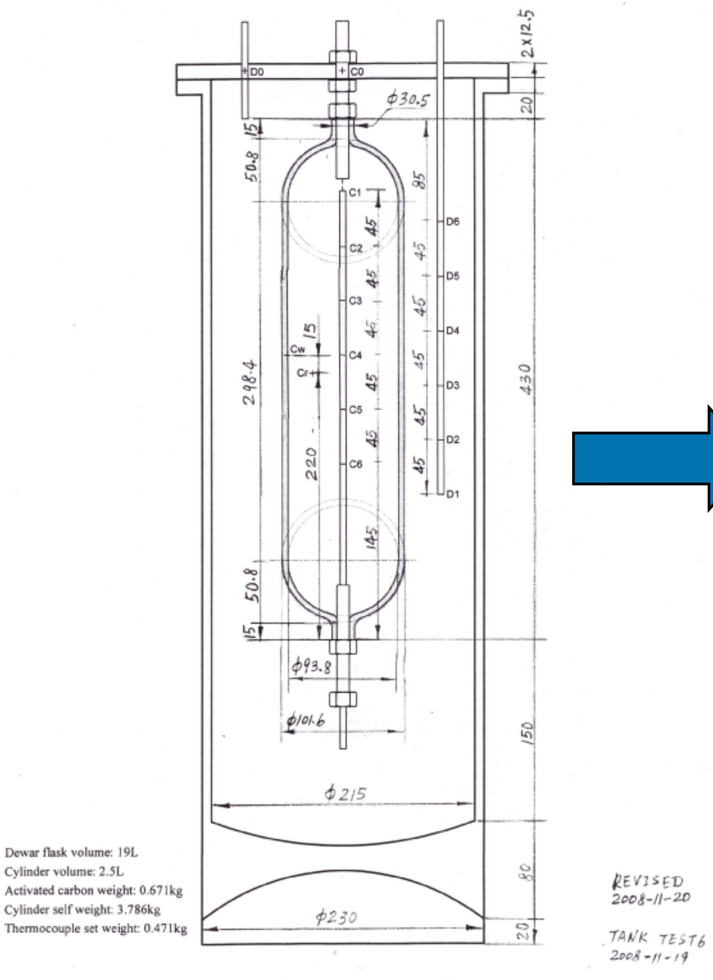
Technical Accomplishments: Adsorbent Scoping Model

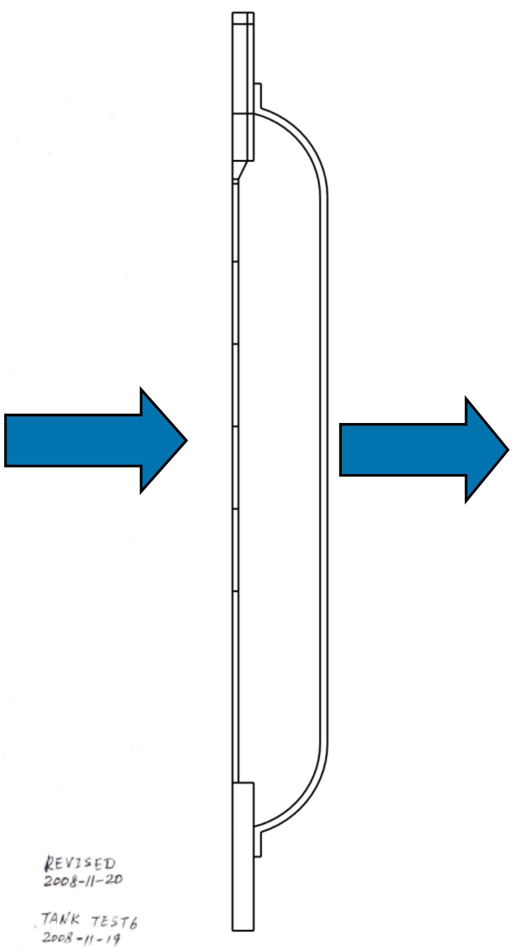
- **Unit cell**
  - Half-thickness of fin & media
  - Central coolant channel
- **Energy balance only**
  - Prescribed pressure transient
- **Executes quickly**
  - Analogous to SRNL heterogeneous cell metal hydride scoping models
  - Suitable for large number of runs
    - Matlab® systematic optimization on a number of design parameters

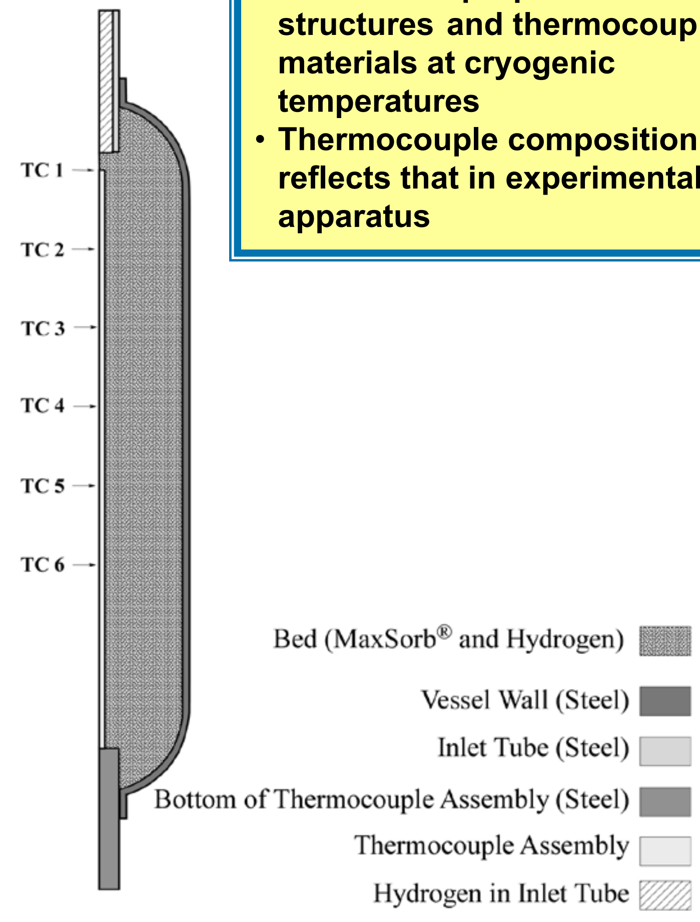
• Optimized Parameters (Use Matlab®-Comsol® Interface)
- **Cooling tube (inner) diameter**
- **Cooling tube thickness**
- **Tube (horizontal) spacing**
- **Fin thickness**
- **Fin-Fin (vertical) spacing**



Technical Accomplishments: Model Validation







- **Model uses properties of structures and thermocouple materials at cryogenic temperatures**
- **Thermocouple composition reflects that in experimental apparatus**

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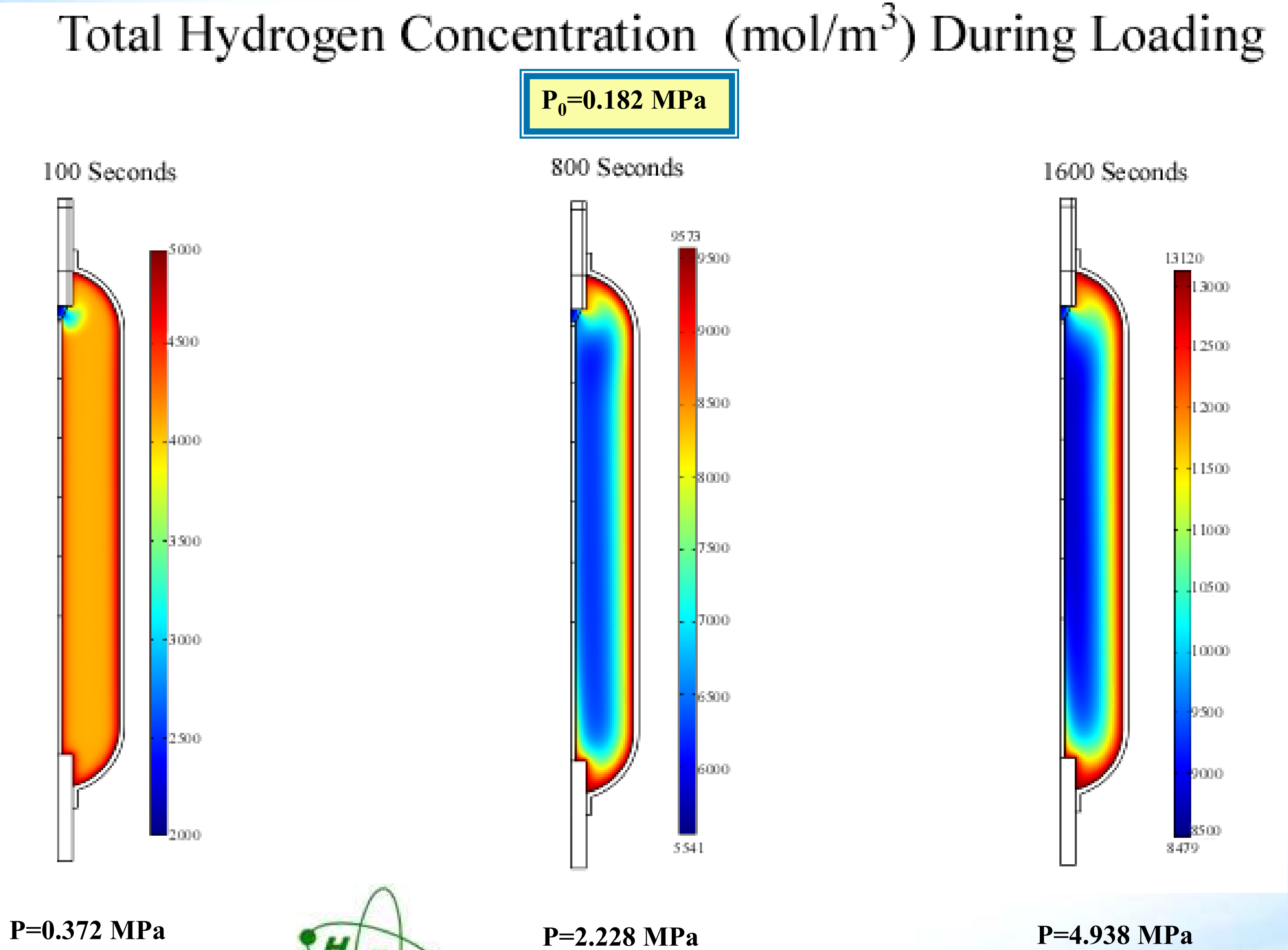
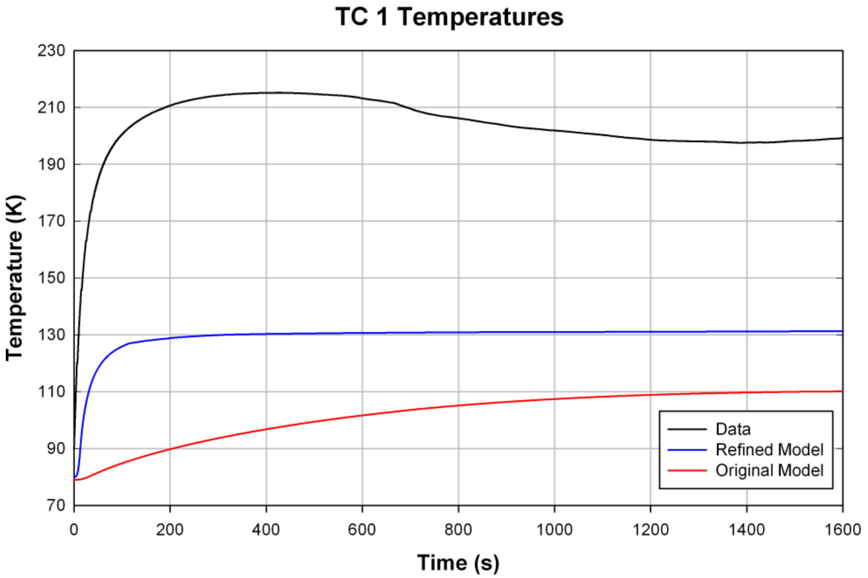
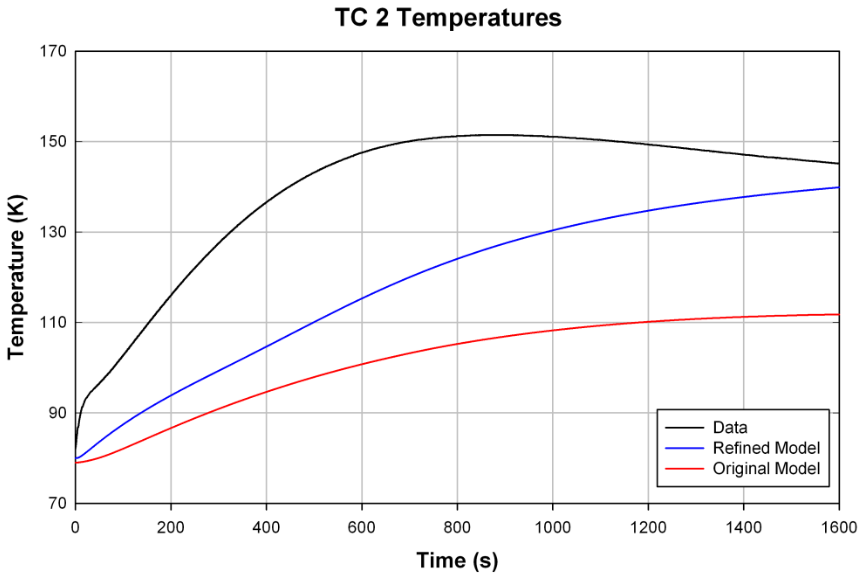
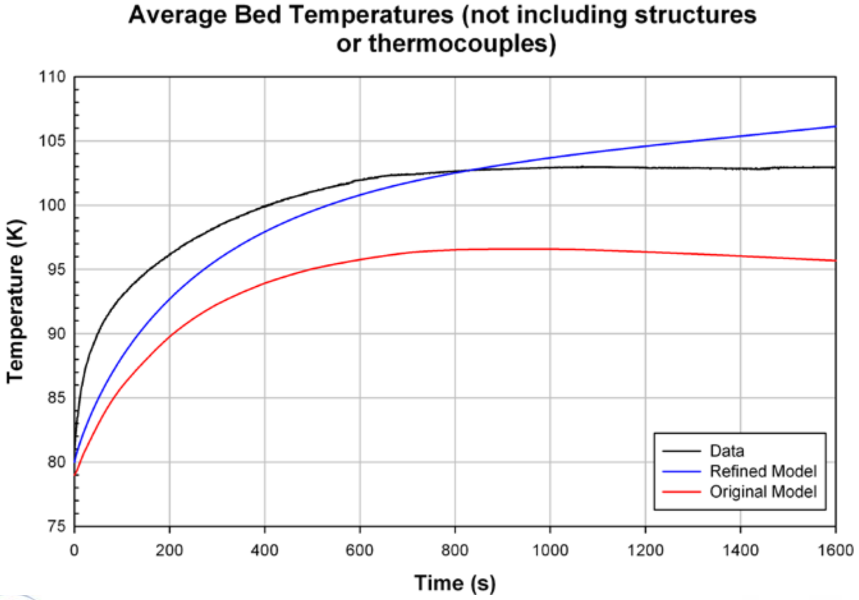
Technical Accomplishments: Model Validation

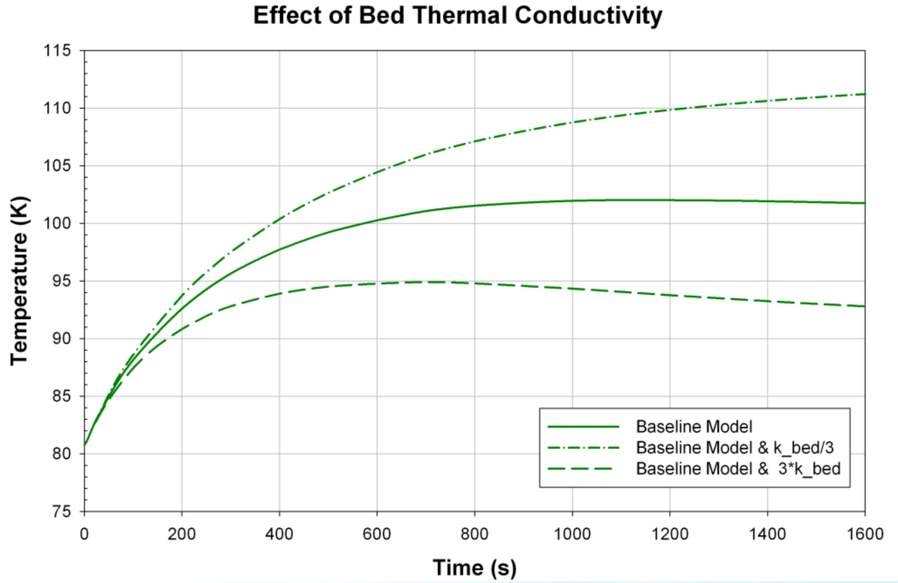


Technical Accomplishments: Model Validation









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Progress: Summary for Adsorbent Modeling

- **Model Development and Validation**
  - Numerical model – Comsol®
  - Model validation against data for MaxSorb®
- **Developed Baseline Scoping Model**
  - Unit cell models – Comsol®

Proposed Future Work: Adsorbent Models

- **Conduct validation experiments that reduce parasitic heat transfer**
  - Use N_2 at temperatures closer to ambient
- **Compare performance of MOF-5® and MaxSorb®**
- **Use baseline models in 2 and 3 dimensions for design and sensitivity studies**
  - Vessel design
  - Structured media
  - Novel concepts
- **Conduct process-specific experiments**
  - Validate models
  - Test conceptual vessel designs
- **Convert models to a form suitable for use in system analysis**
- **Apply models to prototype design**

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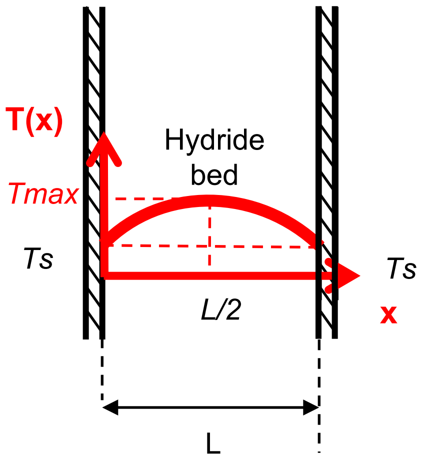
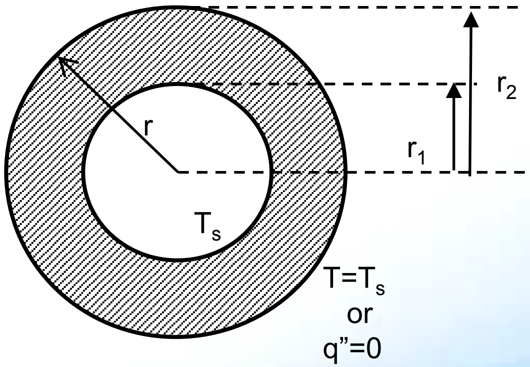
Approach: Acceptability Envelope

- **The "Acceptability Envelope" or "Black Box Analysis" determines the range of parameters necessary for a 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 applied to metal hydrides**
  - Rectangular coordinates (RC)
  - Cylindrical coordinates (CC)





Technical Accomplishments: Acceptability Envelope

For both rectangular and cylindrical geometries

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

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

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

$L^2 = r_1^2 - r_2^2$ **cylindrical**

L= (plate spacing) **rectangular**

Rearrange to get

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

Vessel parameter — $\left(\frac{1}{L^2}\right)$

Media parameters — $\left(\frac{k\ M_{Hyd\_eff}\ \Delta T}{-\Delta H_{overall}\ \rho_{Hydride}}\right)$

Charging/discharging rate — $\frac{\Delta m_{H2}}{\Delta t}$

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

Currently assumes recoverable hydrogen is stored in metal hydride - OK for moderate pressures

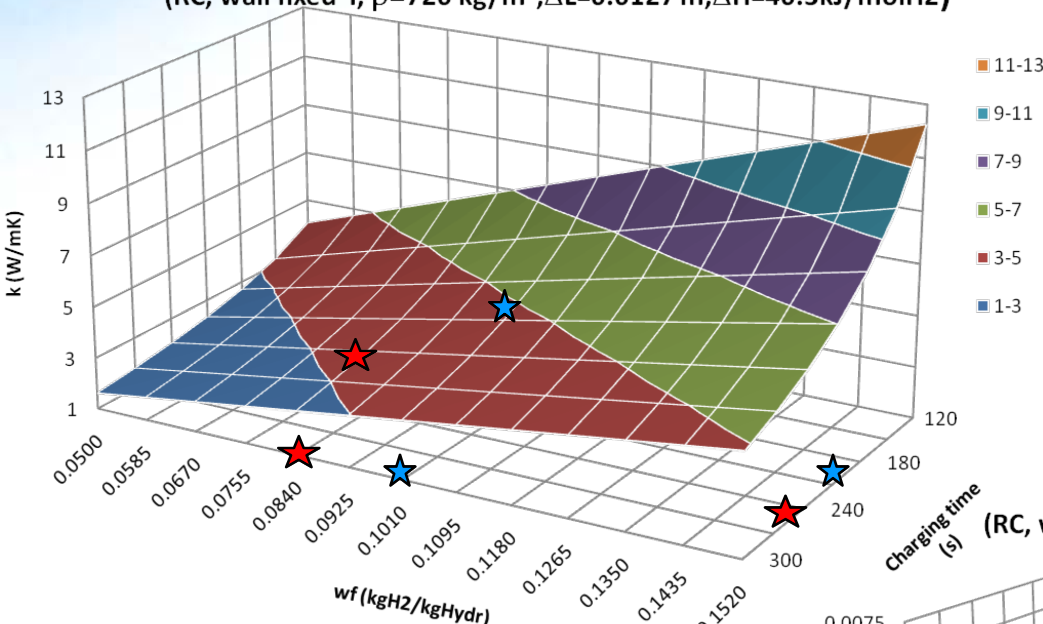
Physical interpretation of parameters

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

Technical Accomplishments: Application of Acceptability Envelope

$NaAlH_4$ System:
Minimum Required Bed Thermal Conductivity (in W/m K)

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



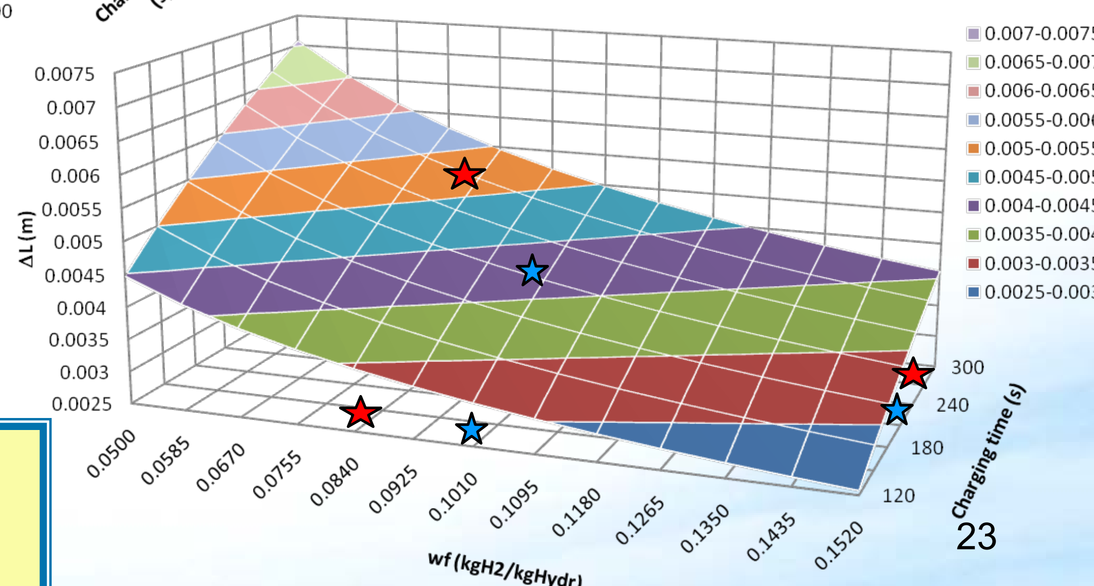
DOE 2010 ★ 5kg H_2 in 4.2 min

DOE 2015 ★ 5kg H_2 in 3.3 min

ΔT=30°C
ΔL is distance between HX surfaces

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

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



If reactions are fast enough to meet target charging times, a high rate of heat removal is required
⇒ Close spacing of HX surfaces
or
⇒ Higher value of k

Alternatives:
Reduce $\Delta H_{overall}$
Increase ΔT_{max}

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Progress: Summary for Acceptability Envelope

- **Model Developed for Metal Hydrides**
  - Based on energy balance
    - Constraints are from DOE Technical Targets
    - Model should be used in conjunction with media kinetics
  - Can be used to identify range of media & component parameters required to meet operational targets
- **Application**
  - Applied to $NaAlH_4$
  - Some general applications have been made

Proposed Future Work: Acceptability Envelope

- **Include effects of system parameters**
  - Mass & volume of storage vessels, fins, tubes, other structures and fittings
- **Complete the application to metal hydrides**
  - Include coupled parameter ranges
  - Evaluate candidate metal hydrides
- **Develop and apply model for adsorbents**

Collaborations

- **Metal Hydride 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 Modeling**
  - Richard Chahine, M. A. Richard (UQTR)
  - Andrea Sudik (Ford)
  - Sudarshan Kumar (GM)
- **Technology Area Interfaces**
  - Scot Rassat, Kriston Brooks, Ewa Ronnebro, Dale King (PNNL)
  - Troy Semelsberger (LANL)
  - Norman Newhouse (Lincoln Composites)
  - Joseph Reiter (JPL)
  - Donald Siegel (U of M)

Project Summary

Relevance

The ultimate goals of the HSECoE are the design and testing of prototype hydrogen storage vessels, the interpretation of test data and the implication for full scale vessels. Within the HSECoE, the Transport Phenomena Technology Area is responsible for the development and application of analyses for storage systems that are necessary to identify and design prototype media and vessel configurations having the best performance relative to the DOE Technical Targets. Storage vessel models developed by this technology area will be essential to interpret data obtained from prototype testing and to relate it to full scale systems.

Approach

In Phase I the Transport Phenomena Technology Area will:

- Evaluate, interpret, and assimilate data for media and vessel components
- Develop and apply and "Acceptability Envelope" to metal hydrides
- Develop general models for scoping and detailed evaluation of storage system designs
  - Validate and test the models

Technical Accomplishments and Progress (as of 3/2010)

Have met/exceeded Phase I objectives:

- Evaluated and interpreted media and component data; assimilated into models
- Developed and applied the "Acceptability Envelope" to metal hydrides
  - Applying to metal hydride vessel-media configurations
  - Developing model for adsorbents
- Developed baseline models for metal hydrides and adsorbents
  - Validated and tested the metal hydride models
  - Initiated validation of adsorbent model
  - Performed optimization studies of vessel configuration for $NaAlH_4$
  - Ready to compare storage system behavior for different media
    - *Metal hydrides in general*
    - *Adsorbents MOF-5® and MaxSorb®*

Collaborations

UQTR, UTRC, PNNL, LANL, JPL, Ford, GM, OSU, Lincoln Composites, U of M – (see previous slide)

Proposed Future Work (Phase I)

- Continue vessel optimization using models
  - Apply to novel design concepts
    - *Micro & mini channel heat exchangers*
    - *Structured media*
  - Develop and test models for adsorbents
- Extend "Acceptability Envelope" to adsorbents and apply
  - Include gravimetric and volumetric constraints
- Preliminary prototype designs

QUESTIONS

SUPPLEMENTAL SLIDES

Technical 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

Technical Accomplishments: 0-D MathCAD® Kinetics Model

Example: $NaAlH_4$ + 4%$TiCl_3$

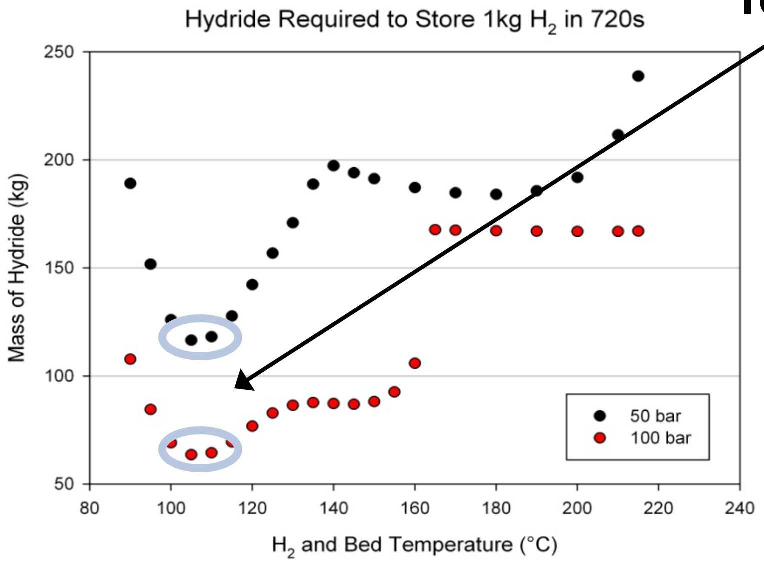
UTRC kinetics and saturation parameters

Assumptions:

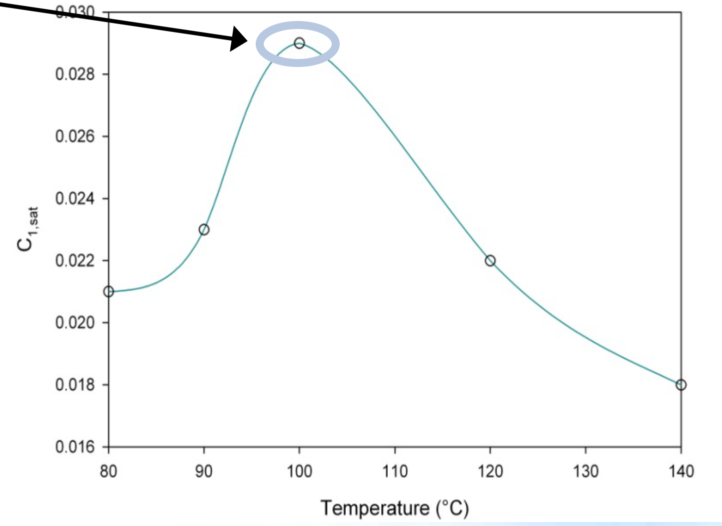
- Isothermal
- Isobaric
- Kinetic limitations only

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 controls optimal temperature



Optimum Temperature Range



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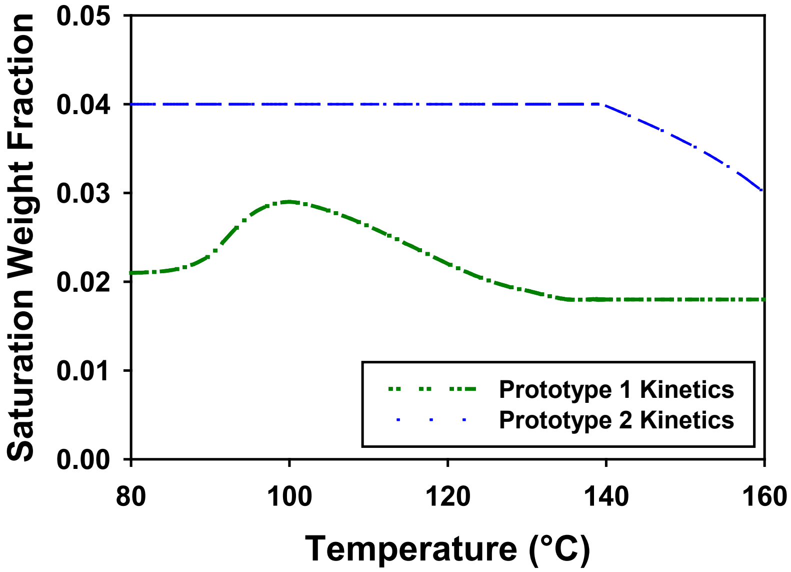
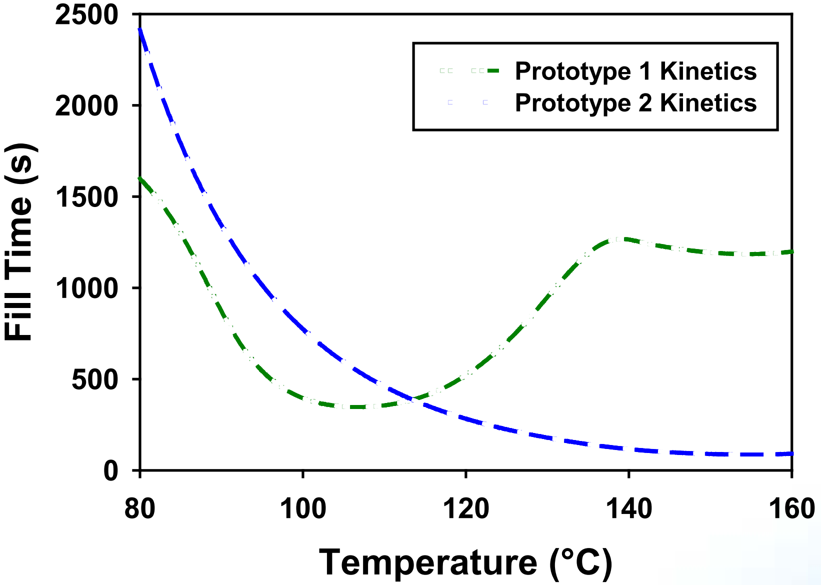
Kinetics Comparison

Saturation Weight Fraction



Fill Time at 200 bar Feed Pressure



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

UTRC Prototype 1 Kinetics

Hydride: $NaAlH_4$ + 4%$TiCl_3$

Mass H_2 Stored

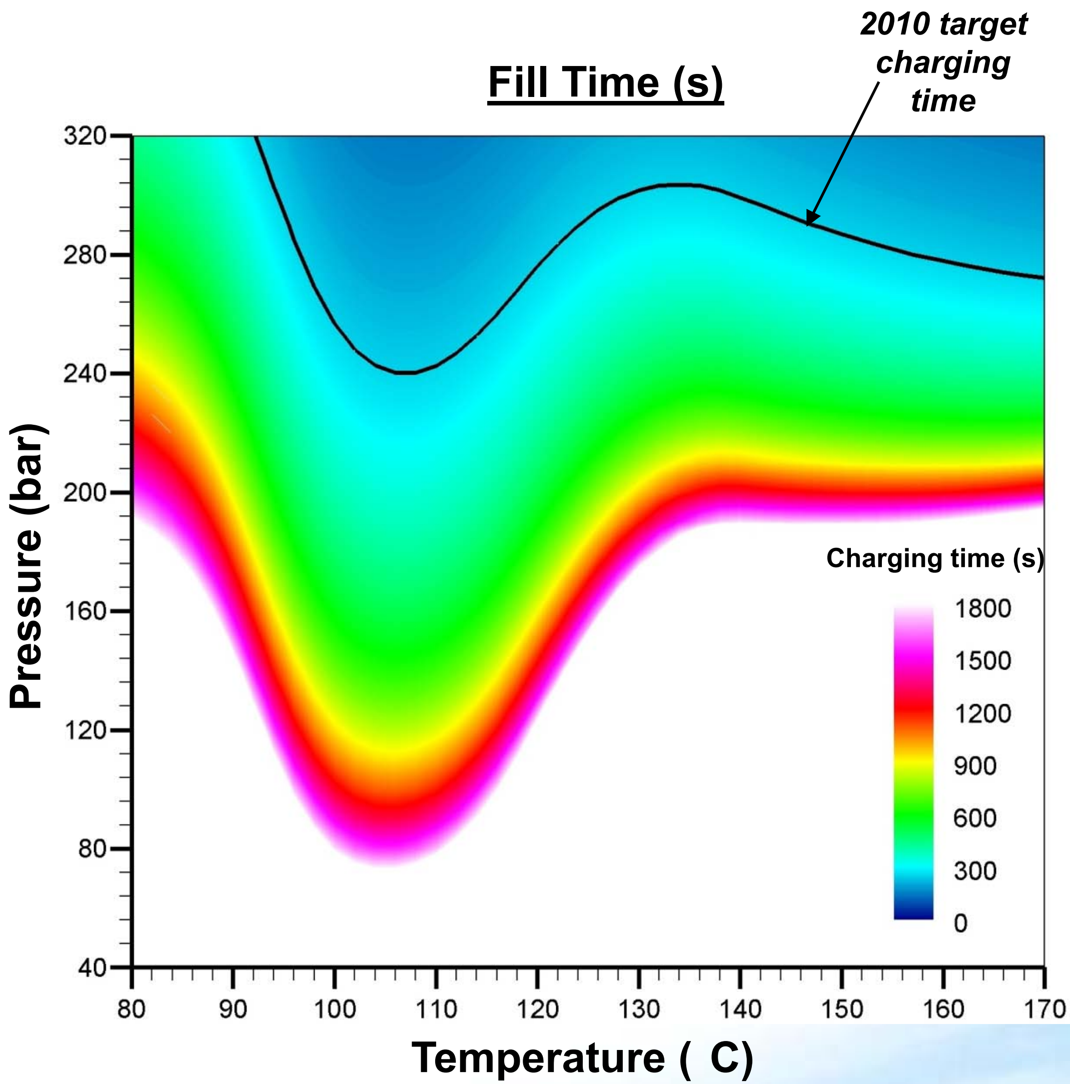
- **5.5 kg in 4.2 min (2010 Target)**
- **Includes compressed gas in voids (~50% porosity)**

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**

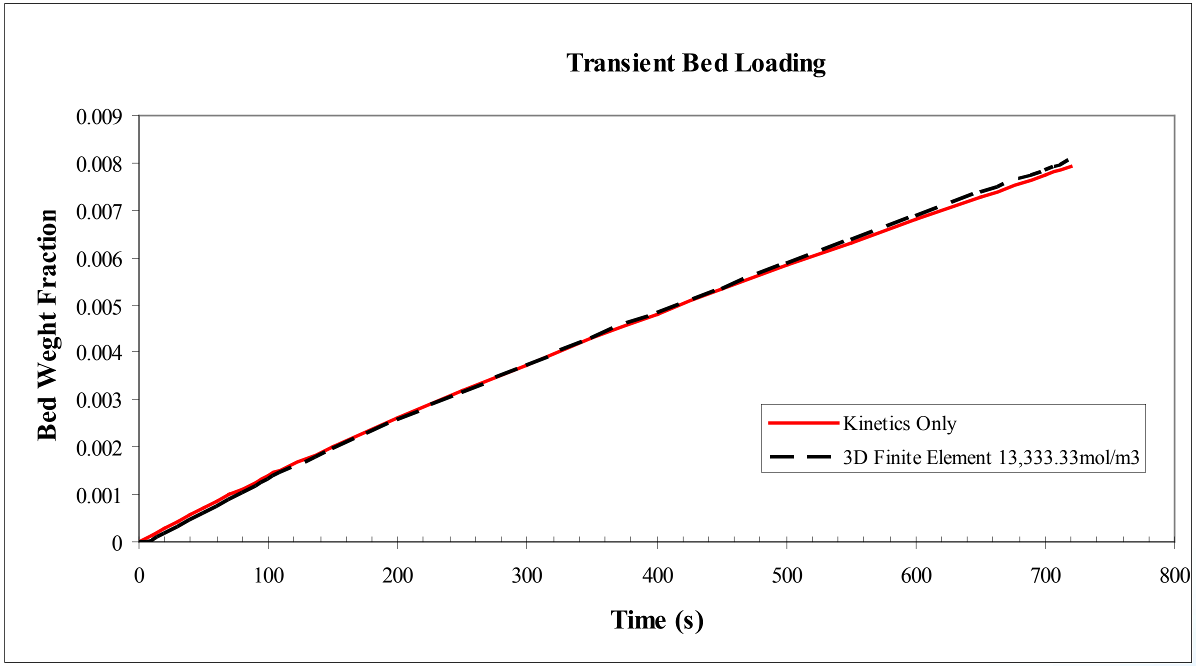


Technical Accomplishments: $NaAlH_4$ Kinetics Vs Storage Vessel Charge Rate

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



For Good Heat Transfer with $NaAlH_4$, Charge Rate Is Limited by Kinetics

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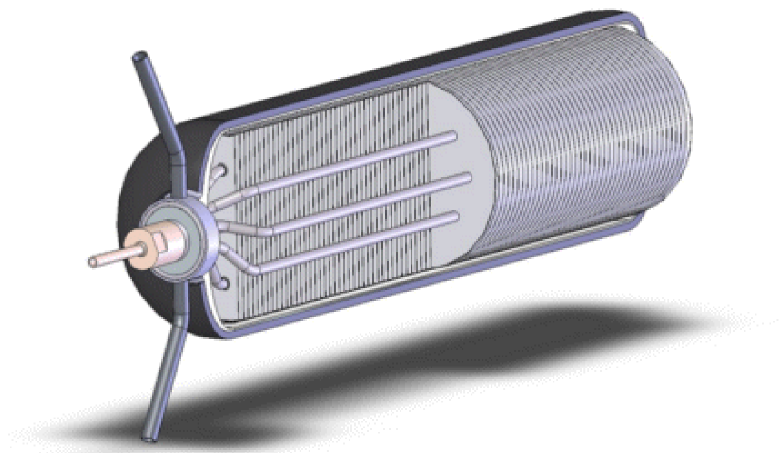
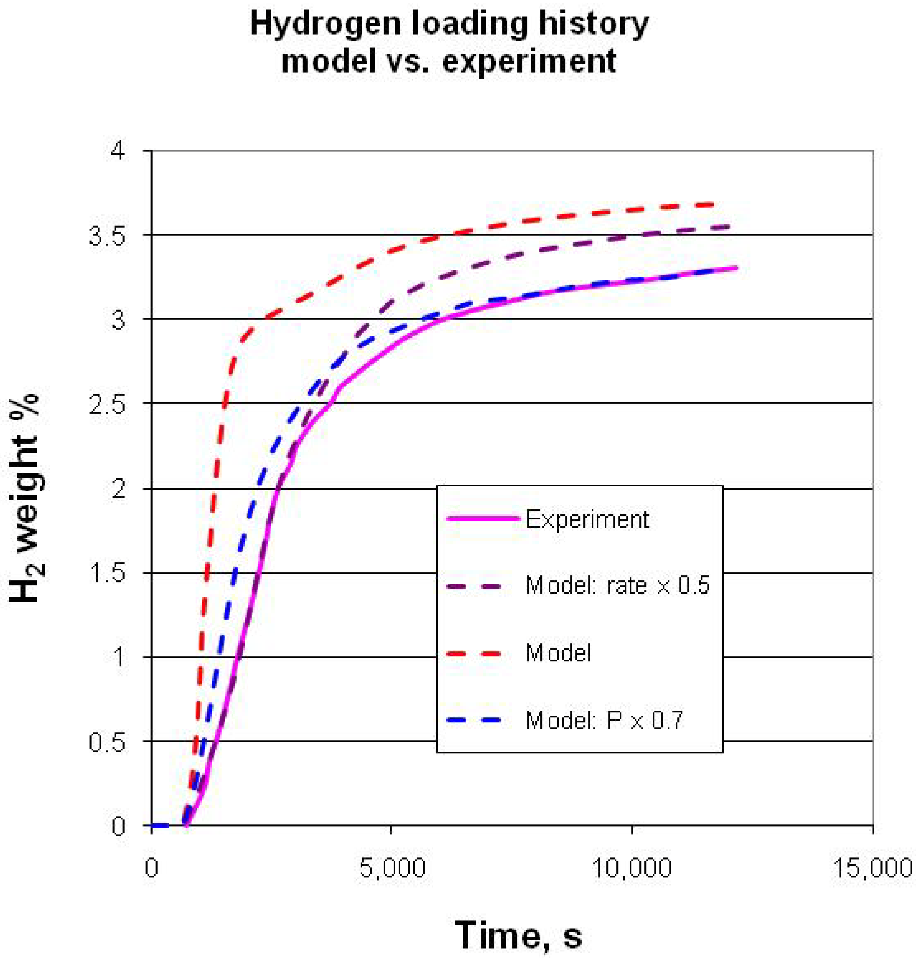
Technical Accomplishments: Metal Hydride Model Validation (UTRC)

Comsol® model validated successfully by UTRC with ABAQUS® model and experimental data from previous DOE contract

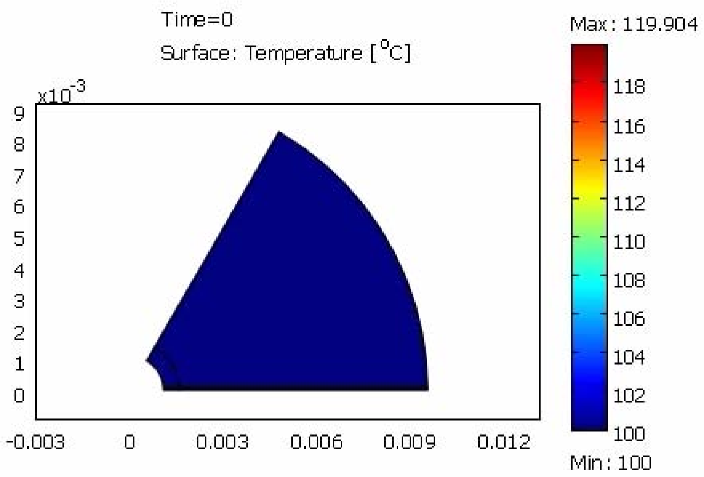


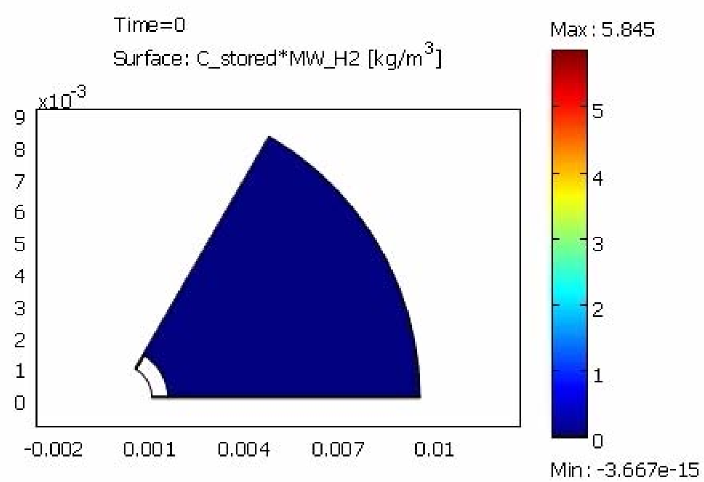


Technical Accomplishments: Systematic Optimization Method Applied to Longitudinal Fins

Store 1 kg of hydrogen in 12 min. (720s)
50 bar feed pressure; $NaAlH_4$+4%$TiCl_3$

	Nelder-Mead
Cooling tube ID:	0.085 in.
Cooling tube thickness:	0.020 in.
Fin length:	0.313 in.
Fin thickness:	0.004 in.
Linear length:	643 m
Media mass:	126 kg
Heat exchanger mass:	16 kg
Heat exchanger vol. %:	3.2%





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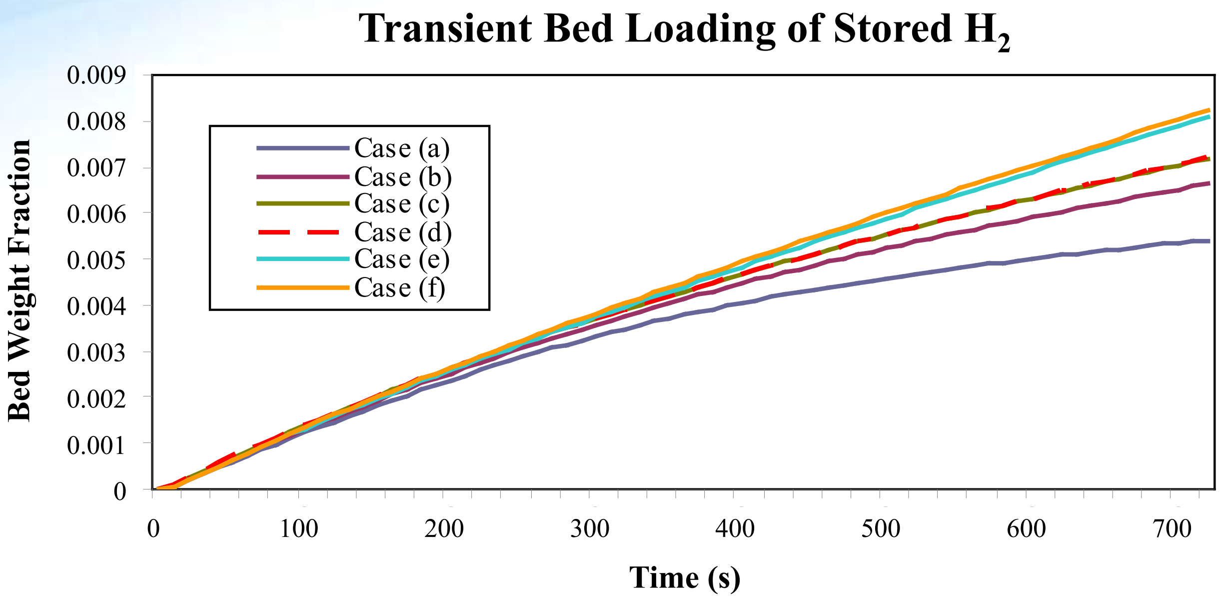
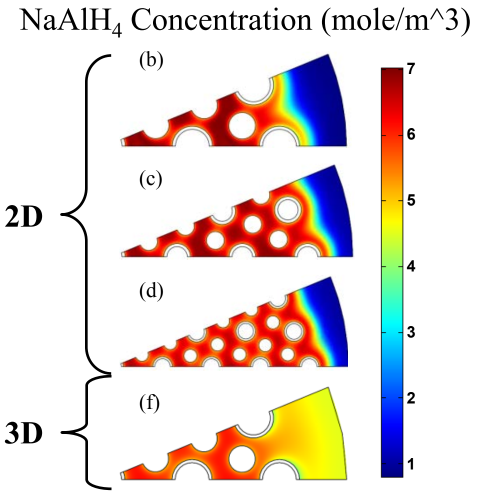
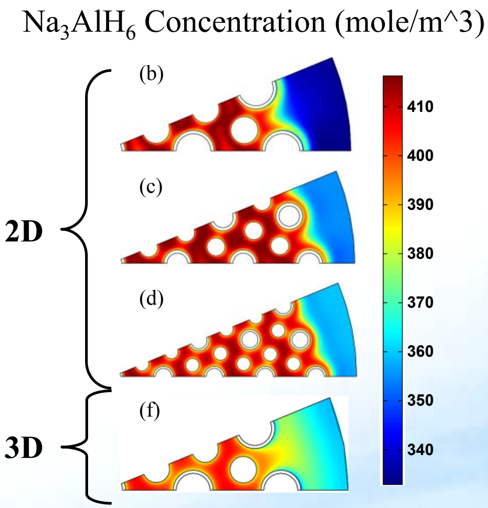
Technical Accomplishments: Preliminary Scoping - Effect of Tube Arrangement on H_2 Charging

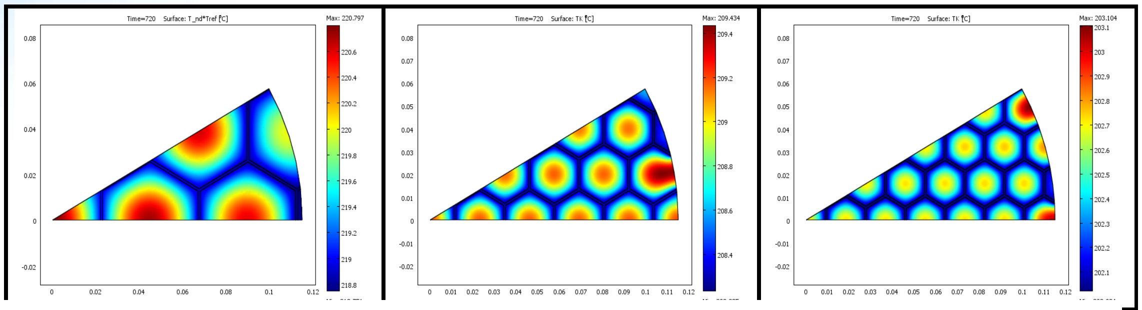




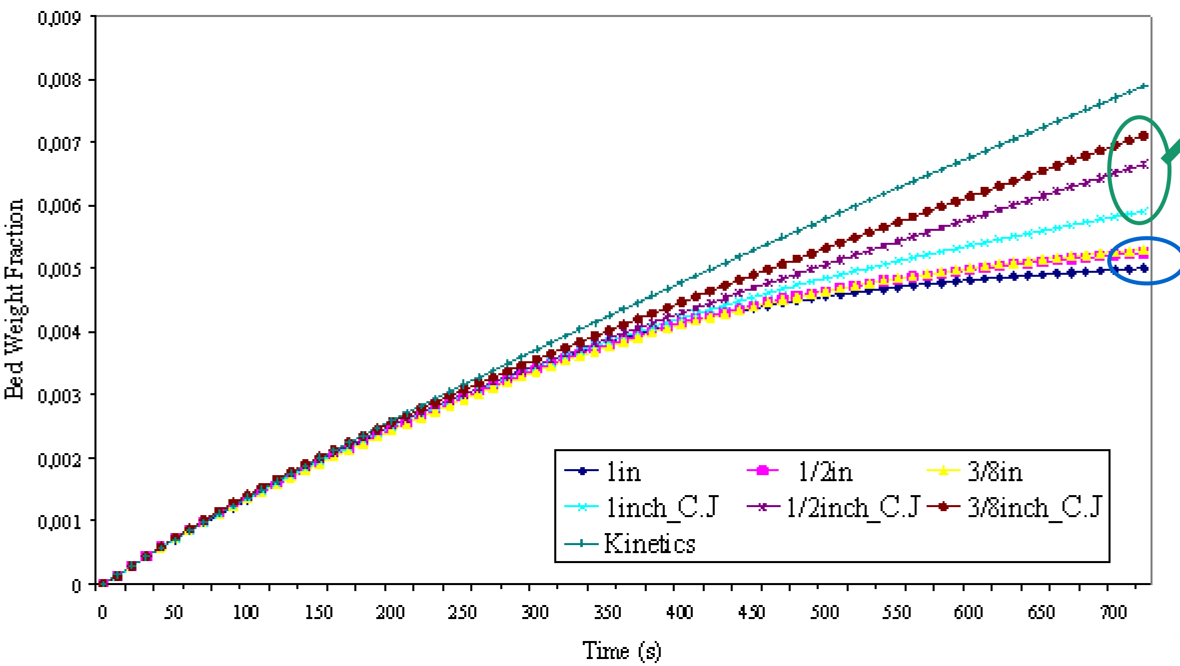


- For the 2D models (cases a – d), increasing the number of heat exchanger tubes results in better utilization of the bed (higher H_2 loading rates).
- No improvement is seen between 49 and 81 cooling tubes (cases c and d, respectively)
  - Suggests the existence of an optimum number of cooling tubes.

Technical Accomplishments: Metallic Honeycomb Structure



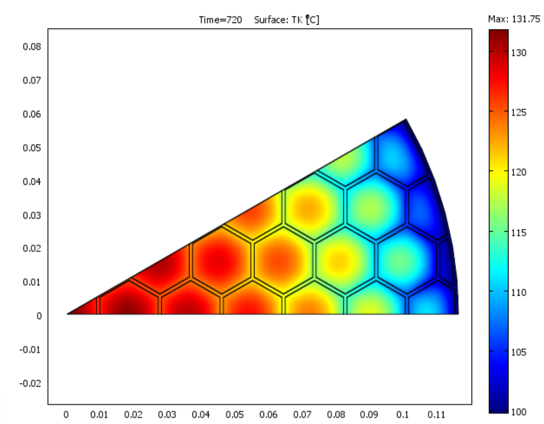
Cell Size



- Decreasing the cell size results in a decrease of the maximum of temperature from 220 to 203°C

- No significant improvement on the bed weight fraction

- Adding a cooling jacket will improve the hydrogen loading rate



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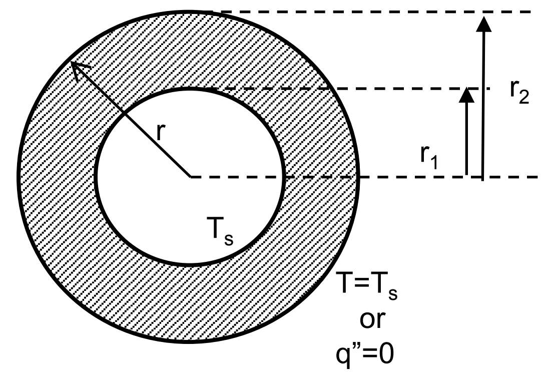
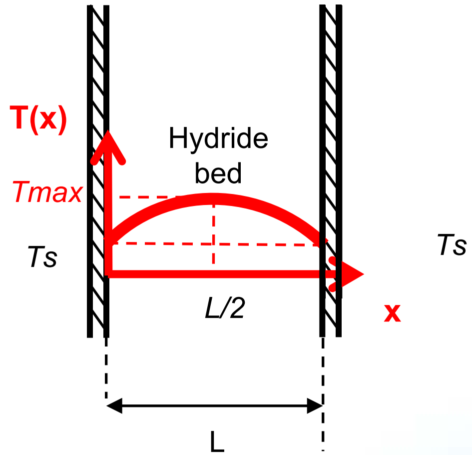
Technical Accomplishments: Acceptability Envelope Development

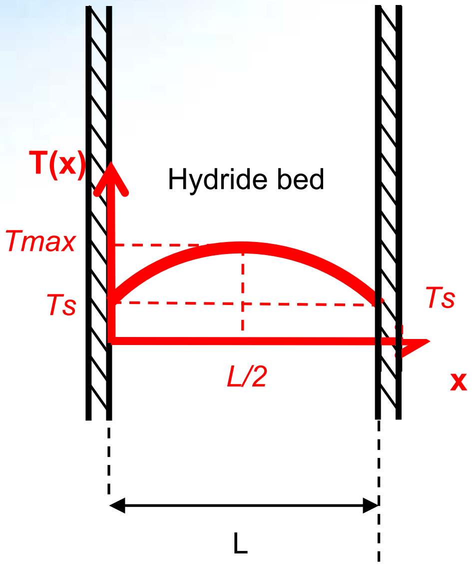
- **Geometry and boundary conditions**
  - Rectangular coordinates (RC)
  - Cylindrical coordinates (CC)
  - Different boundary conditions
    - Fixed wall temperature
    - No heat flux at wall





- **Criteria and media**
  - DOE technical targets
    - 2010, 2015 and Ultimate
  - Storage materials ($NaAlH_4$) current characteristics

Technical Accomplishments: Acceptability Envelope Derivation Physical Model in Rectangular Coordinates



Steady-State Energy Balance

$$k\frac{d^2T}{dx^2}+q'''=0$$

q''' (W/m³) is the rate of thermal energy release during charging or discharging

$$q'''=-\sum_i \Delta H_i \frac{\Delta C_i}{\Delta t} \Rightarrow q'''=-\Delta H_{overall}\frac{\Delta C_f}{\Delta t}=-\Delta H_{overall}\frac{\rho_{Hydride}}{M_{Hyd\_eff}M_{H2}}\frac{\Delta m_{H2}}{\Delta t}$$

where:
ΔH (J/mol) is the enthalpy of reaction
C_i (mol/m³) is concentration of H_2 stored by species i
C_f (mol/m³) is overall concentration of stored H_2
M_{Hyd_eff} is the mass of hydride needed to store the required mass of hydrogen

Solving the Energy Balance Equation for this Geometry Gives:

$$T(x)=-q'''\frac{x(x-L)}{2k}+T_s$$

So that

$$\Delta T=-\frac{L^2}{8k}\Delta H_{overall}\frac{\rho_{Hydride}}{M_{Hyd\_eff}M_{H2}}\frac{\Delta m_{H2}}{\Delta t}$$

where: $\Delta T = T_{max} - T_s$

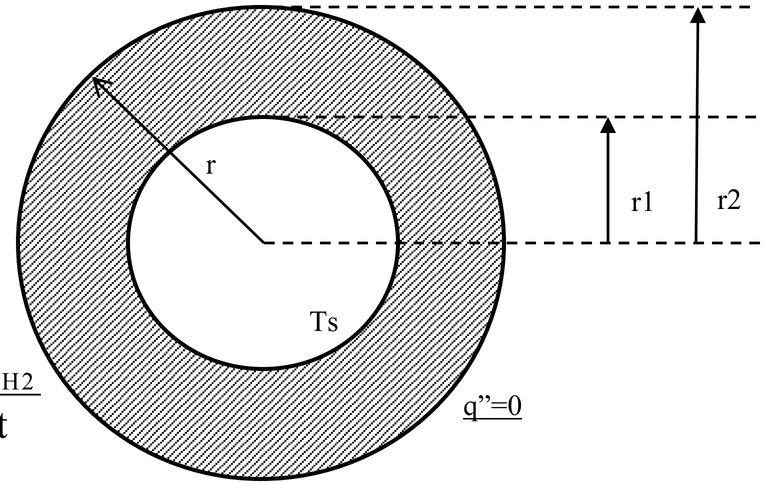
HSECoE

Technical Accomplishments: Acceptability Envelope Derivation
Physical Model in Cylindrical Coordinates

Steady-State Energy Balance

$$k\frac{1}{r}\frac{d}{dr}\left(r\frac{dT}{dr}\right)+q'''=0$$

q''' (W/m³) is the rate of thermal energy release during charging or discharging



$$q'''=-\sum_i \Delta H_i \frac{\Delta C_i}{\Delta t} \Rightarrow q'''=-\Delta H_{overall}\frac{\rho_{Hydride}}{M_{Hyd\_eff}M_{H2}}\frac{\Delta m_{H2}}{\Delta t}$$

where:

ΔH (J/mol) is the enthalpy of reaction

C_i (mol/m³) is concentration of H_2 stored by species i

C_f (mol/m³) is overall concentration of stored H_2

M_{Hyd_eff} is the mass of hydride needed to store the required mass of hydrogen

Solving the Energy Balance Equation for this Geometry Gives:

$$T(r)=T_s+\frac{q'''}{4k}\left[-r^2+2r_2r+\left(r_1^2-2r_1r_2\right)\right]$$

So that

$$\Delta T=-\frac{L^2}{4k}\Delta H_{overall}\frac{\rho_{Hydride}}{M_{Hyd\_eff}M_{H2}}\frac{\Delta m_{H2}}{\Delta t}$$

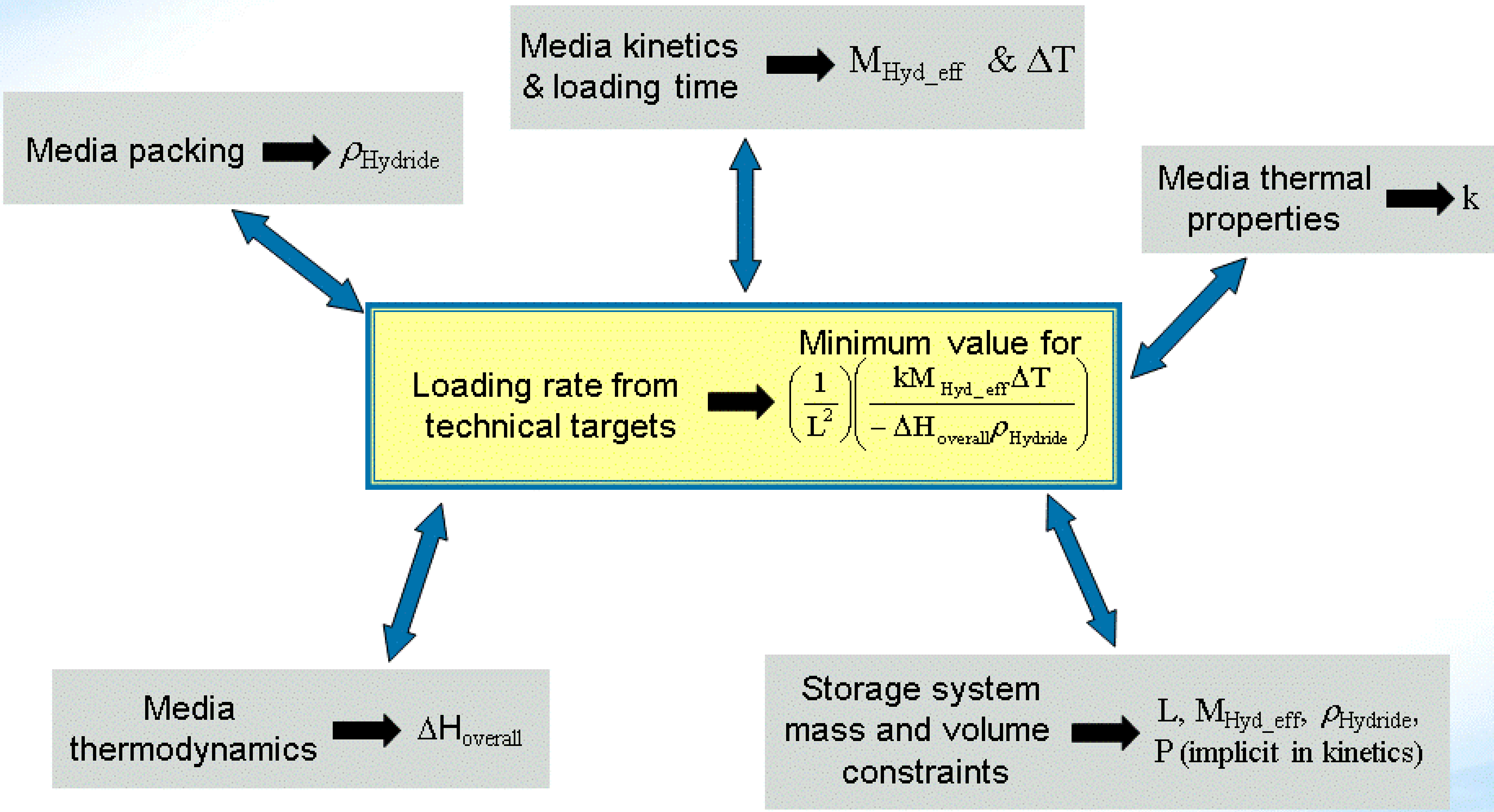
where:

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

$$L^2=r_1^2-r_2^2$$

HSECoE

Approach: Application & Interpretation of Acceptability Envelope



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Approach: Acceptability Envelope Constraints Based on DOE Technical Targets

DOE Technical Targets

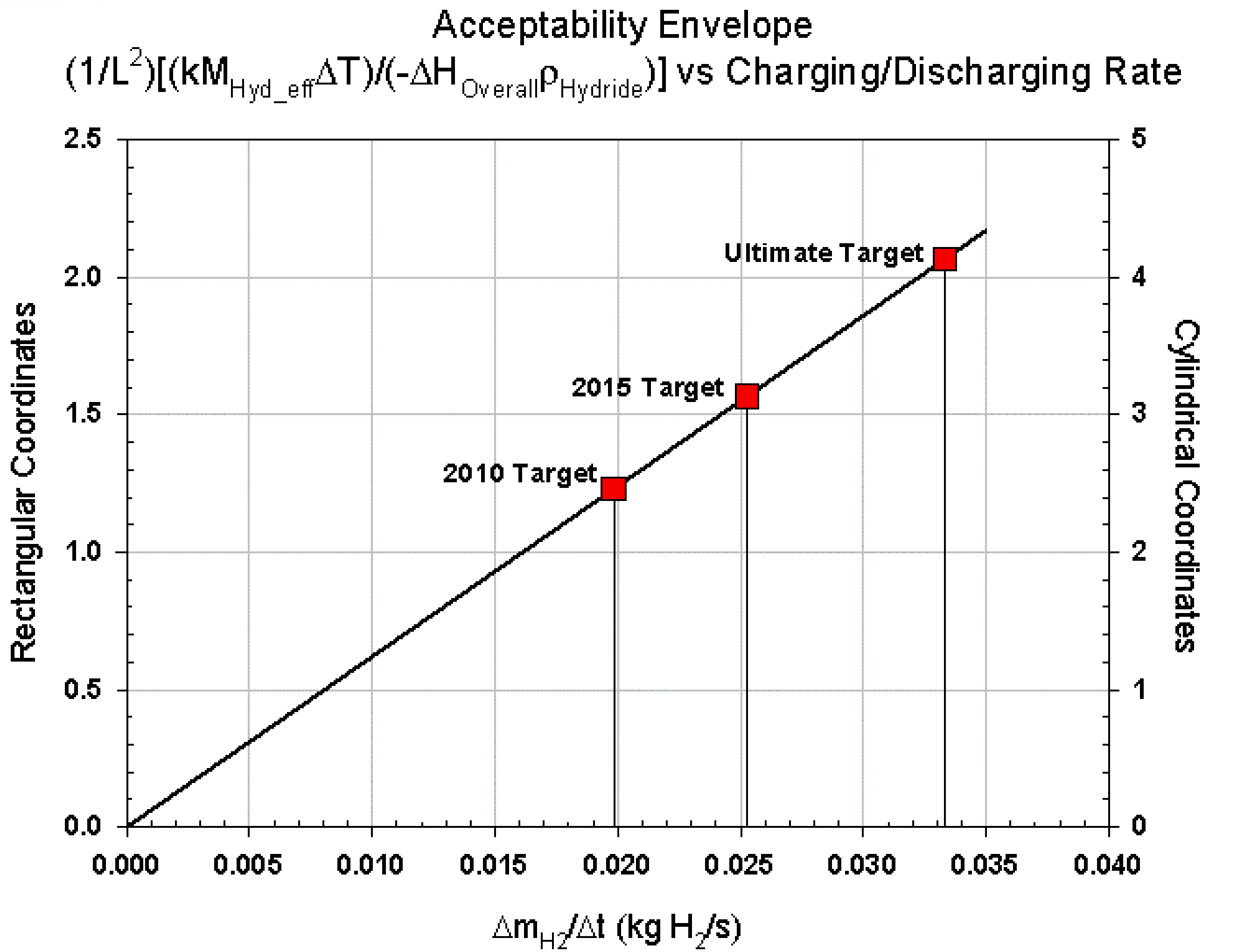
Target	*System Gravimetric Capacity*	*Hydride weight / System weight*	*Δt (min) for 5 kg H_2*	*$\Delta m_{H2}/\Delta t$ (kg/s)*	*M_{Hyd_eff} [kg] for 5 kg H_2*
DOE 2010 year	0.045	0.52	4.2	0.0198	58.1 (Δt = 4.2 min)
DOE 2015 year	0.055	0.55	3.3	0.0253	50.0 (Δt = 3.3 min)
DOE Ultimate target	0.075	0.60	2.5	0.0333	40.0 (Δt = 2.5 min)

- **Parametric analysis applied for fixed ΔT, $\Delta H_{overall}$, $\rho_{Hydride}$ and M_{Hyd_eff} and varying:**
  - Thermal conductivity, *k*
  - Spacing of heat transfer elements, *L*

HSECoE

Approach: Value of Parameter Grouping in Acceptability Envelope

$$\frac{1}{mM_{H2}} \frac{\Delta m_{H2}}{\Delta t}$$



Technical Accomplishments: Overall Summary

- **Have met the following Phase I objectives:**
    - Developed acceptability envelope for metal hydrides
        - *Need to specify gravimetric & volumetric constraints*
    - Performed comparison between metal hydride models & available data
    - Developed baseline models for metal hydrides
        - *Initiated model development for adsorbent media*
    - Performing optimization studies and modeling of vessel configurations
- **Detailed models**
    - Ready to compare storage system behavior for different media
        - Metal hydrides
        - Adsorbents MOF-5® and MaxSorb®
- **Acceptability envelope**
    - Metal hydrides
        - Applying to vessel-media configurations
    - Adsorbents
        - Model is being developed
- **Path forward:**
    - Continue sensitivity analyses
    - Pursue novel concepts
        - *Micro & mini-channel heat exchangers*
        - *Structured media*
    - Conduct preliminary system design