

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

Design and Testing of Metal Hydride and Adsorbent Systems

Theodore Motyka

Assistant Director and SRNL Project Lead

Richard Chahine

Director Hydrogen Research Institute
UQTR

Bruce Hardy

SRNL Transport Phenomena Tech Area Lead

Stephen Garrison

SRNL Tech Team Lead

David Tamburello

SRNL Tech Team Lead

Claudio Corgnale

SRNL Transport Phenomena

Savannah River National Laboratory

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Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Project ID#ST044

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Overview

Timeline

- Start: February 1, 2009
- End: July 31, 2014
- 36% Complete (as of 3/1/11)

Budget

- FY10 Funding: \$1,640,000*
- FY11 Funding: \$ 982,000* (expected)

* Includes \$360,000/\$300,000 for the University of Quebec Trois Rivieres (UQTR) as a subrecipient for FY10/FY11

Barriers

- System Weight and Volume
- H₂ Flow Rate
- Energy Efficiency

Partners



Relevance: Overall Project Objectives

Phase 1: 2009-2011

- Compile all relevant **metal hydride materials data** for candidate storage media and define future data requirements. **Complete**
- Develop engineering and design models to further the understanding of on-board storage **transport phenomena requirements**. **Complete**
- Apply **system architecture approach** to delete specific metal hydride systems not capable of meeting DOE storage targets. **Complete**

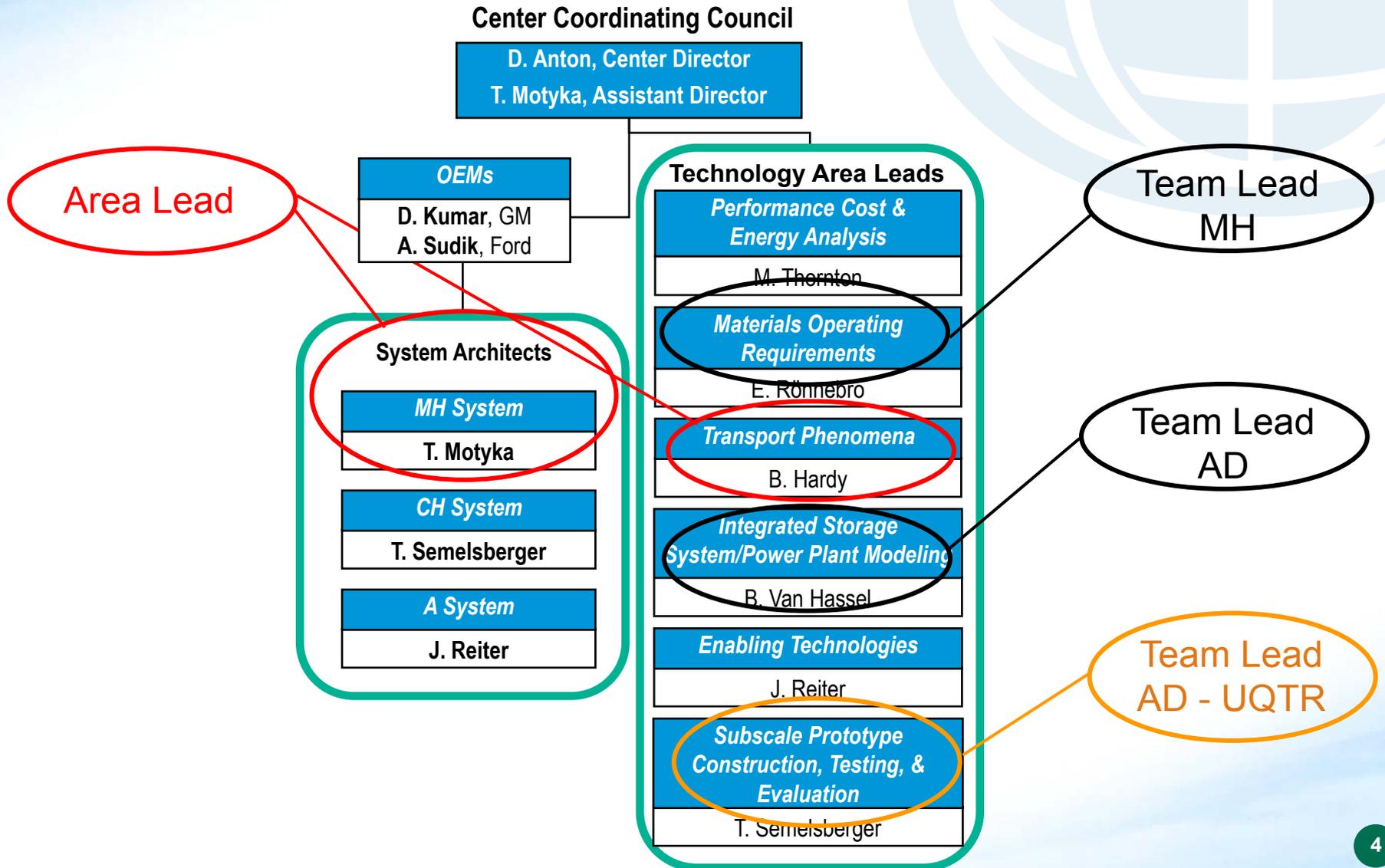
Phase 2: 2011-2013

- 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).

Approach - HSECoE Organization



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

Criteria

Milestones

- **Compiled metal and adsorption hydride data**
 - Chemical kinetics
 - Equilibrium hydrogen capacity
 - Model development
 - Heat transfer parameters
- **Developed hierarchical model**
 - Used model to define “**acceptability envelope**” of metal hydride properties to meet DOE2010 goals
 - Developed **detailed models** for flow through cooling
 - Developed **system models** for adsorbent Go/No-Go Selection

Deliverables (Programmatic Go/No-Go Criteria)

- **Documented selection criteria and assumptions for Metal Hydride Systems with respect to 2010 targets**

Technical Go/No-Go Criteria

- **Selected Metal Hydride Systems for Phase 1 Go/No-Go Decision**

Approach: Phase 2 Milestones, Deliverables, and Go/No-Go Criteria

Milestones

- **Continue to compile metal and adsorption hydride data as required (especially for new materials as well as new forms of materials i.e. compacts, pellets etc.)**
 - Chemical kinetics
 - Heat transfer parameters
- **Develop new heat transfer concepts for both MH and AD systems**
 - Design component heat transfer fixtures for MH and AD systems
- **Develop detailed heat transfer models for both MH and AD new concepts**
 - Model and validate detailed heat transfer models for MH and AD systems
- **Update and validate system models for adsorbent systems**

Deliverables (Programmatic Go/No-Go Criteria)

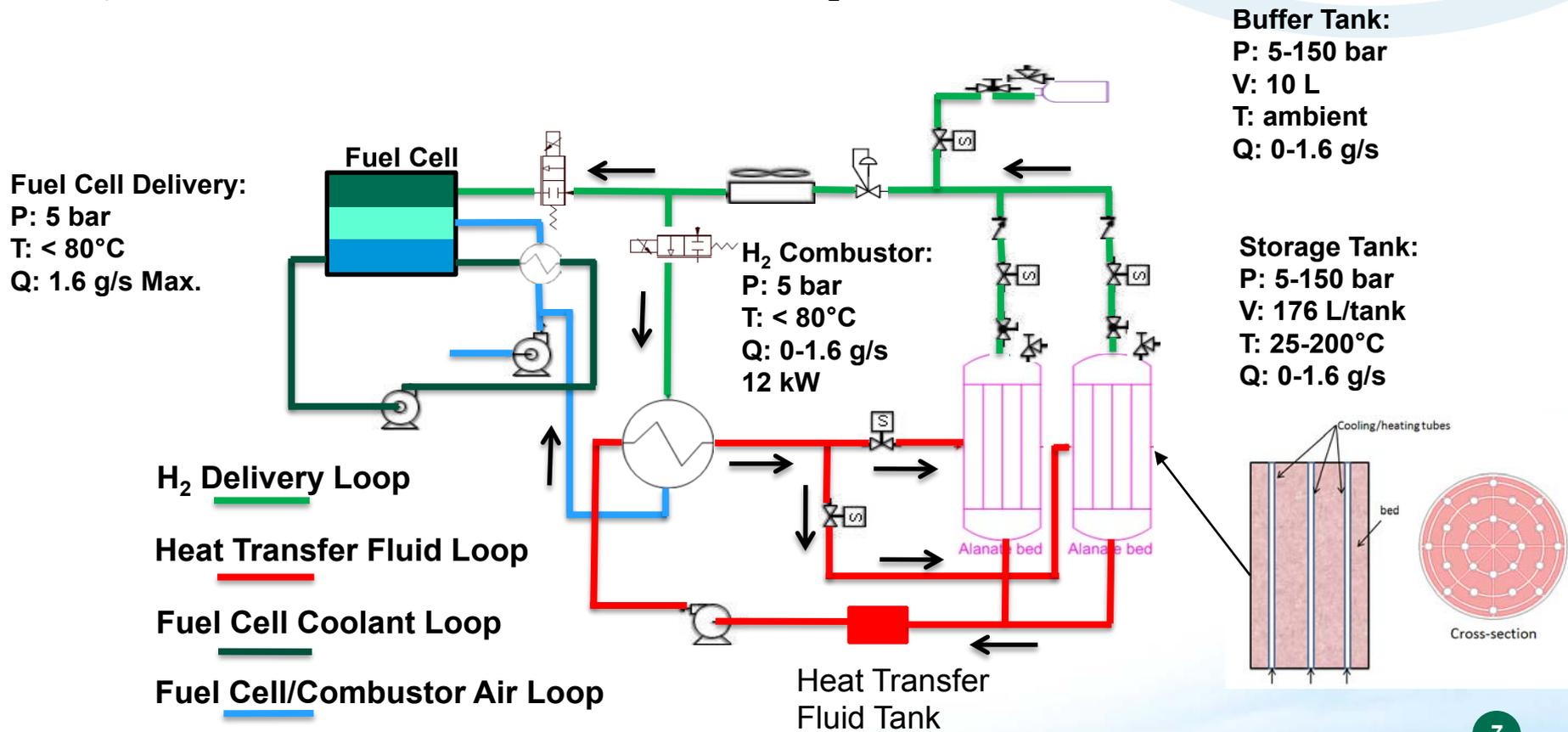
- **Document selection criteria and assumptions for Metal Hydride Systems with respect to 2015 targets**

Technical Go/No-Go Criteria

- **Select Metal Hydride Systems for Phase 2 Decision**

Accomplishments: MH System Architect

- Sodium Alanate (SAH) selected as a model surrogate system
- Dual Vessel SAH Design (w. 4 mol%TiCl₃ & 5 wt% ENG)
- GM1 Design: fin and tube heat exchanger optimized to meet 10.5 min refueling time at the expense of wt %
- Two Type 3 composite tanks with SS liners
- System includes a 10 L buffer tank and a 12 kW H₂ combustor

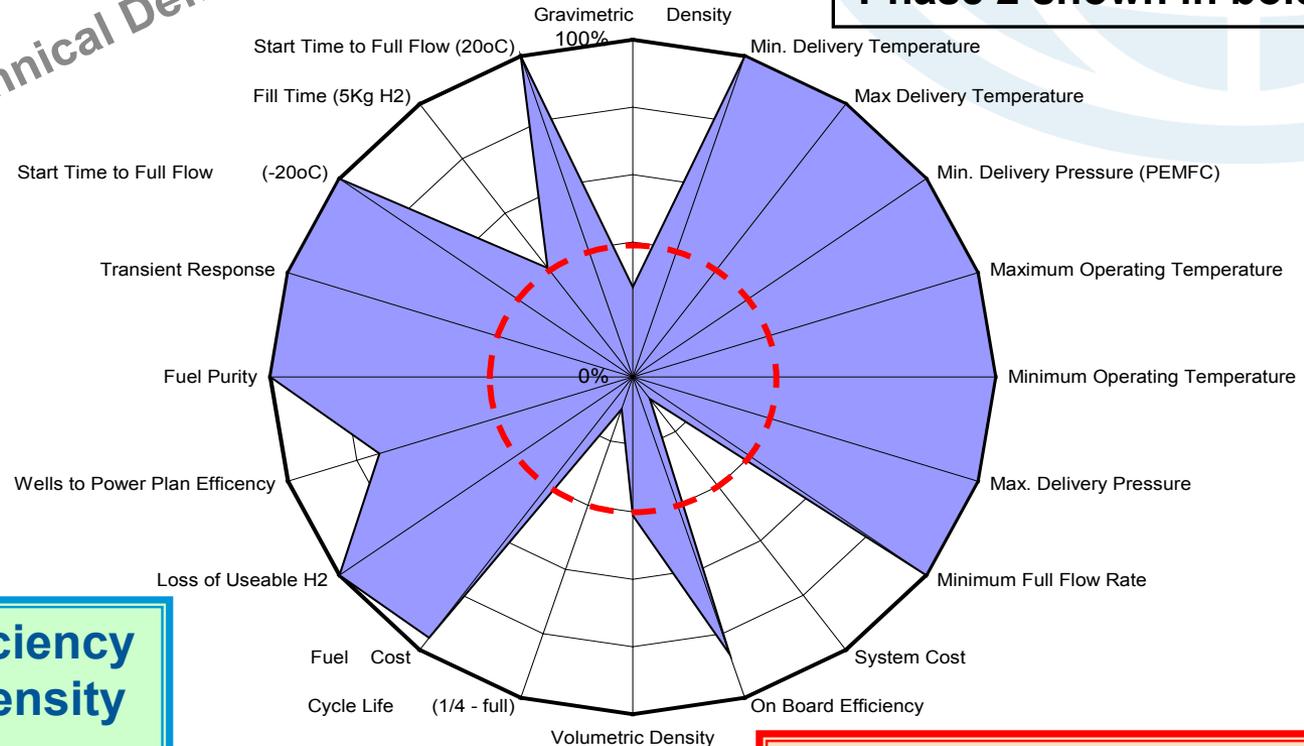


Accomplishments: Metal Hydride System Status

SAH: 2010 Targets

Highlighting Technical Deficiencies

Most significant deficiencies to be addressed first during Phase 2 shown in bold type

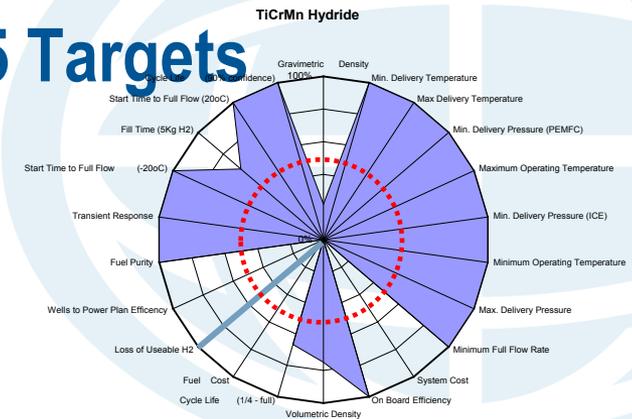


1. Onboard Efficiency
2. Volumetric Density
3. Fill Time
4. Fuel Cost
5. WPP Efficiency (< 2015 targets)

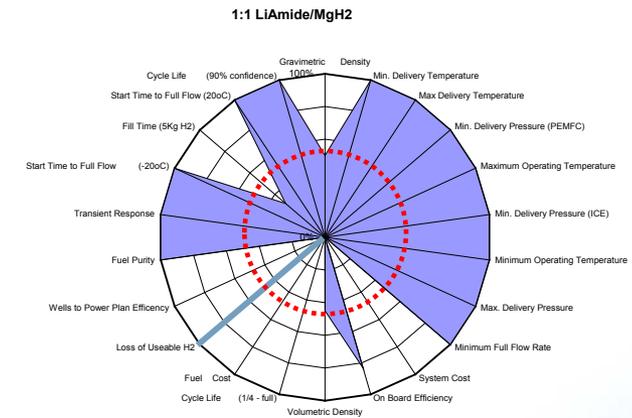
1. **Gravimetric Density**
 2. **System Cost**
 3. **Cycle Life**
- (< 40% 2010 targets)

Accomplishments: Prospects for 2015 Targets

- Gravimetric density has been a major issue for metal hydrides.
- TiCrMn meets many of the 2015 targets except it has a very low gravimetric density
- Materials like 1:1 Li Amide/MgH₂ show promise with a material gravimetric density of > 7 wt%. But because of its current slow kinetic performance it poses additional system challenges.
- A material with a capacity similar to 1:1 Li Amide/MgH₂ but with the kinetics of TiCrMn would be ideal
- Even with such a material several system and component improvements are still needed to overcome various system deficiencies.



Targets below 50%
 Gravimetric density (22%)
 Cost (not calculated)



Targets below 50%
 Volumetric density (45%)
 Fill time (31% due to kinetics)
 Cycle Life (due to material issues)
 Cost (not calculated)

Accomplishments: Identifying Deficiencies and Improvement Areas for MH Systems

- **Gravimetric Density**
 - Improved Tank Designs
 - Improved BOP components
 - Improved Internal Heat Exchanger
- **On Board Efficiency**
 - More Efficient Catalytic Combustor
- **Volumetric Density**
 - Media Compaction
- **System Cost**
 - Lower Cost Tank & BOP Components
- **Fill Time**
 - Improved Internal Heat Exchanger

Accomplishments: Material Operating Requirements

- **Selected sodium aluminum hydride (NaAlH_4) material as initial baseline hydride candidate material for transport phenomena and system modeling development**
- **Database updated for:**
 - NaAlH_4 (with and without catalysts)
 - TiCrMn
 - Mg_2Ni
 - $8\text{LiH}:3\text{Mg}(\text{NH}_2)_2$
- **Additional data added for:**
 - 2:1 $\text{LiNH}_2:\text{MgH}_2$
 - 1:1 $\text{LiNH}_2:\text{MgH}_2$
 - MgH_2 (without catalysts)
- **Developed preliminary kinetic expressions for 2:1 $\text{LiNH}_2:\text{MgH}_2$ and 1:1 $\text{LiNH}_2:\text{MgH}_2$ to support system modeling analyses**
- **Updated and improved the Acceptability Envelop to evaluate metal hydride materials for the Go/No-Go Decision**

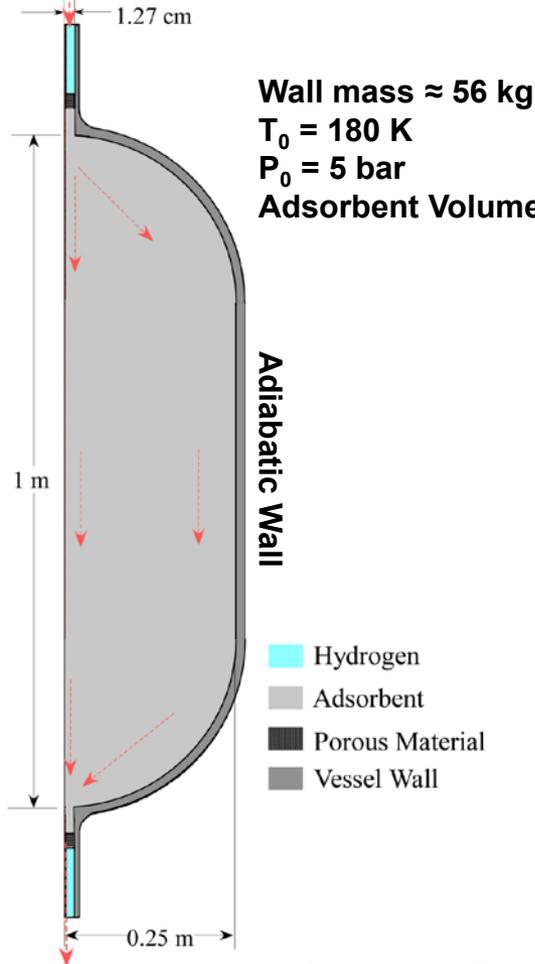
Accomplishments – Transport Phenomena

- **Developed Detailed and Thermodynamic Models for Adsorbent Based Storage Vessels**
 - Applied to MaxSorb (MSC-30™) and MOF-5™ (Basolite™ Z100-H)
 - Validated MaxSorb™ model against test data
- **Applied Models for Charging and Discharging of Storage Vessel**
 - Charging characteristics
 - Charging models were applied for DOE 2015 Technical Target time of 198 seconds (3.3 minutes)
 - Considered stored energy in vessel wall
 - Heat removal by axial and radial convection via flow-through cooling
 - Contributions of pressure work and heat of adsorption
 - Discharging characteristics
 - Resistance heater
 - Flow-through cooling

Accomplishments: Base Case Vessel Geometry and Charging Curve for Flow Through Cooling

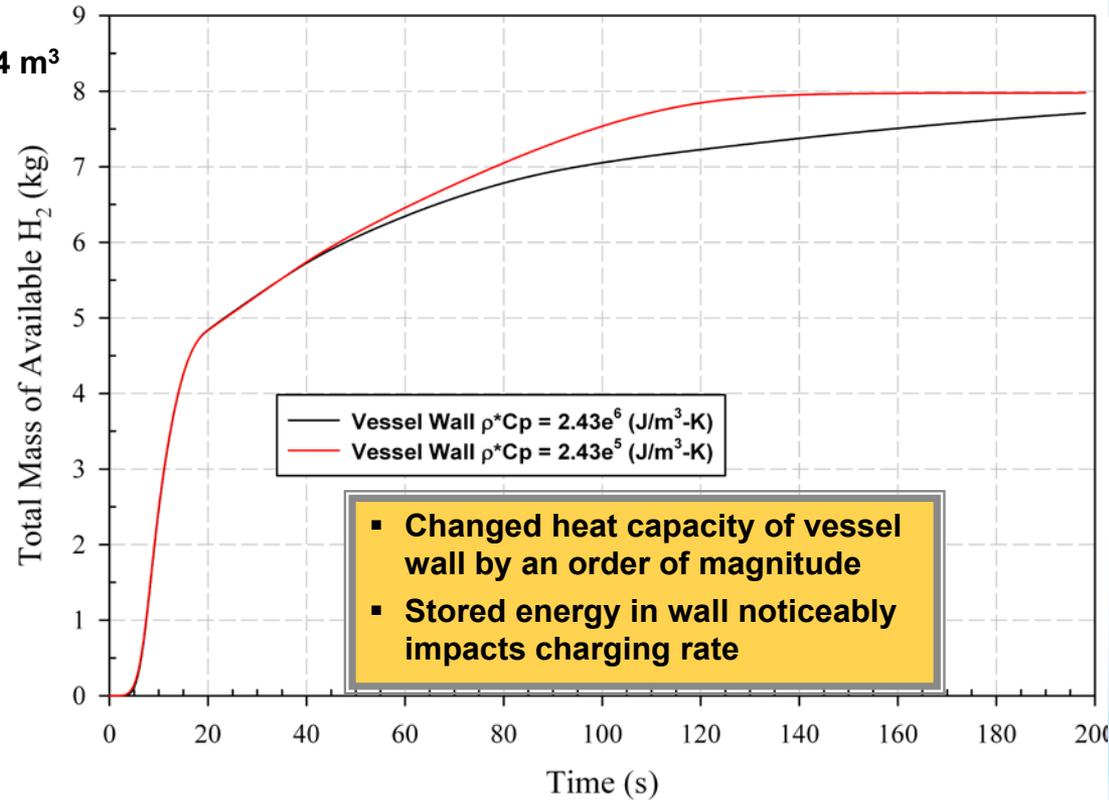
$T_{in} = 80 \text{ K}$
 P_{in} from 5 to 200 bar in 20 sec

Available \Rightarrow Amount Released Upon Return to Initial State



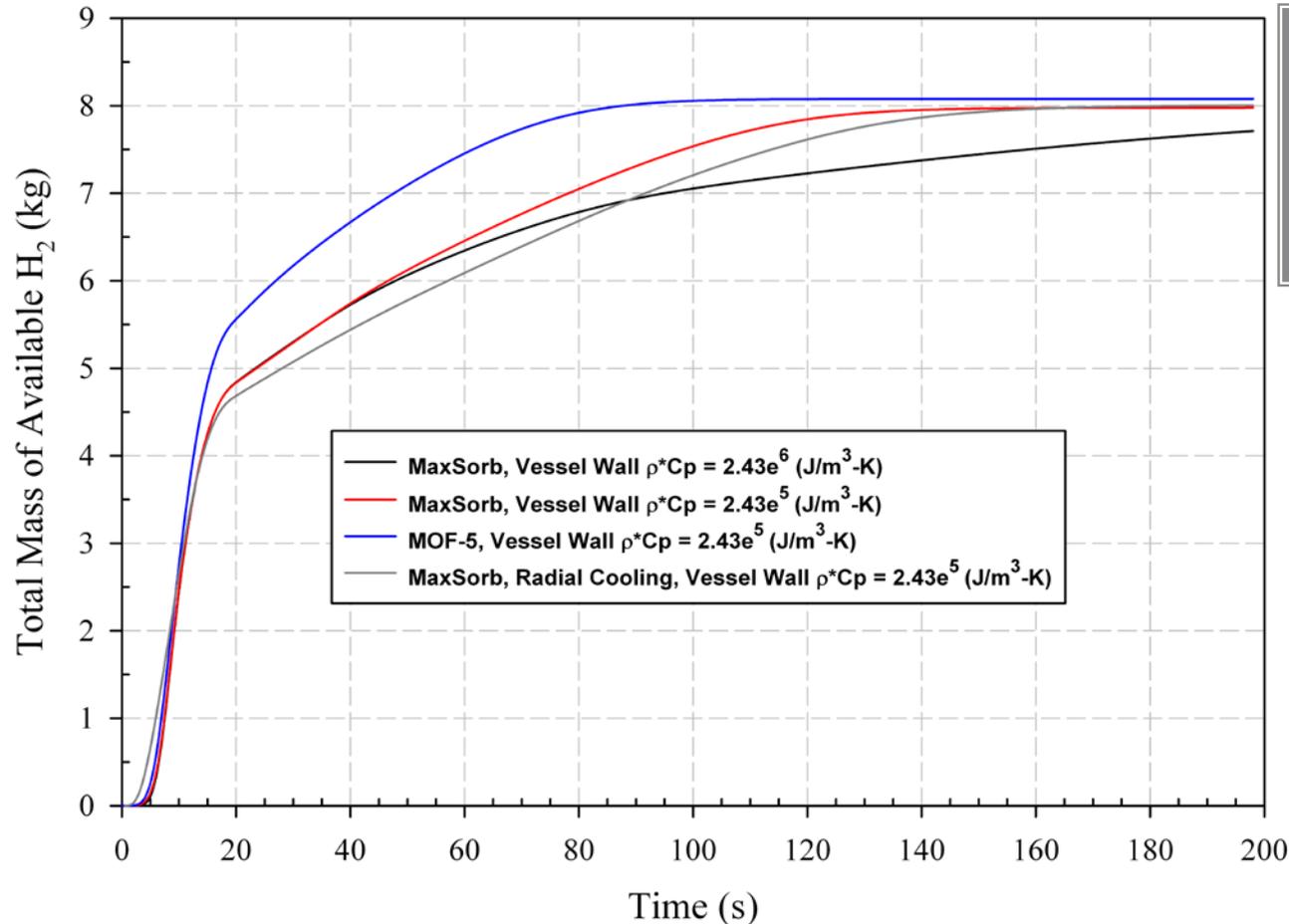
Average exit velocity from
 0 to 9 m/s from 3 to 5 s

MaxSorb Charging Rate - Total Available Hydrogen



Accomplishments: Summary of Charging Curves

Comparison of All Charging Rates Total Available Hydrogen



- **Best charging rate is obtained for MOF-5**
- **Rate can be improved by:**
 - Thermal isolation of wall
 - Reducing wall heat capacity

Accomplishments: State of Exhaust Hydrogen

Each case loads approximately 8 kg of recoverable hydrogen

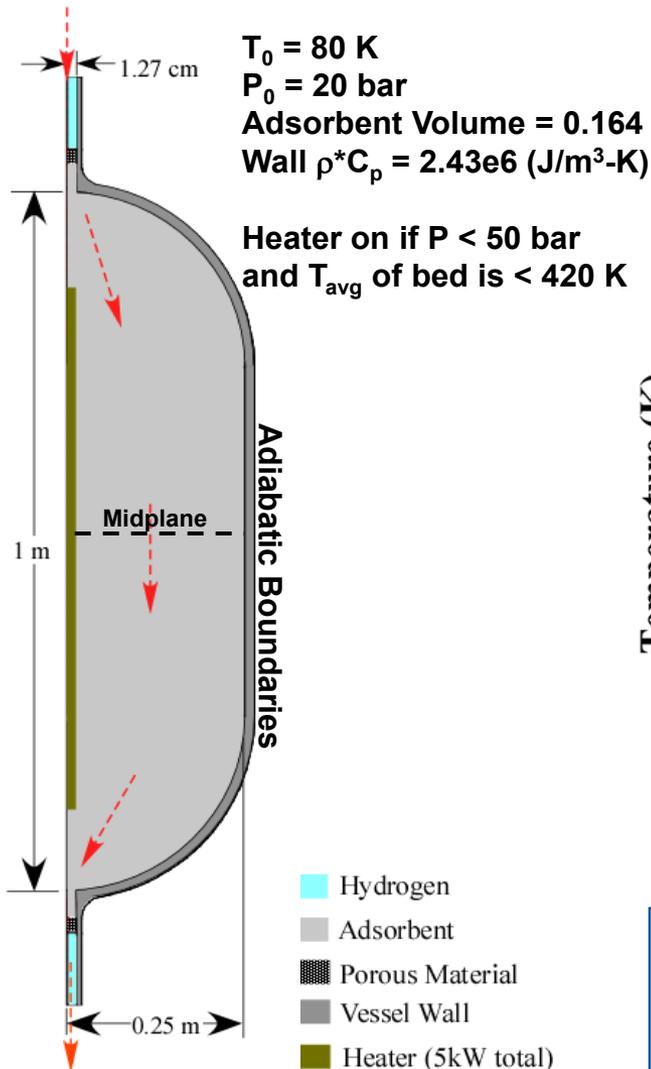
Flow through cooling is most efficient if the mass and average temperature of exhaust hydrogen are minimized (minimize total enthalpy)

Case	Charge Time (s)	Mass of Exhaust H ₂ (kg)	Average H ₂ Exhaust Temperature (K)
MaxSorb Low Wall ρC_p	140	17.19	133.67
MaxSorb Nominal Wall ρC_p	198*	27.51	120.06
MOF-5 Low Wall ρC_p	95	11.61	132.42
MaxSorb Low Wall ρC_p Radial Cooling	155	19.58	137.49

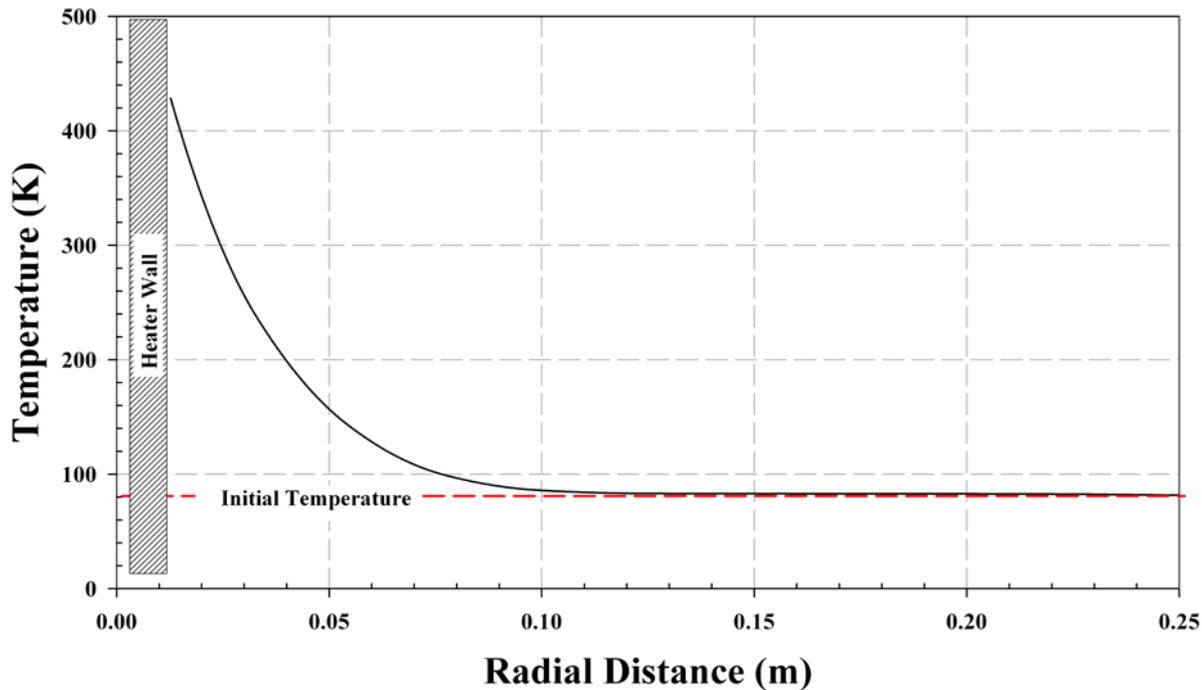
* Had not reached full capacity

Accomplishments: H₂ Discharge – Central Heating Element

No Flow



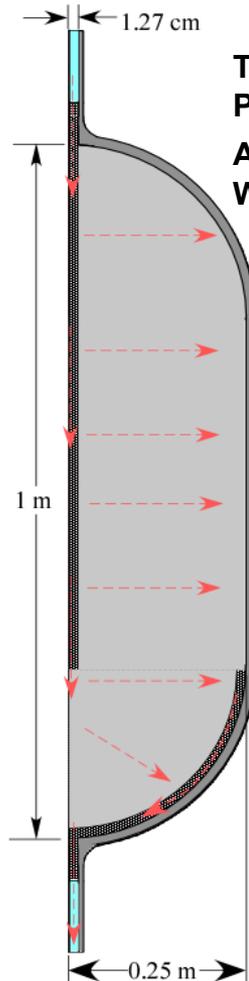
Midplane Temperature Profile at 1800 Seconds



- Pressure increases by 6.2 bar in 1800 seconds – Not very effective!
- A second heating method is required

Accomplishments: H₂ Discharge – Flow Through Heating

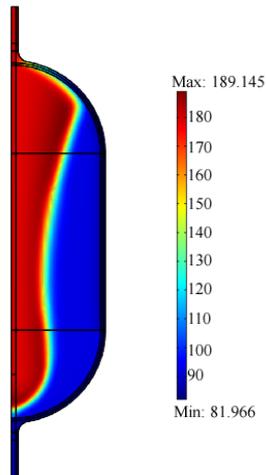
$T_{in} = 180\text{ K}$
 $V_{avg\ in}$ from 0 to 9 m/s in 8 sec



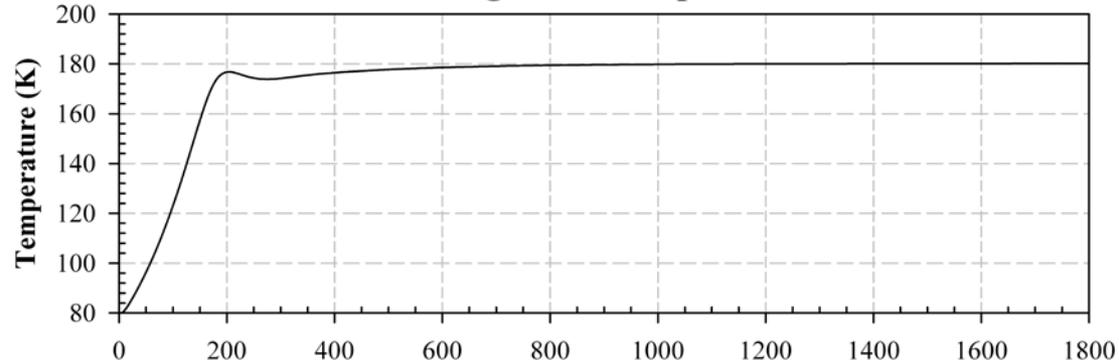
$T_0 = 80\text{ K}$
 $P_0 = 20\text{ bar}$
 Adsorbent Volume $\approx 0.163\text{ m}^3$
 Wall $\rho * C_p = 2.43e6\text{ (J/m}^3\text{-K)}$

- Hydrogen
- Adsorbent
- Porous Material
- Vessel Wall

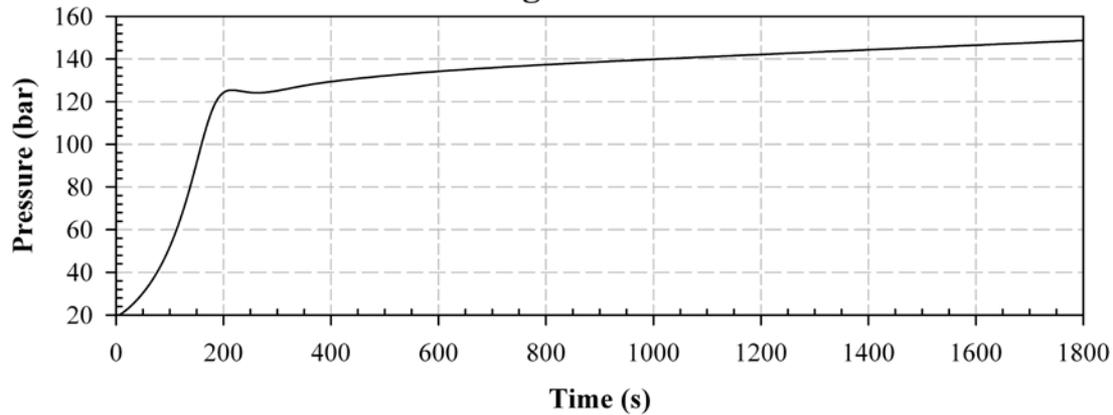
Temperature (K)
 Profile @ 90 sec



Average Bed Temperature

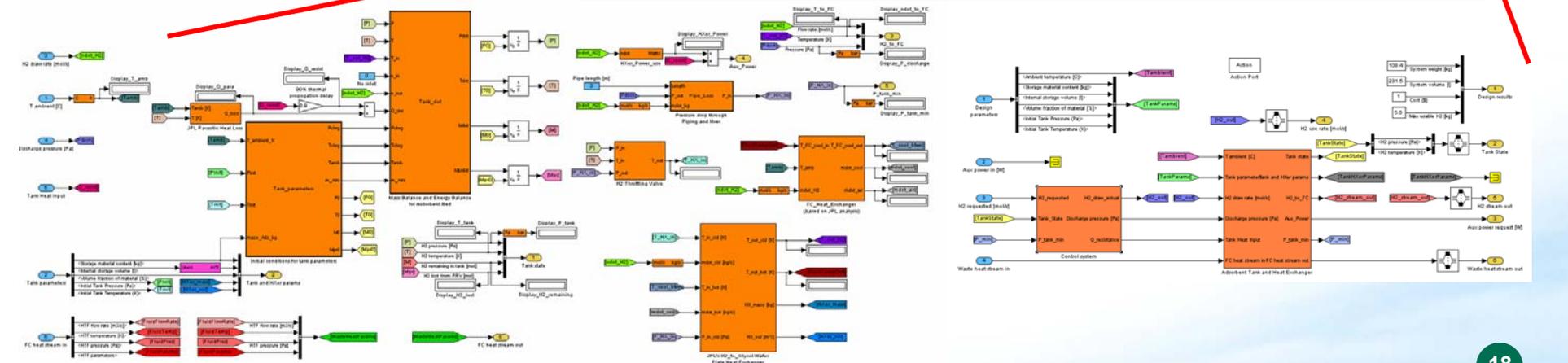
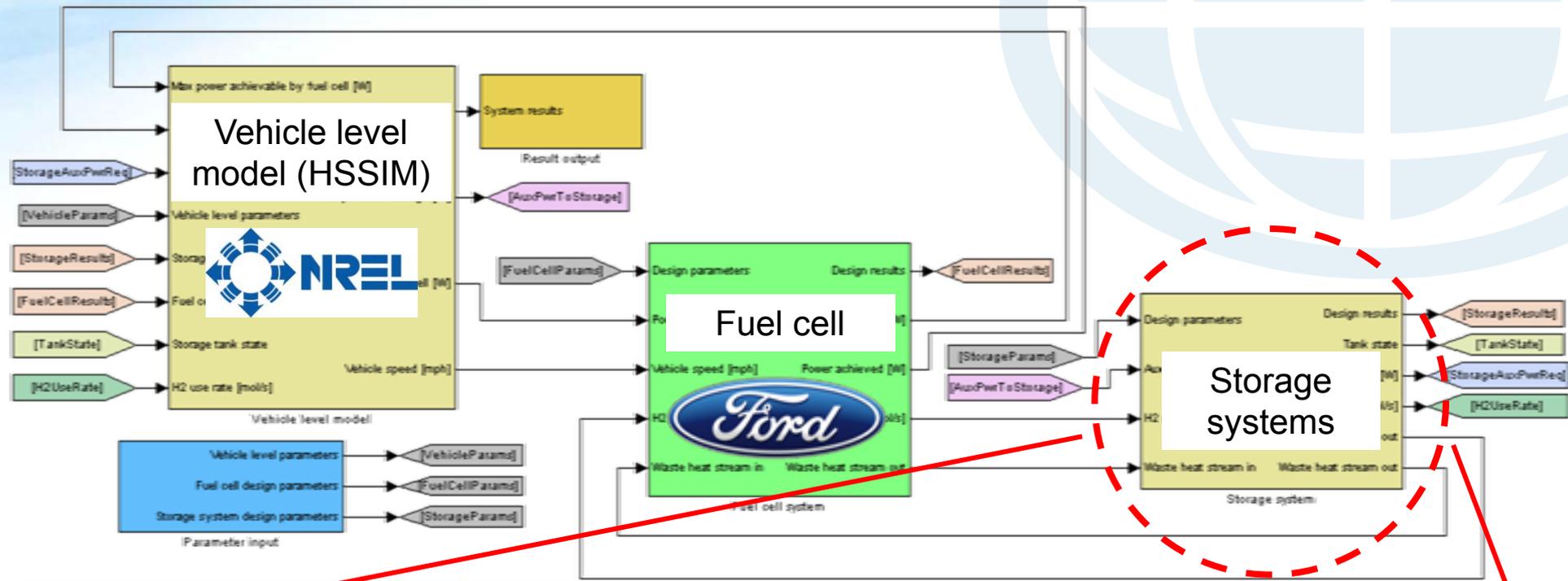


Average Bed Pressure



- Flow through heating provides good time response

Accomplishments: Adsorbent System Modeling



Accomplishments: Adsorbent System Model Selections

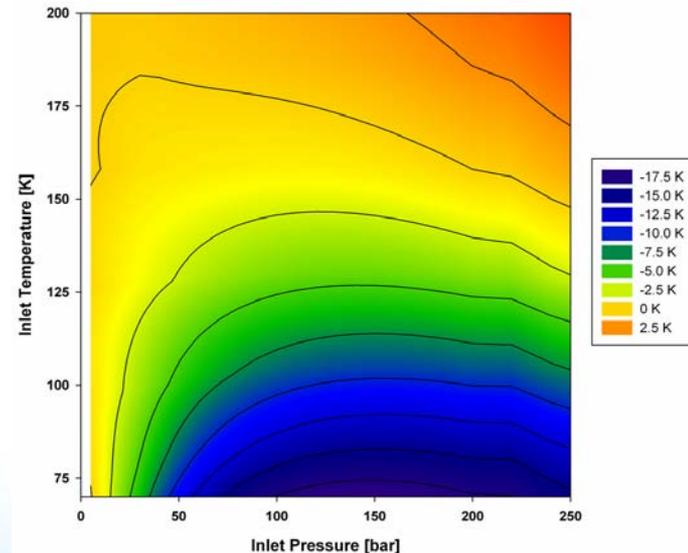
Possible Tank Heat Input methods:

- **Hot-H₂ Recirculation Line**
 - **Pro:** convection is the most effective H₂ desorption method
 - **Con:** requires a compressor – large, heavy, and with high power draw
- **Heat Switches**
 - **Pro:** use ambient temperature to desorb H₂
 - **Con:** application specific – can require significant design work
- **Internal electric heater (currently being used in system model)**
 - **Pro:** small, simple design that uses the fuel cell electricity converted into heat
 - **Con:** must overcome poor adsorbent thermal conductivity
- **Estimate isenthalpic (Joule-Thomson) temperature change for H₂ flow through pressure reducing valve.**
 - As large as **18 K** drop for a 200 bar reduction.

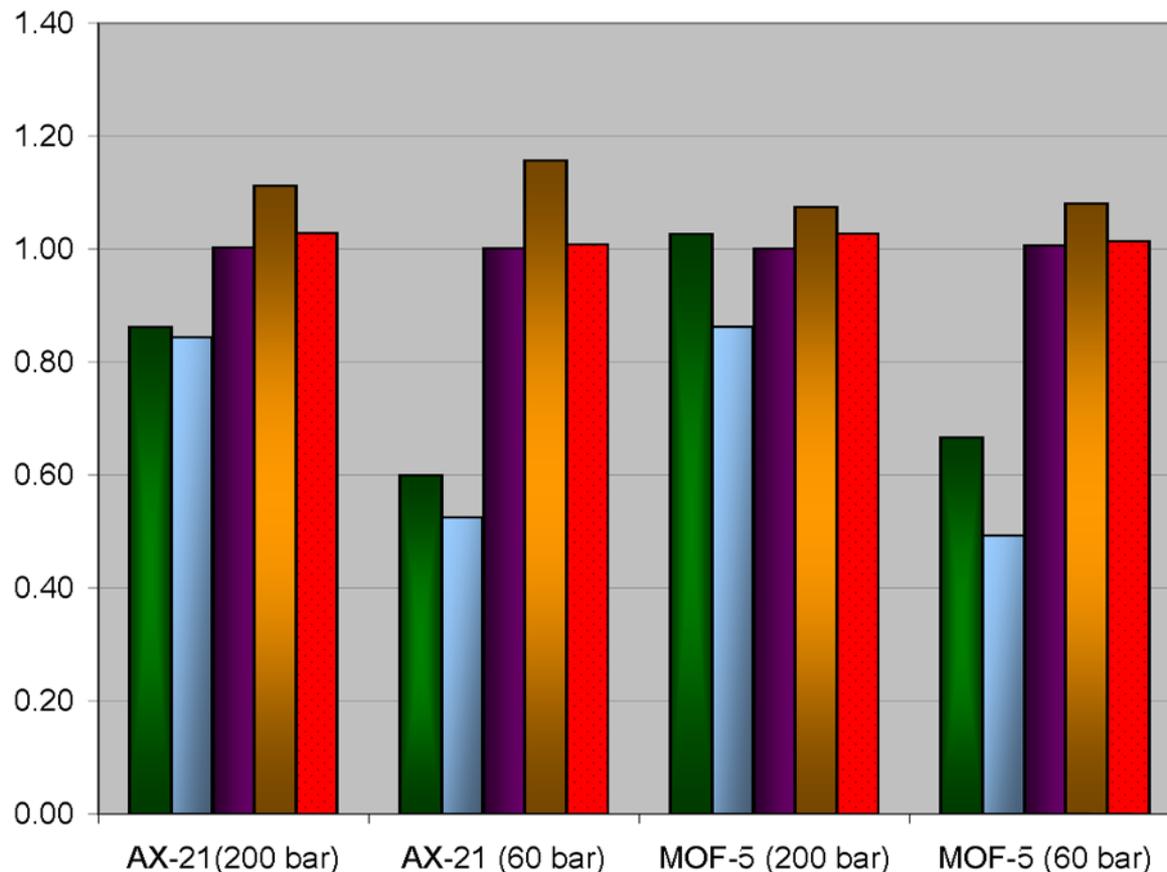
Possible External Tank Heat Exchangers:

- **None / Exposed H₂ Pipe**
 - **Con:** piping would ice, reducing convection
 - **Con:** would need ~36 m of exposed pipe assuming 24 °C ambient air and no icing
- **Air-H₂ Heat Exchanger**
 - **Pro:** simple, inexpensive designs available
 - **Con:** would require a high power deicer
- **Air-Coolant-H₂ Heat Exchanger (currently being used in system model)**
 - **Pro:** uses the Fuel Cell coolant to warm H₂
 - Based on analysis by

JPL

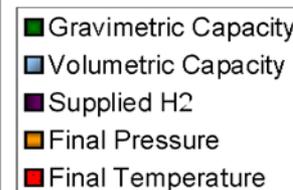


Accomplishments: Comparison to 2010 DOE Tech Targets



Gravimetric Capacity Target
(2010 DOE Technical Target)
4.50%

Volumetric Capacity Target
(2010 DOE Technical Target)
28 g/L



Supplied H₂ Target
5.6 kg

Final Pressure Target
5.0 bar

Final Temperature Target
140 K

- **The system model provides a vehicle for testing an unlimited number of operating conditions and component combinations.**
 - All four systems shown meet 40% of the DOE Capacity Targets while providing 5.6 kg of H₂ to the fuel cell.

Future Work

System Architect

- **Continue MH System Architect Analyses**
 - Follow new material and material property development
 - Assess new component and system designs
 - Provide analyses for Phase 2 Go/No-Go Decision

Experiments

- **Guided by models and of appropriate scale to validate assumptions**
- **Both Metal Hydrides and Adsorbents**
 - Material Operating Requirements
 - Continue updating the database with potential materials
 - Perform kinetic and thermal measurements on materials of interest
 - Bed heat transfer improvements
 - Addition of ENG “mat” to provide directed (anisotropic) heat flux
 - Honeycomb lattice configuration proposed by Bhouri & Goyette of UQTR
 - *Resistively heated for use with adsorbent pressure vessel*
 - *With heat transfer fluid channels for cooling*
 - Compare performance of ENG and honeycomb lattice with traditional tube and fin heat exchangers
 - Novel heat exchangers for compacted media (UQTR/OSU/SRNL)
 - Test selected heat transfer enhancement in actual charging experiment
- **Metal Hydride-Specific Experiments**
 - Structural and thermal bed expansion effects
 - Measurement of expansion forces against heat transfer surfaces
 - Effect of expansion on thermal contact resistance



Future Work – continued

Experiments – continued

● **Adsorbent-Specific Experiments**

- Verify model properties and assumptions
 - Pressure work vs. heat of adsorption, esp. for MOF-5
 - *Inert gas pressurization*
 - Wall contact resistance
 - Flow through cooling configurations
- Viability of flow through cooling concept
 - Mitigation of bypass flow
 - Effects of compaction on hydraulic permeability
 - *Engineering combination of novel heat exchanger concepts and flow through cooling may be required*

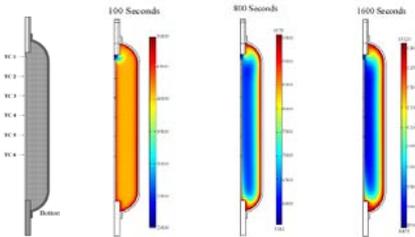
Modeling and Validation

● **Adsorbent Vessel Optimization**

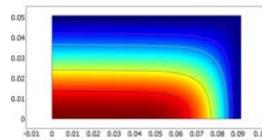
- Minimize impact of pressure work during charging
- Minimize total enthalpy of discharge hydrogen for flow through cooling
 - Requires control of total mass and average specific enthalpy
- Operating conditions
 - Extend dormancy
 - Meet system demands
 - Utilization of *vented* hydrogen
- Thermal interaction with vessel wall
 - Wall cooling methods
 - Reduction of effective thermal mass of the vessel wall
 - Thermal isolation of structural wall from bed

Collaborations

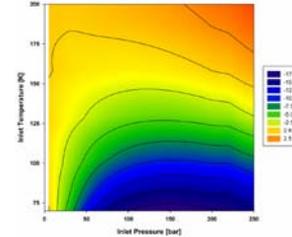
Adsorbent Prototypes:
Design, Testing and
Model Validation



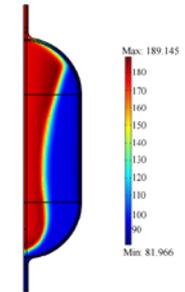
Modular Tank Insert:
Optimization



H₂ Flow and Heat Exchanger:
Modeling and Analysis



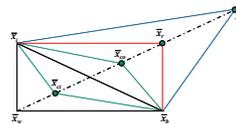
Flow-Through Heat
Transfer Modeling



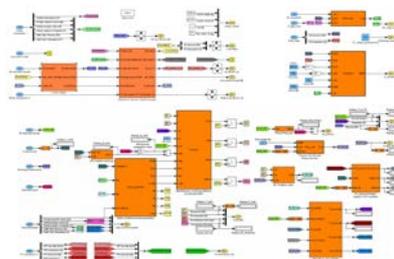
Pressure Vessel Properties
and Wall Thicknesses



Components	Mass [kg]	Volume [L]	Comments
Storage Vessel	186.8	195.8	
Tank component and internals	54.8	78.3	Based on GM's tank analysis
Internal (Tank) IEX	8.5	3.2	Stagnated heat transfer analysis (1-30%)
XX-21 media	36.3	121.3	Assumes 0.3 high density
H ₂ gas stored	7.0	0.3	Weight of H ₂ in subcool
Storage IEX	11.9	6.6	25% to heat exchanger analysis
H ₂ BOP	13.7	14.4	From NEI BOM, TEAC, & PNL
Subtotal	121.6	216.8	
Additional 30%	13.2	21.4	To cover additional volume components
Totals	144.8	237.6	



System Models:
Li:Mg Amide and Adsorbent



Compacted Media:
Properties and Behavior



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 solid-state hydrogen storage systems 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 SRNL/UQTR:

- led in the [collection and screening of material property and engineering data](#) for metal hydride and adsorbent materials including the development of the [Acceptability Envelope](#) methodology.
- led the overall project in [Transport Phenomena](#) modeling and analysis concentrating on metal hydride and adsorbent systems and components designs.
- led [System Architect](#) activities for [metal hydride systems](#) culminating in Go/No-Go for Phase 1

Technical Accomplishments and Progress (as of 3/11)

- Collected material operating data for LiMg-amide metal hydride materials including developing engineering kinetic expressions
- Applied Acceptability Envelope to select metal hydride materials and systems
- Studied 50 bar, 100 bar, and 150 bar sodium alanate optimal systems
- Estimated isenthalpic (Joule-Thompson) temperature change for hydrogen flow through a throttling valve, which can be as large as an 18 K drop
- Developed methodology and estimated pressure drop losses for flow in piping of cryo-adsorbent system for a range of conditions (mass flow rates, temperatures, and pressures) for use in system models
- Developed improved methodology to estimate heat transfer coefficient for turbulent (radial) flow in micro-channel between cooling plates for analysis and COMSOL optimization of modular cryo-adsorbent designs
- Studied in-line heat exchangers for H₂ feed to fuel cell
- Completed System Architect analysis of Sodium Alanate as a model material vs. DOE 2010 Go/No-Go Decision

Collaborations

HSECoE partners, Previous Materials Center members, SSAWG, IPHE, IEA etc.

Proposed Future Work (Phase II)

- Continue MH System Architect analyses
- Provide analyses for Phase 2 Go/No-Go decision
- Investigate thermal and structural effects of bed expansion
- Improve bed heat transfer for metal hydrides and adsorbents (ENG addition. honeycomb lattice) - experiments will be guided by models
- Investigate viability of flow-through concept for adsorbent systems
- Optimize adsorbent system with respect to pressure work, enthalpy of hydrogen discharge flow, dormancy conditions and thermal interaction with container wall



Technical Back-up Slides

Accomplishments: Acceptability Envelope

● Acceptability Envelope or “BlackBox Analysis”

- Based on energy balance
- Relates characteristics of media and system to storage system performance targets
- Combined with DOE Technical Targets, it serves as media screening tool

- Guide for material development
- Defines acceptable media & storage vessel parameter ranges

● Assumptions:

- 1D heat transfer process
 - *Rectangular (RC) and Cylindrical coordinates (CC)*
- Steady state process during charging time
- Constant thermal conductivity inside bed
- Negligible convective heat transfer
- Negligible compression or expansion work

$$\Delta T = \frac{L^2 \cdot \rho_{Bed} \cdot \frac{\Delta H_{overall}}{MW_{H_2}} \cdot \frac{\Delta M_{H_2}}{\Delta t}}{m \cdot k_{eff} \cdot M_{Hydride}}$$

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

Cylindrical

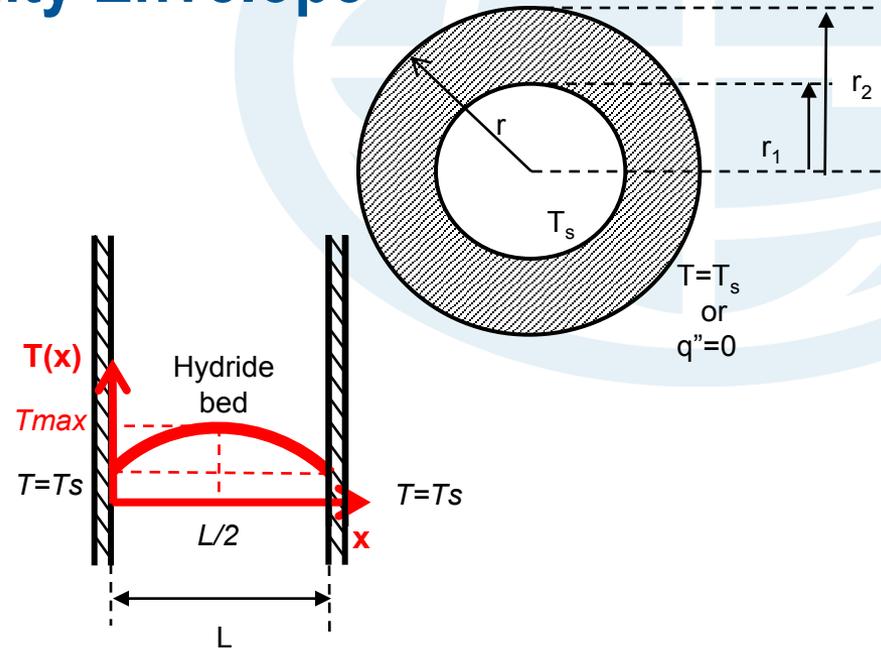
$$L^2 = r_1^2 - r_2^2$$

$$m = 8$$

Rectangular

$$L = (\text{fin spacing})$$

$$m = 4$$



L	Distance between heat transfer surfaces (m)
ΔT	Temperature range required for acceptable chemical kinetics (to give specified charge/discharge rate) (K)
$\Delta H_{overall}$	Overall heat of reaction (kJ/mol H ₂)
ρ_{Bed}	Hydride bed density (kg/m ³)
k_{eff}	Effective bed thermal conductivity (W/m K)
$M_{Hydride}$	Mass of hydride required to load target amount of hydrogen (kg)
MW_{H_2}	Molecular Weight of Hydrogen (kg H ₂ /mol H ₂)
$\frac{\Delta M_{H_2}}{\Delta t}$	Rate of charging/discharging (kg H ₂ /s)

Accomplishments: Modular Tank Insert

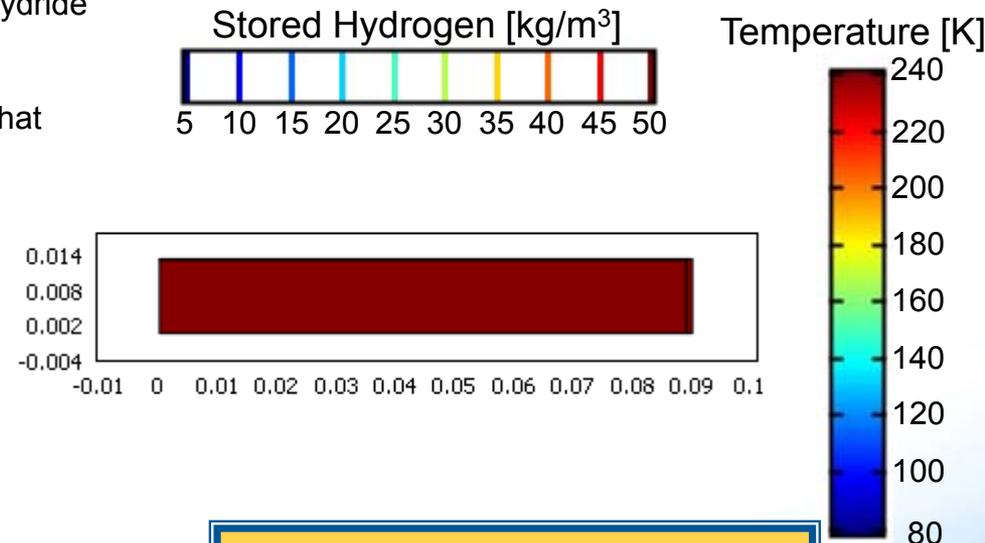
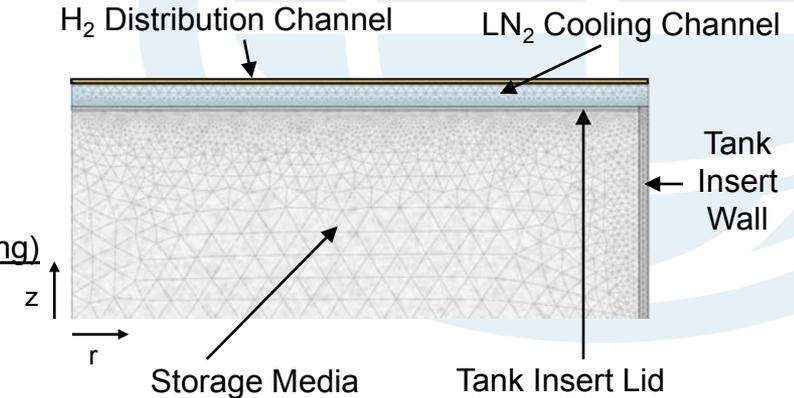
- Store media in modular “cans” or inserts within the pressure vessel, “number-up” to increase size
- Design allows for several engineering improvements
 - Compacted media (possibly w/o binder) – Improved volumetric capacity
 - Integrated hydrogen distribution – Improved H₂ mass transfer
 - Microchannel Heat Exchanger (μ C-HX) – Liquid N₂ cooling (fueling) and heat transfer fins (discharge)
 - Flow-through cooling could still be implemented – Additional, convective, heat transfer

● Modeling and Optimization

- Applied methodology previously developed for metal hydride systems initially to uncompact adsorbent
- Fluid-dynamics dependent heat transfer coefficients
- Systematically and simultaneously found parameters that maximized overall vessel volumetric capacity
 - Tank insert diameter
 - Tank insert thickness
 - Insert cooling channel height
 - Pressure ramp time
 - Return-to-station temperature
- Over 1000 configurations investigated

● Path Forward

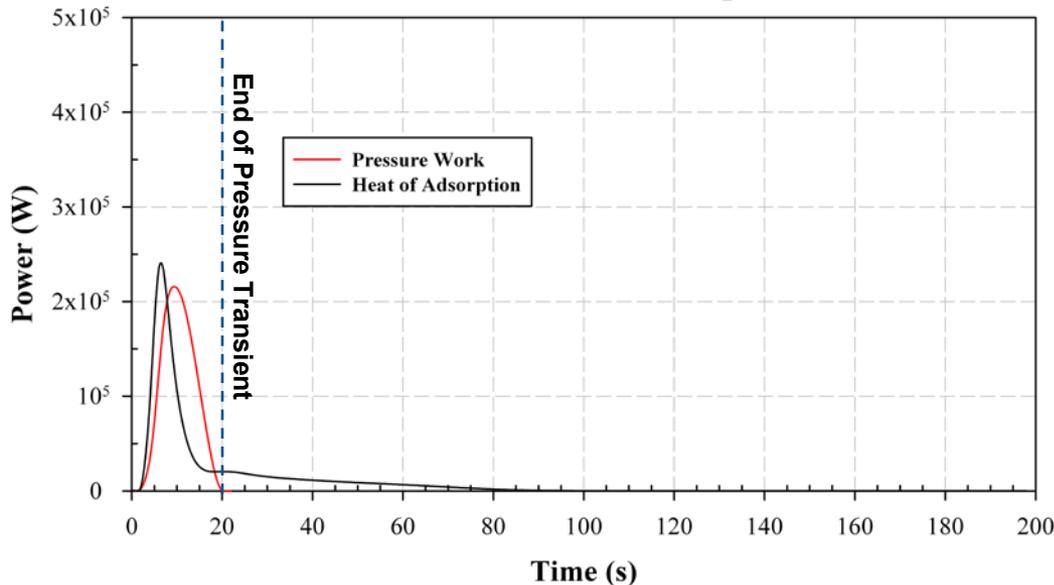
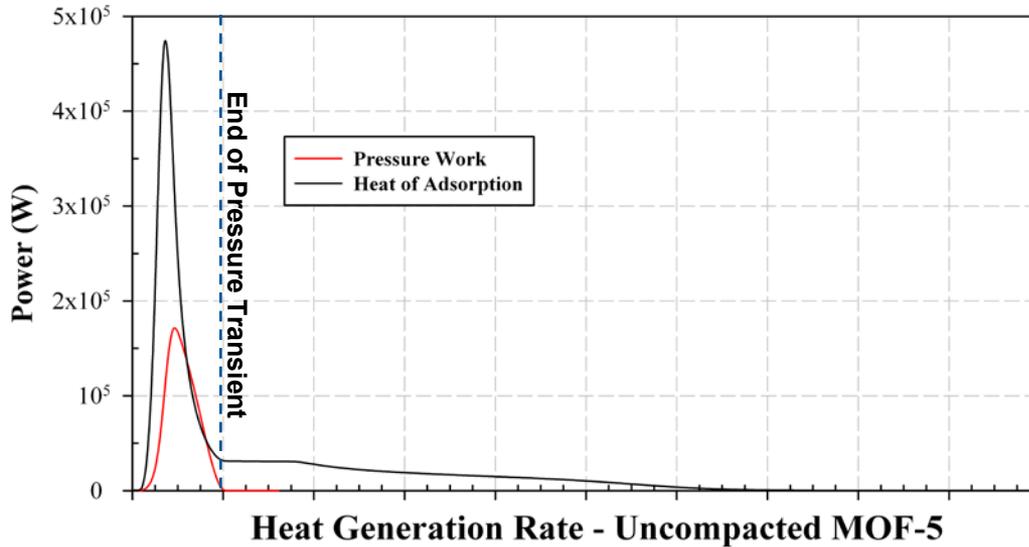
- Extend model and optimization to compacted systems
 - H₂ permeation behavior in compacted system must be experimentally determined
- Optimize on system volumetric capacity
 - Include pressure (vessel wall thicknesses) in optimization
 - Include (estimated) system balance of plant (BOP)
- Model discharge behavior to develop system model for drive cycles
- Collaborate to experimentally test and validate model



Compacted adsorbent media (without a binder) could provide significant **volumetric capacity** improvements!

Accomplishments: Heat Dissipation During Charging

Heat Generation Rate - MaxSorb



$$\text{Generation by Pressure Work} = -\varepsilon \frac{T}{c} \frac{\partial c}{\partial T} \frac{\partial P}{\partial t}$$

$$\text{Generation by Heat of Adsorption} = -\frac{\partial}{\partial t} [\rho_{\text{ads}} (\Delta U_{\text{a}} + n_{\text{a}} (u_{\text{H2O}} - u_{\text{H2}}))]]$$

	Total Pressure Work (MJ)	Total Heat of Adsorption (MJ)
MaxSorb	1.39	4.81
MOF-5	2.03	2.14

- *Difference in pressure work is due to different porosities*
- *Pressure work is more important for MOF-5 because it is approximately equal to the heat of sorption*

Accomplishments: Summary of Adsorbent Cooling and Heating Considerations

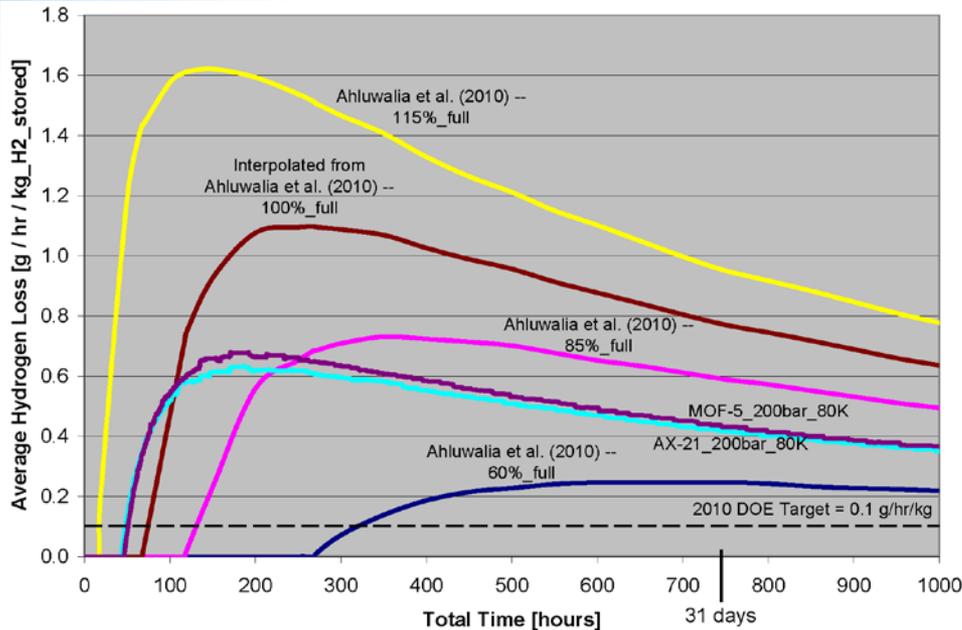
- **Flow Through Cooling is a Viable Concept for Nominal Form of MaxSorb**
 - Optimize vessel design & operation
 - Thermally isolate vessel wall from bed or reduce ρC_p
 - Alternative, novel, heat transfer technologies being pursued by OSU, UQTR and SRNL will likely be needed for compacted adsorbents
 - Optimize charging conditions to minimize total exhaust gas enthalpy
 - Flow through cooling not likely to work for compacted media
 - Need permeability data
- **Charging Conditions and Vessel Geometry Affect Heat Release**
 - Result of pressure work
 - Can be significant
 - This was noted by Hermosilla-Lara, et. al. (2007)¹ and Momen, et. al. (2009)² who claimed pressure work accounted for more than 70% of the energy released during the charging process based on their model and experiments.
- **Need Better Way to Heat Bed**
 - Low bed thermal conductivity requires short thermal transport length
 - Flow through heating can work, but requires pump, valves and possibly combustion of hydrogen

1 Hermosilla-Lara G, Momen G, Marty PH, Le Neindre B, Hassouni K. Hydrogen storage by adsorption on activated carbon: Investigation of the thermal effects during the charging process. *Int J Hydrogen Energy* 2007;32:1542-53.

2 Momen G, Hermosilla G, Michau A, Pons M, Firdaus M, Marty PH, Hassouni K. Experimental and numerical investigation of the thermal effects during hydrogen charging in a packed bed storage tank. *Int J Hydrogen Energy* 2009;52:1495-1503.

Accomplishments: Adsorbent Storage System Dormancy

Comparison with Cryo-compressed (Ahluwalia et al., 2010)



31-day dormancy assumptions

- Ambient temperature at 35 °C
 - CcH₂ uses 50 °C
- Pressure relief set to 25% above rated tank pressure
 - 275 bar CcH₂ tank vents at 345 bar
 - 200 bar Ads tank vents at 250 bar

- 2010 DOE Technical Target for loss of usable H₂ = 0.1 (g/h)/kg_{H2stored}
 - After 31 days – both adsorbent and CcH₂ systems **fail** to meet the target of 0.1 g/hr/kg_{H2stored}
 - CcH₂: 0.77 - 0.80 g/hr/kg_{H2stored}
 - Ads: 0.42 - 0.44 g/hr/kg_{H2stored}
- Lower max average H₂ loss rate
 - CcH₂: 1.09 - 1.10 g/hr/kg_{H2stored}
 - Ads: 0.70 - 0.70 g/hr/kg_{H2stored}
- Venting begins slightly sooner
 - CcH₂: 67 - 68 hours
 - Ads: 44 - 47 hours

• Overall (100% full) adsorbent H₂ loss is **improved** compared to (100% full – interpolated) CcH₂