IV.D.1h SRNL Technical Work Scope for the Hydrogen Storage Engineering Center of Excellence

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Projected End Date: July 31, 2014

Objectives

SRNL and UQTR will:

- Compile property data for sodium aluminum hydride ($NaAlH_4$), a metal hydride, and AX-21, an adsorbent.
- Collect property data for other select metal hydrides and adsorbents.
  - Compile list of available analytical techniques to support materials property data requirements.
- Develop acceptability envelope for storage media and vessels.
- Develop numerical models to adequately predict storage system behavior for $NaAlH_4$ and AX-21 based storage systems.
  - Use the models to design optimized storage systems based on $NaAlH_4$, other metal hydrides, AX-21, and other potential absorbent materials.
- Develop practical and efficient enabling technologies in the areas of hydrogen purification and demonstrate material compatibility for various systems and components for adsorbent and metal hydride storage materials.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

(C) Efficiency

(E) Charging/Discharging Rate

Technical Targets

The goal of the entire Hydrogen Storage Engineering Center of Excellence (HSECoE) is to provide a system model for each material sub-class (metal hydrides, adsorption, chemical storage) which meets the "Technical System Targets: On-Board Hydrogen Storage for Light-Duty Vehicles", Table 3.3.2 in the DOE Multi-Year Research and Development Plan – April 2009. The end of Phase I, Go/No-Go milestone for the entire HSECoE project states that:

1. Four of the DOE 2010 numerical system storage targets are fully met and that,
2. The status of the remaining numerical targets must be at least 40% of the target or higher.

For SRNL's specific technical portion of the HSECoE, SRNL will:

- Compile thermochemical data.
- Bound media operating characteristics for metal and adsorption hydride material.
- Develop and apply numerical models that couple mass, momentum and energy balances with chemical kinetics and/or isotherms to simulate hydrogen uptake and discharge.
- Identify technology gaps.
- Identify preliminary system designs to achieve DOE 2015 hydrogen storage goals.

Accomplishments

- Metal hydride modeling accomplishments:
  - Developed and validated baseline models for metal hydride storage systems.
  - Incorporated improved models into optimization routines.
  - Identified principal issues for design of metal hydride-based storage systems.
  - Began investigating novel concepts/system designs.
- Adsorbent modeling accomplishments:
  - Developed and validated baseline models.

  - Developed an adsorbent unit cell model in Comsol® for optimization.
  - Began investigating novel concepts/system designs.
- Acceptability envelope accomplishments:
  - Model developed for metal hydrides.
- Material operating requirements: metal hydrides:
  - Selected $NaAlH_4$ 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.
- System architect analyses: metal hydride:
  - Completed system architect analysis of $NaAlH_4$ vs. DOE 2010 technical hydrogen storage targets.

Introduction

SRNL and UQTR are involved in several critical aspects of the HSECoE. SRNL is focused primarily modeling, validating, and optimizing hydrogen storage designs for metal hydrides, adsorbents, and, to a lesser extent, chemical hydrides, and system architect analyses of metal hydride systems. SRNL is applying its expertise in modeling dynamic transport phenomena and chemical processes, materials testing, and system modeling to accomplish its objectives in the proposed effort–developing and applying models to identify viable subscale prototype designs, performing design calculations sufficiently accurate for engineering application, and defining the scope and required measurements for experiments with the selected prototypes.

UQTR is developing the governing equations for an adsorbent system that be easily and efficiently implemented by SRNL into a model to accurately predict the adsorption characteristics over a range of temperatures. UQTR is extending its current equations for hydrogen adsorption on activated carbons to any adsorbent used in the storage system design.

Relevance

The ultimate goals of the HSECoE are the design and testing of prototype hydrogen storage vessels, the interpretation of test data, and the implementation 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, SRNL and UQTR will:

- Evaluate, interpret, and assimilate data for media and vessel components.
- Develop and apply an “Acceptability Envelope” based on DOE targets.
- Develop, validate and test general models for scoping and detailed evaluation of storage system designs.
- Obtain material operating requirements for metal hydride and AX-21 materials.
- Perform system architect analysis on candidate metal hydride systems for Phase I Go/No-Go decision.

Results

SRNL and UQTR to date have met and or exceeded their Phase I objectives for all of their major technical areas for the HSECoE. These major technical areas include: transport phenomena, material operating requirements and system architecture. Transport phenomena results are shown below and are divided into metal hydride and adsorbent modeling as well as acceptability envelope development and applications. Results for activities under material operating requirements and system architecture are shown for metal hydrides systems.

Transport Phenomena

Metal Hydride modeling accomplishments:

- Developed and validated baseline models for metal hydride storage systems
  - 0-dimensional kinetics models in MathCad® (Figure 1)
  - 1-, 2-, and 3-dimensional models in Comsol®
    - Consolidated all models into Comsol®
- Incorporated improved models into optimization routines
  - Used Nelder-Mead (Downhill Simplex) optimization scheme
    - With given constraints, optimal designs require very small spacing of heat transfer surfaces

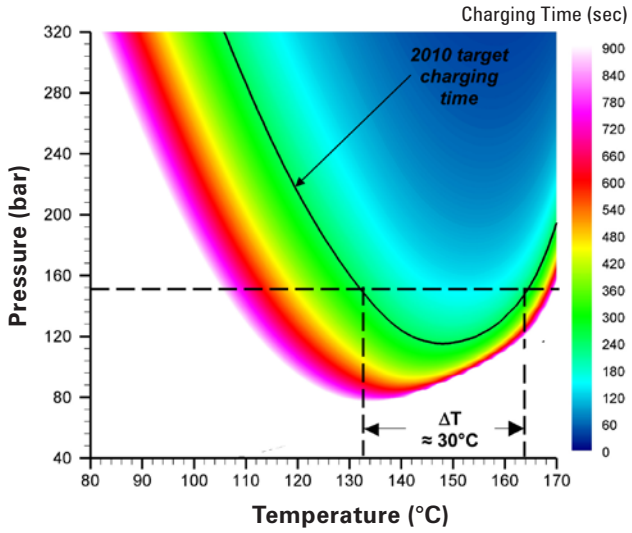


FIGURE 1. Fill times calculated from the 0-dimensional Mathcad Kinetics Model for $NaAlH_4$ based on the UTRC Prototype 2 Kinetics.

- Identified principal issues for design of metal hydride-based storage systems
  - Variations in powder composition and catalyst materials
    - Large impact on the charging and discharging kinetics
    - Large impact on capacity
  - Substantial increase (x50) in $NaAlH_4$ kinetics required to meet 2010 DOE targets for refueling time
    - Heat removal becomes an issue for ΔH associated with most metal hydrides
  - Short refueling times (e.g., 4.2 min vs. 15 min) for the current $NaAlH_4$ kinetics impact
    - System gravimetric capacities
    - System volumetric capacities
- Began investigating novel concepts/system designs (Figure 2)

  - Methods can be easily extended to new metal hydride systems
    - New hydrides, such as 2:1 and 1:1 $LiNH_2$-MgH_2
    - New catalysts for existing hydrides
    - New tank designs
    - Adsorbent systems

Adsorbent modeling accomplishments:

- Model development and validation
  - Numerical models within Comsol®
  - Model validation against experimental data for MaxSorb® (Figure 3)
- Developed baseline scoping models for an adsorbent unit cell in Comsol®

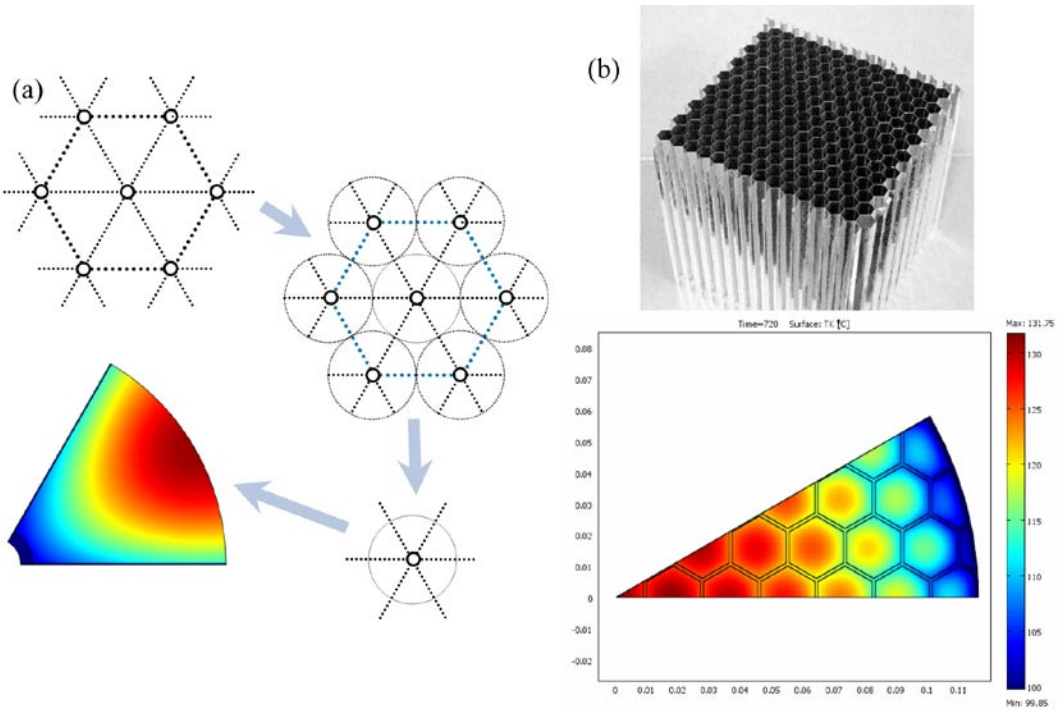


FIGURE 2. Novel concepts for tank designs, such as (a) longitudinal fins or (b) a metallic honeycomb structure.

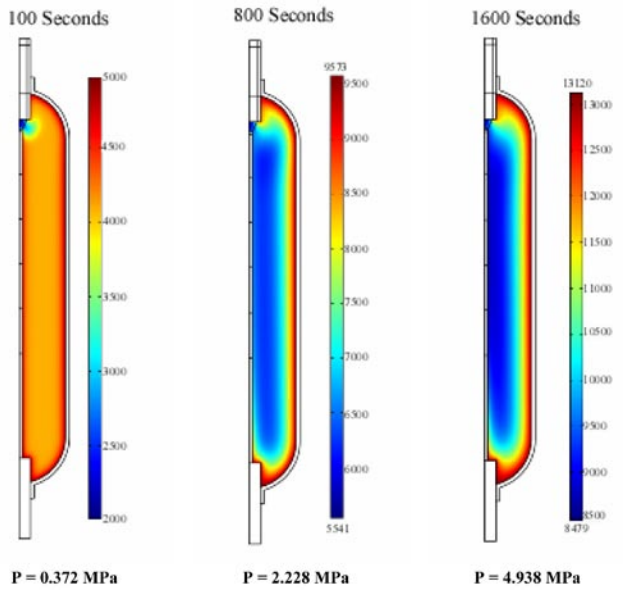


FIGURE 3. Adsorbent model validation showing the total hydrogen concentration (mol/m^3) during loading for a MaxSorb® bed.

- Began investigating novel concepts/system designs

Acceptability envelope accomplishments (Figure 4):

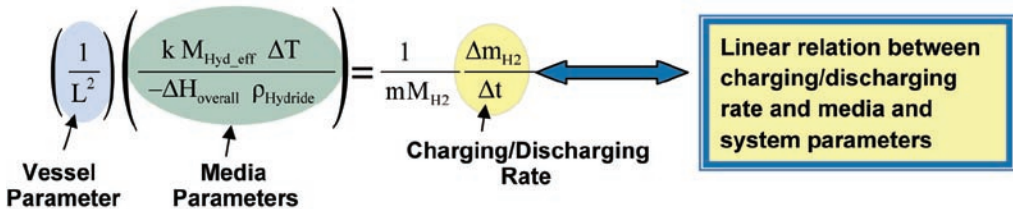
- Model developed for metal hydrides
  - Based on energy balance
    - Constraints are from DOE technical targets
    - Model should be used in conjunction with media kinetics
  - Can be used to identify range of media and component parameters required to meet operational targets
- Application
  - Has been applied to $NaAlH_4$ and other metal hydrides

Material Operating Requirements: Metal Hydrides

- Selected $NaAlH_4$ 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

System Architect Analyses: Metal Hydride

- Completed system architect analysis of $NaAlH_4$ vs. DOE 2010 technical hydrogen storage targets
  - Completed preliminary analysis on other potential metal hydride candidates (Mg, Mg_2Ni, 2:1 $LiNH_2$:MgH_2, and 1:1 $LiNH_2$:MgH_2)



Explanation of terms:

L	Distance between heat transfer surfaces
ΔT	Temperature range for acceptable chemical kinetics (to give charge/discharge rate of DmH2/Dt)
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

FIGURE 4. Basic Equation and Concept for the Acceptability Envelope

Conclusions and Future Directions

Proposed future work for metal hydrides:

- All future work will be dependent upon the results from the acceptability envelope
- More detailed models, as needed
  - 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 convection heat transfer coefficient in coolant tubes dependent on internal diameter and coolant flow rate
  - Include pressure vessel mass
    - Important for hydride (high pressure) storage
  - Incorporate limits based on manufacturability constraints
- Model additional metal hydrides suggested by System Architect and Acceptability Envelope calculations
- Evaluate novel concepts and other unique configurations
  - Longitudinal fins
  - Metal honeycomb structures (UQTR)
    - Cell size
    - Addition of cooling channels
  - Hybrid systems – Combination of high pressure tanks and metal hydrides
- For likely viable systems, convert models to form suitable for Simulink system models

Proposed future work for adsorbents:

- 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 two and three 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 (Simulink®)
- Apply models to prototype design

Proposed future work for the acceptability envelope:

- Include balance of plant contributions
  - Mass and volume of storage vessels, fins, tubes, and other structures and fittings
- Complete the application to metal hydrides
  - Include coupled parameter ranges
  - Evaluate candidate metal hydrides (2:1 and 1:1 $LiNH_2$-MgH_2)
- Develop and apply model for adsorbents

Proposed future work material operating requirements:

- Complete databases for 1:1 $LiNH_2$:MgH_2 material with and without catalysts
- Determine needed engineering properties for all up selected materials

Proposed future work metal hydride system architect analysis:

- 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

FY 2010 Publications/Presentations

1. Quarterly Progress Report, "SRNL HSECoE Technical Work Scope," October 31, 2009, January 31, 2010, April 30, 2010.

2. HSECoE Face-to Face Meeting Presentations: October 2009, March 2010, June 2010.

3. S.L. Garrison, D.A. Tamburello, B.J. Hardy, C. Corgnale, "Optimization of internal heat exchangers for hydrogen storage tanks utilizing metal hydrides," SRNL-TR-2010-00214, In Review.