IV.D.8 Optimization of Heat Exchangers and System Simulation of On-Board Hydrogen Storage System Designs

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Contract Number: DE-FC36-09GO19003

Project Start Date: March 1, 2009
Project End Date: January 31, 2014

Fiscal Year (FY) 2011 Objectives

Main objectives of this project are:

- To develop system simulation models and detailed transport models for on-board hydrogen storage systems using metal hydride and adsorbent materials, and to determine system compliance with the DOE technical targets.
- To develop storage media structures with optimized engineering properties for use in storage systems.
- To design and build an experimental vessel for validation of cryoadsorption models.

Technical Barriers

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

- (A) System weight and volume
- (C) Efficiency
- (E) Charging/Discharging Rates
- (J) Thermal Management

Approach

As part of the Hydrogen Storage Engineering Center of Excellence (HSECoE) team, the GM team is building system models and detailed transport models for on-board hydrogen storage systems using metal hydrides and adsorbent materials. Detailed transport models have been developed for the metal hydride and adsorbent systems with a focus on optimization of heat exchanger design with the objective of minimizing the heat exchanger mass. We are also working on storage media structuring and enhancement studies for the metal hydride and adsorbent materials. Since the hydrogen storage materials are generally characterized by low density and low thermal conductivity, we are conducting experiments to form pellets and add thermal conductivity enhancers to the storage material, and to improve cycling stability and durability of the metal hydride and adsorbent materials. An additional area of focus has been on designing and building a cryoadsorption vessel for validation of cryoadsorption models.

FY 2011 Accomplishments

- Developed two system simulation models for sodium alanate employing different heat exchanger designs and integrated in the framework model.
- Developed and integrated a system simulation model for high-pressure metal hydrides ($Ti_{1.1}CrMn$).
- Optimized three different heat exchanger designs for the metal hydride systems, and identified the design for minimum heat exchanger weight.
- For adsorbent materials, determined optimum pellet size for fast refueling.
- Pelletization and thermal conductivity enhancement of metal hydride and adsorbent materials.

✧   ✧   ✧   ✧   ✧

Results

System Models for Metal Hydride Systems: Three system simulation models have been integrated into a modeling framework developed by the Center for evaluation and comparison on a common basis. For sodium alanate, two system models were developed and integrated – one with a shell and tube heat exchanger with cooling tubes and fins, and second with a helical coil heat exchanger. The third system model is for a high-pressure metal hydride system that contains $Ti_{1.1}CrMn$ and is based on a shell and tube heat exchanger with cooling tubes and fins. The helical coil heat exchanger system for sodium alanate contains multiple beds that were sized to optimize heat

transfer between the alanate bed and the fluid flowing through the helical coil tube. Both systems were run within the framework to determine the sizing adjustments needed to deliver 5.6 kg of useable hydrogen to the fuel cell. Simulations were then run to test the performance of the storage systems for four drive cycles that feature various driving patterns and operating conditions: standard driving, aggressive driving, cold start, and hot start.

A hydrogen mass balance for a simulation of the standard driving cycle with the sodium alanate/helical coil system is presented in Table 1. For comparison, a mass balance for a dual bed sodium alanate system with parallel cooling tubes and fins for heat transfer is also included. Table 2 contains the mass balance for the aggressive driving cycle simulation. These results show that the helical coil heat exchanger design is a better design and is able

TABLE 1. Hydrogen Mass Balance for the Standard Driving Cycle

	H$_2$ Delivered to the Fuel Cell	H$_2$ to Heater	H$_2$ in Bed
Helical Coil	78.4%	20.5%	1.1%
Dual Bed	73.2%	20.8%	6.0%

TABLE 2. Hydrogen Mass Balance for the Aggressive Driving Cycle

|	H$_2$ Delivered to the Fuel Cell	H$_2$ to Heater	H$_2$ in Bed
Helical Coil	75.4%	19.0%	5.6%
Dual Bed	58.2%	15.2%	26.0%

to use most of the hydrogen in the bed for both the normal and the aggressive driving cycles. In the Optimization Study detailed in the following, we present results showing that the helical coil design has much lower mass than the base design. For the Ti$_{1.1}$CrMn storage system, nearly all of the stored hydrogen is delivered to the fuel cell since it does not require a catalytic heater for desorption. While the Ti$_{1.1}$CrMn system has good cold start capability, it has the disadvantage of having a low H$_2$ absorption capacity of approximately 2%. Detailed results are presented in references [1,2].

Optimization of Heat Exchanger Designs: Refueling of metal hydride based hydrogen storage systems is a highly exothermic process. Because of the need for fast refueling rates, thermal management of the storage system is very important. Good heat exchanger design is crucial for a metal hydride-based hydrogen storage system in order to maximize gravimetric and volumetric storage densities of the bed and meet system performance requirements. We have analyzed various heat exchanger designs for sodium alanate-based hydrogen storage systems and systematically optimized the design configurations of these heat exchangers. Optimization is performed by employing an automated COMSOL-MATLAB interface tool to conduct

parametric sweeps of the geometry to optimize the heat exchanger design.

Three different heat exchanger designs are analyzed for sodium alanate-based hydrogen storage systems. The three designs are shown in Figure 1. COMSOL modeling is employed to optimize each design to yield maximum gravimetric capacity with the constraint that the local temperature of the bed should not rise above a pre-specified temperature. Optimized designs for each heat exchanger type have been compared. The helical coil heat exchanger is found to be the most compact and efficient heat exchanger design. The detailed results are presented in references [3,4].

Two-Dimensional (2-D) Analysis of Non-isothermal Adsorption in Cylindrical Pellets: For ease of handling and enhanced volumetric capacity, adsorbent powders are often
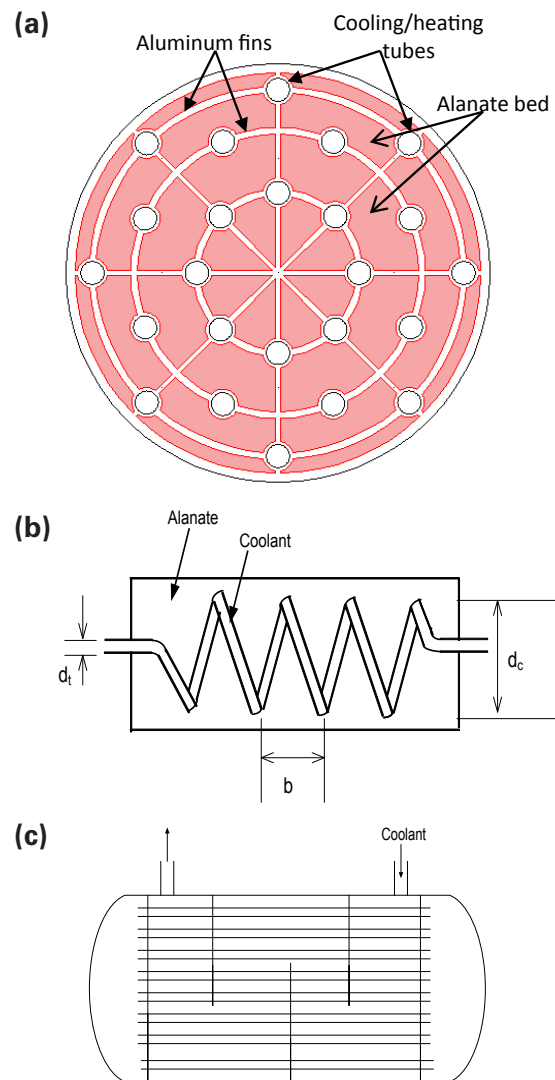
FIGURE 1. (a) Shell and Tube Heat Exchanger with Alanate in Shell; (b) Helical Coil Heat Exchanger; (c) Shell and Tube Heat Exchanger with Alanate in Tubes

compacted into pellets which can be packed in a random or structured fashion in a bed. In either case, one needs to study the intra pellet transport phenomena to arrive at a desired pellet size and aspect ratio. For a random packed bed, often short cylindrical pellets with height identical to diameter are used, since they pack uniformly like spheres.

In the first phase of this study we have analyzed the intra-pellet transport phenomena for short cylindrical pellets at three different sizes, 3 mm, 12 mm and 48 mm. Larger pellets have higher diffusional and thermal resistances, leading to slower adsorption of hydrogen. The aim of this part of the study is to ascertain a typical range of short cylindrical pellet diameters which could be considered for a random packed bed, wherein the intra-pellet transport gradients do not impede achieving short refueling times. A synopsis of these results is discussed below. We are continuing work on the analysis of hockey-puck shaped large pellets which have short heights but large diameters. Such pellets are used in structured packed beds for achieving higher volumetric capacities than a random packed bed.

Model equations were solved to determine the temperature, pressure, and adsorbate concentration fields in short cylindrical pellets. The pressure equilibration occurs quite rapidly, while temperature equilibration is relatively slower. Our analysis shows that simultaneous cooling and adsorption is the rate limiting process. By performing a volume integration of the 2-D total hydrogen content field within the pellet we computed the transient volumetric capacity of the pellet at three different pellet sizes: 3 mm, 12 mm and 48 mm. These results are shown in Figures 2 and 3. The 3 mm pellet reaches its saturation capacity by about 4 seconds, while the 12 mm and 48 mm pellets saturate by about 60 and 600 seconds, respectively. As pellet size increases, a pellet takes longer time to equilibrate with the bulk gas, due to higher diffusional and thermal resistances resulting in a reduced transient volumetric capacity of the pellet. Using very small size pellets increases the bed pressure drop while very large size pellets have poor transient utilization, leading to longer refueling times. This work on single pellet modeling and analysis will help us
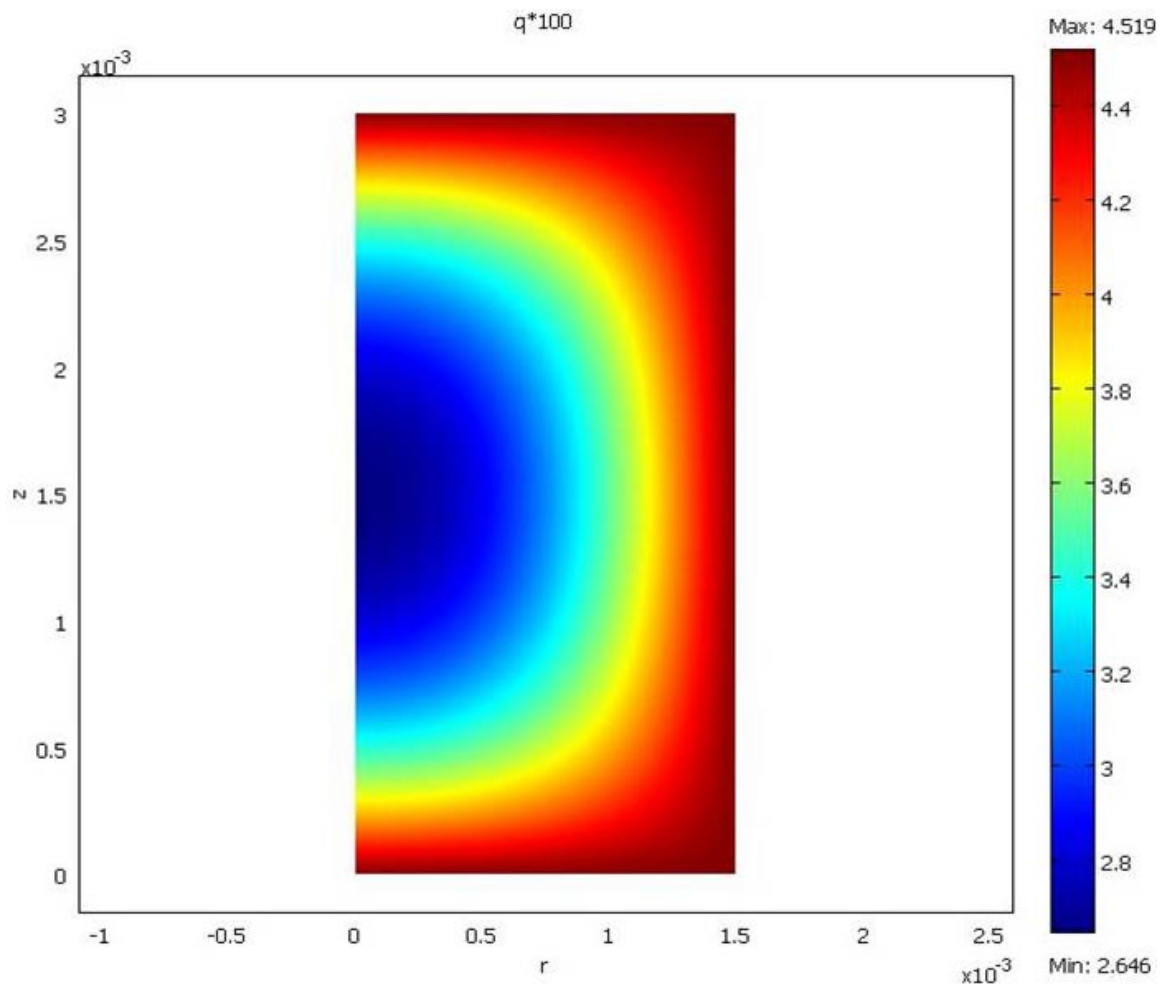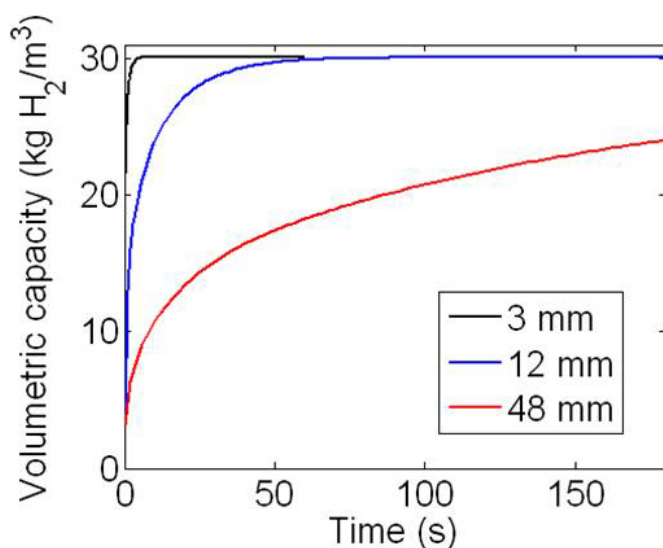

FIGURE 2. Adsorbate Concentration Field in a 3 mm Short Cylindrical Pellet at t = 1 s

FIGURE 3. Transient Volumetric Capacity for Three Different Pellet Sizes

identify an appropriate range of pellet sizes for conventional packed bed design.

Pelletization of Sodium Alanate and AX-21 Powder: Both the metal hydrides and adsorbent materials for hydrogen storage have low densities and low thermal conductivities. Therefore, it is necessary to find ways to pelletize these materials to increase both the density and thermal conductivity without adversely affecting the hydrogen uptake capacity and kinetics. Experiments conducted in our laboratory show that the high thermal conductivity of pelletized titanium doped sodium alanate ($NaH + Al + TiCl_3$) dramatically degrades (up to 80%) within the first 10 cycles due to extensive pellet expansion. Upon further hydrogen cycling, pellets continue to expand leading to complete failure of structural integrity. To counter thermal conductivity degradation two approaches were explored; incorporation of high thermal conductivity additives (expanded natural graphite and graphite flakes) into the alanate before pelletization and mechanical confinement of pellets during cycling. Both forms of graphite additive exhibited similar loss in thermal conductivity over the first 10 cycles. While pellets with graphite additives have a slightly higher thermal conductivity at each cycle compared to pellets without additives, the overall degradation effect of cycling is similar and not favorable.

While the addition of graphite to sodium alanate pellets lessens the decrease in thermal conductivity over 10 cycles compared to pellets without graphite, pellet expansion (previously reported) is not mitigated and has an overwhelming adverse effect on thermal conductivity. Confinement of sodium alanate pellets by mechanical means showed slowed degradation of thermal conductivity over first 10 cycles, compared to unconfined pellets run in parallel, confined pellets had twice the thermal conductivity after 10 cycles (2.57 and 4.80 W/mK, respectively). After

50 cycles, confined pellets had a thermal conductivity of 3.72 W/mK. Unconfined pellets could not be measured after 10 cycles due to expansion. Various methods of confinement have been explored, all showing similar degradation control. Sodium alanate pellets were also observed to fuse to one another during cycling. Fusion of a pellet stack can minimize surface area contact resistance and allow for improved heat transfer between neighboring pellet bodies. The confined fused pellets show a degradation of thermal conductivity.

The increased volumetric capacity of activated carbon through pelletization requires the addition of a binder. Current procedures employ extensive elevated temperature work-up resulting in lengthy processing time per pellet. To expedite pelletization, we are focusing on room temperature binders. The binder is combined with AX-21 resulting in a fibrous network which holds the activated carbon together. The fiber network cold flows under high pressures allowing the AX-21 mixture to be pelletized rapidly under room temperature conditions. The pellet density is improved by a factor of 1.5-1.8 (0.45-0.55 g/cm^3, powder = 0.3 g/cm^3) but the surface area decreases by 20% compared to the powder alone (2,400 and 3,000 m^2/g, respectively). These pellets show gravimetric capacity similar to that of the powder at 77 K but the volumetric capacity is substantially improved through pelletization compared to the powder. Work on identifying the best room temperature binder and pellet properties is continuing.

Future Direction

- Extend the modeling work to short cylindrical pellets that can be used for structured packing of the bed for high volumetric capacity to determine optimum pellet size.

- Optimize binders for pelletizing activated carbon with respect to engineering properties of interest for hydrogen storage.

- Design and build a cryoadsorption vessel for validating the flow-through cooling concept for recharging.

- Conduct experiments to validate the cryoadsorption models for charging and discharging of adsorption based storage beds.

- With the HSECoE team, determine the material properties for metal hydrides that are necessary to meet DOE 2015 hydrogen storage system goals.

FY 2011 Publications/Presentations

1. S. Kumar et al. (2011) Optimization of heat exchangers and system simulation of on-board storage system designs, presented at the 2011 DOE Hydrogen Program Annual Merit Review Meeting, Washington, D.C.

2. M. Raju, J.P. Ortmann, and S. Kumar (2010) System simulation model for high-pressure metal hydride hydrogen storage systems, Int. J. Hydrogen Energy, <u>35</u>, 8742-8754.

3. M. Raju M. and S. Kumar S. (2011) System Simulation Modeling and Heat Transfer in Sodium Alanate based Hydrogen Storage Systems. Int J Hydrogen Energy,36; 1578-1591.

4. M. Sulic, M. Cai, and S. Kumar (2010): Sodium alanate as a practical automotive on-board solid-state hydrogen storage medium, presented at the Int. Symp. on Metal-Hydride systems, Moscow, July 2010.

5. M. Raju and S. Kumar (2010a) Modeling of a Helical Coil Heat Exchanger for Sodium Alanate based On-board Hydrogen Storage System, presented at the *COMSOL 2010 Conference, Boston, MA*.

6. M. Raju and S. Kumar (2010b) Optimization of Metal Hydride based Hydrogen Storage Bed Designs, presented at the *2010 AIChE Annual Meeting, Salt Lake City, UT*.

7. S. Kumar S., M. Raju and V. Senthil Kumar (2010) System Simulation Models for On-Board Hydrogen Storage Systems, presented at the *2010 AIChE Annual Meeting, Salt Lake City, UT*.

References

1. M. Raju, J.P. Ortmann, and S. Kumar (2010) System simulation model for high-pressure metal hydride hydrogen storage systems, Int. J. Hydrogen Energy, 35, 8742-8754.

2. S. Kumar et al. (2011) Optimization of heat exchangers and system simulation of on-board storage system designs, presented at the 2011 DOE Hydrogen Program Annual Merit Review Meeting, Washington, D.C.

3. M. Raju and S. Kumar (2010a) Modeling of a Helical Coil Heat Exchanger for Sodium Alanate based On-board Hydrogen Storage System, presented at the COMSOL 2010 Conference, Boston, MA.

4. M. Raju and S. Kumar (2010b) Optimization of Metal Hydride based Hydrogen Storage Bed Designs, presented at the 2010 AIChE Annual Meeting, Salt Lake City, UT.