IV.B.5 Systems Engineering of Chemical Hydrogen Storage and Cryo-Sorbent Storage, Pressure Vessel, and Balance of Plant for Onboard Hydrogen Storage

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Overall Objectives

- Develop hydrogen storage systems that meet DOE 2020 targets for light duty vehicles based on adsorbents and chemical hydrogen storage (CHS) materials
- Identify, develop, and validate critical components of the chemical hydrogen and cryo-sorbent-based hydrogen storage systems
  - Address system performance, mass, volume, and cost
- Develop and validate models for a CHS system to further the understanding of onboard storage energy management requirements
  - Work with partners to integrate validated models into system framework that will lend insight into overall fuel cycle efficiency
- Mitigate materials incompatibility issues associated with hydrogen embrittlement, corrosion, and permeability through suitable materials selection for balance of plant (BOP) components

Fiscal Year (FY) 2015 Objectives

- Cryo-Adsorbent Hydrogen Storage Design
  - Develop and test prototype of the liquid nitrogen (LN_2) cooled-wall tank concept to increase refueling rate
  - Perform compressive tests of candidate polymer valve and seal materials under cryogenic temperatures with and without saturating the material with high-pressure hydrogen to evaluate each polymer's compatibility in cryo-adsorbent applications
  - Compare cost models for the two cryo-adsorption systems (hexagonal aluminum honeycomb [Hexcell] and modular adsorption tank insert [MATI]) to the Strategic Analysis' independent estimate and update costs to include BOP system upgrades
- Chemical Hydrogen Storage Design
  - Integrate storage system models for exothermic and endothermic systems into the vehicle framework and post the updated model on the Hydrogen Storage Engineering Center of Excellence (HSECoE) website to allow evaluation of other hydrogen storage materials

Technical Barriers

This project addressed the following technical barriers this last year for Hydrogen Storage from the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(B) System Cost

(C) Efficiency

(E) Charging/Discharging Rates

(H) Balance of Plant (BOP) Components

(J) Thermal Management

Technical Targets

The current status of the cryo-sorption material systems versus the DOE Onboard Hydrogen Storage System Technical Targets addressed this fiscal year by PNNL is given in Table 1.

Fiscal Year (FY) 2015 Accomplishments

- Designed, fabricated, and tested LN_2 cooled-wall tank prototype. Compared the results of these prototype tests to the full-scale system and determined (1) that wall cooling to 90 K could be achieved in <3 minutes using 17.9 kg LN_2 and (2) the full scale system design was structurally and thermally sound.

TABLE 1. Cryo-Adsorbent Storage System Progress towards Meeting DOE Technical Targets

Target	Units	2020 DOE Goal	HSECoE Value
System Cost	\$/kWh net	10	35 (Hexcell) 37 (MATI)
	\$/kg H_2 stored	333	486 (Hexcell) 517 (MATI)
System Fill Time (5 kg)	min	3.3	2.7 (tank wall cooling only)
Operational Cycle Life	cycles	1,500	>1,000,000 (tank wall only)

- Updated cost models for the two cryo-adsorbent systems. This update included costs of the “consolidated valve block,” a component of both systems in which multiple valves and instruments were incorporated into a single body. A cross comparison was made between the cost estimates made by PNNL and those produced by Strategic Analysis.
- Developed an approach to evaluating the hydrogen compatibility of polymers for cryo-adsorbent systems by analyzing the combined effects of high pressure H_2 (345 bar) and cryogenic temperatures (77 K).
- Updated the CHS system model, integrated into the framework and documented and released these models to the public on the HSECoE website (hsecoe.org).

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INTRODUCTION

Prior to HSECoE, multiple onboard vehicle-scale hydrogen storage demonstrations were performed. However, none of these demonstrations have simultaneously met all of the DOE hydrogen storage sub-program goals. Additionally, engineering of new cryo-adsorbent and CHS approaches is in its infancy, with ample opportunity to develop novel systems capable of reaching the DOE 2020 targets for light-duty vehicles. The goal of HSECoE, led by Savannah River National Laboratory (SRNL), is to develop and demonstrate low cost, high performing, onboard hydrogen storage through a fully integrated systems design and engineering approach. Toward this end, PNNL is working with HSECoE partners to design and evaluate systems based on slurry chemical and cryo-adsorbent hydrogen storage media.

APPROACH

As part of HSECoE, PNNL has actively contributed to the design and testing of hydrogen storage systems. As these designs are developed, efforts are made to address obstacles to meeting the DOE technical targets. For FY 2015, PNNL’s primary responsibility was to address four issues for the cryo-adsorbent system: (1) rapid refueling, (2) system cost, (3) BOP mass and volume, and (4) hydrogen compatibility. The DOE technical targets require a cool down time of less than 3.3 minutes. One of the major needs is to cool the tank walls themselves. An approach to address this need was developed and a prototype system tested to validate the concept. This year’s work also continued to refine the cost of the two cryo-adsorbent systems. Finally, the compatibility of the polymer materials that may be used within the BOP at low temperatures and high H_2 pressures was investigated.

As the systems are designed, HSECoE has developed models to describe the performance of these systems under a variety of drive cycle scenarios. In past years, PNNL work has focused on the development of the CHS models. The models that have been developed can be used to not only to predict the performance of current CHS materials such as ammonia borane (AB) and alane, but they can also help researchers predict the performance of yet-to-be-developed materials relative to DOE’s technical targets for light-duty vehicles. This fiscal year, these models have been placed on the HSECoE website to allow their use by other researchers.

RESULTS

Liquid Nitrogen Cooled-Wall Tank Testing and Evaluation

During each refueling of cryo-adsorbent systems, the tank and its contents must be re-cooled from approximately 160 K to 80 K. This can be done by flowing cold hydrogen though the adsorbent in the tank in the case of the Hexcell system design, or LN_2 through the microchannels in the case of the MATI system design. Modeling of this process during refueling has demonstrated that while the adsorbent material can be cooled relatively easily using these approaches, the tank wall remains warm. To address this shortcoming, PNNL and Hexagon Lincoln have developed an LN_2 cooled-wall tank approach that utilizes the flow of LN_2 in an annulus between the tank and its insulation to cool the tank wall during refueling. This approach reduces the amount of excess hydrogen fuel required for the Hexcell design and the amount of LN_2 for the MATI design, saving on refueling time and cost.

To evaluate this concept, a 2-liter aluminum Type I tank was instrumented with thermocouples along its interior both axially and radially. This Type I tank was then installed inside of a dewar with a framework that centers it within the dewar cavity (see Figure 1). Insulation is inserted into the exit end of the dewar to allow ports for the flow of LN_2 and to minimize heat loss out of the dewar. Many access ports were designed into the test system and holes were bored through the insulation to provide flow paths for LN_2 and nitrogen steam.

Several different configurations were evaluated to speed the cooling process, including filling from the top, filling

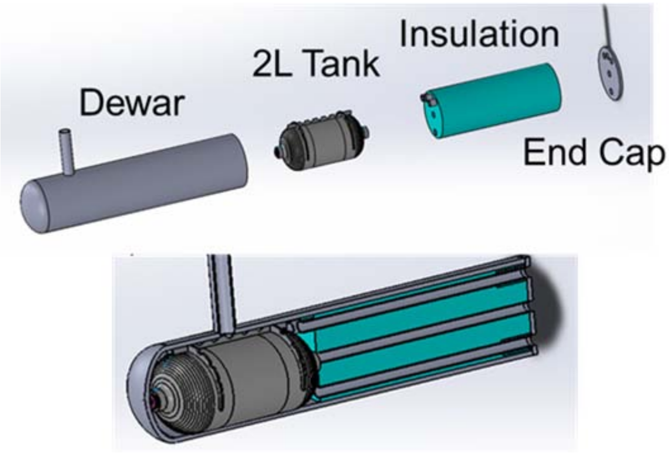

FIGURE 1. Design of the LN_2 cooled-wall tank 2-liter prototype system

from the side, and using a set of spray nozzles in an attempt to quickly cool the tank to the required temperature of 80 K. The best results were achieved with the highest flow rate of LN_2 and by filling the annulus from the rear of the dewar and exhausting the nitrogen gas product from the mouth of the dewar. Although the spray nozzles provided good coverage of the entire surface of the tank, due to its high pressure drop and the limited mass flow rate capacity of the LN_2 supply used in testing, the flow rate attainable was much less than other approaches. As a result, the cooling rate was not improved under test conditions.

The fastest cooling results were compared to modeling an ideal system assuming the tank was totally immersed in LN_2 and cooling is limited by the heat transfer between the LN_2 to the tank as shown in Figure 2. The plot shows that the minimum recorded temperatures match the full immersion cooling rates during the initial stages of cooling. It should be noted that the locations of minimum temperature change throughout the cool down process, which indicates a complex flow pattern of LN_2 within the dewar. Because of the complicated physical phenomenon within the dewar, this analysis is only concerned with the net cooling effect and the ability to recreate that effect in a full scale system.

Using the results of the prototype tests, predictions can be made for the cooling rate of the full-scale system with the same heat flux profiles witnessed in testing. A full scale system as defined by SRNL is an aluminum pressure vessel having a mass of 59.6 kg and having a surface area exposed to the LN_2 cavity of 26,500 cm^2. The results of this analysis are shown in Figure 3. The back fill curve cools the tank from 160 K to 90 K in about 130 seconds, which is well within the DOE target goal of a 3.3 minute refuel rate. However, the desired fully cold temperature is 80 K, which was not demonstrated to be achievable in testing. The 10 K difference in temperature is expected to be addressed via flow-through cooling on the adsorbent material inside the pressure vessel.

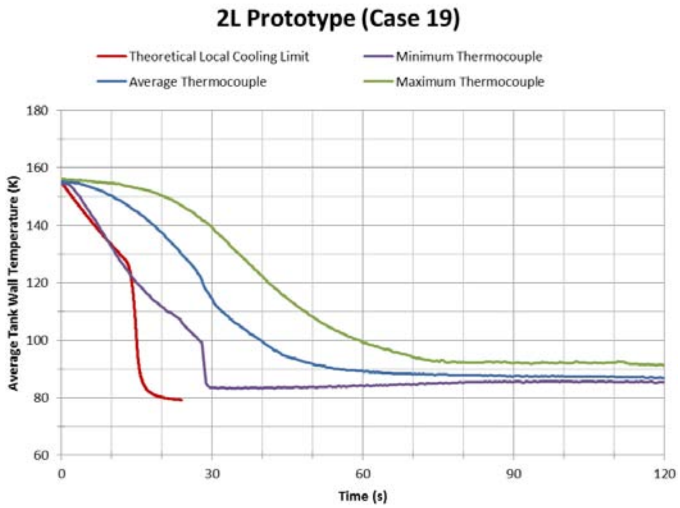

FIGURE 2. The fastest cooling results for the 2-liter prototype system compared to an ideal system

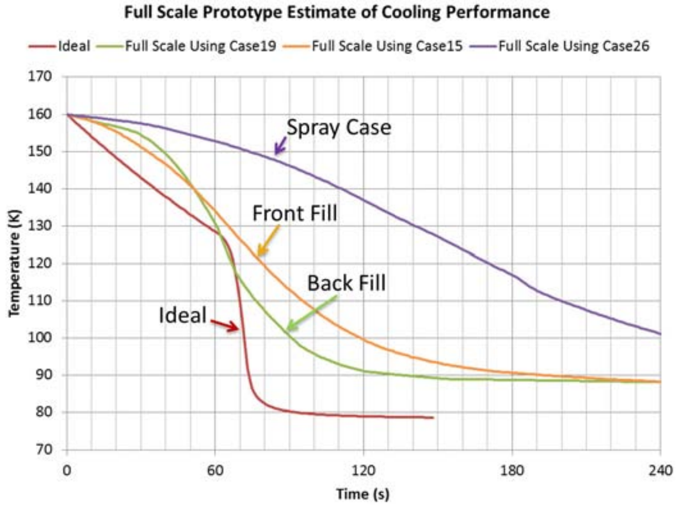

FIGURE 3. Estimated cool down times for a full scale LN_2 cooled-wall system using heat transfer values from the 2-liter prototype

When determining the time required to cool the tank, the flow rate of LN_2 and the resulting amount of LN_2 loss must be considered. Higher flow rates will cool the tank more quickly but excess LN_2 will remain in the annulus after the tank has reached its setpoint temperature. Alternatively, the tank cooling can be slower but designed to reach its setpoint just as the ideal amount of LN_2 evaporates from the annulus. A balance between LN_2 flow rate and usage must be achieved. Table 2 makes performance projections for the full system based on these variables.

In addition to providing information necessary to project full scale system cooling performance, the 2-liter test data demonstrates that the cooling of the aluminum pressure vessel can be significantly non-uniform through time.

TABLE 2. Full System Performance Projections

LN_2 Mass Flow Rate (g/s)	LN_2 Mass Flow Duration (s)	Total LN_2 Delivered During Fill (kg)	Time to 90 K (s)	Temperature at 198 s (K)	LN_2 remaining at 198 s (kg)
188	102	19.2	132	81	1.56
188	93	17.5	144	84	0.52
188	88	16.5	161	89	0.19
150	117	17.5	157	85	0.64
125	140	17.5	172	86	0.74

While the aluminum wall eventually stabilizes to a uniform temperature, rapid localized cooling is apparent, which suggests that thermal stresses are present due to non-uniform thermal expansion of the structure. The thermal stresses were evaluated using a finite element model to determine if thermal fatigue was a problem for this design concept. The results of this modeling study found that localized cooling due to LN_2 boiling on the pressure vessel surface did not cause significant thermal stresses because the surface heat flux is naturally limited (by the Leidenfrost effect) and the thermal conductance of aluminum is so high that the temperature gradients that do occur are relatively gentle. As a result, the finite element study estimated a fatigue life of over 1,000,000 cycles for the full scale system.

Balance of Plant Polymer Compatibility for Cryo-Adsorbent System

The use of polymers is essential to providing adequate seals, pistons, and seats for the components used in the BOP. The compatibility of these polymers in the presence of low temperatures and high H_2 pressures was evaluated. Because PNNL does not currently have the ability to run in situ compression tests in the presence of hydrogen at cryogenic temperatures, an ex situ test was performed as follows. HDPE, PTFE, ECTFE, PCTFE, and PEEK polymer samples were exposed to 345 bar hydrogen for over 72 hours to allow adequate time for H_2 diffusion into the polymer. The H_2 pressure was quickly relieved and the samples were soaked in LN_2 until their temperature was equilibrated. A low temperature compression test was then run following ASTM D695 for rigid plastics.

Stress-strain and modulus curves of the different plastics under compression are shown in Figure 4. Both the hydrogen saturated and baseline tests showed the same qualitative behavior in the stress-strain curves and the failure mechanisms. An increase in the elastic modulus is observed for the hydrogen loaded samples for all materials by a statistically meaningful amount. Conversely, HDPE, PTFE, and ECTFE show a decrease in the yield stress with hydrogen compared to the baseline while there is no statistically significant change for PCTFE and PEEK. Based on these results, it appears that these materials are relatively compatible with a high pressure, low temperature H_2 environment.

Cost Analysis Update for Hexcell and MATI Systems

The cost analysis performed in previous years was updated for the Hexcell and MATI cryo-adsorbent systems. PNNL purchased a design for manufacturing code, Costimator®, that assisted in estimating the cost of those components that are not off the shelf but must be fabricated. The results of the cost analysis were compared to an independent cost study performed by Strategic Analysis. This comparison allowed differences to be addressed and result in improved estimates for both organizations. The results

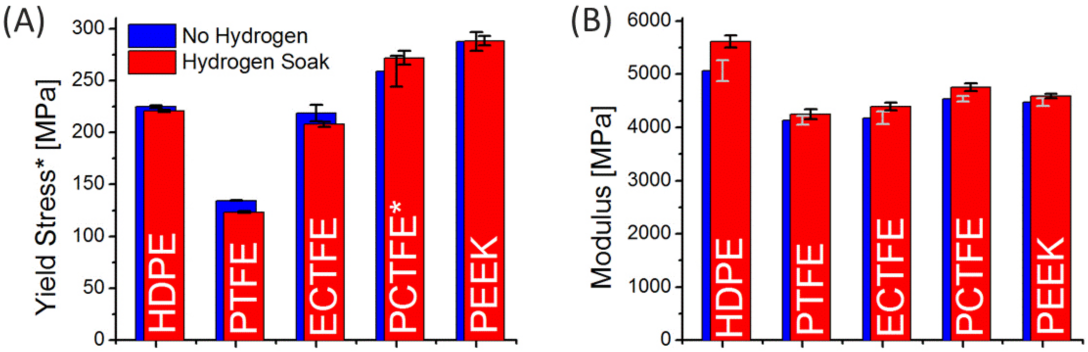

FIGURE 4. (a) Stress-strain and (b) modulus curves for various plastics under compression under LN_2 both with and without a hydrogen soak

of these studies are shown in Table 3. Although individual component costs varied, the overall system cost was consistent between the two organizations.

TABLE 3. Cost Comparison between Strategic Analysis and the HSECoE for Cryo-Adsorbent Systems Hexcell and MATI

Organization	Hexcell System	MATI System
HSECoE	$2,720	$2,897
Strategic Analysis	$2,580	$2,830

Chemical Hydrogen Storage Material Model Development

The CHS models were finalized and incorporated into the vehicle level model (i.e., framework). The graphical user interface allows users to select a representative exothermic CHS material (AB) or an endothermic CHS material (alane). Selected system sizing parameters can be adjusted and the model run to determine if the storage system can meet the four drive cycles available in the model. This newly updated framework with the CHS models and user's manual was uploaded onto HSECoE.org to make it available to the public. Material developers can now modify the thermodynamic and kinetic parameters of the current CHS material to evaluate their newly developed materials relative to the drive cycles with a simulated light-duty fuel cell vehicle.

CONCLUSIONS AND FUTURE DIRECTIONS

The conclusions of the FY 2015 work are as follows:

- Fabricated a 2-liter LN_2 cooled-wall tank prototype and tested it under a variety of conditions. Using the experimental data, the wall cool down time was estimated to be less than the 3.3 minutes required for the full-scale system by the DOE technical targets.
- The thermal mechanical fatigue analysis of the full-scale tank determined that the tank can be subject to over 1,000,000 fully reversing stress cycles to initiate a fatigue crack. This value is much greater than the 1,500 cycles required by the DOE technical targets.
- Polymer materials exposed to high pressure hydrogen followed by cryogenic compressive strength testing showed similar yield and modulus results to those not exposed to hydrogen, suggesting that they are hydrogen compatible under these conditions.
- Cost models developed by Strategic Analysis and HSECoE were compared and their differences reconciled, resulting in an improved cost analysis. The resulting system costs ($/kg H_2) are within 64–68% of the DOE technical targets.

The future direction of this work during FY 2016 is as follows:

- The cryo-adsorbent and CHS reports for HSECoE will be finalized and submitted to DOE.
- Support will continue for users of the vehicle level framework on the HSECoE website. PNNL will address questions and issues for the CHS models as well as develop a pre-processor that provides an estimate of the system sizing based on the material thermodynamic and kinetic parameters.

PATENTS

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FY 2015 PUBLICATIONS/PRESENTATIONS

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Presentations

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