IV.B.2 Systems Engineering of Chemical Hydrogen Storage, Pressure Vessel, and Balance of Plant for Onboard Hydrogen Storage

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Project End Date: June 30, 2015

Overall Objectives

- Develop hydrogen storage systems that meet DOE 2017 targets for light-duty vehicles based on cryo-adsorbent and chemical hydrogen storage materials.
- Identify, develop and validate critical components of the chemical hydrogen and cryo-adsorbent-based materials for performance, mass, volume, and cost.
- Develop and validate models for a chemical hydrogen storage system to further the understanding of onboard storage energy management requirements.
- Work with our partners to integrate our validated models into system framework that will lend insight into overall fuel cycle efficiency.
- Reduce system volume and mass while optimizing system storage capability and performance through value engineering of heat exchangers and balance-of-plant (BOP) components.
- Mitigate materials incompatibility issues associated with hydrogen embrittlement, corrosion, and permeability through suitable materials selection for vessel materials, heat exchangers, plumbing and BOP components.

Fiscal Year (FY) 2014 Objectives

- Chemical Hydrogen Storage Design
  - Develop system models for exothermic and endothermic systems to predict mass, volume, performance
  - Validate models via experimentation
  - Perform cost modeling and manufacturing analysis for the endothermic system design
- Cryo-Adsorbent Hydrogen Storage Design
  - Develop and validate the LN_2-cooled wall approach to refueling and dormancy
  - Perform value engineering of BOP to minimize cost, volume and mass
  - Guide design and technology down selection via cost modeling and manufacturing analysis

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:

(A) System Weight and Volume
(B System Cost
(C) Efficiency
(D) Durability
(E) Charging/Discharging Rates
(G) Materials of Construction
(H) Balance of Plant (BOP) Components
(J) Thermal Management
(O) Hydrogen Boil-Off

Technical Targets

The current status of the chemical hydride and cryo-sorption material systems versus the DOE Onboard Hydrogen Storage System Technical Targets as of the end of Phase 2 is given in Table 1.

FY 2014 Accomplishments

- Developed a cost analysis for the endothermic chemical hydrogen storage materials using alane as a surrogate. Projected system costs of $4,127 or $22/kWh at 500,000 units were calculated.
- Developed a chemical hydrogen storage system model that combines exothermic and endothermic models into a single system and validated it using experimental data from reactor studies performed with ammonia borane (AB) and alane at Los Alamos National Laboratory (LANL).

TABLE 1. Progress towards Meeting DOE Technical Targets for Hydrogen Storage

			Adsorbent System			**Chemical Systyem**		
			Phase 2 ***Actual*** ***(automotive scale)***			**Projected System HSECoE Go/No-Go*What could be built in the future (full scale)***		
Target	Units	2017 DOE Goal (System)	Phase 2 HSECoE Targets (Material)	Phase 2 HSECoE Targets (BOP only)	Phase 2 HSECoE Targets (System)	Phase 2 HSECoE Targets (Material)	Phase 2 HSECoE Targets (BOP only)	Phase 2 HSECoE Targets (System)
Gravametric Capacity	kg H2/kg system	0.055	0.187	0.10	0.0352	0.0872	0.15	0.055
mass	*kg*	*102*		*16.1*	159			*102*
Volumetric Capacity	kg H2/L system	0.04	0.03	0.053	0.0175	0.078	0.132	0.049
Volumetric	*liters*	*140*		*16.9*	320			*114*
System Cost	$/kWh net	6	3.5	5.62	12.74			
	$	*1,119*		*1048*	2376			
Fuel Cost	$/gge at pump	2-6			4.89			
Min Operating Temp	°C	-40			-40			-20
Max Operating Temp	°C	60			60			60
Min Delivery Temp	°C	-40			-40			-20
Max Delivery Temp	°C	85			85			85
Cycle Life	Cycles	1500			1500			1000
Min Delivery Pressure	bar	5			5			5
Max Delivery Pressure	bar	12			12			12
Onboard Efficiency	%	90			92			95
Well to Power Plant Efficiency	%	60			39.2			37
System Fill Time	min	3.3			3.3			2.9
Min Full Flow Rate	(g/s/kW)	0.02			0.02			0.02
	g/s	*1.6*			*1.6*			*1.6*
Start Time to Full Flow (20°C)	sec	5			5			1
Start Time to Full Flow (-20°C)	sec	15			15			1
Transient Response	sec	0.75			0.75			0.5
Fuel Purity	%H2	99.97			99.99			99.97
Permeation, Toxicity, Safety	Scc/h	Meets or Exceeds Standards			s			s
Loss of Useable Hydrogen	(g/h)/kg H2 stored	0.05			0.44			0.05

- Reduced the BOP part count, mass and volume in the design of a consolidated BOP component that combined eight valves and sensors into a single device. Mass and volume of this device was reduced from 5.7 kg and 4.1 liters to 3.9 kg and 0.6 liters.
- Performed proof-of-concept testing for the LN_2-cooled wall concept and measured the estimated cooling rate. Demonstrated the concept's feasibility experimentally and scaled up the results to the full-scale tank design.

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INTRODUCTION

Multiple onboard vehicle-scale hydrogen storage demonstrations have been done, including several studies to examine characteristics that impact systems engineering. However, none of these demonstrations have simultaneously met all of the DOE hydrogen storage program goals.

Additionally, engineering of new chemical hydrogen storage approaches is in its infancy, with ample opportunity to develop novel systems capable of reaching the DOE targets for storage capacity. The goal of the Hydrogen Storage Engineering Center of Excellence (HSECoE), led by Savannah River National Laboratory, 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 the HSECoE, PNNL as a center partner has actively contributed to the design and testing of hydrogen storage systems. This work involves the development of system designs using both slurry chemical hydrogen and cryo-adsorbent hydrogen storage media. As these designs are developed, efforts are made to minimize mass, volume, and cost, in an effort to achieve the DOE technical targets. PNNL's specific responsibility is to identify BOP components for these systems. This year's work has focused on reducing the mass and volume of these BOP components for the cryo-sorbent hydrogen storage systems. As the BOP is developed, PNNL considers the materials incompatibility issues associated with H_2 embrittlement, corrosion and permeability. The Center also develops engineering solutions to overcome deficiencies identified during system development. This year PNNL developed and tested a concept for cooling the walls of the tank during cryo-adsorbent refueling. By cooling the outer walls of the tank with liquid nitrogen, less cold hydrogen has to recirculate through the bed during the refueling. This engineering solution will reduce the cost of refueling.

Once the systems have been designed, the center has developed models to describe the performance of these systems under a variety of drive cycle scenarios. The PNNL work has focused on the development of the chemical hydrogen storage models. These models as well as the design are validated experimentally by testing the key components of the system and comparing them to expected results in the model. The models that have been developed can be used to not only to predict the performance of AB and alane as they are now, 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. In addition to performance modeling, cost modeling is also performed. This is done with a combination of top-down and bottom-up manufacturing analysis. Production rates between 10,000 and 500,000 have been estimated for each system that is developed.

RESULTS

Cryo-Sorbent Hydrogen Storage

PNNL's cryo-sorbent work in the Center has focused on minimizing mass of the BOP and developing a concept for cooling the outer tank wall for faster refueling. In an effort to minimize the BOP cost, mass, and volume, for the cryo-sorbent hydrogen storage system, 11 of the valves and instrumentation interfacing with the storage tank were combined into a single housing. This consolidated BOP component included ports to attach pressure relief valves, a check valve, pressure and temperature sensors, pressure regulators, and isolations valves. By combining these components together, the system installation time is reduced and the system cost minimized. To reduce the housing mass, unnecessary material was removed from the block. The original design had a mass and volume of 5.7 kg and 4.1 L; this was reduced to 3.9 kg and 0.6 L, respectively. The current design installs this consolidated BOP component directly on the top of the tank and is shown in Figure 1.

A structural analysis was performed on this component to understand the impact of pressure and thermal stresses. Evaluating the smallest bridge sections between ports, the system design appears to be adequate for pressure stresses with a demand to capacity ratio of 0.77. Additionally, the thermal gradients and the resultant thermal stresses are small because the heat transfer rates associated with boiling of the liquid nitrogen in the boundary layer are smaller than the heat transfer associated with heat movement through high thermally conductive aluminum.

One approach to refueling the cryo-adsorbent tank uses cold hydrogen in a flow-through mode to cool the tank from an expected 110 K to the required 80 K. Modeling of this process during refueling has demonstrated that while the adsorbent material can be cooled relatively easily, the tank wall remains warm. As a result, it was estimated that 11.4 kg of hydrogen would be required for cooling the adsorbent and tank wall in addition to the 5.6 kg of required for the fill. To address this shortcoming, PNNL and Hexagon Lincoln have developed the LN_2-cooled wall approach that utilizes the flow of liquid nitrogen in an annulus between the tank and its insulation to cool the tank wall during refueling and reduce the waste of hydrogen fuel. The concept is shown in Figure 2.

Work was performed this year to quantify the performance of this approach using a simple proof-of-concept test. A 2" diameter pipe with the same wall thickness expected in the full-scale tank was fabricated to allow liquid nitrogen flow in an annulus on the outside of the pipe. The starting temperature, mass flow rate of LN_2, and annulus thickness could be varied during the experiment and the temperature axially and radially along the pipe were measured during the cooling process. The results of these experiments were analyzed to determine pipe cooling rate. Cooling rate (kW) was normalized by dividing it by the LN_2 mass flow rate (kg/s), yielding kW-s/kg. The results of the

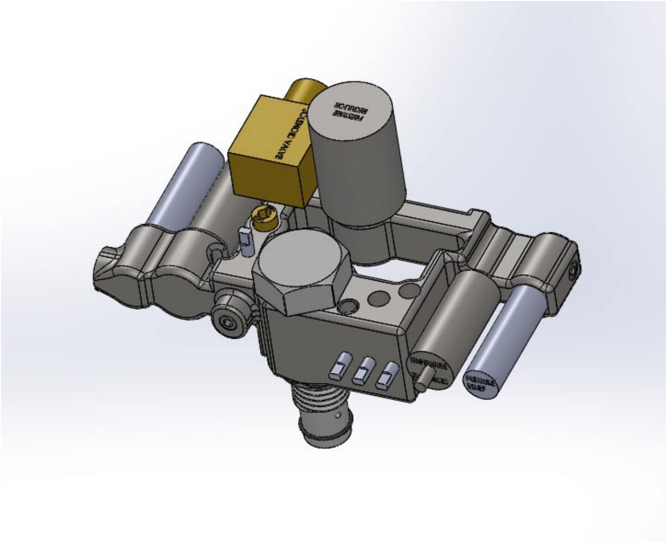

FIGURE 1. Reduced Mass Consolidated BOP Component

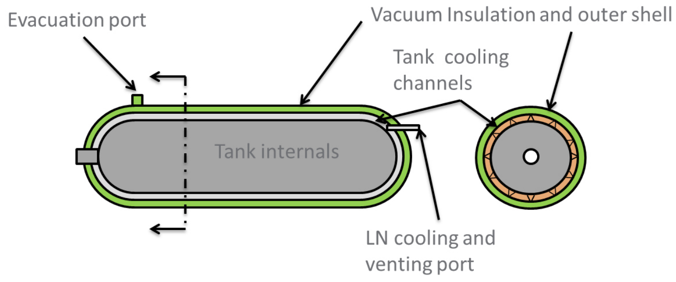

FIGURE 2. LN_2-Cooled Wall Tank Concept for Cooling the Wall of the Cryo-Adsorption Tank

tests indicate two phases of cooling. There is an initial lower cooling rate of ~70 kW-s/kg that is relatively constant as the temperature in the pipe drops until it reaches approximately 130K at which point the cooling rate rises sharply to ~130 kW-s/kg (see Figure 3). This higher cooling rate is associated with nucleate boiling and quickly cools the pipe to its required 77 K. The results of this analysis indicated that higher flows of liquid nitrogen will bring the tank to the higher cooling nucleate boiling regime more quickly and reduce the overall cooling time.

The results of these proof-of-concept tests were extrapolated to estimate the amount of liquid nitrogen to cool a 163 liter full-scale tank from 110 K to 80 K in four minutes. The results of this analysis are shown in Table 2. In addition this analysis demonstrated that combining the initial internal cooling with hydrogen and later cooling with liquid nitrogen will result in an overall reduction in the total gases required.

The use of liquid nitrogen in the tank annulus resulted in concerns relative to the fatigue of the tank wall. As a result, a fatigue stress calculation was performed based on the experimental results. During testing, a maximum of 10°C/inch gradient was observed in the pipe during the cooling process. The stress in the aluminum wall was calculated using finite element analysis and the results indicated a peak thermal stress of 3.2 MPa (von Mises) or 3.4 MPa (stress intensity). The fatigue strength of the aluminum alloy is 100 MPa for 5,000 cycles. These results indicate that significantly higher temperature gradients are needed to challenge the material's fatigue limit.

TABLE 2. Predicted Liquid Nitrogen Usage for 163-L LN_2-Cooled Wall Tank Design

Cooling Rate Assumptions	Cooling Rate (W-s/kg)	Required LN_2 Only (kg)	Required LN_2 + H_2 for 163 L tank (kg)
Average Test	87.1k	66	41 kg N_2 + 5.5 kg H_2
Ideal LN_2 Boiling + Gas Cooling	241k	24	15 kg N_2 + 2 kg H_2

Chemical Hydrogen Storage

With the DOE's decision that chemical hydrogen storage materials would not move into Phase 3, the work in this area was reduced to completion of previous work and final documentation of the center results. In addition the cost modeling done in FY 2013 for the system developed for AB was expanded to provide an estimate for alane. The storage

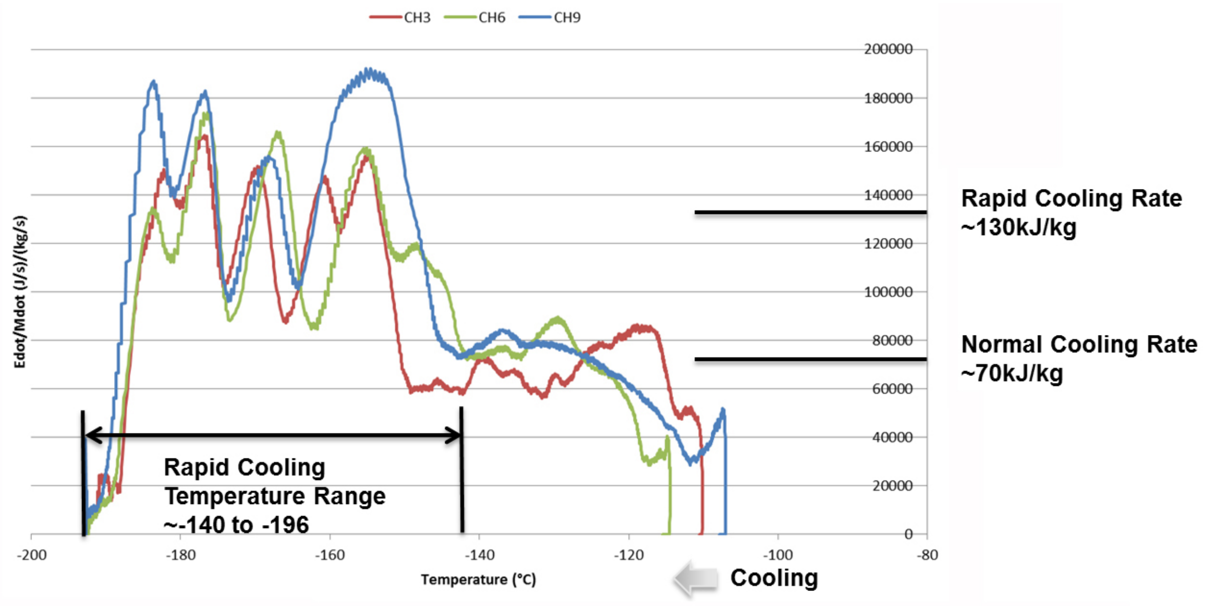

FIGURE 3. Pipe Cooling Rate as a Function of Temperature for the Proof-of-Concept LN_2-Cooled Wall Testing

system models for AB and alane were also completed and incorporated into the vehicle-level model framework.

Using the cost model developed for a slurried AB, only minor changes were required to predict the costs for an alane-based system. Alane does not produce significant impurities during its thermolysis, as a result, borazine and ammonia scrubbers were removed. Furthermore, the alane system uses a recuperator rather than recycle to preheat the feed. The most significant cost increase was the larger amount of alane and slurrying agent required because of its lower hydrogen content. The cost of an alane system for 500,000 units is compared to other automotive systems in Figure 4. The cost of the alane ($26/kg) was significantly higher than the other systems considered. There is, however, considerable uncertainty in its first time production cost.

The chemical hydrogen storage models were finalized and documented. Rather than have separate exothermic and endothermic models using AB and alane as the representative materials, respectively, a single model was developed. Because the systems are very similar, most of the system components are identical. To switch between models, a flag can be set to toggle between the two system configurations and include a recuperator or a recycle stream and to include or not include the impurities clean-up system.

These models were evaluated relative to data sets generated at LANL for a small scale flow-through reactor system. Tests were performed with alane over a range of solids loadings, residence times, auger speeds, and reaction temperatures. The model fit the experimental data reasonably well for alane and AB at low temperatures. The model did not fit the experimental data for AB at high temperatures. As a result, the AB kinetic model was refit to represent the higher temperature experimental data produced at LANL. These models were then documented and incorporated into the vehicle level framework.

CONCLUSIONS AND FUTURE DIRECTIONS

The conclusions of the FY 2014 work are as follows:

- A consolidated BOP component was developed resulting in reduced cost, mass and volume over separate individual components.
- Testing of the LN_2-cooled wall tank concept indicate significant reduction in hydrogen usage to cool the tank during refueling.
- Estimates of the alane-based chemical hydrogen storage system were made for 10,000 to 500,000 units. The 500,000 unit cost of $4,127/system was significantly higher than slurry AB and the cryo-adsorbent systems.
- The transient models developed to predict performance of AB and alane were compared to experimental data and validated before being incorporated in the vehicle level model.

The future direction of this work during FY 2015 is as follows:

- Update cost models and write up cost results for the MATI and Hexcell cryo-adsorbent systems based on addition of consolidated BOP component as well as additional system design detail.

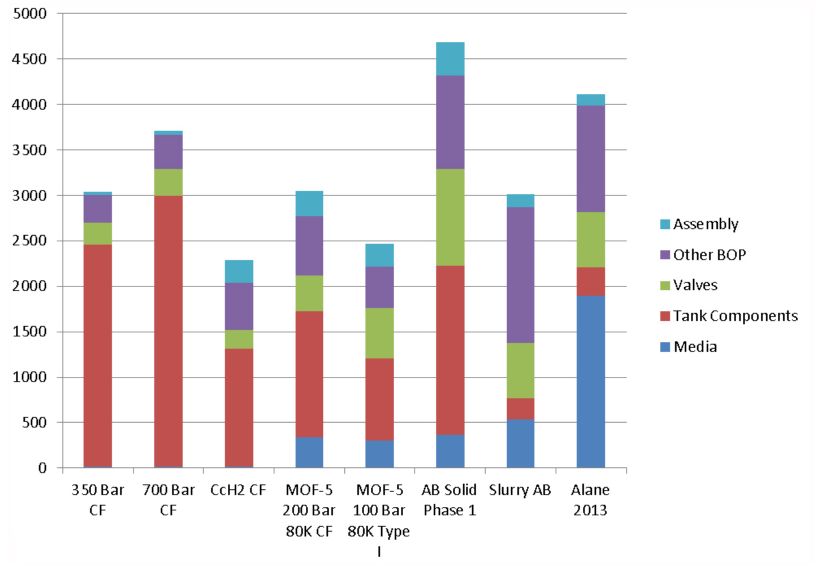

FIGURE 4. Estimated Cost for 500,000 Units Assuming Various Hydrogen Storage Systems

- Design and fabricate the 2-liter scale LN_2-cooled wall tank perform flow through and dormancy tests with and without a surrogate adsorbent material.
- The results of the 2-liter scale LN_2-cooled wall tank tests will be used to estimate the refueling time and dormancy losses for a full-scale tank.
- PNNL will work with other center partners to compile a final report for the cryo-adsorbent work which was performed over the course of the HSECoE.

PATENTS PENDING

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FY 2014 PUBLICATIONS/PRESENTATIONS

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2. Brooks, Kriston P., Troy A. Semelsberger, Kevin L. Simmons, and Bart van Hassel, "Slurry-Based Chemical Hydrogen Storage Systems for Automotive Fuel Cell Applications," *Journal of Power Sources*, Vol. 268, 950-959.

3. Semelsberger, Troy A., Brooks, Kriston P., "Chemical Hydrogen Storage Material Property Guidelines for Automotive Applications," *Journal of Power Sources*, submitted May 2014.

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5. Choi, Young Joon, Matthew Westman, Abhi Karkamkar, Jaehun Chun and Ewa Rönnebro, "Synthesis and Engineering Materials Properties of Fluid Phase Chemical Hydrides for Automotive Applications," *Energy Fuels*, submitted August 2014.

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Presentations

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2. Brooks, Kriston P., R.P. Pires and J.D. Holladay, "Development and Experimental Validation of An Automotive System Model for Slurry-Based Chemical Hydrogen Storage Materials," Innovations of Green Process Engineering for Sustainable Energy and Environment, AIChE Annual Meeting, November 2013.