IV.D.1b Systems Engineering of Chemical Hydride, Pressure Vessel, and Balance of Plant for On-Board Hydrogen Storage

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Objectives

The Pacific Northwest National Laboratory (PNNL) objectives address some of the critical engineering challenges that currently limit design optimization and commercialization of on-board hydrogen storage systems. Each of these objectives and corresponding tasks have been established to advance the state-of-the-art in analysis, design and engineering for chemical hydride storage, pressure/containment vessel construction for metal hydride and cryogenic adsorbent systems, and component miniaturization to achieve PNNL, Hydrogen Storage Engineering Center of Excellence (HSECoE), and DOE goals.

- Demonstrate a high level of performance that meets DOE targets for key components (reactor, solids handling, and heat exchanger) of a solid chemical hydrogen storage system.
- Optimized the design of a structured storage bed and system performance through engineering, including establishment of bulk storage media and system kinetics data to aid in design activities.
- Reduce system volume and weight and optimizing system storage capability, fueling, and dehydriding performance through application of microtechnology and associated architectures to the design of high-efficiency heat exchangers and balance-of-plant (BOP) components.
- Mitigate materials incompatibility issues associated with hydrogen embrittlement, corrosion, and permeability though suitable materials selection for vessel materials, heat exchangers, plumbing, and BOP components.
- Demonstrate the performance of economical, compact, lightweight vessels for a hybrid pressurized metal-hydride and adsorbent system, and containment vessel for a chemical hydride system.
- Guide design and technology down selection, Go/No-Go decision-making, and address vehicle and market impact through cost modeling and manufacturing tradeoff assessments of the three HSECoE prototype storage systems.

Achieving the objectives will enable PNNL, Savannah River National Laboratory (SRNL), and other HSECoE partners to demonstrate on-board hydrogen storage with the potential to meet 2015 DOE technical targets. This technology and design knowledge will be transferred to the participating automotive original equipment manufacturers, thus advancing the hydrogen market sector and production of future hydrogen-powered vehicles.

Technical Barriers

Specific work scope at PNNL is addressing most of the technical barriers, as described by the Fuel Cell Technologies multi-year program plan, in system weight, volume, cost and efficiency, as well as operational constraints in hydrogen delivery and refueling rates, durability and operating temperatures bounds, and materials of construction. This project addresses the following needs in the Fuel Cell Technologies multi-year program plan:

General to All Storage Approaches:

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

Off-board Regenerable Specific:

(S) By-Product/Spent Material Removal

Technical Targets

The Center activities being conducted at PNNL range from process and reactor modeling and component design/engineering to technology application and prototype fabrication for demonstration. The final ultimate goal of the PNNL scope is to demonstrate, with Los Alamos National Laboratory (LANL) partners, a (100-g) scaled chemical hydrogen storage system that meets all the DOE storage performance targets. As a snapshot of progress to date, the spider chart in Figure 1 represents the principal DOE performance targets and status toward achieving those targets as a percentage. The DOE has established an initial in-process review gate of 40% for each of the targets; the dashed line represents this 40% threshold.

Accomplishments

Progress toward meeting formal Fiscal Year (FY) 2010 milestones is on track. Accomplishments achieved to date against these milestones include:

- Initiation of process flow diagram and model development for a solid chemical hydride storage system.
- Established common modeling approaches and platform for use among Center partners.
- Determine functional criteria and design rules based on modeling performance predictions and hydride system needs.
- Complete a conceptual design for a solid chemical hydride reactor that will provide input to the HSECoE's Phase 1 Go/No-Go decision making process, and insight into the ability of such a system to meet the 2015 volumetric capacity target of 1.5 kWh/L.
- Complete COMSOL modeling of configurations.
- Down-select systems to be modeled for transient response.
- Complete preliminary design for fuel element transfer system (solids handling coupled to reactor).
- Complete test station for monolithic fuel element and hydrogen release measurement.
- Provide Rev.0 cost model, structure details and spreadsheet to Center partners for their evaluation.
- Determine bulk kinetics measurements and impact on performance.
- Complete modeling and establish pressure vessel design rules for use with prototypes.

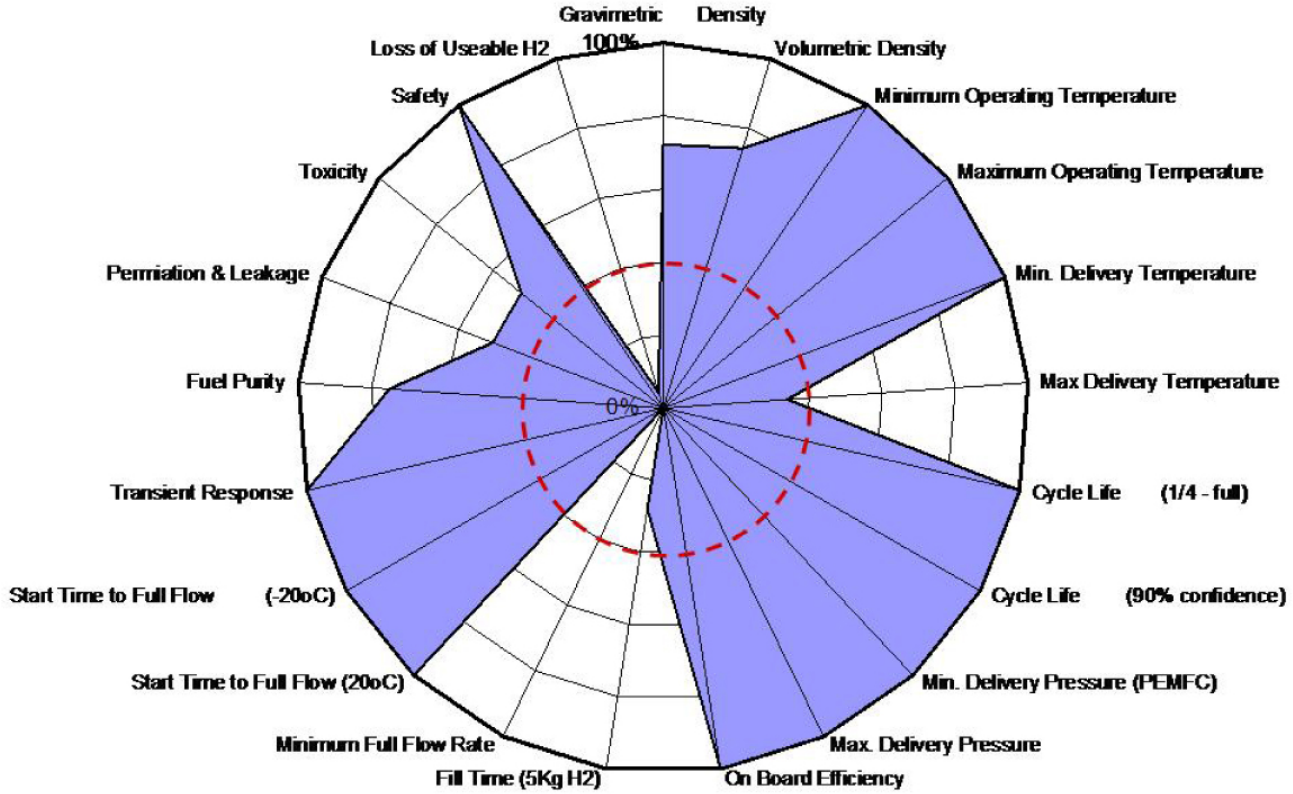

FIGURE 1. Progress toward achieving DOE performance targets for solid ammonia-borane (AB) hydrogen storage. Seventeen targets are above the 40% threshold set as an initial gate target in March 2011.

- Complete identification of known materials compatibility issues and establish corrective action plan for component designs.

Introduction

To date there has been multiple on-board vehicle-scale hydrogen storage demonstrations, including several studies to examine phenomena and characteristics that impact the engineering of hydrogen storage systems. However, none of these demonstrations have simultaneously met all of the DOE hydrogen storage sub-program goals. Additionally, engineering of new chemical hydride approaches specifically is in its infancy, with ample opportunity to develop novel systems capable of reaching the DOE targets for storage capacity. Toward this goal, PNNL is leading efforts as part of the HSECoE led by SRNL, to design and fabricate a 100 g of hydrogen scaled system based on solid or slurry chemical hydride storage media. This system is intended to be demonstrated at LANL during FY 2014 as the HSECoE concludes.

Approach

The PNNL will actively contribute to the five technology areas established as part of the HSECoE led by SRNL. The goal of this center, and PNNL's role, is to develop and demonstrate low-cost, high-performing, on-board solid-state hydrogen storage through a fully integrated systems design and engineering approach.

PNNL will target six key objectives to optimize performance characteristics and reduce the size, weight, and cost of a solid-state hydrogen storage system. This will be accomplished through a carefully engineered and integrated design approach, including application of advanced materials (structural and hydrogen storage), use of micro-scale enhancements of heat and mass transfer, better understanding and tailoring of bulk storage media and system kinetics, and assessments of manufacturing and cost impact based on established models/approaches for technology tradeoff or "viability" studies.

PNNL will also serve multiple leadership roles within the HSECoE technology area structure to help facilitate collaboration across the center partnership and to feed technical results back through and disseminate to other center partners. Achieving the objectives will enable PNNL, SRNL, and other HSECoE partners to demonstrate on-board hydrogen storage with the potential to meet 2015 DOE technical targets. This technology and design knowledge will be transferred to the participating automotive original equipment manufacturers, thus advancing the hydrogen market sector and production of future hydrogen-powered vehicles.

Results

During FY 2010 the basis of a solid chemical hydride reactor design model and system construct was created. Further, system flow sheets were established for a solid monolithic system, which provides preliminary insight into component configurations for chemical hydrides. Flow sheets and design information from component and system models were used to identify knowledge gaps that would be addressed in an experimental program later in FY 2010 and FY 2011. This modeling and experimental data will be used as the basis for down-selection of flow sheets at the end of Phase 1.

To date multiple monolithic fuel element conceptual forms have been considered:

- Disks
  - Five-inch disks, 1/8" thick sequentially inserted into 60-120 3/16" slots.
  - Slots loaded every 2-4 seconds.
  - 170°C oil channels between each slot for preheat/cooling.
- Beads
  - Beads loaded into 60-120 1-1/4" diameter, 5-inch long chambers.
  - Chambers loaded every 3-6 seconds.
  - 170°C oil channels surround each chamber.
- Tape
  - Two-inch wide, 1/8" thick tape runs through reactor at 20 ft/min.
  - Eighteen passes in 3 ft long reactor.
  - 170°C oil channels surround each pass.

Models that represent these physical formats have been drafted, and for FY 2010 are being used to analyze hydrogen mass and heat transfer throughout the dehydrogenization reaction zone and within the fuel storage container. Furthermore, a fourth fuel element type is in the process of being added to the physical domain model that describes the fuel element in a gel or slurry form that may have the added advantage of easier loading on- and off-board the vehicle.

Additionally, a series of models that captures the physiochemical nature of a solid chemical hydride system was drafted that will be use to simulate hydrogen release in monolithic fuels in order to guide system design and determination potential for achieving hydrogen release rate target of 1.6 g H_2/s for an 80 kW fuel cell. This model also incorporates the fuel element engineered form models (e.g. disks, beads, tape) and takes into consideration two different reactor designs and processes routes – batch versus continuous.

The model is built upon a three-tier hierarchy, with the lowest level being a kinetics model that describes

the mass/heat phenomena of the systems; second tier describes the reactor function and physical design, while the highest tier is a BOP component model that follows the process flow diagram configuration. Basic inputs to the model are: reaction rate, reactor design, DOE targets (80 kWe), while outputs are: reactor size, fuel usage, hydrogen loss, and impurity level.

This three-tier series of models are built using a combination of COMSOL, MATLAB and Microsoft Excel, which input/output files are readily transferable between other Center partners. The models once refined and validated experimentally, will be used for sensitivity analyses, understanding reaction residence times, determining reactor size and complexity versus extent of reaction (fuel usage). The modeling effort will also focus on defining fuel element void space (e.g. slot gap size, packing density), ultimate reactor operating pressure, hydrogen loss, and level of impurities.

This initial baseline model utilizes AB in an engineered form, known (or predefined) reactor design dimensions, heat transfer, and diffusion resistance. Figure 2 shows this baseline reactor and storage system. The model is currently being adapted to also include provisions to simulate the functions of a gel or slurry fuel.

To address weight and volume constraints design consideration was given to combining function and components into single units, as well as integrating multiple functionality into the reactor and on-board mass transfer components. As an example, the AB thermohydrolysis reaction and control of kinetics exclusively in the auger rather than ballast tank with the baseline design show in Figure 2. Additionally, the fuel element feed and product tanks are combined into a single unit that works by displacing and refilling the tank volume with fresh and spent fuel, hence minimizing overall system volume. As a result, estimated system volume and weight appears to be within achievable

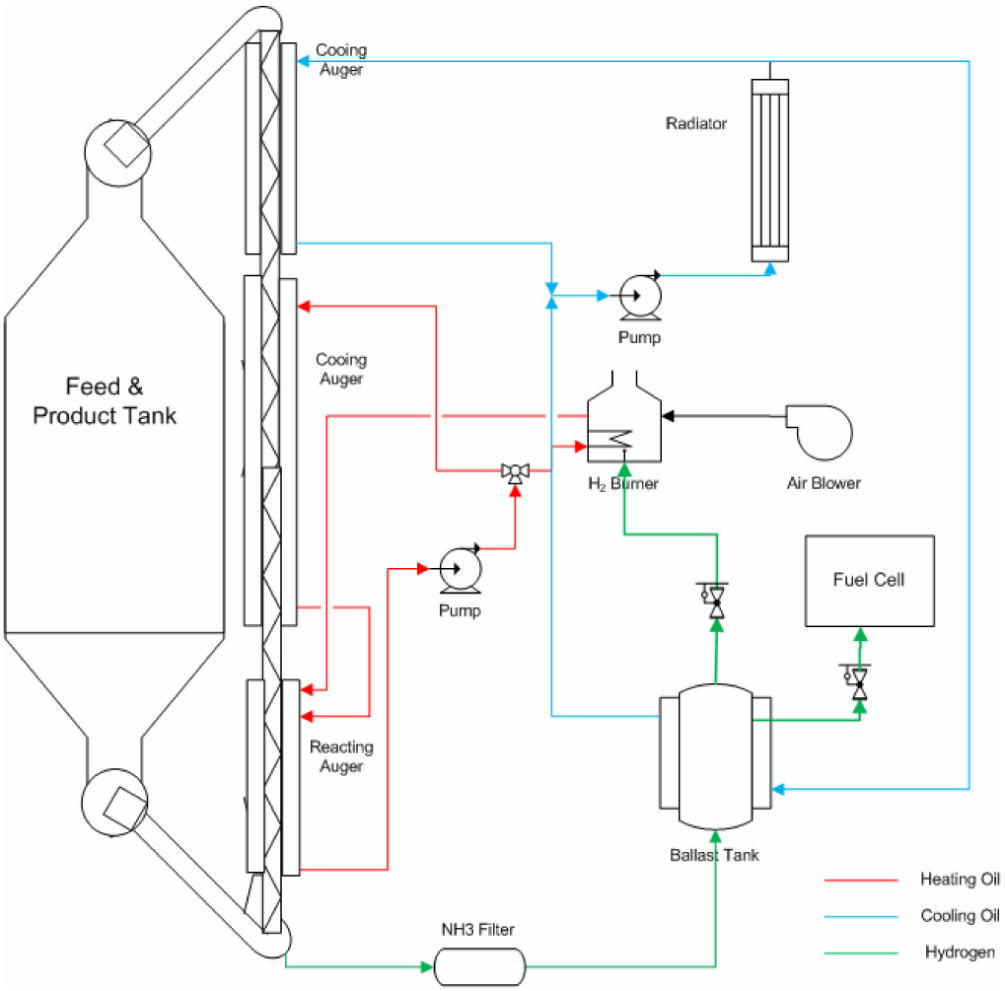

FIGURE 2. Baseline AB bead reactor systems with heated reactive auger for transport of fuel in and out of the reaction zone.

TABLE 1. System Weight and Volume Estimates – Baseline solid AB Bead Reactor with Heated Auger System

Component	Weight	Volume
AB Storage	30.8kg	0L
Feed/Product Tanks	14kg	140L
Ballast Tank (carbon fiber)	29.7kg	9L
Hot Auger (steel)	10.8kg	3.2L
Cold Auger (steel)	20.2kg	6.3L
Burner/Blower	6.3kg	5.7L
Radiator	1kg	1.8L
NH_3 Filter	2.2kg	2.7L
Oil Piping/Pump/Tank	4.7kg	3.5L
Valves/Actuators	5kg	3.5L
Total	125kg	176L

* Total 2010 targets: mass 111 kg; volume 178 liters based on 5 kg of usable hydrogen stored

means relative of the DOE 2010 performance targets. Estimates weights and volumes for the primary systems components are given in Table 1.

Beyond process and kinetics modeling, PNNL has establish the modeling approach, assumptions, and basic structure to simulate various pressure vessel geometries and layered structures, including model parameters that account for basic cost and performance. This effort and model is being used to conduct assessments of materials and design options between Type I-IV pressure vessels, which include a first-order approximation of cost from a materials-of-construction perspective. It was concluded that carbon fiber-wrapped Type-IV tanks is the closest known option to meet 2015 weight targets. However, the trade-off is higher cost of the carbon fiber, which may be a contrite to implementation at this point in time unless options for lower cost carbon fiber and/or tank designs can be developed. Based on this study further analysis will emphasize options for aluminum tanks and liners, as well as modeling lower cost and strength carbon fibers for use in Type-IV tanks.

Additionally in FY 2010 PNNL developed the selection criteria for storage materials to aid in down selecting materials systems for further focus on system modeling and design. These selection criteria are used as a screening tool for subsequent material considerations, and to identify gaps in the property data which will need to be addressed by HSECoE partners or other independent projects. As part of this effort, materials property date collection from the existing materials centers of excellence has been completed.

Conclusions and Future Directions

- A representative systems model of an AB-based bead reactor system was developed and successfully simulated in MATLAB/Simulink environment.
- A COMSOL transport model was developed for a bead and a block system. The heat and mass transfer model used a simple reaction rate expression: (1) Bead reaction can occur within the auger that has been designed assuming a 200°C wall. (2) Heating the outside surface of a block can light off the reaction for the entire block.
- An improved kinetic model has been developed and implemented into the system model.
- Hydrogen loss and impurities assessed for solid AB as material is moved into and out of the pressurized reaction system.
- Materials properties database established for HSECoE partners.
- Screening criteria/questionnaire created.
- Engineering cost model structure established.
- Studies and analysis of pressure vessels performed:
  - Metal hydride hybrid
  - Vessel material of construction sensitivity analysis
  - Liner material assessment
- Materials compatibility and reactivity studies started.

Future planned scope for FY 2011will predominately include implementation of the new reactor designs in MATLAB/Simulink and corresponding simulation analysis for assessing impact on: improve hydrogen delivery temperature; increase volumetric/gravimetric density; include variable transport properties (ρ, Cp, k, zH_2); and address impurities and hydrogen losses in design. Investigation of alternate materials of chemical hydride options, such as alane, will also occur. Additionally, implementation of the new kinetic model in MATLAB/Simulink and corresponding simulation analysis is planned, including the additional of temperature dependent transport properties into models as they become available. This effort will be supported by experimental efforts to determine needed property and kinetics data for each storage material system, as well as for model validation and calibration purposes.