IV.B.1 Hydrogen Storage Engineering Center of Excellence (HSCoE)

Donald L Anton (Primary Contact),
Theodore Motyka, Bruce J Hardy,
David A Tamburello and Claudio Corgnale
Savannah River National Laboratory (SRNL)
Bldg. 999-2W
Aiken, SC 29808
Phone: (803) 507-8551
Email: DONALD.ANTON@SRNL.DOE.GOV

DOE Managers
Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov
Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@ee.doe.gov

Technical Advisor
Robert Bowman
Phone: 818-354-7941
Email: rcbjr1967@gmail.com

Subcontractors
- Pacific Northwest National Laboratory (PNNL), Richland, WA
- United Technologies Research Center (UTRC), E. Hartford, CT
- General Motors Corporation (GM), Dearborn, MI
- Ford Motor Corporation (Ford), Dearborn, MI
- The National Renewable Energy Laboratory (NREL), Golden, CO
- Los Alamos National Laboratory (LANL), Los Almaos, NM
- The Jet Propulsion Laboratory (JPL), Pasadena, CA
- The University of Michigan (UM), Ann Arbor, MI
- The California Institute of Technology (Cal Tech), Pasadena, CA
- Oregon State University (OSU), Corvallis, OR
- Hexagon Lincoln LLC, Lincoln, NB
- University of Québec, Trios Rivieres (UQTR), Trois Rivieres, QC, Canada

Project Start Date: February 1, 2009
Project End Date: June 30, 2015

Overall Objectives

- Develop system models that will lend insight into overall fuel cycle efficiency.
- Compile all relevant materials data for candidate storage media and define future data requirements.
- Develop engineering and design models to further the understanding of onboard storage energy management requirements.
- Develop innovative onboard system concepts for metal hydride, chemical hydrogen storage, and adsorbent materials-based storage technologies.
- Design components and experimental test fixtures to evaluate the innovative storage devices and subsystem design concepts, validate model predictions, and improve both component design and predictive capability.
- Design, fabricate, test, and decommission the subscale prototype components and systems of each materials-based technology (adsorbents, metal hydrides, and chemical hydrogen storage materials).

Fiscal Year (FY) 2014 Objectives

Management Work Scope

- Coordination and facilitation of partner's activities:
  - Organize and conduct one face-to-face Center Technical Meeting
  - Organize and participate in Tech Team Review
  - Publish Integrated model on the HSECoE website
  - Complete construction of Phase 3 prototypes
- Updated prototype system testing plan for both adsorbent and chemical hydrogen systems

Technical Work Scope

- Design and construct two hydrogen cryo-adsorbent test stations capable of evaluating the performance of a 2-liter prototype operating between 80-160 K and 5-100 bar.
  - Test Station #1 – Flow-through cooling concept with a resistance-based heater
  - Test Station #2 – Isolated-fluid cooling/heating concept
- Design and construct two 2-liter adsorbent subscale prototypes:
  - Hexagonal heat exchanger (HexCell) Design – Flow-through cooling concept with a resistance-based hexagonal heat exchanger developed for powder adsorbent
  - Modular Adsorption Tank Insert (MATI) Design – Isolated-fluid cooling/heating concept developed for compacted adsorbent
- Complete test matrix for evaluation of the 2-liter adsorbent system.

- Update the cryo-adsorbent system models with Phase 3 performance data, integrate the models into the framework, document the models, and release them to the public.
- Refine the detailed models (validate) for scale up and alternative hydrogen storage applications.
- Determine minimally acceptable adsorbent material properties to meet the 2017 and ultimate system targets.

Technical Barriers

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

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(D) Durability/Operability

(E) Charging/Discharging Rates

(G) Materials of Construction

(H) Balance-of-Plant (BOP) Components

(J) Thermal Management

(K) System Life-Cycle Assessments

(L) Lack of Tank Performance Data and Understanding of Failure Mechanisms

(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(R) By-Product/Spent Material Removal

Technical Targets

This project directs the modeling, design, build, and demonstration of prototype hydrogen storage systems for each material class (metal hydride, chemical hydrogen storage and hydrogen adsorbent) meeting as many of the DOE Technical Targets for light-duty vehicular hydrogen storage. The current status of these systems versus the Onboard Hydrogen Storage System Technical Targets as of the end of Phase 2 is given in Table 1.

Center Wide Accomplishments

The following are landmark innovations that the HSECoE can claim to have lead which have changed the way we think about hydrogen storage systems and the materials which are used in them. Overall, the DOE Technical Targets

TABLE 1. System Status vs. Technical Targets

			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

were prioritized showing that volumetric density is more important than gravimetric density when range and space are considered. Integration of the hydrogen storage system models including the fuel cell, balance of plant, and vehicle drive cycles were used to determine the empty tank status under the US06 drive cycle.

For metal hydride storage, a metal hydride acceptability envelope showing the interrelationship of the enthalpy, specific heat, thermal conductivity, and gravimetric density in a postulated material's ability to meet the refueling target was accomplished. A microchannel catalytic burner was demonstrated achieving a volumetric density record for oxidizing hydrogen and return the available heat in a useful form to the storage system.

For chemical hydrogen storage the HSECoE identified that a slurry was needed to transport the hydrogen carrier material into and out of a controlled temperature reactor. The definition of slurry storage material characteristics necessary to meet the DOE Technical Targets was identified. An Auger reactor for slurries and a helical reactor for neat liquids allowing the uniform transport of the chemical hydrogen carrier into a thermally controlled reactor for dehydrogenation were shown. Demonstration of a viable 60 wt% alane slurry into an auger reactor with controlled hydrogen discharge.

For adsorbent storage the HSECoE identified the requirement for a liquid nitrogen jacket tank cooling strategy which rapidly dissipates the enthalpy of adsorption and cools the adsorbent allowing achievement of the three minute refueling time technical target. Demonstration of a novel low-cost flow-through heat exchanger design which allows for the rapid cooling of the adsorbent media during refueling and even heat distribution during operation was also shown. Combined metal organic framework (MOF) compaction and augmentation with thermal conductivity enhancements achieved hydrogen adsorption densities 50% greater than conventional powder packing had previously achieved. Development of a microchannel heat exchanger design allowing for the use of compacted adsorbent media achieving a 10% reduction total system volume. Development of the adsorbent acceptability envelope outlines the necessary adsorbent properties using the UNILAN model showing the necessity for adsorbed hydrogen density of ≥120 mol/Kg and an isosteric heat of 4.6 KJ/mol.

Technical Accomplishments

Small-scale (0.5-liter flanged vessel with a HexCell HX) experiments and models for powder MOF-5:

- Verification that physical processes are properly included/represented
- Flow-through cooling hydrogen charging experiments were completed and models were validated
- Resistive heating rod hydrogen discharging experiments were completed and models were validated

- Phase 3 HexCell experiments and model validation:
  - Prototype test station at UQTR was built and tested
  - 2-liter vessel with resistive rod heater within a hexagonal heat exchanger
    - Design completed
    - Assembled and instrumented at UQTR
  - Model for the 2-liter tank in three-dimensional geometry with 90^o symmetry
    - Model running successfully with preliminary test cases
    - Leveraged previous experience from the 0.5-liter tank
  - Test matrix completed
  - Preliminary experiments at UQTR have begun
- Phase 3 MATI experiments and model validation:
  - Prototype design has been completed with OSU
  - Prototype test station at SRNL design completed
    - All components purchased and on site
    - Test station is 80% assembled with electrical left to complete
  - Preliminary test matrix completed

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INTRODUCTION

The HSECoE brings together all of the materials and hydrogen storage technology efforts to address onboard hydrogen storage in light-duty vehicle applications. The effort began with a heavy emphasis on modeling and data gathering to determine the state of the art in hydrogen storage systems. This effort spanned the design space of vehicle requirements, power plant and balance of plant requirements, storage system components, and materials engineering efforts. These data and models will then be used to design components and sub-scale prototypes of hydrogen storage systems which will be evaluated and tested to determine the status of potential systems against the DOE 2017 and Ultimate Full Fleet Technical Targets for Hydrogen Storage Systems for Light-Duty Vehicles.

APPROACH

A team of leading North American national laboratories, universities, and industrial laboratories, each with a high degree of hydrogen storage engineering expertise cultivated through prior DOE, international, and privately sponsored projects has been assembled to study and analyze the engineering aspects of condensed phase hydrogen storage as applied to automotive applications. The technical activities of the HSCoE are divided into three System Architectures: adsorbent, chemical hydrogen storage and metal hydride matrixed with six technology areas: Performance Analysis, Integrated Power Plant/Storage System Analysis, Materials Operating Requirements, Transport Phenomena, Enabling Technologies and Subscale Prototype Construction, Testing and Evaluation. The project is divided into three phases; Phase 1: System Requirements and Novel Concepts, Phase 2: Novel Concept Modeling Design and Evaluation, and Phas 3: Subscale System Design, Testing, and Evaluation.

RESULTS

SRNL and UQTR to date have met and or exceeded their FY 2014 objectives for all of their major technical goals within the HSECoE. These objectives fall within the areas of Transport Phenomena, Adsorbent System Level Modeling, Material Operating Requirements, and System Architecture. Transport Phenomena and Adsorbent System Modeling results are shown below for adsorbent systems.

Transport Phenomena

- Component level experiments for MOF-5 charging and discharging in a 0.5-liter flow-through cooling system were conducted.
  - Flow-through cooling was demonstrated for the charging process.
  - Heating via a resistance rod imbedded in an aluminum hexagon was used for the discharge process.
    - Heating (discharge) experiments along with computational comparisons completed for multiple configurations including heating experiments with empty HexCells, heating experiments with alumina-filled HexCells, and heating experiments with MOF-5 powder-filled HexCells.
    - The HexCell HX distributes thermal energy well.
    - Results are shown for a uniform heater power profile; comparisons are also good for a parabolic heater power profile.
  - Both experimental measurements and numerical models of the heating/discharge technique showed that the HexCell HX distributes thermal energy well.
- Models developed/applied by SRNL replicate the experimental conditions
  - Validation of models against the 0.5-liter experimental data for several flow-through cooling and resistance heater desorption experiments to verify that the physical processes are properly included/represented.
  - Figure 1 shows representative results between the experimental data and computational model for powder MOF-5, initially at 3.5 MPa hydrogen, 77 K at vessel surface, and no outflow.
- 2-liter HexCell prototype experiments and models
  - Designed and assembled vessel and internal components of the 2-liter prototype (as shown in Figure 2) and the HexCell prototype test stand (as shown in Figure 3).
    - The prototype test facility has been completed, with capabilities of hydrogen flow rates up to 1,000 splm.
  - Developed a test matrix
  - Conducted preliminary experiments in ambient temperature and above
  - Created a three-dimensional computational model geometry with a 90^o symmetry (as shown in Figure 2), which is successfully running and shows good agreement with the preliminary ambient temperature experiments.
  - Currently working on solutions for the 2-liter vessel seal leak issue at cryogenic temperatures.
- 2-liter MATI prototype experiments and models
  - Assisted OSU in the design of the 2-liter prototype and its internal components (shown in Figure 4).
  - Designed and began assembly of the MATI prototype test stand, shown in Figure 4, with the following capabilities:
    - Gas supplies:
      - H_2 at 80 K and >100 slpm
      - LN_2 at ~7 bar and 80 K
      - N_2 at >373 K and >100 slpm
    - Data acquisition:
      - Pressure and temperature at all tank inlets/outlets
      - Mass flow control and measurements of all gas/liquid flows
  - Began construction of the MATI prototype test stand, with completion scheduled for August, 2014.

Adsorbent System Level Modeling

- The MATLAB®-version of the cryo-adsorbent system models has been updated to reflect the latest input from all HSECoE partners for both of the HexCell and

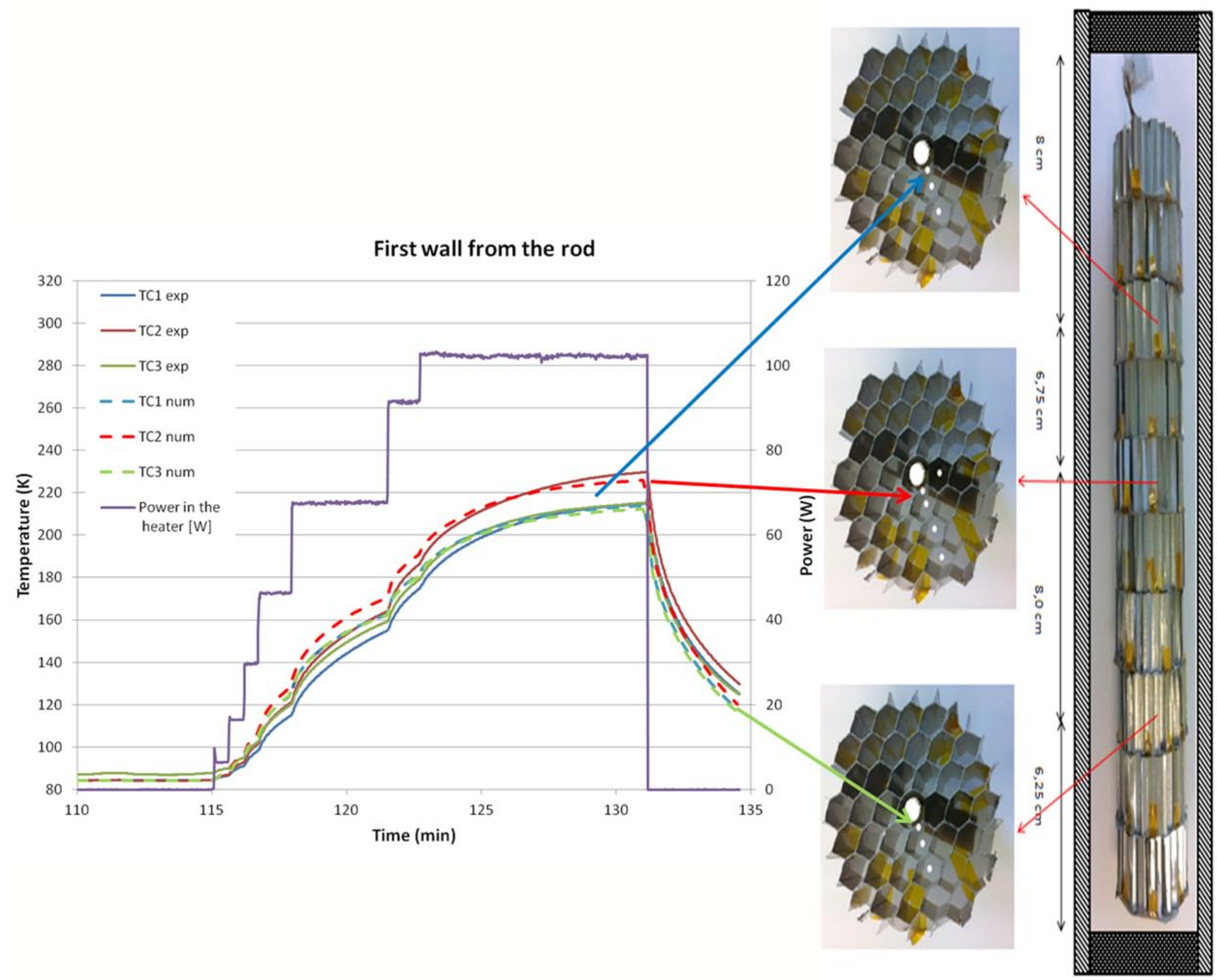

FIGURE 1. 0.5-Liter Vessel Experimental Data and Model Comparison

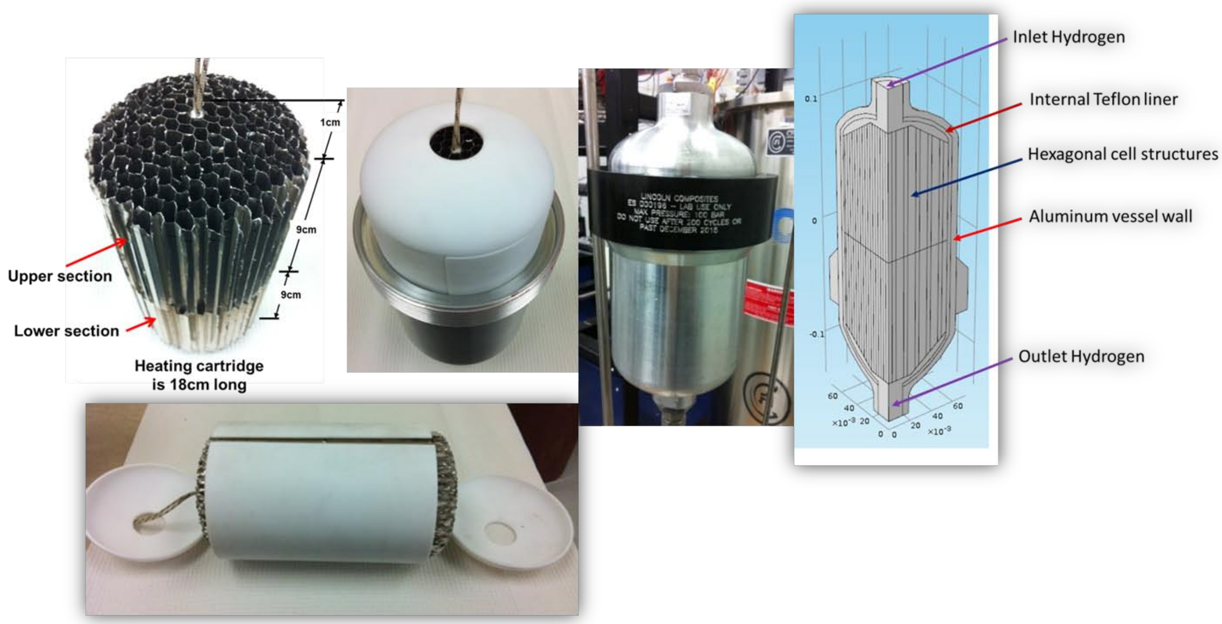

FIGURE 2. 2-Liter HexCell Prototype Assembly and Computational Model

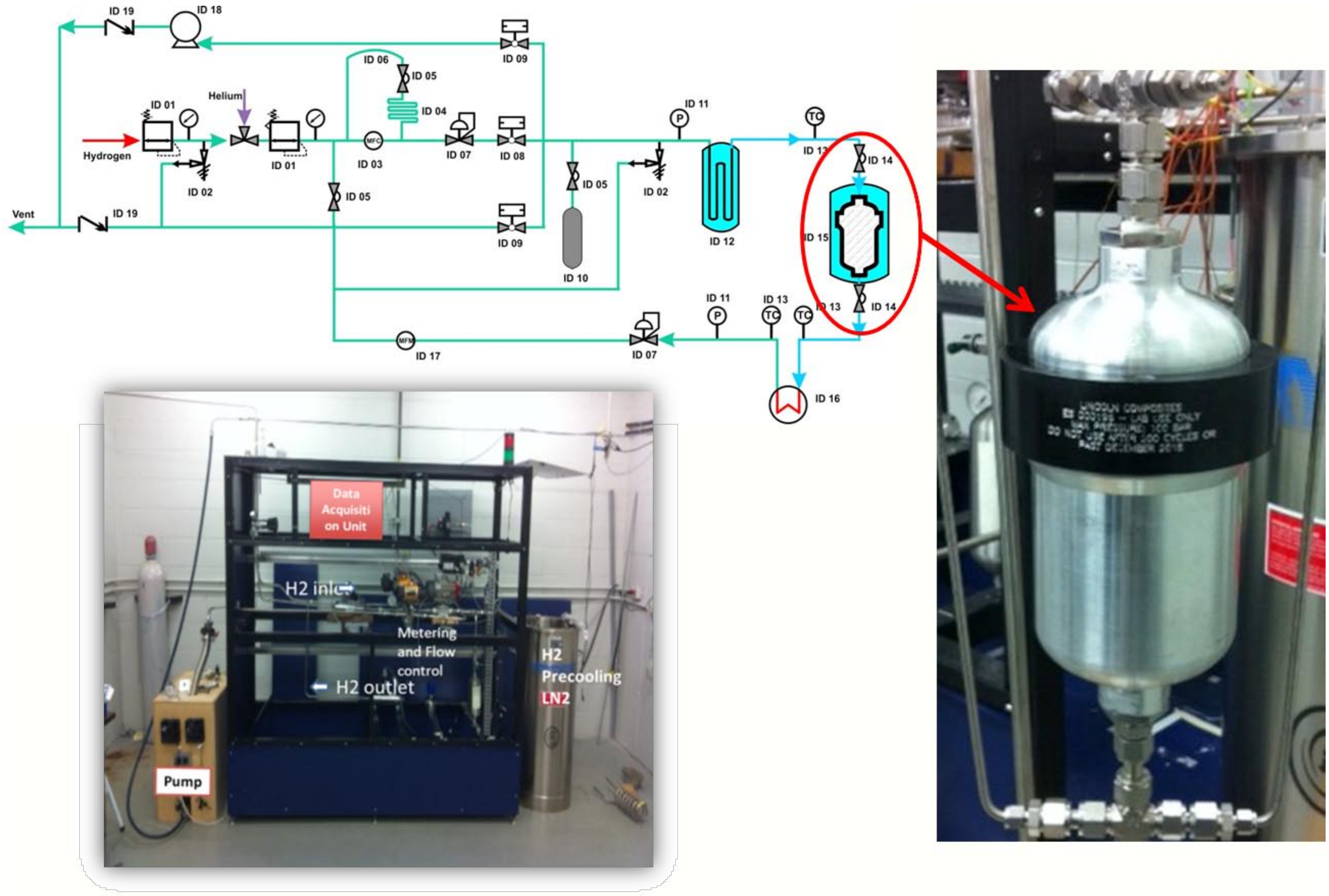

FIGURE 3. 2-Liter HexCell Prototype Test Stand

MATI system designs. Note that the system models have the following capabilities, with all subroutines having expansion abilities should additional options/improvements be available/desirable:

- First-order system and individual component cost estimates.
- Overall system ranks based on a value algorithm developed by Ford that incorporates the system cost, gravimetric capacity, and volumetric capacity.
- Dubinin-Astakhov parameters for hydrogen storage within several cryo-adsorbents (single and multi-component versions are available).
- Internal tank heat exchanger concepts, where the mass and volume of the heat exchanger is adaptable based on the properties (and amount) of the cryo-adsorbent.
- A tank design algorithm, with a wide variety of material and dimensional options, which was developed by PNNL with input from SRNL and Hexagon Lincoln.
- A wide range of thermo-physical property correlations for 0.1 bar < P < 450 bar and 20 K < T < 450 K.
- Excluding pressure and temperature, there are a total of over 60,000 system parameter option combinations.

• The Simulink® version of the cryo-adsorbent system models is being updated from the MATLAB-version in preparation for its inclusion in “Models on the Web.”

CONCLUSIONS AND FUTURE DIRECTIONS

Metal hydride efforts were terminated based on the judgment that no known material was capable of meeting either the 2017 or ultimate targets in a system configuration. Ultimately, a metal hydride is needed which will have a capacity of 10-11 wt% hydrogen and an enthalpy of 25-27 KJ/mole H_2 to avoid the requirement of consuming a significant portion of the stored hydrogen. No metal hydride is currently foreseen that meets this very demanding target.

Chemical hydrogen storage efforts were centered on slurry/solvent materials utilizing flow through reactor

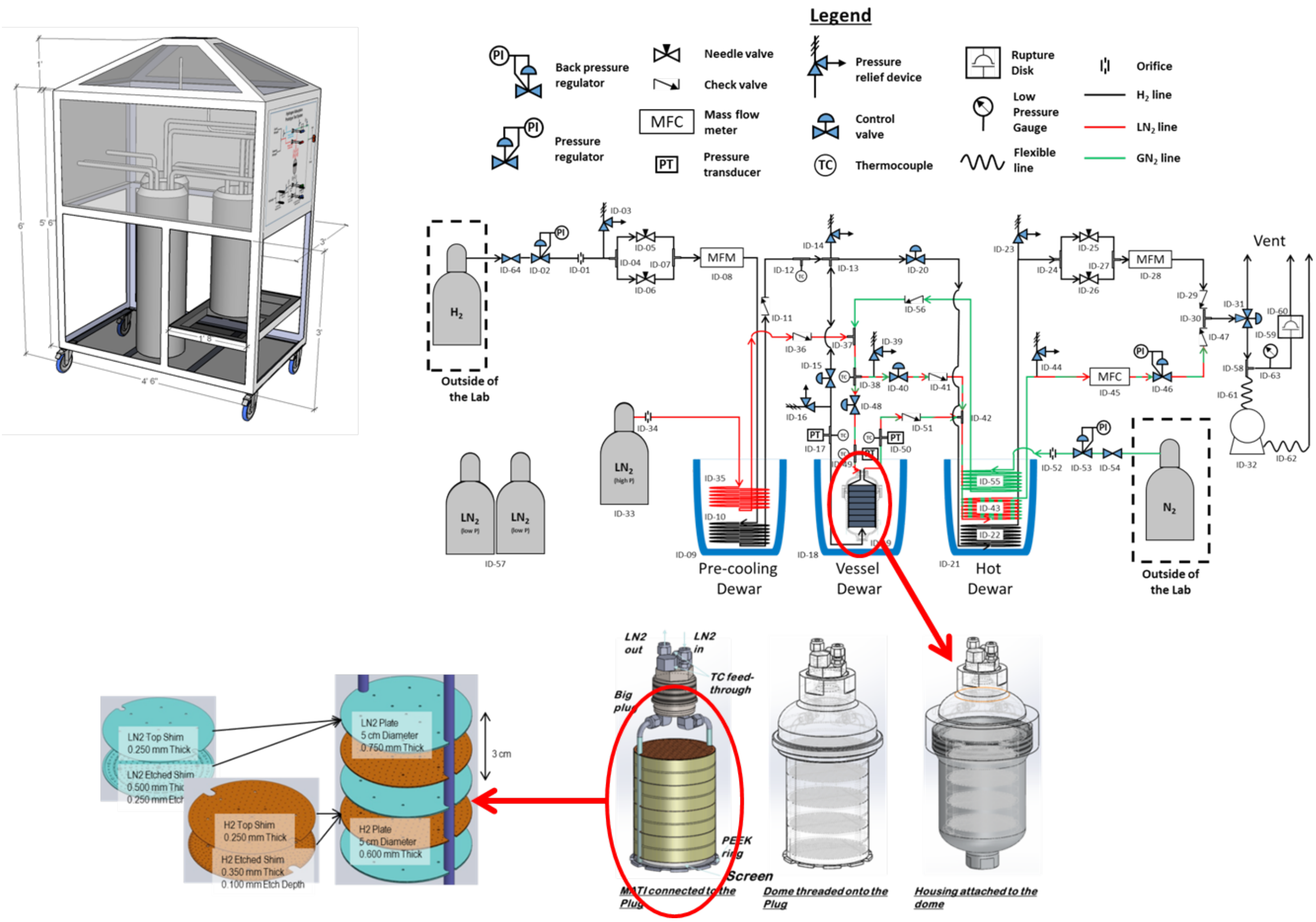

FIGURE 4. 2-Liter MATI Prototype Test Stand

development with dynamic temperature control, high-flow gas liquid separation and impurity trapping. Further studies were conducted on endothermic vs. exothermic chemical hydrogen storage materials with the identification of various start-stop cycles deeply inhibiting attainment of the onboard efficiency target. Ultimately, the chemical hydrogen storage materials efforts were terminated based on the regeneration costs and other associated technology factors outside of the HSECoE scope.

Adsorbent system efforts are concentrated on Phase 3 prototype design, assembly, testing, and modeling, including test station design, construction, and capabilities verification. Two prototypes are being tested (and modeled) in Phase 3; (1) powder MOF-5 in a HexCell that utilizes flow-through cooling during refueling and resistance heating during discharge will be tested at UQTR and modeled at SRNL, and (2) compacted MOF-5 in a MATI utilizing isolated liquid nitrogen during refueling and isolated hydrogen during discharge will be tested at SRNL and modeled at OSU. Several factors affected this selection, including the detailed model analyses with experimental validation, the overall system performance projections, the projected costs, the projected interaction with the forecourt, and the future direction of adsorbent material research.

Future technical work by SRNL in the adsorbent area will include:

- Continue to verify and determine solutions for the 2-liter vessel seal leak issue at cryogenic temperatures.
- Preliminary test plan for the HexCell prototype:
  - Pressure tests the 2-liter vessel without the HexCell structure inside the tank to check the characteristics of the tank (volume, thermal mass, etc.)
  - Performance evaluation of the heating rod (temperature profiles)
  - Flow-through cooling/charging tests with powder MOF-5
  - Heating/desorption tests with powder MOF-5
  - Cycle testing, with charge-discharge-charge, etc.

- Complete construction and capabilities verification of the MATI prototype test stand.
- Preliminary test plan for the MATI prototype:
  - Pressure test the 2-liter vessel without the MATI structure inside the tank to check the characteristics of the tank (volume, thermal mass, etc.)
  - Performance evaluation of the MATI (temperature profiles)
  - Cooling/adsorption tests with compacted MOF-5
  - Heating/desorption tests with compacted MOF-5
  - Cycle testing, with charge-discharge-charge, etc.
- Update Simulink cryo-adsorbent system models to predict full-scale system performance.
  - Make updated system models available for "models on the Web."

FY 2014 PUBLICATIONS/PRESENTATIONS BY SRNL/UQTR

1. Hardy B, Corgnale C, Tamburello D, Anton D. "Acceptability envelope for adsorption based hydrogen storage" Invited presentation at MCARE 2014, Clearwater (FL), USA.

2. Pasini JM, Corgnale C, Van Hassel B, Motyka T., Kumar S, Simmons K. "Metal hydride material requirements for automotive hydrogen storage systems" International Journal of Hydrogen Energy, Volume 38, Issue 23, 2013, Pages 9755–9765

3. "Hydrogen Storage Materials: A System Perspective as to What Is Needed for Transportation Applications", D.L. Anton Invited Presentation at Gordon Conference 2013, Barga, Italy.

FY 2014 PATENTS BY SRNL/UQTR

1. Tamburello et. al., Heat Transfer Unit Method for Prefabricated Vessel, 61/905,557, 12/12/2013.