IV.D.5 Systems Engineering of Chemical Hydrogen, Pressure Vessel, and Balance of Plant for Onboard Hydrogen Storage

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Fiscal Year (FY) 2012 Objectives

The Pacific Northwest National Laboratory (PNNL) objectives address the critical engineering challenges currently limiting onboard hydrogen storage systems for light-duty fuel cell vehicles. Each of the project's objectives and 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 for all systems to achieve PNNL, Hydrogen Storage Engineering Center of Excellence (HSECoE), and DOE goals.

- Demonstrate performance that meets DOE targets for key components (heat exchanger, pumps, and volume exchange tank) of a chemical hydrogen storage system through the use of system modeling and component validation testing.
- 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.
- Demonstrate the performance of economical, lightweight vessels for an 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 onboard hydrogen storage with the potential to meet 2017 DOE technical targets. This technology and design knowledge will be transferred to the participating automotive original equipment manufacturers and non-proprietary information and models will be made available to the fuel cell community, thus advancing the hydrogen market sector and production of future hydrogen-powered vehicles.

Technical Barriers

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

General to All Storage Approaches

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

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 for the PNNL scope is to demonstrate, with Los Alamos National Laboratory (LANL), a scaled chemical hydrogen storage system that meets the 2015 DOE storage performance targets. As a snapshot of progress to date, the spider chart in Figure 1 represents the principal 2017 DOE performance targets and status toward achieving those targets as a percentage with 1a representing exothermic systems with ammonia borane (AB) as the surrogate and 1b representing endothermic systems with alane as the surrogate. The DOE has established an initial in-process review gate of 60% for each of the targets except system cost; the dashed line represents this 60% threshold.

FY 2012 Accomplishments

- Completed development of Simulink® AB Slurry storage system model and integrated it with the fuel cell vehicle system model.
- Completed sensitivity analysis for both AB and alane slurries by doing both a tornado plot type analysis (change one parameter at a time) and Box-Behnken type of sensitivity analysis (vary multiple parameters).
- Demonstrated feasibility of 45 wt% AB slurry: slurry performance is well below upper limit of flow ability before and after hydrogen release.
- Measured key AB slurry properties including viscosity, yield stress, hydrogen release kinetics, and qualitative flocculation/settling before and after hydrogen release.
- Demonstrated 3+ months with no apparent flocculation or settling of a 40 wt% AB slurry.
- Identified key BOP components including a pump and heat exchanger which are a 44% mass reduction and 60% mass reduction, respectively.
- Identified optimal liner thickness to minimize mass and cost while retaining fatigue resistance at cryogenic temperatures.
- Developed cryogenic test plan to test polymer liners for Type-IV vessels and completed testing on seven material candidates.
- Completed sensitivity analysis of mass relative to pressure and volume for Type-I and Type-III vessels. The analysis revealed that changing hydrogen pressure had a larger impact on mass than changing the tank volume at cryogenic conditions.
- Developed cost model tool that will analyze the cost of a pressure vessel at different pressures and different temperatures. The user inputs material, vessel Type (I, III, or IV) pressure, temperature, volume and the model provides manufacturing and material costs.

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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 sub-program goals. Additionally, engineering of new chemical hydride 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 HSECoE, led by 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 fabricate a

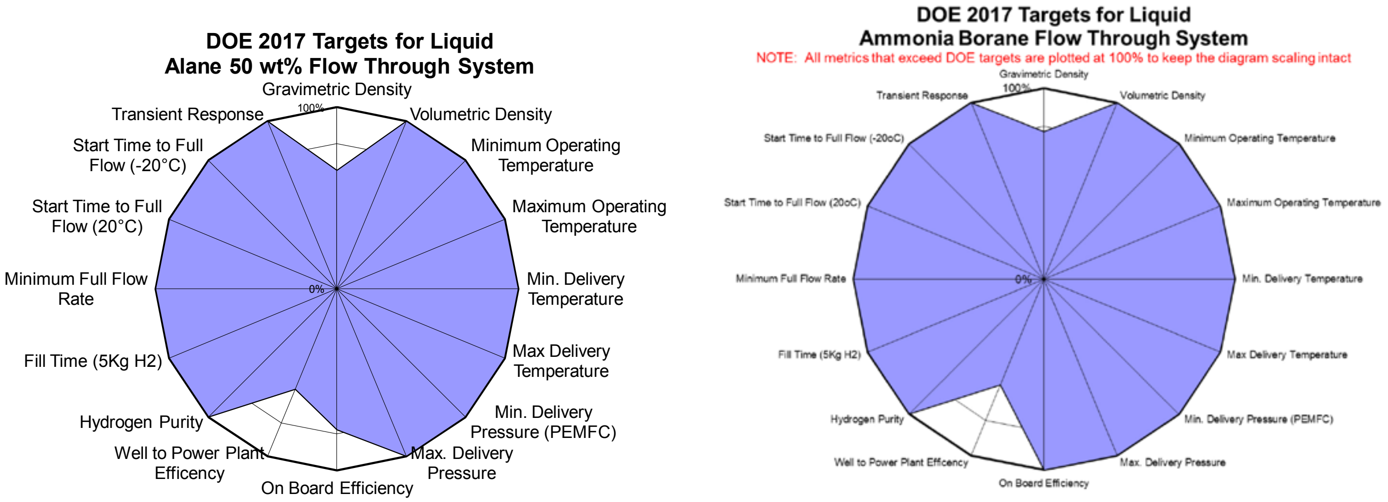


FIGURE 1. a) Progress towards achieving DOE performance targets for an exothermic material slurry with AB as surrogate. b) Progress towards achieving DOE performance targets for endothermic material slurry with alane as surrogate.

system based on slurry chemical hydride storage media. This system will be demonstrated at LANL in Phase 3.

Approach

As part of the HSECoE PNNL actively contributes to all five technology areas and targets six key objectives to optimize performance characteristics and reduce the size, weight, and cost of a H_2 storage system. This is being accomplished through engineering and integrated design approach, including application of advanced materials (structural and H_2 storage), and assessments of manufacturing and cost impact based on established models/approaches for technology tradeoff or "viability" studies.

PNNL serves multiple leadership roles within the HSECoE technology area structure to help facilitate collaboration across the center partnership and to feed technical results to other Center partners. Achieving the objectives enables PNNL, SRNL, and other HSECoE partners to demonstrate onboard hydrogen storage with the potential to meet 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. As appropriate, the models, catalogues, and lessons learned will be made available to the fuel cell community to accelerate fuel cell technology commercialization.

Results

Chemical Hydride Modeling

In the past year the models were updated for both endothermic and exothermic surrogate materials (alane and AB, respectively). The Simulink® models were integrated into the fuel cell vehicle model framework and operated to predict the performance of the hydrogen storage system. Finally, the models were exercised to gain a better understanding of the operating envelope of storage material properties that will meet DOE targets. The model updates included improved kinetic data, additional heat losses, and impacts of viscosity. The heat losses included were for the reactor, the phase separator, the pump, and recycle tubing. These components are assumed to be insulated with one inch of kaowool insulation and heat losses are associated with conduction through this insulation and natural convection to the environment. For the endothermic system a recuperator was added to the Simulink® model to maximize efficiency. These models were integrated with the fuel cell vehicle model framework, and four drive cycles were simulated (city and highway fuel economy [UDDS and HWFET], high-power and acceleration [US06], cold-start city, and air conditioning [SC03]). The simulations showed, among other things, that for endothermic materials like alane, the heat required to maintain full conversion during each of the four drive cycles resulted in onboard efficiencies of less than the DOE 2017 target of 90%. Furthermore, using the current BOP, a storage material such as alane must be loaded to an unrealistic value of 82 wt% slurry to meet the system gravimetric targets. In contrast, the exothermic chemical hydrides model demonstrated that they could meet the DOE onboard efficiency targets for all four drive cycles. The DOE 2017 gravimetric target has not been achieved either, but it is improved from that of the endothermic systems. The impact of varying the heat of reaction, kinetics (pre-exponential factor), chemical hydride mass loading, activation energy, and viscosity was completed by varying a single parameter for a tornado type plot and by varying multiple parameters for a Box-Behnken type of sensitivity analysis. These data will be used by the DOE to develop operating envelopes for directing future materials discovery work.

Chemical Hydride Slurry Development

The focus of PNNL's efforts for the chemical hydride slurry was on the AB surrogate for the exothermic slurry and to increase the loading of AB in the selected liquid carrier while maintaining required performance with respect to flow ability (pump ability). An endothermic slurry is being developed by Brookhaven National Laboratory and the Engineering Center is using their results. For the AB slurry, PNNL evaluated four candidate carrier liquids, seven synthesis techniques and is in the process of examining six additives. We have out-selected development on three carrier liquids, six synthesis techniques, and three additives. We have demonstrated a 40 wt% AB slurry that showed no settling or flocculation after 3+ months and our kinetic tests indicate that the release kinetics were similar to that of the solid AB; however, with a reduced induction period. We believe the induction period reduction was due to improved thermal conductivity of the slurry compared to a solid pellet of AB. The spent fuel did exhibit settling after several hours which will need to be addressed in the system design. The viscosity and yield stress for fresh and spent fuel was also measured (Table 1) and are well within the viscosity limit of 1,500 cP. The results indicate that both the fresh and spent slurry are Bingham plastics.

TABLE 1. Plastic viscosity and yield stress of 45% AB slurry before and after hydrogen release. These results indicate that the slurry is a Bingham plastic.

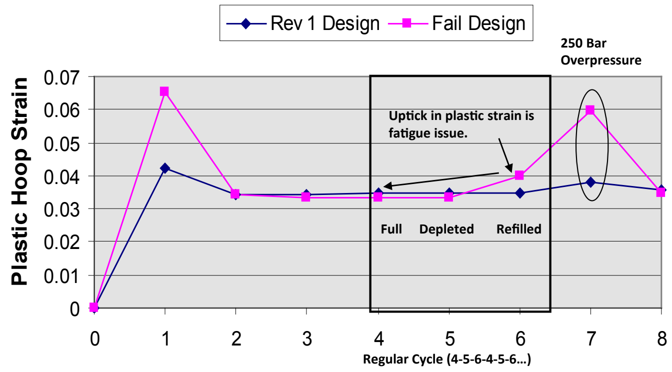
Rheology properties of 45% AB slurry at 25°C	AB slurry before H-release	AB slurry after H-release
Plastic viscosity (cP)	~ 617	~ 442
Yield stress (Pa)	~ 48	~ 3.7

Component Testing

PNNL has begun validating key components (pumps and heat exchanger [HX]) for the chemical hydrogen storage system. PNNL has identified a new pump which is capable of pumping slurries with viscosity up to 50,000 cp, at pressures up to 65 bar, and that has a mass and volume of ~2.5 kg and 1.5 L respectively. This represents a mass reduction of 44% compared to our original system. The HX we identified has a mass and volume of 1.32 kg and 1.3 L which is a 60% and 50% reduction respectively from our baseline system. We have completed initial testing of a test system composed of the prototypic pump, HX, piping, valves, and pressure sensors at room temperature and at -20°C using slurries composed of polyethylene particles and silicon oil and polyimide particles and silicon oil at appropriate loadings to simulate the fresh and spent AB slurry, respectively. No clogging was observed, but tests are on-going.

Vessels

PNNL developed models for estimating the mass of Type-III and -IV tanks subjected to cycling cryogenic temperatures and pressures in the 80-180 K and 200 bar nominal (250 bar max) range. The ring model represents a section of the cylindrical portion of a tank, with aluminum liner and carbon fiber composite overwrap. The quarter-symmetry ring is subjected to a particular pressure and temperature history that covers the autofrettage stage followed by the normal fill-depletion-refill cycle expected of an automotive hydrogen fuel tank. The results of the model determine if a set of wall thicknesses is sufficient or not (Figure 2). We found that a aluminum liner thickness of 9 mm was sufficient. The ring finite element model was employed to evaluate the Type-IV tanks, with the goals of checking the amount of load carried by the liner (minimal) and the amount of strain predicted in the liner material (about 7.5% maximum) for comparison against cryogenic material test data.



200L, 200 Bar Cryo (77-120K)
Fail design 7.5mm Al liner, 7.2 mm shell
Rev 1 design 9.0mm Al liner, 7.2mm shell

FIGURE 2. Type-III wall cylinder finite element analysis to find the optimal tank thickness.

PNNL developed cryogenic (80 K) testing capability for mechanical properties of materials. Staff tested eight candidate liner materials for cryogenic strength and elongation. Staff completed HDPE, Halar, Kynar homopolymer and Kynar copolymer materials, Kel F, polytetrafluoroethyelene, and nylon. In addition, dynamic mechanical analysis for these materials was conducted. Figure 3 contains the results for Halar, Kynar homopolymer, Kynar copolymer, and high-density polyethylene (HDPE). Halar and HDPE have the lowest glass transition temperatures and storage modulus making them the best candidates at this time.

The Center determined that in addition to the Type-III and -IV tanks, a model for Type-I pressure vessels was needed for determining mass and cost as a function of pressure (40 K and 60 bar to 80 K and 200 bar). Therefore, PNNL developed the model for determining wall thicknesses and mass as a function of pressure, temperature, tank radius, and volume. The data from the model is being used as a first order of costing for Type-I tanks and then compare the masses and costs against other tank types for a tradeoff study. The model has been incorporated into the cost model.

Costing

This year the manufacturing and cost analysis task began development of a manufacturing process model to evaluate cost differences between Type-I, Type-III, and Type-IV pressure vessels at different temperatures and pressures

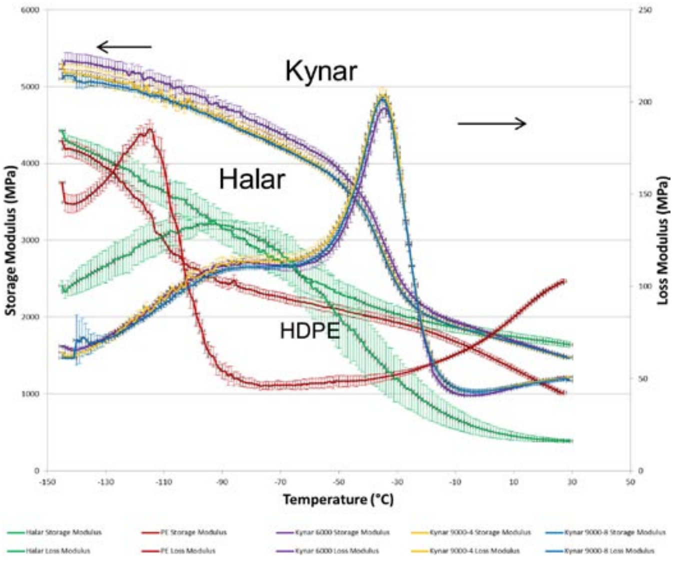
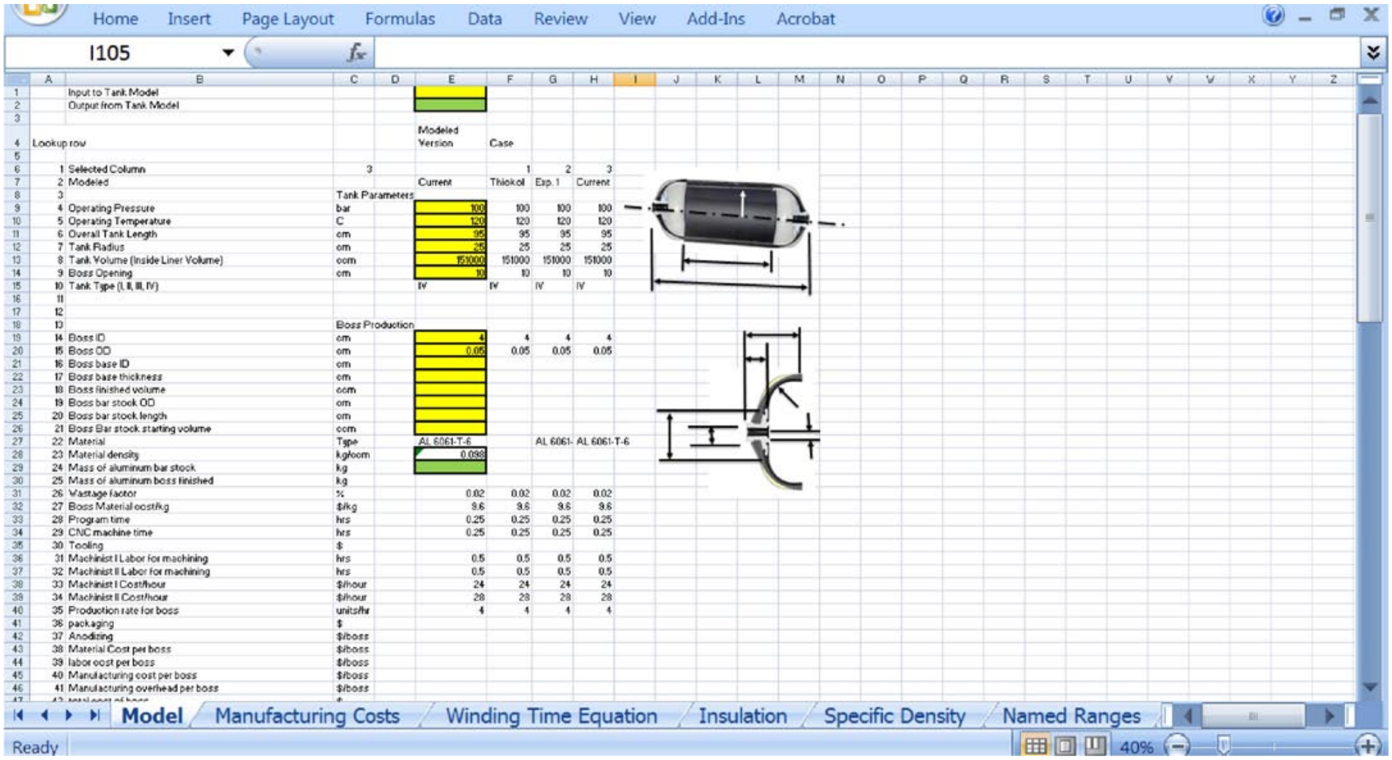


FIGURE 3. Dynamic mechanical analysis for Halar, Kynar homopolymer, Kynar copolymer, and HDPE. Halar and HDPE have the lowest glass transition temperatures and storage modulus making them the best candidates at this time.

(Figure 4). The goal for this model was to provide a high level difference between Type-I and Type-III/IV tanks costs with operating temperatures from -250 to 40°C and from 20 to 200 bar. We have incorporated manufacturing processes based on information from Lincoln Composites, the Jet Propulsion Laboratory, and literature for the Type-III and Type-IV tanks that details the steps required to manufacture the liners and wind the composites onto the tank in addition to capital costs, labor cycle time, quality assurance, insulation (from discussions with the Jet Propulsion Laboratory), installing and processing the vacuum shell, and installing the balance of plant. Only those steps associated with filling the tank with adsorbent and HX are not currently populated.

Conclusions and Future Directions

- Chemical Hydrogen System – Modeling and Validation Exothermic Slurry (AB)
  - Modeled fraction AB critical to meeting DOE mass target
  - Onboard efficiency target can be met with >8 cold-starts/day
  - Performed tornado type (vary one parameter) and Box Benken type (vary multiple parameters) sensitivity analysis
- Chemical Hydrogen System – Modeling and Validation Endothermic Slurry (Alane)
  - Alane cannot meet DOE targets for mass or onboard efficiency for the system specified and conditions evaluated
  - Performed sensitivity tests
  - Performed tornado type (vary one parameter) and Box Benken type (vary multiple parameters) sensitivity analysis.
- Chemical Hydrogen System – BOP
  - Identified key components to reduce mass/volume for pump, radiator (heat exchanger) and performance validation initiated
  - 45 wt% AB slurry demonstrated: Slurry pre- and post-H_2 release
    - Kinetics similar to solid AB without the induction period
    - Viscosity and yield stress for both fresh and spent slurries acceptable
- Vessels
  - Completed the HSECoE tank needs survey for bench top tank production
  - Modeled various cases of Type-I, -III, and -IV tanks of pressure and temperature
  - Tested of Type-IV liner materials at cryogenic temperatures
  - Evaluated mass comparisons between Type-I, -III, and -IV



	A	B	C	D	E	F	G	H
1		Input to Tank Model						
2		Output from Tank Model						
3								
4	Lookup row				Modeled Version	Case		
5								
6	1	Selected Column	3			1	2	3
7	2	Modeled			Current	Thiokol	Exp. 1	Current
8	3		Tank Parameters					
9	4	Operating Pressure	bar		100	100	100	100
10	5	Operating Temperature	C		120	120	120	120
11	6	Overall Tank Length	cm		95	95	95	95
12	7	Tank Radius	cm		25	25	25	25
13	8	Tank Volume (Inside Liner Volume)	ccm		151000	151000	151000	151000
14	9	Boss Opening	cm		10	10	10	10
15	10	Tank Type (I, II, III, IV)			IV	IV	IV	IV
16	11							
17	12							
18	13		Boss Production					
19	14	Boss ID	cm		4	4	4	4
20	15	Boss OD	cm		0.05	0.05	0.05	0.05
21	16	Boss base ID	cm					
22	17	Boss base thickness	cm					
23	18	Boss finished volume	ccm					
24	19	Boss bar stock OD	cm					
25	20	Boss bar stock length	cm					
26	21	Boss Bar stock starting volume	ccm					
27	22	Material	Type		AL 6061-T-6		AL 6061-	AL 6061-T-6
28	23	Material density	kg/ccm		0.098			
29	24	Mass of aluminum bar stock	kg					
30	25	Mass of aluminum boss finished	kg					
31	26	Wastage factor	%		0.02	0.02	0.02	0.02
32	27	Boss Material cost/kg	$/kg		9.6	9.6	9.6	9.6
33	28	Program time	hrs		0.25	0.25	0.25	0.25
34	29	CNC machine time	hrs		0.25	0.25	0.25	0.25
35	30	Tooling	$					
36	31	Machinist I Labor for machining	hrs		0.5	0.5	0.5	0.5
37	32	Machinist II Labor for machining	hrs		0.5	0.5	0.5	0.5
38	33	Machinist I Cost/hour	$/hour		24	24	24	24
39	34	Machinist II Cost/hour	$/hour		28	28	28	28
40	35	Production rate for boss	units/hr		4	4	4	4
41	36	packaging	$					
42	37	Anodizing	$/boss					
43	38	Material Cost per boss	$/boss					
44	39	labor cost per boss	$/boss					
45	40	Manufacturing cost per boss	$/boss					
46	41	Manufacturing overhead per boss	$/boss					

FIGURE 4. Sample page of the cost model which combines costs with predictive models.

- Cost Analysis
  - Updated metal-organic framework-5 cost analysis
  - Cost analysis being combined with vessel design models

Future Work for FY 2013

Chemical Hydrogen System

- Detailed Design, Engineering and Analysis
  - Update component models based on validation testing
  - Complete sensitivity analysis
- Validate Volume Exchange Tank
- Complete Solid-Liquid Slurry Development
  - Additives
  - Scale up synthesis

Pressure Vessel

- Pressure Vessel Engineering
  - Reduce cost, mass
  - Maintain safety
- Materials Compatibility/Reactivity
  - Finalize H_2-wetted material compatibility in components
- Determine BOP and pressure vessel materials compatibility

Cost Analysis

- Work with partners, vendors on reducing cost
- Update analysis with detailed design

FY 2012 Publications/Presentations

Publications List

1. Devarakonda MN, KP Brooks, E Ronnebro, and SD Rassat. 2012. "Systems Modeling, Simulation and Material Operating Requirements for Chemical Hydride Based Hydrogen Storage." *International Journal of Hydrogen Energy* 37(3):2779-2793.

2. Brooks KP, MN Devarakonda, SD Rassat, and JD Holladay. 2011. "Systems Modeling of Chemical Hydride Hydrogen Storage Materials for Fuel Cell Applications." *Journal of Fuel Cell Science and Technology* 8(6):Article No. 061021.

3. Majzoub EH, and E Rönnebro. 2012. "Methodology of Materials Discovery in Complex Metal Hydrides Using Experimental and Computational Tools." *Materials Science and Engineering R*, 73 (2012) 15-26.

4. Devarakonda MN, KP Brooks, and JD Holladay. 2011. "A Solvated Ammonia Borane Model for Chemical Hydrogen Storage in Fuel Cell Applications." PNNL-SA-84798, Pacific Northwest National Laboratory, Richland, WA. Submitted

5. Devarakonda MN, KP Brooks, E Rönnebro, SD Rassat, and JD Holladay. 2011. "Chemical Hydrides for Hydrogen Storage in Fuel Cell Applications." In *SAE World Congress 2012*. Pacific Northwest National Laboratory, Richland, WA.

Presentations List

1. Rönnebro E. 2011. "Fluid Phase Chemical Hydrides-presentation at F2F meeting for the Hydrogen Storage Engineering Center of Excellence." Presented by Ewa Ronnebro (Invited Speaker) at Hydrogen Storage Engineering Center of Excellence Project Meeting, Santa Fe, NM on October 13, 2011. PNNL-SA-83480.

2. Brooks K., S Rassat, M Devarakonda, T. Semelsberger. 2011. "System Modeling of Chemical Hydride Storage Systems." Presented by Kriston Brooks (Invited Speaker) at Hydrogen Storage Engineering Center of Excellence Project Meeting, Santa Fe, NM on October 13, 2011.

3. Brooks K., S Rassat , M Devarakonda. 2011. "Enabling Technology: Slurry Reactor/Gas Phase Separator Concepts." Presented by Kriston Brooks (Invited Speaker) at Hydrogen Storage Engineering Center of Excellence Project Meeting, Santa Fe, NM October 13, 2011.

4. Simmons K. 2011. "Pressure Vessel Breakout Session." Presented by Kevin Simmons (Invited Speaker) at Hydrogen Storage Engineering Center of Excellence Project Meeting, Santa Fe, NM on October 13, 2011.

5. Weimar M, M Veenstra, K Simmons. 2011. "HSECoE On-Board Hydrogen Storage Cost Estimates". Presented by Mark Weimar (Invited Speaker) at Hydrogen Storage Engineering Center of Excellence Project Meeting, Santa Fe, NM on October 13, 2011.

6. Simmons K, N. Klymyshyn, J Reiter, N Newhouse, J Makinson, M Veenstra, J Khalil, D Tamburello. 2012. "D1T11-HSECoE Pressure Vessel and Containment TTR Highlights." Presented by Kevin Simmons (Invited Speaker) at Project review of the Hydrogen Storage Engineering Center of Excellence, Detroit, MI on February 16, 2012.

7. Ronnebro E. 2012. "Materials Operating Requirements for Fluid Phase Chemical Hydrides ." Presented by Ewa Ronnebro (Invited Speaker) at Review of Hydrogen Storage Engineering Center of Excellence, Detroit, MI on February 16, 2012.

8. Brooks K, M Devarakonda, T Semelsberger. 2012. "System Modeling of Chemical Hydride Storage Systems." Presented by Kriston Brooks (Invited Speaker) at Review of Hydrogen Storage Engineering Center of Excellence, Detroit, MI on February 16, 2012.

9. Brooks K, K Simmons, M Devarakonda, T Semelsberger. 2012. "System Modeling and Balance of Plant for the Chemical Hydride Storage Systems." Presented by Kriston Brooks (Invited Speaker) at Review of Hydrogen Storage Engineering Center of Excellence, Detroit, MI on February 16, 2012.

10. Rönnebro E. Karkamkar A. Choi YJ. Chun J. Westman M. 2012. "Materials Engineering of Fluid Phase Chemical Hydrides for Automotive Applications". Presented by Ewa Ronnebro (Invited Speaker) at American Chemical Society, Fuel Chemistry Division, San Diego, CA, March 26, 2012.