Department of Energy Efficiency and Renewable Energy
Fuel Cell Technologies Office

FINAL REPORT

Award Number: DE-FC36-09GO19004
Recipient: Hexagon Lincoln (formerly Lincoln Composites)
Project Dates: 1 February 2009 to 30 June 2015

Development of Improved Composite Pressure Vessels for Hydrogen Storage

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- Savannah River National Laboratory (project lead)
- Pacific Northwest National Laboratory
- Los Alamos National Laboratory
- Jet Propulsion Laboratory
- National Renewable Energy Laboratory
- United Technologies Research Center
- Hexagon Lincoln
- General Motors
- Ford Motor Company
- BASF
- Oregon State University
- Université du Québec à Trois-Rivières
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EXECUTIVE SUMMARY

Hexagon Lincoln started this DOE project as part of the Hydrogen Storage Engineering Center of Excellence (HSECoE) contract on 1 February 2009. The purpose of the HSECoE was the research and development of viable material based hydrogen storage systems for on-board vehicular applications to meet DOE performance and cost targets. A baseline design was established in Phase 1. Studies were then conducted to evaluate potential improvements, such as alternate fiber, resin, and boss materials. The most promising concepts were selected such that potential improvements, compared with the baseline Hexagon Lincoln tank, resulted in a projected weight reduction of 11 percent, volume increase of 4 percent, and cost reduction of 10 percent.

The baseline design was updated in Phase 2 to reflect design improvements and changes in operating conditions specified by HSECoE Partners. Evaluation of potential improvements continued during Phase 2. Subscale prototype cylinders were designed and fabricated for HSECoE Partners' use in demonstrating their components and systems.

Risk mitigation studies were conducted in Phase 3 that focused on damage tolerance of the composite reinforcement. Updated subscale prototype cylinders were designed and manufactured to better address the HSECoE Partners' requirements for system demonstration. Subscale Type 1, Type 3, and Type 4 tanks were designed, fabricated and tested. Laboratory tests were conducted to evaluate vacuum insulated systems for cooling the tanks during fill, and maintaining low temperatures during service. Full scale designs were prepared based on results from the studies of this program.

The operating conditions that developed during the program addressed adsorbent systems operating at cold temperatures. A Type 4 tank would provide the lowest cost and lightest weight, particularly at higher pressures, as long as issues with liner compatibility and damage tolerance could be resolved. A Type 1 tank might be the choice if the liner and damage tolerance issues were not resolved, particularly if the operating pressure was reduced.

Introduction

The Hydrogen Storage Engineering Center of Excellence (HSECoE) started on 1 February 2009. Hexagon Lincoln received Award Number DE-FC36-09GO19004 in response to a proposal submitted under Funding Opportunity Number DE-PS36-08GO98006. The HSECoE was led by Don Anton of Savannah River National Laboratory. Other HSECoE team members were Pacific Northwest National Laboratory (PNNL), Los Alamos National Laboratory (LANL), Jet Propulsion Laboratory (JPL), National Renewable Energy Laboratory (NREL), United Technologies Research Center (UTRC), General Motors (GM), Ford Motor Company (Ford), BASF, Oregon State University (OSU), Université du Québec à Trois-Rivières (UQTR), and the University of Michigan (MU).

The purpose of the HSECoE was the research and development of viable material based hydrogen storage systems for on-board vehicular applications to meet DOE performance and cost targets. The Engineering Center of Excellence used results from the materials based Centers of Excellence developing materials for storage of hydrogen including metal hydrides, chemical hydrogen storage, and adsorbent materials. Initial technical targets (at time of proposal) are given in the following table:

Target ↓ \ Target date	2010	2015
Gravimetric efficiency	2 kWh/kg (6 wt%)	3 kWh/kg (9 wt%)
Volumetric efficiency	1.5 kWh/Liter	2.7 kWh/Liter
Cost efficiency	$4/kWh	$2/kWh

Note: These targets have changed over the course of the project.

Operating ambient temperature was noted as between -40°C and +60°C. Min/max delivery temperature was noted as -40°C and +85°C.

The objectives of Phases 1 and 2 were to utilize an understanding of storage system requirements for light-duty vehicles and to design innovative system concepts and components with the potential to meet DOE performance targets. Phase 3 was for the construction, testing, evaluation, and decommissioning of the subscale prototype(s).

Hexagon Lincoln supported the objectives of Phase 1 by evaluating materials, processes, and design features that would enhance the performance of a composite fuel container regardless of the media contained. Phase 2 efforts included continuation of some Phase 1 topics, design and fabrication of a baseline subscale tank that could be used by HSECoE Partners to further their evaluations, and to address fuel container issues specific to stored media, such as high or low temperature operation. Phase 3 efforts focused on providing a subscale tank that best met the needs of HSECoE Partners in demonstrating their technologies, using the developments from Phases 1 and 2 to the extent possible.

Phase 1

Task 1.1 Establish a Baseline Design

The first task of the project was to establish a baseline design of a hydrogen storage pressure vessel. This design was used to evaluate characteristics that have the potential to improve performance. The baseline vessel is a plastic-lined composite pressure vessel consisting of a high-density polyethylene liner fully wrapped with a carbon fiber-reinforced epoxy. The tank interfaces with a fueling system via a threaded port in a metallic boss at either end of the vessel. Specific operating pressures and temperatures had not been determined for the three different storage technologies at this time, so it was agreed that the baseline vessel would have an operating pressure of 5000 psi and operating temperature limits from -40°F to +180°F. Baseline cylinder properties and operating conditions are listed in Table 1.1.1.

Table 1.1.1: Service conditions and nominal cylinder properties

Service Pressure	5,000 psi (344.7 bar)
Gas Settling Temperature	59°F (15°C)
Maximum Fill Pressure	6,500 psi (448 bar)
Service Life	20 years
Gas Fill Temperature Limits	-40 to 149°F (-40 to 65°C)
Operating Temperature Limits	-40 to 180°F (-40 to 82°C)
Proof Test Pressure	7500 psi (517 bar)
Minimum Rupture Pressure	11,700 psi (807 bar)
Cylinder Diameter	21.4 inches (543.4 mm)
Cylinder Length (unpressurized)	63.0 inches (1600 mm)
Cylinder Length at Maximum Fill Pressure	63.34 inches (1609 mm)
Cylinder Empty Weight (excluding hardware)	231 lbs (105 kg)
Cylinder Volume	15,865 in^3 (260 L)
Cylinder Volume at Service Pressure	16,132 in^3 (264.4 L)
Cylinder interior diameter	19.2 inches (488 mm)

The plastic liner is not a structural component of the pressure vessel. Its primary function is to contain gas at elevated pressures. Due to HDPE's relatively low stiffness, all pressure loads are transferred to the reinforcement. The liner is assembled of two injection molded HDPE domes that contain an aluminum end boss, and a section of extruded HDPE pipe. They are welded together by a fusion welding process.

The end bosses serve several purposes for the baseline design. Most importantly, they are used to connect with the fueling system. They can also be used as a mounting point for the cylinder during operation. They are machined of ASTM B221 certified 6061-T6 aluminum and anodized to prevent corrosion.

The baseline vessel can be mounted into place with two straps around the cylindrical portion of the tank. As mentioned, the bosses can also be used to mount the cylinder in place. One boss is rigidly attached and the other is supported in a sliding mount. There is not a specific system that needs to be used for cylinder mounting, letting customers choose the method that best suits their needs.

The baseline tank is reinforced by a carbon and fiberglass laminate structure. The laminate consists of two layers, both of which are made of a resin impregnated roving wound over the liner. The inner structural layer consists of carbon fiber and resolves the structural load of the internal pressure. The carbon roving used in the baseline is Toray T700S 24K. A sacrificial overwrap of Owens Corning 158B Type 30 fiberglass roving is wound over the structural composite. A foam insert is wound into the sacrificial overwrap as a means to absorb energy from an impact. This feature is described by U.S. Patent 5,476,189. The resin system used in the winding process is a formulation proprietary to Hexagon Lincoln. A paint is applied to the outside of the cylinder to improve aesthetics.

Several aspects of the baseline tank design were identified as areas for possible improvement during Phase 1. They included:

- Alternative reinforcement fibers with higher strength per unit cost
- Alternative resin systems including those with lower cost per unit volume, higher temperature capability, and toughened resin systems
- Alternative liner materials with lower hydrogen permeability
- Alternative boss materials with higher strength or improved fatigue characteristics
- Designs with potentially lower safety factors; Non-Destructive test methods to monitor structural integrity of cylinders, possibly including those with lower a lower factor of safety
- Characterizing safety of the vessel design based on damage versus impact
- External thermal insulation materials if insulation provided by composite is insufficient

Of these proposed design elements, non-destructive testing, thermal insulation materials, and manufacturing processes were not specifically explored by Hexagon Lincoln in Task 1.2.

Milestones accomplished: The baseline design was established and documented.

Task 1.2 Evaluate Potential Improvements

Alternative Reinforcement Fibers

The reinforcement fiber utilized in the baseline design is Toray T700 24K carbon fiber. Initially, five different carbon fibers were identified to have the potential to improve upon the baseline. They were Toray T800 24K, Toho J30743HP 24K, Grafil TRH50 18K, Grafil TRH50 60K, and Hexcel AS7 12K.

Test tanks were wound utilizing each type of fiber. Parameters used in winding of each tank were identical. Each used the same mandrel, wind patterns, tooling, and processing. In order to maintain consistent band cross-sectional area, the number of tows used in winding was adjusted according to each fiber. Number of tows used and band cross section for each type of fiber are given in Table 1.2.1.

One unit of each tank, including the baseline, was subjected to hydrostatic burst without any prior pressurization. Another unit of each tank, except the baseline, was impacted, cycled, and then burst. The impact followed the requirements of ANSI/CSA NGV2 Section 16.8 for the Design Qualification Drop Test. Each tank was cycled 750 times its service life in years, or 15,000 times for a 20-year life. Each tank

was then hydrostatically burst. The reduction of life for each fiber type was used to compare alternate fibers to the baseline. Results of these tests are presented in Table 1.2.1 and Figure 1.2.1.

Table 1.2.1: Performance and construction details of initial alternate fiber test samples

	Performance			Construction	
Fiber**	Virgin Burst (psi)	Burst after Drop/Cycle (psi)	% Reduction	Tows of Carbon Fiber	Band Carbon Cross Section (in^2)
A: Toray T700 24K (Baseline)*	13415	--	--	3	0.00429
B: Toray T800 24K	16009	14599	-9%	5	0.00444
C: Toho J30743HP 24K	12249	10543	-14%	3	0.00433
D: Grafil TRH50 18K	13542	12837	-5%	5	0.00433
E: Grafil TRH50 60K	12152	10193	-16%	2	0.00548
F: Hexcel AS7 12K	11721	9841	-16%	6	0.00414

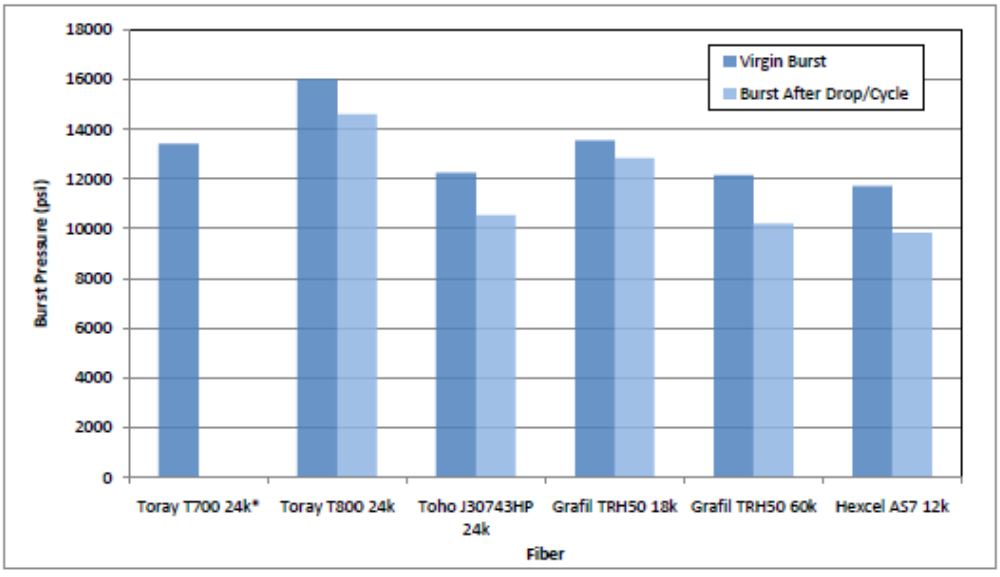

Figure 1.2.1: Comparison of virgin burst to burst after drop and cycle

Toray T800 24K showed the potential to produce a lighter weight vessel, but must be no more than 19% above the cost of the baseline fiber to break even with the baseline. Grafil TRH50 18K was nearest in strength to the baseline, but must cost 5% less to break even. All other fibers are weaker than the baseline, resulting in a tank that must be heavier to maintain strength. This also means that the fibers must be much lower in cost to break even.

After evaluating these alternative fibers, Hexagon Lincoln procured two additional fibers for testing. One type of fiber manufactured by Toho and one by Grafil. These fibers were made with newer processes or were different configurations than those previously tested. Test tanks were made in the same manner and subjected to burst tests. Results comparing these fibers to the baseline Toray T700 24K are presented in Table 1.2.2.

Table 1.2.2: Comparison of additional fibers to baseline

Fiber	Fiber Strength	Fiber Strength (% of baseline)	Stress @ average Failure	Stress @ average Failure (% of baseline)	Translation
Toray T700S::10544-2	742	100.0%	623.2	100.0%	0.84
Toho::10542-2	766	103.2%	635.6	102.0%	0.83
Grafil 37-800 30K	775	104.4%	608.3	97.6%	0.78

These tanks had nearly the same strength as the baseline in burst, indicating interchangeability. This means that there is potential for a decrease in the cost, due in part to market competition, as well as an increase in availability of fibers qualified for use in hydrogen storage.

Alternative Resin Systems

Phase 1 testing of alternative resin systems included acquiring materials and fixtures and making some preliminary comparisons. Hexagon Lincoln tested their own resin hardener against a possible alternative. Both were evaluated for viscosity and gel time. Further tests showed that the Hexagon Lincoln formulation performed better than the alternative resin hardener. The baseline hardener formulation was used in subsequent tests of alternate resin systems.

Fixtures for tensile and dart impact testing, and a mandrel to be used for making ASTM rings were acquired during Phase 1. This mandrel is used to wind rings of composite which can be used for various tests. ASTM rings can be left intact and burst to compare the strengths of various configurations, or they can be cut to size and tested for short beam shear strength or impact strength.

Some sheets of toughened resins were made during Phase 1. Before the testing of these sheets could be completed, Phase 1 was closed. However, much of this testing continued into later phases.

Alternative Liner Design

During phase one, several materials and material treatments were tested with the goal of determining a liner material configuration that effectively reduces hydrogen permeation. Ideally, the configuration would not increase costs, nor would it require major changes to production processes. Two tests were

developed to evaluate the behavior of potential liner materials in hydrogen storage environments. One test determines the permeation characteristics of material coupons. The other test is used to observe the behavior of the material when it is saturated with hydrogen at pressure and depressurized.

Permeation tests are performed by pressurizing one side of the coupon with a hydrogen gas mixture up to 5,000 psi. The amount of gas which permeates through the liner material is then measured by gas chromatograph. Initial tests were performed with a 5% hydrogen, 95% nitrogen mixture. As facilities were updated, tests were performed with 100% hydrogen gas.

Saturation tests were performed by placing material coupons in a high pressure vessel. The vessel would be filled with hydrogen until it reached a pressure of 64.8 MPa (9400 psi). The vessel would be left at this pressure for a set amount of time, and then the vessel would be depressurized over a short time frame. This cycle would repeat up to five times, with the samples being observed after depressurization at several points during cycling.

Material samples were typically HDPE with additives or surface coatings. Three samples of HDPE that were injection molded at low, medium, and high packing pressures were used as a baseline. There was little difference in permeation rates for these three samples. Other material candidates included several forms of Nylon and three engineered polymers from various suppliers. Each material was compared to standard HDPE with respect to permeation rate, saturation behavior, and cost.

Permeation tests showed improvement for all but two alternative configurations. Modifications to HDPE such as nano-clay or TiO_2 fillers reduced permeation by up to 40%. These modifications increase cost over the base HDPE, but with lower impact upon manufacturing.

Nylon typically has over 60% reduction in permeation, but lacks certain mechanical qualities and costs more than HDPE. One type of Nylon tested, PA66 with barrier compounds, was able to reduce permeation by 92-95%. This material is much more expensive than HDPE, potentially doubling the price of the finished pressure vessel.

Three engineered polymers were tested for permeation. Celcon M25, Kynar 2800, and Kurcha 2950 were able to reduce permeation by more than 80%. Similar to Nylon materials, they cost more than other candidates and require modifications to implement into production.

Initial permeation testing of PVDC coated HDPE showed promise. However, problems arose for this and other coated materials when they were saturation tested. The coatings would often blister and peel away from the surface of the coupon. This phenomenon can be seen in Figure 1.2.2. Another issue that was observed during saturation testing is the blistering of the liner material itself. Figure 1.2.3 shows a blister that formed within a sample of HDPE.

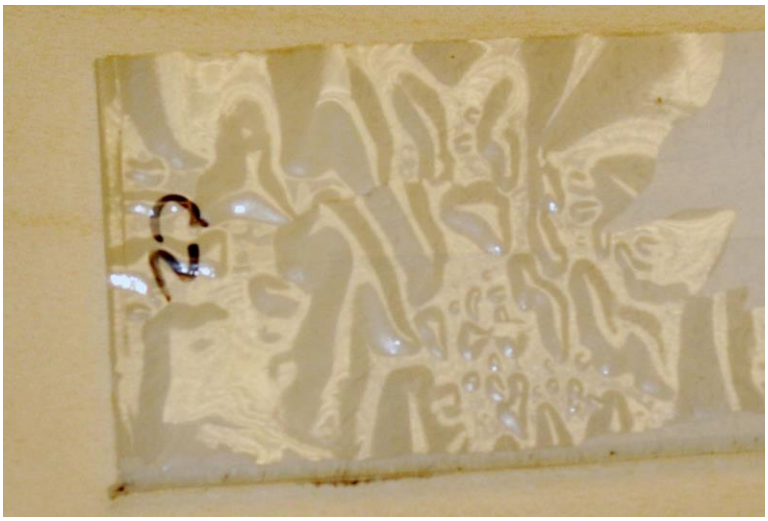

Figure 1.2.2: Example of PVDC coating peeling away from an HDPE substrate after hydrogen saturation

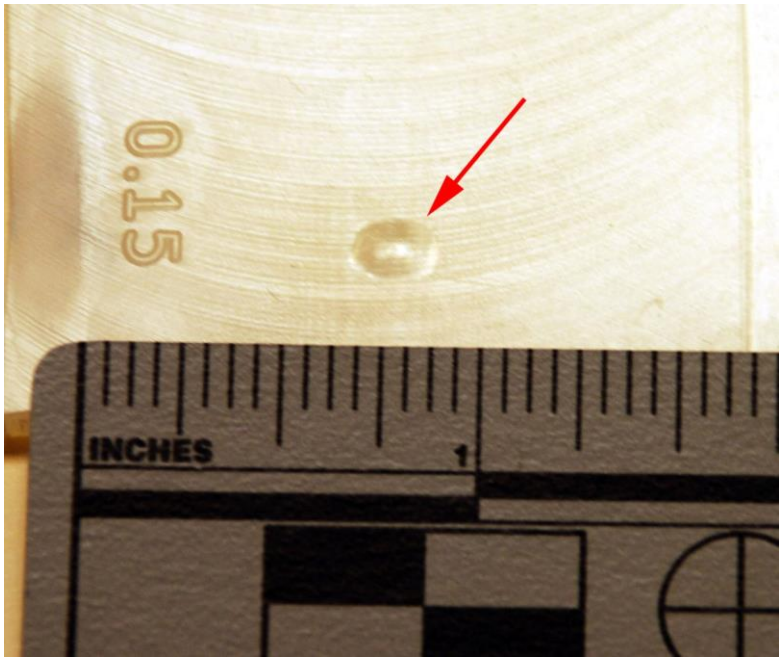

Figure 1.2.3: Hydrogen blister within HDPE liner material

Figure 1.2.4 summarizes the results of the permeation testing performed during Task 1.2. It plots how each material configuration tested compares to the baseline with regards to permeation reduction and cost. The color of each dot indicates the relative complexity of implementing each material. The HDPE baseline is marked by a green dot at (1, 1). Numerous HDPE based liner configurations offer improved permeation behavior with minimal modification to baseline design and processes. Several materials offered much higher reduction in permeation, but at the cost of greater complexity and in some cases,

much higher cost. The two groups indicated on Figure 1.2.4 show the most promise for improving liner performance.

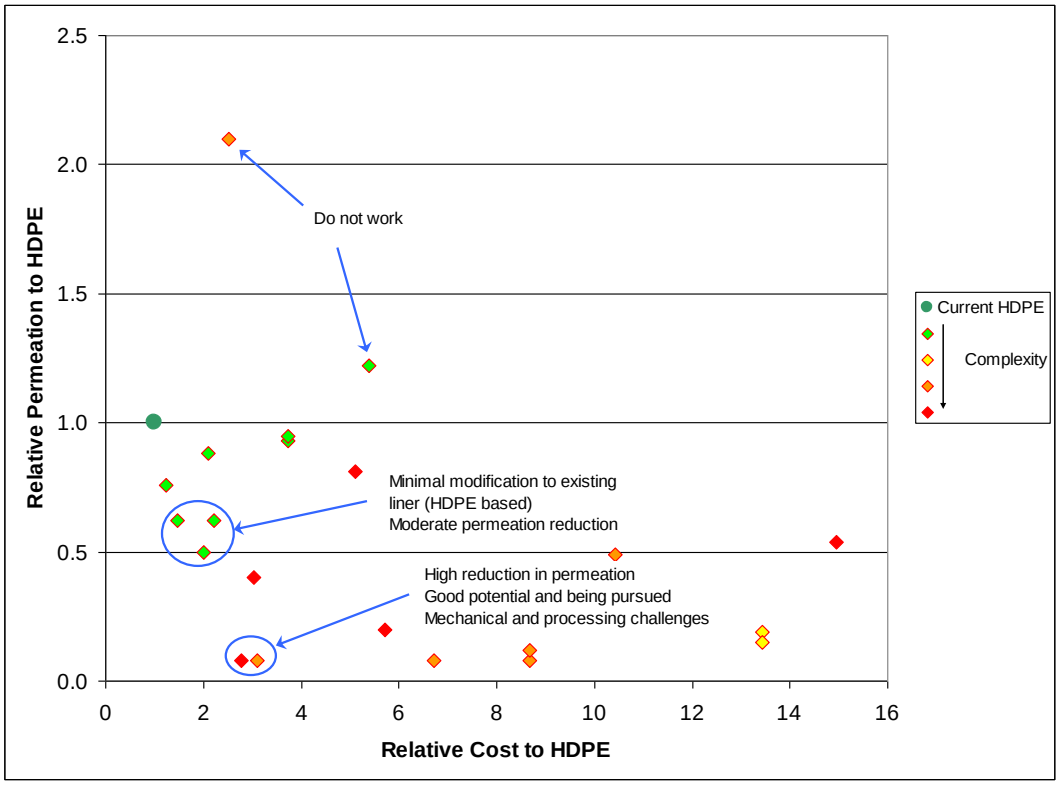

Figure 1.2.4: Chart indicating permeation rates and costs of various liner materials relative to HDPE. The color of the icon indicates complexity of utilizing the material.

Alternative Boss Materials

The boss of the baseline hydrogen storage pressure vessel was specified as 6061-T6 aluminum. The proposed design change was to use 7075-T73 aluminum alloy and heat treat for boss fabrication. Using 7075-T73 aluminum has potential to improve the baseline by reducing weight, increasing strength allowing higher operating pressures, and a decrease in the possibility of shearing boss port threads.

Six near net shape bosses were made from 7075-T6 aluminum with varied surface finishes. One boss had a surface matching manufacturing specification, three had a rough machined surface, another boss had a bead blasted surface, and the last had an oxidized finish. An example of a rough machined surface is shown in Figure 1.2.5.

Figure 1.2.5: Near net shape 7075 aluminum boss with rough machined surface

Figure 1.2.6: Example 7075-T73 near net shape boss

The six bosses were then heat treated to a T73 condition. The two extra bosses with rough machined surfaces were oriented differently when placed into the quenching media. Figure 1.2.6 shows a near net shape boss after heat treatment. Material properties testing evaluated the hardness at various points of the cross section, and mapped the strength properties over various locations throughout the boss.

Potential improvements were confirmed by testing and design reviews. Tensile testing performed on specimens from finished bosses confirmed proper heat treatment and strength increases. Yield strength was twice that of 6061-T6 and 316 SS. Weight of the boss could be reduced to 1/2 that of a 6061-T6 boss and 1/5 that of a 316 SS boss. The cost of a finished boss would be 1-1.5 times that of a 6061-T6 boss and 1/5 that of a 316 SS boss.

Evaluation of Stress Rupture

Damage tolerance and stress rupture behavior have been drivers for the factor of safety used with the design of composite pressure vessels. Most of the available information on these behaviors is from strand testing of materials from the 1970's and 1980's. Information on these behaviors for finished composite cylinders made with current materials is limited. By testing the stress rupture and cyclic fatigue behavior of composite cylinders, a model that more accurately predicts the behavior of a composite cylinder can be developed. This model could then be used to improve cylinder design to meet the goals set by the Department of Energy for hydrogen storage.

A proposal and testing plan was presented to members of the pressure vessel industry at the White Sands Test Facility Composites Seminar in September of 2009 to gain feedback and to gage interest on this subject. The originally intended partners did not agree to proceed with the test plan.

Although testing was not funded, discussions were held with subject matter experts in Type 4 pressure vessel design. They agreed that the move from a safety factor of 2.25 to a safety factor of 2.00 would be appropriate, so long as damage tolerance is accommodated and regular inspections are made.

The proposed test plan is described in the following paragraphs.

Vessels were to be made specifically for this task. They would be subjected to design verification tests, such as burst and burst after impact. Data from these tests would be used to determine the nominal burst strength of the design and the pressure levels to be used in stress rupture testing.

The most important tests proposed for this task are the stress rupture tests. Tanks would be pressurized to one of six pressure levels, determined as a percentage of nominal burst strength. Once pressurized, they would be held at that pressure until failure. A description of these six groups are listed here:

- 95% - This will be about half way between the average burst and minimum burst of the baseline. Vessels held at this level will fail the most quickly, and therefore give the earliest indication of stress rupture behavior. It is expected that some will fail during initial pressurization due to normal scatter in burst pressures. These will be included in the study as failing at a short time interval, which could be evaluated in comparison with other tanks as they rupture.
- 90% - This will be near the minimum burst of the baseline. Vessels held at this level may fail within a reasonable length of time. One or two may also fail during initial pressurization, but will still be included in the data.
- 80% - This is selected as a "mid-range" pressure to get intermediate results between the pressures chosen to get early ruptures, and pressures representative of what could be seen in service. It is also valuable in getting intermediate results for some of the vessels with added loading conditions, and getting early

assessment of whether these added conditions can have a significant effect on the life of pressure vessels in the field.

- 67% - This pressure level represents the loading on aerospace pressure vessels that have the lowest normal factor of safety, equal to 1.5. This adds meaning as a LOTF for these applications. This pressure level also represents the proof test pressure for many applications that have a factor of safety equal to 2.25.
- 56% - This pressure level represents the maximum expected operating pressure for many cylinders in commercial applications where the safety factor is equal to 2.25, such as fuel containers for natural gas and hydrogen powered vehicles. In these applications, a 25% overpressure is allowed during fast filling, and this pressure could be reached in extreme operating conditions with a full fill. This test level would be meaningful as a LOTF for these applications.
- 44% - This pressure level represents the nominal operating pressure for many cylinders in commercial applications where the safety factor is equal to 2.25. It also represents the maximum filling pressure for stationary applications such as the recently developed ASME Section X Class 3 pressure vessels.

Other groups of tanks would be tested to determine the effects of other conditions on the stress rupture behavior of composite cylinders. Three groups would be cycled at stress levels of 80%, 67%, and 56% percent of nominal burst. At this level of stress, none of the tanks are expected to fail soon after loading, but it will be evident if cycling degrades the cylinder.

Three groups would be impacted on the sidewall and then cycled. The impactor will be slightly curved to give a “blunt” impact to the tank. The impact level will produce barely visible damage. More significant damage to a cylinder can be seen and the damaged part can be removed from service. By using barely visible damage, a worst case scenario would be tested. For a more conservative test, an impact level slightly higher than what would cause barely visible damage can be used. The cycle process would follow the same levels as those cycled without impacts.

Three groups of cylinders would be impacted, exposed to chemicals, and cycled. The impact would be used to craze the resin matrix, facilitating the chemical exposure. One of five types of chemicals will be used: an acid, a base, a hydrocarbon, a fertilizer, and a surfactant. These chemicals are the most reactive that may be present at some point during usage. Exposure procedures would follow the environment test of the ANSI/CSA NGV2 standard. Chemicals to be used are listed below:

a) Sulfuric acid - 19% solution by volume in water;

b) Sodium hydroxide - 25% solution by weight in water;

c) Methanol/gasoline - 5/95% concentration of M5 fuel meeting the requirements of *ASTM D4814, Automotive Spark-Ignition Engine Fuel;*

d) Ammonium nitrate - 28% by weight in water; and

e) Windshield washer fluid (50% by volume solution of methyl alcohol and water).

Four other groups of tanks would compare brittle resins to tough resins by cycling and by cycling after impact. This test would complement the task of evaluating toughened resins, by providing more data of their performance in stress rupture situations.

Table 1.2.3 summarizes the various test groups, indicating their test pressure, cycle, other characteristics, and sample size. There would be 10 tanks in each group, except the stress rupture hold tanks at 100%, 95%, 90%, 80%, and 67% of nominal burst. These five groups will each have 20 tanks. All tests that require cycling would be run at a rate of 750 cycles per year, approximating two fill and discharge cycles per day. This is a typical requirement of commercial applications. Temperature would be kept constant for all tests. A temperature near 40°C (104°F) would accelerate test results without significantly altering the reinforcement material.

Table 1.2.3: Test specifications for stress rupture evaluation

Group	Pressure Hold	Cycle	Other	Units
1	Burst	No	No	20
2	95%	No	No	20
3	90%	No	No	20
4	80%	No	No	20
5	67%	No	No	20
6	56%	No	No	10
7	44%	No	No	10
8	80%	750 cycles per year	No	10
9	67%	750 cycles per year	No	10
10	56%	750 cycles per year	No	10
11	56%	750 cycles per year	No	10 [1]
12	80%	750 cycles per year	Impact	10
13	67%	750 cycles per year	Impact	10
14	56%	750 cycles per year	Impact	10
15	56%	750 cycles per year	Impact	10 [1]
16	80%	750 cycles per year	Fluids	10
17	67%	750 cycles per year	Fluids	10
18	56%	750 cycles per year	Fluids	10
19	80%	750 cycles per year	Brittle Resin	10
20	80%	750 cycles per year	Tough Resin	10
21	80%	750 cycles per year	Brittle Resin Impact	10
22	80%	750 cycles per year	Tough Resin Impact	10
23	DVT Burst after impact	No	Yes	10
24	DVT Burst	No	No	10
n/a	Spare			10
Total				300
	Note [1]	Burst 5 units every 10 years		

Acoustic emissions will be monitored during testing. Acoustic emission instrumentation will be used on sample cylinders that are held near expected burst pressure, with and without induced damage. The intent is to characterize the impending failure indications, and confirm that the instrumentation will be useful for monitoring long term tests and for detecting impending rupture. If it should prove useful, the same instrumentation would be used on some or all of the cylinders to monitor damage growth and impending rupture.

Evaluation of Damage vs Impact

Hexagon Lincoln was able to acquire an impact tester for evaluating new fibers, resin formulations, and combinations thereof. This investigation depended heavily upon the evaluation of alternative resin systems, and was not able to be pursued during Task 1.2.

Evaluation of External Thermal Insulation

Hexagon Lincoln, working with PNNL, developed a concept for insulating the vessel and also provided a means for cooling the vessel as part of the filling process for adsorbent materials. This concept was evaluated in Phase 3.

Milestone accomplished: Report (above) on evaluation of design, material, and process improvements.

Task 1.3 Selection of Most Promising Engineering Concepts

The design concepts that were tested in Task 1.2 all showed promise for improving the baseline pressure vessel. Resin toughening and related investigations into stress rupture and damage versus impact, which were not tested during Task 1.2, were still potential areas for improvement that were pursued in later Phases.

The projected cylinder improvements from Phase 1 investigations showed the potential for 11 percent lower weight, 4 percent greater internal volume, and 10 percent lower cost. The specific improvements were determined to be:

- Higher strength boss material (weight reduction *≈3%* due to reduced structural thickness)
- Alternate fiber reinforcements (cost reduction *≈5%* due to competitive pricing)
- Reduced safety factors for carbon fiber (cost reduction *≈5%*, weight reduction *≈4%*, volume increase *≈2%* due to reduced fiber thickness and corresponding reduction in resin)
- Thinner liner resulting from reduced permeation (weight reduction *≈4%*, volume increase *≈2%* due to thinner liner)

Milestones accomplished: Identification of most promising engineering concepts and report on selection (above).

Task 1.4 Evaluate Design Concepts and Propose Go/No Go Decisions for moving to Phase 2

The items selected in Task 1.3 were given the Go decision for inclusion in Phases 2 and 3. Test specimens may not include all features, as the goal is to demonstrate improvements to the fuel container components. To safely do so may require the use of verified design elements instead of newer technology.

Milestones: Design concepts were evaluated, and baseline design summarized (above); likelihood of composite container meeting system and DOE objectives requires higher level evaluation including incorporation of other HSECoE Partner's components and storage media.

Task 1.5 and 1.6 Project Management and Reporting

All HSECoE face-to-face and Technical Team Meetings were attended and presentations made. SSAWG teleconferences were supported. Annual Merit Reviews were attended and presentations made. Input was made to Phase 1 HSECoE report.

Phase 2

Task 2.1 Updated baseline design

The objective was to update the baseline design based on Phase 1 results from the cylinder improvement tasks and the input from project partners, with a focus on cryogenic adsorbent systems.

Service conditions were reviewed at the start of Phase 2, and are shown in Table 2.1.1. It was decided that the nominal service pressure would be set at 200 bar, with a settled temperature of 15°C. Even with adsorbent systems, more gas can be stored at a higher pressure and, if there is some free space, compressed gas is stored that can be used for system startup without need to drive hydrogen off the adsorbent material with added heat. The updated baseline tank could be designed to incorporate the Phase 1 results at the point in time the Phase 2 requirements are finalized.

A design study was conducted towards the end of Phase 2 that compared tanks made with carbon fiber, glass fiber, and aluminum, using the service conditions and cylinder properties from Table 2.1.1. The Type 1 aluminum tank weighed 30 kg, and the glass fiber reinforced Type 4 tank weighed 31 kg. A similarly designed carbon tank would weigh about 11.35 kg. The carbon tank would have a diameter of 440 mm, a length of 950 mm, a volume of 120 L, and a service pressure of 60 bar. The carbon fiber design could be reduced in weight to 8.6 kg if the HDPE liner could be replaced with a resin coating that would not crack or craze at during operation including when exposed to a temperature of 80K.

Table 2.1.1: Service conditions and nominal cylinder properties

	Phase 2 start	Phase 2 end
Service Pressure	200 bar (2900 psi)	60 bar (870 psi)
Gas Settling Temperature	15°C (59°F)	80°K (-315°F)
Maximum Fill Pressure	250 bar (3625 psi)	75 bar (1088 psi))
Service Life	20 years	20 years
Gas Fill Temperature Limits		80 to 160°K (-315 to -171°F)
Operating Temperature Limits (environment)	20 to 373°K (-423 to 212°F)	80 to 355°K (-315 to 180°F)
Proof Test Pressure	300 bar (4350 psi)	90 bar (1305 psi)
Minimum Rupture Pressure	450 bar (6525 psi)	120 bar (1740 psi)
Cylinder Diameter	543.3 mm (21.4 inches)	440 mm
Cylinder Length (unpressurized)	1600 mm (63.0 inches)	950 mm
Cylinder Empty Weight (excluding hardware)		10 kg (22 lbs)
Cylinder Volume		120 L (7323 cu. in.)

Milestone accomplished: Updated baseline design was documented.

Task 2.2 Continue evaluation of improvements

The objective was to continue evaluation of potential material, design and process improvements based on Phase 1 results and input from project partners.

Type 4 pressure vessel

A dome mold was ordered to enable the manufacturing of a subscale Type 4 pressure vessel. The tank was built with the specifications as shown in Table 2.2.1 and was intended to be used for testing at cold temperatures as well as allowing HSECoE partners to place media inside the vessel for further testing. The pressure vessel was designed in collaboration with the project partners, and once testing was completed at Hexagon to confirm the performance of the tank, several pressure vessels were distributed to UQTR, SRNL, Ford, PNNL, JPL and DOE. In Q1 of 2012, 21 of the Type 4 tanks were fabricated. Dimensions and materials are given in Table 2.2.2. Three were burst tested to confirm strength, and three were subjected to cold (LN2) temperatures to develop handling procedures during the time the vessel was being cooled. Two vessels were successfully cooled to LN2 temperature and returned to ambient without apparent damage to the liner. A procedure was written and distributed to HSECoE partners along with the vessels. The procedure can be found in Appendix A (SB 12-04-002).

Table 2.2.1: 6-liter Type 4 tank specifications requirements

Dimension	Value
Design Pressure	200 bar
Max operating pressure	250 bar
Min operating pressure	Vacuum, < 1e-5 torr
Internal liquid volume	~6 liters
Internal liner ID	16.6 cm (6.54 in)
Length/diameter ratio	2:1 aspect ratio
Temperature Range	20°K to 373°K

Table 2.2.2: Actual dimensions and materials of 6-liter Type 4 tank

ID	166 mm
OD (liner)	174 mm
OD (tank)	183 mm
Overall length	372 mm
Boss opening	60.7 mm
Volume	5.68 liters
Fiber	T700-24K
Resin	Epoxy
Liner	HDPE
Bosses	6061 Aluminum

Figure 2.2.1 shows a picture of the completed 6-liter Type 4 pressure vessel. Figure 2.2.2 shows the liner made of injection molded HDPE and associated end bosses. Figure 2.2.3 shows the model and finite element stress analysis for the pressure vessel

Figure 2.2.1: 6-liter Type 4 pressure vessel

Figure 2.2.2: Liner used in the 6-liter Type 4 tank

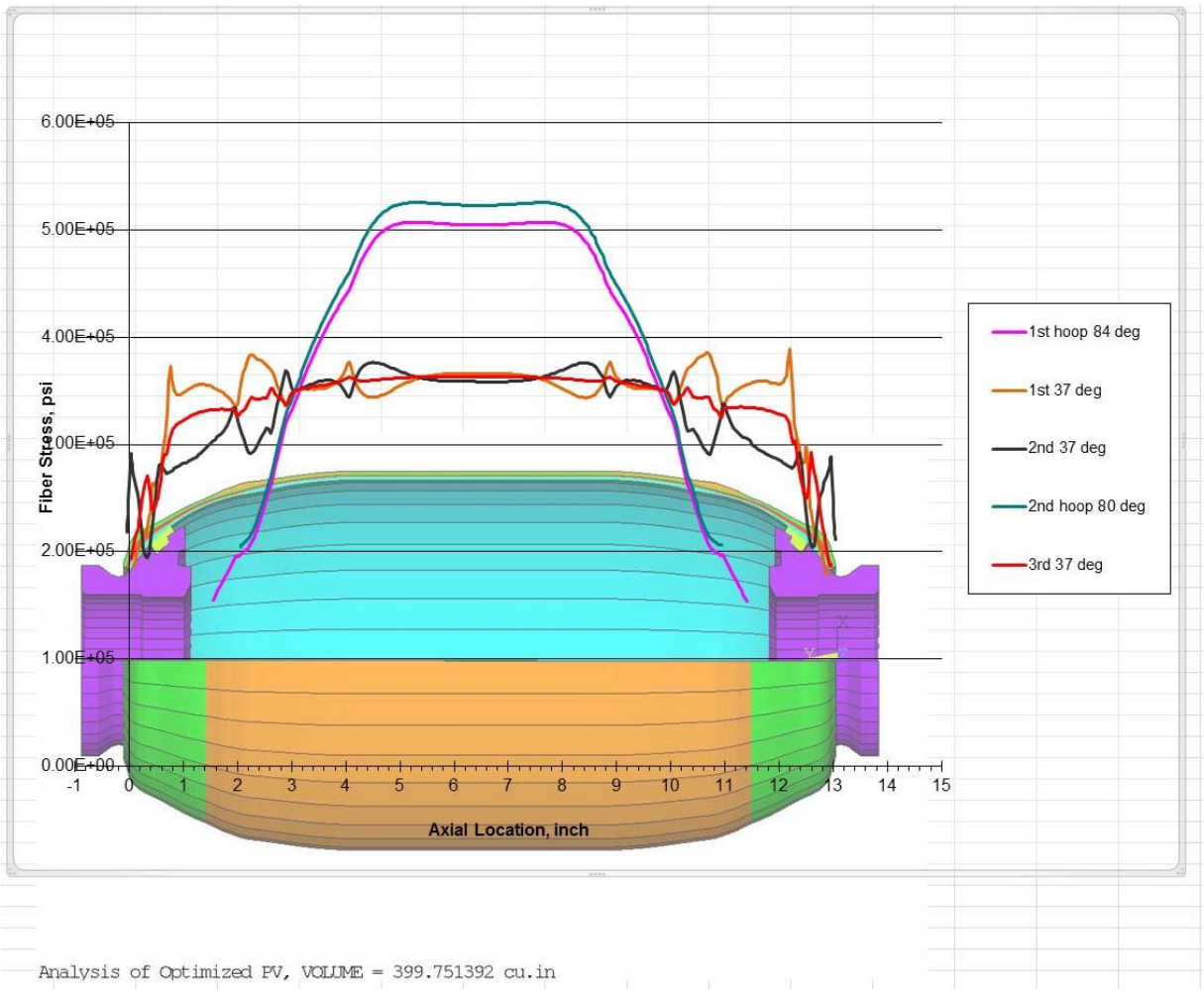

Figure 2.2.3: Stress analysis on the Type 4 vessel

Alternative options for 6-liter tank

A Type 3 design using a stainless steel liner and the same dimensions has been looked at also. It was designed to use the same fiber patterns as the Type 4 tank, and the liner would be made of two halves that would be welded in the center of the liner and that would be entirely wrapped with carbon fiber. An alternative option that was evaluated was a Type 1 tank made out of stainless steel that would have a flange in the middle (two halves bolted together). The excess weight would limit the usefulness of the tank though. The HSECoE team considered the pros and cons for those two options and decided that neither would offer enough benefits and was therefore discarded for the purpose of this task, and the designs were never manufactured.

Four additional Type 4 tanks were made but with a thinner laminate. The reason for these was that JPL would not have been able to do cryogenic bursts on the other tanks due to the pressure limit for their cryogenic burst system. Reducing the laminate resulted in lower burst pressures that would have worked for JPL. However, due to some financial issues at JPL, they ended up not testing the tanks and an alternative source for testing was found later.

Type 1 aluminum vessel

Due to HSECoE's need to have a large opening in the tank in order to accommodate hardware and adsorbent materials being inserted inside the tank, a 3-piece aluminum tank was designed, which would be able to open up, therefore offering a 100% diameter opening. This tank was smaller than the Type 4, at only 2 liters of internal volume. That decision was made by HSECoE partners collectively due to the high cost of the adsorbent materials, hence it was much more cost effective to have a smaller subscale unit. The tank was made out of 6061 aluminum and was designed for a 100 bar service pressure with a 2.25 minimum safety factor. The specifications are shown in Table 2.2.3 below. Initially, there were a variety of designs looked at based on volume (2, 3, 4 or 6 liters) and pressure (60 bar and 100 bar). In the end the decision was made to move further with a 2 liter tank at 100 bar. Figure 2.2.4 shows the assembled 3-piece Type 1 tank. Figure 2.2.5 shows the same tank with the components disassembled.

Table 2.2.3: 3-piece aluminum Type 1 tank specifications

Overall length	10.867 in
Collar OD	6.165 in
Cylinder OD	4.848 in
Wall thickness	0.220 in
Volume	2 liters
Service pressure	100 bar
Actual burst pressure (as tested)	370 bar
Ports	1-1/8"-12

Figure 2.2.4: 3-piece Type 1 tank, assembled

Figure 2.2.5: 3-piece Type 1 tank, disassembled

Testing

Cryogenic tests were outsourced to Cimarron Composites in Q1 2013. A Type 1 tank was sent for a cycle-burst test and one Type 4 tank was sent for a burst test. The Type 1 tank was subject to 200 cycles from 0 to 100 bar using LN2, after which it was burst. The burst pressure was 460 bar (6675 psi), which was expected at 80 K compared with a burst pressure of 372 bar (5400 psi) tested previously at room temperature.

The Type 4 tank was similarly cooled down with LN2 and pressurized to burst, however the liner cracked at 283 bar (4100 psi) and therefore unable to achieve a burst. A replacement tank was then sent for another attempt. In order to prevent the liner from cracking again, the procedure was changed. The tank was pressurized to 138 bar (2000 psi) at room temperature and held for 24 hours. It was then gradually cooled to 77 K while maintaining 138 bar (2000 psi) pressure. Once temperature was stable, the pressure was ramped at a rate of approximately 41 bar/min (10 psi/sec.) Unfortunately, the liner cracked again, this time at around 228 bar (3300 psi). Further work for looking into solutions to prevent the liner from cracking at cryogenic temperature would continue in Phase 3 in parallel with other tasks.

Material testing

Several alternative liner materials were looked at to evaluate properties at ambient and cold temperatures. Impacts tests were performed for HDPE (the standard current liner material), modified EVOH (samples A, B, and C), HDPE with nano-additives, PA, and PTFE. Dog-bone shaped samples were used, and the impact speed was around 2.5 m/s. The energy shown in Figure 2.2.6 provides relative values only, for the purpose of comparison, hence there are no units listed. From the materials tested, HDPE showed the best cold/cryogenic properties.

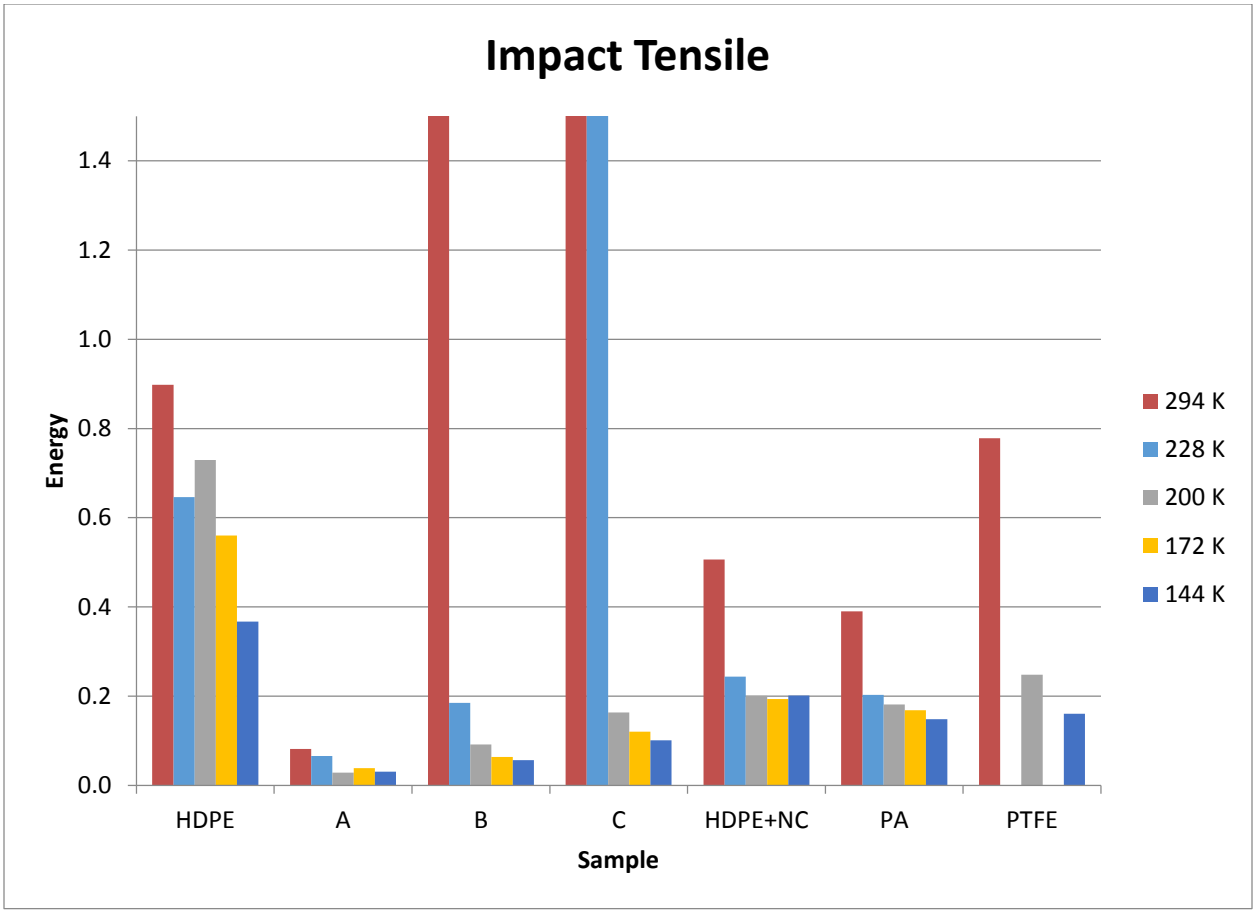

Figure 2.2.6: Impact testing comparison of alternative liner materials

Resin tensile properties were also tested at cold temperature and compared to the properties at ambient temperature. The cold temperature at which they were tested was – 80 degrees F (210°K). As seen in Table 2.2.4, the ultimate tensile strength was a little over 4% lower than at ambient temperature, and the elongation almost 30% lower. Due to that, and the slight loss in strength at cryogenic temperatures of carbon fiber, it is expected that a Type 4 pressure vessel would perform slightly lower at such low temperatures, however at this point the liner is still the limiting factor due to brittleness and cracking issues.

Table 2.2.4: Resin tensile testing, room temp vs cold (-80°F)

	Sample #	UTS (psi)	Elongation (in)	
Room Temp	6	14198	0.29	
	8	14161	0.29	
	10	14292	0.29	
Cold	1	13678	0.19	
	9	13623	0.2	
	11	13464	0.22	
Avg RT UTS	14217		**Avg RT Elong.**	0.29
Avg Cold UTS	13588		**Avg Cold Elong.**	0.203
% difference	4.4%			29.9%

Lab capability upgrades

In 2012 Hexagon Lincoln purchased an Instron impact test machine for the R&D lab to improve the lab's capabilities of testing materials. The machine offers a much greater variety of options that can be used for material testing, as well as better accuracy and control in eliminating variables during testing so that better data can be acquired.

Milestones accomplished: Promising engineering concepts were updated. Proposed technology was demonstrated on a subscale test unit. Phase 2 evaluations of design, material, and process improvements were reported on.

Task 2.3 Prepare for GO/NO-GO decision

The objective of this task was to evaluate the design concepts identified in Task 2.2 against the requirements of the project to confirm that they will be able to meet said requirements, including the ability to meet DOE objects. This was also a preparation for the Go/No Go decision.

A Tech Team review meeting was supported in Southfield, MI at USCAR offices on March 20-21, 2013. Phase 2 activities from the previous tasks were presented, including a comparison of preliminary designs of 60 and 120 L tanks, shown in Table 2.3.1, and results of cryogenic testing on Type 1 and 4 lab prototype vessels. The decision was made following the meeting to go for Phase 3 using adsorbent systems.

Table 2.3.1: Full scale design comparison

Tank	Material	Pressure (bar)	SF	OD (mm)	OAL (mm)	Volume (liter)	Weight (kg)	PV/W
1	Carbon	60	2.25	440	950	120	11.35	634
2	Carbon	60	2.25	390	640	60	5.73	628
3	Glass	60	3.5	400	660	60	15.36	234
4	Glass	100	3.5	410	660	60	26.16	229
5	Carbon	100	2.25	390	640	60	8.16	735
6	Aluminum	60	2.25	390	640	60	16.36	220
7	Aluminum	60	2.25	440	950	120	30.00	240

Carbon Type 4 tanks have the highest performance (Pressure x Volume/Weight). Glass and aluminum tanks are close in performance, but much lower than the carbon tanks. The issue with glass is the poor stress rupture characteristics, and because of that they are required to have a 3.5 safety factor, which means more material and higher weight and cost. Aluminum tanks can be improved by choosing a different alloy and controlling the strength properties of the material, however that will likely make the cost increase as well.

Milestones accomplished: updated design concepts were evaluated and reported on.

Task 2.4 GO/NO-GO sub-scale prototype selection

The objective was to select a sub-scale prototype design that can be used in Phase 3 to confirm the ability to meet DOE performance requirements.

The decision was made that Phase 3 activity would be focused on adsorbent materials, specifically MOF-5. The operating pressure would be 100 bar, and the operating temperature range would be 80°K to 160°K. Sub-scale prototypes would be designed to meet these conditions.

The 3-piece, Type 1, 2-liter tank design was selected as the baseline test unit for Phase 3. This choice was made to minimize risk associated with performance of the prototype tank (avoiding issues with cryogenic performance of polymer or metallic liners), and maximize the ability of HSECoE partners to be able to evaluate components that would be inserted into the tank (multi-piece construction to allow disassembly and re-assembly), while also keeping costs lower due to the small volume of the tank.

Milestones accomplished: Design concepts were evaluated, and baseline design summarized (above); likelihood of composite container meeting system and DOE objectives requires higher level evaluation including incorporation of other HSECoE Partner's components and storage media.

Task 2.5 and 2.6 Project Management and Reporting

All HSECoE face-to-face and Technical Team Meetings were attended and presentations made. SSAWG teleconferences were supported. Annual Merit Reviews were attended and presentations made. Input was made to Phase 2 HSECoE report.

Phase 3

Task 3.1 Risk Assessment and Mitigation

To mitigate risk from using Type IV pressure vessels for hydrogen storage in a full-scale configuration, use of a toughened resin system was proposed to improve durability and reduce susceptibility to impact damage. Epoxy resin toughening agents can be classified into two separate categories: soft segment rubber toughening, and hard particle toughening. From these two categories, a variety of different chemistries are available. For example, some products contain a toughening agent dispersed in an epoxy resin, while some hard particle toughening agents are available in pure powder form, while some rubber based toughening agents are available as a pure liquid rubber, which will phase separate upon curing the resin. During candidate material selection, care was taken to ensure both rubber based and hard particle based toughening agents were included for testing, as well as having a variety of chemistries available from both overall categories.

Candidate materials

Candidate materials chosen for testing were, in addition to the baseline system: core shell rubber particles dispersed in an epoxy resin, an amine terminated butadiene-acrylonitrile rubber in pure form (ATBN), nano-silica particles which were pre-dispersed in an epoxy resin, surface modified silica in powder form, titanium dioxide in powder form, and a pure liquid rubber which phase separates upon curing of the resin. All toughening agents were blended into the resin at manufacturer recommended loading.

Initial materials screening

The first phase of testing was a materials screening, using tests that are relatively quick and inexpensive, and was intended to screen out any materials which are not compatible with the filament winding process, or are incompatible with required service temperatures. The two tests chosen were measuring the glass transition temperature by DSC, and measuring room temperature (23°C) viscosity of the resins. These two properties were chosen, because toughening technologies can have adverse effects on these two properties. Rubber based toughening technologies have a tendency to decrease the glass transition temperature, and blending in a high viscosity toughening agent will increase the overall viscosity of the resin mixture. Any materials not meeting the minimum glass transition temperature of 105°C, or exceeding the maximum allowable room temperature viscosity of 2500 cP were to be disqualified from further testing, in order to maximize resources on those materials that meet the requirements.

Neat resin testing

The second phase of testing was evaluation of neat resin coupons. Each resin formulation was cast into 1/8” thick sheets, and then test specimens were machined to the desired geometry using a three axis CNC mill. Tests chosen were tensile testing (ISO 527), and a three point impact test. An example of a tensile specimen used for testing is shown in Figure 3.1.1. The setup of the three point impact test is shown in Figure 3.1.2. The dimensions of the impact test specimen were 125 mm x 12.7 mm x 3.2 mm. A Charpy tip was used as the impact tool, and a total carriage mass of 20.3 kg was dropped to achieve a 3.0 m/s velocity at impact, to give a total impact energy of 91.4 J. The properties measured were total energy to break the sample, peak force during impact, and total displacement of the sample. After

testing was completed, the four best performing toughened resin systems, along with the baseline, were selected to continue into the next phase of testing.

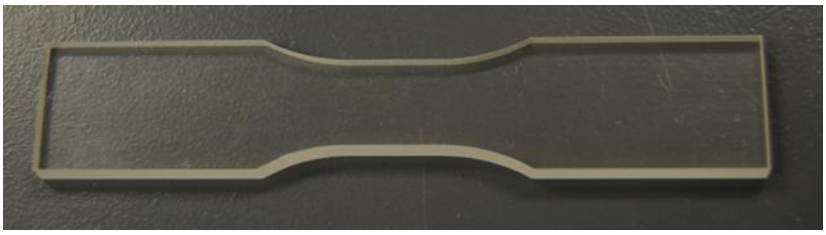

Figure 3.1.1: Neat resin tensile test specimen

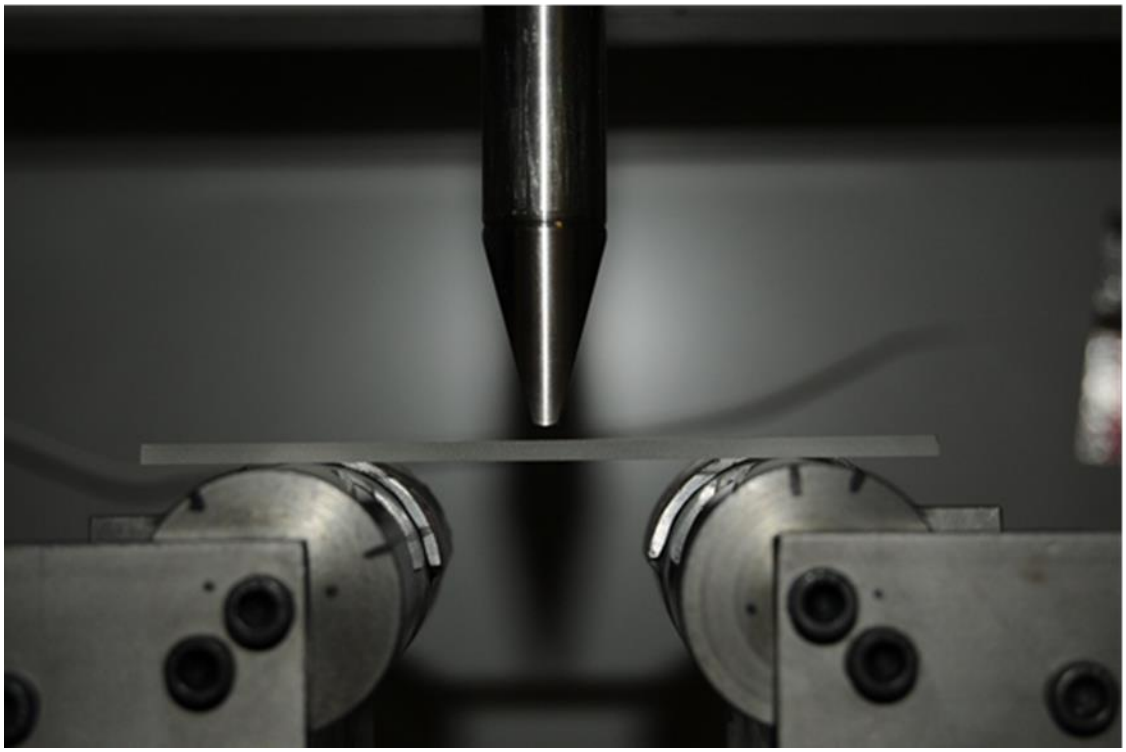

Figure 3.1.2: Three point neat resin impact test setup

Composite coupon testing

After testing of neat resin coupons, the behavior of the toughened resins as used in a composite was investigated, using hoop wound rings as test specimens. Carbon fiber composite rings were produced by winding hoop patterns around a steel mandrel, with a single tow of fiber. In order to isolate the effects of the resin on the performance of the composite, the same lot of carbon fiber was used for production of all rings across all resin formulations. Arcs were cut from rings for short beam shear evaluation in accordance with ASTM D2344, as well as for a three point composite impact test. The same impact fixture and impact tip was used for the composite impact as those used for the neat resin coupon impact. An impact velocity of 2.8 m/s was used, with a 30 kg total mass, giving an impact energy of 117.6 J. The short beam shear test fixture with test sample is shown in Figure 3.1.3, and a composite impact test specimen is shown in the support fixture in Figure 3.1.4. Sections of rings were also taken

for constituent content analysis by matrix digestion in accordance with ASTM D3171, Method I, Procedure B, in order to evaluate the consolidation of each resin into the composite. The remaining rings were evaluated for burst strength in Hexagon Lincoln's hydraulic burst fixture. The assembled burst fixture is shown in Figure 3.1.5, and a burst ring after completion of test is shown in Figure 3.1.6.

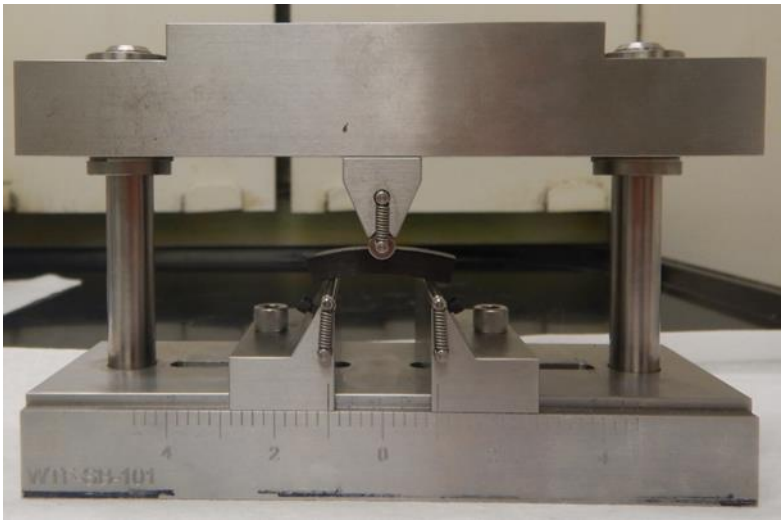

Figure 3.1.3: Short beam shear test fixture with test specimen

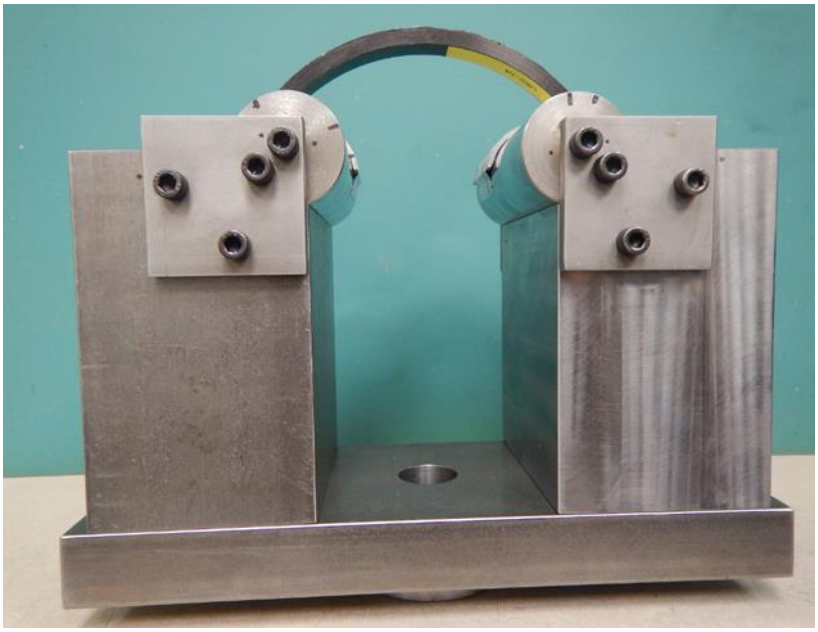

Figure 3.1.4: Composite impact test specimen and fixture

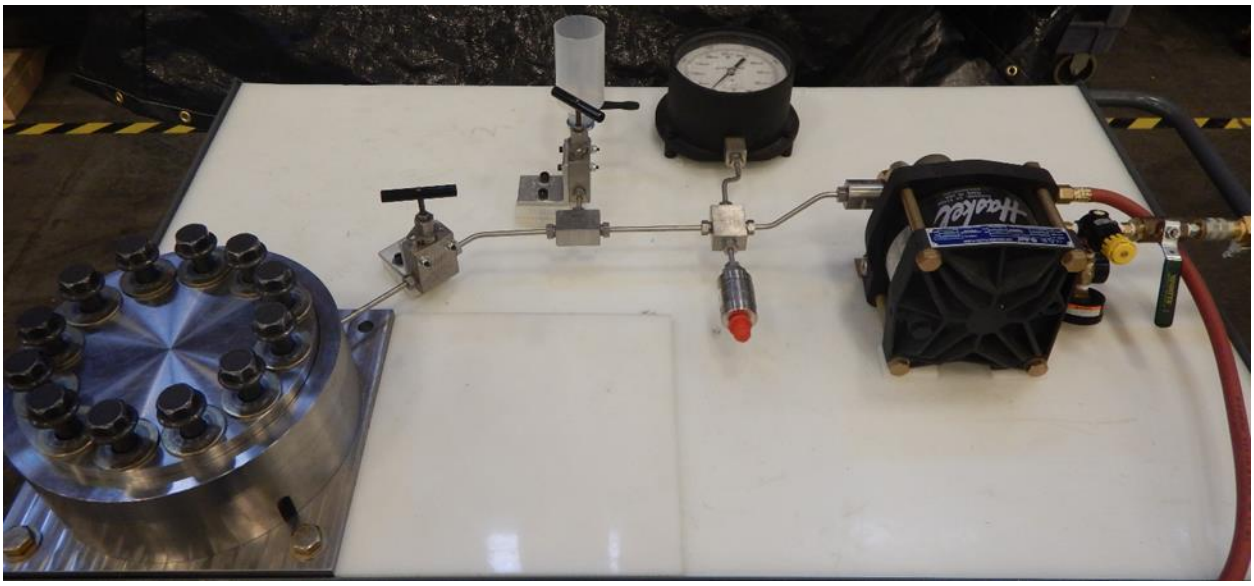

Figure 3.1.5: Hexagon Lincoln hydraulic ring burst fixture

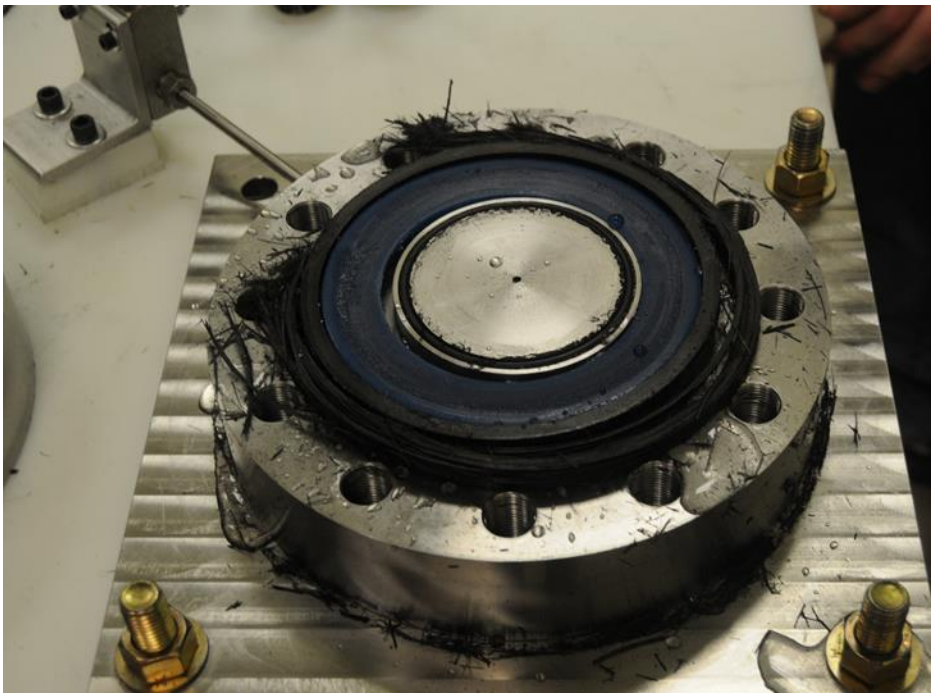

Figure 3.1.6: Burst composite ring after testing

Tank testing

Following the ASTM ring testing, subscale tanks were wound to test the performance of a tank made with the toughened resins. Along with the baseline, the best performing resin system from each category (rubber toughening vs. hard particle toughening) was chosen to make tanks with. In addition, it was decided to wind tanks with a combination of the rubber toughener and hard particle toughener, to investigate if there was any merit in combining the two technologies. The tanks were evaluated for

burst strength, and burst strength after being impacted with 350 J in the middle of the cylinder. The tip used on the impact tool is shown in Figure 3.1.7. Figures 3.1.8 and 3.1.9 show burst tanks in the as-manufactured condition, and after impact, respectively.

Figure 3.1.7: Impact tip used for impacting tanks

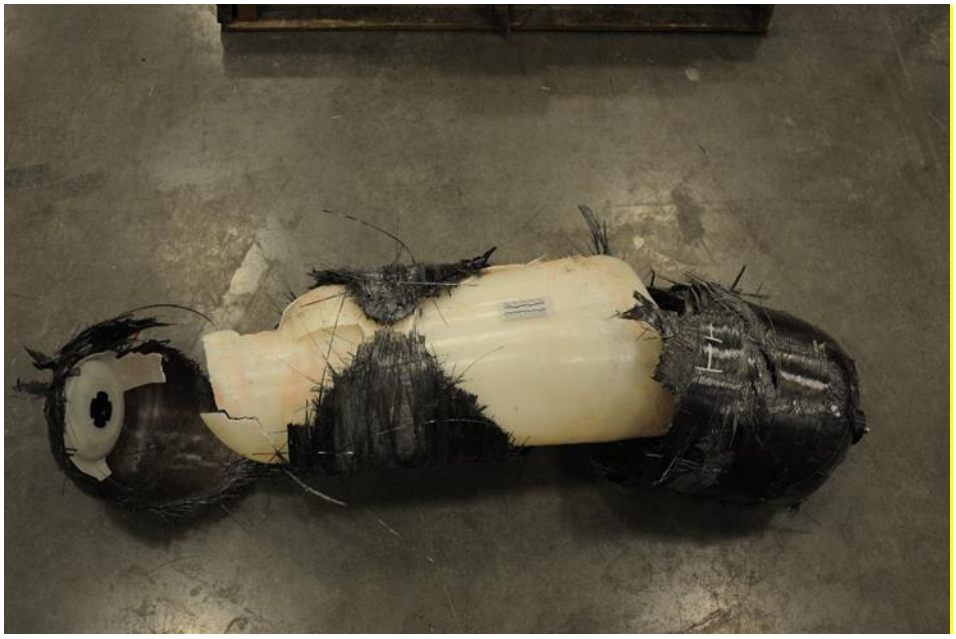

Figure 3.1.8: Tank burst in the as-manufactured condition

Figure 3.1.9: Tank burst after 350 J impact

Initial Material Screening

The results of the initial materials screening are shown in Table 3.1.1. All of the resin formulations were within the allowable limits for viscosity and glass transition temperature, and as a result no resins were removed from testing after the initial screening.

Table 3.1.1: Results from initial materials screening

Material	Glass Transition Temperature (°C)	Viscosity - 23°C (cP)
Baseline	118.3	916
ATBN	116.8	1530
Core shell rubber	118.3	1460
Nanosilica	118.2	1070
Surface modified silica	117.3	960
Titanium dioxide	118.4	930
Phase separating rubber	118.1	1080

Neat Resin Coupon Testing

The results of the tensile testing and three point neat resin impact are summarized in Tables 3.1.2 and 3.1.3 respectively.

Table 3.1.2: Results from neat resin tensile testing

Material	Tensile strength at yield (MPa)	Tensile modulus (MPa)	Strain at break (%)
Baseline	101.1	4264	6.1
ATBN	88.0	3834	5.1
Core shell rubber	90.0	4058	7.3
Nanosilica	101.1	4785	5.7
Surface modified silica	95.5	4544	4.8
Titanium Dioxide	76.0	4374	2.1
Phase separating rubber	86.1	3877	6.8

Table 3.1.3: Results from neat resin three point impact

Material	Total Energy (J)	Peak Force (N)	Total Displacement (mm)
Baseline	1.50	305.6	13.4
ATBN	1.61	258.2	14.7
Core shell rubber	1.89	267.4	16.1
Nanosilica	1.43	309.5	13.5
Surface modified silica	1.19	260.8	12.1
Titanium Dioxide	0.51	188.9	7.9
Phase separating rubber	1.83	288.5	16.5

There are several trends that can be seen from the results of testing neat resin coupons. In general, the rubber tougheners increased elongation at break, while seeing decreases in modulus and tensile strength. Due to the increased elongation at break, the total energy required to break the samples in the three point impact test increased, indicating an increase in toughness. The hard particle tougheners saw an increase in modulus, due to the very hard, stiff particles being dispersed in the resin. The nano-silica formulation retained the same strength, and approximately the same elongation at break. However, the surface modified silica lost strength and elongation at break, and the titanium dioxide material became quite brittle, evidenced by its very low strain at break, and incredibly low energy to fracture in the three point impact. Due to these losses in properties, the surface modified silica and the titanium dioxide were disqualified from further testing.

Composite Coupon Testing

The results from the ASTM ring burst, short beam shear testing, and three point composite impact are shown in Tables 3.1.4, 3.1.5, and 3.1.6.

Table 3.1.4: Results from ASTM ring burst

Material	Burst Pressure (PSI)
Baseline	24724
Phase separating rubber	25086
ATBN	24650
Core shell rubber	25696
Nano-silica	25468

Table 3.1.5: Results from short beam shear testing

Material	Short beam strength (MPa)
Baseline	53.5
Phase separating rubber	47.3
ATBN	50.9
Core shell rubber	54.0
Nano-silica	56.4

Table 3.1.6: Results from three point composite impact

Material	Total Energy (J)	Peak Force (N)	Total Displacement (mm)
Baseline	18.6	2685	35.2
Phase separating rubber	19.3	2721	39.8
ATBN	21.6	2961	38.5
Core shell rubber	23.2	2933	30.0
Nano-silica	20.2	3349	27.5

The largest difference in burst pressure of any rings to the baseline was 3.9%, which falls within one standard deviation of the baseline average. It was determined that the addition of the toughening agents did not have significant effect on the burst pressure, which is mostly controlled by the fiber. The samples prepared with phase separating rubber and ATBN both had a lower short beam strength than the baseline, while the core shell rubber formulation showed no change. The nano-silica modified resin displayed a 5.3% increase in short beam strength.

All specimens made with toughened resin showed an increase in overall toughness, as demonstrated in the three point composite impact test. Total energy required to break each sample was increased from the baseline. The core shell rubber formulation showed the greatest increase in total energy, which parallels the results seen from the neat resin 3 point impact test. The nano-silica formulation increased the toughness of the composite, while also greatly increasing the peak force during impact. It was decided to take the best performing resin system from each category (rubber toughener vs. hard particle toughener) into the tank testing phase, which was the core shell rubber and nano-silica, respectively. In addition, it was decided to test an additional formulation, which was a combination of the core shell rubber and nano-silica materials, to see if there was any benefit from blending the two

materials together, as both materials increased toughness, while the gain in modulus from the nano-silica may offset the loss in modulus from the core shell rubber.

The results from constituent content analysis are shown in Table 3.1.7.

Table 3.1.7: Results from constituent content testing by matrix digestion

Material	Fiber content (Wt. %)	Resin content (Wt. %)	Fiber content (Vol. %)	Resin content (Vol. %)	Void content (Vol. %)
Baseline	67.1	32.9	53.8	40.4	5.8
Phase separating rubber	67.2	32.8	53.2	39.8	7.0
ATBN	69.0	31.0	55.8	38.8	5.4
Core shell rubber	67.4	32.6	54.1	40.5	5.4
Nano-silica	65.2	34.8	52.4	41.1	6.5

The matrix digestion test was performed to ensure that all resin toughening agents did not affect manufacturability of composite parts, and ensure that the fibers were still sufficiently wet out by the resin. While the void content did increase slightly in the case of the phase separating rubber and the nano-silica, the results fell within a fairly narrow range, and no toughening agents were thrown out of consideration on this basis.

Tank Testing

A comparison of the as-is burst pressure and the after impact burst pressure is shown in Table 3.1.8.

Table 3.1.8: Comparison between as-is burst pressure and after impact burst pressure

Material	As-Is burst pressure (PSI)	After impact burst pressure (PSI)	% Reduction in burst
Baseline	10325	6308	39%
Core shell rubber	10410	5134	51%
Nano-silica	10183	6209	39%
Nano-silica + Core shell rubber	10099	5283	48%

All tanks that were burst in the as-wound condition burst within several hundred PSI of the baseline, which indicates little to no change from the baseline. None of the toughening agents were expected to significantly increase the burst pressure in the as-wound condition, but they were expected to improve damage resistance, and maintain a higher burst pressure after impact. However, none of the tanks wound with the toughened resin formulations performed better than the baseline in the burst after impact test. The nano-silica formulation had the same reduction in burst as the baseline, at 39% lower than its corresponding virgin burst, but this result does not show any advantage in using this material over the baseline resin system. The worst performing resin system was the core shell rubber, with a 51% decrease in the burst pressure. These results were disappointing, as all resin formulations

displayed an increase in toughness in the coupon level testing. The highest performing resin system in the coupon testing, the core shell rubber formulation, displayed the worst performance in the burst after impact.

The toughening agents did not improve damage tolerance of pressure vessels, however, several of the toughening agents did show increases in performance of neat resin and composite coupons. These technologies may still show advantages when used in composite pressure vessels, but the formulations may need adjusting to realize the benefits of these materials. In general, the rubber toughening agents tended to show an increase in flexibility, with a greater elongation at break, with a slightly reduced tensile strength and modulus. The hard particle tougheners tended to be stiffer, with an increase in modulus, without losing much in strength. It was also determined that mixing powders in as toughening agents did not provide good results, as demonstrated by the titanium dioxide and surface modified silica particles.

Milestone accomplished: Risk assessment and mitigation related to toughness and impact resistance of the composite laminate were reported (above).

Task 3.2 Scale and design optimization systems

The objective of this task was to design a full scale pressure vessel that would operate at 80°K to 160°K at 100 bar, and support PNNL in designing a full scale, double-wall, vacuum insulated bottle concept tank with LN2 cooling.

Full scale Type 1 and Type 4 tanks were designed based on testing of subscale tanks in Task 3.3, and on the volume required to contain 5.6 kg of usable hydrogen. The required volume for the HexCell/MOF-5 system was 304 liters, while for the MATI/MOF-5 was 264 liters. The value of 304 liters was chosen as the baseline, in part because the HexCell had a lower system cost, and in part because this presented a "worst case" external volume.

Hexagon Lincoln came up with two designs, a Type 1 tank, and a Type 4 tank concept that would be more suitable for cryogenic use, based on work done in Task 3.3. The Type 1 tank shown in Figure 3.2.1 designed to be made out of 6061 aluminum, with similar properties as the 2-liter subscale one. However, this tank would be made out of two halves, which would be joined together by friction stir welding, a process which has been investigated in more detail by PNNL. The reason for making it out of two halves is to facilitate assembly of the internal components, and also because it would help with heat treating.

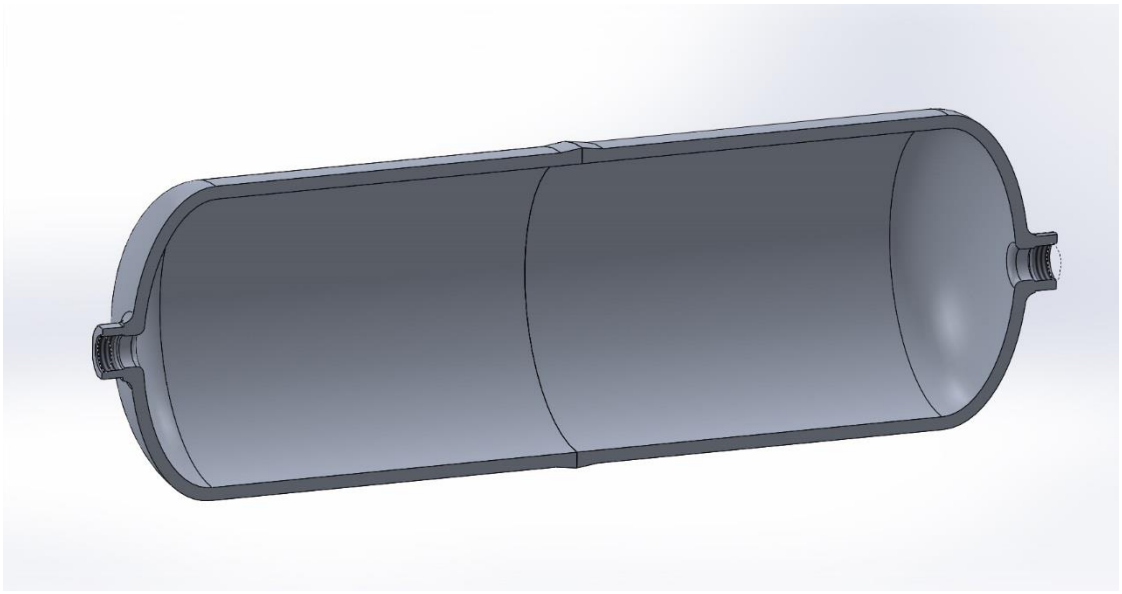

Figure 3.2.1: Full scale Type 1 tank (volume of ~300 liters)

The Type 4 tank, shown in Figure 3.2.2, uses carbon fiber/epoxy composite as its reinforcement, similar to its 2-liter subscale counterpart. The tank would be made with a similar process as the 2-liter subscale, and have a resin liner to limit leakage and permeation. This would allow cold temperature service, as well as maximize the volumetric efficiency by eliminating the traditional polymer liner, and therefore having a larger internal volume. Since this is a design concept at this point, additional consideration may be necessary to determine how to install components into the tank.

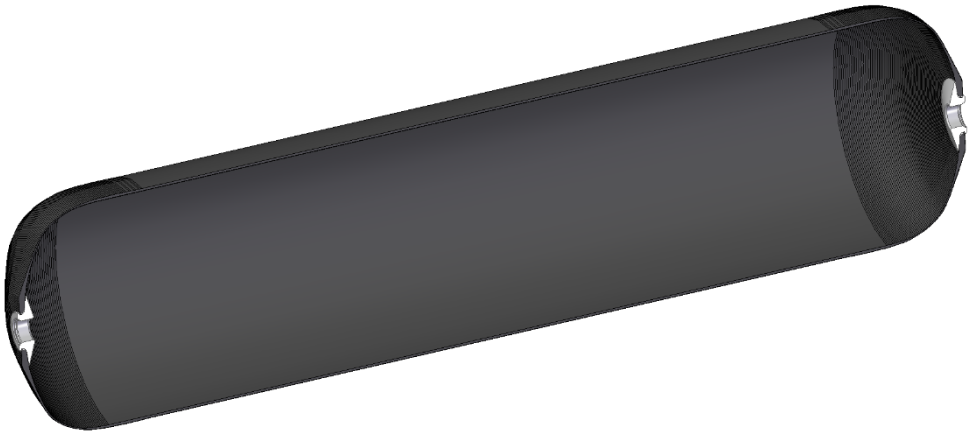

Figure 3.2.2: Full scale Type 4 tank

A Type 3 full scale tank was not designed. Issues with using a Type 3 tank at cryogenic temperatures have not been fully investigated at this point in time, and it is unlikely that it would offer better performance than both a Type 1 and Type 4 full scale tanks.

Table 3.2.1 provides design parameters for the preliminary Type 1 and Type 3 designs. There is room for optimization on both of these if they were actually built and tested. The Type 1 tank weight might

decrease when considering elastic-plastic behavior more carefully, and the weight of the Type 4 tank might increase if more material needs to be added to improve damage tolerance. However, the volumetric density of both designs would not meet DOE goals, causing the tanks to be larger than what OEM's would want to use in a small vehicle.

Table 3.2.1: Type 1 and Type 4 design parameters

Tank design	Type 1	Type 4
Service pressure	100 bar	100 bar
Burst pressure, minimum	225 bar	225 bar
Internal volume	300 L	300 L
Inner diameter	20 inches	19.7
Outer diameter	21.8 inches	20.1 inches
Length	68 inches	65 inches
Wall thickness	0.9 inches	0.2 inches
Weight	390 pounds	55 pounds

Milestone accomplished: Reported on selected vessel designs for full scale systems (above).

Task 3.3 Design subscale systems

The objective was to assess risk associated with implementing the sub-scale and meeting DOE and field performance requirements, as well as means to mitigate risk.

3-piece Type 1 tank

When the decision was made to move on to Phase 3, one of the initial tasks was to re-design the 3-piece Type 1 tank based on input from OSU and some of the other HSECoE partners. OSU requested that the tank have a larger port on one of the domes, and design the port and the fitting for it in such way that the fitting would be inserted from inside. This would allow them to mount the hardware with the MATI adsorbent material to the fitting, then thread the fitting into the dome, and finally assemble the tank.

One of the ports was changed to 2-1/8" – 12 UN port, and the wall thickness of the cylinder was also reduced by 10%, from 5.6 to 5.1 mm (0.220 to 0.200 inches), see Figure 3.3.1. The previous tank had extra margin, so it was possible to reduce the weight of the tank (not counting weight of fittings) and still meet the safety factor with acceptable margin. Weight of the tank was 2.3 kg (5.0 lb), which was about 15% lower than the previous design.

The first tank with reduced weight was burst tested to confirm the design pressure requirements and the burst pressure was 292 bar (4227 psi), after being subjected to 200 cycles from 0 to 100 bar. This was 22% lower than the previous design. Another tank was sent to Cimarron Composites for cryogenic testing. It was also subjected to 200 cycles from 0 to 100 bar using LN2, after which it was burst. The burst pressure was 380 bar (5514 psi), see Figure 3.3.2 well above the required minimum burst of 225 bar. The increase in burst was expected due to the higher strength of the aluminum at lower temperatures.

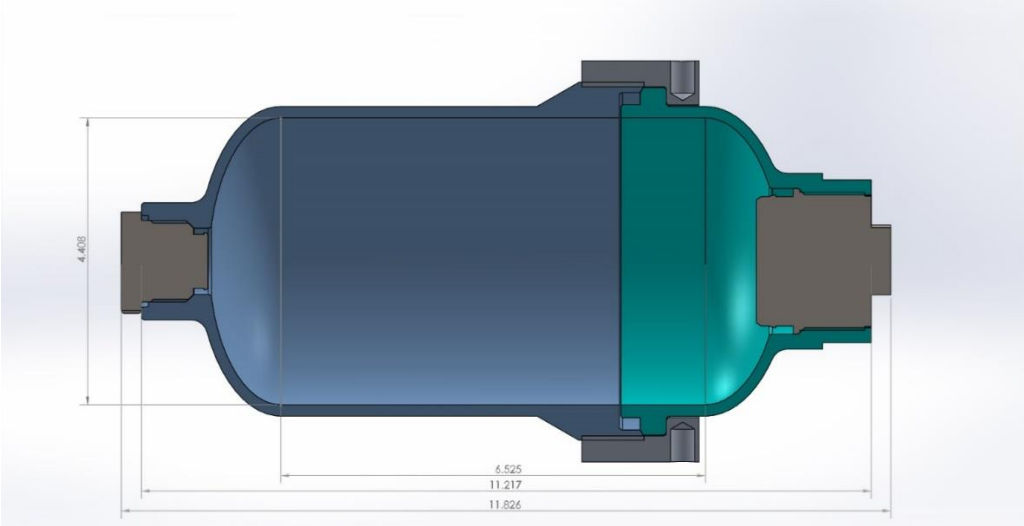

Figure 3.3.1: Cross section of the re-designed 3-piece Type 1 with fittings and overall dimensions

Figure 3.3.2: Test tank burst with LN2. Burst pressure was 380 bar

PTFE insulating liner

HSECoE partners requested a liner that can be used to insulate the subscale tank on the inside when doing cryogenic testing. Several options were looked at initially, and in the end it was decided that the liner would be made out of PTFE, with a thickness of 3.2 mm (0.125 inches) and it would be made out of 3 pieces as well (2 domes and a cylinder portion which would have a slit cut in it axially to allow it to expand or contract along with the aluminum tank), see Figure 3.3.3. Having this liner in the tank would allow the tank to be completely submerged in LN2 for cooling, and then adding heat to drive off the hydrogen in the adsorbent material, without the added heat being absorbed totally by the LN2.

Figure 3.3.3: PTFE liner for the 3-piece aluminum tank next to it

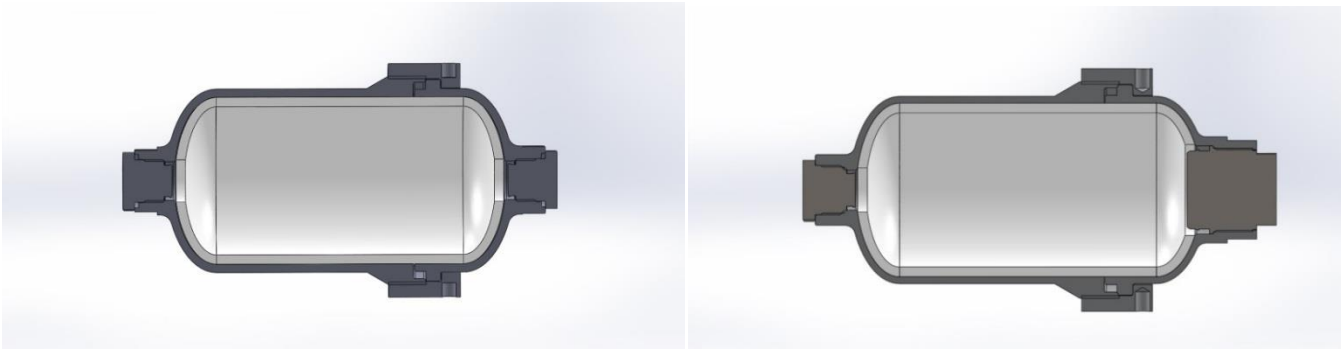

Figure 3.3.4: Cross section of 3D model assemblies showing the PTFE liner inside each of the two 3 piece aluminum tanks

Sealing Issues

With the redesign, there were two types of tanks in use by HSECoE members, which can be seen above in Figure 3.3.4. One had both ports the same size (1-1/8 inch), and the other had a 1-1/4 inch port and a 2-1/8 inch port. The tanks were designed to use spring-energized PTFE seals manufactured by Bal Seal Engineering, see Figure 3.3.5. Those seals were rated for 33°K (-400°F) and similar types have been commonly used in the aerospace industry. Initial testing consisted of 200 room temperature cycles from 0 to 100 bar, followed by a burst test, conducted at Hexagon Lincoln.

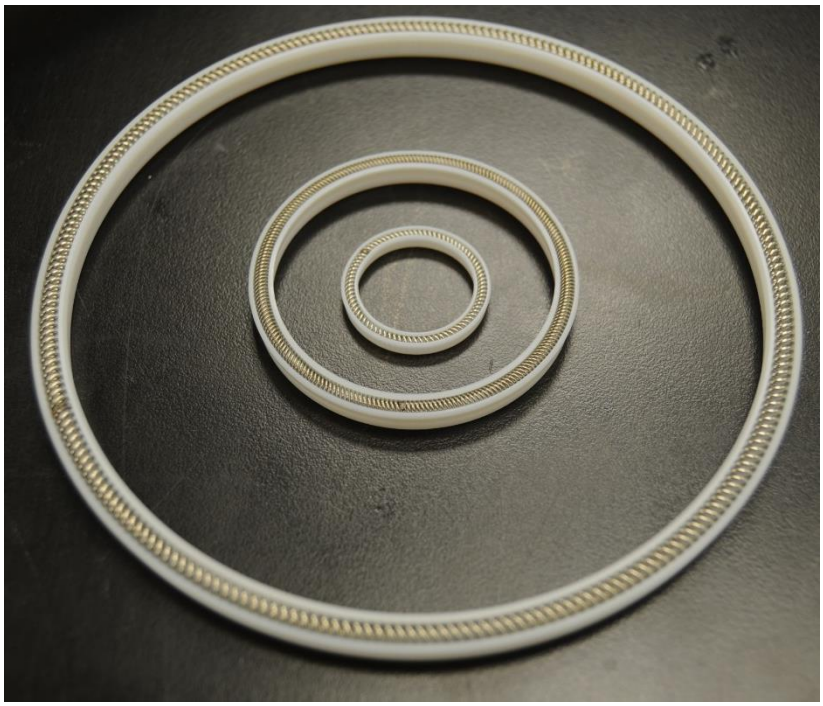

Figure 3.3.5: Cryogenic PTFE seals used in the 3-piece Type 1 tank

Leaks were first observed by UQTR when a MOF-5 filled tank was submerged in LN2 while pressurized to 20.7 bar (300 psi). The tank was leaking from all 3 connections, or seal points. The test was then replicated at Hexagon Lincoln and it was confirmed that there was a leak issue. Hexagon Lincoln, SRNL, and UQTR looked for possible solutions over the course of about 4-5 months in 2014.

UQTR tested out an idea of using a steel washer with gold or indium wire on each side. The idea was that since the wire was much softer, it would be crushed between the washer and the contact points on the tank or the fitting, forming a metal-on-metal seal. Unfortunately, that did not work as expected, and did not solve the leak issue. SRNL tried a similar method, however using a PTFE joint sealant instead of the wire, see Figure 3.3.6.

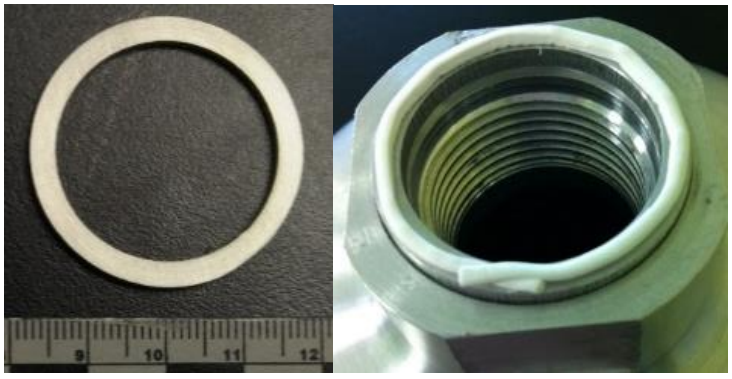

Figure 3.3.6: Left: Aluminum crush seal for the small port end. Right: Teflon sealant applied on the aluminum seal

Hexagon Lincoln managed to seal the small port (1-1/4 inch) by using aluminum crush seals. The seals were made out of 3003 Aluminum, see Figure 3.3.6, which is a very soft alloy, and they were essentially like washers that fit on the fitting, and were crushed in between the fitting flange an the face of the boss. UQTR and SRNL added Teflon sealant gaskets on the aluminum seals, see Figure 3.3.7. They also did not detect any leaks. In order to fix the leak between the two domes (the large seal), Hexagon Lincoln tried multiple things, such as making a soft aluminum crush washer similarly to the small ends. That was unsuccessful, so then the aluminum crush seals were plated with copper, which proved to be unsuccessful as well. Teflon layers were also added to each side of the seal, but that too was unsuccessful. The main problem was that due to the collar design used in the 3-piece tank, it could not be torqued sufficiently to provide enough force to maintain seal of the main body at low temperatures. Other unsuccessful attempts involved using PTFE rings, PTFE wrapped aluminum crush seals, and Plasti Dip coating.

Figure 3.3.7: Teflon sealant on large aluminum seal before compression

A 2-piece stainless steel flange assembly was designed by Hexagon and manufactured, which would allow for more clamping force for the two domes see Figures 3.3.8 and 3.3.9. The clamps were secured by eight Grade 8 bolts, which later on were replaced by A286 bolts after UQTR broke a couple of bolts. The tank was tested using the 2-piece flange assembly with LN2 at 100 bar and no leaks were observed at Hexagon. However, UQTR reported some leaks at 100 bar, and SRNL reported leaks after a few cooling/thawing cycles on the tank.

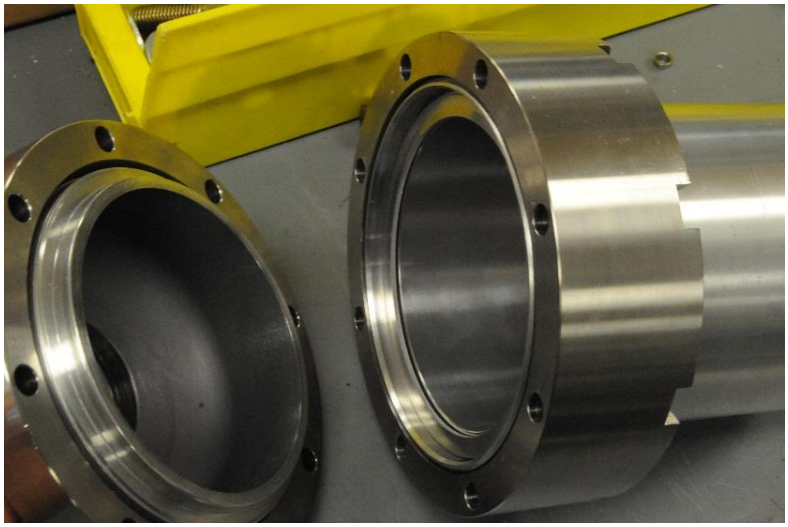

Figure 3.3.8: 2-piece clamp assembly (disassembled)

Figure 3.3.9: 2-piece clamp assembly (assembled)

The large plug from the 2-1/8 inch port was the biggest problem. Due to its design of being inserted from inside, there were not many options to improve its performance. There was no flange that could be used to crush a metal seal, like with the other two. An idea was to make an aluminum cup seal, see Figure 3.3.10, similar to the original PTFE seal. It had to be pushed in place using a press and the fitting had to be modified (machined the step at the base of it to allow the seal to slide on), see Figure 3.3.11. This was unsuccessful, even though after being sprayed with Molykote dry film lubricant, it appeared to not leak. It was deemed to be a marginal solution as the reliability and repeatability of it were questioned, noting that it involved spraying a coating on it, and required a press to be installed, which would not have worked for OSU once the MATI assembly would have been attached to the plug before installing it into the tank.

Figure 3.3.10: Aluminum cup seal for the large port

Figure 3.3.11: Aluminum cup seal installed on modified fitting

Bal Seal Engineering was also contacted during this period of time regarding the sealing issue. They proposed a design revision to all the seals, in which the springs were replaced with stiffer springs. This appeared to work for the small port, but not for the other two. After that, Bal Seal made another revision in which they replaced the seals completely with an approach that used an aluminum reinforcement ring. The new seals did not work either, and in fact they did not even fit on the fittings or in their proper seal cavities due to the reinforcement ring that they added.

Flange tank

Due to the sealing issues experienced with the 3-piece tank, which delayed progress of other HSECoE members on some of the Phase 3 tasks, it was collectively decided that an alternate design approach was needed. That plan involved abandoning the 3-piece aluminum tank, and replacing it with something else that would be more reliable, even if it meant sacrificing weight, ease of use, and other features. After reviewing several options, it was decided that a simple cylinder with flanged ends and flat closures would be designed, see Figure 3.3.12. Twelve bolts would hold the end closures on and flat gaskets would be used. The tank specifications and dimensions can be seen in Table 3.3.1. The gaskets were outsourced from Garlock and they are made out of a knurled steel ring with PTFE rings attached to both knurled surfaces. They are rated for cryogenic applications.

Table 3.3.1: Flange tank specifications

Material	304 Stainless Steel
Inside Diameter	111.8 mm (4.40 inches)
Wall thickness	6.35 mm (0.25 inches)
Flange diameter	177.8 mm (7.00 inches)
Overall length (including bolt heads)	272.5 mm (10.73 inches)
End plate thickness	19.05 mm (0.75 inches)
Total weight	16.8 kg (37 lbs)
Volume	2.1 liters

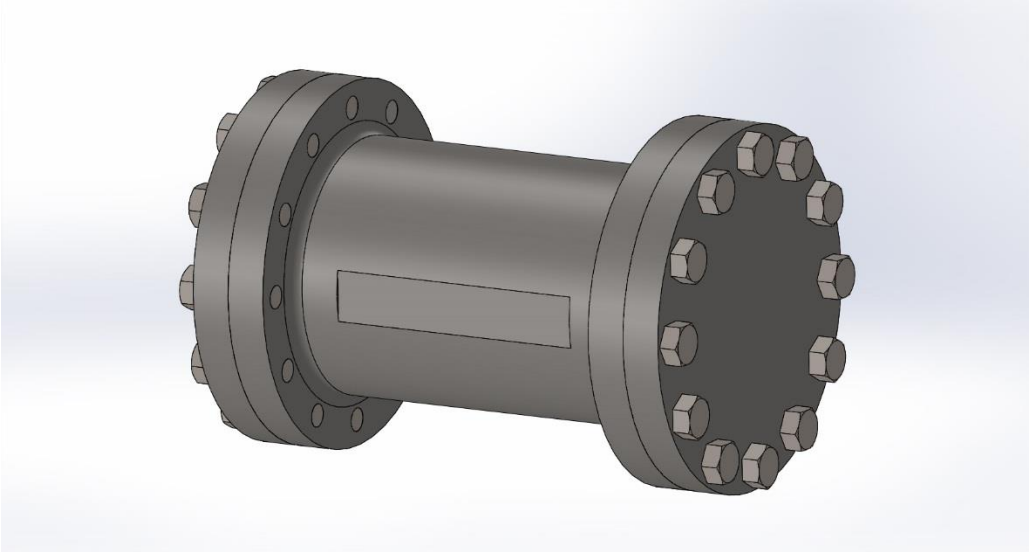

Figure 3.3.12: Flange tank model

Testing done at Hexagon Lincoln consisted of cycle/burst, as it was done for the 3-piece tank in order to confirm safety, and a leak test at 100 bar at 77°K to check leak rate. The flange tank did not show any significant leaks and it did not burst either. It leaked before burst, at around 190-200 bar (2800-2900 psi). Cimarron Composites was also unable to burst the tank with LN2 for the same reason. It leaked at about the same pressure as that tank tested at ambient temperature. The flange tanks were distributed to SRNL, UQTR, and OSU in October 2014, along with spare gaskets, end plates, and PTFE liners made specifically for this design, similar to the ones made for the previous Type 1 tank design.

Monolithic type 1 and type 3

Part of the SMART milestones included the design and development of monolithic Type 1 and Type 3 tanks. The design of the one-piece Type 1 tank and the Type 3 liner were finalized in Q3 of 2014. The metal parts were ordered from Samtech International, and they were delivered at the end of 2014. Both

tank designs had about a 2-liter volume and they were shaped similarly to the inside profile of the 3-piece Type 1 tank. There were some differences in the domes though, due to the manufacturing process used to make them, and the bosses were smaller (3/4 inch-16 AS5202 ports).

Table 3.3.2 shows a comparison in weight between all the subscale tanks used in Phase 2 and 3. The 1-piece Type 1 tank cross-section is shown in Figure 3.3.13. The liner cross-section of the Type 3 tank is shown in Figure 3.3.14. Figure 3.3.15 shows a wound Type 3 tank.

Table 3.3.2: Weight comparison between subscale tanks

Vessel	Wt. (lb)	% weight, compared with vessel 1
1) T1 (1st 3 piece)	5.9	n/a
2) T1 (2nd 3-piece)	5.0	84
3) T1 (1-piece)	3.0	51
4) T3	2.23	38

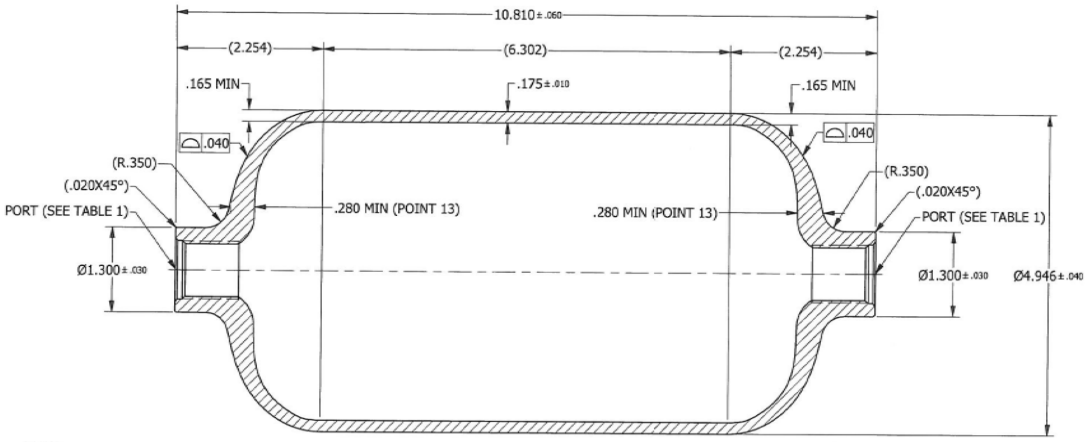

Figure 3.3.13: Cross section of monolithic Type 1 tank

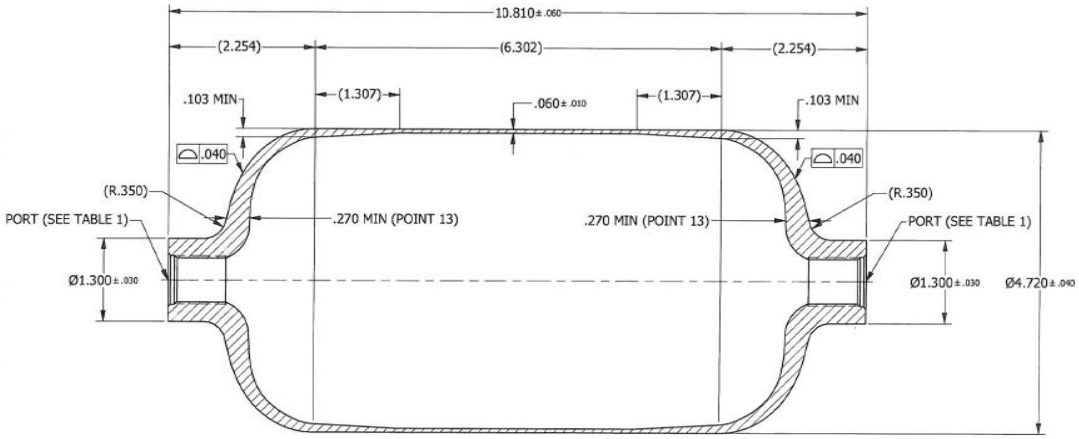

Figure 3.3.14: Cross section of monolithic Type 3 liner

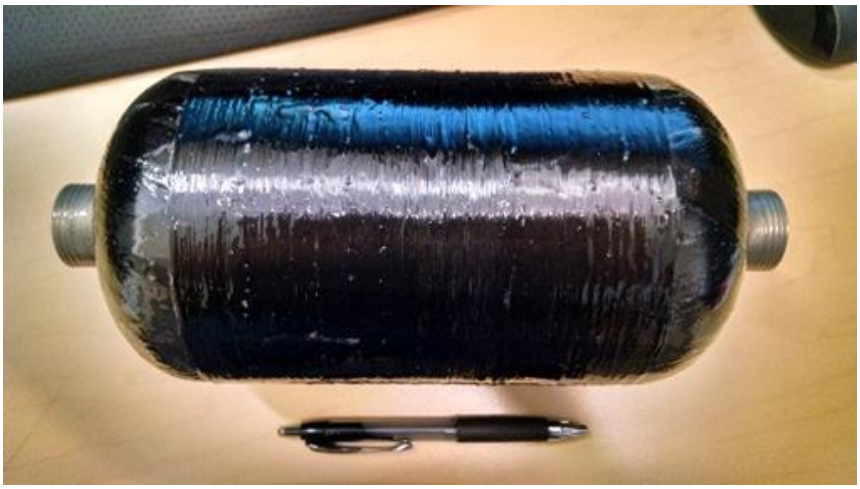

Figure 3.3.15: Type 3 tank

The first Type 3 tank that was wound was burst tested to confirm safety. The tank burst at 318 bar (4615 psi), well above the minimum requirement. A bare liner was also tested to see how much load the liner alone can take. It burst at 102 bar (1480 psi). A Type 1 tank was also burst tested, however the tank did not actually burst. It reached 275 bar (4000 psi), at which point it had yielded and leaked significantly, not allowing the pressure to increase any higher.

Two Type 1 and two Type 3 tanks were then sent to Cimarron Composites for cryogenic tested. One of each of the tanks was burst tested with LN2, and the other two were cycled with LN2 from 0 to 100 bar 200 times, after which they were burst. The Type 1 tanks burst at around 365 and 367 bar (5293 psi and 5316 psi) respectively, while the Type 3 tanks burst at 360 and 368 bar (5224 psi and 5340 psi) respectively. The increased burst pressure was expected due to the increase in the strength of the material at low temperatures. Figure 3.3.16 shows the Type 1 tank after the cryogenic burst test, while Figure 3.3.17 shows the Type 3 tank after the cryogenic burst test.

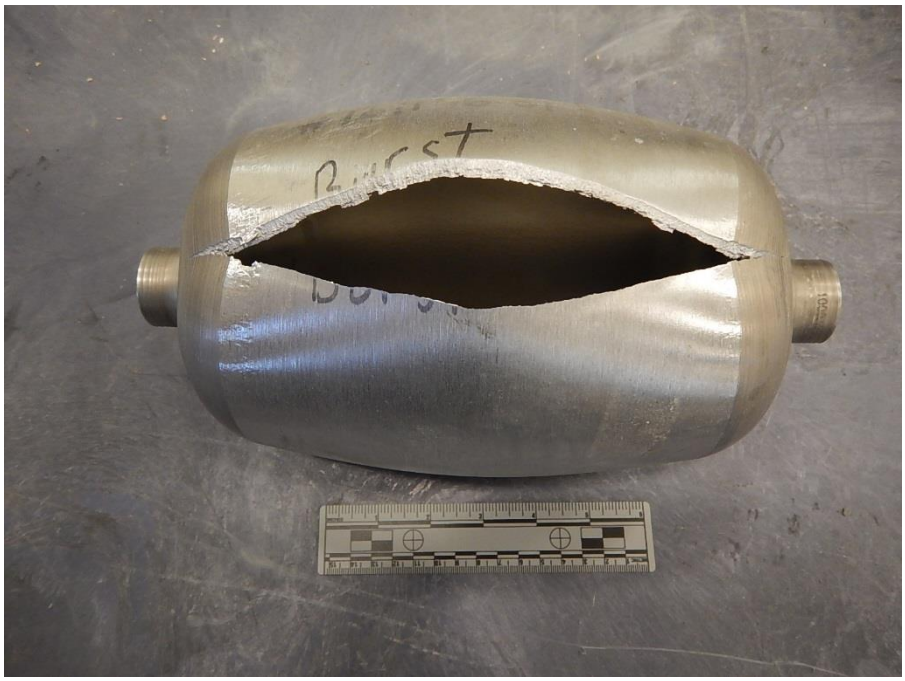

Figure 3.3.16: Type 1 tank after cryogenic burst test

Figure 3.3.17: Type 3 tank after cryogenic burst test

Type 4 tank with resin liner

Type 4 tanks tend to have liner issues at cryogenic temperatures. HDPE is brittle at cryogenic temperatures, and the differences in coefficient of thermal expansion between the liner and composite

causes issues. Other liner technology has been demonstrated to contain H_2 especially at lower temperatures and lower pressures. The development for this project is focused on a liner solution using an epoxy resin material. Experiments are conducted with two types of specialized epoxy resins for the liner and two types of materials used as a carrier for the resin. Carbon fiber and general purpose epoxy resin are used for the tank laminate structure. Two types of removable mandrel materials are used in this project.

While a resin liner may not have the resistance to permeation that a molded polymer has, the driving force for permeation at cryogenic temperatures is reduced as shown by the Arrhenius rate equation. Considering the difference in permeation rates at 80°K to 160°K, versus permeation at 290°K, the key issue is to have a liner that does not leak.

The Type 4 tank was designed to the same criteria for pressure and temperature as the Type 1 and Type 3 tanks discussed above. The mandrel was designed to have essentially the same contour as the metal liner for the Type 3 tank above.

Mandrel options

Two mandrel concepts were used for this program. One was a 3D-printed mandrel, shown in Figure 3.3.18, the other a cast mandrel made from a plaster material, shown in Figure 3.3.19. The tooling for casting the mandrel is shown in Figures 3.3.20 and 3.3.21. Both mandrel concepts made use of soluble materials that could be washed from the inside after the liner and structural composite layers were cured.

Figure 3.3.18: 3D printed mandrel

Figure 3.3.19: Cast mandrel from plaster

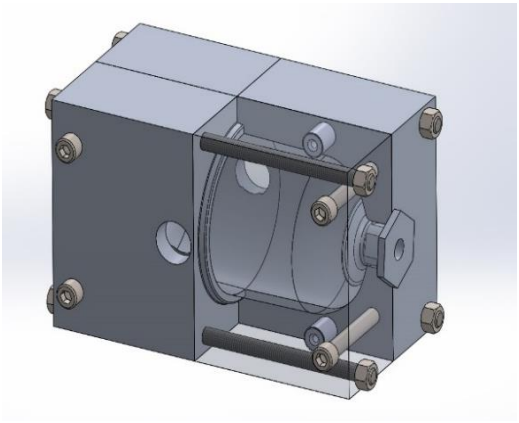

Figure 3.3.20: Solid model of liner casting tooling

Figure 3.3.21: Assembled liner casting tooling

Materials summary

The resin material used for the liner was one of the toughened resin systems discussed in Task 3.1. Two carriers were used for the resin material, a scrim cloth consisting of a synthetic polyester veil, and a braided e-glass material, which were applied over a gel coat on the mandrel. Figures 3.3.22 and 3.3.23 show the polyester veil and e-glass as applied on a mandrel. Infra-red heaters were used to advance the gel coat/liner prior to winding the structural composite.

Figure 3.3.22: Polyester veil with liner resin on soluble mandrel

Figure 3.3.23: Braided cloth with liner resin on soluble mandrel

The composite overwrap consisted of the standard carbon fiber/epoxy resin matrix that has been used for most of the program. The end bosses are machined from stainless steel or aluminum. Figure 3.3.24 shows a completed tank.

Figure 3.3.24: Completed tank with resin liner

Tank manufacture and testing

A total of nine tanks have been fabricated using various combinations of mandrels and carrier materials. Both mandrel approaches have been successfully demonstrated, as have both of the carrier materials. There has been some development of the process of applying the liner resin and carrier, and some development of how the boss is incorporated. Although initial tanks had leaks, the process was updated so that later tanks did not leak.

Tanks were tested at low pressure, less than 10 bar, for leakage. Tanks that passed the leak test were subjected to a proof test at 150 bar (2175 psi) before being subjected to further pressure testing.

Permeation measurements were made on three tanks. Testing was conducted with 100 percent hydrogen at 4.1 bar (60 psi). The first tank permeated at a value of 2.1 scc/min, while the second tank permeated at a value of 0.0005 scc/min, and the third tank permeated at a value of 0.0012 scc/min. This data would suggest that the higher number indicates a minute leak that is not detectable, while the lower number reflects a leak-free condition. The lower numbers indicate that a suitable level of permeation can be achieved with the approach taken for a resin liner, particularly when operating at low temperatures.

Three tanks were subjected to a burst test. The goal was a minimum burst pressure of 225 bar (3263 psi), reflecting a Stress Ratio, or factor of safety, of 2.25 compared with the 100 bar service pressure. The first tank was tested at ambient temperature, reached a pressure of 196 bar (2845 psi) when a leak developed such that a higher pressure could not be reached. The second tank was tested at 80°K, in liquid nitrogen, and achieved a burst pressure of 291 bar (4215 psi). This burst pressure met the design requirement, and indicates it is possible to develop a resin liner that has sufficient capability to contain gases at extreme low temperatures without leakage, and that the composite strength is not degraded significantly by the extreme low temperature. A third tank was tested at 80°K, in liquid nitrogen, and achieved a pressure of 286 bar (4146 psi), when a significant leak developed. This pressure also met the design requirement for burst pressure.

Milestone accomplished: Vessel designs for subscale systems, and development of design/fabrication technology was reported (above).

Task 3.4 Fabricate subscale systems components

The purpose of this task was to support PNNL in the fabrication and demonstration of the thermal insulating tank with the LN2 tank cooling concept, and measurement of the cooling rate and transient heat loss. The plan for testing was to use a Type 1 monolithic tank, and potentially a Type 3 one as well if time and resources allowed.

In Q3 of 2013, Hexagon Lincoln designed a subscale system in order to better understand what the requirements should be for the thermal insulating tank, or Dewar. PNNL conducted evaluations of the cooling rate to support design of the full scale vacuum insulated Dewar, on site at Hexagon Lincoln. The experiment consisted of an aluminum tube inside a stainless steel tube with a specified gap in between the walls. Three different gaps were tested (3 mm, 6 mm, and 9 mm), as seen in Figure 3.4.1, with an

inlet port and an exhaust port, and 15 thermocouples were placed at various points inside the tube. The test setup is shown in Figure 3.4.2.

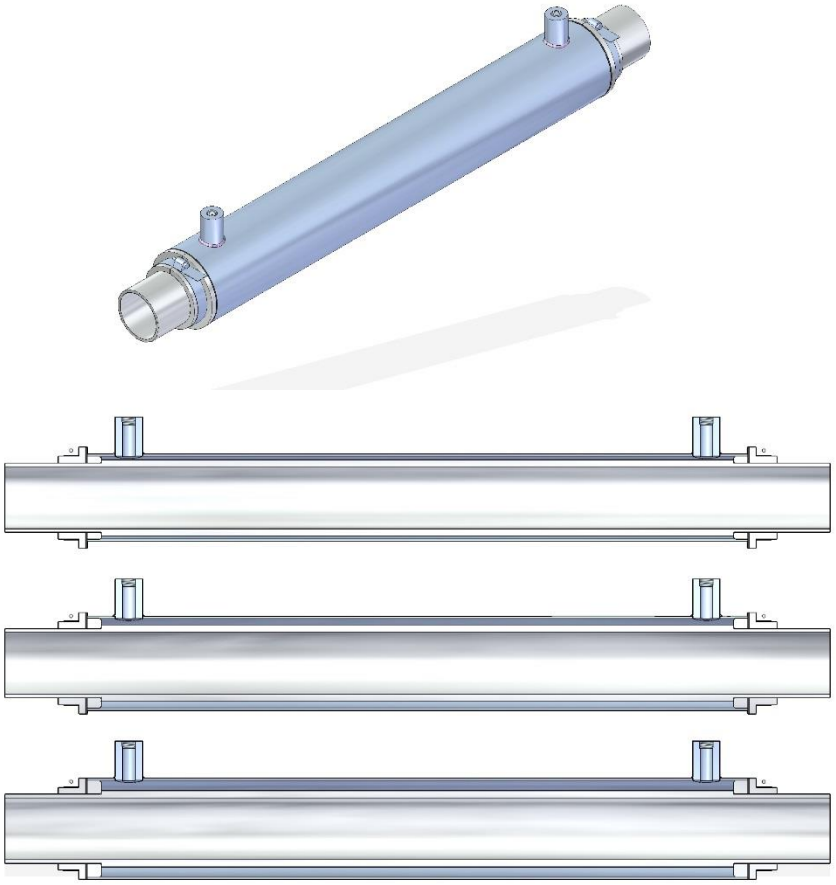

Figure 3.4.1: The 3 tubes used for the initial cooling testing with LN2
From the top: external view, tubes with gaps of 3mm, 6mm, and 9mm

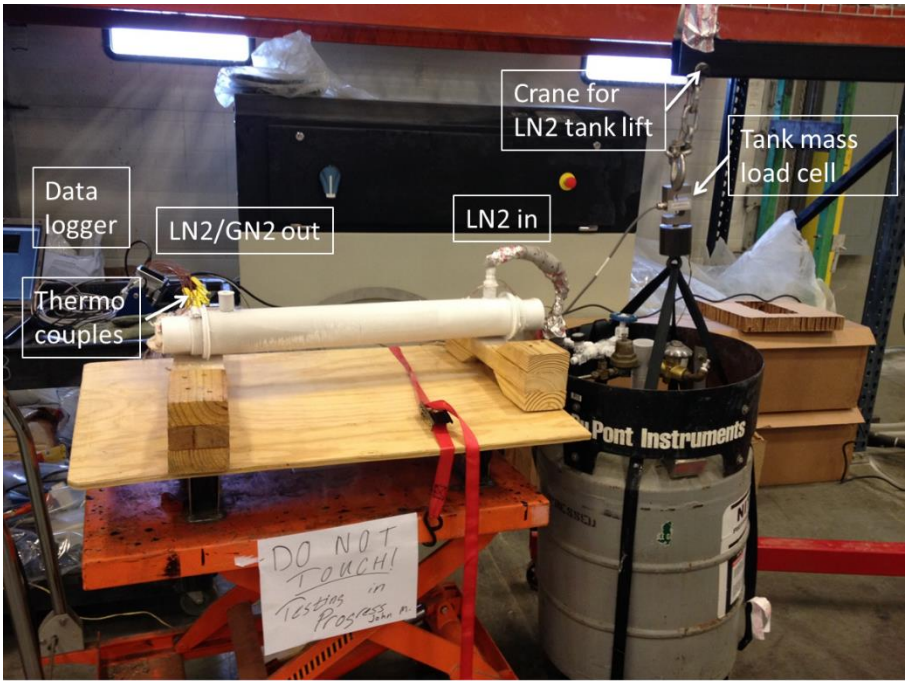

Figure 3.4.2: Test setup for initial LN2 cooling tests

LN2 cooling using subscale Type 1 tank

A vacuum insulated thermal shell, or Dewar, was designed in order to facilitate testing with a 2L subscale tank. The Dewar was fabricated by Cryofab. The design includes a support structure that gives some flow channels allowing the LN2 to flow throughout through and surround the entire tank. Several tests were conducted with an engineer from PNNL on site, in order to understand how the cooling rate is affected by changing the method used, or the LN2 inlet, or the temperature at which the test was started. A total of 13 thermocouples were placed on the inside surface of the tank. This was accomplished by cutting the Type 1 tank in half, mounting the thermocouples, then welding it back together, and then sealing the ports to prevent LN2 from going inside the tank. One other thermocouple was mounted on the end plate of the Dewar, and another on the outside in the middle of the cylinder.

Figure 3.4.3 shows a CAD model of the custom Dewar with the tank assembly to be tested. Figure 3.4.4 shows a photograph of the custom Dewar, while Figure 3.4.5 shows the Dewar end plate with plugs.

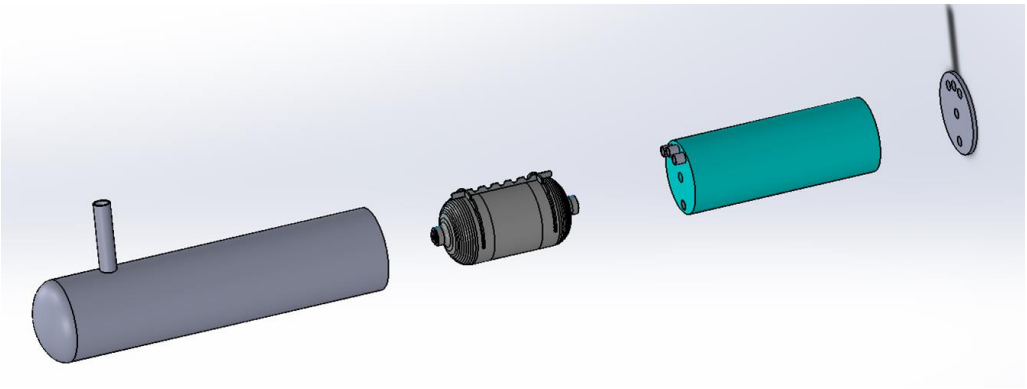

Figure 3.4.3: 3D model of Dewar and tank assembly. From left to right: Dewar, tank with support structure, foam plug, and Dewar end plate with ports

Figure 3.4.4: Custom Dewar

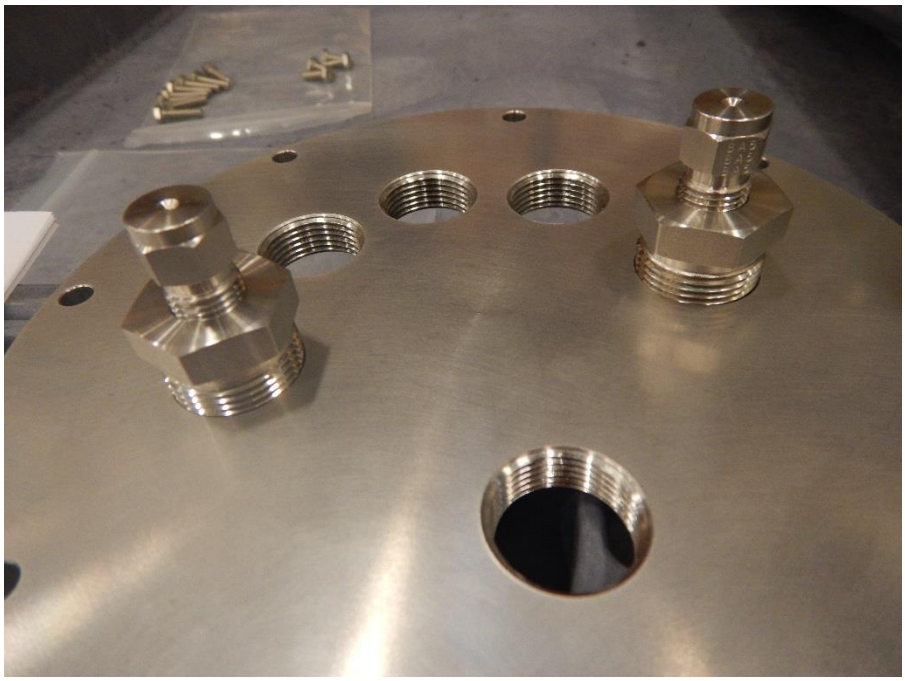

Figure 3.4.5: Dewar end plate including plugs

There were 3 types of fill methods which were tested. The first one involved having a reservoir filled with LN2 (about 5 liters) which was connected to the front of the Dewar via a ball valve. When the valve was opened, the LN2 would enter the Dewar through one of the ports and essentially flood the chamber, cooling the tank. The second method was similar to this, but with the reservoir attached to the back, and the LN2 entering the Dewar from the vent. A couple of the ports on the end plate were then used as vents. The third method was referred to as the “shower test”. The purpose of that method was to be more efficient with the amount of LN2 used for cooling the tank and it involved using a couple of pipes with cuts/holes positioned along the length of the tank on each side, which would spray the LN2 onto the tank. The following Figures 3.4.6, 3.4.7, and 3.4.8 show the setup for each one of those methods.

Figure 3.4.6: Front flood test setup

Figure 3.4.7: Back flood test setup

Figure 3.4.8: Shower test setup

One initial concern for the testing was pressure build-up inside the Dewar, which is why a pressure transducer was installed in one of the ports and pressure data was monitored throughout the first few tests. It was determined that even during the flood tests, pressure build-up was not an issue. The pressure never exceeded 0.035 bar (0.5 psig). First observations were that the second method (back flood) was the quickest way of cooling the tank down to 80°K, and the shower test was the slowest. In general, individual thermocouples mirrored ideal behavior, but the average of all thermocouples did not. The following Figures 3.4.9, 3.4.10, and 3.4.11 are representative of the testing done and data acquired.

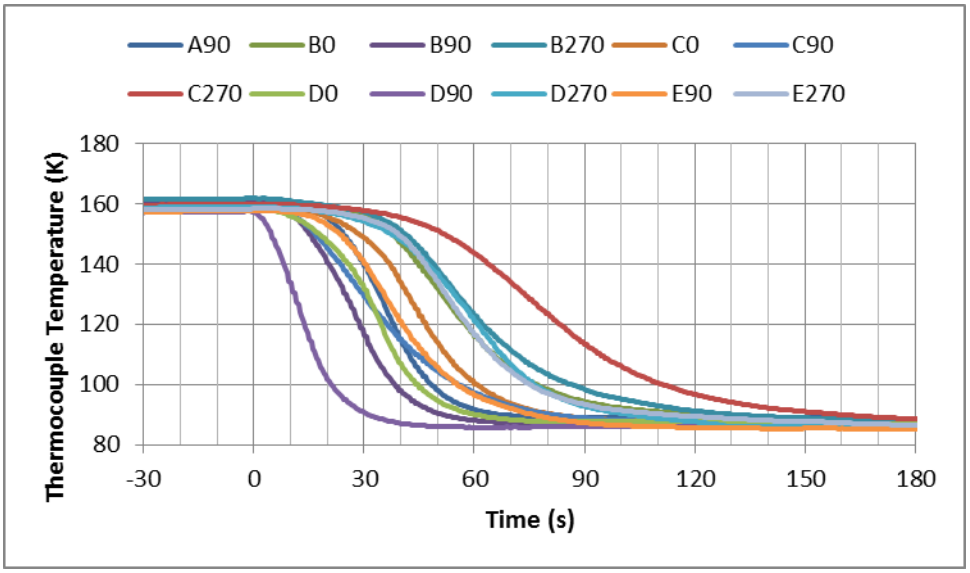

Figure 3.4.9: Individual TC data from 160°K to 85°K, using flood method. One of the TC's had connectivity issues so it was excluded from the data

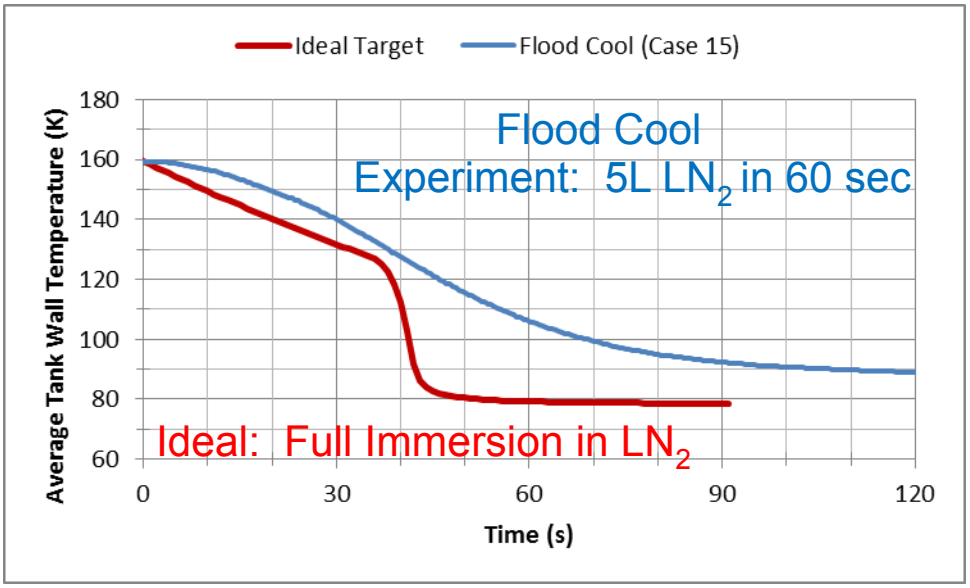

Figure 3.4.10: Average TC data compared to ideal

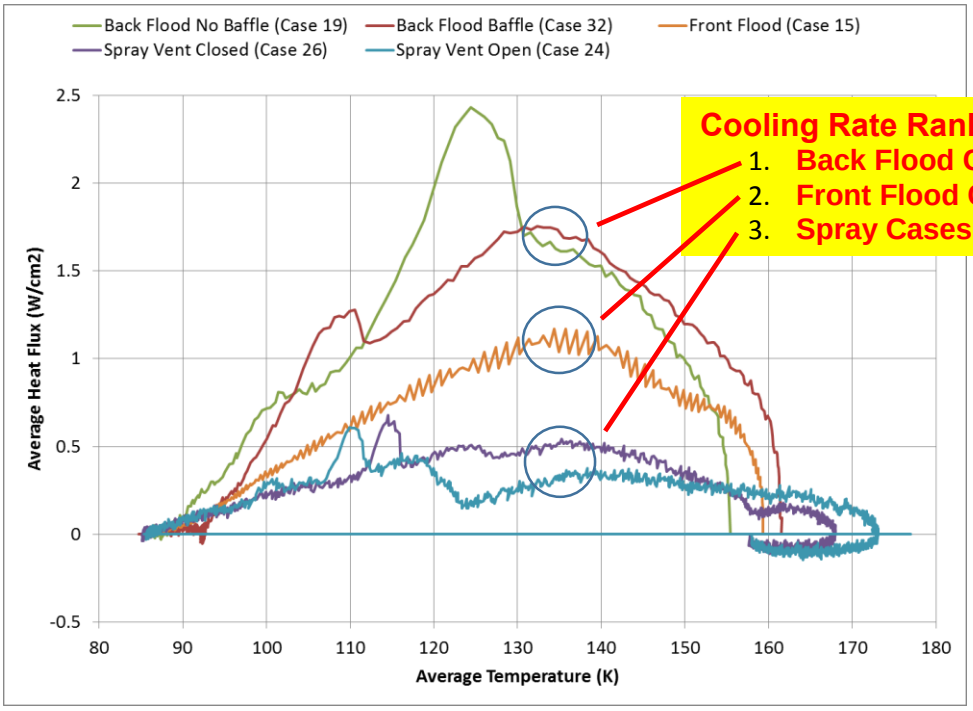

Figure 3.4.11: Heat flux comparison of the 3 methods of cooling

LN2 cooling using Type 3 subscale

After testing with the Type 1 tank was complete, PNNL and Hexagon concurred that testing should be repeated using a Type 3 subscale tank, see Figure 3.4.12, in order to compare the heat transfer properties between the two tank configurations and to determine which would be more beneficial in helping to meet DOE requirements. The liner was also cut in half, and 13 thermocouples were mounted on the interior surface exactly in the same positions as they were on the Type 1 tank, after which the liner was welded back together, and wound with carbon fiber. Since the previous testing already showed which fill method is faster, and the project was nearing its deadline, it was decided that not all the testing would be repeated; instead only testing using the back flood and shower test methods would be done. The purpose of this was to get a better understanding for the difference in heat transfer between a Type 1 and a Type 3 tank. The data collected was sent to PNNL for more detailed analysis, but the main observations were that the Type 3 tank never got as cold as the Type 1 (about 15-20 degrees Kelvin difference), and the cooling took longer by a significant amount of time, see Figures 3.4.13 and 3.4.14.

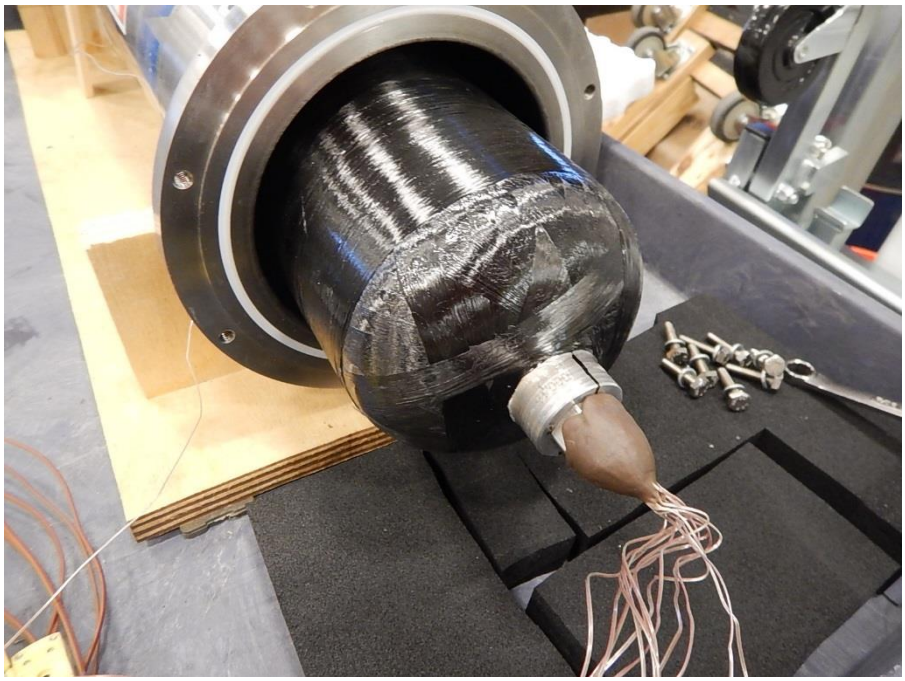

Figure 3.4.12: Setting up with Type 3 tank

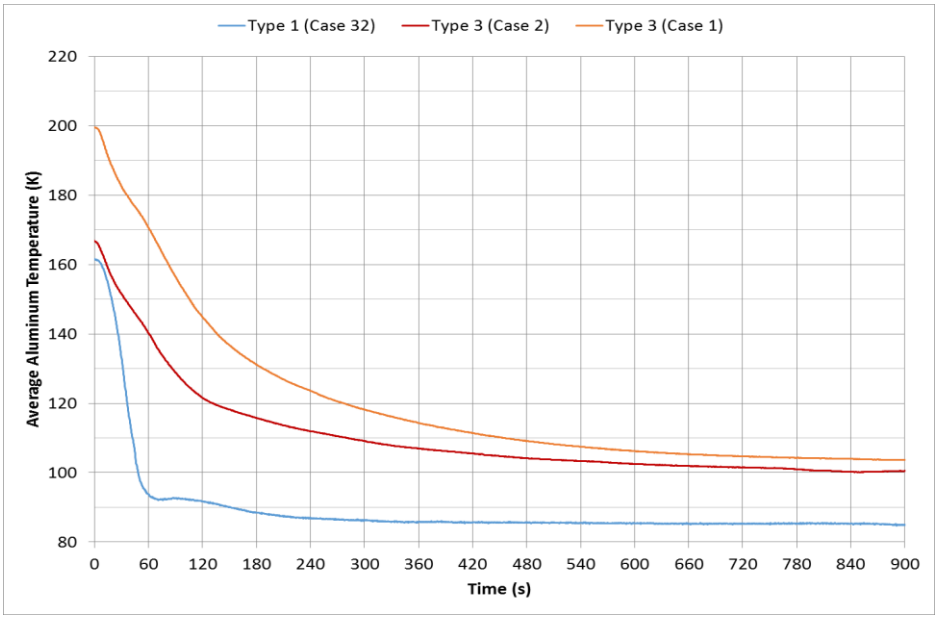

Figure 3.4.13: Comparison data of reservoir cooling tests between Type 1 and Type 3

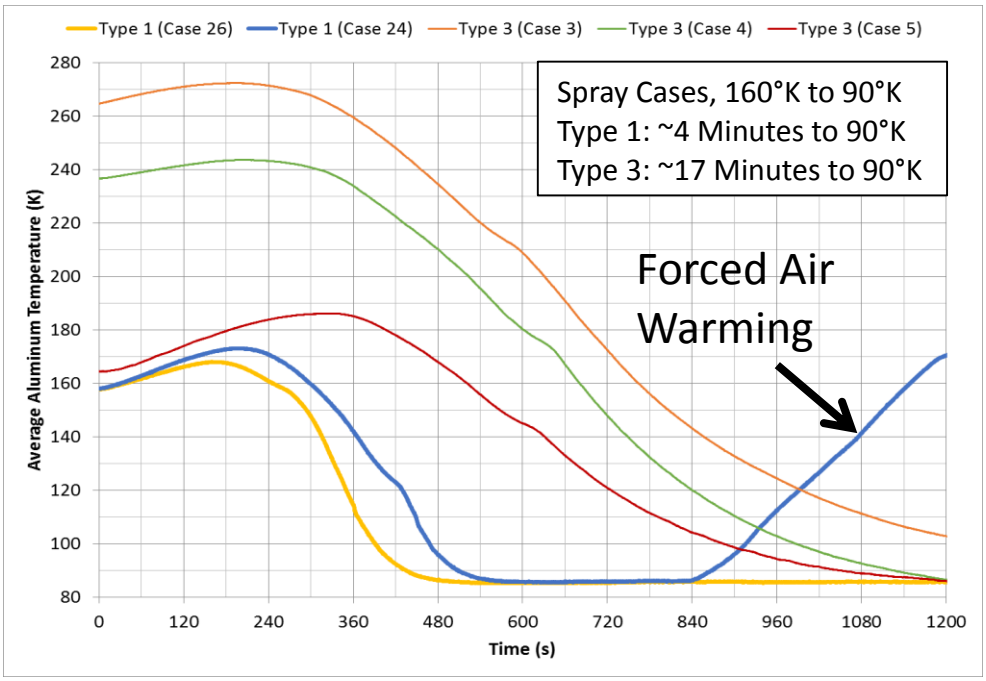

Figure 3.4.14: Comparison data of shower spray tests between Type 1 and Type 3

Milestones accomplished: Subscale vessels were fabricated for system assembly and testing, and distributed to HSECoE partners. Additional subscale vessels were fabricated for the purpose of evaluating and testing design and material options, and reported on (above).

Task 3.5 and 3.6 Project Management and Reporting

This task describes the project management aspects and the goals of Phase 3.

Phase 3 SMART Milestones

1. Report on ability to design and manufacture a baseline, separable Type 1 tank in accordance with size (2L - 6L), pressure (100 bar service pressure), operating temperatures (80°K – 160°K) and interfaces specified by HSECoE team members, and with a 10% reduction in weight per unit volume compared with the Type 1 tank tested in Phase 2.

Result: This task is complete as of 2014Q4 based on the update of the 3-piece aluminum 2 liter Type 1 tank in Phase 3 compared with the Phase 2 tank design. Note that a 3-piece steel tank with flat end closures was subsequently developed to address seal leakage at 100 bar and 80°K. Task completed.

2. With other HSECoE partners, report on the ability to design a full scale , double-wall, vacuum insulated bottle concept tank with the LN2 tank cooling with a modeled cooling rate and transient heat loss for dormancy determination meeting the DOE technical targets.

Result: This task is complete as of 2015Q2. Hexagon Lincoln conducted testing of a prototype 1-piece Type 1 tank, and also a prototype Type 3 tank to simulate filling conditions of the tank inside a vacuum

shell. PNNL, a HSECoE partner, evaluated the data and prepared full scale insulated bottle design. Hexagon has prepared full scale Type 1 and Type 3 fuel tank designs. Hexagon task completed.

3. Report on ability to design and manufacture alternate tank configurations, such as monolithic Type 1, Type 3 with suitable cryogenic liner, and Type 4 with suitable cryogenic liner, that can operate at 100 bar service pressure, at temperatures of 80°K – 160°K, and offer a further 10% reduction in weight compared with the Phase 3 baseline Type 1 tank, and are consistent with safety requirements established by industry for hydrogen fuel containers.

Result: Prototype Type 1, Type 3, and Type 4 tanks have been manufactured and tested. Burst tests at ambient conditions and cryogenic temperatures shown compliance with design requirements. Leak and permeation testing show a suitable liner can be developed for a Type 4 tank using resin in a glass fiber carrier. Full scale designs for Type 1 and Type 4 were developed. Task completed.

4. With other HSECoE partners, fabricate and demonstrate a the thermal insulating tank with the LN2 tank cooling concept and measure the cooling rate and transient heat loss for dormancy determination meeting the DOE technical targets for refueling from 160°K to 77°K in 4.2 minutes using a surrogate adsorbent material.

Result: A vacuum insulated thermal shell was built and delivered to Hexagon Lincoln in 2015Q1. A prototype tank and support structure was installed and thermal testing was conducted. Additional testing was conducted in 2015 Q2, and the results sent to PNNL for evaluation. Hexagon task completed.

Overall

The overall DOE goals for hydrogen storage address 2020 targets for gravimetric capacity (>5%), volumetric capacity (> 0.040 kg H_2/L), and storage system cost (<$12/kWh) and others. Assessment of these goals require assessment of a completed system based on testing conducted on subscale systems and projections to full scale prototypes. The SMART milestones discussed above represent the contributions made by Hexagon Lincoln to meeting the DOE targets for 2020.

All HSECoE face-to-face and Technical Team Meetings were attended and presentations made. SSAWG teleconferences were supported. Annual Merit Reviews were attended and presentations made. Input is being made to the Phase 3 HSECoE report.

Conference Papers/Presentations:

Stress Rupture Testing and Planning for DOE, Norman Newhouse (Hexagon), WSTF 2009 Composite Pressure Vessel and Structure Summit, Las Cruces, NM, September 2009

Potential Diffusion-Based Failure Modes of Hydrogen Storage Vessels for On-Board Vehicular Use, Yehia Khalil (UTRC), Norman Newhouse (Hexagon), Kevin Simmons (PNNL), Daniel Dedrick (SNL), AIChE 2010 Annual Meeting, Salt Lake City, UT, November 2010

Developments in Composite Cylinders for Hydrogen Storage, Norman Newhouse (Hexagon), Kevin Simmons (PNNL), John Makinson (Hexagon), Composite Conference 2012, Las Cruces, NM, August, 2012

Patent Application:

Thermal Insulation Shell System for Composite Pressure Vessel, Norman Newhouse (Hexagon), John Makinson (Hexagon), Kevin Simmons (PNNL), Application Number 14/275,412, 12 May 2014.

Key Observations and Next Steps

The program began with the development of a baseline hydrogen container based on the operating parameters, including pressure and temperature, which were identified. Over the course of the first phase, improvements in materials and processes were demonstrated that led to potential improvements of 11 percent lower weight, 4 percent greater internal volume, and 10 percent lower cost.

Trade studies we conducted in Phase 2 that showed Type 4 (all-composite) tanks could be lighter and more cost effective than other types of construction under the operating conditions that were identified. Operating parameters, particularly pressure and temperature, were modified significantly as material selections for hydrogen storage were refined in Phase 2.

The new operating parameters decreased both pressure and temperature significantly. These parameters were addressed by additional design and development of Type 4 tanks and materials in Phase 2 and Phase 3. Solutions were found for some issues, but there remained some development risk. Differential thermal expansion between the liner and composite reinforcement was one area being addressed by analysis and testing.

Type 1 tanks were manufactured in Phase 3 so that HSECoE partners could demonstrate their technologies without risk. Seal leaks while operating at high pressure and cryogenic temperature resulted in redesign of the Type 1 demonstration tank. The redesigned tank was used successfully in demonstrating the adsorbent technologies.

Components for vacuum insulating the tank and allowing pre-cooling of the tank during the fueling were demonstrated successfully and a patent was applied for.

Trade studies comparing an aluminum Type 1 tank and a carbon/epoxy Type 4 tank showed continued weight benefit using a Type 4 tank, but cost benefits are not clear, and are dependent on addressing design and materials issues. A resin liner with a glass fiber reinforcement was demonstrated to address the issue of differential thermal expansion between liner and composite.

Areas for further investigation include:

- Further development of resin liner and demonstration on a larger size tank
- Demonstration of the ability to assemble a tank with all contents in place
- Identification and/or demonstration of means to seal effectively at high pressure and low temperature that is cost and weight effective.
- Reviewing of the design, material, and test requirements of government regulations and industry standards for vehicle fuel containers, and recommend changes to address the new technology developed.

Service Bulletin 12-04-002
Fill Procedure for Hexagon Lincoln 240208-001 Hydrogen Pressure Vessel

INTRODUCTION

This service bulletin is written to provide safe filling instructions for the Hexagon Lincoln 240208-001 hydrogen pressure vessel. This type of vessel is to be used only by HSECoE partners.

GENERAL INFORMATION

The operator is solely responsible for insuring that the pressure vessel is handled in a safe and responsible manner. The operator should check all local, state and city fire codes before attempting the work described below.

If tank is used at temperatures higher than 10°F (-12°C), there are no fill restrictions as long as the final pressure is not higher than the rated service pressure of the tank (3000 psig).

FILL PROCEDURE FOR CRYOGENIC USE

The pressure inside the tank will greatly decrease when the temperature decreases from room temperature to cryogenic or liquid nitrogen temperature of -320°F (-196°C). At such low temperatures the liner inside the tank becomes brittle and is subject to cracking while shrinking due to the temperature reduction. To avoid cracking the liner, the tank must have a minimum pressure of 400 psig at -320°F (-196°C). This will prevent the liner from shrinking and separating from the laminate. The following steps should be completed to safely pressurize the tank before cooling it to cryogenic temperatures:

1. Condition the tank to room temperature at 68°F ± 18°F (20°C ± 10°C) for a minimum of 4 hours.
2. Pressurize tank to a minimum of 2000 psig, however no higher than the service pressure of 3000 psig.
3. The tank is now ready to be cooled.
4. With an initial pressure of 2000 psig, the pressure will decrease to 400-450 psig at -320°F. At this point, the tank can be further pressurized up to 3000 psig ONLY if a safety vent is used to prevent the pressure from increasing higher than 3000 psig in the case that the temperature of the tank will increase.

CAUTION!

Do not allow a vacuum to form in the container at any time. If a vacuum forms inside the tank it could potentially cause the plastic liner inside to fracture and therefore the gas will leak out.

WARNING!

When used at cryogenic temperatures, there is a risk of seal or liner failure and some gas might leak out. All operations involving use of the pressure vessel with hydrogen should be performed in a well-ventilated area or a fume hood free from heat or ignition sources in order to prevent accumulation and ignition of the hydrogen gas.

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