Conformable Hydrogen Storage Pressure Vessel

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Executive Summary

Existing commercially available hydrogen storage technologies are largely based on bulky and costly pressure vessels. These pressure vessels come in various forms, ranging from Type I steel cylinders to Type III and Type IV composite wrapped cylinders with metallic or polymer liners. In efforts to increase the pressure vessel storage density and meet DOE hydrogen storage targets, manufacturers are making incremental improvements. This approach alone is unlikely to meet DOE hydrogen storage targets and increase adoption of hydrogen fuel cell vehicles.

The project team, led by the Center for Transportation and the Environment (CTE) and consisting of High Energy Coil Reservoirs, LLC (HECR) and The University of Texas at Austin's Center for Electromechanics (UT-CEM), has investigated a transformational hydrogen storage technology using high pressure modulus polymeric pressure vessels. These vessels are constructed by overwrapping an extruded thermoplastic elastomeric resin liner with high performance tensile fiber. This technology is used in commercially available compressed air storage for firefighters. The result is a lightweight, flexible, non-explosive, and non-fragmenting pressure vessel that can be shaped (prior to pressurization) to conform to specific applications. Although this project was funded to investigate the potential for this technology for vehicle applications, a potential significant cost reduction allowed with this approach may make it effective for high pressure ground storage as well.

As part of Phase I of this project, the research team demonstrated a Kevlar™ over-braid that achieves a burst pressure in excess of 3.1X the operating pressure of 700 bar. The conformable vessel is able to achieve this pressure rating with reduced weight and cost when compared to Type IV vessels.

The researchers also identified two potential resins to serve as the liner of the vessel. These resins have excellent hydrogen barrier properties that could enable a liner thickness of 0.06 inches or less; however, difficulties in manufacturing the core due to the extrusion manufacturing processes required testing with prototype resins as commercially available resins were not found that had the required properties. The team was able to build and test a vessel with one such blend, which outperformed the baseline Hytrel resin materials but did not meet the project hydrogen permeability rate goals.

Project Accomplishments and Goals

The overall goal of the Conformable Hydrogen Storage Pressure Vessel project was to develop a game changing approach for compressed hydrogen gas storage that could provide a cost-effective and conformable storage solution for hydrogen. In Phase 1 of the project, the team's goal was to develop and demonstrate a conformable, lightweight 700 bar gaseous hydrogen storage system, which included (1) developing an over-braid design capable of required burst pressures and (2) identifying a low hydrogen permeability core resin material suitable to the pressure vessel manufacturing process. To pass the Go/No Go project gate the initial design must meet a burst pressure requirement of 2170 bar, meet a hydrogen leakage rate requirement of less than 0.05 g/hr/kg H_2 stored at 700 bar, and present no known technical or manufacturing obstacles to producing larger scale, longer vessels.

The hydrogen storage system development began with an initial design including candidate resin down selection and over-braid final development. The team then built test vessels and performed hydrostatic burst testing and hydrogen permeability testing.

Hydrostatic Pressure Testing – To comply with Department of Transportation pressure vessel codes, the pressure vessel must demonstrate a burst pressure of 3.1 X the operating pressure of 700 bar (2170 bar, or 31473 psi). The project team members developed an over-braid using a Kevlar™ weave and an additional proprietary fiber overlay. In designing the weave, the number of axial fibers, longitudinal and cross fiber angles, and the total braiding passes (layers) necessary are critical to support pressure loading. The proprietary fiber overlay was necessary since the thickness of the Kevlar™ required to meet the burst pressure would be too large to safely install the end fittings on the vessel. High Energy Coil Reservoir (HECR) developed and tested over-braid designs for the conformable hydrogen storage pressure vessel. Hydrostatic testing demonstrated a burst pressure of 33,731 psig, thus satisfying the project goal of 3.1X operating pressure, or greater than 31,473 psi. The failure point was on an end fitting and not the braid or overlay itself.

- Project Goal Burst Pressure: 31,473 psig (3X 700 bar)
- Demonstrated Burst Pressure: 33,731 psig – Achieved

Permeability Testing – To achieve a safe and effective hydrogen storage system, the 700 bar pressure vessels must have low permeability with a hydrogen leak rate below 0.05g/hr/kg H_2 stored. The first stage of the project evaluated candidate resin materials with hydrogen permeability low enough when used with the geometric constraints of the conformable pressure vessel design, including small internal volume and high surface area, and manufacturable core liner thickness. The results of this study identified two possible resins, acetal and EVOH (ethylene vinyl alcohol). Acetal is commonly known by DuPont's tradename, Delrin™, while Kuraray markets EVOH in several grades under their tradename EVAL™. To achieve the desired hydrogen leak rate using best available hydrogen permeability data, an acetal liner would need to be 0.049 inches thick, while the EVAL™ resins only need to be 0.005 inches thick. In both cases, these thicknesses were suitable for the corrugation manufacturing process, which require a thickness of 0.020 to 0.060 inches. Due to manufacturing concerns over the brittleness of pure EVAL™ resins, the team fabricated cores with different blends of prototype EVAL resins with higher flexibility trying to balance permeability and manufacturing. The team was only able to test one of these blends, (Blend 1) since other blends (Blend 2 and Blend 3) cracked and failed at relatively low pressures (below 1000 psig). The Blend 1 vessel out performed baseline vessel materials but was still short of the program goal hydrogen leak rate.

Project Activity Summary

Task 1.0 in the Statement of Project Objectives included several subtasks and milestones to develop a Conformable Hydrogen Storage Pressure Vessel. The following section highlights the overall subtasks and project activity.

Subtask 1.1 – Vessel Thermodynamic Modeling

Project partner, UT-CEM, developed a thermodynamic model and simulation using two platforms, a 1-D flow network modeling software called MacroFlow and Matlab/Simulink, to estimate refueling times and heating of the notional conformable pressure vessels.

The UT-CEM chose to perform the 1-D flow network analysis first to quickly and readily identify fueling issues, while working on a more detailed simulation effort in Matlab/Simulink in parallel. The major drawback to the flow network approach was its use of the Ideal Gas Law and not actual pressure and temperature dependent real gas properties. The results showed that with current SAE J2601 fueling rates and temperatures the vessels at the end of the conformable vessel chain would rise to approximately 150°C. Figure 1 shows the layout of the flow network model for two 20 vessel configurations, 10 series and 2 parallel (10s2p) and 20 series and 1 parallel (20s1p), while Figure 2 shows the temperature rise in the vessels.

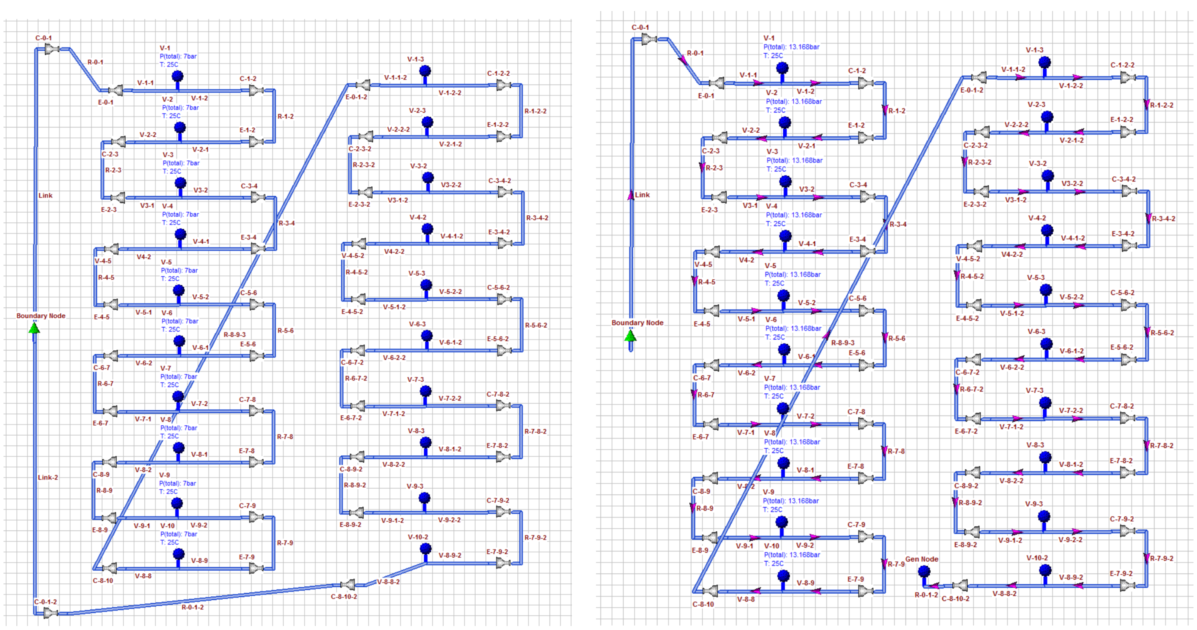

Figure 1. Macroflow network models of 20 vessel conformable storage system. Left: 10 series, 2 parallel configuration. Right: 20 series, 1 parallel configuration.

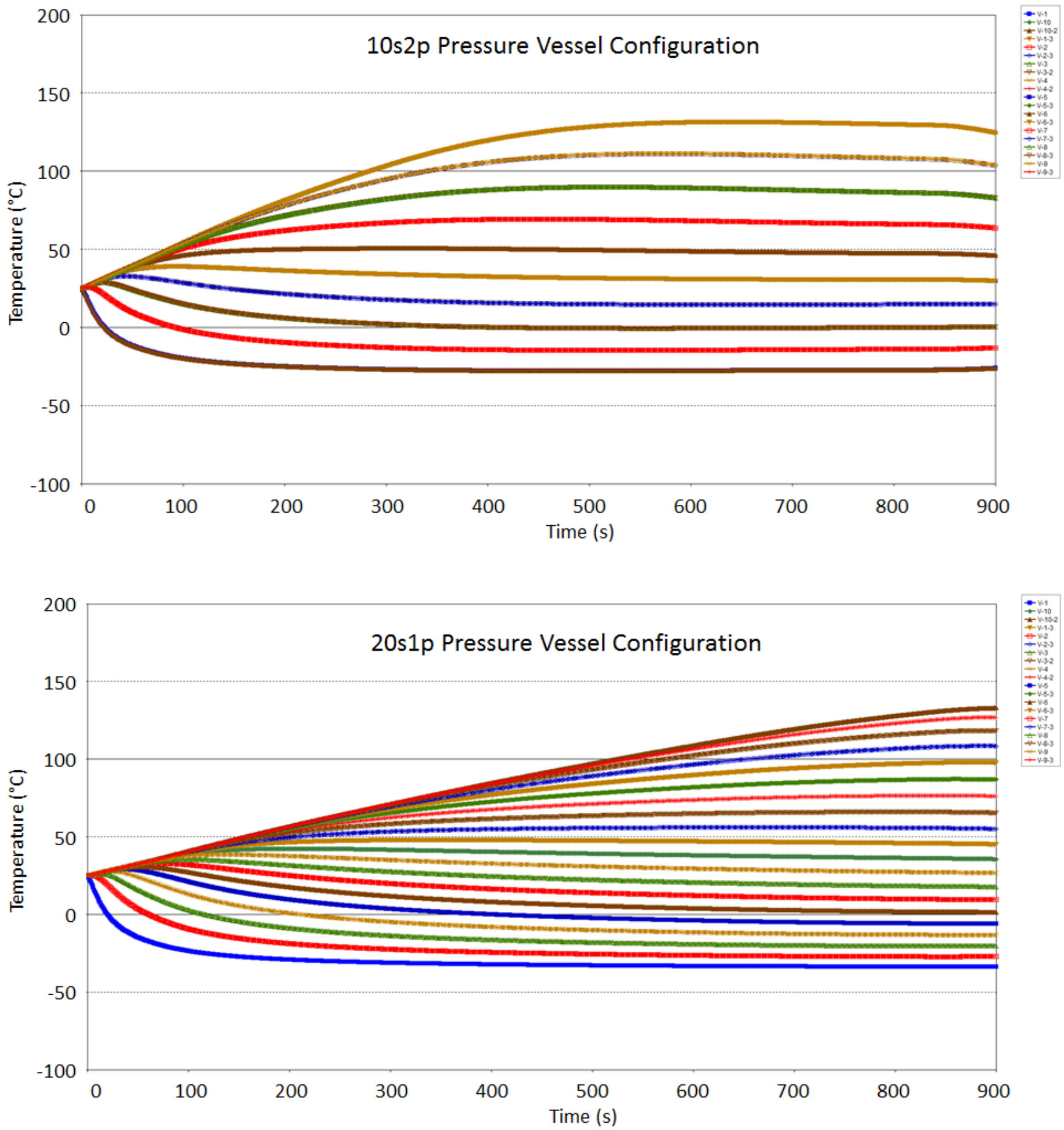

Figure 2. Temperature results of series and parallel configurations. Top: 10s2p configuration. Bottom: 20s1p configuration.

With these 1-D flow network results, it is evident that the temperature rise in the long chain of vessels will be a concern for the usual SAE J2601 fueling protocol which limits the tank temperature to 85°C based on materials used in typical Type III or IV vessels. However, the proposed materials for the conformable storage vessel have working temperatures up to 170°C, in which case the initial temperature results seem less daunting.

Furthermore, UT-CEM investigated the fueling using an alternating fueling manifold approach in which the fueling inlet changes from one end to the other throughout the fuel to mitigate temperature rise in the vessels at the far end of the chain. This approach was shown to greatly reduce the peak temperatures seen in the vessel. Figure 3 depicts this approach with a 140 vessel hydrogen storage system. The preliminary results show that temperatures could be maintained near or below 85°C with the conformable hydrogen storage vessel if an alternating-end fill procedure was established. Note, Figure 3 is meant only to show the possible benefit of this approach and the merits of a potential engineered solution to solve the temperature rise seen with prior fueling modeling.

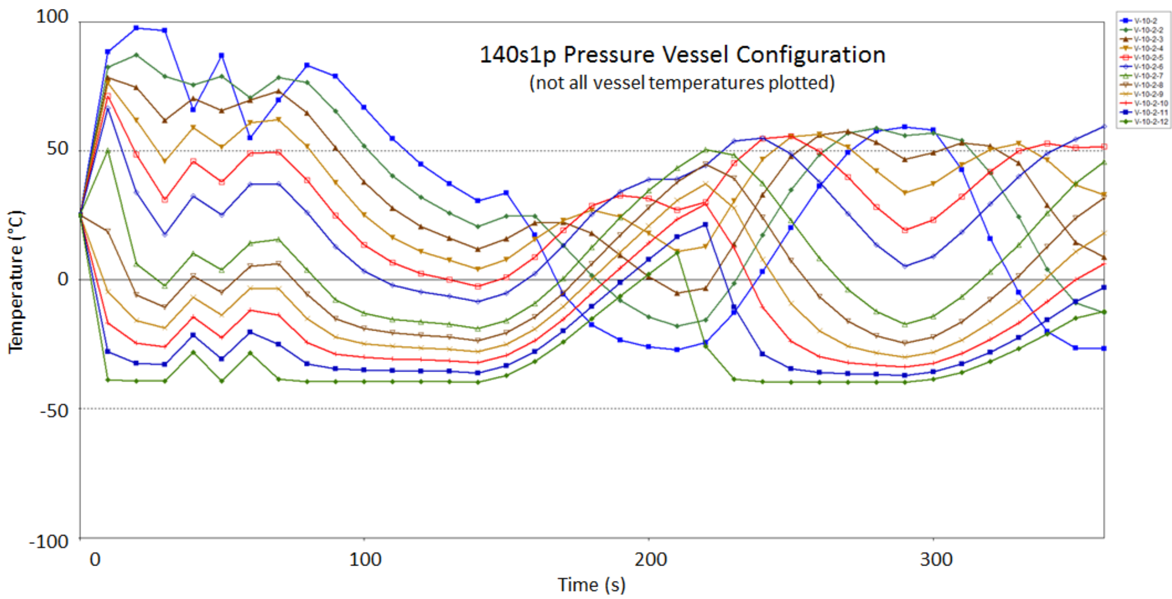

Figure 3. Flow network results for 140 chain vessel with alternating fueling inlet.

UT-CEM was successful in developing the model and validating it against a standard Type IV pressure vessel using the SAE J2601 fueling protocol. Efforts to expand the model to the conformable vessel chain were not carried out to completion in Phase I and were planned for Phase II of the project if it were to be continued.

UT-CEM Pressure Vessel Fueling Model Development

Fueling performance of a conformable hydrogen storage system is evaluated through modeling and simulation for comparison with the SAE J2601-2014 protocol. The evaluation consists of determining the evolution of gas pressure and temperature inside the conformable storage system during the fueling process. Of particular interest are the fill rate and the time required to fill the storage system to its nominal capacity and limiting factors, if any, as compared to fill rates and fill times prescribed by the SAE J2601 protocol for Type III and Type IV compact hydrogen storage systems (CHSSs).

The conformable hydrogen storage vessel considered in this study consists of multiple cylinders connected together by flexible conduits. Figure 4 shows 3 vessels connected together for illustration while the actual number of vessels is 141 with a total volume of ~153 liters. The number of vessels is based on the target H_2 storage of 5.6 kg.

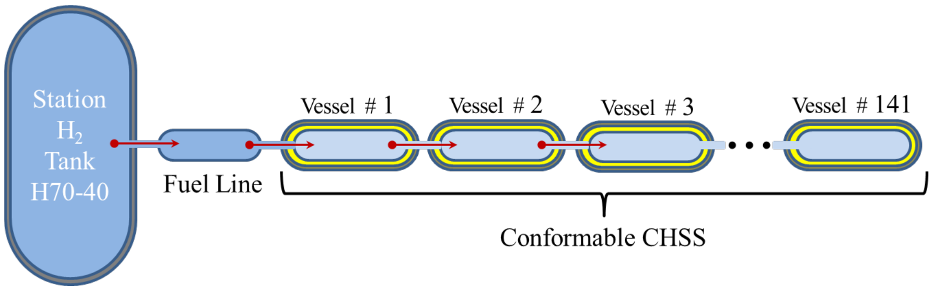

Figure 4. Simplified analysis model of the conformable storage system with 141 vessels connected in series with no bends.

Each of the 141 vessels is a relatively long pipe with length to diameter ratio of 122/3.25 = 37 and made of a Delrin™ liner and a Kevlar™ jacket. Assembled side-by-side the 141 vessels reach a total length of 172 meters which is not a realistic hydrogen reservoir configuration for use in light vehicles but for analysis purposes it provides a first approximation of the actual system. A further simplification of the model consists of representing the 141 vessels by a single pipe with equally spaced obstructions as shown in Figure 5.

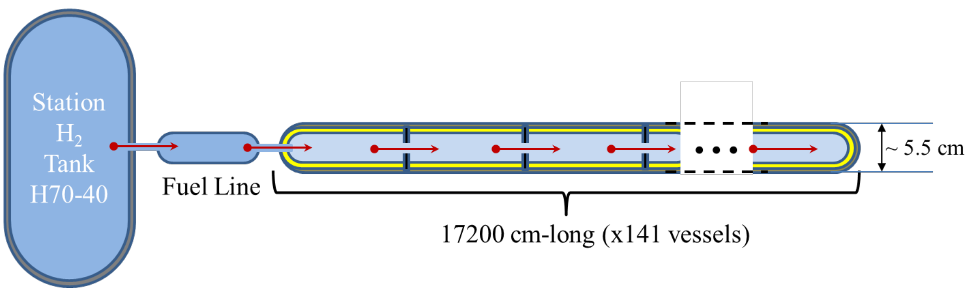

Figure 5. Simplified analysis model with single long pipe and multiple obstructions.

Figure 5 clearly shows the gas flow path as H_2 is filled from one end of the reservoir subject to friction with the liner surface and effects of multiple obstructions as it progresses towards the end section of the reservoir. This simplified representation indicates that, in addition to thermodynamics and heat transfer processes, gas dynamics may play an important role during the filling process for this particular reservoir and, consequently, need to be included in the physics model.

Considering gas dynamics, thermodynamics, and heat transfer processes are present during the filling and referring to a simple model that includes a single vessel, as depicted in Figure 4 and Figure 5, the governing equations describing the filling process are as follows:

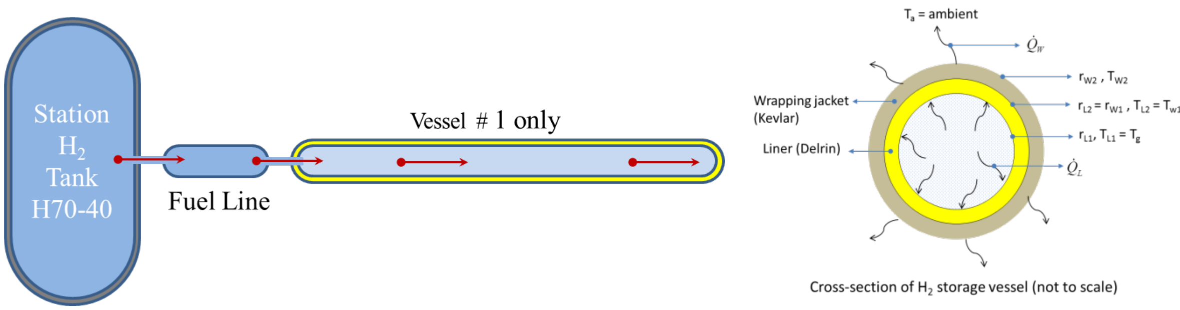

Figure 6. Filling model with a single vessel.

$$\frac{\partial \rho}{\partial t} + \nabla(\rho u) = 0 \qquad (1)$$

$$\rho \frac{\partial u}{\partial t} + \rho u \nabla u = -\nabla p - \frac{f u^2}{2D} \qquad (2)$$

$$\frac{d[me]}{dt} = \dot{Q} + \dot{m}_i (h_i + \frac{u^2}{2}) \qquad (3)$$

$$\dot{Q}_L = \dot{Q} \qquad (4)$$

$$\dot{Q}_L = h_g A (T_g - T_{L1}) \qquad (5)$$

$$\frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial T}{\partial r}) = \frac{1}{\alpha} \frac{\partial T}{\partial t} \qquad (6)$$

$$\dot{Q}_L = -K_L A_L \left. \frac{dT}{dr} \right|_{r=r_{L1}} \qquad (7)$$

$$\dot{Q}_w = -K_w A_w \left. \frac{dT}{dr} \right|_{r=r_{w2}} \qquad (8)$$

$$\dot{Q}_L = \dot{Q}_W \qquad (9)$$

$$\dot{Q}_w = h_a A_w (T_{w2} - T_a) \qquad (10)$$

A state equation or tabulated thermodynamic property data for the H_2 gas are needed to complete the set of model equations that describe the filling of the conformable vessel if the gas properties at the inlet of the vessel are known.

A general description of equations (1) to (10) follows:

Equations (1) and (2) describe the gas dynamics as it progresses from the inlet towards succeeding vessels. They are the continuity and momentum equations which simply state mass conservation and Newton's second law of motion applied to a fluid with density ρ and velocity u. The parameters f and D in the momentum equation are a friction factor and the liner inner diameter.

Equation (3) describes the thermodynamic process. It is the energy balance equation with *m* and *e* the mass and total energy of the gas in the vessel at any time, and *Q* the heat transferred from the gas to the outside through the liner and outer jacket. As defined by equations (4) and (9), Q_L and Q_w are the same as *Q* and are introduced to define the heat transfer from the gas to the liner then from the outer jacket to ambient air. The parameters h_g and h_a are the heat transfer coefficients between the gas and the inner surface of the liner, and between the outer surface of the Kevlar jacket and the ambient air, respectively. K_L and K_w are the thermal conductivities of the liner and the wrapping jacket. The parameters A_L and A_w are the liner inner and the jacket outer surface areas, respectively.

Equations (5) and (10) define the convective heat transfers. Equation (6) is the heat diffusion equation which describes heat conduction in the liner and wrapping jacket with the boundary conditions given by equations (7) and (8).

The H_2 gas inlet properties are not known however, since the gas in the fuel line is subject to heat transfer in addition to the use of a specific dispenser and inlet geometry which will affect the gas properties at the inlet of the vessel. In general, model equations for the gas in the fuel line are similar to the equations just described but since there is no mass accumulation the energy equation will be different and should account for gas mass entering and exiting the fuel line.

For a Type III or Type IV tank as shown in Figure 7, the ratio of length to diameter is an order of magnitude smaller than that of the conformable storage vessel. Consequently, the effect of gas dynamics would be much less important during the filling process. This suggests that a model similar to the model for the conformable H_2 storage vessel just described but without the continuity and momentum equations will be adequate for representing the filling of Type III or Type IV tanks.

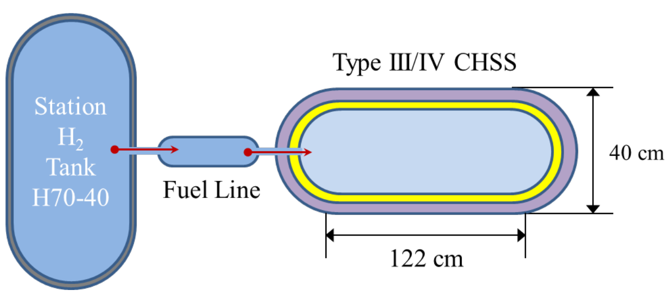

Figure 7. Typical configuration for filling a type III or type IV H_2 tank.

As indicated earlier the materials of the liner and the wrapping jacket used in the conformable hydrogen storage vessel are Delrin™ and Kevlar™, respectively. There are several grades of these materials that can have different properties; typical values of interest are given in Table 1.

Table 1. Some material properties of liner and wrapping jackets.

Properties	Delrin (liner)	Kevlar (wrapping jacket)
Thermal conductivity	0.33 W/m-K	0.04 W/m-k
Heat capacity	1470 J/kg-^{0}C	1420 J/kg-^{0}C
Density	1380 kg/m^3	1440 kg/m^3

An important observation from Table 1 is that the thermal conductivities of the liner and wrapping jacket used in the conformable storage vessel are very low as compared to the thermal conductivities of the metallic liners and carbon-fiber reinforced outer jackets that are used in Type III and Type IV hydrogen tanks. Delrin™ and Kevlar™ are in fact very good heat insulators and will limit heat transfer from the hot gas to ambient air. As a result, if we assume the filling to be adiabatic, *i.e.* no heat loss, model equations (4) to (10) above can be eliminated. In addition, if the effects of viscosity are assumed small, gas dynamics can be neglected as well and the model of charging the conformable vessel reduces to the simplified thermodynamics equation (11) given below:

$$\frac{d[me]}{dt} = \dot{m}_{input}(h_{input} + \frac{u^2}{2}) \qquad (11)$$

If kinetic energy in the gas is small with respect to the internal energy, $e_{internal}$, the input energy equation (11) is reduced to a first order differential equation relating changes of the internal energy to the energy input to the tank as:

$$\frac{d[me_{\text{int}ernal}]}{dt} = \dot{m}_{input}(h_{input}) \qquad (12)$$

If the initial internal energy and mass in the tank are e_{i0} and m_0 respectively, solution of equation (12) gives the internal energy of H_2 gas during filling at any given time t as:

$$e_i(t) = \frac{m0}{m0 + m_{input}(t)}(h_{input} - e_{i0}) + h_{input} \qquad (13)$$

If the vessel is initially empty, i.e. $m_0 = 0$, then simply, $e_i(t) = h_{input}$.

Using a gas state law or tabulated hydrogen property data, pressure and temperature time evolution during the filling can then be determined.

Single Large Vessel Simulation

To validate the physics and modeling assumptions, UT-CEM first simulated the fill of a single large vessel storing 5.6 kg of hydrogen gas. This analysis assumed an adiabatic filling process and neglected friction wall effects. Additional assumptions included:

- ➢ Tank assumed initially filled to 20% of desired mass capacity of 5.6 Kg
- ➢ Assumed 40 ^{0}C ambient temperature
- ➢ Used SAE J2601 recommended pressure rates for filling conditions (11.5 MPa/min)
- ➢ ~ 5 minutes to fill-up tank (or almost filled)

The results are documented in Figure 8. They show great agreement with the anticipated performance when compares to SAE J2601 and verify the underlying model and physics is correct. The tank was able to fill within 5 minutes while maintaining temperatures at 85°C. In this model, the mass flow rate may be adjusted to improve performance.

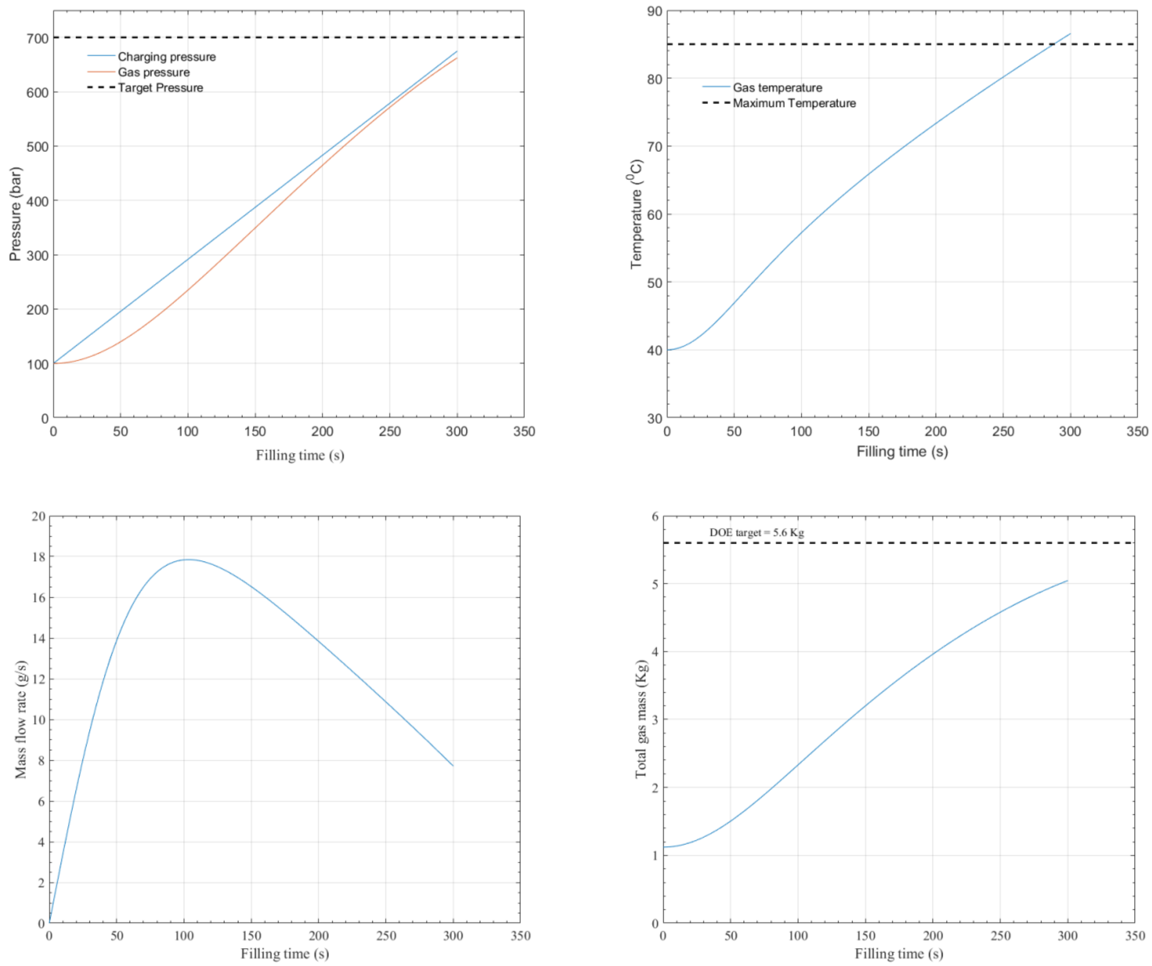

Figure 8. Simulation results for single 5.6 kg storage vessel.

The modeling and simulation confirmed an early concern that compression heating at the end could likely be a significant challenge in long pressure vessel.

Subtask 1.2 – Resin Identification

UT-CEM and affiliated university researchers evaluated several resins during Phase I of the project. Three resins with appropriate characteristics to serve as low permeability liners for a conformable hydrogen storage vessel were identified.

Perhaps the greatest challenge in evaluating the multitude of resins on the market was identifying consistent thermal and permeability properties data across all candidate resins. In an attempt to expand the availability of hydrogen permeability data to include more resins, CheFEM software from the Composite Agency was evaluated. It was hoped that this software would calculate leak rates for candidate resins. However, the results obtained from the software were inconsistent when comparisons were made with known, experimentally measured permeability values.

Water absorption was evaluated as a surrogate for hydrogen permeability. However, direct comparisons of water absorption with hydrogen permeability data showed no apparent correlation between the two properties. The permeabilities of CO_2, N_2, and He were also evaluated as surrogates for hydrogen permeability. Although none of these gases emerged as a clear proxy for hydrogen, acetal and EVAL™ resins showed superior permeability properties across all gases. Table 2 summarizes the permeability data available for a subset of resins evaluated by the team. In the table below stars are shown next to acetal and the two EVAL™ resins. These resins have a predicted permeability that aligns with the maximum core thickness while meeting the target hydrogen leak rate at 700 bar, as well as likely compatibility with the pressure vessel manufacturing processes.

Table 2. Permeability data comparison for several top candidate resins/polymers. Note that current manufacturing processes are setup for a core liner thickness of approximately 0.06 inches, making acetal and EVAL™ the top prospects.

	Permeability (cm^3 (cm)/ atm sec cm^2)				Required thickness to meet 0.05 g/hr-kg H2 stored @ 700 bar		
Resin / Polymer	H_2	CO_2	He	N_2	*(cm)*	*(in)*	
Hytrel 5556	na	1.80E-07	9.90E-08	1.40E-08	na	na	
Acetal	1.50E-10	2.30E-09	na	na	0.0192	0.049	★
Polybutylene terephthalate	1.50E-08	na	na	4.00E-11	1.9171	4.869	
EVALM100	1.62E-11	na	na	na	0.0021	0.005	★
EVAL F101	1.30E-11	1.90E-12	3.70E-10	3.94E-14	0.0017	0.004	★
PCTFE	4.20E-09	3.70E-10	5.20E-08	na	0.5368	1.363	
PTFE	7.40E-08	9.80E-08	na	na	9.4575	24.022	

Due to the lack of consistent permeability data, a preliminary selection matrix consisting of 29 resins (Table 3) was constructed to identify candidates possessing durometry, melt viscosity, melting temperature, and density properties similar to those of Hytrel™ HTR4275, the current resin being used in pressure vessels for other applications. Ideal values for each characteristic were assigned as follows:

- Durometry > 55 (Shore D)
- Melting Temperature 190 +/- 5 °C,

- Melt Mass Flow Rate < 6 g/10 min or Viscosity < 250 Pa · s
- Density > 1.2 g/cm3

Candidates with matrix scores of less than 300 were eliminated in a first round selection resulting in ten resins for further evaluation (Table 4). It is important to note that melt mass flow rate/viscosity data were lacking for nine of the candidate resins. These resins were assigned the lowest rank for this characteristic.

Hydrogen permeability data was unavailable for Hytrel™. There was also no data for specific formulations of Acetal and Crastin. Although, permeability data was available for general formulations of these resins. Six candidate resins were evaluated on the basis of the physical characteristics in the preliminary matrix and hydrogen permeability (Table 5). Three candidate resins demonstrated acceptable permeability characteristics:

1. Acetal
2. EVAL M100
3. EVAL F101

Based on these results acetal, EVAL M100, and EVAL F101 were down selected as potential permeability liners for the conformable hydrogen storage vessel. Hytrel™ HTR4275 served as a baseline for comparison testing.

Table 3. Preliminary resin evaluation decision matrix.

Polymer Resin Evaluation		Density	Subtotal	Melting Temperature	Subtotal	Durometer Scale Reading	Subtotal	Melt Flow Rate Viscosity	Subtotal	Grand Total
		2		4		4		1		
		High density favored, values > 1.2 are preferred		Preferred Temperature 190°C		Hard resin favored, Durometry values of ≥ 55 are preferred		High viscosity favored, values of ≤ 6 (250)are preferred		
#	Resin Properties	g/cm3		°C		Shore D		cm3/10 min or (Pa s)		
1	Hytrel HTR4275 BK316 (Dupont)	1.2 A	4.00	192.0 A	4.00	55.0 A	4.00	6.0 A	4.00	**400.0**
2	Hytrel 5556 (Dupont, also 5555 and 6356)	1.2 A	4.00	201.0 B	3.00	55.0 A	4.00	7.0 B	3.00	**351.0**
3	Crastin S600F10 (Dupont, also CE1085)	1.3 A	4.00	225.0 C	2.00	55.0 A	4.00	7.0 B	3.00	**302.9**
4	Crastin SK605 (Dupont, also SK608 and SK609)	1.5 A	4.00	225.0 C	2.00	55.0 A	4.00	7.0 B	3.00	**302.9**
5	Acetal homopolymer (Aetna)	1.4 A	4.00	190.0 A	4.00	77.0 A	4.00	2.4 A	4.00	**400.0**

6	Zytel RS LC3060 (Dupont)	1.1	B	3.00	223.0	C	2.00	50.0	C	2.00	24.0	D	1.00	**202.2**
7	Zytel RS LC3090 (Dupont)	1.1	B	3.00	225.0	C	2.00	55.0	B	3.00	24.0	D	1.00	**234.3**
8	PCTFE	2.1	A	4.00	212.0	C	2.00	90.0	A	4.00	1.8	A	4.00	**310.9**
9	ECTFE (Halar) (Aetna)	1.7	A	4.00	238.0	C	2.00	78.0	A	4.00	10.7	C	2.00	**291.9**
10	Fluorosint 500 (Aetna)	2.3	A	4.00	327.0	D	1.00	55.0	A	4.00	Not Available	D	1.00	**213.0**
11	Fluorosint 207 (Aetna)	2.3	A	4.00	327.0	D	1.00	50.0	C	2.00	Not Available	D	1.00	**165.6**
12	PVDC (DOW, Saran)	2.1	A	4.00	212.0	C	2.00	90.0	A	4.00	Not Available	D	1.00	**274.1**
13	PFA (Aetna)	2.1	A	4.00	305.0	D	1.00	60.0	A	4.00	3.0	A	4.00	**241.6**
14	FEP (Aetna)	2.2	A	4.00	270.0	D	1.00	55.0	A	4.00	12.6	C	2.00	**226.9**
15	PTFE (Aetna)	2.2	A	4.00	164.0	C	2.00	55.0	A	4.00	200.0	A	4.00	**310.9**
16	PVDF (Aetna)	1.8	A	4.00	172.0	C	2.00	79.0	A	4.00	500.0	D	1.00	**274.1**
17	modified ETFE (Aetna)	1.7	A	4.00	235.0	C	2.00	67.0	A	4.00	Not Available	D	1.00	**274.1**
18	Tivar 1000 UHMW-PE (Aetna)	0.1	B	3.00	135.0	D	1.00	66.0	A	4.00	Not Available	D	1.00	**202.2**
19	MP150 PU (Aetna)	1.2	A	4.00	150.0	D	1.00	60.0	A	4.00	Not Available	D	1.00	**213.0**
20	MP175 PU (Aetna)	1.2	A	4.00	150.0	D	1.00	75.0	A	4.00	Not Available	D	1.00	**213.0**

Table 3 continued. Preliminary resin evaluation decision matrix.

Polymer Resin Evaluation		Density 2 High density favored, values > 1.2 are preferred g/cm3		Subtotal	Melting Temperature 4 Preferred Temperature 190°C °C		Subtotal	Durometer Scale Reading 4 Hard resin favored, Durometry values of ≥ 55 are preferred Shore D		Subtotal	Melt Flow Rate Viscosity 1 High viscosity favored, values of ≤ 6 (250)are preferred cm3/10 min or (Pa s)		Subtotal	Grand Total
#	Resin Properties													
21	PC (Aetna)	1.2	A	4.00	150.0	D	1.00	80.0	A	4.00	Not Available	D	1.00	**213.0**
22	PE, unreinforced (Aetna)	1.3	A	4.00	150.0	D	1.00	83.0	A	4.00	Not Available	D	1.00	**213.0**
23	high-heat ABS (Aetna)	1.1	B	3.00	150.0	D	1.00	88.0	A	4.00	1550.0	D	1.00	**202.2**
24	AG-330 30% glass filled PPSU (Radel, Aetna)	1.6	A	4.00	160.0	D	1.00	80.0	A	4.00	7.6	B	3.00	**235.4**
25	AG-300 PPSU (Aetna)	1.4	A	4.00	160.0	D	1.00	83.0	A	4.00	21.9	D	1.00	**213.0**
26	PEEK	1.3	A	4.00	334.0	D	1.00	62.0	B	3.00	120.0	A	4.00	**217.6**
27	EVAL M100B	1.2	A	4.00	195.0	A	4.00	76.0	A	4.00	4.0	A	4.00	**400.0**
28	EVAL F101A	1.2	A	4.00	183.0	B	3.00	77.0	A	4.00	3.2	A	4.00	**360.3**
29	EVAL F101B	1.2	A	4.00	183.0	B	3.00	77.0	A	4.00	3.2	A	4.00	**360.3**

Table 4. First round resin selection.

#	Polymer Resin Evaluation	Density		Subtotal	Melting Temperature		Subtotal	Durometer Scale Reading		Subtotal	Melt Flow Rate Viscosity		Subtotal	Grand Total
	Weight	2			4			4			1			
		High density favored, values > 1.2 are preferred			Preferred Temperature 190°C			Hard resin favored, Durometry values of ≥ 55 are preferred			High viscosity favored, values of ≤ 6 (250)are preferred			
#	Resin Properties	g/cm3			°C			Shore D			cm3/10 min (Pa s)			
1	Hytrel HTR4275 BK316 (Dupont)	1.2	A	4.00	192.0	A	4.00	55.0	A	4.00	6.0	A	4.00	400.0
2	Hytrel 5556 (Dupont, also 5555 and 6356)	1.2	A	4.00	201.0	B	3.00	55.0	A	4.00	7.0	B	3.00	351.0
3	Crastin S600F10 (Dupont, also CE1085)	1.3	A	4.00	225.0	C	2.00	55.0	A	4.00	7.0	B	3.00	302.9
4	Crastin SK605 (Dupont, also SK608 and SK609)	1.5	A	4.00	225.0	C	2.00	55.0	A	4.00	7.0	B	3.00	302.9
5	Acetal homopolymer (Aetna)	1.4	A	4.00	190.0	A	4.00	77.0	A	4.00	2.4	A	4.00	400.0
6	PCTFE	2.1	A	4.00	212.0	C	2.00	90.0	A	4.00	1.8	A	4.00	310.9
7	PTFE (Aetna)	2.2	A	4.00	164.0	C	2.00	55.0	A	4.00	200.0	A	4.00	310.9
8	EVAL M100B	1.2	A	4.00	195.0	A	4.00	76.0	A	4.00	4.0	A	4.00	400.0
9	EVAL F101A	1.2	A	4.00	183.0	B	3.00	77.0	A	4.00	3.2	A	4.00	360.3
10	EVAL F101B	1.2	A	4.00	183.0	B	3.00	77.0	A	4.00	3.2	A	4.00	360.3

Table 5. Resin hydrogen permeability evaluation decision matrix

#	Polymer Resin Evaluation	Durometer Scale Reading		Subtotal	Melting Temperature		Subtotal	Viscosity		Subtotal	Density		Subtotal	H2 Permeability		Subtotal	Grand Total
	Weight	2			2			1			1			4			
		Hard resin favored, Durometry values of ≥ 55 are preferred			Preferred Temperature 190 +/- 5 °C			High viscosity favored, values of < 6 (250) are preferred			High density favored, values > 1.2 are preferred						
#	Resin Properties	Hardness, Shore D			°C			g/10 min (Pa s)			g/cm3			cm3 (cm)/ atm sec cm2			
1	Acetal	77.0	A	4.00	190.0	A	4.00	2.4	A	4.00	1.42	A	4.00	1.5E-10	B	3.00	356.5
2	Polybutylene terephthalate (Crastin)	55.0	B	3.00	225.0	D	1.00	7.0	B	3.00	1.30	A	4.00	1.5E-08	D	1.00	159.7
3	EVAL M100	76.0	A	4.00	195.0	A	4.00	4.0	A	4.00	1.22	B	3.00	1.6E-11	A	4.00	388.7
4	EVAL F101	77.0	A	4.00	183.0	B	3.00	3.2	A	4.00	1.19	C	2.00	1.3E-11	A	4.00	352.3
5	PCTFE	90.0	A	4.00	212.0	C	2.00	1.8	A	4.00	2.10	A	4.00	4.2E-09	C	2.00	263.9
6	PTFE	55.0	B	3.00	164.0	D	1.00	200.0	A	4.00	2.20	A	4.00	7.4E-08	D	1.00	164.4

Subtask 1.3 – Procure Corrugation Equipment

Project partner HECR worked with third-party vendors to specify corrugation tooling for the hydrogen storage vessels. Due to the higher burst pressure requirement, the hydrogen vessel design has a smaller diameter body necessitating custom tooling. The tooling is a set of 48 interlocking vacuum forming dies used on a specialty corrugation machine, which produces parts through a combination of extrusion and vacuum forming. Figure 9 below shows the tooling ready for shipment from the tooling vendor.

Figure 9 - Corrugation tooling ready for shipment

Test runs with the equipment were performed throughout the third quarter of the project. Figure 10 shows the first sample core using the corrugator equipment heads.

Figure 10. First run sample using corrugator equipment heads.

Subtask 1.4 – Test Vessel Design

HECR developed the pressure vessel design, including both the over-braid and core, in a close working relationship with extrusion and braiding vendors to ensure the pressure vessel design was within their capabilities and processes. For example, the extruders and HECR had to iterate on extrusion rates and temperatures during initial corrugation runs for the core.

HECR also found that the originally intended Kevlar™ over-braid required an additional overlay with a proprietary fiber to meet the 3.1X burst pressure rating. A Kevlar™ only overbraid would have proven too thick to accommodate crimped end fittings.

HECR also found during the project that existing end fittings were not well suited for the pressures the vessel would see. HECR went through several iterations before honing in on a fitting that would survive the burst testing to 2170 bar. An early end fitting failed before the pressure vessel, so subsequent designs had a higher wall thickness for increased strength.

As part of the final design, HECR quantified the manufacturing time and cost of the conformable hydrogen storage vessel versus a standard Type IV cylinder. The baseline for comparison was a single 320 L vessel. Table 6 details the major manufacturing processes, while Table 7 outlines major material costs for each type of pressure vessel. The comparison shows potential for significant cost savings for hydrogen storage systems using the conformable vessel technology.

Table 6. Manufacturing time comparison.

	Manufacturing Process	**Estimated time**
Type IV Hoop Wound Cylinder	Extrude main body	05.-1 hours
	Machine main body	
	Insert conical ends and spin weld in place	
	Spin weld metal bosses for valve mounting	
	Carbon fiber winding	4-5 hours
	Autoclaving	3-4 hours
	Total Time	**7-10 hours**
Conformable Pressure Vessel (HPM Technology)	Extrusion and corrugation	33 minutes
	Braiding	
	Swaging end fittings	5 minutes
	Total time	**38 minutes**

Table 7. Material cost comparison.

	Material	**Cost**
Type IV Hoop Wound Cylinder	Plastic liner material (plastic and metal bosses)	$ 400
	Carbon fiber (400 lbs)	$ 4,800
	Gas for autoclaving	$ 150
	Total	**$ 5350**
Conformable Pressure Vessel (HPM Technology)	Resin	$ 220
	Braid	$ 1200
	Fittings	$ 4
	Total time	**$ 1424**

Subtask 1.5 – Test Vessel Fabrication

With a design and manufacturing process specified, HECR and its vendors fabricated several conformable pressure vessels. The first vessels manufactured were with a Hytrel™ resin. This resin was assumed not to meet the permeability requirements, but was used to validate the production and testing processes to be used with the candidate resins, as Hytrel was readily available and the process was well established. A second set was then fabricated with the EVAL™ resin core. These complete pressure vessels are shown in Figure 11, while Figure 12 shows the EVAL cores prior to over-braiding.

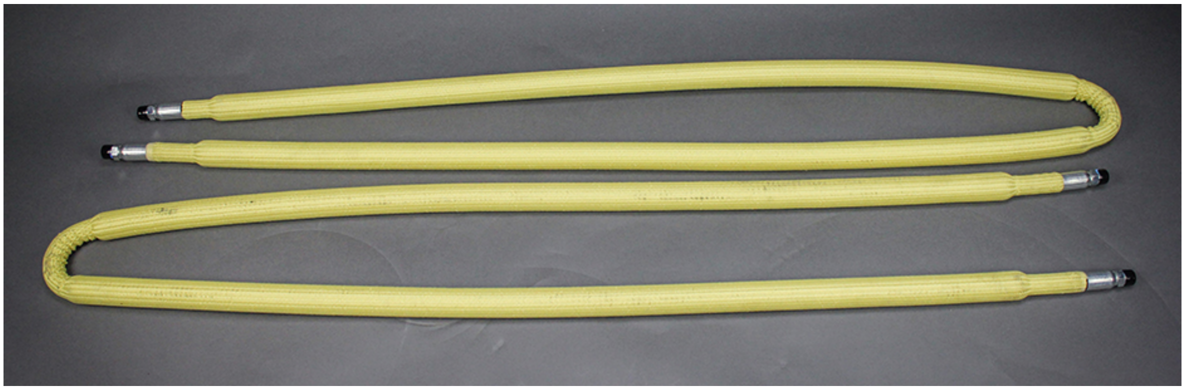

Figure 11. Complete conformable pressure vessel ready for pressure and permeability testing.

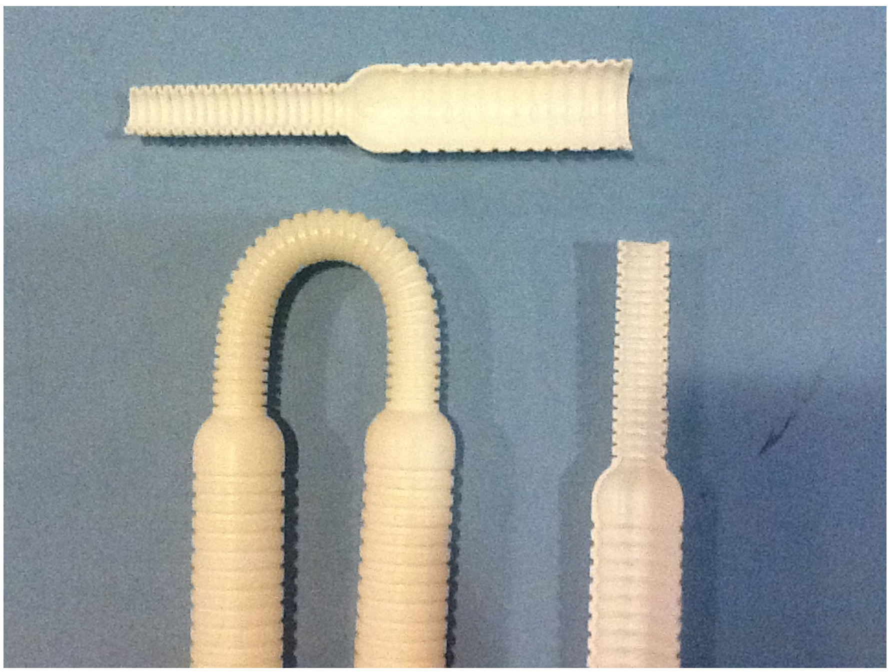

Figure 12. Core liner fabricated using EVAL™ resin.

Subtask 1.6 – Test Vessel Pressure Testing

HECR conducted hydrostatic testing of the conformable vessels during the 4th quarter of the project. Initial difficulties were found with the use of stock fittings. HECR was able to develop a custom fitting suitable for the task. Figure 13 compares the stock fitting (1) to the newly designed fitting (2).

Figure 13. Stock fitting versus newly designed fitting.

During testing HECR also confirmed the need for an additional layer on top of the Kevlar over-braid. Figure 14 shows the failure point of three different Kevlar braid designs, each failing below 10,000 psig. The final solution, also shown in Figure 14, included an overlay on top of the Kevlar braid. For this initial run, the overlay was performed by hand, but could be automated with the braiding process in the future. This pressure vessel failed at 33,731 psig at the end fitting. Attempts were made to temporarily repair the end fitting (see Kevlar wrap over the fitting body in the figure, right image) to test the full capability of the vessel, but this fix was not successful.

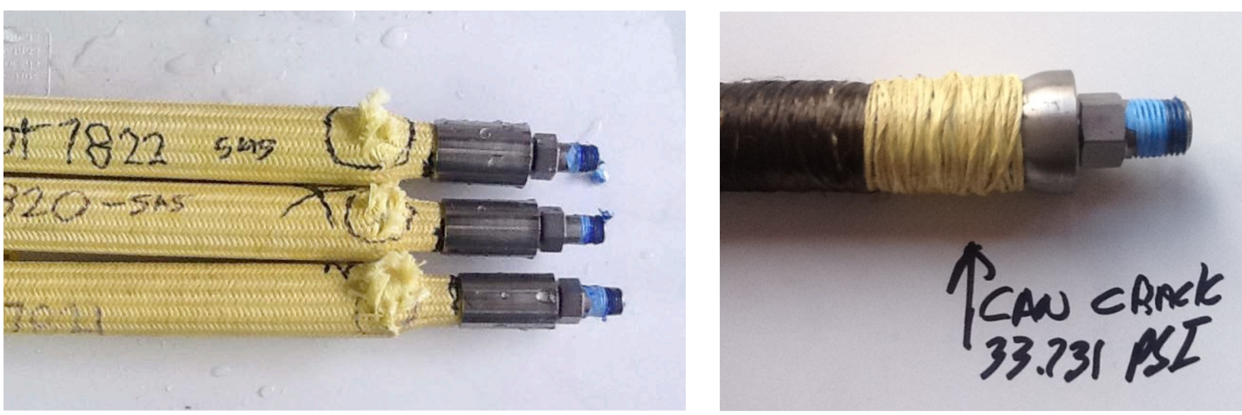

Figure 14. Burst failure point with Kevlar™ only over-braid shown in left image with successful burst pressure achieved with additional overlay (black fiber) in right image.

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Subtask 1.7 – Design and Build Hydrogen Test Cell

UT-CEM completed the design and build of the hydrogen leak test cell during the third quarter of the project. The test cell design underwent a review by the DOE Hydrogen Safety Panel, resulting in the schematic shown in Figure 15. A key safety attribute is the use of Pressure Relief Valves (PRV) for both the pressure vessel and test cell. Furthermore the test cell uses a robust stainless steel design capable of holding 5,000 psig pressure; the maximum pressure at which the pressure vessel will be tested. However, calculations show that since the internal volume of the test cell is much greater than that of the pressure vessel, the maximum pressure that should be seen in the test cell in the event of a sudden rupture in the pressure vessel would be on the order of 500 psig. The final hardware is shown in Figure 16 with a pressure vessel installed and ready for permeability test.

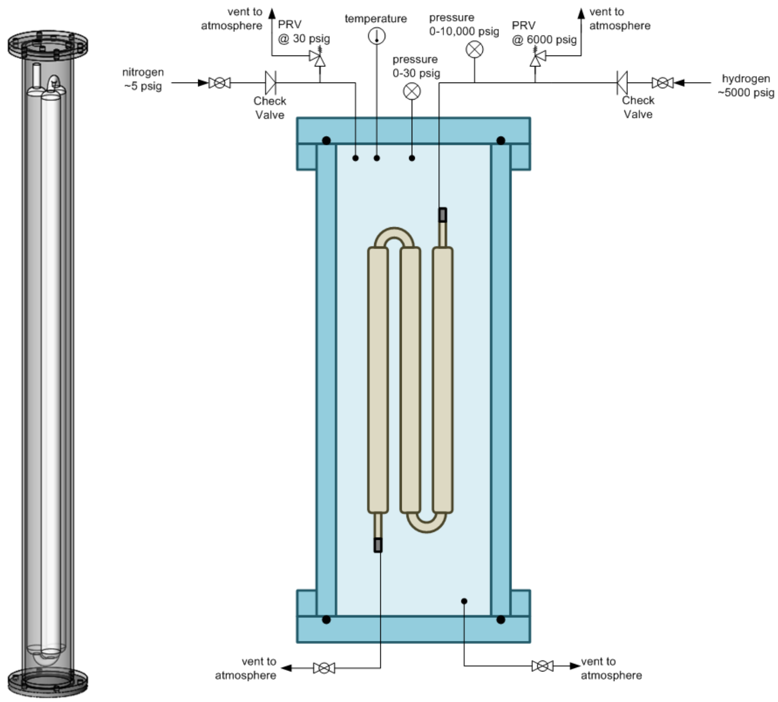

Figure 15. Hydrogen leak test cell design.

Figure 16. Test cell fabrication complete and setup for leakage testing.

Subtask 1.8 – Test Vessel Hydrogen Leakage Testing

During quarter 4, UT-CEM tested several iterations of the hydrogen storage vessels using a Hytrel™ resin material for the core liner.

The first iteration included an off-the-shelf end fitting that was not suited to the full operating pressure and goals of the program but adequate for early testing at test pressures not to exceed 1800 psi. Initial testing at 1000 psi showed high pressure drop rates, >6 psi/hr, but a linear trend indicative of a slow leak, Figure 17. HECR thought the end fitting crimp/swage may not be adequate, so the vessels were returned for re-crimping and then sent back to UT-CEM.

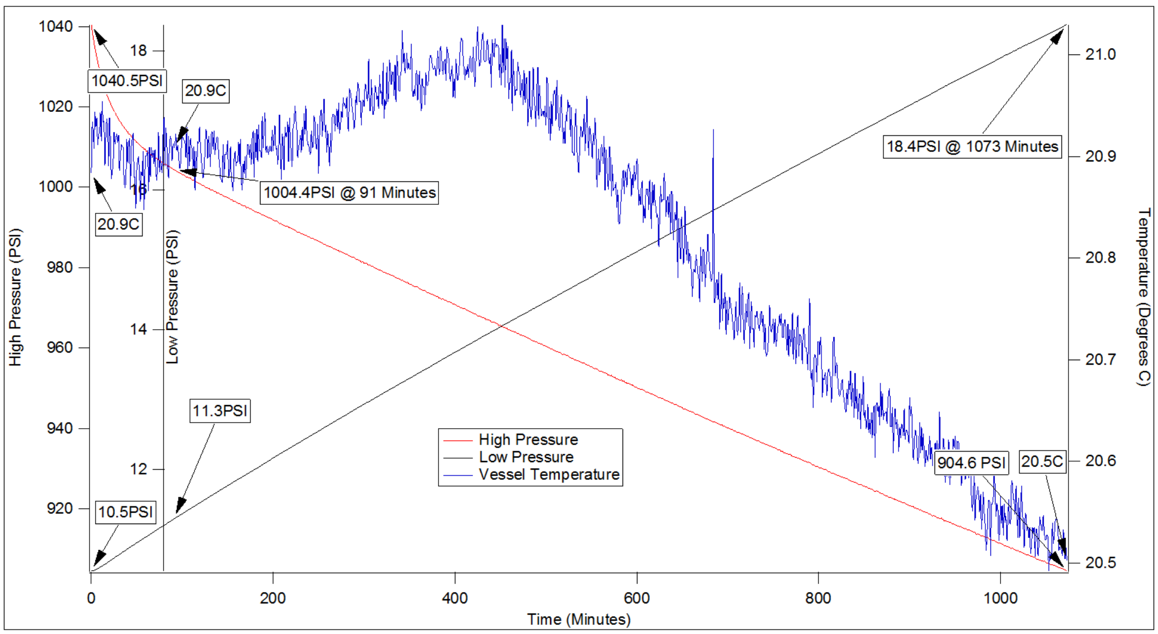

Figure 17. Testing performed at UT-CEM of hydrogen vessels with Hytrel™ core and off-the-shelf end fittings. Leak rate was found to be too high for the goals of the program, and a leak was suspected at the end fitting.

Upon testing the returned vessels at a test pressure of 1300 psi, the linear leak rate changed suddenly at 1158 minutes into the test, see Figure 18. This was indicative of an end fitting failure. With the end fitting under suspicion, the team made no conclusions from this round of testing regarding the permeability of the pressure vessel using a Hytrel™ core. The pressure drop rate up until the failure was still high at 9 psi/hr.

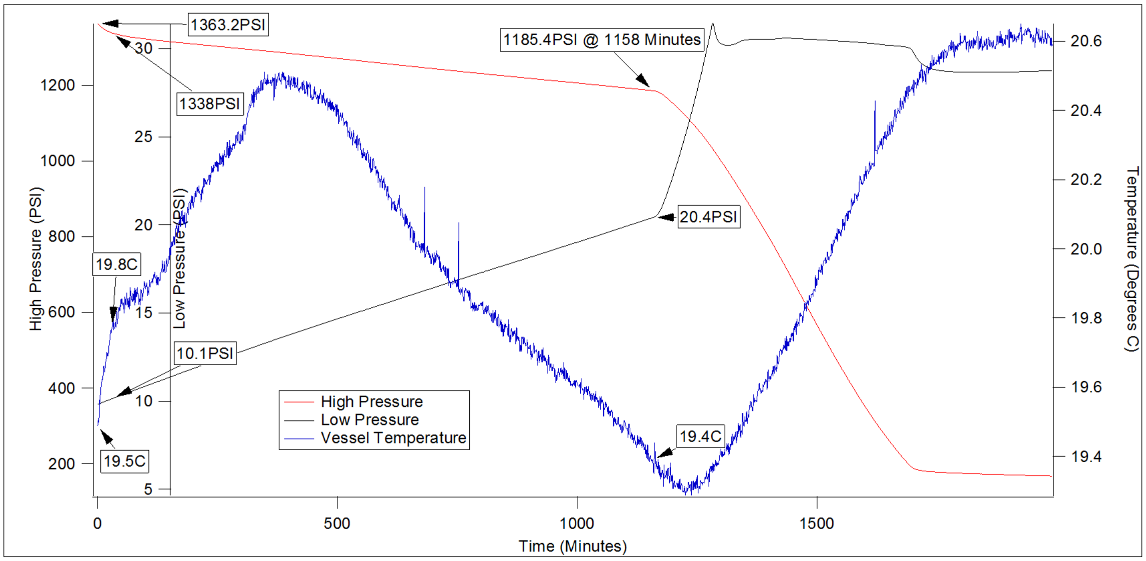

Figure 18. Testing performed after re-crimping the off-the-shelf fitting. Note the fitting failure at 1158 minutes with the pressure plots' slope change.

The second iteration made use of a new, custom fitting. UT-CEM tested two pressure vessels provided by HECR. The first round of testing of the vessels with the new fitting showed higher than anticipated leak rates of approximately 4.5 psi/hr, Figure 19. It was unclear if the leak rates were a result of permeation through the vessel or due to the end fitting. HECR was suspicious of the end fitting crimp/swage, noting that the optimal crimp force is an iterative process, so the vessels were returned and a new set was delivered to UT-CEM. The new set was pressure tested after re-crimping at HECR before delivery to UT-CEM, and the fitting was determined to be leak free.

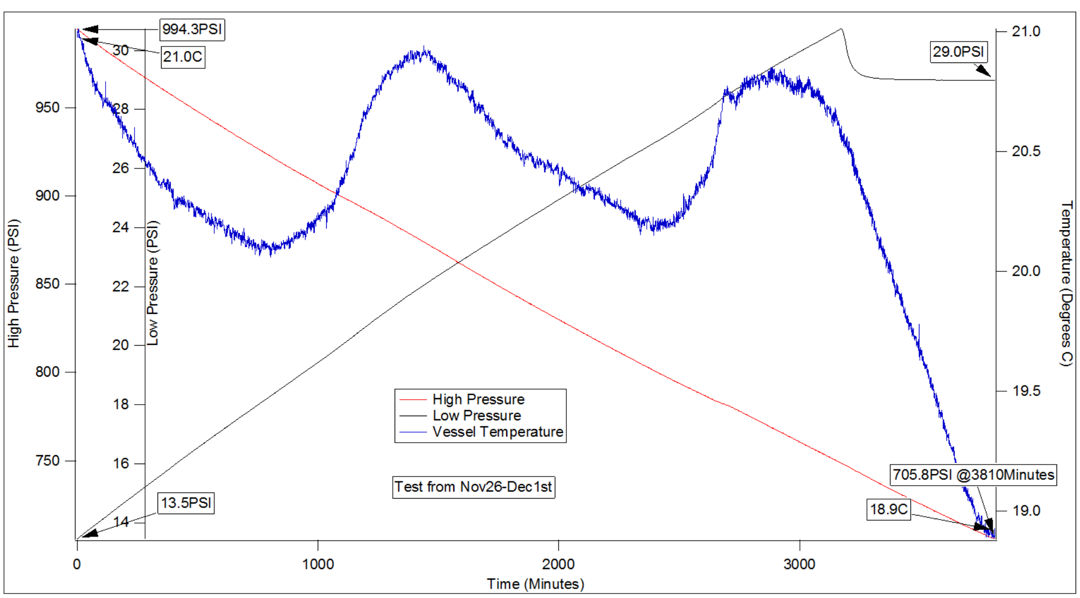

Figure 19. Testing on 12/1 at UT-CEM of hydrogen vessels with Hytrel™ liner and custom end fitting. High leak rate was thought to be due to a leaking end fitting that needed to be re-crimped. Hydrogen loss was most likely due to permeability.

The returned hydrogen vessels with a Hytrel™ core and a custom fitting that was tested by HECR and determined to be leak free were tested in UT-CEM's leak test chamber over a 2 day period in early-January, 2018 (?) (just after this reporting period). The first test was at 1000 psi, see Figure 20, and a follow up test was performed at 1800 psi, see Figure 21.

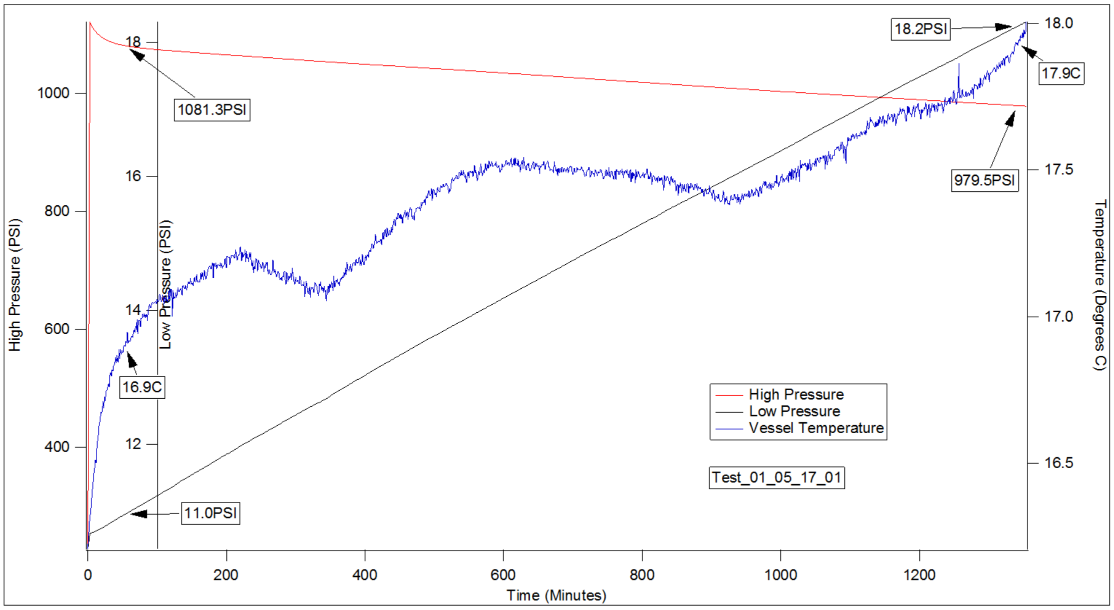

Figure 20. Testing on 1/5 at UT-CEM of hydrogen vessels with Hytrel™ liner and custom end fitting with re-crimp. Testing was done at 1000 psi showing a high leak rate.

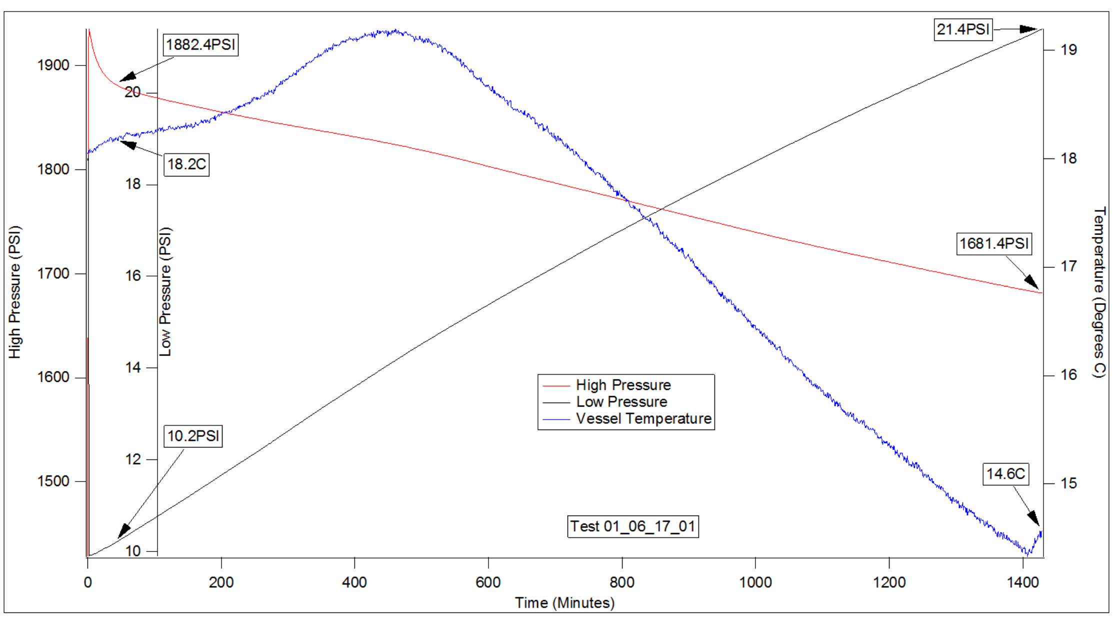

Figure 21. Testing on 1/6 at UT-CEM of hydrogen vessels with Hytrel™ liner and custom end fitting with re-crimp. Testing was done at 1800 psi showing a high leak rate.

In both cases, the leak rate was much higher than needed to meet the goals of the program. The 1000 psi test leaked over 100 psi in just under 21 hours, resulting in a 0.6 g/hr-kgH_2 leak rate, while the 1800 psi test leaked 200 psi in 23 hours, resulting in a 1.0 g/hr-kgH_2 leak rate. (Note, the pressure drop rate during the 1000 psi test was similar to that seen with the testing shown in Figure 17, and thus it is likely the fitting did not need to be re-crimped at that time.)

Hydrogen vessels with an EVAL™ core were evaluated next and showed improved leak results when compared to Hytrel™, but still were not acceptable for program goals and vehicle applications. Figure 22 shows the test results of the vessels constructed with the 60/40 blended EVAL resin sample as the pressure was ramped up at three levels—300 psig, 500 psig, and 1000 psig. Other blends were considered but failed at pressures below 1000 psig without any significant permeability results to report. Due to concerns over the pressure capability of the 60/40 blended vessels, the team did not test at higher pressure. The leak rate at 1000 psig was also already four times greater than the program goal, or 0.2 g/hr-kgH_2.

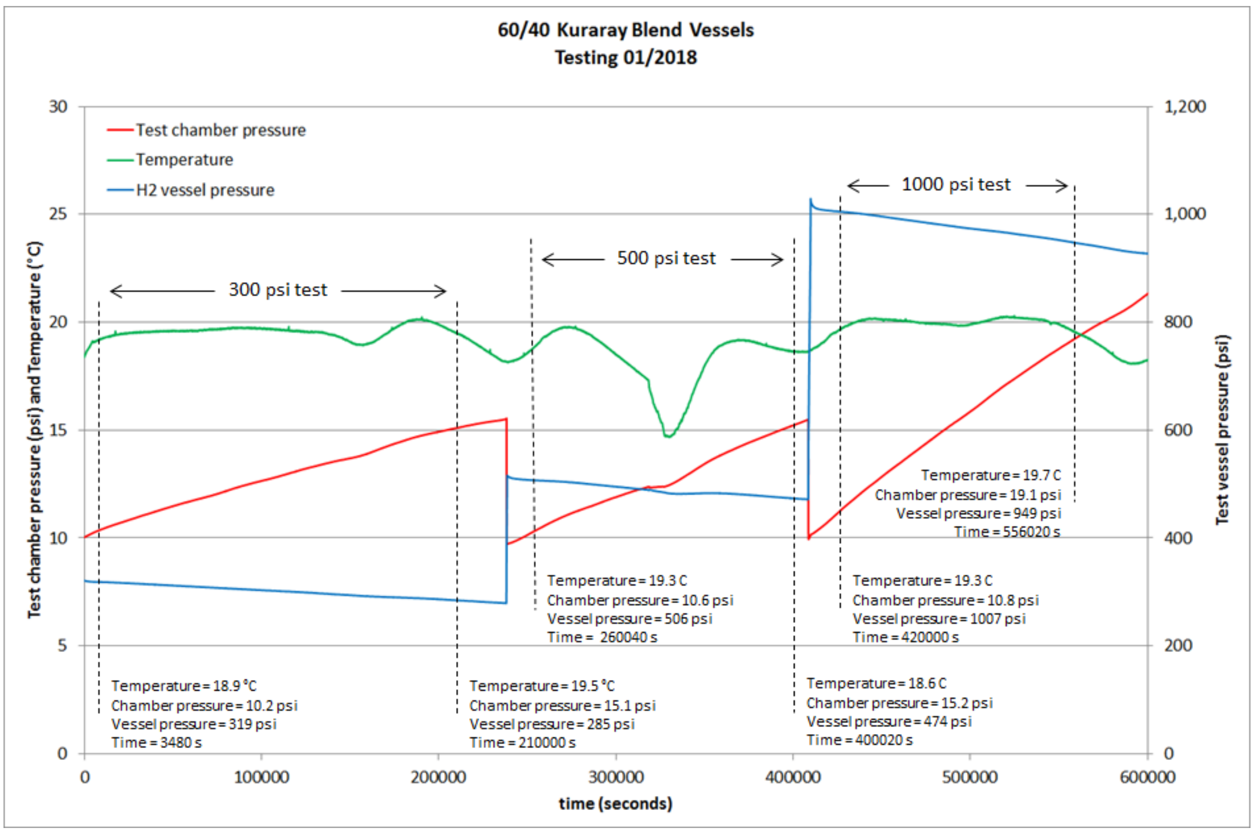

Figure 22. Testing competed on 2/8 at UT-CEM of hydrogen vessels with EVAL™ 60/40 core liners. Testing was done up to 1000 psi showing a high leak rate.

Subtask 1.9 – Test Vessel Thermodynamic Model Validation

Preliminary model validation was performed by comparing results to existing Type IV cylinders. In addition, UT-CEM also began working on validation exercises using computational fluid dynamic codes. Real world validation has yet to occur with actual test data from the pressure vessels since the size of the vessels built were two units long and would not produce significant differences in heating from the first cell to the last.

Subtask 1.10 – Downselect Final Pressure Vessel Design

This team was able to identify a suitable overwrap but the core liner material remains a question at the end of this phase of the project, thus the final pressure vessel design was not completed.

Project Conclusions and Lessons Learned

This project was conceived building on technology HECR had developed in compressed gas storage in a resin core with a tensile fiber overbraid. From the outset of the project the availability of a suitable resin was a known key project risk.

The resin compatibility with corrugation process was more difficult than initially expected. An early task in selecting a resin was to identify a resin with material properties that would work with the process as best as was known. This is shown in Subtask 1.2. The selected material needed to work with requirements that were pulling in different directions. For example the most effective hydrogen barrier materials are typically fairly brittle, and would be difficult to process through the corrugator, and would be difficult to form into a stacked and arranged vessel layout as conceived for a larger capacity vessel.

A key challenge in evaluating the resin for predicted hydrogen permeability is that data of any quality is very difficult to come by, and were rarely for the pressure ranges and material thicknesses this project was interested in. The project team used analogs when possible, like helium and other gas permeability. As there is little comparison data the project team could find, the accuracy of these were not known.

A project assumption from early in the project is that core and overbraiding performed separate functions in the vessel. This meant that the as long as the core was suitable to contain the hydrogen, it would work, and as long as the overbraid design could support the burst pressure, the two components could be tested somewhat independently during the project and then combined for a final successful vessel design. This turned out to be fairly accurate, but was based on a key assumption that the resin core could flex enough to accommodate pressure vessel growth when pressurized. This assumption showed accurate during initial testing with Hytrel, but not during final testing of the project with EVAL cores. During this testing, the pressure vessel cores began leaking, likely due to the core being stretched as the vessel slightly expanded during pressurization.

Although this project did not conclude with a test showing a suitable resin liner that could meet the demanding requirements by the pressure vessel format, the testing did show that the production process could produce prototype vessels as initially proposed. If a suitable resin liner is identified the technology may still provide a pathway for achieving DOE goals for future hydrogen gas storage.

Project Output

To date, the project team has not published results in any publications as it believes additional time, more data and testing is needed to have meaningful, peer reviewable publications. The team has fostered a key collaboration with Kuraray, manufacturers of the EVAL resin.

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