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G. Petitpas, J. Moreno-Blanco, F. Espinosa-Loza,
S. Aceves

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Rapid High Density Cryogenic Pressure Vessel Filling to 345 bar with a Liquid Hydrogen Pump

Guillaume Petitpas, Julio Moreno-Blanco,
Francisco Espinosa-Loza, Salvador M. Aceves

Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore CA 94550

Abstract

This paper presents the results of 24 cryogenic pressure vessel fill experiments with a liquid hydrogen (LH₂) pump manufactured by Linde and installed at the Lawrence Livermore National Laboratory (Livermore, CA) campus. The LH₂ piston pump takes LH₂ from the station Dewar at near ambient pressure (3 bar) and very low temperature (24.6 K) and pressurizes it to the vessel pressure in two stages of compression, up to 875 bar, although the rating of the cryogenic vessel used for these experiments limits fill pressure to 345 bar. Experiments spanned initial vessel temperatures from ambient to 22 K, enabling pump testing over a broad range of conditions. Experimental results confirm many of the virtues that make LH₂ pumping a promising technology for H₂ dispensing, both for filling cryogenic as well as ambient temperature vessels: high throughput (1.67 kg/min, 100 kg/h), low electricity consumption at the station due to high density of LH₂ minimizing compression work, and highest fill density, up to 80 g/L (estimated) when dispensing cryogenic hydrogen at 700+ bar. Analysis of the experiments shows that fill density can be predicted with reasonable accuracy (± 0.7 g/L) by assuming 10 kJ/kg K cryogenic vessel inlet entropy (pump delivery hose outlet entropy). Fill lines are finally generated on a H₂ phase diagram, producing charts that can be used for rapidly determining fill density for any vessel condition at the moment of fill initiation.

Introduction

Cryogenic pressure vessels (also known as cryo-compressed vessels) have fundamental thermodynamic advantages enabling high-density hydrogen (H₂) storage without the boil-off losses typical of cryogenic systems [1]. High density is critical for practical hydrogen-fueled transportation, enabling vehicles with similar driving autonomy and refueling time as today's gasoline vehicles while producing zero regulated and climate changing emissions. High density enables storage of large amount of fuel in a small package that occupies less space onboard the vehicle and weighs less, therefore reducing system cost by reducing the need for expensive structural materials (carbon fiber and metals). Low vessel cost combined with effective liquid hydrogen (LH₂) distribution, storage at the station, and dispensing results in minimum cost of ownership among existing approaches for automotive hydrogen storage [2]. Safety is also improved because cryogenic hydrogen has lower internal energy and therefore expands less in case of vessel failure [3]. Outer vacuum jacket provides an extra layer of protection and volume for H₂ expansion, reducing expansion pressure and thrust [4]. The key outstanding issue of

cryogenic pressure vessels is the need for robust and inexpensive vacuum multilayer insulation (MLI) that can maintain high performance ($<3 \text{ W/m}^2$ heat transfer) for the life of the vehicle, or at least between maintenance intervals. This level of insulation performance typically demands high vacuum quality ($<0.1 \text{ Pa}$).

Cryogenic pressure vessel refueling is also thermodynamically favored. A two-stage LH₂ pump manufactured by Linde enables direct pressurization of dense LH₂, therefore minimizing compression work (hence low electricity consumption) and enabling high throughput (100 kg/h, enough for 5-minute automobile refuels) from a small displacement (0.36 liters) 2-stage piston pump. In addition to this, refueling at densities higher than LH₂ at the Dewar (65 g/L) is possible due to the high compressibility of liquid hydrogen.

In this paper, we describe a series of experiments where a cryogenic pressure vessel was repeatedly filled from different initial conditions. Pressure and temperature were continuously measured during and after the experiment, until temperature equilibration indicated that density could be calculated from pressure and temperature data using standard equations of state [5]. In addition to fill density, we also report refueling time and electricity consumption. Next, we describe a thermodynamic fill model that may allow prediction of fill density based on initial (pressure and density) conditions when the vehicle drives into the station. We conclude the paper with the calculation of vessel fill diagrams that may be used to directly read fill density based on initial vessel conditions.

1. Lawrence Livermore National Laboratory (LLNL) Hydrogen Experimental Facility

LLNL's experimental facility consists of a liquid hydrogen pump that can dispense H₂ up to 875 bar, the refueling hose that accommodates high pressure and low temperature, and the cryogenic pressure vessel. Figure 1 depicts a schematic of the assembly, where the 345 bar 151 L cryogenic pressure vessel is connected to the LH₂ pump via a refuel hose (blue line=inlet), and the vessel outlet can be directed to the vehicle engine or fuel cell (green line), or otherwise released to the atmosphere through the station Dewar vent stack (red lines). The setup is man-operated: one operator controls the pump while another controls the flow using manual valves. During fueling, all valves are closed except the blue line (single flow refueling). The top red valve can be opened during pump operation to precool the refueling hose, while the bottom red valve is used to empty the vessel via the vent stack. The green valve remains closed during all filling experiments. The 345 bar 151 L vessel is installed onboard a Toyota Prius experimental vehicle previously converted to run on hydrogen fuel [6].

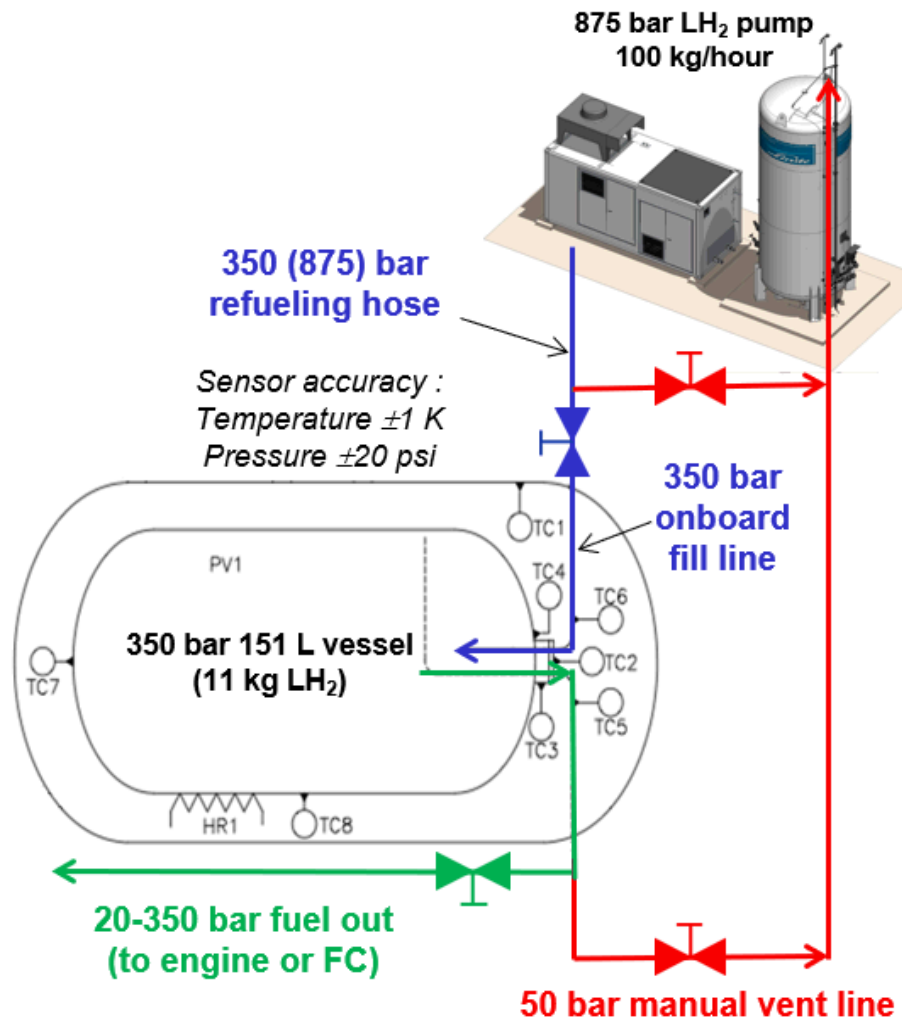


Figure 1. Schematic of the setup used to fill the 345 bar 151 L vessel with the LH₂ pump.



Figure 2. LLNL hydrogen experimental facility. The 345 bar 151 L cryogenic pressure vessel is installed onboard the Toyota Prius experimental vehicle [6]. The LH₂ pump is located inside the white container seen behind the back of the vehicle in this perspective, while the station Dewar for LH₂ storage is on the right.

The Liquid Hydrogen Pump

The LH₂ pump takes liquid hydrogen from the station Dewar (Figure 2) at low pressure (3 bar) and very low temperature (24.6 K) and delivers it as a cryogenic compressed gas at pressures as high as 875 bar and temperatures between 30 and 60 K. The basic operation of the pump is illustrated in Figure 3. The pump operates immersed in LH₂ (colored in blue) inside a secondary Dewar (the pump Dewar), which fills by gravity with LH₂ from the station Dewar. When the piston moves down, a valve opens allowing liquid hydrogen to flood the main cylinder. Upward movement of the piston compresses the hydrogen in the main cylinder to a moderate pressure (6 bar), sufficient to remove the LH₂ from near saturation into a thermodynamic state far removed from saturation that is unlikely to cavitate. The piston shaft is hollow, enabling hydrogen to flow from the main cylinder into the second stage of compression, where the piston pressurizes the hydrogen to the vehicle vessel pressure, up to 875 bar. Hydrogen flows through a check valve on its way to the vehicle vessel.

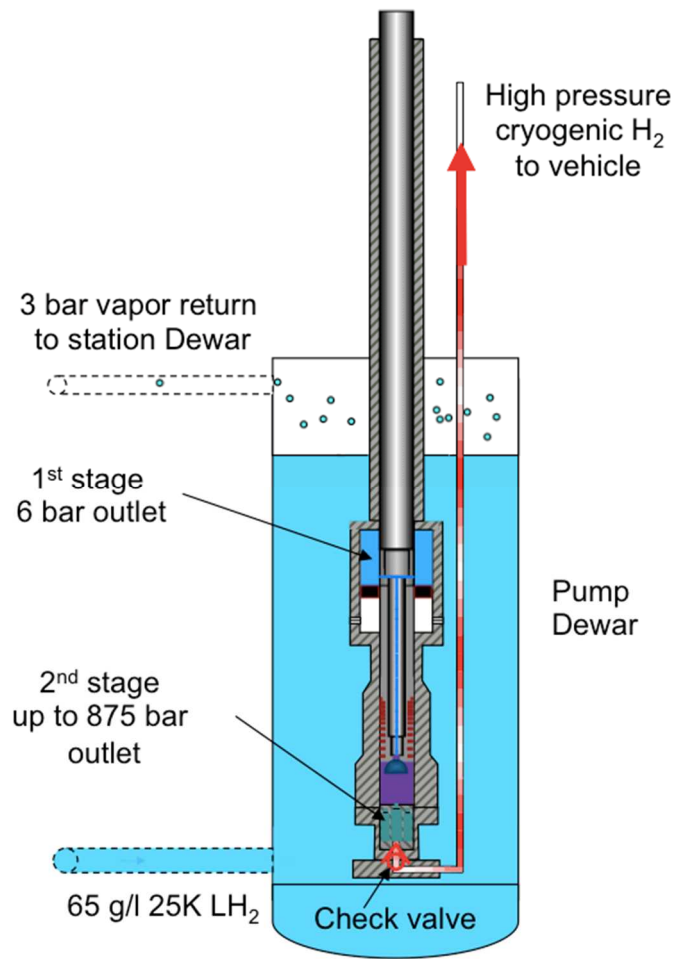


Figure 3. Schematic describing operation of liquid hydrogen pump.

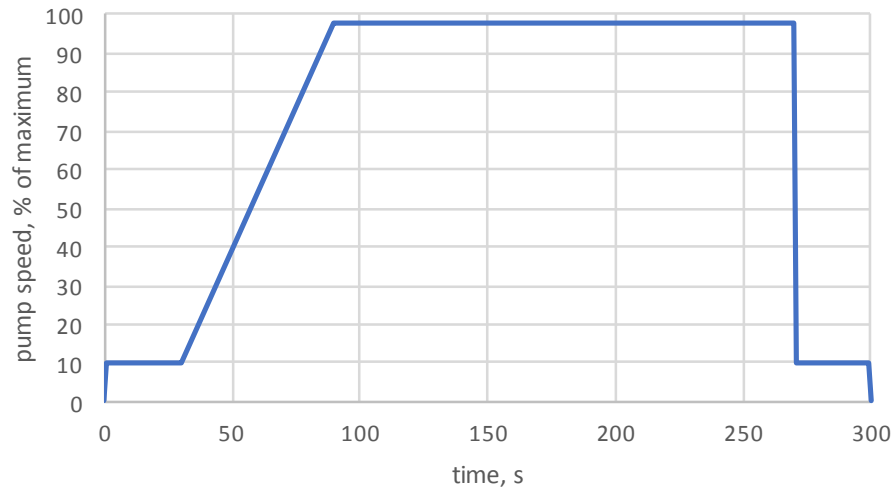


Figure 4. LH₂ pump speed history during a typical fill cycle.

The pump speed profile during a typical fill is illustrated in Figure 4. The pump starts slow (10% of maximum speed), and then ramps up to a steady speed – likely (although not necessarily) the maximum pump speed (1.44 Hertz frequency). The pump slows down to 10% of maximum speed when the target fill pressure is approached, and finally it automatically shuts down when the target pressure is reached. It is therefore apparent that there is a difference between average and maximum H₂ flow rates, and the difference depends on the fraction of time the pump spends at low speed vs. maximum speed. Initial slow operation time and ramp rate are adjustable, and careful tuning of these parameters can increase average fill rate while still allowing gradual pump speed-up, thereby minimizing piston stresses and lengthening maintenance intervals.

The LH₂ pump offers fundamental thermodynamic advantages over today's technologies that compress gaseous hydrogen (typically into a cascade) before dispensing:

1. Higher LH₂ density vs. gaseous hydrogen minimizes compression work [7]
2. Fill directly from the pump without the expense and losses of high-pressure storage (cascade)
3. Lack of cascade means that hydrogen is pressurized only to the vehicle vessel pressure
4. Fill speed is not limited by hydrogen heating
5. No need for hydrogen refrigeration or precooling at the station

These thermodynamic advantages result in practical advantages vs. today's alternative technologies for hydrogen refueling:

- High throughput, 1.67 kg/min (100 kg/h)
- Low station footprint and capital cost [8]
- Low electricity consumption at the station due to high density of LH₂ minimizing compression work
- Highest fill density, up to 80 g/L (estimated) when dispensing cryogenic hydrogen at 700+ bar

The liquid hydrogen pump has the capability for rapid (<5 minute) inexpensive refueling of vehicles with both cryogenic and ambient temperature vessels (by incorporating a heat exchanger in the delivery path) and it is ideal for large stations demanding many consecutive back-to-back refuels. Beyond automobiles, other vehicles such as buses, medium/heavy-duty vehicles, rail, marine, and aircraft can benefit from the high-density hydrogen storage while avoiding the need for precooling during refueling.

Refueling Hose

Hydrogen is dispensed from the pump to the vessel using a refueling hose specifically designed for the application. The hose was insulated to enable transfer of cryogenic hydrogen, rated for high-pressure, and flexible to allow for manipulation and connection to the receiving vessel.

A hose segment rated for 830 bar (12,000 psi) was first pressure tested at liquid nitrogen temperature to ensure safety at cryogenic temperatures. The segment was successfully pressurized to 3800 bar, demonstrating a safety factor in excess of 4 at 875 bar and 10 at 345 bar (Figure 5).

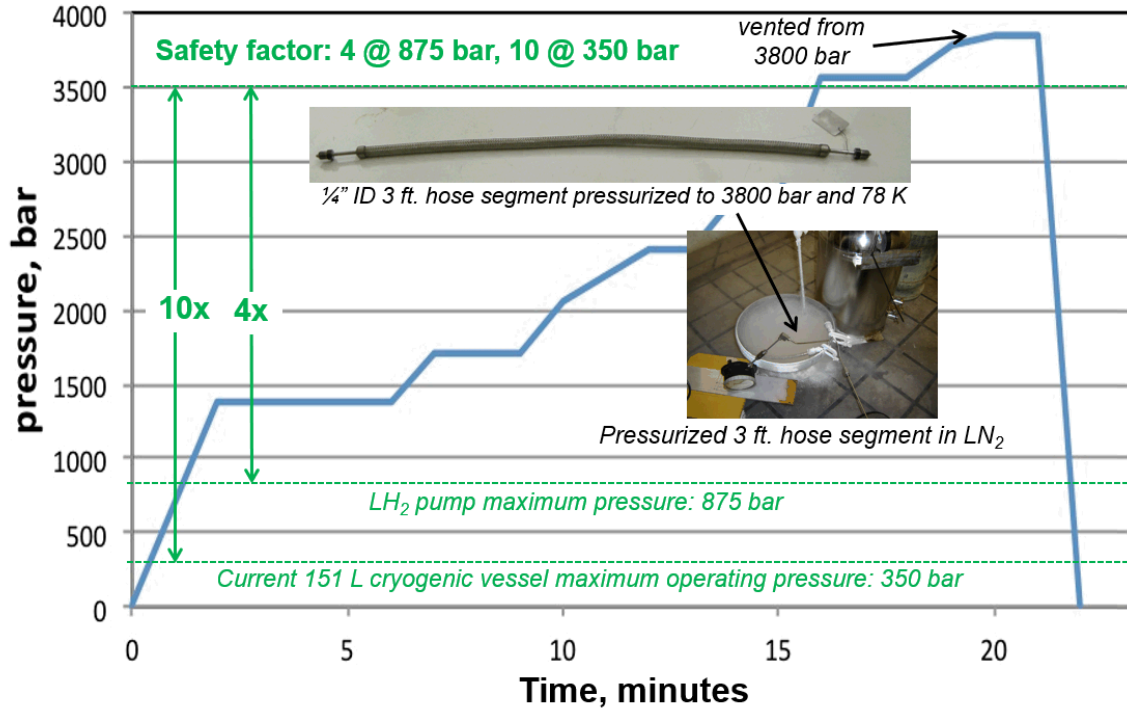


Figure 5. Pressure testing of a segment of the hose at liquid nitrogen temperature and up to 3800 bar.

Three hose segments were then welded together, and vacuum insulated using a flexible outer hose. Figure 6 shows pictures of the hose segments next to the outer hose, before and after welding. The picture in the left shows one of several small fiberglass (G10) rings maintaining the high-pressure hose centered within the outer hose, thereby reducing heat transfer by avoiding direct contact. The outer hose was evacuated after assembly. The total length is approximately 3 meters. Once built and tested, the hose connected the LH₂ pump with the cryogenic pressure vessel onboard the experimental vehicle during refueling (Figure 7).

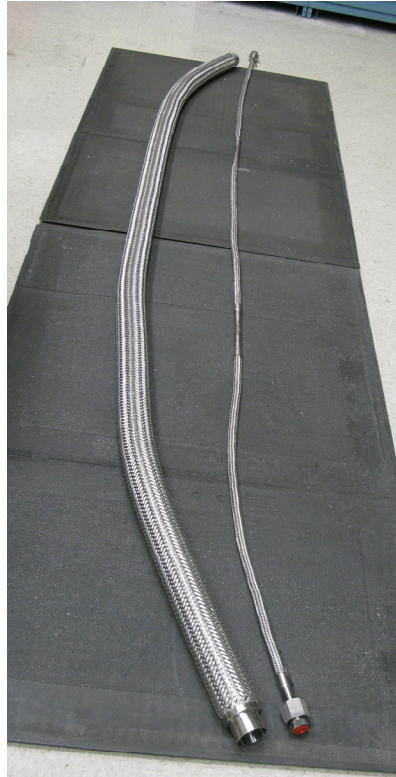
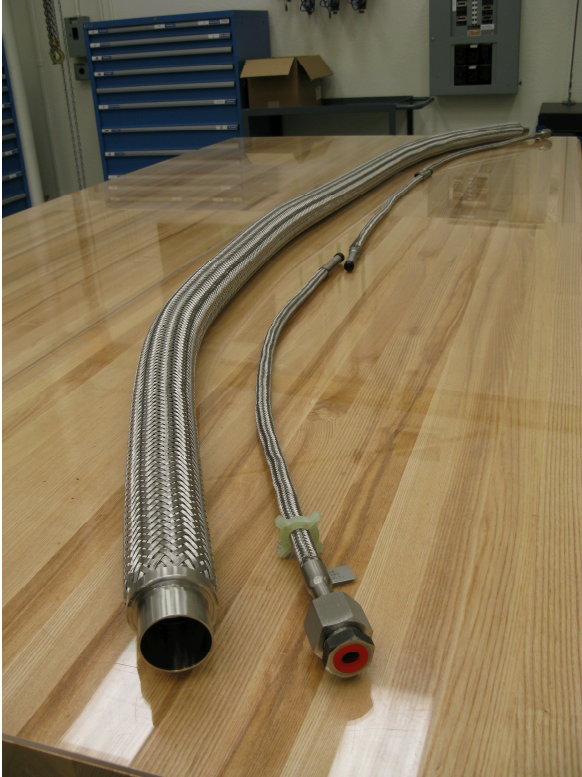


Figure 6. High pressure hose segments next to the vacuum jacket, before (left) and after (right) hose welding.



Figure 7. Vacuum insulated high-pressure refueling hose connected to the cryogenic pressure vessel installed onboard the vehicle.

The Cryogenic Pressure Vessel

Fill experiments were conducted on a cryogenic pressure vessel installed onboard a Toyota Prius experimental hydrogen-fueled vehicle (Figure 2) and described in an earlier publication [6]. The vessel has 151 liters internal volume and 345 bar maximum operating pressure. Vessel rating is therefore considerably lower than the pump rating (875 bar) leaving much of the LH_2 pump performance map unexplored until a stronger vessel is built and tested. The inner (high-pressure) aluminum-lined, carbon fiber wrapped vessel weighs 66.3 kg (37.5 kg aluminum and 28.8 kg composite). Heat transfer from the environment was measured at 4-5 W depending on ambient temperature and vacuum quality [9].

The experimental pressure vessel was instrumented with a pressure indicator as well as three cryogenic diode temperature sensors located in the forward (inlet/outlet) boss (TC2 in Figure 1), opposite end boss (TC7), and mid cylindrical composite layer (TC8), in addition to a thermocouple used to measure ambient temperature (TC1) and other thermocouples to measure inlet/outlet flow temperature (TC3-TC6). These measurements were registered in a portable computer installed onboard the vehicle for continued monitoring and analysis.

2. Experimental results

Table 1 shows technical data for the 24 fill experiments reported here. Fill experiments always started in thermal equilibrium, with the vessel and the hydrogen at the same temperature and the three temperature sensors stable and converged to ± 1 K. Equilibration often demanded ~ 1 hour wait after fill or vent operations. However, faster equilibration is achieved at lower temperature as the specific heat of vessel components (aluminum and carbon fiber-resin composite) drops considerably as the vessel cools down.

We report liner boss temperatures (TC3 location in Figure 1), considered most accurate due to sensor location on the highly conductive aluminum liner, which puts the diode in intimate thermal contact with the hydrogen inside the vessel.

All fill experiments were preceded by fill line precooling, which was accomplished by running the pump at moderate speed (20-50 kgH₂/h) for 5 minutes while releasing the hydrogen through the Dewar vent line. Following fill line precooling, the vessel fill valve was opened, the vent valve was closed, and the pump filled the vessel until it automatically shut down when the pressure vessel reached the target pressure (330-345 bar except for five partial fill experiments 1, 12, 13, 14 and 16).

Fill experiments were followed by a slow hydrogen vent, typically to near ambient pressure, which cools down the vessel due to (near) isentropic H₂ expansion. Venting was once again followed by ~ 1 hour wait, sufficient to reach thermal equilibration in the vessel before the next fill.

Several hydrogen vent operations ended with the vessel in the two-phase region (saturated liquid and vapor). These are labeled in blue in Table 1. In the two-phase region, it is not possible to determine H₂ density from pressure and temperature, and density is determined by modeling H₂ venting, starting from the last fill conditions and assuming that the vessel remains in thermal equilibrium with the hydrogen during the (slow) vent. Modeling applies mass and energy conservation equations to the open vessel and takes into account the fact that the vent tube is located on the upper side of the vessel, and therefore the vessel vents vapor and does not vent LH₂, which deposits at the bottom due to its higher density.

As previously described, set points for the pump speed profile (initial slow period and ramp rate, Figure 3) are adjustable and can be shortened for faster refueling. However, these experiments were conducted with a conservative set of parameters (30 seconds initial slow period and 1-minute ramp time) to reduce stresses in the pump during initial operation.

At the time the experiments were conducted, the LH₂ pump did not have electric power instrumentation and power consumption was read from the substation power meter. Pump electric power consumption measurements reported here are therefore preliminary and likely above the actual energy consumption. No electricity consumption measurements

were taken for experiment 14, and 16 through 24. More accurate values will be reported in a future publication based on improved instrumentation.

Initial experiments (1-15) were conducted with the delivery tube (connecting LH₂ pump outlet to fill hose) uninsulated. Standard practice in cryogenic equipment demands initial operation with no thermal insulation, because thermal contraction and expansion tends to loosen fittings and cause leaks. After initial operation and retightening of all fittings, thermal insulation was applied in March of 2014, and the final series of experiments (16-24) was run with insulated delivery tube.

The experimental sequence started with the vessel at ambient temperature and low pressure (18.9 bar). Experiments 1-5 were conducted in the same day and therefore initiate at progressively colder temperatures, with experiments 4 and 5 initiating within the two-phase region (labeled in blue in Table 1).

Following a weekend and partial warming of the vessel, we conducted a sequence of six experiments (6-11) on one day (8/12). Due to the cold initial temperature (63.2 K) in experiment 6, the vessel rapidly reached the two-phase region and all remaining experiments (7-11) initiated inside the two-phase region.

Three partial fills (Experiments 12-14) and a full fill (15) were conducted during seven days in September, starting near ambient temperature and partially cooling the vessel to 117.7 K at the end of Experiment 15.

The final set of experiments (16-24) was run with thermal insulation on the delivery tube, and they essentially repeat the experimental sequence of the first two days (Experiments 1-11), in an effort to evaluate the effect of thermal insulation. Most of these runs start within the two-phase region (19-23) and show similar fill density. The final fill (24) was conducted after a partial vent to 54.9 bar and therefore started in the single-phase region.

We next list key results from the 24 fill experiments.

- Consecutive fill and vent experiments cool down the vessel and increase the fill density as the internal energy of the system keeps dropping. After several consecutive fills the system reaches steady state, where the vessel cools down as much as possible and density reaches its maximum. This is observed in experiments 10 and 11, as well as in experiments 20 and 21. Successive fills at this point would closely replicate the results of the previous fill.
- The vessel fill density did exceed the density of LH₂ in the Dewar (65 g/L) in most of the experiments that started within the two-phase region. This is due to the high compressibility of LH₂ when pressurized to 345 bar. The maximum density measured (72.4 g/L) is 11% higher than LH₂ density at the Dewar. The LH₂ pump therefore contributes to 11% increased vehicle autonomy by increasing storage density. This density is expected to be the highest possible for a vessel filled to 345 bar when continuously driven for hours.

- Comparing experiments 1-15 with experiments 16-24, we conclude that thermal insulation on the delivery tube had little effect on fill density, despite considerable heat transfer from the environment (calculated at 1 kW for a 10-m long 1.4 cm outer diameter tube exposed to natural convection from the environment). Searching for an explanation, we conducted transient thermal analysis of hydrogen and delivery tube during a typical fill. The first step of the fill process is delivery tube precooling, where H₂ flows at moderate rate for 5 minutes. H₂ flow during these 5 minutes is very cold, because the delivery pressure is low as H₂ is vented to the atmosphere. This cold flow precools the delivery tube to a low temperature. Later, during vessel fill, delivered H₂ heats up due to compression work as the vessel pressurizes. Transient analysis shows that, as the vessel pressurizes, the flowing H₂ becomes warmer than the precooled tube, and therefore the tube absorbs the heat from the environment without significantly transferring heat to the flowing H₂, even though there is substantial heat transfer into the uninsulated tube. This would not be the case in a commercial station where tube precooling is impractical. Commercial stations demand delivery tube insulation to maintain high fill density by keeping the delivery tube cold between fills.
- It is observed that the maximum density experiment (22) has the third highest fill pressure and the second shortest fill time of all the experiments starting within the two-phase region. High pressure and rapid fill combined with thermal insulation of the fill tube explain the highest density measured.
- Peak H₂ flow rates are over 1.67 kg/min (100 kg/h) in most cases. Average H₂ flow rates are typically between 1.1 and 1.4 kg/min due to conservative pump fill profile parameters being used. Operating experience beyond the 24 experiments reported here has enabled faster pump ramp-up rates leading to higher average H₂ flow rate. These results will be reported in a future publication.
- Some experiments have very low H₂ flow rates (0.45-0.75 kg/min), but these are either preliminary or partial fills where the pump spent most of the time in the initial low speed or ramp up period. Average pumping speed rapidly increases as the mass of H₂ dispensed increases, because the pump can then spend more time at maximum speed.
- Electricity consumption is 1.42 kWh/kg H₂ average if the slow and partial fills (1, 12, 13, 14, 17) are excluded. While higher than expected from thermodynamics, this value is considerably lower than necessary for gaseous H₂ pressurization in today's compressors (1.35 kWh/kg H₂ theoretical minimum and ~3 kWh/kg H₂ typical [10]). As previously discussed, improved instrumentation will enable reporting of more accurate electric power consumption figures in a future publication.

Table 1. Summary of results for the 24 pressure vessel fill experiments conducted with the LH₂ pump between August 2013 and April 2014. Values in blue with an * on the experiment number denote initial conditions within the 2-phase region.

Date	#	Initial T	Initial P	Initial rho	Final T	Final P	Final rho	H2 dispensed	Fill time	Average flow	Peak flow	Refuel energy
		K	bar	g/L	K	bar	g/L	kg	min	kg/min	kg/min	kWh/kg
8/8/2013	1	288	19	1.6	219	166	16.7	2.3	5.0	0.45	1.21	2.62
	2	204	85	9.5	153	330	38.8	4.4	6.5	0.67	1.7	1.58
	3	95	2	0.5	87	333	58.5	9.0	6.5	1.38	1.7	1.22
	4*	21	2	5.0	74	341	64.1	8.9	7.0	1.37	1.7	1.45
	5*	21	2	12.5	67	338	66.0	8.0	6.3	1.29	1.7	1.48
8/12/2013	6	63	51	22.4	85	338	59.3	5.6	4.4	1.27	1.7	1.43
	7*	21	2	4.1	71	337	65.8	9.3	6.5	1.43	1.7	1.39
	8*	21	2	11.4	67	338	67.8	8.5	5.8	1.46	1.7	1.29
	9*	21	2	18.0	64	338	69.5	7.8	5.6	1.38	1.7	1.28
	10*	21	2	22.8	62	339	70.3	7.3	5.3	1.38	1.7	1.37
	11*	21	2	22.8	62	338	70.3	7.3	5.1	1.42	1.7	1.37
9/6/2013	12	278	3	0.2	199	183	19.3	2.9	5.1	0.57	1.7	2.44
	13	160	3	0.5	144	49	8.0	1.1	2.3	0.49	0.65	3.54
9/11/2013	14	212	29	3.3	174	124	15.5	1.8	2.4	0.76	1.7	-
9/12/2013	15	163	23	3.4	118	346	48.6	6.8	5.2	1.29	1.7	1.46
4/30/2014	16	290	2	0.2	193	231	24.2	4.0	3.0	1.36	1.7	-
	17	194	232	23.1	178	346	35.3	1.8	3.0	0.61	1.2	-
	18	88	2	0.7	82	346	61.4	9.2	6.6	1.40	1.7	-
	19*	21	2	7.8	72	346	66.2	8.8	6.2	1.42	1.7	-
	20*	21	2	13.1	67	346	68.4	8.4	5.9	1.40	1.7	-
	21*	21	2	18.3	62	337	70.3	7.8	5.7	1.39	1.7	-
	22*	21	2	23.6	59	343	72.0	7.3	5.2	1.40	1.7	-
	23*	21	2	21.2	63	339	69.8	7.3	6.5	1.14	1.7	-
	24	43	55	50.4	64	343	69.4	2.9	2.6	1.10	1.7	-

3. Thermodynamic Fill Model

A detailed physics-based model of hydrogen flow, compression and pressurization through the LH₂ pump would be very useful for a full evaluation and understanding of this promising technology. However, complexity and lack of detailed information due to proprietary issues keep us from developing this model. Instead, we have searched for a simplified thermodynamic model that may replicate experimental results and show promise for predicting fill density within the limits of the experimental effort (up to 345 bar).

It is typical in thermodynamics to model compression processes by comparison with an ideal isentropic process. Outlet pump conditions are then calculated from an exergetic efficiency, defined as the ratio between isentropic and actual pumping work [6]. This approach, however, proved difficult to apply in this case due to the complexity of the process, the broad range of operating conditions (delivery pressure between 2 and 345 bar), and the many loss mechanisms external to the pump such as heat transfer and pressure drop in tubes, valves, fittings, hose, etc. which would have to either be included within a single exergetic efficiency or separately modeled.

Searching for a better approach for developing a thermodynamic fill model, we considered the possibility of assuming constant hydrogen entropy at the cryogenic vessel inlet (or delivery hose outlet). Starting with the entropy at the station Dewar (2 kW/kg K

for saturated LH₂ at 3 bar), this model assumes that entropy increases caused by irreversibilities in the different system components are additive, possibly resulting in a vessel inlet entropy that may remain approximately constant throughout the process. This entropy is unknown a priori, and necessarily higher than the initial entropy (2 kW/kg K) due to irreversibilities.

The assumption of constant vessel inlet entropy was tested against the 24 experiments by modeling each fill, calculating a final fill density, and comparing this to the experimental results. Calculation of the root mean square error reveals that assuming vessel inlet entropy $s=10$ kJ/kg K results in optimum fit to experimental data (Figure 8). The fill density root mean square error is 0.7 g/L – very reasonable for such a simple model.

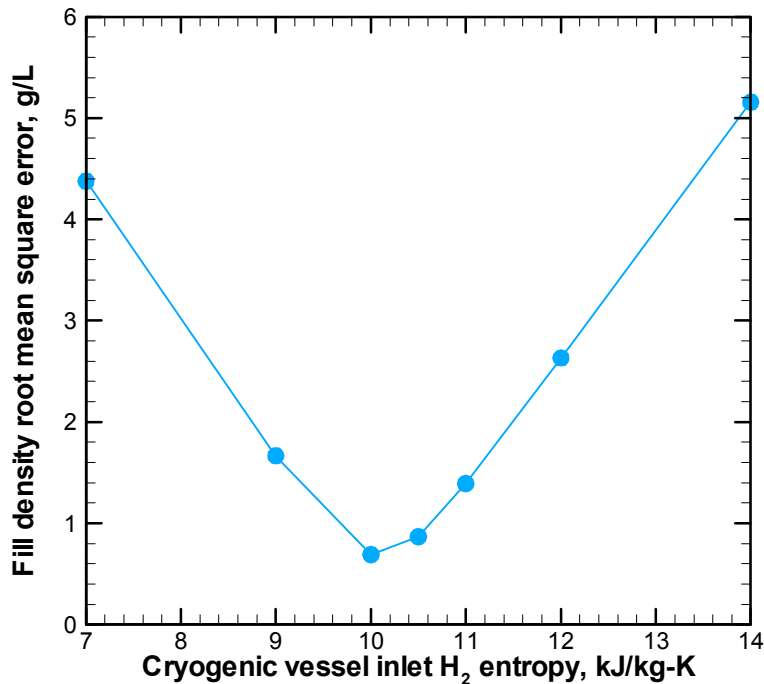


Figure 8. Fill density root mean square error for a thermodynamic fill model that assumes constant cryogenic vessel inlet entropy. RMS error was calculated by comparing fill density model results vs. measured results for the 24 fill experiments.

Figures 9-12 show a comparison between experimental and numerical results (with cryogenic vessel hydrogen inlet entropy=10 kJ/kg K) for temperature vs. density histories for the 24 fill experiments. The following observations can be derived from careful study of the figures.

- The model predicts well the end point on the fill lines, therefore producing accurate estimates of fill density. However, intermediate points are not as well predicted. There are two main reasons for this: (1) The temperature sensor is located outside the vessel and there is a time lag before it equilibrates with the hydrogen temperature inside, and (2) The model assumes thermal equilibrium between hydrogen and vessel, while in reality the vessel takes some time to

equilibrate with the hydrogen. This is especially important at higher temperatures when the specific heat of the vessel materials is higher.

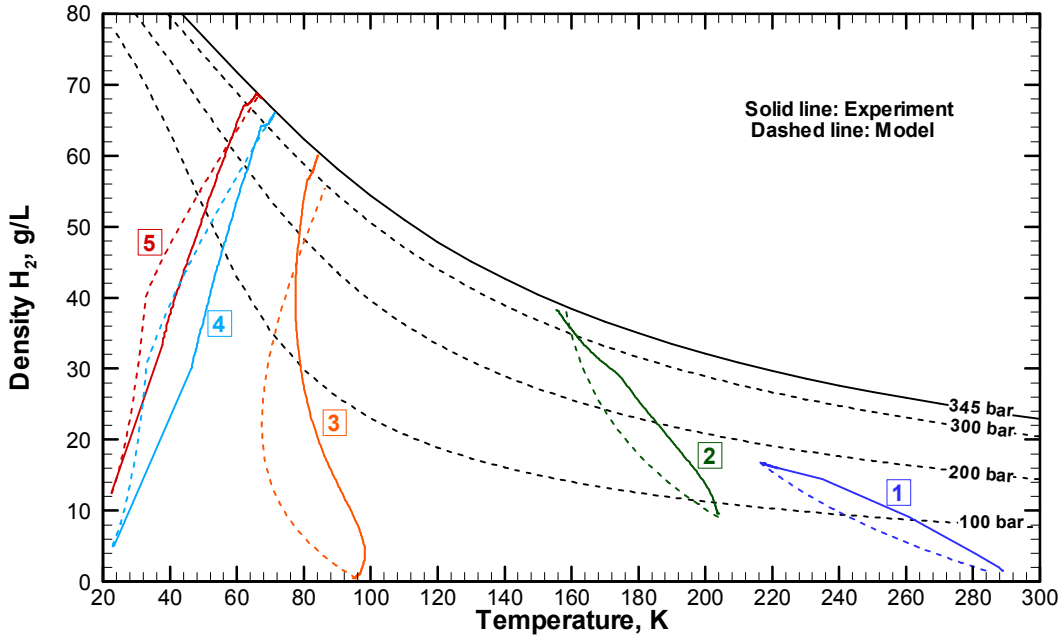


Figure 9. Temperature-density histories during fill for experiments 1-5. The figure shows experimental results (solid lines) and numerical results (dotted lines) calculated with the thermodynamic fill model assuming 10 kJ/kg K vessel inlet entropy.

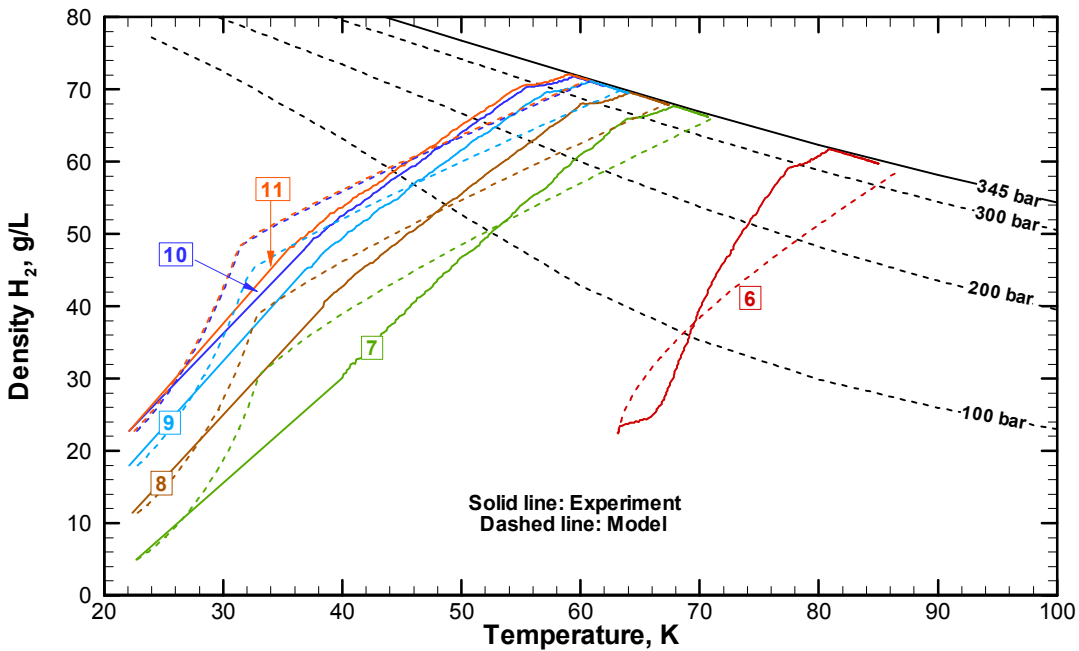


Figure 10. Temperature-density histories during fill for experiments 6-11. The figure shows experimental results (solid lines) and numerical results (dotted lines)

calculated with the thermodynamic fill model assuming 10 kJ/kg-K vessel inlet entropy.

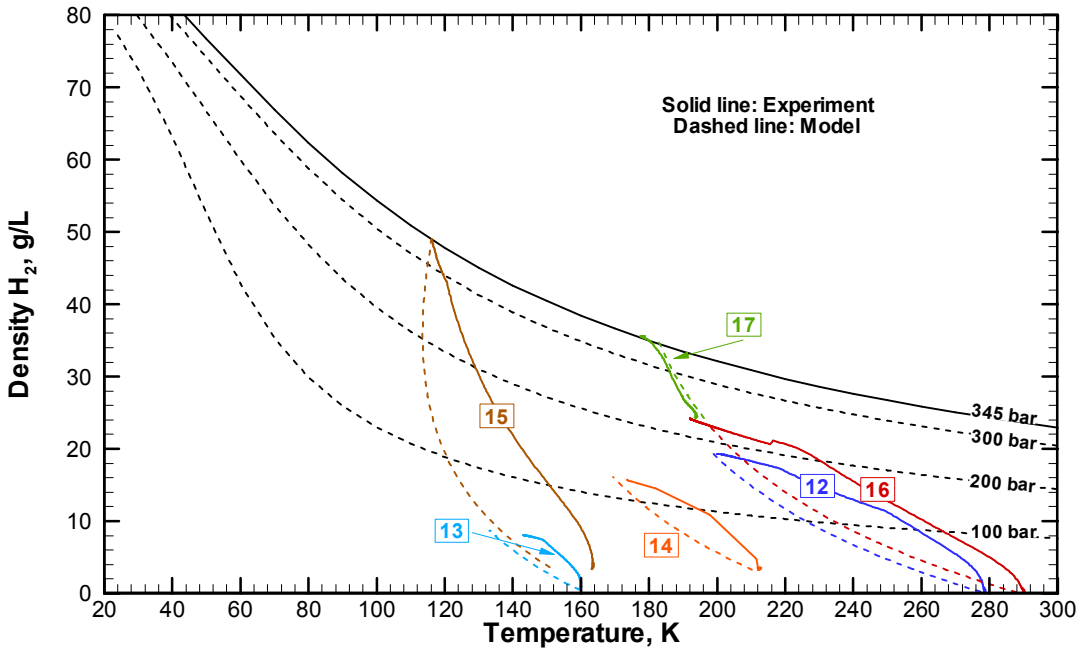


Figure 11. Temperature-density histories during fill for experiments 12-17. The figure shows experimental results (solid lines) and numerical results (dotted lines) calculated with the thermodynamic fill model assuming 10 kJ/kg K vessel inlet entropy.

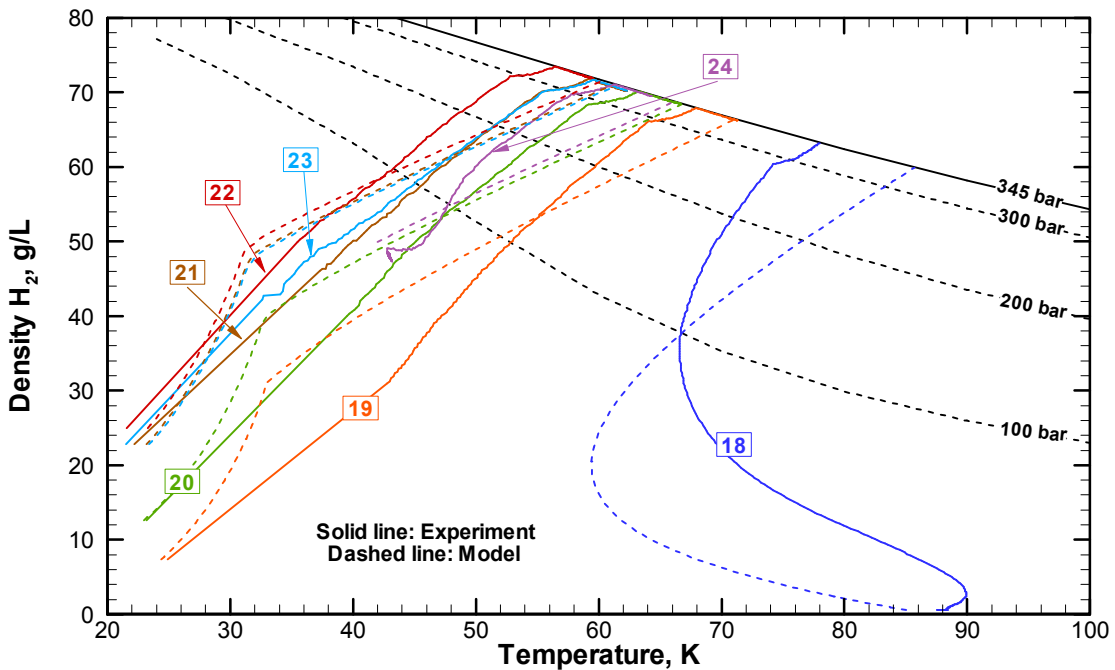


Figure 12. Temperature-density histories during fill for experiments 18-24. The figure shows experimental results (solid lines) and numerical results (dotted lines) calculated with the thermodynamic fill model assuming 10 kJ/kg K vessel inlet entropy.

- Fills that initiate in the two-phase region (4-5, 7-11, 19-22) follow a similar pattern. Initially, the model predicts higher density. This is because, according to the model, the vessel can fill considerably while remaining at low pressure in the two-phase region. Departure from the two-phase region is indicated in the model lines by a sharp change in slope. About two thirds into the fill process, the lines cross and experimental density becomes higher. This can be explained in terms of temperature sensor time lag. As the vessel fills up and pressure increases, hotter hydrogen enters the vessel. However, it takes some time for the temperature sensor to “feel” the hotter temperature, and therefore the sensor reads a low temperature, which translates to higher density. Finally, experimental lines move parallel to the maximum pressure line as temperature equilibration occurs in the vessel after completion of the fill process, increasing experimental temperature at nearly constant pressure.
- Fill experiments initiated at higher temperature (1-3, 12-14, 15-18) can be explained in terms of sensor time lag. Initially, the sensor is slow to detect cooling inside the vessel caused by cold hydrogen entry, and therefore the model predicts lower temperature and higher density at any given pressure. This may not be obvious at first glance from the figures as experimental lines appear on top of model lines. However, for a meaningful comparison, densities should be compared at equal pressure, not at equal temperature. Subsequent temperature equilibration results in the sensor catching up and the two lines reaching similar end points (similar fill density).
- Experiments 6 and 24 are the coldest fills that do not initiate at the two-phase region. In these cases, the vessel heats up as it fills because the hydrogen inlet temperature is higher than the initial vessel temperature.
- Experiment 18 is unique because it starts and ends at (nearly) the same temperature. Initial vessel cooling by low pressure and low temperature hydrogen is later compensated by higher pressure and temperature hydrogen entering the vessel as fill progresses. It is therefore concluded that initially empty vessels near 80 K will fill to approximately the same temperature and 345 bar.

4. Vessel Fill Diagrams

Using the thermodynamic fill model with $s=10$ kJ/kg K and the characteristics of the experimental pressure vessel, we have developed a vessel fill diagram (Figure 13) that can be used to predict fill density for any initial condition. From any initial temperature and pressure (or density) we can follow the red lines up to the target pressure to determine fill density.

Figure 13 is based on an internal energy versus density diagram that has been shown to have advantages for visualization and evaluation of cryogenic vessel processes including cooling during driving and heating during parking [6]. The figure shows constant

pressure lines (green), constant temperature lines (blue), constant entropy lines (black), and a thick black line separating the two-phase region to the left from the single-phase region at the right. Fill lines are shown in red.

Lines up to 345 bar are considered reliable based on the experimental data set presented here. Model extrapolations for up to 875 bar fill pressure are also included in Figure 13 (dashed lines). However, these extrapolations are suspect because (1) no experiments were run beyond 345 bar, so it is unknown whether the $s=10$ kJ/kg K approximation will be valid at higher pressure, and (2) dotted lines consider the thermal mass of the 345 bar experimental vessel. The more massive vessel required for higher pressure fills will increase thermal mass, mitigating temperature changes during both heating and cooling. At low temperature, however, vessel specific heat drops considerably, and therefore vessel mass will have reduced effect on fill processes.

Considering a nearly empty vessel at 80 K and following the red fill line to 345 bar in Figure 13, we confirm that the final fill temperature is close to 80 K, in agreement with experiment 18. We therefore conclude that nearly empty vessels at $T < 80$ K warm up during filling to 345 bar and nearly empty vessels at $T > 80$ K cool down during filling to 345 bar.

We next evaluate the effect of pressure vessel thermal mass on fill diagrams. Figure 14 shows a fill diagram that neglects vessel thermal mass. As expected, vessel thermal mass tends to stabilize temperature, and therefore Figure 13 (including vessel thermal mass) shows less temperature change during filling than Figure 14 (neglecting vessel thermal mass), as can be seen from the slopes of the red fill lines in the figures. This is especially true for warm, nearly empty vessels where the vessel thermal mass has the largest effect on fill temperature and density. As an example, consider a vessel initially at 300 K, 9 g/L, and $s=37$ kJ/kg K near the lower right end of the chart. Considering the thermal mass, the vessel fills to 345 bar, 234 K and 28 g/L (Figure 13), while neglecting thermal mass the vessel fills to 345 bar, 145 K and 42 g/L (Figure 14).

It is also observed from Figures 13 and 14 that fill curves with and without pressure vessel mass become more similar in shape for colder fills. This is also expected, as specific heats of pressure vessel materials rapidly drop to near zero as the vessel cools down. It is therefore interesting to determine whether there may be a region in the phase diagram where fill processes can be accurately analyzed without considering the vessel thermal mass. After careful analysis, we have generated Figure 15, which includes both fill lines considering vessel thermal mass (in red, from Figure 13) and without thermal mass (in blue, from Figure 14). Blue fill lines have been adjusted to intersect red fill lines at $s=23$ kJ/kg K. Figure 15 shows that all fill processes starting at $s \leq 23$ kJ/kg K can be accurately analyzed (within a maximum error of ± 0.5 g/L) while neglecting the vessel thermal mass, and the error is essentially zero within the two-phase region. Vessel thermal mass does play an important role if initial entropy is above 23 kJ/kg K.

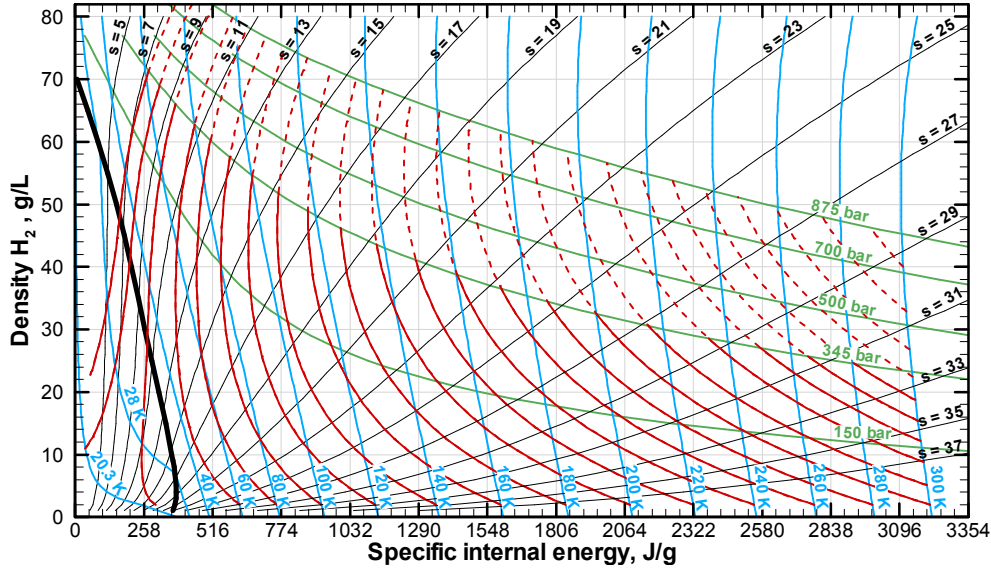


Figure 13. Specific internal energy vs. density chart for H₂ showing LH₂ pump fill lines in red (solid lines to 345 bar and dashed lines for higher pressures) considering the thermal mass of the experimental cryogenic vessel. The figure also shows constant pressure lines (green), constant temperature lines (blue), constant entropy lines (black), and a thick black line separating the two-phase region to the left from the single-phase region at the right. Fill lines assume constant vessel inlet entropy $s_{H_2}=10$ kJ/kg K and thermal equilibrium between the experimental vessel and H₂ inside the vessel.

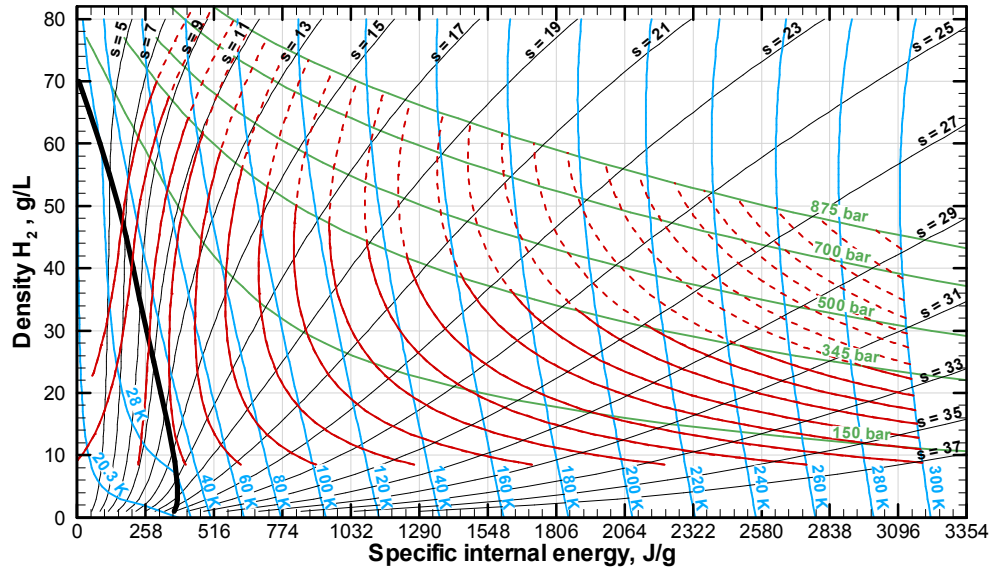


Figure 14. Specific internal energy vs. density chart for H₂ showing LH₂ pump fill lines in red (solid lines to 345 bar and dashed lines for higher pressures) not considering the thermal mass of the experimental cryogenic vessel. The figure also shows constant pressure lines (green), constant temperature lines (blue), constant entropy lines (black), and a thick black line separating the two-phase region to the left from the single-phase region at the right. Fill lines assume constant vessel inlet entropy $s_{H_2}=10$ kJ/kg K and thermal equilibrium between the experimental vessel and H₂ inside the vessel.

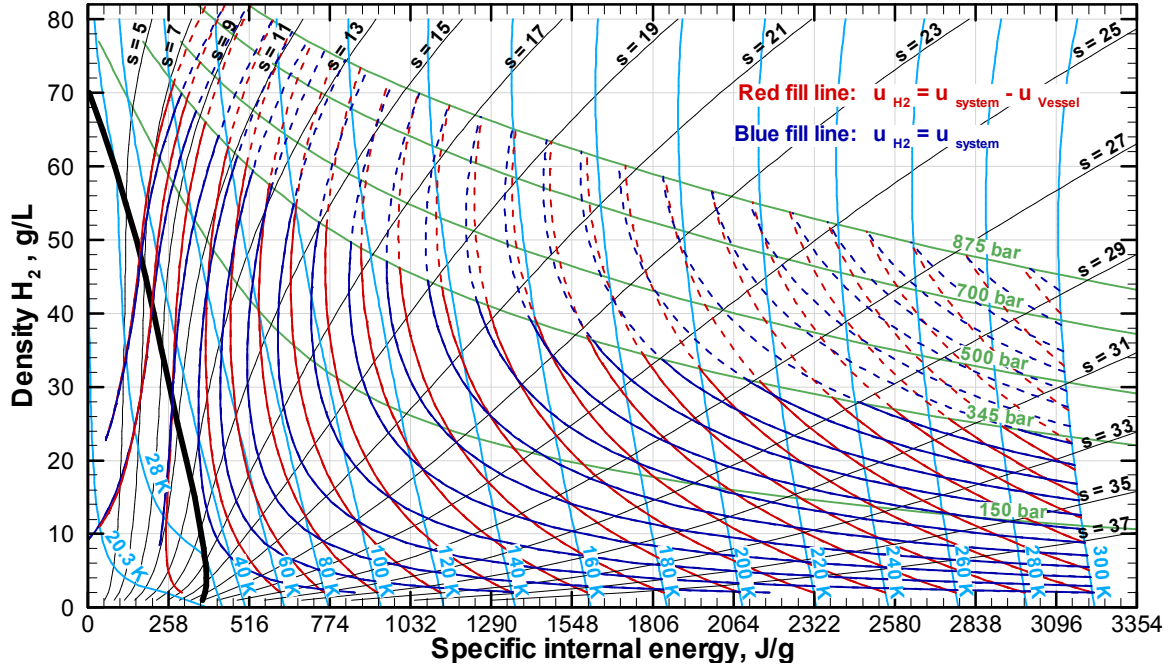


Figure 15. Specific internal energy vs. density chart for H₂ showing LH₂ pump fill lines (solid lines to 345 bar and dashed lines for higher pressures) considering the thermal mass of the experimental cryogenic vessel in red, and not considering the thermal mass of the experimental cryogenic vessel in blue. The figure also shows constant pressure lines (green), constant temperature lines (blue), constant entropy lines (black), and a thick black line separating the two-phase region to the left from the single-phase region at the right. Fill lines assume constant vessel inlet entropy $s_{H_2}=10$ kJ/kg K and thermal equilibrium between the 345-bar experimental vessel and H₂ inside the vessel.

Conclusions

This paper presents the results of 24 cryogenic pressure vessel fill experiments with a liquid hydrogen (LH₂) pump manufactured by Linde and installed at the LLNL campus. The LH₂ piston pump takes LH₂ from the station Dewar at near ambient pressure (3 bar) and very low temperature (24.6 K) and pressurizes it to the vessel pressure in two stages of compression, up to 875 bar, although the rating of the cryogenic vessel used for these experiments limits fill pressure to 345 bar. Experiments spanned initial vessel temperatures from ambient to 22 K, enabling pump testing over a broad range of conditions. The main results from the work are summarized as follows.

- Vessel fill density exceeds the density of LH₂ in the Dewar (65 g/L) in most of the experiments that start within the two-phase region. This is due to the high compressibility of LH₂ when pressurized to 345 bar. The maximum density measured (72.4 g/L) is 11% higher than LH₂ density at the Dewar. The LH₂ pump therefore contributes up to 11% increased vehicle autonomy by increasing storage density.
- Peak H₂ flow rates are over 1.67 kg/min (100 kg/h) in most cases. Average H₂ flow rates are typically between 1.1 and 1.4 kg/min due to conservative pump fill profile

parameters being used. Faster average flow rates have been demonstrated with improved pump speed profiles and will be reported in a future publication.

- Electricity consumption is 1.42 kWh/kg H₂ average if the slow and partial fills are excluded. This value is considerably lower than necessary for gaseous H₂ pressurization in today's compressors (1.35 kWh/kg H₂ theoretical minimum and ~3 kWh/kg H₂ typical [10]).
- Fill densities are well predicted (RMS error=0.7 g/L) with a thermodynamic fill model that assumes constant 10 kJ/kg K inlet vessel entropy.
- The thermodynamic fill model has been applied to generate diagrams that can be used for directly reading fill density for any initial vessel condition.
- Careful analysis of vessel fill diagrams indicates that the thermal mass of the cryogenic vessel can be neglected from calculation of fill density whenever the initial entropy of H₂ inside the vessel is less than 23 kJ/kg-K. This condition applies to very cold or full vessels where the thermal mass of the H₂ dominates the process, as the specific heat of the pressure vessel drops considerably at cold temperatures.

In summary, experimental results confirm many of the virtues that make LH₂ pumping a promising technology for H₂ dispensing, both for filling cryogenic as well as ambient temperature vessels: High throughput (1.67 kg/min, 100 kg/h), low electricity consumption at the station due to high density of LH₂ minimizing compression work, and highest fill density, up to 80 g/L (estimated) when dispensing cryogenic hydrogen at 700+ bar.

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