Metal Hydride Compression

Terry Johnson (Primary Contact), Anne Mallow (SNL), Robert Bowman (Oak Ridge National Laboratory [ORNL]), Barton Smith (ORNL), Lawrence Anovitz (ORNL), Craig Jensen (HHC)
Sandia National Laboratories (SNL)
7011 East Avenue
Livermore, CA 94551-0969
Phone: 925-294-2512
Email: tajohns@sandia.gov

DOE Manager: Neha Rustagi
Phone: 202-586-8424
Email: Neha.Rustagi@ee.doe.gov

Subcontractor:
Hawaii Hydrogen Carriers LLC (HHC), Honolulu, HI

Project Start Date: October 1, 2016
Project End Date: December 31, 2019

Overall Objectives

- Develop and demonstrate on a laboratory scale a two-stage metal hydride compressor with a feed pressure of approximately 100 bar delivering high purity H_2 gas at an outlet pressure ≥875 bar.
- Demonstrate an increase in the technology readiness level (TRL) of this technology from 2 to 5 and enable the development of a comprehensive cost analysis for a production system scaled to 100 kg H_2/h flow rate.
- Demonstrate through engineering analysis that the compressor design is capable of an energy efficiency of ≤4.0 kWh/kg.

Fiscal Year (FY) 2019 Objectives

- Procure metal hydride alloys for low-pressure and high-pressure beds and process into metal hydride/graphite compacts via ball milling, mixing, and compaction using a hydraulic press and custom die sets.
- Order components for and complete the assembly of the prototype compressor beds.
- Complete the assembly of the prototype compressor test facility including the control and data acquisition system, the temperature control system, and the high-pressure hydrogen manifold.
- Complete performance testing of the prototype compressor system.
- Complete a cost analysis for a production system scaled to 100 kg H_2/h flow rate.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- (B) Reliability and Costs of Gaseous Hydrogen Compression.

Technical Targets

This project is developing metal hydride compressor technology that is currently at a TRL of 2. The results of this project will address several of the DOE technical targets for small, forecourt compressors, specifically:

- Specific energy: The 2020 target for 100 bar pipeline delivery is 1.6 kWh/kg. Our project goal is to demonstrate that a metal hydride compressor can achieve a specific energy of less than 4.0 kWh/kg as a first step toward this target.
- Uninstalled capital cost: The 2020 target for 100 bar pipeline delivery is $275,000. A cost analysis for a commercial system will address this target.
- Outlet pressure capability: The 2020 and ultimate targets are 950 bar. We plan to demonstrate a prototype compressor capable of >875 bar pressure with a goal of 950 bar.

FY 2019 Accomplishments

- Completed the design and ordered the custom pellet die sets for the metal hydride/graphite compacts.
- Procured 4 kg each of the low- and high-pressure metal hydrides from Ames

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

Laboratory and ball milled the material to a fine powder.

- Completed production of compacted metal hydride/graphite pellets; 56 center pellets and 26 helical pellets were fabricated for each compressor bed.
- Completed assembly of the two compressor beds that included the metal hydride/graphite pellets, the helical coil heat exchangers, gas distribution tubes, Teflon sleeves, and pressure vessels with seals and thermocouples.
- Pressure checked completed compressor beds to ~1,000 psi after removal from the glove box.
- Completed assembly of the high-pressure hydrogen manifold and integrated with the existing medium-pressure system.
- Completed fabrication of the valve controller for the temperature control manifold.
- Completed the fabrication and assembly of the temperature control manifold, integrated the valve control system, and tested operation.
- Completed all safety documentation and safety reviews for the test facility and prototype compressor.
- Integrated the compressor beds with the test facility and began leak checking the integrated system.
- Completed a preliminary cost analysis for the metal hydride materials and vessels for a commercial system capable of meeting DOE's target of 100 kg/h hydrogen delivery.

INTRODUCTION

Conventional hydrogen compressors often contribute more than half of the cost of hydrogen stations, have poor reliability, and have insufficient flow rates for a mature fuel cell vehicle market. Fatigue associated with their moving parts including cracking of diaphragms and failure of seals leads to failure in conventional compressors, which is exacerbated by the repeated starts and stops expected at fueling stations. Furthermore, the conventional lubrication of these compressors with oil is generally unacceptable at fueling stations due to potential fuel contamination. Metal hydride technology offers a very good alternative to both conventional (mechanical) and newly developed (electrochemical, ionic liquid pistons) methods of hydrogen compression. Advantages of metal hydride compression include simplicity in design and operation, absence of moving parts, compactness, safety and reliability, and the possibility to utilize waste industrial heat to power the compressor. Beyond conventional hydrogen supply via pipelines or tanker trucks, another attractive scenario is the on-site generation and delivery of pure hydrogen at pressure (≥875 bar) for refueling vehicles at electrolysis, wind, or solar hydrogen production facilities in distributed locations that are too remote or widely distributed for cost effective bulk transport.

Metal hydride hydrogen compression utilizes a reversible heat-driven interaction of a hydride-forming metal alloy with hydrogen gas to form the metal hydride phase and is a promising process for hydrogen energy applications [1, 2]. To deliver hydrogen continuously, each stage of the compressor must consist of multiple metal hydride beds with synchronized hydrogenation and dehydrogenation cycles. Multistage pressurization allows achievement of greater compression ratios using reduced temperature swings compared to single-stage compressors. The objectives of this project are to investigate and demonstrate on a laboratory scale a two-stage metal hydride hydrogen gas compressor with a feed pressure of >100 bar and a delivery pressure ≥875 bar of high purity H_2 gas.

APPROACH

The approach for this project is split into three phases to meet the project objectives: (1) feasibility assessment and system design, (2) prototype fabrication, and (3) prototype performance evaluation. In the first phase, candidate hydride materials are selected based on literature review and team experience. Absorption and desorption isotherms of selected hydrides are then measured and compared to system-level requirements to demonstrate feasibility. In parallel, trade studies are performed on different design configurations for the prototype compressor beds and a down-selection is made. Finally, a system-level compressor model is developed and used for feasibility assessment of the hydride materials and bed designs. In the second phase, component fabrication and assembly drawings for compressor beds are developed based on the down-selected designs. Procurement of hydride alloys and fabrication of bed components follows. Once received, the integrated prototype compressor is assembled. In the third and final phase of the project, the prototype compressor is integrated with the test facility and performance testing of the prototype is conducted. This testing will assess the impact of heating rates, state of charge, and temperature ranges on compressor performance as well as degradation behavior. This will include up to 300 hours of operation. Results of the prototype characterization will be documented and used for the conceptual design and cost analysis for a 100 kg H_2/h commercial system in a final report to DOE.

RESULTS

Compressor Bed Fabrication and Assembly

Assembly of the prototype compressor beds was initiated by ordering all bed components (pressure vessels, helical tube heat exchangers, hydrogen distribution tubes, and Teflon liners), bed materials (low-pressure and high-pressure metal hydrides and graphite), and custom die sets to produce the metal hydride/graphite pellets. Once the 4 kg of each metal hydride alloy had been produced by Ames Laboratory it was ball milled at HHC to a fine powder and shipped to Sandia. There the material was pre-mixed with expanded natural graphite to prepare for pellet production. The custom pellet die sets shown in Figure 1 were then used to produce 56 center pellets and 26 helical pellets per bed. Figure 1 shows examples of both pellets. These pellets were then loaded into the helical coil heat exchangers for the low-pressure and high-pressure beds along with the hydrogen distribution tubes that run down the center of the beds. This assembly was then inserted into the Teflon sleeves that are used to insulate the metal hydride from the massive pressure vessels. Based on measurements before and after loading, the low-pressure bed was loaded with 2.8 kg of material and the high-pressure bed was loaded with 2.9 kg of material. Given that the mixture was 15% graphite and 85% metal hydride, each bed was loaded with about 2.4 kg of metal hydride.

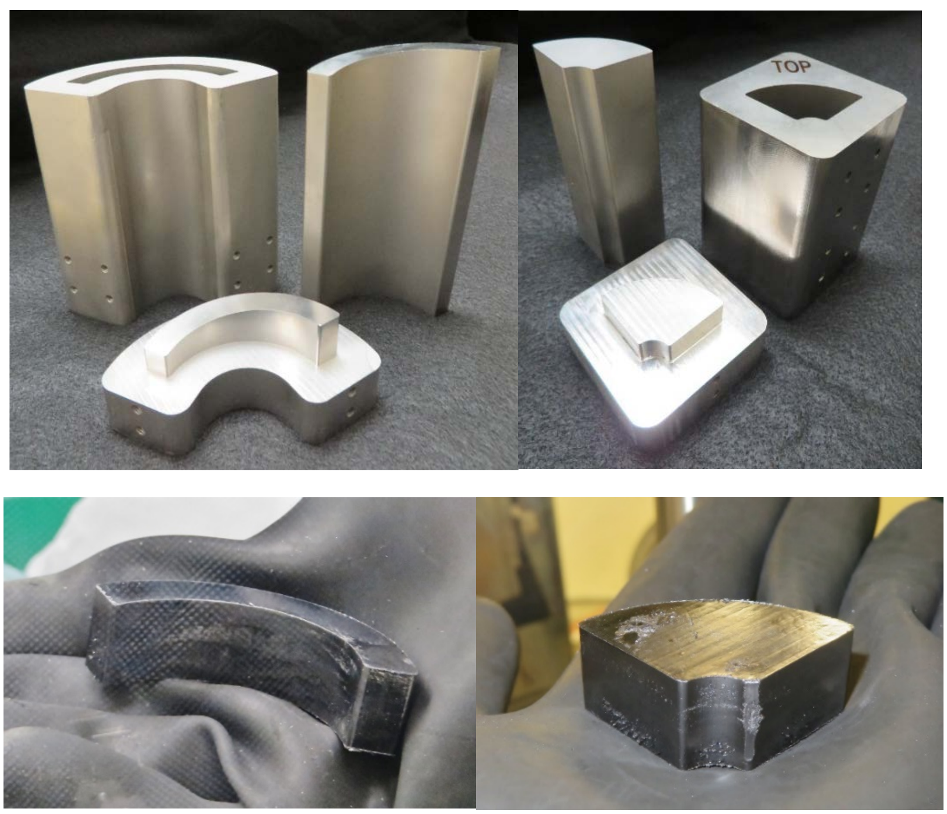

Figure 1. Helix die set and pellet (left) and center die set and pellet (right)

Figure 2 shows one of the vessels being assembled in the Sandia glove box. The Teflon sleeve subassembly was inserted into the vessel body with the heat exchanger tubing protruding through the mating vessel penetrations. Seals were then installed in glands surrounding the tubing. A single thermocouple was inserted into a predrilled hole in the end of the compressor to monitor the metal hydride temperature during operation and sealed with a high-pressure fitting. The hydrogen inlet valve assembly was also attached to the end of the vessel with a high-pressure fitting. This assembly includes a needle valve and an inline filter assembly consisting of one 35 Ωm and one 5 Ωm filter. The filters are used to prevent metal hydride powder from contaminating any downstream components (valves and seals). Finally, the gasket, lid, and nut were installed to seal the vessel body.

Figure 2. Prepping the inner subassembly to be inserted into the pressure vessel

Sealed vessels were then removed from the glove box and pressurized with helium at ~1,000 psi to check for leaks prior to transporting the completed beds to the test facility. The bed thermocouple was also checked to ensure it was operational. Neither bed showed a measurable decrease in pressure during the leak check and a portable He leak detector found no leaks at any of the fittings or seals.

Test Facility

The temperature control system for the compressor prototype, shown in Figure 3, was assembled in early FY 2019 and consists of two oil recirculation loops, one at a low temperature and one at a high temperature. The low-temperature loop consists of a chiller with self-contained pump and heat exchanger. The chiller circulates heat transfer fluid at a specified temperature through the oil manifold and has a cooling capacity of 3 kW. The high-temperature loop is operated with another self-contained unit with a pump to flow heat transfer fluid and a 6 kW resistive heater. Flow from the two oil loops is directed to either the low- or high-pressure bed through a series of 3-way pneumatically operated valves for heating and cooling.

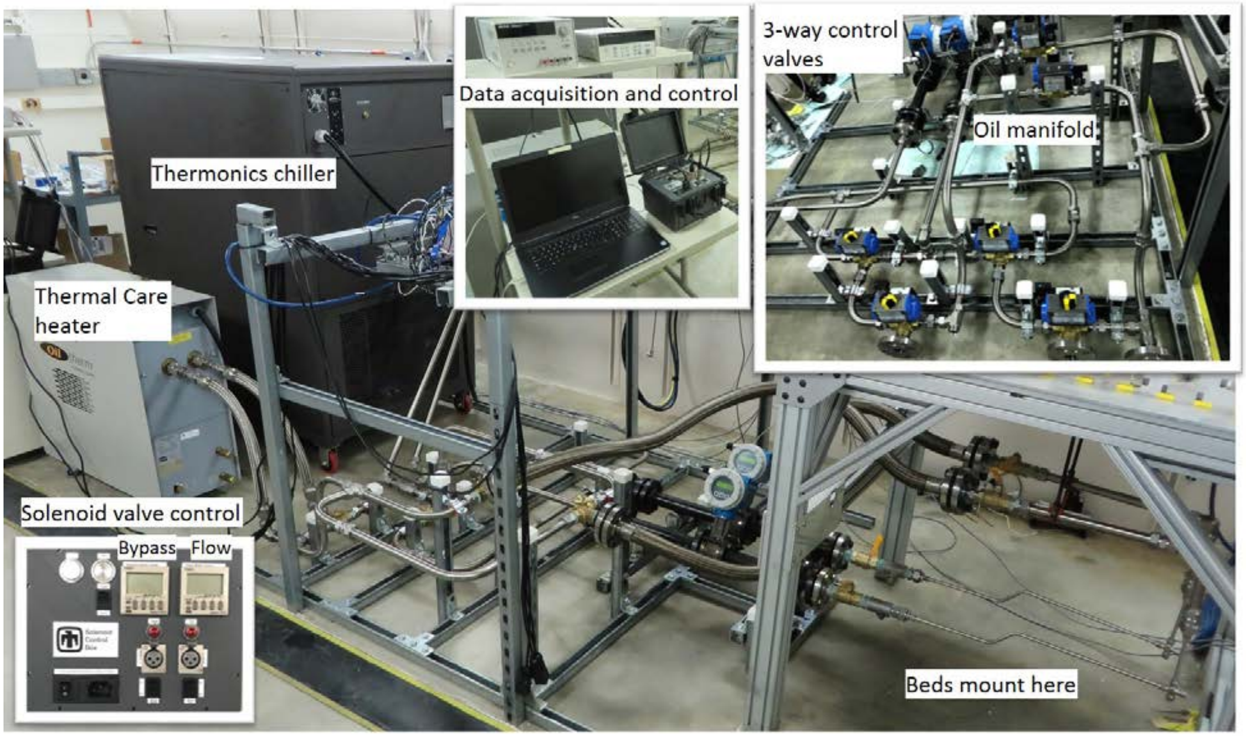

Figure 3. Temperature control system

The high-pressure hydrogen manifold assembly was completed in Q3 of FY 2019 as shown in Figure 4. This manifold was then connected to the existing lower pressure manifold that had been reconfigured for our test setup. The completed manifold allows for closed loop recirculation of hydrogen from the supply volumes into the low-pressure and high-pressure manifold, through the compressor beds and back-pressure regulator, and back to the supply volumes.

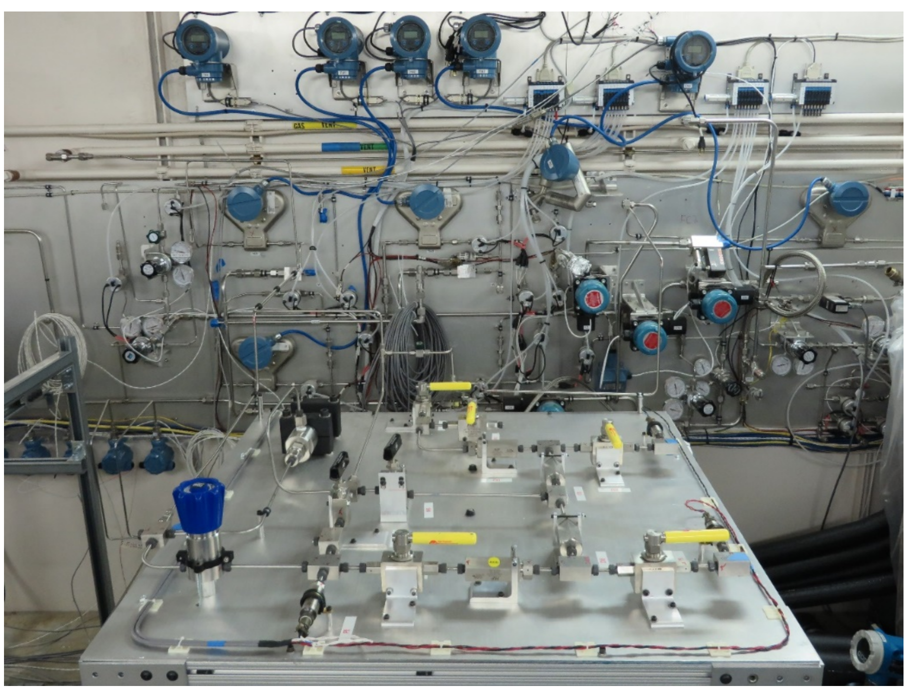

Figure 4. High-pressure hydrogen manifold (near) connected to medium-pressure manifold (far)

A simple data acquisition and control system has been assembled for the metal hydride compressor system and is shown in Figure 3. Data collected will consist of the flow rate and temperature of the two oil loops, supply pressure, intermediate pressure, and delivery pressure of the compressor, internal and external temperatures of the two compressor beds, and delivered hydrogen flow rate. Control of hydrogen flow through the compressor is achieved through the pressure differences across a set of check valves between the supply and the low-pressure bed, the low- and high-pressure beds, and the high-pressure bed and the back pressure regulator set to 875 bar. The pressure of the beds is, in turn, controlled by the temperature of the two hydride beds, which is achieved by directing the flow of the two fluid loops using a series of pneumatically actuated valves. These valves will be controlled by a timer and relay circuit that triggers valves to open or close at preset time intervals chosen based on the desired cycle time of the compressor. Integration testing with the controller and temperature control system was completed in Q3 in parallel with the compressor bed assembly.

Initial Checkout

Once the compressor beds were integrated with the temperature control system and hydrogen manifold, the next step was to purge and leak check the hydrogen system. For this commissioning process, it was planned to perform all leak and pressure checks with helium before switching the manifold over to hydrogen. Once the manifold was purged, the manifold and beds were leak checked at room temperature up to 10,000 psi with no detectable leaks. The final step in the process was to temperature cycle the beds between the operating temperatures of 20°C and 150°C while at 10,000 psi before switching to hydrogen. Unfortunately, seals on both beds failed at 10,000 psi at a temperature of 150°C.

The seals that failed are Parker polypak seals, which are u-cup type seals similar to other ones used on various other high-pressure vessels in the Hydrogen Effects on Materials Laboratory at Sandia. These are used to seal around the heat exchanger tubing where it enters and exits the pressure vessels. These particular seals were recommended by High Pressure Equipment Company (HiP) for our application and should have been rated to 15,000 psi hydrogen and temperature cycling between 20°C and 175°C. These seals are used on other HiP systems for dynamic sealing at up to 20 ksi. Since our application is a static seal, they were confident that these would work well. The seals were also over-pressure tested hydraulically at HiP at up to 22,000 psi and then leak checked with helium at 15,000 psi with no issues. However, they were only tested at room temperature.

Following the seal failures, the beds were removed from the hydrogen and oil manifolds, the oil was drained from the heat exchanger tubes, and they were transported back to the glove box lab and loaded into the glove box to diagnose the failure. It was confirmed that the seals had extruded out of the gland as the result of the combination of pressure and elevated temperature. Investigation into the failure by HiP revealed two mistakes in the design of the seals and glands. First, the polypak seal material was not rated to the operating pressure at a temperature of 150°C. Second, the gland for the seals was designed incorrectly, allowing a much larger gap between the tubing and the gland inside diameter than prescribed by Parker's design guide. The combination of these two mistakes resulted in the seal failure.

HiP has contacted two seal suppliers to design replacement seals. Bal Seal and Gallagher Seal are both designing new seals to meet the appropriate dimensions, pressure rating, temperature rating, and the hydrogen requirements for our application. The goal is to have replacement seals that don't require any modification to the vessels themselves. Once we have determined appropriate replacement seals, HiP will procure them and pressure test them on a surrogate vessel before shipping them to us. We will then install the seals, reassemble the beds, and reintegrate them with the test facility. We will then resume the helium pressure testing with temperature cycling that resulted in the failure of the original seals.

Cost Analysis

A comprehensive cost analysis for a 100 kg H_2/h production compressor system has been started. We have assembled a rough conceptual design for the scaled system and have begun contacting suppliers to provide estimates for the metal hydrides, heat transfer additives, and pressure vessels.

Initial cost estimates for the metal hydrides have been based on scaling calculations for the production-scale system. These scaling calculations are based on several assumptions about the compressor design and performance. First, it is assumed that the system will consist of two beds per stage and two stages, like the prototype system. Operating assumptions include 12-minute half cycles and 1 wt % utilization of the metal hydride capacity. These operating parameters exceed the performance expected by the prototype system. Improved metal hydride performance would be required to provide this level of performance, but literature data suggests that this is feasible. Using these assumptions results in 2,000 kg of alloy required per bed, per stage. That translates to 4,000 kg each of low-pressure and high-pressure alloys. For heat transfer enhancement, the alloys would be combined with 800–1,200 kg of expanded natural graphite (ENG). For reference, a more optimistic assumption of 10-minute half cycles and 1.5 wt % utilization would reduce the required mass of metal hydrides and ENG by 44%.

Initial estimates for at-scale production of metal hydride alloys by vendors in the United States, Japan, and China have been solicited. These estimates show the price of the alloys to be between $17/kg and $43/kg. For 8,000 kg of alloy, this results in a cost of $136,000 to $344,000 per compressor. These cost estimates are promising in that the alloy costs are on par with the target cost for a 100 kg/h compressor. A quote was also received for the ENG. ENG costs for this scale are quoted at $46/kg. For 800–1,200 kg the cost per compressor would be $36,800 to $55,200, a not insignificant amount. For the final cost estimates, HHC will work to refine these values and expand the vendor base from which we are receiving estimates.

The next largest perceived cost for the compressor is that of the pressure vessels. The size and number of pressure vessels per compressor was based on the need to store 2,000 kg of alloy per bed. The original prototype design was based on storing 25 kg of alloy in each vessel. That capacity would result in 80 vessels for each compressor bed. Combining this number of vessels would be impractical for a commercial system, so scaling calculations were performed to reduce the number to 10 vessels per bed. The resulting conceptual design consists of vessels with 12-inch inner diameter and 36-inch internal length. Each vessel would contain a helical coil heat exchanger fabricated from 1-inch diameter tubing and 200 kg of a compacted mixture of metal hydride alloy and graphite. The low-pressure stage would consist of 20 vessels and 850 ft of tubing rated to >4,000 psi. The high-pressure stage would consist of 20 vessels and 850 feet of tubing rated to >13,000 psi.

An initial estimate was obtained for these pressure vessels fabricated from Nitronic 50. For the low-pressure stage, each vessel was quoted at $43,415. For 20 of these vessels the cost would be $868,296. For the high-pressure stage, each vessel was quoted at $56,472 resulting in a cost of $1,129,440 for 20 vessels. Based on these estimates, the total cost per compressor would be almost $2 million. Because of this very high cost, HHC will be exploring other options. Additional vendors will be contacted, and alternative materials and methods of fabrication will be examined. These alternatives will include Type II and Type III composite vessels like those used for high-pressure storage at hydrogen fueling stations.

CONCLUSIONS AND UPCOMING ACTIVITIES

The primary focus of FY 2019 was the assembly of the prototype compressor system including the beds and the test facility. Fabrication and assembly of the compressor beds included the processing of the metal hydride alloys from coarsely crushed ingots into compacted metal hydride/graphite pellets that were then assembled into the helical coil heat exchangers. Heat exchanger assemblies were then installed into the HiP high pressure vessels and leak checked before integrating with the test facility. The compressor test facility was completely assembled in FY 2019 including the hot and cold oil recirculation systems and valve control system for temperature control and the high-pressure hydrogen manifold. Integration of the compressor beds with this test facility was completed and initial checkout was underway when failure of the high-pressure seals temporarily halted progress.

In parallel with the prototype compressor assembly, a comprehensive cost analysis for a 100 kg H_2/h production compressor system was started. A rough conceptual design for the scaled system was developed and suppliers were contacted to provide estimates for the metal hydrides, heat transfer additives, and pressure vessels. Preliminary hydride estimates ranged from $136,000 to $344,000 for the scaled system along with graphite costs of $36,800 to $55,200. With a low-end estimate for these materials at $172,000, the DOE target of $275,000 for the compressor could be feasible. However, initial cost estimates for pressure vessels for the scaled system were nearly $2 million. Additional cost estimates for alternative vessel configurations are being pursued as part of the final cost estimation task.

In FY 2020 the primary goal for the prototype compressor is to complete the performance assessment testing. New seals will be procured and pressure tested by HiP. The compressor beds will then be reassembled at Sandia and integration of the compressor beds with the test facility will resume. Once the beds are integrated with the hydrogen manifold and temperature control system a series of safety checks will be completed to verify safe operations of both the hydrogen and oil systems. Once the system has been verified, the metal hydride beds will be activated and cycled individually to verify hydriding performance. Five to ten cycles may be carried out on each bed until consistent performance is evidenced. Performance testing will then follow. Performance testing of the prototype will be conducted against predicted levels of delivery pressure and hydrogen flow rates. Sufficient testing will be carried out to assess the impact of operating conditions such as heating rates, state of charge, and temperature ranges on performance of the compressor (e.g., discharge pressure and energy consumption) as well as initial monitoring of degradation behavior.

In addition to the prototype performance characterization, the cost estimation for a production-scale compressor will be completed. Cost projections will include refined estimates for metal hydride alloys, high-pressure vessels, and balance of plant components. These estimates will be compiled into a final report from HHC.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Robert C. Bowman, "Status Report on Development of High-Pressure Metal Hydride Compressors," oral presentation at Helmholtz-Zentrum Geesthacht, Geesthacht, Germany, October 10, 2018.
2. T. Johnson, "Metal Hydride Compression," oral presentation at Joint HSTT-HDTT-CSTT Meeting, Southfield, MI, March 12, 2019.
3. T. Johnson, "Metal Hydride Compression," oral presentation at DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington DC, April 30, 2019.

REFERENCES

1. M.V. Lototskyy, Y.A.Yartys, B.G. Pollet, and R.C. Bowman Jr., "Metal Hydride Hydrogen Compressors: A Review," *Int. J. Hydrogen Energy* 39 (2014): 5818.
2. V.A. Yartys, M.V. Lototskyy, V. Linkov, D. Grant, A. Stuart, J. Eriksen, R. Denys, and R.C. Bowman, Jr., "Metal Hydride Hydrogen Compressors: Recent Advances & Future Prospects," *Appl. Phys. A* 122 (2016): 415.
3. T.A. Zotov, R.B. Sivov, E.A. Movlaev, S.V. Mitrokhin, and V.N. Verbetsky, "IMC Hydrides with High Hydrogen Dissociation Pressure," *J. Alloys Compds.* 509S (2011): S839.
4. M. Dieterich, C. Pohlmann, I. Burger, M. Linder, and L. Rontzsch, "Long-Term Cycle Stability of Metal Hydride-Graphite Composites," *Int. J. Hydrogen Energy* 40 (2015): 16375–16382.