Metal Hydride Compression

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Project End Date: September 30, 2019

Overall Objectives

- Develop and demonstrate, on a laboratory scale, a two-stage metal hydride (MH) compressor with a feed pressure of approximately 100 bar delivering high purity hydrogen gas at an outlet pressure ≥875 bar.
- Demonstrate an increase in the technology readiness level 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) 2018 Objectives

- Down-select to one MH alloy for each stage that meets system-level requirements based on laboratory characterization.
- Complete the detailed design of prototype compressor beds for both stages based on trade studies.
- Demonstrate a compressor design that can achieve an energy consumption of ≤4.0 kWh/kg-H_2 under 100–875 bar operation using a system-level model of the compressor.

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 MH compressor technology that is currently at a technology readiness level 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 hydrogen compression from 100 bar inlet is 1.6 kWh/kg. Our project goal is to demonstrate that a MH compressor can achieve a specific energy of less than 4.0 kWh/kg as a first step towards this target.
- Uninstalled capital cost: The 2020 target for 100 bar pipeline delivery is $275,000. An FY 2019 cost analysis for a commercial system will address the R&D needed to achieve this target.
- Outlet pressure capability: The 2020 and ultimate targets are 950 bar. We plan to demonstrate a prototype compressor concept capable of >875 bar pressure with a goal of ultimately achieving 950 bar.

FY 2018 Accomplishments

- In collaboration with Greenway Energy Inc., characterized seven different MH alloys for use in the high-pressure stage of the compressor. Demonstrated two alloys that could produce >875 bar pressure at reasonable temperatures.

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

- Identified the compressor bed design with the best efficiency, manufacturability, and heat transfer through a comprehensive trade study.
- Completed the detailed design of compressor beds based on a helical tube heat exchanger to maximize performance and energy efficiency.
- Engaged several suppliers for the compressor beds and heat exchangers and received quotes for fabrication. Completed final down-selection and ordered components.
- Performed small-scale thermal conductivity and hydrogen cycling experiments to verify stability and effective thermal conductivity of cycled MH/graphite composites.
- Completed the design of the compressor bed loading procedure.
- Completed the design for the compressor test facility, including the hydrogen supply and recirculation system and the temperature control system consisting of hot and cold oil circulation systems, and assessed safety through a failure modes effects and criticality analysis.
- Updated the system-level compressor model with measured thermodynamics and kinetics of the alloys to be used in the prototype compressor as well as the design of the compressor beds. Simulations were then run to demonstrate that the system could meet our go/no-go criteria.

INTRODUCTION

Conventional hydrogen compressors often constitute more than half the cost of hydrogen stations and exhibit insufficient reliability. 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. MH technology offers an alternative to both conventional (mechanical) and newly developed (electrochemical, ionic liquid pistons) methods of hydrogen compression. Advantages of MH compression include simplicity in design and operation, absence of moving parts, compactness, and potential for high reliability.

MH hydrogen compression utilizes a reversible heat-driven interaction of a hydride-forming metal alloy with hydrogen gas to form the MH 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 MH 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 MH hydrogen gas compressor with a feed pressure of >100 bar and a delivery pressure ≥875 bar of high purity hydrogen gas using the scheme shown in Figure 1. Progress to date includes the selection of metal hydrides for each compressor stage based on experimental characterization of their thermodynamics, kinetics, and hydrogen capacities for optimal performance with respect to energy requirements and efficiency. Additionally, final bed designs have been completed based on trade studies and all components have been ordered. The prototype two-stage compressor will be fabricated, assembled, and experimentally evaluated in FY 2019.

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 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 assesses 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 system in a final report to DOE.

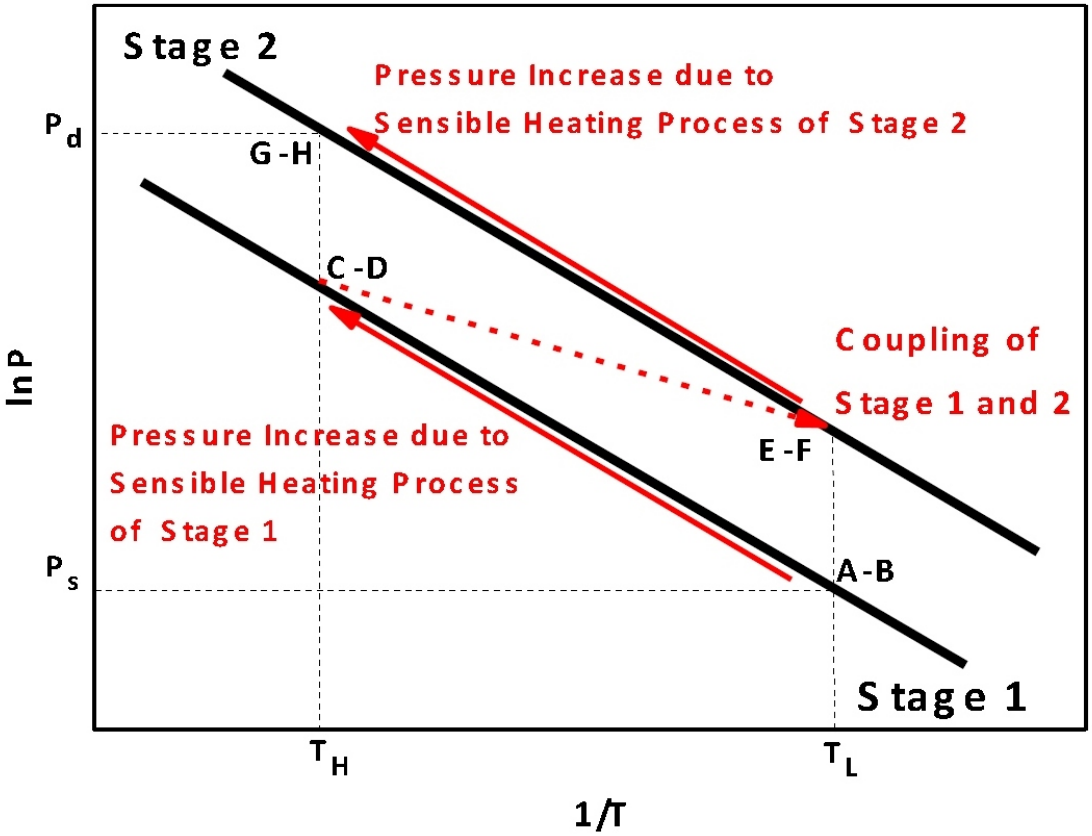

Figure 1. van't Hoff plots illustrating the operation of a two-stage metal hydride hydrogen compression system from the low temperature T_L to the high temperature T_H. The black lines represent the van't Hoff plot for the hydrogenation process for stage 1 (lower black line) and for stage 2 (upper black line). The dashed red line represents the coupling between stage 1 and stage 2. The compression cycle is summarized as follows: Step A: A low-pressure hydrogen supply (e.g., an electrolyzer or pipeline) is attached to the first stage, at pressure P_s. The temperature of stage 1 is maintained at T_L during hydrogenation. Steps B-C: A sensible heating process raises the bed temperature to T_H, increasing the pressure of the stage 1 vessel. Steps D-E: Coupling between stage 1 (dehydrogenation at T_H) and stage 2 (hydrogenation at T_L) occurs. Steps F-G: Stage 2 hydride bed undergoes sensible heating in order to achieve the delivery pressure of P_d. Step H: During dehydrogenation of stage 2 high pressure hydrogen is released from the compressor at P_d.

RESULTS

Metal Hydride Selection and Characterization

The focus in FY 2018 was to identify the best MH for the high-pressure stage of the prototype compressor. To do so required experimental characterization of the pressure-composition-temperature (PCT) behavior of candidate materials. In FY 2017, Oak Ridge National Laboratory (ORNL) had designed and assembled a custom, high-pressure Sievert’s apparatus capable of accurate isotherm measurements up to 1,000 bar and 175°C. This system was used in FY 2018 to characterize several high-pressure alloys chosen based on literature data and synthesized by the Materials Preparation Center at Ames Laboratory (Iowa State University). Three alloy samples were fabricated for this purpose, all of which were titanium-based AB_2-type MHs: (1) $Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_{0.75}V_{0.05}$, (2) $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$, and (3) $TiCrMn_{0.7}Fe_{0.2}V_{0.1}$. These will be referred to as Ames #1, #2, and #3 for brevity. An additional alloy was produced by Ames based on the Ames #2 material, but with nickel substitution for the iron. This material was formulated to try to produce flatter plateau pressures with somewhat lower pressure than Ames #2 and will be referred to as Ames #4.

In addition, our team collaborated with Greenway Energy, the lead for a related hybrid electrochemical-MH compressor project, to characterize several other materials. For their high-pressure stage, Greenway had identified three different materials. These were also titanium-based AB_2 MHs and included $Ti_{1.1}CrMn$, $(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$, and $TiCr_{1.55}Mn_{0.2}Fe_{0.2}$. Greenway had assembled their own high-pressure Sievert's apparatus in early FY 2018 and performed characterization of PCT isotherms on their three materials along with two of our team's alloys.

The following is a brief summary of the results of the characterization of these seven alloys. Of the four alloys chosen by our team, Ames #1 showed a room-temperature absorption isotherm consistent with literature data indicating that it could easily be filled by our low-pressure stage at a reasonable temperature. Desorption pressure from the alloy was then measured at up to 180°C displaying desorption pressures in excess of 875 bar. Although complete isotherms were not measured at these temperatures, the discrete measurements indicated that the alloy was a potential candidate for the high-pressure stage of the compressor. However, the measured desorption pressures would require higher temperature operation than the preliminary design of the compressor assumed.

Ames #2 was found to have the highest desorption pressure capability of all of the alloys tested. Isotherms of this alloy were measured at ORNL and Greenway. As Figure 2 shows, room-temperature absorption requires >400 bar pressure to reach a capacity greater than 1.5 wt%, but at greater than 875 bar, hydrogen can be desorbed from the alloy at 150°C. The figure indicates that while the alloy is viable for the high-pressure stage, highly sloping isotherms prevent it from reaching an ideal compression ratio. In an attempt to correct this characteristic, Ames #4 was produced with the intent that the nickel substitution would flatten and slightly lower the plateau pressures. Unfortunately, the results at Greenway showed that the desorption pressure was lowered too significantly and both the absorption and desorption isotherms remained highly sloped.

Based on literature data, Ames #3 held the most promise for our application with flat plateau pressures that spanned the range of interest for the high-pressure stage of the compressor. However, characterization by Greenway showed that the sample tested did not produce as high a pressure as anticipated. Based on the measurements, the material could be filled at room temperature with about 150 bar hydrogen but might only provide 500–600 bar pressure at 150°C, requiring a higher than desired operating temperature to achieve 875 bar.

Similar results were found by Greenway when characterizing their selected materials. Two of their materials had very sloped isotherms that prevented them from being viable. The third material, $Ti_{1.1}CrMn$, had relatively flat plateau pressures, but provided lower desorption pressures than anticipated. At 170°C, this material only produced 400–500 bar pressure over a reasonable capacity.

Based on the inability of either team to find an ideal high-pressure stage candidate, it was decided that our prototype compressor would maintain the goal of >875 bar output and use the Ames #2 material for our high-pressure stage. This required shifting our low-pressure stage material from Hydralloy C5 to the Ames #3 material. This material would require 150 bar supply pressure but could provide a high enough pressure to fill the Ames #2 alloy.

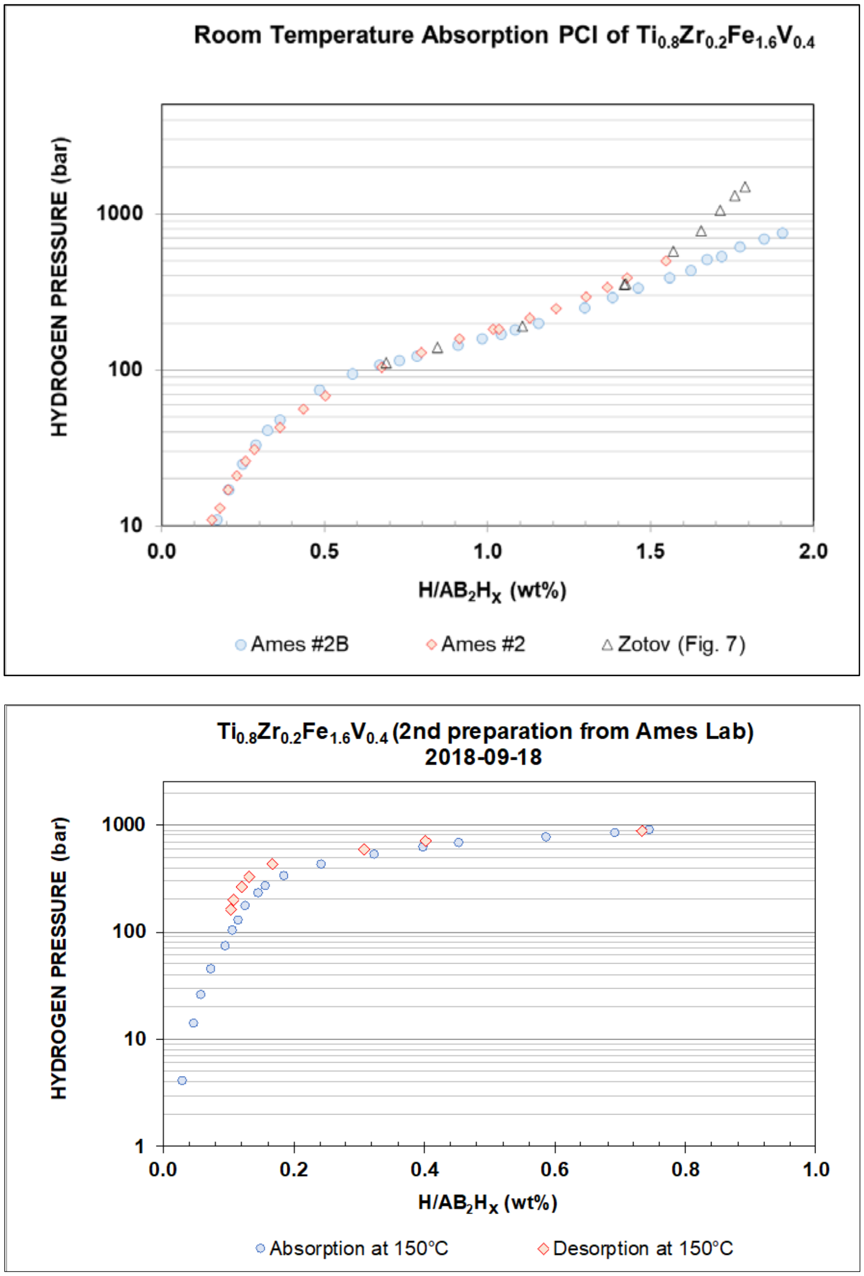

Figure 2. Hydrogen absorption and desorption isotherms measured at ORNL for two preparations of alloy $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$ (Ames #2). Room-temperature data is shown in the top panel along with PCT data obtained by Zotov et al. [3]. Data at 150 °C is shown in the bottom panel.

System Design

An extensive trade study was carried out for the compressor bed designs to determine the best design for each stage. Configurations considered include a shell and tube design with external heating/cooling, a closed ended vessel with internal heating/cooling, and an open-ended vessel with internal heating/cooling. A down-selection to a single design for both low- and high-pressure compressor beds was made in Q1 FY 2018. It was determined that an open-ended vessel with a helical tube heat exchanger had the greatest potential to meet goals for heat transfer, target pressure range (50 bar suction and 875 bar discharge), and energy consumption (4.0 kWh/kg H_2). Scalability of the design to 100 kg/h hydrogen flow and cost for high volume manufacturing was also considered.

The final helical tube design for the prototype compressor is depicted in Figure 3 and consists of a single heat exchanger tube that enters through the pressure vessel lid, spirals through the MH, and exits through the vessel bottom. The helical shape of the tube provides optimal heat transfer distribution within the vessel and requires no manifolds, external or internal. Due to this fact, this heat exchanger design provides the lowest energy burden of the options considered. In addition to the helical tube, the cross-sectional view in Figure 3 shows the hydrogen inlet/outlet at the vessel bottom with a hydrogen distribution tube running the length of the vessel. A Teflon liner, also shown in Figure 3, surrounds the helical tube and MH to thermally insulate the hydride from the vessel, improving energy efficiency. The vessel lid and seal consist of a two-piece design with the T-shaped piece providing the seal with a polymer or metal gasket and the large annular threaded nut providing the force to hold the seal in place. This is a standard design for suppliers of high-pressure reactors such as HiP and Parker/Autoclave, for example.

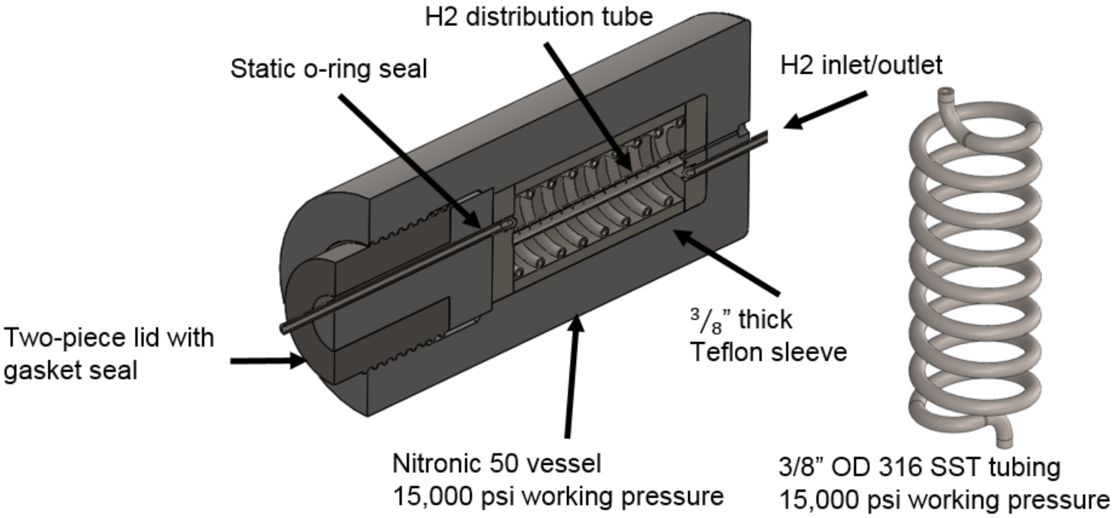

Figure 3. Prototype compressor bed and helical coil heat exchanger

The original design for the compressor prototype included two beds per stage with each bed containing approximately 25 kg of MH. However, due to budget constraints, the prototype was descoped in two ways. Firstly, it was decided that the proof-of-concept could be demonstrated with just one bed per stage. This would not allow for the quasi-continuous flow of hydrogen from the compressor and would cut the flow rate in half but would allow for the demonstration of all other aspects of the system. The second scope change was to reduce the scale of the prototype beds from 25 kg of MH per bed to approximately 3 kg. This required a redesign of the compressor beds but reduced the cost of the prototype significantly and still maintained all of the key design aspects.

A process was identified in FY 2017 to enhance the thermal conductivity of the MH materials using expanded natural graphite (ENG). Enhanced thermal conductivity is necessary to achieve good performance from the compressor beds, which must be alternately heated and cooled to drive the thermodynamic cycles of the MHs. In FY 2018, experiments were carried out to determine the type and amount of ENG to add to the MHs and the required compression force to create robust MH/ENG compacts with good thermal conductivity. Small test compacts (1-inch diameter, 0.25-inch thick) were pressed using a hydraulic press in an argon glove box. These compacts were then measured to verify the thermal conductivity enhancement of the graphite additive. Measurements were made using the transient plane source (TPS) method with a Hot Disk Thermal Analyzer (ThermTest, Inc. TPS2500). This instrument allows for the measurement of anisotropic thermal conductivity (radial and through-thickness), which is expected from compacted ENG, and graphite flake to a lesser degree. Compacts made from Hydralloy C5 and 10% by weight ENG have shown radial conductivity up to 29 W/mK prior to cycling. Based on literature data [4] and tests performed on cycled compacts at Sandia National

Laboratories (SNL), the thermal conductivity is expected to drop by 50% or more after 10 to 20 cycles before stabilizing.

Test Facility

A test facility has been designed to permit performance testing of the prototype 2-stage compressor that operates between 100 bar and 875 bar. The test facility will consist of three primary systems: a high-pressure hydrogen manifold, a temperature control system with hot and cold oil recirculation loops, and a data acquisition and control system.

The high-pressure hydrogen manifold was designed to allow for supply of hydrogen to the prototype compressor at 50 to 150 bar, compression of hydrogen from the low-pressure to the high-pressure stage, delivery of hydrogen from the high-pressure stage at 875 bar, and closed-loop recirculation of the hydrogen back to the supply volumes. The system makes use of existing infrastructure at Sandia's Hydrogen Effects on Materials Laboratory facility including the supply volumes and associated manifold and the manifold and test stand within the high-pressure test cell. The additional manifold section connecting the two beds to each other and the rest of the system is shown in Figure 4.

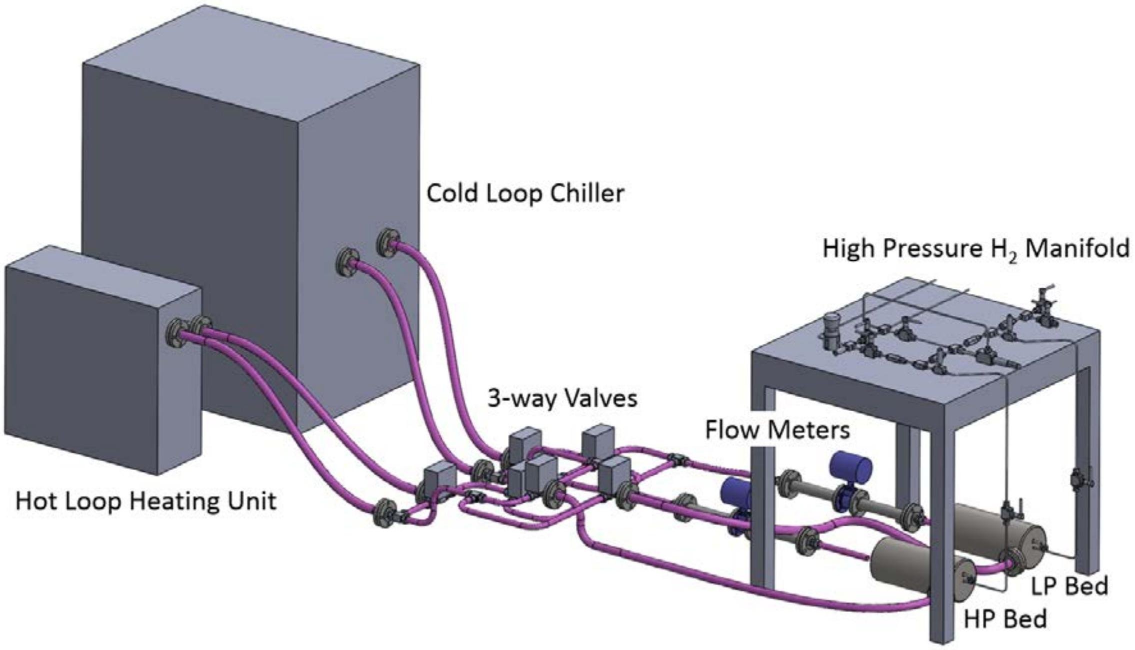

Figure 4. High-pressure hydrogen manifold and temperature control system for the prototype compressor

The temperature control system for the compressor prototype, also shown in Figure 4, 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. The unit has an internal expansion tank to allow for expansion of the fluid at high temperature. Flow from the two oil loops is directed to either the low- or high-pressure bed through a series of 3-way valves for heating and cooling.

A simple data acquisition and control system will be assembled for the system. 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 a 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.

Operation of the system will include a number of hazards including high pressure, high temperature, air-sensitive metal alloys, a combustible liquid, and combustible gases. To ensure the operational safety of the system a failure modes, effects, and criticality analysis was carried out to examine the system for potential failure modes and their associated effects as well as to analyze their relative criticality and risk with respect to safety and programmatic impact. Results from the analysis were used to assist in finalizing and improving the system design and associated testing procedures.

Overall, 346 failure mode effects were identified for the MH compressor system. Out of those, 266 were identified as being negligible in terms of severity. Of the other 70 failure mode effects, one was identified as catastrophic but improbable and 37 were identified as critical. These critical failure modes have been considered further, but none of them have greater than a remote chance of occurring. In all cases, procedures and both passive and active controls and safeguards will be important to insure safe operations. A list of procedures and safeguards has been developed based on this analysis. Procedures will be documented and posted where appropriate. All trained operators will be required to read, understand, and follow these procedures. Safeguards will be fully tested prior to operating the system. We believe that these procedures and controls will prevent or mitigate any significant risks.

CONCLUSIONS AND UPCOMING ACTIVITIES

Work completed in FY 2018 demonstrated that although an ideal combination of MHs for the low- and high-pressure stages of the compressor was not found from the selected candidates, several combinations were viable given either a higher supply pressure or a lower delivery pressure. In addition, a three-stage design was identified based on the measured materials that could compress from 50 to 875 bar. These options were presented to the project sponsor and a final alloy selection was made to deliver 875 bar hydrogen with a two-stage design and 150 bar supply pressure.

The hydride characterization work proved to be much more difficult than anticipated. This points to the need for additional fundamental materials discovery for viable high-pressure MH alloys for this application.

Through the compressor bed design trade study, it was concluded that the helical coil heat exchanger design provided the best combination of performance, manufacturability, and cost. A final detailed design of the bed and heat exchanger was completed and suppliers were engaged to carry out the fabrication for a reduced-scale prototype. Based on system-level simulations, the reduced-scale system should produce a hydrogen flow rate of approximately 120 grams/hour at 875 bar.

The compressor beds and heat exchangers were ordered at the end of Q4 FY 2018 along with the test facility components. In FY 2019, the temperature control system and hydrogen manifold will be assembled, leak checked, and tested. The data acquisition and control system will be designed, procured, and assembled. The custom die sets for the MH/ENG compacts will be fabricated and assembled while the alloys are being produced by Ames Laboratory. Once the alloys are received, they will be processed at Hawaii Hydrogen Carriers where they will be ball milled to a fine powder. The ball milled hydride will then be shipped to SNL for final processing. At SNL, the hydride powder will be mixed with graphite and compacted into shapes for loading into the compressor beds in an argon glove box. Once loaded, the compressor beds will be leak and pressure tested prior to integration in the test facility.

With bed integration complete, system checkout and safety assessments will be carried out prior to hydride activation and initial cycling. The primary performance testing of the prototype MH compressor will then take place. In parallel with this effort, conceptual design and cost analysis for a 100 kg/h commercial system will be carried out by Hawaii Hydrogen Carriers. The performance testing results and cost analysis will then be documented in a final report.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. T. Johnson, "Metal Hydride Compression," Oral presentation at Joint HSTT-HDTT-CSTT Meeting, Southfield, MI, March 28, 2018.
2. T. Johnson, "Metal Hydride Compression," Oral presentation at DOE Annual Merit Review, Washington DC, June 2018.

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