SAND2017-3654PE

Metal Hydride Compression

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Overview

Timeline

- Project Start Date: 10/01/16
- Project End Date: 09/30/19

Budget

- Total Project Budget: $1.8M
  - Total Recipient Share: $180K
  - Total Federal Share: $1.62M
  - Total DOE Funds Spent*: $154K

* As of 3/31/17

Barriers – Hydrogen Delivery

B. Reliability and Costs of Gaseous Hydrogen Compression

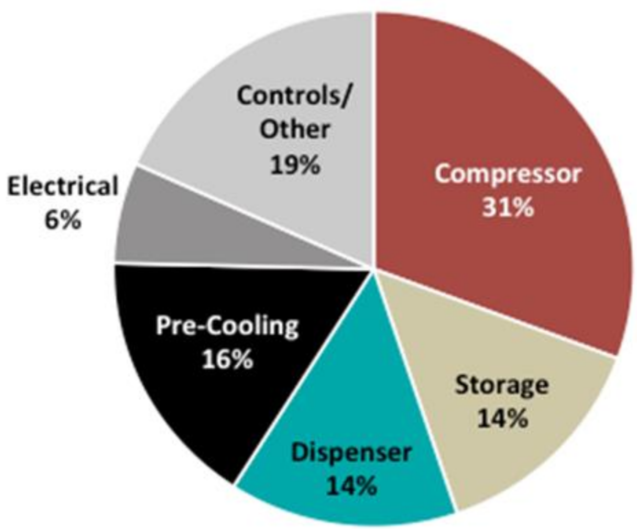
Partners

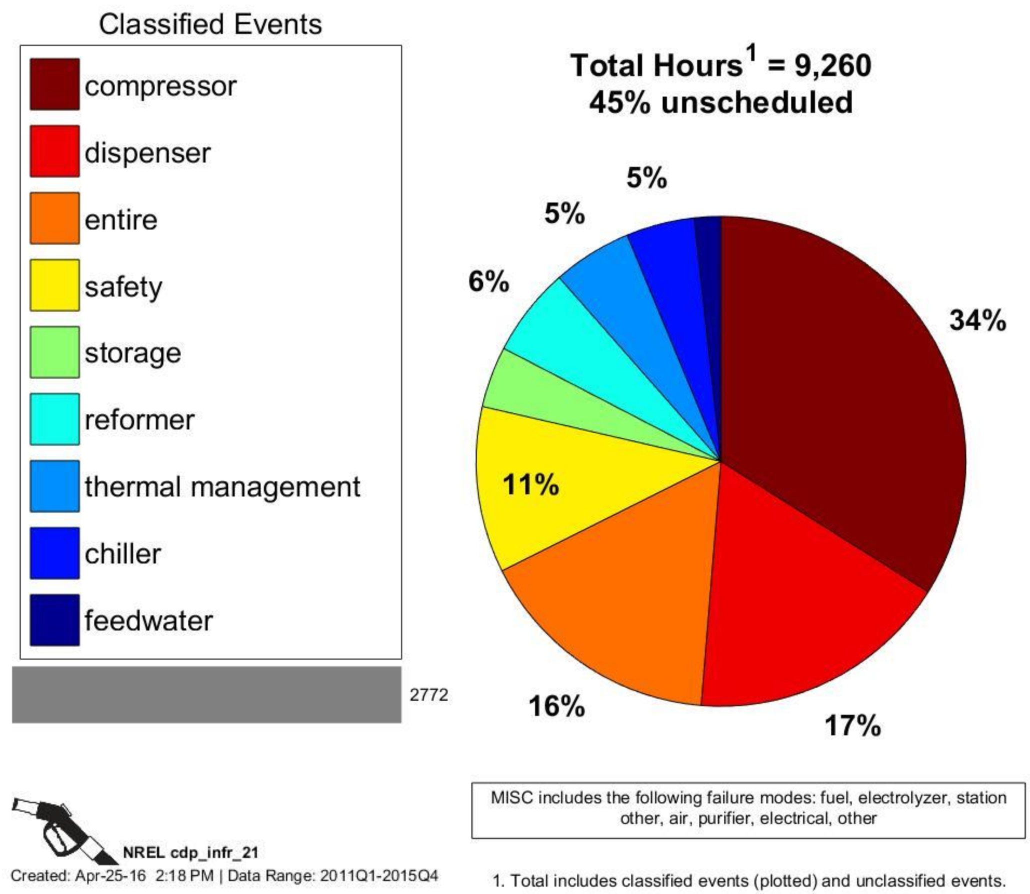
- Lead: Sandia National Laboratories
- Hawaii Hydrogen Carriers, LLC
- Oak Ridge National Laboratory

Relevance: H_2 compressors dominate station costs and downtime

Compressors are largest contributors to maintenance hours

70 Mpa station cost distribution





Compressors represent 31% of total station cost

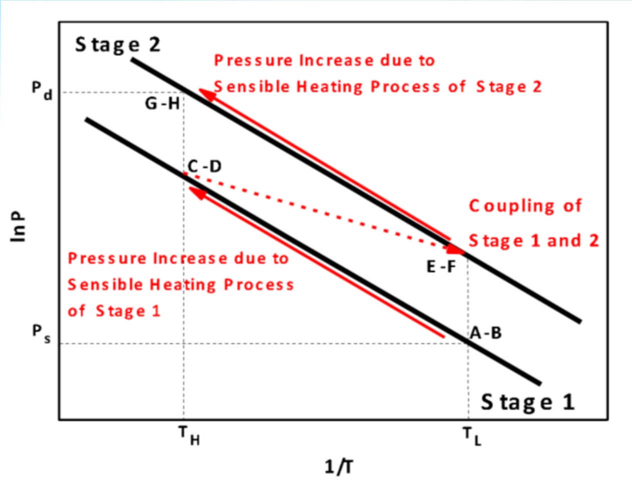
Relevance: Metal hydride compression can improve reliability of 700 bar refueling

Main Objective – *Demonstrate a two-stage metal hydride compressor with a feed pressure of ~50 bar delivering high purity H_2 gas at 1 kg H_2/hr at an outlet pressure of 875 bar.*

- Demonstrate an increase in the TRL of this technology from 2 to 5
- Enable the development of a comprehensive cost analysis for a production system scaled to 100 kg H2/hr
- FY17 Objectives:
  - Demonstrate through laboratory characterization two metal hydrides for each stage that meet system level requirements
  - Demonstrate compressor feasibility through analysis using a system-level compressor model
  - Down select compressor bed designs for both stages based on trade studies

Approach: Two-stage Metal Hydride Compressor

- Two-stage metal hydride compressor
  - Feed pressure 50-100 bar
  - Outlet pressure ≥ 875 bar
  - High purity H_2 gas
- Optimized material for each stage
  - 2-3 candidates per stage will be characterized (thermodynamics, kinetics, and hydrogen capacities) to determine optimum design
- Each stage consists of multiple (2-3) hydride beds
  - synchronized hydrogenation & dehydrogenation cycles
  - size and number of beds will be optimized for continuous pumping at desired pressure with minimal heat input



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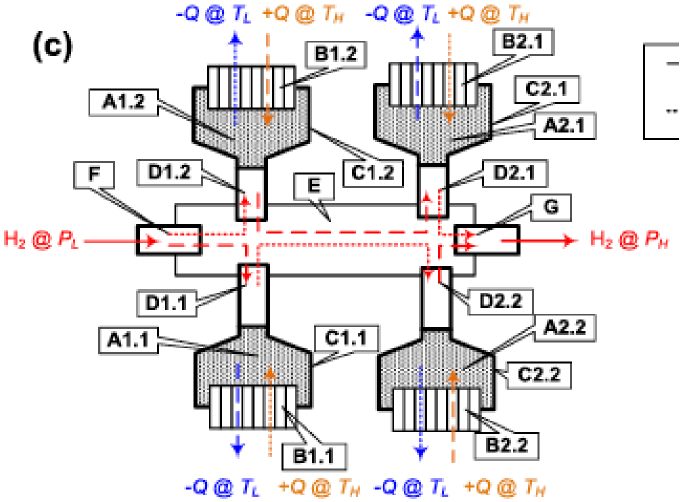
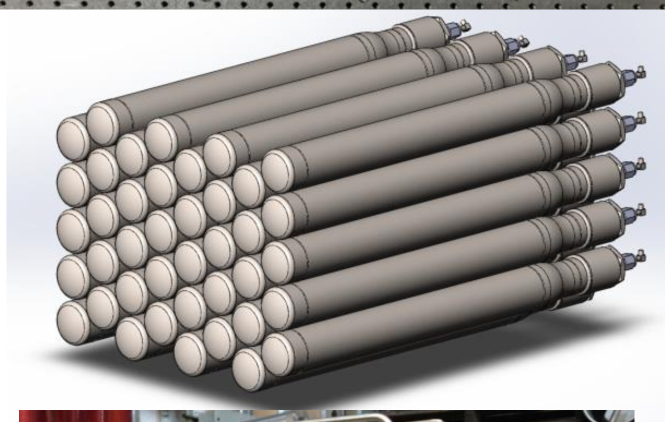
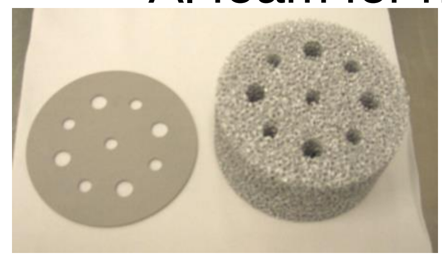


Approach: Trade study to determine bed designs including heat transfer enhancement

External heating/cooling ENG additive for heat transfer



Internal heating/cooling Al foam for heat transfer



Approach: Dynamic system-level model developed for feasibility and design trade studies

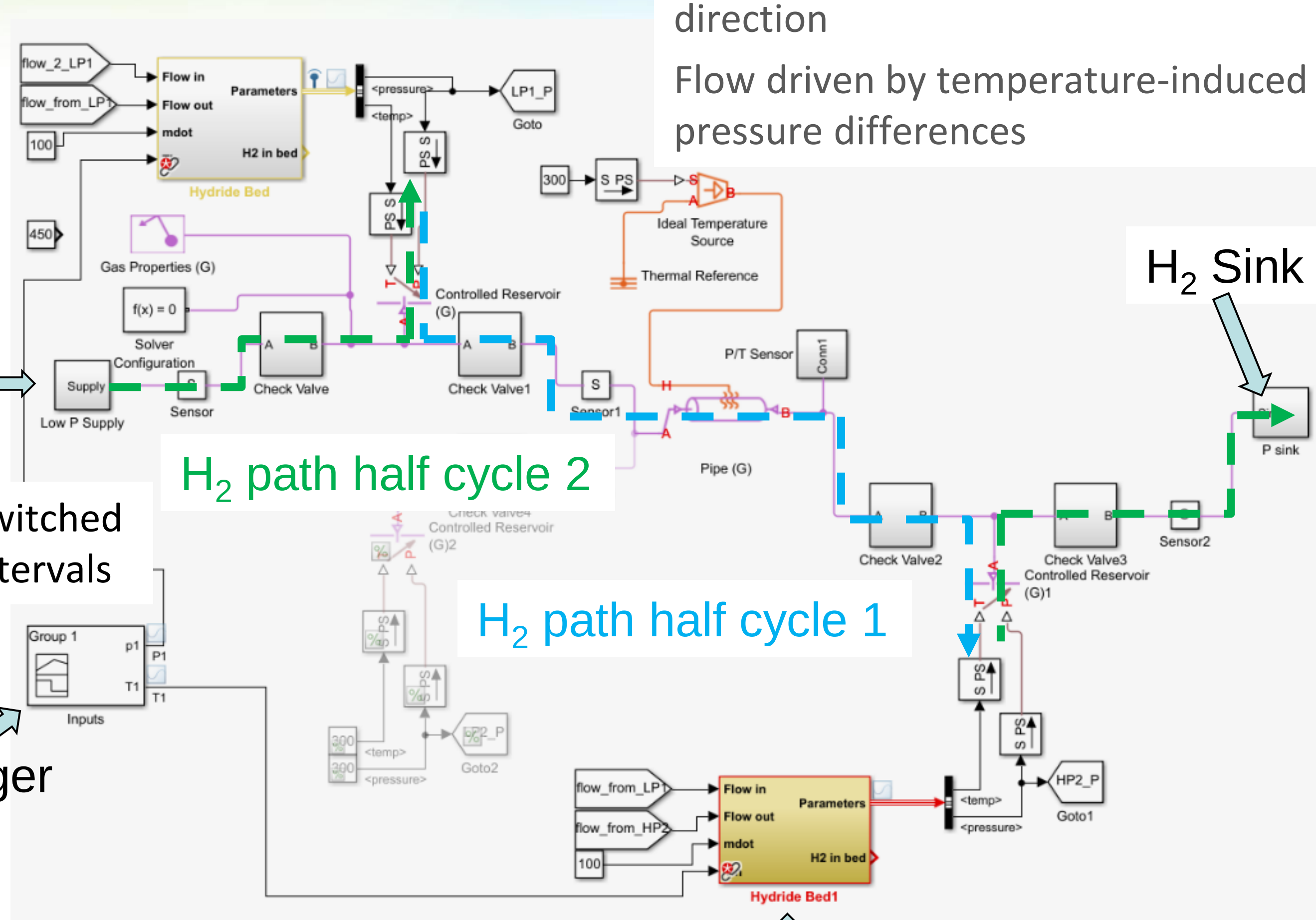
Check valves only allow flow in one direction

Flow driven by temperature-induced pressure differences

LP Bed 1

H_2 Supply

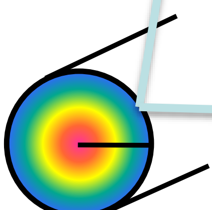
H_2 Sink



Temperature control loops switched between beds at half cycle intervals

Heat Exchanger Temp Control

HP Bed 2



Coupled 1-D heat transfer and chemical kinetics

Approach: Status of Milestones

Type	Milestone Number	Milestone Description	Scheduled Date	Status
Milestone	2.1	At least two candidate alloys identified for both LP and HP	12/16	100%
Milestone	2.2	At least two LP and HP materials fully characterized	4/17	10% (Delayed)
Milestone	3.2.1	Desired effective thermal conductivity determined along with additive type and amount.	7/17	0%
Go/No-Go Decision Point	Go/No-Go #1	Laboratory characterization demonstrates the ability of two metal hydride alloys to compress hydrogen from 100 bar to 875 bar, and engineering simulations using the system-level compressor model reasonably predict that the compressor can achieve an energy consumption of < 2.0 kWh/kg-H2 under 100-875 bar operation relying on process waste heat from co-located equipment.	10/17	0%
Milestone	6.1	Detailed design complete	1/18	0%
Milestone	7.1	Receipt of complete lots of both the LP and HP alloys by 17th month to allow time for processing into powders and confirmation of hydrogen absorption/desorption parameters while the bed assemblies are being fabricated.	3/18	0%
Milestone	7.2	Completed assembly of 2-stage compressor with at least two each LP and HP compressor beds	7/18	0%
Go/No-Go Decision Point	Go/No-Go #2	One LP and one HP hydride must show degradation less than 20% of initial capacity over ~1000 cycles or regeneration potential.	8/18	0%

Accomplishments: Dynamic system model used to predict performance for baseline two-stage design

Baseline Configuration:

- 25 kg of LP hydride ($TiMn_{1.66}Vf_{0.34}$)
- 21.7 kg of HP hydride ($TiCrMn_{0.7}Fe_{0.2}V_{0.1}$)
- 12 minute half cycles
- Heating/cooling of beds with heat transfer fluid
  - Cold loop temperature set to **10 ℃**
  - Hot loop temperature set to **177 ℃**

Results:

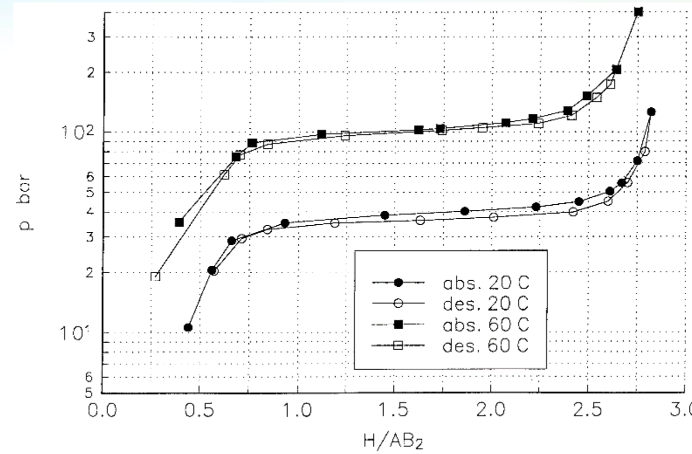
- Utilization = 49.5% for all beds
  - $$Utilization = \frac{Hydrogen\ delivered}{Storage\ capacity}$$
- **1.07 kg/hr average flow rate**
- **Energy usage for heating 12.5 kWh/kg H_2**
- Model used to characterize design space
  - Alloys, cycle times, bed geometry, feed pressure

Accomplishments: Several approaches identified to achieve energy efficiency/cost targets

- Heat recuperator design could reduce the sensible heat requirement of the system by ~40% bringing required heat down to ~10 kWh/kg
- Waste heat utilization:
  - Coupling to an SMR system is possible (heat available at appropriate temperature), but not likely in forecourt
  - Waste-to-energy systems identified with available, high quality heat
    - BESI system at HCATT has 190 kW of steam at ~180 ˚C and cooling water
- Low cost heat:
  - Natural gas burner can provide 10 kWh/kg of heat for about $.25/kg
- Heat pump options:
  - VCC operating between 25 ˚C and 125 ˚C
    - Using R21 gives COP = 2.7 resulting in 3.7 kWh/kg
    - Using methanol gives a COP of 3.2 resulting in 3.1 kWh/kg
  - A natural gas-fired AHP system might produce a COP of ~1.4 with these temperatures requiring 7.1 kWh/kg of heat or $.18/kg

Accomplishments: Five candidate alloys identified for each compressor stage; paired down to two each

- Alloy selection based on thermodynamics reported in literature
  - Minimal hysteresis and flat plateaus
  - Promising pressure at reasonable temperature
- Two high-pressure and low-pressure AB_2 alloys selected for PCT characterization



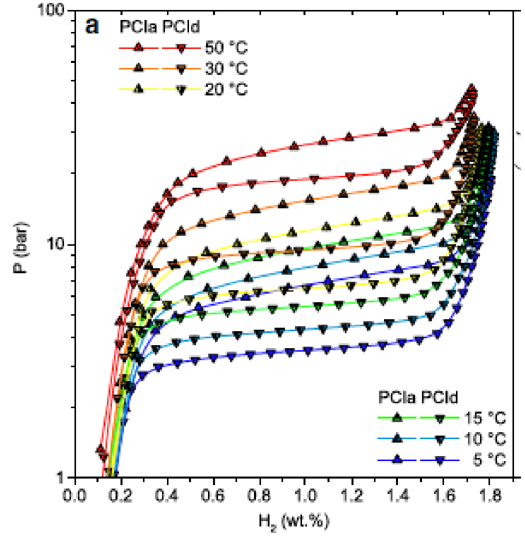
M.T. Hagstrom et al. JALCOM 293–295 (1999) 67

High Pressure Candidates

1. $TiCr_{1.6}Mn_{0.2}$
2. $TiCr_{1.8}$
3. **$Ti_{0.95}Zr_{0.05}Cr_{1.20}Mn_{0.75}V_{0.05}$**
4. $(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$
5. **$TiCrMn_{0.7}Fe_{0.2}V_{0.1}$**

Low Pressure Candidates

1. $MmNi_{4.7}Al_{0.3}$
2. $TiMn_{1.66}Vf_{0.34}$
3. **$Zr_{0.8}Ti_{0.2}FeNi_{0.8}V_{0.2}$**
4. $TiCr_{1.6}Mn_{0.2}$
5. **$Ti_{0.955}Zr_{0.045}Mn_{1.52}V_{0.43}Fe_{0.12}Al_{0.03}$** (Hydralloy C5)



G. Capurso, et al., Appl. Phys. A **122** (2016) 236

Accomplishments: Vendors engaged to supply alloys for low and high pressure beds

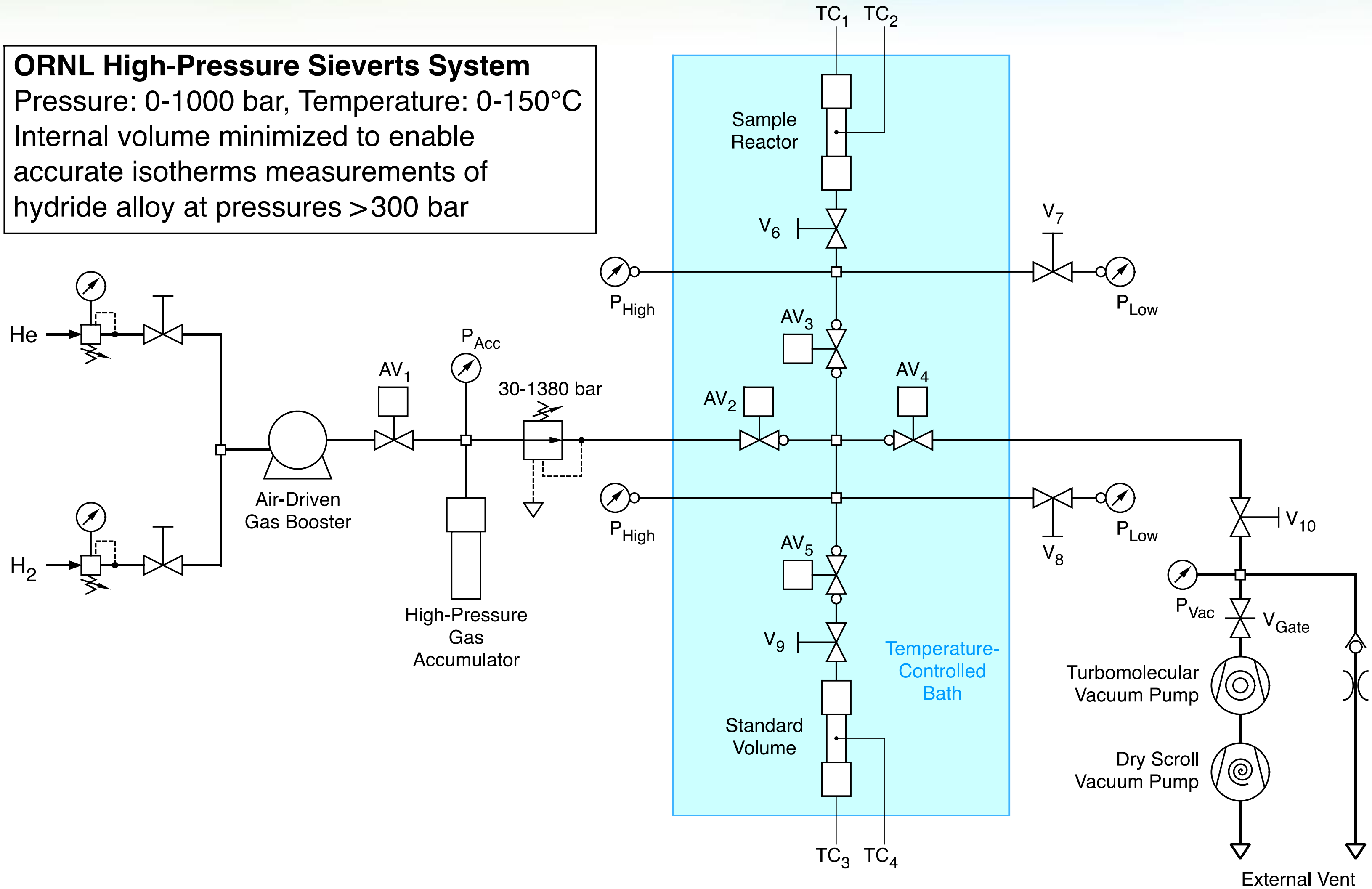
- Vendors contacted: Eutectix, Ergenics, GfE, Ames Laboratory, Sigma Aldrich, Japan Metals and Chemicals (JMC), Japan Steel Works (JSW)
- Sandia owns ~100kg of Hydralloy C5 ($Ti_{0.955}Zr_{0.045}Mn_{1.52}V_{0.43}Fe_{0.12}Al_{0.03}$)
  - Will be characterized for possible LP alloy
- Small samples of LP alloys obtained from GfE and Sigma Aldrich
  - But, similar alloys to Hydralloy C5
- Ames able to produce LP and HP alloys: small batches, expensive
- JMC able to produce LP and HP alloys in large quantities for less cost
  - Procure test quantities (i.e., ~ 50 grams) of three AB_2 alloys
    1. $Zr_{0.8}Ti_{0.2}Fe_{1.0}Ni_{0.8}V_{0.2}$ (Low-Pressure)
    2. $Ti_{0.95}Zr_{0.05}Cr_{1.20}Mn_{0.75}V_{0.05}$ (High-Pressure)
    3. $Ti_{1.0}Cr_{1.0}Mn_{0.7}Fe_{0.2}V_{0.1}$ (High-Pressure)

Accomplishments: High pressure cycling apparatus designed; assembly and calibration in progress

- High-pressure Sievert's system design completed in December
  - Incorporated ideas/practices from JPL hydride temperature cycling station and SNL high-pressure station
  - Used existing infrastructure at ORNL as much as possible
  - Focus on minimizing internal volume to enable measurements of small quantities of hydride alloys
- Safety review completed and design approved in January
- Assembly and system testing began in February
- PCT experiments will determine if
  1. Desorption pressure > 875 bar at T < 150 °C
  2. Alloys properties are stable over ~1000 cycles
- First measurements of high-pressure hydride to be completed in June
- Characterization of high-pressure hydrides to be completed in August

Accomplishments: High pressure cycling apparatus design minimizes internal volume

ORNL High-Pressure Sieverts System
Pressure: 0-1000 bar, Temperature: 0-150°C
Internal volume minimized to enable accurate isotherms measurements of hydride alloy at pressures >300 bar



Accomplishments: PCT system set to characterize low pressure alloys

Suzuki Shokan 2 channel thermo-volumetric analyzer (Sievert’s type apparatus aka PCT) with medium (≥150 atm) pressure capability.

Isotherms of a minimum of 2 candidate AB2 hydrides will be obtained at 25, 70, 100 and 150 ˚C by June 1, 2017.

Responses to Previous Year Reviewer's Comments

- **This project was not reviewed last year**

Collaborations: Experienced team well-suited for executing this project plan

- Sandia National Laboratories
  - Project lead/project management
  - Lead compressor bed and system design (system model, pressure vessel design, heat transfer enhancement)
  - Low pressure hydride degradation assessment
  - Experimental evaluation of the prototype compressor
- Oak Ridge National Laboratory
  - Hydride identification
  - High pressure hydride characterization and degradation assessment
  - Support SNL in developing compressor bed and system designs
- Hawaii Hydrogen Carriers, LLC
  - Low pressure hydride characterization
  - Hydride sourcing and procurement
  - Fabrication of the prototype 2-stage compressor
  - Cost analysis of the commercial system concept.

Remaining Challenges and Barriers

- Challenge: Achieve an energy consumption of < 2.0 kWh/kgH_2 or cost less than \$0.22/kgH_2
  - Metal hydride thermodynamics require 6-7 kWh/kgH_2 minimum for a two-stage compressor; sensible heating requirements and losses push this to ~12 kWh/kgH_2
  - 12 kWh/kgH_2 of heat provided by a natural gas combustion unit (assuming natural gas costs \$0.065/mm-btu, and burners are about 85% efficient) is about \$.30/kg
  - Must show potential for waste heat utilization and/or lower cost heat
- Challenge: Identifying two metal hydride alloys to compress hydrogen from 100 bar to 875 bar within reasonable operating temperatures with degradation less than 20% of initial capacity over ~1000 cycles or regeneration potential
- Challenge: Bed design (especially to >875 bar) that maximizes energy efficiency by minimizing sensible heating, thermal losses, and void volume while also maximizing H_2 flow rate

Proposed Future Work

Remainder of FY17

- Characterize at least two alloys for each stage
  - Produce absorption and desorption isotherms
  - Demonstrate system requirements can be met by at least one alloy for each stage
- Perform trade studies on design configurations for the prototype LP & HP compressor beds and down select
- Complete feasibility assessment using system-level compressor model
  - Demonstrate performance with measured properties and final bed designs
  - Demonstrate path to energy and/or cost targets

FY18

- Perform accelerated cycling tests (~1000 cycles) on hydrides
  - determine degradation rate
  - assess regeneration potential.
- Complete fabrication and assembly drawings of compressor beds
- Procure hydride alloys and fabricate bed components
- Process hydrides, load compressor bed, perform leak and pressure tests then integrate into prototype compressor.
- Configure test facility to enable performance testing.

Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

Potential Follow-on Prototype Demonstration

- Discussions with HCATT/BESI on integration of the prototype system into BESI waste-to-energy system in Peal Harbor, HI or University Park, IL

Tech-to-Market Plan

- Two-year developmental phase
  - HHC will team with an electrolyzer, fueling station supplier, or reformer company to produce a scaled-up, commercial version of the compressor
  - Units will be marketed as upgrades for current hydrogen generation systems, or for localized H_2 production via renewable sources such as solar or wind for residential, businesses or small utility fleets.
- Final two-year phase
  - Further scale-up effort for the development and marketing of larger hydride compressors with output of 10 kg H_2/hr to 100 kg H_2/hr for hydrogen fueling stations

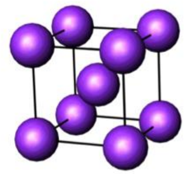
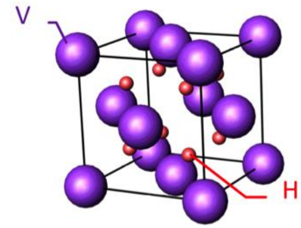
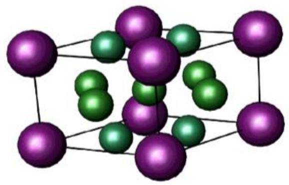
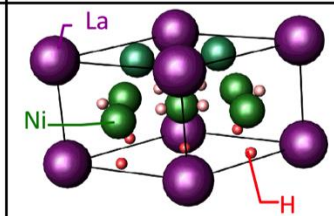
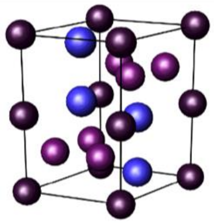
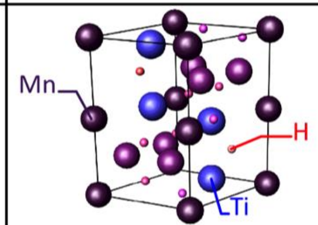
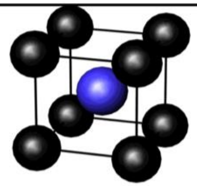
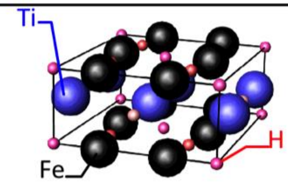
Summary

- A metal hydride compressor has potentially significant advantages over current technology
  - Greatly reduced operating costs
    - Requires little or no maintenance
    - Can be powered by waste heat rather than electricity
  - More Reliable: Simple design and operation with no moving parts
  - High purity H_2 delivery: Oil free operation
- Candidate alloys for low and high pressure stages are readily available in quantities required for a prototype system
- System-level analysis of a baseline design demonstrates feasibility of 50 - 875 bar H_2 compression and delivery at reasonably achievable temperatures
- Metal hydride compressors can be energy efficient by taking advantage of waste heat sources or using heat pumps; inexpensive to operate if low cost heat is available

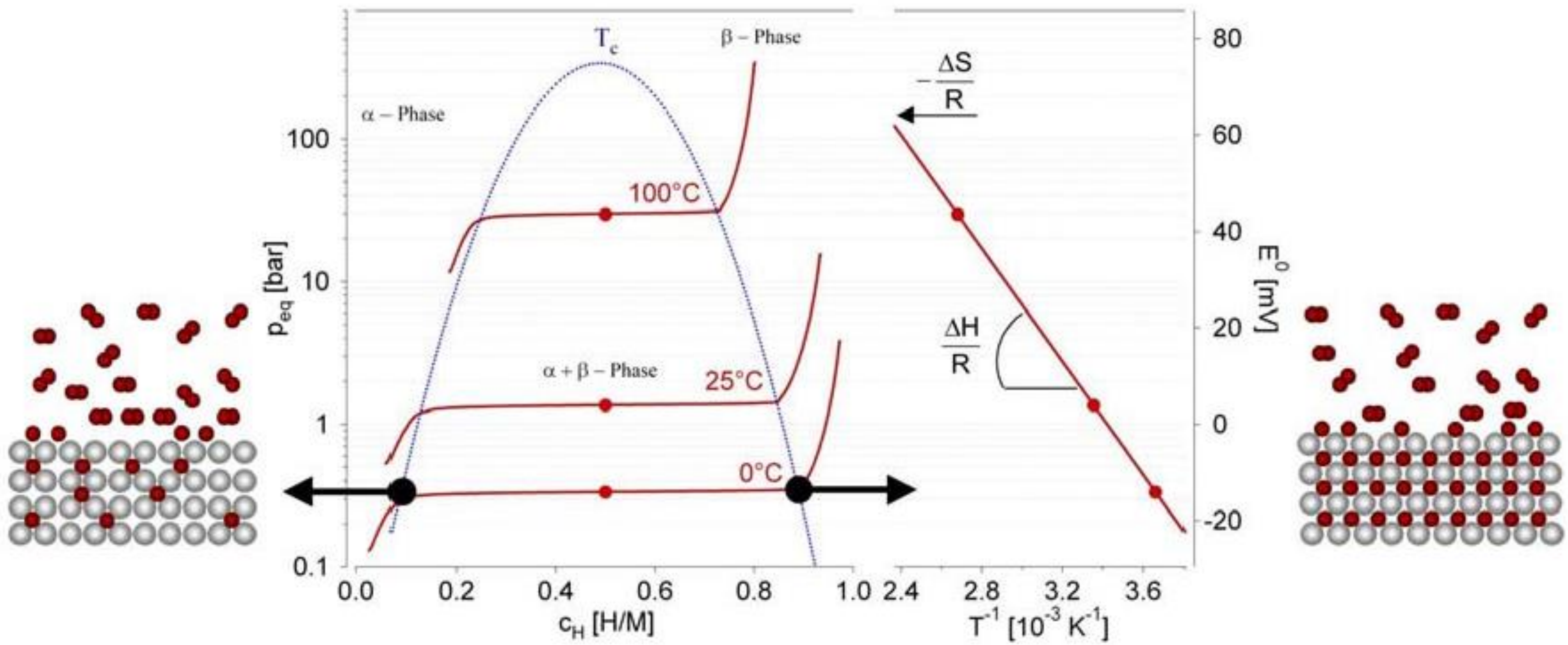
TECHNICAL BACK-UP SLIDES

Interstitial metal hydrides for H_2 compression

AB_5 and AB_2 most commonly used

Group (representative)	Structure of parent alloy	Structure of hydride	$\Delta V/V_0$ [%]
A (BCC-V)			35.5 ($V \rightarrow VH_2$) 30.9 ($V_2H \rightarrow VH_2$)
B ($LaNi_5$)			20.4 ($LaNi_5 \rightarrow LaNi_5H_6$)
C ($TiMn_2$)			19.6 ($TiMn_2 \rightarrow TiMn_2H_{2.5}$)
D (TiFe)			18.3 ($TiFe \rightarrow TiFeH_2$)

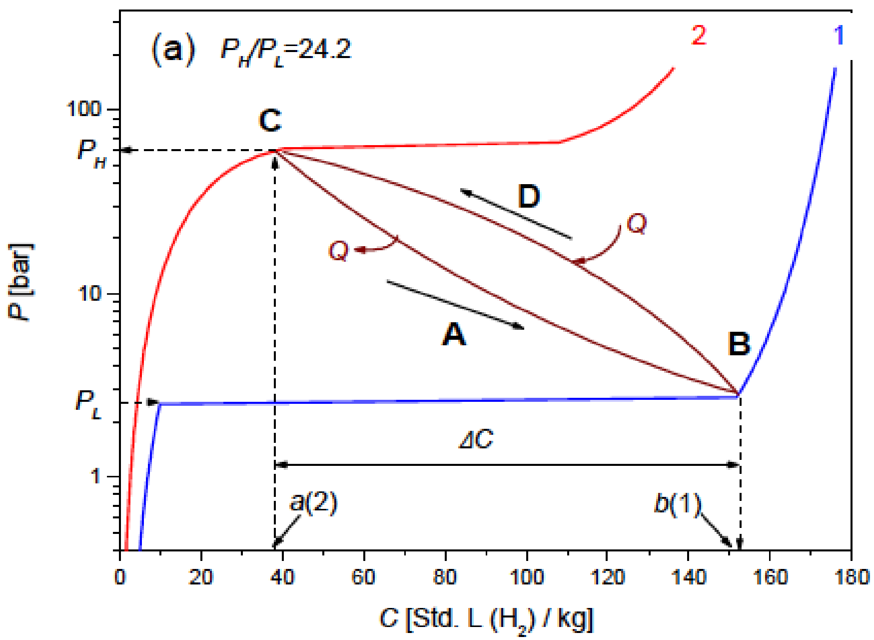
Pressure-Composition-Temperature (PCT) Isotherms for a "Prototype" Metal Hydride

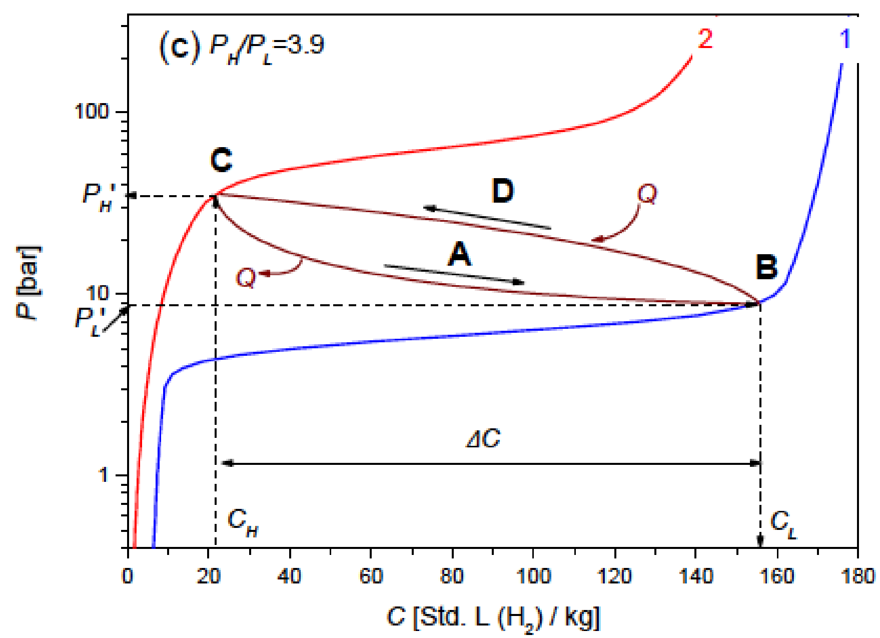


- where α- & β-phases co-exist, a plateau occurs
- plateau pressure is temperature dependent

Estimates of compression ratio must account for real metal hydride properties

Pressure – composition isotherms at T_L=20 °C (1) and T_H=150 °C (2) for H – $La_{0.85}Ce_{0.15}Ni_5$ system





(a) –idealized (flat plateaus, desorption isotherms)

b) – real (sloping plateaus, absorption isotherm at T_L, desorption isotherm at T_H).

M.V. Lototskyy, et al., IJHE 39 (2014) 5818

Metal hydride compressors have advantages over mechanical compression, but other challenges

Advantages

- Simple design and operation
- Absence of moving parts
- Oil-free
- Compact
- Safe and reliable
- Able to utilize waste industrial heat
  - Dramatic decreases in operational costs
  - Advantage with on-site generation

Challenges

- Achieving required pressure range within reasonable operating temperatures
- Capacity degradation over the compressor lifetime
- Hysteresis effects
- Resistance to impurities
- Efficiency
- Minimizing effect of vessel heat capacity

2-Stage 700 bar Compressor Demonstrated Used AB_2 Hydrides

[X. Wang, et al., Int. J. Hydrogen Energy 36 (2011) 9079-9085.]

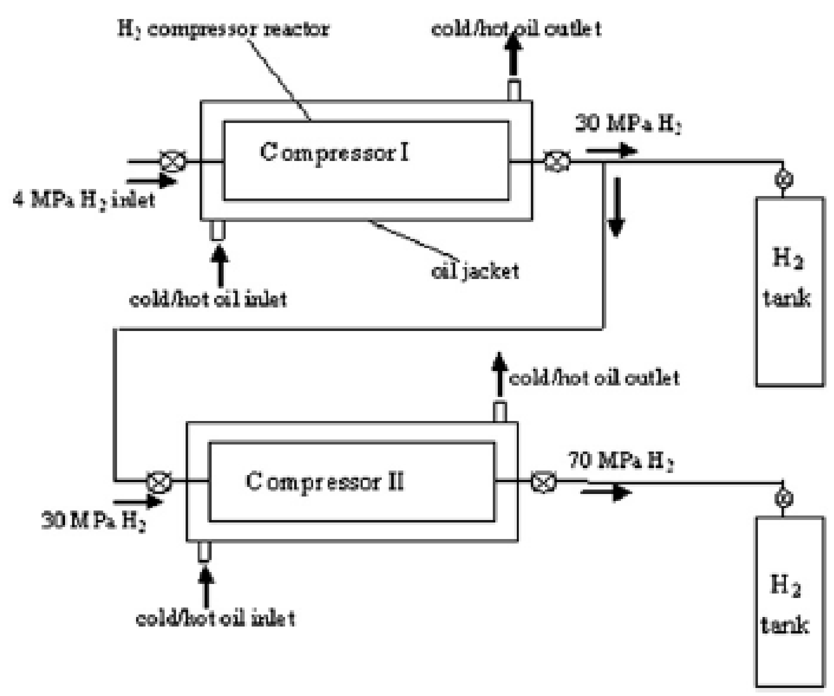


Fig. 6 – Schematic diagram of hydrogen compression system.

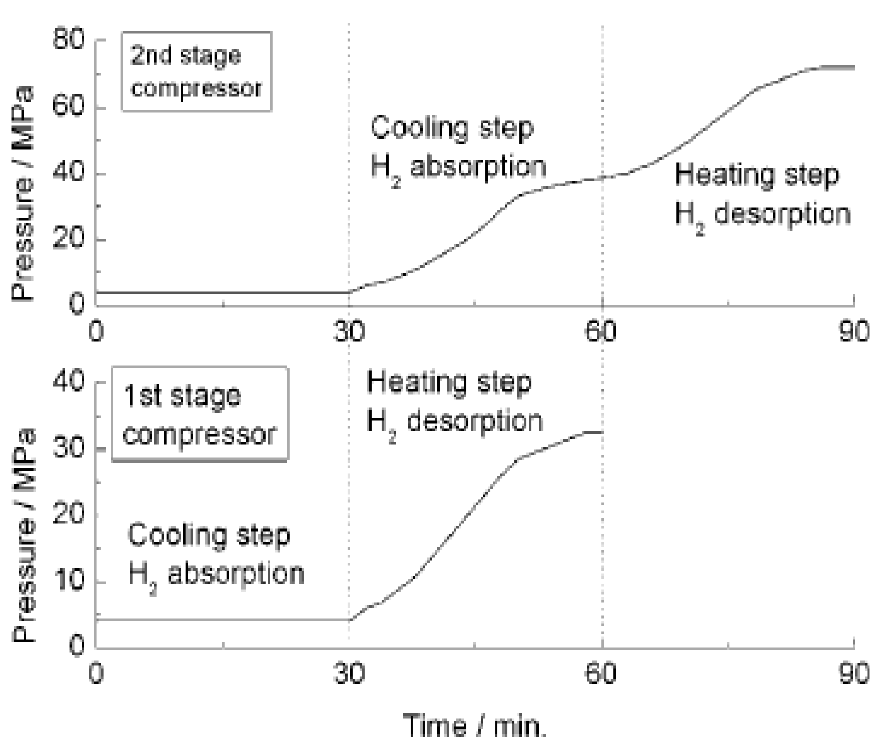


Fig. 7 – Compression performance of the two-stage compression system.

- 1st stage Alloy: $Ti_{0.95}Zr_{0.05}Cr_{0.8}Mn_{0.8}V_{0.2}Ni_{0.2}$
- 2nd stage Alloy: $Ti_{0.8}Zr_{0.2}Cr_{0.95}Fe_{0.95}V_{0.1}$
- Circulated cold (~300 K) and hot (~423 K) oil in beds
- Periodic Pressurization steps and not continuous supply of 700 bar H_2 gas

REVIEWER-ONLY SLIDES

Critical Assumptions and Issues

Issue: Given the fundamental limitation of metal hydride heats of formation, a two-stage MH compressor cannot inherently meet energy efficiency or H_2 delivery cost requirements

Solution: Demonstrate practical application(s) where waste heat from co-located equipment can be used to meet energy requirements and/or low cost heat can be used to meet cost requirements

Assumption: At least one LP and one HP alloy can be obtained that compress hydrogen from 100 bar to 875 bar within reasonable operating temperatures with degradation less than 20% of initial capacity over ~1000 cycles or can be regenerated

Solution: FY17 characterization studies and FY18 degradation studies will prove or disprove this assumption

Issue: Challenging to design compressor beds (especially to >875 bar) that maximize energy efficiency by minimizing sensible heating, thermal losses, and void volume while also maximizing H_2 flow rate

Solution: FY17 design studies along with supporting analyses using the system-level dynamic model should address this issue.

Publications and Presentations

- Johnson, T. A., Oral Presentation at Joint CSTT-HDTT Meeting, "Metal Hydride Compressor for High-Pressure (≥ 875 bar) Hydrogen Delivery," Golden, CO, Nov. 2, 2016
- Bowman, R., Oral Presentation at Joint HSTT-HDTT Meeting, "Metal Hydride Compressor for High-Pressure (≥ 875 bar) Hydrogen Delivery," Southfield, MI, Feb. 16, 2017
- Bowman, R., Oral Presentation at 11th International Symposium on Hydrogen & Energy, "Status of High-Pressure Metal Hydride Compressors for Applications Exceeding 700 Bar," Waikoloa, HI, Feb. 28, 2017