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: $2.05M
  - Total Recipient Share: $180K
  - Total Federal Share: $1.87M
  - Total DOE Funds Spent*: $1.565M

* As of 3/04/19

Barriers – Hydrogen Delivery

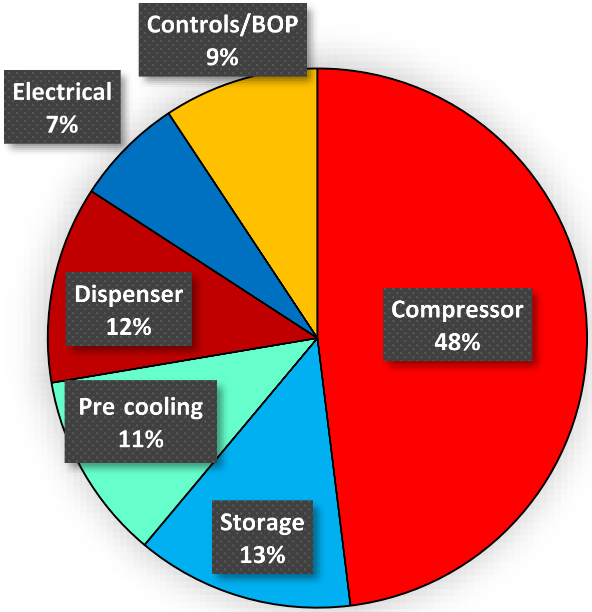
B. Reliability and Costs of Gaseous Hydrogen Compression

Partners

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

Relevance: Hydrogen compressors dominate station costs and downtime

Compressors represent 48% of total station cost

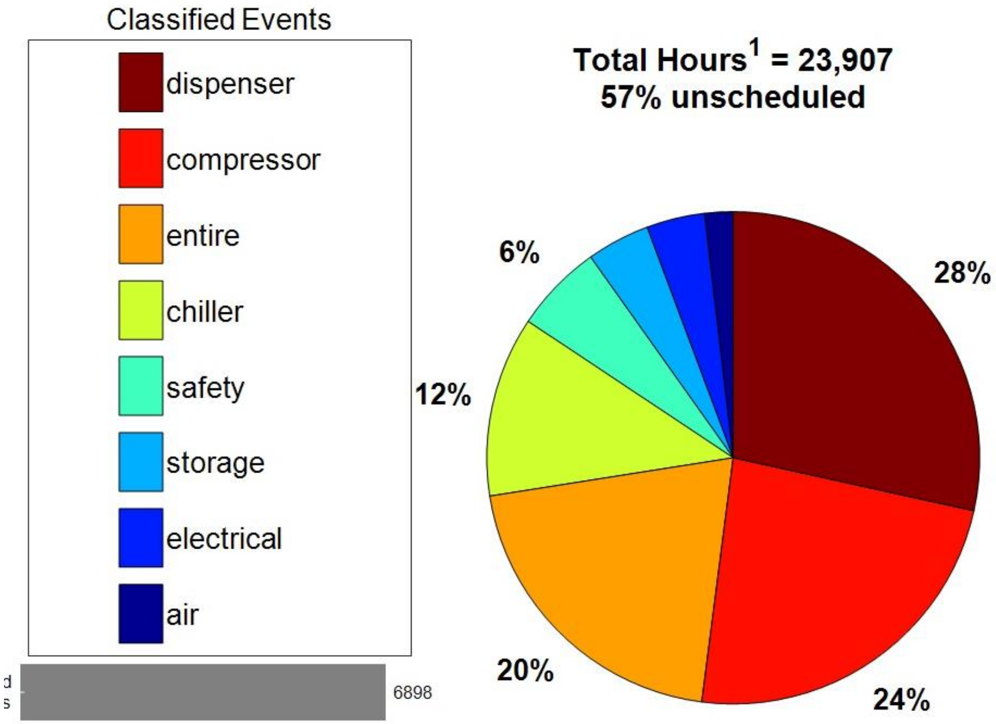


700 bar station cost distribution

Assuming gaseous tube trailer delivery

Source: HDSAM https://hdsam.es.anl.gov/index.php?content=h

Compressors are 2nd largest contributors to maintenance hours



Source:
NREL Composite Data Products, 2018
https://www.nrel.gov/hydrogen/assets/images/cdp-infr-21_20180831.jpg

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

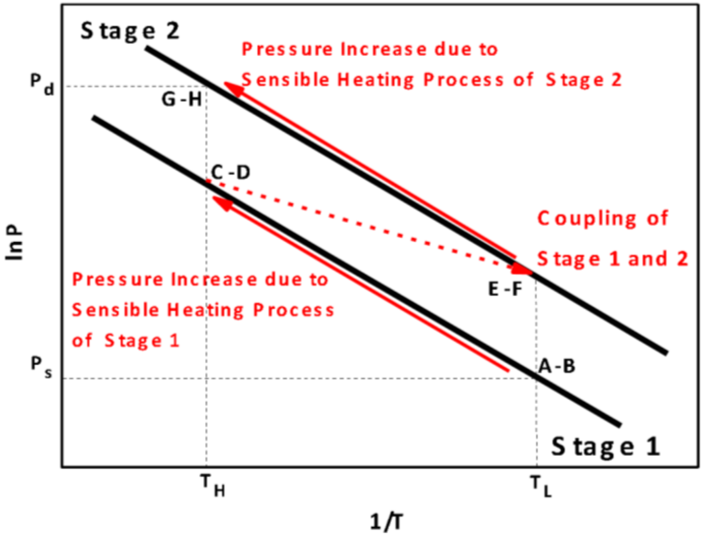
Main Objective – *Demonstrate a two-stage metal hydride compressor with a feed pressure of 150 bar delivering high purity H_2 gas at an outlet pressure of >875 bar.*

- 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 H_2/hr
- Objectives (4/18 to 3/19):
  - Identify a metal hydride alloy for the high pressure stage that meets system level requirements based on laboratory characterization
  - Complete redesign of prototype compressor, order components and assemble the beds
  - Complete the assembly of the prototype compressor test facility

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 optimized for continuous pumping at desired pressure with minimal heat input



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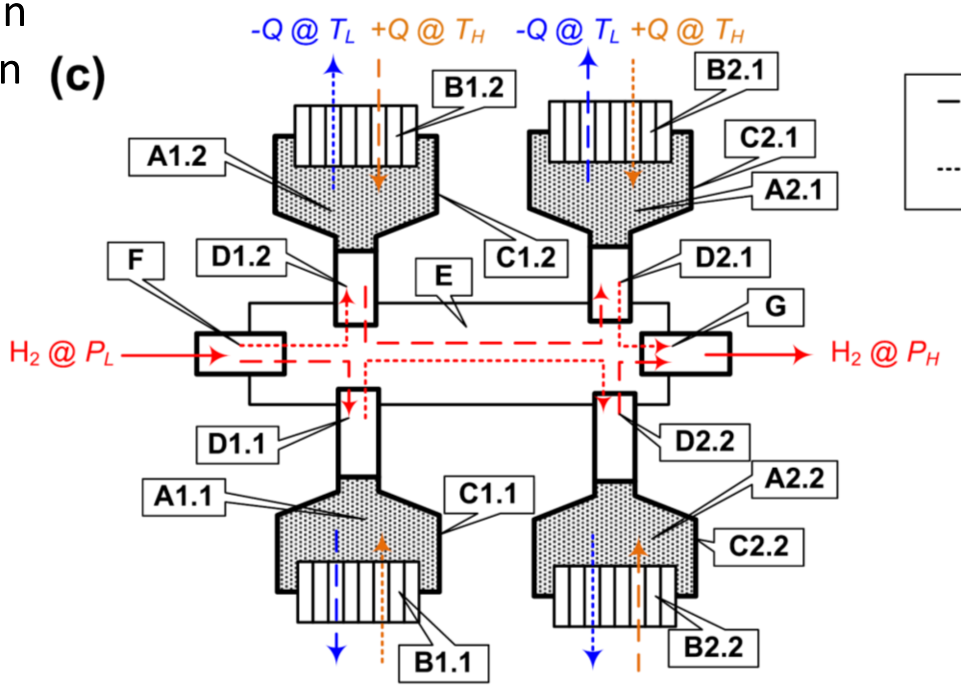


M.V. Lototskyy, Y.A.Yartys, B.G. Pollet, R.C. Bowman Jr., “Metal hydride hydrogen compressors: A review.” Int J. Hydrogen Energy **39** (2014) 5818

Approach: Experimentally demonstrate a scalable system with path to DOE targets

	Inlet pressure (Pipeline)	Outlet Pressure	Flow rate (peak)	Uninstalled Capital Cost	Maintenance Costs (Annual)	Lifetime
FY 2020 Targets	100 bar	950 bar	100 kgH_2/hr	$275K	4% of installed cost	10 years

Path to Targets

- **Pressure**: Literature research to choose candidate alloys; Characterization to verify PCT relationships; Prototype operation to demonstrate synchronized desorption/absorption cycles
- **Flow rate**: Literature research and characterization to provide cycling kinetics; modeling to predict expected flow rate; prototype operation to validate model prediction
- **Costs**: Capital cost estimate from techno-economic analysis based on prototype scaled to 100 kgH_2/hr; maintenance costs based on extrapolation of prototype operation
- **Lifetime**: Based on alloy degradation assessments

Approach: Leverage/collaborate with related projects

- PD137 Hybrid Electrochemical-Metal Hydride Compression (GreenWay Energy)
  - Both projects include a high pressure metal hydride stage
  - Collaboration topics: Material selection, high pressure instrument design, characterization techniques, cost estimates
  - Shared materials lists, materials and instruments
  - Several meetings and e-mail contact over the last year

Approach: Status of Milestones

Type	Milestone Number	Milestone Description	Scheduled Date	Status
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.	12/18	100%
Milestone	7.2	Complete assembly of 2-stage laboratory prototype compressor	3/19	0%
Milestone	9.0	Prototype integrated with test facility and ready for testing	4/19	0%
Milestone	10.0	Demonstrate quasi-continuous 0.12 kg/hr hydrogen flow rate while compressing from 150 to 875 bar	6/19	0%
Milestone	11.0	Final report complete	9/19	0%

Milestones 7.2 and 9.0 are likely to be delayed by at least one month due to late deliveries from suppliers

- High pressure vessels for compressor beds (HiP)
  - Fabrication was behind schedule
  - Determined on 2/26 that parts were machined from wrong material
  - Delivery date currently unknown
- Custom die sets (Header Die and Tool)
  - Delayed by > 3 weeks in part due to weather in the northeast

Accomplishments: Seven high pressure alloys from two vendors characterized between SNL and GWE teams

SNL High Pressure Candidates

1. $Ti_{0.95}Zr_{0.05}Cr_{1.20}Mn_{0.75}V_{0.05}$ [c]
2. $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$ [a,c]
3. $TiCrMn_{0.7}Fe_{0.2}V_{0.1}$ [b]
4. $Ti_{0.6}Zr_{0.4}Fe_{1}Ni_{0.6}V_{0.4}$

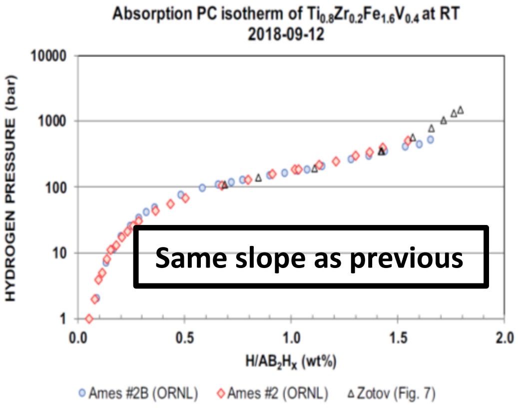
GWE High Pressure Candidates

1. $Ti_{1.1}CrMn$ [a,b]
2. $(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$ [a,b]
3. $TiCr_{1.55}Mn_{0.2}Fe_{0.2}$

[a] *Repeated with new annealing process (10 days at 1200 ℃) meant to improve properties*

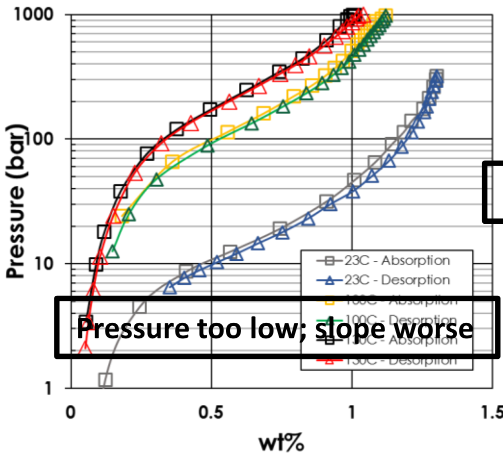
[b] *Samples fabricated by JMC and Ames Lab*

[c] *Demonstrated 875 bar desorption at achievable temperature*



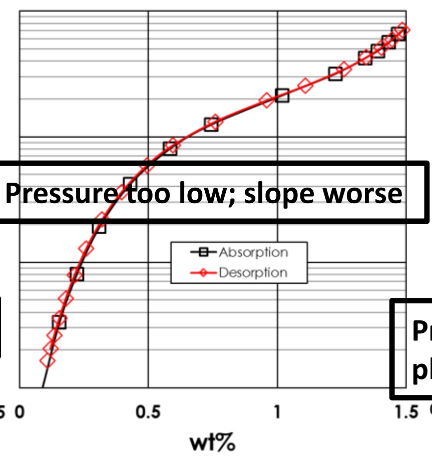
Absorption PC isotherm of $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$ at RT
2018-09-12

Same slope as previous



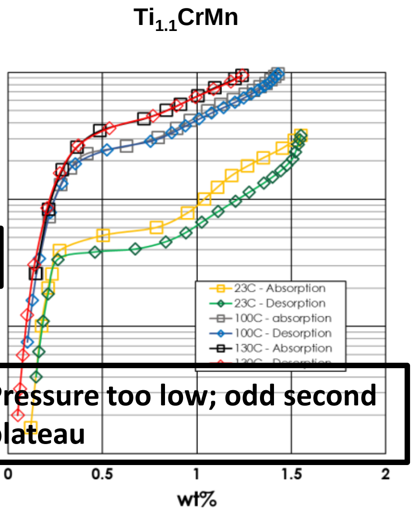
$Ti_{0.6}Zr_{0.4}Fe_{1}Ni_{0.6}V_{0.4}$ - 23, 100 & 130C

Pressure too low; slope worse



$(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$ - 100 C

Pressure too low; slope worse



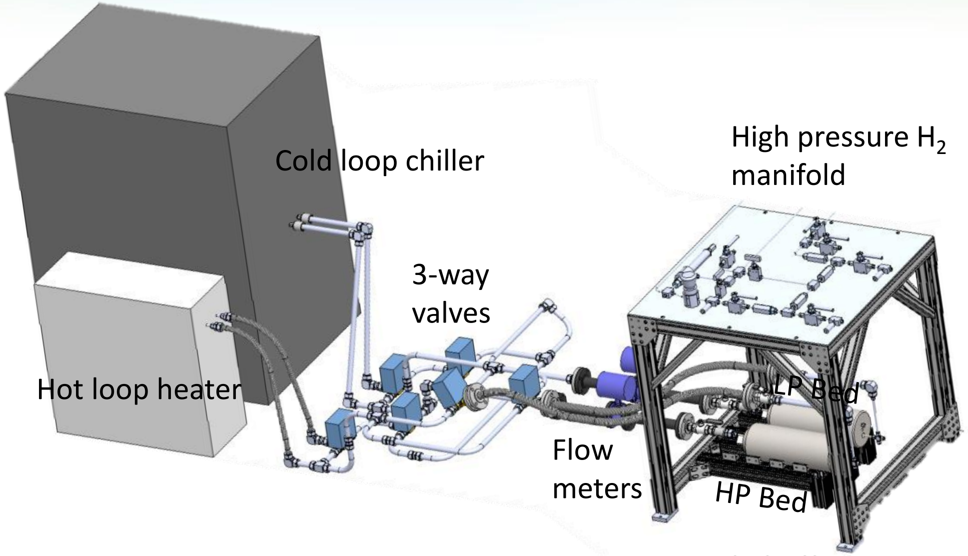
$Ti_{1.1}CrMn$

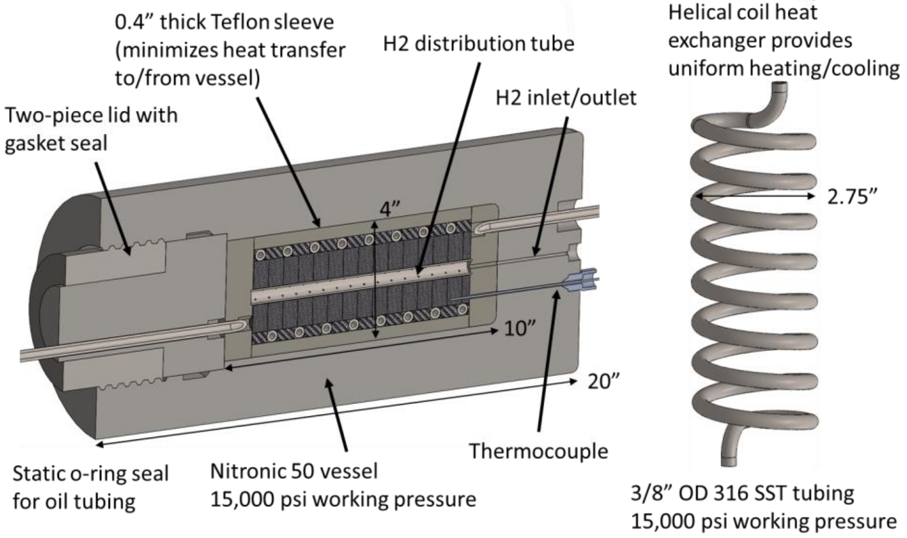
Pressure too low; odd second plateau

Accomplishments: Approved for Phase 2 with reduced-scale prototype; redesigned to reduce cost

Selection from 4 options:

- 2 stage; 1 bed per stage
- ~8X reduction in scale compared to original prototype
  - 3 kg hydride per bed
  - Original – 30”L X 13”OD; 850 lbs
  - New – 20”L X 8”OD; 220 lbs
  - Reduced scale, self-contained oil recirculation systems
  - 0.15 kg/hr flow rate
- Stage 1 = $TiCrMn_{0.7}Fe_{0.2}V_{0.1}$ (Ames #3); Stage 2 = $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$ (Ames #2)
- 150 bar to 875 bar compression; temperatures of ~ 20˚C - 150˚C





Accomplishments: Dynamic system model predicts performance using measured alloy properties

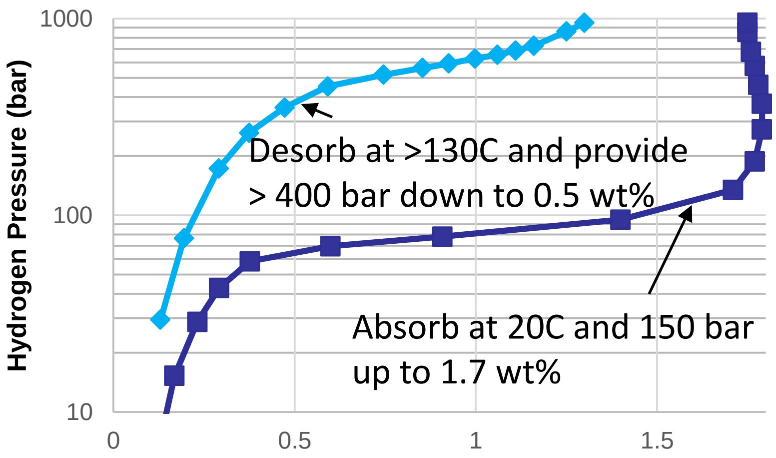
Configuration:

- 25 kg of LP hydride ($TiCrMn_{0.7}Fe_{0.2}V_{0.1}$)
- 21.7 kg of HP hydride ($Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$)
- 15 minute half cycles
- 150 to 875 bar compression
- Heating/cooling of beds
  - Cold loop temperature set to 20 ℃
  - Hot loop temperature set to 160 ℃

Results:

- Utilization = 54% for all beds
  - $$Utilization = \frac{Hydrogen\ delivered}{Storage\ capacity}$$
- **0.90 kg/hr average flow rate**
- **Energy usage for heating 10.9 kWh/kg H_2**

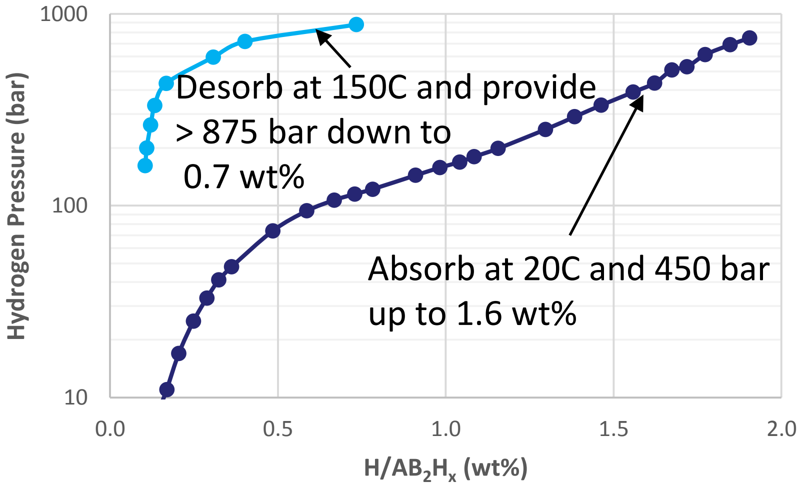
LP Stage - $TiCrMn_{0.7}Fe_{0.2}V_{0.1}$



Desorb at >130C and provide > 400 bar down to 0.5 wt%

Absorb at 20C and 150 bar up to 1.7 wt%

HP Stage - $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$



Desorb at 150C and provide > 875 bar down to 0.7 wt%

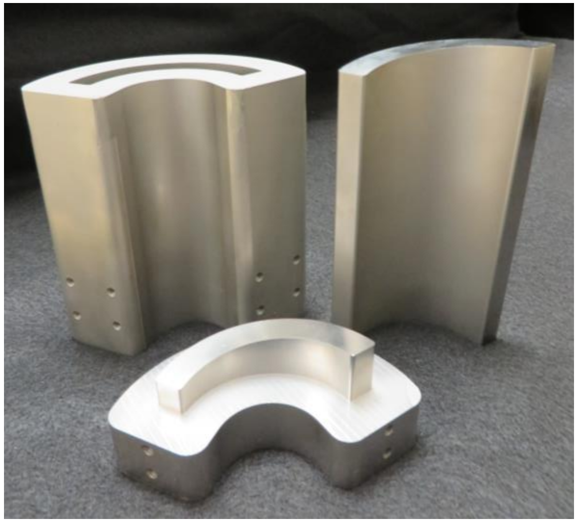
Absorb at 20C and 450 bar up to 1.6 wt%

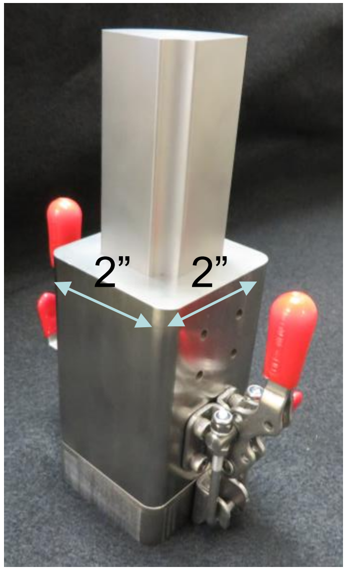
Accomplishments: Ames Lab produced 4 kg each of the AB2 alloys for our compressor beds; HHC ball-milled

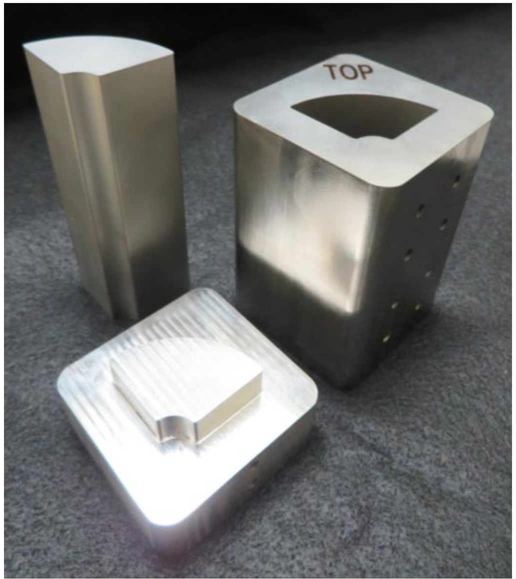
- Plasma arc melted
- Vacuum annealed in Ta vessel
  - 1200 C
  - 240 hours
- Crushed in Ar and shipped to HHC
- Ball milled in planetary mill under Ar
  - Filtered with a 150 mesh sieve
  - 10-100 micron particles

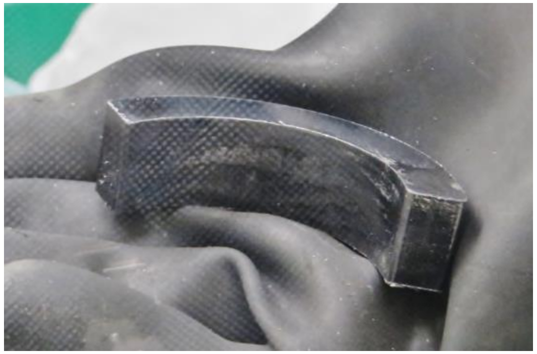
Accomplishments: Two custom die sets produce pellets that conform to internal geometry

Die set parts received 3/11/19

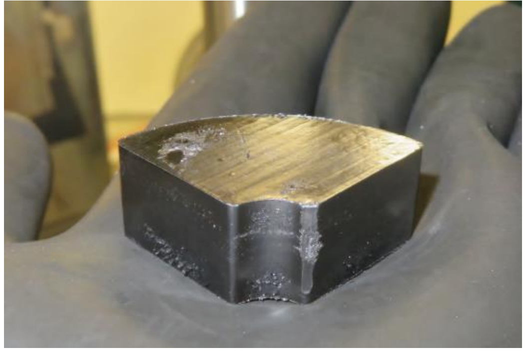




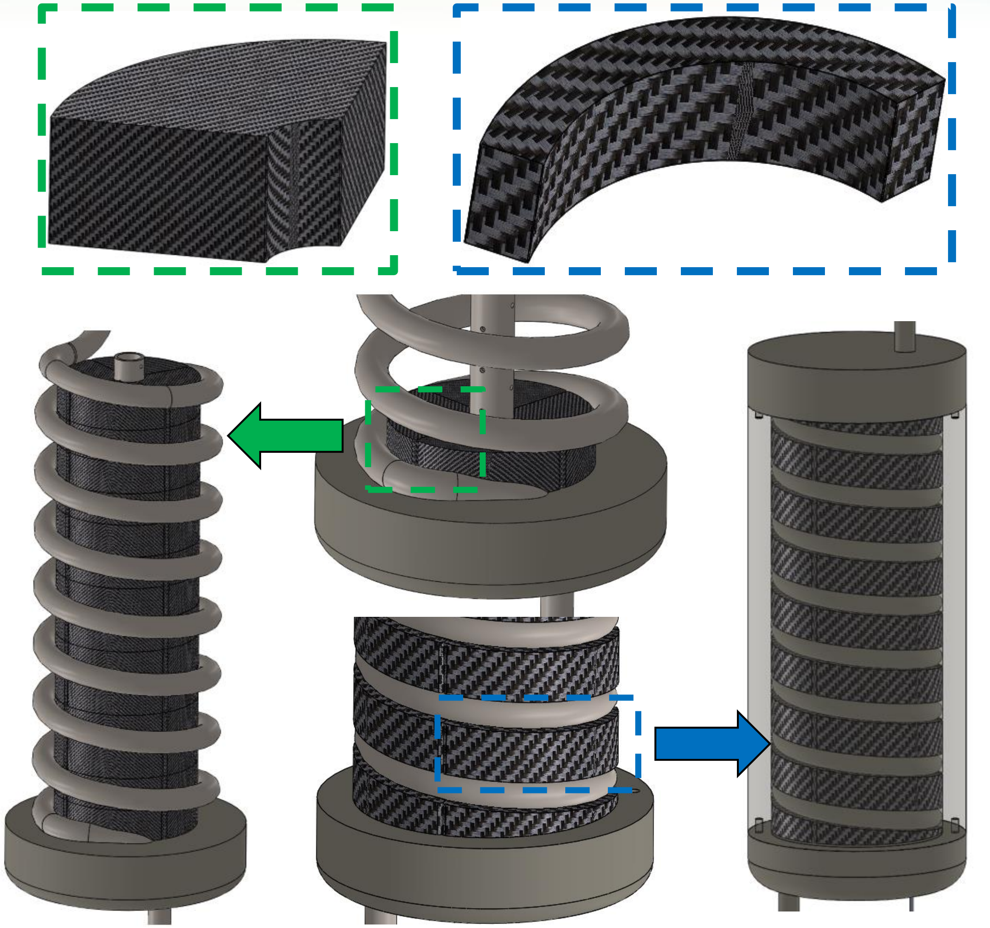




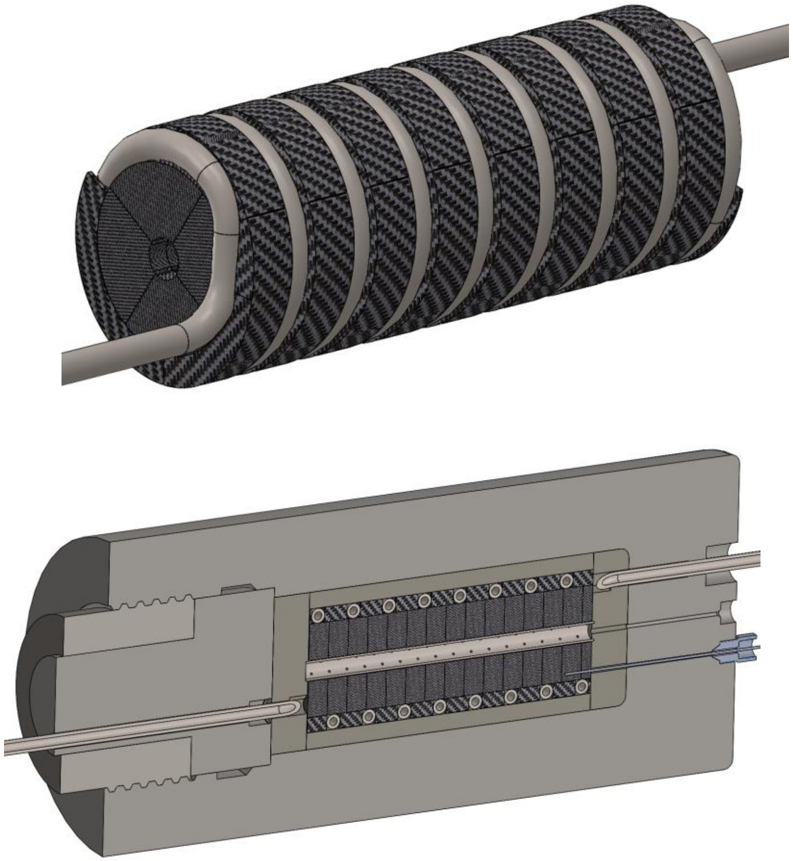
First pellets produced 3/13/19



Accomplishments: Compressor beds will be loaded with compacted metal hydride/graphite composites



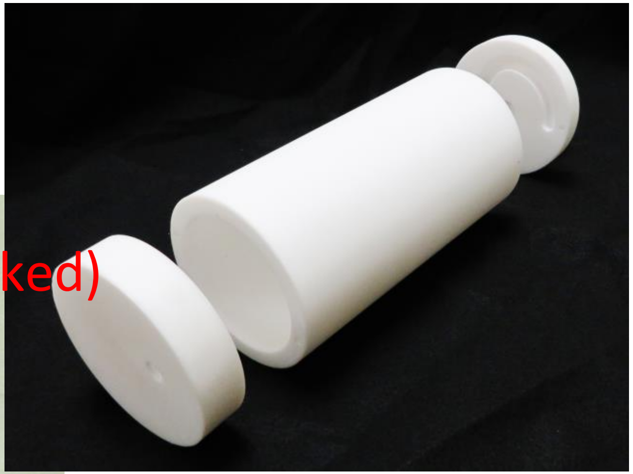
Pre-compressed pellets will be loaded in/around the helical coil and gas distribution tube within the Teflon liner



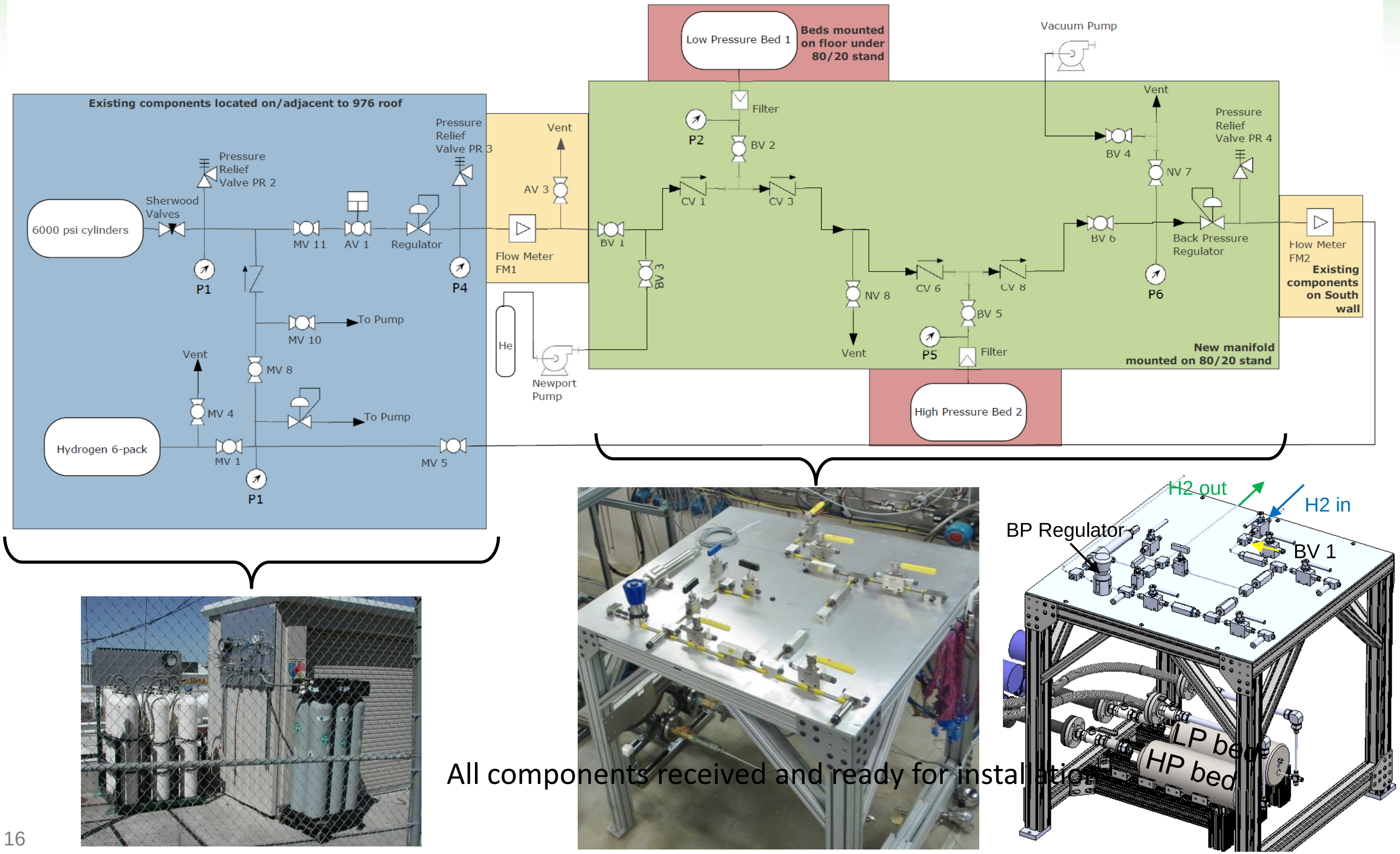
Filled Teflon liner will then be inserted into the Nitronic 50 pressure vessel and sealed

Accomplishments: All compressor components are being fabricated or have already been received

- Helical coils
- Teflon sleeves
- H_2 distribution tubes
- Vessels (being reworked)

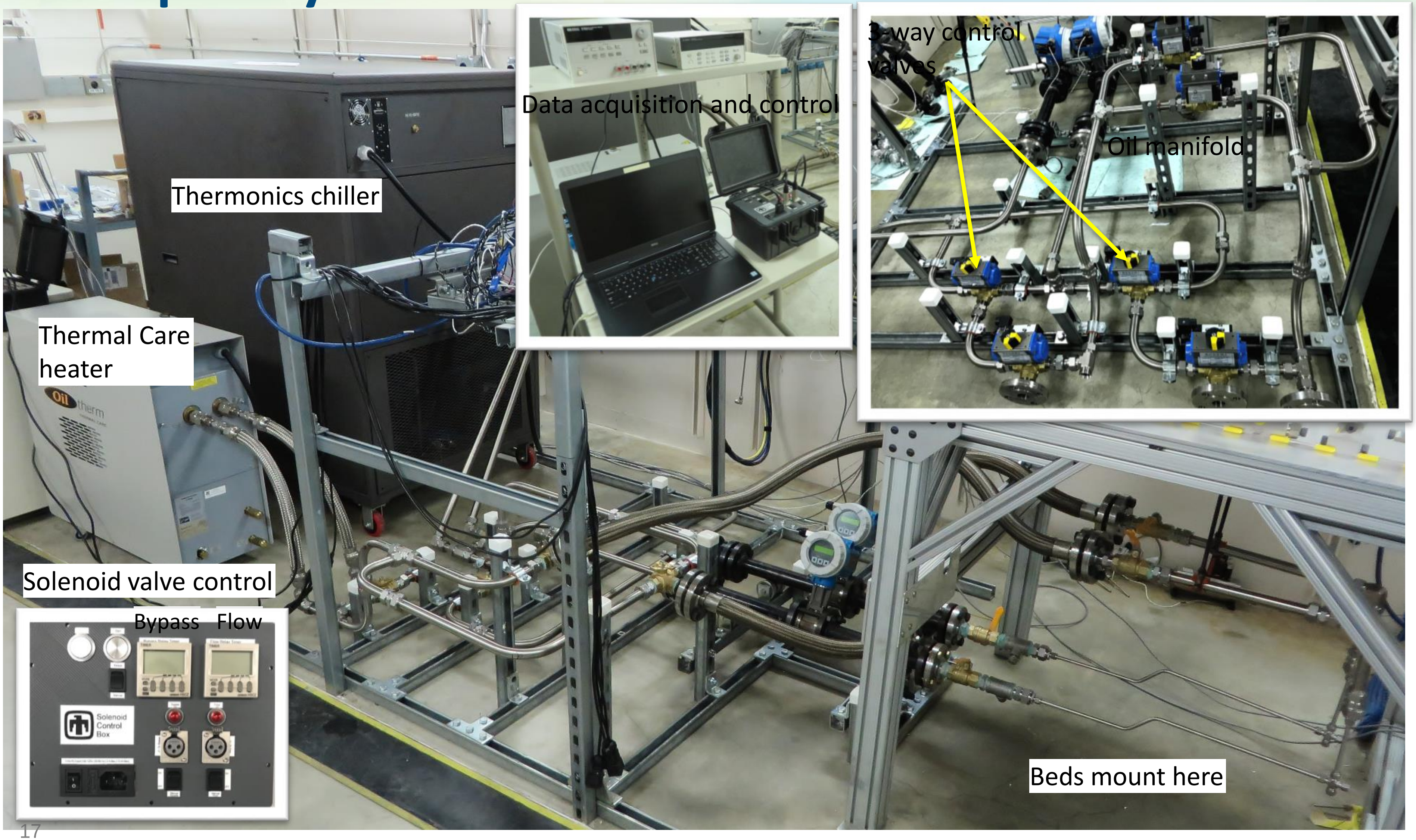


Accomplishments: High pressure manifold for closed loop recirculation of hydrogen ready for assembly



All components received and ready for installation

Accomplishments: Temperature control system completely assembled



Accomplishments: Gathered initial cost projections for metal hydrides and graphite

- Scaling calculations for 100 kg/hr compressor
  - Assumptions: 12 min half cycles, 1 wt% utilization per bed, 2 beds per stage
  - Requires 2000 kg* of alloy per bed, per stage; 4000 kg each of LP and HP alloys; 800-1200 kg of ENG
- Extrapolation from small scale alloy production cost
  - $2,852/kg x 8000 kg = **$22.8M!**
  - Based on specialty production by a non-commercial vendor
  - Industrial production of hydrogen storage alloys is typically at a much larger scale
- Estimates for **at scale production** of alloys by vendors in USA, Japan, and China show price of alloy to be **reduced by ~2 orders of magnitude**
  - $17/kg - $43/kg x 8000 kg = **$136,000 - $344,000**
- **ENG costs** for this scale: $46/kg x 800-1200 kg = **$36,800 - $55,200**

* *Could be reduced to 1111 kg for 10 min half cycles, 1.5 wt% utilization*

Accomplishments: Cost estimates for high pressure vessels next priority

- Scaling calculations for 100 kg/hr compressor
  - 2000 kg alloy per bed requires 80 vessels per bed (based on original prototype design)
- Extrapolation from small scale prototype vessel cost
  - Vessels sized for 25 kg of alloy quoted at ~$25K each for Nitronic 50 vessels rated to 15 ksi
  - 160 vessels for each stage: 160 x $25k = **$4M** for HP stage alone!
- Estimates for at scale production are being pursued
  - Will be based on larger vessel (200 kg per vessel) for practicality
  - Target: 40 vessels per compressor (10 vessels per bed, 2 beds per stage, 2 stages)
  - We are currently contacting vendors to determine the cost of quantity production of these larger low pressure and high pressure vessels

Accomplishments: Responses to Previous Year Reviewer's Comments

"It was not clear if the 20 min for the half cycle proposed is already achieved. In future, more clarification on performance gaps on different aspects and clear separation of predictions from modeling and the results achieved so far will be needed."

All compressor cycling results to-date have been predictions from the dynamic system model. The slide presented that showed this results was titled *Dynamic system model predicts performance using measured alloy properties.*

"Although all necessary elements are there in the planning, it is not clear if some critical bottlenecks can be removed without some re-planning of the tasks and bringing experts in alloy selection. Right now, the risk of not achieving the target seems high."

Both the Sandia and GreenWay Energy teams include experts in metal hydride alloys. These experts selected the most promising materials that had been reported on in the literature. Material development/discovery was outside the scope of both projects. Ultimately, a compromise in the feed pressure was made to achieve 875 bar compression with available alloys.

"More collaborations on the high-pressure alloy phases, and a stronger design effort beyond the helical design of the heat exchanger."

We agree that more effort is needed to develop an optimum high pressure alloy. That effort is, however, beyond the scope of the current project. As for the heat exchanger design, the helical coil design was the result of an extensive design study. We intend to demonstrate that it provides good performance through the prototype testing.

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; Geoffrey Grimmett currently working at Sandia to complete this task
  - Cost analysis of the commercial system concept

Remaining Challenges and Barriers

- Challenge: Identifying a high pressure metal hydride alloy that can compress hydrogen from 200-250 bar to 875 bar within reasonable operating temperatures
- Challenge: Meeting the DOE cost targets for a 100 kg/hr compressor based on alloy costs and high pressure vessel costs
- Challenge: Achieve an energy consumption of < 4.0 kWh/kgH_2 with metal hydride compression from 100 to 875 bar
  - Metal hydride thermodynamics require 6-7 kWh/kgH_2 minimum for a two-stage compressor; sensible heating requirements and losses push this to ~10 kWh/kgH_2
  - Methods to reduce energy consumption (recuperator, waste heat, heat pump) or lower energy cost (cheap heat) are needed to meet DOE requirements

Proposed Future Work

Remainder of FY19

- Process hydrides, mix with ENG and make compacts
- Load compressor beds, perform leak and pressure tests
- Configure test facility
  - Assemble, leak check, fill, and test operation of temperature control system
  - Assemble and leak check hydrogen manifold
- Integrate prototype compressor into test facility
- Activate hydrides and perform initial cycling to assess individual performance
- Test performance of prototype compressor over range of process conditions
- Perform cost analysis for a 100 kg H_2/hr system
- Final report detailing performance of compressor

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

Technology Transfer Activities

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

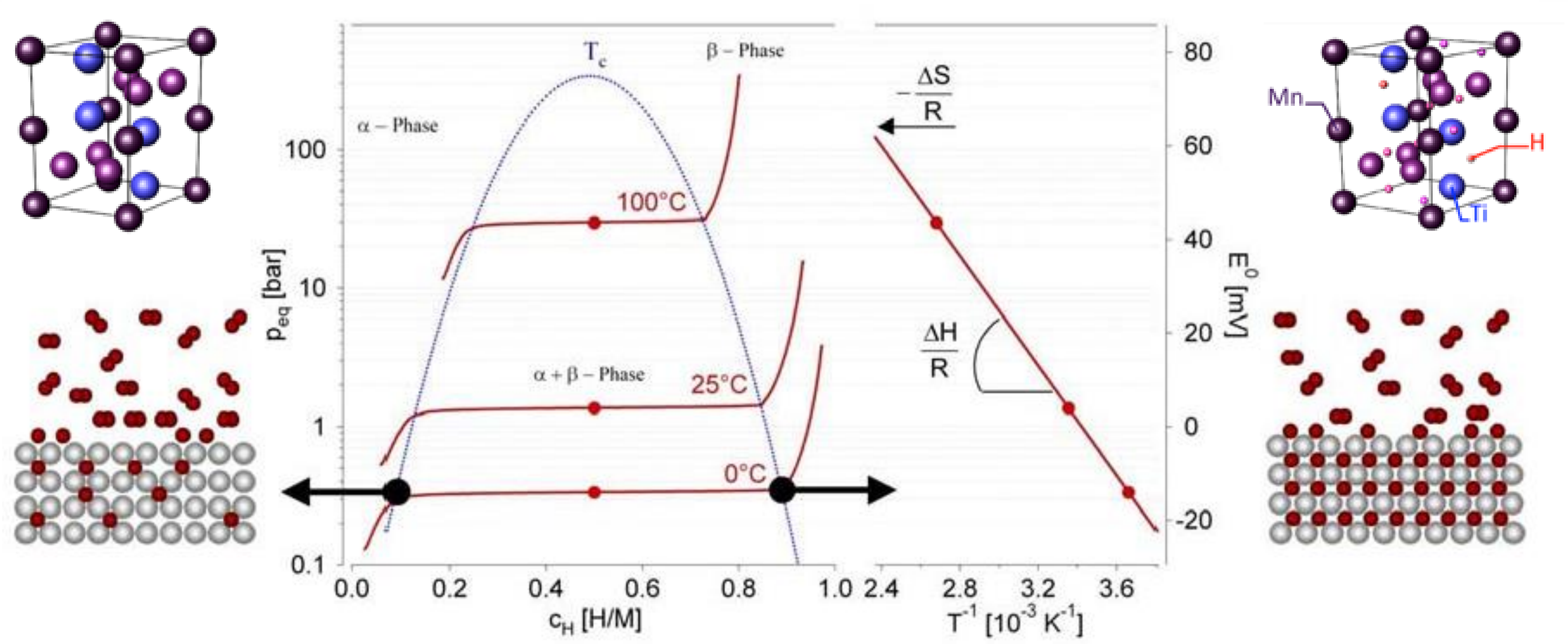
Summary

- 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
- Characterization of multiple alloys for low and high pressure stages resulted in several options for 875 bar compression
- System-level analysis using final bed design and measured hydride properties demonstrates 875 bar H_2 delivery at reasonably achievable temperatures
- Prototype compressor and test facility designed and nearly assembled to demonstrate proof-of-concept performance

TECHNICAL BACK-UP SLIDES

Pressure-Composition-Temperature (PCT) isotherms for a “prototype” interstitial metal hydride

$TiMn_2 \rightarrow TiMn_2H_{2.5}$



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

Approach: Several options for the second phase of the project were proposed

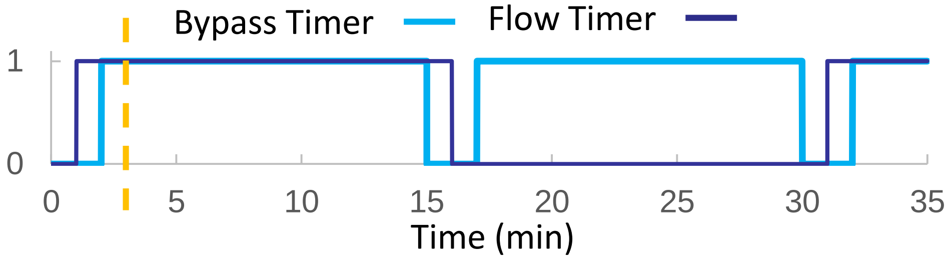
- Compression from 50 bar:
  - Hydralloy C5/$TiCrMn_{0.7}Fe_{0.2}V_{0.1}$
    - 50 to 600 bar compression; temperatures from 20 to 150°C
    - Demonstrates all aspects of the technology except ultimate pressure
- Options to achieve 875 bar:
  - Hydralloy C5/$Ti_{0.95}Zr_{0.05}Cr_{1.20}Mn_{0.75}V_{0.05}$
    - 100 to 875 bar compression; 60 to 190°C temperatures
    - High temperature operation undesirable for energy efficiency
  - $TiCrMn_{0.7}Fe_{0.2}V_{0.1}$/ $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$
    - 150 to 875 bar compression; 20 to 150°C temperatures
    - Higher feed pressure required
  - 3-stage MH compressor;
    - Hydralloy C5/$TiCrMn_{0.7}Fe_{0.2}V_{0.1}$/ $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$
    - 50 bar to 875 bar compression; 20 to 130°C temperatures
    - Third stage makes the design more complicated and likely higher capital cost

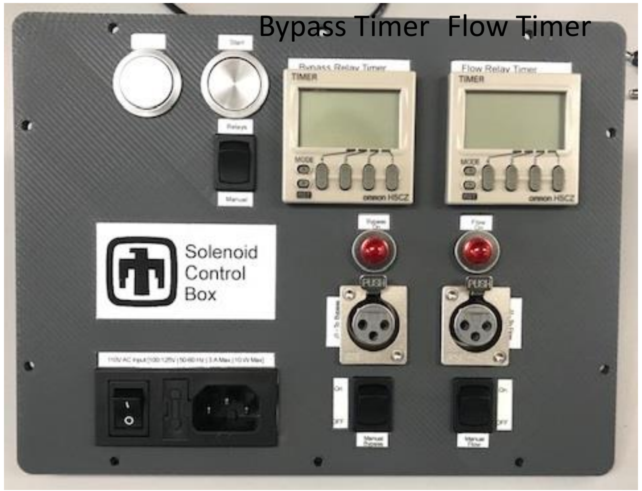
Accomplishments: MH/ENG compacts will be created to fit vessel geometry and loaded in inert environment

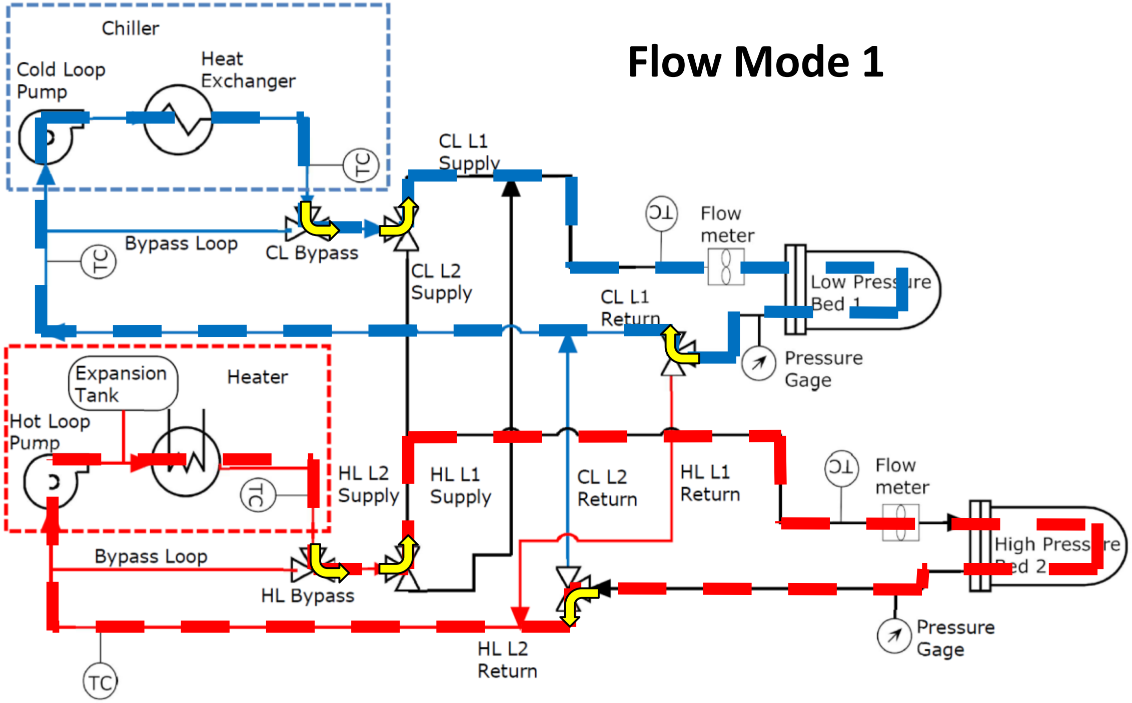
1) MH granules pretreated via high-energy ball milling under argon producing a fine powder
2) Mix with 15 wt% high purity ENG (SGL Carbon) in the as-delivered state in a tubular mixer (Turbula T2F)
3) Uniaxial compaction using a Carver hydraulic press and a custom die set into shaped pellets
4) Compressor bed loaded with pellets and sealed with end caps
5) The whole procedure performed under inert atmosphere to prevent any surface contamination

Accomplishments: Simple control scheme will allow semi-automatic operation of the prototype compressor

Two digital timer relays control the sequencing of the temperature control valves





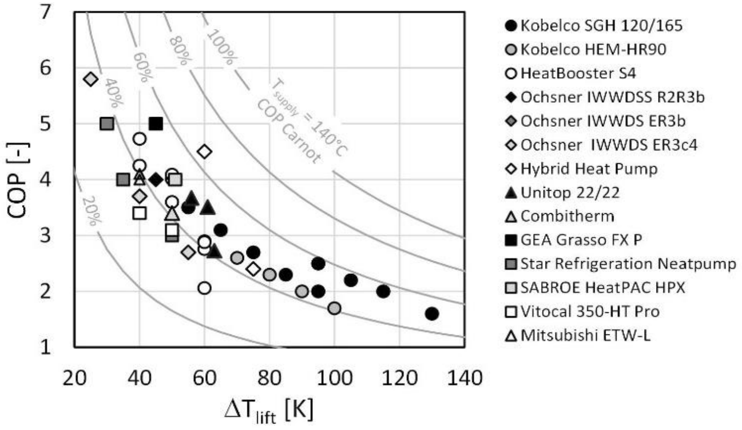


Flow Mode 1

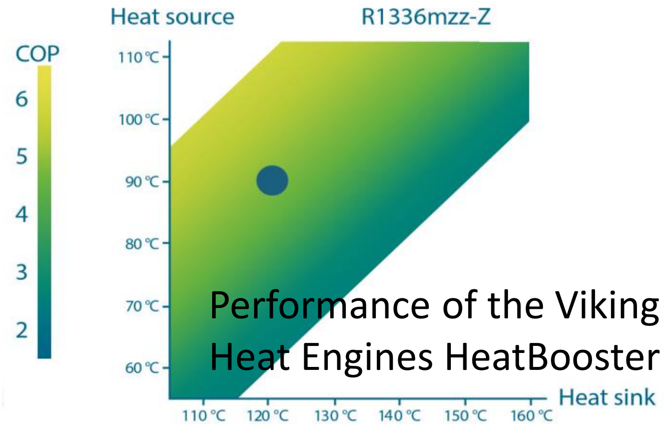
Identified path to energy efficiency using high temperature heat pump (HTHP)/refrigerant

- Heat pump coefficient of performance COP = Heat/Electrical Work
- COP of 2.7 needed to reduce energy consumption to 4.0 kWh/kg
- Many commercially available HTHPs supply temperatures up to 130 ℃, some to 160 ℃, for industrial process heat
- New refrigerants for HTHPs with very low global warming potential
  - e.g. Dupont's R1336mzz-Z (Tc > 170 ℃)
- Cascade heat pump system could reach target COP with 100 ℃ temperature lift
  - Kobelco HTHP operates from 35 ℃ to 90 ℃ with a COP of 5.8
  - HTHP operating from 85 to 135 ℃ with a COP of 4.1 gives net COP of 2.7

COP vs. temperature lift for commercial HTHPs



C. Arpagaus,et al, "Review on High Temperature Heat Pumps." Proceedings of the European Heat Pump Summit, Oct. 2017, Nuremberg, Germany.



Performance of the Viking Heat Engines HeatBooster

http://www.vikingheatengines.com/heatbooster