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Metal Hydride Compression

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Joint Hydrogen Delivery, Safety Codes and Standards, and Storage Tech Team Meeting

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NNSA National Nuclear Security Administration

U.S. DEPARTMENT OF ENERGY

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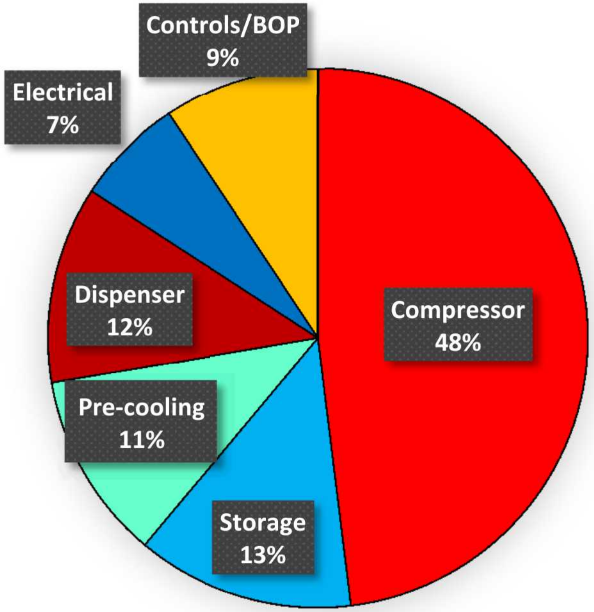
MOTIVATION AND BACKGROUND

Hydrogen compressors dominate station costs and downtime

Compressors represent 48% of total station cost

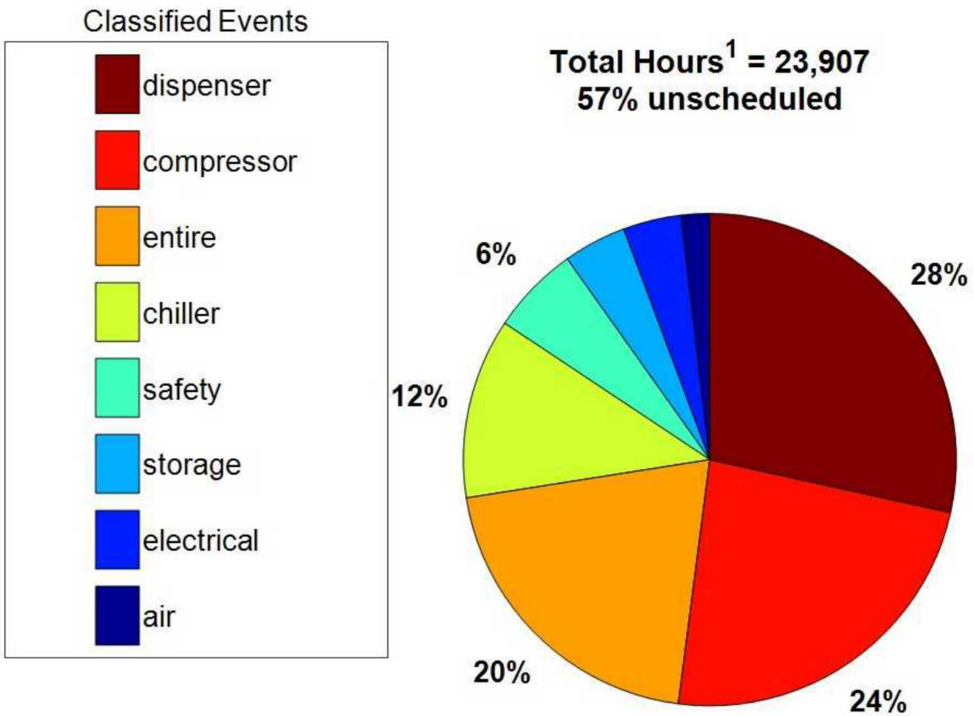


700 bar station cost distribution

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

Metal hydride compression has the potential to improve reliability of 700 bar refueling

Advantages

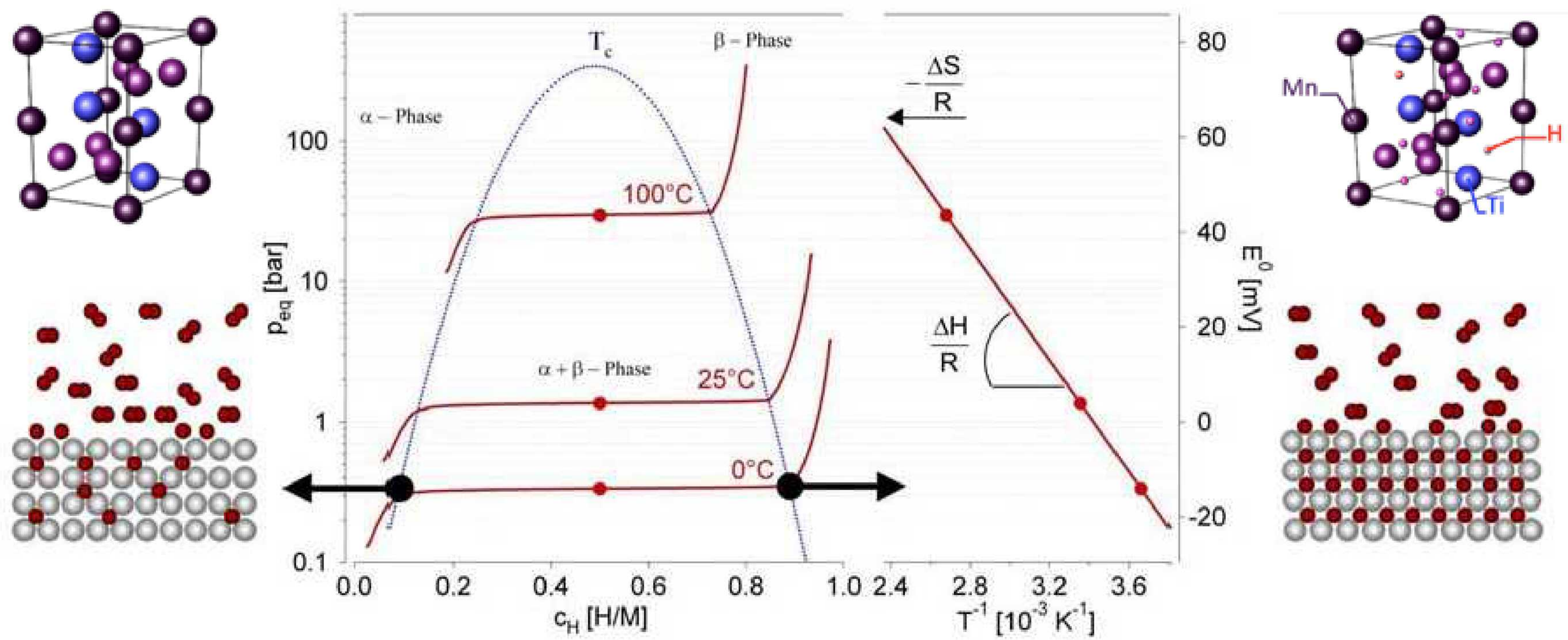
- Simple design and operation
- Absence of moving parts
- Oil-free
- Compact
- Safe and reliable
- Able to utilize waste industrial heat
  - Dramatic decreases in operational costs
  - Advantage with on-site generation

Challenges

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

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

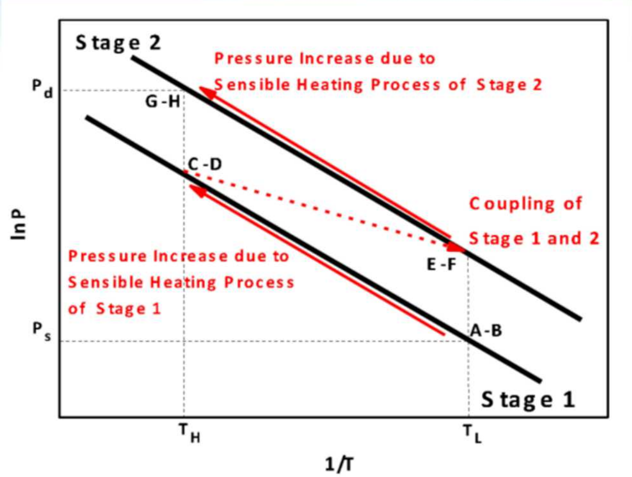
$TiMn_2 \rightarrow TiMn_2H_{2.5}$

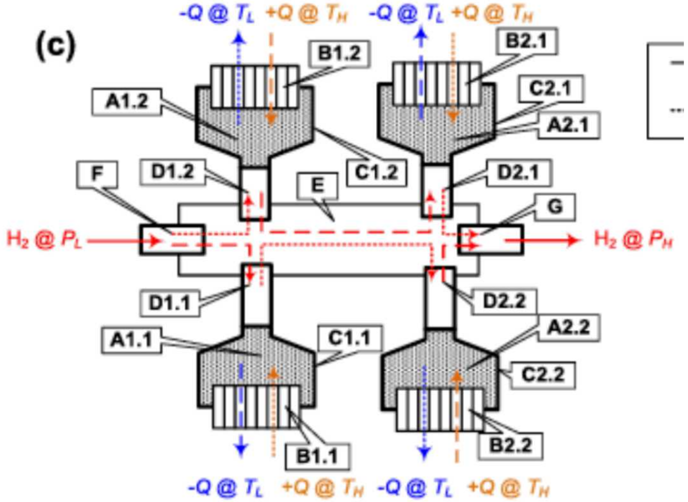


- where α- & β-phases co-exist, a plateau occurs
- plateau pressure is temperature dependent

We will demonstrate a two-stage metal hydride compressor for 875 bar compression

- 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 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





METAL HYDRIDE ALLOY SELECTION

High pressure alloy proved more difficult to find than expected

- Low pressure candidate meeting design requirements was identified early in the project (Hydralloy C5)
- Seven different high pressure metal hydride alloys were characterized in collaboration with GreenWay Energy
  - Demonstrated two alloys that could produce >875 bar pressure at reasonable temperatures
  - Absorption pressure too high for Hydralloy C5

Original SNL High Pressure Candidates

1. $Ti_{0.95}Zr_{0.05}Cr_{1.20}Mn_{0.75}V_{0.05}$
2. $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$
3. $TiCrMn_{0.7}Fe_{0.2}V_{0.1}$

GWE High Pressure Candidates

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

Both teams chose alloys based on literature data

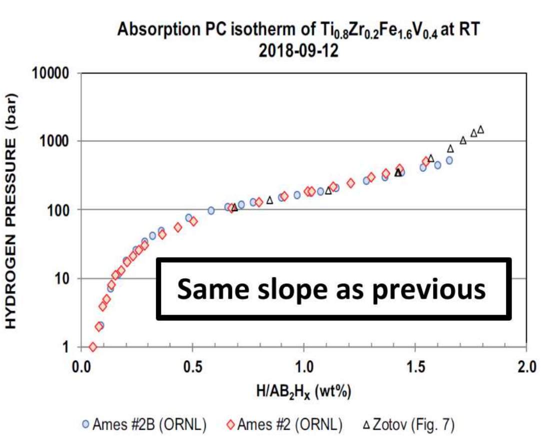
Four new alloy samples characterized; performance not improved

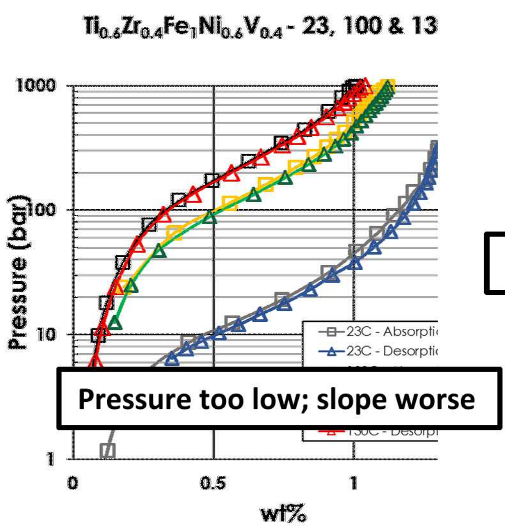
Alloys jointly fabricated by Ames for GWE and SNL teams (3 repeats, 1 new)

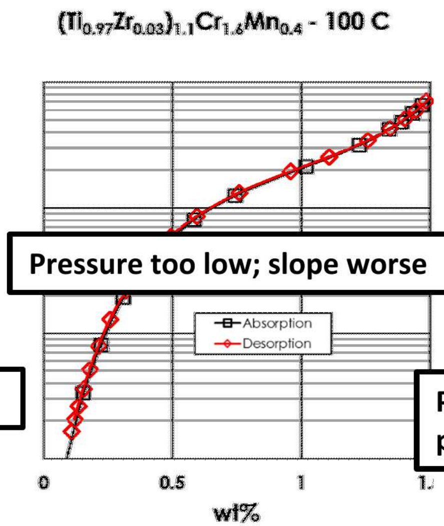
- New annealing process (10 days at 1200 °C) meant to improve properties (i.e. increase plateau pressures and flatten slopes)

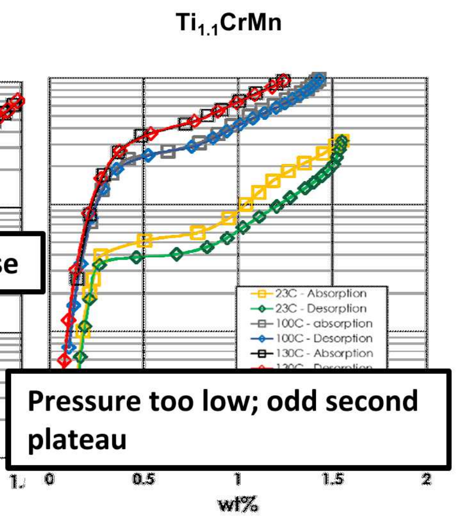
1. $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$ (repeated SNL alloy, original made by AMES)
2. $Ti_{0.6}Zr_{0.4}Fe_{1}Ni_{0.6}V_{0.4}$ (new SNL alloy)
3. $(Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}$ (repeat GWE alloy, original made by JMC)
4. $Ti_{1.1}CrMn$ (repeat GWE alloy, original made by JMC)

*ORNL characterized #1, GWE characterized #2-4









Several options for the second phase of the project were proposed

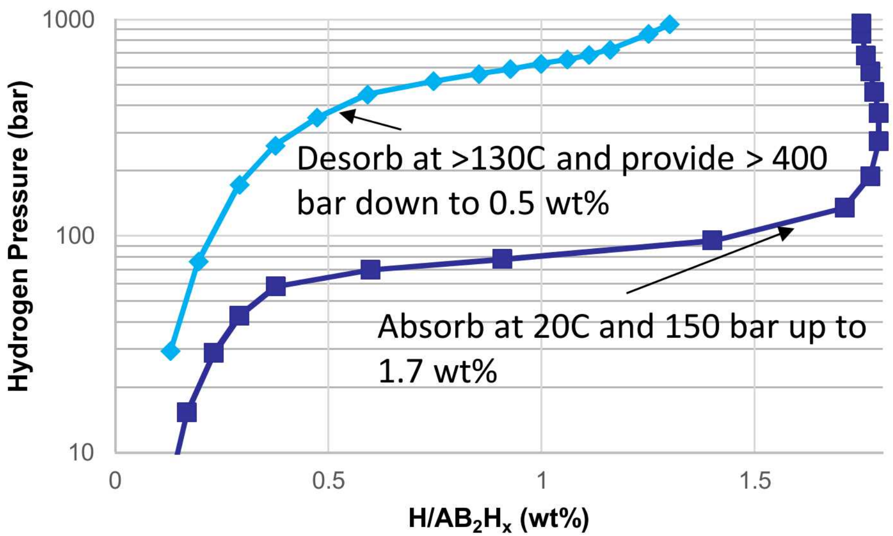
- Compression from 50 bar:
  - Hydralloy C5/$TiCrMn_{0.7}Fe_{0.2}V_{0.1}$
    - 50 to 600 bar compression; temperatures from 20 to 150°C
    - Demonstrates all aspects of the technology except ultimate pressure
- Options to achieve 875 bar:
  - Hydralloy C5/$Ti_{0.95}Zr_{0.05}Cr_{1.20}Mn_{0.75}V_{0.05}$
    - 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

A reduced-scale 2-stage prototype producing 875 bar was selected for the second phase

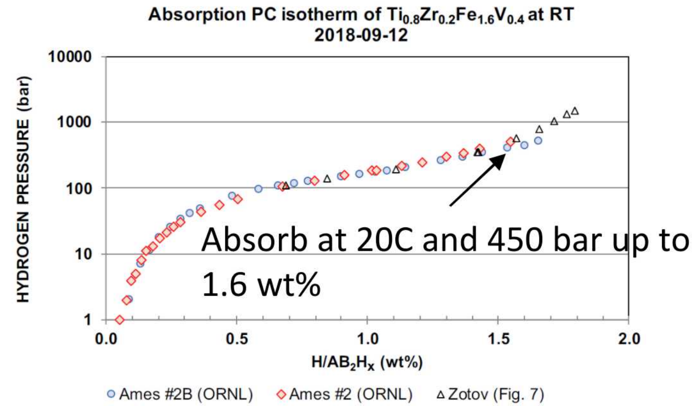
Reduced scale 2-stage prototype

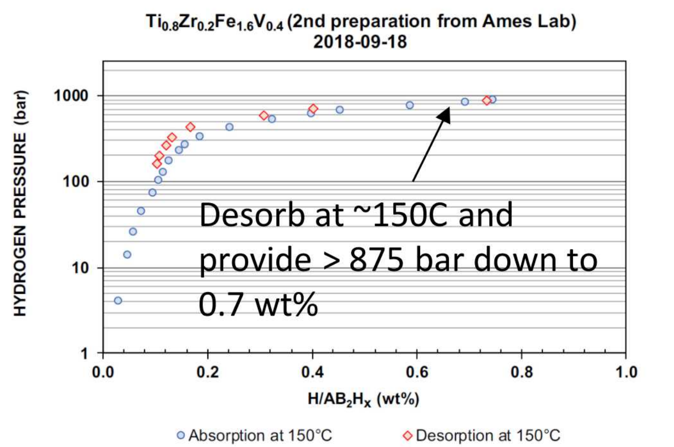
- ~8X reduction in scale compared to original prototype
- Reduced scale, self-contained oil recirculation systems
- 3 kg hydride per bed -> 0.15 kg/hr flow rate

1st Stage - $TiCrMn_{0.7}Fe_{0.2}V_{0.1}$



2nd Stage - $Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$





Dynamic system model predicts performance using measured alloy properties of Ames #3 and Ames #2

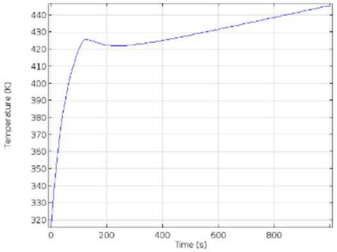
Configuration:

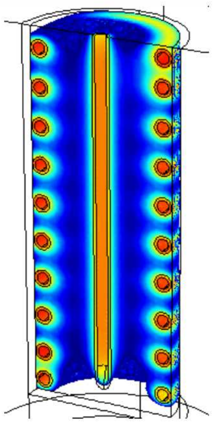
- 25 kg of LP hydride ($TiCrMn_{0.7}Fe_{0.2}V_{0.1}$)
- 21.7 kg of HP hydride ($Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$)
- 15 minute half cycles
- 150 to 875 bar compression
- Heating/cooling of beds with heat transfer fluid
  - Cold loop temperature set to **20 ˚C**
  - Hot loop temperature set to **160 ˚C**

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**

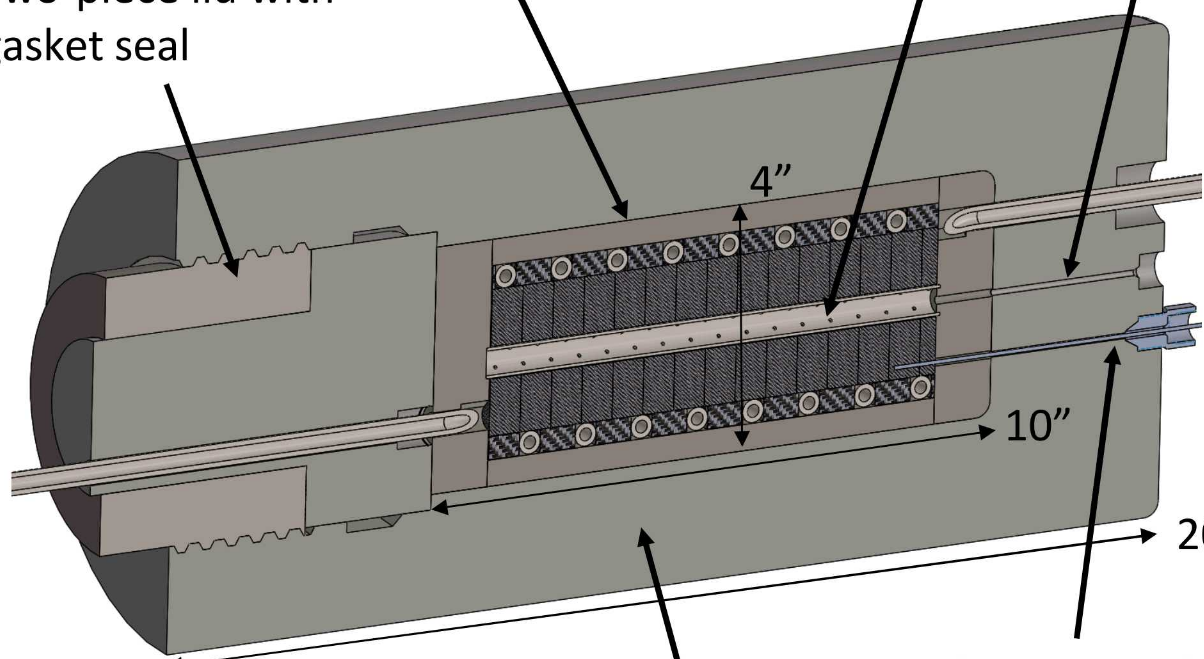
Bed thermal response calibrated to detailed Comsol model

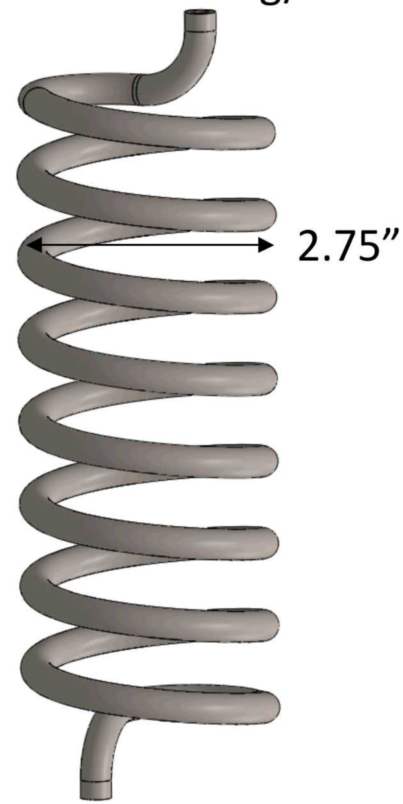




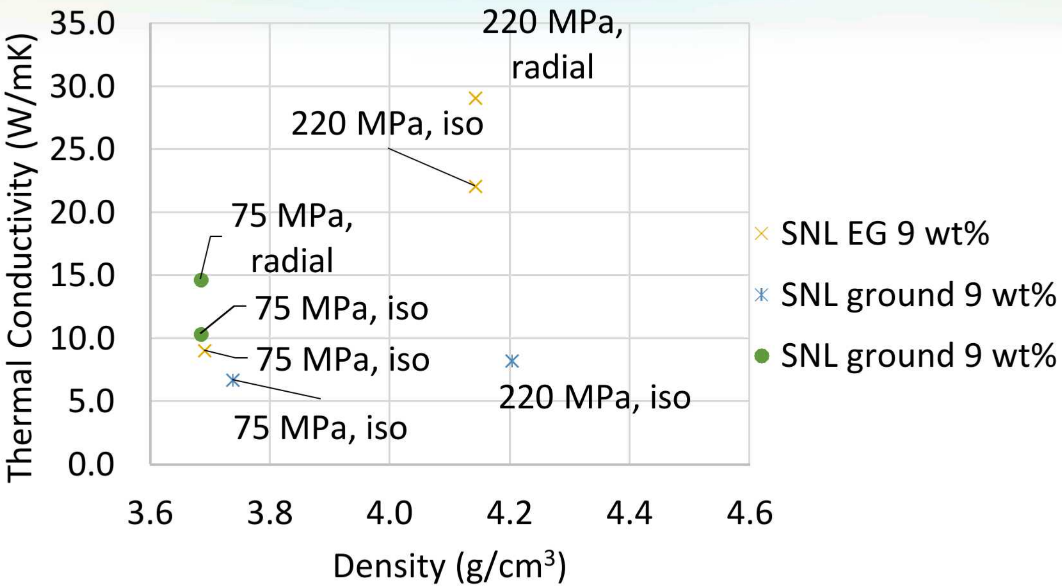
COMPRESSOR PROTOTYPE DESIGN

Bed design based on helical tube heat exchanger maximizes performance and energy efficiency





Thermal management achieved through compacted metal hydride - graphite mixture



- ENG and graphite flake mixed with Hydralloy C5 at 9 wt%
- Compacted at 75 and 220 MPa
- Thermal conductivity measured using hot disk method
- Based on work by Pohlmann, et al (Dresden University, DLR)

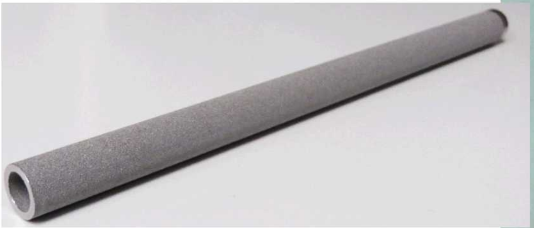
FABRICATION AND ASSEMBLY

Ames Lab produced 4 kg each of Ti-based 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

All compressor components are being fabricated or have already been received

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

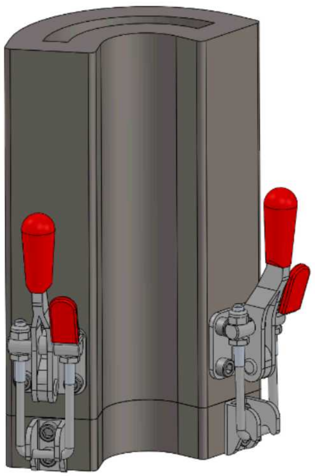


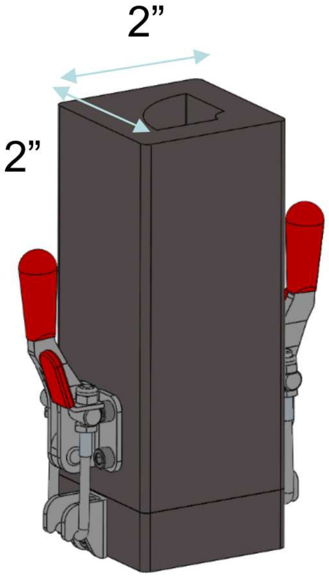
MH/ENG compacts will be created to fit vessel geometry and loaded in inert environment

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

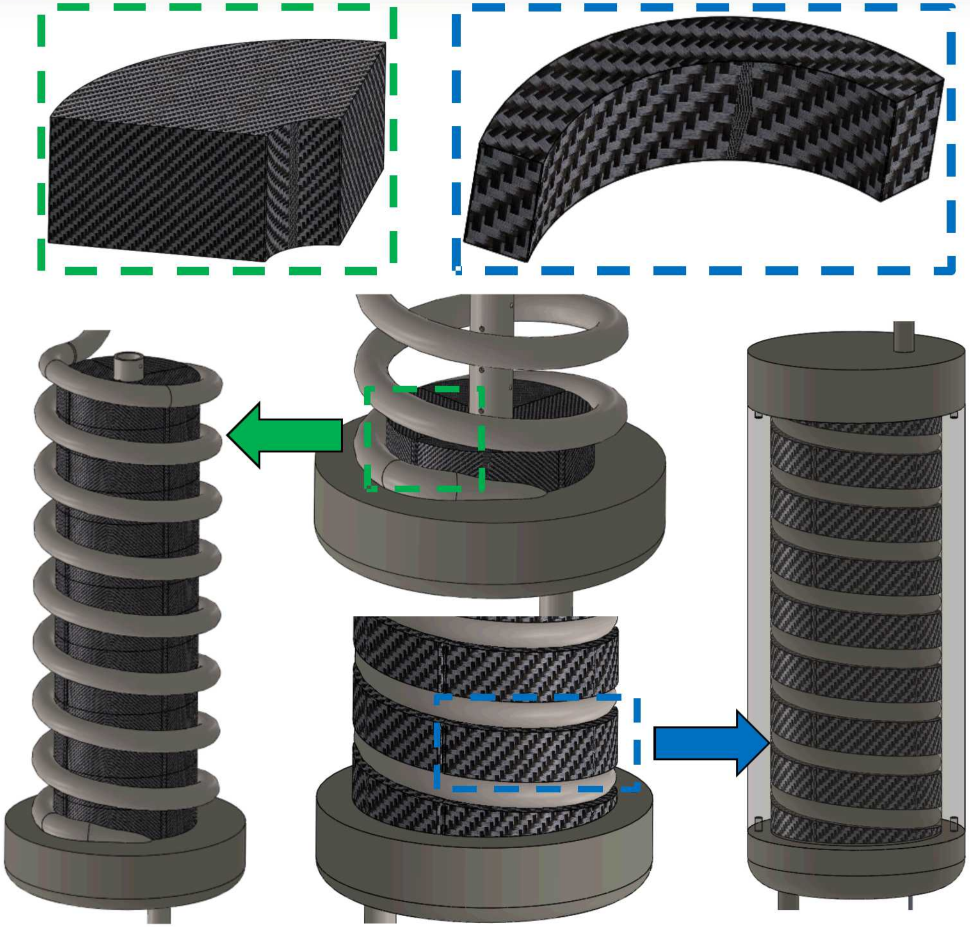
Two custom die sets produce pellets that conform to internal geometry

Die set parts shipped 3/7/19

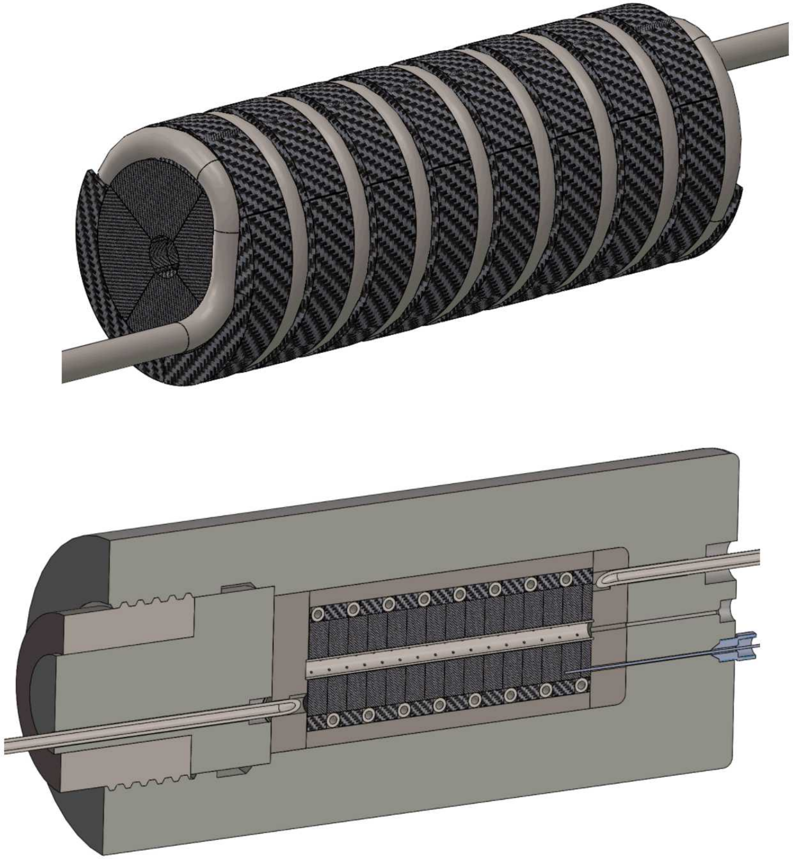




Compressor beds will be loaded with compacted metal hydride/graphite composites



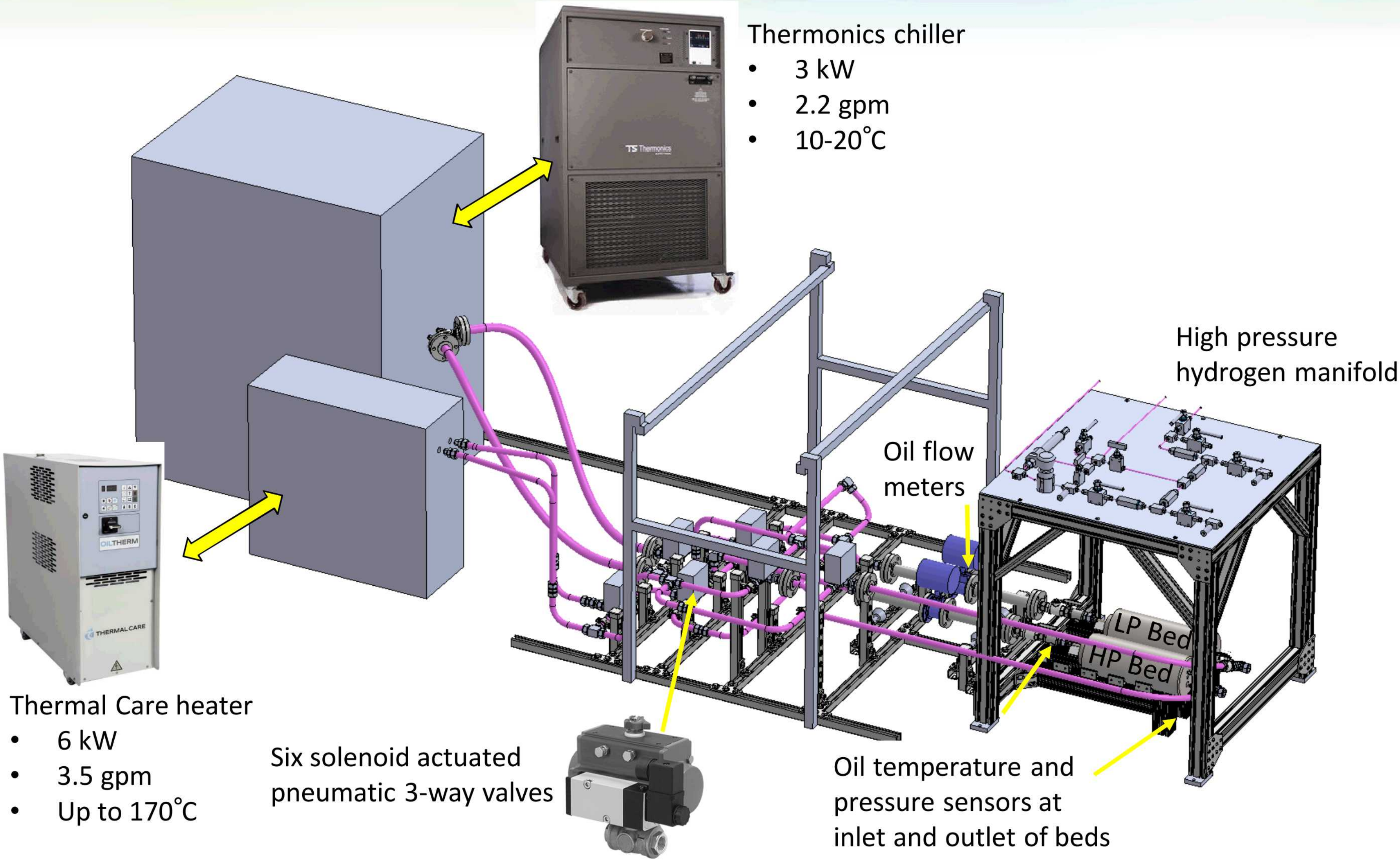
Pre-compressed pellets will be loaded in/around the helical coil and gas distribution tube within the Teflon liner



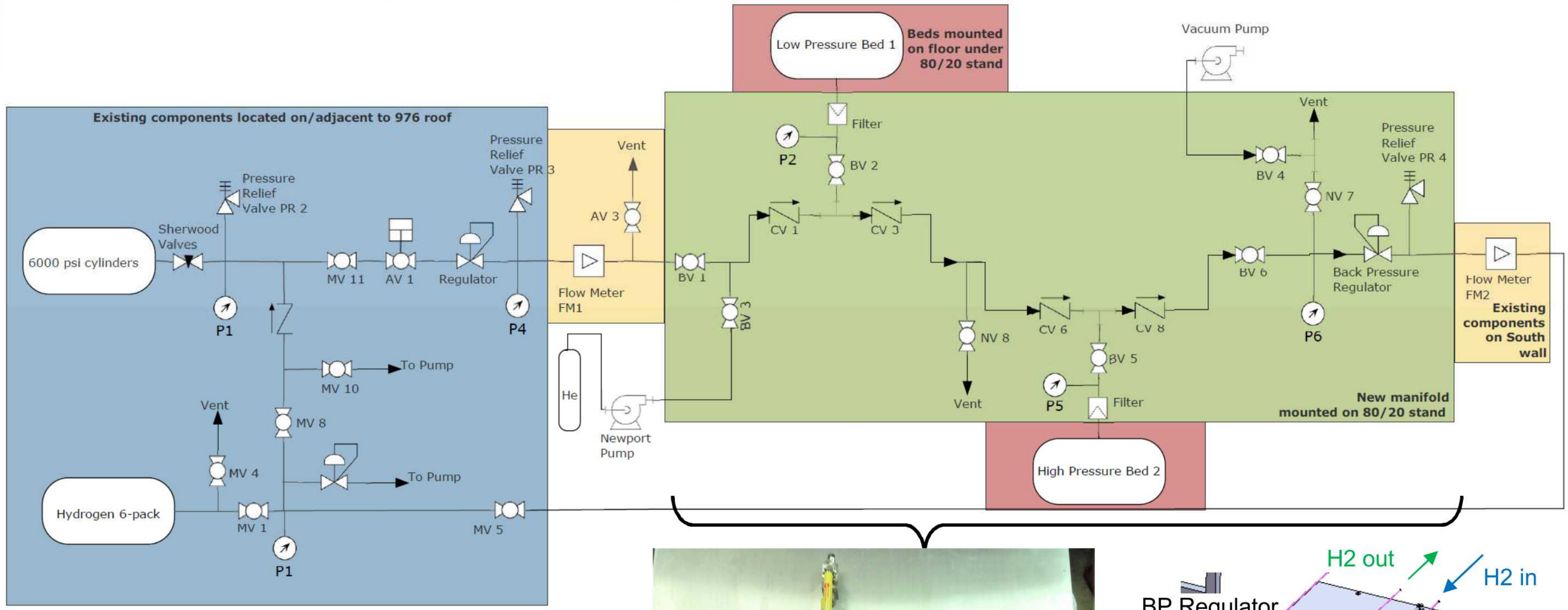
Filled Teflon liner will then be inserted into the Nitronic 50 pressure vessel and sealed

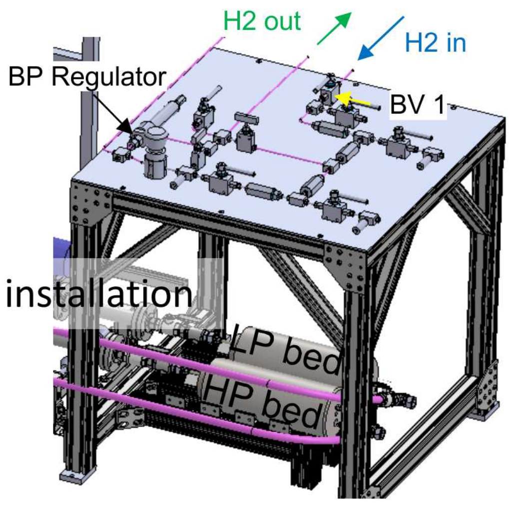
TEST FACILITY

Test facility consists of temperature control system and high pressure hydrogen manifold



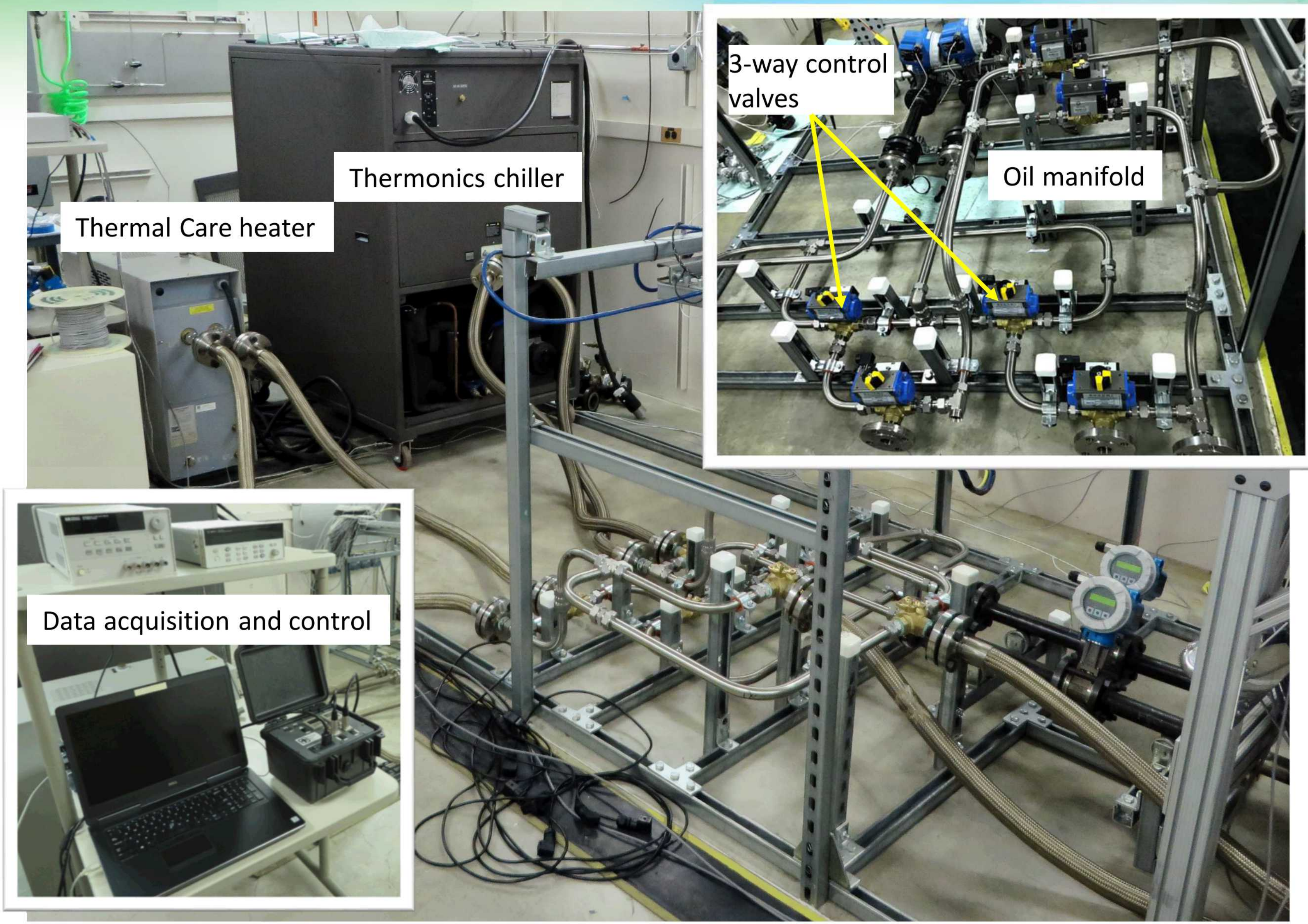
High pressure manifold designed for closed loop recirculation of hydrogen from the compressor





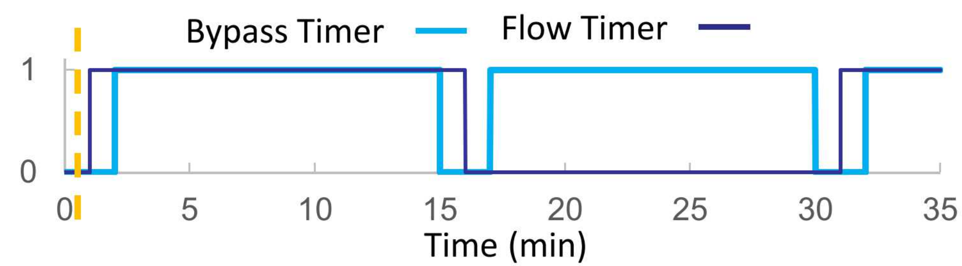
All components received and ready for installation

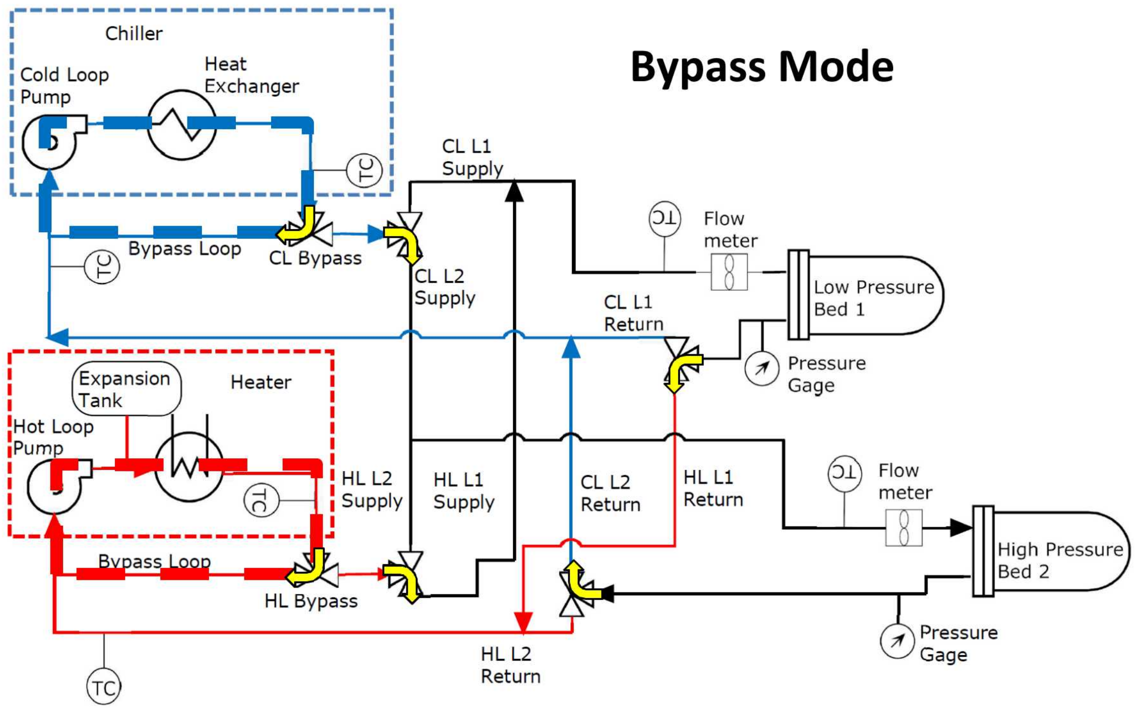
Temperature control system completely assembled



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

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





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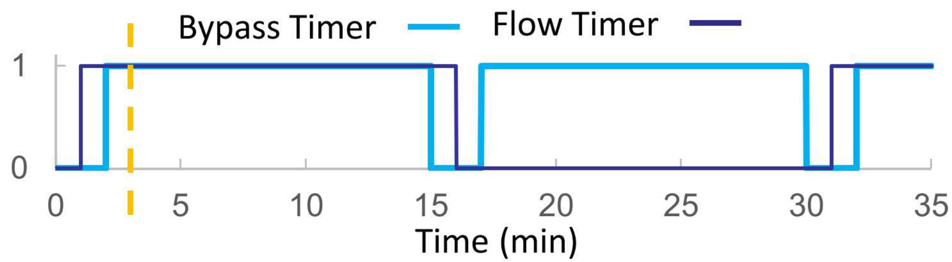

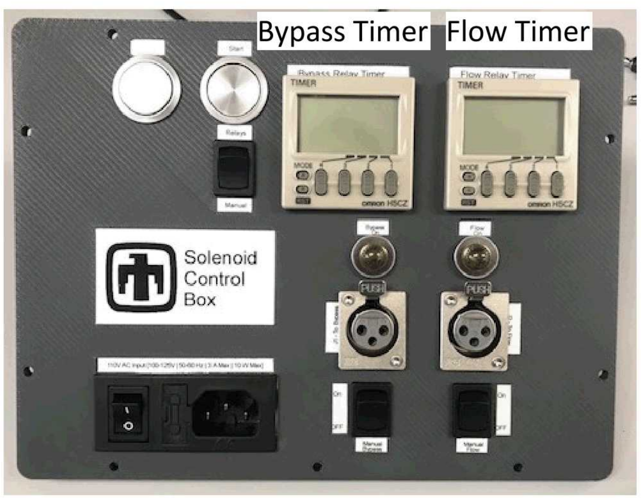

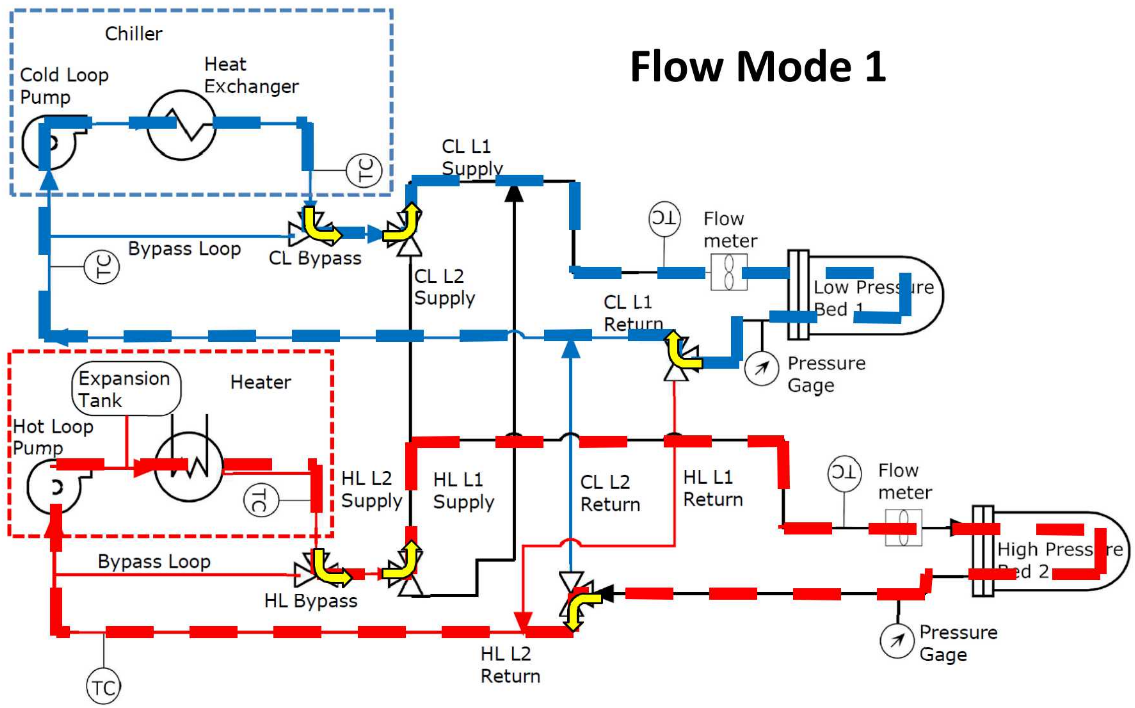

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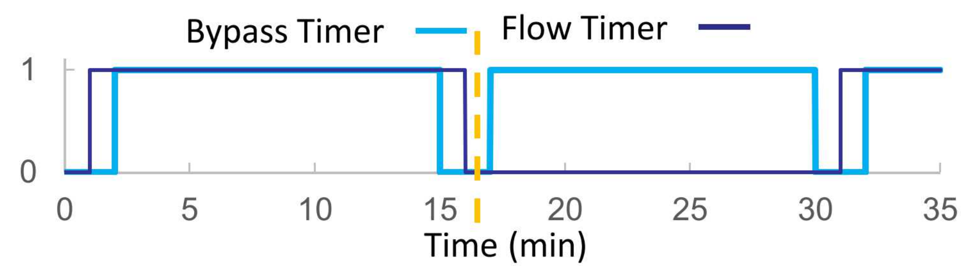

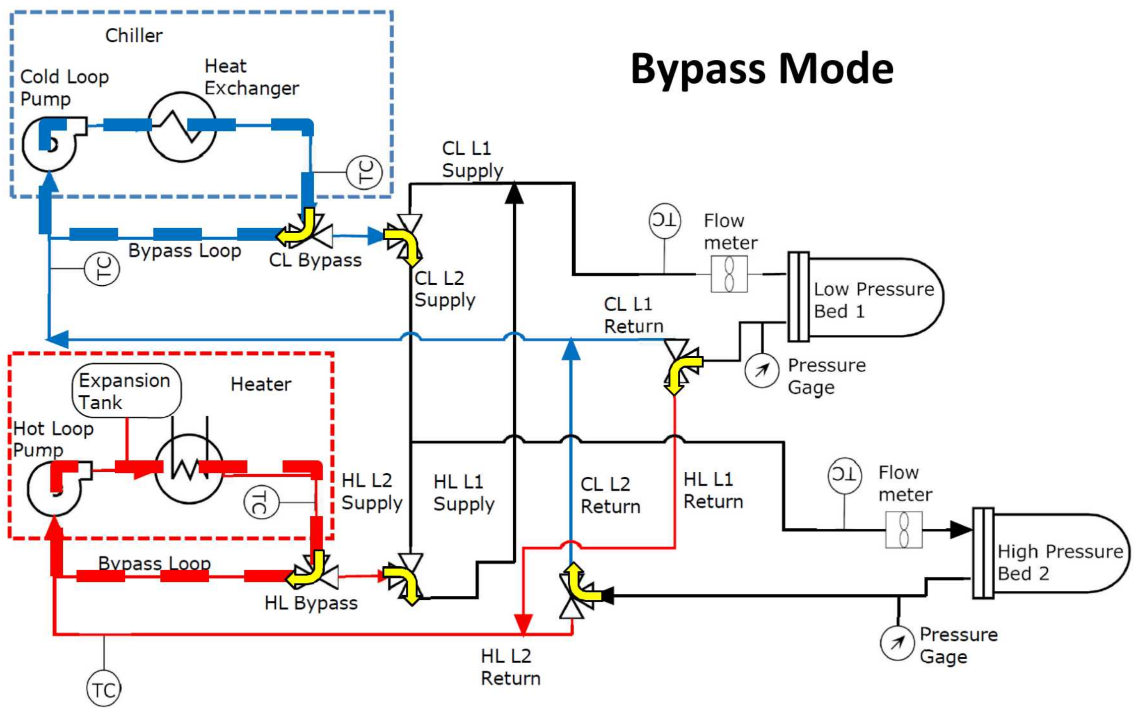

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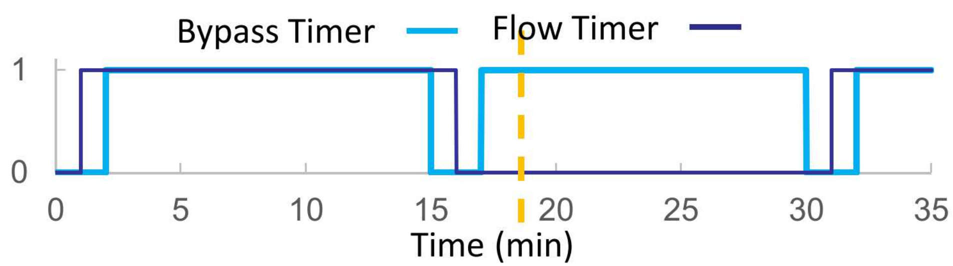
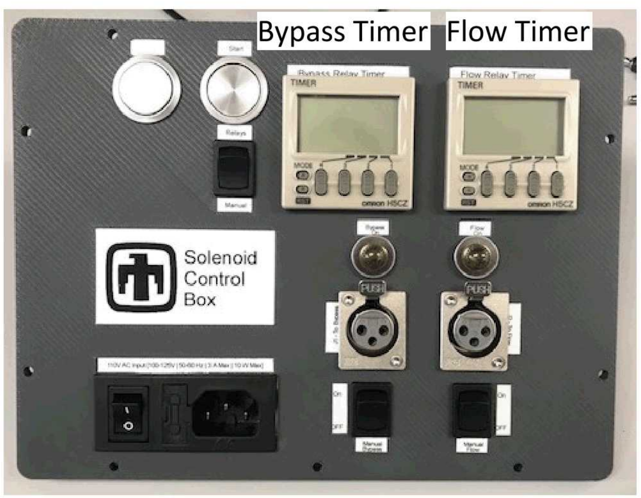
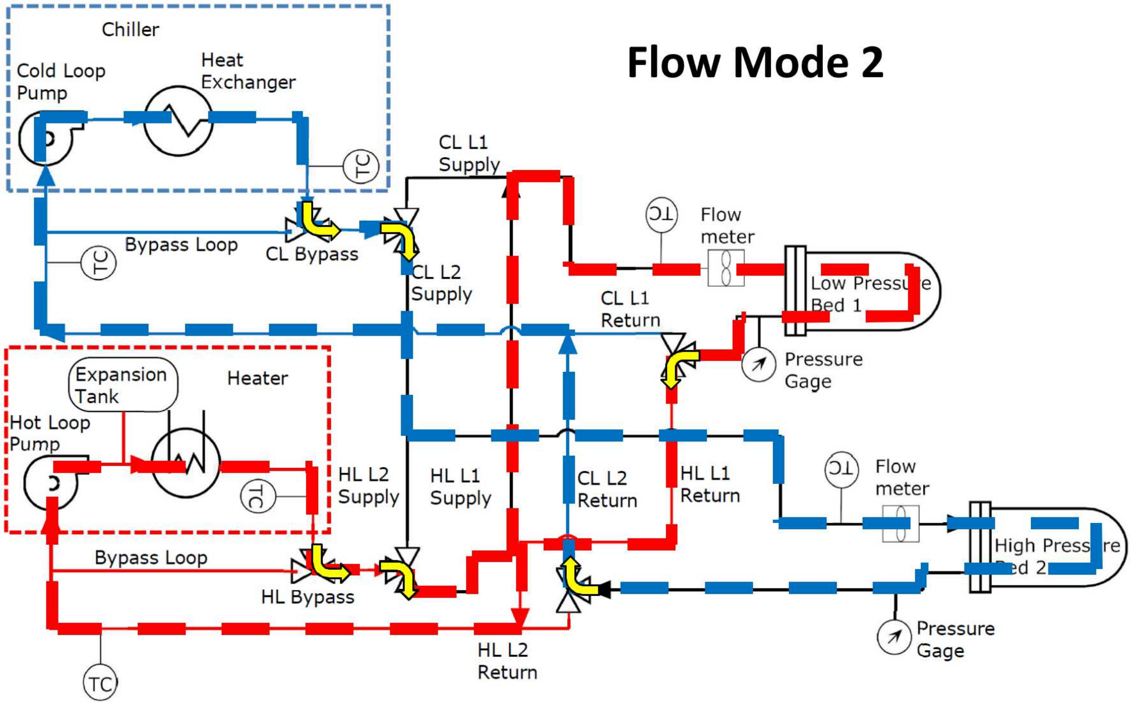




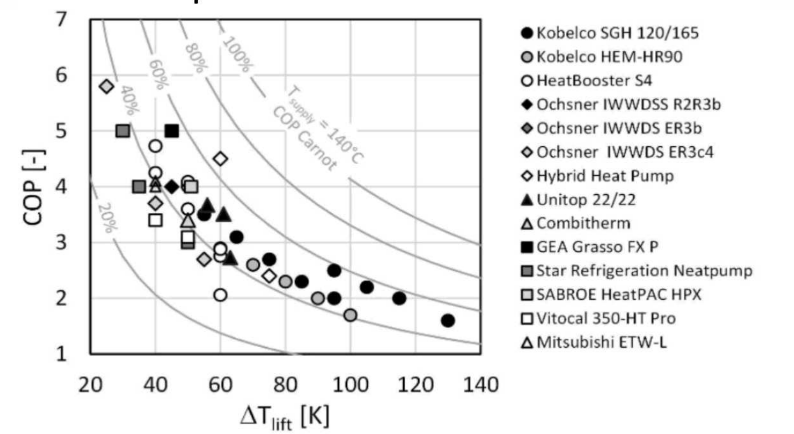


EFFICIENCY AND COST OUTLOOK

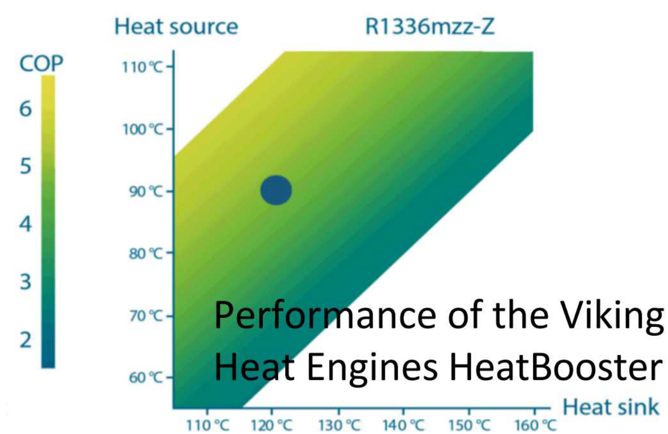
Identified path to energy efficiency using high temperature heat pump (HTHP)/refrigerant

- 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

Early cost projections focused on alloy costs

- 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
- Extrapolation from small scale alloy production cost
  - $2852/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 - $90/kg x 8000 kg = **$136,000 - $720,000**

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

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 or more) 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 larger low and high pressure vessels

PROGRAMMATIC

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

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

BACKUP

Dynamic system-level model used for feasibility and design trade studies

LP Bed 1

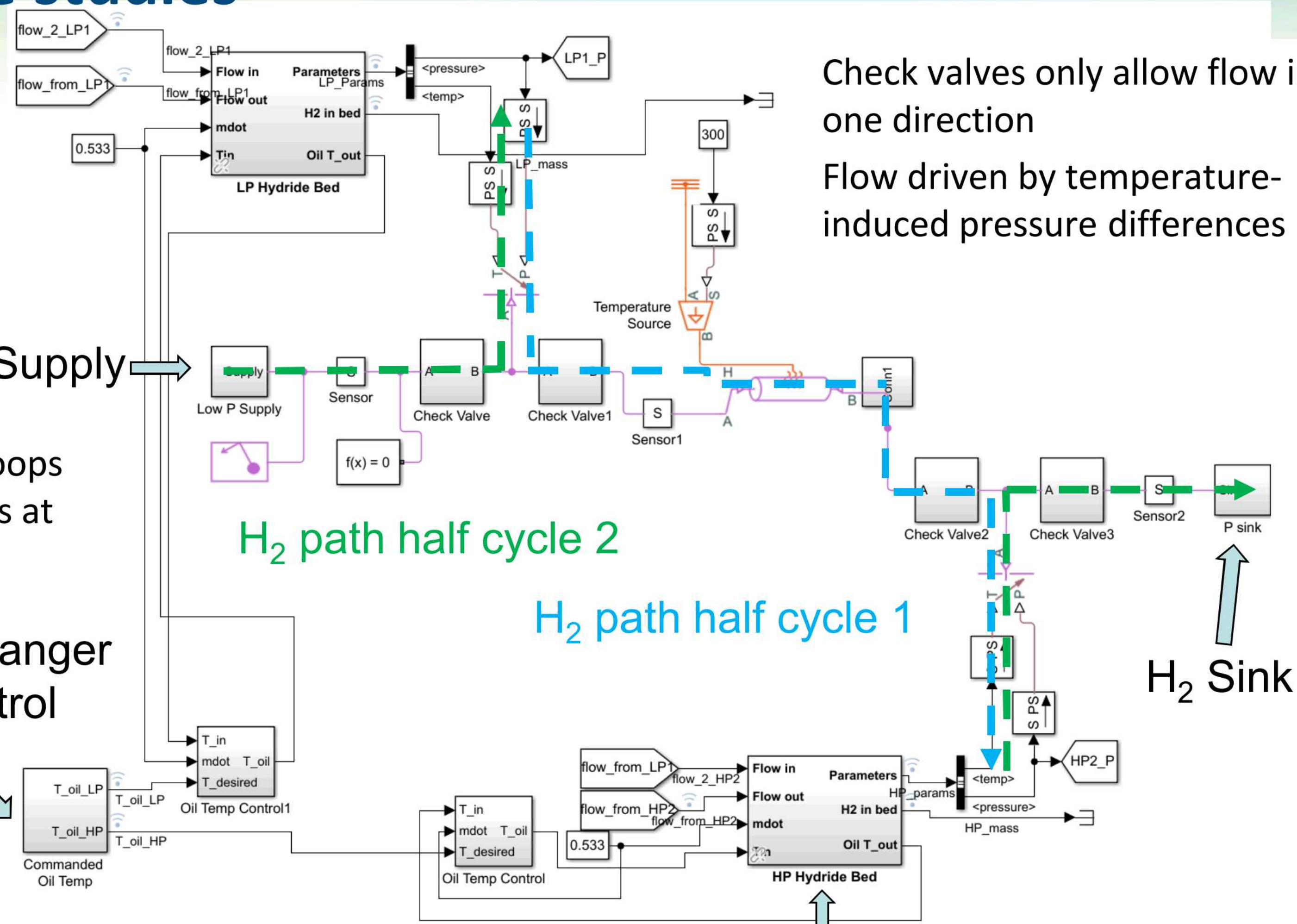
H_2 Supply

Temperature control loops switched between beds at half cycle intervals

Heat Exchanger Temp Control

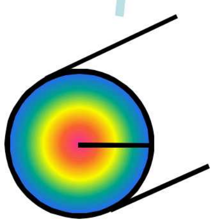
Check valves only allow flow in one direction

Flow driven by temperature-induced pressure differences



H_2 Sink

HP Bed 2



Coupled 1-D heat transfer and chemical kinetics

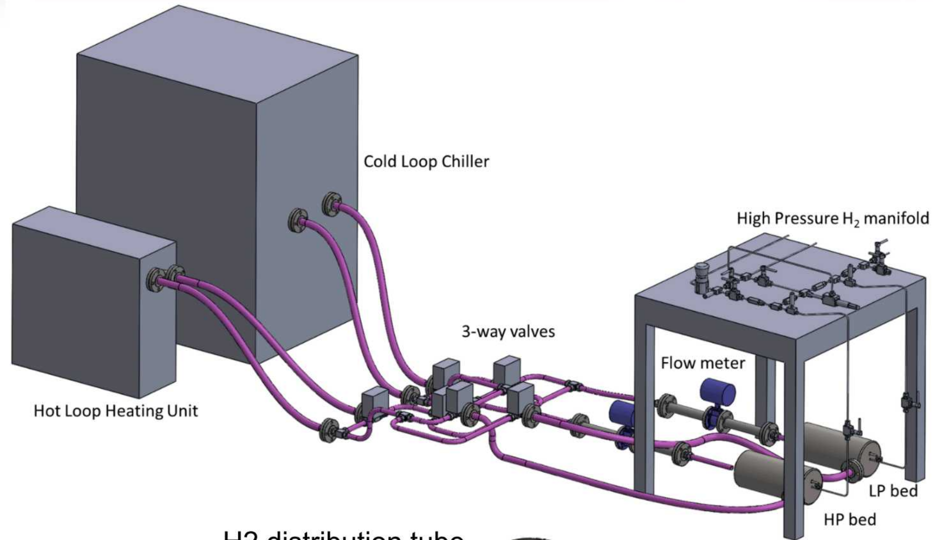
Several approaches identified to achieve energy efficiency/cost targets

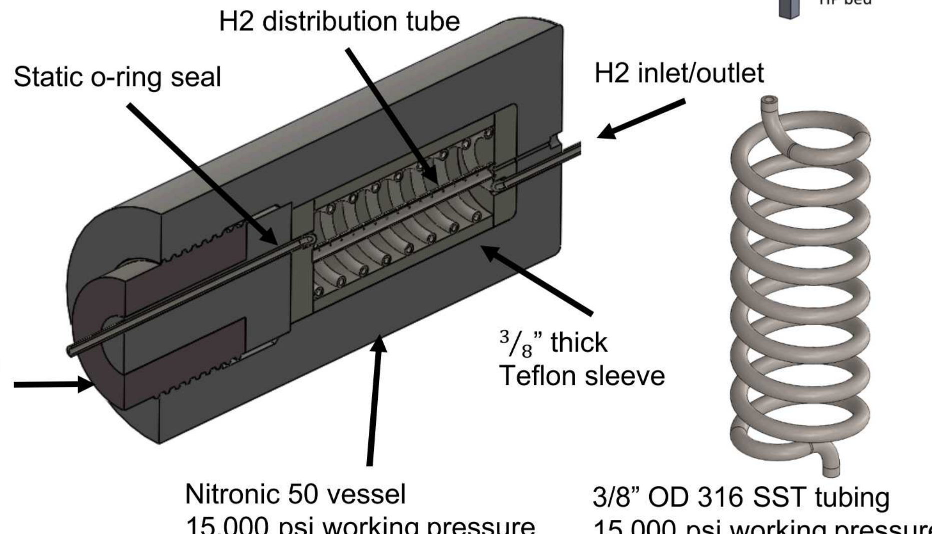
- Heat recuperator design could reduce the sensible heat requirement of the system by ~40% bringing required heat down to ~10 kWh/kg
- Waste heat utilization:
  - Coupling to an SMR system is possible (heat available at appropriate temperature), but not likely in forecourt
  - Waste-to-energy systems 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

2-stage prototype redesigned to reduce cost; flow rate reduced from 1 kg H_2/hr to 150 g/hr

Features:

- 2 stage; 1 bed per stage
- ~8X reduction in scale compared to original prototype
  - 3 kg hydride per bed
  - 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 ~20C to ~150C





Original – 30"L X 13"OD; 850 lbs
New – 19"L X 8"OD; 220 lbs

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

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