SAND2018-3122PE

Metal Hydride Compression

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Hydrogen Delivery Tech Team

March 28, 2018

Project ID PD138

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U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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BACKGROUND

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

Advantages

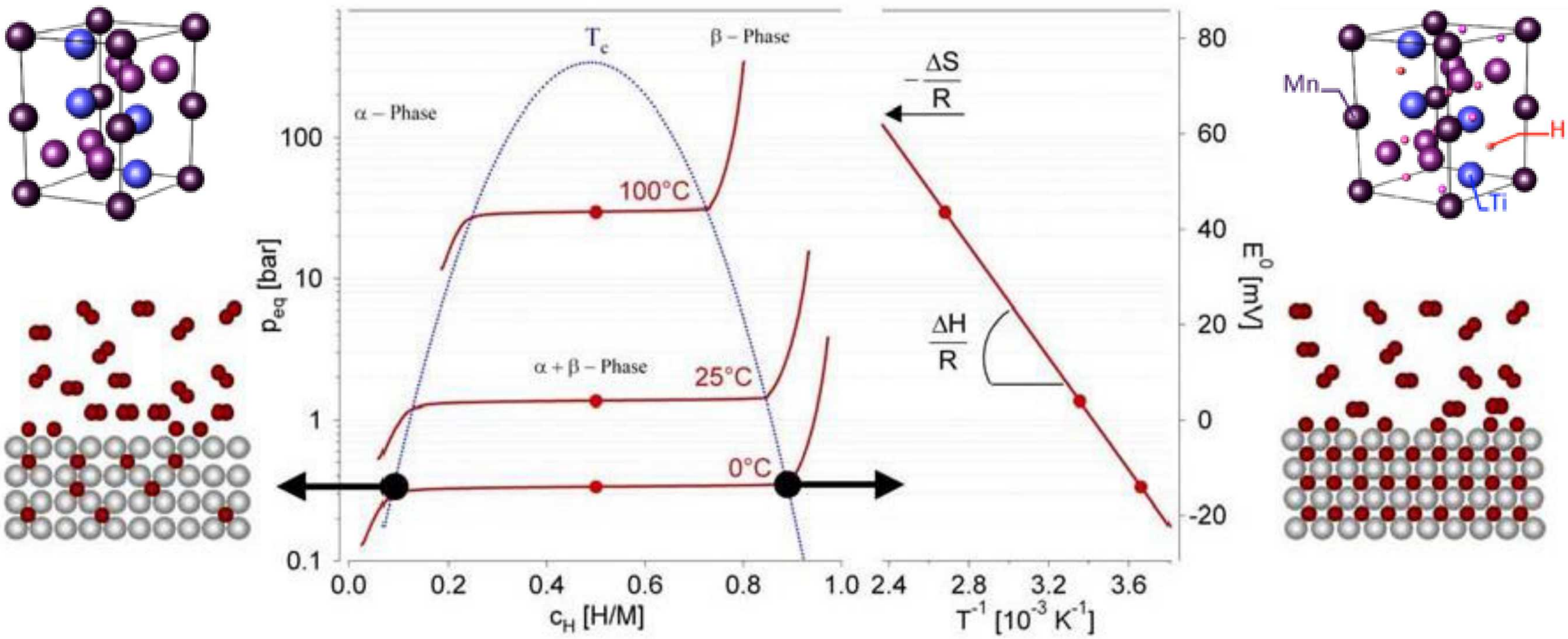
- Simple design and operation
- Absence of moving parts
- Oil-free
- Compact
- Safe and reliable
- Able to utilize waste industrial heat
  - Dramatic decreases in operational costs
  - Advantage with on-site generation

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

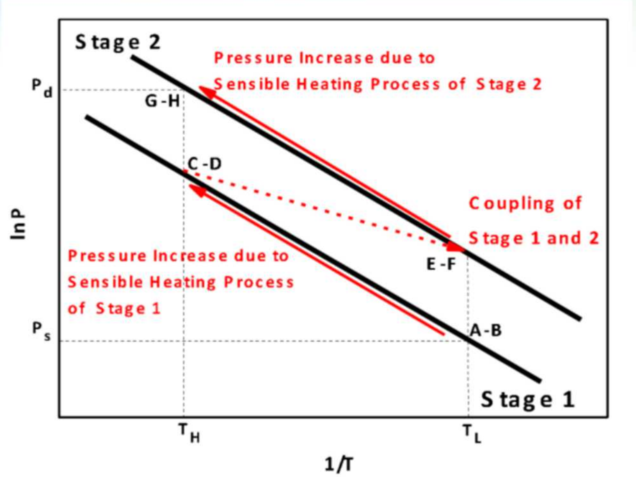
$TiMn_2 \rightarrow TiMn_2H_{2.5}$



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

We will demonstrate a two-stage metal hydride compressor for 50 to 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



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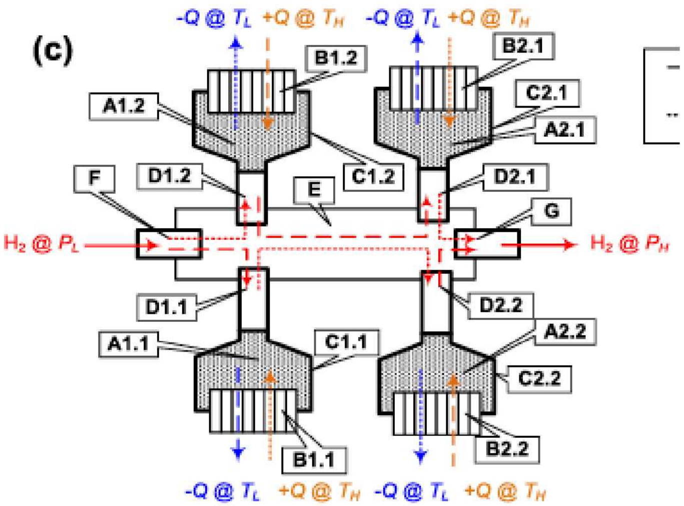


METAL HYDRIDE ALLOY SELECTION

Candidate alloys for each stage were paired down prior to PCT characterization at HHC and ORNL

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

High Pressure Candidates

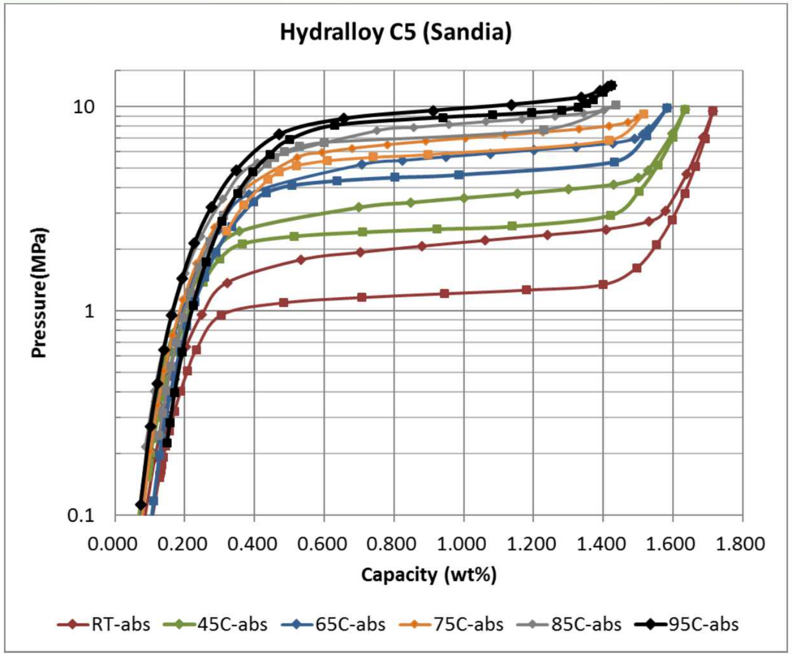
1. $TiCr_{1.6}Mn_{0.2}$
2. $TiCr_{1.8}$
3. **$Ti_{0.95}Zr_{0.05}Cr_{1.20}Mn_{0.75}V_{0.05}$**
4. **$Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$**
5. **$TiCrMn_{0.7}Fe_{0.2}V_{0.1}$**

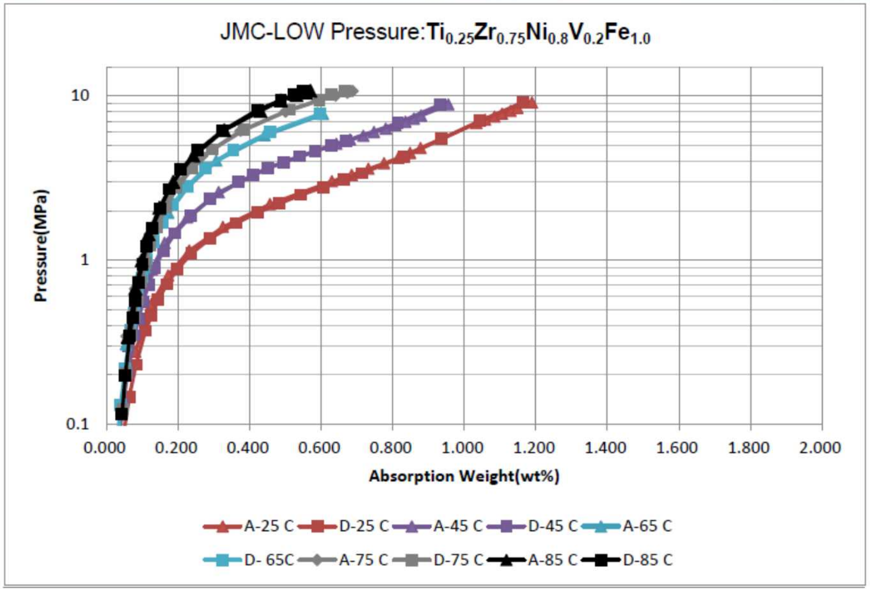
Low Pressure Candidates

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)**

Hydride Suppliers: Ames Lab and Japan Metals and Chemicals

Hydralloy C5 selected for low pressure stage based on performance and availability



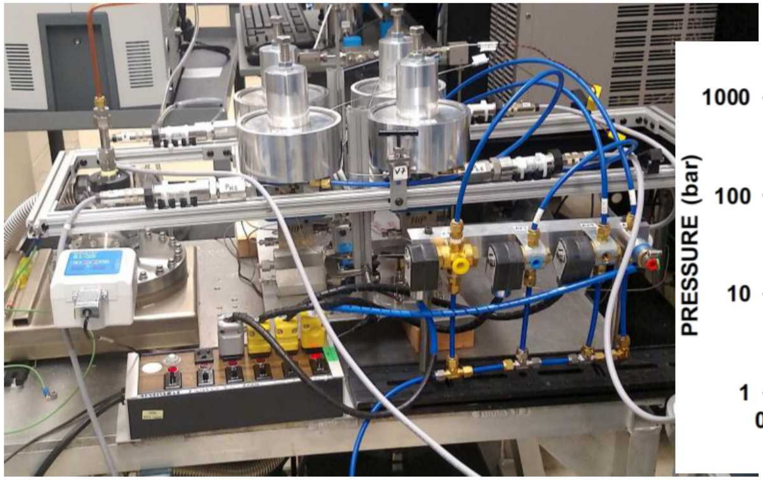


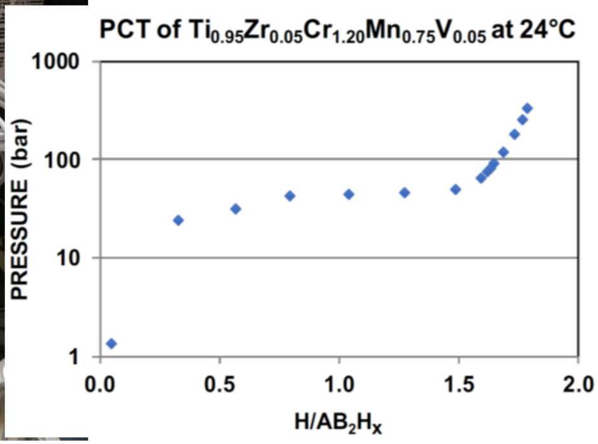
- Isotherms measured at HHC of Hydralloy C5 show promise for low pressure stage
- Sandia has ~100kg in inventory

- Second LP candidate produced by JMC
- Highly sloping isotherms
- Potentially due to lack of annealing

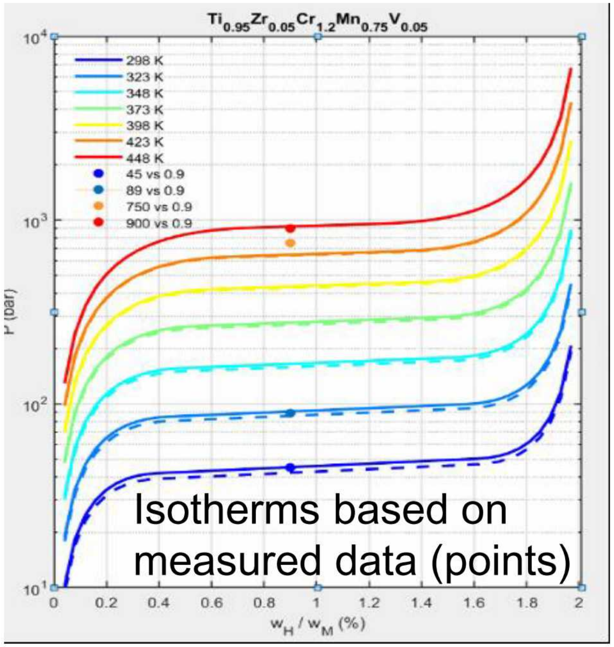
First high pressure candidate measured with ORNL custom Sieverts apparatus; second alloy in progress

- Custom apparatus capable of measurements up to 1000 bar and >150 ˚C
- Absorption isotherm shows that this alloy would easily be filled by our low pressure stage
- Desorption pressure from the alloy was measured up to 180 ˚C displaying desorption pressures in excess of 875 bar





Absorption isotherm at 24 ˚C



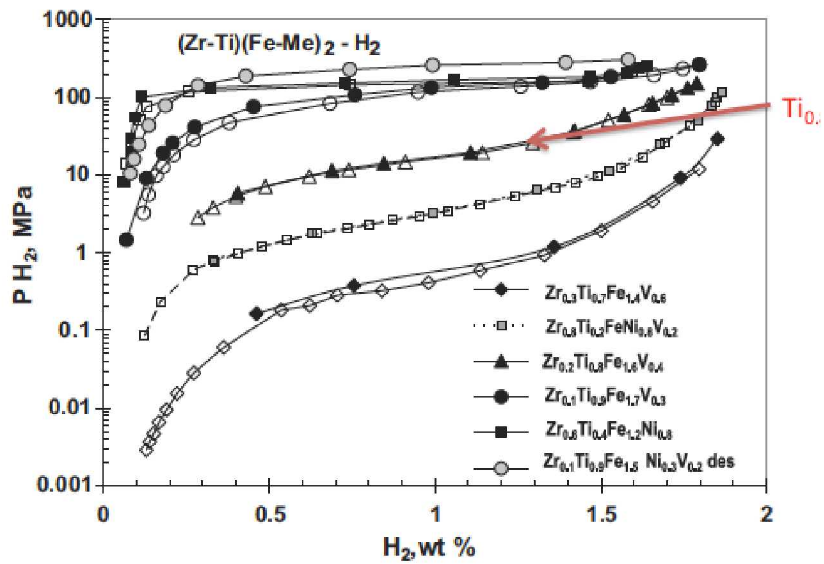
Isotherms based on measured data (points)

Two additional high pressure alloys to be measured at ORNL

$Ti_{0.8}Zr_{0.2}Fe_{1.6}V_{0.4}$ (Ames)

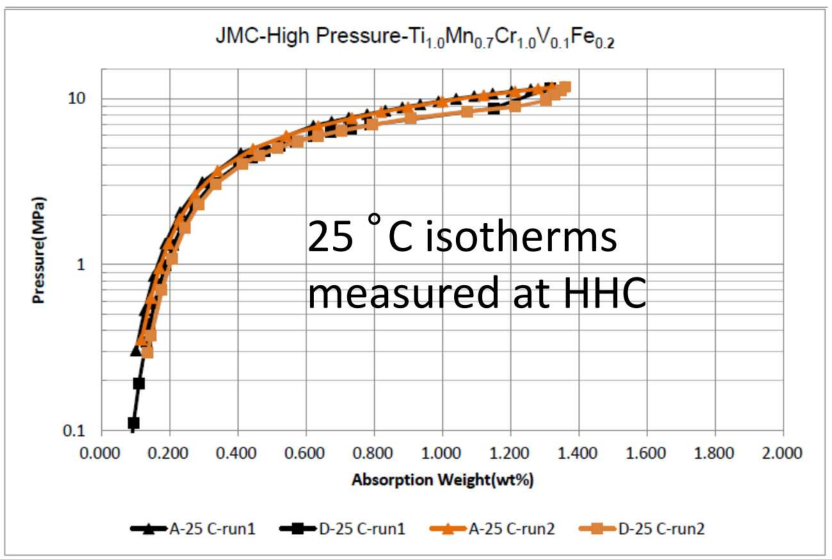
- Low hysteresis, moderate slopes
- Installed in reactor 2/22/18
- Calculate that Pdes = 60.3 MPa @ 90 °C

T.A. Zotov et al., Journal Alloys Compounds **509S** (2011) S839– S843



$TiCrMn_{0.7}Fe_{0.2}V_{0.1}$ (JMC)

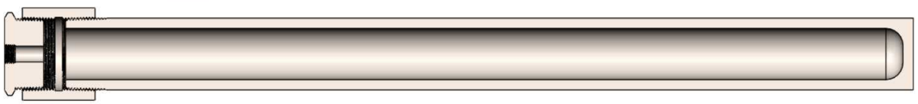
- Intermediate hysteresis, literature isotherms at < 20 °C
- HHC measurement showed high slopes and low capacity
- Ordered a new annealed sample from Ames Lab



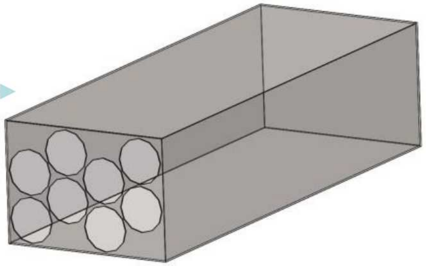
COMPRESSOR BED DESIGN

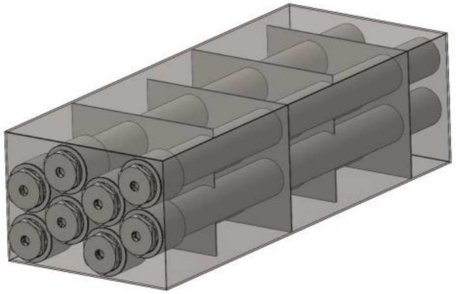
Baseline: Shell and tube consists of tubular pressure vessels arranged in a baffled heat exchanger

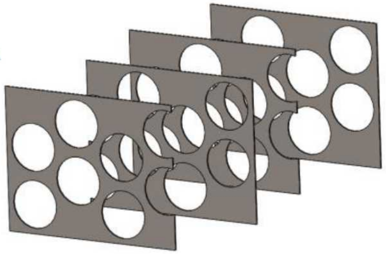
Tube ID: 1.5-2.0”
Wall thickness: 0.3-0.4” (900 bar)
Length: 18 – 24”



Component		Material	Number	Total Mass
Reservoir	7.59 kg	316L SS	8	60.7 kg
Tube	6.31 kg	316L SS		
Coupler	0.74 kg	316L SS		
Reducer	0.54 kg	316L SS		
Shell	8.77 kg	316L SS	1	8.8 kg
Baffles	0.36 kg	316L SS	4	1.4 kg
Total				**70.9 kg**



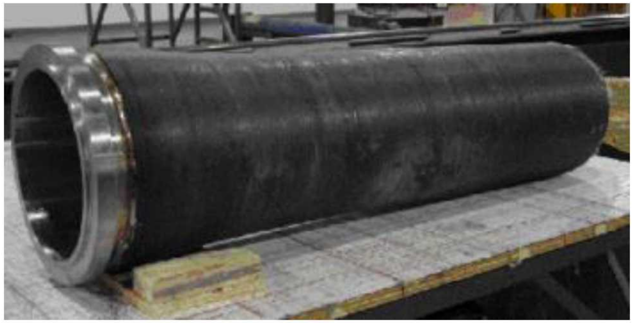




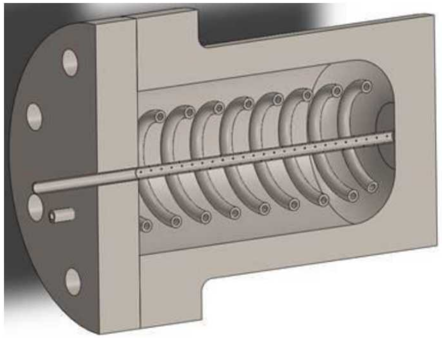
Alternative options: Internal heat exchanger design with several variants

Closed Ended Design
(Carbon fiber composite)

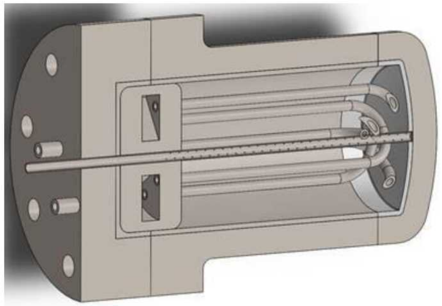
Open Ended Design
(Carbon fiber composite)



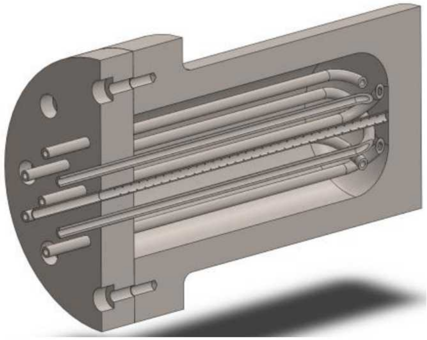
Open Ended Design
(Nitronic 50 w/ insulator)



Helical tube



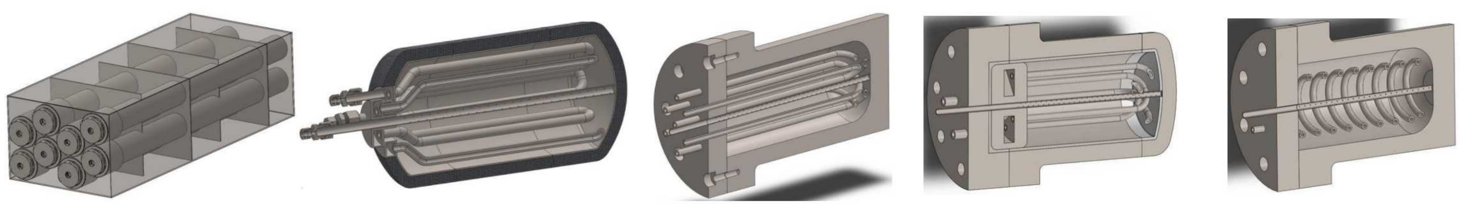
U-tube
internal manifold



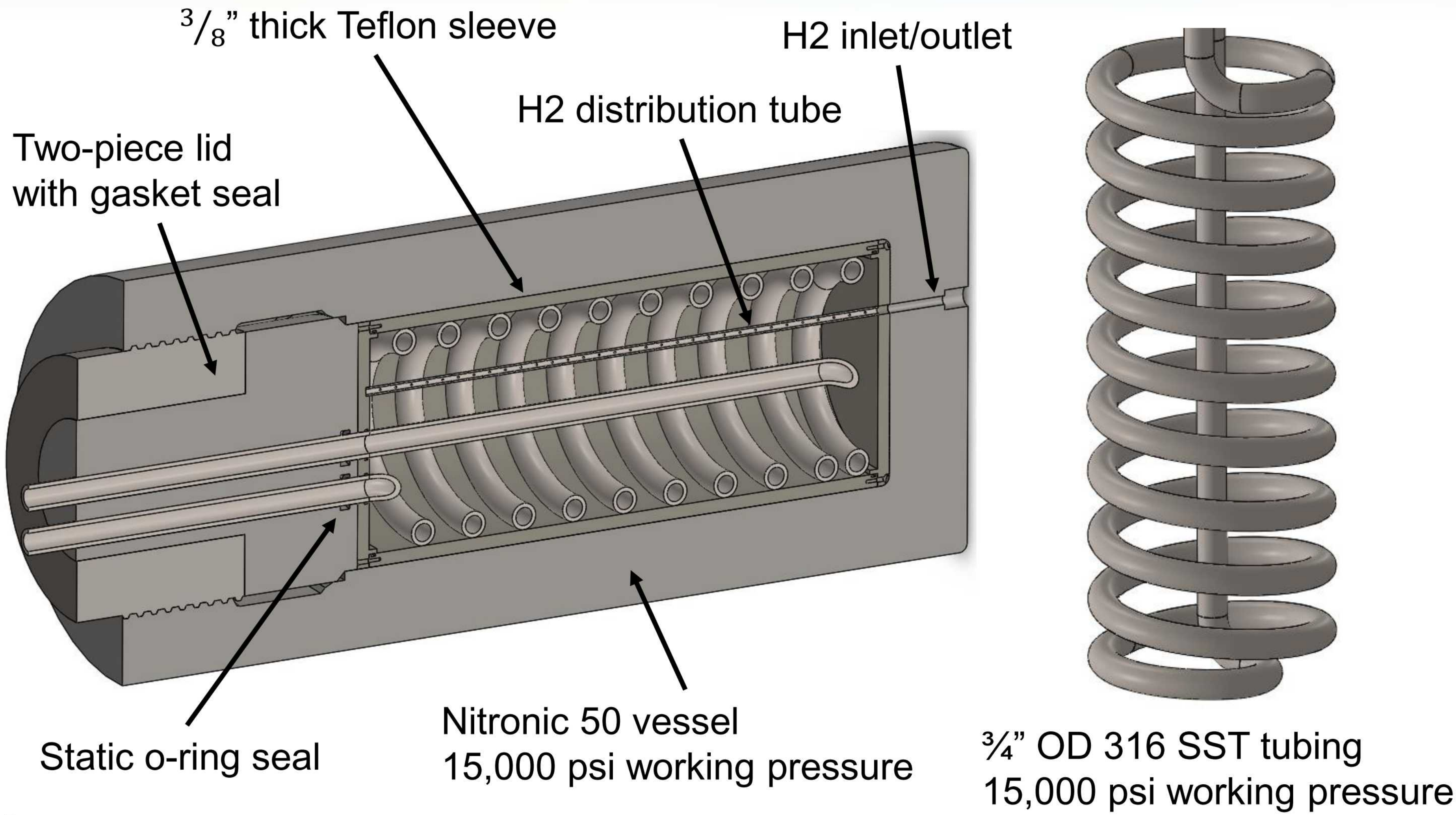
U-tube
external manifold

Trade study points to helical coil design for highest energy efficiency, manufacturability, and heat transfer

	External HX	Internal HX			
	Shell and Tube	Carbon Fiber Composite	External Manifold	Internal Manifold	Helical Coil
Energy Efficiency	Red	Yellow	Yellow	Yellow	Green
Manufacturability	Yellow	Red	Yellow	Yellow	Green
Hydride Loading	Green	Red	Yellow	Yellow	Yellow
Thermal Design	Green	Yellow	Yellow	Yellow	Green
HTF Pressure Drop	Green	Green	Green	Green	Red
Low Cost	Green	Red	Yellow	Red	Yellow

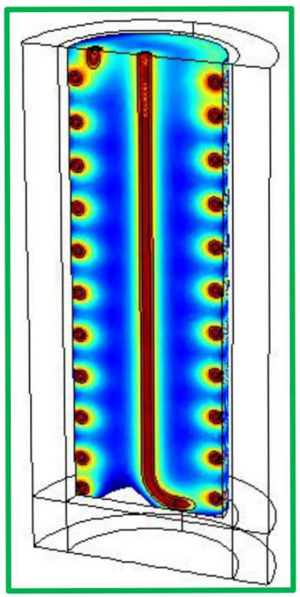


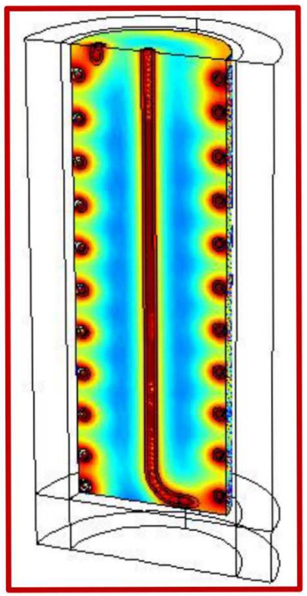
Helical tube heat exchanger design rated for 15,000 psi (1034 bar)



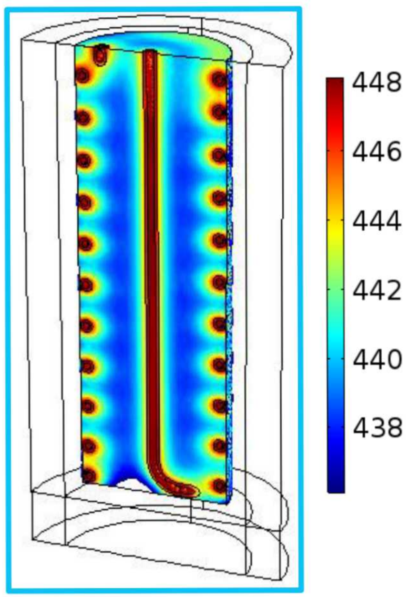
Modeling was used extensively to develop the final helical tube design

- 3D thermal model developed with SolidWorks and Comsol Multiphysics
- Convective heat transfer applied to inner surface of helical tube; based on Nu correlation
- Density, specific heat, and thermal conductivity based on literature values for MH with 10wt% expanded natural graphite (ENG)



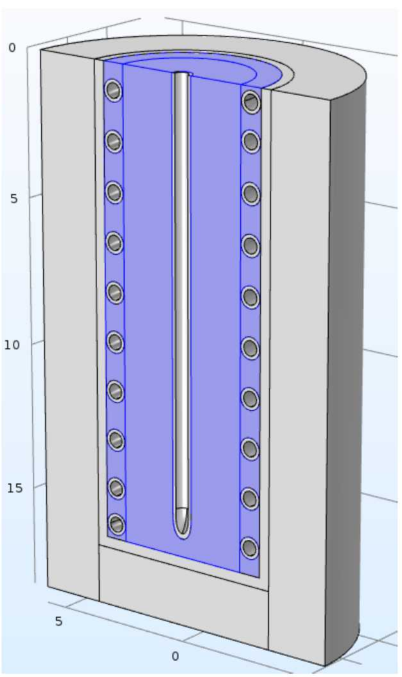


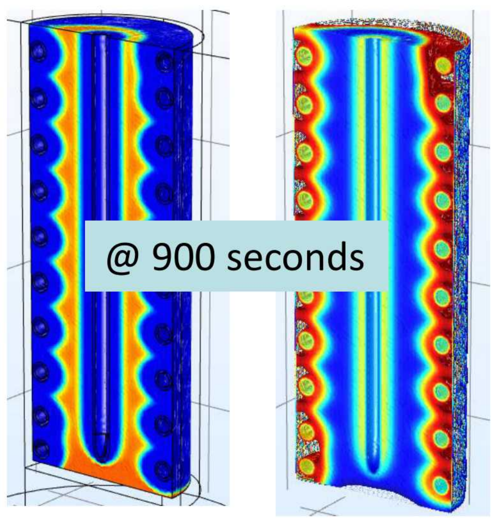
Shell Thickness	Shell Material	$\frac{Q_{shell}}{Q_{total}}$
0.250”	Teflon	17.7%
0.375”	Insulation	2.4%
0.375”	Teflon	14.8%
0.500”	Teflon	13.8%
0.750”	Teflon	13.2%



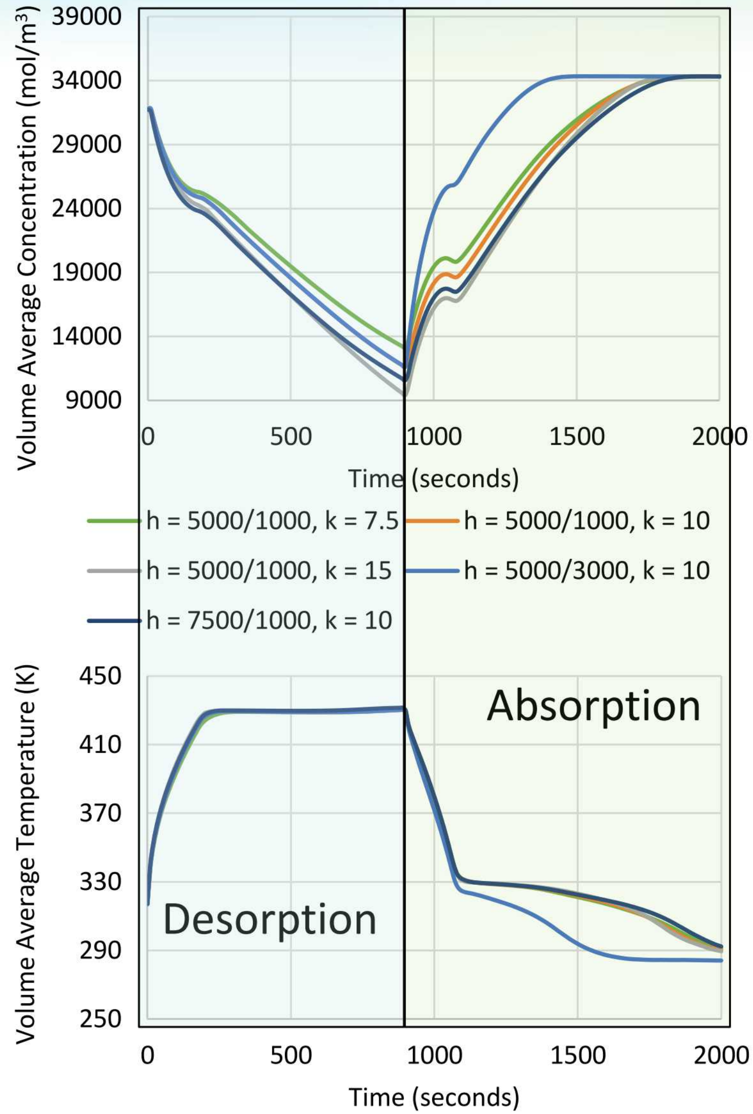
Coupled kinetic-thermal model predicts cycling performance as function of hc and keff

- Desorption Simulation of LP Bed
  - T_{fluid} = 177°C (heating), Tfluid = 10°C (cooling)
  - $h_{c,heating}$ = 5000 to 7500 W/m²K
  - $h_{c,cooling}$ = 1000 to 3000 W/m²K
  - $k_{eff,\ radial}$ = 7.5 to 15 W/mK





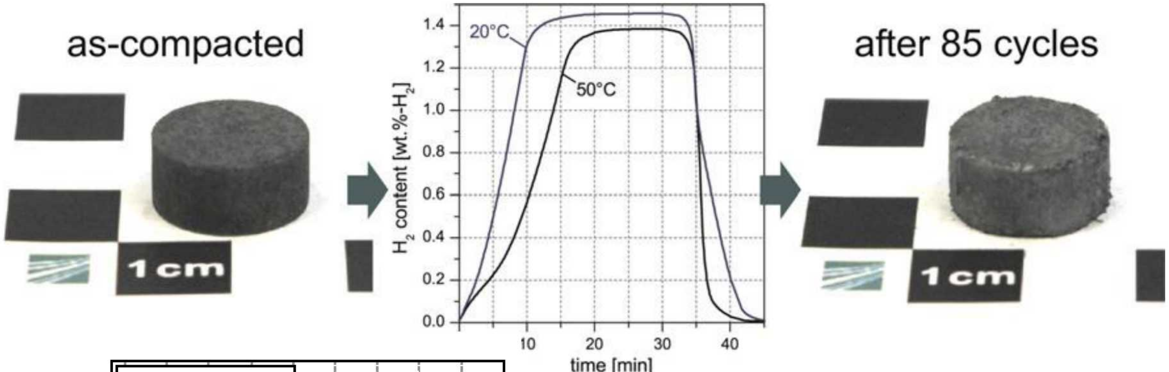
H_2 mol/m³ 420K<T<435K

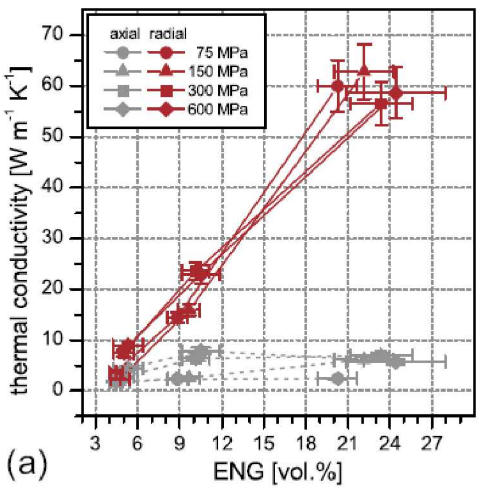


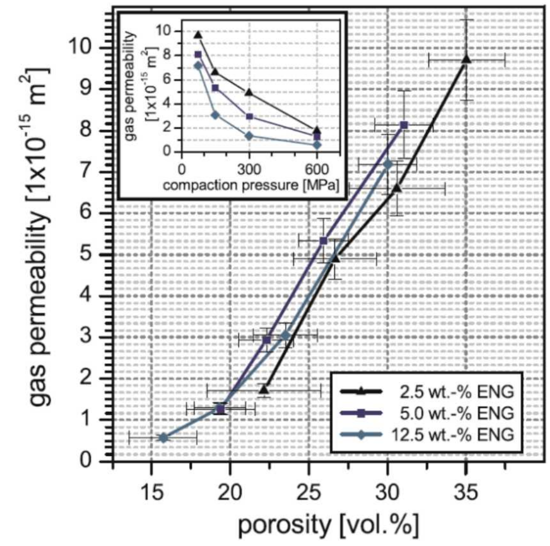
THERMAL MANAGEMENT

Preferred method/process identified for thermal conductivity enhancement

- Based on work by Pohlmann, et al (Dresden University, DLR)
- Overall process: Compaction of a mixture of powdered MH with ENG (75 MPa and 5-10 wt.% ENG) to a packing density of 70%

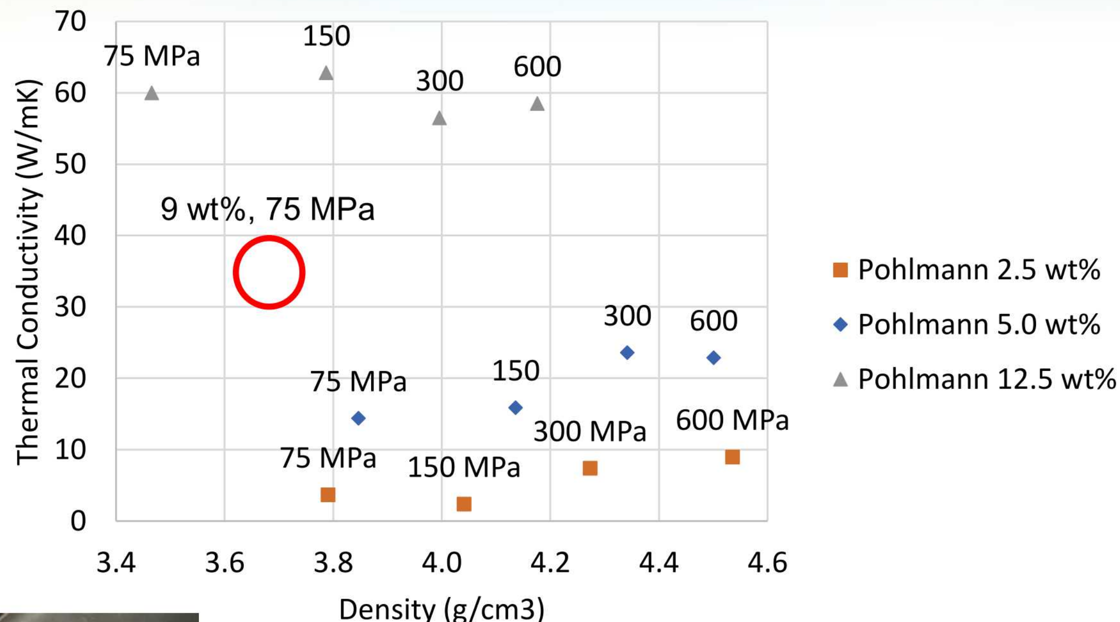






	As-compacted	After 85 cycles
λ_{rad} at 20 °C [W m^{-1} K^{-1}]	14.4	7.4
λ_{rad} at 50 °C [W m^{-1} K^{-1}]	13.9	7.4
k_{gas} [$\times 10^{-15}$ m^2]	8.1	3.9
Φ_{Por} [vol.%]	32.2	33.8

MH/graphite compacts made at Sandia show good thermal conductivity; lower than published values



- ENG and graphite flake mixed with Hydralloy C5 at 9 wt%
- Compacted at 75 and 220 MPa
- Measured k somewhat lower than expected

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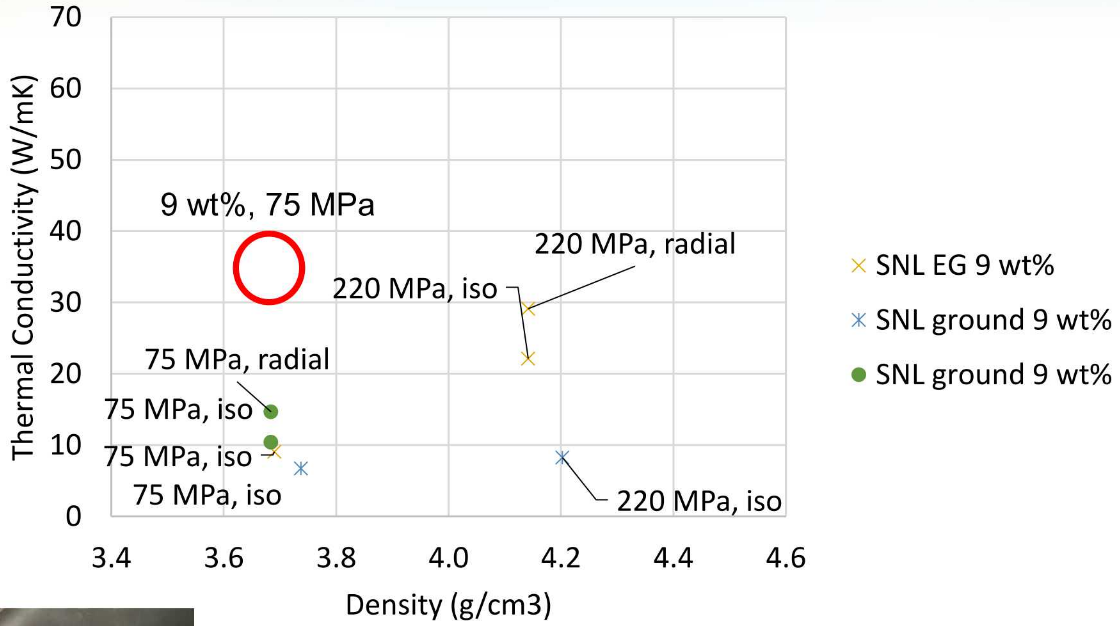

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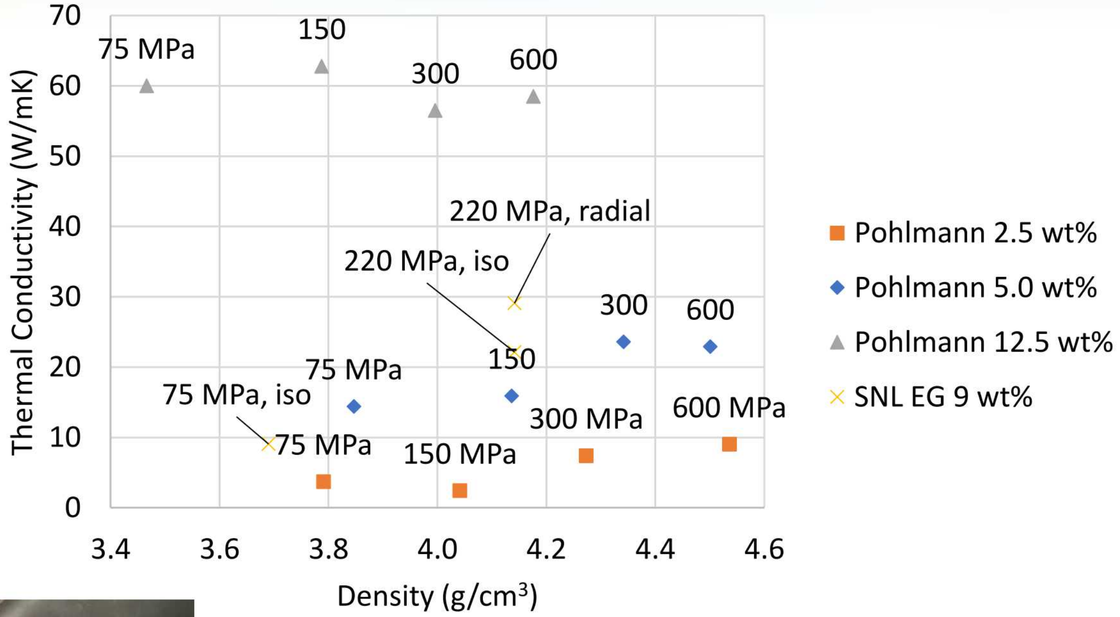
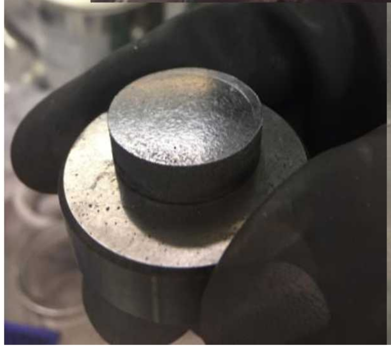




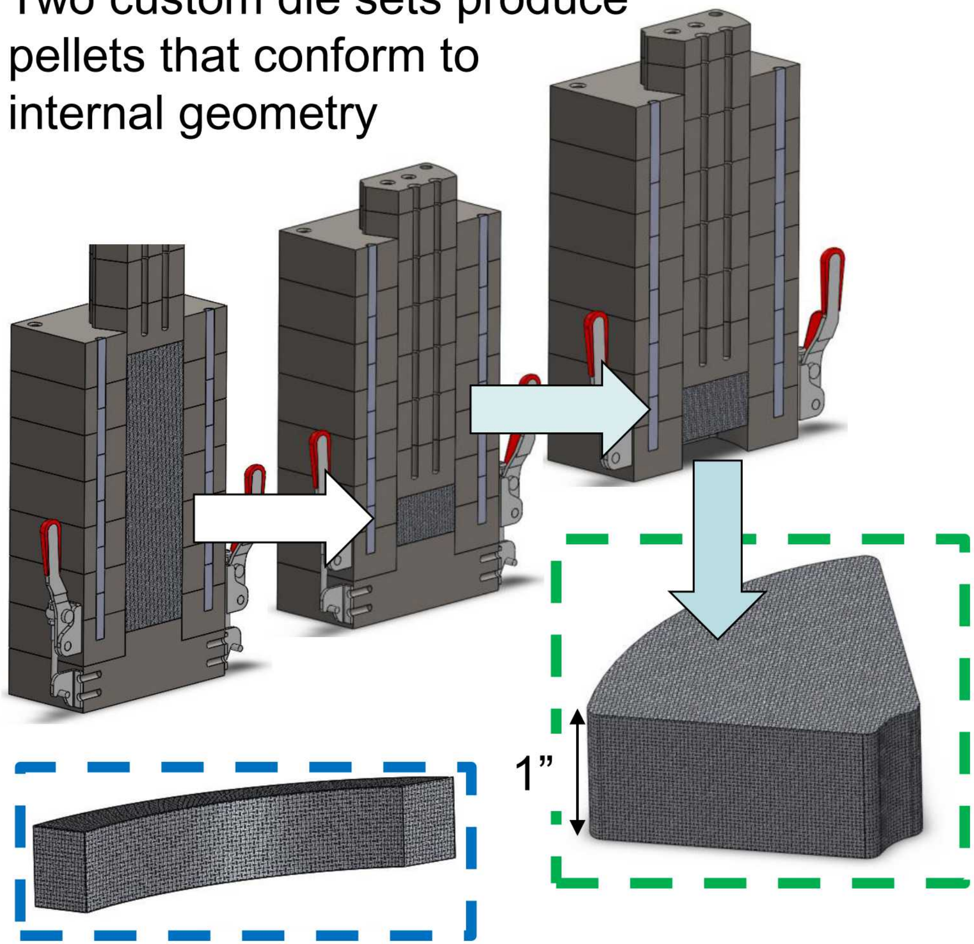
- ENG and graphite flake mixed with Hydralloy C5 at 9 wt%
- Compacted at 75 and 220 MPa
- Measured k somewhat lower than expected

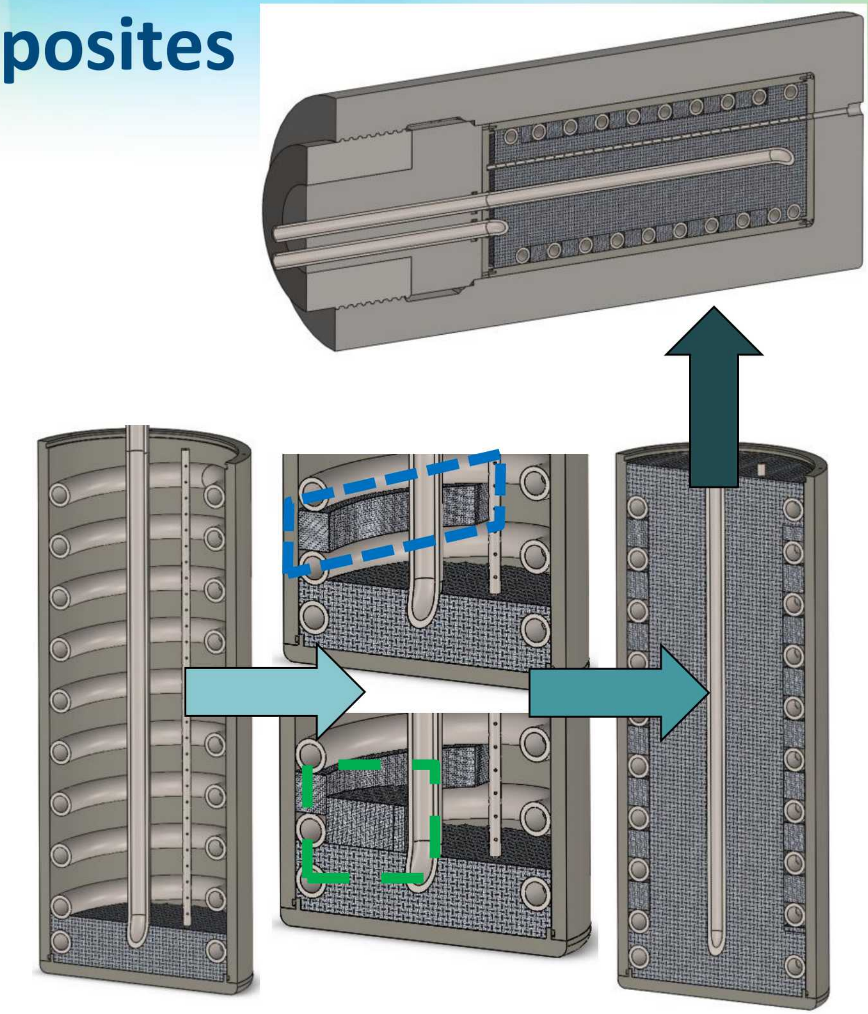
MH/ENG compacts will be created to fit vessel geometry and loaded in inert environment

1) MH granules pretreated via high-energy ball milling under argon producing a fine powder
2) Mix with 10 wt% high purity ENG (delivered by 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.

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

Two custom die sets produce pellets that conform to internal geometry

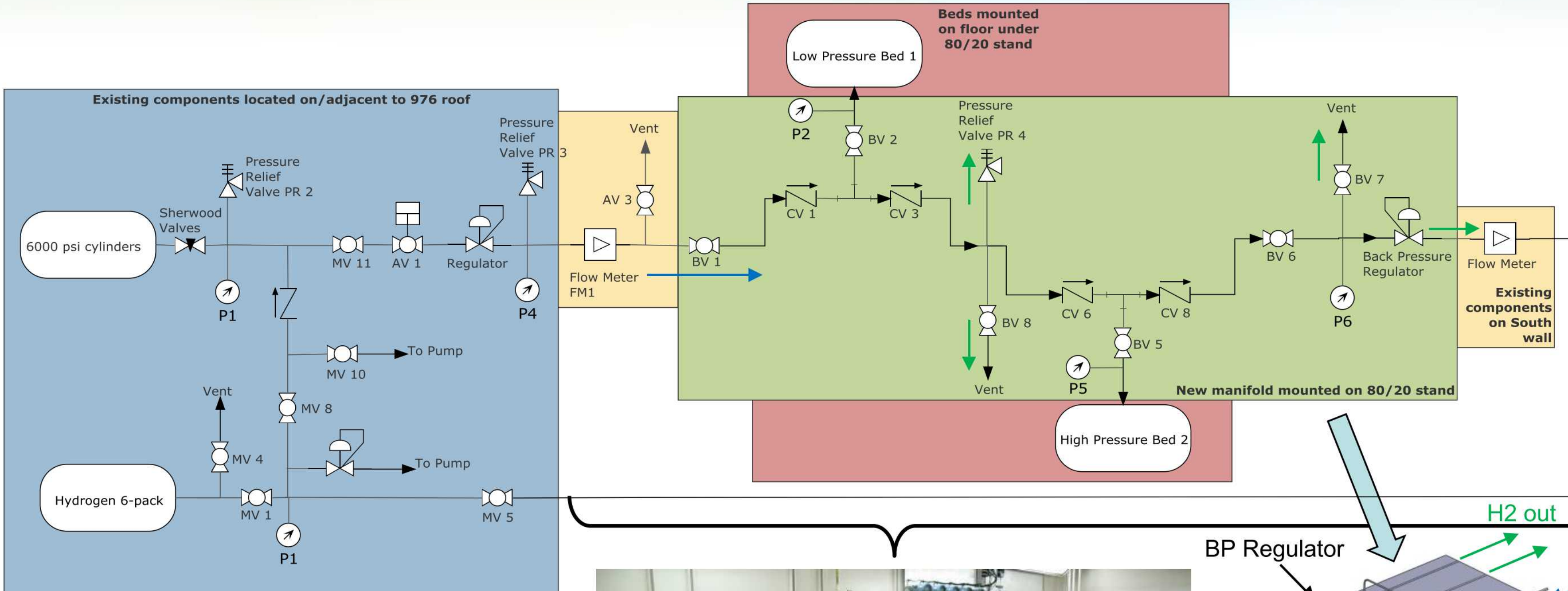


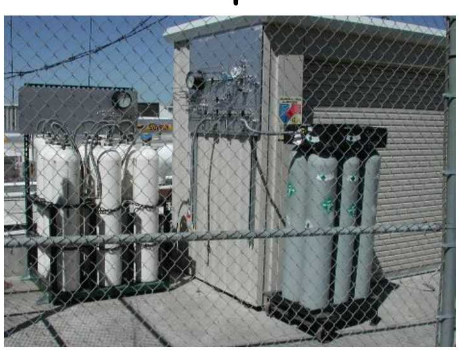


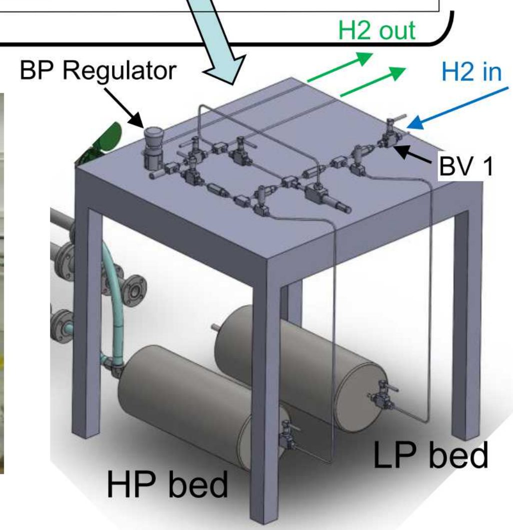
Loading consists of manual compaction and insertion of pre-compressed pellets within insulating liner

SYSTEM-LEVEL DESIGN

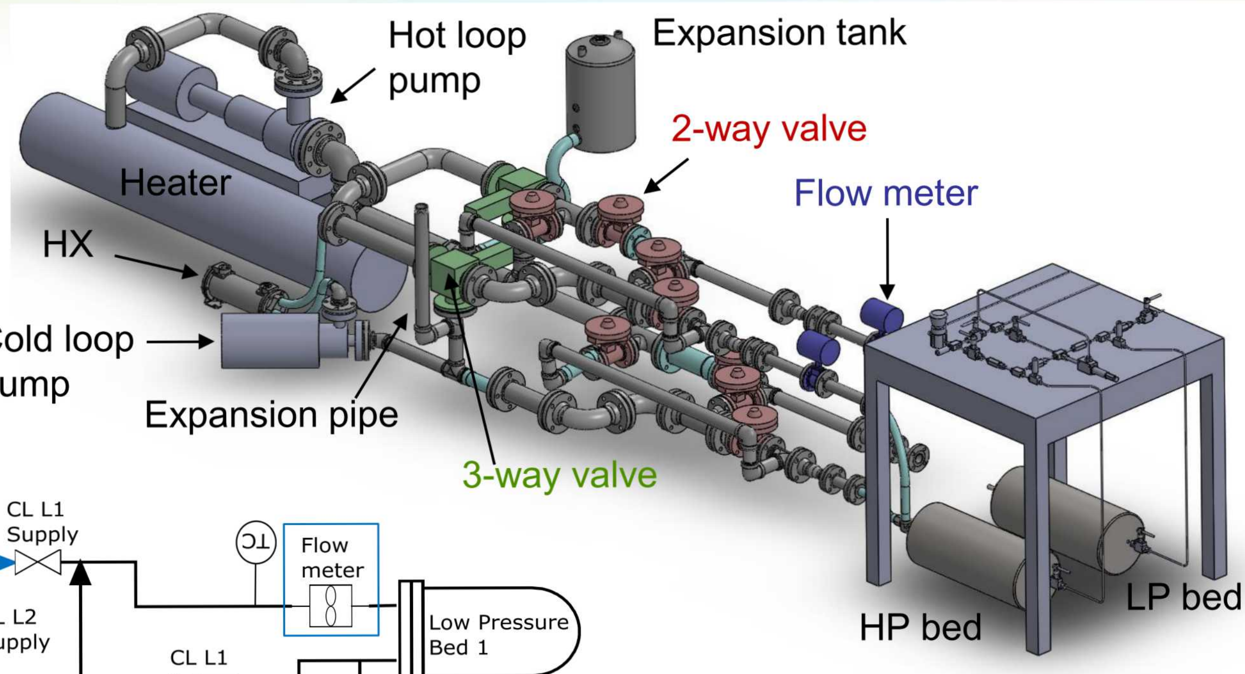
High pressure manifold designed for closed loop recirculation of hydrogen from the compressor

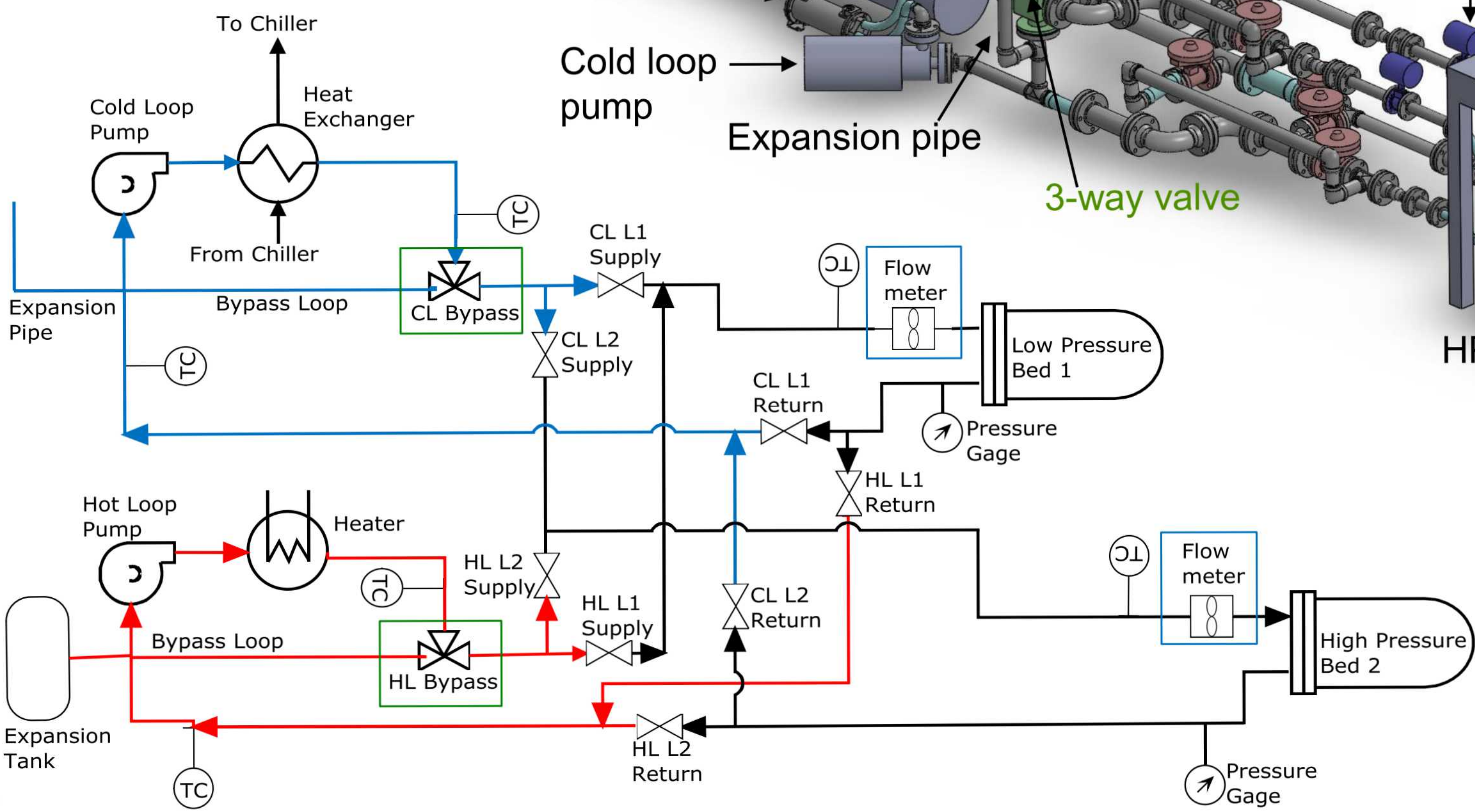






Temperature control system consists of hot and cold oil recirculation loops





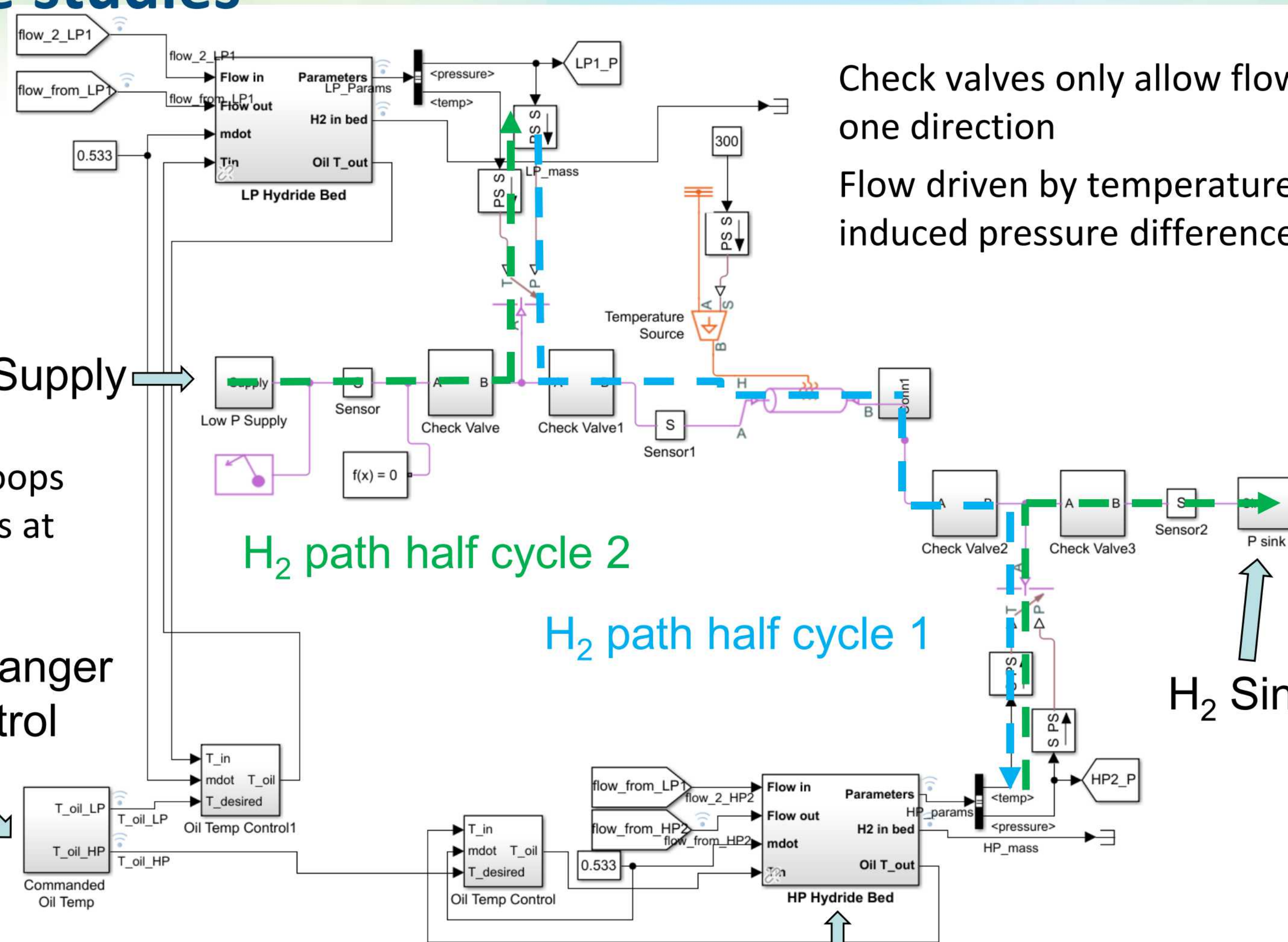
Dynamic system-level model used for feasibility and design trade studies

Check valves only allow flow in one direction

Flow driven by temperature-induced pressure differences

LP Bed 1

H_2 Supply



H_2 path half cycle 2

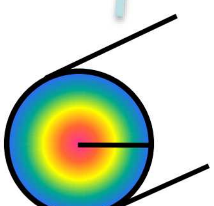
H_2 path half cycle 1

Temperature control loops switched between beds at half cycle intervals

Heat Exchanger Temp Control

H_2 Sink

HP Bed 2



Coupled 1-D heat transfer and chemical kinetics

Sandia National Laboratories

H2FC Hydrogen and Fuel Cells Program

Dynamic system model used to predict performance using measured HP and LP alloy properties

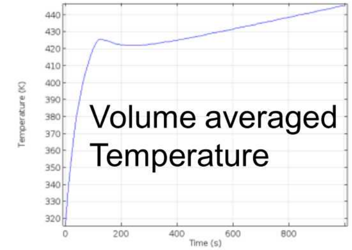
Configuration:

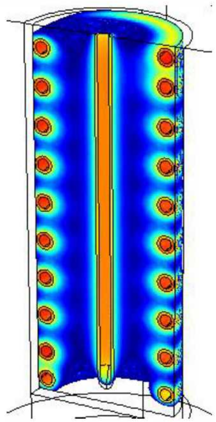
- 25 kg of LP hydride (Hydralloy C5)
- 21.7 kg of HP hydride ($Ti_{0.95}Zr_{0.05}Cr_{1.20}Mn_{0.7}5V_{0.05}$)
- 15-20 minute half cycles
- 100 to 875 bar compression
- Heating/cooling of beds with heat transfer fluid
  - Cold loop temperature set to **60 ℃**
  - Hot loop temperature set to **190 ℃**

Results:

- Utilization = 61% for all beds
  - $Utilization = \frac{Hydrogen\ delivered}{Storage\ capacity}$
- **0.87 kg/hr average flow rate**
- **Energy usage for heating 10.7 kWh/kg H_2**

Bed thermal response calibrated to detailed Comsol model





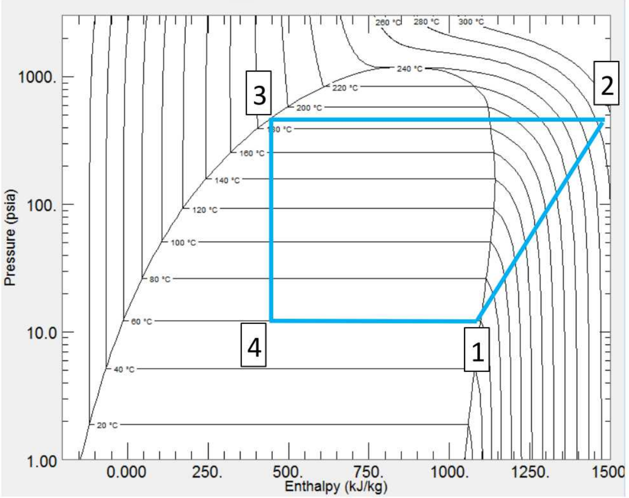
Several approaches identified to achieve energy efficiency/cost targets

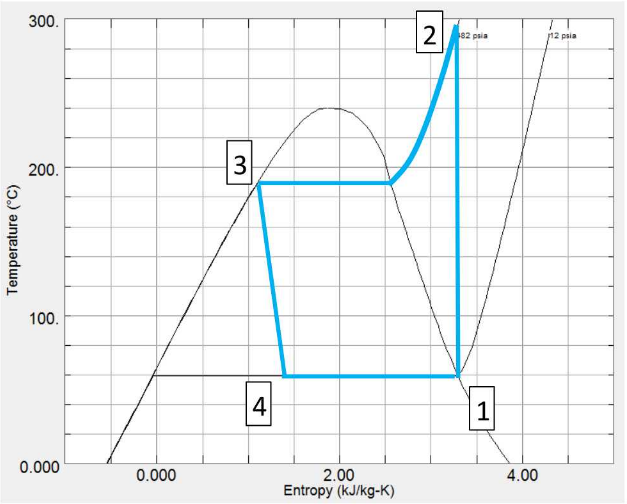
- Heat recuperator design could reduce the sensible heat requirement of the system by ~40% bringing required heat down to ~10 kWh/kg
- Waste heat utilization:
  - Coupling to an SMR system is possible (heat available at appropriate temperature), but not likely in forecourt
  - Waste-to-energy systems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

Heat pump could significantly improve energy efficiency

- Given condenser and evaporator temperatures and a candidate refrigerant, thermodynamic analysis gives heat pump COP
- COP is calculated as (h2-h3)/h2-1)
- VCC with methanol has potentially attractive thermodynamics
- Evaporator at 60 ℃ and 12 psia; condenser at 190 ℃ and 482 psia
- For methanol at these conditions, the COP is 2.63 for idealized system
- Energy consumption for the overall system is 4.06 kWh/kg
- However, actual COP may be closer to 2.0 given realistic compressor efficiency

Theoretical MeOH heat pump cycle

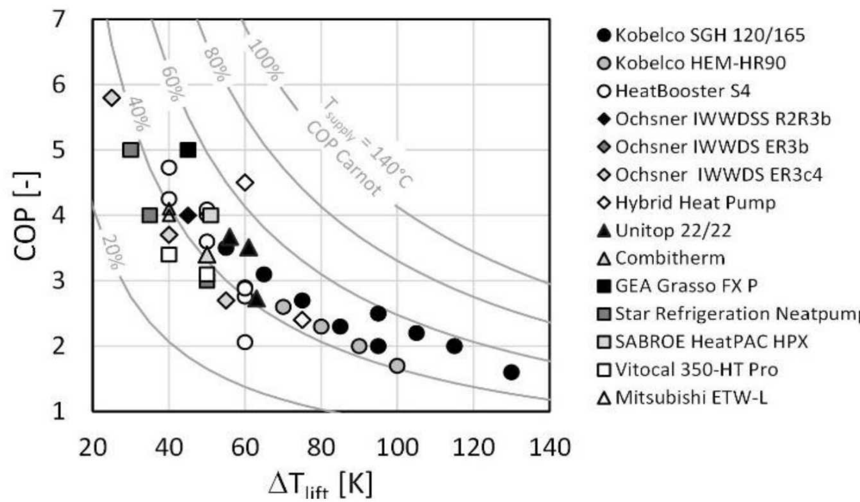


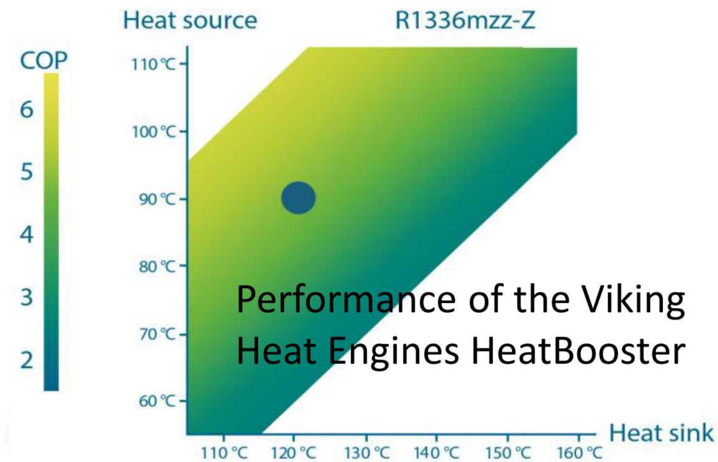


High temperature heat pumps/refrigerants developed for industrial steam generation show promise

- High temperature heat pumps (up to 160 ℃) provide process heat for a number of industries
- Many commercially available HTHPs with supply temperatures from 110 to 130 ℃
- New refrigerants for HTHPs with very low global warming potential
  - e.g. R1336mzz-Z which has a critical temperature of over 170 ℃
- Cascade heat pump system with two loops/fluids might reach target COP
  - Kobelco HTHP has a temperature lift 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 2.675

COP vs. temperature lift for commercial HTHPs





Performance of the Viking Heat Engines HeatBooster

PROGRAMMATIC

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	12/17 (revised)	75%
Milestone	3.2.1	Desired effective thermal conductivity determined along with additive type and amount.	7/17	100%
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 < 4.0 kWh/kg-H2 under 100-875 bar operation relying on innovative heat pump cycle.	2/18 (revised)	95%
Milestone	6.1	Detailed design complete	1/18	100%
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	50%
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%

Proposed Future Work

Remainder of FY18

- Procure HP hydride alloy, compressor beds, and BOP components
- 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

FY19

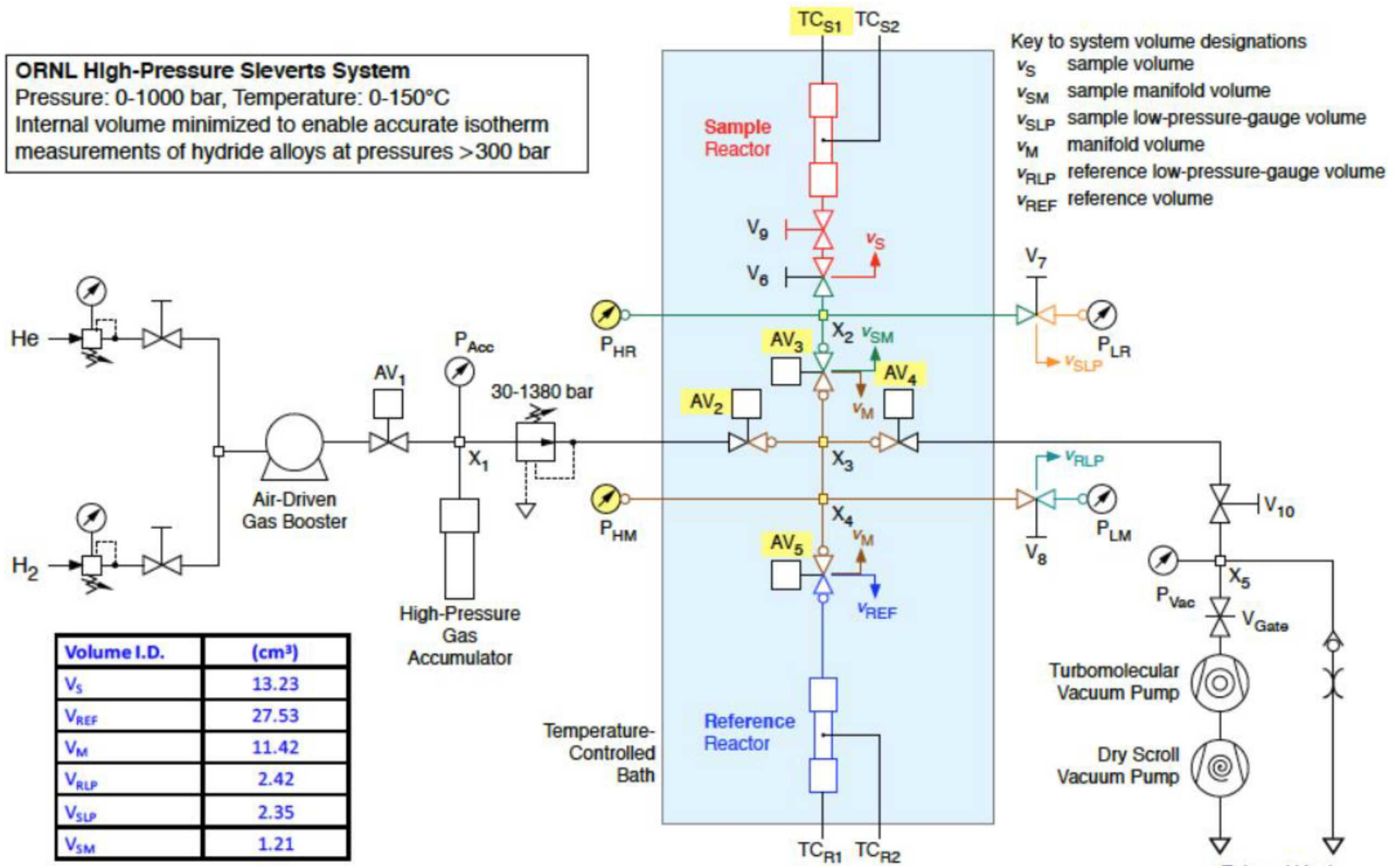
- Integrate prototype compressor into test facility
- Activate hydrides and perform initial cycling to assess individual performance
- Test performance of prototype compressor over range of process conditions
- Perform cost analysis for a 100 kg H_2/hr system
- Final report detailing performance of compressor

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

BACKUP

High pressure Sieverts apparatus designed and built at ORNL

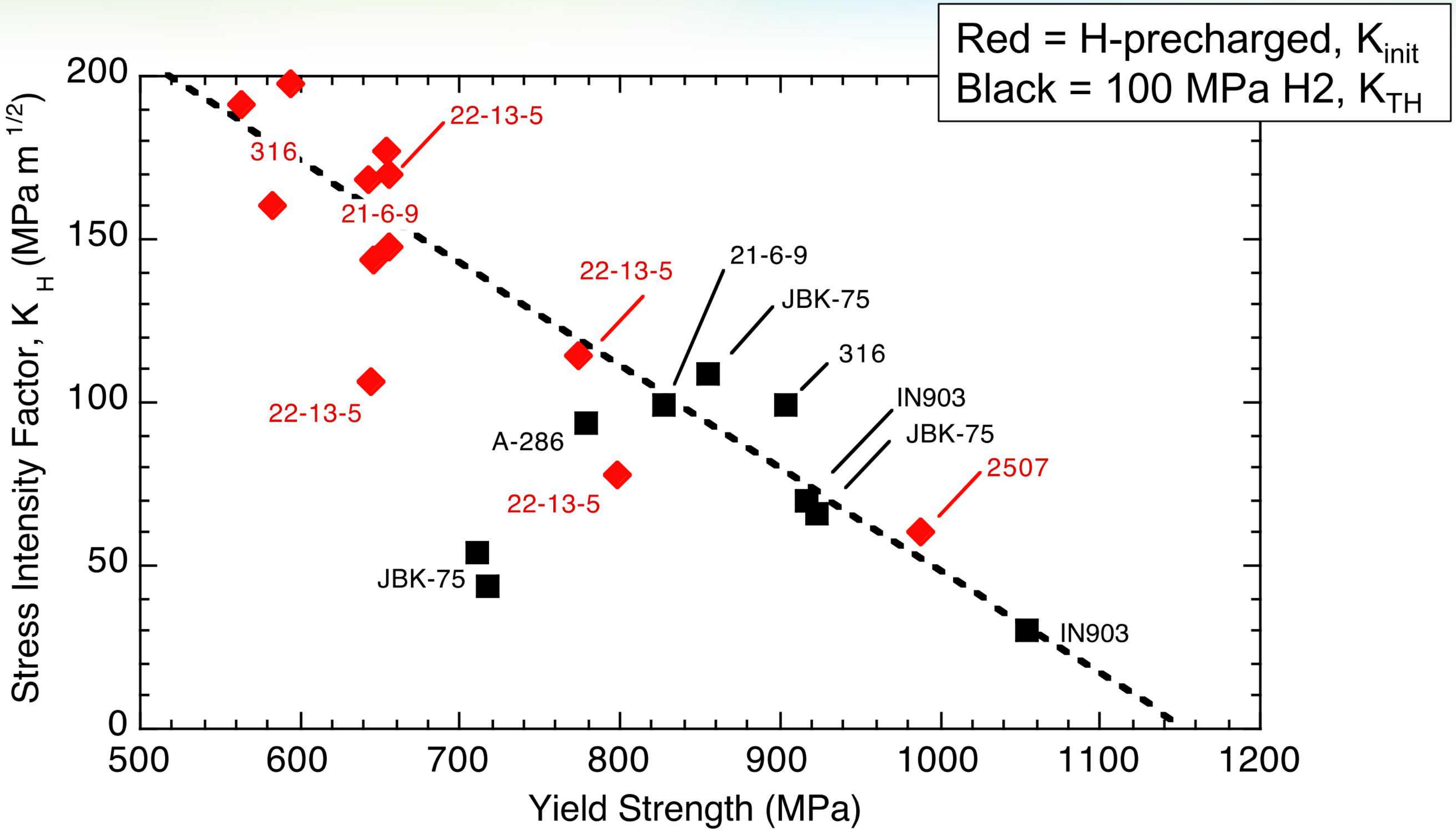
ORNL High-Pressure Sieverts System
Pressure: 0-1000 bar, Temperature: 0-150°C
Internal volume minimized to enable accurate isotherm measurements of hydride alloys at pressures >300 bar



Volume I.D.	(cm³)
V_S	13.23
V_{REF}	27.53
V_M	11.42
V_{RLP}	2.42
V_{SLP}	2.35
V_{SM}	1.21

Calibrated Sieverts Volumes for $Ti_{0.95}Zr_{0.05}Cr_{1.20}Mn_{0.75}V_{0.50}$ Ames-Lab Alloy (57.123 grams in V_S)

Fracture thresholds measured in hydrogen environments



The spread in the XM-19 points represent orientation (also two different strength levels) and the effect of inclusions

Tensile data from high strength XM-19 in the H-precharged condition

	XM-19 (22-13-5)		Sy (MPa)	Su (MPa)	Sy (ksi)	Su (ksi)	Elu	Elt	RA
RT	X	non-charged	916	1099	132.8	159.4	0.053	0.249	0.633
		H-precharged	1045	1178	151.5	170.9	0.092	0.252	0.483
−15°C	X	non-charged	979	1174	142.0	170.4	0.082	0.257	0.625
		H-precharged	1142	1295	165.7	187.9	0.090	0.246	0.465
−50°C	X	non-charged	1063	1276	154.2	185.2	0.104	0.279	0.617
		H-precharged	1209	1400	175.4	203.0	0.147	0.257	0.474