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Magnetocaloric Cryogenic System for High Efficiency Air Separation

Annual Progress Review FWP-73143

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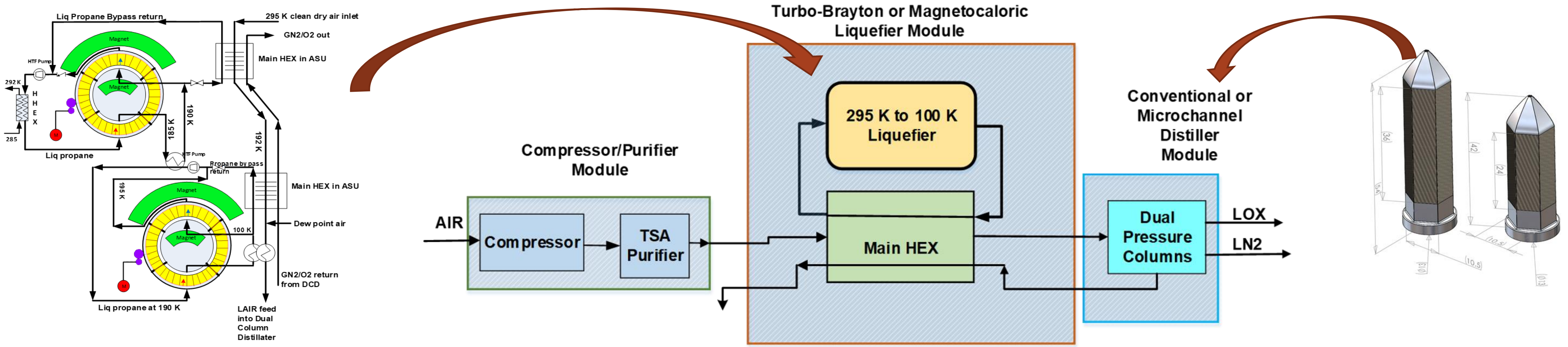
U.S. DEPARTMENT OF ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy

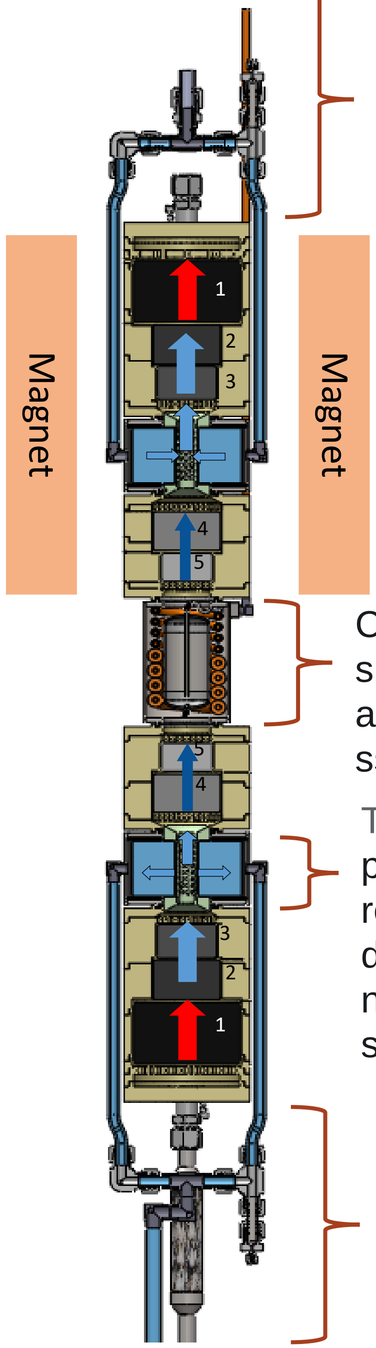
Low-cost LO_2 and LN_2 create a path to low cost LH_2 from small gasification projects with CCU

- The objective of this project is to develop an efficient, compact cryogenic air separation unit (ASU) for production of distributed, low-cost LO_2 and LN_2
- We hope to achieve this goal by replacing two of the three modules of an ASU with two innovative technologies:
  - Replace turbo-Brayton cycle air liquefiers with magnetocaloric liquefiers (MCLs)
    - ✓ Increase ASU energy efficiency by ~40% and decrease capex by ~25%
  - Replace conventional distillation columns with microchannel distillation columns (MCDs)
    - ✓ Reduce distillation footprint by ~10 times



- This presentation summarizes progress made during the past year (since May 2, 2022)

MOLS Prototype Update: Designed to cool from 270 K to 100 K and liquefy ~1 kg/day air at 100 psia



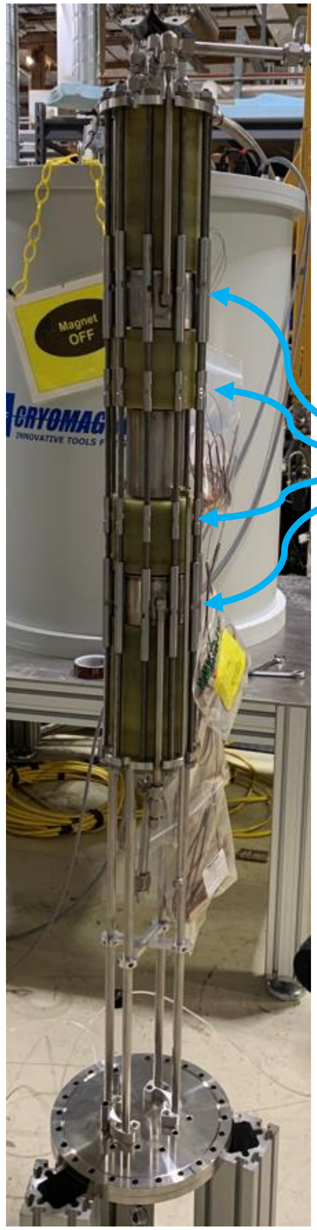
Drive shaft (not shown) is non-magnetic stainless steel (ss)

CHEX and axial support spacers are non-magnetic ss or G-10

Top and bottom passive regenerators for diversion flow are non-magnetic ss spheres

Non-magnetic region at bottom end

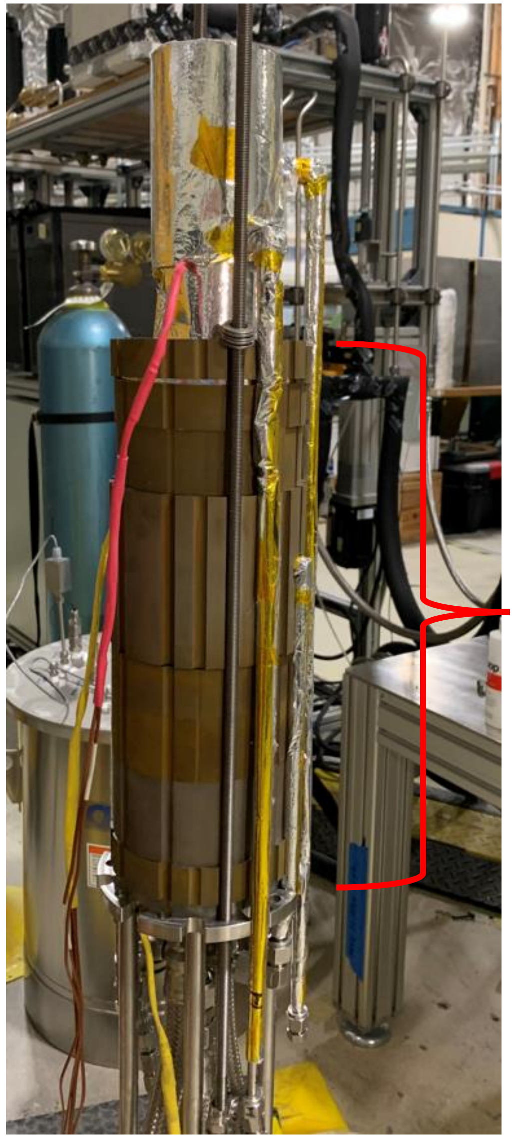
First Iteration w/ Force Balance Rods



Soft Fe to balance forces and reduce AC losses

1st gen worked well in terms of force balance, but magnet heating prevented target cycle frequency of 0.25 Hz

Second Iteration w/ Flux Balancing Exoskeleton



2nd gen uses low carbon steel to fill in gaps in magnetic signature; still saw magnet heating that prevented 0.25 Hz

Plan to modify MOLS assembly to include SS shell to eliminate leaks; critical for propane as HTF

SS shell used in hydrogen liquefier

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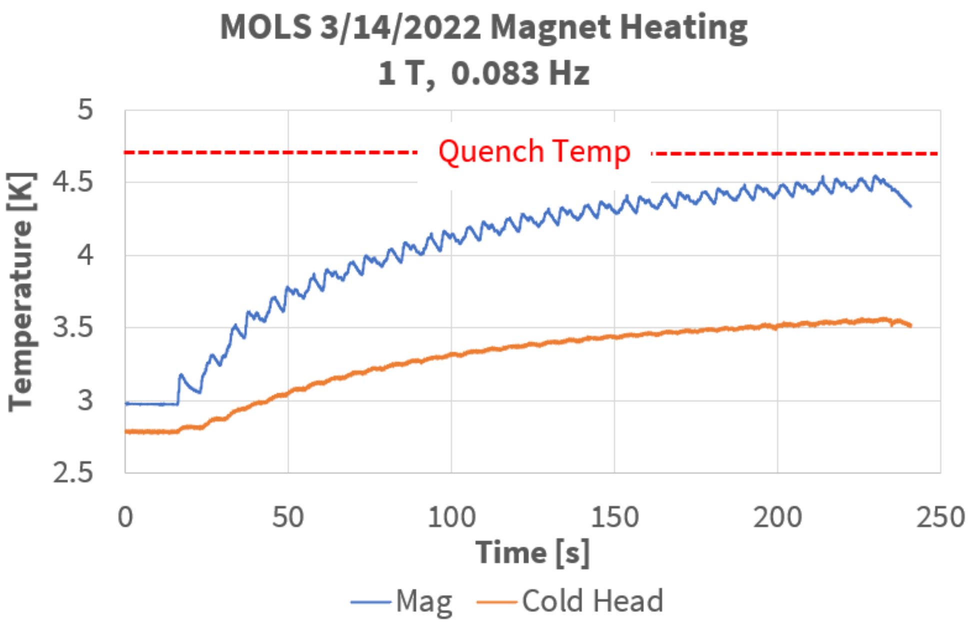
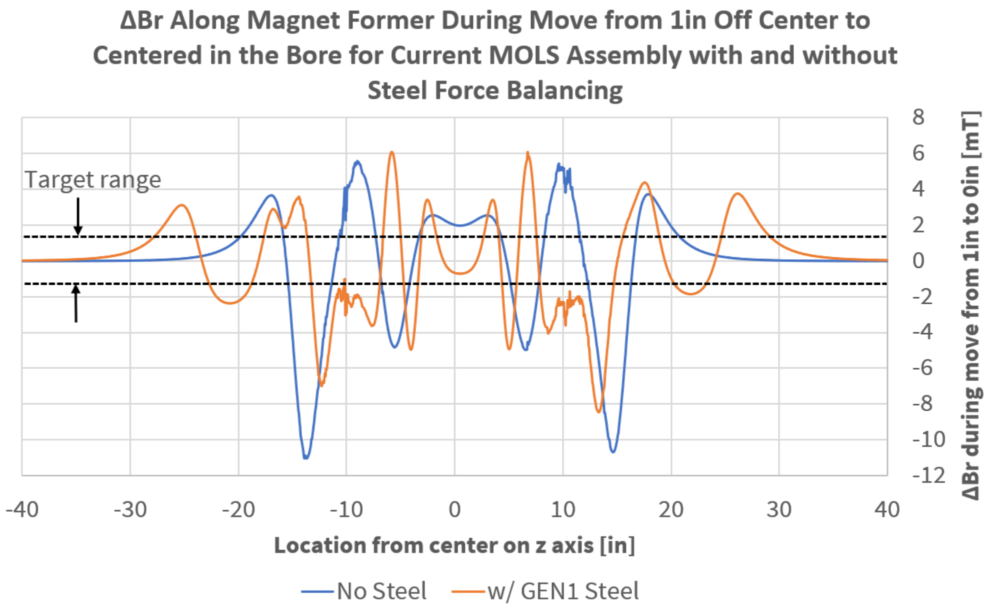
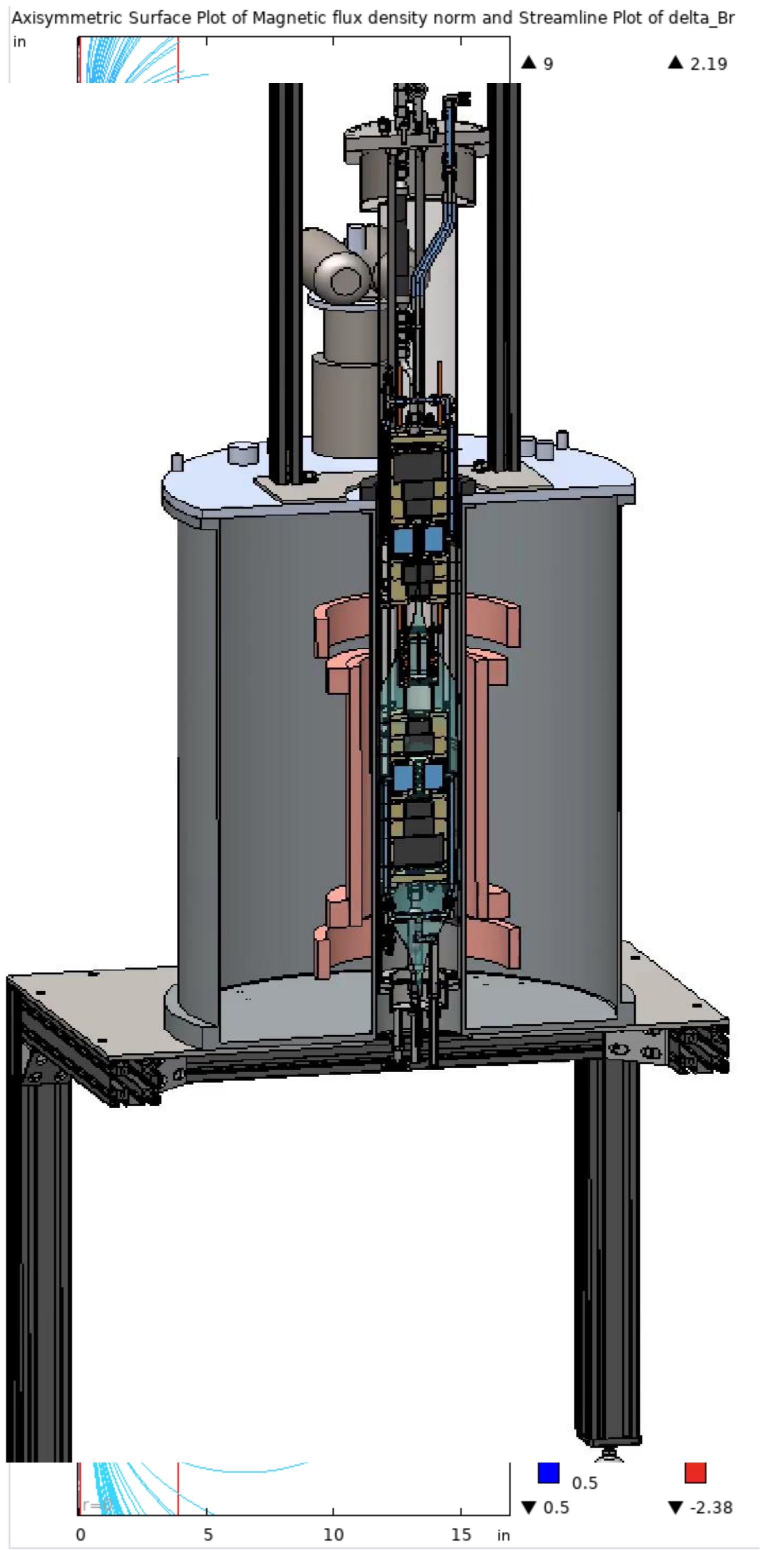
Analysis of results and simulations revealed there are two sources of magnet heating in reciprocating designs

- AC losses are caused by changes in the current in the persistent mode magnet coil to keep the flux density B constant when the magnetization M of objects that move through the bore change where: $B = \mu_0(H + M) = Const.$
- Changes in radial magnetic flux density vector orientations induce eddy currents in magnet structures due to Faraday's Law: $\varepsilon(emf) = -N\frac{d\Phi_B}{dt}$
- Latest tests at 0.25 Hz indicate 5.4 W of magnet heating due to AC losses and eddy currents. At 0.083 Hz, the cryocooler can keep up with eddy current heating. At this lower frequency, MOLS' cooling capacity during start up is too small.
- Force balance and magnetic flux density uniformity issue has been solved which limits both AC and eddy current losses.







A simpler 2-stage rotary MCL overcomes limitations of reciprocating regenerator prototype

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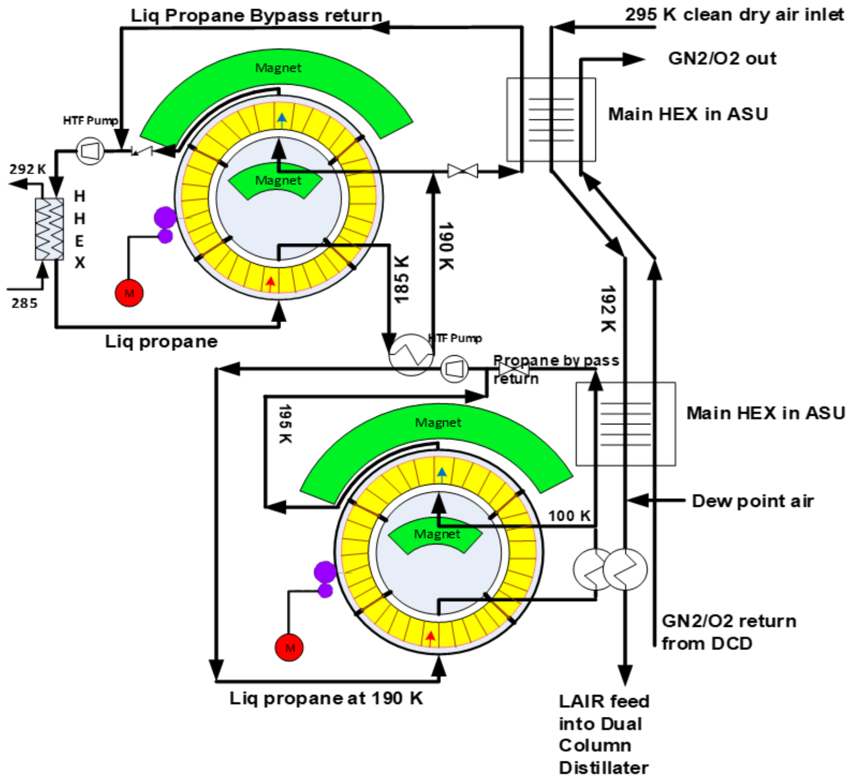
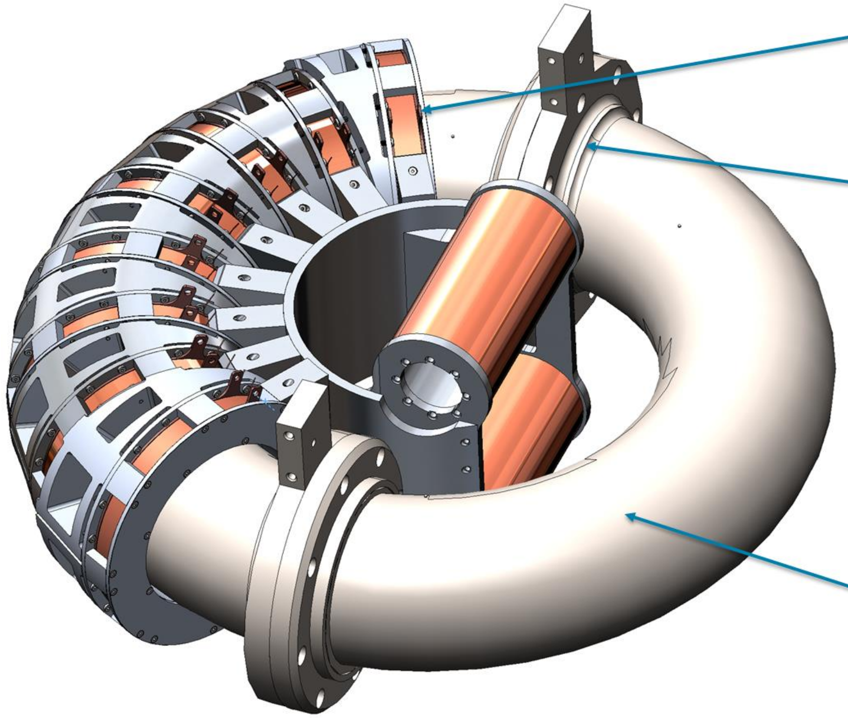
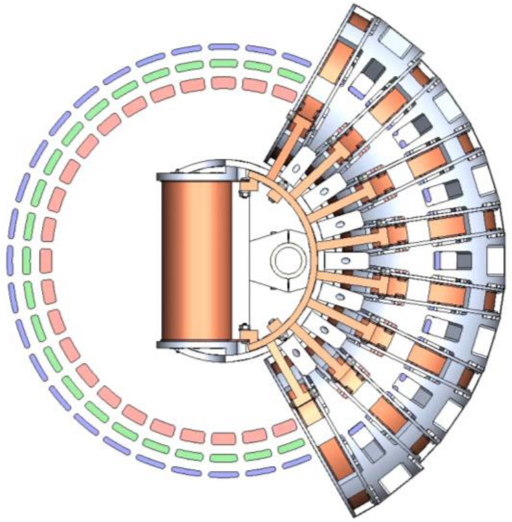
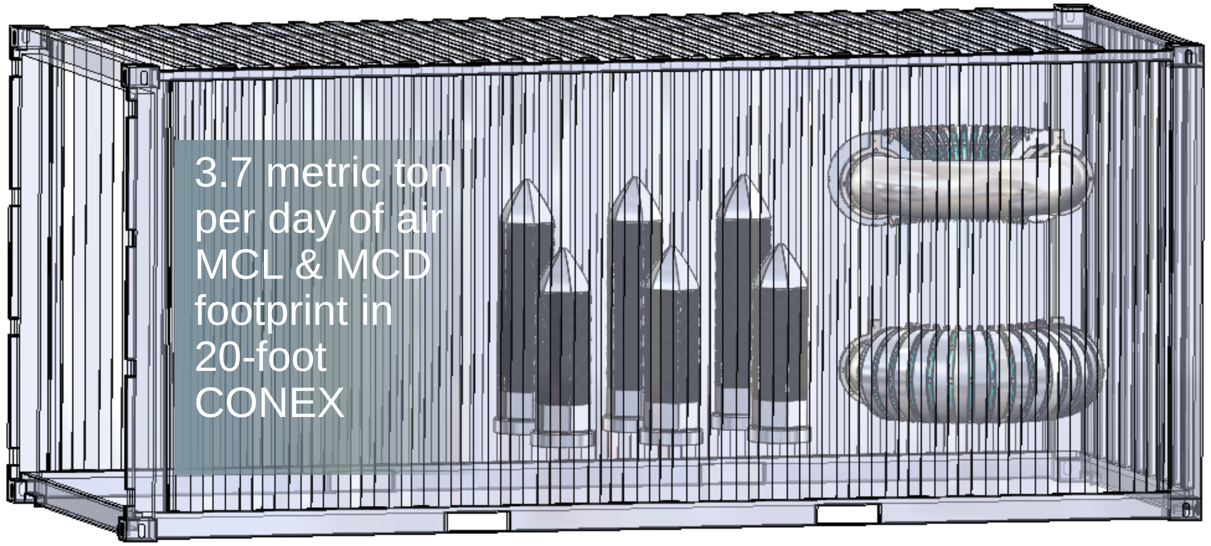




- 4 K conduction-cooled NbTi Partial Tokamak Magnet
- Split housing for assembly into the magnet
  - Filled with liquid propane at 200 psia
  - Low density filler around regenerator
  - HTF flow ports for circulating liquid propane
  - Drive feedthrough
  - Instrumentation feedthrough
  - Adjustable bearing supports
  - Controllable diversion flow channels from demagnetized to magnetized regenerator
- Regenerator mounted into frame in sections to assemble rotating wheel



Propane pump tested and ready



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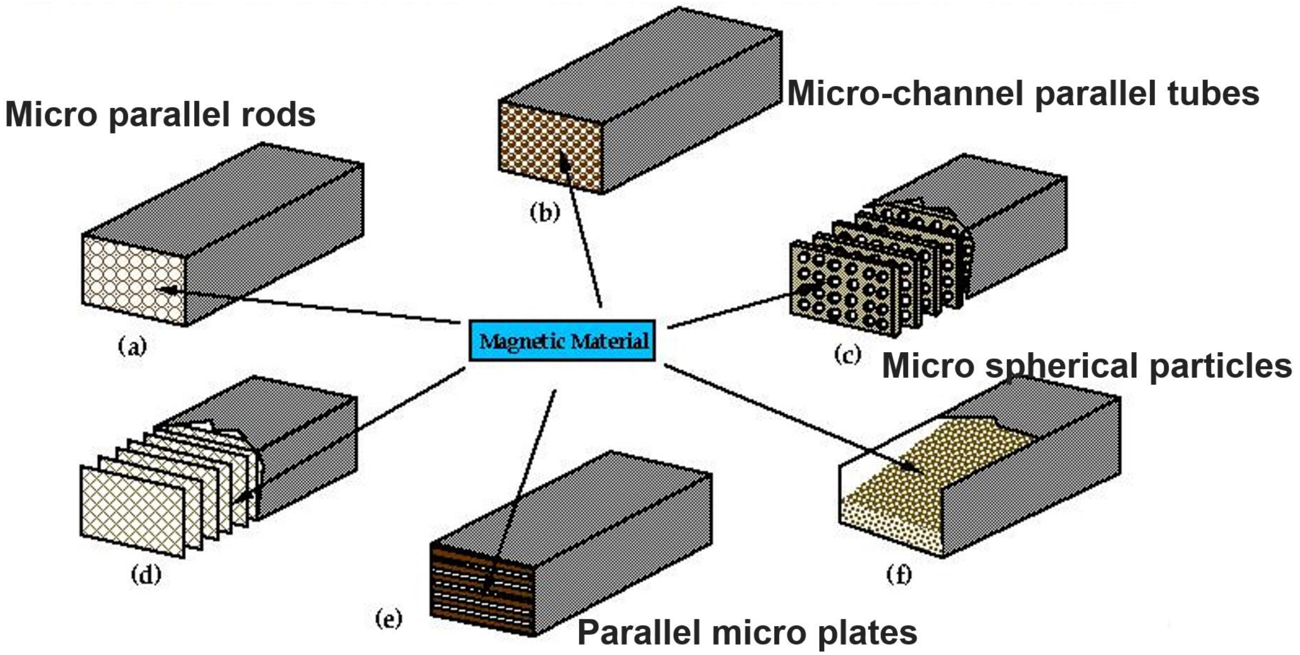
Need to reduce irreversible entropy creation to increase magnetic regenerator efficiency at 1 Hz

$$\mathrm{FOM} = \frac{\dot{W}_{Ideal}}{\dot{W}_{Real}}$$

$$\dot{W}_{Ideal_{Layer}} = \dot{Q}_{C_{Layer}} \left(\frac{T_H}{T_C} - 1\right)$$

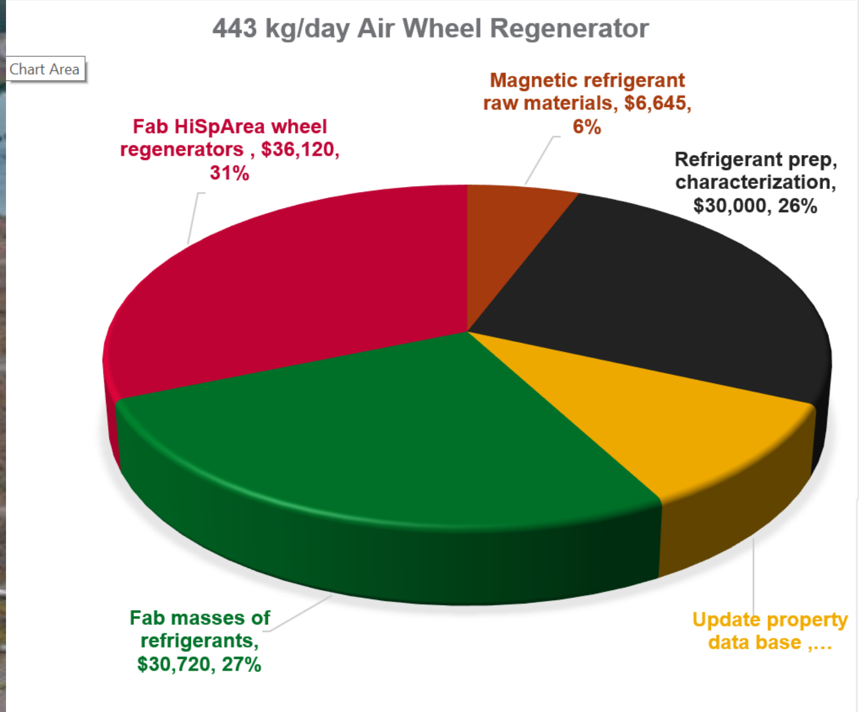
$$\dot{W}_{Real} = \left(\dot{Q}_{CHEX} + \dot{Q}_{LC} + \dot{Q}_{Para}\right)\left(\frac{T_H}{T_C} - 1\right) + T_H * \Delta\dot{S}_{IRRTOTAL}$$

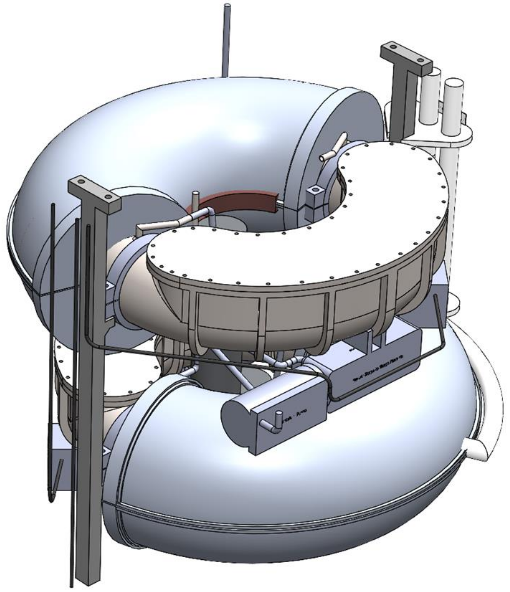
$$\Delta\dot{S}_{IRRTOTAL} = \Delta\dot{S}_{IRR_{HT}} + \Delta\dot{S}_{IRR_{PD}} + \Delta\dot{S}_{IRR_{LC}} + \Delta\dot{S}_{IRR_{EC}} + \Delta\dot{S}_{IRR_{MX}}$$

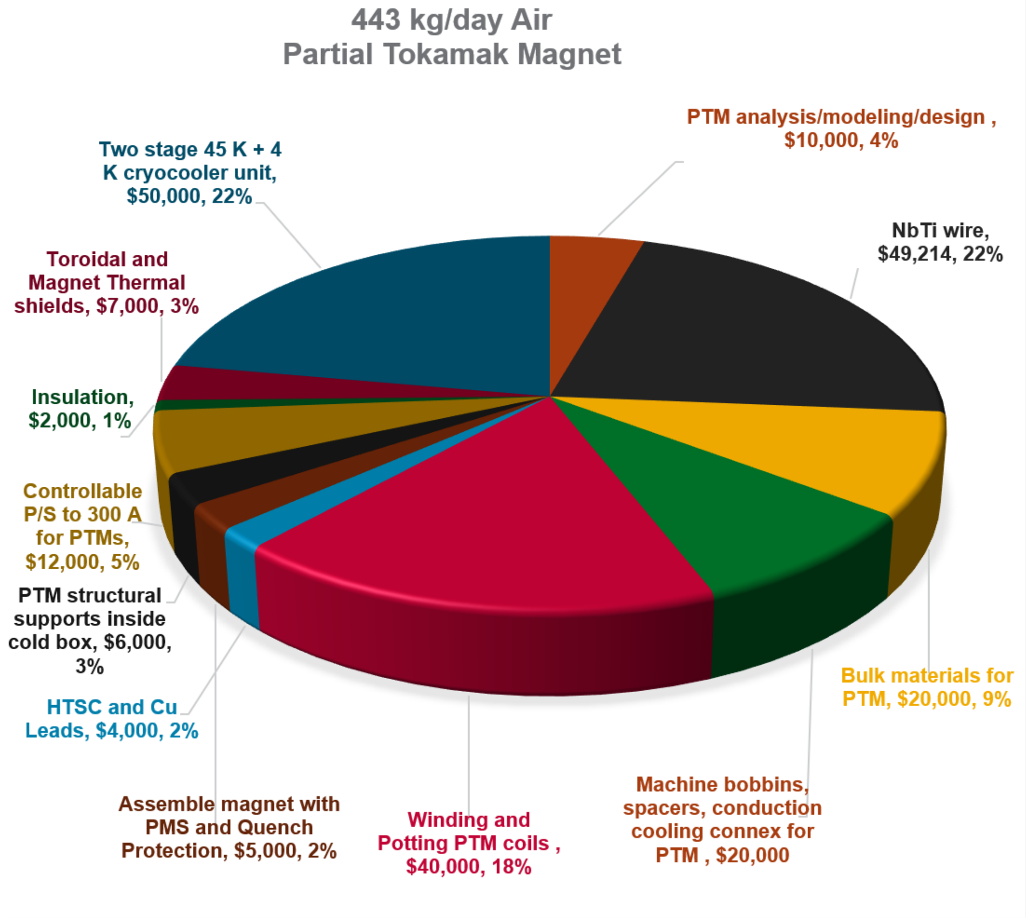


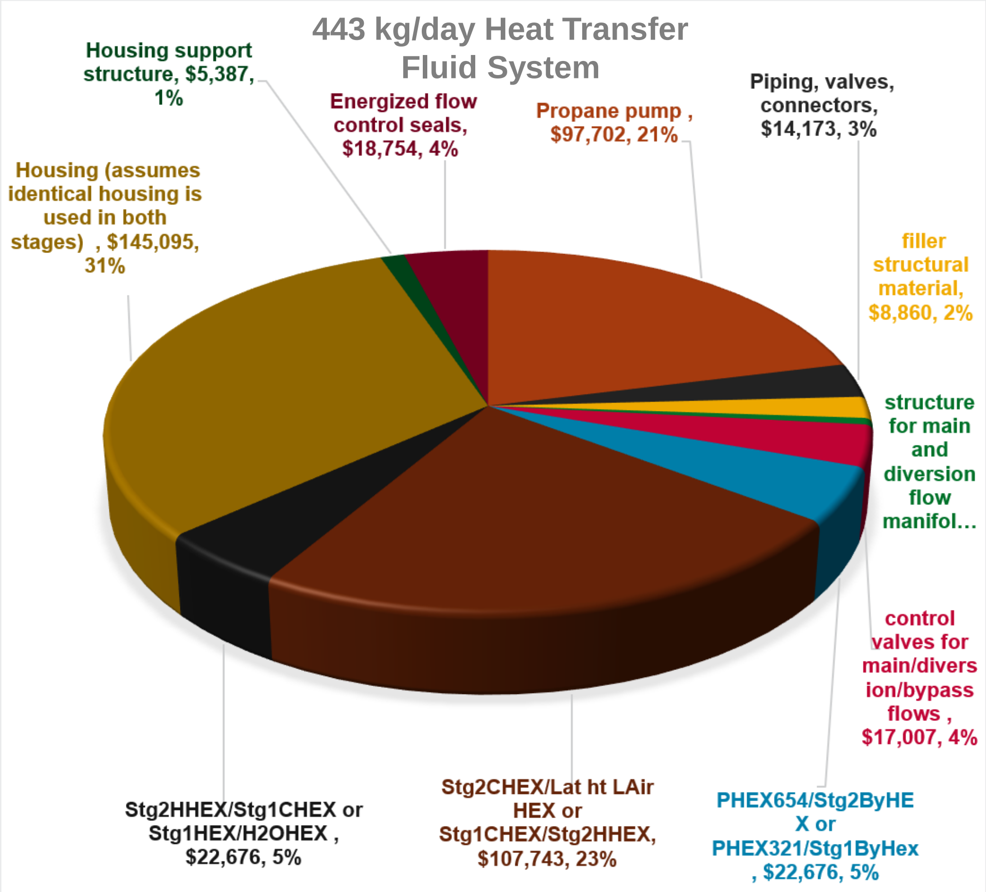
- Increasing frequency of MCL operation from ~0.25 Hz to 1-2 Hz increases specific cooling *power* of magnetic refrigerants by 4-8x $\dot{Q}_{Layer} = \dot{Q}_{HTF}$
- As specific cooling power increases, HTF mass flow rate through regenerators increases by 4-8x
- Regenerator analysis via entropy generation tools
- At 0.5 Hz, FOM with spheres peaks at 0.6
- Micro-channel parallel tube regenerators 1st choice
- Eddy diffusivity and pressure drop are less than for spheres
- Must develop methods to make microchannel regenerator geometries with rare earth alloys
  - Tape casting, hot iso-static, micro-extrusion, pressing, additive manufacture and other methods in oxygen-free environment

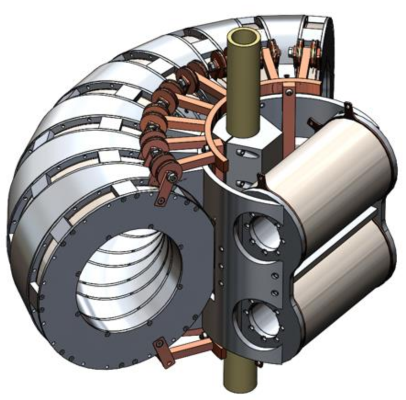
Techno-Economic Analysis Results for MCL Subsystems for 443 kg/day air

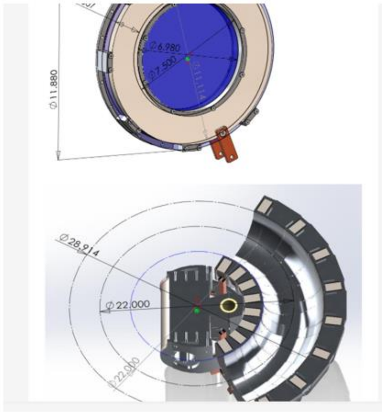




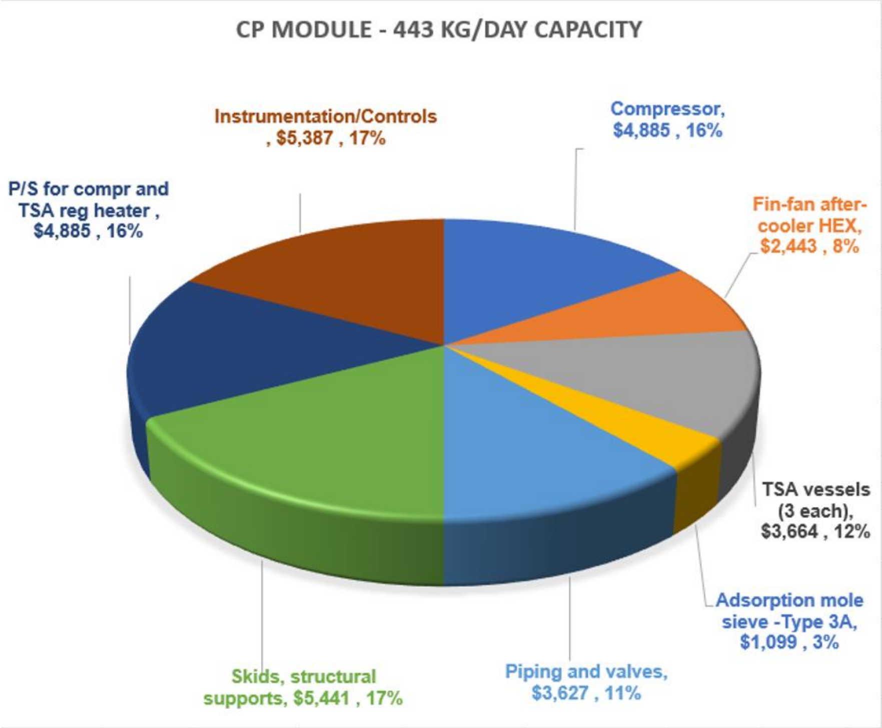


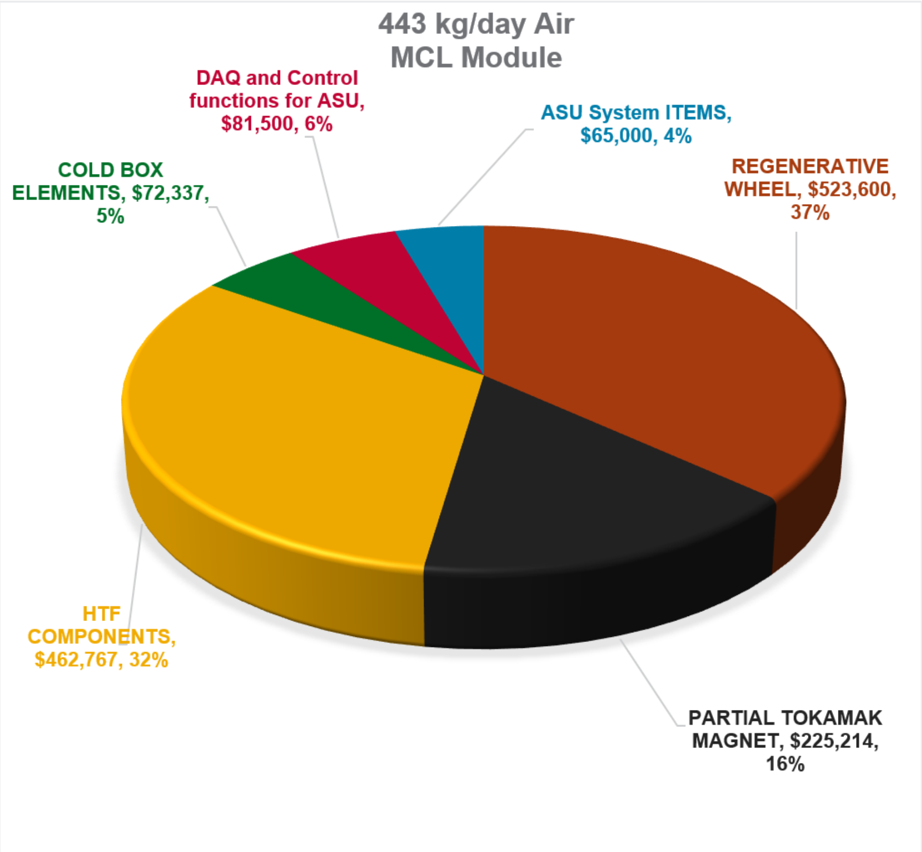


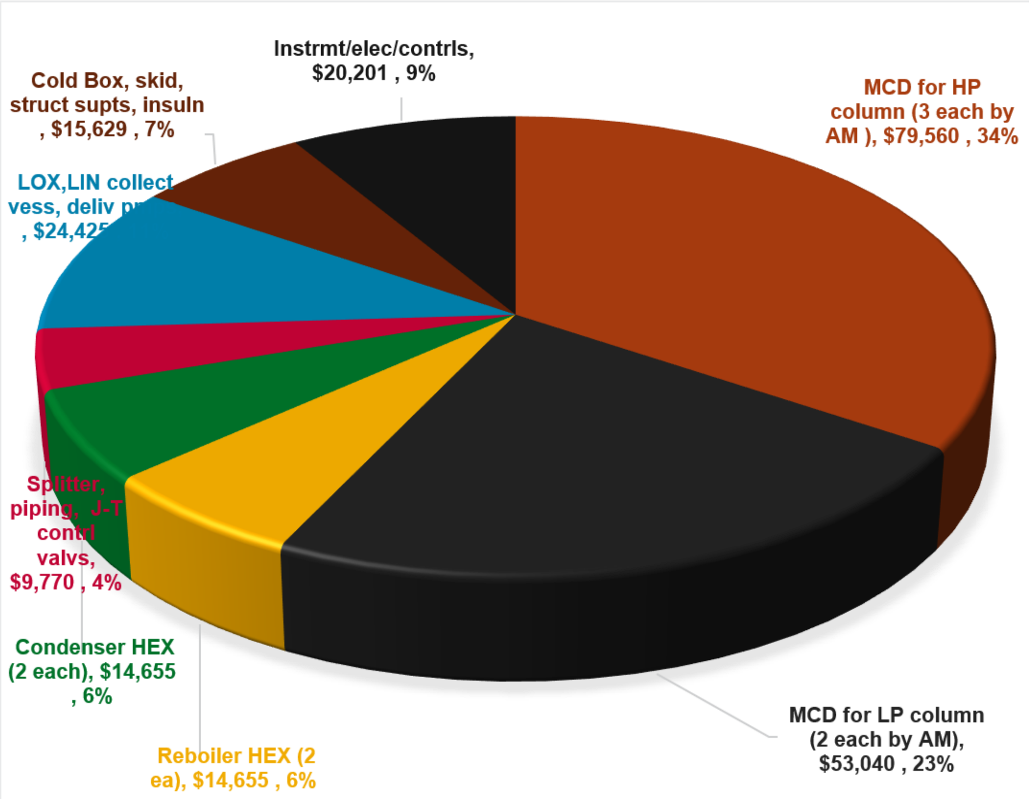




TEA Results for Integrated CP-MCL-MCD ASU







Distillation Module with MCD columns
443 kg/day of liquid air to LOX and LIN

R. Cornelissen & G. Hirs, Energy Conv. Mgmt. 39, 821 (1998)

Module	Energy input by module (conventional) %	Conventional ASU module % Efficiency	MCL/MCD ASU module % Efficiency
Comp/purifier	31%	48	48
Liquefier	58%	25	60
Distillation	10%	46	50

Integrated Air Separation Unit	Compressor-TSA Purifier Module	Magnetic Liquefier Module	Dual MCD distillation module	CAPEX TOTAL	Input power for ASU (kW)	ASU prdtn rate of LO2 (kg/day)	ASU prdtn rate of LN2 (kg/day)	Cost/day of energy	Cost/kg of cryogen ($/kg)
100 kg/day air	$15,950	$722,199	$114,000	$852,149	1.41	12	36	$3.39	$0.071
443 kg/day air	$31,431	$1,440,418	$231,935	$1,703,784	5.85	53	159	$14.03	$0.066
3700 kg/day air	$90,092	$5,511,732	$670,573	$6,272,396	47.94	444	1,332	$115.06	$0.065

Summary

- **MCL with MCD increases ASU energy efficiency by ~40% and decrease capex by ~25%**
- **AC losses and eddy current heating associated with reciprocating design have been solved, but are complex for high efficiency at high frequency**
- **Rotary AMR design eliminates flux uniformity issues, work recovery is built into force imbalance during rotation enabling high frequency (1-3 Hz) and high efficiency (FOM 0.6)**
- **Major risks associated with magnet, rotary seal, and fabrication are being addressed**

Next steps:

- Develop and demonstrate operational efficiency and scalability of small scale ASU for gasification of biomass/waste/methane for liquefaction of hydrogen
- Collaborate with energy company with FEED, EPC, Install/Operate experience to develop ASU to validate capex, efficiency, and overall project economics necessary to license PNNL IP to industrial clients
- PNNL to focus on tasks that reduce technical and cost risks:
  - Simulate heat transfer and HTF flow dynamics for design of more efficient regenerators
  - Investigate best fabrication methods for new regenerator geometries
  - Explore additive manufacturing of various components of ASU subsystems
  - Perfect effective flow control seals in rotary system

PNNL formulated refrigerants

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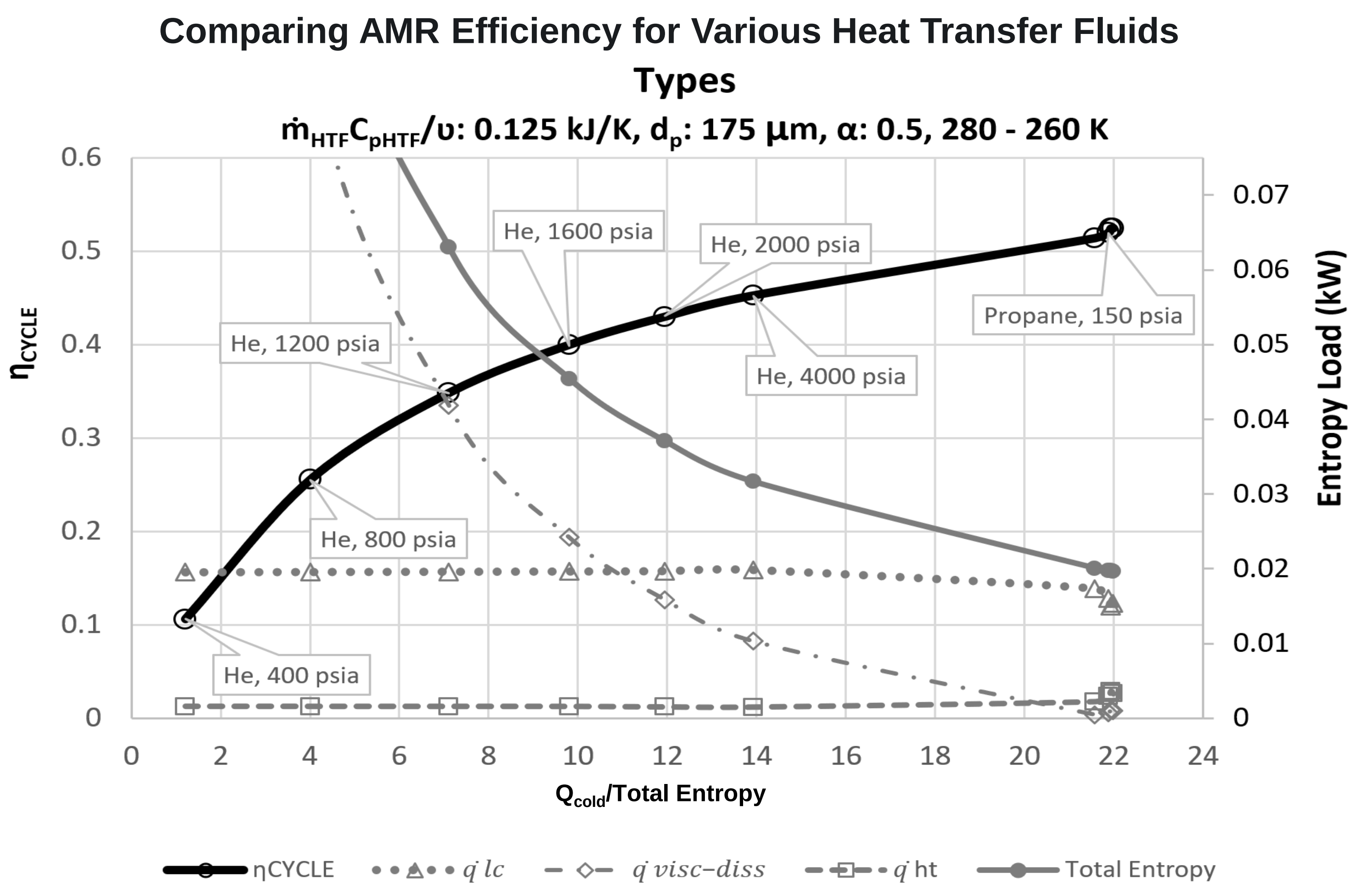
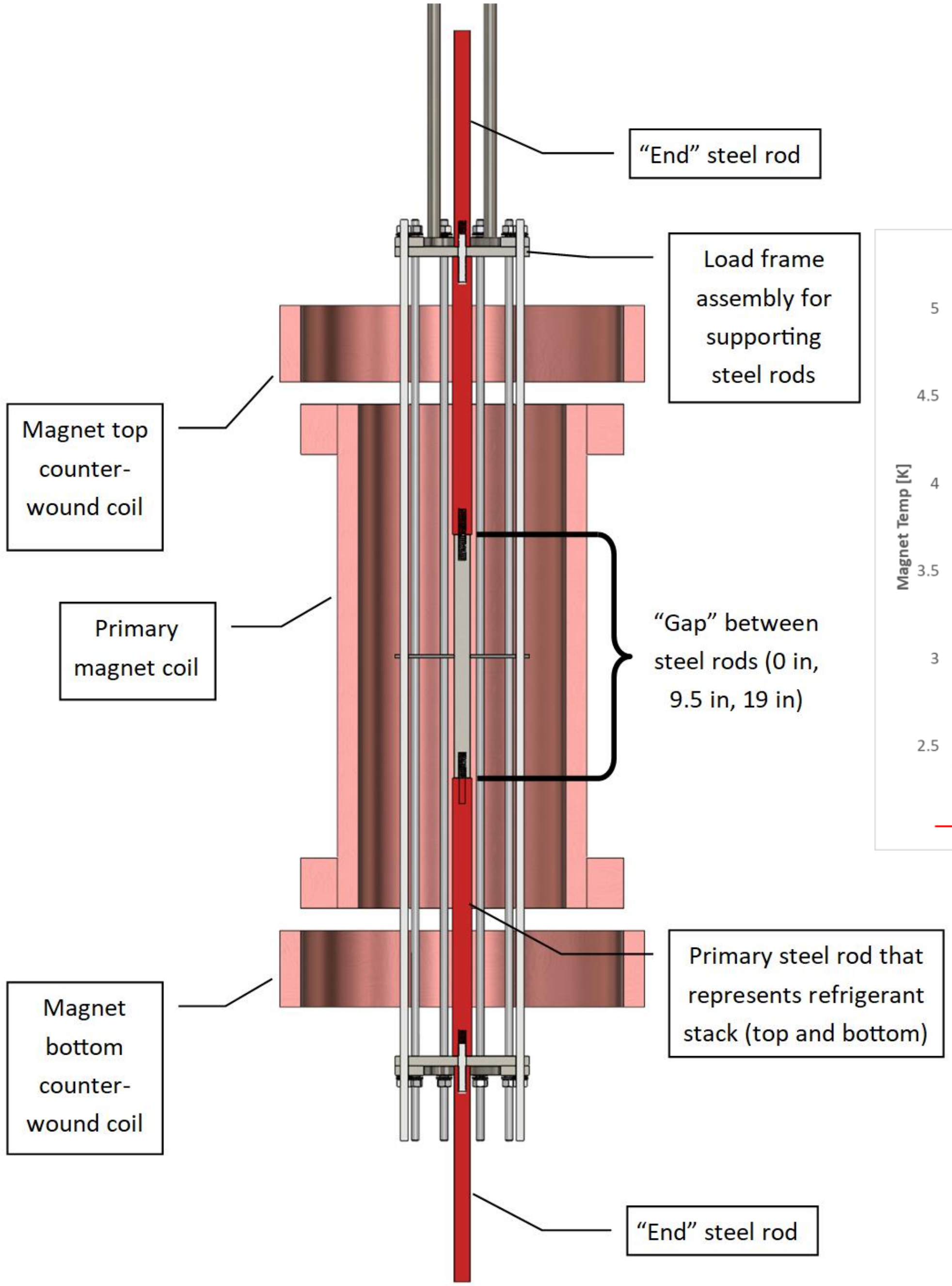
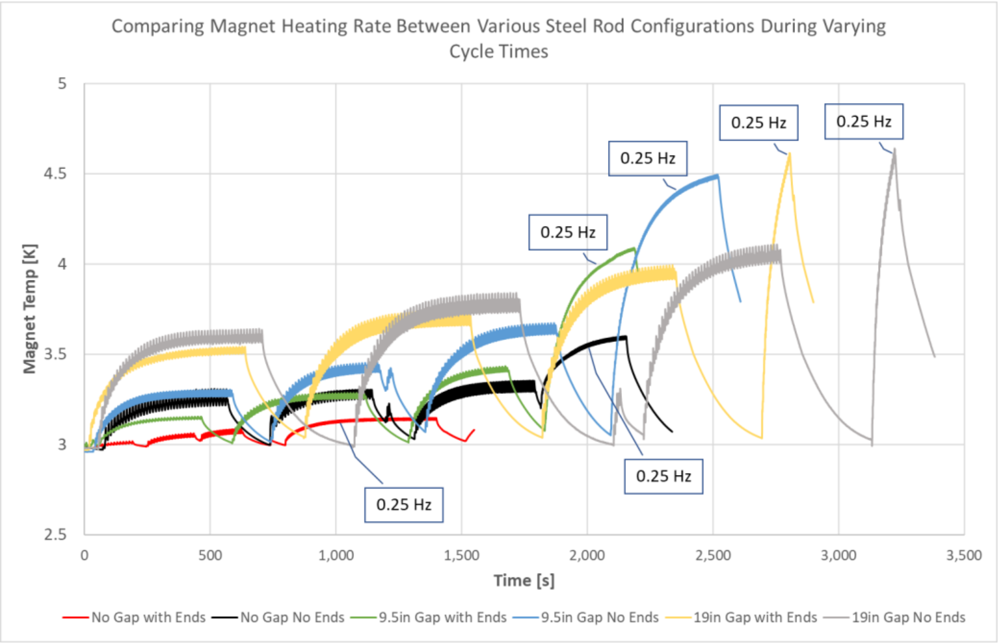
Thank you

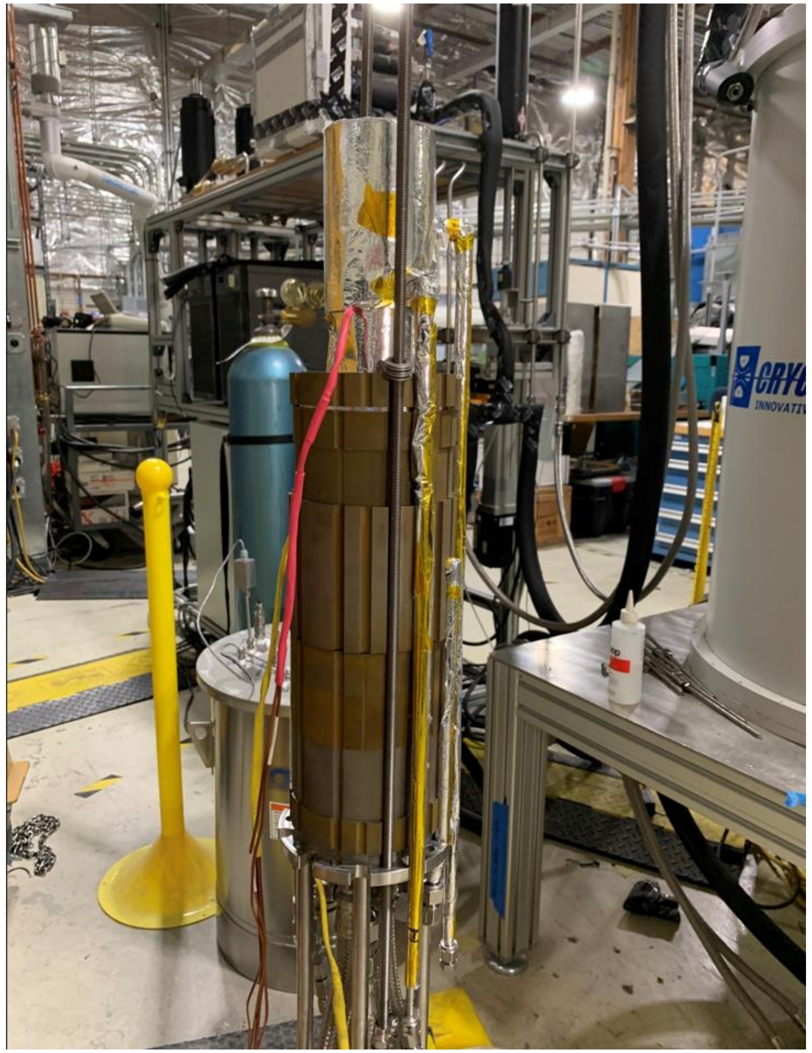
High Density HTF



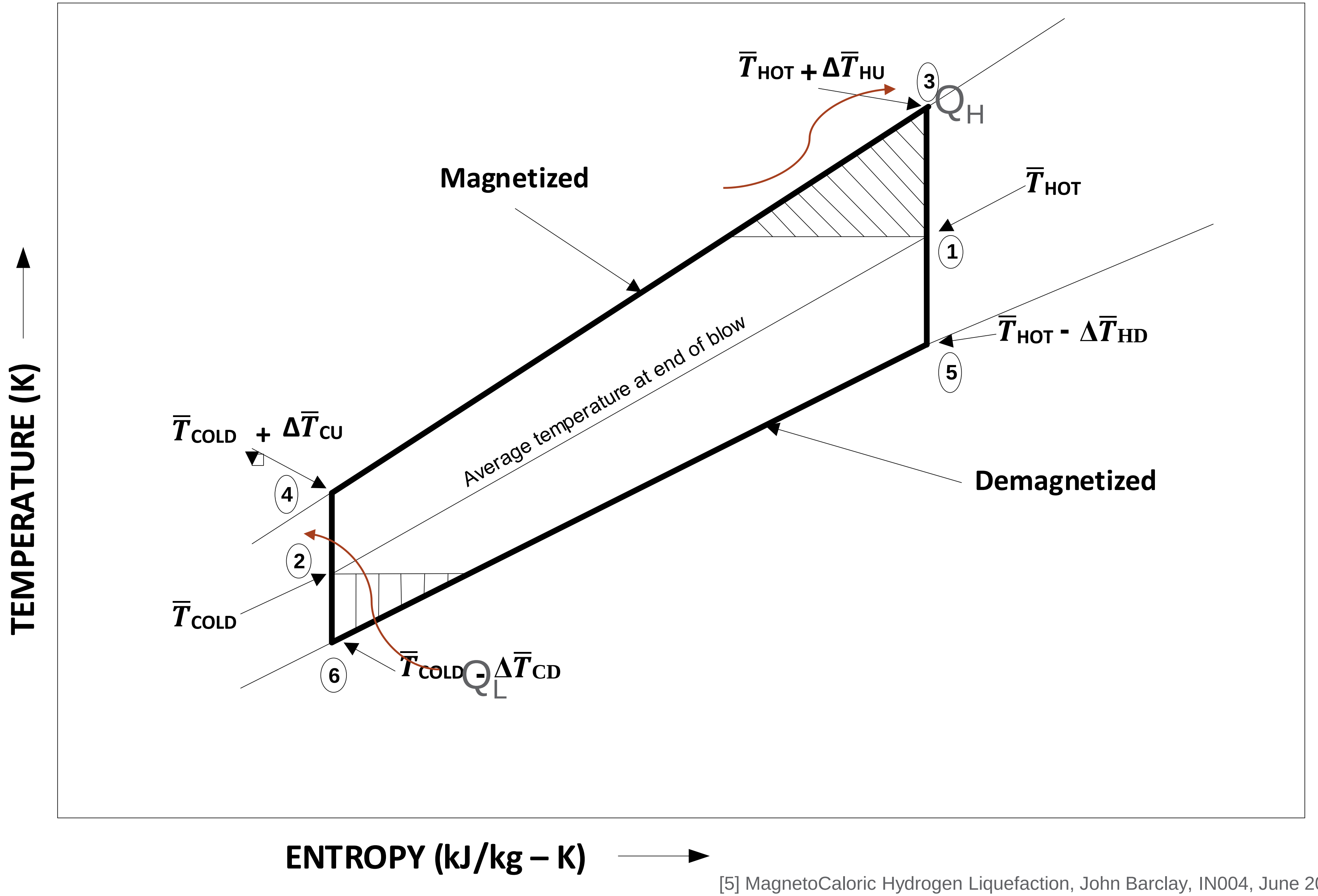
Results from Steel Rod Experiments Applied to MOLS via Steel Exoskeleton





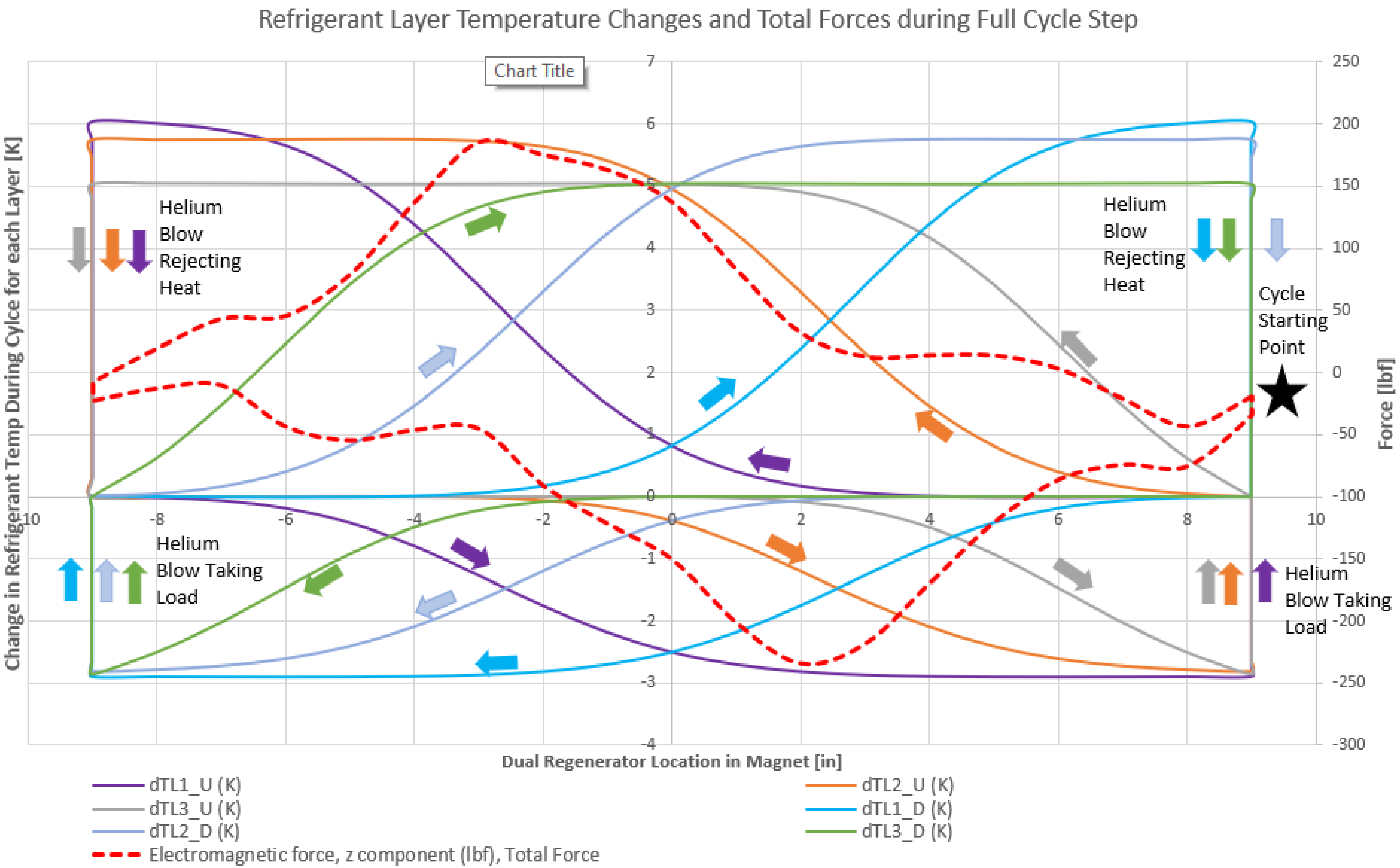


Active Magnetic Regenerative Refrigeration Cycle (AMRR/L)



[5] MagnetoCaloric Hydrogen Liquefaction, John Barclay, IN004, June 2021
https://www.hydrogen.energy.gov/pdfs/review21/in004_barclay_2021_o.pdf

Comparing thermodynamic models to magnetic models to experimental data for work input



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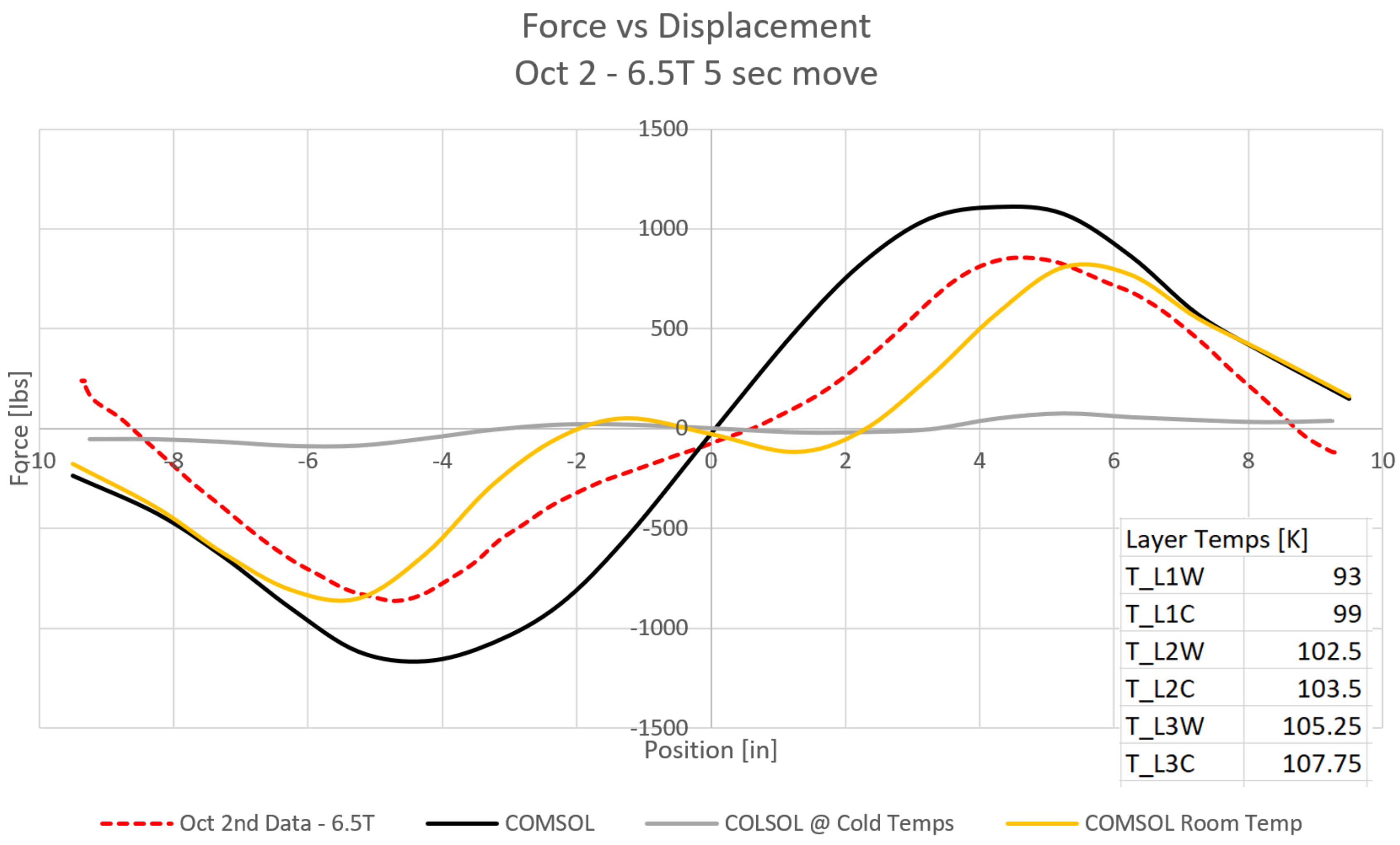

Layer Temps [K]	
T_L1W	93
T_L1C	99
T_L2W	102.5
T_L2C	103.5
T_L3W	105.25
T_L3C	107.75