



MAGNETOCALORIC HYDROGEN LIQUEFACTION

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Pacific Northwest National Lab
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2023 Annual Merit Review and Peer Evaluation Meeting
AMR project **IN004**

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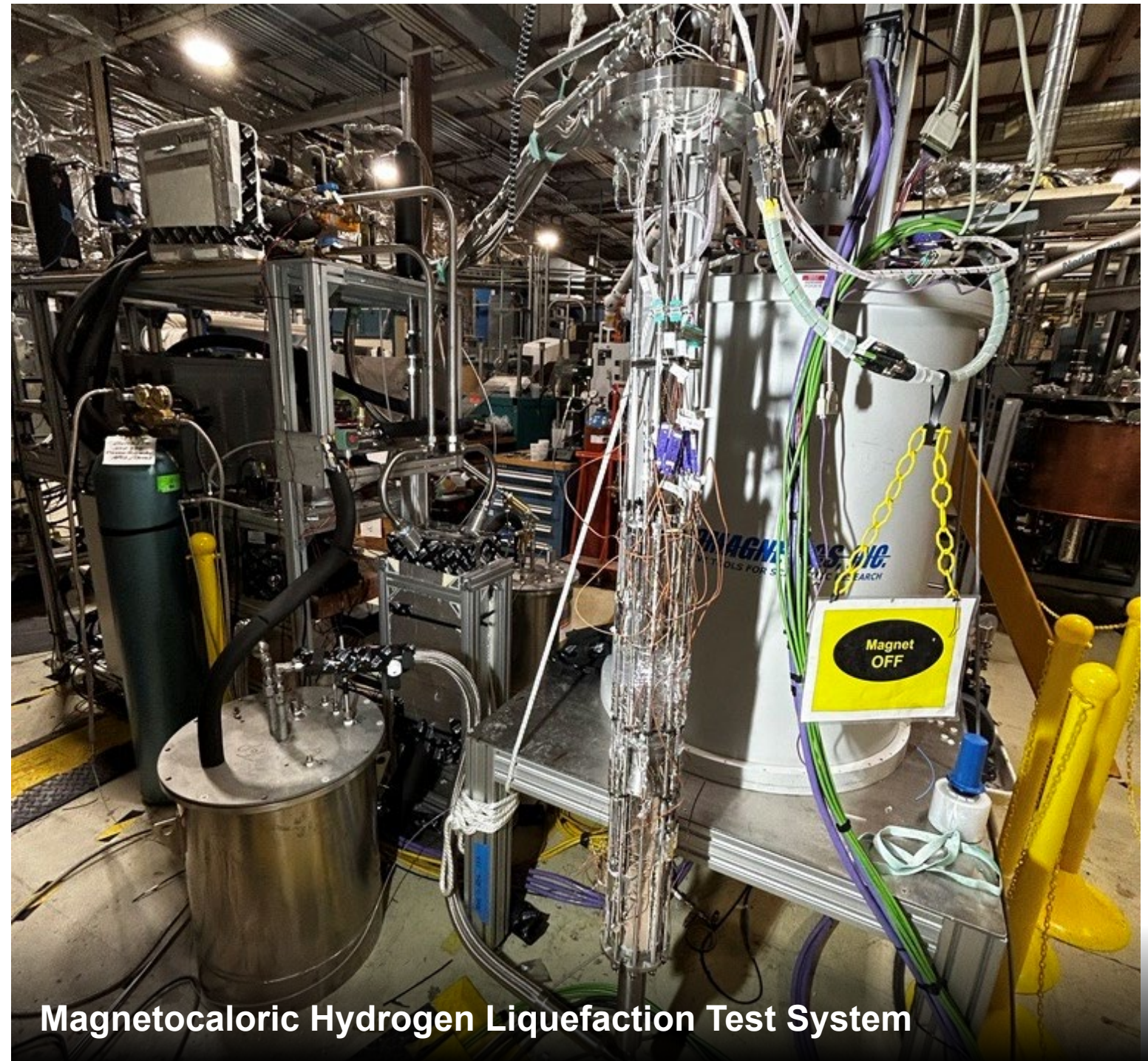




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Project Goal

- The overall project objective is to develop active magnetic regenerative liquefiers (AMRLs) which are ~60% more efficient than and ~20% less expensive than state-of-the-art liquefiers. This means we have to:
 - Prove AMRLs liquefy H₂ efficiently and cost effectively
 - Provide sufficient technical and financial information to industrial decision makers who might consider use
 - Design next 295 K to 20 K AMRL for 3 tonne/day with collaborative partner
 - Enable lower cost LH₂ in the production, storage, transport, and deliver supply chain for truck, rail and marine big-fuel customers



Magnetocaloric Hydrogen Liquefaction Test System

Overview

Timeline and Budget

- Project Start Date: 10/1/2015
- Project End Date: 9/30/2023*
- FY22 DOE incremental funding: \$145 k
- Total DOE funds received to date: \$4.20 MM

*Project continuation by DOE under NCTEs to 9/30/23 due to COVID, vendor, test facility, and technical delays.

Barriers addressed

- Low Hydrogen Liquefier Efficiency
- High Liquefier Capital Costs

Partners

- Co PI-Iver Anderson - AMES Lab
- Co PI-Jun Cui - Iowa State University



We intend to develop highly efficient liquefiers with reduced capital costs that meet DOE targets

Impact

30 tonne/day (small-scale facility)	LN ₂ - Claude cycle (state-of-the-art)	PNNL's MCHL project (AMR cycle)	DOE Target (2020) ¹
FOM (a measure of liquefier efficiency)	0.33 [1.0 is ideal]	0.50 (3 tonne/day)** 0.60 (30 tonne/day)	0.35
Installed Capital cost	\$70 MM ¹	\$49 MM (30 tonne/day)	<\$70 MM
Annual O&M cost	4 % of installed \$	2.8 % of installed \$?
Energy input	12 ¹ kWh/kg H ₂	6-7 kWh/kg H₂	12 kWh/kg H ₂

(¹ see DOE Hydrogen Plans) - specific power depends upon input conditions of GH₂

Highly efficient liquefaction for H₂ is a critical domestic and global need

Impact

- Low cost LH₂ is necessary to achieve to \$1-2/kg target of Hydrogen One Shot for transportation sector
- Hydrogen is most energy-intensive gas to liquefy (starting conditions of GH₂ are important)
 - (14 MJ/119 MJ)/0.35 => 34% of energy content of H₂ used to make LH₂ (at standard conditions)
 - Doubling liquefier efficiency has game changing impacts
- **Magnetocaloric liquefiers (MCL)** have been developed to meet this need
 - Replace gas compression/expansion by magnetization/demagnetization
 - Magnetic field dependent heat capacity of ferromagnetic refrigerants increases efficiency by ~15-20%
 - Adaptive liquefaction rate by varying frequency from ~0.25 Hz to ~1-2 Hz
 - Efficiency comes via minimizing entropy generation in magnetic regenerator design and operation
 - Scales well to ~1-3 metric ton/day for distributed production of LH₂
 - Eliminates high transport cost of LH₂ from large-scale liquefiers
 - Modular to grow with demand from 1-3 metric ton/day to ≥ 30 metric ton/day
 - Versatile – not as constrained by T_{HOT} or T_{COLD}
 - Creates large market for U.S. superconductor wire and magnet manufacturers
 - Niche market economic analysis results are attractive



Make and demonstrate high efficiency liquefiers of cryogenes that confirm model predictions

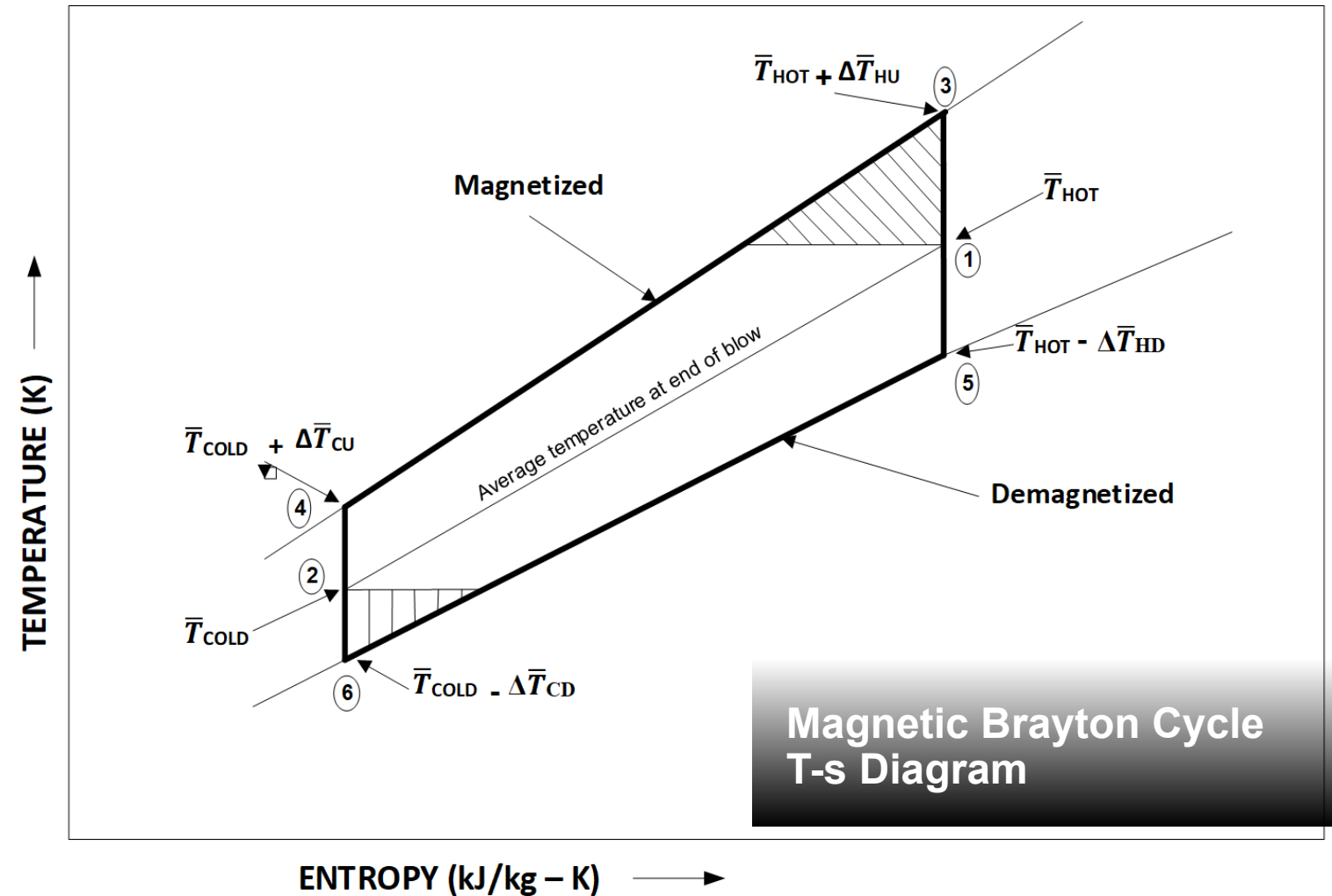
Approach

- Analyze, design, build, and test experimental AMRL prototypes to meet well-defined design basis
- Use **multiple** powerful computational tools to simulate detailed performance before cutting metal
 - COMSOL Multiphysics with AC/DC, Structural, Heat Transfer, and Fluid mechanics modules
 - MathCAD Prime 9.0, FORTRAN, and Excel for performance model calculations used to determine how design choices required to achieve highly efficient design
 - Detailed thermomagnetic, transport, physical, and thermal property data base validated by measurements and literature
 - REFPROP, Solid Works, Visio Pro, Teams, LabVIEW and related tools
 - Measure temperatures, mass flow rates of fluids, pressures, frequency, magnetic forces, magnet current, chiller temperatures, axial position, linear actuator positions/speeds, flammable gas detectors, flame detectors, vent/purge system for H₂ supply/disposal.
 - Acquire lots of precise data with LabVIEW DAQ program as it controls operation during different experiments.
 - Analyze results and compare to predicted performance; e.g., measure heat rejected, and heat absorbed by the MCL to obtain real work rate (difference of heat flow rates) which can be divided by ideal work rate to experimentally obtain FOM.
- Update techno-economic analyses to refine AMRL capital costs
- Capture IP and communicate results via quarterly reports, annual reviews, and peer review papers
- Collaborative outreach toward technology transfer via licensing agreements [technology is at TRL 4-5]

MCHL Efficiency determined by active magnetic regenerator design choices

Approach, cont.

- Calculate optimum ferromagnetic refrigerant layers for liquefier temperature span
- Choose efficiency-optimized magnetic regenerators during design (ΔS_{irrev})
- Create proper heat transfer fluid flows to couple refrigerants to each other and to thermal loads and heat sink
- Use superconducting magnets with large ΔB in refrigerants for large ΔT
- Integration enables the efficient AMR cycle shown on T-S diagram



$$\dot{W}_{\text{realLayer}} = (\dot{Q}_{\text{CHEX}} + \dot{Q}_{\text{LC}} + \dot{Q}_{\text{Para}}) \left(\frac{T_H}{T_C} - 1 \right) + \frac{T_H \int_{T_C}^{T_H} \dot{\Delta S}_{\text{IRR}} dT}{\int_{T_C}^{T_H} dT}$$

Progress

Final assembly and initial tests of MCHL system occurred Oct. 2022

- Leak-tight assembly enabling high-vac (10^{-6} torr) and superinsulation barrier around liquefier to reduce parasitic heat leaks to ~ 0.5 mW
- 28 g He per flow steps of AMR cycle delivers pre-cooled helium heat transfer fluid to hot end of dual regenerators via positive displacement pumps at room temperature, a Tranter recuperative HEX, and two LN2 baths
- LabVIEW controlled 0.5 m reciprocating drive stroke length (0.5 m/s stroke velocity at for 0.25 Hz cycle speed) during magnetization/demagnetization steps of AMR cycle.

Heat transfer
fluid pump cart
(at room temp)

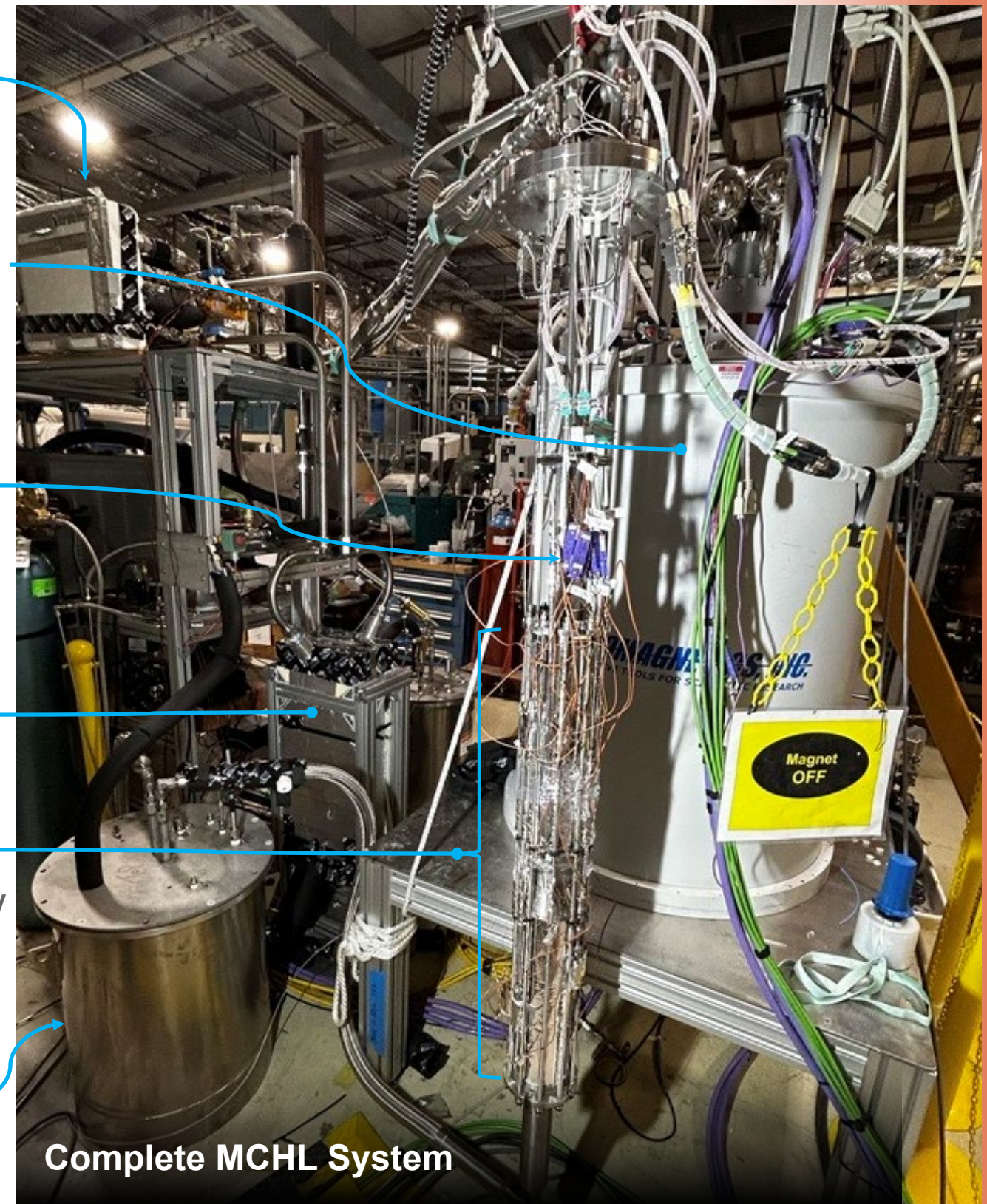
6.5 T solenoid
magnet

Thermocouple and
RTD sensors
located throughout
assembly

Tranter
Recuperative
HEX

3-Layer Dual-
Reciprocating
Magnetocaloric
Liquefier Assembly

LN2 Precooling
Bath (1 of 2)

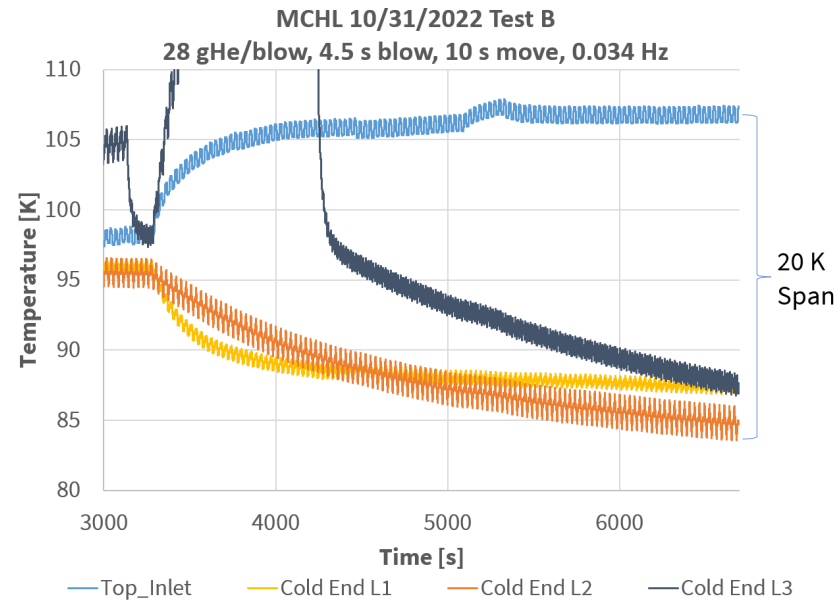


Complete MCHL System

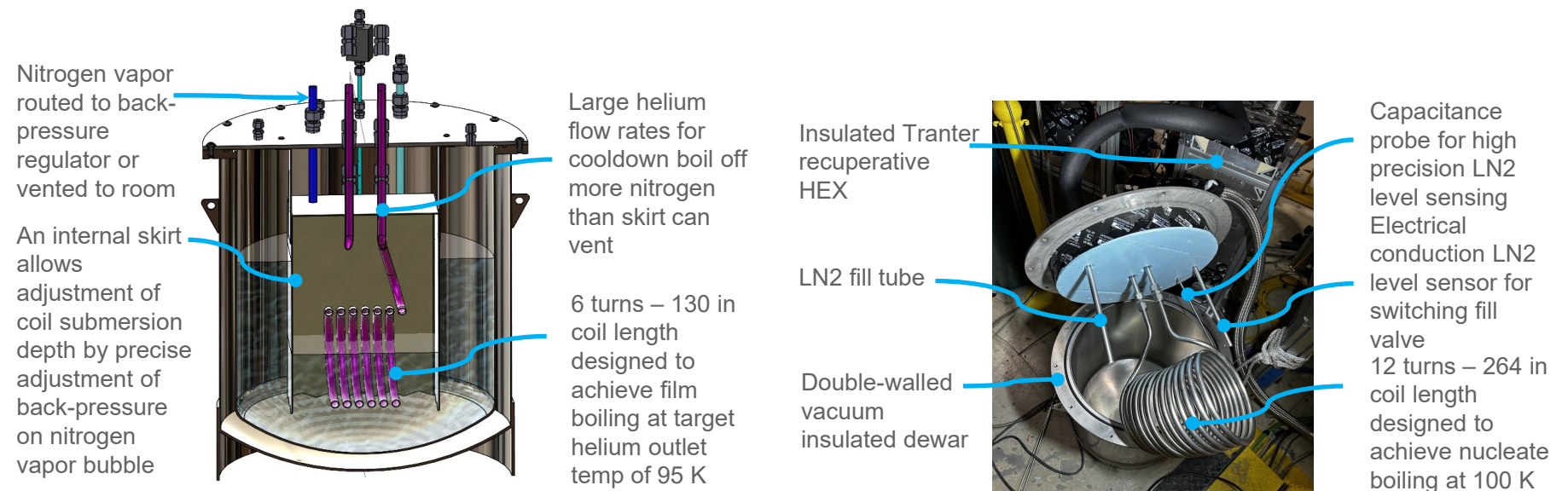
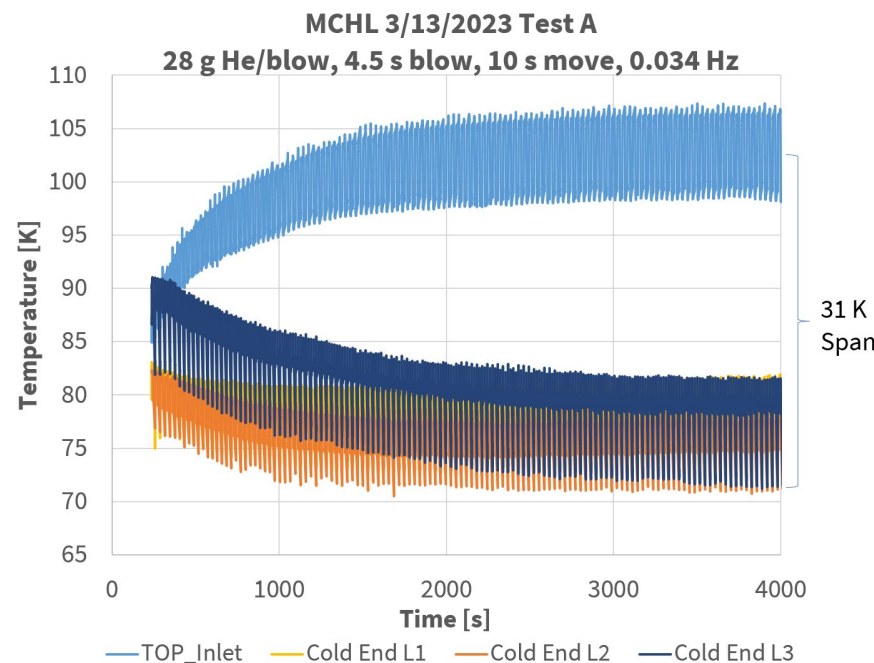


Initial Tests Show Active Cooling by First Layer Achieving 31 K Span – Validating $Gd_xNi_yCo_z$ and Effective Cooldown with Larger LN2 Pre-cooling Coils

Accomplishment



- 1.5 kg newly formulated $Gd_xNi_yCo_z$ refrigerant for first layer shows large magnetocaloric effect in 6.5 T field
 - Tests show first layer capable of rejecting 582 W of heat over 31 K span at 0.25 Hz
- October tests indicate need to modify LN2 pre-cooling coils for improved heat transfer for large 28 g helium flow
 - New coils fabricated and tested validated expected cooldown temperatures and heat rejection rates

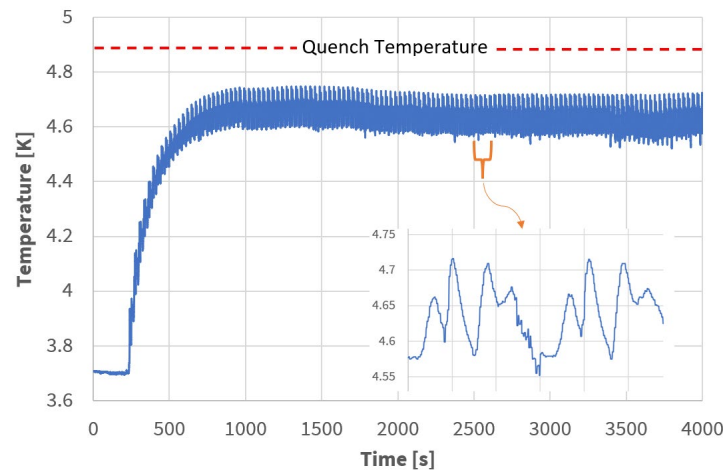


Thorough investigation of magnet heating during operation reveals two heat sources limit cycle rates in reciprocating designs

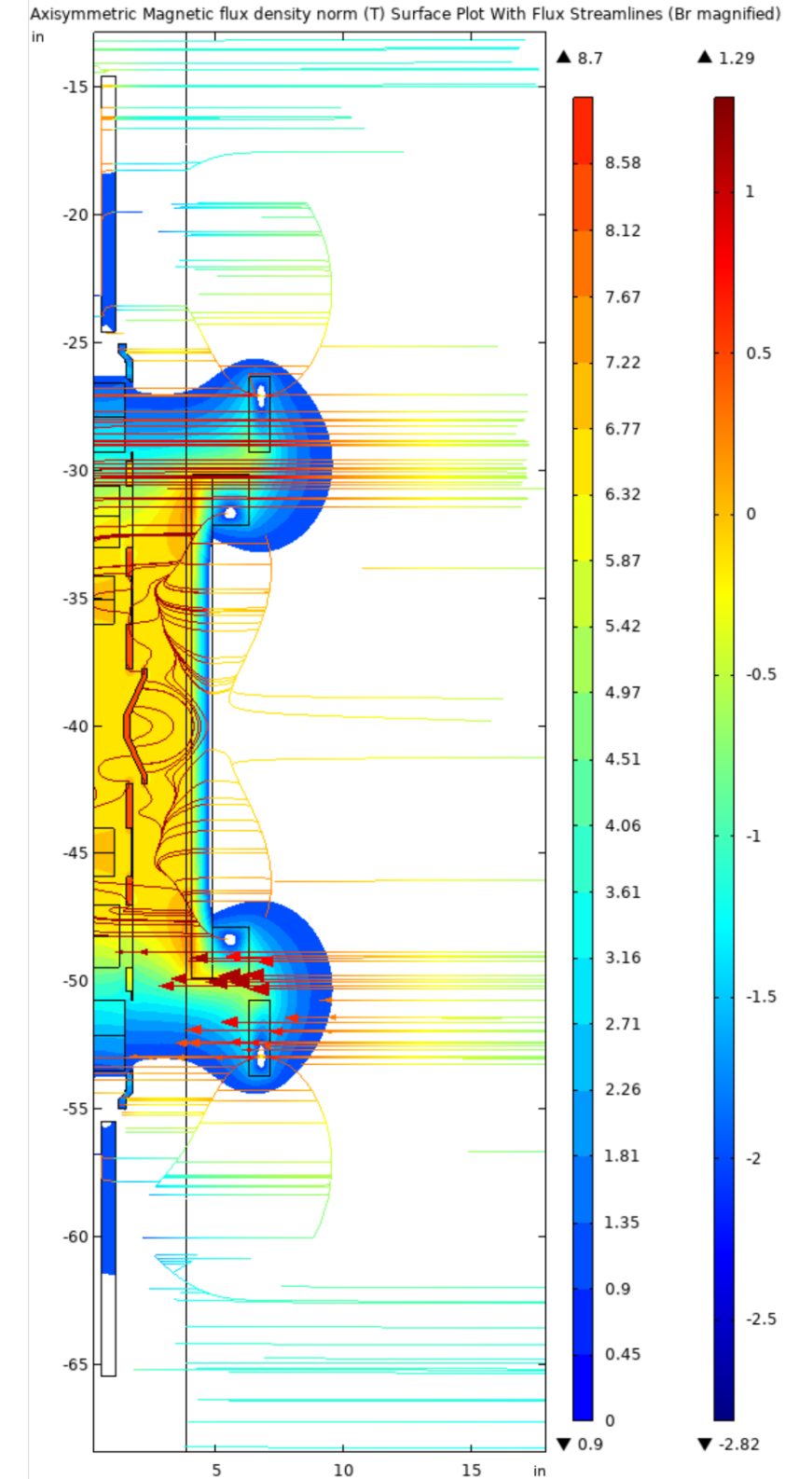
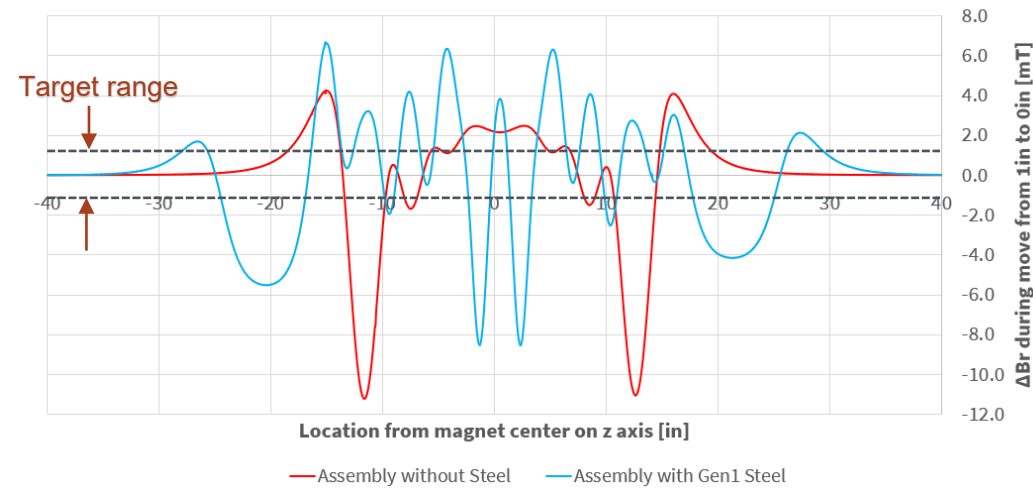
Accomplishment

- AC losses due to changes in free-field in the magnet bore during cycle inherent to reciprocating design due to temperature and field dependent magnetization (M [A/m]) of refrigerant masses
- Changes in magnetic flux vector orientations induce eddy currents in magnet structures due to Farady's Law $\varepsilon(emf) = \frac{d\Phi_B}{dt}$
- Latest tests indicate 8 W of magnet heating due to AC and eddy current losses at cycle frequencies of 0.25 Hz; limiting test frequencies to 0.034 Hz during cooldown resulting in limited available cooling power
- Force balance and flux uniformity solution developed to limit both AC and eddy current losses

MCHL 3/13/2023 Test Magnet Temperatures
0.034 Hz



ΔB_r Along Magnet Former During Move from 1 in Off Center to Centered in Bore for Assembly at 80 K with and without Steel Force Balancing Structure



Force Imbalance During Cycle Corroborates Thermodynamics Models and COMSOL Sims of Work Input and Cycle Efficiency

Accomplishment

- Extended COMSOL model of net force imbalance with field induced temperature changes during the cycle predicts 160.5 W of work input while analytic and phenomenological thermodynamic models predict 157 W

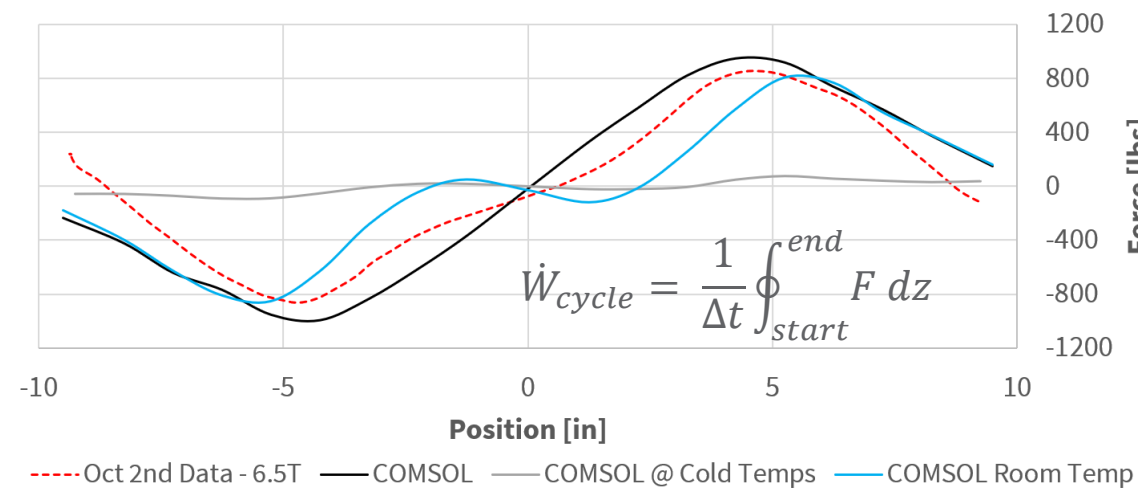
COMSOL net force solution includes temp and field dependent changes in refrigerant magnetization

$$\underbrace{\frac{1}{\Delta t} \oint_{start}^{end} F dz}_{160.5 \text{ W}} = \dot{W}_{real} = \underbrace{\dot{Q}_H - \dot{Q}_C}_{157 \text{ W}}$$

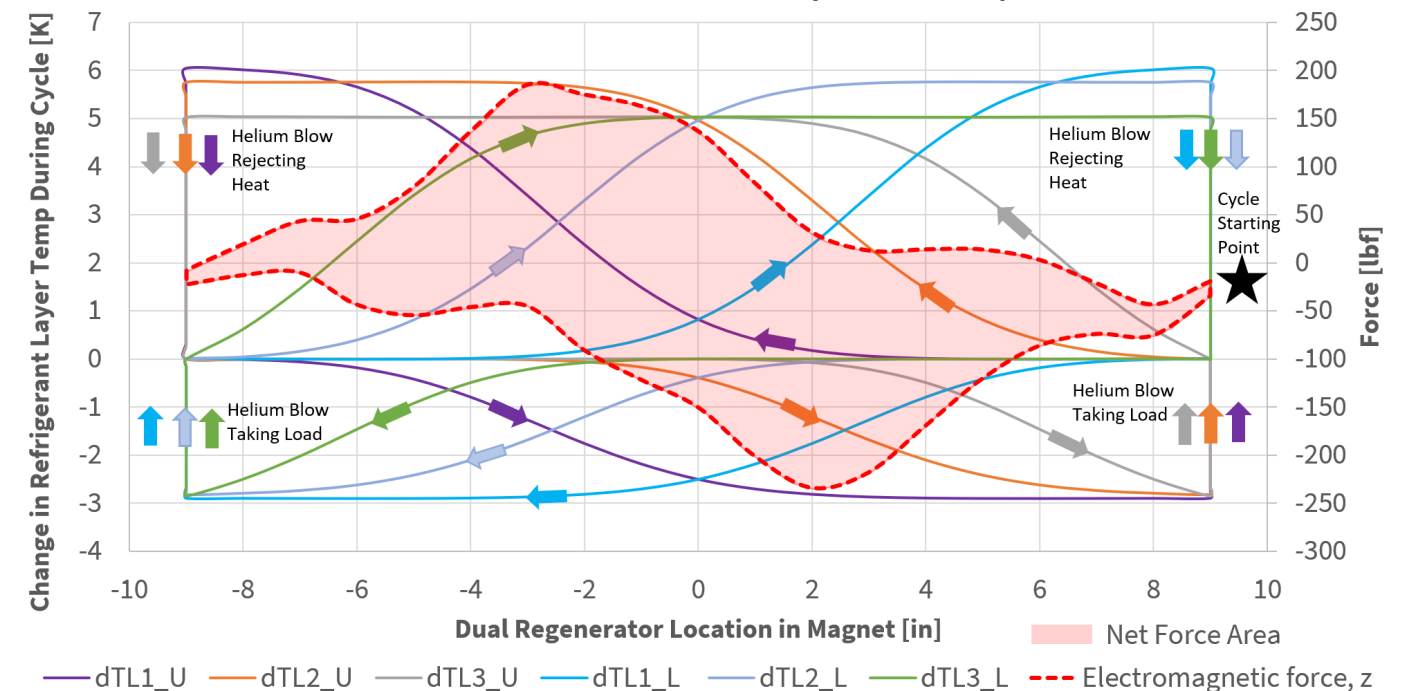
Thermodynamic models include reversible and irreversible work sources

$$\eta_{cycle} = \frac{\dot{W}_{ideal}}{\dot{W}_{real}}$$

MCHL 10/2/2022 Test Force vs Position in Magnet along z
6.5 T, 5 sec move, all 90 K



Refrigerant Layer Temperature Changes and Total Forces during Full Cycle
Total Net Force Imbalance over Cycle = Work Input





Response to 2021-2022 AMR Reviewer's Comments

N/A - No Reviewer Comments from virtual AMR in June 2021

N/A - No Reviews at virtual AMR in June 2022

Responses to 2019 Reviewer's Comments

- *The presentation focused more on the technology's "potential" than actual progress to prove that potential. This is a concern..... Two key aspects are recommended for the approach:*
 - *The project needs to narrow its focus on proving liquid hydrogen (LH₂) temperatures can actually be realized with this technology, and at the efficiency stated – in other words, whether the technology will actually function, an function at the power levels stated.*
 - *There may be gaps as to the expectations of both power efficiency and capital effectiveness. Both should be critically reviewed this year to have a balanced assessment when compared to reality of actual operation and competing technology. Ultimately, the project must determine the "spigot" cost of LH₂ with the capital and operating costs, as well as whether it offers a meaningful reduction in overall cost. This is not stated in direct terms..... Next year's report will be critical to understand if progress is being made on this approach. There are significant deviations from "theory" to "reality", and it is unclear that this project understands.*
- This project is now focused on demonstrating an active magnetic regenerative liquefier that operates between ~100 K and 20 K with enough cooling power to liquefy ~0.5-1 kg/day of LH₂. The design uses dual regenerators, each with 3 layers of ferromagnetic refrigerants, and 400 psia helium gas as the main HTF flow, diversion flows of HTF from the spacers between adjacent layers 1-2 and 2-3 of the demagnetized dual regenerator to the same spacers of the magnetized dual regenerator. A ~2 % portion of the coldest He is separated from the remaining main He flow between demagnetized layer 3 and magnetized layer 3 to as bypass HTF flow which is sent into the process HEX to continuous cool the gaseous hydrogen from ~100 K to ~20 K. Pressurized LN₂ at ~100 K is used as heat sink for 100 K to 20 K stage and to precool the hydrogen process stream.
- Dr. John Barclay assumed the PM/PI role for this project after Dr. Jamie Holladay accepted Group leader position at PNNL. Dr. Barclay has extensive experience with magnetocaloric liquefaction and ~20 years of industrial experience at CEO/CTO in design/manufacturing/installation/operations energy companies that focused on selling small-scale LNG facilities to customers who wanted to convert stranded or waste methane gas into 5,000-10,000 gpd of LNG for transportation or remote power applications. This experience gives him actual experience with cash flow, capital cost of plants, maintenance, and operations.

Collaboration and Technology Transfer Activities

- **Collaboration with Business Development Group at PNNL to License IP**
 - One signed option agreement to license magnetocaloric technology for LH₂ for a specific geographical area
 - Participating in several discussions with interested parties for specific applications of magnetic refrigeration
- **Collaboration with Intellectual Property Group at PNNL to capture IP**
 - Several Invention Disclosure Reports submitted since April 2022 for review to be patented
 - Several new Invention Disclosure Reports are in different stages of preparation\
 - Established NDAs and SharePoint sites to share proprietary technical and confidential business information
- **Discussion with companies who have proven capabilities in a FEED studies of small-scale cryogenic energy systems**
 - Collaborate with PNNL to develop MCL systems for industrial companies with clients for who want to participate in niche applications of efficient and cost-effective liquefiers of cryogenics such as LH₂.
 - Combine industrial know how with PNNL's unique knowledge and experience to model, simulate, design, build, and test of lab-scale hardware lab-scale hardware
- **On going emails re status of MCHL for LH₂ and requests to visit PNNL**

Special Recognition and Awards

- **U.S. Patent 11,555,652** issued January 17, 2023 entitled "Active Magnetic Regenerative Processes and Systems Employing Hydrogen as Heat Transfer Fluid and Process Fluid" by Jamie Holladay and John Barclay
- 4 Non-provisional or PCT Patent Applications Pending Review
- 1 Non-provisional patent application in preparation by patent attorney
- **Invited talk** at the International Superconductivity Symposium 2022 entitled "Magnetocaloric Refrigerators for Cryogen Liquefaction" by John A. Barclay and Corey C. Archipley, December 1, 2022.
- **Invited talk** entitled "Can Process Intensification of Liquefaction Technology for LNG and LH₂ accelerate Adoption for Transportation Use?" To be given by John Barclay at the International Cryogenic Materials Conference in July 8-13, 2023

Publications and Presentations

- **Publications**

- “Methane Liquefaction with an Active Magnetic Regenerative Liquefier”; Cryogenics 128 (2022) 103588 by Corey Archipley, John Barclay, Kerry Meinhardt, Greg Whyatt, Edwin Thomsen, Jamie Holladay, Jun Cui, Iver Anderson, and Sam Wolf
- Integrated vehicular refueling stations for liquefied and compressed hydrogen and natural gas in revision process of International Journal of Hydrogen Energy (2023) by John A. Barclay, Evgueni Polikarpov, and Jamelyn D. Holladay

- **Presentations**

- Seminar on "Magnetocaloric Refrigeration for Energy Systems" to technical staff at Engineering Department of Florida State University and National High Field Magnet Laboratory by John Barclay and Corey Archipley, November 30, 2022
- Guest Lecture by John Barclay for ME-579 Cryogenic Hydrogen course at Washington State University on "Introduction to Magnetocaloric Liquefaction of Hydrogen" (Dr. Jake Leachman's course).

- **Conference papers**

- Accepted paper for oral presentation at Cryogenic Engineering Conference, July 9-13, 2023 entitled "AC Losses and Surprising Magnet Heating in Reciprocating Active Magnetic Regenerative Refrigerators" by Corey Archipley

Remaining FY23 Challenges and Barriers

- **Implement Magnetic Flux Uniformity solution for existing MCHL prototype**
 - Eliminate eddy current heating at start up by redesign of magnetic skeleton
 - Transfer results to MCL for air liquefier prototype
- **Successfully cool from 95 K to 20 K**
 - Measure load curve and performance for different frequencies, heat transfer flow rates, and different magnetic flux densities
- **Liquefy hydrogen with MCHL prototype**
 - Demonstrate effectiveness of o/p catalyst and bypass flow
- **Analyze experimental results and determine efficiency for MCHL**
- **Demonstrate performance to interested parties**
- **Primary barrier is adequate funding to cross Valley of Death for emerging technology transfer**

Proposed Future Work

- **File** several invention disclosures and patent applications to capture additional IP on MCL technology
 - **Advertise** PNNL's increasing collection of issued patents on strategic features of MCL
 - **Work** with several parties who have enquired about efficient liquefaction of hydrogen to discuss IP licensing agreements
- **Publish** peer reviewed paper on successful liquefaction of hydrogen with reciprocating, dual regenerator MCL
- **Present** talks at conferences to describe potential of MCL for DOE strategic goals
- **Publish** numerous papers on results of previously tested MCL prototypes related to efficient liquefaction of hydrogen and other cryogenes
- **Compare** analyzed results of MCHL to predicted performance to validate model
- **Write** final report on MCHL project to HFTO
- **Apply** lessons learned in 3-stage rotary MCL design for LH₂ to span from 295 K to 20 K
 - **Scale up** 1-5 tonne/day capacity
 - **Work** with industrial partner to do complete FEED of small-scale liquefier
- **Secure** additional resources and early adopter industrial partners

Summary

- **Initial shake down runs of MCHL completed, results understood, necessary modifications identified and being made**
- **COMSOL with AC/DC module essential to design uniform magnetic flux density**
- **Validated COMSOL simulations of net magnetic forces for dual regenerators create a good method to measure efficiency of MCHL**
- **After magnetic flux density uniformity modifications are completed MCHL will be reassembled and prepared for next tests to cool toward 20 K**
- **Final leak check of hydrogen process stream delivery and purge system completed**
- **System review by pressure safety personnel done with approval to connect into MCHL**
- **Outreach with numerous interested companies ongoing**
- **Established path toward ~1 metric ton/day MCL for LH₂ is with rotary wheel designs**
- **We've accomplished much, but we are not quite across the finish line.**



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Thank you

