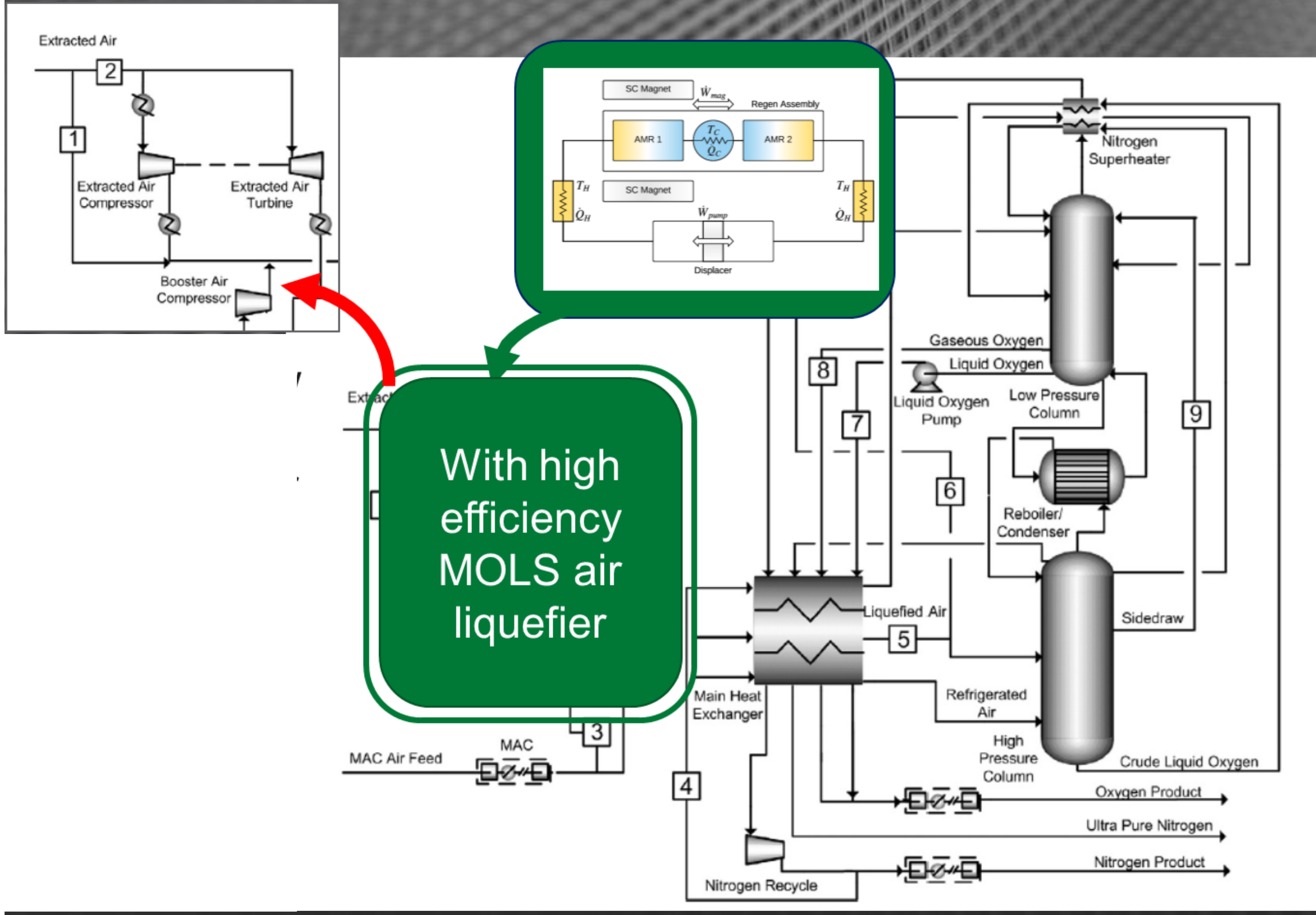
Magnetocaloric Oxygen Liquefaction System (MOLS) for High Efficiency Air Separation

September 2, 2020

John Barclay



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

FWP-73143

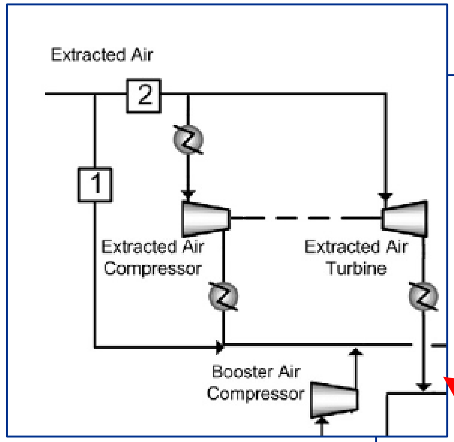
MOLS project summary

- Overall Program Strategic Objective:
  - Effective coal gasification with carbon capture at 1-5 MWe power plants requires small-scale air separation units (ASU) to efficiently produce 10-90 metric tonnes of high purity O2/day. Need alternatives to existing large-scale ASU plants for small-scale gasification.
- PNNL's MOLS Objectives:
  - To develop highly-efficient, small-scale magnetocaloric liquefiers for air coupled with microchannel distillation column to make liquid oxygen (LOX)
  - First year (December 1, 2018 until November 30, 2019)
    - ✓ Designed a multilayer magnetic liquefier; successfully cooled from ~285 K to 135 K with 4 layers
    - ✓ Used to demonstrate liquefaction of methane; identified changes required to reach 100 K for air
    - ✓ Completed techno-economic analysis of ~50 tonne/day of liquid air for ~10 tonne/day of LOX
  - 2nd year of project (January 2, 2020 until December 31, 2020)
    - ✓ Carry over from 1st year due to unexpected delay(s) of new superconducting magnet system
    - ✓ Complete demonstration of a magnetocaloric liquefier cooling to ~100 K to produce ~1 kg/day of air
    - ✓ Complete four new tasks during CY20 directly to increase the efficiency. Reduce cost, and determine scalability of MCL for production of LOX
- CY20 Budget: $1,000,000 plus no-cost carry over of $720,729 to finish 1st year

Project Description:

A MOLS enables efficient, small-scale liquid air to LOX plants (10 tonne/day)

- Three major sources of power consumption at ASU plants
  - Compression of working gases from low to high pressure
  - Separation of pure components from mixtures, e.g. O_2 from air
  - Liquefaction of oxygen and nitrogen gas into LOX and LIN
- Magnetocaloric liquefier (MCL)
  - High surface area magnetic refrigerants thermally coupled by heat transfer fluid enable highly efficient liquefaction
  - Inefficient gas compression-expansion replaced by efficient magnetization/demagnetization



Replace low efficiency compressor - turbine

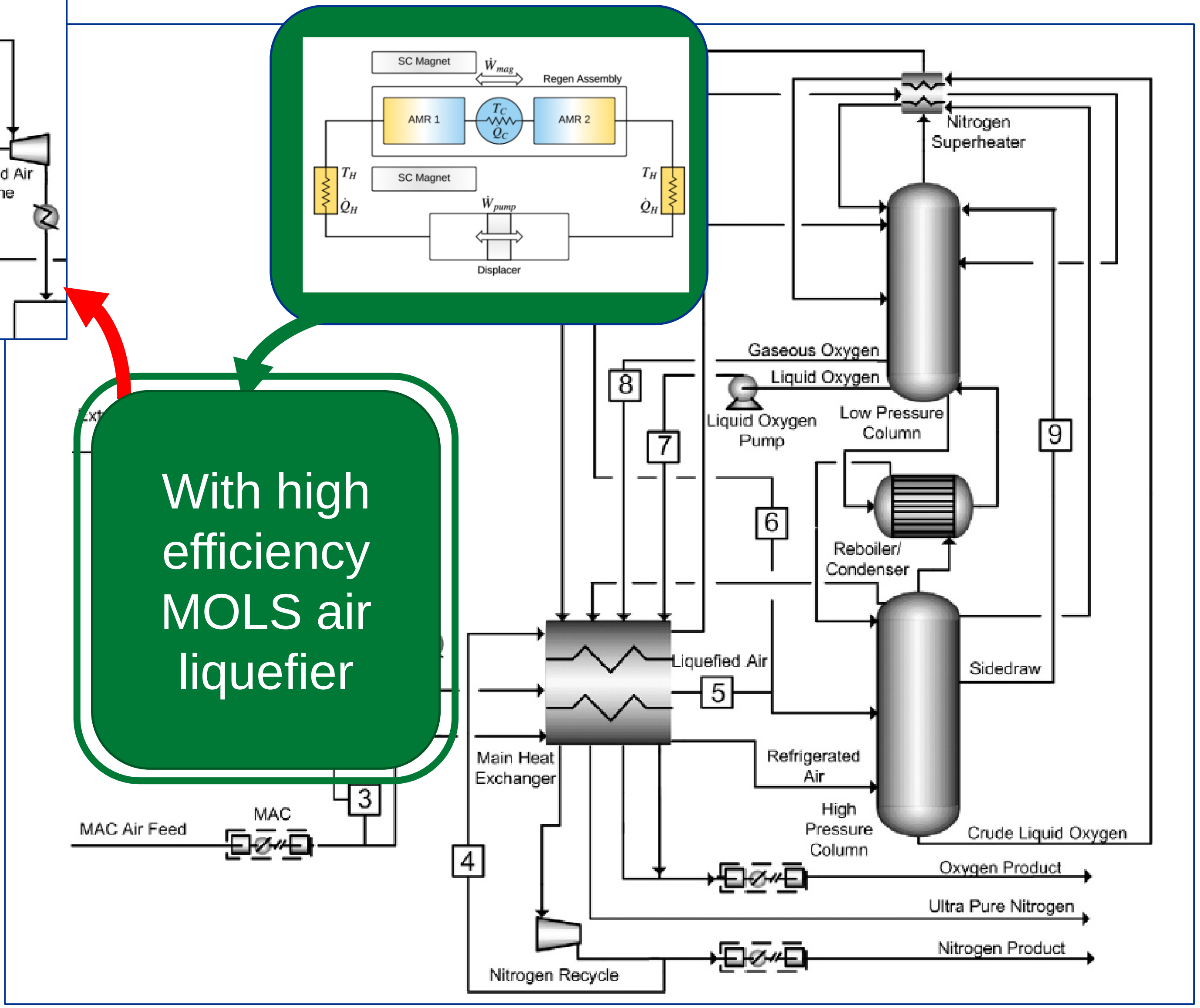
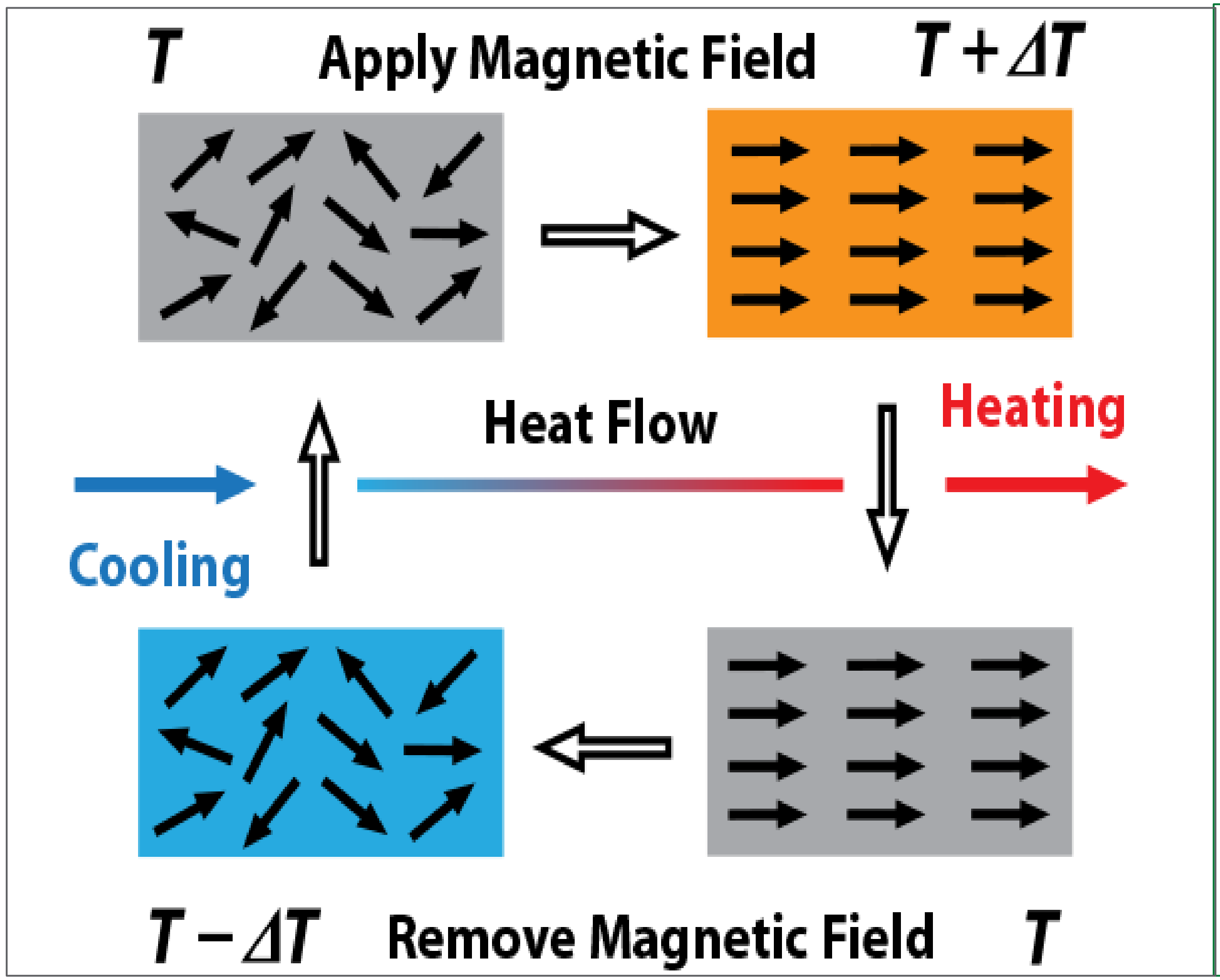


Figure from Jones et al, Fuel Processing Tech 92 (2011) 1685

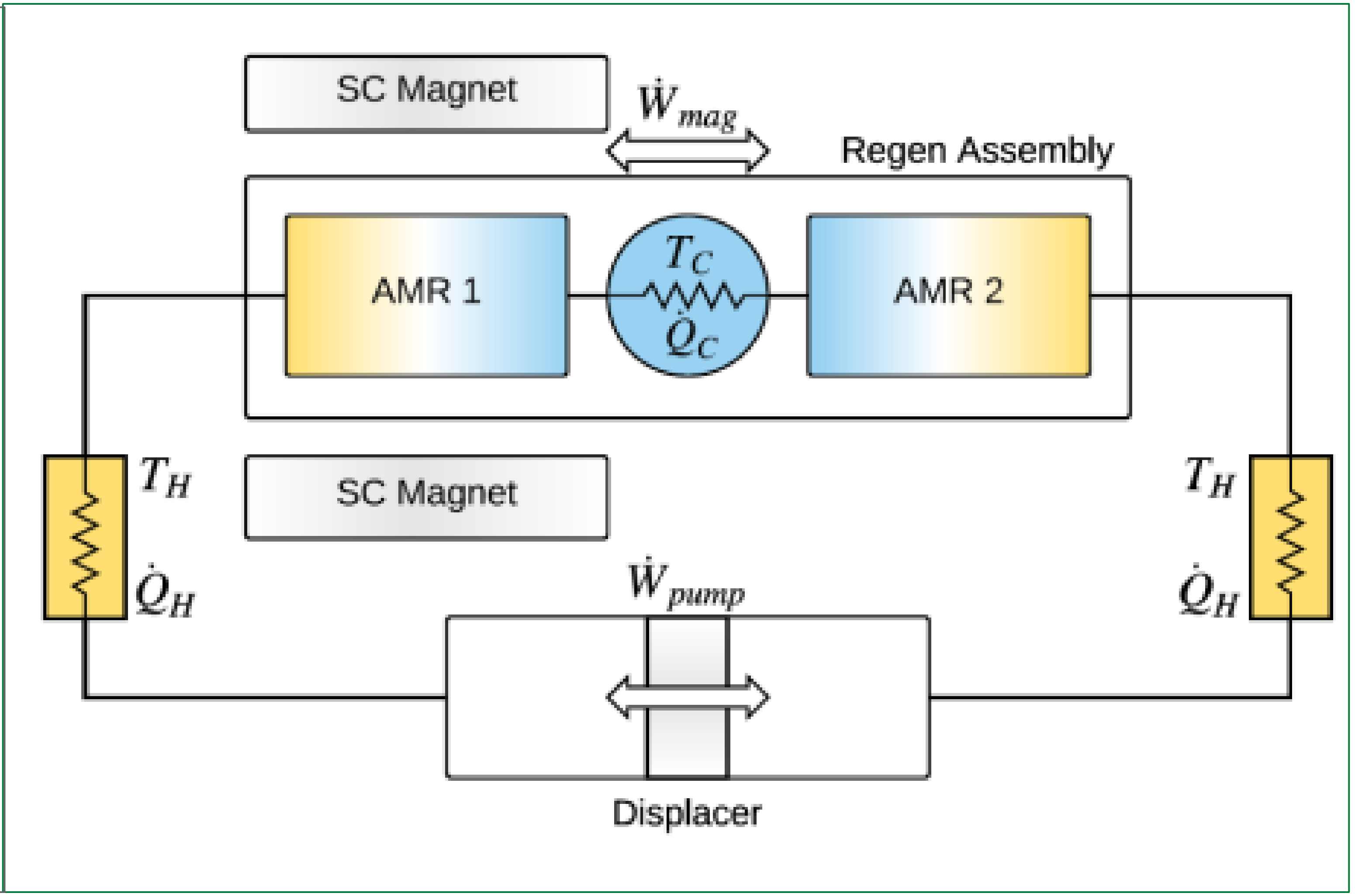
Ref.: G. Chen; CEP; June 2020, pg. 26-33

Active Magnetic Regenerative Refrigeration uses the magnetocaloric effect for efficient cooling

Dual Active Magnetic Regenerator (AMR) design



Goggle search: "Images of Magnetocaloric Effect".



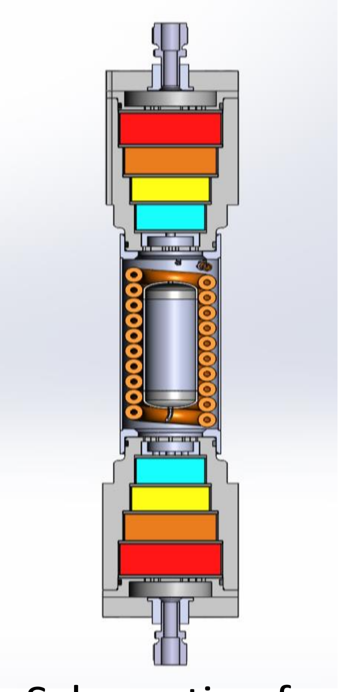
Schematic of active magnetic regenerator:
See R. Teyber, et. al. "Performance of a high-field active magnetic regenerator"; J. *Applied Energy*, ***236***, *426-436 (2019)*

Design of an AMR liquefier to demonstrate efficient liquefaction of air (MOLS)

- Determine design basis to meet project goal
  - Investigate possible magnetic refrigerants for each layer or stage
  - Prepare, characterize, compare, and select; determine thermomagnetic properties
- Performance Modeling to achieve Design Basis
  - Use thermomagnetic, transport, chemical, and physical properties of refrigerants
  - Use Fortran multi-stage model & phenomenological multi-layer model
  - Determine masses of refrigerants, HTF flows, and geometric parameters
- Regenerator Design
  - Irreversible entropy analysis based on lessons learned
- Design superconducting magnet
  - Layers aspect ratio constraint
  - Magnetic force balance
- Heat transfer fluid
  - Diversion flow requirements
  - Optimum layering vs. diversion flow

Progress update:

Two milestones for active magnetic regenerative designs were achieved in CY19

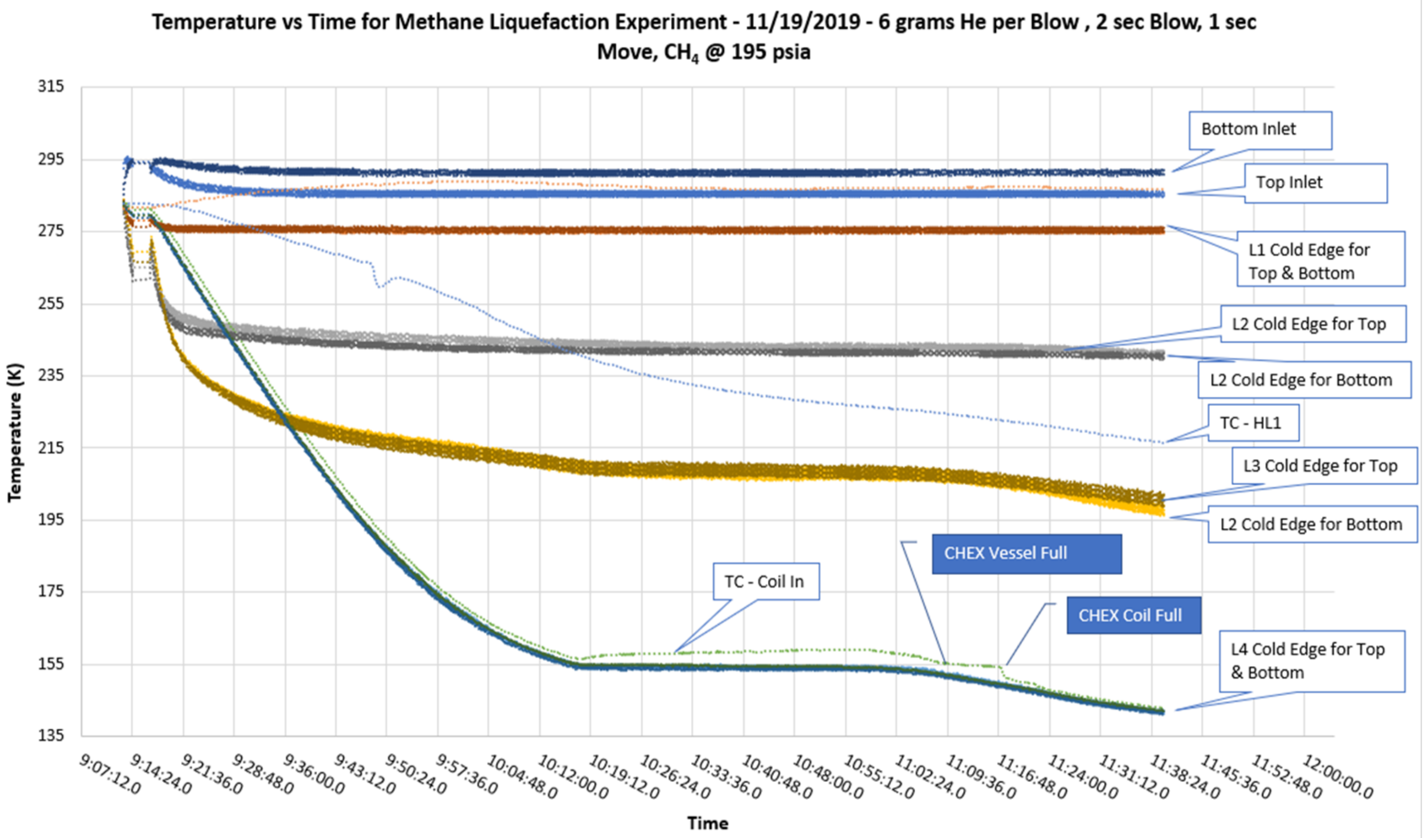


Schematic of dual AMR

Coiled-fin tube exchanger between dual AMRs

Dual AMR

- TCF project with FE funding
- Dual 4-layer active magnetic regenerative refrigerator (AMRR) used to liquefy methane (Nov 2019)
- 195 psia methane feed gas cryopumped into coil-fin heat exchanger cooled by cold He gas from dual magnetic regenerators condensed at 156 K



- MOLS project with FE funding; leverages HFTO project
- 4-layer dual regenerator refrigerants: Gd, $Gd_{0.30}Tb_{0.70}$, $Gd_{0.32}Dy_{0.68}$, $Gd_{0.33}Ho_{0.67}$
- Curie temperatures of refrigerants for each layer: 293 K, 253 K, 213 K, 183 K.
- Expected temperature spans of each layer: 285-245 K, 245-205 K, 205-175 K, 175-145 K
- 400 psia Helium HTF; no diversion flow
- 6 T solenoid magnet; no field profile shaping

CY20 Tasks with 2 tasks carried over from CY19

- **Task 1:** Complete 5-layer dual regenerator liquefier with new magnet to demonstrate cooling to ~100 K and liquefaction of ~1 kg/day of liquid air.
- **Task 2:** Analyze test results, compare with performance models to validate our simulation models, and identify required developments.
- **Task 3:** Model the magnetic force differences for MOLS regenerators in new superconducting magnet to incorporate force-balancing means into design.
- **Task 4:** Design, build, and test a safety-approved HTF subsystem to controllably circulate pressurized ~200 psia liquid propane in regenerators.
- **Task 5:** Develop robust diversion flow valves for multi-layer regenerators
- **Task 6:** Develop and demonstrate a lab-scale microchannel horizontal distillation device for O2 production
- **Task 7:** Project management to achieve milestones and deliverables, communicate progress via reports, and to communicate challenges and changes should any occur.

Progress update:

Magnetic materials with large ΔT vs. T, B for 5-layer dual regenerators were used for MOLS air liquefier prototype

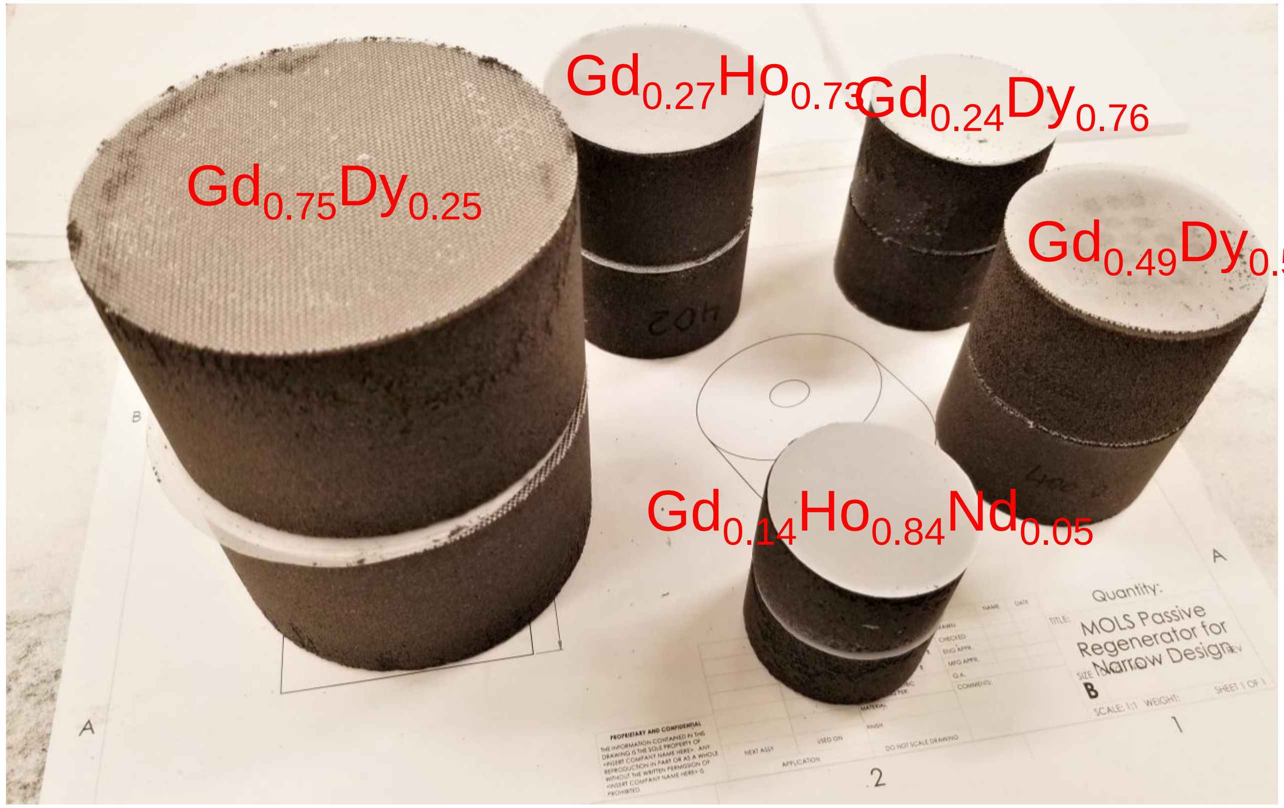
Two improvements

Layer Number	Magnetic Material Molar Composition	Curie Temperature (K)	Ave Thot Temperature (K)	Ave Tcold Temperature (K)
1	$Gd_{0.75}Dy_{0.25}$	263	260	230
2	$Gd_{0.49}Dy_{0.51}$	233	230	200
3	$Gd_{0.24}Dy_{0.76}$	203	200	170
4	$Gd_{0.27}Ho_{0.73}$	173	170	140
5	$Gd_{0.14}Ho_{0.80}Nd_{0.05}$	140	140	100

Progress update:

Magnetic refrigerants and monolithic layers for the 5-layer dual regenerators in MOLS prototype

- Magnetic Refrigerants for 270 K to 100 K liquefier; ~30 K span per layer; one diversion flow
  - $Gd_{0.75}Dy_{0.25}$ (263 K); $Gd_{0.49}Dy_{0.51}$ (233 K); $Gd_{0.24}Dy_{0.76}$ (203 K); $Gd_{0.27}Ho_{0.73}$ (173 K); $Gd_{0.14}Ho_{0.80}Nd_{0.05}$ (140 K)
  - All are ferromagnetic homogeneous RE:RE alloys with excellent magnetic moments
- Characterized and fabricated into 150-250-micron diameter spheres by AMES lab
- Fabricated into monolithic layers for assembly into G-10 regenerator housing at PNNL.

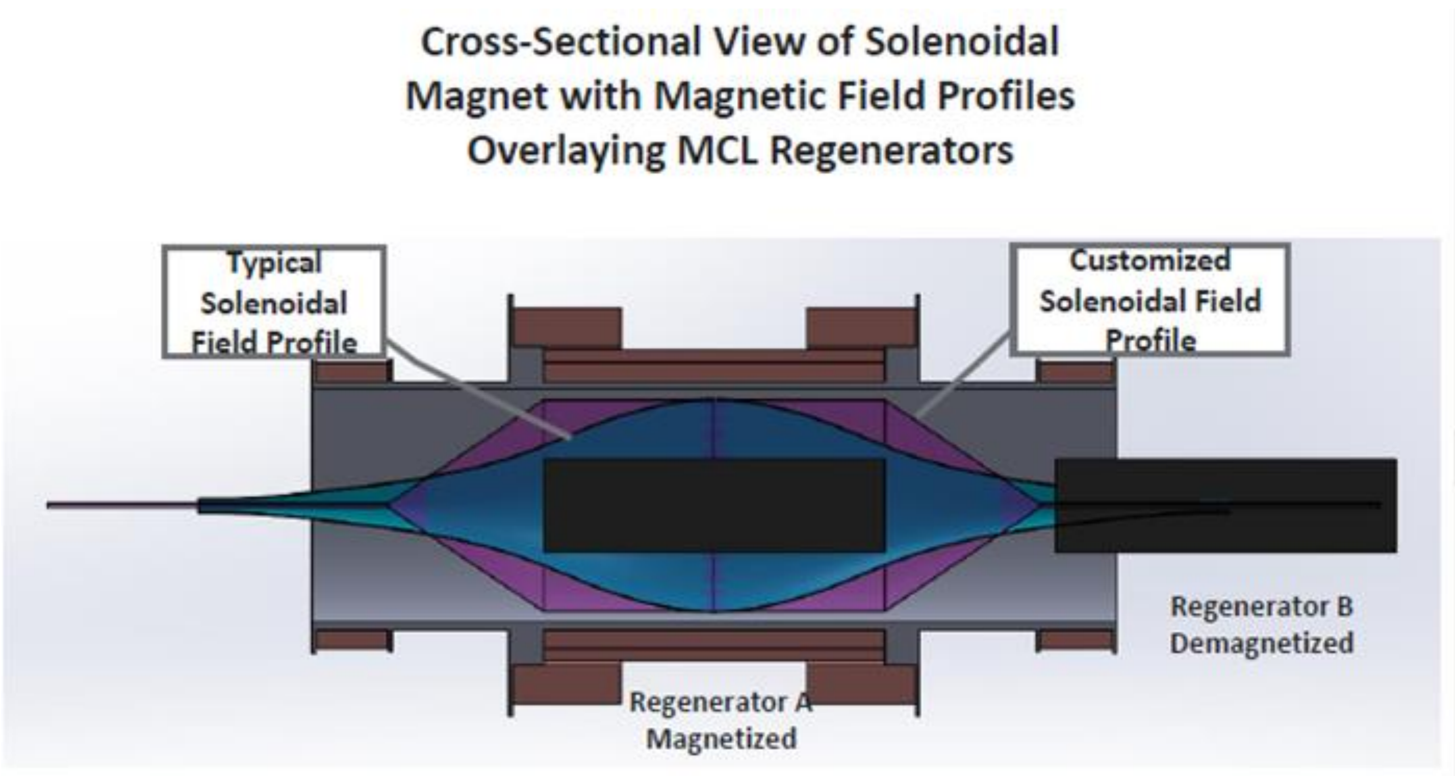


- Dimensions determined by detailed model
- Sphere packing gives porosity **36.5** ± 0.5%
- Mass losses during extraction from molds: **1-4 g** per puck (<0.3%)
- Pressure drop change was measured as a function of gas mass flow rate at three different mean pressures before and after dilute epoxy impregnation: **<1.0% increase**

Progress update:

Optimized superconducting magnet with uniform high-to field changes and better force balancing

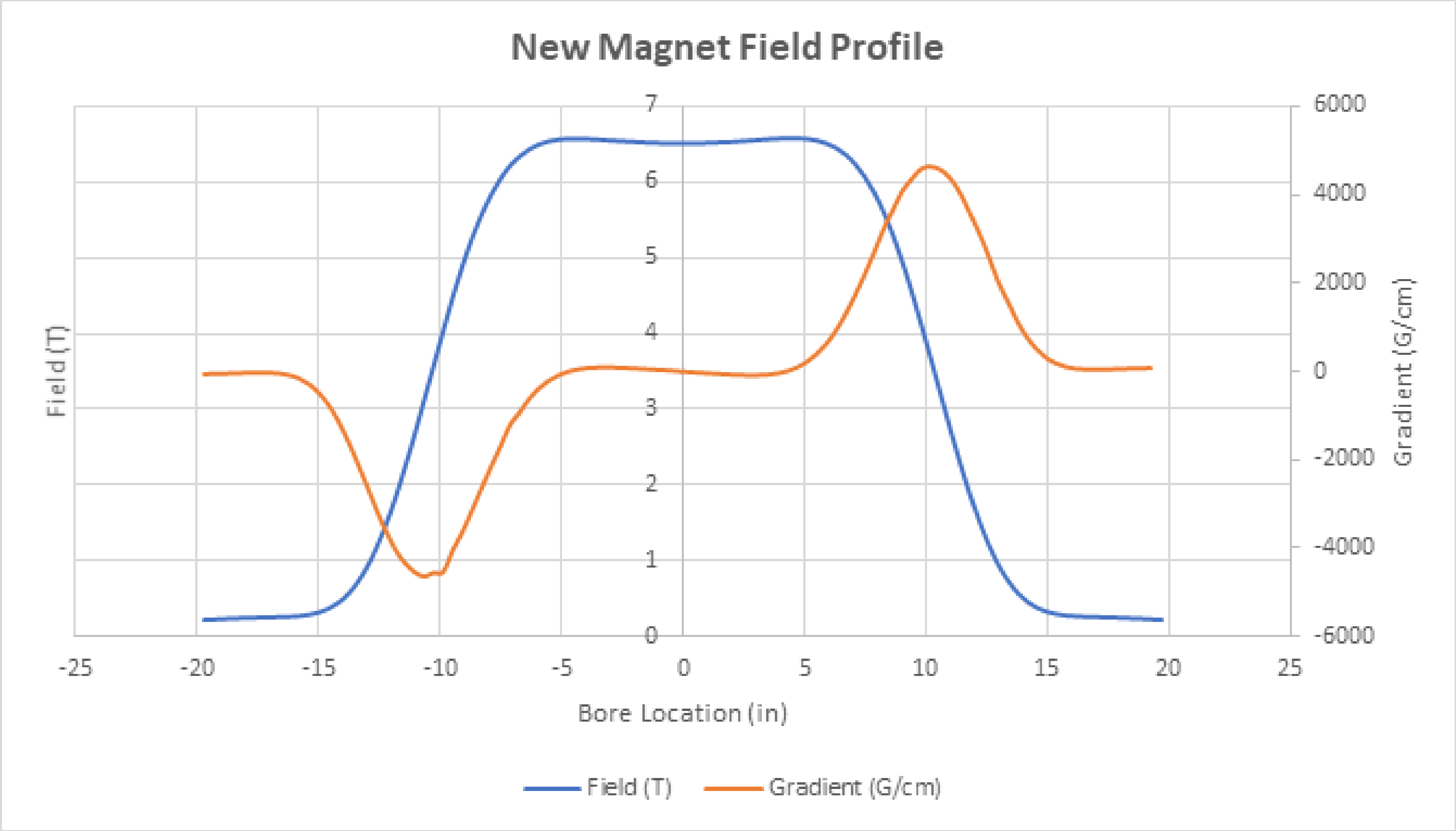
- NbTi; 4 K operation; ~100 A current; added shaping and trim coils; persistent mode switch
  - Constant high field @ ~6.5 T; constant low field @ ~0.15 T
  - Field gradients (dB/dz) leaving high and low field regions are ~same
  - Larger clear bore for larger regenerator diameter; longer high-field region for higher aspect ratio layers



- Magnetic force is determined by field gradient times magnetic moment of refrigerants
- Multilayer regenerators have different masses per layer so magnetic moments per layer differ
- Dual regenerators are mirror images of each other so largest layer leaves high field as smallest layer leaves low field regions
- To avoid this contribution to force imbalance during AMR cycle, need to make regenerators look magnetically similar
- Magnetic force fields in regenerator system modeled in COMSOL to determine amount of soft iron needed around smaller layers within to balance magnetic forces.

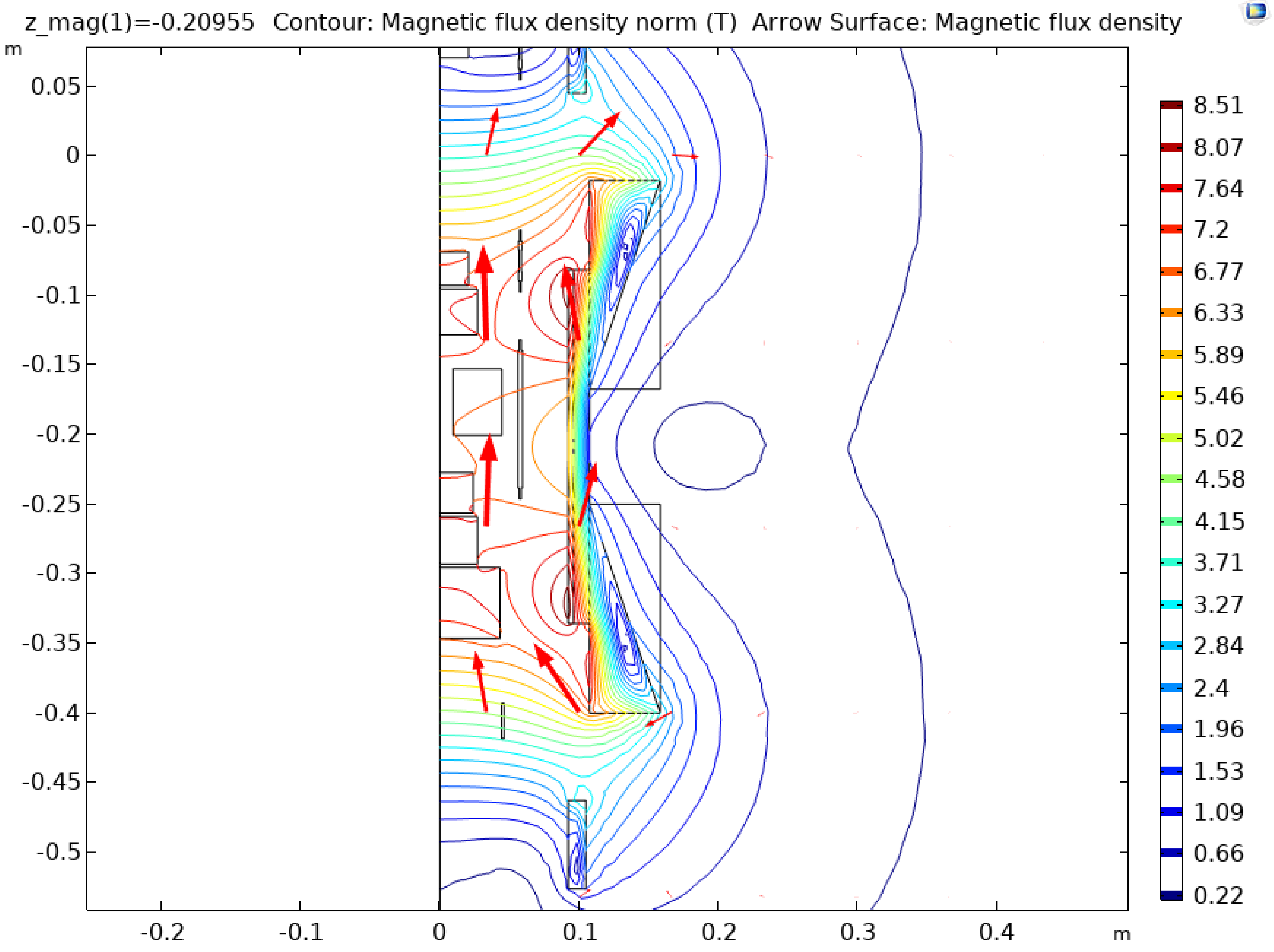
Progress update:

New magnet profile matches our specs very well!



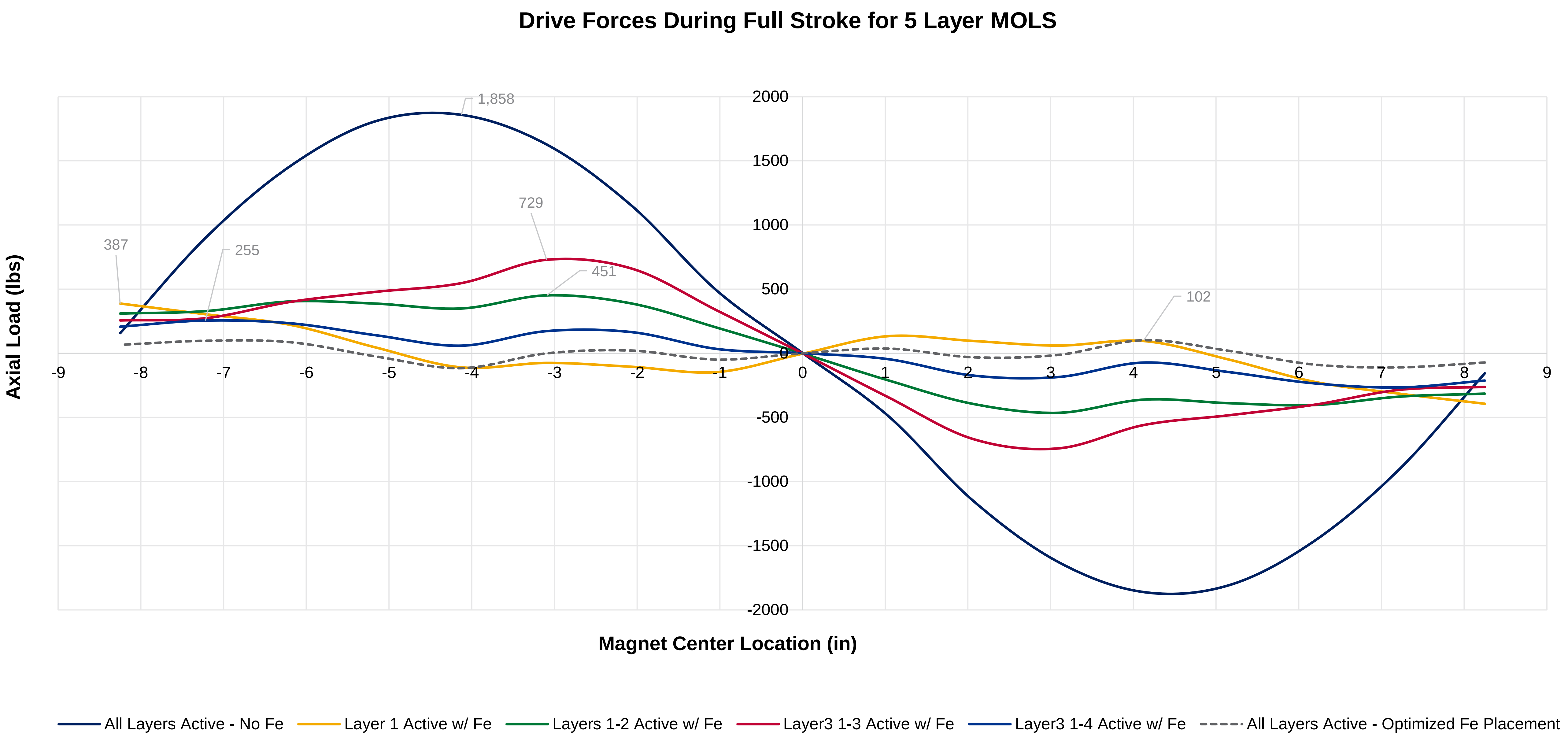
Magnetic field change/layer and force balancing calculations were done for MOLS 5-layer design

- Used COMSOL Multiphysics with AC/DC module (2-D or 3-D)
- Axial symmetry allows a quadrant of s/c magnet windings and magnetic materials of one of dual regenerators
- Magnetic permeability as a f(T, B) for each layer are used
- Calculates $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$ inside the magnetic material
- Calculate actual ΔB in and out of the magnet.



Progress update:

Magnetic forces during cool down of 5-layer dual regenerators with force balancing Fe inserts

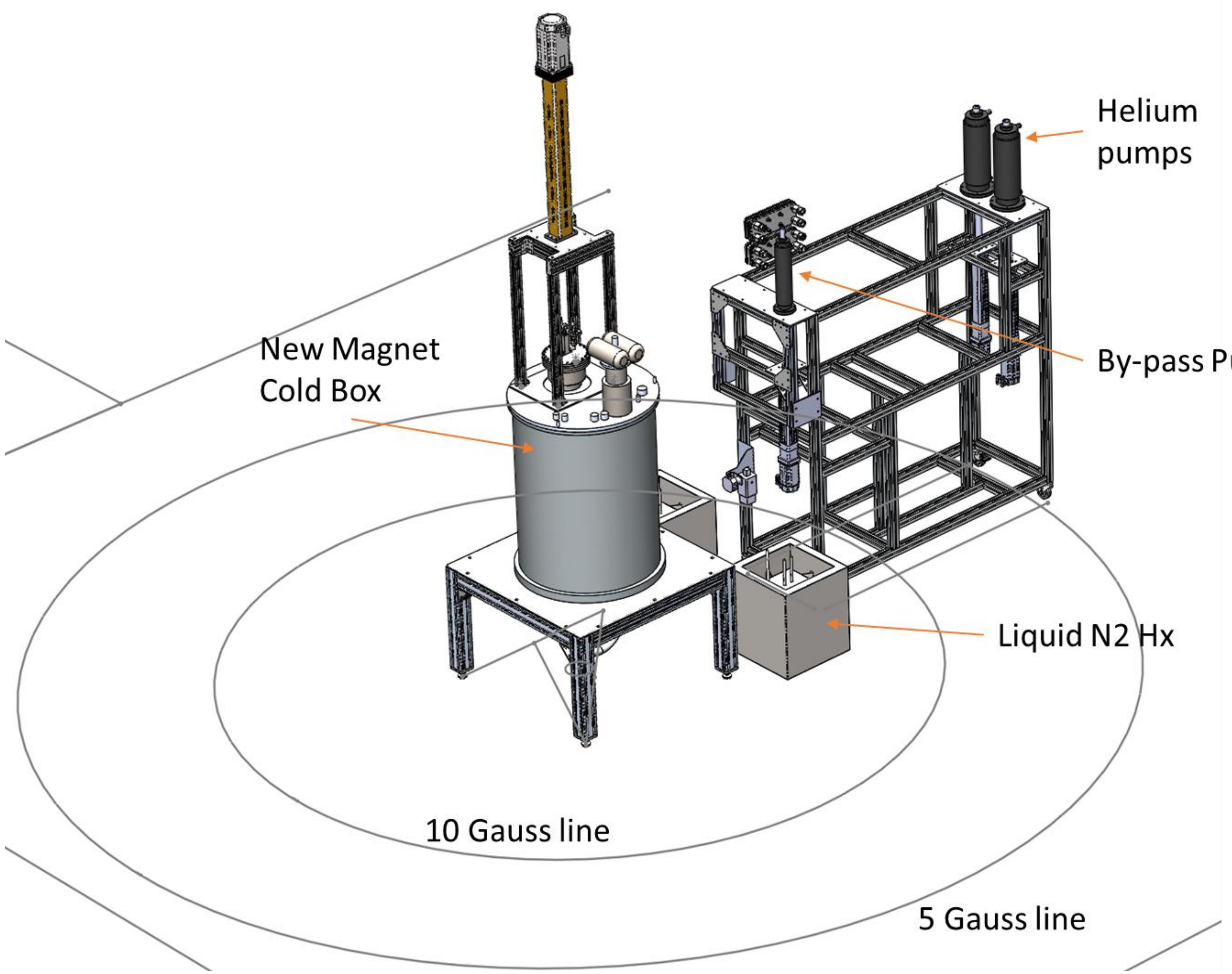


Progress update:

A schematic of high-bay lab arrangement of the new superconducting magnet subsystem

Existing AMR test apparatus

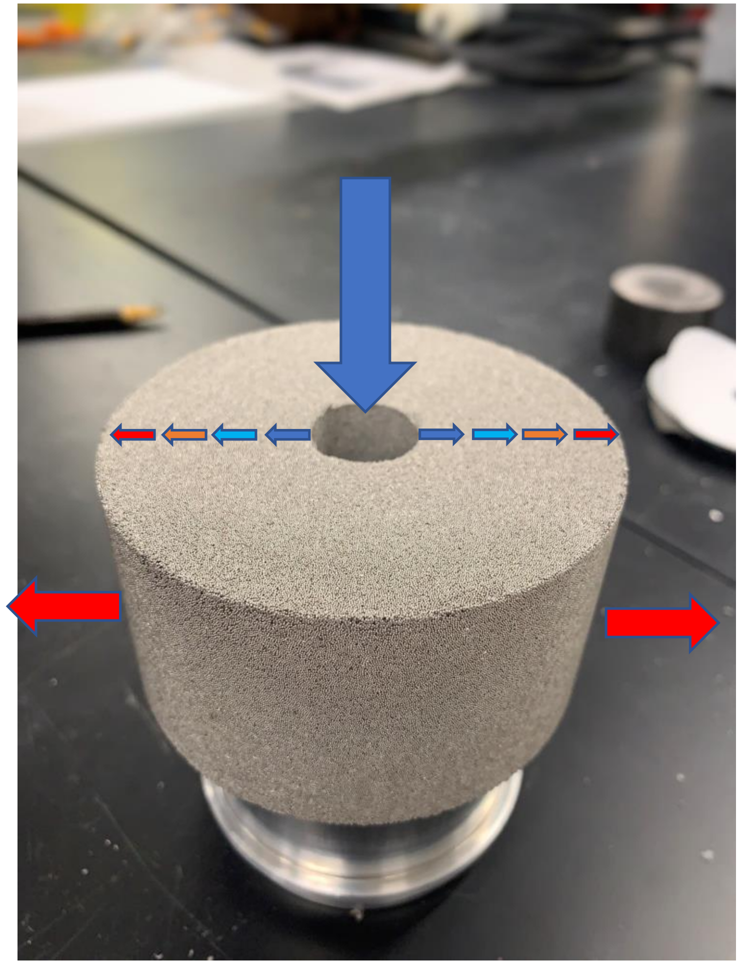
New AMR test apparatus

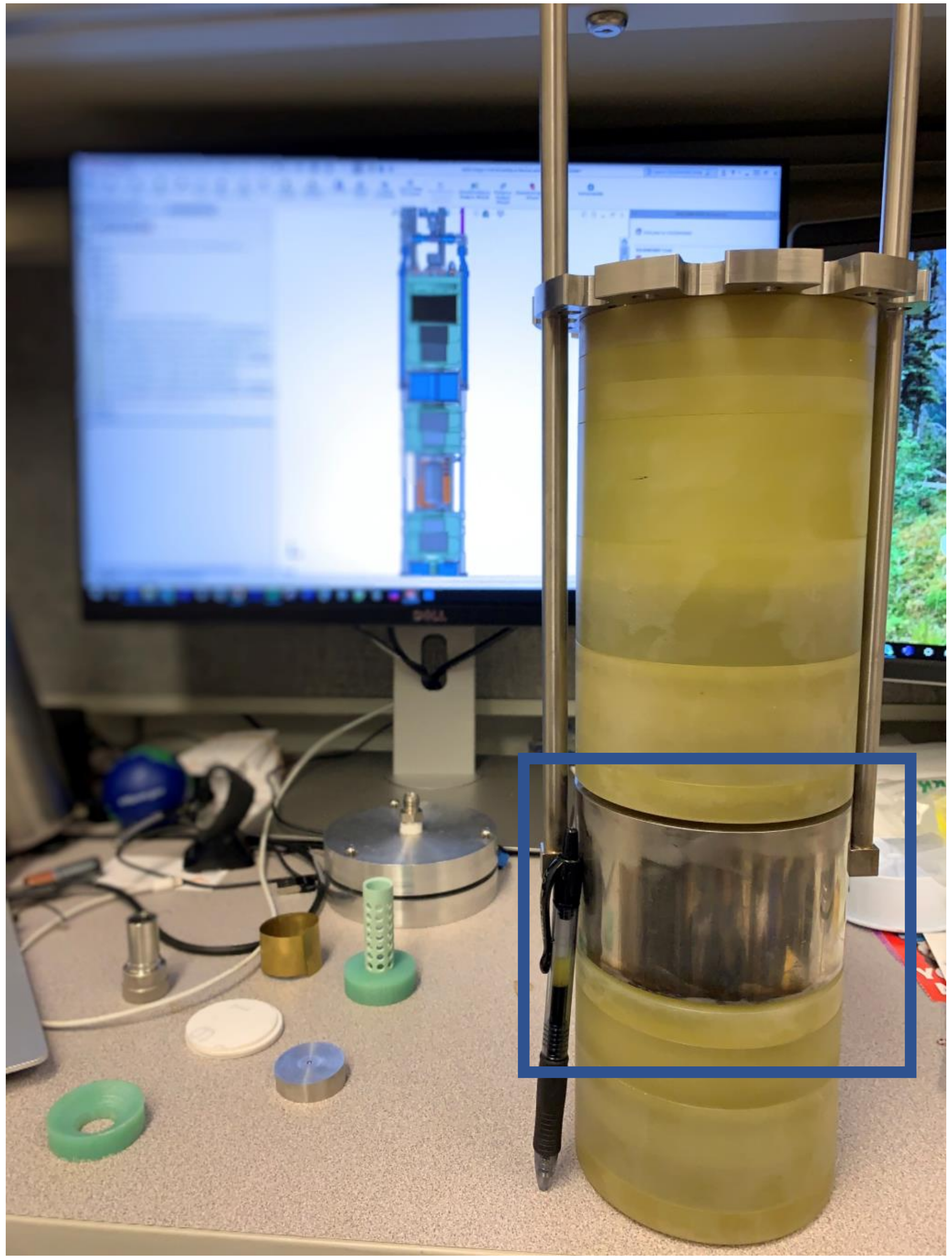


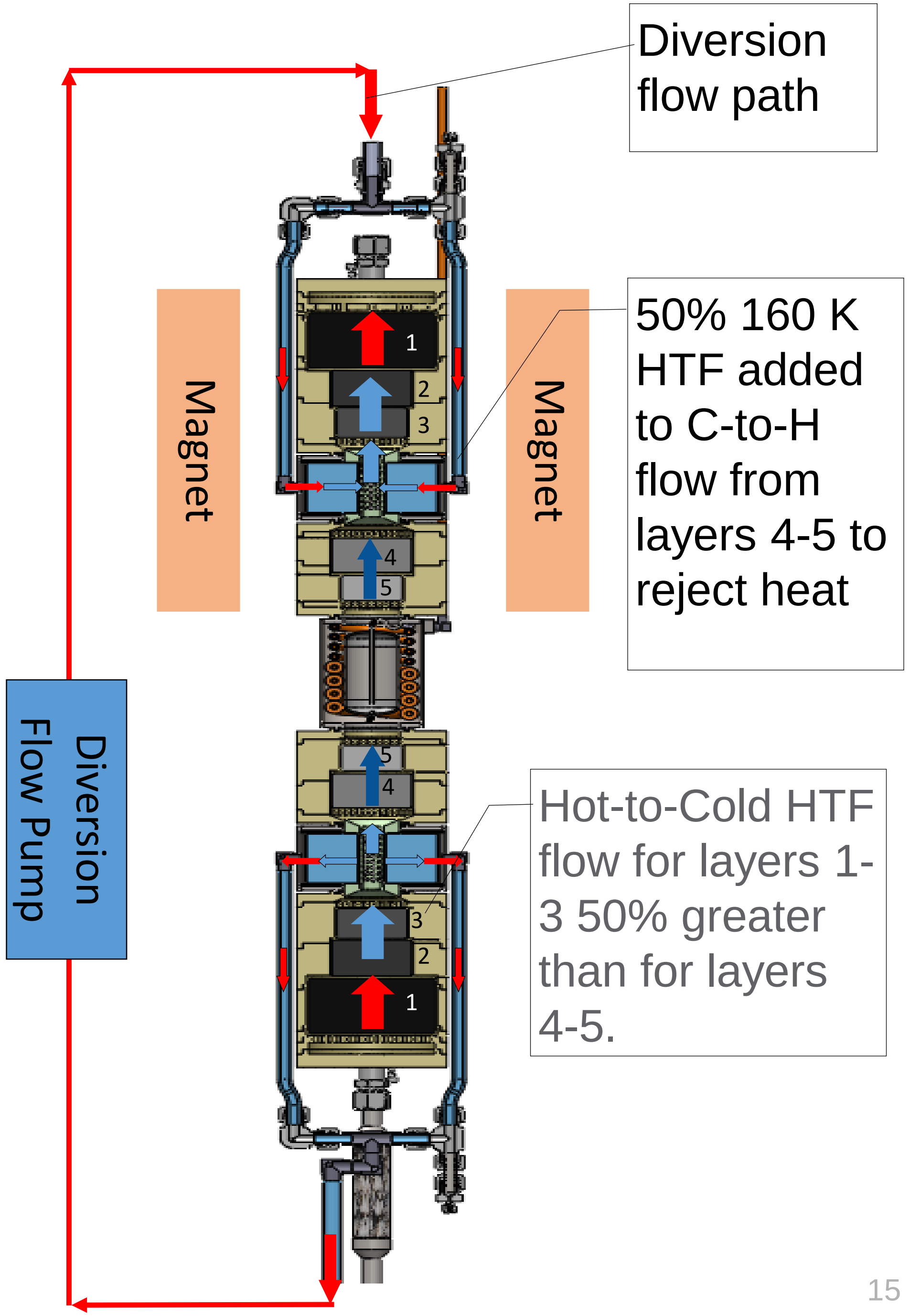
Progress update:

Diversion flow is required to match HTF for layers 50% of H-to-C flow diverted at 160 K in MOLS

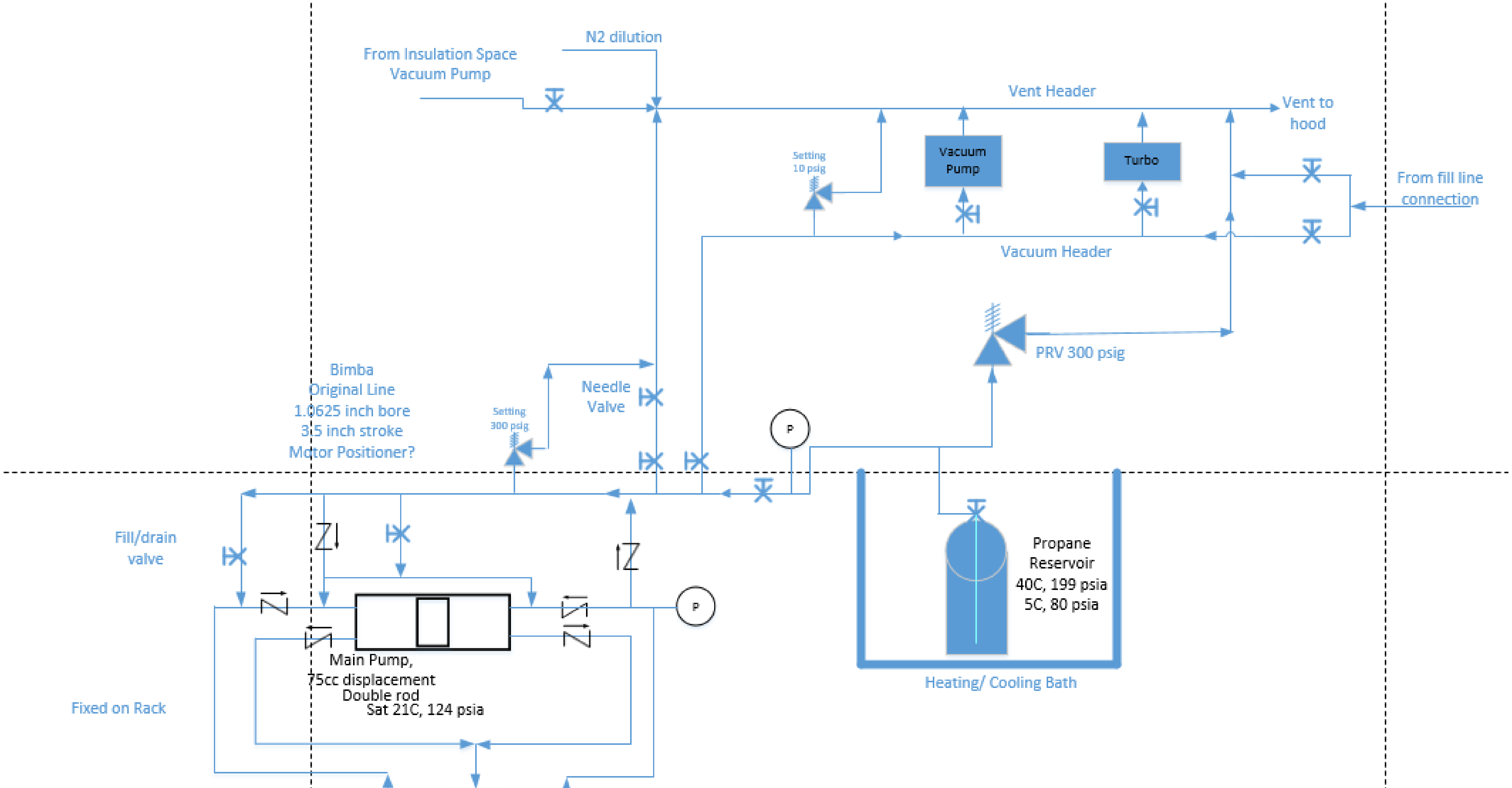
OD (in)	ID (in)	Height (in)	Mass (kg)
3.50	0.75	1.88	1.43







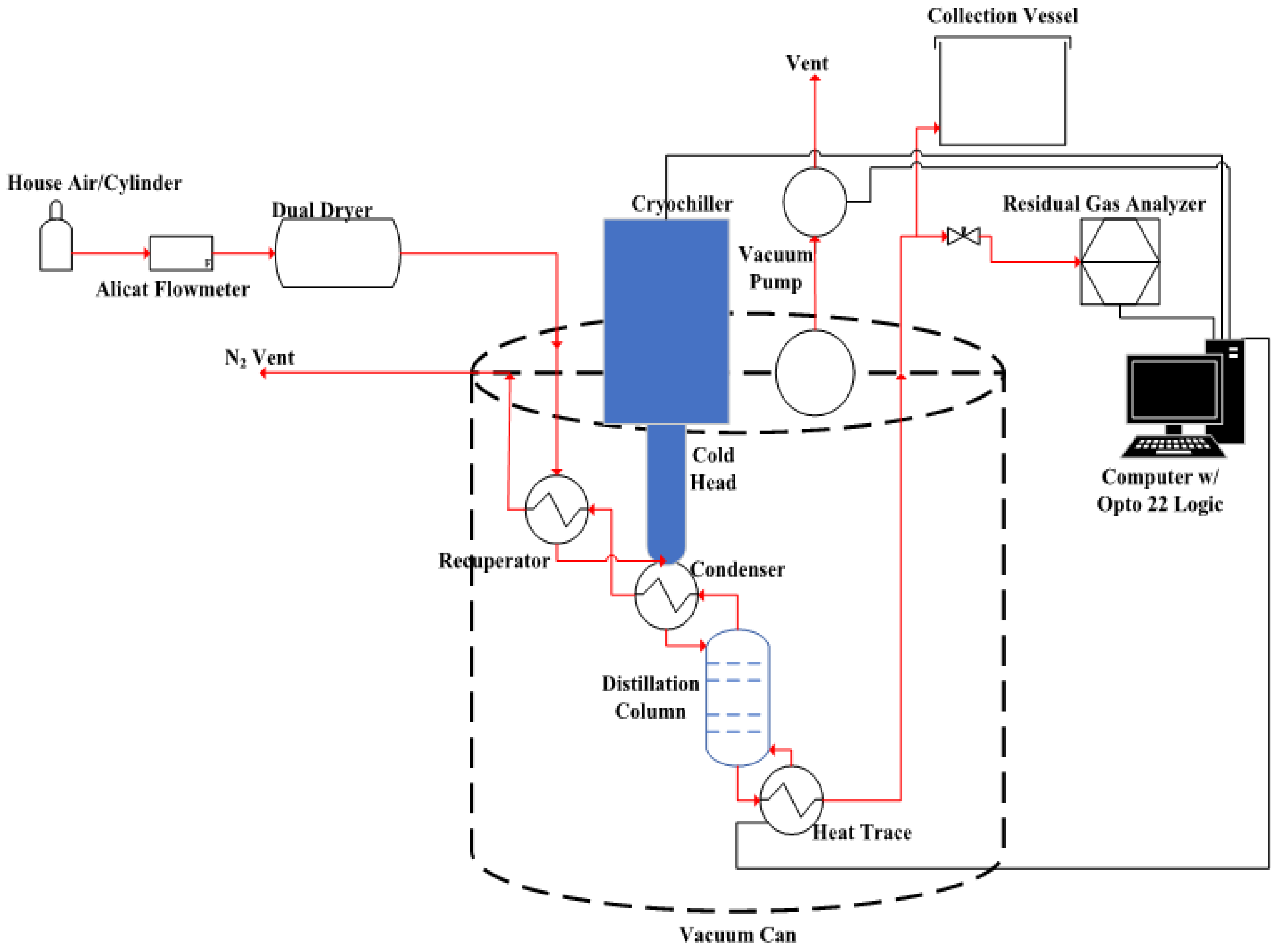
A pressurized liquid propane heat transfer fluid subsystem is being built for testing



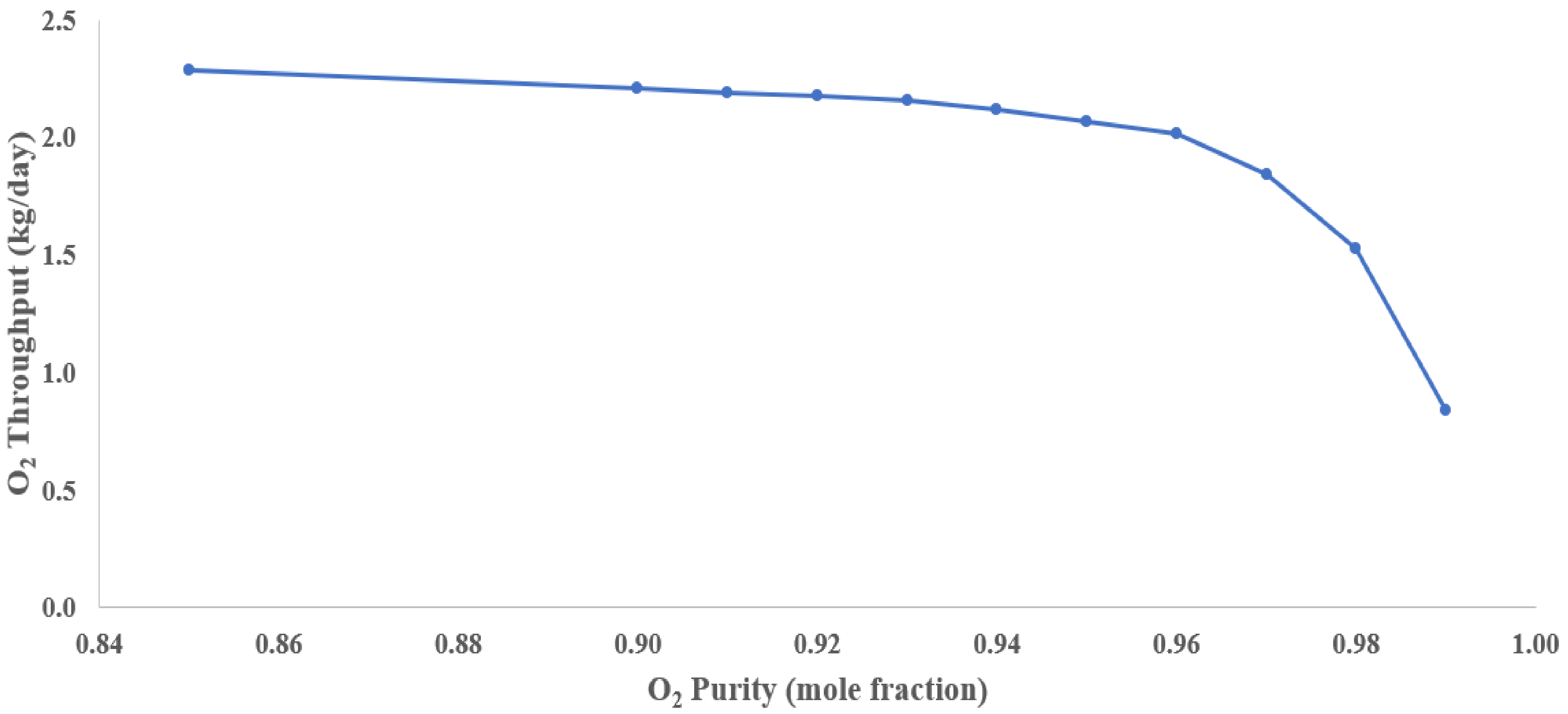
Progress update:

Demonstrate a micro-channel distillation (MCD) column to produce LOX from liquid air

- Continuous distillation of O_2 from cold dry air modeled by using CHEMCAD simulations
  - Multiple variables analyzed
- Process intensification of MCD reduces column length from ~20+ cm to ~4 cm to perform this separation.
- Results indicate that oxygen is easily enriched to > 90 mol% in a relatively short distillation column
- Experienced PNNL team have a test apparatus that will be modified to demonstrate and characterize separation of LOX from liquid air.



Example of a predicted result that will be measured with lab-scale MCD prototype



Techno-economic analysis for MOLS provides insights for future work

- Updated TEA analysis for 10 tonne/day of LOX
- FOM of 0.55 for 6-stage MCL for 46.4 tonne/day liquid air feed to ASU
- Frequency of 0.5 Hz
- HTF pressure drop is limiting FOM
- Rotary instead of reciprocating design
- ASU market demand is strong
  - potential industrial collaborators require pilot scale plant demonstration for new technology.
- Integration with MCD is key attraction

AMRL subsystem - No LN2 used to precool air feedstock	Cost-23,150 kg/ day air liquefier	Cost-46,367 kg/ day air liquefier	% of total cost
Magnetic regenerator subsystem	$1,770,711	$3,541,422	41.6%
Regenerator Housing assembly	$216,000	$432,000	5.1%
Superconducting Magnet subsystem	$833,764	$1,667,528	19.6%
Conduction cooling of magnets	$196,000	$392,000	4.6%
Heat transfer fluid circulators	$192,000	$384,000	4.5%
Chiller, Heat Rejection HEX, Interstage HEX, CHEX, PHEX	$480,000	$960,000	11.3%
Piping and valves	$162,000	$324,000	3.8%
Drive subsystem	$90,000	$180,000	2.1%
Structural subsystem and enclosures	$192,000	$384,000	4.5%
Instrumentation/Controls subsystem	$126,000	$252,000	3.0%
TOTAL	$4,258,475	$8,516,950	100.0%

Concluding remarks

- Objective and Deliverable:
  - Magnetocaloric liquefier can liquefy air at a rate of 1 kg/day
  - Higher FOM and comparable capital cost are possible
  - Techno-economic analysis of existing MCL design
    - ✓ Shows it is possible to reduce the liquefier power by a factor of ~2
    - ✓ Modular 50-100 tonne/day air liquefier for ~10-20 tonne/day of LOX could be built now
    - ✓ Irreversible entropy mechanisms show where performance is limited
    - ✓ Identifies next steps to increase efficiency at higher frequency and reduce capex by ~1/2.
- Next steps
  - Show 5-layer dual regenerator MOLS cools to 100 K and liquefies ~1 kg/day of air
  - Complete demonstrations of MCD for LOX and propane liquid HTF
  - Complete other analysis tasks
  - Develop collaborative partners who are interested in cost sharing and licensing MCL IP.
- Current technical challenges
  - Receive new s/c magnet system; install and shake it down

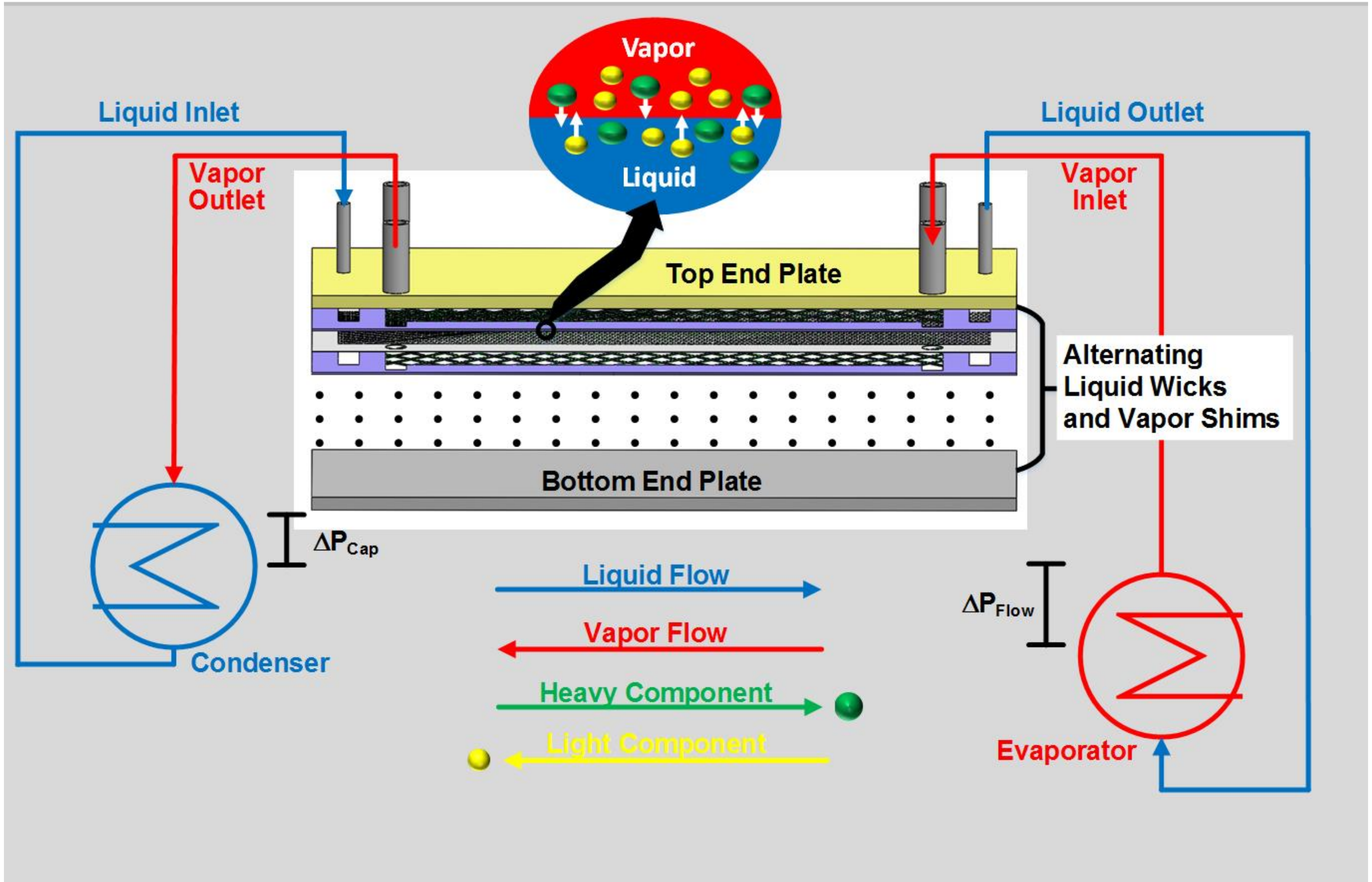
Acknowledgements

- DOE- Fossil Energy
  - Venkat Venkataraman
  - David Lyons
- DOE- Fuel Cell Technology Office
  - Neha Rustagi
- The Team
  - Kerry Meinhardt
  - Corey Archipley
  - Greg Whyatt
  - Mike Powell
  - Danny Bottenus
  - Evgueni Polikarpov
  - John Barclay
  - Jamie Holladay

Thank you

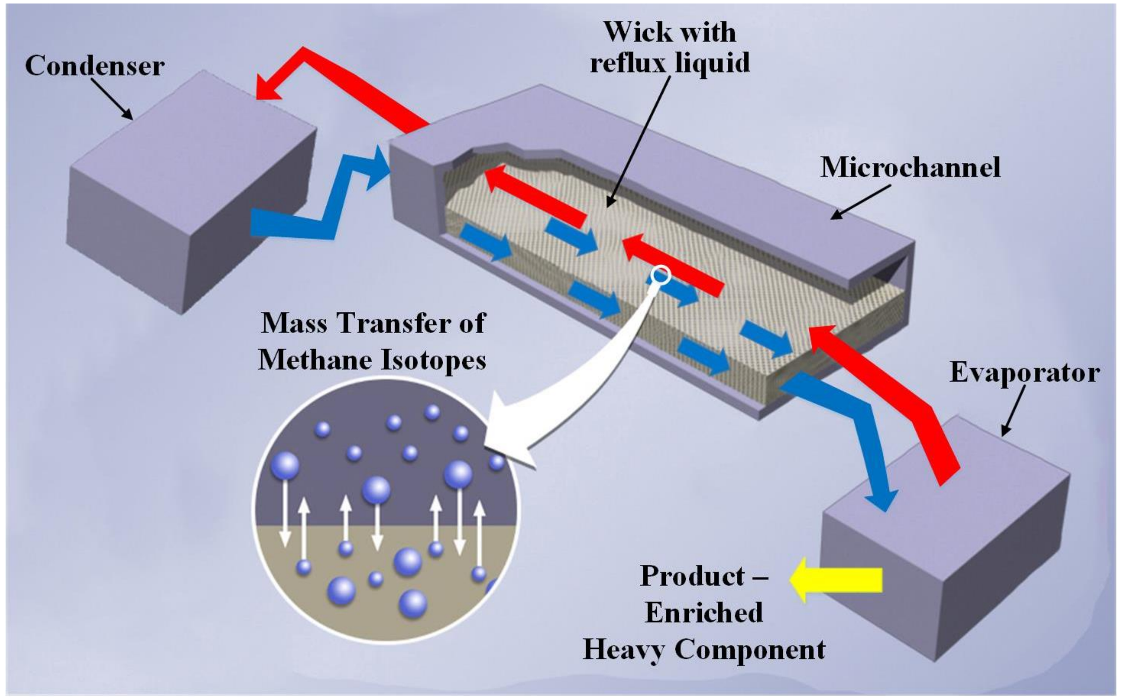
Back-up

Operating principle



Remaining challenges: O_2 separation & purification: microchannel technology

- What about scaling the air separations?
  - Microchannel based distillation to separate the O_2
  - **This is not in current project scope**
- Distillation
  - Mass transfer is dominated by liquid phase diffusivity (*D*)
  - Liquid phase mass transfer is enhanced by increasing liquid phase surface area
  - HETP – Height equivalent to a theoretical plate
    - ✓ Origins in distillation theory relating mass transfer efficiency of packed columns to tray or 'plate' columns
    - ✓ Each 'plate' represents one theoretical stage of separation and HETP is the height of column needed for each stage
    - ✓ Air dual column distillation can have up to 75 stages* (combined)
- Process Intensification
  - The hypothesis is that microchannel architecture can be used to reduce the size of the separations equipment by reducing required residence time via enhanced mass transfer



Comparison to other distillation techniques

Cryogenic Distillation Technique	HETP (cm)
Commercial packing	30-60
Sulzer's best laboratory packing – Best Available Technology (BAT)- theoretical	2-8[a]
Cryogenic microchannel distillation – Velocys Inc.	4.3[b]
PNNL's work in 4" Device	
Propane/propylene	1.0
Methane isotopes	0.5
CFD modeling (Propane/Propylene)	0.1

- Commercial Packing
  - Minimum HETP is ~30 cm
  - **100 separations stages in 30 meters**
- Best Available Technology- theoretical
  - Minimum HETP is ~2 cm
  - **100 separations stages in 2 meters**
- Our Technology
  - HETP of 0.5 cm
  - **100 separation stages in 0.5 m w/ room for improvement**

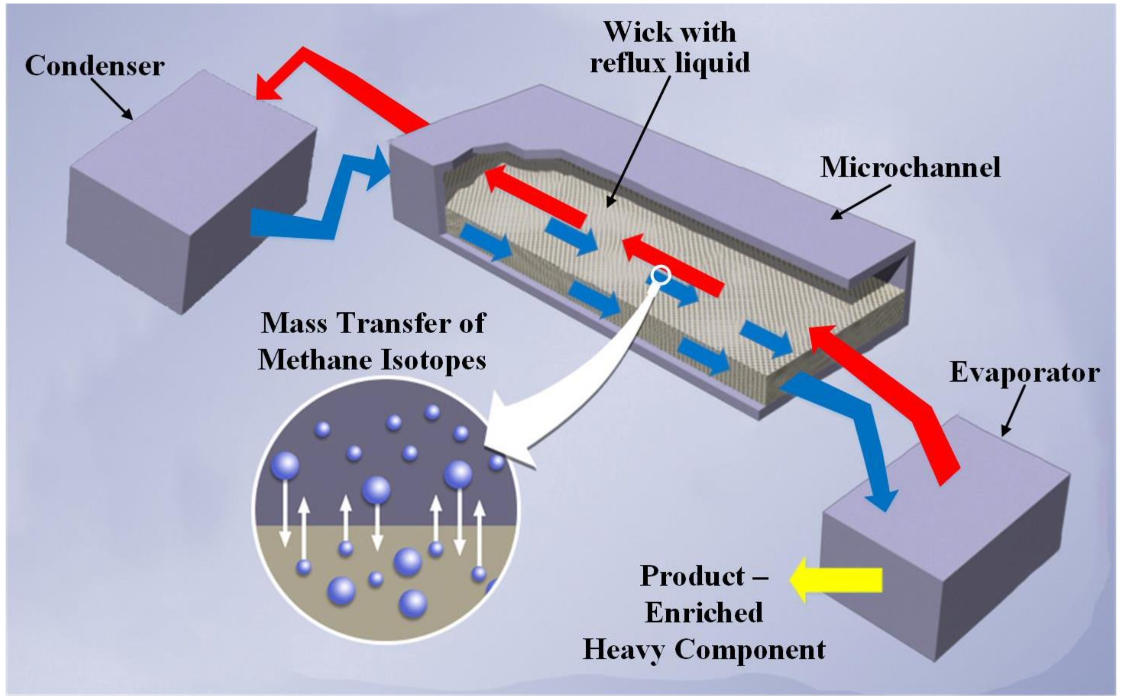
[a] Sulzer Structured Packings for Distillation, Absorption and Reactive Distillation. https://www.sulzer.com/cs/-/media/Documents/ProductsAndServices/Separation_Technology/Liquid_Liquid_Extraction/Brochures/Structured_Packings.pdf
[b] Hickey, T. Advanced Distillation Final Report. Velocys Inc., https://www.osti.gov/scitech/servlets/purl/1000368

Advantages

- Suitable for scale-up by increasing the amount of layered wicks
- Can be operated over a large temperature range
- Can be operated in the **horizontal** or vertical direction
- Microchannel benefits
  - Small Footprint
  - Portable
  - Rapid mass/heat transfer

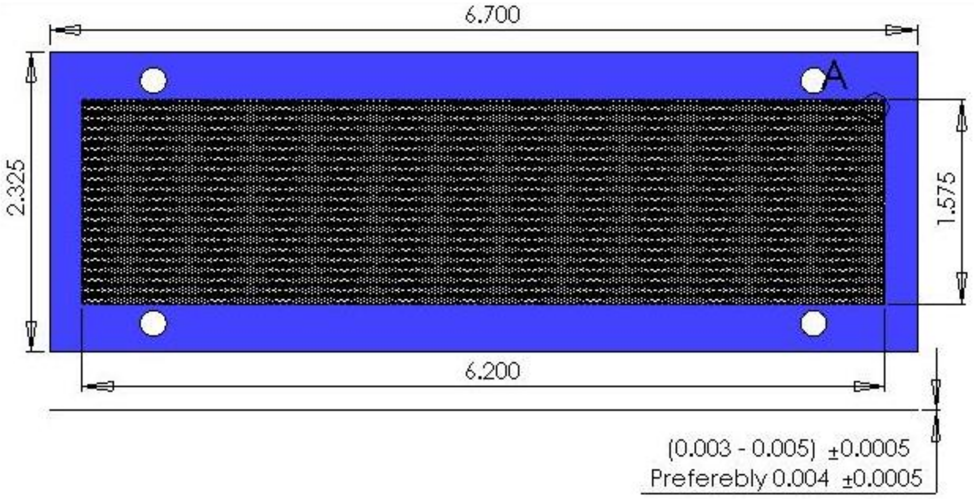
$$HETP \propto \frac{h^2}{D}\frac{\dot{m}}{\rho}$$

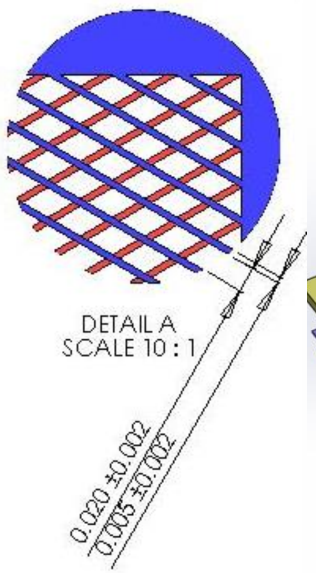
- Microchannel "Cryogenic" distillation
  - 1% Propane in Propylene: α=1.28
  - $^{12}C/^{13}C$ isotopes of methane: α=1.0028

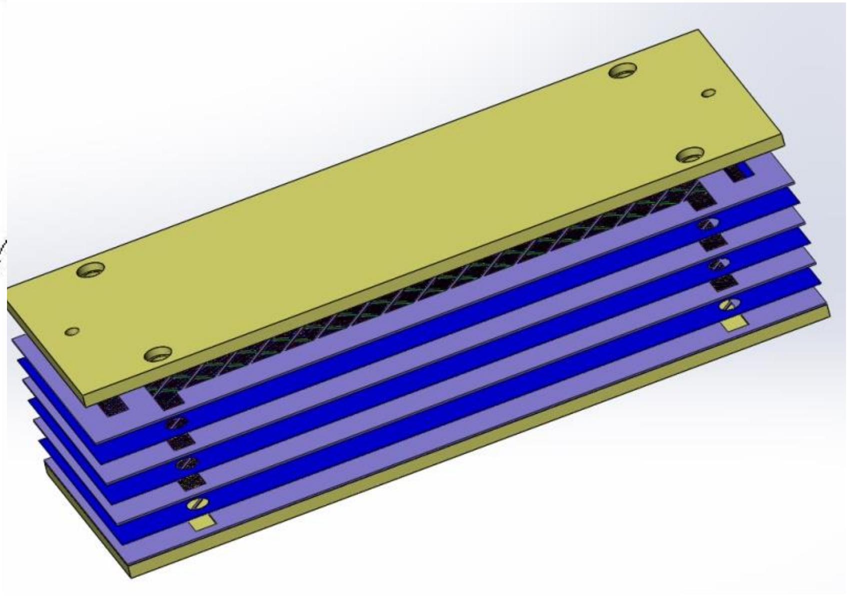


PNNL’s patented microwick technology

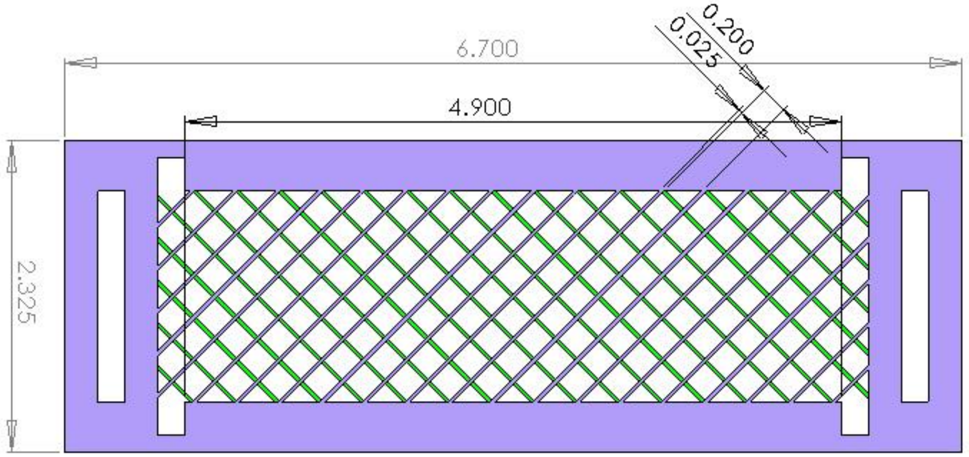
- Thin microchannel wicks for liquid flow – 0.004”

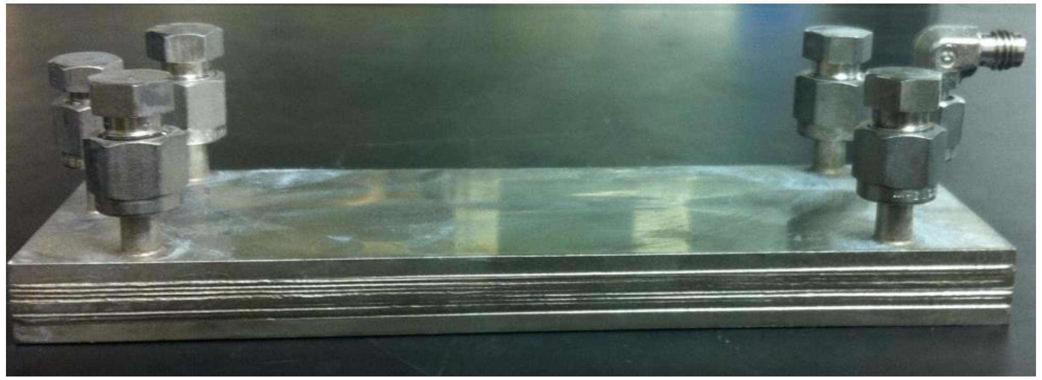






- Thicker microchannel shims for vapor flow – 0.02”





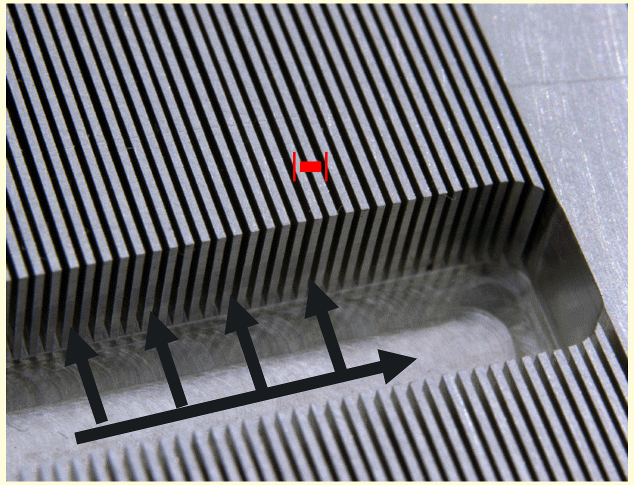
- HETP scales with the square of the wick thickness, *h*: $HETP \propto \frac{h^2}{D}\frac{\dot{m}}{\rho}$

What about oxygen separation?

Note: this is not part of our current scope

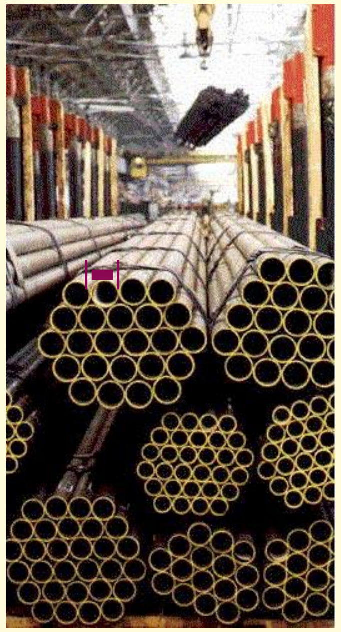
- We can potentially use microchannel architecture for scaling down the distillation

1 – 2 orders of magnitude reduction in hardware size



Vs.

~ 0.01 inch

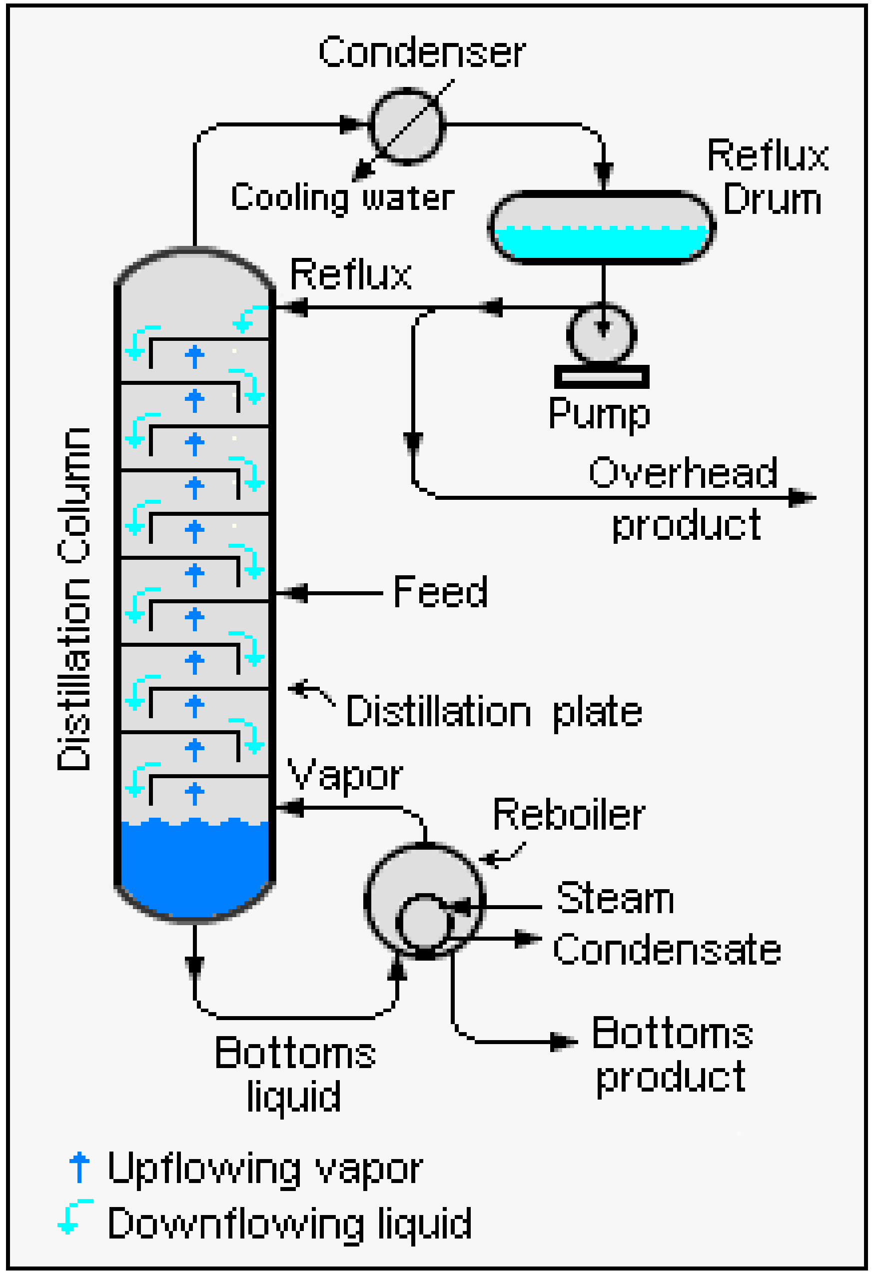


~ 1 inch

- High heat transfer coefficients
- High heat transfer surface area per unit volume
- Low pressure drop achievable through short flow distance

Traditional distillation

- Separation of chemical components via boiling point differences
- Relative volatility (α) – ratio of vapor pressures of components in a liquid mixture
  - $\alpha < 2.4^*$ for 20% O_2 in N_2
- Challenge – enhance mass transfer



https://en.wikipedia.org/wiki/Distillation

* Din, F. Trans of the Faraday Society, 1960. https://pubs.rsc.org/-/content/articlepdf/1960/tf/tf9605600668

Distillation and process intensification by microwick technology

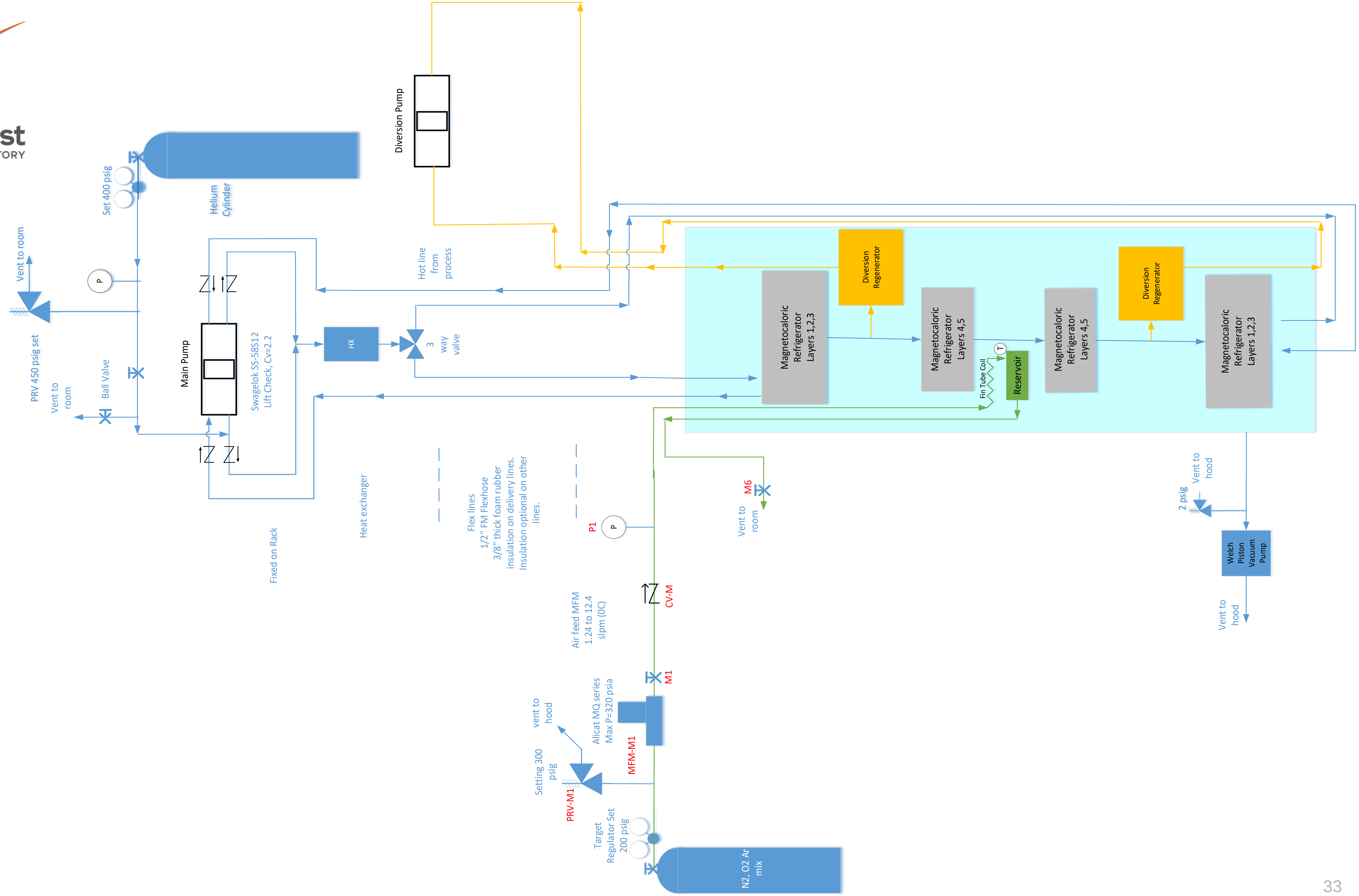
- Distillation
  - Mass transfer is dominated by liquid phase diffusivity (*D*)
  - Liquid phase mass transfer is enhanced by increasing liquid phase surface area
  - HETP – Height equivalent to a theoretical plate
    - Origins in distillation theory relating mass transfer efficiency of packed columns to tray or ‘plate’ columns
    - Each ‘plate’ represents one theoretical stage of separation and HETP is the height of column needed for each stage
    - Air dual column distillation can have up to 75 stages* (combined)
- Process Intensification
  - The hypothesis is that microchannel architecture can be used to reduce the size of the separations equipment by reducing required residence time via enhanced mass transfer
- Microchannel Distillation
  - Enhance mass transfer by incorporating microwicks

http://www.certech.be/en/activities/intensification/

*Jones et al, Fuel Processing Tech 92 (2011) 1685

Design basis for MOLS prototype

- Process gas:
  - Inlet is clean, dry air at 100 psia and 295 K; outlet is liquid air at ~100 psia and ~100 K.
  - Flow synchronized with AMR cooling steps of dual regenerators
- Active Magnetic Regenerative Liquefier subsystem specifications for MOLS
  - Temperature span is ~280 K to ~100 K with cooling of ~30 K/layer
  - Six layers integrated into each ~20cm dual regenerator; one proven refrigerant per layer
  - Ferromagnetic refrigerants have Curie temperatures that are ~30 K apart
  - Validated T, B_a dependent heat capacities and adiabatic temperature changes
  - Layers aspect ratio (L/D) ~0.7; porosity of ~0.37; spheres of ~150-250 μm; monolithic
  - Superconducting magnet; 6.5 T uniform field over 25cm; 0.1 T over 25cm; 13cm change regions
  - Frequency is ≥ 0.25 Hz
  - Heat transfer fluid is liquid that freezes at ~90 K so total pressure drops low from blows
  - Diversion flow valves to adjust flows/layers; bypass flow valve between coldest layers into counterflow process heat exchanger

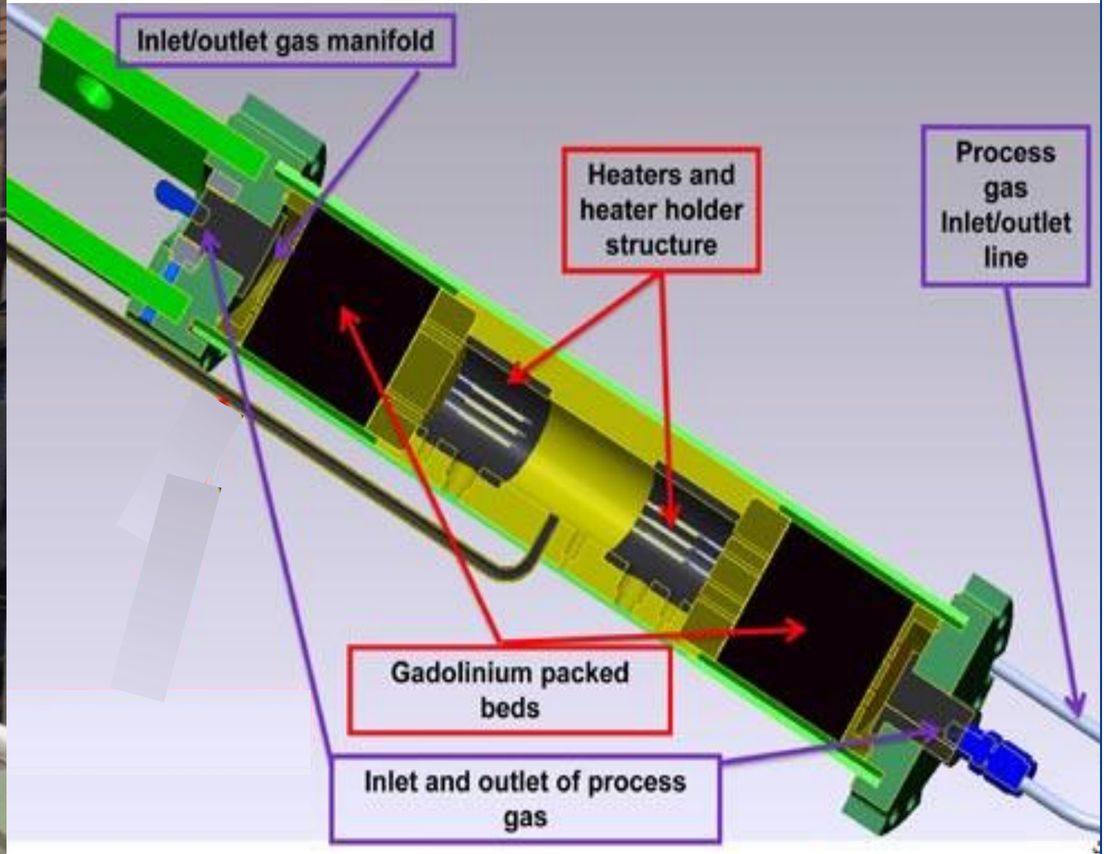


Diversion Pump
Helium Cylinder
Set 400 psig
Vent to room
P
PRV 450 psig set
Vent to room
Ball Valve
Main Pump
Swagelok SS-58S12
Lift Check, Cv=2.2
HX
3 way valve
Hot line from process
Fixed on Rack
Heat exchanger
Flex lines
1/2" FM Flexhose
3/8" thick foam rubber
insulation on delivery lines.
Insulation optional on other lines.
Diversion Regenerator
Magnetocaloric Refrigerator Layers 1,2,3
Magnetocaloric Refrigerator Layers 4,5
Magnetocaloric Refrigerator Layers 4,5
Diversion Regenerator
Magnetocaloric Refrigerator Layers 1,2,3
Fin Tube Coil
T
Reservoir
M6
Vent to room
P1
P
CV-M
Air feed MFM
1.24 to 12.4
slpm (0C)
M1
Alicat MQ series
Max P=320 psia
MFM-M1
vent to hood
Setting 300 psig
PRV-M1
Target Regulator Set 200 psig
N2, O2 Ar mix
Vent to hood
2 psig
Welch Piston Vacuum Pump
Vent to hood

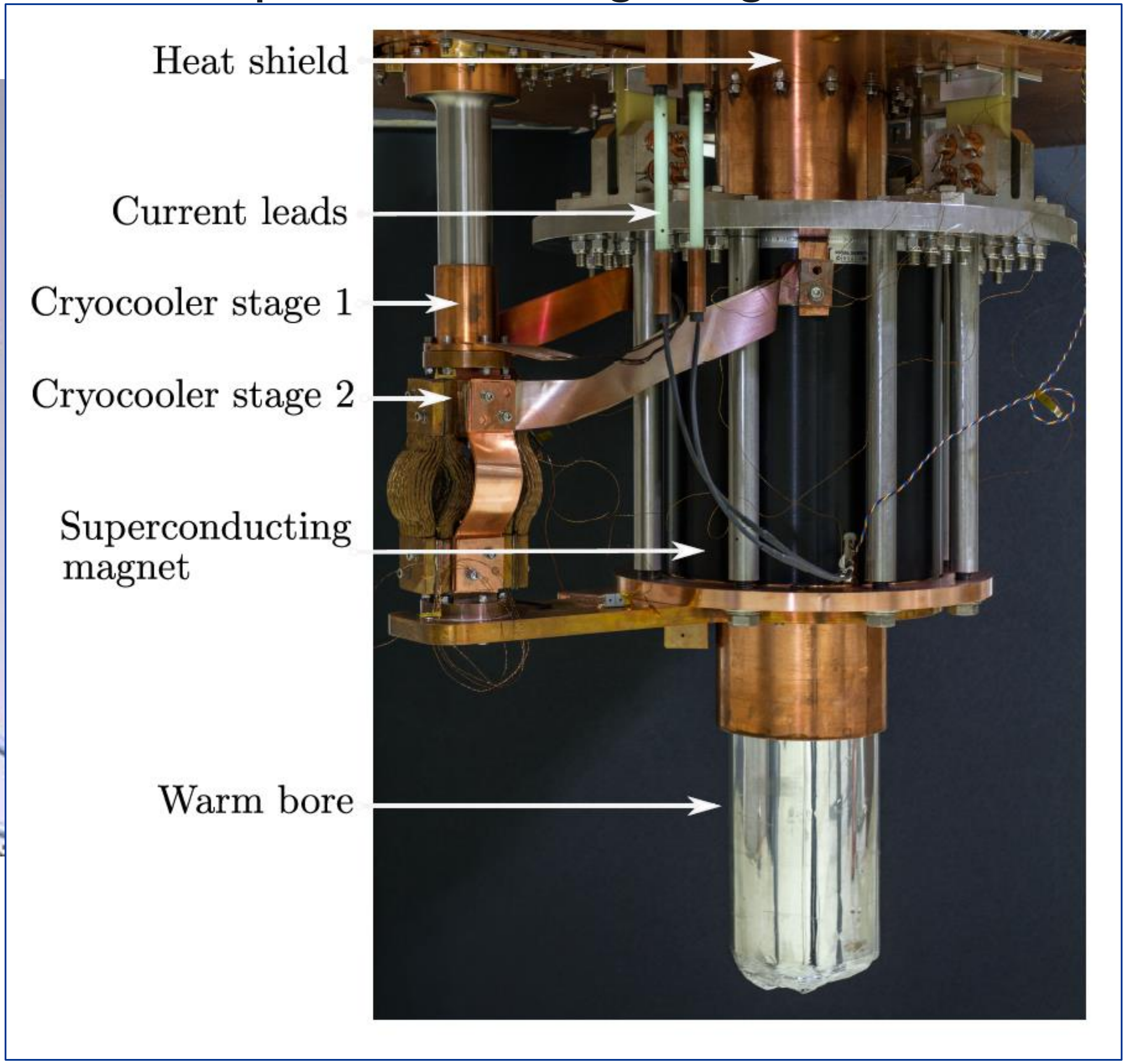
Background:

Dual active magnetic regenerators and super conducting magnet are key subsystems

Active Magnetic Regenerator



Super conducting magnet



Axial thermal conduction ➡ irreversible entropy in low L/D aspect ratio regenerators

$$FOM = \frac{\dot{W}_{ideal}}{\dot{W}_{real}}$$

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

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

$$\Delta\dot{S}_{IRR} = \Delta\dot{S}_{IRR_{HT}} + \Delta\dot{S}_{IRR_{DP}} + \Delta\dot{S}_{IRR_{LC}} + \Delta\dot{S}_{IRR_{EC}}$$

$$\Delta\dot{S}_{IRR_{HT}} = 2 * \left(\frac{\dot{Q}_{Reg}}{NTU + 1}\left(\frac{1}{T_C} - \frac{1}{T_H}\right)\right)$$

$$\Delta\dot{S}_{IRR_{DP}} = \frac{\dot{m}_{He}}{\rho_{He}} * \frac{\Delta p_{Reg}}{T_H}$$

$$\Delta\dot{S}_{IRR_{LC}} = 2 * \left(\frac{\pi * k_{Reg_{eff}} * D_{Reg}}{4 * a_{ratio}} * \frac{(T_H - T_C)^2}{T_H T_C}\right)$$

$$\Delta\dot{S}_{IRR_{EC}} = 2 * \left\{\left(\frac{16}{5 * \pi}\right)\left(\frac{\pi d_p{}^2}{4}\right) * \frac{V_{MM} * \nu^2 * \Delta B^2}{32 * \rho_{eMM} T_{ave}}\right\}$$

$$k_{Reg_{eff}} = k_{MM_{eff}} + k_{He_{static}} + \rho_{He} c_{p_{He}} D_{L_{Reg}}$$

$$\dot{Q}_{LC} = k_{Reg_{eff}} * \frac{\pi\, D_{Reg}}{4\, a_{ratio}} * (T_H - T_C)$$

EXAMPLE

- 280 K to 242 K; 0.25 Hz; 493 gram Gd; 200 micron spheres, 0.37 porosity; 6T field change; 400 psia He HTF @ 4 gm/s;
- $Q_{coldMAX}$= 56W @ 242 K
- D_{layer} =7 cm; L/D_{ratio} = 0.37
- **k_{Regeff} = 2.69 W/m K when**
  $k_{Hestatic}$ = 0.145 W/m K!
- **Q_{dotLC} = 15.1 W**; $Q_{dotPARA}$ = 5 W
- Q_{dotNET} = 56 – 15.1- 5 W = 36 W!
- FOM reduced to 0.47 in this example
- Design needs be changed to increase L/D for FOM = 0.65
- **LONGER Regenerator requires LONGER Magnet**

Diversion of heat transfer fluid flow allows control of cooling power of each layer, but increases complexity