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MagnetoCaloric Hydrogen Liquefaction



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PACIFIC NORTHWEST NATIONAL
LABORATORY

JUNE 2016

PROJECT ID # PD131

Timeline:

- ▶ Project Start Date: 10/1/2015
- ▶ Project End Date: 09/30/2019

Barriers addressed:

- ▶ H: High-Cost Low Energy Efficiency of Hydrogen Liquefaction

Budget:

- Total: \$2.25M
- Federal share: \$2.25M
- Recipient share: \$0
- Total spent: ~\$361k

Partners:

- Emerald Energy NW, LLC:
- AMES/ISU



Relevance:

Magnetocaloric liquefaction is more energy efficient than Claude cycle



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- 1) Demonstrate H₂ liquefaction system liquefying ~ 25 kg/day H₂ with FOM >0.5
- 2) Identify pathway to larger scales with installed capital cost < \$70M 30 tonne/day

30 tonne/day (small facility)	Claude cycles (current)	PNNL's MCHL (projected)	DOE Target (2017) ¹
Efficiency	<40%	70~80%	85%
FOM	<0.3 (small facility) 0.35~0.37 (large facility)	~0.6 (small facility) ~0.7 (large facility)	0.5
Installed Capital cost	\$70M ¹	\$45-70M	~\$70M
O&M cost	4%	2.8%	?
Energy input	10-15 ¹ kWh/kg H ₂	5~6 kWh/kg H₂	12 kWh/kg H ₂

[1] DOE, *Multi-Year Research, Development and Demonstration Plan, 2015*

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

$$\dot{W}_{Real} = \dot{Q}_C \left(\frac{T_H}{T_C} - 1 \right) + \frac{T_H \int_{T_C}^{T_H} \Delta S_{IRR} dT}{\int_{T_C}^{T_H} dT}$$

Approach: MCHL minimizes irreversibilities

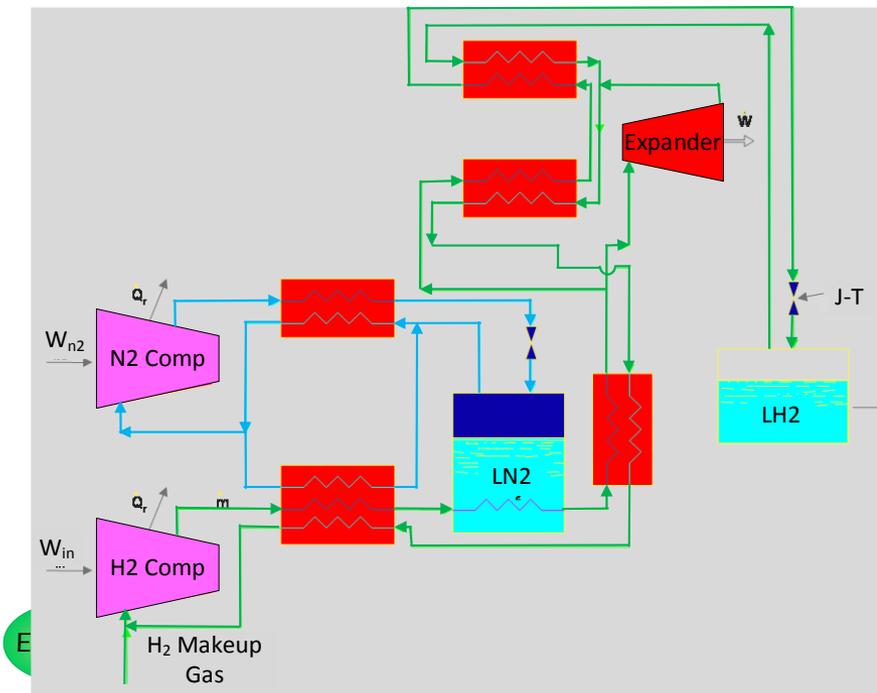


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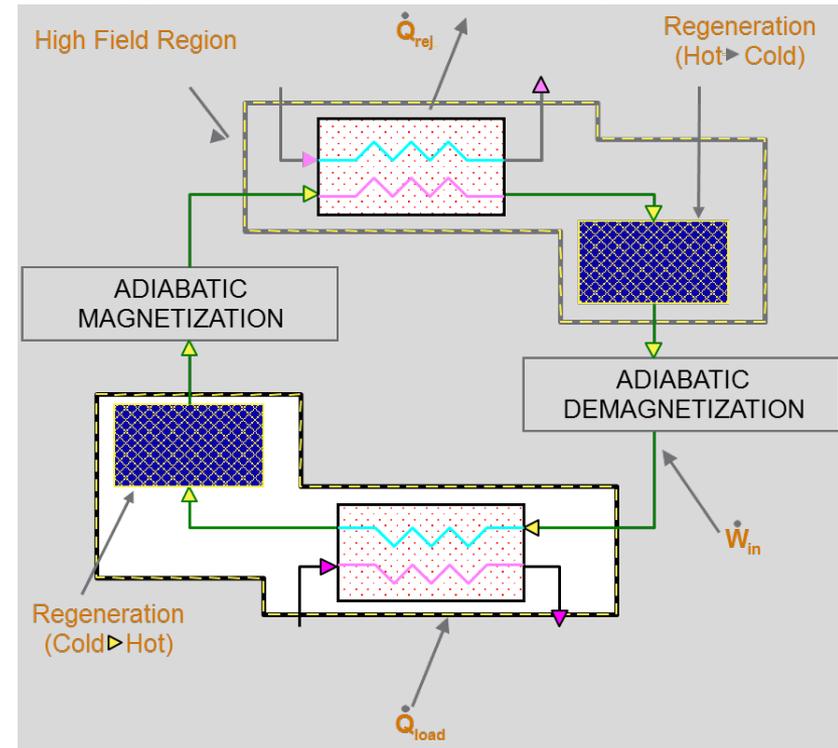
▶ Conventional Claude Liquefier

- Low efficiency, FOM = 36%
 - Theoretical 3.92 kWh/kg H₂
 - Real 10.8 kWh/kg H₂
- Why?
 - LN₂ pre-cooled Claude cycle
 - ~50% irreversibility from compressors



▶ Magnetocaloric Liquefaction

- FOM = 60+% (projected)
- Entropy of solid magnetic materials manipulated by magnetic fields
- Active magnetic regenerative cycle
- Bypass flow of HTF unique to MCL





Approach: Project Plans- 25 kg H₂/Day

▶ GEN-I System

- Refurbish Prometheus prototype and characterize performance
- Measure improvement from by-pass of heat transfer gas
- Test multi-layer regenerator
- Develop GEN-II/GEN-III designs
- Cost analysis

} Validates the models

▶ GEN-II System

- Develop seals for heat transfer gas in rotary designs
- Model magnetic and mechanical forces for non-solenoidal magnets
- Detailed design of all subsystems
- Modify rotating disk for material synthesis
- Fabricate, assemble and test GEN-II with large temperature span
- Refine GEN-III design for efficient 280 K to 20 K operation

▶ GEN-III System

- Demonstrate 25 kg/day H₂ liquefaction
- Cost analysis

Major Milestones Being Met



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Presented by Raffaele Simon 10/5

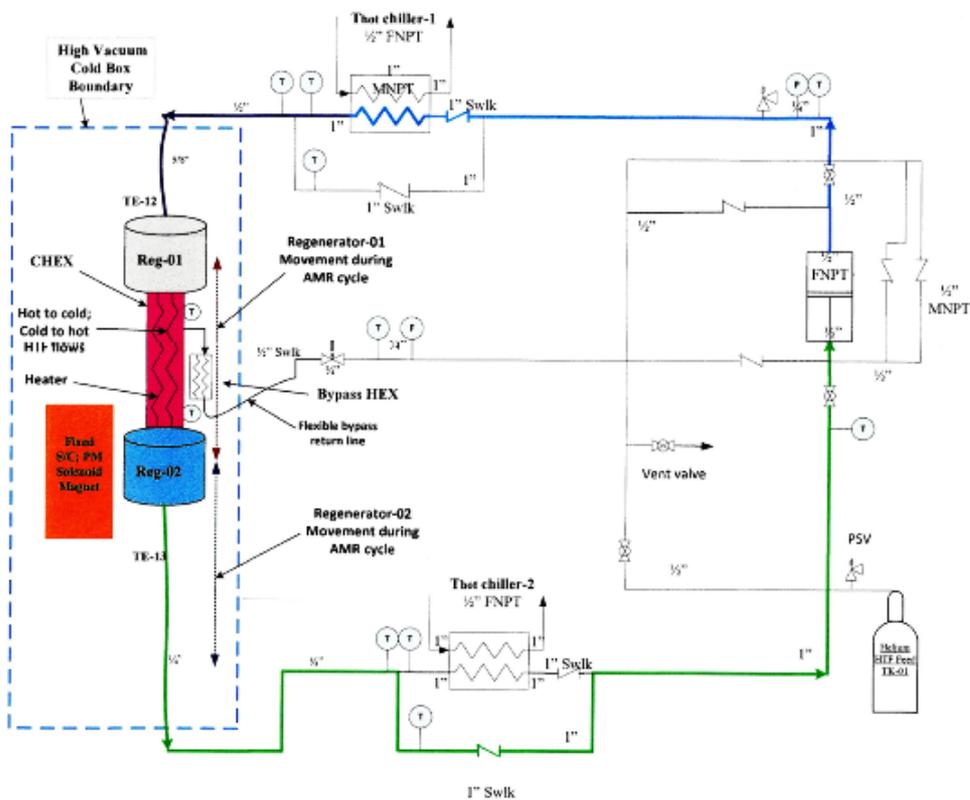
Fiscal Year	Milestone	Status	Comments
2015 Q4	Potential of MCHL technology is quantitatively analyzed. Pathway toward the installed cost of \$6M/ton/day with 10 ton/day capacity and FOM~0.5 efficiency is identified	Complete	
2016 Q1	Demonstrate propane liquefaction	Complete	
2016 Q2	Detailed design of GEN-II	Complete	Seals are a challenge; fixed regenerator design chosen
2016 Q3	Measure M-H-T (magnetization-field-temperature) curves and field-dependent heat capacity vs. temperature of samples from 0.5 kg lots of 8 magnetocaloric powders received from Ames (~200 μm spheres); variable Curie temperatures from ~290 K to ~150 K; up to ~15 K ΔT at ~6.5 T field change	50%	AMES to provide PNNL material. AMES is upgrading rare-earth powder fabrications systems.
2016 Q4	Receive all GEN-II subsystems/components, and test to ensure that they are ready for assembly of the Gen-II multi-layer magnetic dual regenerators.	15%	

Accomplishment: GEN-I PID and Sub-systems Developed

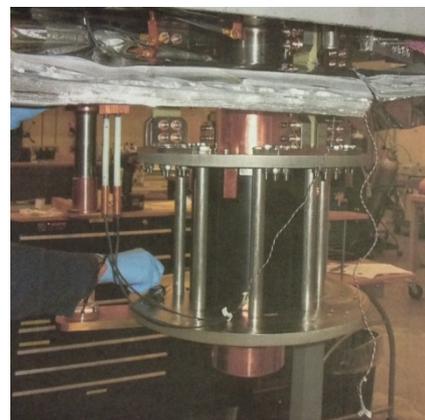


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Dual AMR assembly



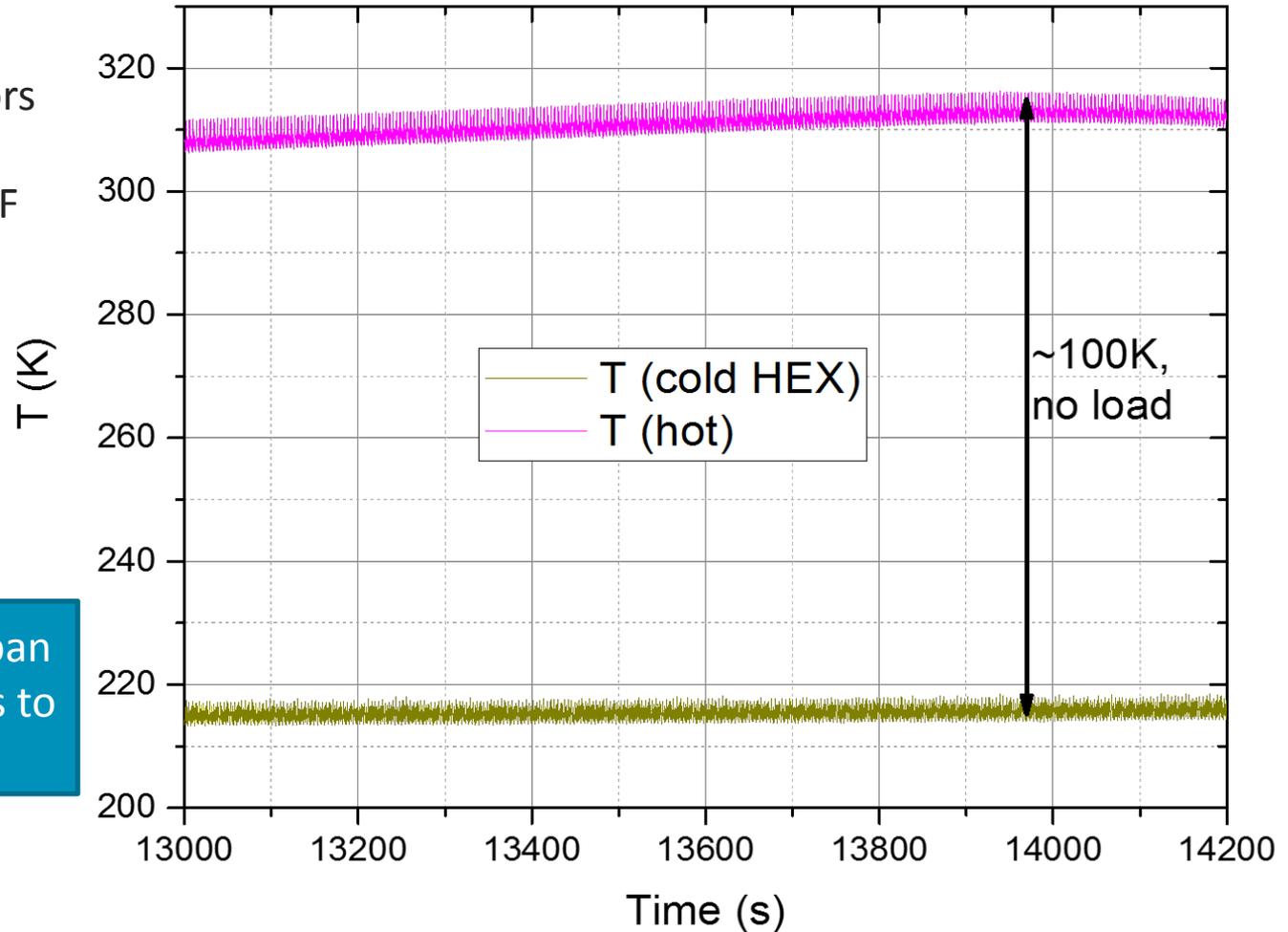
Superconducting magnet



Complete System

Accomplishment: GEN-I: Maximum T Span (No External Load and with $T_{HOT} > T_{Curie}$)

1kg Gd Regenerators
3.3-0.6 Tesla field
200 psia He gas HTF
4 sec AMR cycle



World Record ΔT span
for these conditions to
our knowledge

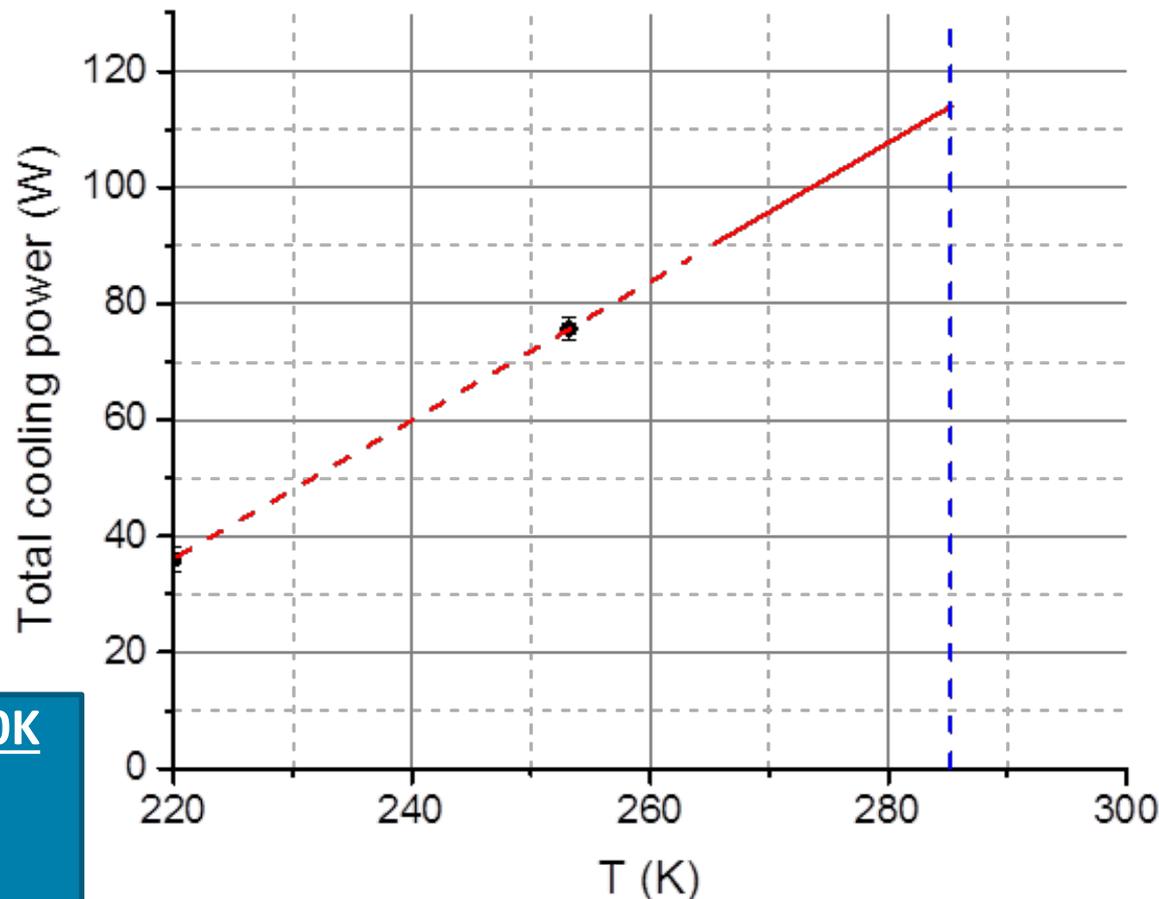
Accomplishment GEN-I: Cooling curve as a function of external applied power via heater in CHEX



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1kg Gd Regenerators
3.3-0.6 Tesla field
200 psia He gas HTF
He mass flow $\sim 20\%$ of max
4 sec AMR cycle
 T_{HOT} set to ~ 285 K
90 W at $T_{\text{COLD}} \sim 265$ K

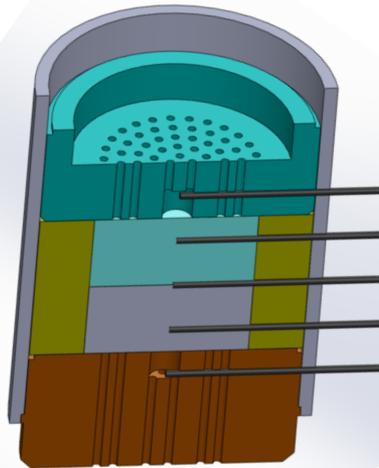


90W achieved @ $\Delta T=20$ K

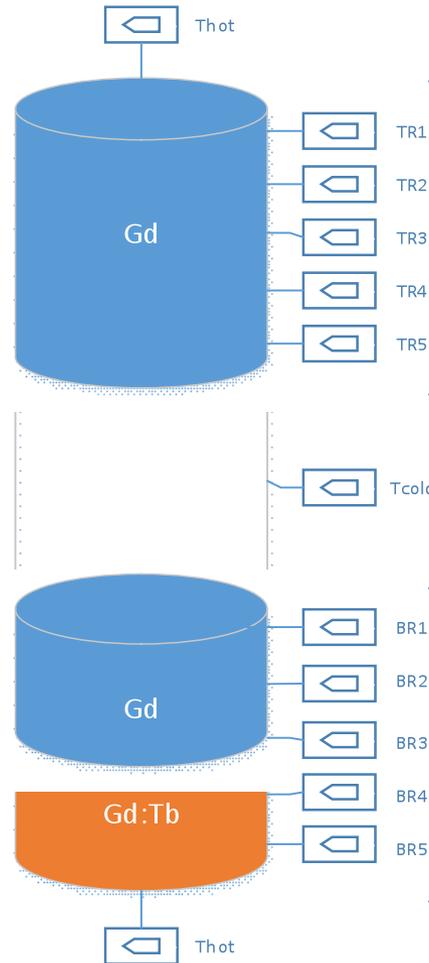
- 54W cooling
- 36W heat leak
- HTF undersized

Accomplishment: GEN-I – Layered Regenerator

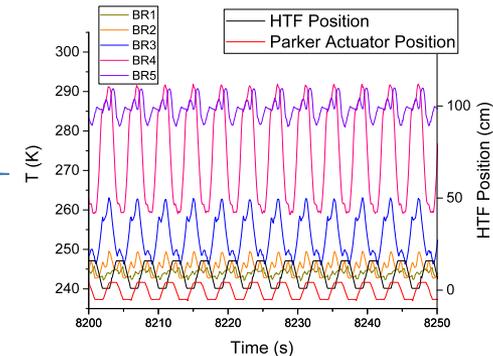
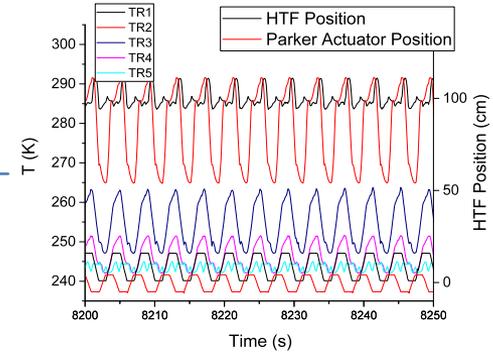
215g Gd Regenerator (upper)
215g Gd/Gd_{0.74}Tb_{0.26}
Regenerator (lower)
3.3 - 0.6 Tesla
200 psia He gas HTF
4 sec AMR cycle



Non-linear T profile that changes with by-pass



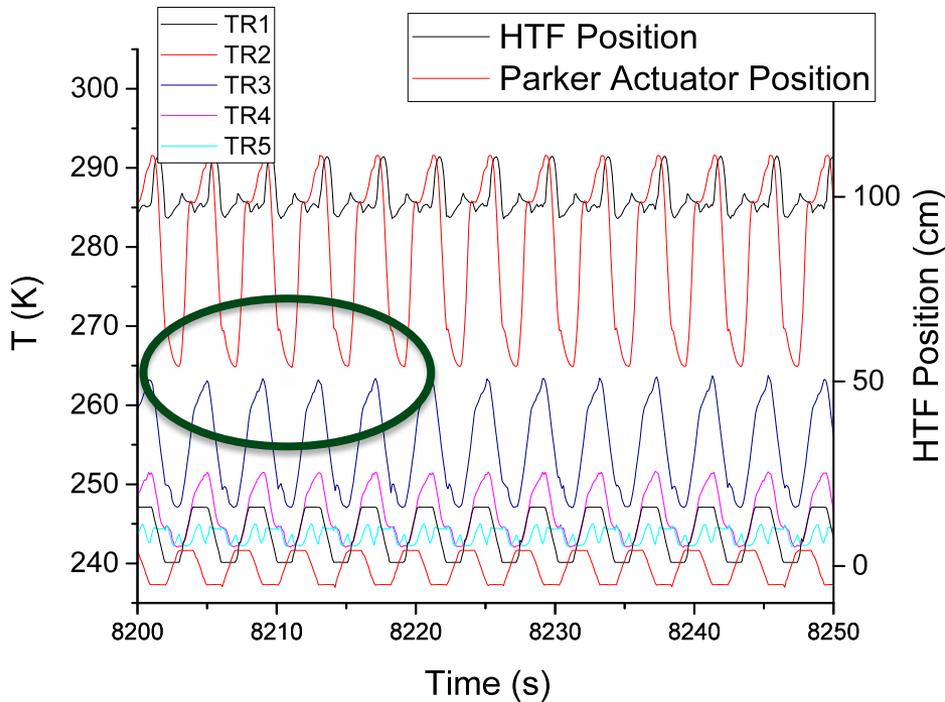
Layered regenerator with the TCs schematic



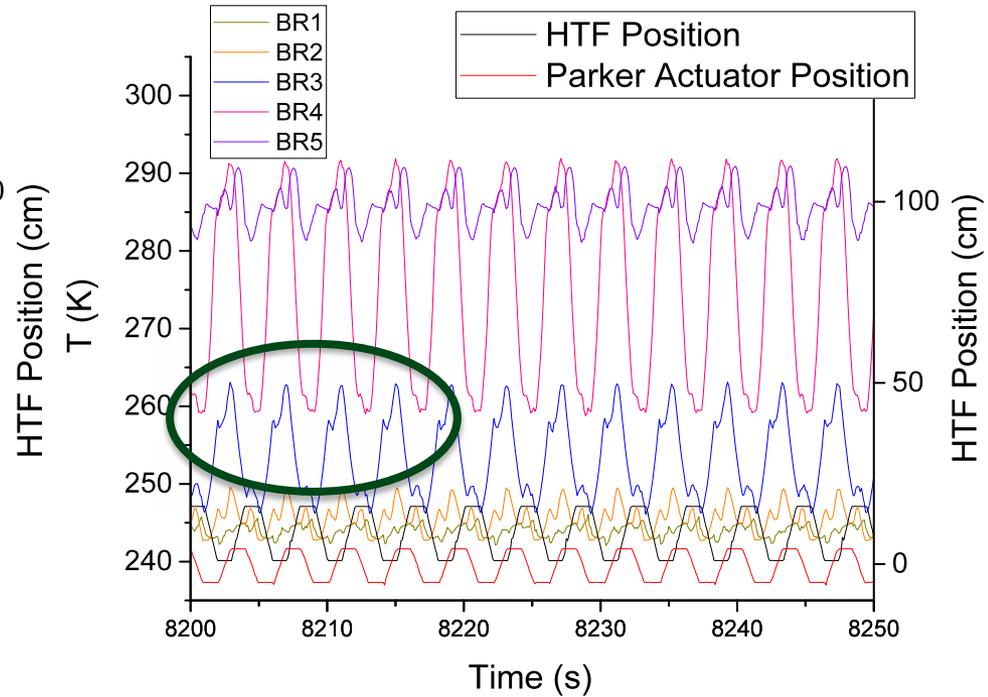
Detailed temperature profiles inside the regenerators

Accomplishment: GEN-I – Layered Regenerator

Gd only



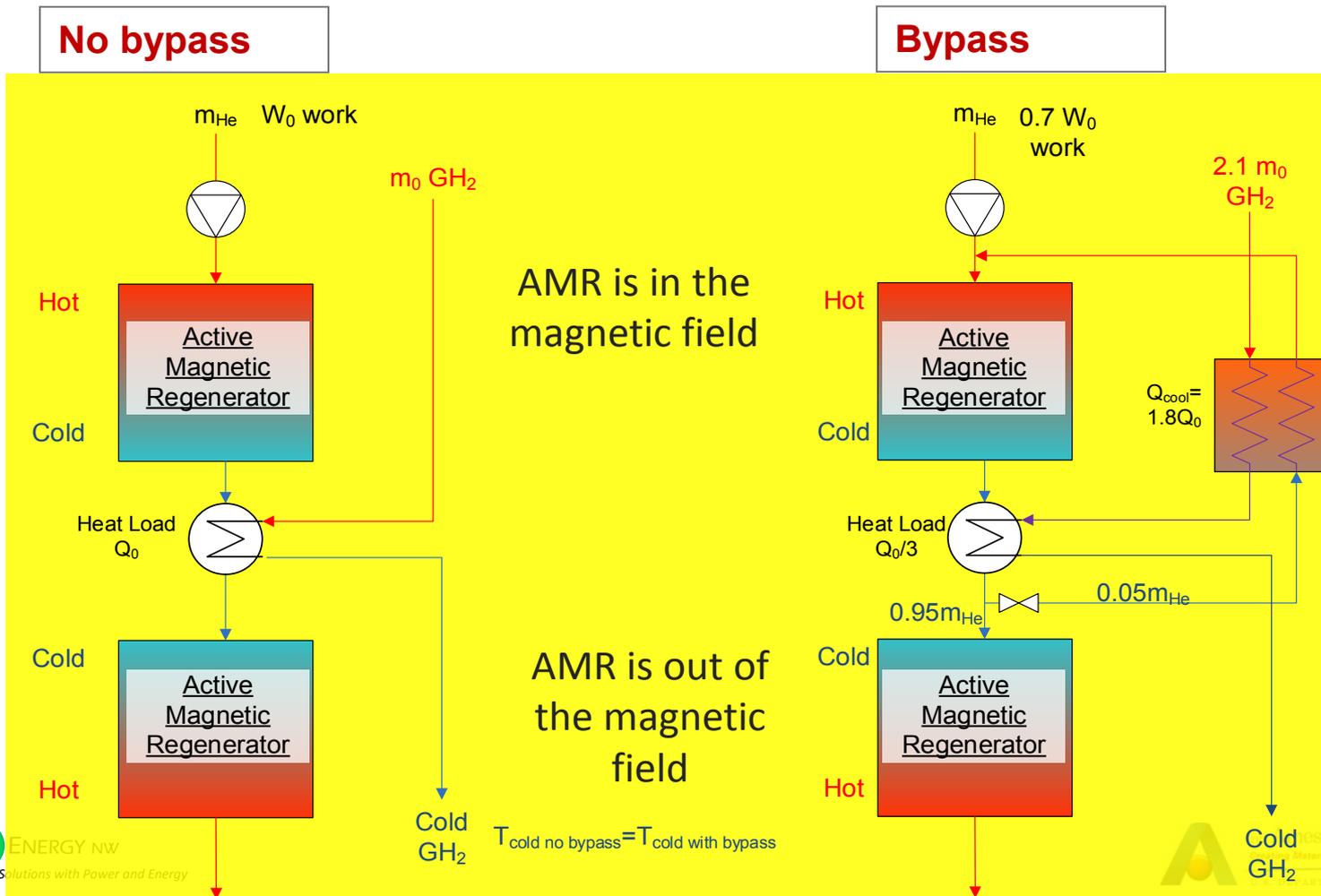
Gd/Gd_{0.76}Tb_{0.24}



Understanding the temperature profile key to designing multi-layer systems

Accomplishment: HTF bypass flow in dual regenerator AMRR improves efficiency

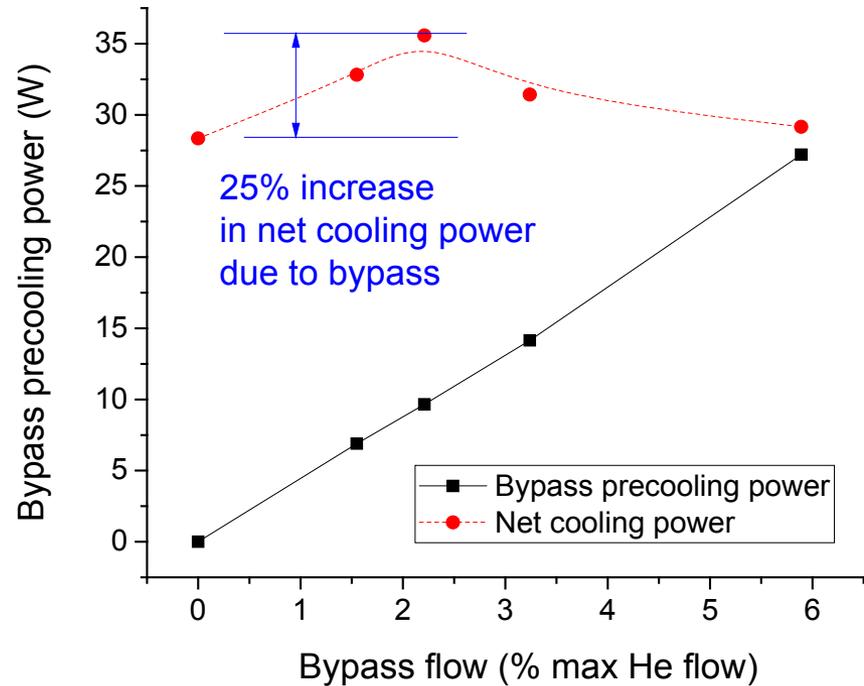
- ▶ Reduces approach ΔT in process HEX for large increase in FOM
- ▶ Eliminates intrinsic irreversibility of AMR cycle in ferromagnetic refrigerants



Accomplishment: Built GEN-I Layered Regenerator with Optimum HTF flow

215g Gd Regenerator (upper)
215g Gd/Gd_{0.74}Tb_{0.26}
Regenerator (lower)
3.3 – 0.6 Tesla field
200 psia He gas HTF
4 sec AMR cycle
HTF flow rate better matched to
magnetocaloric cooling power

- 22% of the magnetic material of original GEN-I regenerators gives 70% of cooling power at optimal HTF flow
- By-pass flow increases cooling by 25%
- Thermal mass difference increases at 6.5-7 T gives > 6% by-pass flow



Accomplishment: Projected Impact of By-Pass - up to 88% reduction in Magnetic Material



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Assuming system is scaled up by:

- 1) Increasing the magnetic field to 7 Tesla
- 2) Increasing HTF size

	No Bypass	6% By-pass	% Improvement
Thermal Load	4.3 kW	2.9 kW	32% reduction
HTF flow	31.3 L He/sec	3.8 L He/sec	87% reduction
Magnetic Material Required	184 kg	22.3 kg	88% reduction
FOM	0.4	>0.75	87% increase

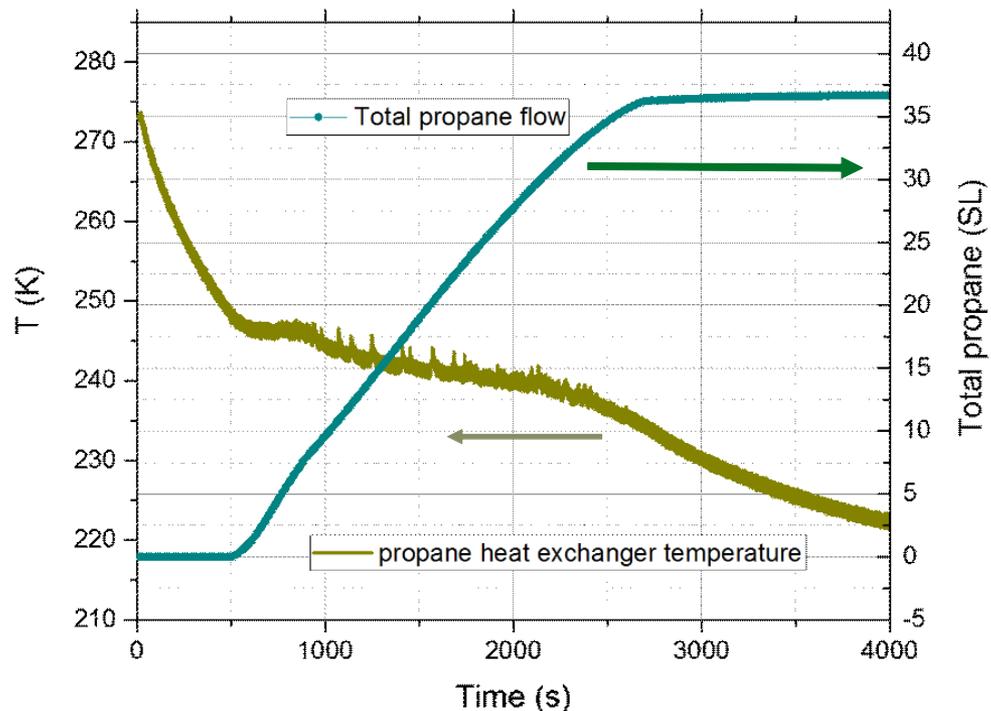
Accomplishment: Propane Liquefaction System



Coiled-fin tube exchanger in
CHEX between dual AMRs



Dual AMR assembly



First ever gas liquefaction
from room temperature
demonstration with MCL
(to our knowledge)

Accomplishment: Design of GEN-II/III System to cool 25 kg H₂/day to 120K



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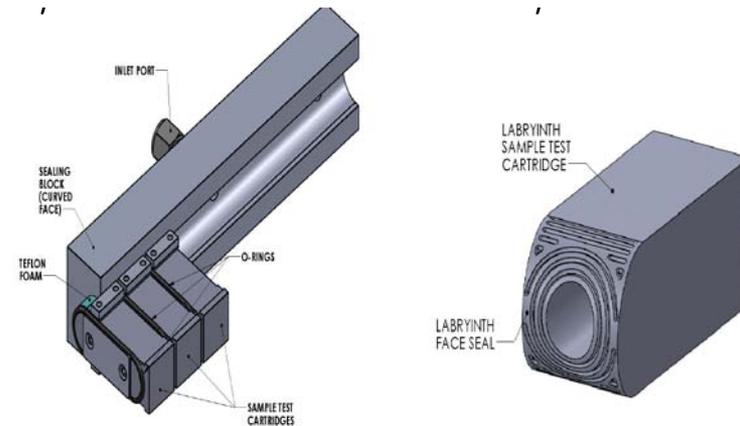
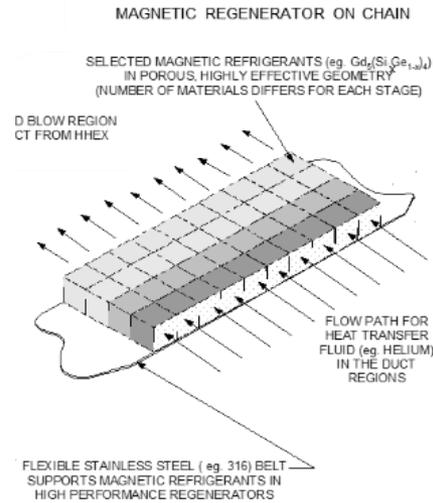
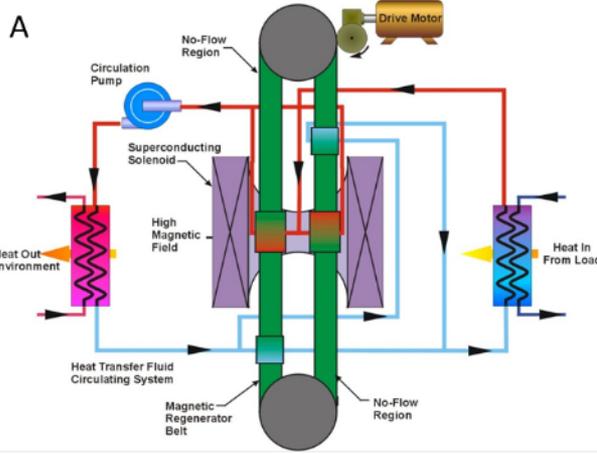
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Advantages

- ▶ > 0.6 FOM
- ▶ Rotary design
- ▶ Unique use of by-pass flow
- ▶ Layered material regenerators
- ▶ Eliminates load imbalance

Risks

- ▶ Seals
- ▶ Chain stresses
- ▶ Never been done before - what don't we know?



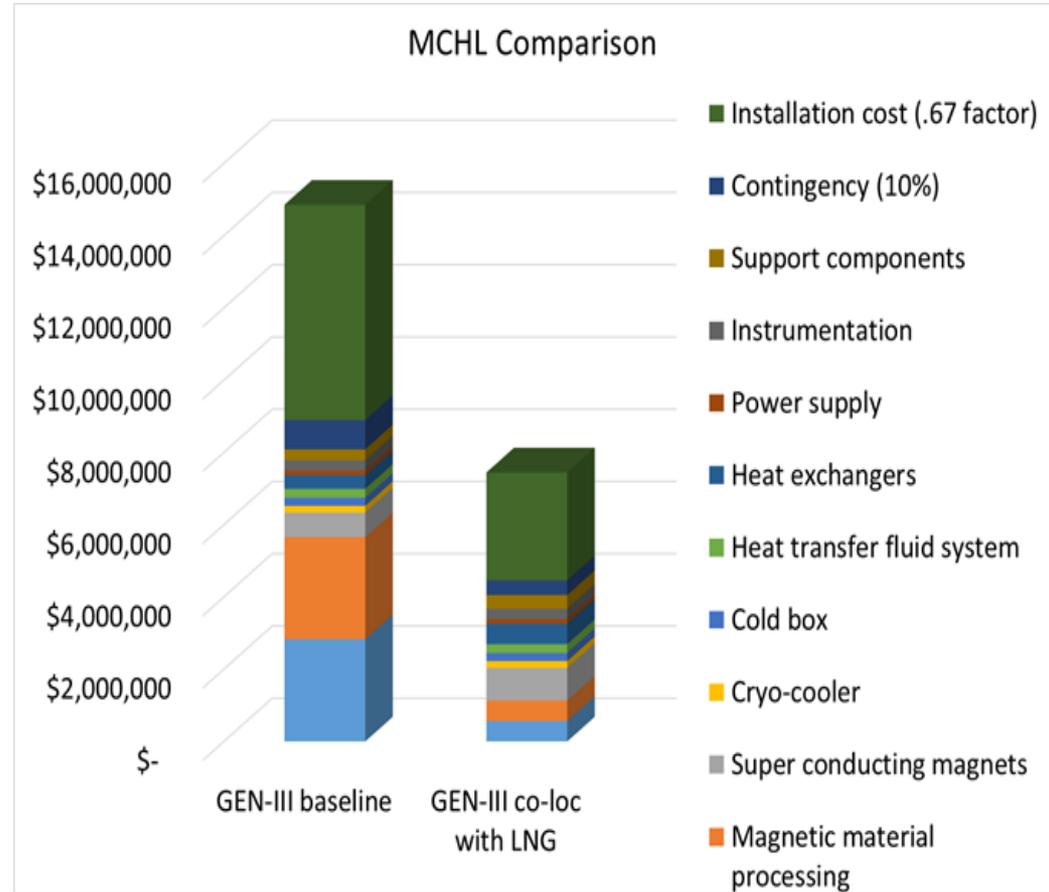
Accomplishment: Preliminary Cost Analysis - \$1.5M / tonne H₂/day

- ▶ Magnetic material (1st stage of 3 stage design 25 kg/day)
 - Wheel (no by-pass) – 184 kg
 - Wheel (GEN-III) (w/by-pass) – 22.3 kg

- ▶ 10 Tonne H₂/day ~\$15M

- ▶ Design option – co-locate with CNG/LNG
 - Use “free cooling” from LNG conversion to CNG
 - ~\$7M

10 tonne H₂ /day

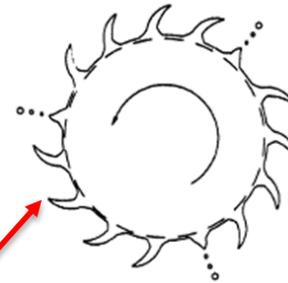
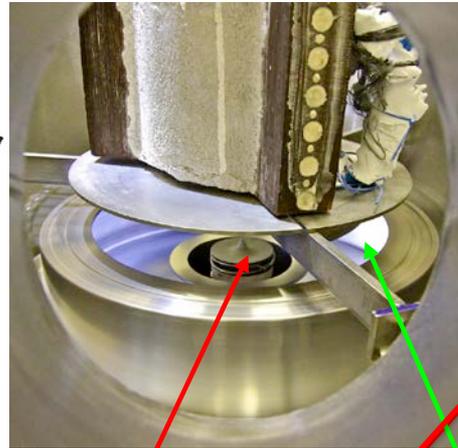
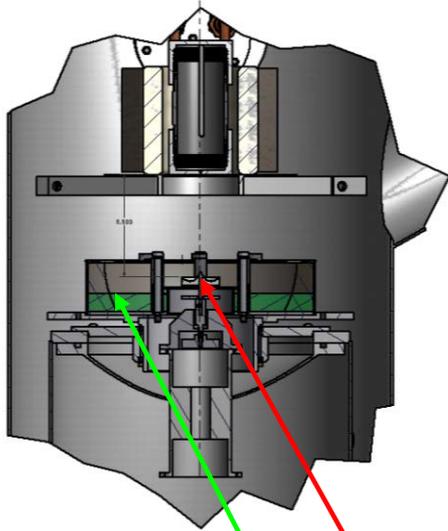


Rotating Disk Atomization System Being Used for Powder Synthesis



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Tantalum atomization disk (molten droplets spun off periphery)

Rotating quench bath filled with vacuum pump oil (quenches/passivates/collects powders)



➤ Current atomizer makes highly reactive, low density calcium.

Co-rotating oil quench bath envelopes powders instantly, providing passivated surface film.

➤ This unique capability is being adapted for making pure rare earth (RE) and RE-RE alloys as spherical powders in the right size for magnetic refrigeration.

Accomplishment: Detailed Gen-II Sub-system design Complete



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Sub-system	% design complete	Notes
Magnetic regenerator	100%	Seals, model
Superconducting magnet	100%	Design complete. Doing upgrades now
Cryocooler subsystem	100%	Complete
Vacuum/Cold-box	100%	Complete
Structural support	100%	Slight modification for GEN-II
Instrumentation, DAQ and control	100%	Complete
Drive	100%	May need tweaks
Fluid subsystem (heat transfer fluid loop and process loop)	100%	May need tweaks

Patent application had not been filed at time of submittal so detailed design not shown.

Accomplishment and Progress: Response to reviewer comments



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- ▶ This is a new start so you will have to wait until next year.

Next Steps: Complete Gen II/III component design and assembly



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- ▶ Finish detailed GEN-II design for multi-layer dual regenerator
- ▶ For two additional magnet designs, do magnetic field/force calculations
- ▶ Do preliminary tests of key elements of GEN-II design
 - Using as many components in GEN-I as possible
- ▶ Finish ordering all materials and components
- ▶ Magnetic materials – AMES will supply finished materials to specs
- ▶ Build / Test GEN-II and use lessons learned to design GEN-III

Patent application had not been filed at time of submittal so detailed design not shown.

Collaborations

Partner	Project Roles
DOE	Sponsorship, steering
Emerald Energy Northwest LLC	Worked with PNNL on: <ul style="list-style-type: none">- Design- Data analysis- Cost analysis
AMES Laboratory / ISU	Materials selection feedback Material synthesis
HDTT	Provide critical feedback and direction
CaloriCool (EMN)	Working with organizers to ensure new materials for our application will be developed



Remaining Challenges and Barriers

- ▶ >2 layer operation
 - Multi-layer AMRs have been a challenge for research groups in the past
 - Our data reveals the problem is in the HTF flow circuits used
 - Mitigation: Incorporate our hypothesis into multi-layer dual regenerators and test new HTF design
- ▶ Rotary design
 - Seals
 - Mitigation: Alternative design with no moving seals under development
- ▶ Rotating disk atomization
 - Currently uses steel crucible - contaminates our magnetic materials
 - Being replaced
 - Quench bath oil identification
 - Speed needs to be increased
 - New drive motor
 - New ceramic bearings

Proposed Future Work



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▶ FY 2016

- Complete model to understand magnetic field and stresses
- Purchase, receive, and test components for GEN-II
- Magnetic materials
 - AMES to provide PNNL with materials and characterization
 - PNNL to validate material performance in GEN-I

▶ FY2017

- Integrate magnetic materials into GEN-II
- Test GEN-II
- Revise GEN-III concept design based on learnings from GEN-II
- Acquire and test remaining components

▶ FY2018

- Receive remaining 14 compositions for the multi-stage GEN-III system
- Construct, commission and test GEN-III system
- Evaluate minimum of 2 non-rare earth based magnetocaloric materials
 - (May be joint with CaloriCool)
- Complete economic analysis



Technology Transfer Activities

▶ Industrial

- Met with multiple companies to discuss application of MCHL
 - Hydrogen liquefaction
 - Stranded NG
 - High value gas separation and recovery

▶ Potential future funding

- Reaching out to other DOE agencies (AMO) for alternative applications

▶ Patents and Licensing

- 4 invention disclosure reports submitted
- 2 provisional patent applications submitted
- 1 additional provisional patent application under development



Summary

▶ Performance

- 100K T span
- First time demonstrated
 - By-pass
 - Layered material with thermocouples
 - Room temperature to liquid C₃H₈

▶ Preliminary Capital Cost Projection

- \$45M – \$75M for 30 tonne/day

▶ Material synthesis

- High production low cost spherical particle production being developed

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FOM	<0.3 (small facility) 0.35~0.37 (large facility)	~0.6 (small facility) ~0.7 (large facility)	0.5
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O&M cost	4%	2.8%	?
Energy input	10-15 ¹ kWh/kg H ₂	5~6 kWh/kg H₂	12 kWh/kg H ₂



Mission

We transform the world through courageous discovery and innovation.

Vision

PNNL science and technology inspires and enables the world to live prosperously, safely and securely.

DISCOVERY

in action

CREATIVITY
integrity *Values* courage Impact
COLLABORATION

Technical Back-up slides



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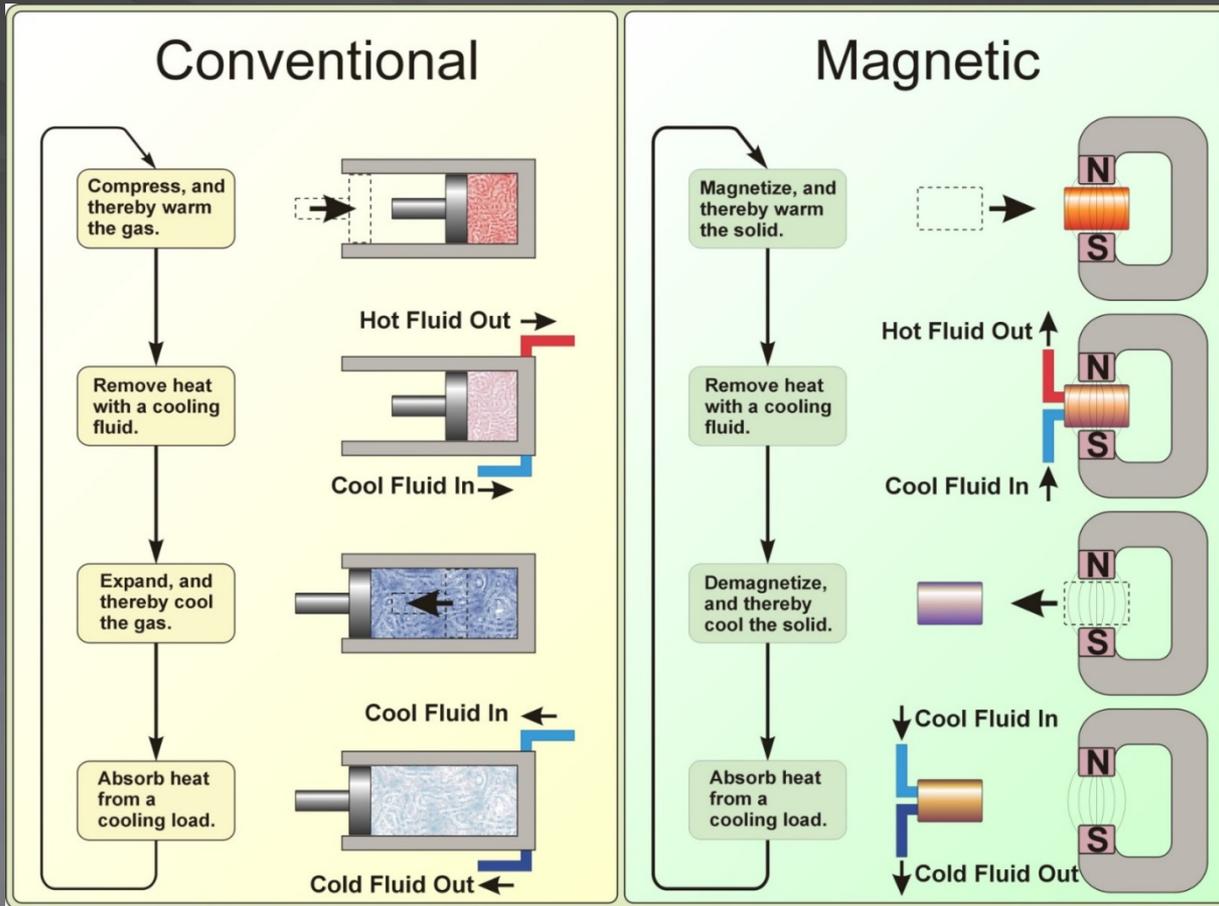
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Background: How magnetocaloric cooling works: Vapor compression analogy



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Advantages

- High efficiency
- Low environmental impact
- Wide cryogenic temperature range

Disadvantages

- Process complexity
- Potential high capital cost
- Market acceptance

Accomplishment: GEN-I System



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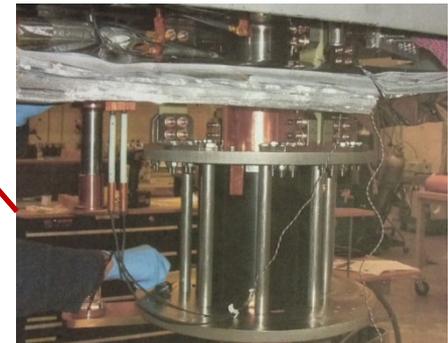


Data acquisition panels



Dual AMR assembly

Heat transfer fluid



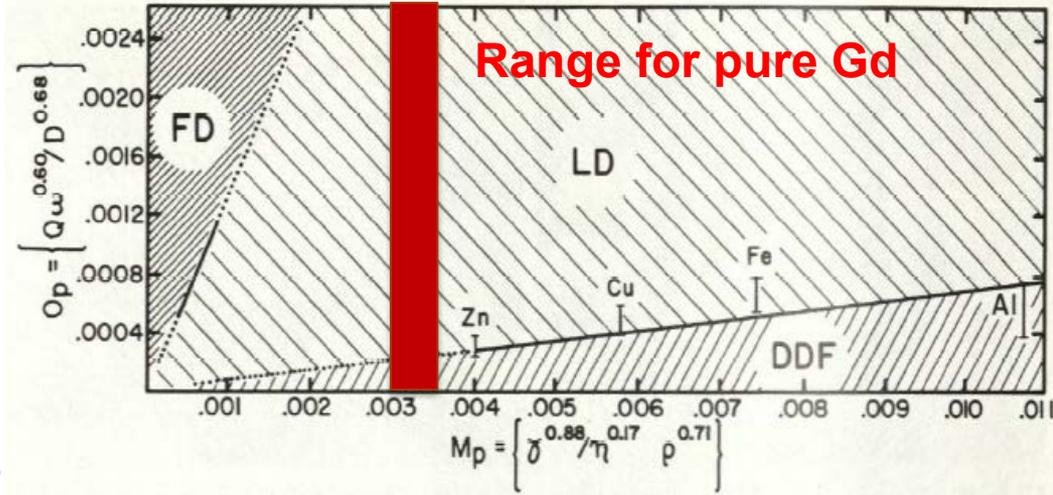
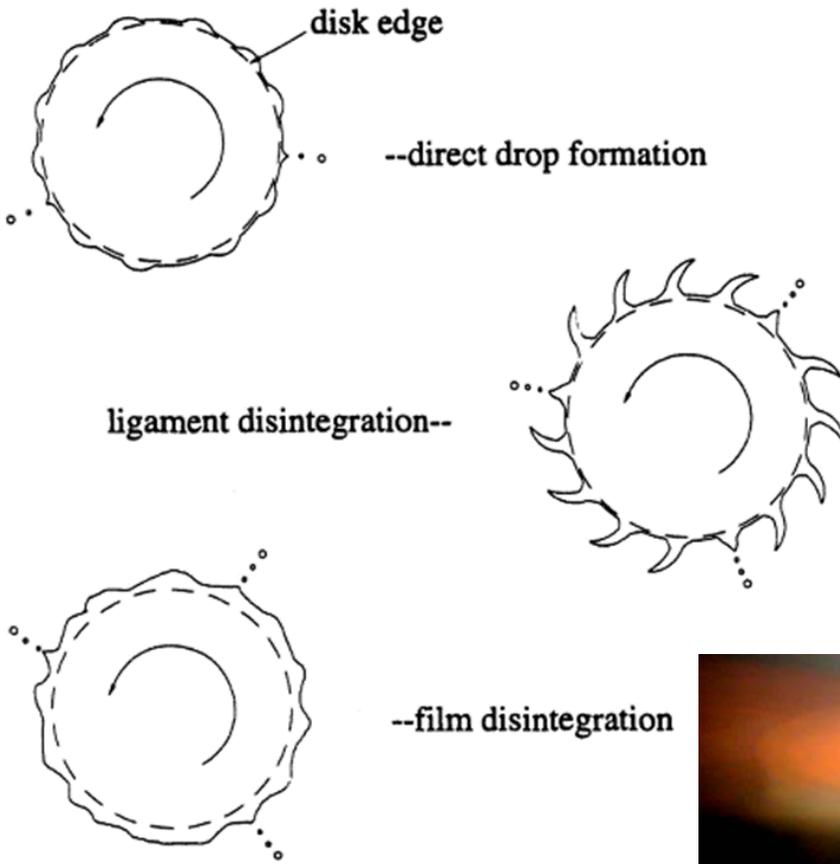
Superconducting magnet

Atomization Mode Selection for Control of Spherical Powder Size



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Champagne and Angers predicted critical liquid flow rates for transitions between 3 modes of centrifugal atomization: lowest flow rate/narrowest size distribution.

Operate in ligament disintegration mode.



Target = 200μm

Current Status and Immediate Plans FY2016



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1. a) **Stopper Rod Control Conversion:** in progress in machine shop (chamber top fixture and fittings designed and being fabricated). ---Completion planned week of May 9.
b) Chamber side access port finished and top viewport being attached with quartz window (on order).---Completion planned week of May 9.
2. a) **Develop Crucible for Gd Melting:** designed for Gd_2O_3 crucible liner and robust YSZ backing.
b) Designed crucible shape and received fugitive graphite mandrels from machine shop.
c) Determined supplier and ordered Gd_2O_3 thermal spray powder.---Delivery scheduled by May 5.
d) Fabricate laminated crucibles by PAS deposition (exclusive Ames Lab capability).---Completion planned by the week of May 9.
3. a) **Add Precise Speed Control to Disk Drive Motor:** Selected and obtained from vendor, control software installed, and motor tests completed.
b) Motor to shaft coupler being fabricated in shop.---Completion planned week of May 3.
- 3.1. a) **Produce Pure Gd Powders:** Procured sufficient commercial high purity Gd to perform trials.
b) Perform initial atomization test runs of pure Gd.---**Completion planned before end of May.**
4. a) **Substitute Ultra-High Speed Disk Bearings:** Develop design and refine selection of ceramic bearing set for durable operation in vacuum and order from vendor.---Completion planned in July.

Accomplishment: Preliminary Cost Analysis. Co-Location <\$1M/tonne H₂/day

