# MagnetoCaloric Hydrogen Liquefaction

JAMIE HOLLADAY
PACIFIC NORTHWEST NATIONAL LABORATORY

JUNE 2016

PROJECT ID # PD131

# Overview

## 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

EMERALD ENERGY NW
Solutions with Power and Energy

EMERALD ENERGY NW
Solutions with Power and Energy

THE Ames Laboratory
Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

# Relevance:
## Magnetocaloric liquefaction is more energy efficient than Claude cycle

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

1) Demonstrate $H_2$ liquefaction system liquefying ~ 25 kg/day $H_2$ 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 $H_2$** | 12 kWh/kg $H_2$ |

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

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

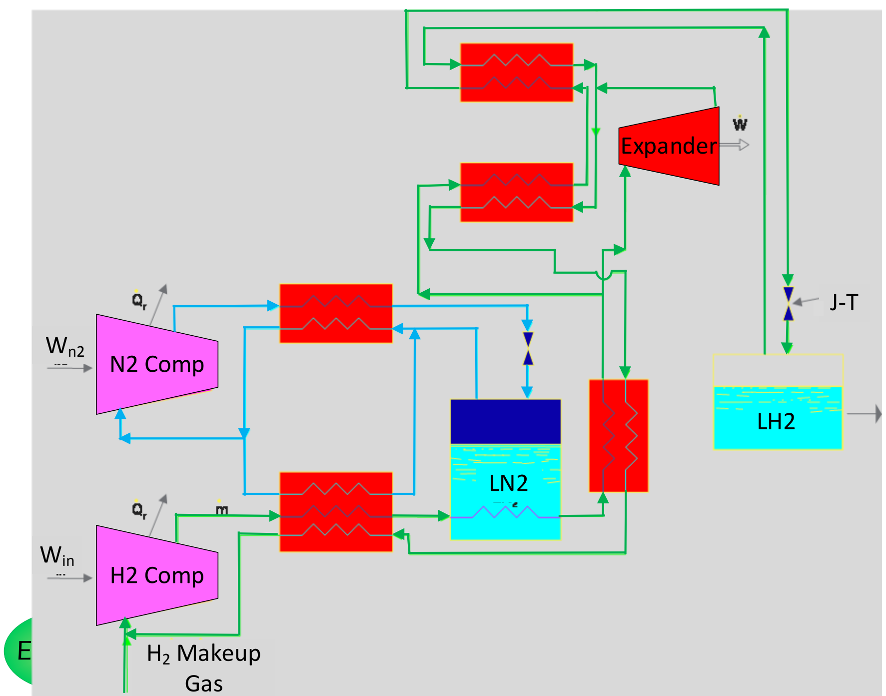
$$\dot{W}_{Real} = \dot{Q}_C\left(\frac{T_H}{T_C} - 1\right) + \frac{T_H \int_{T_C}^{T_H} \Delta S_{IRR}\, dT}{\int_{T_C}^{T_H} dT}$$

EMERALD ENERGY NW
Solutions with Power and Energy

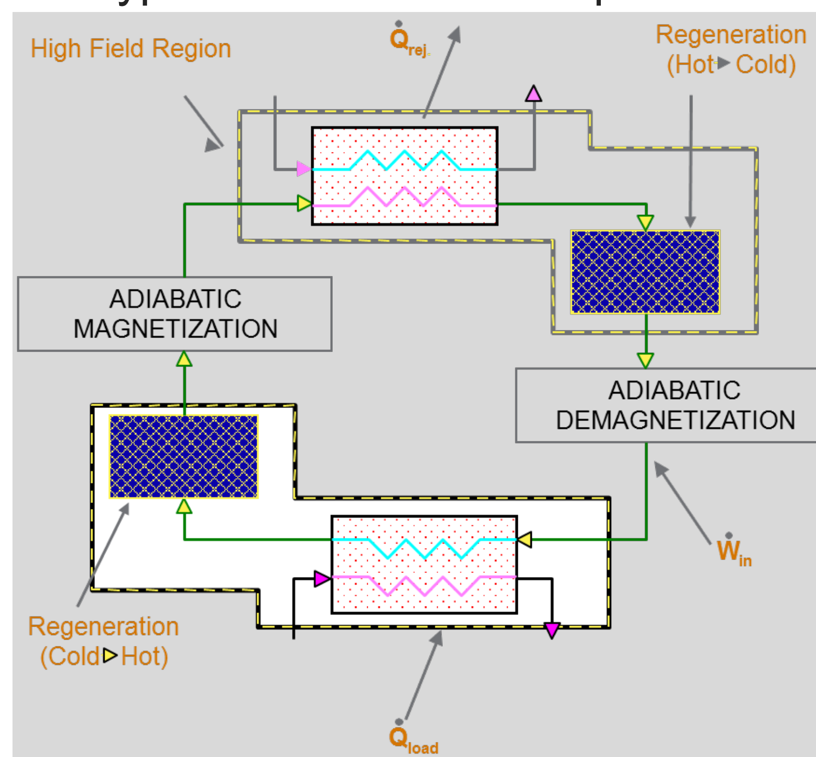
THE Ames Laboratory
Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

# Approach:
# MCHL minimizes irreversibilities

- Conventional Claude Liquefier
  - Low efficiency, FOM = 36%
    - Theoretical 3.92 kWh/kg $H_2$
    - Real 10.8 kWh/kg $H_2$
  - Why?
    - $LN_2$ 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 $H_2$/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 $H_2$ liquefaction
  - Cost analysis

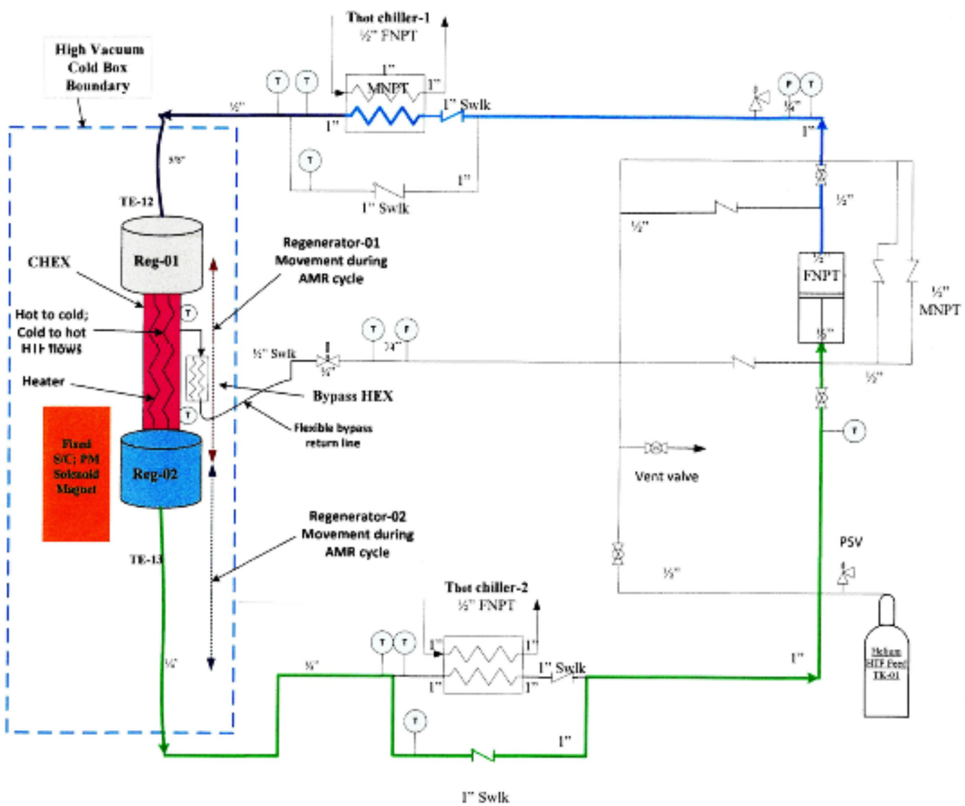
# Major Milestones Being Met

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

| 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 $\Delta T$ 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






Dual AMR assembly

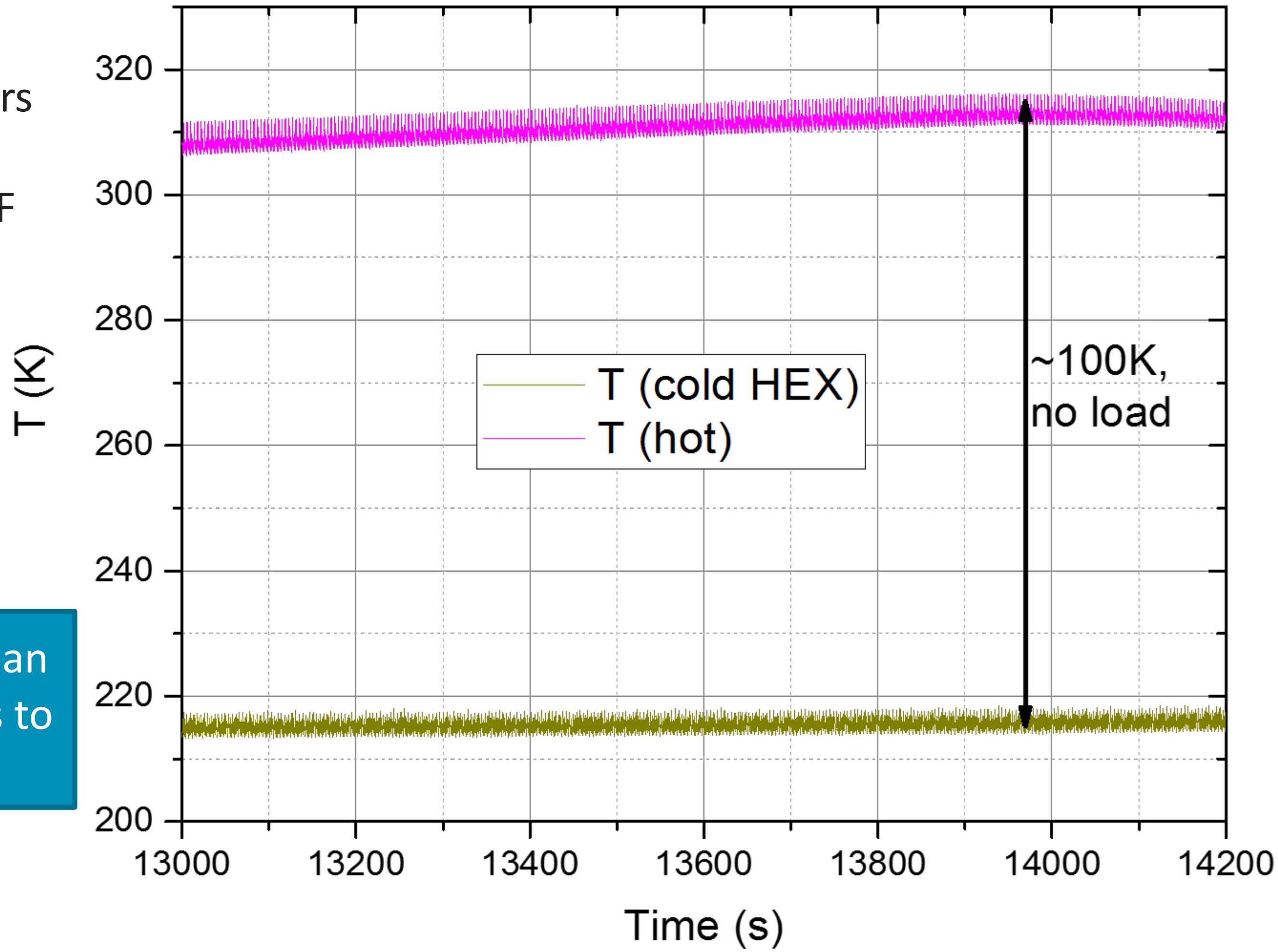
Complete System

Superconducting magnet

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

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by* Battelle *Since 1965*

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

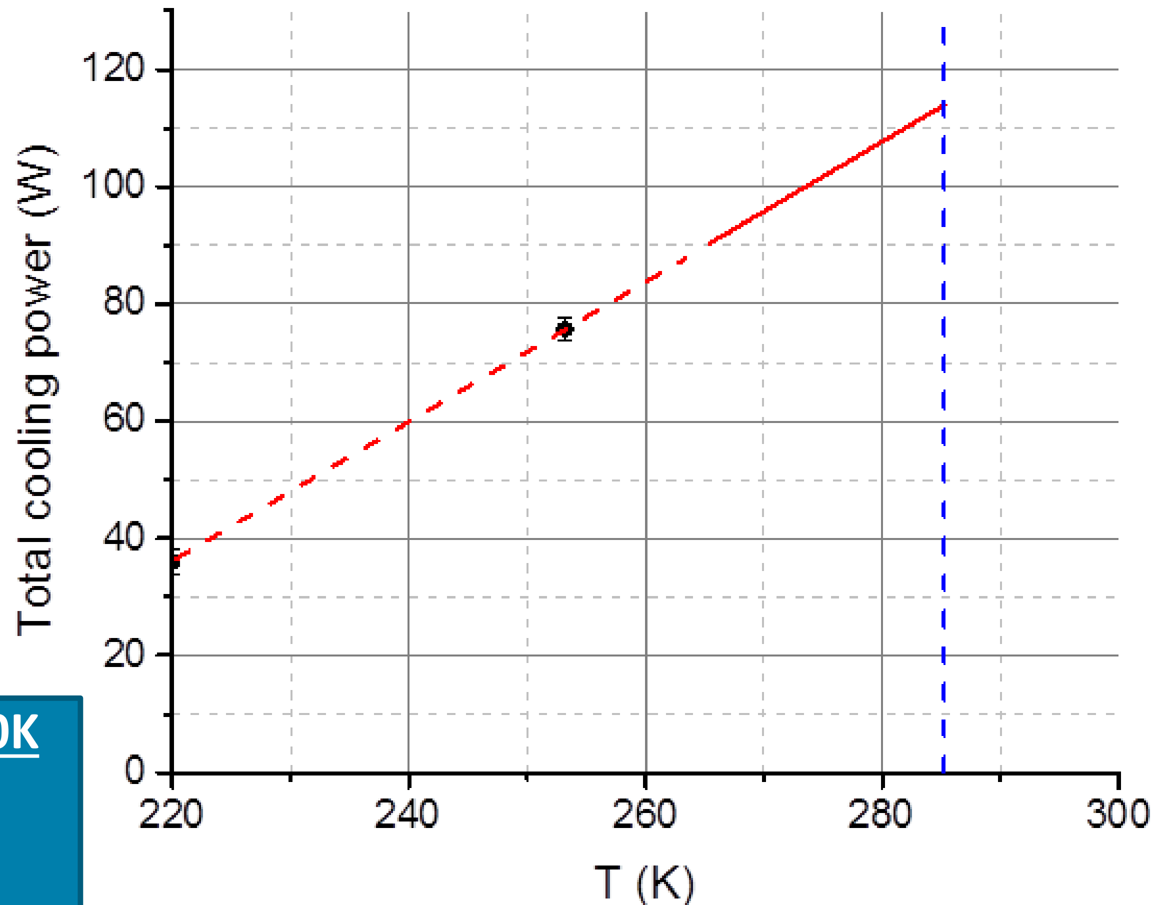



World Record ΔT span for these conditions to our knowledge

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

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by* Battelle *Since 1965*

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

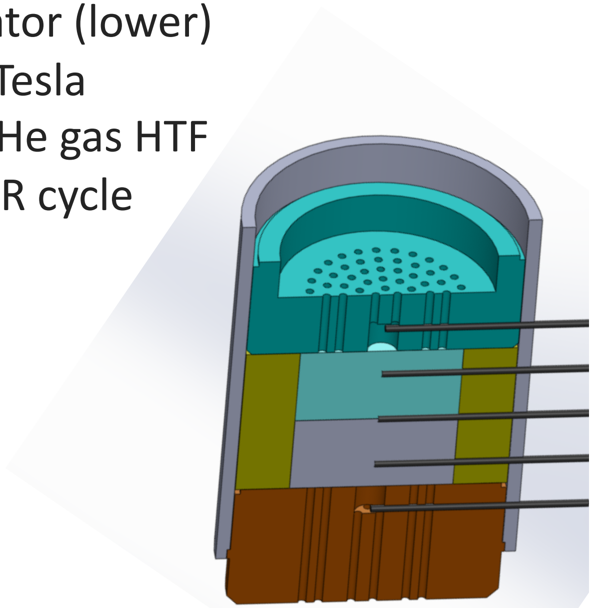



**90W achieved @ ΔT=20K**
- 54W cooling
- 36W heat leak
- HTF undersized

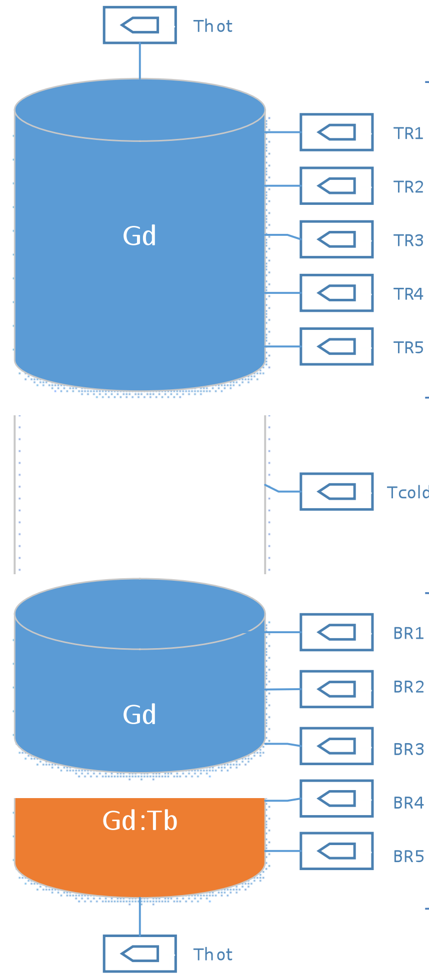
# Accomplishment: GEN-I – Layered Regenerator

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

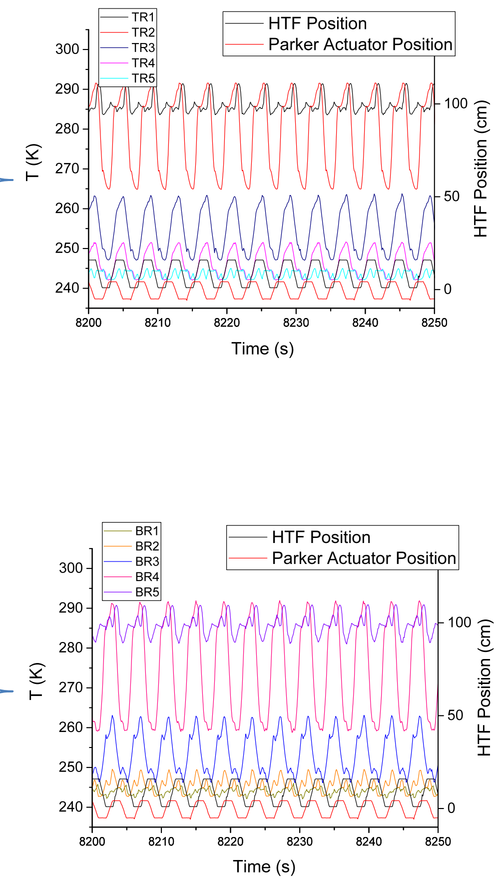
215g Gd Regenerator (upper)
215g Gd/$Gd_{0.74}Tb_{0.26}$ Regenerator (lower)
3.3 - 0.6 Tesla
200 psia He gas HTF
4 sec AMR cycle



Non-linear T profile that changes with by-pass




Layered regenerator with the TCs schematic



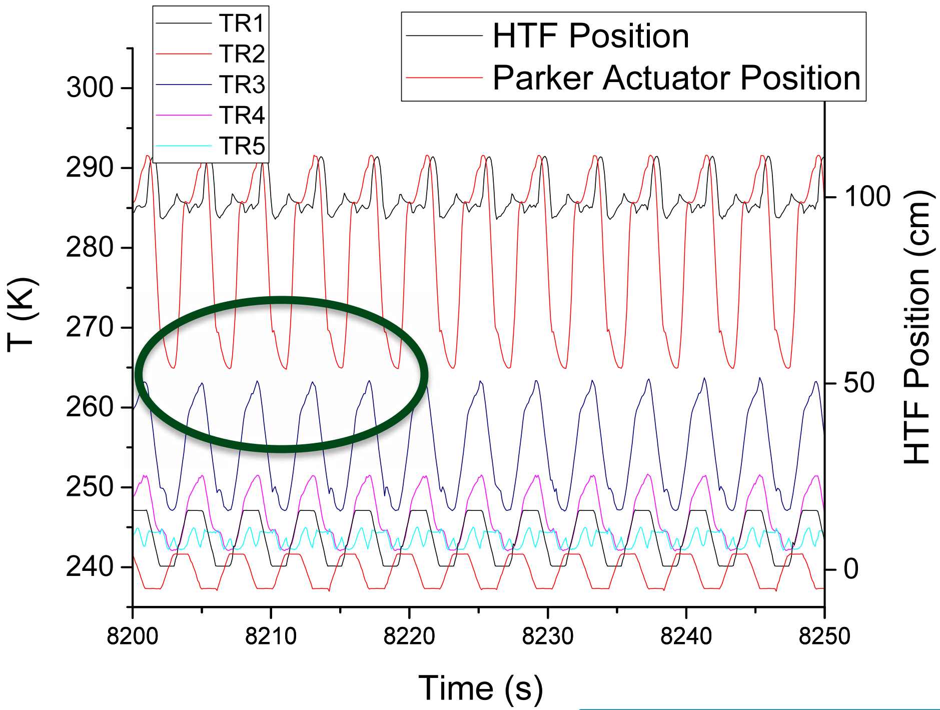

Detailed temperature profiles inside the regenerators

EMERALD ENERGY NW
Solutions with Power and Energy

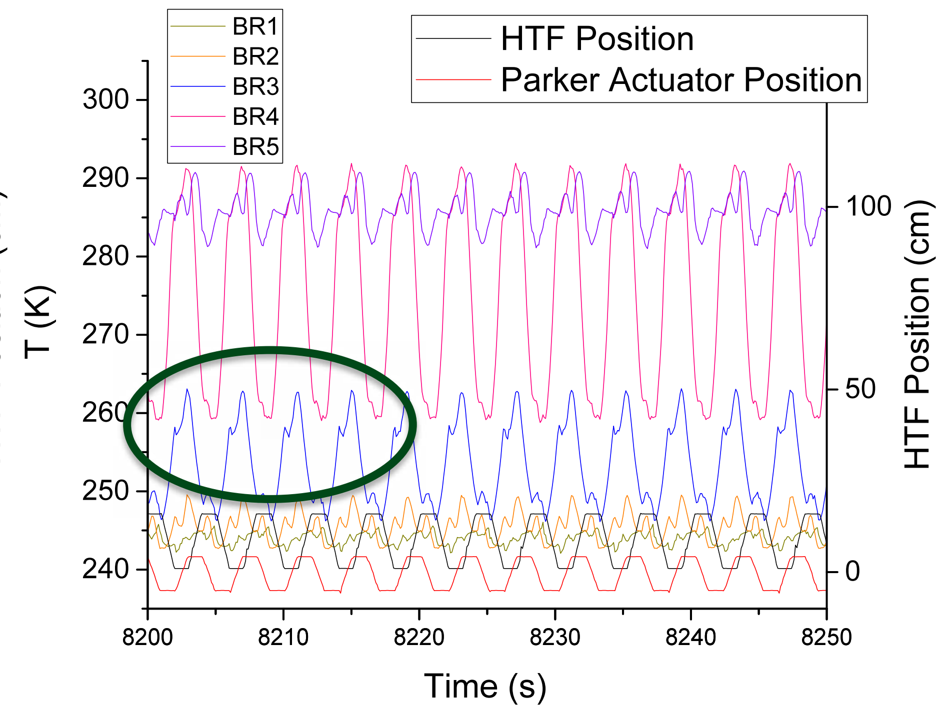
# Accomplishment: GEN-I – Layered Regenerator

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by Battelle Since 1965*

Gd only




$Gd/Gd_{0.76}Tb_{0.24}$




Understanding the temperature profile key to designing multi-layer systems

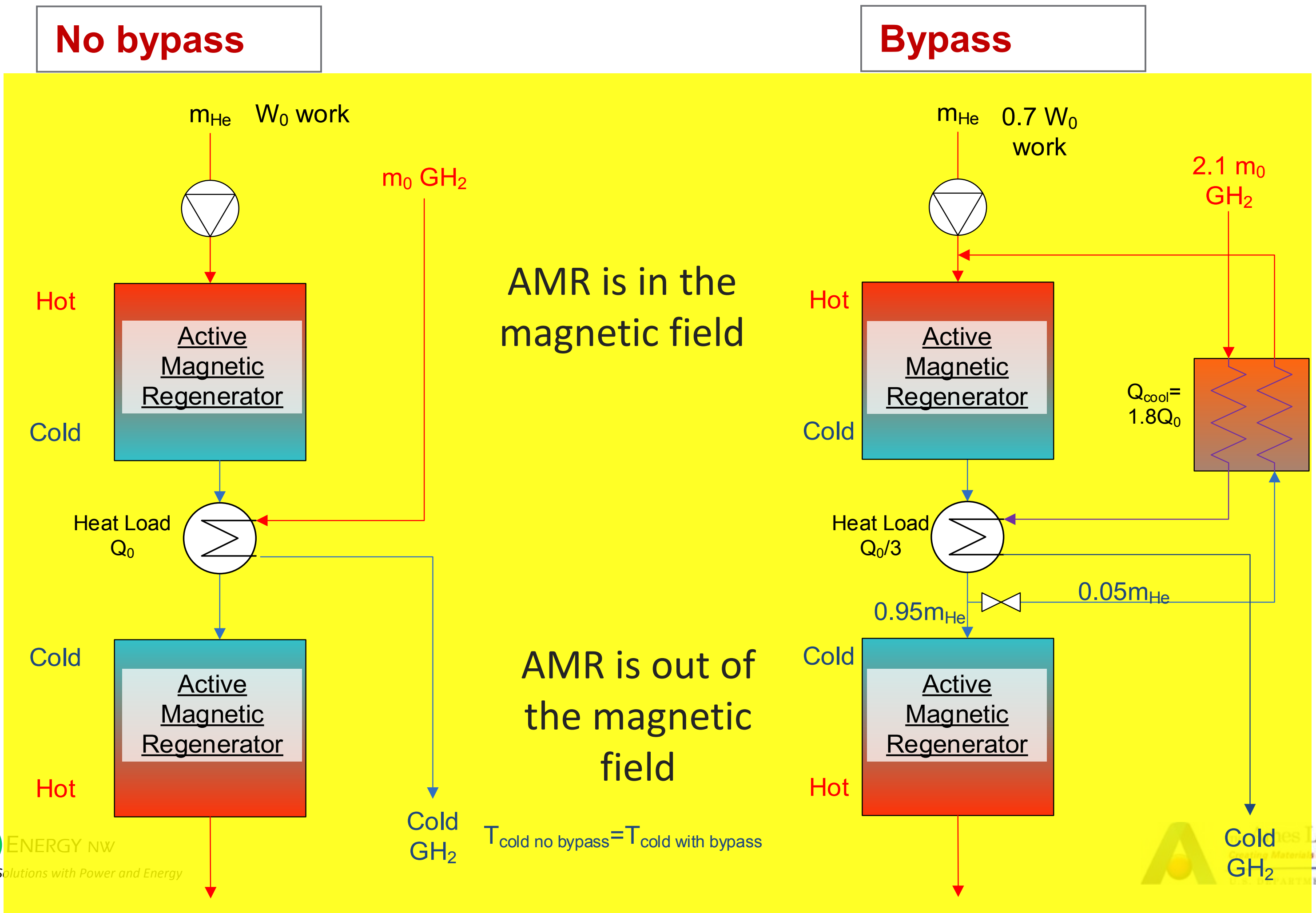
EMERALD ENERGY NW
*Solutions with Power and Energy*

The Ames Laboratory
*Creating Materials & Energy Solutions*
U.S. DEPARTMENT OF ENERGY

# Accomplishment: HTF bypass flow in dual regenerator AMRR improves efficiency

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by Battelle Since 1965*

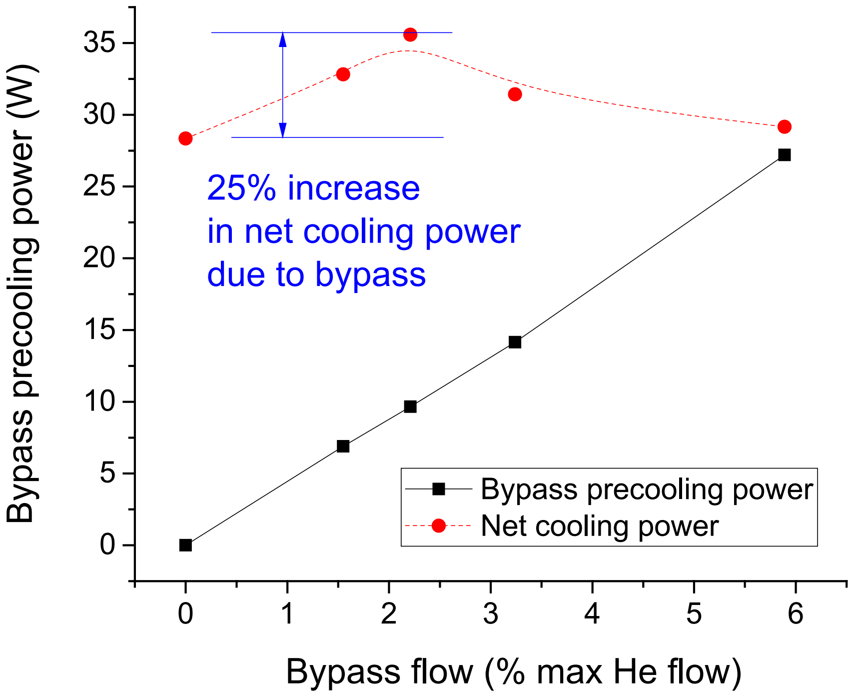
- *Reduces approach ΔT in process HEX for large increase in FOM*
- *Eliminates intrinsic irreversibility of AMR cycle in ferromagnetic refrigerants*



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

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by Battelle Since 1965*

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

EMERALD ENERGY NW
*Solutions with Power and Energy*

THE Ames Laboratory
*Creating Materials & Energy Solutions*
U.S. DEPARTMENT OF ENERGY

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

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by* Battelle *Since 1965*

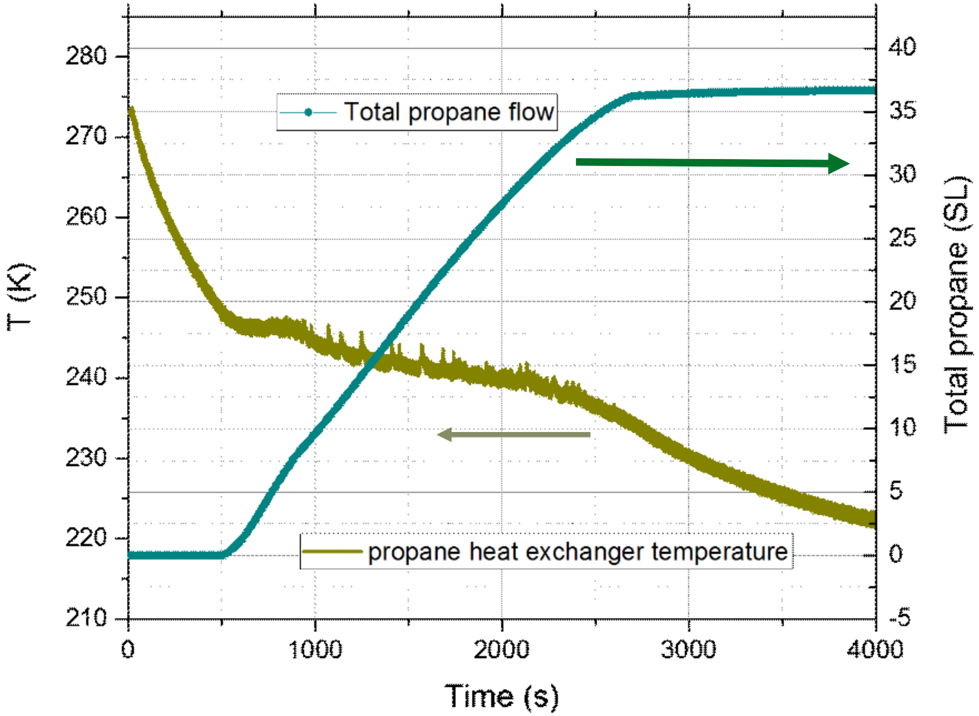
Assuming system is scaled up by:
1) Increasing the magnetic field to 7 Tesla
2) Increasing HTF size

| | 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)

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by* Battelle *Since 1965*

EMERALD ENERGY NW
*Solutions with Power and Energy*

The Ames Laboratory
*Creating Materials & Energy Solutions*
U.S. DEPARTMENT OF ENERGY

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

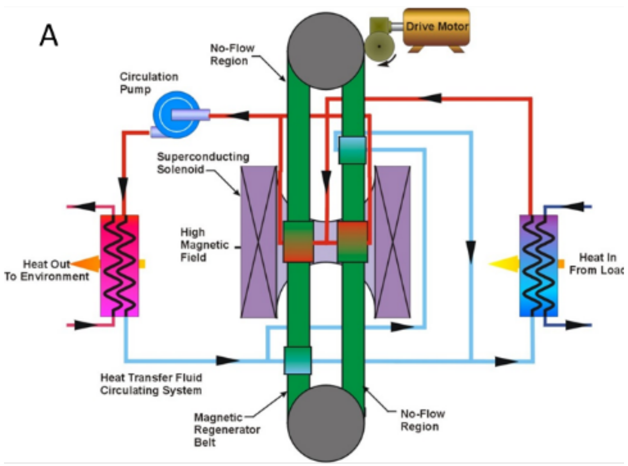


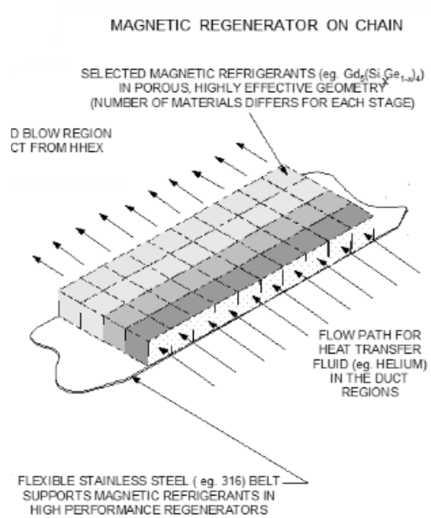
## Advantages

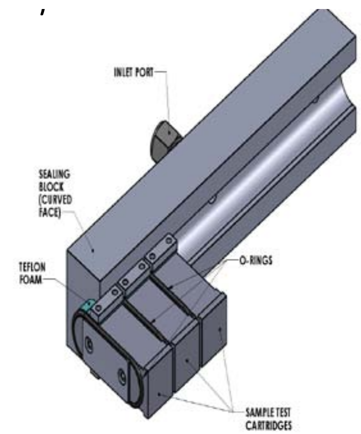
- > 0.6 FOM
- Rotary design
- Unique use of by-pass flow
- Layered material regenerators
- Eliminates load imbalance

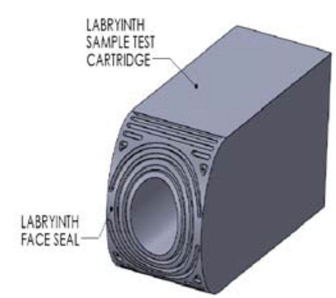
## Risks

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



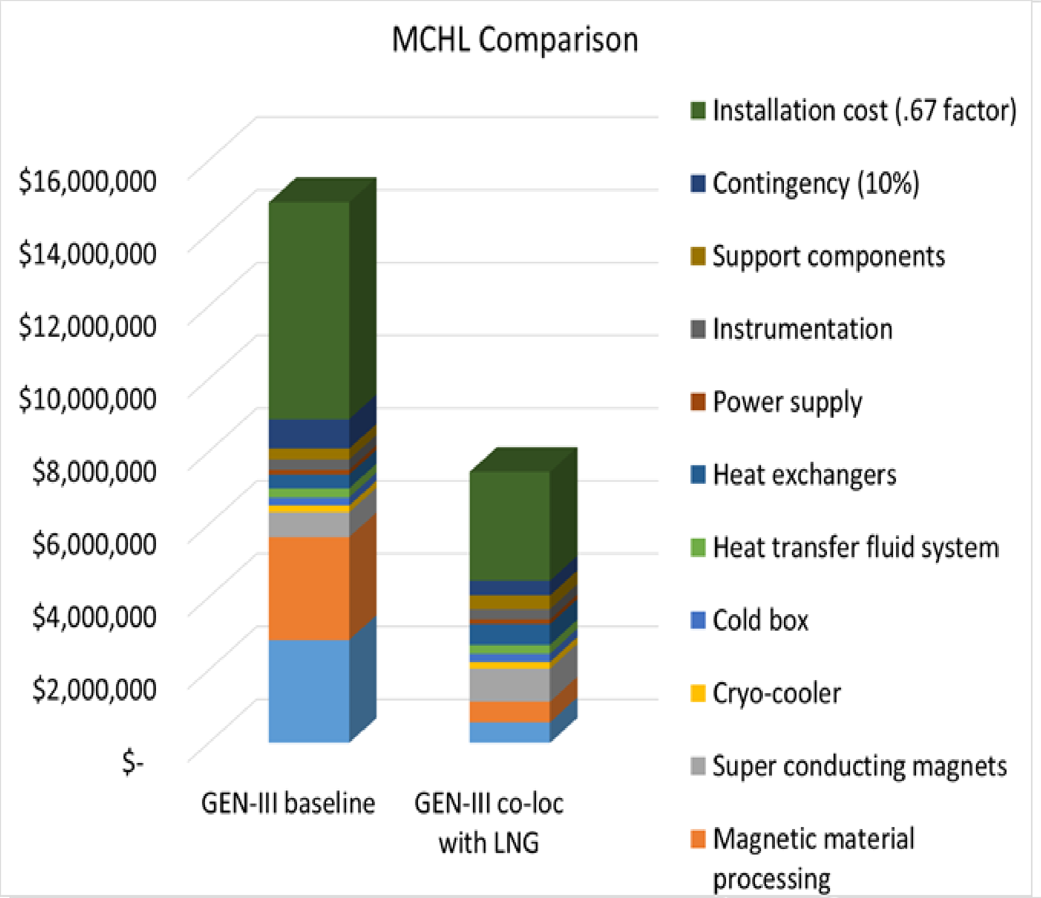



# Accomplishment: Preliminary Cost Analysis - \$1.5M / tonne $H_2$/day

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by Battelle Since 1965*

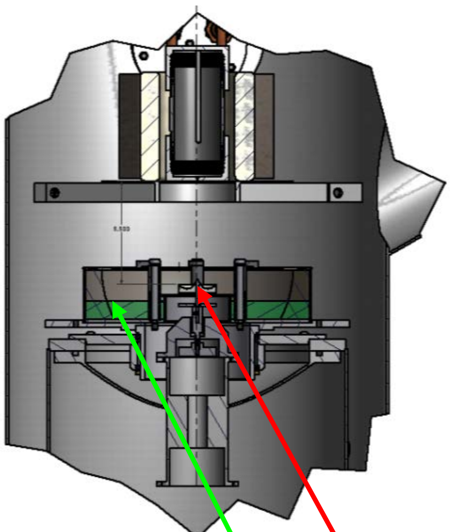
- Magnetic material ( 1st stage of 3 stage design 25 kg/day)
  - Wheel (no by-pass) – 184 kg
  - Wheel (GEN-III) (w/by-pass) – 22.3 kg
- 10 Tonne $H_2$/day ~\$15M
- Design option – co-locate with CNG/LNG
  - Use "free cooling" from LNG conversion to CNG
  - ~\$7M

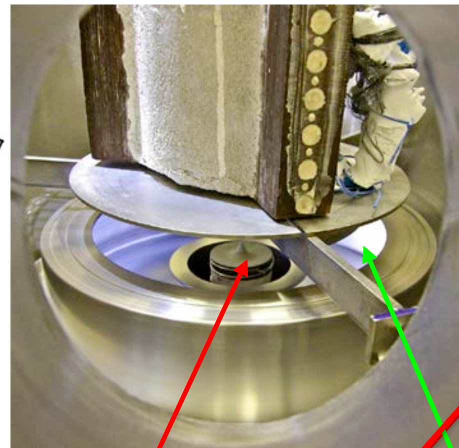
10 tonne $H_2$ /day

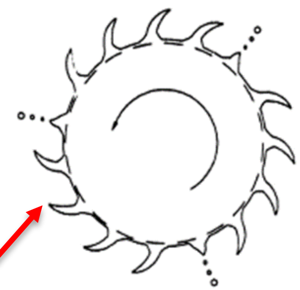


# Rotating Disk Atomization System Being Used for Powder Synthesis









**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



| 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



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

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



- 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

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by Battelle Since 1965*

| Partner | Project Roles |
|---|---|
| DOE | Sponsorship, steering |
| Emerald Energy Northwest LLC | Worked with PNNL on:<br>- Design<br>- Data analysis<br>- Cost analysis |
| AMES Laboratory / ISU | Materials selection feedback<br>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



- 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

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by Battelle Since 1965*

- Performance
  - 100K T span
  - First time demonstrated
    - By-pass
    - Layered material with thermocouples
    - Room temperature to liquid $C_3H_8$
- Preliminary Capital Cost Projection
  - \$45M – \$75M for 30 tonne/day
- Material synthesis
  - High production low cost spherical particle production being developed

| 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 $H_2$** | 12 kWh/kg $H_2$ |

EMERALD
Solutions with Power and Energy

# 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*

## Values

CREATIVITY

integrity

courage

Impact

COLLABORATION

PNNL-SA-94292

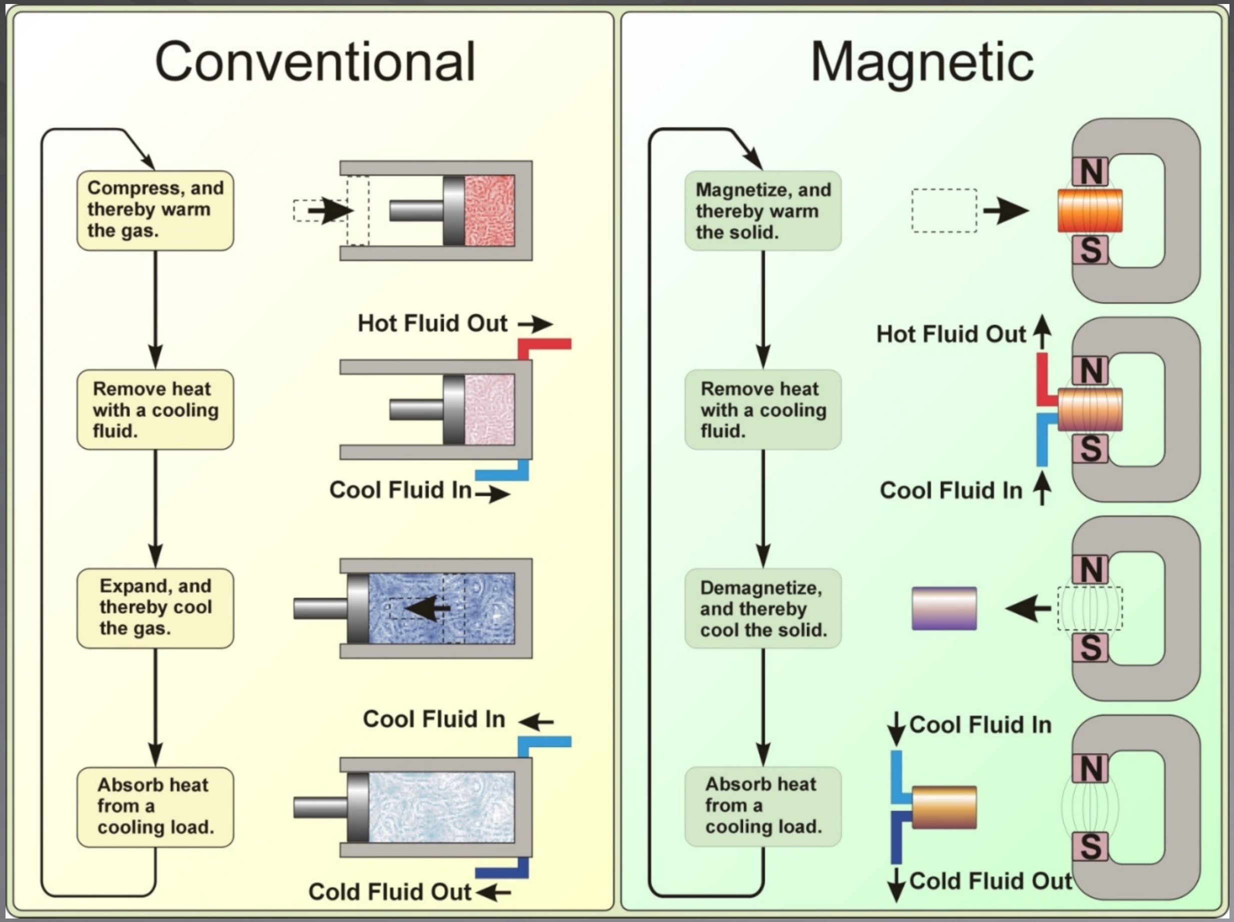
Pacific Northwest
NATIONAL LABORATORY

*Proudly Operated by* Battelle *Since 1965*

# Technical Back-up slides

# Background: How magnetocaloric cooling works: Vapor compression analogy

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by* Battelle *Since 1965*




## Advantages

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

## Disadvantages

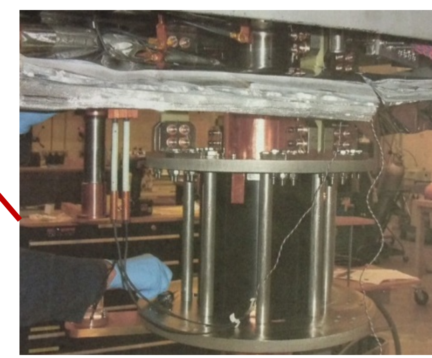
- Process complexity
- Potential high capital cost
- Market acceptance

# Accomplishment: GEN-I System

Data acquisition panels

Heat transfer fluid

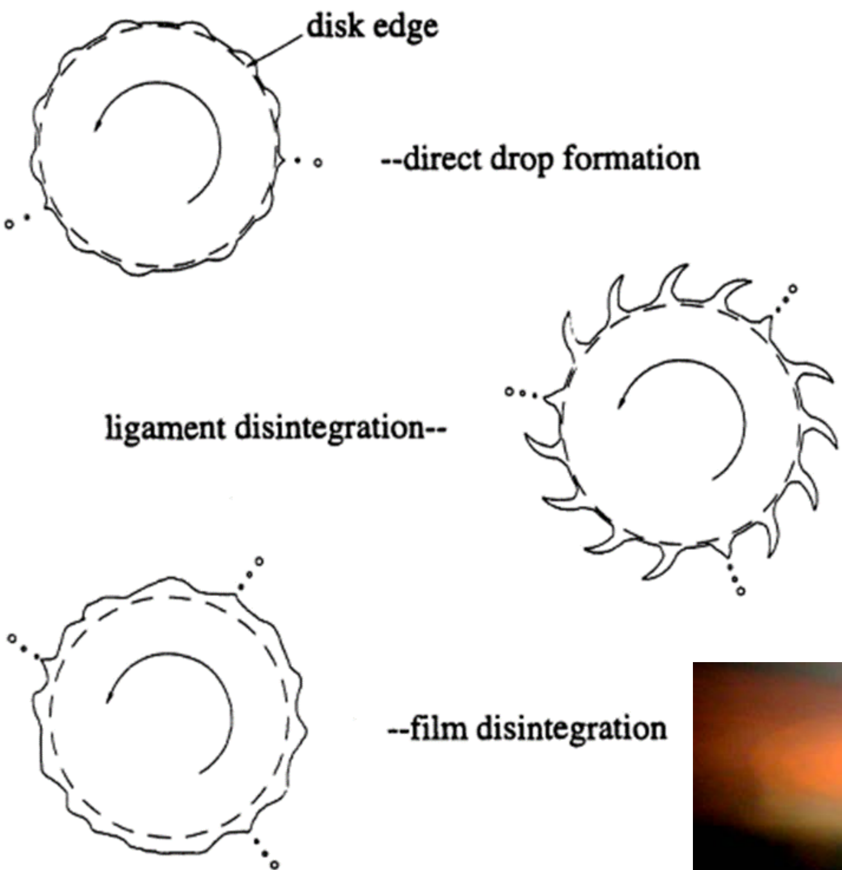
Dual AMR assembly

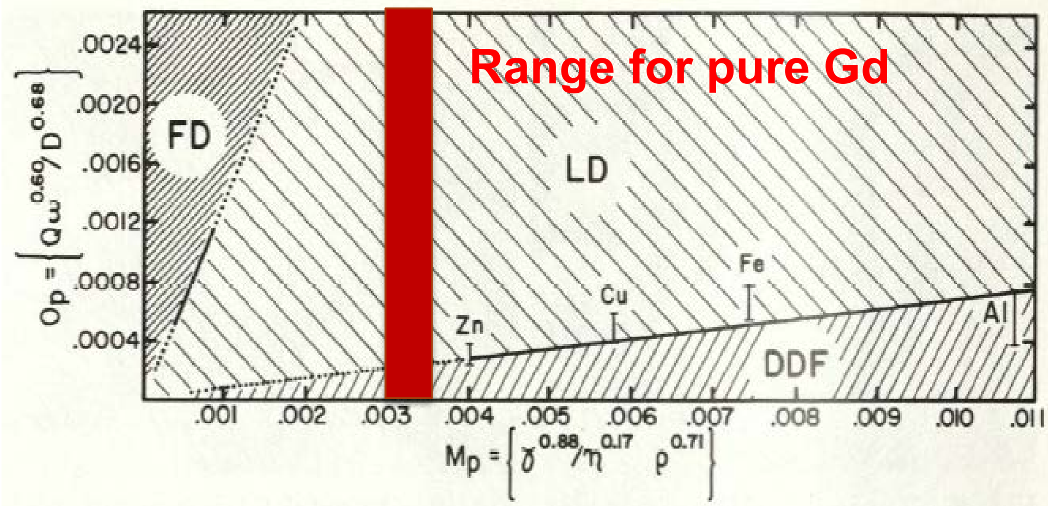


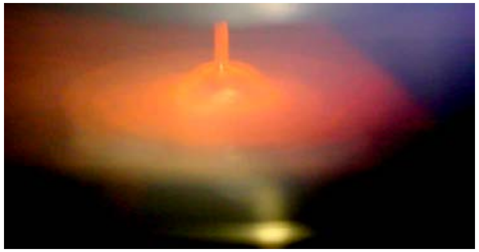
Superconducting magnet

# Atomization Mode Selection for Control of Spherical Powder Size

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



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



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 $H_2$/day

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by* **Battelle** *Since 1965*