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GENERAL ENGINEERING AND RESEARCH

Low-cost Magnetocaloric Materials Discovery

Phase IIB STTR Project ID IN012

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2020 DOE Annual Merit Review
May 25, 2020

Overview

Timeline

Phase I Project Start Date: 06/13/2016
Phase II Project Start Date: 07/31/2017
Phase II Project End Date: 07/30/2019
Phase IIB Project Start Date: 08/19/2019
Phase IIB Project End Date: 08/18/2021

Barriers

H. High-Cost and Low Energy Efficiency of Hydrogen Liquefaction

Ultimate Target: Energy Required < 6 kWh/kg of LH2 at 300,000kg/day facility.

Budget

Total Project Budget: $2,246,899

- Phase I - $150,000
- Phase II - $1,000,000
- Phase IIB - $1,096,899
- Total Phase IIB DOE Funds Spent: $459,695 as of 4/30/2020

Partners

UCSD – Project Partner

US DOE – Project sponsor and funding

California Energy Commission (CEC) – additional development funding

Southern California Energy Innovation Network- Incubator for CleanTech companies

Interactions/collaborations

- Hydrogen Delivery Tech Team
- Other Industrial Collaborators – First Element, Camfridge, Haier, CoolTec-Applications.

Relevance

Objective: Develop low cost energy efficient magnetic refrigeration technology for hydrogen liquefaction.

- Hydrogen is cheaper and safer to transport and store in liquid form, but getting it into liquid form and keeping it in liquid form is not easy.

Barrier

H. High-Cost and Low Energy Efficiency of Hydrogen Liquefaction

- Energy required for H2 Liquefaction at point of production too high.
- Hydrogen boil-off from cryogenic liquid storage tanks needs to be minimized.

DOE Task

Explore new technologies.

PNNL (J. Holladay) – building magnetic refrigeration H2 liquefaction prototype

GE&R Task

1) Discover, develop, and commercialize low cost high performance MCE alloys to enable magnetic refrigeration to move from prototype to production.
2) Demonstrate very small scale magnetic refrigeration for cryogenic applications

DOE Current Targets	FY 2015 Status	FY 2020 Target	Ultimate Target
Small Scale Liquefaction (30,000 kg H2/day)			
Installed Capital Cost ($)	70 million	70 million	-
Energy Required (kWh/kg of H2)	15	12	-
Large Scale Liquefaction (300,000 kg H2/day)			
Installed Capital Cost ($)	560 million	560 million	142 million
Energy Required (kWh/kg of H2)	12	11	6

Approach

Phase I and II Objectives:
Objective: Discover, develop, and commercialize low cost high performance magnetocaloric (MCE) alloys to enable magnetic refrigeration to move from prototype to production.

- **Small scale quantities commercially available on our webstore www.geandr.com**
- **Scale-up and performance development continuing under award from CEC**

Phase IIB Milestones
Objective: Demonstrate small scale magnetic refrigeration for cryogenic applications

3.1 Prototype Model
a) Build a theoretical model to verify feasibility - **Completed**

3.2 Technical and Economic Analysis of Small Scale Magnetic Refrigeration - **Completed**

3.3 Build Partial Prototype (77K – 70K)
a) Design Components
- actuator assembly for magnets
- Heat transfer gas (HTF) system
- MCE container assembly and HTF flow path

- In Progress

b) Test functionality at room temperature
c) Determine changes needed for cryogenic temps
d) Build cryogenic system and characterize

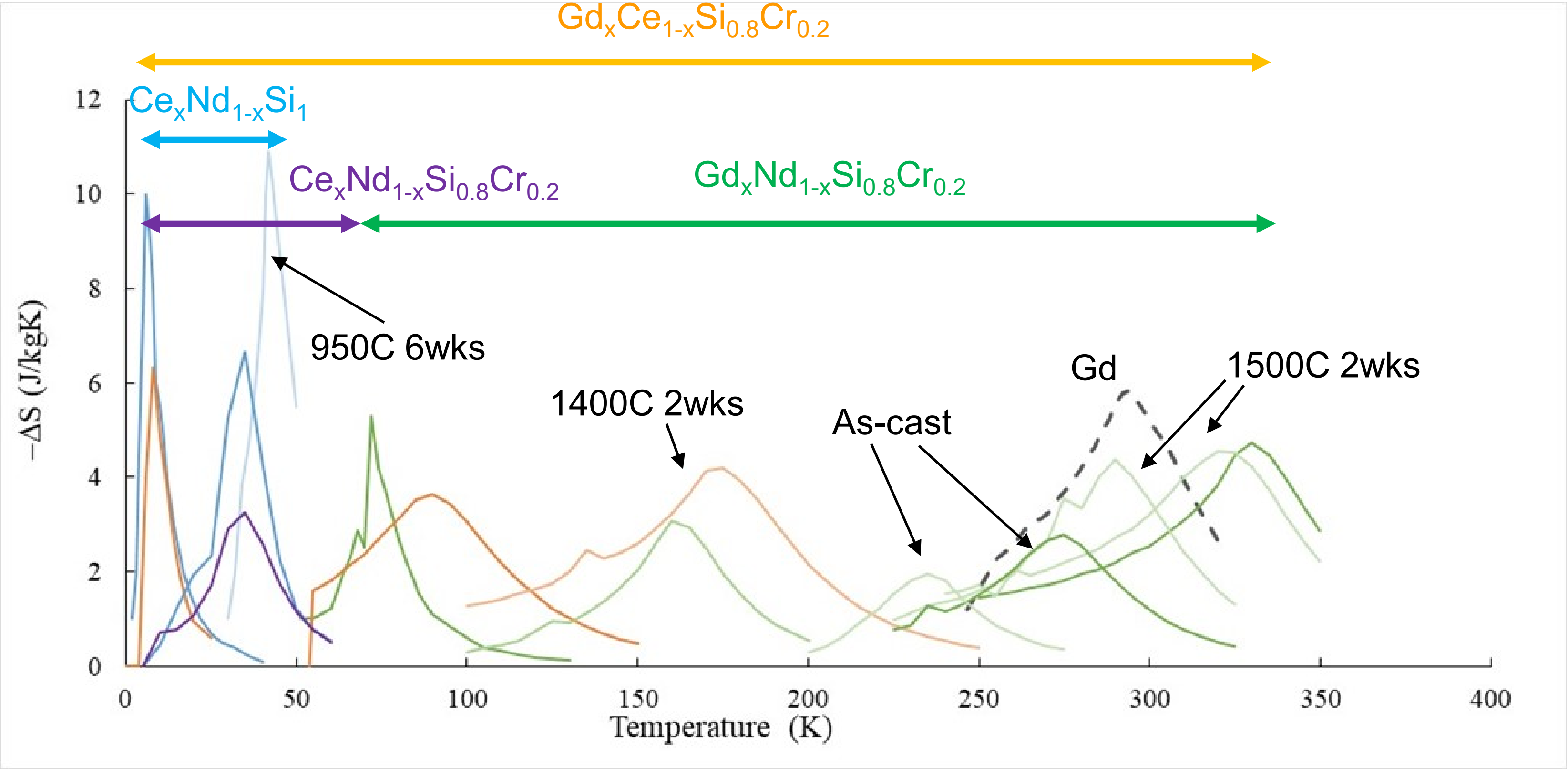
Approach

Why small scale magnetic refrigeration for cryogenic applications?

- An AT-SCALE commercially viable magnetic refrigeration system has yet be demonstrated for ANY application above 4K
- Large scale H2 Magnetic Liquefaction promising – but requires $50M+ investment and several 5+ years to construct
- Small scale cryogenic magnetic refrigerator operating only in the 20-80 regime:
  - Less than $5M to commercialize within ~3years
  - Immediate impact on existing $2B cryocooler market (85% reduction in electrical costs and 60% reduction in capital costs over VCC)
  - Could lower risk for investment into large scale Mag. Ref.
  - Would be useful for a variety of applications that could accelerate path to H2@Scale.
    - LH2 Boil-off losses at fueling stations
    - “Renewable” Power to Gas to LH2

Accomplishments and Progress

GE&R MCE materials performance at 3T field.



- Compositions with any Tc available between 9K – 330K
- Small quantities (5g) available for purchase at geandr.com
- Continued Development under CEC award – Increase performance, Scale-up, optimization, custom forms

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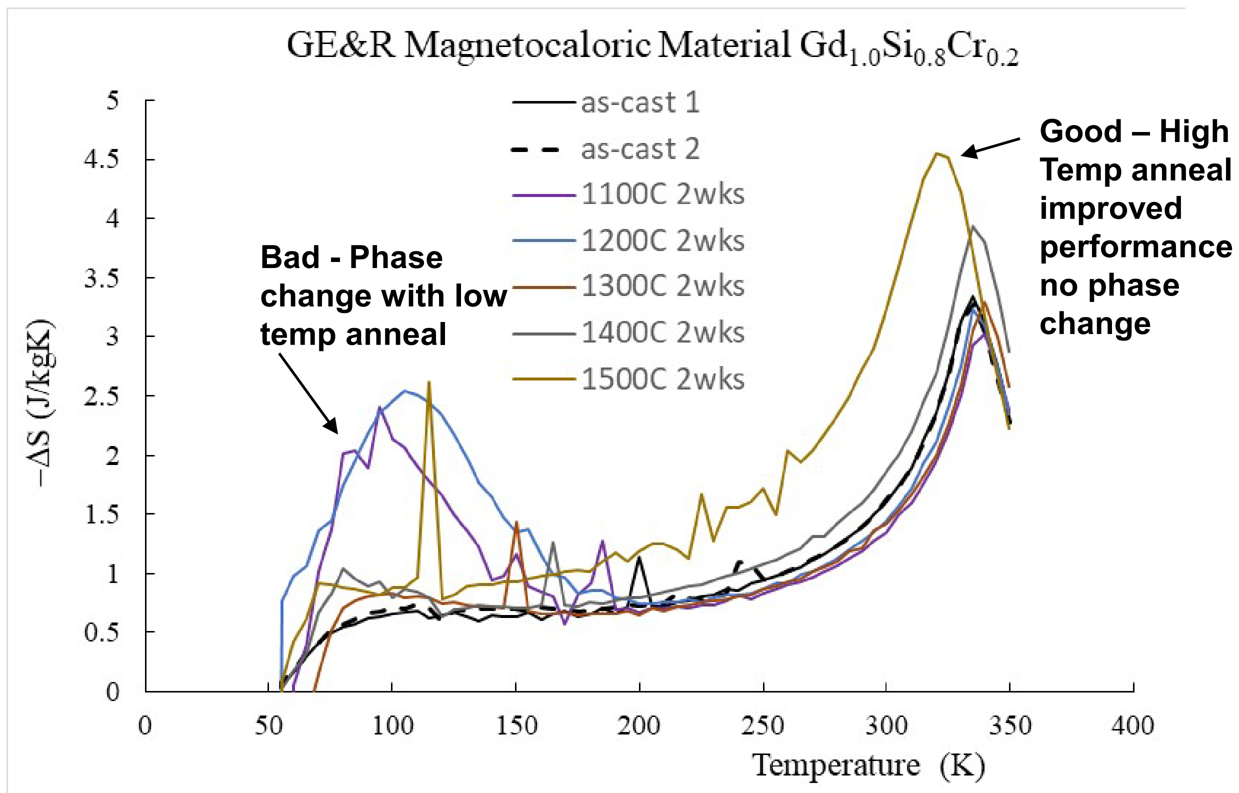
Accomplishments and Progress

Magnetocaloric Materials (MCM) Development
This work is continuing under an award from CEC

- Issue – Materials require long high temp anneals to achieve good properties
- New Anneal Furnace Installed
  - Annealing capability up to 1700C – good results for our 150-320K MCE Materials!
- Collaborative grant awarded to work with PNNL to test their proprietary heat treatment technique (project started in Jan 2020).

New – up to 1700C



Accomplishments and Progress

Magnetocaloric Materials (MCM) Development
This work is continuing under an award from CEC

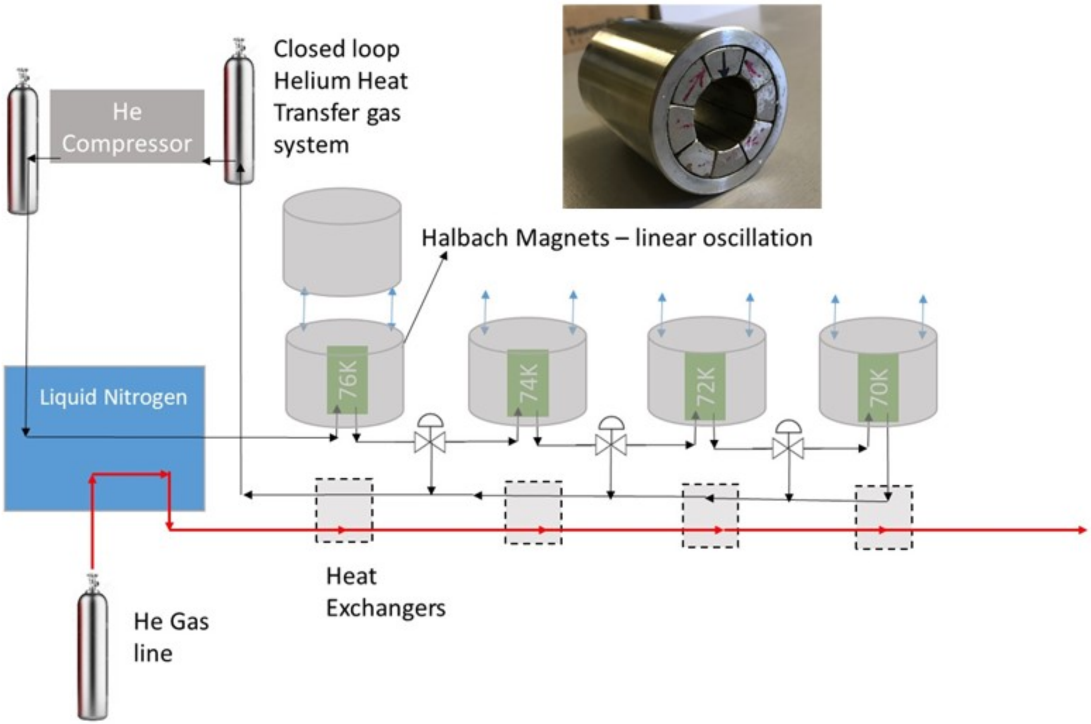
Scale-up

- New atomization furnace purchased by GE&R to scale up in-house casting to ~1kg/day capacity
    - Furnace has ability to form various shaped ingots
    - Using the atomizer – we can form materials into sub mm-sized spheres – Great for Magnetic Refrigeration systems!
    - Furnace arrived in April – we are working to get it installed and running.

Accomplishments and Progress

Phase IIB Prototype

Uses Permanent magnets and LN2 as heat sink, and stages operating from 77K down to ~70K (inset is an actual Halbach magnet).



LN2 is easiest heat sink for prototype

Other options are possible and will depend on end application

- **VCC Cryocooler**
- **LN2 generator**
- **Bulk LN2 delivery**

Accomplishments and Progress

Small Scale (2kW Cooling Power) Cryogenic Magnetic Regenerator Model

Input Parameters	Case 1	Case 2	Case 3	Case 4
Cycling Frequency	1 Hz	10 Hz	1 Hz	10 Hz
Temperature Span at each stage	3 K	3 K	4 K	4 K
Results				
Number of stages	19	19	14	14
Total volume of Magnetic Field (m^3)	0.68	0.12	0.44	0.26
Total Mass of MCE material (kg)	4630	870	3029	1760
Mass flow rate of He heat transfer fluid (kg/s)	4.2	2.3	3.4	3.0
Total Power Input [kW]	13.7	7.8	11	8.8
Cooling Power [kW]	2.1	2.1	2.1	2.1
COP of system	0.15	0.27	0.19	0.24
Fraction of Carnot COP	43%	77%	54%	69%
Estimated Cost for MCE materials and magnets*	~$1.4M	~$260K	~$930K	~$550K

*assumes $75/kg for MCE materials (manufactured by GE&R) and magnet cost of $0.0016/mm^3. These costs can be achieved with bulk purchasing of the raw materials.

Permanent Magnets

Model Results Promising!

Equivalent VCC System Efficiency ~10%
Cost ~$5M

This work has been submitted for publication.

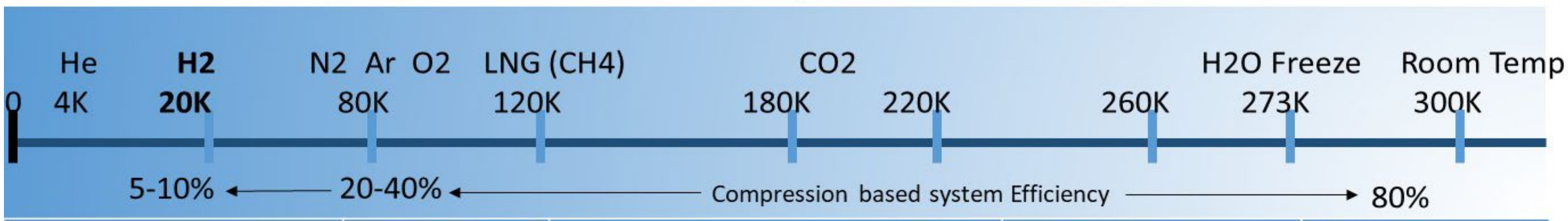
T. Feng, R. Chen, and R. Ihnfeldt, "Modeling of Hydrogen Liquefaction using Magnetocaloric Cycles with Permanent Magnets", *Cryogenics*, currently under review.

Accomplishments and Progress

Technical and Economic Analysis: Small Scale Cryogenic Magnetic Refrigeration Systems, Dr. Robin Ihnfeldt[1], Tianshi Feng[2], Professor Renkun Chen[2], Professor Emeritus Sungho Jin[1], full report available here: https://cdn.shopify.com/s/files/1/0970/1394/files/Technical_and_Economic_Analysis_Small_Scale_Cryogenic_Magnetic_Refrigeration_Systems.pdf?14

Report details current cryogenic markets, technical challenges, and evaluates future impacts of a small scale (<10kW cooling power) high efficiency magnetic refrigeration system.

Cost to produce 10W/day of Cooling at 10K

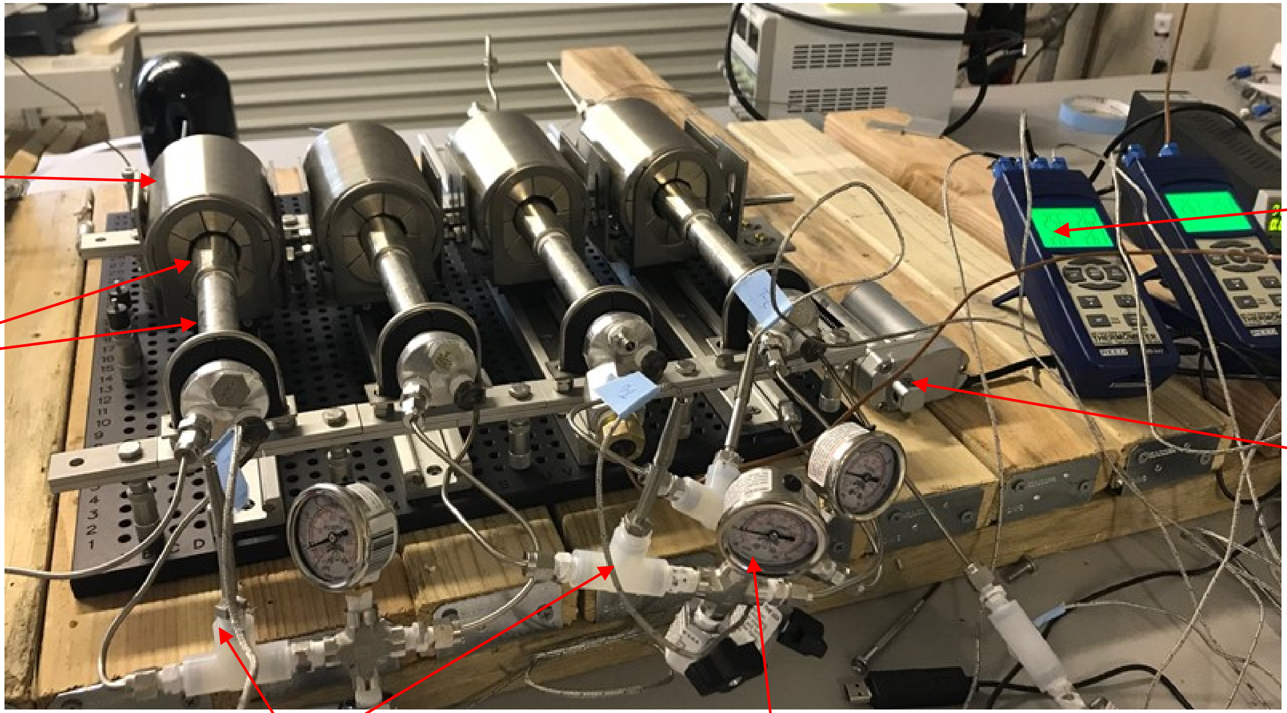


System	10K – 80K	80K – 300K	Total Daily Operating Cost	Cryocooler Cost
a) Liquid Helium	$1640 - $4920		$1640 - $4920	-
b) VCC Cryocooler - Dual System	n=0.05 $6.72	n=0.25 $74.45	$81.17	$125,000
c) Dual System MAG.Ref.	n=0.5 $0.67	n=0.25 $7.92	$8.59	$50,000

Operational and capital costs to produce 10W/day of cooling at 10K using a) liquid helium versus b) commercially available VCC cryocooler and c) replacing the low temperature stage with a theoretical magnetic refrigeration system (n is system efficiency, assumes electricity cost of $0.20/kW-hr).

Accomplishments and Progress

GE&R Prototype

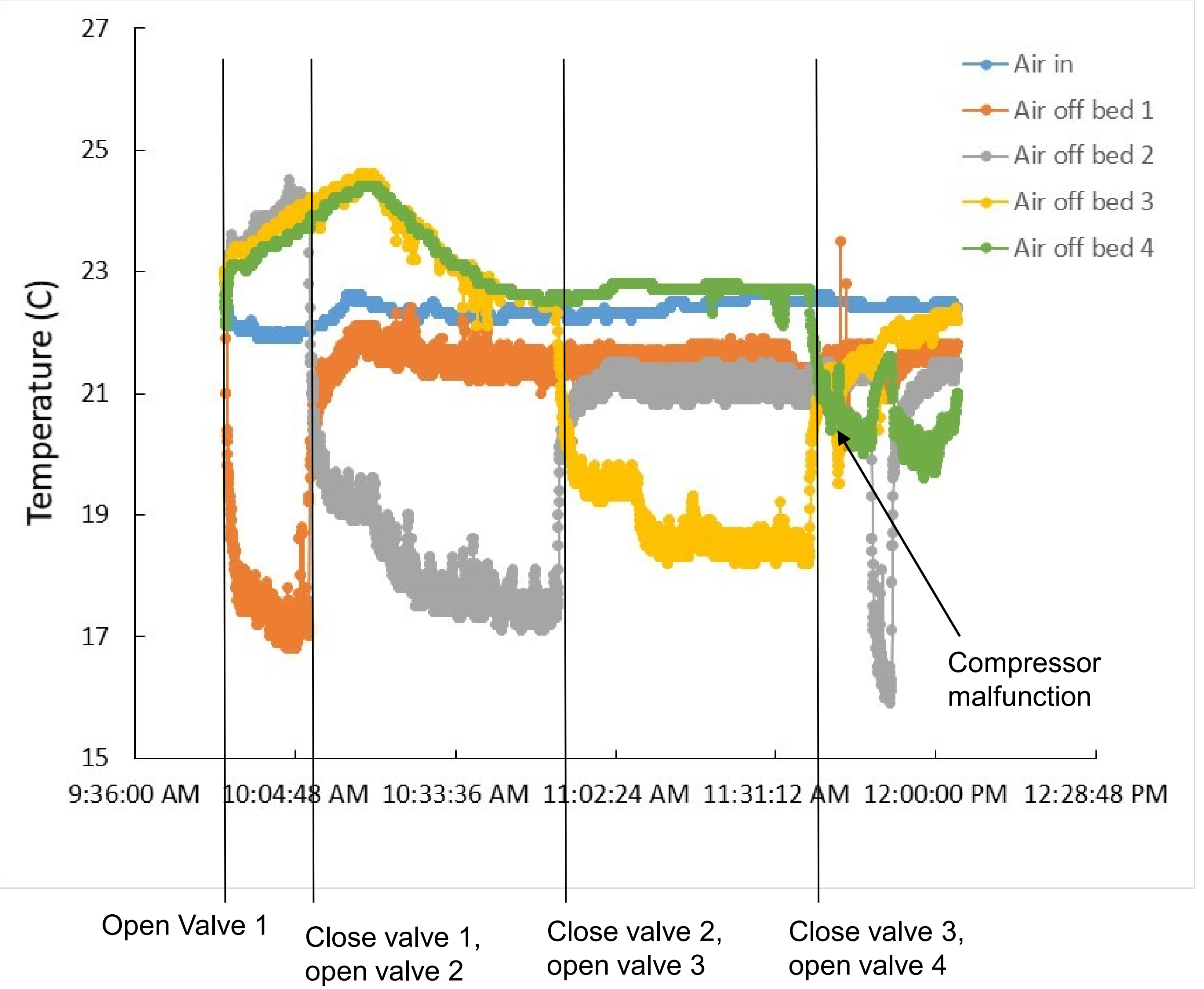


- Initial system built and tested using room temperature MCE (Gadolinium) and mostly off the shelf parts
  - ☐ Verify flow paths and ensure functionality of system setup at room temperature before going to cryo temps
  - ☐ Uses a dual MCE container – where magnet is always working
  - ☐ Heat transfer fluid (HTF) flows through MCE bed, then exits thru pipe in center
  - ☐ Thermocouples measure MCE beds and HTF after exiting each bed
  - ☐ Currently using standard air compressor for HTF (save on cost of Helium)
  - ☐ Oscillator moves magnets, is computer controlled so that we can test different frequencies

Accomplishments and Progress

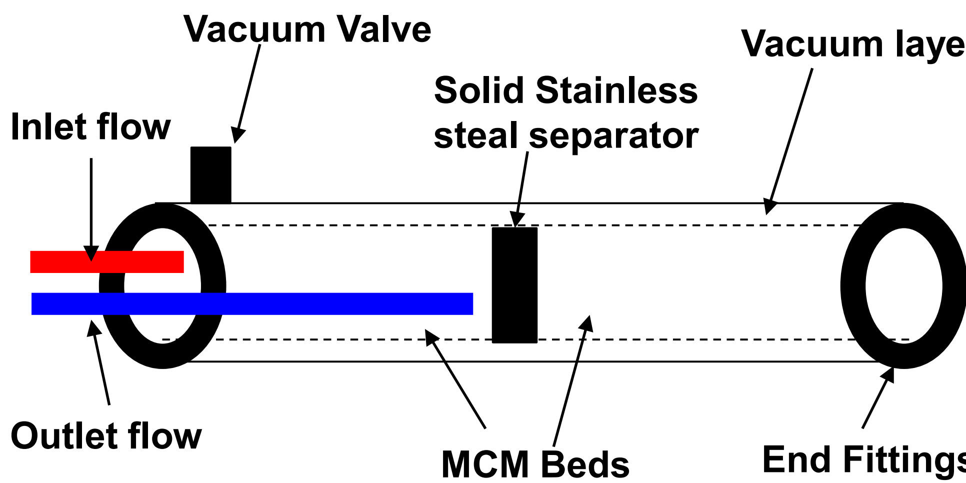
System Functionality Verified

- ☐ Open valves in succession to cool down each bed (from gas expansion)
- ☐ As expected, get DT~1C drop off each bed
- ☐ Testing on room temp system will continue
  - ☐ Understand effects of different parameters (oscillation frequency, HTF flowrate, bypass flow, etc.)
  - ☐ MCE beds are easily removed and repacked so we can test different MCE (plates versus spheres versus ingots, and test different types of packing)



Accomplishments and Progress

Assembly for the Cryosystem



Custom vacuum jacketed MCE container design (new patent application filed!). This is a dual container that has an inner tube insulated by a vacuum layer. The magnet oscillates back and forth across the two containers. Feedthru piping is installed on each end to allow inlet flow to go through the MCE bed, and flow back out the same end.

- ☐ Cryosystem will have other improvements
  - ■ Sub mm-sized MCE pieces (RT system uses ~5mm Gd ingots)
  - ■ System insulation!

Reviewer Responses

- It is not clear that the MCHL project is benefiting from this work; it might be, but it is not clearly stated. Transitioning from a "materials expertise" project to a "system" project is a significant change that does not align with the original objective. It is recommended that this work be done as a separate project or integrated into the MCHL project since it requires substantially different expertise and experience from the materials work. It is also not clear that any evaluation has been completed that would indicate that developing a "boil-off recovery" unit is economically justified or technically possible.

-We are following the MCHL project closely, as their success would be beneficial to our project. The MCE materials for the MCHL project were synthesized by AMES prior to GE&R starting on this work. Once we are able to supply larger quantity materials, we would love to send these to Dr. Holladay and the MCHL team for testing on their system.
-As for the expertise in "materials" versus "system", our team has both. Prior to developing these materials we were building magnetic cooling systems – which gave us the expertise to understand the most important materials properties needed to make these devices function. For the Phase IIB project, we have defined a new scope of work for the system development, and we obtained additional funding from the CEC to continue materials development and scale-up.

- The project's weaknesses are in expanding potentially high-value applications.

We have a two-fold commercialization approach for our technologies:
1) MCE Materials - Sell Magnetocaloric materials for all refrigeration applications.
2) Small Scale Cryogenic Refrigeration – Demonstrate small scale magnetic refrigeration for cryogenic applications and license/sell this technology to strategic partner for deployment.
We believe that the successful demonstration of a full scale prototype with improved efficiency and capital cost over VCC will lower the risk for industrial financing/licensing to move magnetic refrigeration into the cryocooler market, as well as stimulate industrial efforts for the use of magnetic refrigeration in other refrigeration applications (which will in turn lead to growth in our MCE sales).

- The project's weakness is the lack of access to equipment for larger-scale processing of materials.

A new arcmelt furnace was purchased in Aug 2019, and arrived at our facility in March 2020. We are working to get this system installed and running. It will accommodate 1kg/day production of our MCM materials, and has a variety of capabilities for casting differing forms (i.e. ingots, cylindars, or atomization to produce sub mm-sized spheres).

A Collaborative Project

Partner	Project Role
US DOE	Project sponsor and funding
University of California, San Diego (UCSD)	Project partner. Subcontractor. Assisting with cryogenic magnetic refrigeration model and prototype testing.
California Energy Commission (CEC)	Currently funding continued MCE development and scale-up. Also, an award is pending to continue the small scale cryogenic magnetic refrigeration system.
Southern California Energy Innovation Network (SCEIN)	Networking incubator for CleanTech companies in Southern California. GE&R officially accepted into program. They provide network / mentor resources.
Hydrogen Delivery Tech Team	Annual reporting provided to HDTT
Other Industry Partnerships	In Progress – We have engaged the following entities: First Element, Air Liquid, Camfridge, CoolTec-Applications, Denso Corporation, Haier (GE Appliances).
Pacific Northwestern National Lab	Partner – collaboration effort in progress to test PNNL proprietary heat treatment technique on our MCM.

Remaining Challenges and Barriers

Magnetic Refrigeration

For MCE Materials Commercialization –

- This effort will continue to be funded by CEC to scale-up and hit performance targets.
- Complexity of our quaternary materials which operate in the 50K-320K regime require long high temp anneals where preventing phase changes is difficult – significant process development is still needed.

For Cryogenic Refrigeration:

- Functionality of these systems (both large and small scale) at sub 80K temperatures still needs to be verified. Our goal with this Phase IIB is to demonstrate functionality of a partial system operating from ~80K down to ~70K with ~10W of cooling power. Design has been verified at room temperature and we are in process of building the cryo system.
- Significant challenges are expected at cryo temperatures which include:
    - Minimizing and controlling heat losses
    - Accurate characterization of performance as finding compatible thermocouples is difficult
    - Controlling helium HTF may require custom valve development
    - Contamination of helium HTF circulation system / oxidation of MCE

Proposed Future Work

Remainder FY2020 and FY2021

- Testing on room temp system will continue
  - Understand effects of different parameters (oscillation frequency, HTF flowrate, etc.)
  - MCE beds are easily removed and repacked so we can test different MCE (plates versus spheres versus ingots, and test different types of packing)
- Build Cryogenic System operating from 77 – 70K
  - Setup system with custom vacuum jacketed MCE container (this has been designed and built)
  - Setup HTF system with Helium circulation and LN2 heat sink
  - Setup new oscillation system with higher frequency capability
  - Characterize and optimize COP
  - Test different MCM beds (spheres, plates, compositions, etc.)

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

Additional Funding Received

- California Energy Commission Award EPC-18-028 ($1,088,188) 08/2019 – 03/2022
    - Scale-up MCE materials to a 1kg/day production line and form materials into spheres/ thin plates.
- California Energy Commission Award EPC-19-021 ($1,699,066) 06/2020 – 03/2024
    - This award will start when DOE Phase IIB ends (08/2021), and will be used to build a full scale (80K down to 10K) cryogenic magnetic refrigeration system.
- Collaborative Grant with PNNL – CRADA NO. 446 awarded Jan 2020.
    - PNNL will test a proprietary heat treatment technique to see if anneal times for MCE can be reduced

Potential Future Funding

- Applying for additional DOE funding to expand collaborative effort between GE&R and PNNL to include materials characterization with various heat treatments.

Patents

- US Patent Application No. 16476047, Chinese Patent Application No. 2018800006365.1, and European Patent Application No. 18736700.8-1212, filed in July 2019 for our ternary based compounds.
- PCT application (US 62/634078) filed in Feb 2019 for our >50K MCE compositions We will enter national stage (US, Japan, Europe, China) in July 2020
- Provisional Application (US 62/880549) filed July 2019 for our small scale H2 liquefaction system.

Summary Slide

- Scale-up
  - MCE development and scale-up continuing under CEC award.
  - Additional equipment has been purchased to achieve 1kg/day production capacity.

- Theoretical Model of Small Scale Cryogenic Magnetic Refrigeration System
  - Model verifies system feasibility and shows promising results for reducing both capital and operating cost of cryogenic refrigeration

- Techno-Economic Analysis
  - Full analysis of current and future markets for cryogenic refrigeration was performed. Report is published on GE&R website.
  - Analysis shows a high efficiency small scale cryogenic magnetic refrigeration system would be useful for a variety of applications that could accelerate path to H2@Scale.
    - LH2 Boil-off losses at fueling stations
    - “Renewable” Power to Gas to LH2

- Build Partial Prototype System to show functionality from 77K down to 70K.
  - System built and setup to run at room temperature initially, and functionality was verified.
  - This system will continue to be tested to determine effects of various parameters on functionality
  - Cryogenic system is under construction which includes additional engineering to accommodate cryogenic temperatures

Technical Back-Up Slides

Publications and Presentations

[1] T. Feng, R. Chen, and R. Ihnfeldt, “Modeling of Hydrogen Liquefaction using Magnetocaloric Cycles with Permanent Magnets”, Presented at ASME 2019 Conference in Bellevue, WA, July 15, 2019.

[2] R. Ihnfeldt, “High Efficiency Magnetic Refrigeration Enabling HFC-free Refrigeration”, Invited Presentation at the California Energy Commission Technology Showcase, Sacramento, California, on October 25, 2019.

[3] Technical and Economic Analysis: Small Scale Cryogenic Magnetic Refrigeration Systems, Dr. Robin Ihnfeldt[1], Tianshi Feng[2], Professor Renkun Chen[2], Professor Emeritus Sungho Jin[1], accessed here: https://cdn.shopify.com/s/files/1/0970/1394/files/Technical_and_Economic_Analysis_Small_Scale_Cryogenic_Magnetic_Refrigeration_Systems.pdf?14

[4] T. Feng, R. Chen, and R. Ihnfeldt, “Modeling of Hydrogen Liquefaction using Magnetocaloric Cycles with Permanent Magnets”, *Cryogenics*, currently under review.