Low-Cost Magnetocaloric Materials Discovery

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Overall Objectives

- Discover, develop, and commercialize low-cost, high-performance magnetocaloric alloys to enable magnetic refrigeration to move from prototype to production.

Fiscal Year (FY) 2019 Objectives

- Continue to optimize magnetocaloric composition and processing to achieve high performance (ΔT equivalent or better than Gd), low cost (target price ~$400/kg at large scale), and high stability form useful for magnetic refrigeration (spheres and/or thin plates).
- Continue to provide commercially available small quantities of our magnetocaloric effect (MCE) products on the www.geandr.com webstore.
- Build a model of a small-scale (300 kg/day) hydrogen liquefaction magnetic refrigeration system to evaluate feasibility for various commercial applications.

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- (H) High-Cost and Low Energy Efficiency of Hydrogen Liquefaction—The energy required for hydrogen liquefaction at point of production is too high, and hydrogen boil-off from cryogenic liquid storage tanks needs to be addressed and minimized for improved cost and energy efficiency.

Technical Targets

The transportation and storage of hydrogen is safer and more economical when it is in liquid form, but getting it into liquid form and keeping it in liquid form is not easy. Despite significant efforts to improve compression-based liquefaction systems, they remain too inefficient and expensive to meet the DOE hydrogen production and delivery targets shown in Table 1. Therefore, exploration of new refrigeration technologies, such as magnetic refrigeration, is needed.

GE&R is supporting the DOE effort to develop magnetic refrigeration technologies for high-efficiency hydrogen liquefaction. Our goal is to discover, develop, and commercialize low-cost, high-performance MCE alloys to enable magnetic refrigeration to move from prototype to production. Targets for our MCE materials have been defined as follows:

- Cost: $400/kg or less, at large scale
- Performance: equivalent or better than Gd (ΔS $\geq$6 J/kgK in 3T field)
- Forms: sub-mm sized spheres and thin plates.

GE&R is also addressing the issue of hydrogen boil-off from cryogenic liquid storage tanks by building a small scale (<300 kg/day) magnetic refrigeration prototype that uses our magnetocaloric materials. A theoretical model of this system was evaluated in FY 2019, and results

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

are given below. Phase IIB funding was obtained to build a bench-scale prototype.

FY 2019 Accomplishments

- Small scale quantities of our novel second-order response MCE material set for entire temperature range 9-330 K were made commercially available on the www.geandr.com webstore.
- A processing path for scale-up and formation of spheres/thin plates has been identified and equipment tested and verified for compatibility with our compositions.
- Additional funding from the California Energy Commission (CEC) was obtained to fund the scale-up effort to 1 kg/day in-house production.
- A theoretical model of a small-scale (300 kg/day) hydrogen liquefaction prototype was built, and results indicate magnetic refrigeration may be able to provide a low-cost and low-energy solution to prevent boil-off losses at fueling stations—this is a key issue that must be addressed to achieve $3/kg H2@scale retail price.
- Phase IIB Small Business Technology Transfer (STTR) funding was obtained to build a bench-scale prototype of the small-scale hydrogen liquefaction system.

Table 1. DOE Hydrogen Liquefaction Technical Targets

DOE Current Targets	FY 2015 Status	FY 2020 Target	Ultimate Target
Small Scale Liquefaction (30,000 kg H_2/day)			
Installed capital cost ($)	70 million	70 million	-
Energy required (kWh/kg of H_2)	15	12	-
Large Scale Liquefaction (300,000 kg H_2/day)			
Installed capital cost ($)	560 million	560 million	142 million
Energy required (kWh/kg of H_2)	12	11	6

INTRODUCTION

Magnetic refrigeration has long been touted as a promising high efficiency technology to replace vapor compression cycle (VCC) systems. However, there are several major issues that need to be solved to move this technology forward. The technology utilizes the magnetocaloric effect (MCE), which is the temperature variation of a special magnetic material when exposed to a changing magnetic field. Magnetic refrigerators require two main components for operation:

1. MCE materials that function in the desired temperature range
2. Magnetic field force generated by superconducting, electro-, or permanent magnets.

One of the issues inhibiting magnetic refrigeration progress is the lack of commercially available low-cost MCE materials that will actually function, for a long period of time, in a magnetic refrigeration environment such as the active magnetic regenerator, which is in development by several entities [1–6]. GE&R in collaboration with the University of California, San Diego (UCSD), under a Phase I and II STTR grant from DOE, successfully discovered low-cost compositions with second-order, hysteresis-free response to cover the entire 9–330 K temperature range. These materials are now commercially available in small quantities on the www.geandr.com webstore, and they are the highest performance materials on the market. We have also received an award from the CEC, with a start date of August 2019, to scale up our MCE material product line. Under the CEC grant we will bring in additional equipment to manufacture larger-scale quantities of our MCE materials in-house.

Another major issue inhibiting magnetic refrigeration from moving forward is that very little work has been done to design and engineer actual systems that utilize the MCE mechanism. Pacific Northwest National Laboratory (PNNL) has made phenomenal progress building a hydrogen liquefaction magnetic refrigeration system to demonstrate large scale (30 tonne/day) liquefaction from room temperature down to 20 K, which requires MCE materials for the entire 20–300 K temperature range and uses a superconducting magnet [6].

Their results indicate potential for these systems to hit the 50% reduction in energy (6 kW-h/kg) and capital equipment cost ($50 M) for a large scale liquefaction plant (30 metric tonnes/day) compared to current technology [1, 2, 6]; however, there are still some major engineering challenges that need to be addressed to move from their 25 kg/day prototype to the 30 ton/day production plant (i.e., scaling the superconducting magnetic field), and this would require a massive industrial investment in a technology that has, thus far, only been proven at 1/1,000 the scale and has yet to reach the 20 K temperature needed to liquefy hydrogen (last known report their system went down to ~120 K).

APPROACH

Our approach to discovering novel magnetocaloric alloys has been to focus on the following: (1) only second-order response, and (2) high performance, which to date has only been possible with rare-earth elements. Our FY 2018 Phase II report details the reasons for this approach. Further, feedback from industry indicates enthusiasm for the magnetic refrigeration technology, but since practical systems have yet to be achieved, it is too early stage to attract industrial investment. A high-efficiency cost-competitive system for a relevant commercial application needs to be demonstrated to validate this technology and stimulate industrial investment.

The discovery of our high-performance low-cost MCE compositions has opened the door for small-scale systems that utilize permanent magnets. Because of this, we believe small-scale liquefaction applications offer the best immediate (could be taken to market in ~3–4 years) commercial opportunity for magnetic refrigeration due to the following:

1. Small-scale VCC systems have very poor efficiency at cryogenic temperatures (for systems operating in the <70 K region, efficiencies are ~10% of Carnot coefficient of performance (COP)—coefficient of performance is ratio of cooling provided to work required, where Carnot COP is theoretical maximum), so magnetic refrigeration systems with >50% of Carnot COP would provide significant energy cost savings.
2. VCC liquefaction systems are also really expensive (on the order of ~$5 million for 300 kg/day capacity); thus, even if a magnetic refrigeration system cost is the same or higher than that of a VCC system, the efficiency improvement, in many applications, would be worth the extra capital expenditure, as it would offer lower long-term operational cost.

There are a variety of commercial opportunities for high-efficiency small-scale liquefaction systems; however, one major opportunity, which would also be an enabling technology for fuel cell electric vehicles, is the reduction or elimination of boil-off losses at hydrogen fueling stations.

RESULTS

Magnetocaloric Materials

Feedback from end users indicates that the MCE materials need to be formed into sub-mm-sized spheres or thin plates for use in magnetic refrigerators. During the Phase II project, we paid to have our materials tested on equipment from Arcast Inc., which has an atomizer to form sub-mm-sized spheres. It was found that our materials work well in this process, and we have placed an order for this equipment and will install and develop the casting process in-house under the new CEC award. During FY 2019 we also successfully used hot pressing/sintering equipment at UCSD to form our materials into plates/pellets using the atomized powder. Our MCE materials vary in composition depending on the desired temperature range of functionality (i.e., an MCE material that functions in the temperature range near 300 K [room temperature] has a different composition than a material that functions at 10 K). We classify our compositions by their peak ΔS (temperature where the peak MCE properties occur). Under the new CEC award, our goal is to have 1-kg quantities of MCE materials available for every 10 degrees within 20–330 K (for a total of 33 compositions).

The MCE compositions, once formed into an alloy, typically require an anneal to form the crystal structure needed to induce/improve the MCE properties. During FY 2019 we continued to test various annealing processes to both improve the material performance and reduce the processing cost for large-scale manufacturing. Some of the initial heat treatments that yielded the best MCE performance took up to 6 weeks at 950°C. These long anneal times can be costly to implement in large scale due to the high cost of the equipment and facility space needed. Thus, our goal has been to develop heat treatment processes that achieve the required MCE properties in the least amount of time. Several new annealing furnaces have been installed with continuous annealing capability up to 1,700°C. In general, we have found that materials with higher melting temperatures require higher temperature anneals, and materials with more complexity (quaternary versus ternary compounds) take longer; however, there are also some issues with phase separation that can occur, particularly with the quaternary compounds, which add significant complexity to developing effective anneal processes. Figure 1 shows the quaternary compound, $Nd_{0.2}Gd_{0.8}Si_{0.8}Cr_{0.2}$, which as-cast has a peak MCE effect near 300 K, and where various heat treatments produce wildly different results. There is significant phase separation for all anneal temperatures tested thus far, which are 1 week or longer, with no significant improvement achieved with anneal times less than 1 week at these high temperatures. Lower-temperature anneals are in progress. There may also be some compositional variation occurring during melting that becomes exacerbated during anneal. We should be able to control/improve compositional issues with our new arc melt furnace once it is installed.

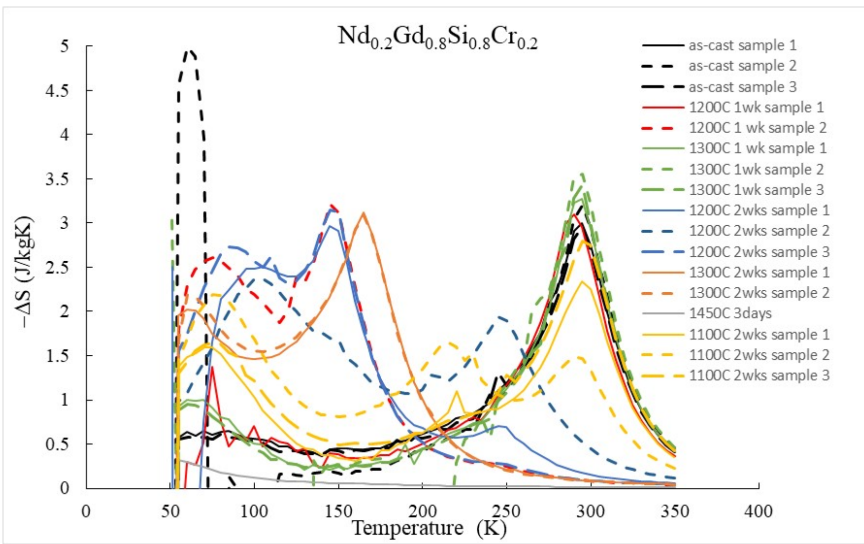

Figure 1. □S versus temperature for various MCE materials at 3T magnetic field with and without (as-cast) various anneal treatments

Additional funding has also been obtained by DOE to support a collaborative effort between GE&R and PNNL to investigate the use of their proprietary heat treatment technique on our MCE materials. Their heat treatment technique was previously developed to reduce the time and cost of anneals for automotive based alloys, and they believe this technique may be effective with our MCE materials as well.

Magnetic Refrigeration Modeling

The goal of the modeling effort is to evaluate the feasibility of a small-scale magnetic refrigeration system cooling 300 kg/day hydrogen from 77 K to its liquefaction point (20.3 K at 1 atm.) using only permanent magnets (max field: 1 Tesla), liquid nitrogen as the heat sink (hence the 77 K hot side temperature), and helium gas as the heat transfer medium fluid. This model was developed following a similar method to that of Andrew Rowe et al. [7, 8], and these initial results were also presented in July 2019 at the ASME conference in Bellevue, Washington [9]. Based on these operation conditions, we have used the model to determine important system performance metrics, such as COP, total mass of the MCE material for each stage, total magnetic field volume, amount of liquid nitrogen needed, and the helium gas flow rate. Using the model, we can also see effects of different designs and identify designs that provide high COP and low MCE materials and magnet mass requirements.

Because our proposed system uses permanent magnets that only have the maximum field intensity of 1 Tesla, we need multiple stages to cool hydrogen from 77 K to 20 K. Figure 2 shows a schematic of the multi-stage system that is being modeled. Table 2 hows the model results for several different design cases using the time-independent model (no bypass). The Case 2 system with a temperature span of 3 K and frequency of 10 Hz achieves 77% of Carnot COP, while also providing the smallest system (lowest cost due to less MCE materials and magnets) than the other example cases shown. These examples illustrate the significant effects that small changes in the system design, such as frequency and/or expected temperature span, have on the system size, cost, and performance. Additionally, the time-independent model has many assumptions, including neglecting the heat losses in the heat exchangers. In reality, fewer heat exchangers would be preferred to reduce both cost and heat losses, thus modeling a by-pass system is in progress.

Table 2. Example Model Results of a 300 kg/day Hydrogen Liquefaction MCE Refrigeration System With Different Temperature Spans and Frequencies

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)	0.679	0.123	0.44	0.63
Total mass of MCE material (kg)	4,630	870	3,029	4,450
Mass flow rate of He heat transfer fluid (kg/s)	2.352	2.252	3.423	4.7
COP of system	0.15	0.27	0.19	0.18
Fraction of Carnot COP	43%	77%	54%	51%
Estimated cost for MCE materials and magnets[a]	~$4 million	~$750,000	~$2.6 million	~$3.7 million

[a] assumes $400/kg for MCE materials and magnet cost of $0.003/mm^3.

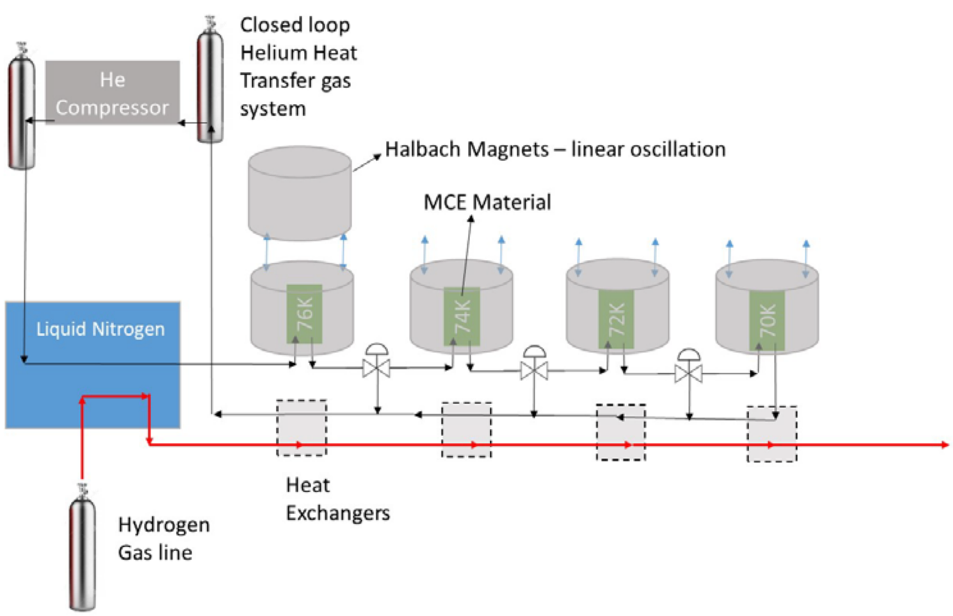

Figure 2. Schematic of the multistage small-scale hydrogen liquefaction system with no bypass flow

CONCLUSIONS AND UPCOMING ACTIVITIES

This project has made progress toward the ultimate goals of increasing the efficiency and lowering the capital cost of hydrogen liquefaction. In FY 2019 we have made progress along the critical path in support of developing magnetocaloric refrigeration technologies, in that we have:

- Continued to provide functioning MCE materials available for purchase on our webstore www.geandr.com in small quantities for any temperature from 9 K to 330 K
- Optimized anneal processing for sub-80 K MCE materials, which achieve double the target performance
- Defined a processing path for scale-up and formation of spheres/thin plates and purchased additional equipment that will be installed in FY 2020
- Built a theoretical model of a small-scale hydrogen liquefaction system, and results look promising for this system to provide low cost and high efficiency.

Upcoming activities will include:

- Under a new CEC award: Install new equipment and develop in-house processing to achieve MCE materials manufacturing capability of 1 kg/day scale to accommodate customer magnetic refrigeration prototype development.
- Under Phase IIB funding: Build a bench-scale gas liquefaction cryogenic magnetic refrigeration prototype.

CONCLUSIONS AND UPCOMING ACTIVITIES

Additional funding received:

- CEC scale-up grant to scale up production of our MCE materials to 1 kg/day
- DOE funding for a collaborative effort between GE&R and PNNL to develop a new heat treatment technique to reduce MCE materials processing time/cost
- DOE Phase IIB STTR funds to build a small-scale cryogenic magnetic refrigeration system with the purpose of demonstrating high-efficiency small-scale hydrogen liquefaction.

Patents:

- PCT application (US2018/012836) filed in February 2018 for our ternary-based compounds. National stage (United States, Europe, China) was entered in July 2019
- PCT application (US 62/634078) filed in February 2019 for our >50 K MCE compositions
- Provisional application (US 62/880549) filed July 2019 for our small-scale hydrogen liquefaction system.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. R. Ihnfeldt, S. Jin, R. Chen, X. Xu, E. Caldwell, and E. Kim, "High Efficiency Magnetic Refrigeration Enabling ZERO Emission Hydrogen Transportation," Presented at the CALSeed Phase II Pitch Competition, San Francisco, CA, October 16, 2018.
2. R. Ihnfeldt, S. Jin, R. Chen, X. Xu, E. Caldwell, and E. Kim, "High Efficiency Magnetic Refrigeration Enabling ZERO Emission Hydrogen Transportation," Presented at the San Diego Innovation Showcase, San Diego, CA, October 25, 2018.
3. R. Ihnfeldt, S. Jin, R. Chen, E. Caldwell, and T. Feng, "Novel, Low-cost Alloys for Magnetocaloric Cooling and Liquefaction," Presented at Hydrogen Delivery Technical Team Review, February 11, 2019.

4. R. Ihnfeldt, S. Jin, R. Chen, X. Xu, E. Caldwell, and T. Feng, "Low-cost Magnetocaloric Materials Discovery," Presentation at DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluation Meeting, Washington, DC, May 1, 2019.
5. 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.

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9. T. Feng, R. Chen, and R. Ihnfeldt, "Modeling of Hydrogen Liquefaction using Magnetocaloric Cycles with Permanent Magnets," Presented at ASME 2019 Conference in Bellevue, Washington, July 15, 2019.