III.10 Magnetocaloric Hydrogen Liquefaction

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Subcontractor:
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Project End Date: September 30, 2018

Overall Objectives

- Quantify and incorporate novel configurations to achieve simpler, more efficient liquefier designs.
- Identify, characterize, and fabricate magnetic materials in shapes suitable for high-performance active magnetic regenerators (AMRs) from 280 K to 20 K.
- Fabricate and characterize improved multi-layer magnetocaloric regenerator performance.
- Design, fabricate, test, and demonstrate a lab-scale magnetocaloric hydrogen liquefier (MCHL) system.
- Demonstrate a lab-scale hydrogen liquefier with a figure of merit (FOM) increase from 0.3 up to 0.5.
- Perform techno-economic analysis on a proposed full-scale (30 tons per day) system.

Fiscal Year (FY) 2016 Objectives

- Complete characterization of first generation (GEN I) system for impact of bypass flow of heat transfer gas on improved engineering liquefier designs in second and third generations (GEN II and GEN III).
- Complete characterization of dual, multi-layer magnetic regenerators.
- Demonstrate gas liquefaction.
- Prepare and characterize candidate magnetocaloric materials for use in GEN II and GEN III system. This physical and thermomagnetic characterization is required to complete the system designs.
- Produce magnetocaloric spherical particles using the rotating disk atomizer. This requires upgrading the apparatus to be able to operate with rare earth materials.
- Finalize GEN II design and order parts.
- Refine the capital equipment cost estimates of a modular scale MCHL system.

Technical Barriers

This project addresses the following technical delivery barrier from the Hydrogen Delivery section (3.2) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(H) High-Cost and Low Efficiency of Hydrogen Liquefaction

Technical Targets

Conventional hydrogen liquefiers at any scale have a maximum FOM of ~0.35 due primarily to the intrinsic difficulty of rapid, efficient compression of either hydrogen or helium working gases (depending on the liquefier design). The novel approach of this MCHL project uses solid magnetic working refrigerants cycled in and out of high magnetic fields to execute an efficient active magnetic regenerative liquefaction cycle that avoids the use of gas compressors. Numerical simulation modeling of high performance MCHL designs indicates certain achievable designs have promise to simultaneously lower installed capital costs per unit capacity and to increase thermodynamic efficiency from an FOM of ~0.35 toward 0.5–0.6. Results from experimental prototypes should support the design and deployment of hydrogen liquefier plants that meet the DOE hydrogen production and delivery targets.

- $70 million capital cost for a turnkey plant with a capacity of 30,000 kg H_2/d
- Operational efficiency of a complete liquefier plant of 75% as defined by DOE and commensurate with a liquefier FOM of approximately 0.5–0.6

FY 2016 Accomplishments

- Set a world record by demonstrating propane liquefaction. To our knowledge this is the first time a magnetocaloric system was used to liquefy a gas from room temperature.
- Demonstrated 25% increase in cooling power using bypass configuration with a layered regenerator.

- Reduced requirement for magnetocaloric materials in liquefaction system by up to 88% through the implementation of a bypass configuration that completely precools the process stream.
- Completed preliminary GEN II designs with rotating belt, rotating wheel, and reciprocating cylinder configurations.
- Projected cost of MCHL system to be \$1.5M/t H_2/d. This is 36% less than current Claude cycle based systems and the DOE targets.
- Upgraded the rotating disk atomizer and demonstrated spherical particle production.
- Characterize magnetization vs. temperature for eight materials to be used in the GEN II system.

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INTRODUCTION

MCHL technology promises cost effective and efficient hydrogen liquefaction because it eliminates gas compressors, the largest source of inefficiency in the traditional Claude cycle liquefiers, and the use of liquid nitrogen to precool the hydrogen. The Claude cycle liquefier is the current industrial choice for hydrogen liquefaction and uses a variety of configurations with processes where helium, hydrogen, or gas mixtures are coolants. In the case of hydrogen as the refrigerant gas and the process gas, the hydrogen feed to the process is first cooled by liquid nitrogen, and then further cooled in counter flow heat exchangers where the cooling power is provided by turbo expansion of a portion of the pre-cooled hydrogen stream. Liquefaction of the pre-cooled, high-pressure hydrogen stream is finally accomplished by throttling in a Joule-Thomson valve into a phase-separator collection vessel. Conventional liquefier technology for hydrogen is limited to an FOM of ~0.35 for a large facility, and of typically less than 0.3 for a smaller facility.

The MCHL initial design (GEN I) is an AMR system which uses regions of high or low magnetic field and reciprocating magnetocaloric materials to transfer heat between hot and cold thermal reservoirs. In one step of the AMR cycle the magnetic material in a high performance regenerator is adiabatically placed in a high magnetic field. The conservation of total entropy in this adiabatic process requires the magnetic refrigerants in the regenerators to increase in temperature to compensate for the increased magnetic order (lower entropy) among the material's magnetic moments. The increased thermal energy is transferred to a heat sink by the cold-to-hot flow of heat transfer fluid. After the cold-to-hot heat transfer fluid flow is completed, the magnetic material is adiabatically removed from the high magnetic field resulting in an increase in entropy among the magnetic moments of the refrigerant in the regenerators so to maintain constant total entropy; the temperature of the magnetic refrigerants decreases in this step. During the subsequent hot-to-cold flow of the heat transfer fluid at constant low magnetic field, the colder magnetic regenerator cools the heat transfer fluid before it exits the regenerator and accepts heat from the thermal load (i.e., the hydrogen process stream). At the end of this flow, the active magnetic regenerative cycle is repeated again at the operating frequency. The principle of operation is shown in Figure 1. The AMR cycle can be highly efficient because the magnetization–demagnetization temperature changes are only a fraction of the adiabatic temperature changes of a gas compression process and the magnetic regenerators can be designed to have much higher effectiveness than a gas-to-gas counter flow heat exchanger, The MCHL project is developing liquefier designs that use magnetocaloric refrigeration to achieve an efficient thermodynamic liquefaction cycle. Detailed modeling of the MCHL technology coupled with experimental validation

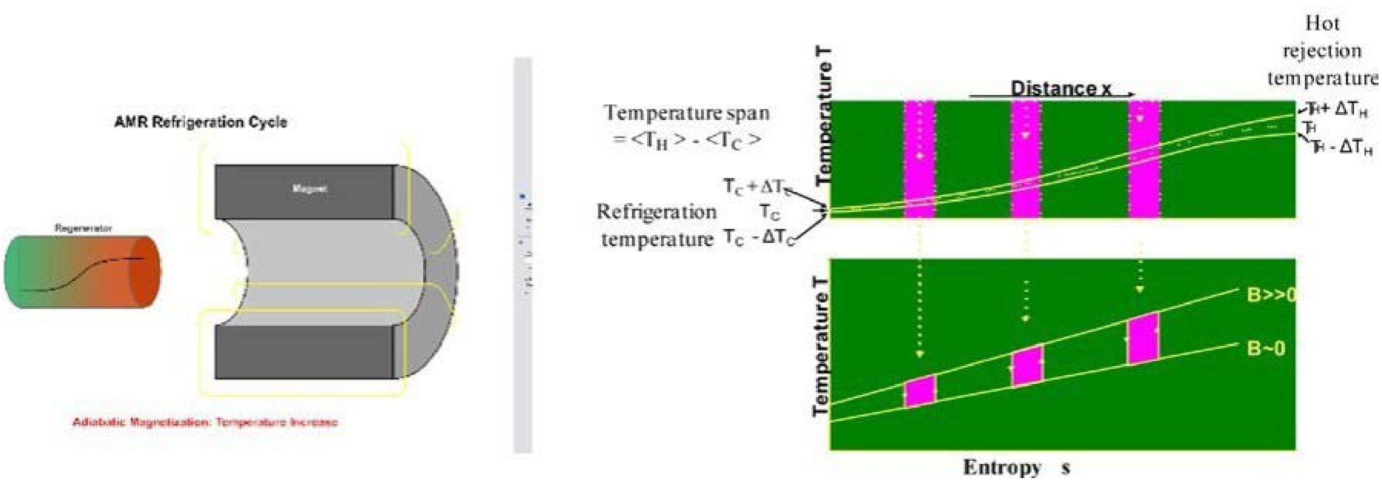
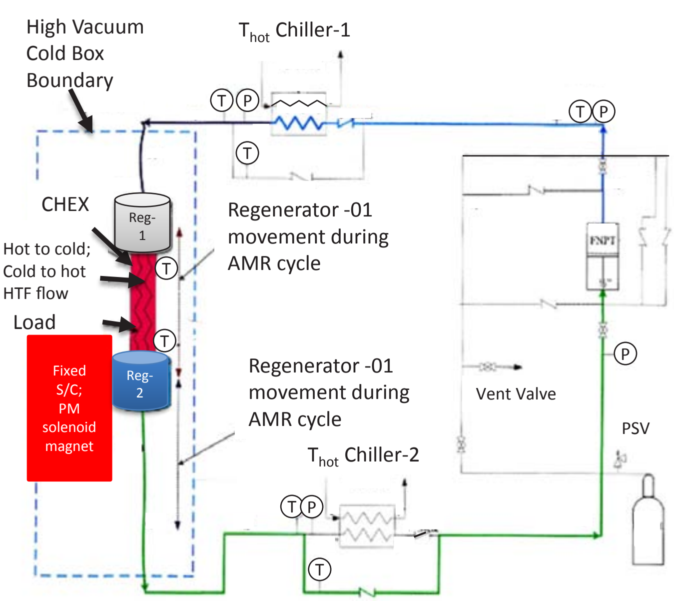


FIGURE 1. Active magnetic regenerative liquefier principle of operation

in prototypes indicate this technology has the potential to simultaneously lower liquefier installed capital costs per unit capacity, delivery cost, and to increase thermodynamic efficiency from an FOM of ~0.3 toward 0.5–0.6.

APPROACH

This project builds upon work first pioneered by Dr. John Barclay (partner). We utilized reciprocating dual regenerator design (GEN I) to evaluate magnetic materials, and better understand the temperature distribution in the regenerators. A simplified process flow diagram of the GEN I unit is shown in Figure 2. The operation and experimental results from FY 2015 are located in the results section of this report. Based upon the results of GEN I, a GEN II MCHL design is being developed. The GEN II initial choice was a rotary regenerator design, which promises to intrinsically balance the magnetic forces upon the magnetic refrigerants going into and out of the high magnetic field region for maximum work recovery. Its continuous magnetic material rotation enables constant magnetic flux, which reduces induced flux jumps that occur in a persistent mode magnet during reciprocating motion of dual magnetic regenerators. The rotary MCHL is an advanced concept that has not been successfully implemented previously. In consideration of the likelihood of encountering unforeseeable technical challenges within limited resources and time, the development of a rotary MCHL will be divided into two phases. In Phase 1, a fully independent prototype (GEN II) will be designed, constructed, and evaluated. GEN II will have only one superconducting (S/C) magnet subsystem, 4 K cryocooler, cold box, heat transfer gas circulator, data acquisition, integrated structures, and drive motors; but, it will incorporate the new novel configuration and have the capability to test several different magnetic wheels that are designed to operate over selected temperature ranges between 280 K and 20 K. For example, the regenerative wheel will be designed for 280–120 K which is the first stage of a multistage MCHL designed specifically to take advantage of the novel configuration. A complete liquefaction system will contain multiple stages, each with a wheel designed to operate over a specific temperature range. Depending on the effectiveness of the new configuration innovations to be done in Phase I, a total of three to four stages may be required rather than six or more without the innovation. This approach will develop the necessary technical knowhow for the rotary system, including an arc shaped superconductor magnet, multilayered refrigerant wheels, fabrication of suitable refrigerant materials, and micro-channel heat exchangers. Phase II focuses on a multi-wheels system (GEN III) capable of liquefying gaseous H_2 (GH_2) from 280 K. The key for a successful Phase II lies in the seamless integration of multiple wheels, magnets, and heat exchange subsystems, as well as successful preparation of refrigerant materials, which will require complete metallurgical understanding of 10–14 different rare earth metals and alloys. All lessons from GEN II will be incorporated into the design of GEN III, which will need multiple magnet subsystems, additional process and heat exchangers, and interconnections among the multiple refrigerant wheels to directly convert gaseous feedstock H_2 to LH_2. The GEN III prototype will be designed, constructed, commissioned, and evaluated. The results will provide a validated, realistic technical and economic assessment of the MCHL technology in general.



PM – Permanent magnet; PSV – Pressure safety valve

FIGURE 2. Process flow diagram of GEN I with bypass

RESULTS

The magnetocaloric materials we are using have a second-order phase transition[1] as they are cooled or heated through a characteristic ordering temperature in external magnetic fields. Magnetic refrigerants with this type of magnetic order are also characterized by a lower total heat capacity in higher magnetic fields compared to that in lower magnetic fields below the ordering temperature (Curie temperature). This is a unique feature of an AMR cycle that we've learned how to exploit. Our design uses dual active magnetic regenerators thermally connected by heat transfer fluid (Figure 3). In this design the heat transfer fluid flows through AMR 1 after AMR 1 is adiabatically removed from a magnetic field to cool it. In this AMR, the heat transfer fluid (HTF) is cooled and then flows to a heat exchanger to cool the process stream. Upon leaving the heat exchanger, the HTF flows to AMR 2 which is magnetized by a high magnetic field (i.e., it is "hotter" than the demagnetized regenerator). The HTF flows from cold to hot and cools hotter AMR 2 and then dumps the excess heat to the environment

[1] Second-order magnetic transitions do not have a latent heat associated with them.

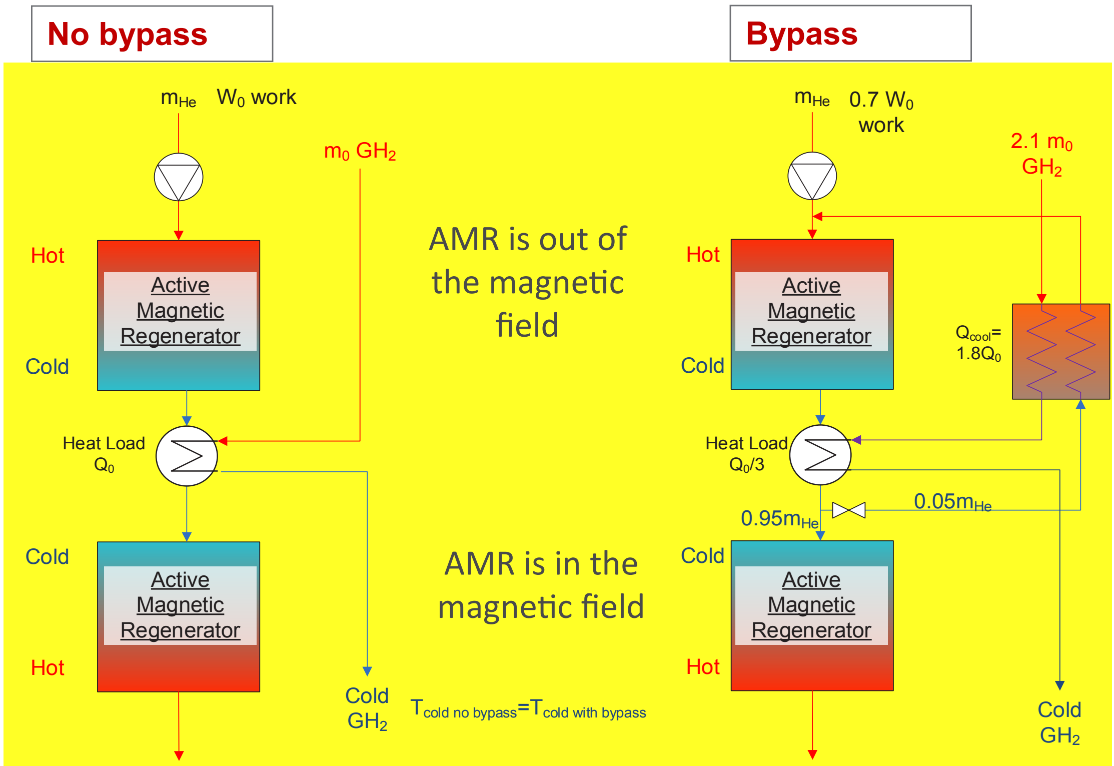


FIGURE 3. Bypass mode operation compared to regular operation with no bypass

in another heat exchanger. Once this heat flow is complete, the AMRs are moved so that AMR 2 is demagnetized which cools it down and AMR 1 is magnetized which heats it up. The HTF flow is reversed and the cooling–heating cycle continued. Because the total heat capacity of the magnetic material subjected to the magnetic field is lower than the magnetic material not subjected to the magnetic field, less HTF is needed to cool the hotter magnetic material in the magnetic field, than to transfer heat in the colder magnetic material outside of the magnetic field. To create the most efficient AMR cycle, a small slip stream of HTF should be removed from the cold heat exchanger (CHEX) prior to the HTF flowing into the hotter AMR. This slip stream can be used to pre-cool the process stream which increases the total cooling power for the same work input. While this theory has been known, it has never been demonstrated nor has the significant impact on improvement of FOM been appreciated. Our GEN II and GEN III designs incorporated the ability to operate in "bypass" mode (Figures 2 and 3). We tested this operation mode and were able to show a 25% increase (Figure 4) in cooling power in our conditions (3.3 to 0.6 Tesla field change). This was extremely promising. We then projected the impact of using bypass configuration to completely pre-cool the process stream at a larger magnetic field change. As shown in Table 1, this design choice resulted in a decrease in magnetic material requirement for the same liquefaction capacity by up to 88%.

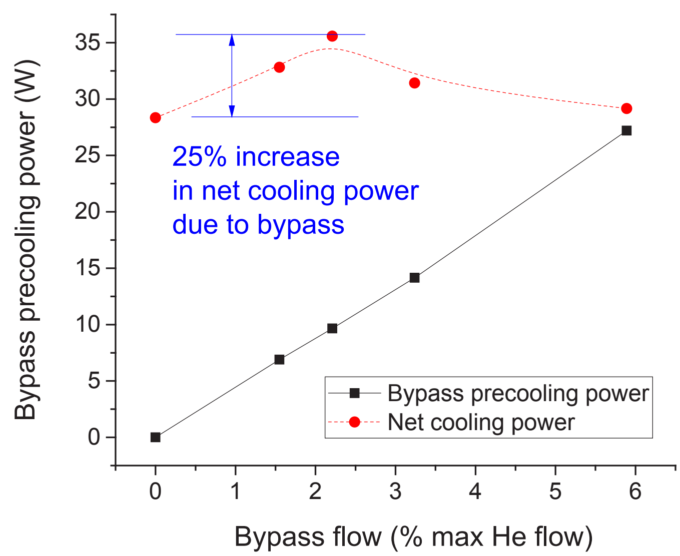


FIGURE 4. 25% increase in cooling power operating in bypass mode. Conditions include 215 g Gd regenerator, 215 g Gd/ $Gd_{0.74}Tb_{0.26}$ regenerator, 3.3–0.6 Tesla field, 200 psia He gas HTF, 4 s AMR cycle.

The ultimate purpose of this work is to efficiently liquefy hydrogen. To demonstrate this potential, we demonstrated the liquefaction of propane gas from room temperature. We built and integrated a simple heat exchanger/condenser into

TABLE 1. Projected Impact of Bypass*

	No Bypass	6% Bypass	% Improvement
Thermal Load	4.3 kW	2.9 kW	32% reduction
HTF Flow	31 L He/sec	~4 L He/sec	87% reduction
Magnetic Material Required	184 kg	22.3 kg	**88% reduction**
FOM	0.4	>0.7	**87% increase**

***assumes the system is scaled by increasing the magnetic field to 7Tesla and increasing the HTF size.**

the CHEX of GEN I for this experiment. The design and operation details are in journal article under preparation. We successfully fed propane from an external tank to the CHEX of GEN I, where it was condensed and collected in a small storage vessel as a liquid. To our knowledge, this is the first time a magnetocaloric system has been used to liquefy a gas from room temperature.

Based upon the experimental results from the GEN I system, we selected a rotary system which used regenerator cartridges mounted on belts for GEN II. The figure of merit of the design is predicted to be 0.6 or higher. It could incorporate layered materials and bypass of the HTF. The primary R&D challenges for GEN II were the performance of the seals between the moving regenerator-belt assembly and the fixed housing, belt drive stresses and the fact that it has not been demonstrated previously for cryogenic temperatures. We developed novel labyrinth face seals which allow the cartridges to move while still retaining a seal. The initial seals still leaked too much, and their spring loading was therefore increased. The increased spring loading reduced the leakage to acceptably small amounts but the friction between the sliding face seals and the rotating belt was too large to be acceptable. This exploratory effort was stopped because of lack of funding for an experimental study of acceptable seals.

We did a preliminary cost analysis of various GEN II and GEN III designs and projected the installed capital cost to be ~$1.5M/t H_2/d. Figure 5 has the breakdown for a 10 t H_2/d system. This cost is a 36% cost reduction compared to the DOE target of $70M for a 30,000 t/d system (which equates to ~$2.33M/t H_2/d). An interesting alternative which was also examined was co-locating the hydrogen liquefier with a compressed natural gas (CNG) plant. In this instance, we can use the cooling from the conversion of liquefied natural gas (LNG) to CNG to precool the hydrogen. By co-locating the projected installed cost decreases substantially to ~$0.7M/t H_2/d.

In addition to the system work, Ames has led an effort for materials analysis and production. We have identified eight materials required for the GEN II system, which is designed to operate from room temperature to about 125 K (sufficient to liquefy methane). Ames has been using their unique capabilities to evaluate the magnetization of materials as a function of temperature, in the range of 320 K to 10 K.

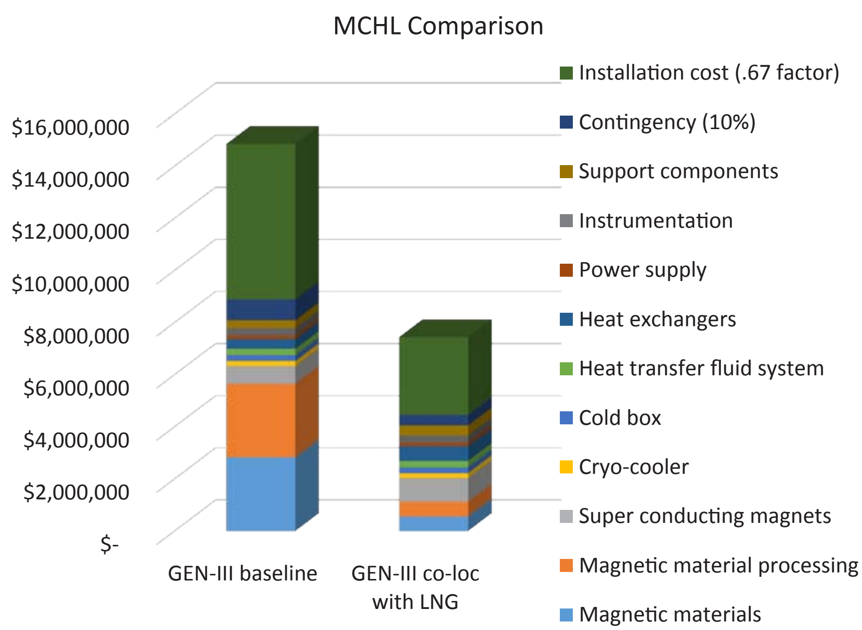


FIGURE 5. 10 t H_2/da installed capital cost for a standalone system and a system co-located with LNG/CNG

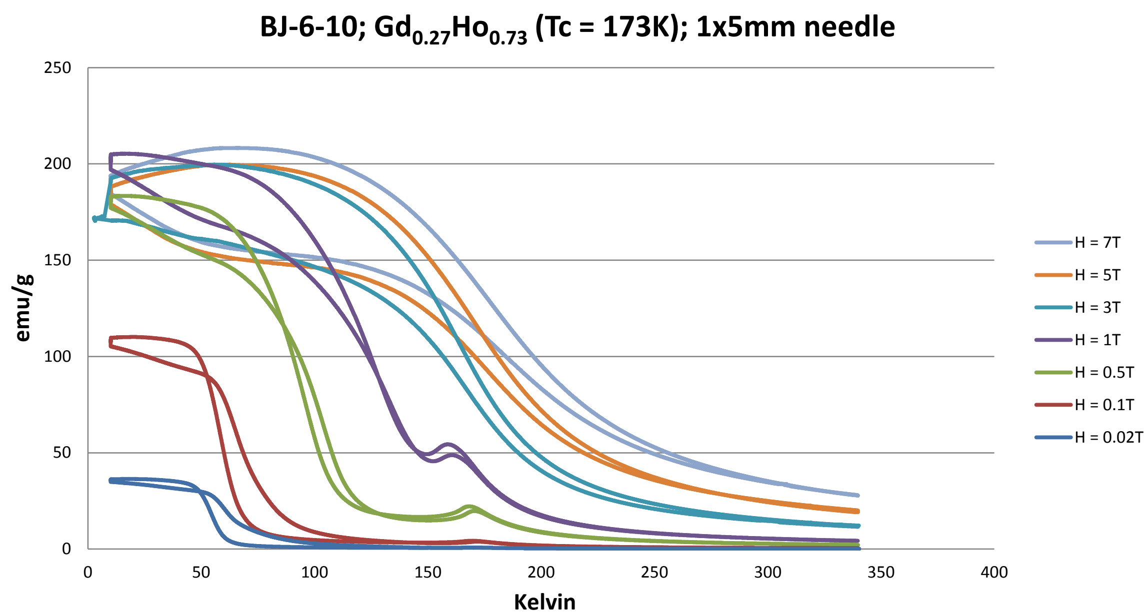


FIGURE 6. Magnetization vs. temperature

The materials evaluated have Curie temperatures ranging from ~293 K to ~150 K. An example of the magnetization vs temperature curves is shown in Figure 6 for $Gd_{0.27}Ho_{0.73}$ (Tc = 173 K). At higher magnetic fields, the magnetization curves indicate that this material has a significant magnetic moment per rare earth atom and a well-defined Curie temperature of ~173 K. The adiabatic temperature changes as a function of magnetic field for materials like this alloy are 1–2 K/Tesla of applied magnetic induction at the Curie temperature. This type of magnetic material also will exhibit the difference in heat capacity at high and low magnetic fields, a requirement for use of bypass flow of the HTF. These initial M (H, T) data support that it is one very promising magnetic refrigerant of the eight used in GEN II.

Our cost projection estimated that materials and processing cost accounted for ~20% of the installed cost of the MHCL. Therefore, in order to reduce capital cost we are looking at lowering the materials processing costs. Ames has a unique rotating disk atomizer system that produces spherical rare earth particles with a low operating cost, and can be up-scaled to relatively high volume. This system was originally designed for low-density calcium production so significant changes were required for use with the rare earth materials used in this project. In the system a crucible melts the metal and, when properly superheated, a stopper rod lifts and drains the molten metal as a stream through an orifice onto the spinning disk. Molten droplets are spun off the periphery of the disk into a co-rotating oil bath. If the disk is rotating at the appropriate speed, perfectly spherical particles with a very narrow size distribution, centered on 180–200 µm are produced. The oil bath quenches the droplets so they solidify and retain a spherical shape. A published empirical correlation has been used to determine the correct disk spinning speed (rpm), based on the surface tension and viscosity of molten Gd. Most of the system upgrades were completed and Gd spheres with ~180 µm diameter have been produced. The rest of the upgrades should be completed by the end of FY 2016. We project that the rotating disk atomizer can reduce manufacturing cost by 10–30% compared to the cost of commercial plasma rotating electrode process (PREP) atomization, while improving quality by adding a thin surface passivation surface film. The chief additional cost for PREP processing is the cost of casting each alloy into a chill mold and for careful machining of the ingot into a precise cylinder. Also, PREP requires an un-atomized cylindrical stub that is constantly necessary for the rotation drive and bearings. Moreover, the ingot used in PREP is constrained to specific size ranges, which is not the case for the rotating disk atomizer. The selected rotating disk method allows a higher yield of the alloy feed stock because the entire charge is melted prior to being poured onto the spinning disk. It works with a wide range of alloys and also with intermetallic compounds. Any shape of charge material that fits into the melting crucible can be melted, which allows scrap and off-size powder to be recycled. Although it has not been measured yet, the effective yield of spheres of the optimum diameter from the spin melting technique may be approximately 30% higher than PREP atomization technique. It is excellent to have both options available. Further advances in regenerator design may also enable higher thermal effectiveness from thin sheets or other high specific area starting materials for the magnetic regenerators.

CONCLUSIONS AND FUTURE DIRECTIONS

We have successfully demonstrated:

- 25% increase in cooling power by using bypass operation.
- Up to 88% reduction in material requirements using bypass operation
- Propane liquefaction, which to our knowledge, is the first gas liquefaction from room temperature using a magnetocaloric system.
- Projected installed system cost of ~$1.5M/t H_2/d which is 36% lower than the DOE targets.
- Magnetization vs. temperature characterization of seven materials for use in GEN II.
- New particle manufacturing process capable of producing high grade, consistent diameter spheres with the potential to reduce materials production cost by 10–30%.

Future directions:

- GEN II system
  - 8-layered system design completed.
  - Components have been ordered and are being received.
  - Upgrades to the vacuum cold box are underway; this should allow for >6 T operation.
  - System will be tested in FY 2017.
- Materials
  - Characterization underway for the key materials.
  - Spinning disk atomizer upgrades will be completed and materials for GEN II and GEN III will be provided by Ames.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Three provisional patent applications have been submitted.

FY 2016 PUBLICATIONS/PRESENTATIONS

Presentations

1. Holladay J.D., J.A. Barclay, J. Cui, K.D. Meinhardt, E. Polikarpov, E.C. Thomsen, and I.E. Anderson. "Advancements in Magnetocaloric Gas Liquefaction at PNNL." Presented at taking the temperature of phase transitions in cool materials, Royal Society, London, United Kingdom. February 8, 2016, PNNL-SA-114806.

2. Holladay J.D., J.A. Barclay, J. Cui, K.D. Meinhardt, E. Polikarpov, E.C. Thomsen, and I. Anderson. 2015. "Advancements in Magnetocaloric Gas Liquefaction." MRS Spring Meeting March 2016. PNNL-SA-113858.

Papers in preparation

1. Holladay J.D., J.A. Barclay, J. Cui, K.D. Meinhardt, E. Polikarpov, E.C. Thomsen, and I. Anderson. 2015. "Advancements in Magnetocaloric Gas Liquefaction." MRS Spring Meeting.

2. Paper on liquefaction under development.