III.6 Magnetocaloric Hydrogen Liquefaction

Jamie Holladay (Primary Contact),
Kerry Meinhardt, Evgueni Polikarpov, Ed Thomsen, Reed Teyber, John Barclay (Emerald Energy NW), Jun Cui (PNNL/Ames Laboratory), Brandt Jensen (Ames), and Iver Anderson (Ames)
Pacific Northwest National Laboratory (PNNL)
PO Box 999, MS: K1-90
Richland, WA 99352
Phone: (509) 371-6692
Email: Jamie.Holladay@pnnl.gov

DOE Manager: Neha Rustagi
Phone: (202) 586-8424
Email: Neha.Rustagi@ee.doe.gov

Subcontractor:
Emerald Energy NW LLC, Bothell, WA

Project Start Date: October 1, 2015
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 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) 2017 Objectives

- Characterize eight magnetocaloric materials for use in second generation (GEN-II) design.
- Synthesize 150–250 µm particles of the magnetocaloric materials.
- Model the GEN-II regenerator using the updated materials properties.
- Adjust GEN-II design based on model results incorporating new hypothesis on layered material performance.
- Demonstrate GEN-II operation from 280 K to 120 K.

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 magnetocaloric hydrogen liquefier (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 (Table 1).

TABLE 1. Comparison of Magnetocaloric Hydrogen Liquefier Current Status to Targets

30 T/d (small facility)	Claude cycles (current)	PNNL's MCHL Targets	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	$70 M[1]	***$45–70 M***	~$70 M
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

O&M – operation and maintenance

FY 2017 Accomplishments

- Identified 13 ferromagnetic materials to span temperatures from 280 K to 20 K for a two-stage magnetocaloric hydrogen liquefier.
- Characterized the eight magnetic materials for use in the GEN-II system.
- Synthesized eight rare-earth alloys into 150–250 µm diameter spheres.
- Validated a new model which uses the materials properties reported by Ames.
- Modeled the GEN-II system.
- Predicted 6–10% bypass to provide optimal cooling of the process stream using the improved, validated model.
- Developed a modified GEN-II design using the model results. The GEN-II design incorporated the new layered regenerator configuration.
- Dual GEN-II regenerators constructed. In process of integrating dual regenerators with other subsystems of GEN-II and testing.
- Improved cooling to superconductive magnet sub-system which allowed its operation up to 7 T from 3.3 T.

✧ ✧ ✧ ✧ ✧

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 turbine 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 current MCHL design is an AMR system which uses regions of high and 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 fabricated into a highly effective 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 (higher entropy) 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 the magnetic regenerators. 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 such as cooling the hydrogen process stream. At the end of this flow, the active magnetic regenerative cycle is repeated again at the operating frequency. To overcome the limited entropy change of magnetic refrigerants, magnetic cooling cycles typically use the active magnetic regenerator in which each differential section of the regenerator undergoes independent Brayton cycles. This allows the temperature spans required for liquefaction to be obtained. A more complete description including simplified process flow diagram and schematics is found in the FY 2016 Annual Progress Report. 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. In addition, the magnetization and demagnetization process are inherently reversible allowing for high efficiency. 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 in prototypes indicate this technology has the potential to simultaneously lower liquefier installed capital costs per unit capacity, decrease delivery cost, and to increase thermodynamic efficiency from an FOM of ~0.3 toward 0.5–0.6.

APPROACH

At a high level the critical path for MCHL project can be summarized as:

- Identify, synthesize and characterize magnetocaloric materials.
- Develop an approach to understand the magnitude and utilize the second order (fero-paramagnetic) phase transaction characteristic in many magnetocaloric

materials to improve system performance while minimizing cost. Below the respective Curie temperatures of such magnetic materials have lower magnetic heat capacity in high magnetic fields compared to low magnetic field. We used the positive influence of this unique thermal characteristic on heat transfer flow in "bypass operation" described in FY 2016 Annual Progress Report as well as in the current report.

- Investigate layered material regenerator compositions, engineering and operation in an attempt to develop layering strategies and to understand how temperature changes within the layers and how different heat transfer fluid in material layers impact performance. This includes detailed models using the materials properties measured as well as experiments.
- Ortho-Para hydrogen conversion for liquefaction. This will include system research for catalyst integration into process heat exchangers or into magnetic regenerators.
- Hydrogen liquefaction by combining the research findings.

This project builds upon work first pioneered by Dr. John Barclay at Emerald Energy NW, LLC, (partner). We have modified the design and updated models previously developed. We have several major efforts occurring simultaneously to complete the critical path for this project's magnetocaloric hydrogen liquefaction research goals. (1) In house synthesized alloy ingots were used for the materials characterization using Ames's magnetic materials characterization capabilities. For use in the MCHL, the materials need to be spherical with a diameter of 150–250 µm. We are using Ames's rotating disk atomization (RDA), a low-cost material synthesis technique, to make the spheres. The RDA synthesized materials will be tested in PNNL's unique reciprocating dual regenerator research system. Details of the dual regenerator design, schematics, etc., as well as initial bypass operation are found in the FY 2016 Annual Progress Report. (2) Bypass operation was tested and identified as a key to achieving high performance operation with minimal materials. (3) The layering and system design efforts are being pursued via modeling and experimental efforts. The materials properties will be used in an advanced modeling sub-task to understand the performance and improve the system design. The models are being validated against experimental data from PNNL's research system. A second-generation device tests materials layering coupled with bypass operation. Material layering is not a new approach; however, the expected performance has not been achieved for cryogenic applications. We hypothesize that the reason for this is that each layer needs to be considered as an individual refrigerator cycle. This results in varying the amount of materials required for each layer and varying the heat transfer fluid flow for each layer. This hypothesis is tested in the second-generation system. (4) Based on the results of the previous work, integration of ortho-para catalysts to aid in hydrogen liquefaction and actual liquefaction tests will be done. This integration and research is part of the future work on this project. Finally, a techno-economic analysis will be used to measure progress against the DOE's efficiency and cost performance targets. An initial techno-economic analysis was reported in FY 2016. This analysis is currently being updated with FY 2017 results and will be completed in FY 2018.

RESULTS

Materials Synthesis and Characterization

Materials with the correct properties combined with innovation system configurations to take advantage of those properties are key to the success of this project. For materials selection, we assumed a 20 K decrease per material which results in a total of 13 materials needed in a two-stage system. Each material needs to have the appropriate Curie temperature, T_c, for operation in the desired temperature range. Molecular field theory was used to identify alloys with the desired T_c which were then synthesized as ingots to measure the properties. These materials are listed in Table 2.

TABLE 2. Materials, Their Target Operating Temperature and Associated Curie Temperatures

Material	Operating Temperature Span	Curie Temperature
	K	K
Gd	280–260	293
$Gd_{0.91}Y_{0.09}$	260–240	274
$Gd_{0.30}Tb_{0.70}$	240–220	253
$Gd_{0.69}Er_{0.31}$	220–200	232
$Gd_{0.32}Dy_{0.68}$	200–180	213
$Gd_{0.15}Dy_{0.85}$	180–160	193
$Gd_{0.27}Ho_{0.73}$	160–140	173
$Gd_{0.16}Ho_{0.84}$	140–120	153
$Gd_{0.23}Er_{0.77}$	120–100	132
$Ho_{0.90}Gd_{0.10}Co_2$	100–80	110
$Ho_{0.95}Gd_{0.05}Co_2$	80–60	90
$Gd_{0.5}Dy_{0.5}Ni_2$	60–40	70
$Dy_{0.75}Er_{0.25}Al_2$	40–20	50

In FY 2017 we have characterized and synthesized the first eight materials for use in the first stage. The RDA system, Figure 1, was used to make the spherical particles. Empirical correlations are available for pure materials to provide guidance for the alloys. Unfortunately, the alloys performed substantially different than the pure materials which caused delays in Ames being able to provide suitable

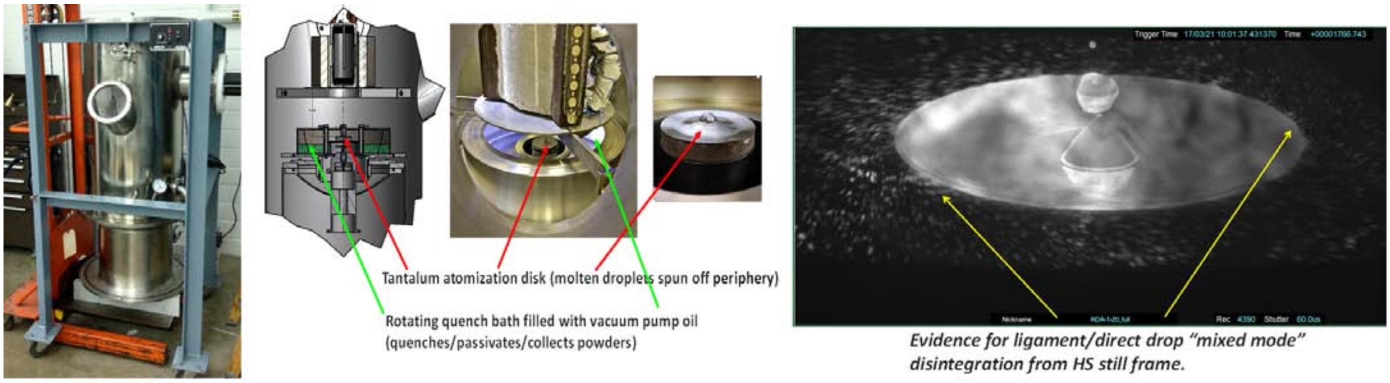

FIGURE 1. Rotating disk atomizer used to synthesize the micron scale spherical magnetocaloric materials. Picture on the far right shows atomization process of $Gd_{0.16}Ho_{0.84}$.

materials to PNNL for the regenerators. One of the major challenges was not in material size, but in achieving spheres. The MCHL system was designed for spherical particles to ensure acceptable pressure drop and uniform fluid flow through the porous regenerators. As flakes will severely limit performance, the spherical particles are needed. In order to eliminate the need to hand separate the particles, PNNL built a simple machine to quickly separate the spherical from non-spherical particles (Figure 2). Several runs were required to obtain sufficient material for each layer of the dual regenerators. The experience from these runs is helping Ames improve their RDA apparatus for rare-earth alloys.

Magnetic property characterizations included Curie temperature (T_c), magnetic moment, and heat capacity measurements from 2 K to 340 K and several magnetic fields between 0 T and 9 T. As shown in Figure 3, the heat capacity for gadolinium below its Curie temperature of 293 K varies by as much as 10% from a change in magnetic field from 0.05 T to 9 T. Similar property performance was measured in the other alloys. These properties were used in the updated model.

Bypass Operation

Bypass operation enables a system to take advantage of the fundamental properties of the second order phase transition in the materials being used. As shown in Figure 3, the magnetocaloric material had a significantly higher heat capacity at low magnetic field compared to high magnetic fields. This translates into the need for a higher heat transfer

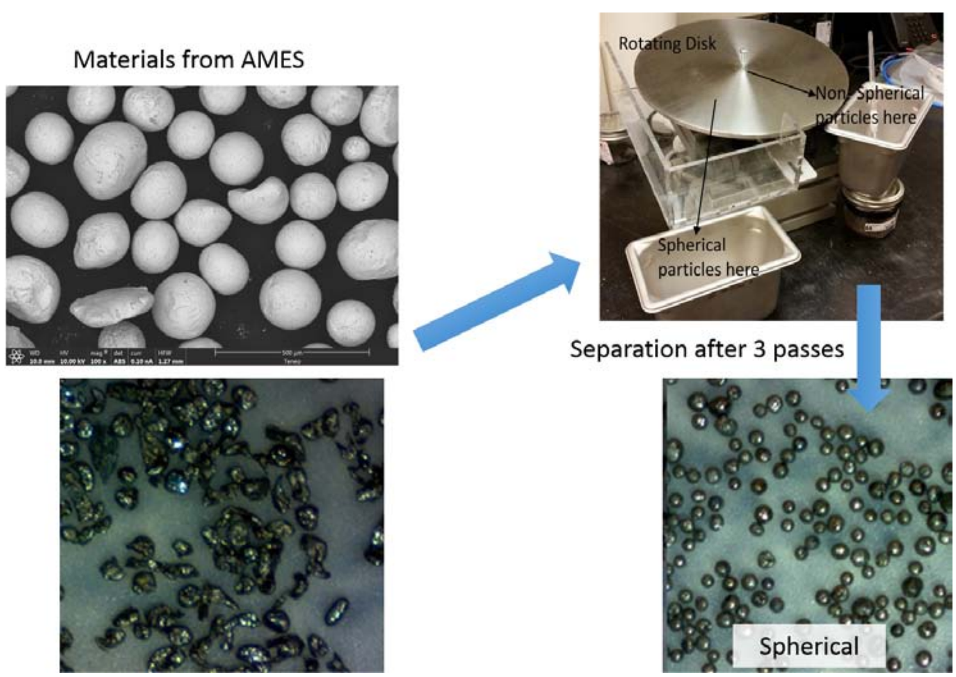

FIGURE 2. Successful separation of spherical particles from non-spherical particles using a simple apparatus

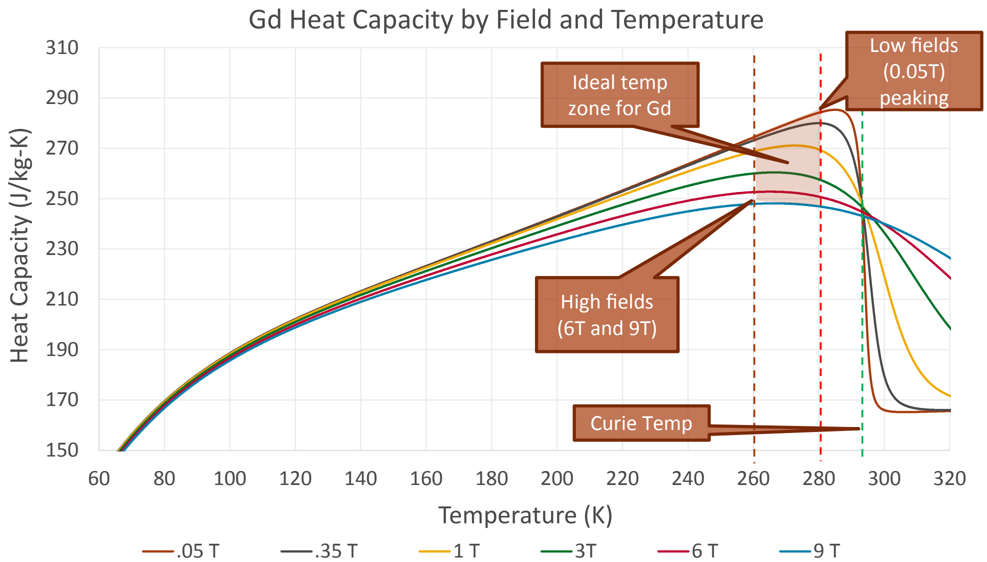

FIGURE 3. Heat capacity is magnetic field dependent

fluid flow through a regenerator located in the low magnetic field than in the high magnetic field. The excess heat transfer fluid can be redirected to bypass the regenerator in the magnetic field to not only improve the AMR performance, but it can be used to pre-cool the process stream to increase the system cooling power and continuously cool the process stream. The system modeling shows identifies 6–10% bypass operation as the optimum and Table 3 shows the impact of a 6% bypass coupled with a 6 T magnetic field change on the regenerator mass for the 280 K to 120 K stage of a 1-Hz MCHL with a 25 kg/d capacity.

Model Validation

Simulations were used to predict performance of the dual regenerators coupled with the reciprocating heat transfer gas flows. Simulations found in the literature used average material properties. For small changes in magnetic field and/or temperature average properties would be sufficient. However, the MCHL system will experience a large change in magnetic field and large temperature change so the average properties would likely result in substantial errors. Thus, large multi-property data bases created using the molecular field model and magnetic thermodynamics based on the materials properties measured by Ames were used. One of the unique features of the PNNL test apparatus is that the regenerators have thermocouples integrated into the dual regenerators which allows the axial temperature distribution in the bed to be measured. Knowing the temperature distribution allowed us to validate the model (Figure 4). The model informed us that one of the key features in the regenerators is the temperature profile and its impact on cooling power. The model showed and was consistent with the experimentally observed data that there was a dramatic change in the temperature profile between zero thermal load and a 50 W applied thermal load in the cold heat exchanger. For example, earlier assumption of regenerator performance was to assume the axial temperature profile moved up and down uniformly along the entire length of the regenerator. That is not what is observed both experimentally and numerically; the cold-end temperatures change much more rapidly than hot-end temperatures. The validated model was used to design an eight-layered regenerator.

Layered System Design and Model Simulation

The most efficient and easiest way to build a magnetocaloric system would be one where each stage is composed of a single material. However, if each stage had a separate high field magnet the capital cost of such a system would make it uneconomical. To lower the capital cost the materials are layered which decreases the balance of plant

TABLE 3. Bypass Operation Results in Significant Improvements in Performance and Reduction in Materials Required

	No Bypass	6% Bypass	% Improvement
Thermal load	4.3 kW	2.9 kW	32% reduction
Heat transfer fluid flow	31.3 L He/sec	3.8 L He/sec	87% reduction
Magnetic material required	184 kg	22.3 kg	88% reduction
Figure of Merit	0.4	>0.75	87% increase

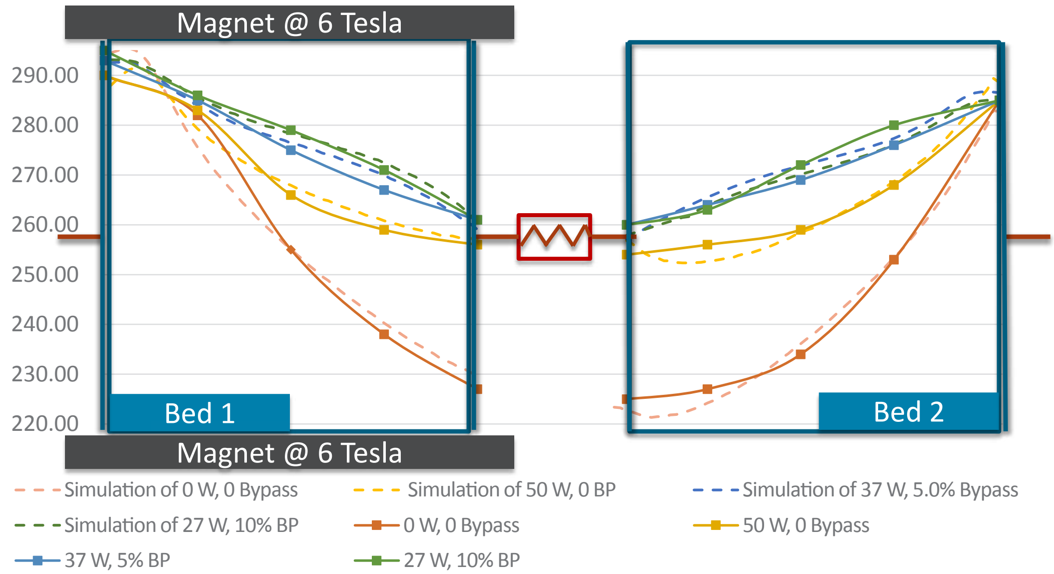

FIGURE 4. Experimental results show temperature profile changes in the regenerator and validate the numerical model

components and therefore the capital cost. In theory, multiple layers should perform equivalently as if each layer was in its own system. However, in practice this has not, to our knowledge, been achieved. We are proposing a new layering approach which we believe will overcome the limitations observed in the past. Our approach is based upon the hypothesis that each layer needs to be considered as its own refrigeration cycle. In this scenario, it results that each layer would have a different heat duty that it needs to account for. For example, layer "A" would have a heat duty of "a", layer "B" would have to reject heat from layer "A" in addition to its own heat duty, so the total heat duty for layer "B" would be "a + b". Similarly, layer "C" would need to accept the heat duty from the previous layers in addition to its own cooling heat duty, "c". Thus layer "C" would have a heat duty of "a+b+c". The implications of this hypothesis are that each layer would need to have different amounts of material and a different heat transfer fluid flow. Current designs do not vary either the material or flow. Using the validated model, we designed an eight-layer system that accounts for the varying enthalpy flow and associated differences in magnetic refrigerant material and heat transfer fluid flow as well as allowed for by-pass flow. Table 4 has the material amounts and heat duty for a device capable of pre-cooling gaseous hydrogen from 280 K to 120 K at a rate of 2.5 kg/d. Figure 5a shows the design and Figure 5b has the model results. Fluid flow was simulated using ANSYS/FLUENT and the header, footer, and packed bed design simulation showed the uniform flow. We have received the materials from Ames, assembled the dual regenerators and are in the process system testing. The results will be reported in the next report.

TABLE 4. Materials, Operating Temperature, and Heat Load for the Eight Layers in the Stage 1 System

Layer	Material	Average T_{HOT}/T_{COLD} (K)	Curie Temp (K)	Mass of Magnetic Material/Layer (grams)	Work Rate/Layer (W)	Q_{HOT} /Layer (W)
1	Gd	280/260	293	268	11.0	132
2	$Gd_{0.91}Y_{0.09}$	260/240	274	258	9.9	110
3	$Gd_{0.3}Tb_{0.7}$	240/220	253	235	8.8	90.7
4	$Gd_{0.69}Er_{0.31}$	220/200	232	202	7.6	71.9
5	$Gd_{0.32}Dy_{0.68}$	200/180	213	172	6.3	54.4
6	$Gd_{0.15}Dy_{0.85}$	180/160	193	139	4.9	38.4
7	$Gd_{0.27}Ho_{0.73}$	160/140	173	100	3.4	23.9
8	$Gd_{0.16}Ho_{0.84}$	140/120	153	57	1.8	11.0

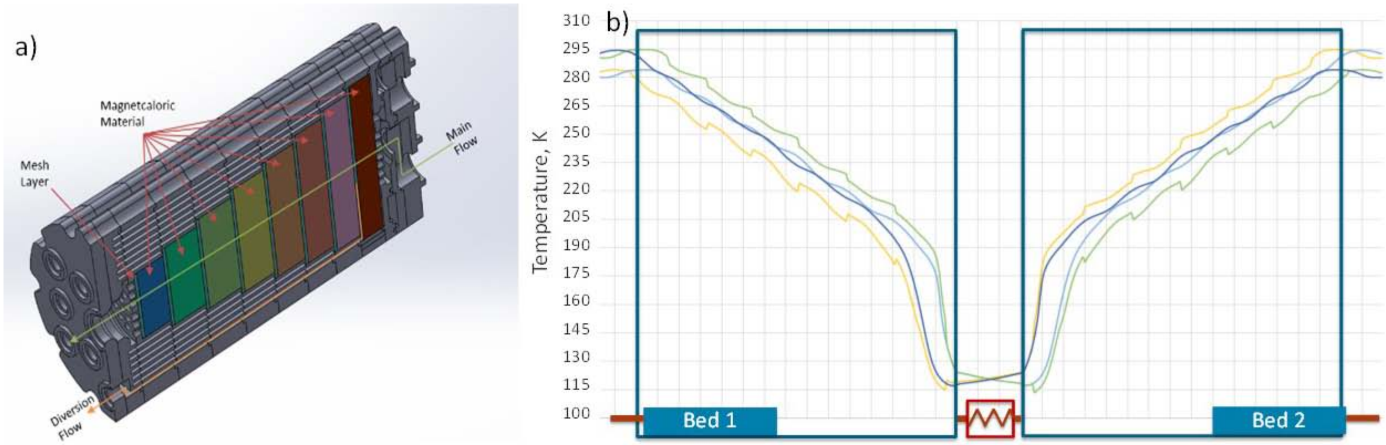

FIGURE 5. Eight-layer system design and simulation results showing the targeted temperature reduction

CONCLUSIONS AND UPCOMING ACTIVITIES

This project has made progress towards the ultimate goals of increasing the system efficiency while maintaining or decreasing the capital cost of hydrogen liquefaction technologies. In FY 2017 we have made progress along the critical path in that we have:

- Identified the 13 materials for a two-stage hydrogen liquefier.
- Characterized and synthesized the eight materials for the first stage.
- Updated the numerical simulation models with measured materials properties and validated the model against experimental data.
- Exercised the model to simulate a novel approach to multi-layered active magnetic regenerative refrigerator system.
- Assembled the fabricated components of the system.

Upcoming activities will include:

- Complete the Stage 1 testing.
- Use the lessons learned from Stage 1 to complete the design of the Stage 2 system.
- Characterize and synthesize the remaining materials for the second stage.
- Build and test the second stage.
- Complete techno-economic analysis.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Patent application: Active magnetic regenerative liquefier using process gas pre-cooling from bypass flow of heat transfer fluid (pending).

2. Patent application: Integrated fueling station (pending).

3. Patent application: Active magnetic regenerative processes and systems employing hydrogen heat transfer fluid (pending).

4. Patent application: Advanced multi-layer active magnetic regenerator systems and processes for magnetocaloric liquefaction (pending).

5. Patent application: Device for Production of Liquid Natural Gas with a 8-stage Active Magnetic Regenerative Liquefier (pending).

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Holladay, J.D., K.D. Meinhardt, E. Polikarpov, E.C. Thomsen, J.A. Barclay, J. Cui, I.E. Anderson, and B. Jensen. 2017. "Magnetocaloric Hydrogen Liquefaction." Presented at Hydrogen Delivery Technical Team Review, Chicago, IL, on March 29, 2017. PNNL-SA-124817.

2. Holladay, J.D., K.D. Meinhardt, E. Polikarpov, E.C. Thomsen, J. Cui, I.E. Anderson, and J.A. Barclay. 2017. "Magnetocaloric Hydrogen Liquefaction." Presented at MRS Spring 2017, Phoenix, AZ, (Invited Speaker) on April 19, 2017. PNNL-SA-125562.

3. Holladay, J.D., J.A. Barclay, K.D. Meinhardt, J. Cui, I.E. Anderson, B. Jensen, E.C. Thomsen, and E. Polikarpov. 2017. "Magnetocaloric Hydrogen Liquefaction." Presented at Fuel Cell Technologies Annual Merit Review, Washington, DC, on June 7, 2017. PNNL-SA-125603.

4. Archipley, C.C., J.A. Barclay, J.D. Holladay, K.D. Meinhardt, E. Polikarpov, and E.C. Thomsen. 2017; "Production of LNG with an Active Magnetic Regenerative Liquefier." Poster presented at the Cryogenic Engineering Conference/International Cryogenic Materials Conference on July 11, 2017 (abstract reviewed prior to acceptance). To be published as paper in cryogenics.

5. Teyber, R., J.D. Holladay, K.D. Meinhardt, E. Polikarpov, E.C. Thomsen, J.A. Barclay, and C.C. Archipley. 2017. "Design and Experimental Analysis of a Superconducting Active Magnetic Regenerative Refrigerator." Under development for paper in cryogenics.