Magnetocaloric Hydrogen Liquefaction

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Project Start Date: October 1, 2015
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

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

Fiscal Year (FY) 2018 Objectives

- Resolve regenerator design and assembly issues such as unexpected spike in thermal expansion coefficient for ferromagnetic rare-earth refrigerants near Curie temperature.
- Demonstrate controlled start-up, cool-down, and steady-state operation of a multilayered regenerator.
- Minimize force imbalance in a reciprocating dual magnetic regenerator design and reduce extra cooling required for flux-jump heat generation from internal current changes due to flux conservation in superconducting magnets during reciprocating AMR cycles.
- Complete detailed efficiency analysis of efficiency-reducing mechanisms within generic magnetic liquefiers to show the means to achieve an FOM >0.65.
- First achievement of 80 K temperature decrease with a four-layer AMR design starting at 280 K.
- Increase spherical particle yield to >85%, a 40% increase over the original design, in the upgraded rotating disk atomizer (RDA).

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.

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 AMR liquefaction cycle that avoids the use of gas compressors. Numerical simulation modeling of high-performance MCHL designs indicates certain achievable designs show promise for simultaneously lowering installed capital costs per unit capacity and increasing 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 (Table 1).

FY 2018 Accomplishments

- Achieved controlled start-up and operation of a four-layer AMR with cooling to ~200 K from room temperature (280 K).
- Reduced net force imbalance in reciprocating dual, multilayer regenerator prototype in ~6 Tesla (T) field changes from >1,000 lb to <100 lb.
- Used force balance to reduce changes in magnetic induction in reciprocating AMR prototype to sufficiently reduce internal heating in a 6-T persistent-mode superconducting magnet due to flux conservation so the existing cryocooler could keep the magnet at <5 K during steady-state operation.
- Improved RDA spherical particle yield by 42% to achieve a yield of spherical particles of 88% for gadolinium (Gd) sphere synthesis.
- FOM >0.7 predicted by detailed analysis for two-stage MCHL 30 tonne/day hydrogen liquefier.
- Identified a series of five magnetocaloric materials with tunable compositions ($Gd_xEr_{1-x}Al_2$ and $Dy_xEr_{1-x}Al_2$) with thermomagnetic characteristics for a 120 K to 20 K operation range to complement existing magnetocaloric materials for 280 K to 120 K operation.

Table 1. Pacific Northwest National Laboratory (PNNL) Magnetocaloric Hydrogen Liquefaction Technical Targets

30 tonne/day (Small Facility)	Claude Cycles (Current) [1]	PNNL's MCHL Targets	2020 DOE Target [1]
Efficiency	<40%	70~80%	N/A
FOM	<0.3 (small facility) 0.35~0.37 (large facility)	~0.6 (small facility) ~0.65 (large facility)	N/A
Operation and maintenance cost	4%	2.8%	–
Energy input	10–15 kWh/kg H_2	5~6 kWh/kg H_2	12 kWh/kg H_2

INTRODUCTION

MCHL technology promises cost-effective and efficient hydrogen liquefaction because it eliminates gas compressors—the largest source of inefficiency in traditional Claude cycle liquefiers—as well as 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 that use helium, hydrogen, or gas mixtures as 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 counterflow heat exchangers in which the cooling power is provided by turbo expansion of a portion of the precooled hydrogen stream. Liquefaction of the precooled, high-pressure hydrogen stream is finally accomplished by throttling 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 typically less than 0.3 for a smaller facility.

The current MCHL design is an AMR system that 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 (HTF). After the cold-to-hot HTF 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 (maintaining constant total entropy), and the temperature of the magnetic refrigerants decreases in the magnetic regenerators. During the subsequent hot-to-cold flow of the HTF at constant low magnetic field, the colder magnetic regenerator cools the HTF before it exits the regenerator and accepts heat from the thermal load, thereby cooling the hydrogen process stream. At the end of this flow, the AMR cycle is repeated at the operating frequency. A more complete description, including a simplified process flow diagram (PFD) and schematics, is found in the FY 2016 Annual Progress Report (APR).

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

APPROACH

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

1. Identify, synthesize, and characterize magnetocaloric materials.
2. Develop an approach to understand the magnitude of the thermomagnetic properties and how to utilize the second order phase transaction characteristic in many magnetocaloric materials to improve liquefier FOM while minimizing cost. The heat capacity below the second order phase transition in ferromagnetic refrigerants is ~10% larger at high magnetic fields than at low magnetic fields. We use this unique characteristic to enable the "bypass of a portion heat-transfer fluid operation" described in the FY 2016 APR as well as in the current report.
3. Investigate layered material operation to understand how temperature changes within the layers and coupled HTF flows through layers impact performance. This will include detailed simulation models using the materials properties measured as well as experiments.

4. Apply well-known catalysts to efficiently execute the ortho-para hydrogen conversion for liquefaction; this will include system design options to best integrate catalysts into compact, micro-channel process heat exchangers.
5. Demonstrate hydrogen liquefaction in an MCHL with appropriate ortho-para (o-p) hydrogen conversion catalysts integrated into the heat exchanger and continuously cooled by bypass heat transfer gas.

This project builds upon work first pioneered by Dr. John Barclay at Emerald Energy Northwest LLC. We have modified the design and updated the previously developed models. The approach is to develop and demonstrate a two-stage system that liquefies hydrogen starting at room temperature (Figure 1). 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 are used for the materials characterization using Ames Laboratory's (Ames) magnetic materials characterization capabilities. For use in the MCHL, the materials need to be spherical with diameters in the range of 150–250µm. We are using Ames' RDA, a tunable, low-cost material synthesis technique, to make kilogram batches of spheres with adjustable diameters from different compositions. The RDA-synthesized materials will be tested in PNNL's versatile, unique reciprocating dual regenerator research system. Details of the dual regenerator design and schematics as well as initial bypass operation are found in the FY 2016 APR.

(2) Bypass operation was tested and identified as a key to achieving high-performance operation with minimal materials (FY 2016 APR).

(3) The proprietary layered regenerator and system design efforts were pursued via modeling and experimental efforts. The materials properties were used in an advanced modeling subtask to understand the performance and improve the system design (FY 2017 APR). The model was validated against experimental data from PNNL's research system as reported in the FY 2017 APR. A second-generation dual regenerator design was developed to test the understanding of layering of different magnetic refrigerants coupled with bypass operation. Layered regenerators are not a new approach; however, expected performance with layered AMRs has not been previously achieved. We hypothesized the reason for this is that each layer needs to be considered as an individual magnetic Brayton cycle refrigerator coupled to adjacent refrigerators with different refrigerants. To accomplish this coupled design means the amount of materials required for each layer must be carefully determined and the corresponding HTF flow for each layer must simultaneously be varied. This hypothesis was tested in the second-generation multilayer design constrained to operate using several of the subsystems from the initial test apparatus. During testing of the new design in FY 2017, challenges regarding magnetic force imbalance, resultant additional heating in the superconducting (s/c) magnet due to flux conservation in persistent-mode s/c magnets, and the need for increased HTF control during start-up, cool-down, and steady-state operation were identified. These challenges were solved in FY 2018 and are reported here.

(4 and 5) Based on the results of the previous work from 280 K to 120 K, the MCHL stage operating between 120 K and 20 K will be designed and built. It will include integration of o-p catalysts into compact, high-performance hydrogen process heat exchangers for the lower-temperature MCHL stage for actual liquefaction tests to be done. This integration and research will be part of the future work on this project. Finally, a more detailed techno-economic analysis update was done to indicate progress against the DOE's efficiency and cost performance targets. An initial techno-economic analysis was reported in FY 2016; this one was done in much more detail using lessons learned and new results from experiments. A detailed FOM analysis was completed in FY 2018.

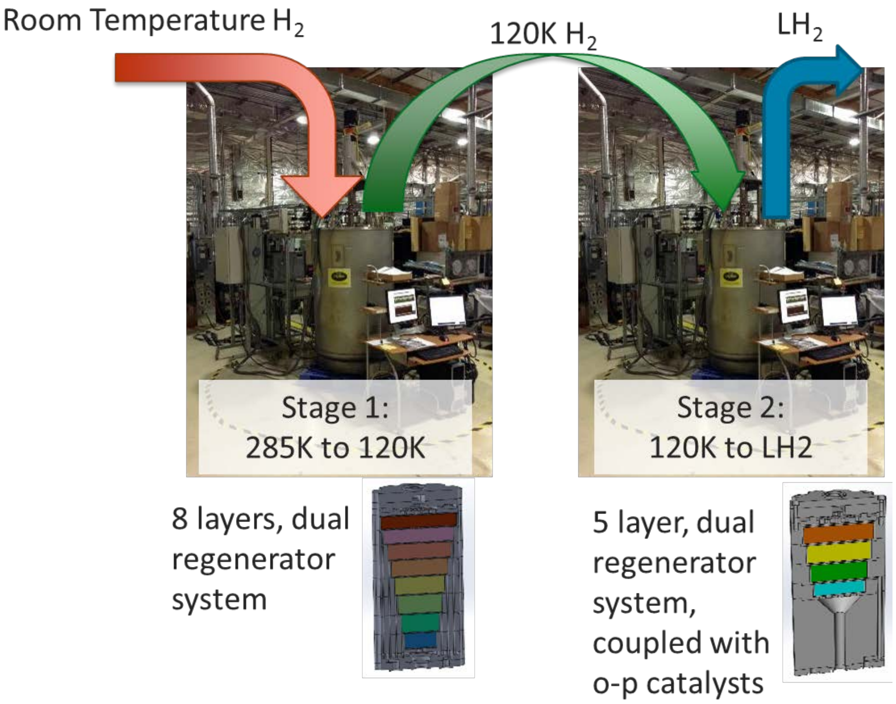

Figure 1. Two-stage, multilayer regenerator, reciprocating magnetocaloric system concept

RESULTS

Minimization of Force Imbalance and Improved Flux Conservation Achieved for Proper Operation

During the MCHL system operation in FY 2017, a net force from the two opposing attractive forces of the magnetic refrigerants toward the center of the high-field, solenoidal magnet occurred as the regenerators move into and out of the magnetic field. In the absence of refrigeration, the dual regenerators at the same temperature and an appropriate distance apart should experience almost the same magnitude force but in opposite directions so the net large compressive forces between the two regenerators should almost cancel each other. In an AMR refrigerator, the average temperature of one regenerator will be several K lower than the other regenerator as they enter and leave the high field region of the cycle. The different temperatures cause a different magnetization entering and leaving the high magnetic field region, which creates a net force imbalance. This is inherent in reciprocating designs because the magnetic work for the AMR cycle is input in this manner into the refrigerator. This additional power is provided by an axial linear drive mechanism in MCHL operation.

However, this AMR cycle force imbalance is magnified in reality because dual magnetic regenerators are separated "lumped" sources of magnetization that must go through the axial magnetic induction (B) gradients that are offset axially entering and leaving a solenoidal magnet. The net magnetic force increases accordingly to several hundreds or even a thousand pounds.

The second effect of different lumped magnetization moving in and out of a persistent-mode superconducting magnet (a constant magnetic flux device) is an increase or decrease in free current field (H) to keep B constant during the AMR cycle. This detrimental change in H causes heating due to flux-jumping as currents change in the s/c magnet. Therefore, a change in the magnetization of the material being moved in and out of the magnetic field is compensated by changing the magnetic field strength H generated by the circulating electric current in the s/c magnet. These changes in the electric current cause the magnet to heat up due to Joule heating and—if the magnet heats up too much—it will quench (at ~5.8 K on the solenoid). During operation in FY 2017, a substantial force imbalance, at times in exceeding 1000 lb_f, was measured. This limited the s/c magnet operation to ~3 T and cycle frequency to ~0.25 Hz. During FY 2018, we developed a generic optimization program to design an addition of shaped pieces of Fe between, above, and below the dual regenerators. The model indicated that if the right mass of Fe of the correct shape was placed in the correct location, the force imbalance could be minimized to less than 50 lb_f [2]. Due to space constraints within the existing magnetic refrigerator prototype, the ideal shape and placement could only be approximated, but the force imbalance was decreased to less than 100 lb_f (a 90% reduction) and, more importantly, the flux-jump heating in the solenoid was sufficiently reduced to enable the cryocooler to keep the magnet below ~5 K even when operating at 6 T and 0.25 Hz.

200 K Temperature Achieved with Innovative HTF Control

Improved HTF flow in the regenerators was achieved by using PNNL-designed and built controllable pneumatic diversion-flow valves to enable control of helium heat transfer gas through each layer as required for proper cool-down and at steady-state operation. (There were no commercially available pneumatic valves that met design requirements.) Several previous attempts by several different groups have been unable to cool to below the Curie temperature of the colder layers of magnetic material. We experienced this result in our initial multilayer magnetic regenerator prototype. After installing compact controllable diversion-flow valves between each set of layers of refrigerants, we were able to use these diversion-flow valves to achieve a start-up from room temperature to steady-state operation with temperature spans for each layer that are below their respective Curie temperatures (293 K, 274 K, 253 K, and 235 K). For start-up, the valves control the flow so that each layer is sequentially cooled down below its respective Curie temperature before the heat transfer gas is adjusted to that required for steady-state operation. During operation, the valves allowed HTF flow control to optimize the temperature distribution in the regenerator (Figure 2), which in turn would increase the efficiency.

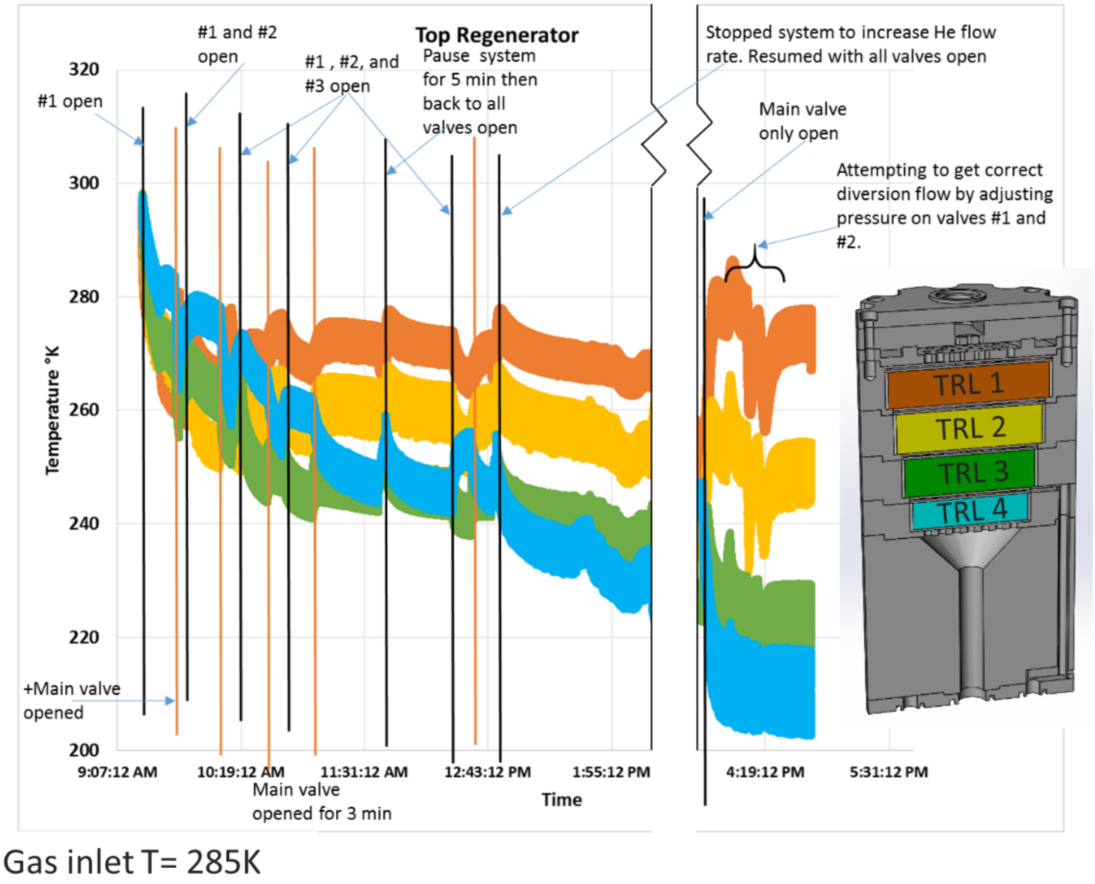

Figure 2. Regenerator temperature profile using adjustable valves to achieve ~200 K

RDA Upgrades Improved Yield of Gd Spherical Particles (150–250 µm) to 88%, a 42% Improvement

Ames' RDA was originally designed for more easily quenched materials, leaving it undersized for the current task of producing rare earth powders, leaving cooling times too small, and allowing flake formation. However, the system for magnetocaloric materials worked, but the yield of spherical material in the desired size range was lower than expected. Recent system upgrades were made to add consistency between runs and improve the quality of powder. The major upgrade was increasing the quench drum diameter by nearly 40% from 12 to 16.5 in. This increases the flight path and cooling time of the droplets, reducing flakes and extending the range of useful disc speeds and superheats. An atomization of pure Gd using the pre-upgraded system was rerun in the upgraded system using identical superheat and disc speed to assess the upgrade. Quantitatively, data gathered from the flake removal process show powder in the desired size range (150–250 µm) is 38% flake in the pre-upgraded system, while the upgraded system reduced the flake to 12% (Figure 3). This is a 42% increase in spherical particles and a spherical particle yield of 88%. Therefore, the upgrade to the RDA has proven effective in improving the quality of the produced powders. We anticipate similar improvement for other alloys.

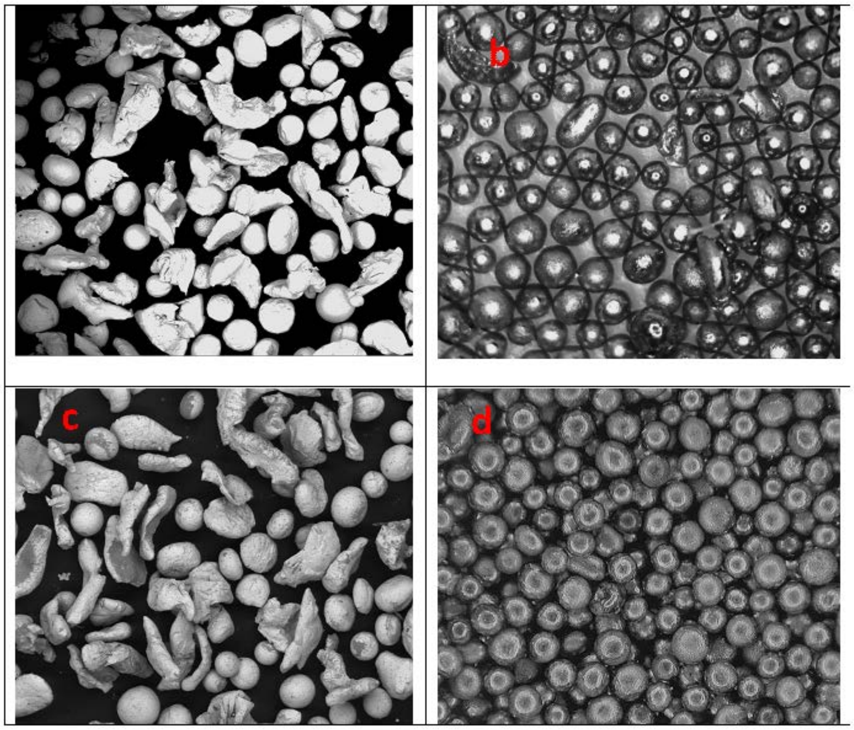

Figure 3. Comparison of 150–250 µm Gd powders produced by the RDA (a) pre-upgrade with flake, (b) post-upgrade with flake, (c) pre-upgrade flake removed, and (d) post-upgrade flake removed

FOM Analysis Shows 0.7 Is Feasible

Finally, a detailed FOM analysis for a 30 tonne H_2/day magnetocaloric-based liquefier was completed. To do the analysis, a PFD was produced for a combination of two modules of quad-regenerator reciprocating refrigerators: one module operating from 280 K to 120 K, in series with the second module operating from 120 K to 20 K. Each quad consisted of two sets of reciprocating dual regenerators with a 90 phase difference in their respective drive actuators and with synchronized 3-way valve control of the flow of HTF through the process heat exchanger to provide continuous cooling to the incoming gaseous hydrogen at 300 psia. The warmer module used liquid propane as the HTF and eight different magnetic refrigerants, each spanning 20 K. The colder module used helium gas at ~800 psia as the HTF and five different magnetic refrigerants, each spanning 20 K (Figure 4). The PFD was used to identify all the mechanisms of the system that contribute to the thermodynamic efficiency. We then calculated the ideal work rate, real work rates, and the resultant FOM for all major sources of inefficiency. The MCHL used 13 refrigerants in two modules to enable bypass flow to continuously cool the 300-psi hydrogen process stream from 280 K to 20 K. The MCHL operated at 1 Hz and 6 T. The real work rate included Carnot work rate/layer; estimates of the parasitic heat leak; cold work sources (e.g., 2nd stage He circulator as part of the HTF); external work input from cryocooler compressor for the s/c; reciprocating drives for the regenerators; HTF pumps; and internal irreversible entropy such as heat transfer between the HTF and magnetic materials, friction within HTF flow with pressure drop, longitudinal thermal conduction in the HTF with mixing effects, and eddy current heating from time-dependent magnetic field as regenerators reciprocate. Table 2 contains the estimated values and the calculated FOM of 0.7.

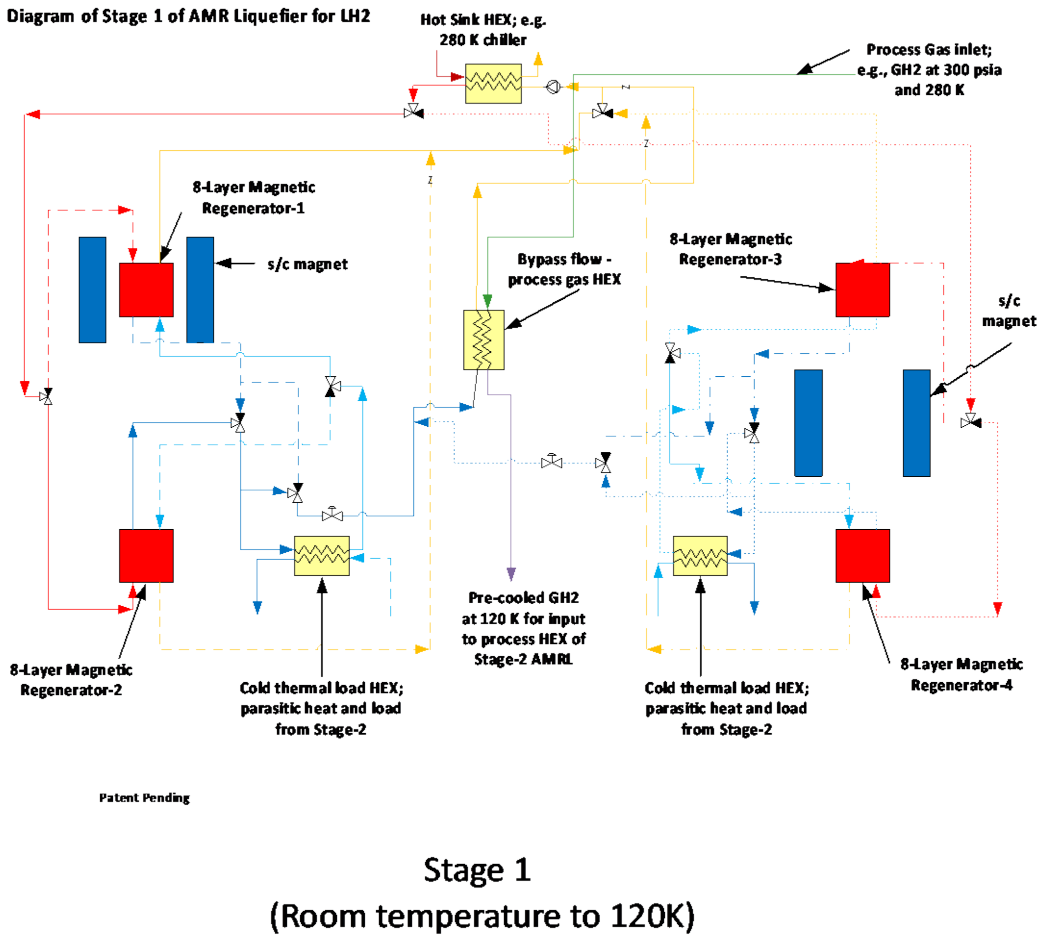

Figure 4. PFD of Stage 1 and Stage 2 of AMR for hydrogen liquefaction

HEX – heat exchanger

Table 2. Inputs for FOM Calculation

	Work Range (kW)
Carnot work for 2-stage, 13-layer device (with bypass flow but without irreversible entropy in regenerators)	2,649
Internal irreversible entropy sources in regenerators	1,075
Parasitic heat leak + cold work sources (e.g., 2nd stage He circulator @ 50% efficiency)	0.6+1.9
Reciprocating drives for regenerators (@ 90% efficiency)	372
HTF pumps at room temperature (@ 50% efficiency)	4.1
Cryocooler compressor power (2 each for 30 tonne/day)	16
Total real work	4,119
Total ideal work	2,996
$\boldsymbol{FOM} = \frac{\dot{\boldsymbol{W}}_{\boldsymbol{Ideal}}}{\dot{\boldsymbol{W}}_{\boldsymbol{Real}}}$	0.73

CONCLUSIONS AND UPCOMING ACTIVITIES

This project has made progress toward the ultimate goals of increasing the system efficiency while maintaining or decreasing the capital cost of hydrogen liquefaction technologies. In FY 2018, we made progress along the critical path in that we:

1. Were the first to achieve cool-down and steady-state operation of a 4-layer dual AMR refrigerator with a temperature decrease to 200 K from 280 K
2. Completed a detailed FOM analysis resulting in a projected FOM of >0.7 for a 30 tonne H_2/day system
3. Developed novel small pneumatic-controlled valves compatible with the cryogenic conditions and effective operation in a high magnetic field
4. Demonstrated controllable diversion flow of HTF in the layered regenerators using the PNNL-developed valves
5. Developed properly shaped and positioned high-permeability materials that—when integrated into the dual regenerator system—reduce the magnetic force imbalance significantly by reducing changes in B required to satisfy flux conservation in s/c solenoids without excessive Joule heating in the magnet
6. Upgraded the RDA to improve the spherical shaped material yield to 88%
7. Identified a good series of tunable magnetic refrigerants for 120 K to 20 K operation with projected thermomagnetic performance for high-performance regenerators.

Upcoming activities will include:

- Demonstrate the stage 1 operation to achieve a temperature of 120 K from 280 K
- Use the lessons learned from stage 1 to complete the design of the stage 2 system operating from 120 K to 20 K
- Characterize and synthesize the remaining materials for the second stage
- Build and test the second stage
- Update techno-economic analysis prepared in Q4 FY18.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Non-Provisional U.S. Patent Application: Production of Liquid Natural Gas and Other Cryogens Using a Multi-Stage Active Magnetic Regenerative Liquefier. Application date 7/2018.
2. Non-Provisional U.S. Patent Application: Active Magnetic Regenerative Processes and Systems Employing Hydrogen as Heat Transfer Fluid and Process Gas. Application date 7/2018.
3. Non-Provisional U.S. Patent Application: Advanced Multi-Layer Active Magnetic Regenerator Systems and Processes for Magnetocaloric Liquefaction. Application date 3/2018.
4. Foreign Patent Application: Active Magnetic Regenerative Processes and Systems Employing Hydrogen as Heat Transfer Fluid and Process Gas. Application date 3/2018.
5. Foreign Patent Application: Advanced Multi-Layer Active Magnetic Regenerator Systems and Processes for Magnetocaloric Liquefaction. Application date 3/2018.

FY 2018 PUBLICATIONS/PRESENTATIONS

Publications

1. J.D. Holladay, R.P. Teyber, K.D. Meinhardt, E. Polikarpov, E.C. Thomsen, C. Archipley, J. Cui, et al. "Investigation of Bypass Fluid Flow in an Active Magnetic Regenerative Liquefier." *Cryogenics* 93 (2018); doi:10.1016/j.cryogenics.2018.05.010.
2. R.P. Teyber, K.D. Meinhardt, E.C. Thomsen, E. Polikarpov, J. Cui, A. Rowe, J.D. Holladay, et al. "Passive Force Balancing of an Active Magnetic Regenerative Liquefier." *Journal of Magnetism and Magnetic Materials* 451 (2018); doi:10.1016/j.jmmm.2017.11.002.
3. J.A. Barclay, K.P. Brooks, J. Cui, J.D. Holladay, K.D. Meinhardt, E. Polikarpov, and E.C. Thomsen. "Propane Liquefaction with an Active Magnetic Regenerative Liquefier." *Cryogenics* (Submitted and in Review 2018).
4. R.P. Teyber, J.D. Holladay, K.D. Meinhardt, E. Polikarpov, E.C. Thomsen, J. Cui, et al. "Performance investigation of a high-field active magnetic regenerator." *Applied Energy* (Submitted and in Review 2018).

Presentations

1. J.D. Holladay, K.D. Meinhardt, E.C. Thomsen, E. Polikarpov, J.A. Barclay, J. Cui, and I.E. Anderson. "MagnetoCaloric Gas Liquefaction: A New High-Efficiency, Low-Cost Gas Liquefaction Technology." Presented by Jamie D. Holladay at Hydrogen and Fuel Cells Working Group, December 8, 2017.
2. J.D. Holladay, K.D. Meinhardt, E.C. Thomsen, E. Polikarpov, J.A. Barclay, C. Archipley, J. Cui, I.E. Anderson, and S. Wolf. "MagnetoCaloric Hydrogen Liquefaction." Presented by Jamie D. Holladay at the DOE Hydrogen and Fuel Cells Program Annual Merit Review, Washington, DC, June 2018.

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2. R.P. Teyber, K.D. Meinhardt, E.C. Thomsen, E. Polikarpov, J. Cui, A. Rowe, J.D. Holladay, et al. "Passive Force Balancing of an Active Magnetic Regenerative Liquefier." *Journal of Magnetism and Magnetic Materials* 451 (2018); doi:10.1016/j.jmmm.2017.11.002.