III.14 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 system
- Demonstrate a lab-scale hydrogen liquefier with a figure of merit (FOM) increase from 0.3 up to 0.5
- Perform technoeconomic analysis on a proposed full-scale (30 tons per day) system

Fiscal Year (FY) 2015 Objectives

- Obtain, refurbish, assemble, and successfully operate the first generation (GEN I) system
- Characterize the performance of the GEN I system using dual Gd regenerators by measuring the maximum temperature differential with heat sink temperature at ~285 K and no external load, with the heat sink temperature held constant at ~285 K, and measure cold temperature as a function of applied thermal load
- Demonstrate multi-layer operation and characterize the temperature distribution through the layered regenerator
- Design a second generation (GEN II) system to take advantage of new configurations and multi-layer design and incorporate several other lessons learned from GEN I operation

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. Results from experimental prototypes should support the design and deployment of hydrogen liquefier plants that meet the DOE hydrogen production and delivery targets.

- Delivery cost of liquid hydrogen (LH_2) at <$2.00/kg
- $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 2015 Accomplishments

- Successfully completed acquisition, refurbishment, assembly, and test of the GEN I prototype with the cooled solenoidal superconducting magnet, dual Gd magnetic regenerators, two electromechanical actuator drives, and the heat transfer fluid subsystems of our reciprocating active magnetic regenerative refrigerator MCHL prototype

- Mechanically and electrically integrated all eight subsystems of our first MCHL prototype into an operational system interfaced to the LabVIEW data acquisition and control program
- Experimentally demonstrated the first cooling curves of our MCHL and began to measure its performance under a variety of different operational parameters such as hot heat sink temperature, cycle frequency, magnetic field strength, heat transfer fluid flow rate, and cooling capability as a function of cold temperature; achieved maximum temperature span of approximately 317 K to 217 K ($\Delta T = 100$ K) with a Gd at 3T net applied magnetic field change
- Demonstrated 40 W external cooling power with ~20 K approach temperature, a heat sink at ~286 K, a cold load temperature of ~266 K and using a Gd regenerator in a 3T field
- Demonstrated a novel configuration that increased the cooling power by 20% without changing the amount of magnetic material required
- Began to incorporate lessons learned from the first prototype into the design of the MCHL GEN II prototype with a rotary configuration with the objective to span from approximately 280 K to 20 K and produce LH_2 with an FOM of ~0.5

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INTRODUCTION

MCHL technology promises cost effective and efficient hydrogen liquefaction because it eliminates compressors, the largest source of inefficiency in the traditional Claude cycle liquefiers, and the need for liquid nitrogen to precool the hydrogen. The Claude cycle liquefier is the current industrial hydrogen liquefaction and uses a variety of processes with helium, hydrogen, or gas mixtures as coolant. The hydrogen feed to the process is first cooled by liquid nitrogen, and then further cooled in multistage heat exchangers where the cooling power is provided by turbo expanders. Liquefaction is finally accomplished by throttling in a Joule-Thomson valve. Conventional liquefier technology for hydrogen is limited to an FOM of ~0.35 for a large facility, and is typically less than 0.3 for a smaller facility.

The MCHL uses an AMR system which uses an alternating magnetic field and magnetocaloric materials to transfer heat between reservoirs. 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 regenerators to increase in temperature to compensate for the increased 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 a decreased regenerator temperature because order among the magnetic moments of the magnetic materials decreases. During a hot-to-cold flow of the heat transfer fluid at constant low magnetic field, the colder magnetic regenerator accepts heat from the thermal load from cooling the hydrogen process stream. The active magnetic regenerative cycle is repeated again at the operating frequency. The principle of operation is shown in Figure 1. The proposed MCHL project uses magnetocaloric refrigeration to achieve an efficient thermodynamic liquefaction cycle. Detailed modeling of the MCHL technology indicates it has the potential to simultaneously lower the 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 to better understand the temperature distribution in the regenerators. A simplified process flow diagram (PFD) of the GEN I unit and the schematic of the GEN I prototype are in Figures 2 and 3, respectively. 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 will be developed.

The GEN II will use a rotary regenerator design, which promises to balance the magnetic force for maximum work recovery. Its continuous magnetic material rotation becomes a constant magnetic flux device, which reduces induced flux jumps which occur in a persistent mode magnet during reciprocating motion of dual magnetic regenerators. The rotary MCHL is an advanced concept. In consideration of the likelihood of encountering unforeseeable technical challenges and due to 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. A block diagram of the process flow for the rotary design is in Figure 4. 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.

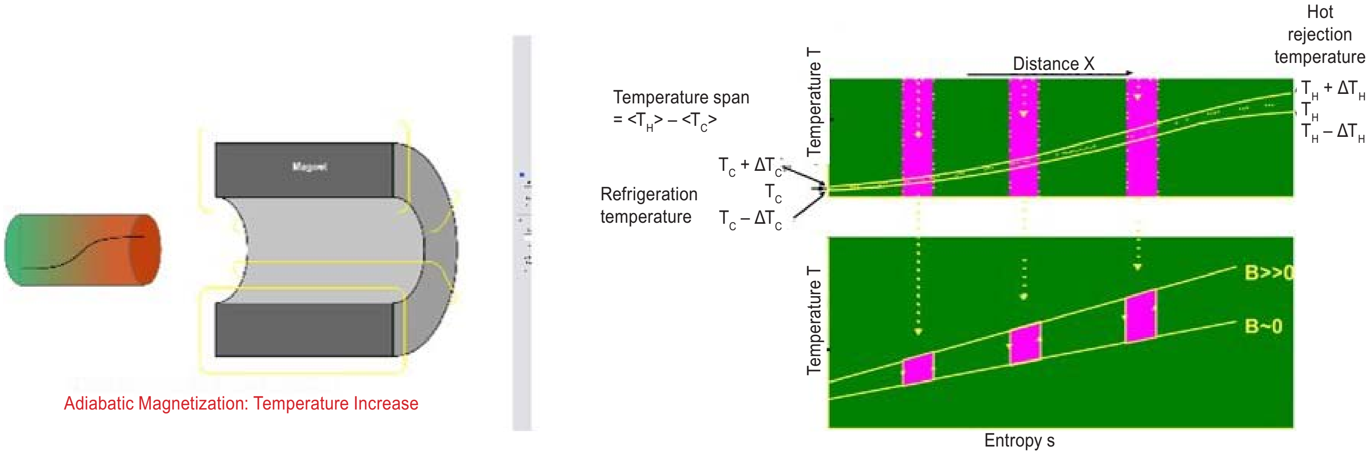
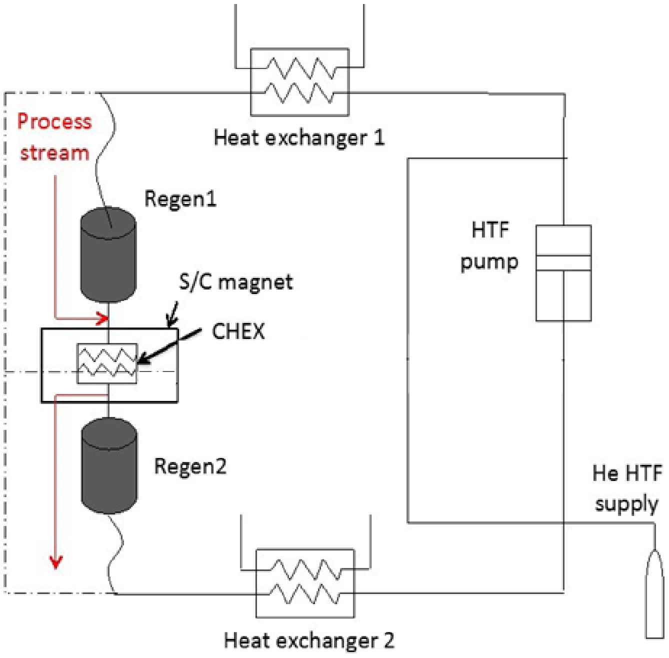


FIGURE 1. Active magnetic regenerative liquefier principle of operation



CHEX – cold heat exchanger; HTF – heat transfer fluid

FIGURE 2. Simplified PFD diagram of GEN I

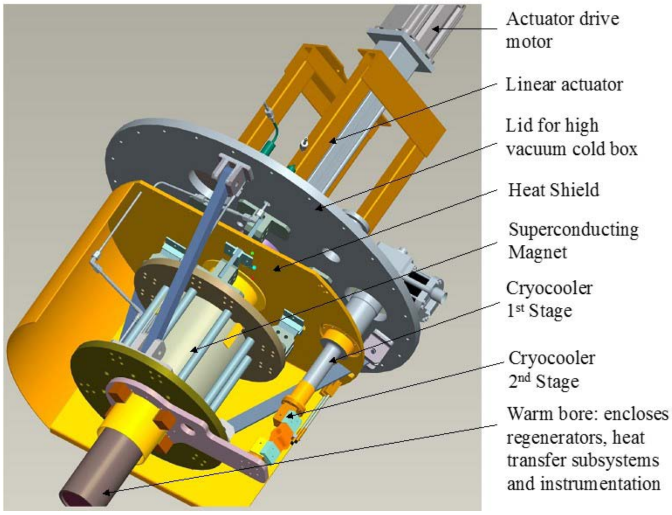
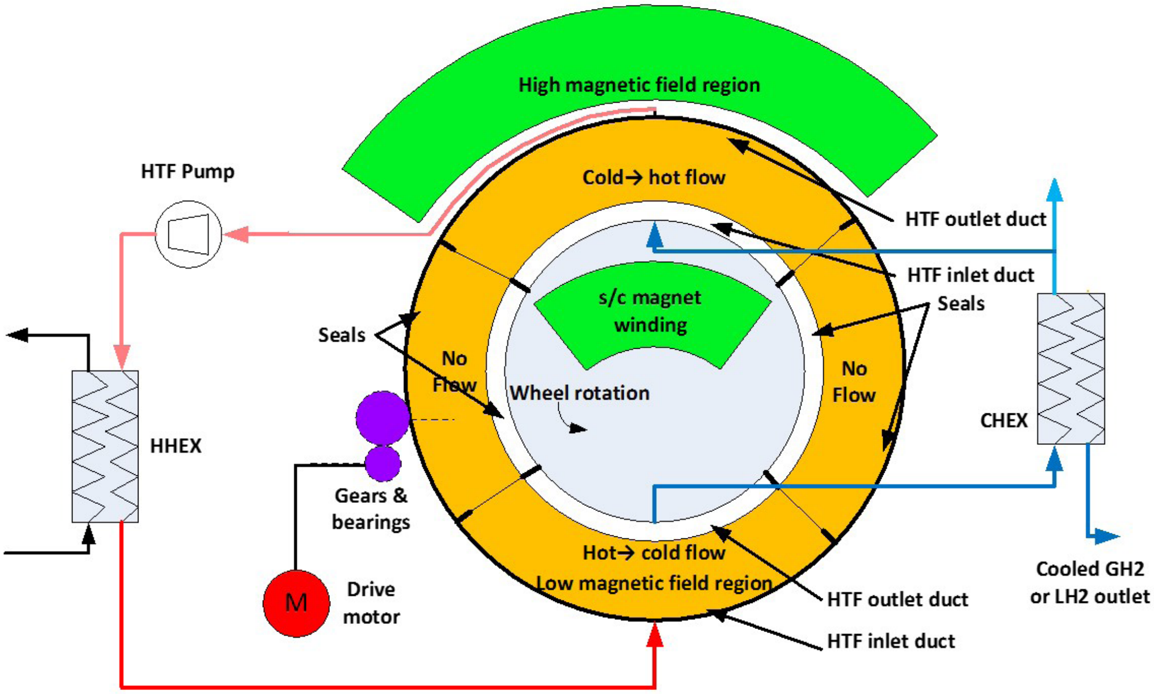


FIGURE 3. Schematic of the GEN-I prototype

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 (third generation [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.

RESULTS

PNNL successfully received and installed the GEN I unit from Prometheus Energy Group Inc, with guidance from EENW. Updates to the system cooling, electronics, sensors,



HHEX – hot heat exchanger

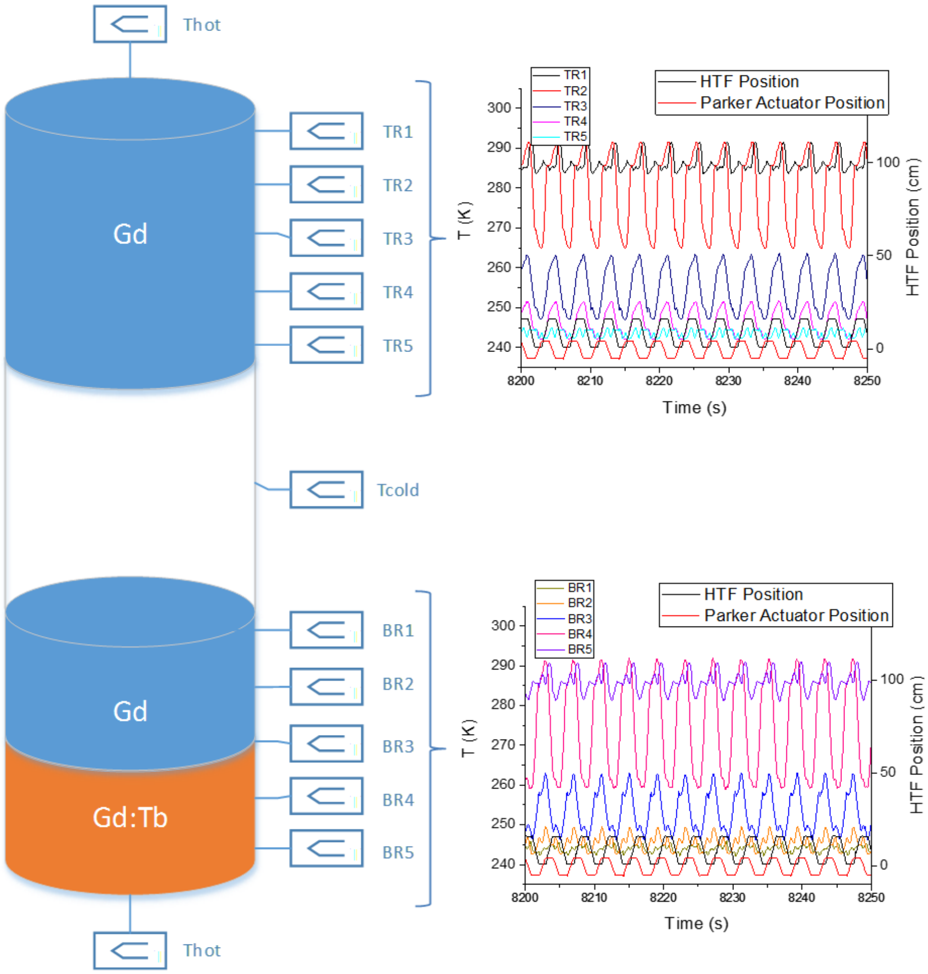
FIGURE 4. A block process flow diagram of the rotary magnetic wheel design

and controls were completed. The GEN I prototype used reciprocating dual magnetic regenerators in an AMR cycle (Figure 2). As indicated in an instance in the AMR cycle by the simplified PFD in Figure 3, the top regenerator is out of the high magnetic field and cooled by the magnetocaloric effect. When the bottom regenerator is in the high magnetic field, it is warmed by magnetocaloric effect. While the regenerators are stationary, helium gas at 200 psia from the double acting reciprocating piston pump flows through the chiller heat exchanger and into the top regenerator where it is cooled from ~T_{HOT} to ~T_{COLD}-ΔT_{COLD} as it flows into the CHEX. In the CHEX it picks up a thermal load from a process stream in a liquefier. The remaining portion of the cold helium gas picks up a thermal load in the CHEX and flows through the bottom regenerator where it is warmed to several degrees above T_{HOT} and returns to the helium pump. A programmable chiller is the thermal sink and cools the helium gas to a desired T_{HOT}. Once the flow segment of the AMR cycle in this snap shot is finished, the helium pump is stopped, Regen2 (bottom regenerator) is moved out of the magnetic field and Regen1 (top regenerator) is moved into the high magnetic field region by the drive actuator. After this magnetization/demagnetization segment of the cycle is completed, the helium flow is reversed and so on. A maximum cycle frequency in GEN I is about 0.5 Hz for all four steps in a complete AMR cycle. The dual regenerators are moved by a linear drive actuator in or out of the superconducting magnet along a programmable trapezoidal shaped motion vs. time curve. PNNL's first tests of GEN I were at 3T magnetic field with 1 kg of Gd spherical particles (~150 µm in diameter) in each dual regenerator. The cycle period was 4 s. The helium pump drive with a 20 cm maximum displacement The chiller kept the average temperature T_{HOT} at the warm end of each magnetic regenerator at ~285 K. With these conditions an average cold temperature measured in the CHEX with no external load (only parasitic heat load) was ~225 K. When T_{HOT} was increased to ~312 K, the maximum cold temperature was ~213 K, i.e., essentially 100 K. These temperature spans of 60 K and ~100 K with a single Gd refrigerant for these test parameters surpasses Prometheus's initial result and others in the literature [1].

The cooling power was assessed by applying varying external thermal loads to the CHEX and measuring the CHEX temperature up to 20 K of the T_{HOT}, i.e., 266 K. The load was applied via an installed heater which allowed accurate measurements. The maximum external load under these conditions was 40 W. The parasitic heat leak in this test configuration for GEN I is ~18 W.

We have developed a novel configuration for which we are in the process of submitting a patent application, so we cannot disclose the details. However, the results of the design increased the cooling power by 20% to ~48 W.

Finally, fabrication and tests with a two-layer magnetic material regenerator in the GEN I system were successfully completed. The only quickly available suitable magnetic refrigerant as ~250 micron spheres we could obtain was $Gd_{0.74}Tb_{0.26}$. This homogeneous rare earth alloy has a Curie temperature of 274 K. We designed and fabricated a new monolithic, layered regenerator comprised of ~108 g of Gd spheres and ~107 g of $Gd_{0.74}Tb_{0.26}$ spheres. A dual regenerator of the same size (~215 g) of only Gd spheres was also fabricated into a monolithic regenerator to compare performance at the same conditions. These two regenerators were assembled into the dual AMR subsystem for GEN I with novel hermetic seals at 200 psia. These new regenerators each had five Type E micro-thermocouples embedded along the central axis of the regenerators to measure temperatures of the magnetic refrigerant and the helium heat transfer gas during the entire four-step AMR cycle. Three different experiments with the layered regenerator provided excellent results. For example, even though the mass of the new Gd and Gd/Tb regenerators was only 215 g each compared to ~1,050 g each for the original Gd regenerators, the temperature span obtained was 43 K with T_{HOT} ~286 K with three quarters of the helium heat transfer gas flow rate. The external load cooling power into the CHEX was ~28.4 W with T_{HOT} at ~285 K and T_{COLD} at ~265 K. (Please note that the parasitic heat leak was the same for the 215 g regenerator as the 1 kg regenerator.) This shows that our improved regenerator design with the layered regenerator operating provided 71% of the cooling power of the original Gd regenerators with only ~20% of the mass of magnetic refrigerant. The improvement in total cooling power due to the novel configuration was ~25% compared to without it. Perhaps the most important result was confirmation that the axial temperature profile from hot to cold in the layered regenerator is nonlinear (Figure 5). To our knowledge, this is the first time the nonlinearity of the temperature distribution has been measured.



Layered regenerator with the TCs schematic

Detailed temperature profiles inside the regenerators

FIGURE 5. Dual regenerator with thermocouple (TC) locations and temperature profiles

CONCLUSIONS AND FUTURE DIRECTIONS

- Successful demonstration of the GEN I system showed the following.
  - A 100 K temperature span was demonstrated.
  - Cooling power of 40 W was demonstrated under optimum efficiency conditions.
  - A novel configuration was demonstrated with the potential of a 20% improvement in cooling power.
  - A multi-layer magnetic material regenerator was demonstrated.
- GEN II system preliminary design takes advantage of these discoveries and other lessons learned from GEN I.
  - It includes a rotary system to improve efficiency, decrease size, and enable other operational improvements.
- Techno-economic analysis is underway.

FY 2016 Work

- GEN I system
  - Magnetic refrigerants specified for GEN II preparation, characterization, and fabrication will be done to validate the performance of materials required for the GEN II system and to test potential new second order magnetic refrigerants provided by Ames.
- GEN II system prototype
  - Single wheel design
    - The rotary design will be proven out.
    - Seals are a major concern and will be an early focus area of the FY 2016 work.
  - A complete PFD and process and instrumentation diagram for each subsystem will be developed, components procured, and each subsystem completed.
- Magnetic materials
  - The shape and size of the magnetic material impacts the performance of the regenerator. Ames will provide tested magnetic refrigerants for this system.

REFERENCES

1. A. Tura, J. Roszmann, J. Dikeos, and A. Rowe, "Cryogenic AMR Test Apparatus," Advances in Cryogenic Engineering, 51, 985–992 (2006).