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MagnetoCaloric Hydrogen Liquefaction

PI: John Barclay
Team: Kerry Meinhardt, Corey Archipley, Greg Whyatt, Evgueni Polikarpov, Ed Thomsen, Jamie Holladay
AMES: Jun Cui, Iver Anderson, Sam Wolf

Pacific Northwest National Laboratory

2020 Doe Annual Merit Review
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Project Id # IN004

Overview

Timeline:

- Project Start Date: 10/1/2015
- Project End Date: 9/30/2020*

*Project continuation and direction determined annually by DOE

Budget:

- FY20 Planned DOE funding: $850k
  - includes $150k for partners
- Total DOE funds received to date: $3.85MM

Barriers addressed:

- High-Cost, Low-Energy Efficiency of Hydrogen Liquefaction

Partners:

- AMES / Iowa State Univ.

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Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

Relevance: We aspire to increase figure of merit, reduce system cost, and meet DOE targets

Project Objectives:

1) Demonstrate magnetocaloric liquefier stage from ~100 K to ~20 K for the first time
2) Demonstrate first H_2 liquefaction of ~1 kg/day with an active magnetic regenerative liquefier at a projected FOM >0.5*
3) Identify scaling pathway to installed capital cost < $70MM for 30 tonne/day

30 tonne/day (small facility)	**Claude cycles (current)**	**PNNL's MCHL project (AMR cycle)**	**DOE Target (2017)[1]**
FOM (a measure of liquefier efficiency)	<0.3 (small facility) 0.35~0.37 (others)	***~0.6 (small facility)***** ***~0.65 (large facility)***	0.5
Installed Capital cost	$70 MM[1]	***$49 MM***	<$70 MM
Annual O&M cost	4% of installed $	***2.8% of installed $***	?
Energy input	10-15[1] kWh/kg H_2	***6-7 kWh/kg H_2***	12 kWh/kg H_2

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[1] DOE, *Multi-Year Research, Development and Demonstration Plan, 2015*

* *Excludes heat transfer fluid pump power and cryocooler compressor power*

** *Installed turn-key system*

$$FOM = \frac{\dot{W}_{Ideal}}{\dot{W}_{Real}}$$

$$\dot{W}_{Real} = \dot{Q}_C\left(\frac{T_H}{T_C} - 1\right) + \frac{T_H \int_{T_C}^{T_H} \Delta S_{IRR}\, dT}{\int_{T_C}^{T_H} dT}$$

Relevance: Technology innovation and cost reduction for LH_2 from source to end-users

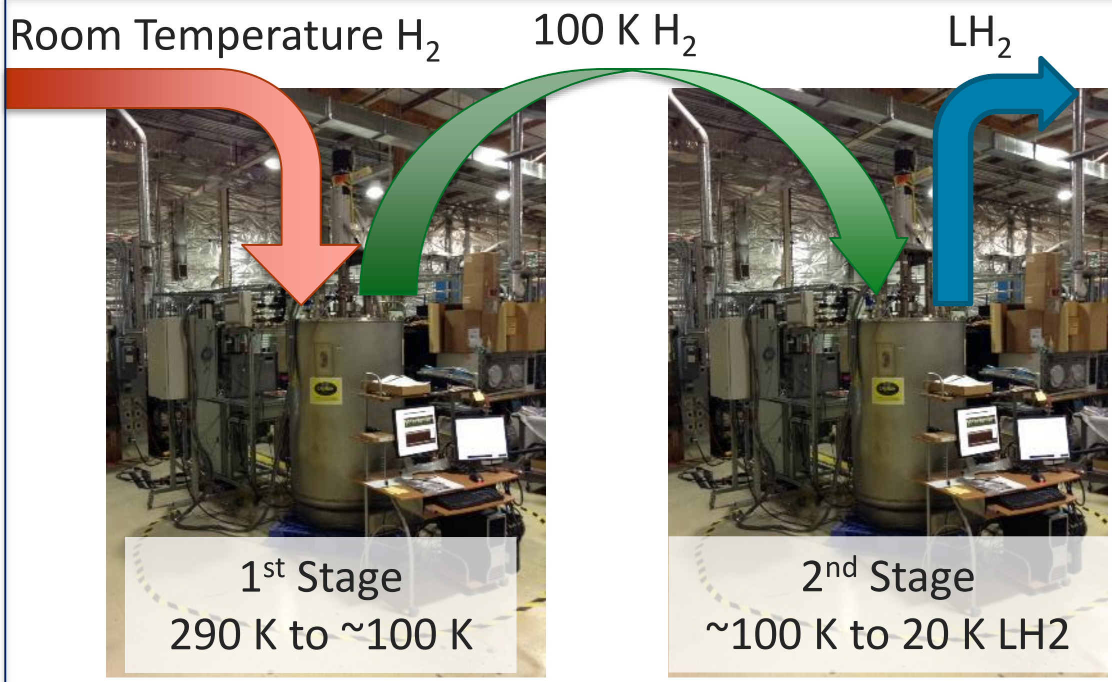
- Objective: Demonstrate increased liquefier FOM to reduce dispensed costs for **LH_2**
- Global energy demand projected to double by ~2050
  - Fuel choices will be driven by economics and environmental compatibility
- GH_2 and NG are used at low pressures
  - Local & on-board storage emphasis on high pressure CH_2 @ 700 and 850 bar; tank weight penalty; volumetric energy density of 700 bar CH_2 is ~56% of LH_2
  - Cost-effective storage, transport, and delivery requires higher volumetric energy density of **LH_2**
- Impact: Hydrogen is most energy-intensive gas to liquefy
  - At 0.1013 MPa, H_2 specific energy is ~14 MJ/kg and its LHV is ~119 MJ/kg
  - Best existing liquefier efficiency FOM is ~0.35 even at very large scale
  - Major barrier is (14/119)/0.35 => 34% of energy content of H_2 to liquefy!
  - Doubling liquefier FOM strongly reduces hydrogen delivery cost!

Approach: Use active magnetic regenerator cycle;
modeled as magnetic Brayton cycles coupled by heat transfer fluid

- Adiabatic temperature changes from magnetocaloric effect near Curie temperature in ferromagnetic refrigerants given by:
  - $\Delta T_S = \frac{T}{\rho}\int_{B_L}^{B_H} \frac{1}{C_{B,T}} * \left(\frac{\partial M}{\partial T}\right)_B \delta B$; ρ is density, C is total heat capacity, M is magnetization, and B is magnetic field.
  - ΔT peaks near Curie temperature; values of 7-12 K for a ~6 T field change
- 25-40 K temperature spans of individual magnetic refrigerants
  - Use multiple refrigerants in regenerators for large temperature spans
- Reciprocating heat transfer fluid (HTF) flows couple active magnetic refrigerants to each other and to cold thermal loads & to heat sinks
- **Steps of an AMR (active magnetic regenerator) cycle are:**
  - Adiabatic magnetization of AMR with no HTF flow
  - HTF flow from cold-to-hot through AMR at constant high field (heat rejection)
  - Adiabatic demagnetization of AMR with no HTF flow
  - HTF flow from hot-to-cold through AMR at constant low field (cooling)

Approach: Two multi-layer AMR liquefier stages to make H_2 starting from room temperature

- The 290 K to 100 K stage uses liquid heat transfer fluid (HTF) to achieve high efficiency
  - Different mass in each of 5 layers in upper stage
  - Different mass flow rates in each layer achieved by diversion flows between layers
  - Unique use of bypass of HTF flow to continuously cool H_2 process gas
- The 100 K to 20 K stage uses helium gas as HTF
  - Different mass in 3 layers plus diversion He flows
  - Heat rejection to 1st stage



Room Temperature H_2

100 K H_2

LH_2

1st Stage
290 K to ~100 K

2nd Stage
~100 K to 20 K LH2

5 layer reciprocating regenerators, liquid HTF, 6 T; heat sink for 2nd stage

3 layer regenerators, coupled to process HEX with o-p catalysts and condensing CHEX

Milestones: Model, Design, Fabricate and Test Prototypes to Understand AMR units

- GEN-I System (FY15-16)
  - ✓ Refurbish single-stage Prometheus prototype and characterize performance
  - ✓ Test by-pass flow of helium gas heat transfer fluid (HTF)
  - ✓ Validate performance simulation models
  - ✓ Develop next GEN designs and do initial cost analysis
- GEN-IIA/B/C Systems (FY17-19)
  - ✓ Reciprocating vs rotary regenerators; investigate rotary seals
  - ✓ Model magnetic and mechanical forces; balance forces
  - ✓ Developed multi-stage and multi-layer regenerators (patents pending)
  - ✓ Improved design of regenerators; controllable HTF diversion flow designs
  - ✓ Fabricate, assemble, test, analyze sequence of GEN-II A, B, C prototypes
  - ✓ First achievement of 135 K from ~285 K with 4-layer dual regenerator design
  - ✓ Validate models; begin GEN-III design after analysis of new results
  - ✓ Complete cost analysis for 30 tonne/day MCHL
- GEN-III System (FY20)
  - ✓ First liquefaction of methane with a magnetocaloric liquefier
  - Design, Build, and Demonstrate 1 kg/day H_2 liquefaction;

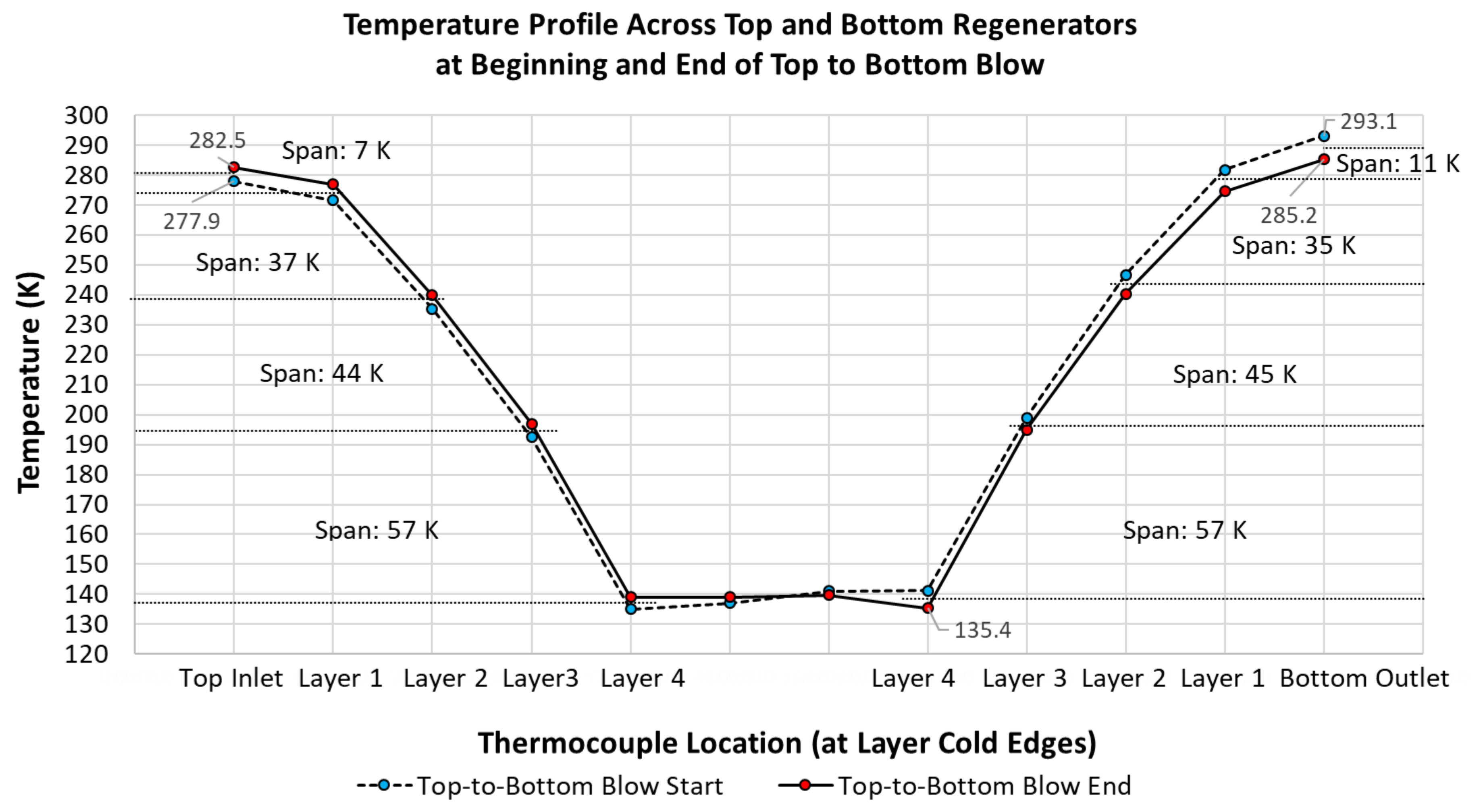
FY20 GEN-III Milestones (as of 3/24/2020)

Date	Milestone	Status*	Comments
3/24/2020	Magnetic Refrigerants	40%	use Gd:X for 30% higher density than $Gd:Er:Al_2$
3/24/2020 COVID-19 delayed	Fabricated spheres of magnetic refrigerants by Ames Lab	10%	Gd:X compounds easier to process than dialuminides; new zirconia coated rotating disk
3/24/2020	Detailed design of 2nd Stage AMR (GEN-III) to cool from 100K to 20K for first production of LH_2	70%	Requires diversion flow between each layer; bypass flow; large mass differences per layer (1:2:4); integrates GH_2 HEX with o/p catalysts
3/24/2020 COVID-19 delayed	Procure and Machine parts for GEN-III regenerators	20%	PNNL shops are on mandatory shut down until mid-June
3/24/2020	Helium pump subsystem flow capacity doubled	70%	Second reciprocating pump added in parallel to existing 400 psia pump
3/24/2020 COVID-19 delayed	LN_2 heat sink and precooling system	50%	Purchasing parts for assembly by crafts
3/24/2020	GH_2 process heat exchangers; o/p catalyst	70%	Purchasing parts for assembly by crafts

Accomplishment:

First time 4-layer AMRR spans ~285 K to ~135 K

(achieved in August 2019 but basis for 290 K to 100 K Stage 1 of MCHL)



Accomplishment:

First liquefication of methane from ~290 K with an AMRL

Done in *FY 20 (11/01/2019) A great precursor for LH_2*

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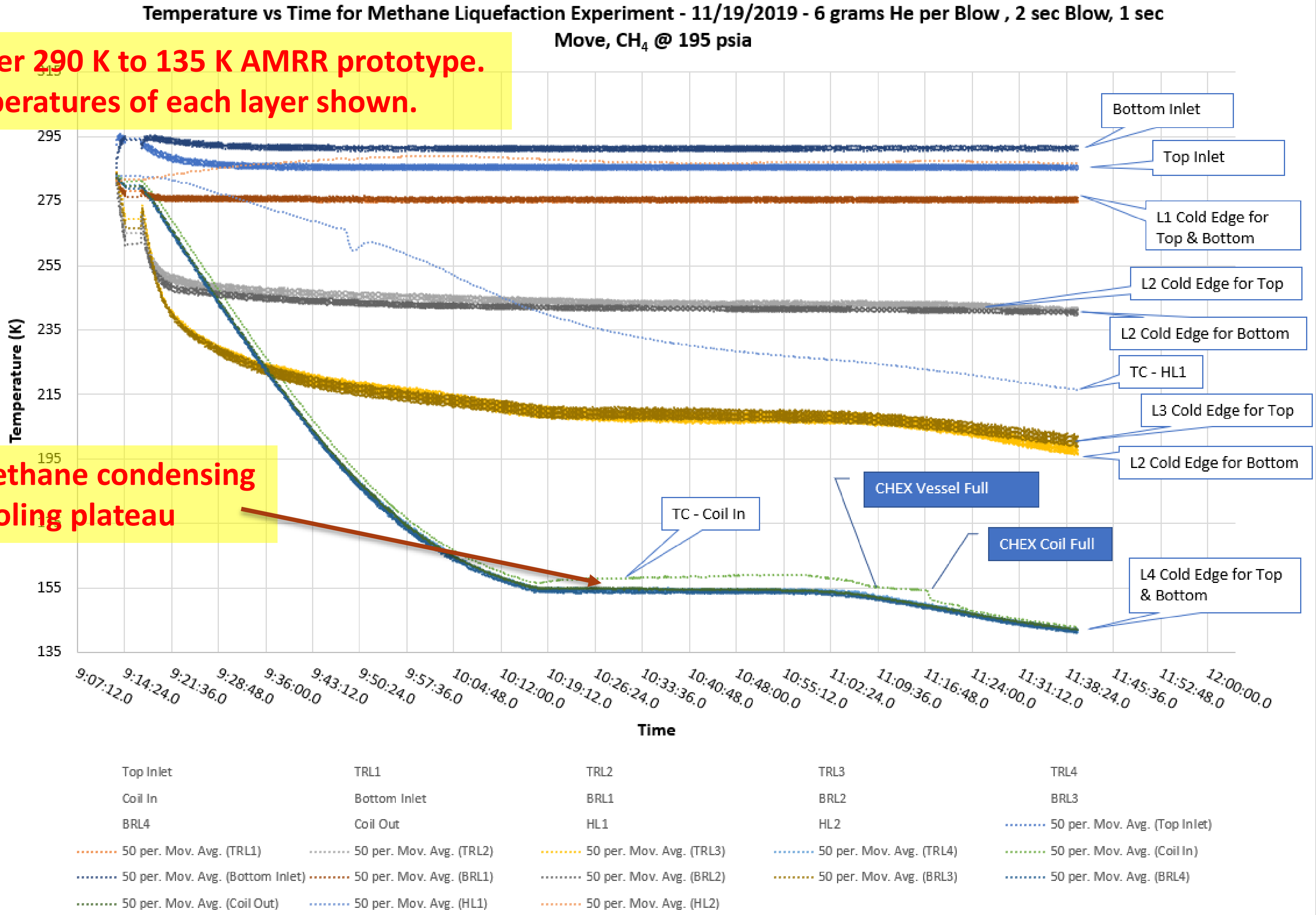
4-layer 290 K to 135 K AMRR prototype. Temperatures of each layer shown.


Temperature vs Time for Methane Liquefaction Experiment - 11/19/2019 - 6 grams He per Blow , 2 sec Blow, 1 sec Move, CH_4 @ 195 psia

Methane condensing cooling plateau

Accomplishment:

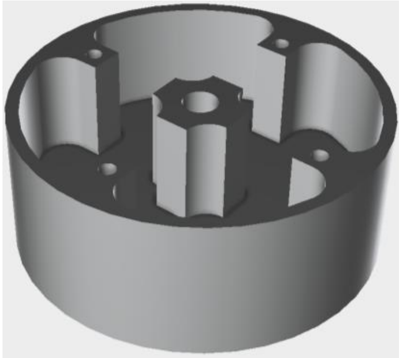
Progress toward GEN-III Design

Some changes required for ~100 K to ~20 K

- Performance Simulation Modeling
  - Numerical Fortran model for AMR from coupled magnetic Brayton cycles
  - Phenomenological multi-layer model validated using Fortran code for 1 layer
- Efficient Regenerator Design
  - Irreversible entropy lessons from analysis of multilayer prototype results
- New Superconducting magnet
  - Aspect ratio constraint requires longer high-field region in large-bore magnet
  - Magnetic force balance requires same magnetic field gradients at two locations
- Three Refrigerants for GEN-III multi-layer regenerators
  - Larger mass ratios due to larger work input rates at colder temperatures
  - Higher density refrigerants than initial Gd:Er:Al_2 choices
- Heat transfer fluid
  - LN_2 precooling stage for GEN-III at ~100 K (upper stage requires liquid HTF)
  - Diversion flow between adjacent layers
  - Bypass flow for process HEX with o/p catalysts

Accomplishment:
Identified magnetic materials for 100 K to 20 K and improved Rotating Disk Atomizer

- AMES continued preparation, characterization, and fabrication into ~200 micron spheres
  - Molten Dialuminides are chemically aggressive and reacted with the Ta disk used in the RDA
  - Several options tried; most promising is a Kovar disk plasma coated with a thin layer of zirconia which should not react with dialuminides



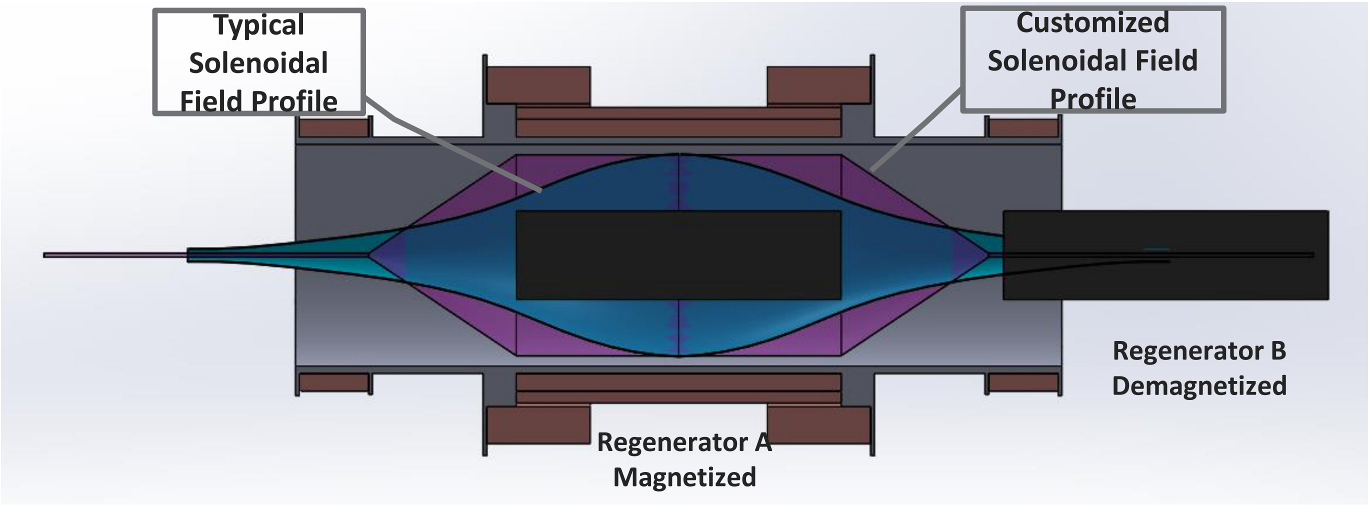
Bottom view of Kovar rotating disk for RDA; machined out to reduce thermal mass

Top of Kovar rotating disk with layered grooves to increase adherence of zirconia coating

Accomplishment:
Superconducting magnet has key features for reciprocating multi-layer regenerators

- Constant high field @ ~6.5 T
- Constant low field @ ~0.15 T
- Field gradients (dB/dz) leaving high and low field regions are ~same
- Larger clear bore for larger mass
- Longer high field region for high aspect ratio layers in regenerator

Cross-Sectional View of Solenoidal Magnet with Magnetic Field Profiles Overlaying MCL Regenerators



Magnet delayed by COVID-19; now due in mid July 2020

Accomplishment:
Preferred design of 2nd stage of MCHL liquefier for LH_2 with continuous bypass flow

- Provides continuous cooling to GH_2 process stream
- Reciprocating design extended to use 4 identical 3-layer regenerators with AMR phased cooling steps
- Stage-2 uses 3 materials to cool H_2 from 100 K and make LH_2 at 20 K
- Single pump for 400 psia He in Stage 2
- One 4 K cryocooler for entire system
- GEN-III will use left half of this Block Process Flow Diagram with only one 6.5 T s/c magnet

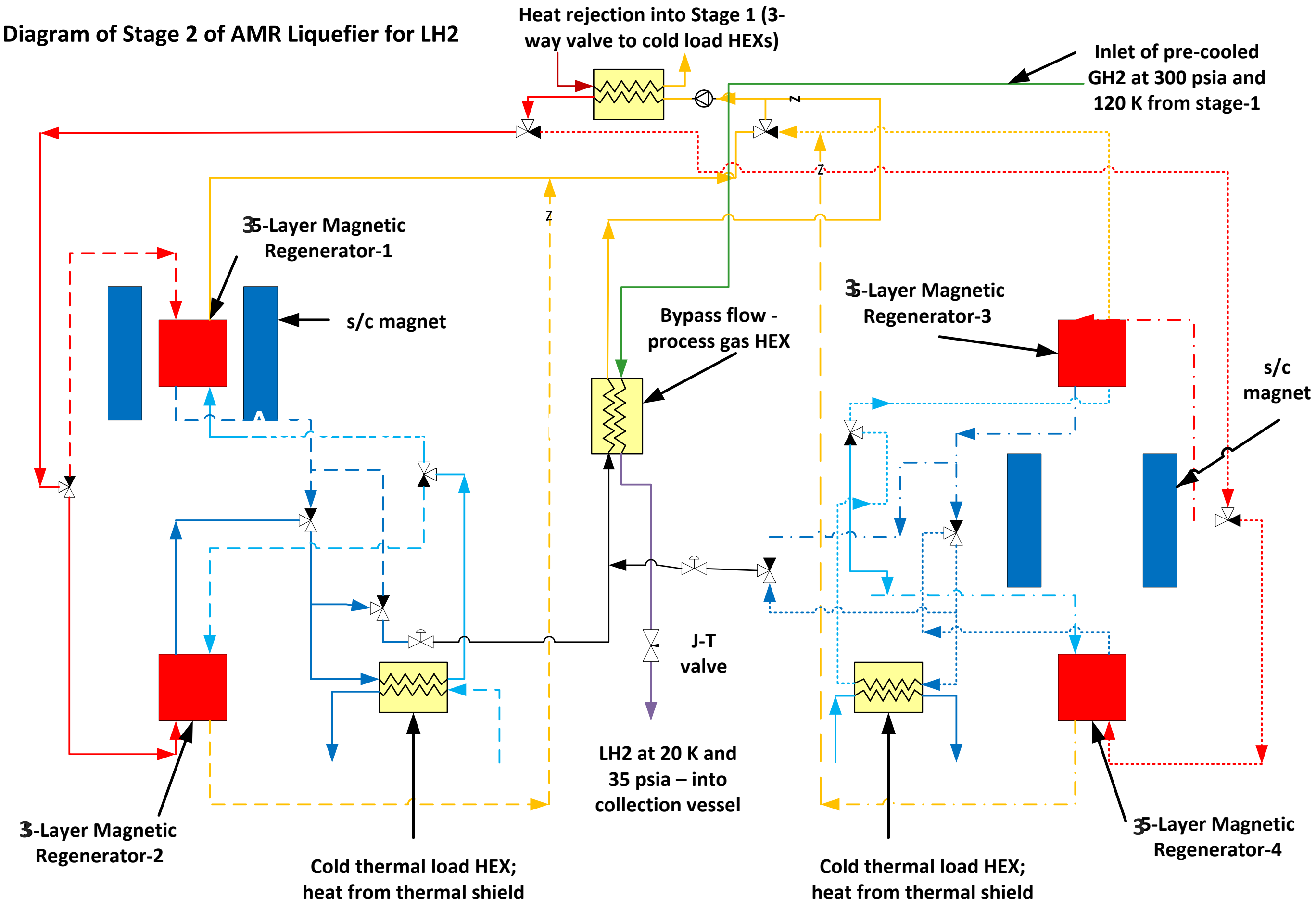


Diagram of Stage 2 of AMR Liquefier for LH2

Heat rejection into Stage 1 (3-way valve to cold load HEXs)

Inlet of pre-cooled GH2 at 300 psia and 120 K from stage-1

35-Layer Magnetic Regenerator-1

s/c magnet

Bypass flow - process gas HEX

35-Layer Magnetic Regenerator-3

s/c magnet

J-T valve

LH2 at 20 K and 35 psia – into collection vessel

35-Layer Magnetic Regenerator-2

Cold thermal load HEX; heat from thermal shield

Cold thermal load HEX; heat from thermal shield

35-Layer Magnetic Regenerator-4

Patent Pending

FY20 Collaborations

Collaborator	**Project Interest/Role**
DOE/EERE/HFTO	Sponsorship, steering - MCHL
DOE/NETL/FE	Efficient Air liquefaction - MOLS
AMES Laboratory / Iowa State University	Materials characterization Material synthesis
HDTT (has 3 big industrial gas or energy companies)	Provide critical feedback and direction and potential future MCL user
Raytheon Technology Research Center	Collaboration on ARPA-E proposal and small ACT contract for highly efficient, low specific mass cryocooler; ~120 K to ~20 K for superconducting devices
Pursuing collaboration with fuel cell electric heavy duty vehicle companies	industrial companies who may want to license and commercialize MCHL

Publications and Presentations

Publications- 5 (pending)

- “Cooling Power of Active Magnetic Regenerative Refrigerators and Liquefiers for Cryogenic Applications” by John Barclay, Corey Archipley, Jamelyn Holladay, Kerry Meinhardt, Evgueni Polikarpov, and Edwin Thomsen
- “Experiments on Cryogenic Multilayer Active Magnetic Regenerative Refrigerators” by John Barclay, Corey Archipley, Jamelyn Holladay, Kerry Meinhardt, Evgueni Polikarpov, and Edwin Thomsen
- “Thermodynamic Efficiency of Active Magnetic Regenerative Refrigerators and Liquefiers for Cryogenic Applications” by Corey Archipley, John Barclay, Jamelyn Holladay, and Kerry Meinhardt
- “Methane Liquefaction with an Active Magnetic Regenerative Liquefier” by John Barclay, Corey Archipley, Kerry Meinhardt, Greg Whyatt, Edwin Thomsen, John Barclay, Jamie Holladay, Jun Cui, Iver Anderson, and Sam Wolf
- “Integrated vehicular refueling stations for liquefied and compressed hydrogen and natural gas” by John Barclay and Jamie Holladay

Patents and licensing

- 8 invention disclosure reports submitted
- 4 non-provisional patents applications submitted
- 2 PCT applications submitted
- Initial discussions with two companies about potential MCL technology licensing

Challenges: We are focusing our efforts to manage impact of COVID-19 and still meet our important milestone to have GEN-III assembled and ready to test by 9/30/2020

- GEN-III: 100 K to 20 K; design, build and demonstrate H_2 liquefaction
    - Higher density Gd:X refrigerant synthesis and fabrication by 8/31/2020
    - Regenerator components procured and/or machined to prepared for the assembly of dual 3-layer regenerators as magnetic refrigerants arrive from AMES no later than 8/31/2020
    - Receive new s/c magnet and install it in APEL-177 after completing several experiments in progress (when mandatory teleworking started on 3/24/2020). Magnet now scheduled for arrival about 7/18/2020
    - Process heat exchanger with o/p catalyst assembled by 7/31/2020
    - Helium pump system with LN_2 precooling subsystems completed by 8/15/2020
    - H_2 gas liquefaction Standard Operating Procedure (SOP) prepared and submitted to safety committee for review, revision, and approval. 8/31/2020
    - Continue to manage and mitigate presence of SARS CoV-2 virus to ensure safety of staff at PNNL.

Proposed Future Work

- FY21

Any proposed future work is subject to change based on funding levels.

  - Finish tests of GEN-III and demonstrate first production of LH_2 with a MCHL
  - Analyze results and document lessons learned from full characterization of GEN-III
  - Integrate designs of a 290 K to 100 K stage and a 100 K to 20 K stage into a complete MCHL system at a scale of 10-50 kg/day of LH_2
    - Develop a rotary wheel design of a MCHL to achieve higher frequency
  - Engage industrial partner(s) to collaboratively design, build, and demonstrate a complete 290 K to 20 K system to provide more precise cost basis for TEA and identify steps required to achieve FOM of ~0.6
  - Explore mutually beneficial transfer technology agreements.

Reviewer Comment	Response
"There should be more efforts made in the lower-temperature stage. This will be more challenging thermally, but the first stage can be approximated by a LN2 supply"	We will be starting the lower-temperature stage this fiscal year. The rare-earth metals and alloys that are excellent refrigerants in the ~280 K to ~120 K range are easy to prepare, characterize, and easily fabricate into spheres for AMRs. DOE's original guidance was to start at room temperature because starting with LN_2 immediately reduces the FOM of a LH_2 liquefier to less than 0.4. The 77 K to 20 K span is also an area where Japanese and Korean groups have pursued but no one has tackled the upper ranges. The work focused on higher-temperatures identified potential AMR design issues that apply and help design lower-temperature stages. Further, with the new Fossil Energy project for 280K to 100K, we will focus the FCTO work exclusively on the lower-temperature stage and the Fossil Energy project will complete the development of the higher-temperature stage; both will leverage what we've learned to date over past 4 years.
"TEA should be considered in FY 2019 rather than FY 2020"	Thank-you for this comment. We updated the TEA as shown in the presentation. The assumptions are in the backup section.
"The longstanding partnership with Ames Laboratory and EENW is good. At some point, however, it would be good to see some private money being invested as matching funds." and "There was no collaboration (or it was not apparent) with industry; this is important for understanding the technical and commercial requirements for the technology. The project does have good collaboration among academia and institutions, however."	We are in discussion with several potential industry partners from ranging from venture capitalists to energy companies to gas providers. They all are intrigued but ask for more proof of claims by liquefaction of natural gas and/or hydrogen beyond lab-scales. We are progressing steadily toward LH_2 and we have a TCF project to make LNG by the end of the FY19. We know working hardware establishes performance credibility required by energy/industrial companies with specific commercial applications suited for MCL technology. To the second comment regarding our lack of industrial partners, Emerald Energy NW is a small business and an industrial partner.
"The presenter claimed that the FOM for the device was 0.73 and that bypassing reduces it to ~0.5. No explanation was given for such a high FOM. It is not clear how such an extraordinarily large FOM can be achieved with the project's design, which involves two heat exchangers."	I think the reviewer mis-typed and meant to say that without bypass the FOM was 0.5 and with bypass it was 0.73. We agree these FOMs are very high values, but they are based on well established thermodynamic analysis for AMR liquefiers of ~10 tonne/day or larger capacity, not lab-scale devices. AMR technology offers unique features that eliminate major sources of lower FOMs in conventional methods, i.e. gas compression and large temperature approaches in process HEXs. A full description of how we calculated the FOM was in our quarterly report to the DOE. In addition, as we learn more, we continue to update our design methods and the FOM calculations. For example, we changed the impact of the pressure drop and the aspect ratios of regenerators on the FOM. With these updates the FOM dropped to ~0.65. We understand that working proof speaks volumes!

Summary and Conclusions

Status of MagnetoCaloric Hydrogen Liquefier

- High-FOM liquefaction of hydrogen is a game-changing goal
- LH_2 demonstration with 5/6 layer, 290K-to-100K prototype with propane HTF coupled to 3-layer 100K-to-20K GEN-III prototype with He HTF is achievable
  - We have validated multi-layer models to guide designs
  - To reduce cost of additional magnets, LN_2 pre-cooler and heat sink for operation at ~100K has been developed
- The magnetic regenerator, heat transfer fluid, and s/c magnet subsystems are understood and validated
  - New magnet will increase performance
  - Magnetic refrigerant supply contingency plans are in place
  - Primary flow, diversion flow, bypass flow, and process flow paths are integrated
- High priority component development goals are:
  - Need continued progress on liquid HTF and diversion flow valve implementation
  - Obtain cost-share partner to develop and demonstrate the integration of a 290 K to 100 K stage and a 100 K to 20 K stage to efficiently produce LH_2.
- Determine scaling and cost projection for licensing potential with hydrogen fuel companies and other end users with design/build capabilities
  - Determine how to move toward 1 Hz operation for scaling up liquefiers to tonne/day capacities

Mission

We transform the world through
courageous discovery and innovation.

Vision

PNNL science and technology inspires
and enables the world to live
prosperously, safely and securely.

DISCOVERY in Action

Values

CREATIVITY
integrity
courage
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COLLABORATION

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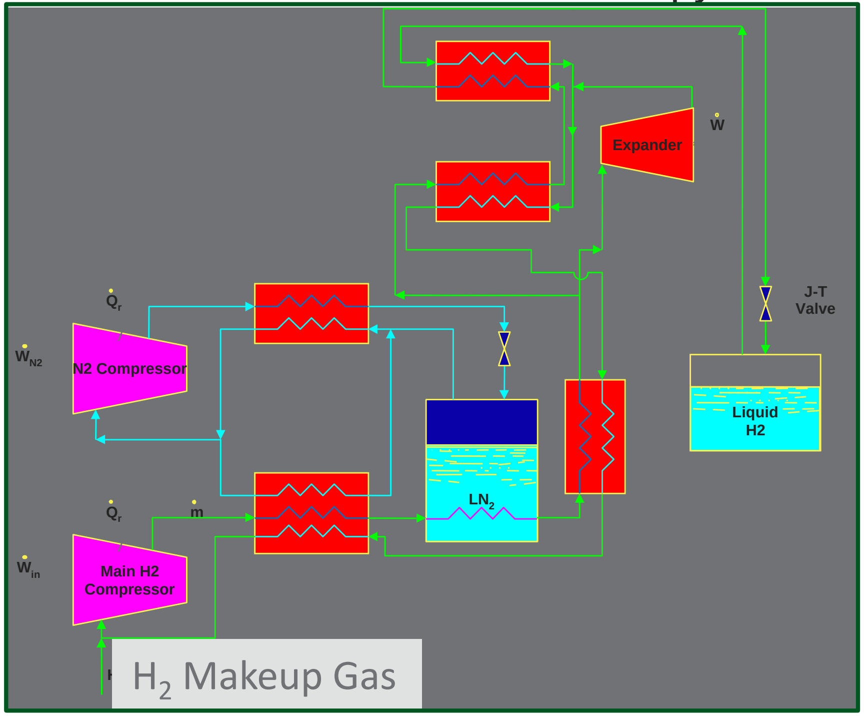
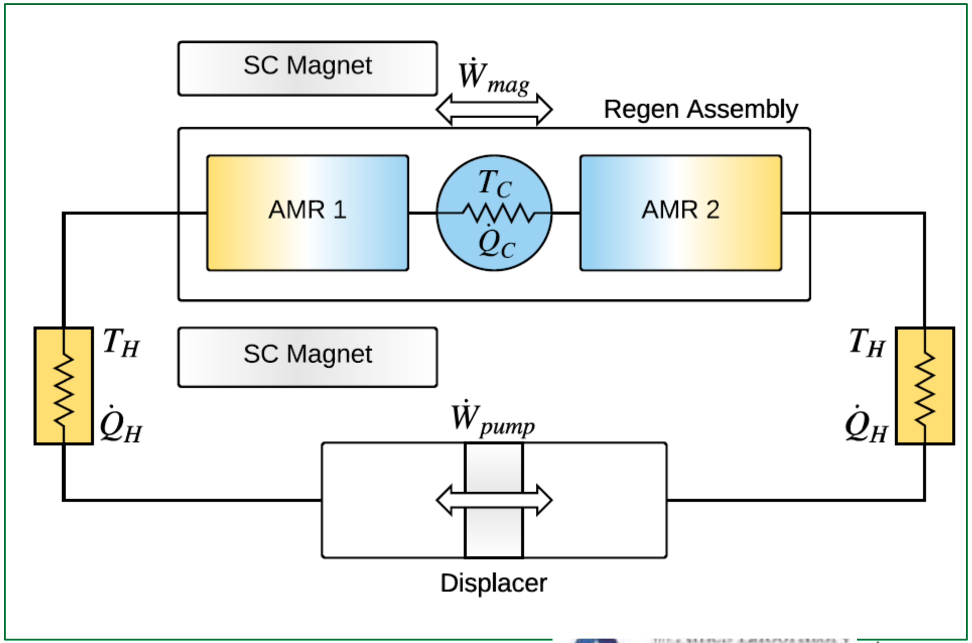
Technical Back-up slides

Approach:
Magnetocaloric liquefaction has potential to increase the FOM by 2x compared to conventional Claude process

- Conventional- Claude Process
  - Low efficiency, FOM = 36%
    - Theoretical 4 kWh/kg H_2
    - Real 11 kWh/kg H_2
  - Why?
    - LN_2 pre-cooled Claude cycle
    - 50% irreversible entropy

- MagnetoCaloric Liquefaction
  - FOM = 60+% (projected)
  - Solid magnetic materials
  - Entropy manipulated by magnetic fields – high reversibility
  - Bypass flow is unique to MCL





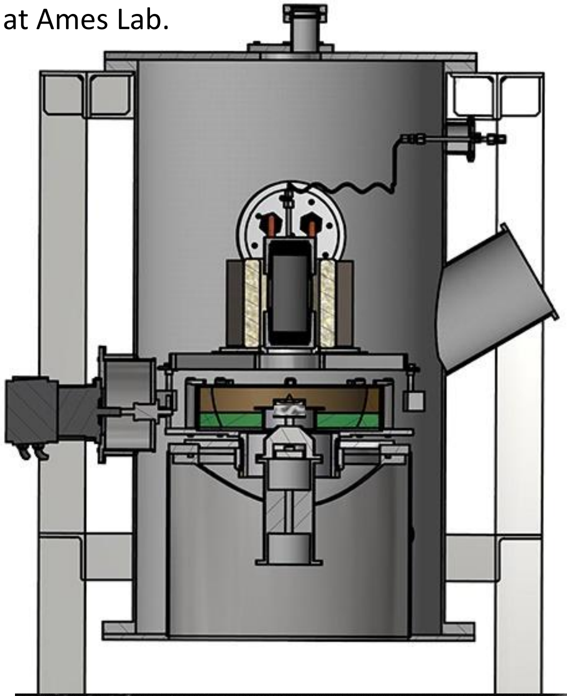
Accomplishment:

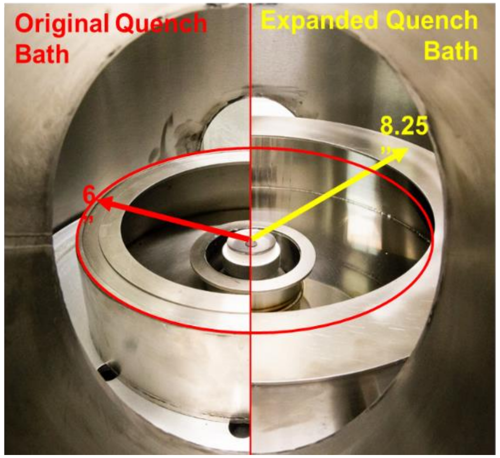
Ortho-para catalyst candidates

- Many options available
  - Ferric oxide (Fe_2O_3) - **we have selected this catalyst for GEN-III**
  - RuO_2
  - Activated 5 carbon
  - Chromic oxides (Cr_2O_3 or CrO_3)
  - Ni metal, NiO/Silica, and nickel compounds (Ni^{2+})
  - Rare earth metals and oxides such as Gd_2O_3, Nd_2O_3, and Ce_2O_3
- Heat exchangers
  - PNNL's patented microchannel architecture
  - Literature many papers
  - Dr. Barclay has experience in designs

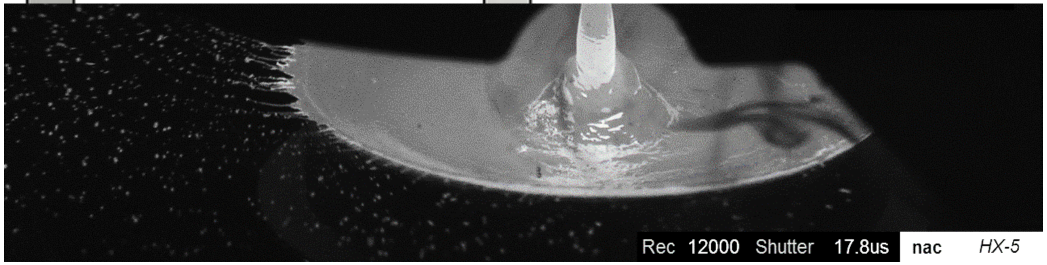
Rotating Disk Atomization (RDA)

Cross section of the RDA designed and built at Ames Lab.





Upgrades to the quench bath has proven successful with consistent reduction of flake content to ~20% compared to pre-upgrade 30-50% due to lengthened flight path for droplet cooling/solidification.



Disk surface during atomization showing droplet formation.

- Droplet break-up by centrifugal forces as liquid metal is poured/spread over a rapidly spinning disk. Droplets spherodize, cool, solidify, and are quenched & collected in co-rotating bath as spherical powder.
- For research on rare earth (RE) alloys, with costly materials and many compositions to prepare, the small (~1kg) batch, fast turnaround RDA process with precise size range and fluid capture is preferred over lab gas atomization, with large (~5kg) batch, 1 week cycle, top size limit (<150µm), and surface passivation needs.
- The upgraded RDA at Ames Lab can produce ~400g of spherical powder in the targeted size range (150-250µm) from a 1-1.5kg charge.
- Challenges are currently being addressed with erosion-resistant materials selection and mechanical stability for extended high RPM runs of disk assembly during atomization of RE-aluminide materials.