N91-19001

1990

NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

MARSHALL SPACE FLIGHT CENTER
THE UNIVERSITY OF ALABAMA

A SURVEY OF TECHNIQUES FOR REFRIGERATION, RELIQUEFACTION, AND PRODUCTION OF SLUSH FOR HYDROGEN

Prepared By: Dan Overcash

Academic Rank: Associate Professor

University and   Lenoir-Rhyne College
Department: Physics and Earth Science

NASA/MSFC:
      Laboratory: Propulsion
      Division: Propulsion Systems
      Branch: Space Propulsion

MSFC Colleague: Leon Hastings

Contract Number: NGT-01-002-099
                          The University of Alabama
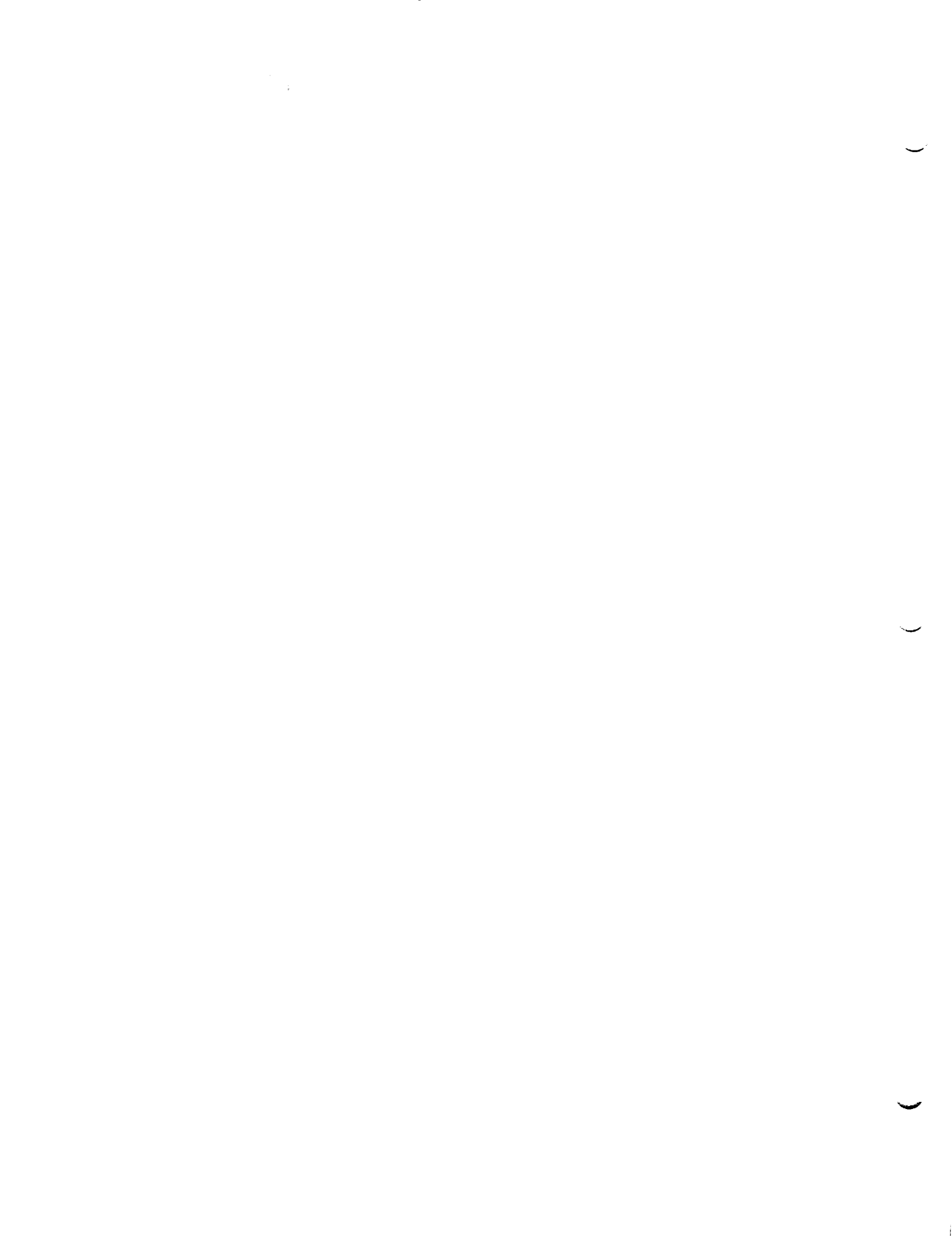
XXXIV

A Survey of Techniques for Refrigeration, Reliquefaction, and Production of Slush for Hydrogen

Techniques surveyed for hydrogen reliquefaction were: Auger; Bubbling Helium; Simon desorbtion; Peltier effect; Joule-Kelvin expansion - Stirling, Brayton, Viulleumier, Rotary reciprocating; Dilution Refrigerator; Adiabatic demagnetization of a paramagnetic salt; and Adiabatic magnetization of a superconductor.

First, I'll briefly consider commercial applications for hydrogen liquefaction then, I'll discuss space refrigeration.

Auger: One end of an auger made of high heat conducting material is immersed in liquid helium and the other end is rotated in hydrogen gas. The cooling power depends on the size of the auger and is slow, massive, and requires liquid helium.

Bubbling Helium Gas: Bubbling liquid helium gas through hydrogen gas slowly forms hydrogen slush but this technique also requires liquid helium and is slow because of the small specific heat of helium.

Simon Desorption: Refrigeration occurs as helium is absorbed by charcoal. This requires liquid helium and has a limited temperature range 20K-50K (36R-90R)[1].

Petlier Effect: Heat can be extracted by passing a current through a thermocouple. A difference in temperature between thermocouple junctins produces a voltage and a current produces a difference in temperature. The peltier heat is equal to the product of the temperature and the Seebeck coefficients. A current of 10 amps through 10 junctions of a Cu-Fe thermocouple at water ice temperature produces 0.74 watts of cooling[1]. In 1838, Levy used an Sb and Bi thermocouple and succeeded in freezing a drop of water[1]. Semiconductors have larger Seebeck coefficients, and good electrical conductivity, but poor thermal conductivity. A p-n junction as gives a heat current of 35 watts but is not usable for hydrogen because the heat is proportional to the temperature (20K) and large currents are needed with the resulting large Joulian heat dissipation.

Joule-Kelvin Expansion: *Stirling cycle.* On a pressure and volume plot, the difference in positive and negative work is the heat absorbed by the refrigeration cycle. In the operation of an ideal stirling refrigerator, a gas is compressed and heat is rejected. The pressure is then lowered at constant volume and the temperature of the gas drops. The gas then expands so the pressure drops and heat is absorbed. The final step in this cycle is a constant volume increase in pressure. In 1982, Myrtle[2] built a

conical Stirling refrigerator to cool from 300K to 9K. Elegant for its simplicity with only one moving part, no moving seals, and 0.6 m x 0.1 m in size, but 8 hours are needed to refrigerate to 9K with its 1 milliwatt cooling. They are sold by North American Phillips, A.D. Little, and Hughes Aircraft. These cycles have a large temperature range and cooling power of 500 watts and can produce 400 liters/hour of liquid hydrogen.[3] They are good commercial refrigerators but their space application is limited by their volume, mass, and support equipment - 5m x 10m x 2m (328 ft^3) for 100 gallons/hour. In a commercial Russian J-K expansion refrigerator, in the condenser, the refrigerant is at as low a temperature as can be obtained and a high pressure. The refrigerant, as a saturated liquid, passes through a narrow opening to a region of lower pressure adiabatically. This "throttling" process occurs at constant enthalpy. Liquefaction of gases by the Joule-Kelvin effect involves isenthalps on a pressure and temperature graph. On an isenthalpic plot for hydrogen, in a region with positive slope, a decrease in pressure causes a decease in temperature. For hydrogen, refrigeration can be obtained for pressure drops in the range 25K to 200K. At 77K (liquid nitrogen) for the maximum pressure to throttle hydrogen is 15MPa (2000 psi).[1] Refrigerators use adiabatic reversible expansion to achieve temperatures within the inversion curve and then Joule-Kelvin expansion is used to liquefy them.

Brayton. Cycles have lower operating pressure levels and have been analyzed by Maddocks and others. They use compressors with after coolers to remove the heat of compression and heat exchangers and expanders. Too many components!

Viulleumirer. A thermal compressor device that offers the possibility of long life and reduced electrical power requirements.

Dilution Refrigerator: Proposed in 1951 and built in 1978, the temperature of a He^3 - He^4 mixture is lowered and the mixture spontaneously separates into two phases. The He^3 floats on top. Lowering the temperature further, the He^4 acts like a vacuum for the dilute gas of He^3 atoms. Upper He^3 atoms are more densely packed and are dispersed among the He^4 atoms, similar to evaporation cooling. Cooling is when the He^3 from the concentrated phase crosses the phase boundary into the dilute phase. A vacuum pump is used to remove the He^3 atoms from the dilute phase, thereby cooling. Transport of He^3 will continue across the boundary because of the 6.4% solubility of He^3 in He^4. He^3 is removed from the dilute phase by osmotic pressure and returned to the still.
    Suppliers of dilution refrigerators are Phillips Research Laboratories, Netherlands, and Astronautics Corp. Many articles may be found in "Cryogenics" articles

concerning: faster He pumps, heat exchangers, condensation stages, without He pumps, entropy of transfer, heat of transport, and dissipation effects.

Recent articles in "Cryogenics" indicate that low temperatures will be essential for some experiments in future space missions but this survey is from 10K-20K and a cooling power of less than 74 Joules per mole of He[3] for dilution refrigerators is small even though they continue to refrigerate below 1.2K and can produce millikelvin temperatures.

Gravity plays an important role in the separation of the lighter He phase from the heavier He phase. H.W. Jackson[3] has demonstrated that electrostriction (5000 volts across a gap of 0.5 mm) is well suited for a mixing chamber aboard spacecraft. Vermeulen and Frossati describe a "powerful" dilution refrigerator but its support equipment is several cubic meters in volume for the necessary pumps.

Astronautics Corporation of America has developed magnetic heat pump which use the magnetocaloric effect to produce refrigeration. Between 2K and 20K, gadolinium garnet (GGG) is used. On an entropy and temperature diagram, a cycle starts by rotating a paramagnetic salt into a magnetic field. This requires work to increase the magnetic energy in the GGG and liberates heat. A heat exchanger removes the heat and from the GGG at a constant temperature as the field is increased and the entropy drops. As the GGG is rotated out of the magnetic field, the temperature drops. A rotating wheel of GGG has been used to produce hydrogen slush. For each kilowatt of cooling power, 34.3 pounds per hour of NPB liquid hydrogen, and 0.93 kW of electrical power and used.

As the GGG rotates into the magnetic field, heat is removed from the wheel by boiling liquid hydrogen. As the wheel rotates out of the field, hydrogen freezes on the wheel and is removed by strippers. J.A. Waynet[5] describes a 1 kilowatt magnetic refrigerator which produces 50% slush @ 550 liters per hour and has a mass of 370 kg and a volume of about 1 cubic meter. A 7 tesla magnetic field is used and the current necessary for this field can be provided by solar cells to a superconducting magnet but a superconducting magnet requires liquid helium. The infrared telescope has successfully used liquid helium in space for a year. This 1 kW refrigerator also uses 27 tons per day of liquid nitrogen. Other candidate cycles in magnetic refrigeration are the Brayton and Ericsson cycles which increase the temperature span and use external thermal agents which act as a thermal flywheel. Superconductors, which can be used as thermal switches in these refrigerators as magnetic fields, are used to turn on and off superconductivity and, therefore thermal conductivity. An active magnetic refrigerator with ortho to para hydrogen

converters, span 77K to 10K, 10 carnot cycle devices are needed. The active magnetic refrigerator (AMR) uses a packed bed of material sandwiched between a hot and a cold reservoir. A heat transfer fluid is shuttled back and forth through the bed by pistons. The bed is magnetized with no flow. Fluid is then passed from the hot reservoir with the bed magnetized. The bed is then demagnetized with no flow. Fluid is then passed from the hot reservoir through the cooled bed. Magnetic refrigerators need to be flight tested and paramagnetic salts with higher specific heats should be found. For the NASP X-30[4], slush hydrogen maintenance by conventional methods are not compatible. The freeze thaw method requires large vacuum pumps and heat exchangers. The auger and helium gas injection system requires large helium refrigeration systems. The largest helium refrigerator ever built is at BNL and provides 10 kwatts of cooling but has 5 cold exchangers which are the size of a gasoline tanker.

Flippen[6] has found for the type II superconductor, Nb, adiabatic magnetization provides cooling. Applying a magnetic field makes the superconductor a normal conductor and refrigerates.

All the refrigerator cycles discussed for adiabatic demagnetization of a paramagnetic salt should be investigated for the magnetization of a superconductor.

Cooling is obtained by converting from ortho to paro hydrogen. The 7 or 8 tesla magnetic field, 70,000 gauss magnetic fields needed for magnetic refrigerators is now obtainable with superconducting magnets with liquid helium cooling and are available from Janis. Future high temperature superconductors, if developed, may bring transition temperatures below space temperatures and provide long term space magnets for magnetic refrigeration to liquify hydrogen. Electrical engineers say high currents may be obtained from solar cells if low power is needed as for superconductors. If spacecraft can be turned so that ceramic superconductors are below 125K, 225R, as of 1987 with 1-2-3 superconductivity is now possible.

Lawless and Clark[7], in 1988 specific heat measurements, found an interesting magnetocaloric stabilization mechanism. Ceramic and epoxies were found that have magnetocaloric cooling and could be used in magnet windings and paramagnetic wheels in cryorefrigerators.

At the Fifth International Cryogenic Conference, R.W. Vance of Aerospace Corporation in California reviewed the state-of-the-art small refrigerators that may be capable of performing in space.

Mason and Stephens described a supercritical helium (SHe) system for a 6 month life time of liquid hydrogen.

A reversed Brayton cycle refrigerator with four expanders was described where high pressure gas passes through a series of counterflow heat exchangers. The compressor rotates 100,000 revolutions/min and are supported by gas bearings that assure long life but these systems are extremely inefficient, less than 1% at 10K.

A Vuileumier refrigerator has a potential long life, low power demands and uses and isotope for thermal compression.

One unit has been flight tested for a short period. Slow piston speeds and low bearing loads produce long life.

Liquid and solid cryogenic propellants, when stored in properly designed dewars, will require small refrigeration loads which can be handled by several of the refrigerators described in this paper for space flights of one year in length.

I encourage this group to investigate and design space cooling systems for the high temperature reservoirs for these refrigeration systems. Since radiation cooling depends on the fourth power of the temperature, higher temperature heat exchangers give increased radiation cooling and higher efficiencies.

I would like to spend the next academic year investigating and testing high temperature superconductors for use is adiabatic refrigerators. Both as magnetic field producers and as a working material for magnetocaloric refrigerators.

Endnotes

1. Zemanski, <u>Heat and Thermodynamics</u>, 6th ed., pp. 25, 441, & 328.

2. K. Myrtle, C. Winter, and S. Gygax, <u>Cryogenics</u>, March 1982, p. 139.

3. H.W. Jackson, <u>Cryogenics</u>, February 1982, p. 59.

4. J.A. Waynet, J.A. Barclay, R.W. Foster, <u>A Portable Magnetic Refrigerator for X-30 Slush Maintenance 5th National Aerospace Plan Technology Symposium</u>, October 1988.

5. J.A. Waynet, J.A. Barclay, P. Claybaker, R.W. Foster, S.R. Jaeger, S. Kral, C. Zimm, <u>Production of Slash Hydrogen Using Magnetic Refrigeration</u>, 7th Intersociety Cryogenic Symposium, Boulder, Colorado, January 1989.