Matthew Frank, P.E., Mark S. Spector, Ph.D., Neil Antin Investigating Low Global Warming Potential (GWP) Alternatives for Navy Refrigeration Systems

ABSTRACT

The American Innovation and Manufacturing (AIM) Act [Public Law 116-260, 2021], as well as the United States (U.S.) ratified (2022) international Kigali Amendment to the Montreal Protocol, calls for a stepwise phasedown to an 85% reduction of the carbon dioxide (CO₂) equivalent emissions from the production and consumption of hydrofluorocarbons (HFCs) by 2036. HFCs are currently used as the refrigerant in air conditioning (AC) plants (commonly called chillers), refrigeration units for chilled/frozen food storage and pumped twophase cooling applications that support various mission critical functions for U.S. Navy ships. This legislation is likely to affect the future availability and cost of these HFC's. The ability to transition to non-HFCs or lower global warming potential (GWP) HFCs is being investigated with a focus on the safety and performance, both thermodynamically and life cycle climate. This paper summarizes findings, challenges, and opportunities from the initial research efforts to identify low-GWP replacements for refrigerants HFC-134a, R-404A and R-407A that are currently used on Navy platforms for the purposes of refrigeration. This paper compliments a previous publication investigating options for Navy chillers [Frank, Spector and Antin, 2023].

BACKGROUND

Gases that trap heat in the atmosphere are known as greenhouse gases. These greenhouse gases have varying Global Warming Potential (GWP) values. GWP is defined as the heat absorbed by the specific gas in the atmosphere as a multiple of the heat that would be absorbed by the same mass of carbon dioxide (CO_2) over a specified period. The U.S. Environmental Protection Agency (EPA) assigns GWP values based on the 100-year GWPs listed in the 2007 Intergovernmental Panel on Climate Change (IPCC) Fourth Report [IPCC, 2007]. The AIM Act (enacted as section 103 in Division S, Innovation for the Environment, of the Consolidated Appropriations Act, 2021 [Public Law 116-260, 2021] and implementing regulations in 40 CFR Subpart 84 (Phasedown of HFCs) and the Senate ratified Kigali Agreement to the Montreal Protocol calls for an 85% reduction of HFCs CO₂ equivalent emissions by 2036 as shown in Figure 1.



Figure 1 – AIM-Act & Kigali Agreement HFC (CO₂ Equivalent) Phasedown

The current dominant use of HFCs is for foam blowing, fire extinguishing systems (examples HFC-125, HFC-227ea and HFC-236fa) and for refrigerants used in vapor compression cooling systems such as air conditioners, chillers, and food storage refrigeration systems. Table 1 lists 18 different HFCs being targeted for phasedown with those highlighted affecting U.S. Navy ships. Note that many refrigerants are blends such as R-404A which is 44% HFC-125, 52% HFC-143a and 4% HFC-134a and is used in some Navy refrigeration systems.

Table 1 – III Cs Targeted for Thasedown					
Chemical	GWP	Chemical	GWP		
HFC-125	3,500	HFC-236cb	1,340		
HFC-134	1,100	HFC-236ea	1,370		
HFC-134a	1,430	HFC-236fa	9,810		
HFC-143	353	HFC-245ca	693		
HFC-143a	4,470	HFC-245fa	1,030		
HFC-152	53	HFC-32	675		
HFC-152a	124	HFC-365mfc	794		
HFC-227ea	3,220	HFC-41	92		
HFC-23	14,800	HFC-43-10mee	1640		

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As these global climate regulations are enforced, there will be a major shift in the global manufacture of HFCs. Most HFCs with GWP >1500 are likely to be phased down almost completely while others such as HFC-134a only partly (but still significantly) phased down while flammable HFC-32 is expected to increase in production since it is a common ingredient in many newer low-GWP refrigerant-blends. This global rearrangement is likely to affect the availability and price of HFCs and create supply chain challenges for the U.S. Navy and other Department of Defense (DoD) agencies.

The AIM Act mandates that the EPA review the availability of acceptable substitutes for certain essential applications including Mission-Critical Military End Uses (MCMEU) not less than once every five years, and the first of these reviews will be published as an Application-Specific HFC Allowances Review and Renewal Rule expected to be finalized prior to 1 October 2025. Additionally, the EPA must allocate the full quantity of HFC production and consumption allowances for MCMEU, which includes Navy shipboard usage for chillers and refrigeration systems.

However, allowances are good if and only if material is available and the EPA regulations implementing the AIM Act (40 CFR Subpart 84) require that Department of Defense (DoD) provide, as part of their annual HFC allowance allocation request for MCMEU, a description of

plans to safely transition to HFCs or HFC blends with a lower exchange value (exchange value is equivalent to GWP) or alternatives to HFCs, including not-in-kind substitutes. All this uncertainty has spurred the DoD to establish various oversight committees to monitor HFC availability and production to mitigate possible supply chain disruptions. In 2022, the Office of Naval Research (ONR) began a program to research low GWP (GWP <700) alternatives for HFC-134a in Naval surface ship chillers with preliminary findings summarized in previous papers [Frank and Spector, 2022], [Frank, Spector and Antin, 2023]. This paper continues the research into low GWP alternatives for shipboard food storage refrigeration applications that currently use HFC-134a, R-404A and R-407A.

Domestic Refrigerant Regulations

The flow-down from the HFC Phasedown is reflected in the October 2023 final EPA Restrictions on the Use of Certain Hydrofluorocarbons under Subsection (i) of the AIM Act [EPA, 2022]. A summary of GWP limits for new equipment that could coincide with equipment on Naval ships is shown in Table 2.

Sectors and Subsectors	GWP Limit	Compliance Date
Retail food refrigeration – stand-alone units	150	January 1, 2025
Industrial process refrigeration systems with refrigerant charge capacities of 200 pounds or greater	150	January 1, 2026
Industrial process refrigeration systems with refrigerant charge capacities less than 200 pounds	300	January 1, 2026
Chillers – industrial process refrigeration with exiting fluid above -30°C (-22°F)	700	January 1, 2026

Table 2 – EPA GWP Limits

The EPA rule prohibits the commercial manufacture and import of equipment containing refrigerants greater than the allowed GWPs by 1 January 2025 or 1 January 2026.

Similarly, several States including California, Washington, and Virginia have recently passed regulations banning the use of HFC-134a and other refrigerants with GWPs greater than 750 like the EPA proposal but became effective 1 January 2024. Any lower GWP limits in the EPA final rule overrides any higher State GWP limit. As long as EPA is still allocating HFC allowances for MCMEU, State legislation and regulations are preempted by the Federal AIM Act. However, this preemption provision expires no later than 27 December 2030. Regardless, MCMEU allowances are good if and only if material is available via domestic production or import.

PRELIMINARY HAZARD ANALYSIS

Similar to the initial assessment for chillers, a preliminary hazard analysis (PHA) was conducted to evaluate low-GWP alternatives for shipboard food storage refrigeration. The Navy starting with DDG-1000 (circa 2008) transitioned from legacy, large reciprocating HFC-134a (GWP-1430) refrigeration condensing units serving complex, distributed piping systems supplying many evaporators (like most supermarkets) to simplified modular refrigeration systems (MRS) comprised of multiple self-contained modular refrigeration units (MRUs). MRS are constructed of commercial off the shelf (COTS) parts such as hermetic scroll compressors that are packaged, tested, and qualified for naval combatants. First generation MRUs operated with R-404A (GWP-3922) while the latest designs operate with R-407A (GWP-2107). MRS provides many benefits that include freeing up valuable machinery space, reduced life cycle costs, reduced refrigerant charge by about 90% and leakage from nominal 25-35% annual to less than 5%. The high maintenance burden and costs associated with legacy HFC-134a refrigeration systems has spurred backfit of MRS with the entire CVN-68 Class recently being converted as an example.

The PHA for Naval surface ship refrigeration systems filtered the 212 refrigerants listed in American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) Standard-34 [2022] down to 14 potential candidates with final selection of the three readily available refrigerants listed in Table 3 as the most suitable to replace the baseline R-404A and R-407A. Early analysis showed no benefit in converting legacy HFC-134a refrigeration systems to a low GWP refrigerant. Replacing the large legacy units with MRS is the better option with its many benefits including its return on investment (ROI).

Refrigerant	HFC	GWP	Intended Use
(Current Refi	rigerants	L
HFC-134a	100%	1430	Legacy distributed refrigeration systems
R-404A (HFC-12 5/HFC-143a / HFC-134a) (33%/52%/4%)	100%	3922	Used 1 st generation MRS
R-407A (HFC-32 /HFC-125 / HFC-134a) (20%/40%/40%)	100%	2107	Used 2 nd generation MRS
Low	er GWP Re	placement	s
R-407H (HFC-32 /HFC-125 /HFC-134a) (32.5%/15%/52.5%)	100%	1495	Possible drop-in replacement for R-407A depending on equipment.
R-449A (Chemours Opteon XP40) (HFC-32 /HFC-125/ HFO-1234yf/ HFC-134a) (24.3%/24.7%/25.3%/25.7%)	74.7%	1397	Possible drop-in replacement for R-404A and R-407A MRS depending on equipment
R-455A (Honeywell Solstice L40x) (CO ₂ / HFC-32/ HFO-1234yf) (3.0%/21.5%/75.5%)	21.5%	148	New MRS with flammable A2L approved hardware with operating pressures like R-404A & R-407A.

Гable 3 – Navy	Food	Storage	Refrigerants
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Note that per ASHRAE Standard 34 [2022], "Zeotropic blends shall be assigned an identifying number in the 400 series. Azeotropes shall be assigned an identifying number in the 500 series. To differentiate among blends having the same components with different proportions, an uppercase letter shall be added as a suffix in serial order of assignment." The saturated gas and liquid temperature (and pressure) for zeotrope's are not the same. The temperature when the zeotrope begins to boil is called the bubble point, and the temperature when it fully boils is called the dewpoint. The difference is called 'glide'. Some zeotrope blends have a very small 'glide' and those less than 0.56°F (1°C) such as R-404A are considered near-azeotropic, while R-407A and its replacements have much higher glides between 11°F (6.1°C) and 22.5°F (12.5°C). Azeotropes and near-azeotropes are preferred for chillers with large vapor space evaporators and condensers, but small refrigeration systems like MRS can accommodate larger glides.

Another property associated with zeotropes is fractionation and is the separation of the liquid blend based on the difference in the vapor pressures of the individual components. So, what leaks into the air, may not be the same blend composition as the liquid and likewise, leakage from the system can alter the liquid composition depending on where the leak occurs. Leakage from the liquid side of the process (downstream of the condenser) does not result in the bulk liquid fractionating, but leakage from the vapor side of the process (downstream of the evaporator) may fractionate. For these reasons, standard practice for zeotrope blends is not to top-off, but to remove and replace charge.

The PHA documents and assesses various risks associated with each alternative refrigerant and includes topics such as pressure vessel safety, flammability, toxicity, ignitions sources (and how they all relate to various leak and rupture events), material compatibility and performance both thermodynamic and life cycle climate. The PHA identified 57 risks, in which additional research and development (R&D), test and evaluation (T&E) and/or analysis is required to mitigate. It is intended to guide the Navy, providing a process that can be used to approve low-GWP refrigerants for shipboard use. The risk relationships are illustrated in Figure 2.





Pressure & Pressure Vessel Safety

The Navy when reviewing alternatives for refrigerant is concerned with the highest and lowest possible pressures. The highest pressure is established at a shutdown saturation pressure at 150 degrees Fahrenheit (°F), or 65.6 degrees Celsius (°C) in the event of a thermal event (fire or weapons effect). The lowest pressure is for freeze applications and is nominal -25°F (-31.7°C) and maximum -40°F (-40°C). A lesson learned from legacy HFC-134a (and the CFC-12 it replaced) refrigeration systems is that these large distributed systems will operate with many components and joints in a vacuum. These low side leaks allow air and moisture to be pulled into the system and are extremely detrimental creating a major maintenance and cost burden, especially as the systems age. The decision to convert the entire CVN68 Class to MRS is a prime example of the benefits.

Reviewing Table 4 (with HFC-134a listed for comparison), the pressure range of the R-400 series refrigerants is quite similar. The three candidates that were evaluated R-407H, R-449A and R-455A are all adequate for the intended purpose with no major impact except for the glide, and there are engineering guides on how to design to accommodate large glides. HoneywellTM in its guidelines for SOLSTICE® L40X (R-455A) [Honeywell, 2020] recommends the following:

Property	R134a	R404A	R407A	R407H	R449A	R455A
Molecular Weight (g/mol)	102.03	97.6	90.1	79.1	86.4	87.5
Saturation Pressure (Psat) -40°F (-40°C)	7.43 psia	19.0 psia	13.7 psia	13.0 psia	14.7 psia	14.1 psia
Psat -25°F (-31.7°C)	11.3 psia	25.5 psia	20.45 psia	19.49 psia	21.7 1psia	20.7 psia
Psat 150°F (65.6°C)	277.6 psia	469.7 psia	443.0 psia	433.3 psia	444.4 psia	416.9 psia
Glide	0.0°F	1.5°F	11.7°F	12.8°F	10.6°F	22.5°F
Specific Volume Liquid 122°F (50°C)	0.0145 ft ³ /lbm	0.0178 ft³/lbm	0.0158 ft³/lbm	0.0162 ft ³ /lbm	0.0166 ft ³ /lbm	0.0175 ft ³ /lbm

Table 4 – Refrigerant Properties

- Use only counter-flow or cross-counter-flow pattern in condenser and evaporator.
- When sizing evaporators, for the coil air to refrigerant temperature difference use the average refrigerant temperature between inlet and dewpoint. Sizing evaporators based on dewpoint will result in undersized evaporators.
- When sizing condensers, the condensing temperature should be the mean of bubble and dew temperature.
- When selecting compressors, for the evaporating side, use the mean temperature defined as 60% of dewpoint and 40% of bubble point temperature. For the condensing side, use the mean temperature defined as: 50% of dewpoint and 50% of bubble point temperature. Using dewpoint temperature leads to oversized compressors.

Additionally, the specific volumes of the candidates R-407H, R-449A and R-455A are similar enough that with the very small charge (8 - 14-lbs) no major change in refrigerant charge is expected and subsequently size of accumulators/receivers and onboard spare refrigerant storage is not affected.

Fire & Toxicity Safety

ASHRAE Standard 34 [2022] classifies the safety aspect of different refrigerants with a capital letter and a number. The first capital letter (A or B) classifies toxicity. "A" being less toxic and "B" being more toxic. Next is a number from 1 to 3 designating flammability with "1" being non-flammable, "2" being flammable and "3" being extremely flammable. Subclass 2L was added, which designates mildly flammable with details specified in Table 5.

Fable 5 -	- Refrigerant	A2L	Flamma	ability
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Parameter	Definition
Test	Exhibits flame propagation when
Condition	tested per ASHRAE-STD-34 at 60°C
	(140°F) and 101.3 kPa (14.7 psia),
	and at 50% relative humidity at 23°C
	(12°C dew point) and:
Lower	$> 0.10 \text{ kg/m}^3$ (0.0062 lb/ft ³), and
Flammable	
Limit (LFL)	
Heat of	<19,000 kJ/kg (8169 BTU/lbm) and
Combustion	
Burning	≤ 10 cm/s (3.9 in/s) when tested at
Velocity	23°C (73.4°F) and 101.3 kPa (14.7
	psia)

An overview of the ASHRAE Standard 34 classifications of the three evaluated low GWP refrigerants along with R-407A (for comparison) and R-454C are summarized in Table 6.

Table 6 – Refrigerant Safety Characteristic

ASHRAE #	ASHRAE Class	ASHRAE OEL ⁽¹⁾ (ppm)	ASHRAE RCL ⁽²⁾ (ppm/%)	UFL/LFL ⁽³⁾ (%)
R-455A	A2L	650	22,000 (2.2%)	12.9/ 11.8
R-454C	A2L	620	19,000 (1.9%)	<15/ 6.3
R-449A	A1	840	100,000 (10%)	na
R-407H	A1	1,000	92,000 (9.2%)	na
R-407A	A1	1,000	83,000 (8.3%)	na
Notes:				

(1) OEL = Occupation Exposure Limit

(1) OLD OCCUPATION EXPOSITIVE Dimit
 (2) RCL = Refrigerant Concentration Limit

(3) UFL = Upper Flammable Limit / LFL = Lower Flammable

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Limit				

Ideally, refrigerants with a safety group designation of "A1" and high exposure limit have been preferred. R-454C (ChemoursTM Opteon XL20) with GWP-149 is essentially a variation of R-455A. It does not contain any CO_2 and the concentration of HFO-1234yf is 3% higher. For flammable refrigerants, ASHRAE sets the refrigerant concentration limit (RCL) to 25% of the lower flammable limit (LFL). The RCL is defined as the refrigerant concentration limit in air, determined in accordance with ASHRAE-34, intended to reduce the risks of acute toxicity, asphyxiation, and flammability hazards in normally occupied, enclosed spaces. The RCL of R-455A is considerably less than 25% of its reported 11.8% LFL. The reason is likely to account for fractionation. For the PHA, the LFL was assumed equal to 6.3% and therefore essentially analyzed both R-454C and R-455A.

Industry testing has shown that the flammability of A2L HFO refrigerants increases with humidity. Navy machinery spaces are typically not air-conditioned but are cooled by ventilation with outside ambient air, and which the humidity levels are often far greater than the ASHRAE standard fire test condition. However, for MRS applications, except for the chilled water cooled, flat-plate condenser, all other refrigerant components are located inside the refrigerated storage space and therefore significant change in flammability characteristics for MRS applications is not expected. The combination of very small charge (8 to 14-lbs), the controlled environment of the refrigerated storage space and the absence of numerous ignition sources significantly mitigates the hazard associated with using an A2L flammable refrigerant in MRS applications. This is not the case for Navy chiller applications in which a large leak has a risk of a vapor cloud explosion due to the semi-confined, Naval machinery space with large refrigerant charge versus compartment volume [Frank, Spector and Antin, 2023].

ASHRAE Standard 15 [2022] 0 specifies numerous requirements when using an A2L refrigerant. For MRS, compliance would not be very difficult. Manufacturers are now producing refrigerant equipment qualified for A2L refrigerants. Additionally, MRS is controlled by a programmable logic controller (PLC) so that

integration with a new refrigerant compartment leak monitor (RCLM) would be easy. The new RCLM would as previous models monitor small leakage using traditional gas sampling with a non-dispersive infrared (NDIR) sensor but incorporate the newly developed remote microelectromechanical system (MEMS) sensors for very high concentrations that meet ASHRAE STD-15 response requirements. The Navy would require the PLC and RCLM be mostly passive. It would incorporate all applicable sensor and time response features minus active control, delegating active control to certified supervisory systems such as the ship's Machinery Control System due to cybersecurity concerns.

As shown in Table 6, the exposure limits for the candidate Low-GWP refrigerants as specified in ASHRAE Standard 34 are 16% to 35% less than legacy HFCs and may not have the same margin of chronic toxicity safety. However, for MRS, the very low expected leakage of less than 5% per year combined with the very small charge, and the limited exposure combined with a new RCLM should mitigate significant human health safety concerns. But a ship at sea for months can present a workplace exposure very different than the standard 8-hours per day, 40-hours per week. Industrial Hygiene and Occupational Toxicology staff with the Navy and Marine Corps Force Health Protection Command would be requested to review all pertinent toxicity data and potentially establish Navy Occupational Exposure Limits (OEL) if necessary.

Simplified models were developed to evaluate refrigerant leakage and levels in a space using representative minimal and maximum ventilation rates during a small leak and pressure boundary failure. This analysis was performed to determine the expected concentrations from these events and the time experienced in the flammable zone, in which the refrigerant concentration is between the lower and upper flammable limits. In general, from an acute toxicity perspective, the lower GWP fluorinated refrigerants do not present substantially greater risk than already presented by R-404A or R-407A. The toxicity risk is mitigated by refrigerated storage spaces being monitored for refrigerant leaks, being single level, not continuously manned, and having easy egress paths.

Analysis of R-455A (and R-454C) indicated that for the 0.75-Ton MRS with 8-lbm charge used in smaller storerooms, a 50-micron defect leak would not raise the space to the LFL (set at 6.3%) when fully packed. This assumed a very low ventilation rate (1-scfm) when accessed and the space was accessed once every 3.33-hours for 40-minutes and is shown in Figure 3 with the LFL shown as the highest dotted line. The different leak rates reflect the different possible operating temperatures and pressures with the lowest at minus 20°F (-28.9°C) and the highest at 68°F (20°C).



Figure 3 - R-455A Build-Up from 50-Micron Leak

In the event of a closed storeroom and pressure boundary failure, modeled as a defect of 0.0625in (1/16"), the total charge is quickly released, and with the door shut, the space will quickly reach the flammable zone. Once the door is opened and nominal ventilation provided (modeled as 27-scfm), the space is quickly ventilated as shown in Figure 4. To mitigate the hazard, a new RCLM with new high range sensors would trigger the appropriate actions for alarms and to secure power to the MRS.



Figure 4 – R-455A 0.625" Pressure Boundary Failure

So, unlike chillers, where the use of flammable refrigerant is dangerous, for MRS, the use of an A2L mildly flammable refrigerant is technically acceptable with the appropriate engineering, operating and maintenance procedures and crew training. Ultimately, for any new design, the Navy's standard process requires the requisite analysis, research, and testing to provide maximum reasonable assurance of ship and crew safety during normal operation, but also in the event of a casualty.

Material Compatibility

In general, the low-GWP fluorinated refrigerants are expected to behave like R-404A and R-407A. Unlike chillers that are large custom designs with service life of 35+ years with routine maintenance and repair performed, MRS is COTs and essentially maintenance free with limited use of non-metallic material. So, while material compatibility for chillers is a major naval technical authorities (NTA) concern, for MRS, the NTA defers to the commercial sector. The Air-Conditioning, Heating and Refrigeration Technology Institute. (AHRTI) as part of its in-depth low-GWP test program has performed extensive oil compatibility testing of many low GWP refrigerants including R-454C and R-455A [Kutak et al, 2022]. The key component for MRS is the compact hermetic compressor and most manufacturers such as Copeland[™] have published data for using their equipment with the new low GWP refrigerants.

In summary, from a material compatibility perspective there is negligible risk with using the new low GWP refrigerants.

Modeling of Navy's MRS

Using a combination of compressor manufacture web-based models and the Navy's own refrigerant compressor modeling program that calculates thermodynamic properties using NIST Reference Fluid Thermodynamic and Transport Properties (REFPROP) [Lemmon, 2018], the thermodynamic performance of low-GWP candidate refrigerants with MRS was evaluated. The highlights are as follows:

- Power efficiency associated with refrigeration for purposes of reduced CO₂ emissions is mostly inconsequential when compared to the impact from refrigerant leakage. Space considerations are very important, and it is important that any refrigerant changes maintain similar space constraints, even at the expense of slightly higher energy usage.
- Analysis of the boiling and condensing heat transfer coefficients [Thome, 2006] indicated that existing MRS heat exchangers operating with R-404A or R-407A should function acceptably with the new low GWP refrigerants.
- All low GWP ASHRAE A1 candidate refrigerants such as R-407H (including R-407F) and R-449A (including R-448A) perform worse than R-404A due to increased motor power. But the difference is relative and well within design boundaries such that no major increase in MRS form, fit or function.
- The overall performance superiority of R-449A plus its HFC composition reduction (25.3%) in comparison to R-407H precludes R-407H as an acceptable replacement of R-404A or R-407A.
- From an overall performance perspective ASHRAE A2L R-455A has the best overall performance for refrigeration capacity as shown in Figure 5. Additionally, R-455A

comprises only 21.5% HFC (HFC-32) representing a 78.5% reduction in HFC.



Figure 5 - Cooling Capacity 45°F Condenser Water – 500-ft³/hr Scroll

- All low GWP ASHRAE A1 candidate refrigerants to replace R-404A will likely require new compressors with liquid injection or economizer vapor injection to control compressor discharge temperature. These low-GWP refrigerants operate with higher discharge temperatures. R-449A may be a drop-in replacement to the few R-407A MRS designs currently using economizer vapor injection. However, the new compressors with modifications for discharge temperature control should fit within the MRU space envelope.
- Analysis indicates that conversion of MRUs to low GWP refrigerants R-449 and R-455A (and similar) should fit within the current shipboard envelopes.

Life Cycle Climate Performance

Life Cycle Climate Performance (LCCP) is an evaluation method to evaluate the global warming impact from manufacturing to disposal. This method analyzes direct emission of refrigerants to the atmosphere through its service life from leaks, servicing, and disposal. It also analyzes indirect emissions from CO₂ that are emitted by generating the electrical power to drive the equipment over its lifetime. The analyses become complex as Navy ships are generally powered by shore power supplied from the electrical grid when in-port and reliant on shipboard power plants at sea. LCCP can also include embodied emissions to capture the global warming effects of manufacturing, transport, installation, and disposal of the equipment. The lower the LCCP is, the better it is for the environment. For simplicity, LCCP was calculated based on direct emissions from leakage and indirect emissions from energy (fuel) consumption. Modeling of annual leakage was performed [Anderson et al, 1994], [ANSI 2022] and Figure 6 shows the defect size to cause a 0.5 ounces per year (limit for leakage from a new joint). The difference between R-404A and R-407A and the other low-GWP various refrigerants is mostly a combination of the different molecular weights and operating pressures shown in Table 3. However, for MRS with its very few mechanical joints, no in-line valves and no mechanical gauges the difference is not very dramatic, likely a change from 1 to 1.5% of the charge per year. In comparison a small legacy 1.5-Ton HFC-134a system with a condensing unit having 52 valves, 7 electro-mechanical pressure switches and 10 mechanical gauges can leak about 25% per year while a larger legacy HFC-134a refrigeration systems leaks as much as 35% per year.





Energy usage for refrigeration systems is a relatively simple calculation since refrigeration systems operate at near constant hours per day, with legacy HFC-134a at 18-hrs/day and MRS at 22-hours/day. Very simply, the climate benefits of any MRS design (including R-404A) with significantly reduced charge and low emissions designs is significantly better than the legacy distributed HFC-134a systems; with at least 35% reduction in GHG emissions for a large ship such as an LHD and at least 60% reduction for a small ship such as a DDG as shown in Figure 7. Beyond the current R-407A, conversion to R-449A or R-455A yields little climate benefit other than reduced HFC reliance due to slightly higher electrical power requirements. The Navy should prioritize funding and in-service resources to complete the conversion of ships to MRS for its many benefits including an ROI.



Figure 7 – GHG Emissions Comparing Legacy HFC-134a with MRS

NEXT STEPS FOR THE FUTURE

Between Federal regulations and individual State regulations along with what the European Union is implementing, the global refrigeration market is in flux. In the MRS equipment sizes of 0.75-Ton and 1.5-Ton, the equipment manufacturers are all developing components that can operate with either A1 or A2L refrigerants, likely discontinuing many legacy components with form and functional replacements. The Navy can design the MRS to accommodate several refrigerant alternatives. The programmable logic control (PLC) based control system should make this relatively easy. The key component is a reliable electronic expansion valve. The MRU would be qualified for use A1 and A2L refrigerants such as R-454C and R-455A. The PLC would have the option to select from a list of authorized refrigerants, which would then load the applicable operating controls and set points.

The MRS business model assumes periodic overhaul based on the approximate 7-to-10-year service life of the COTs disposable hermetic compressors. Additionally, most MRUs are designed to be relatively easy to remove from the ship for overhaul, and the skillset necessary for overhaul is easily within that of the commercial sector. Assuming all MRS would be converted to universal refrigerant designs, there are various options for Fleet implementation as listed in Table 7.

I able / - L	ow GWP MIKS Fleet	t Implementation
Fleet Implementa tion	Options	Risk
New Construction MRS A2L low GWP	Install during new construction or if backfit replace HFC-134a, during a major availability.	 Low schedule risk. Installing Activities will need time to adapt and train with the new requirements for A2L refrigerants. Backfit to Ships with legacy HFC-134a will realize many benefits along with an ROI.
In-Service MRS A1 low GWP	Option 1: Convert by Attrition: Shop convert existing MRS to universal design during routine overhaul and once the ship has a full complement of converted MRUs, then change the ship to Low GWP refrigerant.	 Logistics and staffing are required to continuously monitor the status of MRUs on each ship. Limited climate CO₂ emissions benefit and no ROI.
In-Service MRS A1 low GWP	Option 2: Convert all existing MRS to A1 low GWP during Extended Availability Have a rotating pool of converted universal MRS – full shipset ready to install to expedite schedule	 Lowest schedule risk with least amount of after install logistics and staffing required. Monitor using a simple spreadsheet like was used by the Navy Chlorofluorocarbon (CFC) Elimination Program. Limited climate CO₂ emissions benefit and no ROI.
In-Service MRS A2L low GWP	Option 3: Convert all existing MRS to universal design and A2L low GWP during Ship Overhaul: Have a full shipset of universal design MRUs and new Refrigerant Compartment Leak Monitor Systems ready to install.	 Task may be similar in scope to converting from legacy HFC-134a to MRS. The MRU change-out should be drop-in but the new monitor system and its new ship damage control/machinery control interface may be the time-consuming portion. Installing Activities will need time to adapt and train with the new A2L refrigerant requirements. Limited climate CO₂ emissions benefit and no ROI.

Table 7 – Low GWP MRS Fleet Implementation

WHAT ABOUT R-744/CO₂?

R-744/CO₂ is reemerging as a credible very low GWP (GWP = 1) natural refrigerant, especially for refrigeration, and especially for systems such as MRS that have condensers cooled by chilled water. But CO₂ is a far greater technical challenge than fluorinated refrigerants requiring additional engineering expertise to incorporate additional components of greater complexity with more complex controls. The toxicity and pressure safety aspects of CO₂ are far more complex than fluorinated refrigerants.

First, CO_2 is an asphyxiant, but not like nitrogen. At concentration greater than 14%, which would only dilute the oxygen level to about 18%, CO_2 can be lethal in 1-minute. Accidental discharge of CO_2 flooding fire extinguishing systems have resulted in many injuries and deaths [EPA, 2000].

CO₂ can exist in many different states as shown in Figure 8. What is not shown is that when supercritical, it is no longer possible to differentiate between the liquid and gas phase. Furthermore, the solid, liquid and gas phase will coexist in equilibrium at the triple point. In the supercritical state, it becomes a super-dense fluid with very low surface tension and very high pressures. At -25°F, the pressure is 181 psig, and at the critical point of 87.76°F, the pressure is 1054.4 psig.



An R-744/CO₂ MRS is going to leak. The defect size for CO₂ to leak 0.5-ounces per year at 68°F (20°C) is 1.22-microns and much smaller compared to HFCs in Figure 6. Routine recharging of CO₂ as frequent as quarterly or even monthly will likely be normal.

ASHRAE STD-15 addresses some design aspects for R-744/CO₂ but only for subcritical operation, deferring to engineering analysis for supercritical applications. The American Petroleum Institute (API) has design details for supercritical CO₂, such as how to size safety relief valves. An improperly sized relief valve and associated piping fouled by dry-ice will render overpressure protection useless. When CO_2 is released, it expands twice as much as fluorinated refrigerants, and this may affect structural integrity in the event of pressure boundary failure. NFPA-12, Standard on Carbon Dioxide Extinguishing Systems [2022] does state: "A.5.6.2 Porosity and leakages such as at doors, windows, and dampers, though not readily apparent or easily calculated, have been found to provide sufficient relief for the normal carbon dioxide flooding systems without need for additional venting. Record storage rooms, refrigerated spaces, and ductwork have also been found to need no additional venting when tested under their average system conditions." However, the Fire Industry Association (FIA), [2012] presents a detailed calculation method to determine the required vent area for "non*liquefiable gases and CO_2*". But there is some uncertainty with the structural strength of new shipboard modular panel designs, used for fabricating insulated storerooms.

 CO_2 pressure vessels (and very large CO_2 pipes associated with CO_2 capture) are at risk for boiling liquid evaporating vapor explosion (BLEVE). In the event of a pressure boundary failure, the rapid drop in pressure can causes the liquid to expand extremely rapidly, potentially resulting in an explosion. Proper design of pressure vessels and relief valves mitigates the risk of BLEVE. With all these complexities, beyond the 'natural' environmentally unregulated refrigerant attribute, what makes CO₂ attractive as a refrigerant is exemplified by Figure 9. The theoretical volumetric capacity of CO₂, its heat transfer capacity per volume, is huge. However, this attribute will be difficult to carry over to the system; for instance, the evaporator size will be constrained by airside heat transfer rates with fin spacing to accommodate ice formation.



Figure 9 – Volumetric Capacity

The refrigerant charge for CO₂ is less than fluorinated refrigerants and the components and piping/tubing may be smaller in flow diameter somewhat offsetting the increased wall thickness to accommodate the much high operating pressures. Additionally, R-744/CO₂ is nonflammable, it neither combusts nor does it thermally decompose to any toxic corrosive byproduct below temperatures of about 5000°F.

Feasibility of R-744/CO₂ for potential use in a naval MRS application is being investigated using the PHA process. Thus far, results are positive. Several concerns are listed as follows

 A CO₂ MRS would need to be designed for transcritical operation to account for shutdown conditions as well as transients that are inherent to a Naval combatant. Compact transcritical compressors are commercially available but they are two and four-cylinder reciprocating designs. These are larger and heavier by about 300% and are mounted horizontally versus scroll compressors that are mounted vertically.

- Unlike scroll compressors, reciprocating compressors are less tolerant of liquid flood back; control software must be implemented to prevent this condition to ensure system reliability without maintenance burdens. This becomes a challenge when addressing causalities such as loss of electrical power, loss of chilled water, etc.
- Additionally, not less than two and as many as four electronic/motorized valves would be required. During any transcritical operation, the condenser becomes only a gas cooler. An intermediate expansion valve is used to decrease pressure so that the cooled CO₂ gas decreases in pressure enough to change into a liquid.

Fortunately, most of the necessary components are COTs. The main challenge is packaging to meet military requirements within allocated space/weight constraints. The fiscal reality is that an R-744/CO₂ MRS is going to cost more to purchase and it's going to cost more to maintain and will require specialized training. The benefit of CO₂ is that it's a reasonably safe, an environmentally unregulated compatible refrigerant and eliminates recovery equipment associated with HFCs. These benefits should provide a compelling argument for its use. However, developmental prototypes are necessary to understand all of the variables required for a CO₂-MRS to be successful shipboard.

CONCLUSIONS

The heating, ventilation, and air conditioning (HVAC) industry is in the middle of another major refrigerant transition. However, unlike the relatively orderly transition from ozone depleting substances to HFCs, and the near universal selection of HFC-134a, the transition to low-GWP refrigerants is far more complex. The wide variety of alternatives, each with its own benefits and trade-offs, must be critically evaluated for every application. Further analysis and testing will be required to mitigate individual risks. Some of the main findings for

Navy refrigeration systems and specific to MRS are specified below.

- A universal MRS capable of operating with a variety of fluorinated refrigerants including A2L refrigerants is strongly recommended.
- Absent an R-744/CO₂ MRS, any fluorinated refrigerant for MRS with GWP 300 and less is going to be flammable. Use of an A2L mildly flammable refrigerant for small charge MRSs may be technically acceptable. It can be done safely with detailed engineering, operating/maintenance procedures, and training. While failure to adhere to these attributes is unlikely to cause catastrophic ship damage, damage, and personnel injury or death is possible.
- Use of many different refrigerants in the Fleet presents the same challenge that industry is facing regarding personnel training. Aligning MRS with the commercial sector provides the opportunity for the commercial sector to train Navy personnel. Numerous online training opportunities are being released from reputable organizations such as the AHRI webinar discussing Servicing of A2L refrigerants [AHRI, 2021]0.

The Navy, like the commercial industry and other DoD agencies, is diligently working to find safe, effective, and practical solutions to the global phase-down of HFCs and its corresponding reduction of GWP. The Naval Technical Authorities have established extraordinarily high-quality assurance criteria for acceptable alternatives. In the end, these values are used to protect high value tactical and strategic platforms and systems whose failure could risk National Security, result in serious injury or death to military personnel, or have unintended consequences to civilian populations and the environment.

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