ARE FLUORINATED REFRIGERANTS NEEDED — WILL "NATURAL" REFRIGERANTS SUFFICE?

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Abstract: This paper addresses the historical need for and introduction of fluorinated refrigerants to replace what were then largely "natural" refrigerants. It discusses the heretical question of whether there even are "natural" refrigerants, as contrasted to synthetic but nonfluorinated or more broadly nonhalogenated refrigerants. The paper outlines the successive refrigerant generations, with chemically delineated shifts, from nonfluorinated — use of which continues — to chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) to hydrofluorocarbons (HFCs) to unsaturated HFCs (hydrofluoro-olefins or HFOs) and probably also unsaturated HCFCs (hydrochlorofluoro-olefins or HCFOs). It raises questions on long-term acceptability of them. It briefly explores whether improved manufacturing of components and equipment for air-conditioning and refrigeration systems changes matters. The paper concludes that different needs will require continued use of both nonhalogenated options (notably ammonia, hydrocarbons, and carbon dioxide) and halogenated options with demand for improved efficiency from both.

Keywords: refrigerants, progression, transitions, outlook, historical, natural, fluorinated, unsaturated

1. INTRODUCTION

With recent introduction of yet another class of refrigerants, unsaturated halochemicals, it seems timely to ask two questions. First, is this generation likely to end the periodic churning in refrigerants or be short lived? Second, do we need the new options at all or can we revert to exclusive use of "natural" refrigerants?

2. PROGRESSION IN REFRIGERANTS

2.1 Early Refrigerants

Early references to *coolants* and *refrigerants* (dating back to ancient Egyptian history) were not refrigerants as we know them, but instead fluids (such as water) that provided a cooling effect when evaporated from mats or the skin. The primary method of early cooling for food preservation was use of stored or transported natural ice [1,2]. Oliver Evans proposed the use of a volatile fluid in a closed circuit to freeze water into ice in 1805, but there is no record that he built a working machine [3]. An 1834 patent by Jacob Perkins describes a cycle using a "volatile fluid for the purpose of producing the cooling and freezing … condensing such volatile fluids … and bringing them into operation without waste" [4].

Surprisingly, the first refrigerant actually used in a vapor-compression refrigerant machine was itself a *substitute refrigerant*. Perkins designed the machine to use sulfuric (ethyl) ether, which had not arrived when the apparatus was ready for testing [5]. His assistants, therefore, ran the initial tests with caoutchoucine (a distillate of natural rubber) from Perkins' work as a printer based on the cooling effect felt when it evaporated from their hands. Most of the early refrigerants that followed were volatile fluids familiar to early practitioners from other uses, such as common solvents, other workplace chemicals, and even fuels [6].

2.2 "Natural" Refrigerants

As the first century of mechanical refrigeration progressed, R-717 (ammonia) emerged as and remains today one of the most common industrial refrigerants, especially in the food and beverage industries. Hydrocarbons came into use, and R-290 (propane) in specific was marketed as the "safety refrigerant" because, though highly flammable and explosive, it had neither noxious odor nor problematic toxicity concerns [7]. Nonflammable — and even a suppressant — R-744 (carbon dioxide, CO_2) began use in industrial refrigeration, primarily to produce ice to cool foods during shipping by train and boat. Recent focus on R-744 as a refrigerant includes application in heat pump water heaters for domestic service water use. Not surprisingly, many early refrigerants were what today might be classed as "natural" based on occurrence in nature.

Refrigeration, however, is not natural per se. It is manipulating heat to achieve a cooling effect (heat removal) for comfort, process, or similar uses or to boost heat from low temperature with a heat pump for benefi-

cial use at elevated temperature(s). Under natural conditions, heat (thermal energy) flows in the warmer (higher energy potential) to cooler (lower potential) direction. Whether provided by a vapor-compression, absorption, magnetocaloric, thermoacoustic, or other thermodynamic cycle or process, the direction of heat movement in refrigeration (including in heat pumps) is the opposite, from colder to warmer. The working substance used to reverse the normal flow of heat by thermodynamic manipulation is the refrigerant.

"Natural" refrigerants still move heat in an unnatural direction, but refer to a class of chemicals that occur in nature though some such chemicals are not pursued. R-40 (methyl chloride) is a naturally occurring substance first used as a refrigerant as early as 1878 and widely used in the 1920s and 1930s.[*] It later resurfaced in the 1940s due to wartime shortages of R-12 and in recent years as a dangerous (and often illegal) blend component. R-40B1 (methyl bromide) also saw limited refrigerant use in the late 1930s and 1940s (and more so as a fumigant and pesticide), but its refrigerant use was terminated due to its high toxicity. Both R-40 and R-40B1 are naturally occurring substances, but also major contributors to natural ozone depletion.

Most "natural" refrigerants are not found at sufficient purity or quantity to be directly harvested for use. Instead, they are chemically synthesized. Even then, they typically require further processing to achieve the purity requirements of refrigerants. R-717 (ammonia), for example, is a widely manufactured chemical, typically by a Haber-Bosch process, though mostly for fertilizer use. R-600a (isobutane) now prevalent in domestic refrigerators — notably so in Europe — and R-600 (n-butane) are constituents in natural gas (extracted petroleum gases), but require separation commonly by distillation in fractionating towers. R-704 (helium), used in cryogenics and (along with other options) in Stirling and thermoacoustic cycles, and R-744 (carbon dioxide, CO_2) likewise require industrial separation. The most abundant natural refrigerants, R-718 (water) and R-729 (air), enjoy limited but disparate use. R-718 is the most common refrigerant in large absorption chillers using lithium-bromide (and formerly also but now uncommonly lithium-chloride) solutions as absorbents. Water also is used in smaller absorption equipment (most notably small hotel-room and minibar refrigerators), but as the absorbent with R-717 (ammonia) as the refrigerant. Use of R-729 (air) via Brayton cycles, once more common particularly in aircraft cooling, has fallen but enjoys periodic re-examination in applications such as deep-mine cooling, for which the air also provides ventilation.

Surprisingly, there is no record of a systematic screening of refrigerant candidates until near the end of the first century of mechanical refrigeration. Willis H. Carrier and R. W. Waterfill documented a detailed investigation in 1924 for use with both positive-displacement and turbo-compressors [8]. Their analyses

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[*] Historical accounts from the 1700s that identify methyl chloride as a "refrigerant" refer to use as an anesthetic for amputations, based on evaporative cooling.

Table 1. Historical introduction of refrigerants [6]		
year	refrigerant (/absorbent)	chemical formula or makeup
1830s	caoutchoucine	distillate of india rubber
	sulfuric (ethyl) ether	$CH_3-CH_2-O-CH_2-CH_3$
1840s	methyl ether (R-E170)	CH_3-O-CH_3
1850	water / sulfuric acid	H_2O / H_2SO_4
1856	ethyl alcohol	CH_3-CH_2-OH
1859	ammonia / water	NH_3 / H_2O
1866	chymogene	petrol ether and naphtha (hydrocarbons)
	carbon dioxide	CO_2
1860s	ammonia (R-717)	NH_3
	methyl amine (R-630)	$CH_3(NH_2)$
	ethyl amine (R-631)	$CH_3-CH_2(NH_2)$
1870	methyl formate (R-611)	$HCOOCH_3$
1875	sulfur dioxide (R-764)	SO_2
1878	methyl chloride (R-40)	CH_3Cl
1870s	ethyl chloride (R-160)	CH_3-CH_2Cl
1891	blends of sulfuric acid with hydrocarbons	H_2SO_4, C_4H_{10}, C_5H_{12}, $(CH_3)_2CH-CH_3$
1900s	ethyl bromide (R-160B1)	CH_3-CH_2Br
1912	carbon tetrachoride	CCl_4
	water vapor (R-718)	H_2O
1920s	isobutane (R-600a)	$(CH_3)_2CH-CH_3$
	propane (R-290)	$CH_3-CH_2-CH_3$
1922	dielene (R-1130)[a]	$CHCl=CHCl$
1923	gasoline	Hydrocarbons
1925	trielene (R-1120)	$CHCl=CCl_2$
1926	methylene chloride (R-30)	CH_2Cl_2
[a] blend of *cis-* and *trans-*1,2-dichloroethene isomers		

closely examined R-717 (ammonia), ethyl ether, R-744 (carbon dioxide, CO_2), R-10 (carbon tetrachloride), R-764 (sulfur dioxide), R-718 (water), and others. They found, among other conclusions, that the performance of carbon dioxide would depend on the cycle, and amount of liquid subcooling, but still yields the lowest predicted performance of the fluids analyzed. They also noted that water "gives a low efficiency of performance" and that, for the turbo-compressor option, both ammonia and water would require excessive stages of compression at the conditions needed. They dismissed carbon tetrachloride because it attacks metals, especially in the presence of water, and sulfur dioxide for safety reasons.

So when we now think of "natural" refrigerants as new or at least underutilized alternatives, they have been used almost since the beginning of mechanical refrigeration. Table 1 summarizes the historical introduction of first-generation refrigerants, preceding the advent of fluorochemicals.

2.3 Successive Generations of Fluorinated Refrigerants
As refrigeration use expanded, R-717 (ammonia) became and remains prominent in industrial systems and especially so in food and beverage preparation and storage. R-40 (methyl chloride) came into broad use in building cooling central systems with refrigerant piped to individual apartments. Recurring fires ended such use [for example, 9] and interestingly repeated with recurrences in recent illicit trade [10-13]. Domestic refrigeration (household refrigerators to replace "ice boxes" for home food and beverage preservation) gained rapid popularity in the 1920s but then stalled with consumer responses to refrigerant leaks. As refrigerator use approached a million units in the USA, R-611 (methyl formate, "H-Cooch" from its chemical formula $HCOOCH_3$) and R-764 (sulfur dioxide) emerged as the primary refrigerants. R-611, however, is highly flammable, harmful to the eyes, and toxic if inhaled or ingested, while R-764 is corrosive to the eyes and may cause loss of vision as well as painful skin burns and lesions. Leaks were frequent based on the manufacturing technologies of the time.

The sales impacts forced a second systematic search in 1928 by Thomas Midgley, Jr., with a simple directive that "the refrigeration industry needs a new refrigerant if they expect to get anywhere" [14]. Finding inadequate and suspect data in chemical references, Midgley turned to the periodic table of the elements to identify potential constituents and found eight. All refrigerants then used — in fact all included in Table 1 above — comprised just seven, notably excluding fluorine. Within three days, Midgley and his colleagues Albert L. Henne and Robert R. McNary systematically screened the chemical combinations of the eight elements. They developed both a numbering system (still used) — to ensure that no candidates were overlooked — and essential insights into molecular-composition tradeoffs [15]. The effort led to commercial introduction of R-12 in 1932 and R-11 in 1933, the beginning of chlorofluorocarbon (CFC) usage [16,17].

The key to the second generation of refrigerants, then, was safety and durability afforded by high chemical stability, both outside and inside the system. Additional CFCs came into use in subsequent years as did hydrochlorofluorocarbons (HCFCs), most notably R-22 in 1936. Its use grew in the late 1940s and early 1950s especially for the expanding residential air conditioner market as housing construction increased in southern states of the USA and later in Japan, both with warm climates. R-22 eventually displaced R-12 as the most common refrigerant.

Midgley and his cohorts also identified hydrofluorocarbons (HFCs) as having promise, though subsequent examination led to initial HFC avoidance as immiscible with the mineral oil based refrigeration lubricants then common. Other lubricants were available, notably for use with R-717 (ammonia), but deemed less effective and the combination with HFCs was more expensive at the time. Some HFCs gained acceptance as refrigerant blend components, notably R-152a in R-500 (R-12/152a (73.8/26.2)) first commercialized in the 1950s based on suitability with mineral oils and higher capacity in some uses than R-12 alone.

One of the ironies of refrigerant progressions is that initial connection of CFCs to stratospheric ozone depletion came about based on their very high chemical stabilities, resulting in long atmospheric lifetimes sufficient to survive transport times to high altitudes. Once above the "ozone layer," photolysis of the CFCs liberates chlorine radicals (Cl^-) that react catalytically in ozone destruction reactions. Atmospheric scientists had posited that emissions of nitrous oxide (N_2O), produced by soil bacteria and emissions from supersonic passenger aircraft, could yield nitric oxide (NO) in the stratosphere leading to ozone decomposition. Others had shown that Cl^- was even more efficient than NO at catalyzing destruction of ozone. The origin of chlorine in the stratosphere remained elusive, and some scientist even thought it might be hydrochloric acid (HCl) emissions from the Space Shuttle. These sources were deemed insufficient to explain observed trends in stratospheric ozone. F. Sherwood (Sherry) Rowland and Mario Molina, his postdoctoral research associ-

ate, first connected CFCs to ozone depletion in late 1973 and published a seminal analysis in early 1974 warning of the impacts of increasing CFC releases. Rowland had attended an atmospheric science conference where he discussed his need for a very stable tracer gas not prevalent in the atmosphere — not naturally occurring to avoid stray readings — to calibrate his models of nuclear plume transport with sampling measurements. CFCs came up in the discussions. En route home, he became curious about the ultimate fate of such compounds and suggested further investigation to Molina [18]. The rest is well-documented history and, like the earlier Midgley study, fell into place very quickly once the right questions were asked. So the irony is that CFCs and other halogenated (with bromine and to a lesser extent iodine) organics both came into use and later were phased out predicated on the consequences of their inherent high stability.

The primary substitutes beginning in late 1989 and the 1990s, with phase out of CFCs to protect stratospheric ozone, were HFCs and blends thereof including with hydrocarbons, R-E170 (dimethyl ether), HCFCs, and others. The stability and resulting long atmospheric lifetimes (atmospheric persistence) combined with their infrared absorption properties made HFCs greenhouse gases, some with high global warming potentials (GWPs). HCFC R-123, having very low ozone depletion potential (ODP) and GWP coupled with high performance, gained wide but still transitional use in the 1990s, notably to replace R-11 (a CFC) in centrifugal chillers.

To some extent, refrigerants — or at least HCFC refrigerants with much lower ODP — were victims of other applications of the same chemicals. The strategy of the Montreal Protocol [19] of 1987 was "step down" and later phase out predicated on defined schedules of ozone depleting substances regardless of use other than as feedstock. The Copenhagen Amendments in 1992 added HCFCs (or more accurately enumerated HCFCs). Examination of the two most widely used HCFC refrigerants, the ubiquitous R-22 and less common R-123 (used only in larger centrifugal chillers) showed that their continued use, solely as refrigerants and with care for avoidable leakage reduction, would have no discernable impact on stratospheric ozone [20,21]. The key distinction from other applications of the same chemicals is that refrigerant use (except in Brayton cycles) is inherently non-emissive. Loss minimization from leakage and service actually is essential to maintain both capacity and efficiency and to reduce replacement costs. In contrast, aerosol propellants require emission for use and emission avoidance from fire suppressant, solvent, and foam-blowing uses is impractical.

2.4 New Focus on Unsaturated Compounds

Further focus on greenhouse gas emissions pursuant to the Kyoto Protocol [22], anticipated amendments thereto, and both regional and national regulations is now forcing a further transition. The latest shift is to low-GWP refrigerants, primarily unsaturated fluorochemicals along with continued use — and potentially increased use — of low-GWP non-halogenated ("natural") refrigerants. The short-lived unsaturated halochemicals, primarily unsaturated HFCs also dubbed hydrofluoro-olefins (HFOs), previously were avoided because their lower stability raised concerns of suitability, compatibility, toxicity, and flammability. Also, higher manufacturing and handling costs, including steps to achieve and maintain chemical, isomeric, and even stereo-isomeric (enantiomeric) purity, made them expensive and uncompetitive.

Unsaturates actually have a long chemical history including limited use as refrigerants. The 1924 study by Carrier and Waterfill, addressed above, concluded with selection of R-1130 (dichloroethene), which would now be called an unsaturated hydrochlorocarbon (HCC) or hydrochoro-olefin (HCO), though records suggest it was a blend of the two R-1130 stereo-isomers and possibly also the R-1130a isomer, with commercial introduction in 1922 [8]. They shifted to R-1120 (trichloroethene), also an unsaturated HCC but having only a single isomer, in 1925 when they sought improved capacity and chemical stability. They replaced R-1120 with R-30 (a single-carbon HCC, thus inherently saturated) a year later. Still, trichloroethene remained in wide commercial use as a heat transfer fluid, solvent (including for dry cleaning), disinfectant, food processing extractant including to remove caffeine from coffee, ingredient in inks and paints, limited use anesthetic or analgesic, and chemical intermediate. Use declined with identification as a potential carcinogen and later phase out (except as an intermediate) in the 1990s to protect the stratospheric ozone layer. Current R-1120 classifications are conflicting as to its human carcinogenic potential.

Two unsaturated hydrocarbons, R-1150 (ethylene or systematically ethene) and R-1270 (propylene or propene) came into limited use in the late 1940s and 1950s and remain so today. R-1150 found use in ultralow temperature, industrial refrigeration systems. R-1270 gained acceptance in commercial and industrial chillers (notably in Europe), limited use in commercial refrigeration (notably in the UK), and later as a refrigerant blend component. Propylene had prior use as an anesthetic agent in the 1920s, though not widely due to depression of heart function, and later as an aerosol propellant, both alone and in blends. It remains in

wide use today to produce plastics, alcohols, gasoline, synthetic rubbers, and other chemical products. Accordingly, current focus on unsaturated chemicals as refrigerants has clear precedents; what is new is interest in fluorinated unsaturates.

3. TRANSITIONS

The history of refrigerants can be summarized in four distinct generations, as illustrated in Figure 1 and of which the transition from the third to the fourth now is beginning [23,24].

The preceding discussion traced evolution from familiar workplace chemicals, many of them solvents or fuels and some now dubbed "natural" refrigerants. The key distinction between the **first generation predicated on whatever worked**, and was available, to fluorochemicals specifically selected and manufactured for refrigerant use. This **second generation came about to address safety and durability concerns**. CFCs and HCFCs enabled rapid growth of the air-conditioning and refrigeration industry. Ammonia and water continued dominance in the above cited applications. Linkage of CFCs, HCFCs, and brominated counterparts to ozone depletion in the

Figure 1. Refrigerant Generations Progression

upper atmosphere led to the **third generation to protect the stratospheric ozone layer**. Although loosely considered in third generation selections, growing awareness of the potential severity of climate change impacts spurred a radical shift from highly-stable fluorochemicals to those with short-atmospheric lifetimes (rapid decomposition when released), namely unsaturated HFCs and to a lesser extent unsaturated HCFCs. Implicit in the changes is concurrent attention to improving or at least maintaining application energy use. The dual criteria of low GWP and high efficiency define a **fourth generation of refrigerants selected to minimize global warming** impacts. The third and fourth generations also spawned re-examination of broader use ammonia, carbon dioxide, hydrocarbons, water, and others dubbed "natural" refrigerants.

4. COEXISTENCE AND OUTLOOK

Future demand for refrigeration, including efficient heat pumps, is unambiguous. Our lives depend on it for preservation of foods, beverages, medicines, and other goods. Refrigeration enables many industrial processes ranging from its early uses in textiles and printing for humidity control to precision machining. Increasing dependence on electronics especially in communications and other data centers require heat removal, or perhaps in the future more heat recovery for beneficial use. Air conditioning is no longer just for comfort, but now essential for commercial productivity and health. Such needs will increase as populations grow and even more so if or when climate changes results in global warming and specifically warming in previously cooler regions. These considerations suggest even greater future dependence on refrigerants.

Predicting future refrigerant choices is not easy. Safety concerns will continue and intensify with increasing population density. Risks arise both from occupational exposures and for users from leakage and accidental releases. Elimination of many nonflammable HFC options forces industry resignation to low-flammability refrigerants. This shift may offer opportunities if accompanied by improved manufacturing, equipment and application design, and broader use of leak detectors. Recently added focus on maximum burning velocity (reflected in A2L and B2L safety classifications) manifests new approaches going beyond flame propagation, flammability limits, and heat of combustion [25-27]). And despite competitive zeal for "natural" versus fluorinated refrigerants and highly competitive promotion of individual selections and especially proprietary blend formulations, there is a foreboding sense that all may not be enough. Following three transitions to a fourth generation of refrigerants, it is fair to ask whether even the fourth will survive.

4.1 Uncertainties with Unsaturated Refrigerants

Notwithstanding their exciting promise and manufacturer assurances, credible uncertainties remain for unsaturated halochemicals. A prior paper discussed concerns for these refrigerant including political, competitive, and other questions not addressed herein [24].

Toxicity is a key issue. HCFCs and HFCs introduced in the third generation of refrigerants were examined more exhaustively — "tested to extremes" [28] — than older CFCs, despite anticipated low toxicity, predicated on advances in accepted practices. Whether due to tight lead times to meet changing needs, attempts to minimize exposures of laboratory animals, potential belief that prior testing was excessive, costs, or other reasons, released study data for the new unsaturates suggest less screening than for their predecessors. If true, it is ironic following earlier avoidance of unsaturates due to expected toxicities. Based solely on limited available data, most new unsaturated fluorochemicals may not (or at least not yet) have been vetted through previously demanded chronic animal studies. Openly reported data for the new unsaturates (HFOs and HCFOs) generally stop with subchronic (90-day/13-week repeat exposure studies) rather than more traditional or subsequent chronic studies (two-year repeat exposure studies). This concern is heightened with recollection that some toxic effects in prior refrigerant examinations did not show up until late in chronic studies and would or might not have been observed in subchronic testing alone. Chronic testing (two-year rat study) of R-123 yielded increased incidence of non-malignant tumors in the liver, pancreas, and testis compared to the control group, though primates (including humans) are low-responders to the mechanism (peroxisome proliferation) involved [29,30]. Chronic testing of R-134a produced tumors in the testis and additionally hyperplasia and of R-141b also produced tumors, but in both cases at higher exposure concentrations [31-33]. What is significant is that the tumor findings for R-123, R-134a, and R-141b occurred late in life (late in testing), in chronic studies.

Multiple chemical manufacturers promoted blends of R-1225yc, R-1225ye(E), R-1225ye(Z), and R-1225zc (the last an intermediate in R-245fa manufacture) with R-32, R-E1216, R-1234yf, and others between 2004 and 2007 to replace R-12 and R-134a in mobile air conditioner (MAC) and potentially additional applications. These pursuits terminated in late 2007, some with limited attribution to new toxicity concerns. The timing of these events suggests that the adverse findings may not have been discovered until late in chronic studies, though adverse results from a sub-chronic study were reported for R-1225ye(Z) [34].

Likewise, data on unsaturated HFC (HFO) toxicity for occupancy in a confined, humid cabin subjected to a slow but prolonged leak, such as driving in a humid climate with a full car on a long trip, were not found. An independent test was planned but precluded.

Environmental studies also appear incomplete. Several investigators have assessed trifluoroacetic acid (TFA, a persistent and toxic decomposition product) build up from projected refrigerant emissions, finding safe levels of accumulation [35-39]. The studies, however, do not fully examine the potential for localized buildups in bodies of water with high evaporation and slow refill rates, such as those resulting in salt lakes and marshes or "dead" rivers. Likewise, the studies focus on national (in one on regional) emissions without cross-border contributions and, more importantly, without compounding from non-MAC (from stationary systems) and non-refrigerant (such as from aerosol propellant or blowing agent uses) emissions. Although proposed, predicated on rapid atmospheric decomposition of unsaturated fluorochemicals, full urban studies of hydrofluoric acid (HF) impacts also are needed even though HF also has short atmospheric persistence.

It appears that newer chemicals are assessed based on criteria developed after finding problems in use with older options. Such examination clearly is needed, but not necessarily sufficient without rigorous investigation of potential additional modalities for complication unique to new solutions.

4.2 Options Are Limited

A conflicting perspective would ask what is left if we eliminate all halogenated options for global (stratospheric ozone and climate change) and local (decomposition product) environmental protection as well as rigid risk avoidance for safety. Midgley demonstrated clearly that the number of eligible elements is limited and chemistry shows that the number of options for finite constituents also results in finite candidates. Extensive screening reinforces confidence in "Midgley's eight" and more importantly that future options are limited [40,41]. Studies document concerns with serial elimination of families of chemicals based on serial, single metric approaches rather than more selective approaches based on tradeoffs of low-level offenders among multiple criteria taken together [6,21].

One potential response, focal to this conference, is full reliance on nonhalogenated ("natural") refrigerants. Flurochemicals, notably R-12 in the 1930s and continued with R-134a in the 1990s, replaced nonhalogenated options for domestic refrigeration. Hydrocarbon R-600a (isobutane) later successfully displaced R-12 and R-134a for this application primarily in Europe and to varying extents countries elsewhere. At least one major manufacturer is attempting R-600a use in some models in the USA, where safety regulations and

liability concerns remain impediments. While some automobile manufacturers have replaced R-134a with R-1234yf and others are pursuing R-445A, some formerly considered indirect use of R-152. All such companies clearly considered — and some European manufacturers remain committed to — "natural" R-744 (carbon dioxide) though systems for it are still under development. Some proponents argue for R-290 (propane), R-1270 (propylene), and blends containing them to replace R-22 and its successor R-410A, but products using these hydrocarbons remain a tiny share of the global total based on safety concerns. Others argue for moderate GWP (680 for 100 year integration) R-32, which would have been a preferable choice to R-410A (of which it is a 50% component) in the 1990s. R-717 (ammonia) was and remains the primary refrigerant in industrial food and beverage processing and storage, though some use is made of R-22, R-134a, R-502, and others. R-717 benefits clearly are recognized, but broad acceptance is limited to industrial and isolated settings. With exceptions often spurred by targeted promotion, R-717 use in residential, commercial, and institutional settings is limited by concerns with leaks despite the inherent warning from its pungent odor. Still, worries arising from its flammability (though low), corrosive injury to the mucous membranes, eyes, lungs, gastrointestinal tract, and skin, and even fears of panic from detection of the odor limit applications. Indirect systems, especially in commercial refrigeration, have come and gone, both using fluorochemical options and more recently using R-717 (ammonia) and R-744 (carbon dioxide). One novel approach even uses carbon dioxide as the heat transfer fluid for R-744 and hydrocarbon refrigeration system. R-601a/601 and other hydrocarbon blends had strong advocacies, notably in Australia, but R-134a and R-123 remain the primary (essentially the only) current options for centrifugal chillers. R-717 (ammonia) in the second stage with screw compressors coupled with predominantly R-134a but also R-123 chillers in the first stage as well as in underground chillers are common in deep mines. R-22 and more recently R-410A and others compete with R-744 (carbon dioxide) in heat pump water heaters, an application with disappointing growth but for which R-744 holds promise. More than 40 new single-compound and blended refrigerants based on unsaturates are in testing. This list is not complete either for the applications or refrigerants addressed. It merely summarizes, but briefly, the majority of common refrigerant usage to illustrate that non-fluorinated and fluorinated refrigerants can and do co-exist and can and do compete in some applications. To the extent governments and other regulatory bodies focus on criteria for environmental acceptability, safety provisions for use, and (though currently inadequately) minimum system efficiencies, competition between equipment and system design options including refrigerant selections can only benefit all since cycle refinements and component advances generally are not limited to a single refrigerant. Conversely, mandates for or arbitrary prohibitions of specific refrigerants invariably retard improvements.

The term natural refrigerants is more of a "marketing" term for promotion than — as explained above — an accurate descriptor; most "natural" refrigerants are chemically synthesized and often refined. Such manufacturing is not radically different from fluorochemical processing, for which the primary fluorination method employs hydrofluoric acid (HF) derived from mined — but natural in origin — fluorspar (fluorite, the mineral form of calcium fluoride, CaF_2).[†]

While speculative, the author questions whether the current shift to the fourth generation of refrigerants will be the last. The number of remaining uncertainties as elaborated above and in reference [24], coupled with selecting successors using a single (or essentially a single) criterion, results in an ineffective approach [21]. While international treaties lump refrigerants together with other uses of the same chemicals, refrigerant use need not be inherently emissive. Accordingly, separate regulation of refrigerants (just as chemical feedstock uses are distinct) rather than integral with emissive applications would yield a more scientific and environmentally beneficial approach. Further refinement with consideration of selection implications for efficiency and resulting energy-related emissions also would improve the process. And, objective consideration and reconsideration of nonhalogenated ("natural") refrigerants is integral to such a multi-metric approach.

5. CONCLUSIONS

So fluorinated versus nonfluorinated ("natural")? Are fluorinated refrigerants needed or will "natural" refrigerants suffice? The answer should be obvious that we cannot afford careless elimination of either group, and competition between them on safety (application and fabrication methods rather than chemical safety alone) and performance (especially efficiency) will benefit both.

[†] Zhejiang Province, the venue of this conference, is one of the largest fluorspar producers in the world and the reason Hangzhou is a key center for the chemical industry in China. Fluorspar is a widely occurring mineral with leading production in China, Mexico, Mongolia, Russia, the Republic of South Africa and additional notable deposits in Austria, Canada, Germany, Norway, Switzerland, Kenya, the UK, and the USA.

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