

Refrigerant Transitions ... Again

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ABSTRACT

This paper reviews the progression of refrigerants from inception of mechanical refrigeration to the present. It divides historical and current refrigerants into separate generations and discusses the selection criteria distinguishing them. The four generations include slightly overlapping periods based on whatever worked (1830s-1930s), improved safety and durability (1931-1990s), stratospheric ozone protection (1990s-2010s), and attention to global warming (2012-?). The paper discusses the primary refrigerants employed in each period and goes on to examine the viability of the imminent fourth generation, responding to limits and anticipated limits to acceptable refrigerant global warming potential (GWP). The paper presents factors challenging or likely to challenge the fourth generation refrigerants. Among the potential driving factors are efficiency, momentum, prices, litigation and liability, unforeseen suitability issues, local impacts, and political naïveté. The paper summarizes impacts from these concerns, individually or in combination, and their potential to necessitate a subsequent fifth generation. Notwithstanding the controversial and uncertain nature of predictions, the paper suggests an approach to selecting future refrigerants in the absence of ideal choices and of new chemical families that might better approach them. Despite what many practitioners now consider the second transition during their careers, retiring still new but now familiar candidates (or a third transition including the earlier advent of fluorochemicals), the paper concludes that industry must choose between forward-looking selections, which go beyond minimum mandates, or face refrigerant transitions ... again.

INTRODUCTION

The nature of air conditioning, heat pumping, and refrigeration is use of thermodynamic cycles to move heat in the direction opposite to which it would flow naturally (from cold to hot rather than the natural movement from higher to lower temperatures). The working fluid in such cycles is the refrigerant. Raising its pressure through mechanical compression or chemical (actually a combination of chemical and mechanical) means enables the desired heat movement. The refrigerant removes heat from a colder substance (air or a heat transfer fluid for space conditioning) by evaporating at low pressure and then rejects (or for a heat pump delivers) heat by condensing at raised pressure and temperature.

The refrigerant transitions that transformed the last 80 years, and more memorably the most recent 20-25 years, reflect both successive changes in selection criteria and significant technical developments. From a thermodynamic perspective, essentially all volatile fluids could be used as refrigerants. Studies (Domanski et al., 1994; Domanski, 1995) have documented that all such refrigerants can approach ideal efficiency limits with sufficient cycle optimization. In practice, however, increased cycle complexity with inherent irreversibilities in each step dictates that simple molecules, with suitable boiling and critical point temperatures, in simple cycles have inherent advantages (Calm and Didion, 1997).

In addition to having the desired thermodynamic properties, an ideal refrigerant would be nontoxic, nonflammable, completely stable inside a system, environmentally benign even with respect to decomposition products, and abundantly available or easy to manufacture. It also would be self-lubricating (or at least compatible with common lubricants), stable in the presence of other materials used to fabricate and service refrigeration systems, easy to handle and detect, and low in cost. It would not require extreme pressures, either high or low. There are additional criteria, but no current or potential

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refrigerants are ideal — even based on the partial list — suggesting the necessity for trade-offs in selections (Calm and Didion, 1997).

What has differentiated successive refrigerant transitions has been changing thresholds of acceptability for safety, durability, and environmental restriction indices.

SUCCESSIVE REFRIGERANT GENERATIONS

The author and collaborators have documented historical development and introduction of successive generations of refrigerants defined by the focal selection criteria. Calm and Didion (1997) identified three distinct generations to which Calm (2008) and Calm and Hourahan (2011) added a fourth. The following discussion elaborates and figure 1 summarizes the four generations of refrigerants.

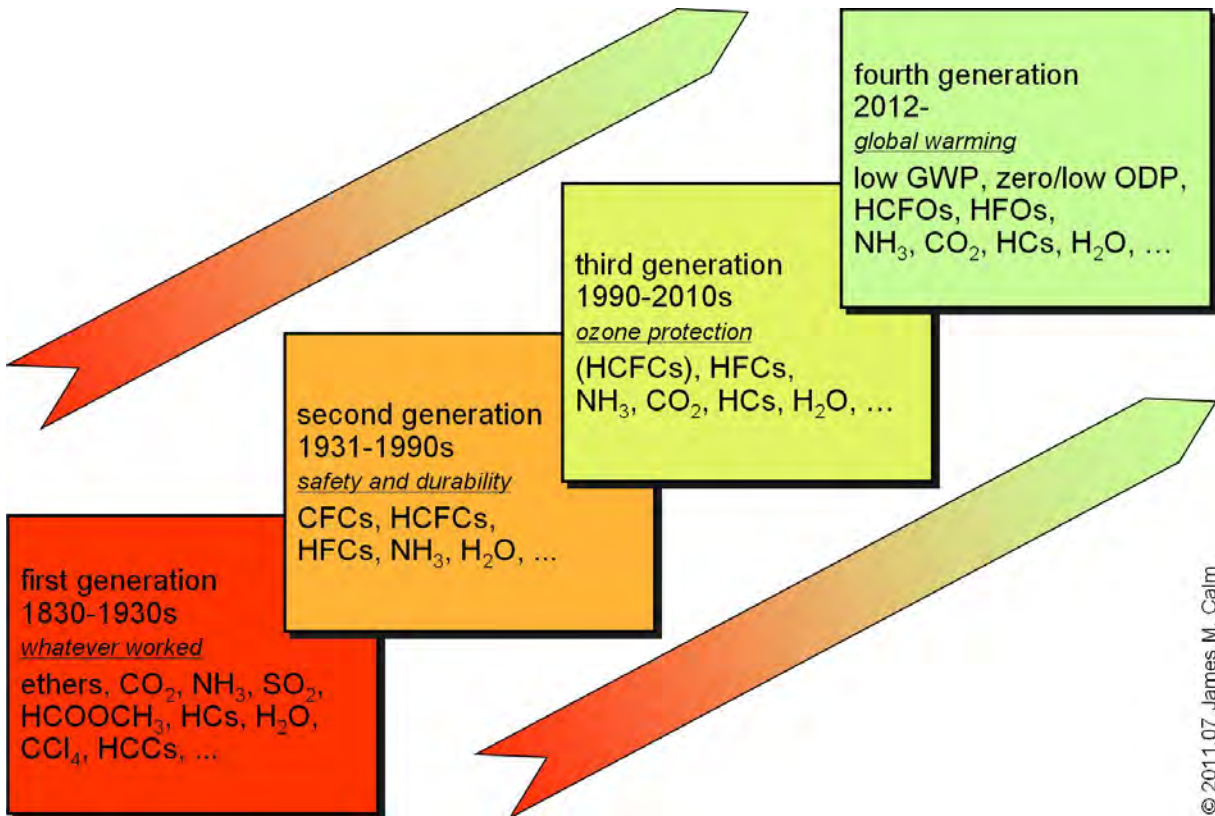


Figure 1. Progression through four refrigerant generations

Whatever Worked (1830s-1930s)

The first generation spanned a period of approximately 100 years beginning with the first documented use (Perkins, 1834; Nagengast, 1996) of vapor-compression refrigeration by Jacob Perkins in the 1830s. His 1834 patent describes a cycle using a “volatile fluid for the purpose of producing the cooling and freezing ... and yet at the same time condensing such volatile fluids, and bringing them into operation without waste” (Perkins, 1834). Earlier 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 poured on mats or the skin to evaporate. The primary method of early cooling was use of stored or transported natural ice (Thévenot, 1979). Oliver Evans proposed the use of a volatile fluid in a closed cycle to

freeze water into ice (Evans, 1805), but there is no record that he built a working machine though his ideas probably influenced Perkins.

The first generation refrigerants were volatile fluids familiar to early practitioners from other uses, such as common solvents, other workplace chemicals, and even fuels. The first refrigerant actually used in Perkins' machine was already a substitute, as the sulfuric (ethyl) ether for which it was designed had not arrived when the apparatus was ready for testing. His assistants, therefore, ran the initial tests with caoutchoucine (a distillate of natural rubber) familiar in Perkins' work as a printer. This substitution highlights availability as a key requisite for refrigerants.

Some of the first generation fluids are among those now promoted as "natural refrigerants," further discussed below, including ammonia, carbon dioxide, hydrocarbons (most notably propane and isobutane), and water (Nagengast, 1989 and 1996).

Surprisingly, there is no record of a systematic screening of refrigerant candidates until near the end of the first generation. Willis H. Carrier and R. W. Waterfill documented a detailed, systematic investigation of candidates for suitability and performance in machines with both positive-displacement and turbo-compressors (Carrier and Waterfill, 1924). Their analyses closely examined ammonia (R-717), ethyl ether, carbon dioxide (R-744), carbon tetrachloride (R-10), sulfur dioxide (R-764), and water (R-718) among others. They concluded, for example, 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.

Improved Safety and Durability (1931-1990s)

The second generation, which lasted approximately 60 years, was distinguished by a shift to fluorochemicals for safety and durability. Repeated leaks, of then prevalent methyl formate (R-611— "H-cooch" from its chemical formula HCOOCH_3) and sulfur dioxide (R-764), retarded early efforts to market domestic refrigerators to replace iceboxes. With direction that "the refrigeration industry needs a new refrigerant if they expect to get anywhere," Thomas Midgley, Jr., and his associates Albert L. Henne and Robert R. McNary scoured property tables to find chemicals with the desired boiling point. They restricted the search to those known to be stable, but neither toxic nor flammable. The published boiling point for carbon tetrafluoride (R-14) drew attention to the organic (containing carbon) fluorides, but they correctly suspected the actual boiling temperature to be much lower than published. Turning to the periodic table of elements, Midgley quickly excluded chemical elements yielding insufficient volatility such as metals. He then eliminated those resulting in unstable and toxic compounds as well as, based on their low boiling points, the inert gases. Just eight elements remained, namely carbon, nitrogen, oxygen, sulfur, hydrogen, fluorine, chlorine, and bromine (Midgley, 1937). Other investigators have repeated Midgley's search with newer methods and modern databases, but they have come to similar findings. McLinden and Didion (1987) documented an extensive screening of industrial chemicals. Of the chemicals meeting their criteria, all but two — both highly reactive and toxic — consisted of the Midgley elements.

Within three days of starting, in 1928, Midgley and his colleagues made critical observations regarding flammability and toxicity of compounds consisting of these elements. They also noted that every known refrigerant at the time combined just seven of these elements — all but fluorine. Their first publication on fluorochemical refrigerants shows how variation of the chlorination and fluorination of hydrocarbons influences boiling points, flammability, and toxicity (Midgley and Henne, 1930).

Commercial production of R-12 began in 1931 followed by R-11 in 1932 (Downing, 1966 and 1984). Chlorofluorocarbons (CFCs) and later, starting in the 1950s, hydrochlorofluorocarbons (HCFCs) — especially R-22 in residential and small commercial air conditioners and heat pumps — dominated the second generation of refrigerants. Ammonia continued as, and remains today, the most popular refrigerant in large, industrial-scale systems for food and beverage processing and storage. Ammonia and water emerged as the primary refrigerants in absorption systems for small and large capacities, respectively.

Stratospheric Ozone Protection (1990s-2010s)

Linkage of released CFCs — including CFC refrigerants — to depletion of stratospheric ozone led to an international agreement, notably the Montreal Protocol (1987), and regional and national regulations to phase out specified ozone-depleting substances (ODSs). The Montreal Protocol and most of the other measures imposed controls including production reduction (“step-down”) and full phase out deadlines for commercialized CFCs such as R-12. They also allowed transition use with later elimination of HCFCs such as R-22. These measures catalyzed the third generation of refrigerants, with focus on ozone protection, starting in the early 1990s (arguably already in 1989) and continuing approximately 20-25 years to the present. The measures also addressed similar chemicals for other applications, such as many widely used aerosol propellants, foam blowing agents, fire suppression agents (notably halons), and solvents. Replacements with near-zero or zero ozone-depletion potential (ODP) came to the forefront with primary focus on hydrofluorocarbons (HFCs), only in limited prior use and then primarily in blends. HFC options were, in fact, well known, but avoided due to their limited miscibility with then common mineral-oil lubricants for compressors. The advent of widespread HFC use forced development of new refrigeration lubricants.

These shifts spawned renewed interest in ammonia, carbon dioxide, hydrocarbons, and water — collectively dubbed “natural refrigerants,” particularly in Europe with accelerated phase out of HCFCs and lesser dependence on HCFCs and HFCs. Proponents of “natural refrigerants” differentiate such candidates from “synthetic refrigerants” to imply environmental superiority. The distinction is somewhat strained as most ammonia and isobutane for refrigerant use is synthesized industrially, rather than gathered or extracted from natural sources, even though both occur naturally. Conversely, methyl chloride (R-40) and methyl bromide (R-40B1), the latter of greater significance as a pesticide and fumigant, are treated as “synthetic” despite their natural abundances. Methyl chloride and methyl bromide together account for greater stratospheric chlorine-bromine loading than the aggregate of all man-made ODSs except CFCs (WMO, 2011; Wuebbles and Calm, 1997). Also, the primary mineral used to produce hydrofluoric acid for manufacture of fluorinated refrigerants is fluorite (commonly called *fluorspar*), a naturally-occurring form of calcium fluoride mined in a number of countries. Distinction between halogenated and nonhalogenated or between fluorinated and nonfluorinated refrigerant alternatives is more accurate than “natural” versus “synthetic.” Since nearly all construction and certainly all refrigeration systems are by character synthetic (man-made rather than naturally occurring), it is unclear that “synthetic” implies undesirable.

Isobutane (R-600a) or in some instances isobutane blends with other hydrocarbons effectively displaced competing R-134a (an HFC) as a replacement for R-12 (a CFC) in domestic refrigerators and refrigerator/freezers in Europe. Isobutane and other hydrocarbons, or hydrocarbon blends, gained acceptance more recently in the Middle East, portions of southeastern Asia, and to varying but generally increasing levels elsewhere. Ammonia (R-717) and to lesser extents — and then in smaller equipment sizes — propane (R-290) and propylene (R-1270) gained increased shares in chillers, primarily in Europe, but all three still hold only a very small fraction of the global total. Both ammonia (R-717) and carbon dioxide (R-744) use grew in commercial refrigeration, sometimes coupled with secondary heat transfer fluids, or in the case of carbon dioxide sometimes with it as a secondary heat transfer fluid. Carbon dioxide use drew significant attention in a nascent rebirth of heat pump water heaters (HPWHs), notably in Japan and later northern Europe, largely influenced by significant utility subsidies. R-134a use in HPWHs actually grew more rapidly on a global basis owing to new regulations prohibiting large-capacity electric-resistance water heaters in the USA. Still, there is further interest in carbon dioxide, including for higher-temperature applications, despite the pressures involved and, for most conditions, a need for transcritical cycles.

Manufacturers commercialized the first alternative fluorochemical refrigerants in late 1989 and, within 10 years, introduced replacements for most ozone-depleting refrigerants. The emphasis was on HFCs and blends of HFCs, alone or with hydrocarbons. R-134a (an HFC) is now the most widely used single-compound refrigerant in new equipment on a worldwide basis. HCFC and HCFC-blend use continued, the latter primarily for aftermarket retrofit applications, at a lesser scale. Private and public research programs systematically examined hydrofluoroether (HFE), fluoro-iodocarbon (FIC), hydrofluoro-iodocarbon (HFIC), and additional nonfluorochemical candidates, but yielded few promising options (Bivens and Minor, 1998; Sekiya and Misaki, 2000; Nimitz and Lankford, 1994).

CFCs are now nearly phased out globally in new equipment, and the retirement of HCFCs, deemed transition options, also is underway. Despite phase out in new equipment, significant amounts of R-22 (an HCFC with atmospheric lifetime

(τ_{atm}) = 11.9 yr, GWP 1790, ODP 0.04) remain in existing equipment and also are used for service (see Calm and Hourahan, 2011, for these, subsequently noted, and additional environmental data). R-123 (also an HCFC) continues in wide use in new centrifugal (turbo-) chillers, for which it still holds nearly a 40% market share globally. Despite scheduled phase out as an HCFC, the case for R-123 is somewhat unique based on its documented, indiscernible impact on stratospheric ozone (Calm et al, 1999; Wuebbles and Patten, 2009). Its consensus ODP of 0.0098 is distinctively low and challenges an older estimate of 0.02 adopted in 1992 for regulatory purposes (Wuebbles and Patten, 2009; WMO, 2011). R-123 offers the highest thermodynamic efficiency of current options, low pressure, extremely low leakage as confirmed in three studies using independent field data, short τ_{atm} (1.3 yr), very low GWP (77), beneficial net-GWP (-25 counting its impact on atmospheric ozone), and fire suppression ability (Kroeze and Reijnders, 1992; Wuebbles and Calm, 1997; Calm et al, 1999; Seager and Theis, 2003; Molina et al., 2004; Calm, 2007; Wuebbles and Patten, 2009; WMO, 2011).

Three points warrant notice. First, refrigerants historically constituted only a minor fraction of total ODS emissions. Most of the CFCs and HCFCs widely commercialized as refrigerants also are or were used in much more emissive applications, including as aerosol propellants, foam blowing agents, and solvents. Some of those refrigerants actually were selected from chemicals already developed for use in other applications, with higher production volumes. Second and at least comparable in importance to the refrigerant replacements, the environmental concerns prompted major changes in design, manufacturing, installation, service, and ultimate disposal procedures to reduce avoidable refrigerant emissions. Third, the ozone layer is recovering despite episodic reports of record ozone holes in the Antarctic (WMO, 2011). The size of the annual Antarctic hole results from variable factors such as southern polar winds and oscillations, which induce the polar vortex, and winter temperature severities that regulate the efficiencies of ozone destruction and natural replenishment. Accordingly, changes from one year to the next, as contrasted to longer-term trends, do not indicate sudden success or failure of efforts to eliminate anthropogenic (of human origin) ODSs. International scientific assessments document that both new ODS releases and residual prior emissions are declining. The progress in ozone recovery is even more evident when measured by global mean ozone rather than columnar ozone isolated in the Antarctic vortex.

The primary targets for third generation refrigerants were zero ODP — more precisely near-zero ODP as even HFCs have very limited ODPs (typically less than 0.00002) — and very low ODP for transition compounds such as HCFCs. Climate change garnered only limited attention, such as avoidance of candidates having extremely high global warming potentials (GWPs), for example perfluorocarbons (PFCs, rigorously dubbed FCs).

Global Warming (2012-?)

Growing awareness of climate change as a more significant and more challenging environmental issue now heralds an imminent fourth generation, to address global warming. This term is a bit misleading, since the impacts of climate change include warming in most regions but cooling in some (for example in parts of Europe). The consequences also include sea level rise and attendant coastal land loss, changes in growing seasons and soil moisture retention (and therefore crop yields), changes in storm frequency and ferocity, and spread of diseases such as malaria now nearly localized to equatorial regions (IPCC, 2007a and 2007b). In short, climate change may impact virtually all aspects of life and raises significant international and intergenerational equity issues (Mahlman, 1998).

One family of chemicals drawing focal attention is fluorochemicals with unsaturated bonds (having more than a single bond connecting adjacent carbon atoms) but still having acceptable toxicity levels (Minor, 2006; Calm, 2008; Brown, 2009; Brown et al., 2010; Leck, 2010; Calm and Hourahan, 2011). Such chemicals — or at least the specific candidates being pursued — typically are stable inside refrigerant circuits, with careful purging of air and water vapor before refrigerant charging, but unstable and subject to rapid decomposition when released to the atmosphere. Such decomposition leads to short τ_{atm} and, therefore, exceptionally low ODP and GWP. Those being actively pursued include three-carbon (propene) and four-carbon (butene) molecules with a single double bond. Proponents describe them as hydrofluoro-olefins (HFOs), hydrochlorofluoro-olefins (HCFOs), or hydrobromofluoro-olefins (HBFOs) to accentuate their short atmospheric lifetimes. Opponents lump them in with the other fluorochemicals (“F-gases”) as HFCs, HCFCs, and HBFCs to imply inclusion or anticipated inclusion in existing control measures. They are identified herein as unsaturated HFCs, HCFCs, and HBFCs, with the “unsaturated” qualifier signifying distinction from saturated compounds (having only single-bonds

between carbon atoms). The first such commercial use, of R-1234yf (an unsaturated HFC) in the automotive sector, began in mid-2012.

Future acceptability of unsaturated fluorochemicals containing bromine, chlorine, or even iodine is uncertain. The Montreal Protocol does not automatically preclude their use as it controls only specifically-enumerated substances (many uncommon CFCs were not controlled or subject to mandatory phase out, but presumably would be added if commercialized). Pursuit of unsaturated HCFCs and HBFCs is testimony that the manufacturers involved do not expect their control under the Montreal Protocol predicated on very short atmospheric lifetimes (τ_{atm}), generally less than two weeks, and consequentially very low ODPs, since only minute quantities would survive the transport time to the stratosphere.

Larger molecules as well as those with more than one double bond or with a triple bond (a haloalkyne) are possible, but typically have higher boiling points than sought and have not attracted the same level of pursuit.

It warrants noting that four of the early (first generation) refrigerants were unsaturated chemicals, so use of unsaturated compounds as refrigerants is not completely new. Two of the four were hydrocarbons, namely ethylene (ethene, R-1150, an unsaturated HC) and propylene (propene, R-1270, also an unsaturated HC). The third was dielene (R-1130, an unsaturated HCC), the first refrigerant used in early centrifugal chillers, starting in 1922 (Grant, 1942; Ingels, 1952). The record does not indicate which or what combination of R-1130 stereoisomers and possibly even the R-1130a isomer was used, but an international search was needed to find a source for it after selection based on published properties (Ingels, 1952). Dielene was succeeded by trielene (R-1120, also an unsaturated HCC) in 1925.

Early candidates, responding to a European directive phasing out fluorinated refrigerants with 100-yr GWP higher than 150 (precluding continued use of R-134a with a GWP of 1370) for mobile air conditioning (MAC) use (European Union, 2006), included blends of unsaturates with R-131i (a fluoro-iodocarbon, FIC, $\tau_{\text{atm}} = 4$ days, GWP 1, ODP 0.008-0.016). Addition of this low-ODP FIC was intended to suppress flammability, but pursuit appears to have stopped predicated on stability (internal reactivity) concerns. Once again, the Montreal Protocol does not automatically preclude R-131i use, but there is uncertainty whether it would be added if commercialized at a significant scale. The GWP limit of 150 was selected to eliminate nearly all saturated fluorochemicals, but to intentionally allow R-152a ($\tau_{\text{atm}} = 1.5$ yr, GWP 133 though 140 in the Kyoto Protocol, ODP 0.000) as a fallback option pending further assessments of carbon dioxide, hydrocarbons, and unsaturated fluorochemicals (European Union, 2006; Kyoto Protocol, 1997; Calm and Hourahan, 2011).

Some manufacturers, especially in Japan and China, have shown interest in R-32 ($\tau_{\text{atm}} = 5.2$ yr, GWP 716, ODP 0.000) to replace R-410A (a blend of R-32 and R-125 in equal fractions by mass, GWP 2100, ODP 0.000) predicated on reduced GWP and increased capacity, but with higher operating pressure and limited flammability. Conventional wisdom is that R-32 alone would amount to only a short-term solution since its GWP exceeds the limit of 150 under consideration (possibly with reduction to 100) for stationary refrigeration. Manufacturers also have considered blends of R-32 with R-131i to mitigate R-32 flammability, but the same internal stability and ODP (albeit very low) concerns remain. Likewise, some manufacturers, notably in China, have pursued R-161 (an HFC, $\tau_{\text{atm}} = 66$ days, GWP 12, ODP 0.000) in blends, but interest thus far has been limited largely due to its high flammability.

Pursuit and certainly advocacy of ammonia, carbon dioxide, hydrocarbons, water, and to a lesser extent dimethyl ether (DME, R-E170, $\tau_{\text{atm}} = 5$ days, GWP 1, ODP 0.000) continues, both alone and in blends (in some instances with R-32, R-41, and R-161). Ammonia does show broader application potential particularly with anticipated costs for unsaturated fluorochemicals, discussed below, or with further regulatory restrictions. Hydrocarbons do likewise in refrigerators, refrigerator/freezers, freezers, dehumidifiers, wine coolers, chilled-water fountains, and other products incorporating small-capacity refrigeration. There is manufacturer interest in scaling up the acceptable charge size limit and likewise reducing system charge size requirements. Future use of hydrocarbons in residential-scale air conditioners and heat pumps with appropriate protective measures may be more restrained by needed regulatory and liability changes than engineering, at least in small capacities.

No attempt to cover all options is intended herein; other papers in this conference address specific candidates and suitability for targeted applications in greater detail. The preceding discussion instead reviews dominant trends to provide a basis for further consideration of potential challenges to the coming fourth generation refrigerants and resulting long-term acceptability.

Not-in-kind alternatives such as absorption, magnetocaloric, and thermo-acoustic refrigeration warrant examination. Indications thus far are that vapor-compression refrigeration will remain the overwhelmingly dominant choice (Brown and Domanski, 2011), primarily based on its efficiency advantages, except in specialty applications such as absorption in mini-bar (very small) refrigerators.

CHALLENGES TO FOURTH-GENERATION REFRIGERANTS

The fourth generation will comprise identified fluorinated refrigerants having both zero (or near-zero) ODP and very low or ultra-low GWP (notably unsaturated HFCs and HCFCs), others still not identified, and nonfluorinated candidates. It is appropriate to ask whether the imminent transition will usher in a period of stability or face new challenges. Predicting the future is at best imprecise, with diminishing certainty as the time period considered extends further out. One approach is to identify factors that might dictate an end to or diminished acceptance of the fourth-generation refrigerants. For example:

- **Efficiency:** The pursuit of low-GWP options to minimize climate change impacts may, in some cases, have the opposite effect. Net Warming Impact (NWI), Total Equivalent Warming Impact (TEWI), Life-Cycle Climate Performance (LCCP), and similar analyses consistently show that greenhouse gas emissions from system energy use significantly exceed the direct impact of refrigerant releases, often by factors exceeding 50. While simple GWP caps may have merit in controlling chemicals requiring release for function (such as aerosol propellants) and for which emission containment is difficult (such as for foam blowing agents), refrigerant release not only is unnecessary for its use but often has greater impact in terms of efficiency reduction due to resulting suboptimal charge. Setting a refrigerant GWP limit without careful assessment of efficiency implications can, and often does, exacerbate net greenhouse gas emissions. Chemical and equipment manufacturers touted both reduced emissions and maintained or improved efficiencies with introduction of the third generation, although the same effort applied to older refrigerants would have yielded even greater performance improvements in most cases. To its credit, the automotive industry and, separately, stationary equipment manufacturers have collaborated in testing alternatives, but that may, for the majority of applications, translate to selecting the least degradation of rather than raising efficiency. The EU MAC directive (European Union, 2006) mentioned above is silent on resulting efficiency consequences except to allow individual Member States to “promote the installation of air-conditioning systems which are efficient, innovative and further reduce the climate impact.” Future attention to climate change measures may dictate greater focus on the performance of alternatives, forcing reconsideration of candidates now being introduced. Even if new refrigerants match the efficiency of what they replace in current designs, they may not have the same potential for future efficiency improvements.
- **Convictions Momentum:** There seems to be an “Atlantic divide.” The dominant perception in Europe or at least northern Europe — and perhaps also in academia globally — is that “F-gases” are evil and doomed. The prevailing perception on the American side (and most Asian countries) is that the progression from the first to subsequent refrigeration generations employed valid engineering selections and, for the third and fourth generations, satisfied mandates. Two possible reasons for the dichotomy are lesser dependence in Europe, and especially northern Europe, on comfort air conditioning along with lesser presence of major, multinational, air-conditioning manufacturers. Nevertheless, one certainty is that nongovernmental organizations and other campaigners will continue to bring pressure on policymakers to proscribe future fluorochemical use, including that of unsaturated fluorochemicals. Such pressures will continue to challenge leading refrigerant candidates and especially so for MAC use, both one of the largest and most frequently challenged refrigerant markets.
- **Prices:** Reliable cost data are not yet available for the new unsaturated HFCs and HCFCs, but anecdotal indications suggest very significant increases over those for current refrigerants. These higher costs are consistent with the added manufacturing complexity (for example a six-step production path for R-1234yf as contrasted to an initial two-step and now a single-step process for R-134a). Higher costs also result from the need for tight process control and cleanup steps, to avoid toxic or otherwise undesired contaminants including isomers and stereoisomers (enantiomers). Anecdotal reports suggest that the initial original-equipment manufacturer (OEM) cost for R-1234yf may be ten or more times (one account indicates 12 times) that for R-134a. The price factor may fall to

four to eight times higher once commercial-scale production plants are completed and supply catches up to demand. Price multipliers also could fall if competitive refrigerants gain acceptance, though the MAC community is seeking to avoid the complications inherent to servicing multiple options. The prices for sales to aftermarket distributors and technicians (who generally purchase refrigerants in smaller containers and net amounts) are likely to be even higher than to OEMs. The very broad patents pending and issued for the new unsaturated fluorochemicals, as well as blends incorporating them, include more extensive claims than for earlier refrigerants. While some of these patents may fall to legal challenges, they may — again at least initially — reduce competition. The resulting refrigerant prices almost certainly will force OEMs to seek low-charge designs where practical and to continue examination of less costly alternatives. The prices also will affect aftermarket service choices, subject to regulatory approvals, and attempts to market — legally or illegally — alternatives of concern. From inception of the third generation, disreputable suppliers have attempted illegal importation of controlled refrigerants from developing countries having delayed transition schedules. They also have misrepresented blends of fluorinated refrigerants with hydrocarbons, such as mixtures of R-12, R-22, or R-134a with n-butane, isobutane, or propane. Likewise, episodic sale and use of adulterated refrigerants has manifested itself several times in stationary and MAC service (AAR, 2011) and most recently in refrigerated transport container systems, “reefers” (Bennett, 2012). Such cases often involve fluorinated refrigerants cut with R-40 or other low-cost or uncontrolled components and misrepresented in *black market* (counterfeit refrigerant) sales. Refrigerant fraud prevention is beyond the scope of this paper except to note that the higher prices anticipated for unsaturated fluorochemical refrigerants in the fourth generation will have a perverse impact. Such high costs will foster illicit substitution of less expensive, often dangerous refrigerants and refrigerant blends, not anticipated and without protective measures in system design, application, and aftermarket service.

- Litigation and Liability: Both nonhalogenated and halogenated refrigerants face uncertainty resulting from future accidents and especially those linked to flammability or increases in operating pressure, unforeseen toxic or environmental consequences, or reduced product durability. Chemical manufacturers are investing enormous sums to qualify new products. Likewise, equipment manufacturers carefully evaluate and test new refrigerants, impacted components, equipment, and system designs. Still, at least in the USA, tort history points to risks in shifts, predicated on assumption that changes introduce hazards not inherent to other options. Notwithstanding anecdotal incidents, European and later other substitution of hydrocarbons, primarily isobutane (R-600a), for R-12 (and its successor, R-134a, in the third generation), proceeded without the level of catastrophic flammability incidents posed early on as concerns. That success prompts upscaling of hydrocarbon substitution, for example use of propane (R-290), propylene (R-1270), and blends with them in air conditioners, heat pumps, small chillers, and commercial refrigeration (the last typically with a secondary heat transfer fluid to isolate the hydrocarbon charge outdoors). These hydrocarbons can be efficient and comparatively inexpensive choices, but the charge sizes for the cited applications are significantly larger than for refrigerators and the historical leak rates are much higher. As usual, early adopters may benefit with advances or get burned — pun intended — with the result. The latter case, if it does happen, would force further refrigerant reconsideration.
- Unforeseen Toxicity, Environmental, or Other Suitability Issues: As mentioned above, technology shifts introduce inherent potential for discovery of adverse secondary impacts. Criteria are well established for both acute (short-term, single exposures as may result from accidental releases) and chronic (long-term, repeat exposures including from occupational handling) toxicity. Such criteria evolve with time and, of necessity, with quantum shifts in either understanding or accepted chemicals. As an example, development of the second generation of refrigerants (driven by safety and durability) included systematic toxicity testing of both then conventional (nonfluorinated) and new, fluorinated candidates (Nuckolls, 1933). The resulting report discusses the nature of life, fire, and explosion hazards and outlines salient concerns for both the chemicals addressed and their decomposition and combustion products. Despite documented earlier awareness of both cardiac function impairment and endogenous epinephrine (adrenaline) sensitization by hydrocarbons and nonfluorinated refrigerants (for example Levy and Lewis, 1911-1912, and Hermann and Vial, 1935), cardiac sensitization by fluorochemicals was not investigated until much later (Burgison et al., 1955; Shulman and Sadove, 1967; Reinhardt, 1969). Likewise, in haste to advance

consensus and regulatory approvals and safety guidance, early data can be conflicting. For example, the documentation for consensus safety exposure limits for R-1234ze(E) (an unsaturated HFC) incorrectly show it to be nonflammable (AIHA, 2011 and 2012) while a consensus safety standard classifies it as “A2L” for “lower flammability” and low burning velocity (ASHRAE, 2011). The risk is exacerbated when pivotal underlying studies are withheld from public scrutiny, as was the case in developing consensus safety guidance for R-1234yf (Calm, 2009). At least two unsaturated HFCs with high early expectations — namely R-1225ye(Z) and (at least pending further studies) R-1243zf — already have fallen out of pursuit, based on unforeseen toxicity findings, after being promoted to and subjected to limited testing for MAC use. The critical point is that full hazard awareness and correct data may not be available at the time of product introduction, particularly for a class of chemicals previously not widely used in similar applications. Screening is based on criteria for known hazards; awareness of or linkage to additional hazards may not emerge until later, as was the case for ozone depletion by CFCs in the 1970s despite commercialization in the 1930s. Breakdown of very-short-lived chemicals — and specifically unsaturated fluorochemicals — may lead to recognition of decomposition effects or interactive decomposition effects with unrelated chemicals in urban environments that are not currently evident or checked, despite intensive scrutiny. Such effects may be less relevant for long-lived compounds with dispersal before most decay occurs.

- **Local Impacts:** A number of regional studies suggest tolerable environmental consequences based on projected emissions of R-1234yf (an unsaturated HFC now considered the leading candidate to replace R-134a) for MAC and related transport use. Henne et al. (2012), Kajihara et al. (2010), and Luecken et al. (2010) examined impacts in Europe, Japan, and the United States, respectively. The well-documented Luecken et al. study, predicated on emission projections for the USA from Papasavva et al. (2009), clearly shows dispersion of some emissions from the United States into as well as resulting decomposition product deposition in Canada and Mexico, but neglects corresponding (additive) emissions from those countries impacting the USA. The Henne, Kajihara, and Luecken studies focused on transformation of R-1234yf into trifluoroacetic acid (TFA), a persistent decomposition product, with lesser consideration of hydrofluoric acid (HF) and other decomposition or potential combustion products. The studies projected that emissions will surpass previously measured levels in background air, but that the airborne and mean rainwater concentrations still will be much lower than safe levels previously determined for even the most sensitive aquatic life-forms. Critics suggest that the analyses are inadequate and/or the findings disqualifying. Greenpeace (2011) notes that R-1234yf “yields more than 90% TFA, or 4 to 5 times as much as HFC-134a” and that if R-1234yf and other unsaturated HFCs become “the refrigerant of choice in multiple sectors worldwide, the concentration of TFA in fresh water bodies could increase dramatically, with unknown effects on ecosystems and human health.” Greenpeace (2011) also suggests, but with limited substantiation and contradictory citations, that unsaturated HFCs acting as volatile organic compounds could exacerbate urban air pollution. Kauffeld (2012) concludes, though he does not provide a detailed rationale, that “unsaturated HFCs are not considered a long term alternative.” Without attempting resolution here, further study is needed to address the combined emissions and TFA consequences from additional refrigerants (in applications other than MAC use) as well as related chemicals in applications other than as refrigerants, for example, as blowing agents, solvents, and fire suppressants. Resulting additional emissions will, at a minimum, increase atmospheric loading of TFA and other decomposition products. Henne et al. (2012) specifically suggest verification with future sampling of TFA in the atmosphere and of accumulation in sensitive areas including endorheic basins (those not ultimately flowing into oceans and subject to mineral and other chemical buildup with successive partial or full evaporation and refill cycles). Tromp et al. (1995), Kotamarthi et al. (1998), and others previously addressed such conditions for fluorochemicals with comparatively longer atmospheric lifetimes, implying greater dispersal before decomposition. Further examination appears warranted for the new unsaturated compounds, with short atmospheric lifetimes (days versus years), to reconfirm evaporative concentration consequences and to address localized air quality impacts in combination with other urban chemicals and their decomposition products.
- **Political Naïveté:** The perceived ease and speed of the first refrigerant substitution (possibly minutes for Perkins’ associates) and introduction of successive generations (within 20 years of the Montreal Protocol and ten years for the Kyoto Protocol) leads politicians to assume that industry protestations can be overcome with concerted

mandates. Notwithstanding the enormous investments entailed, manufacturers responded fairly rapidly to declining manufacturing quotas and scheduled phase-outs of ozone-depleting chemicals. Despite prior insistence that the schedules could not be met, manufacturers actually supported schedule acceleration to consolidate focus on the new solutions once the transition was underway. Likewise, with only a regional mandate for mobile air conditioners, manufacturers again identified new solutions and, with threat of broader regulations, addressed other applications as well. The industry is divided, and proponents of nonhalogenated (“natural”) refrigerants assert further environmental benefits with elimination of halogenated (“synthetic” and primarily fluorochlorocarbons) options. Policymakers, therefore, have come to believe that industry is protecting its products and is too complacent to look further until forced to do so. Regulators, therefore, have been lulled into false confidence and see further mandates as focal, perhaps extending to impossible “repeal of the second law of thermodynamics” if needed for efficiency gains!

The pivotal question is how likely any of the factors discussed or combination of factors is to affect survival of the imminent fourth generation of refrigerants? Without intent to trivialize the uncertainty, the seven concerns raised (and there may be or probably are others) taken together compound the probability. A 90% chance of survival for each of them individually suggests less than a 50% combined likelihood, but the probability undoubtedly differs (lower or higher) for each factor individually. Absent a defensible prediction, determination will depend on how meticulously the air-conditioning and refrigeration industry evaluates the cited and additional concerns. Simple conformance to current or anticipated minimum regulatory requirements risks necessity for future transition to a fifth generation following the imminent fourth generation, just as it followed the third generation for ozone protection with subsequent attention to climate change protection. The sequence is somewhat ironic given much earlier awareness of greenhouse gas mechanisms and the potential for global warming (Fourier, 1824 and 1827; Arrhenius, 1896).

One might also ask when that fifth generation might occur. The first, second, and third generations lasted approximately 100, 60-65, and 20-25 years, respectively. A simple linear regression suggests duration of less than zero years (not introduced?) for the imminent fourth generation, but a forced exponential regression suggests 12 years. There is, however, no causal relationship to justify this regression or resulting projection. Like a trend analysis of seasonal ice cream consumption and drowning frequency, there is an implied codependence on related causation factors. Merely as an observation without implied predictive value, successive refrigerant generations have consistently gotten shorter, reflecting increasing attention to environmental protection and more broadly growing regulatory control of products.

Transition from the first (*whatever worked*) to the second (*safety and durability*) generations resulted primarily from opportunities and technology advances. The next two transitions to the third (*ozone protection*) and fourth generations (*global warming mitigation*) resulted from regulatory changes for environmental protection and, later, perceived business opportunities. Any of the uncertain factors discussed above could drive a further transition, especially if embraced by and further advocated by environmental constituencies and nongovernmental organizations.

NO IDEAL REFRIGERANTS

Calm and Didion (1997) concluded that “the outlook for discovery or synthesis of ideal refrigerants is extremely unlikely” and that “trade-offs among desired objectives, therefore, are necessary to achieve balanced solutions.” They further noted that “fragmented regulation of the chemicals involved, to address individual issues, jeopardizes the prospect of solving subsequently addressed problems.” Wuebbles and Calm (1997) were more specific in demonstrating that the process of successive, single-metric, disqualification steps risks elimination of good overall choices for minor — even indiscernible — impacts in early steps despite offsetting benefits in later steps. Three cases illustrate how pro forma rejection of chemicals or classes of chemicals for known, but inconsequential risks may be more detrimental than beneficial.

- While high flammability was a key constraint in transition from the first to second generation, experience with hydrocarbon domestic refrigerators in the last two decades shows that flammable fluids in small-charge, nearly leak-free systems pose only a limited risk with improvements in equipment fabrication.
- Concerns with marginal and debated flammability in R-245ca — unclassified but likely an A2L refrigerant if classified under current standards (ASHRAE 2010b and 2011) — led to its abandonment as a successor to R-123

in the third generation (though ineligible for the fourth) in low-pressure, centrifugal chillers (Glamm et al., 1996; Keuper, 1996). Alternative pursuit of R-245fa — another R-245 isomer — as a refrigerant and also as a working fluid in organic Rankine cycles (ORCs) resulted from a small flammability difference (crossing an arbitrary test demarcation), despite lower efficiency, higher GWP, higher toxicity, and higher pressure. Studies supporting current efforts to relax restrictions (ASHRAE, 2010a and 2010b; ISO, 2005 and 2008) for refrigerants with very low flammability — namely to differentiate refrigerants classified as “2L” for flammability from those classified as “2” — again show that previously disqualifying criteria resulting from simplistic groupings may not be warranted.

- Eliminating refrigerants, including some HCFCs and HFCs (though not all or even the majority) based solely on non-zero ODP or on GWP thresholds, without regard to offsetting benefits such as higher efficiency, can cause environmental harm in the name of protection.

Nonfluorinated refrigerants can co-exist with halogenated counterparts, and each individual candidate warrants screening on an application by application basis, suggesting a basis for the fifth generation if future findings dictate one.

Fifth Generation – Efficiency and Trade-Offs (2020s-?)

The defining change of a fifth generation could be another shift in chemicals, but such opportunities are becoming increasingly difficult to identify. A more rational, but clearly controversial, approach would simply address the qualifying criteria of low or very-low ODP, GWP, flammability, toxicity, and even cost together (Calm and Didion, 1997; Wuebbles and Calm, 1997). The new screening would re-examine previously discarded candidates including those phased out of prior commercial use for very minor adverse consequences using sequential, rigidly-applied criteria. For example, while zero-ODP may be desirable as long as other candidates exist, elimination of refrigerants solely for having very low ODP from uses with minimal emissions warrants reconsideration if the alternatives result in increased energy use. Likewise, avoidance of refrigerants with marginal occupational exposure limits, and especially those with comparatively high boiling points (more specifically low volatility), may be more stringent than warranted. Tests of such chemicals have shown that spills do not necessarily reach acute or even implicitly lower occupational exposure limits. Indeed, the majority of refrigerants now classified as “B” — higher toxicity — in ASHRAE 34 and ISO 817 still do not reach the defined criteria for “highly toxic” or even “toxic” in widely adopted model construction codes or in U.S. federal regulations for hazardous materials (ASHRAE, 2010b; ISO, 2005 and 2008; ICC, 2012; NFPA, 2012; OSHA, 2012). Several refrigerants classified as “B” in ASHRAE 34 and ISO 817 are still deemed “practically nontoxic” in toxicological reviews.

With recognition that perfect refrigerants — “natural” or “synthetic,” halogenated or nonhalogenated — do not exist, more care is needed in discarding options for negligible or manageable deficiencies. The criteria for the fifth generation may be as simple as allowed trade-offs for individual candidates with very minor defects but having important offsetting benefits with consideration of efficiency, application occupancy, equipment location, charge size, and potential to reduce leakage. The last of these items even suggests distinction for specific chemicals between open (intended release) and closed (release not essential) usage, namely distinction between refrigerant use and applications inherently requiring release for use (such as propellants) rather than regulation by intrinsic chemical composition or properties alone. Even further, ODP, GWP, toxicity, and flammability criteria might be differentiated for equipment or systems with minimal life-cycle releases (operating leakage plus releases during manufacturing, transportation, service, retirement, and amortized accidental catastrophic losses for all of them) versus higher-leakage levels (for example, MAC and commercial refrigeration use until significantly improved from historic levels).

Such a fifth generation might and probably would include new chemicals, but also some previously retired or now being retired based on rigorous and comprehensive re-examination rather than the historic approach of sequential, single-metric eliminations. Doing so would require changes to international treaties such as the Montreal Protocol (possibly not for the Kyoto Protocol) and regional and/or national regulations. It also would make enforcement more difficult, but continued elimination of chemical classes from a finite set may not leave any other option.

A fifth generation would necessarily include new criteria emerging from identified challenges to the fourth generation, of which higher efficiency — not simply asserted potential, but rigorously demonstrated and independently verified improvement in real equipment — will almost certainly be one.

CONCLUSIONS

The history of refrigerants encompassed four distinct intervals divided by changes in selection criteria. The four generations included slightly overlapping periods based on *whatever worked* (1830s-1930s), improved *safety and durability* (1931-1990s), *stratospheric ozone protection* (1990s-2010s), and attention to *global warming* (2012-?). The transitions between successive generations required very large research, development, plant construction, evaluation, product redesign, testing, training, and additional investments, but they also created significant business opportunities. While actual transition to the fourth generation has just begun, a number of challenges are emerging that may dictate later transition to a fifth generation predicated on *efficiency and trade-offs* (2020s-?) in the absence of ideal refrigerants. Among the potential driving factors are efficiency, momentum, prices, litigation and liability, unforeseen suitability issues, local impacts, and political naïveté. Possibly the most important, but also the least predictable uncertainties are whether the need for future transition(s) can be averted and, if not, what the future defining criteria would be. Insight into the driving factors may help in final selections of fourth-generation refrigerants and product designs to use them. While the underlying criteria for the fourth generation may be set, the responses will evolve somewhat and improve with time. The real choice, then, is up to industry, which can respond to immediate requirements (such as GWP limits) alone or attempt to anticipate and respond to future driving factors. If GWP alone, the fourth generation may be short lived and require one or more future refrigerant transitions predicated on further selection criteria. Likewise, policymakers should take a more coordinated approach than sequential steps of elimination. The choices, therefore, are forward-looking selections that go beyond minimum mandates or refrigerant transitions ... again.

NOMENCLATURE

| | |
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| ACR | air conditioning and refrigeration |
| CFC | chlorofluorocarbon, a chemical consisting at the molecular level of <u>chlorine</u> , <u>fluorine</u> , and <u>carbon</u> atoms only |
| FC | a chemical compound consisting of <u>fluorine</u> and <u>carbon</u> atoms only (see fluorocarbon) |
| FIC | fluoro-iodocarbon, a chemical consisting at the molecular level of <u>fluorine</u> , <u>iodine</u> , and <u>carbon</u> atoms only |
| fluorochemical | a chemical compound that includes fluorine and other atoms |
| fluorocarbon | a chemical compound consisting of fluorine and carbon atoms, sometimes (not herein) used less rigorously to refer to compounds consisting of fluorine, carbon, and other atoms (see fluorochemical) |
| GWP | global warming potential, normally and herein relative to carbon dioxide (CO ₂) for 100 yr integration |
| HBFC | hydrobromofluorocarbon, a chemical consisting at the molecular level of <u>hydrogen</u> , <u>bromine</u> , <u>fluorine</u> , and <u>carbon</u> atoms |
| HC | hydrocarbon, a chemical consisting at the molecular level of <u>hydrogen</u> and <u>carbon</u> atoms only |
| HCC | hydrochlorocarbon, a chemical consisting at the molecular level of <u>hydrogen</u> , <u>chlorine</u> , and <u>carbon</u> atoms only |
| HCFC | hydrochlorofluorocarbon, a chemical consisting at the molecular level of <u>hydrogen</u> , <u>chlorine</u> , <u>fluorine</u> , and <u>carbon</u> atoms only |
| HCFO | hydrochlorofluoro-olefin, an unsaturated HCFC |
| HCO | hydrochloro-olefin, an unsaturated HCC |
| HFC | hydrofluorocarbon, a chemical consisting at the molecular level of <u>hydrogen</u> , <u>fluorine</u> , and <u>carbon</u> atoms only |
| HFIC | hydrofluoro-iodocarbon, a chemical consisting at the molecular level of <u>hydrogen</u> , <u>fluorine</u> , <u>iodine</u> , and <u>carbon</u> atoms only |
| HFO | hydrofluoro-olefin, an unsaturated HFC |
| HO | hydro-olefin, an unsaturated HC. The HO designation is not specifically recognized in ASHRAE standard 34 (ASHRAE, 2010b), but is consistent with other terminology therein. |
| MAC | mobile air conditioning |

| | |
|---------------------|---|
| low-GWP | GWP \leq 150. Low-, very-low, and ultra-low and similar descriptors are subjective; Calm and Hourahan (2011) discuss emerging classification schemes. |
| ODP | ozone depletion potential normally and herein relative to R-11 |
| ODS | ozone-depleting substances |
| organofluoride | see fluorocarbon |
| PFC | a fully-fluorinated chemical compound, one consisting of fluorine and carbon atoms only |
| saturated | an organic (carbon-based) chemical compound in which there are no double or triple bonds between carbon atoms |
| τ_{atm} | atmospheric lifetime |
| unsaturated | an organic (carbon-based) chemical compound having one or more pair(s) of carbon atoms connected by a double or triple bond |

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