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Greenhouse Warming Potential of Candidate Gaseous Diffusion Plant Coolants

Lee D. Trowbridge

Enrichment Technical Operations Division

March 1991

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GREENHOUSE WARMING POTENTIAL OF CANDIDATE GASEOUS DIFFUSION PLANT COOLANTS

Lee D. Trowbridge

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ABSTRACT

A preliminary estimate has been made of the greenhouse warming potential (GWP) of coolants under consideration as substitutes for CFC-114 in the gaseous diffusion plants. Coolants are not at present regulated on the basis of GWP, but may well be in the future. Use of c-C_4F_8 or n-C_4F_{10} is estimated to have three to four times the greenhouse impact of an equivalent use of CFC-114. Neither of the substitutes, of course, would cause any ozone depletion. HCFC-124 (a probable commercial substitute for CFC-114, but not presently under serious consideration due to its relatively high UF_6 reactivity) would have much less greenhouse and ozone depletion impact than CFC-114. The GWP estimates derive from a simple model that approximately reproduces literature values for similar compounds. The major uncertainty in these estimates lies in the atmospheric lifetime, especially of the perfluorocarbon compounds, for which little reliable information exists. In addition to GWP estimates for coolants, the overall greenhouse impact of the gaseous diffusion plants is calculated, including indirect power-related CO_2 emissions. This result is used to compare greenhouse impacts of nuclear- and coal-produced electricity.

INTRODUCTION

The search for a substitute for CFC-114, used as a coolant in large quantities in the US DOE's gaseous diffusion plants (GDPs), has aimed at finding a compound that would reduce or eliminate the impact on stratospheric ozone depletion. A fairly unique requirement of the GDPs is for minimal reactivity with UF_6, as the possibility always exists of leakage of small amounts of the coolant into the UF_6 stream. This requirement seems to eliminate use of the popular commercial CFC substitutes, i.e., hydro-fluoro-carbons (HFCs) or hydro-chloro-fluoro-carbons (HCFCs), unless plant operational safety compromises can be made. The compounds that appear usable at this time (namely n-C_4F_{10} and c-C_4F_8) are "greenhouse gases". The greenhouse warming potential (GWP) is not a regulated property yet, but may very well be soon. Delegates from over 130 countries met in February 1991 in Chantilly, Virginia under the auspices of the UN for the first of several negotiating sessions of the Intergovernmental Negotiating Committee on a Framework Convention on Climate Change. This group has been tasked by the UN with drafting a treaty (for signing in June 1992), aimed at controlling greenhouse emissions , analogous to the Montreal Protocol treaty process, which led to international control of ozone-depleting chemicals.[1]

This report is intended to document work, originally presented orally[2,3] in 1990. This work is a preliminary step toward quantifying the greenhouse impact of the candidate GDP coolants.

The greenhouse warming issue, as applied to the GDPs, devolves into two fundamental questions:

(1) What is the greenhouse impact of the candidates under consideration as CFC-114 substitutes?

(2) Should the impact be of concern to DOE and the enrichment enterprise?

At the present time, the answer to the second question is a fairly obvious "yes", largely due to the recent evolution of the politics of the greenhouse warming issue and general concern for global atmospheric changes. The Montreal Protocol is a precedent for the establishment of an international policy protecting the global environment. Control of anthropogenic contributions to the greenhouse effect has many parallels to control of ozone depleting emissions, but in other ways is much different. Greenhouse gas emissions result from a wider scope of human activities, some much more fundamental to the operation of society than are CFC uses. Most notably, energy production and agriculture contribute significantly to greenhouse emission. Since energy production (via fossil fuels) is the main contributor to anthropogenic greenhouse gas emissions, any curative measure that narrowly focuses on a small piece of the problem has the potential for doing more harm than good through energy inefficiency or other unanticipated shifts in fuel usage. Because of such complications, it is impossible at this point to predict with confidence the form that greenhouse gas regulation will take. Nevertheless, the uranium enrichment enterprise needs to be aware if its plans will have an adverse impact on the environment (exclusive of the details of future regulation). Further, the enterprise needs to be prepared to discuss the issue intelligently in the political arena.

Insofar as ozone-depleting gases are concerned, the evolving world strategy in the near term seems to be to substitute CFCs with HCFCs or HFCs. HCFCs are chlorine-containing compounds, and thus can damage the ozone layer. Because of their hydrogen content, however, they have relatively short atmospheric lifetimes, and thus have an influence (i.e. ozone depletion potential, or ODP) only a few percent that of corresponding CFCs. Because they *do* have an impact on the ozone layer, however, they will probably be phased out by the year 2020. HFCs contain no chlorine, and thus pose no threat to the ozone layer. Ultimately, applications that now use CFCs will have to shift to HFCs or other non-ozone-depleting materials.

Ozone depletion control measures are discussed here because the strategy outlined above for commercial CFC replacement tends also to answer the greenhouse question. All the gases referred to are infrared-active, but the relatively short lifetime of the substitutes limits their greenhouse influence.

In public talks at scientific symposia, representatives of CFC manufacturers appear to be taking GWP as seriously as ODP in their search for substitutes, even though GWP is not a regulated property. In addition, international meetings are planned in the near future to discuss GWP regulation, with a structure very similar to the meetings that led to the Montreal Protocol on Ozone Depleting Materials.

In summary, regulation could well come, but may take any of several forms. Greenhouse warming is a more complicated issue than ozone depletion because a wider range of compounds can contribute, among them CO_2 from energy use. It is very likely, for example, that an attempt to reduce greenhouse-gas emissions through narrow regulatory control of a particular compound could lead to energy inefficiencies that would cause an overall *increase* in the greenhouse impact. This report will attempt to put in perspective that energy situation with regard to GDP coolants.

BACKGROUND

Several terms have been mentioned so far and more will be soon that deserve some explanation. Two are Ozone Depletion Potential (ODP) and Greenhouse Warming Potential (GWP). These are numerical evaluations of the relative contribution to the appropriate atmospheric effect of a unit emission of a given compound. They are typically computed by use of atmospheric models. To calculate the ODP of a compound, the model is run with a unit mass injection of the compound in question, and as a base case without that injection. The fractional depletion of stratospheric ozone, integrated over time, is computed from these two runs. The same is done for a reference compound (in the case of ODP this compound is CFC-11). The ratio of the fractional ozone depletion values for the compound in question and the reference compound is termed the Ozone Depletion Potential. GWP is computed similarly, but the parameter of interest is the time-integrated average surface temperature increase due to unit mass injection of the compound. At present, there does not seem to be a consensus on the details of the time integration. The reference compound for GWP calculation may be CFC-11, CFC-12, or CO_2. In this report, GWPs and ODPs will both be referenced to values for CFC-11.

A related pair of acronyms that will be used in this report are Greenhouse Warming Impact (GWI) and Ozone Depletion Impact (ODI). These incorporate the quantities of material emitted, and are defined as the GWP or ODP (as appropriate) times the mass of material emitted. These parameters will be used to allow comparison of emission of different masses of different compounds.

The greenhouse effect *per se* is the trapping of heat in the earth's atmosphere by infrared (IR) absorbing gases. Solar radiation in the visible and IR bands is re-radiated to space largely as IR. Infrared radiation at frequencies absorbed by atmospheric gases does not directly escape, and contributes to warming of the atmosphere (and ultimately the surface of the earth). Naturally occurring gases, mainly H_2O and CO_2, absorb certain bands of the IR spectrum (see Figure 1), but leave the atmosphere transparent in other IR bands. The current concern with greenhouse warming is not that such an effect exists, but that significant changes in its magnitude can be caused by anthropogenic addition of long-lived IR active gases to the atmosphere.

Essentially all gases except homonuclear diatomics (such as N_2 and O_2) and the inert gases (He, Ne, Ar, etc.), absorb infrared radiation. If their absorption bands do not fall in the spectral regions made opaque by H_2O or CO_2, they will also contribute to greenhouse warming. The term "greenhouse gas" is generally taken to mean an infrared active gas with a significant atmospheric lifetime. The class of compounds discussed in this report are all greenhouse gases to some extent. Figure 1 shows the IR absorption spectra of humid air, and of several compounds of interest (CFC-114, HCFC-124, c-C_4F_8, and n-C_4F_{10}). These fluorocarbon compounds are strong IR absorbers, and their absorption bands fall in a relatively transparent region of the spectrum.

These compounds are all saturated (i.e. no double or triple bonds), partially or fully halogenated organics. Depending on the composition, they are referred to by the acronyms CFC (chlorofluorocarbons - $C_xF_yCl_z$), HFC (hydrofluorocarbons - $C_xH_yF_z$), HCFC (hydrochlorofluorocarbons - $C_wH_xCl_yF_z$), or PFC (perfluorocarbons - C_xF_y).

GDP Coolant Substitutes

Currently the GDPs use CFC-114 as a primary coolant. A search is underway for a replacement due to CFC-114's ODP (computed as about 0.7 in most literature, but listed as 1.0 for treaty purposes). It is, however, also a greenhouse gas, with GWP estimated at 3.7 to 4.1.[4]

CFC-114 is not a big commodity material relative to other CFCs. It is used in some large-scale cooling applications, and also for foam blowing. Commercial substitutes for general use will probably be HCFC-124 and perhaps HFC-134 or blends. Most of the GDP requirements are essentially the same as that of other CFC-114 commercial cooling applications. Two requirements, however, are related to the possibility of coolant leakage into the UF_6 stream of the diffusion plant: (1) the molecular weight should differ significantly from that of UF_6 (so that it will separate from the UF_6 - a relatively easy requirement to meet); (2) the material should not be excessively reactive with UF_6.

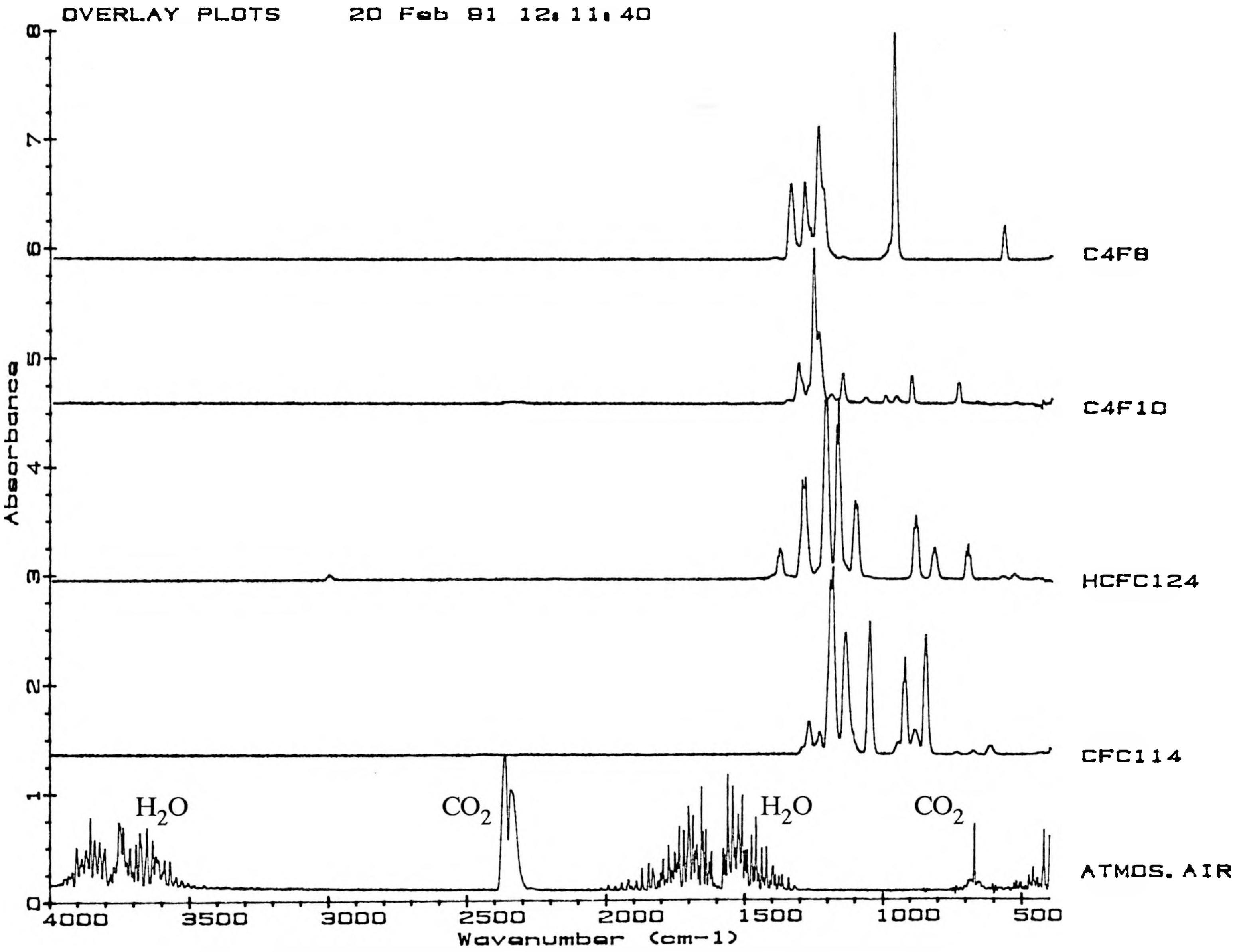

Figure 1 — Infrared spectra for four coolants discussed in this document, and of atmospheric air, showing absorption bands of H_2O and CO_2. The IR absorption bands for all these coolants in general do not coincide with absorptions of H_2O and CO_2.

This latter property is harder to achieve since, in essence, the reactivity of HCFCs and HFCs with OH radicals in the troposphere is responsible for their short lifetime, and is the reason that these compounds are considered as substitutes. The OH radical is chemically similar to (but often less reactive than) atomic fluorine. Thus, at least in a general way, an increase in tropospheric reactivity implies an increase in reactivity in a fluorinating environment. What is important, of course, is the quantitative details of this reactivity. Perhaps an HCFC or HFC can be found with a enough reactivity to have a short lifetime in the atmosphere, but not so much (in UF_6) as to increase risk of fire or explosion in the cascades. One cannot say categorically that no hydrogen-containing organic will meet both requirements, nor can one say that one exists.

We have looked at HCFC-124 and found it to be 100 to 1000 times as reactive with UF_6 and F_2 at simulated plant conditions as is CFC-114.[5] The question of whether this is "too reactive" is open. However, recent moves to negotiate a phase-out of HCFCs by the year 2020 indicate that they may be considered inadequately reactive from an atmospheric standpoint.

One way to eliminate ozone concerns is to eliminate Cl from the molecule. HFCs and PFCs fall into this category. Hydrogen-containing HFCs are potential substitutes for some CFCs (e.g. HFC-134a). We expect reactivity in UF_6 to increase with number of C-H bonds; based on the poor showing of HCFC-124 (which has only one C-H bond), we haven't pursued HFCs, but may in light of possible emphasis on greenhouse warming.

At the outset of the search for substitute coolants, it was suspected that hydrogen-containing compounds might prove too reactive, so the search focussed in early on compounds that contained no hydrogen or chlorine, namely the saturated PFCs. Two that were available on reasonably short notice and were in the general vapor pressure window needed by the existing GDP cooler design were the normal- and cyclo- perfluorobutane, $n\text{-}C_4F_{10}$ and $c\text{-}C_4F_8$. These proved to be relatively unreactive in tests under simulated reaction conditions[6]. These compounds, however, will not have available to them the OH atmospheric destruction mechanism, and thus are likely to have relatively long atmospheric lifetimes. This, combined with their infrared activity, indicates that they will be greenhouse gases.

DISCUSSION

Greenhouse Warming Potential of Candidate Substitute Coolants

The first question posed at the beginning of this report was: "Can we estimate the GWP of these substitutes?". GWP for CFCs (etc.) are typically calculated using elaborate atmospheric models. The model is run with and without a unit quantity of the gas; the average surface temperature change, integrated over time, is taken as the greenhouse warming for that gas. The models consider

1. atmospheric circulation (one- or two-dimensional)
2. atmospheric chemistry and photolysis that can destroy the compound.
3. radiative exchange (solar and thermal radiation), including masking effects of natural IR-absorbing gases (CO_2 and H_2O).

The models yield the atmospheric lifetime and greenhouse effect of the gas in units of, say, degrees surface temperature increase per megaton atmospheric loading. For comparison purposes, this result is typically referenced to $CFCl_3$ (CFC-11) to give the ratio termed the GWP.

GWPs are available in the literature for CFCs and most of their potential commercial substitutes. At present, no one in the scientific literature seems much concerned with perfluorocarbons, presumably because they are not of commercial significance compared to HFCs and HCFCs. Thus, the GWP question has not been answered for us in the case of c-C_4F_8 and n-C_4F_{10}, although values are available for HCFC-124.

Atmospheric modeling is an elaborate, time-consuming, and highly specialized undertaking. For that reason, a shortcut was sought. A simple surrogate model* was devised which seems to adequately reproduce the literature results for several CFCs, HCFCs and HFCs.

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* "surrogate model" - computer modeling jargon for a simple model or arithmetic expression that substantially reproduces the results of a more elaborate (and hence more respectable) simulation.

The model calculates the GWP of compound "x" as:

$$GWP_x = I_x L_x / I_{CFC-11} L_{CFC-11}$$

where I = Integrated IR absorbance at unit pressure and pathlength
L = atmospheric lifetime

Table 1 lists literature values for the integrated IR absorbance (440 cm^{-1} to 1535 cm^{-1}) for several compounds, the predicted atmospheric lifetimes, and the GWP derived from two atmospheric models. Shown in the last column is the GWP predicted by the surrogate model (i.e. the formula above). The GWPs are also plotted on a correlation diagram in Figure 2. The surrogate model, in spite of its simplicity, yields results that vary from the atmospheric model results by typically 30%. Many of the surrogate model's GWPs seem systematically a bit high (or perhaps the reference CFC-11 gives a lower-than-average value for GWP). One could perform a regression fit of the literature GWP vs. surrogate model GWP and get a better empirical reproduction of the literature data. That needlessly complicates this very simple, if approximate, model and will not be done here.

Only two parameters are needed for input to the surrogate model: IR absorbance and atmospheric lifetime. Data is available in the literature on both parameters for several compounds we deal with (CFC-114, CFC-115, HCFC-124), but not for the PFCs n-C_4F_{10} and c-C_4F_8.

Integrated IR absorbance can be easily obtained directly from spectra in our laboratory. Integrated absorbance is calculated per the following equation:

$$\text{Integrated Absorbance} \equiv \frac{1}{\mathbf{P}\ \mathbf{d}} \int \ln(\mathbf{I}/\mathbf{I_0})\ \mathbf{df}$$

where **P** is the partial pressure of the sample, **d** is the path length, **I** is the intensity of the IR beam at frequency **f** with the sample present and $\mathbf{I_0}$ is the intensity with the sample absent. The integration limits, in keeping with Reference 4, are taken as 440 to 1535 cm^{-1}. Modern commercial FTIR spectrometers generally have a peak integration function allowing this integral to be done very easily, the one caveat being that they typically calculate absorbance using the base-10, rather than the natural, logarithm. We use the natural logarithm to be consistent with literature values. The integrated

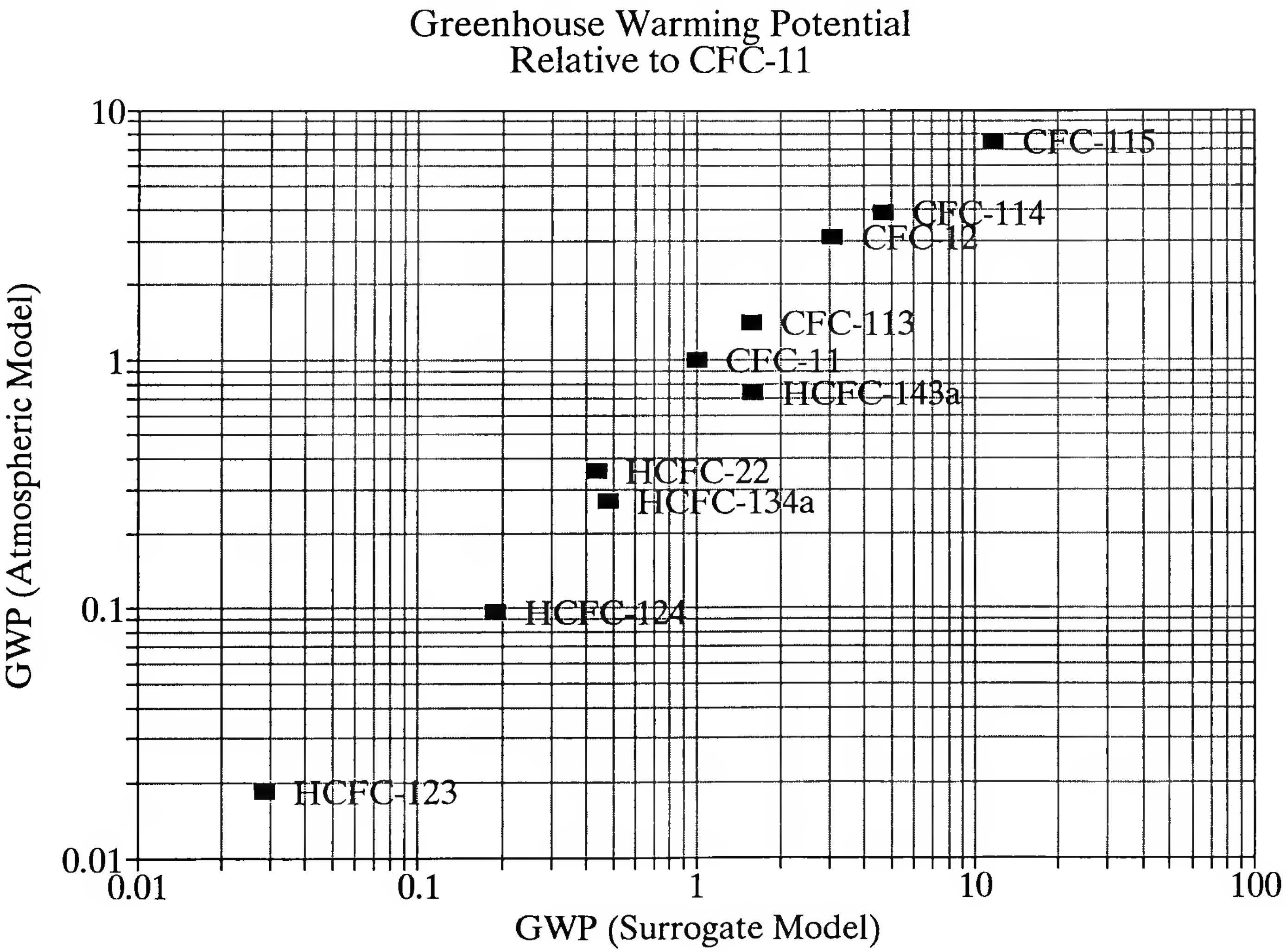

Figure 2: Correlation graph of GWP calculated from surrogate model (this work) and literature values (average of DuPont and A.E.R. values from reference 4)

absorbance has units of atm^{-1}cm^{-2} when pressure is expressed in atmospheres, path length in cm and frequency in cm^{-1}.

Table 1 : Literature values of GWP, IR Strength, compared to surrogate model's calculated GWP

Compound	GWP AER	GWP DuPont	IR Str (atm^{-1}cm^{-2})	Life (years)	Mol Wt (amu)	GWP this work
CFC-11	1	1	2389	60	138	1.00
CFC-12	3.4	2.8	3240	120	121	3.08
CFC-113	1.4	1.4	3401	90	188	1.57
CFC-114	4.1	3.7	4141	200	171	4.65
CFC-115	7.5	7.6	4678	400	155	11.62
HCFC-22	0.37	0.34	2554	15.3	87	0.43
HCFC-123	0.02	0.017	2859	1.6	153	0.03
HCFC-124	0.1	0.092	4043	6.6	137	0.19
HCFC-134a	0.29	0.25	3272	15.5	102	0.48
HCFC-143a	0.76	0.72	3401	41.	84	1.59

Our measured integrated IR absorbances for CFC-114, CFC-115, and HCFC-124 agree with literature values to within about 5%. These values, along with our measurements for n-C_4F_{10} and c-C_4F_8, are shown in Table 2.

Direct use of the integrated absorbance ignores the effects of masking by atmospheric H_2O and CO_2. It would be more proper to weight the spectrum according to the available IR energy at each frequency. From the results in table 1, however, this apparently is an effect that treats all the gases examined more or less the same; all the CFCs, HFCs, HCFCs, and PFCs under consideration have multiple bands, and the strongest ones are in a spectral region that is fairly transparent (1150 to 1280 cm^{-1}). Considering the uncertainties to be discussed later, treating the spectra by this more correct method is, for now, considered a needless elaboration of the model.

Atmospheric lifetime values can by derived be several different techniques. One method is to calculate it theoretically from consideration of atmospheric destruction mechanisms, assuming the reactions, reagent concentrations, and

Table 2 - Integrated IR absorbance

Compound	IR Strength (atm^{-1}/cm^2) Ref 4	This work
$CFCl_3$	2389	
CF_4		1615
n-C_4F_{10}		9037
c-C_4F_8		5530
CFC-114	4141	3988
CFC-115	4678	4922
HCFC-124	4043	4119

rates can be adequately estimated. Atmospheric models may incorporate chemical reactions into their calculations in order to derive a lifetime. That is to say, the atmospheric models that are used to compute GWP and ODP will also calculate the lifetime of the materials in question. Such a calculation need not be done within such a model, however, if the important factors (reactions, concentrations, and rates) are known. Indeed, results calculated from an atmospheric model are not worth much if these factors are not well known. Lifetimes for some compounds have been derived from atmospheric material balance when experimental measurements are available. Unfortunately, we have no definitive information on C_4F_{10} or C_4F_8 along any of these lines, so we are forced to reason by chemical similarity.

Typical atmospheric destruction mechanisms for CFCs, HCFCs, etc. are:

1. Reaction of a C-H bond with OH radicals in the troposphere

2. Reaction of C-Cl or C-Br bonds with atomic O in the stratosphere (this is the reaction chain that destroys ozone; it also destroys the offending precursor molecule.)

3. UV Photolysis (primarily in the stratosphere)

For HCFCs, all three apply, though reaction 1 is sufficiently slow that a small percentage of HCFC will penetrate the stratosphere to do ozone damage. Lifetimes for HCFCs range from 2 to 25 years. For PFCs, only mechanism #3 applies; estimates vary widely for the lifetime of C_xF_y compounds.

Two estimates occur in the literature for CF_4: An early estimate[7] of 14,000 years was based on calculated atmospheric mass balance, atmospheric concentration measurements, and the assumption that no natural CF_4 sources existed. A more recent measurement[8] of concentration concludes that 2/3 of the CF_4 present in the atmosphere is due to natural sources. This is based on vertical concentration profile measurements for CF_4 and C_2F_6, vertical mixing rates, and known changes in the emission rate of these compounds due to anthropogenic sources. The information necessary to compute an atmospheric lifetime from mass balance was all present in this article, but no estimate of lifetime was given. The data suggest a lifetime of less than 100 years (but with large uncertainty). This is considerably lower than estimates for the less stable CFCs, and (considering also the value's uncertainty) may be the reason the author did not actually compute the lifetime from his data.

Lifetime estimates for CF_4, then, though quite uncertain, vary from about 100 to 14,000 years. Chemically, about all we can say about the relationship to our candidate PFCs is that n-C_4F_{10} and c-C_4F_8, having presumably a larger UV absorbance, and also having C-C bonds, are likely shorter-lived than CF_4, though by how much we can't say.

A third estimate appears in the literature for a number of very stable compounds similar to our PFC candidates. A "default" estimate of 500 years has been used by atmospheric modelers for CF_4 and similar "unmeasured" gases[9]. This value seems to be based more on social science than atmospheric science. The 500 year figure is probably a crude way to put a "discount rate" or "present value" on future atmospheric changes. To put it another way, the further we look into the future, the less certain it becomes as to what the desirable anthropogenic temperature change should be. It appears probable that, from a regulatory standpoint, any greenhouse restrictions will adopt some sort of upper limit on the lifetime for long-lived gases.

For purposes of the remainder of this report, we will use a value of 500 years for the best estimate of the lifetime of C_4F_{10} and C_4F_8, with an uncertainty band of $x10^{\pm 1}$ (i.e. 50 to 5000 years). Values for lifetime and the derived GWP are shown in Table 3.

From the surrogate model, the GWP for CFC-114 is calculated to be 4.5. The corresponding values for c-C_4F_8 and n-C_4F_{10} are 13 and 18, which is to say, about 3 and 4 times that of CFC-114 on a unit mass basis. The infrared absorbance is only somewhat larger for these PFCs than for CFC-114; most of the difference lies in the lifetime estimate, which, recall, is quite uncertain.

Table 3 - GWP and ODP for Compounds discussed in this report

Compound	Lifetime (years)	Mol Wt (amu)	GWP (this work)	GWP (Lit[a])	ODP (Lit[d])
$CFCl_3$	60[a]	137.5	1.0	1.0	1.0
CF_4	500[b]	88.	8.8	---	none
C_4F_{10}	500[b]	238.	18.2	---	none
C_4F_8	500[b]	200.	13.3	---	none
CFC-114	200[a]	171.	4.5	4.1	0.7
CFC-115	400[a]	154.5	12.2	7.5	0.4
HCFC-124	6.6[a]	136.5	0.19	0.10	0.02
CO_2	230[c]			0.00078[c]	none

[a] from Ref 4

[b] guesses. Estimates range from < 100 to 14,000 years

[c] from Ref 9

[d] from Ref 10

Greenhouse Impact of GDP Coolants

From the above estimate of GWP, the greenhouse impact of GDP coolants under plausible present and future scenarios can be estimated. The following assumptions are made:

(1) Present coolant losses are 800,000 lbs/year.
(2) Future losses will be 400,000 lbs/year.
(3) GDP annual electric power usage is 2500 MW-yrs now and in the future.
(4) 5% of coolant losses are to the UF_6 stream; any C-H bonds in this 5% are fluorinated to C-F bonds.

The assumption of future loss reductions is predicated on increased emphasis on CFC loss reduction at the GDPs, which for the present is motivated by uncertainty over the availability of coolant, and in the future will be motivated by the increased cost of both CFCs and alternate coolants. Future losses are assumed to be 400,000 lbs/year regardless of the compound used. No attempt has been made to adjust this value for each compound by incorporating physical property differences such as molecular weight and viscosity. In Table 4, the first row shows the present impact of CFC-114 emissions on ozone depletion and greenhouse warming in relative terms. The ODI of current CFC usage is 280 ODP-tons/year, and the GWI is 1800 GWP-tons/year. Cutting CFC loss in half cuts these impact figures in half. Switching to c-C_4F_8 or n-C_4F_{10} will eliminate the ODI, but increase the GWI to 3 or 4 times the "future CFC-114 use" scenario, and 1.5 or 2 times the present CFC-114 effect. The increased greenhouse is directly proportional to the atmospheric lifetimes assumed for these PFCs, and thus just as uncertain as those assumptions.

Table 4 — GDP Impact on Greenhouse Warming and Ozone Depletion

Scenario	Emission (Short-Tons/yr)	ODP	GWP	Scenario Impact ODI	Scenario Impact GWI	GWI Relative to CO_2
Current '114	400	0.7	4.5	280	1800	8 %
Future '114	200	0.7	4.5	140	900	4 %
n-C_4F_{10}	200	---	18.2	0	3600	16 %
c-C_4F_8	200	---	13.3	0	2700	11 %
HCFC-124	200	(*)	(*)	7.8	110	.5%
CO_2 (power usage)	$3.0x10^7$	---	0.00078	0	23000	100 %

* HCFC-124 assumed to enter atmosphere as 95% HCFC-124, 5% CFC-115 (see text). Since the actual emission is a mixture of compounds, no ODP or GWP are shown.

Use of HCFC-124, assuming safety concerns could be adequately answered, would significantly reduce both the GWI and ODI, though not by as much as one would presume from published ODP and GWP values for this compound. HCFC-124 has been shown[5] to be reactive to UF_6 at cascade conditions. Any HCFC-124 leaking into the UF_6 stream will be fluorinated to CFC-115 before eventually escaping to the atmosphere. While HCFC-124 has a relatively short atmospheric lifetime, and consequently low ODP and GWP, CFC-115 does not. Only a small (but variable) proportion of coolant leaks are into the UF_6 stream. This fraction has been estimated variously as between 1% to about 5%. Assuming the higher value of 5%, the effect of HCFC-124, as reported in Table 4, is calculated by treating 95% of the emissions as HCFC-124 and 5% as CFC-115 (using ODP=0.4 and GWP = 7.2 from Ref 4). Under these assumptions, the ODI of HCFC-124 use is 5% and the GWI about 12% that of an equivalent loss rate of CFC-114.

Impact of GDP Power-Related CO_2 Emissions

The discussion so far has considered only the change in greenhouse impact due to coolant losses at the GDPs. In fact, the major impact of diffusion plants on atmospheric emissions of greenhouse gases lies not in coolant loss, but in the CO_2 generated at the fossil fuel power plants which provide the electricity required to operate the GDPs. The delivery to an end-user of one kwh of electricity by a coal-fired power plant generates about 1.25 kg of CO_2 (Computed from figures in Reference 11, per Table 5). While coolant losses are on the order of 300-400 tons per year at present (and will likely be reduced by conservation measures), the CO_2 put into the atmosphere from the generation of the typical annual GDP complex requirement of 2500 MW-yrs of electrical power amounts to about 30 million (short) tons. CO_2 is a much less effective greenhouse gas per unit mass than are CFCs, but the large quantity produces a much larger impact than that of coolant loss. The last column in Table 4 indicates the relative contribution of coolant emissions to that of GDP power-related CO_2 emissions. Current CFC-114 emission has a GWI about 8% that of CO_2 emissions; even the worst alternate coolant, n-C_4F_{10}, would have only about 16% the impact of CO_2. The change from CFC-114 to a PFC coolant would eliminate the ozone depletion impact of the GDPs, and but would slightly increase the greenhouse impact.

Nuclear Power's Impact on Global Warming

A final factor should be considered to place this issue in perspective. Enriched uranium produced by the GDPs ultimately generates electricity which otherwise would be generated by fossil fuels, primarily coal. It is therefore instructive to compare the greenhouse impact of power generation by these two means.

Table 5 lists the approximate US generation of electrical energy by coal and nuclear power for the year 1990 (predicted in 1985 by the Energy Information Agency[11]), the megatons of CO_2 generated, and the equivalent CO_2 emissions per kwh of generated power from each source. The figures for coal power generation represent the power delivered to end-users. The quantity of CO_2 generated was calculated from the total mass of coal used by utilities to generate that power, assuming the average chemical composition of coal to be $(CH)_n$. The impact (equivalent kg CO_2 per kwh) for coal power is simply the quotient of these two figures.

For nuclear power, the 27 million metric tons of CO_2 generated is the same figure previously cited (converted from short tons to metric tons), and is due to the electrical power required by the GDPs for enrichment. It was assumed that the electricity used came completely from coal-fired plants. One could correct for the fact that only about 70% of national electricity production comes from fossil sources (this would reduce the impact figure for nuclear power by 30%). On the other hand, energy use in other parts of the nuclear fuel cycle are ignored, though they are likely to be insignificant compared to enrichment power use. The impact figure for nuclear power includes the effect of both CO_2 and coolant losses under the current use scenario. It was further assumed that all the US nuclear power was supplied solely by US uranium enrichment, and that nuclear power plants consumed all that year's enrichment production (that is not strictly true; there are both imports and exports of enriched uranium).

Table 5 — National Energy Production and Greenhouse Warming

	Generated (10^9 kwh)	10^6 Metric Tons CO_2 generated	Equivalent kg CO_2/kwh
Coal power	2000	2500*	1.25
Nuclear Power	575	27**	0.05***

* Direct emissions of CO_2 from coal-fired power plant

** indirect CO_2 emissions from coal-fired power plants supplying power to gaseous diffusion plants; excludes power costs elsewhere in the uranium fuel cycle.

*** includes also coolant emissions.

Overall, then, nuclear power's greenhouse impact per kwh is about 4% that of coal-generated electricity. Changing the coolant to even the one with the highest GWP would not increase this figure to 5%.

Relative Contribution of GDPs to Ozone and Greenhouse Effect

At present, the relative importance of the ozone depletion and greenhouse warming issues are not known, so it is not possible to rationally trade off improvement in one area to improvement in the other. We can, however, estimate the GDPs relative contribution to each effect as a fraction of the overall national impact.

The approximate annual US consumption of fossil fuels (estimated per reference 11) is 16.7 million barrels/day of petroleum-based fuels, 19 trillion cu ft/year of natural gas, and 960 million short tons/year of coal. Assuming chemical compositions for gas as CH_4, oil as $(CH_2)_n$, and coal as $(CH)_n$, and applying appropriate conversion factors to compute CO_2 emissions from these sources, we calculate that the annual emission of CO_2 will be 2.4×10^{12} kg from oil, 1.1×10^{12} kg from gas, and 2.9×10^{12} kg from coal, for a total of 6.4×10^{12} kg CO_2. Per reference 9, CO_2 emissions in recent years have accounted for about 60% of the effective increase in atmospheric loading of greenhouse gases (weighted by their GWP), so we may approximately calculate the overall national GWI as equivalent to 1.07×10^{13} kg CO_2. The annual GDP-related emissions of CO_2, previously calculated, were 30 million (short) tons of CO_2, or 2.7×10^{10} kg CO_2. Adding 8% for the effect of present CFC-114 emissions, the annual GWI of the diffusion complex is equivalent to 2.9×10^{10} kg CO_2. This represents about 0.3% of the national GWI.

The same sort of calculation can be done for ozone depletion impact. The approximate US consumption of CFCs in 1986 (the reference year for the Montreal Protocol Treaty reductions) was 660 million pounds/year (weighted by ODP). GDP emissions at present are on the order of 600,000 to 800,000 lbs/year. The fractional impact of the GDPs to national ODI is therefore about 0.1%.

Neither of these figures should be construed to imply that GDP impact is a minor fraction of the national impact, and hence unimportant. All emissions are individually minor, but the collective impact can nevertheless be significant. However, on a proportional basis, these two calculations indicate that the GDPs contribute a greater share of the national greenhouse warming impact than they do of the national ozone depletion impact. As stated before, however, we have no way currently to place relative values on ODI and GWI.

CONCLUSIONS

An estimate has been made of the of Greenhouse Warming Potential for coolant candidates using IR spectra and chemical similarity arguments. Some simplifications have been made in the interpretation of the atmospheric infrared activity of the coolants, but this does not lead to much imprecision relative to uncertainty in the atmospheric lifetimes for PFCs. The use of an elaborate atmospheric model will not improve the quality of the answer until this lifetime question is directly or indirectly addressed. There has been some discussion of use of an atmospheric model to address this question, but without knowledge of the atmospheric residence time, or of the chemical processes that determine it, no substantial improvement can be expected in the quality of the answer.

c-C_4F_8 and n-C_4F_{10} are estimated to have GWP values 3 to 4 times that of the currently used CFC-114 under the atmospheric lifetime assumptions used here. Under future conservation scenarios, the actual impact (of the coolant only) would be 1.5 to 2 times that of current coolant emissions.

The primary greenhouse warming impact of the gaseous diffusion complex is due not to its coolant losses, but to its power use. Indirect emission of CO_2 due to GDP power use has a much larger atmospheric impact than the GDP coolant emissions (from 7 to 12 times as large).

Uranium enrichment is carried out to ultimately produce fuel for nuclear power reactors; each kwh generated via nuclear power cuts by 96% the greenhouse warming impact of that kwh relative to coal-generated electricity, a figure which is not substantially altered by use of a strong greenhouse gas as a substitute coolant. Were the operation of the GDPs curtailed because of lack of a suitable substitute coolant, the result would be either a 20-fold increase in greenhouse impact per unit electricity ultimately produced, or the further export of the uranium enrichment industry to overseas suppliers (with an unknown net effect of atmospheric greenhouse gas loading).

The GDP complex's share of the national greenhouse warming impact is about three times larger than its share of the national ozone depletion impact.

Since we cannot at this time make a value comparison between ozone depletion and greenhouse warming, we cannot say whether replacement of CFC-114 with a perfluorocarbon coolant would be, on balance, environmentally harmful or beneficial.

Though the PFC coolants will have little effect on the greenhouse impact of the GDPs (relative to inevitable CO_2 indirect emissions), it would be very desirable to find a substitute coolant that improved or eliminated both greenhouse and ozone impacts. Use of an HCFC or HFC would "solve" both ozone and greenhouse issues, but at the cost of an undetermined degree of increase in operational hazard due to its reactivity with UF_6. Our impression is that DOE would not entertain an increase in perceived operational risk from an alternate coolant. Further, HCFCs may be restricted by the year 2020, though it's difficult to tell at this point whether GDPs will be operating by that time. The CFC substitute program continues to look at HFCs, HCFCs, and more exotic compounds, but all have some plausible disadvantage (e.g. excessive atmospheric lifetime or high UF_6 reactivity).

Greenhouse Warming Potential is not a regulated property yet. There is a good chance it will be regulated, but the form of the regulation is unpredictable. There is therefore no obvious single course of action that should be followed. Pursuing as many options as possible seems prudent. For example, it appears advisable to continue at least a modest level of activity in searching for advanced substitutes while pursuing replacement of CFC-114 by the commercially available PFCs.

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