Atmospheric Treaties and Replacement Refrigerants for Vapour Compression*

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Abstract

Refrigerant gases have many other uses which taken to extremes cause environmental effects like global warming and attract restrictions like the Montreal and Kyoto Protocols. Customs records and manufacturers' data show Australian 1999/2000 refrigerant consumption was about 7400 Mg and increasing. All gases in all applications should expect economically rational restriction before 2005 which implies a price increase for refrigerants in Australia about 4.6 cents/kg GWP or 59 $/kg for R134a.

Keywords: refrigerants, consumption, emissions, global warming

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1 Introduction

In 1834 Jacob Perkins patented a vapour compression refrigerator using diethyl ether. Use of dimethyl ether followed in 1862, hydrocarbon mixtures and carbon dioxide in 1866 and ammonia in 1872. Since then there have been many changes in refrigerants, a massive expansion of world population and wealth and incidentally vapour compression equipment and refrigerants of all kinds.

In the 1970s scientists measured atmospheric changes due to refrigerants and then predicted worse to come (Section 2). Governments met to agree atmospheric treaties (Section 3) and scientists invented potentials to express the relative environmental merit of refrigerants (Section 4). Fluorocarbon refrigerant imports and exports are available from customs data (Section 5) which allows calculation of consumption and potential emissions (Section 6). For natural refrigerants only manufacturers data was available (Section 7). By 2005 fuels and refrigerants with large contributions to global warming will be more expensive (Section 8).

2 Climate Impacts

Halocarbons containing fluorine and chlorine or bromine were successfully marketed as refrigerants from 1930 on. In the 1970s they were found to reduce stratospheric ozone and so increase solar ultraviolet radiation at the earth's surface. The predicted and measured contribution of emissions from hermetic

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refrigeration equipment to ozone depletion were small. However national governments were also concerned about large climate impacts and agreed a series of treaties and amendments known collectively as the Montreal Protocol (UNEP 1998) to phase out consumption of halocarbons containing chlorine or bromine. Australia has import restrictions and Australian manufacture ceased in 1995.

Solar radiation incident on the earth may be reflected by aerosols, clouds or the surface and adsorbed by the atmosphere or surface. The surface adsorbs about 120 W/m^2 on average which convects to the atmosphere, thermally radiates to the sky or evaporates moisture. Many atmospheric gases adsorb the surface thermal radiation making the earth's average temperature about 40 K higher than without adsorption. This is the *greenhouse effect*.

Ice cores from Greenland and Antarctic glaciers give the composition of the atmosphere since 1000 AD. The cores show stable concentrations of anthropogenic greenhouse gases followed by small increases in the 19th century and large increases during the 20th century (IPCC 2001a). *Radiative forcing* is the surface heating effect of an atmospheric change and is positive for greenhouse gases and negative for many aerosols. Radiative forcing from carbon dioxide increased between 1750 and 2000 by about 1.46 W/m^2 and from halocarbons about 0.34 W/m^2 (IPCC 2001a). Radiative forcing increases are magnified by the loss in reflection from snow and ice.

Ocean thermal inertia delays much climate impact of increased radiative forcing by hundreds of years however last century average surface temperatures rose by 0.6 ± 0.2 K and sea levels between 100 and 200 mm (IPCC 2001a). Recent mathematical models of climate predict these measurements. For the 21st century models predict a rise in average temperature from 1.4 to 5.8 K and in sea level 0.09 to 0.94 m depending on assumptions about population and economic activity known as *emission scenarios*. Predicted rainfall changes are unfavourable to Australia. Cereal crops will become more difficult to grow while Australia's customers and competitors have improved growing conditions (IPCC 2001b).

World fossil fuel reserves and resources contain over 5 Eg carbon but the worst 21st century emission scenarios require only 2 Eg. Oil and gas have half the climate impact of coal per energy unit but only about 1 Eg are available (IPCC 2001c). Oil and gas depletion will increases emissions. Limiting anthropogenic radiative forcing from carbon dioxide in 2100 to twice 2000 levels requires a reduction in world consumption of fossil fuel to about 50% of 1990 levels well before 2100. Much of this emission reduction gives a net saving but the rest may cost up to US\$100/MgC_{eq} (IPCC 2001c).

3 Atmospheric Treaties

The United Nations Framework Convention on Climate Change (UNFCCC) (UNEP 1992) came into force on the 21st March 1994. It committed Australia and other economically advanced countries to reduce their global warming emissions (GWE) below 1990 levels by 2000. Many European countries have met this commitment with a combination of conservation, wind, nuclear and natural refrigerants. By 1999 Australia's emissions had increased by 17.4% however uncertain data prevented the inclusion of hydrofluorocarbons (AGO 2001). The Kyoto Protocol (UNEP 1998) offers Australia a less onerous commitment of average 2008 to 2012 emissions no more than 108% of 1990 emissions. Australia has not yet ratified Kyoto. Kyoto had 84 signatories including Australia and 33 ratifications at 19th March 2001 and comes into force after major emitters representing 55% of emissions ratify.

The UNFCCC applies to all anthropogenic greenhouse gas emissions except those covered by the Montreal Protocol (UNEP 1998). The Kyoto Protocol assigns country quotas for total emissions as carbon dioxide equivalent of six of the UNFCCC gases. These six gases are carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride. The global warming potentials (GWP) used as coefficients in calculating the carbon dioxide equivalent of the last five gases are those approved by the Intergovernmental Panel on Climate Change (IPCC 1994).

Neither the Montreal or Kyoto Protocols require of Australia so called *end use controls* such as: licenses, certificates, training courses, codes of practice, recovery, recycling, new equipment or service procedures. Import and production controls include: bounties, excises, subsidies, quotas, tariffs and taxes. End use controls are more expensive and markedly less effective than import and production controls. Polluters like the ineffectiveness of end use controls and activists and regulators often lack the knowledge to assess them. Australia ultimately relied on import and production controls to meet its Montreal commitments.

4 Environmental Potentials

Mathematical modelling of ozone depletion and climate allows comparison of the environmental impacts of different gases. The modelling data also allows calculation of potentials for treaty, legislation and comparison purposes. Whether the appropriate period for potentials is 20, 100 and 500 year depends on the application and the environmental impact of concern. Treaties and legislation use 100 years since many nations are concerned about mitigating 22nd century impacts. For environmental impacts this century like increased drought and flooding 20 years is appropriate. For environmental impacts like a 7 m rise in ocean levels 500 years is appropriate.

The Montreal Protocol (UNEP 1998) annexes tables of ozone depletion potentials (ODP Table 1) relative to R11. Treaty requirements depend on multiplying masses by ODP and summing to give an equivalent mass of R11.

For the UNFCCC (UNEP 1992) and Kyoto (UNEP 1997) reference is made to global warming potentials (GWP) relative to carbon dioxide approved from time to time by the IPCC (1994). WMO (1999) gives revised potentials based on more data with estimated uncertainty ±35%. Table 1 gives the potentials used here. For comparison, ammonia and hydrocarbon refrigerants have ODP 0.0 and GWPs 1 and 3 respectively independent of period (Maclaine-cross and Goedhart 1999).

5 Imports and Exports

The Australian Customs Service maintains a database of imports identified by a ten digit code, the Harmonised Tariff Item Statistical Classification (HTISC). Some HTISC codes for refrigerants with their descriptions are:

Potential	ODP	GWP	GWP	GWP
Source	UNEP	IPCC	WMO	WMO
Year	1998	1994	1999	1999
Period		100	100	20
R22	0.055	1700	1900	5200
R134a	0.0	1300	1600	4100
R141b	0.11	630	700	2100
R123	0.02	93	120	390

Table 1: Ozone depletion (ODP) and global warming (GWP) potentials.

2903491062 Chlorodifluoromethane;

2903300067 1,1,1,2-tetrafluoroethane (HFC 134a) (CAS 811-97-2);

2903491069 1,1-dichloro-1-fluoroethane (HCFC 141b) (CAS 1717-00-6);

2903499064 Halogenated derivatives of acyclic hydrocarbons containing two or more different halogens nes;

2903300068 Fluorinated, brominated or iodinated derivatives of acyclic hydrocarbons (excluding 1,1,3,3,3-Pentafluoro-2(trifluoromethyl) prop-l-ene (PFIB) & excluding 1,1,1,2-Tetrafluoroethane (HFC 134a) (CAS 811-97-2));

8703 Motor cars and other motor vehicles principally designed for the transport of persons (other than public transport type), including station wagons and racing cars.

Refrigerant arrives on container ships and the tanks are weighed at the docks. Imported cars usually arrive with air conditioners charged with R134a. A representative R134a charge of 0.6 kg has been assumed in Table 3.

The ACS export database uses the Australian Harmonised Export Commodity Classification (AHECC) with an eight digit code. Those used here with their descriptions are:

29033000 Fluorinated, brominated or iodinated derivatives of acyclic hydrocarbons;

29034900 Halogenated derivatives of acyclic hydrocarbons containing two or more different halogens nes;

8703 Motor cars and other motor vehicles principally designed for the transport of persons (other than public transport type), including station wagons and racing cars.

AHECC codes 29033000 and 29034900 would contain many products besides refrigerant but code 29034900 contains chlorofluorocarbons being exported.

The HTISC and AHECC codes are used to purchase data from the Australian Bureau of Statistics (ABS). As imports or exports increase broad categories are refined and redefined. The blanks on the left hand side of the tables indicate that the category did not exist at that time. The codes on the right are correct for the last item in the row but for some items the codes and definitions have changed slightly. Code changes are usually introduced to the entire database at an arbitrary time so the first quantity in a new code will be for a reduced period. The data period chosen was the financial year since refrigerant delivery rates are lowest in early winter at its end and tax calculations generate accurate data.

Table 2 summarizes the free on board price of the shipment calculated from the customs value and mass in the ACS databases. The 99/00 step in the R134a import price resulted from shortages caused by Californian regulations requiring R134a as an aerosol propellant.

Financial Year	96/97	97/98	98/99	99/00	Codes
Imports					HTISC
R22	2.26	2.60	3.45	3.86	2903491062
R134a		4.01	4.52	7.08	2903300067
R141b			3.41	3.71	2903491069
Other HCFC	2.74	3.20	4.30	4.96	2903499064
Monohalocarbon	4.92	5.53			2903300068
Exports					AHECC
Monohalocarbon	6.93	5.51	3.69	4.27	29033000
Bihalocarbon	14.49	17.62	20.30	12.33	29034900

Table 2: Bulk import and export prices of refrigerants (Australian $/kg).

Table 3 gives annual imports and exports of fluorocarbon refrigerants from the ACS databases.

Financial Year	96/97	97/98	98/99	99/00	Codes
Imports					HTISC
a R22	2184.21	2216.73	2819.56	1756.65	2903491062
b R134a		721.60	1700.03	2354.80	2903300067
c R141b			442.06	690.82	2903491069
d Other HCFC	312.06	1014.67	534.83	627.06	2903499064
e Monohalocarbon	1624.23	1065.23			2903300068
Exports					AHECC
Monohalocarbon	580.30	712.92	151.00	220.67	29033000
Bihalocarbon	0.17	30.72	25.47	77.94	29034900
Cars *etc.*					
Imported	330823	443375	404548	418333	8703
f R134a (Mg)	198.49	266.03	242.73	251.00	
Exported	55730	47578	62553	98862	8703
g R134a (Mg)	33.44	28.55	37.53	59.32	

Table 3: Australian imports and exports of fluorocarbon refrigerants (Mg).

6 Emissions

Potential emissions are the difference between import and manufacture and destruction and export. *Actual emissions* are the difference between potential emissions and additions to the bank or storage. Potential emissions in a given year usually become actual emissions in some later year. Neither storage nor actual emissions are measurable for refrigerants in a country however when the market stabilizes potential and actual emissions are equal. For replacement fluorocarbon refrigerants in Australia, manufacture and destruction are negligible so potential emissions are the difference between imports and exports.

Table 4 contains estimates of total imports and potential emissions calculated from the data in Tables 1 and 3. Many chemicals not used as refrigerants are include in the monohalocarbon and bihalocarbon exports in Table 3. These exports are believed an upper limit for the uncertainty of potential refrigerant emissions. The GWP used in calculating the UNFCCC potential emissions is exact by treaty and the uncertainty estimate in the UNFCCC GWE is ±10%. The GWP used in calculating the total potential GWE have an uncertainty of ±35% and this is the uncertainty of the GWE. Australia's 1990 anthropogenic carbon dioxide emissions were 348529.97 Gg (AGO 2001). These emissions do not change when GWP values are revised and so are most suitable for comparisons.

Financial Year	96/97	97/98	98/99	99/00	Formulae
h Total imports Mg	4319	5284	5739	5680	$a+b+c+d+e+f$
Ozone depleting Mg	120	128	224	183	$0.055a+0.11c+0.02d$
UNFCCC GWE Gg	2326	2632	2477	3310	$1300(b+e+f-g)$
% 1990 CO_2 Emis.	0.67	0.75	0.71	0.95	
100 yr GWE Gg	7050	7572	8779	7971	$1600(b+e+f-g)+$
% 1990 CO_2 Emis.	2.02	2.17	2.52	2.29	$+1900a+700c+120d$
20 yr GWE Gg	18816	20222	23610	21270	$4100(b+e+f-g)+$
% 1990 CO_2 Emis.	5.40	5.80	6.77	6.10	$+5200a+2100c+390d$

Table 4: Total fluorocarbon refrigerant imports, ozone depleting consumption, potential global warming emissions and their ratio to Australia's 1990 anthropogenic CO_2 emissions.

The Montreal Protocol (UNEP 1998) imposed a cap on Australia's ozone depleting consumption of 548 Mg between 1st January 1996 and 31st December 2003. Australia has a voluntary cap of 220 Mg at present. Tables 3 and 4 show a shift from R22 to R134a after the voluntary cap was reached in 98/99. This increased Australia's UNFCCC GWE but reduced the total refrigerant GWE between 98/99 and 99/00 for both short and medium terms.

From Table 3 one can calculate Australian R134a consumption for 99/00 as 2546 Mg. For refrigeration use transfers to bank are about 75 Mg and actual emissions about 30 Mg. Subtracting these gives 2441 Mg for R134a consumption by mobile air conditioners (MAC). ABS (2000) estimated the total number of enclosed motor vehicles registered in Australia on the 31st October 1999 as 11934797. If 60% of these had MACs charged with R134a, the unit R134a consumption was 341 g/year. R134a emissions from MAC occur as leakage and during maintenance (Maclaine-cross and Goedhart 1999), repairs, collision and disposal.

The carbon dioxide equivalent of 341 g of R134a is 545.4 kg. An average passenger vehicle in Australia during 98/99 used 1684 L (ABS 2000b). One litre of petrol burns to 2.15 kg of carbon dioxide so the fuel consumption emits 3621 kg CO_2. The R134a consumption of a representative Australian MAC is 15.1% of the exhaust global warming emissions of a passenger vehicle.

7 Manufacture

Imports and exports of natural refrigerants are believed negligible for the period of interest but they are not separately recorded in ACS databases. Manufacture is not separately reported by the Australian Bureau of Statistics and the sales data in Table 5 was supplied directly by the refrigerant manufacturers.

Financial Year	95/96	96/97	97/98	98/99	99/00	Formulae
i R290/600a	2.9	10.1	15.9	21.3	24.3	
j R290/170	0.4	0.6	1.3	2.2	2.5	
k R717	694	719	745	772	800	
l All Refrigerants		5789	6825	7352	7359	$h + 3i + 2.5j + 2k$
% HC		0.55	0.74	0.94	1.08	$100(3i + 2.5j)/l$
% Natural		25.39	22.58	21.94	22.82	$100(3i + 2.5j + 2k)/l$

Table 5: Natural and total refrigerant sales (Mg) and natural refrigerant market share.

Australia manufactures large quantities of ammonia for fertiliser but little of refrigerant grade (R717). About half this is actually used as refrigerant. A typical bulk price for refrigerant ammonia is 3 $/kg. The liquid density of ammonia is typically twice that of fluorocarbons making ammonia the cheapest vapour compression refrigerant available on a liquid volume basis. Ammonia is corrosive to aluminium and copper so cannot replace hydrocarbons or fluorocarbons in most existing equipment.

Hydrocarbon refrigerants are made from a variety of feed-stocks and many compositions are available in Australia (Maclaine-cross and Goedhart 1999). They are classified here into medium R290/600a [60/40] and high R290/170 [94/6] pressure grades. A typical bulk price is 9 $/kg but the charge mass of R290/600a is usually one third that of fluorocarbons and of R290/170 40%. Hydrocarbons are effectively about half the price of fluorocarbons and directly replace them in major applications.

8 The Future

A future Australian government will ratify Kyoto because of worse growing conditions expected for Australian agriculture and improved conditions for competing nations (IPCC 2001b). In 1999 Australia was officially 17.4% above 1990 GWE (AGO 2001). When revised with HFCs this will be about 18.2%. This is

10.2% above the Kyoto required average for 2008–2012. Expect effective action before 2005 when Kyoto requires demonstrable progress.

Kyoto applies to emissions but controls will be applied where reliable measurement is easy changing prices throughout the economy to discourage emissions. Greenhouse gas excises and tariffs at ports, wells, generating, metallurgical and chemical plant replacing many existing taxes or equivalent measures are highly probable with net taxation unchanged. These measures would also apply to Montreal gases since many are substitutes for Kyoto gases but with greater GWP. Kyoto imposes no obligation to control exports of coal, gas, oil or anything and explicitly recognizes that developing countries may increase their emissions and imports.

The IPCC (2001c) found the marginal cost of GWE reduction as US$100/Mg$C_{eq}$, Aust $167/Mg$C_{eq}$ or Aust $45.5/Mg$CO_{2\ eq}$. Economic theory says that net incentives must equal this for policy success. For fuels and refrigerants this is equivalent to:—

petrol 11.2 cents/L so 10 cents/L or more reduction possible;

natural gas 2.5 $/GJ possible price increase;

coal 133 $/Mg but less on low grade or high volatile coals;

electricity 6 cents/kWh for 100% coal fired and 0 cents/kWh for renewables;

wood 100 $/Mg for native and 0 $/Mg for plantation;

LPG 7 cents/L so no price change likely;

R717 4.6 cents/kg;

R290/600a 14 cents/kg;

R22 77 $/kg not required by Kyoto but to protect Montreal cap from swapping between R134a and R22 mixtures;

R134a 59 $/kg calculated using Kyoto GWP of 1300 (IPCC 1994).

These values are roughly double some currently applying in Denmark and other European countries but their measures include a phased prohibition of fluorocarbon refrigerants which will be complete well before 2008. Denmark prohibited R22 in 2000 and already taxes carbon dioxide emissions.

The effects of implementing Kyoto in Australia will be:

- Electric utilities will favour natural gas over coal and new plant will be wind or other renewables wherever possible;
- Real energy and electricity prices will rise initially in some states and fall after 10 years as wind turbines are cheaper to purchase and operate;
- Fluorocarbon refrigerants will disappear from MACs in three years and in ten years all refrigeration and air conditioning.

9 Conclusion

Production data from manufacturers and import and export data from Australian Bureau of Statistics gives Australian consumption of replacement refrigerants for vapour compression since 1996 in Tables 3, 4 and 5. Correcting natural refrigerants masses for lower liquid density, the total market has grown to 7400 Mg in 99/00. Ammonia, fluorocarbons and hydrocarbons had 22%, 77% and 1% market shares respectively with hydrocarbons sales growing 15%/year. Typical bulk prices for refrigerants 717, 134a and 290/600a were 2, 8 and 5 $/L liquid respectively.

Australia has easily kept total HCFC consumption below 220 ozone depleting Mg which is well below the 548 Mg Montreal cap. The Kyoto potential GWE of refrigerants had grown from 0 to the equivalent of 0.95% of 1990 carbon dioxide emissions in 99/00. The potential 100 year GWE from all fluorocarbon refrigerants of 2.3% indicates the Kyoto GWEs future value. Australians concerned about predicted increased drought and flooding this century will however focus on the 20 year GWE of 6.1% of 1990 CO_2 emissions.

An economically rational implementation of the Kyoto Protocol in Australia appears highly probable. Electric energy price increases up to 4 cents/kWh in some localities could be expected to last up to 10 years. The price increase in refrigerants would be about 4.55 cents/kg GWP *e.g.,* about 59 $/kg for R134a.

10 Acknowledgement

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11 References

ABS 2000a, *Motor Vehicle Census Australia, 31st October 1999,* Australian Bureau of Statistics, Canberra, 18th August, 32 p.

ABS 2000b, *Survey of Motor Vehicle Use Australia,* Australian Bureau of Statistics, Canberra, 21st July, 43 p.

AGO 2001, *National Greenhouse Gas Inventory 1999,* Australian Greenhouse Office, Canberra, ISBN 1 876536 98 5, April, 207 p.

IPCC 1994, *Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emissions Scenarios,* J.T. Houghton *et al.* eds, Cambridge University Press, 339 p.

IPCC 2001a, *Summary for Policy Makers, Climate Change 2001: The Scientific Basis,* Third Assessment Report of Working Group I, Intergovernmental Panel on Climate Change, `http://www.ipcc.ch/`, Shanghai, 20th January, 20 p.

IPCC 2001b, *Summary for Policy Makers, Climate Change 2001: Impacts, Adaption and Vulnerability,* Third Assessment Report of Working Group II, Intergovernmental Panel on Climate Change, `http://www.ipcc.ch/`, Geneva, 16th February, 17 p.

IPCC 2001c, *Summary for Policy Makers, Climate Change 2001: Mitigation,* Third Assessment Report of Working Group III, Intergovernmental Panel on Climate Change, http://www.ipcc.ch/, Accra, 3rd March, 17 p.

Maclaine-cross, I. and Goedhart, J. 1999, *Hydrocarbon Refrigerants in Australian Cars,* Chapter 11 in Developments and Trends in ODS Phase Out, Yearbook 1997–1999, GTZ Project PROKLIMA, Eschborn Germany, 156 p.

UNEP 1992, *The United Nations Framework Convention on Climate Change,* United Nations Environment Program, New York.

UNEP 1997, *The Kyoto Protocol to the United Nations Framework Convention on Climate Change,* United Nations Environment Program, New York.

UNEP 1998, *The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer,* with amendments up to Montreal 1997, United Nations Environment Program, New York.

WMO 1999, *Scientific Assessment of Ozone Depletion: 1998,* World Meteorological Organization, ISBN 92-807-1722-7, February, Geneva, p. 10.27.