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CLIMATE-SAFE REFRIGERANTS

Zhang Zhaohui and Wang Ruonan

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Abstract

Refrigerant is the working medium of refrigeration and air-conditioning systems. Currently, synthetic refrigerants are the dominant refrigerants for cooling, but the emissions from synthetic refrigerants into the atmosphere will destroy the ozone layer. The global refrigeration and air-conditioning industry is working on a refrigerant substitution based on the provisions of the Montreal Protocol. In selecting new alternative refrigerants, a high level of efficiency, safety, economy, and good climate performance, among other things, will be fully considered. This paper examines cases of countries implementing policies promoting the recycling and reuse of refrigerants. The paper also provides policy recommendations aimed at reducing environmental pollution caused by refrigerant leakage and discharge, as well as a list of climate-safe refrigerants.

Keywords: refrigerant, refrigerant substitution, climate-safe

JEL Classification: O33

Contents

1.	INTRODUCTION.....	1
2.	THE ELEMENTARY KNOWLEDGE OF REFRIGERANTS	2
2.1	What Is Refrigerant?	2
2.2	Classification, Representation Methods, and Designation of Refrigerants (ISO/TC 86/SC 8. 2014)	2
2.3	Evaluation of Refrigerant Safety (ISO/TC 86/SC 8. 2014)	3
3.	CLIMATE-SAFE REFRIGERANTS	6
4.	TRADE-OFFS OF REFRIGERANTS	6
5.	REFRIGERANT LEAKING	8
6.	RECYCLING AND REUSE OF REFRIGERANTS	9
6.1	Japan.....	10
6.2	Europe.....	10
6.3	United States.....	11
6.4	People's Republic of China	12
7.	CONCLUSION AND POLICY RECOMMENDATIONS FOR ASIA	13
	REFERENCES	14
	APPENDIX A: RECOMMENDED REFRIGERANTS	16
	APPENDIX B	21
	APPENDIX C	22

1. INTRODUCTION

Currently, synthetic refrigerants are the dominant refrigerants for cooling, but the emissions from synthetic refrigerants into the atmosphere will destroy the ozone layer. According to the statistics of the China Refrigeration and Air-Conditioning Industry Association (CRAA), more than 300,000 tons of synthetic refrigerants will be used in the People's Republic of China (PRC) in 2020 (Zhang et al. 2022), equivalent to more than 0.5 billion tons of CO₂. Direct refrigerant leakage may occur and be discharged into the atmosphere in the process of refrigerant production and filling, installation, operation, maintenance and transfer of refrigeration equipment, and scrapping of refrigeration equipment and residue of the refrigerant cylinder after use. Moreover, the proportion of refrigerant used in all kinds of recycled and destroyed equipment is still very low. Most of it is eventually discharged into the atmosphere, which leads to the destruction of the ozone layer and intensifies the greenhouse effect.

In 1834, an American physicist invented the vapor compression refrigerator using ether as refrigerant (Calm 1994), which opened a new chapter for the large-scale application of synthetic refrigeration. Industrial technology was less developed at that time, and the choices of refrigerants were mainly based on the consideration of "accessibility." In addition to ether, the refrigerants in use also included carbon dioxide (CO₂), ammonia (NH₃), sulfur dioxide (SO₂), isobutane (HC-600a), propane (HC-290), and other natural substances. These refrigerants are toxic, flammable, or both. Some refrigerants are highly corrosive and unstable, or their working pressures are too high. Due to the limitations of the technical level at that time, accidents have occurred from time to time.

In 1930, an American engineer published the first article on organic fluoride refrigerants, evaluating 15 compounds belonging to the single carbon group containing hydrogen, chlorine, and fluorine (Midgley Jr. and Henne 1930). They selected CFC-12 as the refrigerant. Since then, a series of CFC and HCFC refrigerants have been developed successively. These CFC and HCFC refrigerants are stable, safe, nontoxic, and energy-efficient. Therefore, they have been widely used and have gradually replaced the early natural refrigerants (except NH₃) used for 100 years.

In 1974, Rowland and Molina, two professors at the University of California, suggested for the first time through observation and research that CFCs will diffuse into the atmospheric ozone layer after emission and have a destructive effect on the ozone in the atmosphere (Molina and Rowland 1974). After much scientific research and demonstration, the international community confirmed the ozone-depleting effect of CFCs. It reached the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987, starting the phasing out of CFCs and other ozone depleting substances (ODSs). At the same time, with the development of industrial civilization, global warming has gradually become a major environmental problem that has concerned human society from the 20th century, and some refrigerants also belong to greenhouse gases that can lead to global warming. Therefore, the consumption control of such refrigerants has also attracted great attention from the international community. In October 2016, the Kigali amendment on the reduction of HFCs was agreed at the 28th meeting of the parties to the Montreal Protocol. Its purpose is to promote an effective decrease in the emission of HFCs that is greenhouse gas with a view to achieving the goal of reducing global warming by 0.5°C at the end of the 21st century set by the Paris Agreement (United Nations 2015).

Under these circumstances, the refrigeration and air-conditioning industry together with the chemical industry began to seek climate-safe refrigerants that are more environmentally friendly and still efficient and safe.

The rest of the paper is structured as follows. Section 2 provides background information about refrigerants. Section 3 presents an overview of climate-safe refrigerants. Section 4 discusses trade-offs for the selection of appropriate refrigerants. Section 5 provides policy recommendations for reducing environmental pollution due to refrigerant leakage and discharge. Section 6 reviews countries’ experiences (Japan, the EU, the US, and the PRC) in promoting the recycling and reuse of refrigerants. Section 7 concludes and provides policy recommendations.

2. THE ELEMENTARY KNOWLEDGE OF REFRIGERANTS

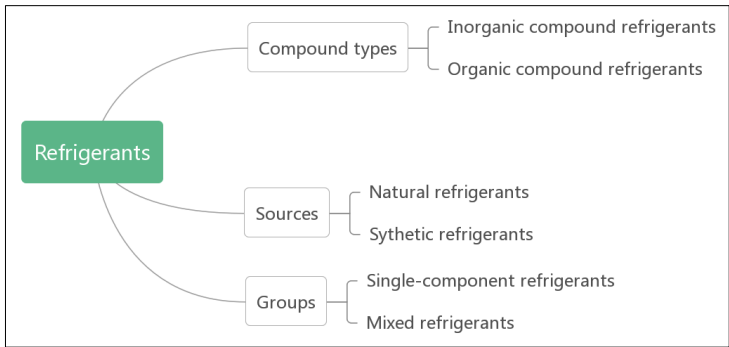
2.1 What Is Refrigerant?

Refrigerant is the working medium in refrigeration (ADB 2021) and air-conditioning equipment, just like blood in the human body. It circulates in the refrigeration system, exchanges energy with the outside through its thermal state, absorbs heat in the low-temperature environment, and releases heat in the high-temperature environment to realize the purpose of refrigeration and heating as a refrigeration working medium.

2.2 Classification, Representation Methods, and Designation of Refrigerants (ISO/TC 86/SC 8. 2014)

Because of their different properties, refrigerants can be classified in many ways. For example, they can be divided into natural refrigerants and synthetic refrigerants, or organic compound refrigerants and inorganic compound refrigerants according to the types of compounds. They can also be divided into single-component and mixed refrigerants according to their components. Within these categories, each category of refrigerant can be further subdivided.

Figure 1: The Classifications of Refrigerants



For convenience, the letter “R” and a group of numbers or letters after it are uniformly stipulated internationally as the abbreviated symbol of a refrigerant. The letter “R” indicates “Refrigerant,” and the chemical composition of the molecule determines the following numbers or letters.

For single-component hydrocarbons and saturated fluorocarbon refrigerants, the composition can be represented by the component identification, the initial letter of the elements contained as the prefix of the refrigerant. If the compound contains hydrogen atoms, the first letter is “H,” the last letter is “C” representing carbon atoms, and the middle letter represents halogen atoms, which are marked in the following order: “C” represents chlorine atoms and “F” represents fluorine atoms.

Saturated fluorocarbon refrigerants include CFC, HCFC, and HFC. CFC, shortened from chlorofluorocarbons, contains three atoms: C (chlorine), F (fluorine), and C (carbon); HCFC, shortened from hydrochlorofluorocarbon, contains four atoms: H (hydrogen), C (chlorine), F (fluorine), and C (carbon); HFC, shortened from hydrofluorocarbon, contains three atoms: H (hydrogen), F (fluorine), and C (carbon).

HFO, unsaturated hydrofluorocarbons, also known as hydrofluoro olefins, contains the same elements as HFC and also contains three atoms: H (hydrogen), F (fluorine), and C (carbon). Because it is the unsaturated fluorohydrocarbon, its last letter is represented by O instead of C, i.e., HFO.

Some refrigerants with simple molecular formulas are also used to be represented directly by a molecular formula. For example, carbon dioxide can be expressed by CO₂, NH₃ can be expressed by NH₃, and water can be expressed by H₂O.

The numbering methods for different types of refrigerants are slightly different. Halogenated hydrocarbons and hydrocarbons of methane, ethane, propane, and cyclobutane are expressed by the molecular number of their chemical composition. Mixed refrigerants are numbered sequentially in 400 and 500 series, of which the 400 series is nonazeotropic mixed refrigerants and the 500 series is azeotropic mixed refrigerants. To distinguish mixed refrigerants with the common refrigerant but different compositions (different mass fractions), a capital letter (A, B, or C) is used after the number. Inorganic compound refrigerants are numbered according to the 700 serial number. The molar mass of the inorganic compound plus 700 is its refrigerant number. For example, the molar mass of CO₂ is 44, and its refrigerant number is R744; the molar mass of NH₃ is 17, and the number of the refrigerant NH₃ is R717.

2.3 Evaluation of Refrigerant Safety (ISO/TC 86/SC 8. 2014)

The safety evaluation of refrigerants includes toxicity and flammability. Refrigerants can be divided into two categories according to their toxic characteristics and four categories according to their flammability, as shown below.

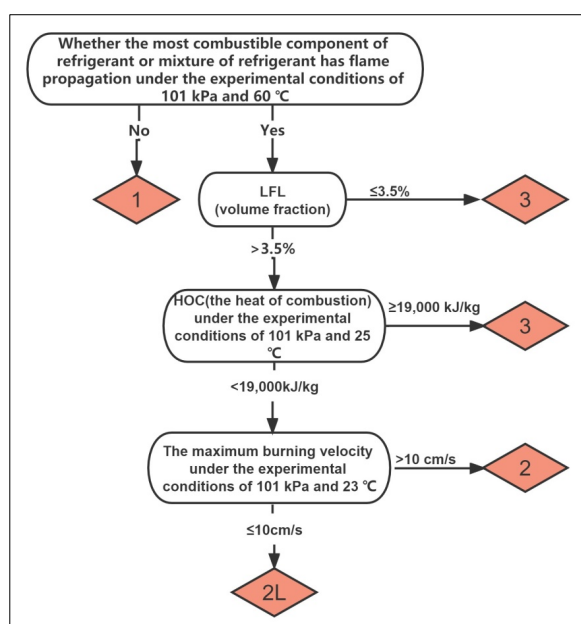
Table 1: The Safety Classification of Refrigerants

	Toxicity	Class A (Lower Chronic Toxicity)	Class B (Higher Chronic Toxicity)
Flammability			
Class 1 (no flame propagation)		A1	B1
Class 2L (lower flammability)		A2L	B2L
Class 2 (flammable)		A2	B2
Class 3 (higher flammability)		A3	B3

Source: ADB (2021).

Toxicity is classified according to the occupational exposure limit (OEL) of refrigerants. Class A (lower chronic toxicity) signifies refrigerants that have an OEL of 400 ppm or greater; Class B (higher chronic toxicity) signifies refrigerants that have an OEL of less than 400 ppm¹. The occupational exposure limit means the time-weighted average concentration for an ordinary eight-hour working day and a 40-hour working week which nearly all workers can be repeatedly exposed without adverse effect. The specific calculation is based on the relevant occupational health regulations or standards of various countries. Chinese regulations on occupational health refer to Occupational exposure limits for hazardous agents in the workplace—Part 1: Chemical hazardous agents (GBZ 2.1. 2019).

Figure 2: Refrigerant Flammability Classification Conditions



The classification of flammability is based on the lower flammability limit of each refrigerant, the combustion heat, and the combustion speed. Class 1 (no flame propagation) requires that the most combustible component of refrigerant or mixed refrigerant does not show flame propagation in the atmospheric test at 101 Kilopascal² (kPa) and 60°C (Figure 2). Other classes (2L, 2, and 3) are provided in Figure 2.³

¹ 0.01 vol % (% volume fraction) is the equivalent of 100 ppm.

² A kilopascal is one thousand times the unit of pressure and stress in the meter-kilogram-second system.

³ Class 2L weak flammability refers to there being flame propagation under the experimental conditions of 101 kPa and 60°C. Lower flammability limit of refrigerant > 3.5% (volume fraction). Under the test conditions of 101 kPa and 25°C, the heat generated by combustion needs to be less than 19,000 kJ/kg. Under the experimental conditions of 101 kPa and 23°C, the maximum burning velocity of refrigerant is ≤ 10 cm/s. Class 2 flammability refers to there being flame propagation under experimental conditions of 101 kPa and 60°C. Lower flammability limit of refrigerant > 3.5% (volume fraction). Under the test

2.4 The Evaluation of Environmental Impacts of Refrigerants

Refrigerants are chemical substances. Some of the refrigerants currently in use belong to ozone-depleting substances (ODSs) and greenhouse gases (GHGs). These two substances are the two prime culprits for the ozone layer hole and global warming, the two central environmental issues causing global concern.

The impact assessment indicators of ozone-depleting substances and greenhouse gases are ODP and GWP, respectively.

ODP (ozone depletion potential) refers to the influence of the ability of gas to escape into the atmosphere on the destruction of the ozone layer. The ozone layer destruction effect of refrigerant R11 is the benchmark. The ODP value of R11 is defined as 1, and the ODP values of other substances are the comparative values relative to R11. The higher the ODP value, the stronger the ability to destroy the ozone layer. The destruction of the ozone layer by refrigerants is mainly caused by the chlorine atom or bromine atom contained in refrigerants. The ODP value depends on the gas stability and atmospheric life of the chemical. For example, although R22 contains a chlorine atom, its atmospheric life is only 11.9 years (World Meteorological Organization (WMO) 2018), and the hydrogen atoms contained are relatively active and basically decomposed before reaching the ozone layer. Therefore, R22 has much less ability to destroy the ozone layer than R11, and the ODP value is only 0.05.

GWP (global warming potential) refers to the ability of greenhouse gases escaping into the atmosphere to affect global warming within a certain period. The GWP is a relative value: The GWP value of CO₂ is determined to be 1, and the GWP value of other substances refers to the mass of CO₂ that produces the same greenhouse effect. The higher its value, the stronger its greenhouse effect. The value of GWP is mainly determined by a substance's ability to absorb long-band radiation, its atmospheric life, and the time frame on which the calculation is based.

LCCP (life cycle climate performance) refers to the climate performance of R&AC equipment throughout its whole life, and it is also an indicator of the greenhouse effect. It needs to consider the environmental impact of refrigerant production, the direct effect of refrigerant emission, and the indirect effect of energy utilization. The environmental impact associated with refrigerant production refers to the ecological effects caused by the energy consumed in the production of refrigerant raw materials and the environmental impact caused by any by-products produced in the process of refrigerant production. The direct effect of refrigerant emission is the greenhouse effect directly caused by refrigerant emissions in R&AC equipment, and its value depends on the GWP and refrigerant emissions. The indirect effect of energy utilization is the greenhouse effect caused by the large amount of energy consumed by R&AC equipment in their operation. Its value depends on the amount of energy consumed by R&AC equipment and the amount of CO₂ emitted per energy production unit. Therefore, the indirect environmental impact of energy utilization of refrigeration and air-conditioning equipment is generally much higher than the direct ecological impact of refrigerant leakage. Compared with the single-index GWP, LCCP can more thoroughly evaluate the effects of climate change on the whole life cycle of refrigeration and air-conditioning equipment.

conditions of 101 kPa and 25°C, the heat generated by combustion is less than 19,000 kJ/kg. Class 3 refrigerants are combustible and explosive, which means that there is flame propagation under the experimental conditions of 101 kPa and 60°C. And the lower flammability limit of refrigerant is $\leq 3.5\%$ (volume fraction) or the heat generated by combustion is $\geq 19,000$ kJ/kg under the test conditions of 101 kPa and 25°C (as shown in Figure 2).

Natural refrigerants have the characteristics of zero ODP and low GWP. CFCs and HCFCs, which are synthetic refrigerants containing chlorine atoms, will destroy the ozone layer when emitted into the atmosphere. At the same time, most of these refrigerants also have high GWP. These refrigerants belong to substances that have been eliminated or are being eliminated following the provisions of the Montreal Protocol. HFCs don't have chlorine atoms, so they have zero ODP and have been widely used as alternative refrigerants to CFCs and HCFCs for many years, but most of them have high GWP and belong to the substances that the Kigali Amendment of the Montreal Protocol should gradually reduce. HFOs are newly developed hydrofluoro olefin refrigerants. They also have zero ODP and lower GWP, but they are expensive because of their complex synthesis process and have many patents for their development, production, and use.

3. CLIMATE-SAFE REFRIGERANTS

Driven by the demand for refrigerant substitution, the global refrigeration and air-conditioning industry and chemical enterprises have worked together to develop a variety of climate-friendly alternative refrigerants in different refrigeration and air-conditioning product areas (Table 2). Some refrigerants have already been widely popularized and applied in an extensive range, while others have been tested in a small range. The characteristics of these refrigerants are described in detail in Appendixes A and B.

Table 2: Potential Climate-Safe Refrigerants and Their Application Sectors

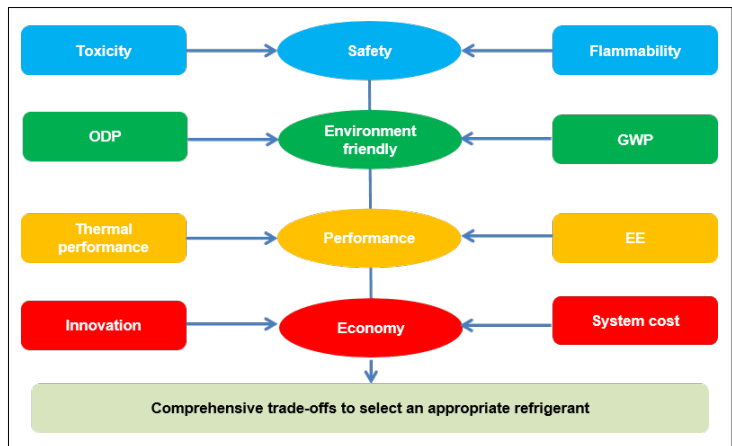
No.	Sector	Product Category	Recommended Alternative Refrigerants
1	Household Refrigeration and Air-conditioning	Room air conditioner	R32, R290
		Domestic refrigerator and freezer	R290, R600a, R1270
		Heat pump water heater	CO ₂ , HFOs
2	Industrial and Commercial Refrigeration and Air-conditioning	Heat pump water heater	CO ₂ , R32, HFOs
		Small chiller (heat pump)	R32, HFOs
		Large and medium-sized chiller (heat pump)	HFOs
		Unitary air conditioner	R32, HFOs
		Multi-connected air-conditioning (heat pump)	R32, HFOs
		Refrigeration and cold storage equipment	NH ₃ , CO ₂ , HFOs
		Automobile air conditioner	HFOs, CO ₂

4. TRADE-OFFS OF REFRIGERANTS

Refrigerant is an important part of the refrigeration system. Its safety level, thermodynamic characteristics, physical and chemical characteristics, and accessibility are related to the safety, reliability, energy efficiency, and manufacturing cost of the refrigeration system. Currently, the global attention given to environmental problems also leads to higher requirements for the ecological properties of refrigerants. Therefore, careful consideration should be given when selecting a new generation of refrigerants.

When selecting refrigerants, particular consideration should be given to the safety performance, environmental protection properties, thermodynamic properties, economic cost, and other aspects of refrigerants, as shown in Figure 3. For the safety of refrigerants, please refer to the refrigerant safety classification in Section 9.2.3. Each country has also established corresponding safety standards or regulations to restrict the refrigerant service conditions, scope, and charges within different safety categories and classifications. The environmental protection properties of refrigerants are described in Section 9.2.4. Currently, the two crucial environmental protection indicators are ODP and GWP. At the same time, the LCCP of the whole life cycle of refrigeration and air-conditioning equipment will also be considered. Appendix C also lists the environmental characteristics and safety classification of some common refrigerants and potential alternative refrigerants.

Figure 3: Comprehensive Considerations When Selecting Refrigerants



Note: EE = energy efficiency.

The essential purpose of refrigeration and an air-conditioning system or equipment is to regulate the temperature, humidity, and air environment of the corresponding space. To achieve this goal, the thermodynamic properties of refrigerants are the most fundamental aspect. These mainly include the pressure, temperature, boiling point, freezing point, specific volume, specific heat capacity, thermal conductivity, enthalpy, entropy, and so on. Generally speaking, a refrigerant with excellent performance will have the following features: (1) an appropriate standard boiling point so that the corresponding saturation pressure will not be too high or too low; (2) at normal working temperature, the latent heat of gasification is strong, which makes great refrigeration capacity; (3) a small temperature rise and low exhaust temperature during compression to avoid overheating of the compressor; (4) in the compression process, the pressure ratio is small, which can improve the volumetric efficiency and realize low energy consumption; (5) good chemical stability, no chemical decomposition under high temperature, and no chemical reaction with lubricating oil, metal, and nonmetallic materials, so as to ensure the long-term service life and reliability of the equipment; (6) good heat transfer characteristics, which can improve the heat exchange efficiency of the heat exchanger; (7) good flow performance, which can reduce the flow

resistance and circulation loss in the refrigerant pipeline and improve the operation efficiency of the machine.

In the highly competitive refrigeration and air-conditioning market, the cost of refrigerants and its influence on the manufacturing cost of a whole machine is also a very important factor that must be considered when selecting refrigerants.

Since ODS elimination has been carried out worldwide, relevant parties in the industry have been trying to explore and develop new and more environmentally friendly alternative refrigerants. Judging from the current technological development, there is no completely ideal alternative refrigerant covering all product fields, meeting zero ODP, low GWP, and being safe, efficient, and economical. According to the current development trend of alternative technology, in the future, applicable refrigerants with different characteristics will be selected in different refrigeration and air-conditioning product fields. The selection of new alternative refrigerants should comprehensively consider the principles of good climate performance, safety, and economy in the service life. A new generation of environmentally friendly refrigerants should have zero ODP, low GWP, low flammability and toxicity, excellent thermophysical properties, and high refrigeration efficiency, and all at a reasonable price.

5. REFRIGERANT LEAKING

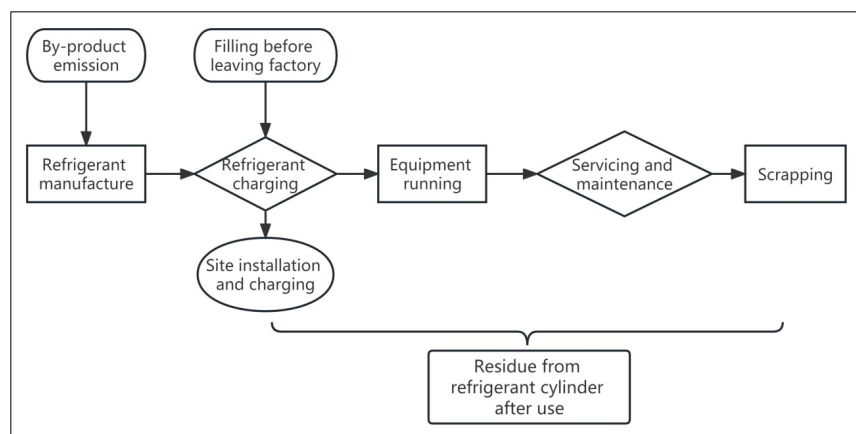
Currently, synthetic refrigerants far exceed natural refrigerants. The emission of CFCs and HCFCs from synthetic refrigerants into the atmosphere will destroy the ozone layer, and these two substances also have high GWP; HFCs do not destroy the ozone layer, but most of them have high GWP. According to the statistics of the China Refrigeration and Air-Conditioning Industry Association, more than 300,000 tons of synthetic refrigerants will be used in the PRC in 2020 (Zhang et al. 2022), equivalent to more than 0.5 billion tons of CO₂. Direct refrigerant leakage may occur and be discharged into the atmosphere in the process of refrigerant production and filling, installation, operation, maintenance and transfer of refrigeration equipment, and scrapping of refrigeration equipment and residue from the refrigerant cylinder after use (Figure 4). Moreover, the proportion of refrigerant used in all kinds of recycled and destroyed equipment is still very low. Most of it is eventually discharged into the atmosphere, which leads to the destruction of the ozone layer and intensifies the greenhouse effect.

To avoid environmental pollution caused by refrigerant leakage and discharge as much as possible, the following measures need to be taken:

- 1) At the national and industrial levels, formulation of relevant management and control regulations and standards, which can effectively urge relevant enterprises to recover and reuse refrigerants and restrict enterprises and users from discharging refrigerants illegally;
- 2) From the perspective of the national government, establishing a complete set of refrigerant recovery, reuse, and treatment systems to promote the recovery and avoid direct discharge of refrigerant;
- 3) Strengthening the training of refrigeration and air-conditioning servicing personnel, professional teachers, and students on good servicing operation, improving the good servicing operation level of maintenance personnel and the installation and servicing level of refrigeration equipment to avoid more refrigerant leakage and discharge at the operational level;

- 4) At the technical level, improving the quality of new production equipment and minimizing the leakage rate and servicing rate of refrigeration and air-conditioning equipment, which is also an effective way to reduce refrigerant emission;
- 5) For new projects and new equipment, selecting climate-friendly and environment-friendly refrigerants as much as possible and using technical means to reduce the amount of refrigerant in the equipment to reduce the impact on the environment after direct leakage of refrigerants;
- 6) Strengthening public awareness of the use of refrigerants through a variety of publicity and responsible training activities.

Figure 4: Possible Links to Refrigerant Leakage



Source: Authors.

6. RECYCLING AND REUSE OF REFRIGERANTS

With the rise of social and economic levels and the improvement of people's living standards, refrigeration and air-conditioning equipment is increasingly widely used. The use of refrigerants is also growing. Therefore, it is necessary to strengthen and improve the management of refrigerants. While selecting climate-friendly and safe refrigerants as much as possible for in-service and scrapped equipment, it is essential to enhance the recovery, reuse, and destruction of refrigerants and reduce the leakage and discharge of refrigerants to minimize their impact on the climate.

Various countries have formulated relevant policies and measures for the recovery and reuse of refrigerants and achieved specific results. These can be summarized as follows:

6.1 Japan

Globally, Japan has done remarkable work and achieved remarkable results in refrigerant recovery. According to a Japanese Ministry of the Environment report, in 2020, the recovery of fluorine-containing refrigerants (CFCs + HCFCs + HFCs) in Japan's commercial refrigeration and air-conditioning sector was about 5,235 tons. The recovery rate of fluorine-containing refrigerant from waste equipment can reach 41% (Ministry of the Environment, Japan 2020). This success is due to Japan's effective refrigerant recycling system and regulations.

In 2015, Japan began to implement the Act on Rational Use and Proper Management of Fluorocarbons (Fluorocarbons Emission Restraining Law) to replace the Fluorocarbons Recovery and Destruction Law (enhanced in 2001) so as to realize the comprehensive management of the whole life cycle of fluorine-containing compounds from "production" to "regeneration or destruction." The Global Warming Countermeasure Plan approved by the Japanese Cabinet in May 2016 has set a higher target for the recovery of fluorocarbon refrigerants. The recovery rate of fluorocarbon refrigerants needs to reach 70% by 2030 (Ministry of the Environment, Japan 2020). Regulations based on the Fluorocarbons Emission Restraining Law were strengthened to obtain this goal. It imposes obligations on stakeholders (users, demolition operators, and scrap and/or recycle operators); for instance, if the fluorocarbons are not recovered when the equipment is scrapped, a direct (nonprobationary) penalty will be imposed on the user. Similarly, when the equipment is scrapped, the user shall show the certificate of fluorocarbon recovery (Shimokyoda 2019).

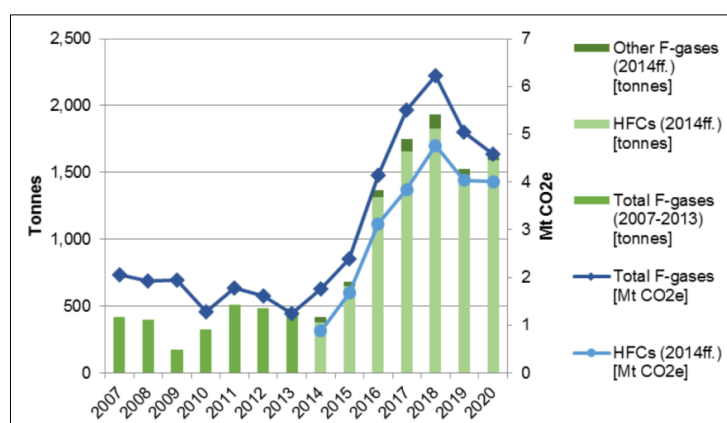
Japan adopts the policy of the government in charge and social organizations as the main body for refrigerant recovery and reuse and establishes a relatively complete industrial chain of refrigerant recovery, reuse, and destruction. There are three laws in Japan aimed at restricting the recovery of products with refrigerant. For vehicle air-conditioners, it is the End-of-life Vehicle Recycling Law. For household AC, refrigerators, and heat pumps, it is the Home Appliances Recycling Law, and for industrial and commercial AC, it is the Act on Rational Use and Proper Management of Fluorocarbons. In the 1990s, the "Refrigerants Recycling Promotion and Technology Center" (RRC), established by the Japan Refrigeration and Air-Conditioning Industry Association (JRAIA), the Japan Association of Refrigeration and Air-Conditioning Contractors (JARAC), and the Japan fluorocarbon Manufacturers Association (JFMA), was especially responsible for the publicity and popularization of refrigerant recovery, the training of recovery technicians, the certification of institutions engaged in refrigerant recovery, the accreditation of institutions involved in the regeneration of recovered refrigerant, refrigerant recovery and reuse research, planning of standards and policies, etc. In 2011, it was incorporated into the newly established Japanese Refrigerants and Environment Conservation Organization (JRECO).

6.2 Europe

Compared with the Montreal Protocol, the EU's Regulation (EC) No. 1005/2009 (known as the ozone regulation) has formulated more advanced and faster reduction plans (EU 2009). After implementing the EU ozone regulation, the consumption of ODSs in the EU has been negative since 2012 (European Environment Agency 2020) (more ODSs were destroyed or exported than were produced or imported).

In 2014, the European Union published a new F-gas regulation (Regulation (EU) No. 517/2014 on fluorinated greenhouse gases), which not only carried out stricter control measures on the use of fluorine-containing gases but also made specific provisions on the emission, leakage detection, and recovery of fluorine-containing gases. According to the European Environment Agency (EEA) report, the greenhouse gas emission reduction of 27 EU countries in 2019 was 24% lower than that in 1990 (European Environment Agency 2021a). Figure 5 shows the recovery of F-gas in the EU from 2007 to 2020 (European Environment Agency 2021b).

Figure 5: The Recovery Situation of F-gas in Europe



Notes: The geographical scope of presented data is the EU-28 except Croatia for 2007–2008, EU-28 for 2009–2019, and EU27+UK for 2020. Annex II F-gases (unsaturated HFCs and HCFCs, HFEs and alcohols, and NF3 and other perfluorinated compounds) were not subject to reporting for the years 2007–2013.

Sources: European Environment Agency 2021b

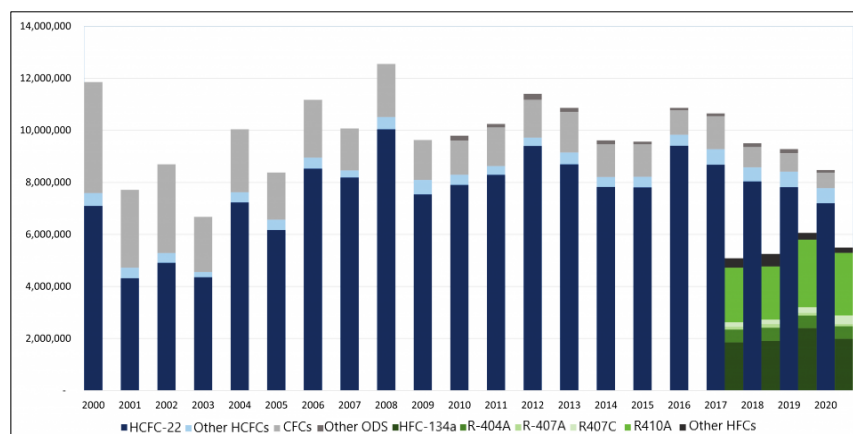
Commented [A1]: There are two references to the EEA for 2021 in the reference list and these need to be distinguished ... Suggest inserting 'a' and 'b' as applicable both in the text and in the reference list ... Do you mean '2021a' or '2021b' here?

6.3 United States

Based on the Clean Air Act, the United States has unified requirements for refrigerant recovery and reuse, personnel certification, and recovery equipment certification, including the production and consumption quota of ozone-depleting substances, the compulsory marking system for equipment containing ozone-depleting substances, and a series of provisions on the use, servicing, disposal, and scrapping of equipment using ozone-depleting substances. At the same time, the US Environmental Protection Agency (EPA) is required to be mainly responsible for formulating and implementing regulations and rules on ODS management. In 2016, the EPA also included HFC substances in the control scope of refrigerants. Figure 6 shows the reclaimed ODS and HFC refrigerant in the United States from 2000 to 2020 (US EPA 2021).

The US Congress enacted the American Innovation and Manufacturing Act (United States Congress 2020) in December 2020. The AIM Act directs the EPA to address hydrofluorocarbons (HFCs) by phasing down production and consumption, maximizing reclamation and minimizing releases from equipment, and facilitating the transition to next-generation technologies through sector-based restrictions.

Figure 6: The Reclaimed ODS and HFC Refrigerant in the United States from 2000 to 2020



Sources: The data on reclaimed ODS and HFC refrigerant in the US are from US EPA, <https://www.epa.gov/section608/summary-refrigerant-reclamation-trends>.

6.4 People's Republic of China

The PRC is currently the world's largest producer and consumer market of refrigeration and air-conditioning equipment, as well as the largest producer and consumer market of refrigerants. Based on the Regulation on the Management of ODSs (Ministry of Ecology and Environment of China 2018), the PRC has formulated a series of regulations and standards at the government and industry levels to effectively promote the good servicing and operation of the refrigeration and air-conditioning industry and the recycling and reuse of refrigerants.

The notice on strengthening the management of the production, sale, and use of HCFCs (Ministry of Ecology and Environment of China 2013) issued by the Ministry of Ecology and Environment of China (MEE) in 2013 stipulates that HCFC production enterprises must hold production quota licenses. The quota and registering system shall be implemented for the equipment production and servicing industry using HCFCs and HFCs. Companies that consume more than 100 tons of HCFCs annually have to apply for quotas from the MEE, while those that consume less than 100 tons have to register with their local environmental protection authorities.

The MEE has established several good servicing operation training centers in the refrigeration servicing industry all over the country to regularly organize the technical workers of servicing enterprises to carry out specialized training and policy publicity. The China Refrigeration and Air-Conditioning Industry Association (CRAA) has developed a series of standards and training materials related to good practice and promoted the classified certification of servicing ability-level enterprises in the servicing sector. The servicing enterprises included in the certification must have related tools and personnel who have obtained relevant certification to promote the recovery and responsible use of refrigerants and strengthen self-discipline within the industry.

7. CONCLUSION AND POLICY RECOMMENDATIONS FOR ASIA

Cooling is inseparable from the use of refrigerants, so choosing a climate-safe refrigerant is crucial to achieving climate-friendly cooling. When choosing a refrigerant, not only ODP and GWP but also safety, economy, energy efficiency, and other factors must be considered. Governments in Asia should promote a new generation and use of environmentally friendly refrigerants with zero ODP, low GWP, low flammability and toxicity, excellent thermophysical properties, high cooling efficiency, cost-effectiveness, excellent climate performance, and other characteristics.

Ozone- and climate-friendly refrigerants that can replace existing refrigerants often have shortcomings such as flammability, toxicity, or high pressure. The promotion of new refrigerants requires the establishment of a complete set of safety and operational service guarantee systems; in addition, despite the huge challenges, relevant laws and regulations also need to be adjusted and updated. The cost of new alternative products will increase significantly within a certain period of time, so the market's acceptance of new alternative products is also a test. The whole society needs to work together to accelerate the market adoption of new alternative products. In order to more effectively promote the wide adoption of new climate-friendly alternative refrigerants, this section lists several recommendations:

- 1) Legislative bodies and government executive departments need to establish and improve relevant laws, regulations, and standards with a view to increasing the development and use of climate-safe refrigerant products.
- 2) Asian governments can strengthen the regulation and supervision of the refrigerant industry and products through establishing or improving the labeling, certification, and registration systems for refrigerant alternatives and developing specific management measures for the identification, certification, and filing of refrigerant substitute products.
- 3) Governments in Asia can include environmentally friendly products (including equipment using climate-safe refrigerants) in the green procurement efforts of the government and public sectors. Widespread use of green and low-carbon products from the perspective of public procurement can help accelerate the market adoption of these products.
- 4) Governments need to help the cooling industry to improve the industrial chain of recovery, reuse, and destruction of refrigerants, and develop effective mechanisms for the supervision and management of the life cycle of refrigerants.
- 5) It is necessary for the government to encourage the refrigeration industry to integrate its forces and make every effort to overcome technical problems such as safety risks and the application efficiency of the new generation of refrigerants.
- 6) Governments need to strengthen technical training, professional development, and market promotion related to green refrigerants.

It is important for Asian governments to work with their cooling industry to design and implement pilot projects to demonstrate the use of new environmentally friendly refrigerants in order to build application cases for the commercialization of new products.

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APPENDIX A: RECOMMENDED REFRIGERANTS

This appendix is mainly based on ADB (2021).

A.1 CO₂

1) CO₂ Characteristics

CO₂ is a natural refrigerant, ODP = 0, GWP = 1, the standard boiling point is -62.9°C , the critical temperature is 31.0°C , and the safety class of CO₂ belongs to A1. CO₂ is nontoxic, noncombustible, has good chemical stability, high refrigerating capacity per unit volume, excellent flow and heat transfer characteristics, etc. As the critical temperature is only 31.0°C , CO₂ operates typically in a transcritical cycle, while the working pressure exceeds 10 MPa, which is 3–5 times that of common refrigerants. The requirements of equipment using CO₂ as a refrigerant for materials, compressors, heat exchangers, valves, and manufacturing processes greatly exceed the needs of conventional equipment, which also leads to a significant increase in the manufacturing cost of CO₂ equipment.

2) The Application Fields of CO₂

The hot water produced by a traditional heat pump water heater generally does not exceed 55°C . If the temperature is higher, the heating coefficient will decrease. CO₂ has a wide range of applications. There is a large temperature slip in the heat release of CO₂ under supercritical conditions, which is conducive to heating hot water to a higher temperature (above 80°C) under extremely low ambient temperature and is highly energy-efficient. Because CO₂ has a larger refrigerating capacity per unit volume, the CO₂ compressor is of small size and has increased volumetric efficiency, but at the same time, the high pressure of CO₂ will bring the problem of difficult sealing. In addition, the pressure difference of the transcritical system is significant, and the throttling loss is enormous. Therefore, using the expander to recover work will significantly improve the system's efficiency.

The COP of a single-stage transcritical CO₂ system is lower than that of R22 and R134a under the same conditions, and a high working pressure is also one of the main shortcomings of the CO₂ transcritical system. These problems can be remedied by improving the cycle mode and optimizing system equipment—for example, parallel compression, quasi-two-stage compression, regenerator, and other optimization technologies (Zhang et al. 2019). When applied in the cascade system, CO₂ is in a subcritical working state, the working pressure of the system is greatly reduced, as is the manufacturing difficulty of the equipment, and the safety and reliability of the system are further improved. Therefore, currently, the CO₂ cascade system is being more and more widely used in low-temperature refrigeration equipment.

The application of CO₂ in the refrigeration and cold storage system has been comprehensively promoted worldwide, and CO₂ heat pump water heaters have been well applied in Japan. The application of CO₂ in automobile air-conditioning is also a research hotspot worldwide.

A.2 NH₃ (ammonia)

1) NH₃ Characteristic

NH₃ (ammonia), a natural refrigerant, ODP = 0, GWP < 1, standard boiling point is -33.3°C, critical temperature is 132.4°C, and the safety class belongs to B2L. It has lower flammability and toxicity. NH₃ has a strong pungent smell, so it is easy to find in the case of a leakage. The refrigeration capacity per unit volume of NH₃ is large, and so are the thermal conductivity and the latent evaporation heat. NH₃ has a small throttling loss, it can be dissolved in water, and it is cheap. NH₃ has had significant applications for more than 100 years as a refrigerant, mainly in refrigeration and cold storage.

2) Solutions to NH₃ Safety Issues

Since there have been some accidents in the use of NH₃ refrigeration and air-conditioning equipment in the past, the toxicity, lower flammability, and corrosivity of NH₃ are often people's concerns. However, according to the investigation and analysis of various accidents, most NH₃ accidents were mainly caused by illegal use or operation. These safety issues also limit its promotion in civil refrigeration and air-conditioning. Therefore, ventilation should be ensured where an NH₃ refrigeration system is used. A concentration monitor and NH₃ leakage alarm should be installed in the refrigeration station and absorb NH₃ with water in time in the case of NH₃ leakage. When NH₃ contains water, it will corrode copper and copper alloy, so copper products should be avoided in the NH₃ refrigeration system. The solubility of NH₃ in mineral oil is very low, so there must be an oil separator, an oil collector, and other related equipment in the NH₃ refrigeration system. As a result, the NH₃ system is more complex and needs more control components than other fluorocarbon refrigerant systems. With the development of technology, the automatic control and leakage monitoring technologies of NH₃ systems have made rapid progress, which improves the application safety of NH₃ systems (Baolong, Wenxing, and Yifan 2009).

3) The Application Fields of NH₃

Currently, NH₃ and NH₃/CO₂ (cascade or CO₂ as a secondary refrigerant system) are mainly used as refrigerants in large and medium-sized refrigeration systems and quick-freeze equipment globally. Compared with the NH₃ system, NH₃/CO₂ cascade or CO₂ as the secondary refrigerant system can reduce the refrigerant charge of NH₃ in the system by more than 80% (Zhang et al 2019), which significantly improves the safety level of the system. The reduction of NH₃ charge in the cascade system promotes the application fields of the NH₃/CO₂ cascade refrigeration system, expanding to the small and medium-sized refrigeration and cold storage sector.

The critical temperature of NH₃ is 132.3°C, which is significantly higher than that of R22 (96.2°C) and R134a (101.1°C), so it can realize a subcritical cycle under high heat source temperature and cold source temperature. Therefore, currently, the application fields of NH₃ are also expanding to the high-temperature heat pump sector.

A.3 Propane (R290)

1) R290 Characteristic

R290 (propane), a natural refrigerant, ODP = 0, GWP = 3, the standard boiling point is -42.1°C, the critical temperature is 96.7°C, it is flammable and explosive, and its safety class belongs to A3. R290 has good environmental characteristics and thermal performance and is compatible with existing common materials and lubricants.

However, it is highly flammable and explosive; therefore, its application is greatly limited. The electronic components in the product need explosion-proof design, and various international standards, including ISO and IEC, put strict limits on the charging amount of R290 refrigerant. According to norms, the refrigerant charge is closely related to the area and height of the installation room. For example, according to ISO 5149, in a room measuring 16 square meters, the charge limiting value of R290 is about 300 g (ISO 5149-1 2014). When the installation system needs more charge and exceeds the refrigerant charge limit specified in the standard, these applications will not be allowed.

2) The Application Fields of R290

R290 has obtained good market application in some products with a slight refrigerant charge, such as room air conditioners, mobile air conditioners, dehumidifiers, small freezers, etc.

A.4 Isobutane (R600a) and propylene (R1270)

R600a (Isobutane), a natural refrigerant, ODP = 0, GWP = 20, standard boiling point is -11.8°C , critical temperature is 134.7°C , and its safety class belongs to A3. It is flammable and explosive, so its application is limited. It is necessary to take strict safety measures according to the standard and meet the strict requirements of refrigerant charge limits. R600a has been widely used in small refrigerators and freezers with a small refrigerant charge.

R1270 (Propylene), a natural refrigerant, ODP = 0, GWP = 2, molecular weight is 42, standard boiling point is -47.6°C , critical temperature is 91.1°C , and its safety class belongs to A3. It is flammable and explosive. The standard boiling point, critical temperature, and freezing point of R1270 are similar to those of R22. The molecular weight of R1270 is much lower than that of R22 and slightly smaller than that of R290. In addition, the lower viscosity of R1270 can greatly reduce the resistance loss of the refrigeration circuit in the air-conditioning system. The latent heat of vaporization for R1270 is about 1.88 times and 1.17 times that of R22 and R290, respectively, so the charge of R1270 is only about half that of R22. R1270 has higher heat transfer efficiency, a better economy, and is easier to obtain. R1270 is soluble in mineral oil and has good oil recovery performance (Ren, Yan, and Song 2006). The R1270 refrigeration system is widely used in petrochemical and other industrial contexts with high security-level requirements.

A.5 HFC-32

R32, ODP = 0, GWP = 675, standard boiling point is -51.7°C , critical temperature is 78.1°C , its safety classification belongs to A2L. HFC-32 is one of the main components of R410A, which is easy to obtain, and the price is low. The discharge temperature of the R32 compressor is higher than that of the R22 and R410A compressors. The increase in exhaust temperature will reduce the viscosity of lubricating oil and affect the long-term service life reliability of the compressor. Therefore, reducing the exhaust temperature of the compressor and developing high-stability lubricating oil is the focus of the development of R32 application technology.

R32 has a large-volume refrigeration capacity and excellent thermodynamic performance. R32 air-conditioning equipment is highly energy-efficient, has a slight refrigerant charge, and has good climate performance in its service life. R32 belongs to HFCs, but the GWP is only a third of that of R410A and 40% of that of R22. Compared

with R410A, the refrigerant charge of R32 air-conditioning equipment can be reduced by about 24%. When it is replaced, the direct emission reduction rate of greenhouse gases will exceed 75% (Rong, Xiaoping, and Xiangfei 2013). Combined with improved energy efficiency, the promotion and adoption of R32 will achieve a better emission reduction effect of greenhouse gases. Currently, R32 is widely used in air-conditioning, VRF systems, unitary air conditioners, and small chillers worldwide.

A.6 HFOs

HFOs belong to unsaturated HFCs. Because these substances have double bonds in their molecular structure, they break easily in the atmosphere. They have a very short atmospheric life, very low GWP, and good environmental performance. They are promoted as being the next generation of low-GWP refrigerants. Table B1 lists the ecological characteristics and alternatives of various potential HFOs. The substances being promoted or tested include HFO-1234yf, HFO-1234ze(E), HCFO-1233zd(E), HFO-1336mzz(Z), and a large number of HFO and HFC mixtures with different composition ratios. Because of the complex synthesis process and many patent barriers, the price of HFOs is much higher than that of traditional HCFCs, HFCS, and natural refrigerants.

HFO-1234yf, ODP = 0, GWP = 4, the standard boiling point is -29°C , the critical temperature is 94.7°C , and its safety class belongs to A2L. Its thermal performance is close to that of HFC-134a, the volumetric refrigeration capacity of HFO-1234yf is about 5% lower than that of HFC-134a, and its COP is equivalent to that of HFC-134a. It is also one of the significant components of many HFO mixtures. HFO-1234yf has been widely used in automobile air conditioners in Europe and the United States.

HFO-1234ze(E), ODP = 0, GWP = 7, HFO-1234ze(E) and HFO-1234yf are isomers. Its molecular weight is 114, the standard boiling point is -19°C , its critical temperature is 109°C , and its safety class belongs to A2L. The volumetric cooling capacity of HFO-1234ze(E) is about 24% lower than that of HFC-134a, and its COP is equivalent to that of HFC-134a. The critical temperature of HFO-1234ze(E) is higher than that of HFC-134a, so it has a certain application prospect in heat pump water heaters and large chillers (heat pump). It is also an important component of many HFO mixtures.

HFO-1233zd(E), ODP = 0.00034, GWP = 4.5, the standard boiling point is 19°C , the critical temperature is 165°C , and its safety class belongs to A1. Its vapor pressure properties are similar to HFC-245fa, and its molecular weight is significant, so it has a good application prospect in centrifugal chillers, high-temperature heat pumps, and Organic Rankine Cycle power generation systems.

HFO-1336mzz(Z), ODP = 0, GWP = 9, the standard boiling point is 33.4°C , the critical temperature is 171.3°C , and its safety class belongs to A1. Because the vapor pressure property of HFO-1336mzz(Z) is similar to that of HCFC-123 (the evaporator is under negative pressure during operation) and its molecular weight is significant, it is expected to become an optional substitute for HCFC-123. It will have good application prospects in centrifugal chillers, high-temperature heat pump systems, and Organic Rankine Cycle power generation systems.

R513A, ODP = 0, GWP = 631, the standard boiling point is -29°C , the critical temperature is 98°C , and its safety class belongs to A1. R513A is a mixture of HFO-1234yf/HFC-134a (component mass ratio 56/44), and its volumetric refrigeration capacity is close to that of R134a under the same working conditions. It has the potential to replace R134a in large and medium-sized chillers.

R514A, ODP = 0, GWP = 7, the standard boiling point is 29.1°C, the critical temperature is 178.1°C, and its safety class belongs to B1. R514A is a mixture of HFO-1336mzz(Z)/HCO-1130 (E) (the mass ratio is 75/25). The vapor pressure property of this refrigerant is similar than that of HCFC-123. It has good potential to replace HCFC-123 in centrifugal chillers (the evaporator is under negative pressure during operation).

R515B, ODP = 0, GWP = 293, standard boiling point is -18.8°C, critical temperature is 108.9°C, and its safety class belongs to A1. R515B is a mixture of HFO-1234ze(E)/HFC-227ea (the mass ratio is 88.0/12.0). The volumetric refrigeration capacity of R515B is equivalent to that of HFO-1234ze(E), about 24% lower than that of HFC-134a. It has the potential to replace R134a in large and medium-sized chillers.

R452B, ODP = 0, GWP = 698, boiling point temperature is -51°C, dew point temperature is -50.3°C, and its safety class belongs to A2L. R452B is a mixture of HFC-32/HFC-125/HFO-1234yf (component mass ratio 67/7/26). The physical properties of R452B are similar to those of R410A. It has a certain potential to replace R410A in small and medium-sized air-conditioning units.

R454A, ODP = 0, GWP = 239, safety level A2L. R454A is a mixture of HFC-32/HFO-1234yf (component mass ratio 35/65). R454C, ODP = 0, GWP = 148, its safety classification is A2L. R454C is a mixture of HFC-32/HFO-1234yf (component mass ratio 21.5/78.5). These two refrigerants have a certain potential to replace R404A and R507A in small and medium-sized refrigeration. R454B, ODP = 0, GWP = 467, its safety class belongs to A2L. R454B is a mixture of HFC-32/HFO-1234yf (component mass ratio 68.9/31.1). The physical properties of R454B are similar to those of R410A. It has a certain potential to replace R410A in small and medium-sized air conditioners.

APPENDIX B

Table B1: Refrigeration Substitution

Next Generation of Refrigerants HFOs	ODP	GWP	Application Sector	To Replace
HFO-1234yf	0	4	Automobile air conditioner	R134a
HFO1234ze(E)	0	7	Heat pump water heater, Large chiller (heat pump)	R134a
HFO-1233zd(E)	0.00034	4.5	Centrifugal chiller, High-temperature heat pump, Organic Rankine Cycle power generation system	R245fa
HFO-1336mzz(Z)	0	9	Centrifugal chiller, High-temperature heat pump, Organic Rankine Cycle power generation system	R123
R513A	0	631	Large and medium-sized chiller	R134a
R514A	0	7	Centrifugal chiller	R123
R515B	0	293	Large and medium-sized chiller	R134a
R452B	0	698	Medium and small air-conditioning units	R410A
R454B	0	467	Medium and small air-conditioning units	R410A
R454A	0	239	Small and medium-sized refrigeration sector	R404A, R507A
R454C	0	148	Small and medium-sized refrigeration sector	R404A, R507A

*ODP and GWP data source: Intergovernmental Panel on Climate Change for its Fourth Assessment Report (IPCC AR4).

Source: ADB (2021).

APPENDIX C

Table C1: ODP, GWP, and Safety Classification of Common Refrigerants

No.	Refrigerants	ODP	GWP	Safety Classification*
1	CFC-11	1	4,750	A1
2	CFC-12	1	10,900	A1
3	HCFC-22	0.055	1,810	A1
4	HCFC-123	0.02	77	B1
5	HCFC-142b	0.065	2,310	A2
6	HFC-134a	0	1,430	A1
7	R410A	0	2,088	A1
8	R407C	0	1,774	A1
9	R404A	0	3,922	A1
10	R507A	0	3,985	A1
11	HFC-32	0	675	A2L
12	NH ₃	0	<1	B2L
13	CO ₂	0	1	A1
14	HC-290	0	3	A3
15	HC-600a	0	20	A3
16	R1270	0	2	A3
17	HFO-1234yf	0	4	A2L
18	HFO-1234ze(E)	0	7	A2L
19	HCFO-1233zd(E)	0.00034	4	A1
20	HFO-1336mzz(Z)	0	4	A1
21	R513A	0	631	A1
22	R514A	0	7	B1
23	R515B	0	293	A1
24	R452B	0	698	A2L
25	R454B	0	467	A2L
26	R454A	0	239	A2L
27	R454C	0	148	A2L

* The refrigerant safety classification shall refer to *Refrigerants – Designation and Safety Classification* (ISO 817:2014). A and B indicate the toxicity of the refrigerant. Class A indicates lower toxicity and Class B indicates higher toxicity. 1, 2L, 2, and 3, respectively, represent the flammability levels of the refrigerant. From 1 to 3, they are nonflame propagation, lower flammability, flammable and higher flammability, respectively.

Source: ADB (2021).