Measures to expand the application range of ammonia refrigerant

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Abstract. To cope with the climate issue, China has clearly stated the goal of carbon peaking and carbon neutrality. Most of the refrigerants currently used are HCFCs and HFCs refrigerants. These refrigerants have high COP and GWP values and can cause a severe impact on the environment. Ammonia refrigerant is an environmentally friendly natural refrigerant, ODP and COP value are zero, and the cost is low, with significant environmental and operational advantages, large unit cooling capacity, moderate condensing temperature, good thermal conductivity, suitable for refrigerator and cold storage refrigeration, but at the same time ammonia is a toxic gas with a strong pungent odor. Studying measures to expand the application range of ammonia refrigerants is conducive to correctly understanding and using ammonia refrigerants and giving full play to the refrigeration potential of ammonia refrigerants. Promoting the utilization of ammonia, a clean energy, and achieve the purpose of environmental protection.

1. Introduction

Energy conservation and environmental protection have become an important theme in the development of the refrigeration industry since the 21st century, and the use of eco-friendly refrigerants may be an effective way to solve the problem of global warming[1].

When selecting a new refrigerant, a thorough evaluation is required. Any substance should assess its overall impact on the global environment, energy efficiency, cost-effectiveness and safety[2]. HCFCs and HFCs have the disadvantages of destroying the ozone layer and aggravating the greenhouse effect. Many laws and regulations have been introduced internationally to freeze and phase out the use of HCFCs and HFCs. Phase-out schedules have been established for countries at different stages of development based on common but differentiated responsibilities. CFCs had been phased out in developed countries and CFCs in developing countries in 2010. Initial CFC alternatives include some hydrochlorofluorocarbons (HCFCs), but they will also be phased out internationally in developed and developing countries in 2020 and 2030. The international conventions that have entered into force play an important guiding role in the process of replacing refrigerants[3, 4].

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2. The use status of ammonia refrigerant

2.1. Ammonia refrigerant characteristics

Ammonia refrigerant is the most widely used medium temperature refrigerant in China. The synthesis process of ammonia refrigerant is mature, and the price of ammonia refrigerant is low. At present, the price of ammonia refrigerant in China is about 3.0 RMB/kg (HCFC-22 is about 20 RMB/kg, HFC-134a is about 80 RMB/kg). Its molar mass is 17, the boiling point at atmospheric pressure is -33.4 ℃, and in the ammonia two-stage compression refrigeration unit, a low temperature of -50 ℃ can be obtained[5]. The pressure of ammonia refrigerant in the condenser and evaporator is moderate (the condensing pressure is generally 0.981MPa, the evaporation pressure is generally 0.098~0.49MPa); the unit volume cooling capacity q_v of ammonia is larger than that of HCFCs-22. Its cooling coefficient (COP) is high, the heat release coefficient is large, the latent heat of ammonia refrigerant is extremely high, at 15 ℃, the latent heat of vaporization is 6.4 times that of R22, is 5.5 times that of R410A, in the unit mass flow, than the refrigeration effect of halogenated hydrocarbon refrigerants used in the vapor compression refrigeration system are better, when the condensing

temperature is 328K and the evaporator temperature is 263K, the mass flow rate of five refrigerants, R134a, R717, R1234ze, R1234yf and R600a, is shown in Figure 1. So at the same temperature, the same cooling capacity, the size of the ammonia compressor is the smallest, which can realize the miniaturization of condenser and other equipment, save materials[6, 7].

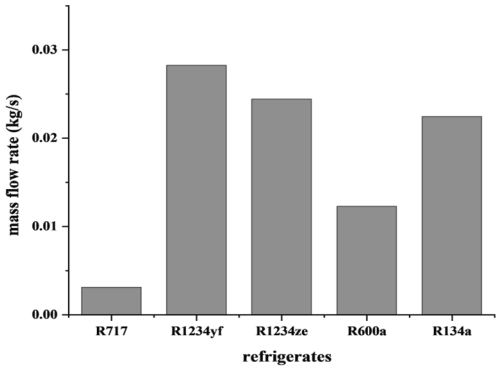

Figure 1. Mass flow of five different refrigerants at the same condensing and evaporating temperatures.

Ammonia refrigerants are easily soluble in water and can be absorbed by water when there is an emergency in the system. Therefore, ammonia refrigerant is a very good eco-friendly "green" refrigerant, which is incomparable with HCFCs and HFCs refrigerants. Table 1 shows the ODP values and GWP values of several commonly used refrigerants.

Table 1. ODP values and GWP values of several commonly used refrigerants

Refrigerant	ODP	GWP100
R22	0.034	1760
R142b	0.057	1980
R407c	0	2690
R134a	0	1430
R32	0	<1
R1234ze	0	<1
R600a	0	20
R290	0	5
R744	0	1
R717	0	0

2.2. Disadvantages of ammonia refrigerants

Ammonia concentration above 5-10 ppm can be detected, but people who work in low concentrations of ammonia for a long time are also difficult to detect ammonia leakage in an environment with ammonia concentration of 100 ppm. The short-term exposure limit for anhydrous ammonia has been reported to be 35 ppm(i.e. 15 minutes working time) , and 5 minutes of contact with anhydrous ammonia above 5000 ppm can lead to death[8]。

Ammonia fire and explosion hazard, according to GB50058 "*Design Code for Power Devices in Explosion and Fire Hazard Environment*", ammonia belongs to the II.AT1 group. In the workshop, its maximum allowable concentration is 43 ppm, the maximum allowable concentration is 0.3 ppm in residential areas, it is classified as B2 in the ANSI/ASHRAE 34-1997 safety level. When the integral number of ammonia gas in the air reaches 0.5%~0.6%, staying in it for 30 min can lead to human poisoning, when the volume fraction reaches 16%~25%, it will explode in case of open flame[9].

The discharge of harmful pollutants and explosions in industrial accidents have an impact on the environment and human health. Figure 2 is a schematic diagram of the ammonia accident. Studies have noted the importance of assessing the risks associated with possible chemical disasters associated with ammonia leakage in storage plants[10, 11]. In 1990, a 4-ton ammonia gas leak occurred in the Cuban city of Matanzas, killing six people and poisoning more than 400[12]. The event demonstrated the need for predictive studies on the massive release of ammonia and its impact on affected populations[13]. Ammonia has a flash point of 700℃ to 780℃ and will not burn or explode in an outdoor environment.

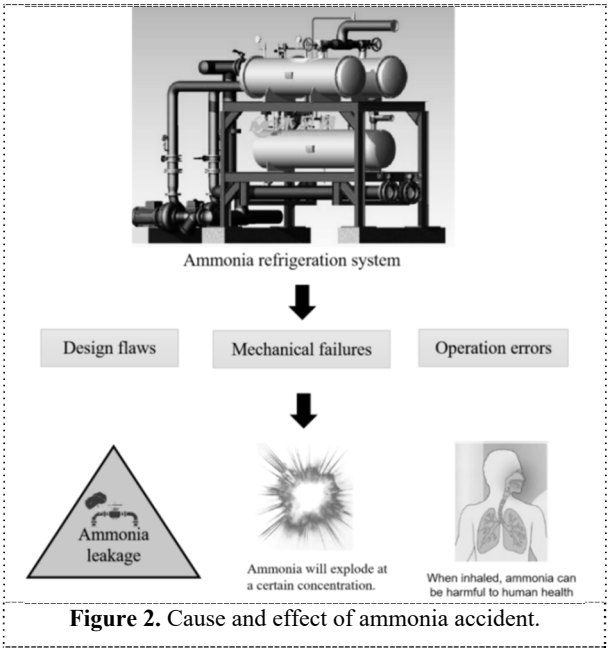

Figure 2. Cause and effect of ammonia accident.

Ammonia has basically no corrosive effect on steel, but when ammonia contains moisture, it has a corrosive effect on zinc, copper, bronze alloys (except phosphor bronze). The pipes, instruments, valves, etc. In the ammonia refrigeration device cannot use copper and copper alloy materials.

In the central air conditioning direct refrigeration system using ammonia refrigerant, even a little leakage will cause serious pollution of indoor air, so its use in air conditioning has been limited.

3. Measures to expand the application range of ammonia refrigerant

The use of ammonia refrigerants instead of ozone-depleting substances is of practical significance. However, sufficient attention must be paid to the toxicity and flammability of ammonia, and the corresponding supporting safety measures must be fully considered when designing and managing the use of refrigeration systems, especially when it comes to civil building air conditioning systems.

3.1. Optimization of ammonia refrigeration system

Ammonia refrigerant is the blood of refrigeration system. Under the condition of meeting the refrigeration demand, reducing the amount of ammonia refrigerant charged in the system can greatly improve the safety of ammonia refrigeration system.

Indirect cooling refrigeration system can be used, the biggest characteristic of indirect cooling refrigeration system is to avoid ammonia refrigerant directly into the cold place. But at the same time, the heat loss caused by heat exchange between refrigerant and secondary fluid should be considered in indirect refrigeration system[14, 15]. CO_2/NH_3 overlapping refrigeration system composed of ammonia and carbon dioxide, is widely used in cold storage, supermarket display cases and other food freezing and refrigeration fields. CO_2 is a non-toxic, tasteless and non-flammable natural working medium. On the premise of meeting the low temperature demand, it can effectively avoid the direct contact between ammonia and frozen food. The CO_2/NH_3 overlapping refrigeration system is shown in the figure3. For lower temperatures, more multiple cooling systems can be used.

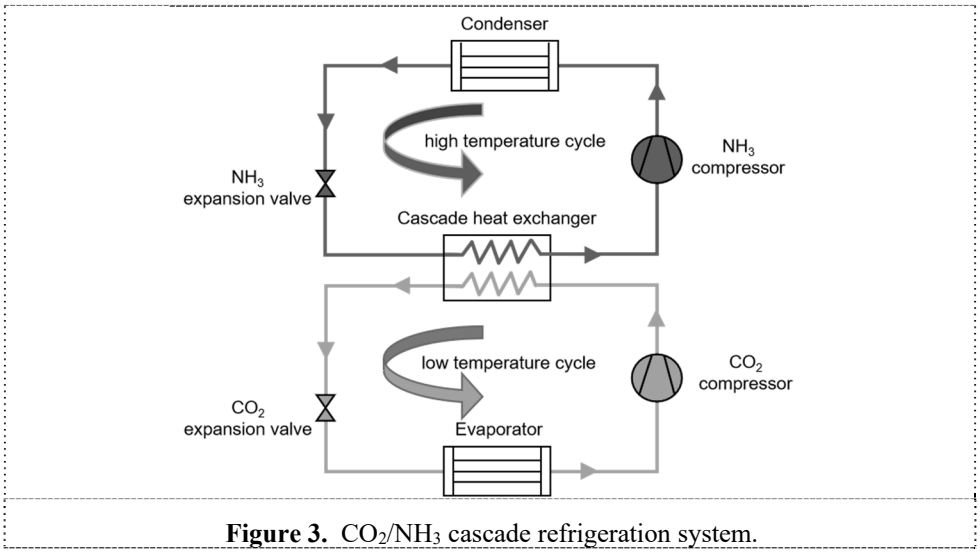

Figure 3. CO_2/NH_3 cascade refrigeration system.

Secondly, the realization of the ammonia refrigeration units can miniaturize the ammonia refrigeration system, reduce the size of the equipment, reduce the weight, avoid the use of full liquid evaporation as far as possible, reduce the amount of ammonia charged in the system, so as to reduce the risk of using ammonia, For enhancing the heat transfer properties of ammonia refrigerants, nanoparticles have high thermal conductivity, and the combination of nanoparticles and fluid will increase the thermal conductivity of the fluid[16, 17], thereby increasing its heat transfer efficiency. Nanomaterials are recognized as an important measure to improve the heat transfer performance of fluids[18].

If the high-pressure liquid storage barrel is canceled in the cold storage, the ammonia storage volume of the system will be significantly reduced[19]. That is, the refrigerant from the condenser outlet is directly introduced into the circulating barrel. The content volume of the system is reduced, greatly reducing the amount of ammonia filled in the system, and also reducing the security risks.

In terms of reducing the amount of ammonia refrigerant charged, the United States used a distributed ultra-lowammonia charge (ULC) refrigeration package[20], which greatly reduced the amount of ammonia in the system. The use of closed coupled components in a compact refrigeration package, along with electronic refrigerant injection control technology, reduces equipment ammonia costs by more than 98%. ULC systems are a promising alternative technology for industrial warehouse cooling in terms of total cost, human safety and environmental benefits.

Simplified refrigeration system, intercooler combined with high pressure stage circulation barrel, in two stage compression system, intercooler is an essential equipment (container). The cold storage combines the intercooler with the high-pressure circulating barrel, that is, the circulating barrel is also used as the intercooler. This eliminates one ammonia storage device in the system and further reduces the amount of ammonia charged to the system.

3.2. Enhance the safety of ammonia refrigeration system

Flame retardants achieve flame retardancy by generating inhibitory radicals during pyrolysis. The addition of flame retardants is important for the safe application of ammonia in the process industry. The combustion flames of ammonia before and after the addition of R125 and R227ea were analyzed for ammonia concentrations located at the lower flammability limit (16.7%), as shown in table 2, the flammability of mixed refrigerants became significantly weaker than that of pure ammonia refrigerants after the addition of flame retardants, and the inhibition of flammability of ammonia refrigerants by R227ea was stronger than that of R125.

Table 2. Combustion effect of ammonia refrigerant with flame retardant added[21].

	t=0 s	t=0.2 s	t=0.4 s
16.7%NH_3	a-1	a-2	a-3
16.7%R125/NH_3	b-1	b-2	b-3
16.7%R227ea/NH_3	c-1	c-2	c-3

Changing the volume ratio of flame retardants/NH_3, the flammability limits of R125/NH_3 and the flammability limits of R125/NH_3 and R227ea/NH_3 decreased gradually with the increase of the volume ratio and finally reached the critical flammability point. With reference to the existing studies, the GWP values and flammability limit ranges of binary mixtures can be calculated from the following two equations:

$$\mathrm{GWP} = GWP_1 \times \frac{X_i}{\mathrm{X_i}+1} + GWP_2 \times \frac{1}{\mathrm{X_i}+1} \quad (1)$$

$$FLR = UFL - LFL \quad (2)$$

where, GWP is the GWP of the binary blend, GWP_1 is the GWP of the flame retardant, and GWP_2 is the GWP of the flammable refrigerant. FLR is the flammability limit range, %. When the GWP value of the refrigerant mixture is 750, the refrigeration percentage of R125 and R227ea in the refrigerant mixture is 0.21 and 0.24, respectively. And the flammability limit range is significantly shortened, and the GWP value can be reduced to realize the safe and environmentally friendly use of ammonia refrigerant [21].

The piping connection in the refrigeration system is welded as much as possible to reduce unnecessary valves. Ammonia refrigeration units can be semi-open air to facilitate better control of the concentration of ammonia vapor in the ammonia plant room. The concentration of ammonia in the engine room should be controlled at 25 ppm or less. The ammonia plant room should be equipped with an ammonia leak warning system, as shown in Figure 4. If a leak occurs, in the first stage, the system will discharge the gas mixture in the plant room to a high altitude away from the building through the fire protection system pipeline, and at the same time, notify the plant room operation management personnel of the warning

signal. In the second stage, if the leak warning system monitors that the concentration of ammonia refrigerant in the room continues to rise, the alarm circuit is turned on and the power to the unit is turned off, stopping the refrigeration system and allowing only the lighting and ventilation systems to operate as usual.

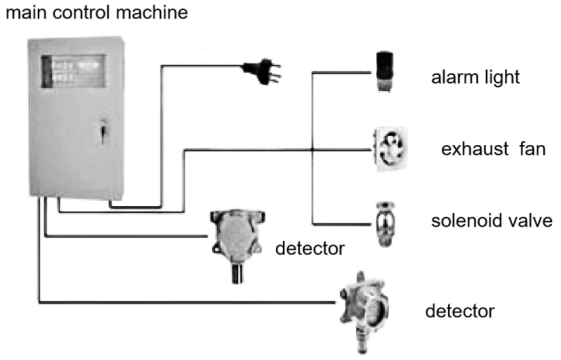

Figure 4. Ammonia leak warning system.

3.3. Operation Management

According to relevant report data, in China, from 2013 to 2017, ammonia leakage, fire accidents caused by ammonia leakage and electrical faults resulted in 161 deaths. However, most accidents are caused by human factors such as improper operation by operators and lack of maintenance of equipment. Ammonia leakage during maintenance usually has a lot to do with improper operation[22 ， 23]. Skilled operation and regular maintenance system are the most effective measures to prevent the leakage of ammonia system, but also related to the safe and reasonable operation of ammonia refrigeration system.

The enterprise shall provide operators with various technical training, which shall cover all the equipment and functions of refrigeration system or unit system, strictly regulate the use, operation and maintenance of ammonia. Strictly implement the fire safety system, leakage prevention system and accident rescue system[24]. Management must establish an emergency plan for ammonia leakage[25]. This must include detecting ammonia leaks, sounding alarms and alerting others around, using personal protective equipment, emergency plant exhaust and electrical isolation, conducting reconnaissance operations and shutdown procedures to effectively respond to emergencies, to ensure the safety and health of operation management personnel, to avoid the loss of national property

4. Conclusions

Ammonia has been used as a refrigerant for refrigeration systems for nearly 150 years. With excellent thermal properties, ODP value of 0 and GWP value of 0, ammonia refrigerant is an environmentally friendly refrigerant with great advantages to replace HCFCs and HFCs. The following measures can be taken to improve the safety of ammonia refrigeration system and expand the application range of ammonia refrigerant. Simplify the ammonia refrigeration system, which can reduce the charge of ammonia refrigerant while ensuring the system cooling capacity. Adding flame retardant, reducing the interface of ammonia refrigeration system piping, setting up early warning system and ammonia drainage system can improve the safety performance of ammonia refrigeration system. Compliance with the relevant standards in operation and management can effectively curb accidents caused by human factors. As the international community becomes more and more environmentally conscious, HCFCs and HFCs refrigerants will definitely leave the stage of history. Ammonia refrigerant will have a very broad application prospect in all fields of refrigeration technology.

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