Introduction to Domestic and International Sulfur Hexafluoride (SF_6) Greenhouse Gas Emission Reduction Technologies for Power Grid Enterprises

Wangchao Dong[1,a*], Yue Zhao[1], Fengxiang Ma[1], Feng Zhu[1], Wei Liu[1], Yumei Song[1], Shan Zhu[1], Han Chen[2,b*]

[1] Power Science Research Institute, State Grid Anhui Electric Power Co., Ltd., Hefei, Anhui, China
[2] Center for New Finance Research, International Institute of Finance, University of Science and Technology of China, Hefei, Anhui Province, China

Abstract: Since its introduction in 1930, sulfur hexafluoride (SF_6) has rapidly become the primary insulation material for high-voltage electrical equipment such as transmission lines, switches, transformers, circuit breakers, and reactors, owing to its exceptional electrical properties. However, the flip side of its excellent performance is its extremely high global warming potential (GWP), which is over 23,000 times that of carbon dioxide (CO_2). Managing SF_6 has thus become a key aspect of emission reduction efforts. The primary strategies for reducing SF_6 emissions include minimizing gas leakage during the production, operation, and maintenance of electrical equipment, as well as purifying and recycling emitted SF_6 gas. Various purification and monitoring methods have been developed for routine operations and have already been implemented by power grid companies globally. In addition to ongoing daily monitoring, research is also underway concerning the transformation, degradation, and substitution of SF_6 gases. Degradation and transformation methods primarily focus on high-temperature degradation, photocatalysis, and arc degradation. In the context of substitution, the idea is to use conventional gases or various organic compounds to form SF_6 mixtures or alternative gases, with the aim of reducing effect of leakage while maintaining performance. Finally, recommendations are made for power grid enterprises to reduce SF_6 emissions, emphasizing the importance of source control and the exploration of alternatives. Effective equipment management to prevent gas leakage, comprehensive monitoring and assessment, as well as the proper handling of unusable SF_6 devices, are also crucial steps in emission reduction efforts.

1.Introduction to Sulfur Hexafluoride Gas

Sulfur hexafluoride (SF_6) is an ultra-high-voltage insulation material that also possesses excellent arc extinguishing properties. Since its introduction in 1930, SF_6 quickly became a preferred insulation material for various high-voltage electrical equipment, including high-voltage transmission lines, circuit breakers, transformers, switches, and reactors. It is widely used as an insulating material in these high-voltage electrical devices.

According to reports from the Intergovernmental Panel on Climate Change (IPCC), nearly 80% of globally produced SF_6 gas is applied in the power industry, aside from its usage in magnesium metal industry (4%), electronics industry (8%), related insulation applications (3%), as well as in particle accelerators, fiber optics production, biomedical applications, etc4.

With technological advancements, scientists have discovered other beneficial properties of SF_6, such as its non-flammable nature, non-corrosiveness, and effective insulation against air, which have expanded its applications into areas like metal smelting, integrated circuit manufacturing, and refrigerant production.

However, while SF_6 boasts various excellent electrical properties, it is also recognized as one of the most potent greenhouse gases with severe global warming potential (GWP). Its GWP is over 23,000 times that of carbon dioxide (CO_2), and it can persist in the atmosphere for approximately 3,200 years, making natural degradation within a human lifespan nearly impossible. Consequently, SF_6 is classified as one of the six greenhouse gases that require strict control of emissions by the Kyoto Protocol.

2.Domestic and International SF_6 Gas Emission Reduction Technologies

In order to protect the environment, fulfill emission reduction obligations, and control SF_6 emissions,

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[a*] First author: Wangchao Dong, dwchhf@live.com
[b*] Corresponding author: aiguningkesi@mail.ustc.edu.cn

countries around the world have undertaken full lifecycle monitoring of SF_6 electrical equipment. Environmental and power departments in various countries have also implemented numerous technologies to restrict the release of SF_6 gas into the atmosphere, and China is no exception. Currently, the annual usage of SF_6 gas in China's power system alone reaches 5,000 to 6,000 tons and is increasing at a rate of 20% annually. The existing stock of SF_6 gas in active equipment within the power industry is approximately 18,000 tons, with a potential recycling capacity of about 600 tons per year. When converted to CO2 equivalent, this amounts to over 14 million tons1. During the Copenhagen World Climate Conference, China pledged to reduce CO2 emissions per unit of GDP by 40% to 45% by 2020 compared to 2005 levels. With the rapid development of the national power grid, especially high-voltage transmission and distribution lines, and the increasing use of GIS and other switchgear, the consumption of SF_6 gas in the power system has significantly increased. Therefore, the rational and proper recovery, purification, and reuse of SF_6 gas has become an urgent issue to address.

2.1Main Technologies for SF_6 Emission Reduction Already in Use

2.1.1Reducing Gas Leaks from SF_6 Electrical Equipment During Production, Operation, and Maintenance

In general, the reasons for SF_6 gas leaks include:

①Leaks at weld seams;
②Leaks at shell defects;
③Leaks at flange joints;
④Leaks in gasket sealing systems;
⑤Leaks at relay connections;
⑥Leaks in GIS (Gas Insulated Switchgear) enclosures.

These leaks can occur due to improper manufacturing processes or inadequate gas refilling operations. The time distribution of SF_6 gas leaks can be divided into three stages:

①During delivery and acceptance, leaks caused by material, processing, and assembly defects.

②During the first winter and summer cycle, leaks resulting from the impact of temperature changes on sealing materials.

③ Leaks occurring as equipment approaches or exceeds its expected service life due to aging and deterioration of sealing materials.

To address this issue, companies like State Grid Corporation of China have made improvements in processes such as efficient synthesis reactions, crude product purification, and fluoride production processes. They have also strengthened the systematic regulations for operational procedures and equipped themselves with SF_6 leak detectors, online monitoring systems, and recovery devices. For instance, State Grid Corporation of China's Hubei branch has improved the method for detecting SF_6 gas leaks in GIS equipment. They comprehensively monitor the SF_6 emissions from the production, operation, and maintenance processes of SF_6 electrical equipment, ensuring compliance with the national standard for industrial sulfur hexafluoride （GB/T 12022-2014）.

2.1.2Purification and Recovery of Emitted SF_6 Gas

During the use of electrical equipment containing SF_6, there is a potential for SF_6 to undergo decomposition, resulting in the formation of toxic and harmful byproducts, including low fluorides. This can pose risks to both human health and the proper functioning of equipment. To address this concern, it is essential to purify and recover the emitted SF_6 gas to eliminate these impurities. In response, State Grid Corporation of China has established multiple SF_6 gas purification and recovery facilities (as shown in Figure 1).

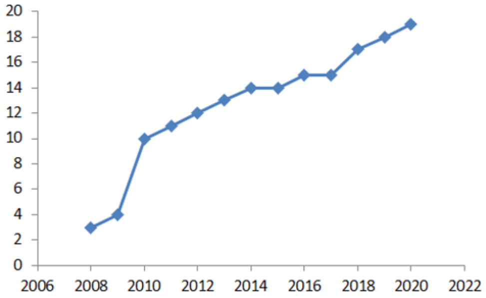

Figure 1 The number of large-scale SF_6 gas purification and recovery facilities in China

The working process of this facility mainly involves collecting the gas from the electrical equipment into the tank through the recovery system of the facility, transporting it to the purification system, removing impurities through the purification system, and then filling the purified gas back into the electrical equipment. This process helps to reduce the emissions of SF_6 and impurities from the electrical equipment to the external environment.

Apart from China, many other countries have also made efforts in the purification and recovery of SF_6 gas. For instance, Solvay Fluor in Germany introduced the "ReUse" program in Europe, proposing on-site treatment of SF_6 waste gas through gas purification vehicles. The Japan Electric Power Company and manufacturers' association have implemented SF_6 recovery plans4; The United States Environmental Protection Agency (USEPA) established SF_6 emission control plans for electrical equipment, magnesium production, die-casting, and other applications as early as 19973.

2.2Partially implemented SF_6 emission reduction technologies

2.2.1Conversion and degradation of SF_6 exhaust gases

SF_6, as a chemically stable non-CO_2 gas, has a long lifecycle with natural degradation mechanisms mainly relying on photolysis and settling, which are inefficient.

Therefore, scientists have proposed various artificial degradation methods to convert SF_6 exhaust gases into non-toxic and harmless products, aiming to reduce the emission of SF_6 gases into the atmosphere. These artificial degradation methods include high-temperature degradation, photocatalytic degradation, arc degradation, etc **错误!未找到引用源。**. In this paper, one of the most advanced degradation methods, the rectifying SiC-Fe_2O_3 heterojunction structure for SF_6 degradation in air, is briefly introduced.

Scientists achieved this by depositing FeOOH onto SiC through self-assembled chemical deposition and designed an in-situ formed SiC-Fe2O3 heterojunction structure during the heating process of SiC-FeOOH composite to catalytically degrade SF_6. The results showed that at 700°C, the initial degradation rate of SF_6 reached 93.6%, with a lifetime of 470 minutes, which is 1.8 times and 1.2 times higher than at 600°C and 650°C, respectively. The degradation amount was 99.0 $mL \cdot g^{-1}$. Especially for high-concentration SF_6 (35 vol%), the degradation amount reached 615.0 $mL \cdot g^{-1}$. Through electron coupling within the heterojunction structure, electrons transferred from SiC to SF_6 through Fe_2O_3, thereby reducing the S-F bond energy. This non-uniform electron distribution heterojunction structure exhibits significant potential in the field of SF_6 degradation in the future4 (as shown in Figure 2).

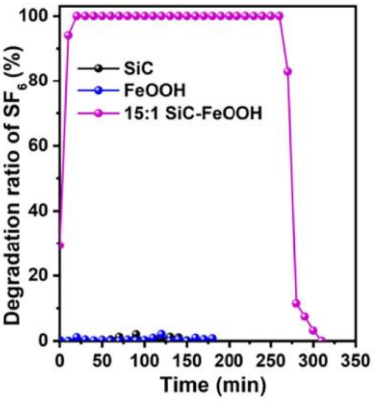

Figure 2 The degradation proportion of SF_6 in SiC, FeOOH, and SiC-FeOOH composite materials.

2.2.2Substituting gases with lower Global Warming Potential (GWP) for SF_6

Due to the Kyoto Protocol explicitly listing SF_6 as one of the six greenhouse gases to be restricted in emissions, seeking alternative gases with excellent insulation and ideal arc-extinguishing properties to replace SF_6 has naturally become one of the research directions in the global scientific community. Currently, there are two main categories of SF_6 substitute gases:

① SF_6 mixed gases

Including dry air and its constituent gases: oxygen, nitrogen, carbon dioxide, and methane. The advantages of these gases lie in their environmental friendliness, safety, and low liquefaction temperature (boiling point). However, their insulation performance is only about 0.3 times that of SF_6. As a result, they cannot be used alone but must be mixed with SF_6 or other substitute gases. The addition of other gases reduces the boiling point of SF_6, addressing the issue of gas liquefaction in cold regions. When SF_6 is mixed with SF_6 in a certain proportion, their insulation strength exhibits a strong synergistic effect. Among them, the mixture of SF_6 and nitrogen in a molar ratio of 7:13 shows the strongest synergistic effect5.Therefore, this mixture is often used in the fields of Gas-Insulated Lines (GIL) and Gas Circuit Breakers (GCB) in power equipment (These will be shown in Table 1).

Table 1 The composition and performance of SF_6 mixed gases

Research Institution	SF6 Mixture Composition	Performance or Application
University of Belgrade	$n(SF_6):n(N_2)=7:13$	The strongest synergistic effect occurs in non-uniform fields, and the synergistic effect in non-uniform fields is more significant than in uniform fields.
ALSTOM (France)	$n(SF_6):n(N_2)=1:4$	240kV GIL has been applied at Swiss airports.
SIEMENS (Germany)	$n(SF_6):n(N_2)=1:4$	A GIL with a voltage level of 550kV and a transmission capacity of 300MW has been developed.
Hyosung (Republic of Korea)	$n(SF_6):n(N_2)=1:3$	In the experiment of 170kV/50kA compressed air GCB, its breaking capacity is equivalent to pure SF_6.
The University of Tokyo	$n(SF_6):n(N_2)=1:3$	In the experiment of blowing air GCB, its breaking capacity is close to 80% of pure SF_6.
Manitoba Hydro(Canada)	$n(SF_6):n(N_2)=1:1$	A high-voltage GCB with a voltage level of 115kV and a breaking current of 40kA has been developed.

Furthermore, CF_4 (carbon tetrafluoride) is a compound that exhibits good arc extinguishing performance and a relatively low liquefaction temperature. By adding an appropriate amount of CF_4 to SF_6, the liquefaction temperature of the gas can be reduced, while slightly sacrificing insulation and arc extinguishing performance. This adjustment allows the gas mixture to meet the requirements of usage in cold regions. Various mature SF_6-CF_4 gas mixtures for circuit breakers have been developed, and they can stably operate under severe cold conditions of -40°C.

Saturated halogenated hydrocarbons primarily rely on the strong electronegativity of molecules to adsorb electrons during the discharge process, thereby enhancing the electrical insulation properties. In chemical processes, hydrogen atoms in compounds can be replaced by halogen atoms to increase the electronegativity of gas molecules. Fluorine and chlorine atoms are commonly used as halogen substitutes to ensure low boiling points of gases. Additionally, bromine and iodine atoms offer advantages at the microscopic level, with multiple electron cloud energy levels and larger collision interfaces, enhancing the ability to block discharges **错误!未找到引用源。**. The insulating properties of individual saturated halogenated hydrocarbons are shown in Table 2.

Table 2 Insulation Performance of Saturated Halogenated Hydrocarbons

Compounds	The relative insulation strength (chemical calculation value) compared to SF_6
CH_3F	0.220
CH_2F_2	0.300
CHF_3	0.270
CF_4	0.594
CF_3Cl	0.672
CF_3Cl_2	0.901
CF_3I	1.217
CHF_2CH_3	0.700
C_2F_6	0.775
C_3F_8	1.080

② Fluorinated compounds

Such as perfluoroketones($C_5F_{10}O$,PFK-5110; $C_6F_{12}O$,PFK-6112, the physical and chemical properties of these two perfluorinated ketones are demonstrated in Table 3), perfluoroisobutylene (C_4F_7N), octafluorocyclobutane (c- C_4F_8), trifluoroiodomethane (CF_3I), etc., are being explored as potential substitutes for SF_6. These gases have characteristics including higher insulation strength compared to SF_6 and lower Global Warming Potential (GWP). However, they also have higher boiling points, which necessitates mixing them with gases like N_2 and CO_2 as mentioned earlier. Additionally, fluorinated compounds with carbon can generate carbon deposits after discharge, potentially leading to reduced insulation performance.

Table 3 Comparison of Physicochemical Properties of Perfluoroketones

Compounds	PFK-5110	PFK-6112
Boiling Point/℃	26.9	49
Lifetime in the Atmosphere/Year	0.040	0.014
GWP_{100}	＜0.21	~0.29
The relative insulation strength (chemical calculation value) compared to SF_6	2.1	2.7
LC_{50}(4h,Rat)/(g/g)	0.02	＞0.1

Among these gases, worth mentioning is trifluoroiodomethane (CF_3I). It has an extremely short atmospheric lifetime (0.005 years) and great development potential. However, it is highly carcinogenic and produces elemental iodine during discharge, which reduces equipment lifespan and poses health and safety risks.

The ideal substitute for SF_6 gas needs to possess high insulation and arc extinguishing strength, low GWP, and a low boiling point. Further research and exploration are required for gases with such characteristics.

3.Conclusion and Suggestions for SF_6 Emission Reduction in Power Grid Enterprises

This paper compiles research findings from both domestic and international reports and provides the following recommendations for SF_6 gas emission reduction in power grid enterprises in China:

Firstly, tackling the source is of paramount importance. This involves two main aspects. On one hand, it is essential to minimize gas leakage from SF_6 electrical equipment during usage, production, operation, and maintenance. On the other hand, there is a need to enhance the degradation and purification recovery of emitted SF_6 gas. Preventing gas leakage can be addressed from three angles:

① For newly acquired SF_6 electrical equipment, a comprehensive documentation system should be established upon receipt. This system should rigorously monitor gas quality, conduct stringent inspections to verify compliance, and closely review essential information such as producer and production date. Simultaneously, strict management measures should be implemented for gas storage areas7.

② For the already operational SF_6 electrical equipment, comprehensive live monitoring is necessary. This encompasses gas composition analysis within the equipment, detection and assessment of gas leakage levels. Maintenance should be carried out for equipment that does not meet application requirements, and regular re-evaluations are essential.

③ For unusable SF_6 electrical equipment, prompt retrieval and proper disposal should be conducted. In terms of degradation and purification of gases, the current SF_6 decomposition methods mainly involve arc decomposition, corona spark and point discharge-induced decomposition, and high-temperature decomposition8. It is also possible to employ high temperature, photolysis, discharge, and catalytic methods to purify SF_6 waste gas into completely non-toxic and harmless gases, ultimately achieving the harmless degradation of SF_6 waste gas.

Next, the search for gases with lower GWP to replace SF_6 is crucial. Currently, there are three main categories of substitute gases that have been extensively studied:

①Conventional Gases: This includes compressed air, N_2 (nitrogen), CO_2 (carbon dioxide), etc. Research has indicated that compressed air and N_2 can be used as substitutes for SF_6 in medium-voltage switchgear insulation, with their application expanding to higher voltage levels.

②Perfluorocarbon (PFC) Gases: Various PFC gases have been considered as substitutes for SF_6 in high-voltage equipment. However, their drawback lies in their high liquefaction temperature, which leads to elevated costs. To address this, a solution is to create mixed buffering gases by combining these PFC gases with N_2 or CO_2.

③Trifluoromethyl Iodide (CF_3I) Gas: CF_3I gas is another category9, known for its high dielectric strength.

It has a global warming potential equivalent to CO_2 and decomposes rapidly in the atmosphere.

These alternative gases offer potential solutions for SF_6 replacement, each with its own advantages and challenges that need to be further explored.

Finally, due to varying costs associated with different mitigation strategies, electric grid enterprises should make reasonable choices based on their own budgets, regardless of the selected emission reduction approach. Governments should also implement robust policies and regulations to provide support. Given the urgent need to address global climate change, and considering SF_6's exceptionally high global warming potential and extended lifespan, the academic community, industries, and governments worldwide must unite their efforts. This collective action should stem from a perspective of long-term human interests and the common destiny of humanity, as we collectively confront the challenges posed by SF_6 's greenhouse gas effect10.

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