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Review

The decomposition products of sulfur hexafluoride (SF_6): Reviews of environmental and health risk analysis

Wen-Tien Tsai *

Graduate Institute of Bioresources, National Pingtung University of Science and Technology, Pingtung 912, Taiwan

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Abstract

Sulfur hexafluoride (SF_6) is being widely used in a variety of industrial processes, commercial products and scientific fields due to its unique characteristics such as relatively low toxicity, extreme inertness and high dielectrics. However, the chemically stable gas is one of the most potent greenhouse gases (GHGs) that cause significantly global warming, and has been, thus, blanketed into the Kyoto Protocol. From the environmental and health points of view, it is necessary to mitigate and control the emissions of the decomposition products from SF_6 destruction processes because most of them (e.g. S_2F_{10}, SF_4 and HF) are highly reactive, corrosive and toxic, and few of them are also potent GHGs. This article aimed to introduce the fully fluorinated gas in industrial/commercial uses, and its toxic decomposition products in their environmental and health hazards, occupational exposure limits and possible exposure sources. Because all SF_6 decomposition products will be converted into fluorides in the discharged effluents and vented gases, the exposure to fluoride, being potential for causing fluorosis or chronic fluorine intoxication, and possible changes in environmental quality were also addressed in this paper. On the other hand, this manuscript also introduced another SF_6 decomposition product, trifluoromethyl sulfur pentafluoride (SF_5CF_3), which is also a powerful greenhouse gas recently detected in the atmosphere, and reviewed its physicochemical properties and atmospheric implications.

Keywords: Sulfur hexafluoride; Decomposition product; Environmental hazard; Occupational exposure; Fluoride; Trifluoromethyl sulfur pentafluoride

Contents

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* Tel.: +886 8 7703202x7399; fax: +886 8 7740134.
E-mail address: wttsai@mail.npust.edu.tw.

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1. Introduction

Sulfur hexafluoride (SF_6), molecular weight 146.07, is a colorless, odorless, nonflammable and heavy gas with excellent electrical characteristics that make it applicable for some special uses in the electrical/electronic equipments, industrial processes, scientific fields and commercial products [1–3]. Due to its low toxicity, thermal stability and high breakdown strength, sulfur hexafluoride had various widespread uses as a gaseous dielectric in electrical/electronic system since mid-1970s, including circuit breaker, high-voltage coaxial line, mini-substation (gas-insulated substation) and transformer, as an etching gas in the semiconductor manufacturing processes, as a blanketing/degassing gas in the light metal (i.e., aluminum and magnesium) casting processes, and as a tracer in a variety of scientific studies such as air/groundwater flow patterns, underground pipe leak detection, and dispersions of air pollutant in the atmospheric environment. However, SF_6 is also a highly radioactively-active gas with high fugacity and very low solubility in water and, thus, is a potent greenhouse gases (GHGs). Following its release into the environment, the compound almost resides in the atmosphere for a very long time. Based on the data adopted by the World Meteorological Organization (WMO) [4], the atmospheric lifetime and 100-year time horizon-global warming potentials (GWP) for SF_6 are 3200 year and 22,450 (relative to CO_2), respectively. Therefore, SF_6 has been considered as one of six target GHGs under the Kyoto Protocol of the United Nations' Framework Convention on Climate Change (UNFCCC) in 1997.

Although SF_6 has been recognized as a physiological inert gas, its decomposition products while producing and/or abating by electrical discharge (e.g. arc, spark or corona) or other destruction methods have aroused concerns about their toxicities in recent years [5–11]. The toxic products containing fluorine and/or sulfur in the SF_6 decomposition may include S_2OF_{10}, CF_4, COF_2, F_2, HF, H_2S, NF_3, F_2O, SiF_4, SO_2, S_2F_{10}, SF_4, SO_2F_2, SOF_2, SOF_4 and $S_2O_2F_{10}$ [5,9,12–16]. Among these highly reactive and toxic species, S_2F_{10}, F_2O and SF_4 are of major concern based on the occupational exposure limits such as American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value-8-h time-weighted average (TLV-TWA) [17]. It can be expected that the exhausts containing SF_6 from the industrial processes shall be availably and widely treated by using various destruction technologies such as plasma discharge, radio frequency (RF) discharge or catalytic methods in order to approach a voluntary reduction goal of PFCs scheduled in the 2008–2012 timeframe according to the Kyoto treaty [9,10]. As a result, the process exhaust generated from the SF_6 decomposition processing must be further controlled using various capture methods such as wet scrubbing and dry adsorption because most of them are toxic and hazardous to human health and the environment. Furthermore, the discharges via the best available control technology system still pose a potential health hazard due to the exposure to the removed fluorides (as F^-) in water bodies and atmospheric air.

Recently, many researches have addressed the decomposition technologies of SF_6 and the formation mechanism/toxicity of its decomposed products, rather than the occupational health hazard and environmental risks of exposing to them and the fluorides produced from the exhaust control in the SF_6 destruction system [9–11]. However, the latter should be more important and significant because the long-term excessive exposure to fluoride is associated with the adverse effects on skeletal fluorosis and bone fractures [18–21]. Trifluoromethyl sulfur pentafluoride (SF_5CF_3), first detected in 1999 [22], is also a SF_6 decomposition product with its atmospheric lifetime and GWP-100-year time horizon on the order of 1000 years and 20,000, respectively, suggesting that it is a highly radioactive-forcing greenhouse gas. This paper aimed to present reviews on commercial/industrial uses for SF_6 and its human health hazards (e.g. chemical/physical information, health hazards, occupational exposure limits and potential risk of fluoride exposure) from the toxic products of SF_6 decomposition. Further, the physicochemical information on SF_5CF_3 and its atmospheric implications were also addressed in this manuscript.

2. Uses of SF_6

SF_6 is a colorless, odorless, tasteless and incombustible gas at normal conditions. Because of its highly chemical stability and excellent electrical characteristics, it has been widely used as acoustic and thermal insulating agents in a diversity of applications such as electron trapper (insulating gas), etching gas, blanketing gas, tracer, refrigerant and filling gas [1–3]. In Taiwan, the principal applications of SF_6 were to be used in the electricity/power sector and industrial processes (i.e., semiconductor manufacturing and light metal processing). In the past decade, annual import of SF_6 was on the fast increase when we compare the data (about 1200 metric tonnes) in 2006 with that (about 20 metric tonnes) in 1996, reflecting that much demand in electricity and the rapid growth in the semiconductor and electronic products manufacturing industry has increased in the large consumption quantities of SF_6 since mid-1990s in Taiwan.

2.1. Insulating gas

Due to its high dielectric strength and also low toxicity as compared to air/nitrogen and polychlorinated biphenyls (PCBs), respectively, SF_6 is being mostly used by the electronic/electrical industries as a gaseous dielectric medium or electron trapper (arc-quenching ability) for high-voltage circuit breaker, switchgear, substations, transformers, capacitors, transmission lines and other electronic/electrical equipments.

2.2. Etching gas

In the past decade, the most commonly used perfluorocarbons (PFCs) in semiconductor industry were CF_4, C_2F_6 and SF_6. In the case of SF_6, it is used in the Tungsten Etch to provide fluorine-radicals for the purpose of etching polycrystalline silicon layer. In Taiwan, the rapid growth in the integrated circuits (IC) manufacturing industry has resulted in the large uses of PFCs since mid-1990s. According to the survey data by Taiwan's Environmental Protection Administration [23], the total use quantity of SF_6 was approximately 200 metric tonnes in 2002.

2.3. Blanketing gas

Because aluminum and aluminium–magnesium alloy possess excellent properties such as light density, high extension, easy heat-dissipation and good electromagnetic shielding, their products have been rapidly used in a variety of electronic/electrical commodities in the past decade, including notebook, cellular phone and video. The blanketing gas mixture composed of air or CO_2 and trace of SF_6 (0.2–0.3 vol.%) is being used in blanketing or protecting molten aluminum and/or magnesium during the casting and degassing processes for purposes of reducing slag waste and improving metal surface [24–26].

2.4. Other applications

Because of its inertness under normal conditions, SF_6 has been also applied to a number of uses, which include (1) using as a tracer gas in the fields of ventilation efficiency in buildings and indoor enclosures, and environmental quality modeling in the atmospheric air, ocean and groundwater [27–29], (2) filling the enclosed space in double pane sound-insulating windows, tires and soles of sport shoes, (3) providing a long-term tamponade (plug) of a retinal hole in retinal detachment repair operations, and employing as a contract agent for ultrasound imaging [30] and (4) additional applications; for example, as a hydrogen source from the reaction with lithium, as a fire suppression agent, as a leak testing agent and as a package gas in the commercial products such as tennis balls.

3. Toxic products of SF_6 decomposition

The fact that any inorganic or organic chemical has the potential to impact the environment and human health has been recognized on a scientific basis. SF_6, also considered as an inert gas, has extremely attractive properties, particularly non-flammability, non-toxicity and high liquid and gaseous dielectrics as compared to commonly used chemicals such as polychlorinated biphenyls and nitrogen. It means that the atmosphere is the most likely fate for their accumulations of emissions under normal conditions. It should be noted, however, that its decomposition products, produced by electrical and thermal decomposition of SF_6 in the presences of other molecules (e.g. H_2O, N_2, silicon, O_2, He, Ar, H_2, air), are all toxic and even corrosive. The toxic products containing fluorine and/or sulfur in the SF_6 decomposition may include S_2OF_{10}, CF_4, COF_2, F_2, HF, H_2S, NF_3, F_2O, SiF_4, SO_2, S_2F_{10}, SF_4, SO_2F_2, SOF_2, SOF_4 and $S_2O_2F_{10}$ [7–16].

3.1. Chemical and physical information on SF_6 decomposition toxic products

From the viewpoints of molecular structures and physical properties, perfluorocarbons such as SF_6 are chemically related to the high stability and low reactivity. Hence, SF_6 is nonpolar and insoluble in water. Following release into the environment,

Table 1
Chemical and physical information on SF_6 decomposition products[a]

Compound	CAS no.	Molecular formula	Molecular weight	Melting point (°C)	Boiling point (°C)	Solubility
Bispentafluorosulfur oxide	42310-84-9	S_2OF_{10}	270.12	−118	31	Sparingly soluble[b]
Carbon tetrafluoride	75-73-0	CF_4	88.01	−128	−186.8	Insoluble
Carbonyl fluoride	353-50-4	COF_2	66.01	−114	−83	Hydrolyzed
Fluorine	7782-41-4	F_2	38.00	−218	−187	HF formed
Hydrogen fluoride	7664-39-3	HF	20.01	−83.1	19.54	Very soluble
Hydrogen sulfide	7783-06-4	H_2S	34.08	−85.5	−60.4	0.5 g/100 mL H_2O (20 °C)
Nitrogen trifluoride	7783-54-2	NF_3	71.01	−208.5	−129	Slightly soluble
Oxygen difluoride	7783-41-7	F_2O	54.00	−223.8	−144.8	6.8 g/100 mL H_2O (0 °C, reacts slowly)
Silicon tetrafluoride	7783-61-1	SiF_4	104.09	−77	−65	Hydrolyzed
Sulfur dioxide	7446-09-5	SO_2	64.06	−75.5	−10.0	8.5 g/100 mL H_2O[b] (25 °C)
Sulfur fluoramide fluorine	81625-84-5	$(SF_5)_2NF$	287.12	–[c]	–	Sparingly soluble[b]
Sulfur fluoride fluorosulfate	81439-35-2	$S_2O_3F_6$	226.12	–	–	Sparingly soluble[b]
Sulfur fluoride peroxide	12395-41-4	$S_2O_2F_{10}$	286.12	–	–	Sparingly soluble[b]
Sulfur pentafluoride	5714-22-7	S_2F_{10}	254.12	−53	26.7	Insoluble
Sulfur tetrafluoride	7783-60-0	SF_4	108.06	−121	−38	Decomposed
Sulfur tetrafluoride oxide	13709-54-1	SOF_4	124.06	–	–	–
Sulfuryl fluoride	2699-79-8	SO_2F_2	102.06	−137	−55	Soluble
Thionyl fluoride	7783-42-8	SOF_2	86.06	−130	−44	Decomposed
Trifluoromethyl sulfur pentafluoride	373-80-8	SF_5CF_3	196.06	−87	−20.3	Insoluble

[a] Most of the data in Table 1 are from the reference [31].

[b] The information was obtained from the databank of SciFinder Scholar (American Chemical Society).

[c] Not available.

the compound possibly reacts with oxidizing molecule (e.g. H_2O) at extreme conditions to a variety of degradation products. Table 1 listed chemical and physical information for SF_6 decomposition products, which were mainly compiled from the Lange's Handbook of Chemistry [31] and Sax's Dangerous Properties of Industrial Materials [32].

Because the SF_6 decomposition products SF_4 and S_2F_{10} have a relative toxicity comparable to other decomposition compounds based on their occupational exposure limits (Section 3.3, described later), additional information on them were further addressed as follows [2,7,33]:

1. Sulfur tetrafluoride (SF_4):

   It is a nonflammable and colorless gas that fumes in humid air and possesses an irritating odor that is similar to sulfur dioxide (SO_2). It is readily hydrolyzed by moisture, forming hydrofluoric acid (HF) and thionyl fluoride (SOF_2) [34],

   $$SF_4 + H_2O \rightarrow 2HF + SOF_2$$

   It can react with most inorganic oxides to produce thionyl fluoride (SOF_2). Other physical properties were given as follows:

   Critical temperature: 90.9 °C.
   Liquid density: 1.919 g/mL (at −73 °C).
   Vapor pressure: 26.4 MPa (at 25 °C).
   Surface tension: 257 mN/m (at −73 °C)

2. Sulfur pentafluoride (S_2F_{10}):

   It, also called disulfur decafluoride, is a highly toxic, colorless and volatile liquid. It is almost insoluble in water but soluble in a variety of organic solvents (e.g. acetone). It can be catalytically decomposed in the presence of water,

   $$S_2F_{10} + H_2O \rightarrow 2HF + SOF_2 + SF_6$$

   The compound is stable to acid, is hydrolyzed by water and alkalies, and at 200 °C in the presence of copper or mercury almost decomposes to SF_4 and SF_6. At 350 °C, it reacts with Cl_2 in Pyrex or Monel to form SF_5Cl. Other physical properties were given as follows:

   Critical temperature: 165 °C.
   Liquid density: 2.08 g/mL (at 25 °C).
   Vapor pressure: 90.0 kPa (at 25 °C).
   Dielectric constant: 2.042 (at 25 °C).
   Surface tension: 257 mN/m (at −73 °C).

3.2. Health hazards

Based on the previous description, the identified products in the SF_6 decomposition system were S_2OF_{10}, CF_4, COF_2, F_2, HF, H_2S, NF_3, F_2O, SiF_4, SO_2, S_2F_{10}, SF_4, SO_2F_2, SOF_2, SOF_4 and $S_2O_2F_{10}$. For example [35], the hydrolysis reaction of SF_6 with water may occur in the presence of an unvented indoor combustion source to produce HF and H_2SO_4. It is well known that airborne H_2SO_4 is a more potent irritant than SO_2 on both acute and chronic effects [36]. On the other hand, HF is a colorless, corrosive gas or liquid (it boils at 19.5 °C). It is well known for its ability to cause severe chemical burns upon dermal contact and even develop skeletal fluorosis in workers heavily exposed to high levels of fluorspar [18].

Table 2 summarized health hazards of SF_6 and its main decomposition products [17,37]. The health hazard similarity which these decomposition products exhibit in the chemical properties such as corrosivity (highly acidic) and reactivity is obvious in the physiological effects. With the exception of SF_6 and NF_3, the gases and the vapors of these decomposed chemicals are irritants of the respiratory system and skin and/or eye contact. Thus, the inhalation of relatively low concentration of these gases and vapors will cause an unpleasant, pungent sensation, which is followed by a feeling of suffocation, coughing and a sensation of constriction in the chest [38]. In the case of skin or eye contact with them will give significant burns and severe irritations that are felt immediately. Due to the

Table 2
Health hazards of SF_6 and its decomposition products

Compound	UN NIOSH[a]		TLV basis-critical effect(s)[b]
	Exposure routes	Target organs	
Sulfur hexafluoride	Inhalation	Respiratory system	Asphyxiation
Carbonyl fluoride	Inhalation, skin and/or eye contact	Eyes, skin, respiratory system, bone	Irritation; bone; fluorosis
Fluorine	Inhalation, skin and/or eye contact	Eyes, skin, respiratory system, liver, kidneys	Irritation
Hydrogen fluoride	Inhalation, skin absorption (liquid), ingestion (solution),skin and/or eye contact	Eyes, skin, respiratory system, bones	Irritation; bone; teeth; fluorosis
Hydrogen sulfide	Inhalation, skin and/or eye contact	Eyes, respiratory system, central nervous system	Sudden death; irritation; central nervous system
Nitrogen trifluoride	Inhalation	Blood, liver, kidneys	Anoxia; blood; liver; kidney
Oxygen difluoride	Inhalation, skin and/or eye contact	Eyes, skin, respiratory system	Irritation; kidney
Sulfur dioxide	Inhalation, skin and/or eye contact	Eyes, skin, respiratory system	Irritation
Sulfur pentafluoride	Inhalation, ingestion, skin and/or eye contact	Eyes, skin, respiratory system, central nervous system	Irritation
Sulfur tetrafluoride	Inhalation, skin and/or eye contact	Eyes, skin, respiratory system	Irritation
Sulfuryl fluoride	Inhalation, skin and/or eye contact (liquid)	Eyes, skin, respiratory system, central nervous system, kidneys	Irritation; central nervous system

[a] The data are from the reference [37].
[b] The data are from the reference [17].

Table 3
SF_6 decomposition products designated as toxic/hazardous substances for specific regulatory purposes[a]

Compound	TSCA[b]/inventory	CERCLA[b]/hazardous substance list	EPCRA[b]/toxics release inventory	CAAA[b]/hazardous air pollutant
Carbonyl fluoride	Reported	–	–	–
Fluorine	Reported	–	Reported	Listed
Hydrogen fluoride	Reported	Listed	Reported	Listed
Hydrogen sulfide	Reported	Listed	–	Listed
Nitrogen trifluoride	Reported	–	–	–
Sulfur dioxide	Reported	Listed	Reported (as H_2SO_4)	–
Sulfur tetrafluoride	Reported	Listed	–	–
Sulfuryl fluoride	Reported	–	Reported	–
Thionyl fluoride	Reported	–	–	–

[a] The data were compiled from the references [32,39].

[b] TSCA: Toxic Substances Control Act; CERCLA: Comprehensive Environmental Response, Compensation and Liability Act; EPCRA: Emergency Planning and Community Right-to-Know Act; CAAA: Clean Air Act Amendments.

harmful hazards to human health and environmental quality, some chemicals from SF_6 decomposition have been regulated by a series of recently enacted laws such as Toxic Substances Control Act (TSCA), Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), Emergency Planning and Community Right-to-Know Act (EPCRA) and Clean Air Act Amendments (CAAA) in the USA, as listed in Table 3 [32,39].

3.3. Occupational exposure limits

Due to its highly chemical stability, it is expected that SF_6 should have no significant health risk on human and has been recognized as physiologically inert. Thus, its occupational exposure limit (OEL), such as American Conference of Governmental Industrial Hygienists threshold limit value, Occupational Safety and Health Administration (OSHA)-permissible exposure limit (PEL) and Deutsche Forschungsgemeinschaft (German Research Foundation, DFG)-maximum allowable concentration (MAK) based on 8-h time-weighted average (TWA) has been set at 1000 ppm, listed in Table 4 [17,40–43]. It is significant that the OEL set at 1000 ppm is the same to the exposure guidance level of hydrofluorocarbons (HFCs) by American Industrial Hygiene Association (AIHA)-Workplace Environmental Exposure Level (WEEL), including HFC-32, HFC-125, HFC-134a, HFC-143a, HFC-152a, HFC-227ea and HFC-236fa [44]. It should be noted, however, that asphyxiation is the critical effect on which the TLV of SF_6 is based (see Table 2), implying that it may occur under the respiratory overexposure [17].

As described above, most of SF_6 decomposition products, produced by electrical dissociation under high temperature and/or pressure in an electrical discharge such as arc, spark, corona and radio frequency power, are harmful for human health. The compounds formed in the SF_6 decomposition may include S_2OF_{10}, CF_4, COF_2, F_2, HF, H_2S, NF_3, F_2O, SiF_4, SO_2, S_2F_{10},

Table 4
Occupational exposure limits of SF_6 and its decomposition products containing fluorine and/or sulfur

SF_6 and its decomposition products	TLV[a]	PEL[b]	MAK[c]	PCS[d]	IDLH[e]
Sulfur hexafluoride (SF_6)	1000 ppm	1000 ppm	1000 ppm	1000 ppm	–[f]
Bispentafluorosulfur oxide (S_2OF_{10}; as F)[g]	2.5 mg m^{-3}	2.5 mg m^{-3}	–	–	250 mg m^{-3}
Carbonyl fluoride (COF_2)	2 ppm	–	–	–	–
Fluorides (as F)	2.5 mg m^{-3}	2.5 mg m^{-3}	2.5 mg m^{-3}	2.5 mg m^{-3}	250 mg m^{-3}
Fluorine (F_2)	1 ppm	0.1 ppm	0.1 ppm	1 ppm	25 ppm
Hydrogen fluoride (HF)	3 ppm (Ceiling)	3 ppm	3 ppm	3 ppm	30 ppm
Hydrogen sulfide (H_2S)	5 ppm	10 ppm	10 ppm	10 ppm (Ceiling)	100 ppm
Nitrogen trifluoride (NF_3)	10 ppm	10 ppm	–	10 ppm	1000 ppm
Oxygen difluoride (F_2O)	0.05 ppm (Ceiling)	0.05 ppm (Ceiling)	–	0.05 ppm	0.5 ppm
Silicon tetrafluoride (SiF_4, as F)[g]	2.5 mg m^{-3}	2.5 mg m^{-3}	–	–	250 mg F m^{-3}
Sulfur dioxide (SO_2)	2 ppm	2 ppm	0.5 ppm	2 ppm	100 ppm
Sulfur pentafluoride (S_2F_{10})	0.01 ppm (Ceiling)	0.01 ppm (Ceiling)	0.025 ppm	0.01 ppm (Ceiling)	1 ppm
Sulfur tetrafluoride (SF_4)	0.1 ppm (Ceiling)	0.1 ppm (Ceiling)	–	0.1 ppm (Ceiling)	–
Sulfuryl fluoride (SO_2F_2)	5 ppm	5 ppm	8.7 ppm	5 ppm	200 ppm
Thionyl fluoride (SOF_2; as F)[g]	2.5 mg m^{-3}	2.5 mg m^{-3}	–	–	250 mg m^{-3}

[a] Threshold limit value, American Conference of Governmental Industrial Hygienists (ACGIH, USA) [17].

[b] Permissible exposure limit, Occupational Safety and Health Administration (OSHA, USA) [40].

[c] Maximum allowable concentration, Deutsche Forschungsgemeinschaft (DFG, Germany) [41].

[d] Permissible Concentration Standard, Council of Labor Affairs (COLA, Taiwan) [42].

[e] Immediately Dangerous to Life or Health, National Institute for Occupational Safety and Health (NIOSH, USA) [43].

[f] Not available.

[g] The limit (i.e., 2.5 mg m^{-3}) for S_2OF_{10}, SiF_4 and SOF_2 was adopted because fluorides will be emitted when they are completely combusted or heated.

SF_4, SO_2F_2, SOF_2, SOF_4 and $S_2O_2F_{10}$ [7–16]. Although the occupational exposure limit is not commonly used as a relative index of toxicity for chemicals, the information is the most common guideline useful for determining their safe levels in order to adopt adequate protection system and handling procedures. Table 4 is an updated summary on the OEL values of the SF_6 decomposition products. Obviously, sulfur pentafluoride or di-sulfur decafluoride (S_2F_{10}) formation is of the most concern because of its high toxicity. Accordingly, the current occupational concentration standard (TLV/PEL) for human exposure in air should not exceed 10 parts per billion (ppb) during any part of the working exposure (i.e., ceiling). In the study by Wang et al. [11], using the lethal concentration (LC_{50}, the concentration causing death in 50% of the exposed animals) values of SF_6 decomposition products, S_2F_{10} was modeled to have a toxicity equivalency factor (TEF) of 1.0 in evaluating total toxicity equivalent emissions of SF_6 decomposed in a RF plasma environment. The approach is analogous to that of reporting toxicity equivalency quantity (TEQ) of polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs) where the TEF of 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (2,3,7,8-TCDD) is set to be 1.0.

Since the equipment or facility using SF_6 is usually sealed or well ventilated, and even designed with the exhaust control system (residual SF_6 abatement) such as plasma-scrubber, the occupational exposure to its decomposition toxic products should be at a minimum. However, it should be noted that the repair or maintenance works of the related compartments could involve welding operations and possibly cause the occupational exposure to final decomposition toxic products including hydrogen fluoride (HF) and sulfur dioxide (SO_2) or sulfuric acid (H_2SO_4), which have been proposed by the following reaction scheme [5,33,35]:

$$SF_6 \quad [\text{spark}] \rightarrow SF_4 + 2F \quad [H_2O] \rightarrow SOF_2 + 2HF \quad [H_2O] \rightarrow SO_2 + 2HF \quad 2[H_2O] \rightarrow H_2SO_4 + 4HF$$

In order to display a relative health risk for personnel emergency exposure to SF_6 decomposition products, the available data on the “immediately Dangerous to Life or Health” (IDLH), it is a situation “that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment.” were also listed in Table 4 [43].

3.4. Health risk of fluoride exposure

On first insight (Table 1) and the description discussed above, most of the SF_6 decomposition products are gases and have very high solubility and/or reactivity in water and humid air at room temperature; therefore, they are likely to remain in water and atmospheric air as fluorides, which may exist in the forms of hydrogen fluoride, fluoride ion and hydrofluoric acid. It should be noted that fluorosis or chronic fluorine intoxication has been attributed to be correlated with fluoride deposition in skeletal tissues (i.e., teeth and bone) of both animals and humans on the bases of clinical and epidemic studies [19,20,38]. Generally, the most significant pathway to exposure to all sources of fluoride is via ingestion [20], including fluoridated public drinking water, soft drinks and fruit juices (beverages), infant formula, cow’s milk, foodstuffs, fluoride supplement tablets and incidental ingestions of soil (by children) and toothpaste containing fluoride. Although atmospheric air was considered as only a small fraction of total fluoride exposure sources, the fluoride concentration in the workplace environment could be elevated in the industrial areas such as semiconductor manufacturing and light metal processing, and even in indoor air owing to the indoor combustion sources, leading to increased exposure by the inhalation route.

Human exposure to fluoride may occur via inhalation from accidental leaks and/or spills from the industrial processes using SF_6 as processing gases. With respect to human risk hazards to potential exposure of fluoride and other harmful species simultaneously existed, the published information is very scarce in the literature. In the study by Guo et al. [35], it was found that SF_6 can react with water vapor under an open flame to generate the dissociation products being mainly H_2SO_4, SO_2 and HF, and, thus, may cause an overexposure to these toxic chemicals during the air quality studies. It should be also noted that the repair works could involve welding (sparks) operations and possibly cause the occupational exposure to highly toxic decomposition products, including sulfur tetrafluoride (SF_4), hydrogen fluoride (HF), thionyl fluoride (SOF_2) and sulfur dioxide (SO_2) [5]. On the other hand, the degradation by-products, including CO, HF, H_2CO (formaldehyde), COF_2, N_2O and SO_2, from the cover (blanketing) gas containing SF_6 and diluent air may be of concern from the standpoint of occupational exposure limits in the magnesium industry [26].

4. Highly radiative-forcing products of SF_6 decomposition

As described above, SF_6 is chemically stable gas with unique characteristics such as non-toxicity, non-flammability and dielectric constant, which make it to be applied in the electric and semiconductor industries. In 1999, Sturges et al. [22] first detected a highly radiative-forcing compound, SF_5CF_3, in the atmosphere. The potential sources of the potent greenhouse gas probably originate as a breakdown product of SF_6 in high-voltage equipment [22,45], as a by-product of fluorochemical manufacturing [46,47], and might be the recombination of SF_5 and CF_3 radicals on aerosol particles in the terrestrial environment [48]. Such systems likely provide a source of trifluoromethyl groups (CF_3^-) from hydrofluorocarbons (e.g. CF_4, CH_2F_2 and CHF_3), perfluorocarbons (e.g. CF_4 and C_2F_6), or fluoropolymers, which may be further attacked by SF_5 radicals formed in the environment of high-voltage discharges containing SF_6. The formation mechanism could be simply expressed as follows:

$$SF_5^* + CF_3^* \rightarrow [SF_5{}^{\bullet}CF_3]^{\neq} \rightarrow SF_5CF_3$$

Table 5
Some atmospheric status and global warming properties for SF_6 and d SF_5CF_3

Compound	Atmospheric concentration (ppt)	Growing rate (% $year^{-1}$)	Radiative efficiency ($W\ m^{-2}$ ppbv)	Atmospheric lifetime (year)	GWP (100-year time horizon)
SF_6[a]	4.2	8	0.52	3200	22,450
SF_5CF_3[b]	0.12	6	0.57	800	17,500

[a] The data were compiled from the references [3,4].

[b] The data were compiled from the references [4,22].

4.1. Chemical and physical information on SF_5CF_3

From the viewpoints of molecular structures, SF_5CF_3 is chemical similar to SF_6. Because of its very low mixing ratio in the atmosphere, its chemical stability and its non-flammability, it has very high potential for use as a refrigerant, tracer gas and electrical insulating gas. As compared to SF_6, it is relatively polar, suggesting that SF_5CF_3 will have a greater affinity for organic matter than SF_6.

According to the results by Silvey and Cady [46], SF_5CF_3 could be prepared by the electrochemical process from the reaction of sulfide (e.g. carbon disulfide and methyl mercaptan) with fluoride (e.g. cobalt trifluoride) at 200–250 °C. Table 1 also listed the data on the boiling point (−20.4 °C) and melting point of SF_5CF_3 (−86.9 °C). Additional information on this gaseous substance were further addressed as follows [46]: chemically stable because there is no hydrolysis observed in the reaction of the gas with 6N sodium hydroxide for 2.5 months at room temperature, only reactive with alkali metals at dull red heat, and readily decomposed by spark-over discharge into CF_4 and SF_4. Other physical properties were given as follows [46]:

> Vapor pressure (P, mm Hg) versus temperature (T, K): $P = 6.71988 - 757.795/T - 53771.9/T^2$.
> Heat of vaporization: 20.51 kJ/mol.

It is well known that the vapor–liquid behavior of pure component can be described in terms of critical properties such as critical temperature (T_c), critical pressure (P_c) and critical density (ρ_c) because they are used in many corresponding state correlations for thermodynamic properties of gases and liquids like boiling point (T_b), heat of vaporization (ΔH_{vap}) and vapor pressure (P, kPa) versus temperature (T, K) [49]. With respect to the critical properties and physicochemical properties of SF_5CF_3, the information was given below [50]: $T_c = 108.1\ ^{\circ}C$, $P_c = 3371$ kPa, $\rho_c = 690\ kg/m^3$, $T_b = -20.3\ ^{\circ}C$, $\Delta H_{vap} = 20.18$ kJ/mol and $\ln P = 158.745 - 22.1236 \ln T - 8021.2/T$ (note: $T < T_b$).

4.2. Environmental hazards of SF_5CF_3

From the data on the infrared absorption spectrum of SF_5CF_3 [51] at 296 K, there are five integrated absorption cross-sections observed in the spectral bands of 400–450, 520–640, 670–780, 840–960 and 1125–1325 cm^{-1}, implying that the greenhouse gas possesses the strongest radiative force (0.59 $W\ m^{-2}\ ppbv^{-1}$) on a basis of molecule. Table 5 listed some atmospheric status and global warming properties of SF_6 and SF_5CF_3 because the chemistry of the former resembles that of the later. Because of its long atmospheric lifetime of approximately 800 years, it is expected not to be degraded in the tropospheric environment by reactions with highly oxidative species (e.g. O_3) and free radicals such as hydroxyl radical [52].

It should be remarked that the atmospheric concentrations of SF_6 and SF_5CF_3 have increased over the past decades (i.e., 1970–1999) with a parallel trend each other [22], suggesting that the source of SF_5CF_3 could be related to the production and industrial uses of SF_6, for example, gas-insulated switchgear [53]. On the other hand, the atmospheric concentration of SF_5CF_3 increased to be about 0.12 pptv in 1999, and is growing at annual rate of 6% $year^{-1}$ or by about 0.008 pptv $year^{-1}$ [22]. Based on its atmospheric concentration, the accumulative amount of SF_5CF_3 in the atmosphere currently seemed to be so small that the contribution of this greenhouse gas to global warming is rather small; nevertheless its impacts on the global climate change would be more significant in the future because of its fast growth rate [54].

5. Conclusions

Though SF_6 reviewed in this paper have been exempted from a series of environmental regulations mainly due to its relatively low toxicity and virtually chemical stability, the perfluorocompound still possess some environmental hazards, especially in global warming, and adverse effect of exposure to its decomposition products, including S_2OF_{10}, CF_4, COF_2, F_2, HF, H_2S, NF_3, F_2O, SiF_4, SO_2, S_2F_{10}, SF_4, SO_2F_2, SOF_2, SOF_4 and $S_2O_2F_{10}$. For the protection of the environmental quality and of human health, the emission of inorganic vapors containing these toxic (irritating) and corrosive species in the workplace environment still needs to be controlled using various wet/dry capture methods to reduce the exposure risk. However, the discharges of fluorides from the controlled vents and effluents could be expected and hence the long-term monitoring and evaluating of its emissions is necessary because fluoride is moderately toxic to human by inhalation in contact with moist body tissues, causing fluorosis in skeletal tissues (i.e., teeth and bone). On the other hand, the most potent greenhouse gas, SF_5CF_3, probably originates from the decomposition reaction of SF_6 with HFCs and/or fluoropolymers in the presence of high-voltage equipments. Its critical properties and some physicochemical information were also addressed in the review paper, showing that the chemistry of this gas resembles that of increased SF_6.

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