Byproducts of Sulfur Hexafluoride (SF_6) Use in the Electric Power Industry

Prepared for

U.S. Environmental Protection Agency
Office of Air and Radiation
Global Programs Division
1200 Pennsylvania Avenue, NW
Washington, DC 20460

Prepared by

ICF Consulting
9300 Lee Highway
Fairfax, VA 22031

January 2002

Forward

This document provides summary information on sulfur hexafluoride (SF_6) byproducts. It was prepared for the U.S. Environmental Protection Agency (U.S. EPA), Global Programs Division by ICF Consulting, Inc., under Contract No. 68-W5-0068, Work Assignment No. 0005AA-83. This document was developed as a service to partners of the *SF_6 Emissions Reduction Partnership for Electric Power Systems*. The information presented in this document does not replace existing regulations or guidance regarding these compounds. Rather, this document was designed solely as an overview of the most significant byproducts identified to date. If you have suggestions and/or information that would improve this document, please send them to

Jerome Blackman / Program Manager
U.S. Environmental Protection Agency
MC 6205-J
1200 Pennsylvania Ave, NW
Washington, DC 20460

or send an electronic mail to Blackman.Jerome@epa.gov. For more information on the *SF_6 Emissions Reduction Partnership for Electric Power Systems*, see http://www.epa.gov/highgwp1/sf6/index.html.

Contents

1. Introduction and Background

Sulfur hexafluoride (SF_6) is a relatively nontoxic gas used in a number of applications for its inert qualities. The dielectric and other physical and chemical properties related to its lack of reactivity have led to the extensive use of SF_6 as an insulating medium in switching equipment (e.g., circuit breakers) by electric utilities. While SF_6 is inert during normal use, when electrical discharges occur within SF_6-filled equipment, toxic byproducts can be produced that pose a threat to health of workers who come into contact with them. This paper discusses these byproducts and how they are formed, and also summarizes relevant health and safety concerns, as well as handling, detection, and safety procedures and guidelines.

U.S. EPA produced this background paper as a service to its partners in the *SF_6 Emission Reduction Partnership for Electric Power Systems*. This is a voluntary program in which partner companies agree to reduce SF_6 emissions through technically and economically feasible actions. SF_6 is a potent and persistent greenhouse gas, with a global warming potential approximately 24,000 times greater than carbon dioxide over a 100-year time horizon and a residency in the atmosphere of more than 3,000 years. Although SF_6 is critical to the reliable distribution of electricity, program participants recognize the importance of careful management and responsible use.

2. Formation and Concentrations of SF_6 Byproducts

Formation of SF_6 Byproducts

SF_6 can decompose into byproducts when exposed to four types of electric discharges (CIGRE[1] 1997):

- partial corona discharges caused by insulation defects;
- spark discharges that occur at insulation defects or during switching operations;
- switching arcs that occur in load break switches and power circuit breakers; and
- failure arcs that occur due to insulation breakdown or switchgear interruption failure.

Each discharge can result in different mixtures and concentrations of byproducts.

Concentrations of SF_6 Byproducts

Numerous studies have characterized the byproducts of SF_6. Dervos and Vassiliou (2000) have summarized the most important ones (considering toxicity and risk) and the amounts of each formed under conditions similar to those found in gas insulated switchgear (GIS) equipment (see Table 1). These data were obtained by exposing SF_6 to repeated sparking under experimental conditions, and thus the decomposition products and concentrations formed under actual conditions can vary depending on the equipment used and the type of electrical discharge (CIGRE 1997).

[1] CIGRE (the International Council on Large Electric Systems) is a permanent non-governmental and non-profit-making international association based in France. This group has established a working group (Study Committee 23) that is focused on concerns related to substations, including SF_6 and its byproducts. The web site established by Study Committee 23 is located at http://www.cigre-b3.org/.

Table 1. Gaseous SF_6 Decomposition Byproducts and Typical Concentrations During Repeated Sparking

Chemical Formula	Chemical Name	Chemical Abstracts Service Registry Number	Experimental Concentration (percent by volume)[a]
HF	Hydrogen fluoride	7664-39-3	1.0
SOF_2 (SF_4)[b]	Thionyl sulfide (sulfur tetrafluoride)	7783-42-8 (7783-60-0)	0.5
SOF_4	Sulfur tetrafluoride oxide	13709-54-1	0.085
SiF_4	Silicon tetrafluoride	7783-61-1	0.085
S_2F_{10} (SF_5)[c]	Disulfur decafluoride	5714-22-7	0.025
SO_2F_2	Sulfuryl fluoride	2699-79-8	0.006
SO_2	Sulfur dioxide	7446-09-5	0.002

Table adapted from Dervos and Vassiliou (2000).

[a] Note that these concentrations represent the measured concentration for the experimental conditions studied. The conditions were designed to simulate a real sparking occurrence; however, actual air concentrations in the vicinity of GIS will vary from these data.

[b] SF_4 is readily hydrolyzed to SOF_2.

[c] S_2F_{10} is referred to by some authors as sulfur pentafluoride or SF_5.

Additional byproducts that may be formed through arcing or other electrical discharges include SF_2, SOF_{10}, $S_2O_2F_{10}$, and H_2S, as well as a number of metal fluorides (e.g., copper fluoride (CuF_2), aluminum fluoride (AlF_3)) and tungsten compounds (e.g., WF_6, WO_3) (CIGRE 1997; U.S. EPA 2001a).

3. Health and Safety Concerns

Information on SF_6 byproducts has improved substantially in recent years. In its 1991 report, CIGRE identified only three gaseous SF_6 byproducts that pose a significant health threat (taking into account reaction quantities and toxicity): SOF_2, SO_2, and HF (Mauthe and Pettersson 1991). More recent research has identified S_2F_{10} as the byproduct of greatest concern due to its relatively high toxicity (James et al. 1993; Dervos and Vassiliou 2000), and occupational safety organizations have examined occupational exposures for several additional gaseous SF_6 byproducts.

Human Health Effects

According to information listed in the Hazardous Substances Databank (HSDB), gaseous SF_6 byproducts such as SF_4, SiF_4, SO_2F_2, SO_2, and HF are extremely irritating to the eyes, nose, and throat (NLM 2001). Other human health effects of these gases include pulmonary edema, skin and eye burns, nasal congestion, and bronchitis due to their corrosive characteristics. Solid byproducts such as AlF_3 and CuF_2 dusts are also irritating to exposed skin and eyes, and the nose, throat, and lungs when inhaled (NLM 2001). If copper salts are inhaled in sufficient concentration so that it reaches the gastrointestinal tract (via cough and mucociliary mechanisms), they act as irritants producing salivation, nausea, vomiting, gastric pain, hemorrhagic gastritis, and diarrhea (NLM 2001).

Several incidents involving human exposure to possible SF_6 byproducts have been reported.

- In the U.S., six workers were exposed during repair work on electrical equipment (Kraut and Lilis 1990). The workers experienced symptoms including burning/watering eyes, nasal irritation/epistaxis, throat irritation, chest tightness/wheezing/shortness of breath, coughing (in one case producing blood), nausea/vomiting, fatigue, and headaches. Most symptoms occurred immediately following or up to one week after the exposure event. Some workers' symptoms did not resolve until a month later or (in one case) a year later. No long-term physical effects were observed. Chemical evaluation at the site qualitatively identified the presence of SF_4.

- In the U.K., two workers collapsed after entering an SF_6 storage tower (James et al. 1993). One of the workers suffered pulmonary edema for the three days following exposure. No long term effects were reported for either worker. Following the incident, both SF_6 and SO_2F_2 were detected at levels that exceeded occupational exposure limits.

- In the Netherlands in 1989, an accident was reported involving two people who were exposed to unidentified substances resulting from a switchgear equipment failure (Mauthe and Pettersson 1991). The equipment contained SF_6; upon failure, a small amount of powder was observed (likely solid metal fluorides). Both people recovered within two weeks.

- A case of serious injury was reported to CIGRE in which an electrician repairing a circuit breaker was exposed to SF_6 decomposition products released by the equipment (Mauthe and Pettersson 1991). The worker lost consciousness and then awakened with a burning sensation in his chest. The worker's lung capacity was reduced by 45 percent. (CIGRE reports that had oxygen been administered more quickly, the damage would have been greatly reduced.)

- Several instances of minor skin irritation from exposure to SF_6 decomposition products have been reported to CIGRE (Mauthe and Pettersson 1991).

These instances of human exposure provide useful anecdotal evidence of the possible human health effects due to exposure to SF_6 byproducts, although specific byproduct compounds were not identified in all cases.

Cell and Animal Toxicity Data

Cell culture toxicity tests have been performed on S_2F_{10} and other SF_6 byproducts (summarized in James et al. 1993). The tests results indicate that S_2F_{10} is more than 43 times more toxic to cell cultures than the other SF_6 byproducts tested (SOF_2, SF_4, SOF_4, SiF_4, SO_2F_2, SO_2, HF). Additionally, whole animal toxicity studies have further characterized the toxicity of S_2F_{10} and other SF_6 byproducts. A complete summary of these data is beyond the scope of this paper, but specific animal toxicity information for SF_4, SiF_4, SO_2F_2, SO_2, HF, AlF_3 can be found in HSDB (NLM 2001). Animal studies indicate that these byproducts are extremely irritating when inhaled. Animals exposed to these gases via inhalation exhibit lung damage (e.g., lung irritation, edema, and hemorrhages) (Dervos and Vassiliou 2000; HSDB 2001).

5. Handling, Detection, and Safety Procedures and Guidelines

Numerous guidelines have been published regarding the handling, detection, and safety of SF_6 gas and its byproducts. These guidelines basically specify that employees minimize exposure to SF_6 byproducts by wearing protective equipment when handling and disposing SF_6 byproducts and by meeting specific exposure concentration standards.

Handling Procedures and Guidelines

SF_6 recycling and handling guidelines are described in detail in CIGRE guide number 117 (CIGRE 1997). Procedures specific to individual manufacturers' equipment types are also reported to be available directly from manufacturers. SF_6 handling procedures as provided by utility partners can be found on U.S. EPA's *SF_6 Emissions Reduction Partnership for Electric Power Systems* web page http://www.epa.gov/highgwp1/sf6/ (U.S. EPA 2001a). These guidelines often include procedures for handling hazardous SF_6 byproducts. U.S. EPA has also prepared a catalog that lists guidelines and standards for the handling and management of SF_6 (U.S. EPA 2001b).

Detection Procedures and Guidelines

SF_6 byproducts are difficult to detect chemically under normal working conditions. The presence of various SF_6 electrical discharge decomposition products and impurities (as well as the presence of SF_6 itself) makes measurement of the different byproducts problematic. A recent report in *Transmission and Distribution World* summarized methods that may allow for on-site and field monitoring of SF_6 byproducts with portable instrumentation (Baumbach et al. 2000). The *NIOSH Pocket Guide to Chemical Hazards* (NIOSH 1997) presents measurement methods and signs and symptoms of exposure for S_2F_{10}, SF_4, SO_2, HF, and SO_2F_2, as well as SF_6.

SF_6 byproducts such as SOF_3 and SF_4 have a strong irritating "rotten egg" odor at low concentrations, and, at high concentrations, are irritating to the eyes, nose, throat, and lungs (U.S. EPA 2001; NLM 2001). Solid byproducts (i.e., metal fluoride byproducts) are white, gray, or tan powders that often can be observed when present and are irritating to exposed skin (Edison Technical Center 1997; U.S. EPA 2001a; NLM 2001). However, these gross physical indicators of the presence of byproducts should not be relied upon as safety mechanisms due to the possibility of severe injury, especially given that the most toxic byproduct, S_2F_{10}, is generally odorless in pure form at typical environmental temperature.

Safety Procedures and Guidelines

Safety precautions for hazardous SF_6 byproducts are often addressed in SF_6 handling procedures for gas-insulated electrical equipment. (See the electric utility partners' SF_6 handling procedures on U.S. EPA's web page http://www.epa.gov/highgwp1/sf6/ (U.S. EPA 2001a). Also see the U.S. EPA catalog – available from the same web page – of SF_6 guidelines and standards (U.S. EPA 2001b).) Many SF_6 handling procedures require the worker to wear protective clothing and an approved respirator when the presence of decomposition products are suspected (e.g., when the SF_6-filled breakers are exposed to a severe arc for an abnormal period of time due to improper operation of the breaker). Industrial hygiene practices can be found in the *NIOSH Pocket Guide to Chemical Hazards* (NIOSH 1997), including respirator selections, exposure limits, signs and symptoms of exposure, and procedures for emergency treatment for S_2F_{10}, SF_4, SO_2, HF, SO_2F_2, fluorides, as well as SF_6.

Table 2 compiles the available occupational safety standards for the gaseous byproducts identified in Table 1 of this paper. SF_6 is included for reference. Table 3 lists exposure limits for fluorides, aluminum, and copper compound dusts. The parameters presented in Tables 2 and 3 are defined below.

- Permissible exposure limit - ceiling (PEL-ceiling): Defined by the Occupational Safety and Health Administration (OSHA), the PEL-ceiling is a specified concentration of the chemical in air that must not be exceeded during any part of the working exposure for any amount of time.

- Recommended exposure limit - ceiling (REL-ceiling): The REL - ceiling is concentration of the chemical in air that should not be exceeded, as recommended by the National Institute for Occupational Safety and Health (NIOSH).

- Recommended exposure limit - time-weighted average (REL-TWA): The REL-TWA is the time-weighted average concentration for up to a 10-hour workday during a 40-hour workweek that should not be exceeded, as recommended by NIOSH.

- Permissible exposure limit - time-weighted average (PEL-TWA): Defined by OSHA, the PEL-TWA is the time-weighted average concentration that must not be exceeded during any 8-hour work shift of a 40-hour work-week.

- Short-term exposure limit (STEL): Defined by OSHA, the STEL is the concentration that must not be exceeded over a 15-minute period.

- Recommended short-term exposure limit (RSTEL): The RSTEL is a 15-minute time-weighted average concentration that should not be exceeded at any time during a workday, as recommended by NIOSH.

- Level immediately dangerous to life or health (IDLH): Developed by NIOSH, the IDLH is the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without irreversible health effects (designed to aid in the selection of a respirator only).

- Threshold limit value - ceiling (TLV-C): Established by the American Conference of Governmental Industrial Hygienists (ACGIH), the TLV-C is a specified concentration of the chemical in air that should not be exceeded during any part of the working exposure for any amount of time.

- Threshold limit value - time-weighted average (TLV-TWA): Established by ACGIH, the TLV-TWA is a the time-weighted average concentration that should not be exceeded based on a normal 8 hour work day/40 hour work week.

Occupational exposure limits were not located for some of the SF_6 byproducts (including SOF_4 and SiF_4). The occupational standards listed in Tables 2 and 3 were developed by occupational health organizations in the United States. CIGRE literature and information in HSDB indicate that international exposure values also exist for some SF_6 byproducts (Mauthe and Pettersson 1991; NLM 2001).

Table 2. Available Inhalation Exposure Limits for SF_6 and Gaseous Byproducts of SF_6

Substance	Parameter	Exposure limit value	Defining organization
S_2F_{10} (SF_5) (sulfur decafluoride or pentafluoride)	PEL-TWA	0.025 ppm	OSHA
	PEL-ceiling [a]	0.01 ppm	OSHA
	REL-ceiling	0.01 ppm	NIOSH
	IDLH	1 ppm	NIOSH
	TLV-C	0.01 ppm	ACGIH
SF_4 (sulfur tetrafluoride)	PEL-ceiling [b]	0.1 ppm	OSHA
	REL-ceiling [c]	0.1 ppm	NIOSH
	TLV-C	0.1 ppm	ACGIH
SO_2 (sulfur dioxide)	PEL-TWA [b]	2 ppm	OSHA
	STEL [b]	5 ppm	OSHA
	REL-TWA	2 ppm	NIOSH
	RSTEL	5 ppm	NIOSH
	IDLH	100 ppm	NIOSH
	TLV-TWA	2 ppm	ACGIH
HF (hydrogen fluoride)	PEL-TWA	3 ppm	OSHA
	STEL [b]	6 ppm	OSHA
	REL-ceiling	6 ppm	NIOSH
	REL-TWA	3 ppm	NIOSH
	IDLH	30 ppm	NIOSH
SO_2F_2 (sulfuryl fluoride)	PEL-TWA	5 ppm	OSHA
	STEL [b]	10 ppm	OSHA
	REL-TWA	5 ppm	NIOSH
	RSTEL	10 ppm	NIOSH
	IDLH	200 ppm	NIOSH
SF_6 (sulfur hexafluoride)	PEL-TWA	1,000 ppm	OSHA
	REL-TWA [c]	1,000 ppm	NIOSH
	TLV-TWA	1,000 ppm	ACGIH

All values listed in this table were cited in ACGIH (1989), James et al. (1993), NIOSH (1997), or OSHA (2000).
ppm = parts per million; ppb = parts per billion; ppm and ppb are given by volume in air.

[a] The PEL-TWA of 0.025 ppm was revised in 1989 to a PEL-ceiling value of 0.01 ppm; however, enforcement of the new limit of 0.01 ppm has been stayed by OSHA, until it publishes a notice in the Federal Register regarding an available sampling and analytical technique.

[b] PEL or STEL was vacated by the U.S. Circuit Court of Appeals on June 30, 1993; however, OSHA may enforce it under the "general duty clause" in Section 5(a)(1) of the Occupational Safety and Health Act. Some states enforce vacated PELs and STELs.

[c] NIOSH has not established an IDLH value for this substance.

Table 3. Available Inhalation Exposure Limits for Solid Byproducts of SF_6

Substance	Parameter	Exposure limit value	Defining organization
Fluorides (measured as fluorine (F))	PEL-TWA	2.5 mg/m^3	OSHA
	TLV- TWA	2.5 mg/m^3	ACGIH
Aluminum soluble salts (measured as aluminum (Al))	PEL-TWA[a]	2 mg/m^3	OSHA
	REL-TWA	2 mg/m^3	NIOSH
Copper dusts (e.g., CuF_2)	PEL-TWA	1 mg/m^3	OSHA
	REL-TWA	1 mg/m^3	NIOSH
	IDLH	100 mg/m^3	NIOSH
	TLV-TWA	1 mg/m^3	ACGIH

All values listed in this table were cited in NLM (2001) and NIOSH (1997)
[a] PEL was vacated by the U.S. Circuit Court of Appeals on June 30, 1993; however, OSHA may enforce it under the "general duty clause" in Section 5(a)(1) of the Occupational Safety and Health Act. Some states enforce vacated PELs.

The Department of Transportation (DOT) provides guidance for emergency response for transportation incidents involving hazardous materials in its *2000 Emergency Response Guidebook*. Health warnings, fire mitigation, evacuation procedures, protective clothing prescriptions, and first aid procedures are available for SO_2F_2 (DOT no. 2191) in Guide 123 and SF_4 (DOT no. 2418) and HF (DOT no. 1052) in Guide 125 (DOT 2000).

5. References

American Conference of Government Industrial Hygienists (ACGIH). 1989. *Threshold Limit Values and Biological Exposure Indices for 1989-1990.* Cincinnati, Ohio.

Baumbach, J.I., Pilzecker, P., Trindade, E., and J. Meinders. 2000. Diagnosing the health of SF_6 switchgear. *Transmission and Distribution World* Vol. 52 (1), Jan 1, 2000, 3 pp.

International Council on Large Electric Systems (CIGRE). 1997. *SF_6 Recycling Guide.* Publication number 117; Task Force 23.10.01. August 1997.

Department of Transportation (DOT). 2000. 2000 Emergency Response Guidebook. A Guidebook for First Responders During the Initial Phase of a Dangerous Materials Incident. Internet site at http://hazmat.dot.gov/gydebook.htm.

Dervos, C.T., and P. Vassiliou. 2000. Sulfur hexafluoride (SF_6): Global environmental effects and toxic byproduct formation. *J. Air and Waste Manage. Assoc.* 50:137-141.

Edison Technical Center. 1997. *Insulating Materials for Distribution Switchgear in Today's Environment.* Internet site located at http://169.207.59.145/Library/TheLine/pdf/97-04/04-97-etc-01.html. Site dated April 1997; accessed September 2000.

Greenberg, L.A., and D. Lester. 1950. The toxicity of sulfur pentafluoride. *Arch. Indust. Hygiene and Occupat. Med.* 2:350-353. [cited in James et al. 1993]

James, D.R., I. Sauers, G.D. Griffin, R.J Van Brunt, J.K. Olthoff, K.L. Stricklett, F.Y. Chu, J.R. Robins, and H.D. Morrison. 1993. Investigation of S_2F_{10} production and mitigation in compressed SF_6-insulated power systems. *IEEE Electrical Insulation Magazine* 9(3):29-51.

Kraut, A. and R. Lilis. 1990. Pulmonary effects of acute exposure to degradation products of sulphur hexafluoride during electrical cable repair work. *British Journal of Industrial Medicine* 47:829-832.

Mauthe,G., and K. Pettersson. 1991. Handling of SF_6 and its decomposition products in gas insulated switchgear (GIS). *Electra*, no. 136:69-89 (Part 1) and no 137:81-105 (Part 2). June 1991. (Publication of Working Group 23, International Council on Large Electric Systems (CIGRE)).

National Institute for Occupational Safety and Health (NIOSH). 1997. *NIOSH Pocket Guide to Chemical Hazards*. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, Washington, D.C. NIOSH Publication no. 97-140; NTIS no. PB-97-177604. Internet site located at http://www.cdc.gov/niosh/npg/pgdstart.html.

National Library of Medicine (NLM). 2001. *Hazardous Substances Databank (HSDB)*. Internet site located at http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.

Occupational Safety and Health Administration (OSHA). 2000. Chemical Sampling Information. January 19. http://www.osha-slc.gov/dts/chemicalsampling/toc/toc_chemsamp.html

Renshaw, B., and M. Gates. 1946. "Di-sulfur decafluoride," in *Chemical Warfare Agents and Related Chemical Problems Parts I-II*, Office of Scientific Research and Development, National Defense Research Committee, Washington, D.C. NTIS no. PB-158508, Chapter 4, pp. 24-29. [cited in James et al. 1993]

Sauers, I., G.D. Griffen, D.R. James, R.J. Van Brunt, J.K. Olthoff, K.L. Stricklett, H.D. Morrison, M. Frechette, et al. 1995. *Investigation of S_2F_{10} production and mitigation in compressed SF_6-insulated power systems*. Final report. Volume 1: Executive Summary. Prepared under Cooperative Research and Development Agreement No. ORNL 90-0002. October 1995. ORNL/M-4314.

Sauers, I. 1998. Plasma Chem. *Plasma Process*. 8: 247-262. [cited in Sauers et al. 1995]

U.S. Environmental Protection Agency (U.S. EPA). 2001a. *SF_6 Emissions Reduction Partnership for Electric Power Systems: SF_6 Handling Procedures*. Internet web site at http://www.epa.gov/highgwp1/sf6/partner_resources/index.html.

U.S. Environmental Protection Agency (U.S. EPA). 2001b. Catalog of Guidelines and Standards for the Handling and Management of Sulfur Hexafluoride (SF_6). Prepared for the U.S. EPA, Office of Air and Radiation, Global Programs Division. Prepared by ICF Consulting, Fairfax, VA, under Contract No. 68-W5-0068. July. http://www.epa.gov/highwp1/sf6/pdf/sf6utility7.pdf.

Van Brunt, R.J., and J.T. Herron. 1990. *IEEE Trans. Electr. Insul.* E1-25: 75-94. [cited in Sauers et al. 1995]