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Investigation of S_2F_{10} Production and Mitigation in Compressed SF_6 -Insulated Power Systems

Final Report
Volume 1: Executive Summary

October, 1995

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Cooperative Research and Development Agreement (CRADA) Number
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Bonneville Power Administration
Canadian Electrical Association
Electric Power Research Institute
Empire State Electric Energy Research Corporation
Hydro-Québec
Oak Ridge National Laboratory
managed by Lockheed Martin Energy Systems, Inc.
National Institute of Standards and Technology
Ontario Hydro Technologies
Tennessee Valley Authority
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ABBREVIATIONS AND ACRONYMS

A	amp
ACGIH	American Conference of Governmental Industrial Hygienists
ASTM	American Society for Testing and Materials
atm	atmosphere (unit of pressure)
BPA	Bonneville Power Administration
C	Coulomb
CAPIEL	European Switchgear Manufacturer's Association (English translation)
CEA	Canadian Electrical Association
CF ₄	carbon tetrafluoride
CIGRÉ	International Conference on Large High Voltage Electric Systems (English translation)
cm	centimeter
cm ⁻¹	inverse centimeters or wavenumbers (= reciprocal of wavelength in cm, e.g. 400 cm ⁻¹ = wavelength of 25 μm)
COPEL/LAC	Companhia Paranaense de Energia (Brazil)
CRADA	Cooperative Research and Development Agreement
cryo-GC	cryogenic enrichment gas chromatograph
DOE	U. S. Department of Energy
DTGS	deuterated triglycine sulfate
EPRI	Electric Power Research Institute
ESEERCO	Empire State Electric Energy Research Corporation
ft	feet
FTIR	Fourier Transform Infrared
g	gram
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectrometer
GIS	Gas-insulated Substation
HF	hydrogen fluoride
h	hour
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronic Engineers
IR	Infrared
J	Joule
KEMA	Institute for the Testing of Electrical Equipment (The Netherlands) (English translation)
kPa	kilopascal
kV	kilovolt
L	liter
m	meter
MCT	mercury cadmium telluride
min	minute
mL	milliliter
MMES	Martin Marietta Energy Systems, Inc. (Lockheed Martin Energy Systems as of August 1995)

mol	mole ($= 6.02 \times 10^{23}$) (refers to the number of molecules of a chemical compound such as S_2F_{10})
ms	millisecond
MS	Mass Spectrometer
MS13X	molecular sieve
NBS	National Bureau of Standards (now NIST)
NIST	National Institute of Standards and Technology
nL	nanoliter ($= 10^{-9}$ L)
OHT	Ontario Hydro Technologies
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration (U. S. Department of Labor)
PEL	Permissible Exposure Level
ppbv	parts per billion by volume ($= 1$ part in 10^9 by volume $= 1$ nL/L)
ppmv	parts per million by volume ($= 1$ part in 10^6 by volume $= 1$ μ L/L)
s	second
SF ₄	sulfur tetrafluoride
SF ₆	sulfur hexafluoride
SOF ₂	thionyl fluoride
SOF ₄	thionyl tetrafluoride
SO ₂	sulfur dioxide
SO ₂ F ₂	sulfuryl fluoride
S ₂ F ₁₀	disulfur decafluoride, or sulfur pentafluoride (name used by ACGIH and OSHA)
S ₂ OF ₁₀	bis-(pentafluorosulfur) oxide
S ₂ O ₂ F ₁₀	bis-(pentafluorosulfur) peroxide
SiF ₄	silicon tetrafluoride
TLV-C	Threshold Limit Value - Ceiling
Torr	unit of pressure (1 Torr = 0.133 kPa)
TVA	Tennessee Valley Authority
TWA	Time Weighted Average
u	(unified) atomic mass unit
~	approximately
μ A	microamp ($= 10^{-6}$ A)
μ L	microliter ($= 10^{-6}$ L)
μ m	micron ($= 10^{-6}$ m $= 10^{-4}$ cm)
μ mol	micromole ($= 10^{-6}$ mole)
°C	degrees Celsius
<	less than

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[†]Gil Addis was the EPRI Steering Committee representative from the beginning of the CRADA in 1990 until his death in April 1994. He will be remembered and greatly missed by us not only for his contributions as a researcher and program manager but also as a friend and colleague.

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ABSTRACT

Volume 1: Executive Summary

A Cooperative Research and Development Agreement (CRADA) was established in 1991 to study the production and mitigation of S_2F_{10} (disulfur decafluoride), one of a number of toxic by-products formed by electrical discharges in the insulating gas SF_6 . Since compressed SF_6 is extensively used as an insulation and current interruption medium in electric power equipment, ensuring the safe operation and maintenance of this equipment is an important issue for utilities, government agencies, and manufacturers. The particular concern for S_2F_{10} is due to 1) its highly toxic nature: the Threshold Limit Value - Ceiling (TLV-C) is 10 ppbv (1 ppbv = 1 part in 10^9 by volume = 1 nL/L), the level which can not be exceeded during any part of the working exposure; and 2) the lack of sensitive detection techniques down to the TLV-C.

Each of the three research laboratories developed a highly sensitive detection method for S_2F_{10} : 1) Oak Ridge National Laboratory (ORNL): gas chromatography/cryogenic enrichment (less than 10 ppbv sensitivity); 2) National Institute of Standards and Technology (NIST): gas chromatography/mass spectrometry/thermal conversion (less than 10 ppbv); 3) Ontario Hydro Technologies (OHT): Fourier transform infrared spectrometry (FTIR) (less than 100 ppbv). These techniques permitted analysis of laboratory experiments and field samples down to very low levels near or below the TLV-C. Toxicity studies using a cell-culture assay verified the high toxicity of S_2F_{10} relative to other typical by-products. A few incidences of human exposure to decomposed SF_6 gas were found to be documented in the literature, but the health effects observed could not be attributed to any one by-product. Studies showed that S_2F_{10} can be produced in the laboratory by corona, spark, and power arc discharges and that the production rates for each type of discharge decrease in that same respective order. In power arcs, SO_2F_2 (thionyl fluoride) is by far the dominant species. Moisture on surfaces, heat, and small cylinder size all promote decay of S_2F_{10} .

Reliable sampling was obtained by using large, dry, 1L stainless steel cylinders for taking samples, keeping them away from heat sources, and by analyzing them as quickly as possible after sampling. Commonly used adsorbing materials such as molecular sieve and activated charcoal were found to be effective in removing S_2F_{10} . Molecular sieve increased the S_2F_{10} decay time constant by about two orders of magnitude. In a limited field survey, S_2F_{10} was found above the TLV-C in only one case (60 ppbv), a bushing which did not have adsorbers present. Only trace amounts (<10 ppbv) of S_2F_{10} were found in other equipment (bushings, breakers, bus duct, and interrupters) which in general had adsorbers in the gas compartments. None of the field samples was found to be highly toxic, consistent with the very low levels of S_2F_{10} found.

A great deal of basic and applied information has been learned about the decomposition products of SF_6 , particularly S_2F_{10} , through this CRADA. Knowledge of production and decay rates allow levels of S_2F_{10} in equipment to be estimated for different types of discharges under certain conditions and thus an assessment of the potential hazard can be made. Such estimates have already been made by some

manufacturers. The field survey, although limited in scope, provided baseline data and demonstrated the feasibility of taking and analyzing field samples using the techniques developed under this CRADA. The survey further indicated that the levels of S_2F_{10} are typically very low or below detection limits in power equipment which has undergone routine operation or non-catastrophic faults, particularly when adsorbers are present, and thus S_2F_{10} was found not to be a problem in such cases. It was found that in power arcs the amount of S_2F_{10} produced is relatively insignificant compared to the amount of the SOF_2 produced. In such cases, the toxicity of the decomposed gas is likely to be determined primarily by SOF_2 and compounds related to its formation such as SF_4 and HF. The toxicity of the gas is significantly affected by S_2F_{10} only when the decomposition is caused by relatively low-level discharges, e.g., corona and spark. The knowledge gained from this CRADA should also be beneficial for the development of routine procedures for gas analysis, so that analysis of the decomposition products of SF_6 will become a standard method for addressing the issues of health and safety, equipment reliability and aging, and diagnostics for GIS (Gas-Insulated Substations).

1. INTRODUCTION

A Cooperative Research and Development Agreement (CRADA) was established in October 1991 to study the production and mitigation of S_2F_{10} (disulfur decafluoride), one of a number of toxic by-products formed by electrical discharges in the insulating gas SF_6 . The particular concern for S_2F_{10} is due to its highly toxic nature, the TLV-C being 10 ppbv (1 ppbv = 1 part in 10^9 by volume = 1 nL/L) and the need for development of sensitive detection techniques down to this level. Because SF_6 is extensively used throughout North America as an insulation and current-interruption medium in power circuit breakers, compressed gas transmission lines and various components in substations, ensuring the safe operation and maintenance of this equipment is an important issue for utilities, government agencies, and manufacturers.

In the presence of an electrical discharge such as an arc, spark, or corona, a portion of the SF_6 decomposes into lower fluorides of sulfur which can react to form a number of chemically active by-products. The handling of these gaseous and solid by-products is therefore a concern during the maintenance or repair of SF_6 -insulated equipment. Although much is known about SF_6 by-products and their formation in typical power system environments, laboratory research funded by the U.S. Department of Energy (DOE) at the Oak Ridge National Laboratory (ORNL) and the National Institute of Standards and Technology (NIST) indicated that, in addition to the already identified by-products, S_2F_{10} was formed under discharge conditions. Because of its highly toxic nature, the issue of whether or not it is present in actual power equipment warranted initiation of a comprehensive research project.

Objectives of the CRADA

The objective of this study was to provide utilities and other interested parties with adequate information for prudent and safe operation of gas-insulated systems. Specific tasks included:

- Development or improvement of detection techniques to permit sensitive detection of S_2F_{10} down to the TLV-C (10 ppbv).
- Investigation of the formation and destruction rates of S_2F_{10} in SF_6 under arc, spark, and corona conditions that simulate practical operating environments.
- Determination of the stability, toxicity, and thermal/chemical properties of S_2F_{10} .
- Review of existing gas-handling procedures, protective equipment, and field sampling techniques, and recommendation of changes if required.

- Dissemination of information for safe gas-insulated systems operation and transfer of relevant technology.

The results from this project will enable realistic estimates of S_2F_{10} production to be made for different electrical discharge conditions in practical systems and will suggest new quantitative chemical analysis procedures that could be employed to assess S_2F_{10} levels in decomposed SF_6 .

The main CRADA research has been conducted at ORNL, NIST, and Ontario Hydro Technologies (OHT). Hydro-Québec, although not a funded research lab under the CRADA, has contributed related information from internal research projects primarily in the area of gas handling and mitigation studies. Each of these organizations has considerable experience in the field of gaseous dielectrics and SF_6 by-product research.

This project undertook a comprehensive, broad study of S_2F_{10} covering development of highly sensitive detection techniques for S_2F_{10} ; basic properties such as production and decay rates; toxicity studies; and practical aspects directly relevant to utilities such as field sampling, field surveys, and mitigation techniques. Volume 1 (Executive Summary) and Volume 2 (Final Report - Extended) present all results of the project through Phase I which were reported on at the S_2F_{10} Workshop held June 9, 1994 in Pittsburgh. Volume 3 will report on Phase II results which will include additional mitigation studies at higher sensitivity and description of a bench model detection system for S_2F_{10} adaptable for use at other laboratories.

2. SF₆ DECOMPOSITION

H. D. Morrison and F. Y. Chu

Ontario Hydro Technologies

About 80% of the world-wide production of sulfur hexafluoride, SF₆, is used for electrical insulation in high-voltage equipment¹. Some of the properties that make SF₆ so useful as a gaseous dielectric are its high dielectric strength, its ability to quench arcs, and its thermal stability. Additionally, SF₆ is non-toxic, non-flammable and non-corrosive, all important safety considerations for widespread industrial use². However, when SF₆ is exposed to electrical discharges, either intentional or accidental, partial decomposition of SF₆ can occur. In the presence of an electric arc, spark, or corona, SF₆ decomposes into lower fluorides of sulfur such as SF₂, SF₄, etc., which in turn can react with electrodes, other equipment materials, and gas impurities to form many chemically active products. Thus, although SF₆ is chemically inert under "normal" conditions, the electrical discharge decomposition products of SF₆ are toxic and corrosive.

The implications of SF₆ decomposition can be grouped into three broad categories: health and safety, equipment reliability and aging, and gas-insulated substations (GIS) diagnostics. From the perspective of health and safety, SF₆ users must be concerned with handling SF₆ and SF₆-filled equipment that may contain decomposition by-products. The toxicity of the by-products dictates that we employ procedures for repair and maintenance that remove the by-products and minimize the release of SF₆. Doing so will help ensure worker safety and demonstrate to our customers and the public that we are responsible corporate citizens, sensitive to their concerns about public and environmental safety. Decomposition of SF₆ within equipment raises concerns about reliability and aging. The corrosive nature of the decomposition products can degrade internal components of GIS, which has important implications for GIS diagnostics. If we can detect various products of decomposition and correctly interpret what we detect, then we can assess the reliability of equipment and the need for maintenance.

Research into SF₆ decomposition by electrical discharges began in the 1970's with investigations sponsored by manufacturers and utilities. The pioneering work by Boudene laid the foundation for much of the research that followed³. In the 1980's many more groups became involved, including the Electric Power Research Institute (EPRI), Canadian Electrical Association (CEA), and DOE as sponsors, with studies conducted at ORNL, NBS (National Bureau of Standards, now NIST), and at the research laboratories of Ontario Hydro and Hydro-Québec, to name a few. Many utilities established safe handling procedures based on this research. Later, various standards groups began to look at SF₆ handling and treatment. Several working groups are now addressing the problems of SF₆ handling within the organizations of the European Switchgear Manufacturer's Association (CAPIEL), International Conference on Large High Voltage Electric Systems (CIGRÉ), International Electrotechnical Commission (IEC), and Institute of Electrical and Electronic Engineers (IEEE). The discovery of S₂F₁₀ as a possible product of SF₆ decomposition, the awareness of its extreme toxicity, and subsequent studies to find

sensitive methods to detect it, eventually led to the formation of the present S_2F_{10} CRADA. The results of the CRADA research on S_2F_{10} and other decomposition products may eventually be incorporated into guides, handbooks, and standards that will govern how we handle SF_6 and its decomposition products.

Many previous reviews of SF_6 decomposition have examined all the various solid and gaseous products formed in discharges. Here we will concentrate on the formation of gaseous products, initiated by electrical dissociation of SF_6 , and influenced by impurities of air and water in the SF_6 . In the American Society for Testing and Materials (ASTM) D2472-92 standard for commercial grade SF_6 , the maximum levels of impurities are equivalent to 2600 ppmv of air (1 ppmv = 1 part in 10^6 by volume = 1μ L/L), 8 ppmv of water, 830 ppmv of CF_4 (carbon tetrafluoride) and acidity equivalent to 2.2 ppmv of HF (hydrogen fluoride), leaving a minimum assay of 99.8 wt% SF_6 (mass fraction of SF_6 = 99.8%). The IEC 376 standard lists similar levels for these impurities and also has limits for hydrolyzable fluorides and mineral oil. Of course, as soon as SF_6 is transferred into GIS equipment, it may no longer meet these standards with respect to air and water. Air can remain from inadequate vacuum pumping, or can be introduced by leaks in transfer lines and in compartment seals. Water is always present. It is adsorbed by every surface in GIS equipment and can only be controlled, but never completely removed. Table 2.1 compares the new SF_6 specification in ASTM D2472-92 with typical concentrations found in operating GIS in North American utilities⁴.

Table 2.1. Comparison of impurities in SF_6

Impurities	ASTM D2472: Maximum levels (ppmv)	Typical Levels in Operation (ppmv)
air	2600	1000 - 10,000
water	8	100 - 500
CF_4	830	100 - 500
acidity (as HF)	2.2	7 - 70

The dissociation of SF_6 in an electrical discharge is represented in Figure 2.1. The diagonal line illustrates the stripping of F atoms to produce the lesser fluorides of SF_6 , all of which are highly reactive. The only stable species on this line are SF_6 and SF_4 . When the discharge current terminates, most of the fragments reform into SF_6 . This self-healing property of SF_6 is partly why SF_6 is so useful as a dielectric. Some of the fragments react with impurities in the gas, mostly oxygen and water, both in and around the discharge volume. Reaction paths above the diagonal in Figure 2.1 occur in the discharge where the reaction partners are atomic oxygen and hydroxyl ions and radicals such as $OH^\cdot$. Reaction paths below the diagonal occur outside the discharge volume where the reaction partners are oxygen and water molecules. Although only some of the possible reactions are represented, the stable end products shown in bold type include all the major species formed in SF_6 discharges. One reaction not shown is the

combination of two SF_5 molecules or ions to form S_2F_{10} , a minor species in concentration but important because of its toxicity.

The degree of dissociation of SF_6 down the diagonal line in Figure 2.1 depends on the discharge temperature. Thus the relative production of secondary compounds, such as SOF_2 and SO_2F_2 , is strongly affected by the temperature of the discharge. The production of S_2F_{10} is more probable in a cold discharge where SF_5 is more abundant, than in a hot discharge where SF_4 is more abundant. Furthermore, S_2F_{10} decomposes rapidly in the gas phase at temperatures above 200°C , so it may only be accumulated in cool zones. Thus, the relative production rates of the various end products depend on the discharge conditions and concentrations of impurities. During laboratory studies of the rate of production of S_2F_{10} , the CRADA researchers also established the production rates of most of the gaseous by-products. Additional properties of S_2F_{10} have been studied as part of the efforts to develop methods for detection and removal of S_2F_{10} from SF_6 . Although S_2F_{10} is insoluble in water, we now know that S_2F_{10} decomposes on heated metal surfaces in the presence of water. This process underlies the method of detection developed at NIST, but it also points up a problem in preserving samples of S_2F_{10} . Surface catalyzed decomposition of S_2F_{10} , especially in the presence of water, makes it difficult to retain standard samples for comparative analysis, and can affect the composition of samples taken in the laboratory or in the field. On the other hand, decomposition on surfaces, such as activated charcoal or other filter materials means that the current procedures used for removing decomposition by-products from SF_6 may also effectively eliminate S_2F_{10} . All these topics are discussed in more detail in subsequent sections.

The studies of S_2F_{10} have also demonstrated that there is still much to be learned from fundamental research on SF_6 decomposition in discharges, especially about the roles of temperature and water vapor. The application of these results to operating GIS is another active area for research. One eventual outcome of the CRADA project should be the development of routine procedures for gas analysis, so that analysis of the decomposition products of SF_6 will become a standard method for addressing the issues of health and safety, equipment reliability and aging, and development of chemical diagnostics for GIS.

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3. TOXICITY OF SF₆ BY-PRODUCTS

G. D. Griffin

Oak Ridge National Laboratory

Toxicity of S₂F₁₀

Electrical decomposition of SF₆ can produce a very wide variety of by-products, many of which may exhibit differing degrees of toxicity, dependent upon exposure concentration, time of exposure, and many other factors. Disulfur decafluoride (S₂F₁₀, also referred to as sulfur pentafluoride) is one of the by-products which may arise from SF₆ decomposition, and it has received much attention in regard to its possible role in adverse health effects arising from exposure to decomposed SF₆. The pure S₂F₁₀ gas is highly toxic, producing pulmonary edema, and was studied as a possible chemical warfare agent in World War II. Apparently because of its potential as a chemical warfare agent, S₂F₁₀ appears very early on Threshold Limit Value lists (e.g., 1954) of the American Conference of Governmental Industrial Hygienists (ACGIH). Threshold Limit Values (TLVs) are recommended limits (i.e., airborne concentrations in the case of the gaseous chemicals) which are intended for the control of potential health hazards in the work place. The current TLV-C for S₂F₁₀ (proposed in 1984) is 0.01 ppmv, ceiling limit, the ceiling limit being that concentration which should not be exceeded during any part of the working exposure¹. The Occupational Safety and Health Administration (OSHA) has set as a Permissible Exposure Level (PEL) a value of 0.025 ppmv for S₂F₁₀, where the PEL is an 8 hour time weighted average (TWA) for a 40 hour work week.² (Please note that the OSHA PEL was changed from a 0.010 ppmv TLV-C to an 8 hour TWA of 0.025 ppmv in 1994.)

Animal toxicology studies in the World War II era indicated that S₂F₁₀ was approximately as toxic as phosgene for a number of animal species. The studies of Greenberg and Lester³, published in 1950, and cited as one of the main sources used in establishing the TLV, involved rat inhalation studies of S₂F₁₀. Exposures of 1 hour to 1 ppmv of S₂F₁₀ produced severe lung congestion, while exposures to 0.1 ppmv for the same time period were without effect. When the exposure period was lengthened to 18 h however, 0.1 ppmv of S₂F₁₀ produced lung irritation, while 0.01 ppmv exposures for the same interval had no effect. If S₂F₁₀ is compared for acute animal inhalation toxicity against other compounds found in decomposed SF₆ (i.e., SOF₂, HF, SO₂F₂, SO₂, SiF₄), S₂F₁₀ appears to be much more toxic, although absolute comparisons are difficult due to both sparseness of data and lack of corresponding conditions of exposures (exposure times vary from 10 min to 4 h).

At Oak Ridge National Laboratory, we have developed a cell culture system which permits exposure of cells in culture to gaseous toxicants. Using this system, it has been possible to compare, on a relative basis, the toxicity of S₂F₁₀ to other by-products of SF₆ decomposition. Cell culture assays have demonstrated that S₂F₁₀ is approximately 2 orders of magnitude more toxic than SOF₂ for cells in culture where toxicity is assessed as reproductive viability of cells. This fact should not be taken in isolation,

however. The absolute concentrations of S_2F_{10} and SOF_2 found in decomposed SF_6 may differ by considerably more than 2 orders of magnitude, so that the relative contributions of S_2F_{10} and SOF_2 (for example) to overall toxicity must be based on the absolute concentrations of each component (as is indeed true for all toxic species), and this will undoubtedly vary from sample to sample.

In a few documented instances in which proper safety precautions were not taken, human exposures to decomposed SF_6 have resulted in observed health effects, such as chest tightness, irritation of eyes and nose, cough, nausea, vomiting, and, in the most severe exposures, pulmonary edema and loss of lung capacity.^{3,4} Whether any of these effects were due to the presence of S_2F_{10} is unclear because only very incomplete gas analysis, if any, was done in each exposure incident. Many of the other by-products of SF_6 decomposition would be expected to produce symptoms similar to those from exposure to S_2F_{10} .

Finally, it must again be emphasized that toxic effects of any toxicant are a function of time of exposure and concentration of toxicant. In a complex mixture of multiple potentially toxic compounds, additive and synergistic toxic effects might occur. It is difficult to say whether it is feasible, by monitoring the concentration of one of the by-products, to ensure that exposure to other decomposition products will be within the limits of safety and compliance given the limited analytical experience to date.

Field Sample Toxicity

During the field survey work, a limited number of samples from various pieces of field equipment were assayed for cytotoxicity (see Section 6. by H. D. Morrison for a discussion of the field survey techniques and results). None of the samples tested were found to be highly cytotoxic. These results are consistent with the fact that all of the field survey samples tested for toxicity had concentrations of S_2F_{10} below 1 ppmv and therefore would be expected to be relatively non-toxic in the cell culture assay, if S_2F_{10} were a significant contributor to the overall toxic effect. In very general terms, the cytotoxicity of the samples correlated with the total amount of decomposition which had occurred. Since one of the most abundant decomposition products is SOF_2 , samples containing higher concentrations of SOF_2 were found to exhibit greater cytotoxicity than those samples with lower overall levels of decomposition products. Due to the very limited nature of this survey it was not possible to show conclusively that there is a definite correspondence between SOF_2 concentration and overall toxicity.

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4. S_2F_{10} DETECTION METHODS

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Each of the three laboratories involved in the research, ORNL, NIST, and Ontario Hydro Technologies, developed a different detection method for S_2F_{10} . The methods are complementary, each having advantages and disadvantages. Due to the difficulty of detecting S_2F_{10} , it was highly beneficial to have separate techniques which allowed cross checking of results at the respective laboratories. Two of the methods proved to be highly sensitive: the Gas Chromatograph/Mass Spectrometer (GC/MS) at NIST and cryo-enrichment GC at ORNL could detect S_2F_{10} to below 10 ppbv which is the threshold limit value. Using the Fourier Transform Infrared (FTIR) method developed at Ontario Hydro Technologies, it was possible to achieve a limit of 100 ppbv. Detection for S_2F_{10} is particularly difficult due to the large background of SF_6 and the interferences from other by-products or impurities.

ORNL (Cryo-enrichment GC): In earlier work at ORNL on S_2F_{10} detection, standard GC and MS methods were used to identify many of the decomposition products of SF_6 including S_2F_{10} . However, to achieve the necessary sensitivity to detect this compound at or below its TLV-C of 10 ppbv, a more sophisticated method was sought. Direct detection of S_2F_{10} can be achieved using a cryogenic enrichment gas chromatograph (cryo-GC) similar to that employed in studies conducted in the Netherlands by the Institute for the Testing of Electrical Equipment (KEMA)¹. The advantage of the cryo-GC is that it allows good separation of the SF_6 and S_2F_{10} peaks and it concentrates the S_2F_{10} in the sample by removing most of the SF_6 . When coupled with an electron-capture detector, it can detect many electronegative samples with a sensitivity in the low ppbv range. Briefly, the four components of this type system are: (1) a liquid nitrogen based cryogenically controlled pre-trap for enrichment of the S_2F_{10} ; (2) a cryogenic injector for retrapping; (3) cryogenic GC with capillary column for separation of the components of the sample; and (4) electron-capture detector for S_2F_{10} and flame photometric detector for monitoring SF_6 . Retention times and detection efficiencies for the relevant by-products from SF_6 have been measured.

This system allows less than 10 ppbv detection of S_2F_{10} in SF_6 using only a 1 mL sample size. The production of S_2F_{10} (approximately 15 ppbv) from one individual 8.9 J spark in a 1.1 L chamber has been observed with this technique². One advantage of this method is that high detection sensitivity of S_2F_{10} is maintained even in highly decomposed SF_6 samples such as produced by an arc discharge.

NIST (GC/MS): The technique being used by NIST to detect S_2F_{10} is a new method utilizing a gas chromatograph/mass spectrometer (GC/MS) in which the S_2F_{10} is converted to SO_2 on a heated jet separator at low pressure before entering the MS³. A surface catalyzed reaction involving H_2O at temperatures above 150 °C is responsible for the conversion. Because of this conversion, peaks corresponding to S_2F_{10} appear on single-ion chromatograms at ion masses characteristic of SO_2 ($m/z = 48$ u (SO^+), 67 u (SOF^+), and 86 u (SOF_2^+)) where there is little or no interference from the SF_6 background. Peaks identifying S_2F_{10} come out of the GC at the time for S_2F_{10} but show up at the ion masses characteristic of SO_2 due to the conversion. Conventional mass-spectral analysis of S_2F_{10} as a

function of temperature clearly shows that S_2F_{10} completely decomposes at low pressure on metal surfaces heated to 270 °C with SOF_2 as the predominant stable product³.

This method has the advantage that very high sensitivity can be achieved with small samples and the analysis time is relatively short. One disadvantage is a loss of sensitivity when high concentrations of SOF_2 (greater than about 500 ppmv) are present in SF_6 . The limit of S_2F_{10} detection in SF_6 using the GC/MS method is estimated to be about 2 ppbv for prepared samples.

Ontario Hydro Technologies (FTIR): Infrared (IR) absorption is the technique which is being used by Ontario Hydro Technologies to detect S_2F_{10} . IR is a non-invasive method which has the potential for adaptation to field use and can be quite sensitive provided there is no interference from other species. In theory it has the advantage of directly identifying species from the IR signature. IR absorption bands for S_2F_{10} have been identified by a number of researchers but many of these bands overlap those for SF_6 and other by-products such as SOF_2 and SO_2F_2 . In the absence of large quantities of discharge products, the 545 cm^{-1} band at 101 kPa (1 atm) provides the most sensitive region for detecting S_2F_{10} . The same band at lower pressure is used for studies of decomposed SF_6 . The stronger band at 825 cm^{-1} provides a check on the measurements at 545 cm^{-1} .

The most sensitive IR measurements have been obtained using a high-resolution Fourier Transform IR (FTIR) system with a 20 m variable path length cell of 6.5 L volume and deuterated triglycine sulfate (DTGS) and liquid nitrogen cooled mercury cadmium telluride (MCT) detectors. Resolution of spectra can be varied between 0.1 cm^{-1} and 1.0 cm^{-1} at pressures from 13 Pa (0.1 torr) to 101 kPa (1 atm). Reference spectra have been taken for S_2F_{10} , SF_6 , and most of the other by-products which may interfere with the detection of S_2F_{10} . These include SF_4 , SOF_2 , SO_2F_2 , SO_2 , and CF_4 . Detection limits for S_2F_{10} with the long path length are 100 ppbv in clean SF_6 and 5 ppmv in highly decomposed SF_6 . Advantages include direct identification from the IR spectra, linear response, and transferable reference spectra. Large sample size (~ 1 L) and long scan times on the order of 30 minutes are two disadvantages.

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5. LABORATORY DISCHARGE STUDIES OF S_2F_{10}

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Production of S_2F_{10} in SF_6 discharges has been established under discharge conditions ranging from corona to power arc. The purpose of these measurements were three-fold: (1) to establish production of S_2F_{10} and evaluate those parameters which influence S_2F_{10} production; (2) to provide absolute rates of production for calculating worse case scenarios; and (3) with the additional analyses of other by-products, to aid in the interpretation of analyses of field samples. Four types of discharges were examined, including corona, spark (capacitively stored energy), spark (from a disconnect switch), and power arc. Corona discharge experiments were performed at NIST and ORNL with gas analyses performed at both sites. Capacitive spark experiments and analyses were performed at ORNL. Both the disconnect switch and power arc experiments were performed at OHT and the gas samples were analyzed at all three sites.

The reactivity and thermal instability of S_2F_{10} causes the net rate of production of S_2F_{10} in electrical discharges to be governed by a production term and a decay term. Factors that influence production include moisture, electrode condition, energy supplied to the discharge, discharge current (for corona discharges), SF_6 pressure, and the presence of oxygen. Decay of S_2F_{10} , occurring primarily on surfaces, is affected by such factors as surface condition, moisture, temperature, S_2F_{10} concentration, and rate of S_2F_{10} diffusion to the walls.

Corona: Corona discharges were produced in a negative point-to-grounded plane geometry in SF_6 , over a pressure range of (100 to 500) kPa. For discharge current in the range of (2 to 80) μA , the charge rate of production, r_q , of S_2F_{10} , measured in $\mu mol/C$, was not constant for total accumulated charge up to around 1 C. Above 40 μA discharge current, the slopes of the S_2F_{10} concentration versus charge curves became nearly parallel, indicating that $d[S_2F_{10}]/dt$ is approximately proportional to the discharge current for current greater than 40 μA . The initial nonlinear behavior of S_2F_{10} production is similar to that observed for SO_2F_2 . The charge rate of production was greatest initially, decreasing and becoming relatively constant after about 0.2 C total accumulated charge. The highest r_q was found to be 15.6 $\mu mol/C$ corresponding to 20 μA at 500 kPa. The initial rate of production generally increased with discharge current and pressure. The charge rate of production of S_2F_{10} was lower for a preconditioned "point" electrode than for a polished electrode. Initial changes in production rate are attributed to changes in discharge behavior or discharge-induced changes in electrode surface conditions. In addition to measured charge rates of production of S_2F_{10} , a plasma chemistry model was developed to account for the reactions responsible for S_2F_{10} production¹. The model of the corona discharge gives reasonable agreement with experimental data on current, water, and oxygen dependence. If decomposition of S_2F_{10} on surfaces is ignored, water is found to increase S_2F_{10} production. In addition to the formation of S_2F_{10} , two other related disulfur compounds, S_2OF_{10} and $S_2O_2F_{10}$, were found to be formed by corona discharges in SF_6 . The yield of the latter compound is significantly enhanced by the presence of O_2 .

Spark discharges: Spark discharges were generated by breakdown between a sphere-plane gap in SF_6 . Energy was supplied by a high-voltage 0.1 μF capacitor. The energy was discharged into a 1.1 L volume chamber. Spark energy was measured by capturing the voltage and current waveforms and integrating the product over the time of the discharge pulse. For conditioned electrodes, the amount of

S_2F_{10} produced is proportional to the number of sparks. The S_2F_{10} yield, measured in mol/J, was relatively constant with a value of $\sim 7 \times 10^{-11}$ mol/J over the energy range (5 to 45) J per spark. At lower energy, below 5 J per spark, the yield increased to 60×10^{-11} mol/J at 2 J per spark. The presence of water or oxygen in SF_6 resulted in a decrease in the spark yield. For example 1% O_2 (by volume) and 1 μ L H_2O (volume of liquid phase injected) in SF_6 reduced the S_2F_{10} yield to 0.778×10^{-11} mol/J and 1.03×10^{-11} mol/J, respectively. Water was found to have a greater effect on reduction of the S_2F_{10} yield for spark discharges in SF_6 than oxygen for equivalent concentrations. The largest yield for S_2F_{10} production in sparked SF_6 , observed under very dry conditions and conditioned electrodes, was 0.37×10^{-9} mol/J.

Disconnect switch: Production of S_2F_{10} in a disconnect switch was investigated using a single phase, 70 kV line-to-ground GIS rated for 115 kV. Sparks were generated in open-close operations (cycles) at a rate of three cycles per minute in a 216 L (7.63 ft³) vessel at an SF_6 pressure of 465 kPa. Experiments were run at 200 open-close cycles per day, which is about 100 times more frequent than under normal operation. Each cycle was composed of multiple sparks for which the energy was not determined.

Production of S_2F_{10} in the disconnect switch was confirmed by both FTIR at OHT and by cryo-GC at ORNL. S_2F_{10} was produced at a rate of $(59 \pm 16) \times 10^{-9}$ mol/cycle. This production rate can be compared to $(2850 \pm 270) \times 10^{-9}$ mol/cycle for the most abundant byproduct observed, SOF_2 , or about a factor of 48 less than for SOF_2 . Decay of by-products were also monitored and the determined decay rate of S_2F_{10} was 7.0×10^{-7} s⁻¹ compared to the SOF_2 rate of 5.2×10^{-8} s⁻¹. It should be noted that the rate of decay of by-products, particularly of S_2F_{10} is dependent on the particular containment vessel for which the surface-to-volume ratio and surface properties have been shown to have significant influence. For example, it was found that in samples taken from the disconnect switch in 150 mL cylinders, S_2F_{10} decayed about 10 times faster than in the switch itself.

Power Arc discharge: Power arc discharges were generated in a co-axial chamber formed by two aluminum pipes with plastic end plates, forming an internal chamber volume of 26.5 L. Four successful arc tests were performed at a nominal SF_6 pressure of about 200 kPa. Arcs were initiated by a trigger-wire fuse which was connected at one end of the pipe where a high-current source delivered about (7 to 10) kA over a time period of (50 to 150) ms. Energy dissipation for the four tests ranged from (0.97 to 2.53) kJ/L. Production of S_2F_{10} in power arcs was observed by all three analytical techniques (cryo-GC, GC/MS, and FTIR). Yields of S_2F_{10} fell in the range (7.5×10^{-12} to 2×10^{-10}) mol/J. Of the three analytical techniques, the cryo-GC method was capable of detecting S_2F_{10} with little or no loss in sensitivity in the presence of large amounts of other by-products, especially SOF_2 , which was generally about four orders of magnitude higher in concentration. As was found in the case of sampling from a disconnect switch, decay of S_2F_{10} in the sample bottle was observed to occur for samples taken from power arcs. Larger sample cylinders (~ 1 L) were preferable to smaller cylinders (150 mL). It was also observed that when high concentrations of SF_4 are present as in the case of power arc discharges, the sample cylinder becomes extremely dry, through hydrolysis of SF_4 , resulting in a retardation of the decay of S_2F_{10} . In one case, S_2F_{10} was found to be stable in the sample cylinder for a period of 50 days, decreasing by about 50% after 200 days.

To summarize, S_2F_{10} was detected under a wide range of discharge conditions including corona, spark, power arc and in a disconnect switch. The ratio of S_2F_{10} to SOF_2 was highest for corona discharge. Both corona and spark were found to be sufficiently reproducible under certain conditions to be potentially used for generating reference samples of S_2F_{10} . While the presence of water tends to increase S_2F_{10}

production in corona discharges, the opposite has been found for spark discharges. The presence of oxygen leads to decreased S_2F_{10} production in both spark and corona. The ratio of S_2F_{10} to SOF_2 is lowest for power arc discharges, among the types of discharges studied. This suggests that for power arc discharges the health risk due to S_2F_{10} is relatively unimportant compared to SOF_2 . Generation of by-products in a disconnect switch is similar to spark discharges produced in laboratory experiments. In the course of studying S_2F_{10} production it was found that another related byproduct, $S_2O_2F_{10}$, is produced in spark and corona discharges, and it appears that from preliminary tests it may also be significantly toxic.

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6. FIELD SAMPLING AND FIELD SURVEY

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Introduction

The main objective for the field survey in this project was to provide a spot check of some representative GIS compartments where S_2F_{10} might be present. Particular attention was paid to equipment in which electrical discharges were known or suspected to have occurred. The survey was not intended to be extensive or exhaustive. Since gas analysis of GIS equipment has become an accepted practice in recent years for diagnosing the condition of the equipment, some procedures and equipment for taking gas samples are generally available. Thus in sampling gas from equipment for S_2F_{10} , we also sought to establish additional guidelines for sampling priorities and procedures.

There are two issues to address when taking gas samples:

- 1) obtaining a sample that is representative of the gas in the compartment, and
- 2) preserving the integrity of that sample for analysis.

The first issue is common to all gas sampling. Procedures to address it include using short, gas-tight connecting lines, and purging or evacuating those connecting lines. The second issue is more complex. As most of the contaminants of interest in GIS equipment are relatively stable, such as air and SO_2 , samples taken to analyze for these contaminants do not require much special care. S_2F_{10} , however, is known to be relatively unstable, so some special care is required in handling samples intended for S_2F_{10} analysis.

Sampling Procedures

From various studies of samples in cylinders and in GIS equipment, we believe that the mechanism for S_2F_{10} decomposition is a surface-catalyzed reaction. In other words, collisions of S_2F_{10} on material surfaces enhance the probability for its decomposition by many orders of magnitude over decomposition in the gas phase. We know that two conditions further enhance the rate of decomposition of S_2F_{10} :

- 1) high temperature and
- 2) water adsorbed on surfaces.

We can exploit this knowledge both to improve our ability to preserve samples for analysis, and to encourage the destruction of S_2F_{10} that may be formed in SF_6 -insulated equipment.

To preserve samples for analysis, sample cylinders should be pre-treated and handled with care. Pre-treatment can be performed either in a laboratory or at the sampling site. Since the material of the cylinder is not as important as various other factors, we recommend the use of stainless steel cylinders

because they are readily available. Before sampling, the cylinder should be dried out as much as possible, preferably by heating while evacuating with a vacuum pump, and then allowing it to cool to ambient temperature. Another method of drying, suitable for laboratory pre-treatment only, is to condition the cylinder with SF_4 and then pump out.

The size and shape of the cylinder should be selected to minimize the interior surface-to-volume ratio, thereby reducing the collision rate of S_2F_{10} with the interior walls. Thus, cylinders of 1000 mL each volume are preferable to cylinders with a volume of 150 mL that are in common use. When taking a sample, the gas pressure in the sample cylinder should be as high as the pressure in the chamber being sampled, i.e. equal pressure, because higher pressures also reduce the rate of wall collisions. After sampling, the inlet of the cylinder valve should be sealed with a plug to prevent accidental contamination or release of the gas sample during shipment to the analysis site. Finally, during shipment the cylinder should not be exposed to temperatures higher than ambient, otherwise all the other precautions will be in vain.

At least one condition in SF_6 -insulated equipment is not generally conducive to preserving S_2F_{10} : the presence of water adsorbed on the interior surfaces. Despite all reasonable efforts to reduce the water in an SF_6 compartment, there will always be water in and on the surfaces of all the materials in a compartment. The other conditions, high pressure and low surface-to-volume ratio, are unavoidable but are not as important as the surface water. We have found that GIS compartments are just as effective at destroying S_2F_{10} as poorly prepared sample cylinders. On the other hand, samples taken in properly prepared cylinders from such compartments are preserved long enough for reliable analysis.

Field Survey Sites and Procedures

A variety of SF_6 -insulated equipment was selected for the field survey from among the utilities participating in the project. Initially, we considered only transmission class GIS equipment rated at more than 300 kV. As Ontario Hydro Technologies (OHT) was responsible for planning the field survey, most of these samples were taken from the company's Claireville station. Samples from gas-to-air bushings, bus duct, and a breaker, all rated for 550 kV, were taken generally after a fault condition had occurred. A second set of samples were obtained from three 345 kV breakers operating in a ring bus configuration at Rochester Gas & Electric where no faults had occurred and switching operations were infrequent. The third site for transmission class samples was Bonneville Power Administration (BPA) where three 500 kV breakers and three bushings open to bus duct were sampled. Again, no faults had occurred in the BPA equipment and switching operations were infrequent.

For all the transmission class samples, a set of stainless steel cylinders with a volume of 1000 mL each were prepared at OHT by heating and pumping. For the Rochester and Bonneville sites, the cylinders were also dried with SF_4 , then pumped and sealed for shipment by air transport. After sampling, the cylinders were shipped by air express courier to either NIST or ORNL. All samples were analyzed at OHT and at either, or both, NIST or ORNL. Analysis at ORNL also involved toxicity testing for some of the samples, which is discussed in detail in Section 3. ORNL also obtained and analyzed samples from the Roane Substation of the Tennessee Valley Authority (TVA).

A final sample set was obtained by Hydro-Québec from some of their distribution class equipment,

25 kV interrupters. These samples were taken in matched pairs with cylinders of 150 mL volume. One of each pair was retained at Hydro-Québec for analysis, and the others were sent to either NIST or ORNL.

Field Survey Results

In all the laboratory studies of the production of S_2F_{10} , we always found SOF_2 present with S_2F_{10} . If we cannot find SOF_2 in a sample, then we conclude that there has been no significant electrical discharge activity and that no S_2F_{10} will be found either. This conclusion was borne out by all the samples. The presence of SOF_2 , however, does not imply that S_2F_{10} is present, only that it could be present.

The highest level of S_2F_{10} found in any of the samples appeared in the first sample set, taken from gas-to-air bushings at Claireville. One of the bushings had failed by arcing internally, so samples were taken from all three phases. The failed bushing contained 4900 ppmv of SOF_2 but only a trace amount of S_2F_{10} (0.01 ppmv), which was essentially the detection limit for the analysis method at ORNL at the time. One of the other bushings had 160 ppmv of SOF_2 , an indicator for recent electrical discharge activity, probably sparking, and also contained 0.06 ppmv of S_2F_{10} . This concentration ratio of SOF_2 to S_2F_{10} , greater than 2500, implies that the SOF_2 may have posed more of a risk to the workers handling the gas than the S_2F_{10} .

None of the samples taken from Rochester Gas & Electric nor from Bonneville Power contained any SOF_2 or any significant amount of S_2F_{10} . Less than 0.015 ppmv of S_2F_{10} was found in two of the samples from Rochester. As one of the breakers had been recently refilled, the S_2F_{10} we found may have been present in trace amounts in gas fill and not produced by electrical discharge.

Two later samples from OHT were taken from compartments where arcing had occurred. One was from a failed bus duct, sampled seven days after the fault, and the other was from a breaker that had tripped three times in about ten minutes and was sampled 15 hours later. Both samples showed high levels of SOF_2 and SF_4 , 900 ppmv to 3500 ppmv. The bus duct contained no S_2F_{10} and the breaker had 0.007 ppmv of S_2F_{10} , with a detection limit of 0.003 ppmv. These samples are consistent with the earlier laboratory studies where we showed that the S_2F_{10} production rate in power arc discharges is orders of magnitude less than the combined SOF_2 and SF_4 production rate.

Finally, the interrupter samples from Hydro-Québec did not contain any S_2F_{10} , although some did contain about 20 ppmv of SOF_2 . In this case, if there had been S_2F_{10} , it may have decayed too rapidly in the 150 mL cylinders to have been detected in the analysis at NIST and ORNL.

Samples were also taken by ORNL from a 161 kV SF_6 breaker at TVA's Roane Transmission Substation and analyzed at ORNL for S_2F_{10} and other by-products. The breaker was operated 3 times on a ring bus which did not break a load and hence did not draw currents comparable to a fault condition. No substantial amounts of decomposition products were observed. These samples provide baseline data and indicate that there are no problems with decomposition products under such routine conditions.

Summary and Conclusions

The preparations for the field survey included developing a reliable procedure for taking samples that might contain S_2F_{10} . Thus, we recommend that samples be taken in stainless steel cylinders of 1000 mL volume. Before sampling, the cylinders must be dried internally, either by heating and pumping, or with the admission of SF_4 and then pumping. After sampling, the cylinders should be transported as quickly as possible to the analysis site, and not exposed to high temperatures. The fact that we were able to see S_2F_{10} above the detection limit in at least two cases does demonstrate that the procedure can work. Certainly, we did not find S_2F_{10} in any samples where these recommendations were not followed.

The samples in the field survey provide a baseline for typical operating SF_6 -insulated equipment. Only one sample contained a significant level of S_2F_{10} (0.06 ppmv). The concentration of SOF_2 in that sample was more than 2500 times higher, and thus was likely to pose more of a risk to workers handling the gas than did the S_2F_{10} . Trace levels of S_2F_{10} were found in a few other samples, perhaps more indicative of subjective interpretation at the detection limit for the methods of analysis than a real presence of S_2F_{10} . Finally, we note that no S_2F_{10} was found without significant levels of SOF_2 also present, but that the presence of SOF_2 does not guarantee the presence of S_2F_{10} .

7. MITIGATION STUDIES

M. F. Fréchette

Hydro-Québec

This section reports on preliminary results pertaining to the mitigation of SF_6 by-products, and in particular S_2F_{10} . Once it was established that S_2F_{10} could be formed, reside, or accumulate in gas-insulated equipment, efficient means of controlling or removing this compound had to be considered. The present context is shaped by the reality of use in the field, where adsorbent materials are commonly used in SF_6 -insulated equipment and gas filtering may be carried out during maintenance.

Adsorption and Current Materials

There is a whole range of solid materials exhibiting ultraporosity which are commonly used for the separation of gas and vapor mixtures. The interactions of by-products with an adsorbent are governed by multiple parameters. Some are linked with the properties of the compounds (e.g. size of molecule, magnitude of dipole moment), others come from the specificity of the material (e.g. pore size and shape, available internal volume). The adsorption process is complex, having to do with the interaction between a molecule and a surface, whether it is the external surface of a solid or the internal convoluted surface of a microporous zeolite crystal.

A rapid survey of adsorbent materials currently used at Hydro-Québec and Ontario Hydro Technologies has allowed the following information to be gathered. Numerous non-standardized materials are in use. For equipment, mainly GIS and breakers, the following materials were identified: aluminum oxide, activated alumina, various synthetic zeolites, and molecular sieve (MS13X)^{††}. Filtering carts utilize several materials in a stack. Typically, it may contain MS13X, activated charcoal, activated alumina, soda lime, soda cartridge, lime cartridge, and particle filters. Worker safety is an issue when maintenance or intervention following a major fault are performed. Respiratory masks are available for protection. Some masks contain adsorbent materials such as ASC carbon, activated charcoal or carbon, with the addition of dust filters.

Of the numerous materials, MS13X and activated charcoal were tested in relation to their interaction with S_2F_{10} . Preliminary results are reported below. These experiments were performed at Ontario Hydro Technologies.

Experimental Investigation

Small-scale experiments were set up, where the adsorption capacity of MS13X for SF_6 and mixtures of by-products, including S_2F_{10} , was measured. In the case of pure SF_6 , a glass vial containing a few grams of MS13X (from 2 g to 10 g) was attached to a vacuum rack. The capacity of adsorption was monitored as a function of the SF_6 pressure, up to a pressure of 133 kPa (1000 Torr). Two mixtures of by-

^{††} Specification of a material or product is made for completeness only and does not imply endorsement by this CRADA.

products were prepared. One consisted of a synthetic mixture of 1.1% S_2F_{10} in SF_6 (by volume). The other was obtained by running a negative corona discharge in SF_6 , thus resulting in the generation of various expected decomposition products. The two mixtures were injected into a cell connected to a Fourier transform infrared (FTIR) spectrometer and tested at a single pressure of 2.93 kPa (22 Torr). A reference spectrum of each mixture was taken showing the presence of S_2F_{10} . A known quantity of the gas mixtures were passed through MS13X and rechecked for S_2F_{10} concentration. A similar experiment dealt with activated carbon.

A series of experiments was carried on using a full-scale setup consisting of a 60 L, 115 kV bus duct. Decomposed SF_6 was obtained by running discharges in a separate spark chamber, resulting in a nominal concentration of 20 ppmv S_2F_{10} in 101 kPa (1 atm) of SF_6 . This gas mixture was used to perform the following three tests. The gas mixture was injected into the evacuated bus duct in the absence of both the cone spacer and sieve. Conditioning of the inner surfaces was achieved this way. The concentration of the by-products was monitored in time by taking gas samples and running analysis by FTIR. The second test consisted in placing one bag (310 g) of MS13X in the bus duct and following the decay of the S_2F_{10} . The third test was done in the presence of a cone while the molecular sieve had been removed. In all cases, the evolution of the S_2F_{10} concentration was monitored over long periods of time (up to a hundred days).

Results and Conclusions

Current adsorbing materials were found to be effective in removing S_2F_{10} . So far, molecular sieve MS13X and activated charcoal have been tested and showed effectiveness. MS13X exhibited a better performance.

MS13X, a porous crystal of sodium aluminosilicate, was found to adsorb SF_6 at an amount of about 1.3 mole(SF_6)/kg(MS13X) at atmospheric pressure. Even in the presence of SF_6 or other by-products, notwithstanding competitiveness and selectivity, S_2F_{10} could be reduced drastically by its interaction with the molecular sieve. While the S_2F_{10} concentration is affected by the presence of metallic surfaces and insulating bulk materials, it was observed that the use of the molecular sieve resulted in an increase of the S_2F_{10} decay time constant by about two orders of magnitude. The experimental decay time constants were found to be stable within 10% throughout.

8. SUMMARY AND CONCLUSIONS

Summary of Results

Conventional analytical methods can not be used to detect trace levels of S_2F_{10} in a background of SF_6 without significant modification. Hence each research laboratory developed a different but complementary type of highly sensitive detection technique. These instruments enabled formation and decay rates of S_2F_{10} to be determined and analyses of samples from field equipment to be made. Gaseous S_2F_{10} can be formed under a variety of conditions in several types of electrical discharges including corona, spark, power arc, and disconnect switches. The ratio of S_2F_{10} to SOF_2 production was highest for corona, but was approximately 5 orders of magnitude lower for arcs. S_2F_{10} was found to be unstable under certain conditions presumably as a result of surface reactions. Moisture on surfaces and heat particularly promote decay of S_2F_{10} .

Toxicity studies using a cell culture (cytotoxicity) assay confirmed that S_2F_{10} is indeed a highly toxic compound consistent with the very limited animal toxicity data available from the literature. Cytotoxicity studies showed that S_2F_{10} was at least 10 to 100 times more toxic than other common by-products. For the few documented human exposures to SF_6 by-products, it was not possible to attribute any health effects specifically to S_2F_{10} or any particular by-product due to uncertainties in the gas analysis performed at the time.

Since S_2F_{10} was found to decay in sample cylinders under certain conditions, special gas handling, sampling, and shipping procedures were developed in order to compare results at the different laboratories. Reliable sampling was obtained by using large, dry, 1 L stainless steel cylinders, keeping them away from heat sources, and analyzing them as quickly as possible after sampling. These sampling methods were used in obtaining results from a survey of in-service equipment. The limited field survey indicated that the levels of S_2F_{10} are typically very low or below detection limits in power equipment which has undergone routine operation or non-catastrophic faults. Hence S_2F_{10} should not be a problem in such cases, particularly when adsorbers are present. Major faults such as power arc discharges or burn through were not available for study. In power arc discharges for example, S_2F_{10} would pose an insignificant risk compared to that associated with SOF_2 which would be produced at levels orders of magnitude higher than S_2F_{10} .

Commonly used adsorbing materials such as molecular sieve and activated charcoal were found to be effective in removing S_2F_{10} . Molecular sieve increased the S_2F_{10} decay time constant by about two orders of magnitude. Hence the presence of adsorbers in some of the field equipment surveyed may have contributed to the very low levels of S_2F_{10} observed.

Conclusions

The objectives of this CRADA given in Section 1 have been accomplished through a collaborative research effort among national laboratories, utility research laboratories, and other government and private

sector utility organizations. The results of this CRADA provide utilities, government agencies, and manufacturers with useful information directly relevant to the safe operation and maintenance of gas-insulated equipment. SF_6 -insulated equipment has become an important part of the transmission and distribution system since its first use in the late 1960s and is now widely used in circuit breakers, GIS, and distribution-class interrupters. Hence issues relating to safe and efficient maintenance of this equipment are important for ensuring not only worker safety but also the availability and reliability of essential components of the transmission and distribution system. The results of the CRADA research on S_2F_{10} and other by-products should also benefit international organizations concerned with standards and practices such as CIGRÉ, CAPIEL, IEC, and IEEE who have working groups addressing gas handling issues. Basic information from the CRADA project is also being used by manufacturers and utilities to estimate possible levels of by-products formed in their equipment and assess the potential hazard. The CRADA has also enhanced the basic knowledge about the chemistry associated with electrical discharges in SF_6 . Much more is now understood about the chemical reactions and processes leading to by-product formation in SF_6 .

The focus of this project has been on one particular by-product of SF_6 , namely S_2F_{10} , which was of particular importance due to its high toxicity. A great deal of information on S_2F_{10} is now available as a result of this CRADA and a number of questions have been answered concerning its formation and existence in power equipment. The field survey, although limited in scope, provided baseline data and demonstrated the feasibility to take and analyze field samples using the techniques developed under this CRADA. The amounts of S_2F_{10} observed in this survey were very low, either below the TLV-C of 10 ppbv or below the detection limit of a few ppbv. Only in one case was S_2F_{10} detected above the TLV-C: a bushing without adsorbers contained 60 ppbv. The question then may be asked whether this quantity of S_2F_{10} is a cause for concern. If gas leakage or other release occurs, then the concentration of by-products within equipment is generally reduced in air by dilution into a much larger volume. A dilution factor argument has thus been proposed to try to assess the limits of by-products allowable in equipment. This argument is based on the fact that SF_6 has a TLV of 1000 ppmv in air. Hence if a release occurs and the SF_6 is kept below its TLV of 1000 ppmv in air, which is a dilution of its concentration by a factor of 1000, then any by-products in the SF_6 would also be reduced in concentration by a factor of 1000 in air. If this argument is valid, then the concentration of S_2F_{10} in air resulting from a release would remain below its TLV-C of 10 ppbv if the amount inside the equipment did not exceed 10 ppmv (i.e. 1000×10 ppbv), provided that the SF_6 released is kept below its limit of 1000 ppmv in air. The amounts of S_2F_{10} observed in the field survey fall well below this 10 ppmv dilution limit and should not be a concern. It should be pointed out that the validity of such a dilution argument was not addressed in this project.

It is also true that in all field samples examined where S_2F_{10} was detected, SOF_2 was also seen, usually at several orders of magnitude higher levels. Hence any mitigation efforts such as filtering or adsorbers would also have to address removal of SOF_2 . For power arcs, the CRADA data show that SOF_2 clearly dominates and that controlling its concentration to below its TLV of 1.6 ppmv should ensure that any S_2F_{10} present will be below its respective TLV-C. In cases other than power arc discharges, not enough information is presently known about production rates under different conditions to show that

monitoring one species, such as SOF_2 , would ensure compliance for other species.

Many results of the S_2F_{10} CRADA have been presented in numerous publications in the literature and at conferences (see Appendix for a bibliography). In addition all results including the field survey were presented at a workshop held on June 9, 1994 in Pittsburgh, PA following the 1994 IEEE International Symposium on Electrical Insulation. The workshop was attended by about 50 people representing utilities, manufacturers, testing laboratories, universities and government laboratories from a number of different countries. A proceedings was made available for this workshop. Volume 2 of the final report of this project will cover the material discussed at the workshop in detail.

There were no inventions or patent disclosures made under this CRADA. However the detection techniques and sampling methods developed provide the guidance which would enable private sector companies and utilities to incorporate these methods into their own gas analysis programs. Specific recommendations have been made for gas sampling techniques and handling practices which will yield reliable results for determination of S_2F_{10} using the detection methods described in this report. The practicality of these methods has been demonstrated in CRADA lab studies and in a field survey in which it was possible to observe trace quantities of S_2F_{10} and other by-products from samples shipped long distances. Since laboratory studies showed that adsorbers and filter materials can significantly reduce the S_2F_{10} concentration as well as that of other by-products, such materials should continue to be used in equipment whenever possible. Although S_2F_{10} was not found to be a problem for the equipment surveyed in this project, users of SF_6 equipment should continue (or initiate if not in place) the practice and increased awareness of safe gas handling methods and procedures as developed by utilities, manufacturers, and international organizations working on this issues. Results from Phase II of this project will report on a detailed prescription for setting up a bench model GC/MS detection system based on the NIST method. This system will be suitable for adaptation to commercially available detection systems which utilities or companies already have or can purchase. This information will be covered in Volume 3 of the final report to be issued in the future.

A number of unanswered questions remain regarding the effectiveness of adsorbers for removal of S_2F_{10} . The preliminary studies conducted so far in this project indicated that common filter materials can significantly reduce the concentration of S_2F_{10} . However, the sensitivity of detection was not high enough to determine if the S_2F_{10} could be removed down to the TLV-C of 10 ppbv. Additional studies on filter materials are planned at ORNL using more sensitive detection techniques and will be reported when complete.

In general more information is needed about the effectiveness of filter materials for all by-products of SF_6 under a wide range of conditions such as pressure, presence of other by-products, saturation effects, adsorption under flow conditions, disposal techniques, etc. Although the field survey conducted covered a typical range of conditions, it was necessarily limited in scope and hence could not check for formation of S_2F_{10} or other by-products under all possible conditions which might occur in practice. Ideally it would be desirable to have a filtering process which would remove any by-products formed to below hazardous levels. However the effectiveness of the filtering would still have to be checked to ensure it is working properly. Filtering issues will also become more important if there is an increased emphasis on recycling

SF₆ to reduce environmental impact of SF₆ as a greenhouse gas. The sensitive detection and sampling methods for by-products developed under this CRADA should also be useful in characterizing and verifying the quality of recycled gas which will have to meet certain criteria to be determined by manufacturers for their equipment. Working groups to study this issue are being formed in organizations such as IEEE.

Finally, the knowledge gained from this CRADA should also be beneficial to the industry for the development of routine procedures for gas analysis, so that analysis of the decomposition products of SF₆ will become a standard method for addressing the issues of health and safety, equipment reliability and aging, and GIS diagnostics.

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