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# Summary of Available Information on Sulfur Hexafluoride (SF6) Byproducts and Safety and Health Considerations for Handling SF6

Sulfur hexafluoride ($SF_6$) is inert and non-toxic. When dissociated in high voltage systems, relatively pure $SF_6$ generally reforms into $SF_6$. However, byproducts, some which are toxic, can develop under certain conditions (Chu 1986). While the types of $SF_6$ byproducts in high voltage systems are understood, the typical concentrations of these byproducts are not well known. The type of byproduct depends upon the conditions of the vessel containing $SF_6$. Specific conditions affecting byproduct formation include energy dissipated in the system, the pressure at which the system operates, the type of solid materials used as insulators or electrodes, and the presence of air and moisture (Sauers 1986). Common byproducts include the following (typically in gas form unless noted otherwise):

- $SOF_2$,
- $SOF_4$,
- $SO_2F_2$,
- $SiF_4$,
- $SO_2$,
- HF,
- $H_2S$
- $SF_4$,
- $S_2F_{10}$,
- $S_2OF_{10}$,
- $CO_2$, $CF_4$,
- $AlF_2$ (solid),
- $WF_6$ (solid), and
- $CuF_2$ (solid).

Silicon-containing materials such as lubricants, grease, or paint near the electrodes can result in the formation of $SiF_4$, and the electrodes can degrade forming metal fluorides (Sauers 1986). Organic insulators can react to also generate $CO_2$, $CF_4$, $S_2OF_{10}$, and $H_2S$ (Braun et al. 1989, Coll et al. 2000, Fu et al 2010, Wang et al. 2011). Many of these byproducts can be of concern from a safety perspective.

## Prevalence of Byproducts and Implications

In evaluating concentrations of byproducts in gas insulated switchgears (GIS), Fu et al. (2010) assessed 220kV and 500kV systems in the field. The byproduct concentrations were found to be lower in the higher voltage 500kV systems than the 220kV systems. Fu et al. (2010) also found that GIS that had operated for longer periods had higher concentrations of byproducts than those operating for shorter periods. The concentrations of the byproducts investigated were generally low.[1]

Oak Ridge National Laboratory (ORNL) investigated the prevalence and toxicity of $SF_6$ byproducts in the 1980s and 1990s. Griffin et al. (1989, 1990) assessed cytotoxicity, the degree to which a compound is destructive to cells, from various byproducts in sparked $SF_6$. The concentration of the most abundant byproduct, $SOF_2$, was 0.5%, which is below any significant cytotoxicity threshold based upon testing of individual gases. However, the concentration of $S_2F_{10}$ was above the lethal concentration (LC50).[2] Sauers et al. (1988) observed that moisture is an effective means of suppressing the formation of $S_2F_{10}$ for spark discharges.

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[1] $CO_2$, $CF_4$, $SOF_2$, $SO_2F_2$, and $S_2OF_{10}$ were all below 0.1% v/v. Concentrations of $SO_2$ were all below 3 µL/L, and concentrations of $H_2S$ were all below 1 µL/L (Fu et al. 2010, Wang et al. 2008).

[2] Griffin et al. (1990) observed $S_2F_{10}$ concentrations of 0.026% (260 ppm), which is above the 80-90 ppm LC50 threshold that is sufficient to result in 50% cell death after 4 hours of exposure.

While byproducts form in GIS and there is the potential for safety concerns in sparked $SF_6$ systems, it is unclear how applicable these experiments are to the conditions of the $SF_6$-containing equipment (e.g., electron microscopes, accelerators, wave guides) commonly used on DOE sites and what the concentrations of byproducts in those systems may be.

## Examples of Handling Practices of $SF_6$

As byproducts may create safety issues in sufficient concentration, their presence may impact $SF_6$ handling procedures. This is the case at a number of electric utilities. ATCO Electric considers any concentration of $SF_6$ byproducts inside a substation building or in a substation yard to be a hazardous atmosphere (ATCO Electric Operations 2003). If byproduct powder is visible from the outside of the $SF_6$-filled equipment, FirstEnergy handling procedures require the use of appropriate personal protective equipment (PPE) such as a HEPA certified respirator with acid vapor cartridges (FirstEnergy 2004). Both National Grid and Northeast Utilities System assume that all in-service $SF_6$ equipment contains decomposition byproducts unless tested. This assumption requires the use of respiratory protective equipment (National Grid 2005, Northeast Utilities System n.d.). Salem Electric recommends having on-hand a dedicated $SF_6$ vacuum, Tyvek® coveralls with a hood, washable boots, nitrile or latex gloves, fitted NIOSH approved organic vapor respirators, and proper gas handling equipment. Salem Electric further instructs its employees to be alert for a rotten egg smell, visible powder around the $SF_6$-containing equipment, gas indicators out of their proper positions, and excessive corrosion (Salem Electric 2008).

It is likely that handling procedures vary according to the type of equipment being accessed for maintenance or $SF_6$ capture for reuse or recycling. Efforts to reach out to DOE sites via the Fugitive Emissions Working Group (FEWG) resulted in additional handling information. Bonneville Power Administration (BPA) presently tests equipment for byproducts using Draeger $SO_2$ tubes if the equipment will be opened and accessed by workers. PPE is required during testing as the byproduct concentration is unknown. Based upon the results of the test, BPA then requires PPE according to the presence of solid and gaseous byproducts. During evacuation of the gas, BPA uses filters to remove the byproducts to aid eventual reprocessing of the gas by a vendor.

Argonne National Laboratory (ANL) provided the $SF_6$ recovery procedure used by SET Environmental, a contractor that has removed $SF_6$ from GISs onsite. As the work is done outside and there is no intended release of $SF_6$, there is no need for respiratory protection, although the presence of any $SF_6$ byproducts in a particular GIS is not known. For the large accelerators, ANL relies on alumina purifiers in the $SF_6$ gas handling system to remove contaminants from the $SF_6$. Additional safety measures include the use of large pressure vessel openings and ventilation blowers before and during entry to the accelerator gas handling system to mitigate potential hazards. ANL conducted an analysis in 1996, as required under former DOE Order (O) 5480.25, which was replaced by DOE O 420.2C, *Safety of Accelerator Facilities,* and concluded that breakdown products of $SF_6$ are not a significant potential hazard.

Solvay, a global supplier of $SF_6$, also suggests treating gaseous decomposition products with activated alumina (Iacoe and Pittroff 2000). This is part of the normal treatment of used $SF_6$ as part of a $SF_6$ reuse program. Additional methods of treatment as identified by Solvay include a molecular sieve for moisture removal and a solid filter to remove solid decomposition products. In order for reuse to be successful, Solvay sets requirements for the gas limiting the amount of degradation products, inert gases, $CF_4$, HF, water, and other impurities. These requirements should be considered when evaluating the potential for reclamation and reuse. For example, at Lawrence Livermore National Laboratory (LLNL), $SF_6$ is often used in combination with $C_4F_8$, and the resultant waste gases are too degraded and contaminated to be recycled or reused.

## Summary of Safety Considerations

Upon review of the available information on $SF_6$ byproducts, there is insufficient data to conclude whether byproducts exist in sufficient concentration to pose a safety risk when capturing or reclaiming $SF_6$ from equipment. When in confined areas and conducting maintenance on $SF_6$ switchgears, it appears that common practice includes the use of HEPA certified respirators with acid vapor cartridges. For large-scale accelerator systems, the handling systems can include alumina purifiers and other treatment methods to remove byproducts from the gas prior to collection. For outdoor areas or spaces with sufficient ventilation, such practices may not be necessary.

## Additional Health and Safety Information

As part of DOE's Worker Safety and Health Program (10 CFR 851), sites should be aware of exposure limits for $SF_6$ byproducts. Sites should default to the threshold limit values (TLVs) set by the American Conference of Governmental Industrial Hygienists (ACGIH) when the TLVs are more protective than the permissible exposure limits (PELs) under 29 CFR 1910. Table 1 lists the TLVs for several $SF_6$ byproducts.

**Table 1. TLVs for selected sulfur hexafluoride byproducts**

| Chemical | TLV-TWA | TLV-STEL | TLV-C |
|---|---|---|---|
| $SF_6$ | 1,000 ppm (5,970 mg/m$^3$) | -- | -- |
| $SO_2F_2$ | 5 ppm (21 mg/m$^3$) | 10 ppm (42 mg/m$^3$) | -- |
| $SF_4$ | -- | -- | 0.1 ppm (0.44 mg/m$^3$) |
| $S_2F_{10}$ | -- | -- | 0.01 ppm (0.10 mg/m$^3$) |
| $SO_2$ | -- | 0.25 ppm (0.65 mg/m$^3$) | -- |
| HF | 0.5 ppm | | 2 ppm |
| $H_2S$ | 1 ppm (1.4 mg/m$^3$) | 5 ppm (7 mg/m$^3$) | |
| $CO_2$ | 5,000 ppm (9,000 mg/m$^3$) | 30,000 ppm (54,000 mg/m$^3$) | |

Note: TWA is the time-weighted average or the average exposure on the basis of an 8 hour day, 40 hours per week work schedule; STEL is the short-term exposure limit or the exposure limit for a duration of 15 minutes, that cannot be repeated more than 4 times per day; C is ceiling limit or absolute exposure limit that should not be exceeded at any time.

In addition to the above references, further information on exposure limits is available through the American Conference of Governmental Industrial Hygienists (ACGIH) at http://www.acgih.org/.

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