# A Novel Purification Process for Used $SF_6$ From Electrical Installations

**International Conference on $SF_6$ and the Environment: December 1-3, 2004 Scottsdale, AZ**

**D.C. Lauzon**
Solvay Fluorides, LLC
3333 Richmond Ave.
Houston, TX 77098
Tel 713 525 6544
Fax 713 525 7805
mailto:daniel.lauzon@solvay.com

**Peter Jannick:** Solvay Fluor GmbH

**ABSTRACT**
In test field studies under highly stressed conditions, one possible toxic $SF_6$ decomposition product formed is disulfur decafluoride or $S_2F_{10}$. This paper presents a test facility for the investigation of the destruction of $S_2F_{10}$ via pyrolysis and the more promising technique of photolysis, specifically photolytic UV destruction. Accordingly, a purification pre-treatment pilot plant was also developed comprising of a photolytic UV reactor for the destruction of $S_2F_{10}$, gas scrubbers for the removal of hydrolysable $SF_6$ decomposition products and membranes for the removal of inert gas.

**INTRODUCTION**
Sulfur hexafluoride ($SF_6$) is a physically stable, non-toxic and inert gas with high dielectric strength and thermal stability. It is generally used in electrical equipment for power transmission and distribution such as gas insulated circuit breakers, gas insulated transmission lines and gas insulated substations. Despite its excellent properties as an insulating and arc-quenching medium in electrical installations, $SF_6$ has also been identified as a very strong greenhouse gas.

The $SF_6$ ReUse Program [1,2] provides a closed loop handling initiative aimed at taking back corrupt $SF_6$ gas from electrical installations thereby minimizing potential emissions. Ultimately, the used gas is fed back into the virgin $SF_6$ production stream, without pre-treatment. The output therefore fulfills all the requirements of virgin gas according to IEC 376 standard.

The used gas collected from various electrical installations often contains operational impurities such as inert gas, switching dust, moisture and oil. More importantly, used $SF_6$ gas may contain decomposition products caused by arcing and faults. As long as the concentration of these impurities falls within the specifications for re-introduction into the virgin $SF_6$ production process stream ($SF_6$-ReUse-Specification), the concept of a closed loop system remains fulfilled.

Occasionally, used gas is collected from electrical installations where severe faults were experienced or gas is received from test operations where the degree of contaminants and decomposition products falls outside the ReUse specification. In this case the used $SF_6$ gas must be disposed of in an environmentally friendly manner, mostly by incineration and at the user's expense. This effectively "breaks" the closed loop handling concept since the used gas is not returned to its virgin state.

In order to keep the loop closed, a purification facility to pre-treat out of specification gas has been developed. The different technologies in existence to remove high concentrations of common impurities such as air, moisture, oil, $SO_2$ and $SO_2F_2$ are briefly discussed. Of greater concern is the potential presence of disulfur decafluoride ($S_2F_{10}$) due to its toxicological profile and is formed in highly stressed $SF_6$ discharges.

The investigation and implementation of a purification pre-treatment facility for decomposition products such as $S_2F_{10}$ would complete the $SF_6$ ReUse program by being able to pre-treat gas that normally would be rejected, so that it can be introduced in the virgin $SF_6$ production stream.

## $SF_6$ PURIFICATION PROCESSES

Table 1 shows the average impurities in used $SF_6$ recovered from test field operations in 2001. The impurity profile is compared to the IEC480 [3] specification for used $SF_6$. Note that the impurities are further classified into inert, hydrolysable and stable/non-hydrolysable.

| Impurity (content) | IEC60480 | Average value | Maximum value | Behavior/Property |
|---|---|---|---|---|
| (SF6) | 96.99% | 97.17% | 99.99% | Inert |
| Air (O2, N2) | 3.0% | 1.59% | 59.74% | Inert |
| CF4 | | 1.15% | 2.70% | Inert |
| SO2 | 50ppm | 300ppm | 1.4% | Hydrolysable |
| SO2F2 | | 200ppm | 1.5% | Hydrolysable |
| S2F10 | Not mentioned | 174ppm | 1.55% | Stable/ Non-hydrolysable |

**Table1**
**Average Impurities in Used $SF_6$ from Test Fields**
**Exceeding the IEC480 Specification in 2001**

Gas impurities such as oxygen and nitrogen can be removed by a membrane separation technique where the main gas flow is separated into a permeate stream and a product stream. Membrane separation units are effective at separating gases with different molecule sizes such as $SF_6$ from $N_2$ and $O_2$ [4].

The soluble gas components such as sulfur oxyfluorides, sulfur dioxide, ($SO_2$) and sulfuryl difluoride ($SO_2F_2$) can be removed from $SF_6$ utilizing gas scrubbers. These components have a high solubility in water compared to $SF_6$ as shown in Table 2. The solubility can be improved even further by using alkaline solutions.

| **Component** | $SF_6$ | $CF_4$ | $N_2$ | $O_2$ | $S_2F_{10}$ | $SO_2$ | $SO_2F_2$ |
|---|---|---|---|---|---|---|---|
| **Solubility (g/kg $H_2O$)** | 0.06 | 0.04 | 0.02 | 0.05 | --- | 164.1 | 1.00 |

**Table 2**
**Solubility of Different Gases at 10°C and 1.013 Bar** [5-8]

Due to its properties, $S_2F_{10}$ is the most challenging to remove. When separated and obtained in a concentrated form, $S_2F_{10}$ presents a waste disposal problem because of its toxicological profile [9], as shown in Table 3. It is also evident that $S_2F_{10}$ could dominate the toxicity profile of any given sample.  For this reason, any closed loop handling concept must find a way to destroy this component.  The most promising destruction methods for $S_2F_{10}$ are pyrolysis [10-11] and photolysis [12].

| Contaminant | $SF_6$ | $CF_4$ | $SO_2F_2$ | $SO_2$ | HF | $SOF_2$ | $SOF_4$ | $SF_4$ | $WF_6$ | $S_2F_{10}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **TLV (ppmv)** | 1000 | 1000 | 5 | 2 | 2 | 1.6 | 0.5 | 0.1 | 0.1 | 0.025 |

**Table 3**
**Threshold Limit Values for Various Gases**

Although the use of gas scrubbers and membranes during the manufacture and purification of $SF_6$ is common practice, the destruction of $S_2F_{10}$ with either pyrolysis or photolysis has yet to be proven on an industrial scale.  Solvay Fluor GmbH initiated a study to investigate these techniques to develop a pre-treatment plant for used $SF_6$.

The photolysis parameters were chosen based on the fact that certain gases are destroyed at certain wavelengths as shown in Figure 1.  Similarly, the pyrolysis parameters were chosen based on literature references stating that $S_2F_{10}$ rapidly decomposes above 250°C (half life = 1.5 seconds).

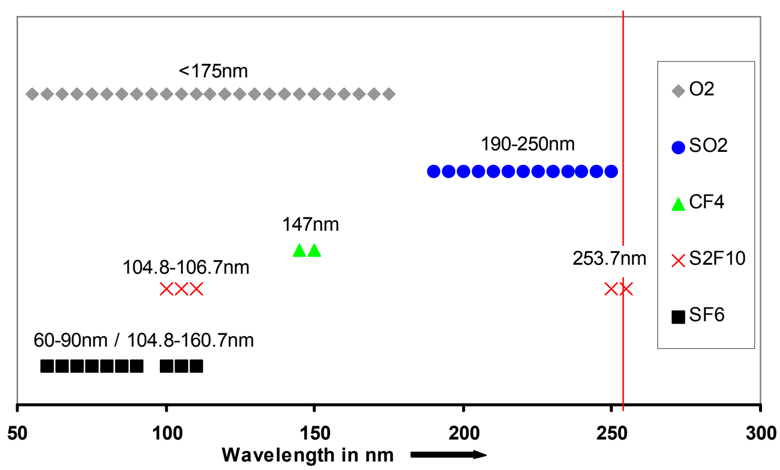


**Figure 1**
**Wavelength for Destruction of Various Gases using Photolysis**

**TEST FACILITY**
The test facility is shown in Figure 2.  Used $SF_6$ from a cylinder (1) is evaporated in an evaporator (2) and the gas pressure is adjusted via a pressure reducer (3).  The $SF_6$ gas stream is regulated by a fine-adjustment regulating valve (4) and fed either into the photolysis reactor (5) or the pyrolysis reactor (6).  The photolysis reactor comprises of a 150 W and 700 W water-cooled 253.7 nm UV lamp with 180 and 520 ml volume operating at 90°C.

For the pyrolysis reactor, a 20 meter spiral shaped copper tube was used with an inner diameter of 2 mm, heated with 750 W heating elements.  Temperatures of 350°C are achievable.  Lastly, the test facility is equipped with a cooling trap where $SF_6$ can be liquefied.  Gas Chromatography is carried out before and after each test series.  The volumetric flow rate, residence time in the reactors (treatment time), temperature and pressure are continuously measured, controlled and recorded with a data acquisition system. In order to avoid any gas release, the system is kept under slight vacuum.

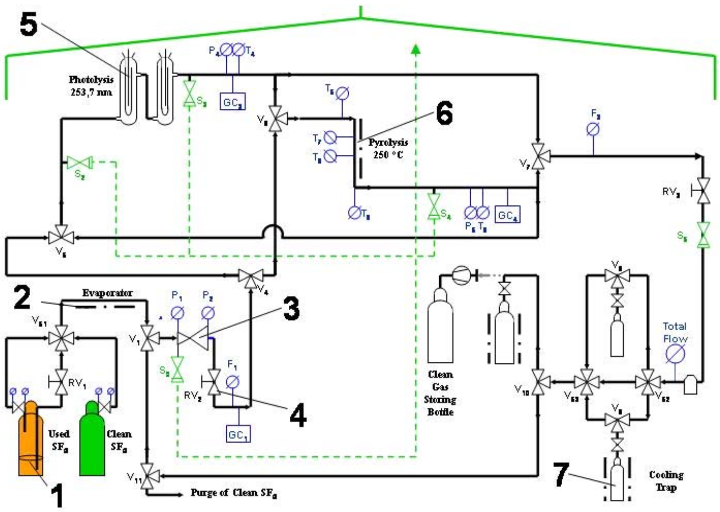


**Figure 2**
**Test Facility for the Investigation of the Destruction of $S_2F_{10}$ Using Photolysis and Pyrolysis**

## PYROLYSIS RESULTS

The trials were conducted at 250°C and 0.8 bar. The residence time in the reactor was 7.6 seconds at a flow rate of 0.5 l/min. The results are shown in Table 3:

| Experiment | $CF_4$ (%) | Air (%) | $SF_6$ (%) | $SO_2F_2$ (ppm) | $S_2F_{10}$ (ppm) | $SO_2$ (ppm) |
|---|---|---|---|---|---|---|
| **Base** | **1.15** | **1.59** | **97.17** | **200** | **174** | **300** |
| **1** | 0.95 | 1.64 | 95.8 | -- | 136 | 610 |
| **2** | 0.91 | 1.69 | 97.7 | -- | 135 | 1740 |
| **3** | 1.25 | 1.58 | 97.02 | -- | 136 | 653 |

**Table 4**
**Impurities Before (Base) and After Pyrolysis**

In this experiment, the concentration of $S_2F_{10}$ was only slightly reduced. The literature suggests that $S_2F_{10}$ should be destroyed under these conditions, but this was not the result here. Note that the $SO_2$ concentration is much higher than the baseline. This is because $SO_2$ is formed from $SO_2F_2$, $S_2F_{10}$ an $O_2$ during the pyrolysis reaction at 250°C.

## PHOTOLOSYS RESULTS

The photolysis trials were conducted using two 700 W ultraviolet lamps at a wavelength of 253.7 nm, at 90°C and 0.8 bar. The residence time of the gas exposed to the lamps was 1.26 seconds at a flow rate of 0.5 l/min in a reactor vessel volume of 700 ml.  The photolysis results are shown in Table 4:

| Experiment | $CF_4$ (%) | Air (%) | $SF_6$ (%) | $SO_2F_2$ (ppm) | $S_2F_{10}$ (ppm) | $SO_2$ (ppm) |
|---|---|---|---|---|---|---|
| **Base** | **1.15** | **1.59** | **97.17** | **200** | **174** | **300** |
| **1** | 1.02 | 1.52 | 97.2 | BDL | BDL | - |
| **2** | 0.92 | 1.55 | 97.2 | BDL | BDL | BDL |
| **3** | 1.23 | 1.60 | 97.8 | 161 | BDL | BDL |

BDL = below detection limit

**Table 5**
**Impurities Before (Base) and After Photolysis**

The concentration of $S_2F_{10}$ after the UV treatment in all 3 trials was below the detection limit (detection limit = 5 ppm).  In 2 out of the 3 tests, the concentration of $SO_2F_2$ was also below the detection limit.  $SF_6$ and air was not influenced by the UV treatment.  Compared to the pyrolysis trials in this study, photolysis seems to be the most appropriate destruction method for $S_2F_{10}$.

**PILOT PLANT**

The various purification processes were arranged in a pilot plant for the pre-treatment of $S_2F_{10}$, $SO_2F_2$, $SO_2$, $O_2$ and $N_2$.  The pilot plant would ensure adequate pre-treatment of the used $SF_6$ gas to comply with the ReUse specifications.  In other words, the pre-treatment pilot plant would ensure that the used $SF_6$ gas would comply with the contaminant concentration limits for introducing the gas into the virgin $SF_6$ production stream.  The pilot plant, shown in Figure 3, consists of a photolysis reactor, an alkaline scrubber and a membrane separation unit.

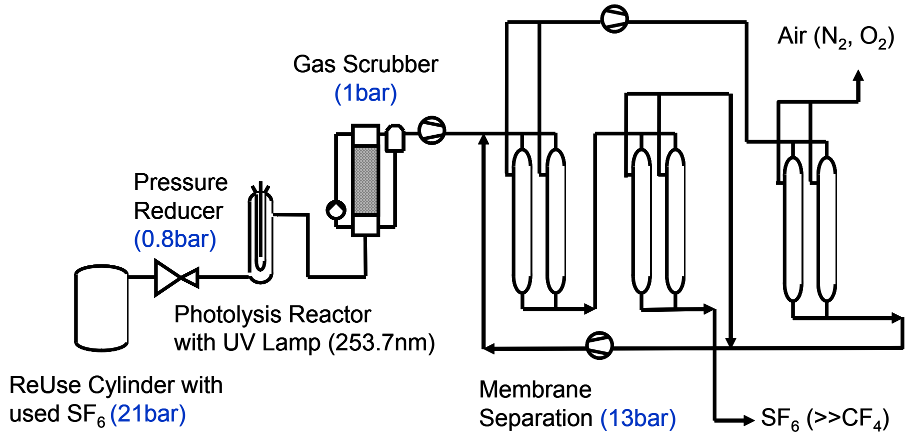


**Figure 3**
**Pilot Plant for the Pre-treatment of Used $SF_6$ Before Reintroduction in the Virgin $SF_6$ Production Process Stream**

The contaminated $SF_6$ flows through a pressure reducer to the different purification processes. $S_2F_{10}$ is efficiently destroyed in the photolysis reactor.  The reaction products along with other hydrolysable components are separated from the $SF_6$ gas stream with an alkaline scrubber while the inert gases such as $N_2$ and $O_2$ are separated in a subsequent step using the membrane separation technology.

**CONCLUSION**

1. Photolysis is a viable method for destroying $S_2F_{10}$ and was implemented in a pilot plant.
2. The pilot plant consists of a photolysis reactor to destroy $S_2F_{10}$, an alkaline scrubber to remove hydrolysable components and a membrane separation unit to remove inert gases.
3. The implementation of a purification pre-treatment facility for decomposition products such as $S_2F_{10}$ would complete the $SF_6$ ReUse program by being able to pre-treat gas that normally would be incinerated, so that it can be introduced in the virgin $SF_6$ production stream.

**REFERENCES**


1. M. Pittroff, H. Krähling, E. Preisegger, *Product Stewardship for $SF_6$*, Proceedings of the 2001 International Symposium on Electrical Insulating Materials, pp. 254-257, Himeji, November 2001
2. D. Lauzon, T. Morris, D. McCreary, M. Pittroff, *The $SF_6$ ReUse Program – a Case Study*, Proceedings of the International Conference on $SF_6$ and the Environment, San Diego, 2002
3. CIGRE 234, *$SF_6$ Recycling Guide,* 2003
4. M. Pittroff, *Separation of $SF_6$/$N_2$ Mixtures,* MEIE 2000, 2nd European Conference on Industrial Electrical Equipment and Environment, pp.61-68, January 2000
5. J.T. Ashton et al., *The Solubility of Certain Gaseous Fluorine Compounds in Water*, J. Chem. Society, pp.1793-1796, 1968
6. M. Trautz, K. Ehrmann, *Beiträge zur Chemie des Schwefels II – Zur Kenntnis der Fluoride und Oxyfluoride des Schwefels,* j. Prakt. Chem. Vol. 142, pp. 79-124, 1935
7. Kirk-Othmer, *Encyclopedia of Chemical Technology*, Vol. 11-16, 4th Edition, John Wiley and Sons, 1994-1996
8. G.H. Cady, S. Misra, *Hydrolysis of Sulfuryl Fluoride*, Inorganic Chemistry, Vol. 13, No. 4, pp.837-841, 1974
9. TLW/TWA ($S_2F_{10}$) = 25 ppb, NIOSH/OSHA, US Department of Labor and Health
10. I. Sauers, et al, *On $S_2F_{10}$ Formation in Spark Breakdown of $SF_6$,* Conference Record, IEEE Symposium on Electrical Insulation, pp. 112-115, June 1988
11. J.T. Herron, *A Critical Review of the Chemical Kinetics of $SF_4SF_5$ and $S_2F_{10}$ in Gas Phase,* Int. J. Chem. Kinetics, pp.129-142, Vol. 19, 1987
12. H.J. Emeleus, K.J. Packer, *The Photochemical Reactions of some Pentafluorosulphur Derivatives with Sulphur Dioxide,* Journal of the Chemical Society, pp. 771-775, 1962