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Characteristics of aerosol by-products generated from sulfur hexafluoride treatment using ionizing energy

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ABSTRACT

Decomposition of SF_6 and its by-products by ionizing radiation were investigated. The SF_6 concentration was decreased as the ionizing radiation intensity increased. When the initial concentration of SF_6 increased, the removal efficiency of SF_6 was decreased. As a result, the ionizing radiation intensity and initial concentration were the influencing factor in the treatment process. The deposited particles and aerosol particles on effluent pipeline and HEPA filters were characterized by scanning electron microscopy (SEM) with the energy dispersion spectrum analysis (EDS), attenuated total reflectance/Fourier transform infrared spectroscopy (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS). The amount of aerosol particles in the HEPA filter was influenced by the ionizing radiation intensity. The detected species in the HEPA filter are S-S, SF_5, SOF_2, SF_4, SO_2F_2, S=O and SOF_4 by FTIR-ATR. This means that the SF_x compounds formed by ionizing irradiation still existed. When we compared with results of removal characteristics using plasma, the input energy of ionizing radiation process was 3–37 times higher than that of plasma. However, the required energy of ionizing radiation process for 1 g of SF_6 removal was 16–160 times lower than the other processes. It is evident that the ionizing radiation process was more efficient process than that of plasma.

1. Introduction

Sulfur hexafluoride (SF_6) is commonly used in various industry processes such as semiconductor and magnesium manufacturing and electric utilities (Bartos, 2001; EPA, 2015). More than 10,000 tons of SF_6 are produced per year, most of which (over 8000 tons) is spent as a gaseous dielectric medium in the electrical industry for current interruption, voltage electrical insulation, and arc quenching in the transmission and distribution of electricity because it is an excellent dielectric (CAPIEL, 2000; EPA, 2014). SF_6 has been reported as a representative greenhouse gas and is inorganic, colorless, odorless, and non-flammable. The life time of SF_6 to disappear into the environment is as much as 3200 years and its GWP (Global Worming Potential) is up to 23,900 times that of CO_2 because it is an extremely stable gas (EPA, 2015). Accordingly, SF_6 concentration in the earth's atmosphere is rapidly increasing (Dervos and Vassiliou, 2000).

Generally, the treatment methods for SF_6 are divided into recovery and reuse by membranes and various decomposition technologies. A study on a membrane for the recovery and reuse of SF_6 has been carried out by research groups (Cho et al., 2011; Lee et al., 2011). On the other hand, diverse techniques including cryogenic capture, pressure swing adsorption, and plasma have been researched to remove SF_6 (Lee et al., 2004). Blundell et al. reported that the cryogenic techniques were effective technique to capture SF_6 gas (Blundell et al., 2007). Shih et al. reported that the SF_6 was decomposed in the radio frequency plasma environment (Shih et al., 2002). SF_6 gas was removed from the SF_6/N_2 mixture by pressure swing adsorption process (Toyoda et al., 2000). However, it has been reported that high energy is needed to obtain a high removal efficiency and an addiction such as H_2 is required to inhibit a re-form of SF_6 (so-called self-healing) in the decomposition reaction (Jakob and Nicholas Perjanik, 1998).

Studies using ionizing radiation were carried out to overcome the limitations (which are high energy consumption, low removal

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efficiency at a high initial concentration of SF_6, by-products, etc.) of these conventional technologies (Ezhov et al., 2004; Lee et al., 2004). The best merit of the ionizing irradiation technology on pollutant treatment is a short reaction time because the electrons are generated during 10^{-18} -10^{-12} s by an electron gun and interact with the gas molecules in a reactor. In addition, free radicals and ions by this reaction are produced during 10^{-8} - 10^{-1} s (Kim, 2002; Kim et al., 2005; Son et al., 2010). Recently, studies on adding H_2 as addition in ionizing irradiation processes for SF_6 decomposition have been conducted to prevent the self-healing of SF_6 (Kim et al., 2013; Ryu et al., 2012). However, in the process for SF_6 control, it was announced that various undesired by-products (such as S_2F_{10}, S containing aerosols/particles, HF) are formed (Son et al., 2016). Some of these by-products are highly toxic and corrosive gases. The LC_{50} (concentration needed to kill 50% of a defined experimental animal population) of S_2F_{10} is 0.1 mg/m^3 (Griffin et al., 1991). The results of experiments with rats by Greenberg and Lester (1950) also reported that S_2F_{10} induces extensive lung damage (edema, lung irradiation from 0.1 ppm, and lung hemorrhages) (Greenberg and Lester, 1950). HF is highly caustic, even attacking glass when in contact with water (Chambers and Holliday, 1975). In addition, breathing in HF at high levels or in combination with skin contact can also cause death from an irregular heartbeat or from fluid buildup in the lungs (Prevention, 2015). Further, it is expected that the performance of SF_6 treatment by ionizing irradiation will decrease because of these by-products. Moreover, the life time of the SF_6 treatment system will be reduced by corrosion and deposition in the reactor, pipelines, and joints.

In this study, we explored the characteristics of aerosol by-products generated from the SF_6 decomposition process by ionizing irradiation. To do so, we investigated the component of sediments deposited with respect to absorbed dose. The aerosol particles and the composition of particles in the HEPA filters after ionizing irradiation were observed using a scanning electron microscope with the energy dispersion spectrum. FTIR-ATR and XPS analyses for characteristics of aerosol by-products were conducted in this study.

2. Experimental method

2.1. Source and reactor of ionizing radiation

A 0.6 MeV mobile electron beam accelerator (maximum power 20 kW, ELV 0.6–33, Korea Atomic Energy Research Institute, Jeongeup-si, Korea) was used to generate electrons.

To decompose SF_6 using ionizing radiation, a rectangular duct-type reactor (length: 680 mm, wide: 190 mm, height: 150 mm and volume: 0.019 m^3) made of stainless steel was used. It was equipped with a thin film (Titanium foil, 50 μm) on the upper part of the reactor allowing the ionizing radiation to penetrate through the film. In order to measure the absorbed dose in a reactor, a cellulose triacetate (CTA) film dosimeter (FTR = 125, Fuji, Japan) and AUV/VIS spectrophotometer (UVIKONxs, SECOMAM, France) were used. The CTA film positions in the reactor were shown in Fig. S1. The CTA films were irradiated by ionizing radiation and analyzed using a AUV/VIS spectrophotometer (wavelength: 280 nm) within 2 h. The ranges of the absorbed dose were estimated to be 211–17,603 kGy (kJ/kg) when the currents were from 1 to 30 mA.

2.2. System setup

A continuous flow system for the removal of SF_6 using ionizing radiation consisted of a standard gas, a mixing chamber, and a reactor with sampling ports. Standard gases (SF_6, 99.999%, H_2, 99.999%, KOREA NOBLE GAS, Korea; N_2, 99.999%, DEOKYANG, Korea; Ar, 99.999%, AIRKOREA INC, Korea), a mass flow controller (MPR-3000, MKP, Korea), and mixing chambers (SUS-304, 2L) were used to adjust to the initial concentrations of SF_6. Sampling ports of SF_6 were located before and after the ionizing irradiation reactor. In addition, to collect aerosol samples, a HEPA filter (260 mm × 230 mm × 30 mm, Doowon corporation, Korea) was installed after the ionizing irradiation reactor. The operation condition of continuous flow system was summarized in Table 1.

2.3. Sampling and analysis

2.3.1. Gaseous compounds

To measure the SF_6 concentration before and after ionizing irradiation, the gases emitted from sampling ports were collected in a bag (Tedlar PVF C-type, 3 L, Dongbang hitech Co, Korea).

A Gas chromatography-mass spectrometer (GC-MS, Shimadzu, GCMS-QP2010 Ultra, and Japan) equipped with a GC-GASPRO (90 m (length) × 0.32 mm (inner diameter), J&W Scientific, USA) was used to quantitatively analyze the SF_6. More detailed information for GS-MS is shown in Table 2.

2.3.2. By-products

The HEPA filter samples (10 mm × 10 mm) were sampled from filter housing after ionizing irradiation. The surface morphology of the HEPA filters was observed using a scanning electron microscope with an energy dispersion spectrum analysis (JEOL, Japan). All samples were sputter-coated with gold-palladium alloy for 60 s. The coated samples were observed under high vacuum conditions. The EDS spectrums were obtained by applying a voltage of 20 kV.

The IR spectra of the HEPA filter were recorded using an Impact 410 − Nicolet FT-IR Spectrometer. The ATR technique was applied on a multiple reflection system using a vertical variable angle (fixed to 45°) with a KRS-5 crystal (thallium bromide–iodide). A total of 32 scans were taken with a 4 cm^{-1} resolution between 4000 and 500 cm^{-1}.

XPS analysis was conducted on a Theta Probe (Thermo Fisher Scientific, UK) spectrometer with a monochromatized AlKα radiation (1486.6 eV). The core-level signals were achieved at an electron takeoff angle of 90°relative to the sample plane. The X-ray energy was adjusted 15 kV at 150 W. The spot size of the sample areas was 400 μm^2.

3. Results and discussion

3.1. Decomposition of SF_6 by ionizing radiation

In general, the SF_6 can decompose into S and $3F_2$ by electrons. SF_6 also can undergo partial dissociation SF_5 and SF_4 releasing fluorine atoms and molecules (Kannari et al., 1986). However, decomposition of SF_5 and SF_4 are hard to decompose into S in the presence of oxygen (Huang et al., 2008). SOF_x formed compounds will be produced in the presence of oxygen during the ionizing irradiation.

Table 1
Operating conditions of SF_6 decomposition by ionizing radiation.

SF_6 concentration	Absorbed dose	Radiation intensity	Flow rate
2%	211 kGy	1 mA	4 ± 0.05 L/min
6%	211 kGy	1 mA	4 ± 0.05 L/min
8%	211 kGy	1 mA	4 ± 0.05 L/min
10%	211 kGy	1 mA	4 ± 0.05 L/min
20%	211–16,892 kGy	20 mA	1–4±0.05 L/min