Decomposition of SF$_6$–R134a effluents by RF plasma

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ABSTRACT

The efficiency of recovery achieved by open or closed loop extraction of RPC exhaust gases is in the range of 90–95% under optimum conditions. For a large detector setup operating on one volume change per day basis, a 5% loss amounts to discharging 50 kg of R134a and 0.5 kg of SF$_6$ into atmosphere every day. The emissions are equivalent to create nearly 50 000 m^3 of carbon dioxide daily. The gas emissions need to be completely converted to safer compounds.

The gases such as R134a and SF$_6$ are stable compounds. In order to decompose these, the mixture is first activated by adding of 50% oxygen and 2% argon and under typical RF plasma conditions of 13.56 MHz, 1 Torr pressure and 0.2 W/cm^2 power density. The chemical reaction takes place on the surface of a silicon electrode. The product of the reaction is mainly SiF$_4$ (gas), which is further hydrolyzed to form HF solution and silicon hydroxide sludge. More than 90% of the effluent gas mixture can be effectively removed by this method.

1. Introduction

Gas filled detectors are most common type of radiation detectors. The RPC type detectors use gas mixtures that are made up of typically isobutane, freon (R134a), argon, carbon dioxide, etc., each gas playing a specific role in the detection process. To keep the running cost down and minimize the discharge of harmful gases into the atmosphere, most detector facilities employ purification and recirculation techniques: closed loop or open loop type. The reported efficiency of gas recovery/recycling process, for open loop or close loop method is in the range of 90–95%. It is evident that at least 5% gas mixture is discharged into the atmosphere.

In the projects of scale of India-based Neutrino Observatory (INO), 28 000 RPCs of size 2 m × 2 m shall be installed with total internal volume of 240 m^3. At 95% efficiency of recovery, nearly 12 m^3 (5%) volume shall be discarded into the atmosphere every day (on one volume change basis). The gas content in the exhaust will be as per Table 1.

The total equivalent CO$_2$ emission is same as burning 25 t of carbon every day.

SF$_6$ and R134a are saturated stable compounds and therefore cannot be recycled by natural processes. SF$_6$ is the toughest of the two. These will accumulate in the atmosphere. Being chemically inactive compounds, these cannot be broken/converted by simple chemistry. Neither they can be adsorbed or polymerized to form

solid end products. The effluent gases are more harmful than equivalent CO$_2$ emission due to the cumulative effect. The problems in safe removal of these gases offset their usefulness as a RPC medium.

2. Plasma decomposition of SF$_6$

It was noticed during reactive ion etching process, commonly used in silicon solar cell manufacturing (semiconductor) industry, that SF$_6$ and other fluorocarbons can be easily broken and made to react under plasma conditions. The process and equipment can be tuned to deplete SF$_6$. The schematic arrangement of plasma processing setup is shown in Fig. 1.

A vacuum reaction chamber is filled with gas mixture at 1 Torr absolute pressure. Two circular electrodes, one with gas injector holes is connected to RF power (13.56 MHz at 0.5 W/cm^2) and other with silicon wafer is placed at ground potential. These plates are spaced 10 mm apart. The gas mixture enters through fine injector holes into the electrode space. The mean free path being sufficiently long at 1 Torr, the electron, while travelling towards ground plates, acquires sufficient energy for interaction with SF$_6$ molecule and starts the following reaction:

$$SF_6 + e^- = (SF_2)^- + 4F. \tag{1}$$

In the presence of oxygen, a cascade of reactions takes place in the plasma zone, starting from SF$_2$ and resulting in the release of a large number of fluorine atoms and other radicals (Fig. 2) [1].

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Table 1
Equivalent CO_2.

Gas (%) in mixture	Emission (m^3/day)	Greenhouse coefficient	Equivalent CO_2 emission (m^3/day)
Freon R134a (95%)	11.40	4200	47880
Isobutane (4.5%)	0.54	–	–
SF_6 (0.5%)	0.06	22400	1350
Total equivalent CO_2 emission/day			49230

Detector operating mode: avalanche.

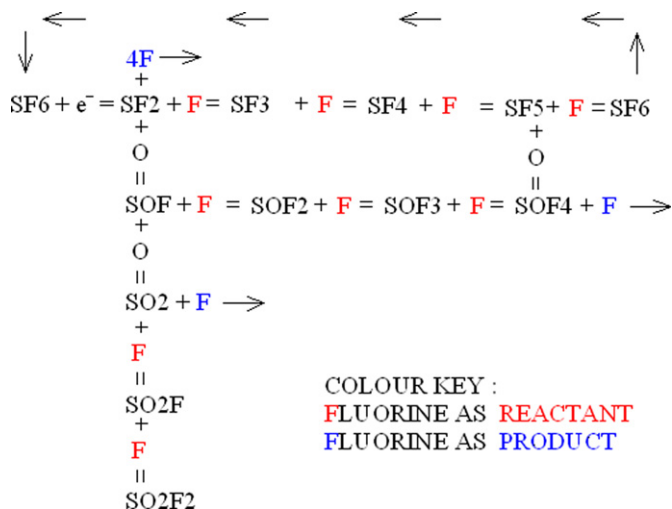Fig. 1. Equipment for plasma decomposition.

Fig. 2. Dissociation reactions in the presence of oxygen.

Mole percentage of the products versus concentration of oxygen in the gas mixture plotted in Fig. 3 [1]. At nearly 50% v/v ratio of oxygen, the formation of the products resulting from the breakup of SF_6 reactant molecule is maximum.

As the gas flows between electrode plates through the plasma zone, a concentration gradient is setup along the radius of the electrodes (Fig. 4) [1,2].

Concentration of stable products builds up to a distance of 5 cm from injector hole and then gradually decreases.

Near the silicon coated ground electrode fluorine reacts with electrode surface to produce gas phase silicon tetra-fluoride.

$$Si + 4F = SiF_4. \tag{2}$$

SiF_4, a gaseous product, is pumped out of reaction chamber for subsequent removal by simple chemical processes.

The present reactive ion etching setup is shown in Fig. 5. It consists of a vacuum chamber, a pumping system and RF power source with matching network.

A combination of MKS mass flow controllers introduce required gas quantity into the vacuum chamber. MKS back-pressure controller valve maintains around 0.3–1.0 Torr pressure inside plasma chamber, measured by Baratron gauges. Advance energy RF generator powers RF electrode up to 300 W.

Exhaust gas is reacted with basic grade activated alumina to remove radicals and halogens. The vacuum pump exhaust is treated with chemical scrubbers to maintain hazardous gas concentrations below TLV (Threshold Limit Value).

3. Factors affecting efficiency of removal of SF_6 by RF plasma

(i) The efficiency of the ionization depends upon localized field strength contour. The shape and dimensions of injector holes play an important part in the field distribution. This factor is being studied by optimizing electrode geometry.

(ii) The reaction between silicon and fluorine is reversible. The accumulation of products and the depletion of reactants brings the net reaction to a halt. It is necessary to separate the products, as they are formed, from gas mixture to maintain the reaction rate.
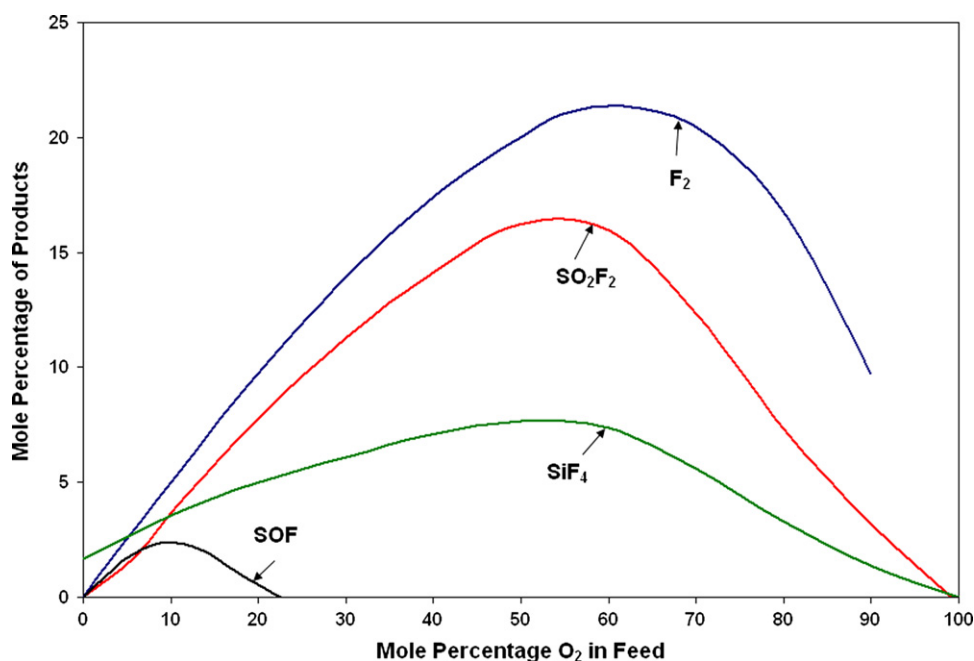
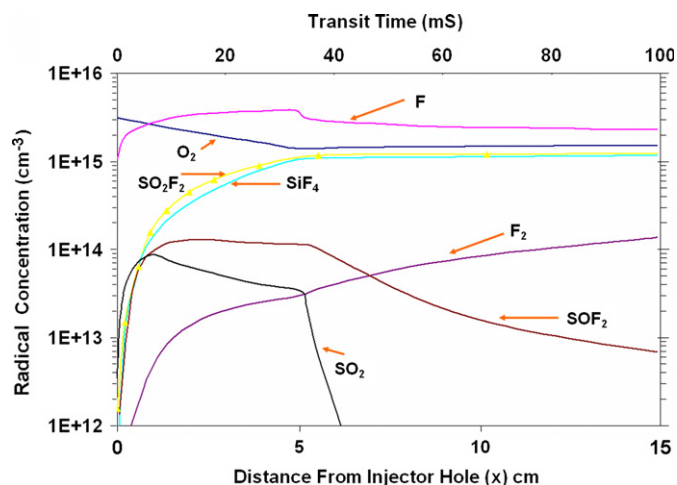Fig. 3. Concentration of products as a function of oxygen molar fraction in reactants.

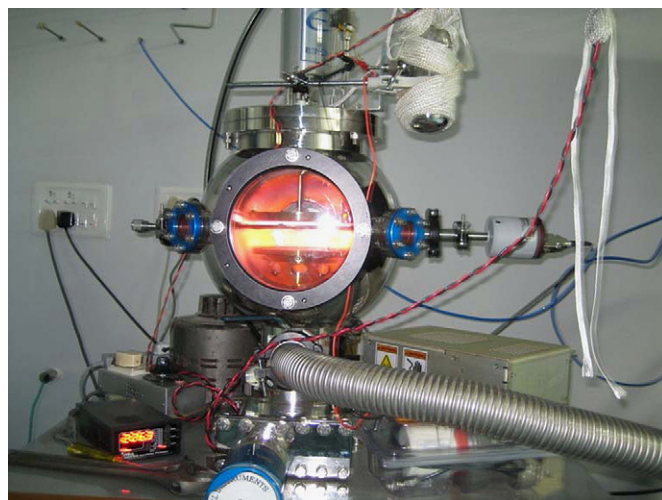Fig. 4. Variation in radical concentration as a function of distance over electrode.

Fig. 5. RIE setup.

(iii) Application of a DC bias is studied to force the reaction in desired direction.
(iv) Electrode surface temperature: At surface temperature of 150 °C, the silicon electrode is highly active.
(v) Multiple electrode design of plasma chamber can improve overall efficiency of SF_6 removal.

4. Proposed plasma scrubber system

Fig. 6 shows the schematic of a pilot scale plasma scrubber for removal of hazardous fluorinated compounds. The gas mixture coming out from recovery/recirculation system will be injected into the plasma chamber through a mass flow controller. The gas mixture will pass between multiple electrodes made of activated silicon–alumina. The RF power density will be in the range of 0.1–0.5 W/cm^2. Ground electrode temperature can be controlled from 30 to 200 °C. The plasma chamber will be

maintained at 1–2 Torr (absolute) pressure range with the help of a butterfly valve coupled with capacitance manometer. The multiple reactions will take place within plasma zone, resulting in the breakup of SF_6 and freon molecules. The breakup products will bond with silicon at ground electrode. The ground electrode will be replaced either continuously through a load-lock or intermittently in a batch type operation. The leftover gas mixture containing fluorine and radicals will be treated with spray of oxidizing and reducing chemical inside wet scrubber, located at outlet of the vacuum system.

This equipment will be fitted with diagnostic tools such as Langmuir probe/optical emission spectroscope for plasma characterization and Residual Gas Analyzer (RGA) for quantitative analysis. The proposed RF plasma scrubber is designed to handle gas flow rates in the range of 0–1 l/min. The performance of this equipment shall be evaluated on the basis of the efficiency of removal of fluorine based gaseous compounds. It will be installed at INO lab, Tata Institute of Fundamental
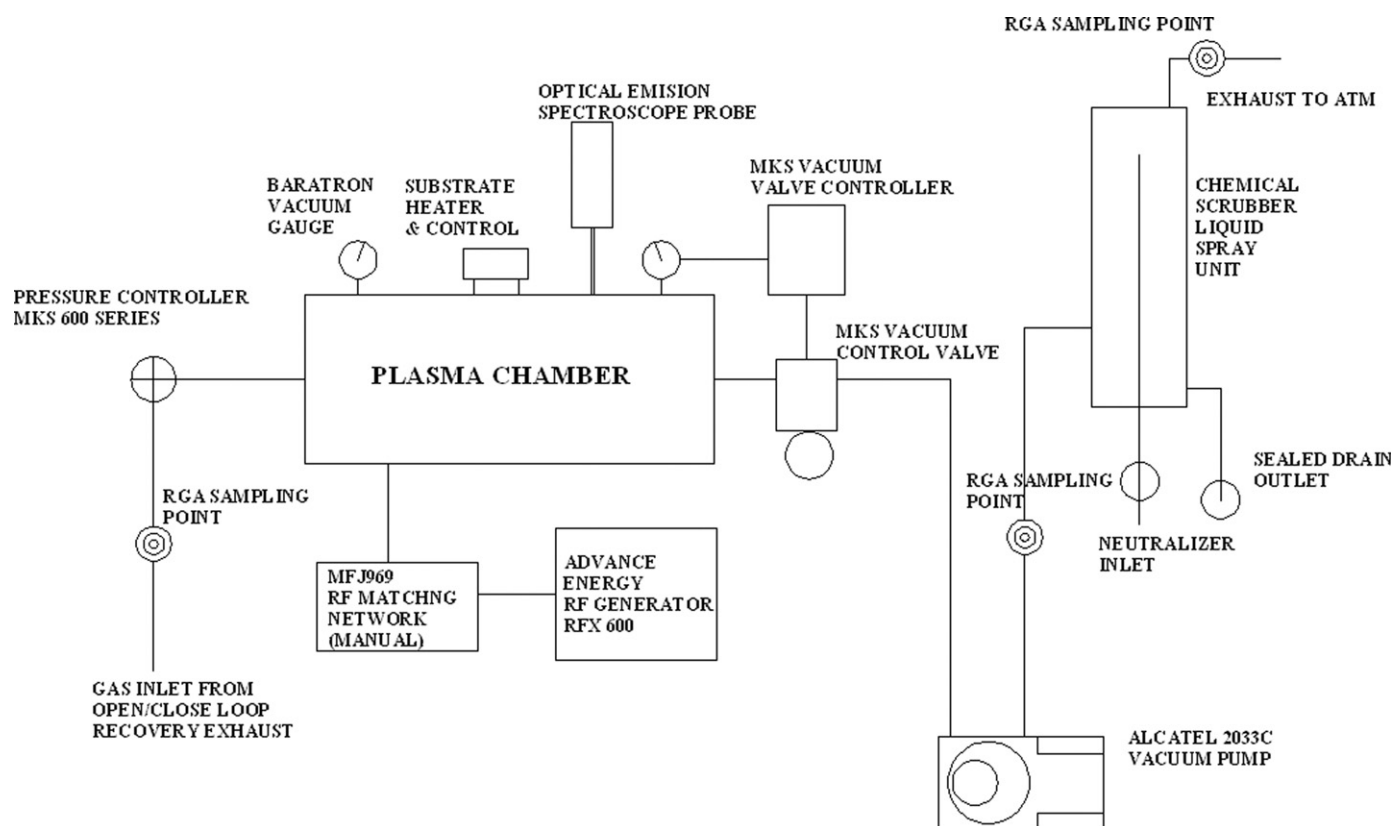
Fig. 6. Schematic of pilot plasma scrubber.

Research (TIFR), Mumbai (INDIA). This project is presently at design stage.

5. Conclusions

It is unsafe to discharge gas mixtures used in RPC detectors in the atmosphere without treatment. Removal of hazardous content from the gas mixture is possible by RF plasma breakdown and in situ reaction with silicon–alumina electrode. Maximum removal rates can be achieved by optimizing process parameters.

References

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[2] Y. Tzeng, T.H. Lin, J. Electrochem. Soc. (Solid State Sci. Technol.) 134 (1987) 2304.