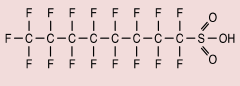
Mass Balance Analysis of Perfluorocompound Decomposition by DC Plasma Generated in Gas Bubbles

Summary

The aqueous solution of perfluorooctanesulfonic acid (PFOS) (55.5 mg/L, 50 mL) was decomposed by a dc plasma generated in argon gas bubbles for 600 min and the mass balances of carbon and fluorine were measured. The mass balances of carbon and fluorine were 57.0% and 72.3% at 600 min, respectively and didn't reach 100%. To detect unknown by-products, the liquid phase and the gas phase products were qualitatively analyzed by high performance liquid chromatography mass spectrometry (HPLC/MS) and Fourier transform infrared spectroscopy (FT-IR). $C_mHF_{2m}SO_3H$ (m=2–8) and $C_lHF_{2l}COOH$ (l=2–7) were detected in the liquid phase and fluorocarbon gases such as CHF_3, C_2HF_5, and C_2F_6 were found in the gas phase. These results indicate that some PFOS is gradually degraded at the C–F, C–C, and C–S bonds, by the collisions of high energy particles. Such processes take relatively long time for detaching F^-. Other PFOS is thermally decomposed by the heat of the plasma (1600 K) and F^- are detached in a short period.

Objectives

Perfluorooctanesulfonic acid (PFOS, $C_8F_{17}SO_3H$)



- Surfactant
- Chemically stable
- Used in semiconductor process
- ✓ Have carcinogenicity

PFOS degradation methods	Concentration, vol., W, %, hours	Efficiency [mg/kWh]
UV254 in 2-Propanol solution (National Inst. Environ. Studies, 2008)	20 mg/L, 750 mL, 30W, 75%(9days)	0.6
Ultrasonic irradiation (Caltech, 2010)	13mg/L, 400 mL, 75W, 70%(2h)	4.5
DC plasma in bubbles (Tokyo Tech, 2010)	60mg/L, 200 mL, 45W, 50%(1h)	26

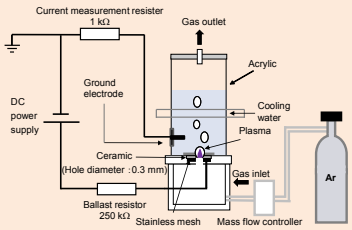
PFOS can be efficiently decomposed by a dc plasma generated in gas bubbles. However, the reaction process of PFOS decomposed by a plasma remains unknown.

Experimental Setup

DC PLASMA INSIDE GAS BUBBLES

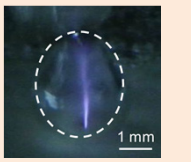
- The plasma is generated inside bubbles in the solution.
- The high-voltage power supply is connected to the plasma reactor through a ballast resistor which stabilizes the plasma current.
- The average current is regulated at 10 mA.

Experimental setup of the plasma reactor



Experimental condition

Gas: Argon
Gas flow rate: 100 sccm
Solution: PFOS 55.5 mg/L, 50 mL

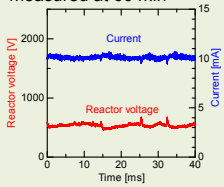


Discharge image in bubbles

Results and Discussions

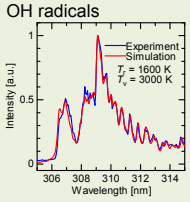
1. Discharge characteristics

Waveforms measured at 60 min



The current fluctuated between 9.5 mA and 10.5 mA.

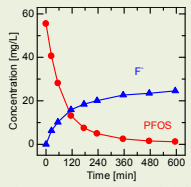
Emission spectrum of OH radicals

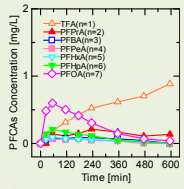


The gas temperature of the plasma was estimated at 1600 K.

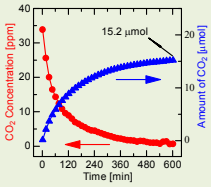
2. Degradation characteristics of PFOS

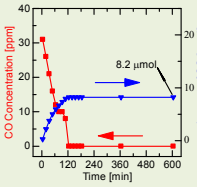
Concentrations of PFOS, PFCAs ($C_nF_{2n+1}COOH$, n=1–7), and F^- in solution.



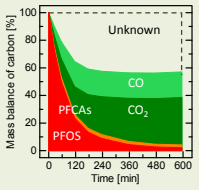


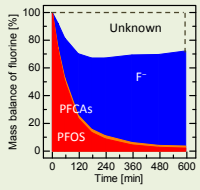
Concentrations of CO_2 and CO in gas.





3. Mass balances of carbon and fluorine





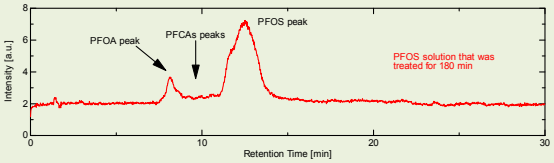
- The mass balances of carbon and fluorine didn't reach 100% during the degradation of PFOS.

➡ Unknown by-products exist!

4. Qualitative analysis to detect the unknown products

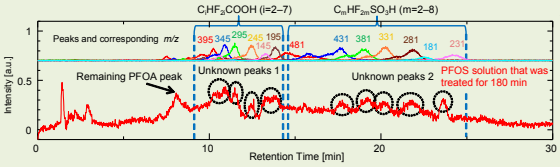
Liquid phase analysis by HPLC/MS

Total ion current chromatogram of PFOS solution treated for 180 min



- PFCAs peaks were detected at 8–12 min.
- PFOS peak was found at 12-14 min.

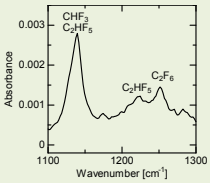
Remove the peaks of PFOS and PFCAs.



◆ $C_mHF_{2m}SO_3H$ (m=2–8, m/z=131, 181, … ,481) and $C_lHF_{2l}COOH$ (l=2–7, 145, 195, …, 395) were detected.

Gas phase analysis by FT-IR

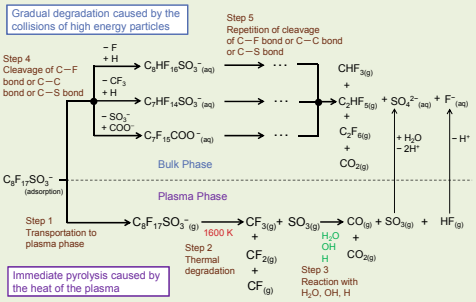
Infrared spectrum of the gas released from the plasma reactor



◆ Fluorocarbon gases such as CHF_3, C_2HF_5,and C_2F_6 were detected.

The unknown by-products were detected as follows: $C_mHF_{2m}SO_3H$ (m=2–8) and $C_lHF_{2l}COOH$ (l=2–7) in the liquid phase and CHF_3, C_2HF_5,and C_2F_6 in the gas phase

5. Proposed reaction process of PFOS decomposition in solution



Gradual degradation

- ◆ A part of PFOS is gradually degraded by the collisions of high energy particles.
- ◆ Intermediates began to adsorb on the gas-liquid interface and degrade after almost all of PFOS in solution is decomposed.

Immediate pyrolysis

- ◆ Other part of PFOS is decomposed by the heat of the plasma (1600 K) in the plasma phase.
- ◆ F^- are generated soon after the decomposition of PFOS.

(K. Tachibana)