Degradation of Perfluoro Compounds and F^- Recovery in Water Using Discharge Plasmas Generated within Gas Bubbles

K. Yasuoka, K. Sasaki, R. Hayashi, A. Kosugi, and N. Takeuchi
Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, Japan

Abstract—Decomposition of perfluoro compounds (PFCs) has been successfully demonstrated using DC plasmas generated within oxygen bubbles in water. A plasma reactor was filled with perfluorooctanoic acid (PFOA) or perfluorooctanesulfonic acid (PFOS) solution (50 mL, 50 mg/L) and DC voltage was applied between the solution and an annular electrode. DC plasma initiated within the central hole of the electrode and slightly expanded along the inner surface of oxygen bubbles formed just above the hole. The typical values of the applied voltage and discharge current were 1.6 kV and 7 mA, respectively. The decomposition ratio of PFOA/PFOS was evaluated by measuring the concentration of fluorine ions (F^-) detached from the PFCs in the solution. The F^- formation ratio and energy efficiency after 30 minutes of operation were 17.4% and 61.0 mg/kWh, respectively, in the PFOA solution and 11.3% and 36.4 mg/kWh, respectively, in the PFOS solution. The recovery of fluorine from the treated solution was tested by adding 200 mg/L of $CaCl_2$. On the basis of the reduction in concentration of calcium ions, we estimated the amount of formed CaF_2 to be 17.7 mg/L after 30 minutes of operation at a discharge current of 10 mA.

Keywords—Bubble, DC discharge, PFCs, PFOA, PFOS, fluorine ion

I. INTRODUCTION

Perfluoro compounds (PFCs) are widely used owing to their chemical stability and physical characteristics. The biopersistence and unexpected toxicity of long-chain PFCs have recently raised environmental concerns, causing changes in effluent control regulations. PFCs such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) cannot be decomposed by the advanced oxidation technology utilizing OH radicals. Therefore, various methods such as UV-induced photochemical reaction [1, 2], sonochemical reaction [3], VUV irradiation [4], S_2O_8-added hot-water treatment at 80°C [5], and microwave-hydrothermal method [6] have been tested to decompose the strong C–F bonds of PFOA. A limited number of reports exist on PFOS degradation using zero-valent iron in subcritical water [7] or by sonochemical methods [3, 8].

Liquid-phase electrical discharge plasmas have been investigated for degradation of persistent organics in water [9, 10]. In liquid-phase plasmas, the generation of hydroxyl radicals, which are the primary reactive species, have been studied extensively by optical emission spectroscopy and chemical probe methods [11]. The hydroxyl radicals are less effective for decomposing PFOA or PFOS in water, so liquid-phase plasmas have not been applied to the decomposition of PFCs. We recently found that the direct plasma-water interaction [12] can easily decompose such PFCs in water with a dielectric barrier plasma [13] or a pulsed plasma [14] in bubbles. DC plasmas within oxygen bubbles showed a faster decomposition rate and a higher energy efficiency than the pulsed plasmas [15].

During the decomposition processes, fluorine ions are generated in the solution. The recovery of fluorine is important as the cost of fluorite has increased. Calcium precipitation has been established as the method of recovering fluorine ions from industrial wastewater [16]. We have examined the manner in which the fluorine ions are recovered by adding a calcium salt such as $CaCl_2$ into PFOA solutions. The goal is the recovery of insoluble CaF_2 crystals during PFOA degradation. In this paper, we report the decomposition of PFOA/PFOS and the recovery of fluorine from PFOA [17] by combining a DC plasma reactor with a calcium precipitation method.

II. EXPERIMENTAL SETUP

A schematic diagram of a DC plasma reactor is shown in Fig. 1. A high-density polyethylene container was used as a reactor chamber in which 50 mL of a 50 mg/L PFOA or 10 mL of a 240 mg/L PFOS solution was filled for degradation experiments. In the recovery experiments, 20 mL of a 200 mg/L PFOA solution was used with and without $CaCl_2$.

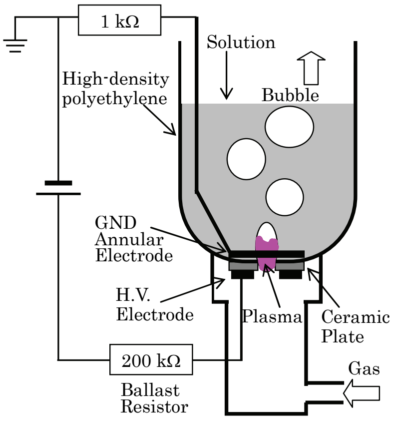

Fig. 1. Schematic diagram of the plasma reactor.

Corresponding author: Koichi Yasuoka
e-mail address: yasuoka@ee.titech.ac.jp

Presented at the Seventh International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy, ISNTP-7, in June 2010

The electrode system consists of a grounded 0.2-mm-thick annular metal plate, a 1-mm-thick dielectric spacer having a 0.2-mm-diameter central hole, and a high-voltage electrode that was separated from the solution with the spacer. Oxygen, argon, or helium gas was fed into the solution through the tiny hole in the ceramic plate at a flow rate of 50–100 sccm. Small gas bubbles formed in the central hole, then expanded into the solution, and finally detached from the ceramic surface after around 10 ms. The high-voltage electrode was connected to a DC voltage source through a 200 kΩ ballast resistor. The polarity of the voltage source was mostly positive. An 1 kΩ resistor was inserted for current monitoring. After applying a high voltage, DC plasmas initiated within the hole and slightly extended along the inner surface of the bubbles. The current value was 7 mA for decomposition and 10 mA for recovery experiments.

The concentration of fluorine ions was measured with a pH/ion-meter (Mettler-Toledo, SevenMulti S80). The calcium ion concentration was determined by measuring the absorbance of the solution with a spectral photometer (JASCO Corp., V-630) after adding a calcium pack test (Kyoritsu Chemical-Check Lab., Corp., WAK-Ca).

III. RESULTS AND DISCUSSION

A. Decomposition of PFOA/PFOS

The molecular structures of PFOA ($C_7F_{15}COOH$) and PFOS ($C_8F_{17}SO_3H$) are shown in Fig. 2. These two compounds differ in the number of carbon atoms in the main chain and the functional groups. Fig. 3 shows the typical voltage and current waveforms when oxygen gas was fed at a flow rate of 100 sccm. The output current from the voltage source was set at 7 mA; however, the frequency response of the voltage source was too slow to maintain a constant plasma current. The solution temperature was kept at around 20°C by a cooling system.

The degradation ratio was evaluated by measuring the fluorine ions generated in the solution. Fig. 4 shows the formation ratio, which is defined as the ratio of the amount of fluorine ions to the initial atomic weight of fluorine in the PFOA solution. The solution conductivity shown with the right-hand axis is a function of the concentration of fluorine ions, but it almost saturated after 50 minutes of operation. The initial concentration and the conductivity of PFOA solution were 240 mg/L and 140 μS/cm, respectively. The reactor voltage was 1.2 kV and an average current was 10 mA. In this case, the flow rate of oxygen was 50 sccm. The formation ratio of fluorine ions rapidly increased for 30 minutes and reached approximately 95% after 100 minutes of operation. At 60 minutes, the decomposition ratio was 85% and the energy efficiency, which is defined as the ratio of the amount of fluorine ions generated in the PFOA solution to the input energy including energy loss with the ballast resistor, was 47 mg/kWh. The decomposing energy efficiencies at 30% of fluorine ions detached from PFOA were 105 mg/kWh with this plasma method, 1.4 mg/kWh for 9 hours [1] and 6.3 mg/kWh for 2 hours [2] operations by photochemical methods.

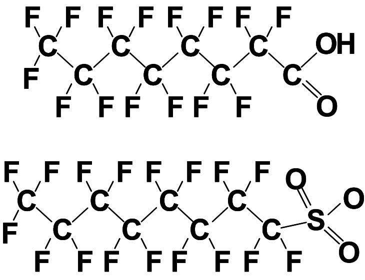

Fig. 2. Molecular structures of PFOA (upper) and PFOS (lower).

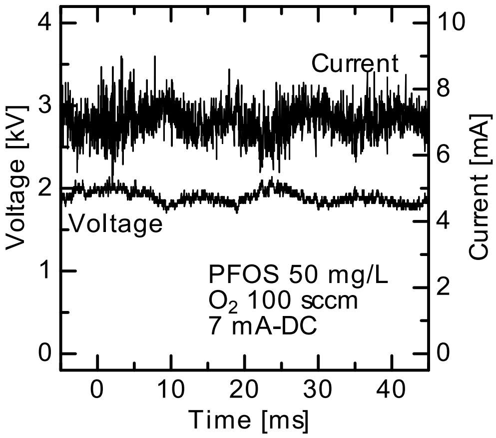

Fig. 3. Typical voltage and current waveforms.

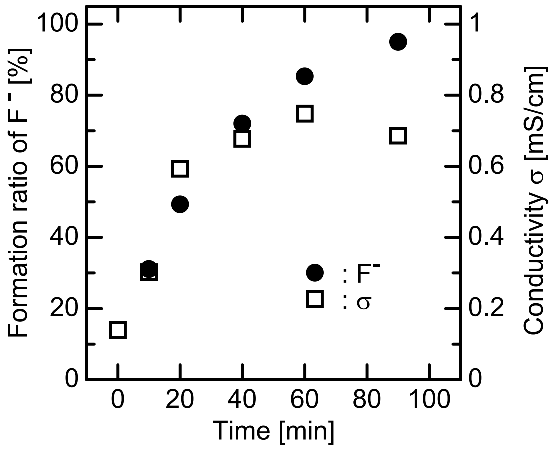

Fig. 4. Formation ratio of fluorine ions and solution conductivity as a function of processing time.

In case of PFOS degradation, sulfate ions (SO_4^{2-}) were generated in the solution in addition to fluorine ions, as shown in Fig. 5. The concentration of ions increased linearly at the beginning of decomposition, and the rate of generation of ions gradually decreased after 60 minutes of operation. The concentration of SO_4^{2-} was approximately one-third of the fluorine ion concentration. The initial values of solution conductivity and pH were 29 μS/cm and 4.4, respectively. The pH was decreased to 3.3 after 60 minutes of operation. At 60 minutes of

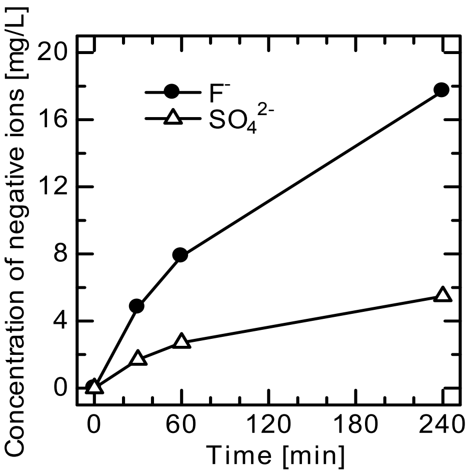

Fig. 5. Concentrations of fluorine and sulfate ions generated in a PFOS solution as a function of processing time.

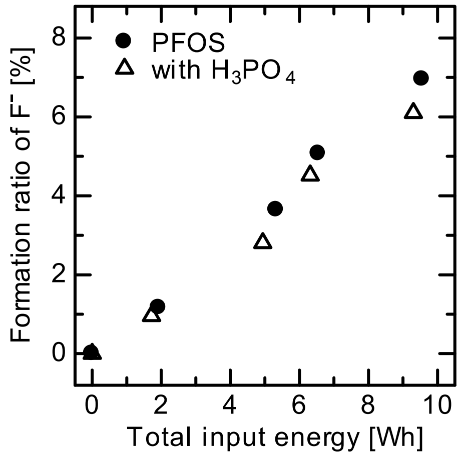

Fig. 6. Formation ratio of fluorine ions in PFOS solution with and without H_3PO_4 as a function of input energy.

operation, the decomposition ratio was 25% and the energy efficiency was 19 mg/kWh. The decomposition rate and efficiency of PFOS are a little lower than those of PFOA degradation.

Fig. 6 shows the formation ratio of fluorine ions as a function of total input energy, with and without H_3PO_4. The hydrated electron may be one of the active species for PFOA/PFOS degradation. Therefore H_3PO_4 which is a scavenger of hydrated electrons was added to the PFOA solution. Addition of H_3PO_4 caused a slight decrease in the formation ratio. This suggests that the effect of the hydrated electron is limited in the degradation of PFOA.

Changing the discharged gas resulted in a change in the contact area between the DC plasma and the solution surface as well as the current densities. As shown in Fig. 7, the highest ratio was obtained with oxygen plasma but the highest energy efficiency was observed with argon plasma. The voltage polarity of the high-voltage source strongly affects the plasma stability and the fluorine formation ratio. Negative polarity led to unstable discharges and a lower efficiency.

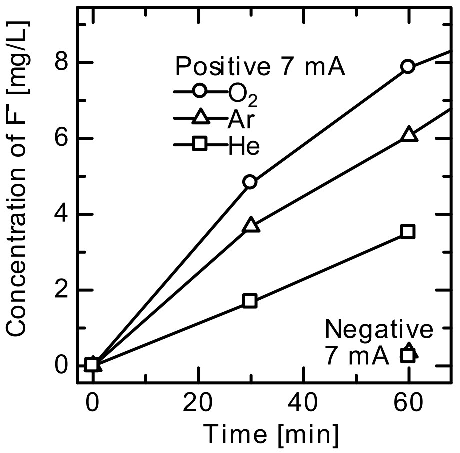

Fig. 7. Concentration of fluorine ions with oxygen, argon, and helium plasmas as a function of processing time and voltage polarity.

The mass balance was evaluated for an initial concentration of 51 mg/L PFOS solution. The initial amounts of fluorine and sulfur atoms were 86.7 μmol and 5.1 μmol, respectively. After 240 min of operation the amounts decreased to 78.5 μmol and 4.5 μmol, respectively. Thus, approximately 10% of fluorine and sulfur atoms disappeared during the operation. The detected byproducts by LC/MS method were PFCSs ($C_nF_{2n+1}COOH$), and no PFASs ($C_nF_{2n+1}SO_3H$) were detected. The disappeared fluorine and sulfur atoms possibly changed into gas compounds.

The possible decomposing processes through which PFOA degrades are shown in Eqs. (1) - (3). In Eq. (1), the unknown reactive species, represented by M, is added to explain the plasma effect on the degradation.

$$C_7F_{15}COO^- + M \rightarrow C_7F_{15}COO\cdot + M + e^- \quad (1)$$

$$C_7F_{15}COO\cdot \rightarrow C_7F_{15}\cdot + CO_2 \quad (2)$$

$$C_7F_{15}\cdot + 2H_2O \rightarrow C_6F_{13}COOH + 3H^+ + 2F^- \quad (3)$$

The processes involved in PFOS degradation are fairly more complicated than those of PFOA degradation, and possible processes are represented by Eqs. (4) – (7). PFOS changes to PFOA through the degradation. The active species M represents direct plasma interactions with the solution surface. PFOA thus generated degrades further through the same processes as for PFOA degradation shown above.

$$C_8F_{17}SO_3^- + M \rightarrow C_8F_{17}SO_3\cdot + M + e^- \quad (4)$$

$$C_8F_{17}SO_3\cdot \rightarrow C_8F_{17}\cdot + SO_3 \quad (5)$$

$$C_8F_{17}\cdot + H_2O \rightarrow C_8F_{17}O^- + H^+ + H \quad (6)$$

$$C_8F_{17}O^- + H_2O \rightarrow C_7F_{15}COO^- + 2H^+ + 2F^- \quad (7)$$

B. Recovery of fluorine atoms by calcium precipitation

Fig. 8 shows the concentrations of fluorine ion with and without $CaCl_2$. The solution contained 200 mg/L PFOA with and without $CaCl_2$ of which initial concentration was 200 mg/L. After 30 minutes of

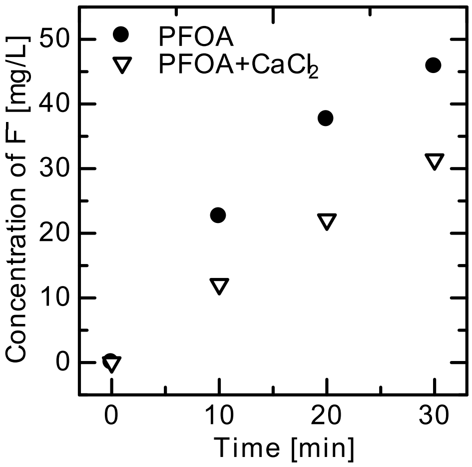

Fig. 8. Concentration of fluorine ions as a function of processing time with and without $CaCl_2$.

TABLE I
CONCENTRATION OF CALCIUM IONS WITH THE PROCESSING TIME IN THE PRESENCE OF $CaCl_2$

Time [min]	0 (initial)	20	30
Calcium ion concentration [mg/L]	45.9	41.8	36.8
Diminished concentration [mg/L]	0	4.1	9.1

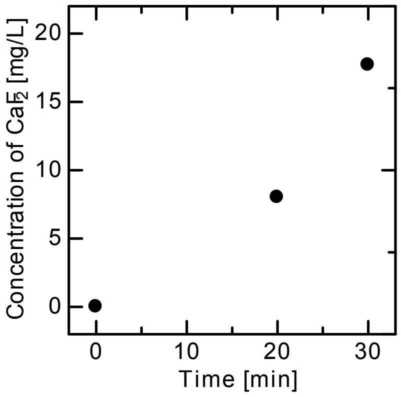

Fig. 9. Estimated formation rate of CaF_2 as a function of processing time in PFOA solution with $CaCl_2$.

operation at 10 mA, the fluorine ion concentrations with and without $CaCl_2$ were 46.0 mg/L and 31.4 mg/L, respectively. The fluorine ion concentration decreased after adding calcium ions. Although CaF_2 crystals were not detected, the reduction may be caused by the production of insoluble CaF_2 in the PFOA solution. However, the change in the amount of decomposed PFOA was not fully understood.

Table I shows the time variation of the concentration of calcium ions when $CaCl_2$ was added and the diminished concentration of calcium ions from the initial value. Around 20% reduction of the concentration was possibly caused by the production of CaF_2. Fig. 9 shows the amount of CaF_2 estimated from the reduction in concentration of calcium ions. The estimated amount of CaF_2 produced after 30 minutes of operation was 17.7 mg.

IV. CONCLUSION

We successfully demonstrated the degradation of PFOA and PFOS solutions by using DC plasmas generated inside gas bubbles in water. The decomposition ratio and efficiency were evaluated by measuring concentration of the fluorine ions generated in the solution. The decomposition ratio of PFOA is slightly higher than that of PFOS, owing to the presence of a sulfo group. Direct plasma interaction with the solution surfaces seems to enhance the degradation of PFOA/PFOS.

Recovery of fluorine from PFOA in water was tested by combining the PFOA decomposition process and the calcium precipitation method. The concentration of fluorine ions in the solution decreased when $CaCl_2$ was added, possibly because of the production of insoluble CaF_2 crystals.

ACKNOWLEDGMENT

This work was supported by a Grants-in-Aid for Scientific Research (KAKENHI: 20360123).

REFERENCES

[1] H. Hori, E. Hayakawa, H. Einaga, S. Kutsuna, K. Koike, T. Ibusuki, H. Kiatagawa, and R. Arakawa, "Decomposition of Environmentally Persistent Perfluorooctanoic Acid in Water by Photochemical Approaches," *Environmental Science & Technology*, vol. 38, pp. 6118-6124, 2004.

[2] H. Hori, A. Yamamoto, E. Hayakawa, S. Taniyasu, N. Yamashita, S. Kutsuna, H. Kiatagawa, and R. Arakawa, "Efficient Decomposition of Environmentally Persistent Perfluorocarboxylic Acids by Use of Persulfate as a Photochemical Oxidant," *Environmental Science & Technology*, vol. 39, pp. 2383-2388, 2005.

[3] H. Moriwaki, Y. Takagi, M. Tanaka, K. Tsuruho, K. Okitsu, and Y. Maeda, "Sonochemical Decomposition of Perfluorooctane Sulfonate and Perfluorooctanoic Acid," *Environmental Science & Technology*, vol. 39, pp. 3388-3392, 2005.

[4] J. Chen and P. Zhang, "Photodegradation of perfluorooctanoic acid in water under irradiation of 254 nm and 185 nm light by use of persulfate," *Water Science & Technology*, vol. 54, pp. 317-325, 2006.

[5] H. Hori, Y. Nagaoka, M. Murayama, and S. Kutsuna, "Efficient Decomposition of Perfluorocarboxylic Acids and Alternative Fluorochemical Surfactants in Hot Water," *Environmental Science & Technology*, vol. 42, pp. 7438-7443, 2008.

[6] Y.-C. Lee, S.-L. Lo, P.-T. Chiueh, Y.-H. Liou, and M.-L. Chen, "Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation," *Water Research*, vol. 44, pp. 886-892, 2010.

[7] H. Hori, Y. Nagaoka, A. Yamamoto, T. Sano, N. Yamashita, S. Taniyasu, S. Kutsuna, I. Osaka, and R. Arakawa, "Efficient Decomposition of Environmentally Persistent Perfluorooctanesulfonate and Related Fluorochemicals Using Zerovalent Iron in Subcritical Water," *Environmental Science & Technology*, vol. 40, pp. 1049-1054, 2006.

[8] C. D. Vecitis, Y. Wang, J. Cheng, H. Park, B. T. Mader, and M. R. Hoffmann, "Sonochemical Degradation of

Perfluorooctanesulfonate in Aqueous Film-Forming Foams," *Environmental Science & Technology*, vol. 44, pp. 432-438, 2009.

[9] B. R. Locke, M. Sato, P. Sunka, M. R. Hoffmann, and J. S. Chang, "Electrohydraulic Discharge and Nonthermal Plasma for Water Treatment," *Industrial & Engineering Chemistry Research*, vol. 45, pp. 882-905, 2006.

[10] M. Malik, "Water Purification by Plasmas: Which Reactors are Most Energy Efficient?," *Plasma Chemistry and Plasma Processing*, vol. 30, pp. 21-31, 2010.

[11] M. Sahni and B. R. Locke, "Quantification of Hydroxyl Radicals Produced in Aqueous Phase Pulsed Electrical Discharge Reactors," *Industrial & Engineering Chemistry Research*, vol. 45, pp. 5819-5825, 2006.

[12] P. Bruggeman and C. Leys, "Non-thermal plasmas in and in contact with liquids," *Journal of Physics D: Applied Physics*, vol. 42, p. 053001 (28 pp), 2009.

[13] K. Sasaki, R. Hayashi, and K. Yasuoka, "Degradation of Perfluoro Compounds by Pulsed Plasmas Generated in Water Bubbles" (in Japanese), *IEEJ Trans. FM*, vol. 130, pp. 985-986, 2010.

[14] K. Sasaki, R. Hayashi, and K. Yasuoka, "Direct Plasma Degradation of Perfluo-rooctanoic Acid in Gas-Liquid Two-Phase Flow Reactor," presented at 19th World Congress & Exhibition, International Ozone Association, Tokyo, Japan, 2009.

[15] K. Yasuoka, R. Hayashi, and K. Sasaki, "Degradation Mechanisms of Persistent Compounds in Water Using Discharge Plasmas Generated Inside Gas Bubbles," in *Proceedings of International Workshop on Plasmas with Liquids (IWPL 2010)*, Japan, I-12, pp. 33–34.

[16] N. Parthasarathy, J. Buffle, and W. Haerdi, "Combined use of calcium salts and polymeric aluminium hydroxide for defluoridation of waste waters," *Water Research*, vol. 20, pp. 443-448, 1986.

[17] N. Takeuchi, A. Kosugi, and K. Yasuoka, "Recovery of Fluorine from Perfluo-ro-compounds in Water During Decomposing Processes by Plasmas," in *Proceedings of International Workshop on Plasmas with Liquids (IWPL 2010)*, Japan, P-14, pp. 97–98, 2010.