

Comparative Evaluation of Destruction Behaviors of Fluorinated POPs and Their Salts by Incineration

Takashi Fujimori^{1*}, Naoya Saito¹, Taichi Murakami¹, Naoki Yamamoto¹, Masaki Takaoka², Hidenori Matsukami³

¹ Faculty of Advanced Science and Technology, Ryukoku University, 1-5 Yokotani, Seta Oe-cho, Otsu, Shiga 520-2194, Otsu, Japan, fujimori@rins.ryukoku.ac.jp

² Department of Environmental Engineering, Graduate School of Engineering, Kyoto University, 615-8540, Kyoto, Japan

³ Center for Material Cycles and Waste Management Research, National Institute for Environmental Studies (NIES), 16-2 Onogawa, 305-8506, Tsukuba, Japan

1 Introduction

Organo-fluorine compounds have been widely used because of their water repellency and thermal/chemical stability. Recently, however, perfluorooctanoic acid (PFOA), its salts, and PFOA-related substances were added to the list of Persistent Organic Pollutants (POPs) for elimination under the Stockholm Convention on POPs, and appropriate decomposition treatment will be required for PFOA waste and stocks. The possibility that perfluorohexanesulfonic acid (PFHxS), which were used as alternatives to perfluorooctanesulfonic acid (PFOS; subject to restriction under the POPs Convention), may also be subject to the POPs Convention in the near future is under discussion. PFOA, PFHxS, and PFOS are referred to as "fluorinated POPs" in this paper. For PFOS, which are already subject to restrictions, decomposition by incineration is being promoted, and an operating condition of 850°C or higher and a residence time of 2 seconds or longer is recommended in Japan.

There are some reports and recommendations on the destruction of PFOA by incineration at high temperatures exceeding 1000°C, and the persistence of PFOA due to its strong carbon-fluorine bonds (C-F) has been considered.^{1,2} However, there are few examples of studies evaluating the destruction behavior of PFOA by incineration in terms of temperature dependence and by the media generated after incineration. As for PFHxS, there is a report on the basic study of the change in thermal weight³, but no examples of decomposition studies by incineration have been found. These salts seem to be at the stage of just coming up for discussion as a subject of study.

The objective of this study was to understand the destruction behavior of fluorinated POPs and their salts by incineration by conducting laboratory-scale incineration tests using pure reagents and detailed media after incineration. Comparative evaluation of destruction characteristics regarding destruction efficiency, temperature dependence, distribution in media after incineration, and by-products was attempted for fluorinated POPs and their salts.

2 Materials and Methods

2.1 Samples

High purity PFOA and PFHxS reagents and aqueous solutions of PFOS were used. NH₄ salt of PFOA, K salt of PFHxS, and K salt of PFOS were used as salts. PFHxS was adjusted to aqueous solution due to its deliquescency. The initial concentrations of PFOS and PFHxS were 41.2% and 37.1%, respectively, according to instrumental analysis. For the application of PFOA, a sample (PFOA-model) simulating major foam extinguishing agent was prepared and used in the experiment. PFOA-model is a mixture of 70% water and 25% ethylene glycol with PFOA. Instrumental analysis showed that the PFOA concentration was 1.2% (coefficient of variation 16%, $n = 6$).

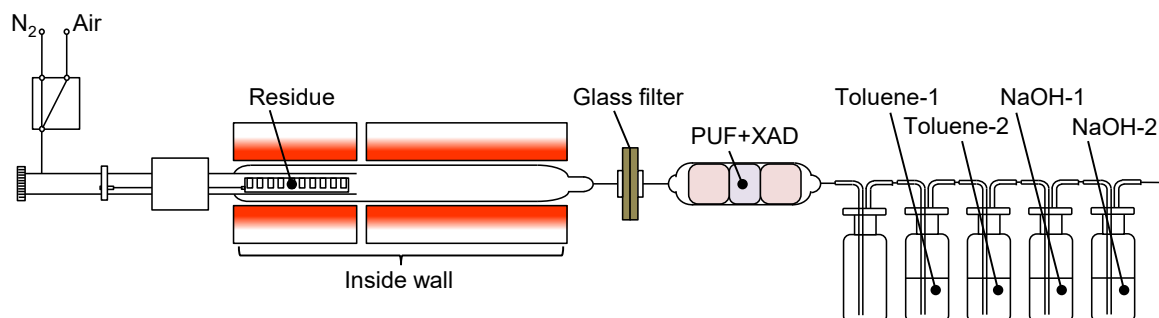


Figure 1: Lab-scale controlled furnace.

2.2 Incineration Test

Incineration tests were conducted using a lab-scale controlled furnace as shown in Figure 1. A glass filter, adsorbent, two toluene traps, and two NaOH traps were connected downstream of the furnace to collect the exhaust gas. Glass fiber filter paper (055120N-SPGFC, As One) was used as the glass filter, and polyurethane foam (PUF, 22 mm O.D. × 76 mm, Restek) and XAD resin (XAD-2, Merck) as the adsorbent. Toluene and 0.1 mol/L NaOH were used in 120 mL each and 50 mL each. Incineration tests were conducted at temperatures of 850°C, 950°C, and 1000°C, with a residence time of 2 seconds and a pure air atmosphere (flow rate of 1.107 L/min). A sample equivalent to about 10 mg was placed in each of the 10 cylindrical holes on the quartz boat. The quartz boat was fed into the quartz tube in the furnace at a speed of 1 cm/30 sec. This was set based on the sample load at a typical municipal solid waste treatment facility (5-10 kg/h/m³).

2.3 Pretreatment and Instrumental Analysis

After incineration, samples were collected in total 9 types: Upstream of quartz tube, sample boat, downstream of quartz tube (referred to as adhered material), glass filter, adsorbent (PUF × 2 combined with XAD), toluene first and second stage, NaOH first and second stage. Toluene samples, NaOH samples, and solid samples were adsorbed on a solid-phase cartridge (Oasis WAX Cartridge, Waters) after adding internal standards as appropriate, extraction, and concentration operations. Subsequently, fractions were separated by elution and nitrogen concentration, and subjected to instrumental analysis by LC/MS. The recovery of the PFOA internal standard of the actual sample by this pretreatment was 49-102%, showing good results. In addition to PFOA, PFHxS, and PFOS, which are the main analytes, we attempted to quantify a total of 16 organofluorine compounds (abbreviated as PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUDA, PFDoA, PFTTrDA, PFTeDA, PFBS, PFHxS, PFHpS, PFOS, and PFDS).

2.4 Destruction Efficiency

The destruction efficiency (DE) of fluorinated POPs by incineration was determined by the following equation.

$$DE [\%] = (A_i - A_{s+l+g})/A_i \times 100$$

Where A_i : Initial amount (g), A_{s+l+g} : Amount in solid, liquid, and gas phase after incineration (g). Data upstream of the quartz tube were not included in the DE calculations because the media in the incinerator and in post-incineration zone were considered appropriate for evaluating destruction by incineration.

3 Results and Discussion

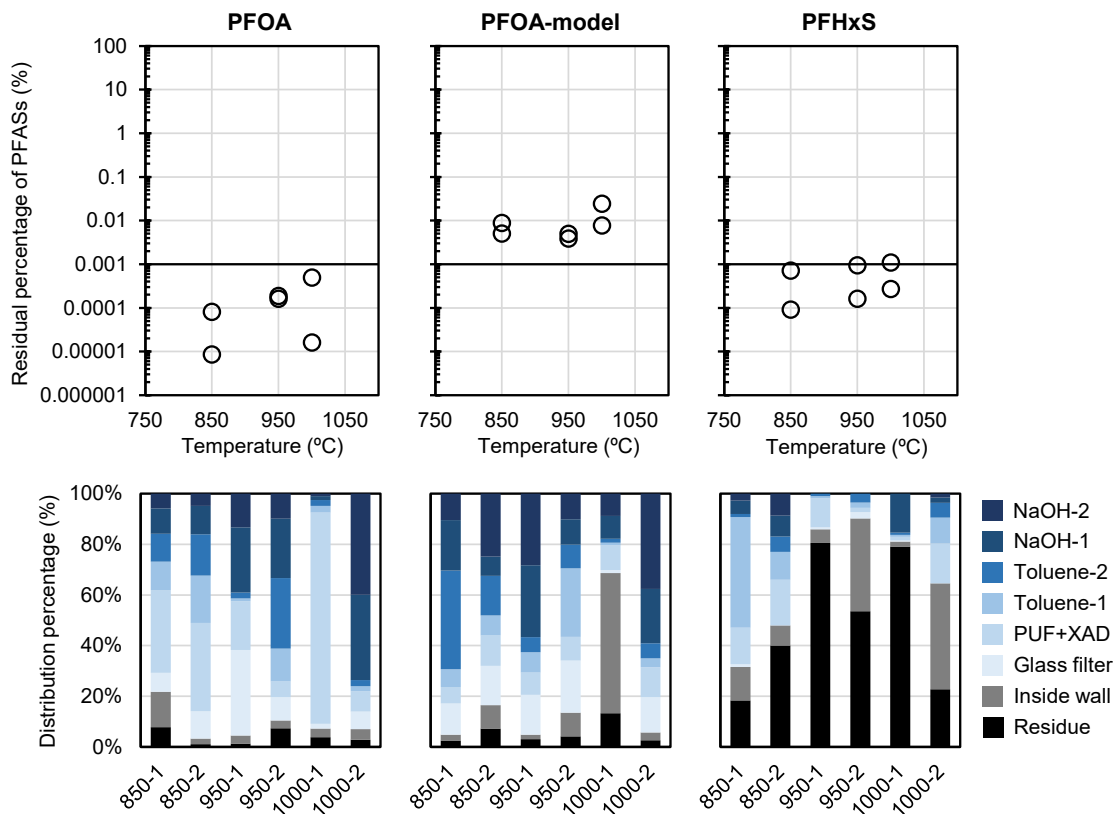


Figure 2: Destruction behavior by incineration (temperature dependence).

3.1 Destruction Efficiency

Figure 2 shows the destruction behavior of PFOA and PFHxS, as well as PFOA-model, organized in terms of temperature dependence. The vertical axis of the scatter plot indicates the residual rate (= 100 – DE) of the substance to be decomposed, and a residual rate below 0.001% is considered to exceed the DE of 99.999% recommended by the Basel Convention for POPs⁴. The reproducibility of the destruction characteristics was examined by conducting two incineration experiments at the same temperature, and the results showed relatively good reproducibility with some exceptions. PFOA and PFHxS showed the DE exceeding 99.999% at 850 – 1000°C, regardless of temperature. Residuals tended to be lower for PFOA than for PFHxS. In other words, destruction of PFOA was easier than that of PFHxS by incineration. On the other hand, PFOA-model tended to be less degradable than pure PFOA alone, and there was no clear effect of incineration temperature, suggesting that the coexisting substances (water and ethylene glycol) in the PFOA-model may have inhibited the efficiency of destruction by incineration.

3.2 Distribution Behavior

The stacked bar graph in the lower part of **Figure 2** shows the distribution behavior of fluorinated POPs to various media after incineration. The distribution behavior of PFOA in the PFOA-model is similar to that of the PFOA-model, indicating that PFOA remaining after incineration, whether in solution or not, accounts for a large proportion of the exhaust gas. PFOA's tendency to vaporize⁵ may have allowed it to migrate into the exhaust gas at a later stage. In contrast, PFHxS tends to be more concentrated in the residue and in the downstream inner wall as solids attached as particles.

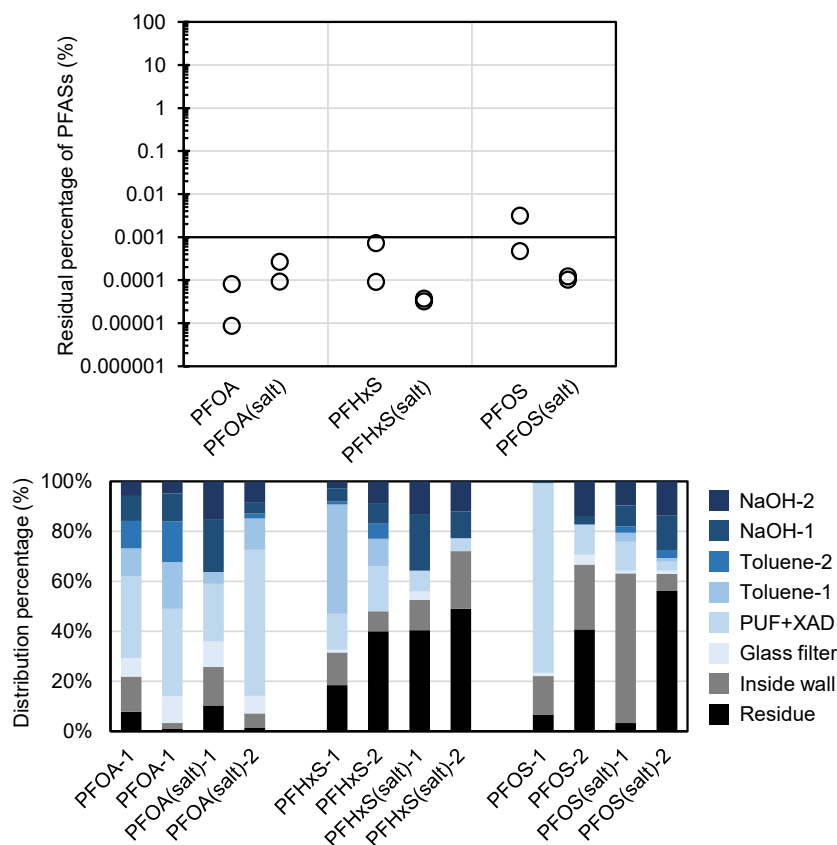


Figure 3: Destruction behavior by incineration (salts).

3.3 Salts

Figure 3 compares the decomposition behavior of PFOA salts and PFHxS salts by incineration under the same incineration temperature conditions (850°C). The salt of each fluorinated compound is indicated as "salt" in parentheses. In the case of PFOA, no significant differences were observed between the pure substance and its salts, showing almost the same decomposition characteristics. The pyrolysis behavior of PFOA salts is not significantly different from that of PFOA. On the other hand, PFHxS tended to show higher destruction rates in its salts. A similar trend was observed for PFOS and its salts. The distribution behavior of PFHxS and PFOS was not clearly different compared to their salts.

3.4 By-products

Trace amounts of fluorinated compounds other than the target substances, which are thought to have been produced by incineration and decomposition, were detected (**Table 1**). Trace amounts of PFHxA and PFHpS with a reduced carbon number were detected by incineration of PFOA and PFOS, respectively. PFHxA was detected by incineration of PFHxS with a sulfo group replaced by a carboxy group. PFOA was also detected by incineration of PFOS with a sulfo group replaced by a carboxy group. Reactions that increase the carbon number were also suggested. For example, PFHxS → PFOS. The detection of sulfo group-containing substances from carboxy group-containing substances is suspected to be a possible experimental origin of very small amounts of contamination.

Table 1: By-products detected by incineration.

	Byproducts					
	PFOS	PFHpS	PFHxS	PFOA	PFHpA	PFHxA
PFOA	✓					✓
PFHxS	✓			✓	✓	✓
PFOS		✓	✓	✓	✓	
PFOA(salt)	✓	✓				
PFHxS(salt)	✓	✓		✓		
PFOS(salt)		✓	✓	✓		

4 Conclusions

In this study, a comparative evaluation of the destruction characteristics of fluorinated POPs and their salts by incineration was conducted. Basic knowledge of the detailed degradation behavior of fluorinated POPs and their salts by incineration was clarified. Pure substances and their salts showed good destruction efficiency in common. On the other hand, the destruction efficiency of PFOA-model, which was simulated as a foam fire extinguishing agent, was about one order of magnitude lower than that of the pure PFOA. The distribution behavior after incineration showed a high ratio of sulfo group-containing compounds migrating to the solid side and carboxy group-containing compounds migrating to the exhaust gas side. Instrumental analysis of 16 substances showed trace amounts of fluorinated compounds as by-products. We plan to conduct future incineration tests on actual foam fire extinguishing agents.

5 Acknowledgments

This work was performed by the Environment Research and Technology Development Fund [JPMEERF20213002, 3-2102(1), (3)] of the Environmental Restoration and Conservation Agency (ERCA) of Japan and Grant-in-Aid for Scientific Research (A) (20H00646 and 20H00634) of the Japan Society for the Promotion of Science (JSPS). We thank Ms. Ayano Terada and Mr. Kento Ito (Kyoto University) for pretreatment and Dr. Satoshi Endo (NIES) for a comment on the physicochemical properties of PFOA.

6 References

1. Winchell et al. Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review. *Water Environ. Res.* 1-18, 2020.
2. Tsang et al. On the incinerability of highly fluorinated organic compounds. *Combust. Sci. Technol.* 139(1), 385-402, 1998.
3. Xiao et al. Thermal stability and decomposition of perfluoroalkyl substances on spent granular activated carbon. *Environ. Sci. Technol. Lett.* 7, 343-350, 2020.
4. UNEP. Technical guidelines: General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants. 2019. UNEP/CHW.14/7/Add.1/Rev.1.
5. Zhang et al. Vapor pressure of nine perfluoroalkyl substances (PFASs) determined using the Knudsen Effusion Method. *J. Chem. Eng. Data* 65(5), 2332-2342, 2020