Summary of the Guideline on the Treatment of Wastes Containing Perfluorooctane Sulfonic Acid (PFOS), and Its Salts in Japan

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A. Introduction

1. Japan designated perfluorooctane sulfonic acid (PFOS), its salts, and perfluorooctane sulfonyl fluoride (PFOSF) as Class I Specified Chemical Substances under the Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture on April 1, 2010, pursuant to the Decision of the Stockholm Convention on Persistent Organic Pollutants on its Fourth Conference of the Parties to add these substances to Annex B. Under the said act, appropriate measures are taken such as developing an approval system for the manufacture and import of these chemical substances, and limiting their use except under certain permitted conditions.

2. The Stockholm Convention prescribes that wastes containing persistent organic pollutants shall be processed for destruction or to irreversibly transform such pollutants so that their hazardous characteristics are no longer detectable, unless the contents of the pollutants in wastes are low enough.

3. To meet this requirement, the Japanese Ministry of the Environment issued in September 2010 the "Technical Guideline for the Environmentally Sound Treatment of PFOS Wastes", which describes the environmentally sound management of wastes containing PFOS and its salts (hereafter referred to as "wastes containing PFOS") and their storage, entrustment of treatment, transport and destruction method, in line with the Waste Management and Public Cleansing Act.

4. This document provides a summary of the "Technical Guideline for the Environmentally Sound Treatment of PFOS Wastes", and as a reference material, introduces an overview of experiments on destruction of wastes containing PFOS, and the calculation method for the emission standards of PFOS and its salts in effluent and residues.

B. Summary of the Technical Guideline for the Environmentally Sound Treatment of PFOS Wastes

1. Backgrounds and Objective

The present technical guideline provides a practical guide concerning the environmentally sound treatment of wastes generated during the manufacture or the use of products containing perfluorooctane sulfonic acid (PFOS) and its salts (hereafter referred to as “wastes containing PFOS”), with the aim of protecting the living condition and improving public health in Japan. This technical guideline is developed in accordance with the decision of the Stockholm Convention on Persistent Organic Pollutants on its Fourth Conference of the Parties in May 2009 to add these substances to Annex B, and in line with the Waste Management and Public Cleansing Act and other related laws in Japan.

2. Scope

This technical guideline applies to wastes (industrial wastes) in solid or liquid forms that are generated during the manufacturing process or the use of products containing PFOS.

3. Storage

3.1 Storage

Wastes containing PFOS should be stored at sites that meet the following criteria:

(1) The sites should be surrounded with a fence,
(2) A signboard that meets the following criteria should be put up at a conspicuous place:
    i. The length of the horizontal and vertical sides of the board should be more than 60 centimeters each,
    ii. The following items must be indicated on the board:
        - The site is for the storage of wastes containing PFOS
        - The type of waste containing PFOS stored at the site
        - The maximum height of wastes containing PFOS piled up at the site
        - The name and contact information of the administrator of the site
        - Other necessary information.
    iii. Appropriate measures should be taken to prevent the scatter, leakage, underground seepage, or the spread of bad odor from the wastes containing PFOS at the site.
(3) The inhabitation of rodents, and the occurrence of mosquitoes, and other pests at the site should be prevented.

(4) Necessary measures, such as setting up partitions, should be taken to avoid contamination of the wastes containing PFOS at the site.

3.2 Storage Container

To store wastes containing PFOS, containers that meet the following criteria should be used.

(1) The container should be sealable.
(2) The container should be easy to store.
(3) The container should be indestructible.

3.3 Labeling

Operators (*1) handling the products containing PFOS such as etching agents for semiconductors, resists, photographic films, fire extinguishers and fire-extinguishing foam, (*2) must comply with the following:

（Technical criteria on specific duties regarding handling of the listed products,

(Storage method, transfer method of the content of product, book and record keeping of the number of stored product, treatment for leakage of the content of product, etc.)

(1) Duty to label listed product in case of transfer or release.

(A label should indicate that the product contains PFOS, the proportion of PFOS content, specific instructions, and contact information of the person in charge of labeling)

*1 Permitted manufacturers, operators using Class I Specified Chemical Substances in business, transporters, storage operators, and others.

*2 Regarding fire extinguishing foams, PFOS is not essential for their manufacture. However, there is a considerable stock of the product containing PFOS, and it is considered difficult to replace these stocks with substitutes within a short period of time because they are used only during disasters. It is therefore necessary to prevent environmental pollution by setting technical criteria on handling and labeling obligation.

4. Monitoring

To entrust the transport or treatment of wastes containing PFOS as industrial wastes, the entruster must issue a control manifest for industrial waste (hereafter referred to as “manifest”), confirm the returned manifest at the completion of transport, intermediate treatment and final disposal at each stage, and keep the returned manifest on file for five years.

5. Transport

The transporter must comply with the following criteria:

(1) Scattering or leakage of the wastes containing PFOS should be prevented during their transport.

(2) Appropriate measures should be taken to prevent adverse effects on the living condition resulting from bad odor, noise, or vibration caused by the transport of wastes containing PFOS.

(2) The transporting vehicle and the container should ensure that no scattering, leakage or bad odor of the wastes containing PFOS will occur.

(4) To avoid mixing with other materials, wastes containing PFOS should be handled separately during the process of collection and transport.

6. Technique for Destruction Treatment

(1) The method of destruction must ensure that PFOS and its salts are completely destroyed. In addition, levels of PFOS and its salts in the effluent and its residues, as well as levels of hydrogen fluoride in the exhaust gas and effluent should not exceed interim emission standards.

(2) Target level of destruction and interim emission standards

1) The destruction level of PFOS and its salts must be over 99.999%.

2) The content of PFOS in the effluent and residues released during the process of destruction shall not exceed the following standards:

i. Effluent:	2 μg/ℓ,
ii. Residue:	3 mg/kg.

3) The contents of hydrogen fluoride in the emission gas as well as fluorine and its compounds in the effluent that were released during the process of destruction shall not exceed the following standards. In case stricter standards are set by other codes or related legislations, they would supersede the following standards:

i. Emission gas: 5mg/m^3N,

ii. Effluent (pursuant to the Water Pollution Control Law):

- Public water except for the sea	8mg/l,
- The sea	15mg/l.

Annex 1

An Overview of the Incineration Experiment I on Wastes containing PFOS and its Salts

1. Objective

The purpose of this experiment was to simulate the condition of liquid PFOS used as fire-extinguishing fluid when treated in commercial incineration facilities for industrial wastes, and to verify the destruction rate of PFOS and its content levels in the flue gas, residues and effluent, as well as the content levels of its by-products.

2. Method

2.1 Commercial waste incineration facility used for the experiment

Fig.1 shows the schematic flow of the commercial waste incineration facility and the sampling points for PFOS.

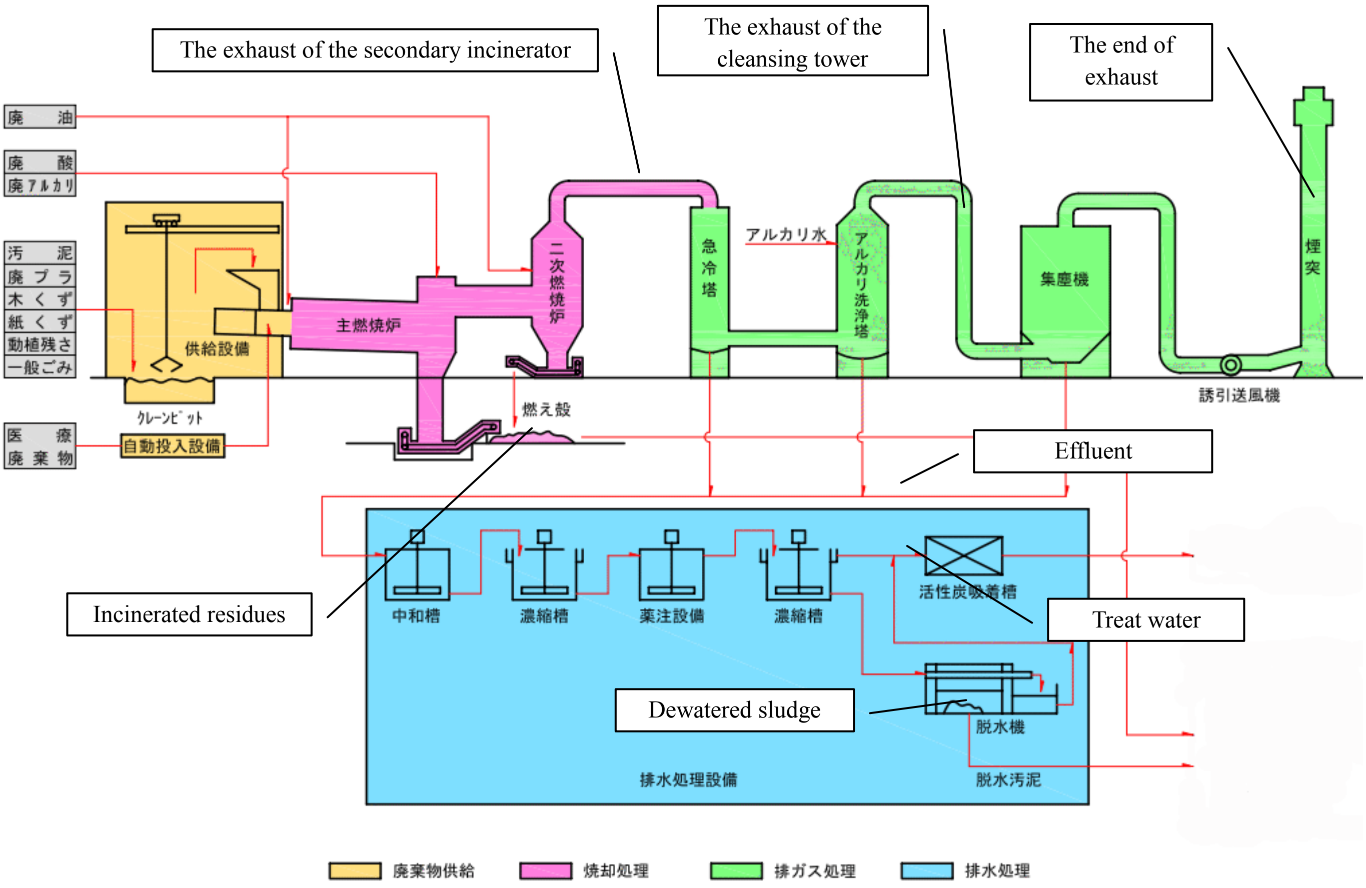

Fig.1 The schematic flow of the incineration facility used for the experiment and the sampling points for PFOS

An overview of the waste incineration facility is described below.

(1) Incinerator

The incinerator consists of a primary furnace (a rotary kiln) and secondary furnace. Incineration temperatures are 1,100 °C in the primary and 900 °C in the secondary furnaces. The combined gas retention time in the primary and secondary furnaces is approximately 8 seconds, and the average retention time for solid materials in the rotary kiln is 1 to 1.5 hours.

(2) Flue gas treatment facility

The flue gas treatment facility includes: the quenching tower that instantly cools down the flue gas from 850-900 °C to 80 °C; the cleansing tower that conducts absorptive treatment of the acidic gas through alkali cyclic water; and the wet-type electric dust collector (a mist Cottrell precipitator) that functions as a dust removal device. After removal of the acidic gas, a portion of the cyclic water is extracted as slurry discharge, and is transferred to the effluent treatment facility.

(3) Effluent treatment facility

The slurry discharge is mixed with those from other incinerators and effluents from other facilities within the site. After heavy metals are fixed using chelate agents and sedimentation separation is conducted using flocculation agents, the effluent and the dehydrated sludge are separated in a dehydrator. The effluent is combined with those from other facilities to be treated at the effluent treatment facility and then released.

2.2 Method of the experiment

This experiment consists of the main incineration test, where the simulated wastes containing PFOS are cast in during the routine waste treatment time, and the blank test, which is incineration without the simulated wastes containing PFOS.

(1) Wastes containing PFOS

The PFOS-containing-simulated-waste used for this experiment is a fire extinguishing foam containing potassium salts of PFOS, which finds application in fire extinguishing equipments among others (hereafter referred to as “fire-extinguishing foam containing PFOS”). The content of PFOS in the simulated waste is approximately 0.67% (the setup value at the time of manufacturing). Presently, a considerable number of fire-extinguishing foams containing PFOS are placed and kept in buildings, and it is expected that these would be discarded after periodic inspections, trainings, disasters, and disposals.

The simulated wastes, 4 kg each, were packed separately in plastic containers, and were continuously cast into the incinerator from the automatic input line for infectious wastes. The input rate per hour was set as 29.4 packs (118kg/h).

(2) Condition of the experiment

Incineration temperatures in the experiment are shown in Table 1.

Table 1 Incineration temperatures during the experiment

Location	Blank test	Main Incineration test
Gas temperature at the exhaust of the primary incinerator	Maximum 1,129°C Average 1,094°C Minimum 1,057°C	Maximum 1,126°C Average 1,088°C Minimum 1,034°C
Gas temperature at the exhaust of the secondary incinerator	Maximum 952°C Average 917°C Minimum 883°C	Maximum 966°C Average 896°C Minimum 832°C
Gas temperature at the exhaust of the cleansing tower	Maximum 80.7°C Average 79.6°C Minimum 78.2°C	Maximum 80.1°C Average 78.9°C Minimum 77.5°C

(3) Items for analysis

The items analyzed at each sampling point are shown in Table 2.

Table 2 Items analyzed at each sampling point

Type of facility	The simulated waste	Other waste	The exhaust of the secondary incinerator	The exhaust of the cleansing tower	The end of exhaust	Incinerated residues	Effluent	Dewatered sludge	Treatment water
Item 1	*	*	*	*	*	*	*	*	*
Item 2			*	*	*				
Item 3	*	*				*		*	
Items for analysis	Item 1: PFOS, PFOA, other related substances of PFOS/PFOA, all fluorine (organic fluorine and inorganic fluorine) Item 2: The amount of gas, the flow rate of gas, the amount of water, the amount of soot and dusts, CO, O_2, Hydrogen fluoride, Fluorocarbons Item 3: The generated amount and input of moisture, ash, and the flammable components during the experiment								

3. Summary of the result

(1) The destruction rate of PFOS

The rate of destruction of PFOS was estimated based on the result of the incineration experiment. The calculation formula for the estimation is as shown below. From the result, the destruction rate was calculated to be more than 99.999%.

Destruction rate = (Total amount of input [*1] – Total amount of emission [*2])/ Total amount of input ×100

*1 The total amount of input (μg): The amount of PFOS in usual waste + the amount of PFOS in waste containing PFOS.

*2 The total amount of emission (μg): The amount of PFOS at the final emission point of flue gas + the amount of PFOS in the residues after destruction + the amount of PFOS in the slurry discharge

*3 The amount for a 5-hour period was used in the estimation. In case the amount was below the minimum determination limit, the minimum determination limit value was applied.

・The destruction rate of PFOS

$$\frac{((73{,}100+4{,}100{,}000{,}000)-(188+316+3{,}950+7.8))\times 100}{(73{,}100+4{,}100{,}000{,}000)}$$

$$= \frac{(4{,}100{,}073{,}100-4{,}461.8)\times 100}{4{,}100{,}073{,}100}$$

$$\fallingdotseq \underline{\mathbf{99.999891\%}}$$

(2) Hydrogen fluoride

It was observed that, in the main test and the blank test, the behaviors of hydrogen fluoride in the flue gas were nearly the same. This result indicates that no effects by the input of the waste containing PFOS occurred. The content of hydrogen fluoride in the final emission of flue gas was at the determination limit（0.5mg/Nm3）, which was below the emission standard under the guideline for the destruction treatment of CFC.

The content of fluorine and its compounds in the effluent was 5.1mg/L in the main test, and 6.9mg/L in the blank test. These data showed no significant differences, and were below the emission standard（8mg/L）.

(3) Fluorocarbons

In the main test and the blank test, the content of fluoric carbons at the emission point of the second furnace and the cleansing tower, and the final emission point were below the determination limit. It was observed that no significant production of fluoric carbons due to incineration of PFOS occurred.

(4) Chlorinated dioxins

In the main test and the blank test, it was observed that the behaviors of chlorinated dioxins were nearly the same. This indicates that no effects by the input of the waste containing PFOS occurred.

The TEQ of chlorinated dioxins in the flue gas, the effluent and the ashes (residues and dehydration sludge) were below the Japanese emission standard.

Annex 2

Target concentrations of PFOS and its salts in effluent and residues released during the destruction treatment process

The target emission concentration of PFOS released during the process of destruction treatment of waste containing PFOS (hereafter referred to as "emission standard reference guide") was calculated according to the methods described below. Since PFOS is highly soluble in water and no evidence of its transition to flue gas was confirmed in the incineration experiment conducted by the Japanese Ministry of Environment, the emission standard reference guide for flue gas was therefore not studied.

1. Emission standard reference guide for effluents

The impact on human health of the intake of PFOS and its salts, resulting from their seepage into the underground water through treated water and other discharges released from the effluent treatment facility, was taken into account when studying the emission standard reference guide for effluents.

According to the primary environmental risk assessment issued by the Japanese Ministry of the Environment ("The environmental risk assessment on chemical substances", Vol.6, May, 2008), ADI for human health is referred to as 0.03mg/kg/day based on NOAEL for rodents. This value was compared with the standard concentration for drinking water in Germany, and the NOAEL of 0.10µg/kg/day, which is equal to the ADI in the said German standard, was the value adopted as the safe side. Calculations were as follows.

Target concentration in drinking water = ADI ×Body weight (50.0kg) × Pathway allocation for water (0.1) ÷ daily intake of water (2L)

The reference standard for effluent was calculated based on the above value and emission standards under the Water Pollution Control Act. The dilution concentration was set at 10:

＝0.2μg/L×10
＝2μg/L

2. Emission standard reference guide for residues

Residues (including incinerated residues and polluted sludge) were regarded as soil, and their impact on human health through food intake and skin absorption was taken into account when studying the emission standard reference guide for residues. As with effluents in section 1, concentrations in residues were calculated, using 0.10μg/kg/day for ADI, as follows.

Target concentrations residues =ADI (0.10μg/kg) ×Body weight (50.0kg) ×Pathway allocation for soil (0.1) ÷(Lifetime average daily intake of soil (108.6mg)+ Lifetime average daily skin contact with soil (463.8mg) ×Absorption rate (0.1)

The basis for each parameter is as follows:

Lifetime average daily food intake of soil = (Daily food intake of soil (children) (200mg/day) ×6 (years) ＋Daily food intake of soil(Adults)(100mg/day)×64(years))÷Years in a lifetime (70 years)

Lifetime average daily skin contact with soil= Daily skin contact with soil per unit skin area(0.5mg/m^2/day) ×Skin area(children)(2800cm^2) ×Rate for sunny day (0.6) ×Rate for touching the soil outdoors (children, 7/7) ×6(years) + Daily skin contact with soil per unit skin area (0.5mg/m^2/day) Skin area(adult)(5000cm^2) × Rate for sunny day (0.6) ×Rate for touching the soil outdoors (adults, weedends: 2/7) ×64 ÷Years in a lifetime.

Absorption rate: Although it is assumed that absorption of PFOS through the skin is rare, information on the absorption rate is insufficient to date. Therefore, the default value used by the Environmental Protection Agency of the United States was employed in this calculation.

Reference：USEPA: RAGS, Part E, Supplemental Guidance for Dermal Risk Assessment, Interim Guidance, 2001.

3. Verification of the emission standard reference guide

The calculated emission standards were compared to the minimum limit of determination of PFOS, its emission concentration and data measured in the environment. Results of the comparisons revealed that the reference emission levels exceeded the minimum limit of determination, as well as the data measured at the point of PFOS generation source (including the experiment on incineration conducted by the Japanese Ministry of Environment). Meanwhile, the standard concentration for drinking water used in the calculation of effluent was confirmed to be very close to the standards for drinking water in other countries (including tentative standards), and exceeded the data measured in the environment.

Table 1 Comparisons of the emission standard reference guide, the minimum limit of determination and data measurements

Items for comparison	Effluent	Residues
Reference emission standard	2μg/L (Reference for the concentration in drinking water: 0.2μg/L)	3mg/kg
Minimum limit of determination (based on the incineration experiment)	0.0002μg/L	0.5μg/kg
Case examples in other countries	[The US] Interim recommendation on human health impact of PFOS in drinking water: 0.2μg/L 1) [Germany]HRIV HRIV※ : 0.3μg/L（drinking water） 2) [England] Initial audit standard: 0.3μg/L（drinking water） 3)	[Minnesota, the US] 9) Residence area: 2mg/kg Industrial area：14mg/kg [Technical Guideline on the waste containing POPs] 10) Low POP content: 50ppm
Data taken in Japan (Emission concentration)	Treated water from a semiconductor manufacturing factory: Maximum 1.6μg/L4) Treated water from a sewage treatment plant: 0.042-0.635μg/L 5) Treated water from a sewage treatment plant: 0.003-0.15μg/L5) Treated water from a final disposal site: ＜ 0.001-0.0043μg/L（PFOA） 6)	[Result of the incineration experiment] Residues from the destruction: Below the minimum limit of determination (0.1μg/kg) Dehydrated sludge: 5-11μg/kg
Data taken in Japan (Concentration in the environment)	0.0007～0.16μg/L（2002）(Fresh water)7) 0.0073～0.011μg/L（2005）（Sea water） 8)	Bottom sediment（Fresh water） 11), 12) <0.000096～0.0043mg/kg Bottom sediment (Sea water) 8), 11) <0.000096～0.00035 mg/kg

※HRIV：permanent tolerable, health-related indication value

reference：

1) USEPA: Provisional Health Advisories for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS), January 8, 2009

2) Ministry of Health at the Federal Environment Agency: Provisional evaluation of PFT in drinking water with the guide substances perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) as examples, Statement by the Drinking Water Commission (Trinkwasserkommission) of the German, June 21, 2006 (revised July 13, 2006)

3) DRINKING WATER INSPECTORATE: Guidance on the Water Supply (Water Quality) Regulations 20001 specific to PFOS (perfluorooctane sulphonate) and PFOA (perfluorooctanoic acid) concentrations in drinking water, October 2009

4) Japan Electronics and Information Technology Industries Association

5) T. Omata, Y. Takashima, T. Nishino, Y. Sasaki, D. Kitano: Identification of the emission sources of PFCs through an investigation on sewage water and discharged water from facilities. Proceeding for the 18th Conference of Environmental Chemistry in Japan: 544-545., 2009

6) M. Yagi, A. Yamaji, I. Shibutani: The behavior of organic fluorine compounds during the treatment of leachate released from final disposal sites. Proceeding for the 18th Conference of Environmental Chemistry: 558-559., 2009

7) K. Harada, N. Saito, K. Inoue, A. Koizumi: Perfluorooctane Sulfonate Contamination of Drinking Water in the Tama River, Japan: Estimated Effects on Resident Serum Levels. Bull. Environ. Contam. Toxicol. 71:31-36., 2003

8) Environmental Health and Safety Division, Environmental Health Department, the Japanese Ministry of Environment: Survey on chemical substances in the environment in fiscal year 2005, 2007

9) Helen Goeden: Issues and Needs for PFAA Exposure and Health Research: A State Perspective, 2008

10) Basel Convention: Updated general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (POPs)

11) Environmental Health and Safety Division, Environmental Health Department, The Japanese Ministry of Environment: Survey on chemical substances in the environment in fiscal year 2003, 2005

12) Osaka Prefectural Government, Japan: Survey on the water quality including perfluorooctanoic acid in waters around Kanzaki River in Osaka, 2007

Annex 3

Amount of waste containing PFOS for treatment

Currently, the treatment of wastes containing PFOS is in progress in accordance with the "Technical Note on the Environmentally Sound Treatment of Wastes containing PFOS" (drafted in September 2010, revised in March 2011) in Japan. The Japanese Ministry of Environment has conducted confirmation experiments on destruction treatment at 13 sites to ensure that the level of destruction is adequate and the treatment is carried out in an environmentally sound manner. The amounts of wastes containing PFOS that were treated at these sites until the end of August 2012 are 847.4t.

Assuming that all 847.4t of the wastes containing PFOS that were treated after the release of the said technical note was fire-extinguishing foam, the content level of PFOS and its salts was estimated as 2.72t (content rate: 0.32% *1). This would account for approximately 2% of 134,370kg, which is the total amount of PFOS and its salts in all fire extinguishing foams that are out in the market.

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*1 The average content rate of PFOS in the fire-extinguishing foam sold in 2008.

*2 Document No. 2 "Mass flow of the waste containing PFOS (revised)" circulated at the second meeting of the panel for the environmentally sound treatment of waste containing PFOS (the fiscal year 2010)