Guidelines on the Destruction of CFCs in Japan

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Office of Fluorocarbons Control Policy Global Environment Bureau Ministry of the Environment Government of Japan

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1. Purpose

Recovery, recycling and destruction of used chlorofluorocarbons (CFCs) are critical measures to the protection of the ozone layer, as well as control of production and consumption of CFCs.

For this purpose, the 4th Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer held in November 1992 adopted a decision to urge the Parties to take all practical measures to recover used CFCs for purposes of recycling, reclamation and destruction. In Japan, the "Conference for Ozone Layer Protection", which consists of eighteen relevant ministries and agencies, compiled details of the "promotion of recovery, recycling and destruction of CFCs" in June 1995 and updated in September 1997. Various programs have been implemented based on this policy.

In order to establish CFC destruction technologies as soon as possible, the Ministry of the Environment conducted short-term CFC destruction tests with rotary kiln and cement kiln in 1994 and 1995, and developed the "Guidelines on the Destruction of CFCs" accordingly in May 1996. In addition, the Ministry conducted demonstration tests over these destruction technologies on long-term and periodic basis as well as other destruction technologies in 1996 and 1997. The Ministry has performed technical evaluation on their feasibility accordingly.

In order to rapidly disseminate the CFC destruction technologies and to promote recovery and destruction of CFCs, this document contains any necessary items to ensure appropriate CFC destruction through updating the previous guidelines based on the results of these evaluations.

2. Current CFC Destruction Technologies and Their Requirements

(1) Current Destruction Technologies

CFC destruction technologies are categorized into: (1) technology using a rotary kiln of waste incinerators (cylindrical rotational incinerator), (2) technology using a rotary kiln incinerator of cement production facilities, and (3) technologies using an existing waste incinerator other than rotary kilns, including those using a municipal solid waste direct fusion furnace and a fixed floor type two-staged combustion furnace, and (4) dedicated CFC destruction technologies, including a high-temperature steam thermal decomposition and a radiofrequency plasma destruction.

The United Nations Environment Program (UNEP) organized the UNEP Ad-hoc Technical Advisory Committee on ODS Destruction Technologies. As the results of studies by the Committee, UNEP recommended seven destruction technologies of the conventional ozone depleting substances destruction technologies, including the rotary kiln method, the cement kiln method and the plasma decomposition method. These methods were approved by the Meeting of the Parties to the Montreal Protocol.

(2) Requirements for Destruction Technologies

The CFC destruction technologies to be disseminated should generally meet the following requirements:

- 1) A high CFC removal efficiency;
- 2) Ensure to treat and dispose of chlorides, fluorides and a trace of toxic by-products in exhaust gasses, effluent water, ashes etc.;
- 3) Facilities with resistance against decomposition products such as chlorides and fluorides; and
- 4) Reasonable costs of equipment and operation.

3. Concept of these Guidelines

In development of these Guidelines, the Ministry took note the importance on protection of the ozone layer, understanding that CFCs do not have direct adverse impacts on human bodies, which is an important difference from other toxic substances such as PCBs.

These Guidelines are designed to compile items required to properly destroy CFCs based on the results from demonstration projects for the CFC destruction conducted by the Ministry of the Environment. The requirements described below are also applicable to destruction of hydrochrorofluolocarbons (HCFC) in principle.

These Guidelines may be reviewed and updated in the light of the latest knowledge and experiences.

4. Requirements for CFC Destruction

As mentioned in the above Paragraph 2.(2), it is necessary to ensure that CFC is efficiently destroyed and that toxic substances are not emitted in a considerable level through the destruction process. Specifically, the following items should be examined or measured and the operation control conditions as described in Paragraph 5. shall be reviewed in case of any inconformity with the requirements, and be corrected to meet the requirements.

(1) Verification of CFC Destruction

- a. The CFC concentration in the exhaust gas, and the quantity of CFC fed for destruction shall be identified. The CFC destruction shall be verified based on removal efficiency.
- b. CFC removal efficiency shall be checked by the CFC concentration in the exhaust gas or decomposition efficiency. The CFC concentration in the final exhaust gas shall be 1 ppm or lower or the decomposition efficiency shall be 99.99% or higher.
- c. In any facilities that destroy CFCs on a regular basis, the CFC destruction efficiency shall be checked according to the previous Paragraph b. at appropriate frequencies depending on the type of facilities (at least once per year). In particular, in introducing the CFC destruction technologies into facilities or drastically changing the operation control conditions of combustion temperatures etc., such check shall be assured.

(2) Measurement of Toxic Substances

- a. It shall be verified that the exhaust gas emitted from the CFC destruction facilities meet the standards specified by the applicable laws and regulations. The following items which could generate or increase through the CFC destruction shall be measured.
 - 1) Concentration of hydrogen chlorides (HCl) in the final exhaust gas
 - 2) Concentration of hydrogen fluorides (HF) in the final exhaust gas
 - 3) Concentration of dioxins in the final exhaust gas
 - 4) Content of fluorides in effluent water, and
 - 5) Concentration of hydrogen ions in effluent water
- b. The measurements shall be pursuant to the procedures set in the applicable laws and regulations and the standards such as the Japanese Industrial Standards (JIS).
- c. The measurements as prescribed in Paragraph a. shall be conducted at least once per year in addition to those required in the applicable laws and regulations. Furthermore, in introducing the CFC destruction technologies into facilities or drastically changing the operation control conditions of combustion temperatures etc. such check shall be assured.

(3) Measurement of Operation Control Conditions

- a. In order to verify the operation control conditions for each destruction method as provided in Paragraphs 5.(1) to 5.(4), the following items shall be measured:
 - 1) Physical conditions of the portions in the facilities where CFCs are destroyed, including the temperatures of combustion, or calcination and reaction
 - 2) Exhaust gas volume after treatment
 - 3) Concentration of carbon monoxide (CO) at the outlet of exhaust gas

If the facilities concerned destroy CFCs through thermal decomposition by incineration, the following item shall be also measured.

- 4) Concentration of oxide (O₂) at the outlet of the incinerator or the secondary combustion chamber
- b. The measurements shall be conducted at practical portions in terms of the structure of each facility. The measurements shall be pursuant to the procedures set in the applicable laws and regulations and the standards such as the Japan Industrial Standards (JIS).
- c. The measurements as provided in Paragraph a. shall be conducted on a daily basis.

5. Major Destruction Technologies and Their Operation Control Conditions

In order to perform appropriate CFC destruction, it is necessary to meet the requirements of selection of facilities and operation control conditions etc. for each type of CFC destruction technologies as follows.

(1) Rotary Kiln Method

a. Selection of Facilities

- (a) The facility shall be equipped with an appropriate exhaust gas treatment system including an anti-ash dust device such as a filter type dust collector and an acid gas treatment device such as a cleansing tower so that it meets the standards for concentration of ash dusts and toxic substances such as hydrogen chlorides generated due to the addition of CFC into wastes. An exhaust gas treatment system should be preferably designed to cool down heated combustion gas as soon as possible.
- (b) If the facility concerned discharges effluent water, it shall be equipped with an appropriate effluent treatment system so that it meets the standards for content of fluorides and concentration of hydrogen ion, etc. as provided by the applicable laws and regulations.
- (c) It shall be equipped with a system to properly deliver and discharge incineration ash dusts so that it prevents their influences on combustion conditions.

b. Operation Control Conditions

It is necessary to operate the incinerator so that successful destruction of CFC and safe control of exhaust gas are ensured. For this purpose, the combustion conditions shall be managed as follows:

- 1) Combustion temperature: 850°C or higher
- 2) CFC gas retention time in the combustion temperature range: two seconds or longer
- 3) Concentration of carbon monoxide (CO) at the exhaust gas outlet (corresponding a value to the oxide concentration of 12%): 100 ppm or lower

c. CFC Feeding Conditions

- (a) Wastes co-combusted with CFC shall have homogenous property as much as possible.
- (b) Quantity of CFC to be fed shall be determined taking into account the halide treatment capacity of the exhaust gas treatment system. In principle, the quantity of CFC should be around 2% of the wastes to be co-combusted.

d. The way of Feeding CFCs

- (a) CFC shall be sprayed at the position close to the burner under the normal operation control conditions.
- (b) Equipment for feeding CFC shall consist of an oil filter, a flow meter and other relevant devices to feed CFC quantitatively.
- (c) The quantity of CFC to be fed shall be properly controlled according to its flow rate.

(2) Cement Kiln Method

a. Selection of Facilities

The facility shall be equipped with a suspension pre-heater type incinerator or a new suspension pre-heater type incinerator and an exhaust gas treatment system for ash dusts so that it meets the standards for concentrations of ash dusts and toxic substances such as hydrogen chlorides generated due to the addition of CFC into raw materials and fuels.

b. Operation Control Conditions

It is necessary to operate the facility in a similar manner to ordinary cement production so that successful destruction of CFC and safe control of exhaust gas are ensured.

c. CFC Feeding Conditions

The quantity of CFC to be fed shall be determined taking into account the capacity of the exhaust gas treatment system and the influence on quality of products, or cement clinker.

d. The way of Feeding CFCs

- (a) CFC shall be sprayed at the position close to the burner before the kiln under the normal operation control conditions.
- (b) Equipment for feeding CFC shall consist of an oil filter, a flow meter and other relevant devices to feed CFC quantitatively.
- (c) The quantity of CFC to be fed shall be properly controlled according to its flow rate.

(3) Destruction Technologies Using Existing Waste Incinerators Other Than Rotary Kilns

Technologies using existing waste incinerators other than rotary kilns include those using municipal solid waste direct fusion furnaces, fixed floor type two-staged combustion furnaces, fluidized bed iron dust furnaces and lime rotary kilns.

For the technologies other than the technology using lime rotary kilns,

- The requirements for selection of facility for the rotary kiln method shall be applied to these technologies.
- The facility shall be operated and controlled under the same operation control conditions as normal incineration so that successful destruction of CFCs and safe control of exhaust gas are ensured.
- Wastes co-combusted with CFC shall have homogenous property as much as possible and halide treatment capacity of the exhaust gas treatment system shall

be taken into consideration, in feeding CFCs.

• CFC shall be sprayed at the bottom of the incinerator (tuyere, etc.). The equipment for feeding CFC shall consist of an oil filter, a flow meter and the other relevant devices to feed CFC quantitatively. The quantity of CFCs to be fed shall be properly controlled according to its flow rate.

For the technology using the lime rotary kilns,

- The facility shall be designed as a coal-fired type facility and other relevant types which contribute to reducing toxic substances. The facility shall be also equipped with an exhaust gas treatment system for ash dusts, etc.
- The facility shall be operated in a similar manner to the cement kiln method.
- CFC shall be fed in a manner that CFC is mixed with air from the bottom of the furnace under the normal operation control conditions, taking into account influences on the quality of burnt lime.

(4) Dedicated CFC Destruction Technologies

Dedicated CFC destruction technologies include the high-temperature steam thermal-decomposition technology and the radiofrequency plasma destruction technology.

a. Selection of Facilities

- (a) The radiofrequency plasma facility shall be equipped with an appropriate exhaust gas treatment system (cleansing tower, absorption tower, etc.) so that it meets the standards provided by the applicable laws and regulations for the concentration of toxic substances such as hydrogen chloride generated through the CFC destruction.
- (b) If exhaust gas is discharged from a lower position, not from a higher position such as chimneys, the radiofrequency plasma facility shall be managed so that it prevents significant increase in the concentration of toxic substances generated through the CFC destruction in the atmosphere around the facilities.
- (c) If CFC is destroyed through thermal decomposition by incineration, the exhaust gas treatment system shall be designed to rapidly cool down the exhaust gas as much as possible.
- (d) If the facility discharges effluent water, it shall be equipped with an appropriate effluent treatment system so that it meets the standards for content of fluorides and concentration of hydrogen ion as provided by the applicable laws and regulations.

b. Operation Control Conditions

It is necessary to operate the facility in accordance with the operation control conditions specific to the type of facility so that successful destruction of CFC and safe control of exhaust gas are ensured.

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1. Requirements for CFC Destruction

(1) Verification of CFC Destruction

[Paragraph 4.(1) of the Guidelines on the Destruction of CFCs]

- a. The CFC concentration in the exhaust gas, and the quantity of CFC fed for destruction shall be identified. The CFC destruction shall be verified based on removal efficiency.
- b. CFC removal efficiency shall be checked by the CFC concentration in the exhaust gas or decomposition efficiency. The CFC concentration in the final exhaust gas shall be 1 ppm or lower or the decomposition efficiency shall be 99.99% or higher.
- c. In any facilities that destroy CFCs on a regular basis, the CFC destruction efficiency shall be checked according to the previous Paragraph b. at appropriate frequencies depending on the type of facilities (at least once per year). In particular, in introducing the CFC destruction technologies into facilities or drastically changing the operation control conditions of combustion temperatures etc., such check shall be assured.
 - (a) To verify the CFC destruction, it is essential to identify the quantity of CFC fed (= CFC concentration in cylinders × the amount of the gas to be supplied) and CFC emission (= CFC concentration in the exhaust gas × the amount of the dry exhaust gas). The CFC concentration or removal efficiency (%) (= (1-(CFC emission/the quantity of CFC fed)) × 100) can be used as an index for the evaluation of CFC destruction. The CFC concentration in the exhaust gas is easy to be understood in the light of the comparison with general ambient concentration, while it cannot evaluate an efficiency of the CFC destruction. On the other hand, the removal efficiency is easily interpreted as an efficiency of the CFC destruction, although the value significantly varies depending on the level of supplied amount if the CFC concentration in the exhaust gas is not more than the determination limit.
 - (b) These Guidelines set the indicative CFC concentration in the exhaust gas of "1 ppm or lower". This is adopted referring to the following information:
 - 1) the Germen Electrical and Electronic Manufacturers' Association (ZVEI: Zentralverband Electrotechnik - und Electronikindustrie e.V.) sets the voluntary exhaust gas limit of 100 mg/Nm³ (=19 ppm) required for plants to recover CFC from waste refrigerators; and
 - 2) the destruction facilities can control the CFC concentration in the exhaust gas more certainly than the above-mentioned CFC recovery plants,
 - (c) The Guidelines specify the indicative removal efficiency of the CFC of 99.99% or higher. This is based on the standards recommended by the United Nations Environment Program (UNEP) Ad-hoc Technical Advisory Committee on ODS Destruction Technologies (hereinafter referred to as the "standards recommended by UNEP").
 - (d) For measurement of the CFC concentration, refer to the measurement procedures in the following table.

Item	Measurement Procedures	Determination Limit	Tolerance
CFC Concentration	 According to the general rules for gas chromatographic analysis by JIS K 0114, analyze the concentration using an electron capture detector. Induce a certain known amount of sample gas to the gas chromatographic spectrometer and determine quantity of the sample using the prepared analytical curve. 	10 ppb	CV = 2 to 5%

Measurement Procedures of CFC Concentration

- (e) For continuous measurement of the CFC concentration, it may be an option to use automatic measurement equipment such as gas chromatographic spectrometers and electron capture detectors.
- (2) Measurement of Toxic Substances

[Paragraph 4.(2) of the Guidelines on the Destruction of CFCs]

- a. It shall be verified that the exhaust gas emitted from the CFC destruction facilities meet the standards specified by the applicable laws and regulations. The following items which could generate or increase through the CFC destruction shall be measured.
- 1) Concentration of hydrogen chlorides (HCl) in the final exhaust gas
- 2) Concentration of hydrogen fluorides (HF) in the final exhaust gas
- 3) Concentration of dioxins in the final exhaust gas
- 4) Content of fluorides in effluent water, and
- 5) Concentration of hydrogen ions in effluent water
- **b.** The measurements shall be pursuant to the procedures set in the applicable laws and regulations and the standards such as the Japanese Industrial Standards (JIS).
- c. The measurements as prescribed in Paragraph a. shall be conducted at least once per year in addition to those required in the applicable laws and regulations. Furthermore, in introducing the CFC destruction technologies into facilities or drastically changing the operation control conditions of combustion temperatures etc. such check shall be assured.
 - (a) Due to its persistency, the CFC would not be effectively decomposed and other by-products such as halide would be generated unless operation control conditions including the combustion temperature and the amount of oxygen are kept appropriately per destruction methods. These Guidelines, therefore, specifies measurement items required for such CFC destruction facilities in the light of verification that the facilities meet the emission standards for toxic substances specified by the applicable laws and regulations for air pollution control etc. as well as in the light of checking the safety of CFC destruction.
 - (b) If any toxic substances that are not specified herein or any CFCs other than the destroyed CFC are potentially generated through the CFC destruction, such

byproducts including phosgene and chlorides shall also be measured.

(c) The standards for toxic substances in exhaust gas specified in the applicable laws and regulations vary depending on types of the facilities concerned. The Air Pollution Control Law specifies such standards for waste incinerators such as rotary kilns and cement kilns as follows:

	Waste Incinerator 1)	Calcination and fusion furnace used for ceramic manufacture ²⁾
Ash Dust	0.04 g/Nm ³ (Burning capacity of 4,000 kg/hr or higher)	0.10 g/Nm ³
	0.08 g/Nm ³ (Burning capacity of not less than 2,000 kg/hr to less than 4,000 kg/hr)	0.05 g/Nm ³ (special emission standard ³⁾)
	0.15 g/Nm ³ (Burning capacity below 2000 kg/hr)	
Hydrogen chloride	700 mg/Nm ³ (O ₂ : 12%)	-
Nitrogen oxide	250 ppm	250 ppm (emission of 100,000 Nm ³ /hr or higher)
		350 ppm(emission below 100,000 Nm ³ /hr)
Sulfuric oxide	According to the K-value	According to the K-value

1) Waste incinerators with the fire grate area of 2 m^2 or larger, or with the burning capacity of 200 kg/hr or higher

2) Furnaces with the fire grate area of one square meter, or with burner's burning capacity of 50 /hr converting to heavy oil, or otherwise, the specific capacity of the transformer of 200 kVA or higher

3) Applied to facilities in the areas listed in the Enforcement Regulations of Air Pollution Control Law

(d) According to the operation records, the facilities concerned achieve the exhaust gas treatment level considerably higher than the legally-binding requirements. The concentrations in the exhaust gas at the final outlet of municipal solid waste incinerators are shown below:

20 to 50 ppm	(Dry type at a low temperature)
20 to 50 ppm	(Half dry type at a low temperature)
20 to 30 ppm	(Wet type)
50 to 100 ppm	(Denitration without catalyzer)
20 to 50 ppm	(Denitration with catalyzer)
80 to 100 ppm	(Low O ₂ combustion control)
60 to 80 ppm	(Water injection in the furnace and low O_2)
60 to 80 ppm	(Exhaust gas circulation and low O_2)
	20 to 50 ppm 20 to 30 ppm 50 to 100 ppm 20 to 50 ppm 80 to 100 ppm 60 to 80 ppm

Source: Incineration Technology of Wastes (1998)

(e) The Air Pollution Control Law sets emission control standards for dioxins in exhaust gas for the "electronic furnace for steal making (except those for cast and/or forged steels)" and the "waste incinerators".

Emission Control Standards of Dioxins in Exhaust Gas from Waste Incinerators under the Air Pollution Control Law

[Unit: ng-TEQ/N		
Capacity of Combustion Chamber	Standards for new facilities	Standards for existing facilities
4 t/hr or higher	0.1	1
2 t/hr to 4t/hr	1	5
Below 2 t/hr	5	10

The Waste Management Law specifies the maintenance and control standards for dioxins in the exhaust gas from waste incinerators (hereinafter referred to as the "Maintenance and Control Standards under Waste Management Law") as the same values listed in the table above.

The Ambient Environment Guidelines specify the standards for dioxins in the air of 0.8 pg-TEQ/m^3 in annual average as a guidance for implementation of the policies.

(f) The Water Pollution Control Law specifies the standards for effluent water discharged to public water as follows:

Concentration of CFC:	15 (mg/l)	
Concentration of hydrogen ions: Effluent water discharged to public water ex		r except the ocean:
		not less than 5.8 to not more than 8.6
	Effluent water discharged to the ocean:	not less than 5.0 to not more than 9.0

Effluent Water Standards under the Water Pollution Control Law

- (g) The facilities regulated by the above mentioned domestic laws and regulations are required to verify that they meet the applicable standards for the concentration of toxic substances in the exhaust gas or the effluent water.
- (h) The concentration of toxic substances in the exhaust gas should not increase, for safety, through CFC destruction which is accompanied with co-combustion of wastes in the existing waste incinerators including rotary kilns, municipal solid waste direct fusion furnaces, fixed floor type two-staged combustion furnaces and cement kilns.
- (i) Some dedicated facilities for CFC destruction may have a lower position of discharging the exhaust gas, and therefore have smaller diffusion and dilution effects. In this case, the concentration of toxic substances in the atmosphere around the facility concerned should meet the occupational environment standards provided by the Industrial Safety and Health Law and the tolerable concentration recommended by the Japan Society of Occupational Health, as an indicative index for verification of the concentration of toxic substances in the exhaust gas.

Hydrogen chloride	Tolerable concentration recommended by JSOH	5 ppm or 7.5 mg/m ³
	Tolerable concentration set by ACGIH	5 ppm or 7.5 mg/m ³
Hydrogen fluoride	Controlled concentration for the Occupational Environment Standards of the Industrial Safety and Health Law	3 ppm
	Tolerable concentration recommended by JSOH	3 ppm or 2.5 mg/m ³
	Tolerable concentration set by ACGIH	3 ppm or 2.6 mg/m ³
Chloride	Controlled concentration for the Occupational Environment Standards of the Industrial Safety and Health Law	0.5 ppm
	Tolerable concentration recommended by JSOH	1 ppm or 2.9 mg/m ³
	Tolerable concentration set by ACGIH	1 ppm or 2.9 mg/m ³
Phosgene	Tolerable concentration recommended by JSOH	0.1 ppm or 0.4 mg/m ³
Dioxins	Countermeasures to Dioxins in Waste Incinerators (Notification by the Ministry of the Health and Welfare)	2.5 pg-TEQ/m ³

Occupational Environment Standards under applicable laws and regulations

* JSOH: Japan Society of Occupational Health

(j) Germany sets emission standards for the exhaust gas in new waste incinerators as follows;
 hydrogen chloride and hydrogen fluoride: 10 mg/Nm³ and 1 mg/Nm³, respectively, for the average for 24 hours; and
 hydrogen chloride and hydrogen fluoride: 60 mg/Nm³ and 4 mg/Nm³, respectively, for the average for 30 minutes
 (either of them are corresponding values to the oxide concentration of 11%)

(k) The United Nations Environment Program (UNEP) Ad-hoc Technical Advisory Committee on ODS Destruction Technologies recommends to the Meeting of the Parties to the Montreal Protocol, the standards for the concentration of toxic substances in the exhaust gas as follows. It is desirable to take measures including improvement of facilities and adjustment of operation control conditions, if necessary, in order to meet the standards recommended by UNEP irrelevant of the CFC destruction technologies.

Exhaust Gas Standards recommended by the UNEP Ad-hoc Technical Advisory Committee on ODS Destruction Technologies

PCDD/PCDF	$< 1.0 \text{ ng-TEQ/Nm}^3$
HCl	$< 100 \text{ mg/Nm}^{3}$
HF	$< 5 \text{ mg/Nm}^3$
HBr/Br ₂	$< 5 \text{ mg/Nm}^3$
particulates	$< 50 \text{ mg/Nm}^3$
CO	$< 100 \text{ mg/Nm}^3$

(1) From the viewpoint of daily control, it is useful to measure the concentration of toxic substances that are indicated to have the correlation with the concentration of dioxins, such as chlorobenzen and chlorophenol.

- (m) There is no standard for the concentration of dioxins in the effluent water due to their low solubility in water. Removal of suspended solids (SS) in the effluent water could lead to removal of dioxins in the effluent water.
- (n) For measurement of toxic substances, refer to the measurement procedures in following table.

Items	Measurement Procedures	Determination Limits	Tolerance
Hydrogen chloride (HCl) concentration	 Measure HCl under the mercuric thiocyanate (II) absorption photometry and ion chromatography analysis provided by JIS K 0107-6. Sampling: Heat a sampling glass tube of which end is filled with filtering material (silica wool) to 150°C or higher. Connect double bubbler tubes containing absorbent of 50 m of 0.1N-NaOH solution (for the ion chromatography analysis, water of 25 m). Collect sample gas at the rate of 2 /min for 60 minutes (for the ion chromatography analysis, 1 /min for 20 minutes). Analysis: Add mercuric thiocyanate (II) and ferrous sulfate (III) ammonium solution. Measure the absorbance of thiocyanate (III) absorption to determine quantity of hydrogen chloride (For the ion chromatography analysis, induce a certain amount of sample solution (10 to 250μ) to the ion chromatograph, and determine quantity of the hydrogen chloride using the prepared analytical curve). 	Exhaust gas: [mercuric thiocyanate (II) absorption photometry] Sampling: 120 1 mg/m ³ N [ion chromatography analysis] Sampling: 20 1 mg/m ³ N	For standard sample: CV = 2 to 4%
Hydrogen fluoride (HF) concentration	 Measure the HF concentration under the lanthanum - alizarin complexion absorption photometry method provided by JIS K 0105-4 Sampling: Place filtering matter in the middle of glass sampling tube (hole diameter of 0.8µm) and heat the tube to 120°C or higher. Connect the double bubbler tubes containing absorbent of 0.1N-NaOH of 50m . Obtain sample gas at the rate of 2 /min for 60 minutes. Analysis: Adjust the pH by adding buffer fluid. Add lanthanum nitrate solution and alizarin complexion solution to color the solution. Measure the absorbance to determine the concentration of hydrogen chloride. 	Exhaust gas: Sampling: 120 0.5 ppm 0.4 mg/m ³ N Sampling: 60 1.0 ppm 0.8 mg/m ³ N	CV = 5 to 10%

Measurement Procedures

<u></u>		
Chloride	1) Measure the Cl_2 concentration under	Exhaust gas
(Cl_2) concentration	either of the 2.2'-amino-bis	[ABTS method]
	(3-ethylbenzothiazoline-6-sulfonic acid)	Sampling: 20
	absorption photometry method (ABTS	0.06 ppm
	method), the 4-pyridinecarboxylic acid-pyrazolone absorption photometry	$0.2 \text{ mg/m}^3 \text{N}$
	method (PCP method) or dichloride 3,	
	3'-dimethyl benzene absorption	[PCP method]
	photometry method (o-tolidine absorption	Sampling: 20
	metric method) specified by JIS K	0.08 ppm
	0106-95.	$0.3 \text{ mg/m}^3\text{N}$
	2) Sampling: Collect sample gas at least	0.5 mg/m N
	twice as principle within continuous time	for toll dimension
	at a same sampling point under the	[o-tolidine absorption
	absorption bulb method used for the	metric method]
	absorbent as specified in the individual	Sampling: 2.5
	above mentioned methods.	0.1 ppm
	3) Analysis: Add the regent provided for the	0.3 mg/m ³ N
	individual above mentioned methods and	
	the like to color the solution of the sample	
	gas. Measure the absorbance to determine	
	the C $_2$ concentration.	
Phosgene	1) Measure the $COCl_2$ concentration under	Exhaust gas
$(COCl_2)$	the ultraviolet spectrophotometric method	Sampling: 20
concentration	provided by JIS K 0090-83.	0.1 ppm
	2) Sampling: Solve 0.25g of aniline in water	$0.4 \text{ mg/m}^3\text{N}$
	to obtain a litter of solution. Adjust the	
	pH of the solution to 6 to 7 by adding	
	hydrochloride acid to obtain absorbent.	
	Use the absorbent to collect sample gas of	
	20 at the rate of 1 /min. under the	
	absorption bulb method.	
	3) Analysis: Extract the formed phosgene	
	derivative in the specified solvent to	
	make extract. Measure the absorbance of	
	the extract at the wave length of around	
	257nm to determine the phosgene concentration.	
Fluorides content	1) Measure the content of fluoride under the	
	lanthanum - alizarin complexion	
	absorption photometry method provided by JIS K 0102-34.	
	2) Sampling: collect effluent using a clean	
	<i>2)</i> Sampling: collect effluent using a clean bucket or a dip to fully fill a polyethylene	
	bottle. Cap the bottle airtight.	
	3) Analysis: dilute the sample, and add the	
	3) Analysis: dilute the sample, and add the lanthanum - alizarin complexion solution	
	to color the extract. Measure the	
	absorbance at the wave length of around	
	620 nm.	
		1

Hydrogen ion concentration (Hydrogen exponent)	 Measure the hydrogen ion concentration under the glass electrode method provided by JIS K 0102-93. Analysis: Rinse the detection part of the constructed pH meter. Dip the detection part in the sample to measure the concentration. 	
Dioxins concentration	 Measure dioxins concentration according to the Manual of Toxic Air Pollutant Measurement Method (issued by the Air Pollution Control Section, Global Environment Bureau of the Ministry of the Environment in October 1997), the Water Quality Inspection Manual for Dioxins (issued by the Water Quality Regulation Section, Water Quality Bureau of the Ministry of the Environment in July 1998) or the Standard measurement Manual of Dioxins in Waste Treatment (issued by the Waste Management Division, the City Water Environment Department of the Environmental Health Bureau of the Ministry of the Health, Labour and Welfare in February 1997). Analysis: Obtain the extract from each sample according to the specified methods. After completion of various refinement processes, analyze the extract under the gas chromatography/mass spectrometry. 	For tetra or penta- chlorodibenzo-p-dioxin, Exhaust gas: 0.008 ng/m ³ N Ash: 0.008 ng/g Effluent: 0.004 ng/
Chlorobenzene concentration Chlorophenol concentration	 Sampling: Collect samples in accordance with the method for dioxins. Analysis: Extract each sample and conduct silica gel column refinement. Then, analyze the extract under the gas chromatography/mass spectrometry or the gas chromatography/electric caption detection method 	Exhaust gas: 10 ng/m ³ N Dust: 10 ng/g Effluent: 10 ng/

(3) Measurement of Operation Control Conditions

[Paragraph 4.(3) of the Guidelines on the destruction of CFCs]

- a. In order to verify the operation control conditions for each destruction method as provided in Paragraphs 5.(1) to 5.(4), the following items shall be measured:
 - 1) Physical conditions of the portions in the facilities where CFCs are destroyed, including the temperatures of combustion, or calcination and reaction
 - 2) Exhaust gas volume after treatment
 - 3) Concentration of carbon monoxide (CO) at the outlet of exhaust gas If the facilities concerned destroy CFCs through thermal decomposition by incineration, the following item shall be also measured.
 - 4) Concentration of oxide (O₂) at the outlet of the incinerator or the secondary combustion chamber
- b. The measurements shall be conducted at practical portions in terms of the structure of each facility. The measurements shall be pursuant to the procedures set in the applicable laws and regulations and the standards such as the Japan Industrial Standards (JIS).
- c. The measurements as provided in Paragraph a. shall be conducted on a daily basis.
 - (a) In thermal destruction technologies, the gas retention time, one of the operation control conditions, is calculated as follows:

Gas retention time (sec) = $\frac{\text{Furnace volume } [\text{m}^3] \times 3,600}{\text{Wet exhaust gas amount } [\text{Nm}^3/\text{hr}] \times (273.15 + \text{furnace temperature } [^{\circ}\text{C}])/273.15}$

(b) For the measurement of the operation control items, see the measurement procedures in the table below.

Items	Measurement Procedures	Determination Limits	Tolerance
Temperature	 Insert the K-type thermo couple to reference points. Record measurements continuously throughout the experiment. For recorded values, calculate the maximum, minimum and average values (use K-type 3.2mm\$\phi\$ sheath and L = 1m). 	100 to 1,200°C: 0.2°C at the FS of 500°C	±0.1% of FS
Exhaust gas flow velocity/rate (1)	 Measure the exhaust gas flow velocity/rate according to JIS Z 8808-7. Measure the flow velocity at the measurement points specified by JIS Z 8808-4.3 using a special pitot tube (western type). Calculate both wet and dry exhaust gas flow rates using the formula specified by paragraphs 7.4.1 and 7.4.2 of JIS Z 8808-4.3. 	Calculate the flow velocity up to around 1.5 m/s at the dynamical pressure of 0.1 mmH ₂ O.	In spite of variation by the dynamical pressure, it is around CV = 5% if it is commutation.

Measurement Procedures for Operation Control Conditions

Exhaust gas flow velocity/rate (2)	1) Measure the exhaust gas flow velocity/rate under the pitot tube method as per JIS Z	0 to 50m/s; 0.5 m/s	Repeatability: FS \pm 0.5 m/s
veroeity/face (2)	8808-7. Insert the sensor of the hot-wire anemometer into the position indicating an average flow velocity to measure and record the flow velocity.	0.5 m/s 0 to 10 m/s; 0.1 m/s	F3 ± 0.5 m/s
	2) Similarly, use the exhaust gas temperatures measured continuously, and calculate a wet exhaust gas flow rate using the formula provided by JIS Z 8808-7.4.		
	 In addition, correct the moisture in the exhaust gas to obtain a dry exhaust gas flow rate. 		
Carbon monoxide (CO) concentration	 Continuously measure the CO concentration by the infrared absorption method of the analysis method classification provided by JIS K 0098-88, or measure under the detection tube method and the like. Record the measurements. 	[0 to 1,000 ppm; 20 ppm] 0 to 250 ppm; 5 ppm	Repeatability: 2% of FS
	2) Collect the sample gas similarly to the method for oxide.		
Oxygen (O ₂) concentration	 Measure the O₂ concentration under the continuous analysis method (the magnetic oxygen automatic meter specified by JIS B 7983) of the analysis method classification provided by JIS K 0301-3. 	0 to 25%; 0.1%	Repeatability: ± 2% of FS
	 To collect the sample gas, fill the silica wool in a stainless sampling tube, and continuously introduce exhaust gas. After cooling, removing moisture and dusts, introduce the gas as dry gas into the automatic measurement equipment. 		

2. Major Destruction Technologies and Their Operation Control Conditions.

(1) Rotary Kiln Method

a. Selection of Facilities

[Paragraph 5.(1) a. of the Guidelines on the destruction of CFCs]

- (a) The facility shall be equipped with an appropriate exhaust gas treatment system including an anti-ash dust device such as a filter type dust collector and an acid gas treatment device such as a cleansing tower so that it meets the standards for concentrations of ash dusts and toxic substances such as hydrogen chlorides generated through due to the addition of CFC into wastes. An exhaust gas treatment system should be preferably designed to cool down heated combustion gas as soon as possible.
- (b) If the facility concerned discharges effluent water, it shall be equipped with an appropriate effluent treatment system so that it meets the standards for content of fluoride, concentration of hydrogen ion, etc. as provided by the applicable laws and regulations.
- (c) It shall be equipped with a system to properly deliver and discharge incineration ash dusts so that it prevents their influences on combustion conditions.
 - (a) CFC destruction facilities shall be equipped with an incineration system that can meet specific operation control conditions to ensure CFC destruction and safety of exhaust gas etc., and also they shall take measures for appropriate treatment of exhaust gas etc..
 - (b) The Structure Standards for Facilities Authorized under the Waste Management Law (hereinafter referred to as the "Structure Standards under the Waste Management Law"), and the Manual for Treatment of Specially Managed Wastes Containing Trichloroethylene etc., issued by the Japan Waste Research Foundation (hereinafter referred to as the "Treatment Manual for Trichloroethylene etc.") have some descriptions relevant to the requirements for the CFC destruction facilities.
 - (c) The Structure Standards under the Waste Management Law specify the following for the facilities to be authorized, in order to reduce dioxins discharged from waste incinerators:
 - 1) To install a device for successively feeding wastes to the combustion chamber at a constant rate under an insulated condition from the outside air.
 - 2) To install a combustion chamber that can meet the following requirements:
 - To keep the combustion gas temperature at 800°C or higher for not less than 2 seconds;
 - To be insulated from the outside air;
 - To install a combustion aid device;
 - To install a device for feeding necessary air for combustion;

- 3) To install a device for cooling down the combustion gas to temperatures of 200°C or lower;
- 4) To install an exhaust gas treatment system with an advanced function to remove ash;
- 5) To install a device for continuously measuring and recording the combustion gas temperature and the carbon monoxide concentration in the exhaust gas; and
- 6) To install equipment to discharge and store ash dusts separately from incineration ash.
- (d) The Treatment Manual for Trichloroethylene etc. requires these facilities to "install an exhaust gas treatment system and a dust collector to ensure preservation of the living environment by eliminating influence from exhaust gas discharged from the chimney of any incinerators". The manual also describes the following items in connection with the specific systems in its interpretation:
 - 1) To use the exhaust gas treatment system with wet gas cleansing equipment or equipment with the similar or superior capacity, to satisfactorily remove hydrogen chloride generated in the decomposition process of trichloroethylene etc..
 - 2) To use the dust collecting system with an electric dust collector or equipment with the similar or superior capacity, to satisfactorily remove ash dust generated in association with incineration of the specially managed industrial wastes containing trichloroethylene etc..

3) To cool down the temperature at the inlet of the dust collector to 200°C or lower by installing an exhaust gas cooling device, for purposes of preventing corrosion by high temperature gas discharged from the combustion chamber and preventing formation of byproducts in cooling process and in the dust collector. This is intended to avoid the temperature of around 300°C as a countermeasure against dioxins.

(e) These Guidelines do not specify detailed provisions for each system due to various facility configurations in the existing waste incinerators, but indicates the points for the exhaust gas treatment system which eventually ensures exhaust gas to be satisfactorily treated.

These Guidelines describe that "An exhaust gas treatment system should be preferably designed to cool down heated combustion gas as soon as possible" for the countermeasures against dioxins. As dioxins are generated in the temperature range from 200°C to 400°C, and the generation reaches the peak at around 300°C, it is necessary to confirm that the exhaust gas treatment system is designed to cool down rapidly, by identifying temperature conditions.

(f) The Waste Management Law specifies appropriate treatments for incineration ash generated through incineration and wastes generated through the treatment of the effluent water from the exhaust gas treatment.

b. Operation Control Conditions

[Paragraph 5.(1) b. of the Guidelines on the destruction of CFCs] It is necessary to operate the incinerator so that successful destruction of CFC and safe control of exhaust gas are ensured. For this purpose, the combustion conditions shall be managed as follows:

1) Combustion temperature: 850°C or higher

2) CFC gas retention time in the combustion temperature range: two seconds or longer

3) Concentration of carbon monoxide (CO) at the exhaust gas outlet (corresponding a value to the oxide concentration of 12%): 100 ppm or lower

- (a) Incineration of wastes itself is generally required to control operation conditions considering the trade-off between reduction of the unburned and increase in nitrogen oxide (NOx) through high-temperature combustion. The Maintenance and Control Standards under the Waste Management Law and the Treatment Manual for Trichloroethylene etc. have some description relevant to the combustion control conditions.
- (b) The Maintenance and Control Standards under Waste Management Law specifies the operation control conditions as follows:
 - 1) To keep the combustion gas temperature in the combustion chamber at 800°C or higher;
 - 2) To rapidly increase the furnace temperature at the start of operation, and keep it high at stop of operation to incinerate wastes completely; and
 - 3) To keep the carbon monoxide concentration in the exhaust gas at 100 ppm or lower.
- (c) The Treatment Manual for Trichloroethylene etc. specifies the operation control conditions as follows:
 - 1) To keep the furnace temperature at the outlet of the combustion chamber at 800°C or higher;
 - 2) To keep the oxide concentration in the exhaust gas at 6% or higher; and
 - 3) To keep the carbon monoxide concentration in the exhaust gas, that is calculated as a corresponding value to the oxide concentration of 12%, at 100 ppm or lower. (200 ppm or lower, in case of existing furnaces).

Its interpretation provides the recommendations for the combustion temperatures in the combustion chamber, the gas retention time in the temperature range, the combustion conditions as follows:

- 1) Preferably to obtain the removal efficiency of 99.99% or higher by installing a afterburning room that ensures the combustion gas retention time for two seconds or longer at 900°C or higher, in order to sufficiently decompose and oxidize trichloroethylene etc. in the gas; and
- 2) To keep the oxygen concentration in the exhaust gas at the combustion room outlet at 6% or higher, and to keep the carbon monoxide concentration in the

exhaust gas, which is calculated as an average value for four hours of the corresponding values to the oxide concentration of 12%, at 100 ppm or lower, in order to sufficiently decompose and oxidize trichloroethylene etc. in the gas.

- (d) The National Federation of Industrial Waste Management Associations specifies a voluntary standard requiring to retain the combustion gas at the temperatures of 850°C or higher for two seconds or longer during incineration, for the industrial waste incineration to control generation of dioxins.
- (e) Existing waste incinerators could have different and limited measurement points for the operation control depending on their type of the furnaces. These Guidelines, therefore, sets combustion temperature, the gas retention time and the carbon monoxide concentration as standard combustion control conditions, referring to the above-mentioned standards.

c. CFC Feeding Conditions

[Paragraph 5.(1) c. of the Guidelines on the destruction of CFCs]
(a) Wastes co-incinerated with CFC shall have homogenous property as much as possible.

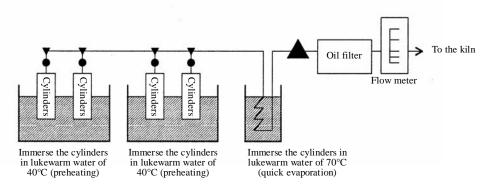
- (b) Quantity of CFC to be fed shall be determined taking into account the halide treatment capacity of the exhaust gas treatment system. In principle, the quantity of CFC should be around 2% of the wastes to be co-incinerated.
 - (a) These Guidelines requires wastes co-incinerated with CFC to have homogenous property as much as possible, in order to stabilize the combustion conditions.
 - (b) Some experiments over the CFC destruction by incineration fed CFCs at the rate of 10% or higher in laboratories. However, in most cases, the rate of CFCs fed is around one to three percent in larger scale experiments such as pilot plants and actual plants, considering the capacity of the system to treat acid gasses such as hydrogen chloride and hydrogen fluoride, and their influences on the facility.
 - (c) The concentrations of hydrogen chloride and hydrogen fluoride increase by feeding CFCs. Feeding CFC 12 at a rate of 1%, for an example, makes both concentrations of hydrogen chloride and hydrogen fluoride before the exhaust gas treatment to 600 ppm in calculation.
 - (d) The existing industrial waste incinerators with the experience of incinerating organic halogenated solvent including trichloroethylene, find no challenges for the facility even if the acid gas concentration is at around 2,000 ppm before exhaust gas treatment.
 - (e) Referring to the results of the CFC destruction experiments, the indicative rate of CFCs feeding is around 2%, taking into account the capacity of acid gas treatment system and their influences on the facilities.

d. The way of feeding CFCs

[Paragraph 5.(1) d. of the Guidelines on the destruction of CFCs]

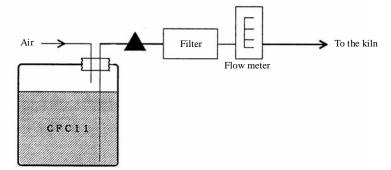
- (a) CFC shall be sprayed at the position close to the burner under the normal operation control conditions.
- (b) Equipment for feeding CFC shall consist of an oil filter, a flow meter and other relevant devices to feed CFC quantitatively.
- (c) The quantity of CFC to be fed shall be properly controlled according to its flow rate.
 - (a) CFCs should be sprayed at the position close to the burner, in order to ensure meeting the combustion temperature and the gas retention time as specified in operation control conditions.
 - (b) Since CFC 12 is delivered in a high-pressured gas cylinder, the general way of feeding CFC is to connect the cylinder with the inlet via a flow meter and feed CFC constantly by the cylinder's own pressure. In the case of feeding a large volume of CFCs, it is necessary to provide heat equal to the latent heat to secure its supply pressure, because the vaporization will cool the cylinder by consuming the latent heat around it. Some devices for soaking the gas cylinder in a hot tub or heating the cylinder in a thermostatic chamber filled with steam at the temperature of 40°C or lower, because the CFC fed will be a considerable volume even if the addition rate is as low as one to two percent, in case of destruction using a waste incinerator.

(Example of Feeding System)



- (c) CFC 113, which is liquid in a room temperature, should be fed constantly from the container such as a drum and a tank by a normal liquid feeding pump.
- (d) Since CFC 11 evaporates more in a high temperature during summer seasons, an easy way of feeding CFC constantly is to cool the CFC 11 in the container such as a drum and a tank by water and feed CFC 11 by pressing air into the container. In this case, the opening of the container shall be equipped with two pipes as illustrated below. One of them is connected with the inlet of pressing air, while the other end shall not reach the liquid surface of CFC 11. For the other pipe, one end

shall reach near the bottom of the container, while the other end shall be connected with the inlet of the kiln via an oil filter and a flow meter.



- (e) It is efficient to recover CFCs using cylinders with a capacity as large as possible, for example those of 20 kg, and of a same shape, because of the gay cylinders shall be replaced sequentially for continuous feeding.
- (f) Close attention should be paid to the feeding method and the connection with cylinders for leakage prevention.

(2) Cement Kiln Method

a. Selection of Facilities

[Paragraph 5.(2) a. of the Guidelines on the destruction of CFCs] The facility shall be equipped with a suspension pre-heater type incinerator or a new suspension pre-heater type incinerator and exhaust gas treatment system for ash dusts so that it meets the standards for concentrations of ash dusts and toxic substances such as hydrogen chlorides generated due to the addition of CFC into raw materials and fuels.

- (a) Cement kilns generally have the following characteristics for CFC destruction:
 - 1) Cement kilns have a structure to absorb acid gas easily, because powdered cement materials are fed from the top of the suspension pre-heater cyclone or new suspension pre-heater cyclone.
 - 2) Cement kilns have a structure to hardly discharge a trace toxic substances into the final exhaust gas, due to its contact heat exchange by material mill and material dryer, installation of an electric dust collector and system to re-feed collected dust into the calcination process.
- (b) For the CFC destruction under the cement kilns, these Guidelines require selecting the facility which can contribute to emission reduction of toxic substances including byproducts, and which is equipped with an exhaust gas treatment system,

so that it meets the standards for concentration of toxic substances in the final exhaust gas provided by the applicable laws and regulations, similarly to the rotary kilns.

b. Operation Control Conditions

[Paragraph 5.(2) b. of the Guidelines on the destruction of CFCs] It is necessary to operate the facility in a similar manner to ordinary cement production so that successful destruction of CFC and safe control of exhaust gas are ensured.

> Since the requirements for the calcination temperature and the gas retention time in the ordinary operation of cement kilns are generally more favorable for CFC destruction than those for rotary kilns used for waste incineration, CFCs are regarded to be destroyed with certainty.

> These Guidelines, therefore, require to operate the facility in a similar manner to ordinary cement production.

c. CFC Feeding Conditions

[Paragraph 5.(2)c. of the Guidelines on the destruction of CFCs] The quantity of CFC to be fed shall be determined taking into account the capacity of the exhaust gas treatment system and the influence on quality of products, or cement clinker.

- (a) In cement kilns, acid gasses such as hydrogen chloride and hydrogen fluoride generated through the CFC destruction will be absorbed in cement clinker. Therefore, these Guidelines require the CFC destruction under cement kilns to take into account the influence on quality of the cement clinker and the cement manufacturing facilities, as well as meet the standards for the acid gas concentration in the final exhaust gas specified by the applicable laws and regulations.
- (b) It is necessary to specify the CFC feeding rate, taking into account the chloride that is already contained in the clinker, caused from the various secondary fuels including waste oil that are used for heat source in manufacturing cement.
- (c) In the past experiments conducted using cement kilns, the indicative CFC feeding rate is set to keep the increment of chloride concentration at 10 ppm or lower in the cement clinker.

d. The way of Feeding CFCs

[Paragraph 5.(2) d. of the Guidelines on the destruction of CFCs]

- (a) CFC shall be sprayed at the position close to the burner before the kiln under the normal operation control conditions.
- (b) Equipment for feeding CFC shall consist of an oil filter, a flow meter and other relevant devices to feed CFC quantitatively.
- (c) The quantity of CFC to be fed shall be properly controlled according to its flow rate.
 - (a) In cement calcination furnaces, cement materials are fed from the end of the kiln, heated and oxidized through combustions of fuels from a burner before the kiln, and then heated and formed as clinkers.
 - (b) Therefore, it is necessary to feed CFCs by spraying from the position close to the burner before the kiln to ensure to keep a sufficient combustion temperature and a gas retention time for certain destruction of CFC. Other requirements for feeding CFCs are the same as those for the rotary kiln incineration.

(3) Destruction Technologies Using Existing Waste Incinerators Other Than Rotary Kilns

[Paragraph 5.(3) of the Guidelines on the destruction of CFCs] Technologies using existing waste incinerators other than rotary kilns include those using municipal solid waste direct fusion furnaces, fixed floor type two-staged combustion furnaces, fluidized bed iron dust furnaces and lime rotary kilns.

For the technologies other than the technology using lime rotary kilns,

- The requirements for selection of facility for the rotary kiln method shall be applied to these technologies.
- The facility shall be operated and controlled under the same operation control conditions as normal incineration so that successful destruction of CFCs and safe control of exhaust gas are ensured.
- Wastes co-combusted with CFC shall have homogenous property as much as possible, and halide treatment capacity of the exhaust gas treatment system shall be taken into consideration, in feeding CFCs.
- CFC shall be sprayed at the bottom of the incinerator (tuyere, etc.). The equipment for feeding CFC shall consist of an oil filter, a flow meter and the other relevant devices to feed CFC quantitatively. The quantity of CFCs to be fed shall be properly controlled according to its flow rate.

For the technology using the lime rotary kilns,

• The facility shall be designed as a coal-fired type facility and other relevant types that contribute to reducing toxic substances. The facility shall be also equipped with an exhaust gas treatment system for ash dusts, etc.

- The facility shall be operated in a similar manner to the cement kiln method.
- CFC shall be fed in a manner that CFC is mixed with air from the bottom of the furnace under the normal operation control conditions, taking into account influences on the quality of burnt lime.

Coal-fired type lime rotary kilns have a structure where lime stones and cokes for materials that are fed from the top of the furnace are oxidized at around 1,200°C, contacting and mixing with the countercurrent flow of combustion air blown from the bottom of the furnace, and are removed as a burnt lime from the bottom of the furnace. The facilities are designed to absorb acid gasses in the burnt lime.

(4) Dedicated CFC Destruction Technologies

a. Selection of Facilities

[Paragraph 5.(4) a. of the Guidelines on the destruction of CFCs]

- (a) The radiofrequency plasma facility shall be equipped with an appropriate exhaust gas treatment system (cleansing tower, absorption tower, etc.) so that it meets the standards provided by the applicable laws and regulations for the concentration of toxic substances such as hydrogen chloride generated through the CFC destruction.
- (b) If exhaust gas is discharged from a lower position, not from a higher position such as chimneys, the radiofrequency plasma facility shall be managed so that it prevents significant increase in the concentration of toxic substances generated through the CFC destruction in the atmosphere around the facilities.
- (c) If CFC is destroyed through thermal decomposition by incineration, the exhaust gas treatment system shall be designed to rapidly cool down the exhaust gas as much as possible.
- (d) If the facility discharges effluent water, it shall be equipped with an appropriate effluent treatment system so that it meets the standards for content of fluorides and concentration of hydrogen ion as provided by the applicable laws and regulations.

b. Operation Control Conditions

[Paragraph 5.(4) b. of the Guidelines on the destruction of CFCs] It is necessary to operate the facility in accordance with the operation control conditions specific to the type of facility so that successful destruction of CFC and safe control of exhaust gas are ensured.

(a) Dedicated CFC destruction technologies include the high-temperature steam thermal-decomposition technology, the radiofrequency plasma destruction

technology, the titanium oxide catalyzer, the liquid injection incineration, the chemical thermal decomposition and the superheated steam reaction.

- (b) It is difficult to indicate universal operation control conditions of these technologies due to their various destruction principles and equipment configurations. However, they are regarded as designed to destroy CFCs efficiently and to meet the level of the concentration of toxic substances including acid gases in the final exhaust gas as required by the applicable laws and regulations. These Guidelines, therefore, do not specify detail requirements for selection of facilities, operation control conditions, CFC feeding conditions and the way of feeding CFCs, but require to keep appropriate conditions verified in process of development of the individual technologies in order to ensure the sufficient destruction, and the treatment of exhaust gas and effluent water.
- (c) Facilities which discharge exhaust gas from a lower position shall take countermeasures to meet the indicative levels as described in Paragraph 1.(2) (i) in the Explanatory Notes. The facilities shall take countermeasures against the exhaust gas to prevent significant increase of the concentration of toxic substances generated through CFC destruction in the atmosphere around the facilities. These countermeasures may include adoption of a structure using absorption by activated carbons as the exhaust gas treatment, and changing the position of the exhaust gas outlet to a higher position.

3. References

(1) Destruction Technologies Approved by the Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer

1) Liquid Injection

A CFC destruction technology by spraying liquid/gaseous CFCs into the furnace with combustion improver, waste oil and waste melting agent from a jet, and burning them.

- Reactor Cracking
 A CFC destruction technology by charging gaseous CFCs into the reaction tower together with oxygen and hydrogen, and then reacting them at the pressure of about 110 kPa and at a high temperature (about 2,000°C).
- 3) Gaseous/Fume Oxidation

A CFC destruction technology by burning liquid CFCs together with combustion improver and air.

4) Rotary Kiln Incineration

A CFC destruction technology by burning liquid/gaseous CFCs in the rotary kiln and the secondary combustion chamber of waste incinerators.

5) Municipal Solid Waste Incinerators (limited to foam products)

A CFC destruction technology by co-combusting CFCs confiscated in solids such as heat insulation materials with municipal solid wastes in the municipal solid waste incinerators.

6) Cement Kiln

A CFC destruction technology by burning liquid/gaseous CFCs in the rotary kiln incinerator in cement manufacturing plants.

7) *Radio Frequency Plasma Decomposition* A technology of destroying liquid/gaseous CFCs using radiofrequency thermal plasma.

(2) CFC Destruction Technologies in Japan

A. Established Technologies

The following technologies are acknowledged to be practical based on the past technological developments:

a. Rotary Kilns

- This is a method to destroy CFCs using a rotary kiln furnace for waste incineration.
- The outline of experiments performed by Fukushima Prefecture under the consignment by the Ministry of the Environment is as follows:

Outline of the Facilities

- The wastes are vaporized and partly decomposed by preheat in rotary kiln. Byproducts that are generated in this process are completely decomposed in the secondary combustion chamber installed in the subsequent stage of the rotary kiln.
- CFCs are fed from a cylinder into the furnace together with other wastes including waste oil and sludge. Exhaust gas is fed to the primary cleansing tower, the secondary cleansing tower and the electric dust collector.

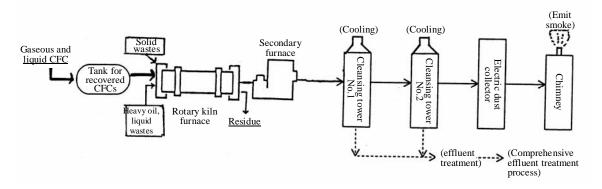


Fig. CFC decomposition process using a rotary kiln

Operation Conditions

• Supply rate of CFC 12	: 39.3 kg/hr (about 1.6% of the weight of the incinerated waste)
Supply rate of HCFC 22	: 36.8 kg/hr (about 1.8% of the weight of the incinerated waste)
Furnace temperature	: 903 - 1,139°C
• Gas retention time in the furnace	: 5.8 - 6.8 seconds

Removal Efficiency

- The concentration of CFC 12 in the exhaust gas was 10 ppb, and the removal efficiency was 99.999% or higher.
- The concentration of HCFC 22 in the exhaust gas was not more than the determination limit (10 ppb), and the removal efficiency was 99.999% or higher.

Concentration of Byproducts

- The concentrations of hydrogen chloride and the hydrogen fluoride were 1.6 76 mg/Nm³ and 0.2 3.2 mg/Nm³ respectively, which did not exceed the emission standards for smoke and soot under the Air Pollution Control Law and the standards recommended by UNEP.
- The concentration of dioxins in exhaust gas was 0.02 ng-TEQ/Nm³, which did not exceed the limits under the Air Pollution Control Law and the standards recommended by UNEP.

b. Cement Kilns

- ≺ This is a method to destroy CFCs using a rotary kiln incinerator of the cement manufacturing facilities.
- ✓ The outline of experiments performed by Fukushima Prefecture under the consignment by the Ministry of the Environment is as follows:

Outline of the Facilities

- Cement materials are transported via the pre-heater to the rotary kiln that is heated and maintained at a high temperature and oxidized.
- CFC 11 and HCFC 22 are fed from a position close to the main burner in the lower part of the rotary kiln and decomposed in a high temperature. Most of hydrogen chloride and hydrogen fluoride that are generated in this process are absorbed in alkaline cement materials during passing through the rotary kiln and the pre-heater.

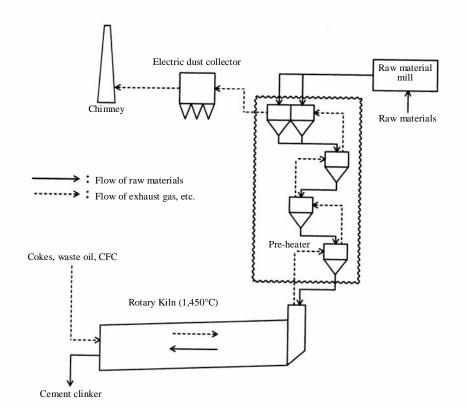


Fig. CFC decomposition process using a cement kiln

Operation Conditions

- The amount of CFCs to be fed was determined taking into account the chlorine concentration in the cement products.
 CFC 11 : 9.1 kg/hr
 HCFC 22 : 9.5 kg/hr
- Furnace temperature : about 1,450°C
- Gas retention time in the furnace : 8 seconds

Removal Efficiency

- The concentration of CFC 11 in the exhaust gas was not more than the determination limit (0.18 ppb) to 0.28 ppb, and the removal efficiency was 99.995%.
- The concentration of HCFC 22 in the exhaust gas was not more than the determination limit (0.54 ppb), and the removal efficiency was 99.994%.

Concentration of Byproducts

- The concentrations of hydrogen chloride and the hydrogen fluoride in the exhaust gas neither exceeded the determination limits (0.4 mg/Nm³ and 2 mg/Nm³) respectively nor the standards recommended by UNEP.
- The concentration of dioxins in the exhaust gas was 0.052 0.064 ng-TEQ/Nm³, and did not exceed the standards recommended by UNEP.

c. Municipal Solid Waste Direct Fusion Furnaces

- ✓ This is a method to destroy CFCs using a municipal solid waste direct fusion furnace with a high temperature fusion furnace and a combustion room.
- ≺ The outline of experiments performed by Ibaraki-Shi, Osaka is as follows:

Outline of the Facilities

- Wastes fed from the upper inlet are thermally decomposed and vaporized in the municipal solid waste direct fusion furnace. The generated gas is completely burnt in the combustion chamber in the subsequent stage.
- CFC 12 is hydrolyzed into hydrogen fluoride, hydrogen chloride and carbon dioxide in a high temperature. The municipal solid waste direct fusion furnace has two high temperature areas, namely the lower part of the fusion furnace and the combustion chamber. Accordingly, there are two decomposition methods for CFC destruction; (1) decomposition by blowing into the fusion furnace from the tuyere, and (2) blowing into the combustion chamber.

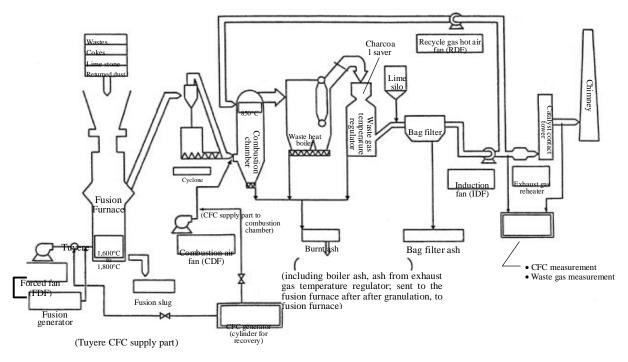


Fig. CFC decomposition process using a municipal solid waste direct fusion furnace

- Supply rate of CFCs 12 : 3 kg/hr
- Waste incineration rate : 6,250 kg/hr
- Furnace temperature

: 1,600 - 1,800°C

• Combustion chamber temperature : 850°C

Removal Efficiency

- In case of blowing into fusion furnace from the tuyere, the concentration of CFC 12 in the exhaust gas was not more than the determination limit (0.5 ppb), and the removal efficiency was 99.996 99.998%.
- In case of blowing into the combustion chamber, the concentration of CFC 12 in the exhaust gas was not more than the determination limit (0.5 ppb) 0.7 ppb, and the removal efficiency was 99.996 99.997%.

- The concentrations of hydrogen chloride and the hydrogen fluoride in the exhaust gas were 9 19 ppm and not more than the detection limit (0.2 ppm) respectively. These values did not exceed the emission standards for smoke and soot under the Air Pollution Control Law and the standards recommended by UNEP.
- The concentration of dioxins in the exhaust gas was not more than the detection limit (0.008 ng-TEQ/Nm³) in either cases of blowing into fusion furnace from the tuyere and blowing into the combustion chamber, and did not exceed the limits scale under the Air Pollution Control Law and the standards recommended by UNEP.

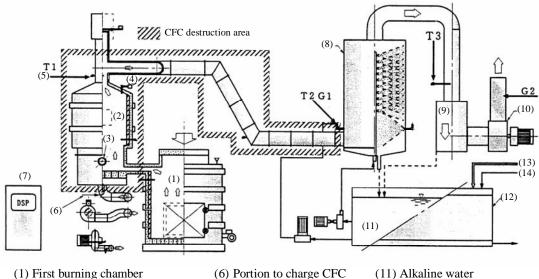
	First Test			Second test		
CFC supply position	Blank	Tuyere	Combustion chamber	Blank	Tuyere	Combustion chamber
HCl concentration (ppm)	5	19	15	17	19	9
HF concentration (ppm)	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cl ₂ concentration (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Concentration of dioxins (ng-TEQ/Nm ³)					<0.008	<0.008

d. Fixed Floor Type Two-staged Combustion Furnaces

- ≺ This is a method to destroy CFCs using the industrial waste incineration furnace to thermally decompose and vaporize mainly waste tires in the first combustion chamber, and then completely burn them in the second combustion chamber.
- ≺ The outline of experiments performed by Hokkaido Prefecture under the consignment by the Ministry of the Environment is as follows:

Outline of the Facilities

- Wastes are thermally decomposed and vaporized in the first combustion chamber, and are completely burnt in the second combustion chamber in the fixed floor type two-staged combustion furnace.
- CFC 12 is fed into the bottom of the second combustion chamber from a cylinder, and is destroyed in the second combustion chamber and in the gas duct. The exhaust gas is guided into the exhaust gas treatment system, and is washed by sprayed alkaline water to cool down to 80°C. The liquid is removed.



(2) Secondary combustion chamber

(3) Combustion aid burner

- (7) Control panel
- (8) Reaction contact tower
- (9) Mist separator
- (4) Oxide concentration meter (5) Thermometer
- (10) Induction fan
- (12) Reaction tank
- (13) Alkaline chemicals
- (14) Makeup water
- Fig. CFC decomposition process using a fixed floor type two-staged combustion furnace

- Supply rate of CFC 12 : 8 kg/hr (about 2% of the weight of the incinerated waste (waste tires) of 400 kg/hr)
- Second combustion chamber : 1,050 1,250°C temperature
- Gas retention time in : 2 seconds or longer the second combustion chamber

Removal Efficiency

- The concentration of CFC 12 in the exhaust gas was not more than the detection limit (0.54 ppb) - 3.7 ppb, and the removal efficiency was not less than 99.99%.
 <u>Concentration of Byproducts</u>
- The concentrations of hydrogen chloride and the hydrogen fluoride in the exhaust gas were 33 42 mg/Nm³ and 6.9 7.1 mg/Nm³, respectively, and did not exceed the exhaust standards for smoke and soot under the Air Pollution Control Law and the standards recommended by UNEP.
- The concentration of dioxins in the exhaust gas was 0.015 0.016 ng-TEQ/Nm³, and did not exceed the limits under the Air Pollution Control Law and the standards recommended by UNEP.

e. Fluidized Bed Iron Dust Furnaces

- This is a method to destroy CFCs using the facilities to treat dusts, industrial sludge and waste liquid generated from sintering plants, blast furnaces, converters and rolling mils and to collect valuable resources such as source of irons for cement and materials for iron manufacturing.
- ✓ The outline of experiments performed by an iron manufacturer in Fukuoka Prefecture is as follows:

Outline of the Facilities

- Sludge is crushed and mixed together with main raw materials, iron-manufacturing dusts, and waste oil and wastewater containing organic matter are directly sprayed into the roasting furnace to be burnt. The heat source during roasting is carbons contained mainly in iron-manufacturing dusts (about 25% of the burnt matter), and waste alkaline liquid is sprayed over to keep the roasting temperature at about 950°C.
- CFCs are fed into the furnace from the bottom of facilities, together with air. Exhaust gas from the roasting furnace is cooled down to about 430°C in the waste heat boiler and the heat is collected as vapor. After dusts in the exhaust gas are removed by the cyclone, the gas is sent to the cooling tower, and then to the desulphurization tower.

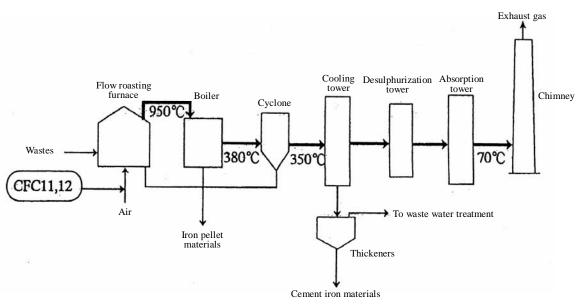


Fig. CFC decomposition process using a fluidized bed iron dust furnace

- CFC 12 is fed at 40 kg/hr, which is corresponding to about 1% of the weight of the incinerated waste (about 4,100 kg/hr). Blast furnace dusts are fed at 6,800 kg/hr.
- CFC 11 is fed at 51 kg/hr, which is corresponding to about 1.6% of the weight of the incinerated waste (about 3,200 kg/hr). Blast furnace dusts are fed at 11,000 kg/hr.
- Roasting temperature: about 950°C
- Gas retention time in the furnace: about 12 13 seconds

Removal Efficiency

- The concentration of CFC 12 in the exhaust gas was 40 60 ppb, and the removal efficiency was 99.97%.
- The concentration of CFC 11 in the exhaust gas was 2 4 ppb, and the removal efficiency was 99.999%.

- The concentrations of hydrogen chloride and the hydrogen fluoride in the exhaust gas were 9.2 10 mg/Nm³, and not more than the determination limit (1.5 mg/Nm³) respectively, and did not exceed the emission standards for smoke and soot under the Air Pollution Control Law and the standards recommended by UNEP.
- The concentration of dioxins in exhaust gas was 0.04 0.3 ng-TEQ/Nm³, and did not exceed the limits under the Air Pollution Control Law and the standards recommended by UNEP.

f. Lime Rotary Kilns

- This is a method to destroy CFCs using a coal-fired vertical lime rotary kiln which is equipment for manufacturing calcined lime.
- The outline of experiments performed by the Gifu Prefectural Institute of Health & Environmental Sciences is as follows:

Outline of the Facilities

- Lime stone and coal charged from the top of the kiln pass through a preheating zone of the lime rotary kiln, and then, they are carried to a calcination zone which is maintained at a high temperature for calcination.
- CFC 12 fed from the inlet of combustion air at the bottom of the calcination kiln is decomposed under a high temperature. Most of hydrogen chloride and hydrogen fluoride generated in the process is absorbed by calcined lime, with alkaline property, during the process to pass through the preheating zone of the kiln.

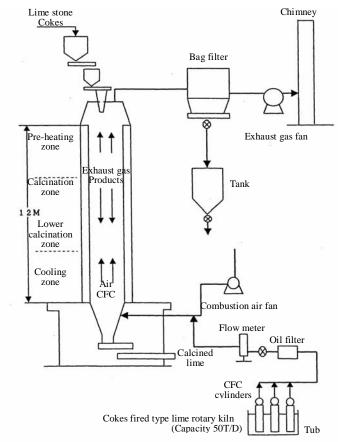


Fig. CFC decomposition process using a lime rotary kiln

• Supply rate of CFC 12	:27 kg/hr
• Temperature of the calcination zone	:1,200°C
• Gas retention period at the calcination zone	:about 7 seconds

Removal Efficiency

• The concentration of CFC 12 in the exhaust gas was less than the determination limit (5.0 ppb) with the removal efficiency not less than 99.99%.

- The concentrations of hydrogen chloride and hydrogen fluoride in the exhaust gas were less than the determination limit (2.0 mg/Nm³ and 0.1 mg/Nm³), respectively, and they did not exceed the standards recommended by UNEP.
- The concentration of dioxins in the exhaust gas was 0.00069 ng-TEQ/Nm³, which was lower than the standards recommended by UNEP.

g. High-Temperature Steam Thermal Decomposition

- ✓ This is a method to thermally decompose CFCs with high-temperature steam.
- The outline of experiments performed by Hiroshima Prefecture under the consignment by the Ministry of the Environment is as follows:

Outline of the Facilities

• In order to maintain the kiln at a high temperature, LPG is supplied as a fuel. CFC 12 and HCFC 22 are thermally decomposed at a high temperature, by the steam which is supplied together with the LPG.

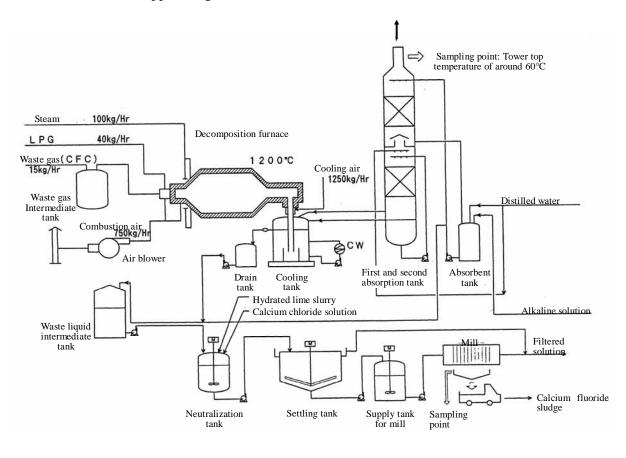


Fig. CFC destruction system under high-temperature steam thermal decomposition method

•	Supply rate of CFCs	: 40 - 165 kg/hr
•	Supply rate of LPG	: 40 kg/hr
•	Supply rate of steam	: 100 - 120 kg/hr
•	Supply rate of combustion air	: 750 kg/hr
•	Temperature of the decomposition kiln	: 1,250°C

Removal Efficiency

- In case of the CFC 12 decomposition, the concentration of CFC 12 in the exhaust gas was not more than the determination limit (3.6 ppb). The removal efficiency was not less than 99.999%.
- In case of the CFC 12 and HCFC 22 decomposition, the concentrations of CFC 12 and HCFC 22 in the exhaust gas were less than the determination limit (4.4 ppb) for the both gases. The removal efficiency was not less than 99.999%.

- The concentrations of hydrogen chloride and hydrogen fluoride in the exhaust gas were not more than the determination limit, (3.0 mg/Nm³) and 0.25 0.49 mg/Nm³, respectively. They did not exceed the standards recommended by UNEP.
- The concentration of dioxins in the exhaust gas was 0.021 0.024 ng-TEQ/Nm³. They did not exceed the standards recommended by UNEP.

h. Radiofrequency Plasma Destruction

- \checkmark This is a method to hydrolyze CFCs with steam in a reaction vessel where the gases are kept in plasma state.
- The outline of experiments under a demonstration project of NEDO (New Energy and Industrial Technology Development Organization) is as follows:

Outline of the Facilities

- Radiofrequency plasma power source is connected to a plasma torch to keep the inside of the torch in plasma state (approx. 10,000°C). CFC 12 and steam are supplied for hydrolysis under a high temperature.
- The exhaust gas is instantly cooled down at the cooling can underneath of the reaction vessel. Hydrogen chloride and hydrogen fluoride are treated in the cooling can and the absorption tower in the subsequent stage.
- Further, hydrogen chloride, hydrogen fluoride and trace amounts of chlorine and fluorine remaining in the exhaust gas are neutralized in the cleansing tower.

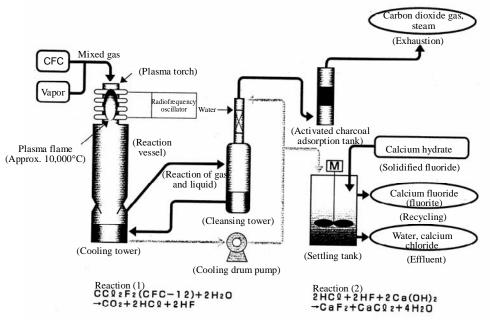


Fig. CFC destruction system under radiofrequency plasma destruction

• Supply rate of CFC 12 : 50 - 80 kg/hr

CFC Removal Efficiency

• The removal efficiency was not less than 99.99%.

- The concentrations of hydrogen chloride and hydrogen fluoride in the exhaust gas were 3.3 37.5 mg/Nm³ and less than the determination limit (0.27mg/Nm³) up to 1.79 mg/Nm³, respectively. They did not exceed the standards recommended by UNEP. Besides, there were no concerns about significant increase of the concentrations in the atmosphere around the facility concerned.
- The concentration of dioxins in the exhaust gas was less than 0.04ng-TEQ/Nm³ and did not exceed the standards recommended by UNEP. Besides, there were no concerns about significant increase of the concentration in the atmosphere around the facility concerned.

j. Titanium Oxide Catalyzer

- \checkmark This is a method to decompose CFCs by catalytic action.
- The outline of experiments performed by Ibaraki Prefecture under the consignment by the Ministry of the Environment is as follows:

Theory of the Decomposition

• CFC 12 that is heated to temperature approx. 440°C and water are reacted on the surface of TiO₂-based catalyst to decompose them to hydrogen fluoride, hydrogen chloride and carbon dioxide (CO₂).

 $CCl_2F_2 + 2H_2O \rightarrow 2HF + 2HCl + CO_2$

Outline of the Facilities

• The pre-heater heats water into steam and is controlled in a feedback basis by the internal temperature of the catalyst tank, which keeps the temperature in the tank constant. In the reaction vessel, CFC 12 is homogeneously mixed and its temperature is maintained at a designated temperature with heat generated through the CFC decomposition in the catalyst tank. Exhaust gas generated under the decomposition process is rapidly cooled down by sprays of alkaline slurry equipped in the exhaust gas cleansing system. During the process, acid gas generated is neutralized and removed.

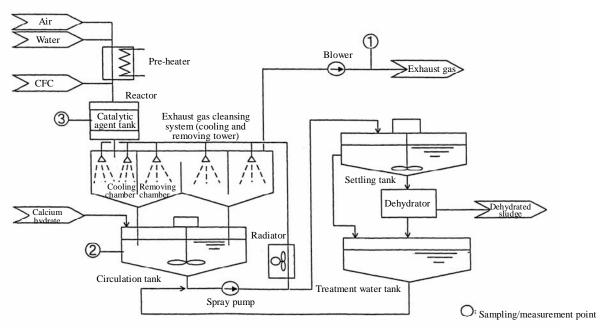


Fig. CFC destruction system under titanium oxide catalyzer

- Temperature of the catalyst tank :
- CFC 12 concentration
- CFC 12 supply rate
- Water supply rate

- : over 440°C
- : 3.0 vol%
- : 1.0 kg/hr
- : 0.66 kg/hr (not less than double of the theoretical molecular value)

CFC Removal Efficiency

- CFC 12 concentration : 0.13 0.26 ppm (0.20 ppm in average) in the exhaust gas
- CFC 12 removal efficiency

: not less than 99.997 - 99.999% (99.998% in average)

- The concentrations of hydrogen chloride and hydrogen fluoride in the exhaust gas were 0.33 0.40 mg/Nm³ and not more than the determination limit (0.2 mg/Nm³), respectively. They did not exceed the standards recommended by UNEP. Besides, there were no concerns about significant increase of the concentrations in the atmosphere around the facility concerned.
- The concentration of dioxins in the exhaust gas was 0.013 ng-TEQ/Nm³. It did not exceed the standards recommended by UNEP. Besides, there were no concerns about significant increase of the concentration in the atmosphere around the facility concerned.
- The concentrations of chlorine and phosgene in the exhaust gas were 0.3 mg/Nm³ and 0.9 mg/Nm³, respectively. There were no concerns about significant increase of the concentrations in the atmosphere around the facility concerned.

B. Other Destruction Technologies

The following methods are acknowledged to be practical based on the past technological development, but still require further improvement.

a. Liquid Injection Incineration

- \checkmark This is a method to decompose CFCs in burning flame.
- \checkmark The treatment of effluent water is an issue to be addressed.
- The outline of experiment performed by Shizuoka Prefecture under the consignment by the Ministry of the Environment is as follows:

Outline of the Facilities

- In liquid injection incineration system, CFC 12 and HCFC 22 are mixed with propane and air, and CFC 12 and HCFC 22 are decomposed in the combustion chamber.
- The gas generated in the combustion process is dispersed into sodium hydroxide aqueous solution in order to remove hydrogen chloride and hydrogen fluoride from the exhaust gas through direct contact of the gas and the liquid.

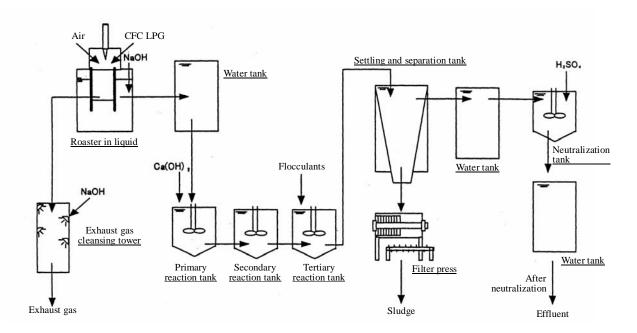


Fig. CFC destruction system under liquid injection incineration method

- Supply rate of CFC 12 : 8.24 8.25kg/hr
- Supply rate of HCFC 22 : 9.66 10.28kg/hr
- Temperature in the chamber : over 800°C

Removal Efficiency

- The concentration of CFC 12 in the exhaust gas was 0.78 3.07 ppm. The removal efficiency was 99.992 99.998%.
- The concentration of HCFC 22 in the exhaust gas was 0.28 0.54 ppm. The removal efficiency was not less than 99.999%.

- The concentrations of hydrogen chloride and hydrogen fluoride in the exhaust gas were 8 14mg/Nm³ and 0.8 2.0mg/Nm³, respectively. They did not exceed the standards recommended by UNEP. Besides, there were no concerns about significant increase of the concentrations in the atmosphere around the facility concerned.
- The concentration of dioxins in the exhaust gas was 0.21 ng-TEQ/Nm³ when CFC 12 was destroyed, and 0.031 ng-TEQ/Nm³ when HCFC 22 was destroyed. They did not exceed the standards recommended by UNEP.
- The fluorine content in the effluent water was 7.3 19.5 mg/l, which is an issue to be addressed. (Some results of measurement exceeded the standard (15 mg/l) specified in the Water Pollution Control Law, although the experiment facility was not subject to the law.)

b. Chemical and Thermal Decomposition

- \checkmark This is a method to decompose CFCs in a tank which is filled with special chemical agents, which are heated to a designated temperature with an electric heating furnace, so as to converse the gas to SiF₄.
- \checkmark The volume of sludge produced from the reaction and the destruction cost are issues to be addressed.
- The outline of experiment performed by Gunma Prefecture under the consignment by the Ministry of the Environment is as follows:

Theory of the Destruction

• CFCs are decomposed at the temperature ranging from 600 to 1,000°C by the action of special chemical agents (silicon compound). A reaction to decompose CFC 12, for instance, is as follows:

$$\begin{array}{l} 1) \ 2\text{CCl}_2\text{F}_2 + \text{SiO}_2 + \text{O}_2 \rightarrow \text{SiF}_4 + 2\text{Cl}_2 + 2\text{CO}_2 \\ 2) \ \text{SiF}_4 + 2\text{Cl}_2 + 2\text{CO}_2 &+ 14\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_2 + 4\text{NaF} + 2\text{NaCl} + 2\text{NaOCl} \\ &+ 2\text{Na}_2\text{CO}_3 + 7\text{H}_2\text{O} \\ 3) \ \text{Na}_2\text{SiO}_2 + 4\text{NaF} + 2\text{NaOCl} + 2\text{Na}_2\text{CO}_3 + 2\text{Na}_2\text{SO}_3 + 7\text{CaCl}_2 \\ &\rightarrow \text{CaSiO}_3 + 2\text{CaF}_2 + 2\text{CaCO}_3 + 2\text{CaSO}_4 + 16\text{NaCl} \\ \end{array}$$

Outline of the Facilities

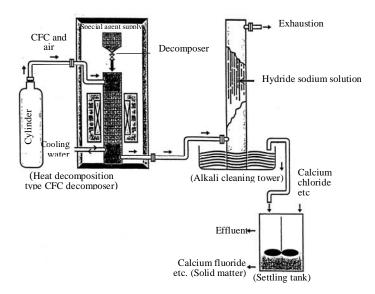


Fig. CFC destruction system under chemical and thermal decomposition method

• Types of fluorocarbons and volume of fluorocarbons to be charged and the decomposition temperatures set for the experiment were as follows:

	Type of fluorocarbons	Decomposing Temperature (°C)	fluorocarbons to be charged (kg/hr)
1	CFC 12	1,000	4
2	CFC 12	1,000	5
3	HCFC 22	500 - 860	2.3
4	HCFC 22	600 - 850	2.7
5	HCFC 22	600 - 850	2.3
6	CFC 12	850 - 940	2.5

Removal Efficiency

• The removal efficiencies of fluorocarbons were not less than 99.99% in any of the above operating conditions.

- The concentrations of hydrogen chloride and hydrogen fluoride in the exhaust gas were not more than the determination limit(1ppm and 0.5ppm), respectively. They did not exceed the standards recommended by UNEP. Besides, there were no concerns about significant increase of the concentrations in the atmosphere around the facility concerned.
- The concentrations of dioxins in the exhaust gas under the operating condition 5 and 6 were 0.18 ng-TEQ/Nm³ and 0.01 ng-TEQ/Nm³, respectively. They did not exceed the standards recommended by UNEP.
- The concentrations of chlorine and phosgene were not more than the determination limit (0.5 ppm and 0.1 ppm, respectively). There were no concerns about significant increase of the concentrations in the atmosphere around the facility concerned.

c. Superheated Steam Reaction

- This is a method to decompose CFCs with superheated steam at the temperature of approx. 650°C. Iron or carbon steel are considered to serve as a reaction aid agent or catalyst in the reaction process.
- \checkmark Corrosion of the reaction chamber is an issue to be addressed.
- The outline of experiment performed by Kagawa Prefecture under the consignment by the Ministry of the Environment is as follows:

Outline of the Facilities

• CFC 12 is fed to an evaporator via a gas flow meter and mixed with evaporated water from a water tank. Then, CFC 12 in the mixed gas is superheated to 650°C at the evaporator and carried to a reaction vessel for hydrolysis reaction with superheated vapor at temperature more than 650°C. In this process, the reaction vessel and the bulkhead plating are considered to serve as a reaction aid agent or catalyst. The gas generated in the decomposition is liquefied in a cooling chamber, neutralized in a neutralization reaction chamber, and then treated at an activated charcoal absorption chamber and waste gas treatment system. On the other hand, the liquid generated in the decomposition is neutralized in the neutralization chamber and aggregated and precipitated subsequently.

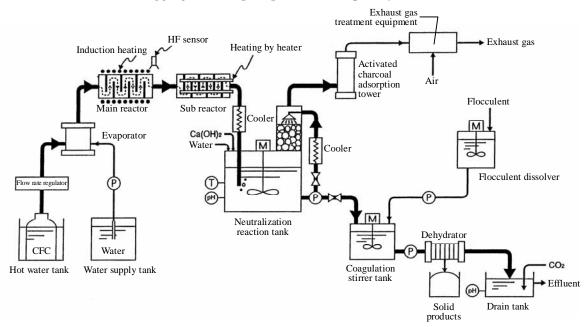


Fig. CFC destruction system under superheated steam reaction method

• Supply rate of CFC 12

- : 1,900 1,970 g/hr : CFC : water = 1 : 10.4
- Supply volume ratios of CFC 12 and water (mole ratio)

Removal Efficiency

- CFC 12 concentration in the exhaust gas : 0.03 2.0ppm
- CFC 12 removal efficiency : more than 99.99%

- The concentrations of hydrogen chloride and hydrogen fluoride in the exhaust gas were 0.2 0.4 mg/Nm³ and not more than the determination limit (0.2 mg/Nm³), respectively. They did not exceed the standards recommended by UNEP. Besides, there were no concerns about significant increase of the concentrations in the atmosphere around the facility concerned.
- The concentration of dioxins in the exhaust gas was not more than 0.0027 0.039 ng-TEQ/Nm³ and did not exceed the standards recommended by UNEP. Besides, there were no concerns about significant increase of the concentration in the atmosphere around the facility concerned.