A-2.6 Studies on Total System for Recovery and Destruction of CFCs

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1. Introduction

It has stopped to produce CFCs since 1996. But, CFCs are stored as refrigerant and adiabator of refrigerators and buildings. According to my investigation, it was estimated that amount of stored CFCs is from 140,000 ton to 220,000 ton. It is necessary to recover and to destruct CFCs, when we disuse them. In this study, social systems for recovery and technologies for destruction of CFCs were investigated.

2. Investigation for Social Systems to Recovery and Destruction

Existing social system for recovery and destruction of CFCs were investigated by hearing, references and questionnaire for 47 prefectures, 75cities and 58 waste incineration plants for chlorinated solvent.
Consequently, it was suggested about existing systems as follows;

(1) Many cities started to recover CFCs in abandoned household refrigerator. These cities were annoyed with space and cost for CFCs gas cylinders. It was wanted to establish early the technologies and systems for destruction of recovered CFCs.

(2) Almost prefectures and cities do nothing as to recovery of adiabator, however, a large amount of CFCs in adiabator was stored. Therefore, effort should be made to recover and destruct adiabator in refrigerators, as well as buildings. Association for Electric Home Appliances is developing recovery and destruction system for abandoned household

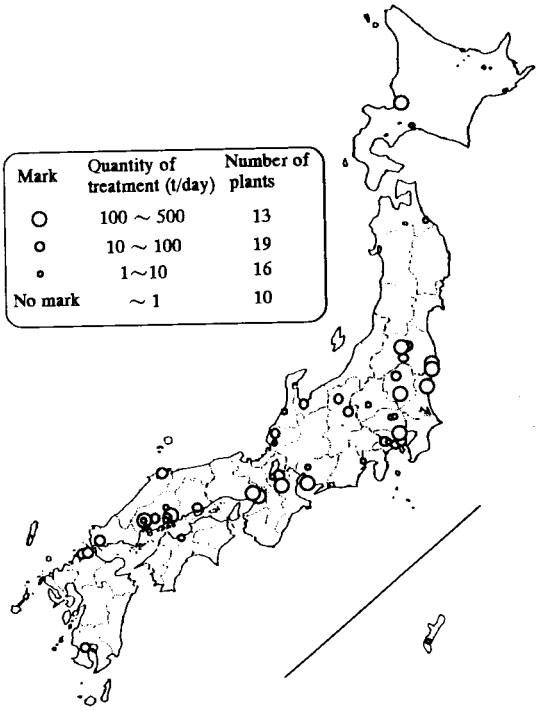

Fig. 1 Distribution of waste incineration plants for chlorinated solvent.

refrigerator, including metal, plastic, and adiabator.

(3) The incineration process is one of the most practical method for destrucion of CFCs. Fifty eight industrial waste incineration plants for chlorinated solvent were the places shown in *Fig.1.* If 32 bigger plants destructed CFCs, accounting for 2% of the total incinerated waste, it was estimated that potential capacity for the destruction of CFCs was 20,000 ton a year. This capacity may be sufficient to destruct recovered CFCs. Therefore, it is necessary that safety, complete, and economical technology for CFCs destruction was established and popularized, and that the nation and prefectures should assist the cost of reconstruction of plants for the destruction of CFCs.

(4) It is economical and effective to use the existing roots and the disposal companies for abandoned refrigerators and others by regional groups, such as Yokohama city's system. Role and cost sharing of this system are as follows; Association for Electric Home Appliances expend and supply equipments for recovering CFCs, home electric shops collect refrigerator and recover CFCs, consumer cooparate collecting refrigerator and share the cost of recovery CFCs, the city publicize and assist to establish the technology for destruction of the recovered CFCs. And the cost of recovery and destruction is estimated a few hundred yen a refrigerator in this system.

3. CFCs Destruction Tests at Waste Incineration Plants

Since cost of transport for gas cylinder is expensive, some existing incineration plants which are suitable for destructing CFCs is necessary at each area in order to recover and destruct CFCs in the whole country. In this stdy, many times tests at the incineration plants of different types were conducted to clearize optimum conditions for destruction of CFCs.

CFCs destruction tests were conducted at four plants whose outlins are shown in *Table 1.* Plants A, B and C were industrial waste incineration plants, and plant D was a steelworks dust reusing plant. These four plants were operated in good conditions for complete destruction of CFCs. The good conditions are as follows; the temperature of incinerator is above 800 ℃ , gas resident time in incinerator is over 2 seconds, O_2 concentration in exhaust gas is over 6%, CO concentration is fairly under 80 ppm. Further, exhaust gas from

Table 1 Outlines of plants for CFCs destruction tests

Plants	A	B	C	D
Incinerator type	Rotary kiln	Rotary kiln	Rotary kiln + atomize incinerator	Fluidized bed incinerator
Incinerator temperature [a](℃)	800～900	850～1,000	800～950	900～950
Gas resident time in incinerator[a](s)	2～3	8～9	7～8	12～13
Waste feed rate(kg/h)	ca. 1,000	ca. 2,500	ca. 2,000	ca. 12,000
Dry flue gas rate (m^3_N/h)	ca. 8,000	ca. 9,000	ca. 18,000	ca. 30,000
O_2 concentration [b](vol%)	11～14	6～7	10～12	6～7
CO concentration [b] (ppm)	ca. 20	< 1	< 1	ca. 6

a) Include secondary combustion chamber

b) Converted to 12% O2 in dry gas at standard conditions

Table 2 Test data of regulation terms to stack gas at plant A

Plant	A				Regulations
CFC	CFC11	CFC12	CFC113	HCFC22	
CFC feed (wt%)	1.8	2.0	2. 0	1.8	
Destruction efficiency (%)	> 99.99	> 99.99	> 99.99	> 99.99	(> 99.99)
HCl (mg/m^3_N)	3	< 9	2	9	100
HF (mg/m^3_N)	Trace (<1.6)	N.D. (<0.5)	N.D. (<0.5)	N.D. (<0.5)	5
NOx (ppm)	55	40	15	13	250
SOx (ppm)	0.4	1.0	0.1	1.7	420
Particulates (mg/m^3_N)	< 5	< 5	< 5	6	20

N.D. indicates "not detected"
Trace indicates "lower than quantitative analysis limit"

Table 3 Test data of volatile organic chlorinated compounds in stack gas at plant A (ppb)

Plant	A			
Destructed CFC	CFC11	CFC12	CFC113	HCFC22
Chloroform	N.D. (<4.0)	N.D. (<1.7)	N.D. (<1.7)	N.D. (<1.7)
Carbon tetrachloride	N.D. (<0.4)	N.D. (<0.3)	N.D. (<0.3)	Trace (<1.5)
1,1,1-trichloroethane	N.D. (<1.4)	N.D. (<0.7)	N.D. (<0.7)	N.D. (<0.7)
Trichloroethylene	N.D. (<3.0)	N.D. (<1.3)	N.D. (<1.3)	Trace (<6.5)
Tetrachloroethylene	N.D. (<0.5)	N.D. (<0.3)	Trace (<1.5)	2.4

N.D. indicates "not detected"
Trace indicates "lower than quantitative analysis limit"
All data are converted to 12%O_2 in dry gas at standard conditions

the incineratiors was cooled rapidly through a boiler, cooling tower or both them, and wastewater and sludge were treated certainly.

CFC11, CFC12, CFC113, HCFC22 were tested. To suppress the concentration of corrosive gas such as HCl and HF in exhaust gas, these flons were fed at a rate of below 2wt% to the total waste for incineration.

Table 2 shows test data of regulation terms to stack gas at plant A. Destruction efficiencies of each flons were over 99.99%, that is, concentrations of flons in the stack gas were below ca.15ppm which is same level in urban air. The all regulations to stack gas were satisfied enough. It is confirmed that these substances were removed by treatment system for exhaust gas. HF regulation to treated wastewater was also satisfied. In case of other plants, results were similar to plant A.

Table 3 shows test data of volatile organic chlorinated compounds which may be generated by insufficient destruction of flons, at plant A. Regardless of kind of flons, these

substances in the stack gas were either not detected or below 3ppb. It is considered that CFCs were destructed completely. In case of other plants, results were similar to plant A.

In any plants, concentrations of PCDDs/PCDFs in stack gas were low level enough than those of municipal waste incinerators. In the two plants, the concentrations of PCDDs/PCDFs were much lower than the guideline value of 1 ng-TEQ/m^3_N by UNEP. In other two plants, occasionaly, the concentrations of PCDDs/PCDFs were over a little the guideline value. In the all plants, concentration of CO in stack gas were low level enough than the guideline of 80 ppm suggested by UNEP. It was suggested that only controling CO concentration is insufficient to decrease PCDDs/PCDFs. Since it was found that the cooling process of gas was very important to decrease PCDDs/PCDF, the two plants were improved.

4. Development of Method for Checking Safety of Stack Gas

In order to destruct CFCs at existing incineration plants, it is necessary that simple method of checking safety of stack gas.

An equipment was designed for sampling acid gas, volatile organic compounds, PCDDs/PCDFs and so on at once (*Fig. 2*).

It was clarified that PCDDs/PCDFs in stack gas could be recovered over 96% with only two bottles containing water and diethylene glycol, respectively.

The determing method of non-volatile total organic halogen (NVTOX) as an index of toxic substances was developed, and the relation between NVTOX and PCDDs/ PCDFs were obtained (*Fig.3*).

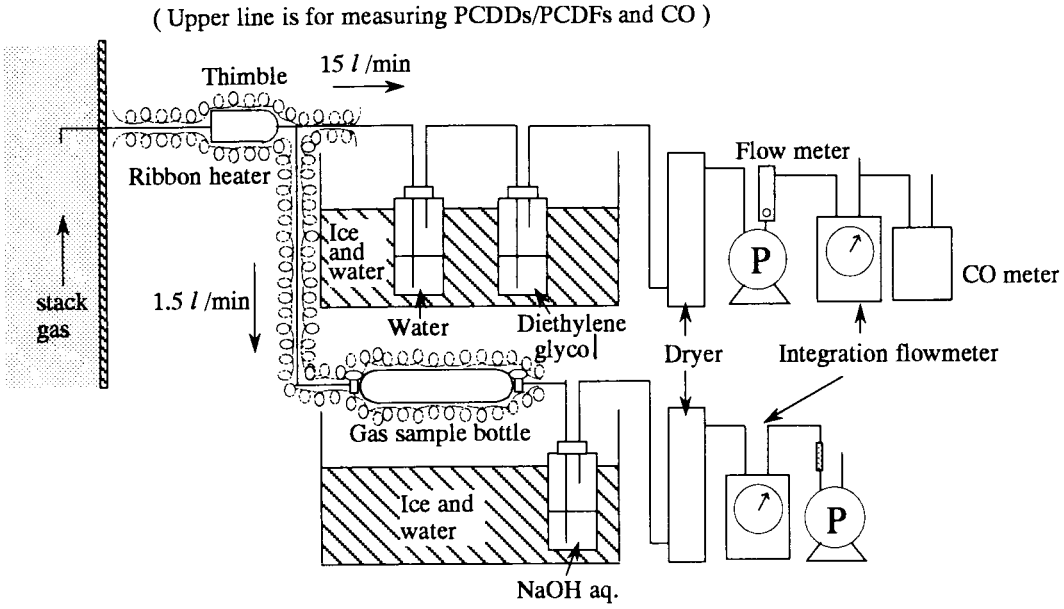

Fig.2 Apparatus for sampling of stack gas

5. Conclusion

(1) It was estimated that potential capacity for destruction of CFCs by 32 waste incineration plants in Japan was 20,000 ton a year.

(2) Yokohama city's system, in which rolls and share of cost are decided for recovery and destruct CFCs in abandoned household refrigerators could be recommended.

(3) CFCs could be destructed completely and the regulations for stack gas and wastewater were satisfied at four plants which were operated good conditons.

(4) It was found that the cooling process of exhaust gas was very important for decreasin PCDDs/PCDFs.

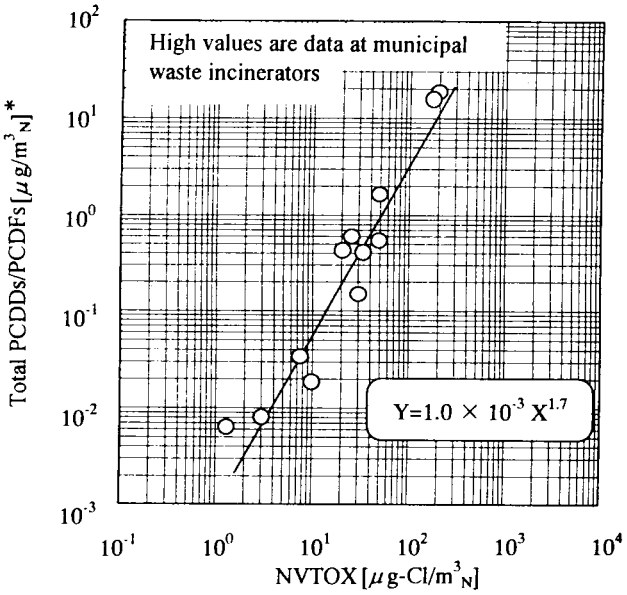

Fig.3 Relation between NVTOX and PCDDs/ PCDFs in incineration plants for municipal waste and industrial waste (*TEQ≒0.01×[PCDDs/PCDFs])

(5) PCDDs/PCDFs in stack gas could be recovered by only two bottles containing water and diethylene glycol, respectively.

(6) Non-volatile total organic halogen (NVTOX) may be useful for an index of toxic substances in stack gas.

6. References

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7. List of Publications

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