

## Destruction of Chlorofluorocarbons (CFCs) in Municipal Solid Waste (MSW) Incineration Plants and Behavior of Organohalogen Compounds

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### 1. Introduction

Chlorofluorocarbons (CFCs) are chemically and thermally stable compounds consumed in large scale (e.g. in refrigerants, solvents, insulating material) during the last decades. They accumulate in the stratosphere contributing to the greenhouse effect<sup>1)</sup> and causing the destruction of the stratospheric ozone<sup>2,3)</sup>. In Japan the CFC manufacture has been completely abolished since the end of 1995, and the HCFC manufacture is planned to be phased out. The collection, reuse and destruction of CFC was decided to be promoted in 1995, and then the guideline for the CFC destructive treatment<sup>4,5)</sup> was established with reference to the guideline of UNEP. In response to this situation, municipal governments have promoted to mainly collect the refrigerant CFC from household refrigerators. However, CFC contained in thermal insulation materials, which is much higher than the refrigerant CFC contained in refrigerators, has not been collected yet. A very few studies on destruction of the heat insulator CFC have been performed<sup>6,7)</sup>. We conducted a study on thermal destruction of CFC in municipal solid waste (MSW) incinerators (stoker furnaces with good combustion practice), aiming at more efficient and easier destruction of CFC at the same site with their collection. CFC is used as refrigerants and also contained in thermal insulation materials of waste refrigerators, which is collected by Kyoto municipal government and is to be decomposed in municipal solid waste (MSW) incinerators. The main purposes are to recognize the CFC destruction rates, the effects on the operation conditions of the facilities, the behavior of acid constituents produced by the destruction, and the content levels of by-products, such as PCDDs/DFs and chlorinated-fluorinated/fluorinated aromatic compounds.

### 2. Experimental Methods

#### 2.1 Facilities and Material supply system

The experiment on destruction of the heat insulator CFC was carried out in the incineration plant (A: 6.25 tons/hr, bag filter, activated carbon injection, wet type gas scrubber) adjacent to the bulky waste crushing facility (C: 40 tons/hr, multiple cyclone, bag filter). The destruction experiment of refrigerant CFC was performed in the incineration plant (B: 10.7 tons/hr, emission gas quenching, activated carbon injection, electric precipitator, wet type gas scrubber).

As for the experiment on destruction of the heat insulator CFC, 3 tons of waste refrigerators were first shredded and input into the incinerator with MSW. In this experiment, the amount of CFC11 added was 10 kg/hr, which amounted to 0.16 % of the total amount of waste input and corresponded to approx. 60 ppm in the combustion air amount. Presently the amount of waste refrigerators collected in Kyoto is about 20,000/yr which is equivalent to 8,000~10,000 kg/yr of CFC11. If the collected refrigerators, or CFC, are decomposed at the same CFC load with the

experiment, the treatment would be completed in 10~30 days annually. In order to understand the situation of CFC11 destruction, CFC 11 was added into the primary combustion air at the rate of 15 kg/hr and 32 kg/hr under the normal operation. These amounts of CFC11 added correspond to approx. 100~300 ppm in the combustion air at the level of concentration.

As for the experiment on destruction of the collected refrigerant CFC, CFC12 was quantitatively added into the combustion air at 16 kg/hr and 47 kg/hr, which amount to 0.15% and 0.44% of the total amount of waste, respectively. These amounts are equivalent to approx. 100~300 ppm in the combustion air. The present amount of refrigerant CFC12 collected is 2,000 kg/yr. If CFC12 is decomposed at this rate, the treatment would be completed in 2~6 days per year.

## 2.2 Measurement items and Analytical method

The concentrations of CFC11 and CFC12 in gas in furnace, in gas at the outlet of the electric precipitator and in the final emission gas were measured. Regarding the CFC sampling and the analytical method, water and acid gases were trapped by an impinger and collected into a 10L-polyester bag. After low temperature concentration, they were analyzed by HRGC-LRMS (Shimadzu QP5050). Acid gases, such as hydrogen chloride, hydrogen fluoride and chlorine, were measured at the same positions described above for CFC and, in addition, at the inlet of the electric precipitator. Additionally aromatic and polyaromatic compounds were measured in the final emission gas.

The analysis of polyhalogenated benzenes and dibenzodioxins/furans was carried out by HRGC/HRMS (Kratos Concept) at a resolution of >10 000. A Supelco SP2331 column (60m, 0.32mm i.d., 0.20 $\mu$ m film thickness) was used for the analysis of the PCDD/F, mixed chlorinated-fluorinated dioxins/furans (PCFDDs/DFs) and fluorinated dioxins and furans (PFDDs/DFs). For analysis of chlorinated and chlorinated-fluorinated benzenes a DB5-MS column (60m, 0.32mm i.d., 0.25 $\mu$ m film thickness) was used. For the chlorinated compounds, quantification was carried out by isotope dilution mass spectrometry. For the chlorinated-fluorinated and fluorinated compounds external standard solutions were used for quantification and determination of the GC-retention times.

## 3. Results and Discussion

### 3.1 Crush of refrigerators and CFC11 concentrations

On the occasion of this experiment on CFC destruction, 56 units of waste refrigerator were investigated. Their average volume was 210 L/unit (56~45 0L/unit) and their average weight was 54 kg/unit (19~88 kg/unit). The heat insulator amounted to 11% of a waste refrigerator, which corresponded to 6 kg/unit. The ratios of other physical constituents were 29% of plastics, 56% of iron, 2.5% of copper and 1.1% of aluminum. The CFC11 contained in polyurethane foams was extracted by methanol and analyzed by GC-MS. The CFC11 concentration was 2.3 g/L, which was equivalent to 480 g/unit on average. The total CFC content in 56 waste refrigerators comes to be approx. 27 kg.

The CFC11 concentration in the off-gas from the waste refrigerator crush was 58 ppm on average, while the concentrations under the blank operation were between 0.01 and 0.4 ppm. This means that the amount in off-gas corresponds to about 30% (26%) of the CFC11 contained in a waste refrigerator and about 70% remains in the thermal insulation material.

### 3.2 Profile of off-gas and Efficiency of CFC Destruction

The CFC concentrations during the experiment on the destruction of the heat insulator CFC and the refrigerant CFC and the destruction rates of those CFCs are shown in Table 1. For the heat insulator CFC, the CFC11 concentration in the combustion gas was 0.017 ppm. The pure CFC11

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concentration was between 0.028 and 0.098 ppm, which was below 1 ppm set by the guideline of Environment Agency. When the collected refrigerant CFC12 was added to the combustion gas, the concentration was between 0.18 and 0.44 ppm, which was also less than 1 ppm. The destruction efficiency of the heat insulator CFC11 was over 99.9% and that of the refrigerant CFC12 was over 99.4%.

Table 1 Concentrations in Off-gas from CFC Destruction and their Destruction rates

| Condition     |                      | Emission gas concentration [ppm] |                 | CFC flow rate [kg/hr]      |                    | Destruction rate [%] |
|---------------|----------------------|----------------------------------|-----------------|----------------------------|--------------------|----------------------|
| Facility /run | CFC Addition         | Before treatment                 | After treatment | Before thermal destruction | Final emission gas |                      |
| A/run1        | no (blank)           | -                                | 0.0047          | -                          | 0.0021             | -                    |
| A/run2        | Heat insulator CFC11 | 63                               | 0.017           | 10                         | 0.0077             | 99.92                |
| A/run3        | Pure CFC11           | 101                              | 0.028           | 15                         | 0.012              | 99.92                |
| A/run4        | Pure CFC11           | 216                              | 0.098           | 32                         | 0.043              | 99.87                |
| B/run5        | no (blank)           | -                                | 0.0024          | -                          | 0.0011             | -                    |
| B/run6        | Refrigerant CFC12    | 98                               | 0.18            | 16                         | 0.087              | 99.46                |
| B/run7        | Refrigerant CFC12    | 292                              | 0.44            | 47                         | 0.21               | 99.55                |

### 3.3. Influence on formation characteristics of Dioxins

For run 1, 2, 5 and 6 we measured PCDDs/DFs and fluorinated and chlorinated-fluorinated aromatic compounds. The concentration of PCDDs/DFs in incinerator A during normal operation conditions with MSW combustion range between 0.061 and 0.25ng-TEQ/Nm<sup>3</sup>. With the addition of the heat insulator including CFC11 in run2, the concentration was 0.052 ng-TEQ/Nm<sup>3</sup> (Table 2). For incinerator B the PCDD/DF concentration during standard operation with MSW lay between 0.67-2.4ng-TEQ/Nm<sup>3</sup>. In run6 with CFC12 addition 1.3 ng-TEQ/Nm<sup>3</sup> were detected. These measurements indicate that the addition of CFC in the chosen amounts cause no additional PCDD/DF formation in the current MSW incineration.

Polyfluorinated dibenzodioxins and dibenzofurans (PFDDs/DFs) were not detected at a detection limit of 0.01ng/Nm<sup>3</sup>. With benzenes, present in three orders of magnitude higher than the dioxins, we could detect trace amounts of monofluorotrichloro- and monofluorotetrachlorobenzenes (0.1-0.2ng/Nm<sup>3</sup>). Which means in about four orders of magnitude smaller concentration compared to the polychlorinated benzenes. This result confirms the former conclusions about the differences in the formation characteristics of fluorinated and fluorinated chlorinated aromatic compounds in thermal processes compared to the chlorinated compounds<sup>8,9</sup>.

In a previous paper we reported about a small formation rate of PFDDs/DFs during CFC combustion<sup>10</sup>. However an extensive analysis of the same samples showed that the assigned peaks were other impurities. Therefore in our experiments with the combustion of CFCs we never detected the formation of PFDDs or PFDFs.

### 4. Conclusion

The results of this experiment on thermal destruction of the heat insulator CFC and the refrigerant CFC in MSW incineration system can be summarized as follows:

- 1) The destruction rate of the heat insulator CFC11 achieved over 99.9% and that of the refrigerant CFC12 did over 99.4%. The CFC concentration in the final emission gas was below 1 ppm.

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- 2) A certain influence was observed on acid gas constituents, such as hydrogen fluoride, produced from the CFC destruction. Although the produced acid gases are removed by the existing emission gas treatment system, the control system of the drainage scrubbing treatment needs further investigation.
- 3) The PCDDs/DFs concentration in off-gas was in the extent of the concentration under the normal MSW incineration. Also we did not find any significant changes in other standard operation parameters.

Table 2 Dioxins from the CFC Destruction Experiment and System Operating Parameters

| Condition                |                            | PCDDs/DFs<br>[ng-<br>TEQ/Nm <sup>3</sup> ] | PFDDs/DFs<br>[ng/Nm <sup>3</sup> ] | Combustion<br>temperature<br>[°C] | CO<br>conc.<br>[ppm] | O <sub>2</sub><br>conc.<br>[%] | Dust<br>collection<br>temp. [°C] |
|--------------------------|----------------------------|--|------------------------------------|-----------------------------------|----------------------|--------------------------------|----------------------------------|
| Facility/<br>run         | CFC<br>addition            |  |                                    |                                   |                      |                                |                                  |
| A/run1<br>& past<br>data | Normal<br>operation        | 0.061~0.25                                 | ND (<0.01)                         | 870~952                           | 31~78                | 11.0~<br>12.6                  | 185~221                          |
| A/run2                   | Heat<br>insulator<br>CFC11 | 0.052                                      | ND (<0.01)                         | 910                               | 28                   | 12.7                           | 193                              |
| B/run5<br>& past<br>data | Normal<br>operation        | 0.67~2.4                                   | ND (<0.01)                         | 885~1075                          | 8.5~<br>30           | 10.6~<br>12.1                  | 177                              |
| B/run6                   | Refrigerant                | 1.3  | ND (<0.01)                         | 889                               | 14                   | 11.7                           | 177                              |

### References

- 1) Rosswall, T., Greenhouse gases and global change: International collaboration, *Environ Sci. Technol.*, 1991, 25, 567.
- 2) Anderson, J.G.; Toohey, D. W. and Brune, W.H., Free radicals within the antarctic vortex: The role of CFCs in antarctic ozone loss, *Science* 1991, 251,39.
- 3) Schoeberl, M.R. and Hartmann, D.L., The dynamics of stratospheric polar vortex and its relation to springtime ozone depletions, *Science* ,1991, 251, 46.
- 4) UNEP: Report of Ad-hoc Technical Advisory Committee on ODS Destruction Technologies (1992)
- 5) Air Quality Bureau, Environment Agency: A guideline for CFC Destructive Treatment (1996)
- 6) Rittmeyer, C. and Vehlow, J.: Decomposition of Organohalogen Compounds in Municipal Solid Waste Incineration Plants, Part I: Chlorofluorocarbons, *Chemosphere*, 26, 2129-2138 (1993)
- 7) Rittmeyer, C., Kaese, P., Vehlow, J. and Vil'hr, W.: Decomposition of Organohalogen Compounds in Municipal Solid Waste Incineration Plants, Part II, *Chemosphere*, 1994, 28, 1455-1465.
- 8) Weber, R., Schrenk, D., Schmitz, H.J., Hagenmaier, A. and Hagenmaier, H.: Polyfluorinated Dibenzodioxins and Dibenzofurans ñ Synthesis, Analysis, Formation and Toxicology, *Chemosphere*, 1995, 30, 629-639.
- 9) Weber, R. and Hagenmaier, H.: Synthesis and Analysis of Mixed Chlorinated-Fluorinated Dibenzop-dioxins and Dibenzofurans and Assessment of Formation and Occurrence of the Fluorinated and Chlorinated-Fluorinated Dibenzop-dioxins and Dibenzofurans, *Chemosphere*, 1997, 34, 13-28.

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- 10) Sakai S., Hiraoka M., and Shiozaki K., Thermal Behavior of Chlorofluorocarbons (CFCs) and Formation of PCDDs/PCDFs & PFDDs/PDFs, *Organohalogen Compounds*, 1995, 23, 347-351.)