

## Formation and Emission Status of PCDDs/PCDFs in Municipal Solid Waste Incinerators in Korea

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### Introduction

As of 1997, the incineration rate of MSW (Municipal Solid Waste) in Korea was recorded to about 5%. It will be increased up to about 15% in the year of 2001 due to the lacks of landfill site further available. But, this incineration-favored policy has faced the problem of dioxins connected with the constructions of further incineration facilities. Accordingly, the government has enforced a series of countermeasures such as the enactment of 0.1ng-TEQ/Nm<sup>3</sup> emission standards, management guidelines, budget assistance for the repair of facilities, technical assistance for GCP (Good Combustion Practice), and designation of agencies for dioxin analysis, etc.

This study was carried out to examine the formation and the emission status of dioxins in the flue gases of MSW Incinerators with the treatment capacity of above 200ton/day, and thus to provide the engineering data for reducing dioxins and furans emitted from MSW incinerators.

### Material and Methods

About 2ton of MSW were analyzed every weeks for three years at 9 sites of MSW incinerators in order to investigate the properties of MSW incinerated. On the basis of these three-year results the characteristics of MSW incinerated were determined. Nine of MSW incinerators with the treatment capacity of above 200ton/day were selected to determine the formation and the emission concentrations of PCDDs/PCDFs. The three times samplings of PCDDs/PCDFs on each incineration sites were performed at the outlets of WHB(waste heat boiler) and the stacks. The Korean Standard Testing Method for Dioxins and Furans was used for sampling and analysis.

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PCDDs/PCDFs were analyzed by HRGC/HRMS(High Resolution Gas Chromatograph/ High Resolution Mass Spectrometer: Micromass Co., Autospec Ultima) above 10,000 resolution with 60m x 0.32mmID x 0.25um of SP-2331. TEQ(Toxic Equivalents as 2,3,7,8-TeCDD) values were calculated by using I-TEF(International-Toxicity Equivalency Factor)

### Results and Discussion

As shown in Table 1, the moisture content of MSW incinerated was average 56% since the proportion of waste food was as high as 50% to total MSW generated. Therefore, the mean calorific value of MSW as LHV was as low as 1,661kcal/kg.

Table 1. Characteristics of MSW incinerated

| Parameters   | Unit               | HWD   | DD     | CW     | IS     | MD     | JD     | SS     | PC     | SK     | Mean   |
|--------------|--------------------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Density      | ton/m <sup>3</sup> | 0.36  | 0.46   | 0.30   | 0.39   | 0.46   | 0.30   | 0.40   | 0.24   | 0.45   | 0.37   |
| Moisture     | %                  | 65.90 | 62.61  | 54.65  | 55.13  | 48.70  | 48.17  | 48.61  | 65.74  | 55.75  | 56.14  |
| Combustibles | %                  | 29.61 | 32.59  | 36.83  | 34.42  | 38.79  | 41.38  | 43.43  | 28.57  | 38.81  | 36.05  |
| Ash          | %                  | 4.49  | 4.80   | 8.52   | 10.45  | 12.51  | 10.45  | 7.96   | 5.69   | 5.44   | 7.81   |
| Total        | %                  | 100.0 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Plastics     | %                  | 10.70 | 18.30  | 15.12  | 13.79  | 14.69  | 27.85  | 14.45  | 9.36   | 13.66  | 15.32  |
| Paper        | %                  | 13.20 | 12.50  | 22.59  | 17.18  | 30.90  | 19.60  | 19.27  | 17.23  | 29.11  | 20.18  |
| Food         | %                  | 67.00 | 51.90  | 42.87  | 58.52  | 31.25  | 44.51  | 50.23  | 60.85  | 41.70  | 49.87  |
| Wood         | %                  | 1.90  | 1.05   | 3.55   | 2.82   | 8.51   | 0.84   | 6.88   | 3.62   | 6.58   | 3.97   |
| Textile      | %                  | 2.60  | 12.45  | 3.96   | 3.90   | 4.12   | 1.21   | 4.58   | 3.40   | 5.49   | 4.63   |
| Metals       | %                  | 2.30  | 2.02   | 3.55   | 1.23   | 5.00   | 3.15   | 2.01   | 2.01   | 0.53   | 2.42   |
| Non-Metals   | %                  | 2.30  | 1.78   | 8.36   | 2.56   | 5.53   | 2.84   | 2.58   | 3.53   | 2.93   | 3.60   |
| Total        | %                  | 100.0 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| HHV          | kcal/kg            | 1,649 | 1,818  | 2,165  | 1,972  | 2,189  | 2,996  | 2,363  | 1,705  | 2,306  | 2,129  |
| LHV          | kcal/kg            | 1,146 | 1,312  | 1,689  | 1,523  | 1,774  | 2,542  | 1,918  | 1,216  | 1,831  | 1,661  |
| C            | %                  | 47.50 | 45.82  | 50.70  | 54.50  | 38.91  | 47.59  | 44.38  | 40.47  | 44.21  | 46.01  |
| H            | %                  | 6.68  | 7.34   | 7.45   | 6.35   | 5.91   | 7.41   | 6.88   | 6.14   | 6.61   | 6.75   |
| O            | %                  | 38.93 | 37.73  | 30.36  | 25.19  | 38.15  | 30.18  | 36.91  | 40.79  | 39.93  | 35.35  |
| N            | %                  | 1.77  | 1.50   | 1.98   | 2.60   | 1.24   | 1.74   | 2.08   | 2.28   | 1.42   | 1.85   |
| S            | %                  | 0.30  | 0.22   | 0.30   | 0.30   | 0.43   | 0.23   | 0.20   | 0.24   | 0.09   | 0.26   |
| Cl           | %                  | 0.33  | 2.59   | 0.69   | 0.61   | 2.86   | 2.40   | 1.59   | 4.40   | 2.29   | 1.97   |
| Total        | %                  | 100.0 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

Note: HHV; High Heating Value, LHV; Low Heating Value

The formation concentrations of PCDDs/PCDFs generated at the outlets of waste heat boilers were in the range of 1.1E-09-9.61ng-TEQ/Nm<sup>3</sup>(average 5.75 ng-TEQ/Nm<sup>3</sup>), while the emission concentrations at the stacks were in the range of 0.02E-04-4.548ng-TEQ/Nm<sup>3</sup>(average 0.924ng-TEQ/Nm<sup>3</sup>). Two major 2,3,7,8-substituted isomers were 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-HxCDF, which were 50% and 64% of total TEQ values at the outlet of WHB and the stack, respectively. From the results of multi-regression analysis, the formation concentration of PCDDs/PCDFs had the relations with r<sup>2</sup>=0.962 as follows : PCDDs/PCDFs(ng-TEQ/Nm<sup>3</sup>) = 3.036(Cl) + 0.094(T<sub>i</sub>) - 0.472(Combustibles) + 0.059(CO) - 0.039(THC) - 3.366(H) + 22.157, while the emission concentration of PCDDs/PCDFs had the relations with r<sup>2</sup>=0.947 as follows : PCDDs/DFs(ng-TEQ/Nm<sup>3</sup>) = 0.007(NOx) - 0.088(SOx)+ 0.047. Where, T<sub>i</sub>(°C) is the temperature at the outlet of waste heat boiler. The unit of Cl, Combustibles and H is %, and the others are ppm.

Table 2. formation of PCDDs/PCDFs at the outlet of WHB in MSW incinerator

| 2,3,7,8-substituted isomers |                     | PCDDs/PCDFs(ng-TEQ/Nm <sup>3</sup> ) |       |       |       |       |       |       |       |       |       |       |
|-----------------------------|---------------------|--------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|                             |                     | MD                                   | CW    | PC    | HWD   | DD    | SK    | JD    | SS    | IS    | Mean  | (%)   |
| 1                           | 2,3,7,8-TCDD        | 0.029                                | 0.079 | 0.583 | 0.040 | 0.028 | 0.433 | 0.038 | 0.159 | 0.186 | 0.175 | 3.04  |
| 2                           | 1,2,3,7,8-PeCDD     | 0.085                                | 0.089 | 1.569 | 0.071 | 0.091 | 0.693 | 0.065 | 0.336 | 0.285 | 0.365 | 6.35  |
| 3                           | 1,2,3,4,7,8-HxCDD   | 0.018                                | 0.012 | 0.457 | 0.019 | 0.031 | 0.123 | 0.017 | 0.072 | 0.048 | 0.088 | 1.54  |
| 4                           | 1,2,3,6,7,8-HxCDD   | 0.100                                | 0.024 | 1.420 | 0.055 | 0.084 | 0.360 | 0.066 | 0.081 | 0.098 | 0.254 | 4.42  |
| 5                           | 1,2,3,7,8,9-HxCDD   | 0.043                                | 0.019 | 0.809 | 0.030 | 0.041 | 0.259 | 0.033 | 0.108 | 0.071 | 0.157 | 2.73  |
| 6                           | 1,2,3,4,6,7,8-HpCDD | 0.080                                | 0.018 | 0.958 | 0.041 | 0.060 | 0.278 | 0.047 | 0.124 | 0.082 | 0.188 | 3.26  |
| 7                           | OCDD                | 0.018                                | 0.006 | 0.210 | 0.009 | 0.009 | 0.075 | 0.016 | 0.025 | 0.016 | 0.042 | 0.74  |
| PCDDs                       |                     |                                      |       |       |       |       |       |       |       |       | 1.269 | 22.09 |
| 8                           | 2,3,7,8-TCDF        | 0.030                                | 0.048 | 0.495 | 0.058 | 0.050 | 0.122 | 0.024 | 0.127 | 0.135 | 0.121 | 2.11  |
| 9                           | 1,2,3,7,8-PeCDF     | 0.034                                | 0.031 | 0.597 | 0.021 | 0.032 | 0.098 | 0.027 | 0.069 | 0.054 | 0.107 | 1.86  |
| 10                          | 2,3,4,7,8-PeCDF     | 0.854                                | 0.461 | 11.07 | 0.499 | 0.886 | 1.621 | 0.541 | 1.909 | 0.967 | 2.090 | 36.37 |
| 11                          | 1,2,3,4,7,8-HxCDF   | 0.162                                | 0.066 | 1.667 | 0.053 | 0.106 | 0.252 | 0.094 | 0.199 | 0.125 | 0.303 | 5.27  |
| 12                          | 1,2,3,6,7,8-HxCDF   | 0.308                                | 0.139 | 2.823 | 0.118 | 0.198 | 0.539 | 0.191 | 0.476 | 0.278 | 0.563 | 9.80  |
| 13                          | 2,3,4,6,7,8-HxCDF   | 0.734                                | 0.139 | 4.438 | 0.117 | 0.199 | 0.511 | 0.336 | 0.690 | 0.270 | 0.826 | 14.37 |
| 14                          | 1,2,3,7,8,9-HxCDF   | 0.078                                | 0.024 | 0.580 | 0.016 | 0.015 | 0.086 | 0.050 | 0.076 | 0.035 | 0.107 | 1.86  |
| 15                          | 1,2,3,4,6,7,8-HpCDF | 0.223                                | 0.068 | 1.515 | 0.031 | 0.053 | 0.238 | 0.119 | 0.207 | 0.097 | 0.283 | 4.93  |
| 16                          | 1,2,3,4,7,8,9-HpCDF | 0.059                                | 0.007 | 0.277 | 0.005 | 0.007 | 0.033 | 0.026 | 0.039 | 0.017 | 0.052 | 0.91  |
| 17                          | OCDF                | 0.042                                | 0.004 | 0.136 | 0.001 | 0.001 | 0.010 | 0.013 | 0.015 | 0.007 | 0.025 | 0.44  |
| PCDFs                       |                     |                                      |       |       |       |       |       |       |       |       | 4.478 | 77.91 |
| PCDDs/PCDFs                 |                     | 2.894                                | 1.232 | 29.61 | 1.183 | 1.892 | 5.732 | 1.701 | 4.713 | 2.771 | 5.748 | 100.0 |

Table 3. Emission concentration of PCDDs/PCDFs at the stack of MSW Incinerators

| 2,3,7,8-substituted isomers |                     | PCDDs/PCDFs at stack (ng-TEQ/Nm <sup>3</sup> ) |       |       |       |        |       |       |       |       |       |       |
|-----------------------------|---------------------|--|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|
|                             |                     | MD   | CW    | PC    | HWD   | DD     | SK    | JD    | SS    | IS    | Mean  | %     |
| 1                           | 2,3,7,8-TCDD        | 0.002  | 0.003 | 0.011 | 0.007 | 0.002  | 0.005 | 0.084 | 0.036 | 0.027 | 0.020 | 2.14  |
| 2                           | 1,2,3,7,8-PeCDD     | 0.004  | 0.002 | 0.025 | 0.030 | 0.005  | 0.008 | 0.234 | 0.137 | 0.036 | 0.053 | 5.78  |
| 3                           | 1,2,3,4,7,8-HxCDD   | 0.001  | 0.000 | 0.006 | 0.010 | 0.001  | 0.001 | 0.043 | 0.031 | 0.007 | 0.011 | 1.21  |
| 4                           | 1,2,3,6,7,8-HxCDD   | 0.002  | 0.001 | 0.018 | 0.024 | 0.003  | 0.003 | 0.132 | 0.070 | 0.015 | 0.030 | 3.23  |
| 5                           | 1,2,3,7,8,9-HxCDD   | 0.002  | 0.001 | 0.009 | 0.017 | 0.002  | 0.002 | 0.061 | 0.040 | 0.008 | 0.016 | 1.70  |
| 6                           | 1,2,3,4,6,7,8-HpCDD | 0.001  | 0.001 | 0.012 | 0.017 | 0.003  | 0.001 | 0.035 | 0.040 | 0.014 | 0.014 | 1.48  |
| 7                           | OCDD                | 0.000  | 0.000 | 0.002 | 0.002 | 0.000  | 0.000 | 0.004 | 0.008 | 0.004 | 0.002 | 0.25  |
|                             | PCDDs               | 0.012  | 0.009 | 0.084 | 0.107 | 0.015  | 0.021 | 0.592 | 0.362 | 0.111 | 0.146 | 15.79 |
| 8                           | 2,3,7,8-TCDF        | 0.000  | 0.001 | 0.011 | 0.006 | 0.002  | 0.004 | 0.063 | 0.006 | 0.025 | 0.013 | 1.43  |
| 9                           | 1,2,3,7,8-PeCDF     | 0.000  | 0.001 | 0.008 | 0.004 | 0.001  | 0.002 | 0.064 | 0.018 | 0.013 | 0.012 | 1.33  |
| 10                          | 2,3,4,7,8-PeCDF     | 0.007  | 0.010 | 0.164 | 0.129 | 0.027  | 0.039 | 2.137 | 0.788 | 0.271 | 0.397 | 42.95 |
| 11                          | 1,2,3,4,7,8-HxCDF   | 0.001  | 0.001 | 0.019 | 0.016 | 0.004  | 0.003 | 0.131 | 0.067 | 0.039 | 0.031 | 3.39  |
| 12                          | 1,2,3,6,7,8-HxCDF   | 0.002  | 0.003 | 0.044 | 0.036 | 0.0009 | 0.007 | 0.371 | 0.194 | 0.097 | 0.085 | 9.17  |
| 13                          | 2,3,4,6,7,8-HxCDF   | 0.002  | 0.003 | 0.074 | 0.041 | 0.008  | 0.009 | 1.056 | 0.399 | 0.175 | 0.196 | 21.22 |
| 14                          | 1,2,3,7,8,9-HxCDF   | 0.001  | 0.000 | 0.009 | 0.006 | 0.001  | 0.001 | 0.049 | 0.025 | 0.019 | 0.012 | 1.34  |
| 15                          | 1,2,3,4,6,7,8-HpCDF | 0.000  | 0.001 | 0.019 | 0.011 | 0.003  | 0.002 | 0.072 | 0.071 | 0.051 | 0.026 | 2.78  |
| 16                          | 1,2,3,4,7,8,9-HpCDF | 0.000  | 0.000 | 0.002 | 0.002 | 0.000  | 0.000 | 0.011 | 0.010 | 0.012 | 0.004 | 0.470 |
| 17                          | OCDF                | 0.000  | 0.000 | 0.000 | 0.000 | 0.000  | 0.000 | 0.002 | 0.002 | 0.007 | 0.001 | 0.15  |
|                             | PCDFs               | 0.014  | 0.020 | 0.350 | 0.252 | 0.056  | 0.068 | 3.956 | 1.580 | 0.709 | 0.778 | 84.21 |
|                             | PCDDs/PCDFs         | 0.026  | 0.029 | 0.434 | 0.359 | 0.007  | 0.088 | 4.548 | 1.942 | 0.820 | 0.924 | 100   |

### Acknowledgements

Thanks for the director of Ko Yoon-Hwa and the deputy director of Yang Jae-Moon, who are working for the Korean MOE(Ministry Of Environment) and made the budget assistance for this project.

### References:

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