Reduction and Behavior of PCDDs/Fs in Fly Ash from Municipal Solid Waste Incinerator by Low Temperature Thermal Treatment

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Introduction

The amount of MSWs increases very rapidly because of the urbanization and industrialization, therefore, various treatment methods for MSWs have been investigated. The most MSWs(47%) have been treated with landfill in Korea[1], but there are many problems such as landfill sites due to shortage and limits for land usage. In accordance with the governmental management policy in Korea, which was decided to reduce landfill while increase incineration ratio, the aspect of increasing fly ash generation will be continued, but hazardous organohalogen pollutants like dioxins are contained in fly ash from MSWIs[2], then a serious second any environmental pollution such as leaching may arise in case of landfill simply. The government manage fly ash from MSWIs as hazardous waste but proper intermediate treatment processes are not developed and supplied so far, it has been reclaimed in designated waste disposal area now, so that cost effective treatment technology, which can reduce organohalogen compounds like dioxins contained in fly ash are requested. In this study, the high potential of dechlorination or decomposition and the relationship between decomposition and detoxification of PCDDs/Fs in fly ash by thermal treatment using low temperature were investigated. The thermal treatment of fly ash with PCDDs/Fs in oxygen deficient atmosphere was found to be an effective method for dechlorination and detoxification of these pollutants at low temperature[3,4,5,6,7,8,9]. Therefore, the result could be used as a basic data for developing intermediate treatment technology that reduces the dioxin in fly ash, it also would be used for recycling of processed fly ash.

Methods and Materials

The facility was a commercial scale MSWI and the ash was collected from fly ash pit (WHB ash + SDA ash / reaction residues + BF ash / reaction residues). The ash was dried at 50 during 24hours and it was sieved and mixed for homogeneous substance. After then, the ash(200g) was treated 3 times at the same condition. The treatment temperature was 300, 450 and 600 and the treatment time was 1hour and 3hours at each temperature in nitrogen atmosphere(0.02kg/cm_3, N_2). The furnace had temperature range up

to 1,000 . The reactor was composed of quartz and sample vessel was used alumina. The analysis of dioxins was used high resolution gas chromatography / high resolution mass spectrometry (HRGC/HRMS, Model : HP 6890N GC, Autospec Ultima, Micromass), DB 5MS columm(60 m, 0.32 mm i.d., 0.25 μm film thickness) and pre-treated according to the JIS Method K0311.

Results and Discussion

Concentration and distribution of PCDDs/Fs in untreated and treated fly ash

Table 1 shows the concentration of PCDDs/Fs of untreated and treated fly ash. The concentration of PCDDs/Fs was reduced as the treatment temperature and time increased. But after treating with the condition at 450 and 3hours, the reduction was not changed much. The portion of PCDFs was increased as the treatment temperature and time increased. Usually, the ratio of TCDD and PeCDD was increased but the ratio of HpCDD and OCDD was decreased as the treatment temperature and time increased. The isomer patterns were not same in all conditions. Hagenmaier[5] reported that the concentration of PCDD/F isomers was not reduced in the same ratio by thermal treatment and the distribution of PCDD/F isomers depended on the treatment temperature because of the thermokinetic and thermodynamic stability of each isomer and decomposition rate depends on compounds in fly ash. Addink[10] also suggested that the pattern of isomer depended on the thermodynamic characteristics of each isomer, like enthalpy and Gibb's free energy, by the treatment time and temperature. Therefore, it is estimated that the trend of distribution of PCDD/F isomers by thermal treatment could not explain without thermodynamic study for isomers and it may not be easy, because the amount of sample and the type of reactor are affected the propagation of heat. Through the concentration reduction of OCDD and OCDF, which are thermally stable at the low temperature (below 500), it is known that OCDD and OCDF are dechlorinated and destroyed at the low temperature under oxygen deficient. Hagenmaier[6] reported that, the fly ash acted as a catalyst because of metals and metal oxides in fly ash and many metals and metal oxides catalyze the low temperature (below 350) decomposition of PCDDs/Fs and related compounds in fly ash. In this study, at 450 within 3hours more than 99% of PCDDs/Fs decomposition was obtained. Hagenmaier[5] reported that the concentration of PCDDs/Fs in fly ash was decreased by about 90% at 280 and within 2hours, Sakai[4] reported more than 99% of PCDDs/Fs decomposition ratio would be obtained at 350 within 1hour under oxygen deficient, respectively. Therefore, it is known that by thermal treatment the decomposition rate depends on the treatment temperature and time and it is estimated that the difference of optimal condition according to studies may be due to the amount of sample and type of reactor.

Table 1. PCDDs/Fs concentrations of untreated and treated fly ash

(Unit : ng/g)

2,3,7,8-substituted Isomers	Untreated fly ash	300		450		600	
		1hr	3hr	1hr	3hr	1hr	3hr
2,3,7,8-TCDF	0.278	0.146	0.401	0.070	0.025	0.010	0.011
1,2,3,7,8-PeCDF	1.805	0.917	1.623	0.215	0.027	0.023	0.025

2,3,4,7,8-PeCDF	0.888	0.386	0.627	0.074	0.010	0.006	0.006
1,2,3,4,7,8-HxCDF	1.200	0.600	0.553	0.070	0.021	0.018	0.014
1,2,3,6,7,8-HxCDF	3.156	1.675	1.729	0.211	0.030	0.024	0.028
2,3,4,6,7,8-HxCDF	5.279	2.572	1.748	0.180	0.041	0.022	0.021
1,2,3,7,8,9-HxCDF	1.294	0.651	0.313	0.040	0.024	0.022	0.010
1,2,3,4,6,7,8-HpCDF	11.197	6.921	3.311	0.384	0.082	0.079	0.058
1,2,3,4,7,8,9-HpCDF	1.686	0.819	0.340	0.035	0.027	0.039	0.026
OCDF	1.941	1.199	0.321	0.055	0.057	0.037	0.025
PCDFs	28.724	15.886	10.966	1.334	0.344	0.280	0.224
2,3,7,8-TCDD	0.383	0.206	13.281	4.332	0.027	0.023	0.011
1,2,3,7,8-PeCDD	1.615	1.140	23.057	5.729	0.032	0.021	0.009
1,2,3,4,7,8-HxCDD	2.231	1.028	6.013	0.919	0.021	0.000	0.009
1,2,3,6,7,8-HxCDD	13.492	4.872	13.334	1.906	0.020	0.026	0.000
1,2,3,7,8,9-HxCDD	7.290	2.857	13.037	2.163	0.037	0.019	0.000
1,2,3,4,6,7,8-HpCDD	138.239	49.450	44.765	4.538	0.184	0.171	0.143
OCDD	76.774	29.640	11.645	1.071	0.123	0.125	0.122
PCDDs	240.105	89.193	125.132	20.658	0.444	0.376	0.294
PCDFs+PCDDs	268.829	105.079	136.098	21.992	0.788	0.656	0.518

TEQ value of PCDDs/Fs in untreated and treated fly ash

Table 2 shows the TEQ value of PCDDs/Fs of untreated and treated fly ash. The TEQ-value of PCDDs/Fs was not reduced as the treatment temperature and time increased. At 300 , 3hours the TEQ value of PCDDs/Fs was increased greatly and at 450 , 1hour was increased also. But at 450 , 3hours it was decreased so much and then it was decreased gradually. The ratio of TCDD and PeCDD was increased greatly as the treatment temperature and time increased. Especially, at 300 , 3hours and 450 ,1hour the ratio of TCDD and PeCDD showed the about 80-90%. For the reduction of toxicity of fly ash, the relationship between concentration and TEQ value of PCDDs/Fs should be considered and in this process not only treatment temperature but also treatment time should be considered, because according to time at the same temperature the result showed very different. Therefore it is known that the reduction of PCDDs/Fs concentration in fly ash has not been always same with reduction of toxicity of fly ash

Table 2. TEQ value of 2,3,7,8-substitute PCDDs/PCDFs of untreated and treated fly ash

(Unit : ng-TEQ/g)

2,3,7,8-substituted Isomers	Untreated fly ash	300		450		600	
		1hr	3hr	1hr	3hr	1hr	3hr
2,3,7,8-TCDF	0.028	0.015	0.040	0.007	0.003	0.001	0.001
1,2,3,7,8-PeCDF	0.090	0.046	0.081	0.011	0.001	0.001	0.001
2,3,4,7,8-PeCDF	0.444	0.193	0.314	0.037	0.005	0.003	0.003
1,2,3,4,7,8-HxCDF	0.120	0.060	0.055	0.007	0.002	0.002	0.001
1,2,3,6,7,8-HxCDF	0.316	0.168	0.173	0.021	0.003	0.002	0.003
2,3,4,6,7,8-HxCDF	0.528	0.257	0.175	0.018	0.004	0.002	0.002
1,2,3,7,8,9-HxCDF	0.129	0.065	0.031	0.004	0.002	0.002	0.001
1,2,3,4,6,7,8-HpCDF	0.112	0.069	0.033	0.004	0.001	0.001	0.001
1,2,3,4,7,8,9-HpCDF	0.017	0.008	0.003	0.000	0.000	0.000	0.000
OCDF	0.002	0.001	0.000	0.000	0.000	0.000	0.000
PCDFs	1.786	0.882	0.905	0.109	0.021	0.014	0.013
2,3,7,8-TCDD	0.383	0.206	13.281	4.332	0.027	0.023	0.011

1,2,3,7,8-PeCDD	0.807	0.570	11.529	2.865	0.016	0.006	0.004
1,2,3,4,7,8-HxCDD	0.213	0.103	0.601	0.092	0.002	0.000	0.001
1,2,3,6,7,8-HxCDD	1.349	0.487	1.333	0.191	0.002	0.003	0.000
1,2,3,7,8,9-HxCDD	0.729	0.286	1.304	0.216	0.004	0.002	0.000
1,2,3,4,6,7,8-HpCDD	1.382	0.494	0.448	0.045	0.002	0.002	0.001
OCDD	0.077	0.030	0.012	0.001	0.000	0.000	0.000
PCDDs	4.940	2.176	28.507	7.742	0.053	0.036	0.017
PCDFs+PCDDs	6.726	3.058	29.413	7.851	0.074	0.050	0.030

Conclusion

In this study, in condition of temperature 450 and retention time 3 hours under nitrogen atmosphere, the removal efficiency of PCDDs/Fs in fly ash was obtained about 99%. However, it is known that the reduction of toxicity of PCDDs/Fs in fly ash by thermal treatment was not found always. Especially, in condition of temperature 300 and retention time 3hrs and at 450 , 1hr the TEQ value was increased. The reduction and behavior of 2,3,7,8-substituted PCDDs/Fs in fly ash from MSWI depend on the treatment temperature and time. By thermal treatment, the relationship between concentration and TEQ value of PCDDs/Fs should be considered. And through the concentration reduction of OCDD and OCDF, which are thermally stable at the low temperature (below 500), it is known that OCDD and OCDF are dechlorinated and destroyed at the low temperature under oxygen deficient. Hagenmaier[6] reported that, the fly ash acted as a catalyst because of metals and metal oxides in fly ash and many metals and metal oxides catalyze the low temperature (below 350) decomposition of PCDDs/Fs and related compounds in fly ash. Therefore, it is estimated that the reduction and behavior of dioxin isomers depend on the thermal characteristic of individual isomer and composition of fly ash.

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