

# Hydrothermal Degradation of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans in Fly Ash from Municipal Solid Waste Incineration under Non-oxidative and Oxidative Conditions

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**ABSTRACT:** Hydrothermal technology was investigated as a degradation method for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in municipal solid waste incineration (MSWI) fly ash at 150, 200, and 250 °C under both non-oxidative and oxidative conditions. The results show that the removal efficiency of PCDDs/PCDFs in fly ash was accelerated by oxidative degradation and increased with an increasing temperature. The distributions of PCDD/PCDF homologues and isomers in fly ash were also analyzed after this hydrothermal process. There were no new isomers generated, and PCDD/PCDF degradation was not significantly dependent upon the position of the chlorine atoms. To further identify the PCDD/PCDF degradation pathways and avoid organic interfering substances in fly ash, octa-chlorinated dibenzo-*p*-dioxin (OCDD)-added aqueous solution degradation trials were conducted. All tetra- to octa-chlorinated PCDD and PCDF congeners were detected under both non-oxidative and oxidative atmospheres after OCDD-added decomposition. The formation of lower chlorinated PCDDs was attributed to a hydrodechlorination reaction, and those PCDF isomers arose as intermediates of OCDD degradation.

## 1. INTRODUCTION

Municipal solid waste incineration (MSWI) has the advantages of both mass and volume reduction and energy recovery. Waste-to-energy incineration has been considered as a mainstream strategy for municipal solid waste (MSW) management in China.<sup>1,2</sup> By 2010, there were 104 MSWI plants, with a combined daily incineration capacity of 84 940 tons, accounting for 18.8% of the total MSW treatment.<sup>3</sup> However, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) generated from MSWI have become of great public concern because of their severe toxicity and negative impacts on human health.<sup>4,5</sup> In addition, MSWI generates considerable volumes of hazardous solid residues, such as fly ash. Because of high concentrations of toxic PCDDs/PCDFs, heavy metals, and water-soluble salts in MSWI fly ash,<sup>6–8</sup> it is classified as a hazardous waste in many countries. Therefore, the treatment of MSWI fly ash is facing new challenges.

Recently, several remediation technologies have been developed for the decomposition of dioxins in fly ash, including thermal treatment,<sup>9,10</sup> photolysis,<sup>11</sup> mechanochemical treatment,<sup>12</sup> non-thermal plasma treatment,<sup>13</sup> chemical reaction,<sup>14</sup> hydrothermal technology,<sup>15–18</sup> etc. Among them, sub- and supercritical water (hydrothermal technology) have been considered to be two of the promising mediums for destroying hazardous organic pollutants,<sup>19–23</sup> because the hydrothermal process can be conducted as a closed system that does not produce any hazardous byproducts, and those products that do arise can be completely converted to inert materials.<sup>24</sup>

The hydrothermal decomposition of dioxins in MSWI fly ash was first conducted by Yamaguchi et al.,<sup>15</sup> who reported that alkaline ingredients with methanol accelerated the decomposition of PCDDs/PCDFs. A strong reductant carbonylhydrazide

is used to enhance the decomposition efficiency of PCDDs/PCDFs in MSWI fly ash during such hydrothermal processing.<sup>16</sup> A mixture of ferric and ferrous sulfate was used as a catalyst to enhance dioxin decomposition by Hu et al.<sup>18</sup> They reported that the high reaction temperature is the most important influencing factor, followed by iron addition. Water washing of the raw fly ash increased the destruction efficiencies of dioxins only slightly. However, those were not examined or reported in the context of whether or not the oxidative atmosphere would have any impact on degradation or the formation of intermediates during the dioxin destruction process. In addition, MSWI fly ash is characterized by high concentrations of related organic compounds, complicated inorganic components, etc. The decomposition of dioxins in fly ash during a hydrothermal process may be subjected to interference from those materials. For example, the formation of PCDFs during polychlorinated biphenyl (PCB) destruction was observed both under oxidative and non-oxidative treatments of sub- and supercritical conditions.<sup>19</sup> Hence, it is difficult to study the reaction pathways of PCDDs/PCDFs in fly ash during hydrothermal processing.

Therefore, the objective of this research was to investigate the effects of hydrothermal processing on the degradation of PCDDs/PCDFs under different oxygen atmospheres in MSWI fly ash. The degradation efficiency of PCDD/PCDF during hydrothermal processing was investigated under both non-oxidative and oxidative conditions. Additionally, the distributions of PCDD/PCDF homologues and isomers were analyzed. Finally, to further study PCDD/PCDF pathways and the

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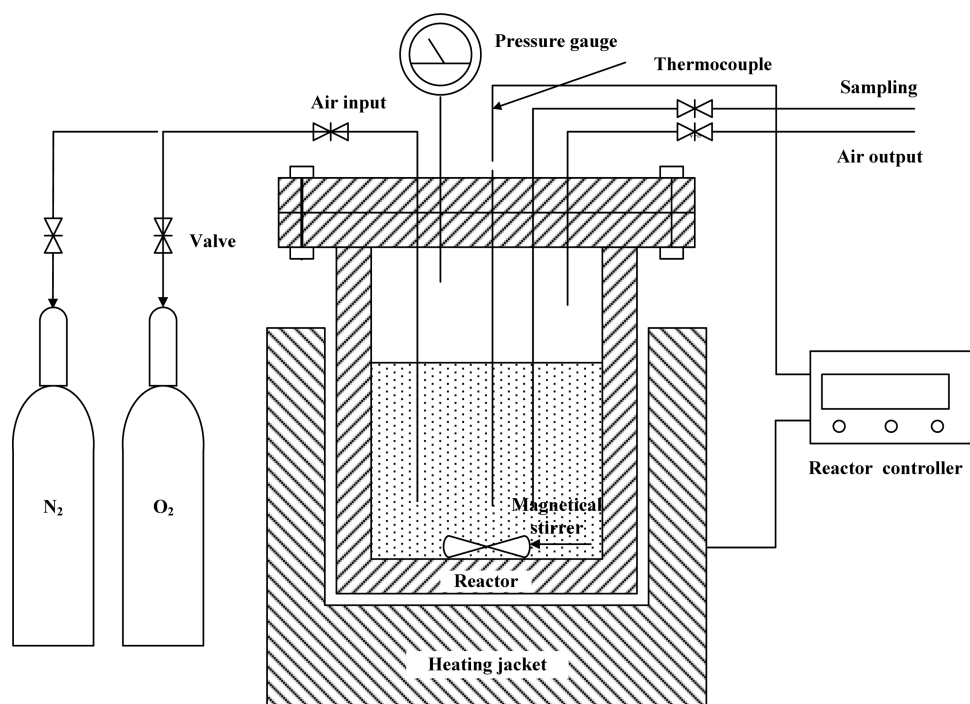


Figure 1. Schematic diagram of the experimental apparatus.

occurrence of byproducts during the hydrothermal process, octa-chlorinated dibenzo-*p*-dioxin (OCDD)-added solution degradation trials were conducted during the hydrothermal process in both cases.

## 2. MATERIALS AND METHODS

**2.1. Fly Ash Sample.** Fly ash was sampled from a commercial MSW and coal co-firing fluidized-bed incineration plant in Changxing, Zhejiang, China, which operates with two lines and a total daily capacity of 600 tons of MSW. The ratio of MSW/coal is about 5:1. The incineration furnace temperature is sustained within the range of 850–950 °C. It is equipped with an air pollution control (APC) system, consisting of a semi-dry scrubber, activated carbon injection, and fabric filter. Activated carbon injection is employed to reduce PCDDs/PCDFs from flue gases. Fly ash was sampled from under the fabric filter. Its elemental composition and that of the corresponding oxide were determined by an X-ray fluorescence (XRF) spectrometer (ThermoFisher, IntelliPower 4200).

**2.2. Equipment and Procedures.** A stainless-steel autoclave was used for the application of this hydrothermal treatment, and a diagram showing the experimental apparatus is provided in Figure 1. The reaction system had a gas supply (oxygen and nitrogen), a cylindrical reactor (with a central magnetic stirrer), a reactor controller, a pressure gauge, and a sampling system together with the gas outlet system. The reactor controller was used to control the operational conditions (e.g., temperature and stirring rate) by a temperature sensor, electric heating jacket, and magnetic stirrer. The pressure varied within the range of 0–20 MPa, according to the temperature. It was monitored by the pressure gauge of the system.

Batches of 20 g of fly ash were prepared and then mixed with 1.0 M NaOH alkali solution, of which the solid/liquid ratio was adjusted to 1:10 (g/mL). PCDD/PCDF degradation in fly ash was then carried out under two different conditions. (1) Non-oxidative experiments: Pure nitrogen was supplied to purge the air inside the reactor 3 times, and then the reactor was heated to the required temperature. The process duration was 12 h with continuous stirring, and three reaction temperatures (150, 200, and 250 °C) were selected. (2) Oxidative experiments: Pure oxygen was supplied to purge the air inside the reactor 3 times, and then the reactor was heated until it reached the

required temperature. Sufficient pure oxygen to produce a pressure of 1.0 MPa in the reactor was fed through the gas pipe. The process was maintained for 2 h with continuous stirring at a constant reaction temperature of 150, 200, and 250 °C.

To further study PCDD/PCDF degradation pathways and avoid interference from organic substances in the fly ash, OCDD-added solution degradation by the hydrothermal process was investigated. A mass of 5000 pg of analytically pure OCDD [99% purity, unlabeled, 10 μg/mL in dimethyl sulfoxide (DMSO), Cambridge Isotope Laboratories, Andover, MA] was used as the reaction reagent. This was added to deionized water with 1 M NaOH alkali solution and then heated to 250 °C for 2 h while being continuously stirred. One experiment was carried out under non-oxidative conditions, and the other experiment was carried out under oxidative conditions. After the experiment, <sup>13</sup>C-labeled compounds (supplied by Wellington Laboratories, Canada) were spiked as internal standards and the mixture solution was then extracted 3 times with 150 mL of methylene chloride in total. Then, the reactor and inside valve were rinsed 3 times with acetone and methylene chloride. The degradation efficiency of PCDDs/PCDFs was calculated from

$$\left(1 - \frac{C_2}{C_1}\right) \times 100\% \quad (1)$$

where  $C_1$  is the concentration of PCDDs/PCDFs (including the total or each amount of homologue, congener, and isomer) in original fly ash in ng kg<sup>-1</sup> and  $C_2$  is the concentration of PCDDs/PCDFs (defined as for  $C_1$ ) in the hydrothermally treated fly ash in ng kg<sup>-1</sup>.

**2.3. High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS) Analysis.** About 1.0 g of raw and treated fly ash was initially treated by 2 M HCl and then filtered. The liquid sample was extracted by methylene chloride (liquid–liquid extraction). The solid sample was dried in a vacuum desiccator, then transferred to the glass thimble of a Soxhlet extractor, and spiked with a mixture of <sup>13</sup>C-labeled PCDD/PCDF internal standards. The spiked sample was extracted for 24 h with 250 mL toluene (Soxhlet extraction). The Soxhlet extraction solution was mixed with liquid–liquid extraction solution. The fly ash mixed extract and OCDD-added solution extract above were concentrated by a rotary evaporator to a volume between 1 and 2 mL, respectively, before the cleanup process. After extraction, a labeled cleanup standard was spiked into the extract.

**Table 1.** Comparison of PCDD/PCDF Concentrations in Original and Treated Fly Ash under Different Oxygen Atmospheric Conditions (ng kg<sup>-1</sup>)

	raw fly ash				under non-oxidative conditions				under oxidative conditions			
temperature (°C)	150	200	250	OCDD-added 250	150	200	250	OCDD-added 250	150	200	250	OCDD-added 250
time (h)	12	12	12	2	2	2	2	2	2	2	2	2
pressure (MPa)	0.5	1.0	3.0	3.0	1.5	2.0	4.0	4.0				
TCDD	15072	12466	2362.0	23.92	1493.7	1948.5	761.94	19.71	197.94			
PeCDD	13618	9435.1	1036.2	14.06	322.93	2026.8	229.82	3.94	23.83			
HxCDD	14781	9449.3	270.8	19.11	110.1	1838.3	101.75	2.37	18.76			
HpCDD	3819	2479.4	26.7	14.5	24.03	509.6	23.04	1.25	3.99			
OCDD	1929	873.26	13.61	45.42	15.05	182.89	5.92	0.89	7.84			
TCDF	31031	16155	3330.1	35.22	1314.1	2728.3	1537.5	27.4	293.05			
PeCDF	22155	12615	953.19	48.28	445.66	2628.1	489.94	15.2	69.1			
HxCDF	11307	6659.7	109.45	22.87	108.07	1438.9	109.24	5.03	30.95			
HpCDF	3525.2	2098.3	29.98	41.29	21.75	412.3	18.41	2.48	12.55			
OCDF	450.74	201.67	10.18	0	3.85	43.03	1.3	0.63	6.21			
I-TEQ (ng of I-TEQ kg <sup>-1</sup> )	3792.0	2333.3	263.68	8.6	46.98	287.25	89.45	1.52	1.83			
∑PCDDs (ng kg <sup>-1</sup> )	49219	34704	3709.2	117.01	1965.8	6506	1122.5	28.17	252.36			
∑PCDFs (ng kg <sup>-1</sup> )	68469	37729	4432.9	147.66	1893.4	7250.5	2156.4	50.73	411.87			
∑PCDDs/PCDFs (ng kg <sup>-1</sup> )	117690	72432	8142.1	264.67	3859.2	13757	3278.9	78.9	664.23			
degradation efficiency of ∑PCDDs/PCDFs (%)		38.45	93.08	99.78	22.82	88.31	97.21	99.93	86.72			
PCDFs/PCDDs ratio	1.39	1.09	1.20	1.26	0.96	1.11	1.92	1.80	1.63			

The PCDD/PCDF was purified by applying the extract to a multi-silica gel column and an alumina column, following the method by the United States Environmental Protection Agency (U.S. EPA) 1613.<sup>25</sup> After cleanup, the extract was reconcentrated and then transferred to a vial. The remaining solvent in the vial was blown down to 20  $\mu$ L under a gentle stream of nitrogen (N<sub>2</sub>). A <sup>13</sup>C<sub>12</sub>-labeled PCDD/PCDF recovery standard mixture was added before the samples were subjected to PCDD/PCDF analysis by HRGC/HRMS (JEOLJMS-800D, JEOL, Japan) with a DB-5MS column (60 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m). The gas chromatography temperature program and mass spectrometer were followed as described by Chen et al.<sup>7</sup> Recovery of internal standards, as determined against external standards, generally varied between 60 and 110%. All satisfied the constraints delineated in the methods of the U.S. EPA 1613.

The congener contents of tetra- to octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans were measured. These 136 isomers were separated into 81 peaks using a DB-5 column, which represented isomers or isomer clusters based on the relative retention time. Isomer or isomer clusters without reference compounds were assumed to have the average recovery and gas chromatography/mass spectrometry response variation of the reference compounds. The concentrations of isomers or isomer clusters within each homologue were plotted according to the sequence of gas chromatographic elution. Isomer clusters that co-elute on DB-5 were expressed by "/". A total of 81 isomers/isomer clusters of tetra- to octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans were used for isomer profiles. Additionally, the average limits of detection (LODs) were defined as 3 times the standard deviation of the lowest calibration point. In the case of values below the LOD, toxicity equivalents (TEQs) were calculated using half of the LOD.

### 3. RESULTS AND DISCUSSION

**3.1. Characteristics of Fly Ash.** Chemical analysis of the original fly ash indicated that SiO<sub>2</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub> were the most abundant oxides, comprising some 34.0  $\pm$  0.24, 26.80  $\pm$  0.22, and 16.29  $\pm$  0.10%, respectively. The high concentrations of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were due to the MSW and co-fired coal. Ca(OH)<sub>2</sub> slurry sprayed in the semi-dry scrubber resulted in high concentrations of elemental Ca. Of the metals evaluated, Fe<sub>2</sub>O<sub>3</sub>, MgO, and TiO<sub>2</sub> were present in significant amounts, comprising some 4.45  $\pm$  0.10, 3.11  $\pm$  0.09, and 1.03  $\pm$  0.05%,

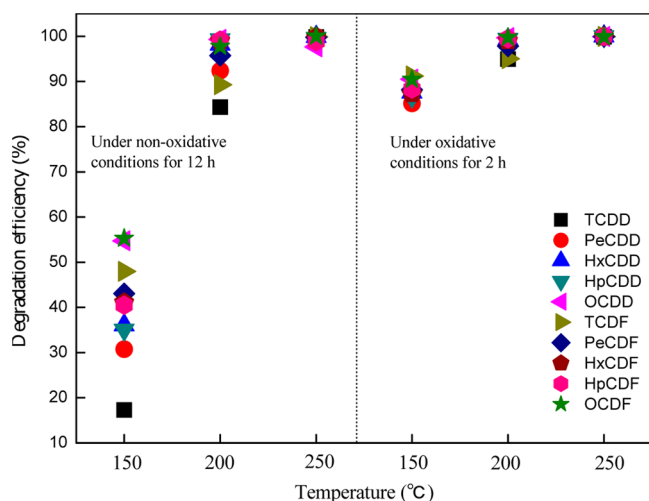
respectively. Of the non-metallic elements, Cl was present in the largest quantity (3.85  $\pm$  0.10%). In addition, minor heavy metal components, such as Cu, Zn, Pb, Mn, etc., were observed.

The total concentration of PCDDs/PCDFs in raw fly ash was 117 690 ng kg<sup>-1</sup>. The I-TEQ value (cumulative concentration of tetra- to octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans) in the original fly ash was 3791.9 ng of I-TEQ kg<sup>-1</sup>, which was higher than the national guidelines for dioxin control in landfill sites receiving MSW incineration fly ash (3000 ng of I-TEQ kg<sup>-1</sup>).<sup>26</sup> Here, 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PeCDF) was the predominant contributor to the toxic equivalent, accounting for 23.66% of 17 PCDD/PCDF congeners. Hepta-chlorinated dibenzo-*p*-dioxins (HpCDDs)/hepta-chlorinated dibenzofurans (HpCDFs) were predominant contributors to the total TEQ value. The total concentration of PCDFs was higher than that of PCDDs, with the PCDFs/PCDDs being in the ratio of 1:1.39.

**3.2. PCDD/PCDF Degradation under Non-oxidative Conditions.** A comparison of PCDD/PCDF concentrations and I-TEQ in original and treated fly ash under different oxygen atmospheric conditions is summarized in Table 1. With respect to PCDDs/PCDFs in treated fly ash under non-oxidative conditions for 12 h, the total concentration of PCDDs/PCDFs decreased to 72 430, 8142.1, and 264.67 ng kg<sup>-1</sup> at 150, 200, and 250 °C, respectively. The corresponding I-TEQ values decreased to 2333.3, 263.68, and 8.60 ng of I-TEQ kg<sup>-1</sup>. The degradation efficiencies of total PCDD/PCDF concentrations were about 38.45, 93.08, and 99.78% at 150, 200, and 250 °C, respectively.

The degradation efficiencies of the PCDD/PCDF homologue at various hydrothermal process temperatures and under different oxygen atmospheric conditions are shown in Figure 2. Generally, the degradation efficiency of each homologue increased with the hydrothermal process temperature. With respect to PCDD/PCDF degradation under non-oxidative conditions, larger differences in removal efficiency between 10 homologues were presented at 150 °C. The degradation efficiencies of OCDD and OCDF, approximately 54.73 and



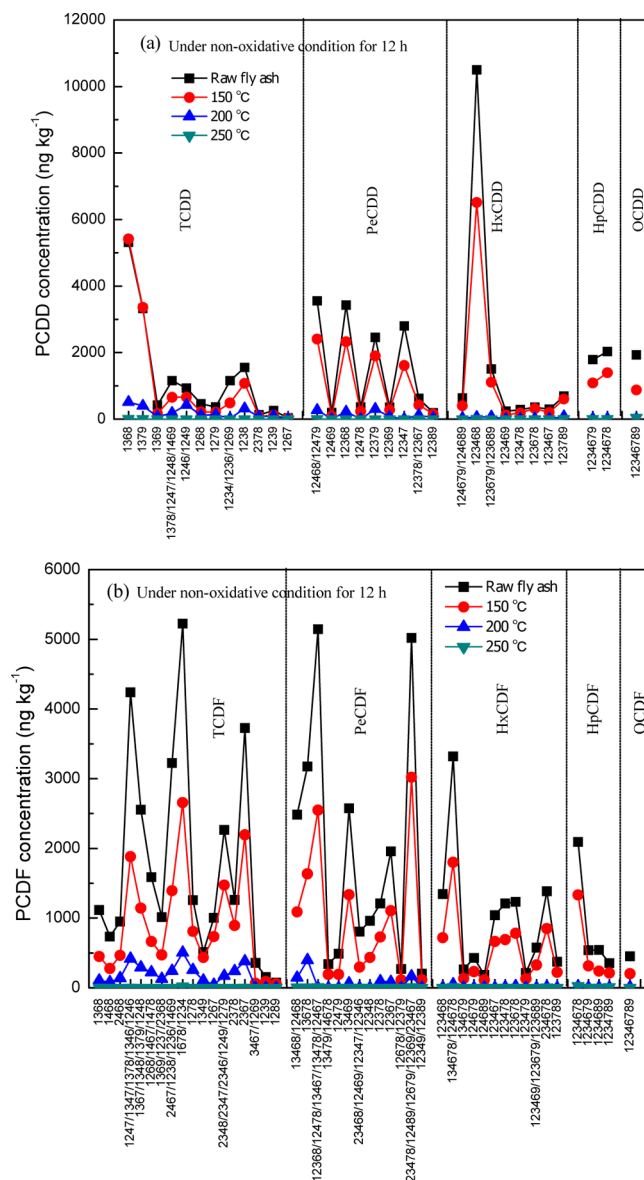


**Figure 2.** Degradation efficiency of PCDD/PCDF homologue profiles at various hydrothermal temperatures under different oxidative conditions.

55.26%, respectively, were better. In comparison to those low chlorinated samples, only 17.29–30.71% of low chlorinated (including tetra- and penta-chlorinated dibenzo-*p*-dioxins) homologues were removed. The difference of degradation efficiency between homologues at 200 °C became smaller. Degradation efficiencies of tetra-chlorinated dibenzo-*p*-dioxin (TCDD) and tetra-chlorinated dibenzofuran (TCDF) were lower than other PCDDs/PCDFs, and the degradation rate of the total PCDD concentration was slightly higher than that of the total PCDFs. The degradation efficiencies of all homologues were practically identical, potentially exceeding 97% at 250 °C. The span-declining trend of homologue degradation efficiency with an increasing temperature indicated that the degradation reaction of PCDDs/PCDFs varied with varying hydrothermal process temperatures.

The PCDD and PCDF isomer concentration profiles of original and treated fly ash under non-oxidative conditions are illustrated in Figure 3, where serial isomer patterns are evident. There were no new isomers generated in any of the treated fly ash. A full range of isomer profiles with only a few isomers or isomer clusters near or below the LOD were evident in original and treated fly ash at 150 °C for 12 h under non-oxidative conditions (see Figure 3). The PCDF removal rate was faster than that of PCDD at 150 °C. At 200 °C, most of the PCDD and PCDF isomers or isomer clusters were close to or lower than the LOD in the treated ash, whereas 10–20% low chlorinated PCDD/PCDF isomers remained after hydrothermal processing. As temperatures increased to 250 °C, more than 99% of the PCDD/PCDF isomers were decomposed.

The total proportional PCDD/PCDF concentration changed practically identically to that of the 2,3,7,8-substituted congeners. For example, the degradation efficiencies of 2,3,7,8-substituted congeners in treated fly ash at 150, 200, and 250 °C were 39.53, 95.72, and 99.45%, respectively. These were practically equal to the total degradation efficiencies (38.45, 93.08, and 99.78% at 150, 200, and 250 °C, respectively). On the other hand, the degradation of efficiencies of 2,3,7,8-substituted penta-chlorinated dibenzo-*p*-dioxin (CDD) and other penta-CDDs at 150 °C were 31.13 and 31.86%, respectively. Therefore, the degradation efficiency of



**Figure 3.** PCDD/PCDF isomer profiles of raw and treated fly ash with various hydrothermal process temperatures under non-oxidative conditions: (a) PCDD isomer profiles and (b) PCDF isomer profiles.

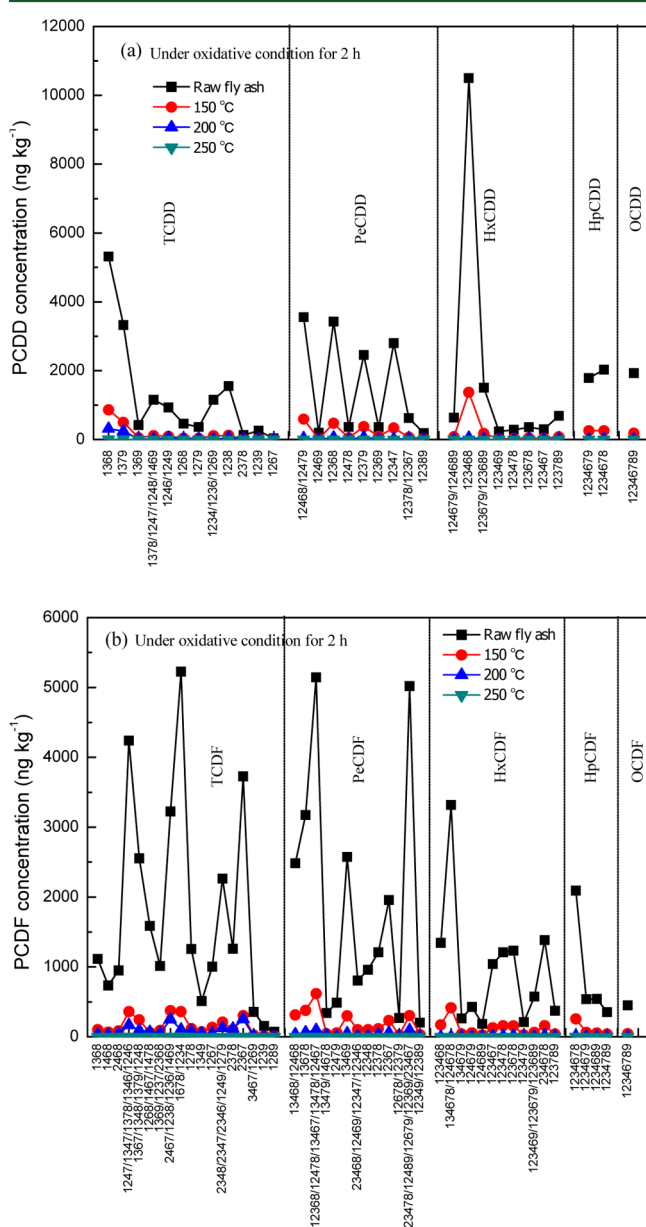
PCDD/PCDF did not rely on the position of the chlorine atoms. This finding was not consistent with the results by Hashimoto et al.,<sup>27</sup> which reported that removal rates of the 2,3,7,8-substituted TCDD were somewhat faster than the 1,4,6,9-position dioxins from contaminated soil under sub-critical water conditions.

In the case of experiments under non-oxidative conditions, acceleration of PCDD/PCDF decomposition was observed with an increase in the temperature as a result of hydrolysis reactions, occurring in hot water accompanied by a thermal reaction.<sup>28</sup> The higher the temperature, the greater the extent of this thermal reaction.

**3.3. PCDD/PCDF Degradation under Oxidative Conditions.** Under oxidative conditions for 2 h, the degradation efficiency of the total PCDD/PCDF concentrations increased to 88.31, 97.21, and 99.93% at 150, 200, and 250 °C, respectively (as shown in Table 1). This denoted a marked improvement compared to those under non-oxidative con-

ditions. The span of decomposition efficiencies between homologues was small (see Figure 2). PCDDs/PCDFs were removed in significant quantities during oxidative degradation. For example, in comparison to 150 °C, the removal rate of TCDD can reach 87.07% under 2 h oxidative conditions, whereas only 17.29% of that was decomposed after 12 h under non-oxidative conditions. These results demonstrated that the hydrothermal degradation reaction varied with changes in the oxygen content of the atmosphere used. Similarly, the degradation efficiencies of PCDDs/PCDFs improved with an increasing temperature. Those results indicated that the decomposition efficiency depended upon not only the temperature but also the oxygen level.

The PCDD and PCDF isomer concentration profiles of original and treated fly ash under oxidative conditions are illustrated in Figure 4. Under oxidative conditions for 2 h, there



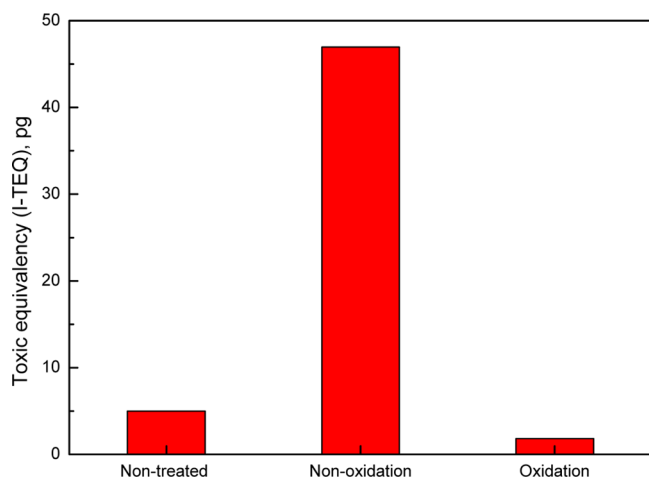
**Figure 4.** PCDD/PCDF isomer profiles of raw and treated fly ash with various hydrothermal process temperatures under oxidative conditions: (a) PCDD isomer profiles and (b) PCDF isomer profiles.

were significant changes of isomer profiles in treated ashes compared to original profiles (see Figure 4). Good degradation effects on PCDD/PCDF isomers were obtained even at mild temperatures (150 °C), and the concentrations of the isomers were reduced by 85.47–90.66%. The removal rate of PCDD isomers was almost the same as those for PCDFs. Because reaction temperatures were as high as 200 °C, most of the PCDD isomers were removed, with small amounts of 1,3,6,8-TCDD and 1,3,7,9-TCDD remaining. The concentration of  $\sum_{6-8}$ PCDF isomers was near the LOD. A total of 3–5%  $\sum_{4-5}$ PCDF isomer content remained after the process. The change of PCDFs/PCDDs ratio from 1.39 (original) to 1.92 (treated at 200 °C) was also consistent with the decomposition trends of the isomers. As a result, the PCDD isomer degradation efficiency was better than that for PCDFs. This degradation efficiency was practically identical to that obtained at 250 °C for 12 h under non-oxidative conditions. Most of the PCDD and PCDF isomers or isomer clusters were close to or lower than the LOD in the treated ash at 250 °C, and the PCDFs/PCDDs ratio became 1.80, indicating a PCDD removal rate faster than that for PCDF. The PCDFs/PCDDs ratios varied from the original at 1.39 to 1.11, 1.92, and 1.80 at 150, 200, and 250 °C, respectively. These indicated that the degradation rate of PCDFs was higher than that of PCDDs at 150 °C. In contrast, the PCDDs decomposed faster than PCDFs at 200 and 250 °C. It remained inconsistent with that under non-oxidative conditions. The reason for this will be discussed in section 3.4.

Moreover, for oxidative decomposition, the degradation of dioxins was rapidly accelerated. This was attributed to a free-radical mechanism, a major contributor to dioxin decomposition, according to the organic degradation in wastewater by wet air oxidation (WAO) technology.<sup>29,30</sup> This type of free radical has a high standard potential and is able to react non-selectively with organic compounds, yielding dehydrogenated or hydroxylated derivatives up to their final mineralization, i.e., their total conversion into CO<sub>2</sub>, water, and inorganic ions.<sup>31–33</sup>

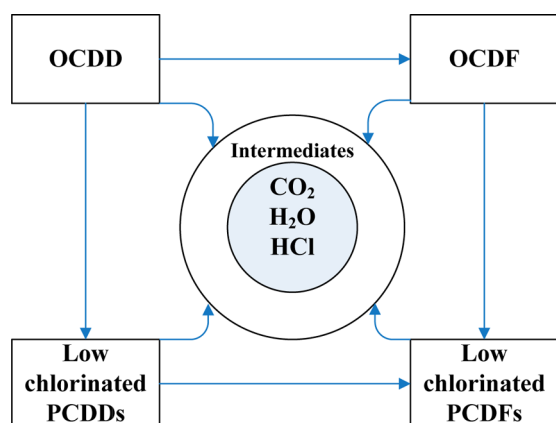
**3.4. Proposed Degradation Pathway.** Water with pure OCDD was chosen as the starting substance for tracing the degradation pathways of and intermediates arising from OCDD degradation. A comparison of the I-TEQ of OCDD-added degradation under different oxidative atmospheres is illustrated in Figure 5. The total OCDD concentration decreased from 5000 to 3859 and 664.2 pg after treatment at 250 °C for 2 h under non-oxidative and oxidative conditions, respectively. The formation of lower chlorinated PCDD/PCDF congeners was observed, resulting in an I-TEQ value that increased up to 8-fold under non-oxidative conditions. However, under oxidative conditions, the reaction rate was greatly accelerated, resulting in up to about a 3-fold decrease in the I-TEQ reaction time (only for 2 h).

It was found that tetra- to octa-chlorinated dibenzo-*p*-dioxin isomers were detected, among which lower chlorinated dibenzo-*p*-dioxin isomers (including tetra- and penta-chlorinated) were predominant, accounting for approximately 92.41 and 87.88% of the total PCDD concentration under non-oxidative and oxidative conditions, respectively. Tetra- to hepta-chlorinated dibenzo-*p*-dioxin isomers detected were attributed to the dechlorination reactions, where higher chlorinated isomers were hydrodechlorinated to form lower chlorinated isomers. Tetra- to octa-chlorinated dibenzofuran isomers were also observed, indicating that PCDFs were intermediates arising during PCDD hydrothermal decomposition. Similarly, the total



**Figure 5.** Comparison of toxic equivalency of OCDD-added solution degradation under non-oxidative and oxidative conditions.

of tetra- and penta-chlorinated dibenzofuran isomers were predominant, accounting for about 92.94 and 87.93% of the total PCDF concentration under non-oxidative and oxidative conditions, respectively. The degradation pathways may be speculated, as shown in Figure 6. The PCDFs/PCDDs ratio



**Figure 6.** Degradation pathways of OCDD-added aqueous solution during hydrothermal processing.

became 0.96 under non-oxidative conditions, indicating that dechlorination and OCDD transformation reactions (transfer to PCDF isomers during OCDD degradation) occurred practically simultaneously. On the contrary, the PCDFs/PCDDs ratio was 1.63 after oxidative degradation. As previously discussed, the PCDD removal rate was faster than that for PCDFs in fly ash at 200 and 250 °C under oxidative conditions. Resulting forms of PCDD were transformed to PCDF isomers.

In comparison to OCDD-added solution degradation efficiency, this removal rate was lower than that in fly ash under both non-oxidative and oxidative conditions. This may have resulted from the catalytic effect(s) of ash composition. It was consistent with previous findings,<sup>34–36</sup> reporting that fly ash shows good catalytic activities for organic compound degradation. The major components of the fly ash used in this study were SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, which results in the fly ash having beneficial catalyst support. Moreover, the minor components of metal oxides present, such as Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, etc., could

also be used as effective catalyst components.<sup>34</sup> Carbon materials contained in MSWI fly ash may accelerate dioxin degradation, because carbon materials could be acting as a catalytic support or a direct catalyst in catalytic WAO of organic pollutants.<sup>37,38</sup> Those results indicated that PCDD/PCDF degradation in fly ash was dependent upon not only the concentration of free radicals but also the ash composition.

#### 4. CONCLUSION

The authors reported the hydrothermal degradation of PCDDs/PCDFs in MSWI fly ash at 150, 200, and 250 °C under non-oxidative and oxidative conditions. The removal rate of PCDDs/PCDFs was accelerated by oxidative degradation; for example, 88.31% of the total PCDD/PCDF was removed at a mild temperature of 150 °C in 2 h under oxidative conditions, while only 38.45% was destroyed at the same temperature in 12 h under non-oxidative conditions. The PCDD/PCDF degradation under oxidative conditions was mainly attributed to the free-radical reaction. Aerating oxygen during the hydrothermal PCDD/PCDF process proved beneficial, in that it decreases the toxicity of the PCDDs/PCDFs and reduced the reaction temperature and time, with the concomitant reduction in energy consumption being claimed implicitly. Therefore, this technology showed potential application to industry.

The results of OCDD-added degradation show that there were coexisting hydrodechlorination reactions and OCDD to PCDF isomer conversions. The formation of PCDF isomers was more liable to occur under oxidative conditions. Finally, the dioxin removal effect in fly ash was better than that in OCDD-added solution during this hydrothermal process. This was due to the composition of the fly ash having a catalytic effect on PCDD/PCDF degradation. However, these points need further research.

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##### Notes

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